Supporting Information

Palladium-Catalysed 5-*endo-trig* Allylic (Hetero)Arylation

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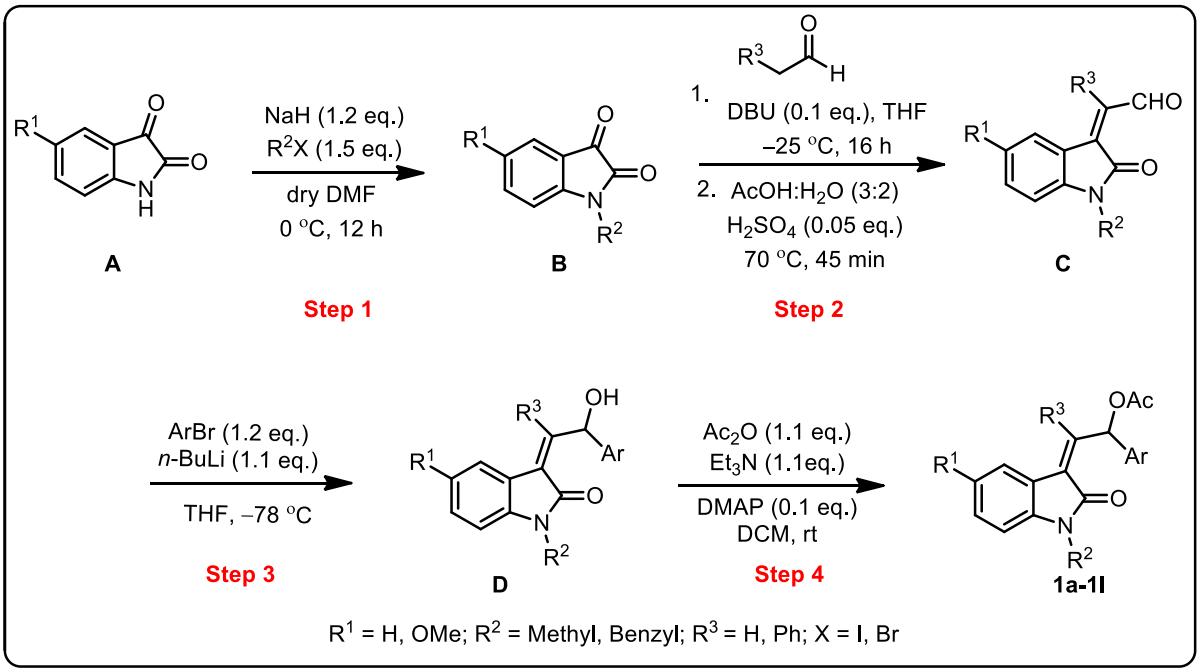
This version of the ESI published 05/08/2020 replaces the previous version published 30/04/2020. The structure of 2l on page 17 has been changed and the name has also been changed accordingly.

General experimental methods: All the starting compounds and catalysts employed in this study were procured from Sigma-Aldrich and were used without further purification. For thin layer chromatography (TLC), silica aluminium foils/TLC plates with fluorescent indicator 254 nm (from Aldrich/Merck) were used and compounds were visualised 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 using 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 utilised to describe peak patterns where appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet and m=multiplet. Proton chemical shifts are given in δ relative to tetramethylsilane (δ 0.00 ppm) in $CDCl_3$ (δ 0.00 ppm) or in $(CD_3)_2SO$ (δ 2.50 ppm) or in $(CD_3)_2CO$ (δ 2.05 ppm). Carbon chemical shifts are internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.1 ppm) or in $(CD_3)_2SO$ (δ 39.5 ppm) or in $(CD_3)_2CO$ at δ 29.9 and 206.7 ppm. Single crystal X-ray analysis was carried on a Rigaku XtaLAB mini diffractometer. High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer. Optical rotations were recorded on Rudolph APIII/2W.

General procedure-1: Synthesis of allylic acetates 1a-1l



Scheme S1: General schematic representation for the synthesis of allylic acetates **1a-1l**

A representative procedure for step-1:

To a solution of isatin **A** (2.94 g, 20.0 mmol) in anhydrous DMF (80 mL) at 0 °C, sodium hydride (60% dispersion in oil, 0.95 g, 24.0 mmol) was added in one portion and stirred for 5 min. Alkyl halide (1.87 mL, 30.0 mmol) was added and the reaction was stirred at 0 °C for 30 min. The reaction mixture was then poured into saturated aqueous ammonium chloride solution and extracted with EtOAc (4 × 30 mL). The combined organic layers were washed with water (3 × 15 mL) and brine (20 mL), then dried over $MgSO_4$, filtered, and concentrated to give crude N-alkyl-isatins **B**, which were used without further purification.

A representative procedure for step-2:

To a solution of N-protected isatin **B** (1.0 g, 4.22 mmol) in THF (8 mL), DBU (130 µL, 0.2 mmol) and propionaldehyde (0.906 µL, 30 mmol) were added, and the reaction mixture was kept at −25 °C for 15 h. After completion of the reaction, the mixture was kept at room temperature followed by the addition of 3:1 mixture of AcOH/H_2O (10 mL) and a few drops of conc. H_2SO_4. This mixture was then refluxed for 45 min. The reaction mixture was diluted with water, extracted with dichloromethane, and washed with brine. The organic layer was separated and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The

crude reaction mixture was purified by silica column chromatography using hexane–ethyl acetate mixture as eluent to obtain compounds **C1-C4** in 60-85% yield.

A representative procedure for step-3:

An oven dried 25 mL long neck round bottom flask was charged with aryl bromide (399 mg, 2.98 mmol), dry THF (5 mL) and kept at -78 ^{o}C. *n*-BuLi (1.6 *M* in hexane, 1.69 mL, 2.7 mmol), was added dropwise at same temperature and stirred for 2 h. Enal **C** (750 mg, 2.7 mmol) dissolved in dry THF (1 mL) was then added within 2 min and stirred at room temperature for 30 min. The reaction mixture was quenched with saturated aqueous ammonium chloride solution and extracted using ethyl acetate. The organic extracts were combined and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product **D** obtained was taken to next step without purification. The corresponding alcohols **D** were obtained in 50-73% yield.

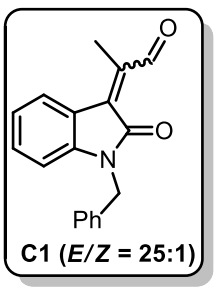
A representative procedure for step-4:

Alcohol **D** (450 mg, 1.09 mmol) was dissolved in dry DCM (6.0 mL) and triethylamine (0.19 mL, 1.3 mmol), acetic anhydride (0.130 mL, 1.3 mmol), DMAP (13 mg, 0.11 mmol) were added sequentially. Then the reaction mixture was stirred until starting material was consumed (as detected by TLC). Upon completion, the reaction mixture was quenched by adding saturated *aq*. NH_4Cl solution and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane–ethyl acetate mixture as eluent (90:10 v/v) to obtain compounds **1a-1l** in 70-90% yield.

Spectroscopic data of newly prepared enals C

2-(1-Benzyl-2-oxoindolin-3-ylidene)propanal (C1)

This compound was isolated as reddish orange solid by following the general procedure-**1,**



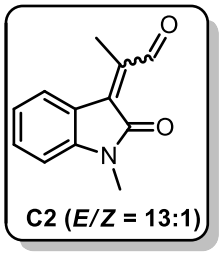
C1 (*E*/*Z* = 25:1)

M.P = 131-133 $^{\circ}$C. R_f = 0.5 (Hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 2937, 1689, 1662, 1601, 1467, 1465, 1344, 1245, 1177, 754. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.39 (s, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.30 (m, 4H), 7.30 – 7.23 (m, 2H), 7.05 (td, *J* = 7.7 and 0.9 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 4.93 (s, 2H), 2.34 (s, 3H). **^{13}C NMR**

(100 MHz, $CDCl_3$): δ 193.78, 167.01, 144.41, 144.06, 135.56, 135.00, 131.64, 128.97 (2C), 127.88, 127.34 (2C), 126.79, 122.85, 122.56, 109.54, 43.59, 12.88. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{16}NO_2$ $(M+H)^+$: 278.1181. Found: 278.1177.

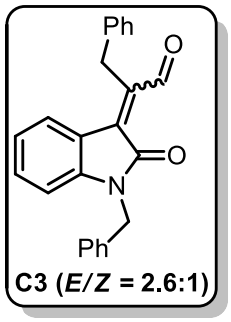
2-(1-Methyl-2-oxoindolin-3-ylidene)propanal (C2)

This compound was isolated as pale red solid by following the general procedure-**1**, M.P = 133-136 °C. R_f = 0.5 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 2937, 1694, 1668, 1602, 1471, 1375, 1241, 1009, 788. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.31 (s, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.38 (td, *J* = 7.8 and 0.9 Hz, 1H), 7.08 (td, *J* = 7.7 and 0.9 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 3.21 (s, 3H), 2.29 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.80, 166.88, 145.20, 143.64, 135.15, 131.69, 126.63, 122.77, 122.40, 108.56, 26.01, 12.70. **HRMS (ESI):** *m/z* calcd for $C_{12}H_{12}NO_2$ $(M+H)^+$: 202.0868. Found: 202.0860**.**



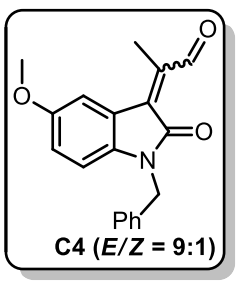
2-(1-Benzyl-2-oxoindolin-3-ylidene)-3-phenylpropanal (C3)

This compound was isolated as pale red solid by following the general procedure-**1**, M.P = 121-123 °C. R_f = 0.5 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3030, 1699, 1667, 1602, 1468, 1349, 1181, 1108, 746. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.43 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.35 – 7.27 (m, 5H), 7.22 – 7.11 (m, 5H), 6.88 (t, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 4.91 (s, 2H), 4.21 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.69, 167.21, 145.55, 144.65, 136.33, 135.38, 131.96, 128.87 (2C), 128.81 (2C), 128.09 (2C), 127.81, 127.32 (2C), 126.65, 126.44, 122.91, 121.35, 109.64, 109.54, 43.56, 31.96. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{20}NO_2$ $(M+H)^+$ 354.1494. Found: 354.1480.



2-(1-Benzyl-5-methoxy-2-oxoindolin-3-ylidene)propanal (C4)

This compound was isolated as blackish red solid by following the general procedure-**1**, M.P = 130-133 °C. R_f = 0.5 (Hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 2937, 1701, 1608, 1589, 1466, 1465, 1361, 1171, 1098, 750. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.39 (s, 1H), 7.36 – 7.26 (m, 5H), 7.24 (d, *J* = 2.4 Hz, 1H), 6.80 (dd, *J* = 8.6 and 2.4 Hz, 1H), 6.62 (d, *J* = 8.6 Hz, 1H), 4.91 (s, 2H), 3.78 (s, 3H), 2.32 (s, 3H). **^{13}C NMR**

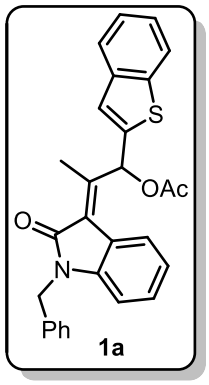


(100 MHz, $CDCl_3$): δ 193.83, 193.78, 166.86, 155.79, 144.23, 138.16, 135.64, 135.31, 128.96, 127.85, 127.33, 123.44, 115.60, 114.47, 110.00, 109.73, 56.05, 43.66, 12.79. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{18}NO_3$ $(M+H)^+$: 308.1287. Found: 308.1300**.**

Spectroscopic data of allylic acetates 1

(*E*)-1-(Benzo[*b*]thiophen-2-yl)-2-(1-benzyl-2-oxoindolin-3-ylidene)propyl acetate (1a)

This compound was prepared following the general procedure-**1** and isolated as pale yellow

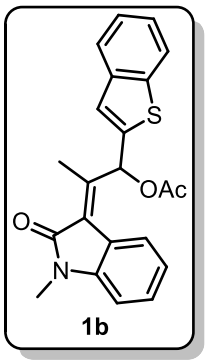


1a

oil. R_f = 0.3 (hexane/EtOAc = 9/1**). IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 2930, 1745, 1693, 1608, 1467, 1357, 1225, 1181, 1028. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.83 (d, *J* = 0.9 Hz, 1H), 7.77 (dd, *J* = 8.2 and 0.9 Hz, 1H), 7.71 (dd, *J* = 6.9 and 1.8 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.46 (s, 1H), 7.33 – 7.20 (m, 7H), 7.14 (td, *J* = 7.7 and 1.0 Hz, 1H), 6.98 (td, *J* = 7.7 and 1.0 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 5.02 (d, *J* = 15.7 Hz, 1H), 4.94 (d, *J* = 15.8 Hz, 1H), 2.43 (s, 3H), 2.20 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.54, 166.82, 149.98, 142.47, 141.35, 139.65, 139.39, 136.14, 129.06, 128.85 (2C), 127.60, 127.38 (2C), 124.71, 124.51, 124.44 (2C), 123.80, 123.06, 122.31, 122.25, 122.15, 109.05, 69.74, 43.53, 27.03, 16.11. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{20}NOS$ $(M\text{-}OAc)^+$: 394.1266. Found: 394.1241.

(*E*)-1-(Benzo[*b*]thiophen-2-yl)-2-(1-methyl-2-oxoindolin-3-ylidene)propyl acetate (1b)

This compound was prepared following the general procedure-**1** and isolated as pale yellow

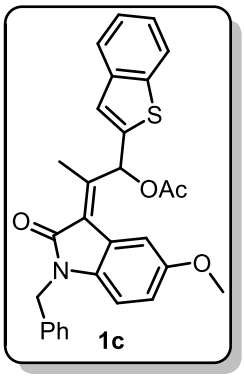


1b

oil. R_f = 0.3 (hexane/EtOAc = 8/2**). IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 2858, 1743, 1694, 1608, 1470, 1371, 1228. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.79 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.43 (s, 1H), 7.35 – 7.16 (m, 3H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 3.24 (s, 3H), 2.40 (s, 3H), 2.19 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.44, 166.72, 149.42, 143.28, 141.26, 139.56, 139.31, 129.07, 124.79, 124.42, 124.36, 124.33, 123.71, 122.82, 122.22, 122.13, 122.02, 107.96, 69.58, 25.94, 21.04, 15.91. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{16}NOS$ $(M\text{-}OAc)^+$: 318.0953. Found: 318.0944**.**

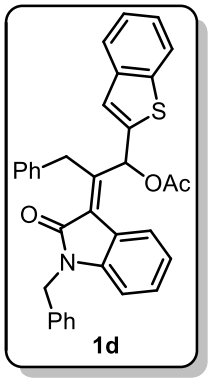
(*E*)-1-(Benzo[*b*]thiophen-2-yl)-2-(1-benzyl-5-methoxy-2-oxoindolin-3-ylidene)propyl acetate (1c)

This compound was prepared following the general procedure-**1** and isolated as pale reddish oil. R_f = 0.4 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2922, 2854, 1746, 1689, 1593, 1488, 1439, 1367, 1227, 1183. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.84 (d, *J* = 0.8 Hz, 1H), 7.81 – 7.76 (m, 1H), 7.72 (dd, *J* = 6.6 and 1. 6 Hz, 1H), 7.46 (s, 1H), 7.36 – 7.28 (m, 6H), 7.28 – 7.21 (m, 1H), 7.16 (d, *J* = 2.3 Hz, 1H), 6.70 (dd, *J* = 8.5 and 2.4 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 5.00 (d, *J* = 15.7 Hz, 1H), 4.93 (d, *J* = 15.7 Hz, 1H), 3.75 (s, 3H), 2.41 (s, 3H), 2.21 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.54, 166.71, 155.42, 150.30, 141.31, 139.66, 139.40, 136.36, 136.21, 128.85 (2C), 127.58, 127.38 (2C), 125.00, 124.51, 124.44, 124.05, 123.81, 122.31, 122.28, 112.79 (2C), 109.09, 69.70, 56.06, 43.61, 21.12, 16.02. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{22}NO_2S$ $(M\text{-}OAc)^+$: 424.1371. Found: 424.1361**.**



(*E*)-1-(Benzo[*b*]thiophen-2-yl)-2-(1-benzyl-2-oxoindolin-3-ylidene)-3-phenylpropyl acetate (1d)

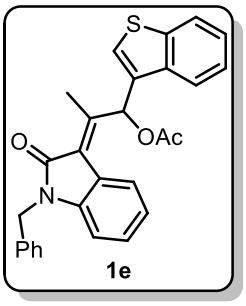
This compound was prepared following the general procedure-**1** and isolated as pale yellow oil. R_f = 0.4 (hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3062, 2925, 1749, 1694, 1608, 1467, 1362, 1223, 1184, 1028. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.97 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.44 (s, 1H), 7.41 – 7.24 (m, 10H), 7.24 – 7.13 (m, 4H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 5.08 (d, *J* = 15.7 Hz, 1H), 5.00 (d, *J* = 15.7 Hz, 1H), 4.31 (d, *J* = 15.3 Hz, 1H), 4.16 (d, *J* = 15.4 Hz, 1H), 1.49 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.63, 166.92, 150.26, 142.87, 141.64, 139.67, 139.46, 136.55, 136.09, 129.72, 128.94 (2C), 128.88 (2C), 128.28 (2C), 127.73, 127.58 (2C), 127.42, 126.60, 124.50, 124.46, 124.43, 123.76, 122.51, 122.34, 122.03, 122.01, 109.17, 69.69, 43.73, 35.97, 20.08. **HRMS (ESI):** *m/z* calcd for $C_{32}H_{24}NOS$ $(M\text{-}OAc)^+$: 470.1579. Found: 470.1559**.**



(*E*)-1-(Benzo[*b*]thiophen-3-yl)-2-(1-benzyl-2-oxoindolin-3-ylidene)propyl acetate (1e)

This compound was prepared following the general procedure-**1** and isolated as pale reddish oil. R_f = 0.3 (hexane/EtOAc = 8/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3062, 2930, 1745, 1694,

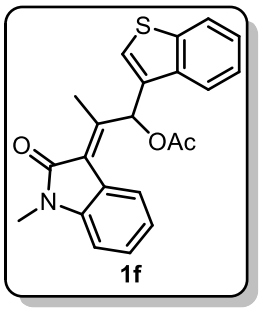
1608, 1467, 1356, 1228, 1181. **^{1}H NMR (400 MHz, DMSO):** δ 8.67 (s, 1H), 8.00 (d, *J* = 7.1 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 1H), 7.80 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.32-7.22 (m, 6H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 4.95 (s, 2H), 2.38 (s, 3H), 2.14 (s, 3H). **^{13}C NMR (100 MHz, DMSO):** δ 169.72, 166.01, 150.23, 141.65, 139.63, 137.30, 136.58, 132.77, 129.15 (2C), 128.68, 127.43, 127.19 (2C), 125.49, 124.77, 124.75, 124.53, 124.12, 123.12, 122.22, 122.14, 122.10, 109.06, 67.73, 42.34, 20.80, 16.86. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{20}NOS$ $(M\text{-}OAc)^+$: 394.1266. Found: 394.1250.



1e

(*E*)-1-(Benzo[*b*]thiophen-3-yl)-2-(1-methyl-2-oxoindolin-3-ylidene)propyl acetate (1f)

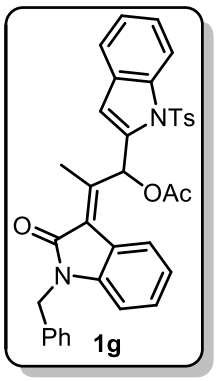
This compound was prepared following the general procedure-**1** and isolated as pale orange oil. R_f = 0.3 (hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 2932, 1745, 1694, 1633, 1608, 1470, 1374, 1226, 1136, 1013. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.89 (d, *J* = 0.8 Hz, 1H), 8.04 (dd, *J* = 7.0 and 1.1 Hz, 1H), 7.82 (dd, *J* = 7.3 and 1.4 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.43 (s, 1H), 7.40 – 7.32 (m, 2H), 7.32 – 7.23 (m, 1H), 7.02 (td, *J* = 7.7 and 0.9 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 3.25 (s, 3H), 2.38 (s, 3H), 2.16 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.75, 166.76, 149.03, 143.42, 140.36, 137.61, 133.40, 129.12, 125.45, 124.72, 124.65, 124.52, 124.10, 123.04, 122.93, 122.77, 122.03, 108.01, 68.69, 26.06, 21.16, 16.94. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{16}NOS$ $(M\text{-}OAc)^+$: 318.0953. Found: 318.0938.



1f

(*E*)-2-(1-Benzyl-2-oxoindolin-3-ylidene)-1-(1-tosyl-1*H*-indol-2-yl)propyl acetate (1g)

This compound was prepared following the general procedure-**1** and isolated as pale yellow solid. M.P = 180-182 °C. R_f = 0.4 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3062, 2926, 1746, 1698, 1608, 1467, 1367, 1229, 1175, 1090, 1020, **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.69 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.21 (m, 5H), 7.25 – 7.12 (m, 5H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.52 (s, 1H), 4.97 (d, *J* = 15.7 Hz, 1H), 4.90 (d, *J* = 15.7 Hz, 1H), 2.45 (s, 3H), 2.27 (s, 3H), 2.19 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.12, 166.29, 148.87, 144.77, 142.80, 137.99, 137.27,

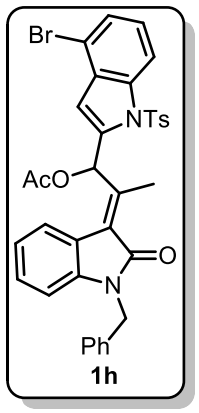


1g

136.34, 135.40, 129.69 (2C), 129.10, 128.83 (3C), 127.89 (2C), 127.58, 127.49 (2C), 126.01, 125.05, 124.68, 123.60, 123.05, 122.08, 121.11, 114.95, 111.16, 109.05, 69.24, 43.52, 21.70, 21.06, 17.81. **HRMS (ESI):** *m/z* calcd for $C_{33}H_{27}N_2O_3S$ $(M\text{-}OAc)^+$: 531.1742. Found: 531.1743.

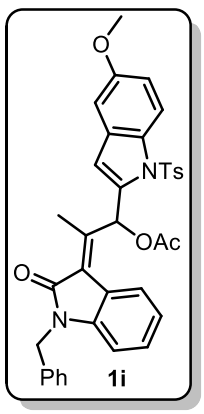
(*E*)-2-(1-Benzyl-2-oxoindolin-3-ylidene)-1-(4-bromo-1-tosyl-1*H*-indol-2-yl)propyl acetate (1h)

This compound was prepared following the general procedure-**1** and isolated as pale yellow semi solid. R_f = 0.4 (hexane/EtOAc = 8/2**). IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 2923, 1747, 1694, 1608, 1467, 1376, 1245, 1171, 1090. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.67 (s, 1H), 8.13 (d, *J* = 7.7 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.27 (m, 5H), 7.29 – 7.17 (m, 4H), 7.12 (t, *J* = 8.1 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.54 (s, 1H), 5.00 (d, *J* = 15.8 Hz, 1H), 4.90 (d, *J* = 15.8 Hz, 1H), 2.47 (s, 3H), 2.30 (s, 3H), 2.20 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.03, 166.31, 148.29, 145.19, 142.83, 138.84, 137.39, 136.24, 135.16, 129.82 (2C), 129.43, 129.19, 128.85 (2C), 127.94 (2C), 127.59, 127.44 (2C), 126.54, 126.24, 125.90, 124.76, 122.98, 122.14, 114.85, 113.93, 110.45, 109.13, 69.04, 43.54, 21.72, 21.02, 17.81. **HRMS (ESI):** *m/z* calcd for $C_{33}H_{26}BrN_2O_3S$ $(M\text{-}OAc)^+$: 609.0848 Found: 609.0837.



(*E*)-2-(1-Benzyl-2-oxoindolin-3-ylidene)-1-(5-methoxy-1-tosyl-1*H*-indol-2-yl)propyl acetate (1i)

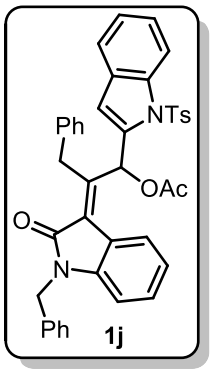
This compound was prepared following the general procedure-**1** and isolated as pale yellow oil. R_f = 0.3 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1746, 1694, 1609, 1467, 1367, 1216, 1163, 1090, 1029. **^{1}H NMR (400 MHz, DMSO):** δ 8.46 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.21 (m, 7H), 7.26 – 7.15 (m, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.99- 6.95 (m, 2H), 6.88 (dd, *J* = 9.2 and 2.2 Hz, 1H), 6.71 (s, 1H), 4.97 (d, *J* = 15.8 Hz, 1H), 4.90 (d, *J* = 15.8 Hz, 1H), 3.65 (s, 3H), 2.42 (s, 3H), 2.25 (s, 3H), 2.08 (s, 3H). **^{13}C NMR (100 MHz, DMSO):** δ 169.36, 165.60, 156.07, 149.92, 145.11, 141.92, 137.99, 136.65, 134.73, 130.79, 129.85



(2C), 129.40, 129.20, 128.65 (2C), 127.44, 127.31 (2C), 127.02 (2C), 124.82, 124.70, 122.24, 122.01, 115.11, 114.08, 111.95, 109.13, 103.79, 68.30, 55.26, 42.42, 21.01, 20.58, 17.40. **HRMS (ESI):** *m/z* calcd for $C_{36}H_{32}N_2O_6S$ $(M+Na)^+$: 643.1897. Found: 643.1890.

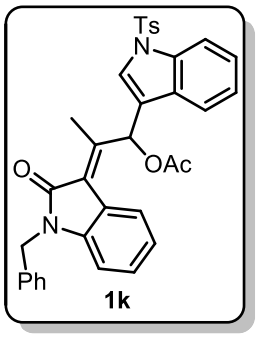
(*E*)-2-(1-Benzyl-2-oxoindolin-3-ylidene)-3-phenyl-1-(1-tosyl-1*H*-indol-2-yl)propyl acetate (1j)

This compound was prepared following the general procedure-**1** and isolated as pale yellow solid. M.P = 182-184 °C. R_f = 0.4 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 1750, 1698, 1607, 1467, 1367, 1224, 1175, 1090, 1021. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.89 (s, 1H), 8.09 (d, *J* = 7.9 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.24 (m, 7H), 7.26 – 7.12 (m, 9H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.54 (s, 1H), 4.97 (s, 2H), 4.44 (d, *J* = 15.0 Hz, 1H), 4.18 (d, *J* = 15.0 Hz, 1H), 2.27 (s, 3H), 1.56 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.82, 166.33, 149.21, 144.71, 143.14, 138.12, 137.26, 136.26, 135.65, 135.35, 129.75, 129.66 (2C), 128.89 (2C), 128.82, 128.69 (2C), 128.56 (2C), 127.84 (2C), 127.68, 127.64 (3C), 126.53, 124.99, 124.51, 123.55, 122.42, 122.05, 121.00, 114.94, 111.57, 109.13, 68.48, 43.72, 38.03, 21.68, 20.27. **HRMS (ESI):** *m/z* calcd for $C_{39}H_{31}N_2O_3S$ $(M-OAc)^+$: 607.2055. Found: 607.2074.



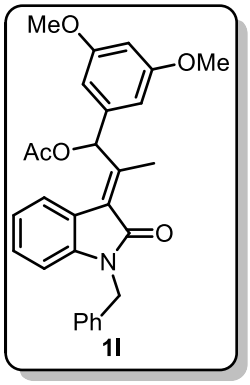
(*E*)-2-(1-Benzyl-2-oxoindolin-3-ylidene)-1-(1-tosyl-1*H*-indol-3-yl)propyl acetate (1k)

This compound was prepared following the general procedure-**1** and isolated as pale yellow oil. R_f = 0.4 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1746, 1697, 1608, 1467, 1366, 1228, 1175, 1090, 1020. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.68 (s, 1H), 8.12 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.23 (m, 6H), 7.28 – 7.14 (m, 4H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.51 (s, 1H), 4.98 (d, *J* = 15.8 Hz, 1H), 4.91 (d, *J* = 15.8 Hz, 1H), 2.45 (s, 3H), 2.29 (s, 3H), 2.19 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.10, 166.30, 148.88, 144.76, 142.83, 138.04, 137.30, 136.36, 135.46, 129.69 (2C), 129.10, 128.84 (3C), 127.89 (2C), 127.58, 127.50 (2C), 126.03, 125.05, 124.69, 123.60, 123.07, 122.08, 121.11, 114.96, 111.15, 109.06, 69.27, 43.54, 21.69, 21.05, 17.81. **HRMS (ESI):** *m/z* calcd for $C_{32}H_{27}N_2O_3S$ $(M-OAc)^+$: 531.1742. Found: 531.1734.



(*E*)-2-(1-Benzyl-2-oxoindolin-3-ylidene)-1-(3,5-dimethoxyphenyl)propyl acetate (1l)

This compound was prepared following the general procedure-**1** and isolated as pale yellow solid. M.P = 134-137 °C. R_f = 0.4 (hexane/EtOAc = 7/3**)**. **IR (thin film, neat):** ν_{max}/cm^{-1} 2934, 2840, 1744, 1694, 1608, 1467, 1429, 1351, 1230, 1157, 1028. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.62 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.21 (m, 5H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.78 – 6.69 (m, 3H), 6.38 (s, 1H), 5.03 (d, *J* = 15.7 Hz, 1H), 4.95 (d, *J* = 15.7 Hz, 1H), 3.75 (s, 6H), 2.28 (s, 3H), 2.19 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.62, 167.05, 160.89 (2C), 151.28, 142.23, 140.85, 136.30, 128.82, 128.78 (2C), 127.55, 127.36 (3C), 124.48, 123.31, 122.04, 108.83, 104.27 (2C), 99.62, 71.44, 55.40 (2C), 43.44, 21.19, 15.98. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{27}NNaO_5$ $(M+Na)^+$: 480.1787. Found: 480.1802.



1l

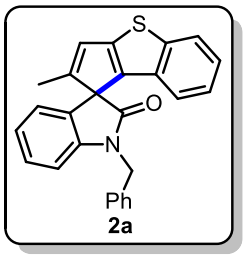
General procedure-2: Synthesis of spirocyclic compounds (2a-2l)

An oven dried 5 mL glass vial was charged with **1a-1l** (0.1 mmol) and 1,2-DCE (1.0 mL) and $PdCl_2$ (0.01 mmol) were introduced. The reaction mixture was stirred at 60 ^oC until **1** disappeared as monitored by TLC. Then the reaction was quenched with water and extracted with EtOAc. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as eluent (9:1 to 4:1) to afford **2a-2l**.

Spectroscopic data of spiroxindoles 2

1'-Benzyl-2-methylspiro[benzo[*b*]cyclopenta[*d*]thiophene-1,3'-indolin]-2'-one (2a)

This compound was isolated as pale brown solid. Following the general procedure-**2**, 30 mg

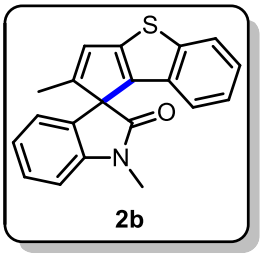


2a

of **1a** afforded 21 mg of **2a** (82% yield). M.P = 168-170 $^{\circ}C$. R_f = 0.4 (Hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2923, 2853, 1694, 1662, 1618, 1599, 1481, 1362, 1289, 1234, 1089, **^{1}H NMR (400 MHz, DMSO):** δ 7.94 (d, *J* = 8 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 5.09 (d, *J* = 15.3 Hz, 1H), 5.03 (d, *J* = 15.3 Hz, 1H), 1.71 (s, 3H). **^{13}C NMR (100 MHz, DMSO):** δ 172.63, 150.25, 146.94, 143.83, 142.55, 140.43, 136.49, 132.32, 129.05 (3C), 128.75 (3C), 127.78, 126.14, 125.80, 124.83, 124.24, 123.16, 123.00, 118.69, 110.12, 64.61, 43.56, 13.34. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{19}NNaOS$ $(M+Na)^+$: 416.1085. Found: 416.1079.

1',2-Dimethylspiro[benzo[*b*]cyclopenta[*d*]thiophene-1,3'-indolin]-2'-one (2b)

This compound was isolated as a pale brown oil. Following the general procedure-**2**, 30 mg



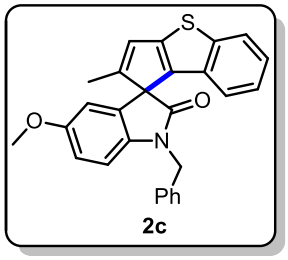
2b

of **1b** afforded 18 mg of **2b** (73% yield). R_f = 0.4 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1716, 1609, 1492, 1468, 1371, 1342, 1259, 1084. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.81 – 7.74 (m, 1H), 7.36 (td, *J* = 7.8, 1.1 Hz, 1H), 7.16 – 7.06 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.98 (dd, *J* = 11.0 and 4.0 Hz, 1H), 6.81 (dd, *J* = 6.6 and 2.3 Hz, 1H), 6.77 – 6.72 (m, 2H), 3.41 (s, 3H), 1.80 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 173.68, 150.45, 147.19, 145.04, 143.47, 140.52, 132.99, 128.98, 126.98,

125.65, 124.73, 123.87, 123.64, 123.37, 122.86, 119.28, 108.64, 65.15, 27.21, 13.74. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{16}NOS$ $(M+H)^+$: 318.0953. Found: 318.0941.

1'-Benzyl-5'-methoxy-2-methylspiro[benzo[*b*]cyclopenta[*d*]thiophene-1,3'-indolin]-2'-one (2c)

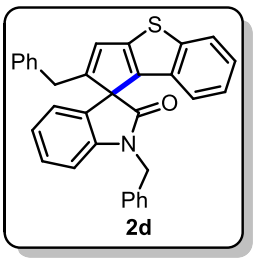
This compound was isolated as reddish brown solid. Following the general procedure-**2**, 25 mg of **1c** afforded 17 mg of **2c** (77% yield). M.P = 170-173 °C. R_f = 0.5 (Hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2923, 2854, 1712, 1600, 1493, 1439, 1337, 1174. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 6.7 Hz, 2H), 7.37-7.31(m, 3H), 7.17 – 7.10 (m, 1H), 7.08 – 7.03 (m, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.79 – 6.72 (m, 3H), 6.34 (d, *J* = 2.5 Hz, 1H), 5.13 (d, *J* = 15.3 Hz, 1H), 4.95 (d, *J* = 15.3 Hz, 1H), 3.61 (s, 3H), 1.85 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 173.46, 156.42, 150.53, 147.22, 143.50, 141.00, 140.80, 137.46, 136.17, 133.05, 128.97(2C), 128.36, 128.03 (2C), 125.76, 124.67, 123.87, 122.90, 119.64, 113.67, 110.38, 110.14, 65.56, 55.75, 44.79, 13.90. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{22}NO_2S$ $(M+H)^+$: 424.1371. Found: 424.1357.



2c

1',2-Dibenzylspiro[benzo[*b*]cyclopenta[*d*]thiophene-1,3'-indolin]-2'-one (2d)

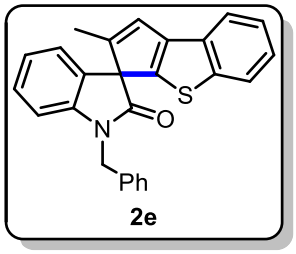
This compound was isolated as pale yellow oil. Following the general procedure-**2**, 35 mg of **1d** afforded 24 mg of **2d** (78% yield). R_f = 0.6 (Hexane/EtOAc = 8/2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.33 (dd, *J* = 14.8 and 7.1 Hz, 3H), 7.29 – 7.17 (m, 4H), 7.13-7.07 (m, 3H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.72 (t, *J* = 8.3 Hz, 2H), 6.52 (s, 1H), 5.11 (d, *J* = 15.3 Hz, 1H), 4.82 (d, *J* = 15.3 Hz, 1H), 3.48 (d, *J* = 16.9 Hz, 1H), 3.33 (d, *J* = 16.9 Hz, 1H). **^{13}C NMR (100 MHZ, $CDCl_3$):** δ 173.44, 154.32, 146.91, 144.12, 143.56, 140.99, 137.75, 136.08, 132.89, 129.51 (2C), 128.98 (2C), 128.93, 128.47(2C), 128.08 (3C), 126.87, 126.65, 126.44, 124.67, 123.91, 123.87, 123.35, 122.99, 119.68, 109.68, 64.80, 44.68, 35.09. **HRMS (ESI):** *m/z* calcd for $C_{32}H_{24}NOS$ $(M+H)^+$: 470.1579. Found: 470.1560.



2d

1'-Benzyl-2-methylspiro[benzo[*b*]cyclopenta[*d*]thiophene-3,3'-indolin]-2'-one (2e)

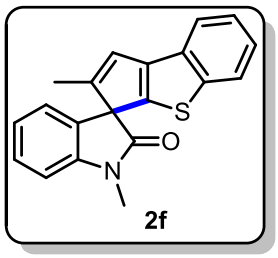
This compound was isolated as pale brown oil. Following the general procedure-**2**, 30 mg of **1e** afforded 20 mg of **2e** (73% yield). R_f = 0.5 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3058, 2933, 1716, 1609, 1486, 1465, 1428, 1341, 1191, 1079. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.34 (m, 5H), 7.33 – 7.17 (m, 3H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.91 (s, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 7.4 Hz, 1H), 5.09 (d, *J* = 15.6 Hz, 1H), 4.98 (d, *J* = 15.6 Hz, 1H), 1.81 (s, 3H). **^{13}C NMR (100 MHZ, $CDCl_3$):** δ 173.91, 149.33, 145.88, 145.13, 143.99, 143.08, 135.86, 132.25, 129.07, 129.01 (2C), 127.92, 127.87, 127.48 (2C), 124.89, 124.63, 124.08, 123.85, 123.71, 123.40, 122.08, 109.84, 66.08, 44.55, 14.03. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{19}NNaOS$ $(M+Na)^+$ 416.1085. Found: 416.1094.



2e

1',2-Dimethylspiro[benzo[*b*]cyclopenta[*d*]thiophene-3,3'-indolin]-2'-one (2f)

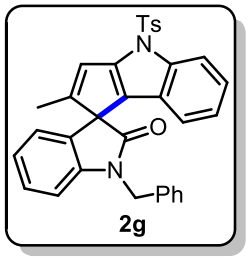
This compound was isolated as pale reddish oil. Following the general procedure-**2**, 25 mg of **1f** afforded 17 mg of **2f** (83% yield). R_f = 0.4 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2958, 1716, 1608, 1490, 1469, 1340, 1245, 1124, 1086, 1017. **^{1}H NMR (400 MHz, DMSO)**: δ 7.96 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.30 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.00-6.97 (m, 2H), 6.72 (d, *J* = 7.4 Hz, 1H), 3.25 (s, 3H), 1.62 (s, 3H). **^{13}C NMR (100 MHz, DMSO):** δ 172.37, 149.27, 145.63, 144.72, 144.04, 142.44, 131.61, 129.29, 126.87, 124.89, 124.39, 124.30, 124.00, 123.13, 122.86, 122.08, 109.51, 65.67, 26.91, 13.31. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{15}NNaOS$ $(M+Na)^+$: 340.0772. Found: 340.0780.



2f

1'-Benzyl-2-methyl-4-tosyl-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indolin]-2'-one (2g)

This compound was isolated as pale yellow solid. Following the general procedure-**2**, 25 mg of **1g** afforded 18 mg of **2g** (83% yield). M.P = 187-190 °C. R_f = 0.5 (Hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3060, 2925, 1716, 1609, 1486, 440, 1372, 1216, 1175. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.28 (m, 3H), 7.22 (dd, *J* = 17.6 and 7.5 Hz, 3H), 7.15 – 7.08 (m, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 2H), 6.65 (d, *J* = 7.1 Hz, 2H), 5.09 (d, *J* = 15.4 Hz, 1H), 4.96 (d, *J* = 15.4 Hz, 1H), 2.33 (s, 3H), 1.84 (s, 3H). **^{13}C**

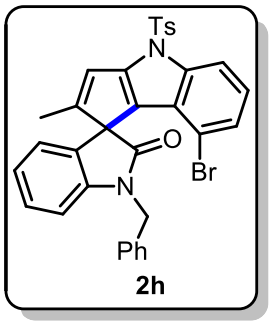


2g

NMR (100 MHz, $CDCl_3$): δ 173.68, 151.98, 147.86, 145.18, 144.07, 138.79, 136.02, 135.18, 130.09 (2C), 128.98 (2C), 128.90, 128.01, 127.70 (3C), 126.97 (2C), 126.64, 125.31, 123.89, 123.55, 123.29, 123.01, 122.67, 117.47, 114.75, 109.70, 62.51, 44.58, 21.73, 14.12. **HRMS (ESI):** *m/z* calcd for $C_{33}H_{26}N_2NaO_3S$ $(M+Na)^+$: 553.1562. Found: 553.1557.

1'-Benzyl-8-bromo-2-methyl-4-tosyl-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indolin]-2'-one (2h)

This compound was isolated as pale brown oil. Following the general procedure-**2**, 40 mg of

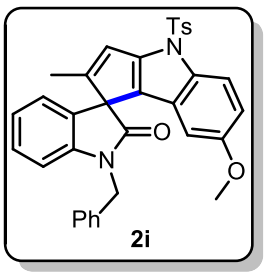


2h

1h afforded 28 mg of **2h** (77% yield). R_f = 0.5 (Hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2930, 1716, 1610, 1487, 1466, 1360, 1171, 1089. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.99 – 7.87 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.39 – 7.30 (m, 3H), 7.28-7.25 (m, 2H), 7.22 (td, *J* = 7.8 and 1.2 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.07 (d, *J* = 1.7 Hz, 1H), 6.99 – 6.86 (m, 3H), 6.62 (d, *J* = 6.8 Hz, 1H), 5.22 (d, *J* = 15.3 Hz, 1H), 4.75 (d, *J* = 15.3 Hz, 1H), 2.35 (s, 3H), 1.78 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 173.82, 153.77, 149.75, 145.61, 144.96, 139.02, 135.94, 134.85, 130.23, 128.91 (2C), 128.88, 128.16 (2C), 127.97 (2C), 127.20, 127.13, 127.04, 127.00 (2C), 124.61, 123.74, 123.16, 123.09, 121.06, 113.49, 111.88, 109.58, 63.03, 45.05, 21.77, 14.01. **HRMS (ESI):** *m/z* calcd for $C_{33}H_{26}BrN_2O_3S$ $(M+H)^+$: 609.0848. Found: 609.0837.

1'-Benzyl-7-methoxy-2-methyl-4-tosyl-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indolin]-2'-one (2i)

This compound was isolated as pale yellow oil. Following the general procedure-**2**, 35 mg of



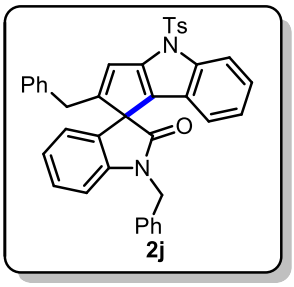
2i

1i afforded 26 mg of **2i** (83% yield). R_f = 0.4 (Hexane/EtOAc = 7/3)**.** **IR (thin film, neat):** ν_{max}/cm^{-1} 2933, 1716, 1609, 1486, 1455, 1434, 1274, 1171, 1088, 1034. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (d, *J* = 9.1 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 7.4 Hz, 2H), 7.36 – 7.27 (m, 3H), 7.21 (dd, *J* = 14.3 and 8.0 Hz, 3H), 7.09 (s, 1H), 6.90 (dd, *J* = 7.6 and 4.8 Hz, 2H), 6.71 (dd, *J* = 9.0 and 2.3 Hz, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 6.11 (d, *J* = 2.2 Hz, 1H), 5.11 (d, *J* = 15.4 Hz, 1H), 4.94 (d, *J* = 15.4 Hz, 1H), 3.56 (s, 3H), 2.32 (s, 3H), 1.82 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 173.61, 156.82, 152.12, 148.79, 145.08, 144.00, 136.02, 134.98, 133.48, 130.01 (2C), 128.96 (2C), 128.90,

127.97, 127.61(2C), 126.88 (2C), 126.55, 126.44, 126.34, 123.46, 123.30, 122.60, 115.51, 110.86, 109.68, 100.89, 62.40, 55.57, 44.53, 21.70, 14.08. **HRMS (ESI):** *m/z* calcd for $C_{34}H_{28}N_2NaO_4S$ $(M+Na)^+$: 583.1667. Found: 583.1680.

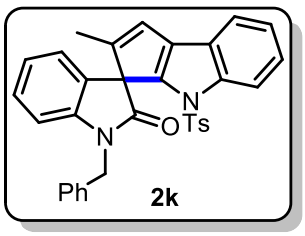
1',2-Dibenzyl-4-tosyl-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indolin]-2'-one (2j)

This compound was isolated as pale yellow oil. Following the general procedure-**2**, 35 mg of **1j** afforded 26 mg of **2j** (83% yield). R_f = 0.6 (Hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2919, 2854, 1713, 1609, 1485, 1465, 1342, 1173. **^{1}H NMR (400 MHz, DMSO):** δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.45 – 7.25 (m, 6H), 7.29 – 7.18 (m, 4H), 7.24 – 7.07 (m, 3H), 6.99-6.93 (m, 3H), 6.89 (s, 1H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 4.92 (d, *J* = 15.5 Hz, 1H), 4.83 (d, *J* = 15.5 Hz, 1H), 3.37 (d, *J* = 16.8 Hz, 1H), 3.29 (d, *J* = 16.7 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR (100 MHz, DMSO):** δ 172.01, 155.93, 146.80, 145.89, 143.80, 137.87, 137.30, 136.44, 133.75, 130.43 (2C), 129.08, 128.95 (2C), 128.73 (2C), 128.29 (2C), 127.73, 127.57, (2C) 126.79, 126.65 (2C), 126.51, 125.31, 124.43, 124.24, 123.42, 123.13, 123.01, 122.27, 117.03, 114.50, 110.03, 61.69, 43.51, 34.67, 21.08. **HRMS (ESI):** *m/z* calcd for $C_{39}H_{31}N_2O_3S$ $(M+H)^+$: 607.2055. Found: 607.2031.

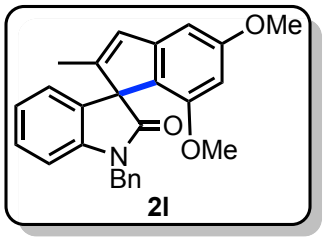


1'-Benzyl-2-methyl-4-tosyl-4*H*-spiro[cyclopenta[*b*]indole-3,3'-indolin]-2'-one (2k)

This compound was isolated as pale yellow oil. Following the general procedure-**2**, 10 mg of **1k** afforded 7.1 mg of **2k** (79% yield). R_f = 0.4 (Hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2922, 2847, 1715, 1610, 1466, 1372, 1175, 1089. **^{1}H NMR (400 MHz, DMSO):** δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.28 (m, 4H), 7.31 – 7.18 (m, 4H), 7.11 (dd, *J* = 8.1 and 6.4 Hz, 3H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 5.09 (d, *J* = 15.4 Hz, 1H), 4.97 (d, *J* = 15.4 Hz, 1H), 2.35 (s, 3H), 1.84 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (100 MHz, DMSO):** δ 172.8, 152.7, 147.6, 146.3, 144.2, 138.2, 136.9, 134.3, 130.9 (2C), 129.5, 129.2 (2C), 128.2, 127.9 (2C), 127.1 (2C), 126.6, 126.0, 124.9, 124.6, 123.6, 123.5, 123.2, 122.3, 117.3, 114.9, 110.6, 62.3, 43.9, 21.5, 14.0. **HRMS (ESI):** *m/z* calcd for $C_{33}H_{26}N_2NaO_3S$ $(M+Na)^+$: 553.1562. Found: 553.1583.



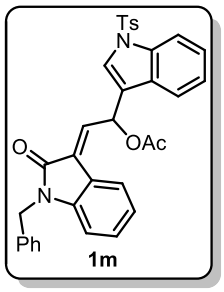
1'-Benzyl-5,7-dimethoxy-2-methylspiro[indene-1,3'-indolin]-2'-one (2l)



This compound was isolated as pale orange solid. Following the general procedure-**2**, 30 mg of **1l** afforded 23 mg of **2l** (89% yield). M.P = 135-137 °C. R_f = 0.5 (Hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 2937, 1713, 1604, 1589, 1486, 1465, 1346, 1228, 1171, 1088. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 1.1 Hz, 1H), 6.54 (d, *J* = 1.6 Hz, 1H), 6.19 (d, *J* = 1.5 Hz, 1H), 5.29 (d, *J* = 15.7 Hz, 1H), 4.80 (d, *J* = 15.7 Hz, 1H), 3.82 (s, 3H), 3.47 (s, 3H), 1.68 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 175.24, 161.98, 154.95, 148.45, 148.22, 144.38, 136.23, 130.12, 128.72 (2C), 128.29, 128.02, 127.57, 127.52 (2C), 124.18, 122.74, 122.66, 109.19, 98.83, 95.94, 65.69, 55.72, 55.27, 44.24, 13.13. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}NaO_3S$ $(M+Na)^+$ 420.1576. Found: 420.1550.

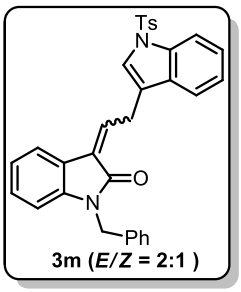
2-(1-Benzyl-2-oxoindolin-3-ylidene)-1-(1-tosyl-1*H*-indol-3-yl)ethyl acetate (1m)

This compound was isolated as white semi solid by following the general procedure-**1**. R_f = 0.4 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1740, 1710, 1447 1370, 1697, 1608, 1467, 1366, 1228, 1175, 1090, 1020. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.34 – 7.22 (m, 4H), 7.22 – 7.12 (m, 7H), 7.04 (dd, *J* = 11.0 and 4.0 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.41 (dd, *J* = 9.1 and 5.3 Hz, 1H), 4.80 (d, *J* = 15.7 Hz, 1H), 4.59 (d, *J* = 15.7 Hz, 1H), 2.27 (s, 3H), 1.90 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 176.87, 170.13, 145.13, 143.33, 135.77, 135.07, 135.01, 129.93 (2C), 128.82 128.75 (2C), 128.59, 128.14, 127.93, 127.59, 127.43, 127.25 (2C), 126.99 (3C), 124.96, 124.37, 123.40, 122.56, 120.81, 120.37, 113.62, 109.34, 66.38, 43.69, 42.65, 20.91.



1-Benzyl-3-(2-(1-tosyl-1*H*-indol-3-yl)ethylidene)indolin-2-one (3m)

This compound was isolated as pale brown oil. Following the general procedure-**2**, 30 mg of **1m** afforded 20 mg of **3m** (73% yield). R_f = 0.5 (Hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 2937, 1701, 1608, 1589, 1466, 1465, 1361, 1171, 1098, 750. **^{1}H NMR (400**



MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.44 (s, 1H), 7.41 – 7.26 (m, 6H), 7.26 – 7.15 (m, 5), 6.99 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 4.98 (s, 3H), 4.05 (d, *J* = 7.5 Hz, 2H), 2.33 (s, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.82, 145.07, 143.19, 137.57, 136.05, 135.50, 135.23, 130.46, 130.06 (2C), 129.49, 128.97, 128.92 (2C), 127.73, 127.43 (2C), 126.93 (2C), 125.20, 123.86, 123.55, 123.44, 122.43, 121.95, 119.48, 118.90, 113.99, 109.47, 43.86, 25.33, 21.72. **HRMS (ESI):** *m/z* calcd for $C_{32}H_{27}N_2O_3S$ $(M+H)^+$: 519.1742. Found: 519.1749.

Expected product was not found from the mass analysis of the crude reaction mixture as well.

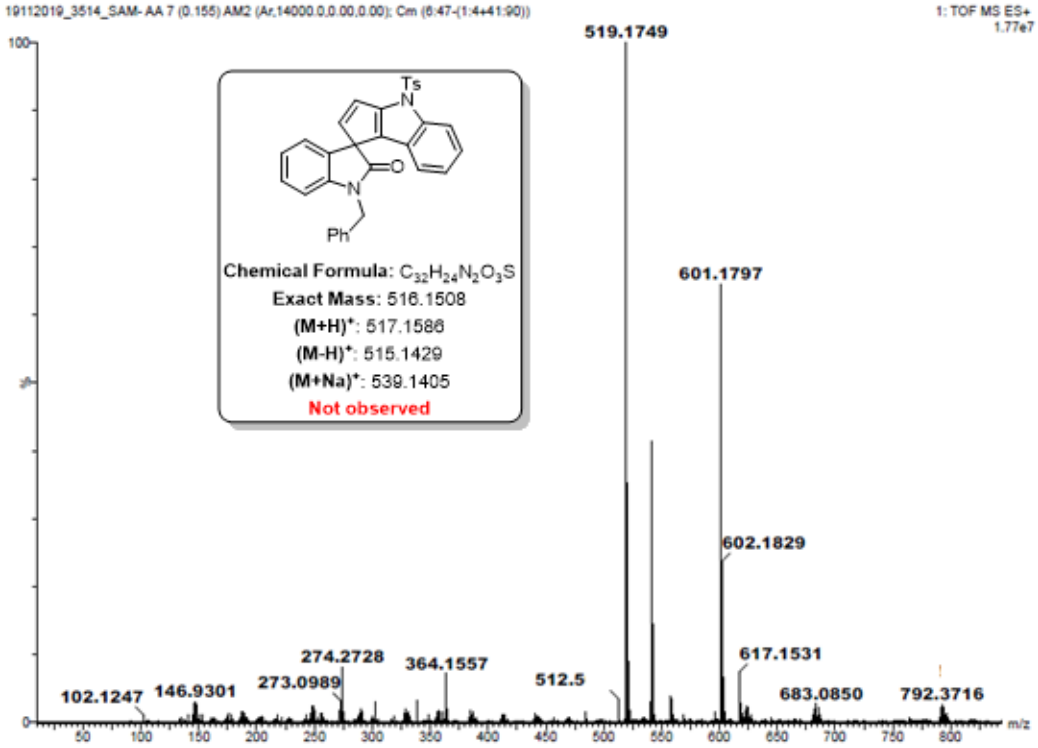
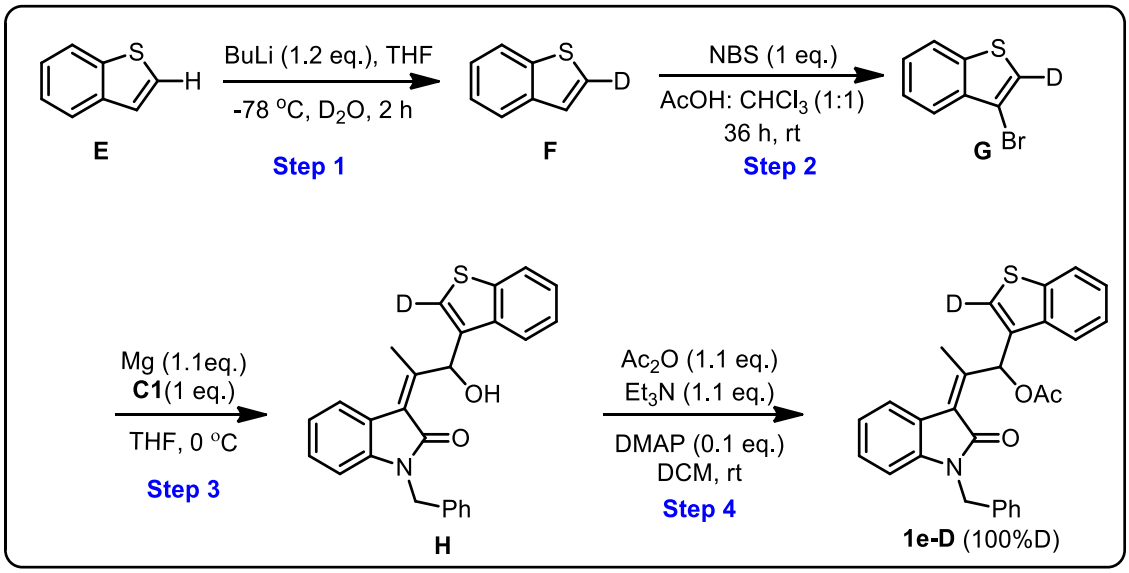


Figure **1S:** HRMS spectrum of the crude reaction mixture of **1m**

General procedure-3: Synthesis of deuterated allylic acetate 1e-D.



Scheme S2: General schematic representation for the synthesis of allylic acetate **1e-D**

A representative procedure for step-1: An oven dried 25 mL long neck RB flask was charged with benzo[*b*]thiophene **E** (1.34 g, 10.0 mmol), 8 mL dry THF and placed at -78 °C. *n*-BuLi (1.6 *M* in hexanes, 7.5 mL, 12 mmol) was added dropwise at the same temperature and stirred for 2 h. D_2O (0.25 mL) was added and stirring continued for 1 h. The reaction mixture was quenched with saturated aq. NH_4Cl solution and extracted with ethyl acetate. The organic layer was dried and the residue was chromatographed on silica to give **F**.

A representative procedure for step-2: To a solution of **F** (1.3 g, 9.6 mmol) in chloroform (20 mL) and acetic acid (20 mL), *N*-bromosuccinimide (1.71 g, 9.6 mmol) was added stepwise and stirred at room temperature for 24 h. The reaction mixture was diluted with chloroform (20 mL) was added and the resulting mixture was successively washed with a saturated sodium thiosulfate solution (20 mL), a saturated sodium carbonate solution (20 mL) and water (15 mL). The extracted organic layer was then dried over $MgSO_4$. The resulting red liquid was then filtered over a pad of silica, eluting with hexane/ethyl acetate to afford **G** as colorless oil.

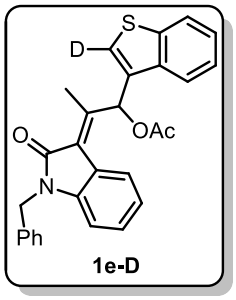
A representative procedure for step-3: To a 50 mL RB flask equipped with magnetic stir bar, **C1** (500 mg, 1.8 mmol), anhydrous THF (5.0 ml) were added under N_2 atmosphere and stirred at 0 °C for 2-3 min. Benzo[*b*]thiophen-3-ylmagnesium bromide solution of **G** which was prepared from magnesium (56 mg, 2.34 mmol), **G** (425 mg, 2 mmol) and a catalytic amount of iodine in 10 mL of dry THF was added dropwise with stirring at 0 °C and stirring

was continued for 1 h. The reaction mixture was quenched with dil. HCl and extracted twice with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated and **H** was purified by silica gel column chromatography.

A representative procedure for step-4: Alcohol **H** (450 mg, 1.09 mmol) was dissolved in dry DCM (6.0 mL) and triethylamine (0.19 mL, 1.3 mmol), acetic anhydride 0.130 mL, 1.3 mmol), DMAP (13 mg, 0.11 mmol) were added to it one by one. Then the reaction mixture was stirred until starting material disappeared (as detected by TLC). Upon completion, the reaction mixture was quenched by adding saturated *aq*. NH_4Cl solution and extracted with DCM. The combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using 10% ethyl acetate/hexane as an eluent to afford **1e-D (**83% yield, 100% D).

1-(2-Deuterobenzo[*b*]thiophen-3-yl)-2-(1-benzyl-2-oxoindolin-3-ylidene)propyl acetate (1e-D)

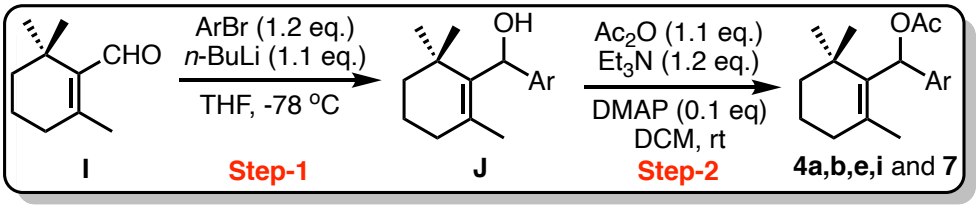
This compound was prepared following the general procedure-**3** and isolated as pale reddish



1e-D

oil. R_f = 0.3 (hexane/EtOAc = 8/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3062, 2930, 1745, 1694, 1608, 1467, 1356, 1228, 1181. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.96 (s, 1H), 8.11 – 8.04 (m, 1H), 7.88 – 7.80 (m, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.29 (m, 6H), 7.29 – 7.21 (m, 1H), 7.16 (td, *J* = 7.7 and 0.9 Hz, 1H), 6.99 (td, *J* = 7.7 and 0.9 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 5.03 (d, *J* = 15.7 Hz, 1H), 4.97 (d, *J* = 15.7 Hz, 1H), 2.40 (s, 3H), 2.19 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 169.73, 166.85, 149.48, 142.47, 140.33, 137.59, 136.21, 133.32, 129.05, 128.86 (2C), 127.60, 127.37 (2C), 125.29, 124.72, 124.64, 124.61, 123.21, 123.04, 122.82, 122.10, 109.01, 68.80, 43.50, 21.20, 16.97. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{19}DNOS$ $(M\text{-}OAc)^+$: 395.1328. Found: 395.1315.

General procedure-4: Synthesis of allylic acetates 4a,b,e,i and 7



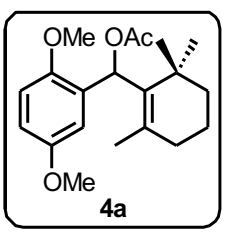
Scheme S3: General representation for the synthesis of allylic acetates

A representative procedure for step-1: An oven dried 25 mL long neck RB flask was charged with aryl bromide (975 mg, 3.95 mmol), 5 mL dry THF and placed at -78 °C. *n*-BuLi (1.6 *M* in hexanes, 2.26 mL, 3.6 mmol), was added dropwise at same temperature and stirred for 2 h. Enal **I** (500 mg, 3.28 mmol) dissolved in 1 mL dry THF, was added dropwise over 2 mins and stirred at room temperature for 30 min. The reaction mixture was quenched with saturated *aq*. ammonium chloride solution and extracted using ethyl acetate. The organic extracts were combined and dried over anhydrous sodium sulphate and concentrated. The crude product **J** was taken to next step without purification.

A representative procedure for step-2: Alcohol **J** (400 mg, 1.25 mmol) was dissolved in dry DCM (6.0 mL) and triethylamine (0.20 mL, 1.3 mmol), acetic anhydride (0.13 mL, 1.3 mmol), DMAP (15 mg, 0.11 mmol) were added. Then the reaction mixture was stirred until starting material disappeared (by TLC). Upon completion, the reaction mixture was quenched by adding saturated *aq*. NH_4Cl solution and extracted with DCM. The combined organic layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate/hexane as an eluent to afford **4a,b,e,i** and **7**.

Spectroscopic data of allylic acetates 4 and 7

(2,5-Dimethoxyphenyl)(2,6,6-trimethylcyclohex-1-en-1-yl)methyl acetate (4a)



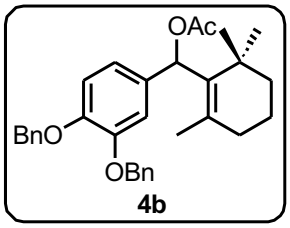
4a

This compound was prepared following the general procedure-**4** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2933, 2867, 2834, 1739, 1588, 1495, 1464, 1429, 1239. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.93 (s, 1H), 6.82 (d, *J* = 1.2 Hz, 2H), 6.76 (s, 1H), 3.80 (s, 3H), 7.76 (s, 3H), 2.14-2.05 (m, 2H), 2.03 (s, 3H), 1.35 (s, 3H), 1.71-1.62

(m, 2H), 1.50-1.43 (m, 2H), 1.24 (s, 3H), 0.77 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.5, 152.9, 152.2, 134.2, 134.1, 128.5, 116.8, 112.6, 111.3, 69.5, 55.8, 55.6, 40.0, 34.7, 33.8, 29.0, 27.9, 22.4, 21.1, 19.0. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{25}O_2$ $(M\text{-}OAc)^+$: 273.1855. Found: 273.1858.

(3,4-Bis(benzyloxy)phenyl)(2,6,6-trimethylcyclohex-1-en-1-yl)methyl acetate (4b)

This compound was prepared following the general procedure-**4** and isolated as colorless oil.

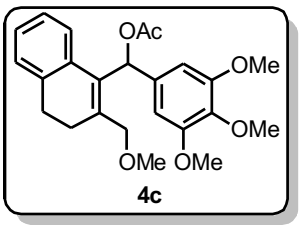


4b

R_f = 0.4 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2928, 1736, 1509, 1453, 1377, 1235, 1135, 1020, 734. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49-7.47 (m, 2H), 7.43-7.33 (m, 8H), 6.90-6.88 (m, 1H), 6.77-6.74 (m, 2H), 6.60 (s, 1H), 5.19 (s, 4H), 2.11 (s, 3H), 2.00-1.95 (m, 2H), 1.65-1.58 (m, 2H), 1.46-1.42 (m, 2H), 1.43 (s, 3H), 1.04 (s, 3H), 0.87 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.4, 148.1, 147.9, 137.4, 137.3, 135.4, 134.9, 133.7, 128.54 (2C), 128.52 (2C), 127.8, 127.6, 127.3 (2C), 126.9 (2C), 119.9, 114.4, 114.3, 72.4, 71.25, 71.22, 39.8, 34.6, 33.5, 28.7, 28.2, 21.8, 21.4, 19.1. **HRMS (ESI):** *m/z* calcd for $C_{30}H_{33}O_2$ $(M\text{-}OAc)^+$: 425.2481. Found: 425.2500.

(2-(Methoxymethyl)-3,4-dihydronaphthalen-1-yl)(3,4,5-trimethoxyphenyl)methyl acetate (4c)

This compound was prepared following the general procedure-**4** and isolated as pale yellow

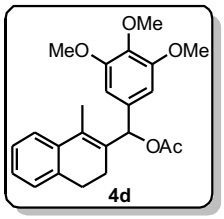


4c

oil. R_f = 0.4 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2936, 1741. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.33 (d, *J* = 7.6 Hz, 1H), 7.19-7.09 (m, 4H), 6.59 (s, 2H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.19 (d, *J* = 12 Hz, 1H), 3.84 (s, 3H), 3.60 (s, 6H), 3.38 (s, 3H), 2.80 (t, *J* = 7.7 Hz, 2H), 2.49 (d, *J* = 8.8 Hz, 2H), 2.18 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.2, 153.2 (2C), 139.3, 137.3, 136.8, 134.6, 133.1, 131.3, 127.2, 126.8, 125.2, 103.5 (2C), 72.2, 72.0, 60.8, 58.4, 56.11 (2C), 56.10, 28.4, 26.4, 21.3. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{25}O_4$ $(M\text{-}OAc)^+$: 354.1831. Found: 354.1777.

(1-Methyl-3,4-dihydronaphthalen-2-yl)(3,4,5-trimethoxyphenyl)methyl acetate (4d)

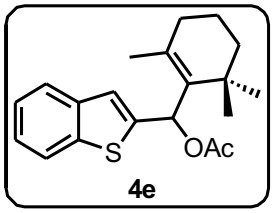
This compound was prepared following the general procedure-**4** and isolated as colorless oil. R_f = 0.4 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2937, 2839, 1739, 1590, 1415, 1234, 1012, 762. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40 (d, *J* = 7.8Hz, 1H), 7.26-7.16



(m, 3H), 6.98 (s, 1H), 6.60 (s, 2H), 3.87 (9H), 2.75-2.71 (m, 2H), 2.37-2.32 (m, 4H), 2.21 (s, 3H), 2.18-2.09 (m, 1H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 170.0, 153.2 (2C), 137.3, 136.3, 136.0, 134.8, 132.9, 130.0, 127.1, 127.0, 126.5, 123.8, 103.1 (2C), 74.2, 60.8, 56.1 (2C), 28.5, 23.1, 21.2, 14.6. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{23}O_3$ (M-OAc)$^+$: 323.1647. Fo1und: 323.1662.

Benzo[*b*]thiophen-2-yl(2,6,6-trimethylcyclohex-1-en-1-yl)methyl acetate (4e)

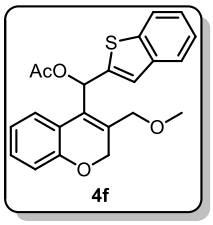
This compound was prepared following the general procedure-**4** and isolated as pale reddish



oil. R_f = 0.4 (Hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2932, 2867, 1742, 1436, 1458, 1366, 1232, 1014, 957. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.82-7.73 (m, 2H), 7.38-7.30 (m, 2H), 7.14 (s, 1H), 6.94 (s, 1H), 2.24 (s, 3H), 2.14-2.12 (m, 2H), 1.78 (s, 3H), 1.74-1.71 (m, 2H), 1.60-1.49 (m, 2H), 1.18 (s, 3H), 1.13 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 170.1, 146.0, 139.9, 139.5, 136.9, 135.6, 124.2, 124.1, 123.4, 122.1, 121.8, 69.5, 39.8, 34.8, 33.7, 28.9, 28.1, 22.2, 21.3, 19.2. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{21}S$ (M-OAc)$^+$: 269.1364. Found: 269.1353.

Benzo[*b*]thiophen-2-yl(3-(methoxymethyl)-2H-chromen-4-yl)methyl acetate (4f)

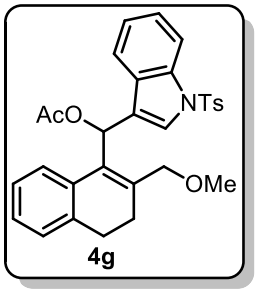
This compound was prepared following the general procedure-**4** and isolated as pale reddish



oil. R_f = 0.3 (hexane/EtOAc = 8/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3062, 2939, 1457, 1375, 1224, 1098. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.76 (d, *J* = 7.1 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.34 (s, 2H), 7.31 – 7.22 (m, 1H), 7.16 (s, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.79 (t, *J* = 7.6 Hz, 1H), 4.85 (d, *J* = 14.7 Hz, 1H), 4.77 (d, *J* = 14.7 Hz, 1H), 4.44 (d, *J* = 12.7 Hz, 1H), 4.28 (d, *J* = 12.8 Hz, 1H), 3.35 (s, 3H), 2.17 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 169.90, 154.65, 142.61, 139.87, 139.53, 132.71, 129.33, 128.31, 125.99, 124.58, 124.52, 123.81, 122.35, 122.18, 121.42, 121.26, 116.39, 69.44, 68.58, 66.56, 58.66, 21.16. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{16}O_2S$ (M-OAc)$^+$: 321.0949. Found: 321.0940.

(2-(Methoxymethyl)-3,4-dihydronaphthalen-1-yl)(1-tosyl-1*H*-indol-3-yl)methyl acetate (4g)

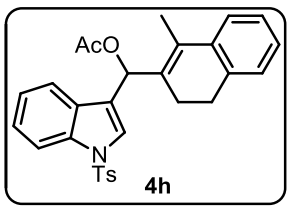
This compound was prepared following the general procedure-**4** and isolated as pale reddish oil. R_f = 0.4 (Hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2923, 1742, 1599, 1447, 1373, 1230, 1175, 1097, 982. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.02 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J*= 7.8 Hz, 1H), 7.49-7.46 (m, 2H), 7.43 (d, *J*= 1.0 Hz, 1H), 7.38-7.34 (m, 1H), 7.30-7.26 (m, 1H), 7.22-7.16 (m, 4H), 7.10-7.06 (m, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 4.23 (d, *J* = 12.0 Hz, 1H), 3.39 (s, 3H), 2.86-2.82 (m, 2H), 2.63-2.48 (m, 2H), 2.37 (s, 3H), 2.19 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.0, 145, 139.6, 136.9, 135.5, 134.9, 133.1, 130.6, 129.9 (2C), 129.0, 127.5, 126.9, 126.8 (2C), 125.9, 125.32, 125.30, 125.06, 123.5, 121.0, 120.2, 113.8, 71.8, 67.3, 58.4, 28.3, 26.3, 21.6, 21.2. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{25}NO_3S$ (M-OAc)$^+$: 456.1633. Found: 456.1626.



4g

(1-Methyl-3,4-dihydronaphthalen-2-yl)(1-tosyl-1*H*-indol-3-yl) methyl acetate (4h)

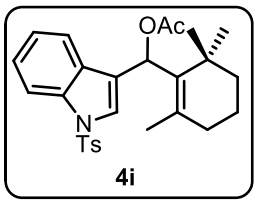
This compound was prepared following the general procedure-**4** and isolated as pale brownish oil. R_f = 0.4 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2933, 1740, 1598, 1449, 1372, 1229, 1176, 1089, 1021, 920, 812, 757, 663, 575, 540. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00-7.97 (m, 1H), 7.78-7.76 (m, 2H), 7.58 (d, *J* = 1.2 Hz, 1H), 7.43-7.40 (m, 2H), 7.35-7.31 (m, 2H), 7.26-7.24 (m, 4H), 7.20-7.18 (m, 2H), 2.71-2.65 (m, 2H), 2.38-2.37 (m, 6H), 2.32-2.29 (m, 2H) 2.22 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.0, 145.0, 136.1 (2C), 135.4, 135.0, 131.4, 130.6, 129.9 (2C), 128.6, 127.2, 127.1, 126.8 (2C), 126.5, 125.0, 123.9, 123.8, 123.4, 120.8, 119.9, 113.8, 69.4, 28.4, 23.0, 21.6, 21.2, 14.6. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{24}NO_2S$ (M-OAc)$^+$: 426.1528. Found: 426.1535.



4h

(1-Tosyl-1*H*-indol-3-yl)(2,6,6-trimethylcyclohex-1-en-1-yl)methyl acetate (4i)

This compound was prepared following the general procedure-**4** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2928, 1734, 1597, 1446, 1372, 1174, 1018, 974, 812, 747. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.74-7.72 (m, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 1.2 Hz, 1H), 7.34 (td, *J* = 7.8 Hz, 1H), 7.29-7.21 (m, 4H), 6.83 (s, 1H), 2.35 (s, 3H), 2.22-2.05 (m, 2H), 2.09 (s, 3H), 1.79 (s, 3H), 1.72-1.68 (m, 2H), 1.55-1.51 (m, 2H), 1.18 (s, 3H), 0.87 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.1, 145.0, 135.6, 135.02, 135.00, 134.9, 129.8 (2C), 129.5, 126.8 (2C), 126.4,

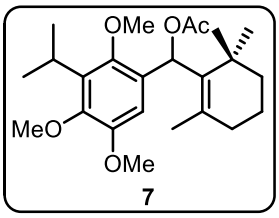


4i

124.8, 123.5, 122.0, 119.9, 113.8, 66.5, 39.8, 34.6, 33.6, 29.2, 27.8, 22.3, 21.5, 21.3, 19.0. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{28}NO_2S$ $(M\text{-}OAc)^+$: 406.1841. Found: 406.1839.

(3-Isopropyl-2,4,5-trimethoxyphenyl)(2,6,6-trimethylcyclohex-1-en-1-yl)methyl acetate (7)

This compound was prepared following the general procedure-**4** and isolated as pale reddish oil. R_f = 0.4 (Hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2933, 1738, 1480, 1236, 1105, 1042, 954. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.82 (s, 1H), 6.77 (s, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.70 (s, 3H), 3.42-3.35 (m, 1H), 2.13-2.06 (m, 2H), 2.06 (s, 3H), 1.80 (s, 3H), 1.70-1.60 (m, 2H), 1.52-1.46 (m, 2H), 1.38-1.34 (m, 6H), 1.26 (s, 3H), 0.74 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.6, 150.8, 149.3, 148.8, 135.2, 135.0, 133.3, 126.7, 111.8, 70.0, 62.0, 60.6, 55.8, 40.2, 34.7, 33.9, 29.3, 27.9, 26.1, 22.6, 21.9, 21.8, 21.3, 19.0. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{33}O_3$ $(M\text{-}OAc)^+$: 345.2430. Found: 345.2418.



7

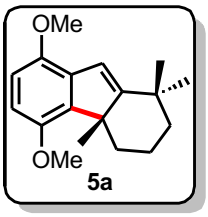
General procedure-5: Screening of reaction parameters for the synthesis of (5a-5i, 8)

An oven dried 5 mL glass vial was charged with **4** (0.15 mmol), and solvent (1.0 mL) and catalyst (0.015 mmol) were introduced. Stirring continued at 80 ^{o}C until **4a** disappeared as monitored by TLC. Then the reaction was quenched with water and extracted with EtOAc. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel flash chromatography using hexane/ethyl acetate as eluent, to afford **5**.

Spectroscopic data of cyclopentene-fused arenes and heteroarenes 5

5,8-Dimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydro-1*H*-fluorene (5a)

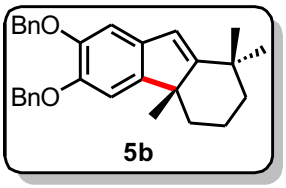
This compound was prepared following the general procedure- **5** and isolated as pale reddish



oil. 25 mg of **4a** afforded 22 mg of **5a** (88% yield). R_f = 0.5 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1752, 1493, 1461, 1383, 1251, 1086. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.71-6.69 (m, 1H), 6.62-6.59 (m, 1H), 6.48 (s, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 2.57-2.52 (m, 1H), 2.00-1.89 (m, 1H), 1.67-1.57 (m, 2H), 1.47 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H), 1.17-1.01 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 164.1, 149.9, 147.2, 142.6, 131.8, 116.2, 109.0, 107.4, 55.9, 55.6, 52.5, 42.7, 35.8, 35.6, 31.4, 25.4, 19.9, 19.4. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{25}O_2$ $(M+H)^+$: 273.1855. Found: 273.1844.

7,8-Bis(benzyloxy)-1,1,4a-trimethyl-2,3,4,4a-tetrahydro-1*H*-fluorene (5b).

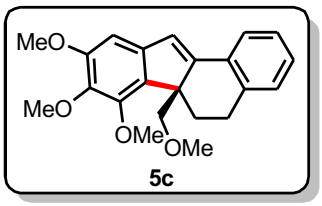
This compound was prepared following the general procedure-**5** and isolated as colorless oil.



30 mg of **4b** afforded 21 mg of **5b** (81% yield). R_f = 0.5 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2958, 2926, 1614, 1484, 1453, 1317, 1137, 1027, 736. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.54-7.29 (m, 10H), 6.97 (d, *J* = 12.2 Hz, 2H), 6.30 (s, 1H), 5.22-5.20 (m, 4H), 2.16-2.09 (m, 1H), 2.00-1.96 (m, 1H), 1.71-1.60 (m, 2H), 1.36 (s, 3H), 1.33 (s, 3H), 1.28 (s, 3H), 1.18-1.10 (m, 1H), 1.05-0.91 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.4, 148.57, 148.51, 146.4, 137.8, 137.7, 135.9, 128.48 (2C), 128.40 (2C), 127.7 (4C), 127.3 (2C), 120.2, 110.5, 108.0, 72.6, 71.7, 50.9, 42.7, 38.2, 35.5, 31.3, 25.3, 23.5, 19.8. **HRMS (ESI):** *m/z* calcd for $C_{30}H_{33}O_2$ $(M+H)^+$: 425.2481. Found**:** 425.2475.

7,8,9-Trimethoxy-6a-(methoxymethyl)-6,6a-dihydro-5*H*-benzo[*a*]fluorine (5c)

This compound was prepared following the general procedure-**5** and isolated as colorless oil.

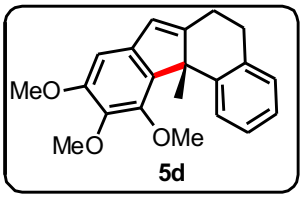


5c

30 mg of **4c** afforded 20 mg of **5c** (78% yield). R_f = 0.5 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2935, 2366, 1604, 1576, 1465, 1354, 1237, 1109, 1022, 761. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69-7.67 (m, 1H), 7.29-7.23 (m, 3H), 6.79 (s, 1H), 6.77 (s, 1H), 4.02 (s, 3H), 4.01-3.99 (m, 1H), 3.92 (s, 6H), 3.65 (d, *J* = 9.0 Hz, 1H), 3.13 (s, 3H), 2.97-2.79 (m, 2H), 1.64 (dt, *J* = 13.1 and 6.5, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 153.5, 150.7, 150.2, 140.1, 139.9, 135.7, 133.3, 132.0, 128.9, 127.5, 126.3, 125.3, 123.3, 101, 74.2, 60.9, 60.8, 60.5, 59.5, 56.14, 56.13, 54.6. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{26}O_4$ $(M+H)^+$: 353.1753. Found: 354.1744.

7,8-Bis(benzyloxy)-1,1,4a-trimethyl-2,3,4,4a-tetrahydro-1*H*-fluorene (5d).

This compound was prepared following the general procedure-**5** and isolated as colorless oil.

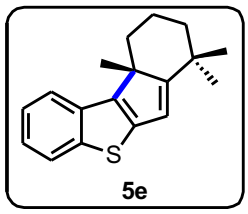


5d

30 mg of **4d** afforded 21 mg of **5d** (80% yield). R_f = 0.5 (Hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2933, 2839, 1601, 166, 1408, 1355, 1199, 1109, 1021, 988. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.20 (d, *J* = 7.8 Hz, 1H), 7.28-7.13 (m, 3H), 6.65 (s, 1H), 6.33 (s, 1H), 4.11 (s, 3H), 3.95 (s, 3H), 3.90 (s, 3H), 3.31-3.26 (m, 1H), 3.05-2.1 (m, 3H), 1.70 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 156.5, 15.34, 150.8, 142.7, 140.0, 139.7, 136.1, 134.2, 128.9, 128.4, 126.3, 126.2, 121.2, 100.2, 60.9, 56.8, 56.1, 32.6 (2C), 24.7, 23.2. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{23}O_3$ $(M+H)^+$: 323.1647. Found**:** 323.1662.

7,7,10a-Trimethyl-8,9,10,10a-tetrahydro-7*H*-benzo[*b*]indeno[1,2-*d*]thiophene (5e)

This compound was prepared following the general procedure-**5** and isolated as pale yellow solid. M.P = 78-80 °C. 30 mg of **4e** afforded 22 mg of **5e** (92% yield).

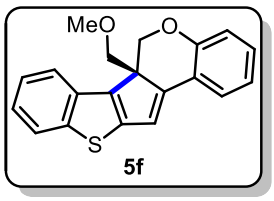


5e

R_f = 0.5 (Hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2928, 2863, 1564, 1456, 1424, 1323, 1293, 1186, 756, 729. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.40-7.36 (m, 1H), 7.26-7.22 (m, 1H), 6.48 (s, 1H), 2.44 (dd, *J* = 13.0 and 1.5 Hz, 1H), 2.07-2.02 (m, 1H), 1.69-1.17 (m, 2H), 1.55 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H), 1.27-1.17 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 168.6, 150.5, 143.6, 141.3, 133.9, 124.1, 124.0, 122.0, 119.9, 116.4, 50.6, 43.2, 37.6, 36.3, 31.2, 25.5, 21.7, 19.5. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{20}S$ $(M+H)^+$: 268.1286. Found: 268.1323.

6a-(Methoxymethyl)-6,6a-dihydrobenzo[4',5']thieno[2',3':4,5]cyclopenta[1,2-c] chromene (5f)

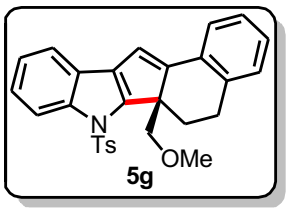
This compound was prepared following the general procedure-**5** and isolated as colorless oil.



23 mg of **4f** afforded 35 mg of **5f** (78% yield). R_f = 0.7 (Hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3057, 2919, 1608, 1580, 1473, 1331, 1212, 1103, 756. **^{1}H NMR (400 MHz, DMSO):** δ 7.98 – 7.91 (m, 2H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.18 (m, 3H), 7.05 – 6.94 (m, 2H), 5.06 (d, *J* = 10.4 Hz, 1H), 3.83 (dd, *J* = 19.0 and 9.1 Hz, 2H), 3.18 (s, 3H), 3.04 (d, *J* = 9.0 Hz,1H). **^{13}C NMR (100 MHz, DMSO):** δ 152.66, 146.44, 146.21, 143.42, 142.90, 134.45, 129.72, 125.05, 124.79, 123.78, 123.15, 122.41, 121.46, 119.97, 119.23, 116.59, 72.31, 69.49, 59.00, 51.49. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{17}O_2S$ $(M+H)^+$: 321.0949. Found: 321.0935.

6a-(Methoxymethyl)-7-tosyl-5,6,6a,7-tetrahydrobenzo[4,5]indeno[1,2-*b*]indole (5g)

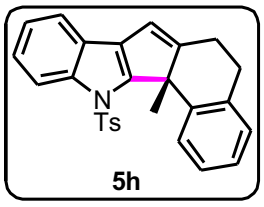
This compound was prepared following the general procedure-**5** and isolated as colorless oil.



50 mg of **4g** afforded 38 mg of **5g** (86% yield). R_f = 0.5 (Hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2923, 1596, 1447, 1366, 1173, 1109, 980, 852, 756. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00-7.96 (m, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.62 (dd, *J* = 8.8 Hz and 2.8, 1H), 7.30-7.25 (m, 5H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.00 (s, 1H), 4.41 (d, *J* = 9.0 Hz, 1H), 3.90 (d, *J* = 9.0 Hz, 1H), 3.27-3.12 (m, 2H), 3.10 (s, 3H), 3.05-2.99 (m, 1H), 2.34 (s, 3H), 1.86-1.76 (m, 1H) **^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.4, 148.9, 144.6, 140.3, 135.8, 134.6, 132.4, 131.5, 129.7 (2C), 128.7, 127.1, 126.8 (2C), 126.5, 124.9, 124.4, 123.9, 123.5, 119.8, 116.5, 114.8, 73.2, 59.2, 54.0, 29.7, 26.4, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{25}NO_3S$ $(M+H)^+$: 456.1633. Found: 456.1623.

12*b*-Methyl-12-tosyl-5,6,12,12*b*-tetrahydrobenzo[6,7]indeno[1,2-*b*]indole (5h)

This compound was prepared following the general procedure-**5** and isolated as pale reddish

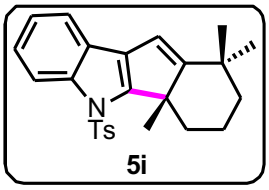


oil. 30 mg of **4h** afforded 20 mg of **5h** (79% yield). R_f = 0.5 (Hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1598, 1446, 1371, 1175, 1090, 813, 742, 703, 665, 574, 542. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.11 (d, *J* = 8.3 Hz, 1H), 7.76 (td, *J* = 19.5 and 7.5 Hz, 4H), 7.38-7.34 (m, 1H), 7.28-7.14 (m, 6H), 6.92 (s, 1H), 3.34 (dd, *J* = 12.1and 5.5 Hz,

1H), 3.10-3.01 (m, 3H), 2.32 (s, 3H), 1.57 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.4, 144.7, 140.7, 138.9, 136.0, 135.4, 132.1, 129.8 (2C), 128.6, 127.8, 127.1, 126.7 (3C), 126.4, 126.3, 123.7, 122.3, 118.5, 114.7, 114.5, 52.5, 32.4, 26.7, 24.2, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{24}NO_2S$ $(M+H)^+$: 426.1528. Found: 426.1506.

1,1,4a-Trimethyl-5-tosyl-1,2,3,4,4a,5-hexahydroindeno[1,2-*b*]indole (5i)

This compound was prepared following the general procedure-**5** and isolated as pale yellow oil. 30 mg of **4i** afforded 20 mg of **5i** (78% yield). R_f = 0.5 (Hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 3029, 2929, 1487, 1449, 1370, 1075, 963, 761, 694. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.16-8.14 (m, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.53-7.50 (m, 1H), 7.30-7.23 (m, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.43 (s, 1H), 2.98 (dd, *J* = 12.6 and 1.6 Hz, 1H), 2.30 (s, 3H), 2.00 (td, *J* = 13.9 and 3.2 Hz, 1H), 1.75-1.68 (m, 2H), 1.65 (s, 3H), 1.35 (s, 3H), 1.30 (s, 3H), 1.25-1.17 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.4, 152.7, 144.4, 140.9, 135.4, 129.5 (2C), 129.3, 126.7 (2C), 125.1, 123.7, 123.6, 119.3, 115.5, 113.1, 52.0, 42.1, 36.2, 35.1, 31.6, 26.2, 22.1, 21.5, 19.2. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{28}NO_2S$ $(M+H)^+$: 406.1841. Found: 406.1821.



5i

Kinetic Isotope Effect Experiments

To determine kinetic isotope effects in the palladium-catalysed allylic arylation reaction, **1e** and **1e-D** were subjected to optimised reaction conditions. The reaction progress was monitored by HPLC analysis using Daicel Chiralpak IB Column (90:10 n-Hexane/2-Propanol, 1 mL/min, 254 nm), and yield of the product was used for plotting the graph.[1] Figure 2 indicates faster reaction rate for **1e-D** as compared to **1e**. Initially, reaction rate was similar in both cases which may be consider as induction period. Afterwards, it exponentially increased. From Figure 3, it was found that $k_H/k_D = 0.51$, which strongly indicates that the C-C bond forming cyclisation event involved an ene-type allylic arylation step rather than C-H activation. Otherwise, typical metal-catalysed C-H functionalisation processes involve the C-H bond cleavage in the rate determining step.[2]

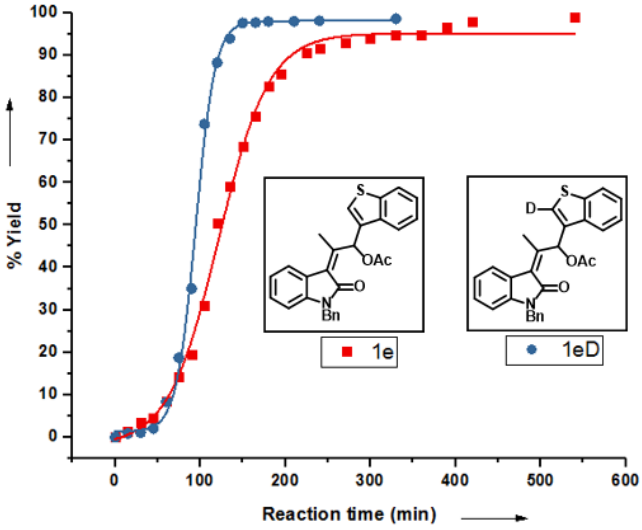


Figure **2S**: A full reaction profile of **1e** (red) and **1e-D** (blue)

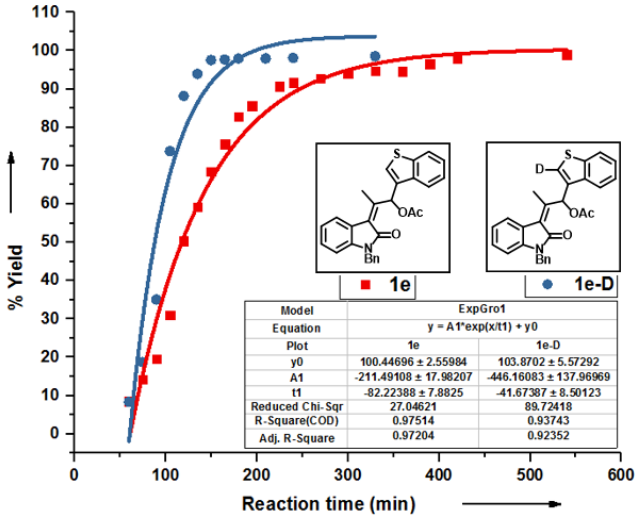
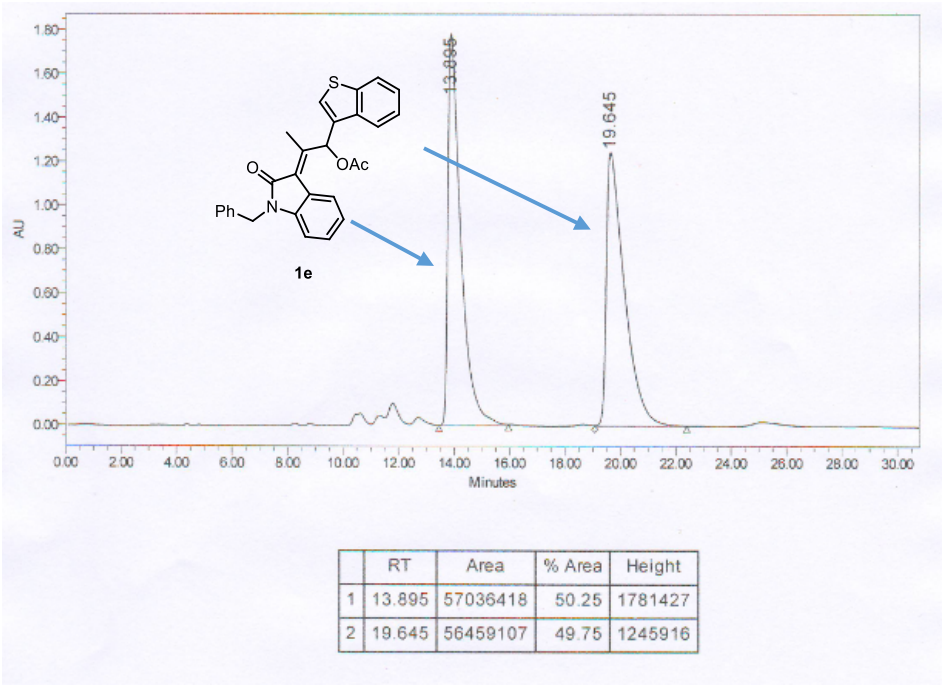
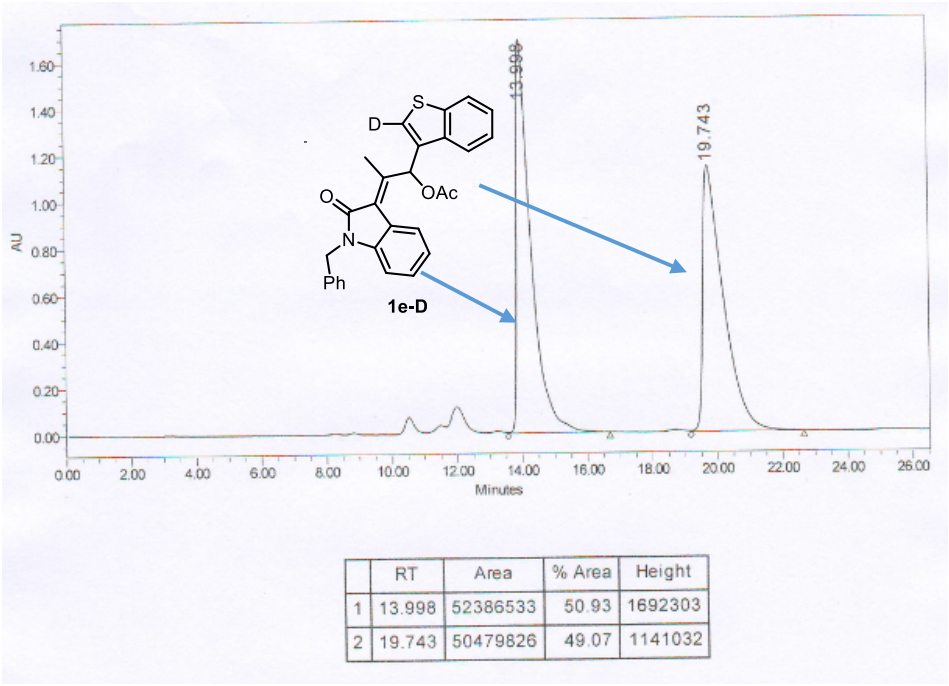


Figure **3S**: Kinetic isotope effect was determined for the reactions of **1e** (red) and **1e-D** (blue)



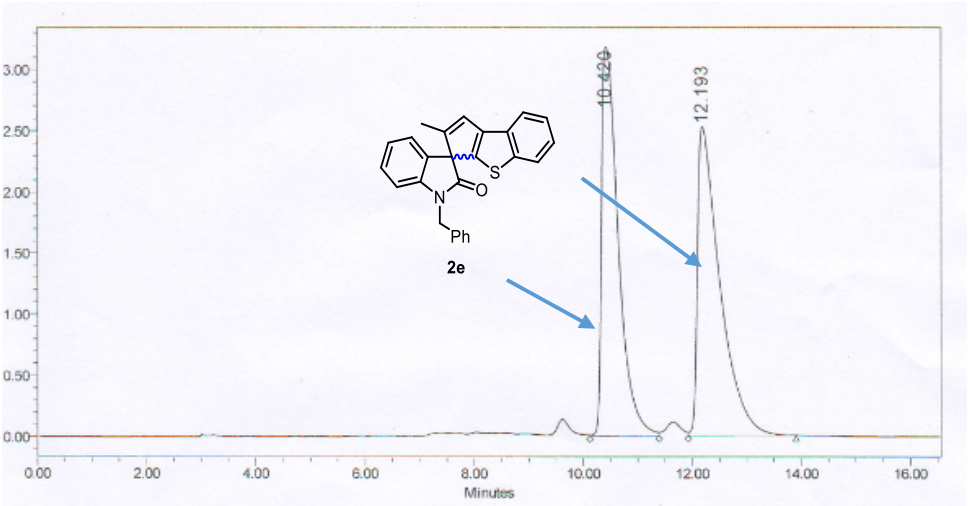
	RT	Area	% Area	Height
1	13.895	57036418	50.25	1781427
2	19.645	56459107	49.75	1245916

Figure **4S**: HPLC Spectrum of **1e**



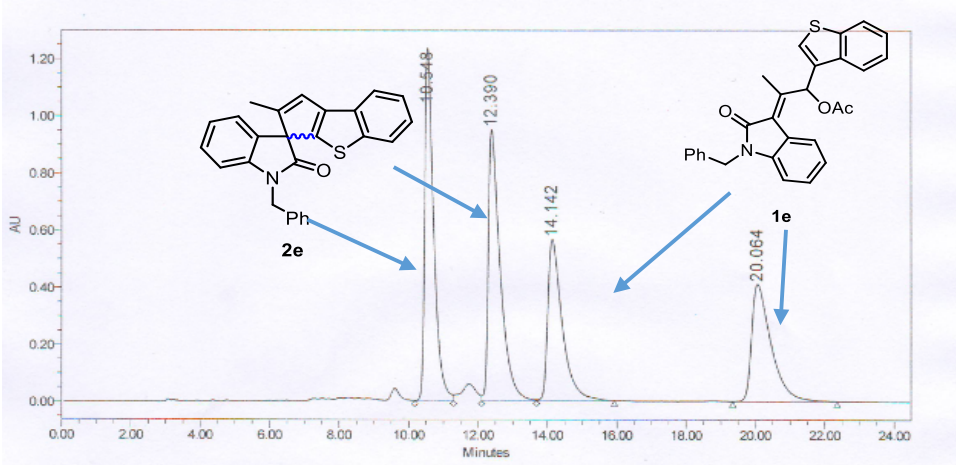
	RT	Area	% Area	Height
1	13.998	52386533	50.93	1692303
2	19.743	50479826	49.07	1141032

Figure **5S**: HPLC Spectrum of **1e-D**



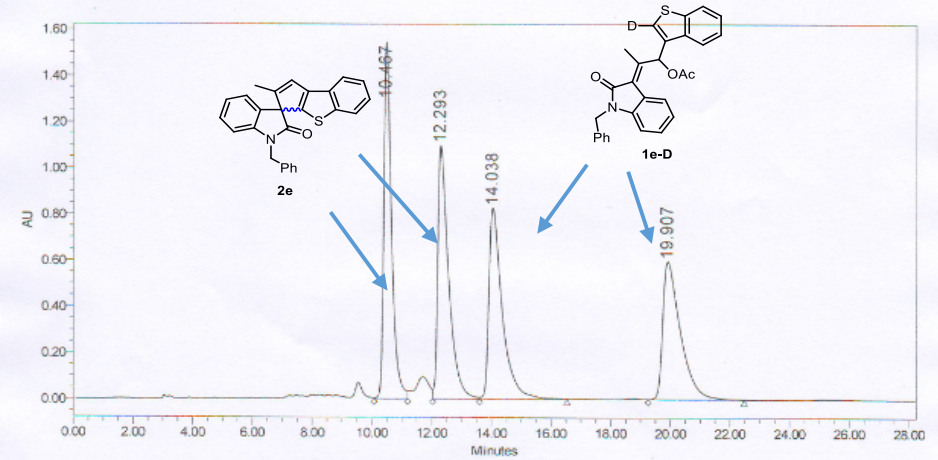
	RT	Area	% Area	Height
1	10.420	67591194	48.49	3173299
2	12.193	71793670	51.51	2522377

Figure **6S**: HPLC Spectrum of **2e**



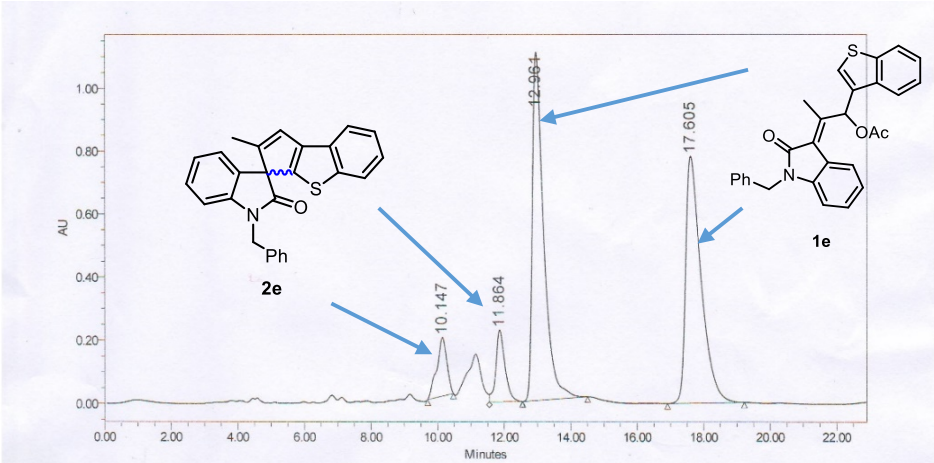
	RT	Area	% Area	Height
1	10.548	22398511	29.01	1234002
2	12.390	22520140	29.17	948615
3	14.142	16298689	21.11	563281
4	20.064	15990655	20.71	410369

Figure **7S**: HPLC Spectrum of **1e** and **2e**



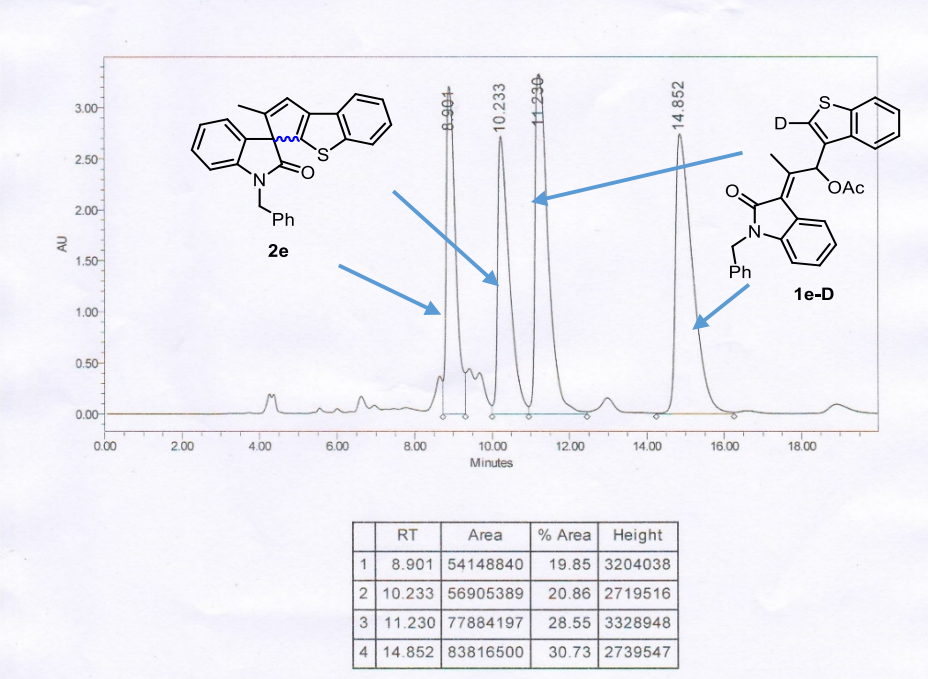
	RT	Area	% Area	Height
1	10.467	27404878	26.15	1542801
2	12.293	27438795	26.18	1096196
3	14.038	25565635	24.39	825506
4	19.907	24405781	23.28	594680

Figure **8S**: HPLC Spectrum of **1e-D** and **2e**



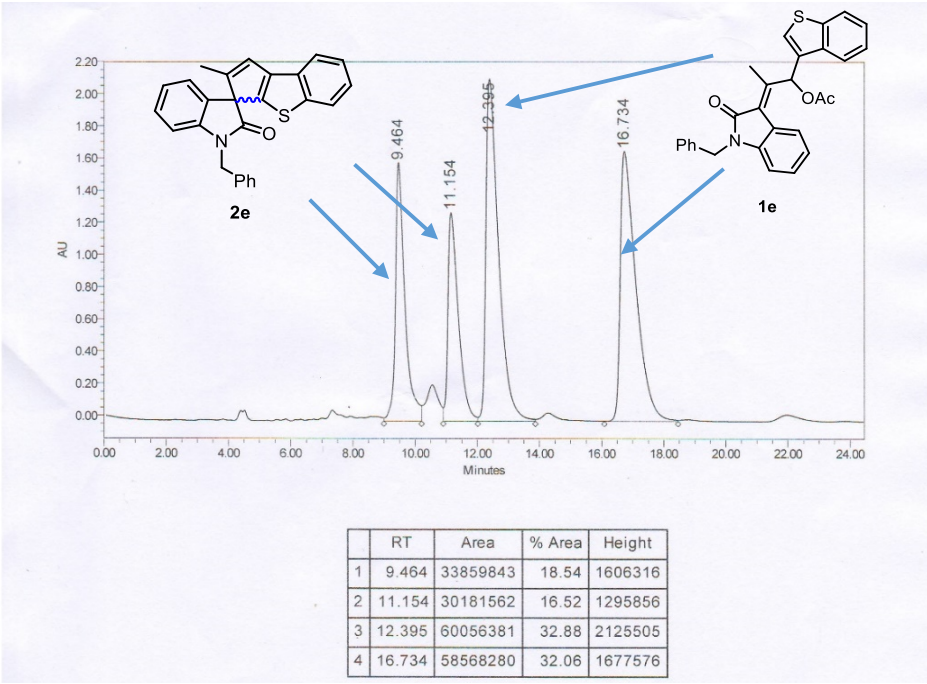
	RT	Area	% Area	Height
1	10.147	3904650	6.58	184750
2	11.864	4280099	7.21	226199
3	12.961	25829585	43.53	1104297
4	17.605	25321697	42.68	781908

Figure **9S**: HPLC Spectrum of crude reaction mixture of **1e** and **2e** after 90 min



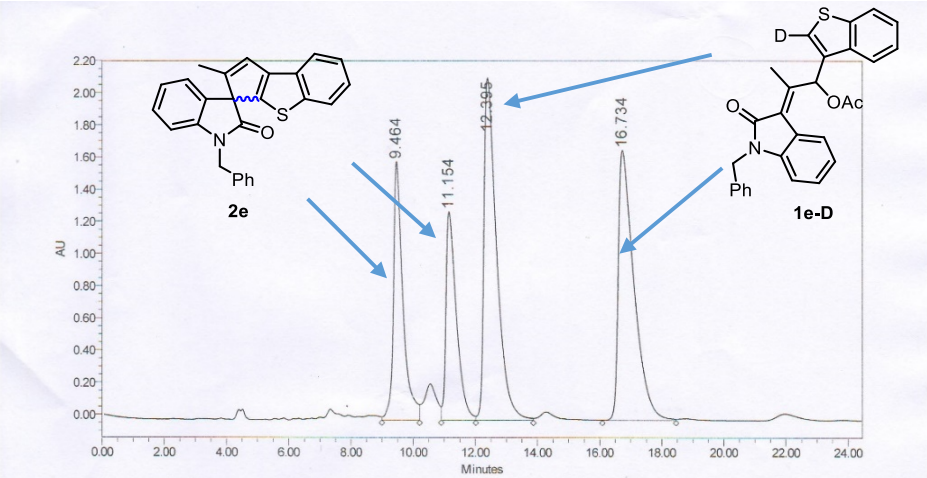
	RT	Area	% Area	Height
1	8.901	54148840	19.85	3204038
2	10.233	56905389	20.86	2719516
3	11.230	77884197	28.55	3328948
4	14.852	83816500	30.73	2739547

Figure **10S:** HPLC Spectrum of crude reaction mixture of **1e-D** and **2e** after 90 min



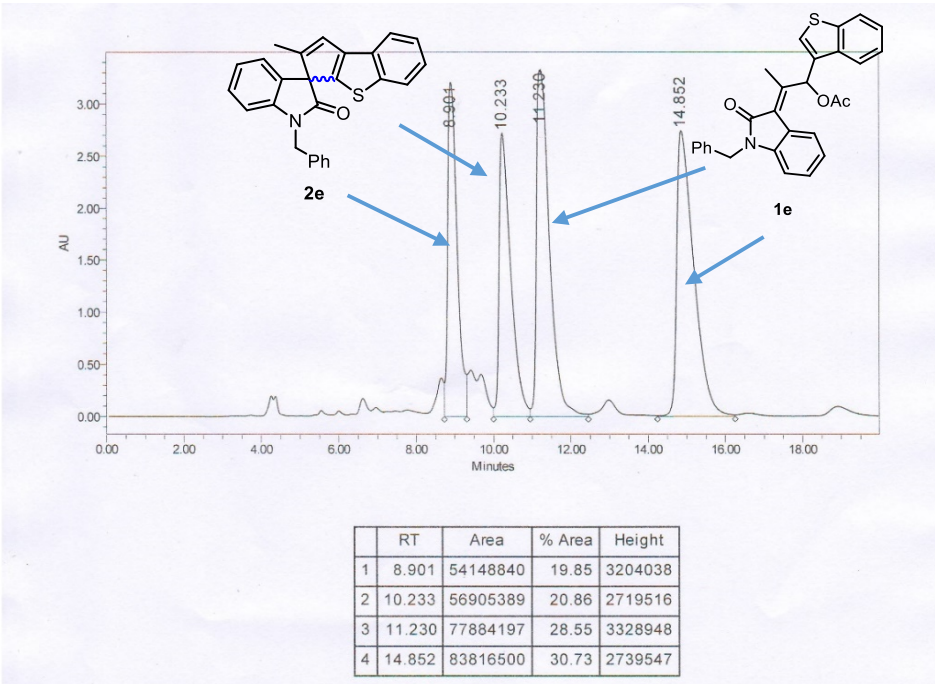
	RT	Area	% Area	Height
1	9.464	33859843	18.54	1606316
2	11.154	30181562	16.52	1295856
3	12.395	60056381	32.88	2125505
4	16.734	58568280	32.06	1677576

Figure **11S**: HPLC Spectrum of crude reaction mixture of **1e** and **2e** after 105 min



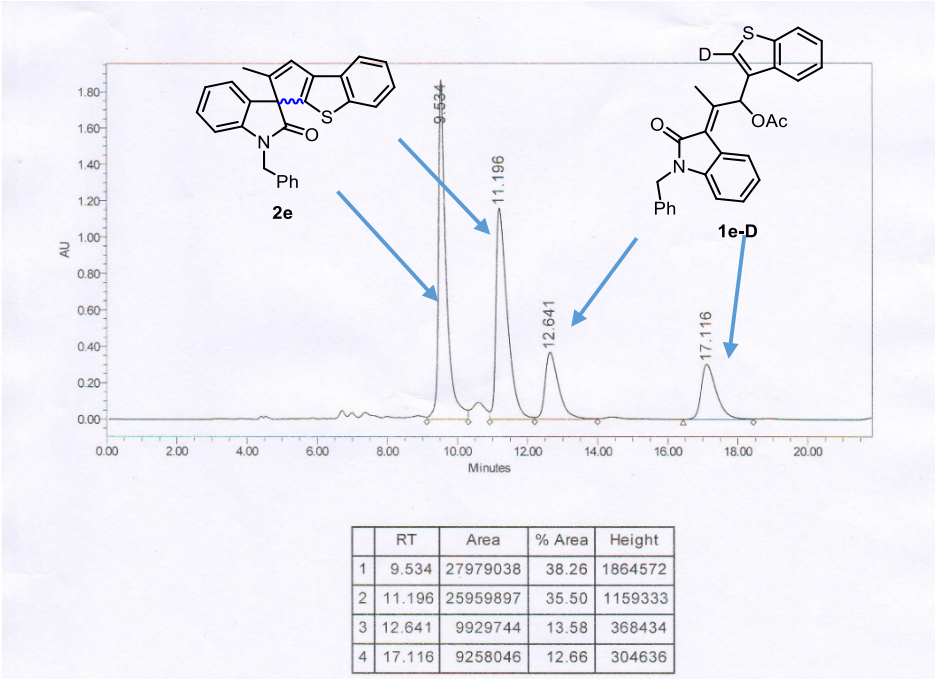
	RT	Area	% Area	Height
1	9.464	33859843	18.54	1606316
2	11.154	30181562	16.52	1295856
3	12.395	60056381	32.88	2125505
4	16.734	58568280	32.06	1677576

Figure **12S**: HPLC Spectrum of crude reaction mixture of **1e-D** and **2e** after 105 min



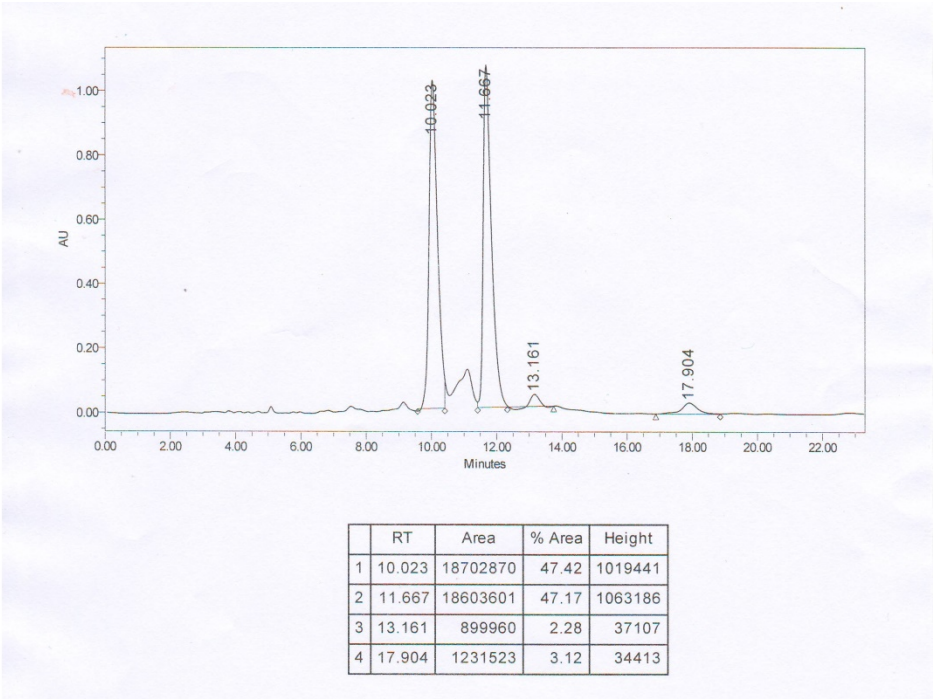
	RT	Area	% Area	Height
1	8.901	54148840	19.85	3204038
2	10.233	56905389	20.86	2719516
3	11.230	77884197	28.55	3328948
4	14.852	83816500	30.73	2739547

Figure **13S**: HPLC Spectrum of crude reaction mixture of **1e** and **2e** after 120 min



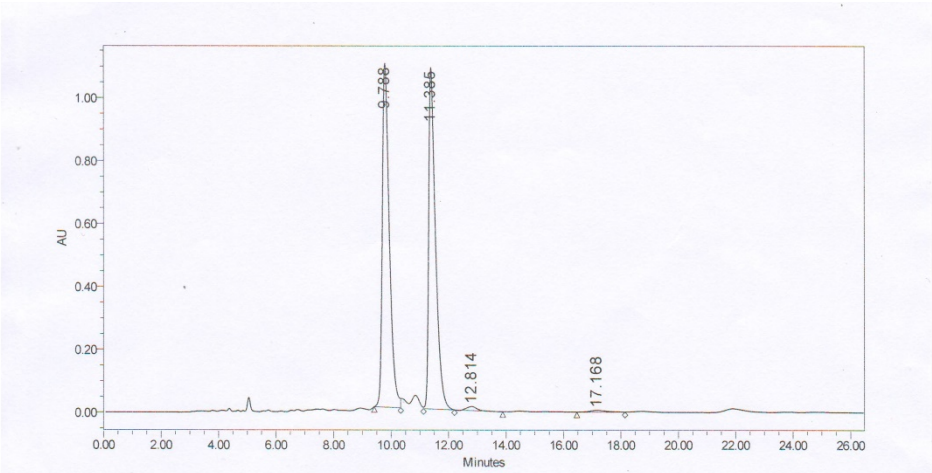
	RT	Area	% Area	Height
1	9.534	27979038	38.26	1864572
2	11.196	25959897	35.50	1159333
3	12.641	9929744	13.58	368434
4	17.116	9258046	12.66	304636

Figure **14S**: HPLC Spectrum of crude reaction mixture of **1e-D** and **2e** after 120 min



	RT	Area	% Area	Height
1	10.023	18702870	47.42	1019441
2	11.667	18603601	47.17	1063186
3	13.161	899960	2.28	37107
4	17.904	1231523	3.12	34413

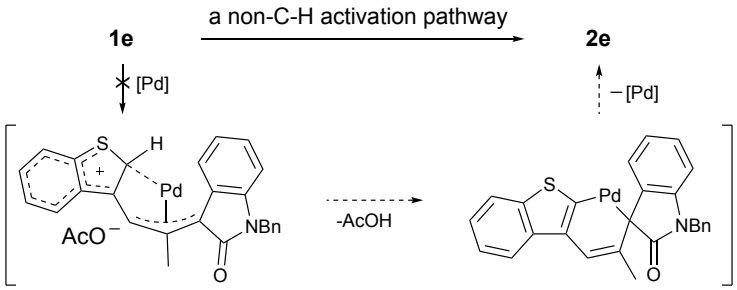
Figure **15S**: HPLC Spectrum of crude reaction mixture of **1e-D** and **2e** after 330 min



	RT	Area	% Area	Height
1	9.788	18362040	49.54	1092682
2	11.385	18139134	48.94	1085764
3	12.814	322276	0.87	12812
4	17.168	241306	0.65	5712

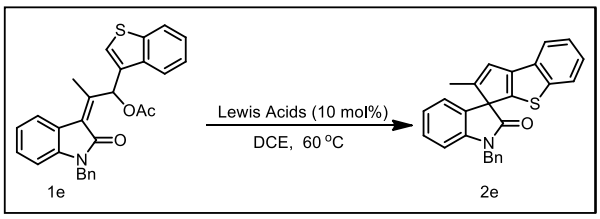
Figure **16S**: HPLC Spectrum of crude reaction mixture of **1e-D** and **2e** after 330 min

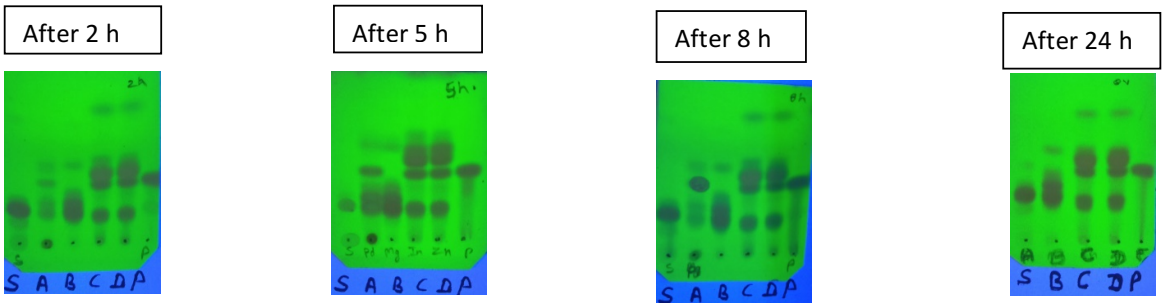
From these experiments, it was concluded that the conversion of **1e** to **2e** involves a non-C-H activation pathway.



Experiments to rule out the Lewis acidic nature of $PdCl_2$

To rule out $PdCl_2$ acting as a Lewis acid, we have performed the reaction of **1e** with Lewis acids such as $PdCl_2$, $MgBr_2$, $InCl_3$, $ZnCl_2$. These reactions hardly gave any desired product **2e** (except $PdCl_2$).





I II III IV

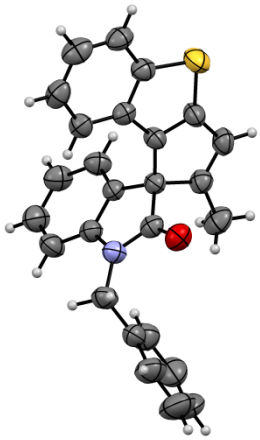
S - Starting compound (**1e**)

A - $PdCl_2$ B - $MgBr_2$ C - $InCl_3$ D - $ZnCl_2$

P - Expected product (**2e**)

*After 8 h, the reaction with $PdCl_2$ (A) was almost complete (can be seen from the TLC plate III). So, the TLC plate IV (checked after 24 h) did not have the spot corresponding to the $PdCl_2$ reaction.

Crystal Structure of 2a (CCDC 1965370): Structure of the spiroxindole **2a** was confirmed by single crystal X-ray diffraction analysis.

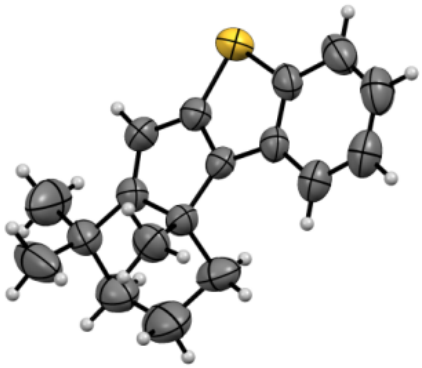


Crystal Data: for $C_{26}H_{19}NOS$ (M =393.48 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 9.8555(12) Å, b = 9.9916(8) Å, c = 11.3490(15) Å, β = 114.698(16)°, V = 1015.3(2) Å^3, Z = 2, T = 298.0(2) K, μ(MoKα) = 0.176 mm^{-1}, *Dcalc* = 1.287 g/cm^3, 7711 reflections measured (5.678° ≤ 2Θ ≤ 50°), 3578 unique (R_{int} = 0.0326, R_{sigma} = 0.0592) which were used in all calculations. The final R_1 was 0.0455 (I > 2σ(I)) and wR_2 was 0.1002 (all data).

Crystal data and structure refinement for SAM_03_81_RT	
Identification code	SAM_03_81_RT
Empirical formula	$C_{26}H_{19}NOS$
Formula weight	393.48
Temperature/K	298.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.8555(12)
b/Å	9.9916(8)
c/Å	11.3490(15)
α/°	90
β/°	114.698(16)
γ/°	90
Volume/Å^3	1015.3(2)
Z	2
ρ_{calc}g/cm^3	1.287
μ/mm^{-1}	0.176

F(000)	412.0
Crystal size/mm^3	0.21 × 0.16 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.678 to 50
Index ranges	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-13 \leq l \leq 13$
Reflections collected	7711
Independent reflections	3578 [R_{int} = 0.0326, R_{sigma} = 0.0592]
Data/restraints/parameters	3578/1/263
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0455, wR_2 = 0.0850
Final R indexes [all data]	R_1 = 0.0706, wR_2 = 0.1002
Largest diff. peak/hole / e $Å^{-3}$	0.17/-0.21
Flack parameter	0.03(5)

Crystal Structure of 5e (CCDC 1965374): Structure of the cyclopentannulated heteroarene **5e** was confirmed by single crystal X-ray diffraction analysis.



Crystal Data: for $C_{18}H_{20}S$ (M =268.40 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 10.0356(14) Å, b = 9.5429(9) Å, c = 16.215(2) Å, β = 104.664(13)°, V = 1502.3(3) Å^3, Z = 4, T = 298.00(2) K, μ(MoKα) = 0.200 mm^{-1}, *Dcalc* = 1.187 g/cm^3, 5325 reflections measured (4.996° ≤ 2Θ ≤ 49.978°), 2636 unique (R_{int} = 0.0469, R_{sigma} = 0.0726) which were used in all calculations. The final R_1 was 0.1098 (I > 2σ(I)) and wR_2 was 0.3510 (all data).

Crystal data and structure refinement for sb 08 sbc	
Identification code	sb 08 sbc
Empirical formula	$C_{18}H_{20}S$
Formula weight	268.40
Temperature/K	298.00(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.0356(14)
b/Å	9.5429(9)
c/Å	16.215(2)
α/°	90
β/°	104.664(13)
γ/°	90
Volume/Å^3	1502.3(3)
Z	4
ρ_{calc}g/cm^3	1.187
μ/mm^{-1}	0.200

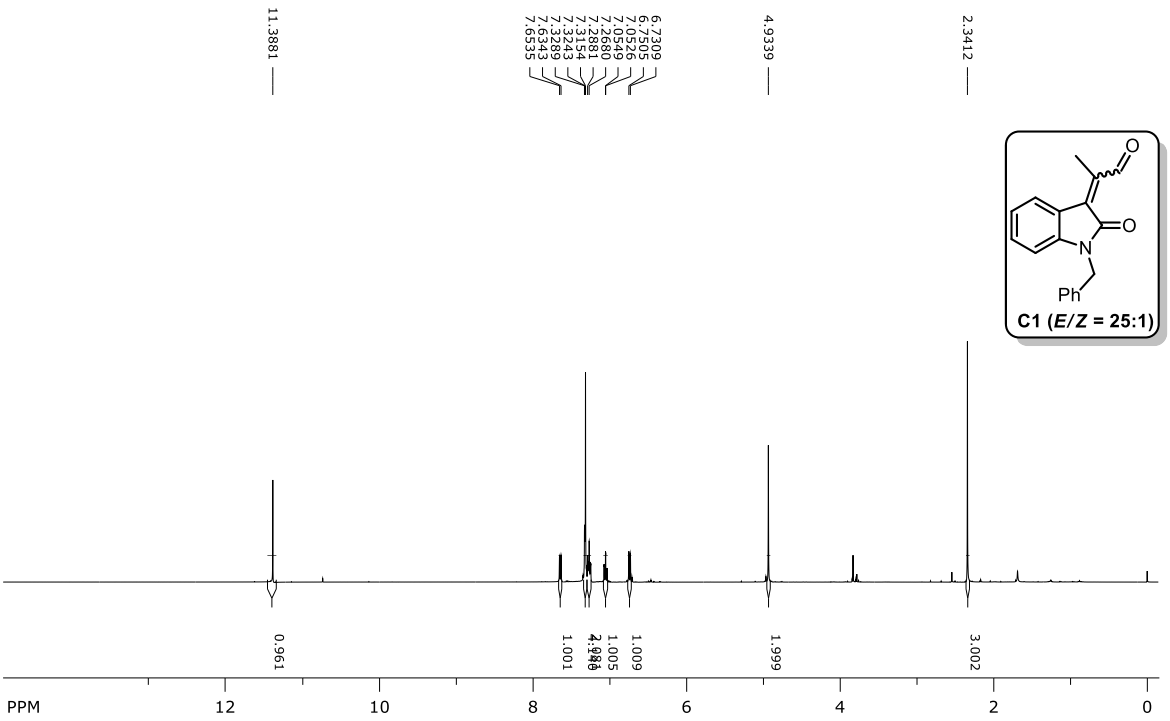
F(000)	576.0
Crystal size/mm^3	0.3 × 0.25 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.996 to 49.978
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -19 ≤ l ≤ 19
Reflections collected	5325
Independent reflections	2636 [R_{int} = 0.0469, R_{sigma} = 0.0726]
Data/restraints/parameters	2636/0/175
Goodness-of-fit on F^2	1.115
Final R indexes [I>=2σ (I)]	R_1 = 0.1098, wR_2 = 0.2943
Final R indexes [all data]	R_1 = 0.1569, wR_2 = 0.3510
Largest diff. peak/hole / e $Å^{-3}$	1.16/-0.47

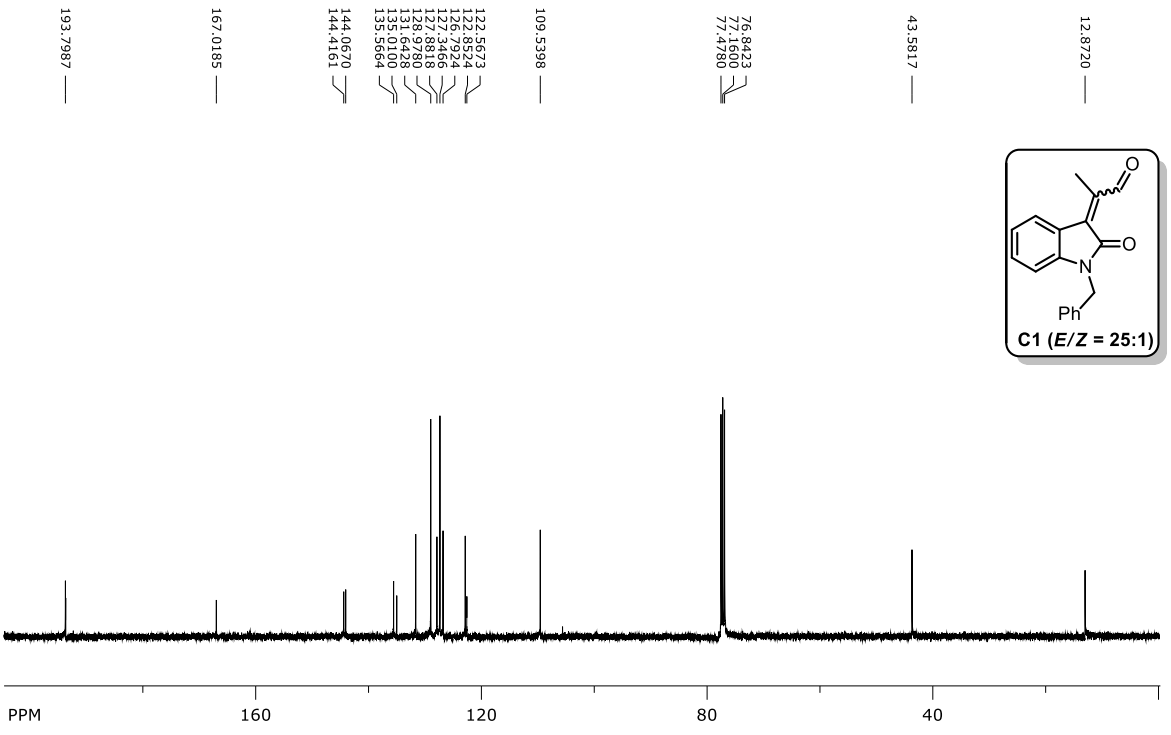
References

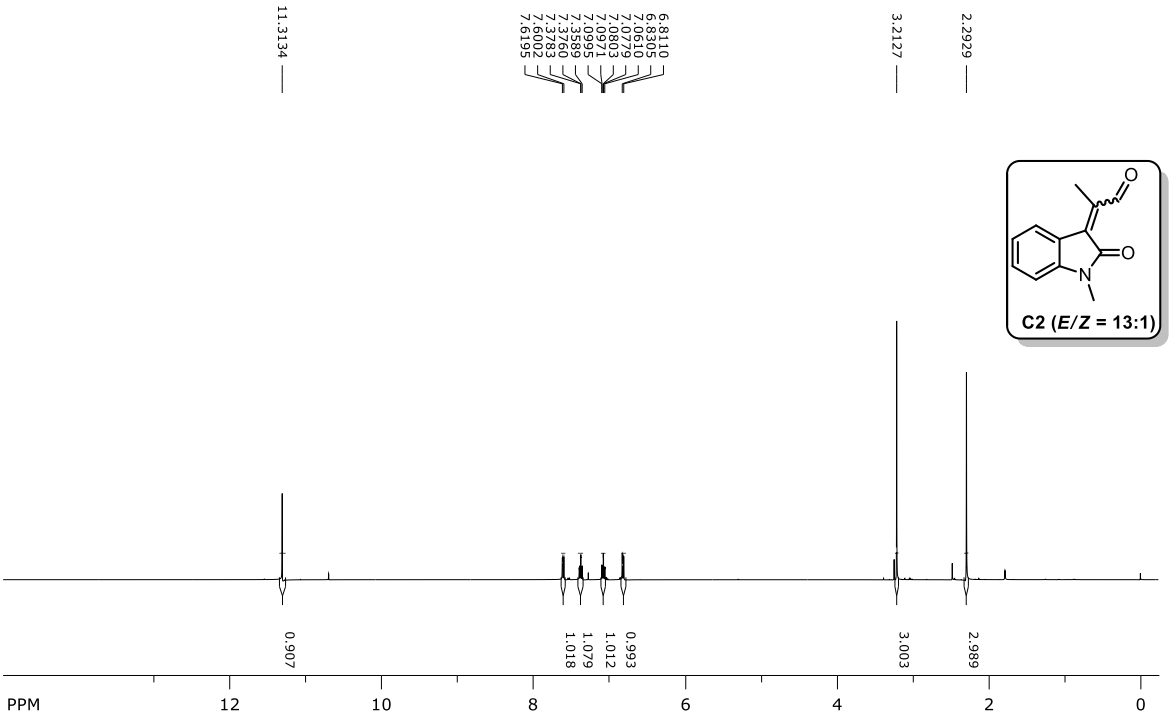
1. (*a*) D. C. Truhlar, B. C. Garrett. In *Isotope Effects in Chemistry and Biology*; A. Kohen, H.-H. Limbach, Eds.; Taylor & Francis: New York, 2006; pp 579-620; (*b*) H. Gu and S. Zhang, *Molecules*, 2013, 18, 9278 and references cited therein.

2. For the study of kinetic isotope effects in organometallic reactions, see: (*a*) W. D. Jones, *Acc. Chem. Res.*, 2003, 36, 140; (*b*) J.-J. Li, R. Giri and J.-Q. Yu, *Tetrahedron*, 2008, 64, 6979; (*c*) A. García-Rubia, B. Urones, R. G. Arrayas and J. C. Carretero, *Chem. Eur. J.*, 2010, 16, 9676; (*d*) M. Gomez-Gallego and M. A. Sierra, *Chem. Rev.*, 2011, 111, 4857; (*e*) E. M. Simmons and J. F. Hartwig, *Angew. Chem. Int. Ed*., 2012, 51, 3066.

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



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PPM
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10
8
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2
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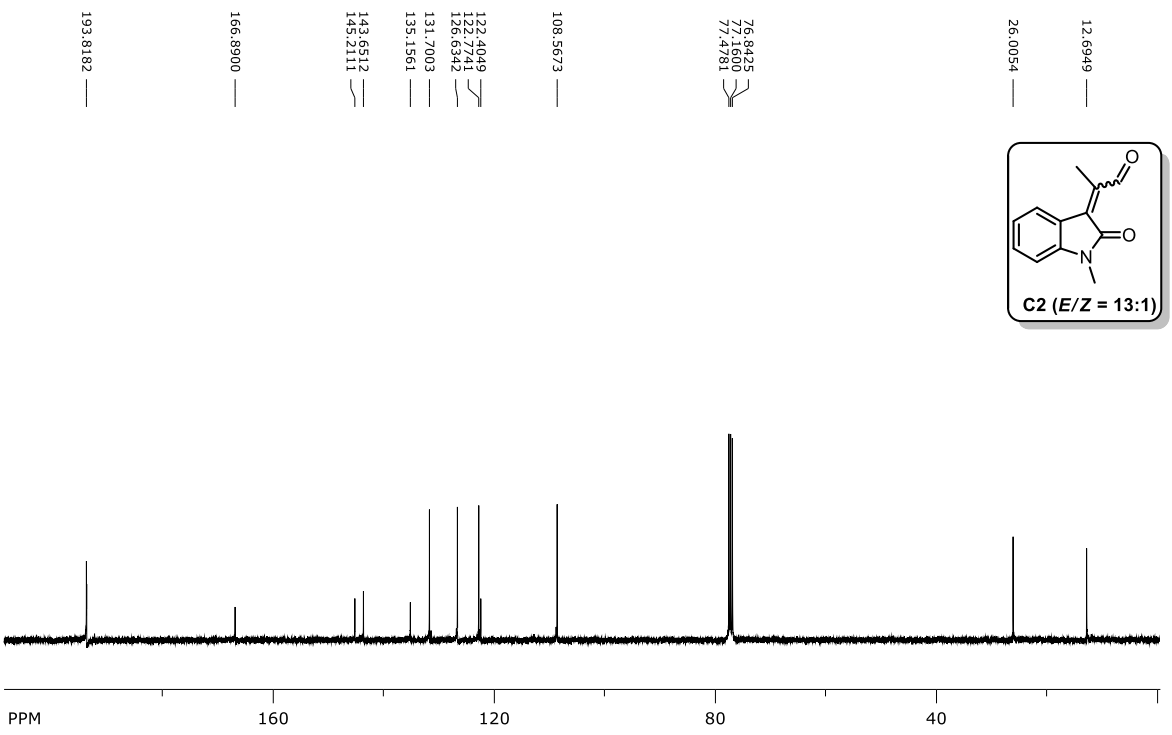
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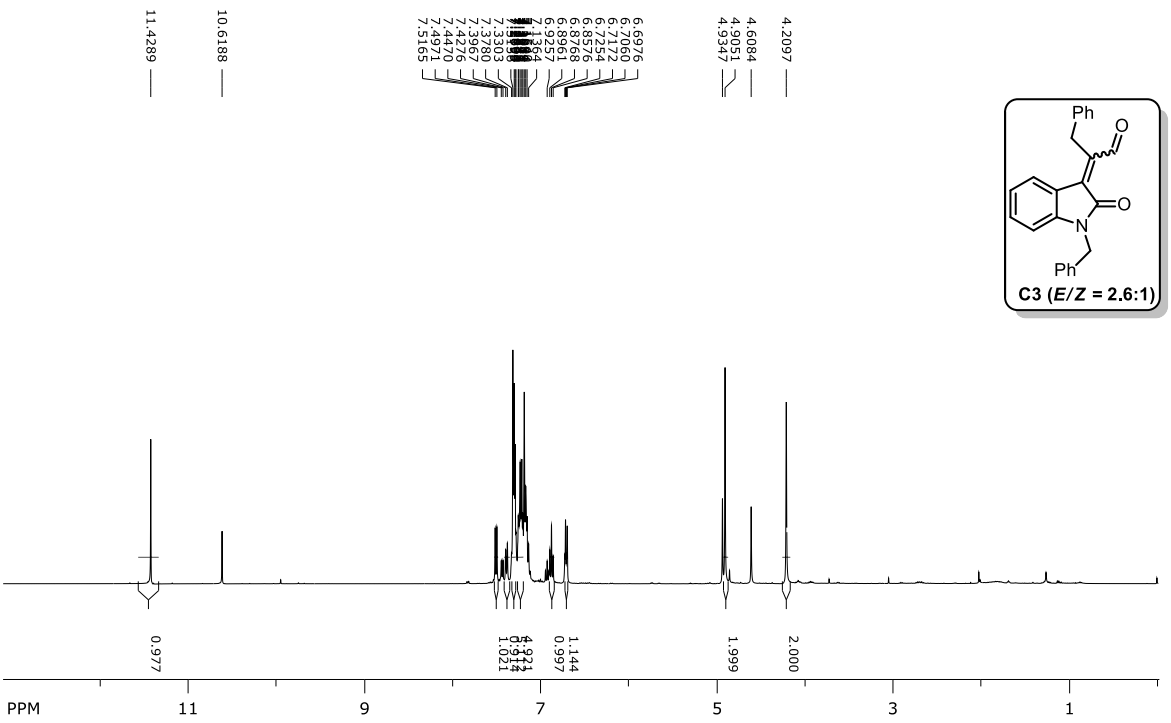
80
40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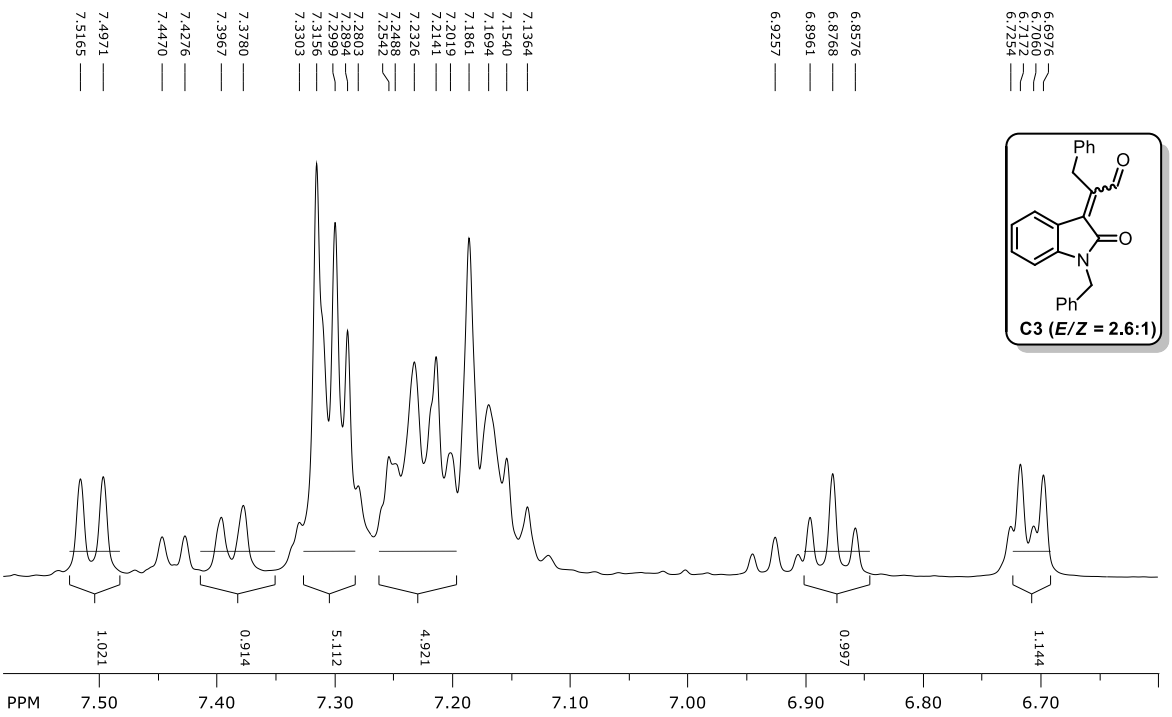
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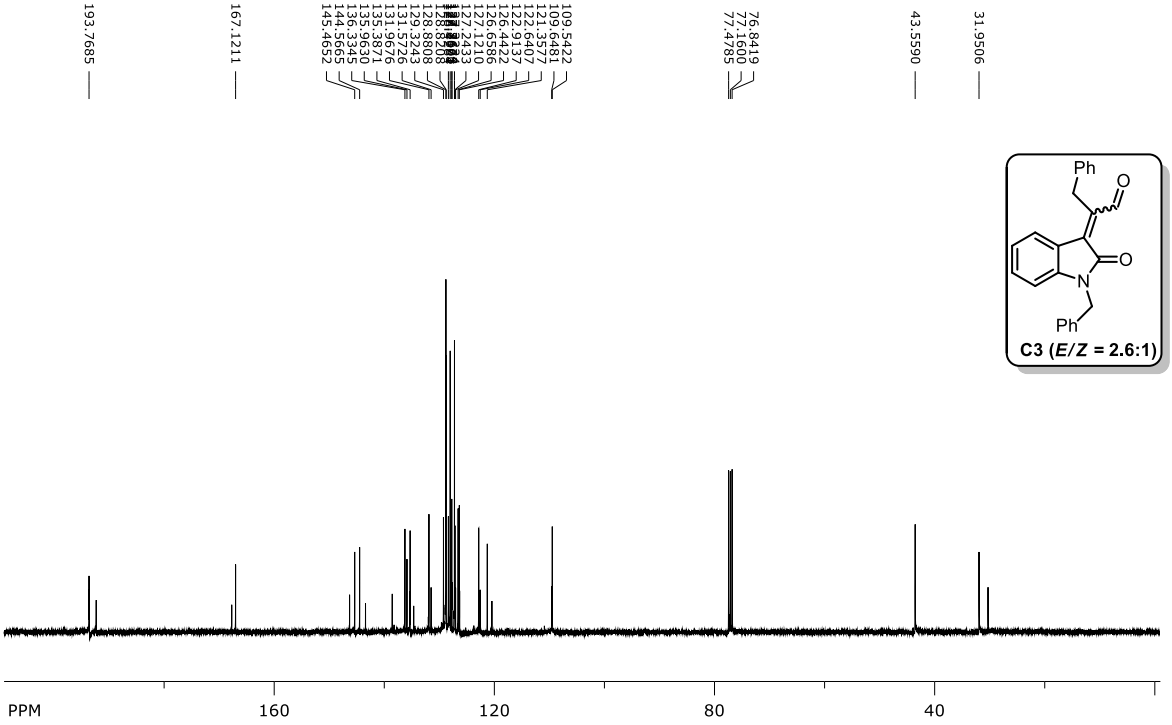
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80
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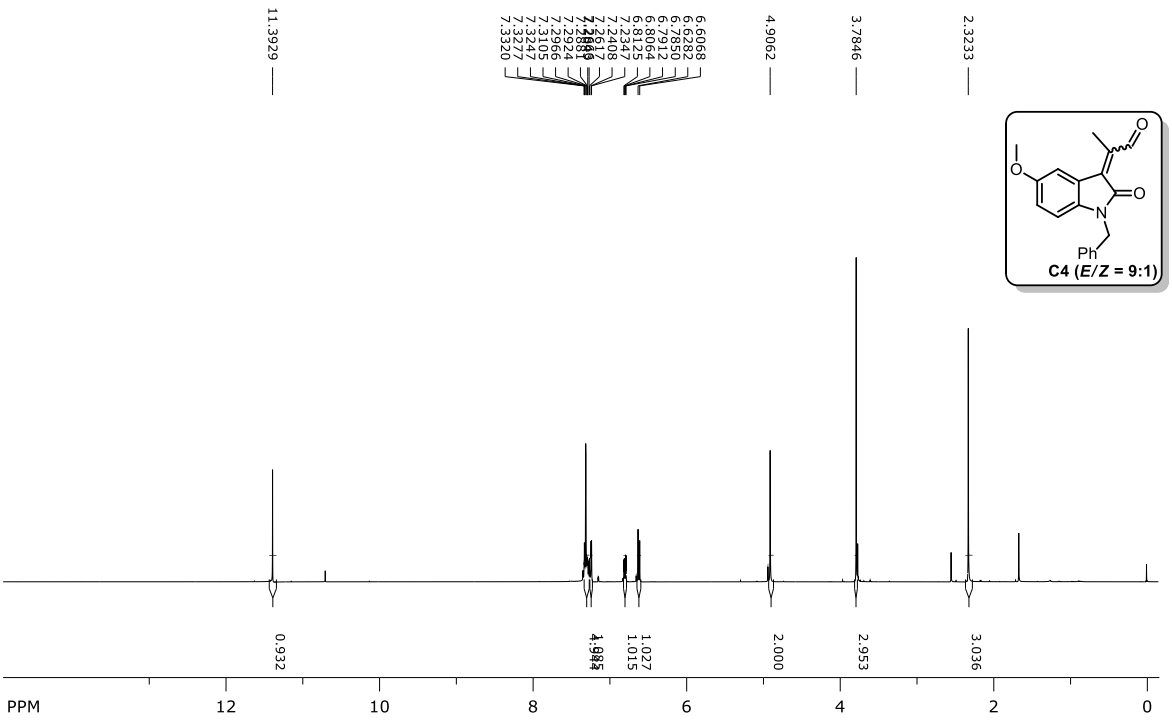
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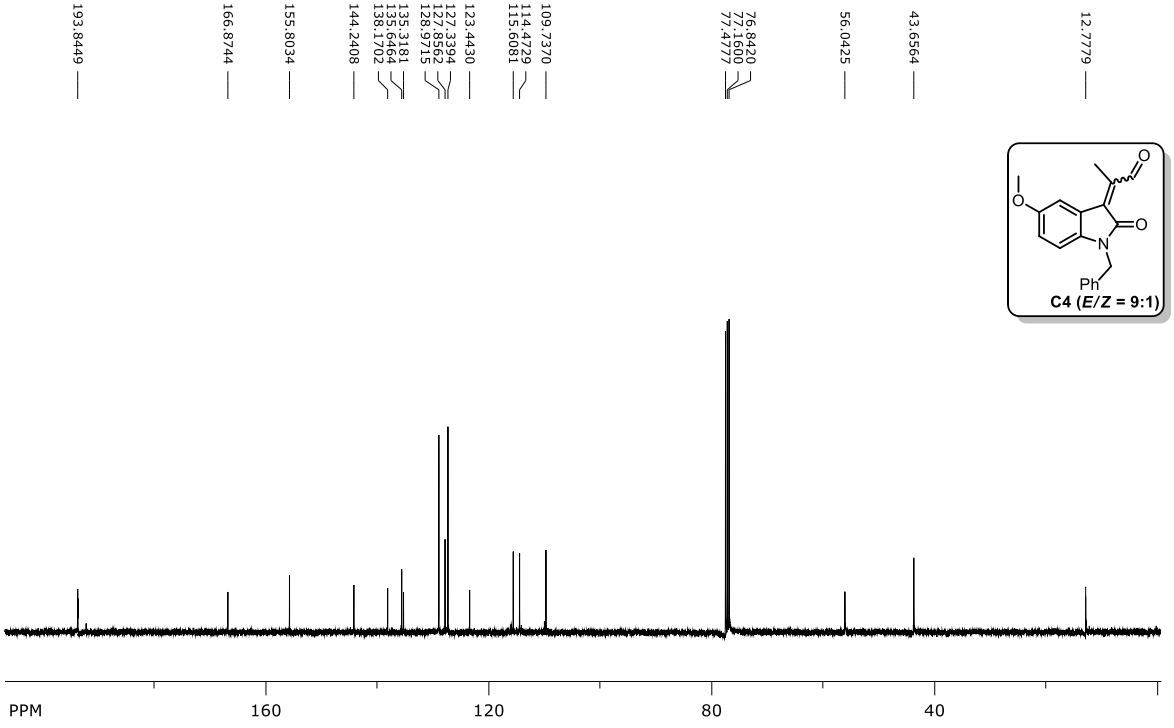
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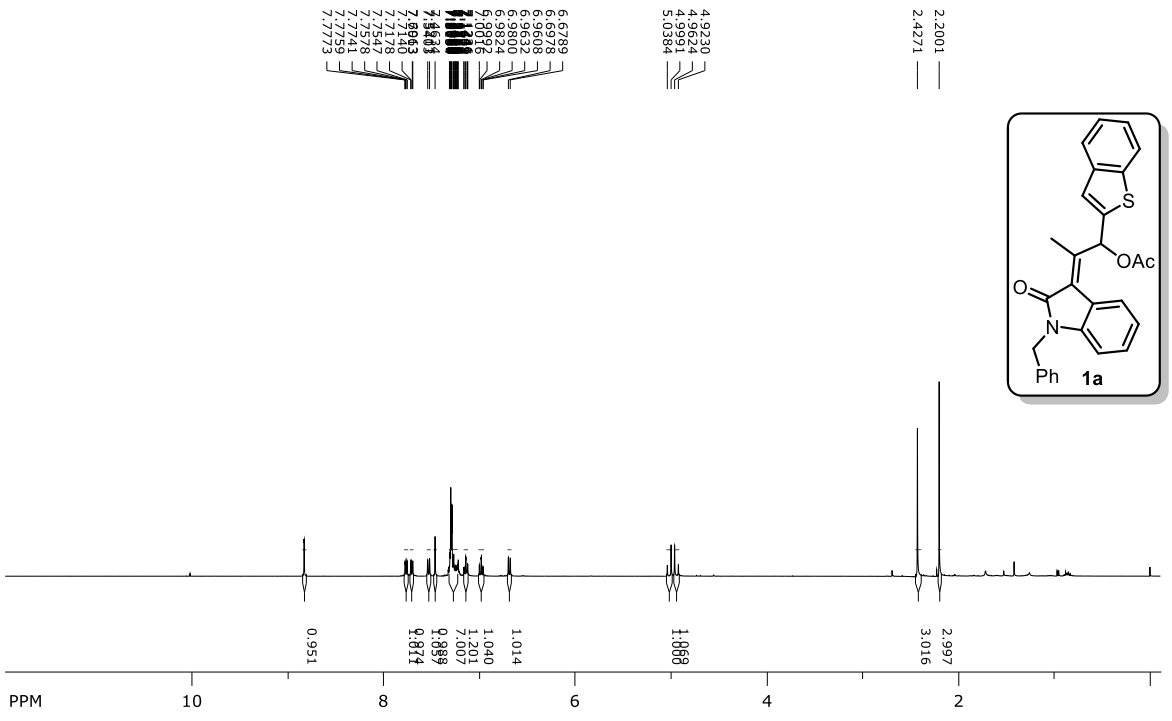
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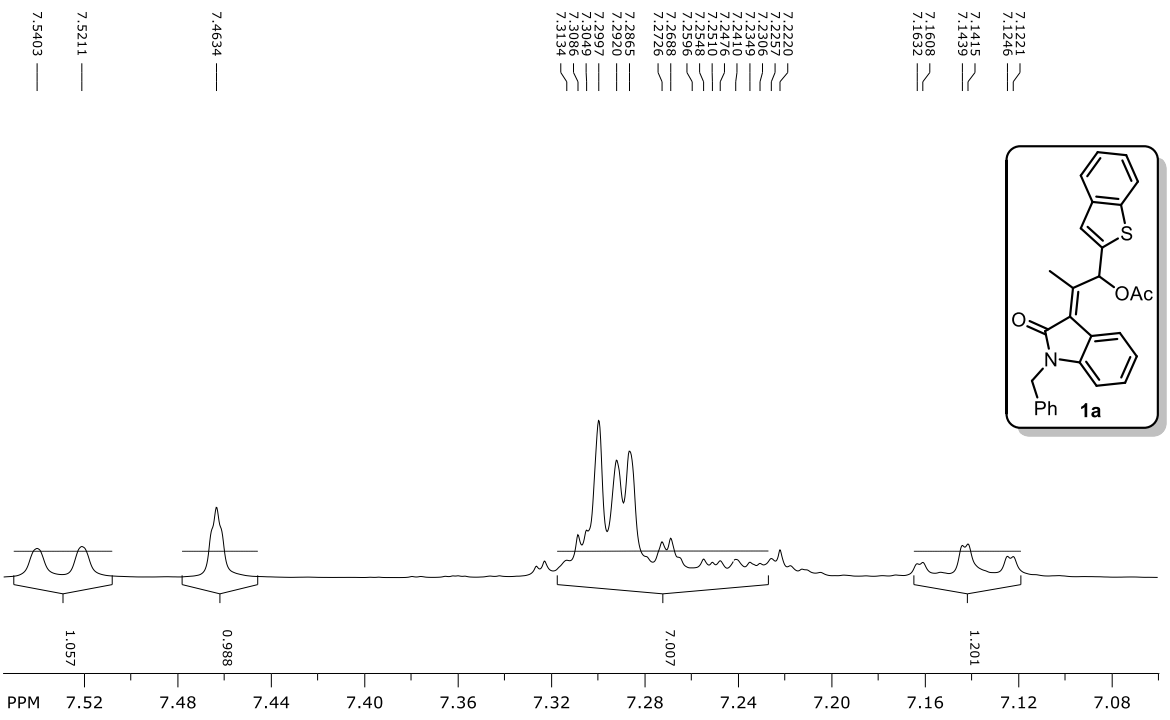
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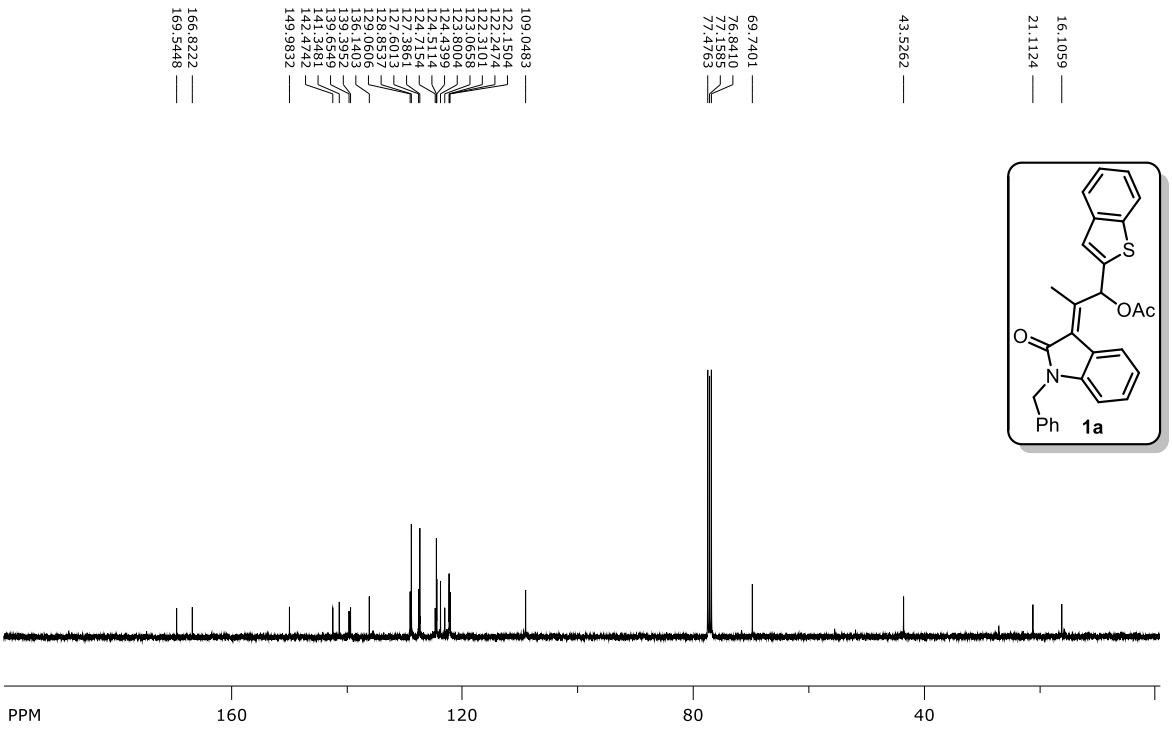
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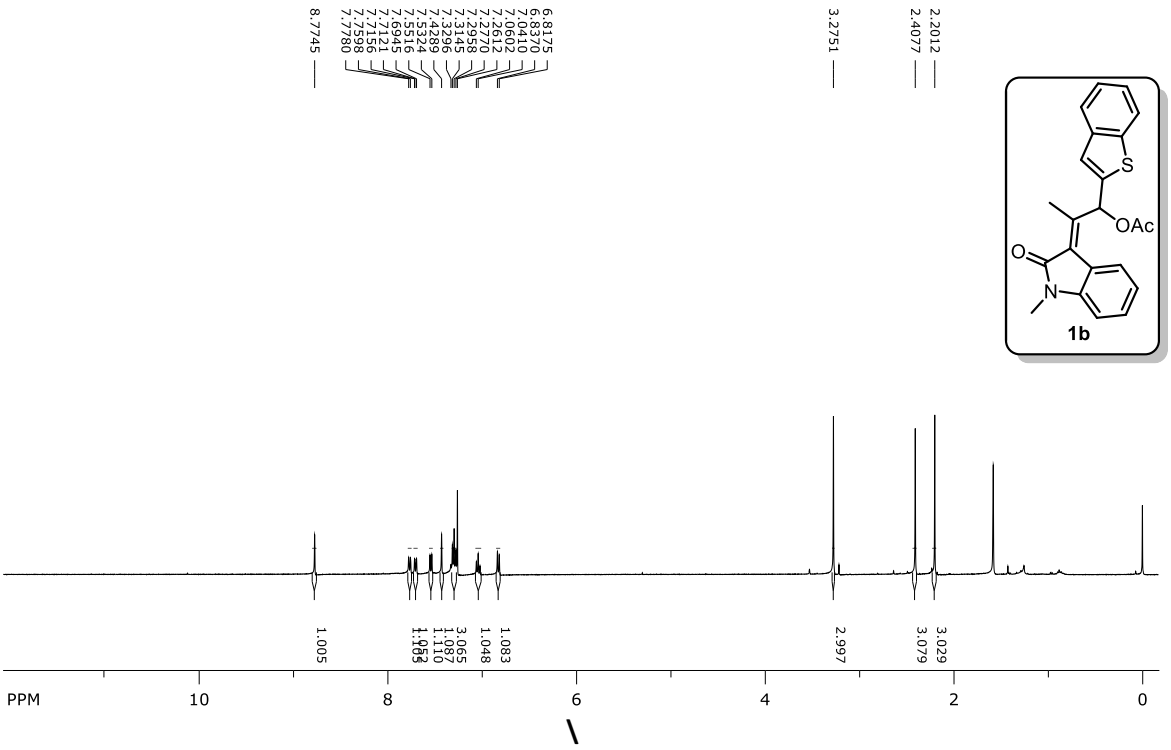
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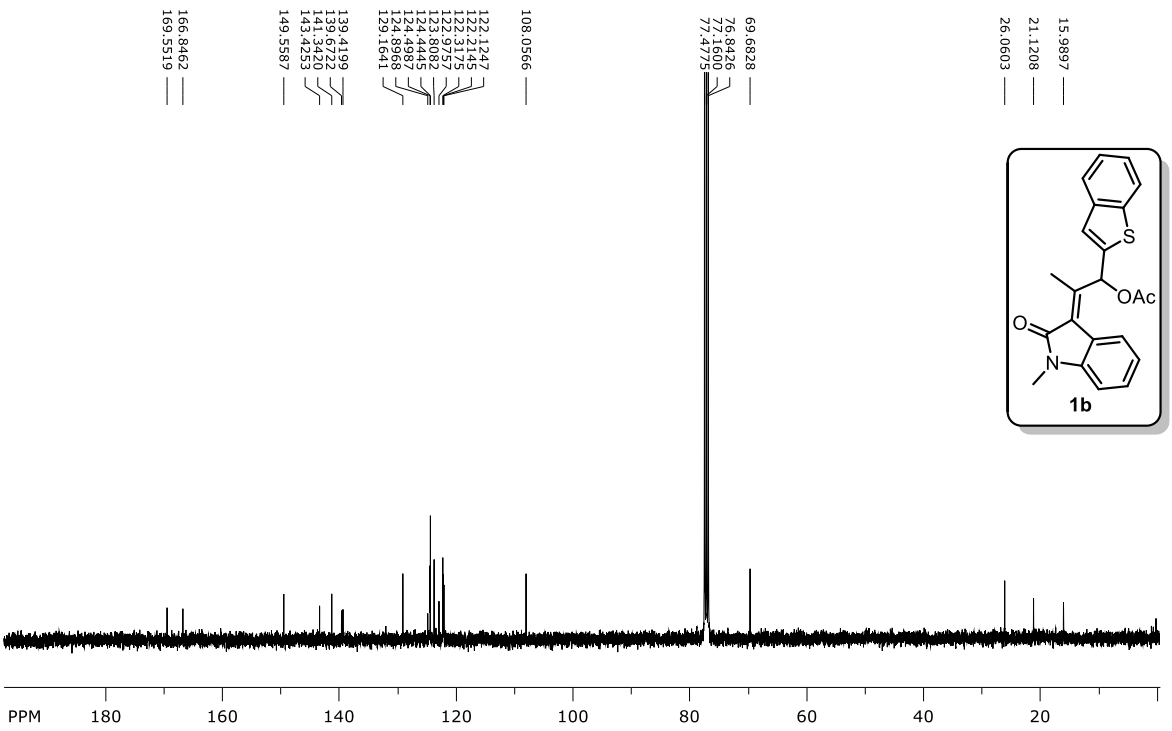
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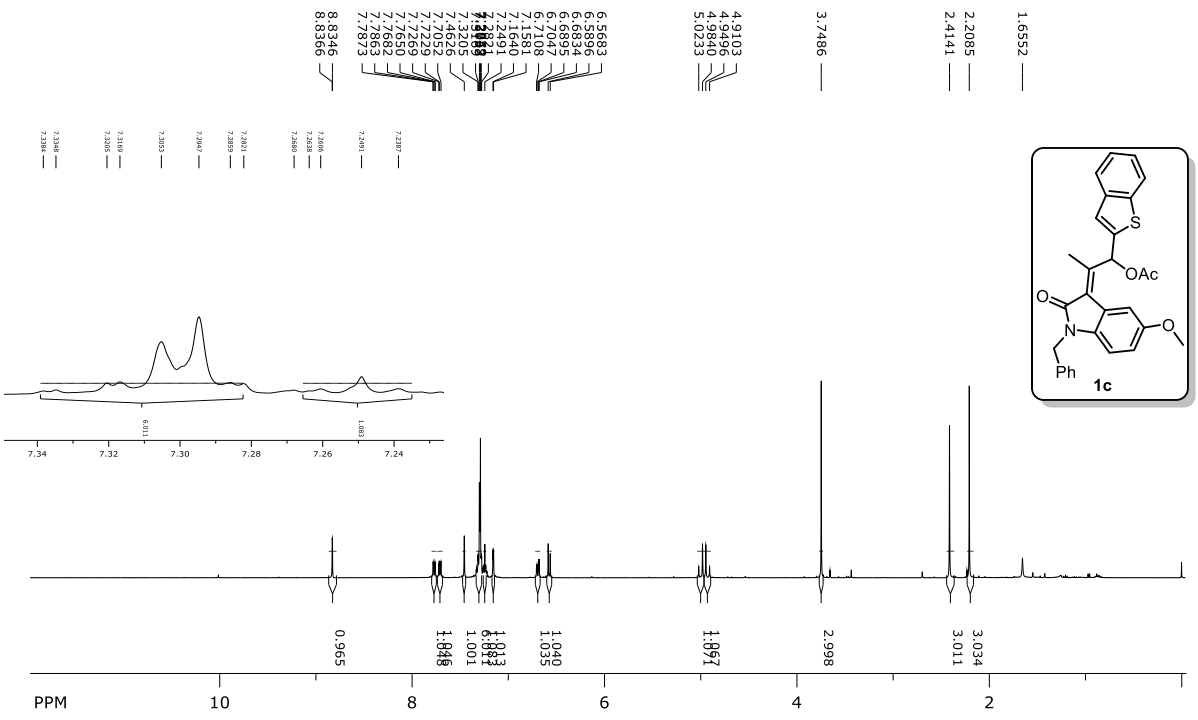
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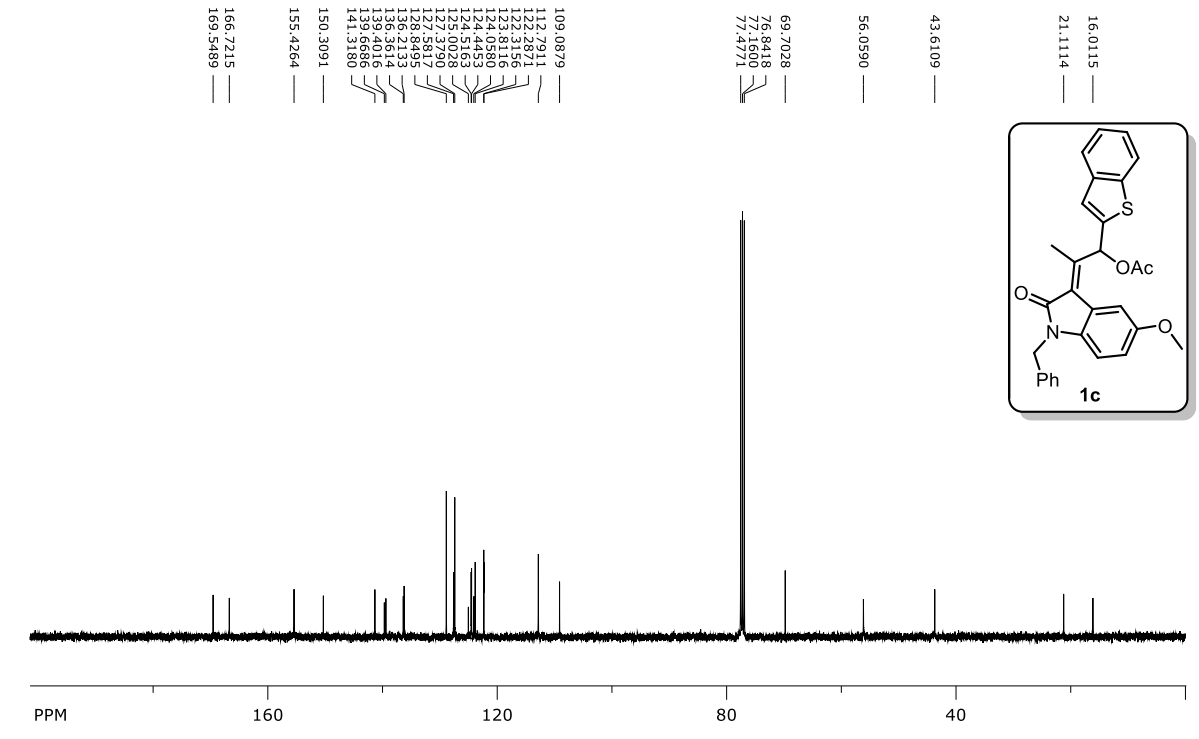
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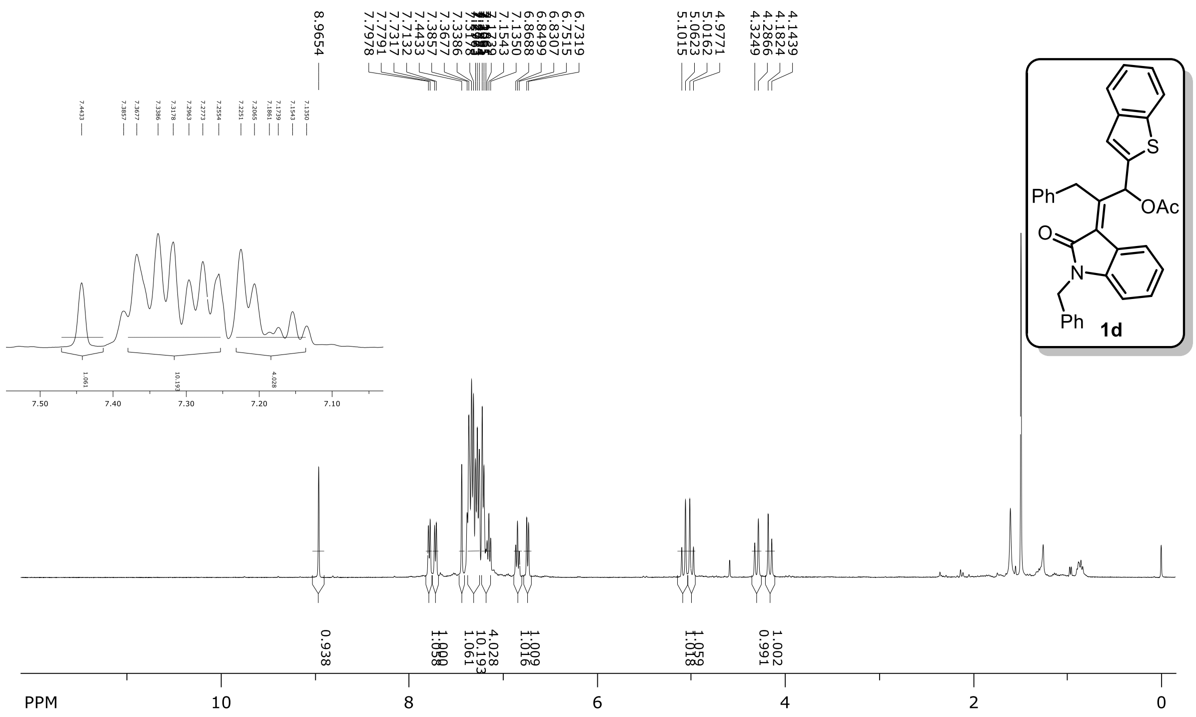
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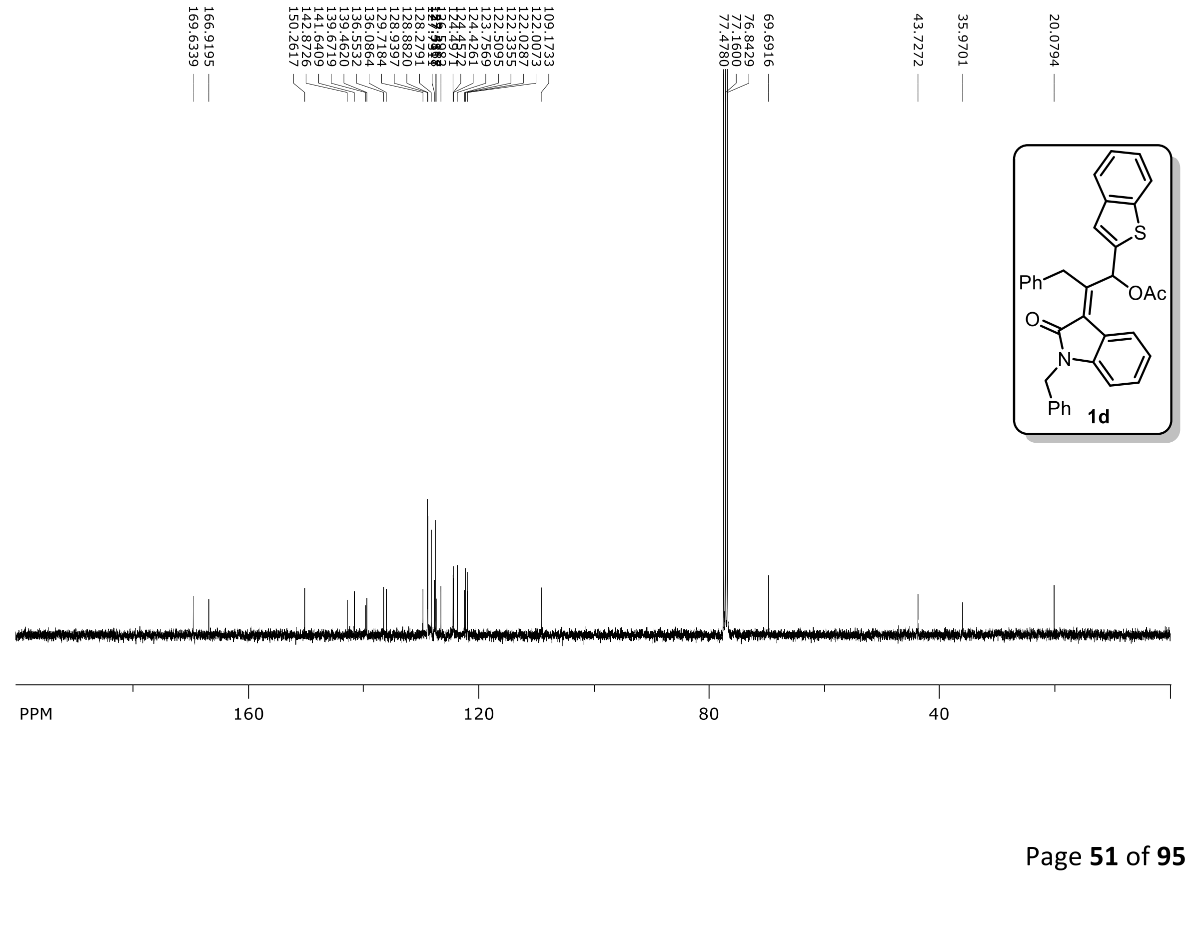
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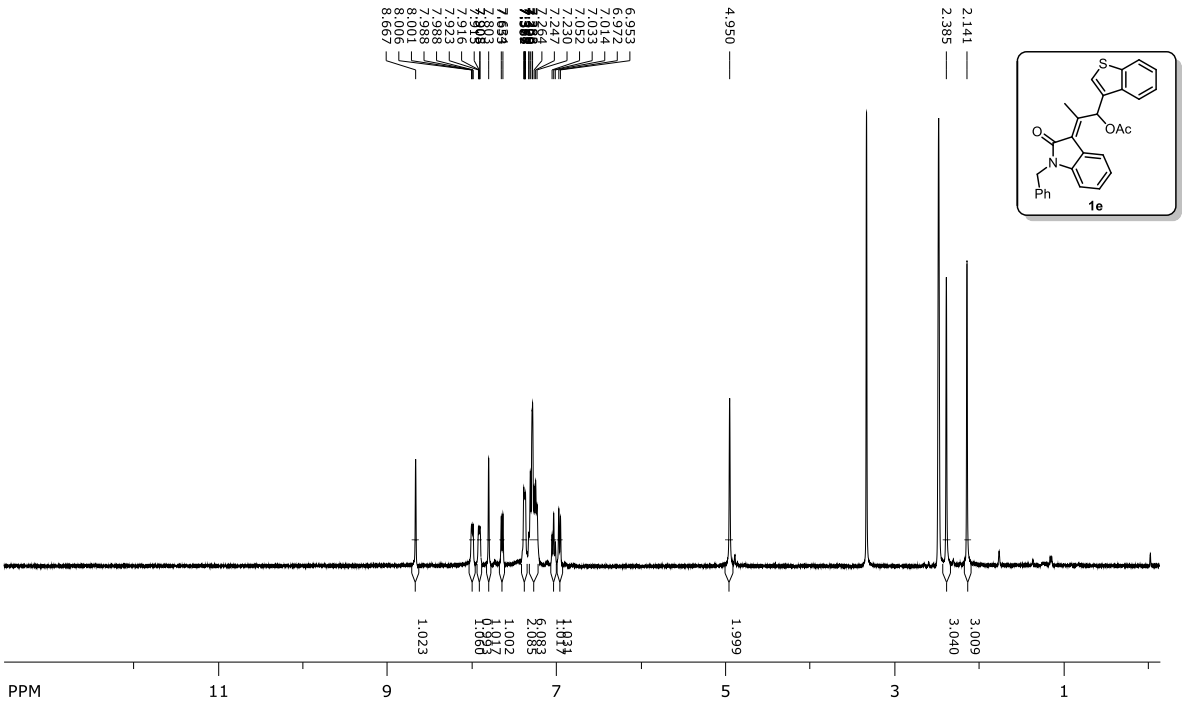
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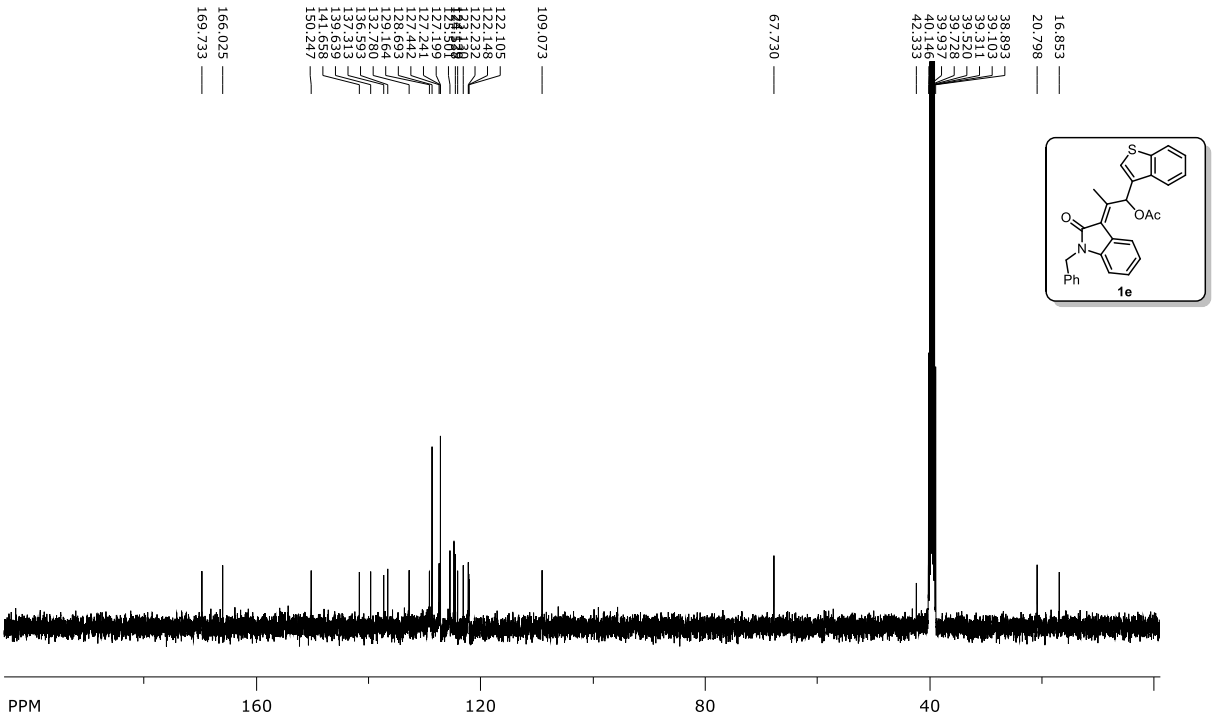
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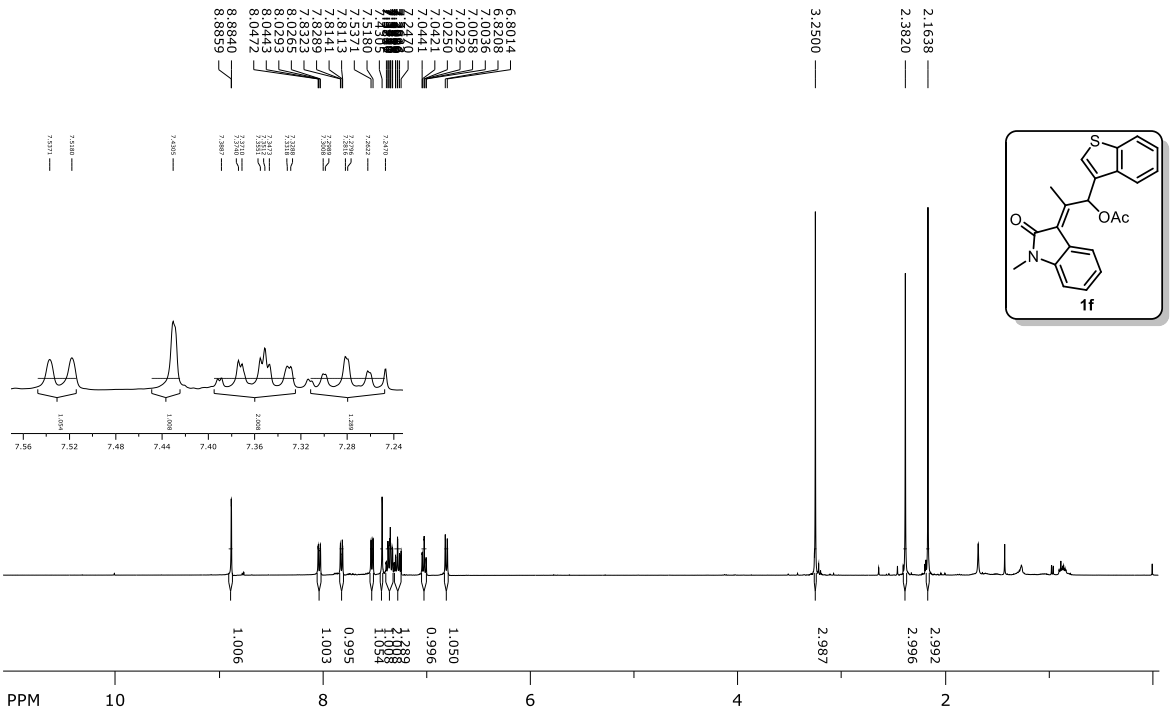
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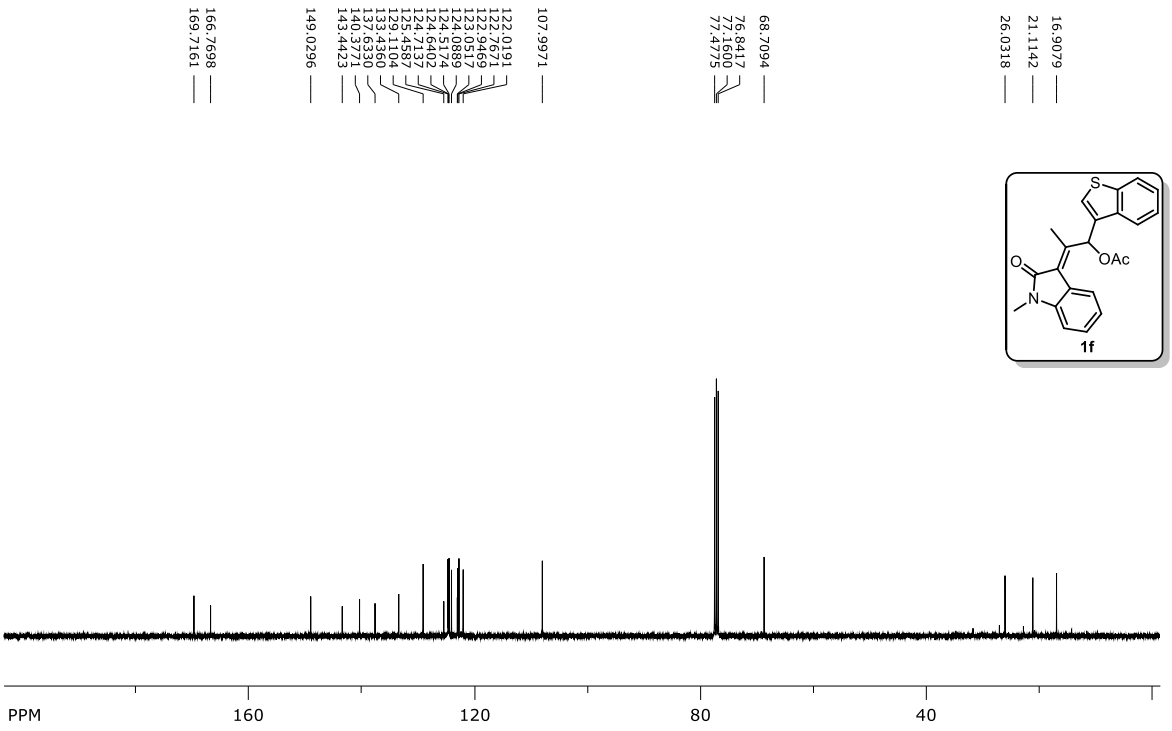
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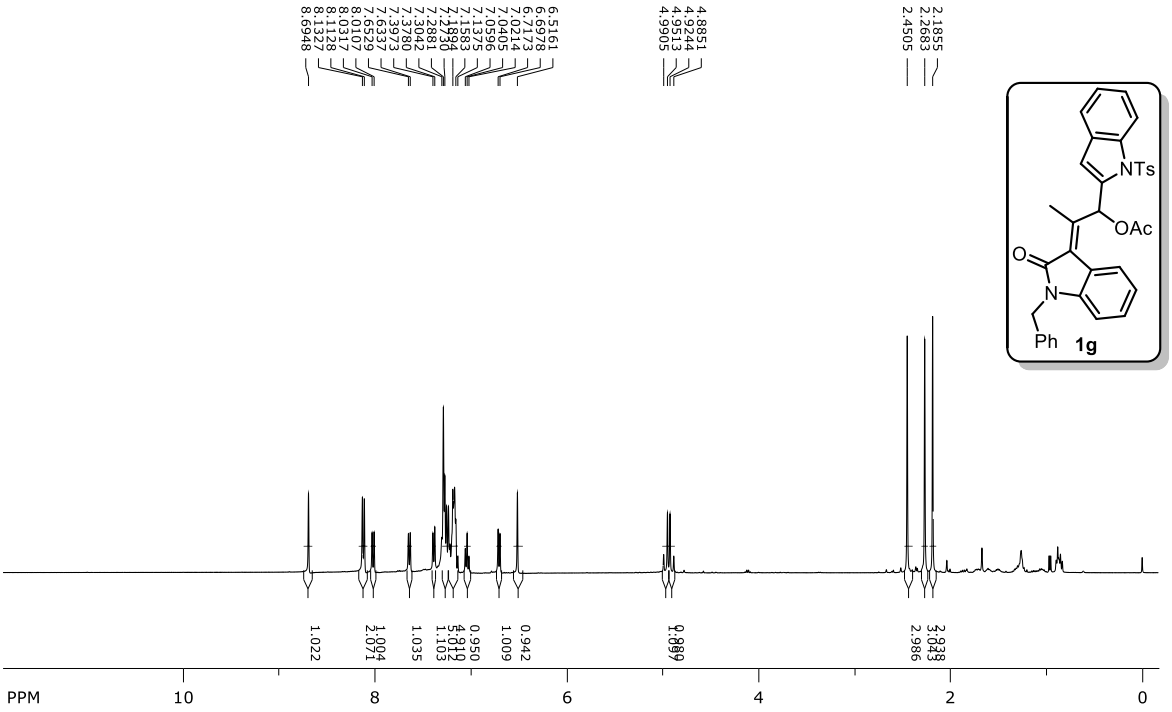
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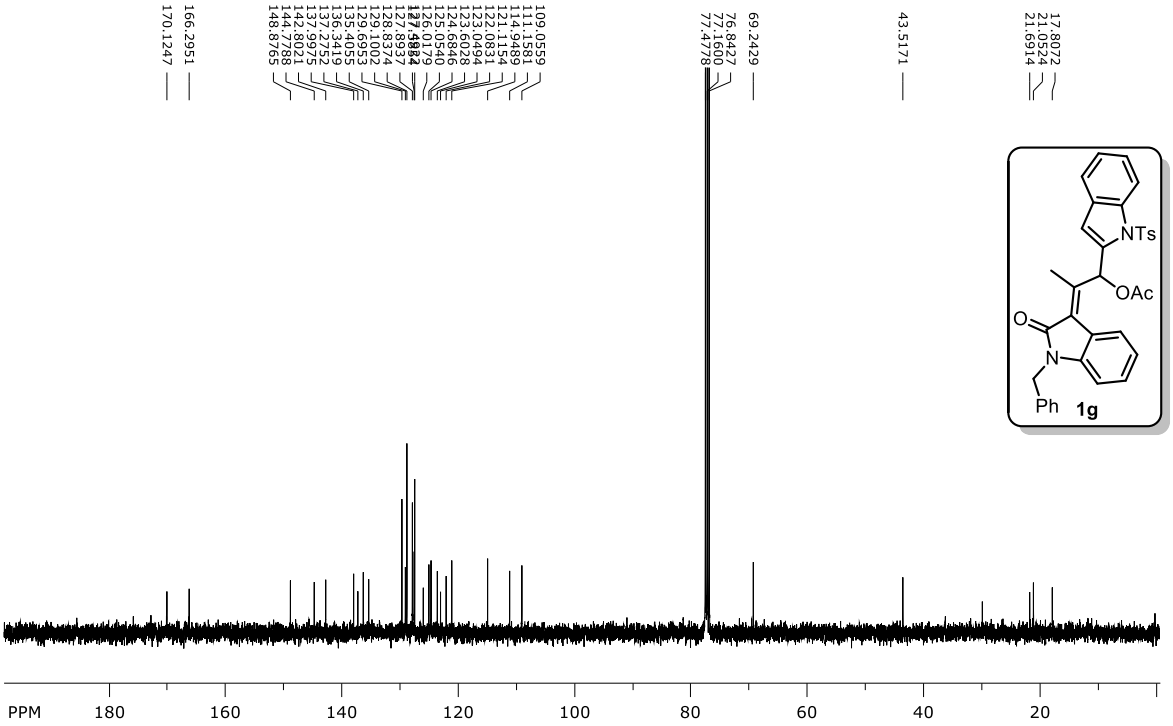
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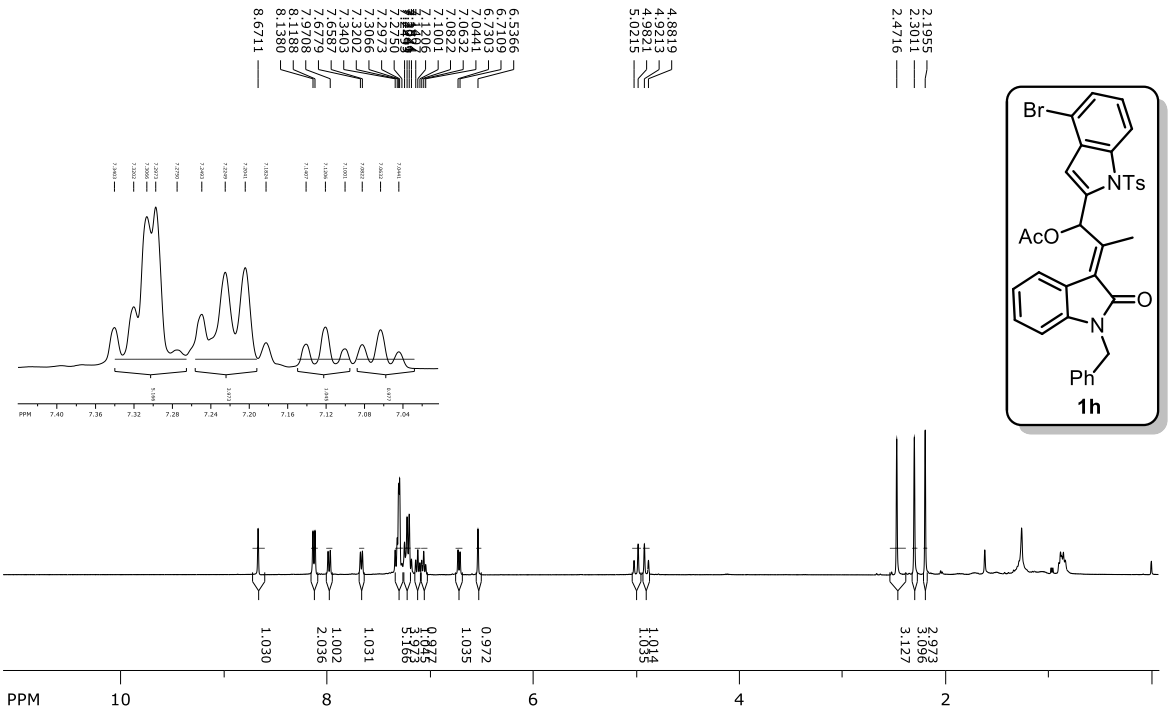
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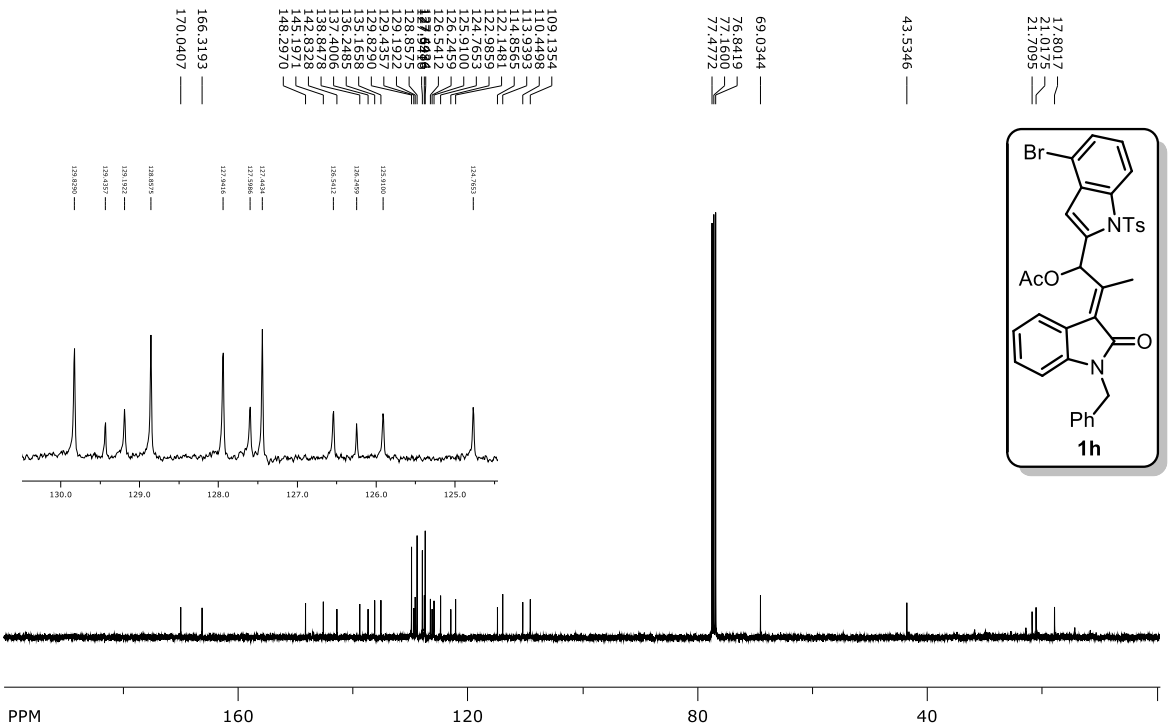
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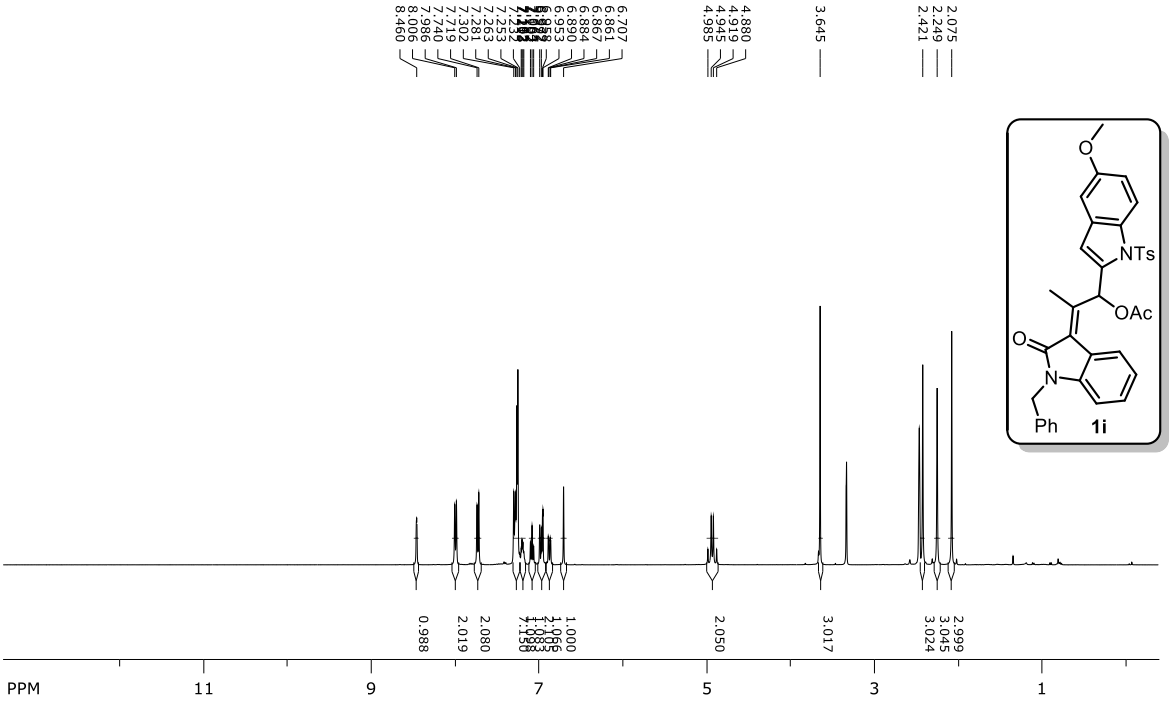
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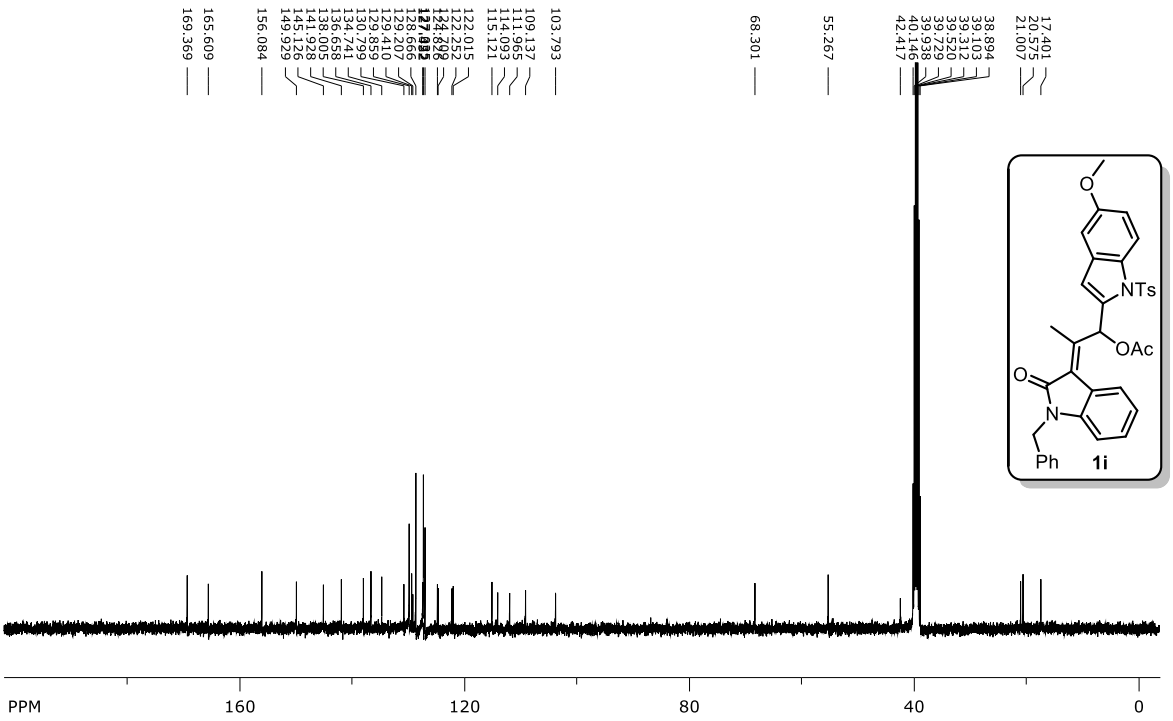
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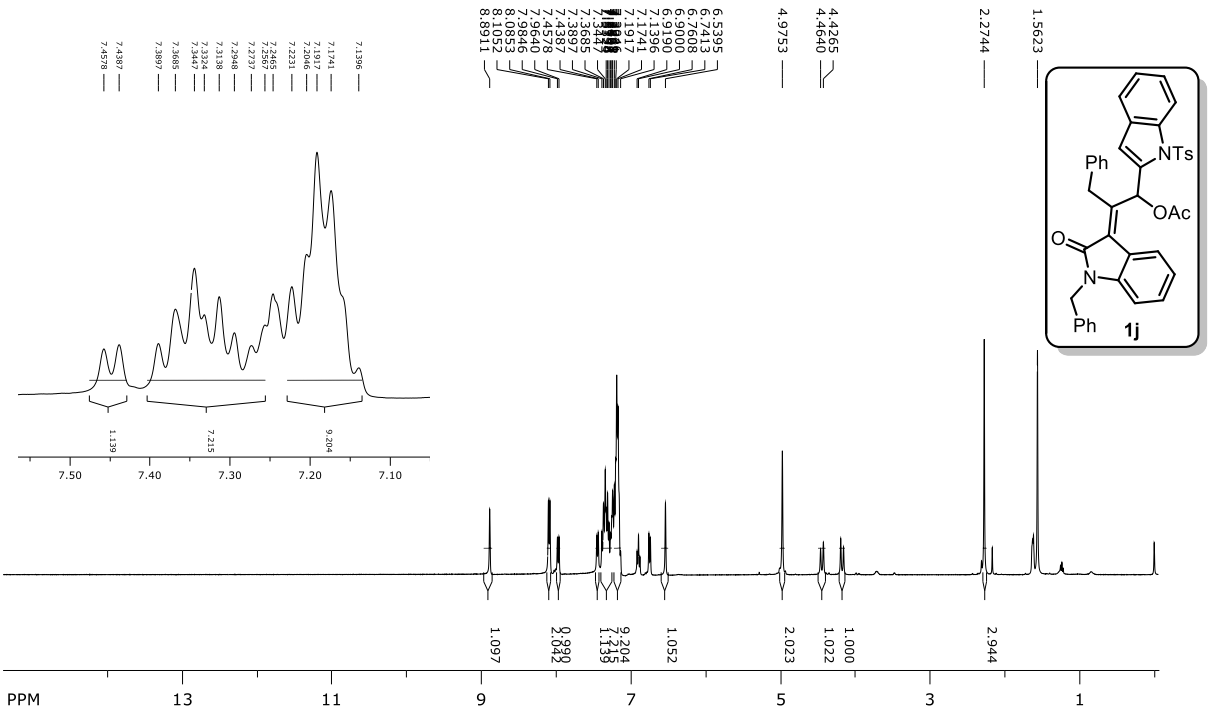
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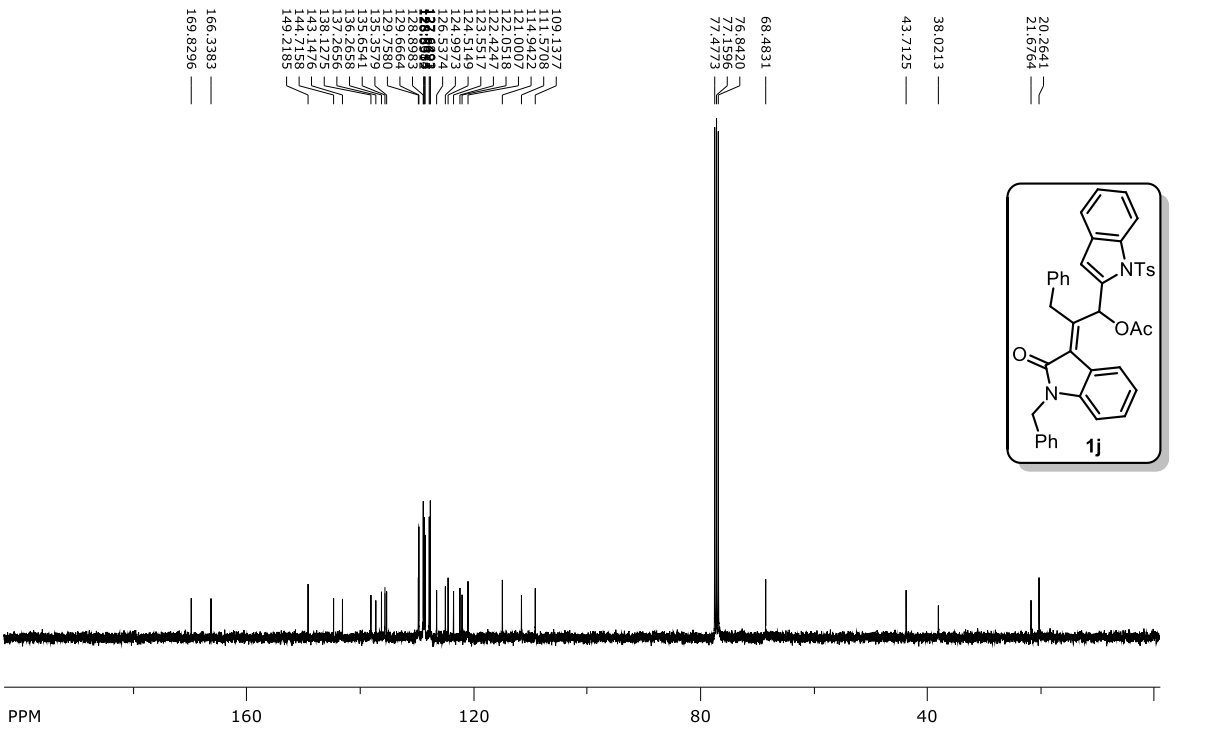
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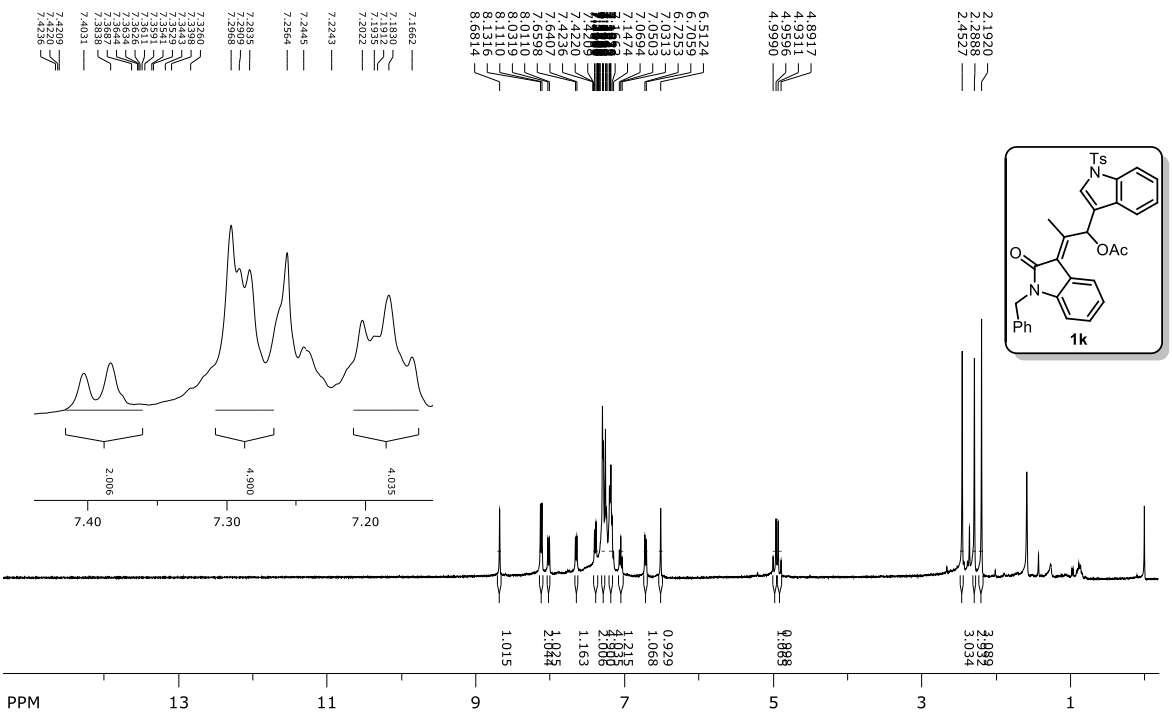
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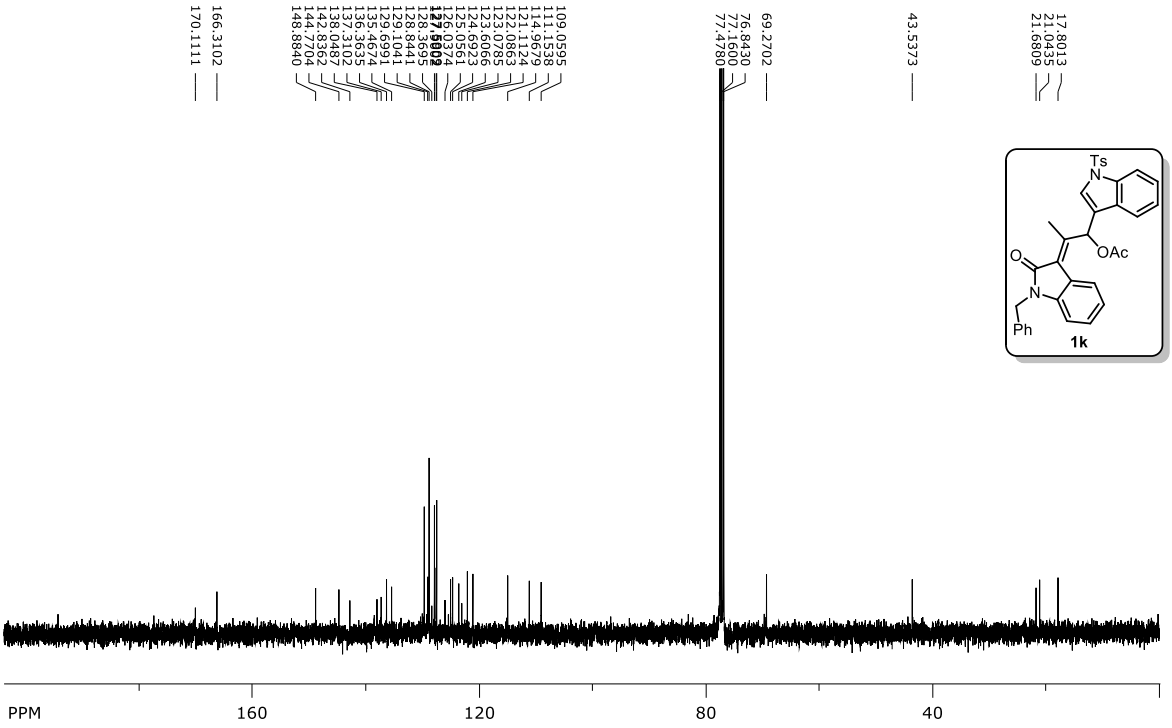
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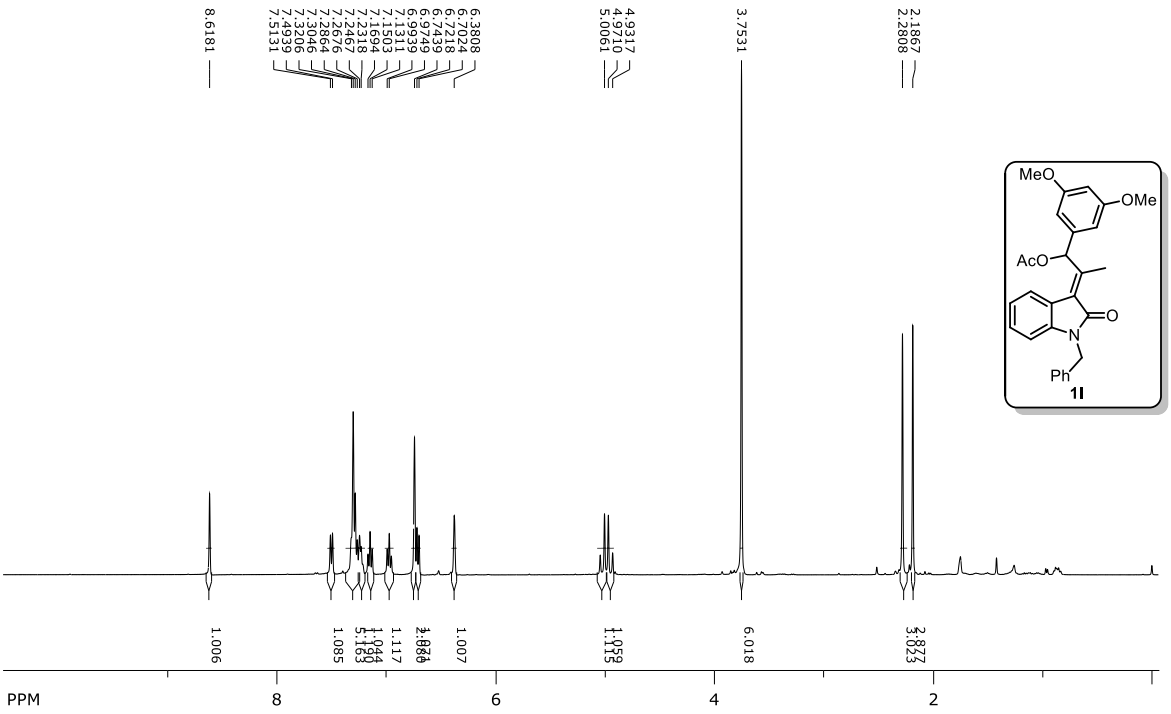
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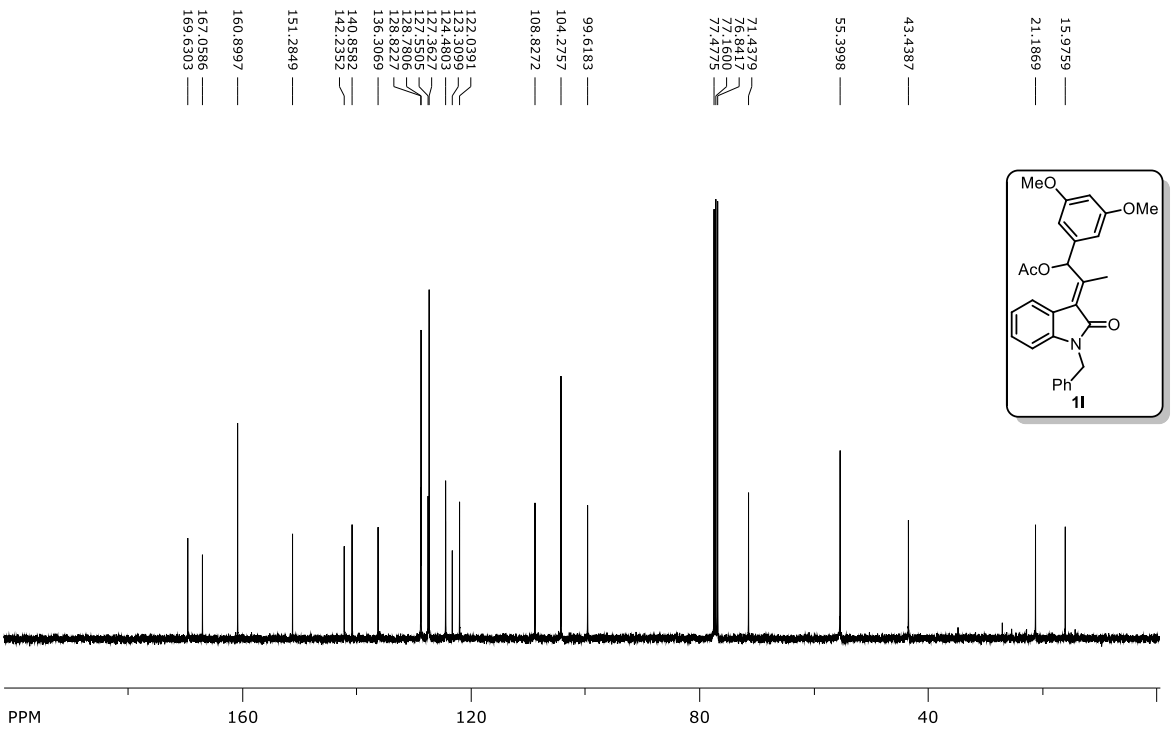
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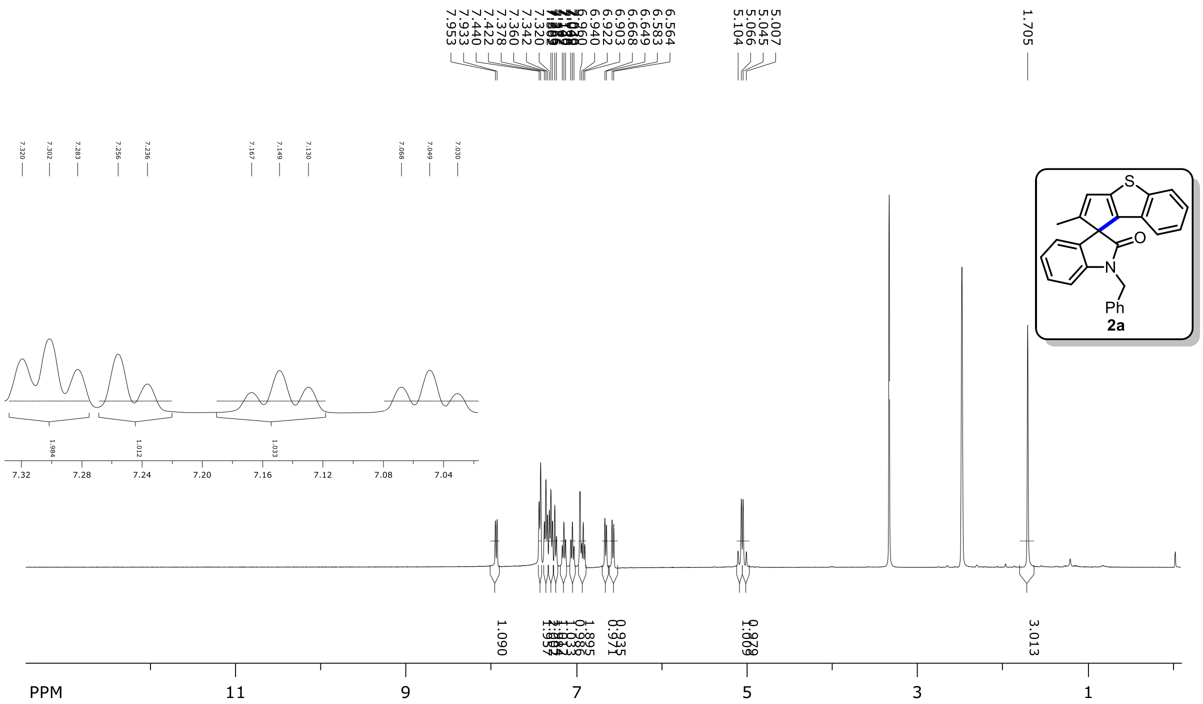
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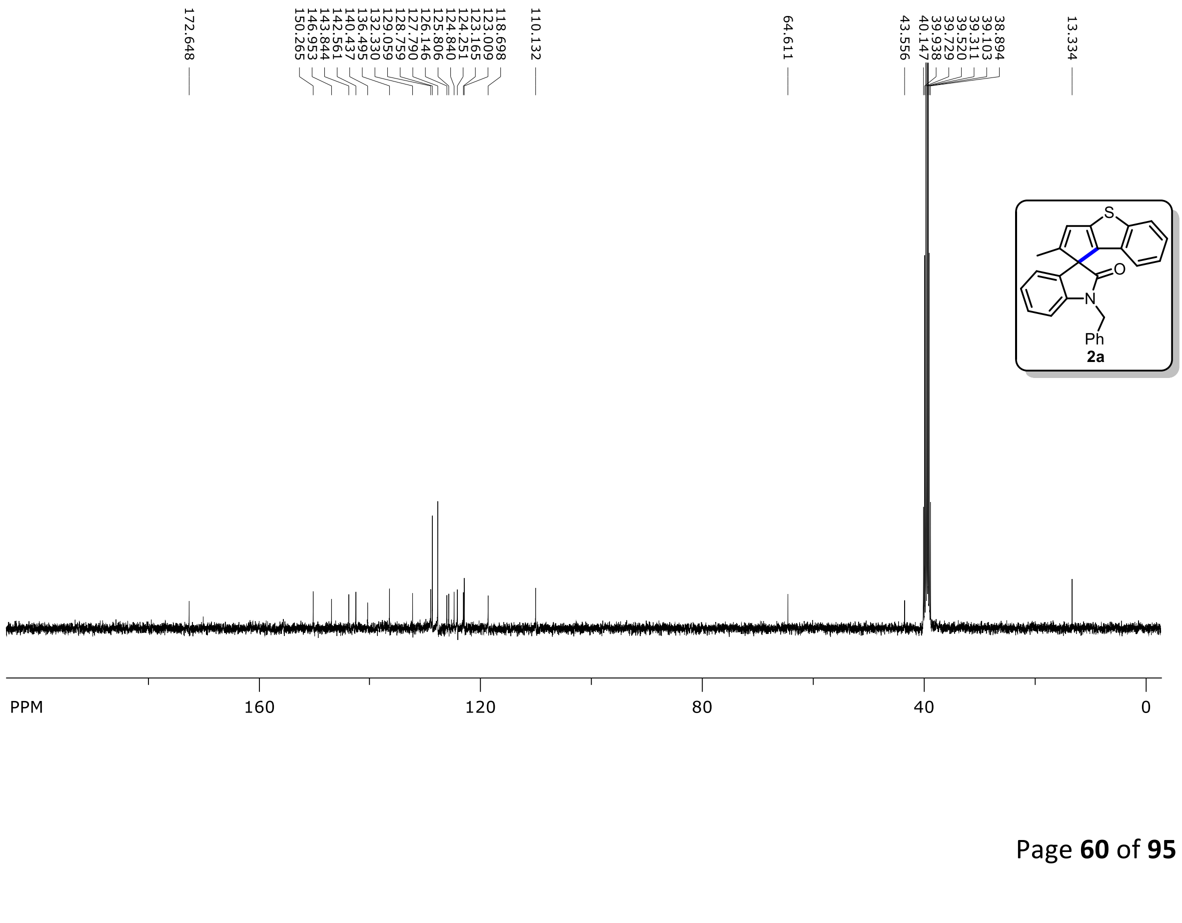
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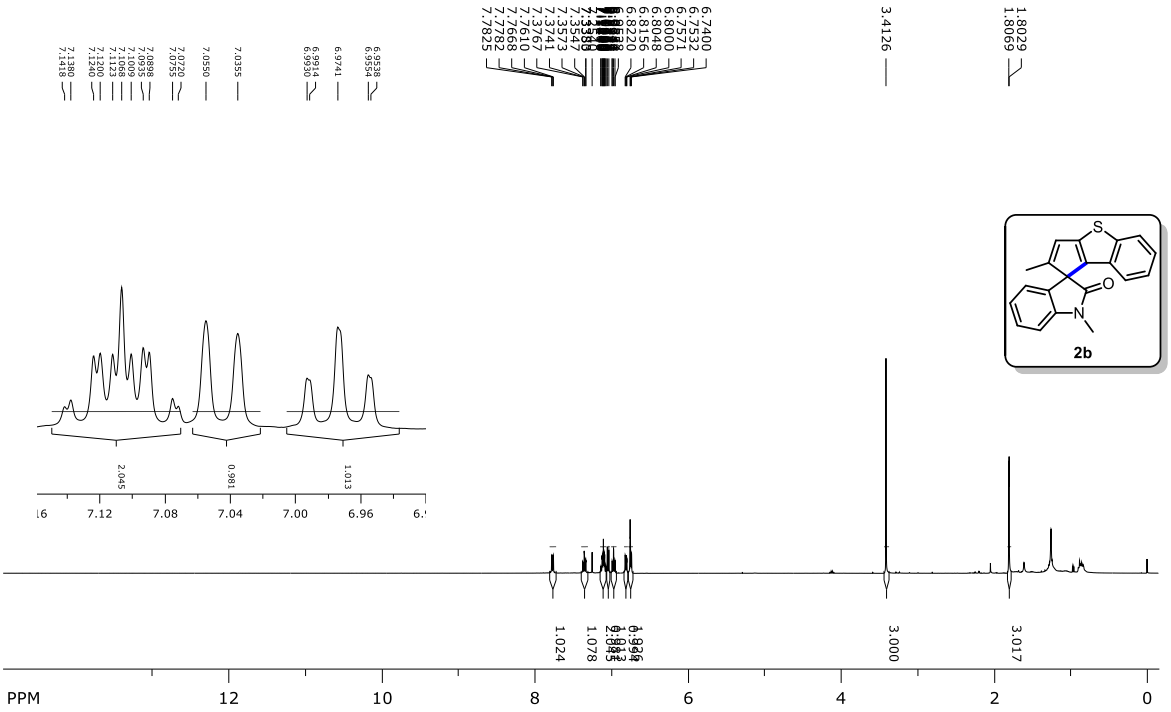
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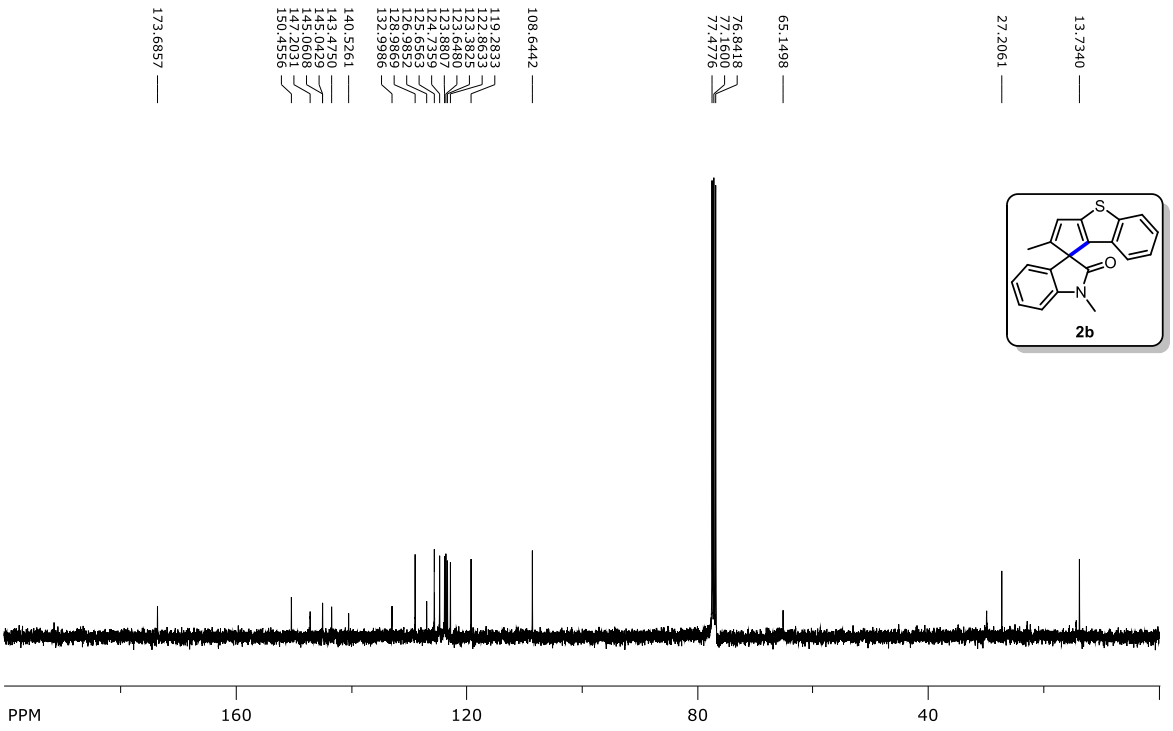
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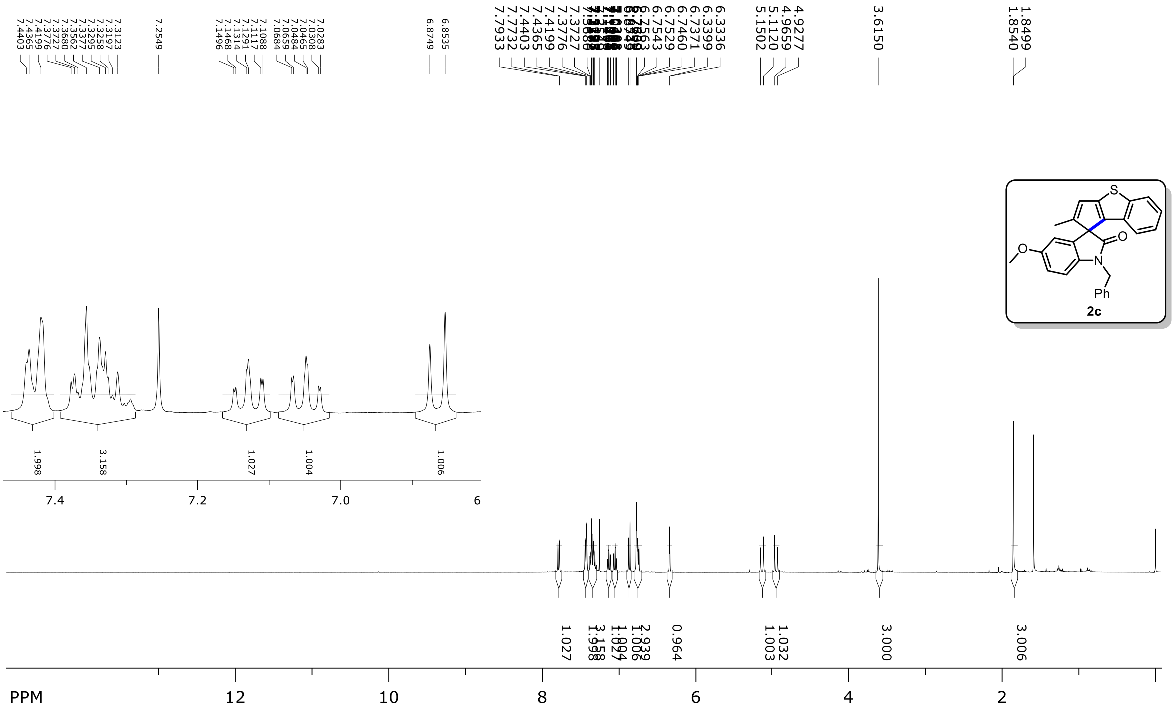
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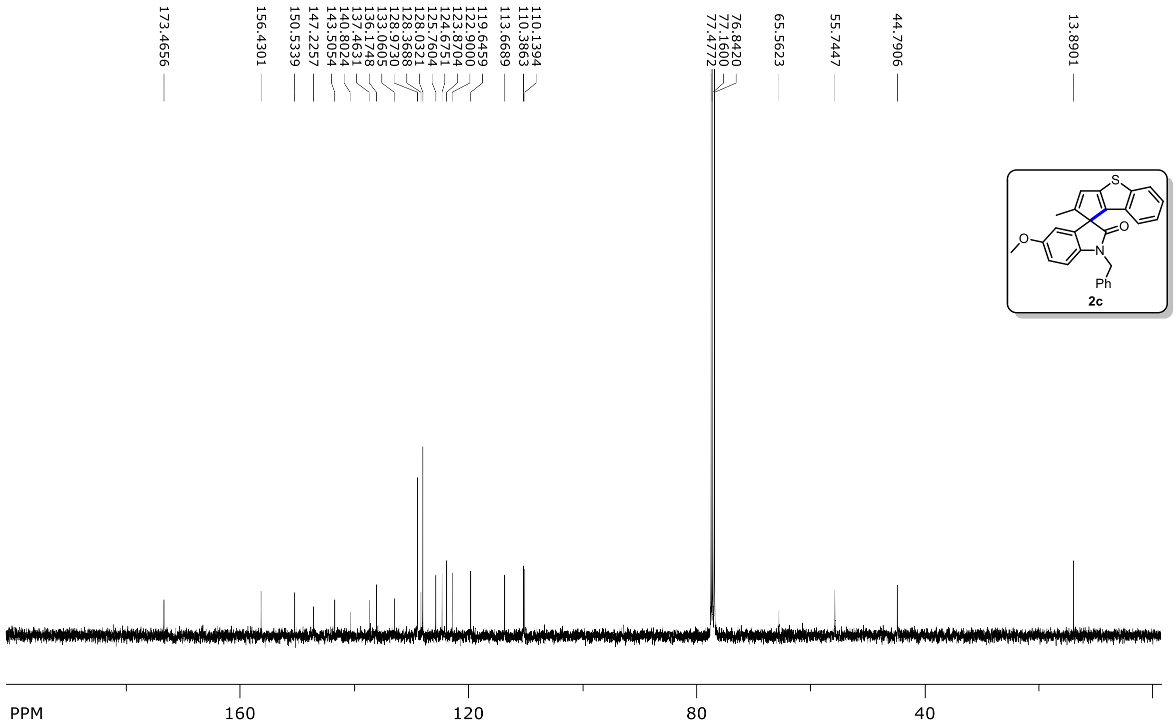
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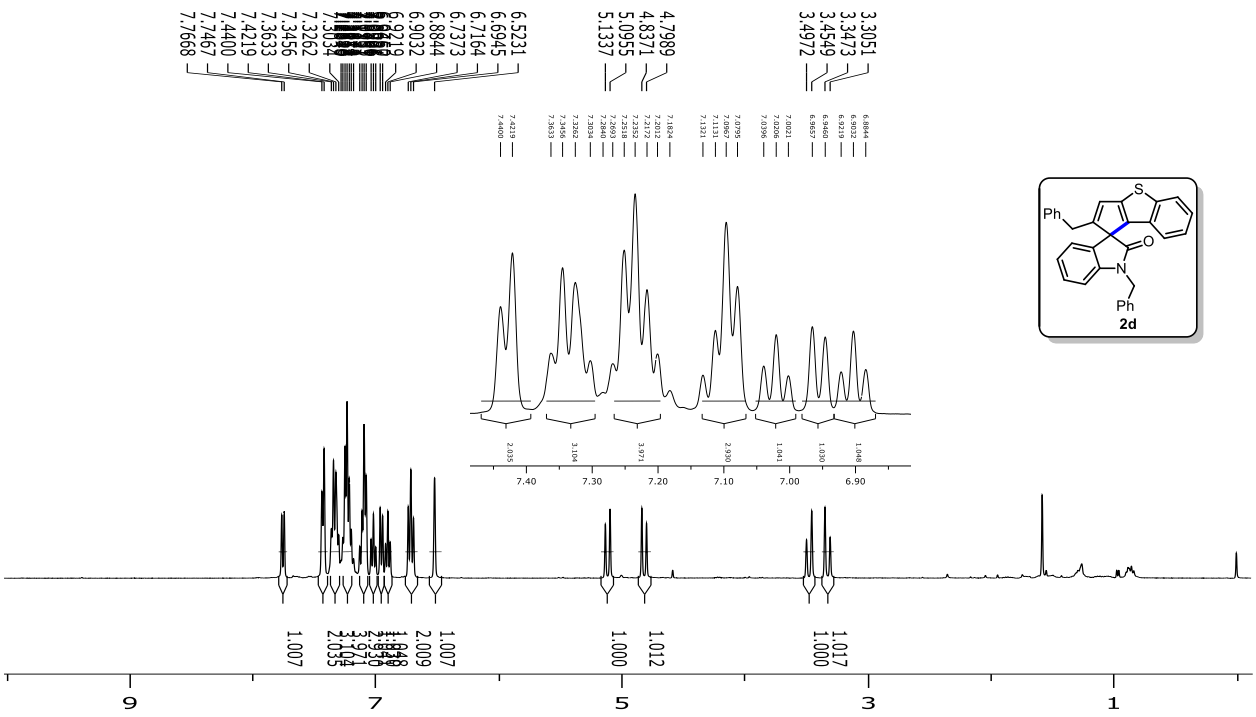
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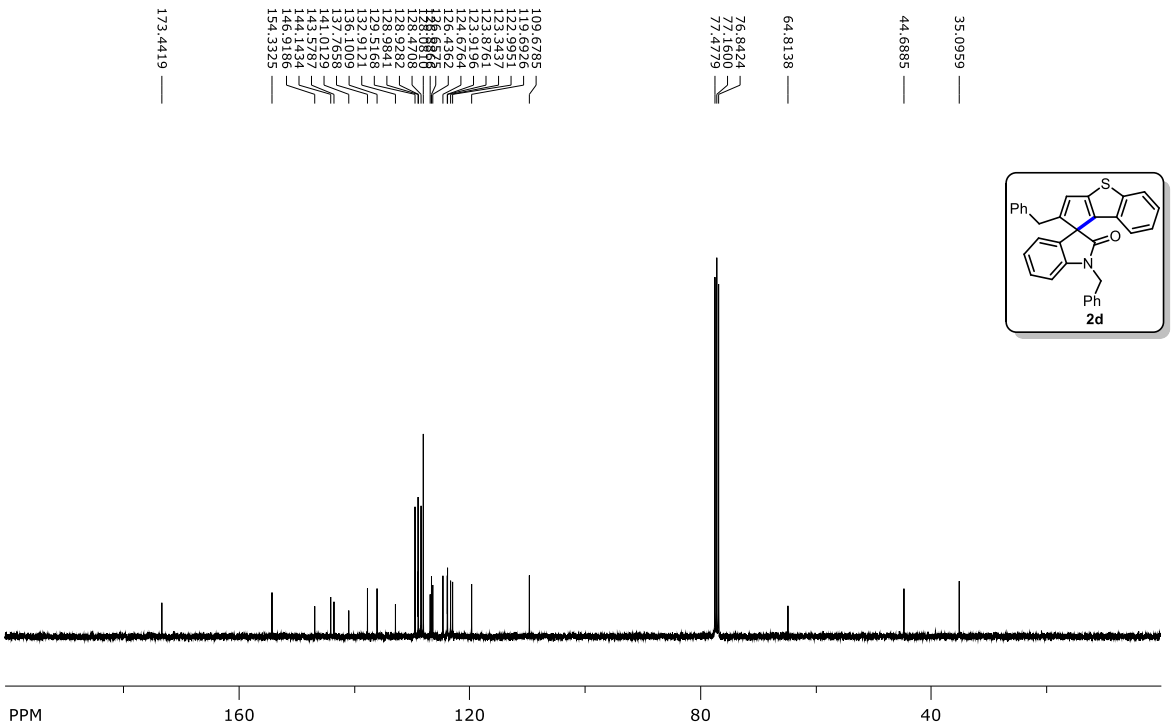
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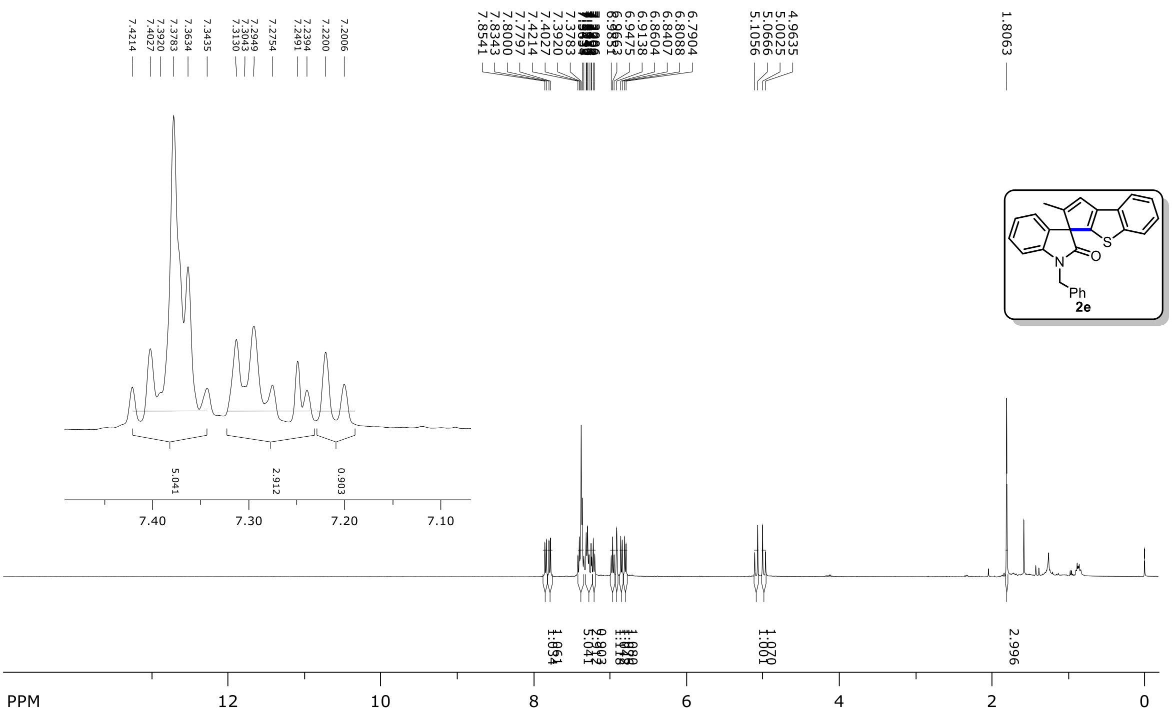
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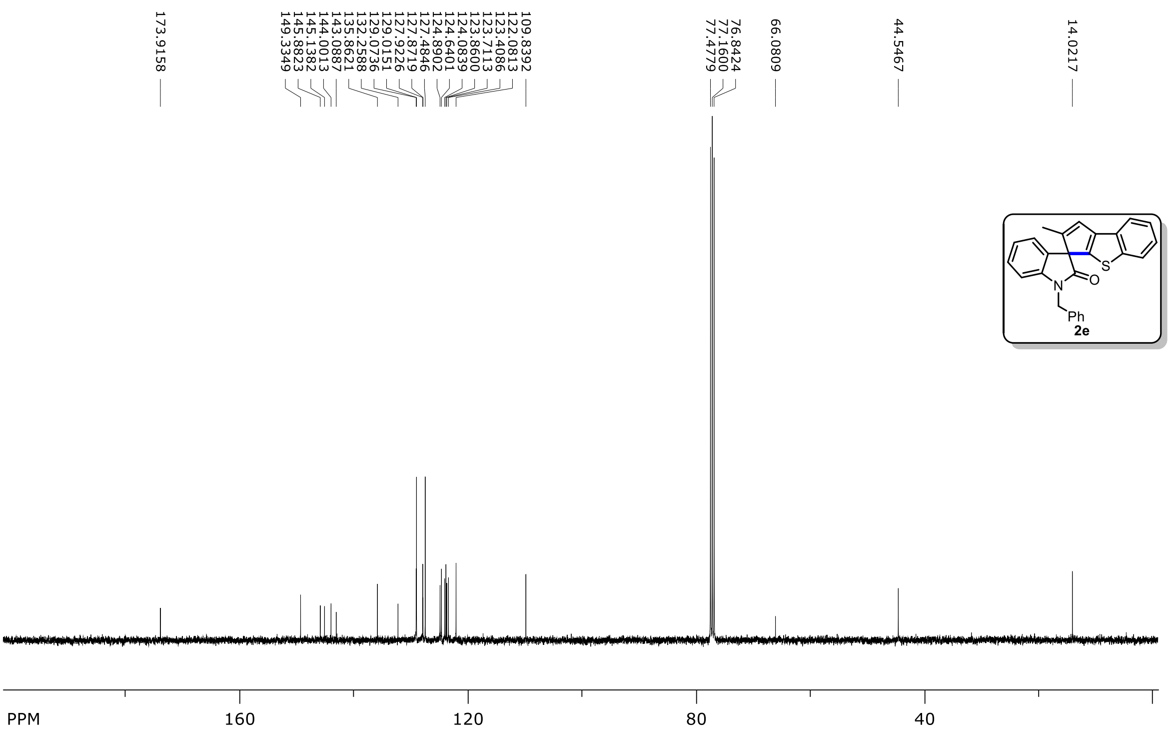
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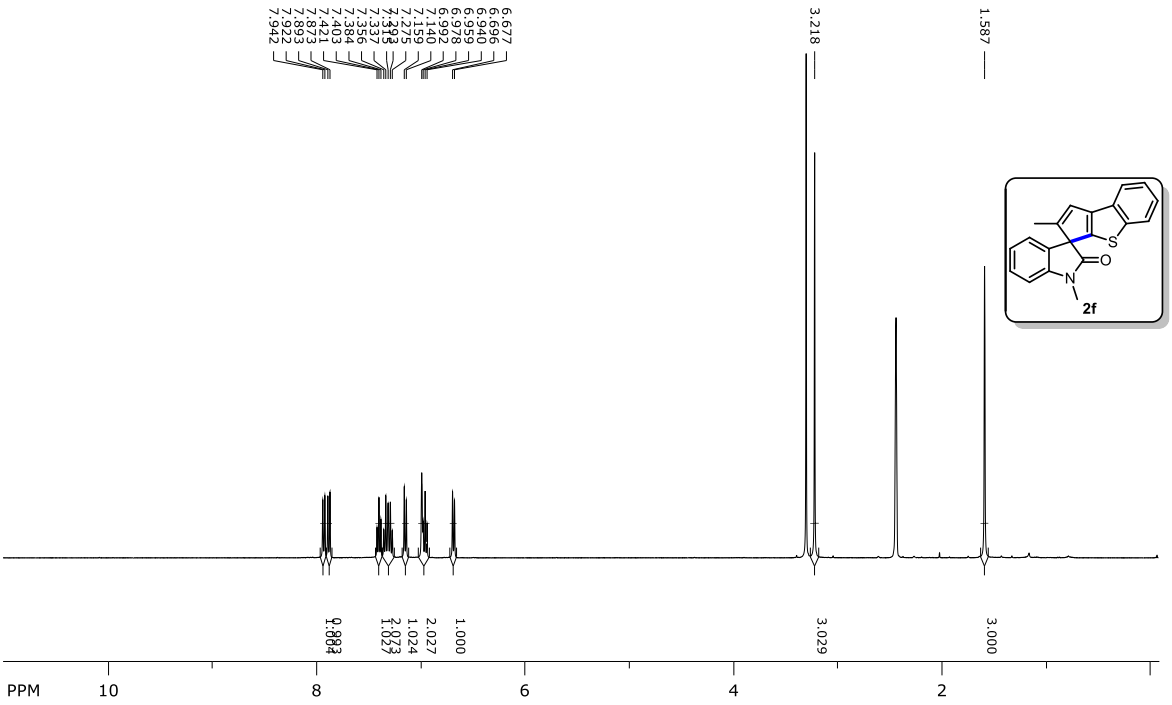
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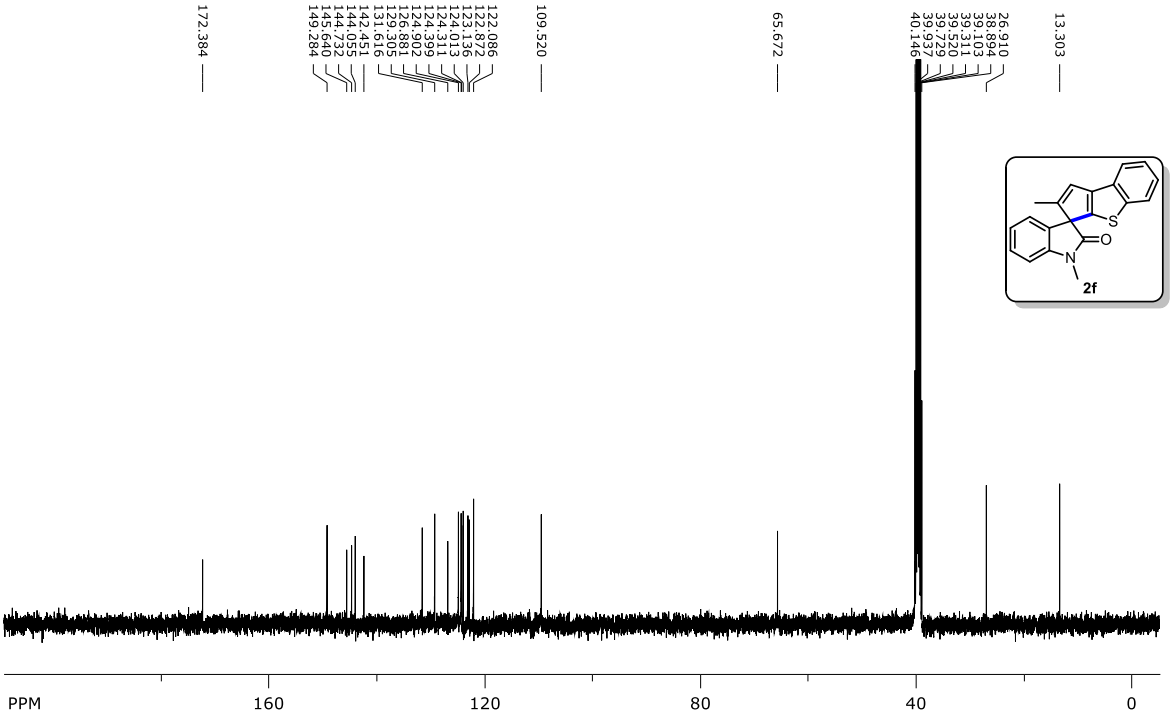
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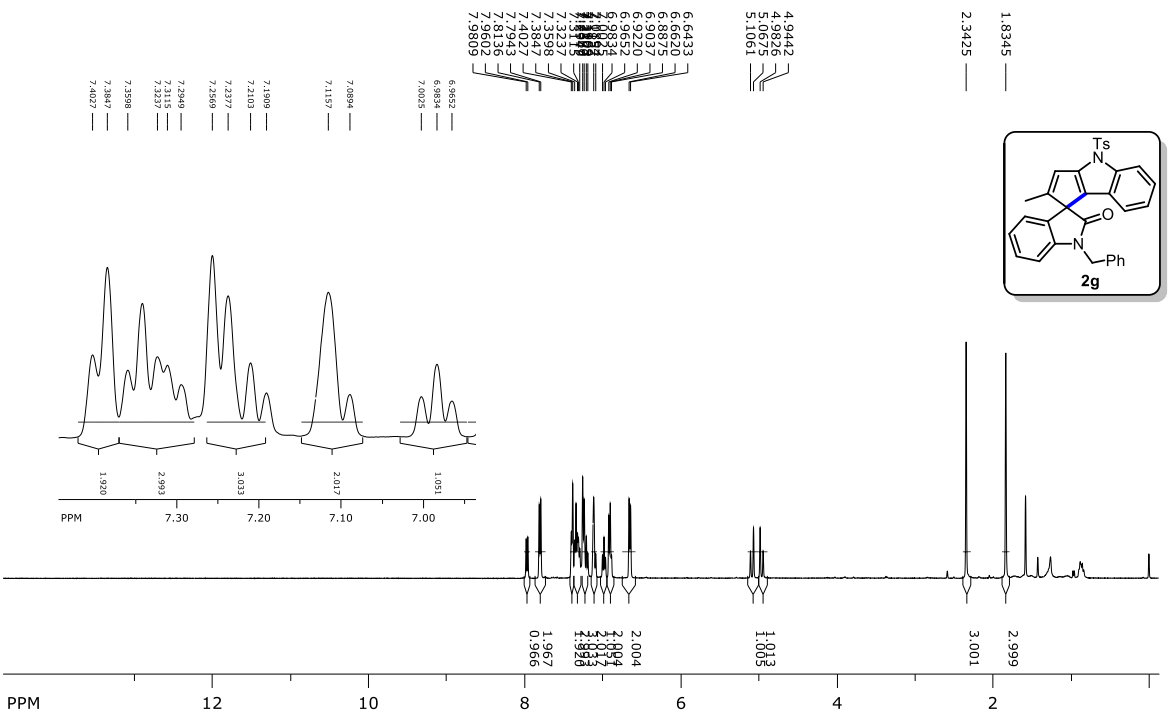
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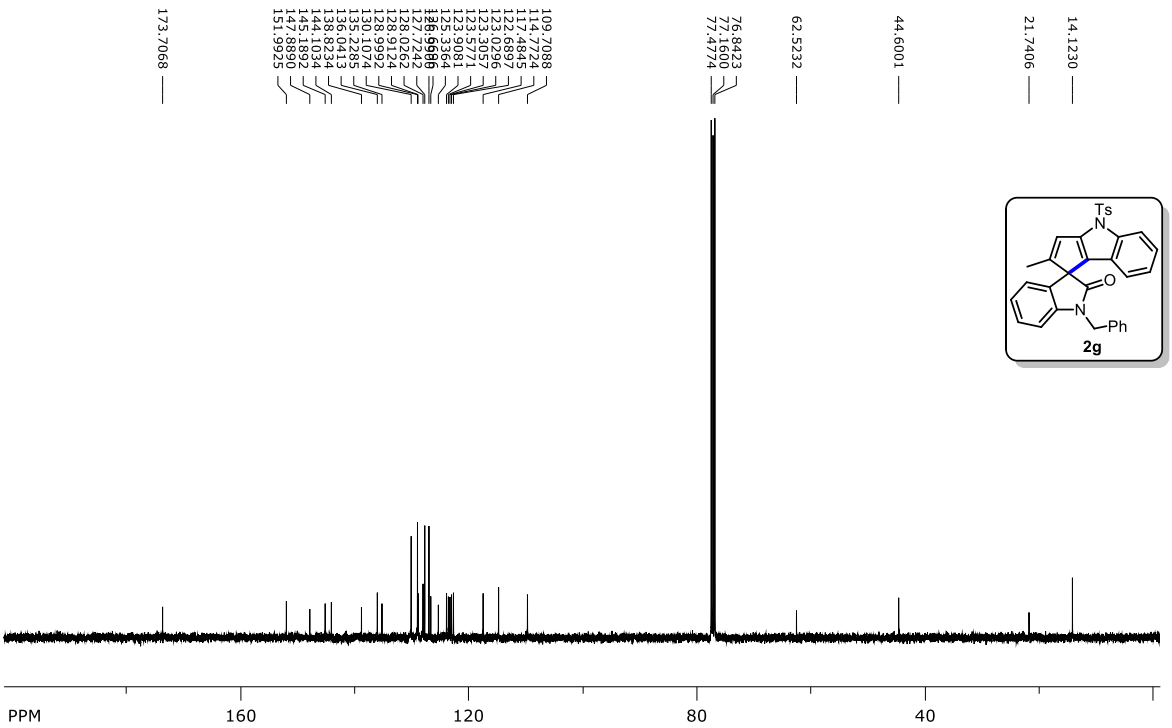
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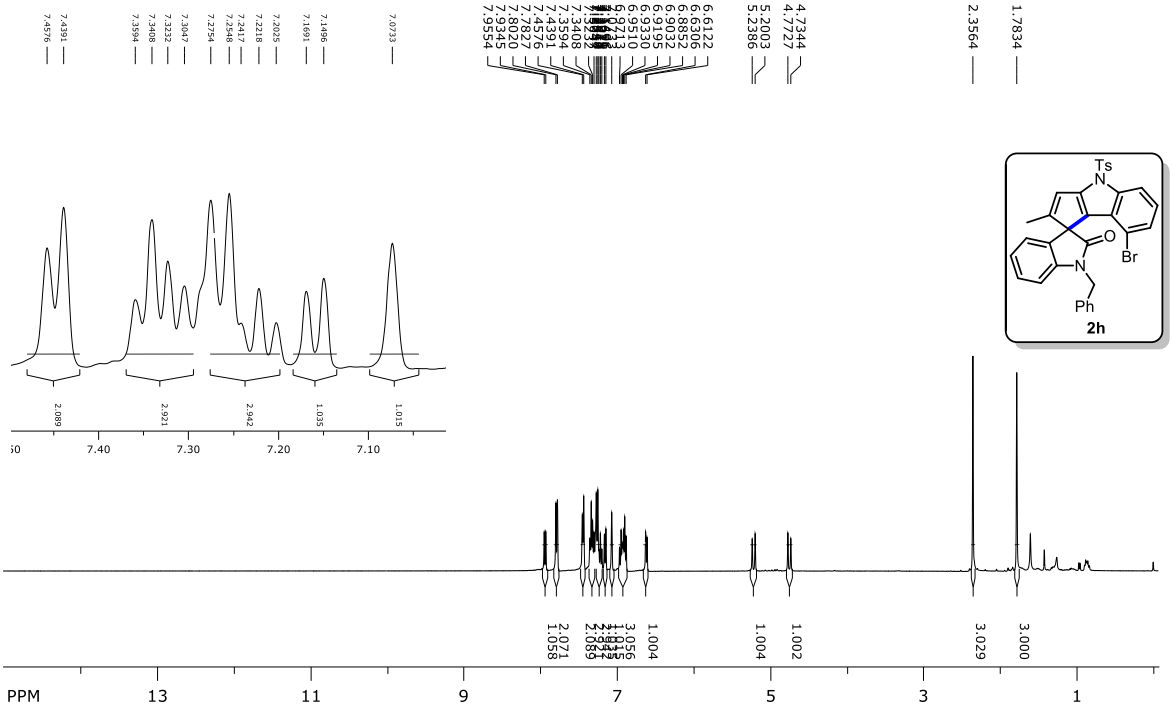
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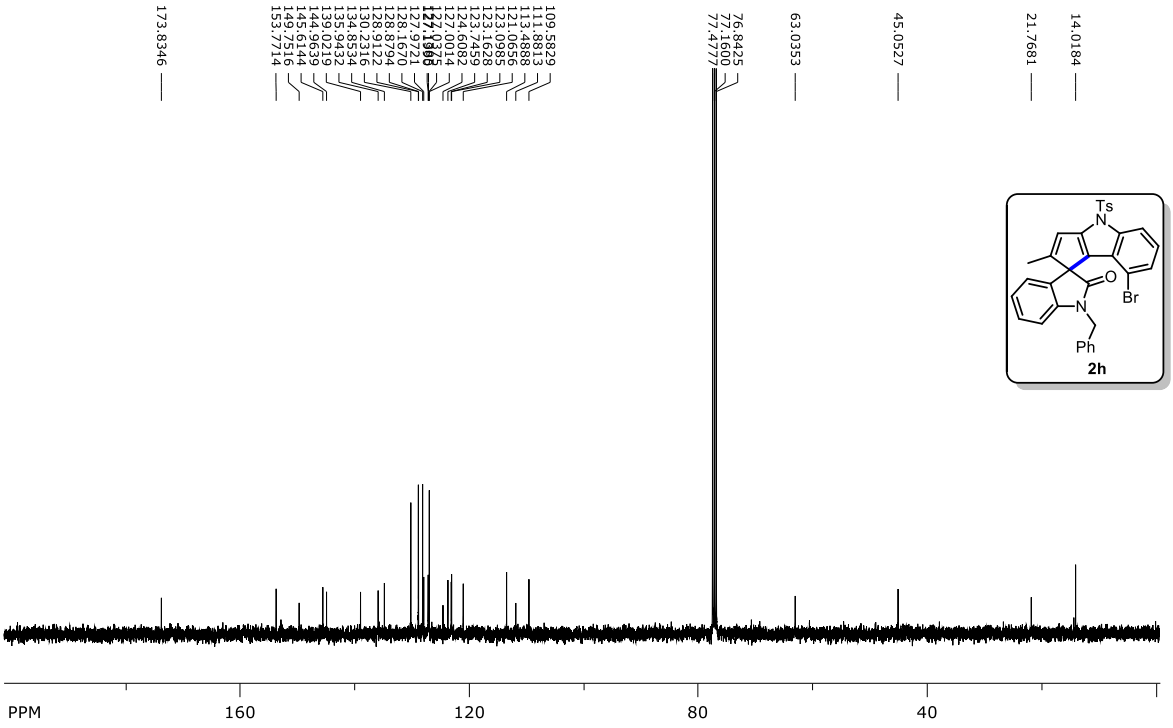
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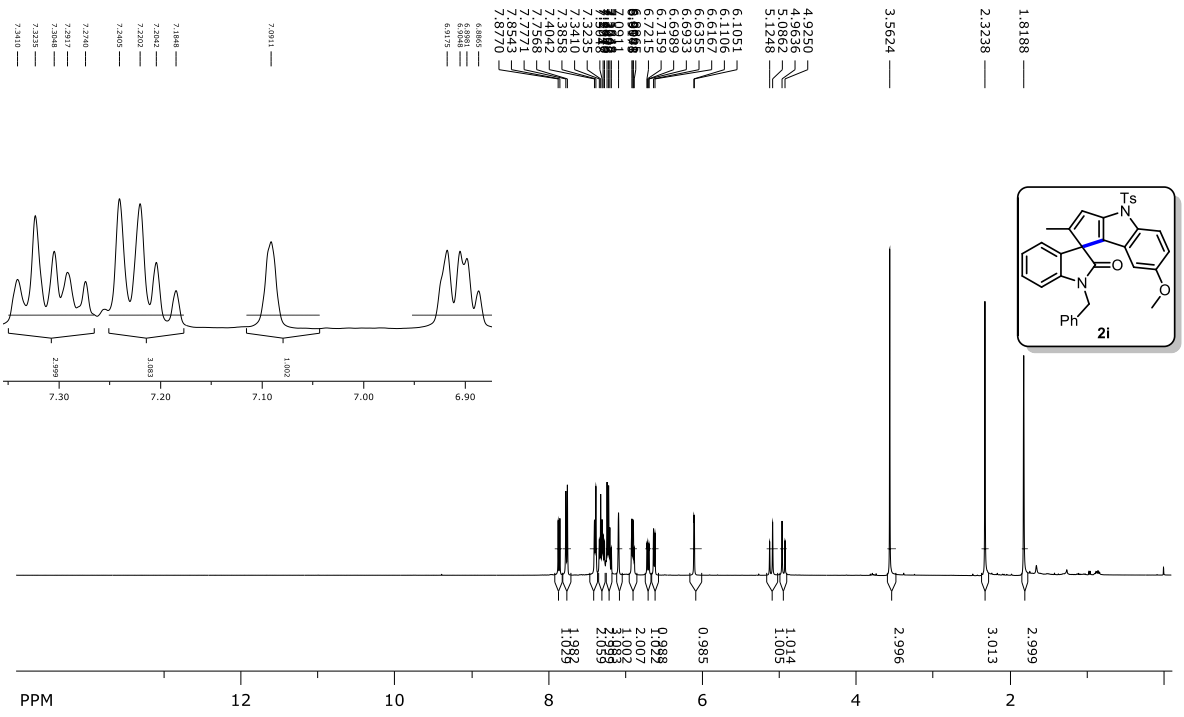
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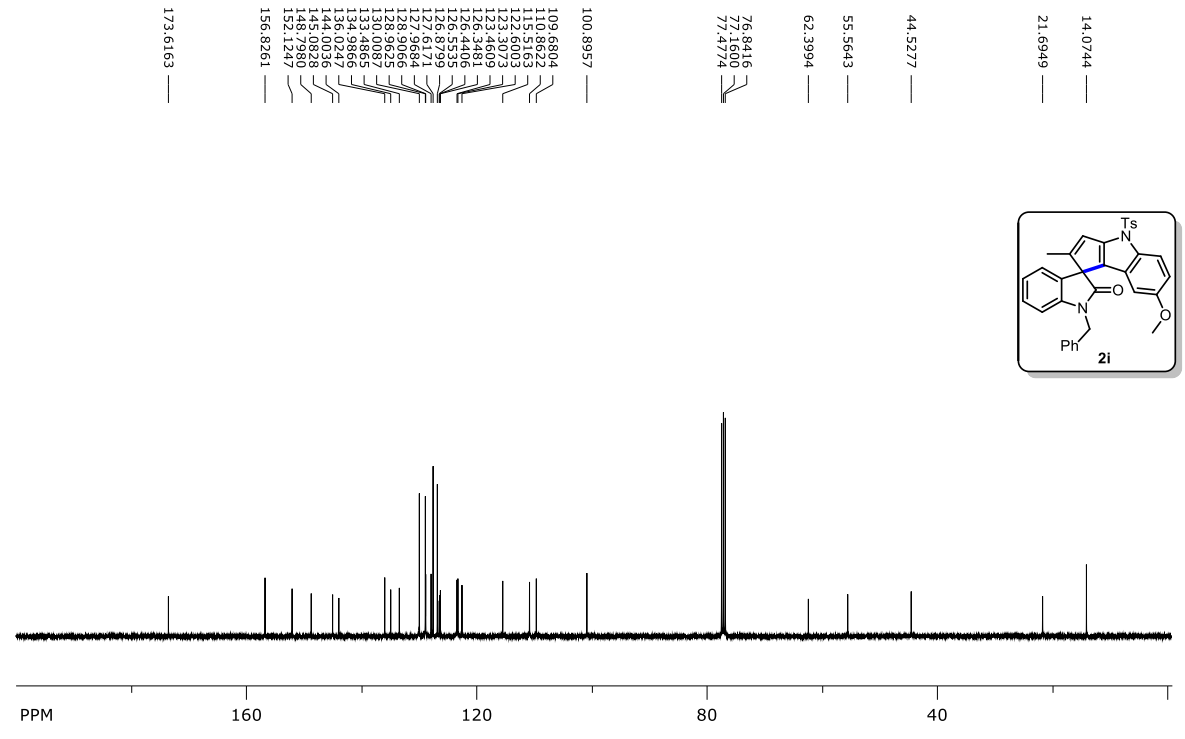
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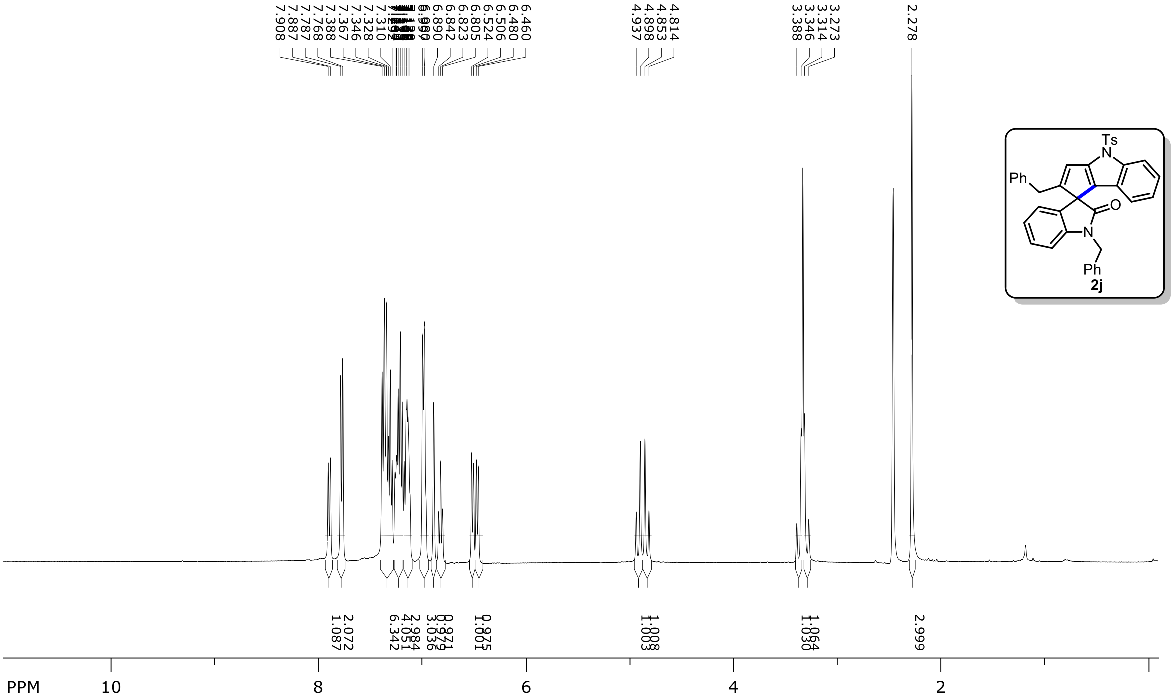
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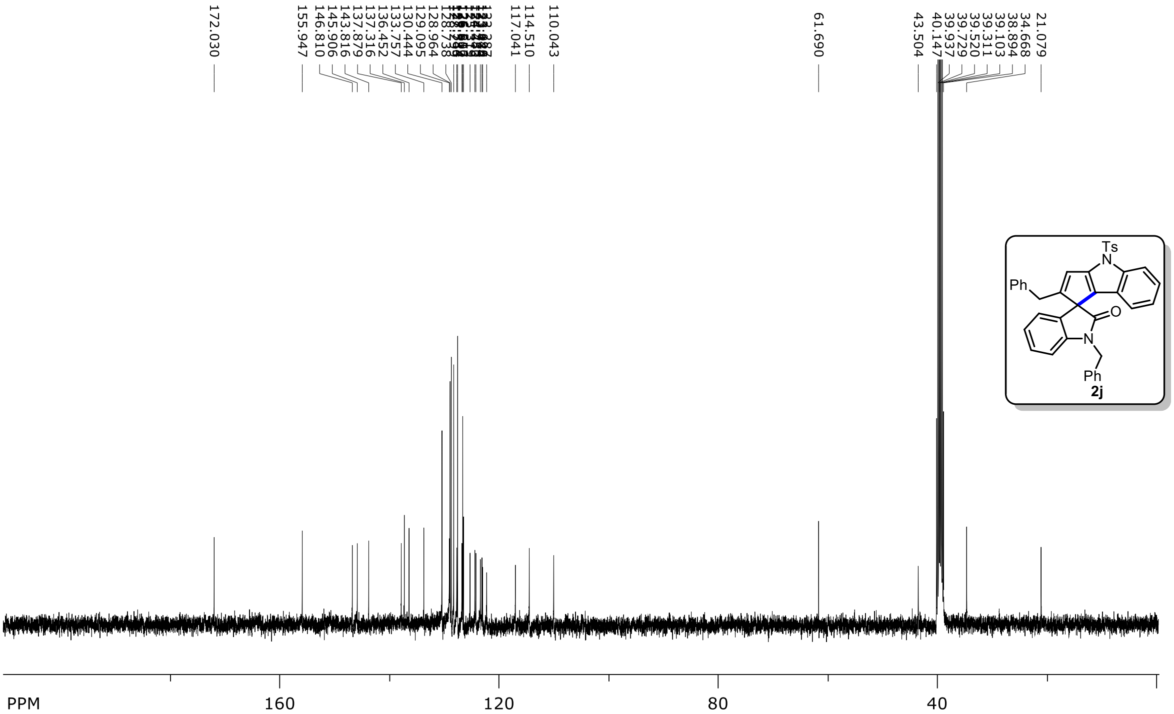
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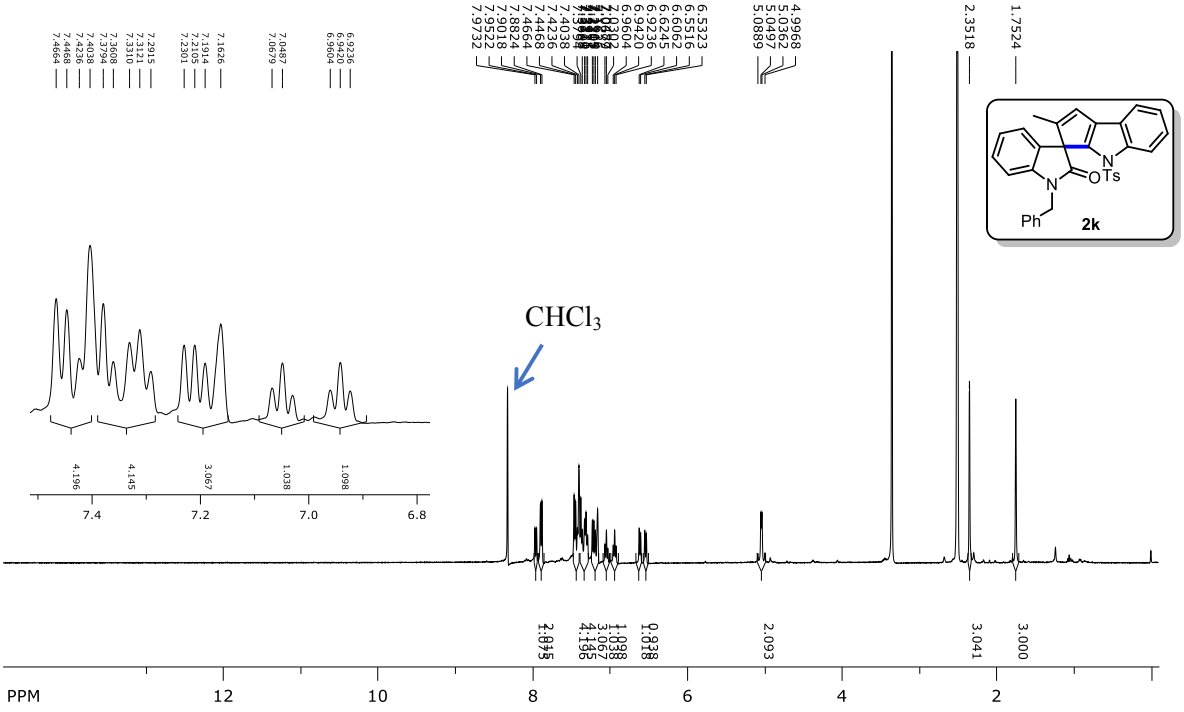
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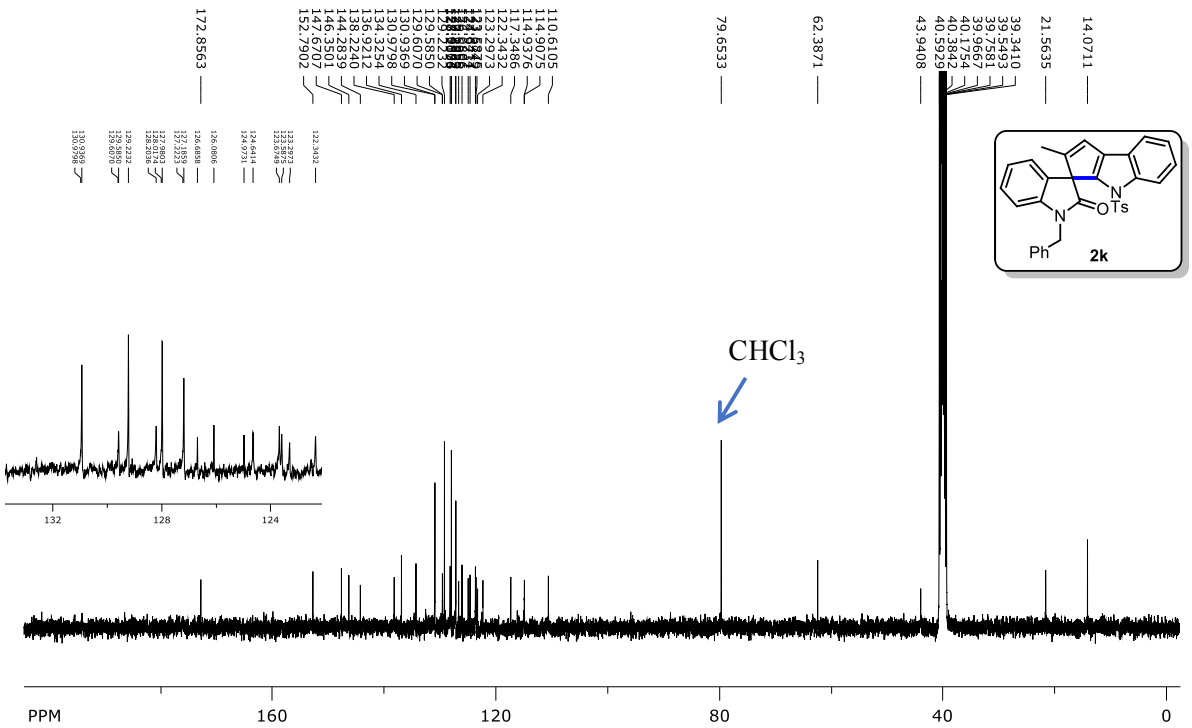
Ph
Ts
PPM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2k
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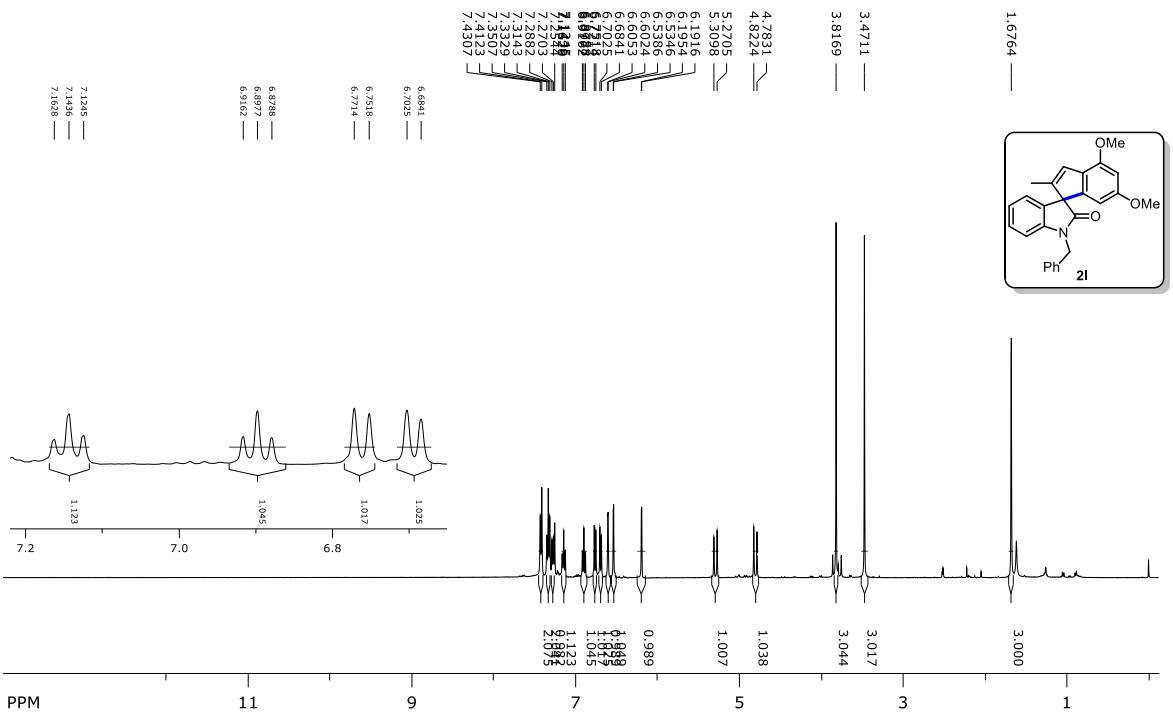
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6.6053
6.6841
6.7025
7.2703
7.2882
7.3143
7.3507
7.4123
7.4307
7.1245
7.1436
7.1628
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6.8977
6.9162
6.7518
6.7714
6.6841
6.7025
OMe
OMe
N
O
Ph
2l
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1.045
1.017
1.025
7.2
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1.038
3.044
3.017
3.000
PPM
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7
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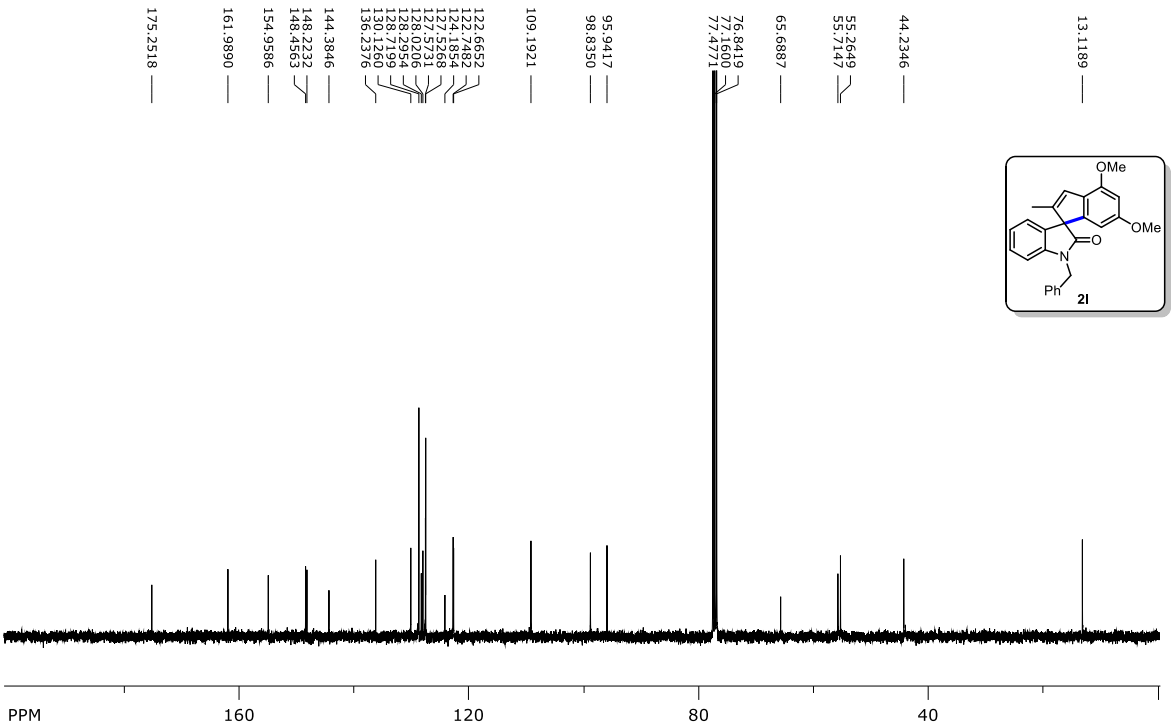
3
1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OMe
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Ph
2l
PPM
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80
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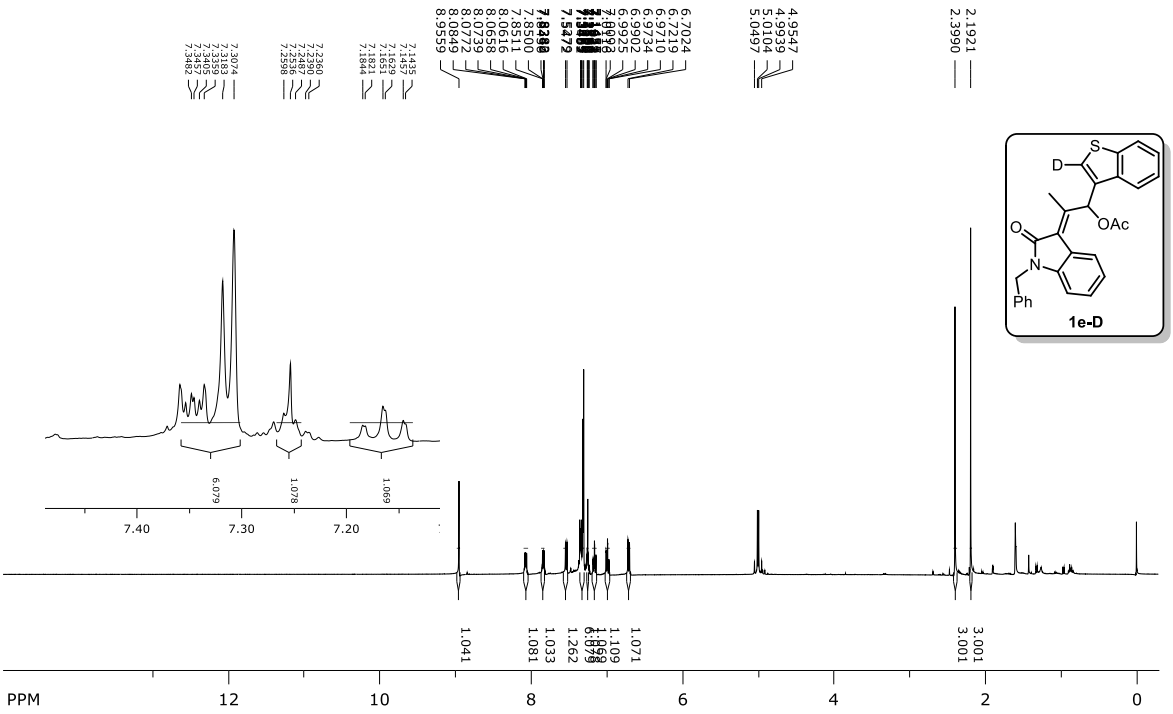
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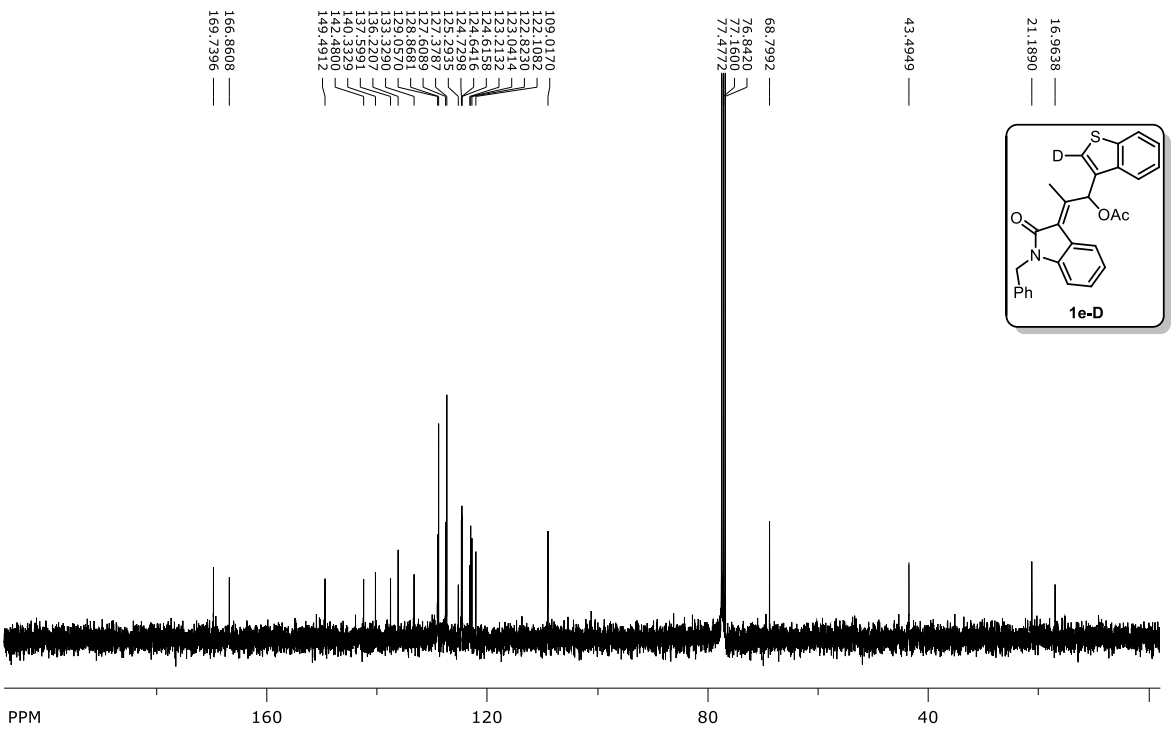
PPM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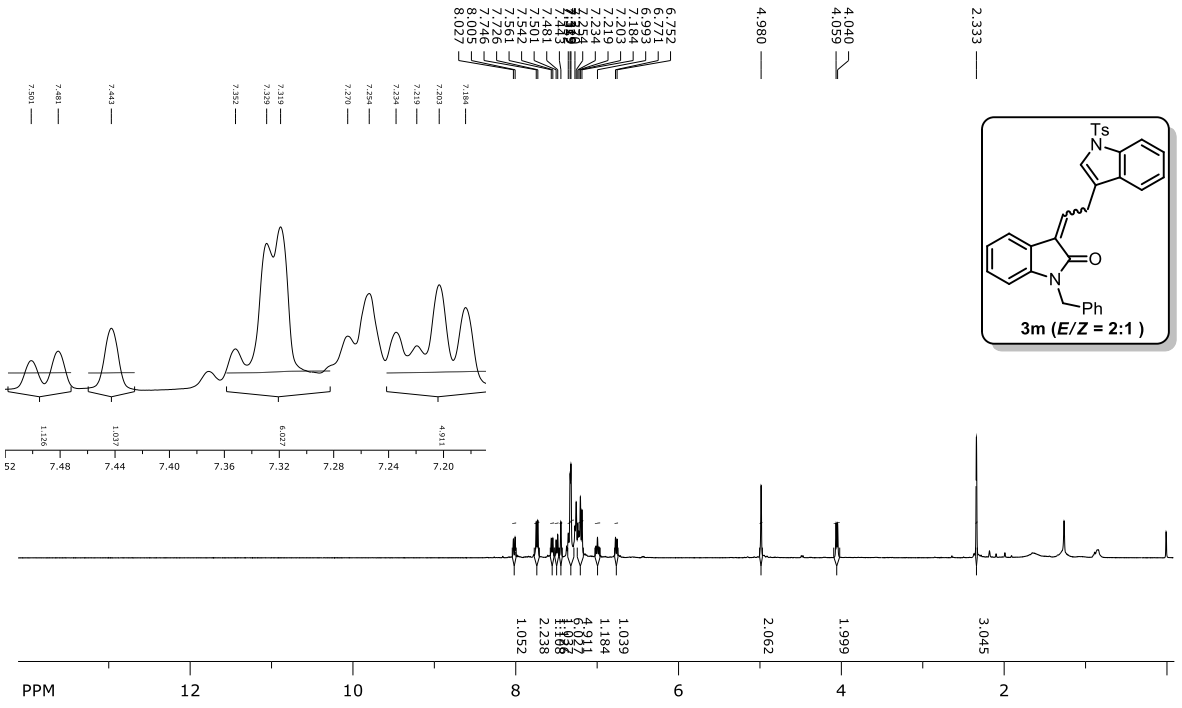
PPM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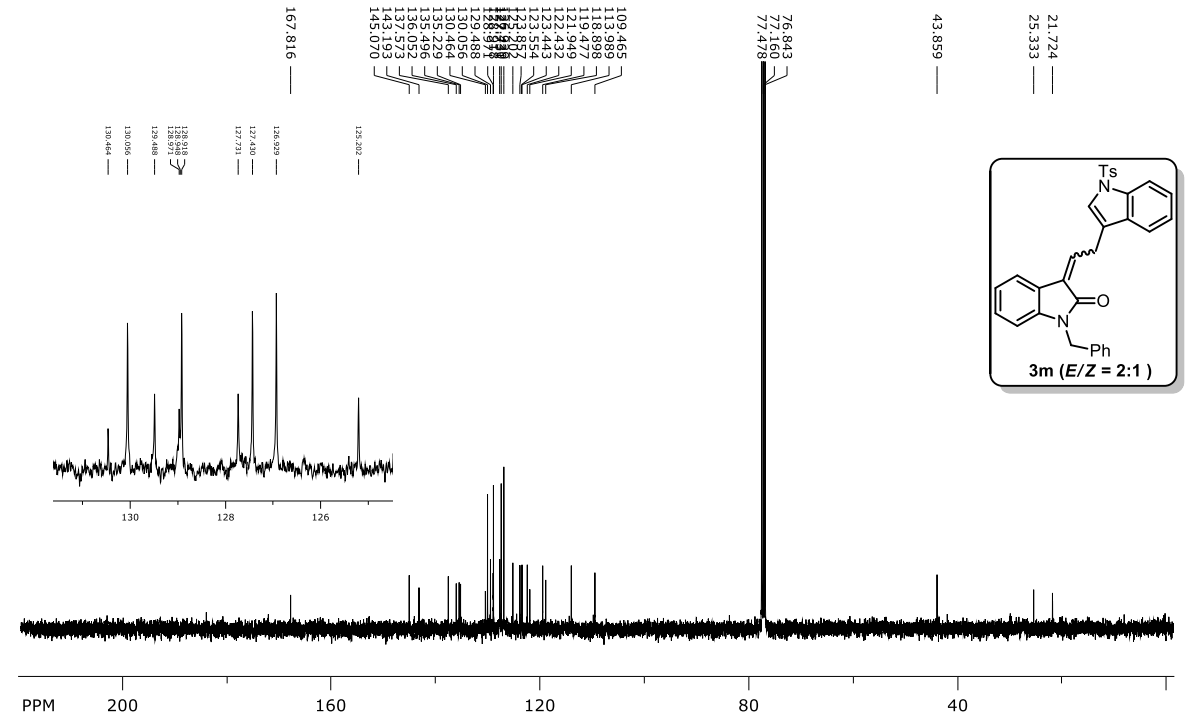
N
O
N
Ph
3m (E/Z = 2:1)
PPM
12
10
8
6
4
2


Ts
N
O
N
Ph
3m (E/Z = 2:1)
PPM
200
160
120
80
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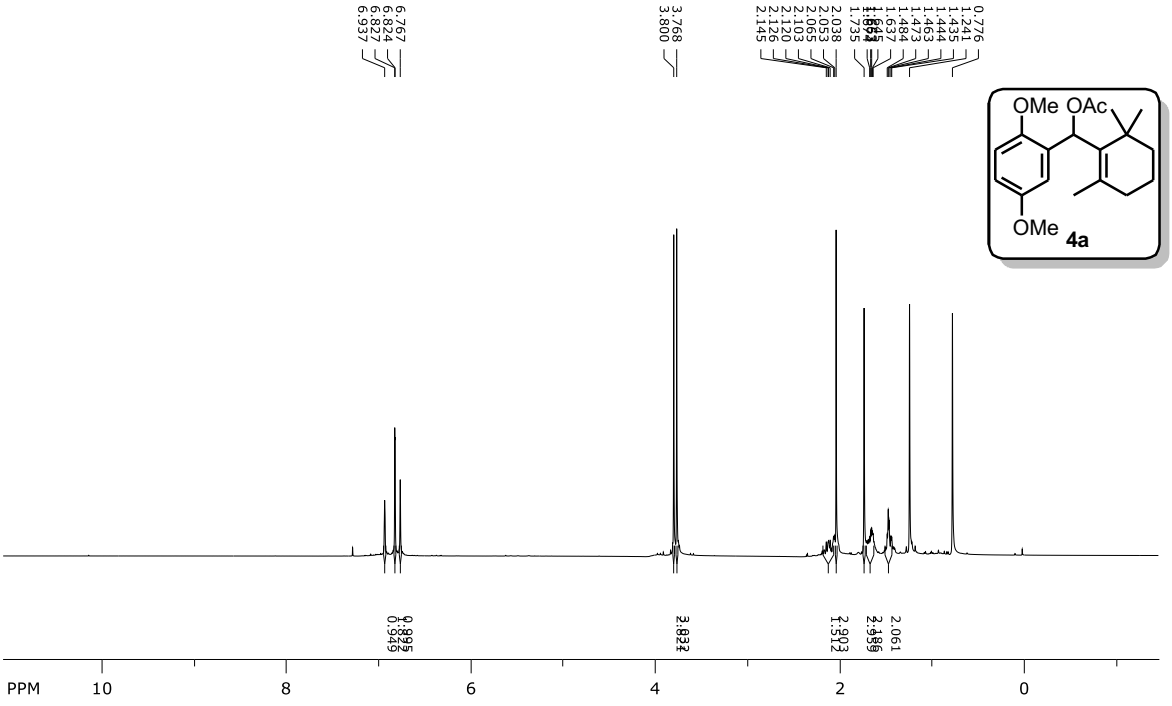
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1.637
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1.473
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1.435
1.251
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OMe
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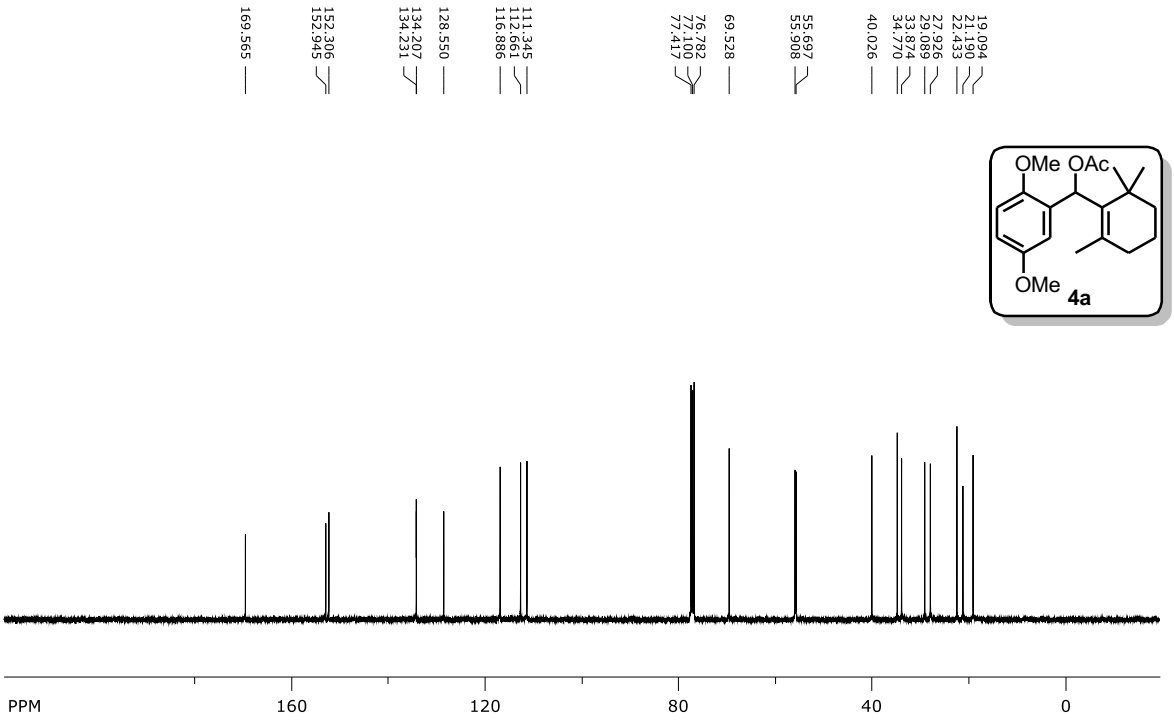
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112.661
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76.782
69.528
55.908
55.697
40.026
34.770
33.874
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27.926
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21.190
19.094
OMe
OAc
OMe
4a
PPM
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120
80
40
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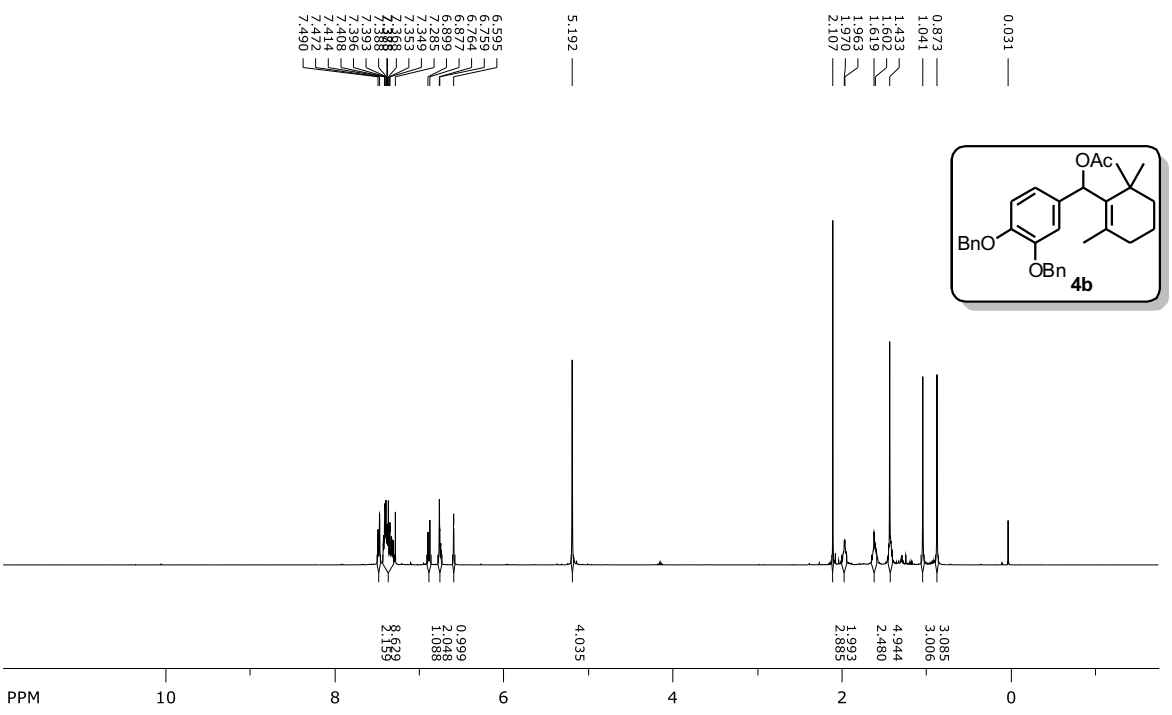
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7.368
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7.396
7.408
7.414
7.472
7.490
5.192
2.107
1.970
1.963
1.619
1.602
1.433
1.041
0.873
0.031
OAc
BnO
OBn
4b
8.629
2.159
0.999
2.068
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6
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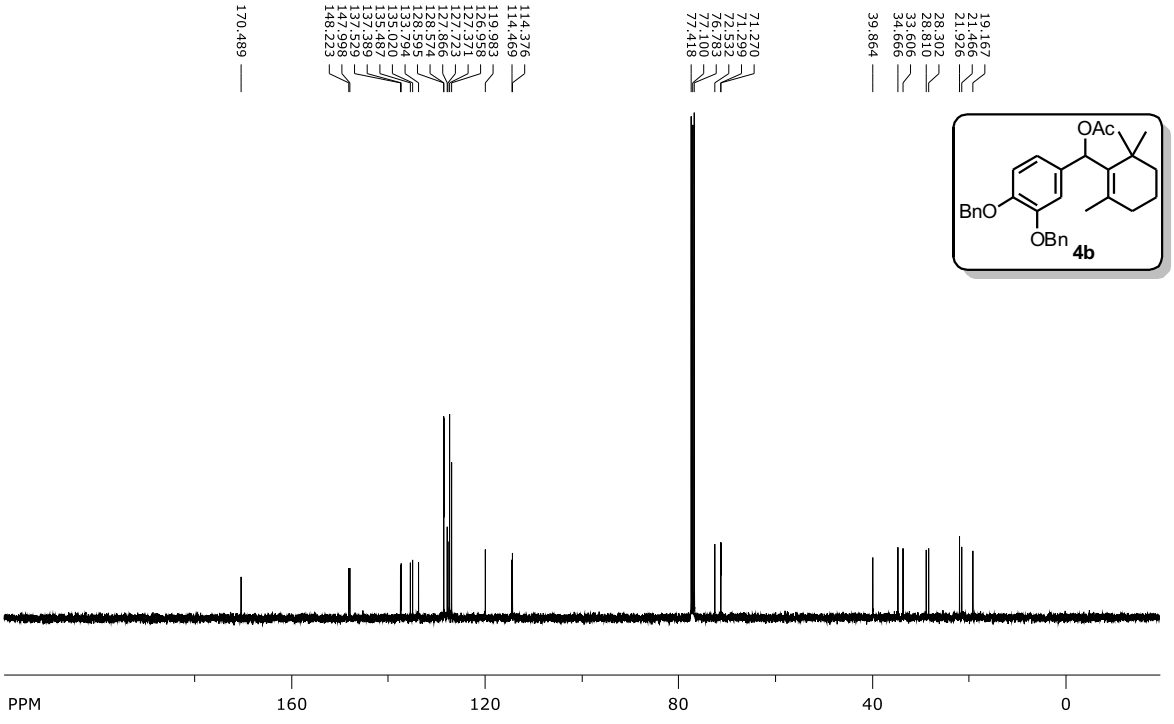
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77.418
77.100
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71.270
39.864
34.666
33.606
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OBn
4b
PPM
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120
80
40
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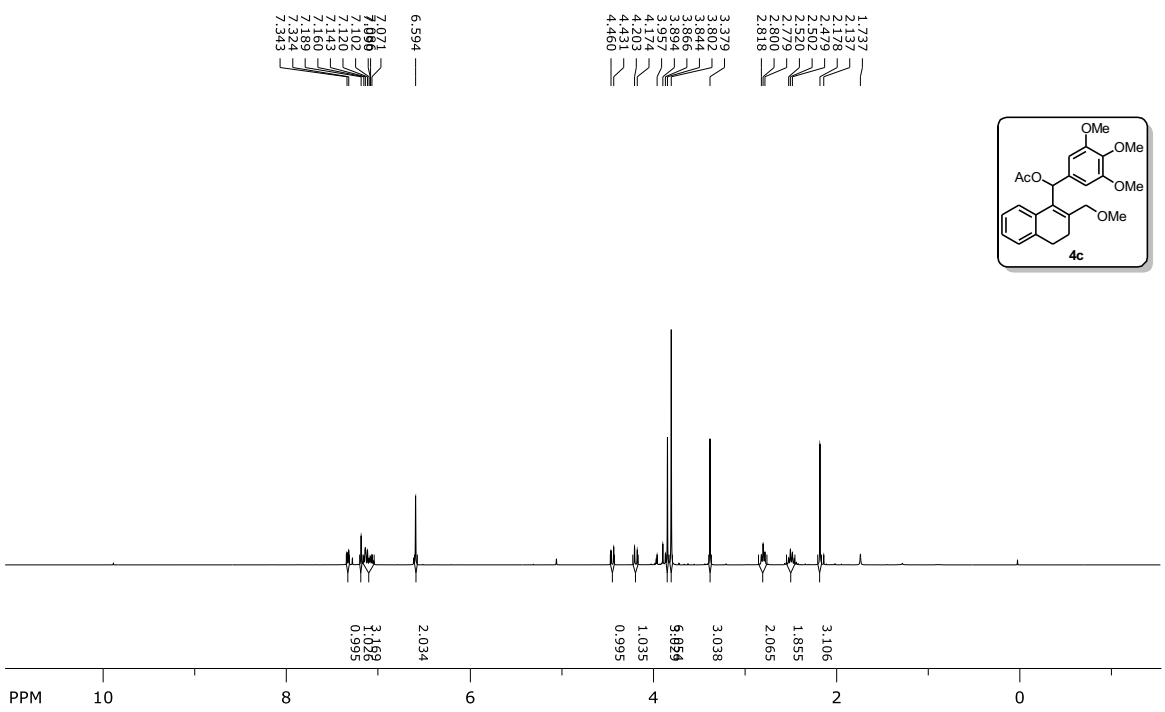
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4.174
3.866
3.844
3.802
3.379
2.818
2.808
2.520
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2.479
2.178
2.137
1.737
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OMe
AcO
OMe
OMe
4c
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1.000
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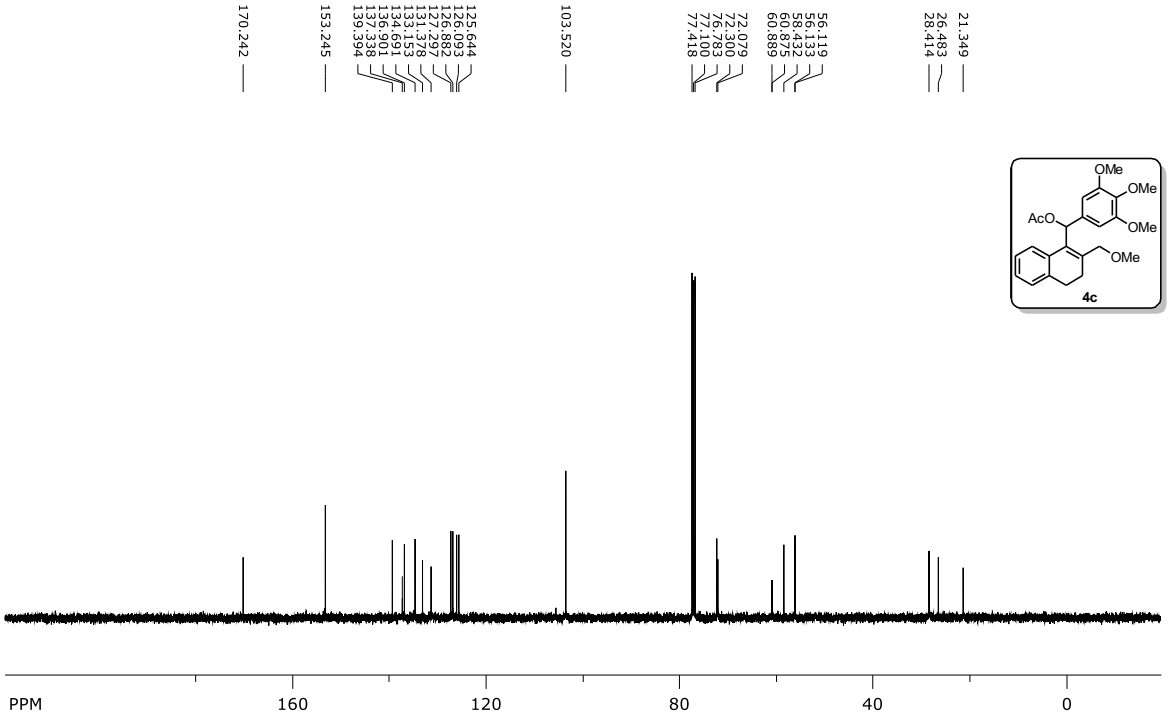
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OMe
AcO
OMe
OMe
4c
PPM
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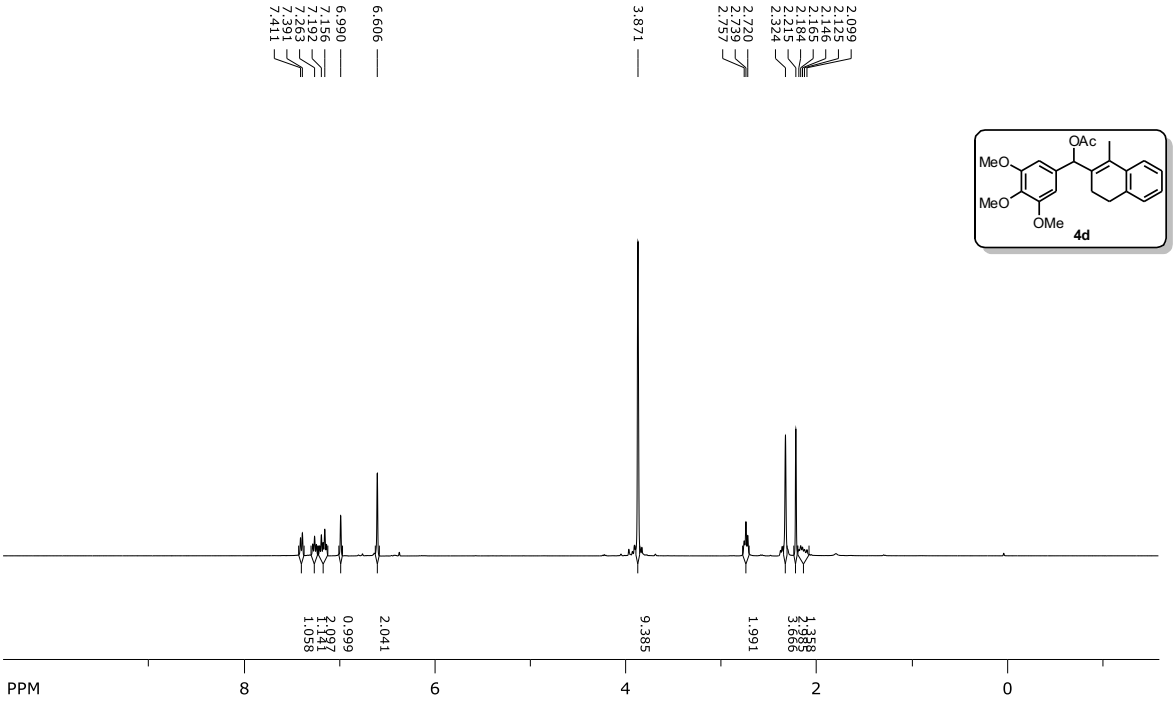
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2.215
2.182
2.146
2.125
2.099
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MeO
MeO
OMe
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0.999
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3.666
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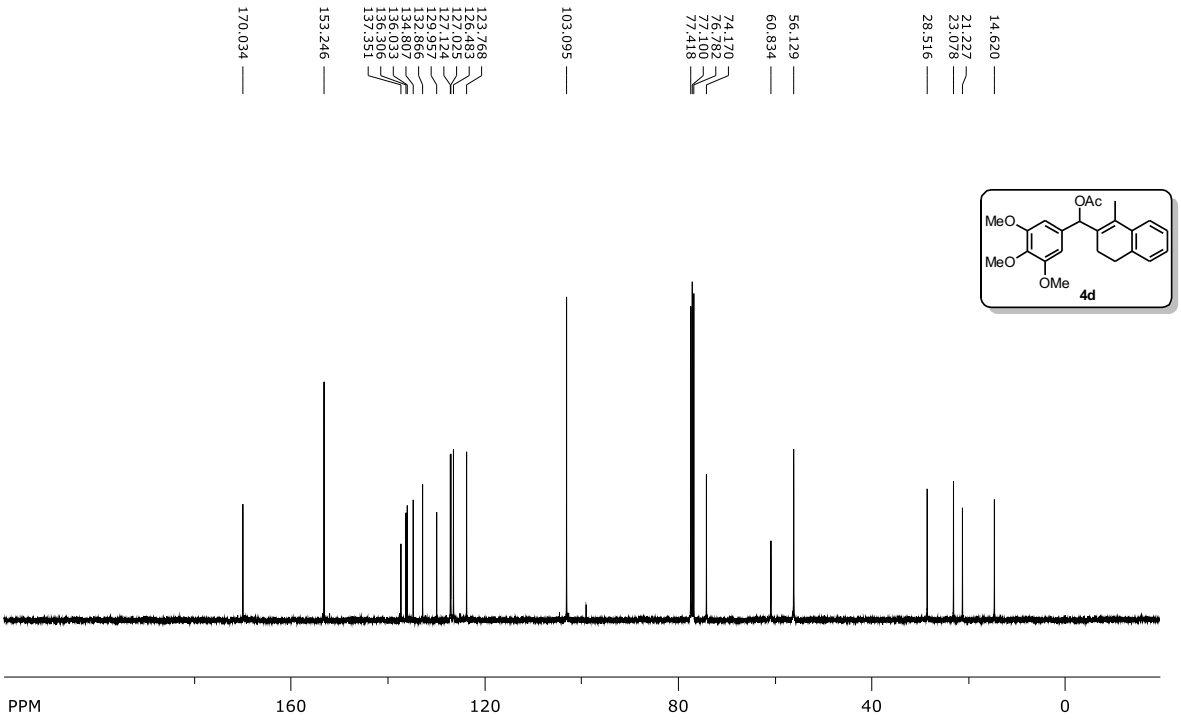
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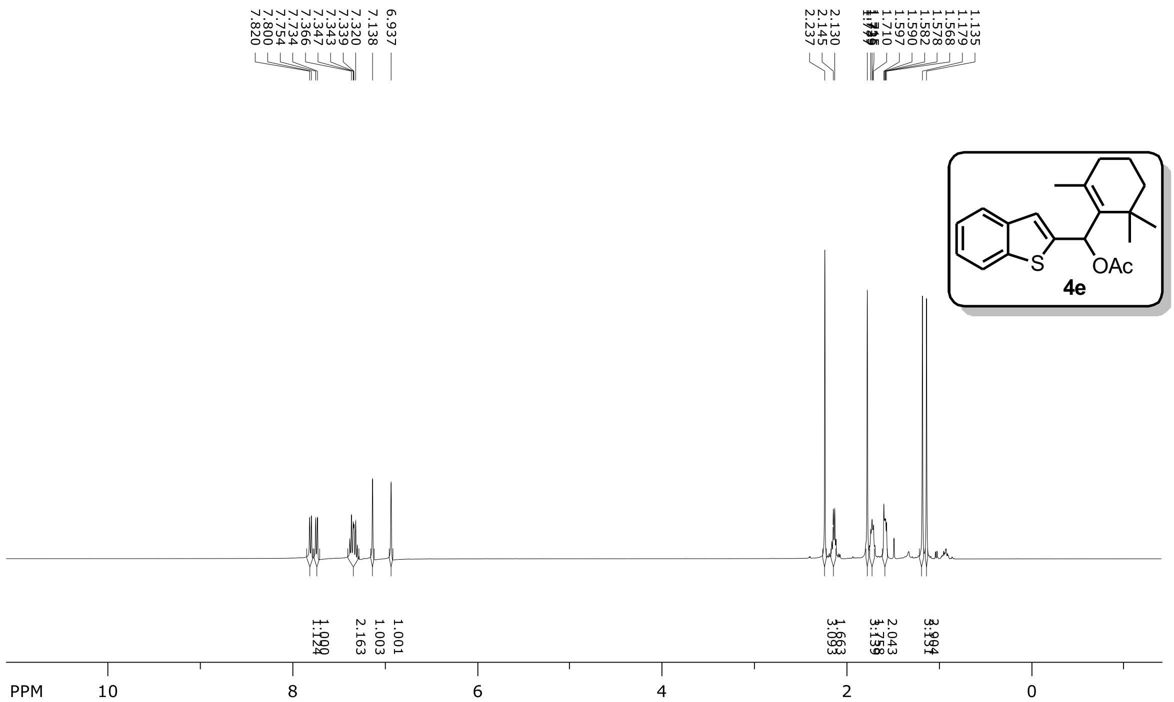
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1.590
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1.568
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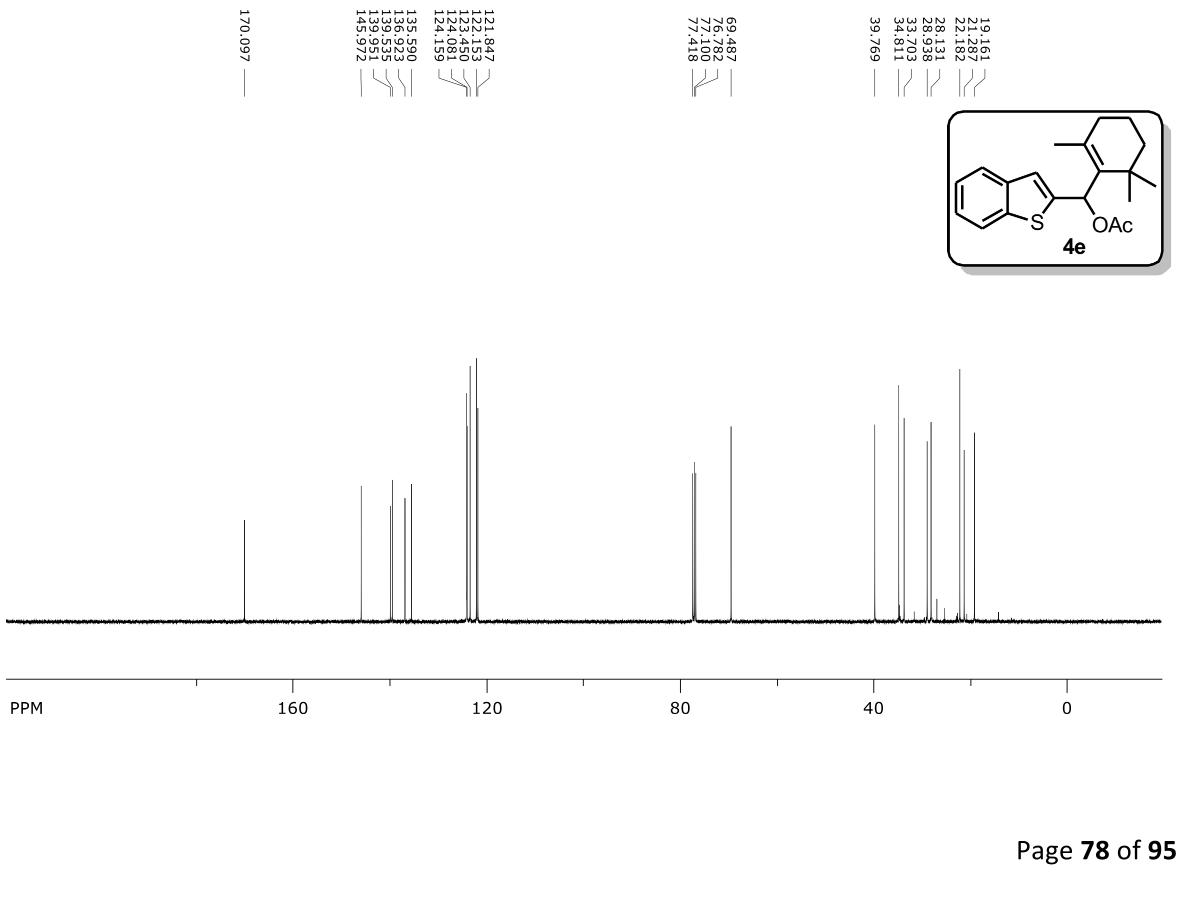
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4e
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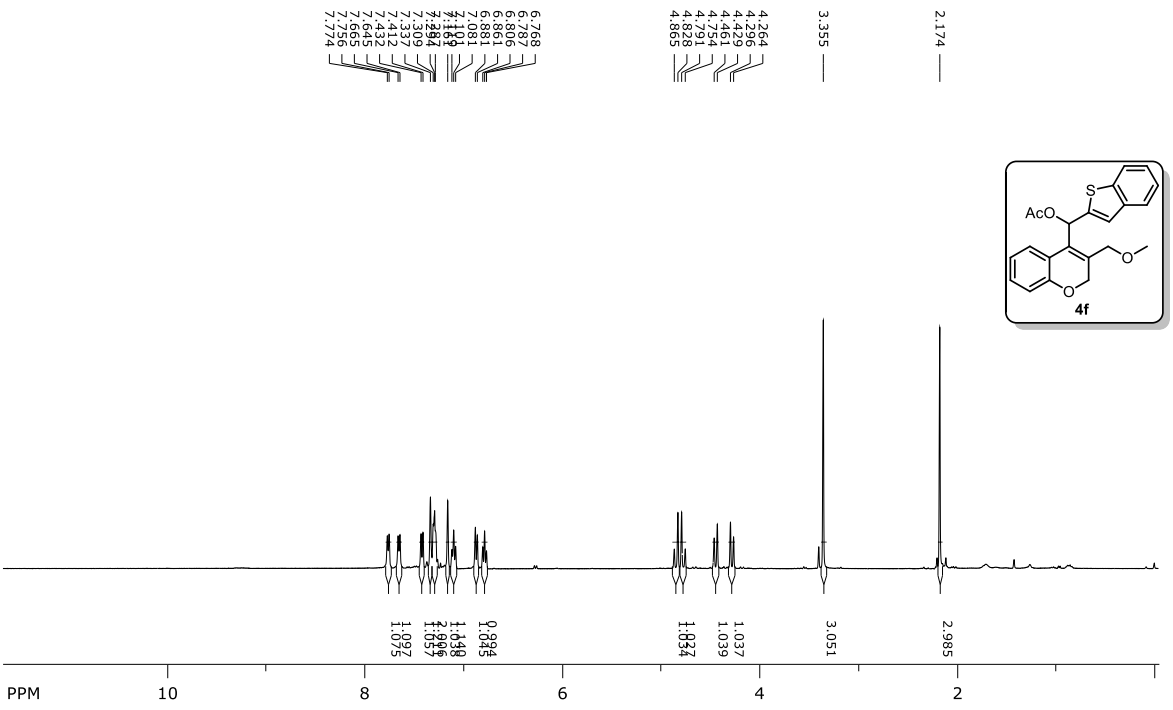
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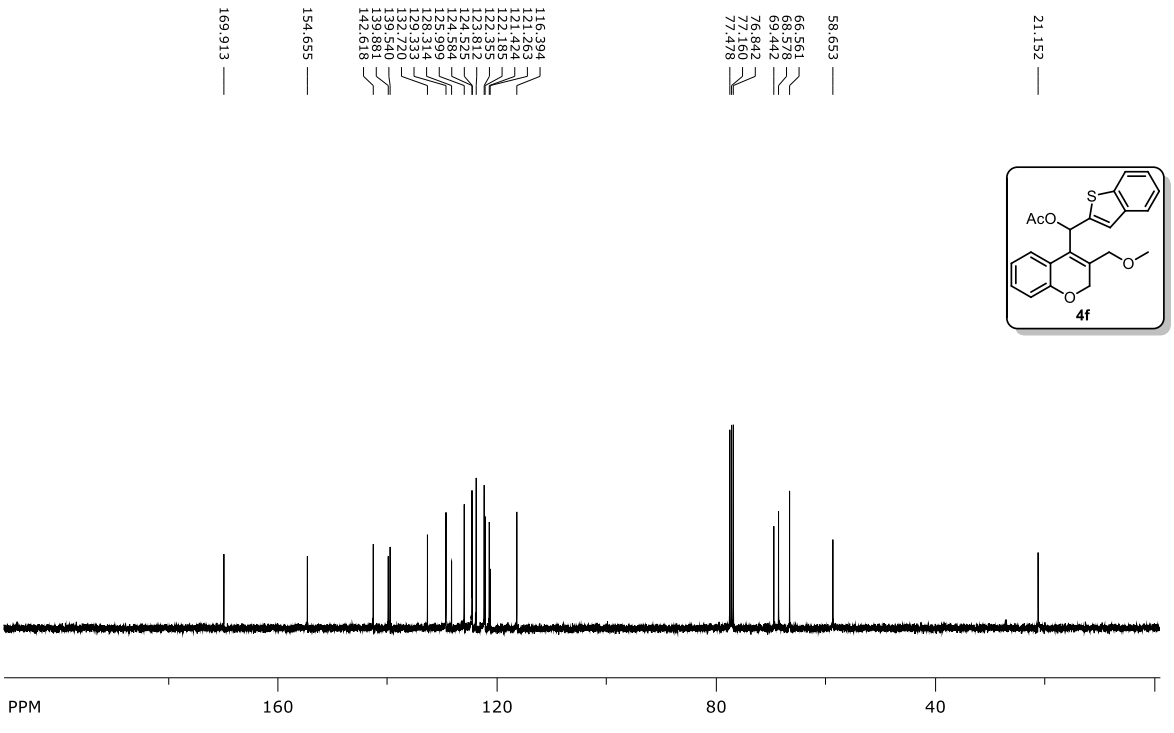
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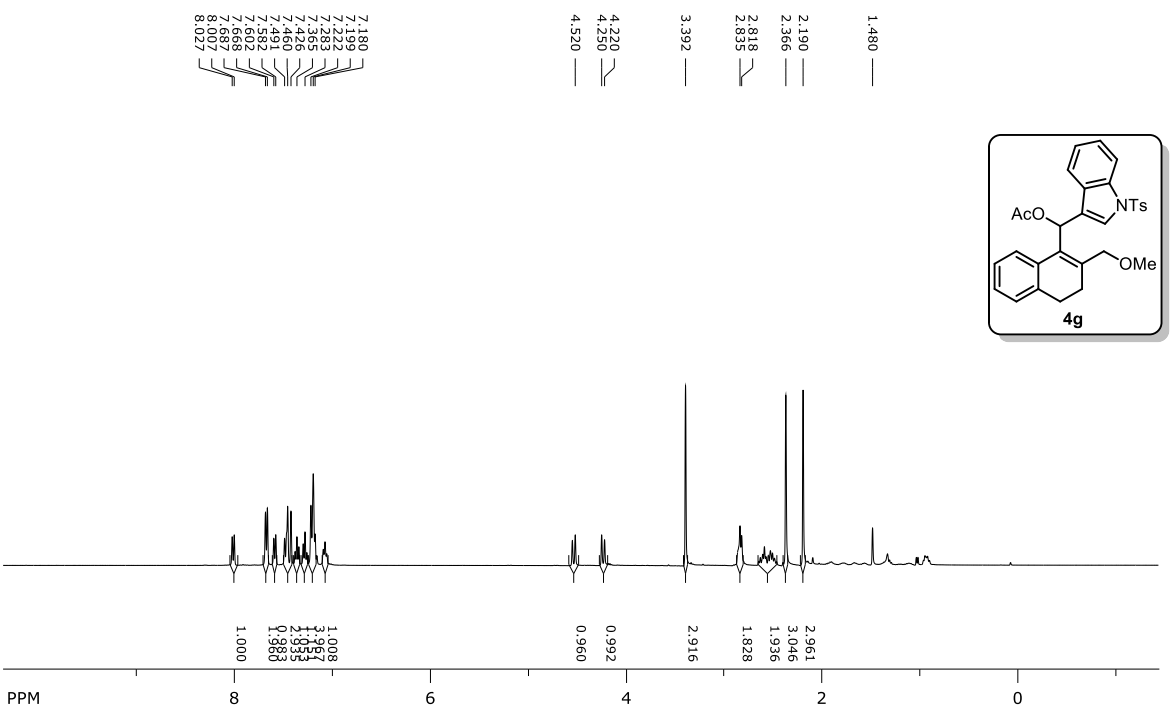
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7.180
4.520
4.250
4.220
3.392
2.835
2.818
2.366
2.190
1.480
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OMe
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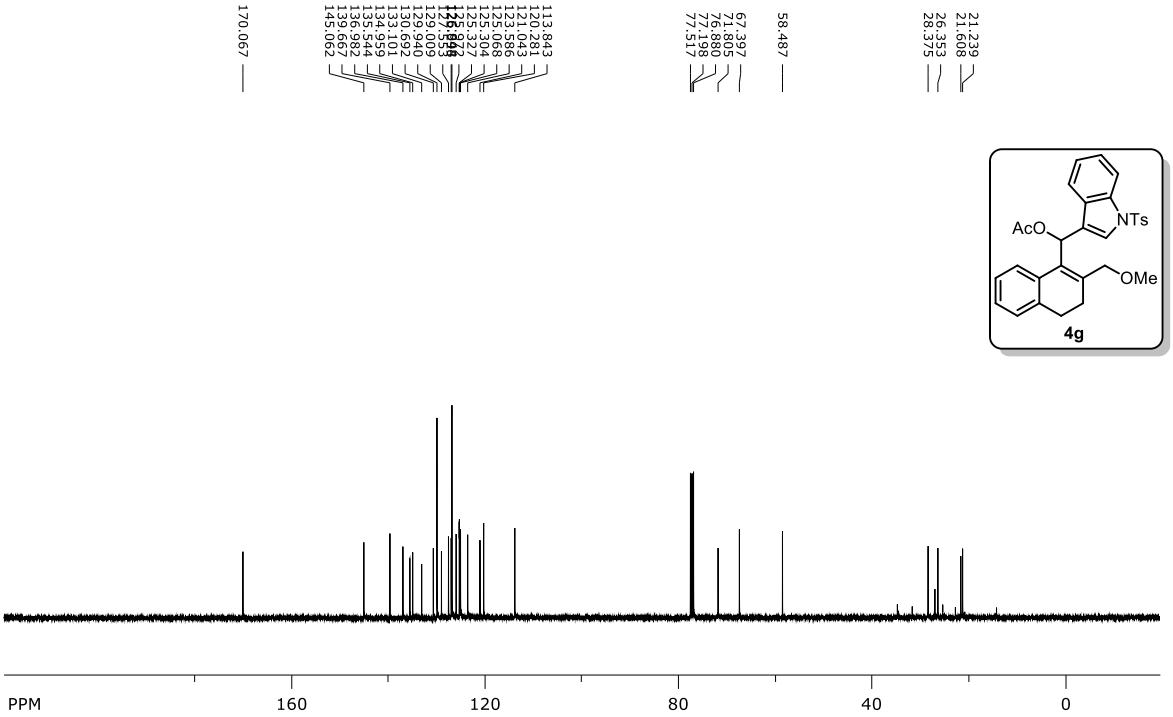
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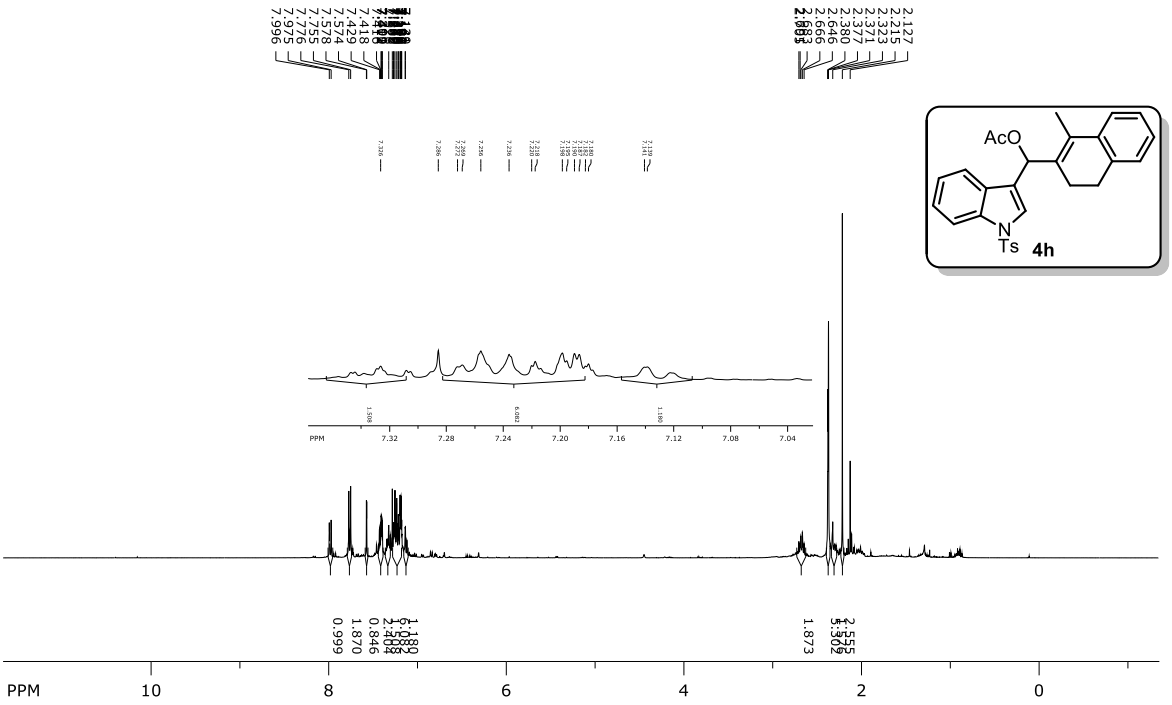
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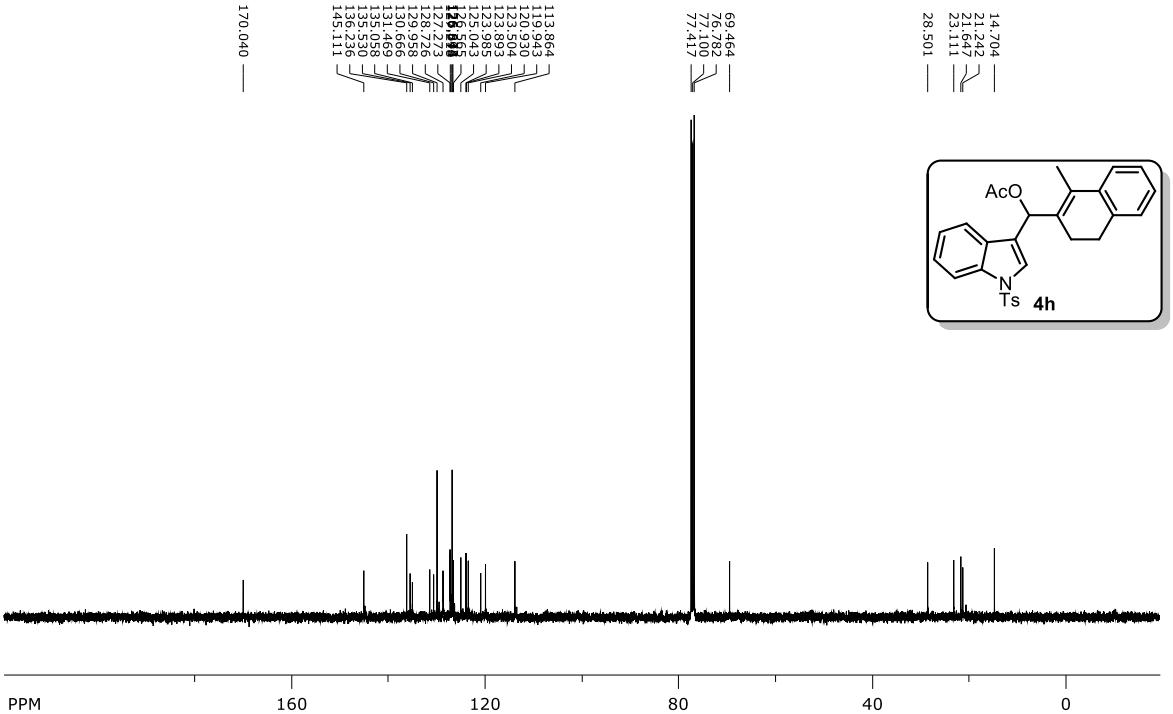
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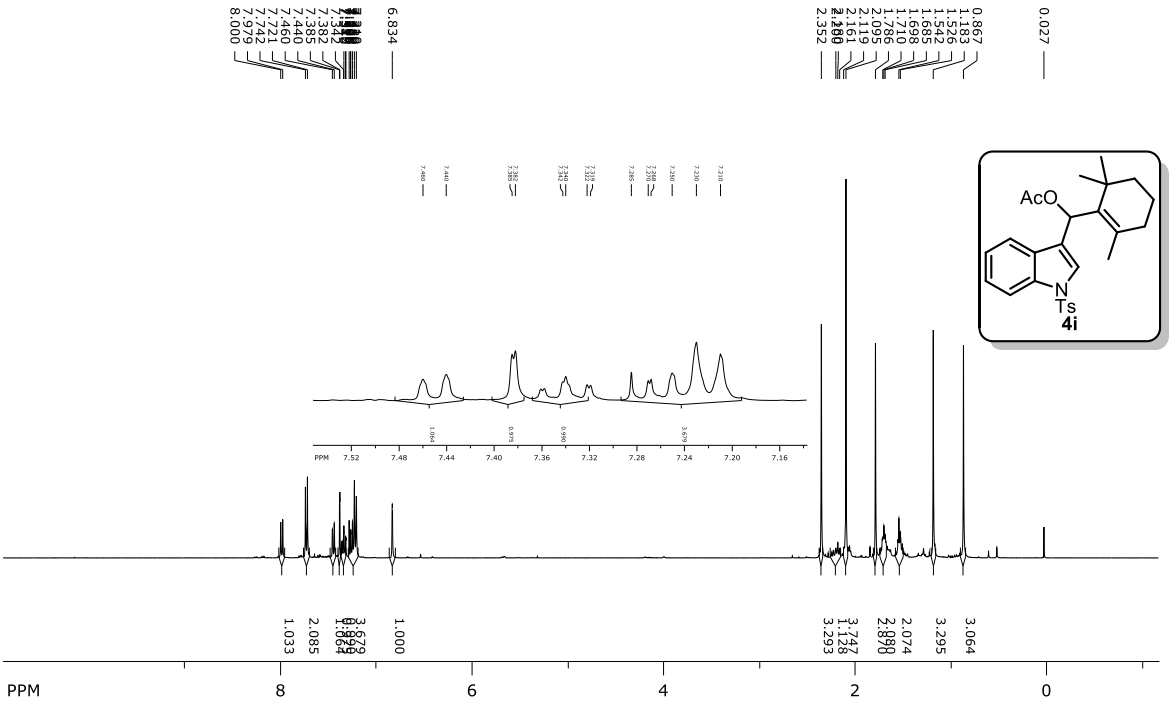
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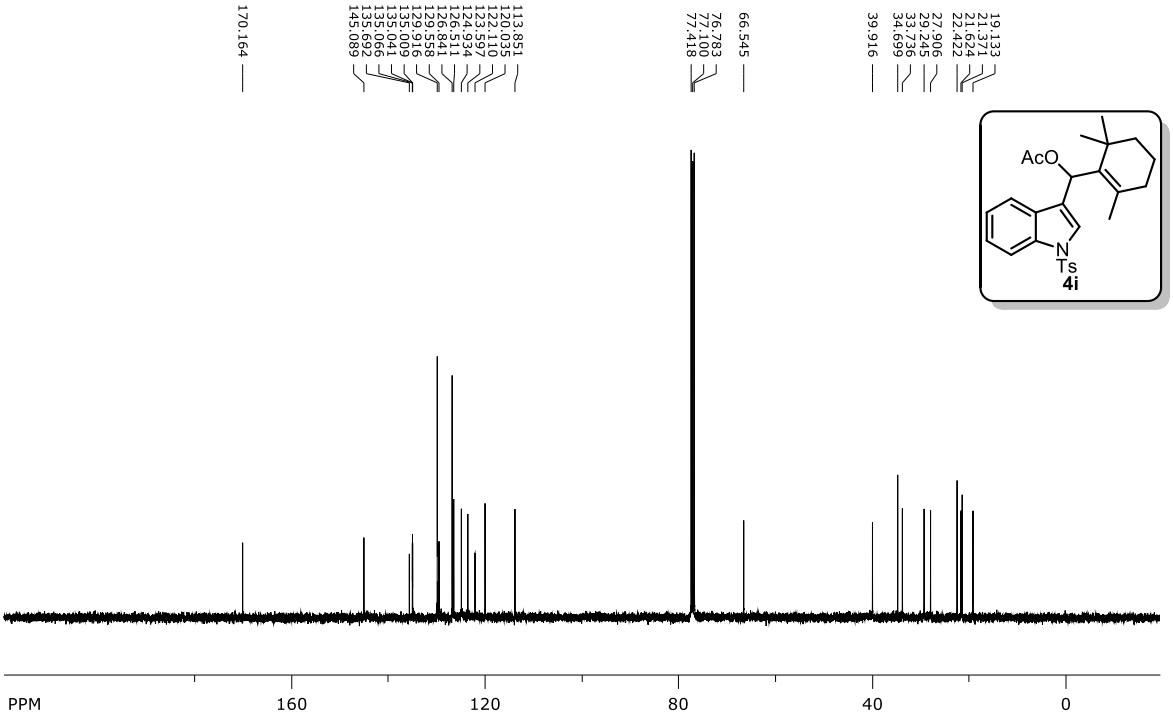
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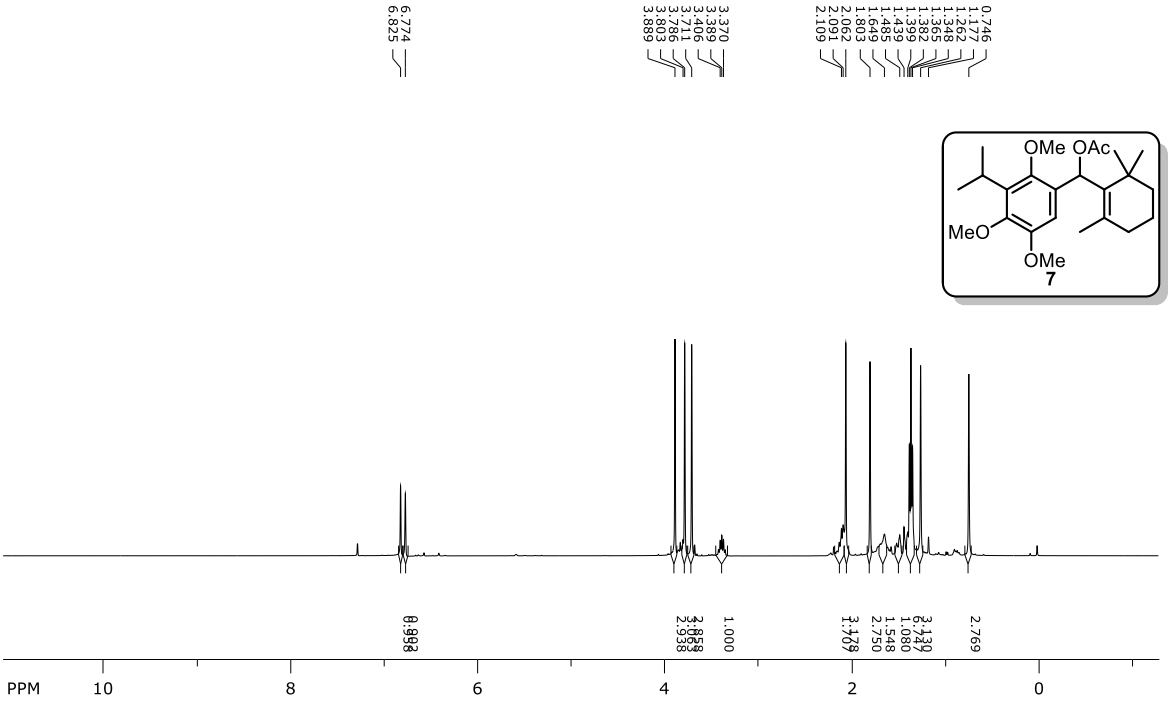
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MeO
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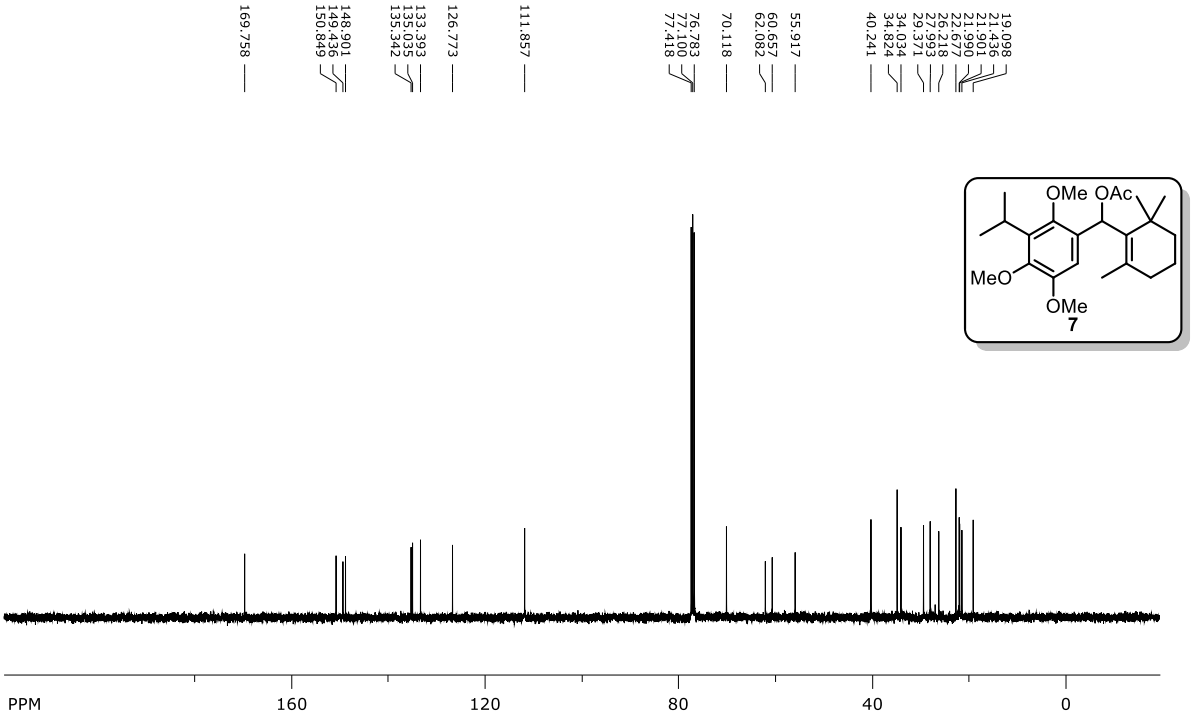
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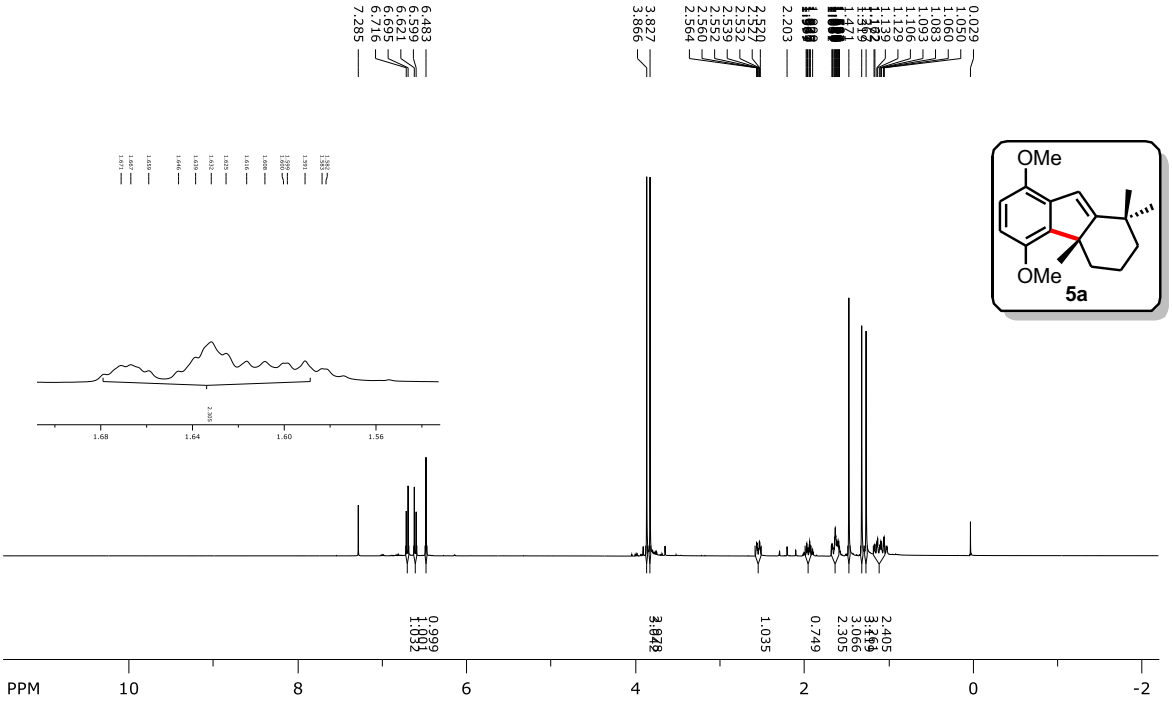
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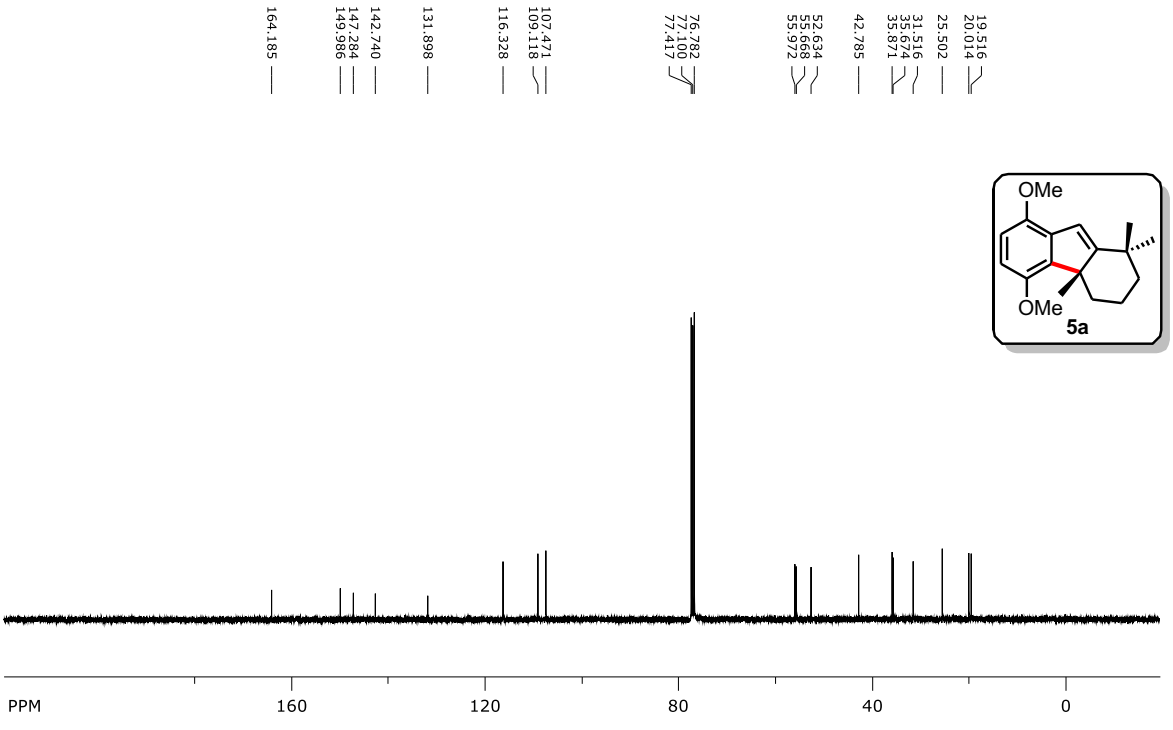
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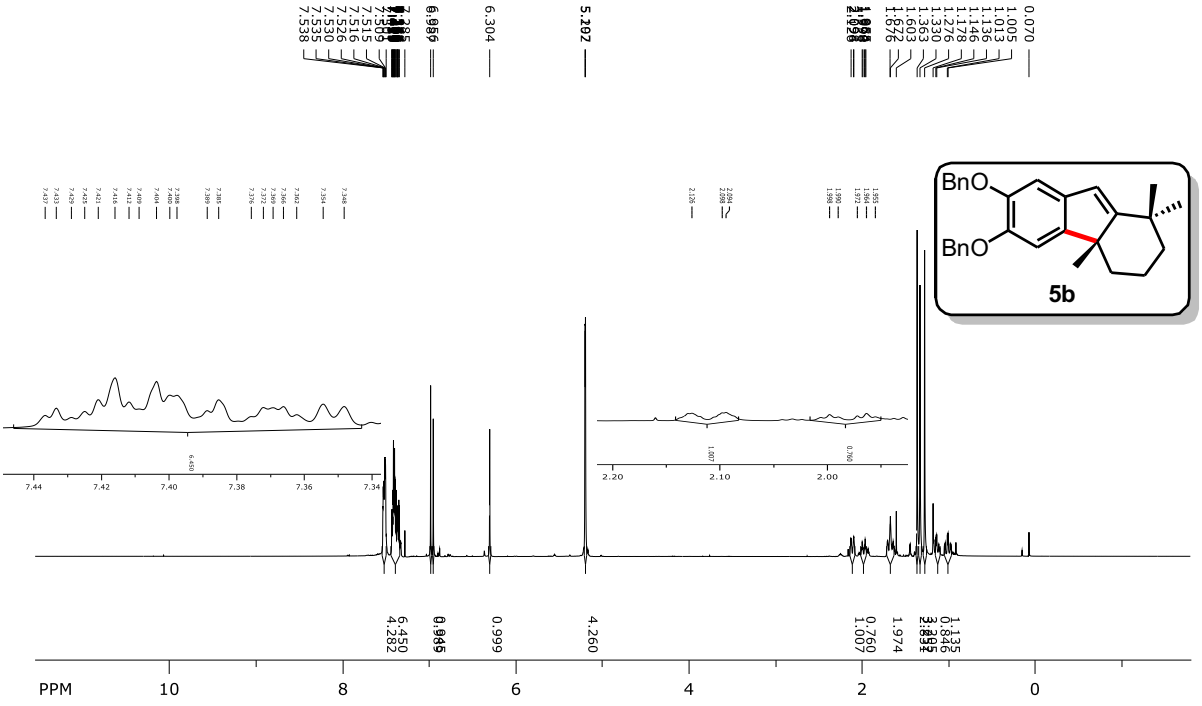
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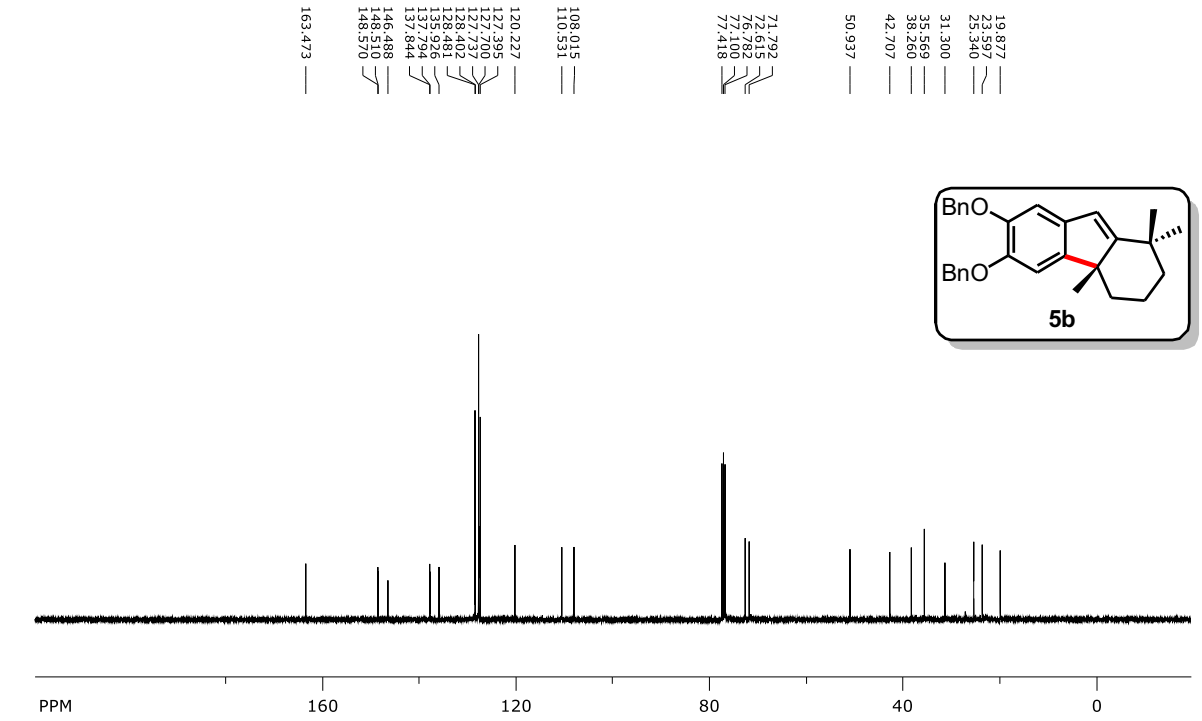
BnO
BnO
5b
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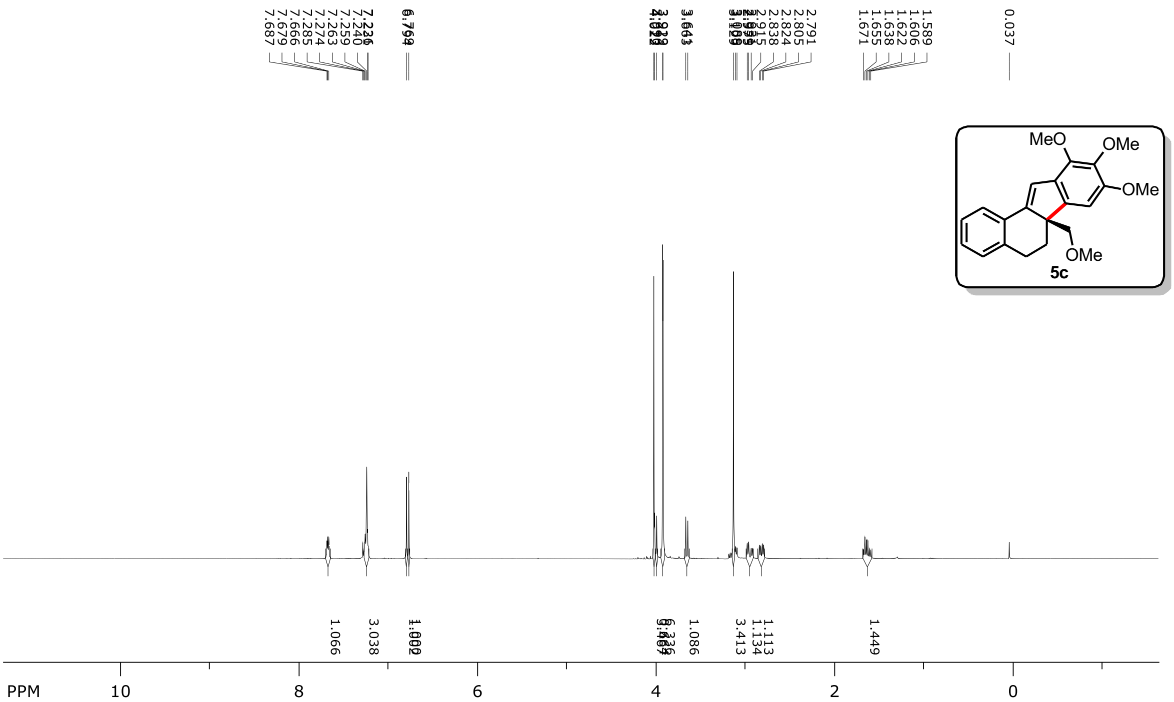
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OMe
OMe
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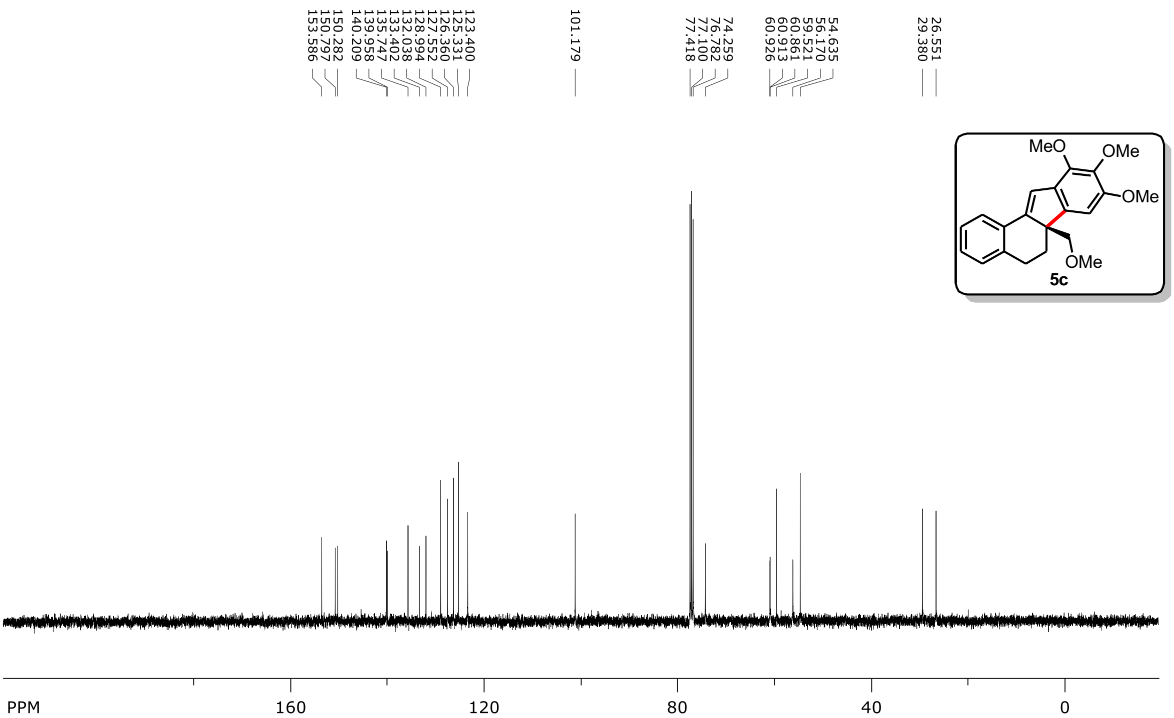
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OMe
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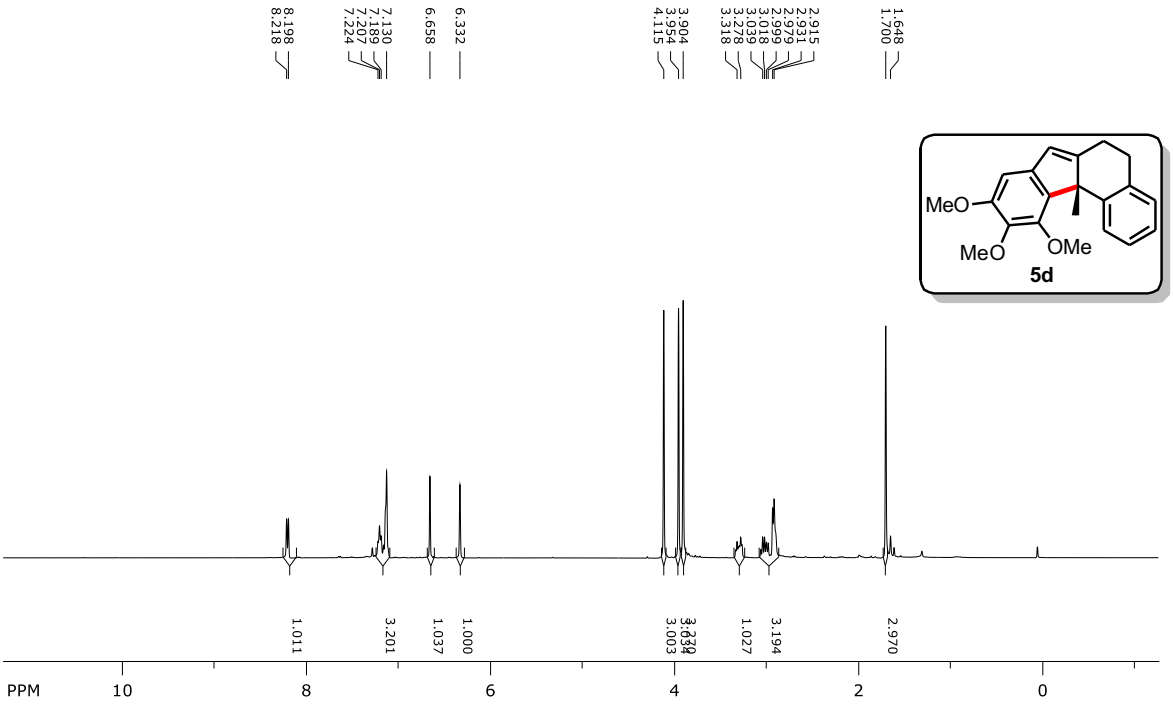
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MeO
OMe
5d
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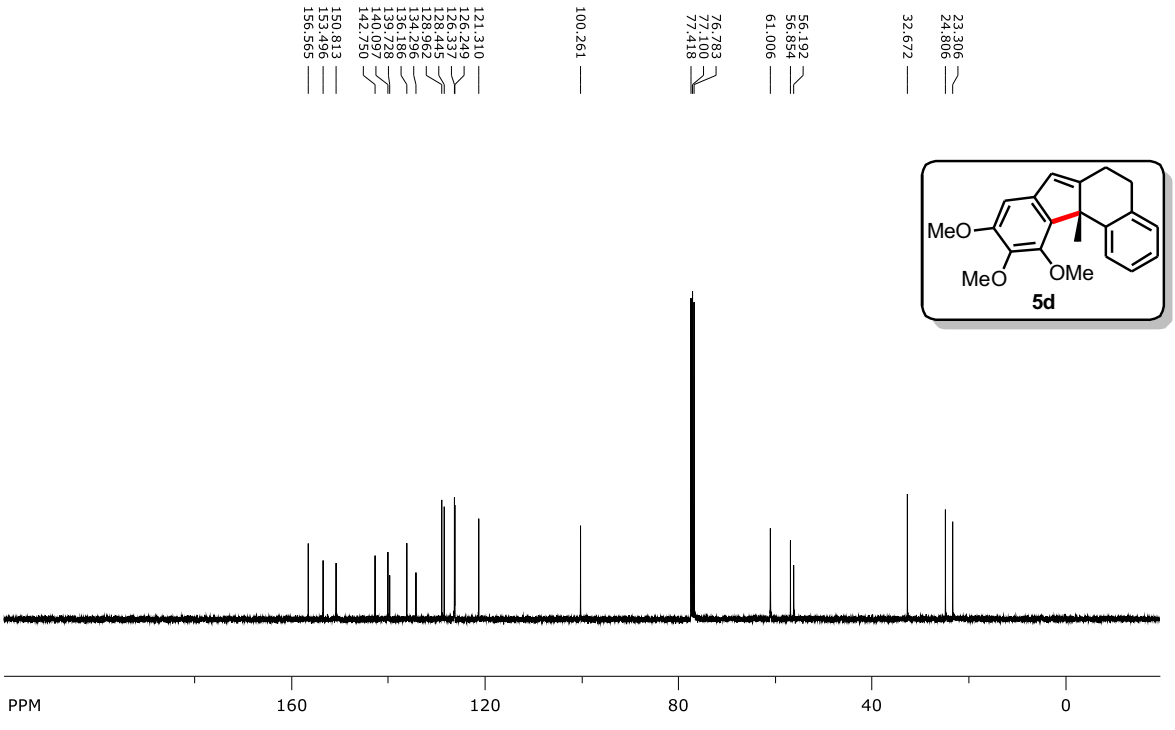
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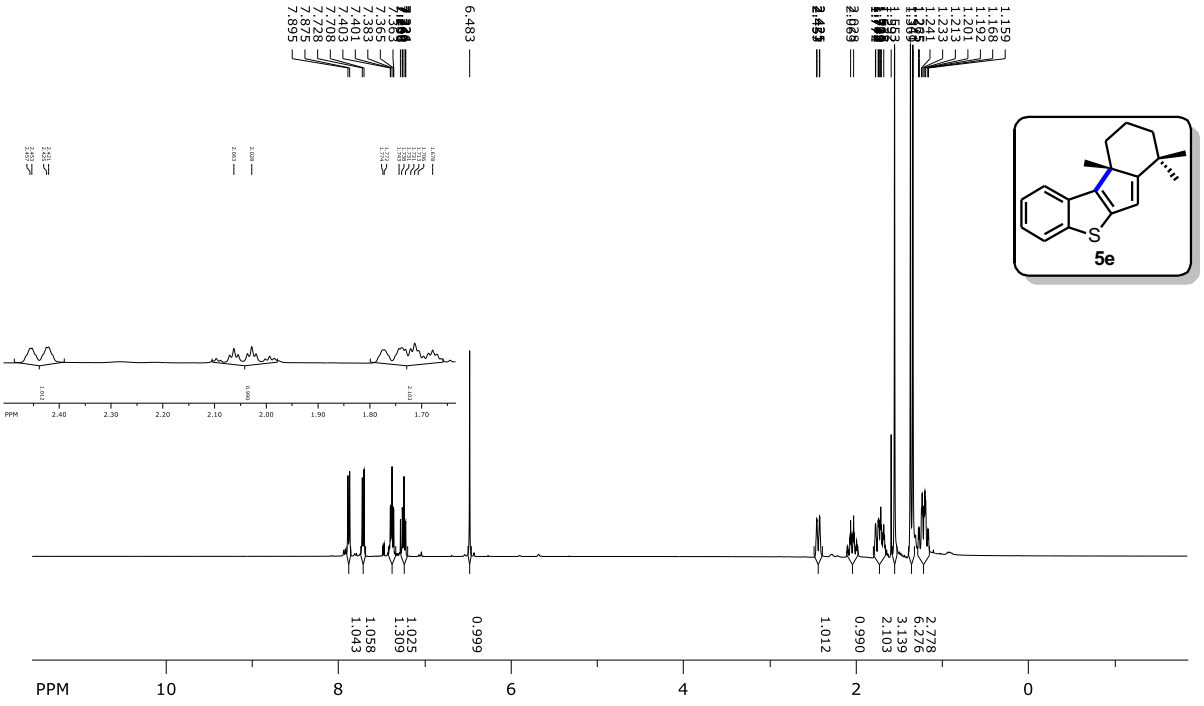
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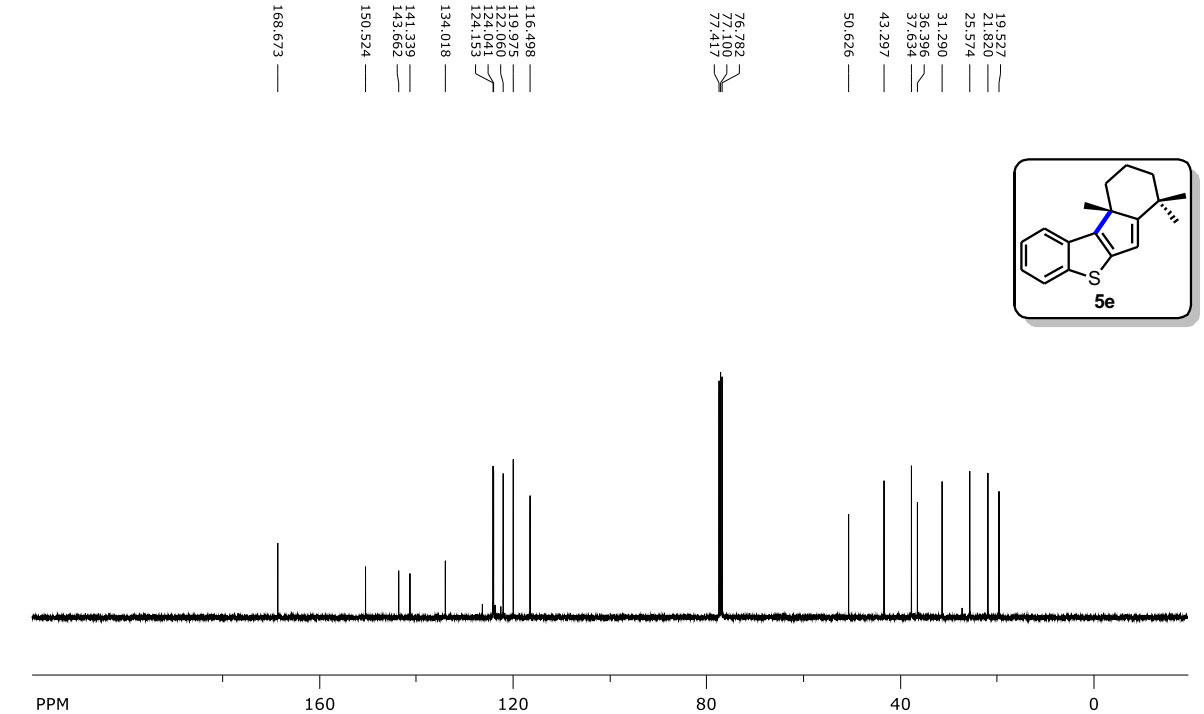
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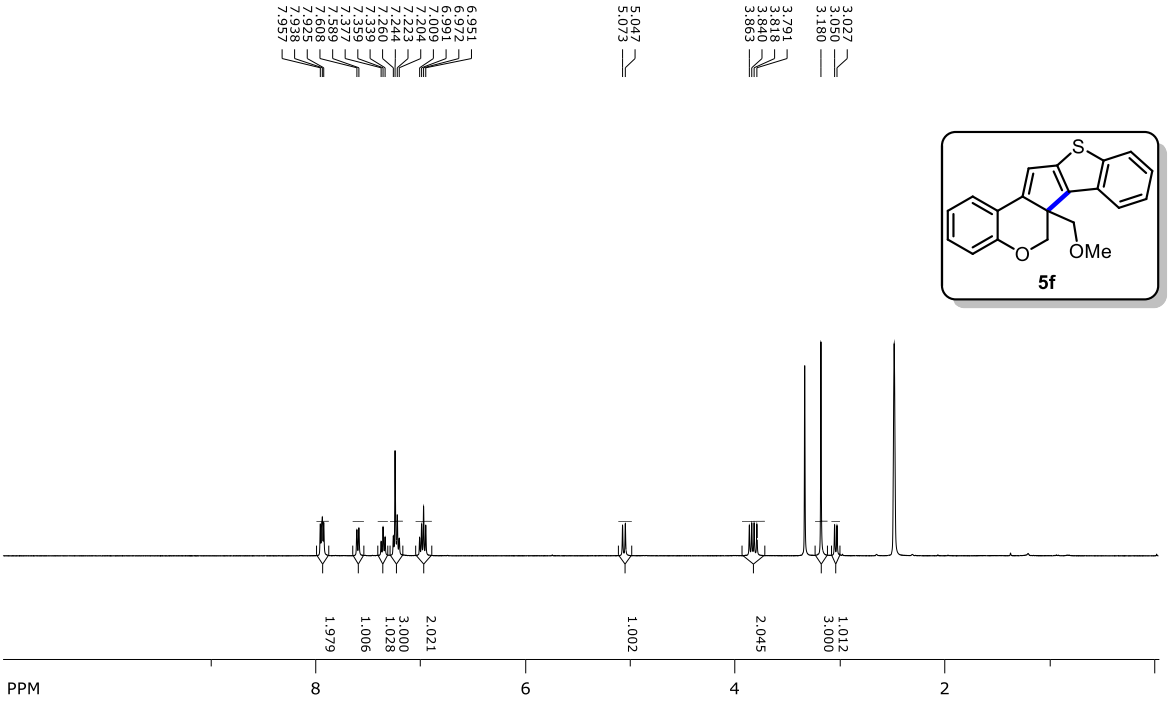
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S
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OMe
5f
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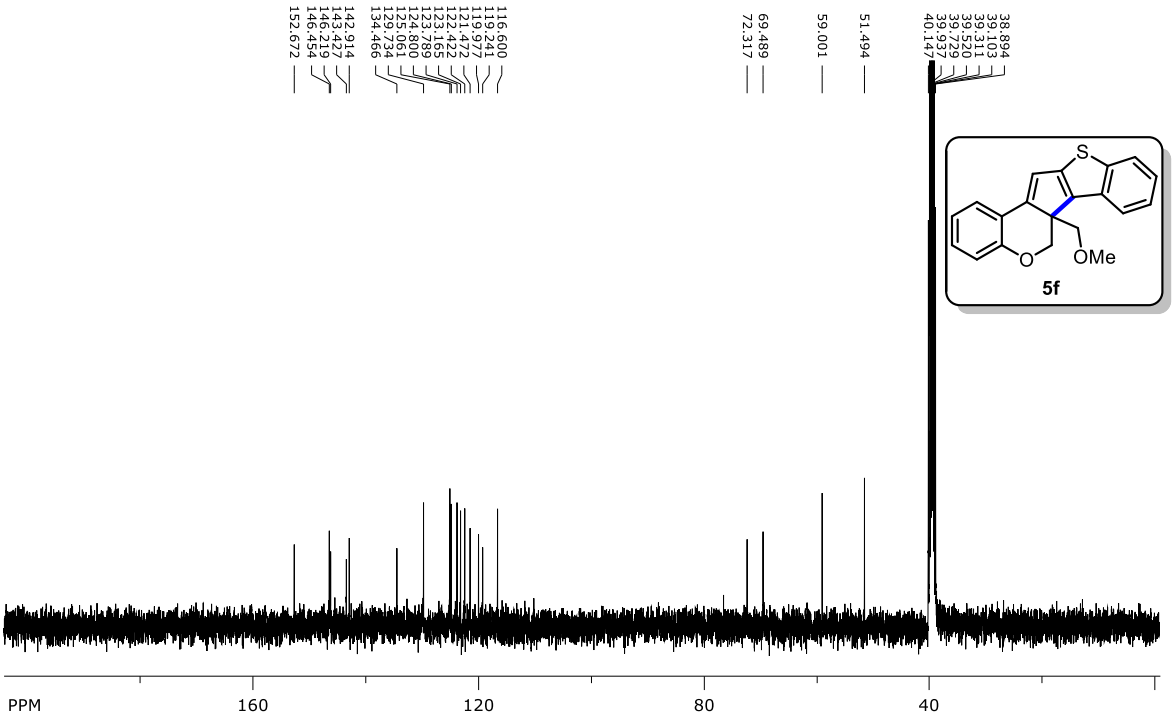
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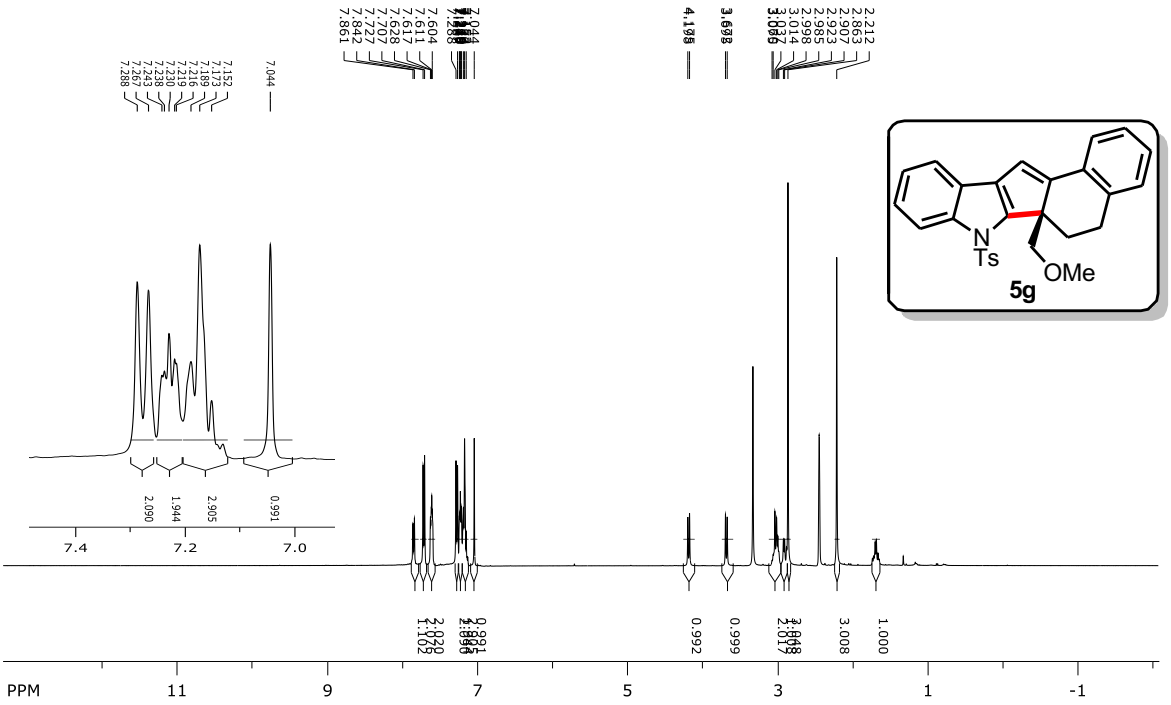
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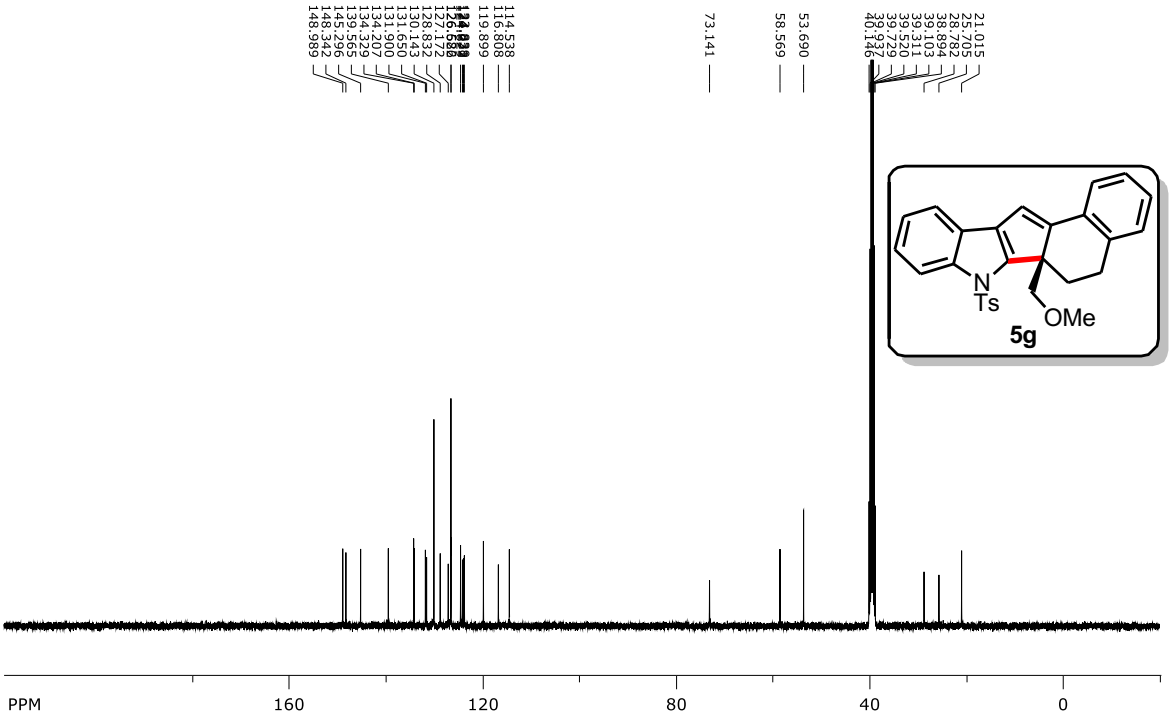
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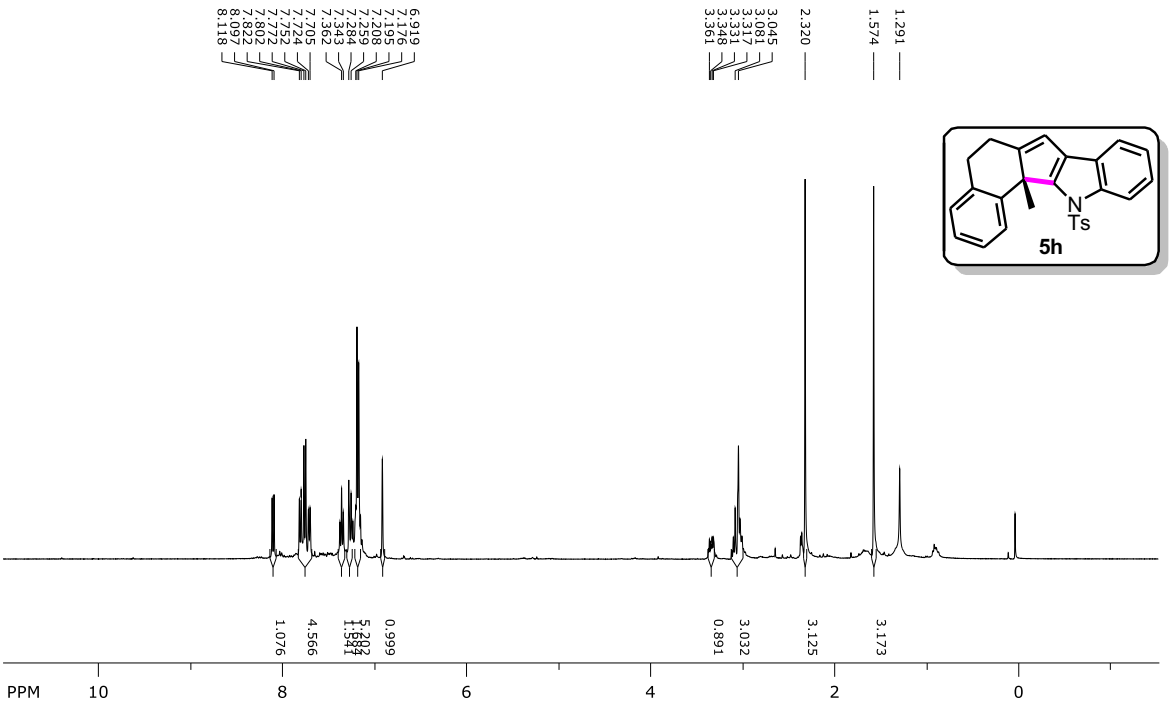
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3.317
3.081
3.045
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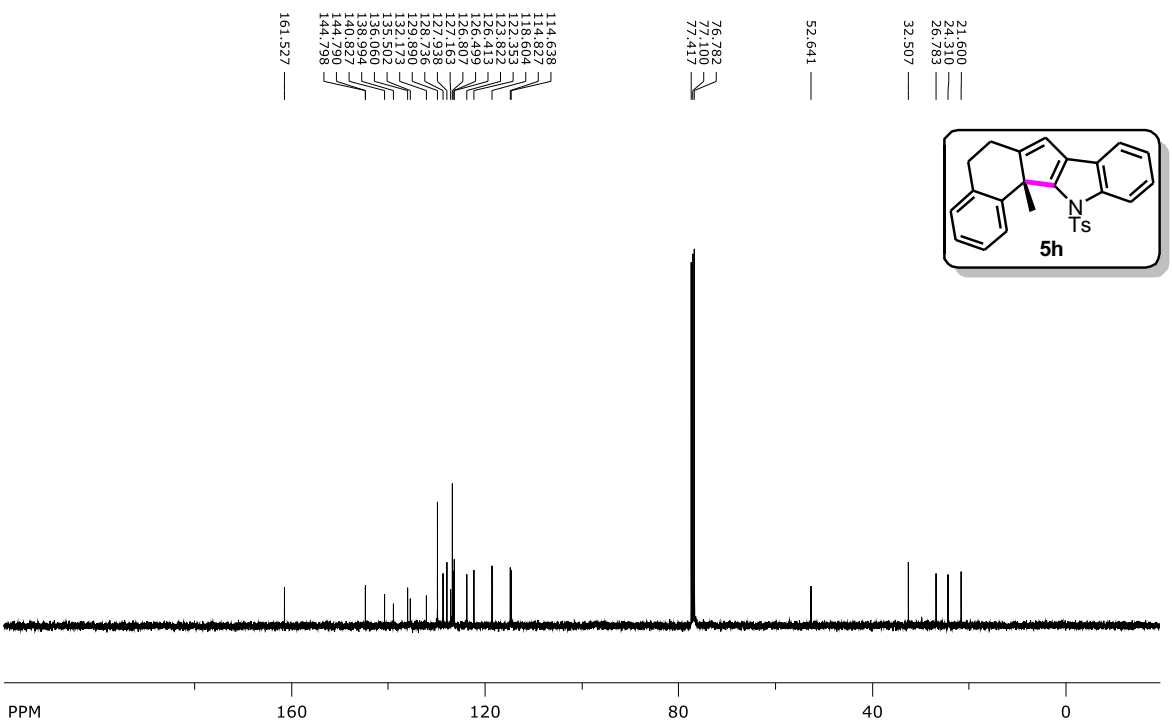
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114.638
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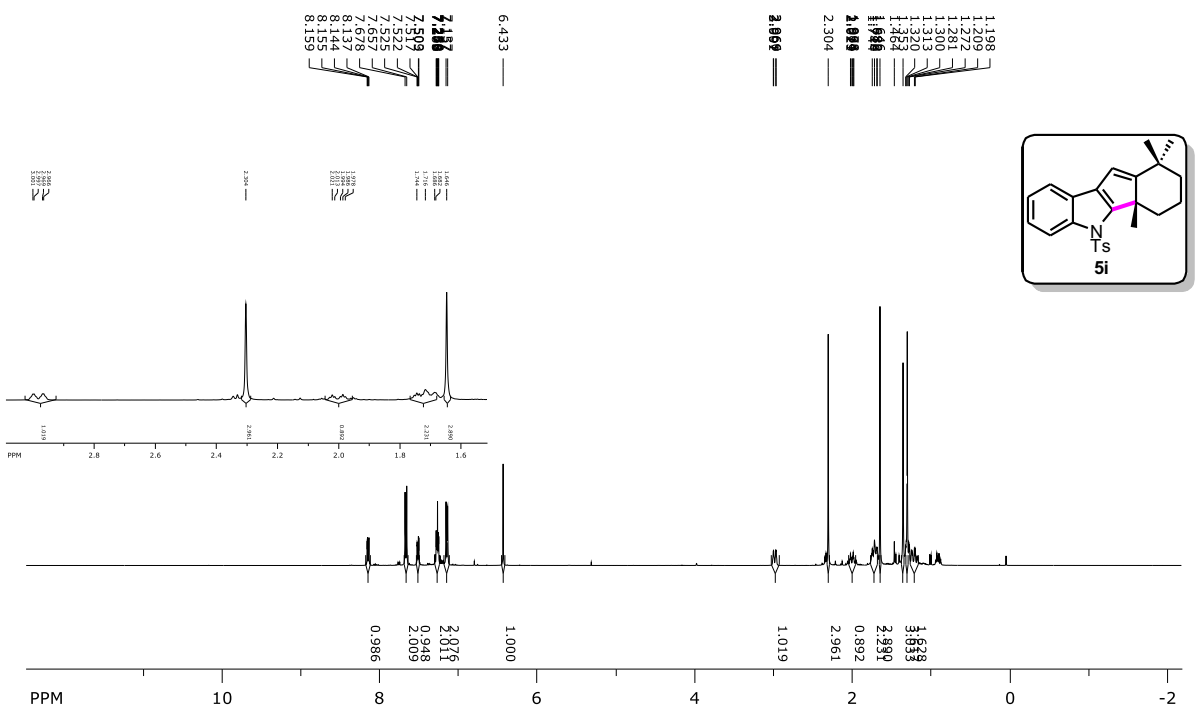
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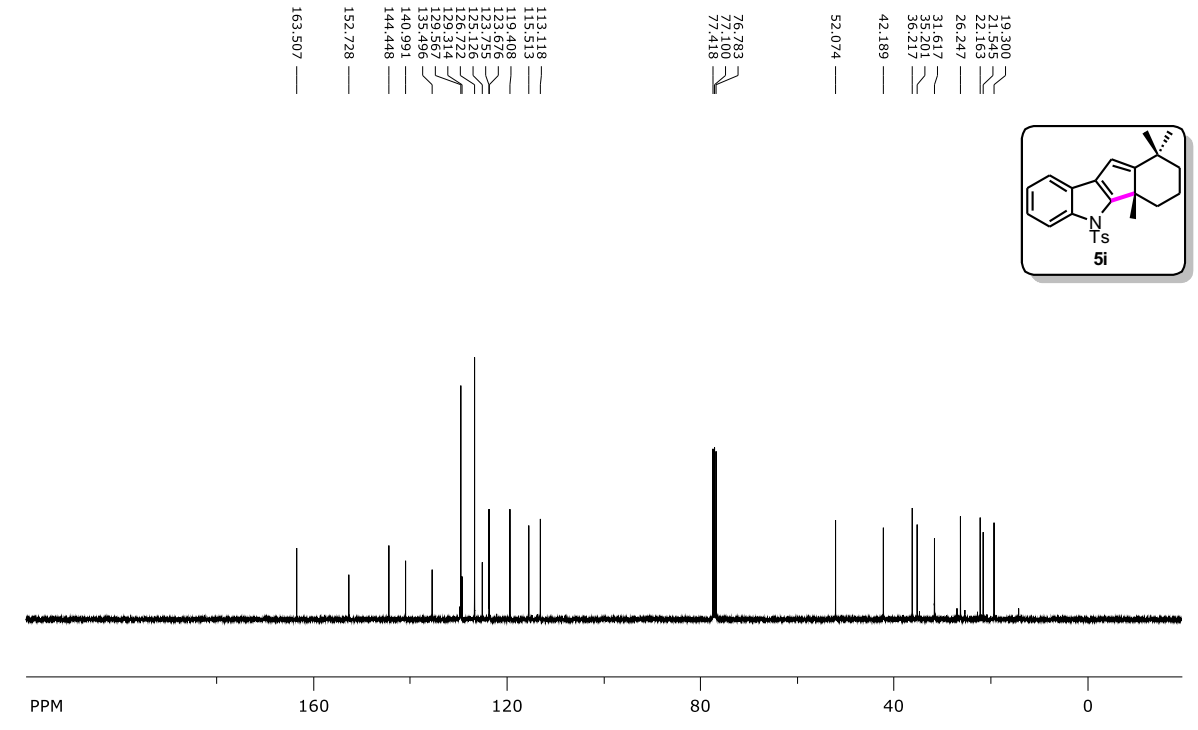
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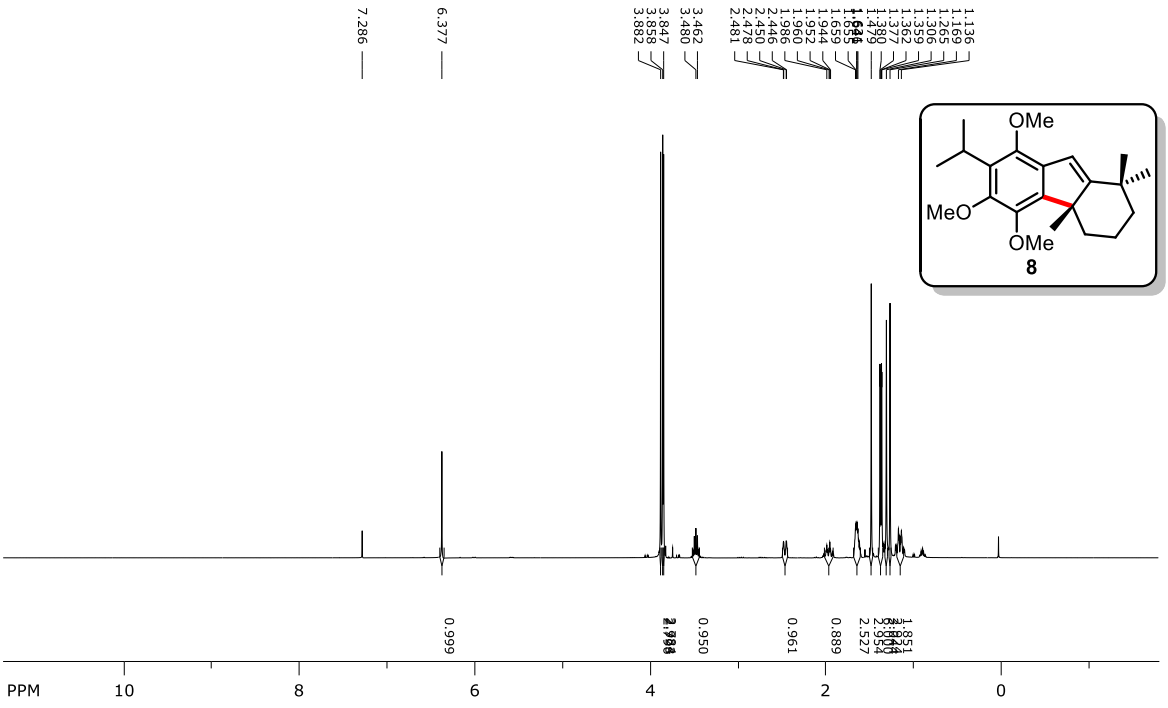
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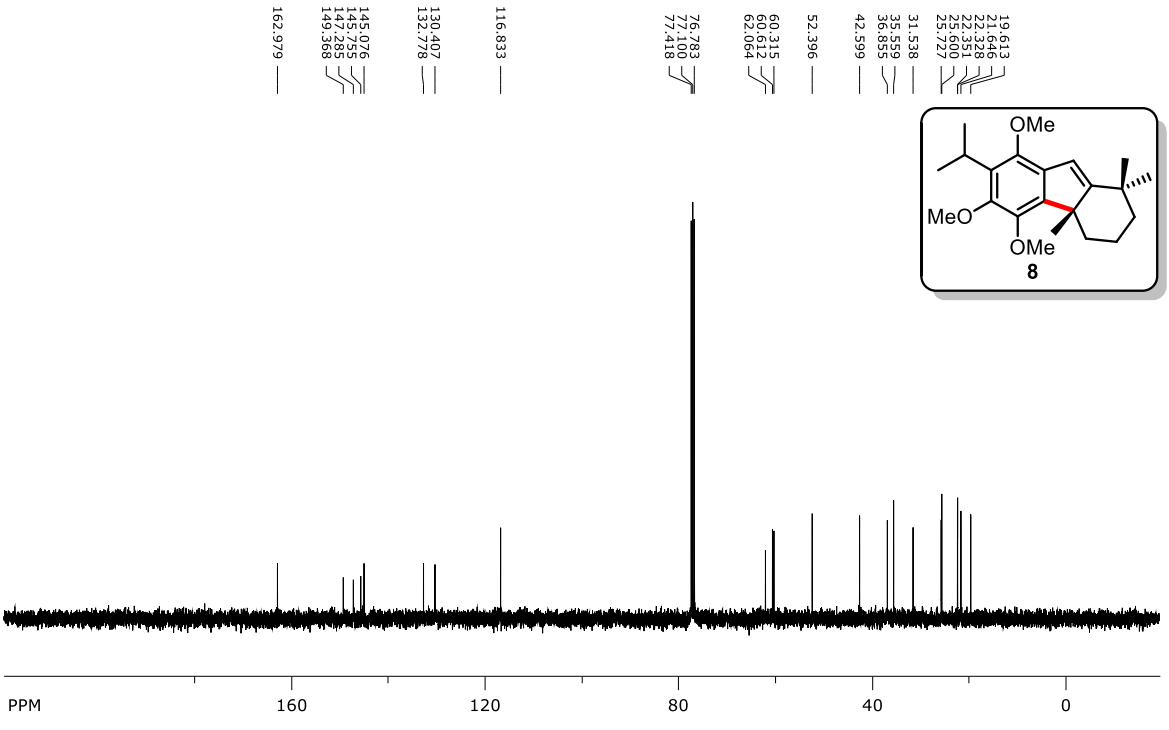
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OMe
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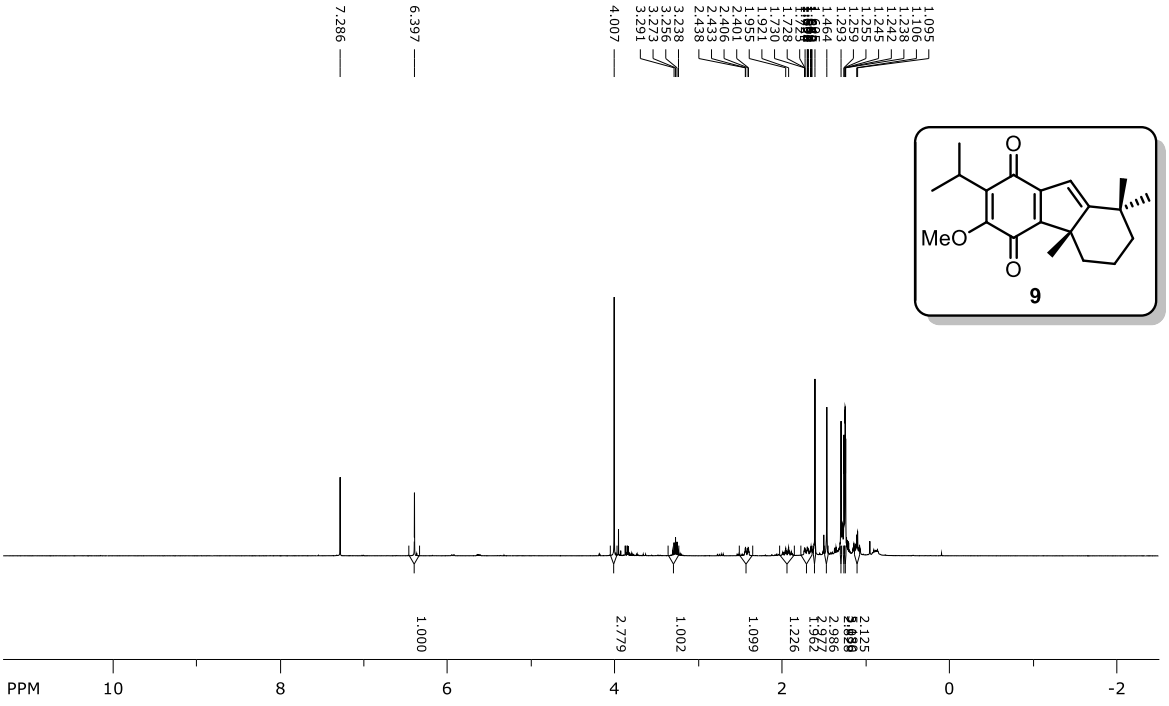
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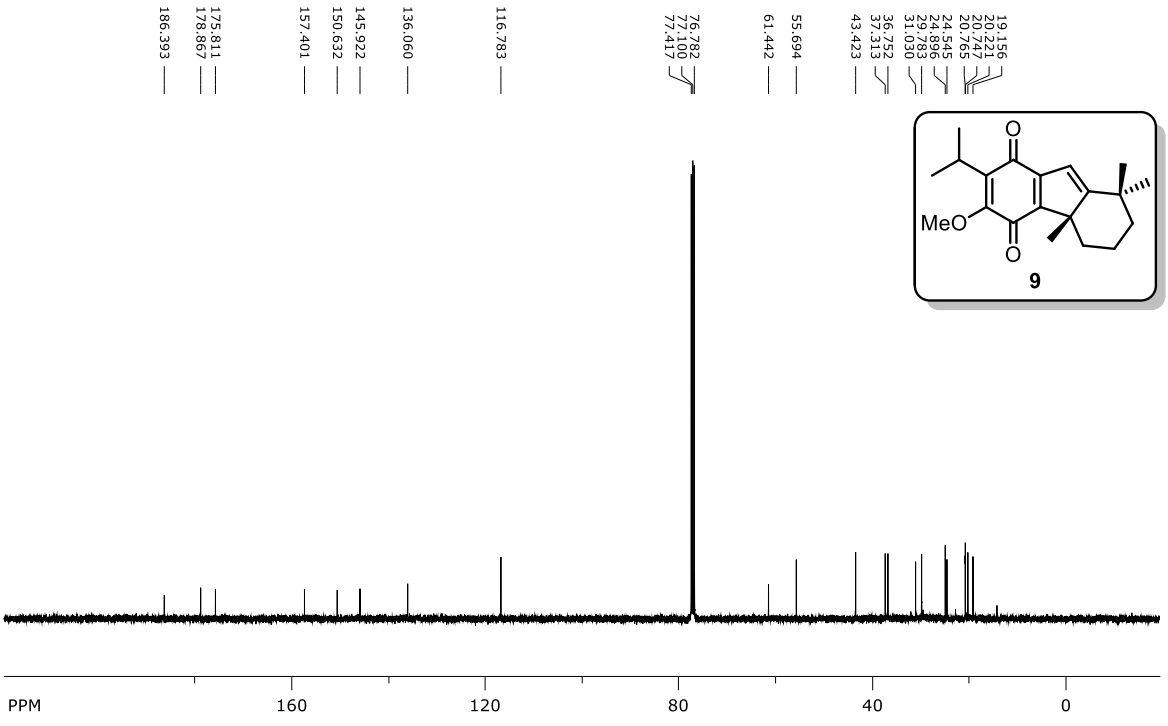
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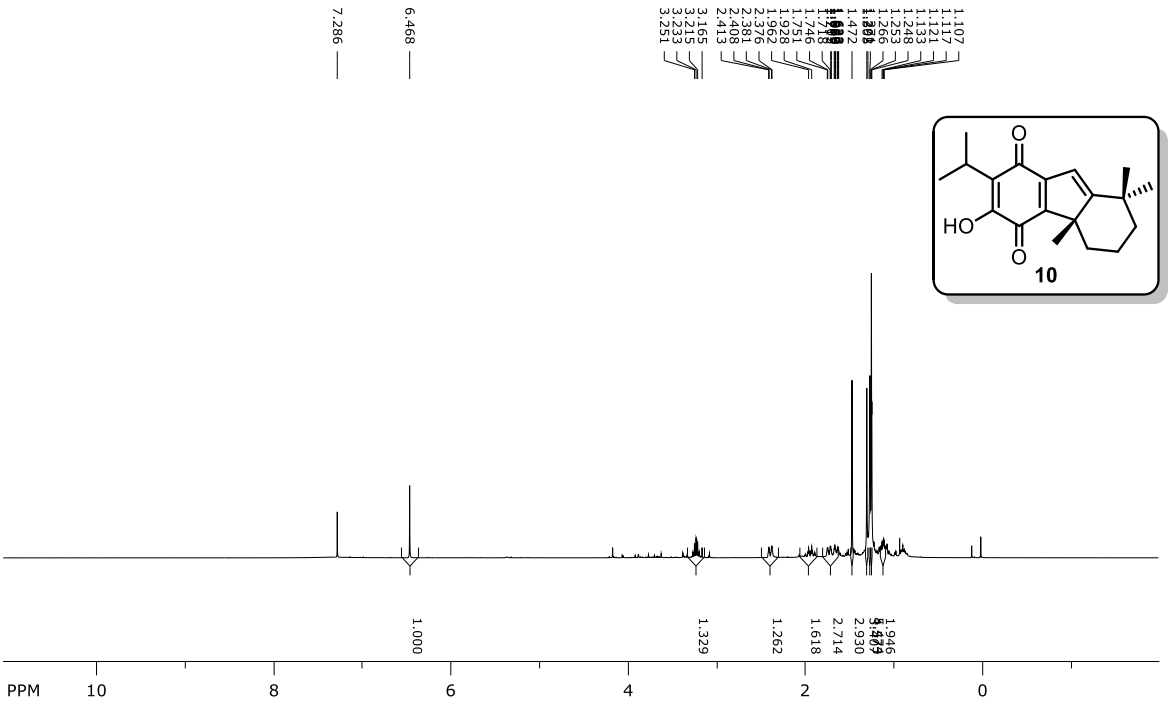
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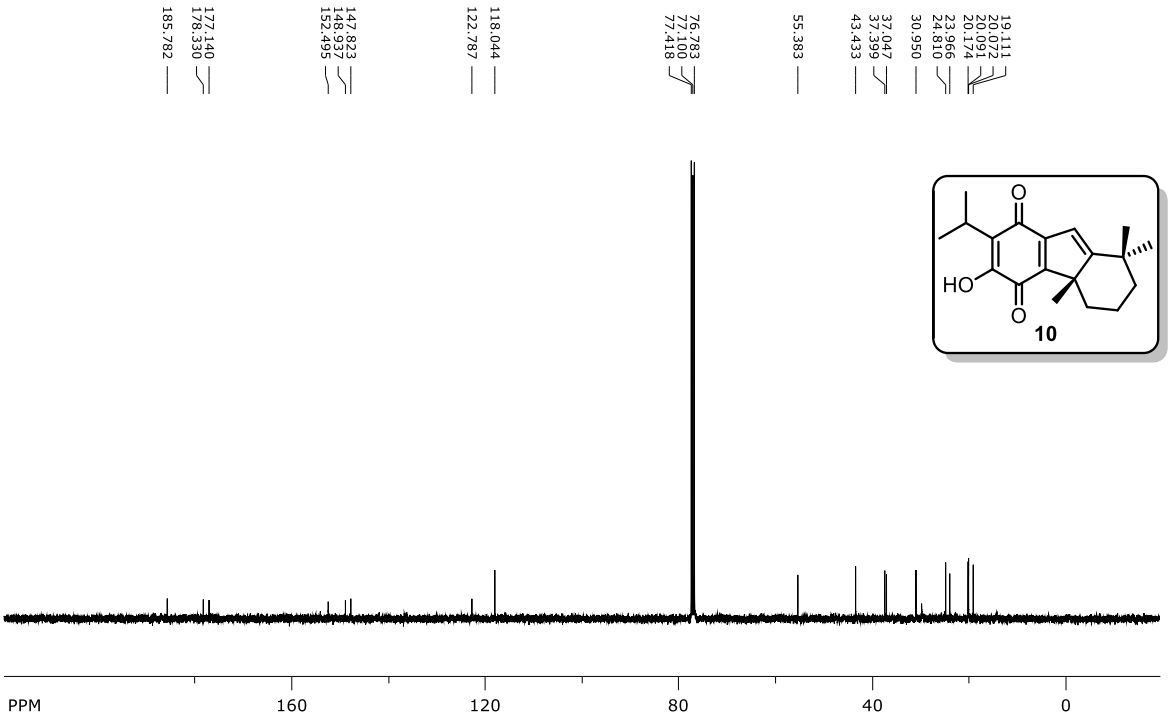
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20.072
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HO
O
O
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