Supporting Information

Sulfur(IV)-Mediated Transformations: From Ylide Transfer to Metal-Free Arylation of Carbonyl Compounds

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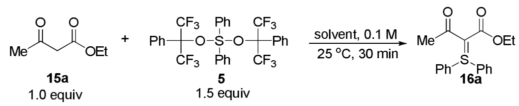
Part I Experimental part

General information

Unless otherwise indicated, all glassware was oven dried by a heat gun before use and all reactions were performed under an atmosphere of Argon. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. β-Ketoesters were prepared according to the procedures reported in the literature.[1] Reaction progress was monitored by thin layer chromatography (TLC) performed on plastic plates coated with keiselgel F_{254} with 0.2 mm thickness or GC-MS. Visualization was achieved by ultraviolet light (254 nm). Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.). Neat infra-red spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavelengths (ν) are reported in cm^{-1}. Mass spectra were obtained using a Finnigan MAT 8200 or (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). Melting points were recorded using a BÜCHI Melting Point thermometer (B-540). All ^{1}H NMR, ^{13}C NMR spectra were recorded on Bruker AV-500 in $CDCl_3$. Chemical shifts were given in parts per million (ppm, δ), referenced to the peak of tetramethylsilane, defined at δ = 0.00 (^{1}H NMR), or the solvent peak of $CDCl_3$, defined at δ = 77.0 (^{13}C NMR). Coupling constants were quoted in Hz (*J*). ^{1}H NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), septet (se), octet (o). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br).

[1] Brown, D. S.; Marples, B. A.; Smith, P.; Walton, L. *Tetrahedron* **1995**, *51*, 3587.

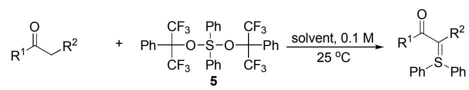
1.1 Survey of solvents' effect on the formation of sulfonium ylide 16a[a]



solvent	Et_2O	DCM	$CHCl_3$	PhMe	THF	MeCN	$MeCO_2Et$
yield (%)[b]	99	99	99	95	95	99	99

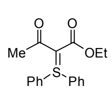
[a] Reaction conditions: **15a** (0.2 mmol), **5** (0.3 mmol), dry solvent (2 mL, 0.1M), 30 min to 2h. [b] Isolated yield based on **15a**.

1.2 General procedure to prepare diphenylsulfonium ylides[2]



Typical procedure. Take the preparation of **16aa** as a representative example (Table 2). A dry schlenk tube equipped with a stir bar was charged with Martin's sulfurane **1** (201.8 mg, 0.3 mmol). Sulfurane **5** was dissolved by diethyl ether (2 mL, 0.1M), followed by the addition of ketoester **15a** (26 μL, 0.2 mmol) via a syringe. After stirring at room temperature for 30 min, GC-MS showed a complete conversion of **15a**. The solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel (*n*-hexane/ethyl acetate = 1/3) to give the corresponding sulfonium ylide.

Ethyl 3-oxo-2-(diphenylsulfuranylidene)butanoate (16a)

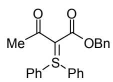


Compound **16a** was obtained in 99% yield as a white solid, R_f = 0.56 (ethyl acetate); mp 93-94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.51 (m, 4H), 7.43-7.37 (m, 6H), 4.02 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.0, 166.4, 131.1, 129.8, 129.4, 129.3, 75.5, 59.2, 29.7, 14.4; IR (neat) ν

[2] ^{1}H NMR and ^{13}C NMR spectra for compounds **16a** to **16g**, **16j**, and **16l** to **16t** see: Huang, X.; Goddard, R.; Maulide, N. *Angew. Chem. Int. Ed.* **2010**, *49*, 8979.

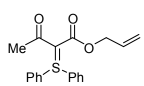
1649, 1585, 1570, 1368, 1320, 1087, 754; EIMS *m/z* (%): 314 (100), 186 (68), 121 (48), 77 (30), 43 (50); HRMS-(EI) (*m/z*): M^+ calcd for $C_{18}H_{18}O_3S$, 314.0977; found 314.0973.

Benzyl 3-oxo-2-(diphenylsulfuranylidene)butanoate (16b)



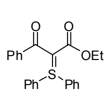
Compound **16b** was obtained in 88% yield as a white solid, R_f = 0.43 (*n*-Hexane/ethyl acetate = 1/4); mp 97-98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.54 (m, 4H), 7.49-7.46 (m, 2H), 7.43-7.40 (m, 4H), 7.32-7.23 (m, 5H), 5.10 (s, 2H), 2.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.1, 166.1, 136.8, 131.1, 129.7, 129.4, 129.3, 128.3, 127.9, 127.7, 75.4, 65.2, 29.8; IR (neat) ν 1663, 1600, 1578, 1317, 1306, 1225, 1053, 736; EIMS *m/z* (%): 376 (48), 186 (52), 91 (100); HRMS-(EI) (*m/z*): M^+ calcd for $C_{23}H_{20}O_3S$, 376.1133; found 376.1133.

Allyl 3-oxo-2-(diphenylsulfuranylidene)butanoate (16c)



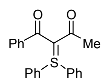
Compound **16c** was obtained in 74% yield as a white solid, R_f = 0.43 (*n*-Hexane/ethyl acetate = 1/4); mp 69-70 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.59 (m, 4H), 7.52-7.45 (m, 6H), 5.90-5.83 (m, 1H), 5.26-5.22 (m, 1H), 5.16-5.14 (m, 1H), 4.59-4.58 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.0, 166.1, 133.2, 131.2, 129.7, 129.39, 129.36, 117.0, 75.2, 64.1, 29.8; IR (neat) ν 1664, 1588, 1313, 1264, 1049, 741, 683; EIMS *m/z* (%): 326 (29), 186 (100), 43 (37); HRMS-(EI) (*m/z*): M^+ calcd for $C_{19}H_{18}O_3S$, 326.0977; found 326.0979.

Ethyl 3-oxo-3-phenyl-2-(diphenylsulfuranylidene)propanoate (16d)

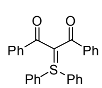


Compound **16d** was obtained in 88% yield as a white solid, R_f = 0.39 (*n*-Hexane/ethyl acetate = 2/1); mp 143-144 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.62 (m, 4H), 7.46-7.40 (m, 8H), 7.29-7.22 (m, 3H), 3.83 (q, *J* = 7.1 Hz, 2H), 0.79 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.6, 166.2, 142.9, 131.3, 129.8, 129.53, 129.47, 129.2, 127.5, 127.2, 75.6, 59.3, 13.8; IR (neat) ν 1675, 1560, 1327, 1306, 1244, 1043, 747; EIMS *m/z* (%): 376 (50), 186 (25), 105 (100), 77 (40); HRMS-(EI) (*m/z*): M^+ calcd for $C_{23}H_{20}O_3S$, 376.1133; found 376.1130.

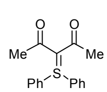
1-Phenyl-2-(diphenylsulfuranylidene)butane-1,3-dione (16e)


Compound **16e** was obtained in 99% yield as a white solid, R_f = 0.38 (*n*-Hexane/ethyl acetate = 1/4); mp 154-155 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.62 (m, 4H), 7.53-7.46 (m, 8H), 7.44-7.34 (m, 3H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.7, 190.0, 142.8, 131.3, 129.8, 129.54, 129.46, 129.3, 128.1, 127.3, 90.5, 30.4; IR (neat) ν 1607, 1582, 1570, 1327, 787, 752; EIMS *m/z* (%): 346 (70), 186 (68), 105 (100), 77 (60); HRMS-(ESIpos) (*m/z*): $[M+Na]^+$ calcd for $C_{22}H_{18}O_2NaS$, 369.0920; found 369.0919.

1,3-Diphenyl-2-(diphenylsulfuranylidene)propane-1,3-dione (16f)[3]


Compound **16f** was obtained in 99% yield as a white solid, R_f = 0.20 (*n*-hexane/ethyl acetate = 1/1); mp 184-185 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73-7.68 (m, 4H), 7.43-7.38 (m, 6H), 7.33-7.29 (m, 4H), 7.00-6.92 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.8, 141.8, 131.4, 129.7, 129.6, 129.4, 128.6, 127.3, 90.0, (one carbon overlapped); IR (neat) ν 1537, 1326, 1298, 875, 727.

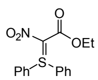
3-(Diphenylsulfuranylidene)pentane-2,4-dione (16g)


Compound **16g** was obtained in 99% yield as a white solid, R_f = 0.23 (ethyl acetate); mp 167-168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 4H), 7.53-7.45 (m, 6H), 2.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 131.3, 131.0, 129.4, 129.3, 88.9, 30.0; IR (neat) ν 1609, 1591, 1575, 1364, 1315, 749; EIMS *m/z* (%):

[3] Nozaki, H.; Nakamura, K.; Takaku, M. *Tetrahedron* **1969**, *25*, 3675.

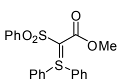
284 (55), 186 (30), 147 (32), 77 (20), 43 (100); HRMS-(EI) (*m/z*): M^+ calcd for $C_{17}H_{16}O_2S$, 284.0871; found 284.0869.

Ethyl 2-nitro-2-(diphenylsulfuranylidene)acetate (16h)



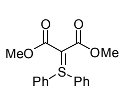
Diethyl ether was used as solvent. Compound **16h** was obtained in 98% yield as colorless oil. R_f = 0.33 (hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.51, (m, 6H), 7.48-7.45 (m, 4H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3, 132.3, 129.9, 129.4, 127.2, 94.0, 60.6, 14.3; EIMS *m/z* (%): 317 (21), 271 (39), 197 (54), 186 (100), 121 (30); HRMS-(ESIpos) (*m/z*): $[M+Na]^+$ calcd for $C_{16}H_{15}NO_4SNa$, 340.0614; found 340.0612.

Methyl 2-(diphenylsulfuranylidene)-2-(phenylsulfonyl)acetate (16i)



Diethyl ether was used as solvent. Compound **16i** was obtained in 99% yield as a white solid. R_f = 0.22 (hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (bs, 2H), 7.53 (d, *J* = 7.5 Hz, 4H), 7.47-7.44, (m, 2H), 7.42-7.37 (m, 5H), 7.34-7.20 (m, 2H), 3.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 145.1, 131.6, 131.4, 130.3, 129.6, 129.1, 128.3, 126.8, 66.0, 50.9; EIMS *m/z* (%): 398 (30), 367 (7), 257 (100), 186 (50), 125 (55); HRMS-(ESIpos) (*m/z*): $[M+Na]^+$ calcd for $C_{21}H_{18}O_4S_2Na$, 421.0539; found 421.0538.

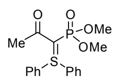
Dimethyl-2-(diphenylsulfuranylidene)malonate (16j)



Compound **16j** was obtained in 85% yield as a white solid, R_f = 0.32 (*n*-hexane/ethyl acetate = 1/4); mp 126-127 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.52 (m, 4H), 7.45-7.38 (m, 6H), 3.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 131.2, 130.2, 129.3, 129.1, 59.8, 50.9; IR (neat) ν 1709, 1581, 1562, 1192, 1045, 746;

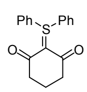
EIMS *m/z* (%): 316 (20), 285 (20), 207 (100), 186 (40), 77 (28); HRMS-(ESIpos) (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{16}O_4NaS$, 339.0661; found 339.0663.

Dimethyl 2-(diphenylsulfuranylidene)-2-oxopropylphosphonate (16k)



Diethyl ether was used as solvent. Compound **16k** was obtained in 99% yield as a white solid. R_f = 0.22 (hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 4H), 7.49-7.42, (m, 6H), 3.69 (d, *J* = 11.5 Hz, 6H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.7 (d, *J* = 19.1 Hz), 131.1, 130.6 (d, *J* = 3.1 Hz), 129.4, 129.2, 58.4 (d, *J* = 213.0 Hz), 52.0 4 (d, *J* = 5.6 Hz), 27.8; ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.3; EIMS *m/z* (%): 350 (100), 257 (74), 186 (71), 148 (59), 121 (70); HRMS-(ESIpos) (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{19}O_4PSNa$, 373.0634; found 373.0637.

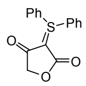
2-(Diphenylsulfuranylidene)cyclohexane-1,3-dione (16l)



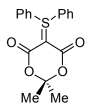
Compound **16l** was obtained in 57% yield as a white solid, R_f = 0.47 (ethyl acetate/methanol = 8/1); mp 183-184 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.57 (m, 4H), 7.46-7.38 (m, 6H), 2.43 (t, *J* = 6.4 Hz, 3H), 1.91 (p, *J* = 6.4 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 131.5, 129.9, 129.6, 128.7, 89.3, 38.1, 20.2; IR (neat) ν 1584, 1569, 1297, 1176, 753; EIMS *m/z* (%): 296 (100), 185 (28), 121 (50), 77 (25); HRMS-(EI) (*m/z*): M^+ calcd for $C_{18}H_{16}O_2S$, 296.0871; found 296.0869.

3-(Diphenylsulfuranylidene)furan-2,4(3*H*,5*H*)-dione (16m)

Compound **16m** was obtained in 73% yield as a white solid, R_f = 0.21 (ethyl acetate); mp 179-180 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.78 (m, 4H), 7.63-7.60 (m, 2H), 7.56-7.53 (m, 4H), 4.52 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.3, 172.7, 132.6, 130.2, 129.8, 128.7, 72.1, 67.2; IR (neat) ν 1725, 1643, 1629, 1344, 1316, 1025, 742; EIMS *m/z*

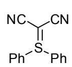
 (%): 284 (90), 226 (38), 186 (100), 121 (76), 77 (60); HRMS-(EI) (*m/z*): M^+ calcd for $C_{16}H_{12}O_3S$, 284.0507; found 284.0505.

5-(Diphenylsulfuranylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (16n)



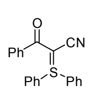
Compound **16n** was obtained in 88% yield as a white solid, R_f = 0.49 (*n*-hexane/ethyl acetate = 1/4); mp 215-216 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71-7.69 (m, 4H), 7.60-7.57 (m, 2H), 7.54-7.51 (m, 4H), 1.71 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 132.2, 129.9, 129.6, 128.5, 103.5, 60.4, 26.2; IR (neat) ν 1653, 1311, 1055, 751; EIMS *m/z* (%): 328 (10), 270 (15), 186 (25), 121 (100), 77 (28); HRMS-(ESIpos) (*m/z*): $[M+Na]^+$ calcd for $C_{18}H_{16}O_4NaS$, 351.0662; found 351.0658.

2-(Diphenylsulfuranylidene)malonodinitrile (16o)



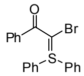
Compound **16o** was obtained in 90% yield as a white solid, R_f = 0.65 (*n*-hexane/ethyl acetate = 1/4); mp 144-145 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.57 (m, 2H), 7.56-7.53 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.1, 130.7, 130.1, 128.5, 117.6, 17.5; IR (neat) ν 2190, 2165, 1476, 1441, 728; EIMS *m/z* (%): 250 (28), 186 (100), 109 (95), 77 (25); HRMS-(ES) (*m/z*): M^+ calcd for $C_{15}H_{10}N_2S$, 250.0565; found 250.0566.

3-Oxo-2-(diphenylsulfuranylidene)-3-phenylpropanenitrile (16p)



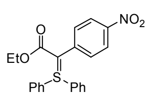
Compound **16p** was obtained in 98% yield as a white solid, R_f = 0.53 (n-hexane/ethyl acetate = 1/4); mp 130-131 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.85 (m, 2H), 7.58-7.47 (m, 10H), 7.39-7.30 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.8, 137.8, 132.6, 131.1, 130.4, 130.2, 129.21, 129.17, 128.0, 120.2, 58.0; IR (neat) ν 2167, 1590, 1563, 1333, 750; EIMS *m/z* (%): 329 (30), 186 (20), 105 (100), 77 (34); HRMS-(ESIpos) (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{16}NOS$, 330.0947; found 330.0947.

2-(Diphenylsulfuranylidene)-2-bromo-1-phenylethanone (16q)



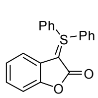
The reaction was run in chloroform. Compound **16q** was obtained in 76% yield as a pale yellow solid, R_f = 0.32 (ethyl acetate); mp 100-101 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.47 (m, 11H), 7.40-7.35 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.7, 141.0, 132.0, 131.1, 130.9, 129.9, 128.9, 128.1, 127.5, 57.7; IR (neat) ν 1543, 1322, 1300, 742, 706; EIMS *m/z* (%): 384 (15), 382 (15), 277 (21), 279 (21), 186 (70), 105 (100), 77 (60); HRMS-(ES) (*m/z*): M^+ calcd for $C_{20}H_{15}OBrS$, 382.0027; found 382.0027.

2-(Diphenylsulfuranylidene)-ethyl 2-(4-nitrophenyl)acetate (16s)



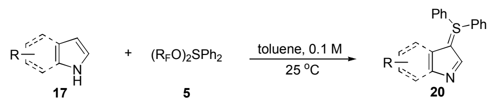
After stirring at room temperature for 40 hours in diethyl ether, TLC showed that ethyl 2-(4-nitrophenyl)acetate was not completely consumed. Concentrated, the residue was purified by chromatography on silica gel. Compound **16s** was obtained in 69% yield as a yellow solid, R_f = 0.47 (hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.08-8.05 (m, 2H), 7.91-7.89 (m, 2H), 7.68-7.65 (m, 4H), 7.63-7.66 (m, 6H), 4.03 (q, *J* = 7.1 Hz, 2H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 165.7, 149.3, 141.1, 131.8, 131.3, 130.0, 129.3, 124.1, 123.8, 59.4, 58.9, 14.6; IR (neat) ν 1643, 1574, 1485, 1299, 1273,1052, 847, 749.

3-(Diphenylsulfuranylidene)-benzofuran-2(3*H*)-one (16t)



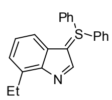
Compound **16t** was obtained in 74% yield as a yellow oil, R_f = 0.26 (hexane/ethyl acetate = 1/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.05 (m, 2H), 7.57-7.55 (m, 4H), 7.51-7.47 (m, 2H), 7.45-7.42 (m, 4H), 6.99 (dd, *J* = 0.8 Hz, *J* = 0.5 Hz, 1H), 6.83 (dt, *J* = 1.3 Hz, *J* = 7.5 Hz, 1H), 6.78 (dt, *J* = 1.0 Hz, *J* = 7.6 Hz, 1H), 6.58 (dd, *J* = 1.0 Hz, *J* = 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 148.4, 132.1, 130.2, 129.8, 128.9, 128.0, 122.0, 120.5, 113.6, 109.5, 52.4; IR (neat) ν 1686, 1644, 1577, 1273, 1243, 741, 683; EIMS *m/z* (%): 318 (15), 241 (11), 186 (100).

1.3 General procedure to prepare indole or pyrrole sulfonium ylides



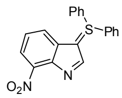
Typical procedure. Take the preparation of **20c** as a representative example (scheme 4). A dry schlenk tube equipped with a stir bar was charged with Martin sulfurane **5** (201.8 mg, 0.3 mmol). Sulfurane **5** was dissolved by toluene (2 mL, 0.1M), followed by the addition of indole (23.4 mg, 0.2 mmol). After stirring at room temperature for 2 hours, TLC showed a complete conversion of indole. The solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel (dichloromethane/methanol/triethyl amine/ammonium hydroxide = 10/1/1/1) to give the corresponding sulfonium ylide.

7-Ethyl-3-diphenylsulfonioindolide (20a)



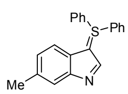
Compound **20a** was obtained in 95% yield as a pale yellow solid, R_f = 0.43 (ethyl acetate/methanol/triethyl amine/ammonium hydroxide = 10/2/2/1); mp 183-184 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.48-7.37 (m, 10H), 6.92 (q, *J* = 7.4 Hz, 2H), 6.4 (t, *J* = 7.5 Hz, 1H), 3.10 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 147.8, 135.3, 132.0, 130.7, 130.2, 128.7, 127.8, 120.1, 119.2, 114.0, 74.8, 24.6, 14.8; IR (neat) ν 1439, 1426, 1397, 1215, 1151, 743; EIMS *m/z* (%): 329 (100), 252 (80), 220 (40), 143 (80); HRMS-(EI) (*m/z*): M^+ calcd for $C_{22}H_{19}NS$, 329.1238; found 329.1236.

7-Nitro-3-diphenylsulfonioindolide (20b)



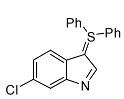
Compound **20b** was obtained in 99% yield as a yellow solid, $R_f = 0.19$ (ethyl acetate/methanol/triethyl amine/ammonium hydroxide = 100/5/5/1); mp 184-185 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.87 (dd, *J* = 7.5 Hz, *J* = 0.5 Hz, 1H), 7.55-7.44 (m, 10H), 7.35 (dd, *J* = 7.3 Hz, *J* = 0.5 Hz, 1H), 6.89 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5, 143.2, 139.1, 132.6, 132.4, 130.5, 129.3, 128.6, 122.3, 118.4, 117.9, 78.8; IR (neat) ν 1501, 1332, 1295, 1229, 1160, 744, 734; EIMS *m/z* (%): 346 (100), 237 (91), 223 (56), 191 (30); HRMS-(ESIpos) (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{15}N_2O_2S$, 347.0849; found 347.0848.

6-Methyl-3-Diphenylsulfonioindolide (20c)



Compound **20c** was obtained in 99% yield as a pale yellow solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.53 (s, 1H), 7.46-7.43 (m, 6H), 7.39-7.36 (m, 4H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1, 148.2, 132.0, 130.5, 130.22, 130.17, 128.6, 125.3, 121.6, 119.6, 115.9, 74.8, 21.4; IR (neat) ν 1441, 1408, 1170, 796, 746; EIMS *m/z* (%): 315 (81), 238 (100), 223 (55), 206 (55); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{21}H_{18}NS$, 316.1154; found 316.1152.

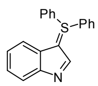
6-Chloro-Diphenylsulfonioindolide (20d)



Compound **20d** was obtained in 99% yield as a pale yellow solid, $R_f = 0.19$ (ethyl acetate/methanol/triethyl amine/ammonium hydroxide = 40/4/1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.67 (d, *J* = 1.7 Hz, 1H), 7.46-7.36 (m, 10H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.80 (dd, *J* = 8.4 Hz, *J* = 1.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 149.8, 132.2, 130.3, 130.1, 128.5, 126.5, 126.0, 120.1, 119.5, 116.6, 75.4;

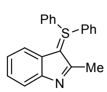
IR (neat) ν 1443, 1406, 1157, 741, 682; EIMS *m/z* (%): 335 (82), 258 (76), 223 (100); HRMS-(EI) (*m/z*): M^+ calcd for $C_{20}H_{15}NClS$, 336.0608; found 336.0606.

3-Diphenylsulfonioindolide (20e)



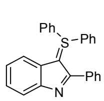
Compound **20e** was obtained in 99% yield as a pale yellow solid, R_f = 0.34 (dichloromethane/methanol/triethyl amine/ammonium hydroxide = 10/1/1/1); mp 187-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.51-7.39 (m, 10H), 7.09-7.02 (m, 2H), 6.91-6.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 147.7, 132.2, 130.4, 130.3, 128.8, 127.9, 120.9, 120.2, 119.6, 116.2, 75.5; IR (neat) ν 1667, 1443, 1410, 1156, 737; EIMS *m/z* (%): 301 (80), 224 (100), 192 (90), 186 (10), 77 (35); HRMS-(EI) (*m/z*): M^+ calcd for $C_{20}H_{15}NS$, 301.0925; found 301.0922.

2-Methyl-3-diphenylsulfonioindolide (20f)



Compound **20f** was obtained in 99% yield as a pale solid, R_f = 0.29 (dichloromethane/methanol/triethyl amine/ammonium hydroxide = 25/5/5/1); mp 188-200 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 1H), 7.46-7.35 (m, 10H), 6.97-6.94 (m, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.75-6.72 (m, 1H), 2.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 150.1, 131.8, 130.3, 130.1, 129.1, 128.6, 120.2, 119.2, 118.6, 115.7, 71.7, 15.7; IR (neat) ν 1336, 1251, 738; EIMS *m/z* (%): 315 (72), 238 (100), 223 (50), 206 (50); HRMS-(ESIpos) (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{18}NS$, 316.1154; found 316.1153.

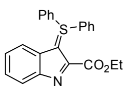
2-Phenyl-3-diphenylsulfonioindolide (20g)



. Compound **20g** was obtained in 99% yield as a pale solid, R_f = 0.40 (ethyl acetate/methanol/triethyl amine/ammonium hydroxide = 100/5/5/1); mp 102-103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77-7.74 (m, 1H), 7.68-7.44 (m, 2H), 7.48-7.24

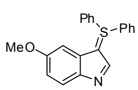
(m, 13H), 7.05-7.00 (m, 1H), 6.83-6.73 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 150.6, 136.0, 131.9, 130.2, 130.1, 129.8, 129.6, 128.7, 128.1, 127.8, 120.9, 119.9, 119.8, 116.5, 71.4; IR (neat) ν 1442, 1334, 1259, 738, 683; EIMS *m/z* (%): 377 (90), 300 (100), 268 (44); HRMS-(ESIpos) (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{20}NS$, 378.1310; found 378.1314.

Ethyl 2-carboxylate-3-diphenylsulfonioindolide (20h)



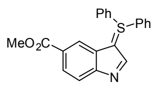
Compound **20h** was obtained in 99% yield as a pale solid, R_f = 0.53 (ethyl acetate/methanol/triethyl amine/ammonium hydroxide = 100/5/5/1); mp 161-162 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 1H), 7.49-7.38 (m, 10H), 7.05-7.02 (m, 1H), 6.78-6.74 (m, 1H), 6.49 (d, *J* = 7.7 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 149.3, 144.9, 132.1, 130.2, 129.6, 129.2, 129.0, 122.2, 121.5, 121.4, 116.7, 79.1, 60.9, 14.3; IR (neat) ν 1693, 1201, 736; EIMS *m/z* (%): 373 (63), 329 (70), 300 (60), 223 (100), 105 (60), 77 (22); HRMS-(ESIpos) (*m/z*): $[M+H]^+$ calcd for $C_{23}H_{20}NO_2S$, 374.1209; found 374.1211.

5-Methoxy-3-diphenylsulfonioindolide (20i)



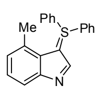
Compound **20i** was obtained in 94% yield as a pale yellow solid, R_f = 0.35 (ethyl acetate/methanol/triethyl amine/ammonium hydroxide = 10/2/2/1); mp 189-190 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.46-7.38 (m, 10H), 6.71-6.69 (m, 1H), 6.53 (d, *J* = 2.5 Hz, 1H), 3.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 148.3, 146.6, 131.9, 130.7, 130.2, 129.0, 128.6, 120.4, 109.1, 99.6, 73.6, 55.6; IR (neat) ν 1475, 1443, 1412, 1146, 1034, 745; EIMS *m/z* (%): 331 (100), 254 (90), 222 (68); HRMS-(EI) (*m/z*): M^+ calcd for $C_{21}H_{17}NOS$, 331.1031; found 331.1029.

Methyl 5-carboxylate-3-diphenylsulfonioindolide (20j)



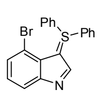
Compound **20j** was obtained in 99% yield as a pale yellow solid, R_f = 0.55 (ethyl acetate/methanol/triethyl amine/ammonium hydroxide = 10/2/2/1); mp 197-198 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.89 (d, *J* = 1.0 Hz, 1H), 7.75-7.70 (m, 2H), 7.50-7.40 (m, 10H), 3.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 154.0, 150.5, 132.4, 130.4, 130.0, 128.7, 127.9, 121.7, 121.3, 119.3, 118.7, 77.2, 51.6; IR (neat) ν 1689, 1410, 1300, 1247, 1156, 743; EIMS *m/z* (%): 359 (84), 282 (63), 250 (100), 223 (62); HRMS-(ESIpos) (*m/z*): $[M+H]^+$ calcd for $C_{22}H_{18}NO_2S$, 360.1053; found 360.1052.

4-Methyl-3-diphenylsulfonioindolide (20k)



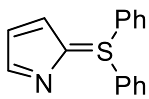
Compound **20k** was obtained in 90% yield as a pale yellow solid, R_f = 0.35 (ethyl acetate/methanol/triethyl amine/ammonium hydroxide = 15/3/1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.57 (m, 2H), 7.51-7.42 (m, 10H), 6.99-6.96 (m, 1H), 6.79 (d, *J* = 7.1 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) one carbon missed δ 145.0, 132.3, 132.0, 130.4, 128.8, 128.7, 125.9, 121.8, 120.5, 117.3, 76.5, 21.1; IR (neat) ν 1443, 1424, 1249, 1164, 740, 683; ESI *m/z* (%): $[M+H]^+$: 316; HRMS-(ESIpos) (m/z): $[M+H]^+$ calcd for $C_{21}H_{18}NS$, 316.1155; found 316.1151.

4-Bromo-3-diphenylsulfonioindolide (20l)



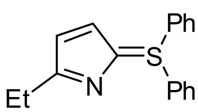
Compound **20l** was obtained in 99% yield as a white solid, R_f = 0.45 (ethyl acetate/methanol/triethyl amine/ammonium hydroxide = 40/4/1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 1H), 7.52-7.43 (m, 10H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 146.6, 132.3, 131.4, 130.4, 129.3, 129.1, 123.5, 120.9, 119.0, 109.3, 77.8; IR (neat) ν 1443, 1428, 1182, 744, 684; EIMS *m/z* (%): 381 (60), 379 (57), 304 (41), 302 (39), 272 (40), 270 (41), 223 (100); HRMS-(ESIpos) (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{15}NBrS$, 380.0103; found 380.0100.

2-Diphenylsulfoniopyrrolide (20m)



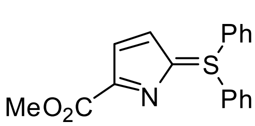
Compound **20i** was obtained in 98% yield as a brown solid, R_f = 0.57 (ethyl acetate/methanol/ammonium hydroxide = 95/5/5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64-7.63 (m, 4H), 7.48-7.41 (m, 7H), 6.87 (dd, *J* = 3.5 Hz, *J* = 1.2 Hz, 1H), 6.35 (q, *J* = 1.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.0, 132.2, 131.6, 130.2, 129.5, 120.4, 111.2, 104.4; IR (neat) ν 1475, 1441, 1351, 1016, 741, 721; EIMS *m/z* (%): 251 (79), 174 (42), 142 (100), 115 (37); HRMS-(EI) (*m/z*): M^+ calcd for $C_{16}H_{13}NS$, 251.0769; found 251.0766.

2-Ethyl-5- diphenylsulfoniopyrrolide (20n)



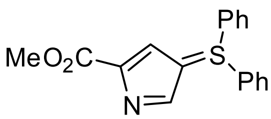
Compound **20n** was obtained in 52% yield as a brown oil, R_f = 0.57 (ethyl acetate/methanol/ammonium hydroxide = 10/1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71-7.69 (m, 4H), 7.51-7.44 (m, 6H), 6.90 (d, *J* = 3.4 Hz, 1H), 6.27 (d, *J* = 3.4 Hz, 1H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.2, 133.3, 131.6, 129.9, 129.4, 121.1, 108.8, 101.8, 25.0, 15.5; IR (neat) ν 1474, 1444, 1019, 741, 682; EIMS *m/z* (%): 279 (64), 264 (32), 202 (40), 186 (34), 170 (100); HRMS-(ESIpos) (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{18}NS$, 280.1154; found 280.1157.

Methyl 2-carboxylate-5-diphenylsulfoniopyrrolide (20o)



Compound **20o** was obtained in 83% yield as a white solid, R_f = 0.62 (ethyl acetate/methanol/triethyl amine/ammonium hydroxide = 100/5/5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.41 (m, 10H), 7.07 (d, *J* = 3.7 Hz, 1H), 6.51 (d, *J* = 3,7 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 140.4, 132.5, 130.5, 130.3, 129.6, 117.8, 117.4, 113.6, 51.0; IR (neat) ν 1700, 1441, 1336, 1157, 745, 680; EIMS *m/z* (%): 309 (100), 278 (32), 250 (28), 200 (49), 172 (31); HRMS-(ESIpos) (*m/z*): $[M+Na]^+$ calcd for $C_{18}H_{15}NO_2NaS$, 332.0716; found 332.0713.

Methyl 2-carboxylate-4-diphenylsulfoniopyrrolide (20o')

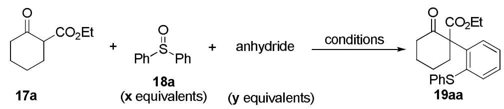


Compound **20o'** was obtained in 16% yield as a colorless oil, Rf = 0.40 (ethyl acetate/methanol/triethyl amine/ammonium hydroxide = 40/5/5/2); 1H NMR (300 MHz, $CDCl_3$) δ 7.58-7.43 (m, 11H), 7.12 (d, J = 1.4 Hz, 1H), 3.78 (s, 3H); 13C NMR (75 MHz, $CDCl_3$) δ 164.9, 139.3, 138.0, 132.7, 131.1, 130.6, 129.0, 116.6, 90.0, 51.1; IR (neat) ν 1714, 1475, 1444, 1155, 1103, 747, 728, 683; MS-(ESIpos) m/z: [M+H]+ 310; HRMS-(ESIpos) (m/z): $[M+H]^+$ calcd for C18H16NO2S, 310.0896; found 310.0894.

1.4 Optimization of conditions for α-arylation of β-ketoesters.

Acetic anhydride was ineffective (table S1, entries 1 and 2). In contrast, stronger activating reagents led to shorter reaction times and higher yields of the desired product (entries 3, 4 and 5). Further tuning of the ratios of reactants, solvents and concentrations led to two sets of optimal reaction conditions (entries 10 and 11).

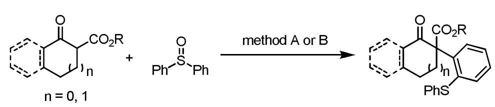
Table S1. Optimization of the direct arylation of β-ketoester **17a** with diphenyl sulfoxide.[a]



Entry	x	y	Anhydride	Reaction time (h)	Solvent	Conc. (M)	Yield[b] (%)
1	1	2	Ac_2O	24	CH_2Cl_2	0.25	-[c]
2	1.2	2		48			-[c]
3	1.2	2	TFAA	36	CH_2Cl_2	0.25	64
4	1	2	Tf_2O	0.5			66
5	1.2	2					79
6	2	2					53
7	1.2	2			$EtNO_2$		60
8	1.2	2			Et_2O		-[c]
9	1.2	2			PhMe		35
10	**1.2**	**1.5**			**CH_2Cl_2**	**0.5**	**80**
11	**1.2**	**1.5**		**24**	**MeCN**	**0.5**	**79**

[a] All reactions were performed at 25°C and Tf_2O was employed unless mentioned otherwise; [b] Yields refer to pure, isolated material obtained after column chromatography; [c] Yield not determined. TFAA = trifluoroacetic anhydride; Tf_2O = trifluoromethanesulfonic anhydride; Ac = acetyl.

1.5 Direct arylation of carbonyl compounds with sulfoxides[4]



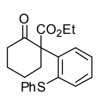
Typical procedure for method A (Table 4): Triflic anhydride (126 μL, 0.75 mmol) was added to a solution of β-ketoester **17a** (82 μL, 0.50 mmol) and diphenyl sulfoxide **18a** (121 mg, 0.60 mmol) in CH_2Cl_2 (1 mL, 0.5 M) under Argon at -70 °C, and the reaction mixture was allowed to warm up to room temperature, typically 25 °C, and stirred at this temperature for 30 min. The mixture was poured into saturated aqueous $NaHCO_3$ (15

[4] ^1H NMR and ^{13}C NMR spectra for compounds **19aa** to **19na**, **19ab**, **19ac**, and **19ae** to **19aj**, see: Huang, X.; Maulide, N. *J. Am. Chem. Soc.* **2011**, *133*, 8510.

mL), and extracted with CH_2Cl_2 (20 mL x 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel, *iso*-Hexane/ethyl acetate = 6/1, and provided the desired product.

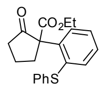
Typical procedure for method B (Table 5): Trifluoroacetic anhydride (104 μL, 0.75 mmol) was added to a solution of β-ketoester **17a** (82 μL, 0.50 mmol) and diphenyl sulfoxide **18a** (121 mg, 0.60 mmol) in CH_3CN (1 mL, 0.5 M) under argon at 25 ^{o}C, and stirred at this temperature for 24 h. TLC showed a complete conversion of **17a**. The mixture was poured into saturated aqueous $NaHCO_3$ (15 mL), and extracted with CH_2Cl_2 (20 mL x 3). The combined organic layers were dried over andydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel, *iso*-Hexane/ethyl acetate = 6/1, and provided the desired product.

Ethyl 2-oxo-1-(2-(phenylthio)phenyl)cyclohexanecarboxylate (19aa)



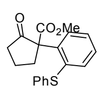
Compound **19aa** was obtained as white solid, 142 mg, 80% yield, m.p 98-99 ^{o}C, R_f = 0.39 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.34 (m, 1H), 7.20-7.16 (m, 1H), 7.15-7.12 (m, 3H), 7.08-7.04 (m, 4H), 4.12-4.07 (m, 2H), 2.63-2.58 (m, 3H), 2.53-2.50 (m, 1H), 1.91-1.86 (m, 1H), 1.77-1.73 (m, 1H), 1.66-1.64 (m, 1H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.5, 170.7, 141.5, 138.1, 136.3, 135.0, 128.8, 128.7, 128.1, 127.94, 127.86, 126.1, 67.7, 61.8, 41.0, 36.6, 25.9, 22.4, 13.9; IR (neat) ν 1700, 1707, 1215, 1136, 1024, 739; EIMS *m/z* (%): 354 (100), 309 (7); HRMS-(ESIneg) (*m/z*): M^+ calcd for $C_{21}H_{21}O_3S$, 353.1217; found 353.1215.

Ethyl 2-oxo-1-(2-(phenylthio)phenyl)cyclopentanecarboxylate (19ba)



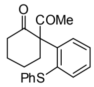
Compound **19ba** was obtained as colorless oil, 155 mg, 91% yield, R_f = 0.40 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.30 (m, 1H), 7.16-7.10 (m, 4H), 7.07-7.04 (m, 3H), 7.01-6.99 (m, 1H), 4.07-4.01 (m, 1H), 3.92-3.89 (m, 1H), 2.99 (p, *J* = 6.9 Hz,1H), 2.44 (t, *J* = 7.7 Hz, 2H), 2.28 (p, *J* = 6.6 Hz,1H), 2.00 (o, *J* = 6.8 Hz, 1H), 1.78-1.70 (m, 1H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.6, 170.1, 141.4, 137.3, 136.1, 134.4, 128.80, 128.77, 128.1, 127.8, 127.7, 126.2, 67.0, 61.8, 38.8, 36.4, 19.4, 13.7; IR (neat) ν 1750, 1717, 1227, 1023, 732, 690; EIMS *m/z* (%): 340 (100), 295 (5), 239 (63), 211 (60); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{20}H_{20}O_3SNa$, 363.1025; found 363.1023.

Methyl 2-oxo-1-(2-(phenylthio)phenyl)cyclopentanecarboxylate (19ca)



Compound **19ca** was obtained as colorless oil, 127 mg, 78% yield, R_f = 0.31 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.34 (m, 1H), 7.20-7.14 (m, 4H), 7.10-7.07 (m, 3H), 7.02-7.00 (m, 1H), 3.47 (s, 3H), 3.07-3.01 (m, 1H), 2.47 (t, *J* = 7.9 Hz, 2H), 2.27 (p, *J* = 6.6 Hz, 1H), 2.08-2.00 (m, 1H), 1.81-1.72 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.9, 170.7, 141.6, 137.2, 136.4, 134.3, 128.9, 128.7, 128.3, 128.0, 127.7, 126.3, 67.1, 52.9, 39.1, 36.8, 19.4; IR (neat) ν 1750, 1720, 1230, 733, 690; EIMS *m/z* (%): 326 (100), 239 (59), 211 (56); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{19}H_{18}O_3SNa$, 349.0869; found 349.0866.

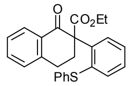
2-Acetyl-2-(2-(phenylthio)phenyl)cyclohexanone (19da)



Compound **19da** was obtained as white solid, 82 mg, 51% yield, m.p 107-108 ^{o}C, R_f = 0.32 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.33 (m, 1H), 7.19-7.09 (m, 7H), 6.93-6.91 (m, 1H), 2.70-2.66 (m, 1H), 2.57-2.54

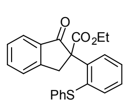
(m, 1H), 2.41-2.38 (m, 1H), 2.24-2.20 (m, 1H), 2.07 (s, 3H), 1.93-1.85 (m, 2H), 1.68-1.63 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.1, 204.8, 142.8, 137.2, 135.9, 135.0, 129.2, 129.0, 128.19, 128.15, 127.9, 126.6, 74.0, 42.0, 35.2, 27.9, 25.4, 22.2; IR (neat) ν 1701, 1580, 1130, 1121, 755, 691; EIMS *m/z* (%): 324 (40), 282 (100), 265 (60), 173 (52); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{20}H_{20}O_2SNa$, 347.1076; found 347.1077.

Ethyl 1-oxo-2-(2-(phenylthio)phenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (19fa)



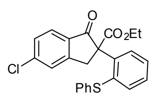
Compound **19fa** was obtained as pale yellow solid, 110 mg, 55% yield, 38 mg of β-ketoester **17f** was recovered. m.p 139-140 °C, R_f = 0.38 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.8 Hz, *J* = 1.0 Hz, 1H), 7.39-7.35 (m, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.15-7.01 (m, 8H), 6.92 (dd, *J* = 7.9 Hz, *J* = 1.2 Hz, 1H), 4.15-4.11 (m, 1H), 4.01-3.98 (m, 1H), 2.99-2.98 (m, 1H), 2.84-2.79 (m, 2H), 2.57-2.52 (m, 1H), 1.09 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.7, 171.1, 143.2, 140.3, 138.0, 136.7, 134.9, 133.6, 128.9, 128.62, 128.58, 128.5, 128.3, 128.0, 127.8, 126.9, 126.1, 64.6, 61.8, 32.6, 26.0, 13.8; IR (neat) ν 1730, 1675, 1247, 1192, 754, 738; EIMS *m/z* (%): 402 (62), 293 (68), 247 (42), 220 (100); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{25}H_{22}O_3SNa$, 425.1181; found 425.1182.

Ethyl 1-oxo-2-(2-(phenylthio)phenyl)-2,3-dihydro-1H-indene-2-carboxylate (19ga)



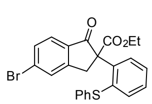
Compound **19ga** was obtained as pale yellow oil, 160 mg, 82% yield. R_f = 0.33 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.50-7.47 (m, 1H), 7.33-7.26 (m, 3H), 7.17-7.05 (m, 8H), 4.42 (d, *J* = 17.3 Hz, 1H), 4.10-4.04 (m, 1H), 3.89-3.82 (m, 1H), 3.11 (d, *J* = 17.3 Hz, 1H), 1.04 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.0, 169.6, 152.9, 142.6, 136.8, 135.8, 135.7, 134.8, 134.5, 128.9, 128.8, 128.1, 128.0, 127.9, 127.7, 126.31, 126.27, 124.7, 67.1, 62.2, 41.7, 13.7; IR (neat) ν 1741, 1708, 1464, 1209, 1003, 732, 689; EIMS *m/z* (%): 388 (100), 343 (10), 314 (57), 237 (39); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{24}H_{20}O_3SNa$, 411.1025; found 411.1023.

Ethyl 5-chloro-1-oxo-2-(2-(phenylthio)phenyl)-2,3-dihydro-1H-indene-2-carboxylate (19ha)



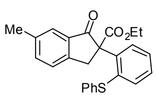
Compound **19ha** was obtained as pale yellow oil, 185 mg, 90% yield. R_f = 0.55 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 1H), 7.35-7.33 (m, 1H), 7.28-7.26 (m, 2H), 7.17-7.07 (m, 8H), 4.39 (d, *J* = 17.6 Hz, 1H), 4.11-4.05 (m, 1H), 3.91-3.84 (m, 1H), 3.08 (d, *J* = 17.6 Hz, 1H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 169.3, 154.3, 142.33, 142.30, 136.7, 135.9, 134.3, 133.4, 129.0, 128.7, 128.6, 128.3, 128.1, 128.0, 126.5, 126.4, 125.8, 67.3, 62.4, 41.3, 13.8; IR (neat) ν 1743, 1709, 1597, 1580, 1203, 899, 732, 689; EIMS *m/z* (%): 422 (100), 348 (62), 299 (44), 271 (55); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{24}H_{20}O_3ClS$, 423.0816; found 423.0814.

Ethyl 5-bromo-1-oxo-2-(2-(phenylthio)phenyl)-2,3-dihydro-1H-indene-2-carboxylate (19ia)



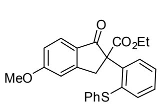
Compound **19ia** was obtained as yellow oil, 189 mg, 81% yield. R_f = 0.41 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.61 (s, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.49-7.47 (m, 1H), 7.30-7.20 (m, 8H), 4.52 (d, *J* = 17.6 Hz, 1H), 4.25-4.19 (m, 1H), 4.05-3.98 (m, 1H), 3.22 (d, *J* = 17.6 Hz, 1H), 1.20 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.7, 169.3, 154.3, 142.3, 136.7, 135.9, 134.3, 133.7, 131.4, 131.3, 129.6, 129.0, 128.7, 128.3, 128.1, 127.9, 126.4, 125.8, 67.2, 62.4, 41.2, 13.8; IR (neat) ν 1721, 1709, 1594, 1580, 1204, 893, 734, 689; EIMS *m/z* (%): 469 (26), 468 (100), 467 (26), 394 (65), 284 (44), 176 (37); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{24}H_{19}O_3BrSNa$, 489.0131; found 489.0132.

Ethyl 6-methyl-1-oxo-2-(2-(phenylthio)phenyl)-2,3-dihydro-1H-indene-2-carboxylate (19ja)



Compound **19ja** was obtained as white solid, 147 mg, 73% yield. m.p 102-103 ^{o}C, R_f = 0.43 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.48-7.46 (m, 2H), 7.34-7.21 (m, 9H), 4.52 (d, *J* = 17.2 Hz, 1H), 4.25-4.19 (m, 1H), 4.04-3.97 (m, 1H), 3.21 (d, *J* = 17.2 Hz, 1H), 2.44 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.0, 169.7, 150.3, 142.8, 137.7, 137.1, 136.9, 135.7, 135.1, 134.5, 128.9, 128.8, 128.04, 127.99, 127.92, 126.3, 126.0, 124.6, 67.5, 62.2, 41.4, 20.9, 13.8 ; IR (neat) ν 1715, 1707, 1215, 1023, 734, 689; EIMS *m/z* (%): 402 (100), 356 (26), 328 (75), 279 (53), 251 (68), 220 (53); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{25}H_{22}O_3SNa$, 425.1182; found 425.1181.

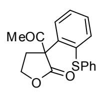
Ethyl 5-methoxy-1-oxo-2-(2-(phenylthio)phenyl)-2,3-dihydro-1H-indene-2-carboxylate (19ka)



Compound **7ka** was obtained as pale yellow oil, 87 mg, 42% yield. R_f = 0.48 (*iso*-Hexane/ethyl acetate = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.6 Hz, 1H), 7.36-7.34 (m, 1H), 7.23-7.09 (m, 8H), 6.85 (dd, *J* = 8.6 Hz, *J* = 2.1 Hz, 1H), 6.74 (d, *J* = 1.7 Hz, 1H), 4.39 (d, *J* = 17.4 Hz, 1H), 4.11-4.06 (m, 1H), 3.91-3.86 (m, 1H), 3.76 (s, 3H), 3.05 (d, *J* = 17.5 Hz, 1H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.9, 170.2, 166.3, 156.2, 143.0, 137.1, 135.8, 134.4, 129.0, 128.8, 128.2, 128.14, 128.08, 126.6, 126.3, 116.2, 109.1, 67.3, 62.2, 55.7, 41.7, 13.8; IR (neat) ν

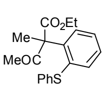
1699, 1595, 1261, 1219, 1022, 734, 690; EIMS *m/z* (%): 418 (100), 372 (20), 344 (54), 295 (37), 267 (69), 236 (50); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{25}H_{22}O_4S$, 419.1311; found 419.1313.

3-Acetyl-3-(2-(phenylthio)phenyl)dihydrofuran-2(3H)-one (19la)



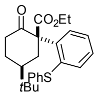
Compound **19la** was obtained as white solid, 93 mg, 60% yield. m.p 77-78 °C, R_f = 0.48 (*iso*-Hexane/ethyl acetate = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.36 (m, 1H), 7.26-7.14 (m, 8H), 4.35-4.30 (m, 1H), 4.10-4.05 (m, 1H), 3.49-3.43 (m, 1H), 2.21-2.17 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.7, 173.9, 138.5, 134.6, 134.2, 134.1, 130.4, 129.4, 129.0, 128.6, 128.0 127.5, 67.0, 66.2, 32.7, 27.3; IR (neat) ν 1760, 1709, 1475, 1193, 1159, 1020, 741, 732, 689; EIMS *m/z* (%): 312 (35), 270 (100), 197 (42), 147 (31), 43 (42); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{18}H_{16}O_3SNa$, 335.0712; found 335.0709.

Ethyl 2-methyl-3-oxo-2-(2-(phenylthio)phenyl)butanoate (19ma)



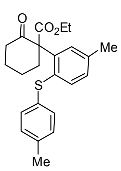
Compound **7al** was obtained as white solid, 68 mg, 41% yield. R_f = 0.39 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.34 (m, 1H), 7.23-7.20 (m, 1H), 7.18-7.06 (m, 7H), 4.12-4.07 (m, 2H), 2.30 (s, 3H), 1.75 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.8, 171.8, 142.9, 137.3, 136.1, 134.6, 128.9, 128.8, 128.3, 128.1, 127.8, 126.3, 65.7, 61.8, 28.1, 22.4, 13.8; IR (neat) ν 1709, 1581, 1204, 1013, 734, 689; EIMS *m/z* (%): 328 (37), 286 (63), 240 (100), 211 (96), 197 (61); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{19}H_{20}O_3SNa$, 351.1025; found 351.1021.

Ethyl 5-tert-butyl-2-oxo-1-(2-(phenylthio)phenyl)cyclohexanecarboxylate (19na)[5]



Compound **7am** was obtained as colorless oil, 155 mg, trans/cis = 1/9, 75% yield. R_f = 0.39 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.4 Hz, 1H), 7.34-7.19 (m, 8H), 4.25-4.22 (m, 1H), 4.07-4.03 (m, 1H), 3.02 (dt, *J* = 7.4 Hz, *J* = 3.5 Hz, 1H), 2.71 (se, *J* = 6.4 Hz, 1H), 2.51-2.48 (m, 1H), 2.34-2.89 (m, 1H), 2.01-1.96 (m, 1H), 1.64-1.61 (m, 1H), 1.54-1.51 (m, 1H), 1.21 (t , *J* = 7.1 Hz, 3H), 0.94 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 171.1, 140.0, 137.2, 136.2, 135.9, 128.98, 128.95, 128.7, 128.2, 127.7, 126.4, 67.4, 61.7, 41.7, 39.9, 37.5, 32.5, 29.3, 27.4, 13.9; IR (neat) ν 1732, 1708, 1477, 1222, 736, 690; EIMS *m/z* (%): 410 (100), 301 (64), 239 (42), 197 (38), 57 (56); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{25}H_{30}O_3SNa$, 433.1808; found 433.1811.

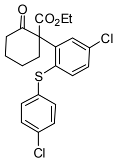
Ethyl 1-(5-methyl-2-(p-tolylthio)phenyl)-2-oxocyclohexanecarboxylate (19ab)



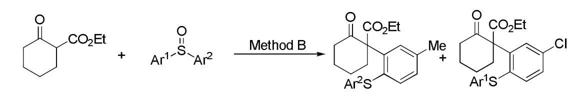
Compound **19ab** was obtained as colorless oil, method A: -40°C, 80 mg, 40% yield; method B: 113 mg, 59%. R_f = 0.40 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 1H), 7.11-7.05 (m, 5H), 6.97 (d, *J* = 0.9 Hz, 1H), 4.29-4.25 (m, 2H), 2.76-2.60 (m, 4H), 2.35 (s, 3H), 2.32 (s, 3H), 2.04-1.99 (m, 2H), 1.90-1.86 (m, 1H), 1.78-1.73 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 171.0, 141.5, 137.8, 136.3, 136.0, 135.0, 131.8, 129.7, 129.1, 128.9, 67.9, 62.0, 41.2, 36.8, 25.9, 22.7, 21.4, 21.0, 14.1; IR (neat) ν 1720, 1710, 1202, 1015, 804, 735; EIMS *m/z* (%): 382 (100), 187 (39),; HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{23}H_{26}O_3SNa$, 405.1495; found 405.1496.

[5] A study on arylation of β-ketoesters using aromatic lead reagents with similar stereo chemistry, see: Elliott, G. I.; Konopelski, J. P.; Olmstead, M. M. *Org. Lett.* **1999**, *1*, 1867.

Ethyl 1-(5-chloro-2-(4-chlorophenylthio)phenyl)-2-oxocyclohexanecarboxylate (19ac)

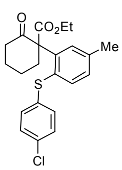


Compound **19ac** was obtained as colorless oil, method A: -40^{o}C, 110 mg, 50% yield; method B: 92 mg, 42%. R_f = 0.47 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.3 Hz, 1H), 7.15-7.10 (m, 4H), 7.01-6.99 (m, 2H), 4.14-4.03 (m, 2H), 2.77-2.73 (m, 1H), 2.62-2.56 (m, 2H), 2.40-2.35 (m, 1H), 1.96-1.95 (m, 1H), 1.84-1.79 (m, 2H), 1.69-1.66 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 170.4, 143.2, 136.2, 134.2, 133.8, 132.4, 130.0, 129.1, 128.4, 128.3, 67.2, 62.2, 40.9, 36.8, 26.0, 22.2, 13.9; IR (neat) ν 1721, 1696, 1476, 1240, 1206, 808; EIMS *m/z* (%): 422 (91), 279 (41), 207 (100); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{21}H_{20}Cl_2O_3SNa$, 445.0402; found 445.0408.



17a, 0.5 mmol **18d**, 0.6 mmol **19ad**, *48% yield* **19ad'**, *3% yield*

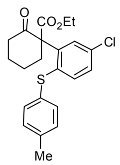
Ethyl 1-(5-Methyl-2-(4-chlorophenylthio)phenyl)-2-oxocyclohexanecarboxylate (19ad)



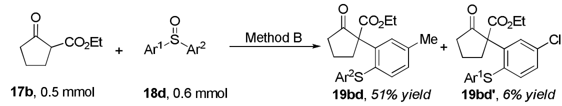
Compound **19ad** was obtained as colorless oil, method B: major product, 96 mg, 48%. R_f = 0.24 (*n*-Pentane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.9 Hz, 1H), 7.21-7.18 (m, 2H), 7.10-7.05 (m, 3H), 6.99 (d, *J* = 1.3 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.72-2.67 (m, 3H), 2.54-2.48 (m, 1H), 2.36 (s, 3H), 2.02-1.94 (m, 2H), 1.88-1.85 (m, 1H), 1.75-1.73 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.6, 170.8, 141.9, 138.6, 137.3, 136.8, 131.6, 130.4, 129.3, 129.2, 128.9, 128.8, 67.6, 61.9, 41.0, 36.9, 25.8, 22.4, 21.4, 13.9; IR (neat) ν 1710, 1475, 1238, 1203, 812, 730; EIMS *m/z* (%): 404 (40), 402 (100), 259 (61), 187

(64); HRMS-(ESIpos) (m/z): $[M+Na]^+$ calcd for $C_{22}H_{23}ClO_3SNa$, 425.0949; found 425.0951.

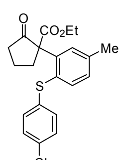
Ethyl 1-(5-chloro-2-(p-tolylthiophenyl)-2-oxocyclohexanecarboxylate (19ad')



Compound **19ad'** was obtained as colorless oil, method B: minor product, 7 mg, 3%. R_f = 0.26 (*n*-Pentane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (t, J = 8.24 Hz, 2H), 7.11-7.07 (m, 1H), 7.05-6.96 (m, 5H), 4.20-4.10 (m, 2H), 2.71-2.67 (m, 1H), 2.64-2.58 (m, 2H), 2.50-2.44 (m,1H), 2.23 (s, 3H), 1.95-1.80 (m, 3H), 1.71-1.63 (m, 1H), 1.20 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 170.5, 142.5, 136.9, 136.5, 135.2, 133.7, 133.4, 129.9, 129.8, 128.2, 128.1, 67.5, 62.2, 41.0, 36.6, 26.0, 22.4, 21.0, 14.0; IR (neat) ν 1729, 1710, 1237, 1205, 805; EIMS m/z (%): 404 (40), 402 (100), 281 (5), 279 (14); HRMS-(ESIpos) (m/z): $[M+Na]^+$ calcd for $C_{22}H_{23}ClO_3SNa$, 425.0949; found 425.0950.

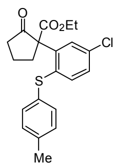


Ethyl 1-(5-Methyl-2-(4-chlorophenylthio)phenyl)-2-oxocyclopentanecarboxylate (19bd)



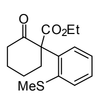
Compound **19bd** was obtained as colorless oil, method B: major product, 99 mg, 51%. R_f = 0.24 (*n*-Pentane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 7.9 Hz, 1H), 7.10 (dt, J = 8.7 Hz, J = 1.9 Hz, 2H), 6.99 (dd, J = 7.9 Hz, J = 1.2 Hz, 1H), 6.96 (dt, J = 8.7 Hz, J = 2.0 Hz, 2H), 6.83 (d, J = 1.2 Hz, 1H), 4.05 (dq, J = 10.8 Hz, J = 7.1 Hz, 1H), 3.91 (dq, J = 10.8 Hz, J = 7.1 Hz, 1H), 2.97 (p, J = 6.9 Hz, 1H), 2.46 (t, J = 7.8 Hz, 2H), 2.25 (s, 3H), 2.23-2.19 (m, 1H), 2.06-1.98 (m, 1H), 1.83-1.78 (m, 1H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.7, 170.2, 142.1, 138.7, 136.89, 136.88, 131.7, 129.8, 129.3, 129.2, 128.9, 128.7, 67.0, 62.0, 39.0, 36.7, 21.3, 19.5, 13.8; IR (neat) ν 1750, 1717, 1475, 1221, 1091, 812, 728; EIMS *m/z* (%): 390 (39), 388 (100), 245 (10); HRMS-(ESIpos) (*m/z*): $[M+Na]^+$ calcd for $C_{21}H_{21}ClO_3SNa$, 411.0792; found 411.0795.

Ethyl 1-(5-chloro-2-(p-tolylthiophenyl)-2-oxocyclopentanecarboxylate (19bd')



Compound **19bd'** was obtained as colorless oil, method B: minor product, 12 mg, 6%. R_f = 0.26 (*n*-Pentane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22-7.14 (m, 1H), 7.10-7.08 (m, 1H), 7.05-6.99 (m, 5H), 4.12 (dq, *J* = 10.9 Hz, *J* = 7.1 Hz, 1H), 4.02 (dq, *J* = 10.9 Hz, *J* = 7.1 Hz, 1H), 2.02 (p, *J* = 6.9 Hz, 1H), 2.49 (td, *J* = 7.7 Hz, *J* = 2.6 Hz, 2H), 2.34-2.28 (m, 1H), 2.24 (s, 3H), 2.11-2.02 (m, 1H), 1.87-1.78 (m, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.1, 169.8, 142.1, 137.1, 136.1, 134.8, 133.2, 132.8, 130.2, 130.0, 128.3, 127.9, 66.8, 62.3, 38.9, 36.2, 21.0, 19.6, 13.9; IR (neat) ν 1752, 1719, 1225, 805, 735; EIMS *m/z* (%): 390 (39), 388 (100), 267 (1), 265 (4); HRMS-(ESIpos) (*m/z*): $[M+Na]^+$ calcd for $C_{21}H_{21}ClO_3SNa$, 411.0792; found 411.0792.

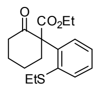
Ethyl 1-(2-(methylthio)phenyl)-2-oxocyclohexanecarboxylate (19ae)



Compound **19ae** was obtained as colorless oil, 82 mg, 56%. R_f = 0.29 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.8 Hz, *J* = 1.3 Hz, 1H), 7.19 (td, *J* = 7.5 Hz, *J* = 1.4 Hz, 1H), 7.12 (td, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H), 6.99 (dd, *J* = 7.9 Hz, *J* = 1.3 Hz, 1H), 4.25-4.15 (m, 2H), 2.60-2.47 (m, 4H), 2.28 (s, 3H), 1.95-1.90 (m, 2H), 1.76-1.75 (m, 1H), 1.68-1.65 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 170.8, 141.2, 137.7, 133.6, 128.0, 127.5, 126.9, 67.7, 61.8, 40.9, 37.0, 25.9, 22.4, 19.6, 13.9; IR (neat) ν 1709, 1236, 1205, 1130, 749;

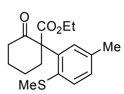
EIMS *m/z* (%): 292 (71), 245 (30), 201 (100); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{16}H_{20}O_3SNa$, 315.1025; found 315.1027.

Ethyl 1-(2-(ethylthio)phenyl)-2-oxocyclohexanecarboxylate (19af)



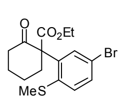
Compound **19af** was obtained as colorless oil, 88 mg, 57%. R_f = 0.26 (*iso*-Hexane/ethyl acetate = 5/1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.7 Hz, *J* = 1.4 Hz, 1H), 7.18-7.10 (m, 2H), 6.99-6.98 (m, 1H), 4.26-4.13 (m, 2H), 2.78 (q, *J* = 7.43 Hz, 2H), 2.64-2.47 (m, 4H), 2.02-1.86 (m, 2H), 1.79-1.73 (M, 1H), 1.67-1.59 (m, 1H), 1.21-1.16 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 170.8, 141.5, 136.3, 133.9, 127.71, 127.68, 126.9, 67.8, 61.8, 41.0, 30.6, 25.8, 22.5, 13.94, 13.88; IR (neat) ν 1729, 1710, 1237, 1204, 728; EIMS *m/z* (%): 308 (18), 245 (3), 215 (100), 20 (24); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{17}H_{22}O_3SNa$, 329.1182; found 329.1180.

Ethyl 1-(5-methyl-2-(methylthio)phenyl)-2-oxocyclohexanecarboxylate (19ah)



Compound **19ah** was obtained as colorless oil, 73 mg, 48%. R_f = 0.39 (*iso*-Hexane/ethyl acetate = 5/1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.9 Hz, 1H), 7.00 (dd, *J* = 7.9 Hz, *J* = 1.2 Hz, 1H), 6.77 (d, *J* = 1.3 Hz, 1H), 4.28-4.15 (m, 2H), 2.62-2.40 (m, 4H), 2.24 (s, 3H), 2.22 (s, 3H), 2.02-1.87 (m, 2H), 1.80-1.74 (m, 1H), 1.67-1.58 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 170.9, 141.6, 137.0, 134.3, 133.9, 128.9, 128.4, 67.7,61.8, 41.0, 37.2, 25.7, 22.6, 21.2, 19.9, 13.9; IR (neat) ν 1729, 1709, 1202, 813; EIMS *m/z* (%): 306 (100), 259 (37), 215 (88); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{17}H_{22}O_3SNa$, 329.1182; found 329.1180.

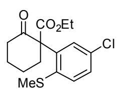
Ethyl 1-(5-bromo-2-(methylthio)phenyl)-2-oxocyclohexanecarboxylate (19ai)



Compound **19ai** was obtained as colorless oil, 85 mg, 45%. R_f = 0.26 (*iso*-Hexane/ethyl acetate = 5/1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (s, 2H), 7.12

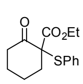
(app t, J = 1.1 Hz, 1H), 4.24-4.17 (m, 2H), 2.67-2.51 (m, 3H), 2.41-2.38 (m, 1H), 2.26 (s, 3H), 1.95-1.89 (m, 2H), 1.81-1.76 (m, 1H), 1.67-1.61 (m, 1H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.8, 170.4, 143.0, 137.2, 134.8, 131.0, 130.6, 120.9, 67.3, 62.1, 40.9, 37.0, 25.9, 22.3, 19.5, 13.9; IR (neat) ν 1728, 1710, 1206, 907, 726; EIMS *m/z* (%): 372 (69), 370 (67), 325 (31), 281 (100); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{16}H_{19}O_3BrSNa$, 393.0130; found 393.0129.

Ethyl 1-(5-chloro-2-(methylthio)phenyl)-2-oxocyclohexanecarboxylate (19aj)



Compound **19aj** was obtained as colorless oil, 72 mg, 44%. R_f = 0.38 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 1H), 7.17 (dd, J = 8.4 Hz, J = 2.3 Hz, 1H), 6.99 (d, J = 2.3 Hz, 1H), 4.26-4.16 (m, 2H), 2.67-2.52 (m, 3H), 2.42-2.36 (m, 1H), 2.26 (s, 3H), 1.95-1.90 (m, 2H), 1.82-1.76 (m, 1H), 1.70-1.63 (m, 1H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.8, 170.4, 142.9, 136.5, 134.7, 132.9, 128.1, 127.8, 67.4, 62.1, 40.9, 37.0, 25.9, 22.3, 19.7, 13.9; IR (neat) ν 1729, 1709, 1205, 907, 728; EIMS *m/z* (%): 326 (100), 235 (55), 211 (37); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{16}H_{19}O_3ClSNa$, 349.0636; found 349.0636.

Ethyl 2-oxo-1-(phenylthio)cyclohexanecarboxylate (9)[6]



Compound **9** was obtained as colorless oil, 92 mg, 66%. R_f = 0.30 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 7.5 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.33-7.29 (m, 2H), 4.21-4.09 (m, 2H), 2.67 (d, J = 7.5 Hz, 1H), 2.50-2.40 (m, 2H), 2.02-2.00 (m, 1H), 1.88-1.70 (m, 3H), 1.62-1.55 (m, 1H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.9, 168.3, 137.1, 129.6, 128.5, 67.4,

[6] T, Tetsuaki, A. Tsutomu, F. Xie, U. Shuji, I. Chuzo, I. Toshimasa, I. Yasuko, M. Naoyoshi, *Synlett* **2000**, 32.

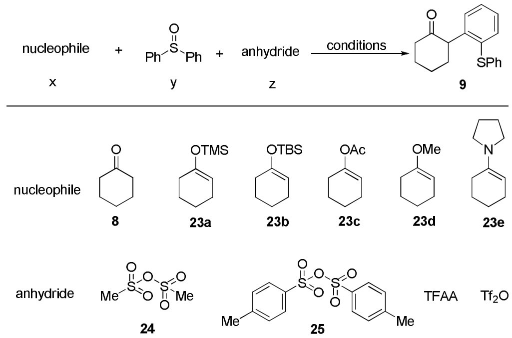
61.8, 40.8, 27.0, 22.8, 13.8; EIMS *m/z* (%): 278 (100), 250 (17), 176 (22), 110 (36), 67 (41); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{15}H_{18}O_3SNa$, 301.0869; found 301.0867.

1.6 Condition optimization of the arylation of cyclohexanone derivatives

We probed a wide range of reaction conditions and cyclohexanone derivatives. As the results in table S2 show, solvents have huge impacts on the reaction. When the reaction was run in high polar solvents, the reaction was dominated by the self-reduction of the sulfoxide (entries 3-5).[7] Similar results were obtained when the preformed enolate **23** was used instead of the normal ketone **8** (entry 6). To our delight, changing the reaction medium to toluene, and using toluenesulfonic anhydride **29** as activating reagent, the desired product **9** was isolated in much higher yield (entry 7). Several other solvents, such as acetone, diethyl ether and ethyl acetate, were also tested for this reaction, no improvements were observed (entries 8-10). Because of the low stability of **23** in the acidic environment, the effects of other preformed enolates were examined. Changing the protecting group from TMS to TBS or acyl group, resulted in no conversion of both reactants (entries 10 and 11). However, when 1-methoxycyclohex-1-ene **26** or bench stable enamine **27** were applied to the system, no arylated products were detected (entries 13 and 14). Raising the temperature to 50 ^{o}C, resulted in a higher reaction rate and slight yield increase, along with significant amounts of diphenyl sulfide (entry 15). Interestingly, adding the nucleophile **23a** and anhydride **25** in portions, gave the arylated product in high isolated yield (entry 16). In comparison, the addition of cyclohexanone in a similar manner, only trace product can be detected by TLC (entry 17).

[7] For a review on hypervalent Organosulfur Compounds, see: Furukawa, N.; Sato, S. *Top. Curr. Chem.* **1999**, *205*, 89.

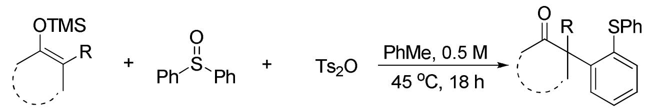
Table S2. Condition optimization of the arylation of cyclohexanone derivatives.[a]



entry	Nucleophile	anhydride	x/y/z	temp. (°C)	reaction time (h)	Solvent	yield (%)
1	**8**	TFAA	1:1.2:1.5	25	20	MeCN	9[b]
2	**8**	Tf_2O	1:1.2:1.5	25	1	DCM	-[c]
3	**8**	**24**	1:1.2:1.5	25	16	DCM	-[d]
4	**8**	**25**	1:1.2:1.5	25	16	DCM	-[d]
5	**8**	**25**	1:1.2:1.5	25	16	$MeNO_2$	-[d]
6	**23a**	**25**	1:1.2:1.5	25	20	DCM	-[d]
7	**23a**	**25**	1:1.2:1.5	25	20	PhMe	29[b]
8	**23a**	**25**	1.5:1:1.5	25	20	Me_2CO	33[e]
9	**23a**	**25**	1.5:1:1.5	25	20	Et_2O	13[e]
10	**23a**	**25**	1.5:1:1.5	25	20	AcOEt	30[e]
11	**23b**	**25**	1.5:1:1.5	25	20	AcOEt	-[c]
12	**23c**	**25**	1.5:1:1.5	25	20	Me_2CO	-[c]
13	**23d**	**25**	1.5:1:1.5	25	20	Me_2CO	-[c]
14	**23e**	**25**	1.5:1:1.5	25	20	Me_2CO	-[c]
15	**23a**	**25**	1.5:1:1.5	50	2	PhMe	32[b]
16	**23a**	**25**	**4:1:3**	**45**	**18**	**PhMe**	**65[b, f]**
17	**8**	**25**	4:1:3	45	5	PhMe	-[c, f]

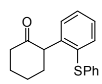
[a] The reaction was run in 0.5 mmol scale, and the concentration was 0.5 M. [b] Isolated yield after column chromatography. [c] Yield not determined. [d] Yield not determined, diphenylsulfide was obtained as main product. [e] NMR yield, using dibromomethane as internall standard. [f] **23a** and **25** were added in portions, each time in 0.5 mmol scale in an interval of 1 h. After the final addition of **23** (3h), the reaction was continuing stirred at 45 °C for 15 h.

1.7 Arylation of silyl enol ethers with diphenyl sulfoxide



Typical procedure: To a solution of silyl enol ether (0.5 mmol, 105 μL) and diphenyl sulfoxide (104 mg, 0.5 mmol) in dry toluene (1 mL, 0.5 M), was added toluenesulfonic anhydride (163 mg, 0.5 mmol). After stirring at 45 °C for 1h, 1.0 equivalent of silyl enol ether and anhydride were added to the mixture. 1h later, another potion of each was added. After stirring at 45 °C for one more hour, 1.0 further equivalent of silyl enol ether was added to the reaction mixture. After stirring for 15h at 45 °C, the mixture was allowed to cool to room temperature, poured into saturated aqueous $NaHCO_3$ (15 mL), and extracted with CH_2Cl_2 (20 mL x 3). The combined organic layers were dried over andydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel, *iso*-Hexane/ethyl acetate = 7/1, and provided the desired product.

2-(2-(phenylthio)phenyl)cyclohexanone (9) [8]



Compound **9** was obtained as colorless oil, 92 mg, 65% yield, R_f = 0.46 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.19-7.13 (m, 4H), 7.08-7.05 (m, 3H), 4.25-4.21 (m, 1H), 2.42-2.24 (m, 2H), 2.11-2.05 (m, 2H), 1.96-1.87 (m, 2H), 1.79-1.67 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.5, 141.7, 137.4, 134.8, 133.3, 129.3, 129.0, 128.8, 128.5, 127.7, 126.1, 54.8, 42.2, 35.0, 27.6, 25.6.

2-methyl-2-(2-(phenylthio)phenyl)cyclohexanone (26)

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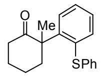
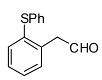
8 Martin, J. C.; Franz, J. A.; Arhart, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 4604-4611.



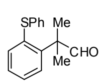
Compound **26** was obtained as colorless oil, 95 mg, 64% yield, R_f = 0.37 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.9 Hz, *J* = 1.2 Hz, 1H), 7.30 (dd, *J* = 7.8 Hz, *J* = 1.3 Hz, 1H), 7.24 (dt, *J* = 7.5 Hz, *J* = 1.4 Hz, 1H),7.16-7.11 (m, 3H), 7.10-7.06 (m, 3H), 2.52-2.48 (m, 1H), 2.39-2.33 (m, 2H), 2.04-2.02 (m, 1H), 1.82-1.80 (m, 1H), 1.79-1.72 (m, 3H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.5, 148.0, 137.3, 136.1, 133.2, 128.9, 128.8, 128.2, 127.5, 127.1, 126.3, 54.8, 41.2, 39.1, 26.6, 24.9, 21.8; EIMS *m/z* (%): 296 (56), 225 (29), 187 (100); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{19}H_{20}OSNa$, 319.1127; found 319.1126.

2-(2-(Phenylthio)phenyl)acetaldehyde (27)



Compound **27** was obtained as colorless oil, 38 mg, 33 % yield, R_f = 0.49 (*iso*-Hexane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.57 (t, 1H), 7.39-7.36 (t, *J* = 1.8 Hz, 6H), 7.28-7.05 (m, 8H), 3.77 (d, *J* = 1.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.3, 136.4, 135.6, 135.1, 134.7, 131.9, 129.8, 129.7, 129.2, 129.1, 127.1, 49.2; IR (neat) ν 1713, 1581, 736, 685; EIMS *m/z* (%):228 (88), 200 (100), 165 (37); HRMS-(EI) (*m/z*): M^+ calcd for $C_{19}H_{20}OS$, 228.0609; found 228.0611.

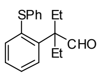
2-Methyl-2-(2-(phenylthio)phenyl)propanal (28)



Compound **28** was obtained as colorless oil, 93 mg, 73% yield, R_f = 0.54 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.39 (dd, *J* = 7.9 Hz, *J* = 1.5 Hz, 1H), 7.35 (dd, *J* = 7.8 Hz, *J* = 1.4 Hz, 1H), 7.29 (dt, *J* = 7.4 Hz, *J* = 1.5 Hz, 1H), 7.20-7.12 (m, 3H), 7.09-7.06 (m, 1H), 7.03-7.01 (m, 2H), 1.40 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.2, 147.0, 137.2, 136.3, 132.4, 129.0, 128.7, 128.35, 128.33, 127.4, 126.3, 51.0, 24.7; IR (neat) ν 1712, 1583, 735, 685; EIMS *m/z* (%):

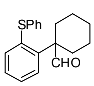
256 (49), 228 (100), 211 (46), 134 (378); HRMS-(ESIpos) (*m/z*): M^+ calcd for $C_{16}H_{16}OSNa$, 279.0814; found 279.0813.

2-Ethyl-2-(2-(phenylthio)phenyl)butanal (29)



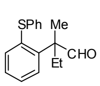
Compound **29** was obtained as pale yellow oil, 65 mg, 46 % yield, R_f = 0.30 (pentane/diethyl ether = 15/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.41-7.29 (m, 3H), 7.23-7.05 (m, 4H), 7.02-7.98 (m, 2H), 2.10-1.86 (m, 4H), 0.71 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.5, 144.5, 137.8, 137.1, 132.-8, 129.4, 129.0, 128.3, 128.2, 128.0, 126.2, 57.9, 26.7, 8.0; IR (neat) ν 1714, 1582, 1025, 736, 689; EIMS *m/z* (%): 284 (67), 256 (69), 227, (100), 197 (56); HRMS-(EI) (*m/z*): M^+ calcd for $C_{18}H_{20}OS$, 284.1235; found 284.1235.

1-(2-(Phenylthio)phenyl)cyclohexanecarbaldehyde (30)



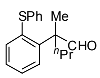
Compound **30** was obtained as colorless oil, 63 mg, 43 % yield, R_f = 0.49 (*iso*-Hexane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.0 (s, 1H), 7.46 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1H), 7.32-7.24 (m, 2H), 7.17-7.06 (m, 4H), 7.20-7.12 (m, 3H), 6.99-6.97 (m, 2H), 2.23-2.19 (m, 2H), 1.89-1.82 (m, 2H), 1.67-1.56 (m, 5H), 1.36-1.33 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.7, 148.3, 137.6, 136.6, 132.8, 129.0, 128.44, 128.39, 128.10, 127.98, 1326.3, 53.9, 33.9, 25.5, 22.7; IR (neat) ν 1716, 1583, 1020, 737, 688; EIMS *m/z* (%): 296 (45), 268 (100), 197 (87); HRMS-(ESIpos) (*m/z*): $[M+Na]^+$ calcd for $C_{19}H_{20}OSNa$, 319.1127; found 319.1126.

2-Methyl-2-(2-(phenylthio)phenyl)butanal (31)



Compound **31** was obtained as colorless oil, 85 mg, 63% yield, R_f = 0.57 (*iso*-Hexane/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.38-7.34 (m, 2H), 7.32 (dt, *J* = 7.2 Hz, *J* = 1.5 Hz, 1H), 7.21-7.14 (m, 3H), 7.07 (tt, *J* = 7.4 Hz, *J* = 1.2 Hz, 1H), 7.03-7.00 (m, 2H), 2.00 (q, *J* = 7.5 Hz, 2H), 1.35 (s, 3H), 0.69 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.8, 145.5, 137.5, 136.6, 132.5, 129.0, 128.7, 128.5, 128.3, 128.2, 126.3, 54.7, 29.7, 21.4, 8.3; IR (neat) ν 1713, 1581, 1024, 735, 688; EIMS *m/z* (%): 270 (43), 242 (96), 211 (100), 197 (52); HRMS-(ESIpos) (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{18}OSNa$, 293.0971; found 293.0972.

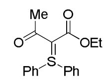
2-Methyl-2-(2-(phenylthio)phenyl)pentanal (32)



Compound **32** was obtained as pale yellow oil, 57 mg, 40 % yield, R_f = 0.43 (pentane/diethyl ether = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.39-7.27 (m, 3H), 7.22-6.66 (m, 6H), 1.92-1.87 (m, 2H), 1.36 (s, 3H), 1.25-1.18 (m, 2H), 0.92-0.82 (m, 2H), 0.73 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.7, 145.8, 137.5, 136.8, 132.4129.0, 128.60, 128.55, 128.2, 128.1, 126.3, 54.6, 39.3, 22.0, 17.2, 14.4; IR (neat) ν 1714, 1582, 736, 689; EIMS *m/z* (%): 284 (50), 256 (100), 211 (87), 197 (48); HRMS-(ESIpos) (*m/z*): $[M+Na]^+$ calcd for $C_{18}H_{20}OSNa$, 307. 1127; found 307.1129.

1.8 X-ray crystal structure of 16a and 19aa

The crystal was prepared by slow diffusion of pentane to the solution of **16a** in dichloromethane, and was found suitable for X-ray crystal analysis.



16a

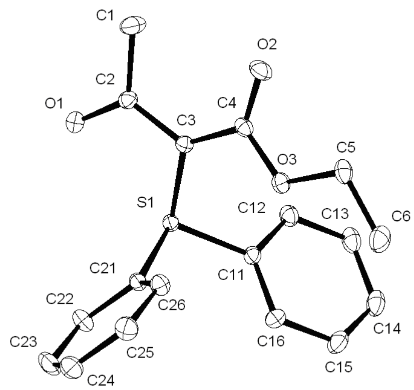
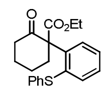


Figure S1. Solid state structure of **16a.**

The crystal was prepared by slow diffusion of pentane to the solution of **19aa** in diethyl ether, and was suitable for X-ray crystallographic analysis. Cambridge Crystallographic Data Centre number: 798559



19aa

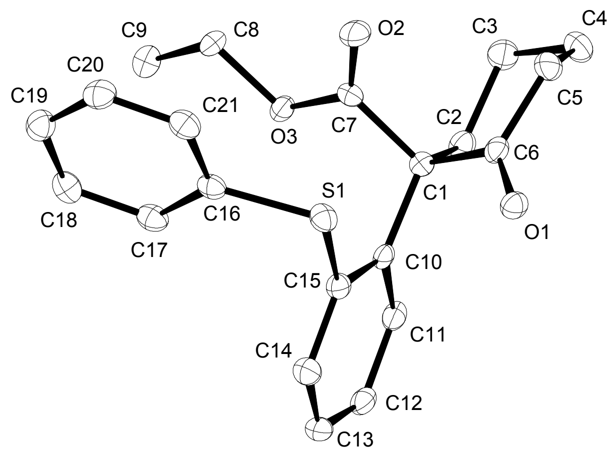
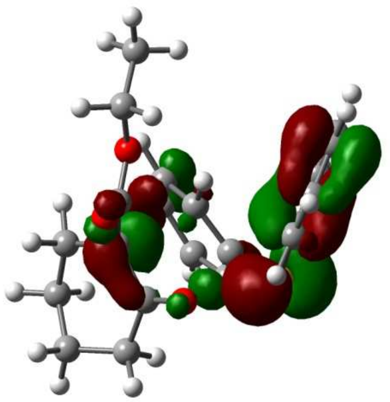


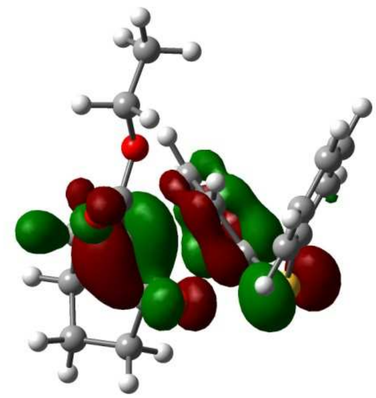
Figure S2. Solid state structure of **19aa**

Part II Mechanistic studies

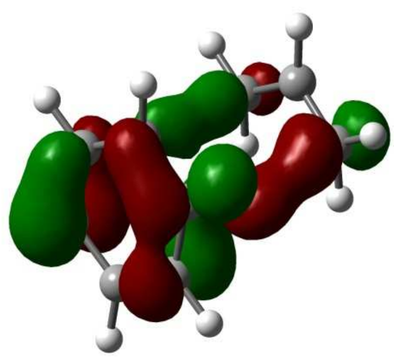
2.1 Computational details



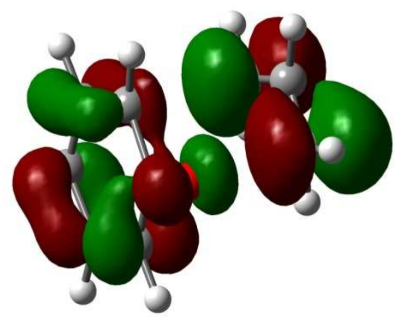
TS (38→39) HOMO



TS (38→39) LUMO



HOMO



LUMO

Ortho-Claisen rearrangement of allyl phenyl ether

Figure S3. Frontier molecular orbitals of **TS (38→39)** and of a transition state for a typical sigmatropic rearrangements (B3LYP).

Table S3. Optimized geometries (B3LYP-I, Cartesian coordinates in Å) and single-point energies of reactants, intermediates and transition states (in a.u.). Notation: E = total electronic energy from B3LYP-I (in parenthesis: B3LYP-II), Tc = thermal correction at 298K to obtain the Gibbs free energy (B3LYP-I), Nimag = number of imaginary frequencies (B3LYP-I). See main paper for notation of the species and for computational methodology.

15a
E = -460.3907561 (-460.406968)
Tc = 0.117416 Nimag = 0

6	1.094034	0.497672	-0.797980
6	1.985042	-0.266845	0.184630
6	3.298344	-0.764737	-0.366258
1	3.813743	0.024062	-0.923502
1	3.931906	-1.130563	0.443037
8	1.643023	-0.459592	1.341648
6	-0.256603	0.841623	-0.210399
8	-1.132319	-0.160308	-0.366976
8	-0.516579	1.895229	0.345857
6	-2.467371	0.025871	0.189629
1	-2.906634	0.916200	-0.268251
1	-2.367217	0.201287	1.264085
6	-3.267581	-1.225010	-0.112381
1	-4.277713	-1.113345	0.293942
1	-3.348336	-1.390471	-1.190927
1	-2.809286	-2.106501	0.345882
1	1.609029	1.424923	-1.070294
1	0.981608	-0.097797	-1.709831
1	3.104713	-1.581879	-1.071829

$^{-}OC(CF_3)_2Ph$
E = -1020.4393113 (-1020.467863)
Tc = 0.086435 Nimag = 0

8	-0.795009	0.000466	-1.869297
6	-1.195949	-1.281213	0.091291
9	-1.119148	-1.371611	1.454964
9	-0.600395	-2.403976	-0.389852
9	-2.516134	-1.393416	-0.205925
6	-0.540307	0.000125	-0.562553
6	-1.195270	1.281450	0.092040
6	0.986971	-0.000170	-0.193631
6	1.502473	-0.001054	1.113065
6	1.886206	0.000632	-1.265996
6	2.884129	-0.001217	1.333633
1	0.838483	-0.001654	1.969200
6	3.267463	0.000528	-1.049240
1	1.470126	0.001277	-2.267568
6	3.773052	-0.000415	0.254285
1	3.263363	-0.001957	2.352002
1	3.947126	0.001165	-1.897376
1	4.845541	-0.000519	0.428027
9	-1.116345	1.372053	1.455576
9	-2.515945	1.393394	-0.203172
9	-0.600608	2.404218	-0.390177

34
E = -1881.5821275 (-1881.6475001)
Tc = 0.257009 Nimag = 0

8	0.100403	0.050943	0.137004
6	1.676702	0.676132	-1.676579
9	2.962295	0.599769	-2.053345
9	1.395686	1.960041	-1.389493
9	0.917330	0.321729	-2.737712
16	-1.356822	0.004368	-0.740644
6	-2.197679	-1.319943	0.123307
6	-1.889763	-1.660599	1.444560
6	-3.175195	-1.990252	-0.621283
6	-2.603170	-2.703238	2.036221
1	-1.106014	-1.148295	1.989685
6	-3.884839	-3.020905	-0.002201
1	-3.380202	-1.722924	-1.652849

5
E = -2902.0432356 (-2902.1631825)
Tc = 0.368413 Nimag = 0

8	1.771568	-0.448495	-0.127931
6	2.469241	1.401461	1.273925
9	3.138034	2.578280	1.339615
9	2.967420	0.606210	2.243435
9	1.184748	1.676233	1.608404
16	-0.223401	-0.525445	0.192062
6	-0.205762	-1.979911	-0.907272
6	0.316097	-1.827535	-2.193580
6	-0.765566	-3.187629	-0.484324
6	0.284151	-2.916581	-3.067838
1	0.749010	-0.888140	-2.510207
6	-0.783004	-4.269429	-1.366625
1	-1.187351	-3.288416	0.508102

6	-3.599484	-3.375317	1.319387	6	-0.258641	-4.136811	-2.655984
1	-2.376341	-2.988791	3.057927	1	0.689393	-2.806132	-4.068646
1	-4.648022	-3.552021	-0.560766	1	-1.210489	-5.212964	-1.042498
1	-4.148193	-4.184362	1.790477	1	-0.275366	-4.981318	-3.337953
6	-2.094881	1.522373	-0.194530	6	0.055939	-1.290148	1.838408
6	-2.119338	2.546562	-1.155756	6	-0.756354	-0.930653	2.915762
6	-2.633711	1.692727	1.089422	6	1.108624	-2.196990	1.999061
6	-2.682490	3.773876	-0.808165	6	-0.501656	-1.484996	4.174128
1	-1.718310	2.389388	-2.151339	1	-1.591162	-0.258691	2.785178
6	-3.187347	2.927495	1.415548	6	1.342241	-2.751116	3.257959
1	-2.630345	0.887492	1.813900	1	1.742750	-2.458407	1.163200
6	-3.210294	3.963408	0.472247	6	0.542844	-2.394238	4.348449
1	-2.712126	4.574900	-1.538717	1	-1.132490	-1.204656	5.011630
1	-3.607382	3.079386	2.403959	1	2.154566	-3.460309	3.381683
1	-3.650350	4.919516	0.736704	1	0.732259	-2.825220	5.326618
6	1.407911	-0.220726	-0.418570	6	2.566227	0.684705	-0.117727
6	1.468834	-1.739573	-0.789051	6	2.112130	1.657922	-1.263111
6	2.386717	0.168660	0.699116	6	4.040178	0.264090	-0.379339
6	3.628648	-0.467632	0.846400	6	5.104213	1.180065	-0.355389
6	2.047149	1.226877	1.556402	6	4.310964	-1.081549	-0.658548
6	4.510059	-0.054105	1.846960	6	6.411270	0.750449	-0.601062
1	3.930425	-1.274340	0.191115	1	4.931500	2.228080	-0.147674
6	2.933557	1.631603	2.555530	6	5.618787	-1.507319	-0.905640
1	1.095335	1.732022	1.452655	1	3.492528	-1.789300	-0.681780
6	4.166405	0.992683	2.705396	6	6.674970	-0.593593	-0.877105
1	5.466625	-0.556171	1.950175	1	7.221559	1.472975	-0.576075
1	2.655692	2.448419	3.213918	1	5.807979	-2.554964	-1.120497
1	4.854607	1.308495	3.483222	1	7.691700	-0.923936	-1.068122
9	2.583155	-2.055981	-1.472898	9	2.839602	2.796845	-1.343451
9	0.413151	-2.084595	-1.562336	9	0.818952	2.033690	-1.134257
9	1.416580	-2.497716	0.316678	9	2.222240	1.035408	-2.459792
				8	-2.113714	-0.681784	0.504716
				6	-3.029387	0.170300	-0.130164
				6	-2.663488	1.672659	-0.135034
				6	-2.940361	2.530717	-1.211063
				6	-2.088915	2.219541	1.022291
				6	-2.635627	3.892389	-1.131532
				1	-3.395960	2.163597	-2.120848
				6	-1.788301	3.579472	1.102780
				1	-1.873505	1.587146	1.873037
				6	-2.059690	4.423791	0.023723
				1	-2.853811	4.534445	-1.979394
				1	-1.340573	3.973956	2.009643
				1	-1.825073	5.482251	0.082677
				6	-4.339951	-0.009012	0.726368
				6	-3.309553	-0.382270	-1.574078
				9	-4.823874	-1.269246	0.676156
				9	-5.331039	0.815541	0.319985
				9	-4.098802	0.268107	2.024842
				9	-3.445737	-1.720633	-1.579134
				9	-2.281090	-0.086394	-2.402967
				9	-4.435521	0.125144	-2.135056

(15a + $^{-}$OC(CF$_3$)$_2$Ph) E = -1480.8300702 (-1480.8789143) Tc = 0.218943 Nimag = 0				**TS(15a→35)** E = -1480.8212153 (-1480.8772223) Tc = 0.221548 Nimag = 1 (-1248.85 cm^{-1})			
6	-2.838811	1.169842	0.549669	6	-2.299078	0.970355	1.008100
6	-3.139188	2.653248	0.366802	6	-2.362118	2.433493	0.904706
6	-4.420455	3.176485	0.970178	6	-2.781153	3.108113	-0.387089
1	-4.352386	3.119570	2.063664	1	-2.669709	4.189131	-0.280028
1	-4.591285	4.211661	0.670848	1	-2.179700	2.750253	-1.227018
8	-2.357868	3.383341	-0.227490	8	-2.016799	3.140520	1.869411

6	-3.626679	0.315610	-0.422772	6	-3.146738	0.101359	0.184283
8	-3.644081	-0.968630	-0.038088	8	-3.354821	-1.098406	0.805553
8	-4.159309	0.726324	-1.442052	8	-3.613252	0.329250	-0.930933
6	-4.312042	-1.921641	-0.916881	6	-4.101917	-2.098004	0.073642
1	-3.826035	-1.884291	-1.895505	1	-3.587932	-2.303742	-0.870378
1	-5.353249	-1.609185	-1.033839	1	-5.094457	-1.700437	-0.160348
6	-4.196947	-3.290290	-0.276133	6	-4.189828	-3.337899	0.944556
1	-4.690621	-4.029807	-0.914495	1	-4.751525	-4.115926	0.417257
1	-3.149466	-3.583186	-0.158394	1	-3.194021	-3.729889	1.173782
1	-4.679896	-3.307729	0.705532	1	-4.704880	-3.122375	1.886035
1	-1.767935	0.974112	0.378301	1	-0.987513	0.667711	0.719000
8	0.302196	0.599330	0.115625	8	0.250709	0.444449	0.846091
6	1.113534	-1.464475	-0.739808	6	1.084427	1.034858	-1.317005
9	2.069738	-2.442426	-0.696665	9	1.831759	0.673606	-2.394102
9	1.038028	-1.074878	-2.039263	9	1.565702	2.226462	-0.891998
9	-0.058650	-2.090107	-0.460221	9	-0.166355	1.263361	-1.784873
6	1.359966	-0.208482	0.187053	6	1.090885	0.001553	-0.136322
1	-3.080931	0.851531	1.569317	1	-2.280719	0.652919	2.052077
1	-5.270374	2.553749	0.671415	1	-3.820150	2.860336	-0.624911
6	1.523992	-0.712298	1.676346	6	0.584015	-1.393056	-0.646716
6	2.714439	0.454650	-0.250387	6	2.543822	-0.150490	0.394702
6	2.646127	1.787285	-0.673081	6	2.782649	0.169859	1.736704
6	3.965534	-0.184056	-0.245536	6	3.617609	-0.587281	-0.398189
6	3.793672	2.474061	-1.080448	6	4.065448	0.057918	2.280360
1	1.672077	2.264318	-0.672135	1	1.950533	0.507180	2.342150
6	5.115870	0.500856	-0.652146	6	4.900296	-0.698933	0.146599
1	4.058632	-1.215365	0.073683	1	3.469598	-0.843046	-1.439935
6	5.035858	1.832597	-1.070860	6	5.130400	-0.377276	1.487200
1	3.717006	3.508580	-1.404690	1	4.229752	0.311684	3.323765
1	6.074961	-0.009934	-0.640232	1	5.718723	-1.038230	-0.481799
1	5.930650	2.362350	-1.385746	1	6.128103	-0.464973	1.907521
9	2.502229	-1.643899	1.895280	9	1.300363	-1.918414	-1.676377
9	0.382995	-1.264699	2.162918	9	-0.701779	-1.342132	-1.068502
9	1.818119	0.334940	2.490878	9	0.629743	-2.297828	0.359036

(35 + HOC(CF_3)$_2$Ph) E = -1480.831974 (-1480.8872175) Tc = 0.222754 Nimag = 0				**(34 +35)** E = -2341.5143652 (-2341.6127089) Tc = 0.387050 Nimag = 0			
6	2.699411	-0.642704	1.143555	6	-3.763834	-1.589123	-0.827945
6	2.703619	-2.064692	1.105738	6	-2.413832	-1.362658	-0.777528
6	3.268032	-2.813259	-0.096456	6	-1.446974	-2.496372	-1.013303
1	4.359829	-2.719889	-0.124122	1	-0.857013	-2.706529	-0.114795
1	3.003761	-3.870132	-0.010680	1	-1.981456	-3.407214	-1.286780
8	2.238929	-2.754381	2.059423	8	-1.934035	-0.139014	-0.570603
6	3.330193	0.234067	0.206427	6	-4.812314	-0.611098	-0.578900
8	3.245973	1.553727	0.628648	8	-6.040859	-1.178162	-0.772184
8	3.895907	-0.033976	-0.865180	8	-4.694326	0.562331	-0.231261
6	3.832476	2.551384	-0.227936	6	-7.195340	-0.335217	-0.544062
1	3.355543	2.511400	-1.213137	1	-7.128198	0.540466	-1.196931
1	4.897372	2.333396	-0.364170	1	-7.178656	0.013768	0.493249
6	3.626895	3.905593	0.429058	6	-8.434502	-1.159978	-0.838052
1	4.061997	4.690158	-0.199060	1	-9.327156	-0.547753	-0.674102
1	2.561693	4.122474	0.558775	1	-8.441319	-1.503978	-1.877045
1	4.110992	3.944976	1.410230	1	-8.492574	-2.033069	-0.180603
1	0.682470	-0.348287	0.693164	1	-4.096443	-2.587236	-1.085649
8	-0.237127	-0.054765	0.922648	1	-0.742398	-2.243008	-1.812329
6	-1.258700	-1.687395	-0.508698	16	-0.108285	0.119858	0.051050
9	-2.054852	-1.922688	-1.575800	6	-0.289902	1.827986	-0.555606
9	-1.750063	-2.397028	0.527516	6	-0.618585	2.009468	-1.900214
9	-0.042654	-2.201441	-0.803185	6	-0.058959	2.908392	0.296216
6	-1.159909	-0.174405	-0.119453	6	-0.720672	3.310765	-2.397940
1	2.370446	-0.190383	2.075772	1	-0.801976	1.159890	-2.546748

1	2.899266	-2.407181	-1.041166
6	-0.650397	0.682614	-1.325746
6	-2.524933	0.345925	0.364167
6	-2.635786	0.850359	1.666620
6	-3.658635	0.331348	-0.463309
6	-3.861193	1.332140	2.134652
1	-1.765742	0.864920	2.310261
6	-4.881273	0.813667	0.009677
1	-3.603451	-0.051074	-1.474686
6	-4.987905	1.315773	1.309251
1	-3.930440	1.719408	3.146723
1	-5.748921	0.794920	-0.642707
1	-5.939696	1.690107	1.674126
9	-1.433195	0.591107	-2.423986
9	0.598023	0.318010	-1.697491
9	-0.596808	1.984027	-0.974712

6	-0.169593	4.203523	-0.214763
1	0.207572	2.751339	1.334490
6	-0.499372	4.406165	-1.558368
1	-0.977633	3.462408	-3.441488
1	0.003479	5.050851	0.441111
1	-0.583684	5.415228	-1.949750
6	-0.672843	0.244893	1.806512
6	0.203962	-0.065514	2.850162
6	-1.996912	0.623677	2.063720
6	-0.259123	-0.006321	4.168643
1	1.234697	-0.315275	2.652246
6	-2.435597	0.688801	3.387893
1	-2.680709	0.845811	1.253965
6	-1.574664	0.370138	4.441910
1	0.422843	-0.250132	4.977130
1	-3.460016	0.987102	3.588134
1	-1.926785	0.417693	5.467751
8	1.718676	0.487282	0.632335
6	2.796775	-0.050943	-0.074097
6	4.015907	0.140320	0.904409
6	3.049406	0.832239	-1.349031
6	2.689195	-1.557121	-0.413932
6	3.174602	-2.119418	-1.604931
6	2.134422	-2.413648	0.549893
6	3.091580	-3.497228	-1.826733
1	3.623738	-1.506103	-2.374978
6	2.056545	-3.789537	0.329932
1	1.761913	-2.012453	1.483296
6	2.534067	-4.338698	-0.862506
1	3.468471	-3.907568	-2.758609
1	1.621922	-4.428108	1.092913
1	2.472882	-5.408533	-1.037282
9	4.272677	0.646905	-1.905654
9	2.130008	0.555777	-2.304693
9	2.945523	2.145310	-1.074144
9	5.154597	-0.407116	0.421882
9	3.764578	-0.449514	2.092879
9	4.276478	1.441328	1.158780

TS(35→36)
E = -2341.500302 (-2341.5945057)
Tc = 0.382572 Nimag = 1 (-27.70 cm^{-1})

6	-2.979513	-1.369628	-1.761106
6	-1.984751	-2.371818	-1.782788
6	-1.047072	-2.382420	-2.992411
1	-1.131261	-3.348568	-3.503995
1	-1.257828	-1.585756	-3.711655
8	-1.784241	-3.259641	-0.899984
6	-4.021457	-1.224631	-0.792403
8	-4.852071	-0.157588	-1.120180
8	-4.257296	-1.894438	0.223418
6	-5.961269	0.100146	-0.240573
1	-5.586072	0.321087	0.764908
1	-6.587805	-0.795762	-0.171431
6	-6.740772	1.274592	-0.807207
1	-7.593260	1.500077	-0.157698
1	-6.113465	2.169494	-0.871585
1	-7.123623	1.047052	-1.807404
1	-3.008518	-0.669609	-2.588307
1	-0.009602	-2.288569	-2.651751
16	-0.043761	0.177363	0.316461
6	-1.012161	1.668242	0.192232

35 + $^{-}OC(CF_3)_2Ph$
E = -2341.5410652 (-2341.6352825)
Tc = 0.379269 Nimag = 0

6	-1.333775	0.719686	-0.727984
6	-1.561088	0.791968	-2.254641
6	-1.015156	-0.329855	-3.095655
1	-0.983051	-0.013037	-4.139006
1	-0.020729	-0.626232	-2.750817
8	-2.118139	1.769450	-2.720814
6	-1.919040	1.930463	-0.007185
8	-1.036017	2.923995	-0.038295
8	-3.019893	1.989720	0.507149
6	-1.452386	4.204916	0.537301
1	-1.690536	4.035618	1.590259
1	-2.358669	4.527043	0.018558
6	-0.307771	5.179052	0.355126
1	-0.592867	6.146449	0.780165
1	0.592859	4.830079	0.868245
1	-0.077876	5.323746	-0.704421
1	-0.226849	0.653526	-0.559398
1	-1.669410	-1.207012	-3.021848
16	-1.834504	-0.940336	-0.049343
6	-1.904305	-0.700694	1.748390

6	-1.390643	2.020837	-1.112166	6	-0.671761	-0.484731	2.374325
6	-1.371520	2.442449	1.304295	6	-3.100122	-0.813035	2.458415
6	-2.127106	3.189286	-1.302407	6	-0.657162	-0.351771	3.765176
1	-1.128356	1.392356	-1.955286	1	0.241477	-0.411007	1.783043
6	-2.107890	3.605560	1.092060	6	-3.056271	-0.689889	3.849621
1	-1.097734	2.149731	2.310159	1	-4.042905	-0.990524	1.955852
6	-2.481233	3.979414	-0.205000	6	-1.841717	-0.456002	4.500961
1	-2.429130	3.473648	-2.304610	1	0.286993	-0.175297	4.270677
1	-2.394948	4.216815	1.941004	1	-3.976511	-0.774683	4.418522
1	-3.058761	4.885546	-0.357537	1	-1.818322	-0.359481	5.581900
6	-0.413740	-0.558252	1.906696	6	-3.490221	-1.358341	-0.615023
6	0.107389	-0.040065	3.099755	6	-3.630478	-2.696725	-1.010142
6	-1.238299	-1.687312	1.862030	6	-4.553724	-0.451201	-0.693677
6	-0.231484	-0.675938	4.292848	6	-4.869540	-3.134674	-1.481046
1	0.776291	0.812379	3.100360	1	-2.791302	-3.382368	-0.953818
6	-1.571320	-2.295338	3.076605	6	-5.780623	-0.906790	-1.179435
1	-1.603377	-2.102844	0.922483	1	-4.424528	0.576171	-0.377249
6	-1.074242	-1.794704	4.281893	6	-5.940462	-2.240914	-1.568072
1	0.166093	-0.297603	5.228789	1	-4.989718	-4.168600	-1.786861
1	-2.211316	-3.171497	3.069469	1	-6.612955	-0.214063	-1.249246
1	-1.332239	-2.282025	5.216841	1	-6.900183	-2.582781	-1.942501
8	1.480515	0.838780	0.681334	8	1.322268	-0.153475	-0.067422
6	2.623473	0.568894	-0.168060	6	2.644039	0.014534	-0.222627
6	3.812779	1.020567	0.760598	6	3.148376	1.064852	0.839904
6	2.512933	1.546019	-1.388066	6	2.917006	0.583226	-1.666681
6	2.782441	-0.901981	-0.551671	6	3.473131	-1.300239	-0.045805
6	3.195668	-1.311157	-1.829508	6	4.869219	-1.385405	-0.171384
6	2.555882	-1.876354	0.436463	6	2.754543	-2.462695	0.256528
6	3.364073	-2.668142	-2.111327	6	5.524638	-2.608548	0.004519
1	3.394843	-0.595360	-2.615638	1	5.457678	-0.506475	-0.405460
6	2.720012	-3.230369	0.146059	6	3.407716	-3.685954	0.433232
1	2.255778	-1.587297	1.436323	1	1.677224	-2.381732	0.347070
6	3.125407	-3.631180	-1.129053	6	4.797804	-3.763739	0.308052
1	3.680237	-2.966883	-3.105527	1	6.605463	-2.655079	-0.095960
1	2.532633	-3.967507	0.919952	1	2.830779	-4.576400	0.667984
1	3.253884	-4.684978	-1.355193	1	5.309577	-4.712194	0.444704
9	3.664237	1.638986	-2.078095	9	4.207286	0.943759	-1.926637
9	1.549771	1.116504	-2.234932	9	2.588043	-0.345836	-2.601788
9	2.169139	2.784025	-0.997597	9	2.163652	1.678917	-1.936008
9	4.989925	0.801629	0.147563	9	4.471884	1.391719	0.770738
9	3.806192	0.325566	1.910812	9	2.943295	0.585987	2.093747
9	3.747285	2.326742	1.078975	9	2.474222	2.239590	0.761170

TS(36→16a) E = -2341.5356879 (-2341.6339353) Tc = 0.379642 NImag = 1 (-1096.69 cm^{-1})				**(16a + HOC(CF_3)$_2$Ph)** E = -2341.5723308 (-2341.6596874) Tc = 0.385163 NImag = 0			
6	-1.142101	0.768297	-0.473265	6	-1.969602	-0.211518	0.124196
6	-1.177886	1.300945	-1.891936	6	-0.630041	-0.203407	-0.403824
6	-0.866325	0.343432	-3.023472	6	-0.387482	-0.003324	-1.897981
1	-0.534550	0.923101	-3.886638	1	0.688204	-0.004847	-2.074861
1	-0.103012	-0.384855	-2.740961	1	-0.840350	-0.802821	-2.491500
8	-1.405198	2.484610	-2.109644	8	0.370069	-0.344738	0.339693
6	-1.589892	1.725081	0.600901	6	-2.385042	-0.386653	1.513671
8	-0.749208	2.755513	0.692086	8	-1.392675	-0.703456	2.369748
8	-2.565128	1.577782	1.324543	8	-3.554190	-0.264725	1.887678
6	-1.069992	3.789126	1.669573	6	-1.773107	-0.882935	3.760148
1	-1.060615	3.333110	2.663260	1	-2.513052	-1.686257	3.821488
1	-2.079930	4.154034	1.464418	1	-2.239555	0.038709	4.119927
6	-0.030316	4.883376	1.535240	6	-0.513782	-1.217295	4.536663
1	-0.245343	5.673749	2.261351	1	-0.767634	-1.366132	5.591182
1	0.974364	4.499092	1.733165	1	-0.052043	-2.135926	4.162075
1	-0.048342	5.323141	0.533717	1	0.217834	-0.406307	4.471108

1	0.125627	0.400560	-0.316361	1	1.928062	-0.415039	-0.120054
1	-1.772551	-0.201930	-3.313119	1	-0.799777	0.945305	-2.255217
16	-1.904734	-0.898215	-0.401443	16	-3.245594	-0.005538	-1.057172
6	-1.931652	-1.408534	1.340995	6	-4.469983	-1.336285	-0.919723
6	-0.700572	-1.777064	1.892781	6	-4.260267	-2.420687	-1.779276
6	-3.126808	-1.525341	2.051806	6	-5.563770	-1.293208	-0.051168
6	-0.675207	-2.253332	3.206017	6	-5.154997	-3.493331	-1.750904
1	0.213275	-1.671365	1.316507	1	-3.416766	-2.431640	-2.462121
6	-3.081279	-2.017684	3.358308	6	-6.457138	-2.366697	-0.044802
1	-4.073486	-1.239707	1.610687	1	-5.709581	-0.449500	0.610076
6	-1.860526	-2.377764	3.936628	6	-6.252697	-3.465518	-0.886313
1	0.274172	-2.535080	3.650277	1	-4.997799	-4.338955	-2.412742
1	-4.004069	-2.112778	3.921660	1	-7.310788	-2.344146	0.625403
1	-1.834059	-2.757309	4.953302	1	-6.951757	-4.295987	-0.871411
6	-3.622724	-0.863354	-0.956270	6	-4.169612	1.525690	-0.729331
6	-4.001738	-1.972088	-1.725244	6	-5.323663	1.770344	-1.480595
6	-4.507928	0.190740	-0.703486	6	-3.646122	2.484912	0.136333
6	-5.300342	-2.030660	-2.235339	6	-5.978548	2.995094	-1.332525
1	-3.297436	-2.773150	-1.926056	1	-5.714782	1.024948	-2.165469
6	-5.798270	0.120416	-1.233129	6	-4.309447	3.708263	0.269953
1	-4.200434	1.033224	-0.097326	1	-2.739920	2.285936	0.696793
6	-6.195389	-0.984932	-1.992550	6	-5.474455	3.963479	-0.458225
1	-5.603318	-2.886653	-2.829395	1	-6.879111	3.190158	-1.906190
1	-6.493855	0.931960	-1.044932	1	-3.911797	4.457415	0.947344
1	-7.201450	-1.028928	-2.397728	1	-5.985996	4.914622	-0.348991
8	1.204491	-0.339826	-0.280025	8	2.827714	-0.676003	-0.489953
6	2.511197	0.048058	-0.196524	6	3.901898	0.102694	-0.071422
6	2.775114	0.588375	1.254148	6	4.017657	-0.016120	1.485825
6	2.772017	1.180559	-1.249204	6	3.631323	1.584315	-0.499847
6	3.477287	-1.136424	-0.476217	6	5.191303	-0.415929	-0.737651
6	4.875908	-1.013721	-0.455647	6	6.441986	0.180796	-0.512475
6	2.913408	-2.386532	-0.759142	6	5.108648	-1.522713	-1.592892
6	5.687471	-2.122369	-0.714159	6	7.586013	-0.324661	-1.135006
1	5.346011	-0.062032	-0.240490	1	6.540194	1.036853	0.143197
6	3.725700	-3.494323	-1.017356	6	6.255800	-2.025159	-2.212831
1	1.834167	-2.477129	-0.774444	1	4.147512	-1.987930	-1.769676
6	5.117018	-3.366883	-0.995763	6	7.498461	-1.428600	-1.987145
1	6.767469	-2.008753	-0.694178	1	8.545462	0.148780	-0.950024
1	3.268809	-4.455644	-1.234611	1	6.173489	-2.884217	-2.871985
1	5.750154	-4.226422	-1.195794	1	8.389677	-1.819250	-2.469172
9	4.009081	1.739184	-1.193013	9	4.581154	2.454667	-0.087766
9	2.623383	0.689768	-2.503199	9	3.566428	1.667387	-1.846004
9	1.887758	2.197549	-1.122034	9	2.450560	2.035595	-0.017569
9	4.016210	1.107452	1.454086	9	4.989514	0.759005	2.020452
9	2.626705	-0.416356	2.151673	9	4.288113	-1.293701	1.828554
9	1.896582	1.554867	1.601923	9	2.862282	0.323369	2.100236

17a E = -577.1363319 (-577.1616141) Tc = 0.183663 Nimag = 0				Diphenyl sulfoxide E = -936.7077149 (-936.7322283) Tc = 0.144835 NImag = 0			
6	-0.440607	0.024017	-0.020113	16	-0.002373	1.292310	-0.890218
6	-1.501833	0.893748	-0.015962	6	-1.390891	0.306176	-0.236678
6	-2.937994	0.453913	0.012660	6	-2.138011	-0.458741	-1.134786
1	-3.364509	0.649850	-0.981772	6	-1.720531	0.367619	1.119776
8	-1.358818	2.229780	-0.044704	6	-3.221067	-1.204438	-0.655514
6	0.902745	0.582919	-0.020484	1	-1.886001	-0.473661	-2.191342
8	1.881427	-0.335342	0.021687	6	-2.808322	-0.372839	1.586020
8	1.160091	1.804810	-0.052824	1	-1.140951	0.990268	1.794170
6	3.254933	0.144574	0.024021	6	-3.554451	-1.161687	0.700917
1	3.394281	0.792086	0.894054	1	-3.807112	-1.805290	-1.344111

1	3.415201	0.740405	-0.878683	1	-3.074095	-0.335039	2.638130
6	4.161381	-1.069667	0.070642	1	-4.399462	-1.735598	1.068969
1	5.205306	-0.740560	0.073931	6	1.380816	0.240811	-0.314180
1	3.984710	-1.658784	0.975612	6	2.152789	0.673439	0.762855
1	4.006621	-1.710971	-0.802267	6	1.682319	-0.937161	-1.003481
1	-3.479133	1.106563	0.707715	6	3.237506	-0.107449	1.176835
6	-3.102495	-1.024992	0.384901	1	1.905618	1.606465	1.258906
1	-4.125870	-1.346281	0.164135	6	2.766166	-1.710459	-0.580110
1	-2.955012	-1.149745	1.465729	1	1.086568	-1.254084	-1.854889
6	-0.646744	-1.481551	-0.003678	6	3.542303	-1.297509	0.509380
1	-0.398589	-1.877013	0.991893	1	3.843871	0.217896	2.016867
1	0.058612	-1.952356	-0.696321	1	3.007480	-2.629629	-1.105223
6	-2.082393	-1.882270	-0.371073	1	4.386851	-1.899260	0.831146
1	-2.234327	-1.754917	-1.451740	8	0.067932	2.576800	-0.056918
1	-2.233171	-2.944950	-0.151510				
1	-0.377695	2.408537	-0.069531				

$(CF_3SO_2)_2O$
E = -1847.630344 (-1847.6464949)
Tc = 0.005983 Nimag = 0

8	-0.051209	-0.394209	0.623383
16	-1.350213	-0.738250	-0.418950
8	-1.939848	-1.996473	-0.006904
8	-0.982191	-0.443961	-1.790338
6	-2.403230	0.693440	0.268686
9	-1.790443	1.843521	0.021327
9	-2.577180	0.526222	1.572673
9	-3.572406	0.647507	-0.362846
16	1.557149	-0.818777	0.380213
8	2.082983	-1.049038	1.709287
8	1.658892	-1.773331	-0.706502
6	2.191758	0.872594	-0.216266
9	1.899796	1.793113	0.694586
9	3.509550	0.770696	-0.363426
9	1.620554	1.171422	-1.376328

37
E = -1822.7187725 (-1822.7541709)
Tc = 0.160287 Nimag = 0

16	0.596570	0.071336	-0.772511
6	1.998715	-0.902220	-0.263990
6	2.850962	-1.283611	-1.309051
6	2.221162	-1.274182	1.068045
6	3.986945	-2.030688	-0.993451
1	2.640970	-1.008504	-2.337451
6	3.353270	-2.035397	1.353272
1	1.525067	-1.004774	1.853619
6	4.235574	-2.403787	0.330043
1	4.663413	-2.331512	-1.785983
1	3.542987	-2.342830	2.376021
1	5.114078	-2.995327	0.566211
6	0.844342	1.738862	-0.246410
6	0.165896	2.695023	-1.023710
6	1.664134	2.097870	0.834955
6	0.302976	4.040472	-0.690771
1	-0.446282	2.393181	-1.867027
6	1.784792	3.448130	1.148098
1	2.200119	1.353237	1.409739
6	1.106250	4.413462	0.391806
1	-0.210499	4.792867	-1.279096
1	2.413280	3.748600	1.979275
1	1.212938	5.463399	0.644474
8	-0.568922	-0.425972	0.400841
16	-1.832432	-1.454348	-0.027111
8	-1.930049	-2.423525	1.045375
8	-1.718766	-1.805755	-1.431675
6	-3.255864	-0.211228	0.190242
9	-3.203493	0.308497	1.410499
9	-4.391972	-0.881896	0.023628
9	-3.148456	0.745138	-0.724864

(17a + 37)
E = -2399.8415846 (-2399.9213077)
Tc = 0.359314 Nimag = 0

6	0.332290	-3.462746	1.512301
6	0.282220	-2.156257	0.659350
6	-0.122276	-0.967571	1.512251
6	0.600783	-0.818328	2.834294
6	0.660047	-2.135301	3.632691
6	1.181747	-3.290286	2.775142

TS(17→38)
E = -2399.8273958 (-2399.9086964)
Tc = 0.358688 Nimag = 1 ($-1098.02 cm^{-1}$)

6	1.940229	-1.729793	2.312557
6	0.814473	-1.226777	1.370131
6	-0.362577	-0.726308	1.983142
6	-0.490720	-0.458735	3.452067
6	0.532952	-1.192932	4.321431
6	1.922910	-1.078386	3.696871

1	-0.691500	-3.748316	1.779213
1	0.737476	-4.256218	0.877108
1	1.616419	-0.491866	2.560007
1	0.130082	-0.009521	3.396570
1	1.305002	-1.971695	4.502298
1	-0.338736	-2.374323	4.017167
1	2.227734	-3.109481	2.497500
1	1.159684	-4.222754	3.348848
8	-0.939663	-0.092673	1.209318
6	-0.582824	-2.394235	-0.566320
8	0.162862	-2.602438	-1.650780
8	-1.802497	-2.447249	-0.544774
6	-0.530015	-2.960341	-2.889605
1	-1.196024	-2.135156	-3.153852
1	-1.133702	-3.849794	-2.692702
6	0.525950	-3.203989	-3.947443
1	0.033949	-3.471812	-4.887609
1	1.127654	-2.306663	-4.118268
1	1.188973	-4.025449	-3.660932
1	1.301380	-1.910006	0.335000
8	2.150631	0.342721	-0.226125
16	3.309383	1.077670	0.349882
8	3.330660	2.529038	0.049819
8	3.634953	0.710681	1.749135
6	4.766470	0.405544	-0.630508
9	5.917037	0.986289	-0.238169
9	4.609808	0.640165	-1.948180
9	4.891599	-0.924753	-0.456846
16	-2.130258	0.562062	-0.757154
6	-3.744434	0.287220	-0.241437
6	-4.359422	0.944422	0.860686
6	-4.422759	-0.739393	-0.959949
6	-5.659209	0.608475	1.189722
1	-3.808193	1.656392	1.462150
6	-5.732269	-1.035622	-0.625898
1	-3.919489	-1.262580	-1.764782
6	-6.349473	-0.365520	0.442999
1	-6.139714	1.083546	2.037387
1	-6.273346	-1.793665	-1.180301
1	-7.368729	-0.619799	0.714995
6	-1.714443	2.206010	-0.469019
6	-0.314226	2.470475	-0.477551
6	-2.662135	3.263507	-0.356068
6	0.121712	3.773729	-0.320176
1	0.407118	1.660900	-0.560549
6	-2.196340	4.558601	-0.226670
1	-3.723632	3.072712	-0.442962
6	-0.813015	4.815614	-0.193085
1	1.187263	3.973199	-0.291200
1	-2.902949	5.378943	-0.171275
1	-0.464546	5.837692	-0.085689

1	1.837503	-2.815315	2.417638
1	2.896036	-1.549011	1.816785
1	-0.383163	0.632758	3.554598
1	-1.526260	-0.675064	3.737983
1	0.506632	-0.759256	5.325176
1	0.248968	-2.247391	4.416702
1	2.213998	-0.022430	3.627736
1	2.669643	-1.572713	4.326002
8	-1.474550	-0.312120	1.381355
6	0.653776	-2.044323	0.103806
8	1.791039	-2.635690	-0.234598
8	-0.389947	-2.159013	-0.524140
6	1.779556	-3.480226	-1.432669
1	1.463607	-2.860607	-2.275229
1	1.040257	-4.269717	-1.278385
6	3.179355	-4.028295	-1.611578
1	3.200504	-4.664169	-2.502006
1	3.904535	-3.221155	-1.748379
1	3.479654	-4.632789	-0.750916
1	1.296940	-0.081830	0.903007
8	1.704054	1.072931	0.428183
16	3.152476	1.361681	-0.001735
8	3.546379	2.735152	0.332901
8	4.074048	0.264428	0.317953
6	2.989571	1.349352	-1.876185
9	4.182195	1.608675	-2.431793
9	2.114476	2.284256	-2.275626
9	2.565035	0.151395	-2.305785
16	-1.657108	0.170939	-0.315119
6	-3.066557	-0.829387	-0.737434
6	-4.065869	-1.147690	0.190715
6	-3.096758	-1.277669	-2.063697
6	-5.134333	-1.932191	-0.240991
1	-4.006636	-0.817009	1.220866
6	-4.188693	-2.042110	-2.476654
1	-2.294531	-1.042859	-2.754692
6	-5.200128	-2.369457	-1.569308
1	-5.914918	-2.199862	0.463048
1	-4.235485	-2.393141	-3.501776
1	-6.039162	-2.976173	-1.894071
6	-2.253204	1.807448	-0.018904
6	-1.237756	2.782656	0.053752
6	-3.613613	2.147397	0.076254
6	-1.600560	4.111973	0.249581
1	-0.192738	2.502048	-0.032015
6	-3.951616	3.484385	0.261633
1	-4.389808	1.398253	-0.009744
6	-2.951747	4.461346	0.351960
1	-0.830873	4.873444	0.311698
1	-4.997100	3.764965	0.329165
1	-3.229138	5.500984	0.493187

38
E = -1437.799793 (-1437.8620894)
Tc = 0.336925 Nimag = 0

6	-4.047417	-0.750810	-0.304169
6	-2.624886	-0.463062	0.151527
6	-1.579150	-1.017741	-0.492084
6	-1.681055	-1.972886	-1.650252
6	-3.104197	-2.523582	-1.822653
6	-4.129355	-1.395460	-1.690680
1	-4.526073	-1.400016	0.442933

TS(38→39)
E = -1437.7840414 (-1437.859195)
Tc = 0.337277 Nimag = 1 (-128.86 cm^{-1})

6	2.674811	1.524138	0.020250
6	1.380209	1.006034	-0.529217
6	1.385851	-0.034894	-1.598688
6	2.691479	-0.718441	-1.951324
6	3.952518	0.086243	-1.606418
6	3.885461	0.602765	-0.166473
1	2.850689	2.464654	-0.535279

1	-4.600857	0.192558	-0.282066	1	2.544671	1.849775	1.057709
1	-1.366755	-1.467770	-2.574232	1	2.701271	-1.674791	-1.409892
1	-0.971346	-2.792565	-1.486166	1	2.636682	-0.968155	-3.015034
1	-3.182340	-3.018427	-2.795523	1	4.833363	-0.546954	-1.746781
1	-3.293769	-3.285243	-1.056063	1	4.054501	0.931282	-2.298912
1	-3.939846	-0.637222	-2.461852	1	3.834011	-0.237900	0.532484
1	-5.143216	-1.773834	-1.856938	1	4.787191	1.169230	0.084472
8	-0.274585	-0.758047	-0.013069	8	0.330361	-0.331878	-2.159924
16	0.930888	-0.477146	-1.158901	16	-0.664564	-2.436551	-0.520000
6	2.340297	-1.027010	-0.221651	6	-2.191496	-1.508530	-0.384562
6	3.038961	-0.205037	0.671217	6	-2.885884	-1.454236	0.834565
6	2.719775	-2.356782	-0.461955	6	-2.744859	-0.966667	-1.551637
6	4.129004	-0.743637	1.353190	6	-4.129551	-0.822766	0.882542
1	2.755358	0.828407	0.827626	1	-2.468809	-1.904924	1.729033
6	3.809918	-2.877059	0.234279	6	-3.997213	-0.350641	-1.490823
1	2.178916	-2.971114	-1.174408	1	-2.199032	-1.012985	-2.486692
6	4.510441	-2.073114	1.139097	6	-4.686668	-0.272651	-0.277042
1	4.682347	-0.121351	2.048345	1	-4.667176	-0.773892	1.824226
1	4.114282	-3.903825	0.062196	1	-4.427613	0.073854	-2.392341
1	5.362919	-2.480271	1.673246	1	-5.658040	0.210062	-0.234848
6	0.993374	1.306573	-1.239534	6	0.412049	-1.778685	0.679273
6	1.360588	1.844203	-2.479570	6	1.435169	-2.626978	1.160236
6	0.659198	2.110121	-0.143079	6	0.309936	-0.442033	1.188312
6	1.425438	3.232930	-2.607359	6	2.244712	-2.200597	2.198934
1	1.590478	1.201508	-3.323246	1	1.546192	-3.627426	0.754975
6	0.717286	3.494865	-0.297877	6	1.110012	-0.065721	2.300229
1	0.344161	1.667728	0.794248	1	-0.568322	0.142970	0.960055
6	1.105268	4.053035	-1.521546	6	2.069917	-0.923898	2.791498
1	1.712597	3.668795	-3.558243	1	3.006784	-2.869567	2.585708
1	0.457264	4.135997	0.537747	1	0.950868	0.909379	2.747110
1	1.147233	5.131906	-1.630860	1	2.686255	-0.635201	3.636002
6	-2.535184	0.459451	1.325214	6	0.288004	2.054212	-0.617064
8	-1.504243	0.221629	2.149945	8	-0.276713	2.373028	0.536443
8	-3.372519	1.326161	1.537466	8	0.090191	2.601339	-1.686281
6	-1.427655	1.039967	3.356260	6	-1.236565	3.488808	0.527377
1	-2.374228	0.943816	3.894236	1	-2.037532	3.230385	-0.168709
1	-1.307195	2.084973	3.057174	1	-0.711392	4.370969	0.154475
6	-0.254326	0.539892	4.174729	6	-1.735359	3.667100	1.944714
1	-0.175958	1.135899	5.089355	1	-2.450878	4.494774	1.964946
1	-0.390707	-0.507792	4.458746	1	-2.242889	2.766695	2.302001
1	0.685365	0.635080	3.622784	1	-0.913671	3.907304	2.625306

($39 + {}^{-}OSO_2CF_3$) E = -2399.4562655 (-2399.5419484) Tc = 0.348798 NImag = 0				**TS(39→19aa)** E = -2399.4472369 (-2399.5376629) Tc = 0.347919 NImag = 1 (-1055.00 cm^{-1})			
6	1.843787	2.869246	0.428461	6	0.798765	3.052943	0.708300
6	0.525048	2.143657	0.077776	6	-0.149606	1.894989	0.277462
6	0.403616	1.948276	-1.460040	6	-0.184802	1.791173	-1.269884
6	1.036132	3.023187	-2.317637	6	0.037420	3.083559	-2.030691
6	1.200487	4.363666	-1.591938	6	-0.336503	4.337322	-1.230844
6	2.033937	4.227143	-0.299187	6	0.443389	4.432443	0.099492
1	1.889160	3.011877	1.511324	1	0.794683	3.107776	1.799816
1	2.668238	2.203221	0.162620	1	1.810817	2.770821	0.408899
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1	0.450693	3.109928	-3.237783	1	-0.506028	3.014017	-2.977494
1	1.672396	5.084138	-2.266505	1	-0.149418	5.226524	-1.840283
1	0.209081	4.772295	-1.364349	1	-1.415857	4.328629	-1.039412
1	3.096864	4.329665	-0.541254	1	1.378762	4.978189	-0.062811
1	1.782357	5.049108	0.375458	1	-0.140302	5.016941	0.816363
8	-0.153304	0.972421	-1.931663	8	-0.364195	0.725556	-1.833388
16	2.220143	-0.559722	-0.860462	16	2.451972	0.317513	-0.820796
6	3.677067	-1.569110	-0.561479	6	4.071648	-0.441072	-0.647379

6	3.544774	-2.962689	-0.511363	6	4.296731	-1.709231	-1.198989
6	4.936530	-0.959410	-0.495060	6	5.122388	0.281497	-0.065203
6	4.690094	-3.750745	-0.371750	6	5.579563	-2.262027	-1.150713
1	2.564476	-3.423048	-0.578377	1	3.479770	-2.255937	-1.658533
6	6.073609	-1.758939	-0.354873	6	6.400203	-0.281086	-0.019658
1	5.027375	0.120415	-0.549746	1	4.942459	1.269666	0.345589
6	5.950817	-3.150676	-0.292711	6	6.628893	-1.550680	-0.560880
1	4.594654	-4.831054	-0.328602	1	5.756066	-3.245332	-1.575456
1	7.052337	-1.293075	-0.298589	1	7.215420	0.274982	0.432778
1	6.837825	-3.767631	-0.187567	1	7.624511	-1.982380	-0.527437
6	1.625816	-0.152002	0.715038	6	1.637387	-0.001783	0.712091
6	2.221999	-0.647094	1.880662	6	2.214875	-0.867193	1.653366
6	0.395007	0.723100	0.806341	6	0.306686	0.564412	0.980394
6	1.665012	-0.396885	3.125454	6	1.614273	-1.104715	2.882424
1	3.117494	-1.251349	1.814939	1	3.159547	-1.345158	1.429050
6	-0.136996	0.870633	2.190420	6	-0.200556	0.353786	2.327684
1	-0.398476	0.189788	0.241653	1	-0.348018	-0.463742	0.494770
6	0.459516	0.338937	3.287665	6	0.400197	-0.487681	3.231617
1	2.158347	-0.802939	4.003668	1	2.100281	-1.777787	3.582163
1	-1.066215	1.417124	2.303646	1	-1.139863	0.819292	2.596520
1	0.029771	0.464605	4.274545	1	-0.052058	-0.664988	4.200650
6	-0.678575	3.026348	0.525414	6	-1.589232	2.270657	0.738510
8	-1.816793	2.629641	-0.040789	8	-2.530098	1.840713	-0.100547
8	-0.580232	3.945907	1.313902	8	-1.817237	2.898654	1.756182
6	-3.040071	3.357491	0.311523	6	-3.920771	2.147408	0.242662
1	-2.907197	4.397728	0.003964	1	-3.994057	3.222750	0.421102
1	-3.150992	3.324481	1.398077	1	-4.155831	1.619894	1.170325
6	-4.190571	2.682167	-0.404427	6	-4.789634	1.695560	-0.912018
1	-5.119444	3.204416	-0.154387	1	-5.835683	1.913637	-0.675014
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8	-1.599975	-1.690255	0.293144	8	-0.824165	-1.697189	0.059184
16	-2.991131	-2.068576	0.650287	16	-2.097319	-2.354917	0.565452
8	-3.110809	-3.302159	1.465139	8	-1.863575	-3.692589	1.134576
8	-3.856201	-0.942645	1.077604	8	-2.977142	-1.441565	1.313721
6	-3.732112	-2.574724	-1.003071	6	-3.003633	-2.697414	-1.046396
9	-3.050515	-3.604651	-1.544739	9	-2.275744	-3.502157	-1.837941
9	-3.704383	-1.552752	-1.881835	9	-3.252739	-1.557966	-1.710676
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E = -2399.4955446 (-2399.5822313)
Tc = 0.349054 NImag = 0

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6	0.624478	1.839147	0.061565
6	0.025621	1.299082	-1.254833
6	0.555406	1.882157	-2.538748
6	1.033343	3.331797	-2.369179
6	2.156444	3.448790	-1.316060
1	2.440240	2.782508	0.744687
1	2.685264	1.523502	-0.454890
1	1.395995	1.243699	-2.845887
1	-0.219105	1.778445	-3.303403
1	1.377157	3.710099	-3.336076
1	0.177556	3.957112	-2.088635
1	3.129936	3.336655	-1.804595
1	2.137155	4.451485	-0.879949
8	-0.881901	0.462030	-1.284498
16	1.811810	-1.064205	-0.619443
6	3.561192	-1.369799	-0.338117
6	4.194828	-2.227068	-1.251638
6	4.306584	-0.766202	0.683548

6	5.566040	-2.469908	-1.145013	
1	3.619005	-2.706857	-2.037948	
6	5.676489	-1.025967	0.788310	
1	3.829001	-0.104116	1.397396	
6	6.312696	-1.873055	-0.123855	
1	6.046118	-3.135467	-1.856390	
1	6.245188	-0.557257	1.586193	
1	7.376984	-2.069217	-0.037816	
6	1.198163	-0.515652	0.982879	
6	1.220926	-1.443879	2.034972	
6	0.643897	0.772339	1.178856	
6	0.731567	-1.113573	3.296529	
1	1.628779	-2.433213	1.854742	
6	0.146800	1.075002	2.458109	
1	-1.693684	-0.177912	-0.240178	
6	0.191362	0.155362	3.505804	
1	0.762048	-1.843894	4.098990	
1	-0.276380	2.052409	2.658183	
1	-0.202525	0.433629	4.478233	
6	-0.257610	3.044199	0.507490	
8	-1.535983	2.903955	0.156348	
8	0.185053	3.995751	1.120511	
6	-2.460779	3.972781	0.541310	
1	-2.088021	4.907765	0.115758	
1	-2.445860	4.052739	1.631024	
6	-3.829908	3.603749	0.010403	
1	-4.540650	4.390221	0.282548	
1	-3.819269	3.513127	-1.079625	
1	-4.180217	2.661156	0.440507	
8	-2.298024	-0.666997	0.460845	
16	-3.585708	-1.351453	-0.125007	
8	-4.541333	-1.540844	0.960478	
8	-3.996922	-0.758074	-1.395476	
6	-2.925329	-3.065333	-0.540410	
9	-2.455992	-3.662178	0.559842	
9	-1.941724	-2.968904	-1.442676	
9	-3.919605	-3.801644	-1.050639	

Complete citation of reference 29

Gaussian 09, *Revision B.01*, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

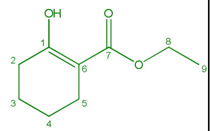
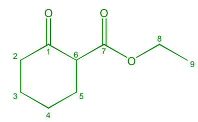
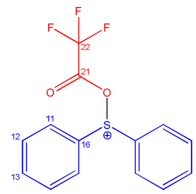
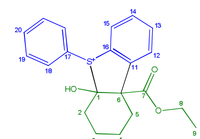
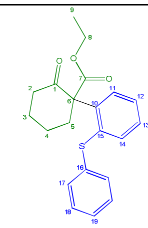
2.2 NMR investigation

NMR kinetic study of the α-arylation reaction of the ketoester 17a and characterization of intermediate J.

An NMR-based kinetic study was performed on an Avance III 500MHz spectrometer equipped with a dual-channel 1H/BB probehead with z-gradient from Bruker Biospin GmbH in order to follow the reaction represented in scheme 13 using ^{1}H and ^{13}C NMR. Standard 1D ^{1}H and ^{13}C spectra were recorded at 298K at intervals of 23 mins beginning shortly after adding TFAA (1.5 eq) to a mixture of **17a** (0.5 M) and **18a** (0.6 M) in CD_3CN in a 5-mm NMR tube. All corresponding NMR data were processed and analysed with Topspin 3.0 and kinetic model fitting was performed with the Program Potterswheel 3.0 running under MATLAB R2009b. Based on the number of species observed in the NMR spectrum, the entire reaction was defined by six rate constants (k_1,k_{-1}, k_2, k_3, k_4 and k_{-4}) as shown in **Figure 6** in the text. Other short-lived intermediates, which are invisible to NMR such as species **38** and **39** as determined from DFT, were pooled as a single intermediate for the kinetic fitting. Other assumptions included the initial concentration of the keto and enol form of **17a** which were set to 70:30 based on initial conditions prior to adding TFAA.

A full ^{1}H and ^{13}C characterization of all the major species at play, including the stable intermediate **J**, was completed based on correlation experiments including ^{1}H/^{1}H DQF-COSY, ^{1}H/^{1}H-NOESY, ^{1}H/^{13}C-HSQC, ^{1}H/^{13}C-HMBC performed on the reaction mixture cooled from room temperature down to 253 K (-20 °C) after 5 hours, and are presented in Table S4. ^{1}H and ^{13}C spectra also shown in figures S4-S9.

Table S4. ^{13}C and ^{1}H chemical shift assignment (at 500MHz and 125MHz, resp.) of reaction mixture, cooled down to 253K 5 hours after addition of TFAA at room temperature. Chemical shifts are referenced to residual CH_3CN.

Atom No.	 **17a-enol**		 **17a-keto**		 **37**		 **J**		 **19aa**	
	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
1	173.92	--	208.41	--			115.37	--	206.88	--
2	29.68	2.19	42.36	2.38, 2.30			30.36	2.07, 1.95	41.9	2.79, 2.52
3	22.73	~1.44	30.87	2.09, 1.94			22.71	1.62, 1.42	26.87	1.93, 1.83
4	23.15	o/l	24.12	o/l			20.51	1.81, 1.40	23.2	1.70, 1.79
5	23.05	o/l	28.1	1.94, 1.65			28.13	2.96, 2.38	37.48	2.57, 2.51
6	98.46	--	58.03	3.42			64.01	--	68.43	--
7	173.37	--	171.43	--			170.89	--	171.82	--
8	61.35	4.13	61.72	4.11			65.05	4.20	63.07	4.11, 3.99
9	14.58	1.20	14.57	1.20			14.03	1.19	14.26	1.13
10										
11					125.71	7.71	139.84	--	143.16	--
12					130.93	7.52	127.42	7.77	129.59	7.328
13					133.12	7.52	135.68	7.86	129.52	7.249
14							133.26	7.73	129.22	7.208
15							130.60	7.59	137.62	7.386
16					143.97		129.14	--	135.73	--
17							122.46	--	139.35	--
18							137.26	7.89	130.18	7.221
19							?		129.13	7.074
20							?		127.29	7.15
21					159.2					
					q 37Hz					
22					116.0					
					q 285Hz					

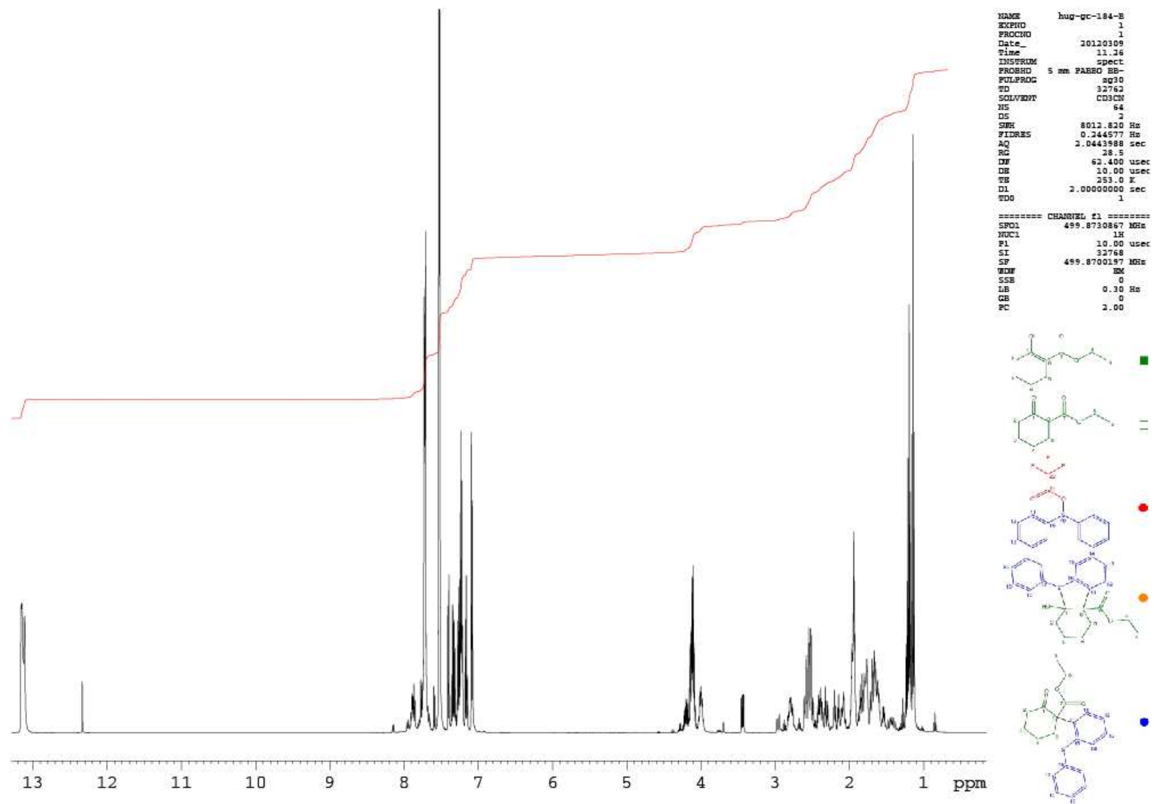


Figure S4. ^{1}H spectrum of α-arylation reaction of the ketoester **17a**.

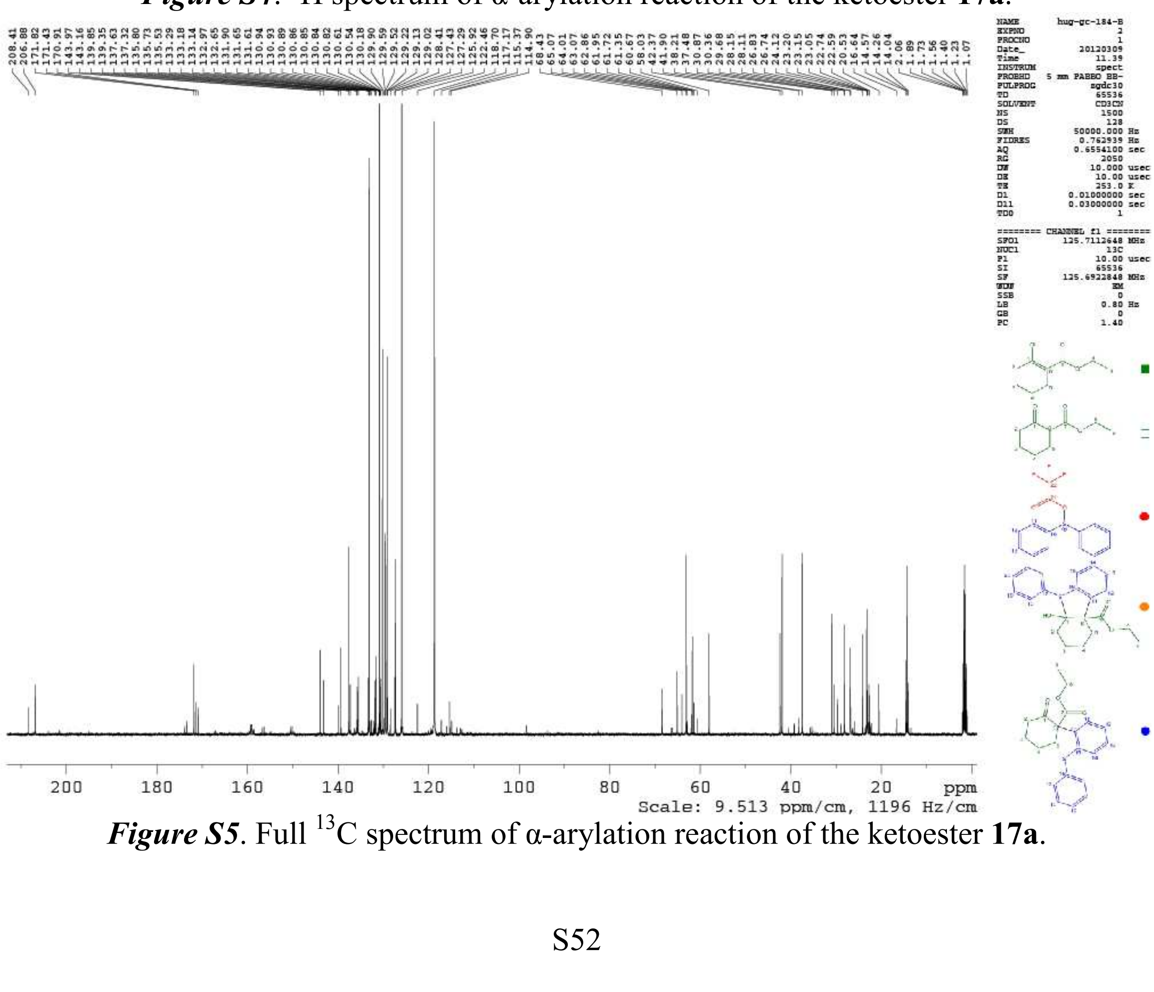


Figure S5. Full ^{13}C spectrum of α-arylation reaction of the ketoester **17a**.

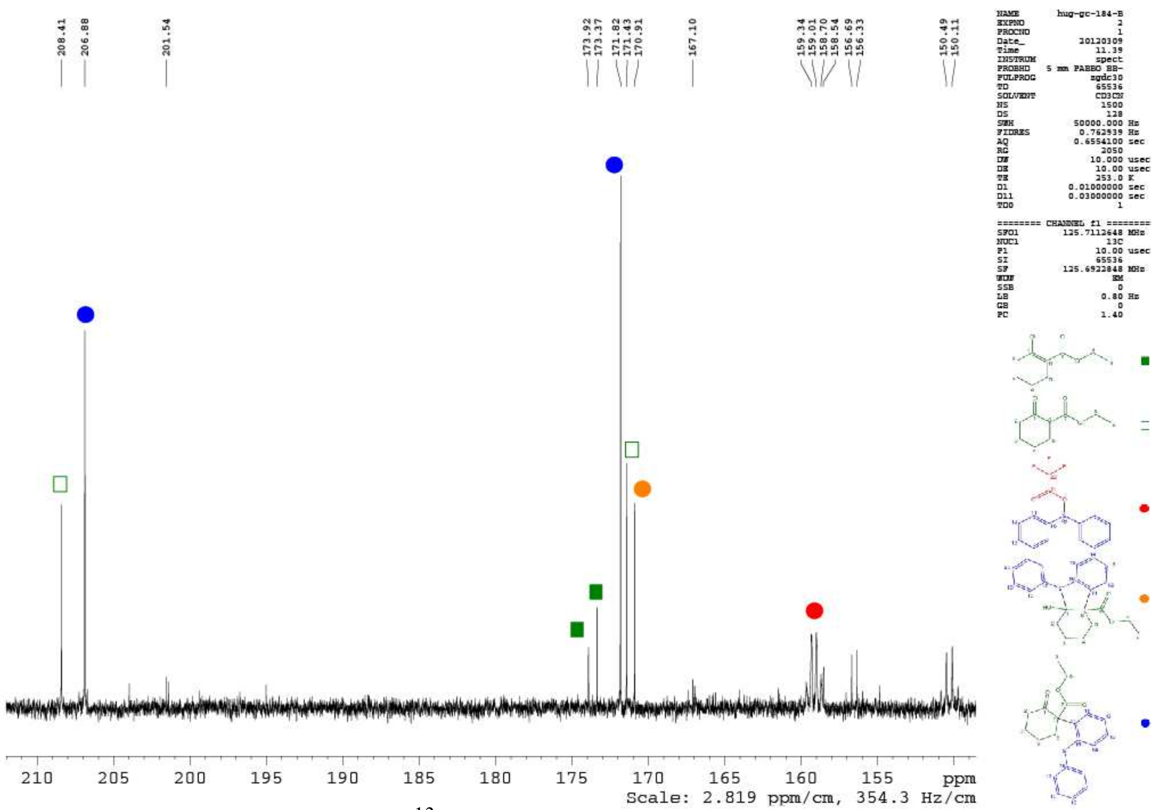


Figure S6. Low field region of ^{13}C spectrum of α-arylation reaction of the ketoester **17a**.

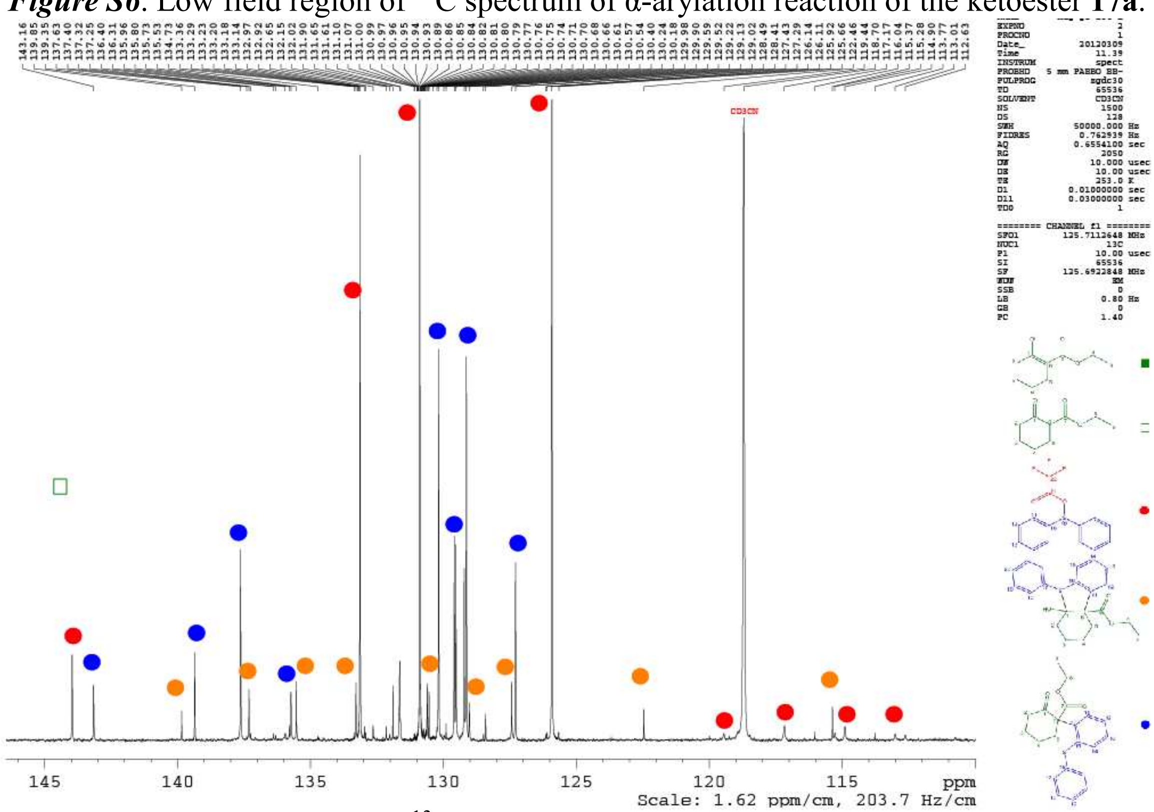


Figure S7. Aromatic region of ^{13}C spectrum of α-arylation reaction of the ketoester **17a**.

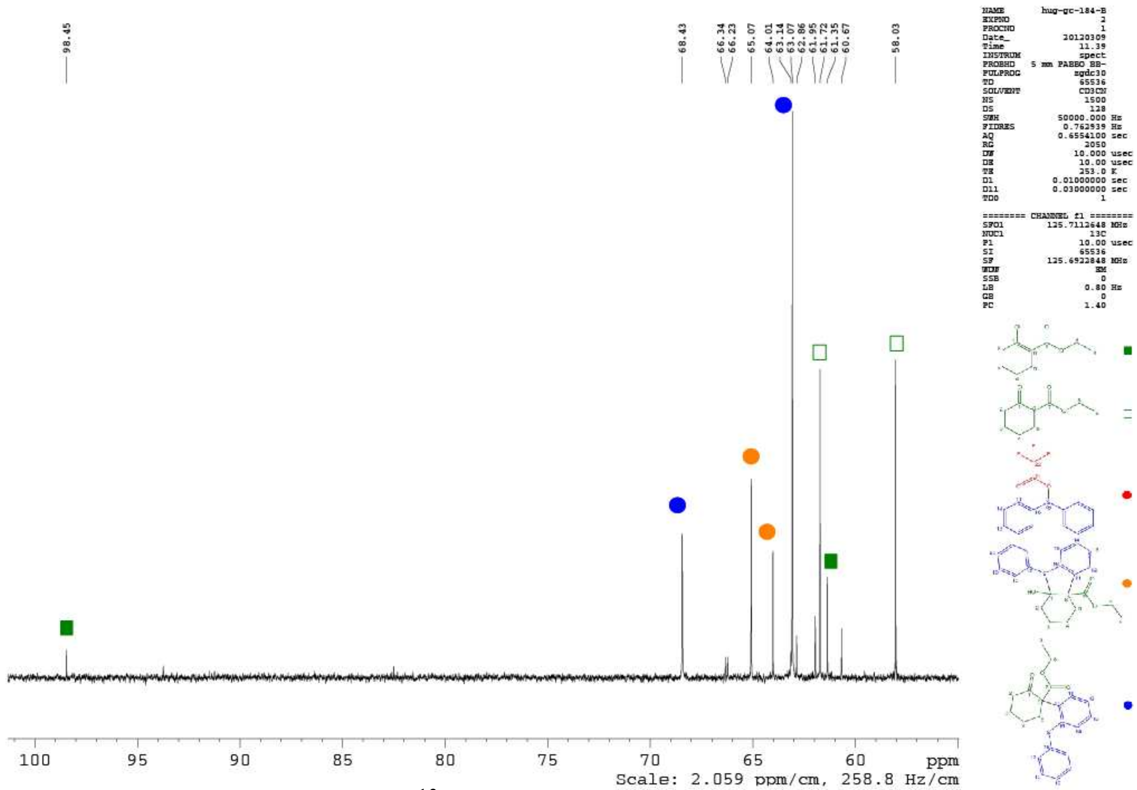


Figure S8. Mid-field region of ^{13}C spectrum of α-arylation reaction of the ketoester **17a**.

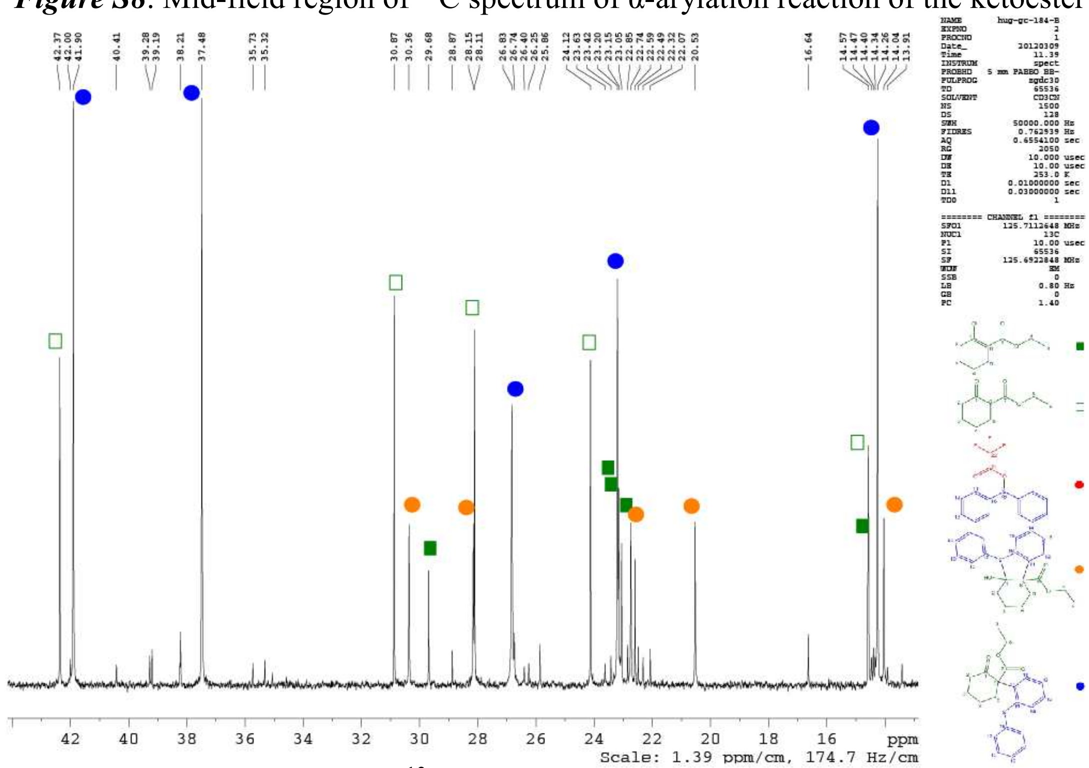
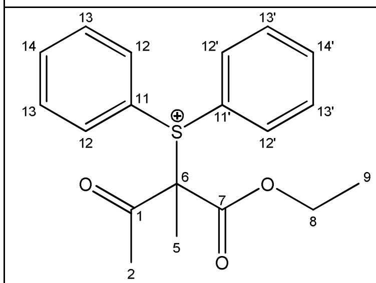


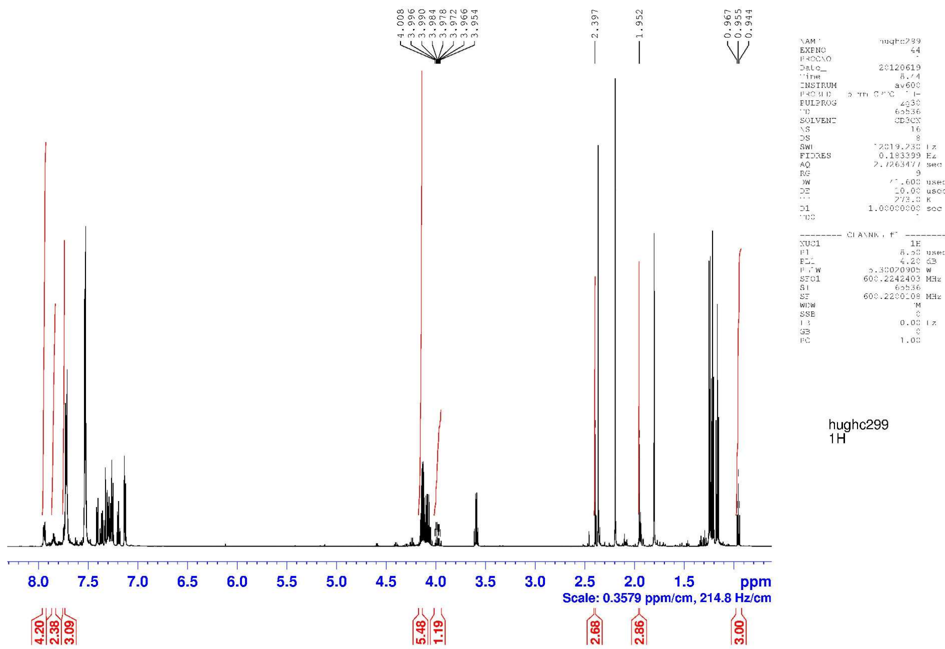
Figure S9. Aliphatic region of ^{13}C spectrum of α-arylation reaction of the ketoester **17a**.

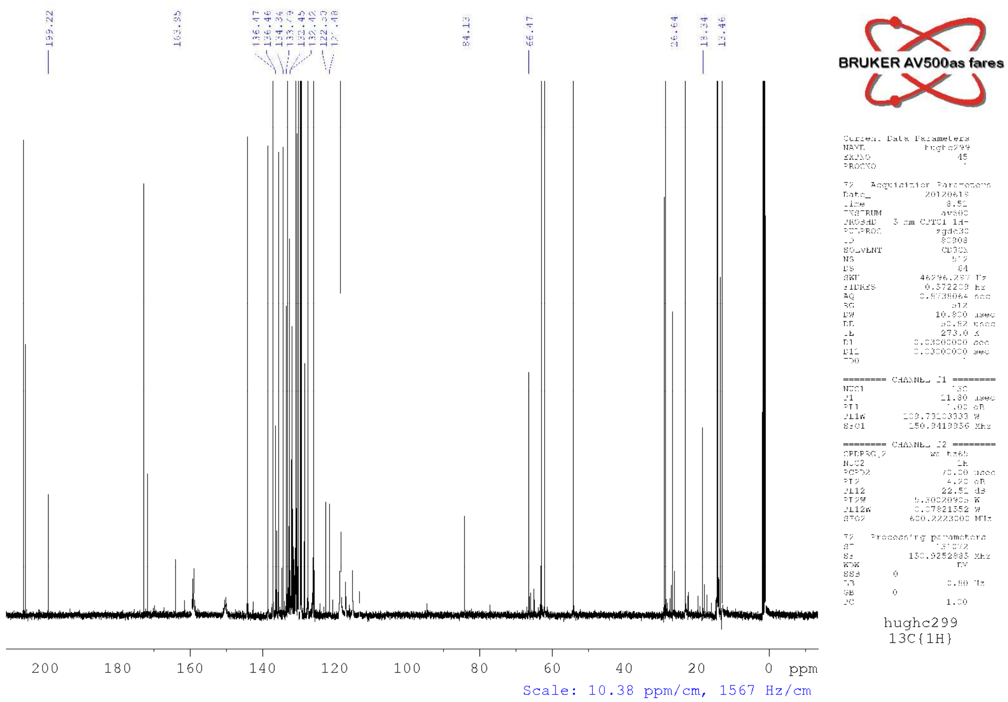
Table S5: ^{13}C and ^{1}H chemical shift assignment (at 600MHz and 150MHz, resp.) of reaction mixture, measured at 273K. Chemical shifts are referenced to residual CH_3CN.

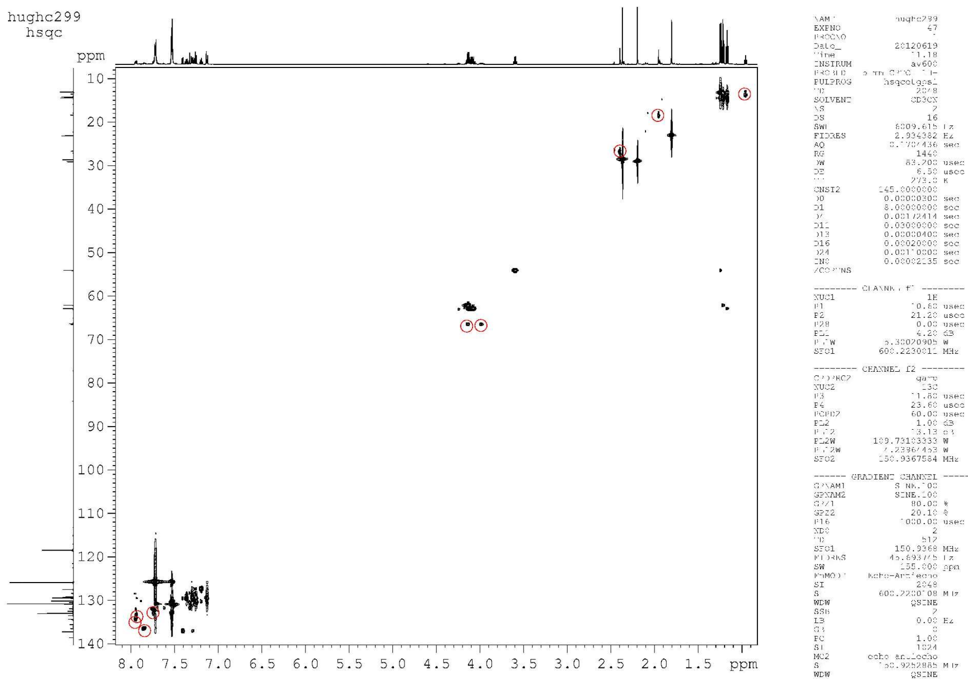


40

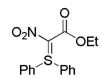
Atom No.	^{13}C	^{1}H
1	199.22	
2	26.64	2.40
5	18.34	1.95
6	84.13	
7	163.95	
8	66.47	3.98,4.14
9	13.46	0.96
11, 11’	121.48, 122.50	
12, 12’	136.46, 136.47	7.85, 7.85
13, 13’	132.42, 132.45	7.75, 7.73
14, 14’	133.49, 134.34	7.94, 7.95


4.008
3.996
3.990
3.984
3.978
3.972
3.966
3.954
2.397
1.952
0.967
0.955
0.944
hughc299
1H
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
Scale: 0.3579 ppm/cm, 214.8 Hz/cm
4.20
2.38
3.09
5.48
1.19
2.68
2.86
3.00

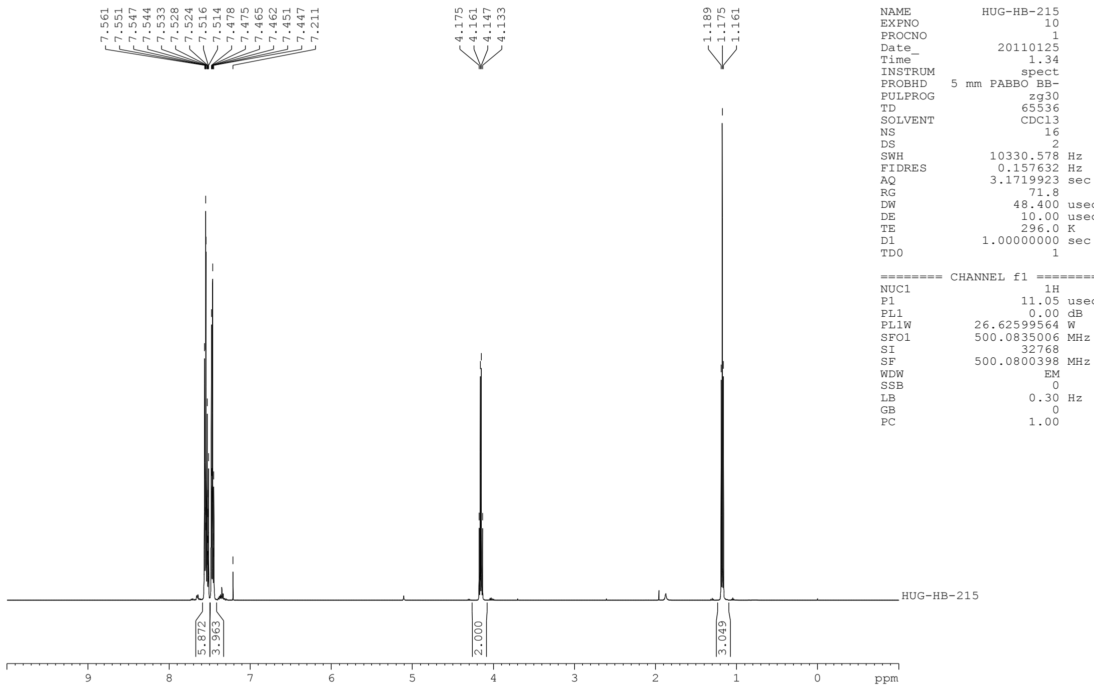

199.22
163.85
84.13
66.47
19.34
BRUKER AV500as fares
hughc299
13C{1H}
200 180 160 140 120 100 80 60 40 20 0 ppm
Scale: 10.38 ppm/cm, 1567 Hz/cm

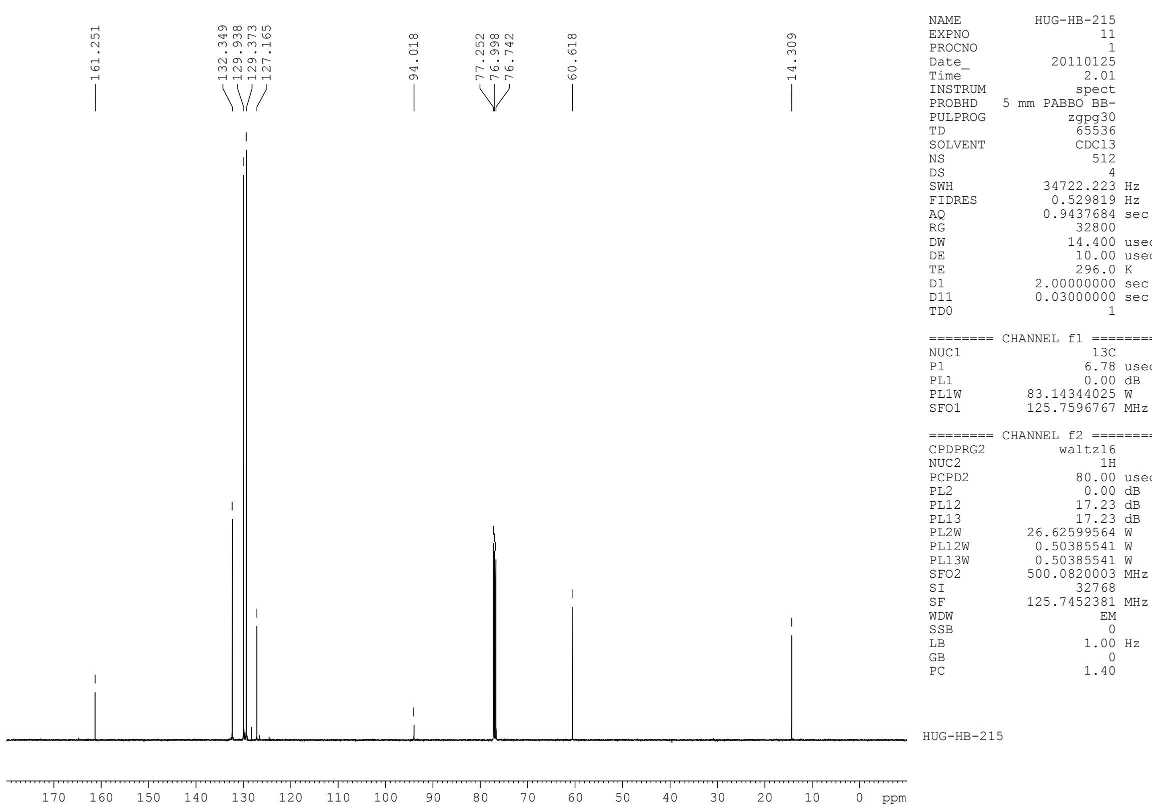

hughc299
hsqc

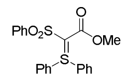
Part III NMR spectra



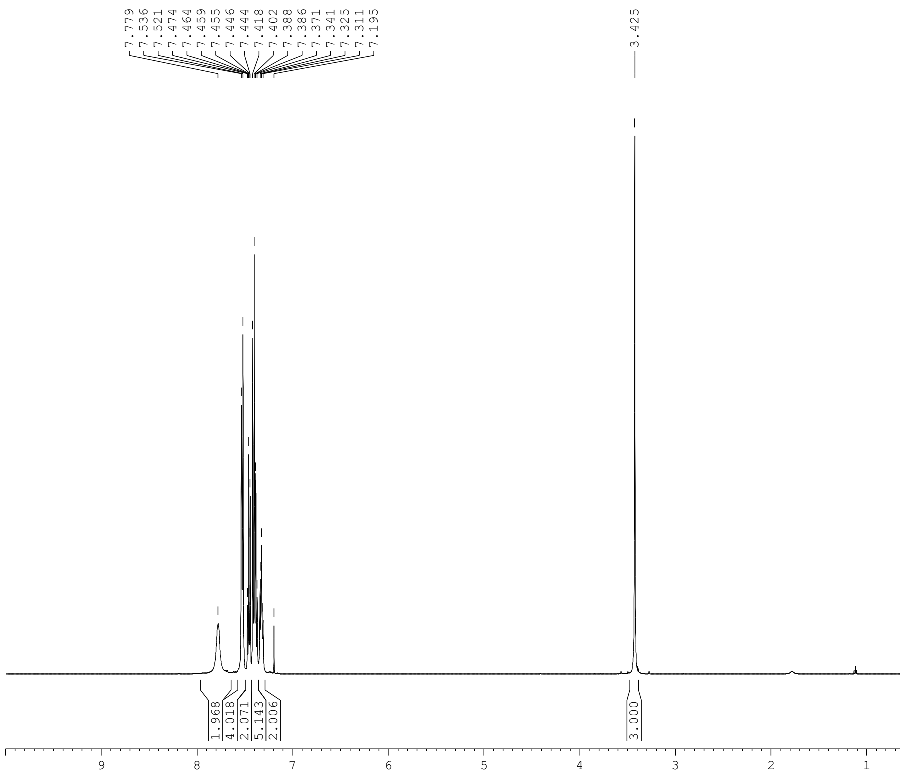
16h



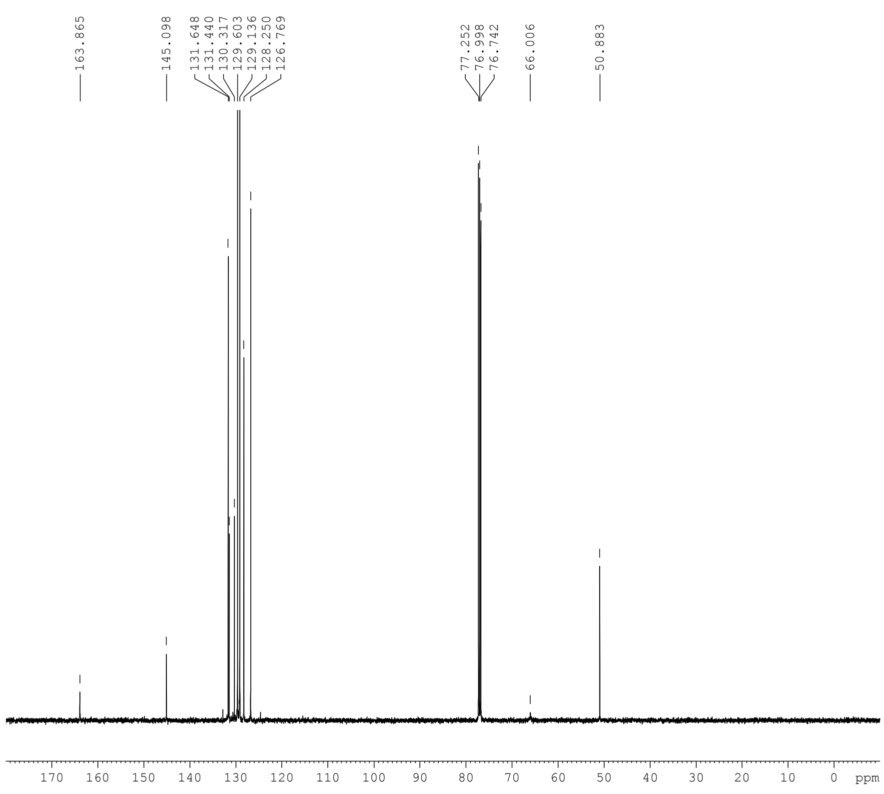




16i

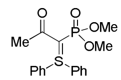



```
NAME           HUG-HB-294
EXPNO                  10
PROCNO                  1
Date_            20110420
Time                10.57
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ           3.1719923 sec
RG                   80.6
DW              48.400 usec
DE               10.00 usec
TE               296.0 K
D1          1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1               11.05 usec
PL1               0.00 dB
PL1W       26.62599564 W
SFO1       500.0835006 MHz
SI                  32768
SF         500.0800476 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

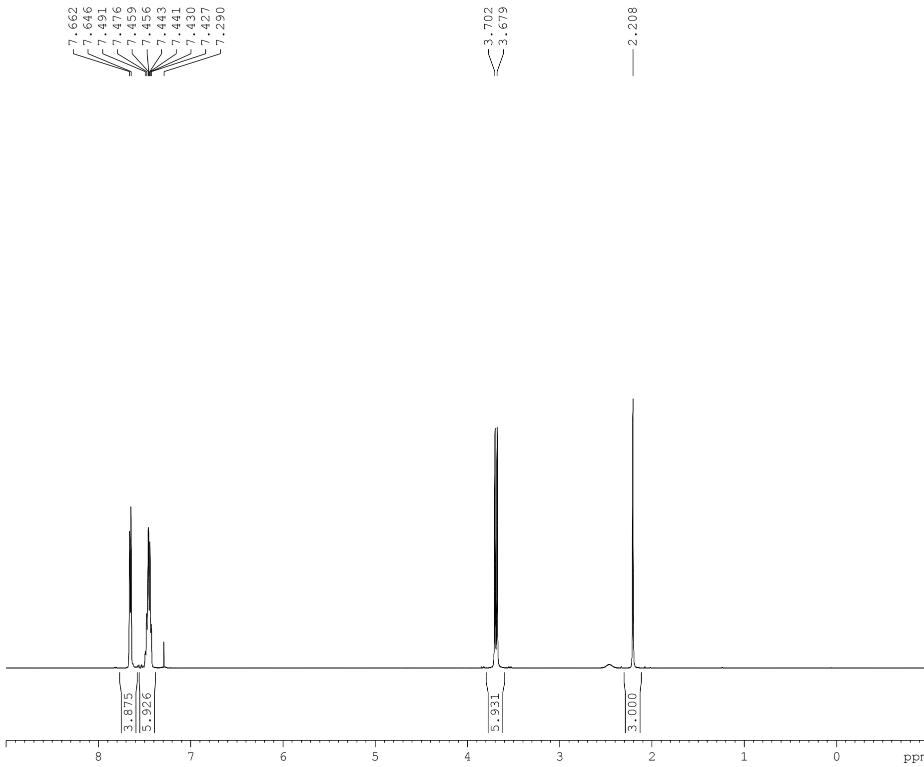



```
NAME           HUG-HB-294
EXPNO                  11
PROCNO                  1
Date_            20110420
Time                22.33
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    512
DS                      4
SWH          34722.223 Hz
FIDRES        0.529819 Hz
AQ           0.9437684 sec
RG                  32800
DW              14.400 usec
DE               10.00 usec
TE               296.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                6.78 usec
PL1               0.00 dB
PL1W       83.14344025 W
SFO1       125.7596767 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             17.23 dB
PL13             17.23 dB
PL2W       26.62599564 W
PL12W       0.50385541 W
PL13W       0.50385541 W
SFO2       500.0820003 MHz
SI                  32768
SF         125.7452349 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

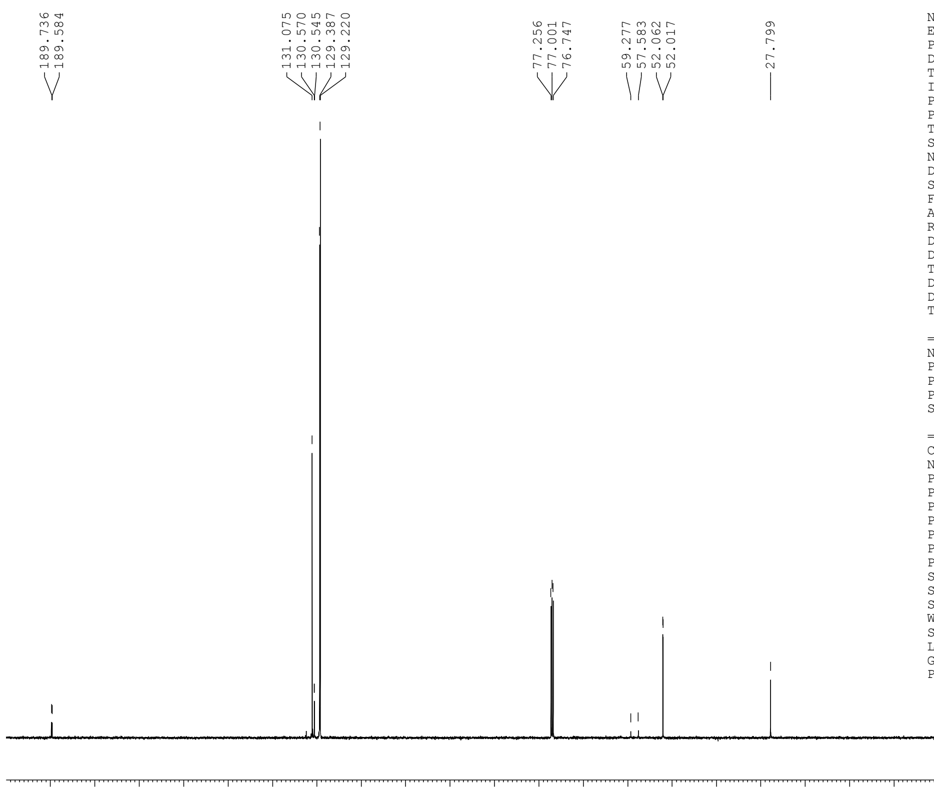
HUG-HB-294



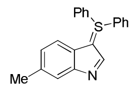
16k



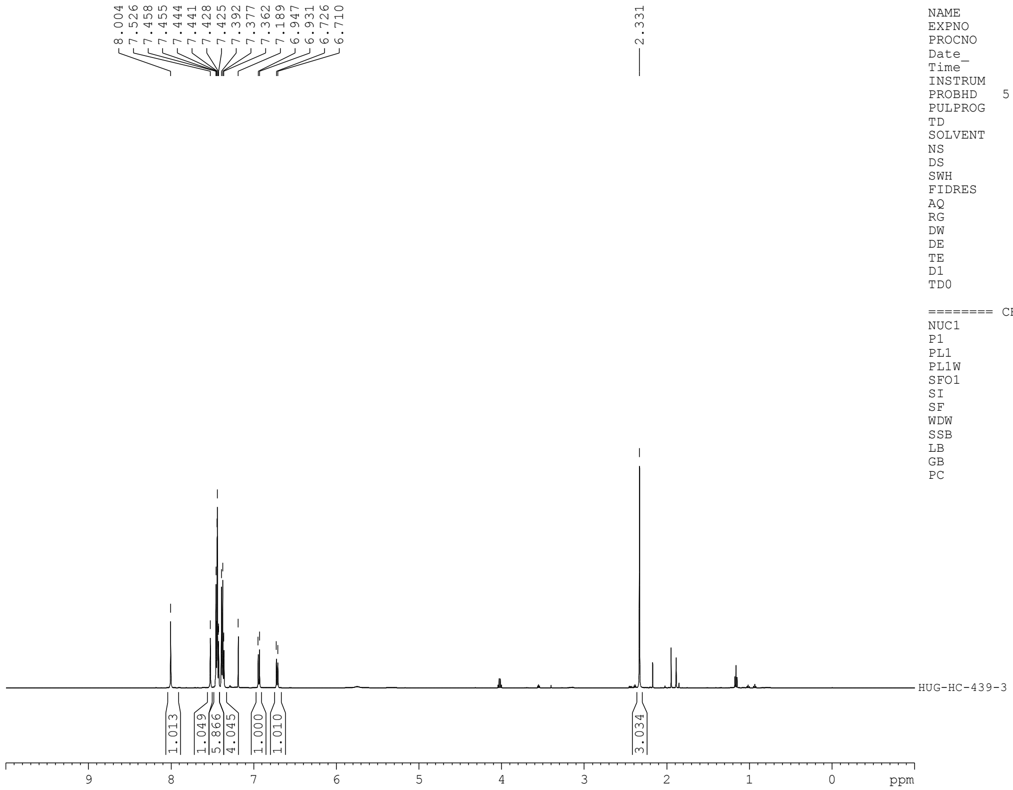

```
NAME         HUG-HB-296
EXPNO                10
PROCNO                1
Date_          20110420
Time              11.07
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719923 sec
RG                   64
DW               48.400 usec
DE                10.00 usec
TE                296.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                11.05 usec
PL1                0.00 dB
PL1W        26.62599564 W
SFO1        500.0835006 MHz
SI                32768
SF          500.0800000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```




```
NAME         HUG-HB-296
EXPNO                12
PROCNO                1
Date_          20110420
Time              23.32
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                32800
DW               14.400 usec
DE                10.00 usec
TE                296.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 6.78 usec
PL1                0.00 dB
PL1W        83.14344025 W
SFO1        125.7596767 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              17.23 dB
PL13              17.23 dB
PL2W        26.62599564 W
PL12W        0.50385541 W
PL13W        0.50385541 W
SFO2        500.0820003 MHz
SI                32768
SF          125.7452349 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



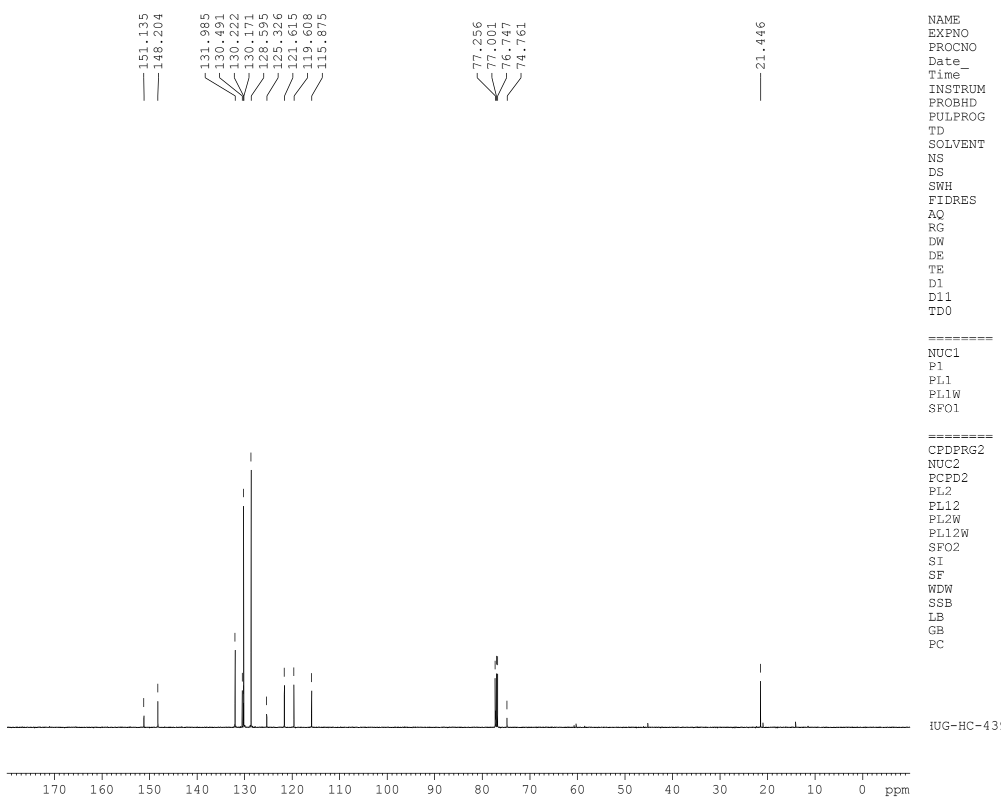
20c



NAME	HUG-HC-439-3	
EXPNO	10	
PROCNO	1	
Date_	20130405	
Time	17.41	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	10330.578	Hz
FIDRES	0.157632	Hz
AQ	3.1719923	sec
RG	57	
DW	48.400	usec
DE	6.50	usec
TE	296.0	K
D1	1.00000000	sec
TD0	1	

======== CHANNEL f1 ========

NUC1	1H	
P1	11.05	usec
PL1	0.00	dB
PL1W	26.62599564	W
SFO1	500.3530899	MHz
SI	32768	
SF	500.3500468	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	



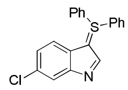
NAME	HUG-HC-439-3	
EXPNO	11	
PROCNO	1	
Date_	20130406	
Time	2.25	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgdc30	
TD	65536	
SOLVENT	CDCl3	
NS	1500	
DS	4	
SWH	34722.223	Hz
FIDRES	0.529819	Hz
AQ	0.9437684	sec
RG	32800	
DW	14.400	usec
DE	10.00	usec
TE	296.0	K
D1	0.01000000	sec
D11	0.03000000	sec
TD0	1	

======== CHANNEL f1 ========

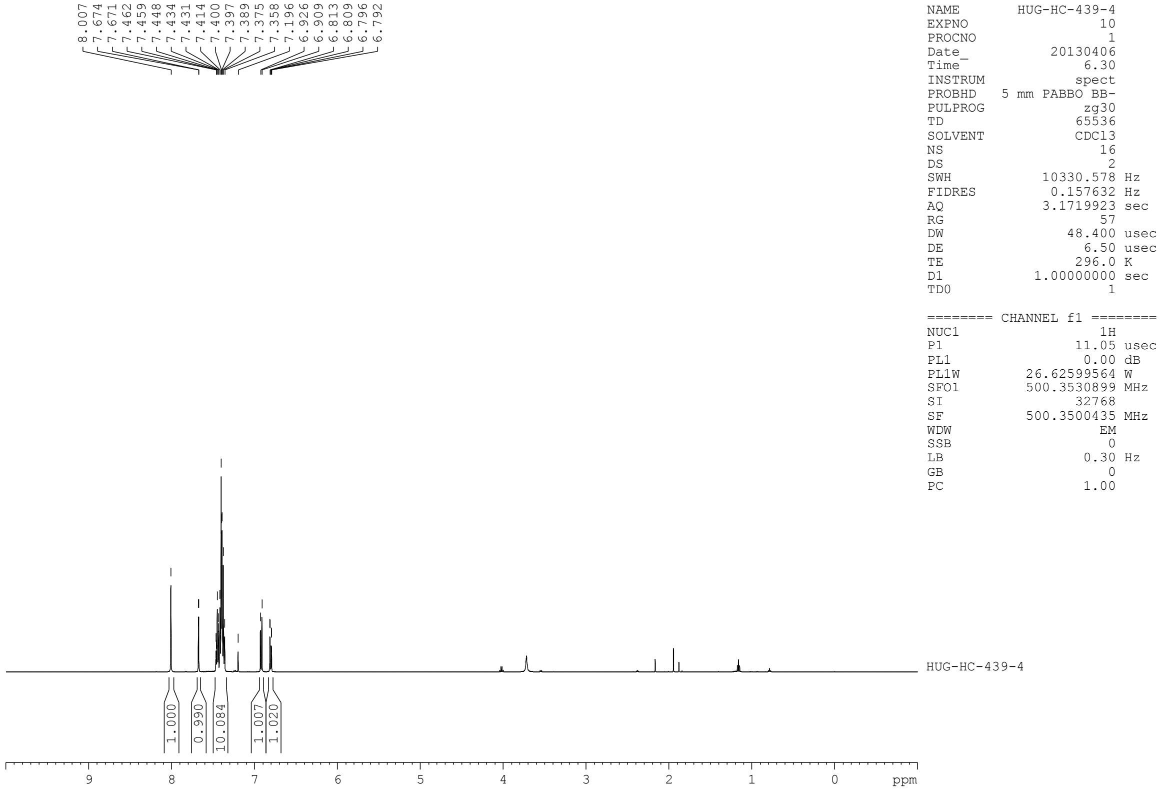
NUC1	13C	
P1	6.78	usec
PL1	0.00	dB
PL1W	83.14344025	W
SFO1	125.8275761	MHz

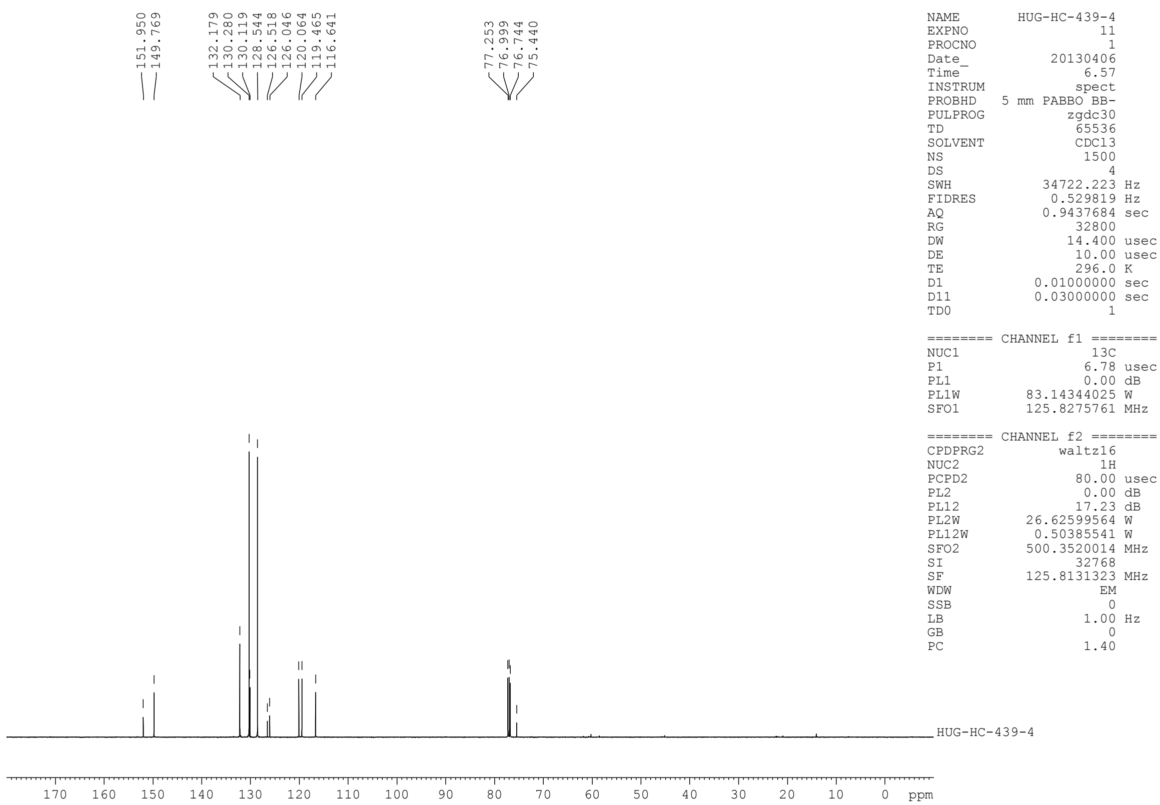
======== CHANNEL f2 ========

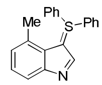
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	17.23	dB
PL2W	26.62599564	W
PL12W	0.50385541	W
SFO2	500.3520014	MHz
SI	32768	
SF	125.8131333	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	


Ph
S
Ph
Cl
N

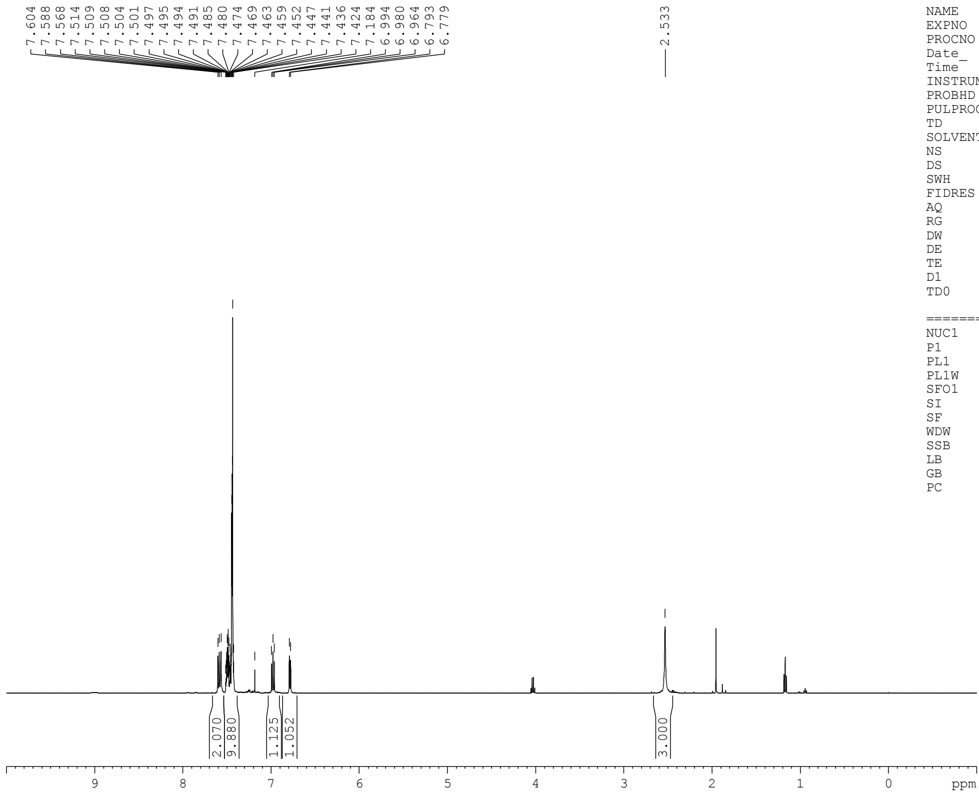
20d


8.007
7.674
7.671
7.462
7.459
7.448
7.434
7.431
7.414
7.400
7.397
7.389
7.375
7.358
7.196
6.926
6.909
6.813
6.809
6.796
6.792
NAME HUG-HC-439-4
EXPNO 10
PROCNO 1
Date_ 20130406
Time 6.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 57
DW 48.400 usec
DE 6.50 usec
TE 296.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 0.00 dB
PL1W 26.62599564 W
SFO1 500.3530899 MHz
SI 32768
SF 500.3500435 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
HUG-HC-439-4
1.000
0.990
10.084
1.007
1.020
9
8
7
6
5
4
3
2
1
0
ppm

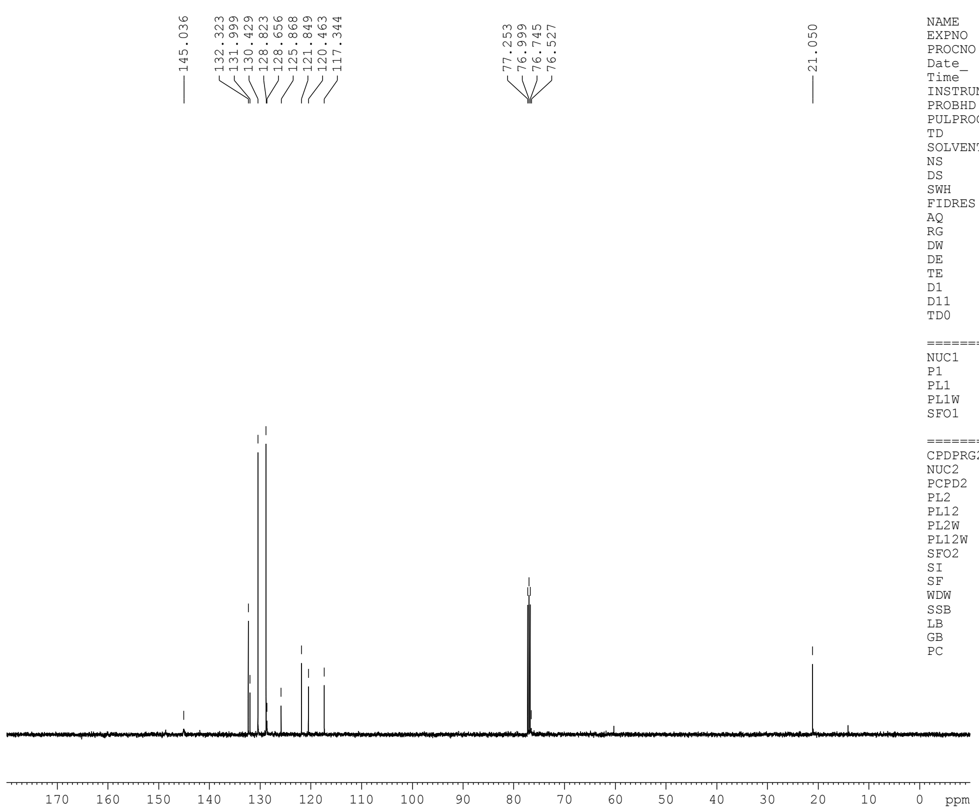

151.950
149.769
132.179
130.280
130.119
128.544
126.518
126.046
120.064
119.465
116.641
77.253
76.999
76.744
75.440
NAME HUG-HC-439-4
EXPNO 11
PROCNO 1
Date_ 20130406
Time 6.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1500
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 32800
DW 14.400 usec
DE 10.00 usec
TE 296.0 K
D1 0.01000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 6.78 usec
PL1 0.00 dB
PL1W 83.14344025 W
SFO1 125.8275761 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 17.23 dB
PL2W 26.62599564 W
PL12W 0.50385541 W
SFO2 500.3520014 MHz
SI 32768
SF 125.8131323 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
HUG-HC-439-4
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



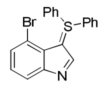
20k



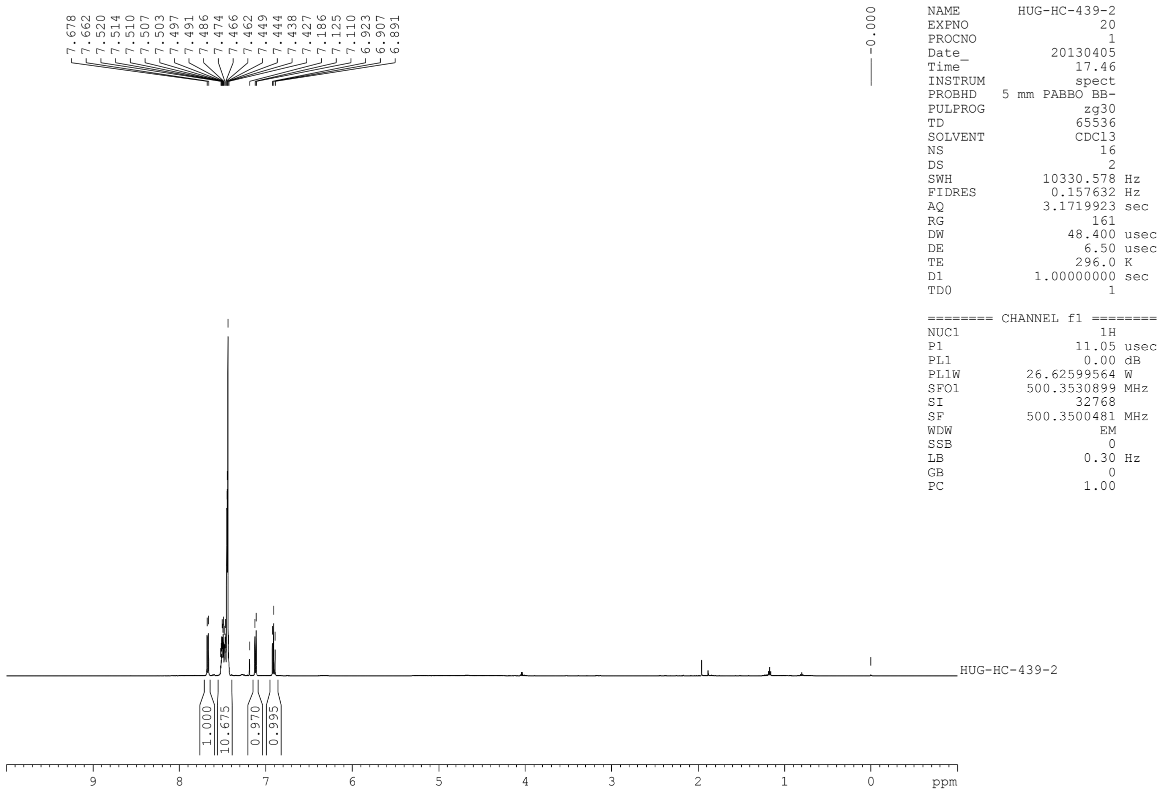
NAME	HUG-HC-439A
EXPNO	20
PROCNO	1
Date_	20130326
Time	14.34
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	71.8
DW	48.400 usec
DE	6.50 usec
TE	296.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.05 usec
PL1	0.00 dB
PL1W	26.62599564 W
SFO1	500.3530899 MHz
SI	32768
SF	500.3500492 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

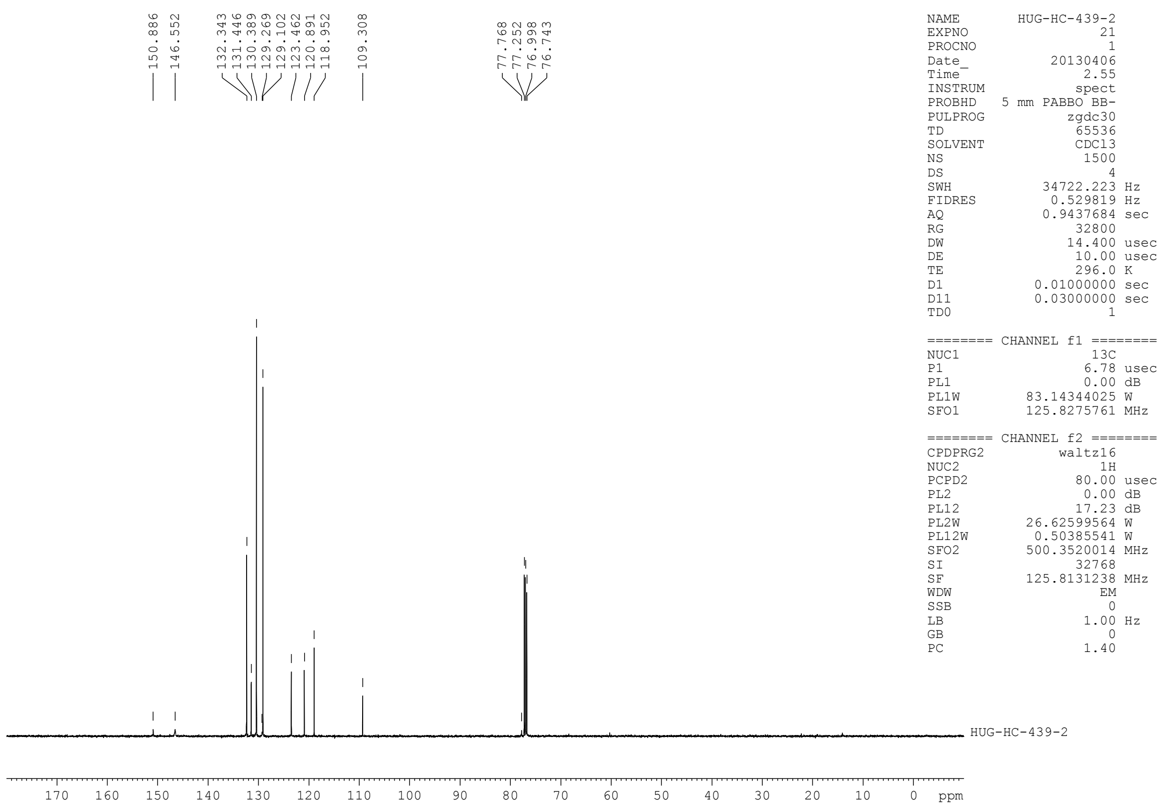


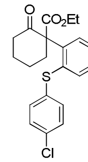
NAME	HUG-HC-439A
EXPNO	21
PROCNO	1
Date_	20130326
Time	14.39
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	256
DS	4
SWH	34722.223 Hz
FIDRES	0.529819 Hz
AQ	0.9437684 sec
RG	32800
DW	14.400 usec
DE	10.00 usec
TE	296.0 K
D1	0.01000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	6.78 usec
PL1	0.00 dB
PL1W	83.14344025 W
SFO1	125.8275761 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	17.23 dB
PL2W	26.62599564 W
PL12W	0.50385541 W
SFO2	500.3520014 MHz
SI	32768
SF	125.8131280 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40


Br
Ph
S
Ph
N

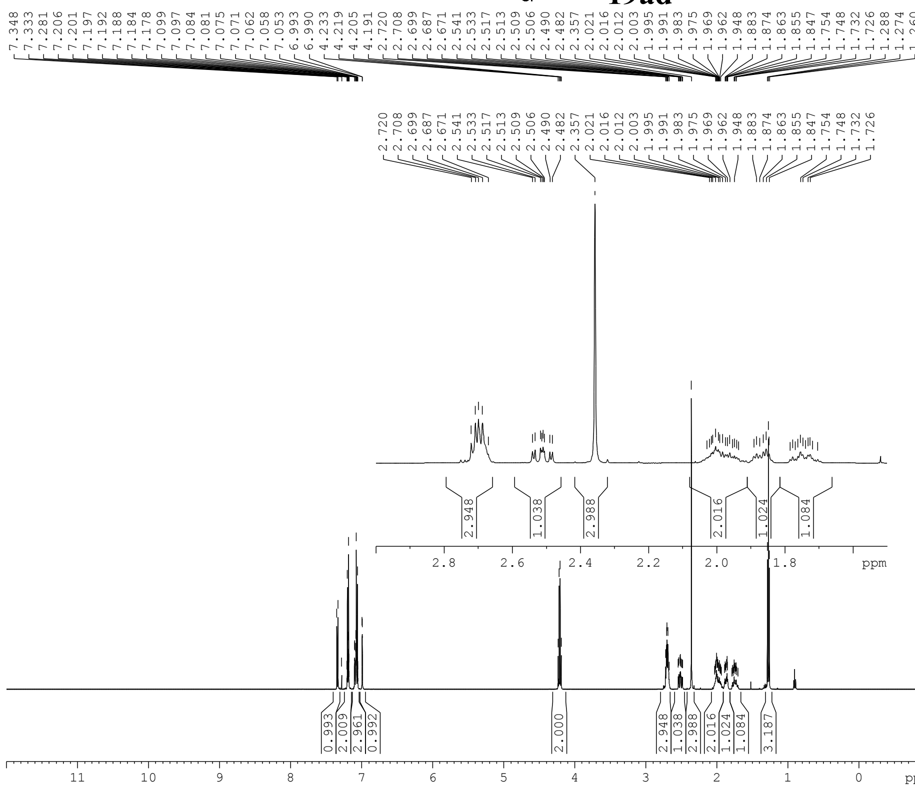
20l


7.678
7.662
7.520
7.514
7.510
7.507
7.503
7.497
7.491
7.486
7.474
7.466
7.462
7.449
7.444
7.438
7.427
7.186
7.125
7.110
6.923
6.907
6.891
0.000
1.000
10.675
0.970
0.995
HUG-HC-439-2
9 8 7 6 5 4 3 2 1 0 ppm
NAME HUG-HC-439-2
EXPNO 20
PROCNO 1
Date_ 20130405
Time 17.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 161
DW 48.400 usec
DE 6.50 usec
TE 296.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 0.00 dB
PL1W 26.62599564 W
SFO1 500.3530899 MHz
SI 32768
SF 500.3500481 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

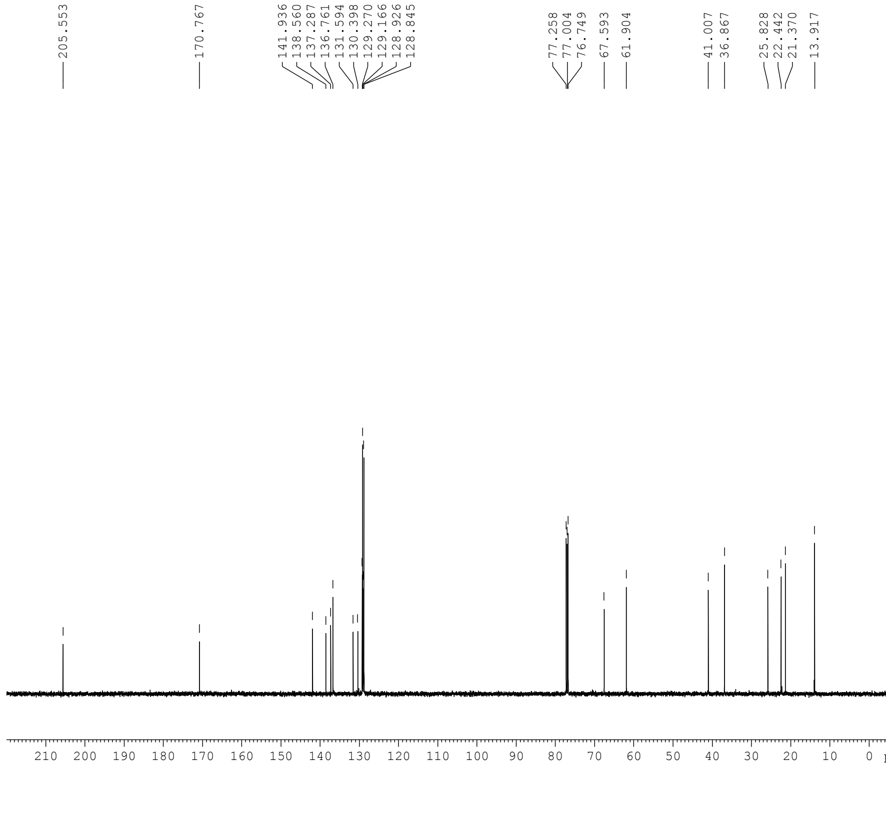

150.886
146.552
132.343
131.446
130.389
129.269
129.102
123.462
120.891
118.952
109.308
77.768
77.252
76.998
76.743
HUG-HC-439-2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
NAME HUG-HC-439-2
EXPNO 21
PROCNO 1
Date_ 20130406
Time 2.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1500
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 32800
DW 14.400 usec
DE 10.00 usec
TE 296.0 K
D1 0.01000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 6.78 usec
PL1 0.00 dB
PL1W 83.14344025 W
SFO1 125.8275761 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 17.23 dB
PL2W 26.62599564 W
PL12W 0.50385541 W
SFO2 500.3520014 MHz
SI 32768
SF 125.8131238 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



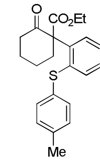
19ad



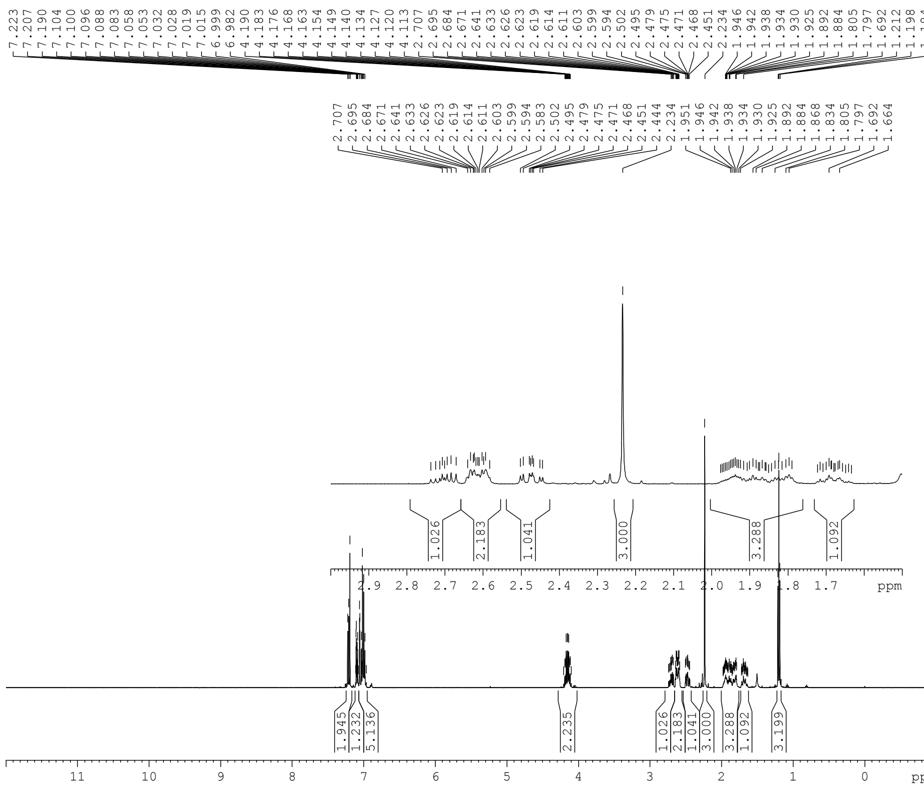

```
NAME       HUG-HC-444B-2
EXPNO                 10
PROCNO                 1
Date_           20130403
Time               19.21
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                  45.2
DW                48.400 usec
DE                  6.50 usec
TE                 296.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.05 usec
PL1                 0.00 dB
PL1W         26.62599564 W
SFO1         500.3530899 MHz
SI                 32768
SF           500.3500000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



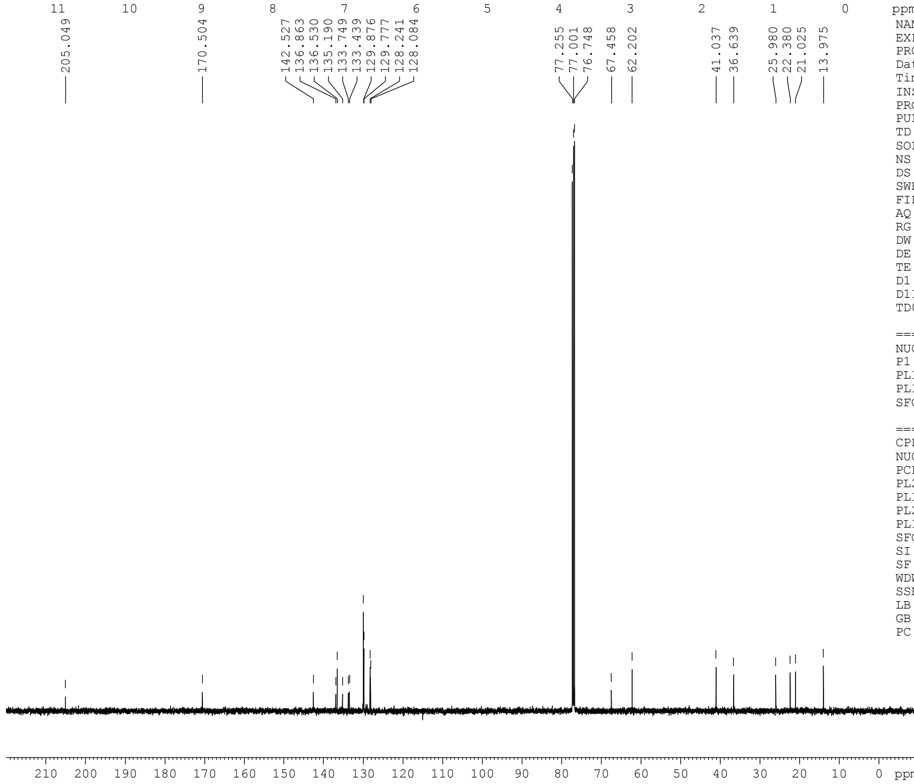

```
NAME       HUG-HC-444B-2
EXPNO                 11
PROCNO                 1
Date_           20130403
Time               19.27
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            34722.223 Hz
FIDRES          0.529819 Hz
AQ             0.9437684 sec
RG                 32800
DW                14.400 usec
DE                 10.00 usec
TE                 296.0 K
D1            0.01000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  6.78 usec
PL1                 0.00 dB
PL1W         83.14344025 W
SFO1         125.8275761 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.23 dB
PL2W         26.62599564 W
PL12W         0.50385541 W
SFO2         500.3520014 MHz
SI                 32768
SF           125.8131217 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



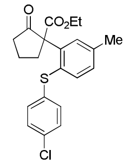
19ad'



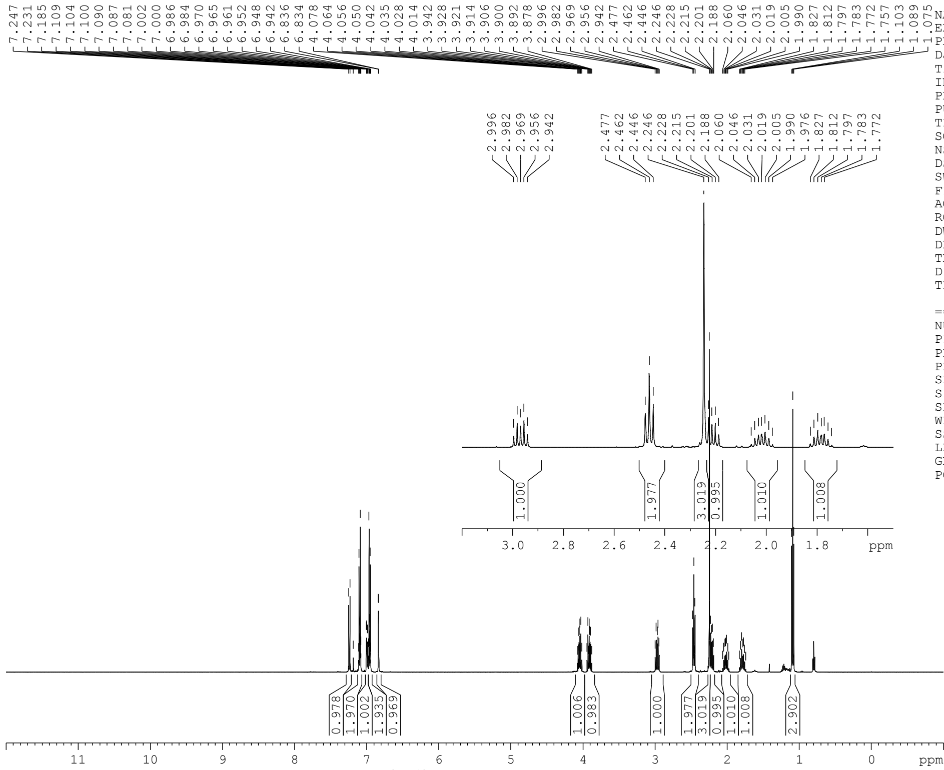
NAME	HUG-HC-444B-1
EXPNO	10
PROCNO	1
Date_	20130403
Time	19.16
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	287
DW	48.400 usec
DE	6.50 usec
TE	296.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.05 usec
PL1	0.00 dB
PL1W	26.62599564 W
SFO1	500.3530899 MHz
SI	32768
SF	500.3500458 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



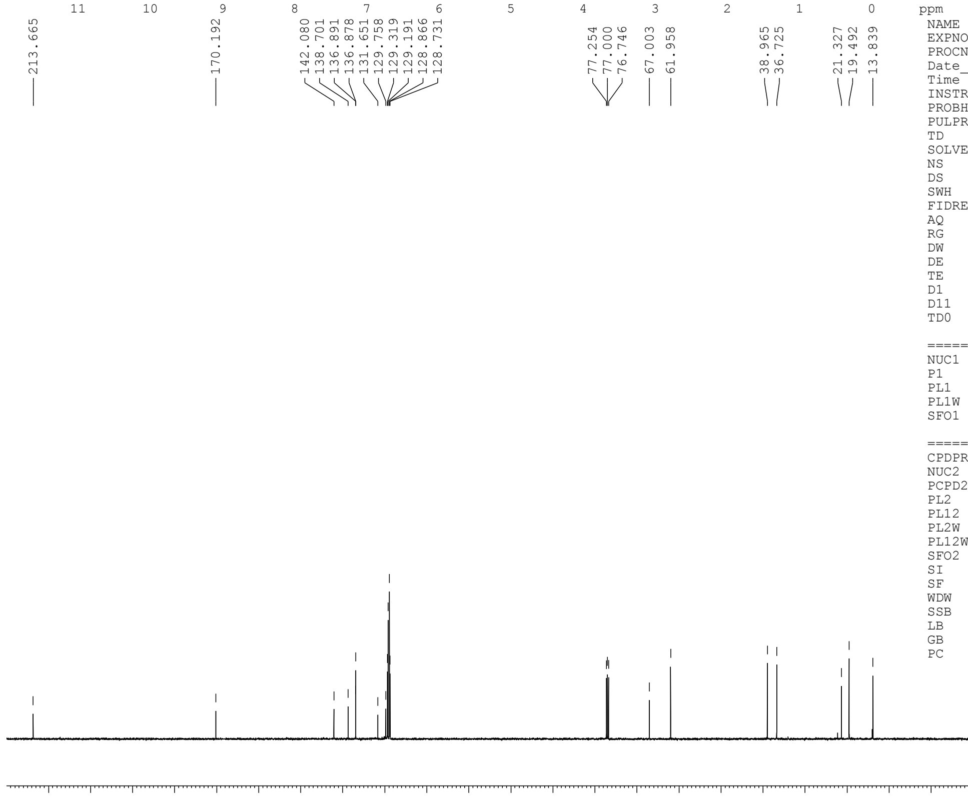
NAME	HUG-HC-444B-1
EXPNO	11
PROCNO	1
Date_	20130404
Time	4.16
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	1500
DS	4
SWH	34722.223 Hz
FIDRES	0.529819 Hz
AQ	0.9437684 sec
RG	32800
DW	14.400 usec
DE	10.00 usec
TE	296.0 K
D1	0.01000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	6.78 usec
PL1	0.00 dB
PL1W	83.14344025 W
SFO1	125.8275761 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	17.23 dB
PL2W	26.62599564 W
PL12W	0.50385541 W
SFO2	500.3520014 MHz
SI	32768
SF	125.8131111 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



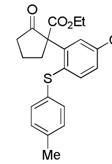
19bd



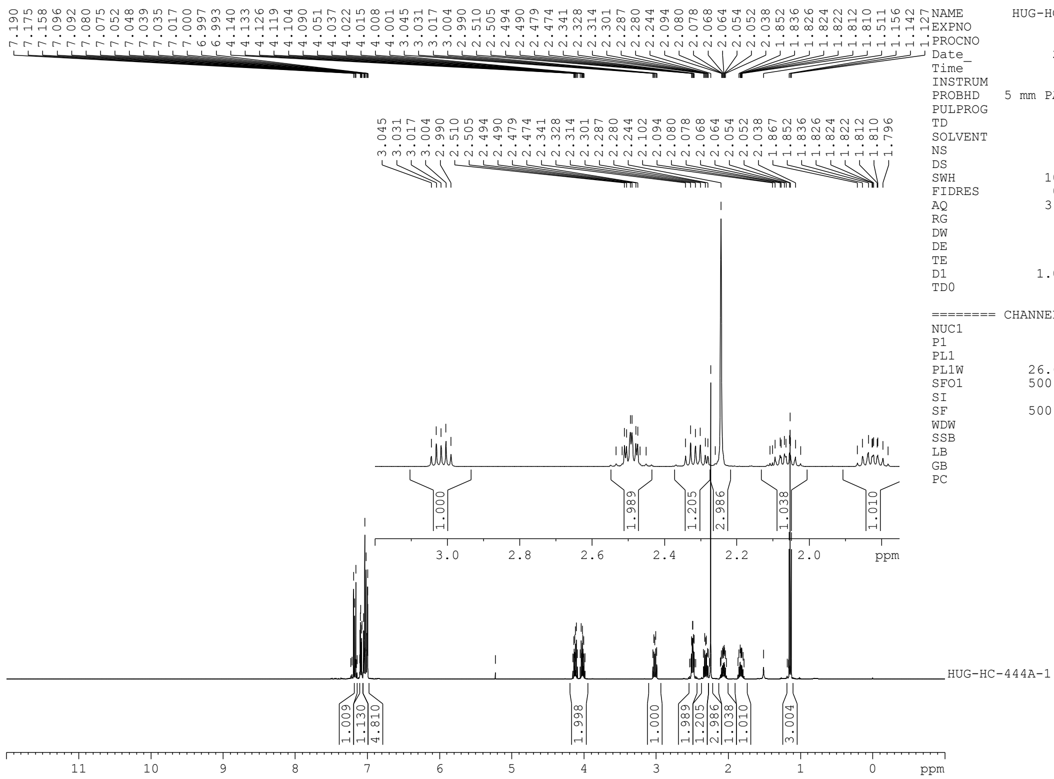

```
NAME       HUG-HC-444A-2
EXPNO                 10
PROCNO                 1
Date_           20130403
Time               16.42
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                  45.2
DW                48.400 usec
DE                  6.50 usec
TE                 296.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.05 usec
PL1                 0.00 dB
PL1W         26.62599564 W
SFO1         500.3530899 MHz
SI                 32768
SF           500.3500481 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



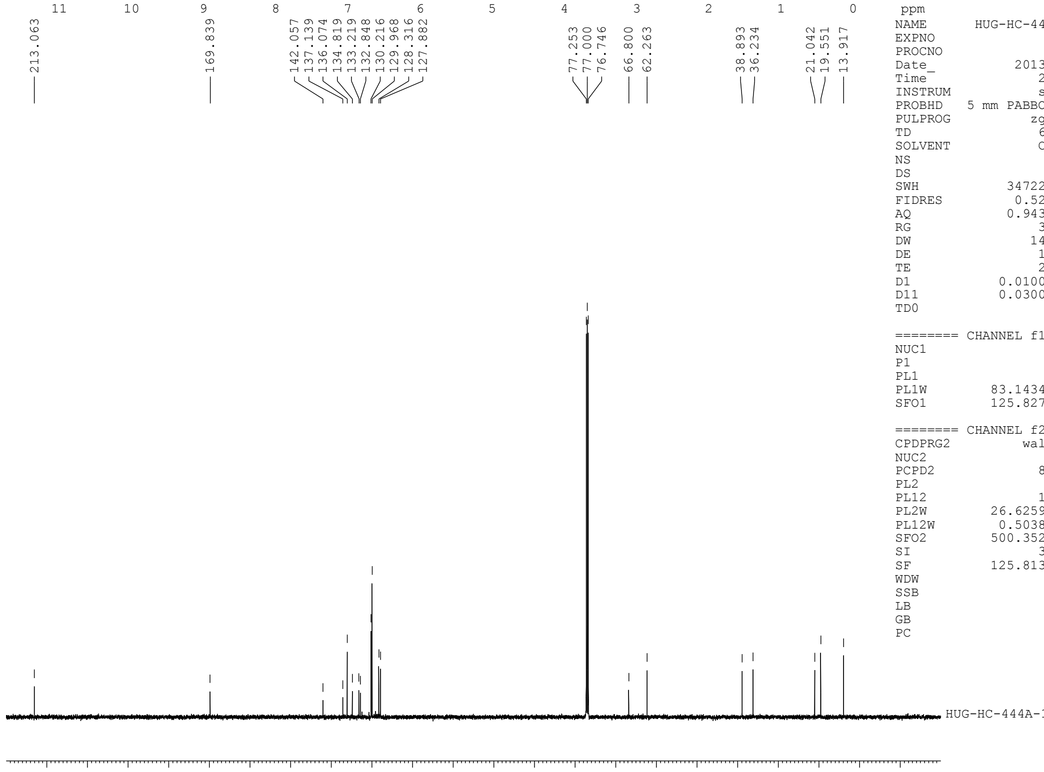

```
NAME       HUG-HC-444A-2
EXPNO                 12
PROCNO                 1
Date_           20130403
Time               16.48
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            34722.223 Hz
FIDRES          0.529819 Hz
AQ             0.9437684 sec
RG                 32800
DW                14.400 usec
DE                 10.00 usec
TE                 296.0 K
D1            0.01000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  6.78 usec
PL1                 0.00 dB
PL1W         83.14344025 W
SFO1         125.8275761 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.23 dB
PL2W         26.62599564 W
PL12W         0.50385541 W
SFO2         500.3520014 MHz
SI                 32768
SF           125.8131217 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



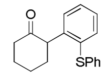
19bd’



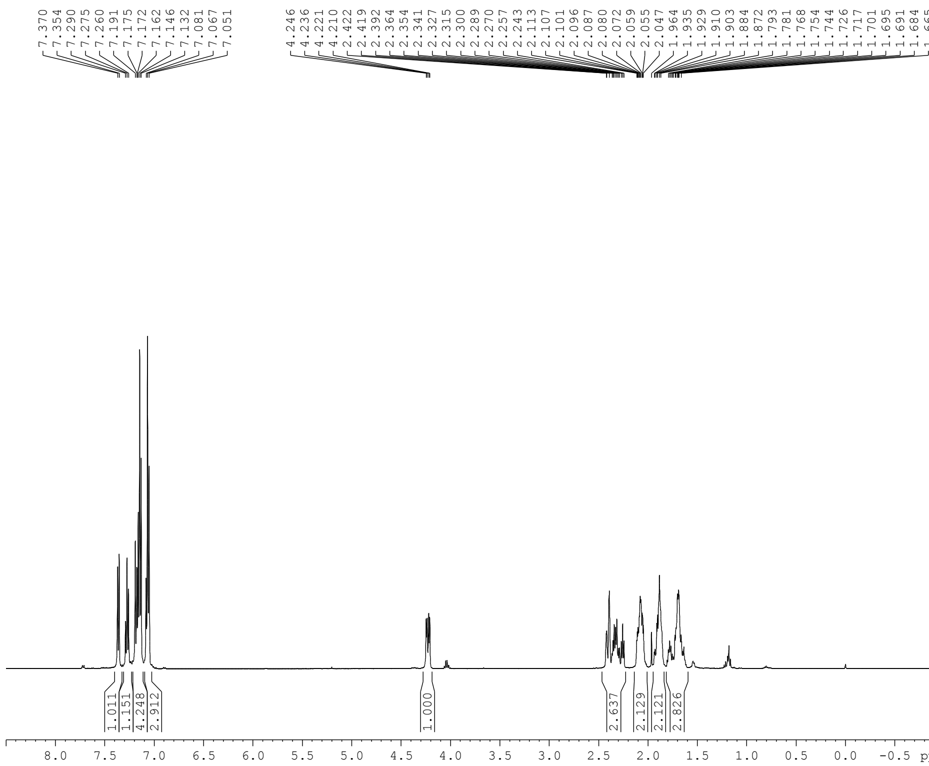

```
NAME        HUG-HC-444A-1
EXPNO                  10
PROCNO                  1
Date_            20130403
Time                16.38
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ           3.1719923 sec
RG                    161
DW              48.400 usec
DE                6.50 usec
TE               296.0 K
D1          1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1               11.05 usec
PL1               0.00 dB
PL1W       26.62599564 W
SFO1       500.3530899 MHz
SI                  32768
SF         500.3500461 MHz
WDW                    EM
SSB                     0
LB                0.30 Hz
GB                      0
PC                   1.00
```




```
NAME        HUG-HC-444A-1
EXPNO                  12
PROCNO                  1
Date_            20130403
Time                22.49
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgdc30
TD                  65536
SOLVENT             CDCl3
NS                   1500
DS                      4
SWH          34722.223 Hz
FIDRES        0.529819 Hz
AQ           0.9437684 sec
RG                  32800
DW              14.400 usec
DE               10.00 usec
TE               295.9 K
D1          0.01000000 sec
D11         0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                6.78 usec
PL1               0.00 dB
PL1W       83.14344025 W
SFO1       125.8275761 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             17.23 dB
PL2W       26.62599564 W
PL12W       0.50385541 W
SFO2       500.3520014 MHz
SI                  32768
SF         125.8131121 MHz
WDW                    EM
SSB                     0
LB                1.00 Hz
GB                      0
PC                   1.40
```

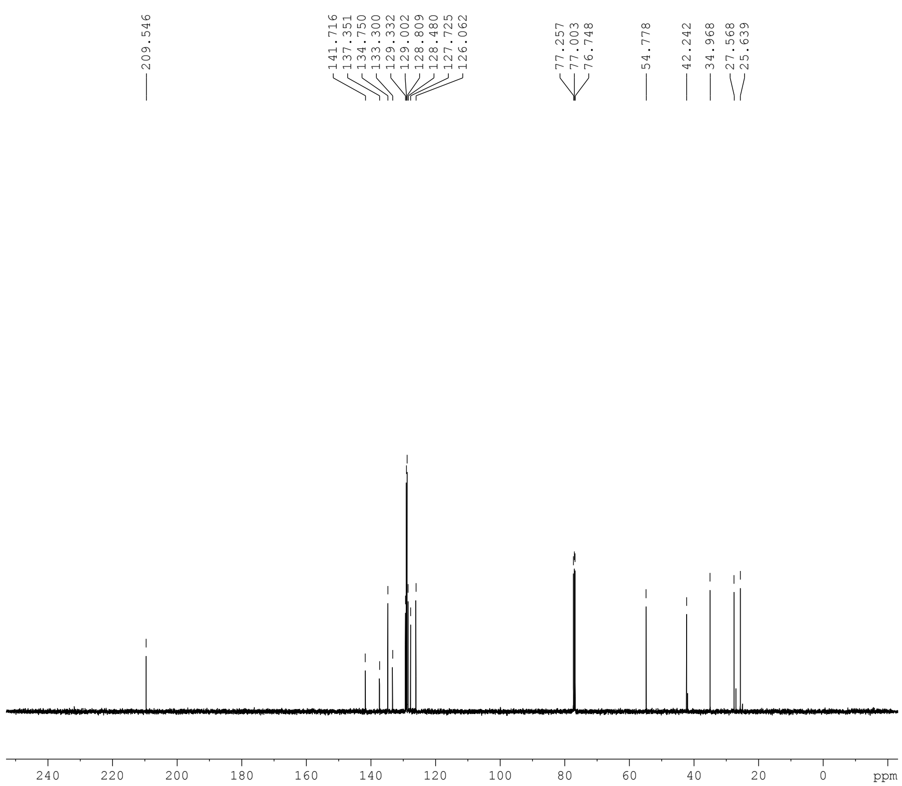


9



NAME HUG-HB-165
EXPNO 10
PROCNO 1
Date_ 20101213
Time 18.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 90.5
DW 48.400 usec
DE 10.00 usec
TE 296.0 K
D1 1.00000000 sec
TD0 1

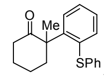
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 0.00 dB
PL1W 26.62599564 W
SFO1 500.0835006 MHz
SI 32768
SF 500.0800595 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



NAME HUG-HB-165
EXPNO 11
PROCNO 1
Date_ 20101213
Time 18.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 32800
DW 14.400 usec
DE 10.00 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 6.78 usec
PL1 0.00 dB
PL1W 83.14344025 W
SFO1 125.7596767 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 17.23 dB
PL13 17.23 dB
PL2W 26.62599564 W
PL12W 0.50385541 W
PL13W 0.50385541 W
SFO2 500.0820003 MHz
SI 32768
SF 125.7452275 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



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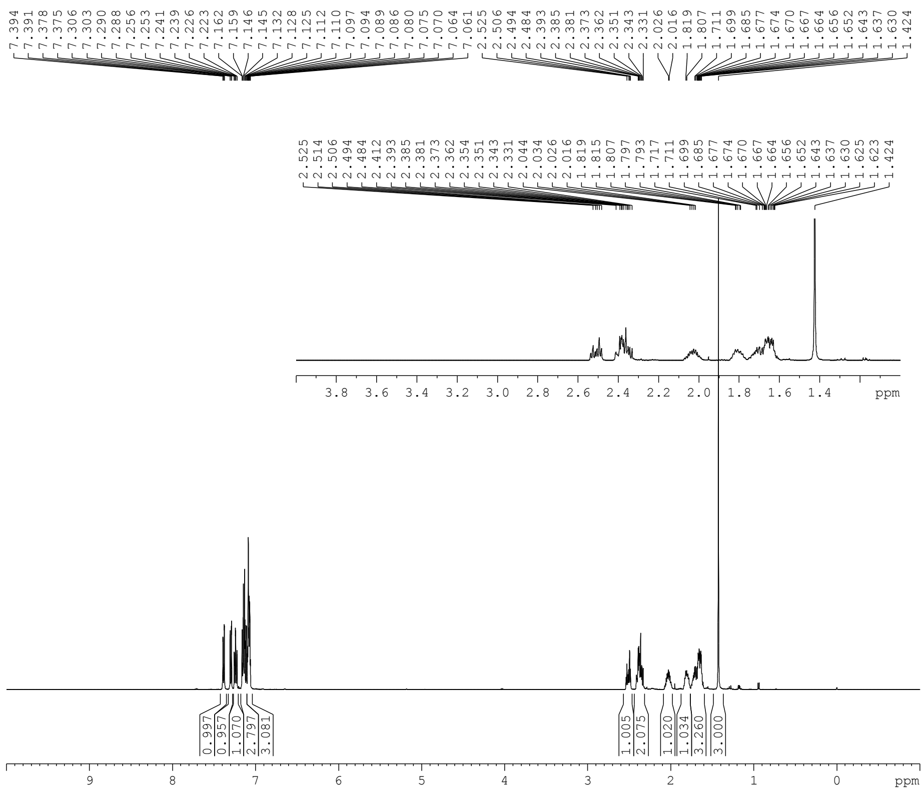
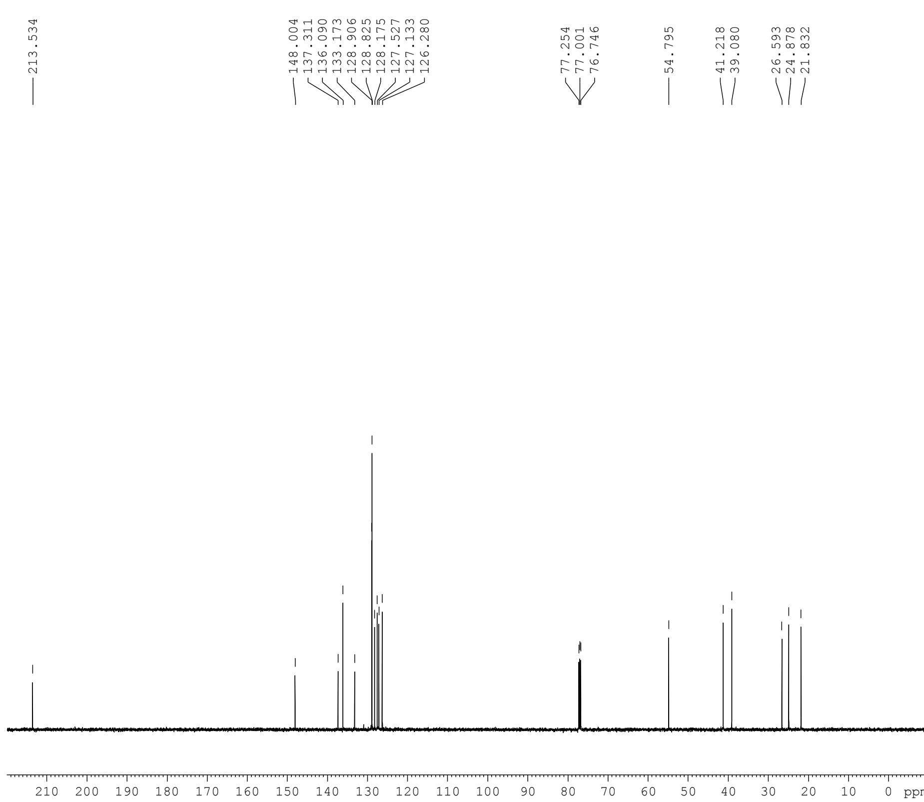


NAME HUG-HB-358
EXPNO 10
PROCNO 1
Date_ 20110608
Time 14.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 57
DW 48.400 usec
DE 10.00 usec
TE 296.0 K
D1 1.00000000 sec
TD0 1

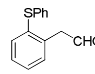
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 0.00 dB
PL1W 26.62599564 W
SFO1 500.0835006 MHz
SI 32768
SF 500.0800640 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



NAME HUG-HB-358
EXPNO 11
PROCNO 1
Date_ 20110608
Time 14.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 32800
DW 14.400 usec
DE 10.00 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 6.78 usec
PL1 0.00 dB
PL1W 83.14344025 W
SFO1 125.7596767 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 17.23 dB
PL13 17.23 dB
PL2W 26.62599564 W
PL12W 0.50385541 W
PL13W 0.50385541 W
SFO2 500.0820003 MHz
SI 32768
SF 125.7452339 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



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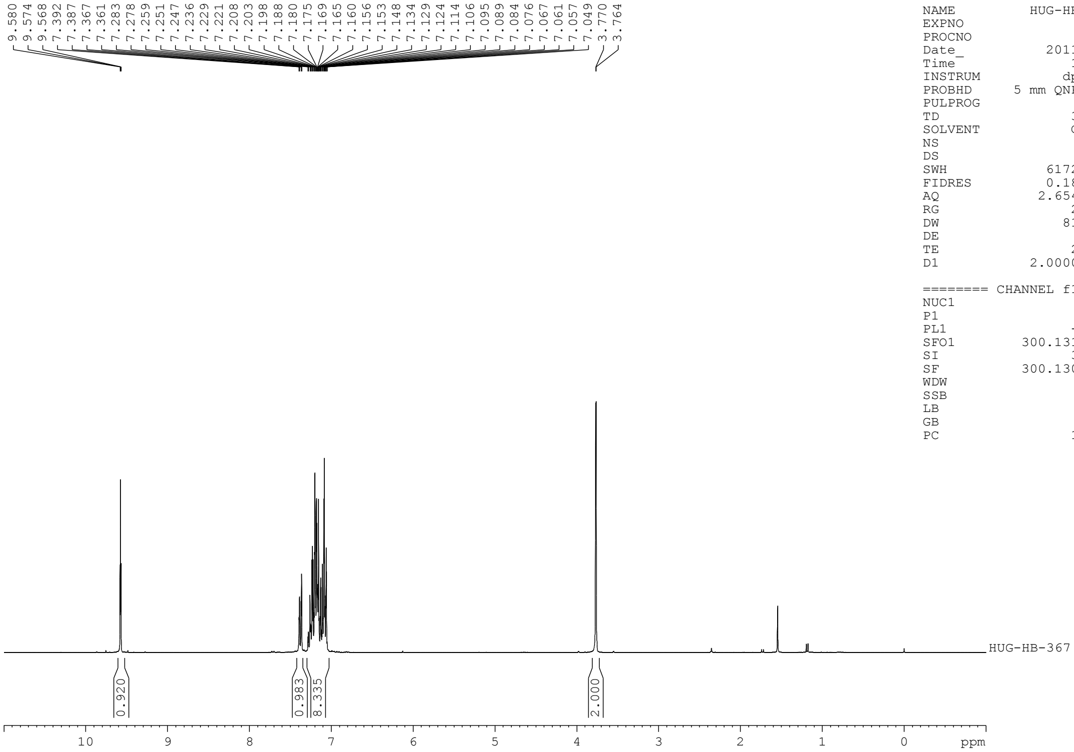
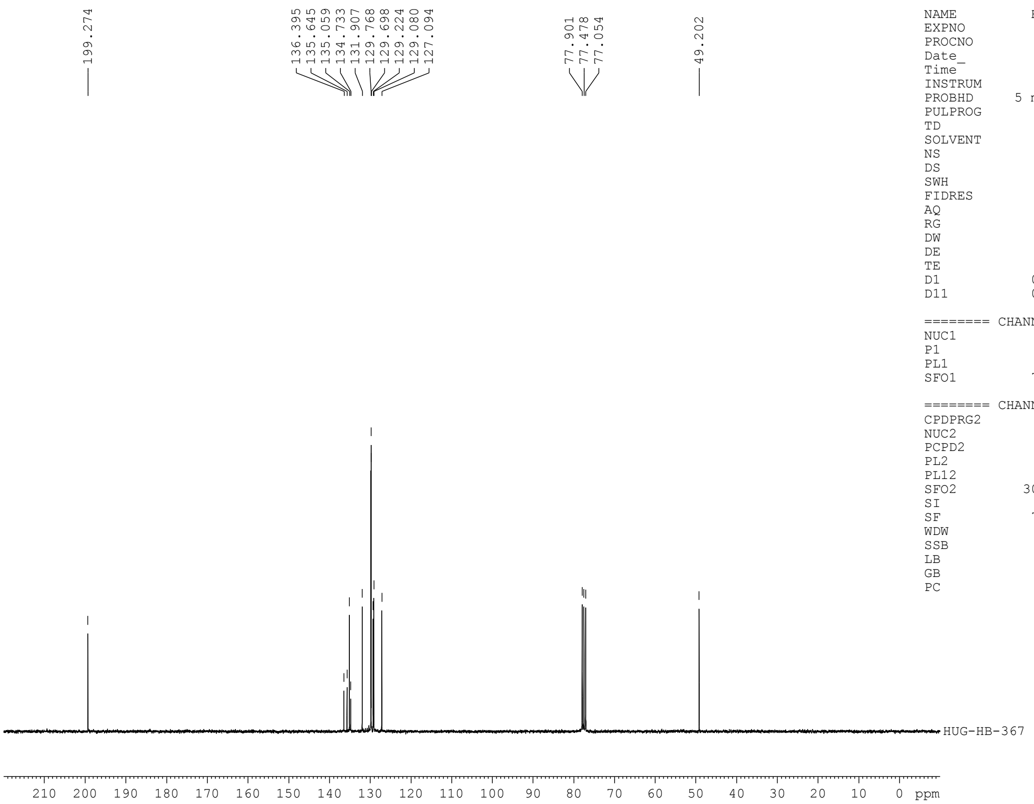
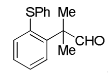



```
NAME          HUG-HB-367
EXPNO                 10
PROCNO                 1
Date_           20110614
Time               12.52
INSTRUM           dpx300
PROBHD     5 mm QNP 1H/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ             2.6542580 sec
RG                 203.2
DW                81.000 usec
DE                  4.50 usec
TE                 297.2 K
D1            2.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.30 usec
PL1                -6.00 dB
SFO1         300.1318534 MHz
SI                 32768
SF           300.1300346 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                 18.00
```




```
NAME          HUG-HB-367
EXPNO                 11
PROCNO                 1
Date_           20110614
Time               15.30
INSTRUM           dpx300
PROBHD     5 mm QNP 1H/
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                  1200
DS                     2
SWH            21231.422 Hz
FIDRES          0.323966 Hz
AQ             1.5434228 sec
RG                 16384
DW                23.550 usec
DE                  4.50 usec
TE                 297.2 K
D1            0.03000000 sec
D11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  6.60 usec
PL1                -6.00 dB
SFO1          75.4760670 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               16.20 dB
SFO2         300.1312005 MHz
SI                 32768
SF            75.4677190 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



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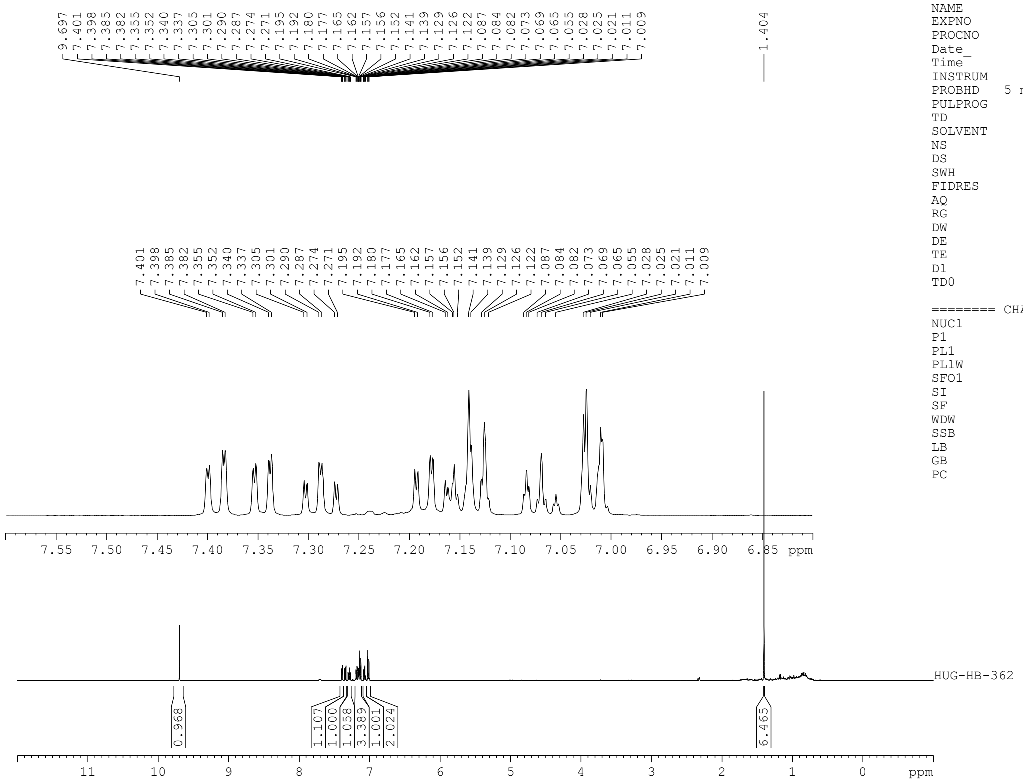
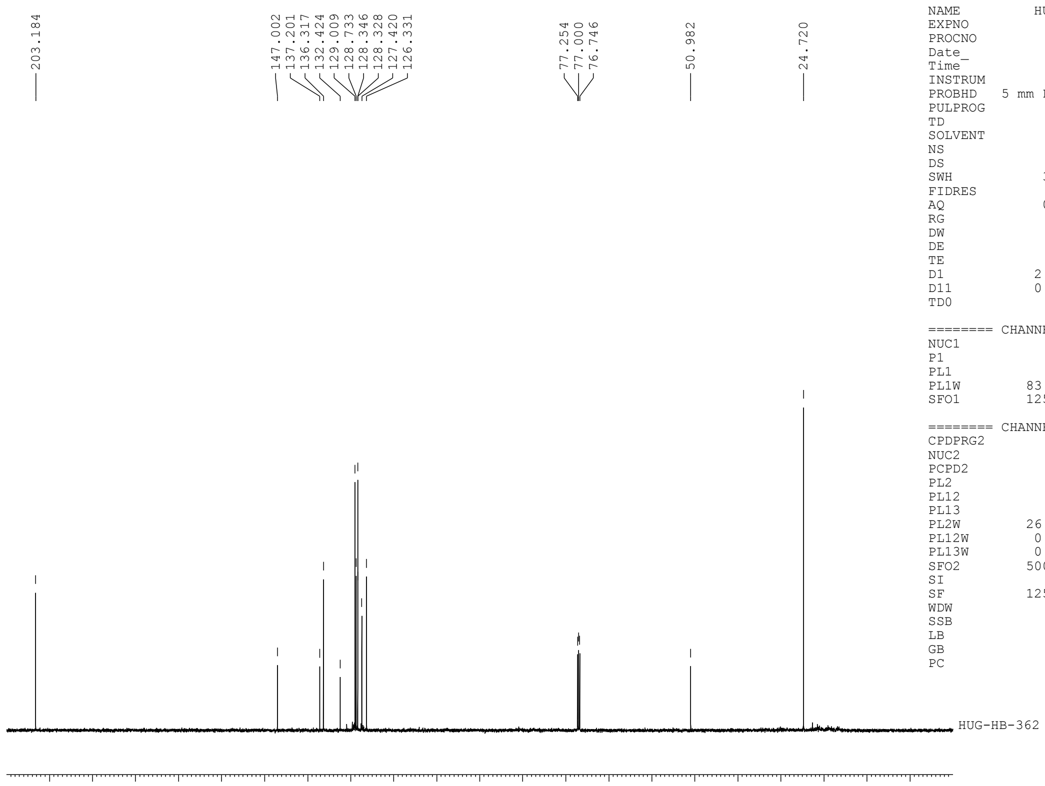
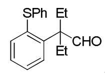


NAME	HUG-HB-362
EXPNO	10
PROCNO	1
Date_	20110610
Time	9.01
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	28.5
DW	48.400 usec
DE	10.00 usec
TE	296.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.05 usec
PL1	0.00 dB
PL1W	26.62599564 W
SFO1	500.0835006 MHz
SI	32768
SF	500.0800632 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



NAME	HUG-HB-362
EXPNO	11
PROCNO	1
Date_	20110610
Time	9.09
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	128
DS	4
SWH	34722.223 Hz
FIDRES	0.529819 Hz
AQ	0.9437684 sec
RG	32800
DW	14.400 usec
DE	10.00 usec
TE	296.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	6.78 usec
PL1	0.00 dB
PL1W	83.14344025 W
SFO1	125.7596767 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	17.23 dB
PL13	17.23 dB
PL2W	26.62599564 W
PL12W	0.50385541 W
PL13W	0.50385541 W
SFO2	500.0820003 MHz
SI	32768
SF	125.7452318 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



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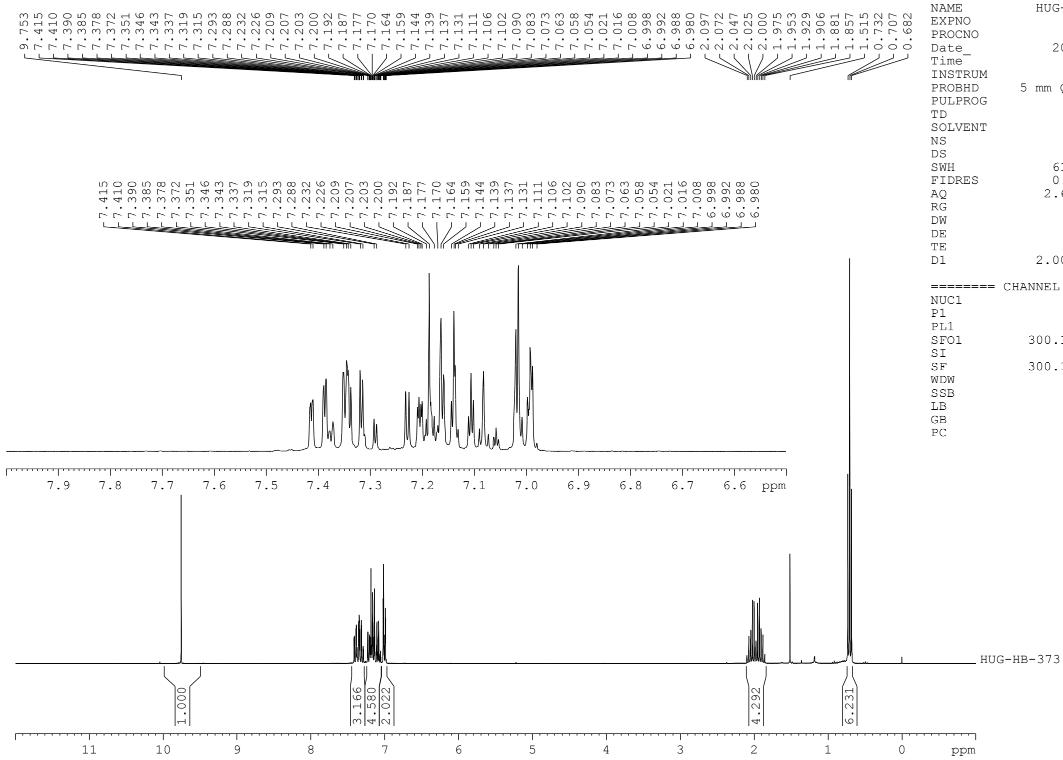
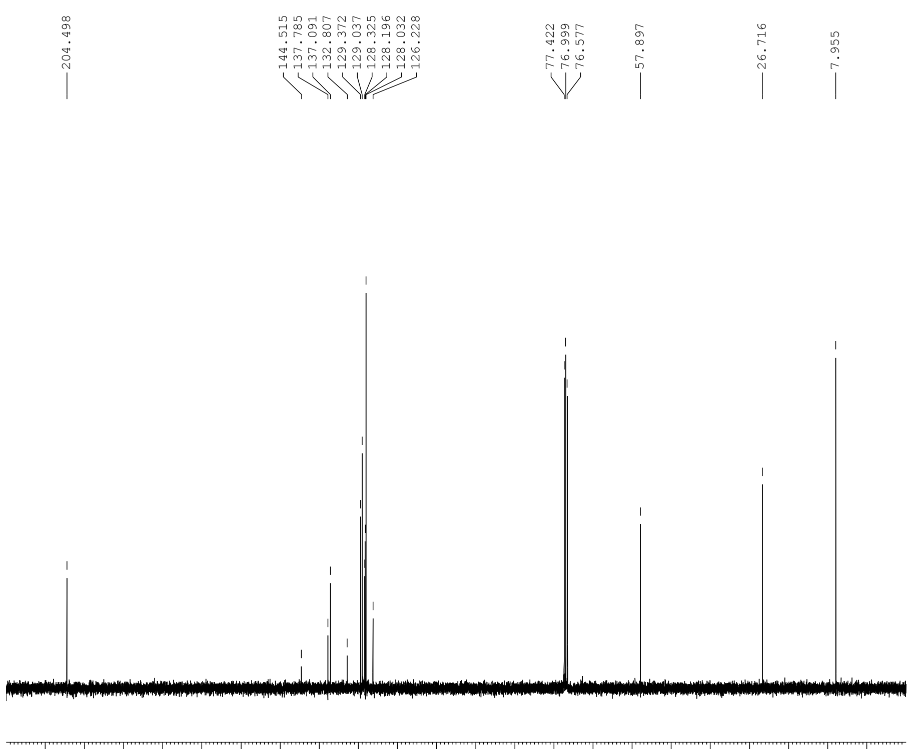
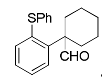



```
NAME          HUG-HB-373
EXPNO                 10
PROCNO                 1
Date_           20110617
Time                7.00
INSTRUM           dpx300
PROBHD      5 mm QNP 1H/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH          6172.839 Hz
FIDRES       0.188380 Hz
AQ          2.6542580 sec
RG                 322.5
DW            81.000 usec
DE              4.50 usec
TE               296.2 K
D1        2.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1              7.30 usec
PL1             -6.00 dB
SFO1      300.1318534 MHz
SI                 32768
SF        300.1300281 MHz
WDW                   no
SSB                    0
LB               0.00 Hz
GB                     0
PC                 18.00
```




```
NAME          HUG-HB-373
EXPNO                 11
PROCNO                 1
Date_           20110617
Time                7.32
INSTRUM           dpx300
PROBHD      5 mm QNP 1H/
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                  1200
DS                     2
SWH         21231.422 Hz
FIDRES       0.323966 Hz
AQ          1.5434228 sec
RG               14596.5
DW            23.550 usec
DE              4.50 usec
TE               296.2 K
D1        0.03000000 sec
D11       0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1              6.60 usec
PL1             -6.00 dB
SFO1       75.4760670 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2          80.00 usec
PL2             -6.00 dB
PL12            16.20 dB
SFO2      300.1312005 MHz
SI                 32768
SF         75.4677514 MHz
WDW                   no
SSB                    0
LB               0.00 Hz
GB                     0
PC                  1.40
```


SPh
CHO

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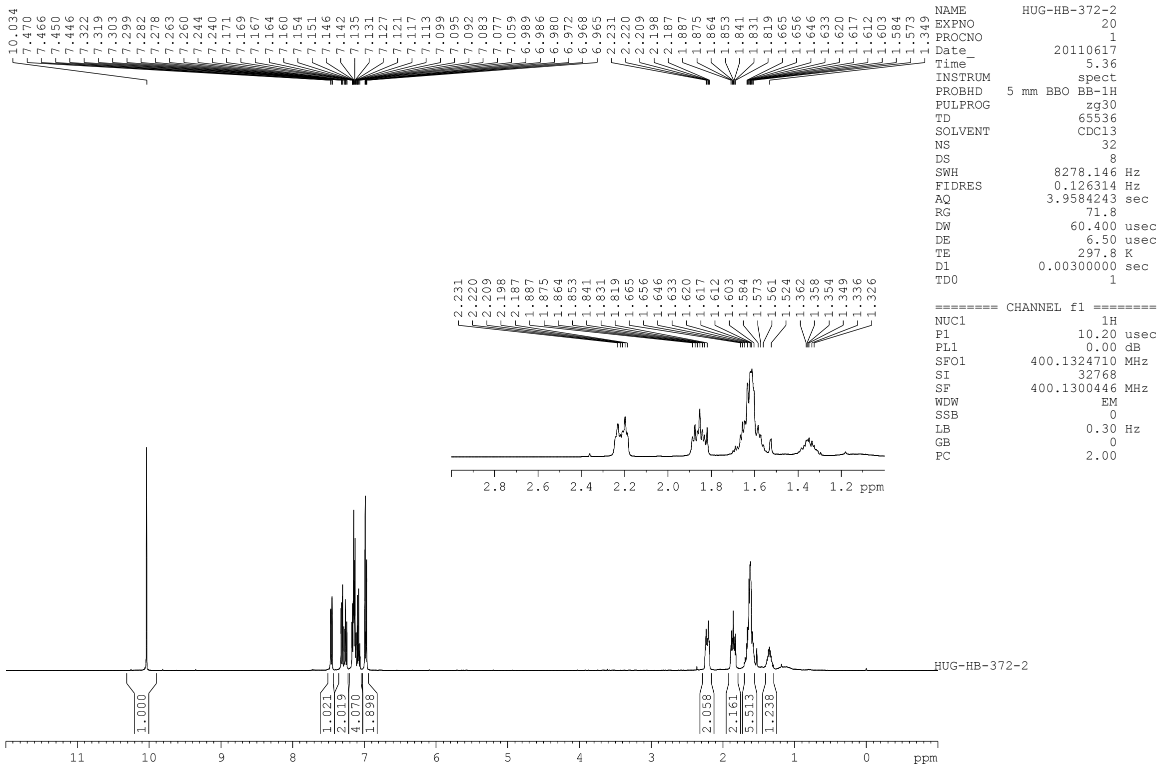
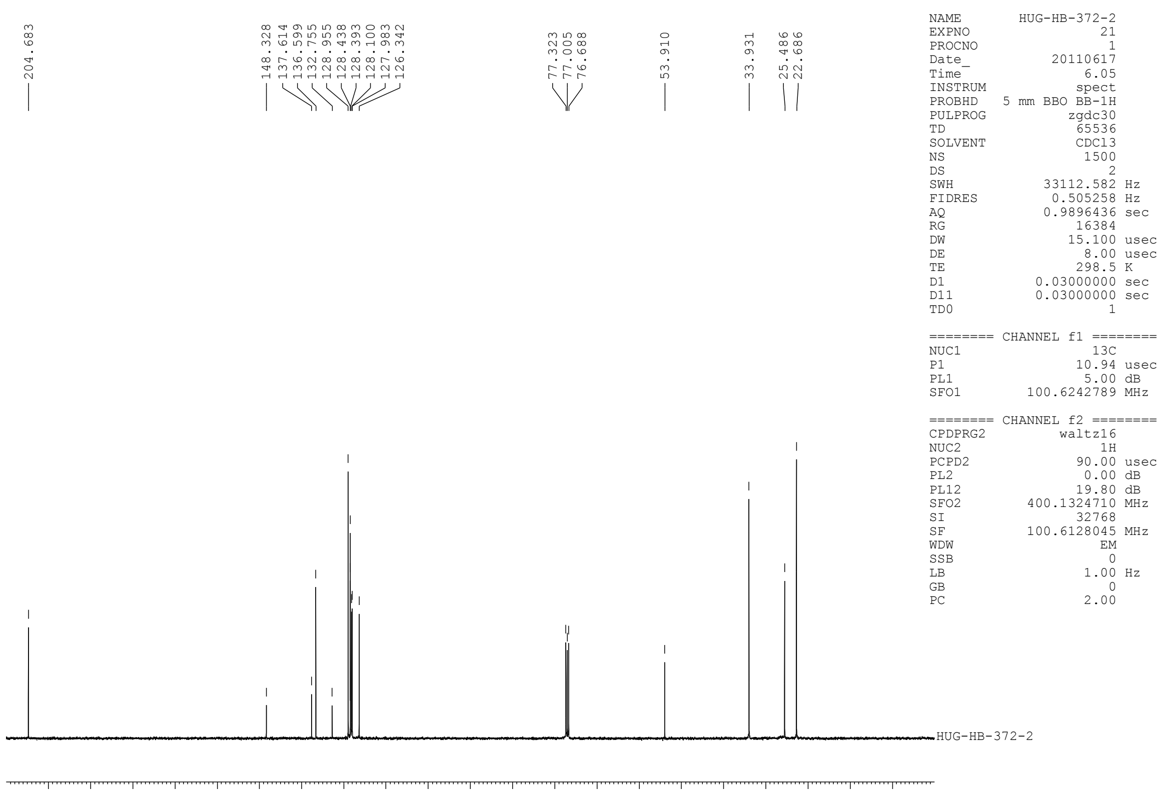
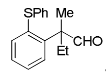

NAME HUG-HB-372-2
EXPNO 20
PROCNO 1
Date_ 20110617
Time 5.36
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 71.8
DW 60.400 usec
DE 6.50 usec
TE 297.8 K
D1 0.00300000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.20 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
SI 32768
SF 400.1300446 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00
HUG-HB-372-2
1.000
1.021
2.019
4.070
1.898
2.058
2.161
5.513
1.238
ppm


204.683
148.328
137.614
136.599
132.755
128.955
128.438
128.393
128.100
127.983
126.342
77.323
77.005
76.688
53.910
33.931
25.486
22.686
NAME HUG-HB-372-2
EXPNO 21
PROCNO 1
Date_ 20110617
Time 6.05
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.505258 Hz
AQ 0.9896436 sec
RG 16384
DW 15.100 usec
DE 8.00 usec
TE 298.5 K
D1 0.03000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.6242789 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.80 dB
SFO2 400.1324710 MHz
SI 32768
SF 100.6128045 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
HUG-HB-372-2
ppm


SPh
Me
CHO
Et

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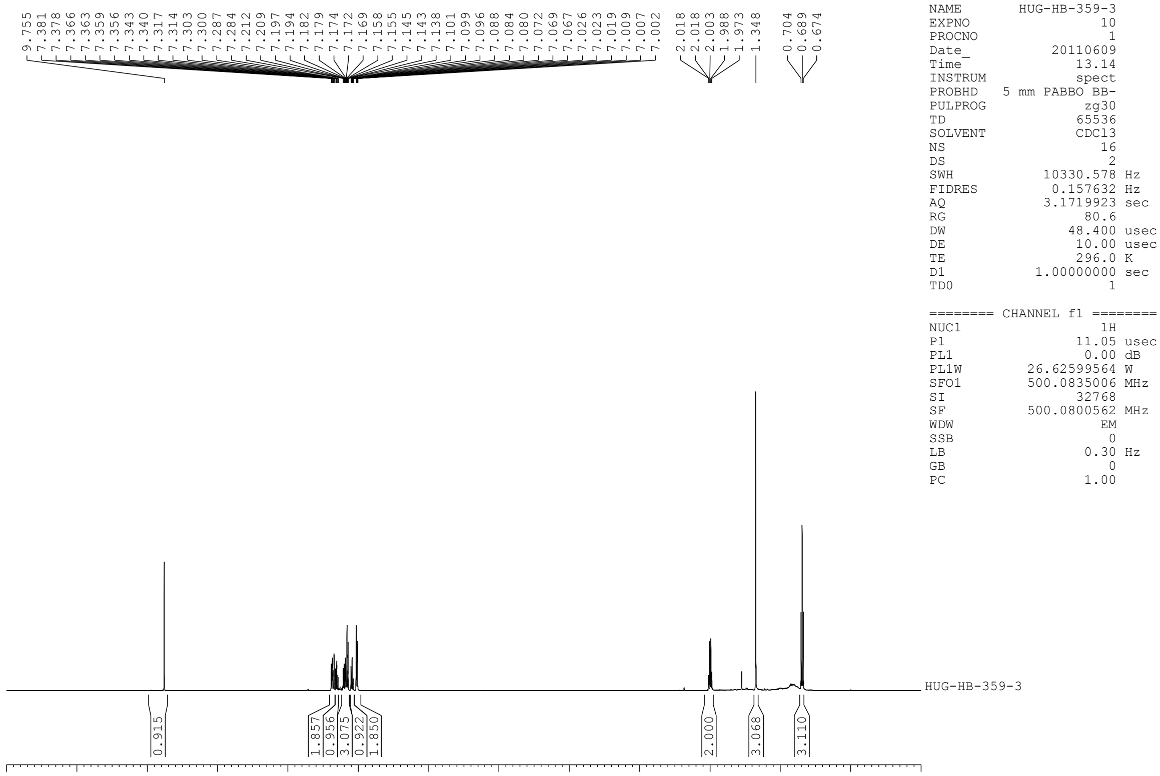
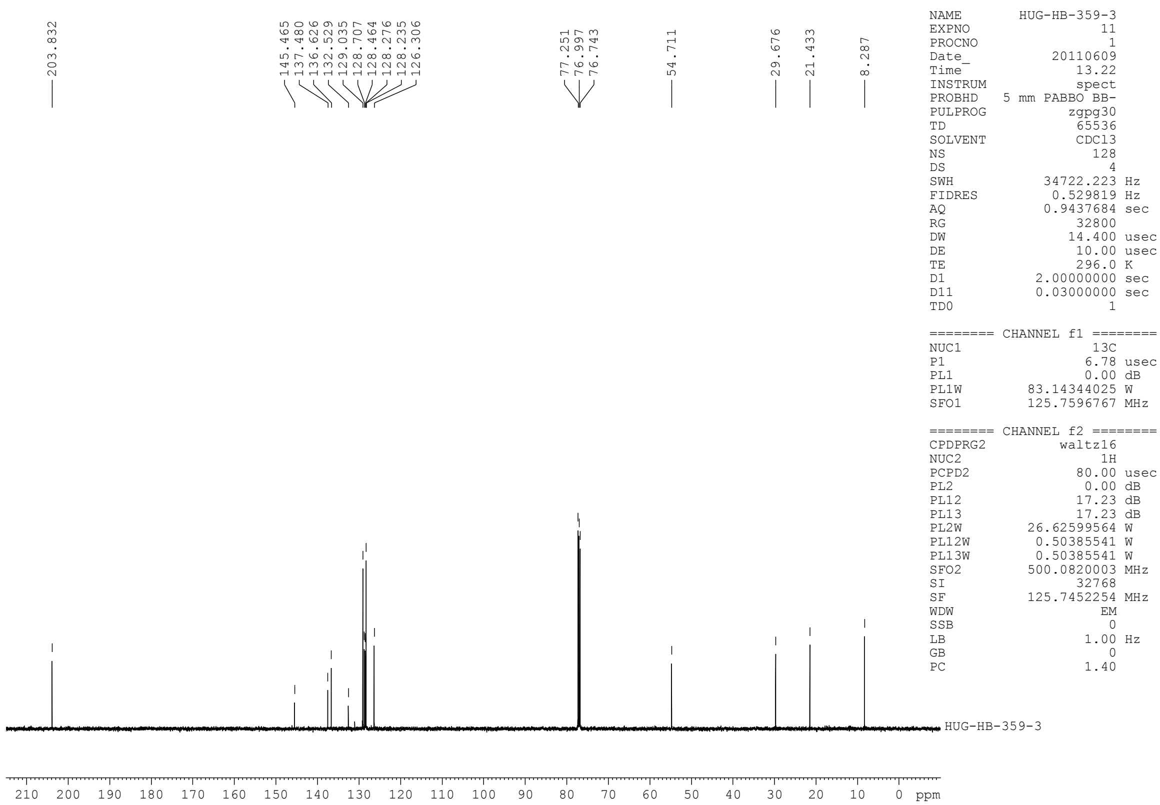
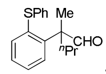
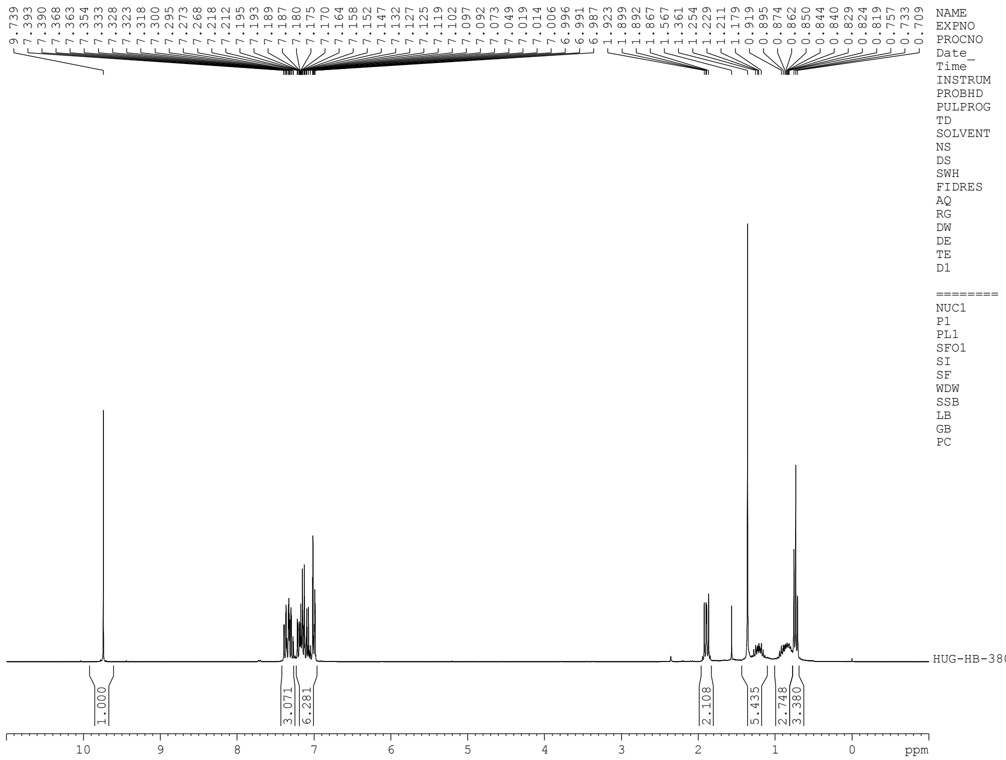

9.755
7.381
7.378
7.366
7.363
7.359
7.356
7.343
7.340
7.317
7.314
7.303
7.300
7.287
7.284
7.212
7.209
7.197
7.194
7.182
7.179
7.174
7.172
7.169
7.158
7.155
7.145
7.143
7.138
7.101
7.099
7.096
7.088
7.084
7.080
7.072
7.069
7.067
7.026
7.023
7.019
7.009
7.007
7.002
2.018
2.018
2.003
1.988
1.973
1.348
0.704
0.689
0.674
0.915
1.857
0.956
3.075
0.922
1.850
2.000
3.068
3.110
11
10
9
8
7
6
5
4
3
2
1
0
ppm
HUG-HB-359-3
NAME HUG-HB-359-3
EXPNO 10
PROCNO 1
Date_ 20110609
Time 13.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 80.6
DW 48.400 usec
DE 10.00 usec
TE 296.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 0.00 dB
PL1W 26.62599564 W
SFO1 500.0835006 MHz
SI 32768
SF 500.0800562 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


203.832
145.465
137.480
136.626
132.529
129.035
128.707
128.464
128.276
128.235
126.306
77.251
76.997
76.743
54.711
29.676
21.433
8.287
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
HUG-HB-359-3
NAME HUG-HB-359-3
EXPNO 11
PROCNO 1
Date_ 20110609
Time 13.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 32800
DW 14.400 usec
DE 10.00 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 6.78 usec
PL1 0.00 dB
PL1W 83.14344025 W
SFO1 125.7596767 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 17.23 dB
PL13 17.23 dB
PL2W 26.62599564 W
PL12W 0.50385541 W
PL13W 0.50385541 W
SFO2 500.0820003 MHz
SI 32768
SF 125.7452254 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

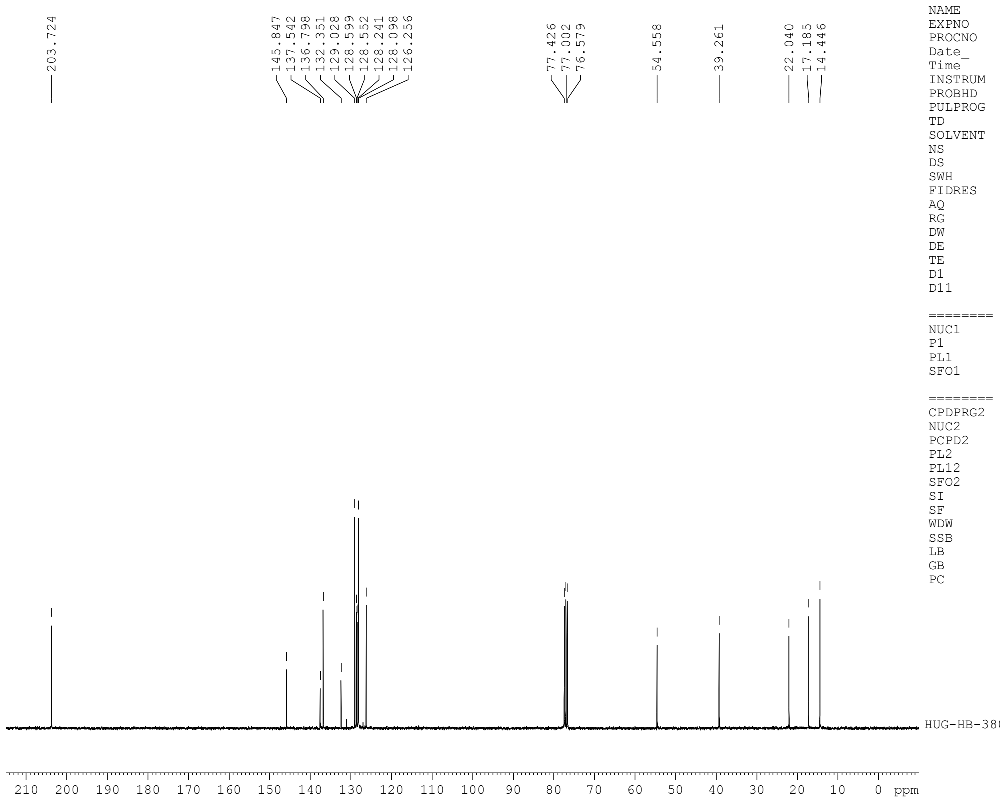


32




```
NAME            HUG-HB-380
EXPNO                   10
PROCNO                   1
Date_             20110622
Time                 12.02
INSTRUM             dpx300
PROBHD      5 mm QNP 1H/
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      32
DS                       0
SWH              6172.839 Hz
FIDRES           0.188380 Hz
AQ              2.6542580 sec
RG                     128
DW                  81.000 usec
DE                    4.50 usec
TE                   297.2 K
D1              2.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.30 usec
PL1                  -6.00 dB
SFO1           300.1318534 MHz
SI                   32768
SF             300.1300318 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                   18.00
```




```
NAME            HUG-HB-380
EXPNO                   11
PROCNO                   1
Date_             20110622
Time                 13.21
INSTRUM             dpx300
PROBHD      5 mm QNP 1H/
PULPROG             zgdc30
TD                   65536
SOLVENT              CDCl3
NS                    1200
DS                       2
SWH             21231.422 Hz
FIDRES           0.323966 Hz
AQ              1.5434228 sec
RG                 14596.5
DW                  23.550 usec
DE                    4.50 usec
TE                   297.2 K
D1              0.03000000 sec
D11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    6.60 usec
PL1                  -6.00 dB
SFO1            75.4760670 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -6.00 dB
PL12                 16.20 dB
SFO2           300.1312005 MHz
SI                   32768
SF              75.4677540 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```