Supporting Information

Polysubstituted Cyclopenta[*b*]indoles via Relay Gold(I)/Brønsted Acid Catalysis

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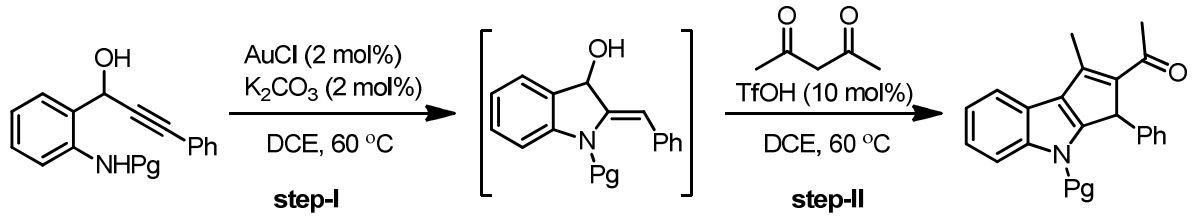
General experimental methods: Starting compounds such as 2-nitrobenzaldehydes, 2-aminobenzaldehydes, alkynes, Gold(I) catalysts and other Lewis/Brønsted acids etc., were purchased from Sigma-Aldrich and were used without further purification. For thin layer chromatography (TLC), silica aluminum foils with fluorescent indicator 254 nm (from Aldrich) were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), and acetic acid (10 mL) in ethanol (900 mL) followed by heating. Column chromatography was performed using SD Fine silica gel 100-200 mesh (approximately 15–20 g per 1 g of the crude product). Dry THF was obtained by distillation over sodium and stored over sodium wire. IR spectra were recorded on a Perkin–Elmer FT IR spectrometer as thin films or KBr pellet, as indicated, with ν_{max} in inverse centimetres. Melting points were recorded on a digital melting point apparatus Stuart SMP30 and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Biospin Avance III FT-NMR spectrometer. NMR shifts are reported as delta (δ) units in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations are utilized to describe peak patterns when appropriate: br=broad, s=single, d=doublet, t=triplet, q=quartet and m=multiplet. Proton chemical shifts are given in δ relative to tetramethylsilane (δ 0.00 ppm) in $CDCl_3$. Carbon chemical shifts are internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.1 ppm). Single crystal X-ray analysis was carried on a Bruker AXS KAPPA APEX II system. High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer.

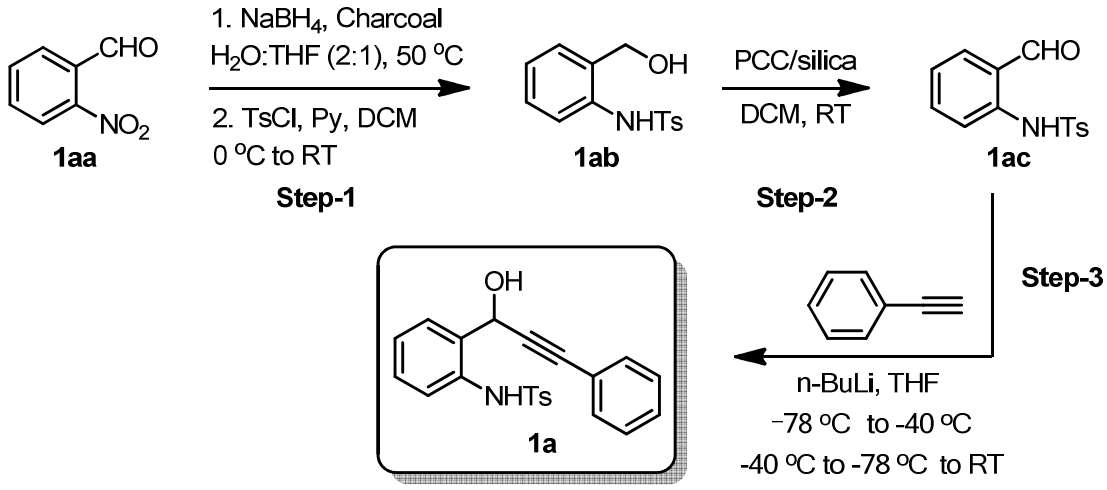
Screening of protecting groups in the relay Au(I)/Brønsted acid catalyzed domino process. From the following table, it is evident that N-tosyl protecting group is efficient in generating cyclopentannulated indole. N-Acetate or N-Boc group containing propargyl alcohols failed to generate even step-I product (indoline).



Entry	N-Protecting group	Time (h)	Yield (%)
1	Ac	48	NP
2	Boc	48	NP
3	Ts (**1a**)	18	90
4	Ms (**1aMs**)	24	83

NP – No Product

General procedure for the preparation of 1-(2-aminophenyl)prop-2-ynols (1a-1m).



Step-1: [1, 2]

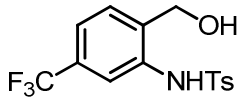
In a 25 mL round bottom flask equipped with magnetic stirrer and a condenser, a solution of 2-nitrobenzaldehyde **1aa** (2 g, 13.24 mmol) in a mixture of water-THF (15 mL, 2:1) was prepared. Charcoal (4 g) was then added, and the reaction mixture was stirred for 10 min at room temperature. To the resulting mixture, $NaBH_4$ (1.8 g, 47.3 mmol, 3.5 equiv) was

[1] Z. Behzad and S. Davood, *Synth. Commun*., 2006, **36**, 2699.
[2] B. W. Boal , A. W. Schammel and N. K. Garg, *Org Lett*., 2009, **11**, 3458.

added portion wise for 2 h with stirring at 50-60 °C. At the end of the reaction, the reaction mixture was simply filtered and dried over anhydrous Na_2SO_4, concentrated under vacuo.[1]

Without further purification, the 2-amino benzylalcohol was dissolved in 50 mL of dry dichloromethane and cooled to ice temperature. Pyridine (15.9 mmol, 1.2 equiv) was added drop wise at ice temperature. p-Toluene sulfonylchloride (14.56 mmol, 1.1 equiv) dissolved in 30 mL of dichloromethane was added slowly. After stirring the reaction mixture for 12 h at room temperature, the solvent was removed in vacuo and the residue was dissolved in ethyl acetate, washed with saturated (aq.) $NaHCO_3$, and the layers were separated. The aqueous layer was further extracted with dichloromethane. The organic layers were combined, dried over Na_2SO_4, concentrated under vacuo. The residue was purified by silica gel column chromatography (40% hexane/ethyl acetate) to afford N-(2-(hydroxymethyl)phenyl)-4-methylbenzenesulfonamide **1ab**.[2]

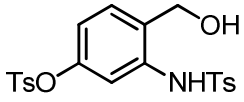
Spectroscopic data of some important and the newly synthesized amino benzylalcohols is presented below.



1ib

N-(2-(Hydroxymethyl)-5-(trifluoromethyl)phenyl)-4-methylbenzenesulfonamide (1ib)

Colourless oil. R_f = 0.5 (hexane/EtOAc = 2/3). IR (thin film, neat): ν_{max}/cm^{-1} 3461, 3178, 2970, 1597, 1437, 1352, 1216, 1164, 1132, 823, 749. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15 (br s, 1H), 7.70-7.66 (m, 3H), 7.34 (dt, *J* = 8.7 and 0.8 Hz, 1H), 7.27-7.21 (m, 3H), 4.51 (s, 2H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.4, 137.1, 136.1 (q, *J* = 232.0 Hz), 134.1, 131.6, 131.2, 129.8 (2CH), 129.0 (q, *J* = 32.0 Hz), 127.1, 121.4, 121.7 (q, *J* = 3.0 Hz), 119.5 (q, *J* = 3.0 Hz), 63.5, 21.6. HRMS (ESI): *m/z* calcd for $C_{15}H_{13}F_3NO_3S$ $(M-H)^+$: 344.0528, Found: 344.0549.



1jb

4-(Hydroxymethyl)-3-(4-methylphenylsulfonamido)phenyl 4-methylbenzenesulfonate (1jb).

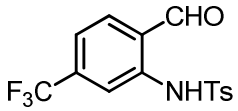
Colourless solid. M.P = 156-158 °C. R_f = 0.5 (hexane/EtOAc = 3/2). IR (thin film, neat): ν_{max}/cm^{-1} 3416, 3256, 2970, 1596, 1492, 1366, 1216, 1040, 907, 735. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.67-7.65 (m, 2H), 7.61-7.59 (m, 2H), 7.34-7.30 (m, 3H), 7.23 (dd, *J* = 8.5 and 0.5 Hz, 2H), 6.88 (d, *J* = 2.5 Hz, 1H), 6.72 (dd, *J* = 8.8 and 2.8 Hz, 1H), 4.30 (s,

2H), 2.47 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.2, 145.7, 144.1, 136.4, 135.1, 133.3, 131.9, 129.8 (2CH), 129.7 (2CH), 128.4 (2CH), 126.9 (2CH), 129.2, 123.0, 122.4, 63.2, 21.7, 21.6. HRMS (ESI): *m/z* calcd for $C_{21}H_{20}NO_5S_2$ $(M–OH)^+$: 430.0783, Found: 430.0762.

Step-2:[3]

The amino benzylalcohol **1ab** was dissolved in 10 mL of dichloromethane and treated with pyridinum chlorochromate (PCC, 1.2 equiv) adsorbed on silica gel (1 g). After complete oxidation to the aldehyde, the reaction mixture was concentrated under vacuo. The residue was purified by silica gel column chromatography (30-40% EtOAc/hexane) to obtain **1ac**.

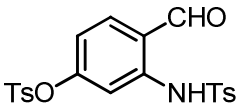
Spectroscopic data of some important and the newly synthesized amino aldehydes is presented below.[3]



1ic

N-(2-Formyl-5-(trifluoromethyl)phenyl)-4-methylbenzenesulfonamide (1ic).

Colourless amorphous solid. M.P = 118-120 ^oC. R_f = 0.5 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3345, 3180, 1682, 1581, 1511, 1408, 1330, 1165, 1132, 951, 870, 566. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.8 (s, 1H), 9.90 (s, 1H), 7.99 (m, 1H), 7.82-7.75 (m, 3H), 7.42-7.39 (m, 1H), 7.30-7.28 (m, 2H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.4, 144.8, 140.3, 136.9, 136.5 (q, *J* = 231.0 Hz), 129.9 (2CH, 1C), 127.3 (2CH), 123.3, 121.5, 119.2 (q, *J* = 3.0 Hz), 114.6 (q, *J* = 3.0 Hz), 21.4. HRMS (ESI): *m/z* calcd for $C_{15}H_{11}F_3NO_3S$ $(M–H)^+$: 342.0412, Found: 342.0419.



1jc

4-Formyl-3-(4-methylphenylsulfonamido)phenyl 4-methylbenzenesulfonate (1jc).

Colourless amorphous solid. M.P = 108-110 ^oC. R_f = 0.6 (hexane/EtOAc = 3/2). IR (thin film, neat): ν_{max}/cm^{-1} 3467, 3187, 3064, 2970, 2863, 1676, 1596, 1583, 1491, 1372, 1291, 1142, 1040, 955, 659. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.7 (s, 1H), 9.71 (s, 1H), 7.78-7.72 (m, 2H), 7.67-7.65 (m, 2H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.83-7.31 (m, 3H), 7.28-7.25 (m, 2H), 7.04 (dd, *J*

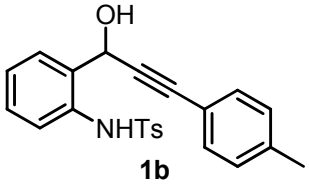
[3] (a) K. Hirano, A. T. Biju, I. Piel and F. Glorius, *J. Am. Chem. Soc.*, 2009, **131**, 14190; (b) L. Yu. Ukhin and L. G Kuzmina, *Russ. Chem. Bull.*, 2004, **53**, 2262.

= 9.2 and 2.6 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.8, 146.1, 144.6, 144.2, 138.6, 135.9, 131.5, 130.0 (2CH), 129.9 (2CH), 129.8, 129.2, 128.4 (2CH), 127.2 (2CH), 122.2, 118.9, 21.8, 21.6. HRMS (ESI): *m/z* calcd for $C_{21}H_{18}NO_6S_2$ $(M-H)^+$: 444.0576, Found: 444.0575.

Step-3:[4]

To a stirred solution of the alkyne (2.2 equiv) in anhydrous THF at −78 °C was added n-butyllithium (2.0 M in cyclohexane solution, 2.2 equiv) drop wise, and the resulting solution was allowed to stir at the same temperature for 10 min. The reaction was warmed to −40 °C. The resulting mixture was stirred at the same temperature for 1 h. After 1 h reaction mixture was cooled to −78 °C. The aminoaldehyde **1bc** (1 mmol) was dissolved in THF (2 mL) and added to the reaction mixture drop wise at −78 °C and allowed to stir for 1 h at the same temperature. The reaction mixture was slowly warmed up to room temperature and stirred for a further 1 h. Upon completion, the reaction mixture was quenched by adding saturated aq. NH_4Cl (1 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (20-30% EtOAc/hexane) to afford **1b** in 80-90% yields.

Some of the 1-(2-aminophenyl)prop-2-ynols employed in this study are already known in the literature with complete characterization data.[4] Spectroscopic data of some important and the newly synthesized amino propargyl alcohols is presented below.

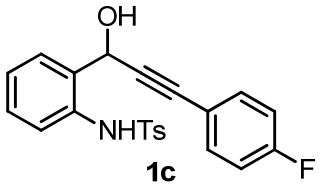


1b

N-(2-(1-Hydroxy-3-(p-tolyl)prop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1b). Colourless solid. M.P = 153-155 ^oC. R_f = 0.5 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3446, 3276, 2897, 2356, 2229, 1597, 1494, 1330, 1158, 1021, 815. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (br s, 1H), 7.72-7.70 (m, 3H), 7.58 (dd, *J* = 7.7 and 1.6 Hz, 1H), 7.48 (dd, *J* = 8.2 and 1.1 Hz, 1H), 7.32-7.28 (m, 2H), 7.19-7.13 (m, 5H), 5.50 (d, *J* = 5.5 Hz, 1H),

[4] For alcohol **1a, 1g** and **1l**: D. Susanti, F. Koh, J. A. Kusuma, P. Kothandaraman and P. W. H. Chan, *J. Org. Chem.,* 2012, **77**, 7166.
For alcohol **1f**: P. Kothandaraman, B. Q. Koh, T. Limpanuparb, H. Hirao and P. W. H. Chan, *Chem. Eur. J.,* 2013, **19**, 1978.

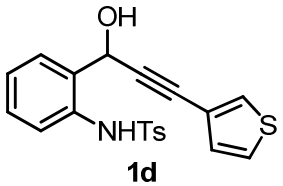
2.70 (d, *J* = 5.5 Hz, 1H), 2.38 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.9, 139.2, 136.7, 135.5, 131.7 (2CH), 130.7, 129.7 (2CH, C), 129.1 (2CH, C), 128.3, 127.2 (2CH), 125.1, 122.7, 118.7, 88.7, 85.5, 63.5, 21.5. HRMS (ESI): *m/z* calcd for $C_{23}H_{20}NO_2S$ $(M–OH)^+$: 374.1215, Found: 374.1201.



1c

N-(2-(3-(4-Fluorophenyl)-1-hydroxyprop-2-yn-1-yl)phenyl)-4-methylbenzene sulfonamide (1c).

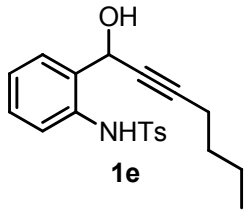
Colourless amorphous solid. M.P = 152-154 ^oC. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3434, 3250, 2934, 2221, 1599, 1506, 1330, 1228, 1158, 1090, 923. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (br s, 1H), 7.73-7.70 (m, 2H), 7.57-7.55 (m, 1H), 7.47-7.44 (m, 2H), 7.40 (dd, *J* = 8.2 and 1.1 Hz, 1H), 7.28 (td, *J* = 7.7 and 1.6 Hz, 1H), 7.20-7.16 (m, 3H), 7.06-7.01 (m, 2H), 6.56 (s, 1H), 3.06 (br s, 1H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.8 (d, *J* = 248.2 Hz, 1C), 143.9, 136.6, 135.4, 133.4, 133.7 (2CH), 131.0, 129.7 (2CH), 128.4, 127.2 (2CH), 125.3, 122.8, 118 (d, *J* = 3.7 Hz), 115.8, 115.6 (d, *J* = 3.5 Hz), 87.2, 86.2, 63.3, 21.5. HRMS (ESI): *m/z* calcd for $C_{22}H_{17}FNO_3S$ $(M–H)^+$: 394.0913, Found: 394.0909.



1d

N-(2-(1-Hydroxy-3-(thiophen-3-yl)prop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1d).

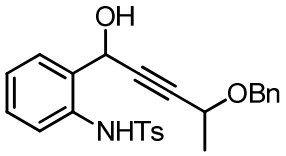
Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3430, 3263, 3107, 2925, 2232, 1597, 1492, 1400, 1330, 1157, 1090, 926, 813, 759. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (br s, 1H), 7.73-7.70 (m, 2H), 7.57-7.52 (m, 2H), 7.45 (dd, *J* = 8.2 and 1.1 Hz, 1H), 7.32-7.28 (m, 2H), 7.22-7.21 (m, 2H), 7.16-7.13 (m, 2H), 5.52 (s, 1H), 2.77 (br s, 1H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.9, 136.7, 135.5, 130.7, 129.8 (2CH), 129.7, 129.6 (2CH), 128.4, 127.2 (2CH), 125.6, 125.2, 122.8, 120.8, 86.0, 83.7, 63.5, 21.5. HRMS (ESI): *m/z* calcd for $C_{20}H_{16}NO_3S_2$ $(M–H)^+$: 382.0572, Found: 382.0575.



1e

N-(2-(1-Hydroxyhept-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1e).

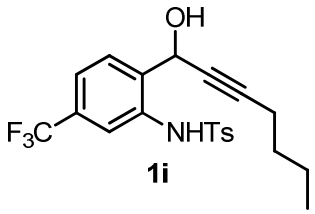
Colourless amorphous solid. M.P = 93-95 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3487, 3262, 2956, 2165, 1598, 1493, 1331, 1159, 1091, 924, 759. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71-7.68 (m, 2H), 7.51-7.49 (m, 2H), 7.29-7.23 (m, 3H), 7.13 (td, *J* = 7.5, 7.5 and 1.3 Hz, 1H), 5.23 (s, 1H), 2.40 (s, 3H), 2.29 (td, *J* = 7.2 and 2.0 Hz, 2H), 1.56-1.51 (m, 2H), 1.46-1.40 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.8, 136.8, 135.5, 131.2, 129.6 (2CH), 129.4, 128.1, 127.1 (2CH), 125.0, 122.7, 89.6, 77.6, 63.0, 30.4, 22.0, 21.5, 18.5, 13.5. HRMS (ESI): *m/z* calcd for $C_{20}H_{23}NNaO_3S$ $(M+Na)^+$: 380.1296, Found: 380.1299.



1h

N-(2-(4-(Benzyloxy)-1-hydroxypent-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1h).

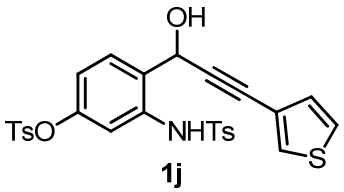
Colourless amorphous solid. M.P = 102-105 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3413, 3171, 2983, 2862, 2213, 1597, 1456, 1380, 1276, 1119, 986, 738. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71-6.68 (m, 2H), 7.53 (dd, *J* = 7.5 and 1.5 Hz, 1H), 7.38-7.34 (m, 6H), 7.25-7.22 (m, 3H), 7.15 (td, *J* = 7.5 and 1.5 Hz, 1H), 5.38 (s, 1H), 4.77 (d, *J* = 11.5 and 2.8 Hz, 1H), 4.54 (dd, *J* = 11.8 and 5.3 Hz, 1H), 4.35-4.30 (m, 1H), 2.38 (s, 3H), 1.52 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.9, 137.6, 136.7, 135.4, 131.1, 129.7 (2CH), 129.6, 128.4 (2CH), 128.3, 128.0 (2CH), 127.8, 127.1 (2CH), 125.3, 122.9, 88.4, 82.7, 70.8, 64.5, 62.6, 21.5, 21.4. HRMS (ESI): *m/z* calcd for $C_{25}H_{25}NNaO_4S$ $(M+Na)^+$: 458.1402, Found: 458.1406.



1i

N-(2-(1-Hydroxyhept-2-yn-1-yl)-5-(trifluoromethyl)phenyl)-4- methylbenzene sulfonamide (1i).

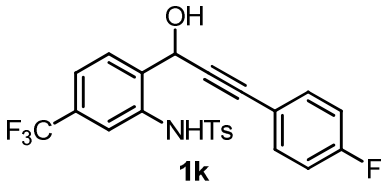
Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3469, 3252, 2198, 1579, 1507, 1470, 130, 1232, 1131, 1091, 968, 665, 565. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.16 (br s, 1H), 7.73-7.71(m, 3H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.36-7.34 (m, 1H), 7.27-7.25 (m, 2H), 5.29 (s, 1H), 2.41 (s, 3H), 2.29 (dt, *J* = 7.3 Hz and 5.2 Hz, 2H), 1.56-1.51 (m, 2H), 1.47-1.40 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): 144.3, 136.3, 136.2, 138.8, 131.7, 131.4, 129.8 (2CH), 128.7, 127.1, 127.1 (q, *J* = 245.0 Hz), 121.3 (q, *J* = 6.0 Hz), 110.3 (q, *J* = 4.0 Hz), 90.8 (2C), 62.8, 30.3, 22.0, 21.5, 18.4, 13.5. HRMS (ESI): *m/z* calcd for $C_{21}H_{21}F_3NO_2S$ $(M–OH)^+$: 408.1245, Found: 408.1246.



1j

4-(1-Hydroxy-3-(thiophen-3-yl)prop-2-yn-1-yl)-3-(4-methylphenylsulfonamido)phenyl 4-methylbenzenesulfonate (1j).

Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3481, 3269, 2926, 2235, 1596, 1493, 1374, 1266, 1194, 1031, 790. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 c(br s, 1H), 7.69-7.66 (m, 4H), 7.53 (dd, *J* = 8.8 Hz, 1H), 7.34 (dd, *J* = 5.0 and 3.0 Hz, 1H), 7.28-7.21 (m, 6H), 7.14 (dd, *J* = 4.9 and 1.0 Hz, 1H), 6.84 (dd, *J* = 8.9 and 2.9 Hz, 1H), 5.36 (br s, 1H), 2.43 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.1, 145.6, 144.2, 136.4, 134.7, 132.0, 130.1, 129.8 (2CH, C), 129.7 (2CH), 128.4 (3CH), 127.1 (2CH), 123.5, 123.3, 124.4, 120.5, 84.9, 84.3, 62.9, 21.7, 21.6. HRMS (ESI): *m/z* calcd for $C_{27}H_{22}NO_6S_3$ $(M–H)^+$: 552.0609, Found: 552.0604.

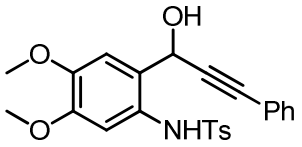


1k

N-(2-(3-(4-Fluorophenyl)-1-hydroxyprop-2-yn-1-yl)-5-(trifluoromethyl)phenyl)-4-methylbenzenesulfonamide (1k).

Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3469, 3252, 2199, 1599, 1507, 1420, 130, 1232, 1131, 1091, 968, 665, 565. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15 (br s, 1H), 7.75-7.73 (m, 2H), 7.71 (d, *J* = 1.3 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.48-7.44 (m, 2H), 7.39-7.37 (m, 1H), 7.28-7.21 (m, 2H), 7.09-7.03 (m, 2H), 5.62 (s, 1H), 3.01 (br

s, 1H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.9 (d, *J* = 249.7 Hz, 1C), 144.4, 136.3, 136.1, 133.9, 133.8, 133.4, 132.0, 129.8 (2CH, 1C), 128.9 (q, *J* = 246.0 Hz), 127.3 (2CH), 121.5 (q, *J* = 3.8 Hz), 118.9 (q, *J* = 3.8), 117.5 (d, *J* = 4.0 Hz), 115.9, 115.7, 88.0, 85.2, 63.2, 21.5. HRMS (ESI): *m/z* calcd for $C_{23}H_{16}F_4NO_2S$ $(M–OH)^+$: 446.0838, Found: 446.0839.



1l

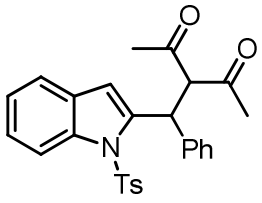
N-(2-(1-Hydroxy-3-phenylprop-2-yn-1-yl)-4,5-dimethoxyphenyl)-4-methyl benzenesulfonamide (1l).

Colourless amorphous solid. M.P = 58-60 ^oC. R_f = 0.5 (hexane/EtOAc = 1/1). IR (thin film, neat): ν_{max}/cm^{-1} 3446, 3276, 2897, 2356, 2229, 1597, 1494, 1330, 1158, 1130, 1021, 815. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.09 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.38-7.34 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.1 (s, 1H), 6.72 (s, 1H), 5.51 (s, 1H), 3.88 (s, 3H), 3.74 (s, 3H), 3.08 (br s, 1H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.1, 147.2, 144.0, 136.1, 131.7 (2CH), 129.7 (2CH), 128.8, 128.4 (2CH), 127.4 (2CH), 127.1, 126.8, 122.0, 110.9, 109.2, 87.7, 81.1, 62.0, 56.0, 55.9, 21.5.

General procedure for optimization of reaction parameters (Table 1).

To a 0.05 M solution of the alcohol **1a** in an appropriate solvent, catalyst (2 mol%) and co-catalyst (2 mol%) were added and stirred at 60 ^oC until the alcohol was consumed as monitored by TLC. Upon disappearance of alcohol (**1a**), acetylacetone (1.1 equiv) and an acid (20 mol%) were added and continued stirring at 60 ^oC until indoline (**3a**) and acetylacetone adduct (**4a**) disappeared. Reaction mixture was quenched with aqueous saturated sodium bicarbonate solution (1-2 mL). Diluted the reaction mixture with DCM or EtOAc (1-2 mL) and the layers were separated. The aqueous layer was further extracted with DCM or EtOAc (1-2 mL). The organic layers were combined, dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (20% EtOAc/hexane) to afford product **5a**.

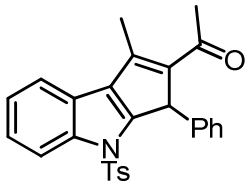
In some cases the acetylacetone adduct **4a** was also isolated, complete characterization data is presented below.



4a

3-(Phenyl(1-tosyl-1*H*-indol-2-yl)methyl)pentane-2,4-dione (4a).

Colourless solid. M.P = 176-178 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2924, 2939, 1720, 1716, 1594, 1491, 1467, 1371, 1275, 1170, 1121, 749. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04-8.02 (m, 1H), 7.52-7.50 (m, 1H), 7.30-7.22 (m, 9H), 6.99 (d, *J* = 8.7 and 0.6 Hz, 2H), 6.68 (s, 1H), 5.85 (d, *J* = 12.3 Hz, 1H), 4.51 (d, *J* = 12.3 Hz, 1H), 2.27 (s, 3H), 2.10 (s, 3H), 1.88 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.5, 202.4, 144.6, 140.7, 136.8, 135.5, 129.4 (2CH, C), 129.2 (2CH, C), 128.8 (2CH, C), 127.3, 126.8, 124.7, 123.6, 120.8, 114.8, 109.7, 75.9, 43.7, 31.7, 27.5, 21.5. HRMS (ESI): *m/z* calcd for $C_{27}H_{25}NNaO_4S$ $(M+Na)^+$: 482.1402. Found: 482.1381.



5a

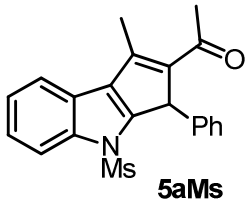
1-(1-Methyl-3-phenyl-4-tosyl-3,4-dihydrocyclopenta[b]indol-2-yl)ethanone (5a).

Colourless amorphous solid. M.P = 195-197 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2924, 2919, 1630, 1511, 1481, 1447, 1371, 1275, 1171, 1091, 749. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97-7.95 (m, 1H), 7.81-7.79 (m, 1H), 7.37-7.19 (m, 7H), 7.03-6.97 (m, 4H), 5.27 (q, *J* = 2.0 Hz, 1H), 2.84 (d, *J* = 2.0 Hz, 3H), 2.29 (s, 3H), 2.18 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.7 (C=O), 152.2, 148.6, 144.9, 142.1, 139.6, 135.4, 134.8, 129.6 (2CH), 129.5, 129.4, 128.6 (2CH, C), 127.2, 127.1 (2CH), 124.4, 124.1, 123.8, 119.5, 114.6, 52.8 (CH), 30.4 (CH_3), 21.5 (CH_3), 15.6 (CH_3). HRMS (ESI): *m/z* calcd for $C_{27}H_{24}NO_3S$ $(M+H)^+$: 442.1477, Found: 442.1484.

General procedure for the synthesis of polysubstitued cyclopenta[*b*]indoles via realy Au(I)/Brønsted acid catalyzed one-pot process (Table 2).

A 5 mL glass vial was charged with alcohol (0.1 mmol), catalyst (2 mol%) and co-catalyst (2 mol%) in 1 mL of dichloroethane (DCE) and stirred at 60 ^{o}C until the alcohol was consumed as monitored by TLC. Upon disappearance of alcohol, 1,3-dicarbonyls (1.1 equiv)

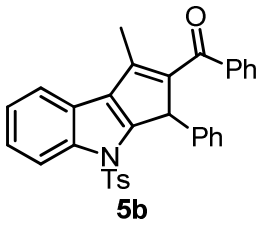
and triflic acid (10 mol%) were added and continued stirring at 60 ^{o}C until indoline and 1,3 dicarbonyl adducts disappeared. Reaction mixture was quenched with aqueous saturated sodium bicarbonate solution (1-2 mL). Diluted the reaction mixture with dichloromethane (1-2 mL) and the layers were separated. The aqueous layer was further extracted with solvent (1-2 mL). The organic layers were combined, dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (20-30% EtOAc/hexane) to afford polysubstituted cyclopenta[*b*]indoles.



5aMs

1-(2-Methyl-4-(methylsulfonyl)-3-phenyl-3,4-dihydrocyclopenta[*b*]indol-1-yl)ethanone (5aMs).

Colourless solid. M.P = 130-132 ^{o}C. R_f = 0.5 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 2924, 2919, 1630, 1511, 1481, 1447, 1371, 1275, 1171, 1091, 749. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96-7.94 (m, 1H), 7.88-7.86 (m, 1H), 7.42-7.29 (m, 3H), 7.27-7.17 (m, 4H), 5.17 (q, *J* = 2.0 Hz, 1H), 2.89 (d, *J* = 2.0 Hz, 3H), 2.37 (s, 3H), 2.17 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.7, 152.3, 149.4, 141.3, 140.0, 134.6, 129.2 (2CH, 1C), 128.7 (2CH), 127.6 (2CH), 124.6, 124.0, 119.7, 114.2, 52.4, 41.5, 30.2, 15.7. HRMS (ESI): *m/z* calcd for $C_{21}H_{20}NO_3S$ $(M+H)^+$: 366.1164, Found: 366.1149.

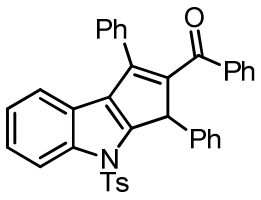


5b

(1-Methyl-3-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-2-yl(phenyl)methanone (5b).

Colourless solid. M.P = 195-197 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3503, 2915, 2852, 1608, 1474, 1445, 1375, 1174, 750. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07-8.05 (m, 1H), 7.77-7.05 (m, 1H), 7.59-7.53 (m, 2H), 7.53-7.46 (m, 1H), 7.44-7.31 (m, 4H), 7.22-7.11 (m, 5H), 7.11-6.98 (m, 4H), 5.55 (q, *J* = 2.0 Hz, 1H), 2.34 (d, *J* = 2.0 Hz, 3H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.9 (C=O), 152.0, 145.9, 145.7, 144.9, 143.2, 140.7, 139.8, 135.3, 134.9, 131.6, 130.0, 129.6 (2CH), 128.6, 128.5 (2CH), 128.4 (2CH), 128.2 (2CH), 127.1 (2CH), 126.9, 124.4, 124.1, 123.8, 119.3, 114.7, 63.4 (CH),

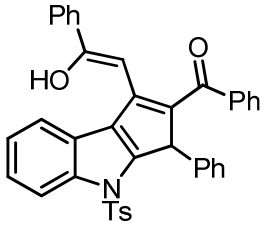
21.5 (CH_3), 16.6 (CH_3). HRMS (ESI): *m/z* calcd for $C_{32}H_{26}NO_3S$ $(M+H)^+$: 504.1633, Found: 504.1637.



5c

(1,3-Diphenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-2-yl)(phenyl)methanone (5c).

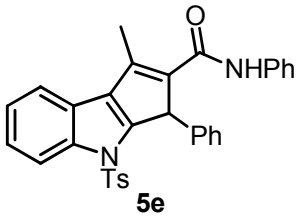
Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3057, 2918, 1658, 1608, 1467, 1375, 1174, 839, 750. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.50-7.52 (m, 1H), 7.42-7.29 (m, 7H), 7.27-7.20 (m, 6H), 7.20-7.12 (m, 4H), 7.09-6.98 (m, 4H), 5.75 (s, 1H), 2.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.4, 151.9, 147.1, 145.0, 143.3, 139.8, 138.3, 135.2, 135.0, 133.9, 131.3, 129.7 (2CH), 129.3 (2CH), 129.2 (2CH, C), 128.7 (2CH, C), 128.6, 128.3, 127.9 (2CH), 127.4 (2CH), 127.2 (2CH, C), 124.4, 124.0, 123.6, 120.0, 114.6, 53.7 (CH), 21.5 (CH_3). HRMS (ESI): *m/z* calcd for $C_{37}H_{28}NO_3S$ $(M+H)^+$: 566.1790, Found: 566.1793.



5d

1-((2-Hydroxy-2-phenylvinyl)-3-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-2-yl)(phenyl)methanone (5d).

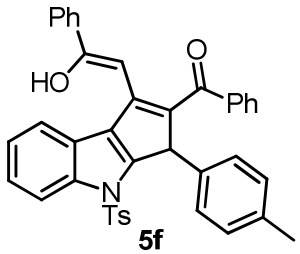
Yellow coloured solid. M.P = 225-227 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 3004, 2945, 2910, 1639, 1563, 1446, 1371, 1275, 1187, 767, 664. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 16.15 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.72-7.68 (m, 2H), 7.64-7.55 (m, 3H), 7.46-7.40 (m, 3H), 7.36-7.29 (m, 7H), 7.28-7.25 (m, 2H), 7.21-7.16 (m, 2H), 7.13-7.09 (m, 2H), 7.06-7.00 (m, 2H), 6.00 (s, 1H), 5.61 (s, 1H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 182.2, 181.8, 152.3, 147.8, 145.0, 140.9, 139.6, 135.7, 135.4, 135.1, 134.8, 131.6, 129.7 (2CH), 129.2, 129.1, 128.9 (2CH), 128.8 (4CH), 128.6 (2CH), 128.3 (2CH), 127.2 (2CH), 127.1, 126.6 (2CH), 124.5, 123.6, 119.7, 115.0, 104.5, 97.1, 52.5, 21.5. HRMS (ESI): *m/z* calcd for $C_{39}H_{30}NO_4S$ $(M+H)^+$: 608.1896, Found: 608.1904.



5e

1-Methyl-N,3-diphenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indole-2-carboxamide (5e).

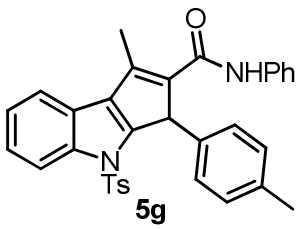
Colourless solid. M.P = 185-187 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 3094, 2924, 2856, 1658, 1597, 1529, 1495, 1372, 1174, 750. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.02-7.98 (m, 1H), 7.82-7.78 (m, 1H), 7.44-7.30 (m, 6H), 7.26-7.24 (m, 4H), 7.21-7.01 (m, 7H), 5.17 (q, *J* = 1.8 Hz, 1H), 2.90 (d, *J* = 1.8 Hz, 3H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.1(C=O), 150.0, 148.0, 144.9, 139.6, 138.0, 135.4, 134.9, 130.0, 129.6 (3CH), 129.5 (2CH), 129.3 (2CH), 128.8 (2CH), 128.3, 126.9 (2CH), 124.5, 124.1, 123.9, 123.8, 119.6 (2CH), 119.5, 114.7, 52.3 (CH), 21.5 (CH_3), 15.0 (CH_3). HRMS (ESI): *m/z* calcd for $C_{32}H_{27}N_2O_3S$ $(M+H)^+$: 519.1742, Found: 519.1757.



5f

(1-(2-Hydroxy-2-phenylvinyl)-3-(p-tolyl)-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-2-yl)(phenyl)methanone (5f).

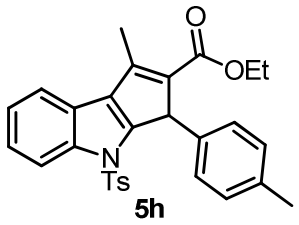
Yellow coloured solid. M.P = 240-242 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 3178, 2965, 2930, 1629, 1563, 1436, 1376, 1275, 1197, 767, 664. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 16.15 (s, 1H), 8.02 (d, *J* = 7.2 Hz, 1H), 7.72-7.76 (m, 2H), 7.64-7.56 (m, 3H), 7.47-7.29 (m, 3H), 7.35-7.29 (m, 3H), 7.28-7.06 (m, 8H), 7.05-6.99 (m, 2H), 6.00 (s, 1H), 5.57 (s, 1H), 2.38 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 182.3 (C=O), 181.8, 152.4, 147.7, 144.8, 140.9, 139.7, 136.7, 135.5, 135.2, 135.0, 132.4, 131.6, 129.6 (2CH), 129.2 (2CH), 129.0 (2CH), 128.9, 128.9, 128.8 (4CH), 128.3 (2CH), 127.2 (2CH), 126.6 (2CH), 124.6, 123.6, 123.5, 119.7, 114.5, 91.1, 52.2, 21.6 (CH_3), 22.3 (CH_3). HRMS (ESI): *m/z* calcd for $C_{40}H_{32}NO_4S$ $(M+H)^+$: 622.2052, Found: 622.2070.



5g

1-Methyl-N-phenyl-3-(p-tolyl)-4-tosyl-3,4-dihydrocyclopenta[*b*]indole-2-carboxamide (5g).

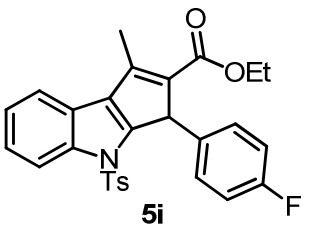
Colourless solid. M.P = 193-195 ^{o}C. R_f = 0.5 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3056, 2915, 1632, 1596, 1374, 1221, 1176, 1087, 818. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03-8.00 (m, 1H), 7.81-7.79 (m, 1H), 7.38-7.34 (m, 2H), 7.29-7.24 (m, 5H), 7.20 (m, 3H), 7.13-7.14 (m, 2H), 7.05-6.92 (m, 3H), 5.13 (q, *J* = 2.0 Hz, 1H), 2.89 (d, *J* = 2.0 Hz 3H), 2.43 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.1 (C=O), 150.1, 148.0, 144.8, 139.7, 138.2 (2CH), 135.0, 134.5, 132.1, 132.0, 130.1 (2CH), 130.0, 129.5 (2CH), 129.1, 128.8 (2CH), 127.0 (2CH), 124.4, 124.1, 123.9, 123.7, 119.5 (2CH), 119.4, 114.7, 51.9 (CH), 21.5 (CH_3), 21.2 (CH_3), 15.0 (CH_3). HRMS (ESI): *m/z* calcd for $C_{33}H_{29}N_2O_3S$ $(M+H)^+$: 533.1899, Found: 533.1877.



5h

Ethyl 1-methyl-3-(p-tolyl)-4-tosyl-3,4-dihydrocyclopenta[*b*]indole-2-carboxylate (5h).

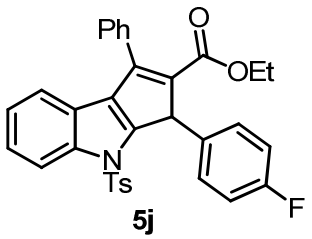
Colourless solid. M.P = 166-168 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 3064, 2981, 2931, 1693, 1597, 1373, 1275, 1174, 982, 703, 682. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03-8.01 (m, 1H), 7.79-7.76 (m, 1H), 7.36-7.37 (m, 2H), 7.11-7.09 (m, 2H), 7.09-6.97 (m, 6H), 5.19 (q, *J* = 2.0 Hz, 1H), 4.11 (m, 2H), 2.80 (d, *J* = 2.0 Hz, 3H), 2.37 (s, 3H), 2.31 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.5 (C=O), 151.7, 148.8, 144.7, 139.6, 136.3, 135.1, 133.1, 132.8, 129.5 (2CH), 129.3, 129.0 (2CH), 128.8 (2CH), 127.1 (2CH), 124.2, 124.1, 123.7, 119.3, 114.6, 59.6, 52.3, 21.5 (CH_3), 21.2, (CH_3) 14.8 (CH_3), 14.1 (CH_3). HRMS (ESI): *m/z* calcd for $C_{29}H_{28}NO_4S$ $(M+H)^+$: 486.1739, Found: 486.1733.



5i

Ethyl 3-(4-fluorophenyl)-1-methyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indole-2-carboxylate (5i).

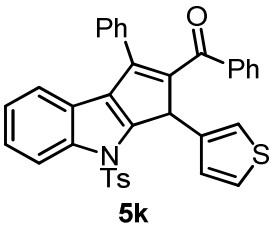
Colourless solid. M.P = 143-145 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3056, 2981, 2930, 1693, 1598, 1507, 1373, 1174, 1219, 737, 575. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05-8.02 (m, 1H), 7.78-7.77 (m, 1H), 7.36-7.28 (m, 2H), 7.16-7.14 (m, 2H), 7.06-7.05 (m, 4H), 6.89 (t, *J* = 8.8 Hz, 2H), 5.19 (q, *J* = 2.0 Hz, 1H), 4.17-4.05 (m, 2H), 2.80 (d, *J* = 2.0 Hz, 3H), 2.32 (s, 3H), 1.81 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.4, 162.0 (d, *J* = 243.1 Hz), 151.2, 149.2, 145.0, 139.7, 135.1, 132.9, 131.7 (d, *J* = 3.5 Hz), 130.6 (d, *J* = 31.4 Hz), 129.6 (2CH, 1C), 129.5, 126.8 (2CH, 1C), 124.4, 124.0, 123.8, 119.3 (d, *J* = 11.2) 115.0, 114.3 (d, *J* = 11.6 Hz), 59.7 (CH_2), 51.8 (CH), 21.5 (CH_3), 14.8, (CH_3) 14.1(CH_3). HRMS (ESI): *m/z* calcd for $C_{28}H_{25}FNO_4S$ $(M+H)^+$: 490.1488, Found: 490.1488.



5j

Ethyl 3-(4-fluorophenyl)-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[b]indole-2-carboxylate (5j).

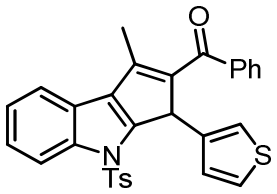
Colourless solid. M.P = 153-155 ^{o}C. R_f = 0.5 (hexane/EtOAc = 8/2). IR (thin film, neat): ν_{max}/cm^{-1} 3049, 2971, 2930, 1690, 1595, 1504, 1373, 1170, 1219, 737. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04-8.02 (m,1H), 7.66-7.63 (m, 2H), 7.54-7.48 (m, 3H), 7.35-7.31 (m, 2H), 7.21-7.15 (m, 5H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.94 (t, *J* = 8.8 Hz, 2H), 5.41 (s, 1H), 4.05 (dq, *J* = 10.8 and 7.2 Hz, 1H), 3.96 (dq, *J* = 10.9 and 7.1 Hz, 1H), 2.34 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.3, 151.7 (d, *J* = 127.8 Hz), 145.1, 139.8, 135.0, 134.0, 133.2, 131.3 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 8.0 Hz), 129.7 (2CH, C), 128.9 (2CH, C), 128.8, 128.5, 127.9 (2CH, C), 126.7 (2CH, C), 124.5, 123.7 (d, *J* = 3.6 Hz), 119.9, 115.1 (d, *J* = 11.0 Hz, 2C), 114.5, 59.9, 52.2, 21.5, 13.8. HRMS (ESI): *m/z* calcd for $C_{33}H_{27}FNO_4S$ $(M+H)^+$: 552.1645, Found: 552.1619.



5k

Phenyl(1-phenyl-3-(thiophen-2-yl)-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-2-yl) methanone (5k).

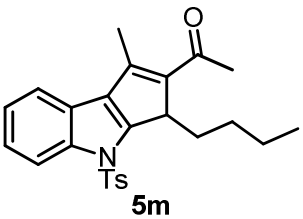
Colourless solid. M.P = 208-210 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3068, 2915, 2852, 1612, 1578, 1174, 1092, 836, 747. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.39-7.34 (m, 8H), 7.24-7.12 (m, 8H), 7.02 (t, *J* = 7.9 Hz, 2H), 6.86 (dd, *J* = 5.0 and 1.3 Hz, 1H), 5.97 (s, 1H), 2.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.5 (C=O), 150.9, 146.8, 145.0, 142.1, 139.9, 138.3, 135.1, 134.6, 133.8, 131.4 (2CH), 129.8 (2CH), 129.2 (2CH), 129.1 (2CH), 128.6 (2CH), 127.9 (2CH), 127.5 (2CH), 127.1 (2CH), 126.8, 125.1, 124.0, 123.7, 123.6, 120.0, 114.7, 49.0 (CH), 21.6 (CH_3). HRMS (ESI): *m/z* calcd for $C_{35}H_{26}NO_3S_2$ $(M+H)^+$: 572.1354, Found: 572.1359.



5l

(1-Methyl-3-(thiophen-2-yl)-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-2-yl)(phenyl) methanone (5l).

Colourless solid. M.P = 190-191 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2925, 2878, 1612, 1519, 1446, 1372, 1172, 1088, 745. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (dt, *J* = 8.2 and 0.9 Hz, 1H), 7.74-7.71 (m, 1H), 7.59-7.49 (m, 3H), 7.44-7.34 (m, 4H), 7.28-7.25 (m, 2H), 7.11-7.05 (m, 4H), 6.62 (dd, *J* = 4.9 and 1.4 Hz, 1H), 5.74 (q, *J* = 2.0 Hz, 1H), 2.37 (d, *J* = 2.0 Hz, 3H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.6 (C=O), 151.9, 145.8, 145.0, 141.9, 140.8, 139.8, 135.0, 134.7, 131.6, 129.7 (2CH), 128.4 (2CH, C), 128.3 (2CH), 127.0 (2CH), 126.7, 125.0, 124.5, 124.2, 123.8, 123.5, 119.3, 114.8, 48.7 (CH), 21.5 (CH_3), 15.7 (CH_3). HRMS (ESI): *m/z* calcd for $C_{30}H_{24}NO_3S_2$ $(M+H)^+$: 510.1198, Found: 510.1205.

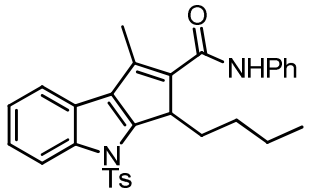


5m

1-(3-Butyl-1-methyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-2-yl)ethanone (5m).

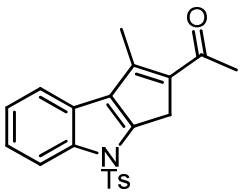
Colourless solid. M.P = 102-104 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 2958, 2927, 2858, 1658, 1598, 1498, 1371, 1174, 1089, 750, 665. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.17-8.11 (m, 1H), 7.74-7.64 (m, 3H), 7.38-7.25 (m, 2H), 7.21-7.13 (m, 2H),

4.83 (m, 1H), 2.72 (d, *J* = 1.9 Hz, 3H), 2.61-2.52 (m, 1H), 2.49 (s, 3H), 2.32 (s, 3H), 2.30-2.22 (m, 2H), 1.15-1.08 (m, 2H), 0.71 (t, *J* = 7.4 Hz, 3H), 1.15-1.08 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.7 (C=O), 151.8, 147.5, 145.2, 141.4, 140.9, 134.6, 131.6, 129.8 (2CH), 126.6 (2CH), 125.0, 124.4, 122.4, 119.1, 115.5, 48.0 (CH), 30.5, 29.9, 25.0, 22.7, 21.6, 15.8, 13.9. HRMS (ESI): *m/z* calcd for $C_{25}H_{28}NO_3S$ $(M+H)^+$: 422.1790, Found: 422.1804.



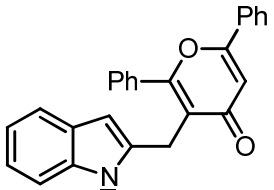
5n

3-Butyl-1-methyl-N-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indole-2-carboxamide (5n).
Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 2958, 2957, 1598, 1530, 1498, 1442, 1371, 1174, 1023, 750, 665. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15-8.07 (m, 1H), 7.76-7.61 (m, 4H), 7.45-7.29 (m, 6H), 7.23-7.13 (m, 3H), 4.31 (m, 1H), 2.74 (d, *J* = 1.9 Hz, 3H), 2.58 (m, 1H), 2.33 (s, 3H), 1.47-1.14 (m, 3H), 0.97-0.85 (m, 2H), 0.74 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.4, (C=O) 140.9, 145.2, 143.6, 140.8, 138.0, 135.5, 134.6, 131.5, 129.8 (2CH), 129.1 (2CH), 126.6 (2CH), 124.9, 124.3 (2CH), 124.2, 120.0 (2CH), 119.1, 115.4, 47.8, 30.0, 25.6, 22.7, 21.5, 14.7, 13.8. HRMS (ESI): *m/z* calcd for $C_{30}H_{31}N_2O_3S$ $(M+H)^+$: 499.2055, Found: 499.2062.



5o

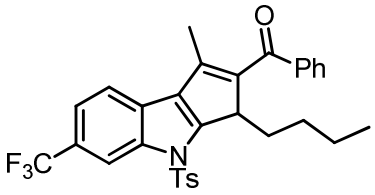
1-(1-Methyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-2-yl)ethanone (5o).
Colourless solid. M.P = 185-187 ^oC. R_f = 0.5 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3082, 2922, 2856, 1646, 1598, 1493, 1369, 1275, 1174, 1090, 915, 748. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13-8.06 (m, 1H), 7.85-7.79 (m, 3H), 7.74-7.69 (m, 4H), 4.04 (q, *J* = 2.4 Hz, 2H), 2.76 (t, *J* = 2.4 Hz, 3H), 2.45 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.7 (C=O), 149.2, 146.8, 145.6, 139.8, 134.9, 134.4, 131.2, 130.1 (2CH), 126.6 (2CH), 124.6, 124.4, 123.9, 119.3, 114.5, 36.2 (CH_2) 29.6 (CH_3) 21.6 (CH_3) 15.6 (CH_3). HRMS (ESI): *m/z* calcd for $C_{21}H_{20}NO_3S$ $(M+H)^+$: 366.1164, Found: 366.1169.



5p

2,6-Diphenyl-3-((1-tosyl-1*H*-indol-2-yl)methyl)-4*H*-pyran-4-one (5p).

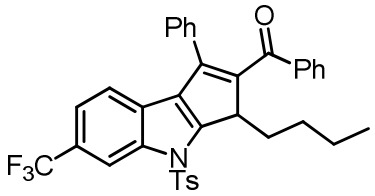
Colourless solid. M.P = 272-274 ^{o}C. R_f = 0.5 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3343, 2928, 2846, 1614, 1565, 1514, 1474, 1372, 1219, 1187, 1009, 749. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.2 Hz, 1H), 7.84-7.73 (m, 5H), 7.58-7.51 (m, 3H), 7.49-7.40 (m, 6H), 7.38-7.25 (m, 4H), 6.29 (s, 1H), 4.24 (s, 2H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 179.4, 163.3, 162.8, 144.7, 139.5, 137.0, 135.7, 132.0, 131.5, 131.2, 130.7, 129.9 (2CH), 129.6, 129.1 (2CH, C), 128.8 (2CH, C), 128.1 (2CH, C), 126.8 (2CH), 125.9 (2CH), 123.9, 123.4, 122.1, 120.4, 36.2, 21.6. HRMS (ESI): *m/z* calcd for $C_{33}H_{26}NO_4S$ $(M+H)^+$: 532.1583, Found: 532.1583.



5q

(3-Butyl-1-phenyl-4-tosyl-6-(trifluoromethyl)-3,4-dihydrocyclopenta[*b*]indol-2-yl) (phenyl)methanone (5q).

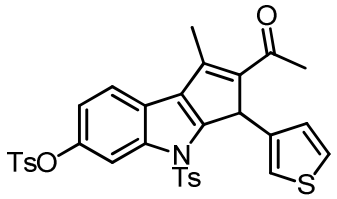
Colourless oil. R_f = 0.5 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 2957, 2923, 2883, 1629, 1577, 1515, 1148, 1325, 1173, 1124, 981, 813. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.82-7.66 (m, 4H), 7.63-7.48 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.61 (m, 1H), 2.52-2.39 (m, 2H), 2.36 (s, 3H), 2.18 (d, *J* = 2.0 Hz, 3H), 1.17 (m, 2H), 1.03-0.78 (m, 2H), 0.75 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.3, 153.9, 144.5, 144.6, 142.6, 140.4, 140.1, 134.3, 132.2, 130.9 (q, *J* = 256.0 Hz), 130.1 (3CH), 128.8 (3CH), 128.6 (3CH), 127.4, 126.7, 121.0 (q, *J* = 3.0 Hz), 119.3, 112.8 (q, *J* = 3.0 Hz), 49.1, 29.5, 26.5, 22.6, 21.6, 15.8, 13.8. HRMS (ESI): *m/z* calcd for $C_{31}H_{29}F_3NO_3S$ $(M+H)^+$: 552.1820, Found: 552.1824.



5r

(3-Butyl-1-phenyl-4-tosyl-6-(trifluoromethyl)-3,4-dihydrocyclopenta[*b*]indol-2-yl) (phenyl)methanone (5r).

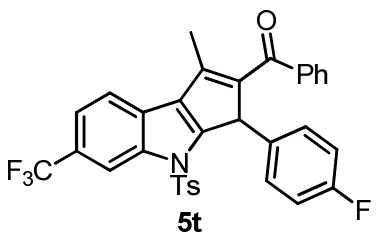
Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 2959, 2929, 2873, 1619, 1577, 1515, 1148, 1325, 1173, 1124, 981, 813. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.56-7.52 (m, 2H), 7.48-7.42 (m, 2H), 7.29-7.23 (m, 5H), 7.19-1.08 (m, 5H), 4.79 (t, *J* = 4.0 Hz, 1H), 2.69-2.56 (m, 1H), 2.36 (s, 3H), 2.34-2.27 (m, 1H), 1.29-1.17 (m, 2H), 1.12-0.87 (m, 2H), 0.76 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.3, 153.7, 145.6, 144.5, 142.7, 140.1, 138.1, 134.2, 133.8, 131.7, 130.1 (2CH), 129.3 (2CH), 129.1 (3CH), 128.5 (q, *J* = 267.0 Hz), 128.0 (3CH), 127.7 (2CH), 127.2, 126.7, 126.4, 120.8, 120.3 (q, *J* = 2.0 Hz), 120.0, 112.6 (q, *J* = 2.0 Hz), 49.5, 29.5, 26.5, 22.6, 21.6, 13.8. HRMS (ESI): *m/z* calcd for $C_{36}H_{29}F_3NO_3S$ $(M-H)^+$: 612.1820, Found: 612.1829.



5s

2-Acetyl-1-methyl-3-(thiophen-3-yl)-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-6-yl 4-methylbenzenesulfonate (5s).

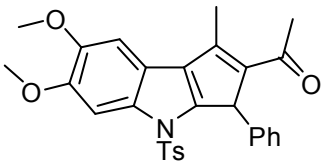
Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 3/2). IR (thin film, neat): ν_{max}/cm^{-1} 2926, 2924, 1654, 1592, 1521, 1450, 1367, 1157, 1245, 1024, 690. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 9.0 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 3H), 7.41-7.31 (m, 6H), 7.19 (dd, *J* = 5.6 Hz and 3.0 Hz, 1H), 6.92 (dd, *J* = 9.0 Hz and 2.4 Hz, 1H), 6.68 (dd, *J* = 5.0 Hz and 1.2 Hz, 1H), 5.44 (q, *J* = 1.9 Hz, 1H), 2.67 (d, *J* = 1.9 Hz, 3H), 2.49 (s, 3H), 2.33 (s, 3H), 2.18 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.8, 152.3, 147.5, 145.9, 145.6, 145.4, 140.9, 137.7, 134.6 (2CH), 132.3, 129.9 (2CH), 129.8 (2CH), 128.7, 128.6 (2CH), 127.5, 127.0 (2CH), 125.5, 124.6, 124.5, 118.7, 115.2, 113.3, 48.1, 30.1, 21.7, 21.5, 15.3. HRMS (ESI): *m/z* calcd for $C_{32}H_{27}NO_6S_3$ $(M)^+$: 617.1000. Found: 617.1046.



5t

(3-(4-Fluorophenyl)-1-methyl-4-tosyl-6-(trifluoromethyl)-3,4-dihydrocyclopenta[*b*] indol-2-yl)(phenyl)methanone (5t).

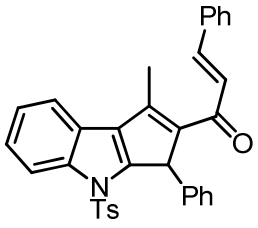
Colourless amorphous solid. M.P = 128-131 ^{o}C. R_f= 0.5 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3503, 2960, 2925, 1638, 1449, 1363, 1218, 1173, 1091, 917, 733, 665, 542. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.62-7.50 (m, 4H), 7.45-7.39 (m, 2H), 7.24-7.17 (m, 2H), 7.11-7.09 (m, 2H), 7.04-6.96 (m, 2H), 6.88-6.79 (m, 2H), 5.56 (d, *J* = 2.0 Hz, 1H), 2.35 (s, 3H), 2.33 (d, *J* = 2.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.3, 161.2 (d, *J* = 244.1 Hz), 153.7, 145.6, 144.5, 143.6, 140.2, 139.1, 134.5, 132.0, 130.5 (d, *J* = 2.9 Hz), 130.0 (2CH, C), 129.9 (2CH), 129.5 (q, *J* = 265.0 Hz), 128.5 (2CH, C), 128.4 (2CH), 126.8 (2CH), 126.4, 120.8 (q, *J* = 3.0 Hz), 119.6, 115.5, 115.3, 112.2 (q, *J* = 3.0 Hz), 52.7, 21.5, 15.7. HRMS (ESI): *m/z* calcd for $C_{33}H_{24}F_4NO_3S$ $(M+H)^+$: 590.1413, Found: 590.1416.



5u

1-(6,7-Dimethoxy-1-methyl-3-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-2-yl)ethanone (5u).

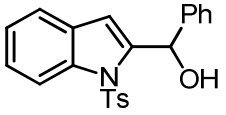
Colourless amorphous solid. M.P = 174-176 ^{o}C. R_f= 0.5 (hexane/EtOAc = 1/1). IR (thin film, neat): ν_{max}/cm^{-1} 3060, 2917, 1649, 1579, 1492, 1366, 1301, 1169, 1086, 907. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.28-7.23 (m, 3H), 7.71 (s, 3H), 7.06-6.99 (m, 4H), 6.17 (s, 1H), 3.97 (s, 6H), 2.81 (s, 3H), 2.30 (s, 3H), 2.15 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.9, 150.7, 148.8, 147.8, 147.4, 145.0, 142.1, 135.7, 134.9, 134.0, 130.0, 129.7 (2CH), 129.4, 128.6 (2CH), 127.2, 126.9 (2CH, 1C), 117.0, 101.2, 98.7, 56.4 ($2CH_3$), 52.9, 30.5, 21.6, 15.8.



5v

1-(1-Methyl-3-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-2-yl)-3-phenylprop-2-en-1-one (5v).

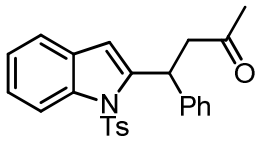
Pale yellow solid. M.P = 114-116 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2924, 2919, 1610, 1511, 1481, 1447, 1371, 1275, 1171, 1091, 749. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00-7.98 (m, 1H), 7.89-7.81 (m, 1H), 7.61-7.47 (m, 3H), 7.45-7.34 (m, 8H), 7.21-7.11 (m, 2H), 7.07-6.96 (m, 5H), 5.47 (q, *J* = 2.0 Hz, 1H), 2.91 (d, *J* = 2.0 Hz, 3H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 186.2, 152.3, 149.5, 144.9, 142.7, 141.8, 139.7, 135.3, 135.2, 134.8, 130.3, 130.0, 129.7 (2CH), 129.3, 129.0, 128.8 (2CH), 128.7 (2CH), 128.6, 128.2, 127.3, 127.2, 127.1 (2CH), 125.5, 124.5, 123.9, 119.6, 114.7, 52.7, 21.5, 15.9. HRMS (ESI): *m/z* calcd for $C_{34}H_{28}NO_3S$ $(M+H)^+$: 530.1790, Found: 530.1798.



6

Phenyl(1-tosyl-1*H*-indol-2-yl)methanol (6).

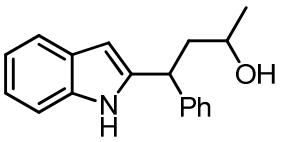
Colourless oil. R_f = 0.5 (hexane/EtOAc = 3/2). IR (thin film, neat): ν_{max}/cm^{-1} 3547, 3163, 2925, 1567, 1493, 1451, 1368, 1172, 1053, 916, 701. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.12 (m, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.46-7.41 (m, 6H), 7.32 (ddd, *J* = 8.4, 7.3 and 1.4 Hz, 2H), 7.28-7.20 (m, 2H), 6.42 (d, *J* = 4.5 Hz, 1H). 6.19 (s, 1H), 3.68 (d, *J* = 4.8 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.1, 143.9, 140.7, 137.3, 135.5, 129.9 (2CH), 128.8, 128.3 (2CH), 127.9, 127.0 (2CH), 126.4 (2CH), 125.0, 123.8, 121.2, 114.7, 112.2, 69.3, 21.6. HRMS (ESI): *m/z* calcd for $C_{22}H_{18}NO_2S$ $(M–OH)^+$: 360.1058, Found: 360.1021.



9

4-Phenyl-4-(1-tosyl-1*H*-indol-2-yl)butan-2-one (9).

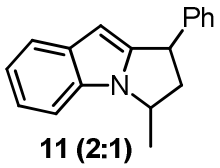
Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2958, 973, 2872, 1713, 1513, 1475, 1372, 1308, 1211, 1188, 1175, 1090, 748. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.2 Hz, 1H), 7.58-7.53 (m, 3H), 7.33-7.18 (m, 7H), 7.15-7.11 (m, 2H), 6.44 (s, 1H), 5.40 (t, *J* = 7.4 Hz, 1H), 3.34 (dd, *J* = 17.2 and 7.6 Hz, 1H), 3.08 (dd, *J* = 17.1 and 7.6 Hz, 1H), 2.32 (s, 3H), 2.17 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.8, 144.6, 143.5, 141.8, 135.6, 129.6 (2CH), 129.2, 128.6 (2CH), 128.1 (2CH, C), 126.8, 126.7 (2CH), 124.0, 123.6, 120.4, 115.1, 109.8, 51.0, 39.5, 30.1, 21.5. HRMS (ESI): *m/z* calcd for $C_{25}H_{23}NO_3SNa$ $(M+Na)^+$: 440.1296, Found: 440.1287.



10 (1:1)

4-(1*H*-Indol-2-yl)-4-phenylbutan-2-ol (10).

Colourless oil. R_f = 0.5 (hexane/EtOAc = 3/2). IR (thin film, neat): ν_{max}/cm^{-1} 3537, 3063, 2925, 1597, 1493, 1451, 1368, 1172, 1053, 916, 701. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.40 (br s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.37-7.22 (m, 6H), 7.15-7.07 (m, 2H), 6.40 (s, 1H), 4.40-4.35 (m, 1H), 3.92-3.66 (m, 1H), 2.32 (ddd, *J* = 12.1, 8.6 and 6.7 Hz, 1H), 2.14 (ddd, *J* = 12.1, 8.6 and 6.7 Hz, 1H), 1.29 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.1, 142.4, 136.1, 128.8 (2CH, 1C), 128.3 (2CH), 126.9, 121.3, 120.0, 119.6, 110.5, 98.4, 66.0, 44.5, 41.7, 24.0. HRMS (ESI): *m/z* calcd for $C_{18}H_{18}NO$ $(M–H)^+$: 264.1389, Found: 264.1380.



11 (2:1)

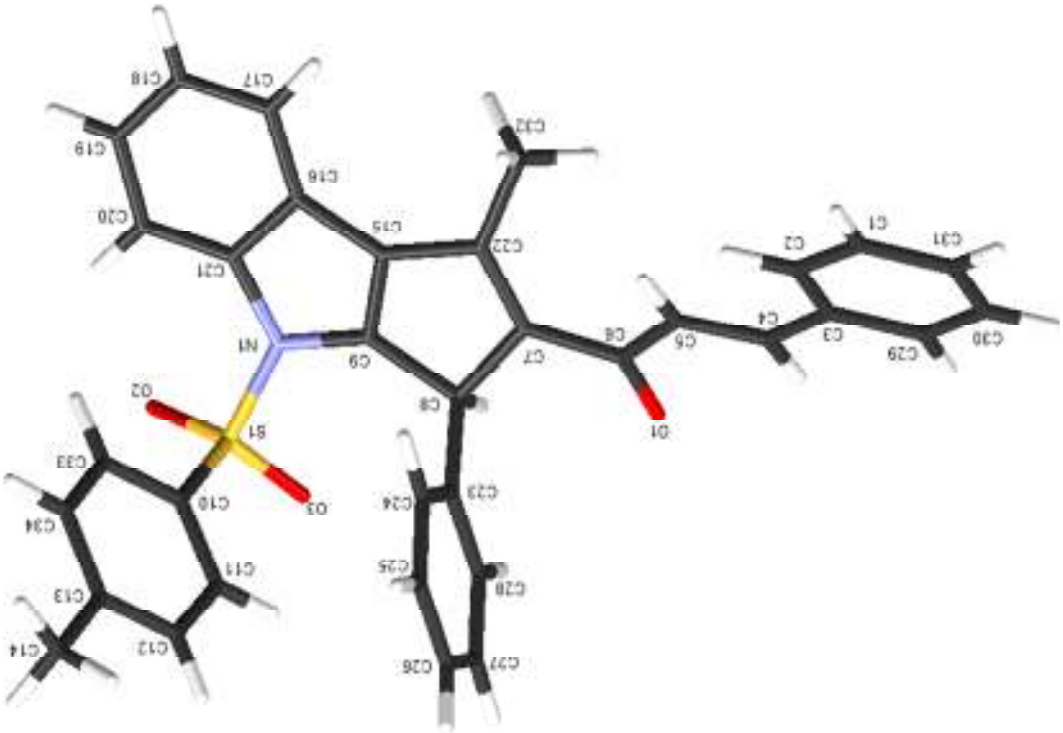
3-Methyl-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (11 major).

Colourless oil. R_f = 0.5 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 2915, 1567, 1451, 1430, 1192, 1153, 926, 701. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60-7.58 (m, 2H), 7.40-7.36 (m, 5H), 7.19-7.16 (m, 2H), 6.12 (s, 1H), 4.54 (t, *J* = 8.5 Hz, 1H), 4.77 (qt, *J* = 8.5 and 6.7 Hz, 1H), 3.23 (ddd, *J* = 12.7, 8.5 and 6.7 Hz, 1H), 2.22 (ddd, *J* = 12.8, 8.5 and 7.8 Hz, 1H), 1.74 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.8, 142.9, 133.4, 132.2, 128.6 (2CH, C), 127.6 (2CH), 120.8, 120.3, 119.1, 109.7, 93.5, 53.2, 47.7, 43.2, 20.9. HRMS (ESI): *m/z* calcd for $C_{18}H_{18}N$ $(M+H)^+$: 248.1439, Found: 248.1475.

3-Methyl-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (11 minor).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.45 (m, 2H), 7.40-7.36 (m, 5H), 7.18-7.16 (m, 2H), 6.10 (s, 1H), 4.78-4.74 (m, 2H), 2.76-2.70 (m, 2H), 1.57 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.3, 142.8, 133.3, 132.2, 131.9, 127.7 (2CH, C), 126.8 (2CH), 120.7, 120.2, 109.5, 93.3, 51.7, 47.0, 42.2, 20.0.

Crystal structure of 5v (CCDC 1029309): Structure of the cyclopentannulated indole **5v** was confirmed by single crystal X-ray diffraction analysis.



Another view of the crystal structure of indole **5v**

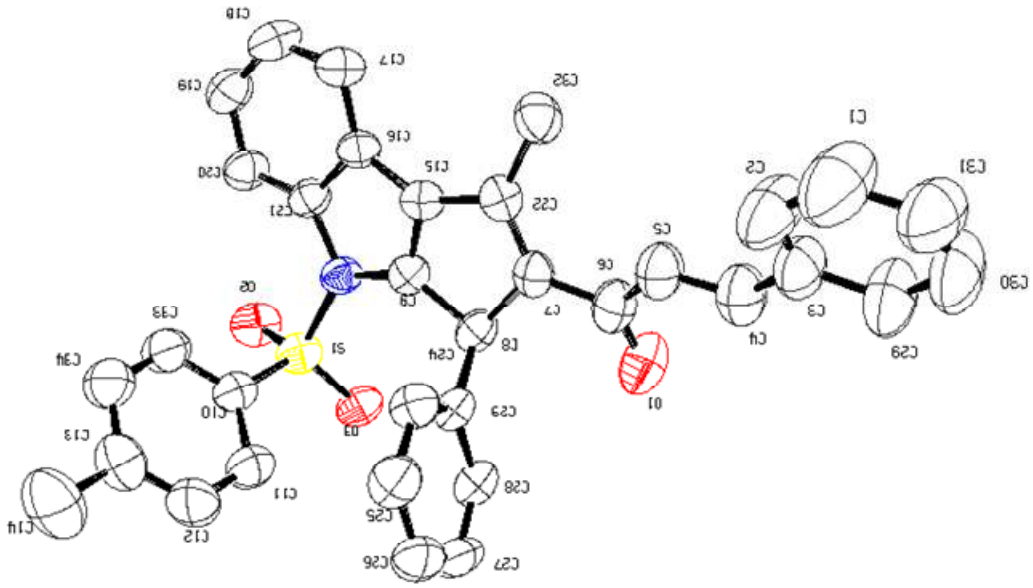


Fig 1S. ORTEP diagram of **5v** (CCDC 1029309).

A specimen of $C_{34}H_{27}NO_3S$ was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using a monoclinic unit cell yielded a total of 22157 reflections to a maximum θ angle of 25.24° (0.83 Å resolution), of which 3925 were

independent (average redundancy 5.645, completeness = 98.7%, R_{int} = 6.91%, R_{sig} = 5.76%) and 2599 (66.22%) were greater than $2\sigma(F^2)$. The final cell constants of a = 6.1013(8) Å, b = 15.039(2) Å, c = 23.894(3) Å, β = 90.877(8)°, volume = 2192.2(5) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I).

The final anisotropic full-matrix least-squares refinement on F^2 with 355 variables converged at R1 = 6.40%, for the observed data and wR2 = 18.10% for all data. The goodness-of-fit was 1.080. The largest peak in the final difference electron density synthesis was 0.344 $e^-/Å^3$ and the largest hole was -0.285 $e^-/Å^3$ with an RMS deviation of 0.091 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.605 g/cm^3 and F(000), 1112 e^-.

Table 1. Sample and crystal data for SCI_234_SM_SE_11_48.

Identification code	SCI_234_SM_SE_11_48	
Chemical formula	$C_{34}H_{27}NO_3S$	
Formula weight	529.62	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 6.1013(8) Å	α = 90°
	b = 15.039(2) Å	β = 90.877(8)°
	c = 23.894(3) Å	γ = 90°
Volume	2192.2(5) $Å^3$	
Z	4	
Density (calculated)	1.605 g/cm^3	
Absorption coefficient	0.193 mm^{-1}	
F(000)	1112	

Table 2. Data collection and structure refinement for SCI_234_SM_SE_11_48.

Theta range for data collection	1.60 to 25.24°
Index ranges	-7<=h<=7, -16<=k<=17, -28<=l<=28
Reflections collected	22157
Independent reflections	3925 [R(int) = 0.0691]
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014 (Sheldrick, 2014)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints /	3925 / 0 / 355

parameters		
Goodness-of-fit on F^2	1.080	
Δ/σ_{max}	0.005	
Final R indices	2599 data; I>2σ(I)	R1 = 0.0640, wR2 = 0.1539
	all data	R1 = 0.1080, wR2 = 0.1810
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1000P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Extinction coefficient	0.0190(20)	
Largest diff. peak and hole	0.344 and -0.285 eÅ^{-3}	
R.M.S. deviation from mean	0.091 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for SCI_234_SM_SE_11_48.

	x/a	y/b	z/c	U(eq)
S1	0.71389(15)	0.99604(6)	0.20634(4)	0.0466(3)
O1	0.0698(5)	0.24283(18)	0.04479(12)	0.0731(8)
O2	0.6686(4)	0.91187(14)	0.21787(10)	0.0534(7)
O3	0.9193(3)	0.02321(15)	0.20237(10)	0.0510(7)
N1	0.6055(4)	0.01402(17)	0.14834(11)	0.0407(7)
C1	0.5889(10)	0.5273(4)	0.9093(3)	0.120(2)
C2	0.6393(8)	0.4587(3)	0.9405(2)	0.0962(17)
C3	0.8414(8)	0.4361(3)	0.94580(18)	0.0705(12)
C4	0.9092(8)	0.3652(3)	0.97712(17)	0.0684(11)
C5	0.7955(7)	0.3097(3)	0.00145(16)	0.0628(11)
C6	0.8856(7)	0.2433(2)	0.03427(16)	0.0555(10)
C7	0.7564(6)	0.1800(2)	0.05659(14)	0.0430(8)
C8	0.8246(5)	0.1391(2)	0.10799(14)	0.0423(8)
C9	0.6528(5)	0.0785(2)	0.11459(14)	0.0406(8)
C10	0.5853(5)	0.0595(2)	0.25016(14)	0.0425(8)
C11	0.6883(6)	0.1246(3)	0.27405(16)	0.0579(10)
C12	0.5872(8)	0.1720(3)	0.31024(16)	0.0681(11)
C13	0.3883(8)	0.1576(3)	0.32257(16)	0.0632(11)
C14	0.2799(9)	0.2123(3)	0.3613(2)	0.0933(15)
C15	0.5159(5)	0.0832(2)	0.07491(14)	0.0408(8)
C16	0.3658(5)	0.0193(2)	0.08188(14)	0.0403(8)

	x/a	y/b	z/c	U(eq)
C17	0.1940(6)	0.9925(2)	0.05409(16)	0.0523(9)
C18	0.0852(6)	0.9263(3)	0.07283(18)	0.0612(11)
C19	0.1441(6)	0.8850(3)	0.11794(17)	0.0591(10)
C20	0.3143(6)	0.9094(2)	0.14640(15)	0.0495(9)
C21	0.4221(5)	0.9764(2)	0.12786(14)	0.0416(8)
C22	0.5794(6)	0.1468(2)	0.03836(14)	0.0442(8)
C23	0.8545(5)	0.2022(2)	0.15184(13)	0.0418(8)
C24	0.6939(6)	0.2534(2)	0.16568(15)	0.0506(9)
C25	0.7207(7)	0.3127(3)	0.20399(16)	0.0589(10)
C26	0.9083(7)	0.3229(3)	0.22751(16)	0.0586(10)
C27	0.0675(7)	0.2730(3)	0.21393(16)	0.0578(10)
C28	0.0425(6)	0.2132(2)	0.17554(15)	0.0494(9)
C29	0.9863(9)	0.4835(3)	0.9213(2)	0.0916(15)
C30	0.9306(10)	0.5509(3)	0.8909(2)	0.0981(17)
C31	0.7344(11)	0.5723(4)	0.8853(2)	0.1014(18)
C32	0.4644(6)	0.1634(3)	0.98803(14)	0.0565(10)
C33	0.3865(6)	0.0433(3)	0.26236(16)	0.0566(10)
C34	0.2872(6)	0.0928(3)	0.29771(17)	0.0653(11)

Table 4. Bond lengths (Å) for SCI_234_SM_SE_11_48.

S1-O3	1.323(2)	S1-O2	1.326(2)
S1-N1	1.550(3)	S1-C10	1.627(3)
O1-C6	1.148(4)	N1-C9	1.297(4)
N1-C21	1.340(4)	C1-C31	1.261(7)
C1-C2	1.306(7)	C1-H1	0.93
C2-C3	1.284(6)	C2-H17	0.93
C3-C29	1.284(6)	C3-C4	1.364(6)
C4-C5	1.236(5)	C4-H18	0.93
C5-C6	1.379(5)	C5-H15	0.93
C6-C7	1.351(5)	C7-C22	1.261(4)
C7-C8	1.429(4)	C8-C9	1.399(4)
C8-C23	1.423(4)	C8-H14	0.98

C9-C15	1.256(4)	C10-C33	1.275(5)
C10-C11	1.292(5)	C11-C12	1.286(5)
C11-H5	0.93	C12-C13	1.272(5)
C12-H4	0.93	C13-C34	1.294(5)
C13-C14	1.409(5)	C14-H3	0.96
C14-H24	0.96	C14-H2	0.96
C15-C16	1.339(4)	C15-C22	1.355(4)
C16-C17	1.297(4)	C16-C21	1.316(4)
C17-C18	1.282(5)	C17-H9	0.93
C18-C19	1.290(5)	C18-H8	0.93
C19-C20	1.286(5)	C19-H7	0.93
C20-C21	1.286(4)	C20-H6	0.93
C22-C32	1.406(5)	C23-C28	1.282(4)
C23-C24	1.293(4)	C24-C25	1.287(5)
C24-H13	0.93	C25-C26	1.276(5)
C25-H12	0.93	C26-C27	1.273(5)
C26-H26	0.93	C27-C28	1.292(5)
C27-H11	0.93	C28-H10	0.93
C29-C30	1.289(6)	C29-H16	0.93
C30-C31	1.245(7)	C30-H30	0.93
C31-H31	0.93	C32-H21	0.96
C32-H20	0.96	C32-H19	0.96
C33-C34	1.285(5)	C33-H23	0.93
C34-H22	0.93		

Table 5. Bond angles (°) for SCI_234_SM_SE_11_48.

O3-S1-O2	120.71(15)	O3-S1-N1	105.88(15)
O2-S1-N1	105.36(14)	O3-S1-C10	109.37(16)
O2-S1-C10	108.79(16)	N1-S1-C10	105.66(15)

C9-N1-C21	106.4(3)	C9-N1-S1	126.2(2)
C21-N1-S1	126.5(3)	C31-C1-C2	121.5(6)
C31-C1-H1	119.3	C2-C1-H1	119.3
C3-C2-C1	118.9(5)	C3-C2-H17	120.6
C1-C2-H17	120.6	C2-C3-C29	118.4(5)
C2-C3-C4	123.0(5)	C29-C3-C4	118.7(5)
C5-C4-C3	128.2(5)	C5-C4-H18	115.9
C3-C4-H18	115.9	C4-C5-C6	122.3(4)
C4-C5-H15	118.8	C6-C5-H15	118.8
O1-C6-C7	119.0(4)	O1-C6-C5	120.6(4)
C7-C6-C5	120.4(4)	C22-C7-C6	130.1(4)
C22-C7-C8	111.3(3)	C6-C7-C8	118.6(3)
C9-C8-C23	116.0(3)	C9-C8-C7	99.7(3)
C23-C8-C7	112.2(3)	C9-C8-H14	109.5
C23-C8-H14	109.5	C7-C8-H14	109.5
C15-C9-N1	111.1(3)	C15-C9-C8	111.7(3)
N1-C9-C8	137.0(3)	C33-C10-C11	120.1(4)
C33-C10-S1	120.3(3)	C11-C10-S1	119.5(3)
C12-C11-C10	118.9(4)	C12-C11-H5	120.6
C10-C11-H5	120.6	C13-C12-C11	122.0(4)
C13-C12-H4	119.0	C11-C12-H4	119.0
C12-C13-C34	118.2(4)	C12-C13-C14	120.7(5)
C34-C13-C14	121.1(5)	C13-C14-H3	109.5
C13-C14-H24	109.5	H3-C14-H24	109.5
C13-C14-H2	109.5	H3-C14-H2	109.5
H24-C14-H2	109.5	C9-C15-C16	108.3(3)
C9-C15-C22	109.4(3)	C16-C15-C22	142.1(3)
C17-C16-C21	118.3(3)	C17-C16-C15	135.1(3)
C21-C16-C15	106.6(3)	C18-C17-C16	118.8(4)
C18-C17-H9	120.6	C16-C17-H9	120.6
C17-C18-C19	121.8(4)	C17-C18-H8	119.1
C19-C18-H8	119.1	C20-C19-C18	121.2(4)
C20-C19-H7	119.4	C18-C19-H7	119.4
C19-C20-C21	117.0(4)	C19-C20-H6	121.5
C21-C20-H6	121.5	C20-C21-C16	123.0(3)
C20-C21-N1	129.3(3)	C16-C21-N1	107.7(3)
C7-C22-C15	108.0(3)	C7-C22-C32	129.7(3)
C15-C22-C32	122.2(3)	C28-C23-C24	119.1(3)
C28-C23-C8	121.0(3)	C24-C23-C8	119.7(3)

C25-C24-C23	120.4(4)	C25-C24-H13	119.8
C23-C24-H13	119.8	C26-C25-C24	120.0(4)
C26-C25-H12	120.0	C24-C25-H12	120.0
C27-C26-C25	120.0(4)	C27-C26-H26	120.0
C25-C26-H26	120.0	C26-C27-C28	120.6(4)
C26-C27-H11	119.7	C28-C27-H11	119.7
C23-C28-C27	119.9(4)	C23-C28-H10	120.0
C27-C28-H10	120.0	C3-C29-C30	121.0(5)
C3-C29-H16	119.5	C30-C29-H16	119.5
C31-C30-C29	120.6(5)	C31-C30-H30	119.7
C29-C30-H30	119.7	C30-C31-C1	119.6(6)
C30-C31-H31	120.2	C1-C31-H31	120.2
C22-C32-H21	109.5	C22-C32-H20	109.5
H21-C32-H20	109.5	C22-C32-H19	109.5
H21-C32-H19	109.5	H20-C32-H19	109.5
C10-C33-C34	120.0(4)	C10-C33-H23	120.0
C34-C33-H23	120.0	C33-C34-C13	120.8(4)
C33-C34-H22	119.6	C13-C34-H22	119.6

Table 6. Torsion angles (°) for SCI_234_SM_SE_11_48.

O3-S1-N1-C9	-32.2(3)	O2-S1-N1-C9	-161.1(3)
C10-S1-N1-C9	83.8(3)	O3-S1-N1-C21	160.4(3)
O2-S1-N1-C21	31.5(3)	C10-S1-N1-C21	-83.6(3)
C31-C1-C2-C3	-1.3(11)	C1-C2-C3-C29	1.8(9)
C1-C2-C3-C4	-179.4(6)	C2-C3-C4-C5	5.1(8)
C29-C3-C4-C5	-176.2(5)	C3-C4-C5-C6	-176.7(4)
C4-C5-C6-O1	8.1(7)	C4-C5-C6-C7	-174.9(4)
O1-C6-C7-C22	-152.1(4)	C5-C6-C7-C22	30.8(6)
O1-C6-C7-C8	25.5(5)	C5-C6-C7-C8	-151.6(3)
C22-C7-C8-C9	-0.4(4)	C6-C7-C8-C9	-178.5(3)
C22-C7-C8-C23	-123.8(3)	C6-C7-C8-C23	58.1(4)
C21-N1-C9-C15	-0.7(4)	S1-N1-C9-C15	-170.2(2)
C21-N1-C9-C8	-173.9(4)	S1-N1-C9-C8	16.7(6)

C23-C8-C9-C15	121.2(3)	C7-C8-C9-C15	0.5(4)
C23-C8-C9-N1	-65.6(5)	C7-C8-C9-N1	173.6(4)
O3-S1-C10-C33	-177.1(3)	O2-S1-C10-C33	-43.3(3)
N1-S1-C10-C33	69.4(3)	O3-S1-C10-C11	0.5(3)
O2-S1-C10-C11	134.3(3)	N1-S1-C10-C11	-113.0(3)
C33-C10-C11-C12	0.3(6)	S1-C10-C11-C12	-177.3(3)
C10-C11-C12-C13	-1.1(7)	C11-C12-C13-C34	0.3(7)
C11-C12-C13-C14	-178.2(4)	N1-C9-C15-C16	0.6(4)
C8-C9-C15-C16	175.6(3)	N1-C9-C15-C22	-175.4(3)
C8-C9-C15-C22	-0.5(4)	C9-C15-C16-C17	-178.5(4)
C22-C15-C16-C17	-4.6(8)	C9-C15-C16-C21	-0.2(4)
C22-C15-C16-C21	173.7(4)	C21-C16-C17-C18	0.7(6)
C15-C16-C17-C18	178.9(4)	C16-C17-C18-C19	-1.0(6)
C17-C18-C19-C20	0.6(7)	C18-C19-C20-C21	0.0(6)
C19-C20-C21-C16	-0.3(6)	C19-C20-C21-N1	-178.4(4)
C17-C16-C21-C20	-0.1(5)	C15-C16-C21-C20	-178.7(3)
C17-C16-C21-N1	178.4(3)	C15-C16-C21-N1	-0.2(4)
C9-N1-C21-C20	178.9(3)	S1-N1-C21-C20	-11.6(5)
C9-N1-C21-C16	0.6(4)	S1-N1-C21-C16	170.0(2)
C6-C7-C22-C15	177.9(4)	C8-C7-C22-C15	0.2(4)
C6-C7-C22-C32	2.2(7)	C8-C7-C22-C32	-175.5(3)
C9-C15-C22-C7	0.2(4)	C16-C15-C22-C7	-173.7(4)
C9-C15-C22-C32	176.2(3)	C16-C15-C22-C32	2.4(7)
C9-C8-C23-C28	128.1(4)	C7-C8-C23-C28	-118.2(4)
C9-C8-C23-C24	-56.5(5)	C7-C8-C23-C24	57.2(4)
C28-C23-C24-C25	-2.2(5)	C8-C23-C24-C25	-177.7(3)
C23-C24-C25-C26	1.9(6)	C24-C25-C26-C27	-1.6(6)
C25-C26-C27-C28	1.6(6)	C24-C23-C28-C27	2.2(5)

C8-C23-C28-C27	177.6(3)	C26-C27-C28-C23	-1.9(6)
C2-C3-C29-C30	-1.7(8)	C4-C3-C29-C30	179.5(5)
C3-C29-C30-C31	1.0(10)	C29-C30-C31-C1	-0.4(11)
C2-C1-C31-C30	0.6(11)	C11-C10-C33-C34	1.3(6)
S1-C10-C33-C34	178.8(3)	C10-C33-C34-C13	-2.1(6)
C12-C13-C34-C33	1.3(7)	C14-C13-C34-C33	179.8(4)

Table 7. Anisotropic atomic displacement parameters ($Å^2$) for SCI_234_SM_SE_11_48.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0450(6)	0.0411(6)	0.0535(6)	0.0026(4)	-0.0086(4)	0.0045(4)
O1	0.0525(18)	0.073(2)	0.094(2)	0.0128(16)	0.0161(15)	-0.0043(15)
O2	0.0642(16)	0.0291(13)	0.0664(16)	0.0071(11)	-0.0123(13)	0.0032(11)
O3	0.0305(13)	0.0590(16)	0.0632(16)	0.0005(12)	-0.0088(11)	0.0028(11)
N1	0.0420(16)	0.0360(16)	0.0439(16)	0.0018(13)	-0.0055(13)	-0.0047(13)
C1	0.082(4)	0.107(4)	0.171(6)	0.058(5)	-0.021(4)	-0.013(3)
C2	0.068(3)	0.083(4)	0.138(5)	0.045(3)	-0.011(3)	-0.011(3)
C3	0.085(3)	0.052(3)	0.074(3)	0.009(2)	0.008(3)	-0.014(2)
C4	0.080(3)	0.056(3)	0.070(3)	0.008(2)	0.013(2)	-0.004(2)
C5	0.070(3)	0.053(2)	0.066(3)	0.013(2)	0.005(2)	-0.010(2)
C6	0.053(3)	0.053(2)	0.061(2)	0.000(2)	0.014(2)	0.000(2)
C7	0.045(2)	0.0385(19)	0.046(2)	-0.0011(16)	0.0085(16)	0.0020(17)
C8	0.0343(18)	0.0385(19)	0.054(2)	-0.0023(16)	0.0034(15)	-0.0002(15)
C9	0.0411(19)	0.0341(19)	0.046(2)	-0.0046(16)	0.0019(17)	0.0017(15)
C10	0.043(2)	0.0358(19)	0.048(2)	0.0063(15)	-0.0077(16)	0.0008(16)
C11	0.057(2)	0.053(2)	0.064(3)	-0.007(2)	0.000(2)	-0.013(2)
C12	0.084(3)	0.059(3)	0.061(3)	-0.016(2)	0.004(2)	-0.015(2)
C13	0.076(3)	0.056(3)	0.059(3)	0.001(2)	0.009(2)	0.012(2)
C14	0.119(4)	0.082(3)	0.080(3)	-0.020(3)	0.021(3)	0.015(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C15	0.0410(19)	0.037(2)	0.044(2)	-0.0042(16)	-0.0025(17)	0.0048(16)
C16	0.040(2)	0.0365(19)	0.045(2)	-0.0027(15)	-0.0043(16)	0.0012(15)
C17	0.052(2)	0.052(2)	0.052(2)	-0.0021(18)	-0.0116(18)	-0.0011(19)
C18	0.048(2)	0.060(3)	0.075(3)	-0.004(2)	-0.014(2)	-0.011(2)
C19	0.058(2)	0.052(2)	0.068(3)	0.001(2)	0.000(2)	-0.016(2)
C20	0.053(2)	0.039(2)	0.057(2)	-0.0014(17)	-0.0040(18)	-0.0079(18)
C21	0.039(2)	0.0379(19)	0.048(2)	-0.0052(16)	-0.0008(16)	-0.0004(16)
C22	0.050(2)	0.038(2)	0.045(2)	0.0012(16)	0.0034(16)	0.0047(17)
C23	0.035(2)	0.040(2)	0.051(2)	0.0009(16)	0.0030(16)	-0.0040(16)
C24	0.046(2)	0.049(2)	0.057(2)	-0.0062(19)	-0.0015(17)	0.0013(18)
C25	0.057(3)	0.049(2)	0.072(3)	-0.013(2)	0.010(2)	-0.0003(19)
C26	0.064(3)	0.050(2)	0.062(2)	-0.0139(19)	0.001(2)	-0.011(2)
C27	0.051(2)	0.056(2)	0.066(3)	-0.004(2)	-0.011(2)	-0.018(2)
C28	0.037(2)	0.049(2)	0.062(2)	0.0008(19)	0.0025(18)	-0.0055(17)
C29	0.089(4)	0.079(3)	0.107(4)	0.033(3)	0.019(3)	-0.010(3)
C30	0.102(4)	0.079(4)	0.113(4)	0.043(3)	0.013(4)	-0.016(3)
C31	0.097(4)	0.083(4)	0.123(5)	0.040(3)	-0.019(4)	-0.020(4)
C32	0.059(2)	0.058(3)	0.053(2)	0.0082(18)	0.0005(18)	0.0025(19)
C33	0.048(2)	0.059(2)	0.062(2)	-0.010(2)	-0.0019(19)	-0.003(2)
C34	0.051(2)	0.076(3)	0.069(3)	-0.015(2)	0.004(2)	0.002(2)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for SCI_234_SM_SE_11_48.

	x/a	**y/b**	**z/c**	**U(eq)**
H1	0.4425	0.5432	-0.0954	0.144
H17	0.5305	0.4269	-0.0414	0.115
H18	1.0600	0.3576	-0.0194	0.082
H15	0.6438	0.3128	-0.0025	0.075
H14	0.9617	0.1067	0.1023	0.051

	x/a	y/b	z/c	U(eq)
H5	0.8331	0.1370	0.2652	0.069
H4	0.6619	0.2183	0.3280	0.082
H3	0.3178	0.1938	0.3987	0.14
H24	0.1244	0.2073	0.3555	0.14
H2	0.3239	0.2730	0.3560	0.14
H9	0.1504	0.0209	0.0212	0.063
H8	-0.0395	-0.0926	0.0534	0.073
H7	0.0621	-0.1632	0.1301	0.071
H6	0.3575	-0.1201	0.1789	0.059
H13	0.5582	0.2473	0.1478	0.061
H12	0.6034	0.3481	0.2145	0.071
H26	0.9286	0.3667	0.2545	0.07
H11	1.2029	0.2796	0.2318	0.069
H10	1.1607	0.1782	0.1651	0.059
H16	1.1338	0.4690	-0.0745	0.11
H30	1.0379	0.5839	-0.1269	0.118
H31	0.6953	0.6212	-0.1365	0.122
H21	0.3453	0.2034	-0.0050	0.085
H20	0.4077	0.1085	-0.0267	0.085
H19	0.5616	0.1896	-0.0385	0.085
H23	0.3135	-0.0043	0.2457	0.068
H22	0.1408	0.0818	0.3055	0.078

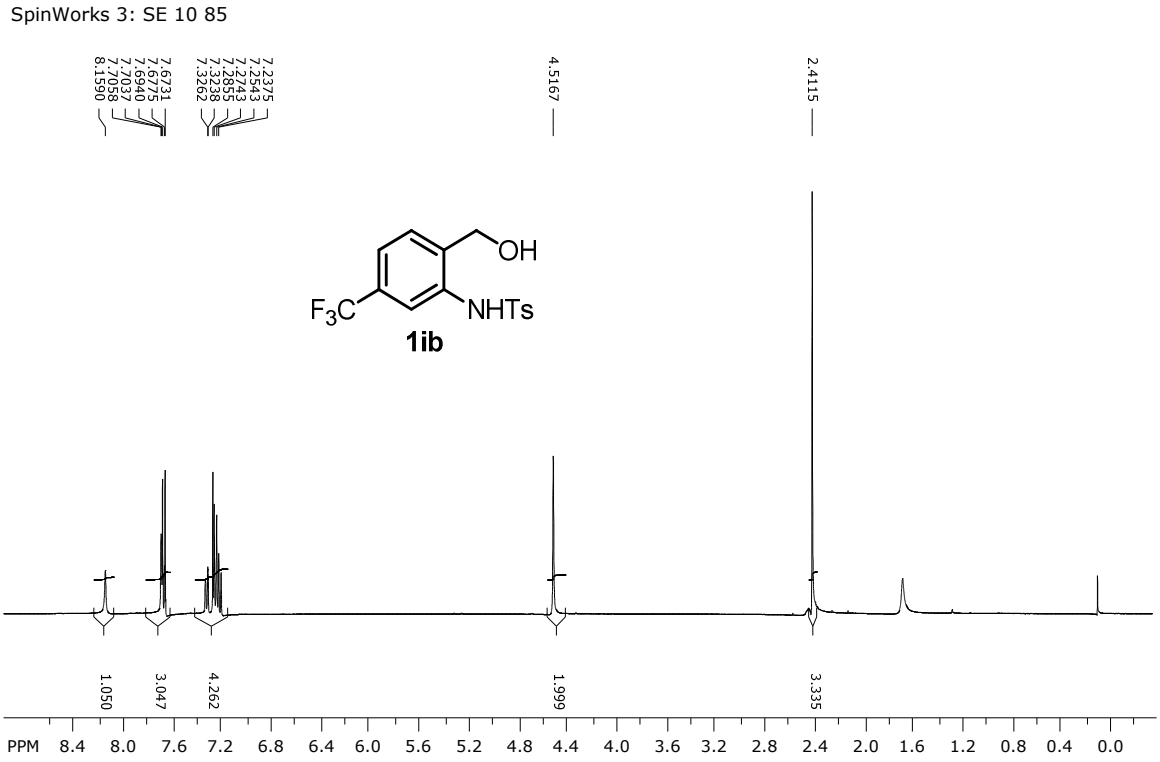
Table 9. Hydrogen bond distances (Å) and angles (°) for SCI_234_SM_SE_11_48.

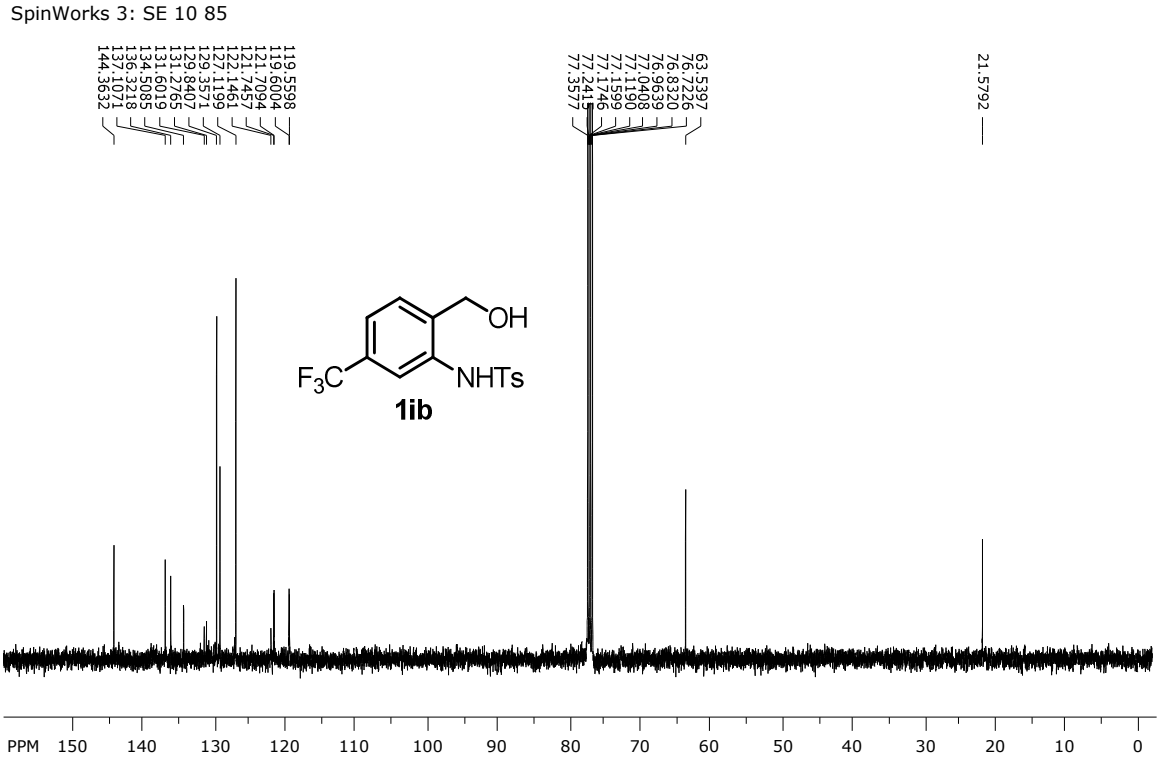
	Donor-H	Acceptor-H	Donor-Acceptor	Angle
C33-H23···O3	0.93	2.64	3.186(4)	118.4
C20-H6···O2	0.93	2.16	2.734(4)	119.4
C33-H23···O3	0.93	2.64	3.186(4)	118.4
C20-H6···O2	0.93	2.16	2.734(4)	119.4
C33-H23···O3	0.93	2.64	3.186(4)	118.4
C20-H6···O2	0.93	2.16	2.734(4)	119.4
C20-H6···O2	0.93	2.16	2.734(4)	119.4
C33-H23···O3	0.93	2.64	3.186(4)	118.4

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
C20-H6···O2	0.93	2.16	2.734(4)	119.4
C33-H23···O3	0.93	2.64	3.186(4)	118.4
C20-H6···O2	0.93	2.16	2.734(4)	119.4
C33-H23···O3	0.93	2.64	3.186(4)	118.4

^{1}H and ^{13}C-NMR spectra of all new compounds reported in this study

(**Note**: In general, in a ^{1}H NMR spectrum recorded in $CDCl_3$, a peak at around δ 1.6 refers to moisture in the solvent/sample and a peak at about δ 1.2 refers to oil/grease present in the sample. In a ^{13}C NMR spectrum recorded in $CDCl_3$, a peak at about δ 29.7 usually represents oil/grease)





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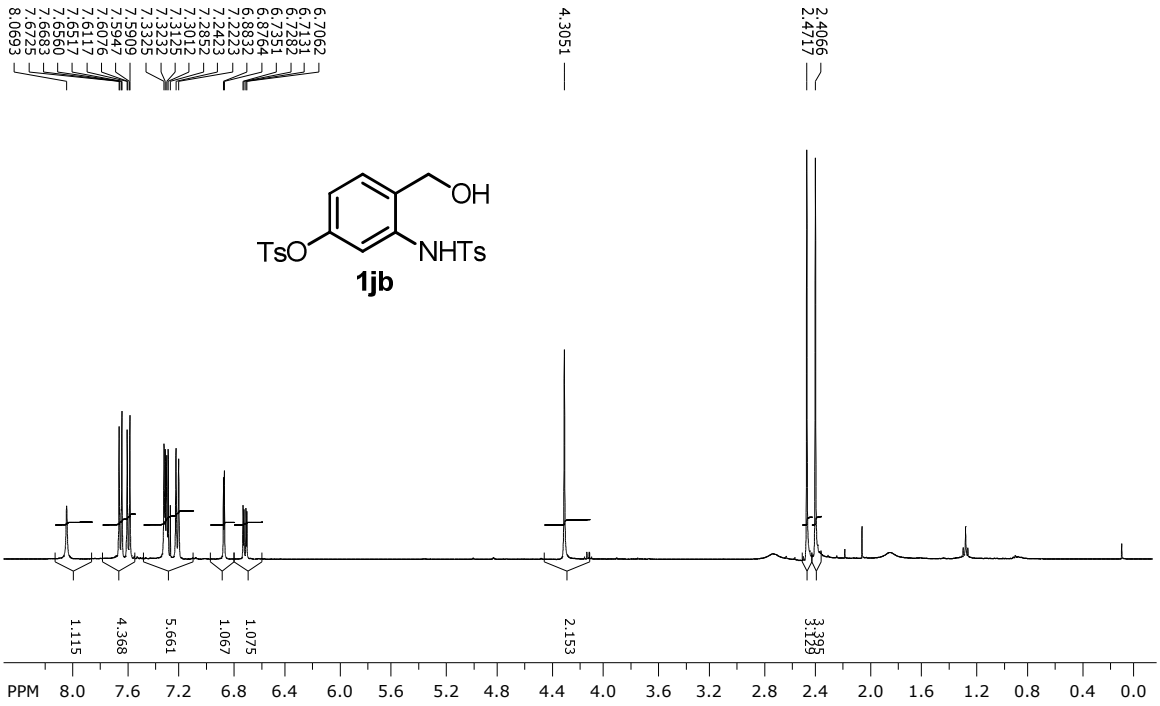

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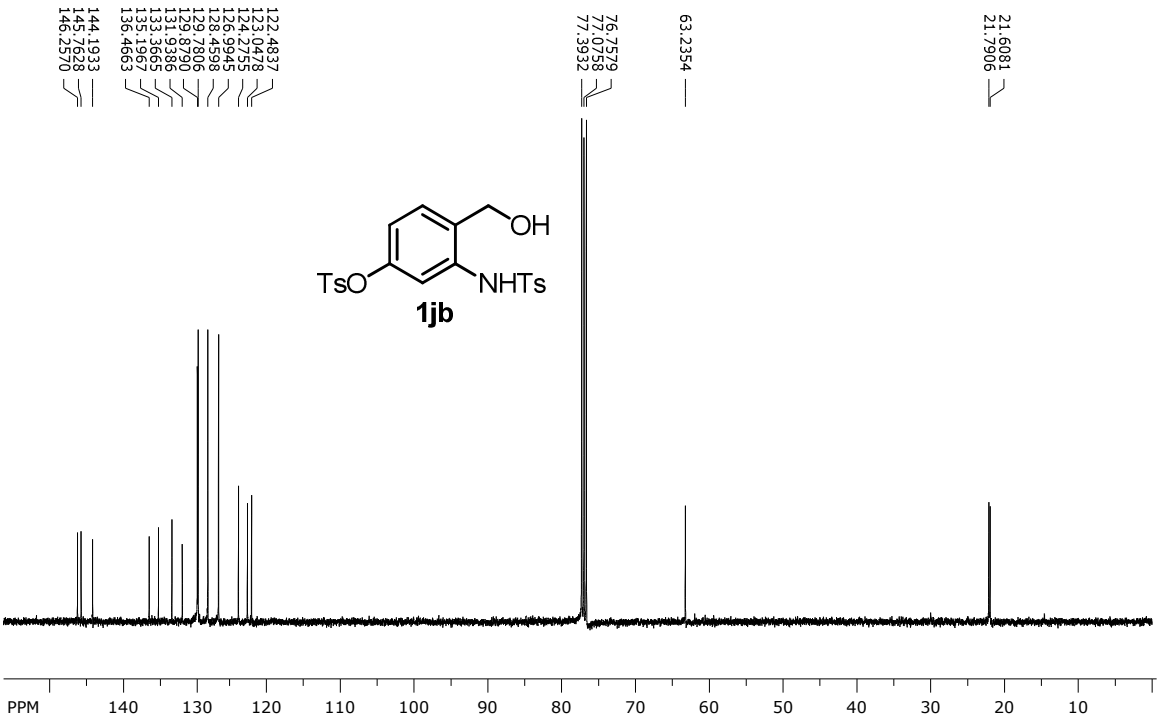

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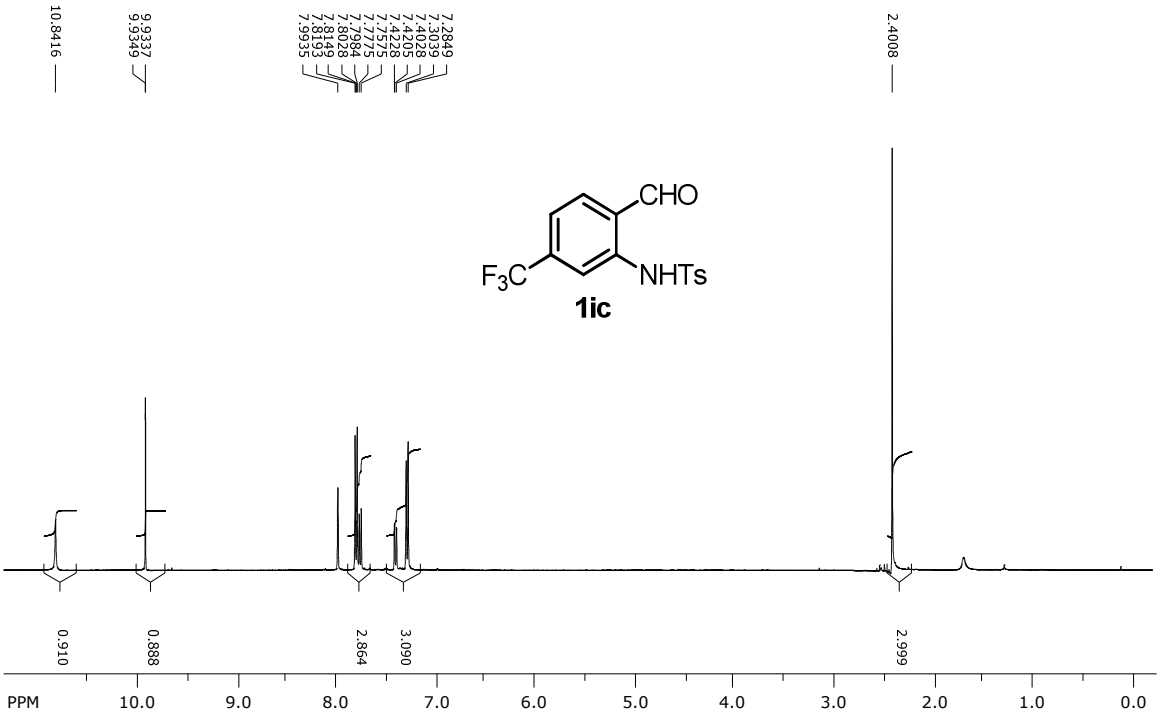

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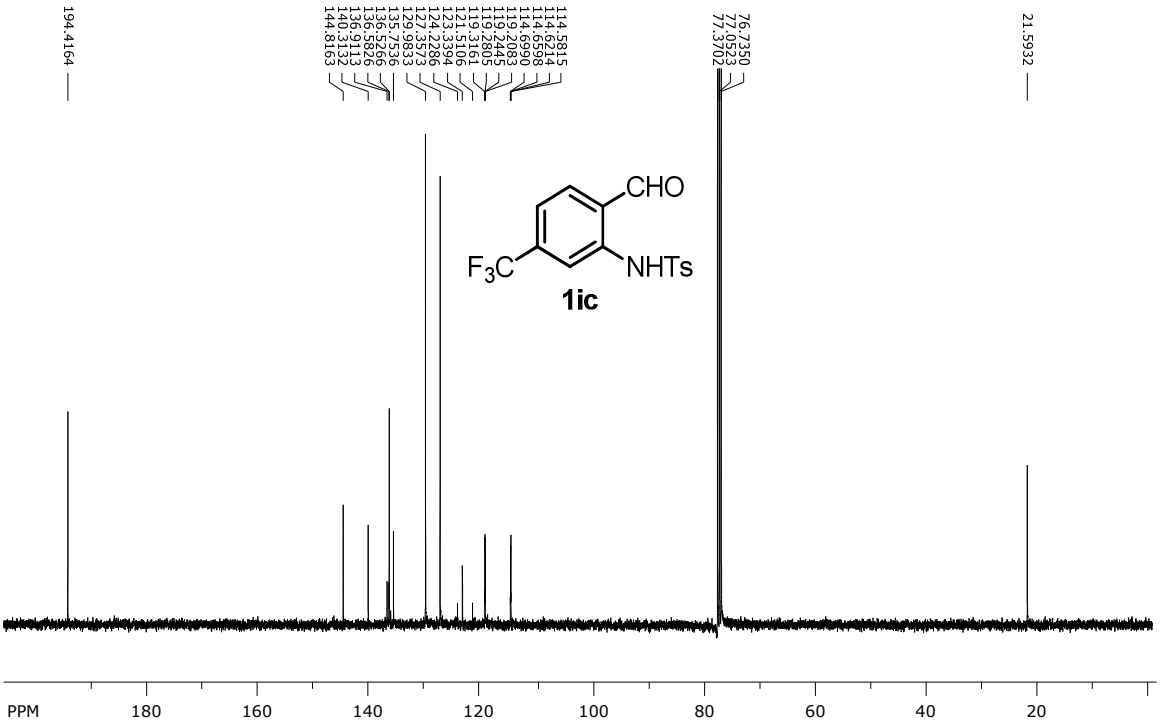

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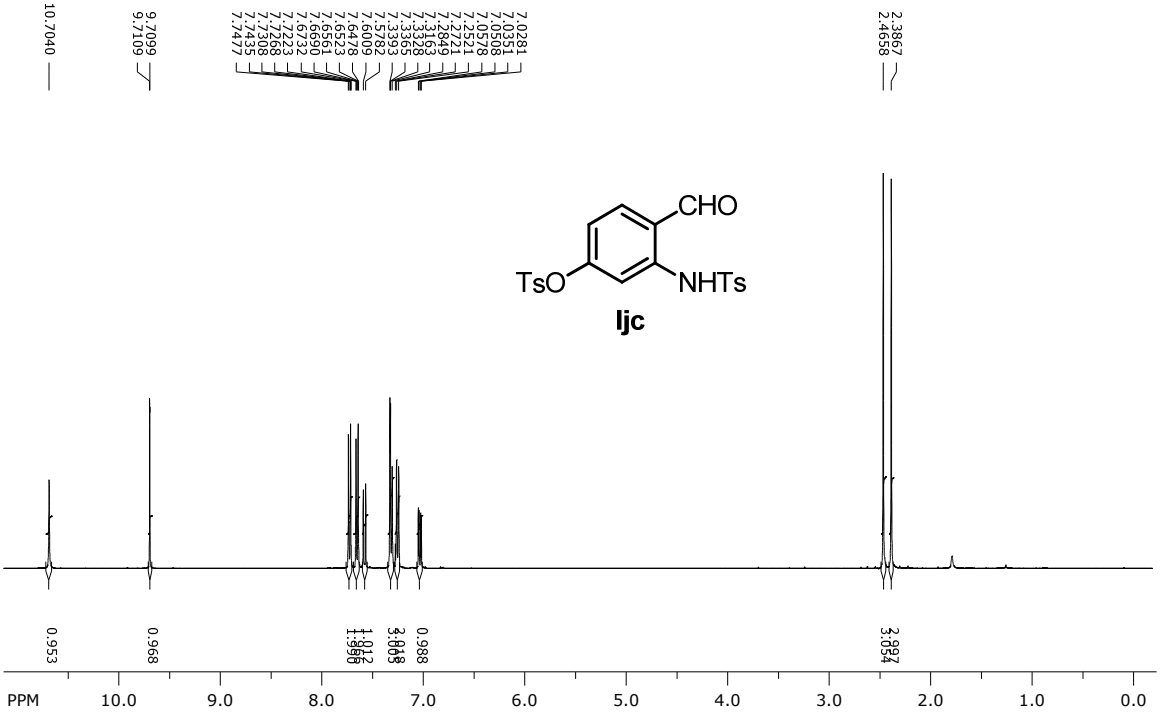

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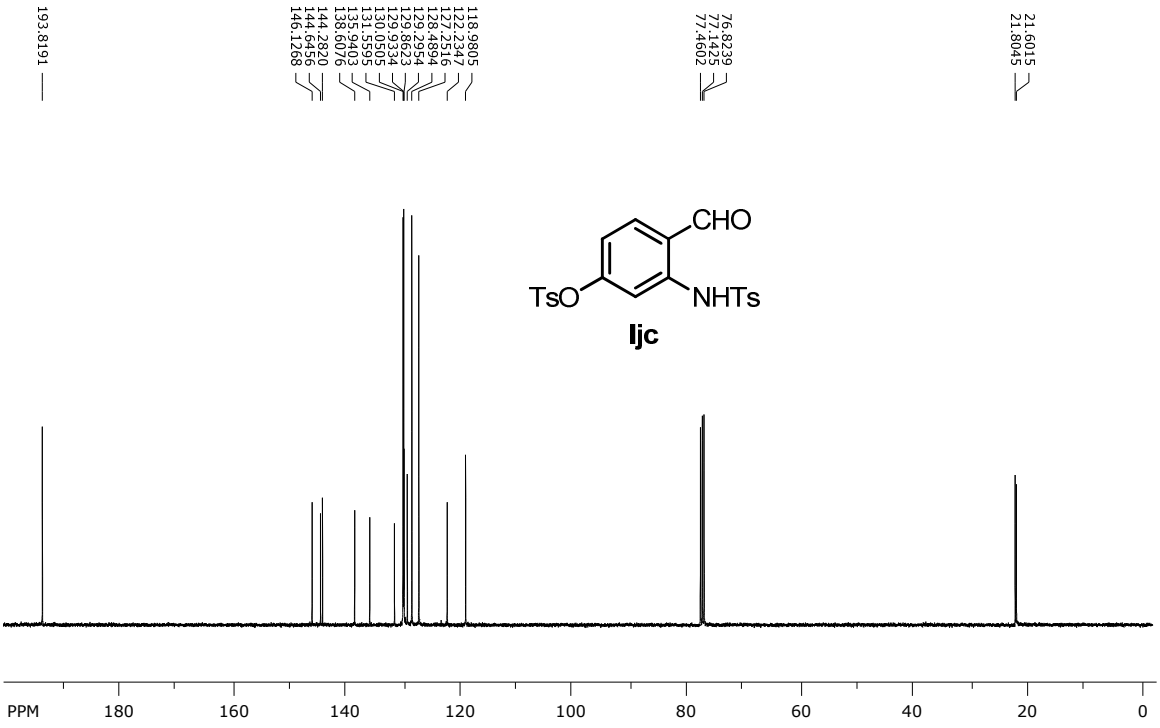

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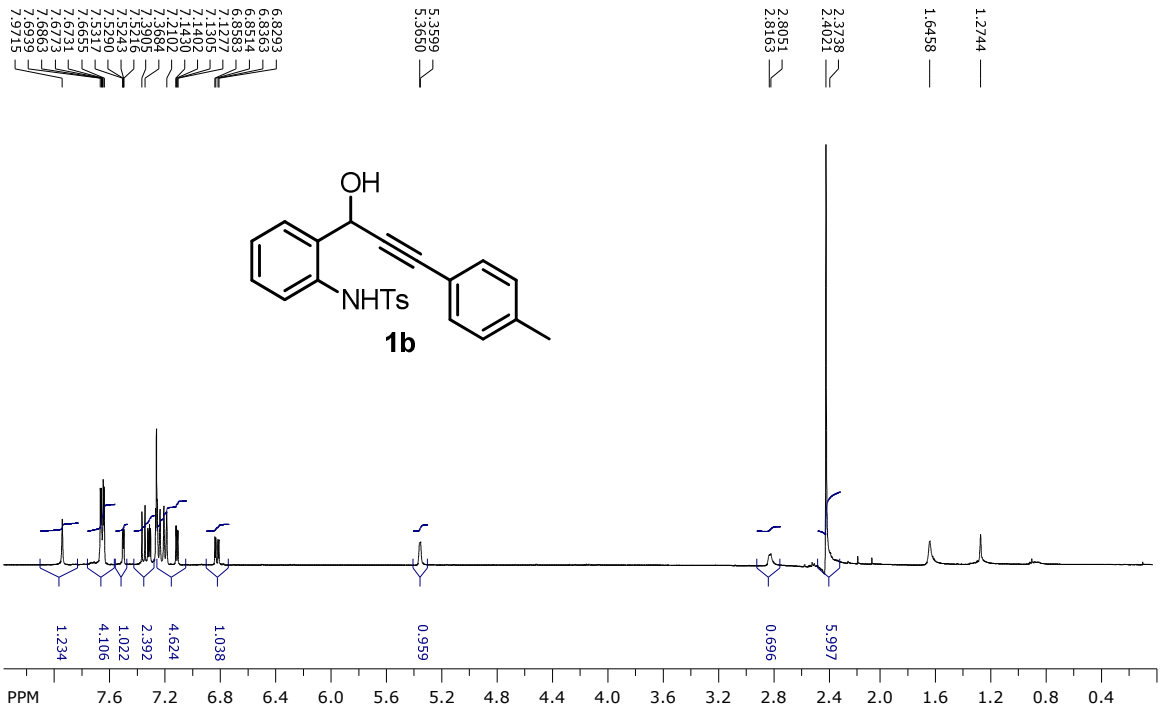

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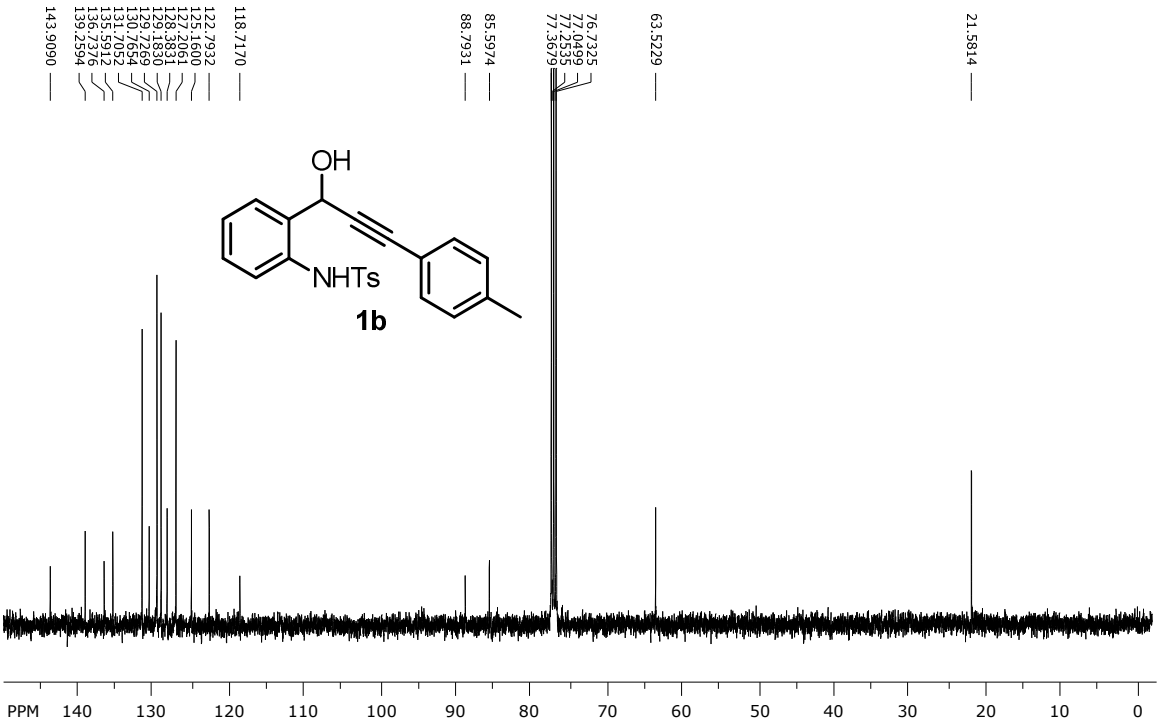

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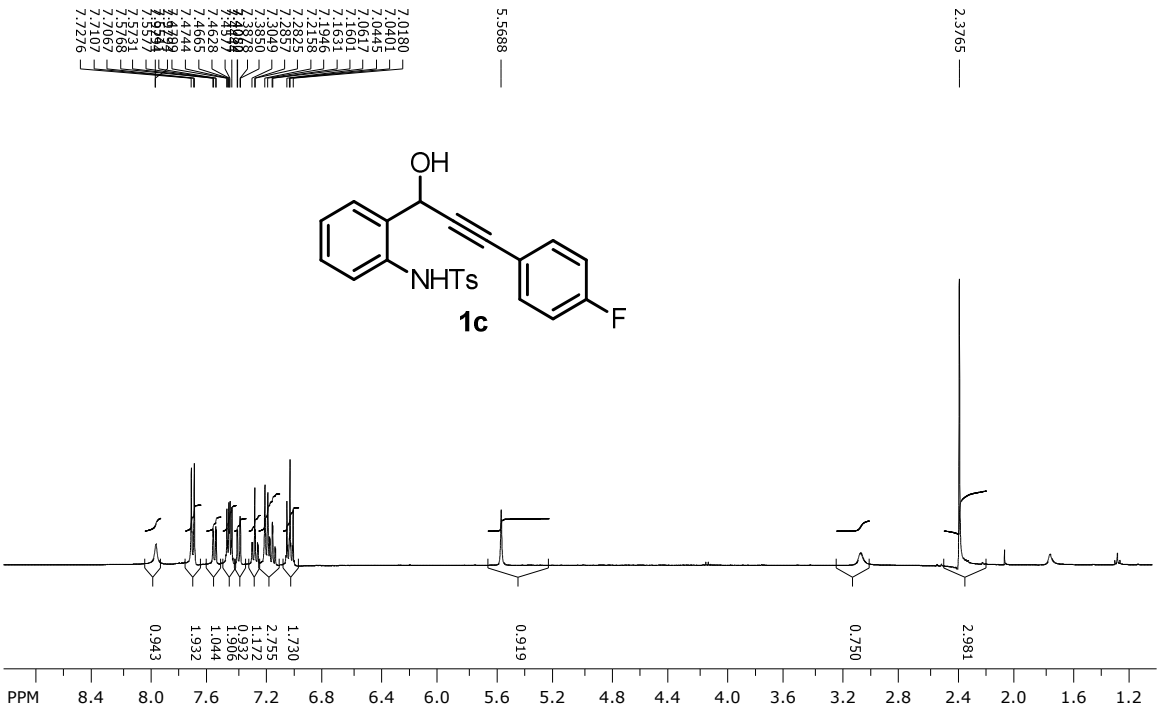
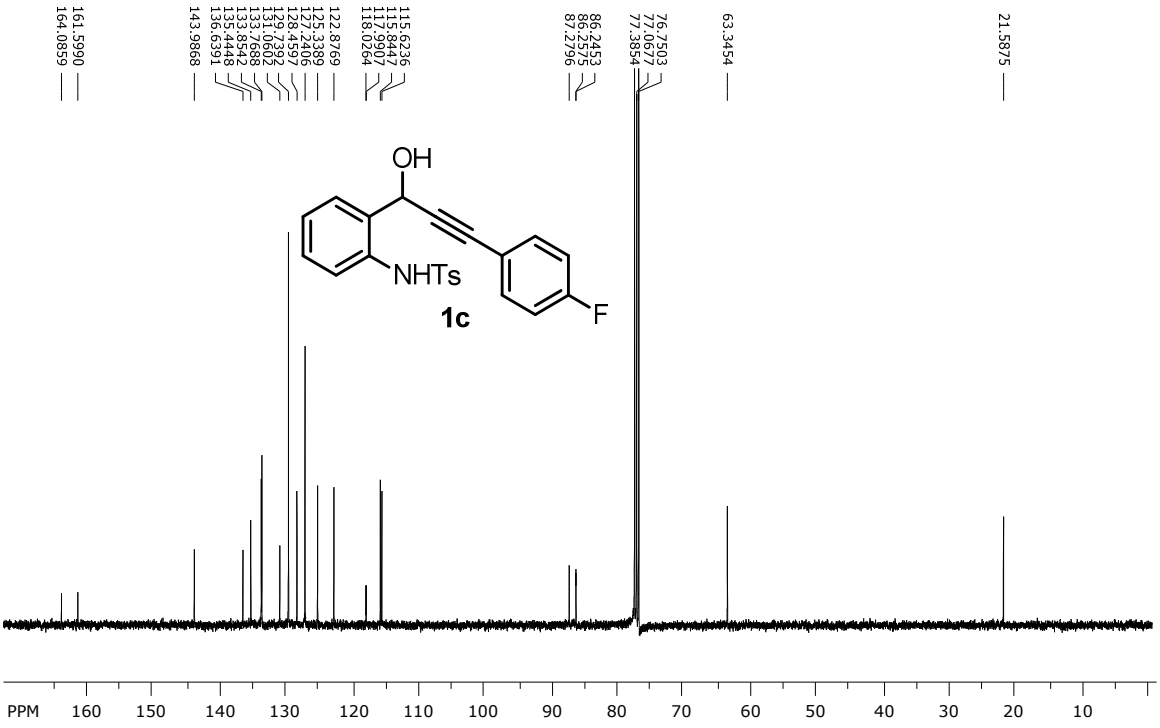
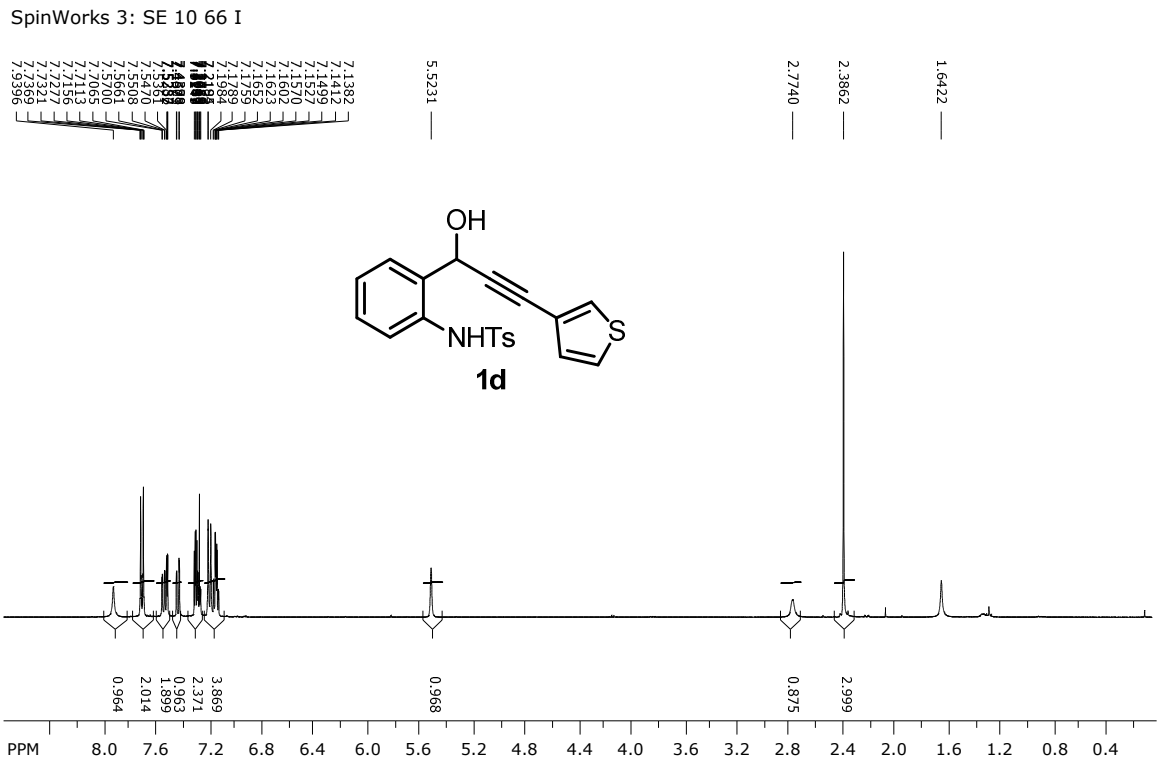
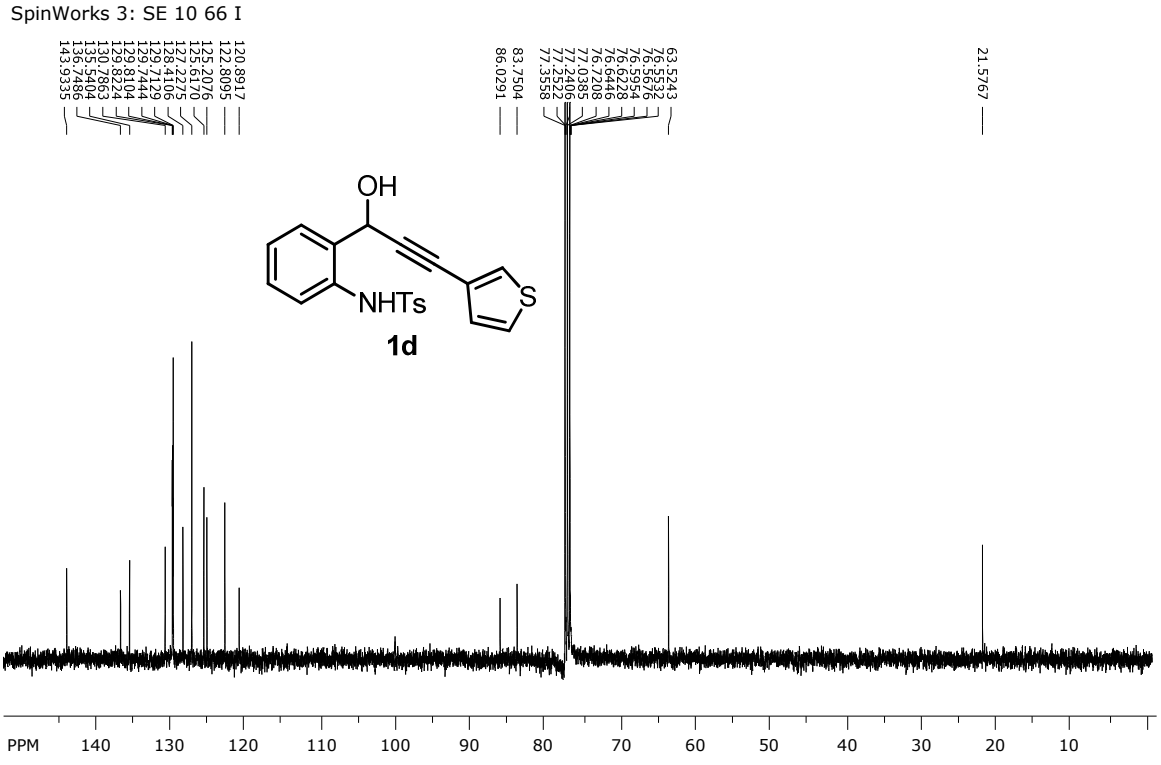


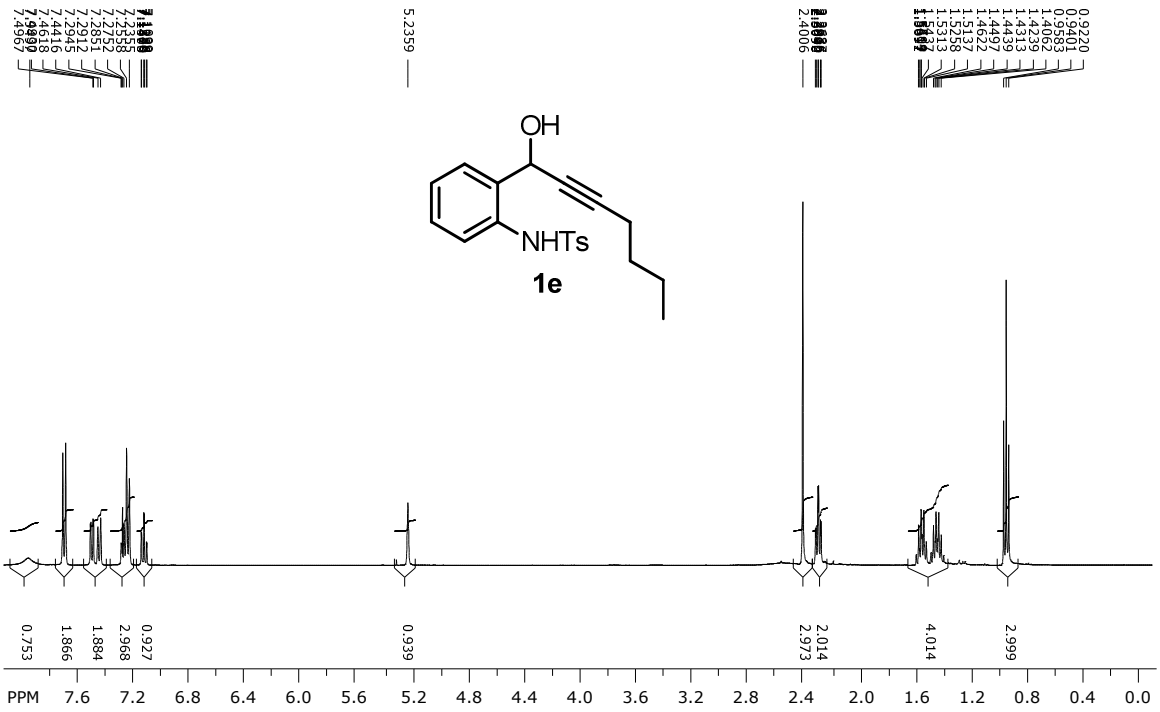
SpinWorks 3: SE 10 66 B



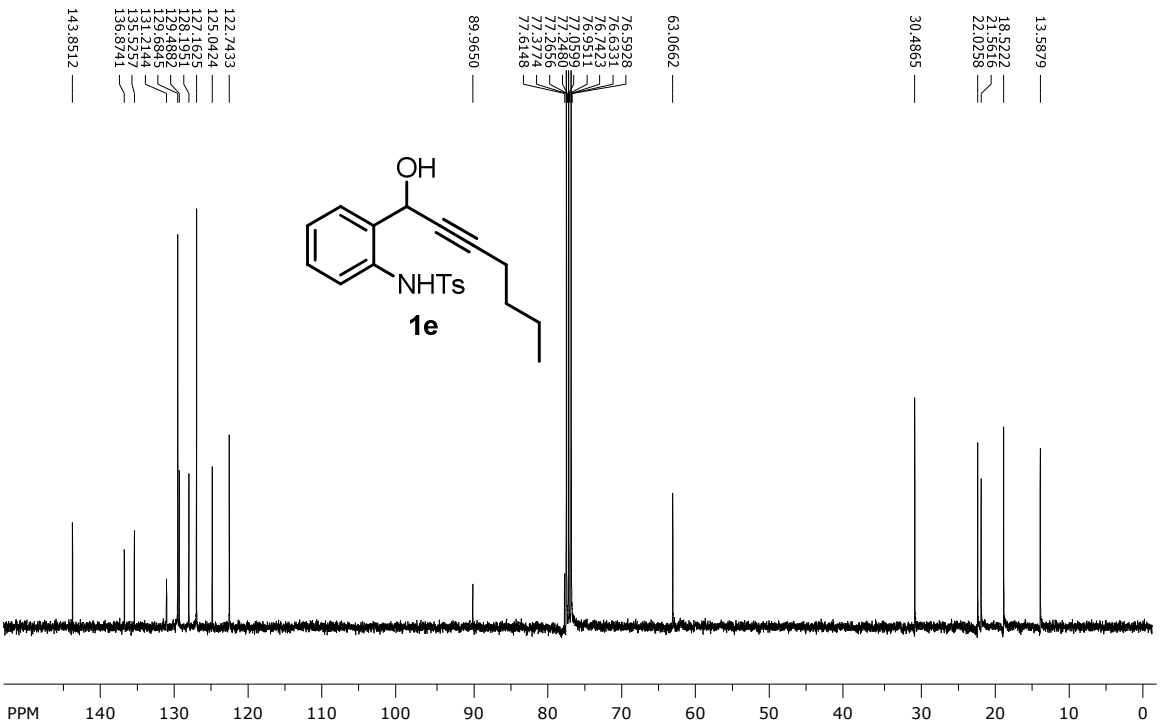

SpinWorks 3: SE 10 66 I
7.9396
7.7369
7.7221
7.7155
7.7113
7.7065
7.5700
7.5661
7.5508
7.5470
7.1759
7.1652
7.1623
7.1602
7.1570
7.1527
7.1499
7.1412
7.1382
5.5231
2.7740
2.3862
1.6422
OH
NHTs
S
1d
0.964
2.014
1.899
0.963
2.371
3.869
0.968
0.875
2.999
PPM
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4


SpinWorks 3: SE 10 66 I
143.9335
136.7486
135.5404
130.7863
129.8224
129.8104
129.7444
129.7129
128.4106
127.2270
125.2076
122.8095
120.8917
86.0291
83.7504
77.3558
77.2405
77.0385
76.7208
76.6446
76.6228
76.5954
76.5676
76.5532
63.5243
21.5767
OH
NHTs
S
1d
PPM
140
130
120
110
100
90
80
70
60
50
40
30
20
10

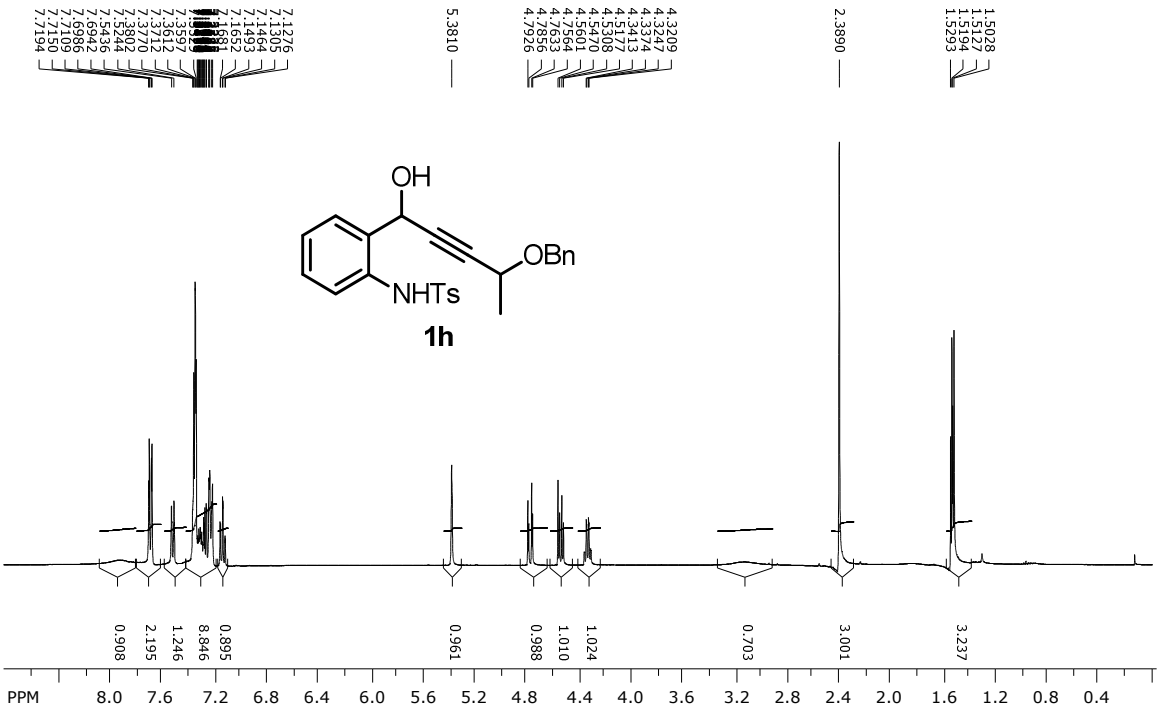
SpinWorks 3: SE 10 050 A



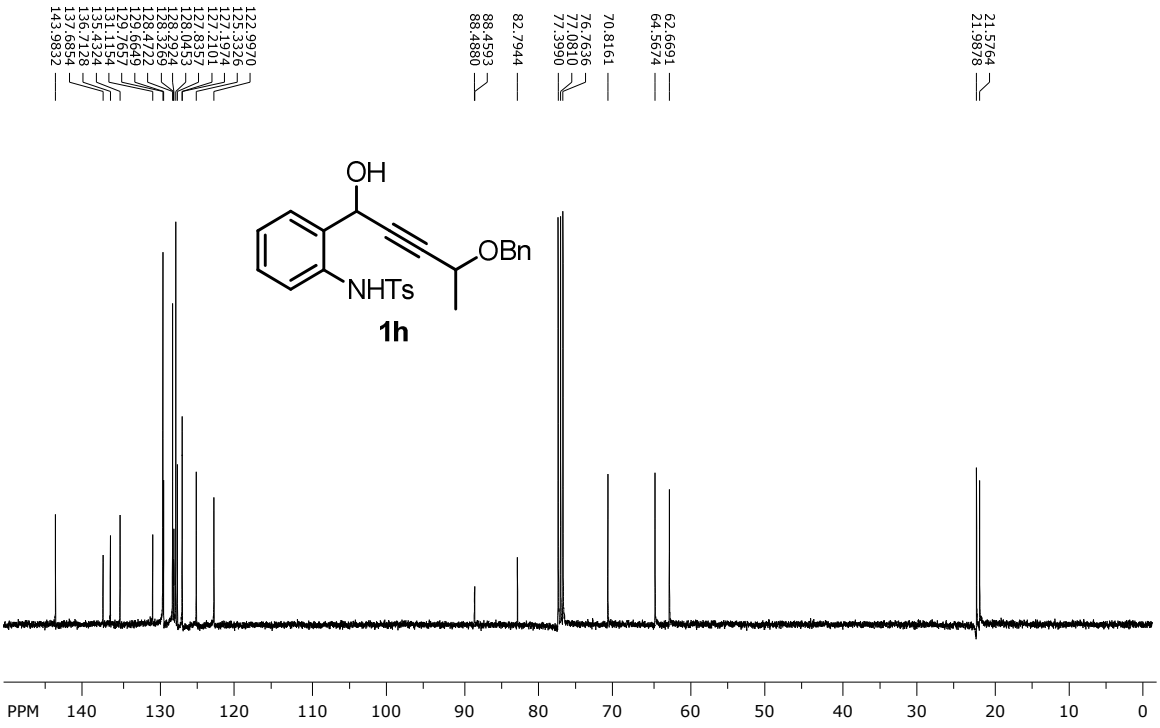
SpinWorks 3: SE 10 050 A



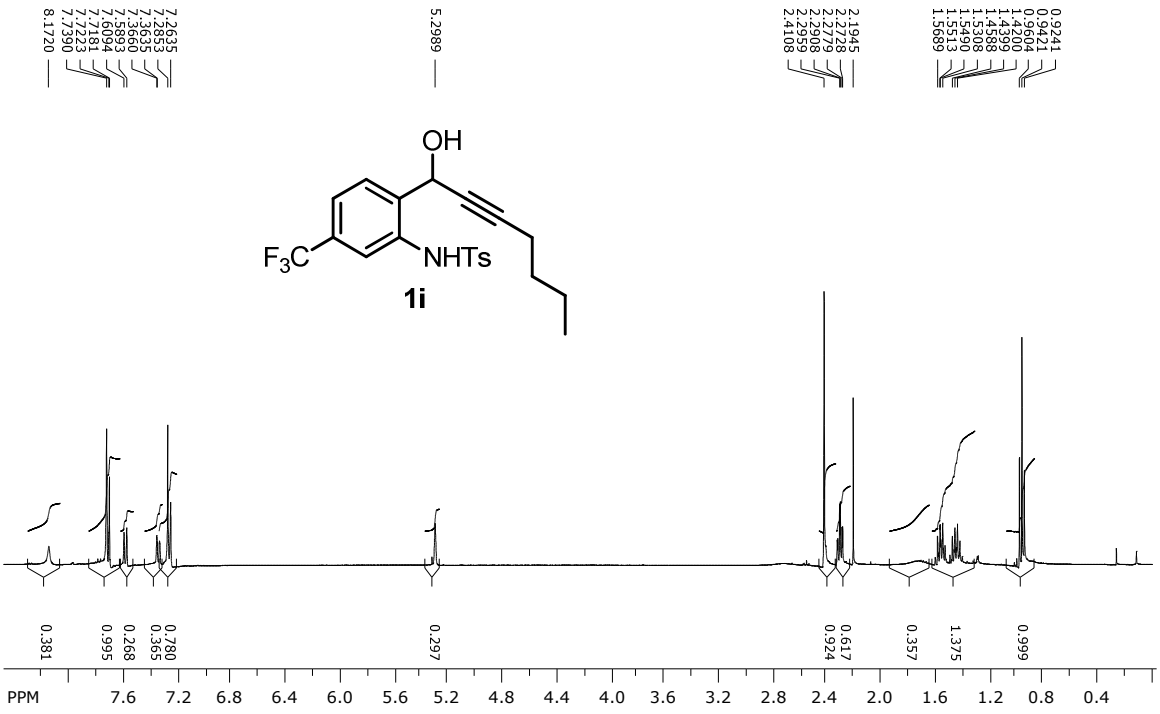
SpinWorks 3: SE 10 88 5



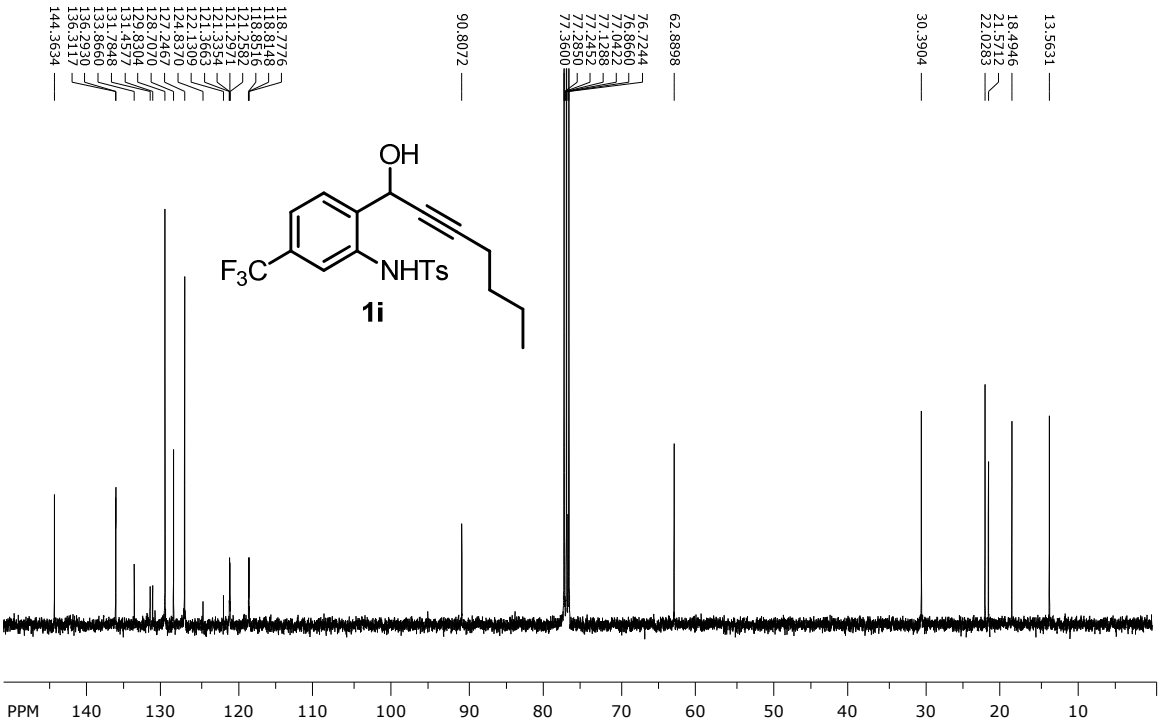
SpinWorks 3: SE 10 88 5



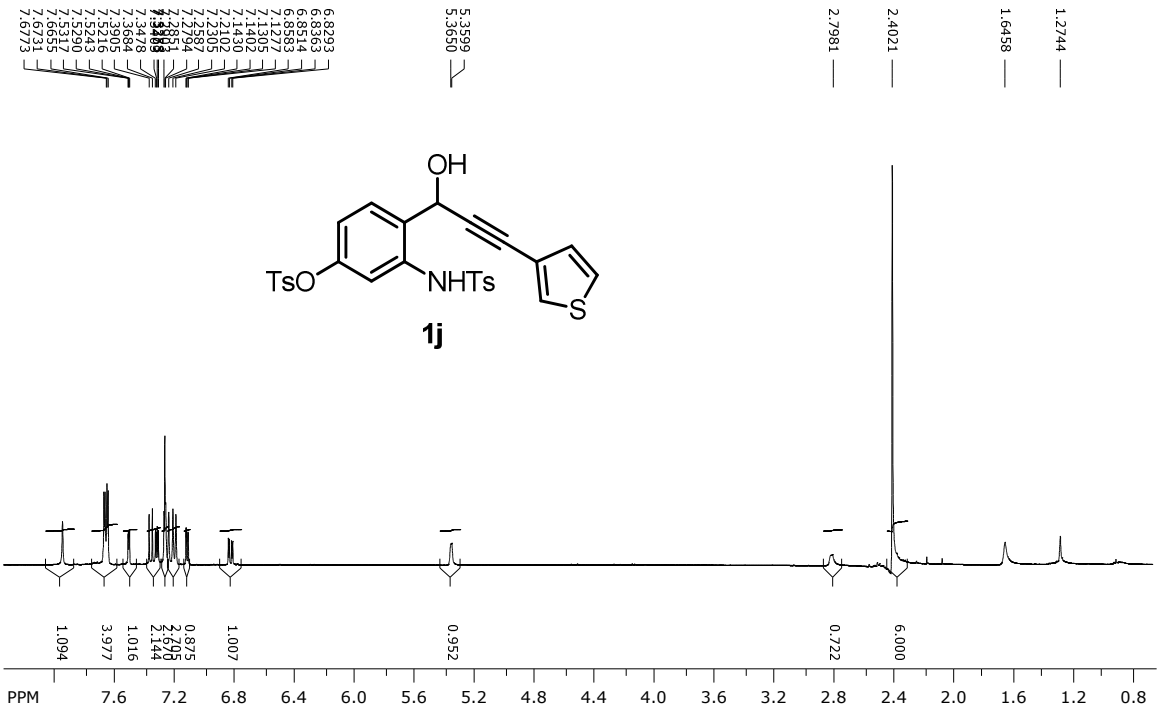
SpinWorks 3: SE 10 98 B



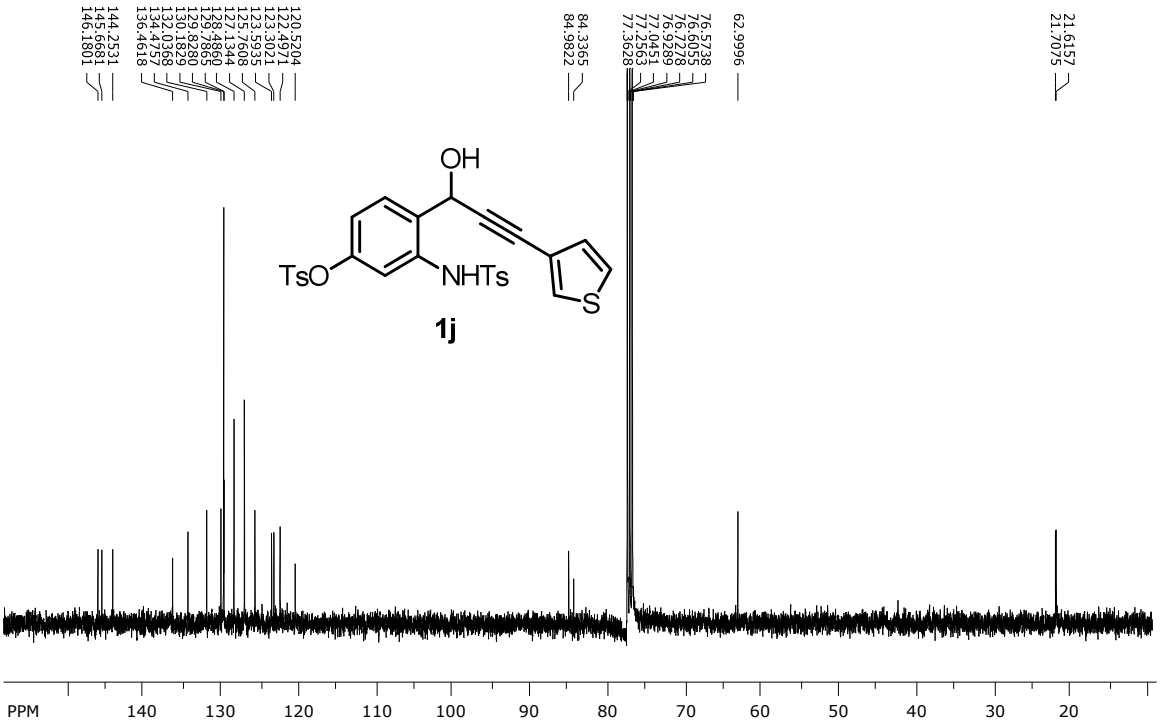
SpinWorks 3: SE 10 97 B



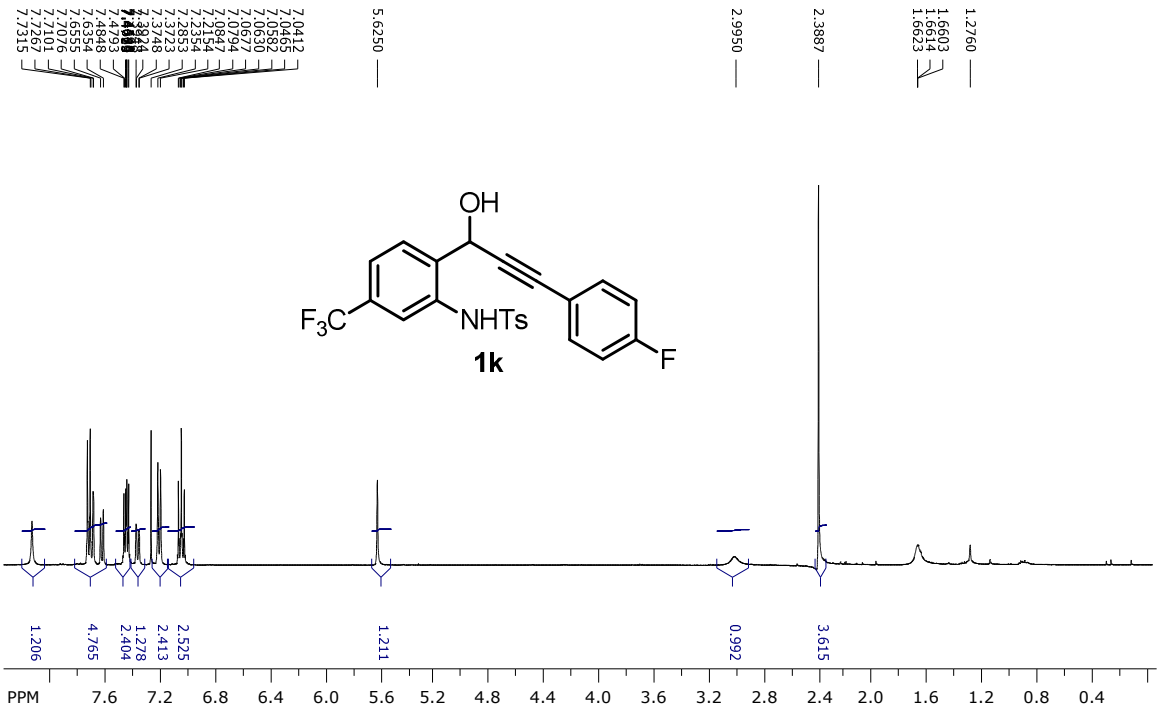
SpinWorks 3: SE 10 06 B



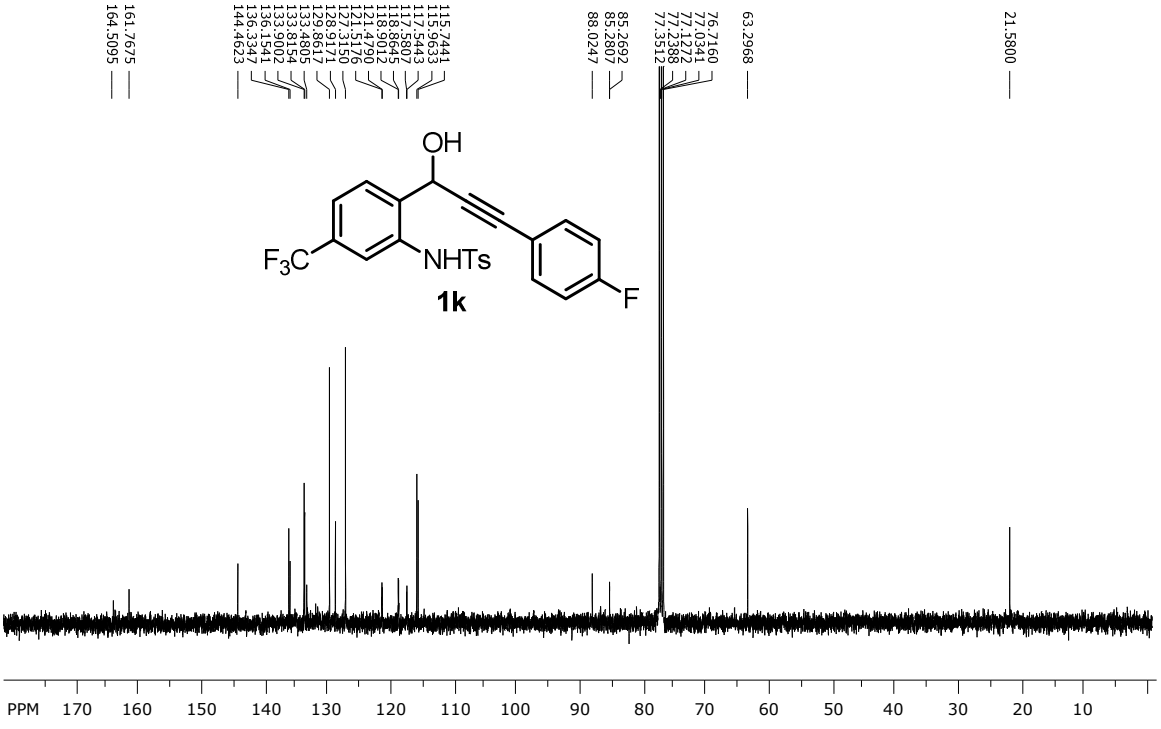
SpinWorks 3: SE 10 06 B



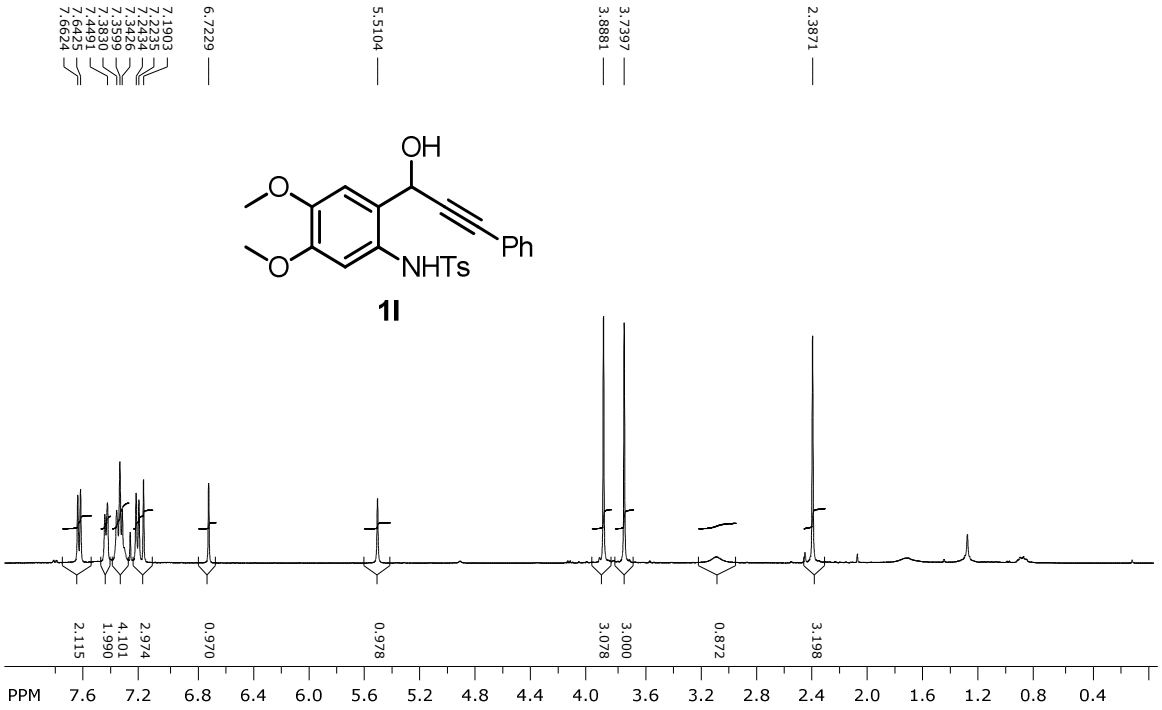
SpinWorks 3: CE 10 97 A



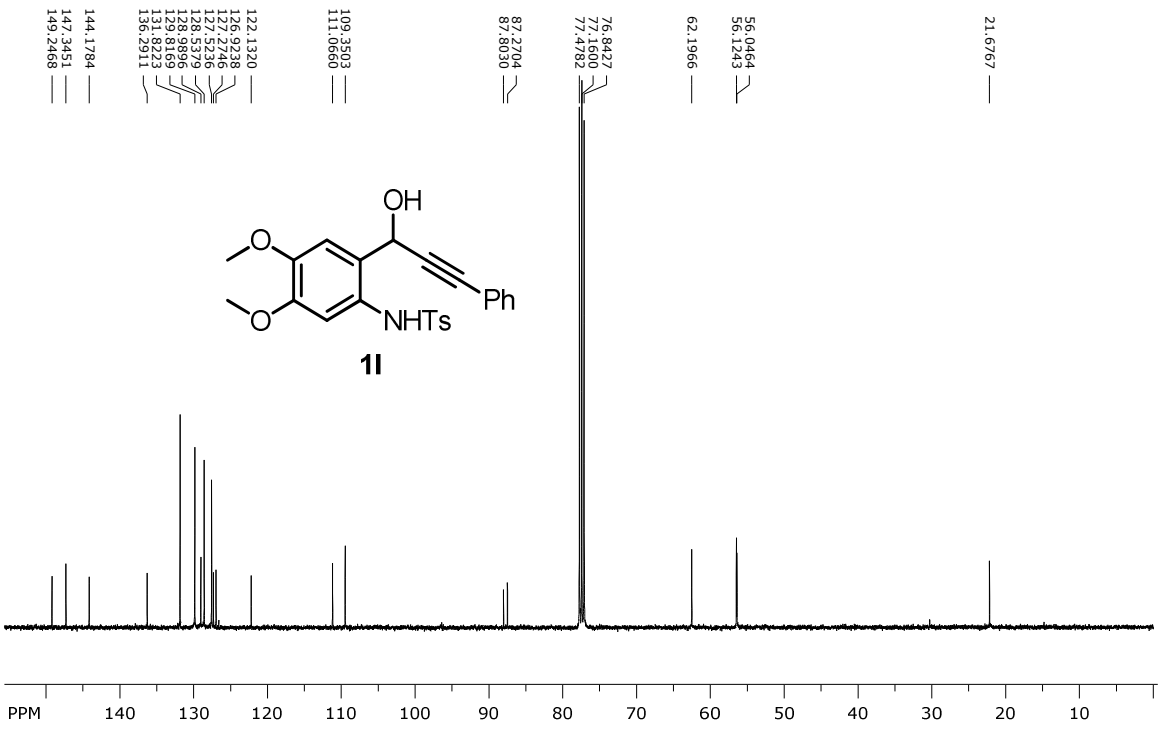
SpinWorks 3: CE 10 97 A



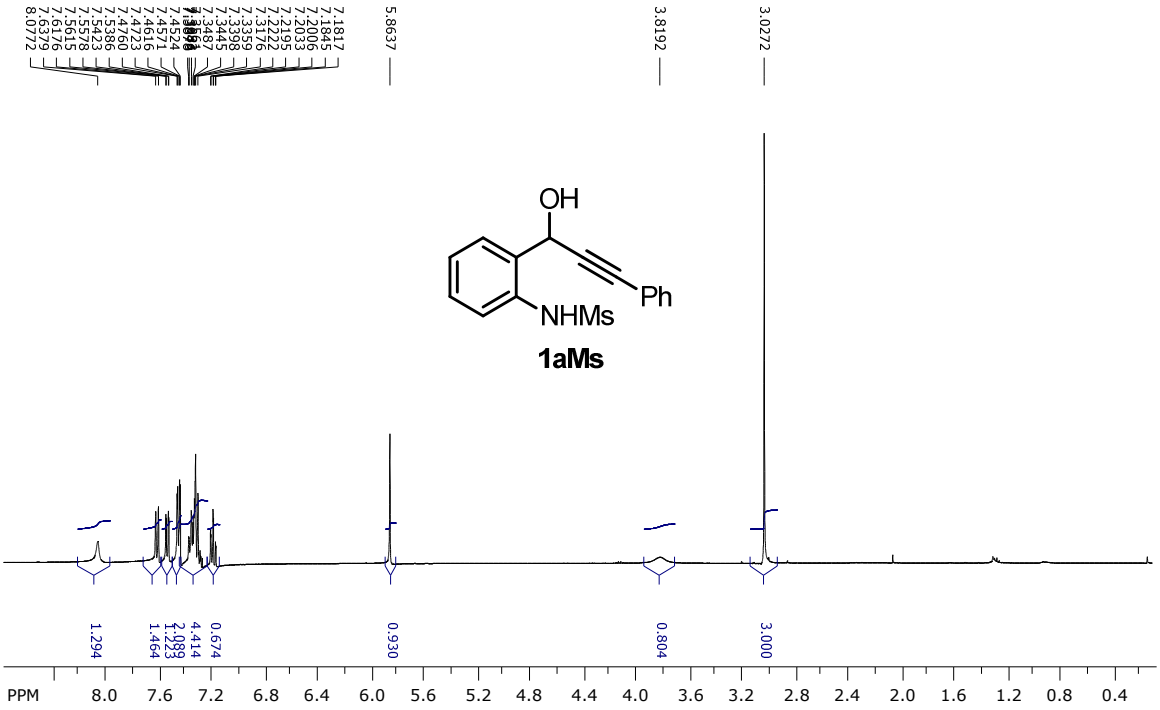
SpinWorks 3: SE-11-273



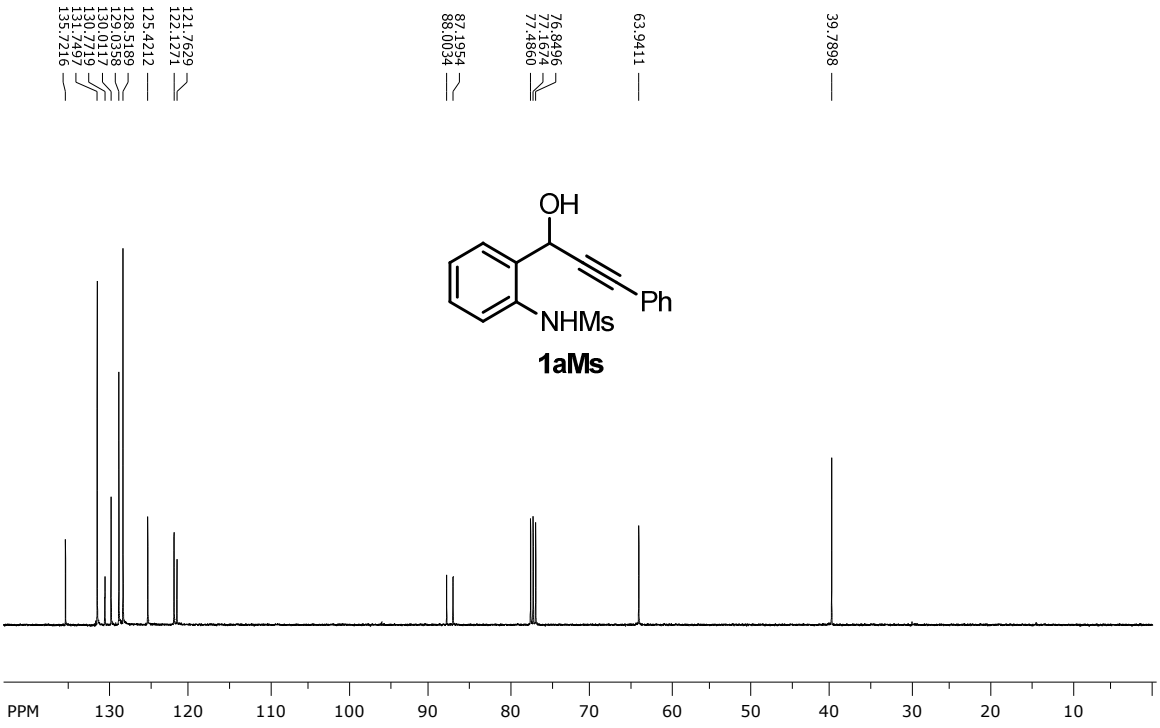
SpinWorks 3: SE 11 273

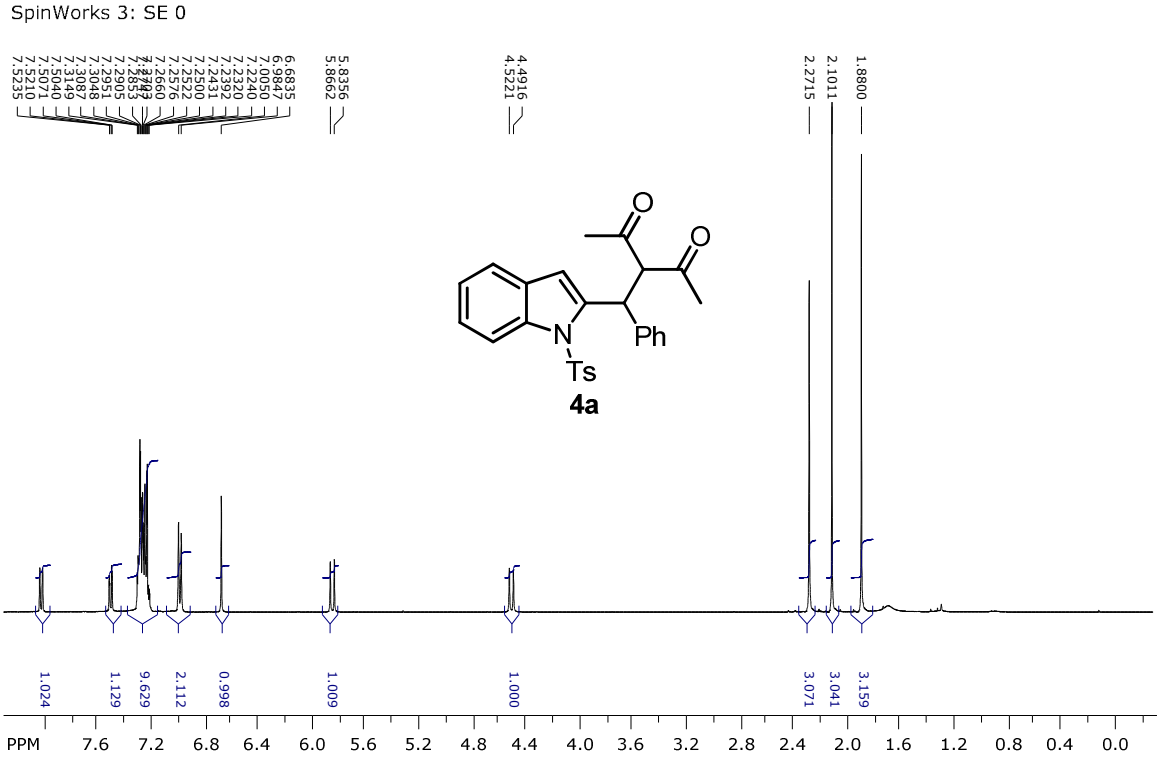


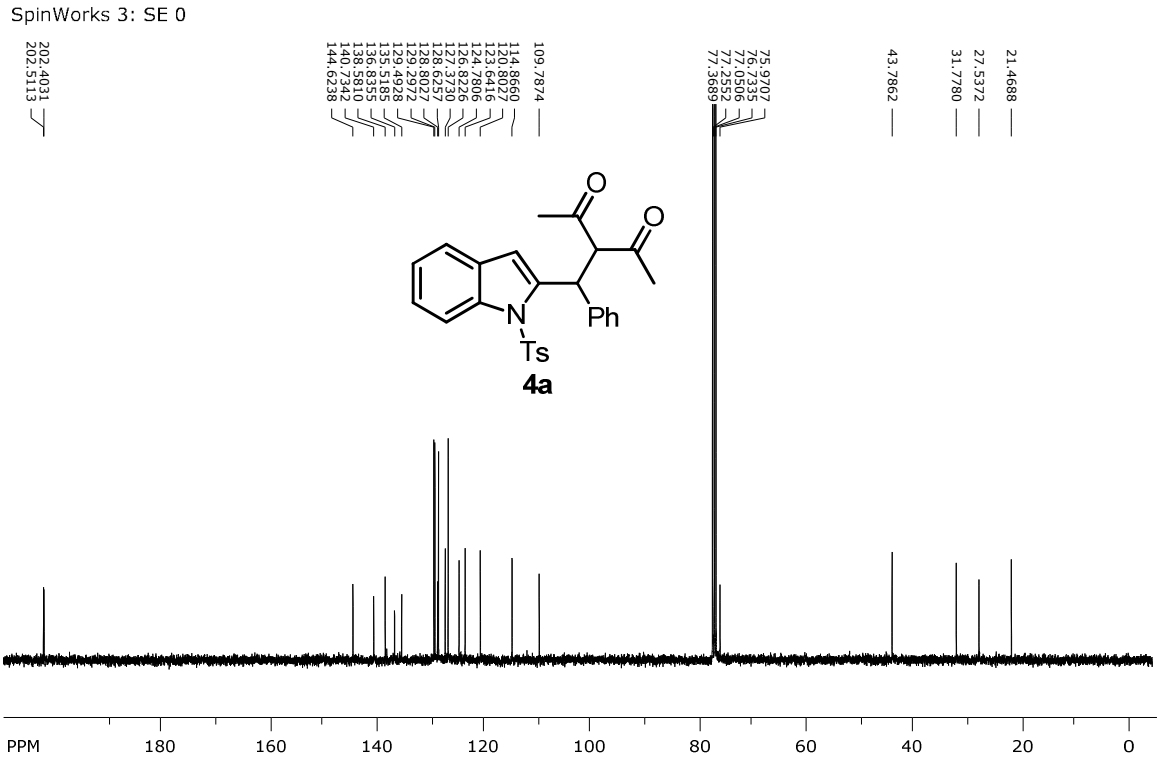
SpinWorks 3: se 11 15

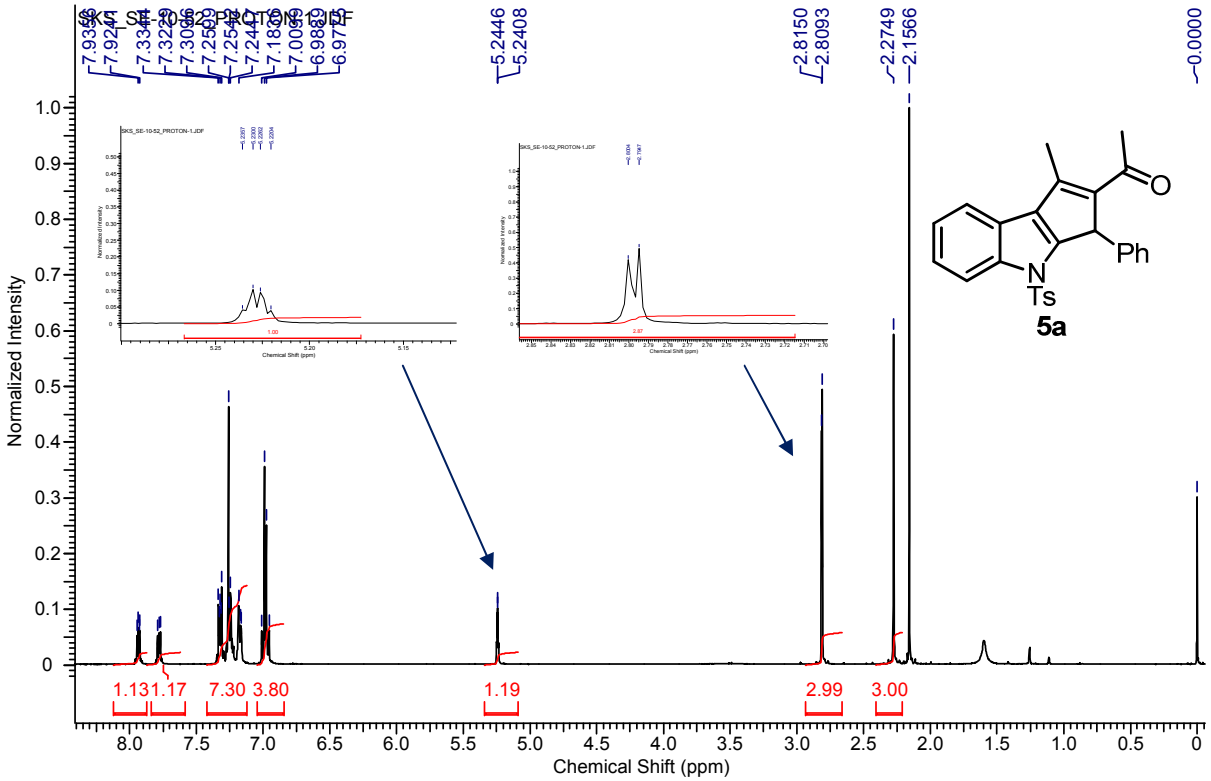


SpinWorks 3: se 11 15

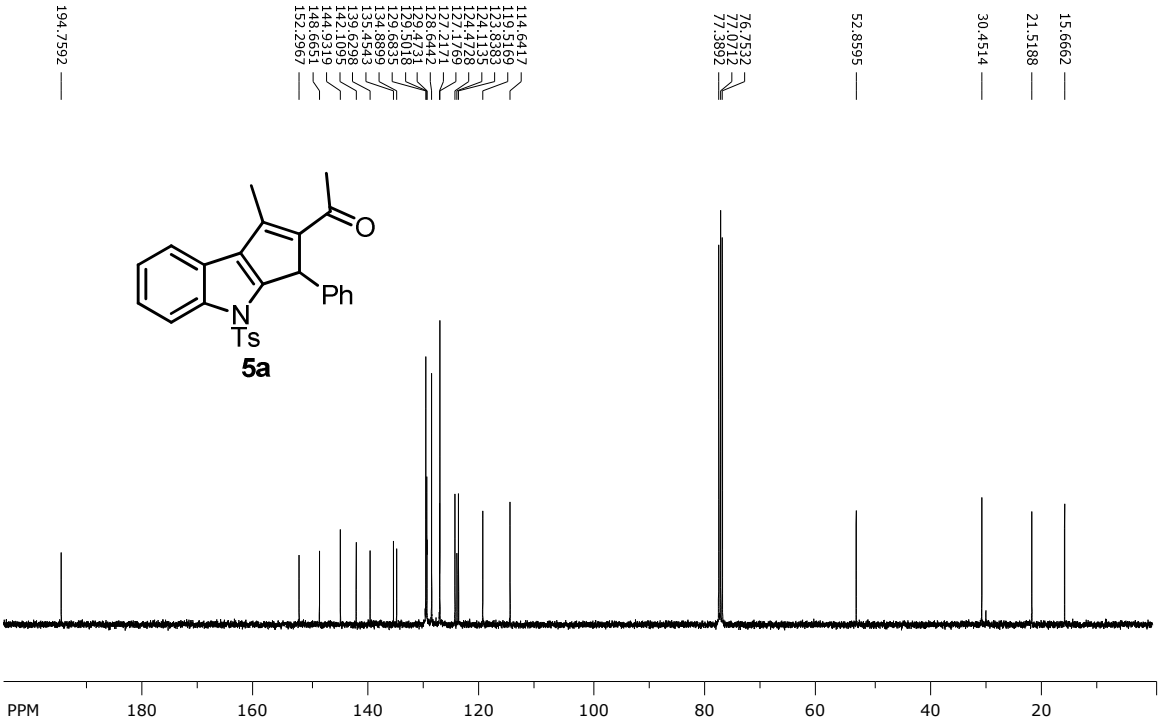



SpinWorks 3: SE 0
7.5235
7.5210
7.5071
7.5040
7.3082
7.3048
7.2951
7.2905
7.2660
7.2576
7.2522
7.2500
7.2431
7.2392
7.2320
7.2240
6.0847
6.0835
5.8662
5.8356
4.5221
4.4916
2.2715
2.1011
1.8800
Ts
Ph
4a
1.024
1.129
9.629
2.112
0.998
1.009
1.000
3.071
3.041
3.159
PPM
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

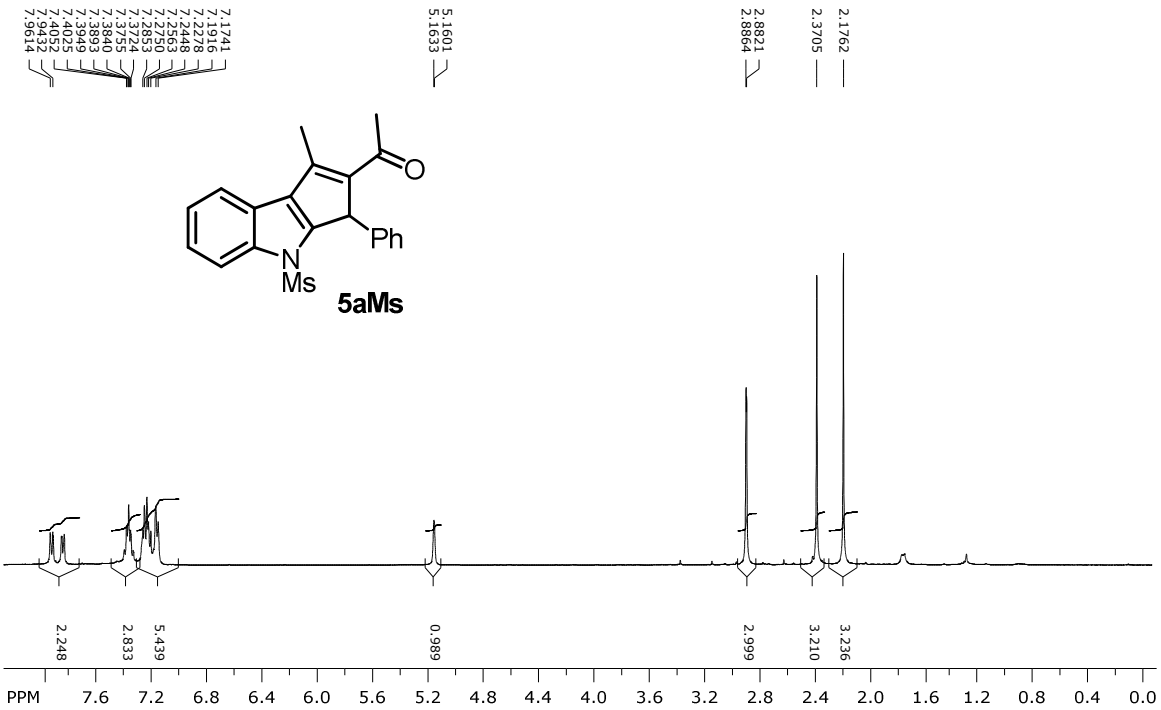

SpinWorks 3: SE 0
202.4031
202.5113
144.6238
140.7342
138.5810
136.8355
135.5185
129.4928
129.2972
128.8027
128.6257
127.3730
126.8226
124.7806
123.6416
114.8660
109.7874
77.3689
77.2252
77.0505
76.7335
75.9707
43.7862
31.7780
27.5372
21.4688
Ts
Ph
4a
PPM
180
160
140
120
100
80
60
40
20
0



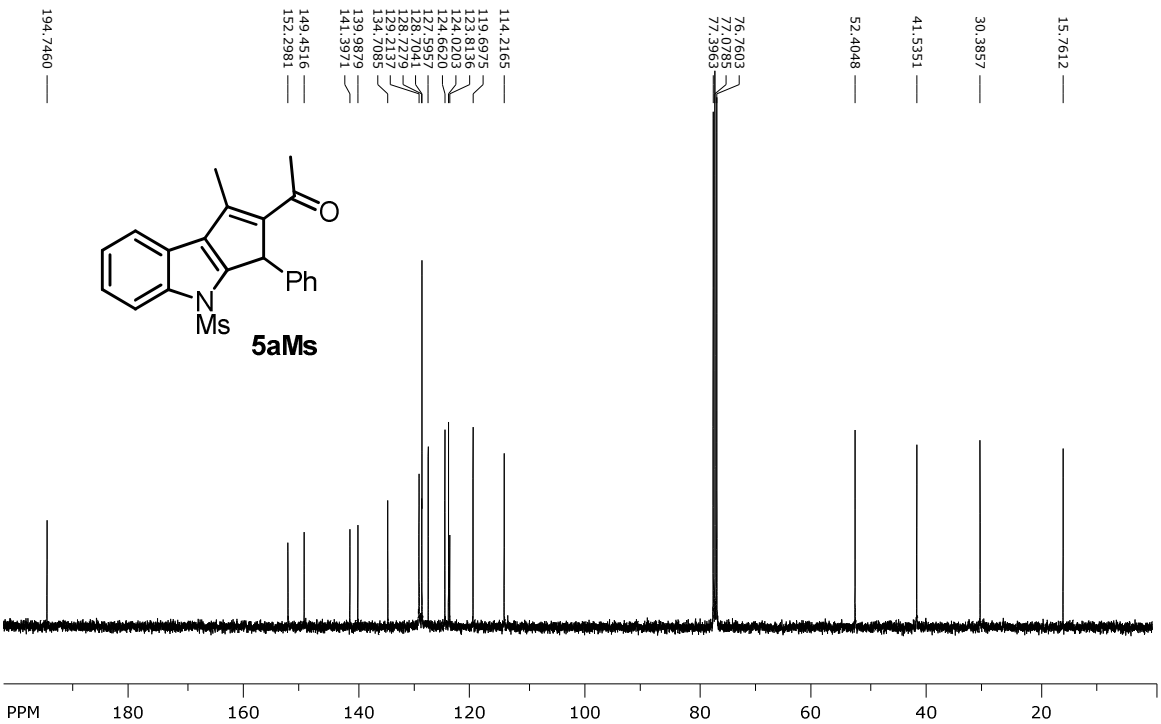
SpinWorks 3: SE 10 52

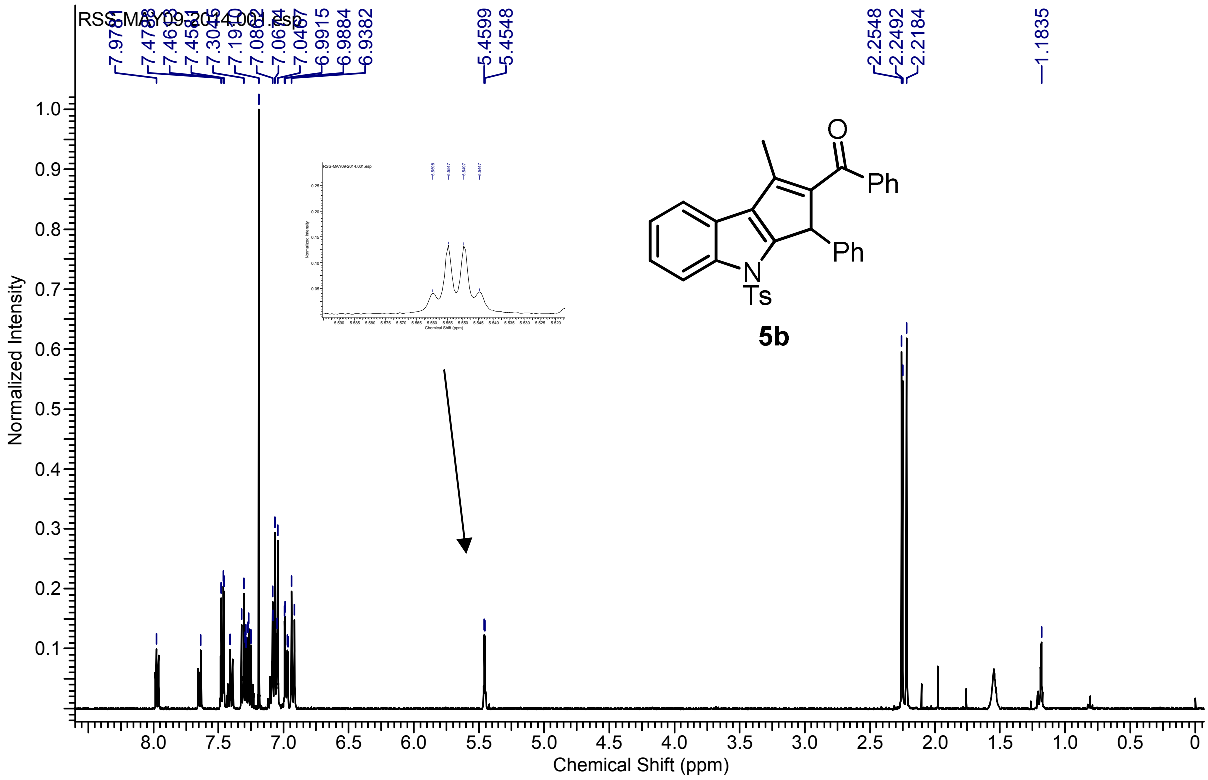


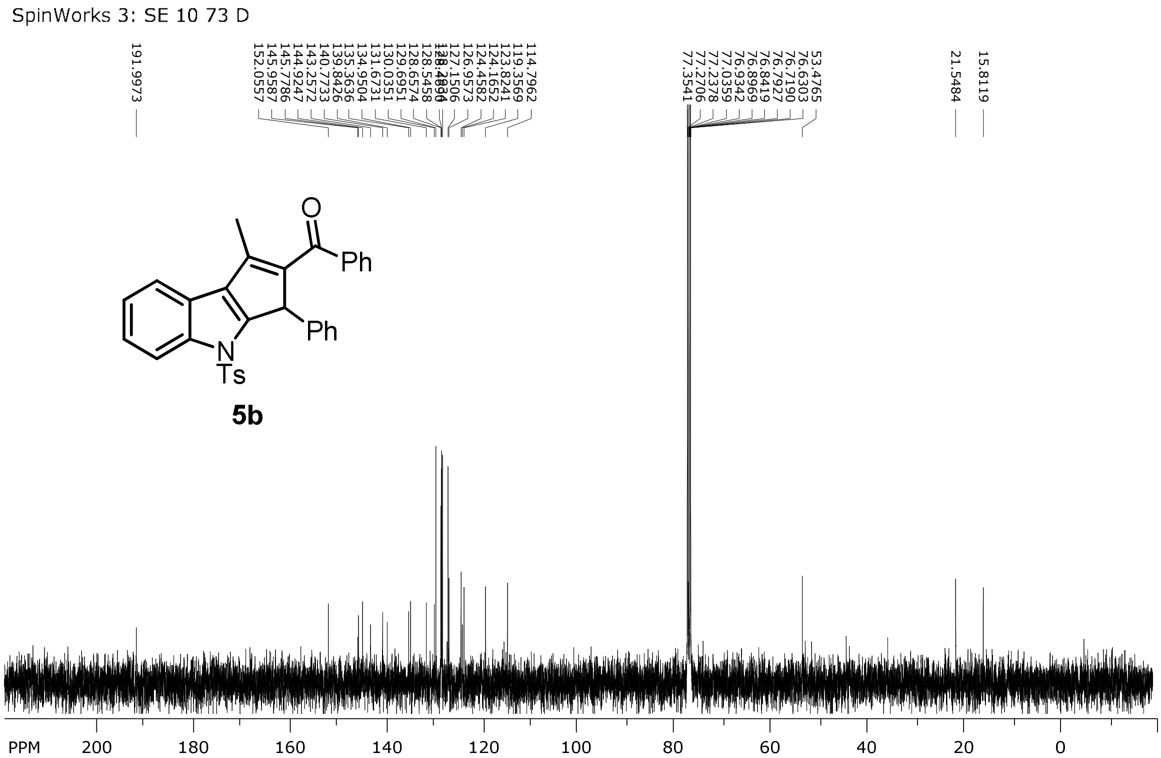
SpinWorks 3: se-11-21-c



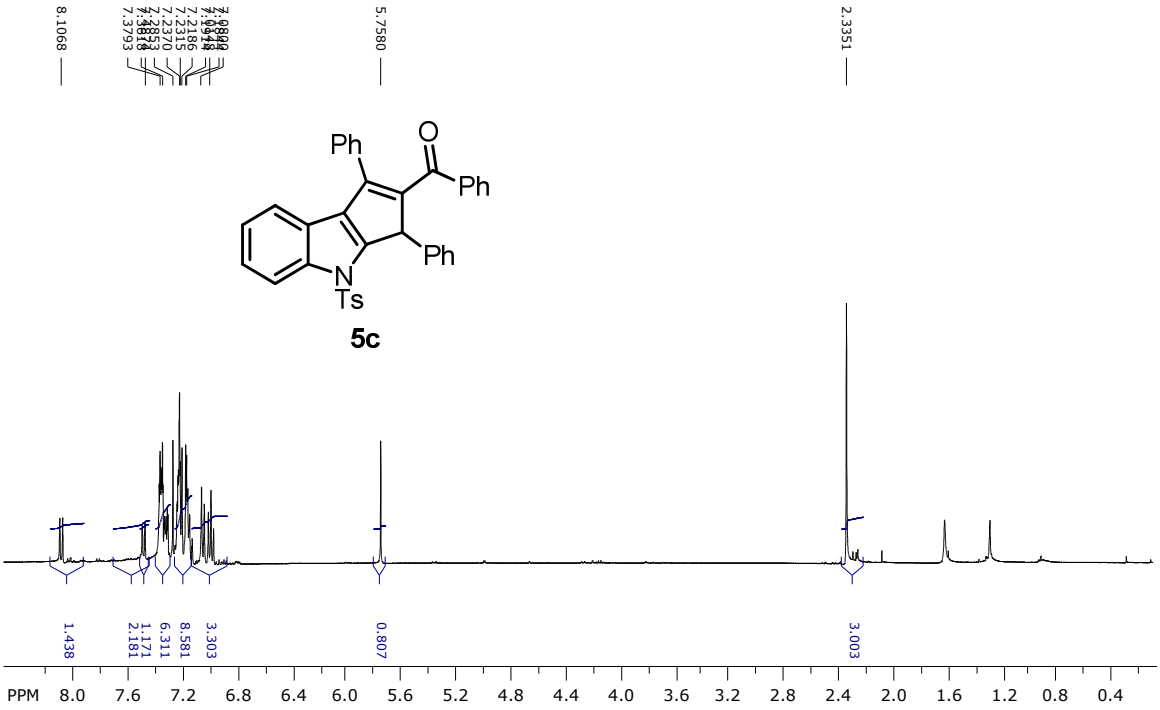
SpinWorks 3: SE 11 21 C




RSS-MAY09-2014.001.esp
Normalized Intensity
Chemical Shift (ppm)
5.4599
5.4548
2.2548
2.2492
2.2184
1.1835
O
Ph
N
Ts
Ph
5b

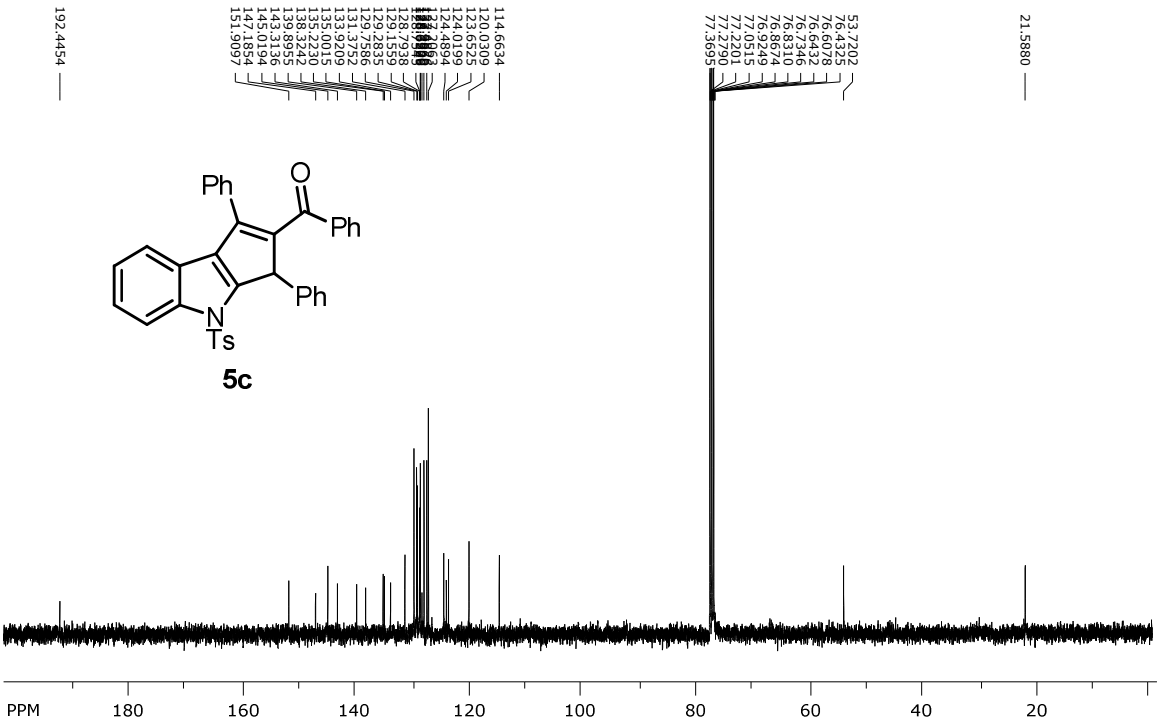

SpinWorks 3: SE 10 73 D
191.9973
21.5484
15.8119
O
Ph
N
Ts
Ph
5b
PPM

SpinWorks 3: SE 10 73 A



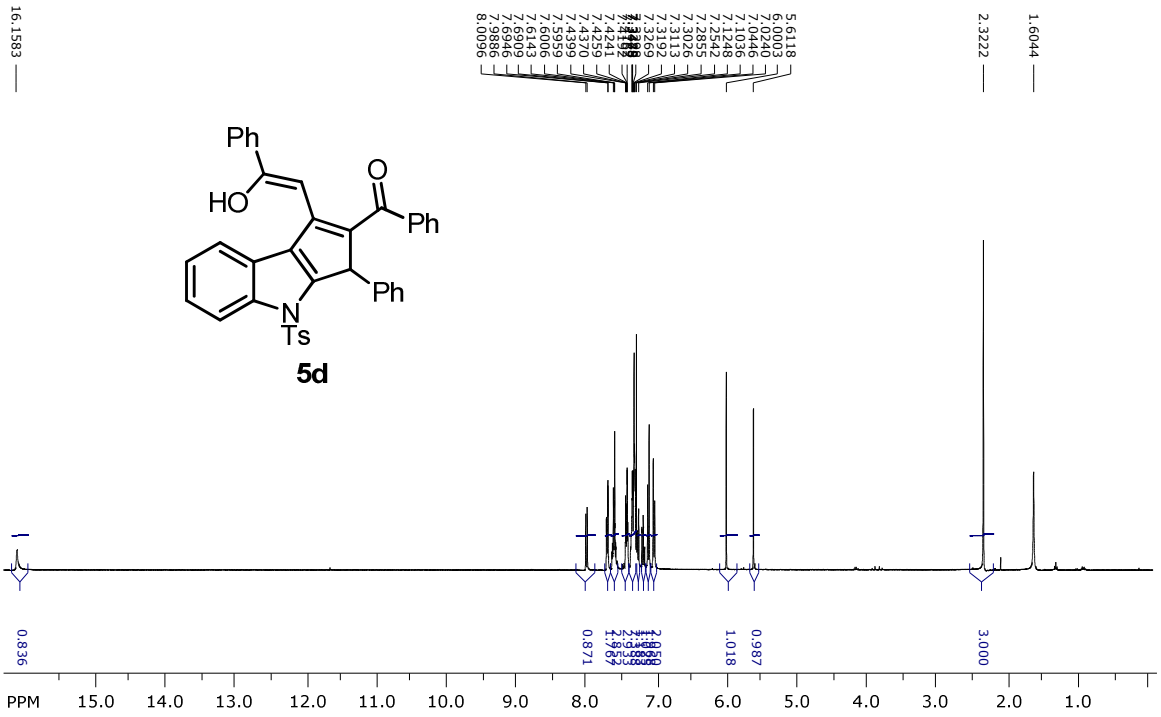
5c

SpinWorks 3: SE 10 73 A

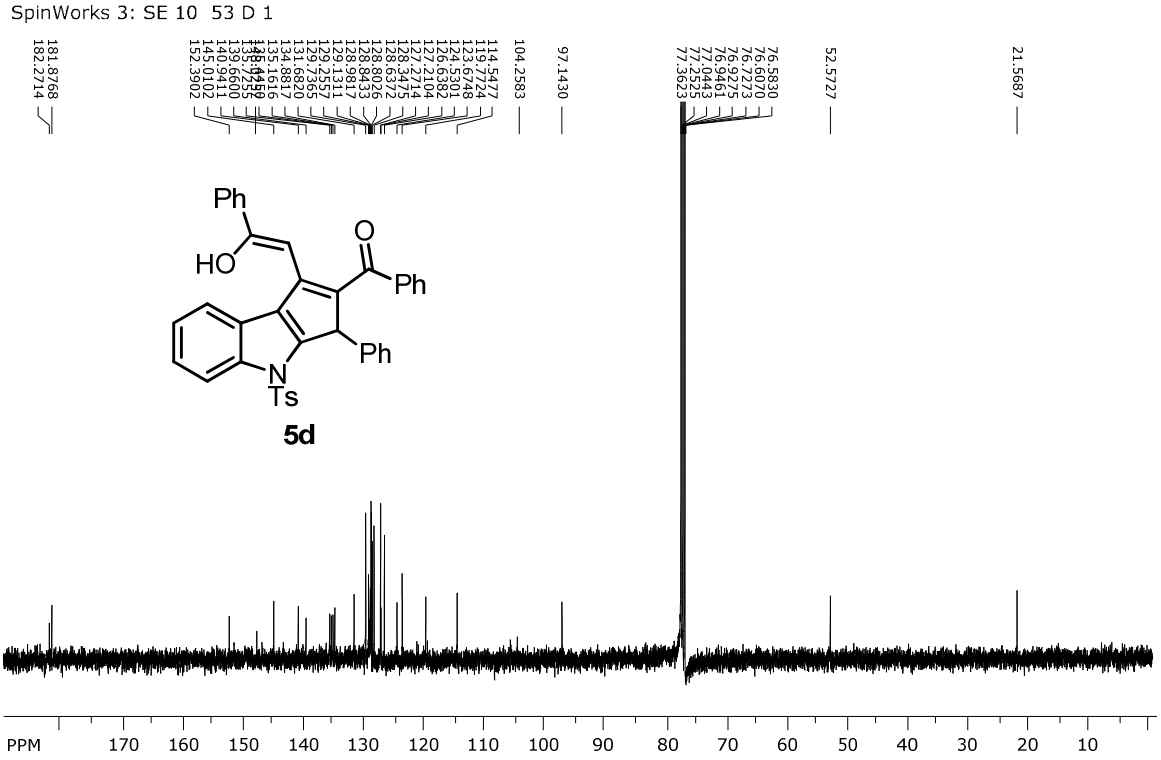


5c

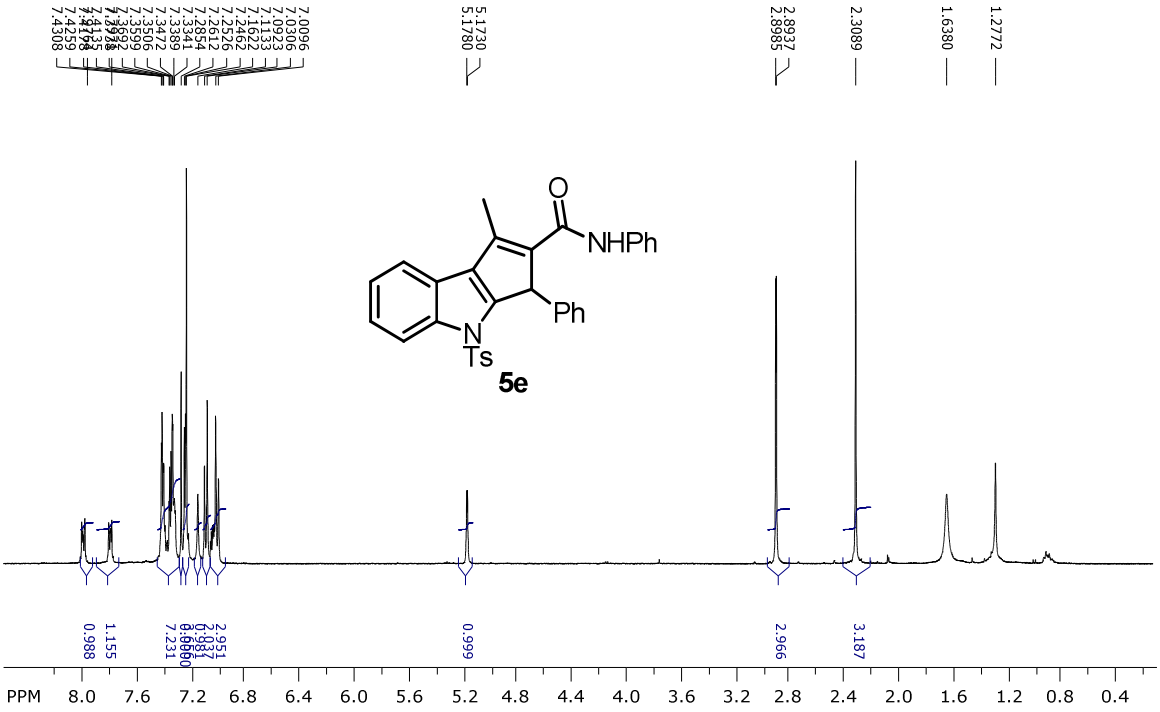
SpinWorks 3: SE 10 53 D 1



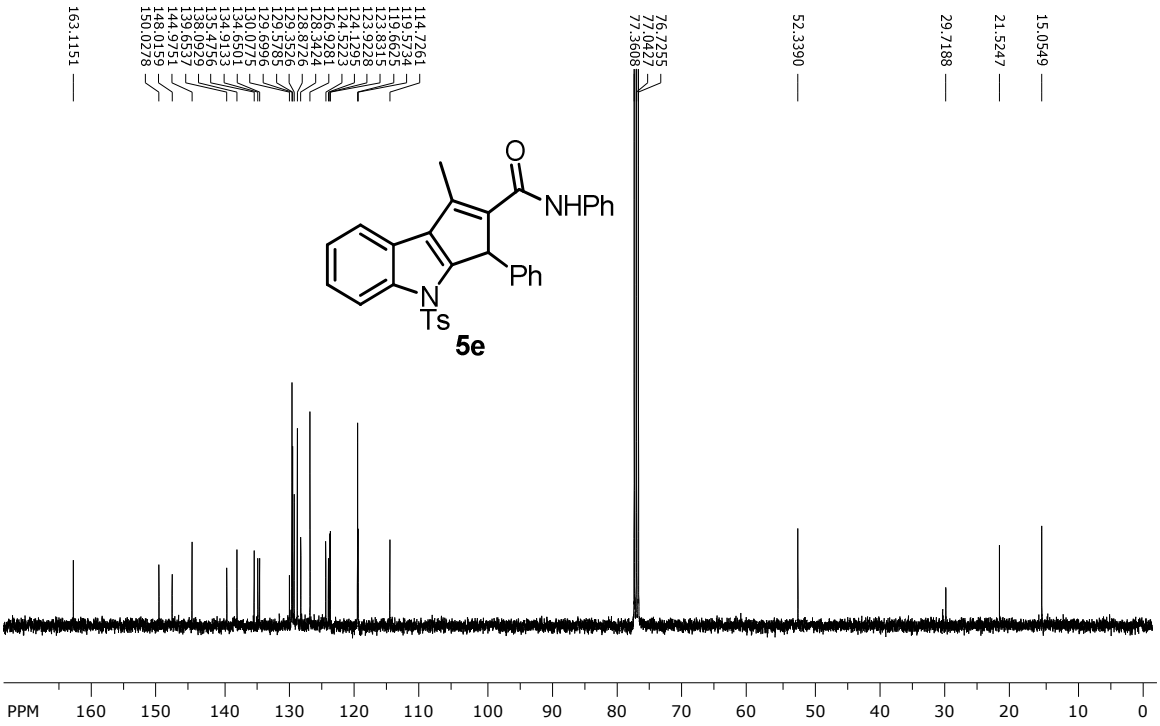
SpinWorks 3: SE 10 53 D 1

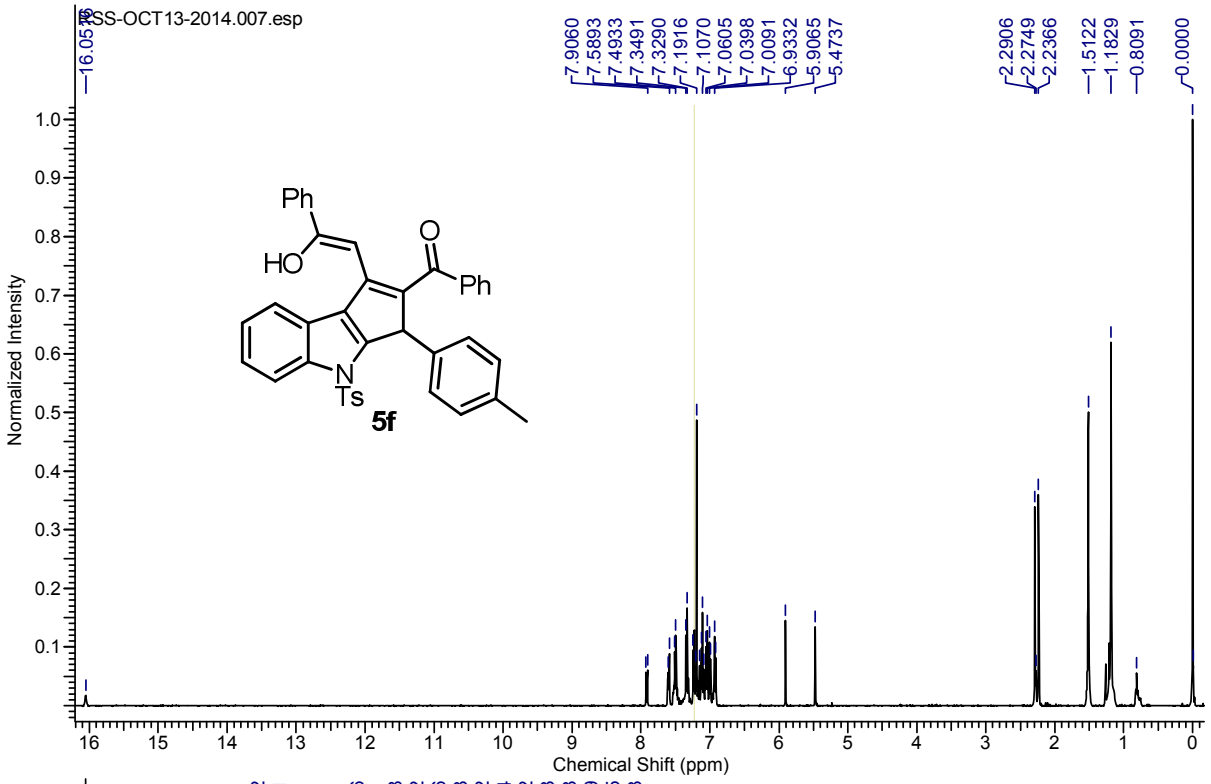


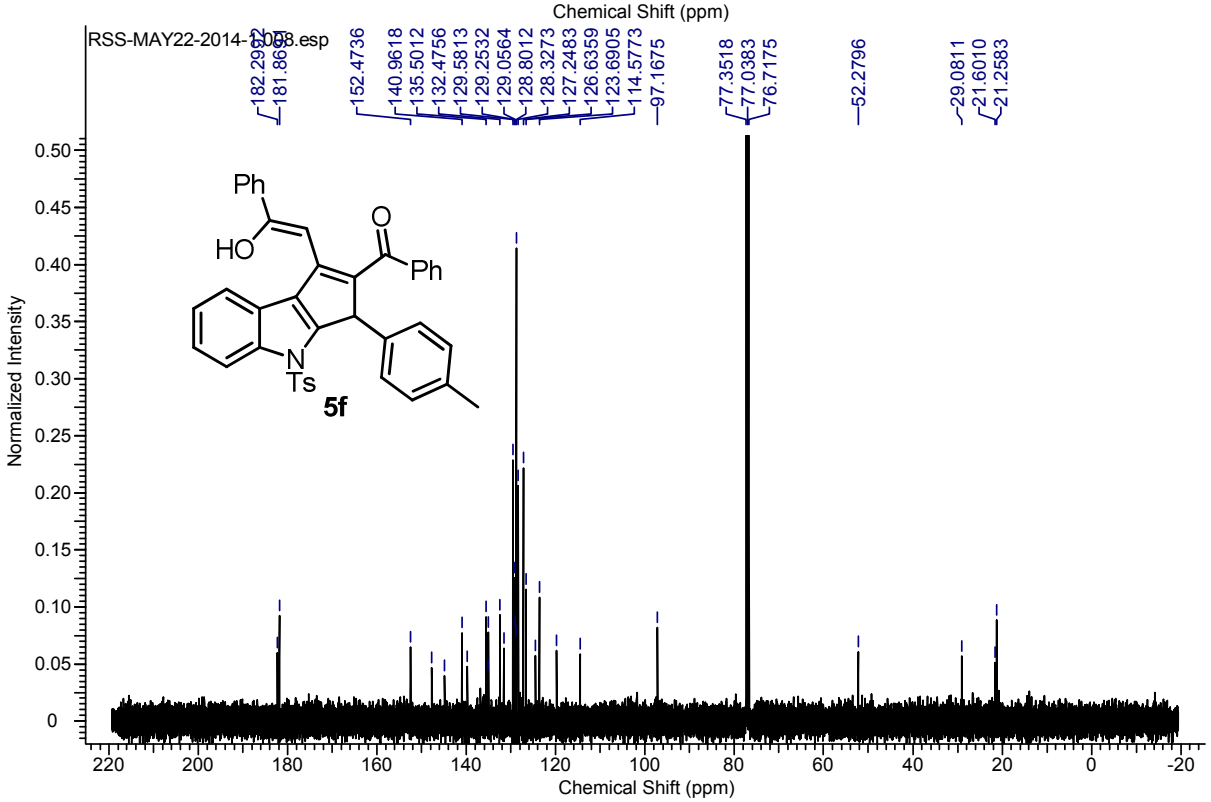
SpinWorks 3: se-10-53-f



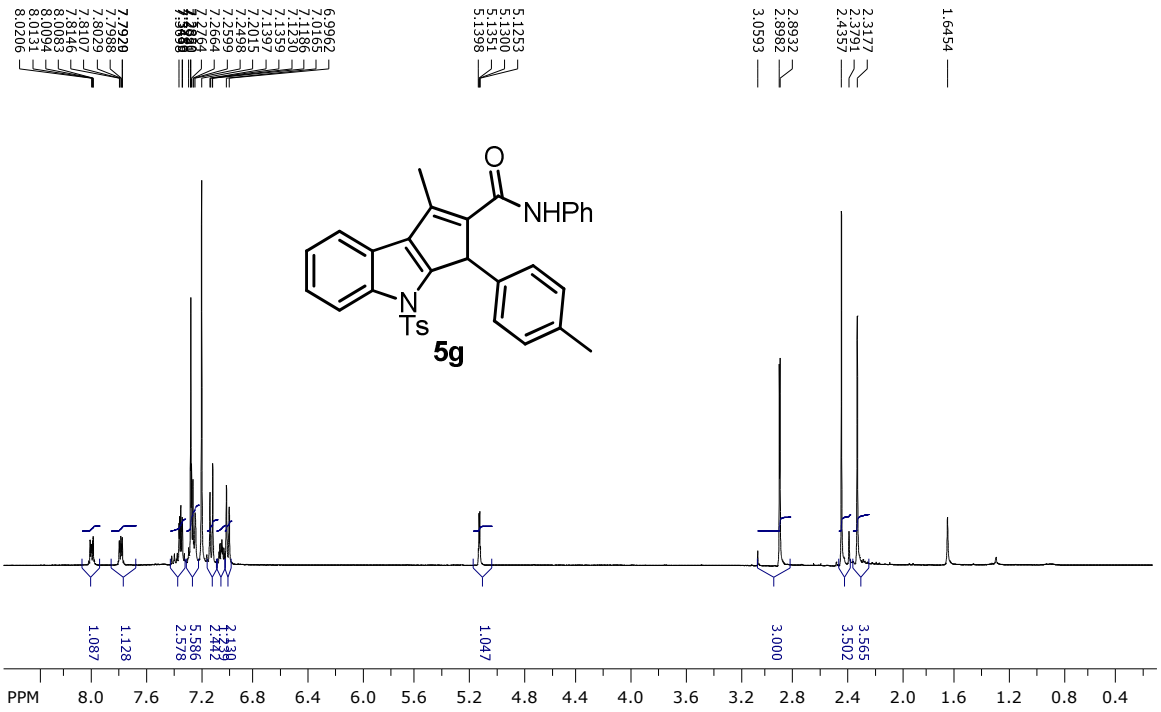
SpinWorks 3: SE 10 53 F



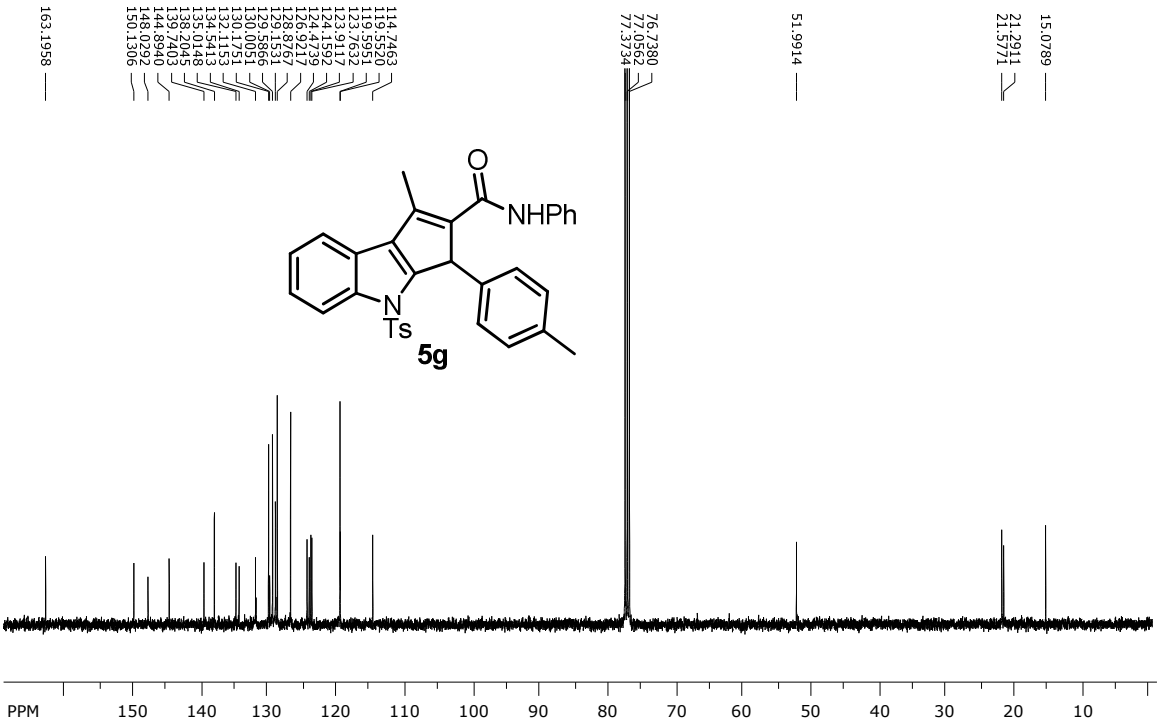

RSS-OCT13-2014.007.esp
16.0578
7.9060
7.5893
7.4933
7.3491
7.3290
7.1916
7.1070
7.0605
7.0398
7.0091
6.9332
5.9065
5.4737
2.2906
2.2749
2.2366
1.5122
1.1829
0.8091
0.0000
Normalized Intensity
Chemical Shift (ppm)
Ph
HO
O
Ph
N
Ts
5f


RSS-MAY22-2014-1008.esp
182.2992
181.8668
152.4736
140.9618
135.5012
132.4756
129.5813
129.2532
129.0564
128.8012
128.3273
127.2483
126.6359
123.6905
114.5773
97.1675
77.3518
77.0383
76.7175
52.2796
29.0811
21.6010
21.2583
Normalized Intensity
Chemical Shift (ppm)
Ph
HO
O
Ph
N
Ts
5f

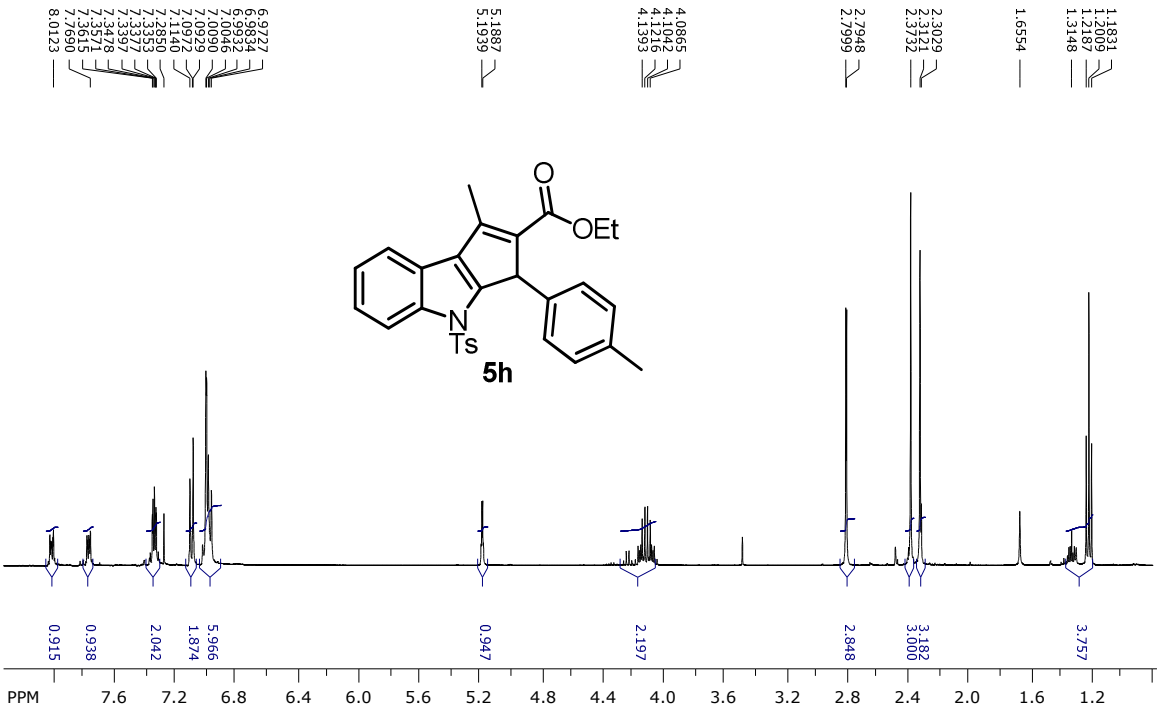
SpinWorks 3: SE 10 81 F



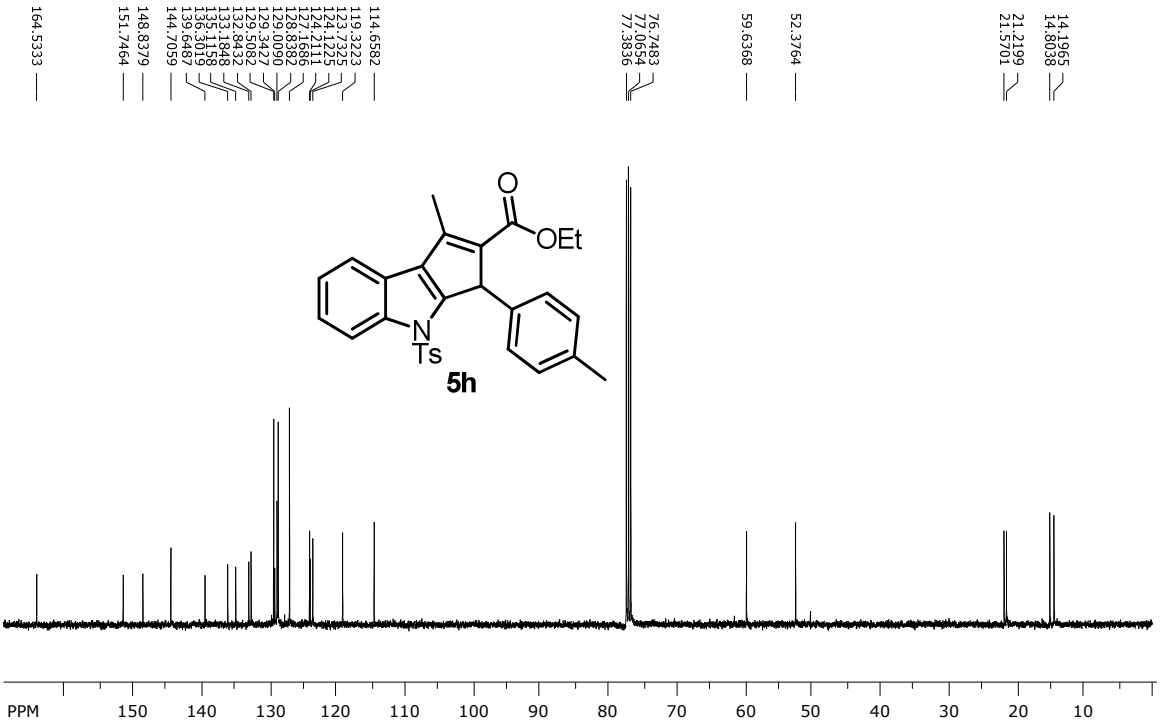
SpinWorks 3: SE 10 81 F



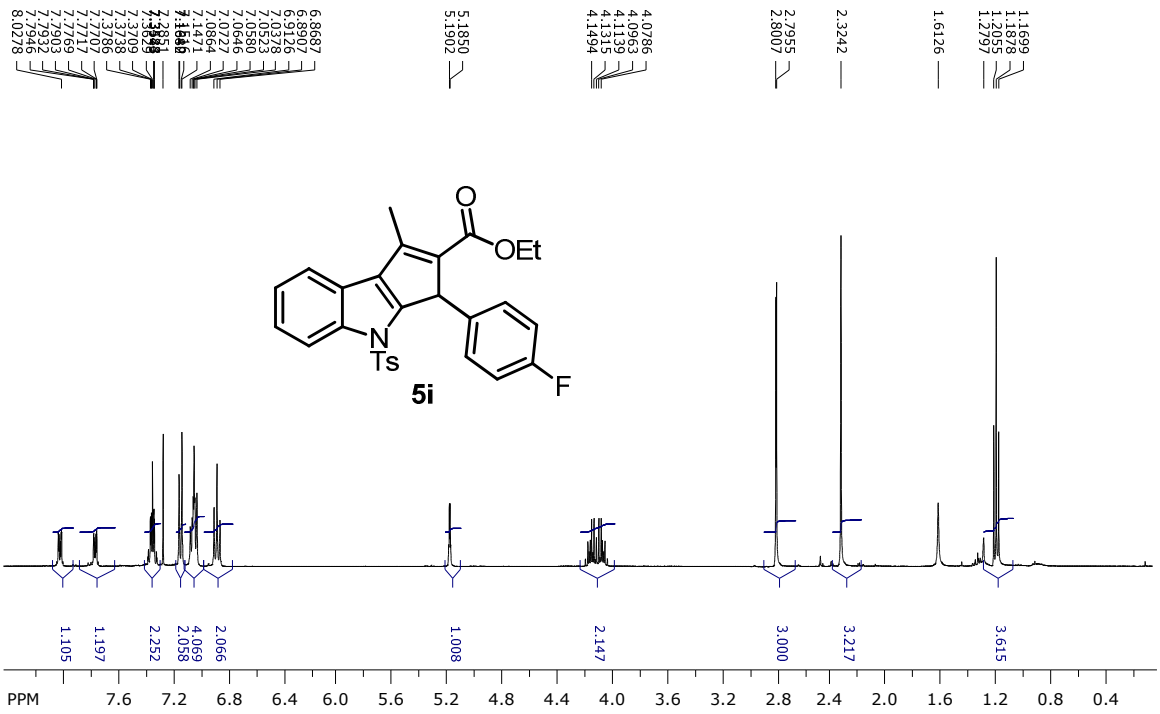
SpinWorks 3: SE 10 81 G



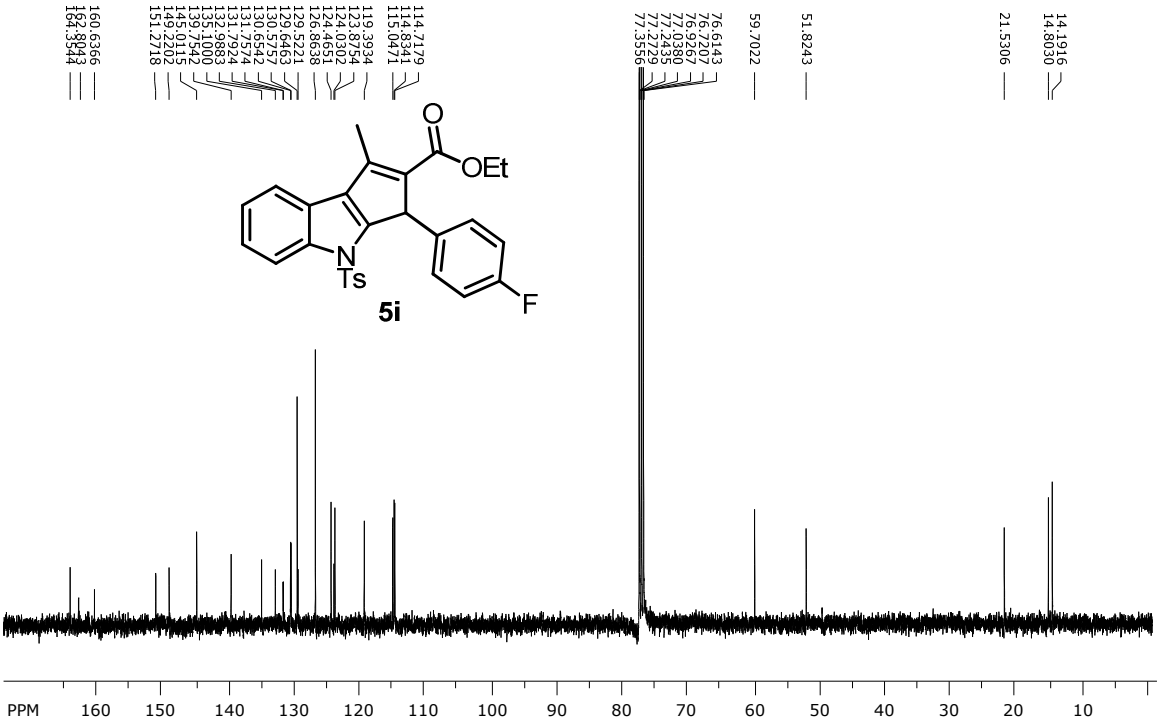
SpinWorks 3: SE 10 81 G

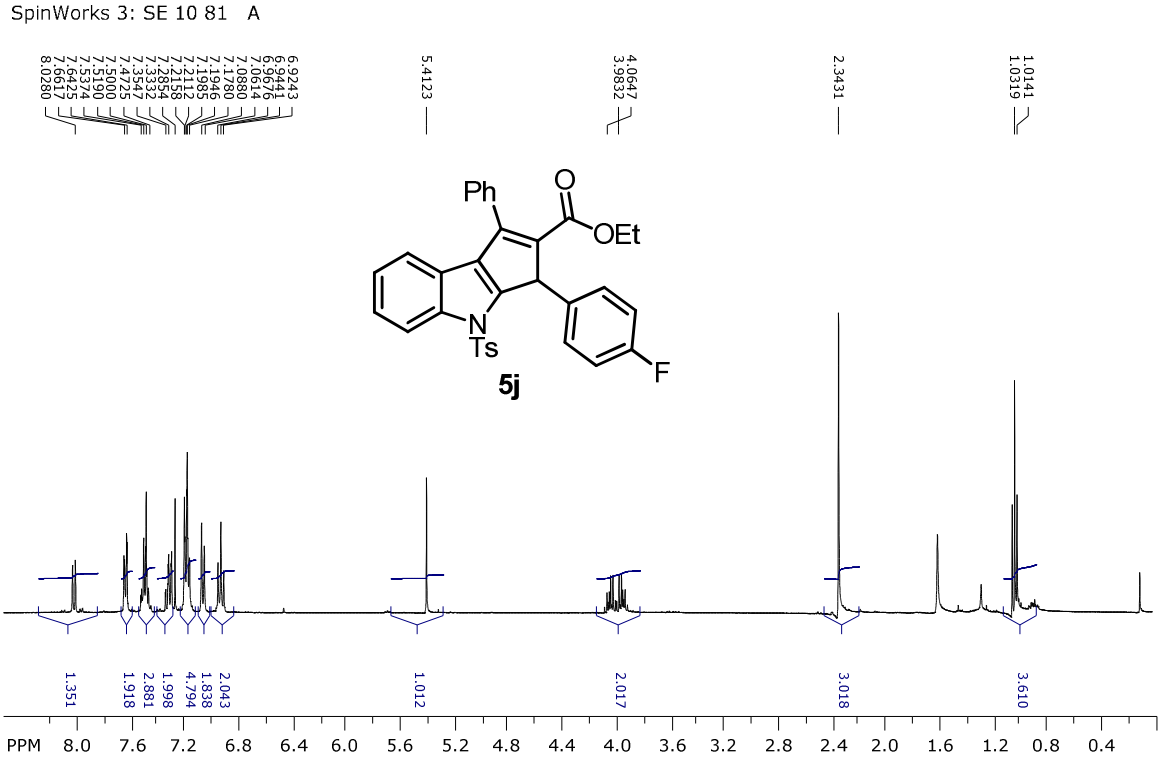


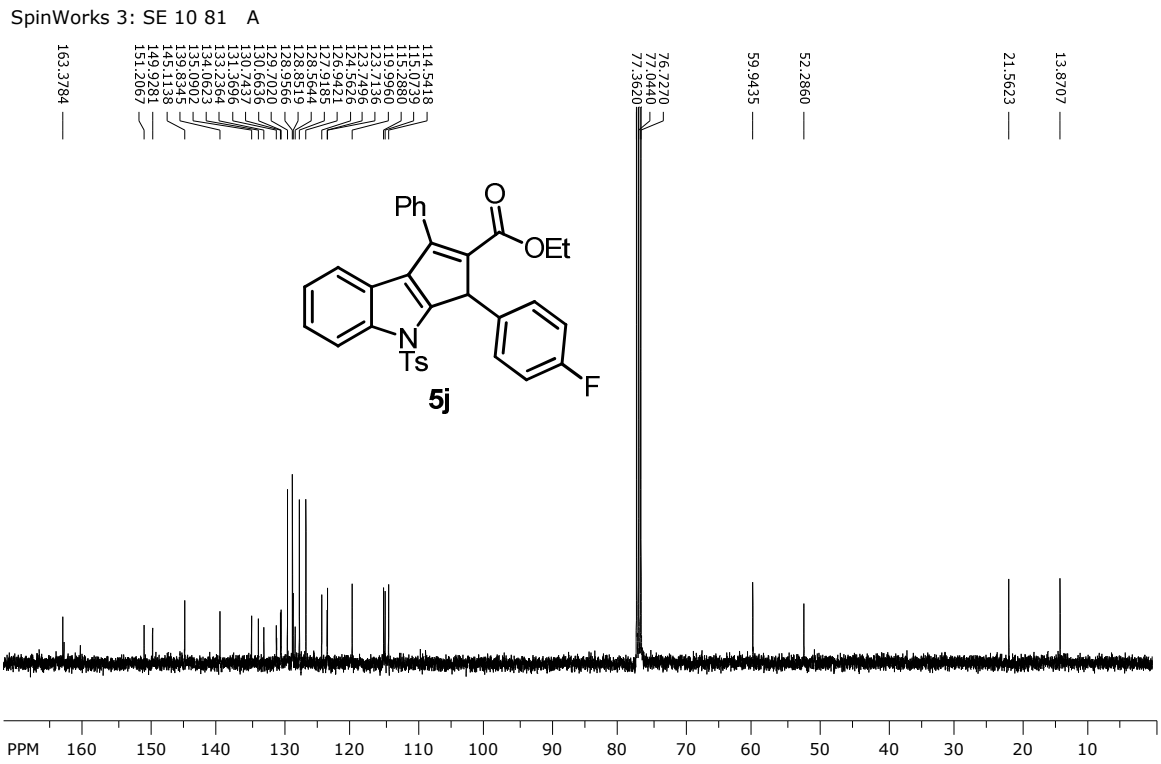
SpinWorks 3: SE 10 78 C



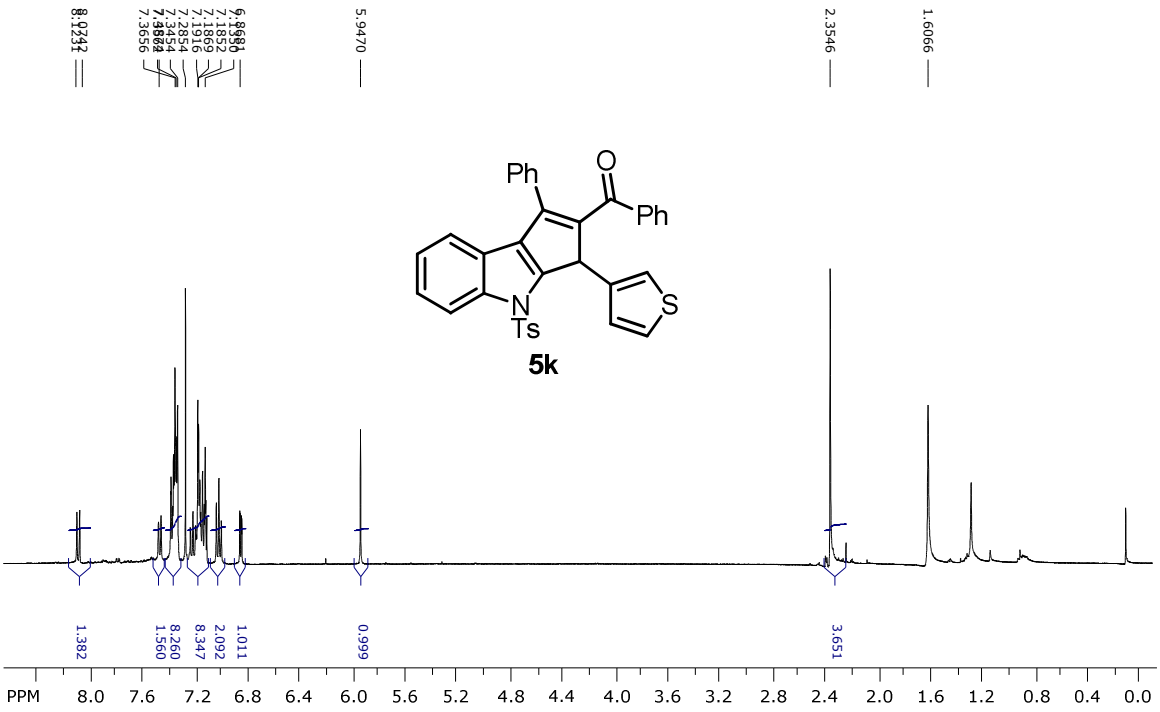
SpinWorks 3: SE 10 78 C




SpinWorks 3: SE 10 81 A
8.0280
7.6617
7.6425
7.5374
7.5190
7.5000
7.4752
7.3332
7.2854
7.2158
7.2112
7.1985
7.1946
7.1780
7.0880
7.0614
6.9676
6.9441
6.9243
5.4123
4.0647
3.9832
2.3431
1.0319
1.0141
Ph
O
OEt
N
Ts
F
5j
1.351
1.918
2.881
1.998
4.794
1.838
2.043
1.012
2.017
3.018
3.610
PPM 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4

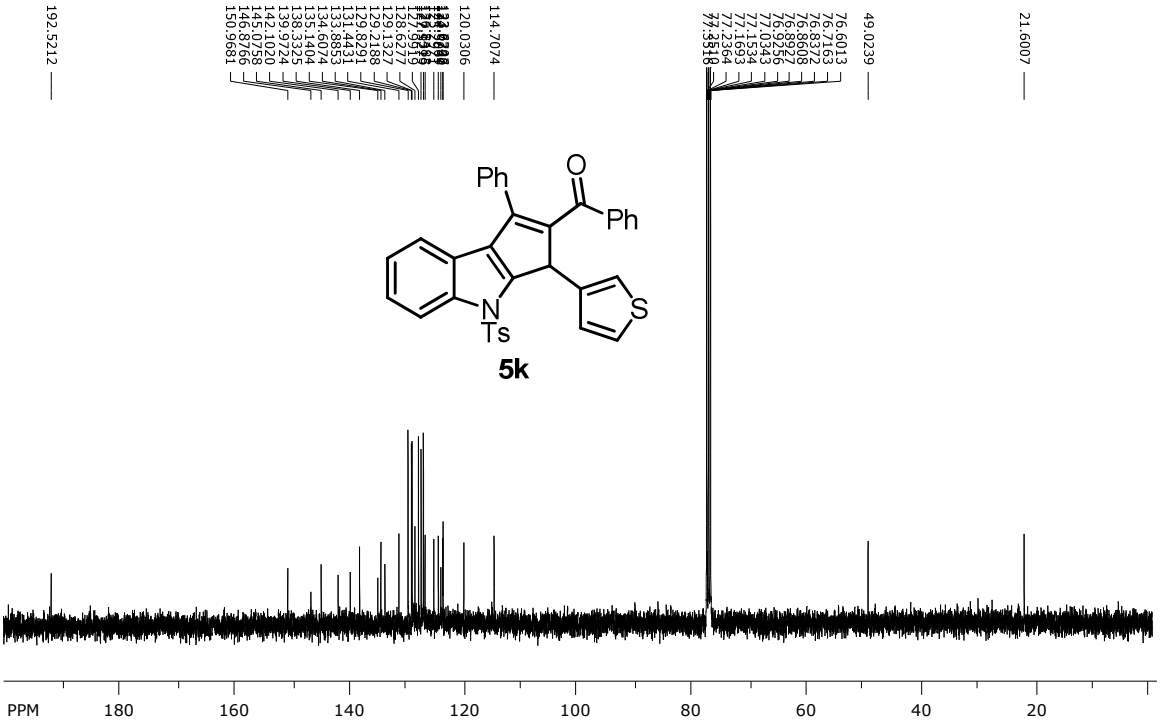

SpinWorks 3: SE 10 81 A
163.3784
151.2067
149.9281
145.1138
135.8942
134.0623
133.2364
131.3696
130.7437
130.6636
129.7020
128.9566
128.8519
128.5644
127.9185
126.9421
124.5626
123.7496
119.9960
115.2880
115.0739
114.5418
77.3620
77.0440
76.7270
59.9435
52.2860
21.5623
13.8707
Ph
O
OEt
N
Ts
F
5j
PPM 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

SpinWorks 3: SE 10 089 A



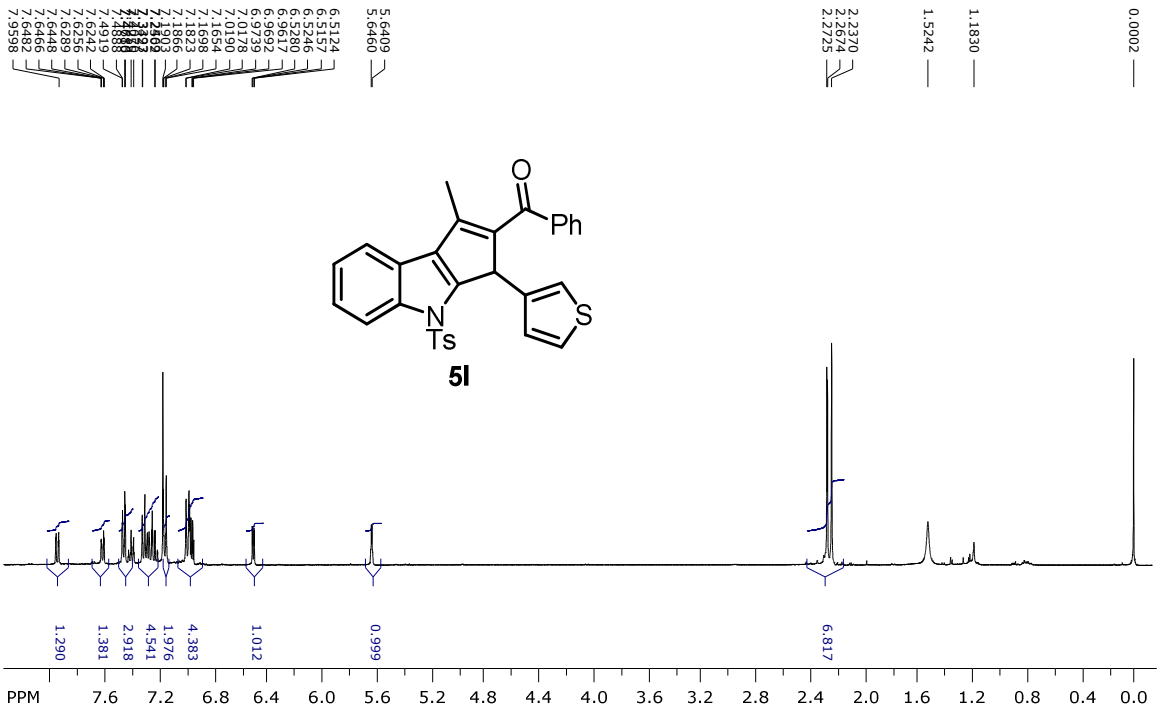
5k

SpinWorks 3: SE 10 089 A



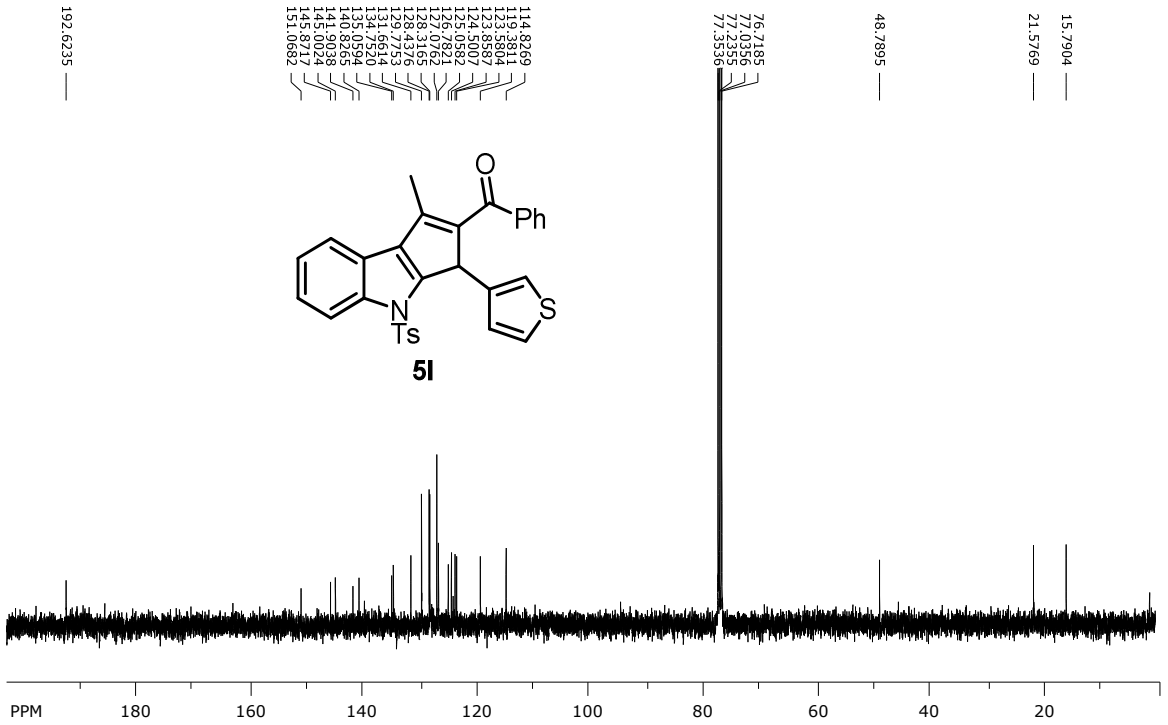
5k

SpinWorks 3: SE 1089 B



5l

SpinWorks 3: SE 1089 B



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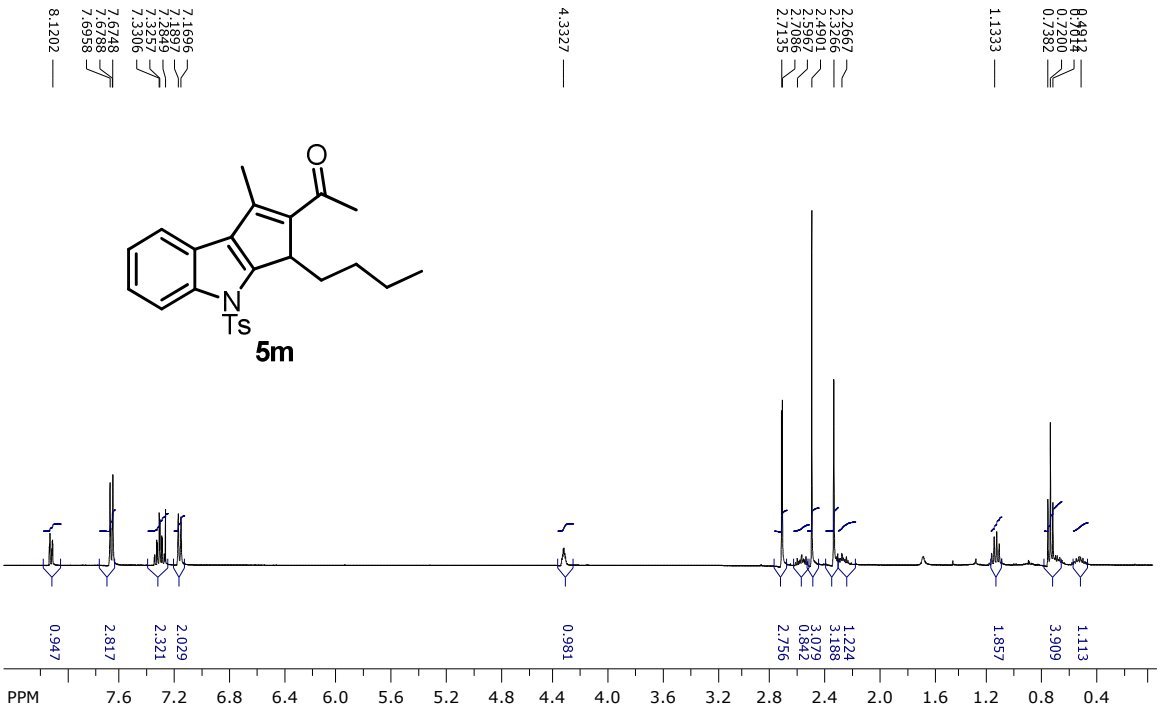
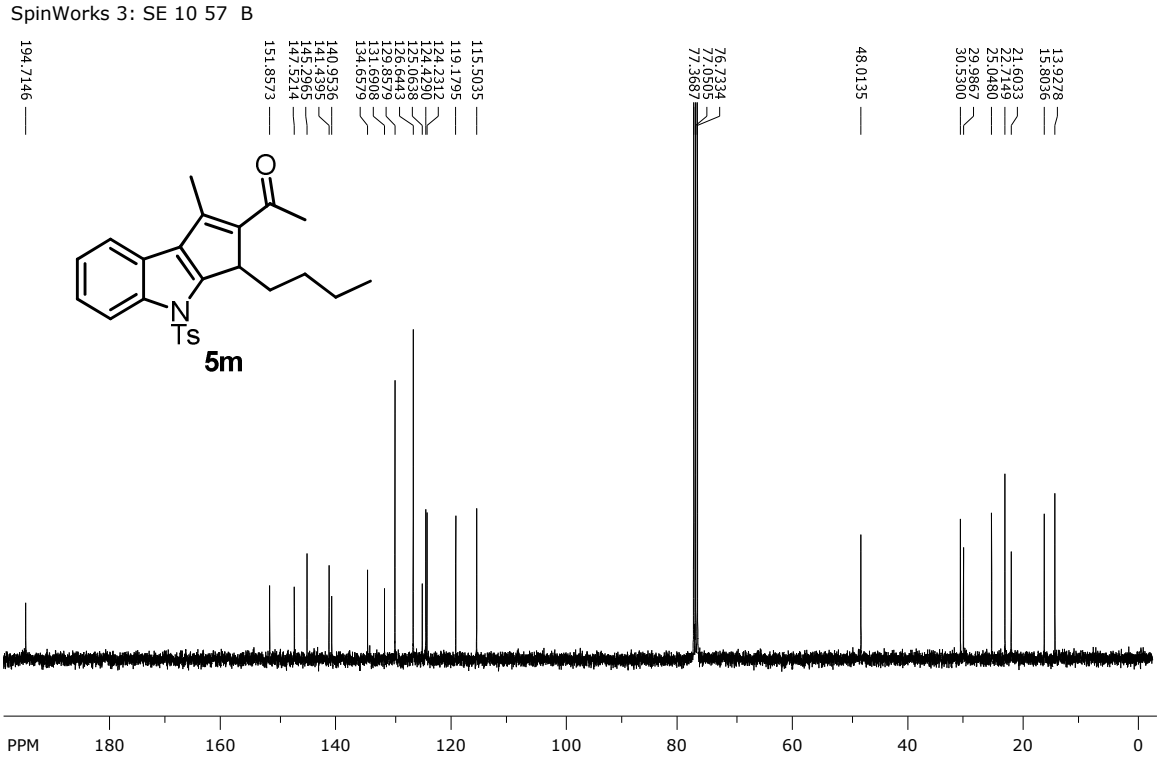
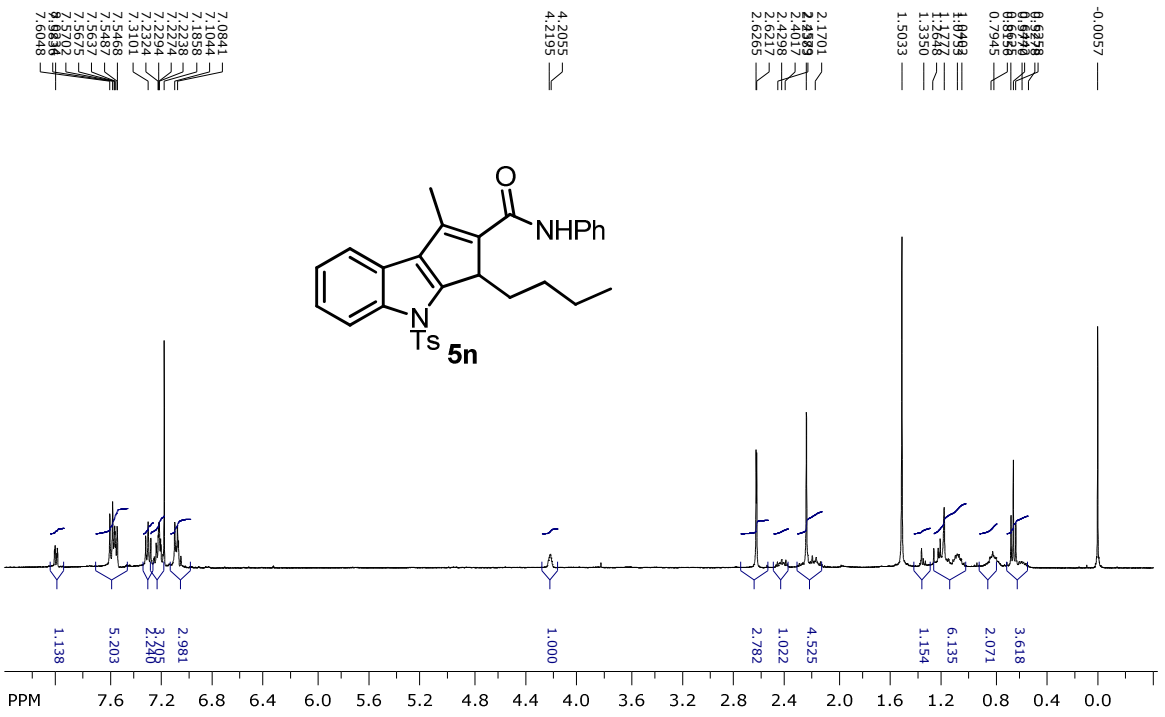
SpinWorks 3: SE 10 57 B



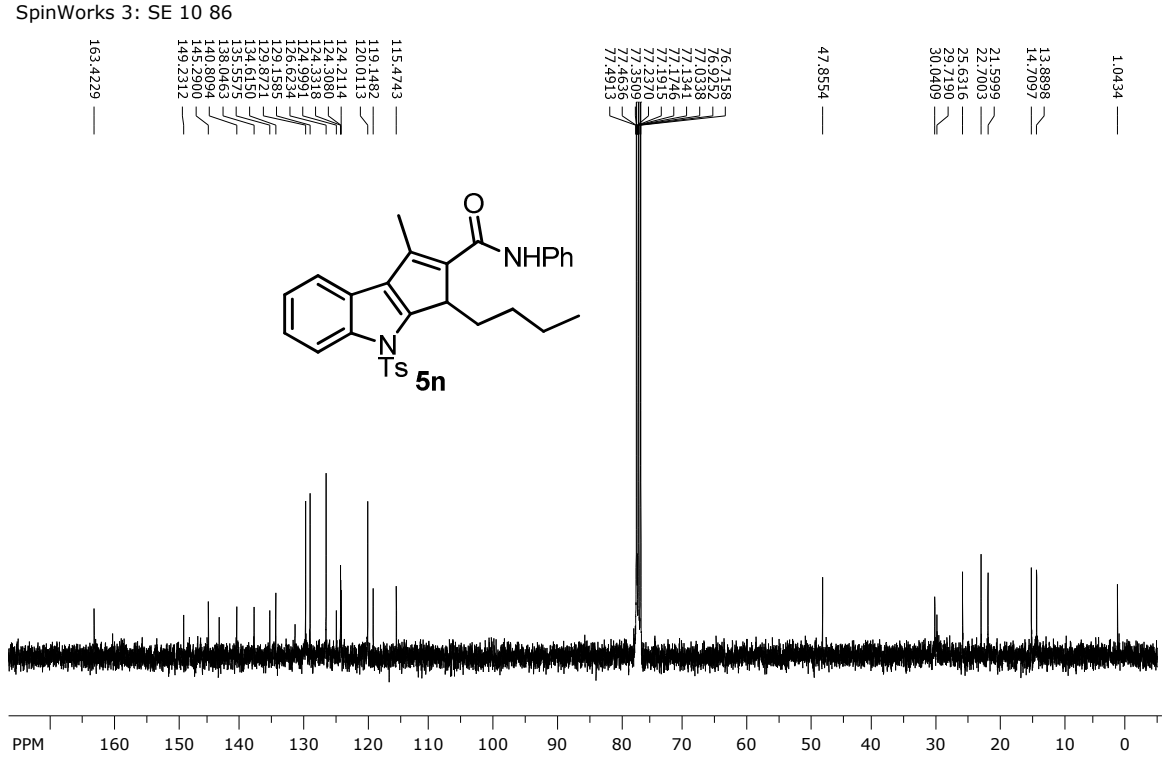
SpinWorks 3: SE 10 57 B



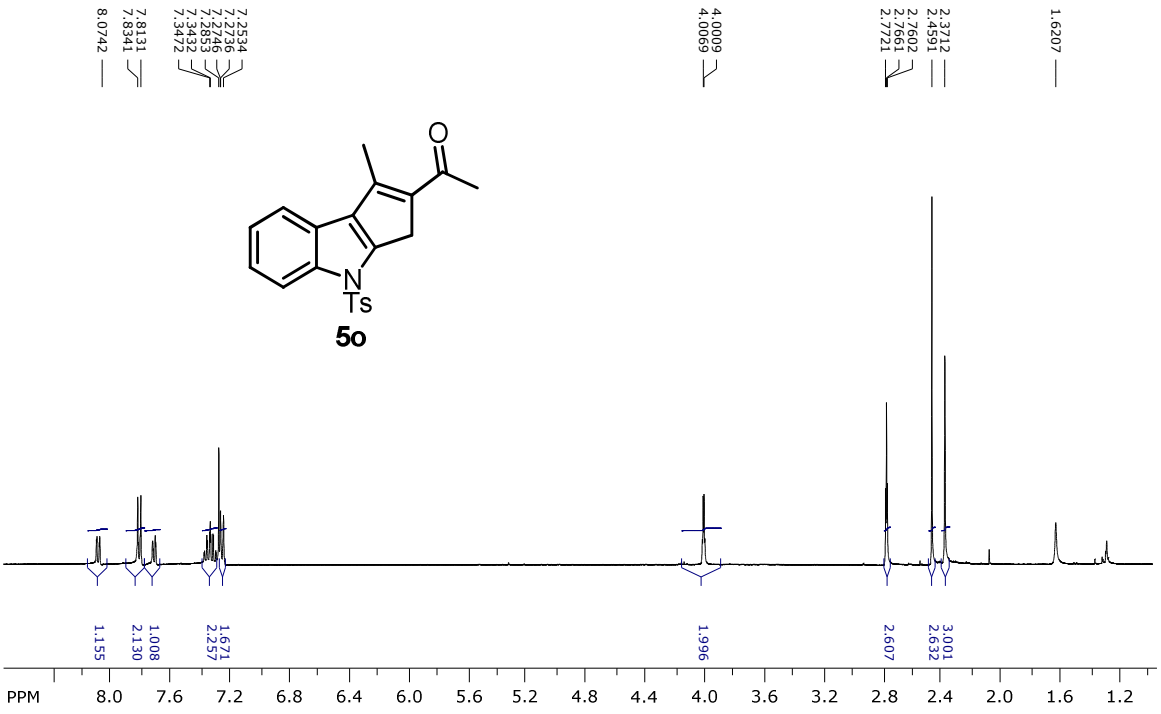
SpinWorks 3: SE 10 86



SpinWorks 3: SE 10 86



SpinWorks 3: se 10 90a



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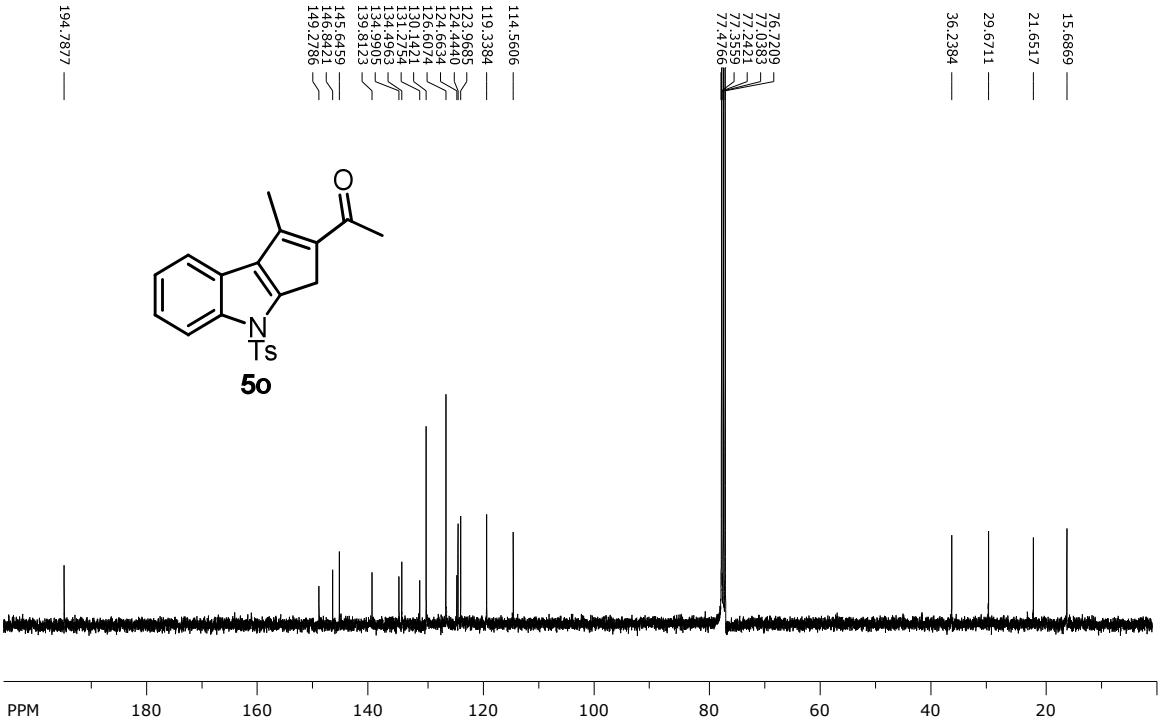
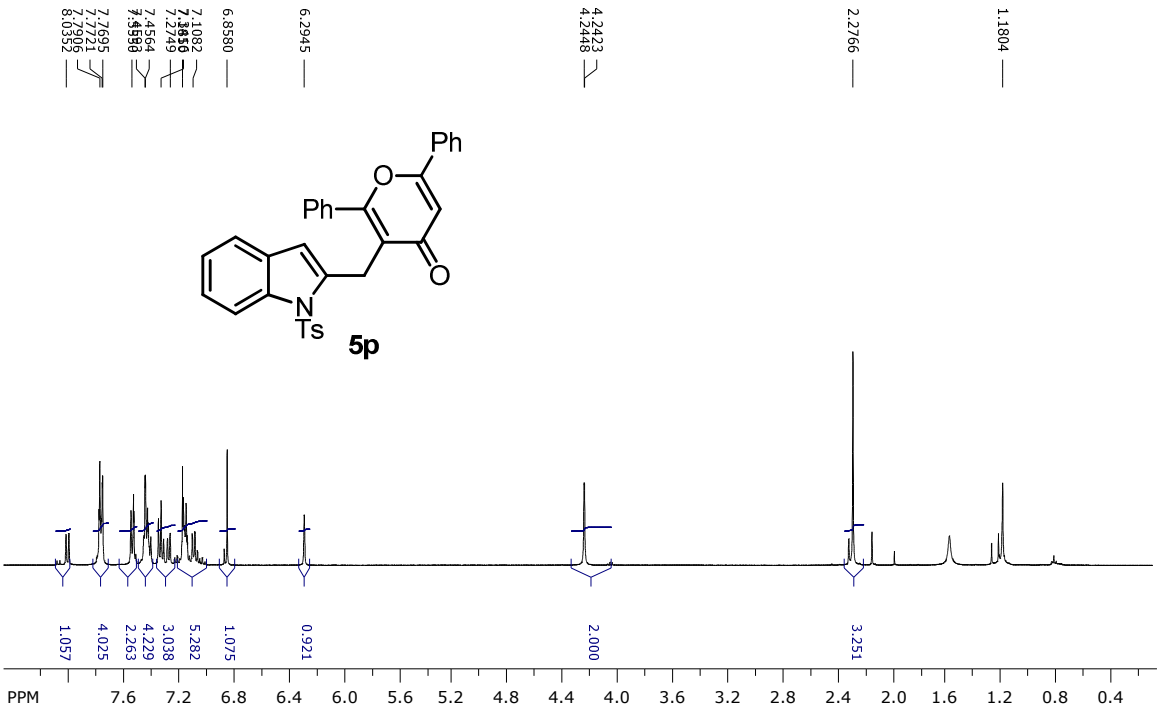


SpinWorks 3: SE 10 90 D



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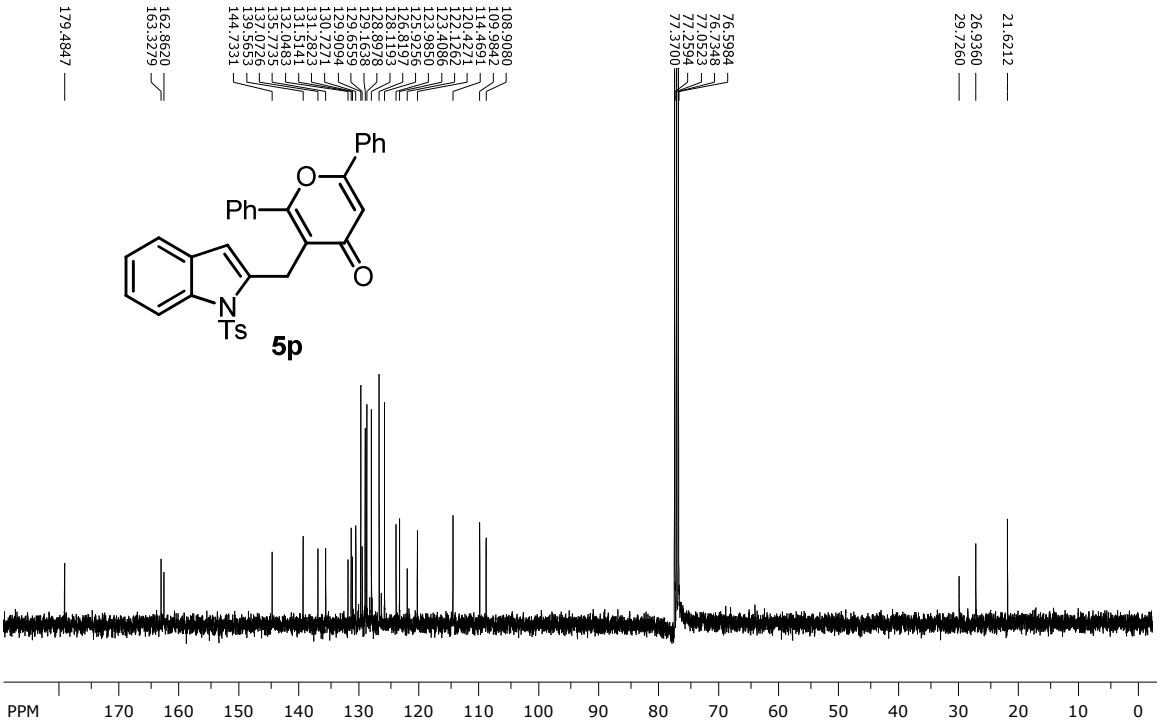
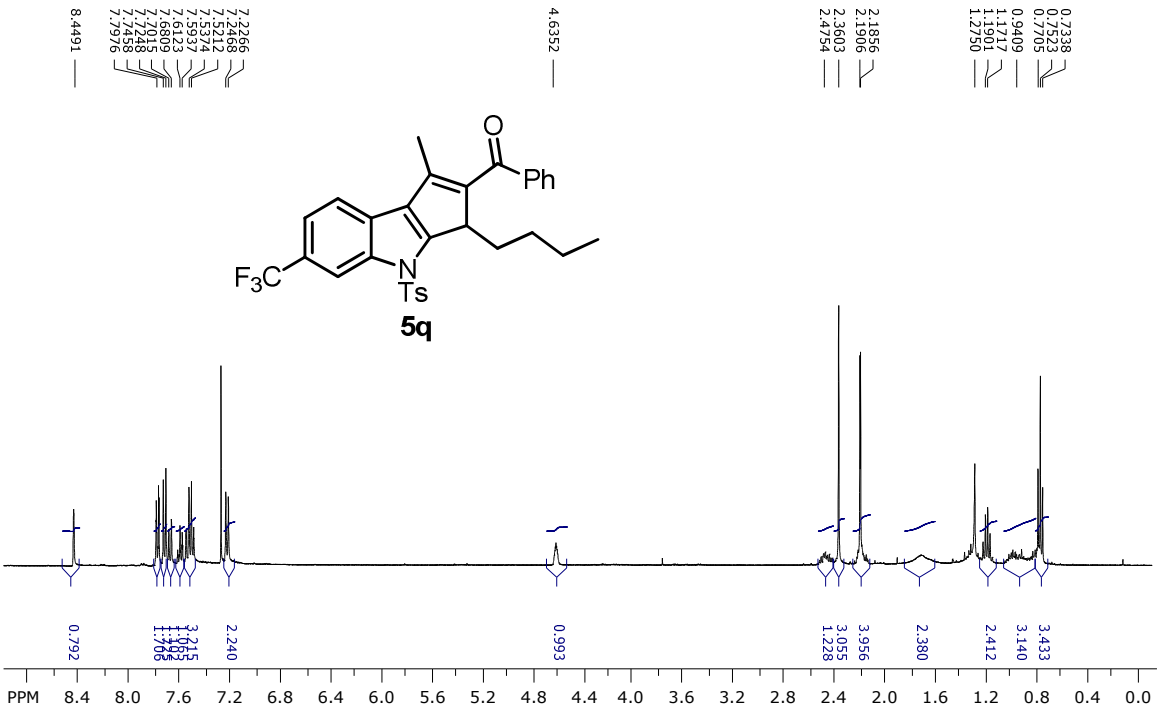


SpinWorks 3: SE 10 98 B 2



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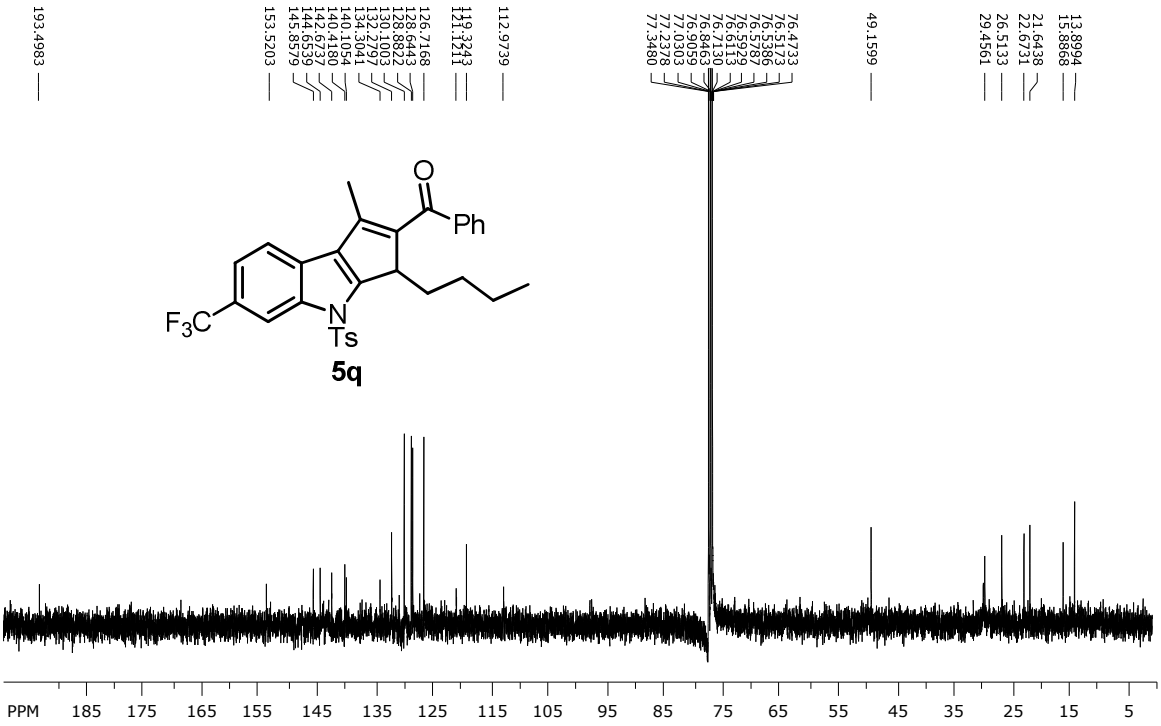
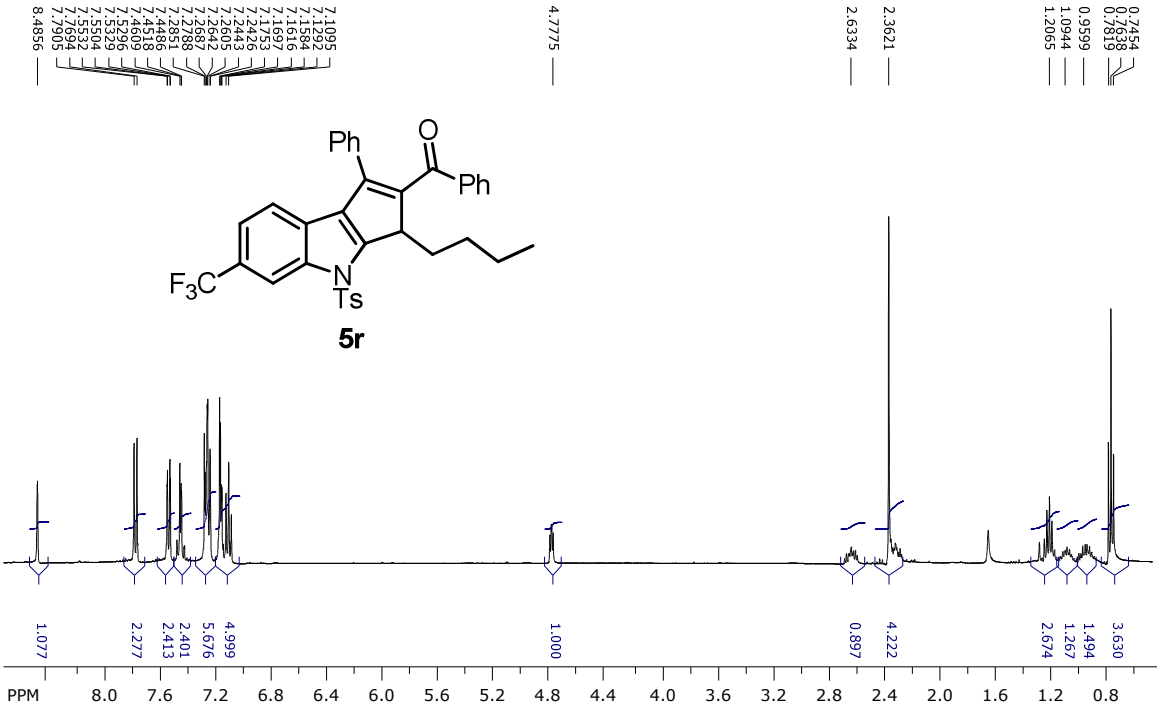


SpinWorks 3: SE 10 98 B 1



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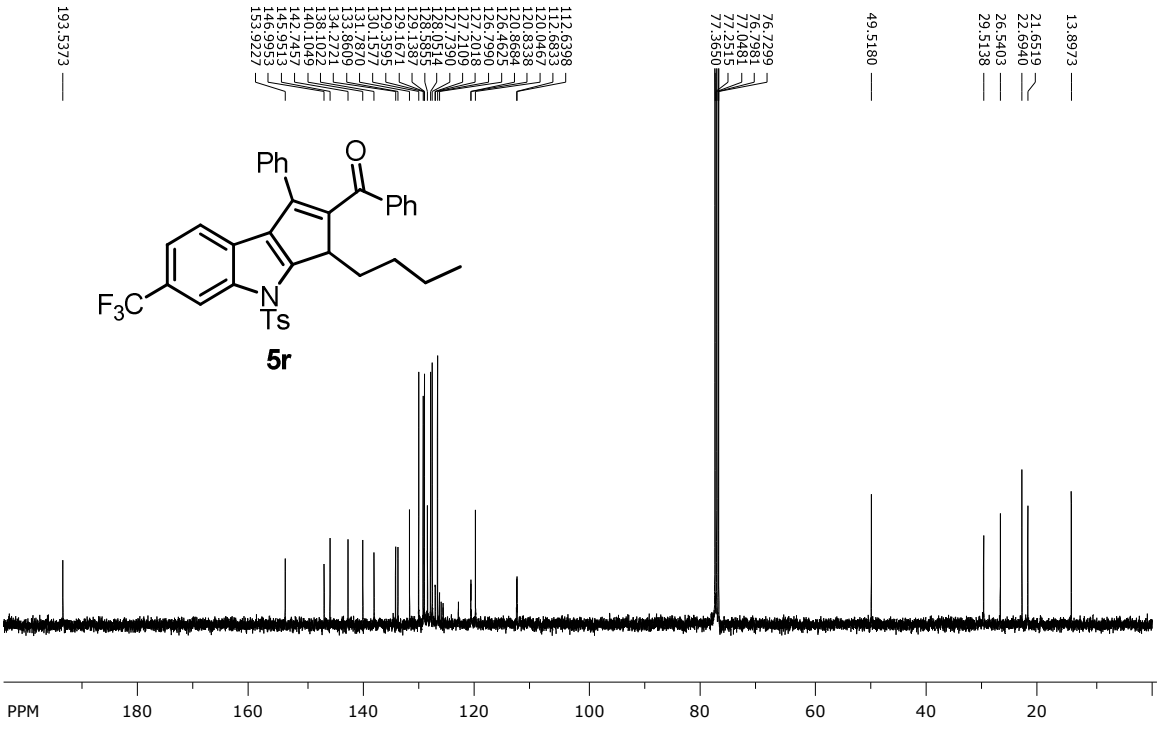
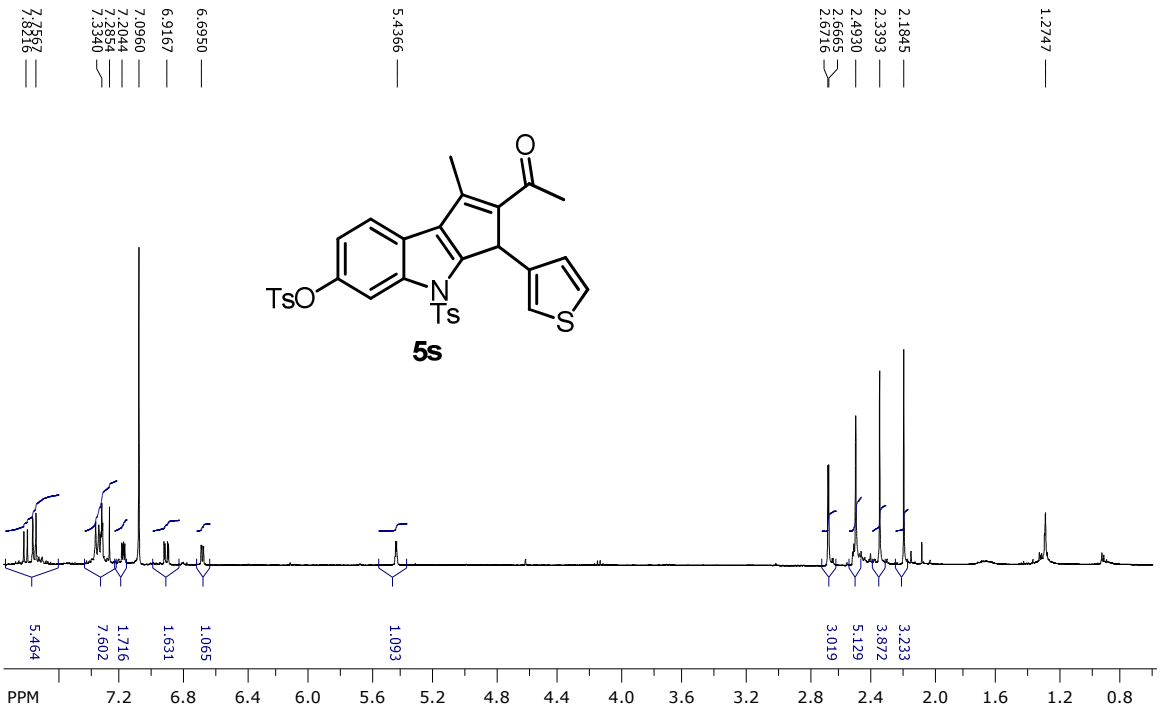


SpinWorks 3: SE 10 11 A



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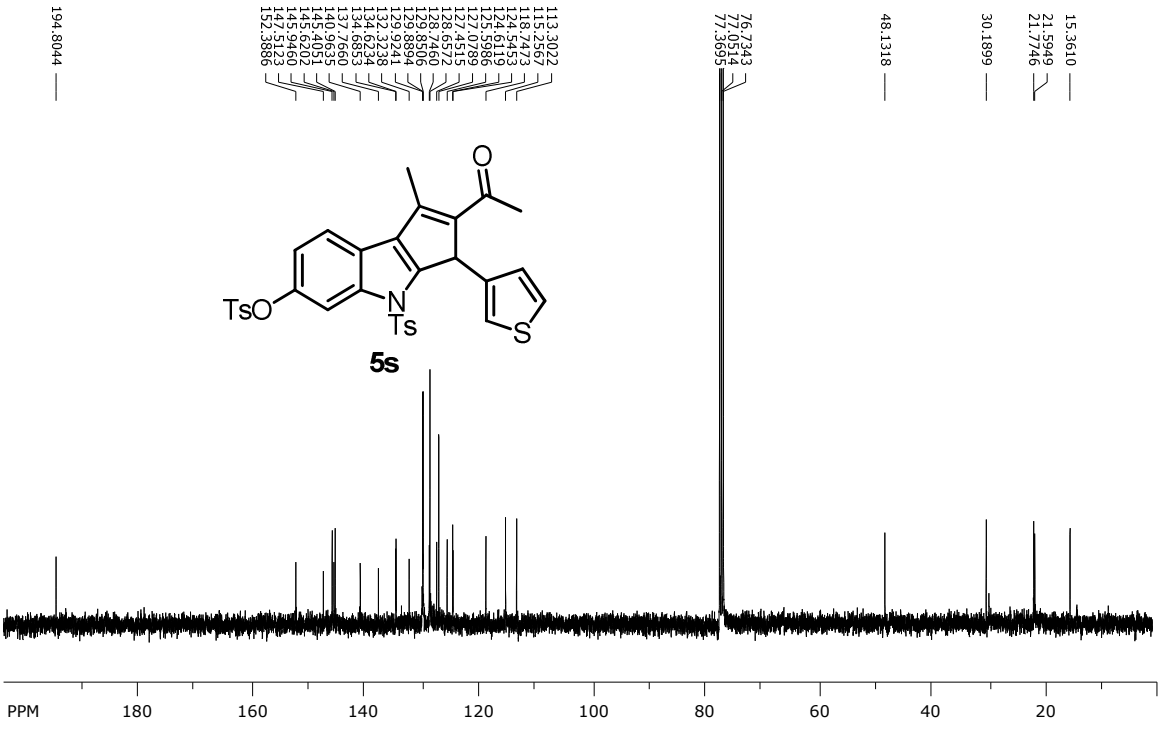

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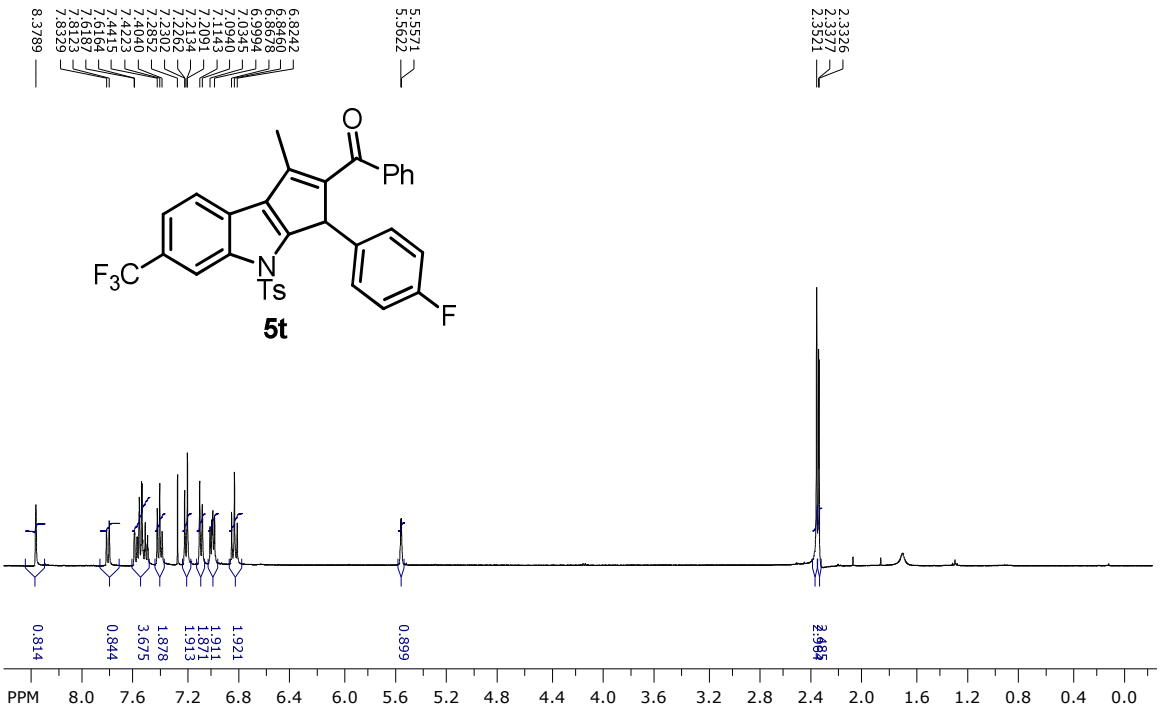
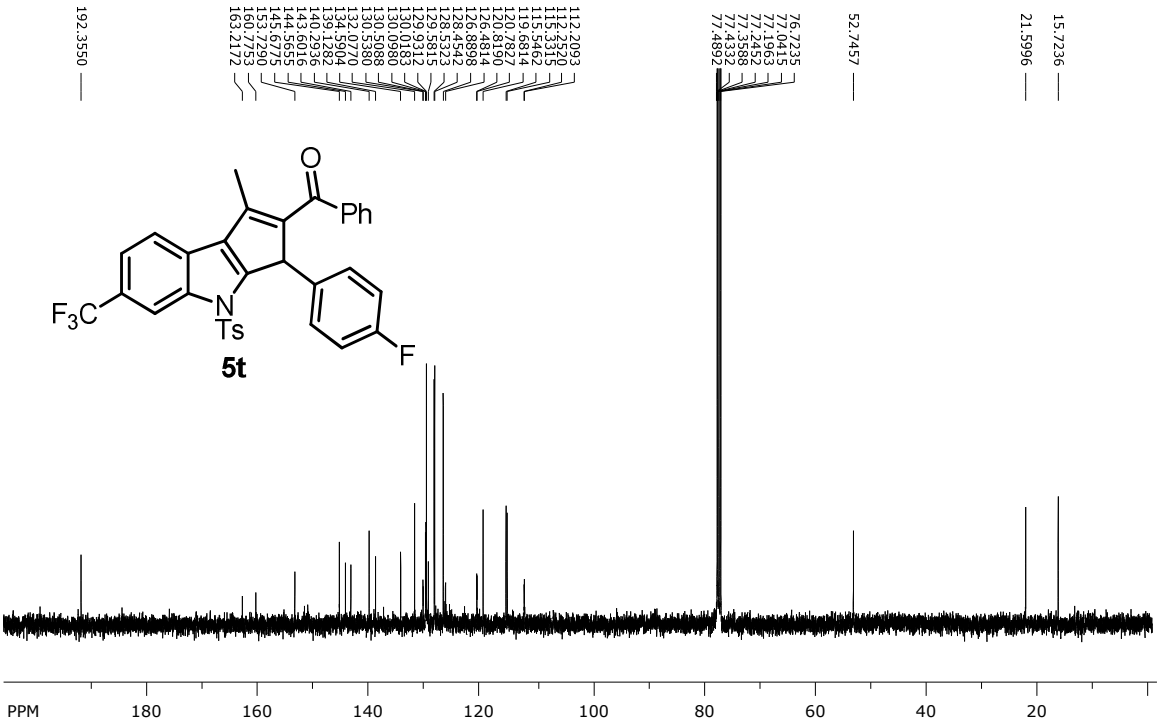
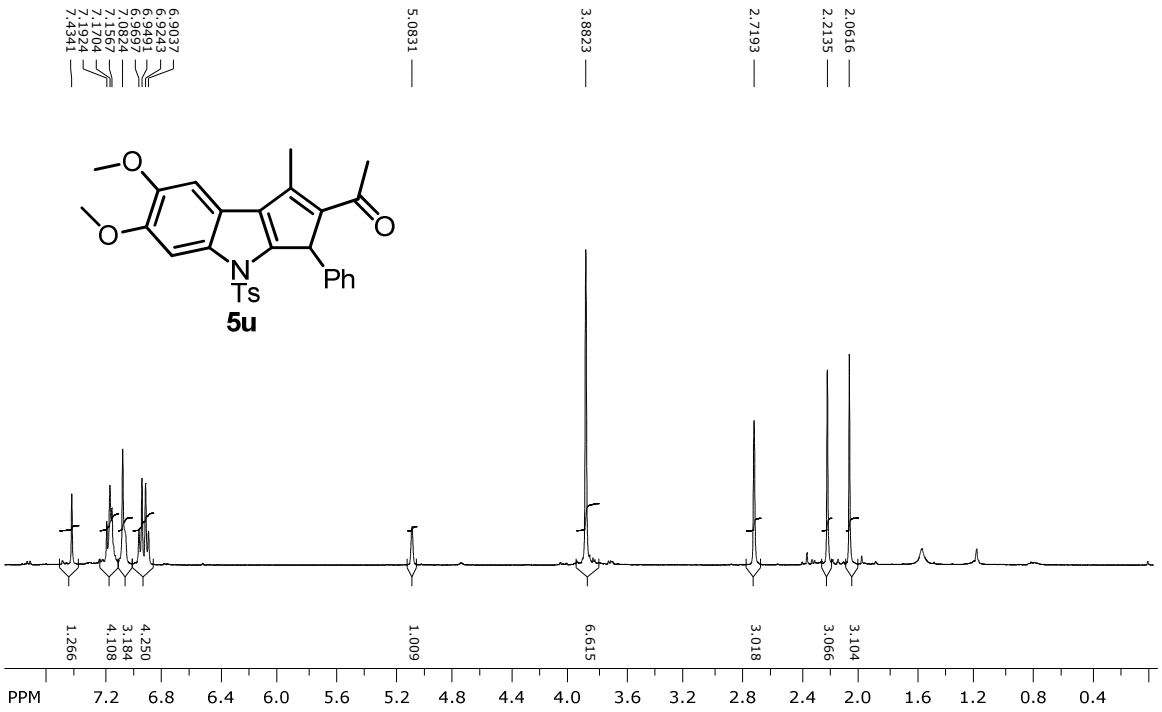


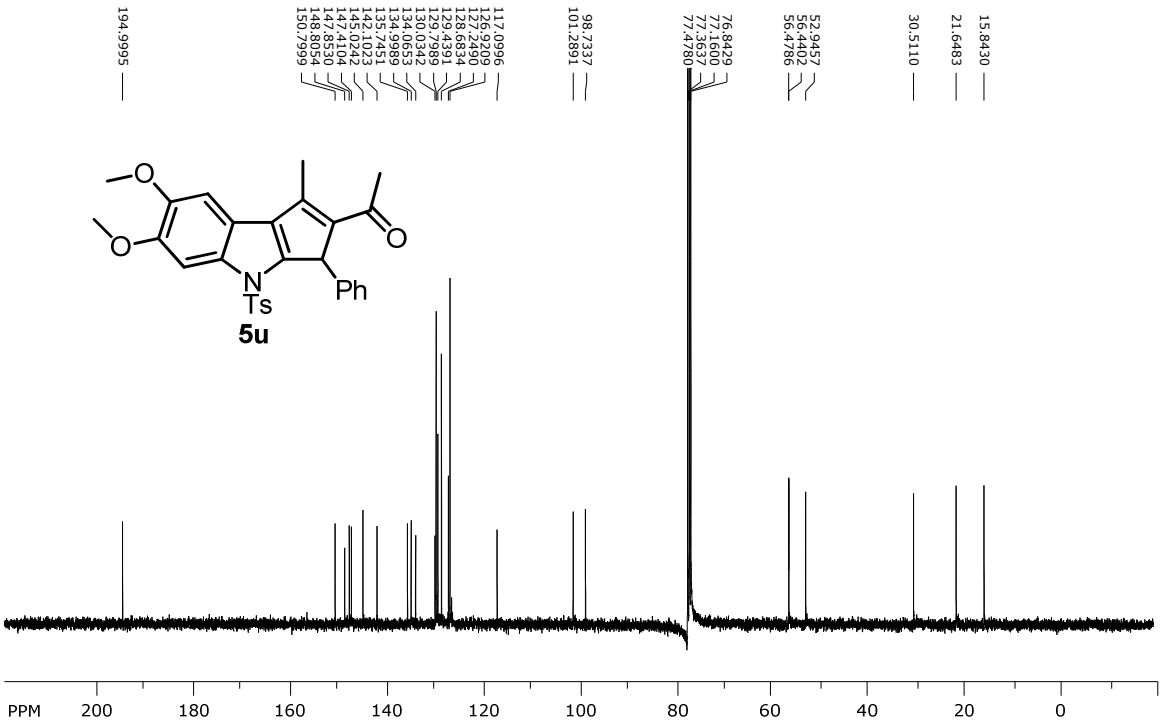
SpinWorks 3: SE 10 98 A 1

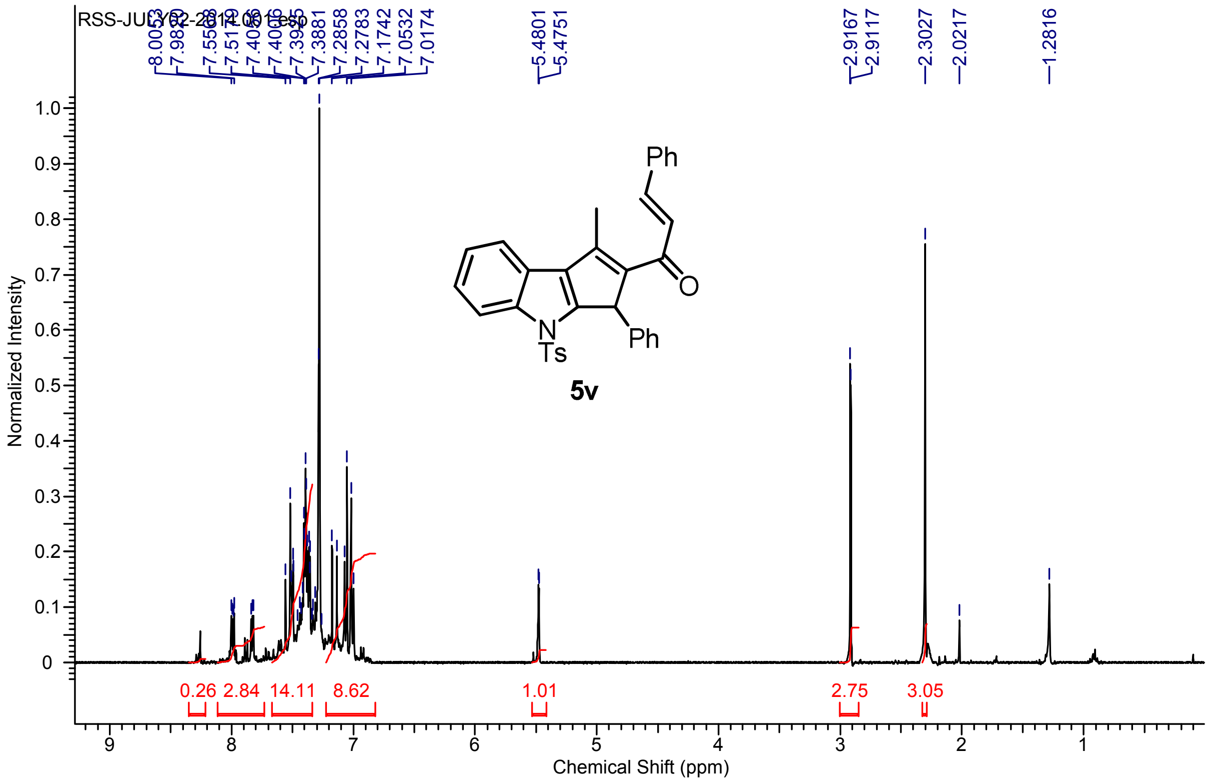


SpinWorks 3: SE-11-274



SpinWorks 3: SE 11 274

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7.3950
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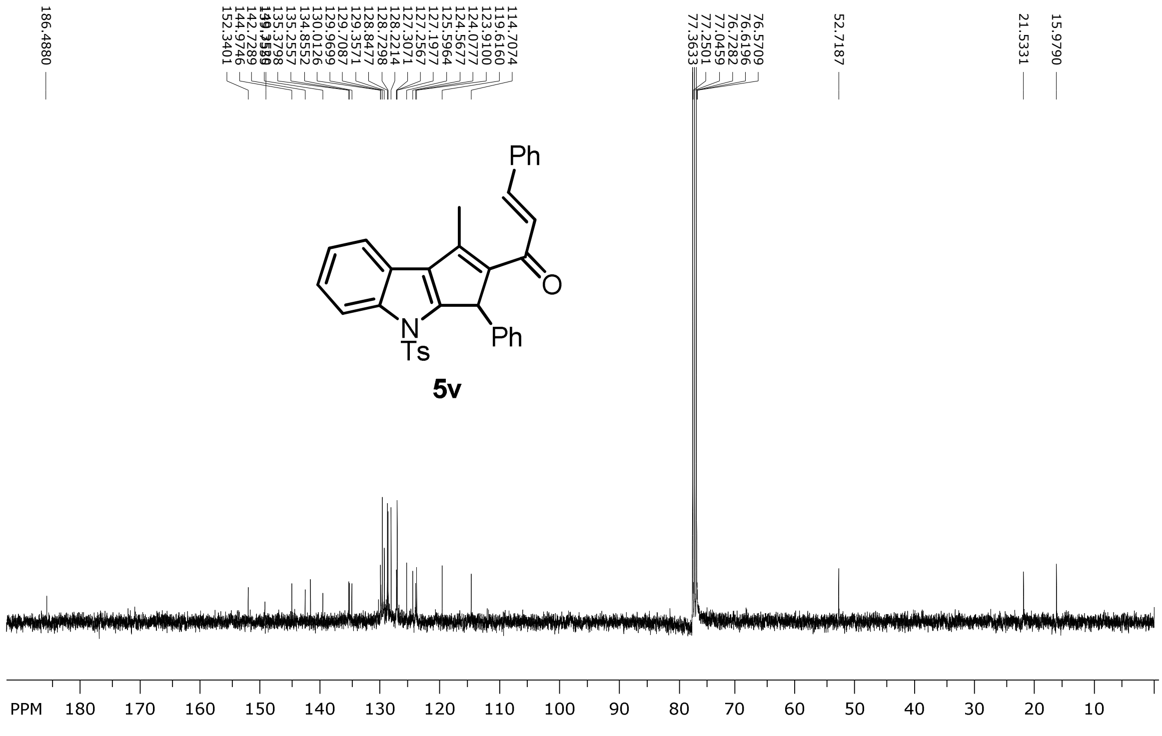
7.2783
7.1742
7.0532
7.0174
5.4801
5.4751
2.9167
2.9117
2.3027
2.0217
1.2816
Normalized Intensity
0.26
2.84
14.11
8.62
1.01
2.75
3.05
Chemical Shift (ppm)
Ph
O
N
Ts
Ph
5v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144.9746
142.7289
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135.3798
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129.7087
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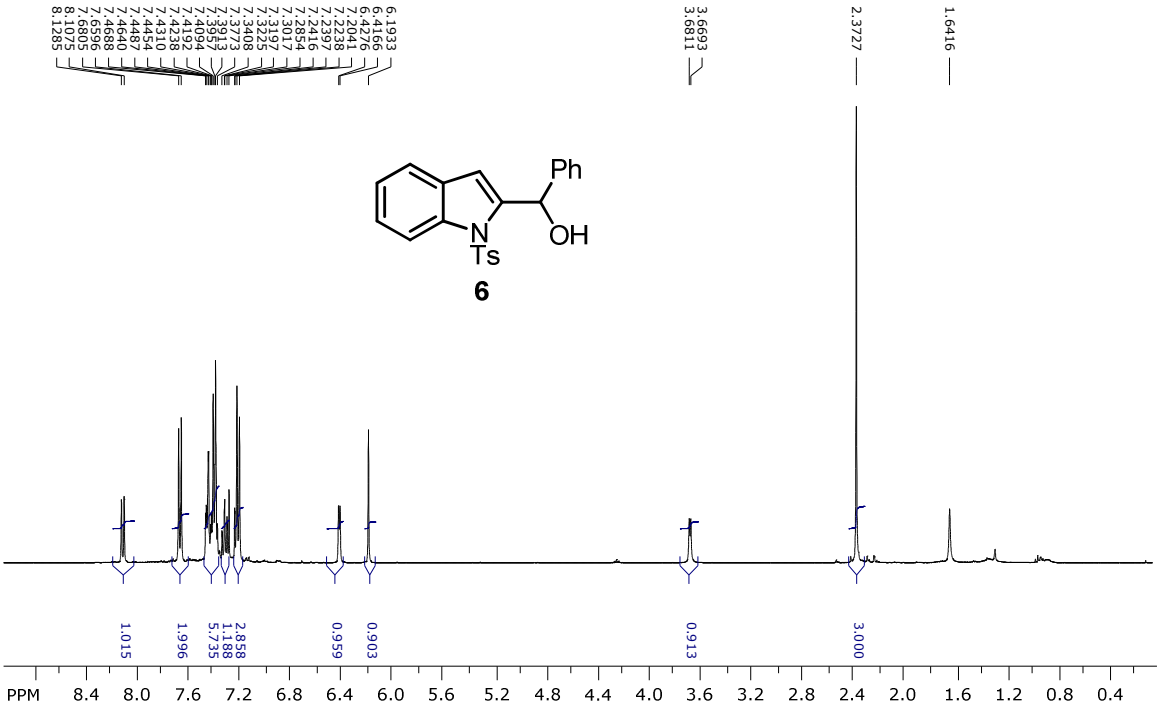
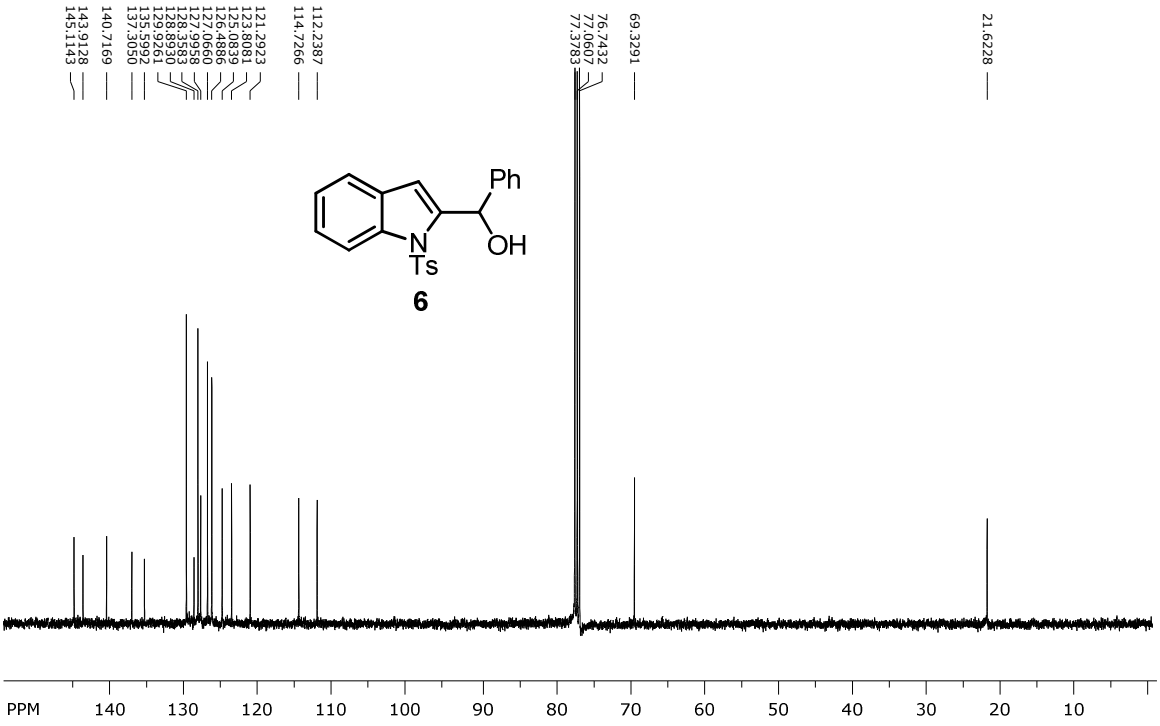
128.8477
128.7298
128.2214
127.3071
127.2567
125.5964
124.5677
124.0777
123.9100
119.6160
114.7074
77.3633
77.2501
77.0459
76.7282
76.6196
76.5709
52.7187
21.5331
15.9790
Ph
O
N
Ts
Ph
5v
PPM

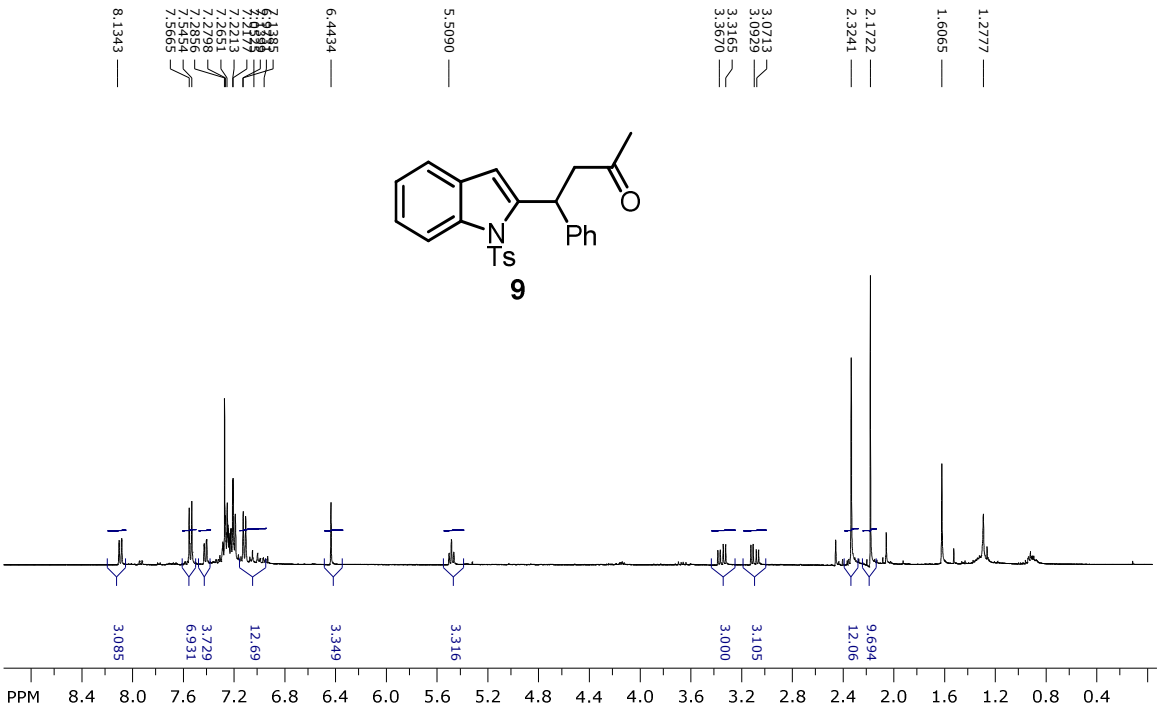
SpinWorks 3: se-11-1



SpinWorks 3: SE 11 1

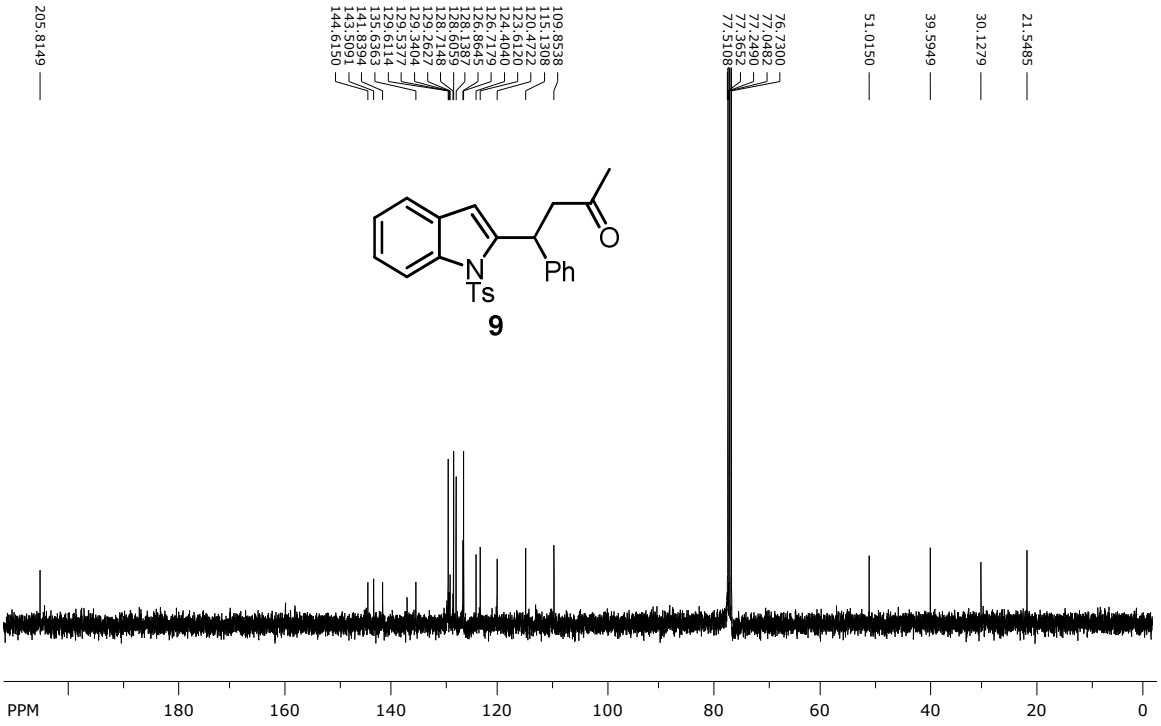


SpinWorks 3: SE 10 53 A



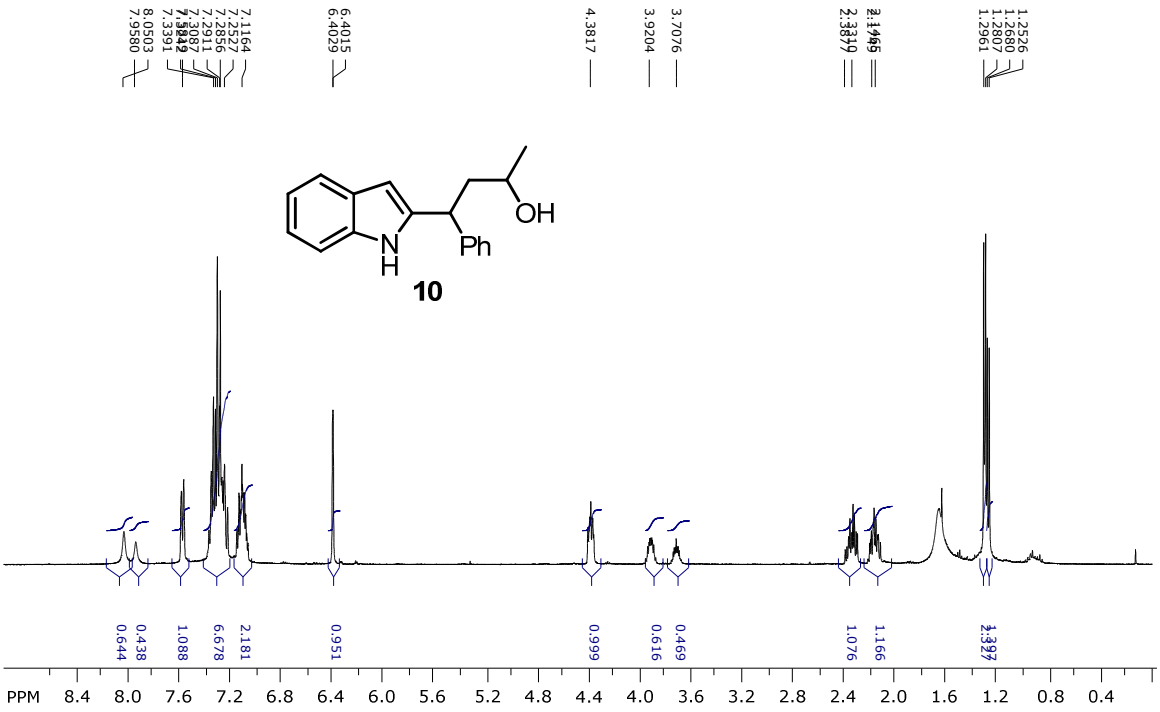
9

SpinWorks 3: SE 10 53 A

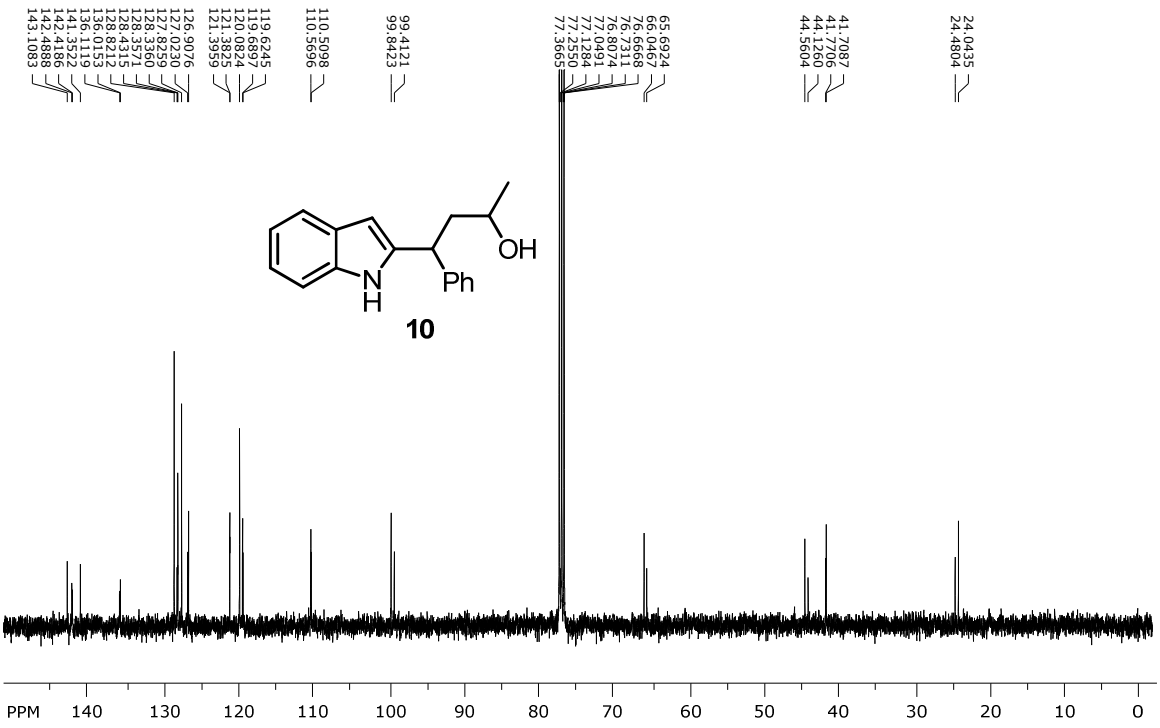


9

SpinWorks 3: se-10-89-a



SpinWorks 3: SE 11 223



SpinWorks 3: SE 11 223 2