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A highly efficient thiourea catalyzed dehydrative nucleophilic substitution reaction of 3-substituted oxindoles with xanthydrols

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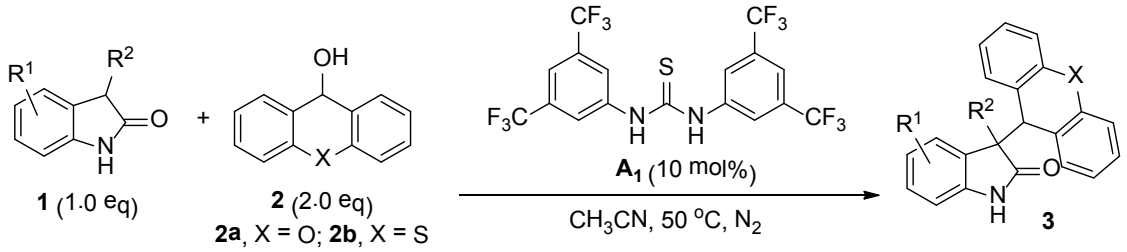
General: Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products were carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX-400 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

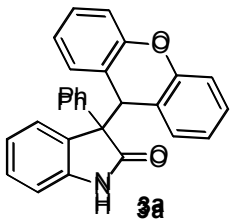
All reactions were run under N_2 atmosphere. Anhydrous THF and toluene were prepared by distillation over sodium-benzophenone ketyl prior to use. Anhydrous acetone was distilled over anhydrous $CaSO_4$ and stored over MS 4Å. Anhydrous DMF was prepared by first distillation over anhydrous $CaSO_4$ and then from MS 4 Å. Anhydrous halogenated solvents and CH_3CN were prepared by first distillation over P_2O_5 and then from CaH_2. Anhydrous Ethyl acetate was prepared by first dried in anhydrous Na_2SO_4 and then distilled over P_2O_5 and stored over MS 4Å. Anhydrous CH_3NO_2 was prepared by first dried in anhydrous Na_2SO_4 and then distilled under reduced pressure. Oxindoles **1** were prepared according to literature report.[1] 9H-xanthen-9-ol (**2a**) and 9H-thioxanthen-9-ol (**2b**) were prepared through the reduction of corresponding ketone using $NaBH_4$.[2] $In(OTf)_3$ and CuCl were purchased individually from Strem chemicals and Aldrich. Thiourea catalysts **A1-A4**[3a] , $\mathbf{B_1}$-$\mathbf{B_2}$[3b], $\mathbf{C_1}$-$\mathbf{C_2}$[3c] were prepared according to the literature methods.

[1] Y. Hamashima, T. Suzuki, H. Takano, Y. Shimura and M. Sodeoka, *J. Am. Chem. Soc*., 2005, **127**, 10164.
[2] X.- Q. Zhu, Z. Dai, A. Yu, S. Wu and J.-P. Cheng, *J. Phys. Chem. B*., 2008, **112**, 11694.
[3] (a) C. B. Tripathi and S. Mukherjee, *J. Org. Chem*., 2012, **77**, 1592; (b) C. -H. Chien, M. –K. Leung, J. –K. Su, G. –H. Li, Y.-H. Liu and Y. Wang, *J. Org. Chem*., 2004, **69**, 1866; (c) V. Štrukil, M. D. Igrc, M. E. Maksić and T. Friščić, *Chem. Eur. J*., 2012, **18**, 8464.

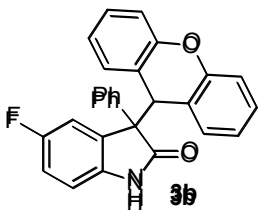
General procedure for the dehydrative nucleophilic substitution reaction of 3-substituted oxindoles with 9H-xanthen-9-ol (2a) and 9H-thioxanthen-9-ol (2b)



Under an atmosphere of N_2, to a flame-dried Schlenk tube were added $\mathbf{A_1}$ (12.5 mg, 0.025 mmol, 0.1 eq), oxindole **1** (0.25 mmol, 1.0 eq), **2a** or **2b** (0.5 mmol, 2.0 eq) and 1.0 mL of anhydrous CH_3CN. The reaction mixture was heated to 50 °C and stirred till almost full conversion of **1** by TLC analysis. The solvent was removed under reduced pressure and the residue was subjected to column chromatography using petroleum ether/ethyl acetate as the eluent to afford the desired product **3**.

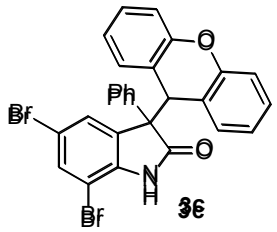


Column chromatography afforded the desired product **3a** in 81% yield as white solid. Mp 213-215 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74-7.72 (m, 2H), 7.58-7.56 (m, 1H), 7.48 (s, 1H), 7.36-7.33 (m, 3H), 7.20-7.12 (m, 2H), 7.05-7.01 (m, 2H), 6.96-6.91 (m, 2H), 6.73-6.64 (m, 3H), 6.59-6.57 (m, 1H), 6.44-6.42 (m, 1H), 5.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.82, 153.54, 152.80, 140.62, 136.36, 129.97, 129.86, 128.73, 128.47, 128.45, 128.22, 128.18, 127.79, 127.66, 127.05, 122.74, 122.20, 121.49, 120.16, 119.82, 116.06, 115.72, 109.11, 63.24, 48.57; IR (neat): 2928, 1713, 1475, 1253, 878, 739, 696 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{27}H_{19}NNaO_2$ $[M+Na]^+$: 412.1308, Found: 412.1305.

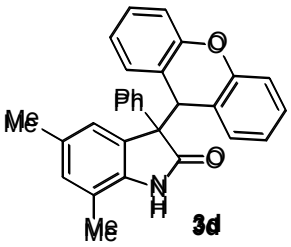


Column chromatography afforded the desired product **3b** in 76% yield as white solid. Mp 252-253 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71-7.69 (m, 2H), 7.57-7.55 (m, 1H), 7.38-7.31 (m, 4H), 7.23-7.19 (m, 1H), 7.10-7.05 (m, 2H), 6.95-6.92 (m, 1H), 6.88-6.83 (m, 1H), 6.77-6.69 (m, 2H), 6.52-6.49 (m, 1H), 6.42-6.36 (m, 2H), 5.15 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 177.54, 158.17, 155.83, 153.05, 152.28, 138.34, 136.27, 130.02, 129.82, 128.91, 128.73, 128.65, 128.54, 128.33, 128.21, 127.69, 122.86, 122.40, 119.86, 119.79, 115.81, 115.64, 115.04, 114.81, 114.53, 114.27, 109.82,

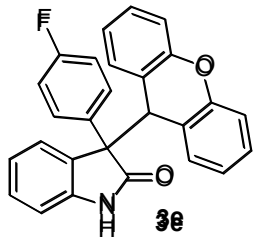
109.74, 63.10, 46.87; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -120.77; IR (neat): 3250, 1714, 1480, 1253, 1095, 755, 697, 650 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{27}H_{18}FNNaO_2$ $[M+Na]^+$: 430.1214, Found: 430.1202.



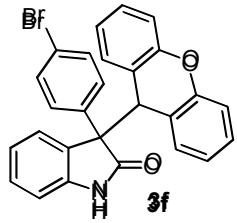
Column chromatography afforded the product **3c** in 83% yield as white solid. Mp 234-236 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.64 (m, 2H), 7.55-7.53 (m, 2H), 7.45-7.44 (m, 1H), 7.40-7.36 (m, 3H), 7.24-7.22 (m, 1H), 7.14-7.06 (m, 2H), 6.97-6.93 (m, 1H), 6.82-6.80 (m, 1H), 6.74-6.70 (m, 1H), 6.59-6.58 (m, 1H), 6.41-6.39 (m, 1H), 5.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.18, 153.54, 152.59, 139.42, 135.12, 133.21, 129.78, 129.74, 128.98, 128.65, 128.46, 128.35, 128.12, 123.03, 122.45, 119.30, 118.93, 116.14, 116.09, 114.35, 102.37, 65.10, 49.10; IR (neat): 3190, 1708, 1455, 1253, 898, 757, 699, 632 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{27}H_{17}Br_2NNaO_2$ $[M+Na]^+$: 567.9518, Found: 567.9501.



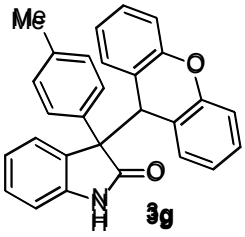
Column chromatography afforded the desired product **3d** in 80% yield as yellow solid. Mp 190-192 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (s, 1H), 7.75-7.73 (m, 2H), 7.55-7.53 (m, 1H), 7.34-7.29 (m, 3H), 7.21-7.17 (m, 1H), 7.00-6.97 (m, 2H), 6.83-6.77 (m, 2H), 6.71-6.68 (m, 2H), 6.43-6.41 (m, 1H), 6.20 (s, 1H), 5.12 (s, 1H), 2.22 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.41, 153.73, 152.71, 137.05, 136.69, 130.66, 130.00, 129.84, 129.82, 128.83, 128.38, 128.06, 128.00, 127.49, 126.60, 125.94, 122.53, 122.01, 120.24, 119.71, 117.84, 115.76, 115.61, 63.76, 48.63, 21.14, 16.14; IR (neat): 2974, 2893, 1695, 1477, 1255, 1089, 1049, 880, 750, 696, 644 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{29}H_{23}NNaO_2$ $[M+Na]^+$: 440.1621, Found: 440.1608.



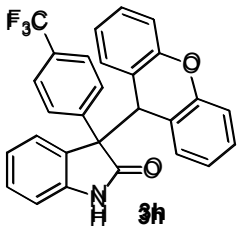
Column chromatography afforded the desired product **3e** in 89% yield as white solid. Mp 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73-7.70 (m, 2H), 7.56-7.54 (m, 1H), 7.24-7.12 (m, 3H), 7.08-7.01 (m, 4H), 6.96-6.93 (m, 2H), 6.76-6.72 (m, 2H), 6.65-6.63 (m, 1H), 6.58-6.56 (m, 1H), 6.42-6.40 (m, 1H), 5.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.87, 163.54, 161.09, 153.53, 152.75, 140.61, 132.21, 132.18, 130.51, 130.43, 129.90, 129.74, 128.61, 128.29, 127.62, 126.95, 122.75, 122.30, 121.65, 119.93, 119.62, 116.17, 115.79, 115.10, 114.89, 109.26, 62.63, 48.78; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -114.75; IR (neat): 3300, 1713, 1476, 1256, 812, 743, 679 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{27}H_{18}FNNaO_2$ $[M+Na]^+$: 430.1214, Found: 430.1203.



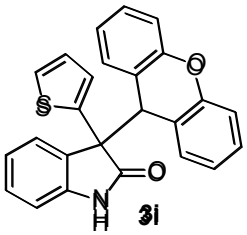
Column chromatography afforded the desired product **3f** in 75% yield as white solid. Mp 218-220 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62-7.60 (m, 2H), 7.54-7.52 (m, 2H), 7.47-7.45 (m, 2H), 7.24-7.20 (m, 1H), 7.17-7.13 (m, 1H), 7.07-7.03 (m, 2H), 6.96-6.88 (m, 2H), 6.79-6.71 (m, 2H), 6.63-6.58 (m, 2H), 6.46-6.44 (m, 1H), 5.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.49, 153.52, 152.46, 140.59, 135.57, 131.26, 130.49, 129.87, 129.74, 128.70, 128.66, 128.35, 127.59, 126.60, 122.76, 122.43, 122.04, 121.70, 119.84, 119.47, 116.21, 115.80, 109.31, 62.87, 48.59; IR (neat): 3290, 1706, 1474, 1250, 1098, 1007, 816, 767, 673 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{27}H_{18}BrNNaO_2$ $[M+Na]^+$: 490.0413, Found: 490.0404.



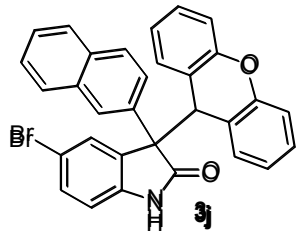
Column chromatography afforded the desired product **3g** in 86% yield as white solid. Mp 223-224 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.55 (m, 3H), 7.26 (s, 1H), 7.22-7.11 (m, 4H), 7.03-7.01 (m, 2H), 6.94-6.88 (m, 2H), 6.74-6.70 (m, 2H), 6.62-6.56 (m, 2H), 6.50-6.48 (m, 1H), 5.13 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.38, 153.53, 152.77, 140.80, 137.30, 133.31, 130.07, 129.82, 128.86, 128.56, 128.38, 128.34, 128.14, 127.63, 127.31, 122.68, 122.19, 121.39, 120.30, 119.87, 115.99, 115.65, 109.19, 63.14, 48.24, 21.03; IR (neat): 3300, 1707, 1454, 1251, 1099, 1020, 812, 744, 698, 630 cm^{-1}; MS (ESI): 426 $[M+Na]^+$; HRMS (ESI): Exact mass calcd for $C_{28}H_{21}NNaO_2$ $[M+Na]^+$: 426.1448, Found: 426.1465.



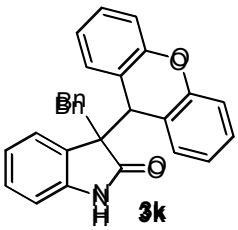
Column chromatography afforded the desired product **3h** in 91% yield as white solid. Mp 193-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.02 (s, 1H), 7.89-7.87 (m, 2H), 7.61-7.59 (m, 2H), 7.54-7.52 (m, 1H), 7.24-7.16 (m, 2H), 7.06-6.96 (m, 3H), 6.88-6.84 (m, 1H), 6.74-6.62 (m, 4H), 6.40-6.38 (m, 1H), 5.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 178.39, 153.58, 152.83, 140.68, 140.59, 129.72, 129.21, 128.91, 128.81, 128.47, 127.68, 126.43, 125.07 (q, J = 4.0 Hz), 122.82, 122.47, 121.88, 119.71, 119.36, 116.37, 115.90, 109.49, 63.30, 48.85; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.49; IR (neat): 3360, 2975,1702, 1455, 1323, 1251, 1049, 974, 881, 748 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{28}H_{18}F_3NNaO_2$ $[M+Na]^+$: 480.1182, Found: 480.1177.



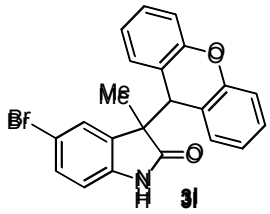
Column chromatography afforded the desired product **3i** in 65% yield as white solid. Mp 180-182 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51-7.50 (m, 2H), 7.30-7.28 (m, 1H), 7.26-7.24 (m, 1H), 7.15-7.04 (m, 4H), 6.98-6.90 (m, 3H), 6.84-6.80 (m, 1H), 6.75-6.72 (m, 2H), 6.59-6.56 (m, 2H), 4.94 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.34, 153.48, 152.71, 140.42, 140.17, 129.73, 129.67, 128.79, 128.66, 128.35, 128.05, 127.52, 126.53, 126.46, 125.81, 122.77, 122.38, 121.86, 119.84, 119.46, 115.99, 115.75, 109.19, 61.11, 50.29; IR (neat): 2892, 1698, 1618, 1475, 1255, 747, 714, 653 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{25}H_{17}NNaO_2S$ $[M+Na]^+$: 418.0872, Found: 418.0853.



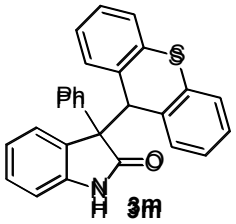
Column chromatography afforded the desired product **3j** in 82% yield as white solid. Mp 253-255 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16-8.14 (m, 1H), 7.95-7.93 (m, 1H), 7.88-7.86 (m, 1H), 7.75-7.73 (m, 2H), 7.66 (s, 1H), 7.58-7.57 (m, 1H), 7.52-7.44 (m, 2H), 7.32-7.30 (m, 1H), 7.21-7.17 (m, 1H), 7.08-7.02 (m, 2H), 6.92-6.89 (m, 1H), 6.79-6.77 (m, 1H), 6.69 (s, 1H), 6.60-6.57 (m, 1H), 6.51-6.49 (m, 1H), 6.42-6.41 (m, 1H), 5.30 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 177.05, 153.21, 152.39, 141.49, 133.95, 132.37, 132.16, 131.32, 130.12, 129.63, 129.57, 129.41, 128.94, 128.63, 128.22, 127.76, 127.41, 127.22, 126.53, 126.34, 122.90, 122.43, 119.90, 119.66, 115.77, 115.72, 112.75, 111.00, 63.37, 46.48; IR (neat): 3218, 1716, 1476, 1256, 814, 751, 691 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{31}H_{20}BrNNaO_2$ $[M+Na]^+$: 540.0570, Found: 540.0558.



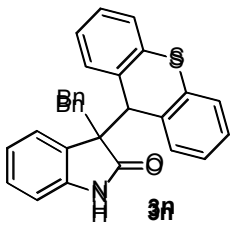
Column chromatography afforded the desired product **3k** in 65% yield as white solid. Mp 265-266 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.48 (m, 1H), 7.42-7.36 (m, 2H), 7.23-7.18 (m, 2H), 7.07-7.01 (m, 2H), 6.97-6.85 (m, 6H), 6.78-6.72 (m, 4H), 6.24-6.22 (m, 1H), 4.64 (s, 1H), 3.43 (AB, J = 12.4 Hz, 1H), 3.07 (AB, J = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.62, 153.86, 152.77, 140.44, 135.51, 131.08, 130.02, 129.28, 128.84, 128.39, 128.03, 127.49, 126.25, 125.10, 122.83, 122.79, 121.62, 120.85, 120.62, 116.82, 115.73, 108.49, 61.06, 46.82, 41.25; IR (neat): 3304, 2972, 1694, 1455, 1253, 1051, 903, 760, 698, 655 cm^{-1}; MS (ESI): 426 $[M+Na]^+$; HRMS (ESI): Exact mass calcd for $C_{28}H_{21}NNaO_2$ $[M+Na]^+$: 426.1465, Found: 426.1452.



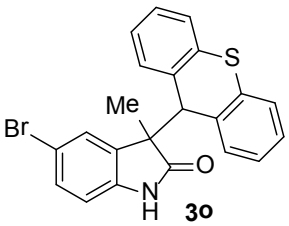
Column chromatography afforded the desired product **3l** in 85% yield as white solid. Mp 240-242 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (s, 1H), 7.40-7.29 (m, 3H), 7.19-7.17 (m, 3H), 7.09-7.01 (m, 1H), 6.93-6.89 (m, 1H), 6.79-6.77 (m, 1H), 6.57 (s, 1H), 6.44-6.42 (m, 1H), 4.38 (s, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.59, 153.69, 152.63, 139.06, 133.30, 130.73, 129.03, 128.98, 128.23, 127.69, 122.79, 122.73, 120.47, 119.96, 116.65, 116.00, 114.68, 110.23, 55.04, 46.56, 21.06; IR (neat): 3252, 2966, 1713, 1668, 1476, 1253, 1097, 815, 765, 695, 612 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{22}H_{16}BrNNaO_2$ $[M+Na]^+$: 428.0257, Found: 428.0248.



Column chromatography afforded the desired product **3m** in 79% yield as white solid. Mp 206-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.81-7.79 (m, 2H), 7.68-7.66 (m, 1H), 7.37-7.31 (m, 3H), 7.26 (s, 1H), 7.22-7.00 (m, 6H), 6.88-6.85 (m, 2H), 6.66-6.59 (m, 3H), 5.32 (s, 1H); ^{13}C NMR (100 MHz,): δ = 178.34, 141.13, 136.67, 134.89, 133.12, 132.35, 131.04, 130.44, 129.67, 129.51, 128.84, 128.53, 128.09, 127.48, 127.17, 127.04, 126.82, 125.76, 125.61, 125.57, 125.16, 121.30, 109.11, 63.25, 56.16; IR (neat): 2924, 1693, 1469, 1208, 1038, 789, 734, 695, 632 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{27}H_{19}NNaOS$ $[M+Na]^+$: 428.1080, Found: 428.1072.



Column chromatography afforded the desired product **3n** in 63% yield as white solid. Mp 215-216 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57-7.55 (m, 1H), 7.45-7.43 (m, 1H), 7.40-7.33 (m, 4H), 7.07-7.02 (m, 3H), 6.99-6.90 (m, 5H), 6.83-6.76 (m, 4H), 6.26-6.24 (m, 1H), 4.77 (s, 1H), 3.47 (AB, *J* = 12.8 Hz, 1H), 3.09 (AB, *J* = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.55, 140.69, 135.51, 134.90, 133.04, 132.33, 131.49, 130.73, 130.63, 130.17, 128.21, 128.08, 127.52, 127.39, 127.17, 126.86, 126.70, 126.19, 125.80, 125.74, 125.69, 121.23, 108.40, 61.05, 54.32, 41.61; IR (neat): 2924, 1698, 1468, 1037, 909, 748, 697, 651 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{28}H_{21}NNaOS[M+Na]^+$: 442.1236, Found: 442.1230.

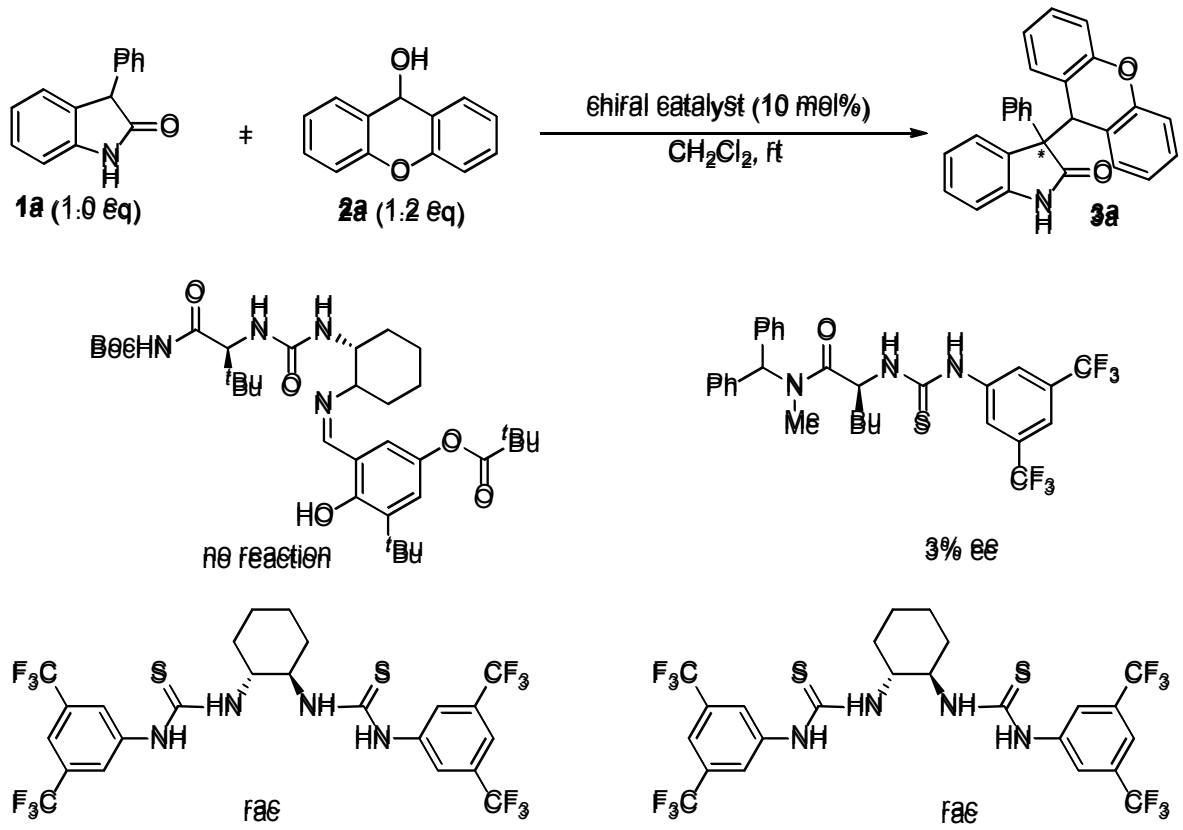


Column chromatography afforded the desired product **3o** in 79% yield as white solid. Mp 214-215 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.42 (m, 2H), 7.38-7.31 (m, 4H), 7.22-7.20 (m, 1H), 7.08-7.05 (m, 3H), 6.71-6.70 (m, 1H), 6.45-6.43 (m, 1H), 4.50 (s, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):

δ = 181.11, 139.08, 134.68, 133.40, 132.83, 132.10, 131.12, 130.74, 130.57, 130.06, 129.28, 127.70, 127.05, 126.56, 125.93, 125.78, 125.75, 114.62, 109.99, 55.08, 54.07, 21.77; IR (neat): 3341, 2924, 1708, 1469, 1377, 1278, 1048, 880, 746, 616 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{22}H_{16}BrNNaOS$ $[M+Na]^+$: 444.0028, Found: 444.0026.

The catalytic asymmetric version of 1a with 2a catalyzed by chiral (thio)urea catalysts

To a 5.0 mL vial were successively added chiral (thio)urea (0.005 mmol, 0.1 eq), **1a** (10.5 mg, 0.05 mmol), **2a** (19.8 mg, 0.1 mmol, 2.0 eq) and 0.5 mL of anhydrous CH_2Cl_2. The mixture was stirred at room temperature. Generally, the reaction proceeded very slowly and **1a** could not be consumed even after 48 h. The ee value of the product **3a** was determined by HPLC analysis of a sample taken from the reaction mixture. Unfortunately, since almost no enantioselectivity was observed when several widely used chiral ureas were examined, so we did not check the yield of **3a**.



The high resolution mass data for the complex of 1a and A_5

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry

Chinese Academy of Sciences

High Resolution MS Data Report

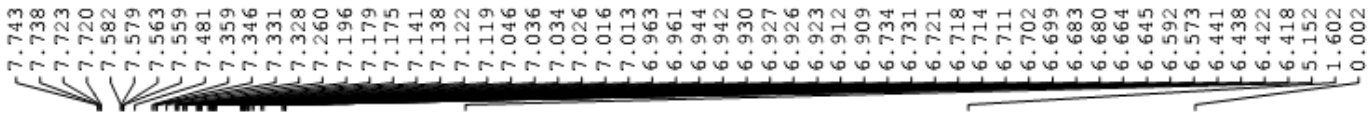
Instrument

Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS

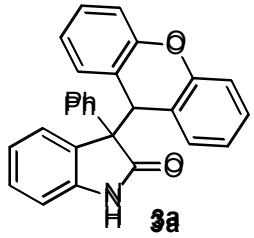
Card Serial Number	F130793
Analysis Name	D:\Data\zfj2013\20130605_000054.d
Sample Name	CL-437
Acquisition Date	3/26/2013 2:27:07 PM
Operator:	zfj
Ionization Mode	ESI-Positive
Ion Mass (Measured)	460.1439

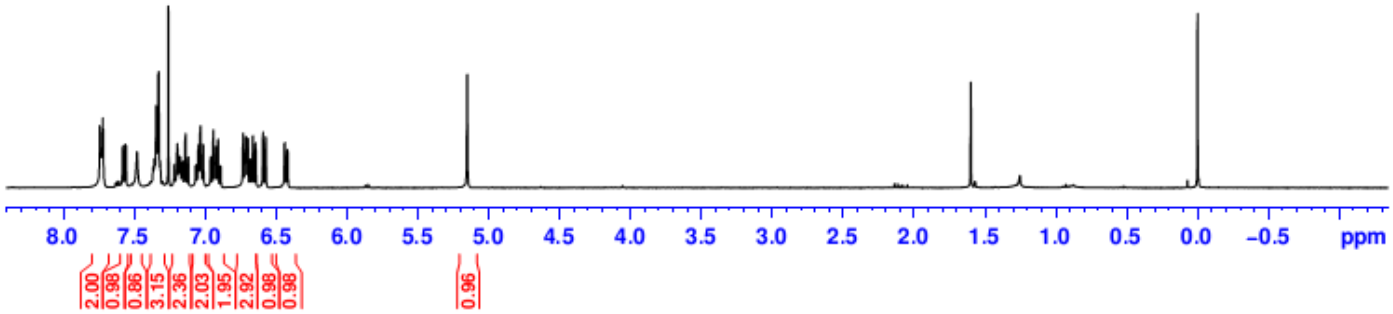
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 20 H 25 N 2 Na 1 O 9	0.032	460.1452	2.86	0.69	1.32	9.00	ok	odd
C 17 H 27 N 1 Na 1 O 12	0.046	460.1425	-2.96	-5.15	-1.36	4.50	ok	even
C 24 H 25 N 2 Na 1 O 4 S 1	0.047	460.1427	-2.58	-4.86	-1.19	13.00	ok	odd
C 27 H 23 N 3 Na 1 O 1 S 1	0.055	460.1454	3.25	0.83	1.49	17.50	ok	even

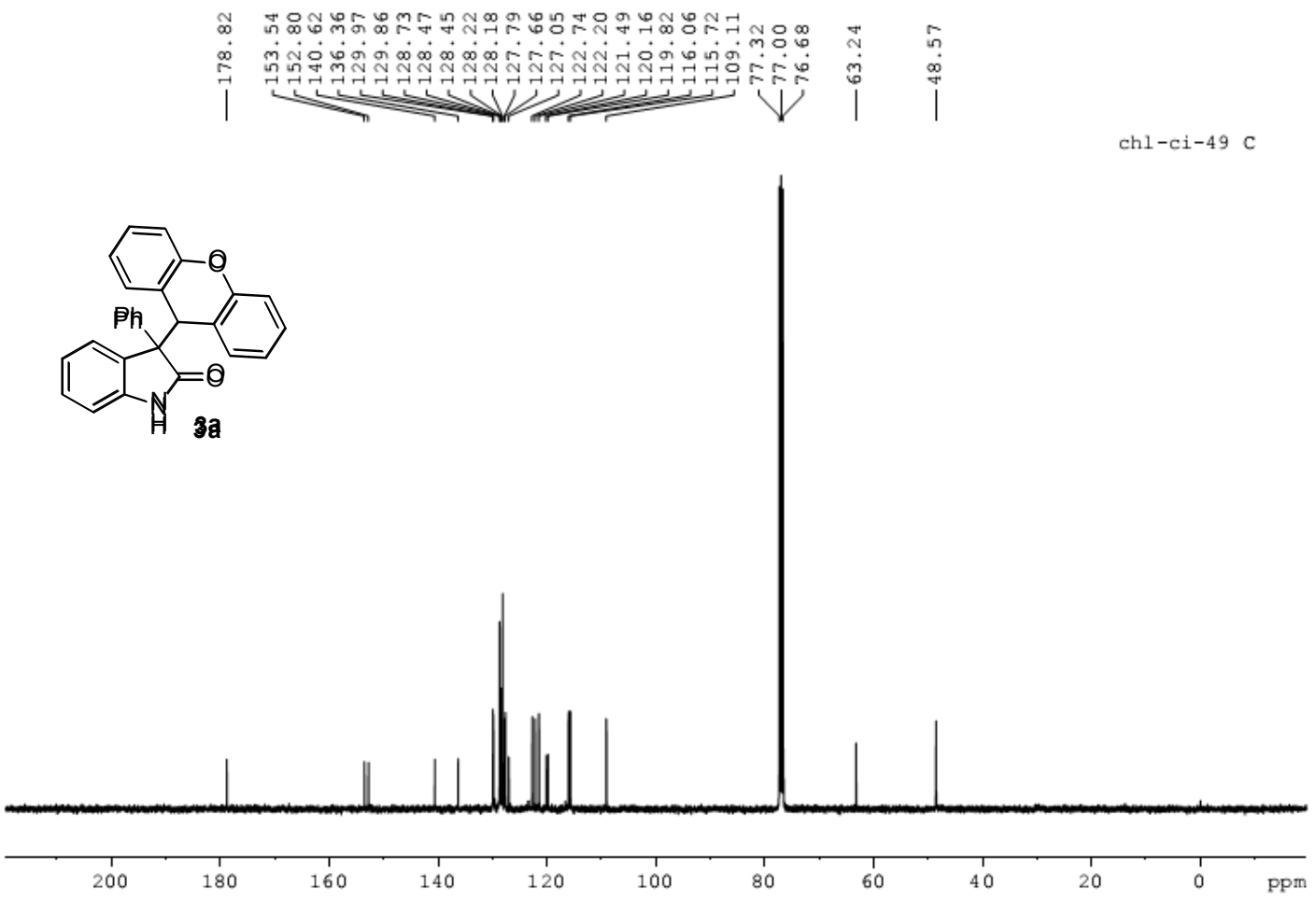
Bruker Daltonics DataAnalysis 3.4 printed: 4/20/2013 3:30:09 PM Pag1 of 1

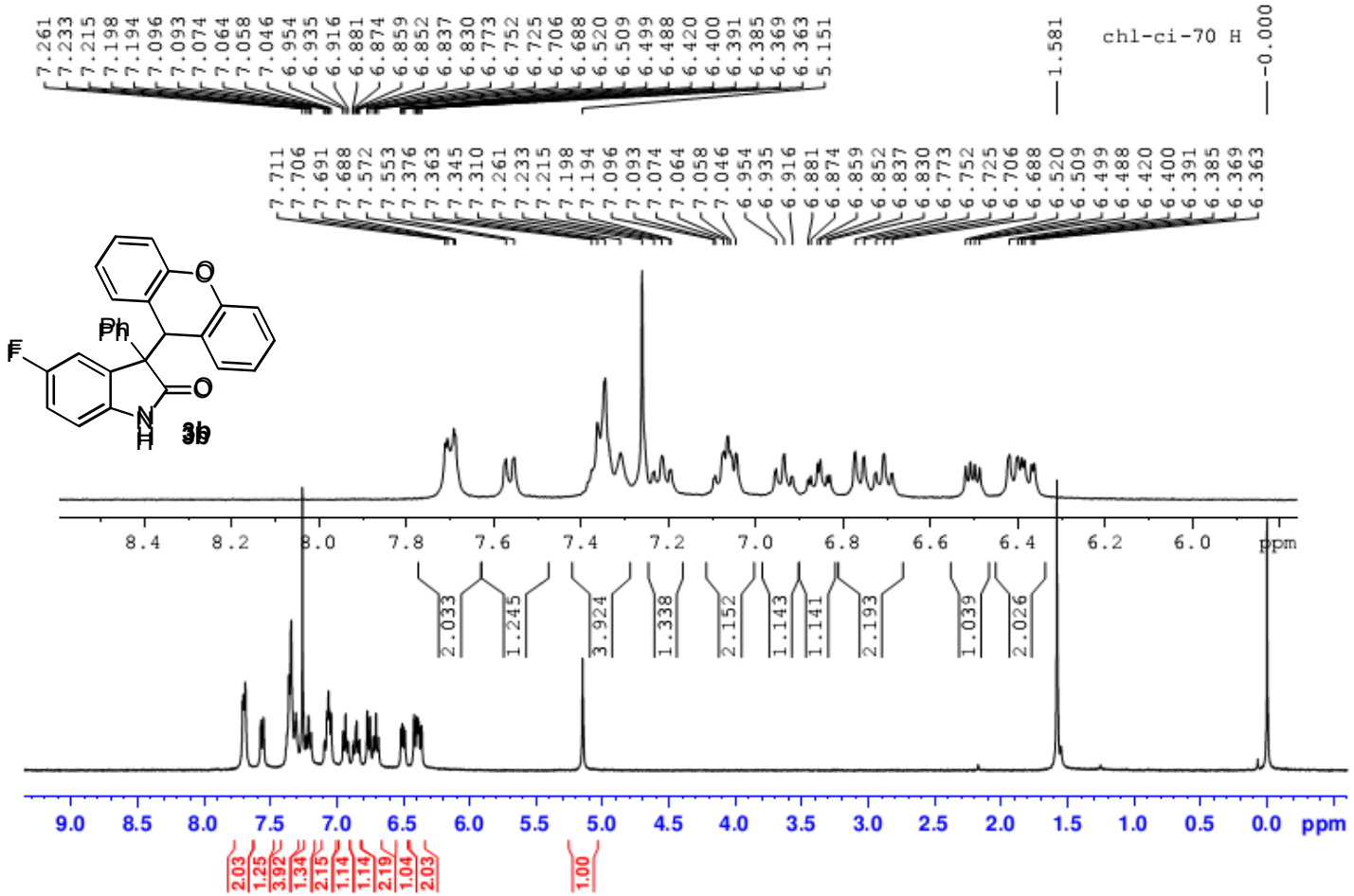


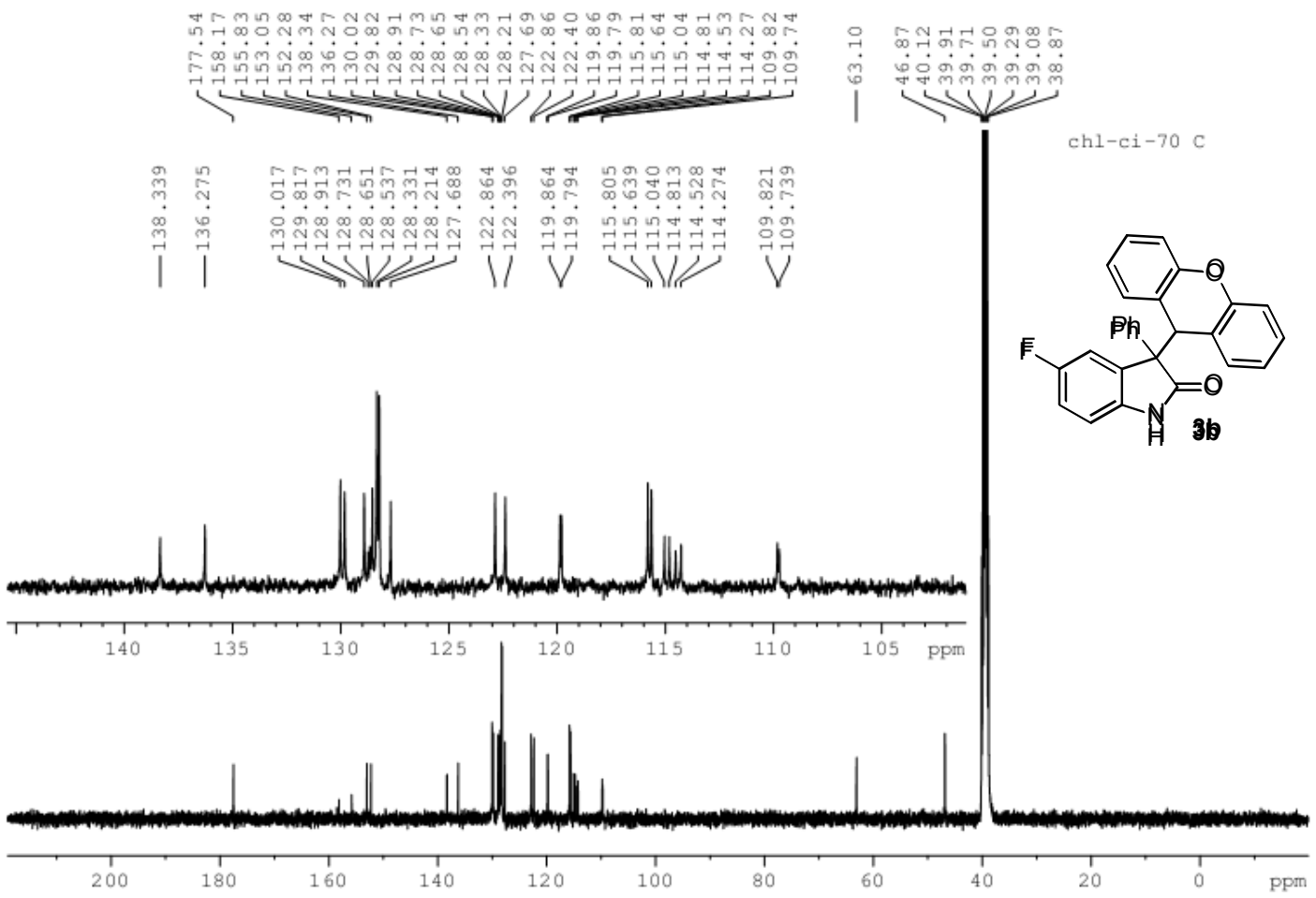
chl-ci-49 H

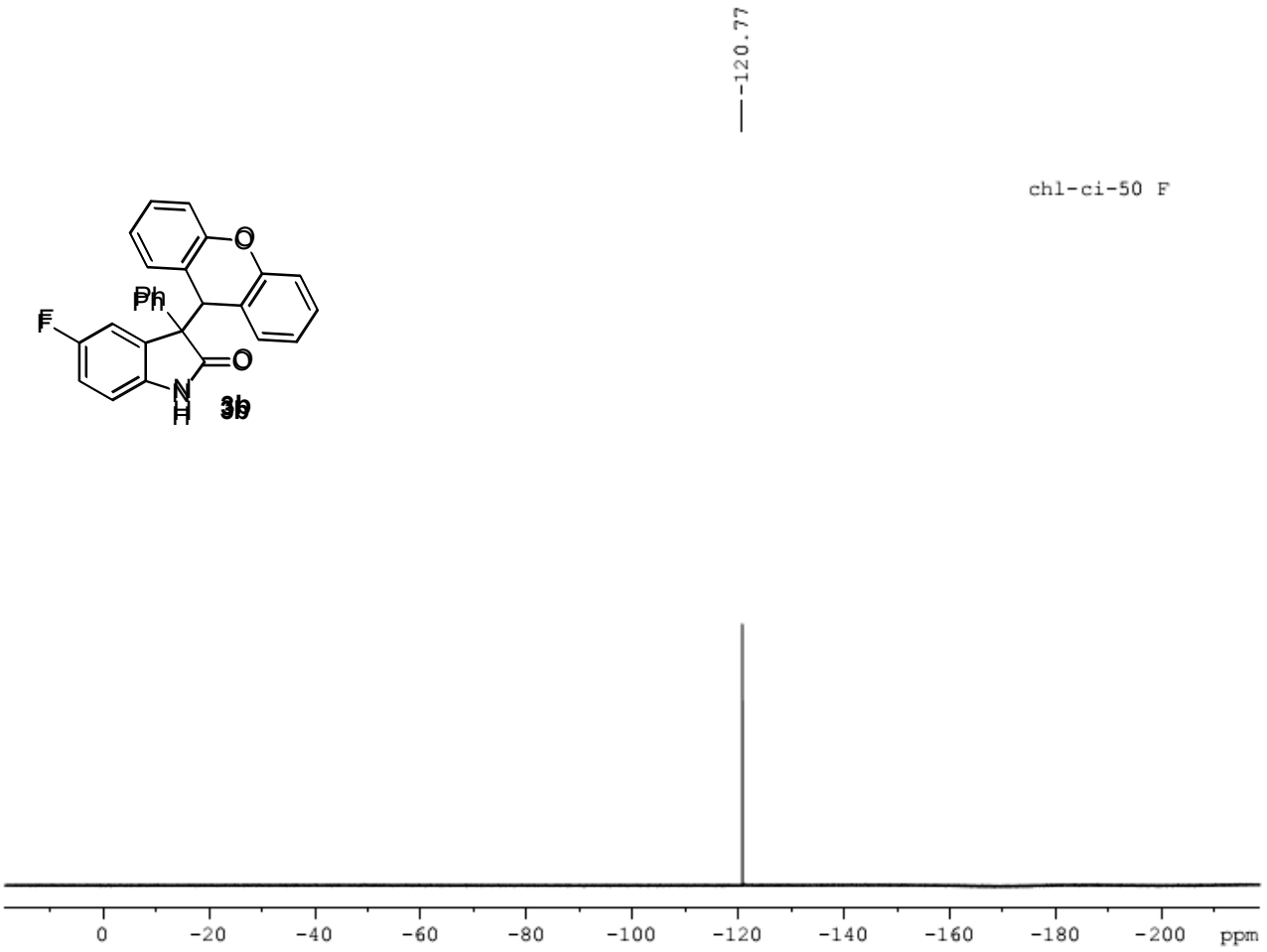


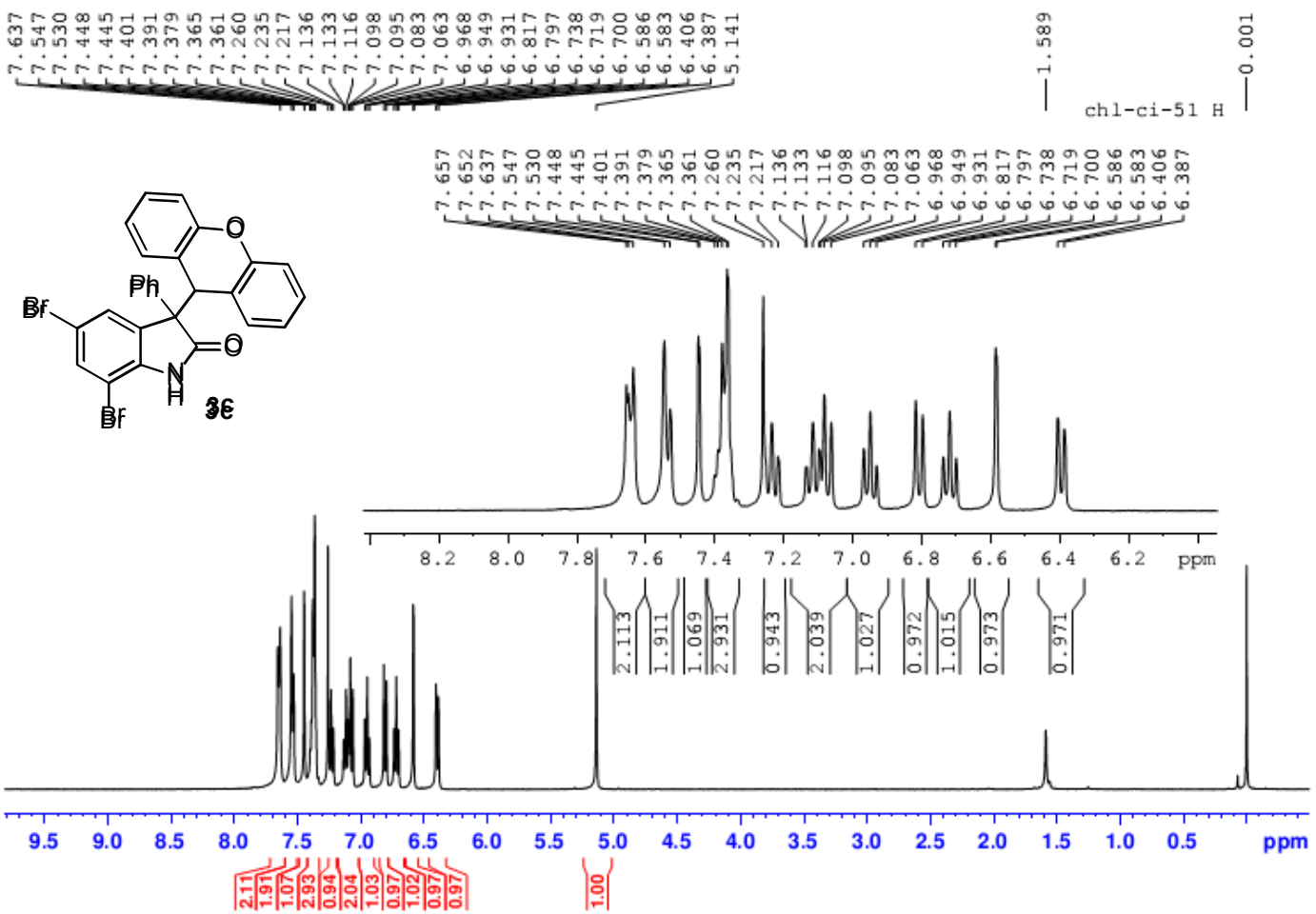


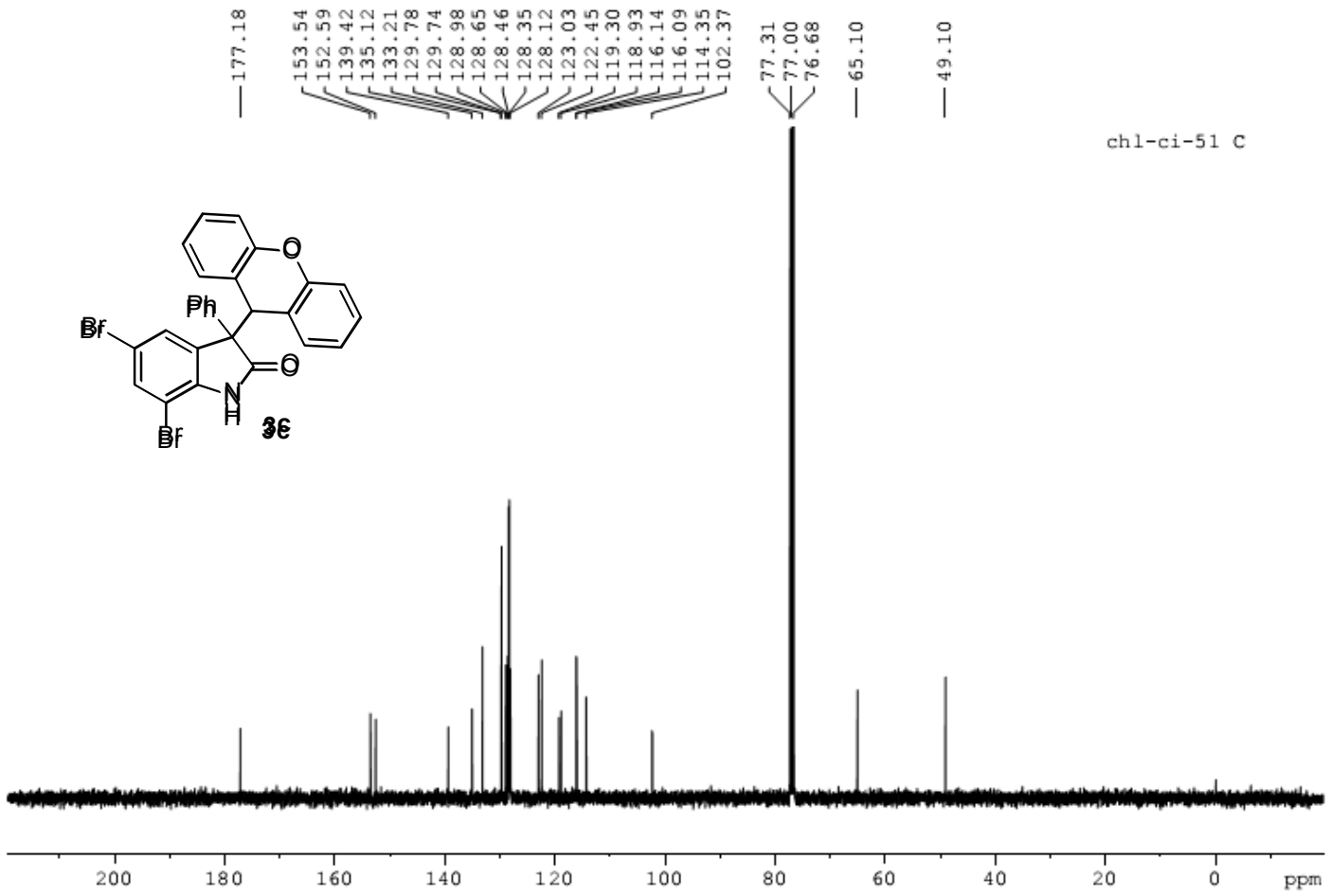


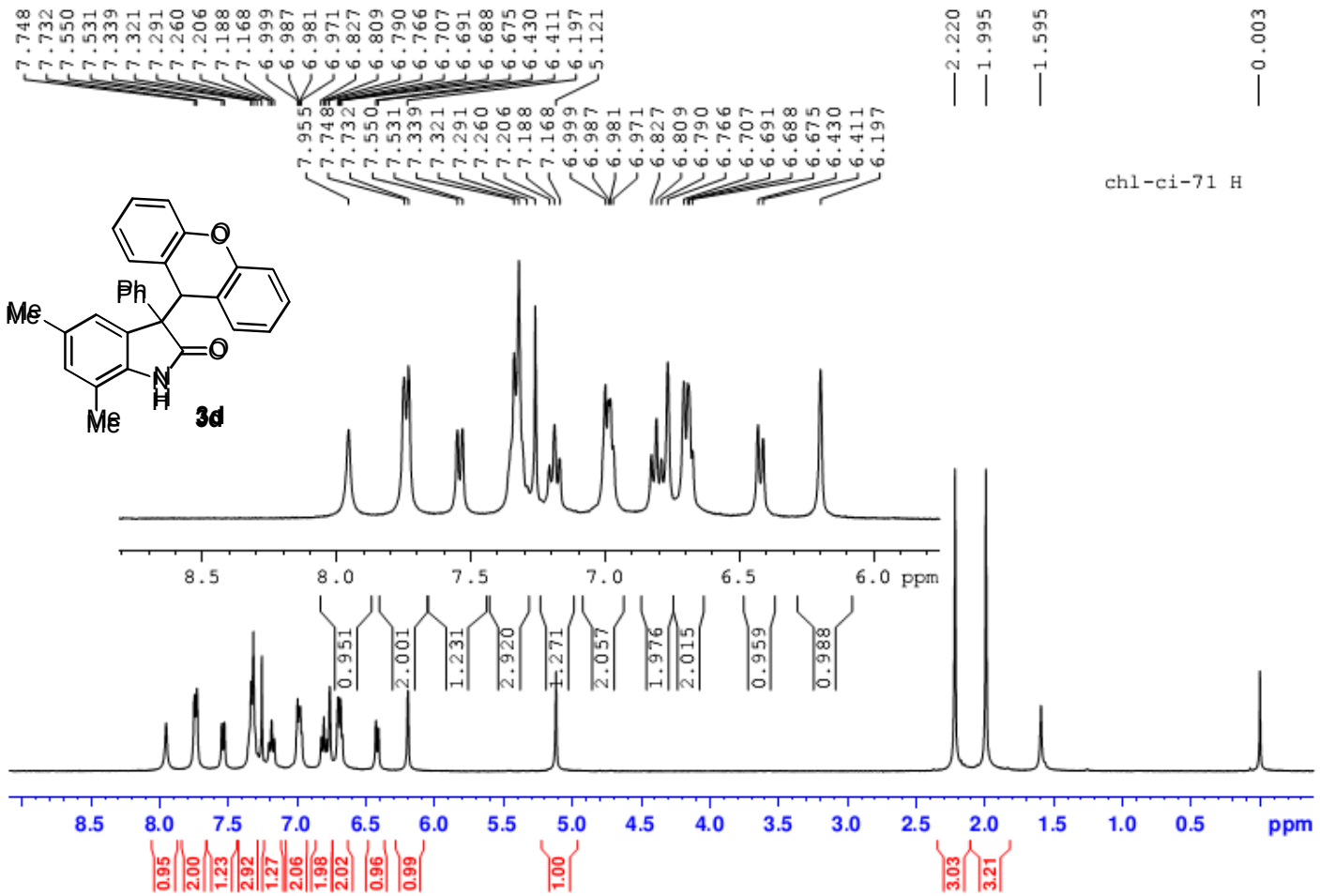


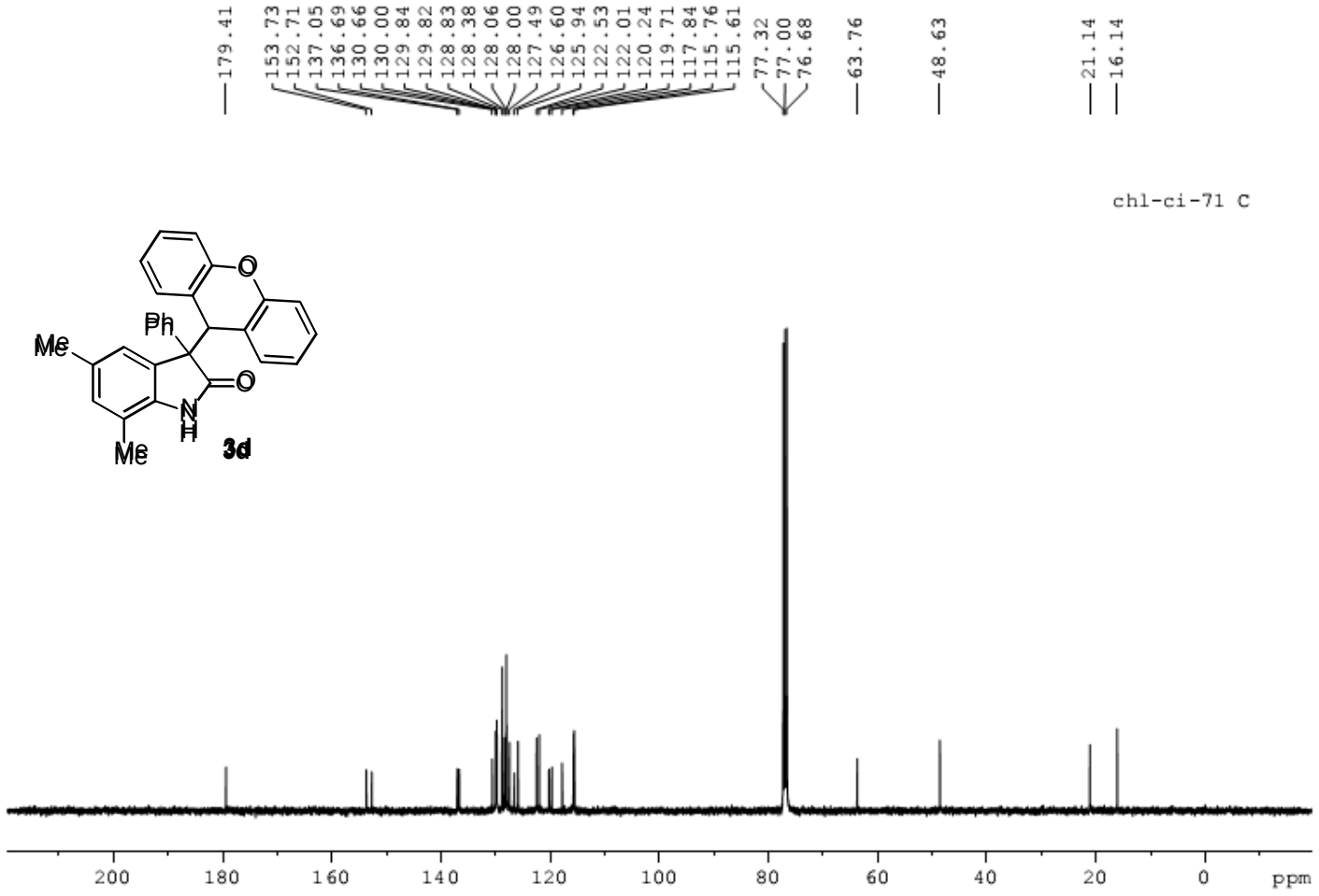


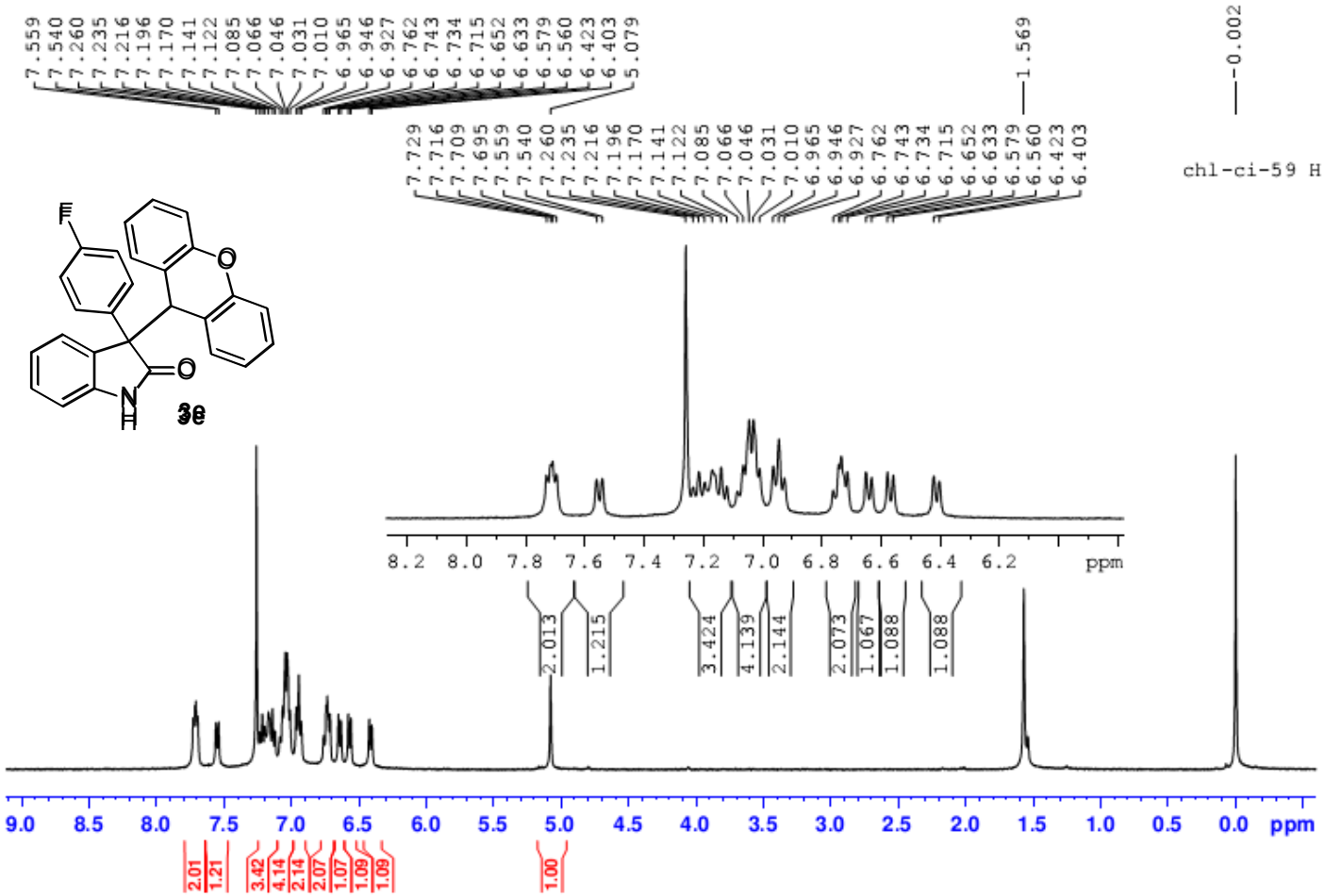


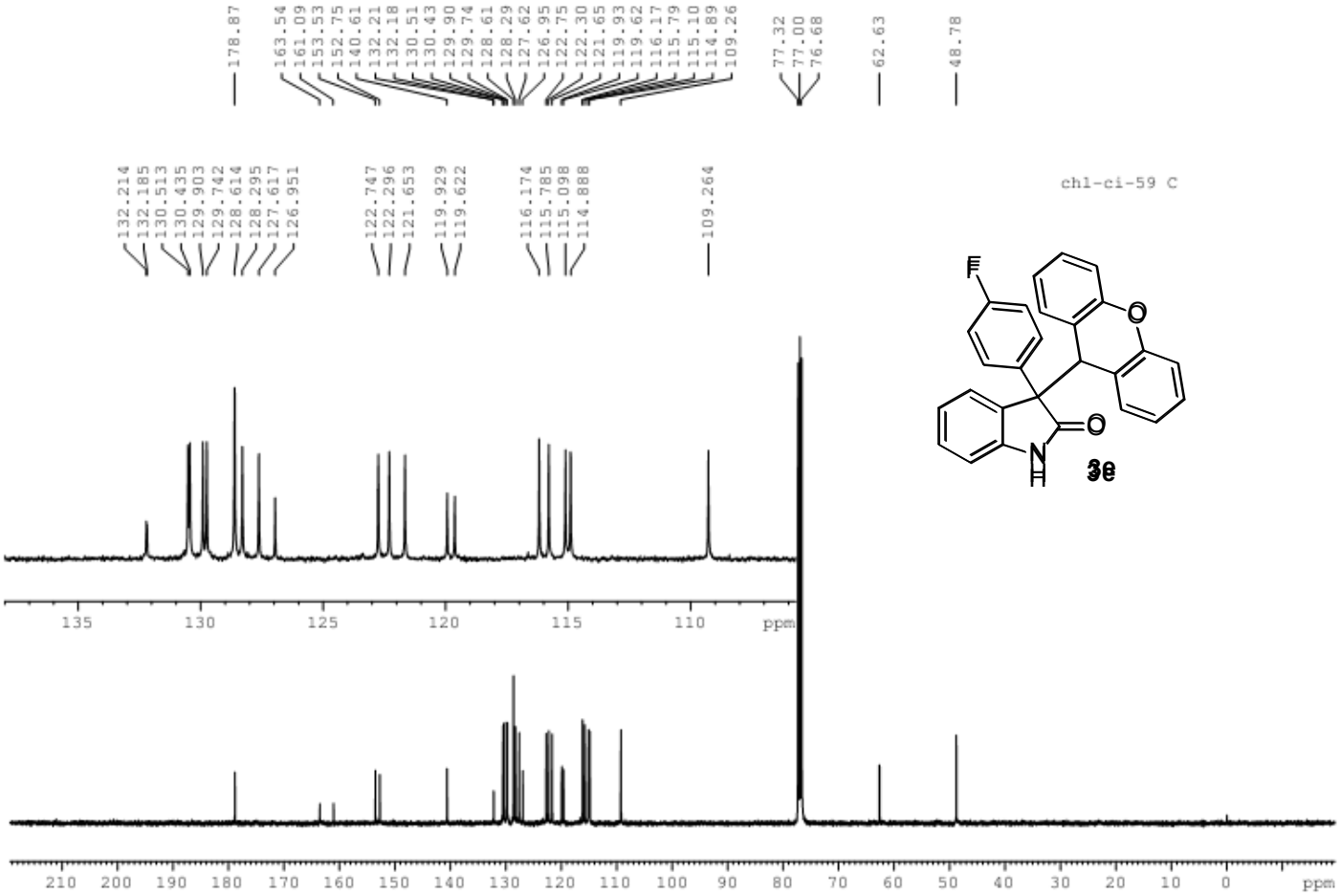












3e