Eosin Y Photoredox Catalyzed Net Redox Neutral Reaction for Regiospecific Annulation to 3-Sulphonylindoles via Anion Oxidation of Sodium Sulfinate Salts

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General information: ^{1}H and ^{13}C NMR spectra were recorded using a 500/400 MHz NMR spectrometer. The chemical shifts were referenced to signals at 7.26 and 77.0 ppm, respectively, and $CDCl_3$ was used as the solvent with TMS as the internal standard. High-resolution mass spectra were obtained with a HRMS Thermo-scientific Bruker Daltonic mass spectrometer ESI. The mass spectra were taken on an LC−MS (ESI) mass spectrometer. TLC was performed by using commercially prepared 100−400 mesh silica gel plates (GF254), and visualization was effected at 254 nm and a solution of $KMnO_4$. All 2-alkynyl arylazides[1] **1a−1o** were prepared from 2-iodoanilines and sodium sulfinates[2] **2c**, **2d**, **2e** and **2f** were synthesized according to the literature. All other reagents and solvents were obtained from commercial sources and used without further purification unless otherwise stated. The structures of known compounds were corroborated by comparing their ^{1}H NMR and ^{13}C NMR data with those in the literature. Column chromatography was performed by using Merck silica gel 100-200 mesh.

References:

1 (a) Q. Liu, P. Chen, G. Liu *ACS Catal.* 2013, **3**, 178. (b) Z. Zhang, F. Xiao, B. Huang, J. Hu, B. Fu, Z. Zhang. *Org. Lett*., 2016, **18,** 908.
2 (a) J. Liu, X. Zhou, H. Rao, F. Xiao, C.-J. Li, G.-J. Deng. *Chem. Eur. J.* 2011, **17**, 7996. (b) L. K. Liu, Y. Chi, K.-Y. Jen. *J. Org. Chem.* 1980, **45**, 406.

General Procedure for 3a-u: In dry Schlenk tube, 1-azido-2-(phenylethynyl)benzene (**1a**, 0.14 mmol, 30 mg), Eosin Y (0.006 mmol, 4.4 mg), phenyl sodium sulfinate (**2a**, 0.41 mmol, 67.4 mg) and DMF:H_2O (9:1, 1.5 mL) were added and backfilled with Nitrogen (three times). The solution was stirred at room temperature with the irradiation of Green LEDs (12 W strip of LED) for 48h under nitrogen. After the reaction was completed as monitored by TLC, the reaction mixture was diluted with ether and extracted with ether (10 mL × 3). Organic layer was washed with saturated brine solution three times and dried over anhydrous Na_2SO_4.

The solvent was then removed under vacuum. The residue was purified with silica gel column chromatography (gradient eluent of EtOAc:petroleum ether: 2:8) to give the corresponding products **3a**.

2-phenyl-3-(phenylsulfonyl)-1H-indole (3a). Pale yellow solid; (37 mg, 81%); mp 183-184 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.86 (brs, 1H), 8.24 (d, *J* = 7.3 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.35 – 7.44 (m, 4H), 7.20 – 7.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 143.8, 142.7, 134.5, 132.3, 130.2, 130.0, 129.8, 128.6, 128.1, 126.3, 125.9, 123.9, 122.6, 120.8, 112.8, 111.3; HRMS (ESI, m/z): Calcd for $C_{20}H_{15}NO_2S+H^+$: 334.090, found 334.082.

5-methyl-2-phenyl-3-(phenylsulfonyl)-1H-indole (3b). Pale yellow solid; (32 mg, 74%); mp 164-165 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (brs, 1H), 8.07 (s, 1H), 7.67 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 6.6 Hz, 2H), 7.50 – 7.36 (m, 4H), 7.35 – 7.22 (m, 3H), 7.12 (d, *J* = 8.3 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 142.6, 132.8, 132.2, 132.1, 130.2, 130.1, 129.6, 128.6, 128.1, 126.2, 126.1, 125.5, 120.2, 112.2, 110.9, 21.7.; m/z: 348 ($[M+H]^+$).

5-chloro-2-phenyl-3-(phenylsulfonyl)-1H-indole (3c). White solid; (28 mg, 72%); mp 182-183˚C (petroleum ether-EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (brs, 1H), 8.34 (d, *J* = 2.0 Hz, 1H), 7.67 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.61 – 7.42 (m, 6H), 7.38 – 7.26 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 143.5, 132.9, 132.4, 130.1, 129.9, 129.5, 128.73, 128.4, 128.1, 126.9, 126.1, 124.3, 120.1, 112.6, 112.3.; m/z: 368 ($[M+H]^+$).

5-bromo-2-phenyl-3-(phenylsulfonyl)-1H-indole (3d). White solid; (26 mg, 72%); mp 185-186 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (brs, 1H), 8.47 (d, *J* = 1.2 Hz, 1H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.56 – 7.37 (m, 7H), 7.34 – 7.22 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 143.5, 133.1, 132.5, 130.1, 129.5, 128.7, 128.3, 127.5, 127.1, 126.3, 123.5, 116.2, 112.6.; m/z: 412 ($[M+H]^+$).

2-phenyl-3-(phenylsulfonyl)-5-(trifluoromethyl)-1H-indole (3e). White solid; (29 mg, 69%); mp 184-185 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (brs, 1H), 8.62 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.68-7.38 (m, 8H), 7.34-7.26 (m, 2H);^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 143.3, 135.8, 132.6, 130.3, 130.1, 129.3, 128.79, 128.3, 126.4, 125.4, 124.9 (q, *2JC,F* = 31.5 Hz), 124.8 (q, *1JC,F* = 272.1 Hz), 120.8 (q, *3JC,F* = 3.2 Hz), 114.3, 111.8; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -60.89 (s).; m/z: 402 ($[M+H]^+$).

3-(phenylsulfonyl)-2-(p-tolyl)-1H-indole (3g). White solid; (38 mg, 84%); mp 175-176 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.69 (brs, 1H), 8.21 (d, *J* = 7.4 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.40–7.17 (m, 9H), 2.39 (s, 3H); ^{13}C NMR

(100.6 MHz, $CDCl_3$): *δ* 144.0, 143.0, 140.0, 134.5, 132.2, 130.0, 128.9, 128.6, 127.1, 126.3, 126.0, 123.8, 122.6, 120.8 , 112.6, 111.2, 21.4.; m/z: 348 ($[M+H]^+$).

2-(4-ethylphenyl)-3-(phenylsulfonyl)-1H-indole (3h). White solid; (35 mg, 80%); mp 176-177 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.34 – 8.25 (m, 1H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.46 – 7.25 (m, 8H), 2.76 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 144.0, 143.0, 134.5, 132.1, 130.1, 128.6, 127.66, 127.3, 126.3, 126.0, 123.8, 122.5, 120.7, 112.5, 111.2, 28.7, 15.3.; HRMS (ESI, m/z): Calcd for $C_{22}H_{19}NO_2S+H^+$: 362.1215, found 362.1211.

2-(4-nbutylphenyl)-3-(phenylsulfonyl)-1H-indole (3i). White solid; (34 mg, 81%); mp 173-174 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.26 - 8.20 (m, *J* 1H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.31 - 7.23 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.57 (m, 2H), 1.44 – 1.33 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.9, 143.1, 134.5, 132.1, 130.0, 128.5, 128.1, 127.2, 126.2, 126.00, 123.7, 122.5, 120.6, 112.1, 111.3, 35.4, 33.3, 22.3, 13.9.; HRMS (ESI, m/z): Calcd for $C_{24}H_{23}NO_2S+H^+$: 390.1528, found 390.1525.

2-(4-bromophenyl)-3-(phenylsulfonyl)-1H-indole (3j). White solid; (32 mg, 78%); mp 178-179 ˚C (petroleum ether-EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (brs, 1H), 8.27 – 8.21 (m, 1H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.29 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 141.2, 134.6, 132.4, 131.7, 131.4, 128.9, 128.7, 126.3, 125.7, 124.5, 124.2, 122.8, 120.8, 113.3, 111.4.; m/z: 412 ($[M+H]^+$).

2-(4-ethoxyphenyl)-3-(phenylsulfonyl)-1H-indole (3k). Pale yellow solid; (31 mg, 73%); mp 222-223 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (brd, 1H), 8.27 (d, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.55 – 7.48 (m, 2H), 7.45 – 7.35 (m, 2H), 7.34 – 7.25 (m, 4H), 6.98 – 6.69 (m, 2H), 4.10 (q, *J* = 6.9 Hz, 2H), 1.48 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 143.9, 142.9, 134.4, 132.1, 131.5, 128.6, 126.2, 126.0, 123.7, 122.5, 121.9, 120.6, 114.1, 112.1, 111.2, 63.57, 14.8.; HRMS (ESI, m/z): Calcd for $C_{22}H_{20}NO_3S+H^+$:378.1164, found 378.1159.

3-(phenylsulfonyl)-2-(pyridin-2-yl)-1H-indole (3l). Pale yellow solid; (30 mg, 65%); mp 191-192 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.72 (d, *J* = 8.1 Hz, 1H), 8.61 (d, *J* = 4.3 Hz, 1H), 8.38 – 8.26 (m, 1H), 7.88 (d, *J* = 7.5 Hz, 2H), 7.84 (td, *J* = 7.9, 1.7 Hz, 1H), 7.48 – 7.24 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 149.0, 147.4, 143.9, 138.9, 137.0, 134.3, 132.5, 128.9, 127.3, 126.13, 126.06, 124.6, 124.2, 122.8, 121.5, 112.3, 111.6.; m/z: 335 ($[M+H]^+$).

2-(isobutyl)-3-(phenylsulfonyl)-1H-indole (3m). Thick oil; (22 mg, 46%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (brs, 1H), 8.07 – 8.02 (m, 1H), 7.99 – 7.94 (m, 2H), 7.500 – 7.39 (m, 3H), 7.33 – 7.29 (m, 1H), 7.25 – 7.20 (m, 2H), 3.05 (d, *J* = 7.5 Hz, 2H), 2.18 – 2.06 (m, 1H), 0.97 (d, *J* = 6.6

Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 144.3, 134.3, 132.3, 128.9, 128.5, 126.2, 125.5, 123.2, 122.2, 119.9, 112.1, 110.9, 35.5, 29.4, 22.5; HRMS (ESI, m/z): Calcd for $C_{18}H_{19}NO_2S$ $+H^+$: 314.1215, found 314.1215.

2-cyclopropyl-3-(phenylsulfonyl)-1H-indole(3n). Thick oil; (19 mg, 38%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (brs, 1H), 8.10 – 7.95 (m, 3H), 7.52 – 7.40 (m, 3H), 7.27 – 7.15 (m, 4H), 3.21 – 2.98 (m, 1H), 1.25 – 1.17 (m, 2H), 0.91-0.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 144.2, 133.6, 132.3, 128.9, 126.2, 125.9, 123.2, 122.3, 119.4, 112.71, 110.91, 8.8, 8.0; HRMS (ESI, m/z): Calcd for $C_{17}H_{15}NO_2S$ $+H^+$: 298.0902, found 298.0898.

2-phenethyl-3-(phenylsulfonyl)-1H-indole (3o). Thick oil; (24 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (brs, 1H), 8.05 (d, *J* = 7.2 Hz, 1H), 7.99 – 7.93 (m, 2H), 7.51 – 7.39 (m, 3H), 7.32 – 7.12 (m, 8H), 3.49 (t, *J* = 7.5 Hz, 2H), 3.05 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 144.1, 140.3, 134.2, 132.4, 129.0, 128.8, 128.55, 126.6, 126.1, 125.3, 123.3, 122.3, 119.9, 111.5, 110.9, 35.8, 28.9; HRMS (ESI, m/z): Calcd for $C_{22}H_{19}NO_2S+H^+$: 362.1215, found 362.1213.

3-((4-methylphenyl)sulfonyl)-2-phenyl-1H-indole (3p). White solid; (34 mg, 71%); mp 193-194 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (brs, 1H), 8.27 – 8.20 (m, 1H), 7.56 (d, *J* = 8.1 Hz, 4H), 7.53 – 7.27 (m, 6H), 7.09 (d, *J* = 8.2 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 142.4, 141.1, 134.5, 130.2, 130.2, 129.8, 129.2, 128.1, 126.4, 125.8, 123.9, 122.5, 120.9, 113.4, 111.2, 21.4.; m/z: 348 ($[M+H]^+$).

3-((4-fluorophenyl)sulfonyl)-2-phenyl-1H-indole (3q). Pale yellow solid; (30 mg, 63%); mp 194-195 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (brs, 1H), 8.30 – 8.20 (m, 1H), 7.70 – 7.60 (m, 2H), 7.53 (dd, *J* = 9.6, 8.2 Hz, 2H) 7.53 – 7.35 (m, 4H), 7.34 – 7.26 (m, 2H), 6.95 (t, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.85 (d, *JC-F* = 254.2 Hz), 142.6, 140.0, 134.5, 130.2, 129.9, 129.1, 128.2, 125.7, 124.1, 122.8, 120.7, 115.9, 115.6, 113.0, 111.3; HRMS (ESI, m/z): m/z Calcd for $C_{20}H_{14}FNO_2S$+H:352.0808, found 352.0806.

3-((4-chlorophenyl)sulfonyl)-2-phenyl-1H-indole (3r). White solid; (35 mg, 69%); mp 192-193 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (brs, 1H), 8.28 – 8.20 (m, 1H), 7.58 – 7.54 (m, 4H), 7.53 – 7.37 (m, 4H), 7.34 – 7.28 (m, 2H), 7.25 (dt, *J* = 9.2, 2.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 142.4, 138.7, 134.5, 130.2, 130.0, 129.9, 128.9, 128.2, 127.7, 125.7, 124.1, 122.8, 120.7, 112.6, 111.4.; m/z: 368 ($[M+H]^+$).

3-((4-bromophenyl)sulfonyl)-2-phenyl-1H-indole (3s). White solid; (41 mg, 73%); mp 194-195 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (brs, 1H), 8.28 - 8.20 (m, 1H), 7.59 – 7.55 (m, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.54 – 7.37 (m, 4H), 7.35 – 7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 142.8, 134.4, 131.9, 130.2, 130.1, 129.9, 128.2, 127.9, 127.2, 125.7, 124.2, 122.9, 120.8, 112.8, 111.3.; m/z: 412 ($[M+H]^+$).

3-(naphthalen-2-ylsulfonyl)-2-phenyl-1H-indole (3t). Pale yellow solid; (24 mg, 43%); mp 191-192 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (brs, 1H), 8.39 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.25 (d, *J* = 1.6 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.69 – 7.44 (m, 8H), 7.44 – 7.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 140.7, 134.6, 134.4, 132.0, 130.3, 130.1, 129.9, 129.3, 128.9, 128.4, 128.2, 127.7, 127.3, 127.1, 125.9, 124.1, 122.7, 122.1, 121.0, 113.4, 111.1.; m/z: 384 ($[M+H]^+$).

3-(methylsulfonyl)-2-phenyl-1H-indole (3u). White solid; (18 mg, 48%); mp 170-171 ˚C (petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (brs, 1H), 8.20 - 8.10 (m, 1H), 7.75 – 7.65 (m, 2H), 7.52-7.40 (m, 4H), 7.38 – 7.27 (m, 2H), 2.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 134.4, 130.1, 130.0, 129.8, 128.4, 125.9, 124.2, 122.7, 120.7, 111.3, 45.4.; m/z: 272 ($[M+H]^+$).


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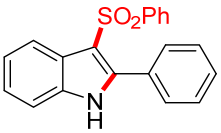
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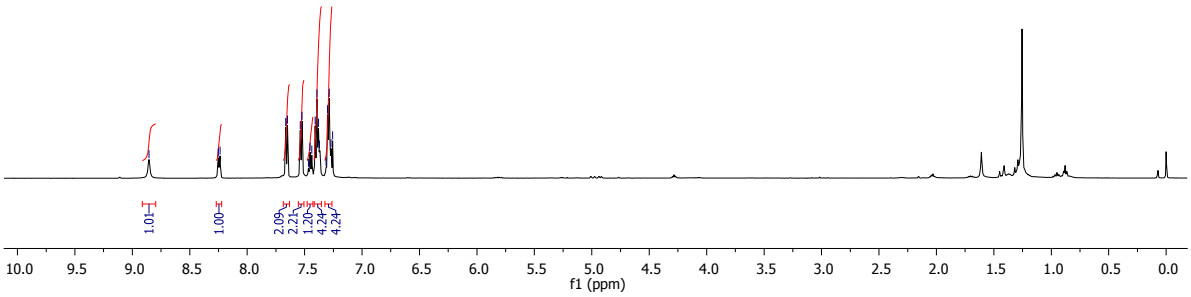
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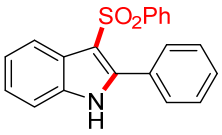
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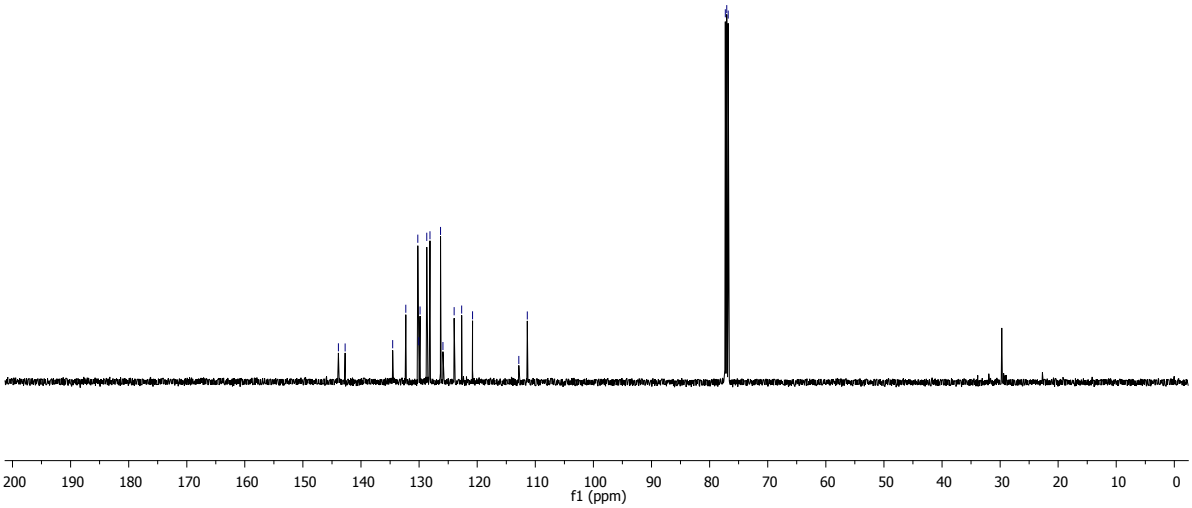
3a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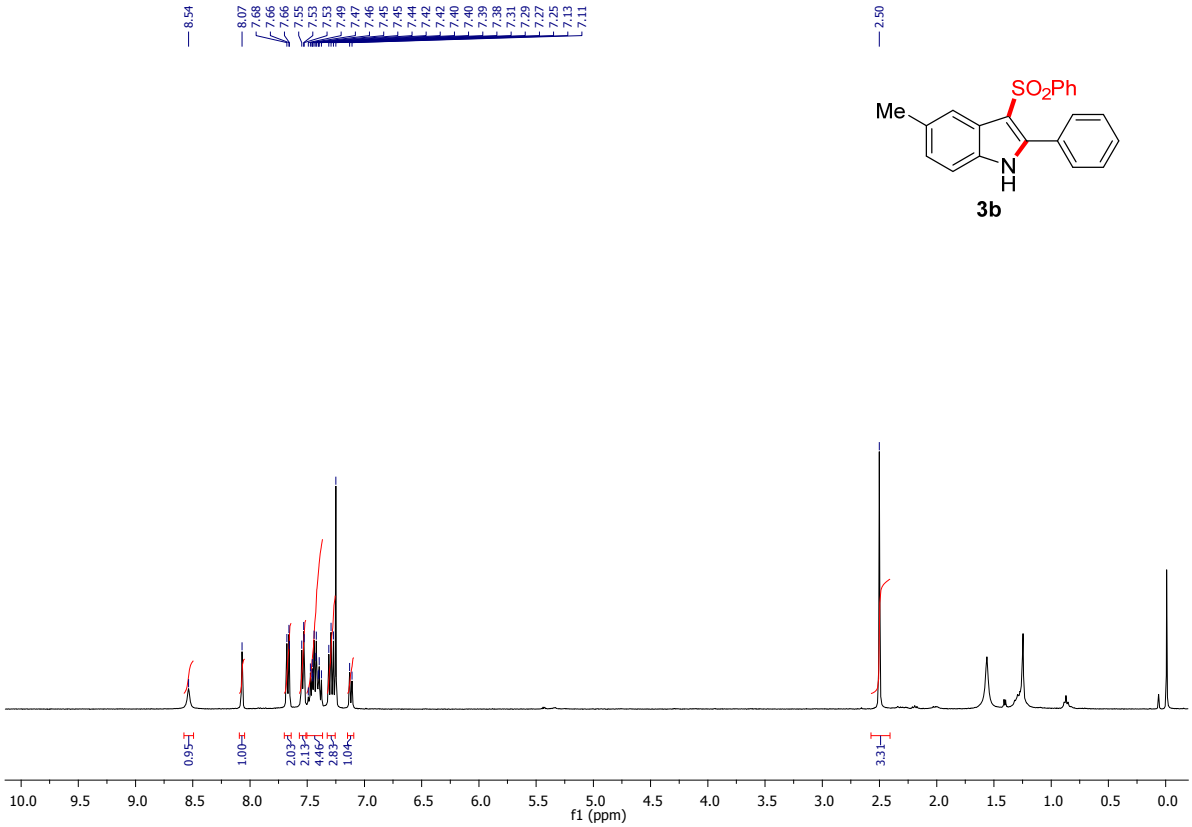
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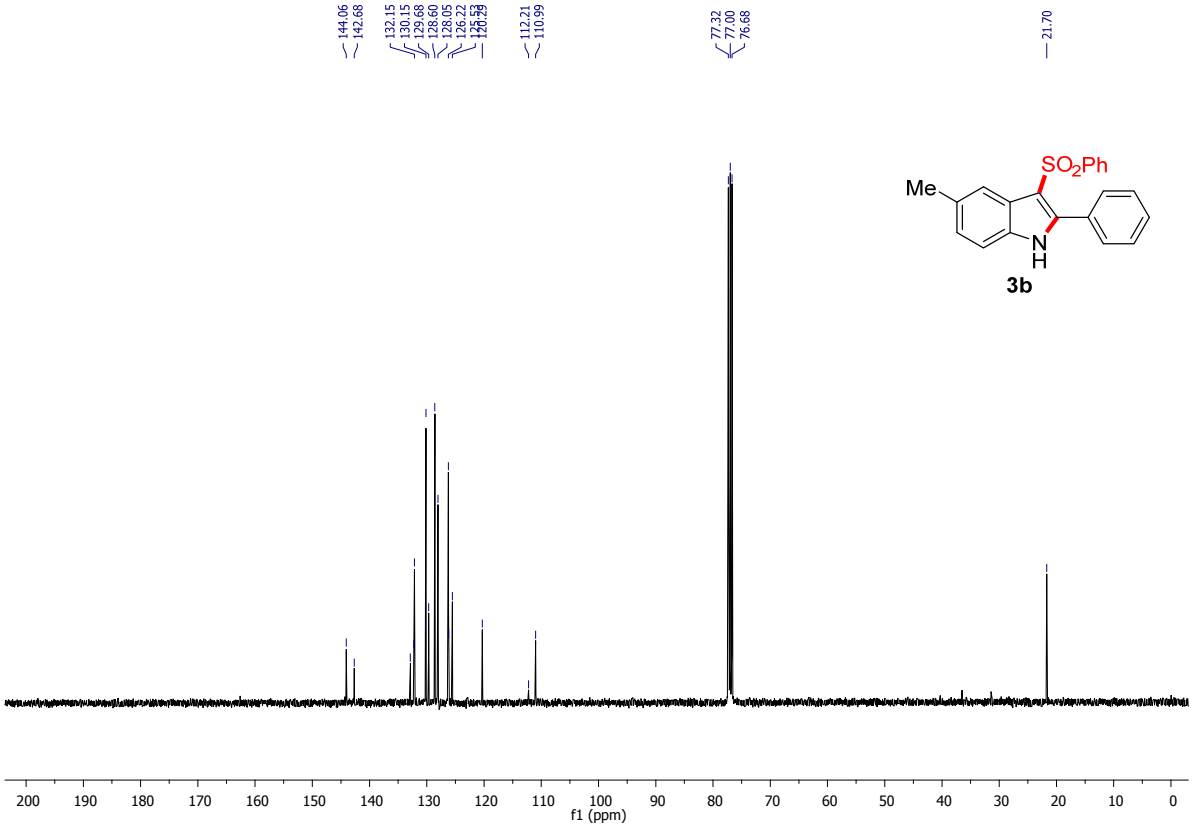
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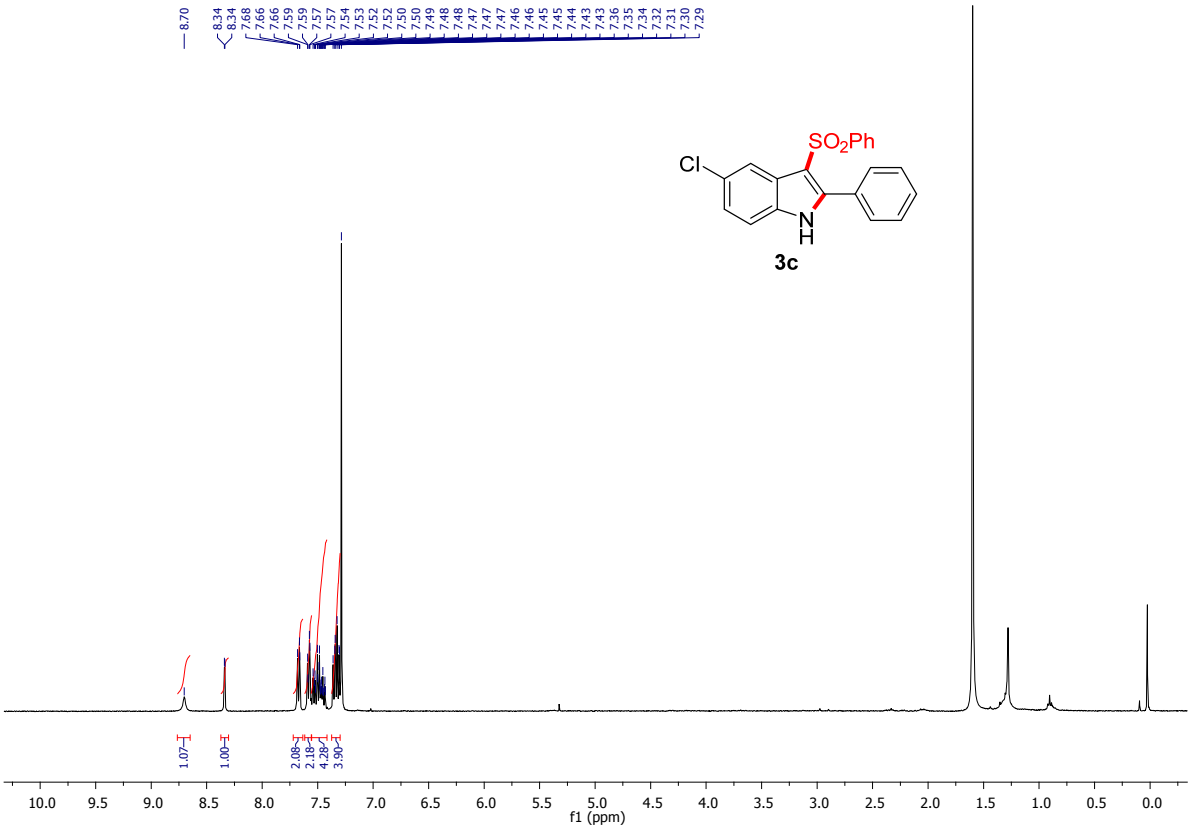
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SO2Ph
Cl
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H
3c
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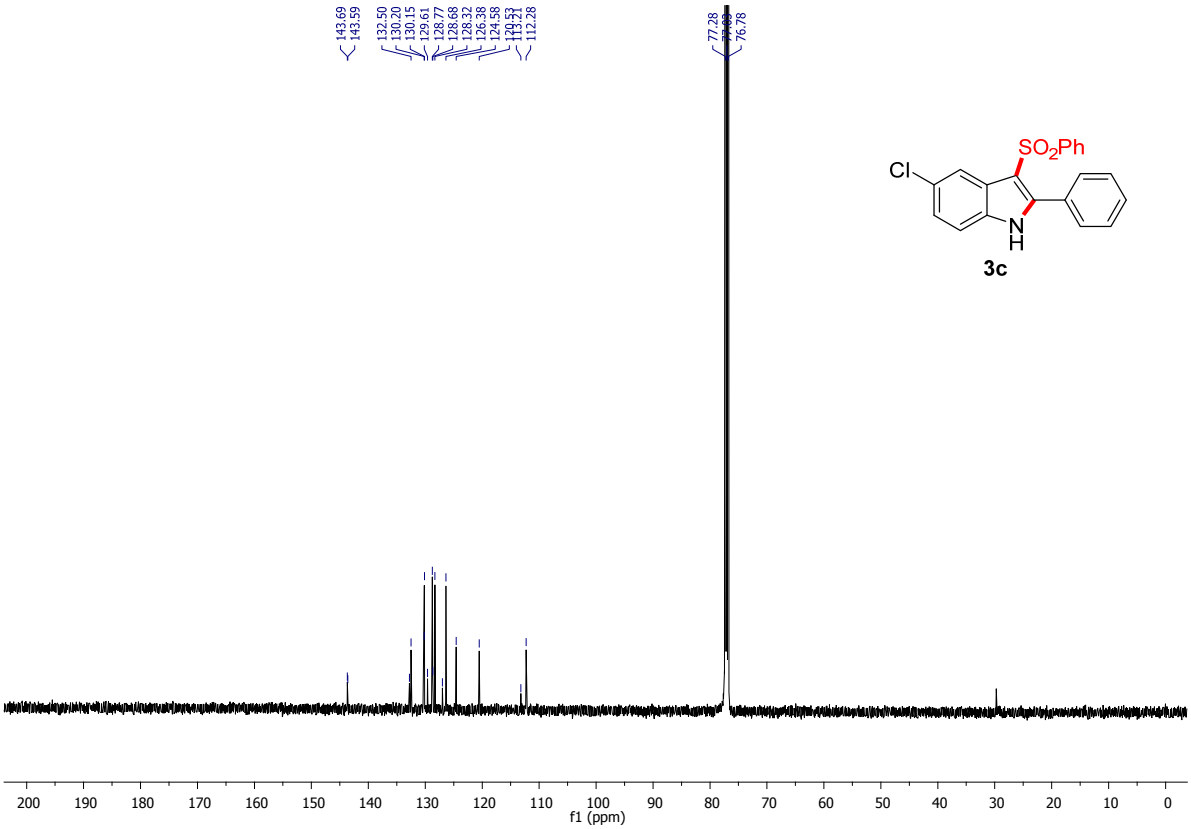
1.00
2.08
2.18
4.28
3.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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143.59
132.50
130.20
130.15
129.61
128.77
128.68
128.32
126.38
124.58
120.53
113.21
112.28
77.28
77.03
76.78
SO2Ph
Cl
N
H
3c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.75
8.75
8.46
8.46
7.64
7.64
7.62
7.62
7.54
7.54
7.52
7.52
7.52
7.52
7.50
7.50
7.48
7.48
7.45
7.45
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.41
7.39
7.39
7.39
7.39
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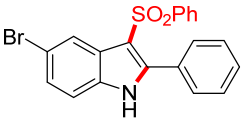
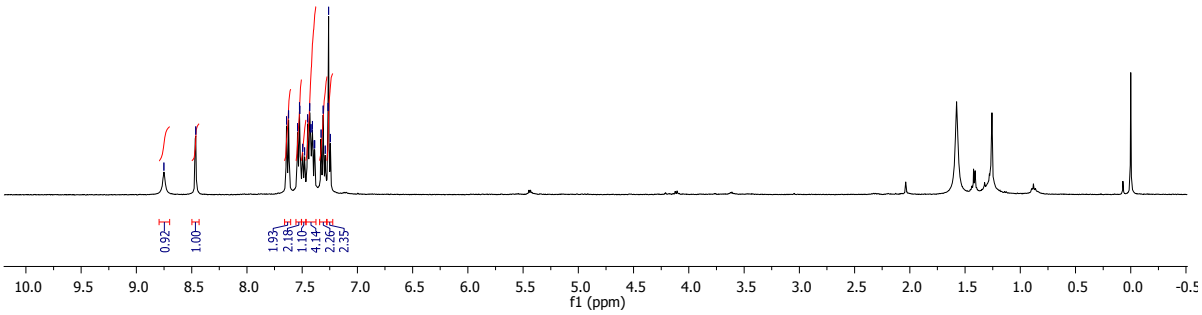
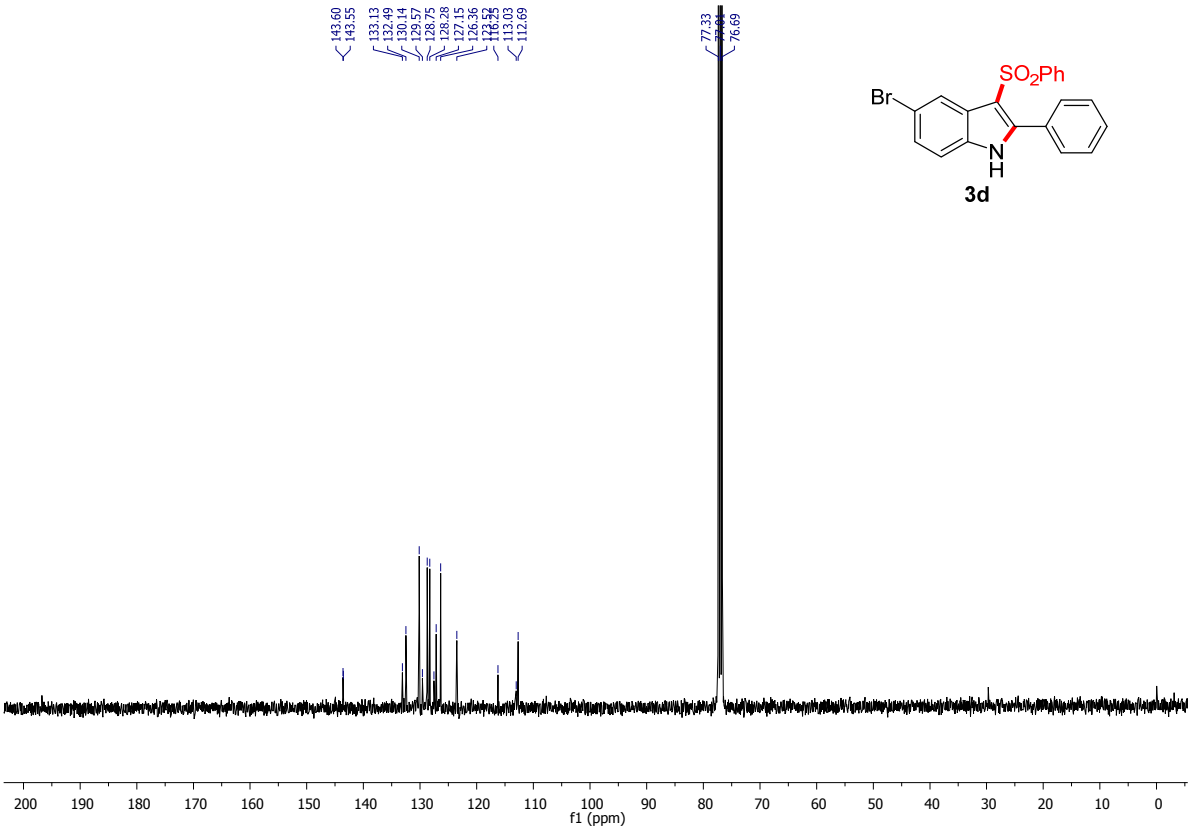
7.27
7.27
7.26
7.26
7.24
7.24


SO2Ph
Br
N
H

3d

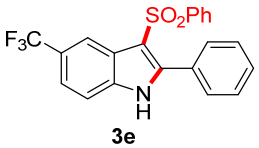

0.92
1.00
1.93
2.18
1.10
4.14
2.26
2.35
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.60
143.55
133.13
132.49
130.14
129.57
128.75
128.28
127.15
126.56
113.03
112.69
77.33
77.01
76.69
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

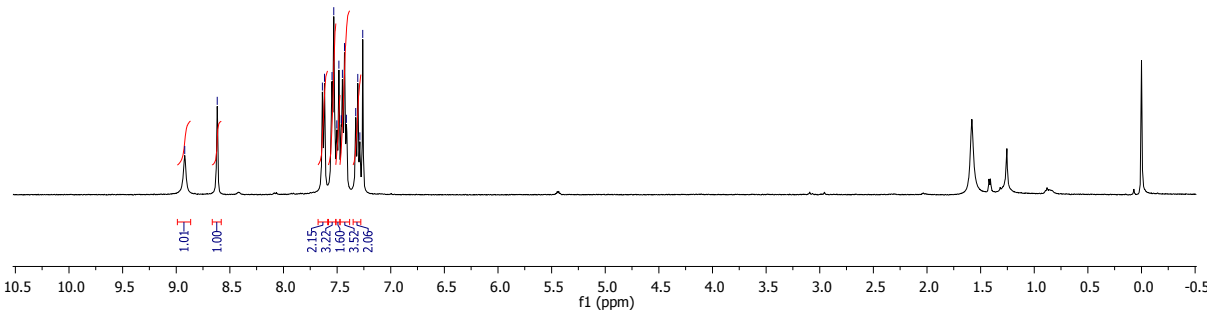
SO2Ph
Br
N
H

3d

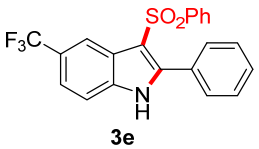

8.92
8.62
7.64
7.62
7.55
7.53
7.50
7.48
7.46
7.45
7.43
7.41
7.33
7.31
7.29
7.26


SO2Ph
F3C
N
H

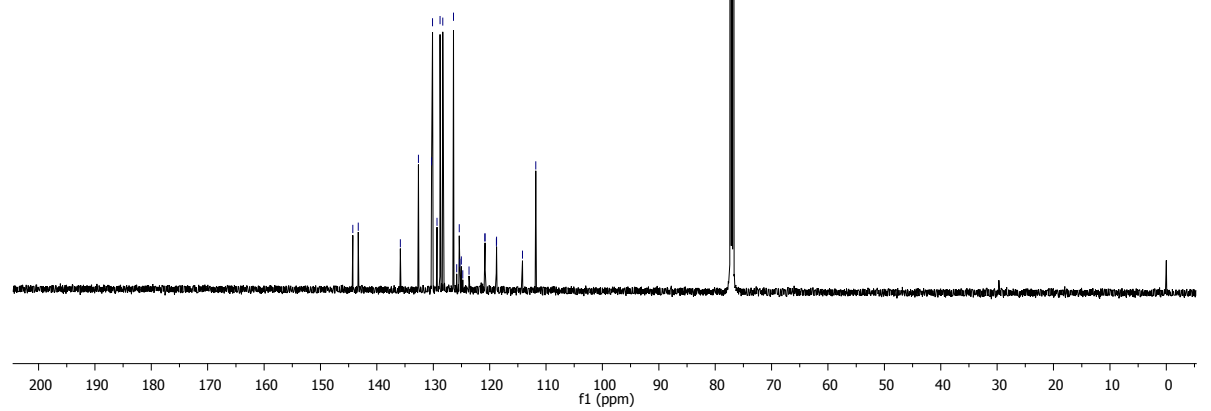
3e

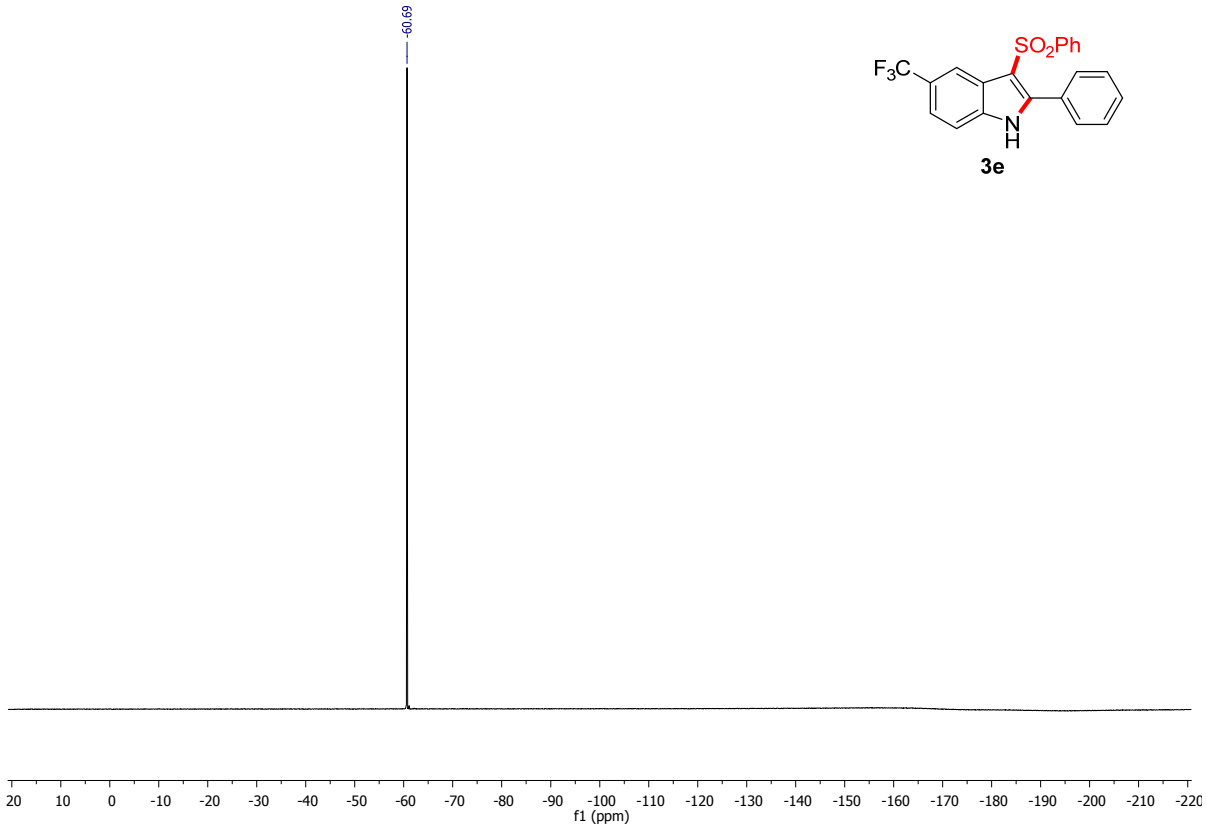

1.01
1.00
2.15
3.22
1.60
3.52
2.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

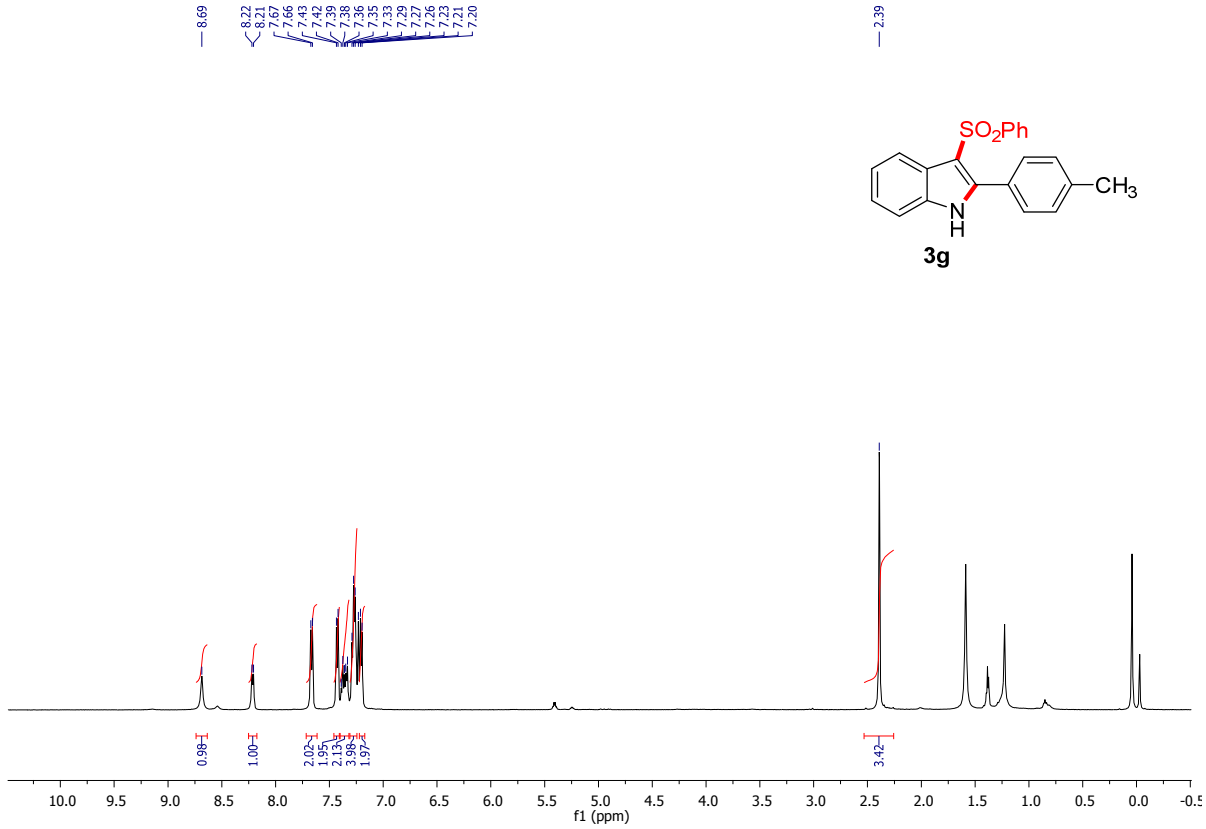

144.27
143.31
135.83
132.64
130.29
130.12
129.34
128.79
128.31
126.40
125.83
125.40
125.28
125.03
124.77
123.67
120.83
120.81
118.80
118.77
114.18
111.82
77.27
77.02
76.76

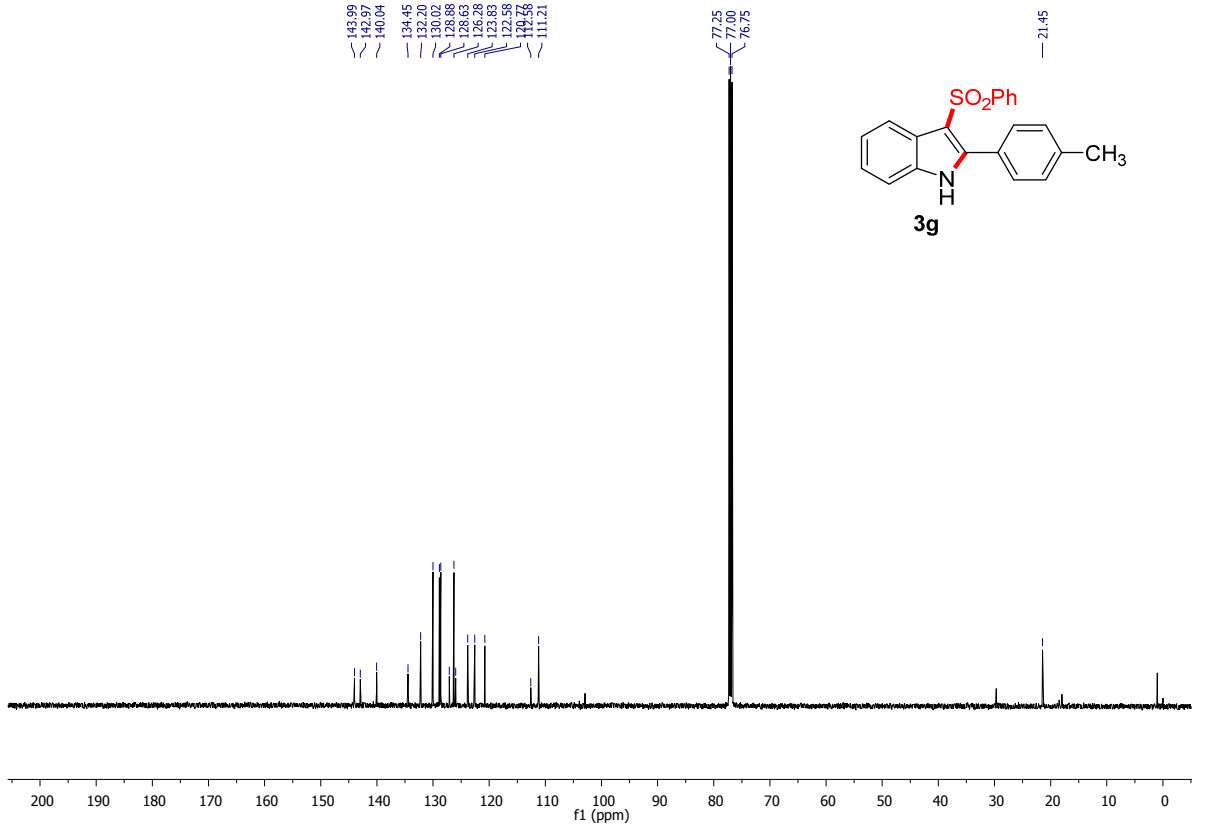

SO2Ph
F3C
N
H

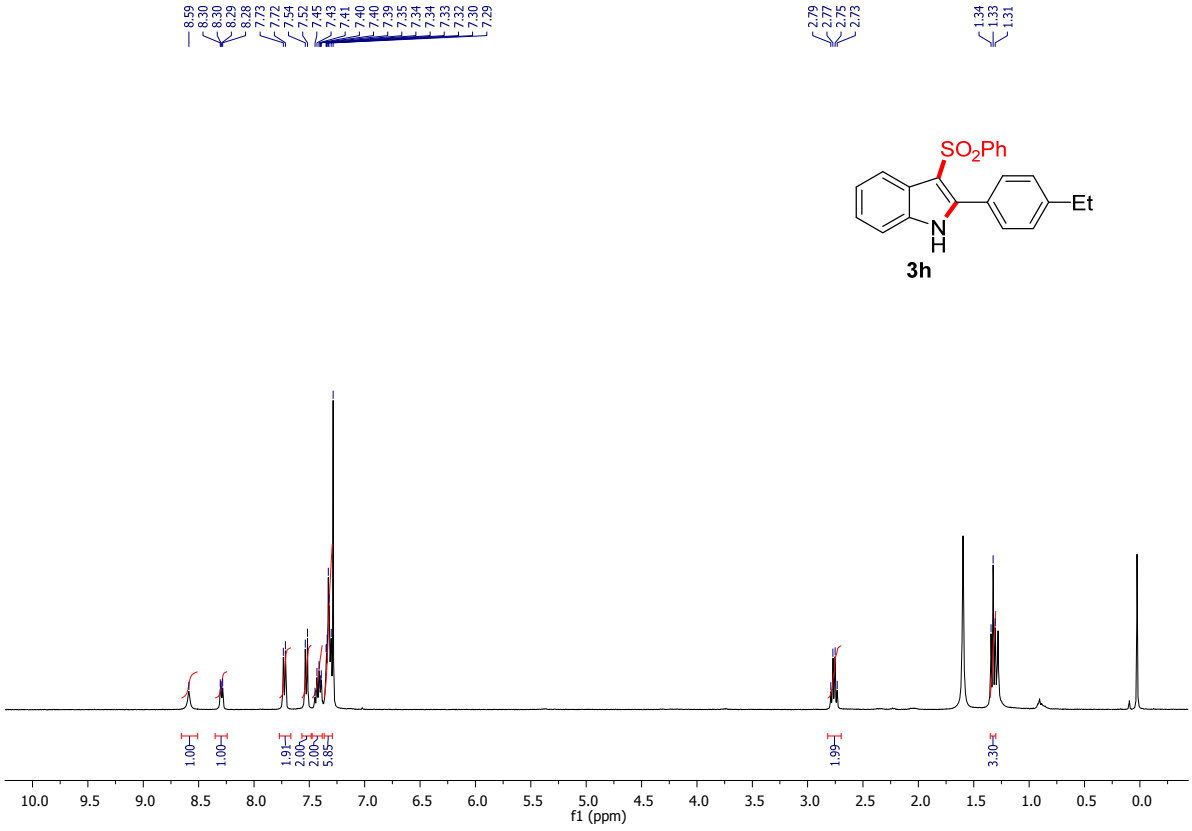
3e

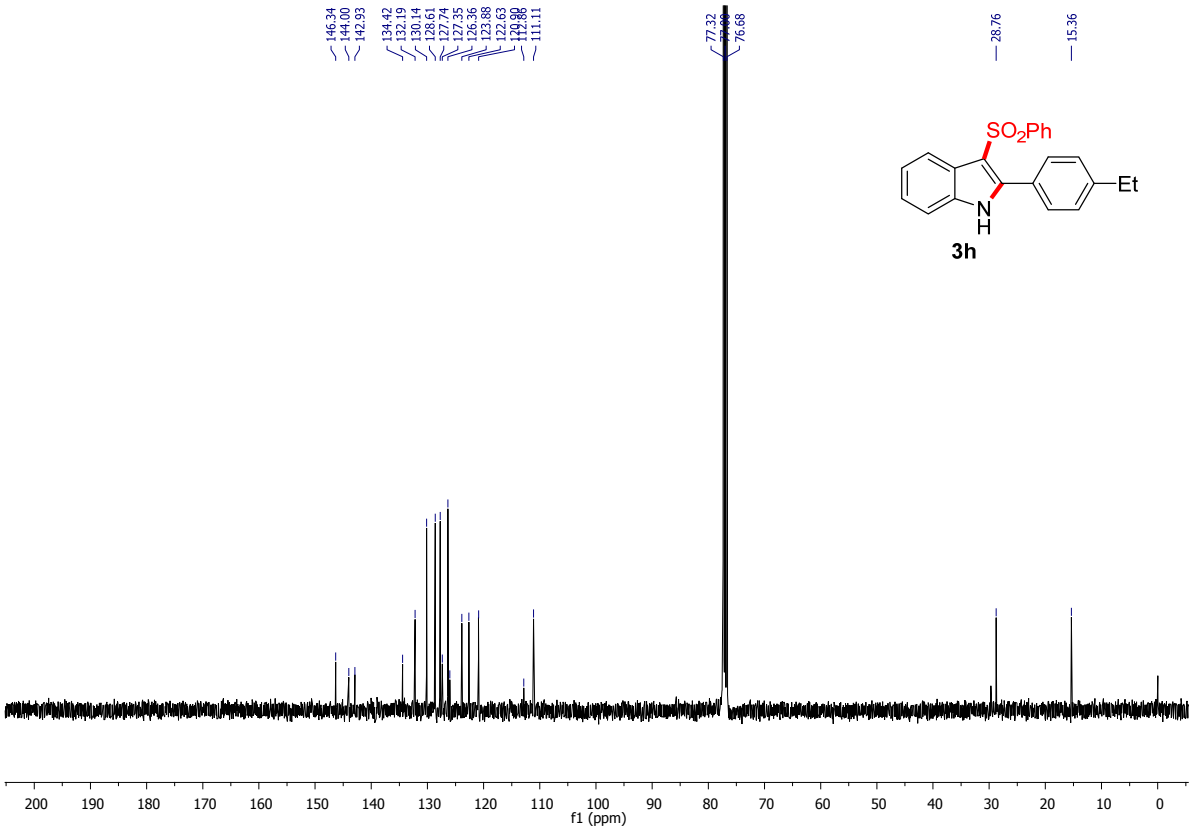

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

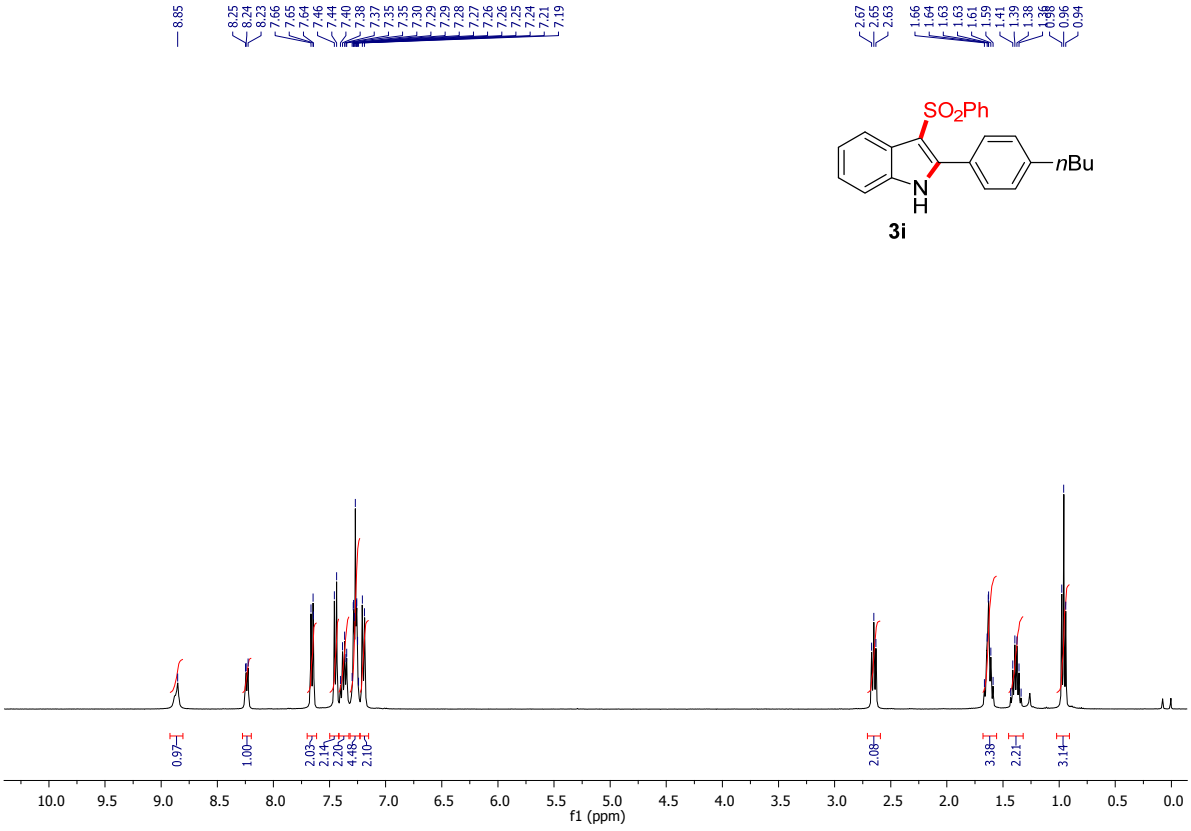

-60.69
SO2Ph
F3C
N
H
3e
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

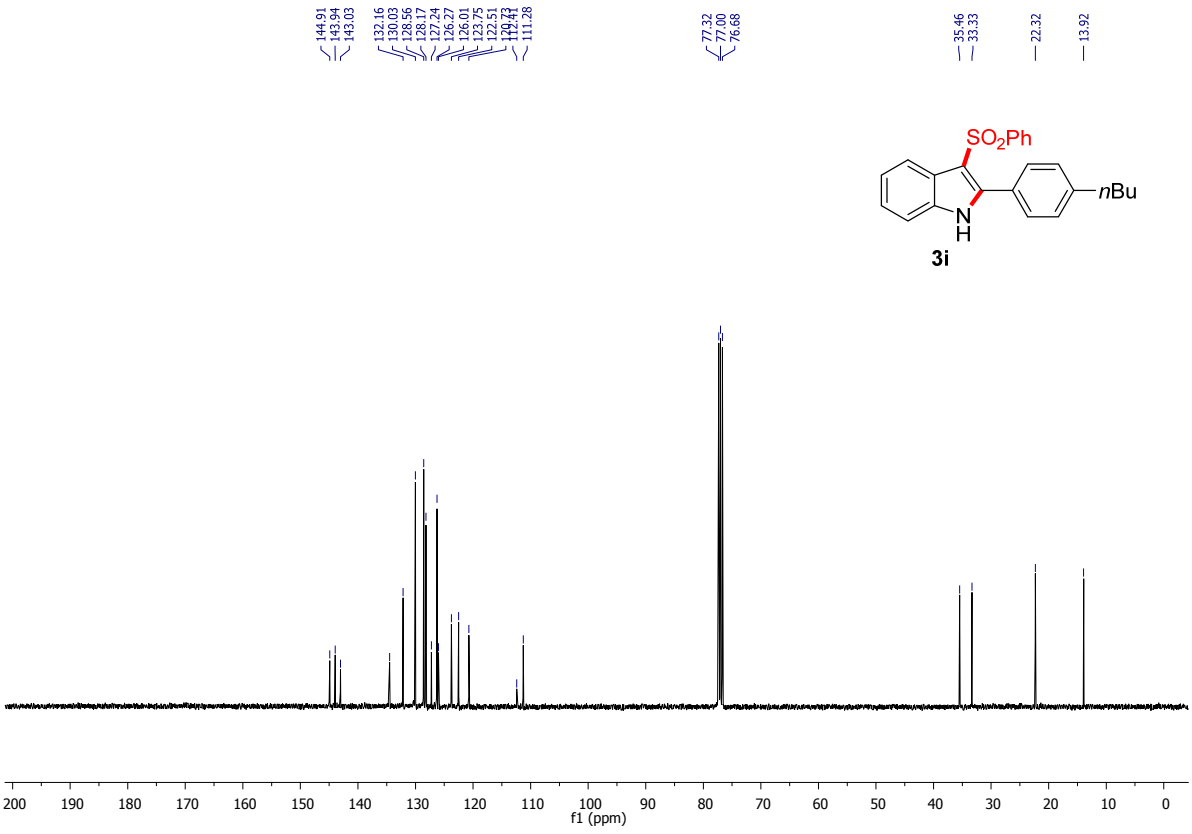

8.69
8.22
8.21
7.67
7.66
7.43
7.42
7.39
7.38
7.36
7.35
7.33
7.29
7.27
7.26
7.23
7.21
7.20
2.39
SO2Ph
CH3
N
H
3g
0.98
1.00
2.02
1.95
2.13
3.98
1.97
3.42
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


143.99
142.97
140.04
134.45
132.20
130.02
128.88
128.63
126.28
123.83
122.58
111.21
77.25
77.00
76.75
21.45
SO2Ph
CH3
N
H
3g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

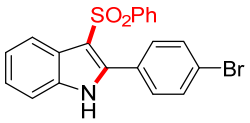

8.59
8.30
8.30
8.29
8.28
7.73
7.72
7.54
7.52
7.45
7.43
7.41
7.40
7.40
7.39
7.35
7.34
7.34
7.33
7.32
7.30
7.29
2.79
2.77
2.75
2.73
1.34
1.33
1.31
SO2Ph
Et
N
H
3h
1.00
1.00
1.91
2.00
2.00
5.85
1.99
3.30
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


146.34
144.00
142.93
134.42
132.19
130.14
128.61
127.74
127.35
126.36
123.88
122.63
120.90
112.88
111.11
77.32
77.00
76.68
28.76
15.36
SO2Ph
Et
N
H
3h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

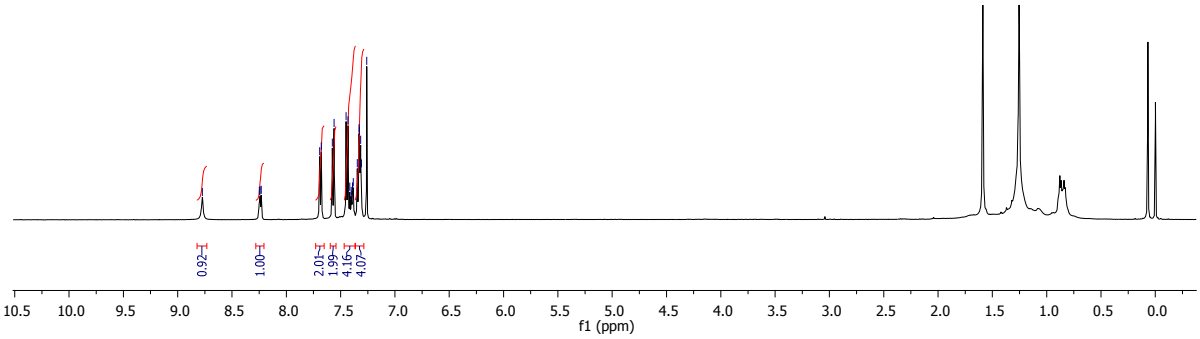

8.85
8.25
8.24
8.23
7.66
7.65
7.64
7.46
7.44
7.40
7.38
7.37
7.35
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.21
7.19
2.67
2.65
2.63
1.66
1.64
1.63
1.63
1.61
1.59
1.41
1.39
1.38
0.98
0.96
0.94
SO2Ph
nBu
N
H
3i
0.97
1.00
2.03
2.14
2.20
4.48
2.10
2.08
3.38
2.21
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.91
143.94
143.03
132.16
130.03
128.56
128.17
127.24
126.27
126.01
123.75
122.51
111.28
77.32
77.00
76.68
35.46
33.33
22.32
13.92
SO2Ph
nBu
N
H
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

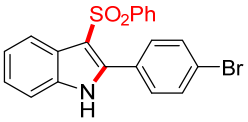

8.77
8.25
8.24
8.23
7.69
7.68
7.58
7.56
7.45
7.43
7.42
7.40
7.40
7.39
7.38
7.35
7.33
7.33
7.32
7.32
7.31
7.26


SO2Ph
Br
N
H

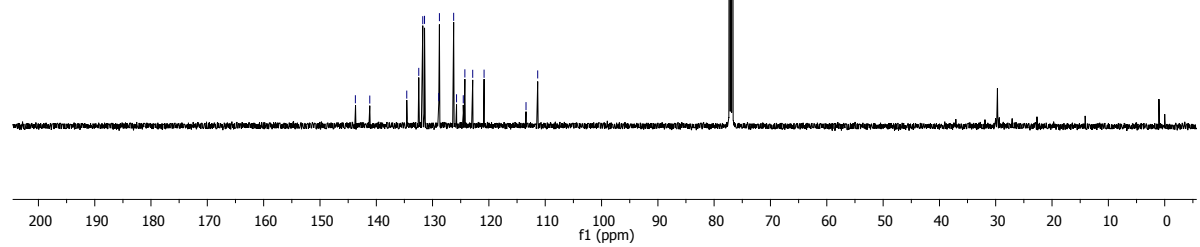
3j

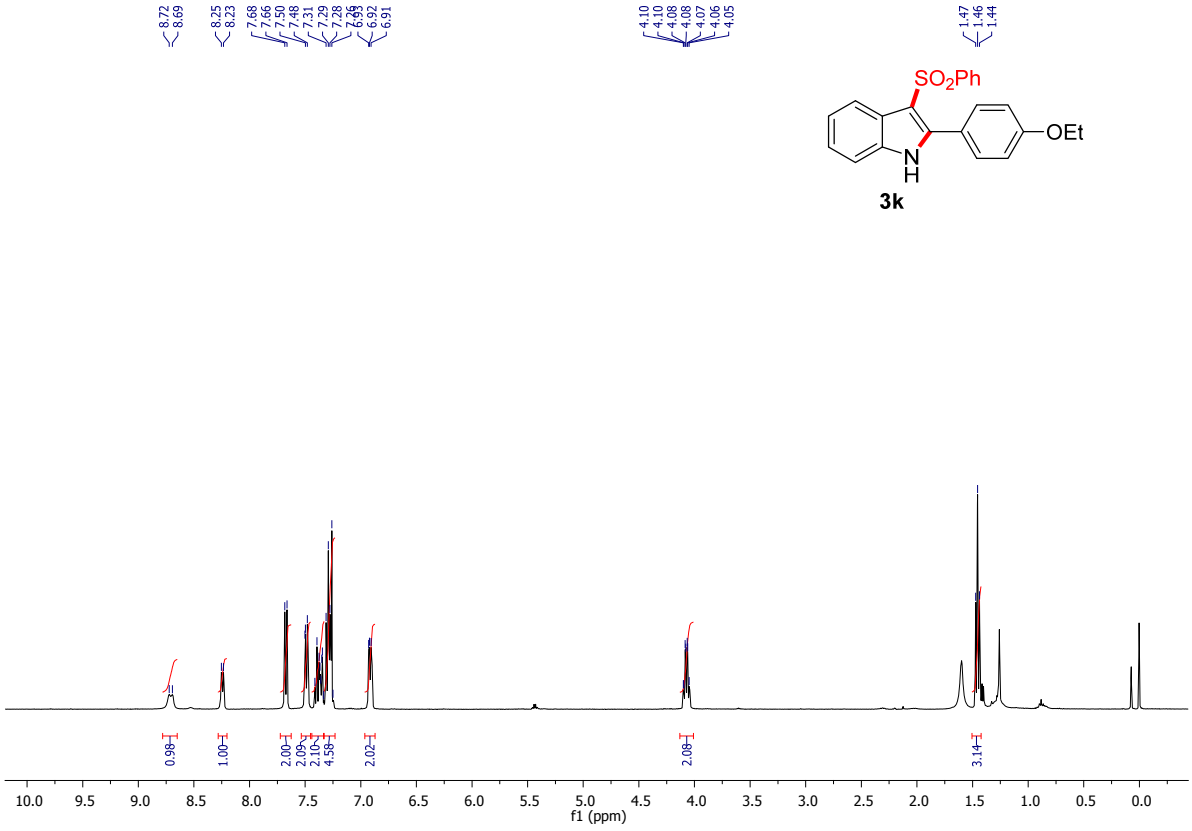

0.92
1.00
2.01
1.99
4.16
4.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

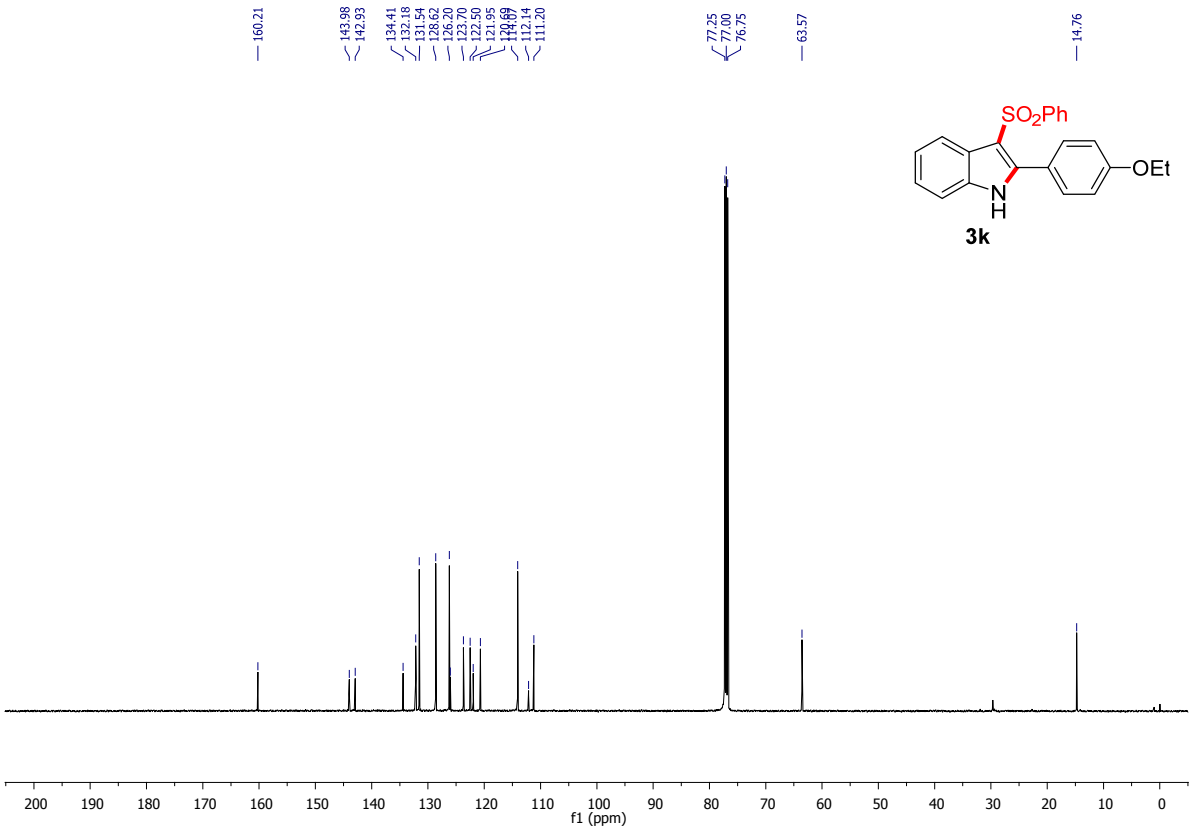

143.70
141.15
134.58
132.45
131.73
131.43
128.78
126.26
124.27
122.87
120.86
115.40
111.34
77.25
76.75

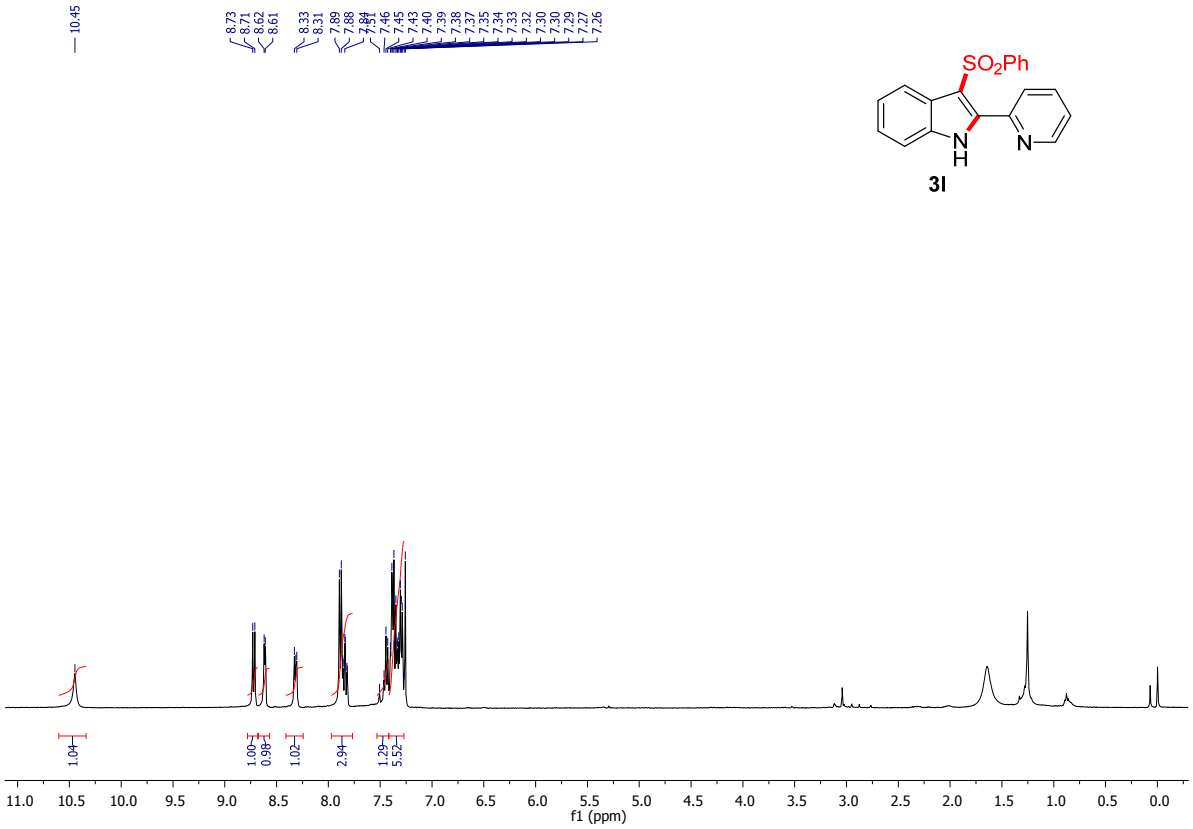

SO2Ph
Br
N
H

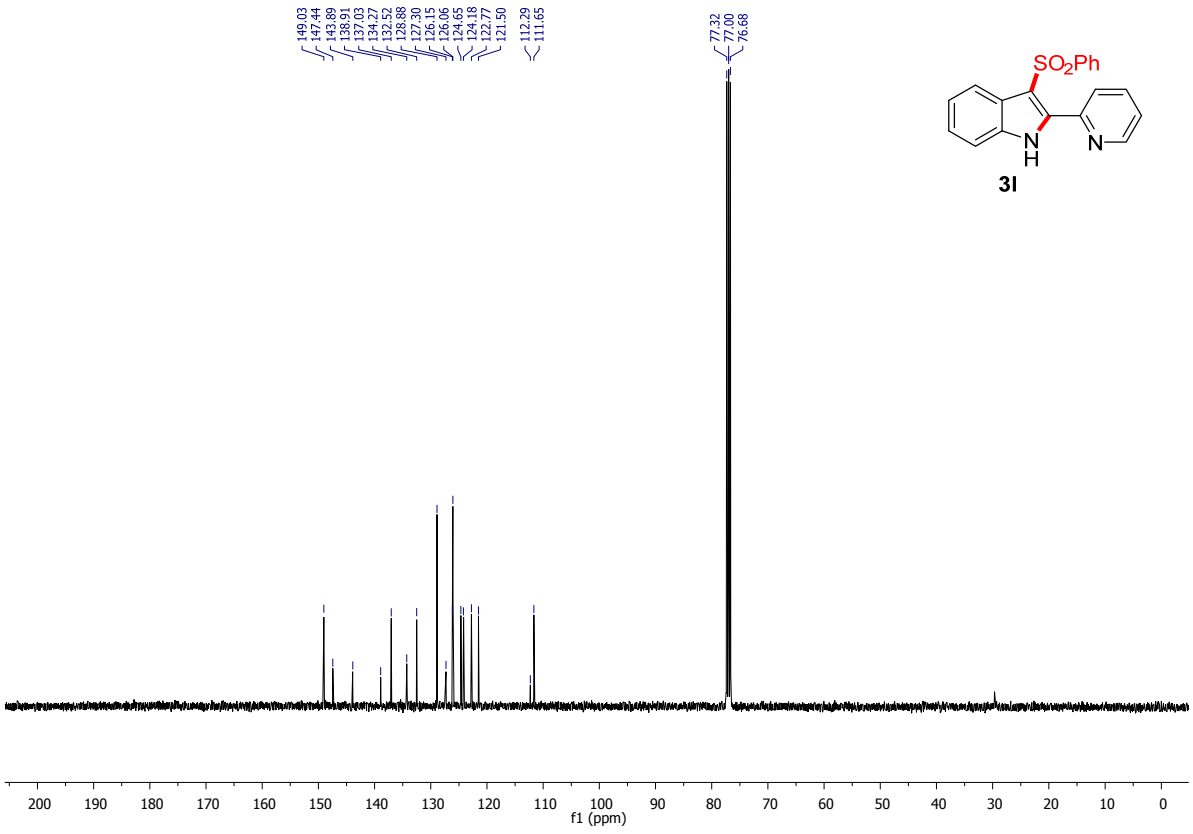
3j

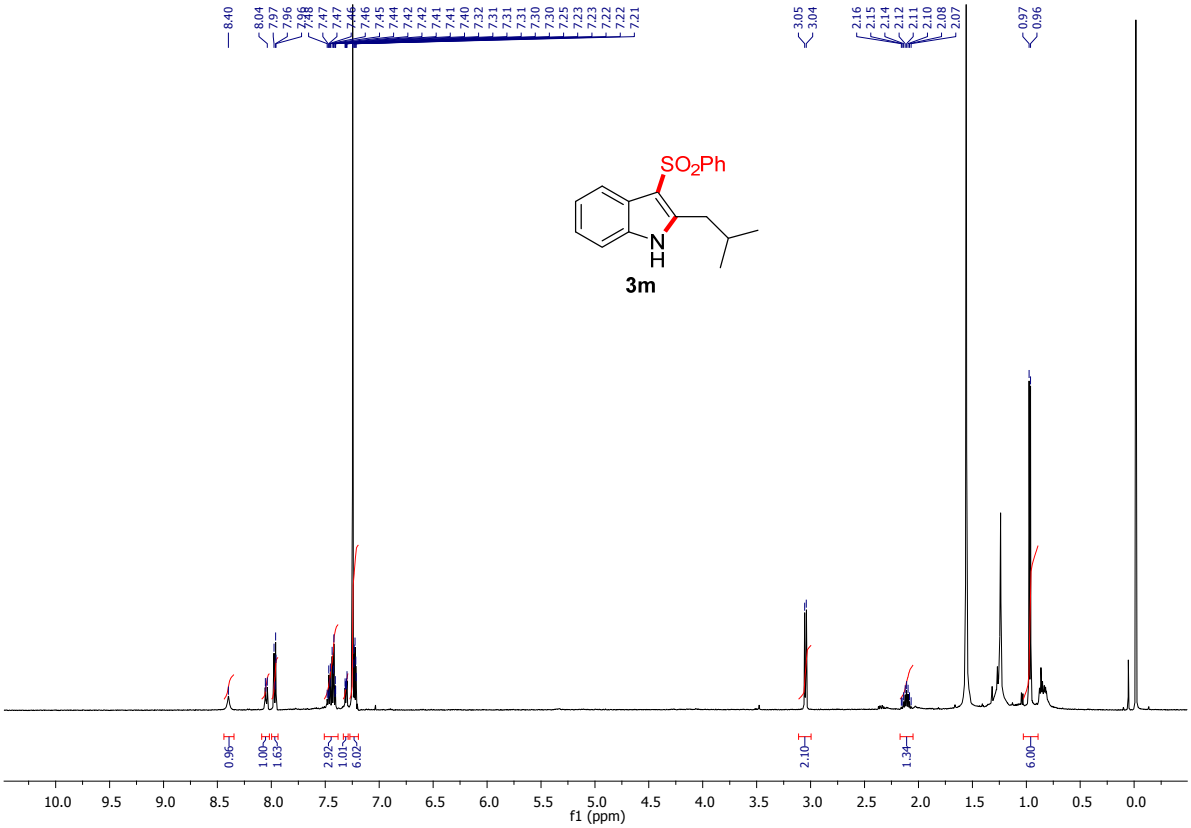

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

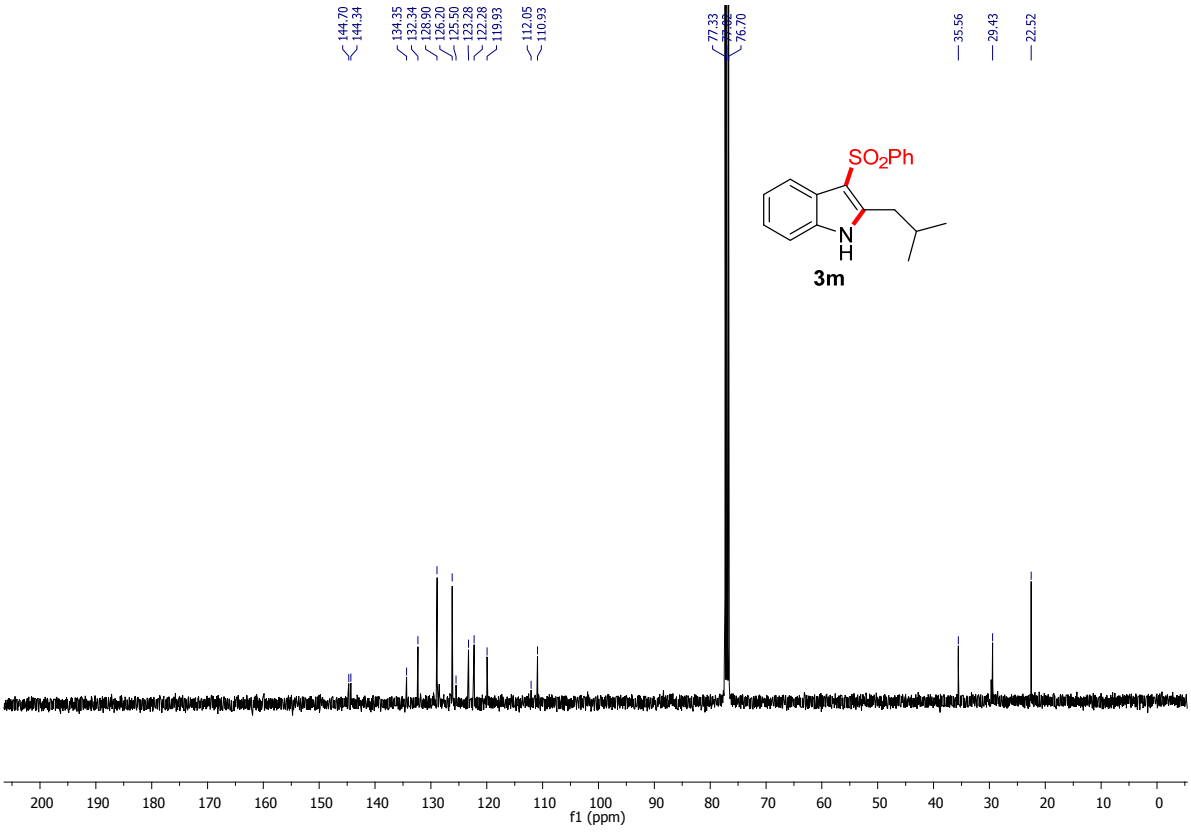

8.72
8.69
8.25
8.23
7.68
7.66
7.50
7.48
7.31
7.29
7.28
6.92
6.91
4.10
4.08
4.07
4.06
4.05
1.47
1.46
1.44
SO2Ph
OEt
N
H
3k
0.98
1.00
2.00
2.09
2.10
4.58
2.02
2.08
3.14
f1 (ppm)

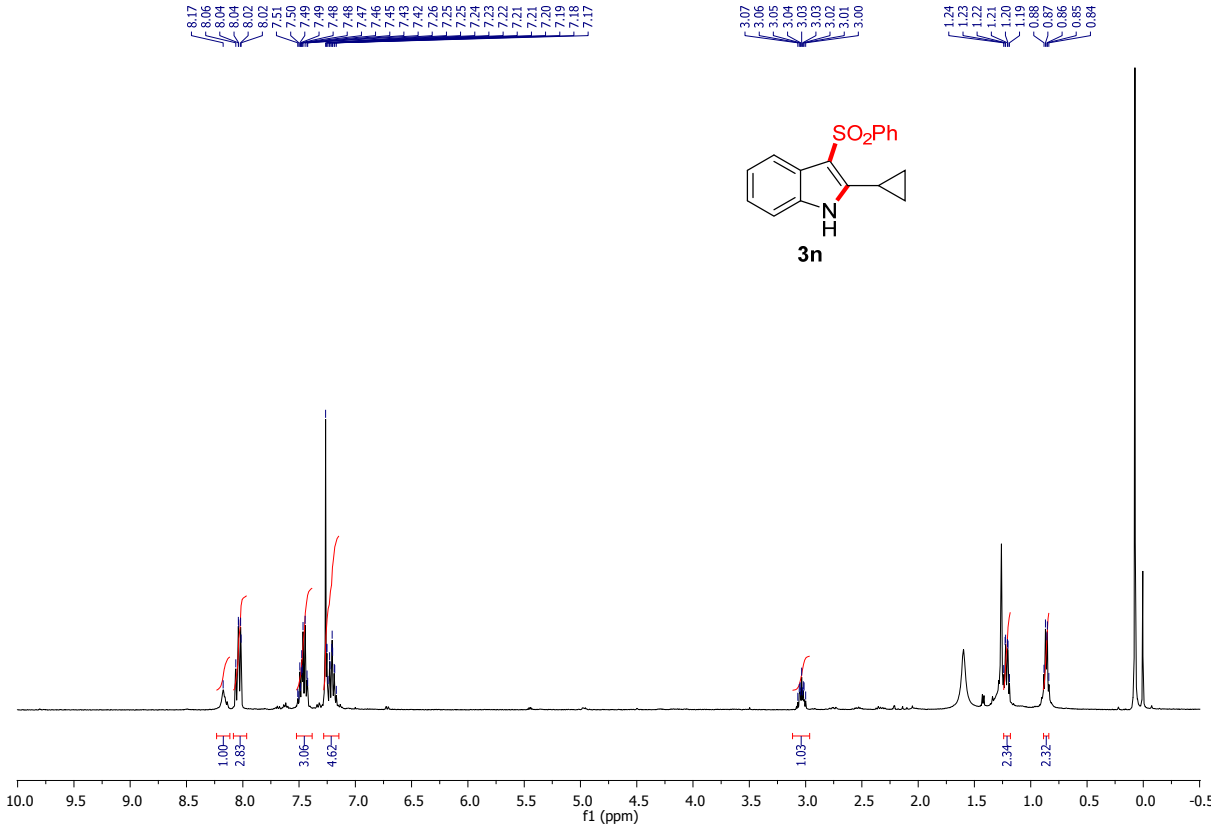

160.21
143.98
142.93
134.41
132.18
131.54
128.62
126.20
123.70
122.50
121.95
112.14
111.20
77.25
77.00
76.75
63.57
14.76
SO2Ph
OEt
N
H
3k
f1 (ppm)

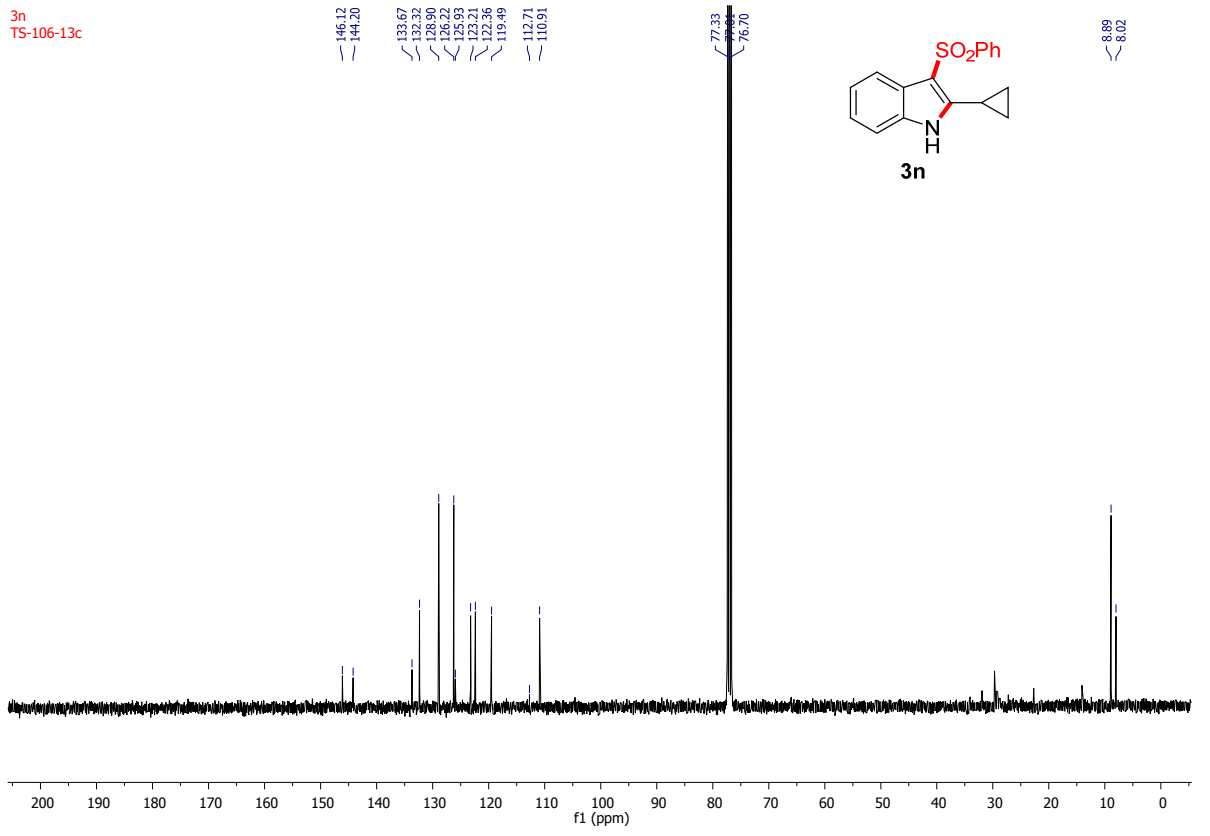

10.45
8.73
8.71
8.62
8.61
8.33
8.31
7.89
7.88
7.46
7.45
7.43
7.40
7.39
7.38
7.37
7.35
7.34
7.33
7.32
7.30
7.30
7.29
7.27
7.26
SO2Ph
N
H
N
3l
1.04
1.00
0.98
1.02
2.94
1.29
5.52
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

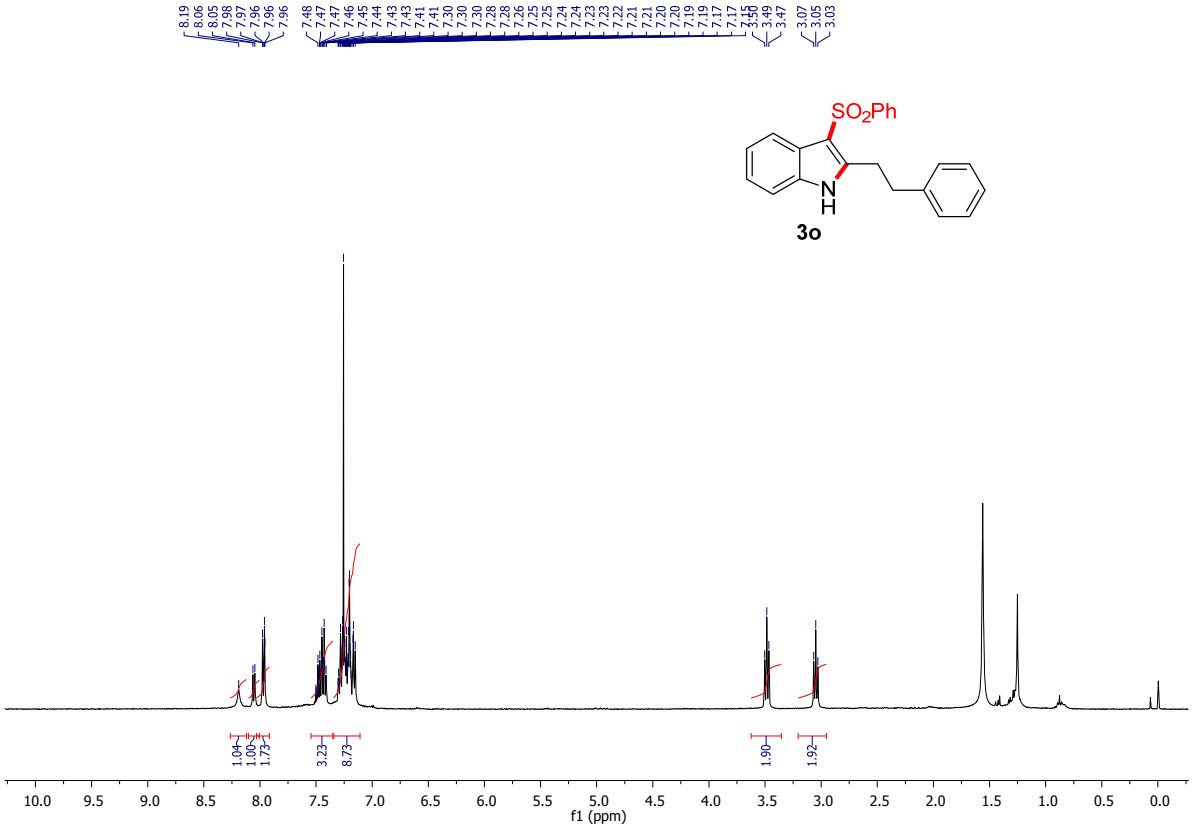

149.03
147.44
143.89
138.91
137.03
134.27
132.52
128.88
127.30
126.15
126.06
124.65
124.18
122.77
121.50
112.29
111.65
77.32
77.00
76.68
SO2Ph
N
H
N
3l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

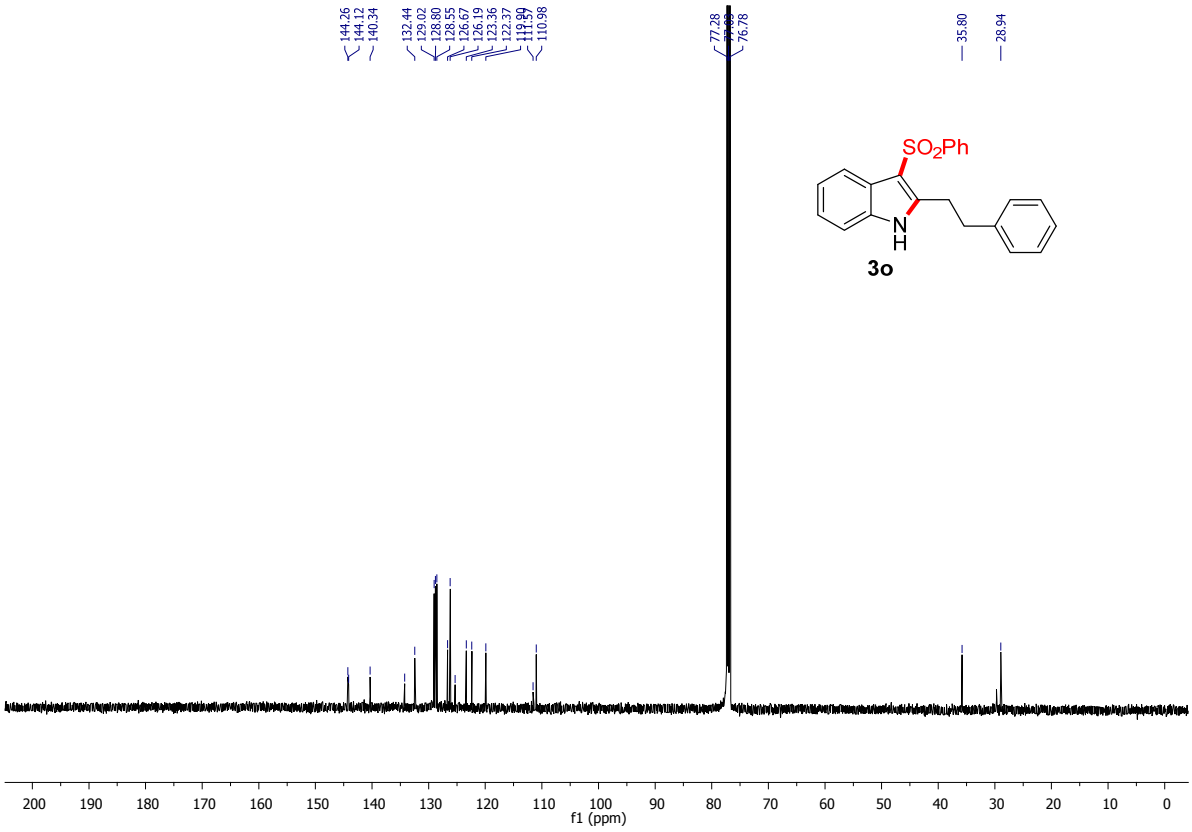

8.40
8.04
7.97
7.96
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.42
7.42
7.41
7.41
7.40
7.32
7.31
7.31
7.30
7.30
7.25
7.23
7.23
7.22
7.22
7.21
3.05
3.04
2.16
2.15
2.14
2.12
2.11
2.10
2.08
2.07
0.97
0.96
SO2Ph
N
H
3m
0.96
1.00
1.63
2.92
1.01
6.02
2.10
1.34
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

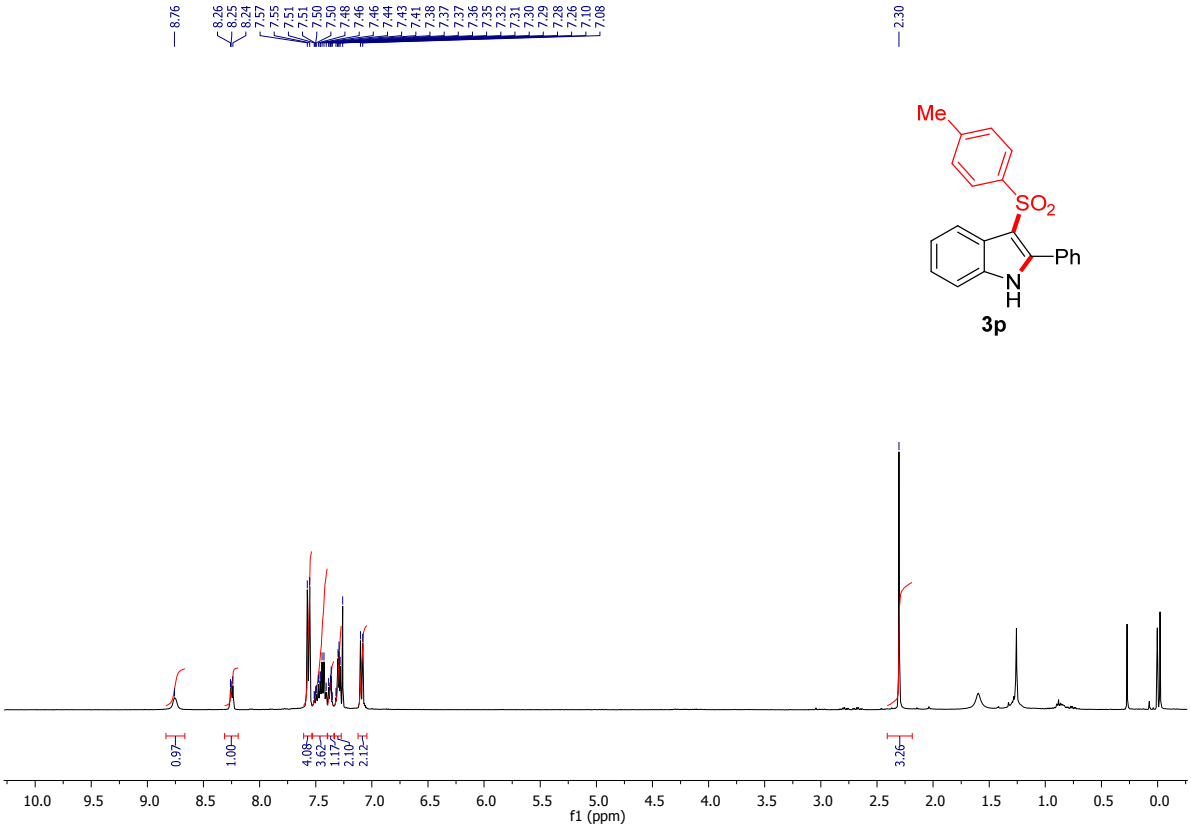

144.70
144.34
134.35
132.34
128.90
126.20
125.50
123.28
122.28
119.93
112.05
110.93
77.33
77.08
76.70
35.56
29.43
22.52
SO2Ph
N
H
3m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

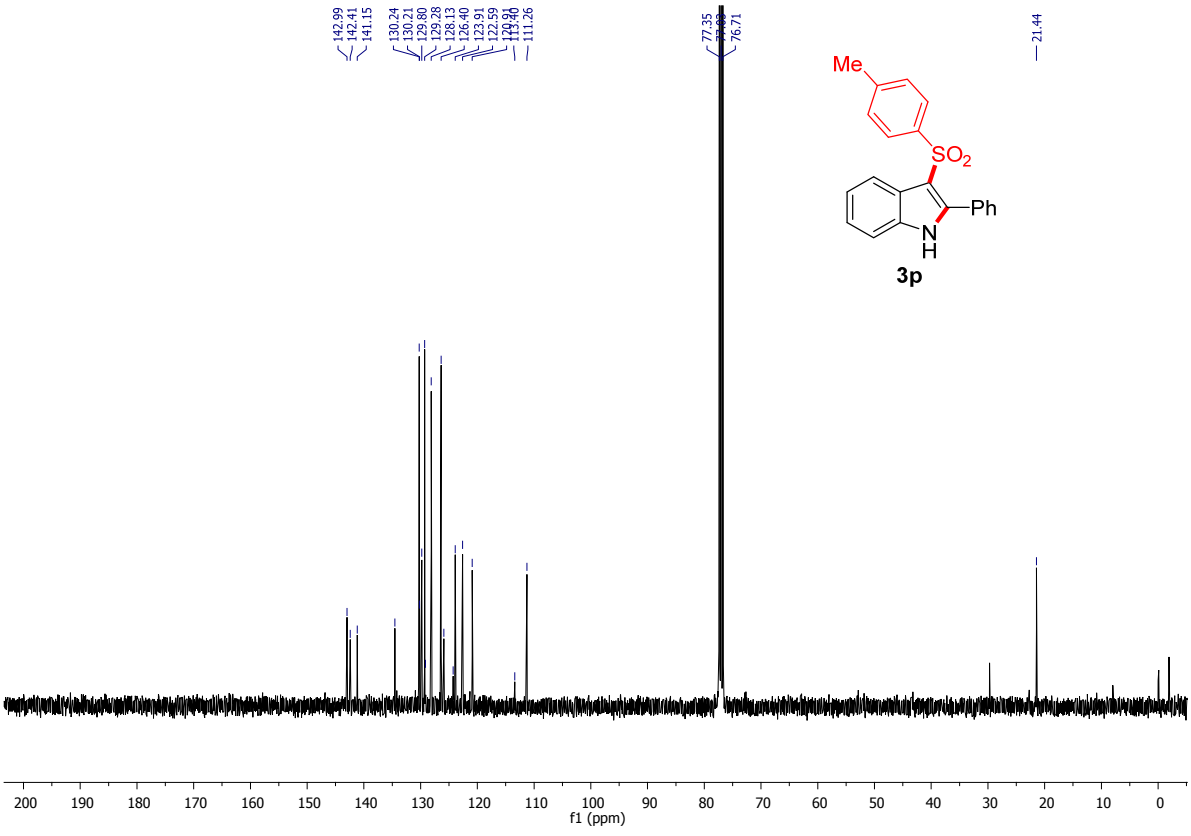

8.17
8.06
8.04
8.04
8.02
8.02
7.51
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.45
7.43
7.42
7.26
7.25
7.25
7.24
7.23
7.22
7.21
7.21
7.20
7.19
7.18
7.17
3.07
3.06
3.05
3.04
3.03
3.03
3.02
3.01
3.00
1.24
1.23
1.22
1.21
1.20
1.19
0.88
0.87
0.86
0.85
0.84
SO2Ph
N
H
3n
1.00
2.83
3.06
4.62
1.03
2.34
2.32
f1 (ppm)

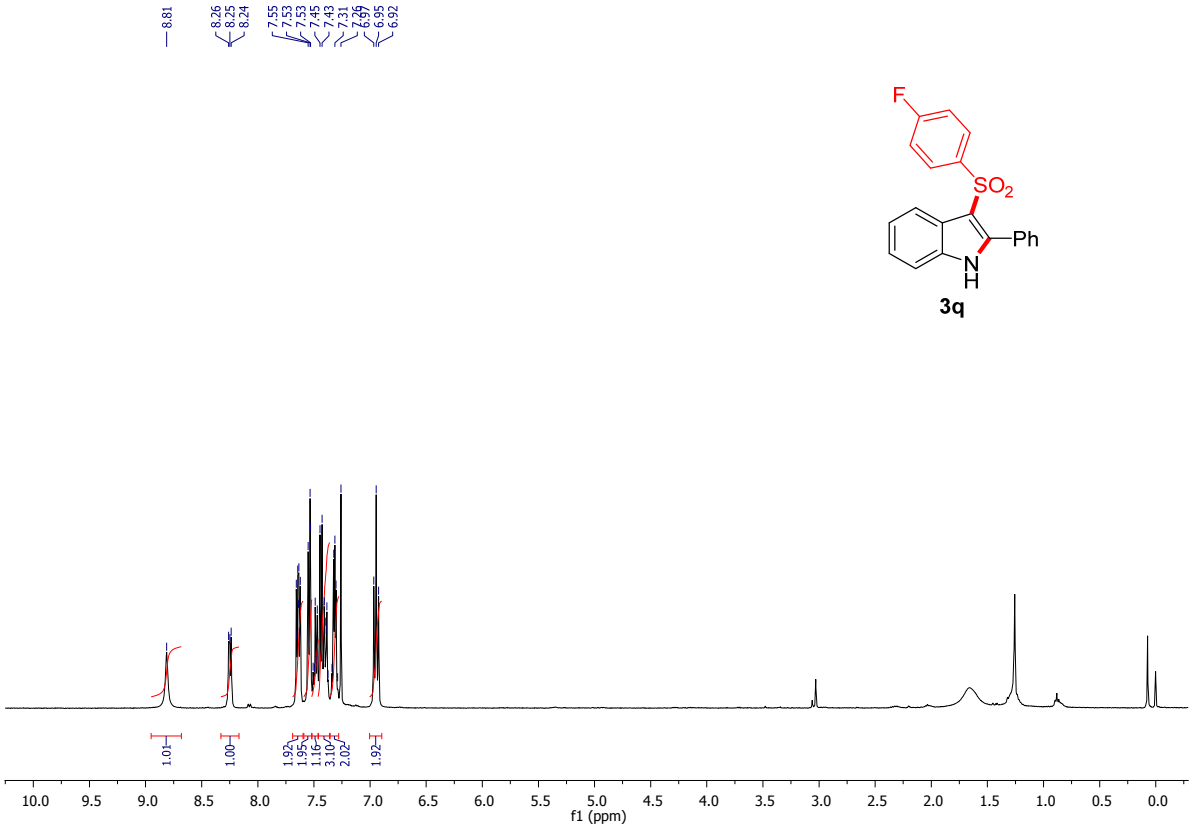

3n
TS-106-13c
146.12
144.20
133.67
132.32
128.90
126.22
125.93
123.21
122.36
119.49
112.71
110.91
77.33
77.04
76.70
8.89
8.02
SO2Ph
N
H
3n
f1 (ppm)

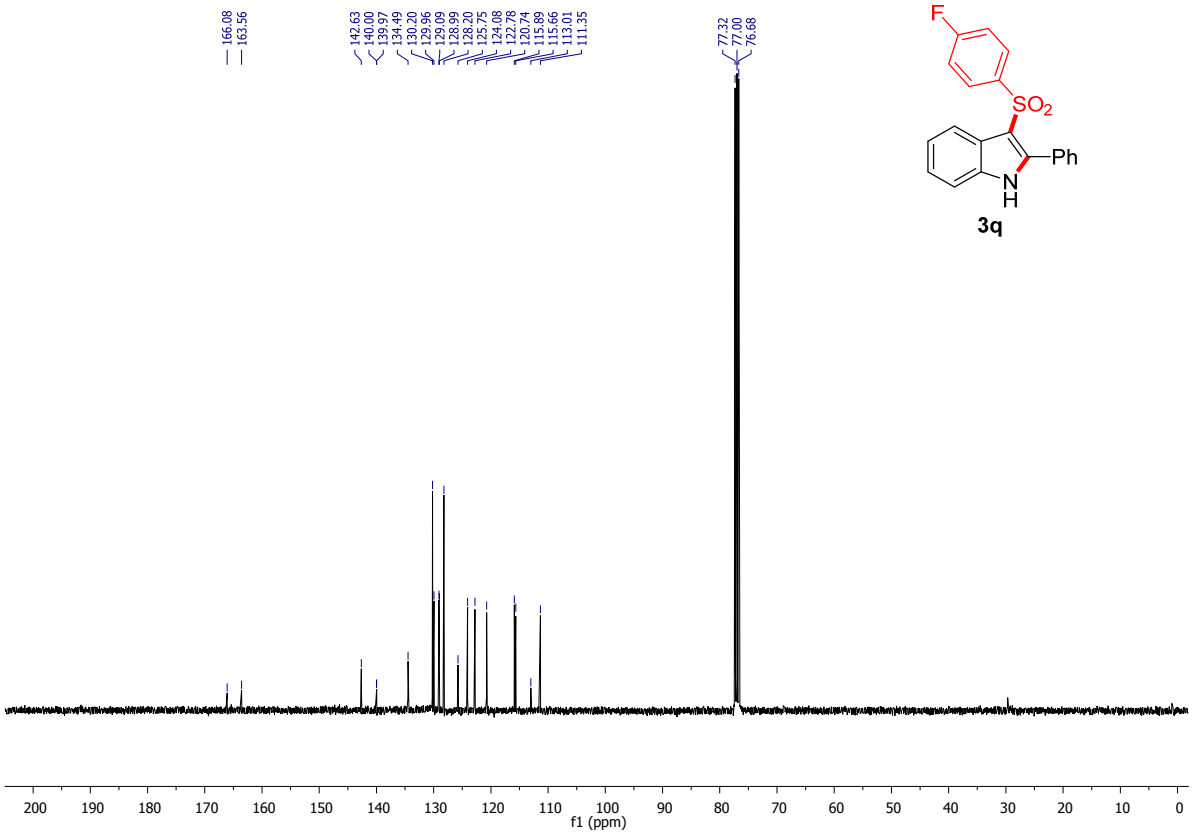

8.19
8.06
8.05
7.98
7.97
7.96
7.96
7.96
7.48
7.47
7.47
7.46
7.45
7.44
7.43
7.43
7.41
7.41
7.30
7.30
7.28
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.17
7.17
3.50
3.49
3.47
3.07
3.05
3.03
SO2Ph
N
H
3o
1.04
1.00
1.73
3.23
8.73
1.90
1.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

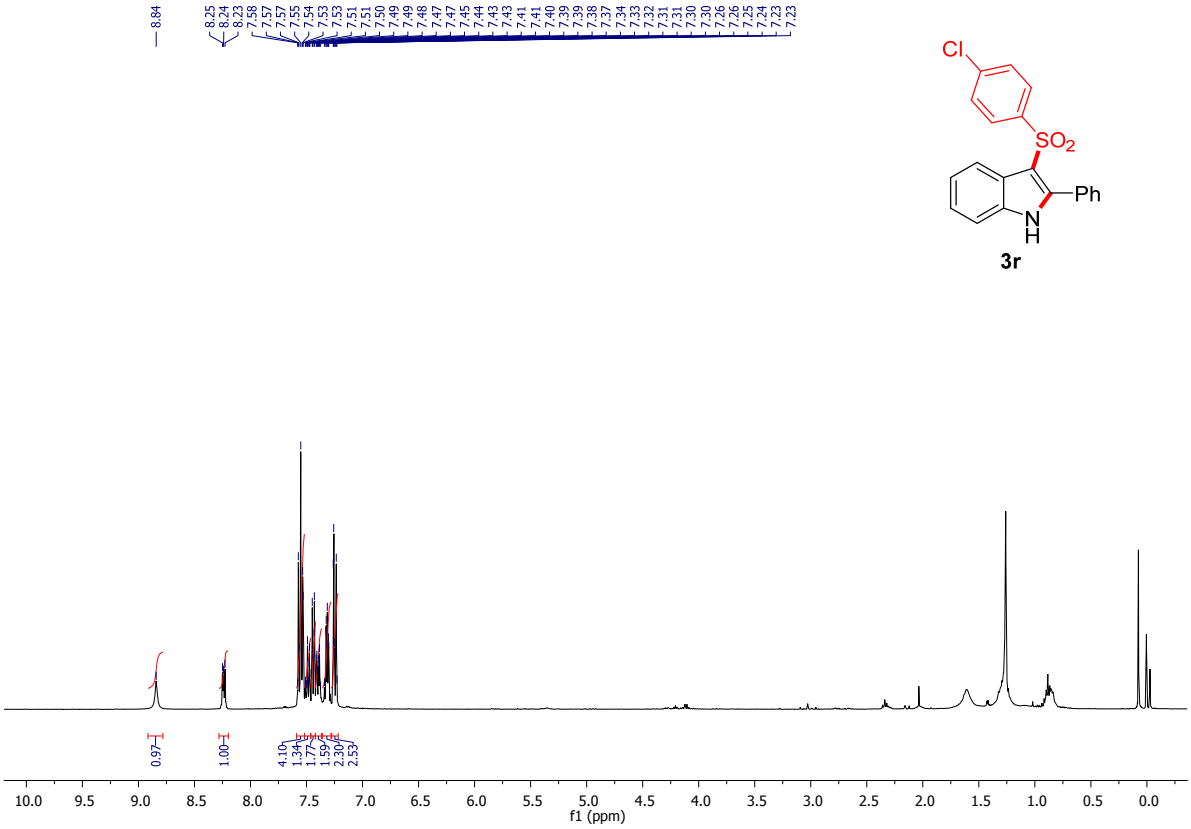

144.26
144.12
140.34
132.44
129.02
128.80
128.55
126.67
126.19
123.36
122.37
119.69
111.57
110.98
77.28
77.03
76.78
35.80
28.94
SO2Ph
N
H
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

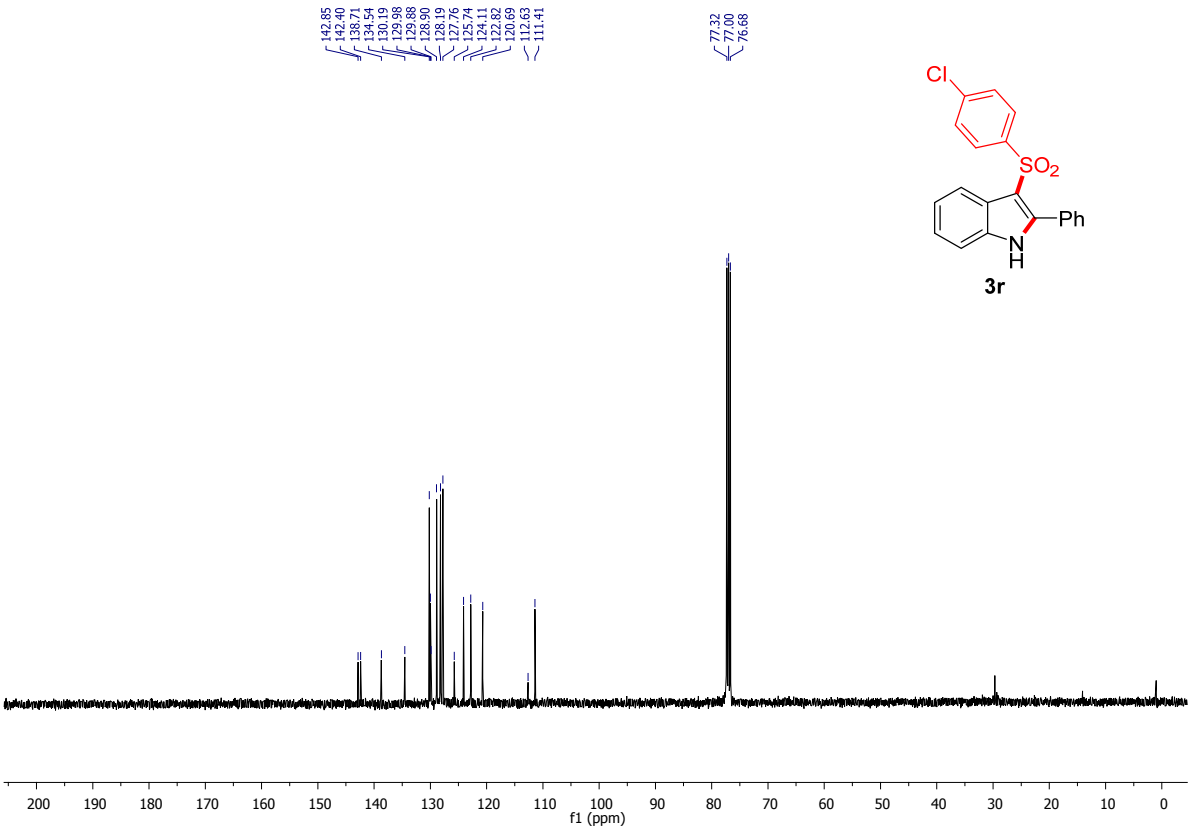

8.76
8.26
8.25
8.24
7.57
7.55
7.51
7.51
7.50
7.50
7.48
7.46
7.46
7.44
7.43
7.41
7.38
7.37
7.37
7.36
7.35
7.32
7.31
7.30
7.29
7.28
7.26
7.10
7.08
2.30
Me
SO2
Ph
N
H
3p
0.97
1.00
4.08
3.62
1.17
2.10
2.12
3.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


142.99
142.41
141.15
130.24
130.21
129.80
129.28
128.13
126.40
123.91
122.59
111.26
77.35
76.71
21.44
Me
SO2
Ph
N
H
3p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.81
8.26
8.25
8.24
7.55
7.53
7.53
7.45
7.43
7.31
7.26
6.97
6.95
6.92
F
SO2
Ph
N
H
3q
1.01
1.00
1.92
1.95
1.16
3.10
2.02
1.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.08
163.56
142.63
140.00
139.97
134.49
130.20
129.96
129.09
128.99
128.20
125.75
124.08
122.78
120.74
115.89
115.66
113.01
111.35
77.32
77.00
76.68
F
SO2
Ph
N
H
3q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.84
8.25
8.24
8.23
7.58
7.57
7.57
7.55
7.54
7.53
7.53
7.51
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.45
7.44
7.43
7.43
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.34
7.33
7.32
7.31
7.31
7.30
7.30
7.26
7.26
7.25
7.24
7.23
7.23
Cl
SO2
Ph
N
H
3r
0.97
1.00
4.10
1.34
1.77
1.59
2.30
2.53
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.85
142.40
138.71
134.54
130.19
129.98
129.88
128.90
128.19
127.76
125.74
124.11
122.82
120.69
112.63
111.41
77.32
77.00
76.68
Cl
SO2
Ph
N
H
3r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.66
8.27
8.26
8.24
7.58
7.56
7.56
7.54
7.53
7.52
7.50
7.50
7.49
7.47
7.45
7.45
7.43
7.43
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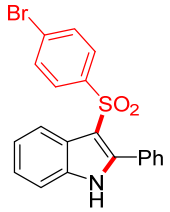
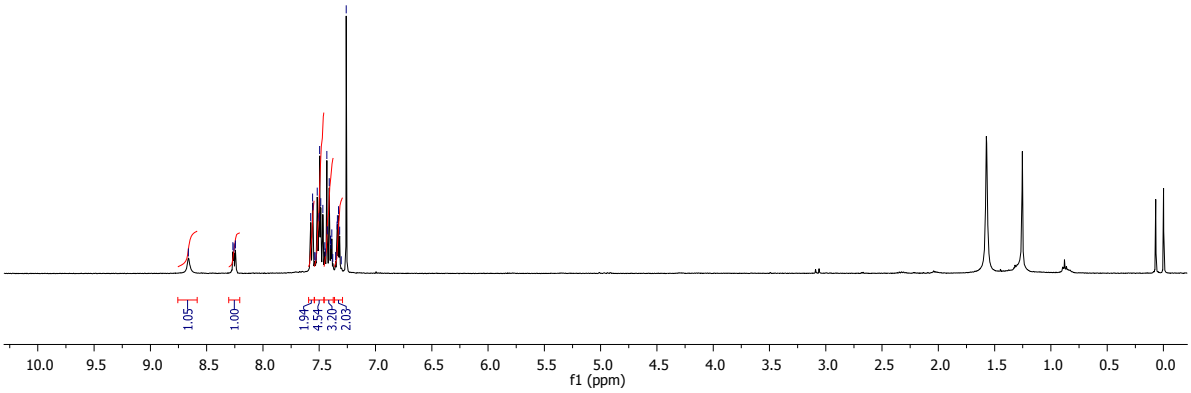
7.34
7.34
7.33
7.32
7.30
7.26

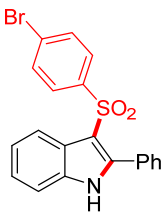

Br
SO2
Ph
N
H

3s

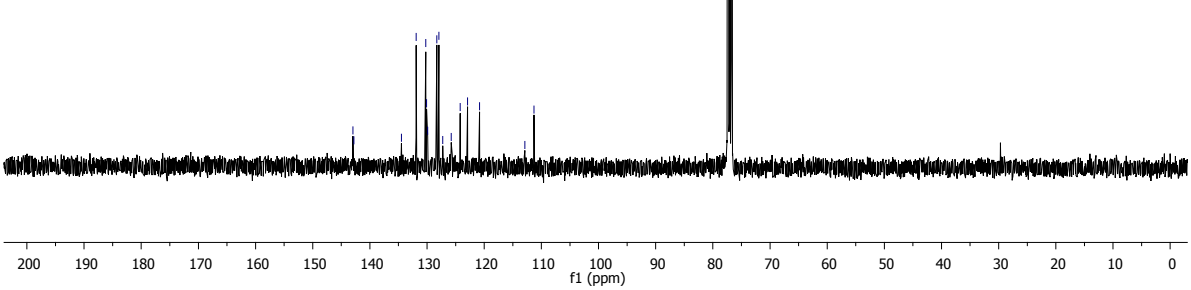

1.05
1.00
1.94
4.54
3.20
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

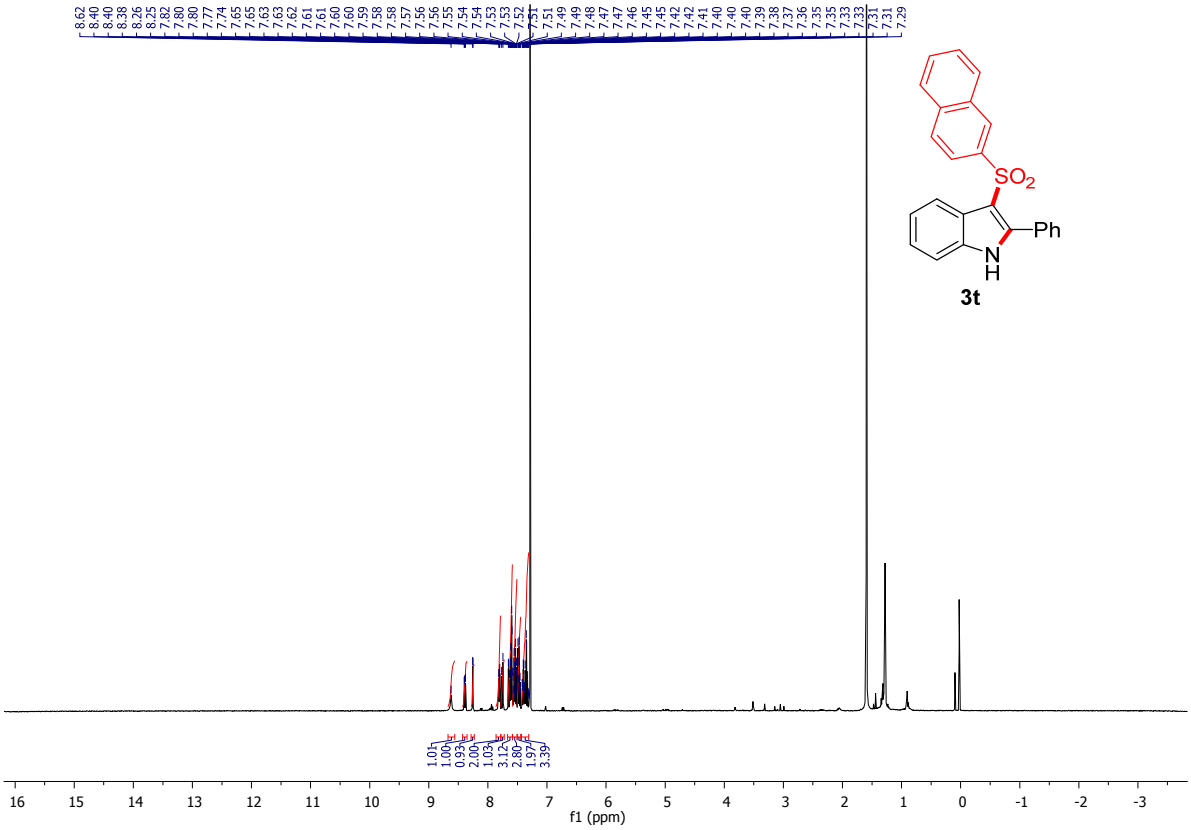

142.96
142.81
131.91
130.23
130.10
129.90
129.29
127.94
125.76
125.21
122.91
112.89
111.31

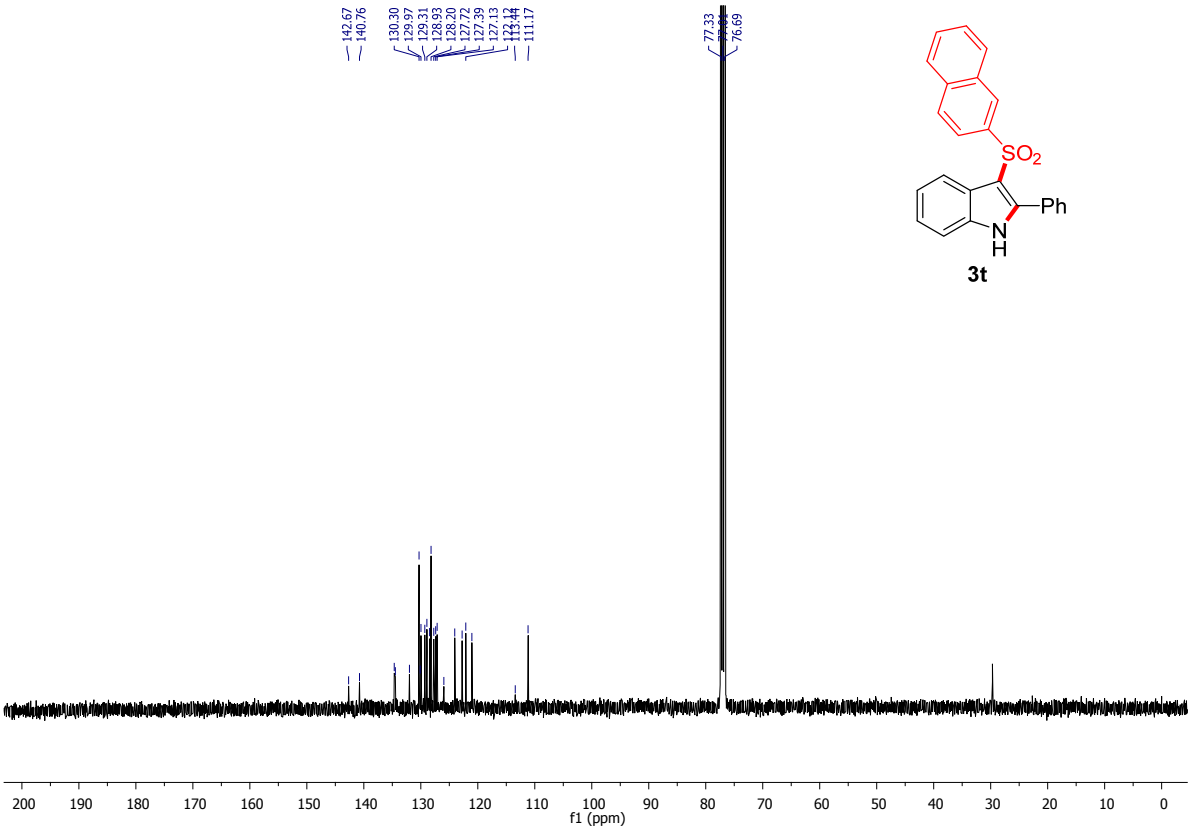

77.34
76.70

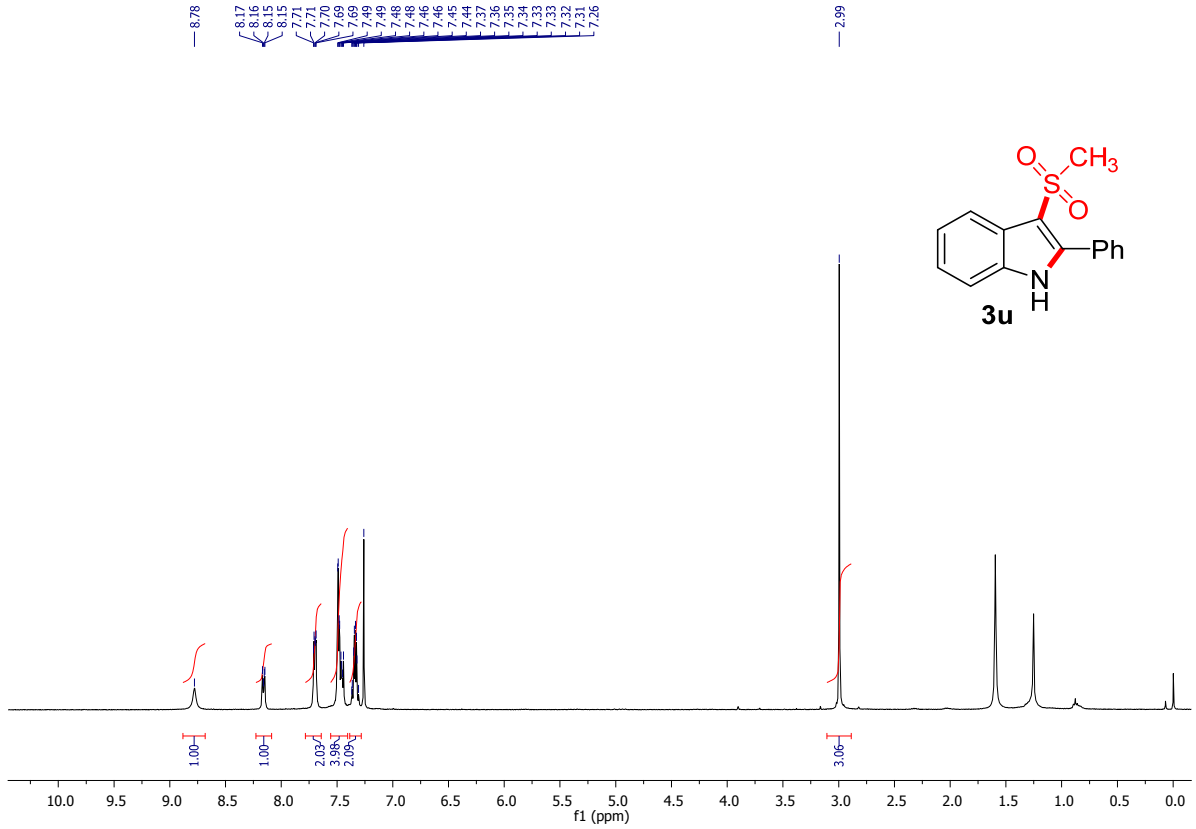

Br
SO2
Ph
N
H

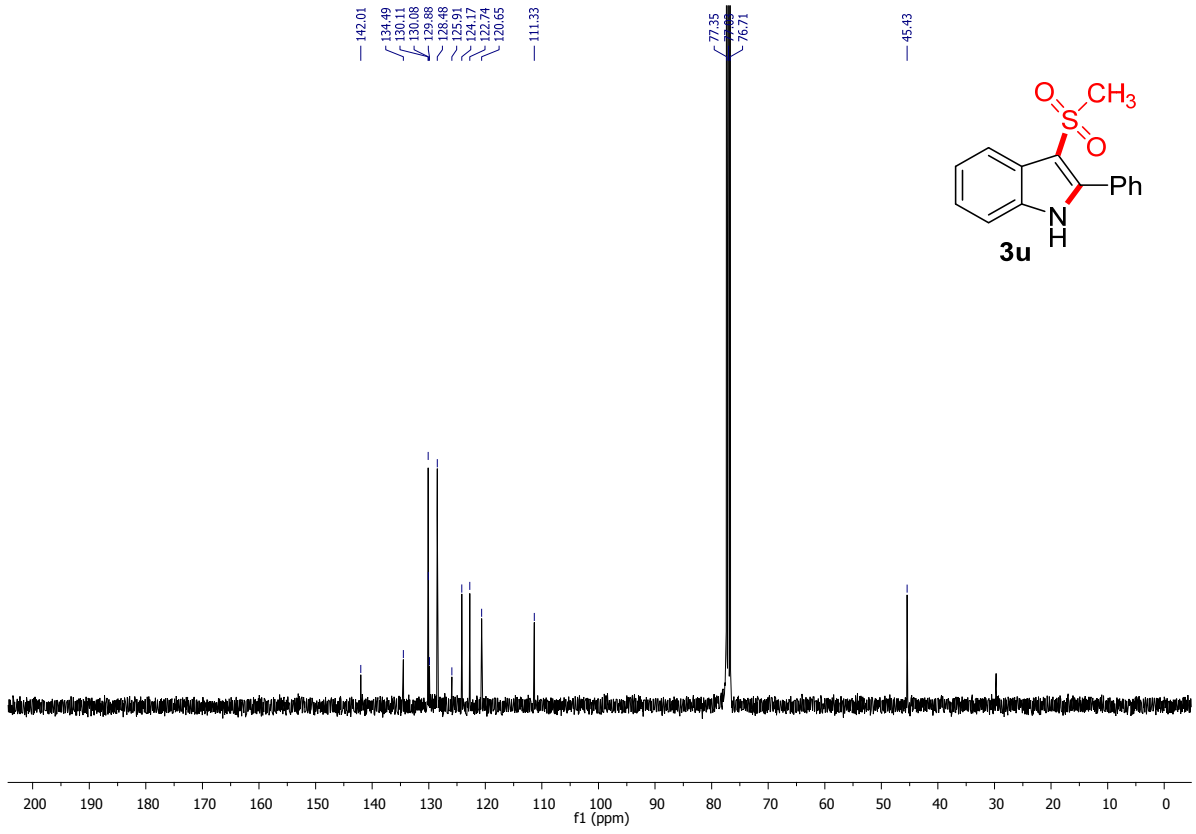
3s


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.62
8.40
8.40
8.38
8.26
8.25
7.82
7.80
7.80
7.77
7.74
7.65
7.63
7.63
7.62
7.61
7.61
7.60
7.60
7.59
7.58
7.58
7.57
7.56
7.56
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.42
7.42
7.41
7.40
7.40
7.40
7.39
7.38
7.37
7.36
7.35
7.33
7.33
7.31
7.31
7.29
1.01
1.00
0.93
2.00
1.03
3.12
2.80
1.97
3.39
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)
SO2
Ph
N
H
3t


142.67
140.76
130.30
129.97
129.31
128.93
128.20
127.72
127.39
127.13
111.17
77.33
76.69
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
SO2
Ph
N
H
3t


8.78
8.17
8.16
8.15
8.15
7.71
7.71
7.70
7.69
7.69
7.49
7.49
7.48
7.48
7.46
7.46
7.45
7.44
7.37
7.36
7.35
7.34
7.33
7.33
7.32
7.31
7.26
2.99
O
CH3
S
O
Ph
N
H
3u
1.00
1.00
2.03
3.98
2.09
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.01
134.49
130.11
130.08
129.88
128.48
125.91
124.17
122.74
120.65
111.33
77.35
76.71
45.43
O
CH3
S
O
Ph
N
H
3u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)