Enantioselective Synthesis of Axially Chiral Biaryls by the Pd-Catalyzed Suzuki-Miyaura Reaction: Substrate Scope and Quantum Mechanical Investigations

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Supporting Information

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D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision E.01; Gaussian, Inc.: Wallingford CT, 2004.

Part II. Experimental conditions and procedures.

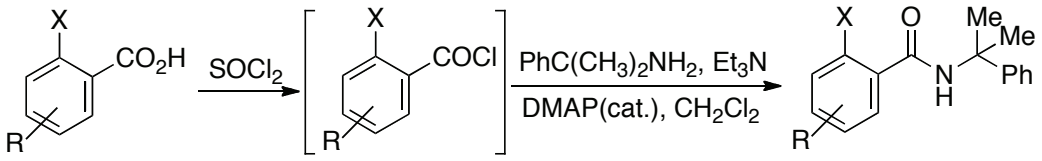
GENERAL CONSIDERATIONS

Reagents. Unless otherwise stated, all reactions were carried out in resealable screw-cap Schlenk tubes under an argon atmosphere using standard Schlenk techniques for the manipulation of solvents and reagents. Anhydrous solvents (CH_2Cl_2, THF, diethyl ether and toluene) were obtained by passage through successive alumina and Q5 reactant-packed columns on a solvent purification system. $Pd_2(dba)_3$ was purchased from Aldrich, $Pd(OAc)_2$ was a gift from BASF. All reagents were purchased from commercial sources and used as received. *o*-tolylboronic acid and 2-ethylphenylboronic acid were purchased from Alfa Aesar, 2-ethoxy-1-naphthaleneboronic acid was purchased from Aldrich. Cumyl amine was purchased from TCI. 2-methyl-1-naphthaleneboronic acid,[1] diphenyl (1-bromo-2-naphthyl)phosphonate,[2] (1-chloro-2-naphthyl)diisopropylphosphine oxide[2] were prepared according to the literature procedure. Flash chromatography was performed with EM Science silica gel 60 (230-400 mesh)[3] or using a Biotage SP4 instrument with prepacked silica cartridges.

Analytical Methods. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR (where applicable), ^{31}P NMR (where applicable), IR spectroscopy and in most cases, elemental analysis. ^{1}H NMR and ^{13}C NMR spectra and melting points (where applicable) are included for all known compounds and for all new compounds not characterized by elemental analysis. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 300 MHz or Bruker 400 MHz. Infrared spectra were recorded on a Perkin-Elmer Model 2000 FT-IR using NaCl plates (thin film). Optical rotations were measured on Jacsco P-

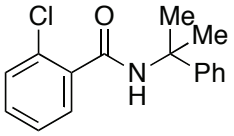
1010 polarimeter with a sodium lamp (589 nm) at ambient temperature (21-22 °C) and are reported as follows: $[\alpha]_\lambda$ (c g/100mL, the concentration of the samples is given in g 100 mL^{-1}). Analytical high performance liquid chromatography (HPLC) was performed on a Agilent 1100 Series system equipped with a multiple wavelength UV detector (deuterium lamp, 190-600 nm) using a Daicel Chiralcel®, or Chiralpak® and HPLC-grade isopropanol and hexanes as the eluting solvents. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. All ^1H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for $CHCl_3$ (7.27 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77 ppm) and were obtained with ^1H decoupling. Melting points were obtained on a Mel-Temp capillary melting point apparatus. Gas chromatographic analyses were performed on Hewlett-Packard 6890 gas chromatography instrument with a FID detector using 25m x 0.20 mm capillary column with cross-linked methyl siloxane as the stationary phase. The yields reported in tables 2 refer to isolated yields and represent an average of at least two independent runs. The pure compounds are estimated to be ≥ 95% pure as determined by ^1H NMR and GC analysis and/or combustion analysis.

General Procedure for the Synthesis of Aryl Halides

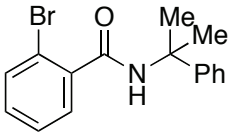


A mixture of ortho-halo acid (5.0 mmol) and $SOCl_2$ (8 mL) was heated to reflux for 3 h. The resulting mixture was then cooled down to room temperature and concentrated with the aid of a rotary evaporator. To the resulting residue, benzene (15 ml) was added and the resulting solution was concentrated with the aid of a rotary evaporator. Then the residue was dissolved in CH_2Cl_2 (10 mL) and added to a solution containing cumyl amine (1.2 eq), Et_3N (1.5 eq), DMAP (5%) and CH_2Cl_2 (10 mL). The mixture was then stirred at room temperature for 2 h. The resulting mixture was diluted with ether (40 mL) and washed twice with 1N HCl (20 mL), twice with sat. $NaHCO_3$ and once with brine.

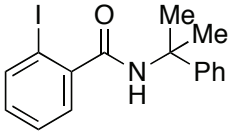
The organic layer was dried and concentrated in vacuo. The crude product was directly used for the Suzuki-Miyaura coupling process.



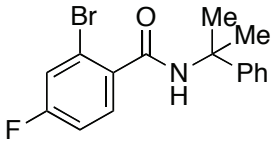
2-chloro-N-(2-phenyl-2-propyl)benzamide (Table 2, entry a) The title compound was obtained in 90% yield as a white solid from 2-chlorobenzoyl chloride and cumyl amine by using the general procedure. MP = 100.5-101.5 °C; IR (thin film): 3275, 1653, 1540 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 7.0, 1,6 Hz, 1H), 7.47 (d, J = 7.6 Hz, 2H), 7.35-7.23 (m, 6H), 6.51 (s, 1H), 1.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 146.4, 135.8, 131.0, 130.3, 130.04, 130.00, 128.4, 127.0, 126.7, 124.8, 56.7, 29.0. Elemental analysis for $C_{16}H_{16}ClNO$: C, 70.20; H, 5.89. Found: C, 69.90; H, 5.79.



2-bromo-N-(2-phenyl-2-propyl)benzamide (Table 2, entry b) The title compound was obtained in 95% yield as a white solid from 2-bromobenzoyl chloride and cumyl amine by using the general procedure. MP = 115-116 °C; IR (thin film): 3276, 1653, 1540 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58-7.49 (m, 4H), 7.40-7.30 (m, 3H), 7.29-7.21 (m, 2H), 6.34 (s, 1H), 1.83 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 146.4, 138.4, 133.2, 131.0, 129.5, 128.4, 127.5, 126.7, 124.8, 119.1, 56.8, 28.8. Elemental analysis for $C_{16}H_{16}BrNO$: C, 60.39; H, 5.07. Found: C, 60.21; H, 5.01.

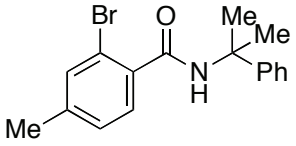


2-iodo-N-(2-phenyl-2-propyl)benzamide (Table 2, entry c) The title compound was obtained in 88% yield as a white solid from 2-iodobenzoyl chloride and cumyl amine by using the general procedure. MP = 135-136 °C; IR (thin film): 3246, 1655, 1548 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.8 Hz, 2H), 7.42-7.34 (m, 4H), 7.28-7.24 (m, 1H), 7.08 (t, J = 7.4 Hz, 1H), 6.05 (s, 1H), 1.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 146.4, 142.6, 139.7, 130.8, 128.3, 128.2, 128.1, 126.8, 124.8, 92.3, 56.7, 28.7. Elemental analysis for $C_{16}H_{16}INO$: C, 52.62; H, 4.42. Found: C, 52.88; H, 4.41.

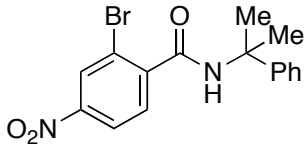


2-bromo-4-fluoro-N-(2-phenyl-2-propyl)benzamide(Table 2, entry f) The title compound was obtained in 83% yield as a white

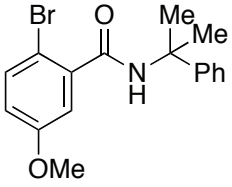
solid from 2-bromo-4-fluorobenzoic acid by using the general procedure. MP = 100-100.5 °C; IR (thin film): 3231, 1648, 1597 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50-7.45 (m, 3H), 7.39-7.32 (m, 2H), 7.30-7.23 (m, 2H), 7.02 (ddd, J = 8.7, 7,8, 2.4 Hz, 1H), 6.46 (s, 1H), 1.79 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 162.5 (d, J = 252.5 Hz), 146.3, 134.6 (d, J = 3.8 Hz), 131.1 (d, J = 8.8 Hz), 128.3, 126.7, 124.8, 120.4 (d, J = 24.5 Hz), 119.7 (d, J = 9.5 Hz), 114.7 (d, J = 21.1 Hz), 56.8, 28.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ –108.9. Elemental analysis for $C_{16}H_{15}BrFNO$: C, 57.16; H, 4.50. Found: C, 57.29; H, 4.43.



2-bromo-4-methyl-N-(2-phenyl-2-propyl)benzamide (Table 2, entry h) The title compound was obtained in 95% yield as a white solid from 2-bromo-4-methylbenzoic acid by using the general procedure. MP = 131-132 °C; IR (thin film): 3275, 1651, 1539 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.40 (d, J = 7.8 Hz, 1H), 7.36-7.31 (m, 3H), 7.25-7.20 (m, 1H), 7.10 (d, J = 7.8 Hz, 1H), 6.40 (s, 1H), 2.31 (s, 3H), 1.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 146.4, 141.5, 135.3, 133.5, 129.6, 128.3, 128.2, 126.6, 124.8, 118.8, 56.6, 28.8, 20.8. Elemental analysis for $C_{17}H_{18}BrNO$: C, 61.46; H, 5.46. Found: C, 61.17; H, 5.42.

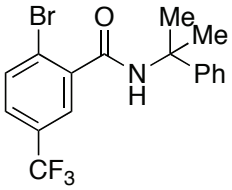


2-bromo-4-nitro-N-(2-phenyl-2-propyl)benzamide (Table 2, entry j) The title compound was obtained in 93% yield as a white solid from 2-bromo-4-nitrobenzoic acid by using the general procedure. MP = 166-167 °C; IR (thin film): 3273, 1651, 1526 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 2.1 Hz, 1H), 8.12 (dd, J = 8.4, 2.2 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.46-7.43 (m, 2H), 7.36-7.31 (m, 2H), 7.26-7.22 (m, 1H), 6.33 (s, 1H), 1.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 148.3, 145.8, 144.0, 130.0, 128.5, 128.3, 127.1, 124.8, 122.5, 119.8, 57.3, 28.7. Elemental analysis for $C_{16}H_{15}BrN_2O_3$: C, 52.91; H, 4.16. Found: C, 53.08; H, 4.01.

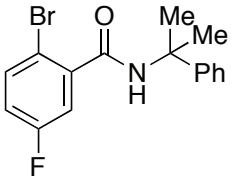


2-bromo-5-methoxy-N-(2-phenyl-2-propyl)benzamide (Table 2, entry k) The title compound was obtained in 95% yield as a white solid from 2-bromo-5-methoxybenzoic acid by using the general procedure. MP = 111-112.5 °C; IR (thin film): 3279, 1653, 1540 cm^{-}

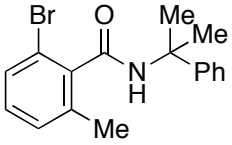
[1]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 7.5 Hz, 2H), 7.42 (d, J = 8.7 Hz, 1H), 7.37 (t, J = 7.2 Hz, 2H), 7.29-7.23 (m, 1H), 7.09 (d, J = 3.0 Hz, 1H), 6.80 (dd, J = 8.7, 3.0 Hz, 1H), 6.44 (s, 1H), 3.78 (s, 3H), 1.83 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 158.8, 146.3, 138.8, 134.0, 128.3, 126.7, 124.8, 117.6, 114.7, 109.2, 56.8, 55.5, 28.8. Elemental analysis for $C_{17}H_{18}BrNO_2$: C, 58.63; H, 5.21. Found: C, 58.86; H, 5.40.



2-bromo-N-(2-phenyl-2-propyl)-5-(trifluoromethyl)benzamide (Table 2, entry m) The title compound was obtained in 96% yield as a white solid from 2-bromo-5-(trifluoromethyl)benzoic acid by using the general procedure. MP = 110-111 °C; IR (thin film): 3267, 1653, 1547 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.63 (m, 2H), 7.49-7.26 (m, 6H), 6.56 (s, 1H), 1.78 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 146.0, 139.1, 133.8, 129.9 (q, J = 35.0 Hz), 128.4, 127.3, 126.9, 126.3, 124.8, 123.3 (q, J = 270.4 Hz), 123.1, 57.0, 28.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.1. Elemental analysis for $C_{17}H_{15}BrF_3NO$: C, 52.87; H, 3.91. Found: C, 53.02; H, 3.83.

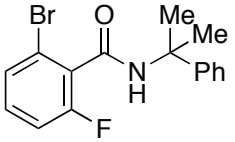


2-bromo-5-fluoro-N-(2-phenyl-2-propyl)benzamide (Table 2, entry n) The title compound was obtained in 91% yield as a white solid from 2-bromo-5-fluorobenzoic acid by using the general procedure. MP = 140-140.5 °C; IR (thin film): 3259, 1663, 1540 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.47 (m, 3H), 7.37 (t J = 7.7 Hz, 2H), 7.29-7.23 (m, 1H), 7.19 (dd, J = 8.4, 3.3 Hz, 1H), 6.96 (ddd, J = 9.0, 7,8, 3.3 Hz, 1H), 6.52 (s, 1H), 1.79 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3 (d, J = 1.9 Hz), 161.9 (d, J = 247.7 Hz), 146.5, 140.2 (d, J = 6.5 Hz), 135.0 (d, J = 7.7 Hz), 128.7, 127.1, 125.1, 118.6 (d, J = 22.2 Hz), 117.1 (d, J = 23.9 Hz), 113.6 (d, J = 3.4 Hz), 57.2, 29.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ –114.0. Elemental analysis for $C_{16}H_{15}BrFNO$: C, 57.16; H, 4.50. Found: C, 57.29; H, 4.38.

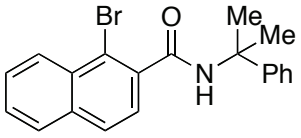


2-bromo-6-methyl-N-(2-phenyl-2-propyl)benzamide (Table 2, entry o) The title compound was obtained in 80% yield as a white solid from 2-bromo-6-methylbenzoic acid by using the general procedure. MP = 164-166 °C; IR (thin film): 3276, 1653, 1539 cm^{-1}; ^{1}H NMR (400 MHz,

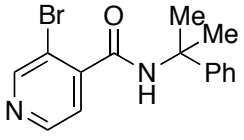
$CDCl_3$) δ 7.54-7.51 (m, 2H), 7.36-7.31 (m, 3H), 7.26-7.22(m, 1H), 7.10-7.03 (m, 2H), 6.00 (s, 1H), 2.34 (s, 3H), 1.83 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 146.6, 138.9, 137.2, 129.9, 129.8, 129.1, 128.3, 126.9, 125.0, 119.3, 56.7, 28.3, 19.4. Elemental analysis for $C_{17}H_{18}BrNO$: C, 61.46; H, 5.46. Found: C, 61.18; H, 5.32.



2-bromo-6-fluoro-N-(2-phenyl-2-propyl)benzamide (Table 2, entry p) The title compound was obtained in 91% yield as a white solid from 2-bromo-6-fluorobenzoic acid by using the general procedure. MP = 152.5-153.5 °C; IR (thin film): 3283, 1655, 1546 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.39-7.32 (m, 3H), 7.29-7.16 (m, 2H), 7.04 (t, J = 8.4 Hz, 1H), 6.17 (s, 1H), 1.81 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 159.2 (d, J = 250.0 Hz), 146.2, 131.1 (d, J = 8.6 Hz), 128.5 (d, J = 3.5 Hz), 128.3, 127.8 (d, J = 21.8 Hz), 126.8, 124.9, 120.5 (d, J = 4.8 Hz), 114.8 (d, J = 21.8 Hz), 57.1, 28.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ –113.0. Elemental analysis for $C_{16}H_{15}BrFNO$: C, 57.16; H, 4.50. Found: C, 57.19; H, 4.40.

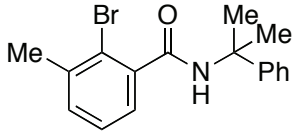


1-bromo-N-(2-phenyl-2-propyl)-2-naphthamide (Scheme 3, entry a) The title compound was obtained in 92% yield as a white solid from 1-bromo-2-naphthoic acid by using the general procedure. MP = 158-159 °C; IR (thin film): 3311, 1667, 1534 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.62-7.58 (m, 1H), 7.55-7.51 (m, 3H), 7.42 (d, J = 8.4 Hz, 1H), 7.36 (t, J = 7.7 Hz, 2H), 7.27-7.23 (m, 1H), 6.33 (s, 1H), 1.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 146.5, 136.8, 134.3, 131.7, 128.4, 128.13, 128.11, 128.0, 127.7, 127.3, 126.8, 125.1, 124.8, 119.5, 56.9, 28.8. Elemental analysis for $C_{20}H_{18}BrNO$: C, 65.23; H, 4.93. Found: C, 65.28; H, 4.85.

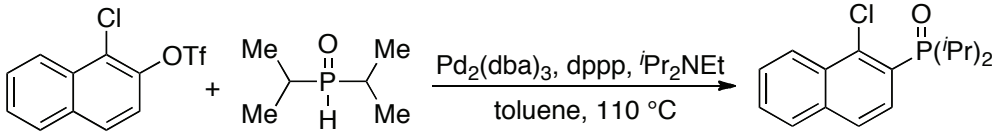


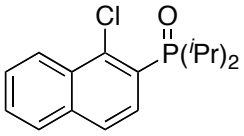
3-bromo-N-(2-phenyl-2-propyl)isonicotinamide (Scheme 3, entry b) The title compound was obtained in 80% yield as a yellow solid from 3-bromoisonicotinic acid by using the general procedure. MP = 128-130 °C; IR (thin film): 3268, 1653, 1546 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.44 (d, J = 4.3 Hz, 1H), 7.43 (d, J = 7.6 Hz, 2H), 7.34-7.21 (m, 4H), 6.61

(s, 1H), 1.75 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 152.4, 148.5 145.8, 144.7, 128.4, 126.9, 124.7, 123.3, 117.0, 57.1, 28.7. Elemental analysis for $C_{15}H_{15}BrN_2O$: C, 56.44; H, 4.74. Found: C, 56.52; H, 4.63.



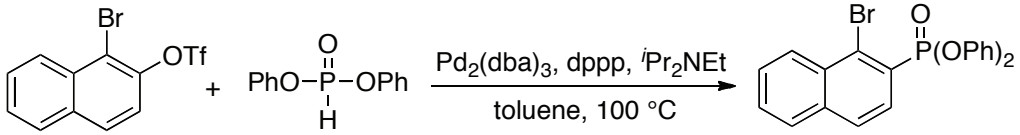
2-bromo-3-methyl-N-(2-phenyl-2-propyl)benzamide (Scheme 3, entry c) The title compound was obtained in 90% yield as a white solid from 2-bromo-3-methylbenzoic acid by using the general procedure. MP = 134-135.5 °C; IR (thin film): 3284, 1653, 1540 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.47 (m, 2H), 7.36-7.32 (m, 2H), 7.25-7.17 (m, 4H), 6.10 (s, 1H), 2.41 (s, 3H), 1.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 146.5, 139.7, 139.0, 131.5, 128.4, 127.2, 126.8, 126.2, 124.8, 121.5, 56.8, 28.7, 23.5. Elemental analysis for $C_{17}H_{18}BrNO$: C, 61.46; H, 5.46. Found: C, 61.21; H, 5.38.

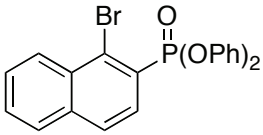




(1-chloro-2-naphthyl)diisopropylphosphine oxide (Figure 2) A solution of 1-chloro-2-naphthyl trifluoromethanesulfonate (3.10 g, 10 mmol, 1.0 equiv), and diisopropylphosphine oxide (1.61 g, 12 mmol, 1.2 equiv), *N,N*-diisopropylethylamine (2.61 mL, 15 mmol, 1.5 equiv), $Pd_2(dba)_3$ (228 mg, 0.25 mmol, 5 mol% Pd), and 1,3-bis(diphenylphosphino)propane (206 mg, 0.50 mmol, 5 mol%) in toluene (20 mL) under Ar was stirred at 110 °C for 40 h. The mixture was then cooled to room temperature and filtered through celite. The solution was concentrated, and purified by flash chromatography on silica gel to give 1.56 g (53%) of the title compound as an off white solid. MP = 104-106 °C; IR (thin film): 2968, 1466, 1185 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34-8.30 (m, 1H), 8.17 (t, J = 9.0 Hz, 1H), 7.88-7.82 (m, 2H), 7.61-7.55 (m, 2H), 2.73-2.62 (m, 2H), 1.37 (d, J = 7.2 Hz, 3H), 1.32 (d, J = 7.2 Hz, 3H), 0.97 (d, J = 7.2 Hz, 3H), 0.92 (d, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) Due to the complexity of the spectra all the peaks are listing without take into consideration C-P couplings. δ 135.84, 135.82, 132.8, 132.7, 130.5, 130.4, 130.2, 130.1, 128.9, 128.14, 128.11, 127.9, 127.5, 127.0, 126.9, 124.6, 27.6, 26.8, 16.97,

16.92, 16.27, 16.22; ^{31}P NMR (121 MHz, $CDCl_3$) δ 55.5. Elemental analysis for $C_{16}H_{20}ClOP$: C, 65.20; H, 6.84. Found: C, 64.91; H, 6.84.

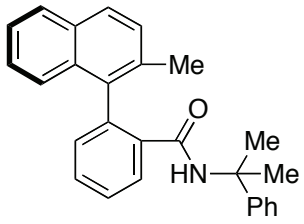




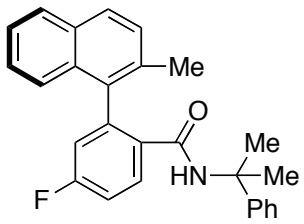
diphenyl (1-bromo-2-naphthyl)phosphonate (Scheme 2, entry c) A solution of 1-bromo-2-naphthyl triflate (3.55 g, 10 mmol, 1.0 equiv), diphenyl phosphonate (2.30 mL, 12 mmol, 1.2 equiv), *N,N*-diisopropylethylamine (2.61 mL, 15 mmol, 1.5 equiv), $Pd_2(dba)_3$ (228 mg, 0.25 mmol, 5 mol% Pd), and 1,3-bis(diphenylphosphino)propane (206 mg, 0.50 mmol, 5 mol%) in toluene (20 mL) under Ar was stirred at 110 °C for 40 h. The mixture was then cooled to room temperature and filtered through celite. The solution was concentrated, and purified by flash chromatography on silica gel to give 3.11g (71%) of the title compound as a white solid. IR (thin film): 1589, 1489, 1187 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, J = 8.7 Hz, 1H), 8.19 (dd, J = 12.9, 8.4 Hz, 1H), 7.86 (ddd, J = 12.3, 8.7, 3.6 Hz, 2H), 7.64-7.60 (m, 2H), 7.32-7.27 (m, 7H), 7.17-7.11 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) Due to the complexity of the spectra all the peaks are listing without take into consideration C-P couplings. δ 150.3, 150.2, 136.21, 136.18, 132.5, 132.3, 130.5, 130.4, 129.6, 129.1, 128.62, 128.58, 128.5, 128.28, 128.26, 128.24, 127.8, 127.6, 127.3, 125.12, 125.10, 124.6, 120.5, 120.4; ^{31}P NMR (121 MHz, $CDCl_3$) δ 9.6. Elemental analysis for $C_{22}H_{16}BrO_3P$: C, 60.16; H, 3.67. Found: C, 60.00; H, 3.52.

General Procedure for the Palladium-catalyzed Asymmetric Suzuki-coupling: An oven-dried resealable Schlenk tube was charged with the $Pd(OAc)_2$ (2.5-5.0 mol%), (*S*)-KenPhos (L : Pd = 1.2 : 1), aryl halide (1.0 mmol, 1.0 equiv), arylboronic acid (1.5-2.0 mmol, 1.5-2.0 equiv), and K_3PO_4 (3 equiv). The Schlenk tube was capped with a rubber septum and twice evacuated and backfilled with argon. THF (2.5-3 mL per mmol aryl halide) was injected into the Schlenk tube. The septum was replaced with a teflon screwcap. The Schlenk tube was sealed, and the mixture was stirred vigorously at the indicated temperature (room temperature–80 °C) for 24–40 h. The reaction was monitored by TLC or GC analysis. The reaction mixture was then cooled to room

temperature, diluted with ethyl acetate and water, extracted, the combined organic layers was dried over androus Na_2SO_4 and concentrated. The crude material was purified by flash chromatography on silica gel.

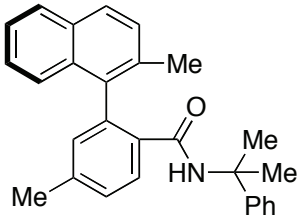


(*R*)-2-(2-methyl-1-naphthyl)-*N*-(2-phenyl-2-propyl) benzamide (Table 2, entry b) The reaction was conducted for 40 h according to the general procedure (5 mol% Pd, 6 mol% (*S*)-KenPhos and 2.0 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 10% ethyl acetate in hexanes to 15% ethyl acetate in hexanes) gave 311 mg (83%) desire product as a white solid. MP = 86-87.5 °C. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 3% ^{i}PrOH, 97% hexane, T_{major}: 10.4 min (*R*), T_{minor}: 12.3 min (*S*)] provided the product with (93% ee). $[\alpha]_D$ = –30.5 (*c* = 0.33, $CHCl_3$); IR (thin film): 3421, 1660, 1510 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07-8.04 (m, 1H), 7.89 (t, J = 8.7 Hz, 2H), 7.60-7.50 (m, 2H), 7.50-7.46 (m, 2H), 7.44-7.35 (m, 2H), 7.26-7.22 (m, 1H), 7.10-7.08 (m, 3H), 6.74-6.71 (m, 2H), 5.65 (s, 1H), 2.23 (s, 3H), 1.06 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 146.1, 136.5, 136.4, 136.2, 134.1, 132.7, 132.1, 130.7, 130.5, 129.9, 128.8, 128.2, 128.1, 128.0, 127.9 (2C), 127.0, 126.1, 125.4, 125.2, 124.4 (2C), 55.1, 28.2, 27.7, 20.6. Elemental analysis for $C_{27}H_{25}NO$: C, 85.45; H, 6.64. Found: C, 85.42; H, 6.58.

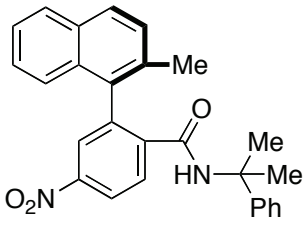


(*R*)-4-fluoro-2-(2-methyl-1-naphthyl)-*N*-(2-phenyl-2-propyl)benzamide (Table 2, entry f) The reaction was conducted for 40 h according to the general procedure (5 mol% Pd, 6 mol% (*S*)-KenPhos and 1.5 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 9% ethyl acetate in hexanes) gave 330 mg (83%) desire product as a white solid. MP = 101.5-103.5 °C. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 10% ^{i}PrOH, 90% hexane, T_{major}: 6.4 min (*R*), T_{minor}: 7.3 min (*S*)] provided the product with (93% ee). $[\alpha]_D$ = –29.7 (*c* = 0.59, $CHCl_3$); IR (thin film): 3413, 1662, 1511 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (dd, J = 8.7, 6.0 Hz, 1H), 7.90 (t, J = 8.7 Hz, 2H), 7.53-7.42 (m, 3H), 7.38-7.35 (m, 1H), 7.23 (ddd, J = 8.7,

8.1, 2.7 Hz, 1H), 7.12-7.08 (m, 3H), 6.95 (dd, J = 9.0, 2.4 Hz, 1H), 6.74-6.70 (m, 2H), 5.63 (s, 1H), 2.26 (s, 3H), 1.06 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 163.7 (d, J = 250.8 Hz), 146.0, 139.1 (d, J = 8.2 Hz), 135.0 (d, J = 1.4 Hz), 134.0, 132.7 (d, J = 8.9 Hz), 132.3 (d, J = 3.2 Hz), 132.2, 132.0, 128.7, 128.6, 128.3, 127.9, 127.2, 126.2, 125.7, 124.9, 124.3, 117.4 (d, J = 21.3 Hz), 115.2 (d, J = 21.0 Hz), 55.0, 28.2, 27.7, 20.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ –110.1. Elemental analysis for $C_{27}H_{24}FNO$: C, 81.59; H, 6.09. Found: C, 81.44; H, 6.09.

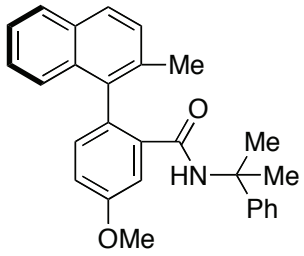


(*R*)-4-methyl-2-(2-methyl-1-naphthyl)-*N*-(2-phenyl-2-propyl)benzamide (Table 2, entry h) The reaction was conducted for 40 h according to the general procedure (5 mol% Pd, 6 mol% (*S*)-KenPhos and 2 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 15% ethyl acetate in hexanes) gave 322 mg (82%) desire product as a white solid. MP = 179-181 °C. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 2.5% ^{i}PrOH, 97.5% hexane, T_{major}: 12.1 min (*R*), T_{minor}: 14.1 min (*S*)] provided the product with (94% ee). $[\alpha]_D$ = +8.9 (*c* = 0.41, $CHCl_3$); IR (thin film): 3393, 1658, 1520 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.50-7.33 (m, 5H), 7.10-7.03 (m, 4H), 6.74-6.71 (m, 2H), 5.66 (s, 1H), 2.43 (s, 3H), 2.24 (s, 3H), 1.06 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 146.2, 140.8, 136.4, 134.0, 133.2, 132.7, 132.1, 131.23, 131.18, 130.1, 128.81, 128.76, 128.12, 128.05, 127.9, 126.9, 126.1, 125.44, 125.36, 124.3, 54.9, 28.3, 27.8, 21.3, 20.6. Elemental analysis for $C_{28}H_{27}NO$: C, 85.46; H, 6.92. Found: C, 85.21; H, 6.95.

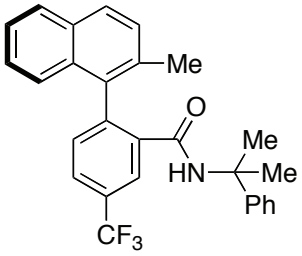


(*S*)-2-(2-methyl-1-naphthyl)-4-nitro-*N*-(2-phenyl-2-propyl)benzamide (Table 2, entry j) The reaction was conducted for 40 h according to the general procedure (2.5 mol% Pd, 3 mol% (*R*)-KenPhos and 2 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 15% ethyl acetate in hexanes) gave 382 mg (90%) desire product as a white solid. MP = 85 °C (Dec.). Separation of enantiomers by Chiral HPLC [Daicel Chiracel® AD-H

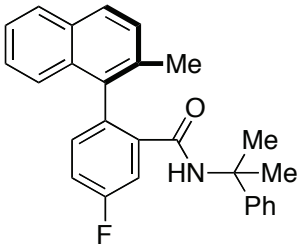
column, flow rate 1.0 mL/min, 10% ^{i}PrOH, 90% hexane, T_{minor}: 28.6 min (*R*), T_{major}: 46.9 min (*S*)] provided the product with (88% ee). $[\alpha]_D$ = –25.1 (*c* = 1.23, $CHCl_3$); IR (thin film): 3414, 2978, 1670, 1521 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, J = 8.6, 2.3 Hz, 1H), 8.14 (d, J = 8.6 Hz, 1H), 8.12 (d, J = 2.3 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.51-7.47 (m, 1H), 7.47 (d, J = 8.5 Hz, 1H), 7.43-7.39 (m, 1H), 7.22 (d, J = 9.3 Hz, 1H), 7.08-7.04 (m, 3H), 6.66-6.64 (m, 2H), 5.65 (s, 1H), 2.19 (s, 3H), 1.03 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 148.7, 145.5, 142.3, 138.2, 134.4, 133.6, 132.2, 132.0, 131.3, 129.1, 128.8, 128.6, 128.0, 127.6, 126.5, 126.0, 125.8, 124.4, 124.2, 122.9, 55.6, 28.0, 27.5, 20.6. Elemental analysis for $C_{27}H_{24}N_2O_3$: C, 76.39; H, 5.70. Found: C, 75.90; H, 5.72.



(*R*)-5-methoxy-2-(2-methyl-1-naphthyl)-*N*-(2-phenyl-2-propyl)benzamide (Table 2, entry k) The reaction was conducted for 40 h according to the general procedure (5 mol% Pd, 6 mol% (*S*)-KenPhos and 2 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 15% ethyl acetate in hexanes to 20% ethyl acetate in hexanes) gave 340 mg (83%) desire product as a white solid. MP = 135.5-137 °C. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 5% ^{i}PrOH, 95% hexane, T_{major}: 8.6 min (*R*), T_{minor}: 10.0 min (*S*)] provided the product with (94% ee). $[\alpha]_D$ = –33.4 (*c* = 0.85, $CHCl_3$); IR (thin film): 3419, 1666, 1604, 1509, 1293 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.60 (s, 1H), 7.47-7.41 (m, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.39-7.37 (m, 2H), 7.10 (s, 2H), 7.08-7.05 (m, 3H), 6.71-6.69 (m, 2H), 5.69 (S, 1H), 3.89 (s, 3H), 2.21 (s, 3H), 1.02 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 159.2, 146.1, 137.1, 136.0, 134.5, 133.1, 132.1, 132.0, 128.8, 128.6, 128.13, 128.07, 127.9, 126.9, 126.2, 125.4, 125.3, 124.3, 117.9, 113.6, 55.5, 55.0, 28.2, 27.7, 20.7. Elemental analysis for $C_{28}H_{27}NO_2$: C, 82.12; H, 6.65. Found: C, 81.99; H, 6.71.

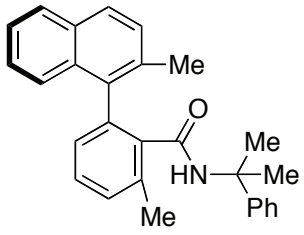


(*R*)-2-(2-methyl-1-naphthyl)-*N*-(2-phenyl-2-propyl)-5-(trifluoromethyl)benzamide (Table 2, entry m) The reaction was conducted for 40 h according to the general procedure (2.5 mol% Pd, 3 mol% (*S*)-KenPhos and 2 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 9% ethyl acetate in hexanes) gave 389 mg (87%) desire product as a white solid. MP = 109-110.5 °C. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 1% ^{i}PrOH, 99% hexane, T_{major}: 9.2 min (*R*), T_{minor}: 10.5 min (*S*)] provided the product with (89% ee). $[\alpha]_D$ = –20.3 (*c* = 0.70, $CHCl_3$); IR (thin film): 3415, 1669, 1517, 1333 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.53-7.46 (m, 2H), 7.42 (d, J = 6.9, 1.5 Hz, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.27 (d, J = 9.0 Hz, 1H), 7.11-7.08 (m, 3H), 6.73-6.69 (m, 2H), 5.69 (s, 1H), 2.22 (s, 3H), 1.08 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 145.7, 140.3, 136.9, 134.7, 134.1, 132.2, 132.0, 131.6, 130.5 (q, J = 32.9 Hz), 128.79, 128.76, 128.4, 128.0, 127.4, 127.1 (q, J = 3.5 Hz), 126.4, 125.8, 124.8, 124.30, 124.28, 122.0, 55.3, 28.1, 27.6, 20.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0. Elemental analysis for $C_{28}H_{24}F_3NO$: C, 75.15; H, 5.41. Found: C, 75.29; H, 5.44.

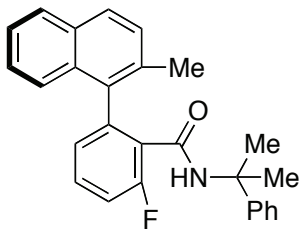


(*S*)--5-fluoro-2-(2-methyl-1-naphthyl)-*N*-(2-phenyl-2-propyl)benzamide (Table 2, entry n) The reaction was conducted for 40 h according to the general procedure (5 mol% Pd, 6 mol% (*R*)-KenPhos and 1.5 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 9% ethyl acetate in hexanes) gave 338 mg (85%) desire product as a colorless oil. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 10% ^{i}PrOH, 90% hexane, T_{minor}: 5.9 min (*R*), T_{major}: 6.7 min (*S*)] provided the product with (92% ee). $[\alpha]_D$ = +32.0 (*c* = 0.81, $CHCl_3$); IR (thin film): 3416, 2977, 1667, 1510 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (t, J = 8.4 Hz, 2H), 7.79 (dd, J = 9.6, 2.7 Hz, 1H), 7.52-7.40 (m, 3H), 7.36-7.17 (m, 3H), 7.11-7.07 (m, 3H), 6.72-6.69 (m, 2H), 5.69 (s, 1H), 2.23 (s, 3H), 1.06 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 162.3 (d, J = 246.2 Hz), 145.8, 138.2 (d, J = 6.9 Hz), 135.1, 134.4, 132.7, 132.6, 132.5,

132.3 (d, J = 3.6 Hz), 132.1, 128.8, 128.3 (d, J = 12.4 Hz), 128.0, 127.2, 126.3, 125.6, 125.0, 124.3, 117.8 (d, J = 21.3 Hz), 116.9 (d, J = 23.2 Hz), 55.2, 28.1, 27.6, 20.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ –113.9, Elemental analysis for $C_{27}H_{24}FNO$: C, 81.59; H, 6.09. Found: C, 81.61; H, 6.23.

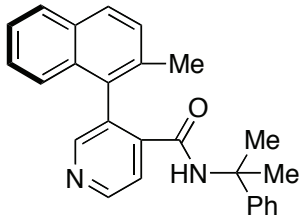


(*R*)—2-methyl-6-(2-methyl-1-naphthyl)-*N*-(2-phenyl-2-propyl)benzamide (Table 2, entry o) The reaction was conducted for 40 h according to the general procedure (5 mol% Pd, 6 mol% (*S*)-KenPhos and 1.5 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 9% ethyl acetate in hexanes) gave 315 mg (80%) desire product as a white solid. MP = 114-116 °C. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 2% ^{i}PrOH, 98% hexane, T_{minor}: 7.4 min (*R*), T_{major}: 8.6 min (*S*)] provided the product with (48% ee). $[\alpha]_D$ = –42.5 (*c* = 0.42, $CHCl_3$); IR (thin film): 3420, 2974, 1672, 1502 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.48-7.30 (m, 6H), 7.10-7.07 (m, 4H), 6.67-6.64 (m, 2H), 5.36 (s, 1H), 2.47 (s, 3H), 2.24 (s, 3H), 1.06 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 146.2, 138.3, 136.2, 136.0, 135.9, 135.0, 133.3, 131.8, 129.5, 128.9, 128.7, 128.3, 128.0, 127.6, 127.5, 126.6, 126.2, 125.0, 124.8, 124.4, 55.5, 28.4, 26.7, 20.7, 19.4. Elemental analysis for $C_{28}H_{27}NO$: C, 85.46; H, 6.92. Found: C, 85.11; H, 6.94.

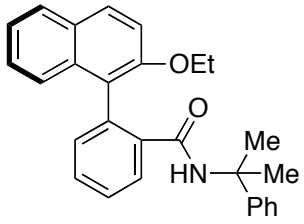


(*R*)—2-fluoro-6-(2-methyl-1-naphthyl)-*N*-(2-phenyl-2-propyl)benzamide (Table 2, entry p) The reaction was conducted for 40 h according to the general procedure (5 mol% Pd, 6 mol% (*S*)-KenPhos and 2 equiv of boronic acid). The title product was purified by Biotage (eluted with gradient: 0-30% ethyl acetate in hexanes) gave 183 mg (46%) desire product as a white solid. MP = 121-123 °C. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® AD-H column, flow rate 1.0 mL/min, 10% ^{i}PrOH, 90% hexane, T_{major}: 6.5 min (*S*), T_{minor}: 7.5 min (*R*)] provided the product with (90% ee). $[\alpha]_D$ = –67.9 (*c* = 0.60, $CHCl_3$); IR (thin film): 3418, 2977, 1675, 1508 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 8.7 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.53-7.34 (m, 5H), 7.29-7.19 (m, 2H), 7.09-7.05 (m, 3H), 6.69-

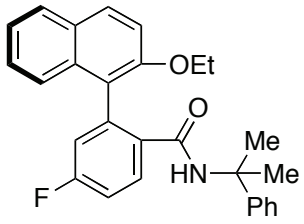
6.53 (m, 2H), 5.44 (s, 1H), 2.24 (s, 3H), 1.09 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 159.7 (d, J = 248.6 Hz), 145.8, 139.1 (d, J = 3.6 Hz), 134.9, 134.3 (d, J = 2.0 Hz), 132.9, 131.7, 130.5 (d, J = 8.8 Hz), 128.8, 128.3, 128.0, 127.9, 126.9 (d, J = 17.6 Hz), 126.7, 126.2, 126.0 (d, J = 3.2 Hz), 124.9, 124.7, 124.3, 115.1 (d, J = 21.5 Hz), 56.0, 28.3, 27.4, 20.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ –116.0. Elemental analysis for $C_{27}H_{24}FNO$: C, 81.59; H, 6.09. Found: C, 81.37; H, 6.00.



(*S*)-3-(2-methyl-1-naphthyl)-*N*-(2-phenyl-2-propyl)isonicotinamide (Scheme 3, entry b) A oven-dried resealable Schlenk tube was charged with the $Pd(OAc)_2$ (5 mol%), (*S*)-KenPhos (6 mol%), aryl halide (0.5 mmol, 1.0 equiv), arylboronic acid (1.0 mmol, 2.0 equiv), and K_3PO_4 (3 equiv). The Schlenk tube was capped with a rubber septum and twice evacuated and backfilled with argon. Toluene (1.5 mL) was injected into the Schlenk tube. The septum was replaced with a teflon screwcap. The Schlenk tube was sealed, and the mixture was stirred at 80 °C for 20 h. Then $Pd(OAc)_2$ (5 mol%) (*S*)-KenPhos (6 mol%), arylboronic acid (1.0 mmol, 2.0 equiv) was added to the reaction mixture and washed with 0.3 mL of toluene, the Schlenk tube was sealed and stirred at 80 °C for another 20 h. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate and water, extracted, the combined organic layers was dried over androus Na_2SO_4 and concentrated. The title product was purified by flash chromatography (eluted with 50% ethyl acetate in hexanes to 100% ethyl acetate) gave 162 mg (85%) desire product as a yellow sticky oil. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® AD-H column, flow rate 1.0 mL/min, 10% ^{i}PrOH, 90% hexane, T_{major}: 13.1 min (*R*), T_{minor}: 17.0 min (*S*)] provided the product with (70% ee). $[\alpha]_D$ = –14.4 (*c* = 1.0, $CHCl_3$); IR (thin film): 3411, 1674, 1518 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81 (d, J = 5.1 Hz, 1H), 8.54 (d, J = 0.6 Hz, 1H), 7.94-7.90 (m, 3H), 7.53-7.41 (m, 3H), 7.27 (d, J = 9.0 Hz, 1H), 7.11-7.06 (m, 3H), 6.68-6.65 (m, 2H), 5.74 (s, 1H), 2.23 (s, 3H), 1.07 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 151.7, 149.9, 145.5, 143.0, 135.0, 132.7, 132.01, 131.97, 131.1, 129.0, 128.7, 128.4, 128.0, 127.4, 126.4, 125.8, 124.6, 124.2, 123.1, 55.4, 27.9, 27.6, 20.7.

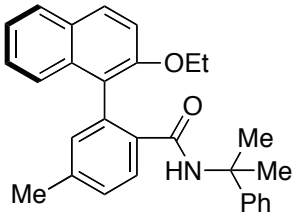


(*S*)--2-(2-ethoxy-1-naphthyl)-N-(2-phenyl-2-propyl) benzamide (Table 2, entry e) The reaction was conducted for 40 h according to the general procedure (5 mol% Pd, 6 mol% (*S*)-KenPhos and 2 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 10% ethyl acetate in hexanes) gave 327 mg (80%) desire product as a colorless oil. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 10% ^{i}PrOH, 90% hexane, T_{major}: 6.4 min (*S*), T_{minor}: 7.8 min (*R*)] provided the product with (91% ee). $[\alpha]_D$ = +22.9 (*c* = 0.48, $CHCl_3$); IR (thin film): 3418, 2979, 1667, 1510 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.91 (m, 2H), 7.85 (dd, J = 6.7, 1.6 Hz, 1H), 7.53-7.46 (m, 2H), 7.4-7.30 (m, 2H), 7.30 (d, J = 9.0 Hz, 1H), 7.26-7.19 (m, 2H), 7.06-6.97 (m, 3H), 6.72-6.68 (m, 2H), 6.24 (s, 1H), 4.12-3.98 (m, 2H), 1.21 (t, J = 7.0 Hz, 3H), 1.21 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 152.7, 146.3, 137.7, 133.8, 133.5, 131.5, 129.9, 129.8, 129.2, 129.0, 127.9, 127.8, 127.2, 126.1, 125.0, 124.4, 124.10, 124.08, 114.3, 64.9, 55.3, 28.9, 27.4, 15.0. Elemental analysis for $C_{28}H_{27}NO_2$: C, 82.12; H, 6.65. Found: C, 81.86; H, 6.77.

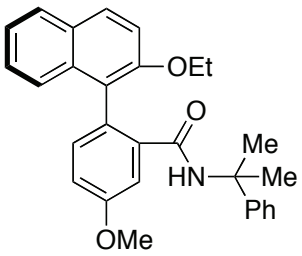


(*S*)--2-(2-ethoxy-1-naphthyl)-4-fluoro-N-(2-phenyl-2-propyl)benzamide (Table 2, entry g) The reaction was conducted for 40 h according to the general procedure (5 mol% Pd, 6 mol% (*S*)-KenPhos and 2 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 9% ethyl acetate in hexanes) gave 346 mg (81%) desire product as a colorless oil. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 10% ^{i}PrOH, 90% hexane, T_{major}: 6.6 min (*S*), T_{minor}: 8.2 min (*R*)] provided the product with (90% ee). $[\alpha]_D$ = +19.6 (*c* = 0.35, $CHCl_3$); IR (thin film): 3419, 2979, 1667, 1512 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99-7.94 (m, 2H), 7.89-7.86 (m, 1H), 7.43-7.38 (m, 2H), 7.32 (d, J = 9.0 Hz, 1H), 7.27-7.16 (m, 2H), 7.09-6.98 (m, 3H), 6.94 (dd, J = 9.3, 2.7 Hz, 1H), 6.73-6.70 (m, 2H), 6.17 (s, 1H), 4.17-4.00 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H), 1.19 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 163.4 (d, J = 248.9 Hz), 152.6, 146.2, 136.2 (d, J = 8.7 Hz), 133.8 (d, J = 3.1 Hz), 133.4, 131.7 (d, J = 8.7 Hz), 130.3, 128.9, 127.94, 127.91, 127.5, 126.2, 124.6, 124.4, 124.2, 122.7, 118.2 (d, J

= 21.1 Hz), 114.9 (d, J = 20.9 Hz), 114.1, 64.8, 55.4, 28.8, 27.4, 14.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ –111.4. Elemental analysis for $C_{28}H_{26}FNO_2$: C, 78.66; H, 6.13. Found: C, 78.39; H, 6.10.

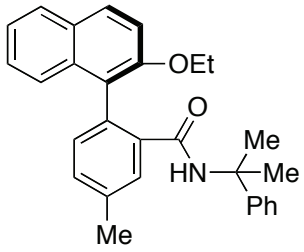


(*S*)-2-(2-ethoxy-1-naphthyl)-4-methyl-N-(2-phenyl-2-propyl)benzamide (Table 2, entry i) The reaction was conducted for 40 h according to the general procedure (5 mol% Pd, 6 mol% (*S*)-KenPhos and 2 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 10% ethyl acetate in hexanes) gave 343 mg (81%) desire product as a colorless oil. $[\alpha]_D$ = +43.1 (*c* = 1.40, $CHCl_3$); Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 5% ^{i}PrOH, 95% hexane, T_{major}: 8.6 min, T_{minor}: 10.4 min] provided the product with (92% ee). IR (thin film): 3418, 2978, 1664, 1511 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 9.3 Hz, 1H); 7.88-7.85 (m, 2H), 7.40-7.26 (m, 6H), 7.05-6.98 (m, 4H), 6.73-6.70 (m, 2H), 6.20 (s, 1H), 4.15-4.02 (m, 2H), 2.41 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.21 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 152.7, 146.4, 140.0, 134.7, 133.8, 133.4, 132.0, 129.7, 129.4, 129.0, 128.6, 128.4, 127.85, 127.8, 127.2, 126.1, 125.0, 124.4, 124.2, 124.0, 114.3, 64.8, 55.2, 28.9, 27.5, 21.3, 15.0. Elemental analysis for $C_{29}H_{29}NO_2$: C, 82.24; H, 6.90. Found: C, 81.76; H, 6.86.

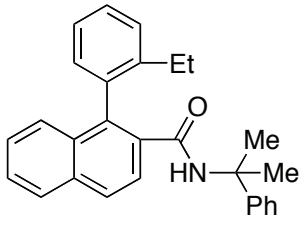


(*S*)--2-(2-ethoxy-1-naphthyl)-5-methoxy-N-(2-phenyl-2-propyl)benzamide (Table 2, entry l) The reaction was conducted for 40 h according to the general procedure (5 mol% Pd, 6 mol% (*S*)-KenPhos and 2 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 20% ethyl acetate in hexanes) gave 369 mg (84%) desire product as a white solid. MP = 112-114 °C. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 10% ^{i}PrOH, 90% hexane, T_{major}: 6.4 min (*S*), T_{minor}: 7.7 min (*R*)] provided the product with (91% ee). $[\alpha]_D$ = +18.7 (*c* = 0.44, $CHCl_3$); IR (thin film): 3416, 1667, 1508 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 9.0 Hz, 1H), 7.84-7.81 (m, 1H), 7.47 (d, J = 2.6 Hz, 1H), 7.37-7.32 (m, 4H), 7.04-6.87 (m, 5H), 6.71-6.68 (m,

2H), 6.25 (s, 1H), 4.11-3.97 (m, 2H), 3.89 (s, 3H), 1.22 (t, J = 7.0 Hz, 3H), 1.17 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 159.0, 153.0, 146.3, 138.5, 134.2, 132.7, 129.7, 129.0, 127.9, 127.8, 127.2, 126.1, 125.6, 125.0, 124.4, 124.0, 123.8, 117.2, 114.4, 113.0, 64.8, 55.4, 55.3, 28.7, 27.5, 15.0. Elemental analysis for $C_{29}H_{29}NO_3$: C, 79.24; H, 6.65. Found: C, 79.17; H, 6.65.

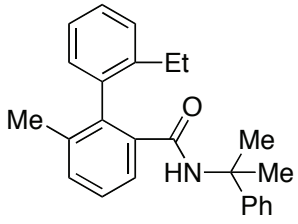


(*R*)--2-(2-ethoxy-1-naphthyl)-5-methyl-N-(2-phenyl-2-propyl)benzamide: The reaction was conducted for 40 h according to the general procedure (5 mol% Pd, 6 mol% (*R*)-KenPhos and 2 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 9% ethyl acetate in hexanes) gave 360 mg (85% containing about 5% inpurity) desire product as a colorless oil. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 5% ^{i}PrOH, 95% hexane, T_{minor}: 8.2 min (*S*), T_{major}: 10.3 min (*R*)] provided the product with (90% ee). $[\alpha]_D$ = –22.1 (*c* = 0.69, $CHCl_3$); IR (thin film): 3419, 1667, 1512 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 9.0 Hz, 1H), 7.87-7.84 (m, 1H), 7.76-7.75 (m, 1H), 7.40-7.25 (m, 5H), 7.11 (d, J = 7.8 Hz, 1H), 7.05-6.97 (m, 3H), 6.73-6.70 (m, 2H), 6.23 (s, 1H), 4.16-3.98 (m, 2H), 2.47 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H), 1.21 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 152.8, 146.4, 137.6, 137.4, 134.0, 131.4, 130.8, 130.5, 129.73, 129.67, 129.0, 127.9, 127.8, 127.1, 126.1, 125.0, 124.4, 124.1, 124.0, 114.4, 64.8, 55.3, 28.9, 27.5, 21.2, 15.0.

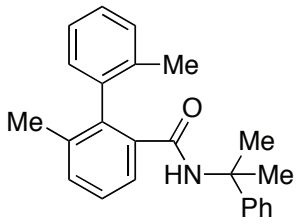


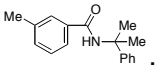
1-(2-ethylphenyl)-N-(2-phenyl-2-propyl)-2-naphthamide (Scheme 3, entry a) The reaction was conducted at room temperature for 30 h according to the general (5 mol% Pd, 6 mol% (*R*)-KenPhos and 2 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 9% ethyl acetate in hexanes) gave 315 mg (80%) desire product as a white solid. MP = 109-111 °C. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 3% ^{i}PrOH, 97% hexane, T_{major}: 12.3 min, T_{minor}: 14.2 min] provided the product with (88% ee). $[\alpha]_D$ = –8.6 (*c* = 0.94, $CHCl_3$); IR (thin film): 3417, 2970, 1653, 1506 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, J = 8.7 Hz, 1H), 7.91 (t, J = 7.8 Hz,

2H), 7.55-7.50 (m, 3H), 7.42-7.36 (m, 3H), 7.29-7.19 (m, 4H), 7.13-7.10 (m, 2H), 5.82 (s, 1H), 2.32 (q, J = 7.5 Hz, 2H), 1.41 (s, 3H), 1.38 (s, 3H), 0.97 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 146.4, 143.1, 137.4, 136.0, 134.2, 132.8, 132.2, 130.3, 130.0, 128.8, 128.1, 128.0, 127.9, 127.1, 126.9, 126.46, 126.42, 126.40, 126.0, 124.7, 55.6, 28.6, 28.2, 26.1, 14.4. Elemental analysis for $C_{28}H_{27}NO$: C, 85.46; H, 6.92. Found: C, 85.00; H, 6.86.



2'-ethyl-6-methyl-N-(2-phenyl-2-propyl)-[1,1'-biphenyl]-2-carboxamide (Scheme 3, entry c) The reaction was conducted at room temperature for 30 h according to the general procedure (5 mol% Pd, 6 mol% (*R*)-KenPhos and 2 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 9% ethyl acetate in hexanes) gave 250 mg (70%) desire product as a white solid. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 3% ^{i}PrOH, 97% hexane, T_{major}: 9.7 min, T_{minor}: 11.1 min] provided the product with (81% ee). $[\alpha]_D$ = +11.8 (*c* = 0.82, $CHCl_3$); IR (thin film): 3418, 2978, 1664, 1510 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.70 (m, 1H), 7.41-7.38 (m, 2H), 7.36-7.26 (m, 3H), 7.23-7.17 (m, 3H), 7.15-7.10 (m, 2H), 7.05-7.03 (m, 1H), 5.63 (s, 1H), 2.34 (q, J = 7.7 Hz, 2H), 1.98 (s, 3H), 1.33 (s, 3H), 1.27 (s, 3H), 1.02 (td, J = 7.5, 0.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 146.4, 142.1, 138.7, 137.7, 136.6, 136.0, 131.9, 129.2, 129.0, 128.4, 128.1, 127.6, 127.1, 126.5, 126.3, 124.7, 55.5, 28.7, 28.1, 25.9, 20.6, 14.1. Elemental analysis for $C_{25}H_{27}NO$: C, 83.99; H, 7.61. Found: C, 83.73; H, 7.65.



2',6-dimethyl-N-(2-phenyl-2-propyl)-[1,1'-biphenyl]-2-carboxamide (Scheme 3, entry d) The reaction was conducted at room temperature for 30 h according to the general procedure (5 mol% Pd, 6 mol% (*S*)-KenPhos and 2 equiv of boronic acid). The title product was purified by flash chromatography (eluted with 9% ethyl acetate in hexanes) gave 307 mg product which contains about 20 mol% (by ^{1}H NMR) of inseparable 

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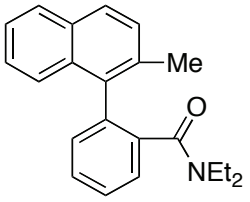
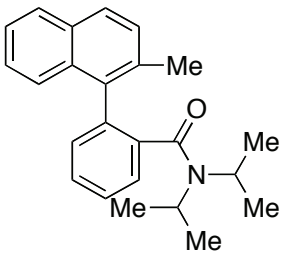
Separation of enantiomers by Chiral HPLC [Daicel Chirapak® AD-H column, flow rate 1.0 mL/min, 2% ^{i}PrOH, 98% hexane, T_{minor}: 36.3 min, T_{major}: 39.2 min] provided the product with (80% ee). $[\alpha]_D$ = –3.0 (*c* = 0.40, $CHCl_3$); IR (thin film): 3416, 2973, 1653, 761 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (dd, J = 7.2, 2.1 Hz, 1H), 7.38-7.29 (m, 5H), 7.26-7.16 (m, 4H), 7.11-7.07 (m, 2H), 5.66 (s, 1H), 2.05 (s, 3H), 2.00 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 146.4, 139.2, 137.9, 136.42, 136.37, 136.1, 131.8, 130.8, 129.1, 128.1, 128.08, 127.5, 126.8, 126.5, 126.4, 124.6, 55.5, 28.6, 28.1, 20.4, 19.8.

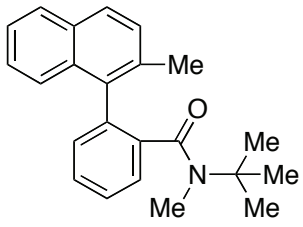


N,N-diethyl-2-(2-methyl-1-naphthyl)benzamide (Table 1, entry c) The reaction was conducted for 24 h according to the general procedure (0.20 mmol ArOTf as reprensentative starting material) using (*R*)-KenPhos as ligand. The title product was purified by flash chromatography (eluted with 5% ethyl acetate in hexanes to 15% ethyl acetate in hexanes) gave 54 mg (85%) desire product as a white solid. MP = 135.0-137.0 °C. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® AD-H column, flow rate 1.0 mL/min, 5% ^{i}PrOH, 95% hexane, T_{minor}: 8.8 min, T_{major}: 11.7 min] provided the product with (71% ee). $[\alpha]_D$ = +60.6 (*c* = 0.57, $CHCl_3$); IR (thin film): 2972, 1633, 1427 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J = 7.5 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.30-7.19 (m, 3H), 7.16-7.06 (m, 5H), 3.25 (br, 1H), 2.93 (br, 1H), 2.32 (br, 2H), 2.08 (s, 3H), 0.63 (s, 3H), 0.02 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 137.8, 136.8, 135.0, 131.6, 131.1, 128.5, 127.7, 127.4, 127.3, 126.1, 125.2, 124.4, 42.6, 37.5, 21.1, 13.7, 11.2. Elemental analysis for $C_{22}H_{23}NO$: C, 83.24; H, 7.30. Found: C, 82.74; H, 7.34.

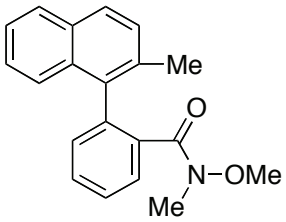


N,N-diisopropyl-2-(2-methyl-1-naphthyl)benzamide (Table 1, entry d) The reaction was conducted for 36 h according to the general procedure (0.20 mmol) using (*R*)-KenPhos as ligand. The title product was purified by flash chromatography (eluted with 5% ethyl acetate in hexanes to 10% ethyl acetate in hexanes) gave 53 mg (76%) desire product as a colorless oil. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® AD-H column, flow rate 1.0 mL/min, 5% ^{i}PrOH, 95% hexane, T_{minor}: 5.2 min, T_{major}: 6.8 min] provided the product with (82% ee). $[\alpha]_D$ = +67.6

(c = 1.55, $CHCl_3$); IR (thin film): 2967, 1632, 1338 cm^{-1}; ^1H NMR of major rotamer (300 MHz, $CDCl_3$) δ 7.82 (d, J = 7.2 Hz, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.50-7.44 (m, 2H), 7.41-7.28 (m, 6H), 3.68-3.56 (m, 1H), 3.08-2.96 (m, 1H), 2.36 (s, 3H), 1.39 (d, J = 6.9 Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H), 0.78 (d, J = 6.9 Hz, 3H), -0.01 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 139.2, 135.9, 134.9, 132.6, 131.6, 131.2, 128.7, 127.95, 127.86, 127.5, 127.3, 126.2, 125.8, 125.3, 124.2, 50.0, 45.1, 21.4, 21.1, 20.4, 19.7, 19.5. Elemental analysis for $C_{24}H_{27}NO$: C, 83.44; H, 7.88. Found: C, 83.42; H, 7.98.

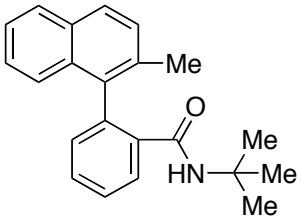


N-(tert-butyl)-N-methyl-2-(2-methyl-1-naphthyl)benzamide (Table 1, entry e) The reaction was conducted for 36 h according to the general procedure (0.20 mmol) using (*R*)-KenPhos as ligand. The title product was purified by flash chromatography (eluted with 5% ethyl acetate in hexanes to 10% ethyl acetate in hexanes) gave 54 mg (82%) desire product as a white solid. MP = 94 °C (dec.). Separation of enantiomers by Chiral HPLC [Daicel Chiracel® AD-H column, flow rate 1.0 mL/min, 1% ^{i}PrOH, 99% hexane, T_{minor}: 13.7 min, T_{major}: 15.7 min] provided the product with (75% ee). $[\alpha]_D$ = +98.1 (c = 0.46, $CHCl_3$); IR (thin film): 2977, 1637, 1377 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, J = 7.5 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.49-7.30 (m, 8H), 2.41 (s, 3H), 2.29 (s, 3H), 0.87 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 140.2, 136.1, 135.4, 131.6, 131.1, 128.6, 128.2, 127.6, 127.3, 125.0, 124.5, 55.8, 34.5, 26.9, 21.0. Elemental analysis for $C_{23}H_{25}NO$: C, 83.34; H, 7.60. Found: C, 83.26; H, 7.66.

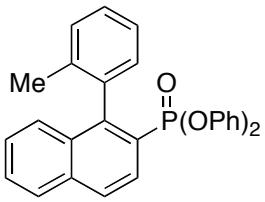


N-methoxy-N-methyl-2-(2-methyl-1-naphthyl)benzamide (Table 1, entry f) The reaction was conducted for 36 h according to the general procedure (0.20 mmol) using (*R*)-KenPhos as ligand. The title product was purified by flash chromatography (eluted with 15% ethyl acetate in hexanes to 25% ethyl acetate in hexanes) gave 46 mg (75%) desire product as a colorless oil. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 2% ^{i}PrOH, 98% hexane, T_{minor}: 22.4 min, T_{major}: 25.5 min] provided the product

with (80% ee). $[\alpha]_D$ = +71.5 (*c* = 0.95, $CHCl_3$); IR (thin film): 2932, 1656, 1378 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, J = 7.5 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.58-7.50 (m, 3H), 7.40-7.30 (m, 5H), 3.13 (br, 3H), 2.77 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 137.2, 136.3, 136.2, 134.0, 132.6, 132.0, 130.6, 130.3, 129.5, 128.8, 128.08, 128.05, 127.9, 126.9, 125.3, 125.1, 50.4, 27.6, 20.5.



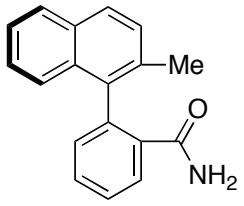
N-(tert-butyl)-2-(2-methyl-1-naphthyl)benzamide (Table 1, entry g) The reaction was conducted for 40 h according to the general procedure (0.2 mmol) using (*R*)-KenPhos as ligand. The title product was purified by flash chromatography (eluted with 8% ethyl acetate in hexanes to 15% ethyl acetate in hexanes) gave 43 mg (68%) desire product as a white solid. MP = 85 °C (dec.). Separation of enantiomers by Chiral HPLC [Daicel Chiracel® AD-H column, flow rate 1.0 mL/min, 5% ^{i}PrOH, 95% hexane, T_{minor}: 9.1 min, T_{major}: 10.0 min] provided the product with (87% ee). $[\alpha]_D$ = +31.7 (*c* = 0.70, $CHCl_3$); IR (thin film): 3422, 1664, 1516 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.01-7.98 (m, 1H), 7.89-7.85 (m, 1H), 7.84 (d, J = 8.7 Hz, 1H), 7.57-7.50 (m, 2H), 7.46-7.40 (m, 2H), 7.36 (dd, J = 6.6, 1.5 Hz, 1H), 7.34-7.31 (m, 1H), 7.23-7.20 (m, 1H), 5.07 (s, 1H), 2.20 (s, 3H), 0.65 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 137.2, 136.3, 136.2, 134.0, 132.6, 132.0, 130.6, 130.3, 129.5, 128.8, 128.08, 128.05, 127.9, 126.9, 125.3, 125.1, 50.4, 27.6, 20.5. Elemental analysis for $C_{22}H_{23}NO$: C, 83.24; H, 7.30. Found: C, 83.07; H, 7.48.



Diphenyl (1-(o-tolyl)-2-naphthyl)phosphonate (Scheme 2, entry c) The reaction was conducted at 70 °C in toluene (6 mL/mmol) for 16 h according to the general procedure. The title product was purified by flash chromatography (eluted with 15% to 25% ethyl acetate in hexanes) gave 405 mg (90%) desire product as a white solid. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® AD-H column, flow rate 1.0 mL/min, 10% ^{i}PrOH, 90% hexane, T_{major}: 22.4 min, T_{minor}: 24.7 min] provided the product with (84% ee). ^1H NMR (300 MHz, $CDCl_3$) δ 8.40 (dd, J = 12.9, 8.7 Hz, 1H), 8.06 (dd, J = 8.4, 4.2 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.65-7.59 (m, 1H), 7.48-7.19 (m, 10H), 7.12-7.06 (m, 2H), 6.96-6.87 (m, 4H), 1.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) Due to the

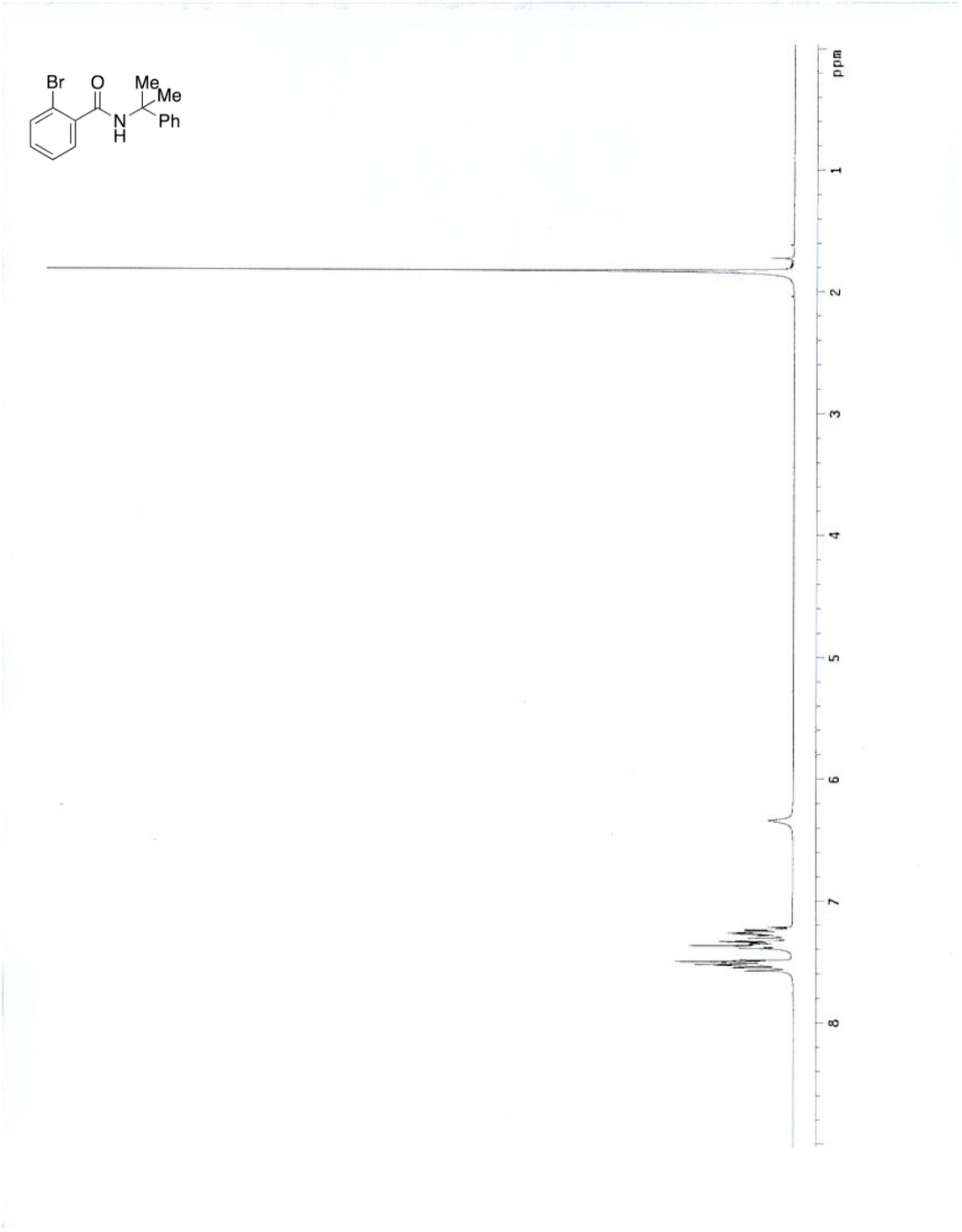
complexity of the spectra all the peaks are listing without take into consideration C-P couplings. δ 150.36, 150.29, 150.25, 150.17, 145.97, 145.83, 137.74, 137.72, 137.36, 137.29, 135.34, 135.30, 132.53, 132.30, 130.76, 130.74, 129.49, 129.41, 129.40, 129.36, 129.35, 128.42, 128.33, 128.27, 128.24, 128.05, 128.04, 127.7, 127.5, 127.19, 127.17, 127.04, 127.02, 124.98, 124.73, 124.71, 124.64, 124.63, 124.46, 121.89, 120.55, 120.49, 120.36, 120.30, 19.86. ^{31}P NMR (121 MHz, $CDCl_3$) δ 12.0. Elemental analysis for $C_{29}H_{23}O_3P$: C, 77.32; H, 5.15. Found: C, 77.10; H, 5.05.

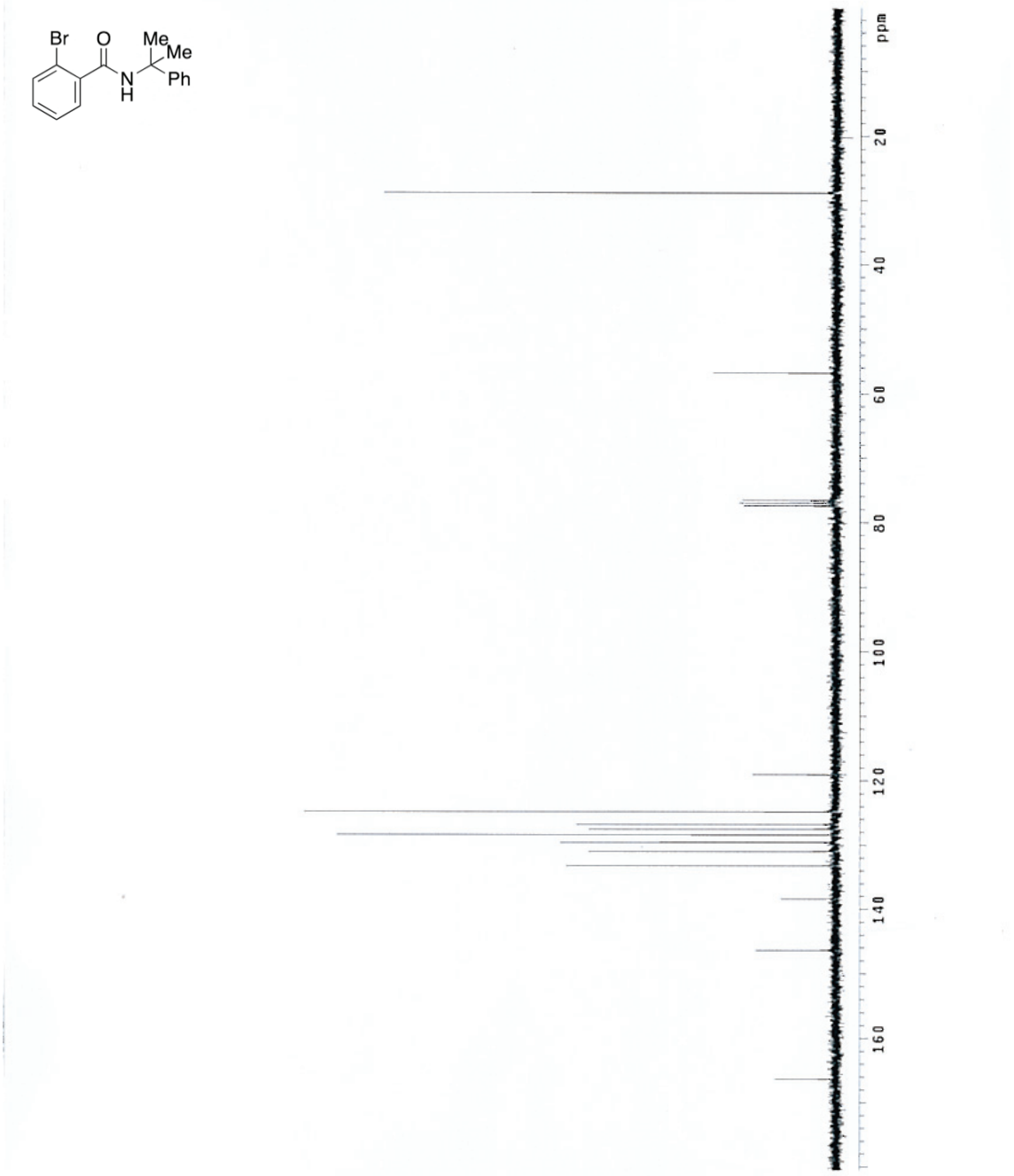
Deprotection of Cumyl Group



(*R*)--2-(2-methyl-1-naphthyl)benzamide (Figure 4) A vial containing 53 mg of **(*R*)-2-(2-methyl-1-naphthyl)-*N*-(2-phenyl-2-propyl) benzamide** (0.14 mmol, 93% ee) and a stir bar was cooled down to 0 °C, 3.0 mL of ice-cold TFA was added, then the reaction mixture was warmed to room temperature and stirred for 2.5 h. The resulting mixture was then concentrated with the aid of a rotary evaporator. The resulting residue was diluted with ether (30 mL) and washed with sat. $NaHCO_3$ and brine. The organic layer was dried, concentrated. The title product was purified by flash column chromatography (eluted with 30% ethyl acetate in hexanes) gave 35 mg (96%) as a white solid. MP = 110-112 °C. Separation of enantiomers by Chiral HPLC [Daicel Chiracel® OD-H column, flow rate 1.0 mL/min, 10% ^{i}PrOH, 90% hexane, T_{minor}: 9.5 min (*S*), T_{major}: 12.1 min (*R*)] provided the product with (93% ee). $[\alpha]_D$ = +15.6 (*c* = 0.50, $CHCl_3$); IR (thin film): 3467, 3120, 1669, 1594, 1379 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 7.6, 1.5 Hz, 1H), 7.81 (dd, J = 11.4, 8.3 Hz, 2H), 7.57-7.48 (m, 2H), 7.42-7.38 (m, 2H), 7.32 (t, J = 6.8 Hz, 1H), 7.26-7.23 (m, 1H), 7.15-7.14 (m, 1H), 5.81 (s, 1H), 5.21 (s, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 137.3, 135.8, 134.0, 133.9, 132.2, 132.0, 131.3, 131.1, 130.2, 128.8, 128.2, 128.1, 128.0, 126.8, 125.4, 125.1, 20.5. Elemental analysis for $C_{18}H_{15}NO$: C, 82.73; H, 5.79. Found: C, 82.54; H, 5.83.

Part III. Compound characterization data including several representative chiral HPLC spectra.

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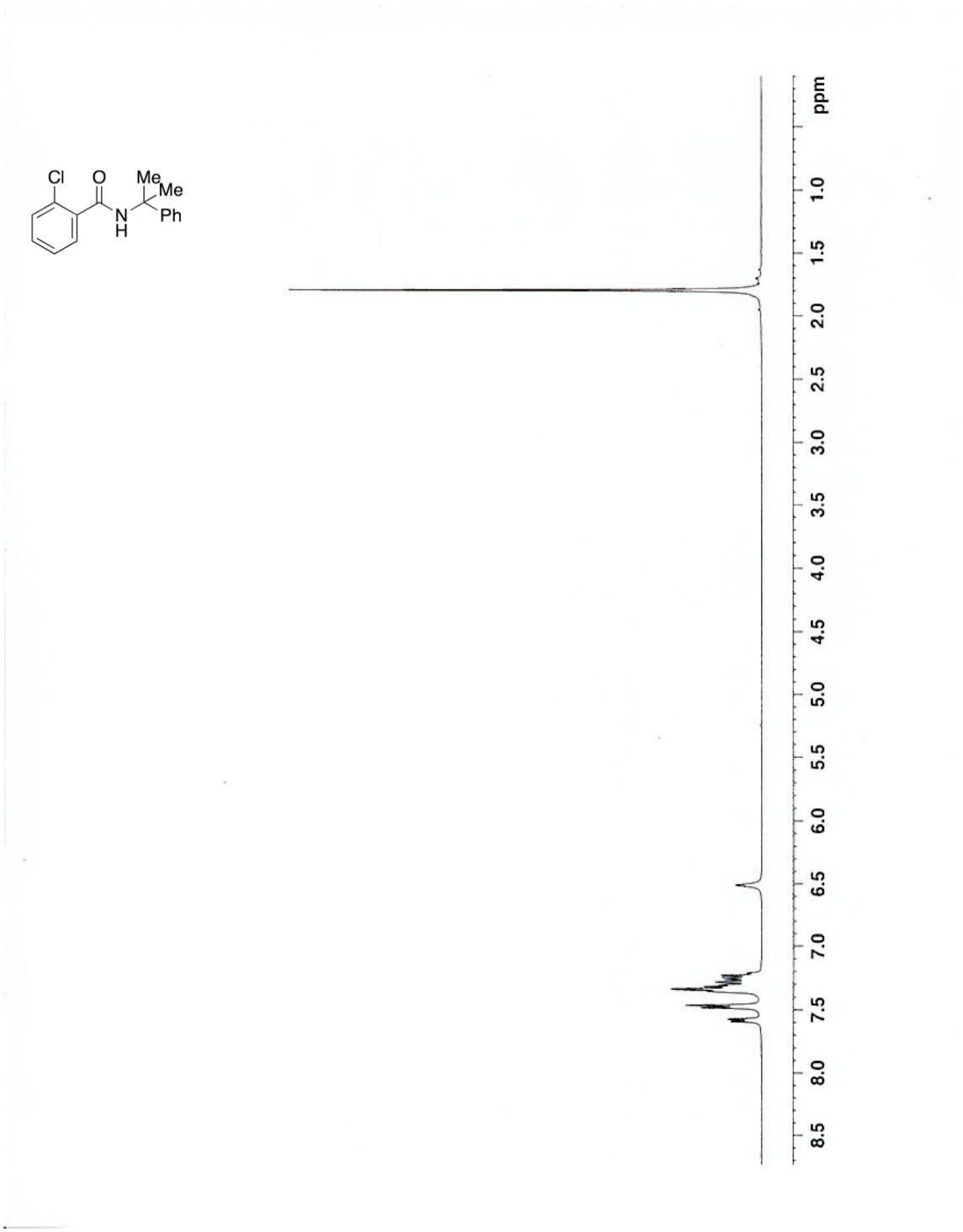
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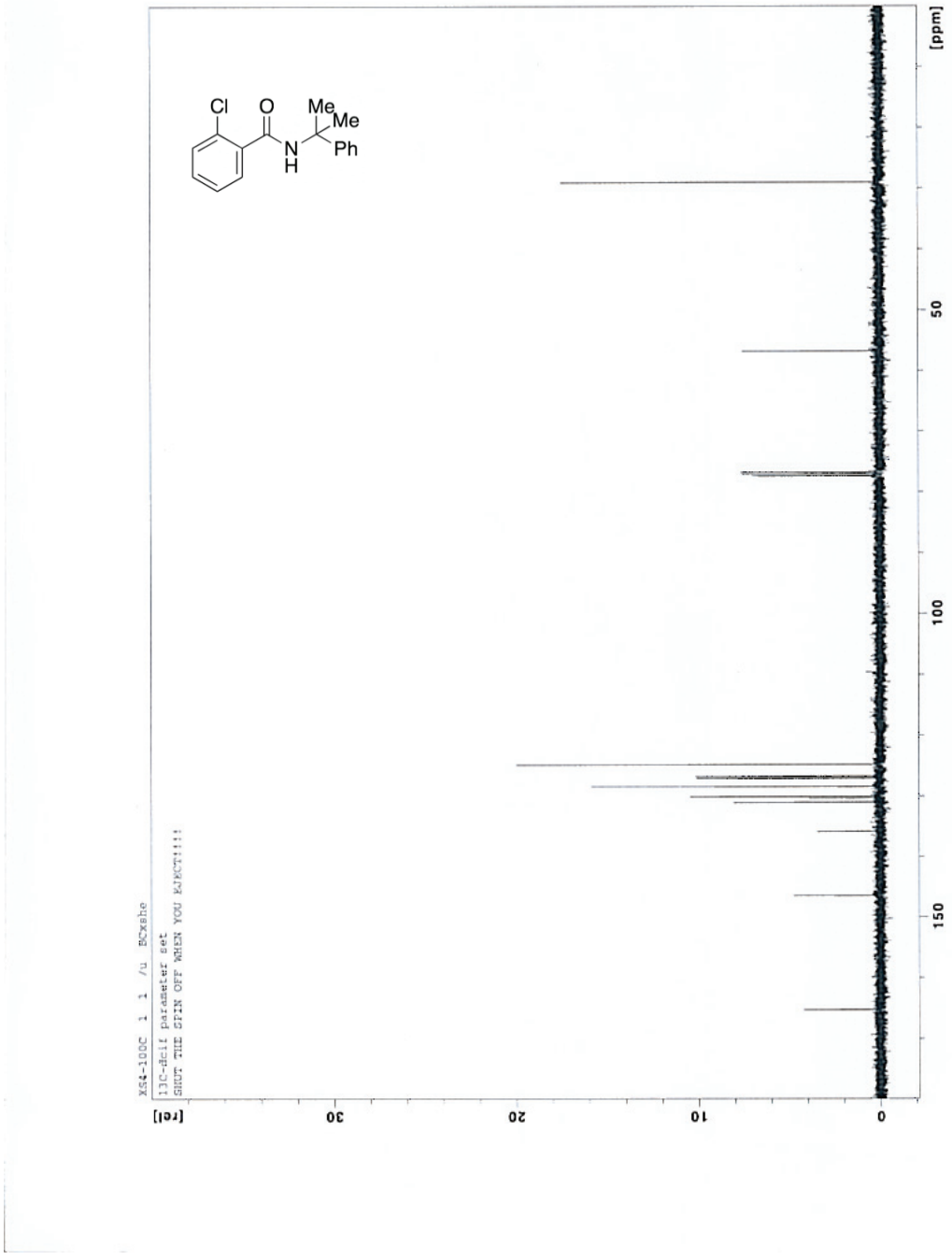
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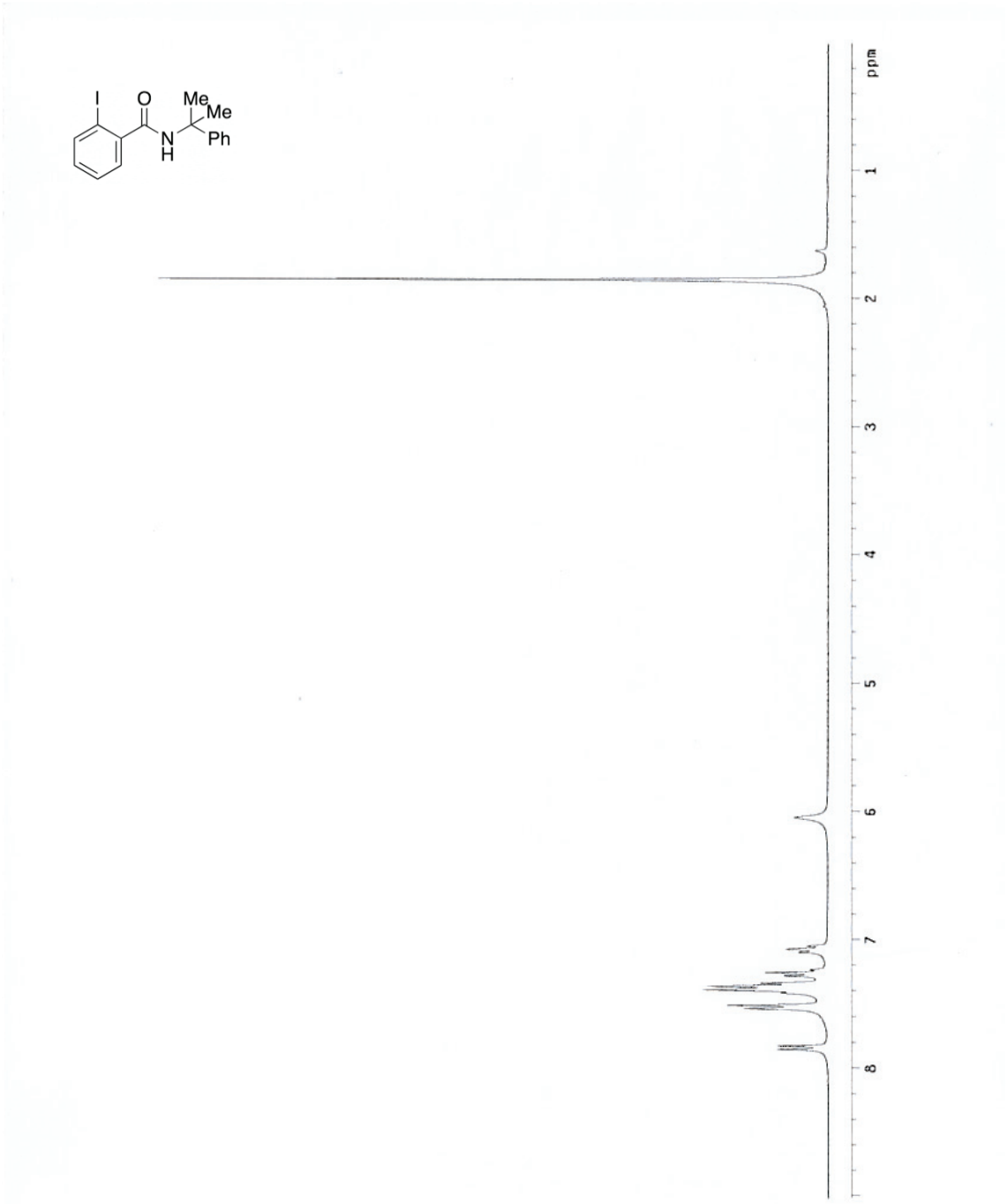
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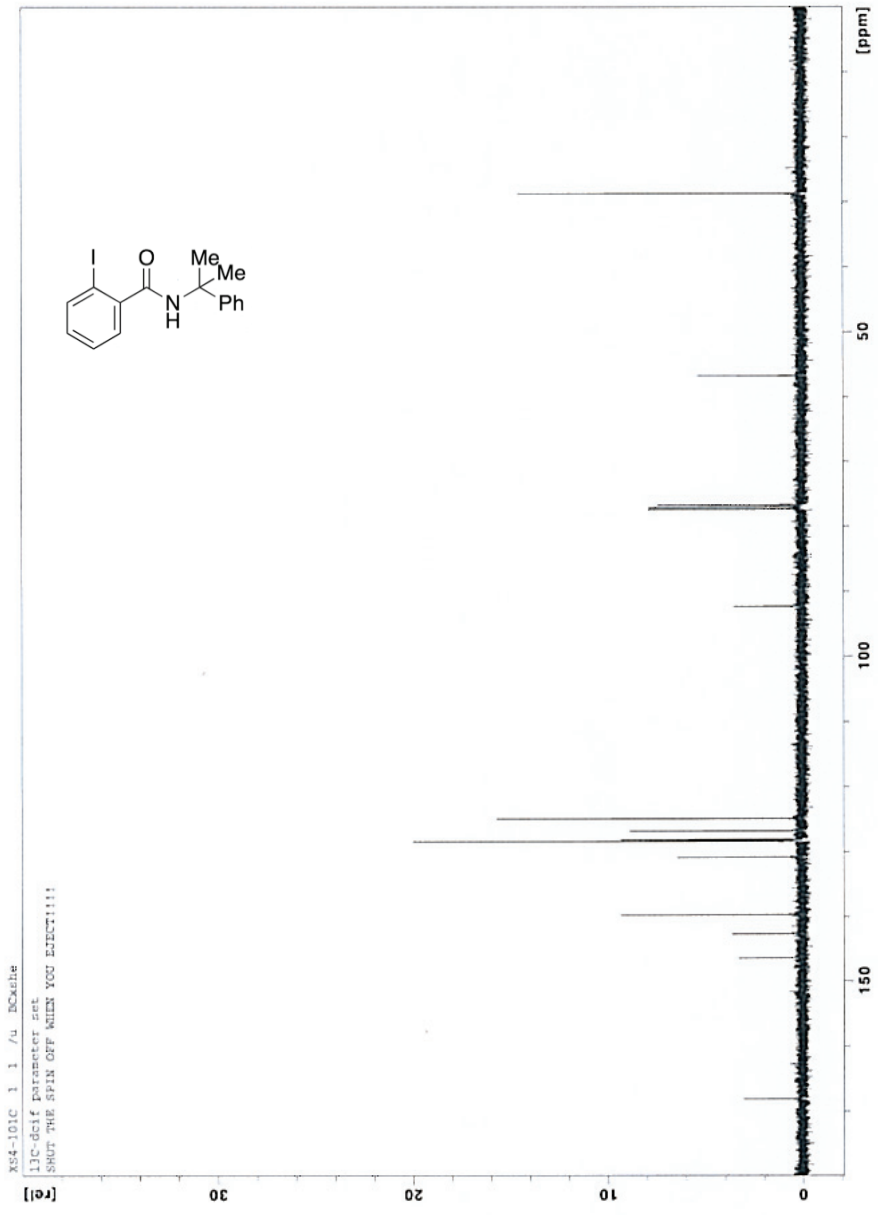
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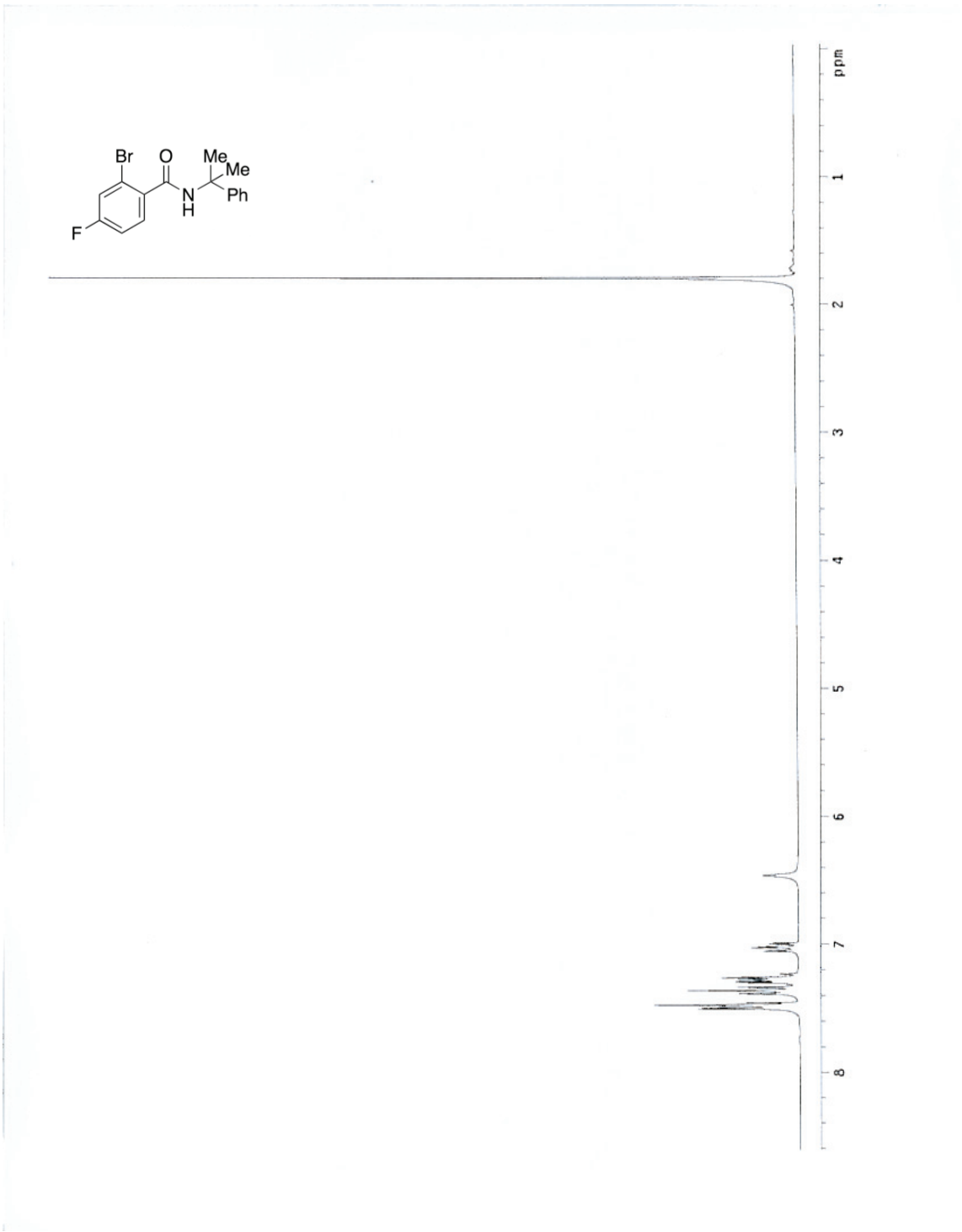
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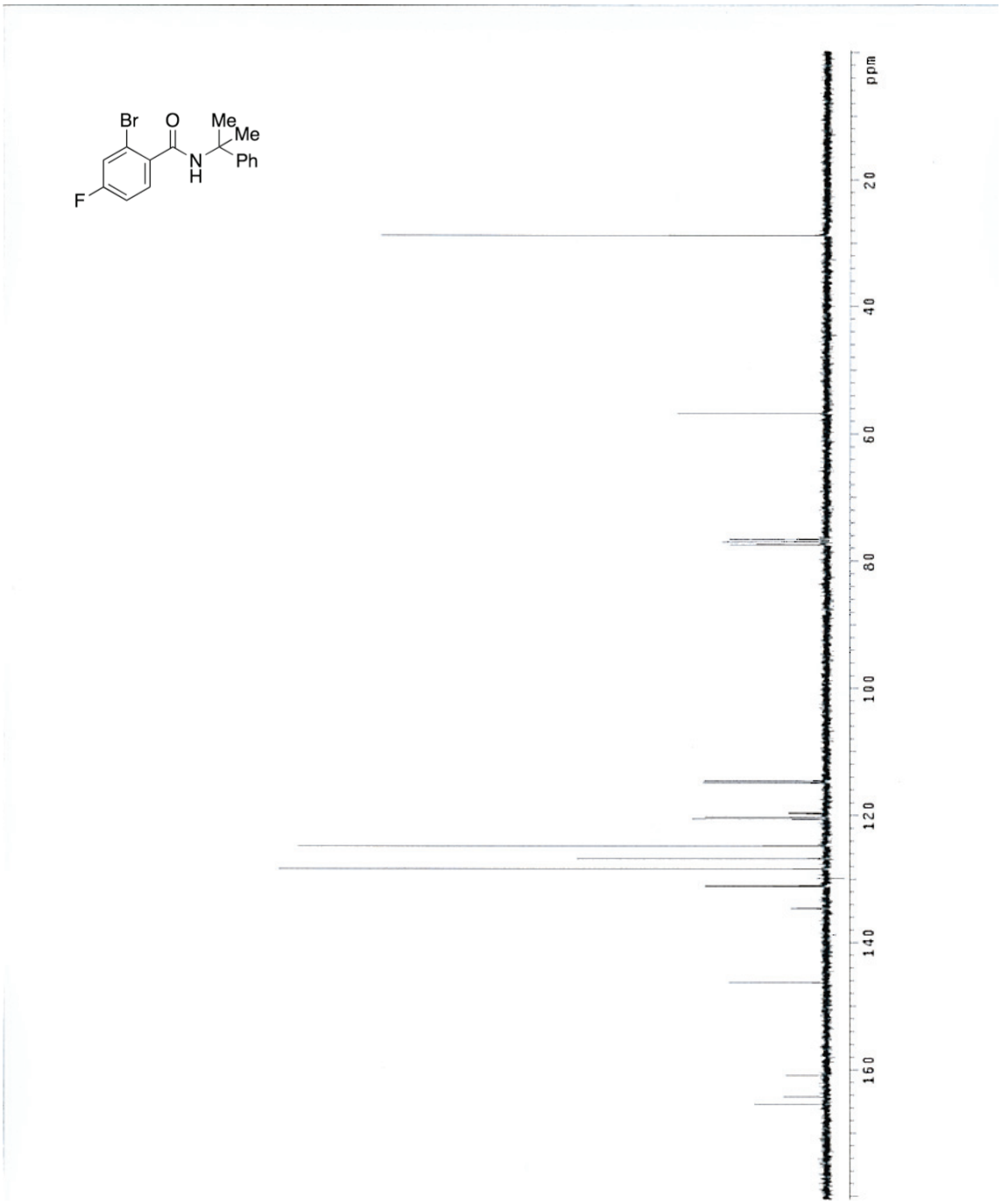
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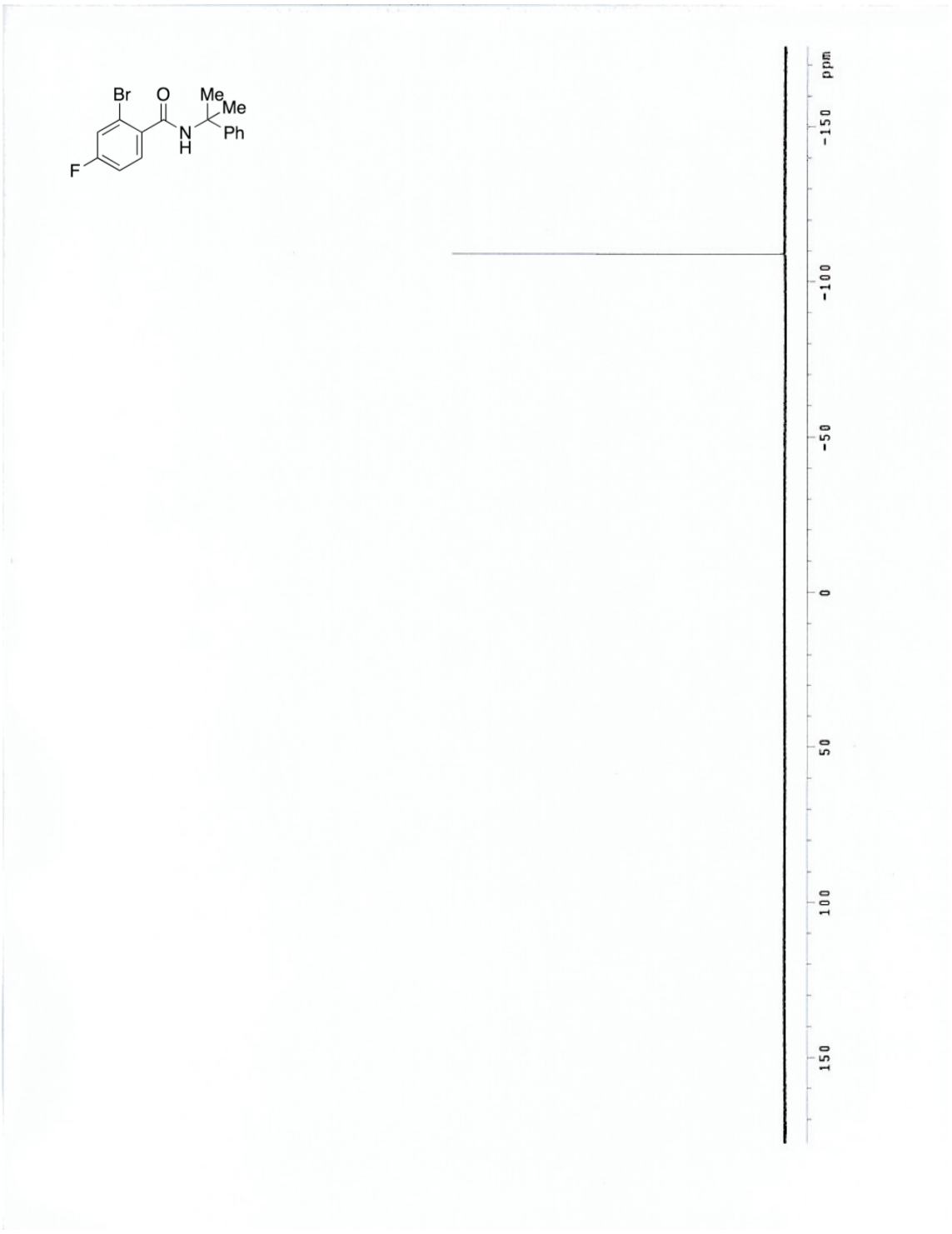
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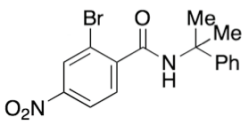
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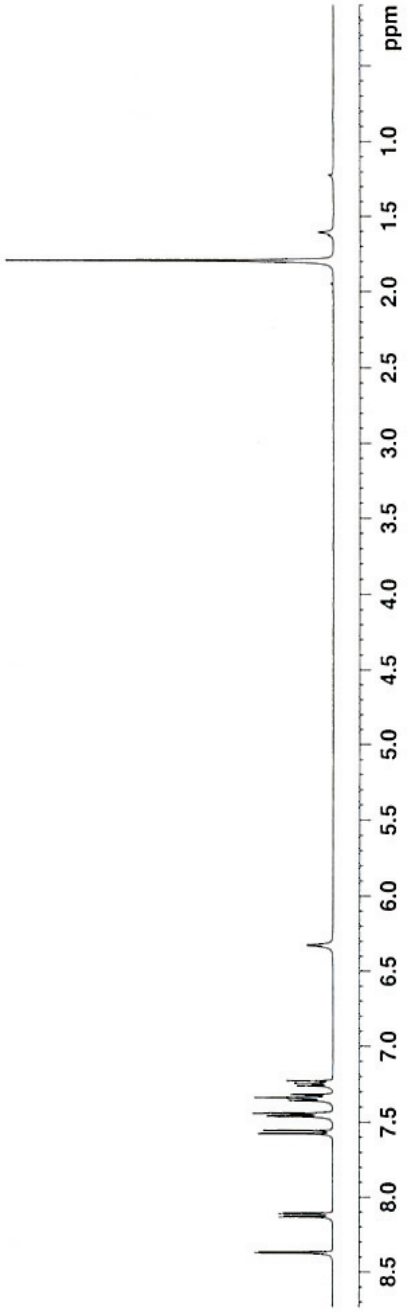
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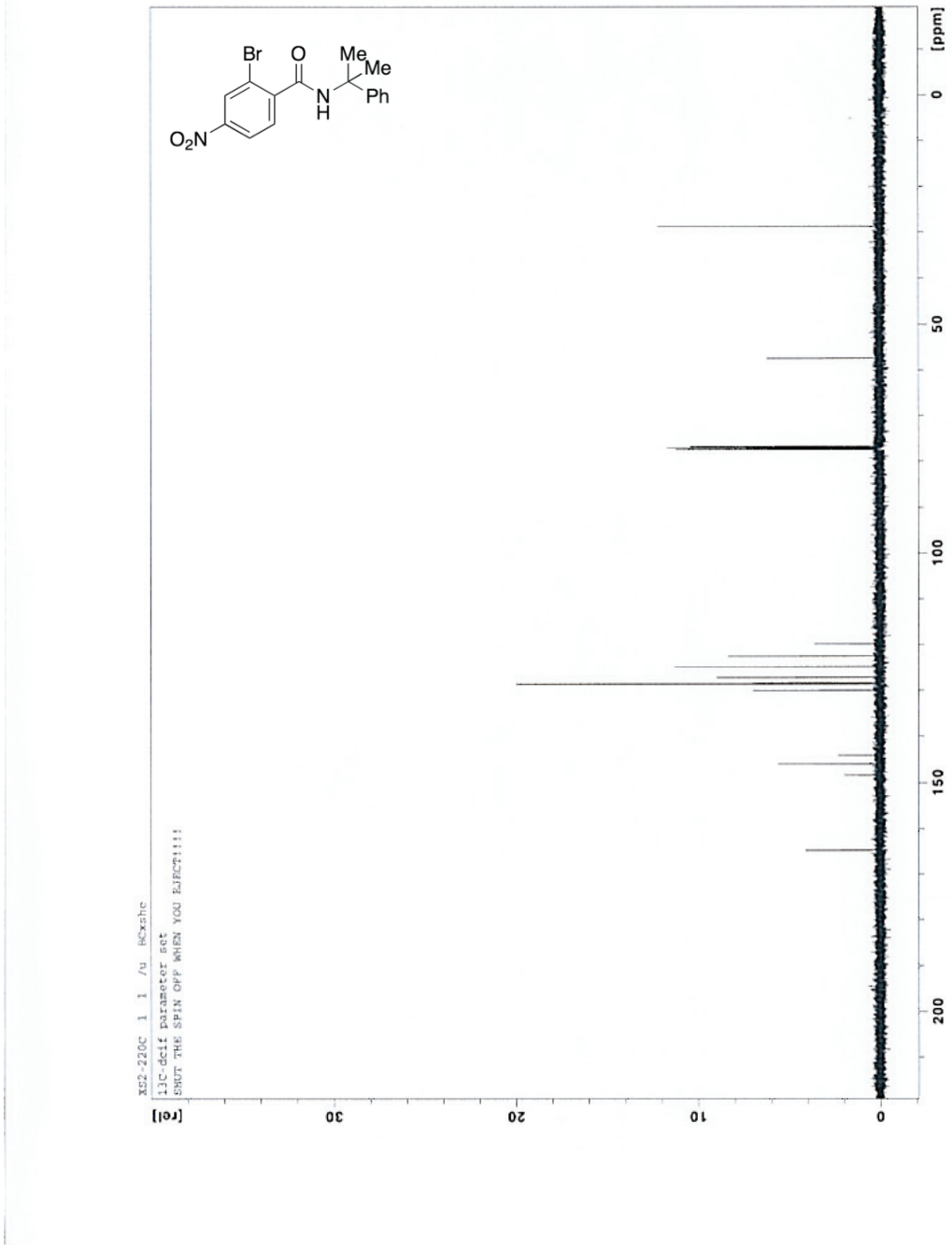
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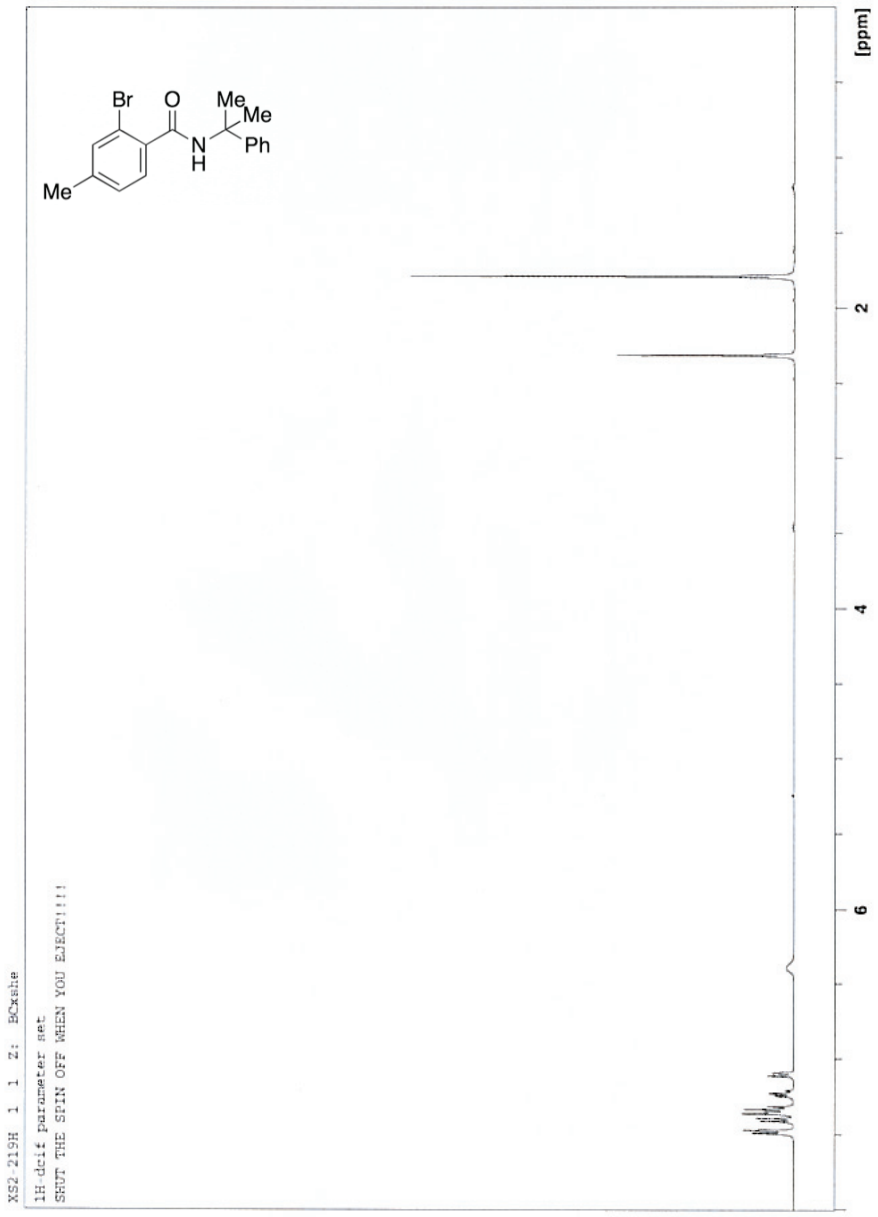
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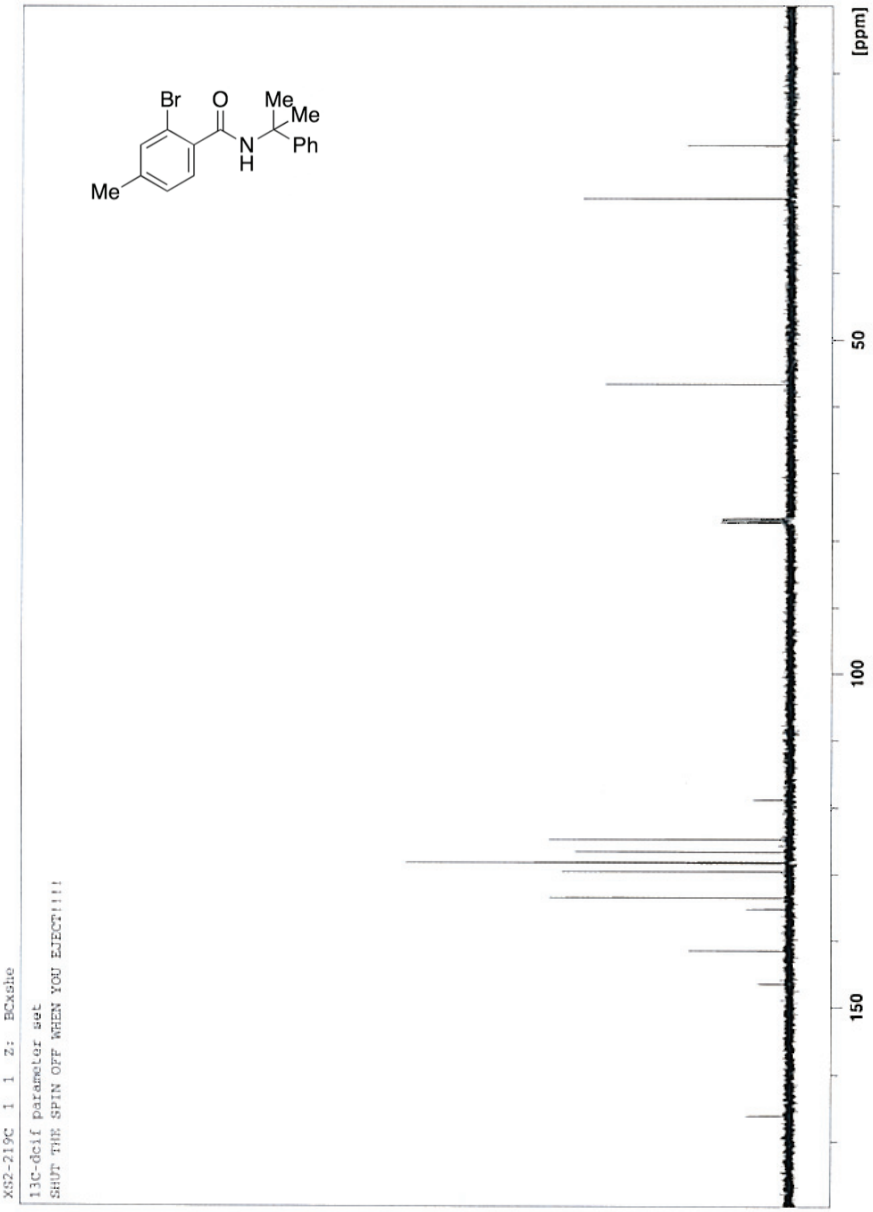
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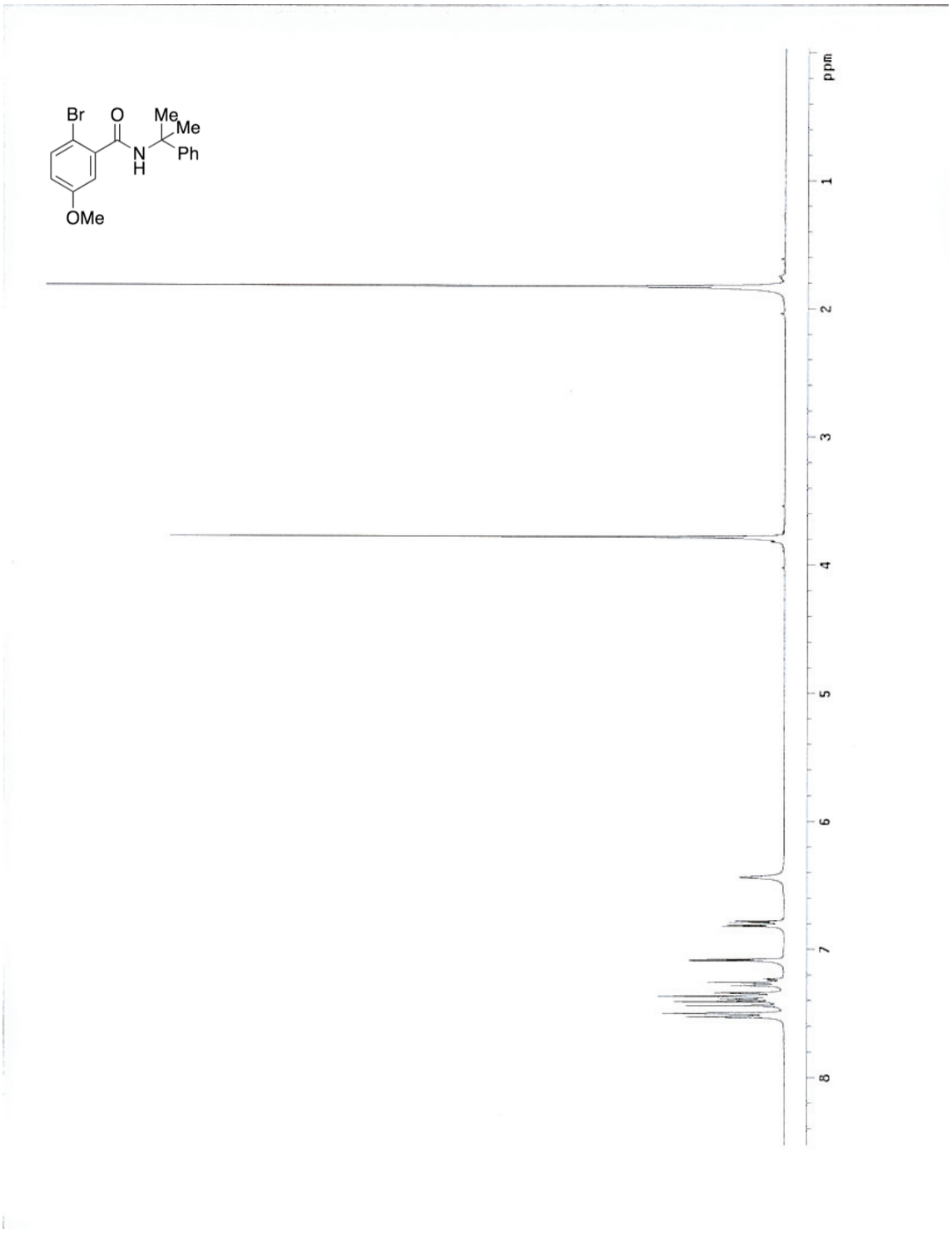
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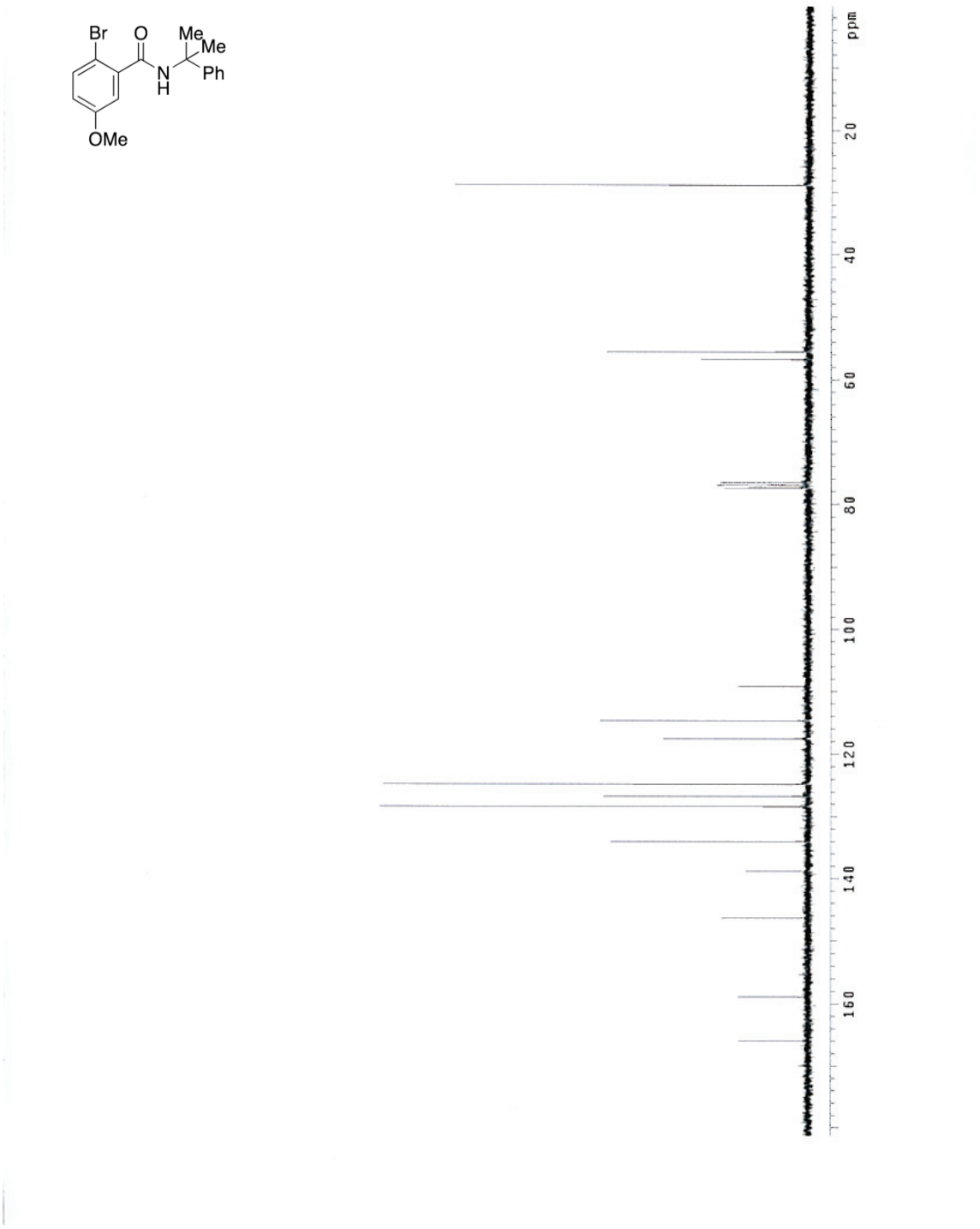
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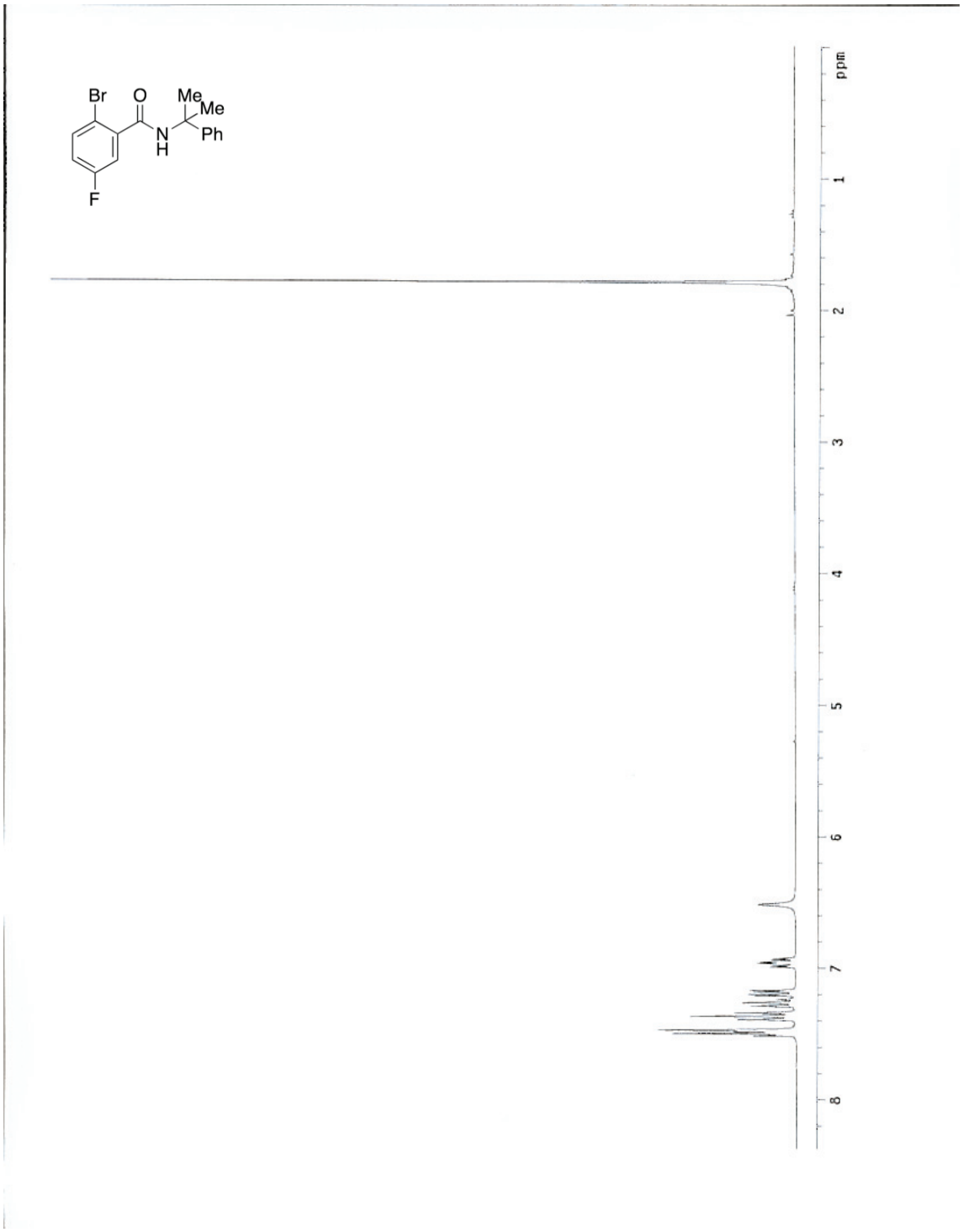
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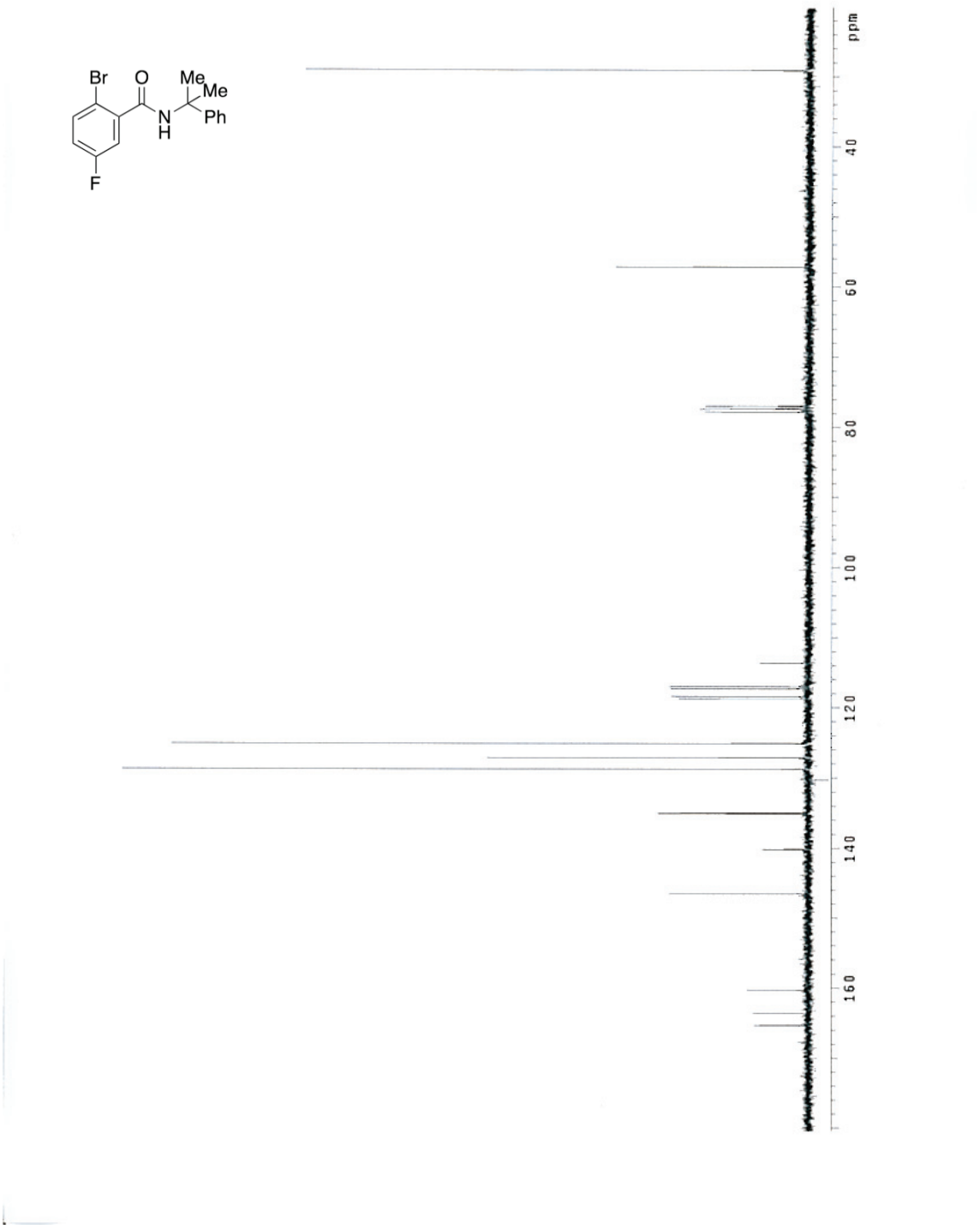
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Me
Me
N
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Ph
F
ppm
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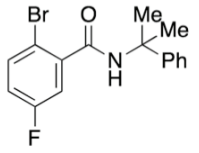
Br
O
Me
Me
N
H
Ph
F


ppm
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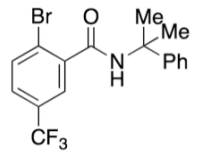
-100
-150


Br
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Me
Me
N
H
Ph
CF3

ppm
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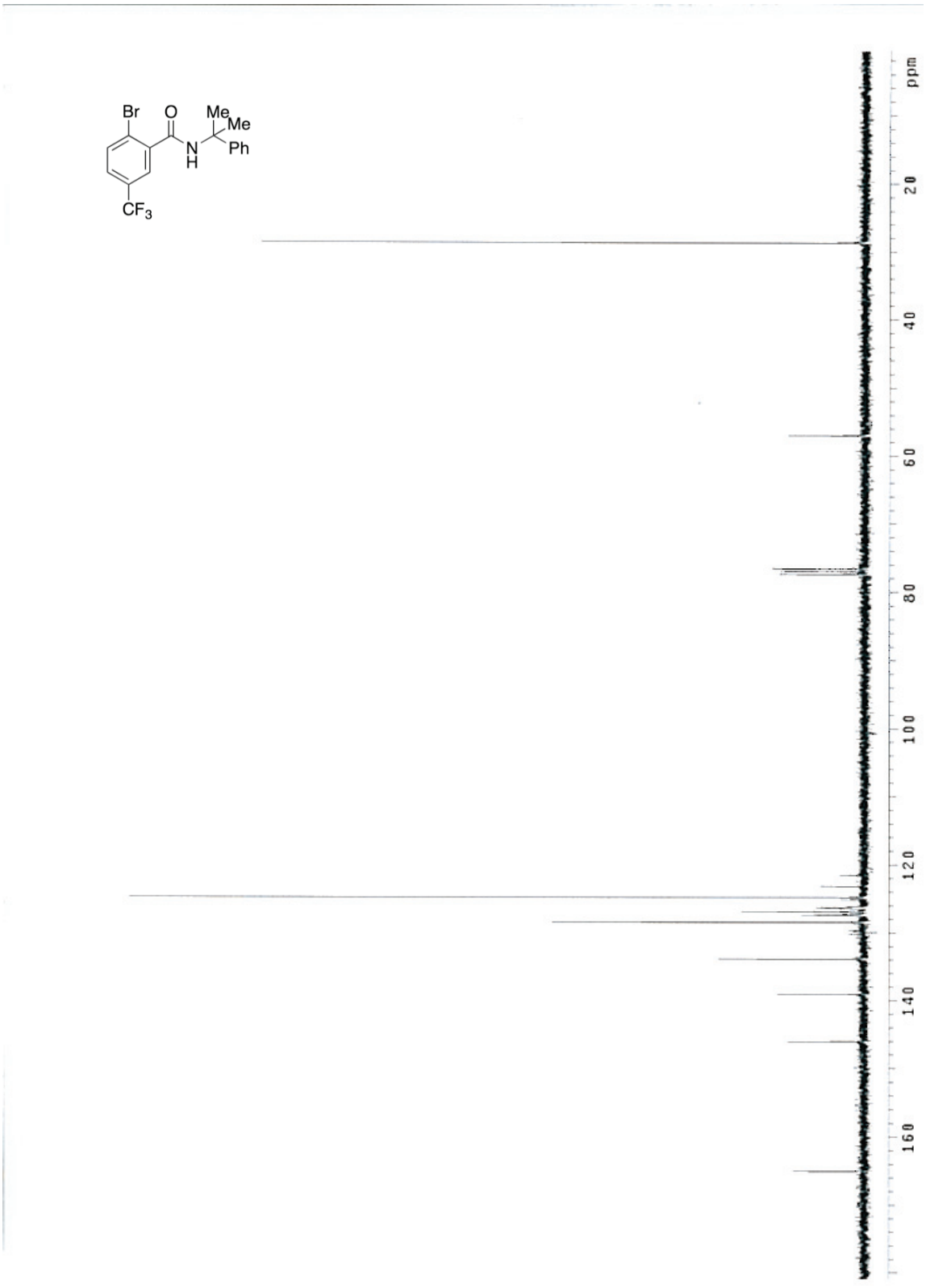
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O
Me
Me
N
H
Ph
CF3
ppm
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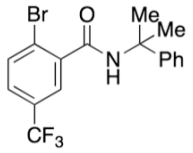
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Me
Me
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H
Ph
CF3

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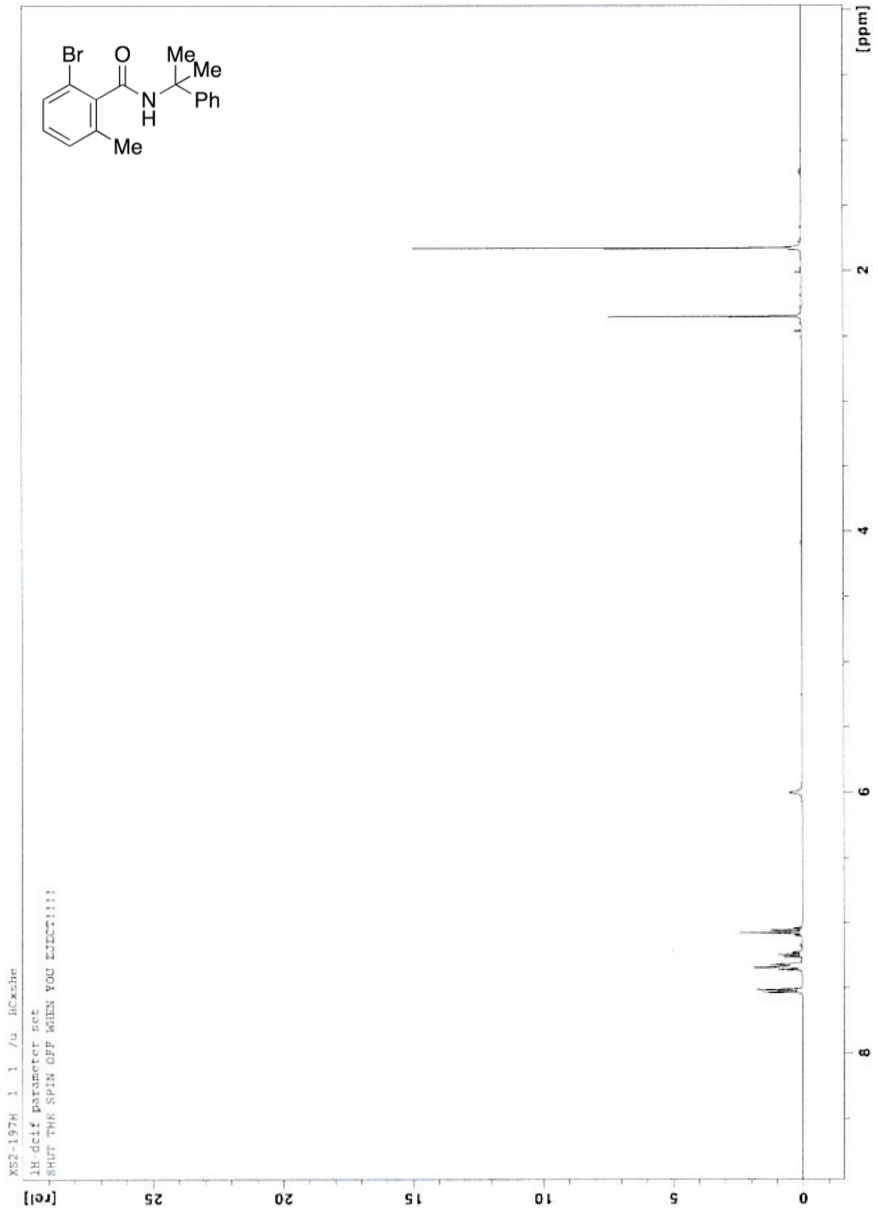
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Me
Me
Ph
N
H
Me
[ppm]
2
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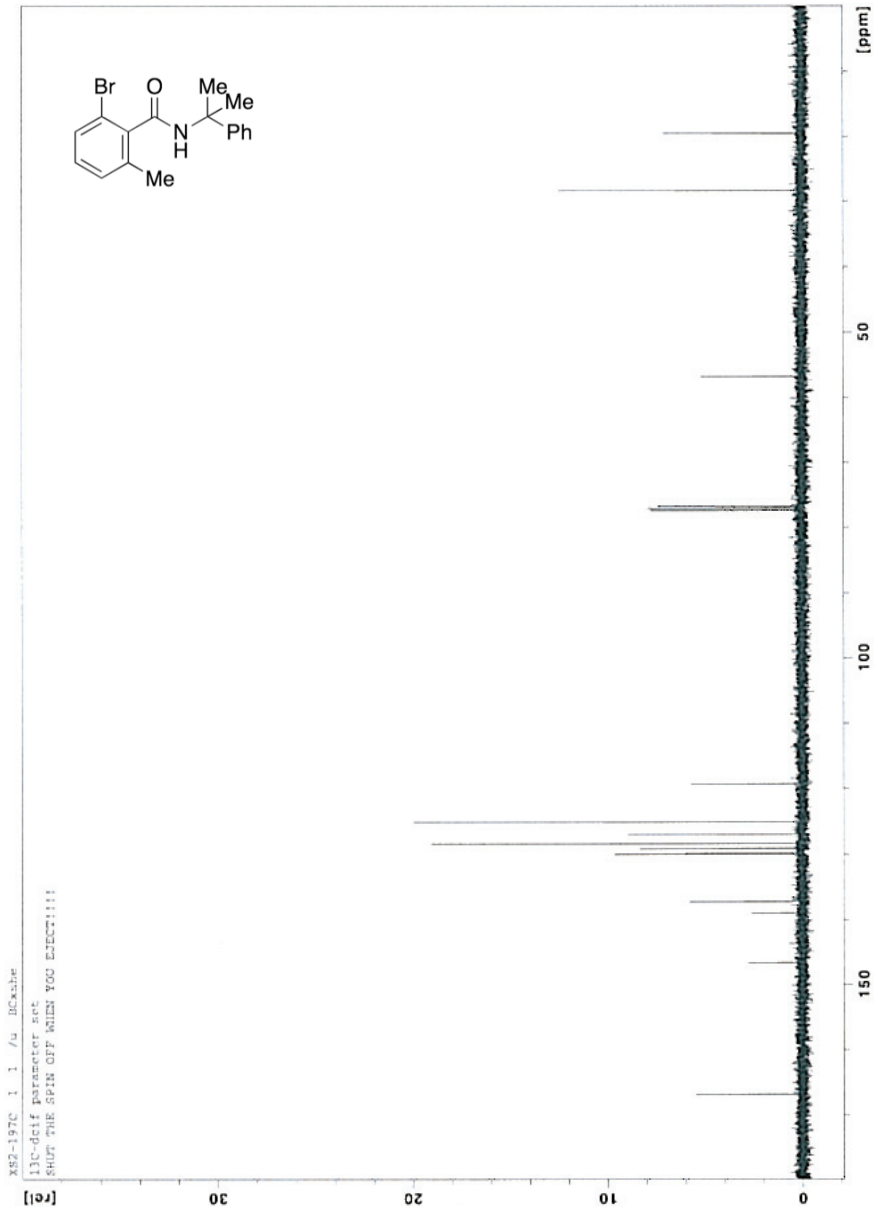
6
8
0
5
10
15
20
25
[rel]
XS2-197H 1 1 /u BCxshe
1H dcif parameter set
SHUT THE SPIN OFF WHEN YOU EJECT!!!!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Me
Ph
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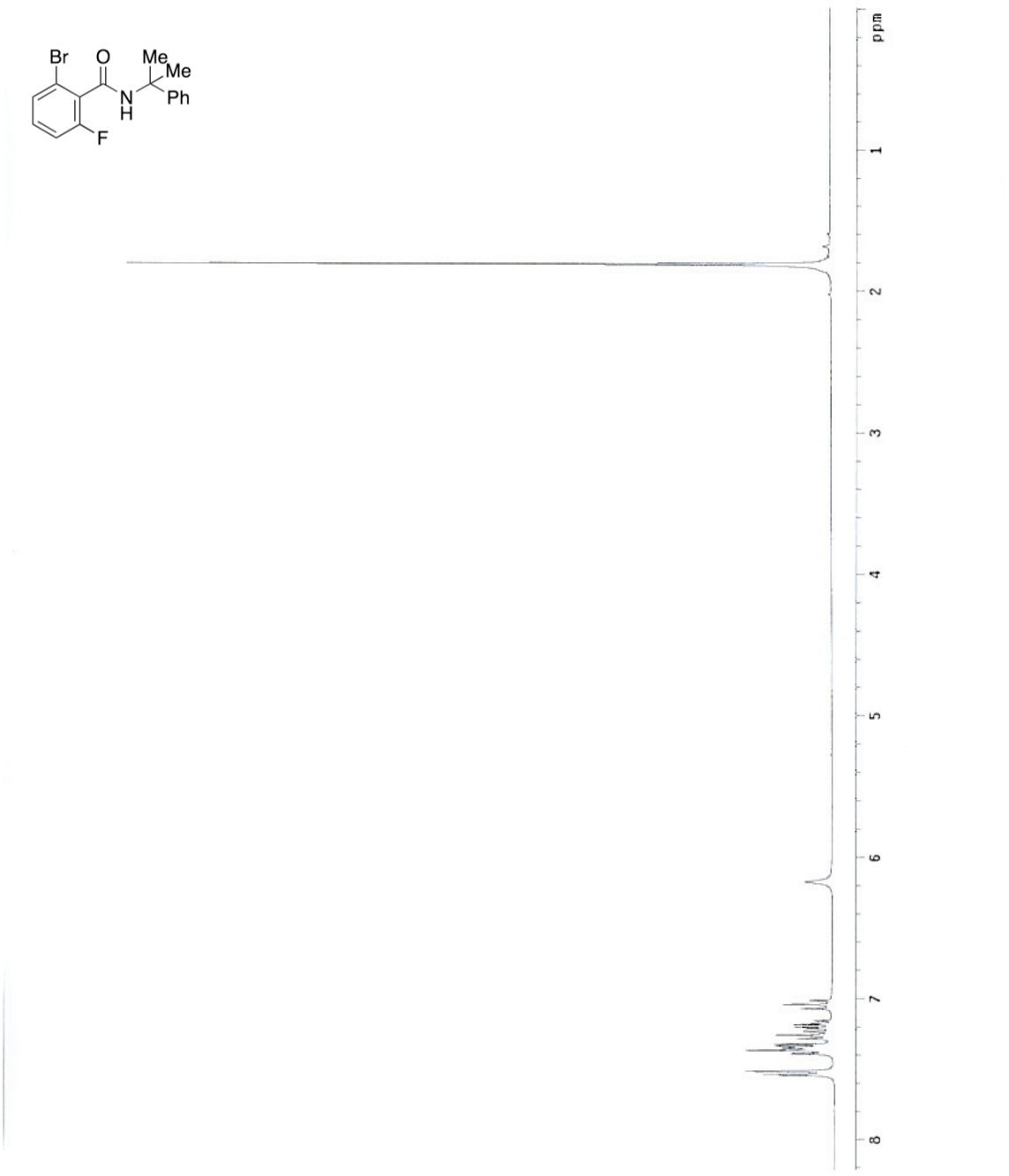
30
[rel]


Br
O
Me
Me
N
H
Ph
F
ppm
1
2
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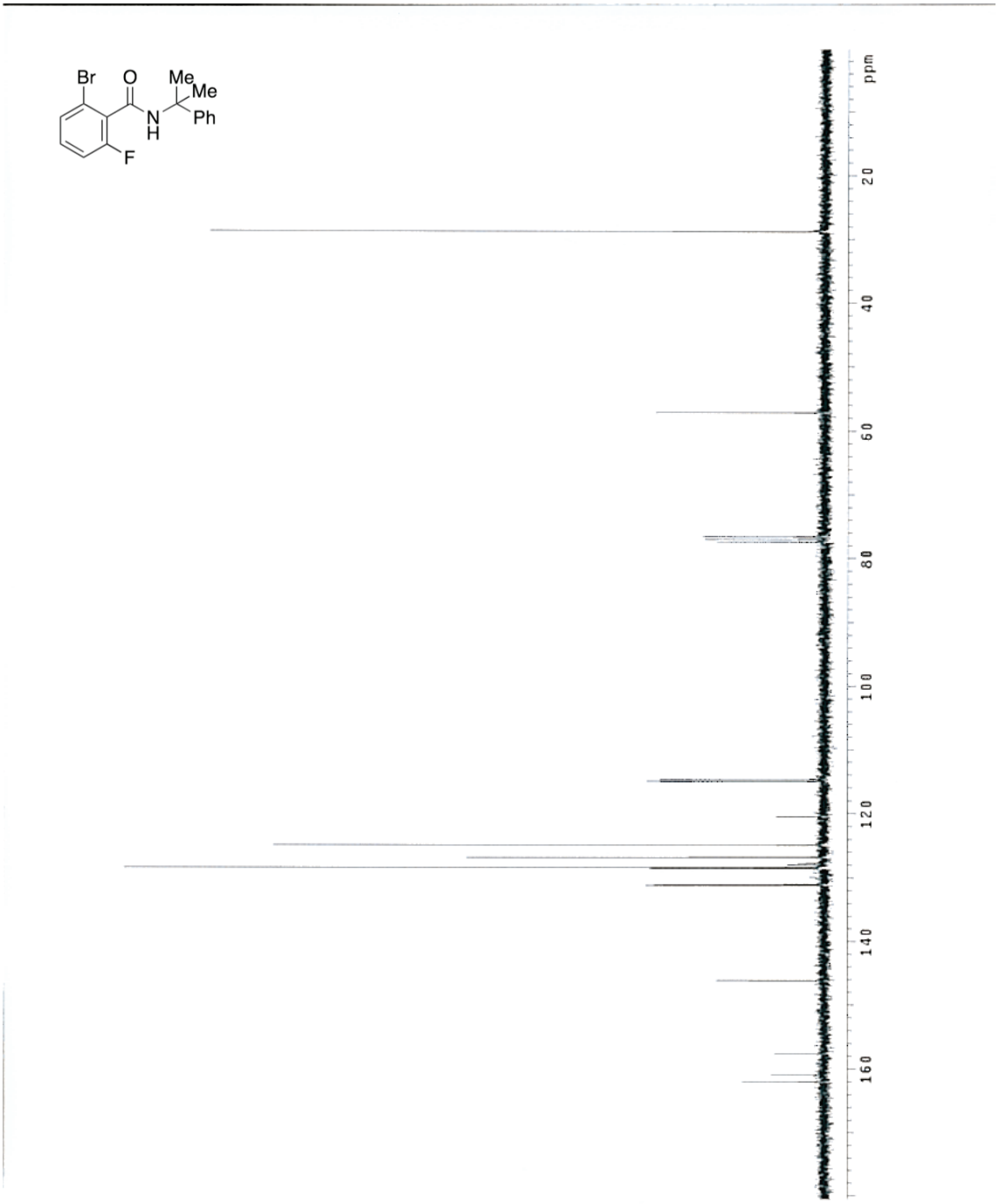
4
5
6
7
8


Br
O
Me
Me
N
H
Ph
F
ppm
20
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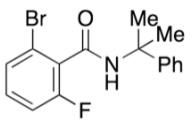
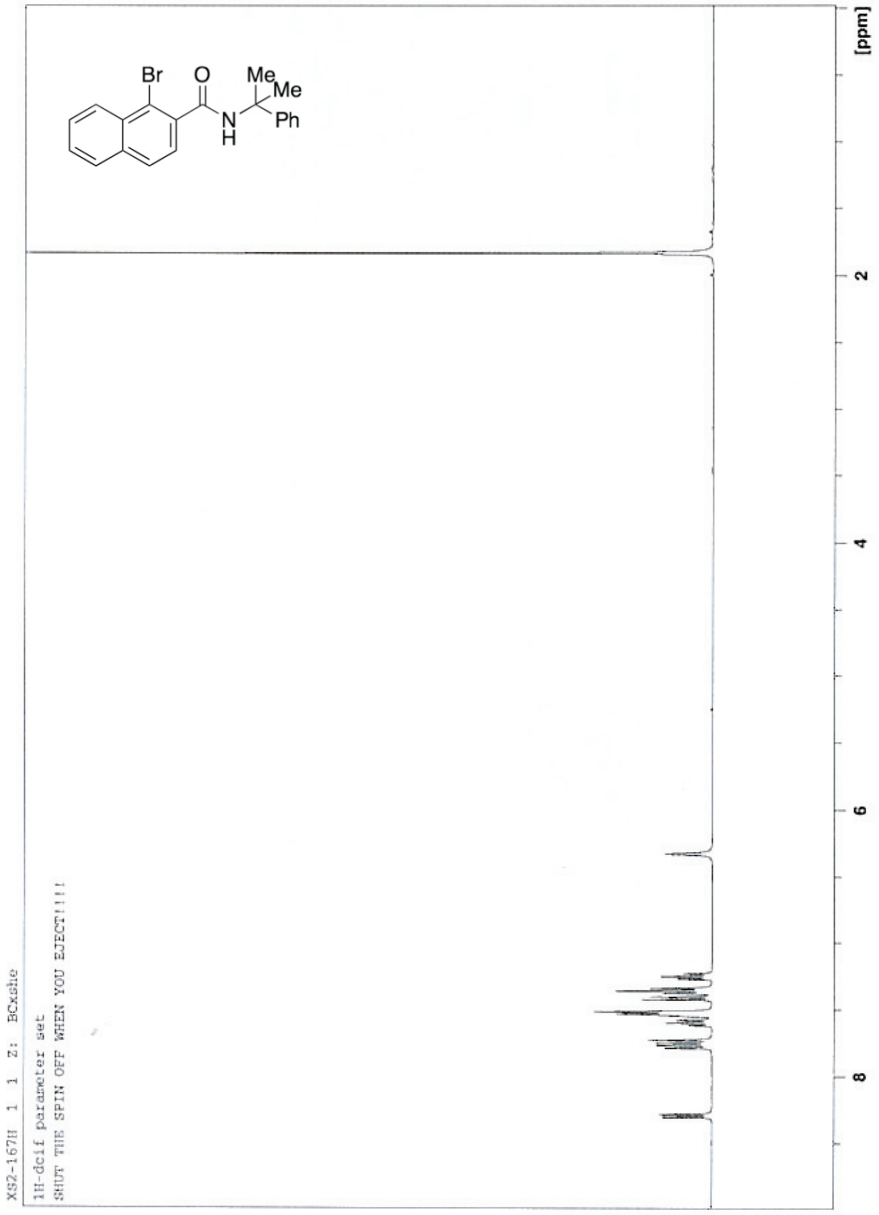
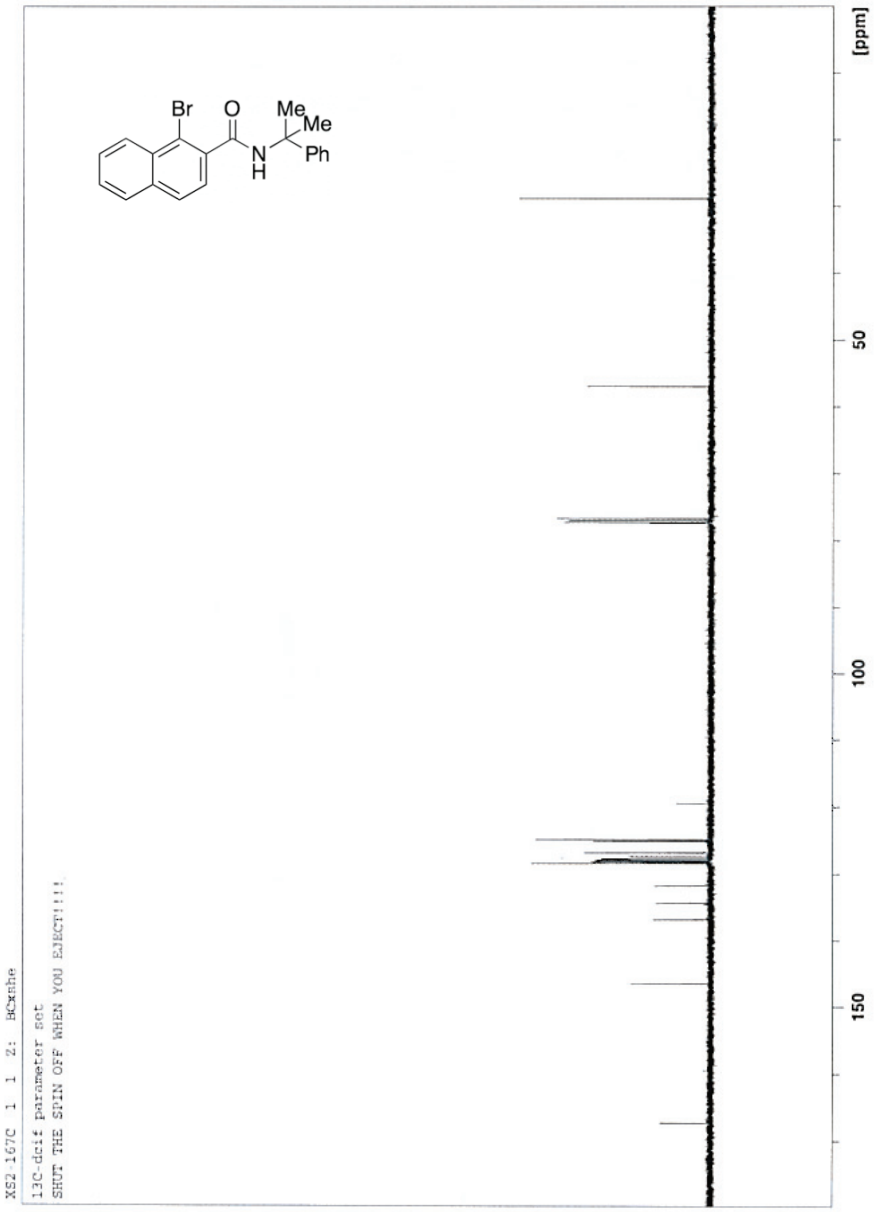
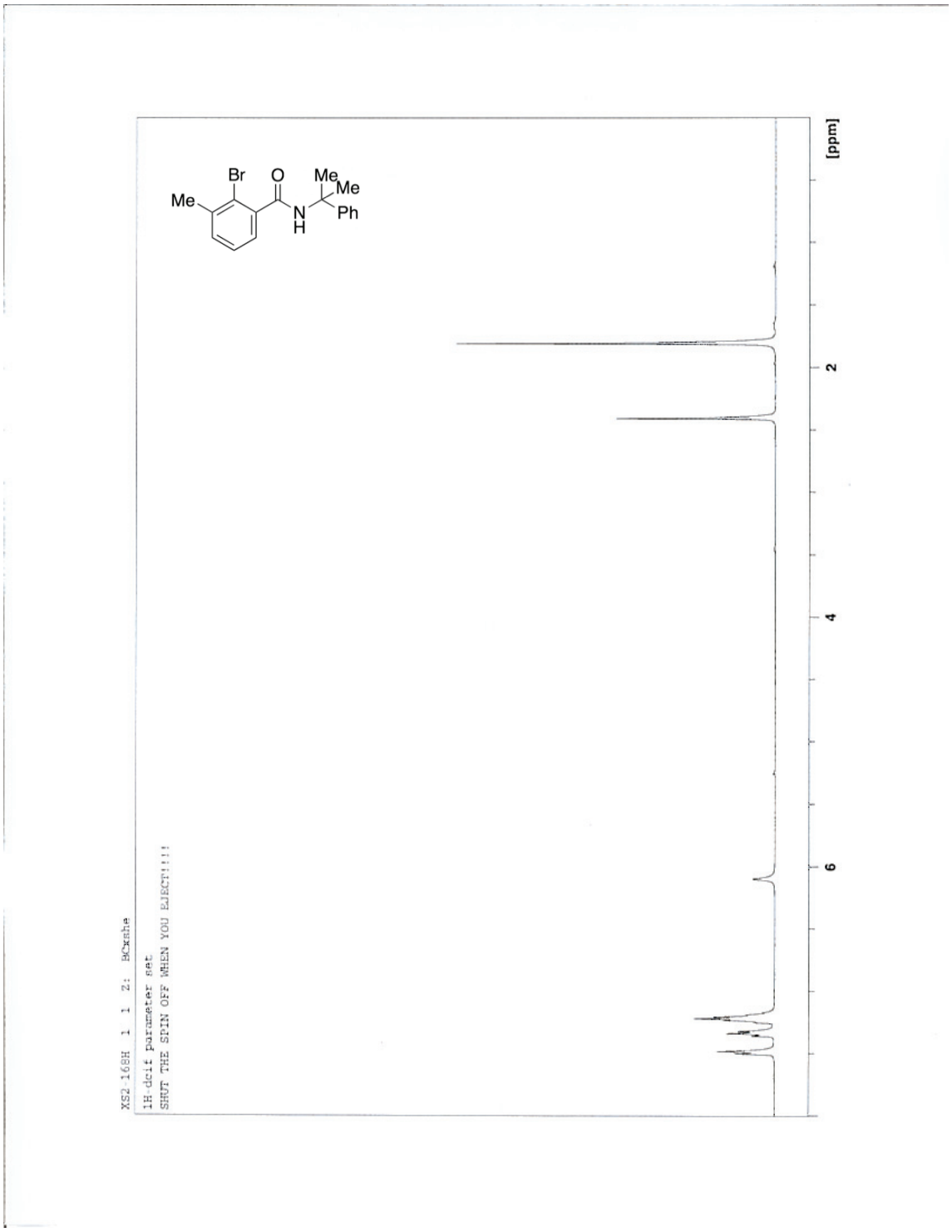
80
100
120
140
160

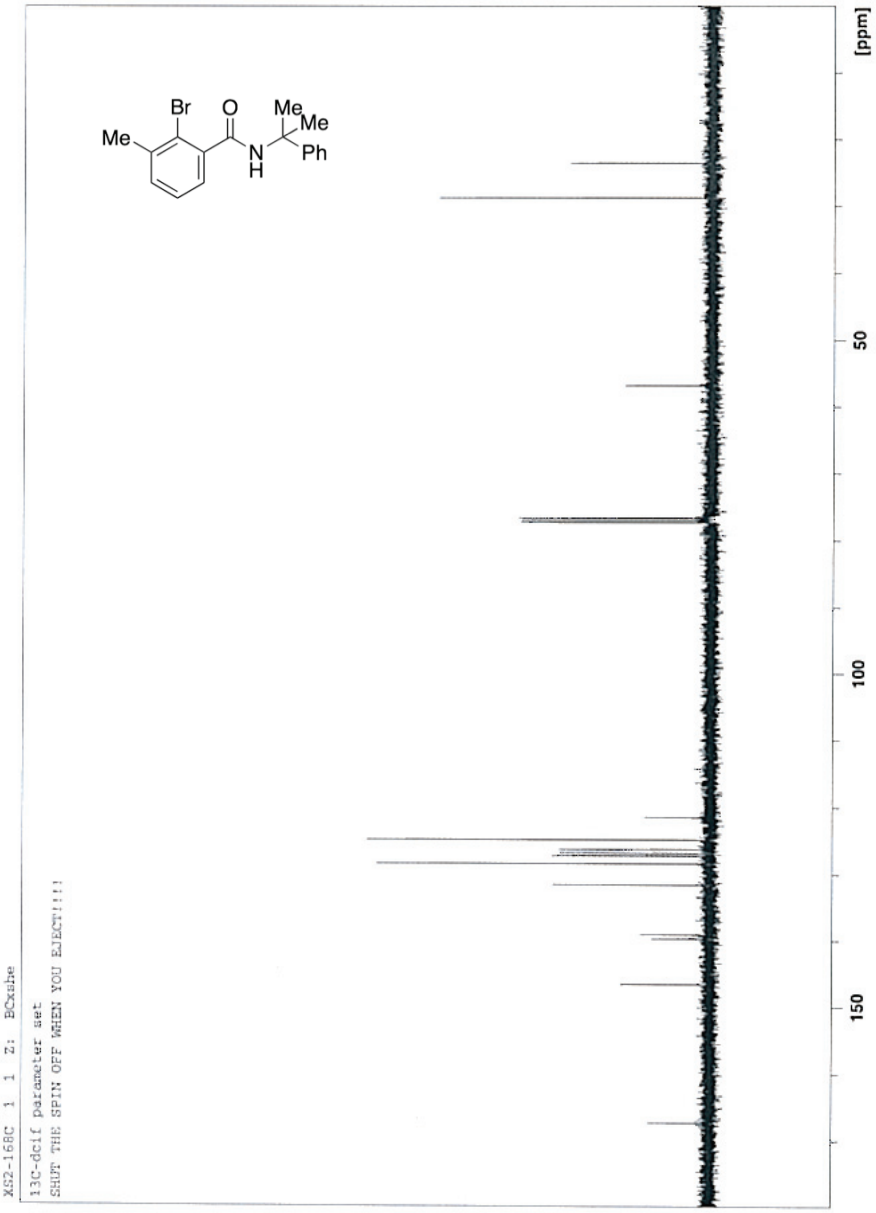

Br
O
Me
Me
N
H
Ph
F

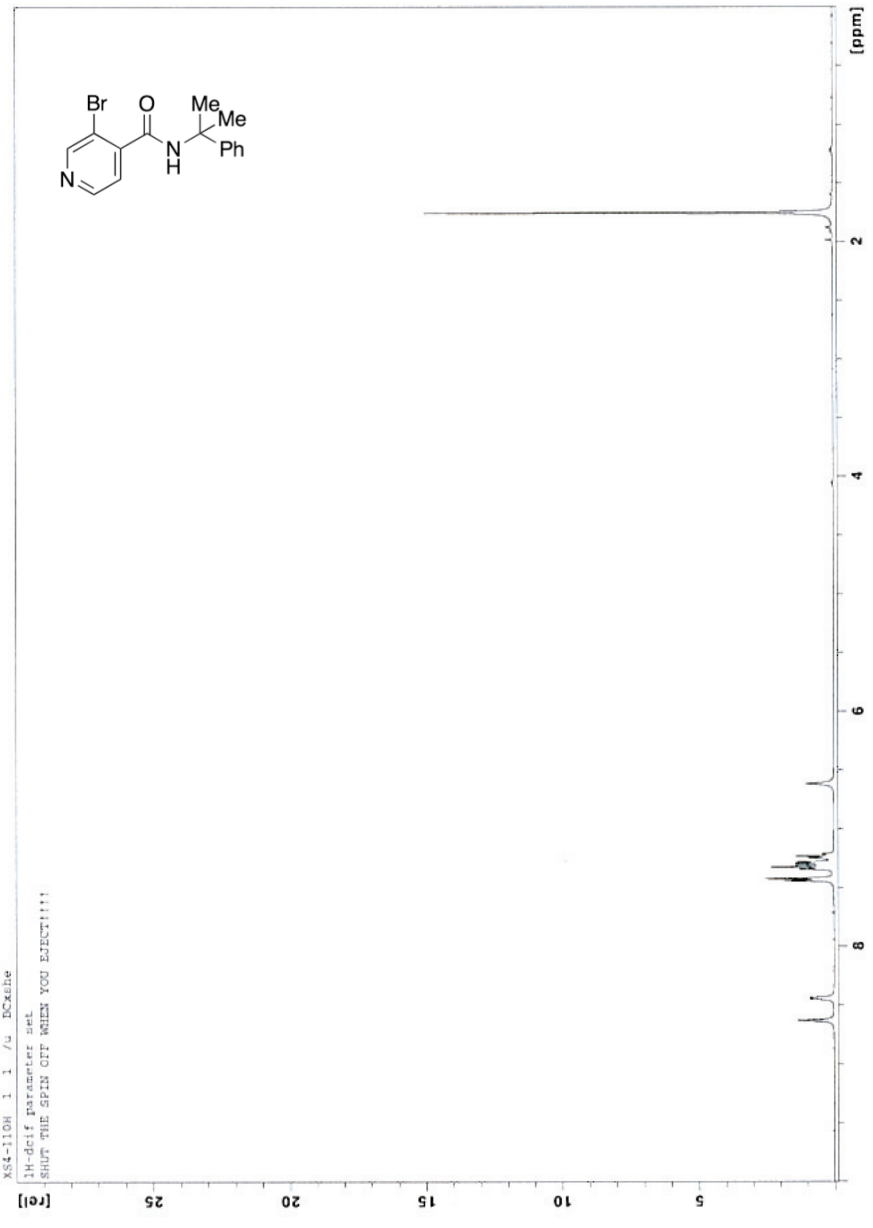

ppm
-150
-100
-50
0
50
100
150

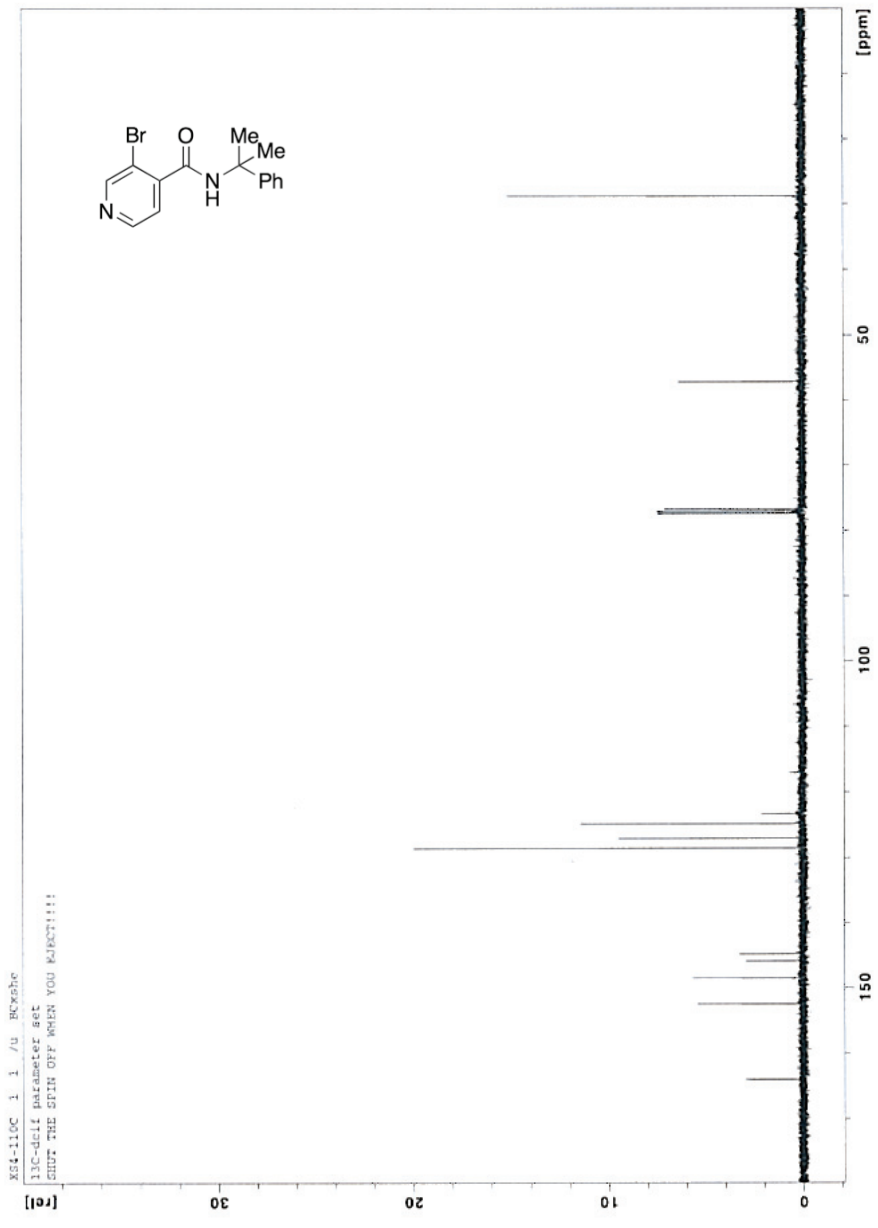

Br
O
Me
Me
N
H
Ph
XS2-167H 1 1 Z: BCxshe
1H-deif parameter set
SHUT THE SPIN OFF WHEN YOU EJECT!!!!
8
6
4
2
[ppm]


Br
O
Me
Me
N
H
Ph
XS2-167C 1 1 2: BCxnhe
13C-dcif parameter set
SHUT THE SPIN OFF WHEN YOU EJECT!!!!
150
100
50
[ppm]

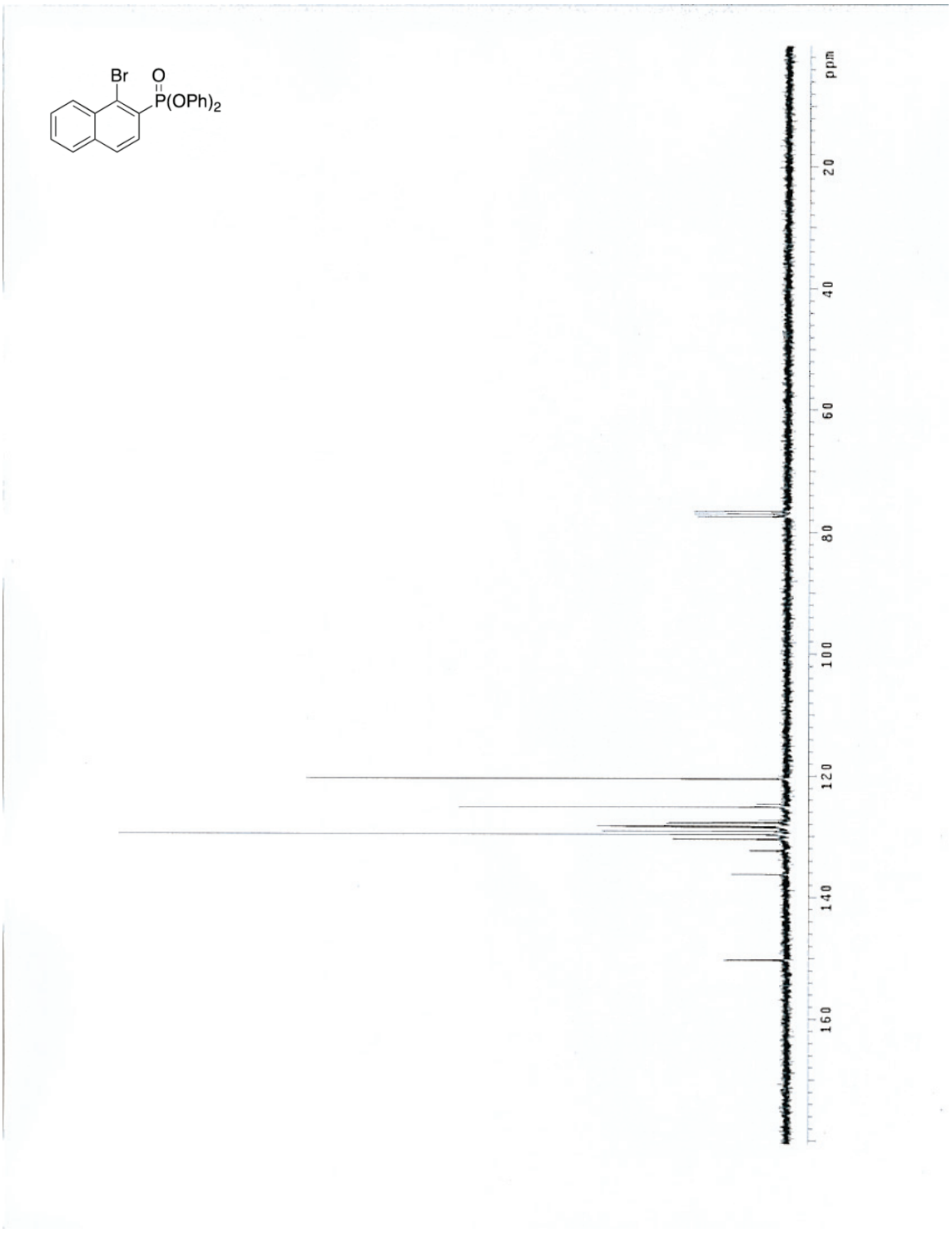

Br
O
Me
Me
Me
N
H
Ph
XS2 168H 1 1 2: BCxnhe
1H dcif parameter set
SHUT THE SPIN OFF WHEN YOU EJECT!!!!
[ppm]
2
4
6


XS2-168C 1 1 2: BCxsbe
13C-dcif parameter set
SHIFT THE SPIN OFF WHEN YOU EJECT!!!!
Br
O
Me
Me
Me
N
H
Ph
[ppm]
50
100
150


Br
O
Me
Me
N
H
Ph
N
[ppm]
2
4
6
8
5
10
15
20
25
[rel]
KS4-110H 1 1 /u DCaube
1H-dcif parameter set
SHUM TUBE SPIN OFF WHEN YOU EJECT!!!!


Br
O
Me
Me
N
H
Ph
N
[ppm]
150
100
50
0
10
20
30
[rel]
KS4-110C 1 1 /u BCrabe
13C-dept parameter set
GUYS TAKE SPIN OFF WHEN YOU EJECT!!!!


Br
O
P(OPh)2
ppm
1
2
3
4
5
6
7
8
9


Br
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P(OPh)2
ppm
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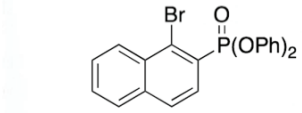
60
80
100
120
140
160


Br
O
P(OPh)2

9.586
ppm
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-40
-20
0
20
40
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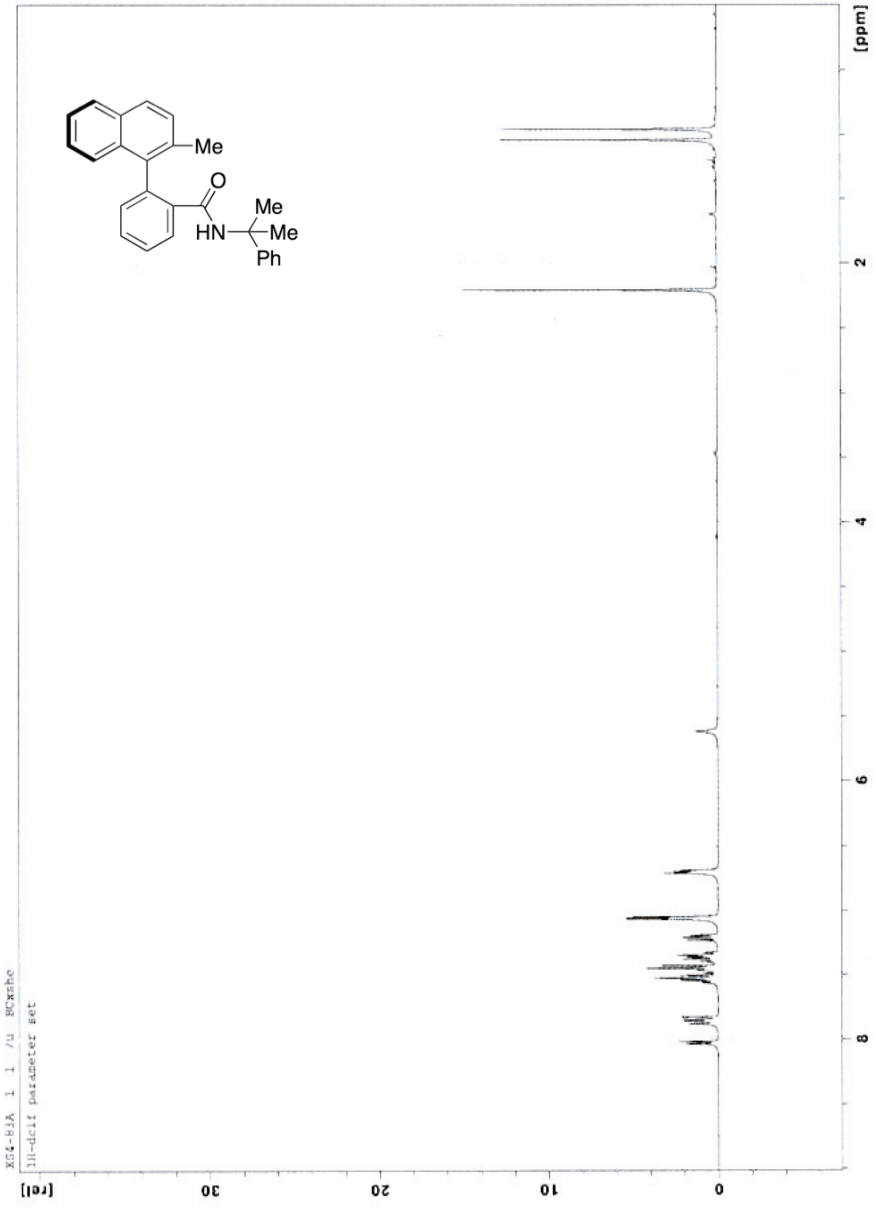
80
100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HN
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Ph
[ppm]
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6
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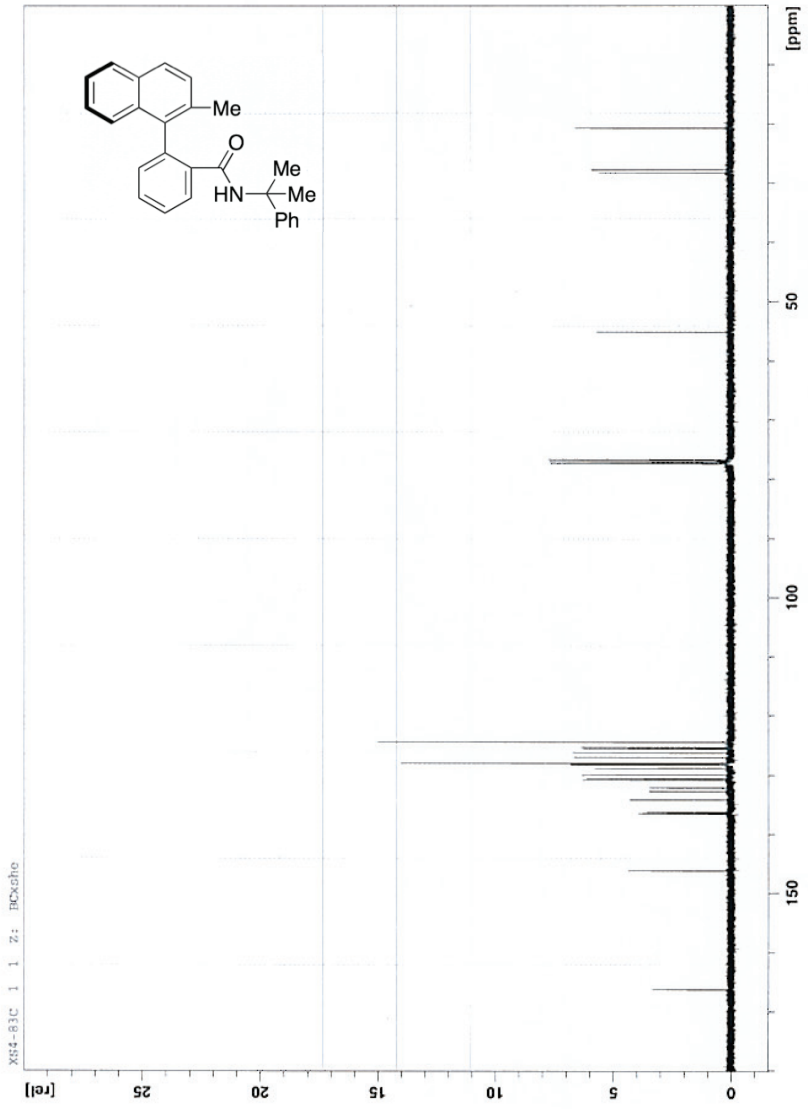
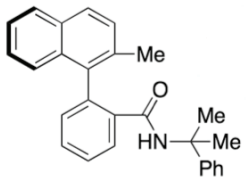
0
10
20
30
[rel]


Me
O
HN
Me
Me
Ph
[ppm]
50
100
150
[rel]
0
5
10
15
20
25

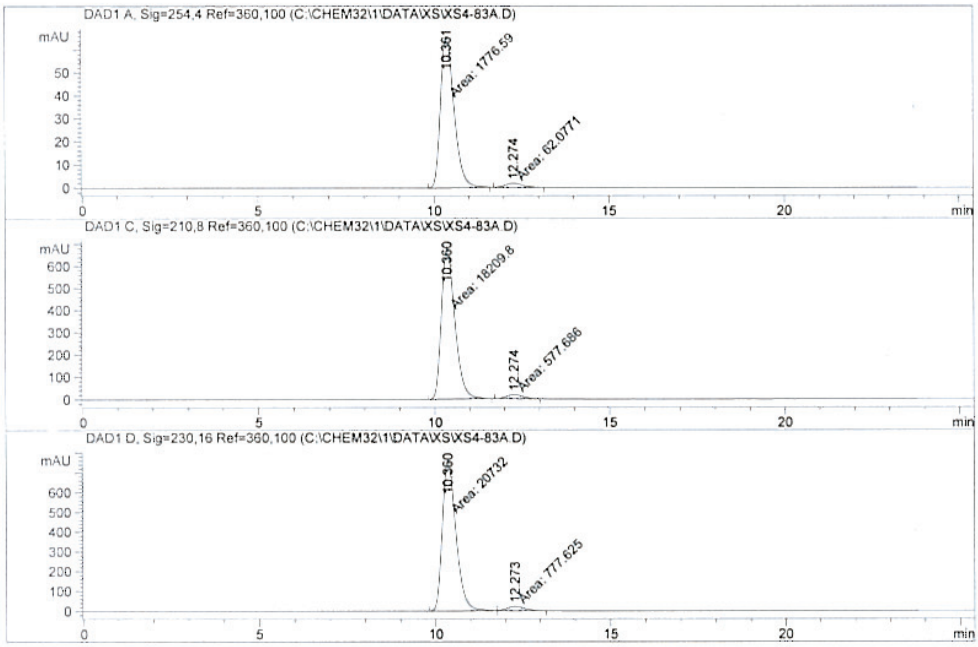
Data File C:\CHEM32\1\DATA\XS\XS4-83A.D
Sample Name: XS4-83A

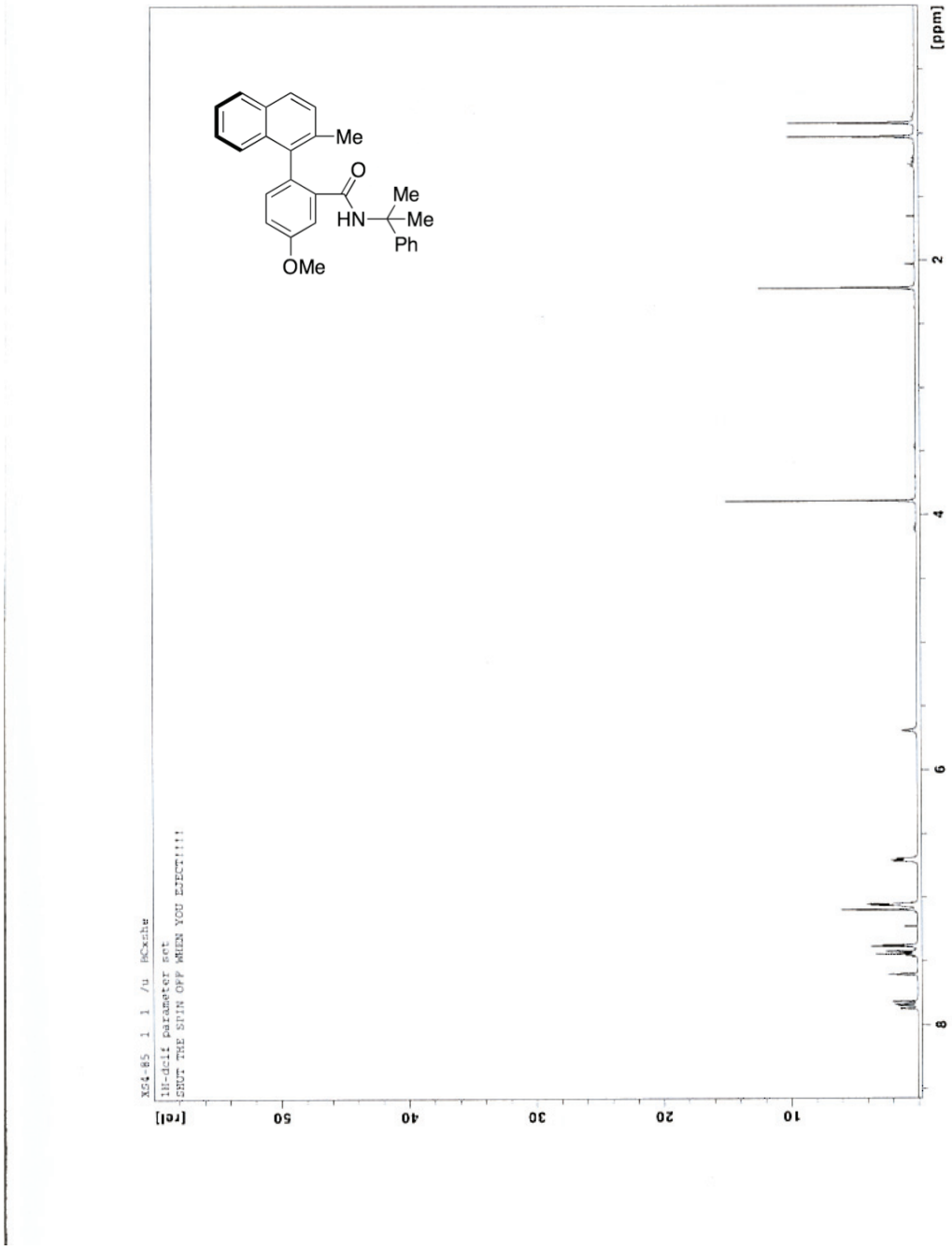
Acq. Operator : XS
Acq. Instrument : Instrument 1 Location : Vial 1
Injection Date : 5/16/2009 5:59:09 PM
Inj Volume : 0.2 µl
Acq. Method : C:\CHEM32\1\METHODS\JGF30.M
Last changed : 5/16/2009 5:49:34 PM by XS
(modified after loading)
Analysis Method : C:\CHEM32\1\DATA\XS\XS4-83A.D\DA.M (JGF30.M)
Last changed : 5/16/2009 6:25:04 PM by XS
Method Info : 60% n-Hexane
40% i-propanol
0.5 ml/min

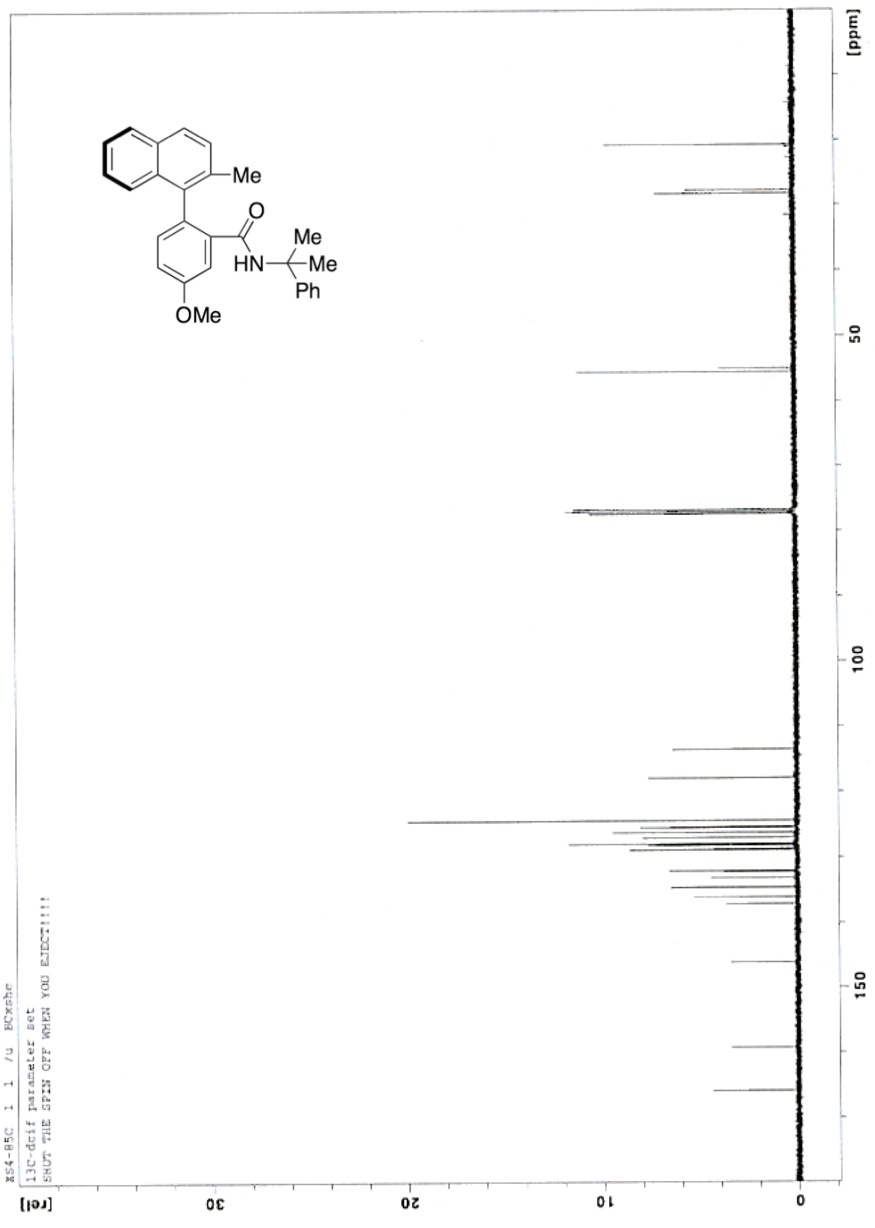
Sample Info : OD-H 3% IPA 1.0ML/MIN



93% ee

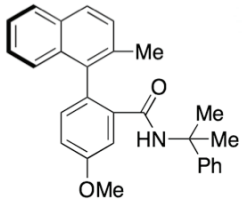



Me
O
HN
Me
Me
Ph
OMe
[ppm]
2
4
6
8
10
20
30
40
50
[rel]
X54-85 1 1 /u PCcche
1H-dcif parameter set
SHUT THE STIR OFF WHEN YOU EJECT!!!!


Me
O
HN
Me
Me
Ph
OMe
[ppm]
150
100
50
0
10
20
30
[rel]
AS4-85C 1 1 /u BCxshe
13C-dsif parameter set
SHUT THE SPIN OFF WHEN YOU EJECT!!!!

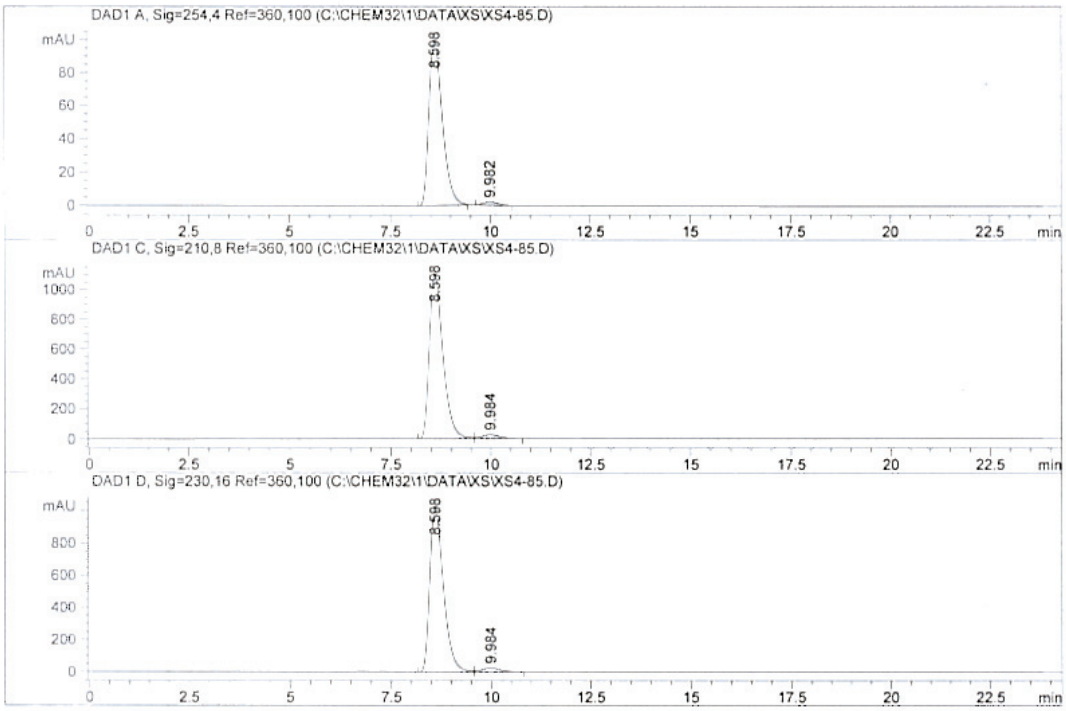
Data File C:\CHEM32\1\DATA\XS\XS4-85.D
Sample Name: XS4-85

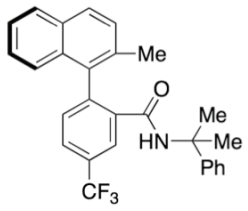
Acq. Operator : XS
Acq. Instrument : Instrument 1 Location : Vial 1
Injection Date : 5/19/2009 1:05:36 PM
Inj Volume : 0.5 µl
Acq. Method : C:\CHEM32\1\METHODS\JGF30.M
Last changed : 5/19/2009 1:04:50 PM by XS
(modified after loading)
Analysis Method : C:\CHEM32\1\DATA\XS\XS4-85.D\DA.M (JGF30.M)
Last changed : 5/19/2009 1:30:33 PM by XS
Method Info : 60% n-Hexane
40% i-propanol
0.5 ml/min



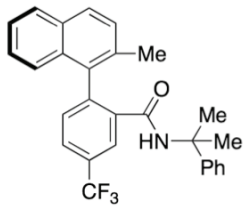
Sample Info : OD-H 5% IPA 1.0ML/MIN

94% ee




Me
O
HN
Me
Me
Ph
CF3

ppm
1
2
3
4
5
6
7
8
9


Me
O
HN
Me
Me
Ph
CF3

ppm
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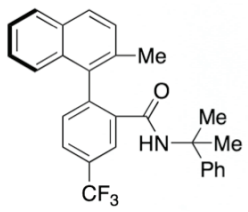
80
100
120
140
160


Me
O
HN
Me
Me
Ph
CF3


ppm
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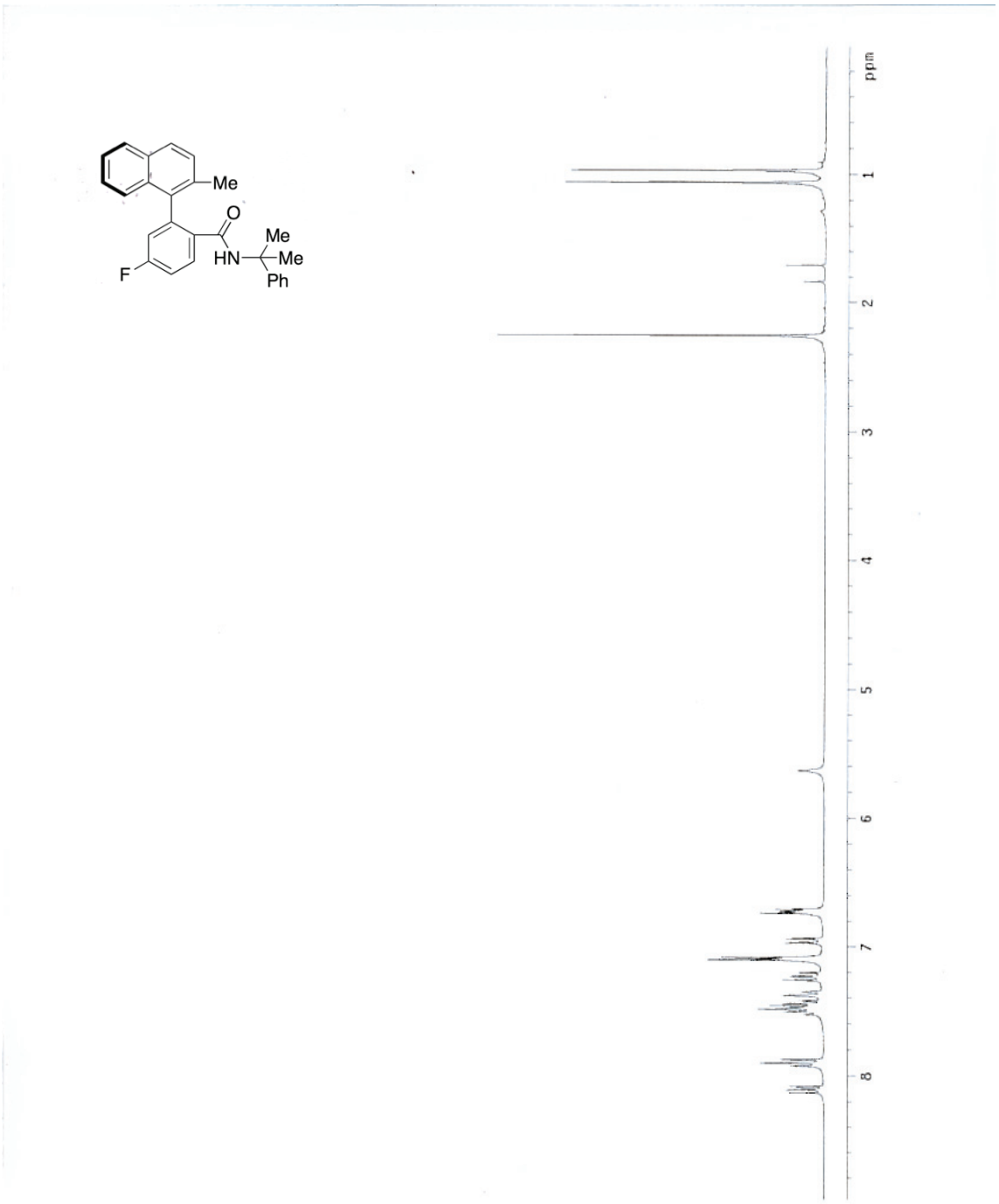
100
150


Me
O
Me
HN
Me
Ph
F
ppm
1
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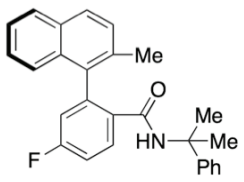
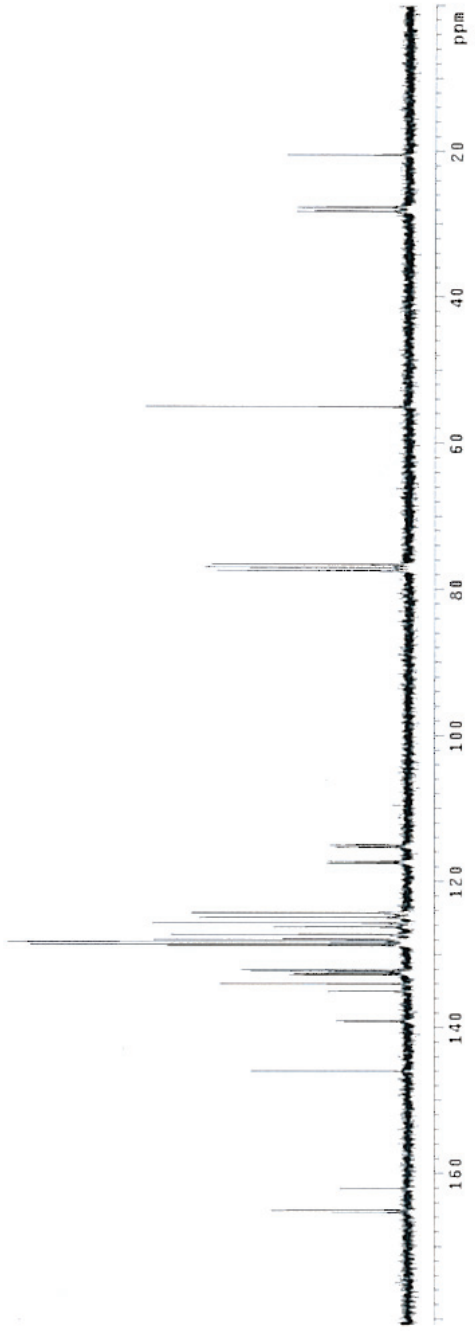
6
7
8


Me
O
Me
HN
Me
Ph
F


ppm
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100
120
140
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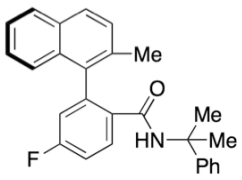
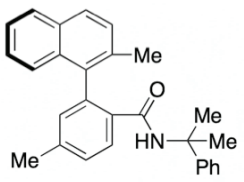
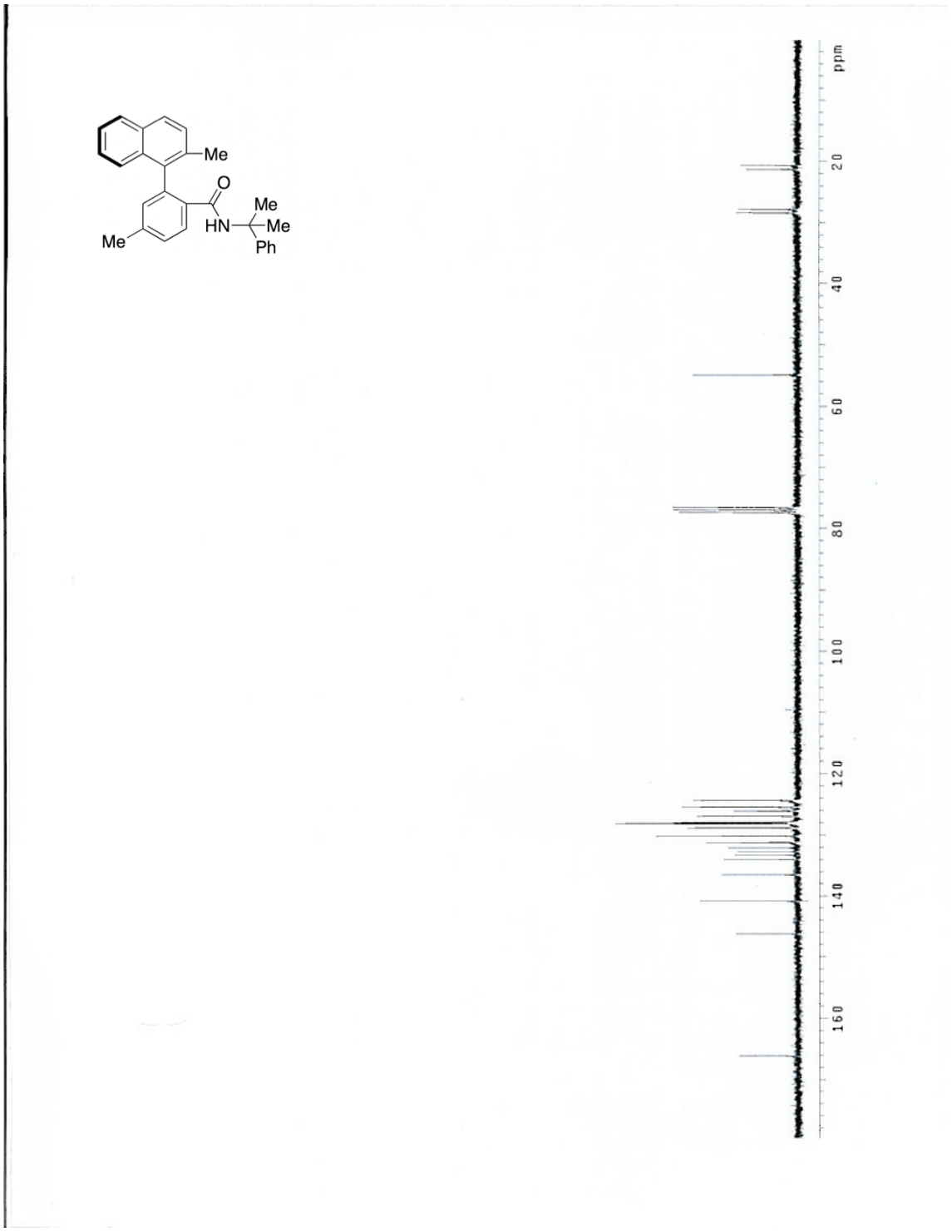

Me
O
Me
HN
Me
Ph
F


ppm
-150
-100
-50
0
50
100
150

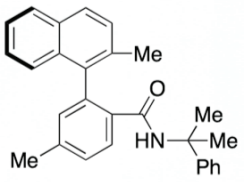

Me
O
Me
HN
Me
Me
Ph

ppm
1
2
3
4
5
6
7
8

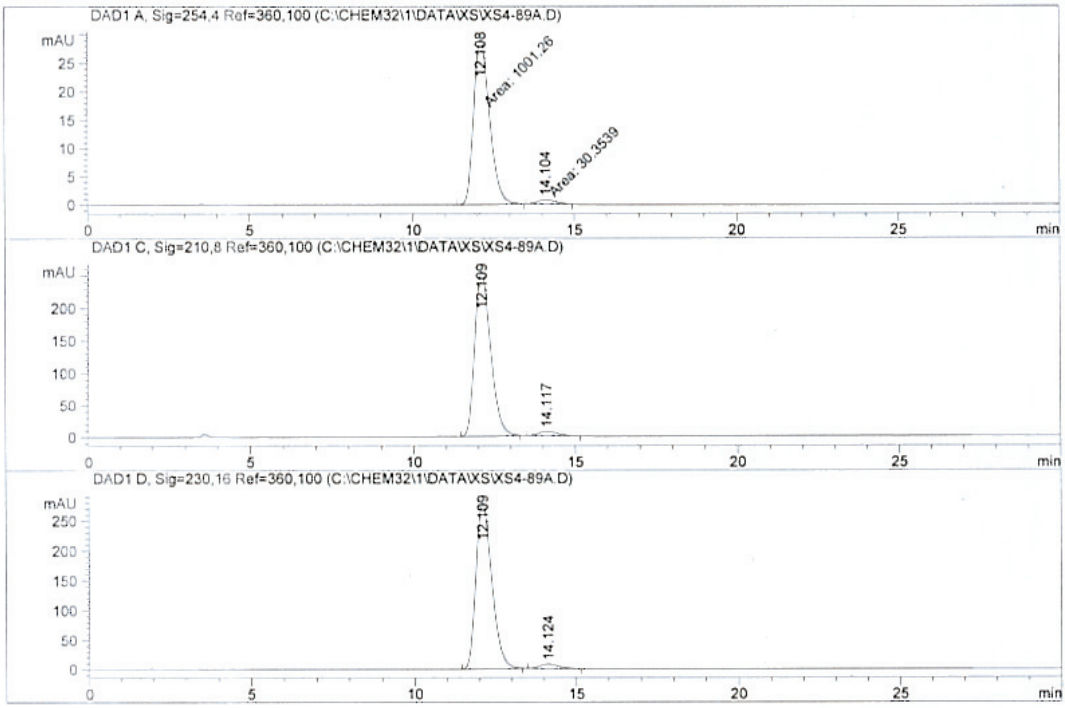

Me
O
Me
HN
Me
Me
Ph
ppm
20
40
60
80
100
120
140
160

Data File C:\CHEM32\1\DATA\XS\XS4-89A.D
Sample Name: XS4-89A

Acq. Operator : XS
Acq. Instrument : Instrument 1 Location : Vial 21
Injection Date : 6/22/2009 12:42:59 PM
Inj Volume : 0.6 µl
Acq. Method : C:\CHEM32\1\METHODS\ELLIOT-2.M
Last changed : 6/22/2009 12:42:15 PM by XS
(modified after loading)
Analysis Method : C:\CHEM32\1\DATA\XS\XS4-89A.D\DA.M (ELLIOT-2.M)
Last changed : 6/22/2009 1:24:28 PM by jACLYN
(modified after loading)
Sample Info : OD-H, 2.5% IPA IN HEXANE, 1.0ML/MIN

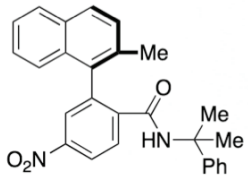


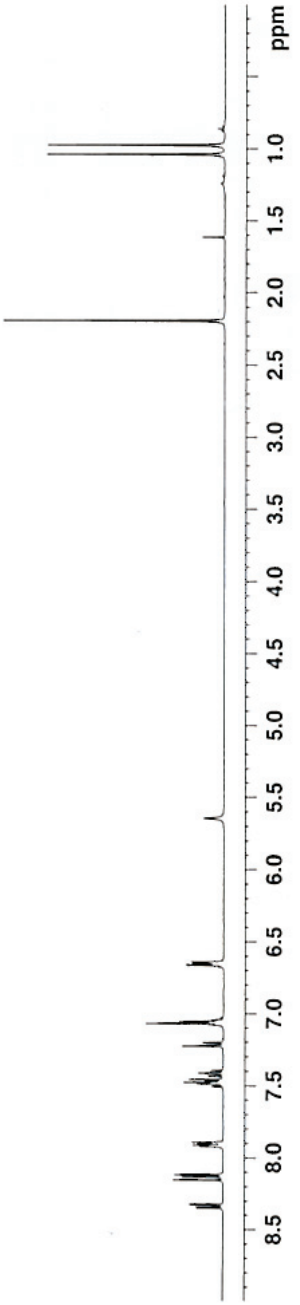
94% ee



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Me
O
Me
HN
Me
Ph
O2N


ppm
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2.0
2.5
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4.5
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5.5
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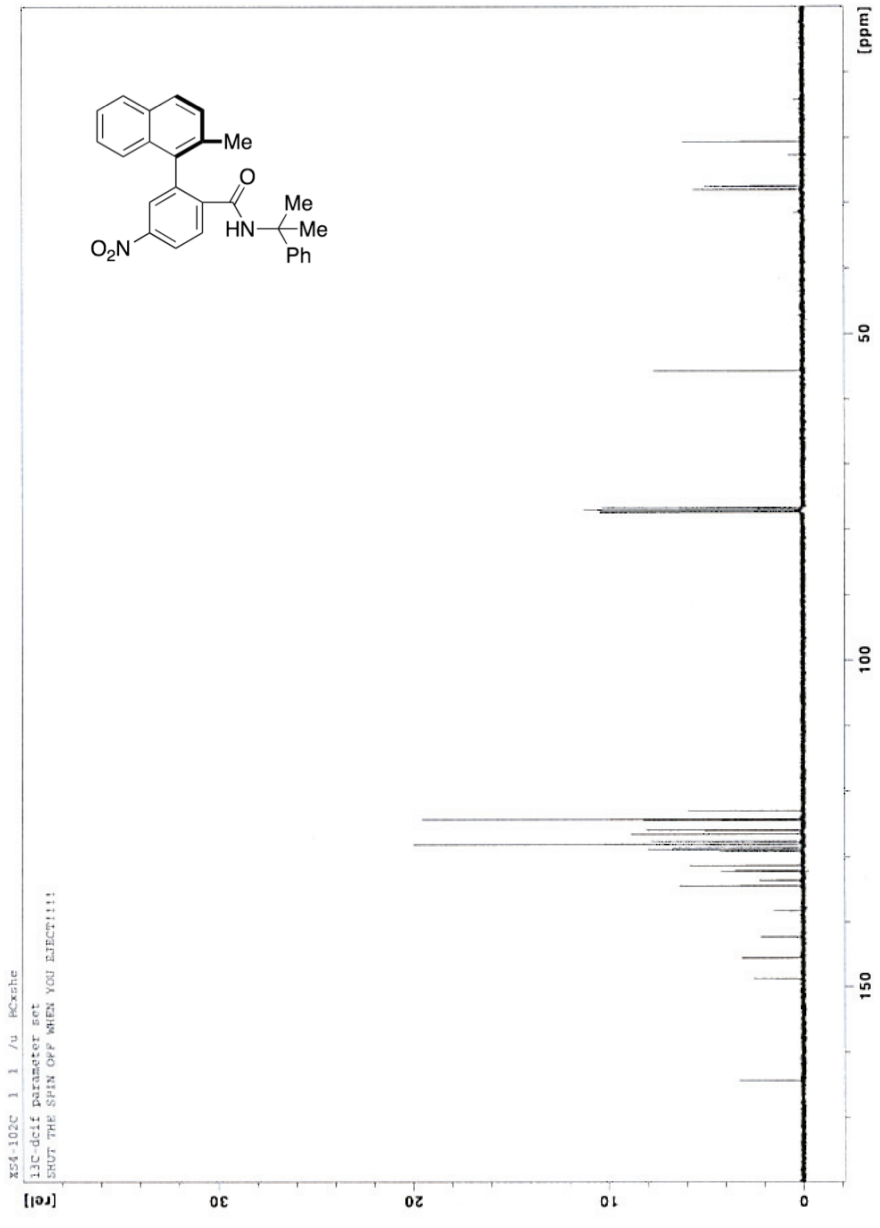
6.5
7.0
7.5
8.0
8.5


Me
O
Me
HN
Me
Ph
O2N
[ppm]
150
100
50
0
10
20
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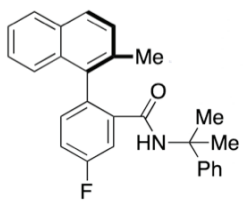
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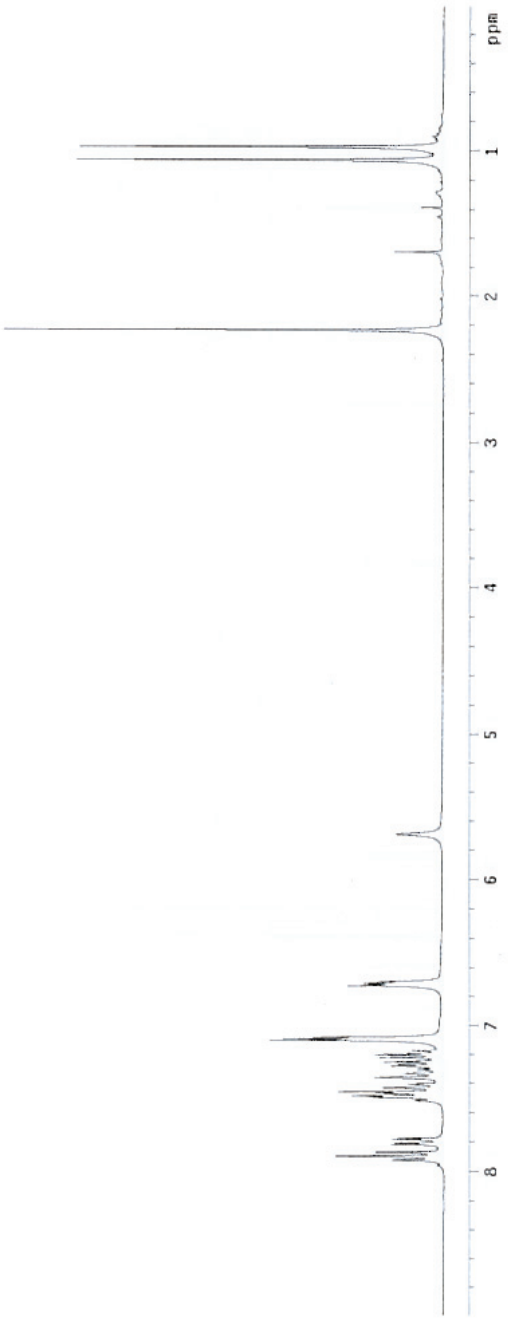
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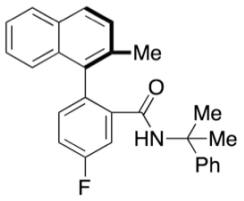
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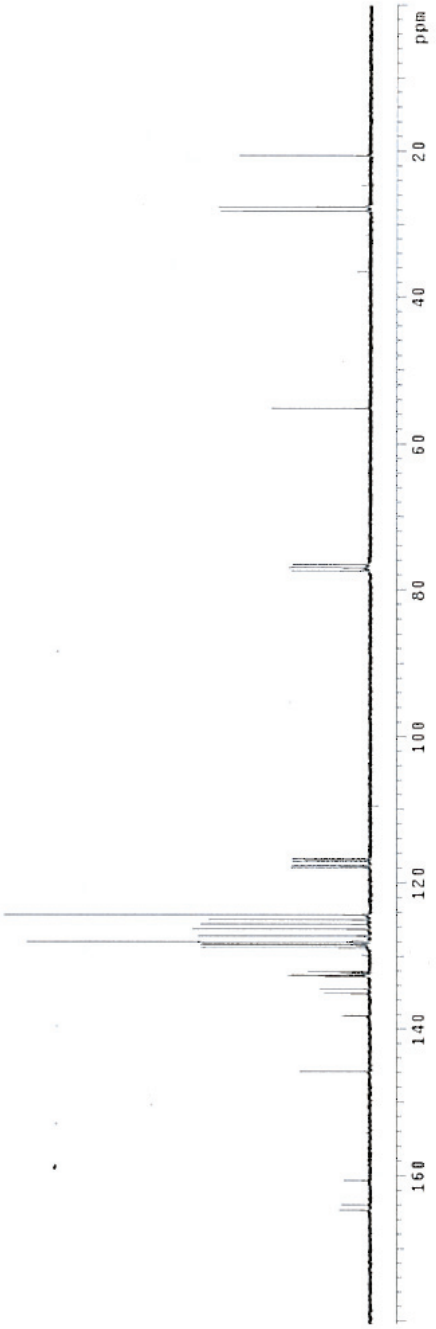
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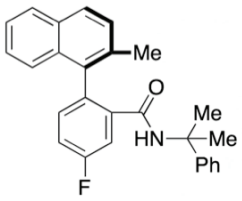
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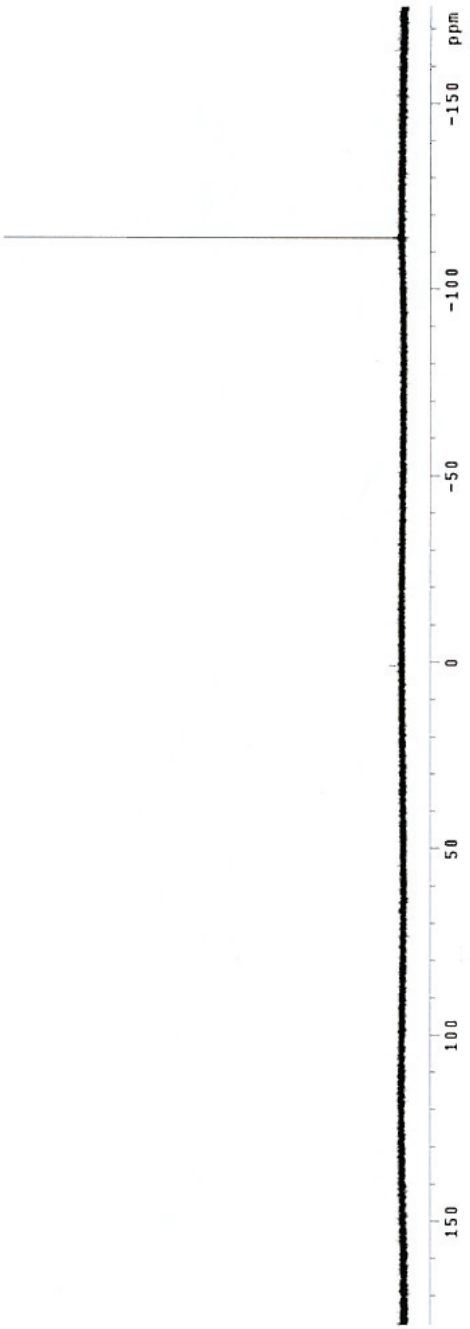
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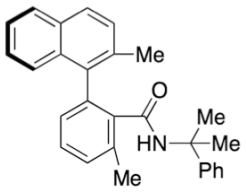
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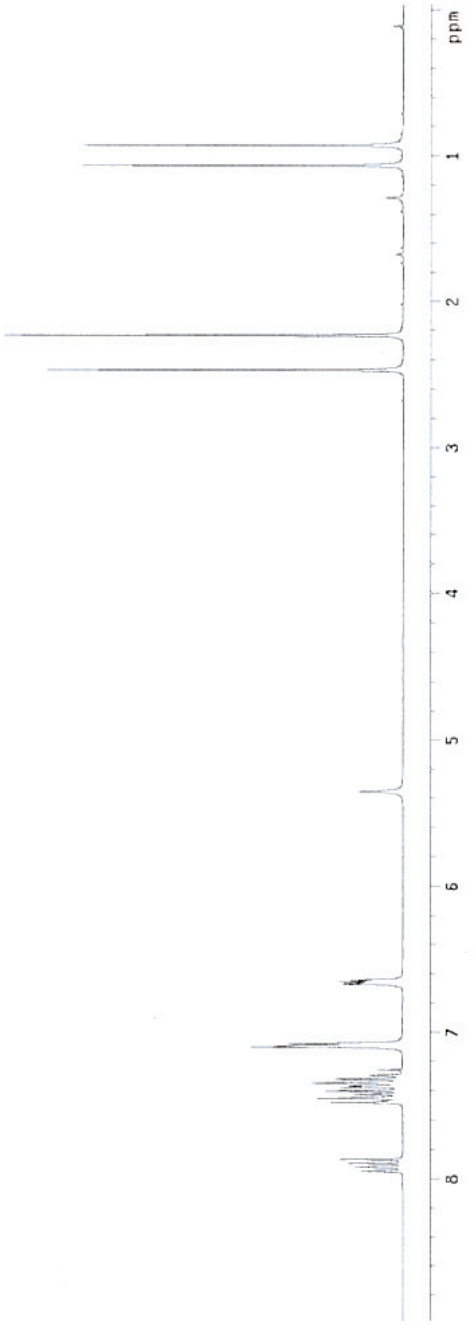
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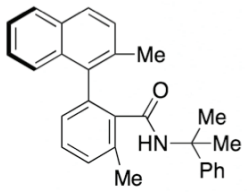
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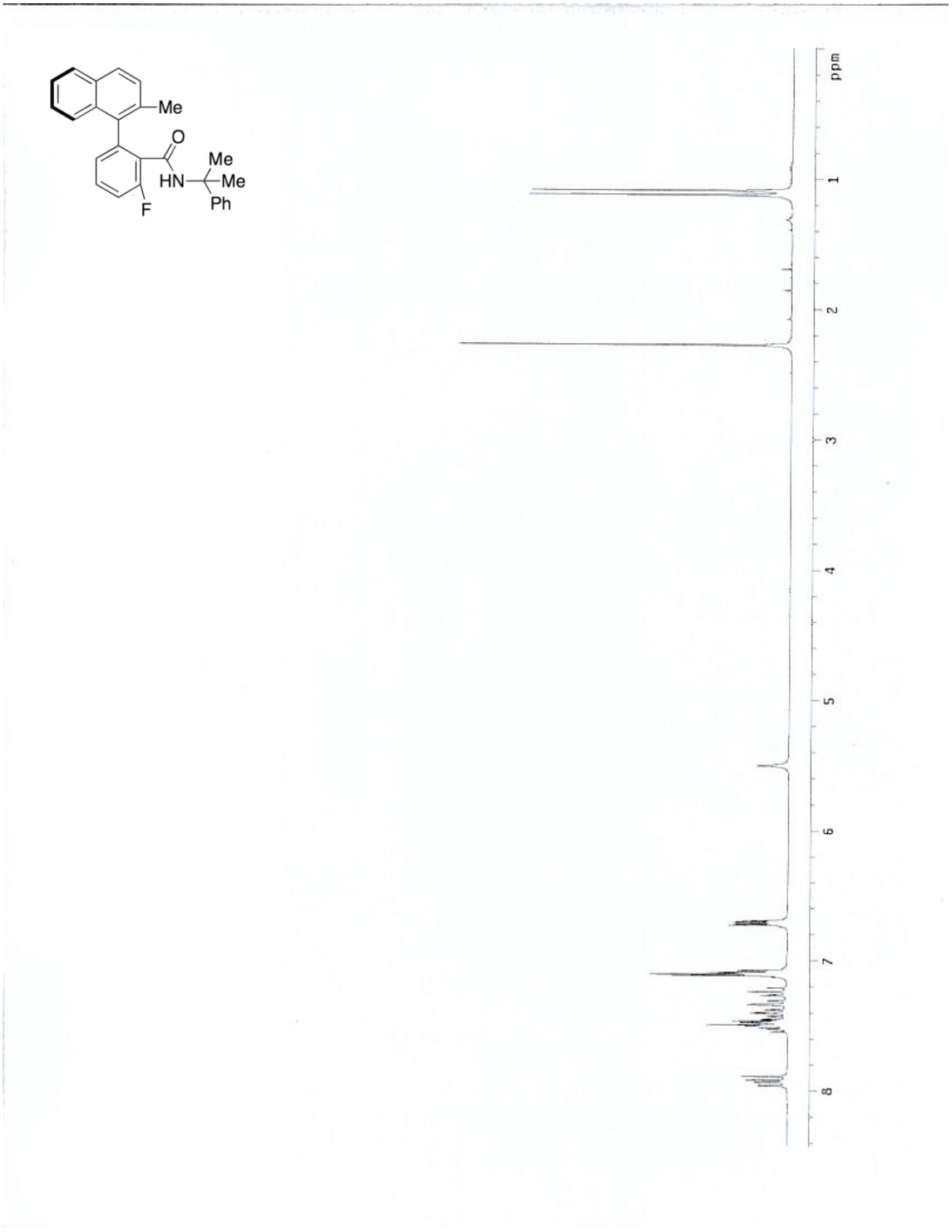
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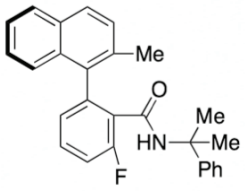
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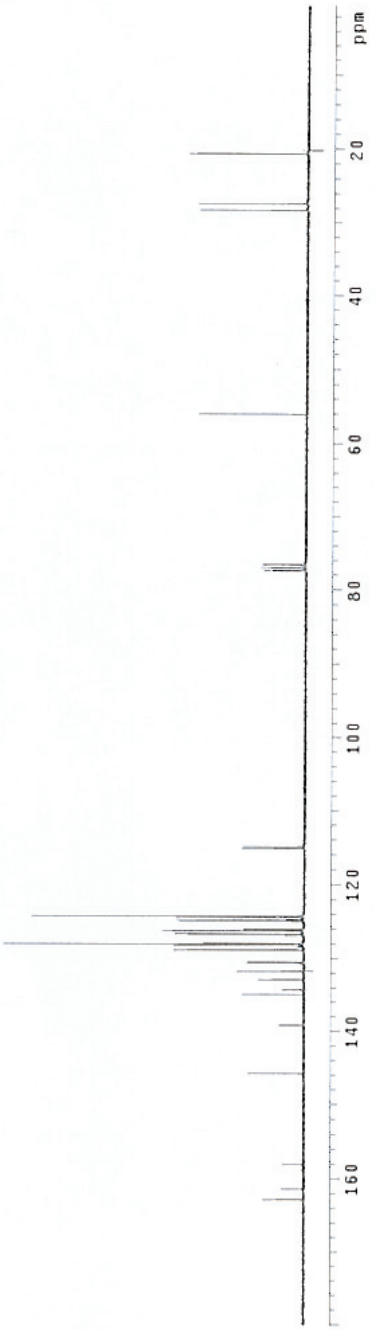
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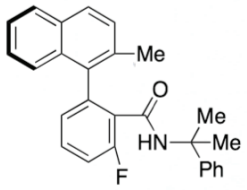
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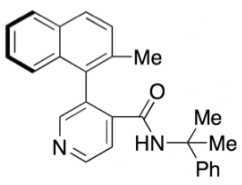
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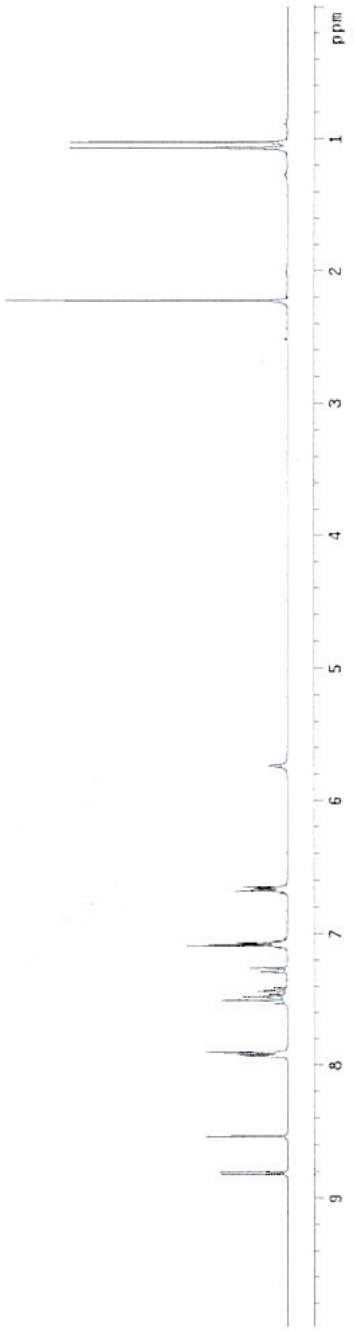
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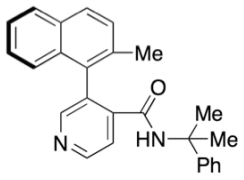
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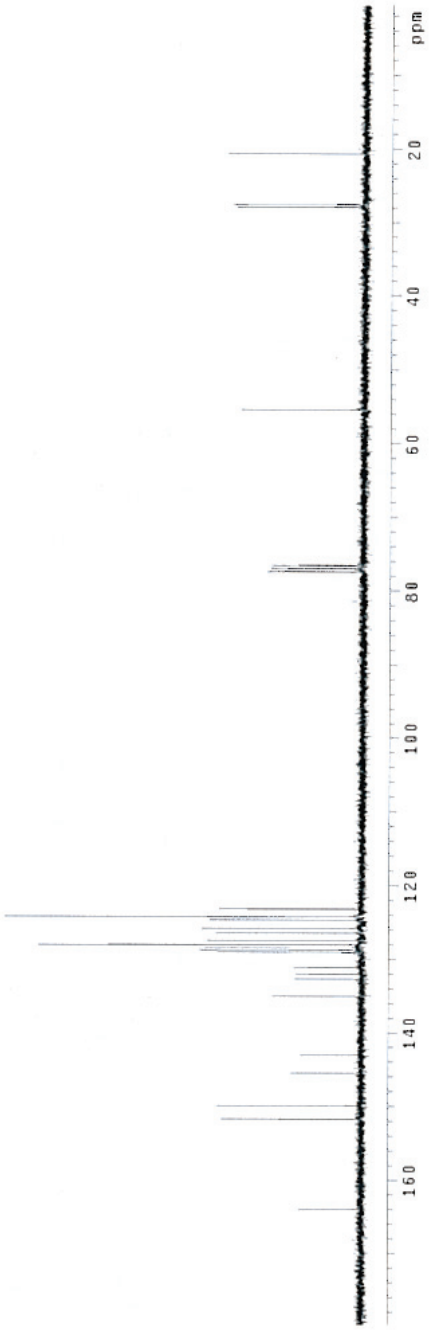
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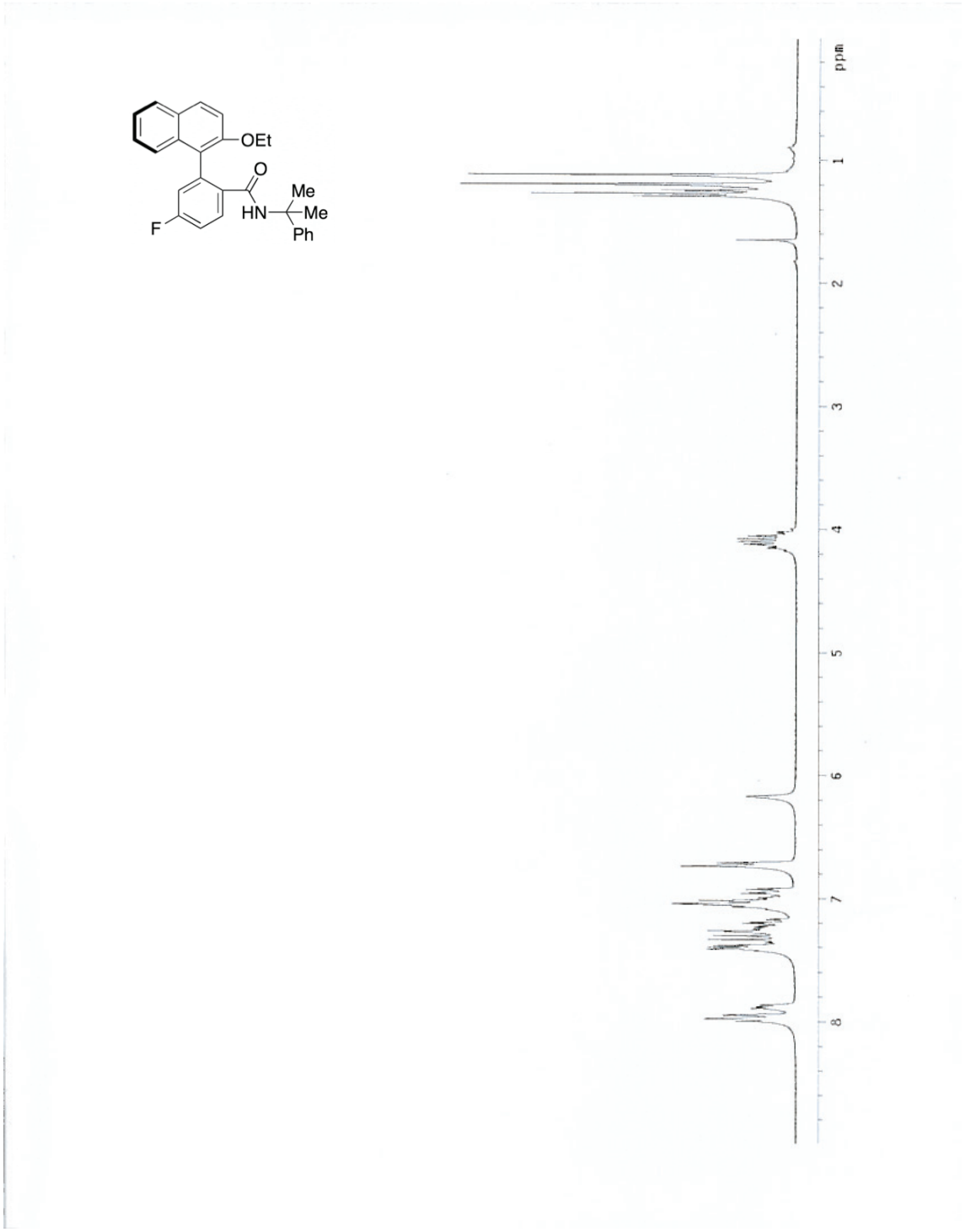
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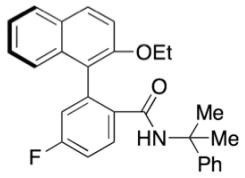
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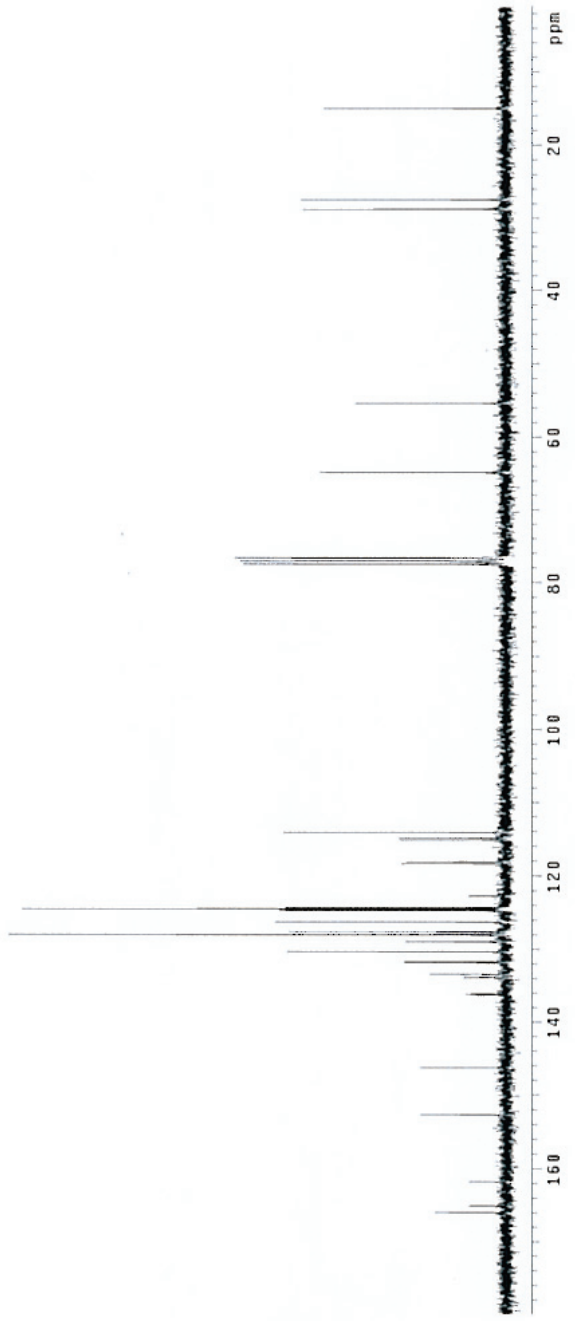
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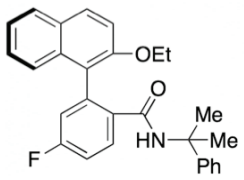
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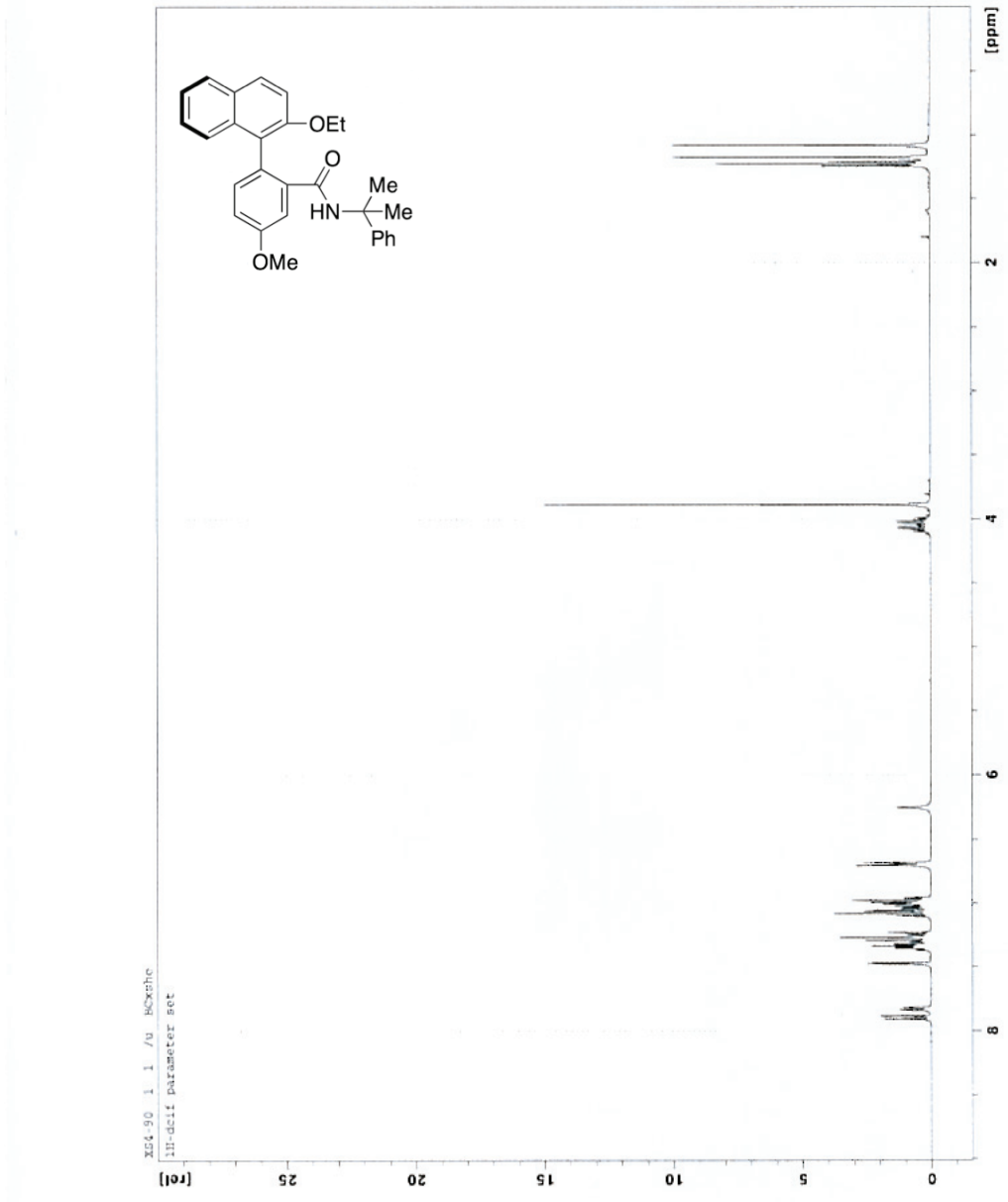
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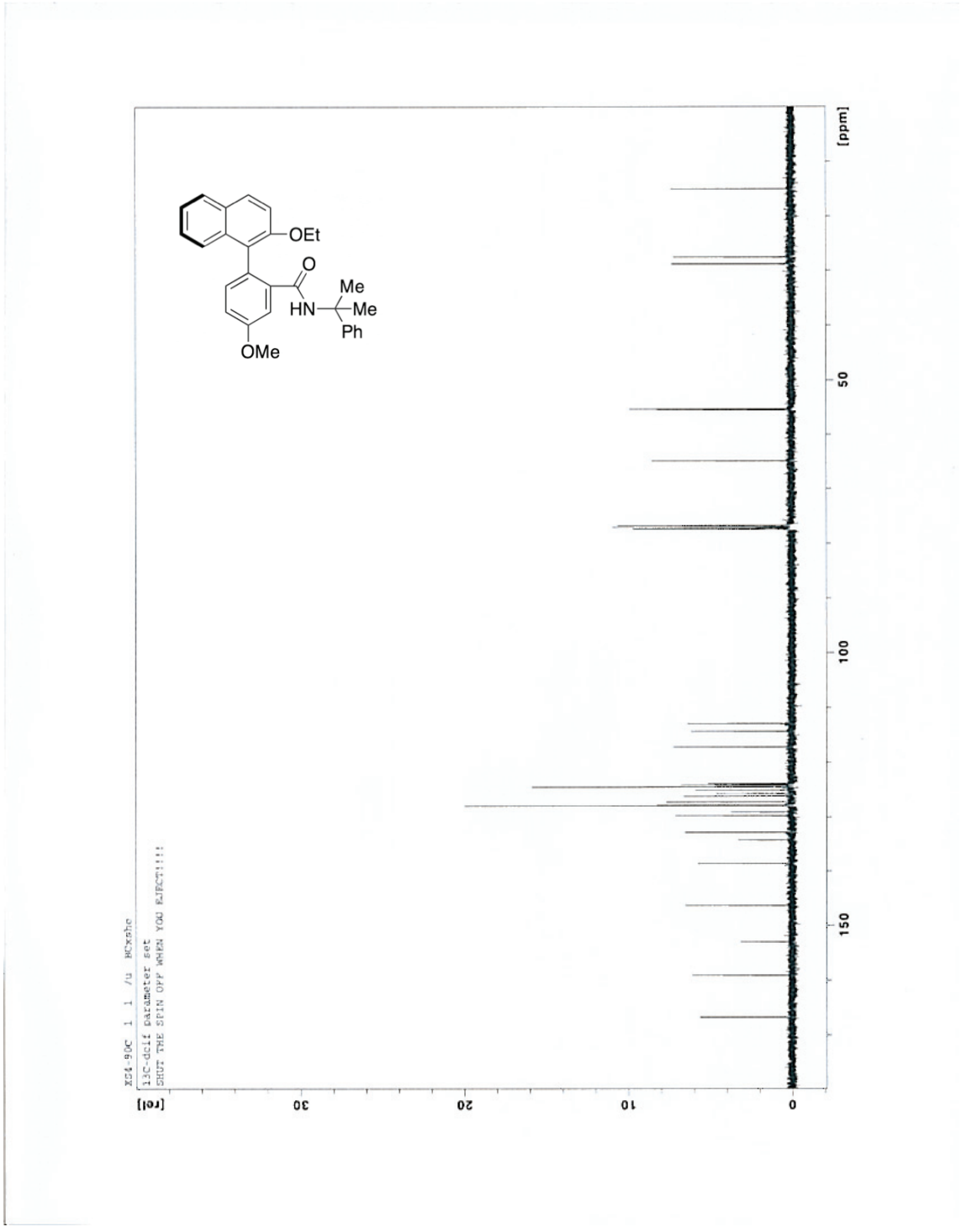
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Acq. Instrument : Instrument 1 Location : Vial 91
Injection Date : 7/10/2008 6:03:27 PM
Inj Volume : 0.5 µl
Acq. Method : C:\CHEM32\1\METHODS\AMTSTANDARD.M
Last changed : 7/10/2008 6:02:40 PM by XS
(modified after loading)
Analysis Method : C:\CHEM32\1\DATA\XS\XS2-191.D\DA.M (AMTSTANDARD.M)
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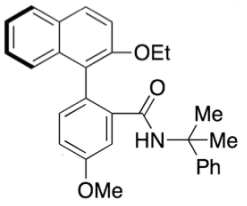
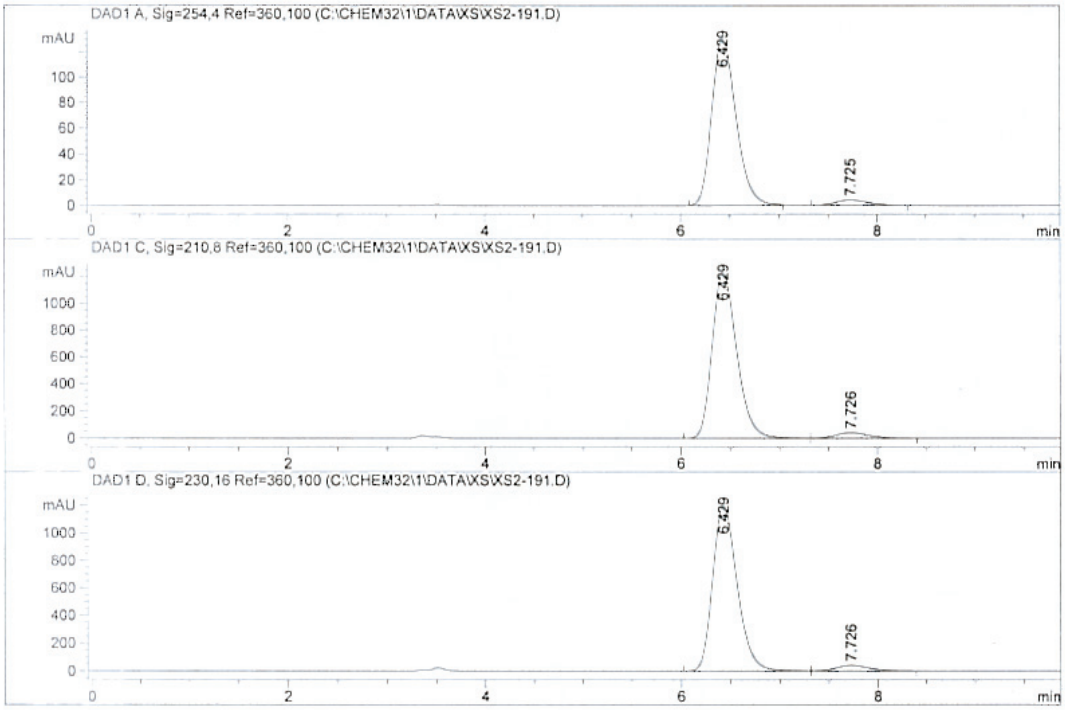
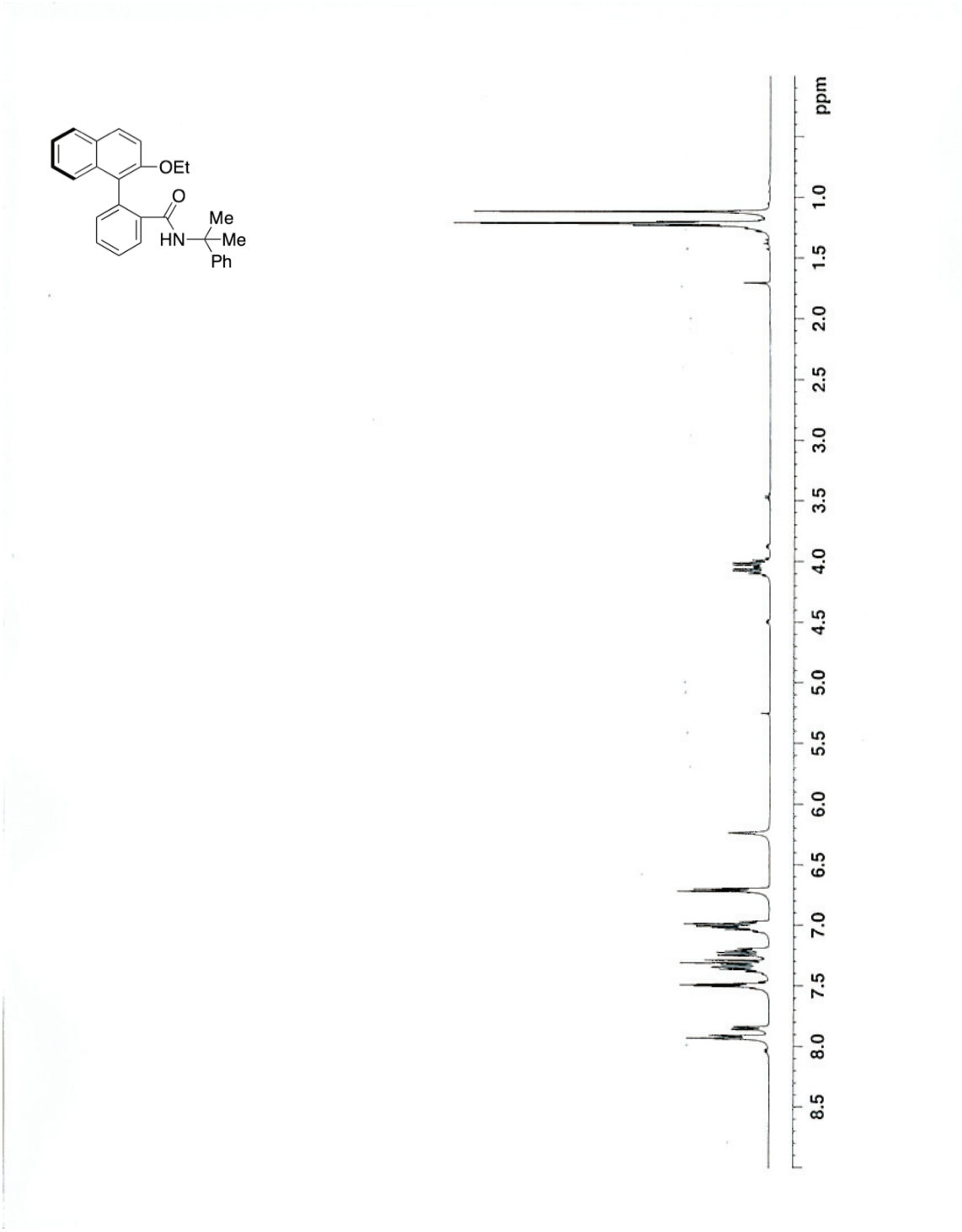
Method Info : 60% n-Hexane
40% i-propanol
0.5 ml/min

Sample Info : OD-H 10%IPA 1ML/MIN



91% ee

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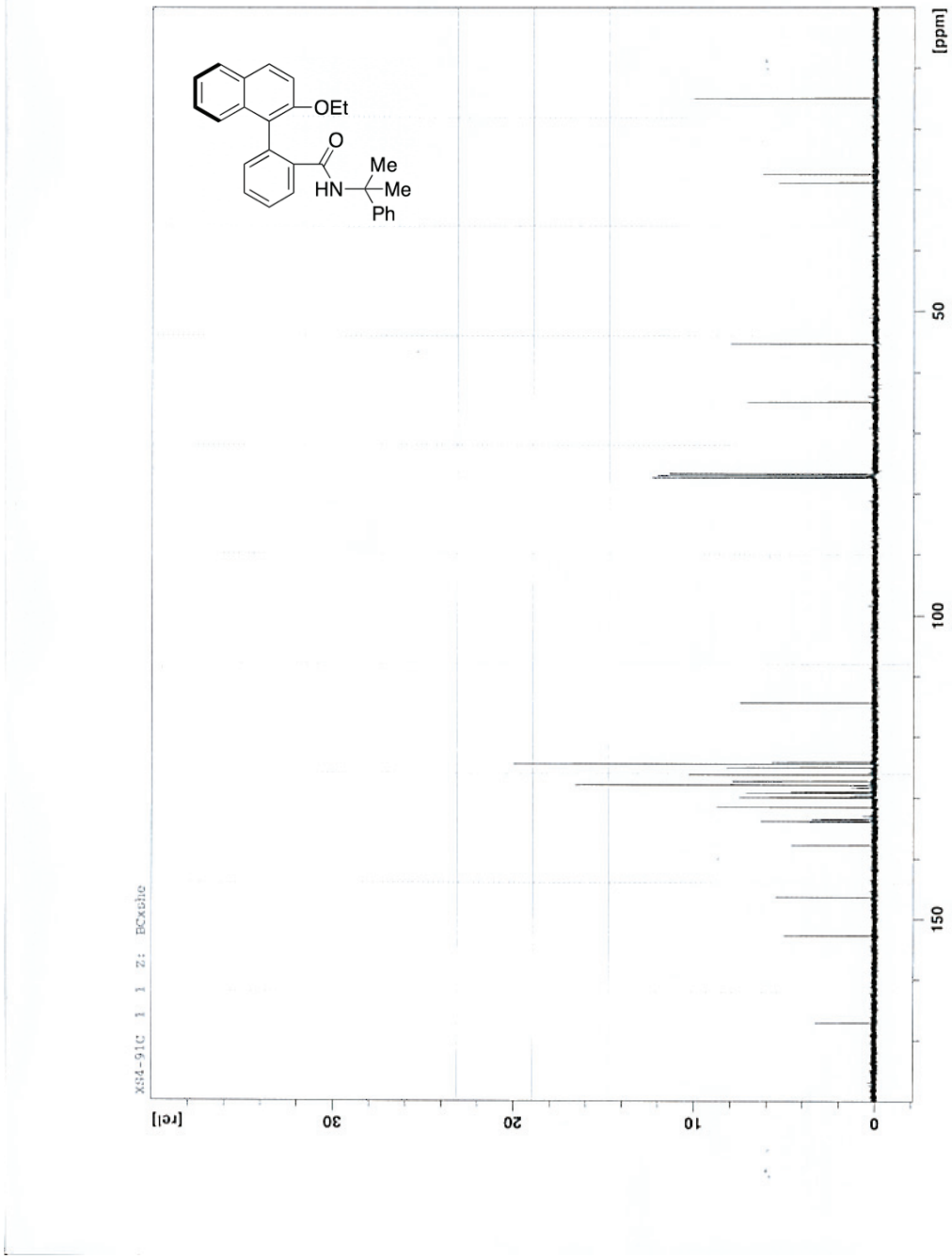
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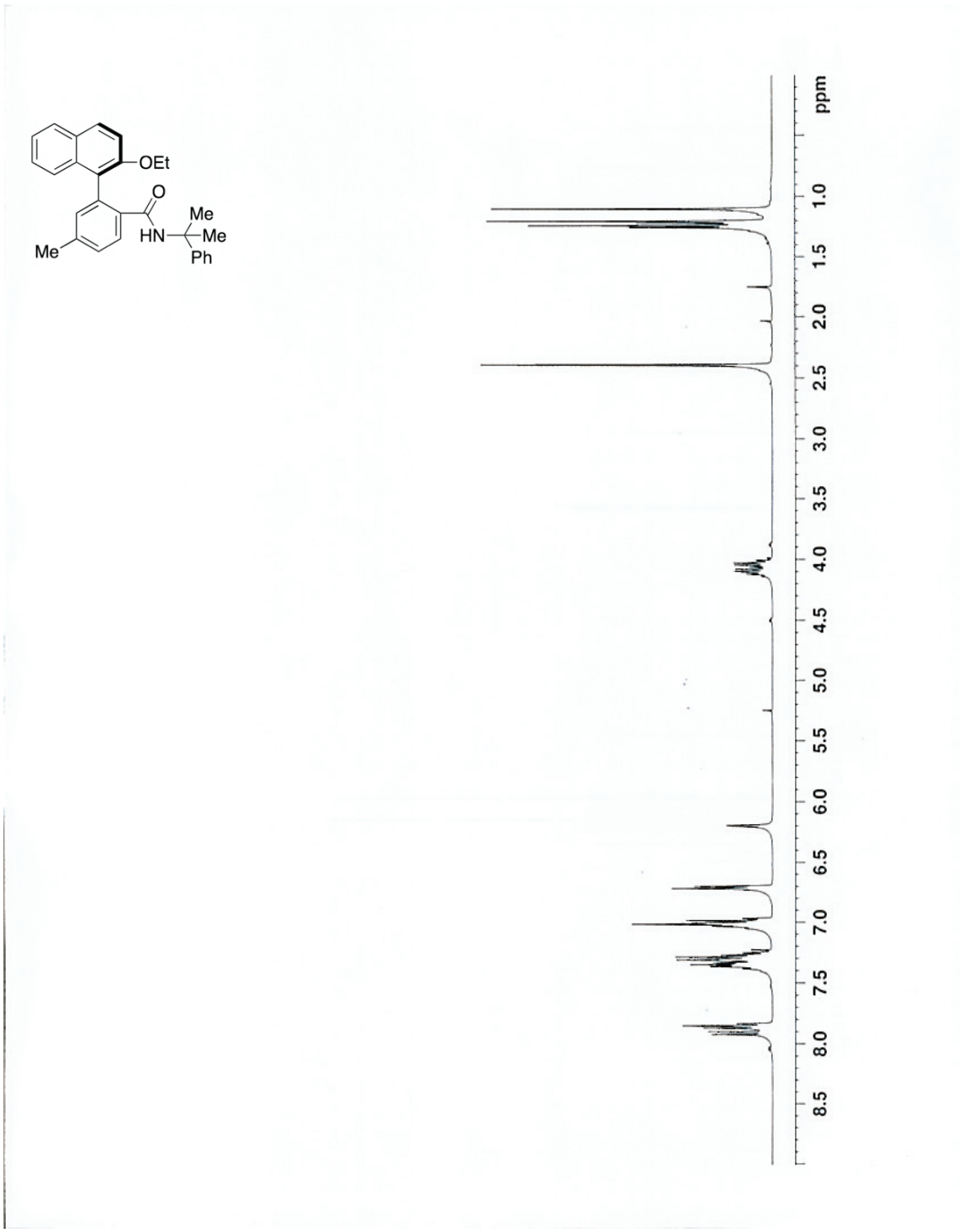
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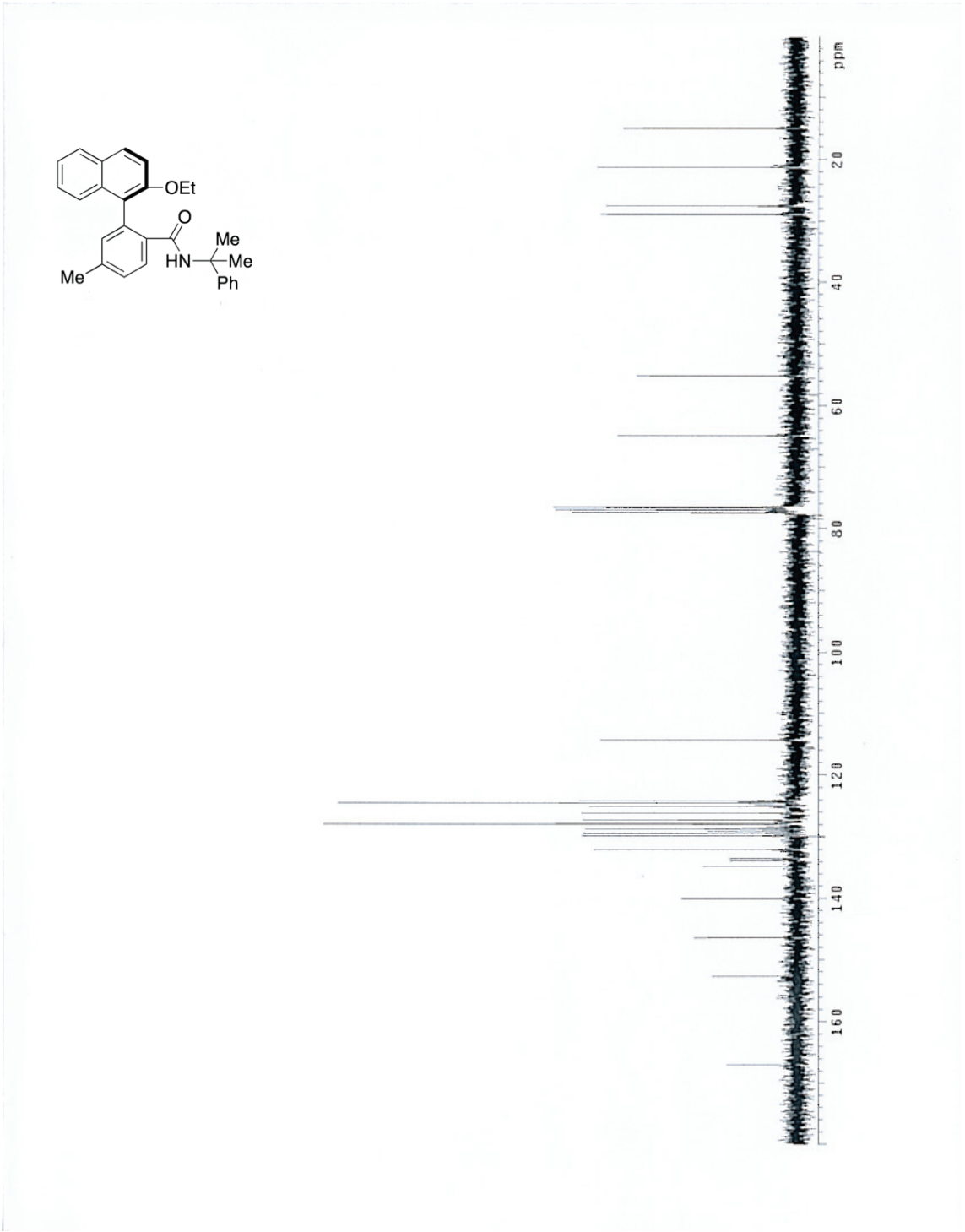
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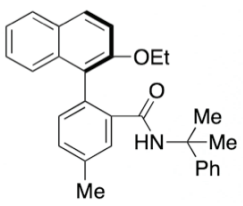
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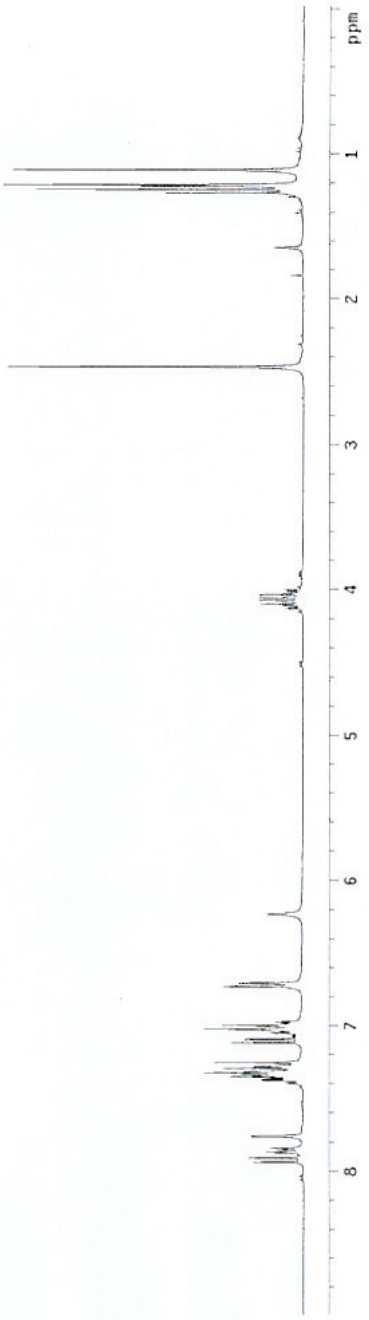
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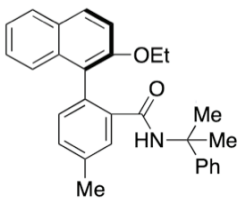
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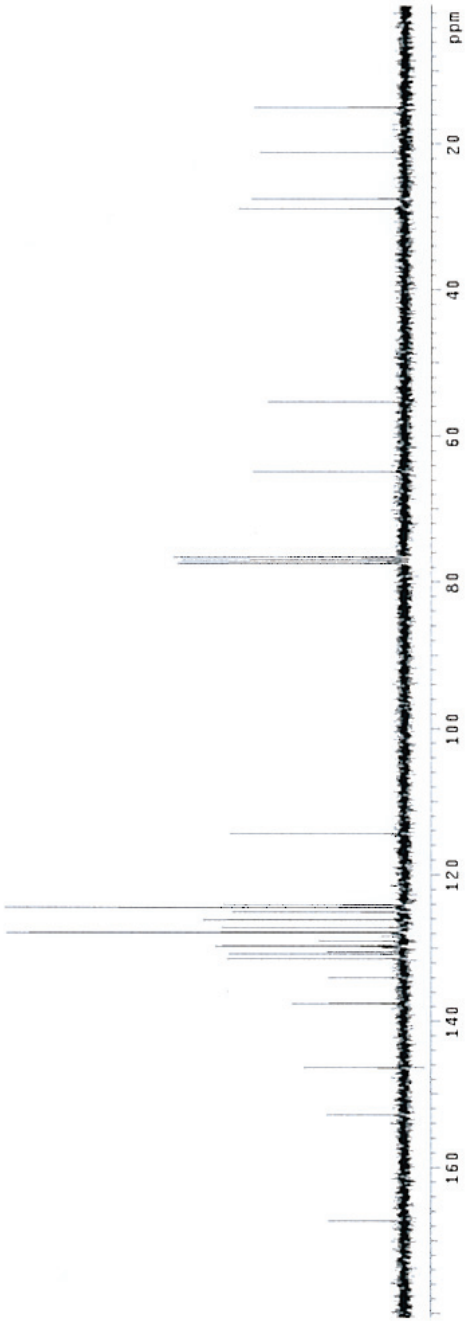
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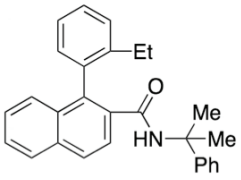
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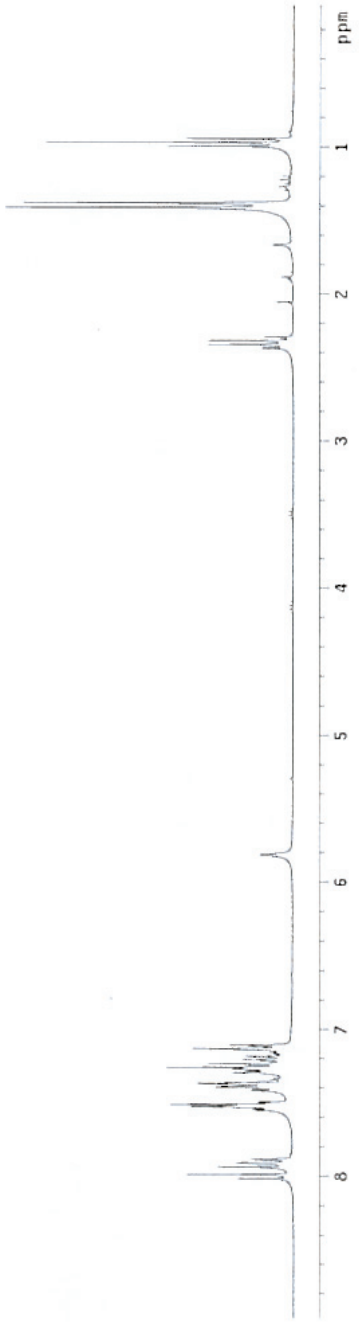
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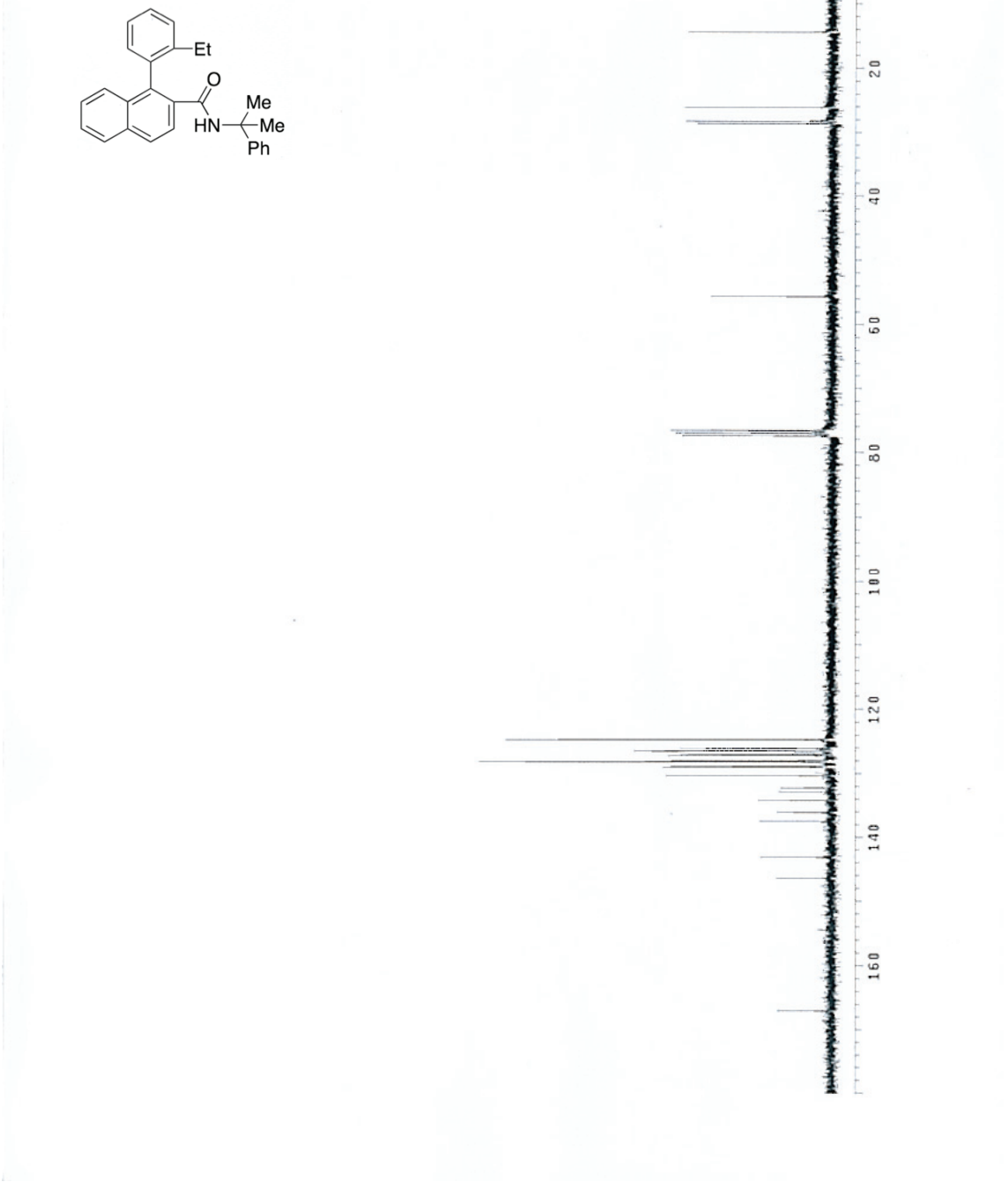
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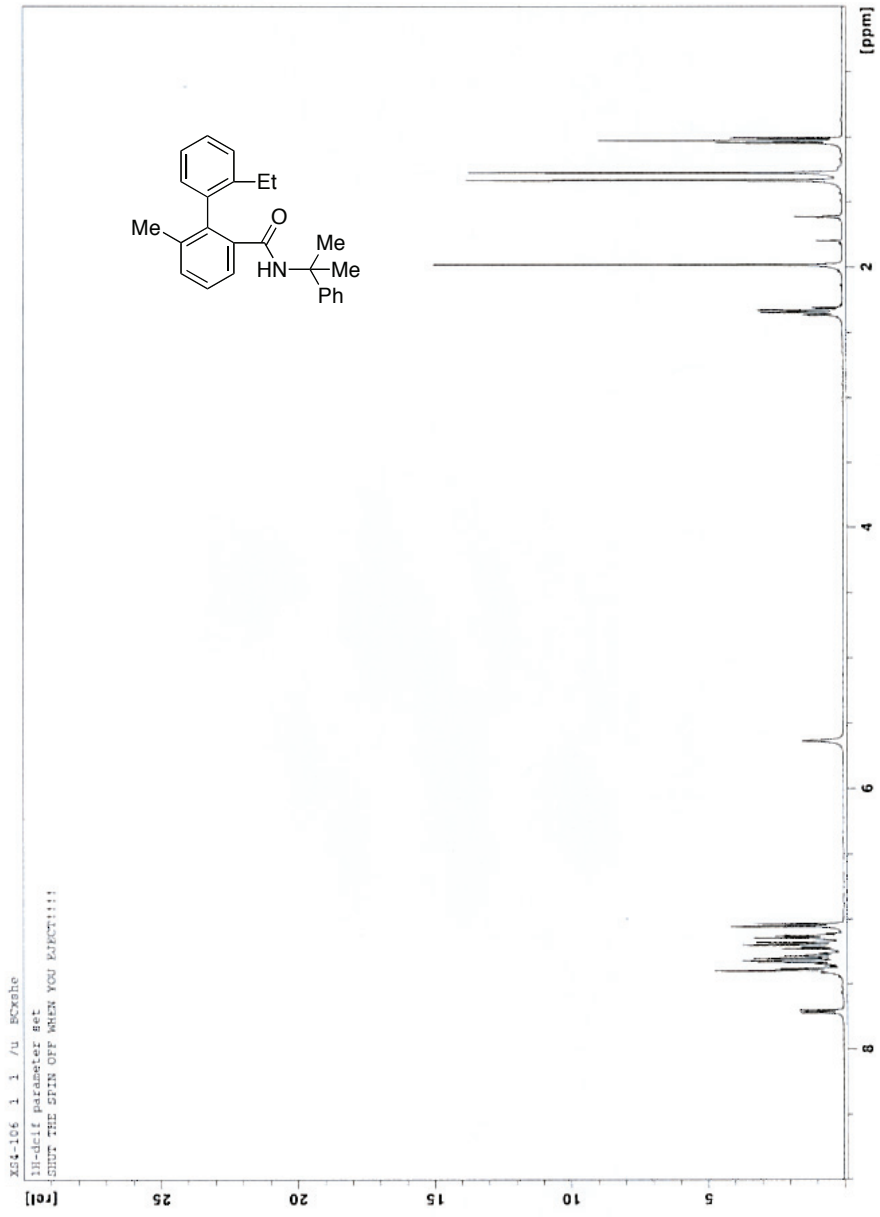
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XS4-106 1 1 /u SCxehe
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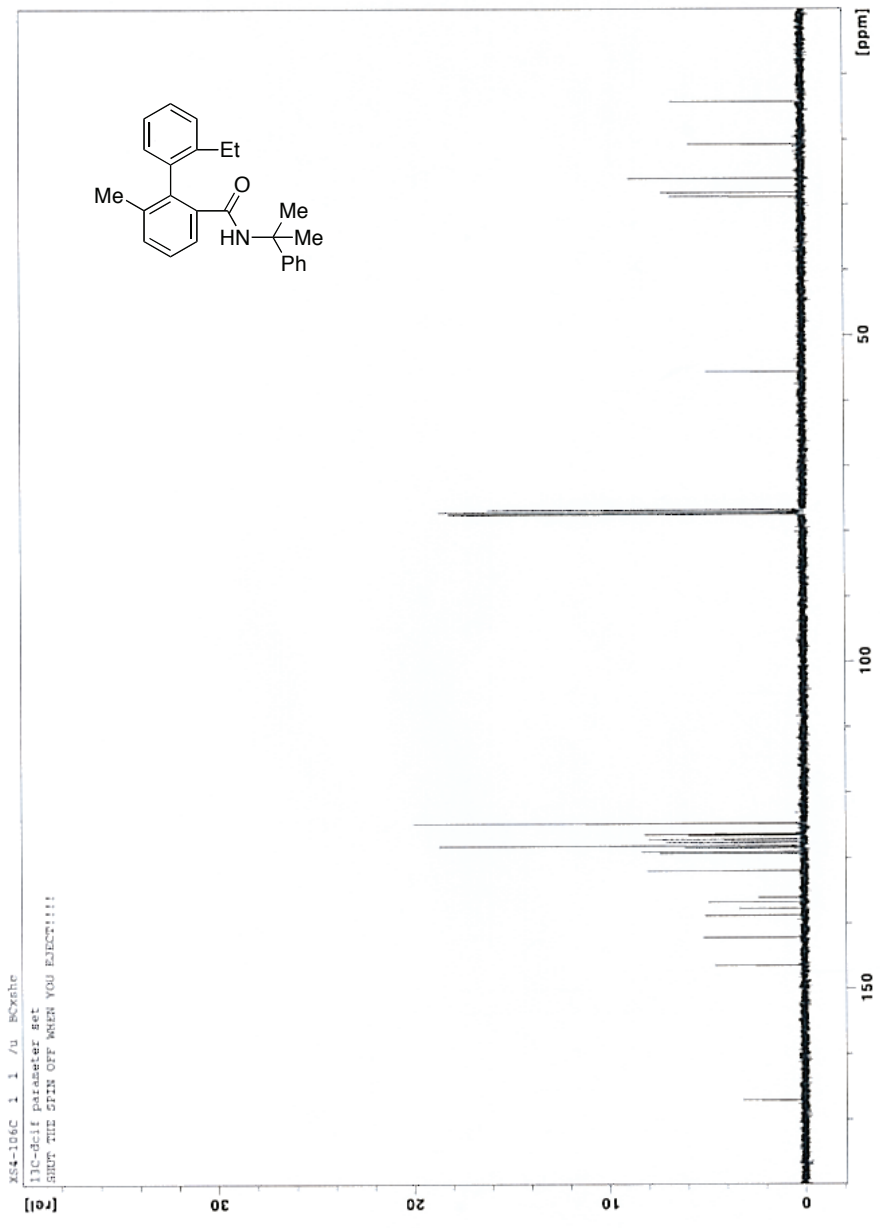
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XS4-106C 1 1 /u BCXehe
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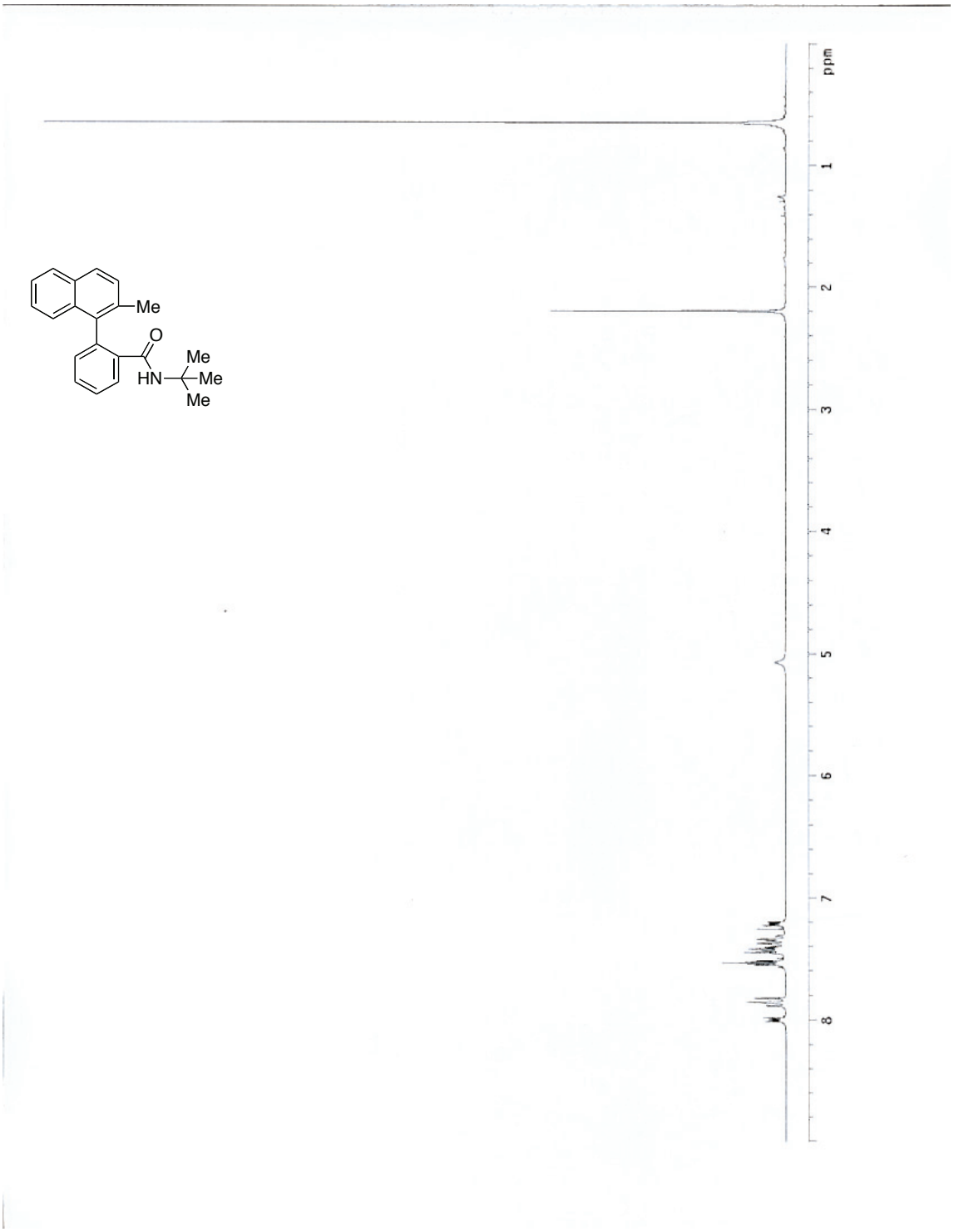
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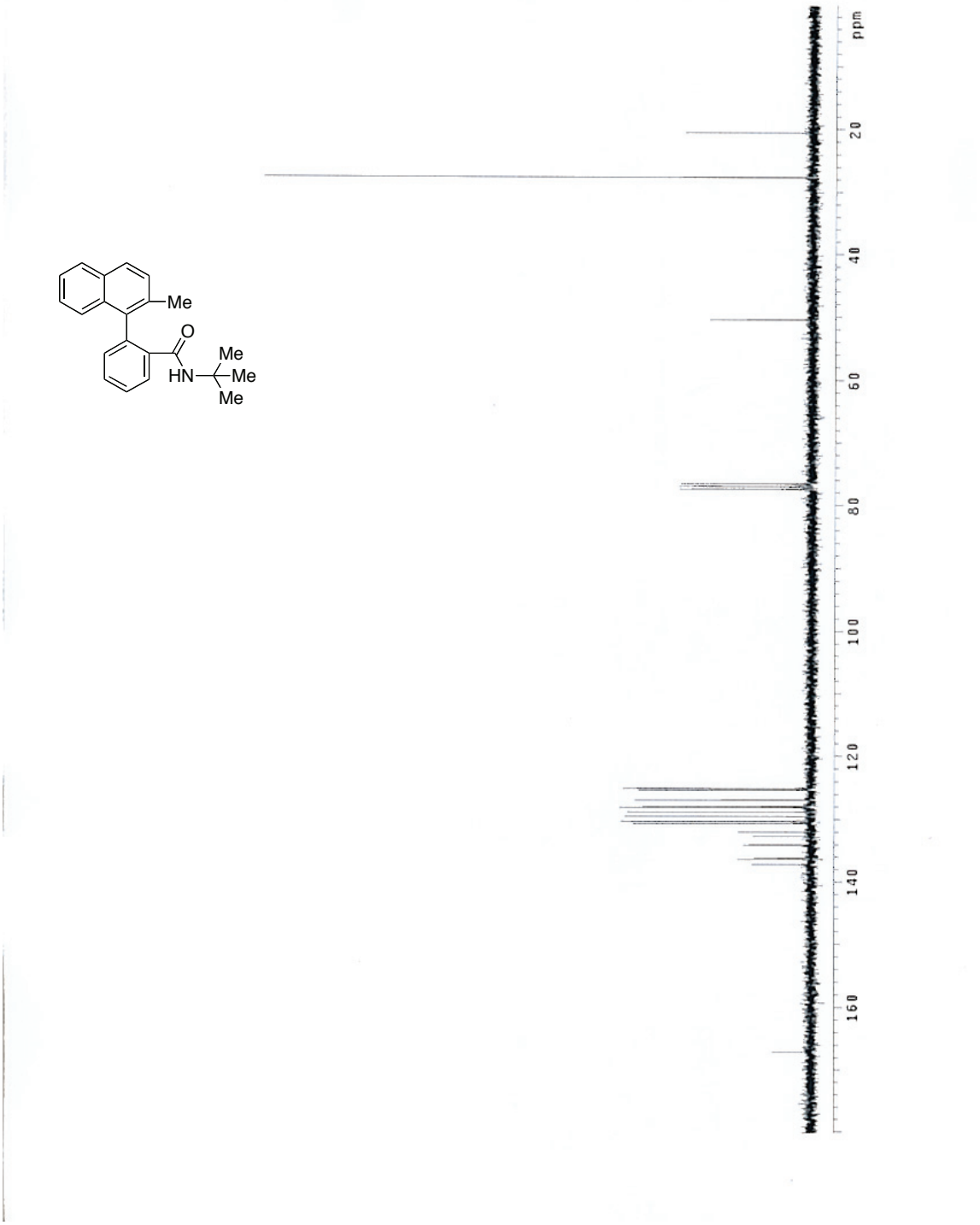
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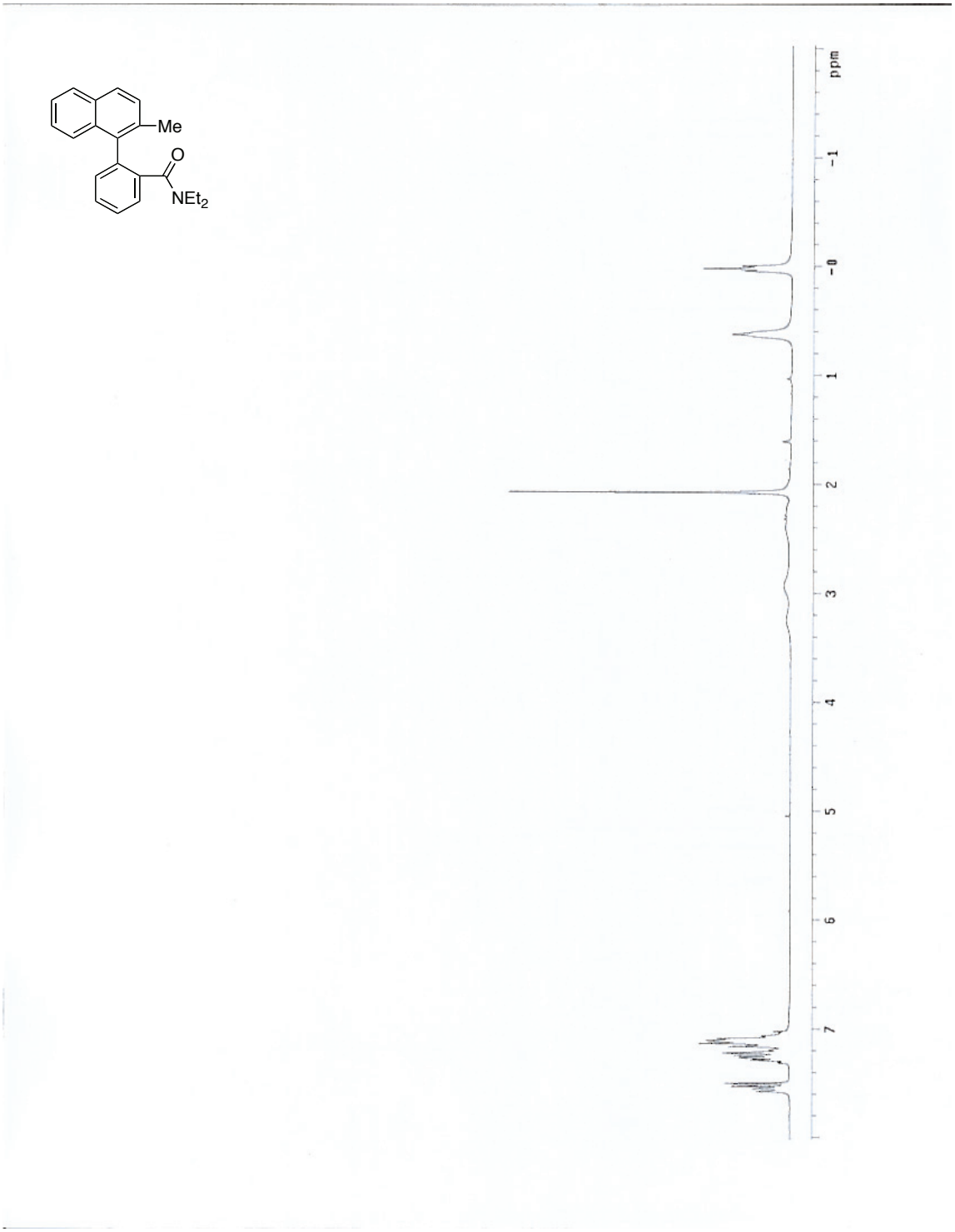
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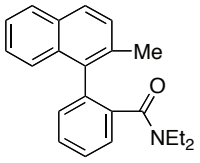
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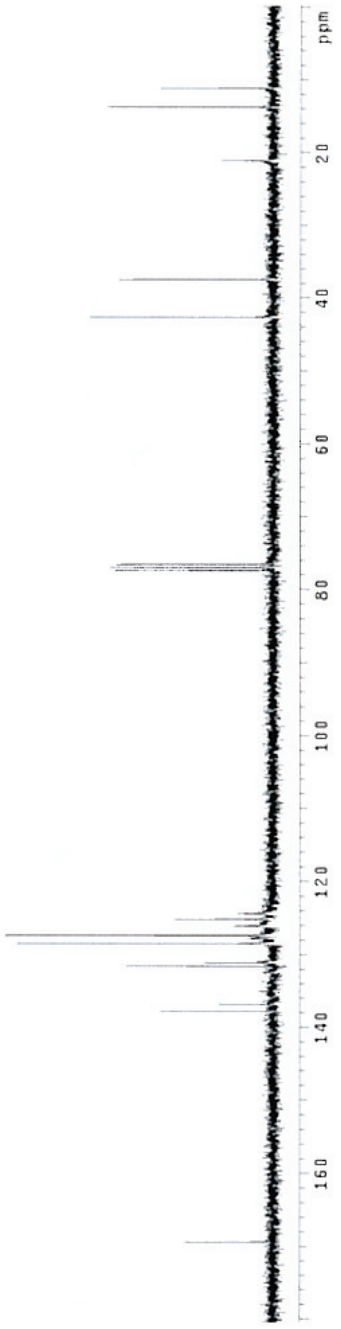
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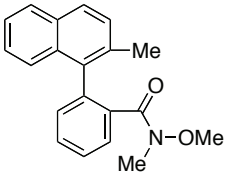
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Me

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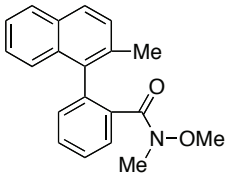
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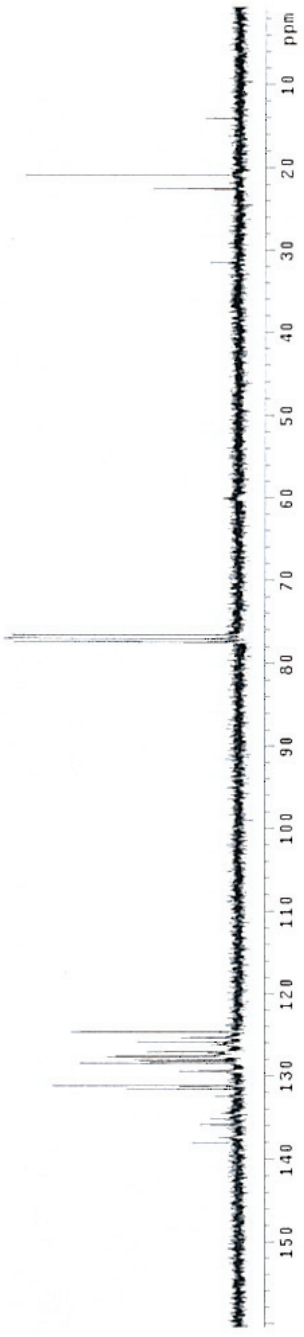
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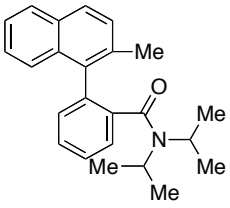
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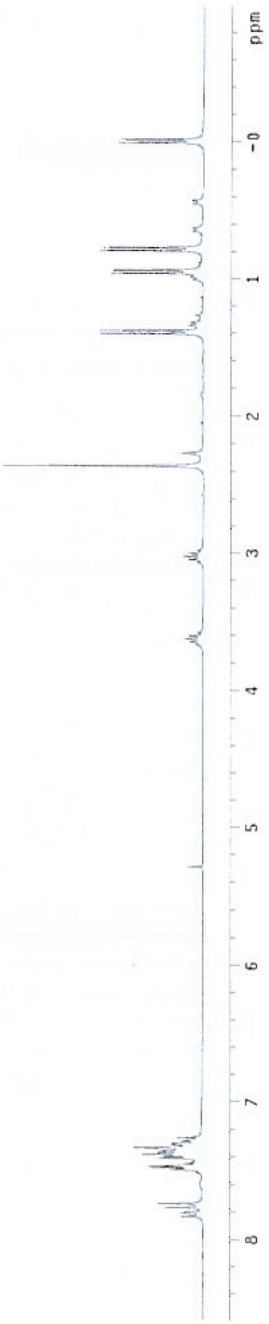
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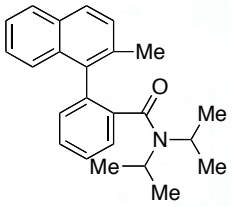
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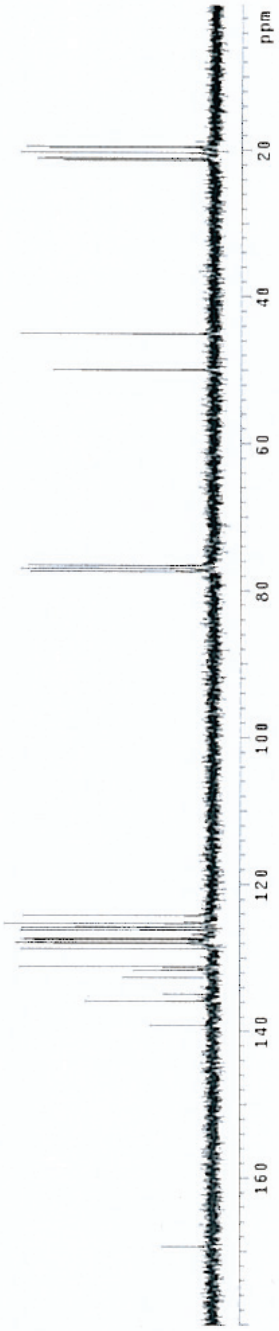
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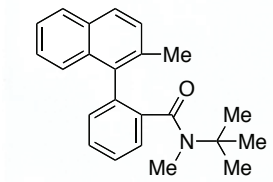
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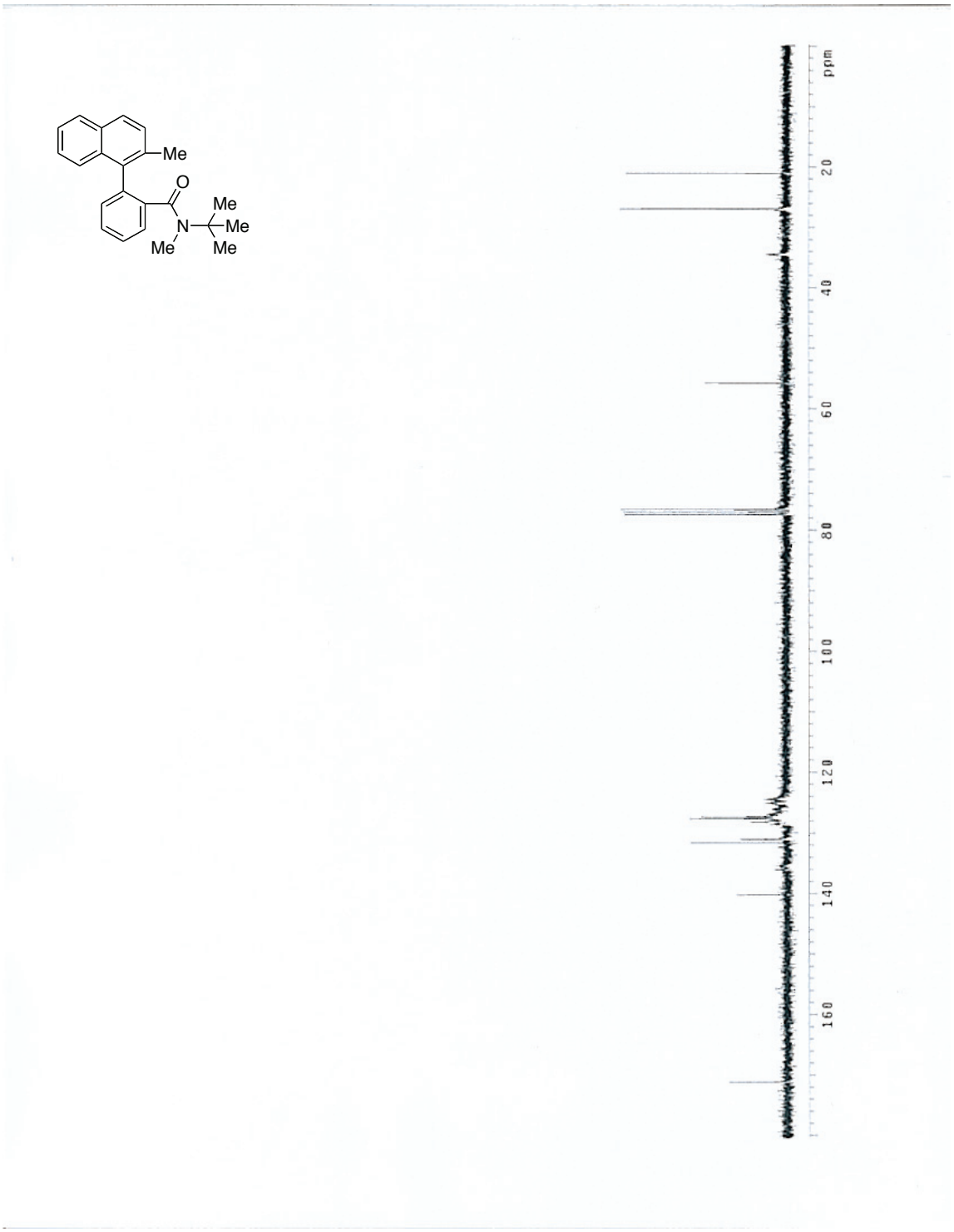
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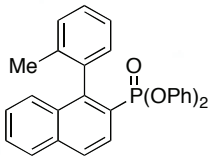
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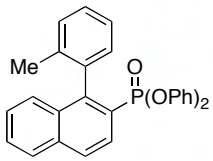
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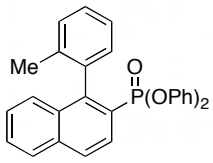
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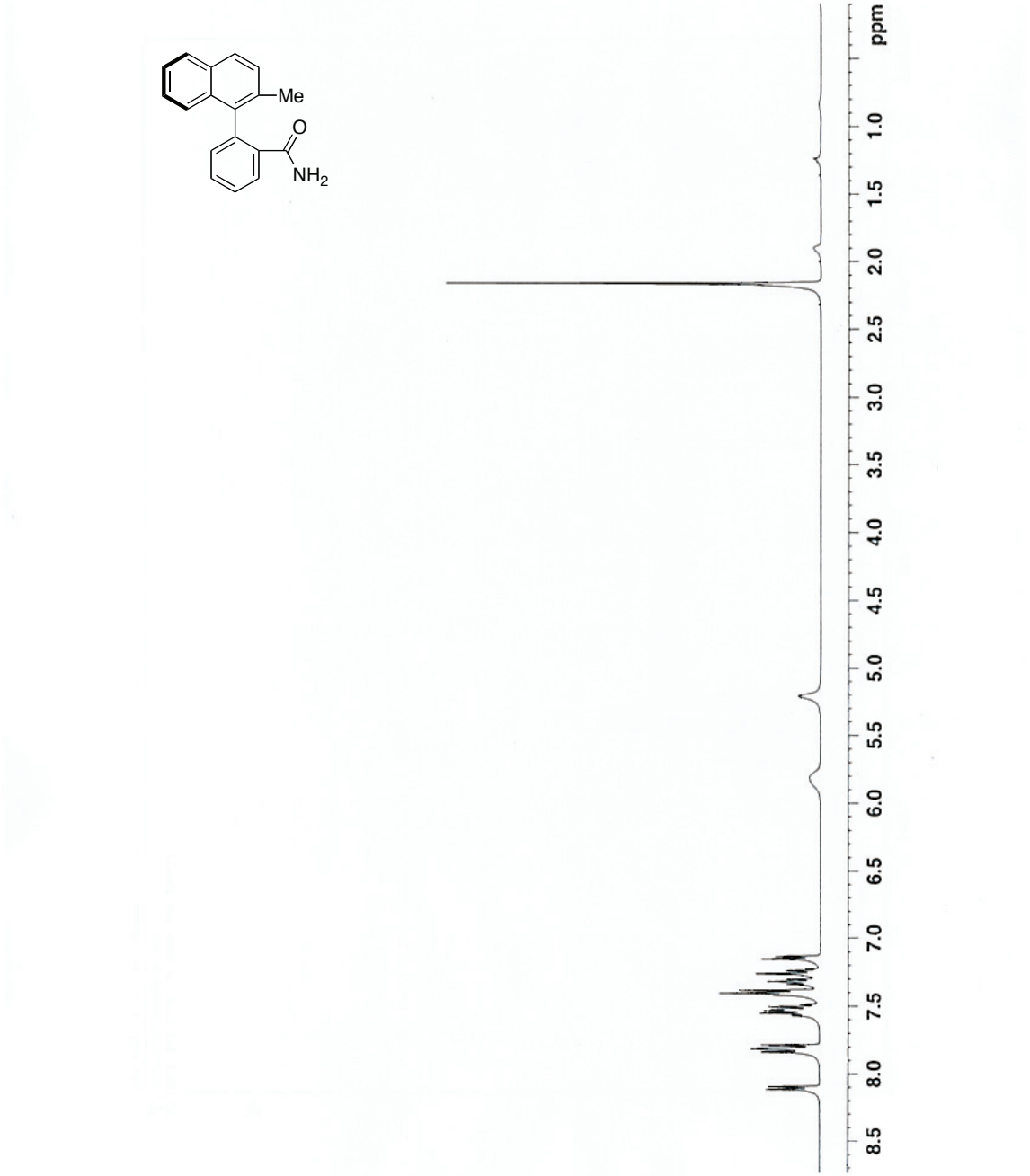
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NH2
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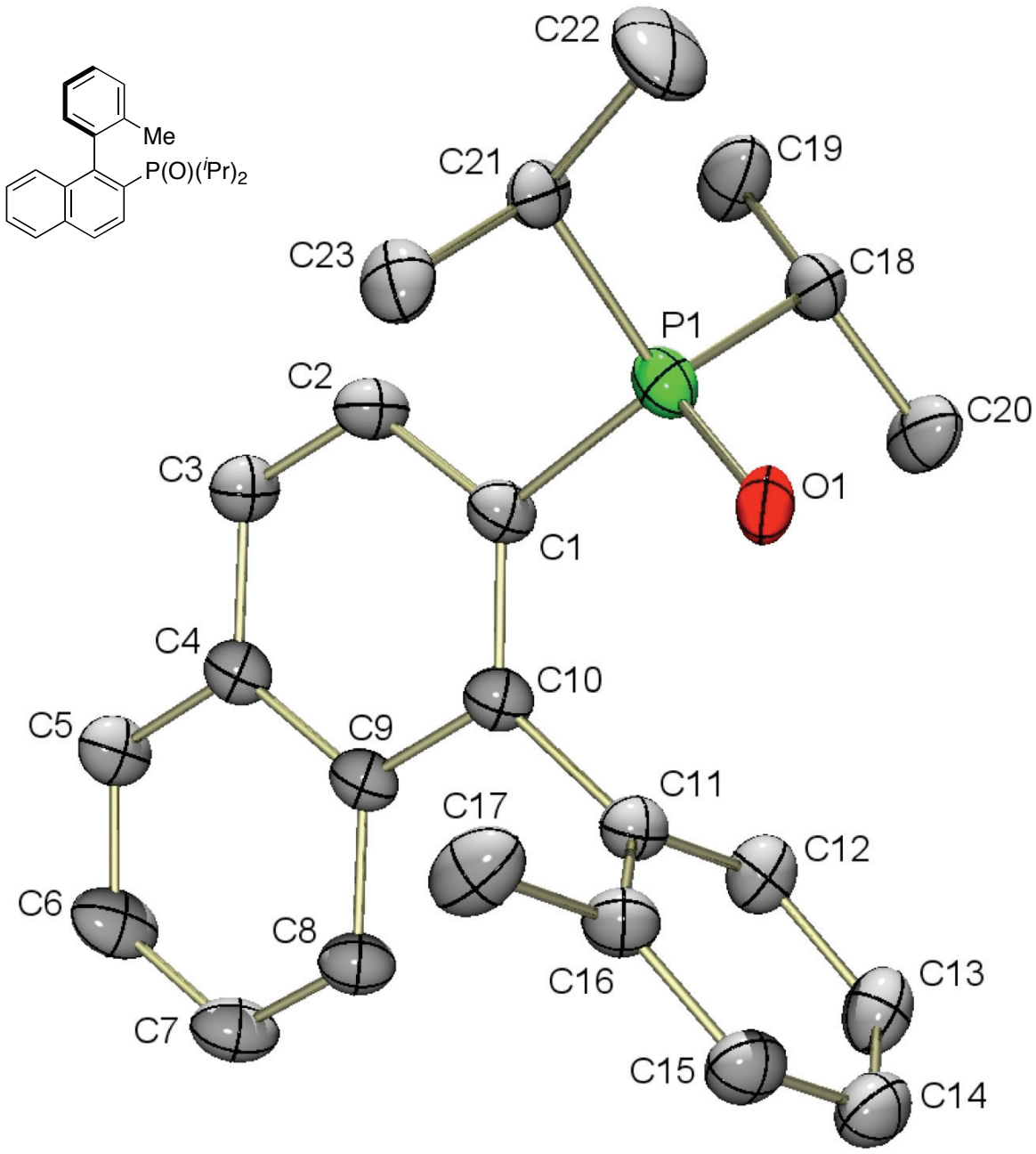
13C-dc1f parameter set
SHUT THE SPIN OFF WHEN YOU EJECT!!!!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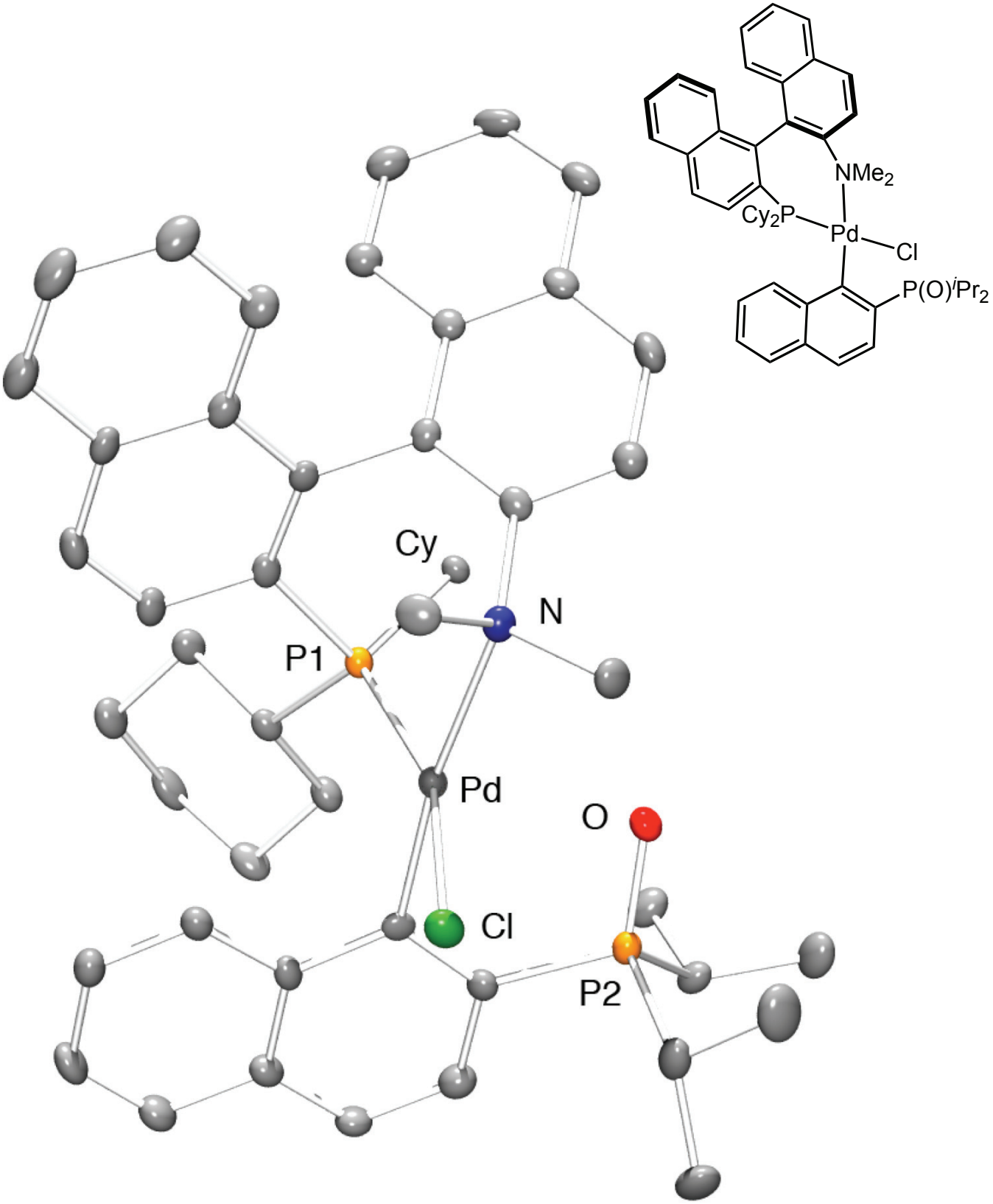
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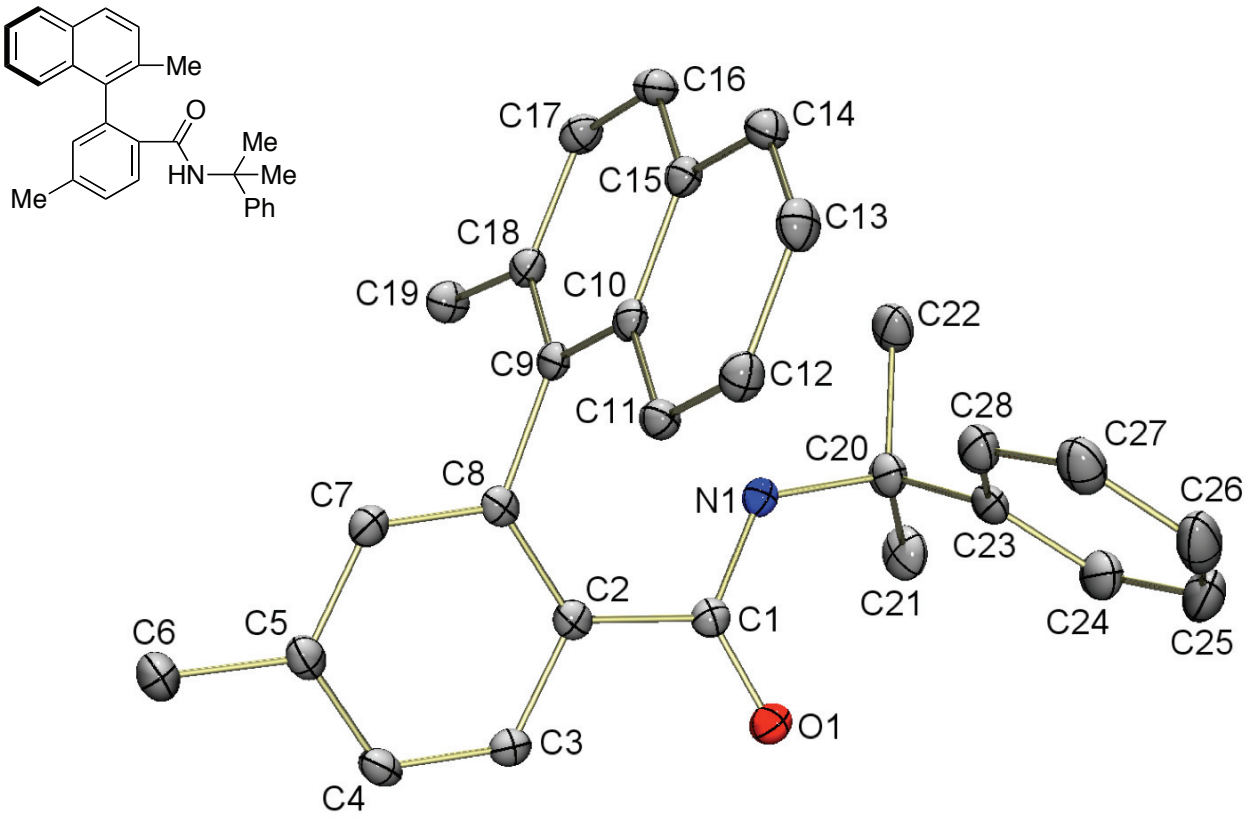
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C12
C11
C28
C27
C20
C8
C7
N1
C26
C23
C2
C21
C1
C24
C6
C5
C25
O1
C3
C4

Part IV. Interconversion of intermediates formed after transmetalation.

Computational studies have revealed four low-energy intermediates formed after transmetalation of the (KenPhos)Pd(naphthylphosphonate)(bromide) complex with tolyl boronic acid (Figure S1). The energies of these intermediates are within 3 kcal/mol of the lowest energy complex. Significantly, the palladium atom in these intermediates have square-planar geometries. Here, the oxygen atom belonging to the phosphonate substituent is bound to palladium and the bound tolyl ligand is trans to the phosphonate oxygen. These functional groups share a plane with the naphthylphosphonate ligand which is, in turn, trans to the phosphine atom belonging to the KenPhos ligand.

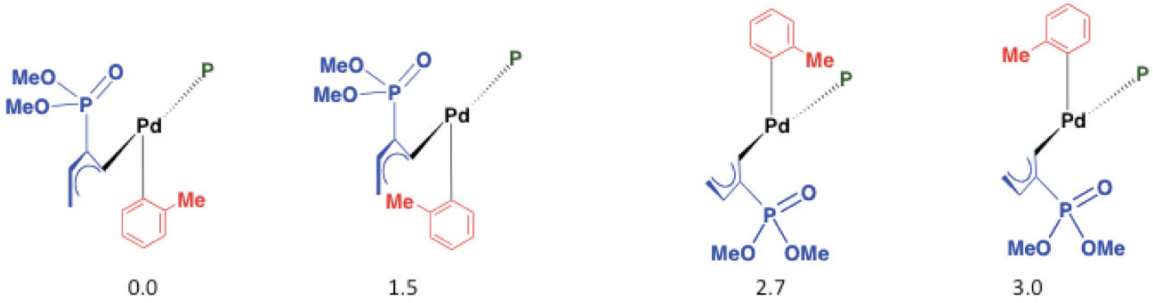

Figure S1. Square-planar complexes formed after transmetallation. The KenPhos ligand and some of the atoms belonging to the naphthylphosphonate ligand have been deleted for clarity. The energies below each structure are in kcal/mol.

Additional intermediates were also located that were at least 4 kcal/mol less stable than the lowest energy square-planar intermediate (Figure S2). Similar to the result that we found for the oxidative addition complex and the transition states, the geometry of these complexes are more accurately described as “T-shaped”.

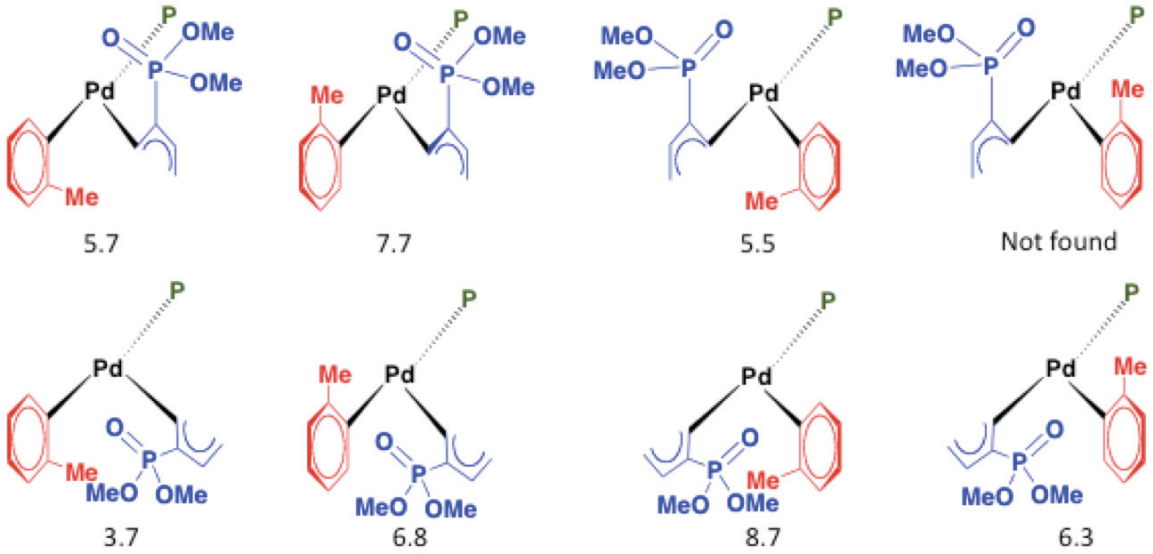

Figure S2. “T-shaped” complexes formed after transmetallation. The KenPhos ligand and some of the atoms belonging to the naphthylphosphonate ligand have been deleted for clarity. The energies below each structure are in kcal/mol.

Overall, these results suggest that transmetalation initially leads to the formation of the low-energy square-planar complexes. These square-planar complexes can be readily interconverted by rotation of the bound tolyl ligand around the Pd-C bond (Figure S3). In addition to this rotational motion, the tolyl group can also “oscillate” in either direction to form the “T-shaped” complexes which are the reactive intermediates that lead to the transition states discussed in the main article.

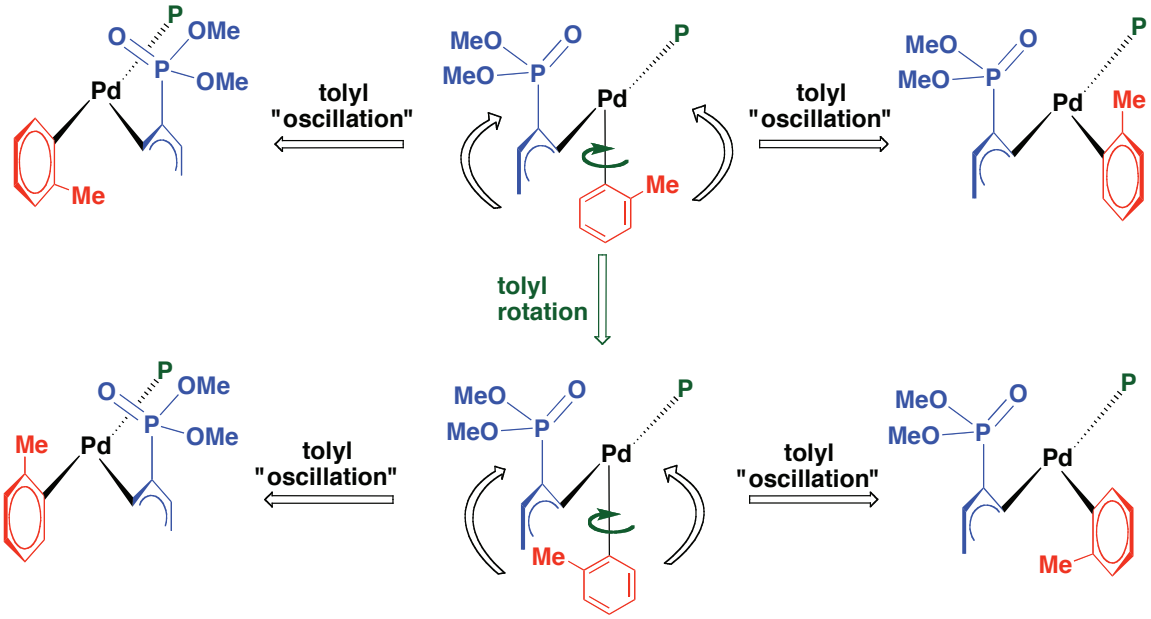

Figure S3. Interconversion of square-planar complexes to “T-shaped” reactive intermediates by rotation and “oscillation” of the bound tolyl addend. The KenPhos ligand and some of the atoms belonging to the naphthylphosphonate ligand have been deleted for clarity. The energies below each structure are in kcal/mol.

In an effort to obtain a barrier for rotation of the tolyl group, we have computed the free energy surface for the rotation of the tolyl addend around the Pd-C(tolyl) single bond for one of the low energy square-planar complexes by performing a relaxed potential scan of the dihedral angle defined by the C1-C2-Pd3-P4 as shown below in Figure S4. The free energy barrier was calculated to be 11.5 kcal/mol. In comparison, the activation free energy for reductive elimination of the coupled tolylnaphthylphosphonate product starting from this intermediate is 22.9 kcal/mol. Taken together, these results suggest that, as expected, rotation around the Pd-C single bond in these complexes is fast compared to reductive elimination.

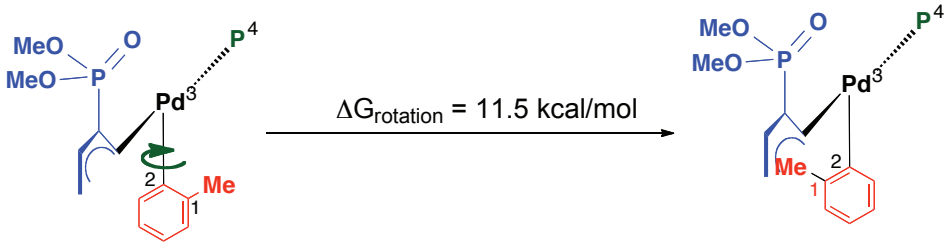

Figure S4. Interconversion of square-planar complexes by rotation of the tolyl addend around the Pd-C single bond. The free energy barrier for interconversion is given in kcal/mol.

Part V. Cartesian coordinates and energies for stationary points.

TS1

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C	5.601107	-1.788075	0.355350
C	5.249825	-0.572589	0.881064
C	4.065479	0.097824	0.469811
C	3.229196	-0.414555	-0.538808
C	2.663026	1.004100	-1.883008
C	2.305274	2.293901	-1.418462
C	2.413318	3.431266	-2.220554
C	2.945248	3.318134	-3.500828
C	3.348514	2.064326	-3.954273
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Sum of electronic and thermal Free Energies= -2474.357446

TS2

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H	-3.790298	4.859102	2.834948
H	-5.121096	2.077793	-1.059829
C	-5.198894	4.586053	1.240752
H	-5.788043	5.462972	1.495085
C	-5.559882	3.788900	0.129898
H	-6.424666	4.060448	-0.469604
H	6.021478	-0.088981	2.621405
C	3.832475	-2.557387	-0.588494
P	2.497248	2.540437	0.552091
C	4.599103	-3.672054	-0.317089
H	4.417548	-4.595970	-0.859897
H	3.049747	-2.627175	-1.324647
H	4.582521	1.880159	2.248131
C	5.615022	-3.617673	0.661147
H	6.222407	-4.494912	0.867930
C	5.823187	-2.447417	1.354861
H	6.593131	-2.389999	2.120945
O	1.386509	2.809259	-0.464939
O	2.017824	2.671103	2.164289
O	3.707115	3.724576	0.471335
C	1.468536	3.929692	2.580999
H	2.230320	4.716158	2.537934
H	0.606864	4.205188	1.964434
H	1.149596	3.794011	3.617009
C	3.478989	4.869494	-0.363013
H	3.174195	4.574643	-1.371394
H	2.709902	5.526502	0.058671
H	4.432132	5.402179	-0.400032
C	1.958482	-1.910877	-3.255430
H	1.200366	-1.832388	-4.044373
H	2.564688	-2.796749	-3.488033
H	1.427481	-2.080984	-2.316404

H 4.003921 2.028367 -1.491190

Sum of electronic and thermal Free Energies= -2474.352212

TS3

Pd 1.226054 -0.044338 -0.837017
P -0.665686 -0.620327 0.653767
C 3.545155 -1.761073 -1.115188
C 4.680340 -2.494221 -0.635822
C 5.542277 -1.898650 0.318307
C 5.228978 -0.673992 0.843695
C 4.087528 0.056295 0.412218
C 3.263420 -0.403091 -0.639622
C 2.807524 0.833778 -2.031714
C 2.504172 2.231466 -2.004341
C 2.865845 3.025065 -3.107485
C 3.496798 2.512918 -4.234442
C 3.770317 1.147735 -4.281079
C 3.431314 0.338974 -3.201125
C 0.007870 -0.839405 2.459374
C 0.813687 -2.145899 2.598504
C -0.998124 -0.678535 3.614292
C -1.761796 -2.153489 0.232229
C -0.889057 -3.269836 -0.378805
C -2.658424 -2.708372 1.353056
C -1.702879 0.976651 0.775907
C -1.043302 1.981401 1.551565
C -1.581186 3.228353 1.732634
C -2.810932 3.582294 1.125437
C -3.460682 2.618963 0.289229
C -2.887462 1.300046 0.114085
C -3.623837 0.360269 -0.797988
C -4.836770 -0.251141 -0.329426
C -5.572896 -1.139296 -1.181931
C -5.076105 -1.391990 -2.483908
C -3.922601 -0.793207 -2.925575
C -3.174340 0.098161 -2.100744
N -1.963245 0.660862 -2.591904
C -1.965857 2.101010 -2.858939
C -1.286149 -0.065558 -3.661011
C 1.699192 2.953851 -0.940355
H 0.149142 -3.016019 2.519277
H 1.546552 -2.225929 1.787099
H -1.541044 0.267954 3.521191
H -1.747217 -1.477571 3.583972
H -0.183040 -3.654081 0.368682
H -0.279783 -2.864132 -1.193434
H -2.411247 -1.783111 -0.563647
H -0.071137 1.774247 1.983826

H	-1.054553	3.964597	2.335238
H	-3.580476	-0.989339	-3.935327
H	-5.629834	-2.059296	-3.140547
H	-2.036605	-3.072839	2.179898
H	-3.303064	-1.920962	1.756739
H	-2.528862	2.348140	-3.777171
H	-0.932700	2.438519	-2.990815
H	-2.403434	2.651347	-2.028050
H	-1.243299	-1.132171	-3.424989
H	-0.258937	0.305551	-3.732494
H	-1.760272	0.059587	-4.652046
H	0.736764	-0.023308	2.520697
H	3.696722	-0.706486	-3.266394
H	2.618653	4.084551	-3.071083
H	4.261831	0.706931	-5.144738
H	3.767677	3.167078	-5.059182
H	1.624791	2.417190	0.003661
H	2.131291	3.942238	-0.743205
H	0.673663	3.118604	-1.294149
C	-1.762873	-4.427997	-0.890279
H	-2.388633	-4.067255	-1.720164
H	-1.122837	-5.220619	-1.299406
C	-3.523628	-3.875613	0.841085
H	-4.125251	-4.274329	1.668252
H	-4.233105	-3.497475	0.093155
C	-2.667952	-4.986835	0.217081
H	-3.309599	-5.784041	-0.180192
H	-2.042405	-5.447795	0.996448
C	1.529291	-2.197261	3.960559
H	2.282498	-1.397760	3.997569
H	2.072311	-3.146414	4.057537
C	-0.270438	-0.728516	4.971143
H	-1.000301	-0.637064	5.786243
H	0.401075	0.138711	5.052038
C	0.546492	-2.019718	5.127093
H	1.085937	-2.017898	6.083291
H	-0.139010	-2.879984	5.156778
C	-5.343348	-0.030858	0.986147
C	-6.768520	-1.744778	-0.708582
C	-4.664796	3.020856	-0.360062
C	-3.385019	4.868842	1.303252
C	-6.502536	-0.636911	1.417811
H	-6.864035	-0.447514	2.425079
C	-7.230412	-1.500405	0.563875
H	-8.146210	-1.967139	0.915873
H	-4.801949	0.628844	1.654667
H	-7.311958	-2.409276	-1.376656
H	-2.872258	5.579293	1.947599
H	-5.171681	2.321900	-1.014741

C	-4.557494	5.215023	0.671405
H	-4.988420	6.202419	0.813287
C	-5.196706	4.278853	-0.173822
H	-6.117319	4.552656	-0.682344
H	6.428027	-2.434476	0.648690
C	2.693474	-2.432461	-2.041088
P	3.761932	1.544732	1.434617
C	2.936067	-3.722597	-2.464156
H	2.254696	-4.197039	-3.165229
H	1.821669	-1.902568	-2.413511
H	5.860231	-0.236731	1.608260
C	4.067194	-4.425771	-1.992927
H	4.259632	-5.440188	-2.332392
C	4.917509	-3.817639	-1.099466
H	5.788008	-4.346439	-0.718088
O	2.347562	1.760827	1.988318
O	4.889841	1.491415	2.693749
O	4.427345	2.808961	0.575703
C	4.469586	0.937334	3.947257
H	5.218855	1.243406	4.681150
H	3.485564	1.317744	4.235280
H	4.437787	-0.158401	3.897300
C	4.431623	4.106022	1.195580
H	5.081975	4.107702	2.075777
H	4.822061	4.794146	0.443485
H	3.418404	4.405857	1.482500

Sum of electronic and thermal Free Energies= -2474.354612

TS4

Pd	1.149448	-0.156696	-0.805209
P	-0.611019	-0.568626	0.900296
C	3.911517	-1.436667	-0.047526
C	5.219945	-1.376233	0.536977
C	5.747142	-0.122728	0.952507
C	4.950406	0.988865	0.904442
C	3.678211	0.950428	0.268227
C	3.180971	-0.210074	-0.371484
C	2.720519	-0.157362	-2.242957
C	3.180101	0.930141	-3.047910
C	3.427750	0.705828	-4.413526
C	3.225416	-0.525694	-5.029708
C	2.777395	-1.592813	-4.256254
C	2.555982	-1.406688	-2.893735
C	0.120712	-0.648686	2.693205
C	1.076837	-1.847657	2.848267
C	-0.850022	-0.585496	3.889910
C	-1.634241	-2.178544	0.584817
C	-0.733660	-3.288905	0.007815

C	-2.490620	-2.714307	1.744459
C	-1.800227	0.919530	0.954256
C	-1.435277	1.943068	1.879563
C	-2.143225	3.109277	2.001186
C	-3.265243	3.362000	1.175406
C	-3.619366	2.384533	0.192093
C	-2.865080	1.152507	0.083358
C	-3.297534	0.184784	-0.982100
C	-4.500072	-0.568522	-0.735935
C	-4.982956	-1.508046	-1.703930
C	-4.246211	-1.667207	-2.900982
C	-3.108494	-0.938600	-3.133744
C	-2.597214	0.010836	-2.192283
N	-1.386162	0.686714	-2.499138
C	-1.363598	2.156674	-2.424483
C	-0.673368	0.252450	-3.702927
C	3.424053	2.332569	-2.555410
H	0.504117	-2.785132	2.847831
H	1.774556	-1.894015	2.006726
H	-1.551496	0.249286	3.795385
H	-1.455616	-1.497088	3.928823
H	-0.004589	-3.616664	0.760665
H	-0.158087	-2.892112	-0.836890
H	-2.311066	-1.875169	-0.216333
H	-0.560316	1.807929	2.500223
H	-1.840992	3.859717	2.728205
H	-2.598036	-1.077290	-4.077007
H	-4.602069	-2.368146	-3.652755
H	-1.840261	-3.034927	2.568058
H	-3.146180	-1.928637	2.135797
H	-1.854599	2.603532	-3.305916
H	-0.324632	2.490039	-2.381932
H	-1.857873	2.518303	-1.530082
H	-0.495384	-0.824321	-3.687381
H	0.300395	0.744674	-3.718136
H	-1.205740	0.517627	-4.633707
H	0.755462	0.246570	2.711202
H	2.246469	-2.269983	-2.325937
H	3.786049	1.542257	-5.009646
H	2.612457	-2.572363	-4.698405
H	3.427150	-0.647932	-6.090709
H	4.192195	2.355908	-1.773567
H	3.771415	2.966263	-3.377787
H	2.517584	2.776764	-2.137480
C	-1.576922	-4.494270	-0.443245
H	-2.218880	-4.185909	-1.281268
H	-0.918537	-5.285700	-0.825109
C	-3.333755	-3.920337	1.288627
H	-3.913250	-4.304511	2.138324

H	-4.062433	-3.588686	0.537117
C	-2.455373	-5.031737	0.696087
H	-3.080312	-5.859532	0.336715
H	-1.810517	-5.446671	1.485641
C	1.864388	-1.740856	4.166959
H	2.519163	-0.859407	4.116202
H	2.521026	-2.613464	4.275327
C	-0.061412	-0.460649	5.207684
H	-0.759178	-0.425341	6.054638
H	0.486935	0.493442	5.213377
C	0.932333	-1.618346	5.381509
H	1.518066	-1.483349	6.300039
H	0.371058	-2.556972	5.504096
C	-5.243619	-0.444441	0.476402
C	-6.166580	-2.251298	-1.449883
C	-4.709782	2.689259	-0.673372
C	-4.014452	4.563444	1.283076
C	-6.386631	-1.181360	0.697912
H	-6.929489	-1.058815	1.631505
C	-6.863001	-2.093564	-0.273809
H	-7.768115	-2.664850	-0.087367
H	-4.901099	0.245945	1.237962
H	-6.510483	-2.951181	-2.208343
H	-3.727489	5.286622	2.043044
H	-4.985992	1.979215	-1.443580
C	-5.073180	4.814315	0.440840
H	-5.639760	5.737302	0.529374
C	-5.415691	3.866600	-0.551438
H	-6.243571	4.068376	-1.225901
H	6.745532	-0.076323	1.378979
C	3.344289	-2.726008	-0.221246
P	2.664667	2.438952	0.596171
C	4.047601	-3.882298	0.056875
H	3.569155	-4.849552	-0.072625
H	2.303698	-2.793347	-0.514708
H	5.295184	1.926571	1.328148
C	5.376152	-3.809874	0.524847
H	5.935969	-4.719912	0.724051
C	5.939905	-2.577361	0.771522
H	6.941495	-2.503728	1.189302
O	1.378687	2.782672	-0.163420
O	2.434078	2.269783	2.261452
O	3.783894	3.708049	0.553617
C	1.972831	3.424743	2.975213
H	2.744139	4.202786	2.990920
H	1.052996	3.823854	2.532844
H	1.773683	3.093015	3.996934
C	3.390364	4.982640	0.026497
H	2.421842	4.920308	-0.477442

H 3.331813 5.709927 0.844491
H 4.158921 5.299707 -0.684432

Sum of electronic and thermal Free Energies= -2474.351207

TS5

Pd 1.110062 0.378062 -0.694421
P -0.690437 -0.309807 0.858299
P 4.182464 -1.819020 -0.456801
C 4.057317 -0.134905 0.272252
C 5.100510 0.140209 1.198079
C 5.128748 1.303730 1.920869
C 4.058555 2.224869 1.807201
C 3.006231 1.971993 0.862429
C 3.036787 0.796427 -0.001679
C 2.672815 1.000778 -1.978382
C 3.017625 2.251790 -2.568514
C 3.350901 2.270873 -3.934086
C 3.345603 1.131572 -4.735739
C 3.016408 -0.091186 -4.160639
C 2.711400 -0.151405 -2.799905
C -0.064026 -0.164033 2.686922
C 1.018783 -1.215525 2.996724
C -1.108816 -0.117142 3.818065
C -1.428009 -2.073445 0.607050
C -0.309403 -3.067767 0.231817
C -2.306833 -2.636710 1.736598
C -2.052006 1.023955 0.755022
C -1.769563 2.190008 1.532048
C -2.581352 3.293552 1.525061
C -3.742007 3.329505 0.714298
C -4.026716 2.198482 -0.115194
C -3.160377 1.037269 -0.092574
C -3.536682 -0.102576 -0.995729
C -4.644051 -0.931461 -0.601244
C -5.061290 -2.025153 -1.428674
C -4.356457 -2.260676 -2.633039
C -3.307391 -1.459365 -3.005558
C -2.869635 -0.358713 -2.206336
N -1.744636 0.398939 -2.632177
C -1.943175 1.829337 -2.890308
C -0.909887 -0.192150 -3.676525
O 2.912743 -2.579096 -0.848823
O 5.107232 -2.705224 0.647956
O 5.343580 -1.639261 -1.639756
C 4.403986 -3.448751 1.651033
C 5.699509 -2.802989 -2.403035
C 3.087167 3.585191 -1.858559
H 5.882533 -0.598678 1.333569

H	0.565257	-2.213499	3.057463
H	1.758955	-1.244864	2.190024
H	-1.887790	0.622916	3.607695
H	-1.612937	-1.086142	3.902869
H	0.359425	-3.225842	1.086896
H	0.321096	-2.666378	-0.566942
H	-2.055370	-1.948101	-0.278854
H	-0.876098	2.218268	2.142853
H	-2.337122	4.155734	2.141517
H	-2.811237	-1.660047	-3.946608
H	-4.665666	-3.082234	-3.275184
H	-1.698340	-2.781969	2.638410
H	-3.109222	-1.937222	1.995450
H	-2.476882	2.000508	-3.841627
H	-0.963673	2.313331	-2.952115
H	-2.505743	2.301638	-2.089368
H	-0.658654	-1.225740	-3.426912
H	0.023711	0.371849	-3.732799
H	-1.381895	-0.169598	-4.675491
H	4.013834	-2.781439	2.430402
H	5.134672	-4.129840	2.093731
H	3.579776	-4.018693	1.212079
H	4.813425	-3.259380	-2.856261
H	6.210106	-3.537416	-1.771340
H	6.375722	-2.452064	-3.184856
H	0.457423	0.801462	2.663541
H	2.481876	-1.121598	-2.373508
H	3.622380	3.225936	-4.378663
H	3.004788	-1.002698	-4.753663
H	3.607511	1.203609	-5.788334
H	2.122196	3.898780	-1.450703
H	3.793862	3.569515	-1.023651
H	3.415585	4.359929	-2.558697
C	-0.917715	-4.418403	-0.182898
H	-1.508356	-4.280175	-1.100787
H	-0.112983	-5.122323	-0.429877
C	-2.909193	-3.995220	1.329233
H	-3.504437	-4.396622	2.159912
H	-3.603579	-3.842704	0.492325
C	-1.820385	-4.997087	0.917077
H	-2.277736	-5.937258	0.581979
H	-1.204366	-5.245209	1.794854
C	1.705727	-0.896743	4.337146
H	2.252752	0.052091	4.241653
H	2.455184	-1.667380	4.561714
C	-0.425123	0.210514	5.159163
H	-1.172622	0.224328	5.963005
H	0.000734	1.223645	5.109649
C	0.690764	-0.793415	5.486054

H	1.197397	-0.510001	6.417582
H	0.243391	-1.783147	5.661935
C	-5.352942	-0.728979	0.620993
C	-6.153612	-2.841979	-1.030244
C	-5.171170	2.278274	-0.961265
C	-4.600470	4.460235	0.693654
C	-6.405602	-1.540510	0.983279
H	-6.925061	-1.357760	1.920295
C	-6.819330	-2.607727	0.150546
H	-7.654073	-3.236817	0.446846
H	-5.054695	0.080563	1.277136
H	-6.452154	-3.660563	-1.681377
H	-4.362639	5.303354	1.338146
H	-5.404463	1.446085	-1.614653
C	-5.704859	4.494111	-0.126481
H	-6.356160	5.363772	-0.136672
C	-5.984924	3.390684	-0.965370
H	-6.851141	3.419101	-1.620957
H	5.941849	1.508667	2.612205
C	1.905904	2.876930	0.871624
C	3.992117	3.368737	2.650653
C	1.848705	3.960489	1.722374
H	0.986665	4.621856	1.695749
C	2.913008	4.220926	2.615784
H	2.873120	5.084243	3.275012
H	4.810467	3.542685	3.345609
H	1.086776	2.688609	0.182495

Sum of electronic and thermal Free Energies= -2474.356047

TS6

Pd	0.999855	0.458932	-0.530123
P	-0.641714	-0.520437	1.062202
P	3.130627	-1.768523	-1.821643
C	3.721421	-0.624130	-0.516545
C	4.986008	-1.007774	0.004084
C	5.566858	-0.332086	1.043710
C	4.826762	0.677992	1.714028
C	3.531447	1.058490	1.224603
C	3.007779	0.519249	-0.036982
C	2.569078	1.800823	-1.290467
C	2.076666	3.141420	-1.134414
C	2.399474	4.102778	-2.109049
C	3.163439	3.819793	-3.236263
C	3.624372	2.518257	-3.411587
C	3.338301	1.553508	-2.451382
C	0.095178	-0.648338	2.848489
C	1.222845	-1.700274	2.890592
C	-0.848304	-0.829544	4.054296

C	-1.584160	-2.162519	0.663043
C	-0.617375	-3.230089	0.117834
C	-2.491821	-2.745354	1.757734
C	-1.916958	0.895404	1.160680
C	-1.735369	1.843462	2.212244
C	-2.497304	2.979350	2.315196
C	-3.498778	3.266560	1.355977
C	-3.680839	2.354359	0.267619
C	-2.868672	1.162794	0.172282
C	-3.134662	0.230613	-0.978124
C	-4.313807	-0.594312	-0.884060
C	-4.622758	-1.539105	-1.915828
C	-3.731743	-1.647820	-3.009041
C	-2.622712	-0.847144	-3.099816
C	-2.302192	0.129666	-2.107106
N	-1.139636	0.947655	-2.293769
C	-1.408847	2.397463	-2.338113
C	-0.287783	0.590554	-3.442911
O	1.648663	-1.797209	-2.217815
O	3.721816	-3.289156	-1.376756
O	4.199548	-1.533201	-3.095230
C	2.963259	-4.076552	-0.454818
C	4.034904	-2.358378	-4.259955
C	1.165149	3.666129	-0.035093
H	5.496077	-1.857751	-0.437667
H	0.793374	-2.707840	2.804441
H	1.900830	-1.560154	2.041703
H	-1.668983	-0.104845	4.034090
H	-1.310721	-1.820873	4.021953
H	0.058227	-3.565185	0.916797
H	0.005465	-2.804841	-0.675596
H	-2.219747	-1.861927	-0.171405
H	-0.967358	1.673879	2.955682
H	-2.336139	3.672754	3.137470
H	-1.981709	-0.959410	-3.962651
H	-3.942846	-2.369219	-3.795096
H	-1.880119	-3.085237	2.602468
H	-3.179735	-1.983206	2.140990
H	-2.024586	2.663164	-3.213731
H	-0.453541	2.921316	-2.411476
H	-1.915464	2.734714	-1.438365
H	0.055173	-0.441381	-3.363311
H	0.596137	1.229470	-3.415921
H	-0.798003	0.754194	-4.407978
H	2.868966	-3.574043	0.515841
H	3.520586	-5.007252	-0.323640
H	1.967044	-4.296275	-0.850148
H	3.020223	-2.268849	-4.661693
H	4.247448	-3.405402	-4.022052

H	4.756578	-1.991017	-4.992553
H	0.593797	0.323700	2.951840
H	3.780732	0.581265	-2.603630
H	2.011104	5.110671	-1.976191
H	4.226947	2.249148	-4.275327
H	3.390962	4.600569	-3.957269
H	0.510405	2.896073	0.376007
H	1.740683	4.112030	0.784411
H	0.521684	4.455258	-0.439277
C	-1.405737	-4.441978	-0.412110
H	-1.996705	-4.125920	-1.283740
H	-0.708033	-5.210642	-0.770702
C	-3.283108	-3.952869	1.219727
H	-3.903354	-4.372516	2.022832
H	-3.972818	-3.616010	0.434699
C	-2.343952	-5.028133	0.653403
H	-2.926461	-5.858714	0.233885
H	-1.742121	-5.451045	1.472341
C	2.010603	-1.598922	4.209335
H	2.537453	-0.635156	4.234724
H	2.783423	-2.377848	4.237726
C	-0.058575	-0.700681	5.371399
H	-0.736437	-0.837633	6.224069
H	0.348292	0.318183	5.454695
C	1.092754	-1.715799	5.434877
H	1.670880	-1.578107	6.357657
H	0.671757	-2.731617	5.478717
C	-5.203329	-0.535458	0.231012
C	-5.787690	-2.346339	-1.820005
C	-4.668748	2.681291	-0.706662
C	-4.301545	4.435235	1.442892
C	-6.325687	-1.332043	0.298310
H	-6.983827	-1.256865	1.159932
C	-6.631384	-2.245830	-0.738078
H	-7.522071	-2.864584	-0.673373
H	-4.993257	0.151196	1.042273
H	-5.997297	-3.048818	-2.623506
H	-4.145295	5.110152	2.281272
H	-4.818658	2.014723	-1.547900
C	-5.251656	4.712503	0.487121
H	-5.860295	5.609540	0.560947
C	-5.429807	3.824650	-0.600072
H	-6.175169	4.046438	-1.359151
H	6.553161	-0.606423	1.407582
C	2.775392	1.937349	2.037862
C	5.327903	1.266612	2.905370
C	3.268966	2.471830	3.213865
H	2.646012	3.133533	3.810418
C	4.573915	2.153608	3.642218

H	4.971312	2.585733	4.556992
H	6.320758	0.976733	3.241965
H	1.762411	2.157031	1.741065

Sum of electronic and thermal Free Energies= -2474.350811

TS7

Pd	1.157021	0.304736	-0.647477
P	-0.684203	-0.620362	0.733127
P	4.490207	-1.422995	-0.041268
C	4.113952	0.309548	0.435296
C	5.034776	0.830930	1.385598
C	4.853528	2.055362	1.969657
C	3.687310	2.805046	1.678746
C	2.756603	2.312785	0.704393
C	3.000969	1.055379	-0.011203
C	2.698733	1.149299	-1.901572
C	2.862440	0.183736	-2.944277
C	3.250432	0.624448	-4.222074
C	3.473640	1.961603	-4.526580
C	3.286174	2.911982	-3.525087
C	2.908877	2.504918	-2.249645
C	-0.015619	-0.977124	2.517623
C	0.981862	-2.151505	2.506103
C	-1.032403	-1.133096	3.663849
C	-1.541148	-2.222412	0.077596
C	-0.508802	-3.110400	-0.648805
C	-2.368083	-3.039247	1.085819
C	-1.968163	0.766562	1.000315
C	-1.585805	1.697719	2.014720
C	-2.322614	2.815641	2.303564
C	-3.501289	3.109532	1.575583
C	-3.887903	2.223155	0.520229
C	-3.101836	1.040303	0.233015
C	-3.590538	0.165676	-0.887521
C	-4.732766	-0.671645	-0.636943
C	-5.251519	-1.517700	-1.671898
C	-4.614262	-1.500334	-2.935933
C	-3.532981	-0.689069	-3.169069
C	-2.994009	0.166065	-2.159597
N	-1.840172	0.939409	-2.453506
C	-1.958773	2.398369	-2.398014
C	-1.043592	0.532939	-3.606990
O	3.359266	-2.455747	-0.004088
O	5.770817	-1.901137	0.955477
O	5.337386	-1.286326	-1.472260
C	5.462068	-2.697871	2.107716
C	5.901853	-2.485184	-2.028648
C	2.524181	-1.293049	-2.859054

H	5.902646	0.234361	1.640669
H	0.442943	-3.093762	2.340050
H	1.702661	-2.049869	1.688114
H	-1.742190	-0.299343	3.678158
H	-1.622528	-2.044486	3.520012
H	0.248777	-3.476870	0.054479
H	0.033458	-2.518043	-1.393531
H	-2.225160	-1.837954	-0.681750
H	-0.673897	1.530567	2.574206
H	-2.000183	3.493225	3.090603
H	-3.088968	-0.683753	-4.157083
H	-5.002994	-2.130121	-3.732982
H	-1.713959	-3.423010	1.878602
H	-3.124989	-2.409309	1.565788
H	-2.477556	2.799111	-3.287025
H	-0.954391	2.832947	-2.362205
H	-2.500863	2.716677	-1.511015
H	-0.871606	-0.546307	-3.589078
H	-0.071455	1.030207	-3.547241
H	-1.503226	0.802685	-4.575459
H	5.108705	-2.067131	2.933118
H	6.395294	-3.185325	2.400021
H	4.703165	-3.448994	1.872416
H	5.132721	-3.251510	-2.171772
H	6.694050	-2.872588	-1.380421
H	6.320507	-2.197165	-2.994890
H	0.579703	-0.075544	2.712444
H	2.811158	3.272543	-1.495291
H	3.359721	-0.125142	-5.003922
H	3.447106	3.968783	-3.722814
H	3.784601	2.254577	-5.526049
H	2.439355	-1.676170	-1.842851
H	1.566110	-1.480015	-3.362874
H	3.279497	-1.888010	-3.386218
C	-1.201136	-4.304238	-1.328645
H	-1.860646	-3.930701	-2.126218
H	-0.447653	-4.938518	-1.813098
C	-3.050751	-4.235740	0.396276
H	-3.604193	-4.819991	1.143139
H	-3.793738	-3.863288	-0.321876
C	-2.032821	-5.124361	-0.332736
H	-2.545925	-5.946234	-0.848889
H	-1.360065	-5.588408	0.404171
C	1.714549	-2.236661	3.856955
H	2.333505	-1.336113	3.986477
H	2.403381	-3.091356	3.848348
C	-0.299354	-1.218003	5.016643
H	-1.029460	-1.352890	5.825422
H	0.209240	-0.261914	5.211498

C	0.734598	-2.354621	5.033635
H	1.278511	-2.358670	5.987256
H	0.209584	-3.319436	4.969307
C	-5.375874	-0.724990	0.635910
C	-6.375738	-2.347566	-1.414058
C	-5.050155	2.567505	-0.230602
C	-4.279963	4.263370	1.855910
C	-6.461376	-1.543798	0.857461
H	-6.929511	-1.559205	1.838187
C	-6.975634	-2.362866	-0.176140
H	-7.835397	-2.999936	0.011684
H	-4.999563	-0.107279	1.443051
H	-6.751985	-2.973927	-2.219839
H	-3.965183	4.916245	2.666767
H	-5.362236	1.927327	-1.047311
C	-5.403084	4.555572	1.116561
H	-5.992076	5.441658	1.336946
C	-5.784061	3.697752	0.058968
H	-6.665321	3.930845	-0.532680
H	5.579156	2.445839	2.678132
C	1.577384	3.088542	0.500060
C	3.422770	4.023044	2.363471
C	1.335636	4.259540	1.188225
H	0.416472	4.809085	1.005303
C	2.273991	4.741324	2.127705
H	2.084826	5.668238	2.663050
H	4.151368	4.369634	3.092817
H	0.841500	2.729053	-0.213388

Sum of electronic and thermal Free Energies= -2474.352748

TS8

Pd	1.186484	0.433055	-0.429495
P	-0.690460	-0.490618	0.969857
P	3.587639	-1.862210	-1.465137
C	4.100849	-0.403430	-0.482183
C	5.441004	-0.515764	-0.011375
C	5.930334	0.322535	0.952687
C	5.032987	1.186284	1.638846
C	3.670550	1.279381	1.202411
C	3.226937	0.617828	-0.028627
C	2.480355	1.880030	-1.273615
C	2.078835	3.119557	-0.714083
C	2.040193	4.306504	-1.441718
C	2.440454	4.308676	-2.775280
C	2.860462	3.111490	-3.346397
C	2.887586	1.895105	-2.642424
C	-0.189756	-0.617657	2.840190
C	0.798597	-1.774391	3.077573

C	-1.307198	-0.629868	3.900434
C	-1.570083	-2.137003	0.471018
C	-0.532691	-3.177706	0.002540
C	-2.549060	-2.756108	1.483939
C	-1.940524	0.957414	0.962983
C	-1.629875	1.991967	1.898589
C	-2.358799	3.148406	1.988400
C	-3.458074	3.375341	1.125013
C	-3.767832	2.380862	0.143676
C	-2.988193	1.162598	0.064219
C	-3.373835	0.176848	-1.001916
C	-4.559821	-0.611246	-0.801219
C	-4.967108	-1.566753	-1.789602
C	-4.169000	-1.715404	-2.949477
C	-3.045793	-0.950129	-3.136558
C	-2.626158	0.024438	-2.180782
N	-1.443651	0.777150	-2.423044
C	-1.609009	2.226529	-2.599162
C	-0.528782	0.248224	-3.435478
O	2.132380	-2.000447	-1.925837
O	4.134057	-3.190606	-0.575465
O	4.751626	-1.983432	-2.661948
C	3.366106	-3.635750	0.543949
C	4.683033	-3.119370	-3.538967
H	6.081908	-1.277110	-0.445039
H	0.283809	-2.737559	2.964736
H	1.595731	-1.744177	2.326748
H	-2.011495	0.192605	3.738946
H	-1.885556	-1.556195	3.824726
H	0.070948	-3.511299	0.858098
H	0.160792	-2.737267	-0.721099
H	-2.140808	-1.840671	-0.411634
H	-0.785048	1.870609	2.565141
H	-2.095254	3.905764	2.723075
H	-2.472515	-1.079431	-4.045793
H	-4.465455	-2.438800	-3.705694
H	-2.000845	-3.075871	2.379379
H	-3.296969	-2.023306	1.805520
H	-2.039983	2.466210	-3.587357
H	-0.629377	2.706498	-2.520824
H	-2.255829	2.645042	-1.832114
H	-0.281811	-0.795093	-3.226358
H	0.395271	0.827262	-3.386233
H	-0.922503	0.334438	-4.464675
H	3.370319	-2.888331	1.346733
H	3.851264	-4.547224	0.901865
H	2.334546	-3.857542	0.254755
H	3.705019	-3.174359	-4.028687
H	4.872488	-4.045451	-2.987403

H	5.462610	-2.966421	-4.288182
H	0.394200	0.301086	2.977035
H	1.706724	5.220865	-0.957427
H	3.177102	3.102866	-4.387024
H	2.434343	5.224315	-3.360837
C	-1.242896	-4.398822	-0.608013
H	-1.775458	-4.083366	-1.517051
H	-0.497059	-5.139805	-0.923695
C	-3.252677	-3.987114	0.880597
H	-3.916445	-4.433810	1.632562
H	-3.894540	-3.664526	0.050455
C	-2.241369	-5.026741	0.375197
H	-2.765985	-5.868212	-0.096008
H	-1.689903	-5.443106	1.232029
C	1.400058	-1.689100	4.492161
H	2.012737	-0.779017	4.564151
H	2.077956	-2.536327	4.658603
C	-0.703768	-0.534258	5.314627
H	-1.506654	-0.563864	6.062584
H	-0.203699	0.438871	5.431018
C	0.309160	-1.659446	5.573308
H	0.761821	-1.544150	6.566478
H	-0.219507	-2.624432	5.581013
C	-5.359198	-0.505019	0.375940
C	-6.140537	-2.341968	-1.586058
C	-4.846980	2.653001	-0.747067
C	-4.231425	4.563708	1.201004
C	-6.489142	-1.274206	0.547640
H	-7.078307	-1.166278	1.454539
C	-6.893390	-2.200769	-0.443277
H	-7.789791	-2.796917	-0.296912
H	-5.069226	0.198170	1.148111
H	-6.430082	-3.053841	-2.355866
H	-3.976421	5.300376	1.959356
H	-5.094136	1.927883	-1.513156
C	-5.275237	4.784396	0.331962
H	-5.860982	5.697270	0.396389
C	-5.577916	3.817795	-0.654903
H	-6.395330	3.994540	-1.348796
H	6.970329	0.271708	1.263369
C	2.770116	1.971513	2.054306
C	5.448548	1.886307	2.802168
C	3.188144	2.608015	3.207789
H	2.462705	3.113657	3.839911
C	4.551015	2.594476	3.570899
H	4.883111	3.111703	4.467218
H	6.493154	1.818904	3.097543
H	1.714481	1.946242	1.804960
C	3.358760	0.693229	-3.414111

H 3.491829 0.949166 -4.470518
H 4.325755 0.337156 -3.044625
H 2.656840 -0.142030 -3.356425
H 1.796581 3.173686 0.325016

Sum of electronic and thermal Free Energies= -2474.354448

TS9

Pd 1.613728 -0.711776 -0.866893
P -0.713213 -1.031873 0.013166
C 4.524822 -0.897545 -2.341492
C 5.516334 -1.888081 -2.454945
C 5.703927 -2.891064 -1.506641
C 4.890242 -2.910381 -0.379377
C 3.916546 -1.923542 -0.218595
C 3.686382 -0.919407 -1.189710
C 2.946280 0.875937 -0.569560
C 3.493815 1.305028 0.654180
C 3.938070 2.642307 0.850875
C 3.813527 3.587291 -0.133072
C 3.157215 3.260578 -1.344580
C 2.703826 1.914943 -1.559181
C -0.440576 -2.173968 1.555741
C 0.126751 -3.547628 1.154526
C -1.607825 -2.314158 2.548202
C -1.935585 -1.894511 -1.198365
C -1.124110 -2.710201 -2.230056
C -3.054898 -2.756983 -0.589088
C -1.419825 0.534931 0.843112
C -0.481971 1.022127 1.807043
C -0.724016 2.142541 2.555441
C -1.919711 2.882388 2.381955
C -2.862721 2.436424 1.401978
C -2.600917 1.240046 0.623026
C -3.668705 0.850858 -0.361639
C -4.871730 0.245336 0.138876
C -5.947029 -0.074238 -0.755199
C -5.795517 0.232010 -2.129504
C -4.643888 0.814523 -2.596591
C -3.557020 1.136434 -1.729951
N -2.364667 1.684891 -2.276430
C -2.042569 3.074552 -1.943192
C -2.100948 1.412219 -3.682344
H -0.629938 -4.137096 0.619319
H 0.976305 -3.419401 0.472246
H -1.972956 -1.324730 2.846252
H -2.451272 -2.837280 2.083078
H -0.597367 -3.533267 -1.727929
H -0.350152 -2.077376 -2.682874

H	-2.396421	-1.058528	-1.730171
H	0.453517	0.491348	1.953626
H	0.010530	2.480027	3.282829
H	-4.564235	1.053749	-3.651066
H	-6.611137	0.009541	-2.814012
H	-2.614247	-3.595504	-0.035334
H	-3.646960	-2.178483	0.124582
H	-2.665116	3.786664	-2.515121
H	-0.991847	3.264551	-2.182950
H	-2.189464	3.265572	-0.882532
H	-2.281540	0.357356	-3.908371
H	-1.046389	1.627823	-3.878480
H	-2.701422	2.027531	-4.378376
H	0.374395	-1.646555	2.062938
C	-2.040449	-3.289371	-3.322467
H	-2.473159	-2.461052	-3.903822
H	-1.445908	-3.887855	-4.024884
C	-3.971686	-3.327442	-1.687276
H	-4.745959	-3.955324	-1.227762
H	-4.495215	-2.500407	-2.185822
C	-3.176964	-4.131627	-2.724856
H	-3.841108	-4.492894	-3.520797
H	-2.749847	-5.024627	-2.244400
C	0.576330	-4.324788	2.404748
H	1.414442	-3.787883	2.869956
H	0.953370	-5.313707	2.112326
C	-1.153640	-3.098636	3.794560
H	-1.999153	-3.220414	4.484515
H	-0.391450	-2.512965	4.328195
C	-0.566526	-4.468109	3.421060
H	-0.211594	-4.987033	4.321028
H	-1.359938	-5.097590	2.989930
C	-5.042633	-0.083169	1.516840
C	-7.126119	-0.687656	-0.252975
C	-4.042596	3.217008	1.226472
C	-2.187892	4.049752	3.144574
C	-3.343587	4.771934	2.952996
H	-3.539248	5.664035	3.541828
C	-4.275935	4.348617	1.978422
H	-5.186635	4.919946	1.819259
C	-6.195688	-0.683171	1.972364
H	-6.294627	-0.923066	3.027736
C	-7.254545	-0.987780	1.083237
H	-8.160087	-1.457296	1.457444
H	-4.771303	2.915094	0.483788
H	-1.454412	4.363788	3.883639
H	-4.244067	0.142067	2.214324
H	-7.927396	-0.917934	-0.951644
H	6.482512	-3.636445	-1.647738

H	4.173948	4.600441	0.024150
H	3.318740	-1.948772	0.685148
H	5.010919	-3.671015	0.387493
C	4.468319	0.104849	-3.472060
H	5.253587	-0.117359	-4.201563
H	3.512685	0.086228	-4.003127
H	4.617301	1.131054	-3.123829
H	6.158365	-1.866512	-3.332944
C	1.956178	1.668248	-2.745468
C	2.908341	4.256256	-2.329128
C	1.709573	2.655598	-3.675309
H	1.145963	2.423903	-4.575078
C	2.202538	3.965813	-3.473103
H	2.015470	4.738324	-4.214397
H	3.273952	5.264030	-2.146373
H	1.572207	0.662689	-2.901317
H	4.366776	2.915893	1.807188
P	3.597819	0.241073	2.154950
O	2.469424	-0.750458	2.443685
O	5.075491	-0.560480	2.251529
O	3.758752	1.409895	3.355559
C	6.260169	0.090828	1.779859
H	7.074301	-0.618680	1.941329
H	6.188374	0.320660	0.711444
H	6.461492	1.009847	2.343332
C	3.661374	0.941179	4.711233
H	2.710406	0.425479	4.873867
H	4.488613	0.263511	4.949369
H	3.719744	1.831124	5.341141

Sum of electronic and thermal Free Energies= -2474.353336

TS10

Pd	-1.426513	-0.459251	0.319082
P	0.868992	-0.958132	-0.668810
C	-3.218070	-2.747573	0.765321
C	-4.075564	-3.780849	0.349652
C	-5.042831	-3.604365	-0.633021
C	-5.154291	-2.354957	-1.238388
C	-4.326518	-1.311173	-0.833119
C	-3.349440	-1.457096	0.172331
C	-3.184044	0.383295	0.935124
C	-3.384159	1.519468	0.114093
C	-3.951260	2.722104	0.625496
C	-4.358181	2.818281	1.928603
C	-4.215854	1.712673	2.801740
C	-3.630201	0.491638	2.315780
C	0.452955	-1.667043	-2.429104
C	-0.186629	-3.066011	-2.321281

C	1.541435	-1.656897	-3.519517
C	2.174746	-2.119451	0.160466
C	1.494836	-3.264197	0.934892
C	3.287296	-2.662474	-0.752463
C	1.729107	0.709693	-1.045146
C	1.253459	1.345541	-2.233045
C	1.738273	2.554252	-2.660151
C	2.706890	3.255765	-1.902896
C	3.145165	2.683967	-0.666634
C	2.649394	1.389714	-0.242745
C	3.183534	0.862817	1.059653
C	4.537084	0.375597	1.092758
C	5.091694	-0.138613	2.311011
C	4.275913	-0.150548	3.468294
C	2.992869	0.332560	3.431291
C	2.414823	0.859911	2.235688
N	1.071709	1.312425	2.258377
C	0.812253	2.722795	1.958492
C	0.235630	0.857968	3.363519
H	0.567230	-3.806068	-2.017516
H	-0.971901	-3.068102	-1.557216
H	2.014666	-0.673141	-3.599504
H	2.336811	-2.367331	-3.271068
H	0.972040	-3.935517	0.240274
H	0.735209	-2.856919	1.608809
H	2.639635	-1.469514	0.904354
H	0.461940	0.879239	-2.802954
H	1.371578	2.992249	-3.585945
H	2.409826	0.334550	4.344194
H	4.686168	-0.532879	4.400361
H	2.851378	-3.325377	-1.510105
H	3.782700	-1.843774	-1.285527
H	1.039517	3.370747	2.823917
H	-0.246272	2.843058	1.706718
H	1.403336	3.061660	1.111378
H	0.341035	-0.220774	3.503178
H	-0.808293	1.061514	3.112713
H	0.457975	1.365281	4.320438
H	-0.352717	-0.988974	-2.732268
C	2.531387	-4.070654	1.738319
H	2.961573	-3.421839	2.515247
H	2.032731	-4.898258	2.260061
C	4.323453	-3.464091	0.056810
H	5.088943	-3.863912	-0.621192
H	4.841950	-2.790596	0.751700
C	3.659651	-4.603041	0.843575
H	4.405546	-5.135213	1.448124
H	3.245223	-5.339260	0.138280
C	-0.785846	-3.486003	-3.676186

H	-1.619739	-2.811476	-3.915579
H	-1.210613	-4.495168	-3.595934
C	0.931215	-2.055994	-4.876781
H	1.711637	-2.054451	-5.649276
H	0.189268	-1.301453	-5.176175
C	0.255369	-3.433352	-4.804009
H	-0.213166	-3.679927	-5.765729
H	1.023624	-4.201008	-4.624928
C	5.368625	0.347938	-0.066788
C	6.426402	-0.625172	2.334415
C	4.062929	3.444073	0.116651
C	3.216899	4.512166	-2.324877
C	4.116843	5.207102	-1.550133
H	4.500061	6.168853	-1.880310
C	4.533944	4.666471	-0.311798
H	5.233567	5.219432	0.309335
C	6.658204	-0.134093	-0.014495
H	7.265703	-0.137598	-0.915701
C	7.201780	-0.622336	1.197828
H	8.221995	-0.994929	1.225712
H	4.395181	3.051802	1.070402
H	2.873351	4.918380	-3.273593
H	4.975187	0.716674	-1.006858
H	6.822890	-1.002647	3.274454
H	-5.691011	-4.427342	-0.922296
H	-4.787324	3.743097	2.305429
H	-4.487218	-0.356791	-1.310704
H	-5.892418	-2.176404	-2.016072
C	-2.135992	-3.170166	1.743660
H	-2.563293	-3.649260	2.635427
H	-1.477382	-3.907957	1.270608
H	-1.501477	-2.335647	2.052701
H	-3.950098	-4.762100	0.804832
C	-3.520659	-0.572928	3.250242
C	-4.636419	1.812666	4.155088
C	-3.936699	-0.451758	4.559332
H	-3.835487	-1.297556	5.234218
C	-4.499545	0.756303	5.024762
H	-4.826234	0.846217	6.057305
H	-5.072706	2.751273	4.488995
H	-3.108425	-1.510227	2.924117
H	-4.026785	3.586733	-0.022420
P	-2.956150	1.640401	-1.688243
O	-1.932028	0.737587	-2.367742
O	-4.389887	1.538735	-2.590779
O	-2.602512	3.284147	-1.790906
C	-5.523519	2.350440	-2.273218
H	-6.268400	2.137342	-3.043611
H	-5.938249	2.098245	-1.290386

H	-5.270944	3.416712	-2.298658
C	-2.071893	3.749808	-3.042802
H	-1.087749	3.312286	-3.227781
H	-2.744658	3.505933	-3.872650
H	-1.985158	4.833873	-2.944280

Sum of electronic and thermal Free Energies= -2474.348451

TS11

Pd	1.633175	-0.656825	-0.909641
P	-0.676472	-1.076763	-0.013786
C	4.446441	-0.024514	-2.525020
C	5.557147	-0.616615	-3.117584
C	6.045770	-1.822138	-2.618902
C	5.386914	-2.410334	-1.547136
C	4.256852	-1.839263	-0.932145
C	3.763574	-0.588722	-1.421383
C	2.907014	0.932352	-0.561575
C	3.388366	1.330376	0.703884
C	3.605637	2.698669	1.027311
C	3.337666	3.698081	0.131114
C	2.783156	3.383662	-1.134222
C	2.554168	2.012014	-1.483283
C	-0.457044	-2.264872	1.504380
C	0.022525	-3.664182	1.078421
C	-1.631058	-2.360193	2.495141
C	-1.899188	-1.879322	-1.265953
C	-1.093340	-2.693592	-2.303255
C	-3.056591	-2.721088	-0.699337
C	-1.367339	0.479563	0.851731
C	-0.427284	0.925467	1.833554
C	-0.660301	2.024088	2.616319
C	-1.845678	2.783901	2.460744
C	-2.790526	2.379259	1.464784
C	-2.541486	1.202650	0.651586
C	-3.619168	0.851093	-0.337089
C	-4.827978	0.251287	0.157538
C	-5.914869	-0.028922	-0.735812
C	-5.768980	0.309740	-2.103096
C	-4.612177	0.886373	-2.564318
C	-3.514298	1.170823	-1.698190
N	-2.320726	1.722876	-2.238407
C	-1.992222	3.102808	-1.870769
C	-2.072379	1.488572	-3.654482
H	-0.775319	-4.197813	0.545793
H	0.868935	-3.582592	0.387953
H	-1.943120	-1.359362	2.813031
H	-2.500084	-2.827871	2.017197
H	-0.603949	-3.546789	-1.813747

H	-0.291236	-2.074221	-2.724830
H	-2.323377	-1.016376	-1.785576
H	0.501258	0.379591	1.970292
H	0.072946	2.327936	3.359628
H	-4.536917	1.151496	-3.612885
H	-6.593123	0.117229	-2.786488
H	-2.653369	-3.584608	-0.156264
H	-3.645052	-2.140913	0.015479
H	-2.628636	3.830493	-2.406873
H	-0.947866	3.302371	-2.128273
H	-2.115764	3.261251	-0.801735
H	-2.263549	0.441926	-3.908589
H	-1.018225	1.701290	-3.854244
H	-2.675434	2.127703	-4.326471
H	0.385522	-1.791705	2.021799
C	-2.005952	-3.214467	-3.427356
H	-2.402634	-2.357934	-3.993210
H	-1.416718	-3.811480	-4.135475
C	-3.967931	-3.237424	-1.828603
H	-4.768106	-3.854142	-1.399318
H	-4.458705	-2.383491	-2.314621
C	-3.177973	-4.037554	-2.873077
H	-3.837836	-4.357286	-3.690098
H	-2.786763	-4.955638	-2.409620
C	0.434436	-4.487683	2.311884
H	1.304427	-4.009462	2.782947
H	0.753112	-5.490903	1.999463
C	-1.221278	-3.190694	3.726912
H	-2.072481	-3.277035	4.415145
H	-0.428708	-2.656268	4.269925
C	-0.710638	-4.584252	3.331266
H	-0.381302	-5.135157	4.221841
H	-1.538278	-5.163217	2.893814
C	-4.994078	-0.109844	1.527907
C	-7.099666	-0.636605	-0.240259
C	-3.960427	3.179175	1.310006
C	-2.102819	3.929988	3.258680
C	-3.249259	4.671348	3.086303
H	-3.436653	5.546753	3.702271
C	-4.182972	4.289625	2.095938
H	-5.086197	4.876521	1.951524
C	-6.153044	-0.703367	1.977010
H	-6.247819	-0.968543	3.026706
C	-7.223093	-0.968765	1.088835
H	-8.133174	-1.433490	1.457991
H	-4.689836	2.909460	0.555737
H	-1.368349	4.211634	4.009733
H	-4.187214	0.084753	2.224959
H	-7.909620	-0.836280	-0.938349

H	6.920113	-2.297047	-3.056545
H	3.525507	4.736897	0.388950
H	5.737475	-3.367806	-1.166314
H	6.041747	-0.122367	-3.955877
C	1.956934	1.762067	-2.753573
C	2.439514	4.415609	-2.050753
C	1.639248	2.780774	-3.628145
H	1.202393	2.544725	-4.594723
C	1.886291	4.127615	-3.276313
H	1.636585	4.927080	-3.968949
H	2.624791	5.446031	-1.756642
H	1.753239	0.732286	-3.031896
H	3.987677	2.944159	2.010063
P	3.658202	0.159413	2.092732
O	2.516484	-0.769585	2.508622
O	5.065674	-0.727530	1.846289
O	4.123444	1.201216	3.331992
C	6.240160	-0.032596	1.402750
H	7.024052	-0.789064	1.332132
H	6.084351	0.418647	0.417217
H	6.536089	0.738836	2.122383
C	4.129300	0.643936	4.657251
H	3.152064	0.218849	4.903211
H	4.896717	-0.132788	4.749072
H	4.361230	1.472347	5.329694
H	4.129905	0.928022	-2.924490
C	3.616097	-2.711179	0.130910
H	4.383212	-3.134049	0.788255
H	2.896649	-2.187402	0.758584
H	3.096635	-3.550288	-0.350960

Sum of electronic and thermal Free Energies= -2474.350657

TS12

Pd	-1.680043	-0.384672	0.915379
P	0.641470	-0.933984	0.141152
C	-3.198592	0.650257	3.074579
C	-3.881340	0.423845	4.266788
C	-4.960568	-0.455184	4.283240
C	-5.317343	-1.096927	3.101726
C	-4.628584	-0.910883	1.891068
C	-3.525933	-0.005200	1.861320
C	-3.123885	0.965303	0.239604
C	-3.789817	0.657653	-0.968591
C	-4.574146	1.619361	-1.667777
C	-4.677055	2.907948	-1.219285
C	-3.832731	3.345895	-0.163185
C	-2.997017	2.396047	0.510602
C	0.528852	-2.368525	-1.155103

C	-0.100875	-3.638022	-0.553821
C	1.800298	-2.686033	-1.959562
C	1.720713	-1.516507	1.629482
C	0.777783	-2.083489	2.715371
C	2.871049	-2.500005	1.348394
C	1.426207	0.439884	-0.924732
C	0.530487	0.772854	-1.987433
C	0.845295	1.699627	-2.944316
C	2.084525	2.384831	-2.901063
C	2.982390	2.107610	-1.820761
C	2.635298	1.122614	-0.814049
C	3.629530	0.922672	0.295748
C	4.829571	0.179570	0.030209
C	5.822296	0.021149	1.053857
C	5.594199	0.622395	2.315762
C	4.448096	1.338756	2.555892
C	3.444743	1.508122	1.556449
N	2.255860	2.226656	1.866503
C	2.085422	3.536277	1.233268
C	1.856557	2.266990	3.266331
H	0.575143	-4.087922	0.185618
H	-1.033595	-3.378547	-0.043002
H	2.205725	-1.771415	-2.406881
H	2.579870	-3.089994	-1.303783
H	0.277793	-2.986607	2.339579
H	-0.016172	-1.358218	2.938032
H	2.148190	-0.586823	2.014270
H	-0.441522	0.293544	-2.034082
H	0.135115	1.927004	-3.735600
H	4.309020	1.804335	3.525359
H	6.347175	0.519582	3.093954
H	2.466069	-3.432966	0.937647
H	3.558448	-2.093555	0.602683
H	2.681282	4.316658	1.740857
H	1.029966	3.824315	1.274220
H	2.384147	3.503663	0.187959
H	1.938189	1.274059	3.717319
H	0.806283	2.574825	3.318234
H	2.439804	2.980178	3.878184
H	-0.216912	-1.962034	-1.847568
C	1.548625	-2.430323	4.001089
H	1.944163	-1.503826	4.444152
H	0.859163	-2.860115	4.739083
C	3.641764	-2.832363	2.640136
H	4.442643	-3.548042	2.413727
H	4.131316	-1.922090	3.012131
C	2.712292	-3.393068	3.724377
H	3.273350	-3.587100	4.647754
H	2.309040	-4.361776	3.393314

C	-0.392010	-4.668025	-1.659495
H	-1.176824	-4.260749	-2.310968
H	-0.799500	-5.584181	-1.212122
C	1.491910	-3.714983	-3.063522
H	2.411106	-3.955920	-3.613752
H	0.800086	-3.265431	-3.791632
C	0.860133	-4.991431	-2.488102
H	0.612255	-5.690977	-3.297301
H	1.597763	-5.501578	-1.850148
C	5.075880	-0.444488	-1.228691
C	6.997642	-0.731537	0.787592
C	4.205036	2.840179	-1.781532
C	2.436283	3.344044	-3.887180
C	3.631957	4.022094	-3.822042
H	3.892238	4.753483	-4.582329
C	4.520654	3.766248	-2.752785
H	5.462826	4.304728	-2.694230
C	6.223173	-1.172254	-1.454418
H	6.381977	-1.637086	-2.423880
C	7.199899	-1.318677	-0.439835
H	8.101684	-1.892993	-0.633194
H	4.902012	2.664295	-0.970880
H	1.734979	3.534166	-4.696312
H	4.340670	-0.342207	-2.018554
H	7.735841	-0.835770	1.579616
H	-5.522190	-0.635101	5.196208
H	-5.328954	3.621386	-1.716082
H	-6.159867	-1.784816	3.106273
H	-3.572789	0.945872	5.169146
C	-2.005117	2.914360	1.384001
C	-3.746097	4.722344	0.174950
C	-1.913254	4.263628	1.667129
H	-1.133743	4.624747	2.333006
C	-2.817008	5.177220	1.084004
H	-2.753929	6.235511	1.323007
H	-4.409363	5.419943	-0.331383
H	-1.264571	2.226163	1.779108
H	-5.113836	1.307682	-2.556166
P	-3.500742	-0.856129	-1.957630
O	-2.830433	-2.126473	-1.422985
O	-5.003319	-1.177579	-2.662545
O	-2.658142	-0.166195	-3.247127
C	-5.387728	-2.537200	-2.912208
H	-6.458601	-2.608479	-2.704593
H	-5.204604	-2.790874	-3.963050
H	-4.835280	-3.229222	-2.270850
C	-2.424889	-0.988041	-4.398332
H	-1.974458	-1.947007	-4.118966
H	-3.359273	-1.162777	-4.944205

H	-1.732405	-0.433127	-5.034850
H	-2.395513	1.369776	3.095913
C	-5.129047	-1.704363	0.713994
H	-5.952500	-2.356927	1.021628
H	-5.512425	-1.046586	-0.075803
H	-4.344464	-2.324579	0.274820

Sum of electronic and thermal Free Energies= -2474.352511

TS13

Pd	1.281422	0.066179	0.299076
P	-0.955870	-0.875894	0.867945
C	3.319727	-1.770422	0.742747
C	3.943703	-2.780747	1.467938
C	4.412641	-2.518215	2.753174
C	4.218828	-1.248118	3.284547
C	3.563609	-0.212313	2.591321
C	3.102794	-0.472146	1.268221
C	3.119237	1.010190	-0.002876
C	3.063855	2.386663	0.485402
C	4.016994	3.367826	0.044150
C	4.984699	3.009430	-0.926402
C	4.913476	1.779999	-1.531032
C	3.969736	0.806745	-1.112398
C	-0.898370	-1.758933	2.597505
C	-0.042618	-3.040105	2.551109
C	-2.234944	-2.022114	3.316272
C	-1.688337	-2.121948	-0.415283
C	-0.550851	-2.965629	-1.031149
C	-2.853721	-3.009601	0.053261
C	-2.149644	0.581670	1.173570
C	-2.028170	1.156023	2.476677
C	-2.748763	2.253812	2.867362
C	-3.645544	2.883093	1.969591
C	-3.748925	2.367562	0.638238
C	-2.975900	1.209196	0.240800
C	-3.112351	0.748478	-1.182445
C	-4.306872	0.044033	-1.560955
C	-4.472559	-0.426813	-2.905131
C	-3.433486	-0.183193	-3.835370
C	-2.303517	0.502677	-3.467894
C	-2.116393	0.998126	-2.141852
N	-0.913060	1.680511	-1.817002
C	-1.026587	3.085024	-1.407951
C	0.213355	1.508293	-2.731308
H	-0.559050	-3.812631	1.966794
H	0.913938	-2.844655	2.055546
H	-2.846772	-1.115212	3.356027
H	-2.815719	-2.766662	2.761764

H	-0.106009	-3.616134	-0.266070
H	0.253667	-2.318464	-1.396891
H	-2.061910	-1.467633	-1.205727
H	-1.338850	0.717710	3.188393
H	-2.636142	2.652895	3.872806
H	-1.539748	0.687101	-4.213063
H	-3.546282	-0.536019	-4.858011
H	-2.515806	-3.671560	0.860636
H	-3.668829	-2.397870	0.455359
H	-1.174666	3.748145	-2.278794
H	-0.106077	3.383038	-0.896893
H	-1.857943	3.229633	-0.723098
H	0.400176	0.449527	-2.924596
H	1.103728	1.918336	-2.247461
H	0.078368	2.039589	-3.691850
H	-0.324953	-1.038025	3.195224
C	-1.089217	-3.835344	-2.180920
H	-1.425579	-3.179324	-2.997248
H	-0.275076	-4.448448	-2.587905
C	-3.379640	-3.882064	-1.102365
H	-4.184832	-4.531053	-0.733360
H	-3.826615	-3.235027	-1.868974
C	-2.258519	-4.722178	-1.730399
H	-2.647617	-5.301879	-2.577703
H	-1.894871	-5.453339	-0.992304
C	0.204812	-3.574623	3.974022
H	0.824001	-2.851093	4.523844
H	0.786713	-4.503643	3.921380
C	-1.982778	-2.546099	4.742628
H	-2.941509	-2.747721	5.237973
H	-1.484458	-1.763057	5.333735
C	-1.109368	-3.808984	4.733750
H	-0.902747	-4.137107	5.760678
H	-1.665207	-4.626427	4.250507
C	-5.350871	-0.244692	-0.632015
C	-5.653738	-1.126669	-3.271313
C	-4.617589	3.049775	-0.262941
C	-4.412803	4.013866	2.354998
C	-5.252896	4.636529	1.460467
H	-5.836157	5.501542	1.764050
C	-5.347721	4.148469	0.136642
H	-6.003329	4.644191	-0.574250
C	-6.482739	-0.930139	-1.015437
H	-7.261096	-1.131389	-0.284056
C	-6.645045	-1.373827	-2.349885
H	-7.545301	-1.908822	-2.639181
H	-4.704380	2.695330	-1.283161
H	-4.318472	4.381190	3.374335
H	-5.248660	0.085589	0.395305

H	-5.756492	-1.465884	-4.299692
H	4.921516	-3.283792	3.332998
H	5.578164	1.543485	-2.355026
H	5.728215	3.738818	-1.236751
C	2.011693	2.846406	1.329667
C	3.932152	4.702323	0.528601
H	4.681049	5.418643	0.198465
H	1.255845	2.130580	1.640478
C	2.905733	5.096340	1.355741
H	2.843706	6.125093	1.701146
C	1.920781	4.159150	1.741952
H	1.094791	4.469505	2.376111
P	3.893781	-0.651840	-2.224594
O	2.562526	-1.398514	-2.366688
O	5.228129	-1.561834	-1.813948
O	4.454630	-0.089684	-3.716655
C	5.478603	-2.757038	-2.571963
H	5.754843	-2.509133	-3.601896
H	6.311591	-3.256853	-2.073971
H	4.600369	-3.411314	-2.572835
C	3.486094	0.415649	-4.643082
H	3.083776	1.379144	-4.305110
H	4.016225	0.560023	-5.587356
H	2.665735	-0.294954	-4.781874
H	4.581385	-1.035698	4.287995
H	4.061681	-3.764732	1.020704
C	3.428952	1.089893	3.347197
H	3.981261	1.905287	2.870157
H	2.389910	1.418178	3.437369
H	3.825656	0.971118	4.360580
H	2.953903	-2.011411	-0.246811

Sum of electronic and thermal Free Energies= -2474.353768

TS14

Pd	1.392883	0.000368	0.110970
P	-0.883343	-0.776633	0.827615
C	3.516551	-1.044446	2.051181
C	3.805224	-1.193344	3.417611
C	3.511370	-0.213572	4.361185
C	2.908433	0.967201	3.929922
C	2.630995	1.147920	2.578802
C	2.917317	0.168497	1.594362
C	3.282932	0.847390	-0.107061
C	3.402813	2.309533	-0.090579
C	4.605700	2.954953	-0.525207
C	5.642124	2.175708	-1.113486
C	5.390270	0.866954	-1.431746
C	4.203414	0.216815	-0.993377

C	-0.760422	-1.458242	2.642826
C	0.025372	-2.782521	2.693735
C	-2.056956	-1.557563	3.467314
C	-1.755281	-2.121456	-0.249942
C	-0.705984	-3.117626	-0.791038
C	-2.951145	-2.866267	0.368860
C	-1.977668	0.774491	1.042463
C	-1.664293	1.510098	2.227545
C	-2.277179	2.694214	2.542835
C	-3.250922	3.253604	1.679841
C	-3.552690	2.567853	0.460072
C	-2.894493	1.318085	0.142116
C	-3.239401	0.683101	-1.174113
C	-4.502138	0.014430	-1.320659
C	-4.848217	-0.600476	-2.569510
C	-3.918524	-0.535976	-3.636589
C	-2.721778	0.120387	-3.489316
C	-2.362310	0.755590	-2.264561
N	-1.106770	1.415689	-2.148302
C	-1.143802	2.878765	-2.085999
C	-0.038335	0.955058	-3.026656
H	-0.562006	-3.587111	2.233086
H	0.954611	-2.691309	2.121301
H	-2.606716	-0.611019	3.443534
H	-2.719792	-2.316705	3.037486
H	-0.293089	-3.713702	0.033212
H	0.138666	-2.587194	-1.241621
H	-2.122080	-1.551203	-1.106714
H	-0.907719	1.129676	2.903412
H	-2.016950	3.217262	3.460205
H	-2.039017	0.171126	-4.329993
H	-4.171546	-1.002777	-4.585843
H	-2.613233	-3.456122	1.230203
H	-3.704239	-2.160396	0.735143
H	-1.347580	3.327806	-3.075255
H	-0.173298	3.245943	-1.735980
H	-1.909757	3.218989	-1.391207
H	0.037823	-0.134669	-2.997013
H	0.906145	1.363712	-2.654171
H	-0.152977	1.283208	-4.077220
H	-0.112173	-0.710252	3.116628
C	-1.349083	-4.067109	-1.817104
H	-1.672430	-3.483378	-2.691714
H	-0.597908	-4.781526	-2.177746
C	-3.587802	-3.823203	-0.657491
H	-4.417723	-4.366250	-0.186457
H	-4.024090	-3.233933	-1.474802
C	-2.558475	-4.808834	-1.229160
H	-3.025914	-5.445338	-1.991967

H	-2.215985	-5.481667	-0.428264
C	0.341423	-3.167809	4.150128
H	1.028295	-2.421995	4.574364
H	0.871936	-4.128792	4.170090
C	-1.737337	-1.939472	4.925483
H	-2.669935	-2.030053	5.497622
H	-1.160673	-1.127355	5.392894
C	-0.930984	-3.244484	5.006069
H	-0.675401	-3.469979	6.049543
H	-1.557130	-4.076905	4.651016
C	-5.440376	-0.089493	-0.251394
C	-6.098925	-1.261552	-2.707786
C	-4.502930	3.173284	-0.413837
C	-3.906589	4.474504	1.989104
C	-4.828406	5.021055	1.125809
H	-5.325233	5.955759	1.370998
C	-5.122066	4.361424	-0.090098
H	-5.843569	4.794998	-0.777441
C	-6.643463	-0.739873	-0.415745
H	-7.339833	-0.799375	0.416512
C	-6.984204	-1.329699	-1.656959
H	-7.938771	-1.835221	-1.773898
H	-4.742720	2.687423	-1.352254
H	-3.660835	4.971776	2.924609
H	-5.198036	0.357016	0.706423
H	-6.341947	-1.714786	-3.666251
H	3.752734	-0.369082	5.409406
H	6.097289	0.309043	-2.038989
H	6.572901	2.653702	-1.406577
C	2.313588	3.140985	0.281176
C	4.705895	4.369065	-0.452981
H	5.635866	4.837728	-0.766991
H	1.362100	2.669456	0.514718
C	3.638955	5.141109	-0.045600
H	3.726739	6.223959	-0.013612
C	2.419657	4.519964	0.296771
H	1.559497	5.124629	0.571648
P	3.770021	-1.259162	-1.974020
O	2.329801	-1.781164	-1.862173
O	4.995768	-2.370682	-1.746751
O	4.194893	-0.859240	-3.560901
C	4.946316	-3.584370	-2.516811
H	5.077396	-3.370314	-3.581796
H	5.772325	-4.200288	-2.155702
H	3.997350	-4.106724	-2.357017
C	3.286798	-0.057283	-4.320163
H	3.188184	0.945975	-3.887077
H	3.718557	0.026183	-5.320336
H	2.301153	-0.529809	-4.383395

H	2.199860	2.092652	2.284498
H	2.661328	1.755752	4.636598
C	3.870444	-2.198854	1.155685
H	4.103327	-3.088000	1.751272
H	3.060551	-2.455373	0.467508
H	4.757909	-1.974713	0.553700
H	4.268186	-2.122660	3.742228

Sum of electronic and thermal Free Energies= -2474.352290

1. Cammidge, A. N.; Crepy, K. V. L. *Tetrahedron* **2004**, *60*, 4377.
2. Yin, J.; Buchwald, S. L. *J. Am. Chem. Soc*. **2000**, *122*, 12051
3. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.