Supporting Information

Phosphine- and water-promoted pentannulative aldol reaction

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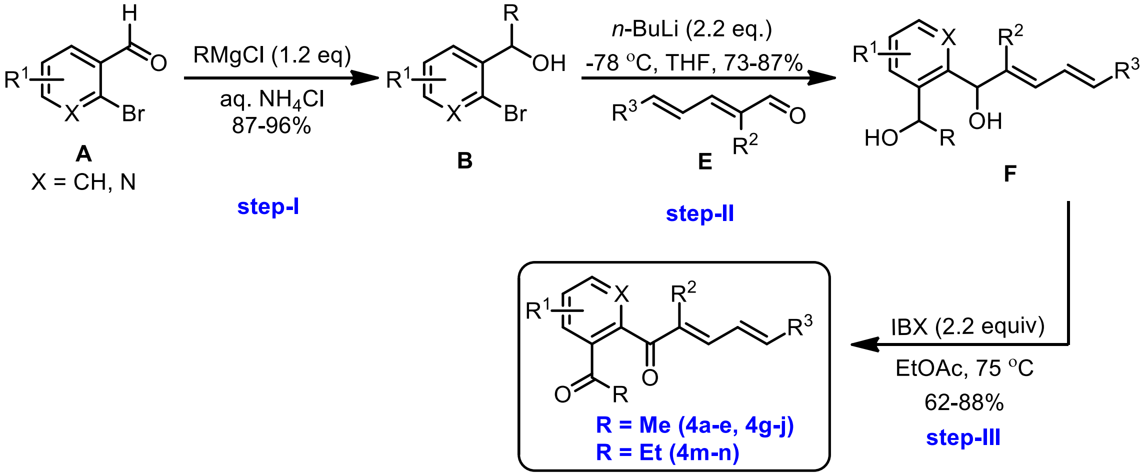
General experimental methods: All the starting compounds and catalysts employed in this study were procured from Sigma-Aldrich, Avra Chemicals and were used without further purification. For thin layer chromatography (TLC), silica aluminium foils with fluorescent indicator 254 nm (from Aldrich) were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), and acetic acid (10 mL) in ethanol (900 mL) followed by heating. Column chromatography was performed using SD Fine silica gel 60-120 mesh (approximately 15–20 g per 1 g of the crude product). Dry THF was obtained by distillation over sodium and stored over sodium wire. IR spectra were recorded on a Perkin–Elmer FT IR spectrometer as thin films or KBr pellet, as indicated, with ν_{max} in inverse centimetres. Melting points were recorded on a digital melting point apparatus Stuart SMP30 and were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Biospin Avance III FT-NMR spectrometer. NMR shifts are reported as delta (δ) units in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations are utilized to describe peak patterns when appropriate: br = broad, s = 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 $CDCl_3$ (7.26 ppm) or in $(CD_3)_2SO$ (δ 2.50 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). Single crystal X-ray analysis was carried on a Bruker AXS KAPPA APEX II system. High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer.

General procedure-1: Syntheses of the dienone-ketones 4a-e, 4g-j and 4m-n.

The dienones (**4a-e, 4g-j and 4m-n**) employed in this study were prepared as in Scheme 1S. *n*-Butyllithium reaction 2-bromobenzyl alcohols **B** followed by alkylation with an appropriate dienal **E** generated diols **F**. IBX oxidation of the diols **F** led to the formation of dienone-ketones **4**.



Scheme 1S. Syntheses of the dienones **4a-e, 4g-j and 4m-n.**

Representative procedure for step-I (Scheme 1S): To an oven dried 25 mL RB flask, 2-bromobenzaldehyde **A** (2.0 mmol) and anhydrous THF (10 mL) were added. Appropriate Grignar reagent (2.4 mmol) at 0 °C under nitrogen atmosphere and continued stirring at room temperature until **A** disappeared (as monitored by TLC). The reaction mixture was quenched with saturated aq. NH_4Cl and extracted with ethyl acetate. Organic extracts were combined and dried over anhydrous sodium sulphate and concentrated to afford 2-bromo alcohol **B**. The crude reaction mixture was taken forward to the next step without further purification.

Representative procedure for step-II (Scheme 1S):[1] An oven dried 25 mL long neck RB flask was charged with 2-bromobenzyl alcohol **B** (1.0 mmol), dry THF (5 mL) and placed at −78 °C. *n*-BuLi (1.6 *M* in hexanes, 2.2 mmol) was added drop wise at the same temperature and stirred for an hour. Then, α-methyl *trans*-cinnamaldehyde (1.3 mmol) dissolved in 1 mL of dry THF was added dropwise over 2 mins and stirred at room temperature for 30 mins. The reaction mixture was quenched with saturated aq. NH_4Cl solution and extracted using ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The

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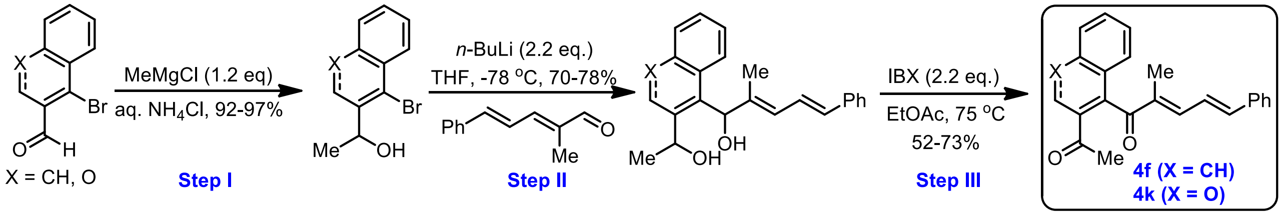
[1] B. Satpathi and S. S. V. Ramasastry, *Angew. Chem. Int. Ed.*, 2016, **55**, 1777.

product was purified by silica gel column chromatography using hexane/ethyl acetate (10:3) as eluent to afford the diol **C**.

Representative procedure for step-III (Scheme 1S): The diol **C** (1.0 mmol) was dissolved in ethyl acetate (10 mL) and IBX (2.2 mmol) was added. The resulting suspension was immersed in an oil bath set to 75 °C and stirred until diol **C** disappeared as monitored by TLC. The reaction mixture was cooled to room temperature and filtered through a Buchner funnel. The filter cake was washed with 3×5 mL of ethyl acetate. Organic extracts were combined and washed with saturated sodium bicarbonate solution to remove excess iodobenzoic acid. The extract was dried over anhydrous sodium sulphate and concentrated under vacuum. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the enone **4**.



Scheme 2S. Syntheses of the dienone-ketones **4f** and **4k.**

Representative procedure for step-I, II and III (Scheme 2S): Reactions were performed by following the general procedure described for step-I, II and III, Scheme 1S.

General procedure-2: Syntheses of the dienone-ketones 4l and 4o.

The dienones **4l** and **4o** were synthesized by following literature methods, Scheme 4S.[2] Direct α-alkylation of benzothiophene-3-carboxaldehyde **G** afforded **H**, which upon Grignard reaction and IBX oxidation generated the dienone-ketones **4l** and **4o**.

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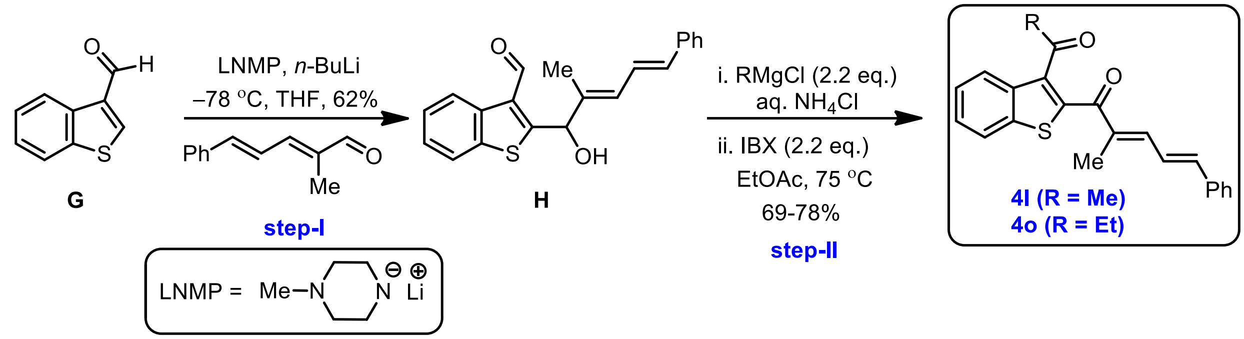
[2] (a) S. Dhiman and S. S. V. Ramasastry, *Indian J. Chem., Sect. A*, 2013, **52,** 1103; (b) R. P. Shirke and S. S. V. Ramasastry, *J. Org. Chem.*, 2015, **80**, 4893; (c) B. Satpathi, S. V. Wagulde and S. S. V. Ramasastry, *Chem. Commun.*, 2017, **53**, 8042.

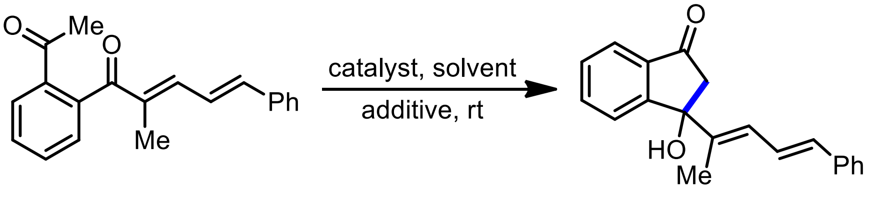


Scheme 3S. Syntheses of the dienone-ketones **4l** and **4o.**

Representative procedure for step-I (Scheme 3S): To a solution of *N*-methylpiperazine (NMP, 0.18 mL, 1.6 mmol) in THF (5 mL) at −78 °C was added *n*-BuLi (1.6*M* in hexane, 1.0 mL, 1.6 mmol). After 15 min, benzothiophene-3-carboxaldehyde **G** (200 mg, 1.2 mmol) was added and then the reaction mixture was stirred for an additional 30 min. A hexane solution of *n*-BuLi (2.0 mL, 3.2 mmol) was added and the mixture was stirred for an additional 15 min and then the mixture was warmed to −30 °C in 2 h. The solution was again cooled down to −78 °C and an appropriate dienal (1.5 mmol) dissolved in dry THF (1.0 ml), was added drop wise over 5 min. The mixture was warmed to room temperature over 30 min. The reaction progress was monitored by TLC. Reaction mixture was quenched with saturated aqueous ammonium chloride solution and extracted with ethyl acetate. 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 to afford dienol **H.**

Representative procedure for step-II (Scheme 3S): To an oven dried 25 mL RB flask, alcohol **H** (1.0 mmol) and anhydrous THF (10 mL) were added. Appropriate Grignard reagent (2.2 mmol) at 0 °C under nitrogen atmosphere and continued stirring at room temperature until **A** disappeared (as monitored by TLC). The reaction mixture was quenched with saturated *aq*. NH_4Cl and extracted with ethyl acetate. Organic extracts were combined and dried over anhydrous sodium sulphate and concentrated to afford the diol. The crude diol was further subjected to IBX oxidation (procedure as described in step III, scheme 1S) to afford the dienone-ketones **4l** and **4o**.

General procedure-3: Optimization of the reaction parameters for 4a.

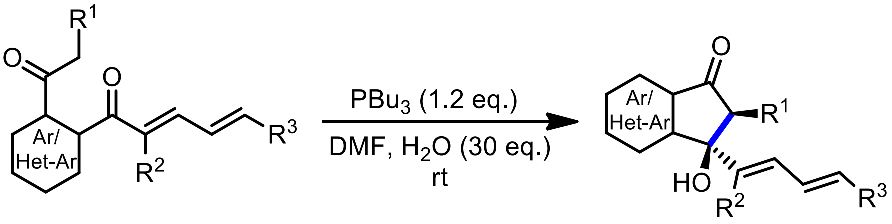


4a **5a**

Scheme 4S. Optimization of reaction parameters for aldol reaction

Representative procedure: An oven dried 5 mL glass vial was charged with **4a** (30 mg, 0.11 mmol). An appropriate solvent (1 mL), additive and a catalyst (1.2 mmol) were introduced at room temperature (rt) and stirring continued at rt until **5a** disappeared as monitored by TLC. The reaction mixture was extracted using ethyl acetate. All the volatiles were removed under reduced pressure. The crude product was purified by silica gel chromatography using hexane/ethyl acetate (10%) as eluent, to afford **5a** as a pale yellow solid.

General procedure-4: Evaluating the substrate scope for 5.



4 **5**

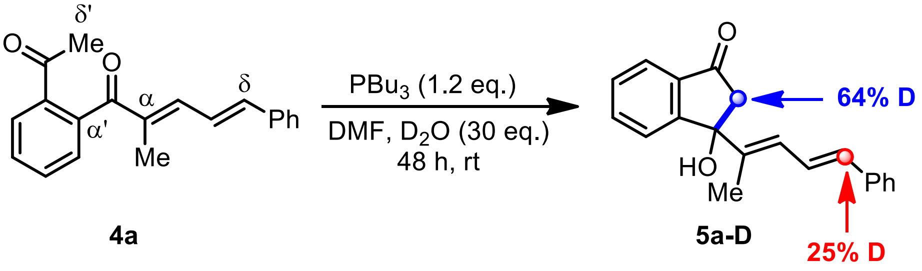
Scheme 5S. Synthesis of cyclopentannulated arenes and heteroarenes **5** via aldol reaction

Representative procedure: An oven dried 5 mL glass vial was charged with **4** (30 mg, 0.11 mmol). An appropriate solvent (1 mL), water (3.3 mmol) and PBu$_3$ (1.3 mmol) were introduced at room temperature (rt) and stirring continued at rt until **5** disappeared as monitored by TLC. The reaction mixture was extracted using ethyl acetate. All the volatiles were removed under reduced pressure. The crude product was directly purified by silica gel chromatography using hexane/ethyl acetate as eluent to afford **5**.

Efforts to gain mechanistic insights about the phosphine-mediated intramolecular aldol reaction

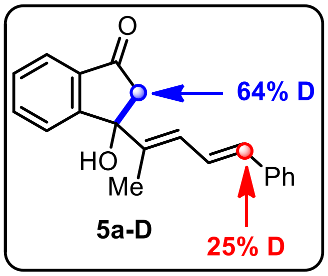
1. Aldol reaction of 4a in the presence of D_2O

The role of water was investigated in the aldol reaction by carrying out the reaction of **4a** using D_2O instead of H_2O, which resulted in the formation of **5a-D** in 81% yield (Scheme S18). The *D*-incorporation in **5a-D** at δ-position was 25% and at δ'-position, it was realized to be 64%.



Scheme 6S: Aldol reaction of **4a** in presence of D_2O

3-Hydroxy-3-((2*E*,4*E*)-5-phenylpenta-2,4-dien-2-yl)-2,3-dihydro-1*H*-inden-1-one (5a-D).



This compound was isolated as white solid. Following the general procedure-4, 50 mg of **4a** afforded 40.4 mg of **5a-D** (81% yield). M.P = 133-135 °C. $R_f = 0.3$ (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3420, 2926, 1710, 1600, 1459, 1285, 1047, 753. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.53-7.50 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.01 (dd, *J* = 15.5 and 11.0 Hz, 2H), 6.62 (d, *J* = 15.5 Hz, 0.75H), 6.56 (d, *J* = 11.0 Hz, 1H), 3.07 (d, J_{AB} = 19.2 Hz, 0.37H), 2.89 (d, J_{AB} = 19.2 Hz, 0.33H), 2.33 (s, 1H), 1.72 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.4-203.3 (m, C=O), 156.8 (d, *J* = 2.2 Hz), 139.1, 137.4, 136.4 (d, *J* = 1.3 Hz), 135.6, 133.6, 129.6, 128.6 (2C), 127.6, 126.4 (2C), 124.7, 124.5, 124.4, 123.4, 80.0 (t, *J* = 5.5 Hz), 52.0-51.5 (m, CD_2), 13.9. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{15}D_3O_2$ $(M)^+$: 293.1495. Found: 293.1488.

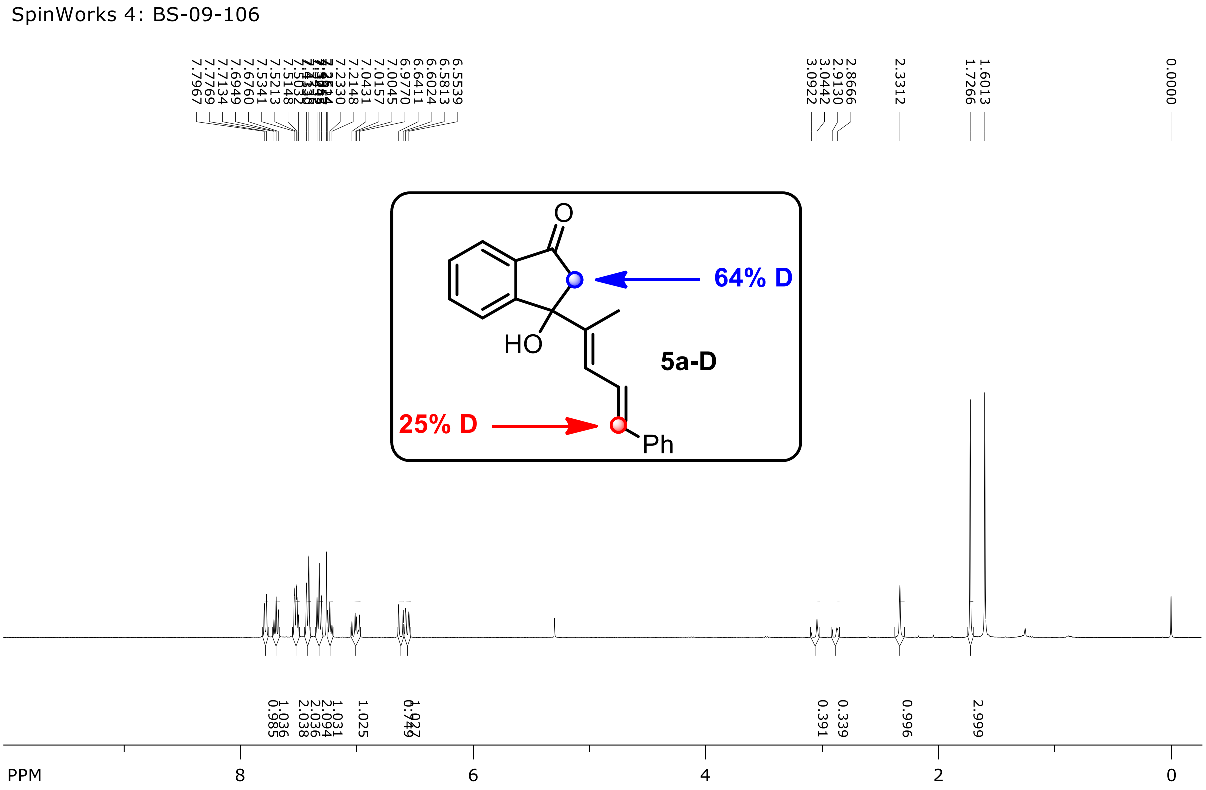


Figure 1S: ^{1}H NMR spectrum of **5a-D**

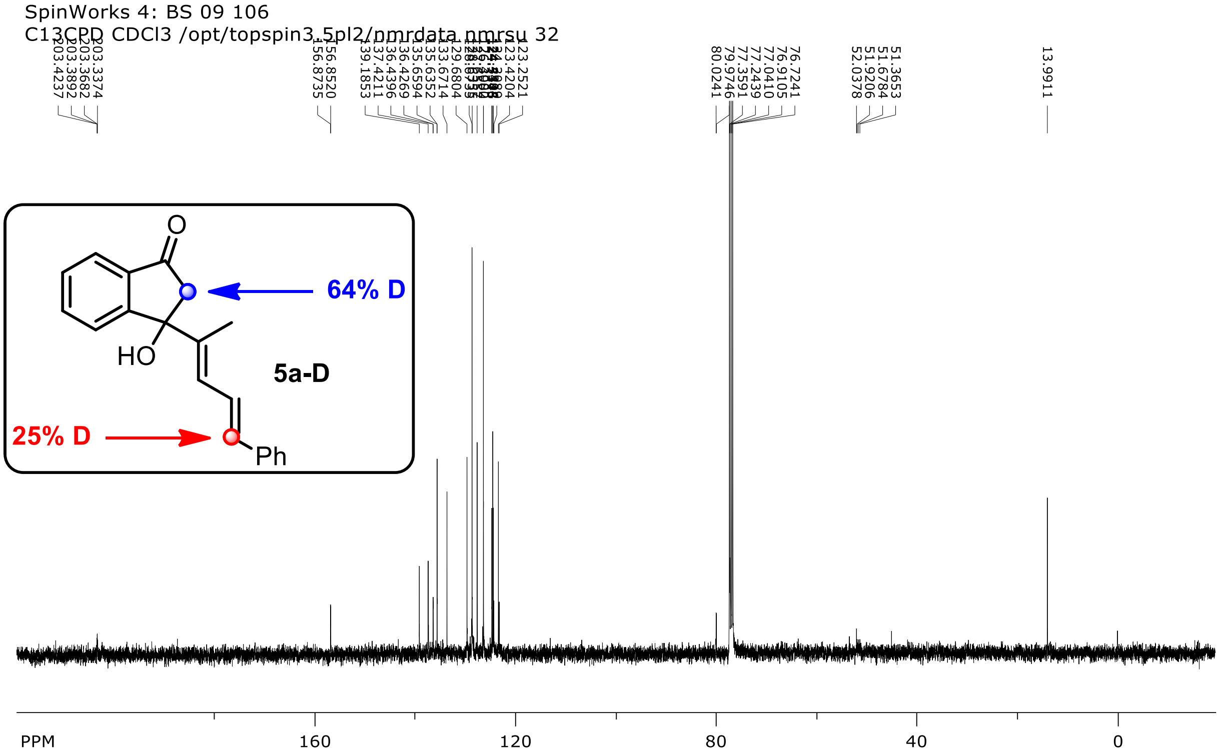


Figure 2S: ^{13}C NMR spectrum of **5a-D**

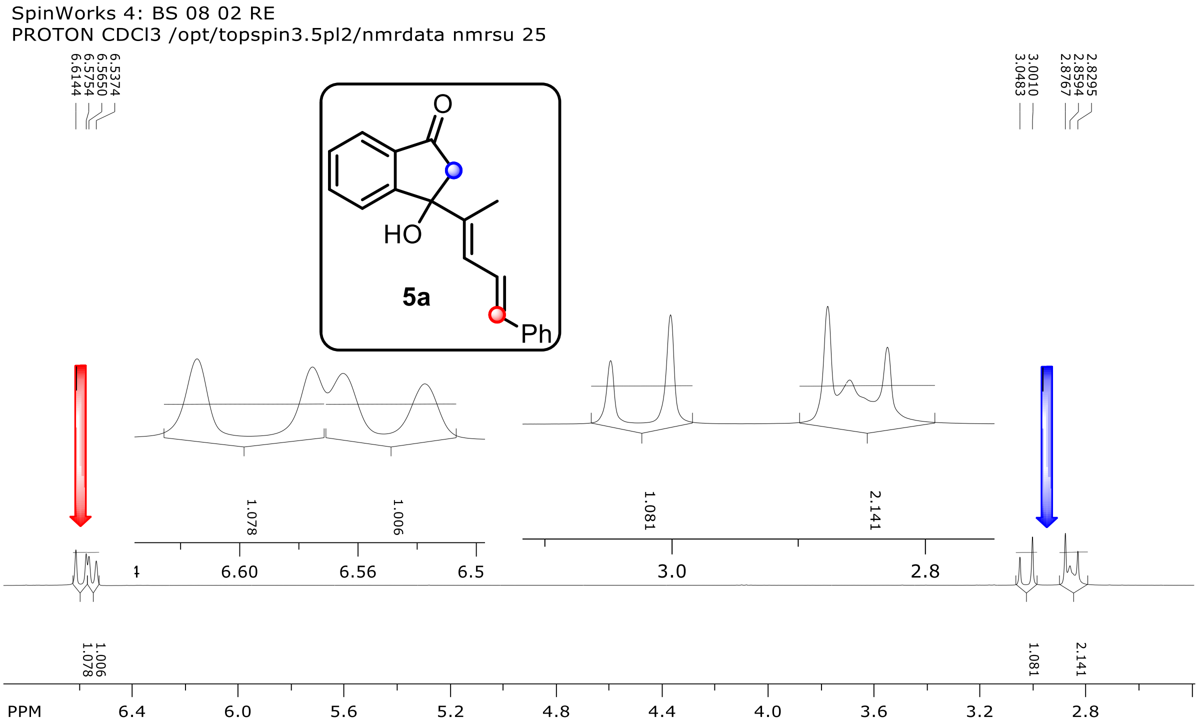


Figure 3S: Expanded ^{1}H NMR spectrum of **5a**

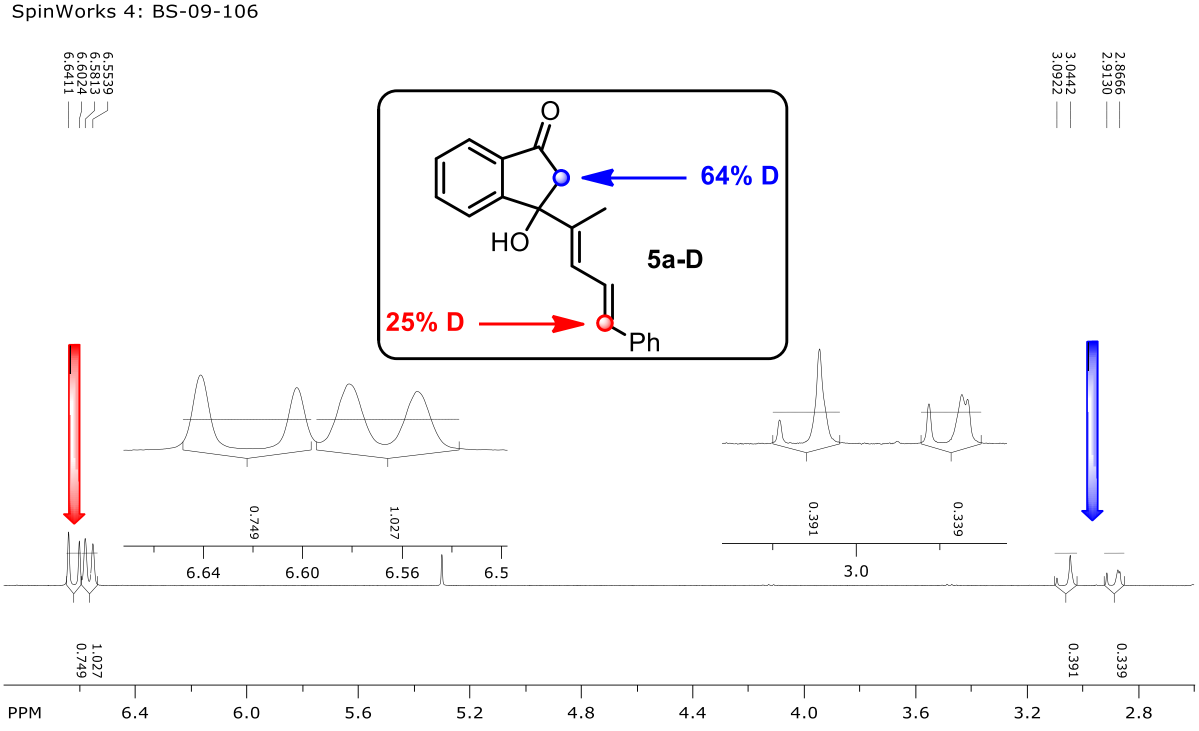
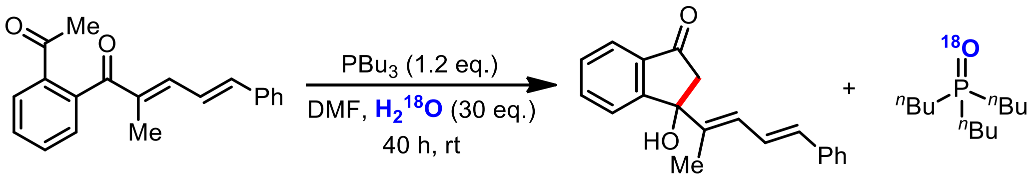


Figure 4S: Expanded ^{1}H NMR spectrum of **5a-D**

2. Aldol reaction of 4a in the presence of $H_2{}^{18}O$

The role of water in the phosphine-mediated aldol reaction was further elucidated by performing the aldol reaction of **4a** in the presence of ^{18}O-labelled water. The crude reaction mixture was analyzed by HRMS. The HRMS spectra as shown below (Figures 5S and 6S), revealed the abundance of $P(^{18}O)Bu_3$ $[(M+H)^+$ found: 221.1913] increased ~550% (Figure 6S) more than the respective abundance of $P(^{18}O)Bu_3$ $[(M+H)^+$ found: 221.1910] obtained from the H_2O reaction (Figure 5S). This experiment further confirms the nucleophilic addition of water on to the phosphonium center during the course of the reaction triggering the elimination of phosphine oxide.



4a **5a**

Scheme 7S: Reaction of **4a** in presence of $H_2{}^{18}O$

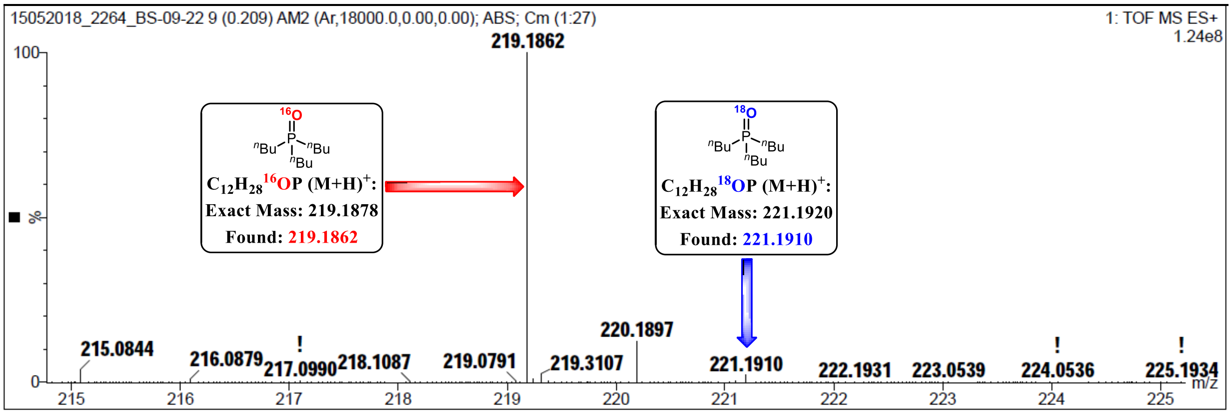


Figure 5S: HRMS spectrum of the crude reaction mixture of H_2O reaction of **4a**

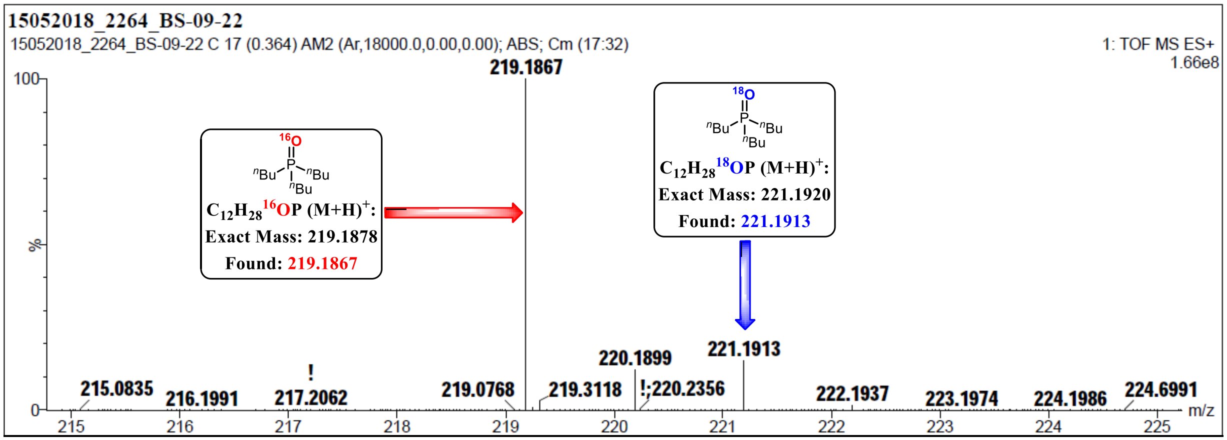
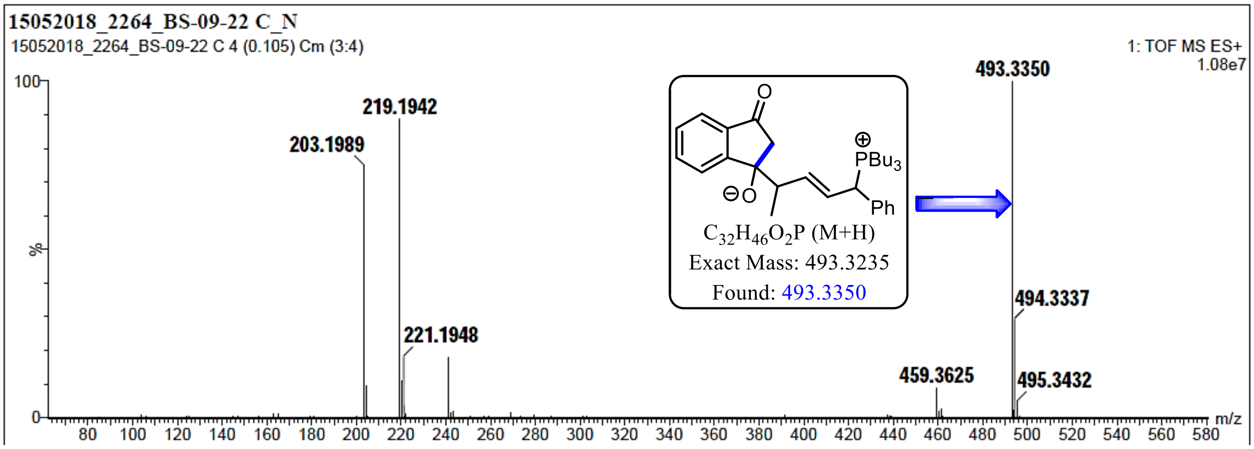


Figure 6S: HRMS spectrum of the crude reaction mixture of $H_2{}^{18}O$ reaction of **4a**

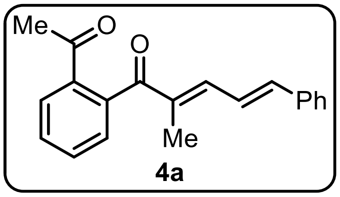
Evidence that favours Lewis basic character of PBu_3

HRMS data of the crude reaction mixture of **4a** indicates the presence of PBu_3-adduct of **4a** (see the spectrum pasted below). Thus, this evidence points to the fact that the role of PBu_3 is Lewis basic rather than Brønsted basic.



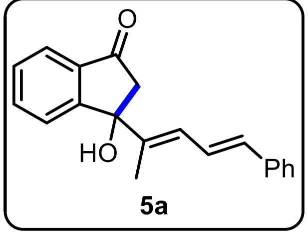
Spectroscopic data of the newly synthesized compounds during this study

(2*E*,4*E*)-1-(2-Acetylphenyl)-2-methyl-5-phenylpenta-2,4-dien-1-one (4a). This compound was prepared by following the general procedure-1 and isolated as Pale yellow solid. M.P = 106-107 °C. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat): ν_{max}/cm^{-1}** 3037, 2924, 1682, 1648, 1617, 1359, 1285, 1012, 756. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.42-7.40 (m, 2H), 7.35-7.26 (m, 4H), 7.13 (dd, *J* = 15.5 and 11.2 Hz, 1H), 6.63 (d, *J* = 15.5 Hz, 1H), 6.55 (d, *J* = 11.2 Hz, 1H), 2.54 (s, 3H), 2.20 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 199.9, 198.4, 141.3, 141.0, 139.5, 137.7, 137.0, 136.4, 132.1, 129.5, 129.2, 128.9, 128.8 (2C), 128.2, 127.1 (2C), 124.3, 27.5, 12.1. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{19}O_2$ (M+H)$^+$: 291.1385. Found: 291.1397.



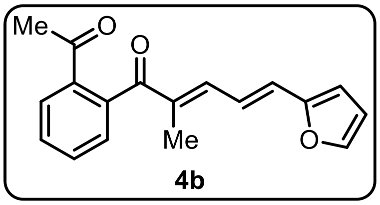
4a

3-Hydroxy-3-((2*E*,4*E*)-5-phenylpenta-2,4-dien-2-yl)-2,3-dihydro-1*H*-inden-1-one (5a). This compound was isolated as pale yellow solid. Following the general procedure-4, 40 mg of **4a** afforded 35.7 mg of **5a** (89% yield). M.P = 119-120 °C. R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3418, 3025, 2930, 1695, 1595, 1499, 1286, 738. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.51-7.46 (m, 2H), 7.41-7.39 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.24-7.20 (m, 1H), 7.00 (dd, *J* = 15.4 and 11.4 Hz, 1H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.55 (d, *J* = 11.1 Hz, 1H), 3.02 (d, J_{AB} = 18.9 Hz, 1H), 2.85 (d, J_{AB} = 18.9 Hz, 1H) 2.85 (s, 1H), 1.70 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 203.6, 156.9, 139.2, 137.4, 136.3, 135.6, 133.6, 129.6, 128.6 (2C), 127.6, 126.4 (2C), 124.7, 124.6, 124.4, 123.3, 80.0, 52.0, 13.9. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{19}O_2$ (M+H)$^+$: 291.1385. Found: 291.1371.



5a

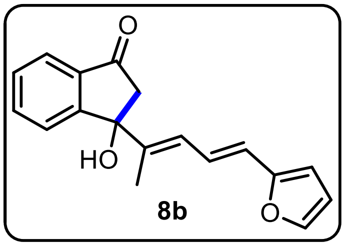
(2*E*,4*E*)-1-(2-Acetylphenyl)-5-(furan-2-yl)-2-methylpenta-2,4-dien-1-one (4b). This compound was prepared by following the general procedure-1 and isolated as Pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1683, 1645, 1606, 1476, 1358, 1260, 1074, 757. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.85 (dd, *J* = 7.6 and 1.2 Hz, 1H), 7.58-7.51 (m, 2H), 7.41 (d, *J* = 1.6 Hz, 1H), 7.33 (dd, *J* = 7.5 and 1.4 Hz, 1H), 7.00 (dd, *J* = 15.2 and 11.3 Hz, 1H), 6.49 (d, *J* = 11.6 Hz, 1H), 6.42 (d, *J* = 15.3 Hz,



4b

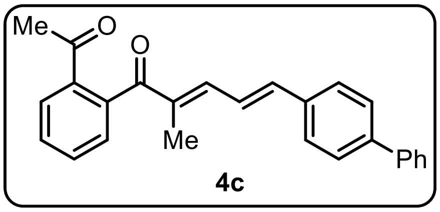
1H), 6.40-6.39 (m, 1H), 6.35 (d, *J* = 3.5 Hz, 1H), 2.52 (s, 3H), 2.17 (d, *J* = 1.0 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 199.6, 198.5, 152.5, 143.6, 141.3, 140.7, 137.6, 137.1, 132.0, 129.4, 129.1, 128.2, 126.0, 122.6, 112.1, 111.5, 27.6, 12.1. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{17}O_3$ (M+H)$^+$: 281.1178. Found: 281.1164.

3-((2*E*,4*E*)-5-(Furan-2-yl)penta-2,4-dien-2-yl)-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (5b).



8b

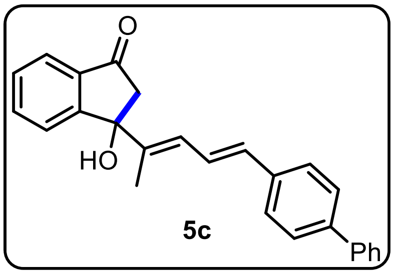
This compound was isolated as pale yellow oil. Following the general procedure-4, 40 mg of **4b** afforded 36 mg of **5b** (88% yield). R$_f$ = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3427, 2927, 2859, 1697, 1602, 1236, 1059, 737. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.52-7.48 (m, 2H), 7.36 (d, *J* = 1.3 Hz, 1H), 6.89 (dd, *J* = 15.4 and 11.2 Hz, 1H), 6.50 (d, *J* =11.3 Hz, 1H), 6.40-6.37 (m, 2H), 6.27 (d, *J* = 3.2 Hz, 1H), 3.04 (d, J_{AB} = 19.0 Hz, 1H), 2.86 (d, J_{AB} = 19.0 Hz, 1H), 2.61 (s, 1H), 1.69 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 203.4, 156.9, 153.2, 142.2, 139.4, 136.3, 135.6, 129.6, 124.5, 124.3, 123.3, 123.0, 120.9, 111.6, 108.6, 80.0, 51.9, 13.9. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{15}O_2$ (M-OH)$^+$: 263.1072. Found: 263.1042.



4c

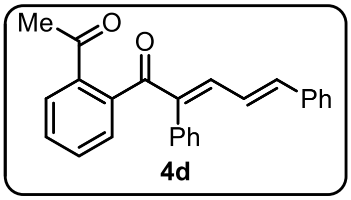
(2*E*,4*E*)-5-([1,1'-Biphenyl]-4-yl)-1-(2-acetylphenyl)-2-methylpenta-2,4-dien-1-one (4c). This compound was prepared by following the general procedure-1 and isolated as white solid. M.P = 168-170 ^{o}**C.** R$_f$ = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3032, 1683, 1648, 1615, 1484, 1358, 1263, 1009, 762. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.88 (dd, *J* = 8.0 and 1.1 Hz, 1H), 7.61-7.53 (m, 6H), 7.52-7.41 (m, 4H), 7.36-7.35 (m, 2H), 7.17 (dd, *J* = 15.2 and 11.2 Hz, 1H), 6.67 (d, *J* = 15.3 Hz, 1H), 6.58 (dd, *J* = 11.2 and 0.9 Hz, 1H), 2.55 (s, 3H), 2.22 (*J* = 1.0 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 199.8, 198.4, 141.5, 141.4, 141.0, 140.3, 139.0, 137.7, 137.1, 135.4, 132.1, 129.4, 129.2, 128.8 (2C), 128.2, 127.6, 127.5 (2C), 127.4 (2C), 126.9 (2C), 124.3, 27.6, 12.2. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}O_2$ (M+H)$^+$: 367.1698. Found: 367.1683.

3-((2*E*,4*E*)-5-([1,1'-biphenyl]-4-yl)penta-2,4-dien-2-yl)-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (5c). This compound was prepared by following the general procedure-4 and isolated as Pale yellow solid. M.P = 201-203 ^{o}C. R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3421, 2917, 2852, 1703, 1597, 1059, 982, 764. **^{1}H NMR (400 MHz, $(CD_3)_2SO$):** δ 7.76 (dt, *J* = 7.6 and 1.0 Hz, 1H), 7.69-7.60 (m, 6H), 7.57-7.52 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.20 (dd, *J* = 15.6 and 11.2 Hz, 1H), 6.65 (d, *J* = 15.5 Hz, 1H), 6.49 (d, *J* = 11.2 Hz, 1H), 6.05 (s, 1H), 3.01 (d, J_{AB} = 18.8 Hz, 1H), 2.75 (d, J_{AB} =18.8 Hz, 1H), 1.68 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.8, 158.5, 141.9, 140.1, 139.3, 137.0, 136.2, 135.8, 132.2, 129.5, 129.4 (2C), 127.8, 127.4 (2C), 127.2 (2C), 126.8 (2C), 125.8, 125.7, 124.4, 122.7, 79.1, 52.2, 14.1. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{22}NaO_2$ $(M+Na)^+$: 389.1517. Found: 389.1512.



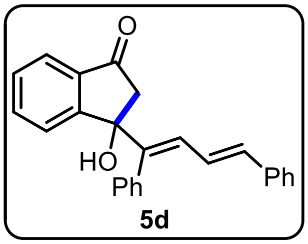
5c

(2*E*,4*E*)-1-(2-Acetylphenyl)-2,5-diphenylpenta-2,4-dien-1-one (4d). This compound was prepared by following the general procedure-1 and isolated as Pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3058, 1680, 1654, 1611, 1491, 1444, 1267, 1240, 1084, 1054, 975, 700. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.84 (dd, *J* = 7.9 and 0.8 Hz, 1H), 7.61 (dt, *J* = 7.4 and 1.2 Hz, 1H), 7.53 (dt, *J* = 7.6 and 1.4 Hz, 1H), 7.47-7.43 (m, 5H), 7.38-7.35 (m, 1H), 7.29-7.23 (m, 5H), 6.92-6.83 (m, 2H), 6.76-6.73 (m, 1H), 2.54 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.4, 198.1, 141.8, 141.7, 141.6, 140.8, 137.0, 136.2, 135.2, 132.2, 130.6 (2C), 129.4, 129.3, 129.0, 128.7 (2C), 128.4, 128.1 (2C), 127.8, 127.2 (2C), 125.3, 27.4. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{21}O_2$ $(M+H)^+$: 353.1542. Found: 353.1530.



4d

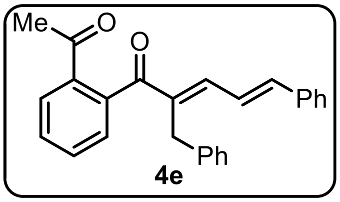
3-((1*E*,3*E*)-1,4-Diphenylbuta-1,3-dien-1-yl)-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (5d). This compound was isolated as pale yellow oil. Following the general procedure-4, 40 mg of **4d** afforded 34 mg of **5d** (85% yield). R_f = 0.4 (Hexane/EtOAc = 2/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3418, 3030, 2926, 1711, 753. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 3.6 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.54-7.50 (m, 1H), 7.27-7.15 (m, 8H), 6.84-6.80 (m, 3H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.47 (d, *J* = 10.8 Hz, 1H), 3.12 (d, J_{AB} = 18.8 Hz, 1H), 2.84 (d, J_{AB} = 18.8 Hz,



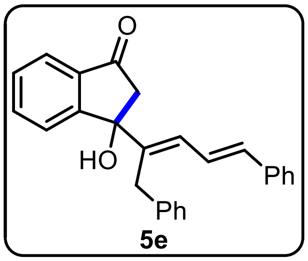
5d

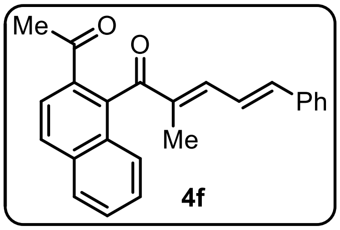
1H), 2.59 (s, 1H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 202.7, 156.5, 145.5, 137.1, 136.8, 136.6, 135.4, 134.4 (2C), 127.9, 19.7, 128.5 (2C), 128.3 (2C), 127.8, 127.7, 127.3, 126.5 (2C), 125.7, 125.1, 123.2, 79.4, 52.7. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{21}O_2$ (M+H)$^+$: 353.1542. Found: 353.1534.

(2*E*,4*E*)-1-(2-Acetylphenyl)-2-benzyl-5-phenylpenta-2,4-dien-1-one (4e). This compound was prepared by following the general procedure-1 and isolated as Pale yellow solid. M.P = 107-109 °C. R$_f$ = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat): ν_{max}/cm^{-1}** 3028, 1613, 1438, 1360, 1261, 740**. ^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.84 (d, *J* = 7.2 Hz, 1H), 7.55-7.53 (m, 2H), 7.37-7.25 (m, 10H), 7.21-7.15 (m, 2H), 6.79 (d, *J* = 11.2 Hz, 1H), 6.70 (d, *J* = 15.4 Hz, 1H), 4.06 (s, 2H), 2.52 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 198.9, 198.7, 143.5, 141.1, 140.9, 140.0, 139.7, 137.6, 136.2, 131.8, 129.3, 129.2, 129.1, 128.8 (2C), 128.5 (4C), 128.2, 127.2 (2C), 126.0, 124.2, 31.8, 27.8. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}O_2$ (M+H)$^+$: 367.1698. Found: 367.1679.

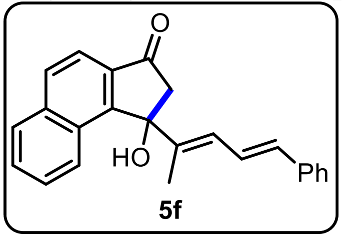


3-((2*E*,4*E*)-1,5-Diphenylpenta-2,4-dien-2-yl)-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (5e). This compound was isolated as pale yellow oil. Following the general procedure-4, 30 mg of **4e** afforded 26 mg of **5e** (87% yield). R$_f$ = 0.2 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3422, 3059, 3029, 2926, 1709, 1602, 1455, 1285, 1058, 749. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.51-7.48 (m, 1H), 7.46-7.44 (m, 1H), 7.39-7.36 (m, 2H), 7.33-7.18 (m, 8H), 7.13-7.11 (m. 2H), 7.04 (dd, *J* = 15.2 and 11.2 Hz, 1H), 6.69 (d, *J* = 15.2 Hz, 1H), 6.68 (d, *J* = 11.0 Hz, 1H), 3.77 (d, J_{AB} = 15.7 Hz, 1H), 3.49 (d, J_{AB} =15.7 Hz, 1H), 2.95 (d, J_{AB} = 19.0 Hz, 1H), 2.80 (d, J_{AB} =19.0 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 203.2, 156.8, 142.1, 139.3, 137.1, 136.3, 135.3, 134.9, 129.6, 128.7 (2C), 128.6 (2C), 128.5, 128.0 (2C), 127.8, 127.6, 126.5 (2C), 124.9, 124.5, 123.2, 80.3, 52.9, 34.1. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}O_2$ (M+H)$^+$: 367.1698. Found: 367.1671.

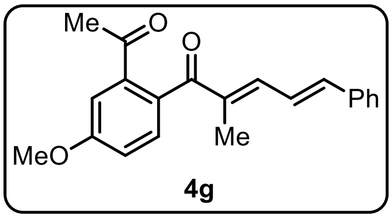



4f

(2*E*,4*E*)-1-(2-Acetylnaphthalen-1-yl)-2-methyl-5-phenylpenta-2,4-dien-1-one (4f). This compound was prepared by following the general procedure-1 and isolated as white solid. M.P = 152-153 ^{o}**C.** R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3060, 2921, 1682, 1646, 1616, 1463, 1426, 1382, 1279, 1243, 1074, 736. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.01-7.91 (m, 3H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.60 (dt, *J* = 6.8 and 1.2 Hz, 1H), 7.52 (dt, *J* = 8.1 and 1.3 Hz, 1H), 7.36-7.34 (m, 2H), 7.31-7.24 (m, 3H), 7.13 (dd, *J* = 15.2 and 11.3 Hz, 1H), 6.49-6.45 (m, 2H), 2.65 (s, 3H), 2.33 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 200.6, 198.0, 140.9, 140.2, 139.5, 138.5, 136.3, 135.1, 132.0, 130.8, 129.1, 128.8, 128.7 (2C), 128.6, 127.9, 127.7, 127.4, 127.0 (2C), 125.1, 124.3, 28.0, 12.0. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{21}O_2$ (M+H)$^+$: 341.1542. Found: 341.1524.

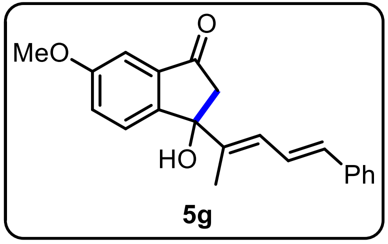

5f

1-Hydroxy-1-((2*E*,4*E*)-5-phenylpenta-2,4-dien-2-yl)-1*H*-cyclopenta[*a*]naphthalen-3(2*H*)-one (5f). This compound was isolated as pale yellow oil. Following the general procedure-4, 40 mg of **4f** afforded 35.2 mg of **5f** (88% yield). R_f = 0.3 (Hexane/EtOAc = 2/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3429, 3055, 2924, 1693, 1453, 1278, 746. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.35 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.68-7.61 (m, 2H), 7.57-7.53 (m, 1H), 7.40 (d, *J* = 3.3 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24-7.18 (m, 1H), 7.03 (dd, *J* = 15.4 and 11.0 Hz, 1H), 6.76 (d, *J* = 11.0 Hz, 1H), 6.61 (d, *J* = 15.6 Hz, 1H), 3.08 (s, 1H), 3.05 (d, J_{AB} = 19.0 Hz, 1H), 2.92 (d, J_{AB} = 19.0 Hz, 1H), 1.62 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 203.3, 155.4, 139.7, 137.5, 135.0, 133.3, 131.1, 129.2, 129.14, 129.13, 128.6 (2C), 127.6, 127.5, 126.3 (2C), 126.0, 124.6, 124.5, 118.6, 80.8, 53.5, 13.8. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{19}O_2$ (M-H)$^+$: 339.1385. Found: 339.1363.


4g

(2*E*,4*E*)-1-(2-Acetyl-4-methoxyphenyl)-2-methyl-5-phenylpenta-2,4-dien-1-one (4g). This compound was prepared by following the general procedure-1 and isolated as Pale yellow oil. R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2933, 2849, 1688, 1604, 1486, 1358, 1284, 1177, 1010, 751. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.44-7.42 (m, 2H), 7.36-7.25 (m, 5H), 7.13 (dd, *J* = 15.4 and 11.2 Hz, 1H), 7.09-7.05 (m, 1H), 6.65 (d, J = 15.7 Hz, 1H), 6.63 (d, J = 11.3 Hz, 1H), 3.91 (s, 3H), 2.49 (s, 3H), 2.17 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 199.5, 199.2, 160.3, 141.0, 140.4, 139.5, 137.9, 136.4, 132.8, 130.3, 128.9 (2C), 127.1 (2C), 124.3, 115.9, 114.9, 55.7, 28.2, 12.4. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{21}O_3$ (M+H)$^+$: 321.1491. Found: 321.1476.

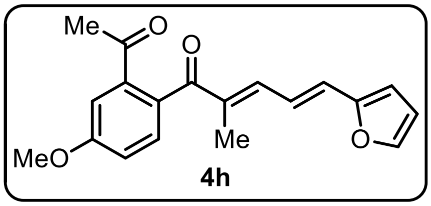
3-Hydroxy-6-methoxy-3-((2*E*,4*E*)-5-phenylpenta-2,4-dien-2-yl)-2,3-dihydro-1*H*-inden-1-one



5g

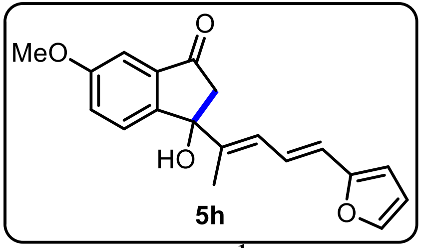
(5g). This compound was isolated as white solid. Following the general procedure-4, 40 mg of **4g** afforded 36 mg of **5g** (84% yield). R$_f$ = 0.3 (Hexane/EtOAc = 2/1). **IR (thin film, neat):** ν$_{max}$/cm^{-1} 3058, 2926, 2854, 2749, 1762, 1694, 1643, 1609, 1459, 1386, 1282, 1081, 745. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.43-7.39 (m, 3H), 7.33-7.30 (m, 2H), 7.25-7.22 (m, 2H), 7.18 (d, J = 2.4 Hz, 1H), 7.00 (dd, J = 15.5 and 11.1 Hz, 1H), 6.60 (d, J = 15.5 Hz, 1H), 6.53 (d, J = 11.1 Hz, 1H), 3.86 (s, 3H), 3.06 (d, J_{AB} = 18.9 Hz, 1H), 2.89 (d, J_{AB} = 18.9 Hz, 1H), 2.34(s, 1H), 1.72 (d, J = 0.9 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 203.2, 161.0, 149.6, 139.4, 137.9, 137.4, 133.5, 128.6 (2C), 127.6, 126.3 (2C), 125.5, 124.7, 124.6, 124.5, 104.4, 79.6, 55.7, 52.6, 13.9. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{21}O_3$ (M+H)$^+$: 321.1491. Found: 321.1485.

(2*E*,4*E*)-1-(2-Acetyl-4-methoxyphenyl)-5-(furan-2-yl)-2-methylpenta-2,4-dien-1-one (4h).



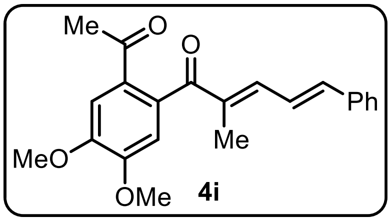
4h

This compound was prepared by following the general procedure-1 and isolated as Pale yellow oil. R$_f$ = 0.4 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν$_{max}$/cm^{-1} 2938, 2843, 1687, 1642, 1603, 1479, 1358, 1286, 1219, 1010, 740. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.42 (s, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 1.5 Hz, 1H), 7.05 (dd, J = 8.0 and 2.6 Hz, 1H), 7.00 (dd, J = 15.3 and 11.5 Hz, 1H), 6.57 (d, J = 11.5 Hz, 1H), 6.45 (d, J = 15.4 Hz, 1H), 6.41-6.36 (m, 2H), 3.90 (s, 3H), 2.46 (s, 3H), 2.17 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 199.6, 198.9, 160.3, 152.5, 143.5, 140.8, 140.5, 137.9, 132.7, 130.3, 126.0, 122.6, 115.9, 114.8, 112.1, 111.5, 55.6, 28.2, 12.3. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{19}O_4$ (M+H)$^+$: 311.1283. Found: 311.1267.



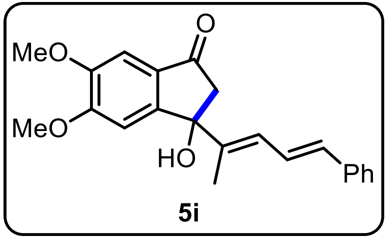
5h

3-((2*E*,4*E*)-5-(Furan-2-yl)penta-2,4-dien-2-yl)-3-hydroxy-6-methoxy-2,3-dihydro-1*H*-inden-1-one (5h). This compound was isolated as pale yellow oil. Following the general procedure-4, 30 mg of **4h** afforded 25.8 mg of **5h** (86% yield). R$_f$ = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3422, 2928, 2849, 1708, 1605, 1488, 1282, 1056. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.40 -7.38 (m, 2H), 7.25 (dd, *J* = 8.4 and 2.6 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 6.92 (dd, *J* = 15.4 and 11.2 Hz, 1H), 6.48 (d, *J* = 11.2 Hz, 1H), 6.42-6.38 (m, 2H), 6.28 (d, *J* = 3.2 Hz, 1H), 3.88 (s, 3H), 3.07 (d, J_{AB} = 19.0 Hz, 1H), 2.90 (d, J_{AB} = 19.0 Hz, 1H), 2.25 (s, 3H), 1.72 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 203.2, 161.0, 153.2, 149.6, 142.1, 139.6, 137.8, 125.5, 124.7, 124.2, 123.1, 120.8, 111.6, 108.5, 104.4, 79.6, 55.7, 52.5, 13.9. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{17}O_3$ (M-OH)$^+$: 293.1178. Found: 293.1152.



4i

(2*E*,4*E*)-1-(2-Acetyl-4,5-dimethoxyphenyl)-2-methyl-5-phenylpenta-2,4-dien-1-one (4i). This compound was prepared by following the general procedure-1 and isolated as white solid. M.P = 110-112 °C. R$_f$ = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2933, 2851, 1672, 1646, 1614, 1448, 1344, 1279, 1206, 1021, 745. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.35-7.26 (m, 4H), 7.12 (dd, *J* = 15.6 and 11.2 Hz, 1H), 6.82 (s, 1H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.54 (d, *J* = 11.2 Hz, 1H), 4.00 (s, 3H), 3.95 (s, 3H), 2.48 (s, 3H), 2.20 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 199.6, 197.0, 152.0, 148.8, 140.5, 139.5, 138.0, 136.3, 135.5, 129.8, 128.9, 128.8 (2C), 127.0 (2C), 124.3, 111.9, 110.8, 56.3, 56.2, 27.6, 12.3. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{23}O_4$ (M+H)$^+$: 351.1596. Found: 351.1580.

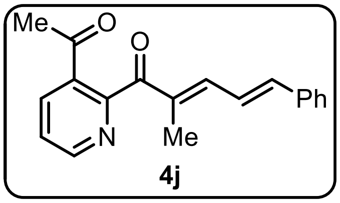


5i

3-Hydroxy-5,6-dimethoxy-3-((2*E*,4*E*)-5-phenylpenta-2,4-dien-2-yl)-2,3-dihydro-1*H*-inden-1-one (5i). This compound was isolated as pale yellow oil. Following the general procedure-4, 40 mg of **4i** afforded 36 mg of **5i** (90% yield). R$_f$ = 0.3 (Hexane/EtOAc = 1/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3414, 2931, 1697, 1594, 1499, 1296, 1062, 735. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.26-7.23 (m, 1H), 7.16 (s, 1H), 7.02 (dd, *J* = 15.5 and 11.0 Hz, 1H), 6.86 (s, 1H), 6.62 (*J* = 15.5

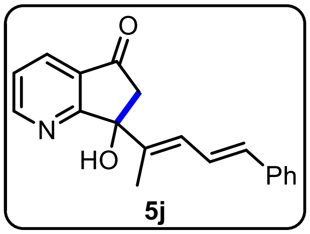
Hz, 1H), 6.59 (d, J = 11.1 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.03 (d, J_{AB} = 18.8 Hz, 1H), 2.83 (d, J_{AB} = 18.8 Hz, 1H), 2.55 (s, 1H), 1.70 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 201.9, 156.1, 151.9, 151.0, 139.3, 137.4, 133.4, 129.6, 128.6 (2C), 127.6, 126.3 (2C), 124.5, 124.4, 105.1, 103, 56.5, 56.2, 52.3, 13.8. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{23}O_4$ $(M+H)^+$: 351.1596. Found: 277.1575.

(2*E*,4*E*)-1-(3-Acetylpyridin-2-yl)-2-methyl-5-phenylpenta-2,4-dien-1-one (4j). This compound was prepared by following the general procedure-1 and isolated as Pale yellow oil. R_f = 0.2 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3057, 2926, 1687, 1614, 1565, 1434, 1360, 1277, 1021, 737. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.77 (dd, J = 4.8 and 1.6 Hz, 1H), 8.14 (dd, J = 8.0 and 1.6 Hz, 1H), 7.50 (dd, 8.0 and 4.8 Hz, 1H), 7.45-7.43 (m, 2H), 7.36-7.29 (m, 3H), 7.19 (dd, J = 15.5 and 11.2 Hz, 1H), 6.77-6.70 (m, 2H), 2.56 (s, 3H), 2.22 (d, J = 0.9 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 197.9, 196.4, 158.2, 151.3, 143.6, 140.6, 136.8, 136.3, 135.6, 133.1, 129.0, 128.8 (2C), 127.2 (2C), 124.2, 123.6, 28.0, 11.8. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{18}NO_2$ $(M+H)^+$: 292.1338. Found: 292.1353.



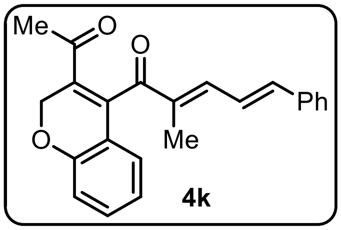
4j

7-Hydroxy-7-((2*E*,4*E*)-5-phenylpenta-2,4-dien-2-yl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridin-5-one (5j). This compound was isolated as colourless oil. Following the general procedure-4, 30 mg of **4j** afforded 25.5 mg of **5j** (85% yield). R_f = 0.2 (Hexane/EtOAc = 1/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3416, 3031, 2927, 1722, 1584, 1422, 1280, 1067, 750. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.87 (dd, J = 8.8 and 1.6 Hz, 1H), 8.09 (dd, J = 7.8 and 2.4 Hz, 1H), 7.46 (dd, J = 7.8 and 4.8 Hz, 1H), 7.38-7.36 (m, 2H), 7.32-7.27 (m, 2H), 7.24-7.20 (m, 1H), 6.98 (dd, J = 15.2 and 11.0 Hz, 1H), 6.56 (d, J = 15.2 Hz, 1H), 6.41 (d, J = 11.0 Hz, 1H), 3.80 (s, 1H), 3.04 (s, 2H), 1.74 (d, J = 0.9 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 201.0, 174.4, 156.0, 138.6, 137.4, 133.8, 132.2, 130.0, 128.6 (2C), 127.6, 126.4 (2C), 125.5, 124.3, 124.2, 80.2, 51.2, 13.9. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{16}NO$ $(M-OH)^+$: 274.1232. Found: 274.1247.



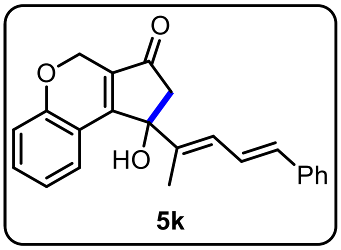
5j

(2*E*,4*E*)-1-(3-Acetyl-2*H*-chromen-4-yl)-2-methyl-5-phenylpenta-2,4-dien-1-one (4k). This compound was prepared by following the general procedure-1 and isolated as Pale yellow oil. R_f = 0.6 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3427, 2962, 2927, 1710, 1602, 1461, 1378, 1287, 1060, 767. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.45-7.43 (m, 2H), 7.36-7.27 (m, 5H), 7.13 (dd, *J* = 15.2 and 11.2 Hz, 1H), 7.00-6.89 (m, 4H), 6.80 (d, *J* = 15.2 Hz, 1H), 5.06 (s, 2H), 2.23 (s, 3H), 2.18 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 197.9, 194.8, 154.8, 143.7, 142.8, 141.6, 136.1, 136.0, 132.5, 129.3, 128.8 (2C), 127.3 (2C), 126.2, 123.8, 122.4, 120.8, 116.7, 64.7, 29.0, 11.4. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{20}O_3$ $(M)^+$: 344.1412. Found: 344.1414.



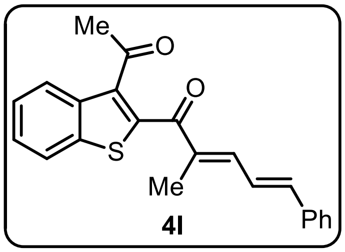
4k

1-Hydroxy-1-((2*E*,4*E*)-5-phenylpenta-2,4-dien-2-yl)-1,2-dihydrocyclopenta[*c*]chromen-3(4*H*)-one (5k). This compound was isolated as pale yellow oil. Following the general procedure-4, 30 mg of **4k** afforded 28.8 mg of **5k** (96% yield). R_f = 0.5 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3419, 3034, 2925, 2859, 1697, 1633, 1483, 1397, 1345, 1041, 753. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.52 (d, *J* = 7.1 Hz, 1H), 7.43-7.41 (m, 2H), 7.33-7.20 (m, 2H), 7.01 (dd, *J* = 10.8 Hz, 1H), 6.63 (d, *J* = 15.4 Hz, 1H), 5.06 (d, *J*AB = 14.8 Hz, 1H), 5.02 (d, J_{AB} = 14.8 Hz, 1H), 3.07 (s, 1H), 2.79 (d, J_{AB} = 18.6 Hz, 1H), 2.69 (d, *J*AB = 18.6 Hz, 1H), 1.78 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 201.0, 162.1, 156.2, 137.6, 137.3, 133.6, 133.5, 131.5, 128.6, (2C), 127.7, 126.8, 126.4 (2C), 124.9, 124.4, 121.9, 117.8, 116.9, 80.4, 62.7, 52.1, 13.4. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{21}O_3$ $(M+H)^+$: 345.1491. Found: 345.1479.



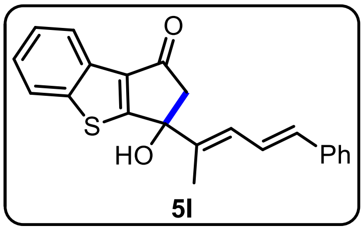
5k

(2*E*,4*E*)-1-(3-Acetylbenzo[*b*]thiophen-2-yl)-2-methyl-5-phenylpenta-2,4-dien-1-one (4l). This compound was prepared by following the general procedure-2 and isolated as Pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3050, 2927, 2854, 1676, 1641, 1608, 1502, 1428, 1282, 1225, 756. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.26-8.24 (m, 1H), 7.88-7.86 (m, 1H), 7.51-7.45 (m, 4H), 7.37-7.31 (m, 3H), 7.21-7.11 (m, 2H), 6.85 (d, *J* = 10.4 Hz, 1H), 2.47 (s, 3H), 2.21 (s, 3H). **^{13}C NMR (100**

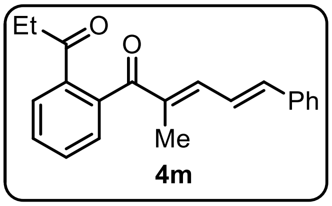


4l

MHz, $CDCl_3$): δ 196.3, 192.0, 145.2, 145.1, 142.3, 139.5, 137.3, 137.1, 136.6, 135.9, 129.5, 128.9 (2C), 127.5 (2C), 126.5, 126.0, 125.2, 123.5, 122.2, 31.5, 12.3. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{19}O_2S$ $(M+H)^+$: 347.1106. Found: 347.1123.

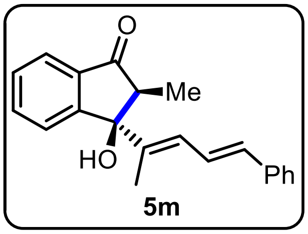

5l

3-Hydroxy-3-((2*E*,4*E*)-5-phenylpenta-2,4-dien-2-yl)-2,3-dihydro-1*H* benzo[*b*]cyclopenta[*d*]-thiophen-1-one (5l). This compound was isolated white solid. Following the general procedure-4, 30 mg of **4l** afforded 26.5 mg of **5l** (88% yield). M.P =126-129 °C. R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3410, 3057, 2927, 1695, 1466, 1385, 966, 736. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.18-8.16 (m, 1H), 7.79-7.77 (m, 1H), 7.46-7.38 (m, 4H), 7.32-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.98 (dd, *J* = 15.7 and 10.7 Hz, 1H), 6.60 (d, *J* = 15.2 Hz, 1H), 6.59 (d, *J* = 10.6 Hz, 1H), 3.29 (d, J_{AB} = 18.3 Hz, 1H), 3.25 (s, 1H), 3.16 (d, J_{AB} = 18.3 Hz, 1H), 1.84 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.0, 175.8, 145.2, 140.5, 137.8, 137.3, 134.3, 130.7, 128.7 (2C), 127.8, 126.5 (2C), 126.4, 126.2, 125.3, 124.2, 123.9, 123.5, 79.1, 56.7, 13.6. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{18}OS$ $(M-OH)^+$: 329.1000. Found: 329.1017.


4m

(2*E*,4*E*)-2-Methyl-5-phenyl-1-(2-propionylphenyl)penta-2,4-dien-1-one (4m). This compound was prepared by following the general procedure-1 and isolated as Pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3126, 3060, 2848, 2749, 1699, 1642, 1601, 1476, 1360, 1242, 1011, 746. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.85 (dd, *J* = 7.9 and 1.2 Hz, 1H), 7.58-7.50 (m, 2H), 7.43-7.40 (m, 2H), 7.35-7.25 (m, 4H), 7.13 (dd, *J* = 15.4 and 11.2 Hz, 1H), 6.64 (d, *J* = 15.4 Hz, 1H), 6.58 (d, *J* = 11.2 Hz, 1H), 2.91 (q, *J* = 7.2 Hz, 2H), 2.20 (d, *J* = 0.9 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.5, 199.8, 141.2, 139.5, 137.6, 137.3, 136.4, 131.7, 129.2, 128.9, 128.8 (2C), 128.7, 128.6, 128.3, 127.1 (2C), 124.3, 33.0, 12.2, 8.1. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{21}O_2$ $(M+H)^+$: 305.1542. Found: 305.1533.

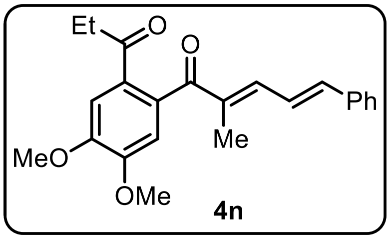
3-Hydroxy-2-methyl-3-((2*E*,4*E*)-5-phenylpenta-2,4-dien-2-yl)-2,3-dihydro-1*H*-inden-1-one (5m). This compound was isolated as white solid. Following the general procedure-4, 30 mg of



5m

4m afforded 24.3 mg of **5m** (81% yield). M.P = 153-155 ^{o}C. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3419, 2927, 2855, 1708, 1600, 1455, 1265, 752. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.79 (d, *J* =7.6 Hz, 1H), 7.67 (dt, *J* = 7.5 and 1.2 Hz, 1H), 7.52-7.43 (m, 4H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 11.1 Hz, 1H), 6.66 (d, *J* = 15.6 Hz, 1H), 2.87 (q, *J* = 7.3 Hz, 2H), 1.98 (s, 1H), 1.76 (d, *J* = 0.8 Hz, 3H), 1.26 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 206.4, 155.8, 138.3, 137.5, 135.7, 135.3, 133.4, 129.7, 128.6 (2C), 127.6, 126.4 (2C), 125.6, 124.5, 123.7, 81.3, 52.1, 14.3, 9.0. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{19}O$ (M-OH)$^{+}$: 287.1436. Found: 287.1429.

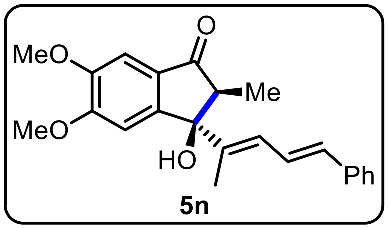
(2*E*,4*E*)-1-(4,5-Dimethoxy-2-propionylphenyl)-2-methyl-5-phenylpenta-2,4-dien-1-one (4n).



4n

This compound was prepared by following the general procedure-1 and isolated as white solid. R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2937, 1646, 1614, 1355, 1277, 1020, 743. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.44-7.42 (m, 2H), 7.35-7.28 (m, 4H), 7.11 (dd, *J* = 15.3 and 11.2 Hz, 1H), 6.83 (s, 1H), 6.65 (d, *J* = 15.3 Hz, 1H), 6.55 (dd, *J* = 11.2 and 1.0 Hz, 1H), 3.99 (s, 3H), 3.94 (s, 3H), 2.84 (q, *J* = 7.2 Hz, 2H), 2.20 (d, *J* = 1.0 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 200.1, 199.5, 151.7, 148.9, 140.6, 139.4, 137.9, 136.4, 135.3, 130.0, 128.9, 128 (2C), 127.0 (2C), 124.2, 111.2, 110.9, 56.2 (2C), 33.0, 12.3, 8.3. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{25}O_4$ (M+H)$^{+}$: 365.1753. Found: 365.1741.

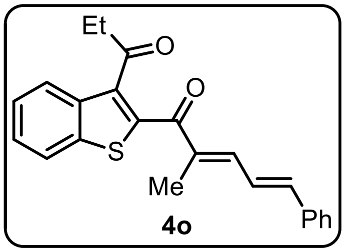
3-Hydroxy-5,6-dimethoxy-2-methyl-3-((2*E*,4*E*)-5-phenylpenta-2,4-dien-2-yl)-2,3-dihydro-1*H*-inden-1-one (5n).



5n

This compound was isolated as pale yellow oil. Following the general procedure-4, 30 mg of **4n** afforded 25.0 mg of **5n** (83% yield). R_f = 0.3 (Hexane/EtOAc = 2/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3444, 2971, 2936, 1697, 1595, 1499, 1293, 1111, 749. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.44-7.40 (m, 2H), 7.34-7.29 (m, 2H), 7.18 (s, 1H), 7.00 (dd, *J* = 15.4 and 11.0 Hz, 1H), 6.92 (s, 1H), 6.63 (d, *J* = 11.1 Hz, 1H), 6.59 (d, *J* = 15.4 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 2.87 (q, *J* = 7.3 Hz, 2H), 1.68 (s, 1H), 1.47 (s, 3H), 1.17 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 203.0, 155.8, 150.7, 138.5, 137.4, 133.2, 129.0, 128.6 (2C), 127.6, 126.3 (2C), 126.0, 125.2, 124.6, 105.1, 103.3, 83.4, 57.4, 56.4, 56.2, 15.1, 9.9. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{23}O_3$ $(M-OH)^+$: 347.1647. Found: 347.1634.

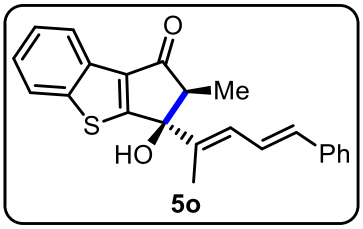
(2*E*,4*E*)-2-Methyl-5-phenyl-1-(3-propionylbenzo[*b*]thiophen-2-yl)penta-2,4-dien-1-one (4o).



4o

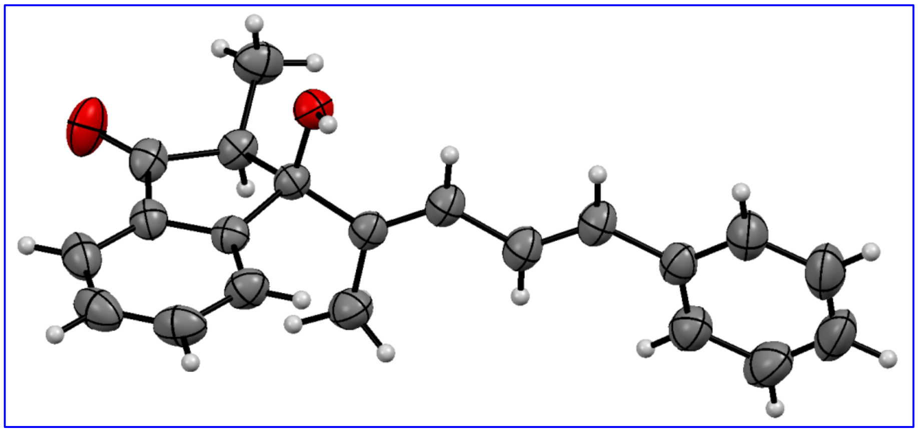
This compound was prepared by following the general procedure-2 and isolated as Pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3057, 2980, 2937, 1675, 1606, 1502, 1456, 1361, 1282, 1226, 1069, 740. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.11-8.08 (m, 1H), 7.87-7.85 (m, 1H), 7.49-7.45 (m, 4H), 7.37-7.30 (m, 3H), 7.19-7.11 (m, 2H), 6.84 (d, *J* = 14.4 Hz, 1H), 2.73 (q, *J* = 7.2Hz, 2H), 2.20 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 200.5, 191.6, 144.7, 143.3, 142.1, 139.9, 138.6, 137.0, 136.8, 136.0, 19.4, 128.9 (2C), 127.5 (2C), 126.7, 125.9, 124.9, 123.4, 122.3, 37.8, 12.4, 8.3. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{21}O_2S$ $(M+H)^+$: 361.1262. Found: 361.1244.

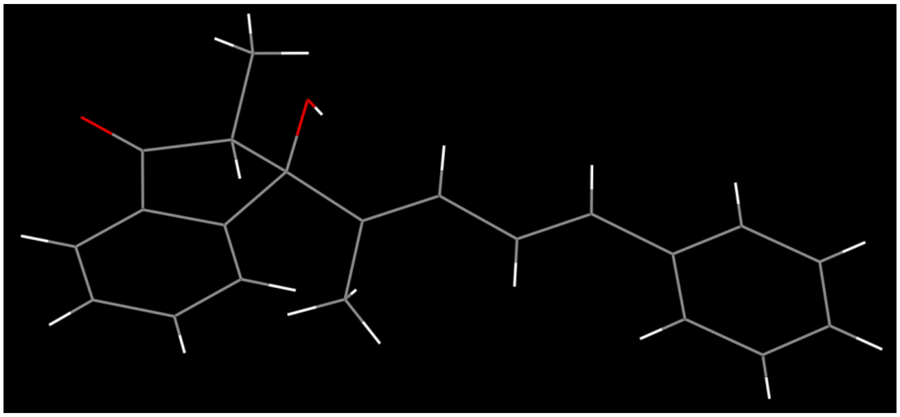
3-Hydroxy-2-methyl-3-((2*E*,4*E*)-5-phenylpenta-2,4-dien-2-yl)-2,3-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-1-one (5o). This compound was isolated as pale yellow oil. Following the general procedure-4, 30 mg of **4o** afforded 26.5 mg of **5o** (88% yield). R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3422, 3057, 2978, 2933, 1690, 1463, 1387, 1093, 746. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.23-8.21 (m, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.49-7.38 (m, 4H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.24-7.20 (m, 1H), 7.00 (dd, *J* = 15.4 Hz and 11.0 Hz, 1H), 6.57 (d, *J* = 15.4 Hz, 1H), 6.47 (d, *J* = 10.9 Hz, 1H), 3.23 (q, *J* = 7.5 Hz, 2H), 3.07 (s, 1H), 1.70 (s, 3H), 1.20 (d, *J* = 7.5 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 196.9, 174.0, 145.0, 139.7, 137.2, 136.9, 134.0, 130.8, 128.6 (2C), 127.7, 127.2, 127.6 (2C), 126.3, 126.1, 124.2, 124.1, 123.4, 82.9, 61.7, 14.9, 10.8. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{21}O_2S$ $(M+H)^+$: 361.1262. Found: 361.1247.



5o

Crystal structure of 5m (CCDC 1865325): Structure of the **5m** was confirmed by single crystal X-ray diffraction analysis.





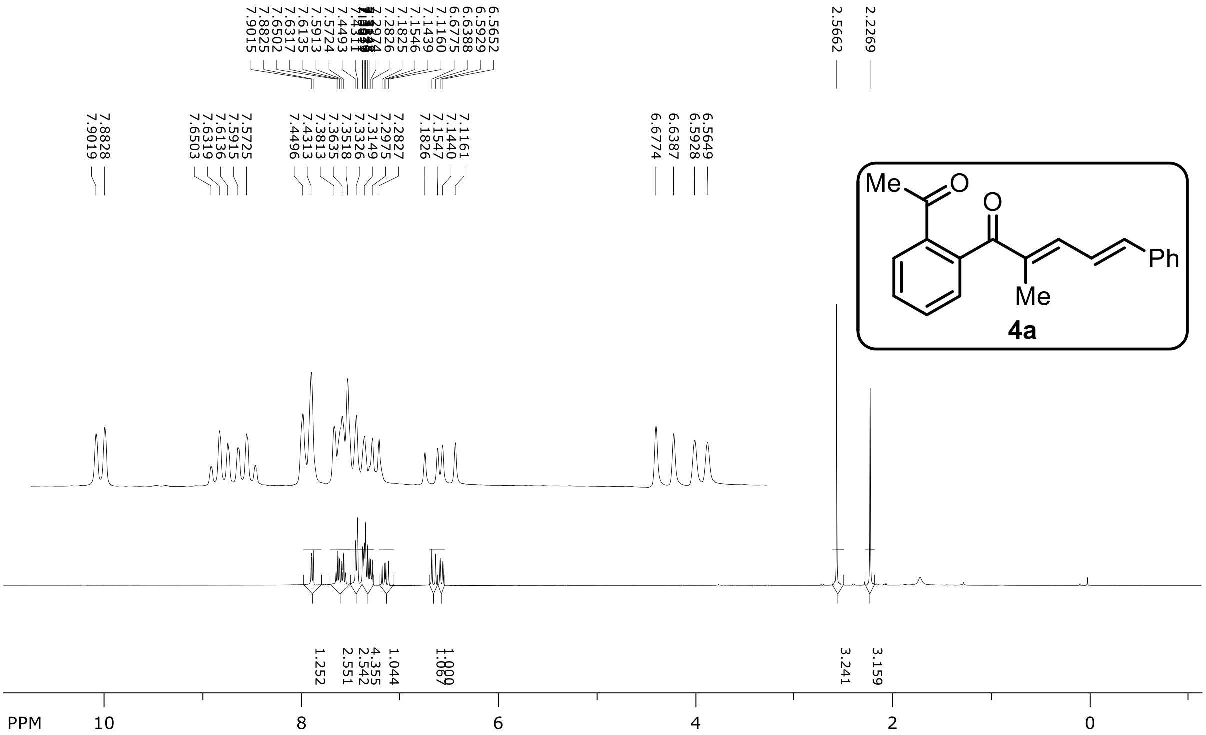
Crystal Data for $C_{21}H_{20}O_2$ (M =304.39 g/mol): triclinic, space group P-1 (no. 2), a = 6.299(4) Å, b = 11.213(7) Å, c = 12.297(8) Å, α = 92.294(8)°, β = 92.253(9)°, γ = 96.879(8)°, V = 860.7(9) Å^3, Z = 2, T = 296.15 K, μ(Mo Kα) = 0.074 mm^{-1}, $Dcalc$ = 1.1744 g/cm^3, 10039 reflections measured (3.32° ≤ 2Θ ≤ 49.78°), 3003 unique (R_{int} = 0.0263, R_{sigma} = 0.0240) which were used in all calculations. The final R_1 was 0.0391 (I>=2u(I)) and wR_2 was 0.1119 (all data).

Table 1S: Crystal data and structure refinement for 5m

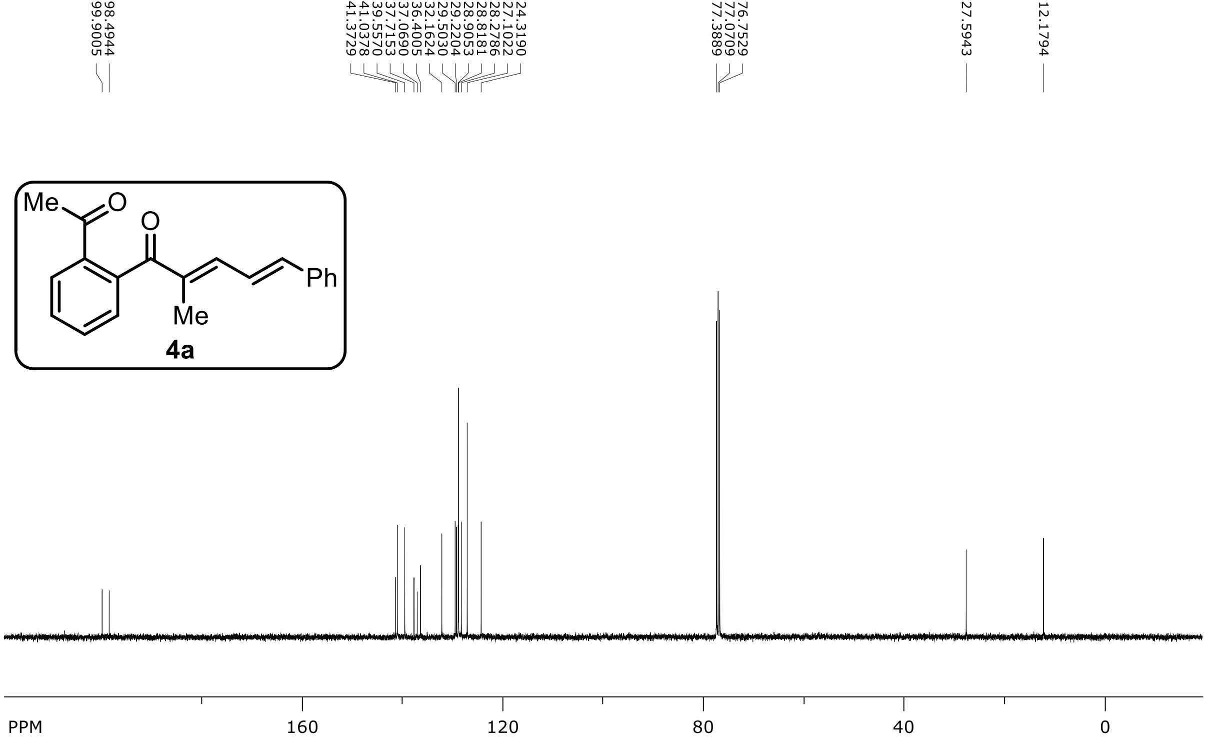
Identification code	5m
Empirical formula	$C_{21}H_{20}O_2$
Formula weight	304.39
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1

a/Å	6.299(4)
b/Å	11.213(7)
c/Å	12.297(8)
α/°	92.294(8)
β/°	92.253(9)
γ/°	96.879(8)
Volume/Å^3	860.7(9)
Z	2
ρ$_{calc}$g/cm^3	1.1744
μ/mm^{-1}	0.074
F(000)	324.2
Crystal size/mm^3	0.2 × 0.15 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.32 to 49.78
Index ranges	$-7 \leq h \leq 7$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$
Reflections collected	10039
Independent reflections	3003 [R_{int} = 0.0263, R_{sigma} = 0.0240]
Data/restraints/parameters	3003/0/212
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0391, wR_2 = 0.1025
Final R indexes [all data]	R_1 = 0.0497, wR_2 = 0.1119
Largest diff. peak/hole / e Å^{-3}	0.17/-0.19

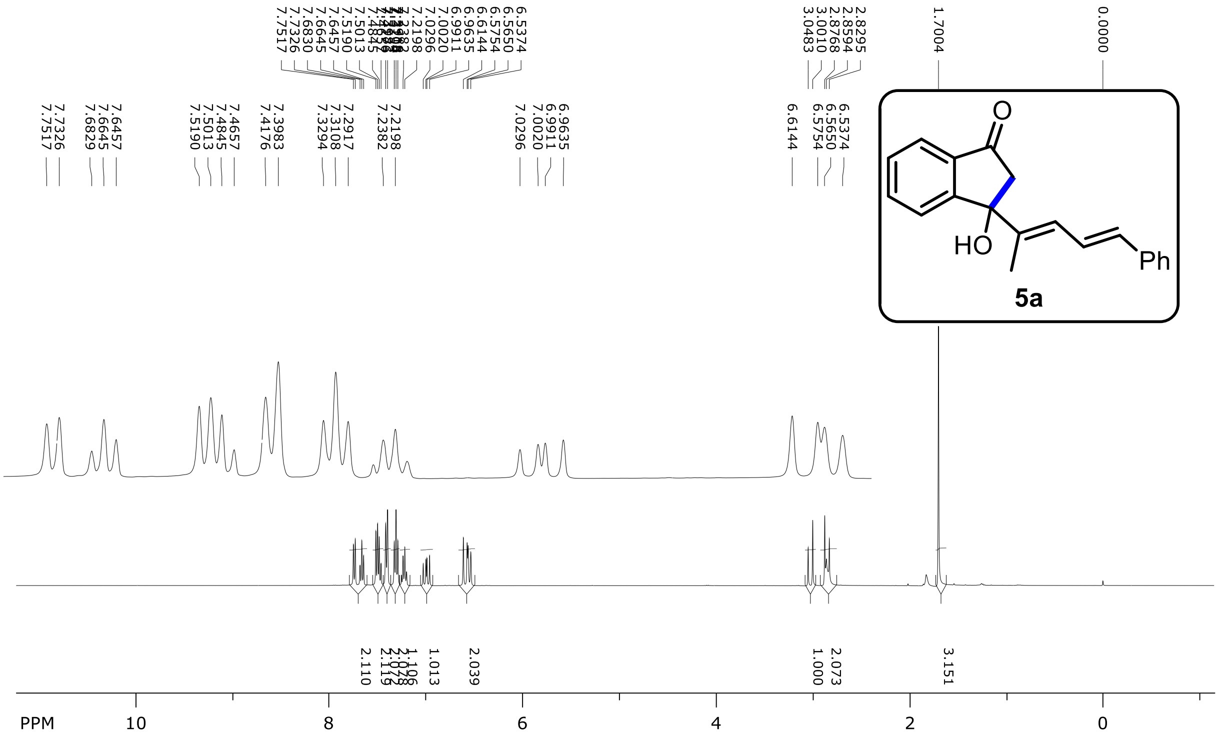
SpinWorks 4: BS 08 01
PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 21



SpinWorks 4: BS 08 01
C13CPD256 CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 21



SpinWorks 4: BS 08 02 RE
PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 25



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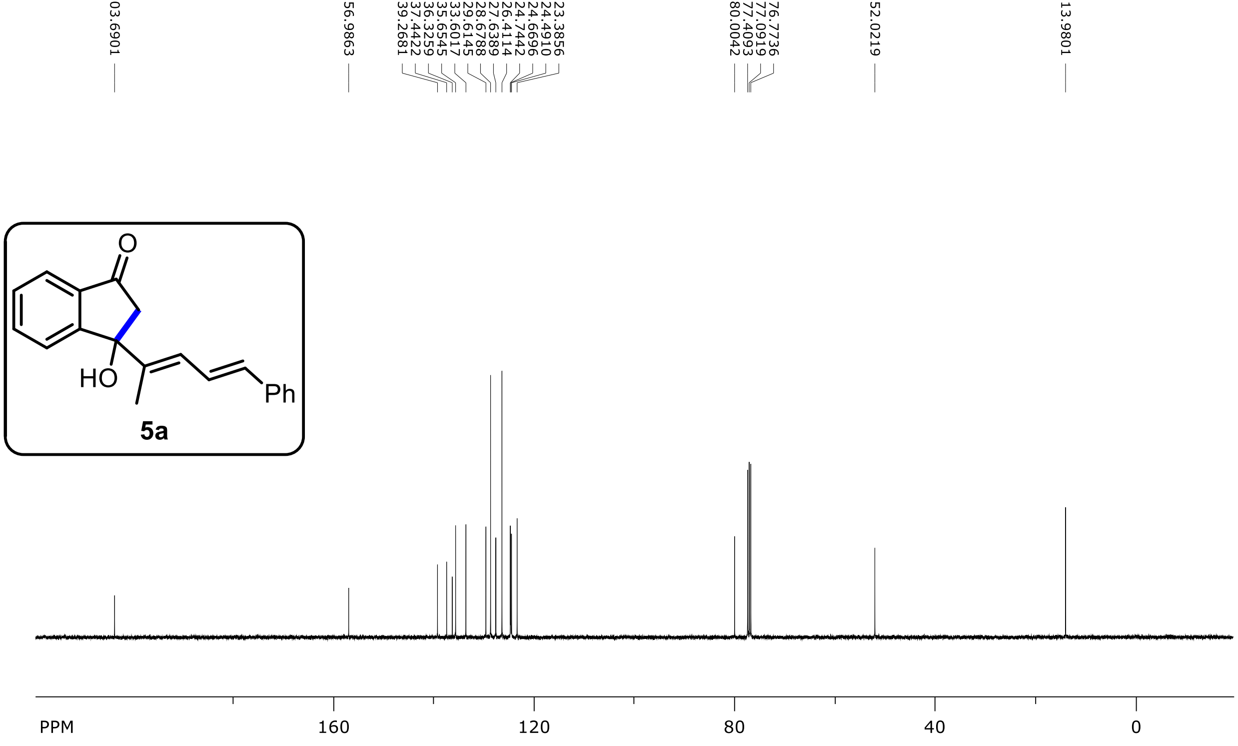
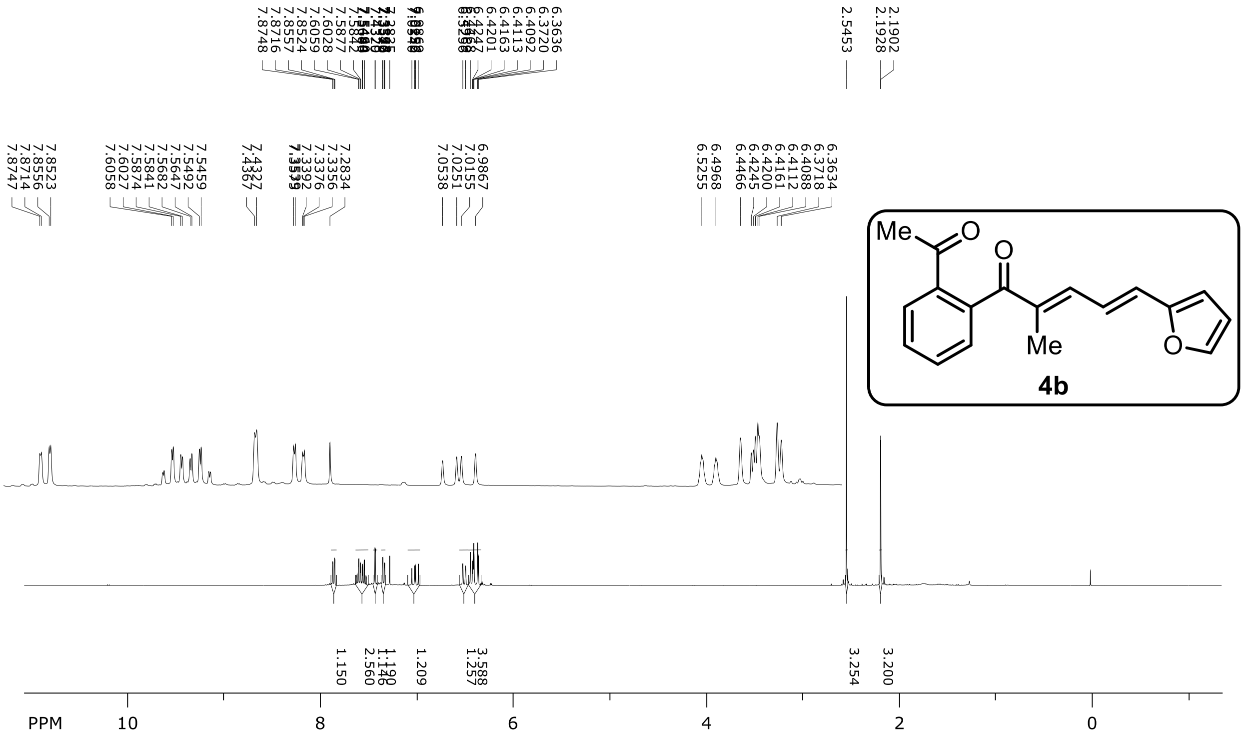


SpinWorks 4: BS-08-13



SpinWorks 4: BS 08 13
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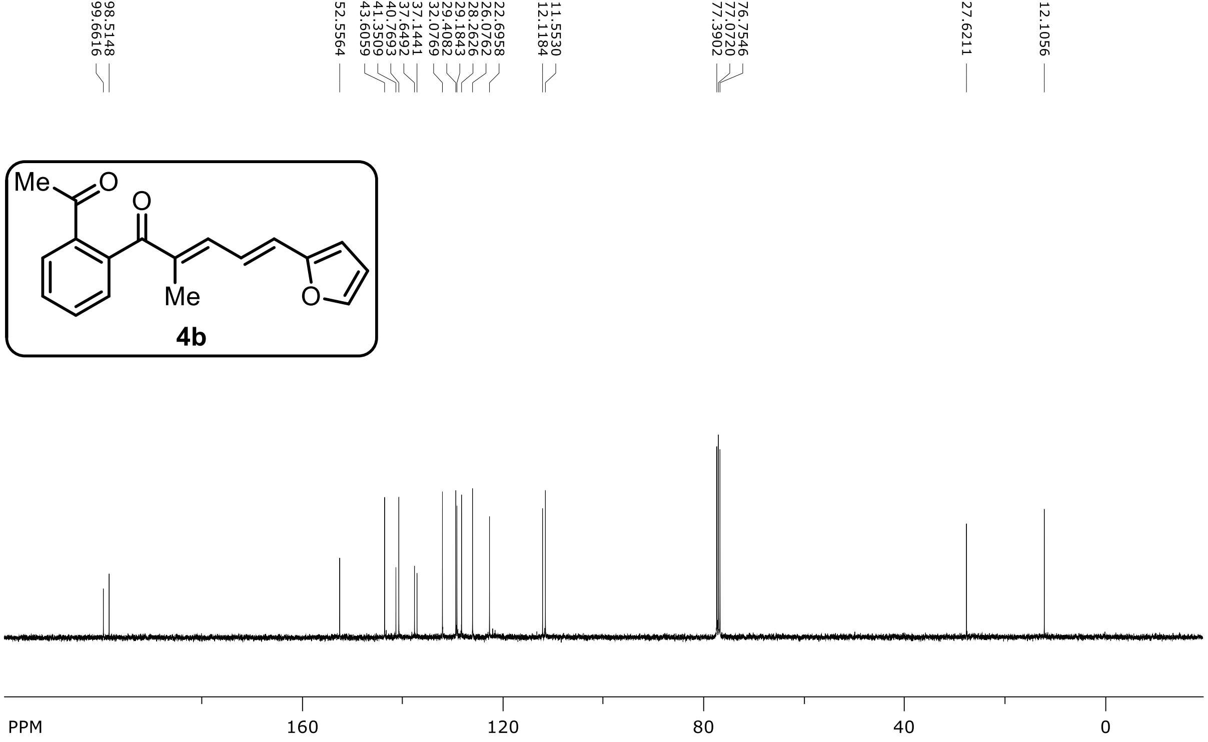
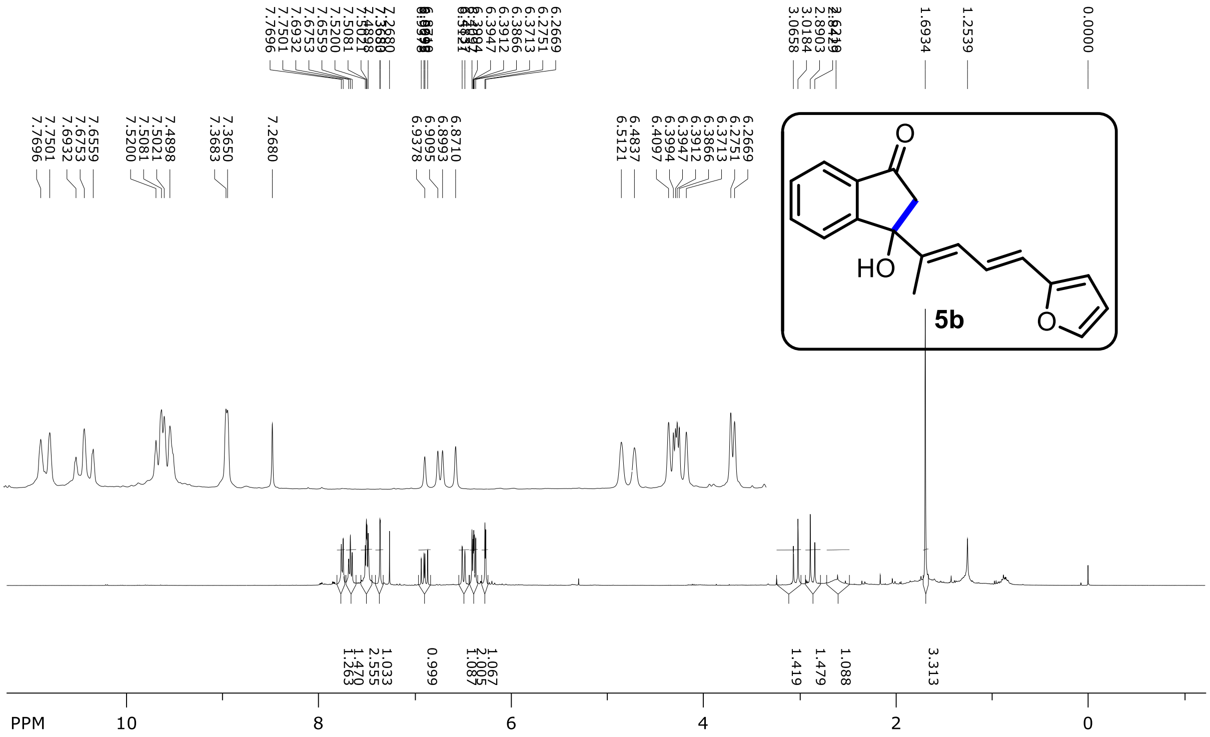
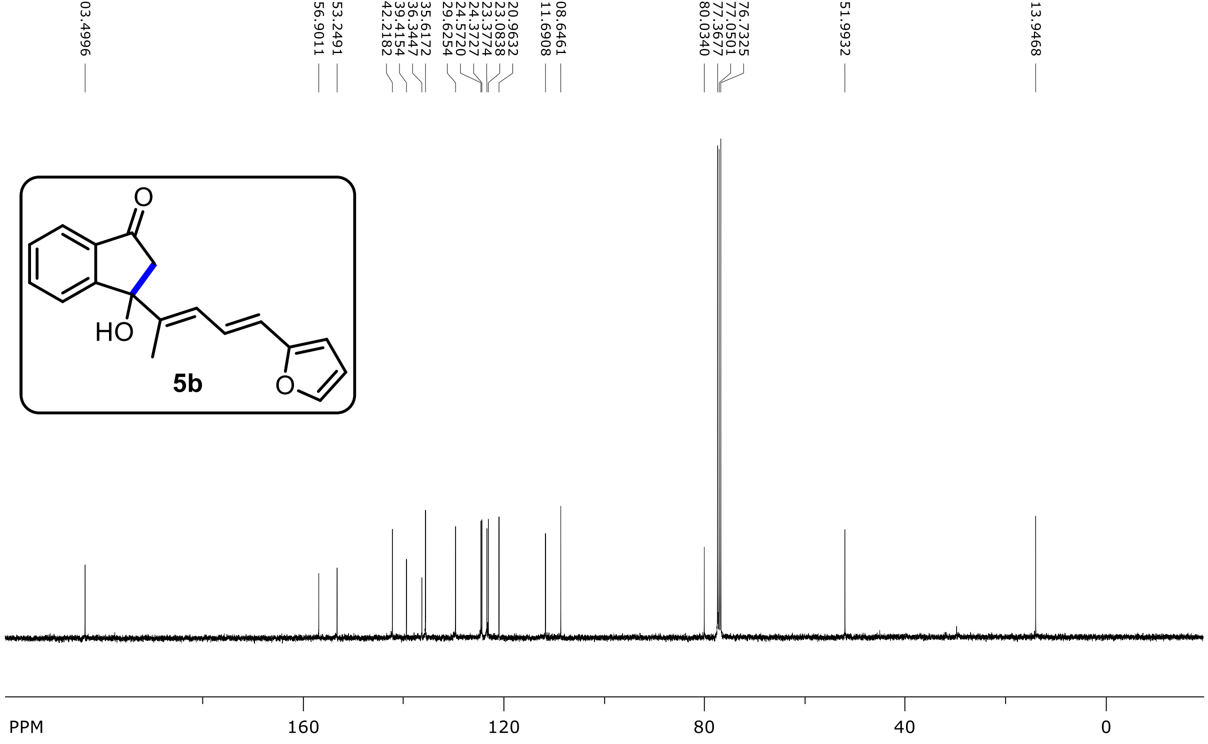


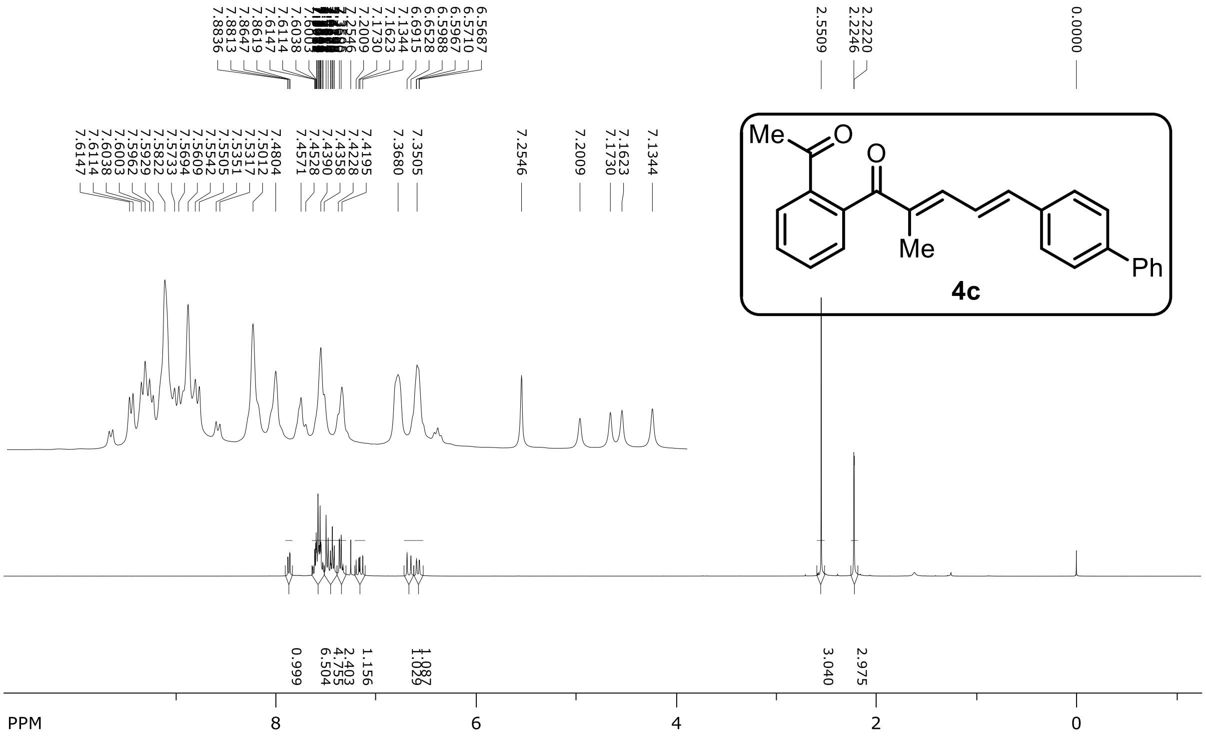
SpinWorks 4: BS-09-41



SpinWorks 4: BS 09 41
C13CPD CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 59



SpinWorks 4: BS-08-140



SpinWorks 4: BS 08 140
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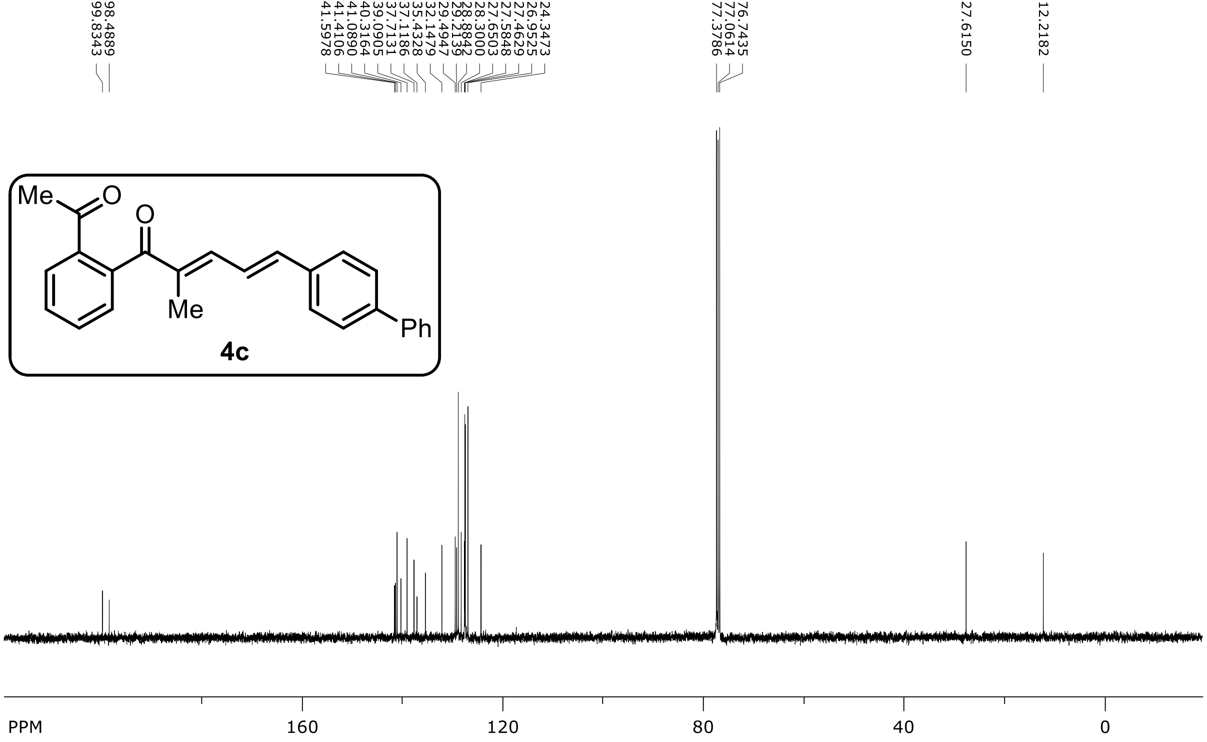
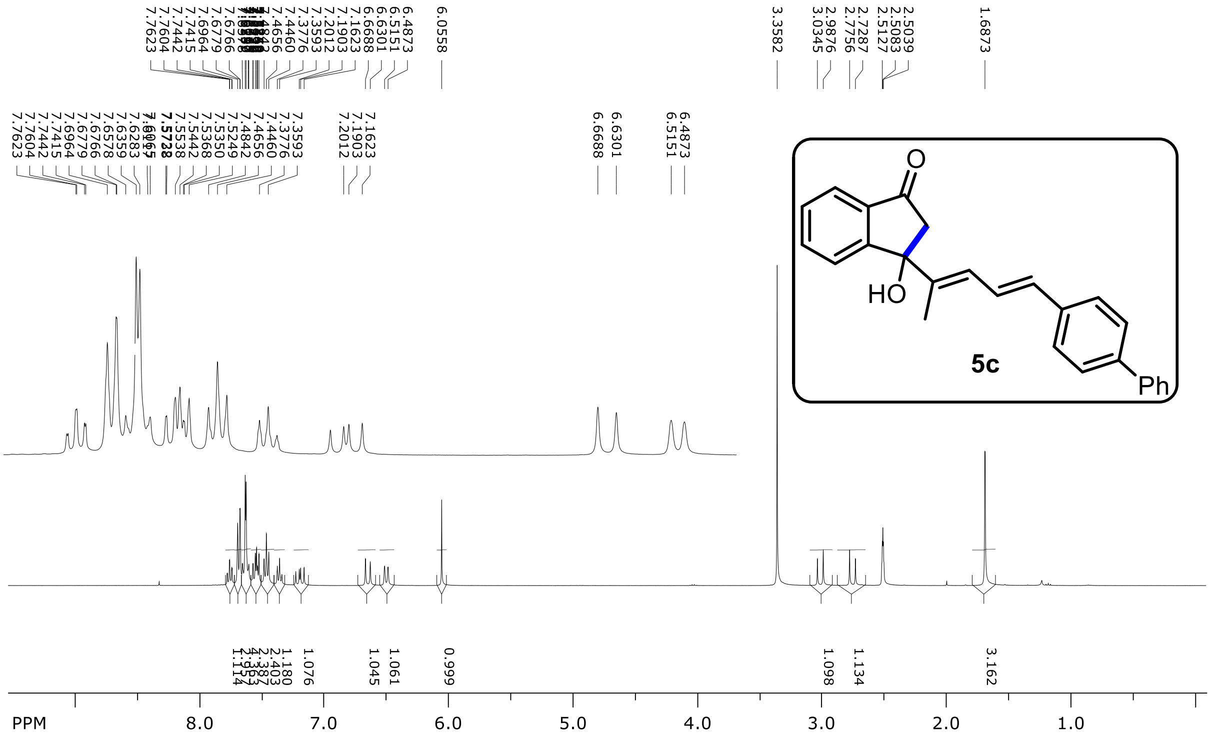
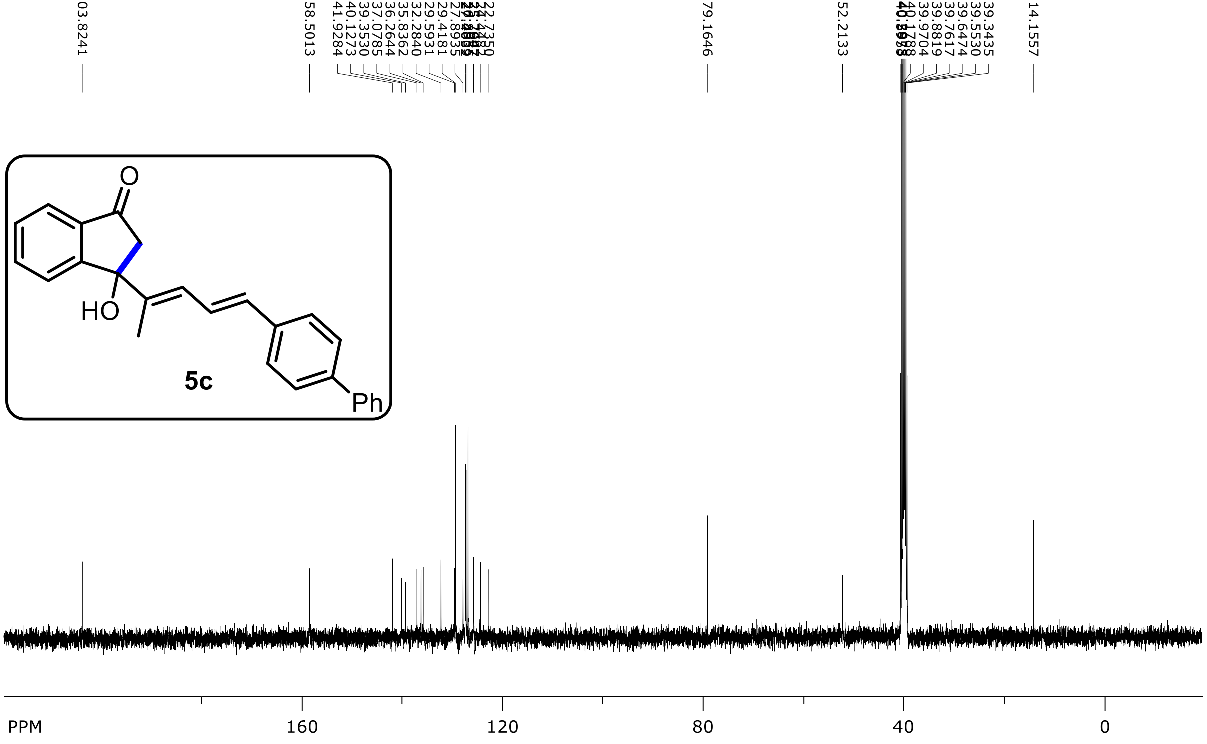


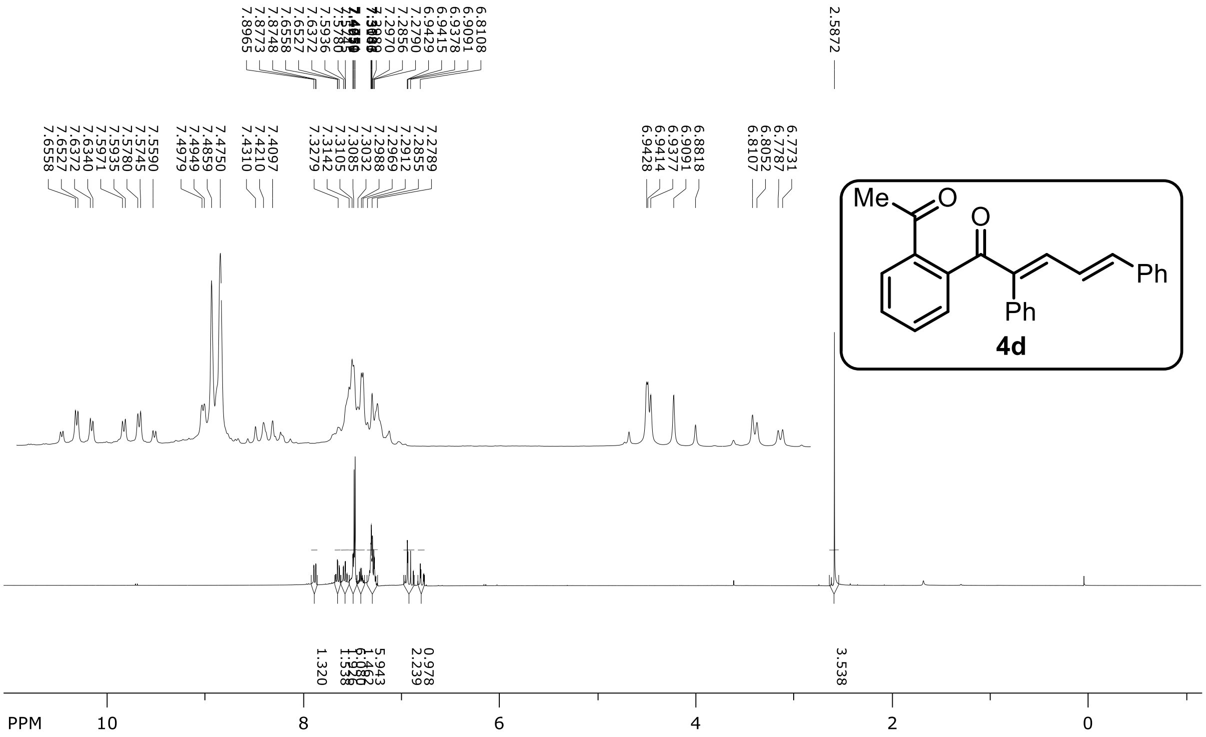
SpinWorks 4: BS-08-142



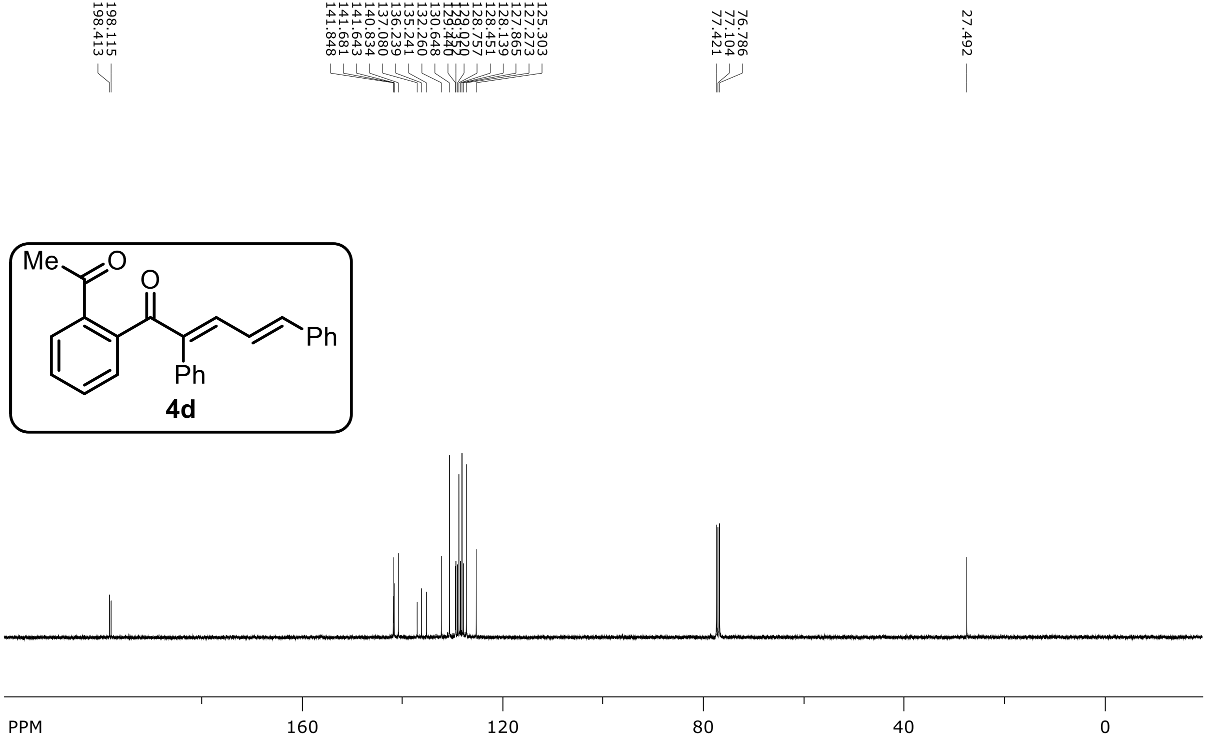
SpinWorks 4: BS 08 142
C13CPD256 DMSO /opt/topspin3.5pl2/nmrdata nmrsu 28



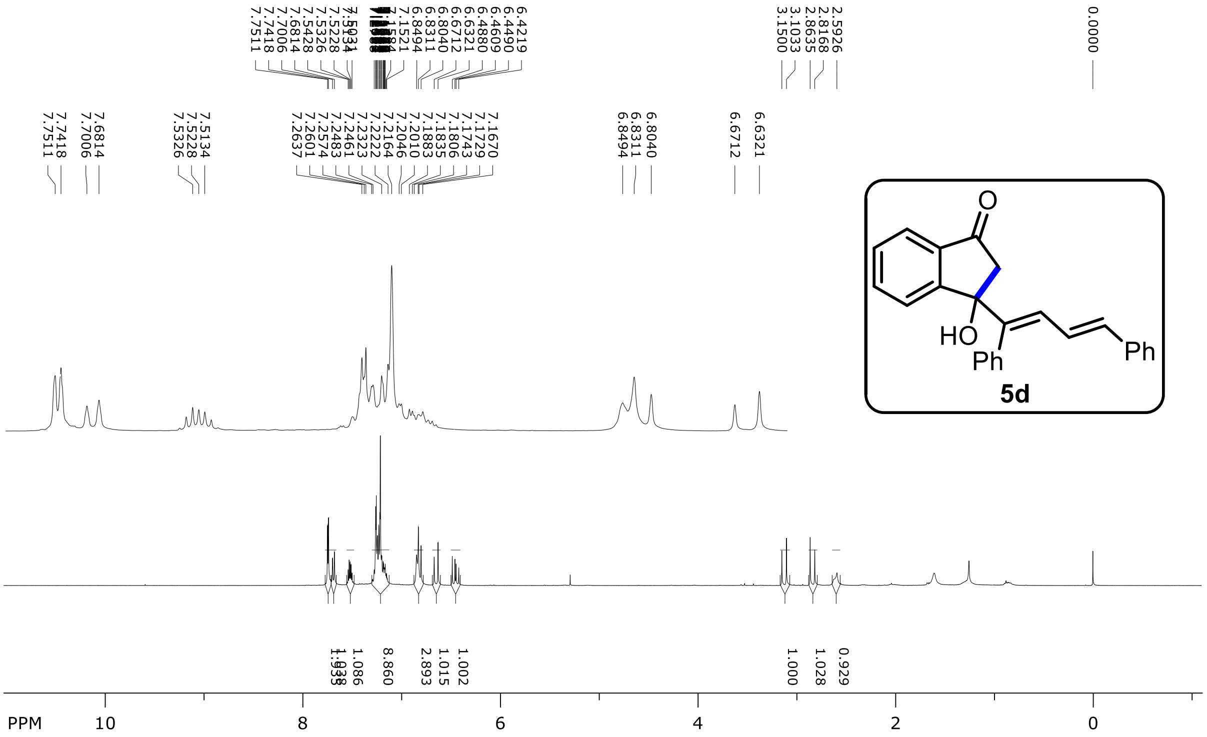
SpinWorks 4: BS-09-43



SpinWorks 4: BS 09 43
C13CPD256 CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 33



SpinWorks 4: BS-09-44



SpinWorks 4: BS-09-44
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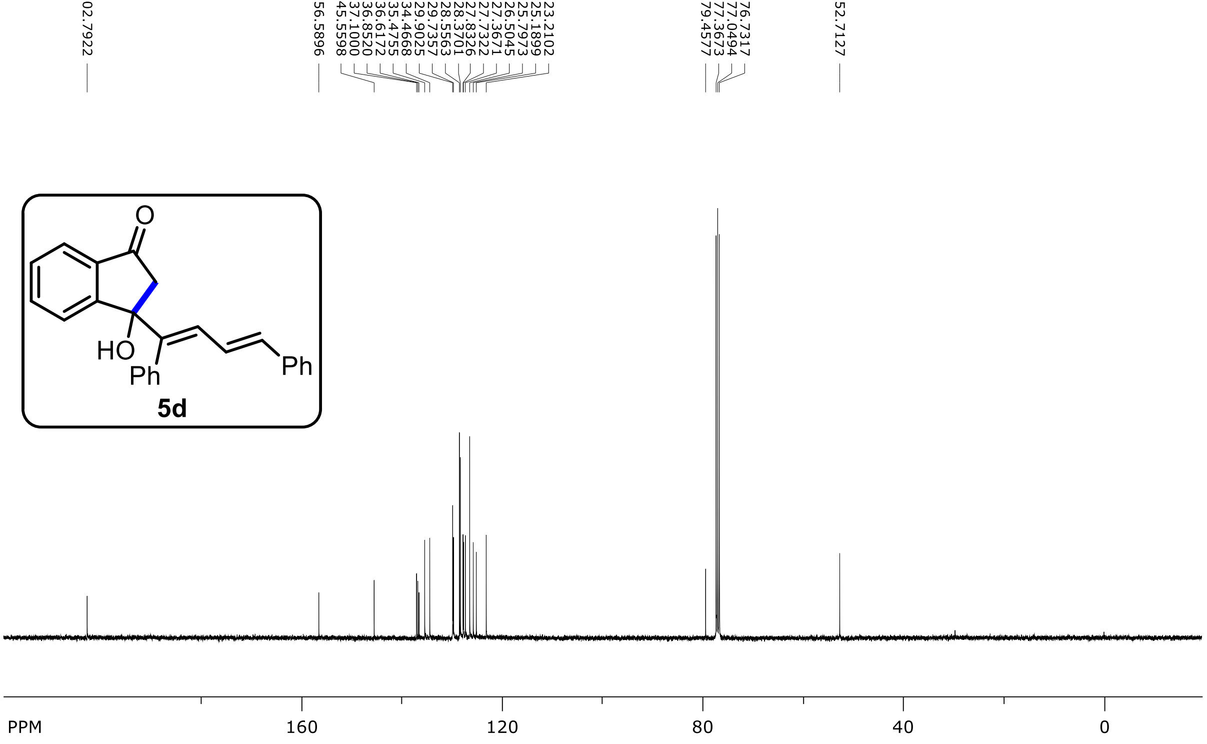
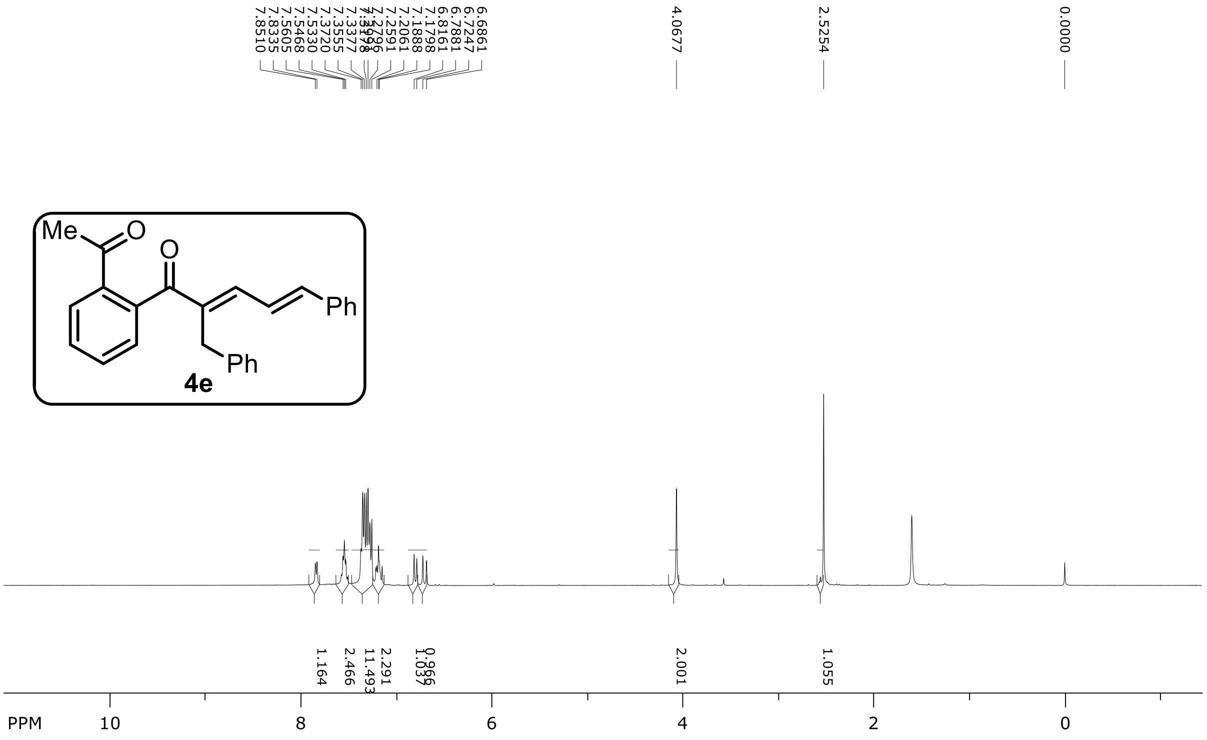


SpinWorks 4: BS 08 51
PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 28



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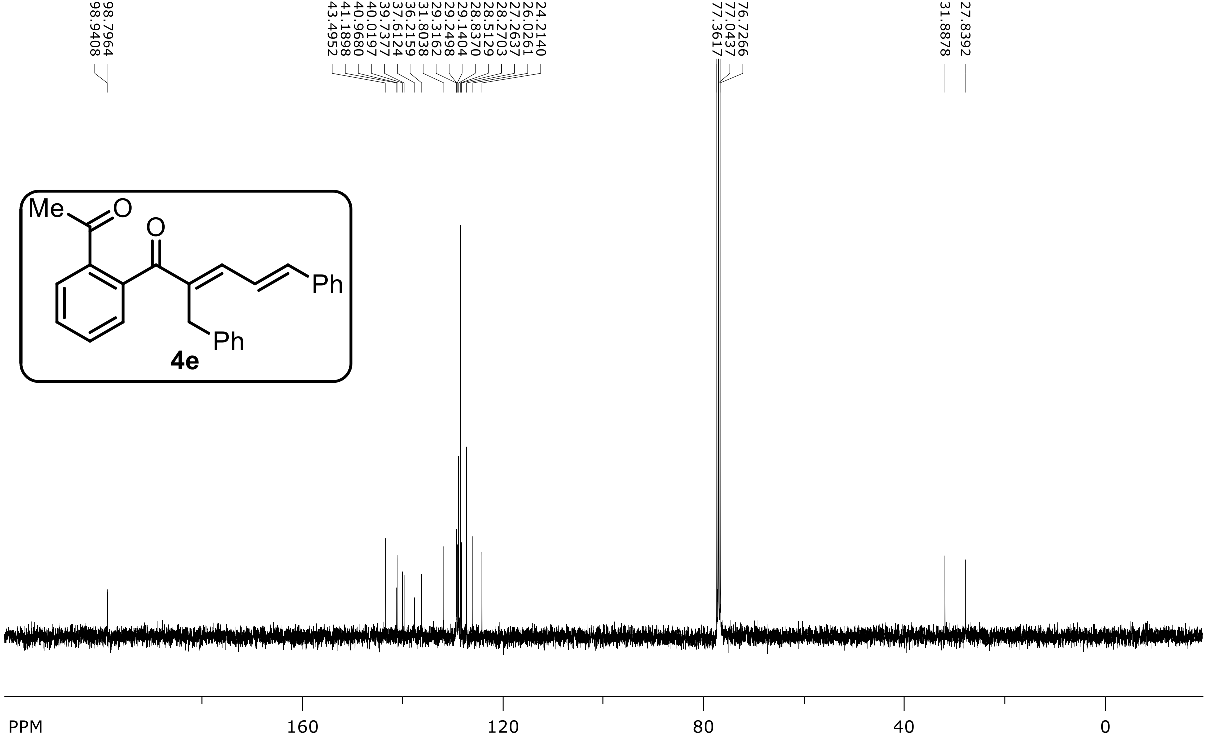

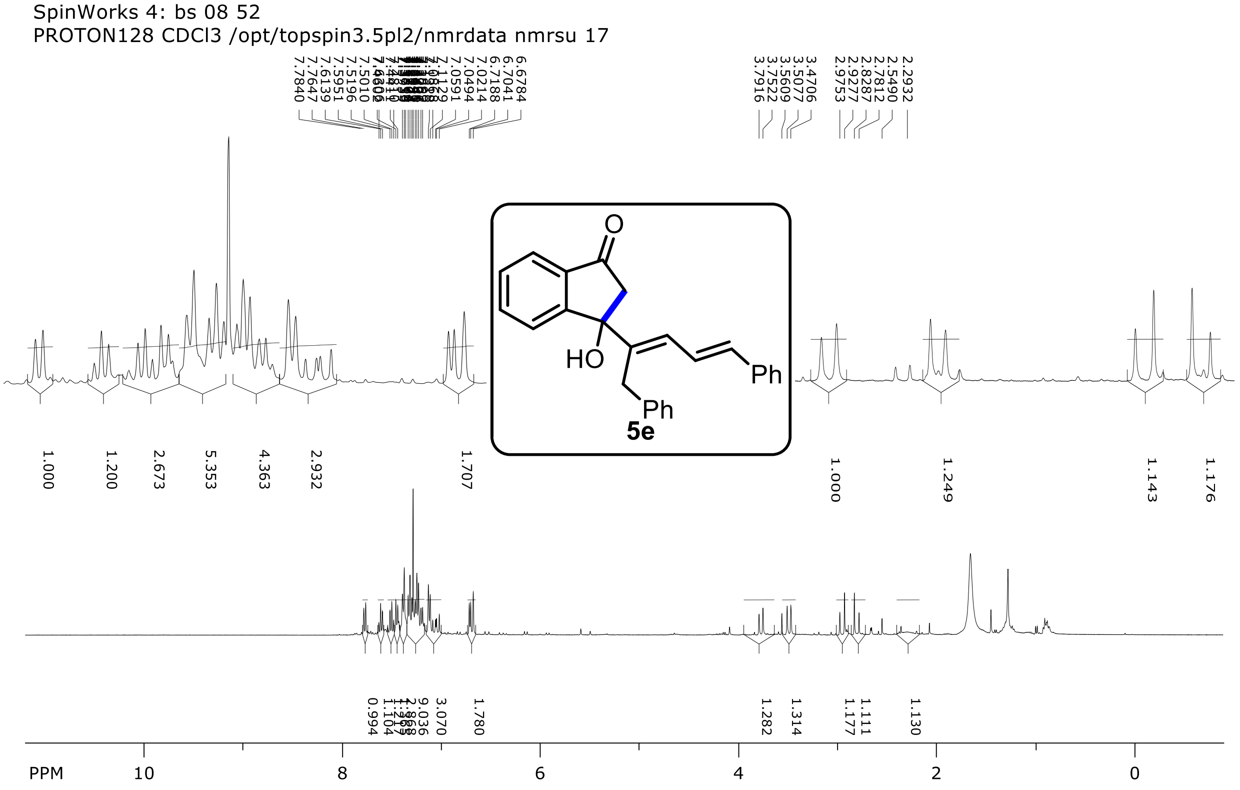
SpinWorks 4: bs 08 52
PROTON128 CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 17
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7.6139
7.5951
7.5196
7.5010
7.0494
7.0591
7.1129
7.0214
6.7188
6.7041
6.6784
3.7916
3.7522
3.5609
3.5077
3.4706
2.9753
2.9277
2.8287
2.7812
2.5490
2.2932
O
HO
Ph
Ph
5e
1.000
1.200
2.673
5.353
4.363
2.932
1.707
1.000
1.249
1.143
1.176
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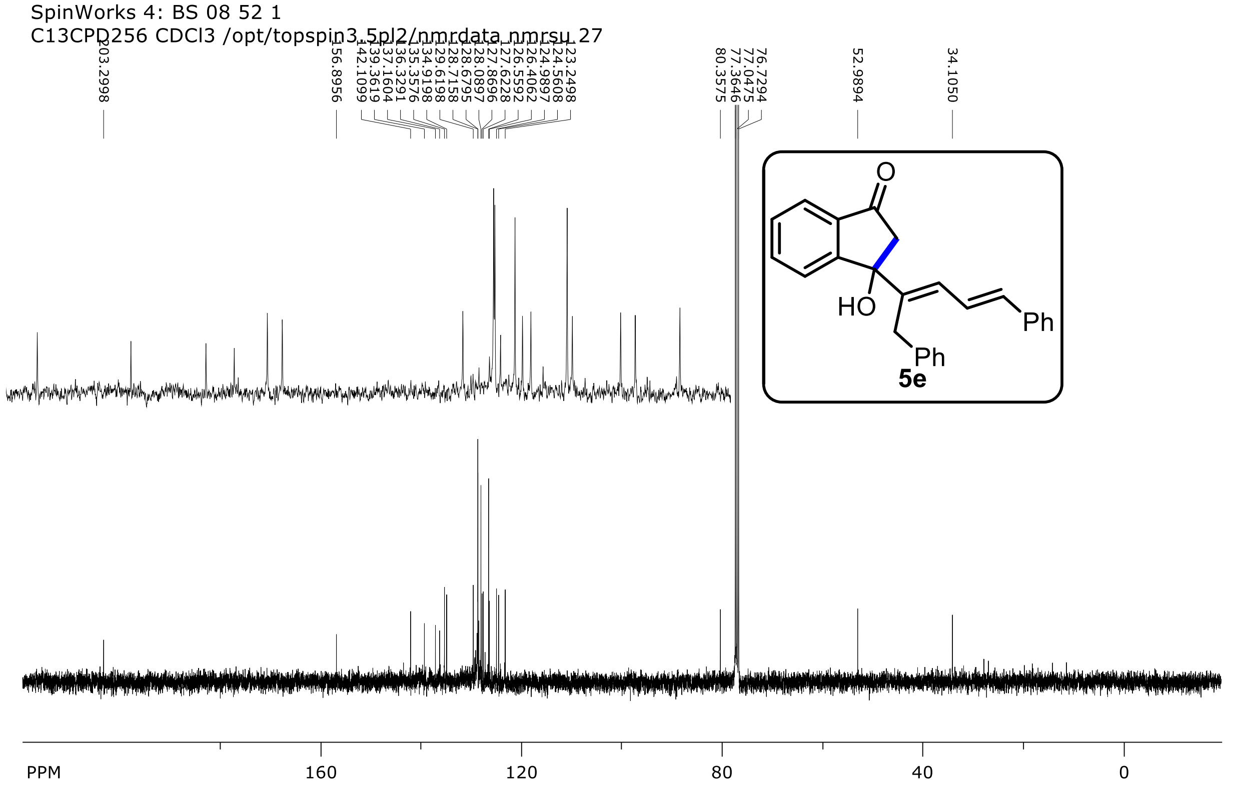
6
4
2
0


SpinWorks 4: BS 08 52 1
C13CPD256 CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 27
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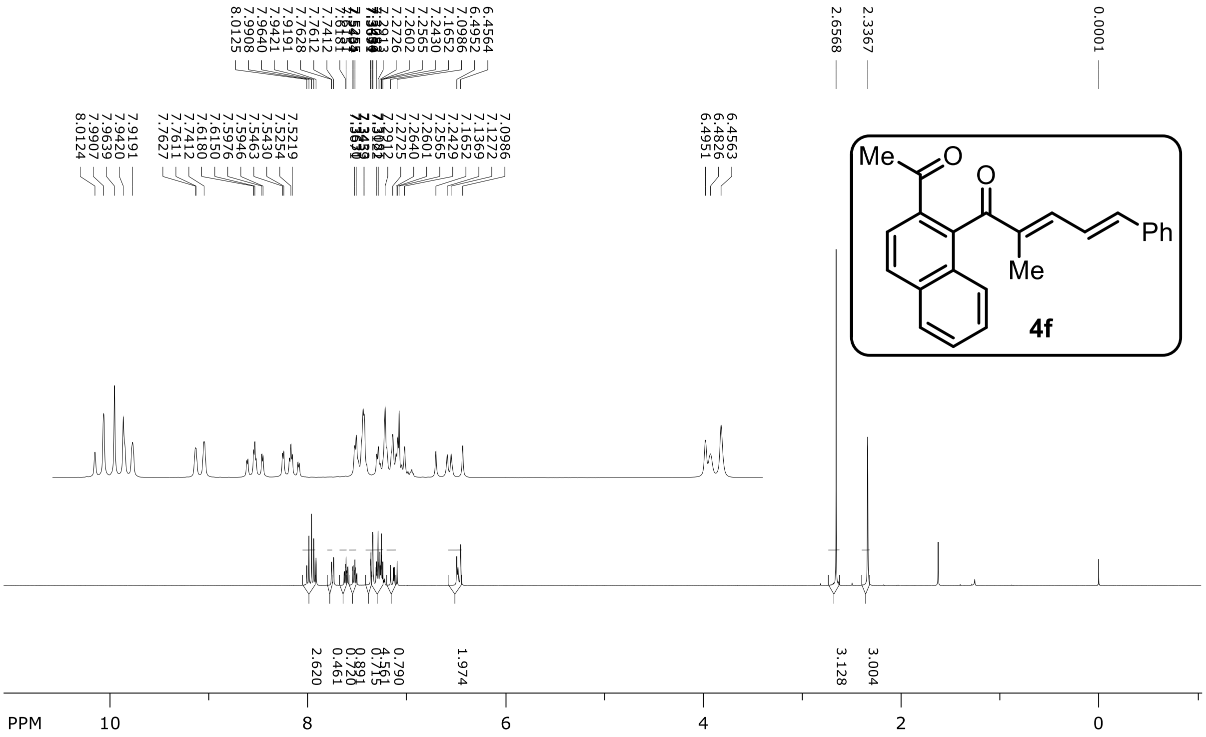
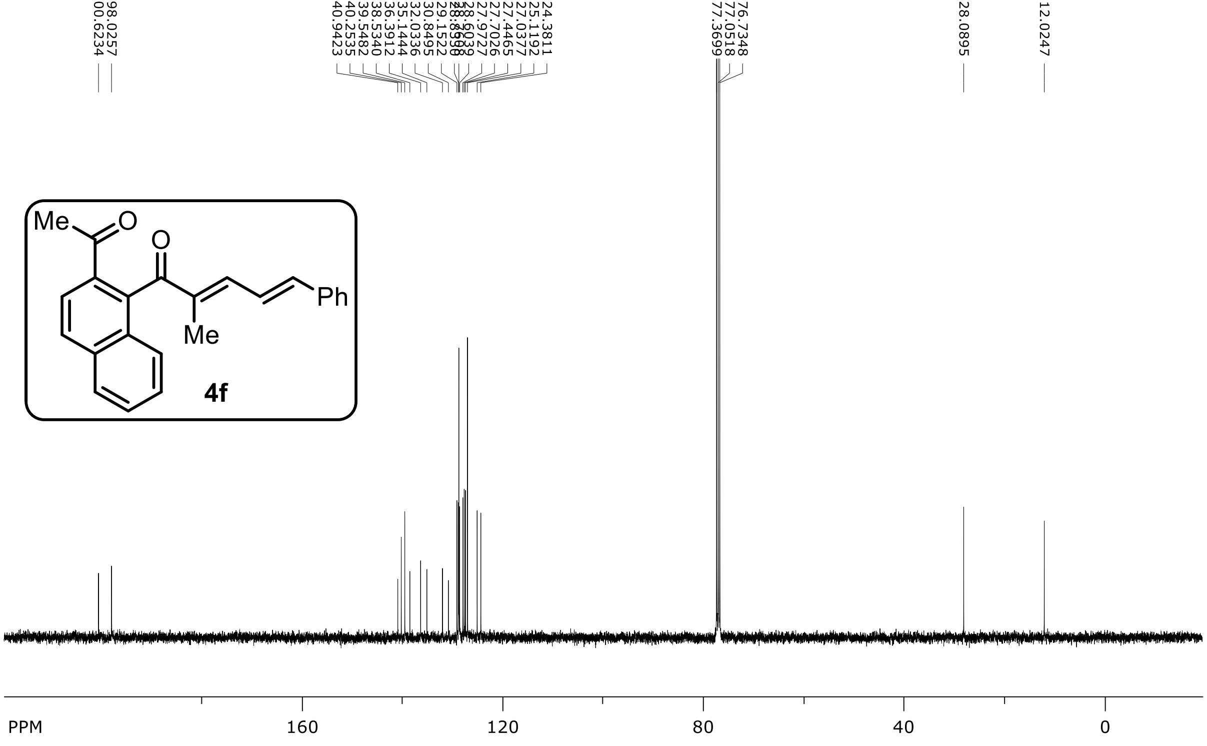
156.8956
142.1099
139.3619
137.1604
136.3291
135.3576
134.9198
129.6198
128.7158
128.6795
128.0897
127.8696
127.6228
126.5592
126.4062
124.9897
124.5608
123.2498
80.3575
77.3646
77.0475
76.7294
52.9894
34.1050
O
HO
Ph
Ph
5e
PPM
160
120
80
40
0

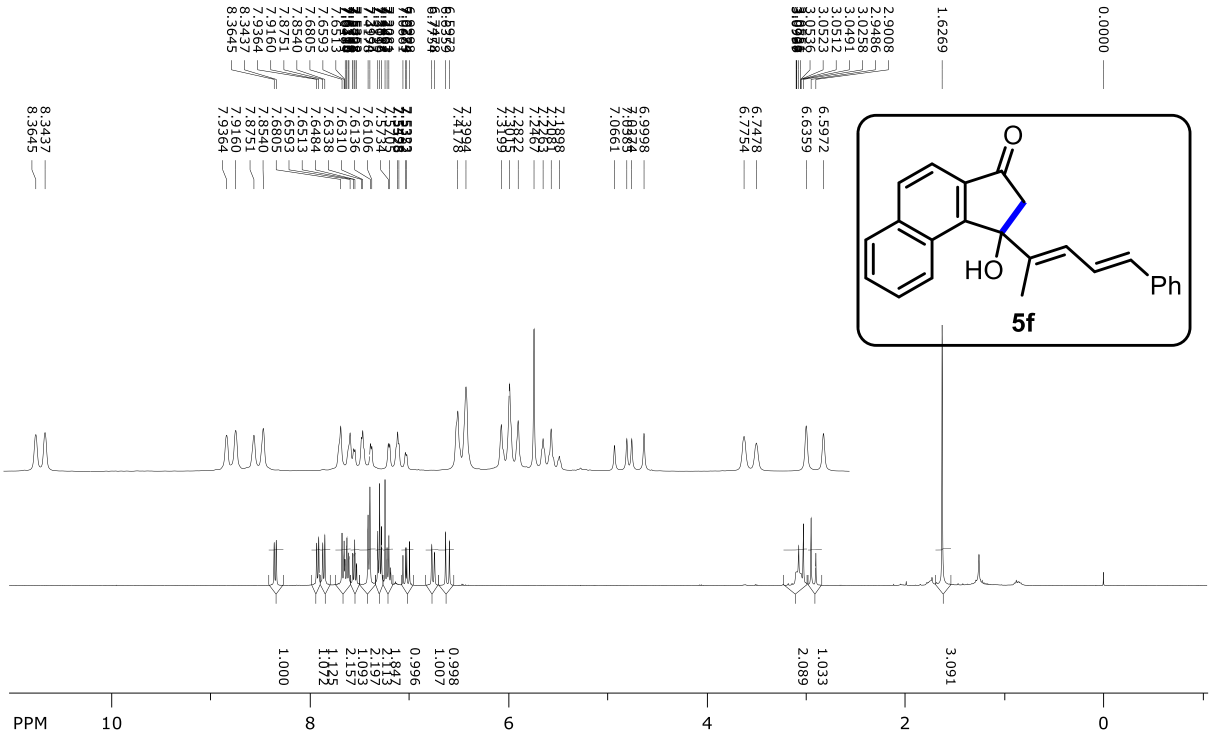
SpinWorks 4: BS-08-270



SpinWorks 4: BS 08 270
C13CPD256 CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 53



SpinWorks 4: BS-08-271-Re



SpinWorks 4: BS 08 271
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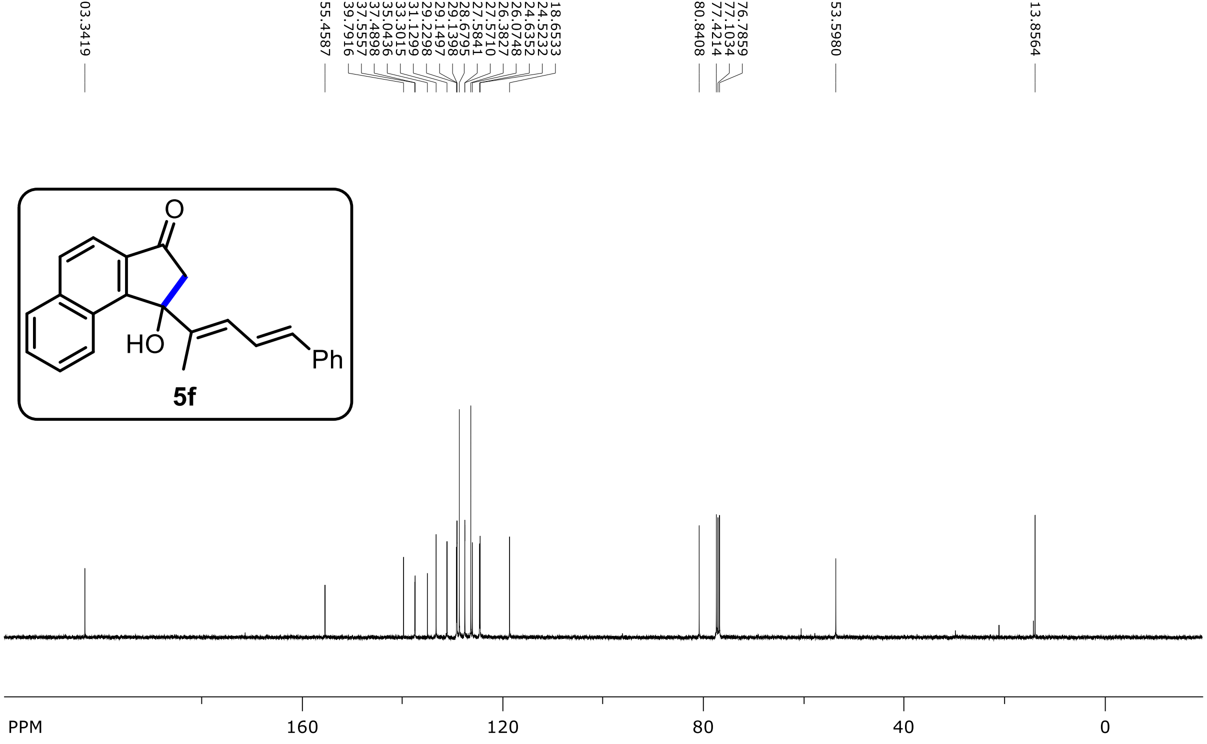
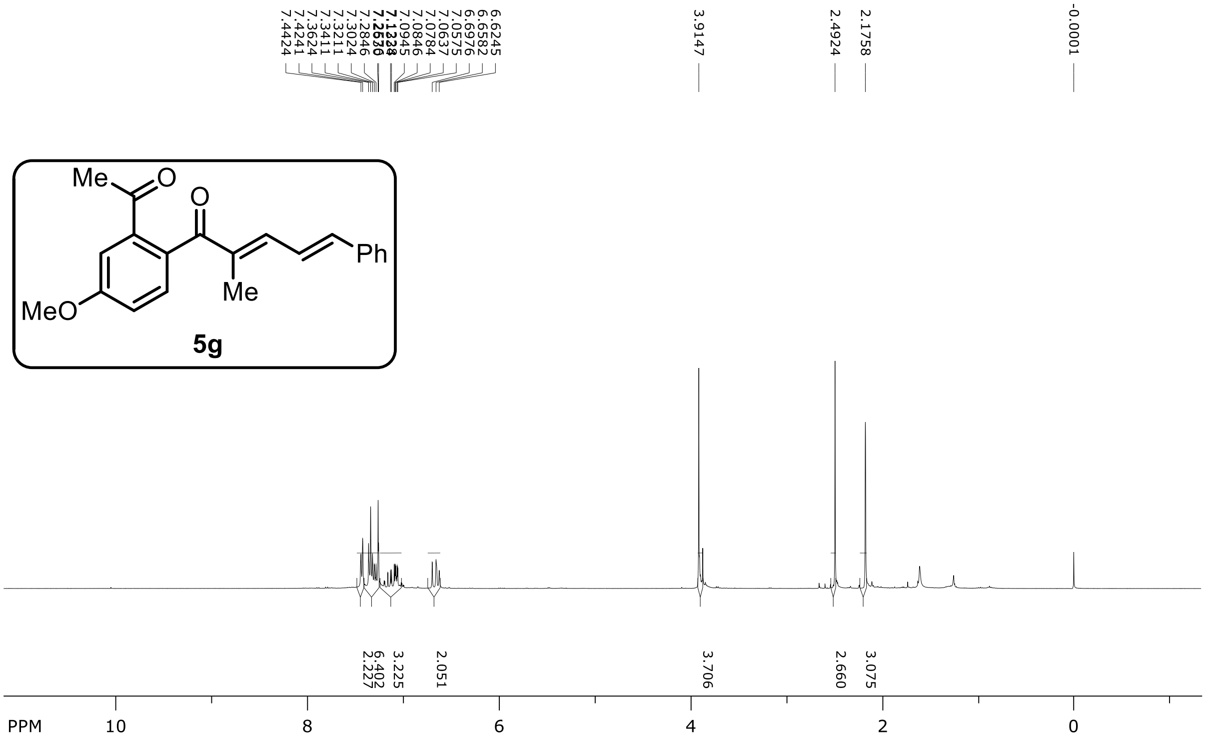


SpinWorks 4: BS-09-34



SpinWorks 4: BS 09 34
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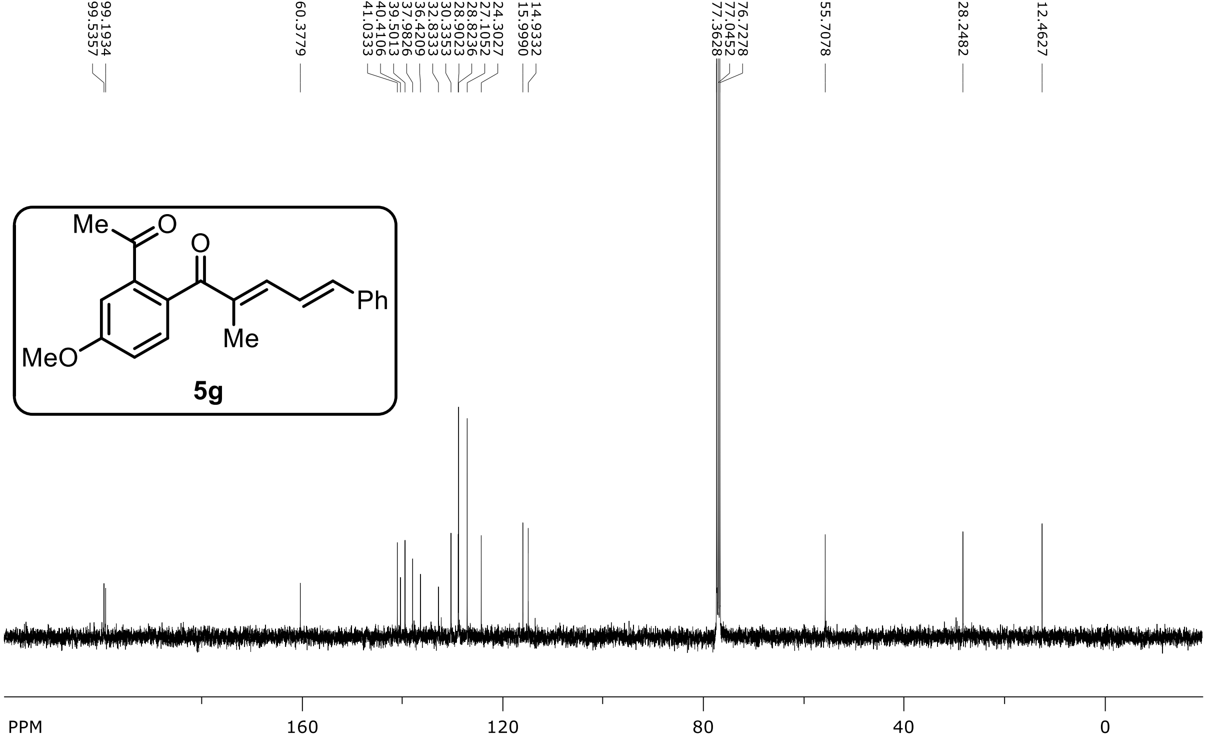
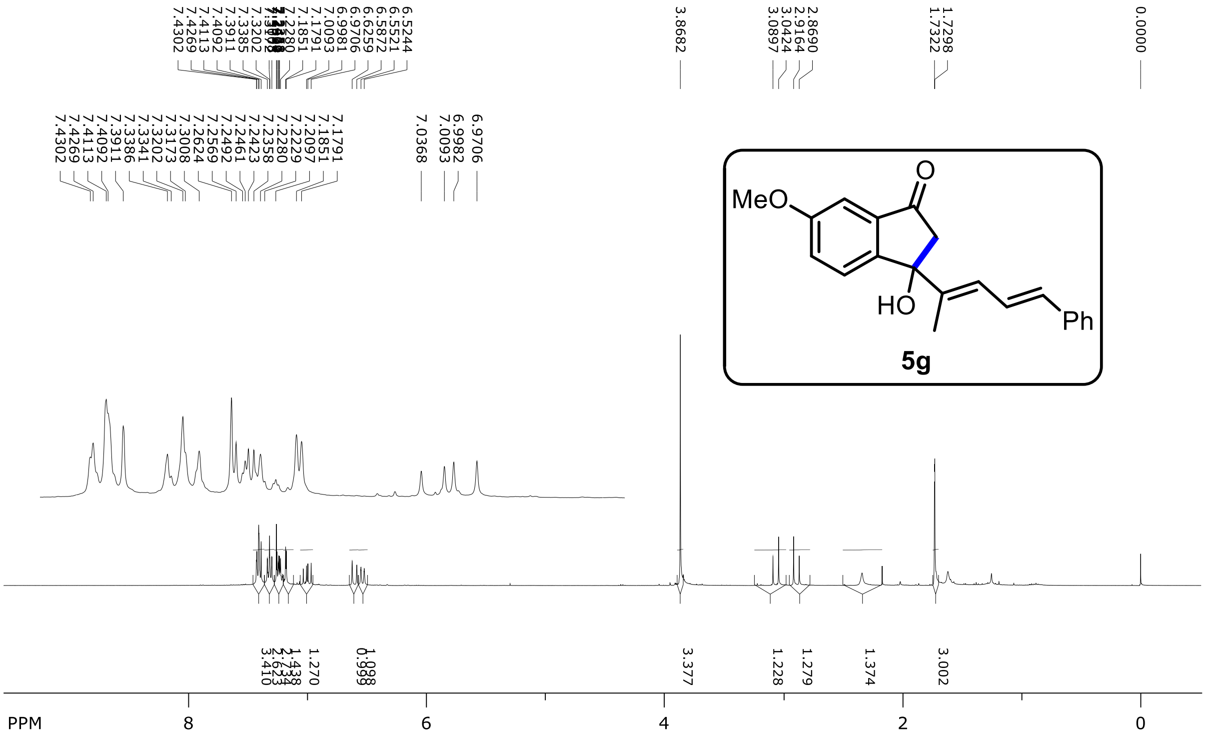


SpinWorks 4: BS-09-35



SpinWorks 4: BS 09 35
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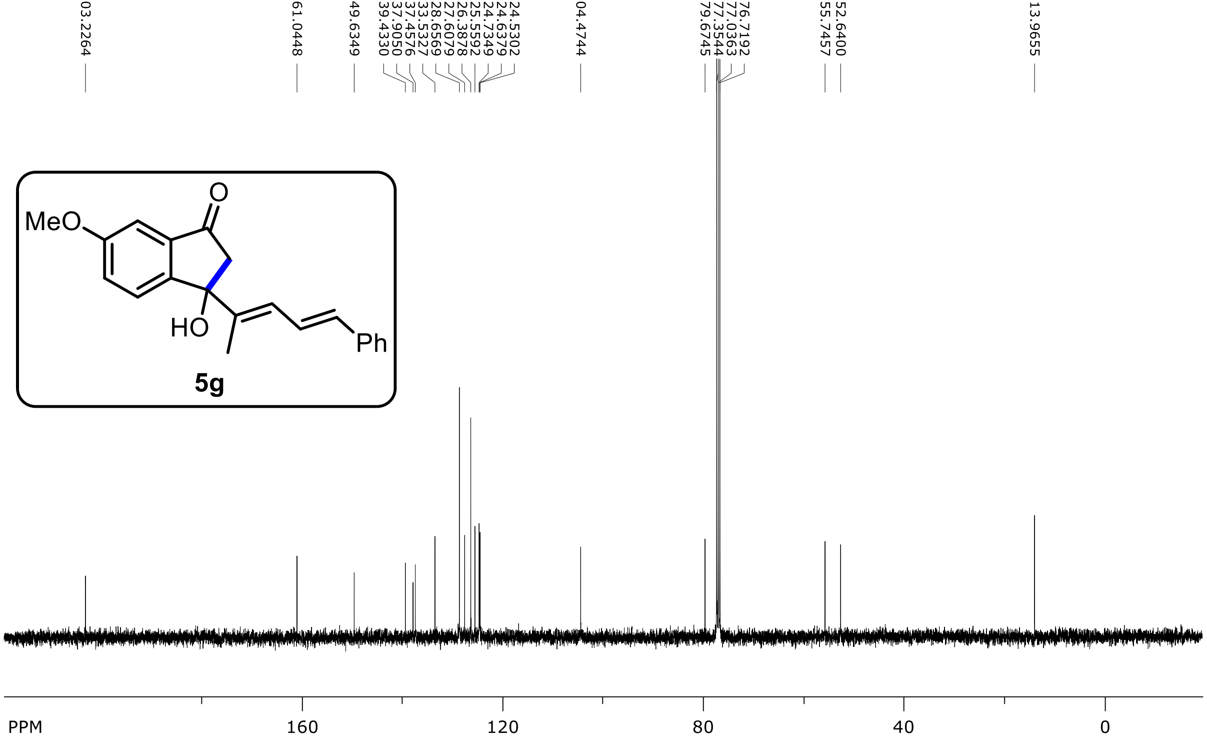
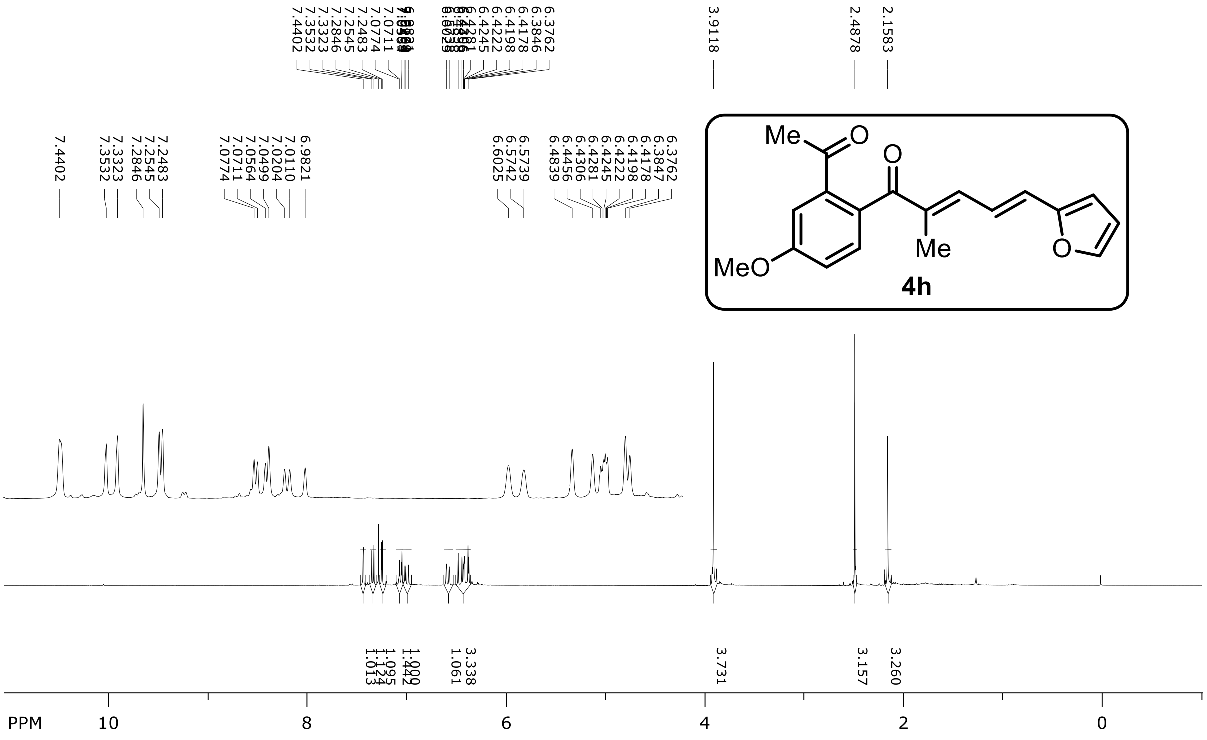


SpinWorks 4: BS-08-98



SpinWorks 4: BS 08 98
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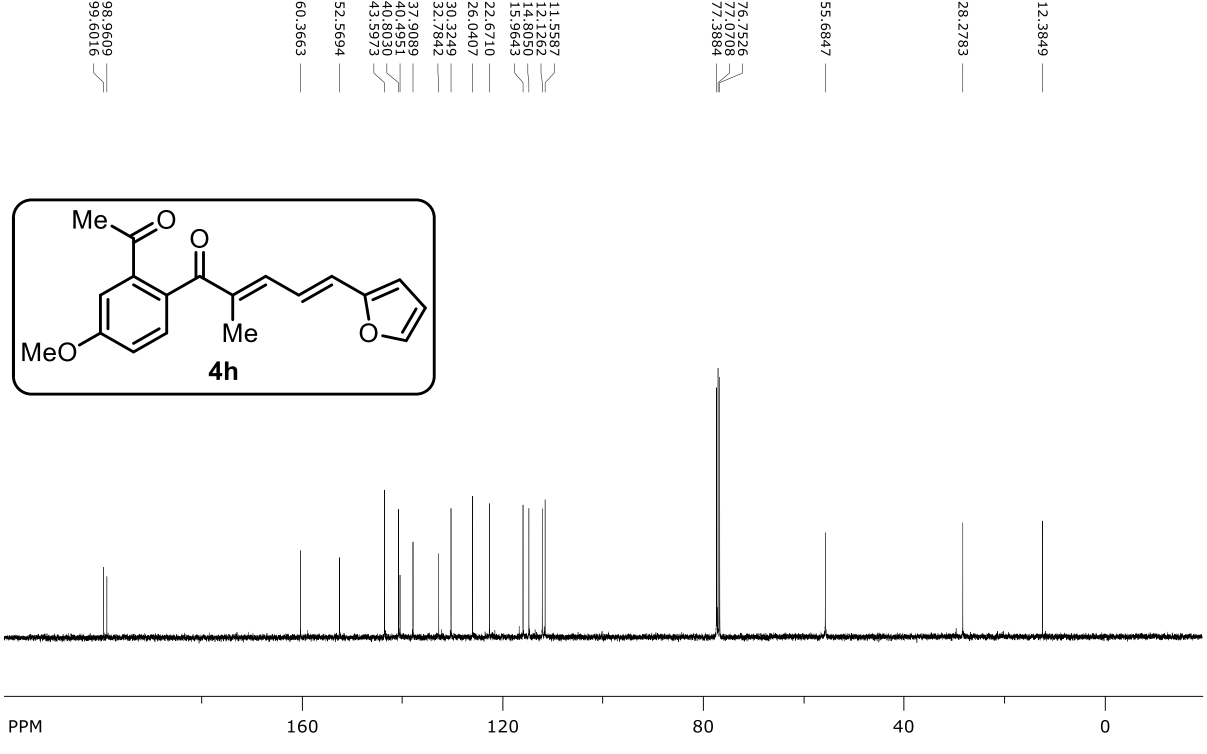
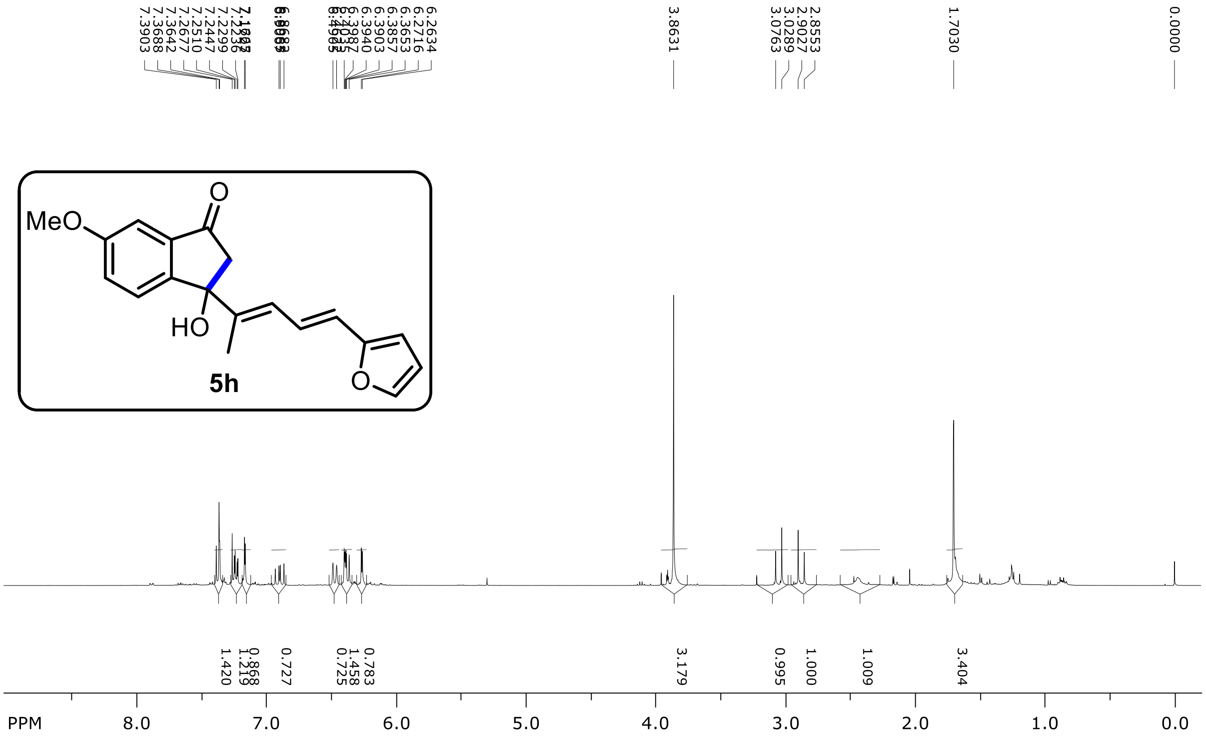
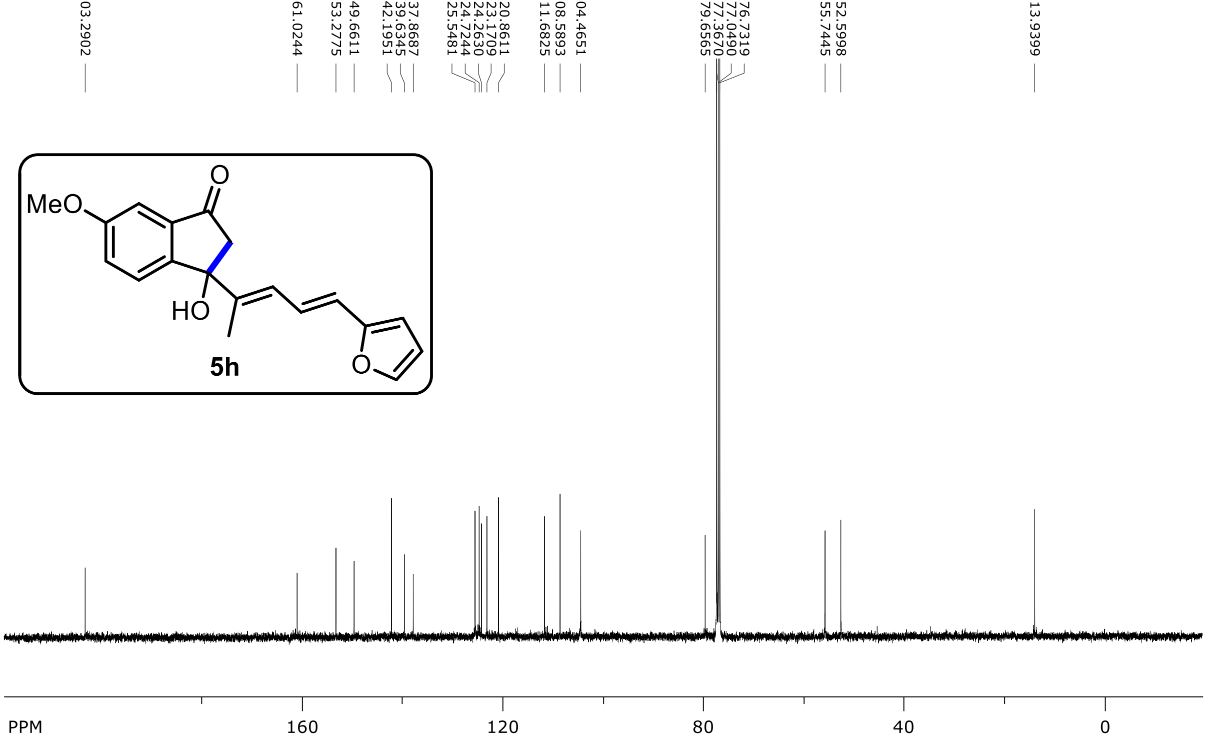


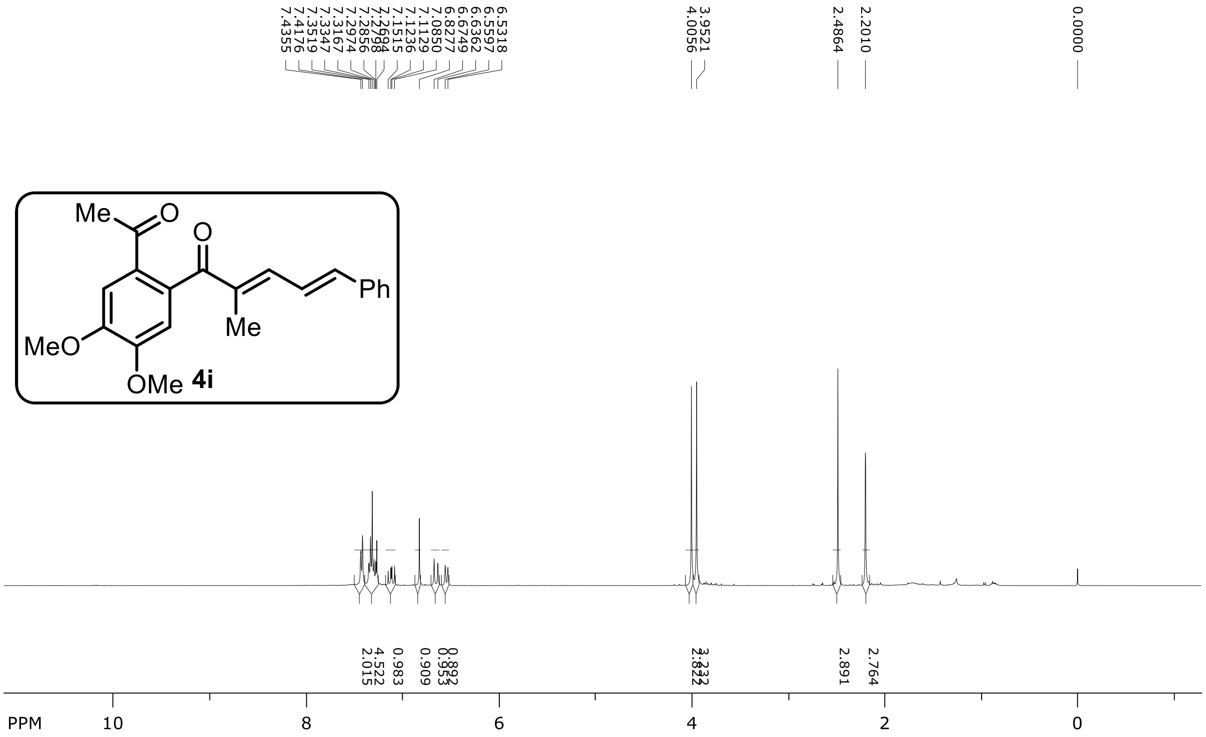
SpinWorks 4: BS-09-43



SpinWorks 4: BS 09 42???/43
C13CPD CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 52



SpinWorks 4: BS-08-22



SpinWorks 4: BS 08 22
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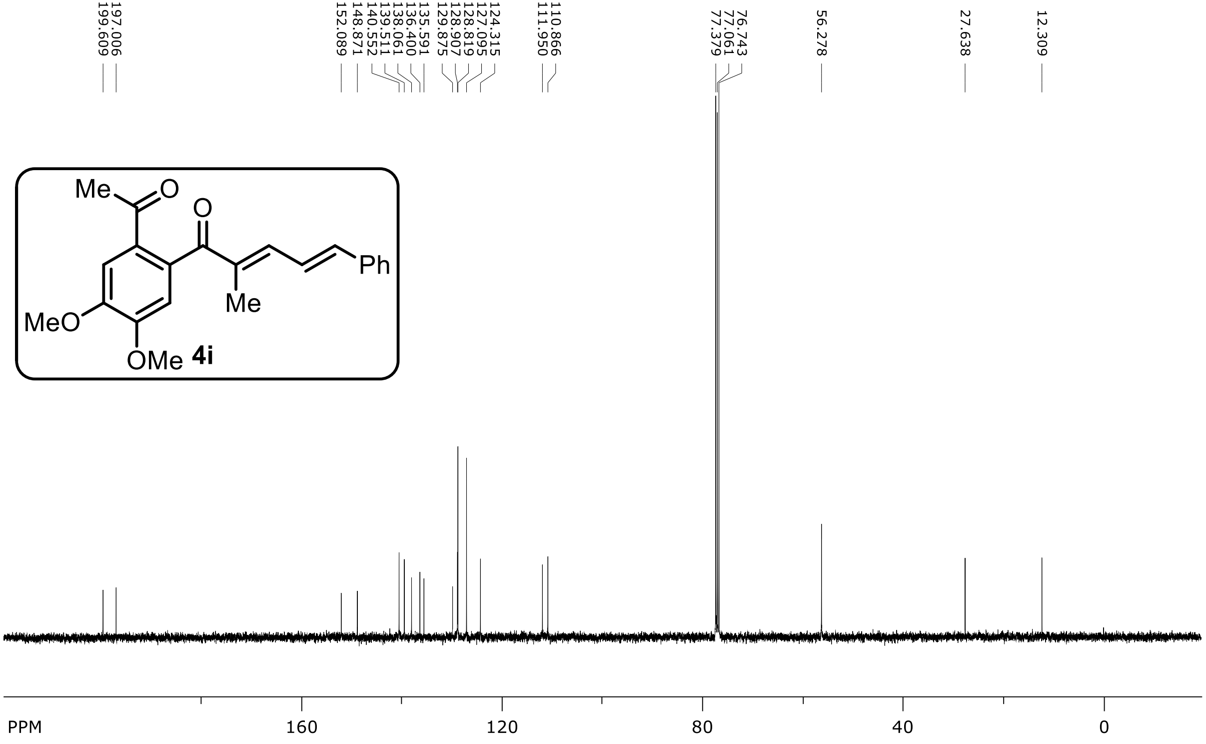
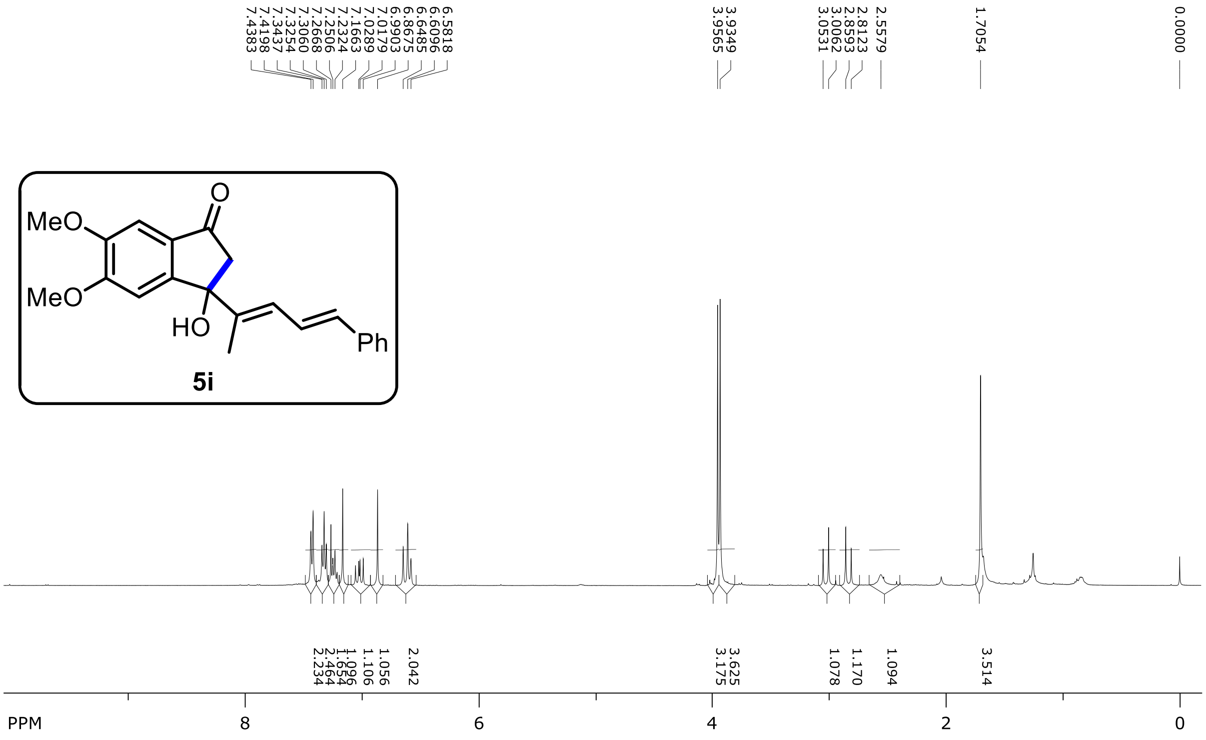


SpinWorks 4: BS-08-30-1



SpinWorks 4: BS 08 30 1
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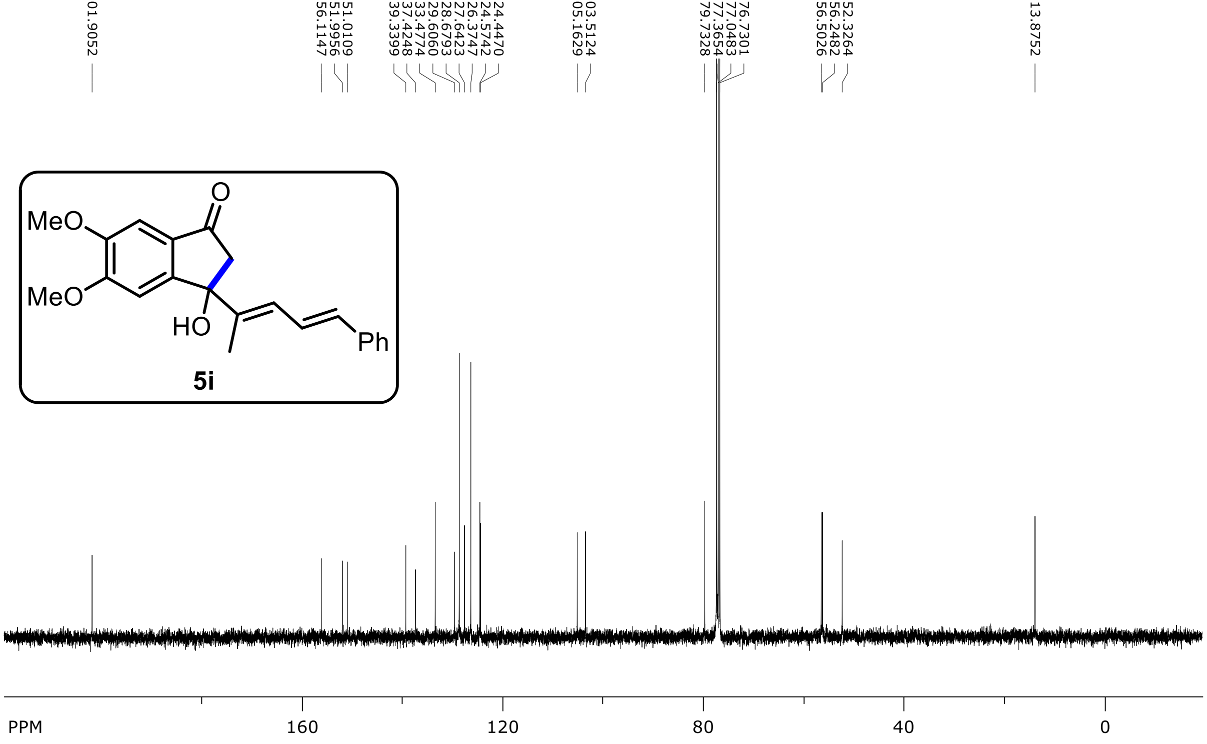
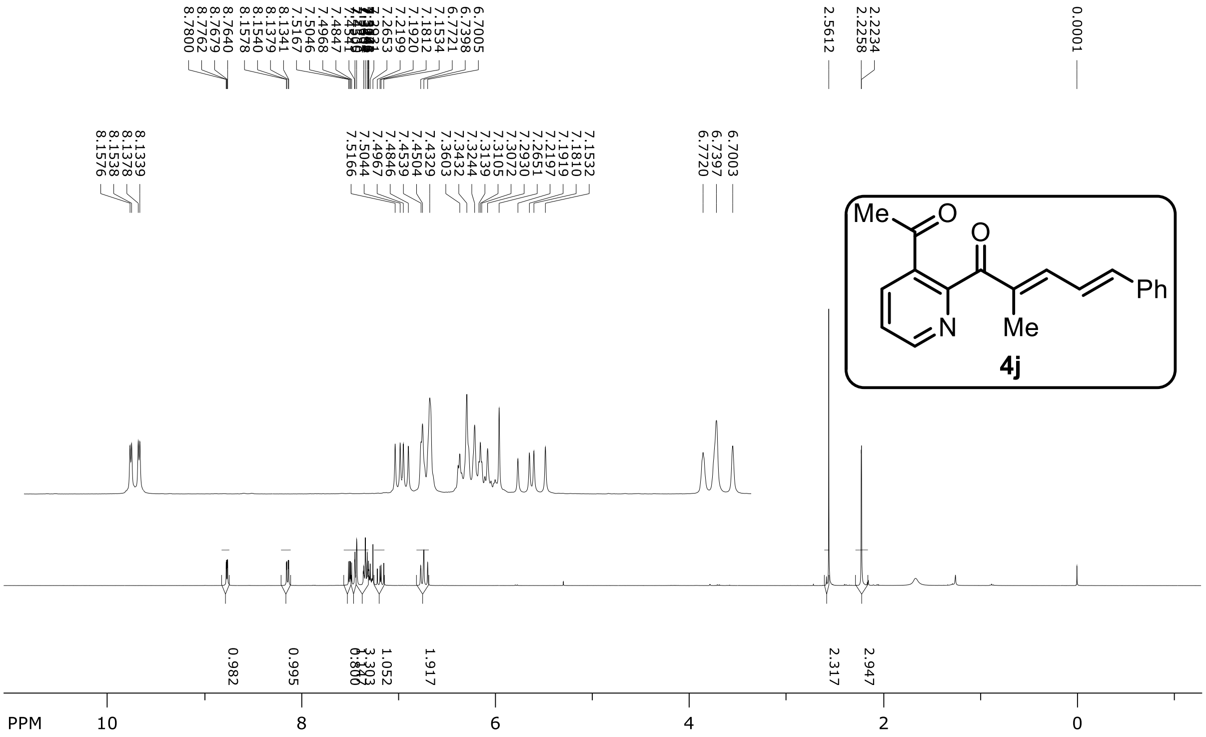


SpinWorks 4: BS-08-329-re



SpinWorks 4: BS 08 329 RE
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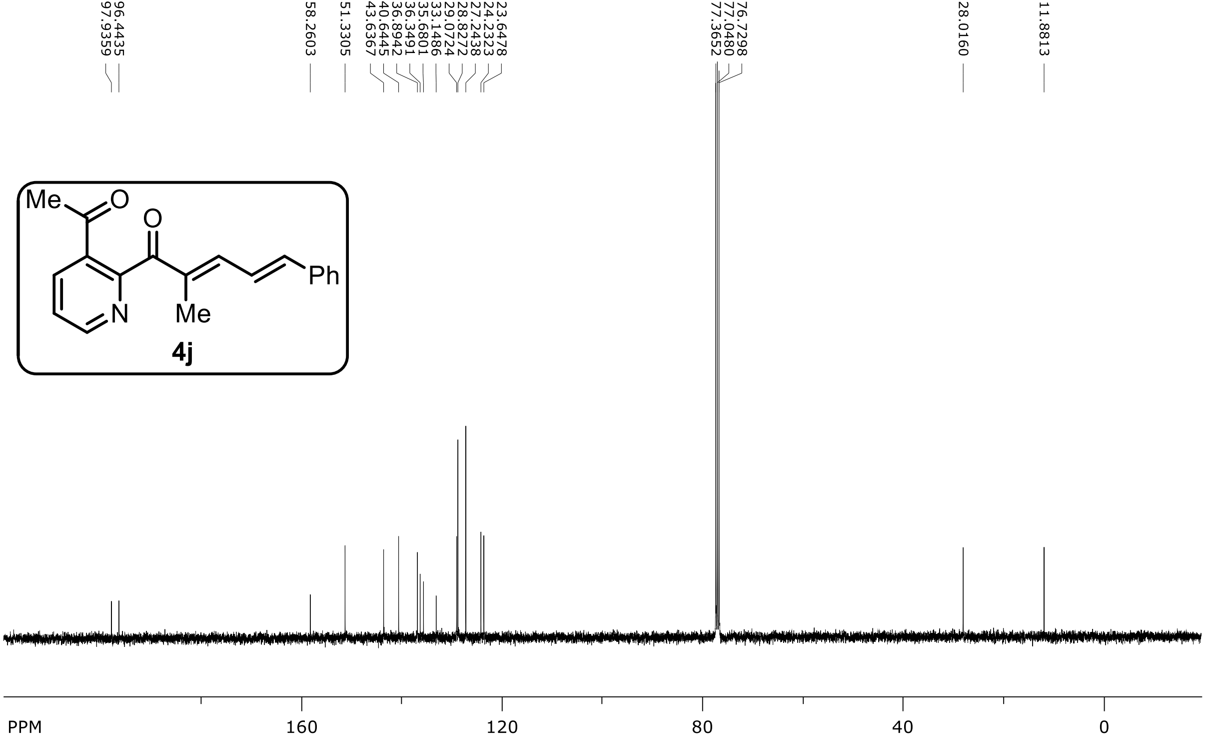
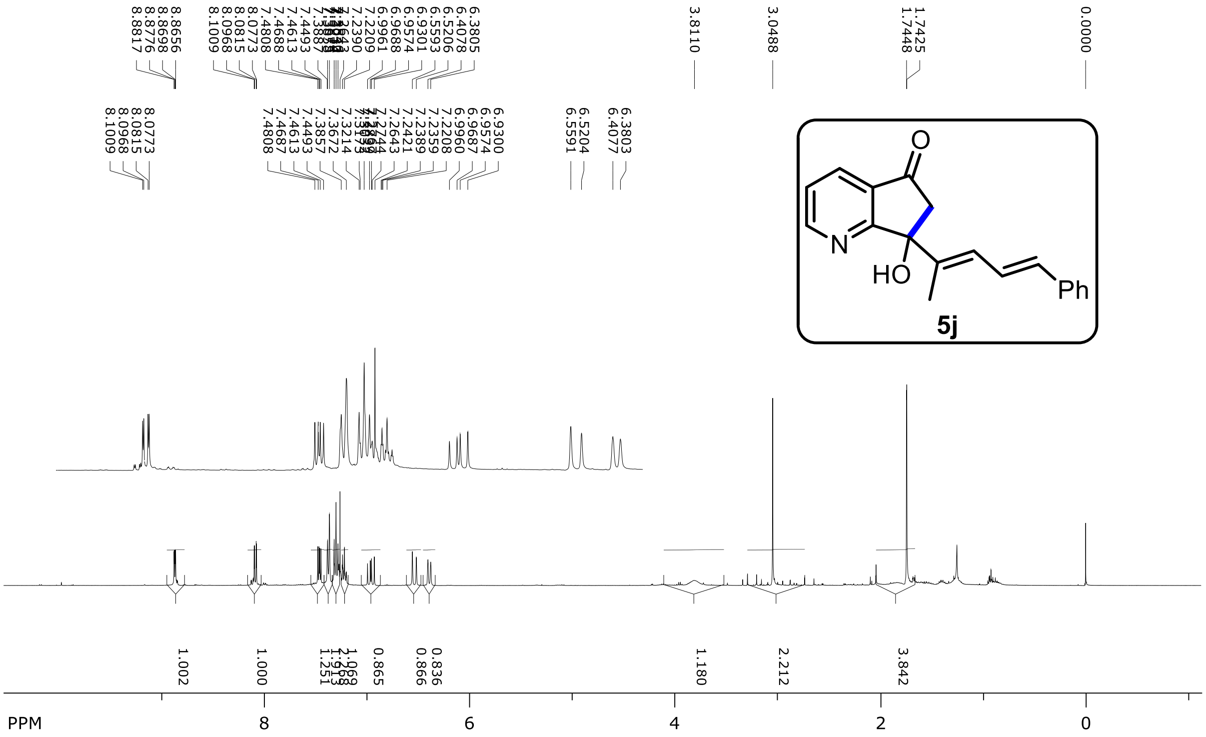


SpinWorks 4: bs-08-331



SpinWorks 4: BS 08 331
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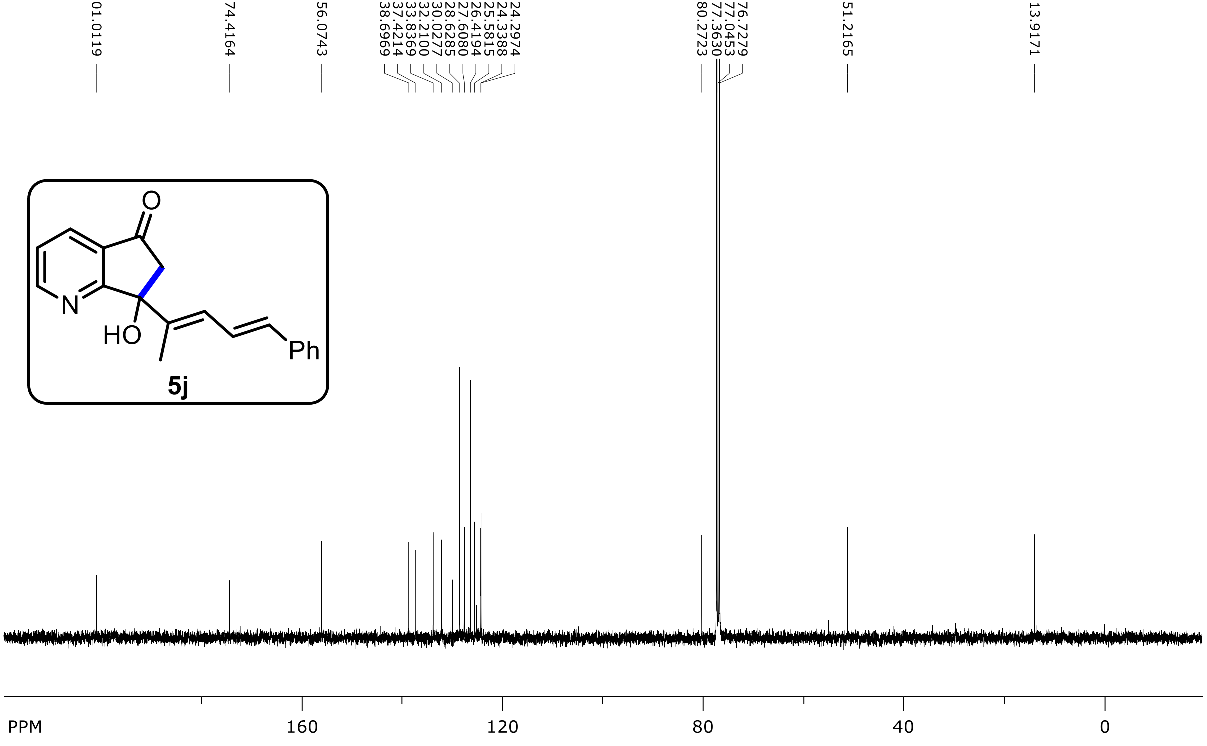
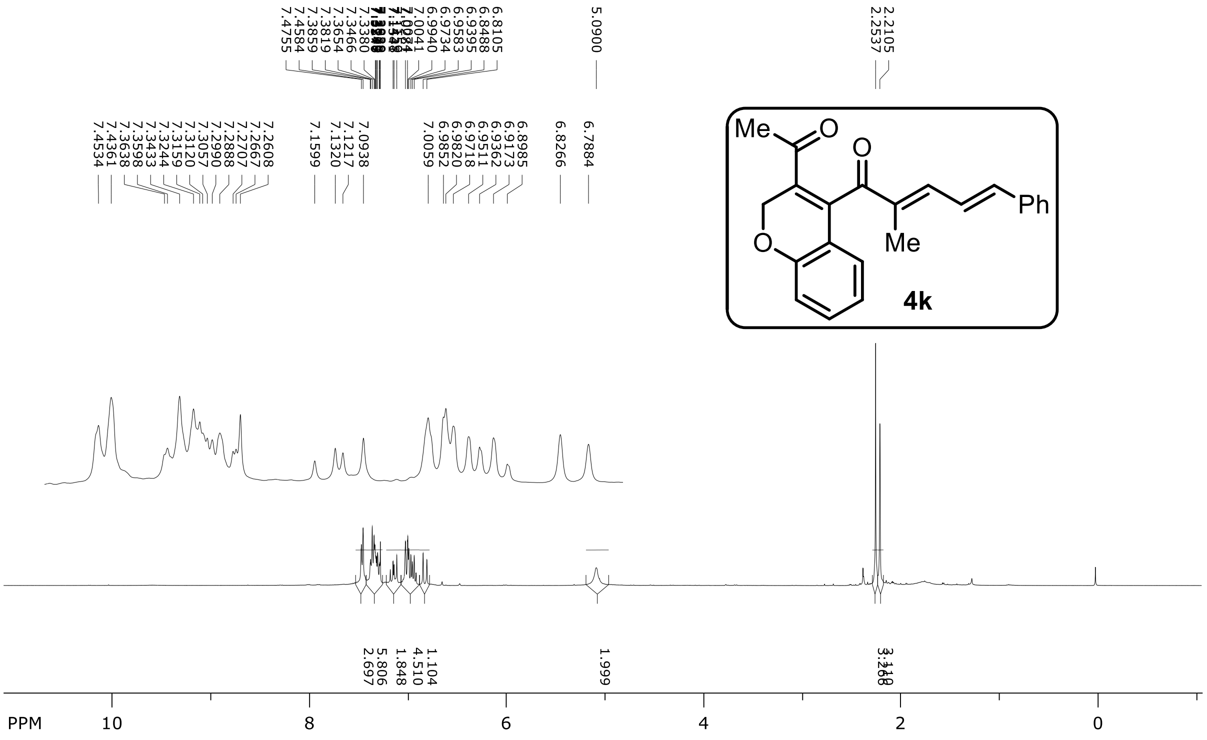


SpinWorks 4: BS-08-70



SpinWorks 4: BS 08 70
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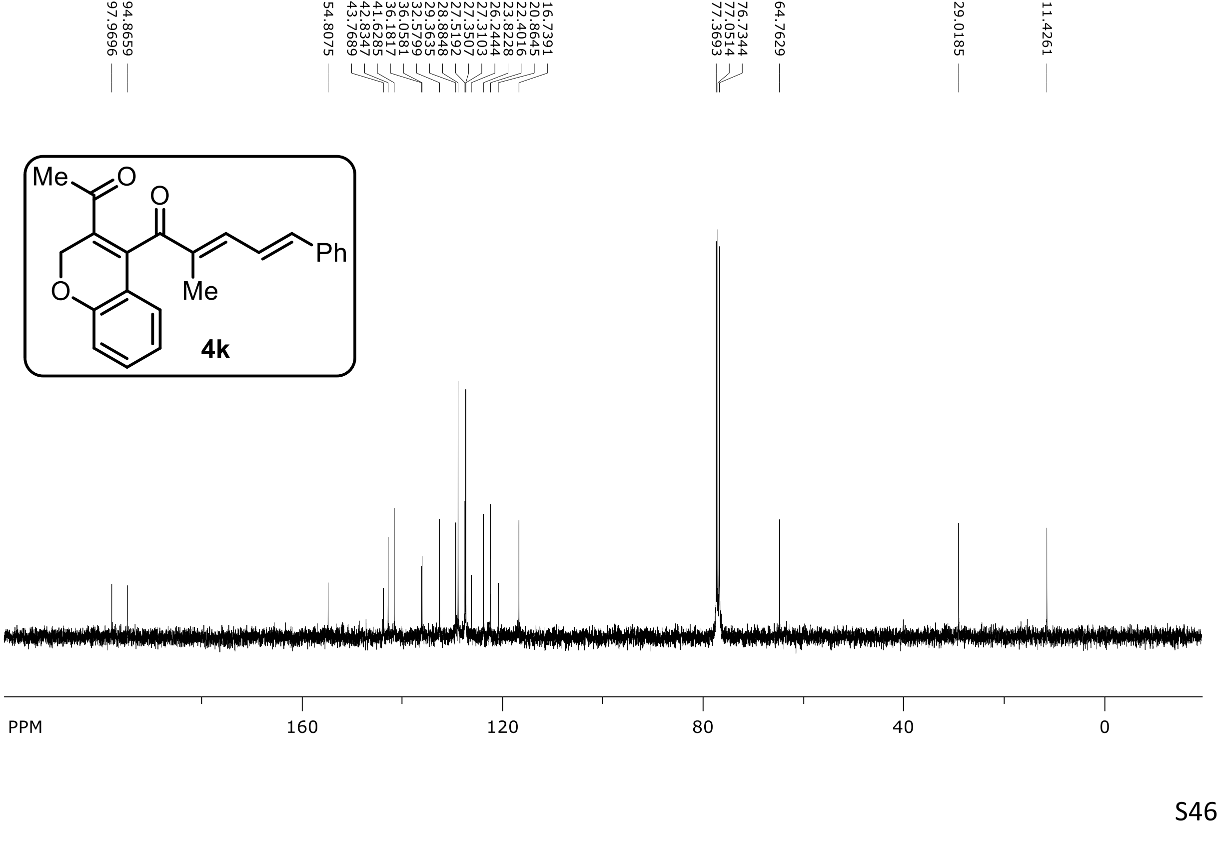
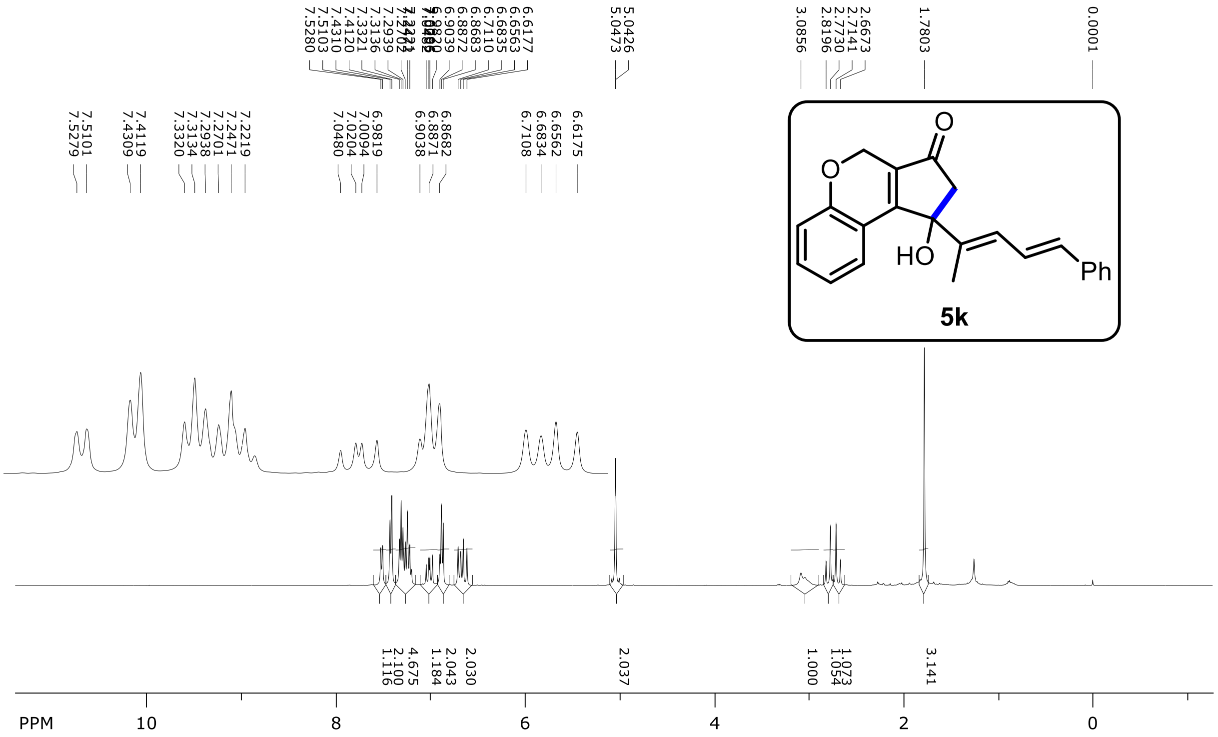


SpinWorks 4: BS-08-73



SpinWorks 4: BS 08 73
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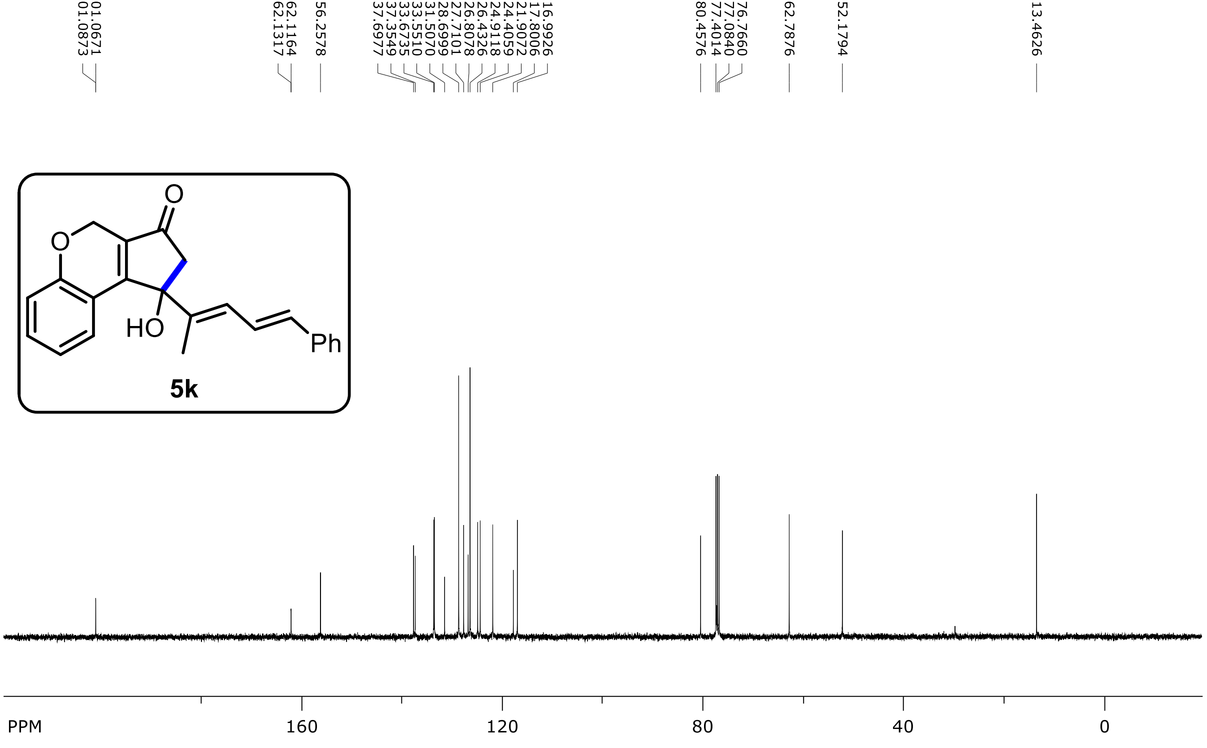
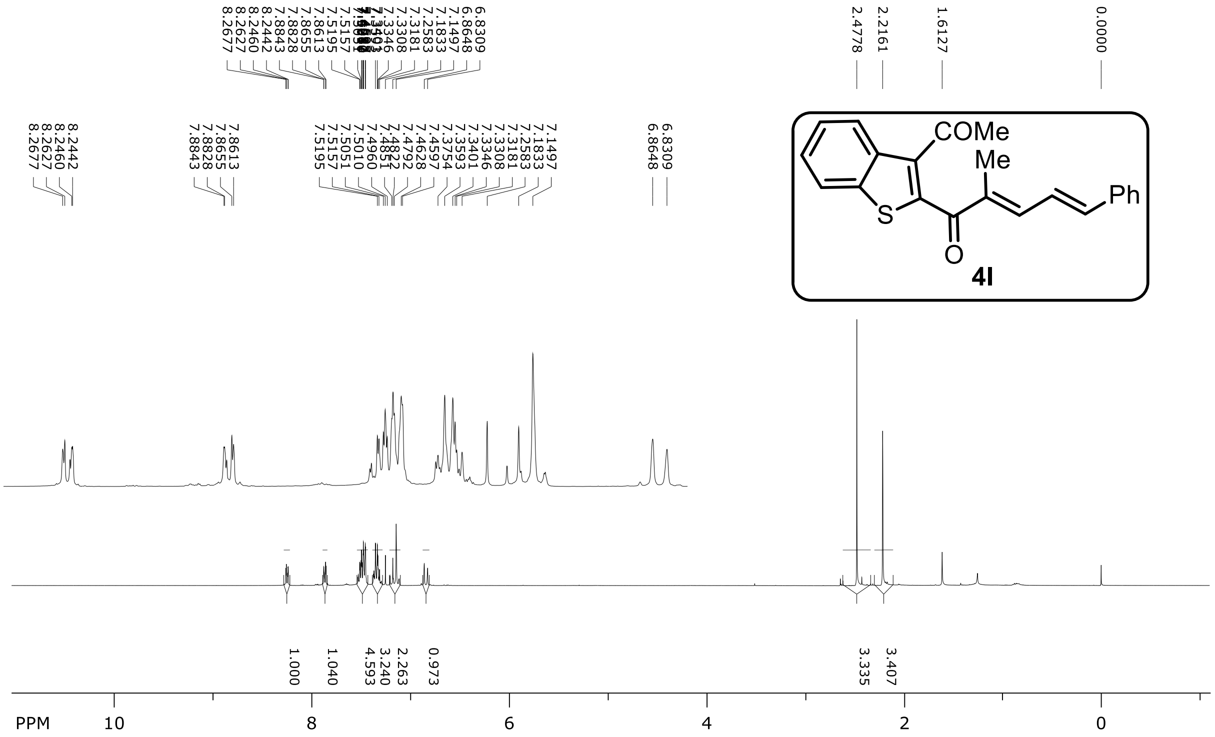


SpinWorks 4: BS-08-320-Re



SpinWorks 4: BS 08 320
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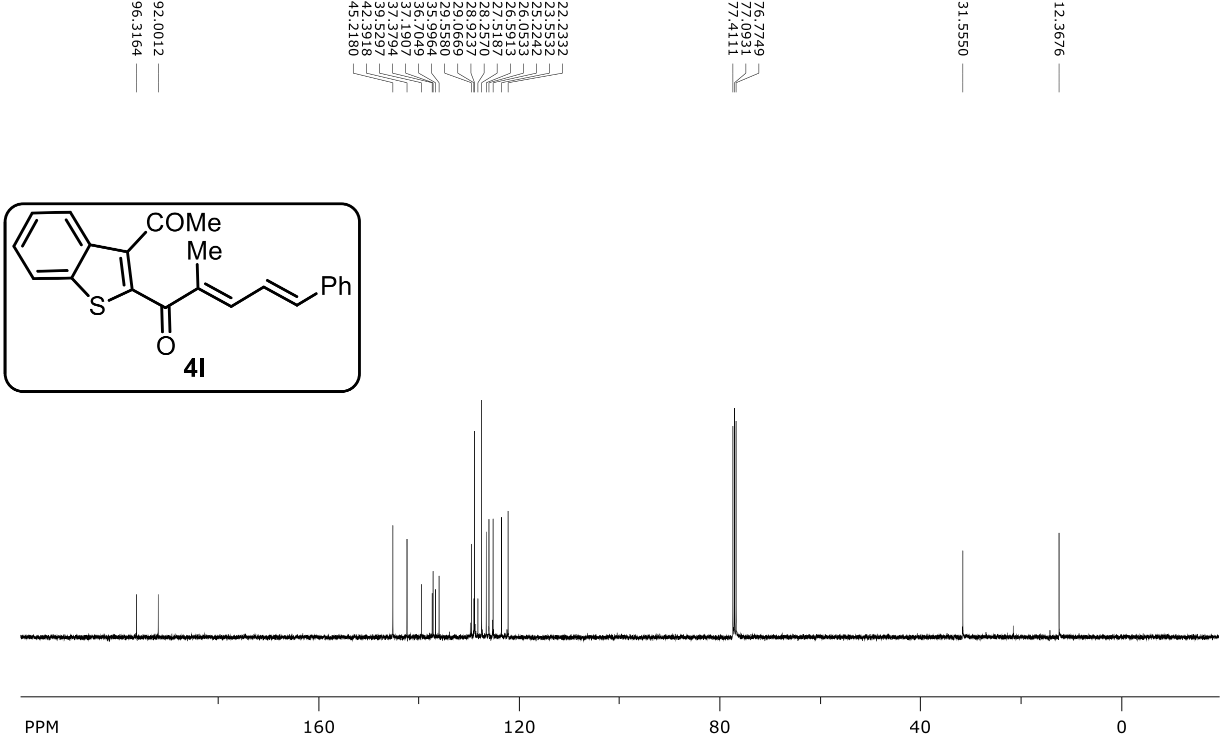

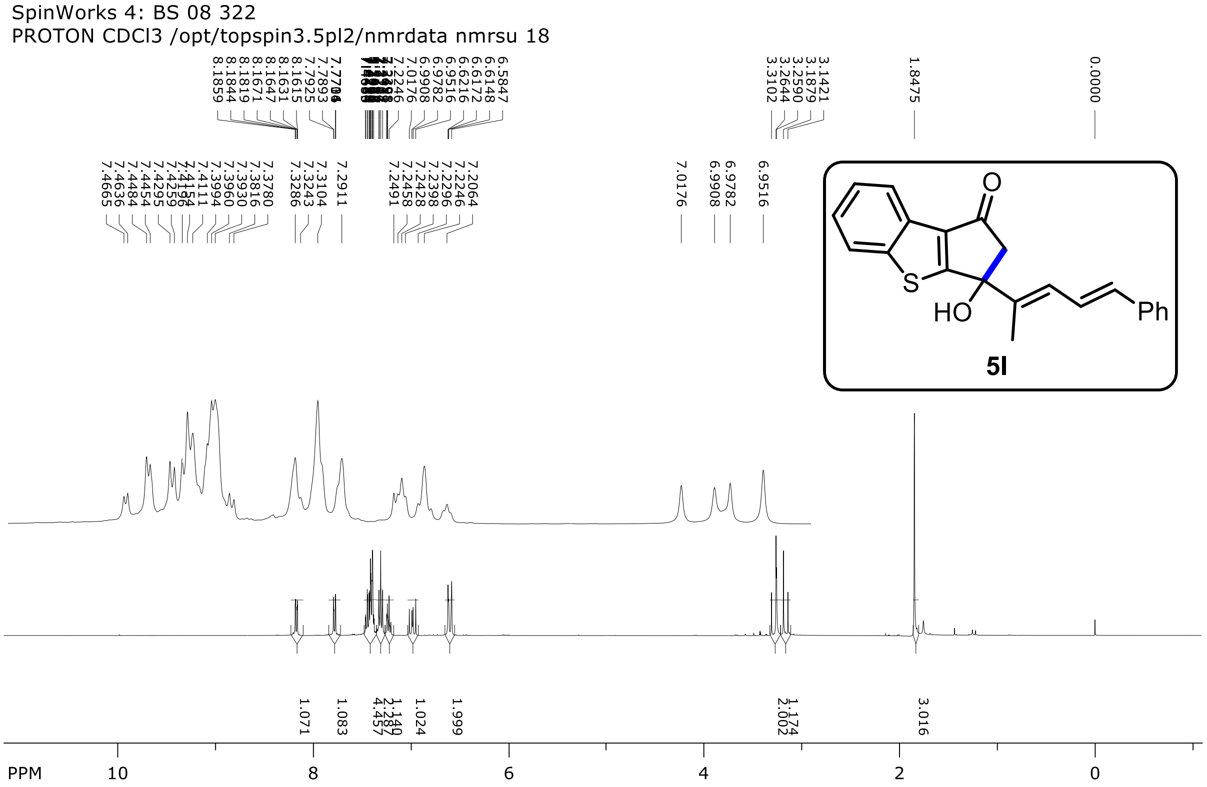
SpinWorks 4: BS 08 322
PROTON CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 18
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8.1647
8.1631
8.1615
7.7925
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7.0176
6.9908
6.9782
6.9516
6.6216
6.6172
6.6148
6.5847
3.3102
3.2644
3.2590
3.1879
3.1421
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7.4636
7.4484
7.4454
7.4295
7.4256
7.4154
7.4111
7.3994
7.3960
7.3930
7.3816
7.3780
7.3286
7.3243
7.3104
7.2911
7.2491
7.2458
7.2428
7.2398
7.2296
7.2246
7.2064
7.0176
6.9908
6.9782
6.9516
O
S
HO
Ph
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PPM
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6
4
2
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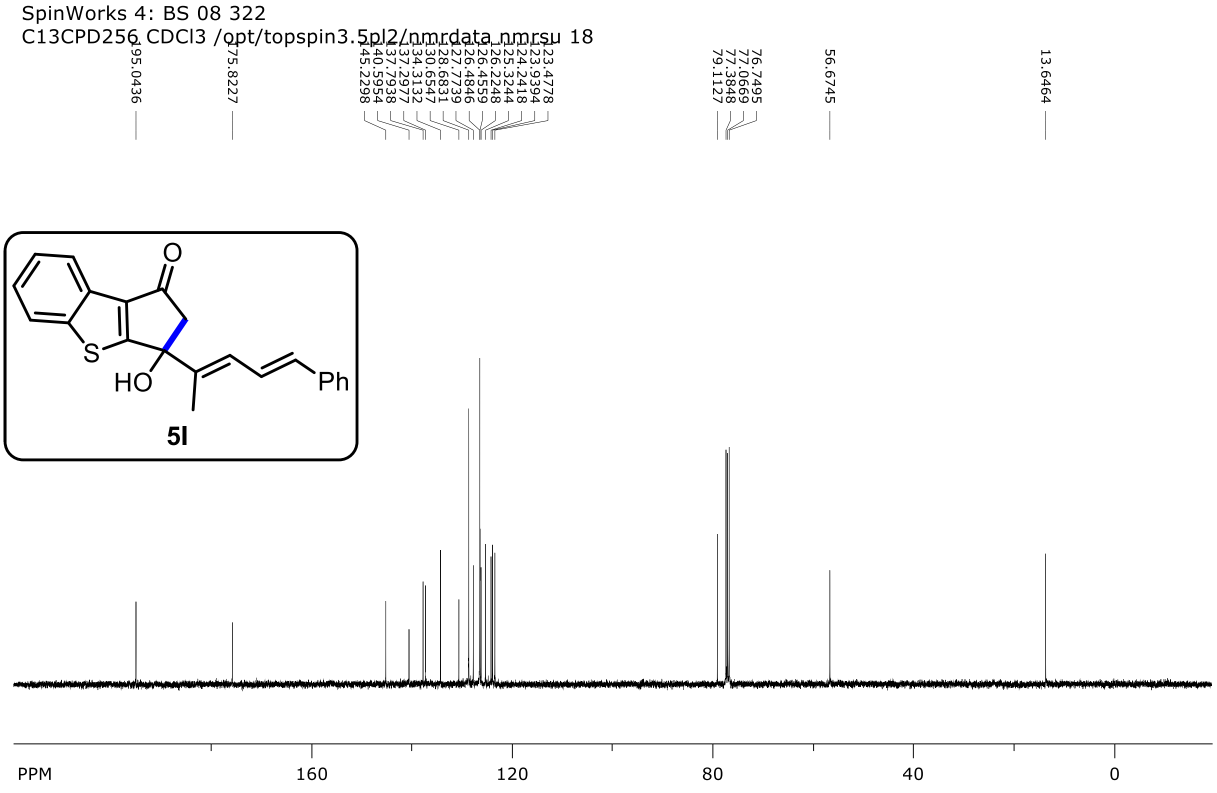
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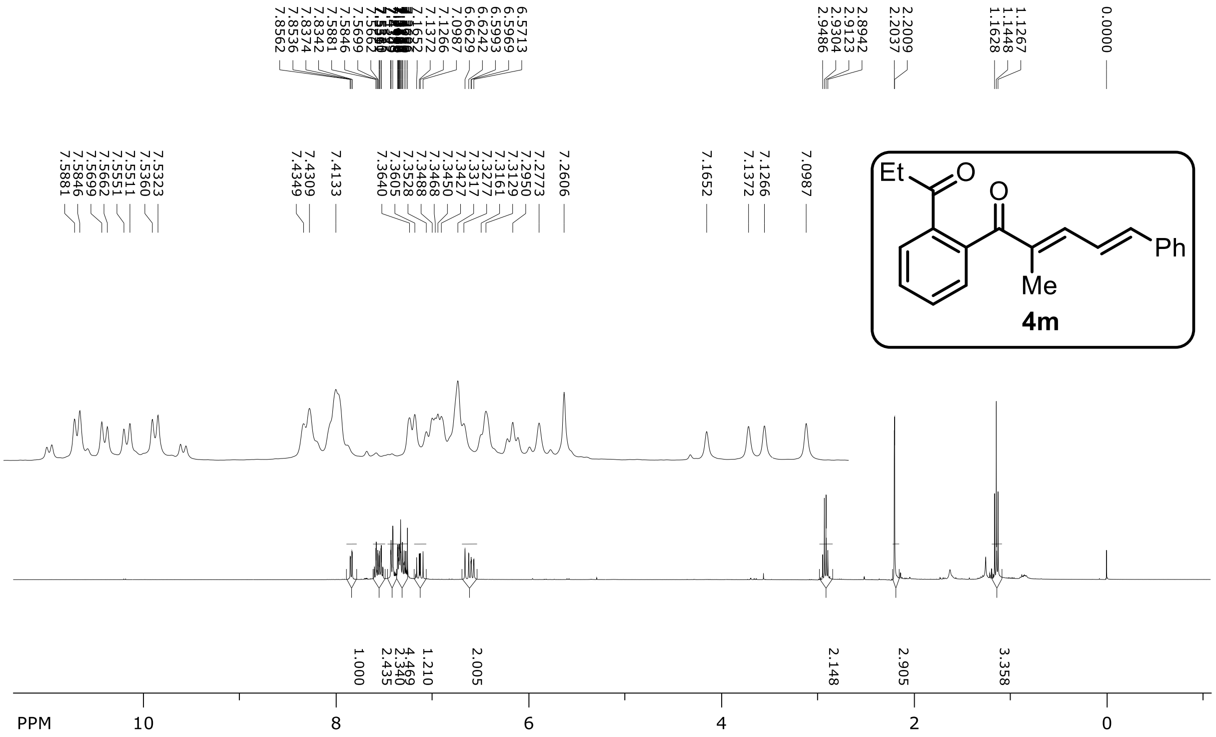
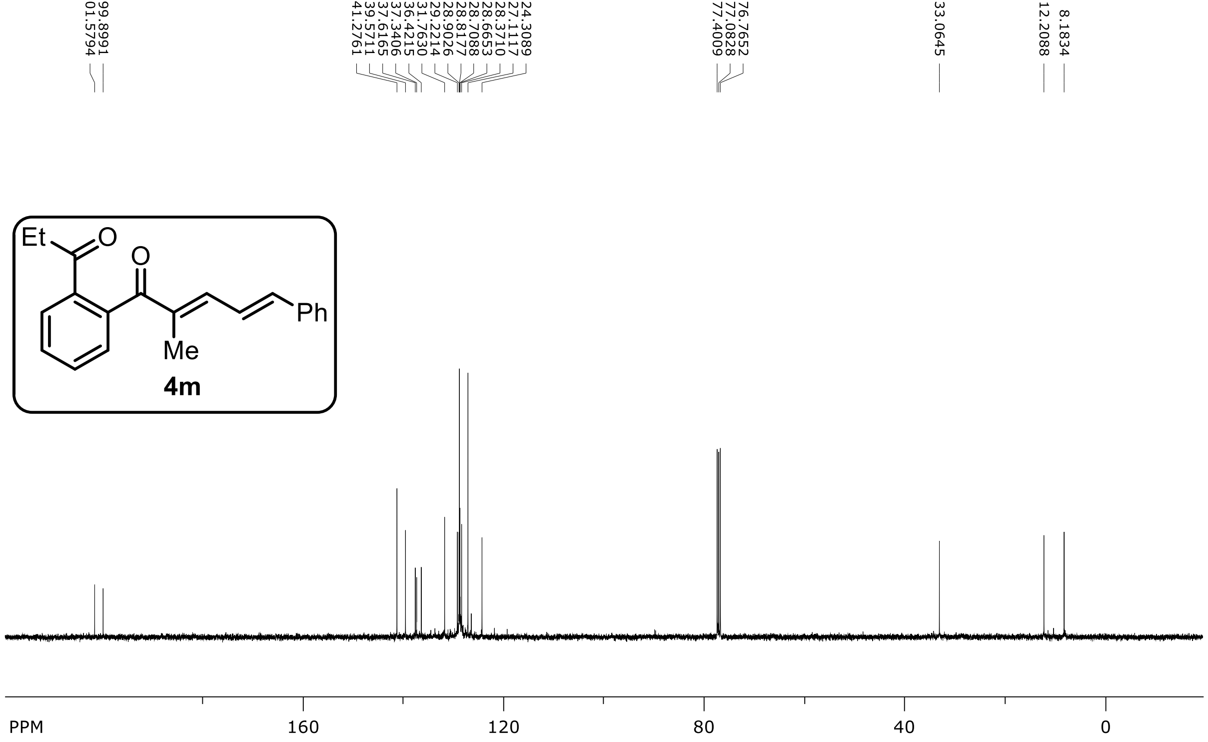
134.3132
130.6547
128.6831
127.7739
126.4846
126.4559
126.2248
125.3244
124.2418
123.9394
123.4778
79.1127
77.3848
77.0669
76.7495
56.6745
13.6464
O
S
HO
Ph
5l
PPM
160
120
80
40
0

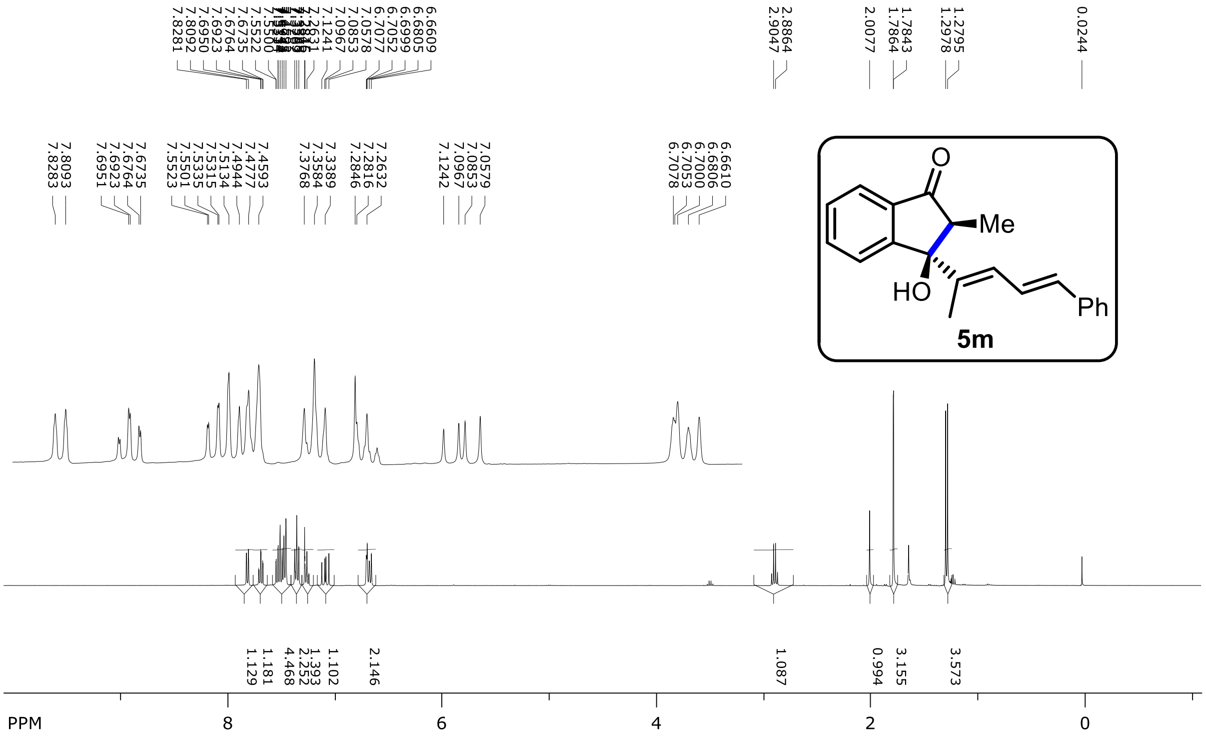
SpinWorks 4: BS-09-05-Re



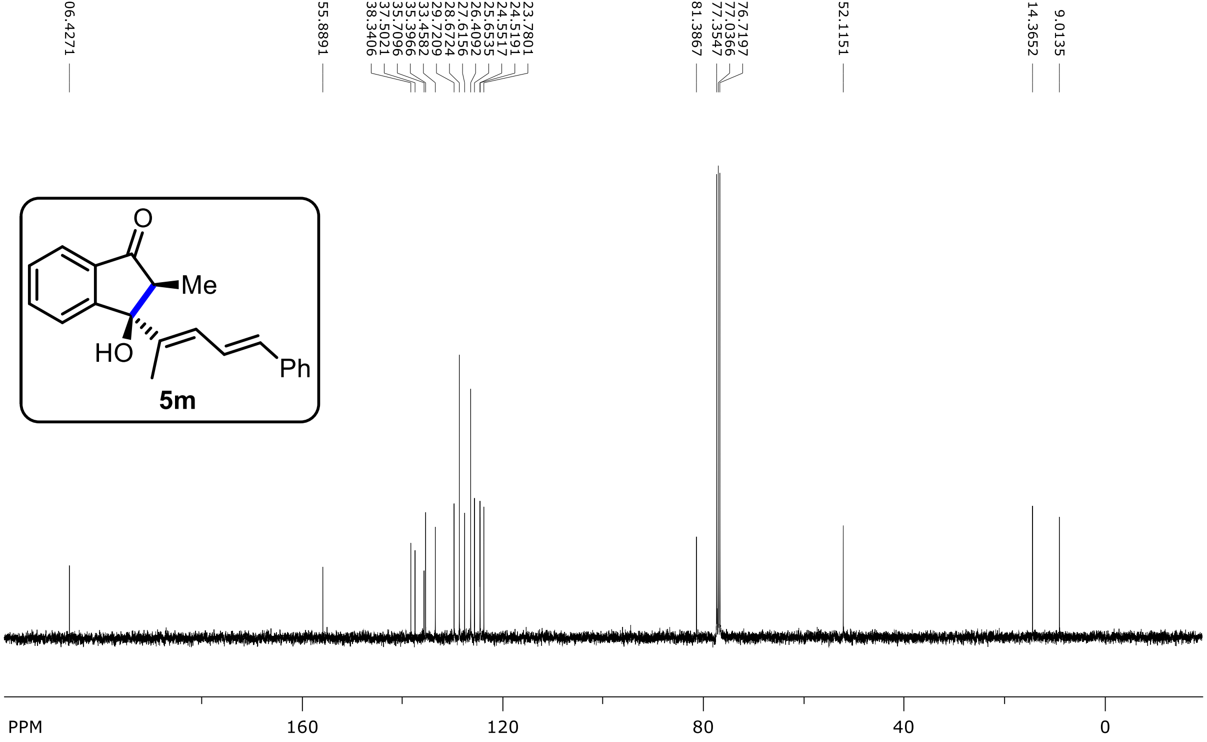
SpinWorks 4: BS 09 05
C13CPD256 CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 13



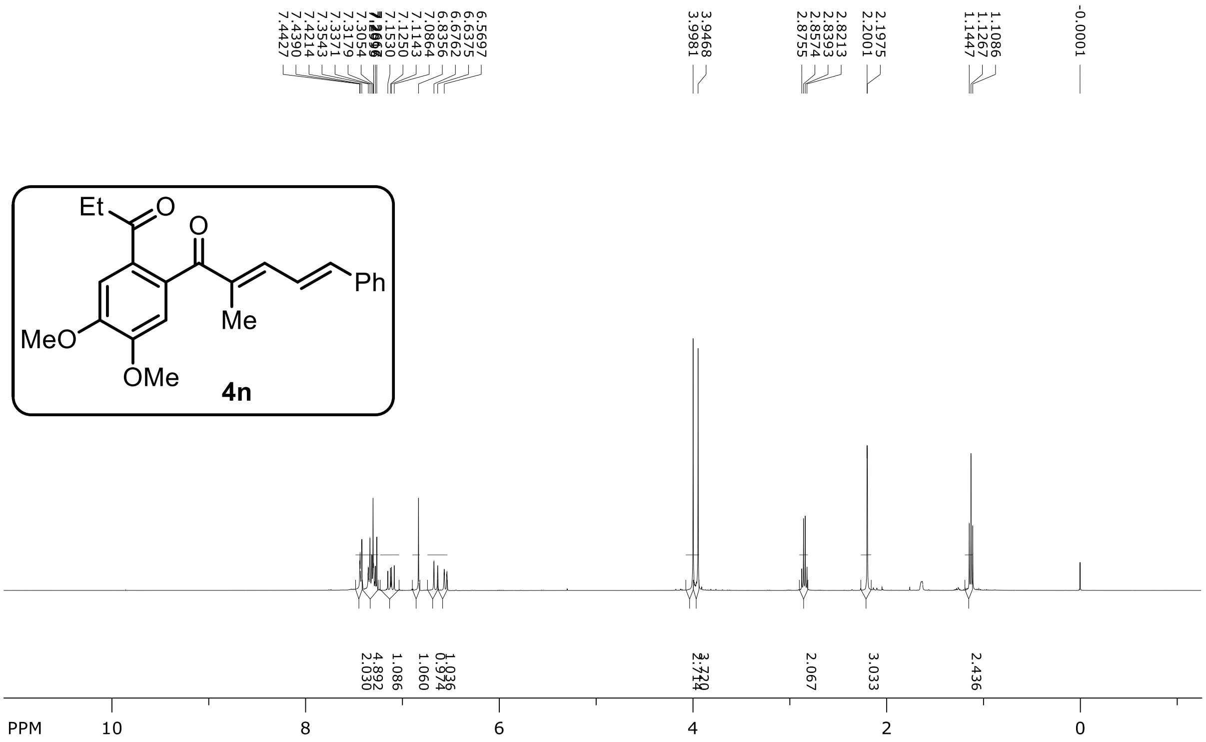
SpinWorks 4: bs-09-06



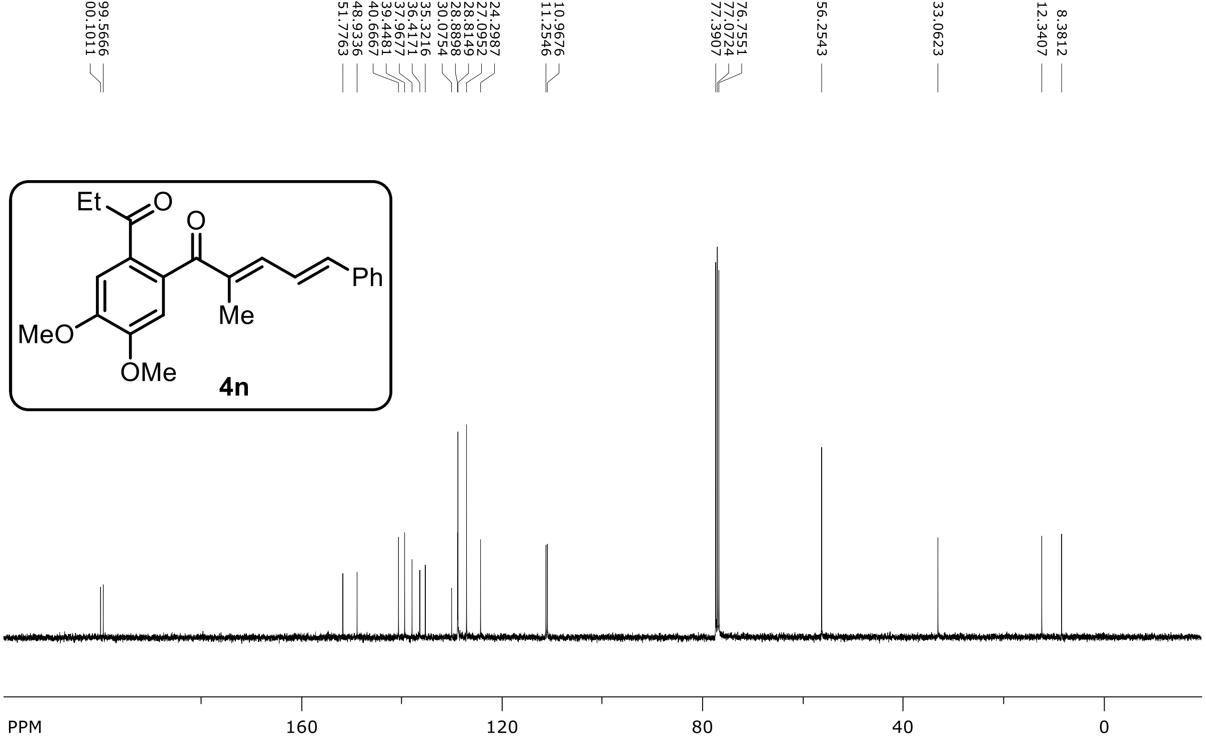
SpinWorks 4: BS 09 06
C13CPD256 CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 57



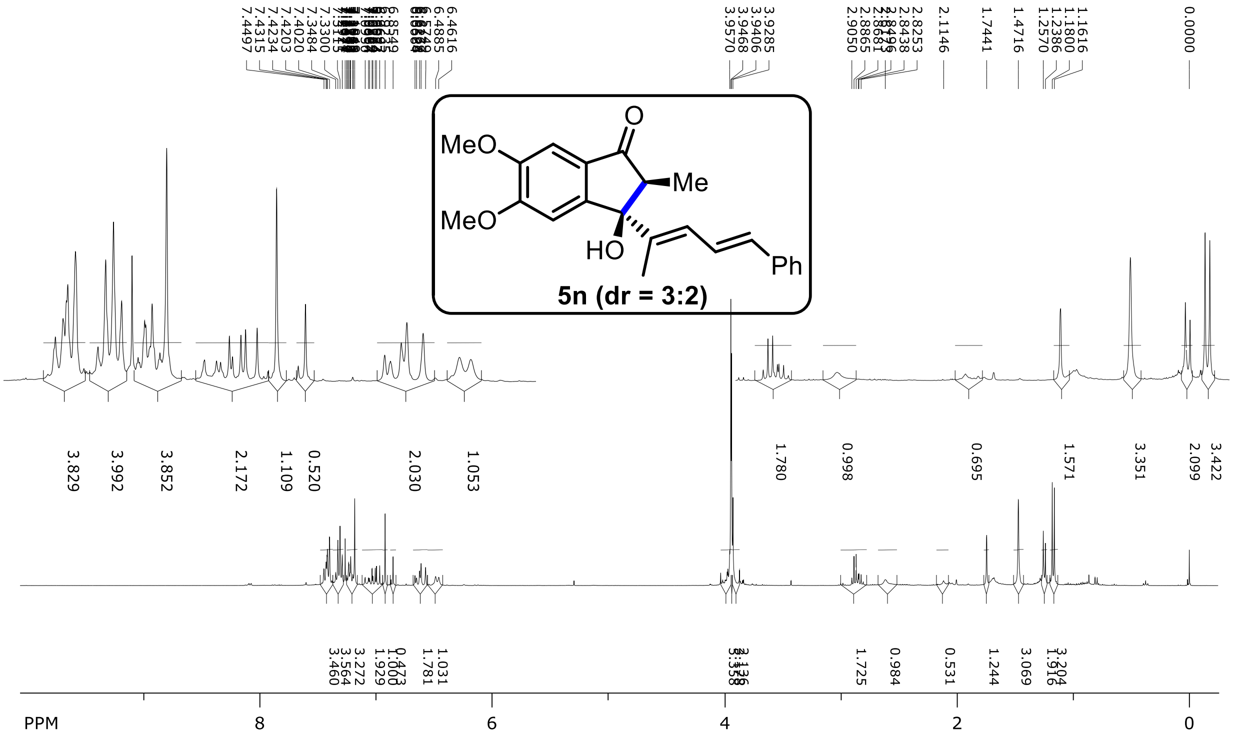
SpinWorks 4: BS-09-25



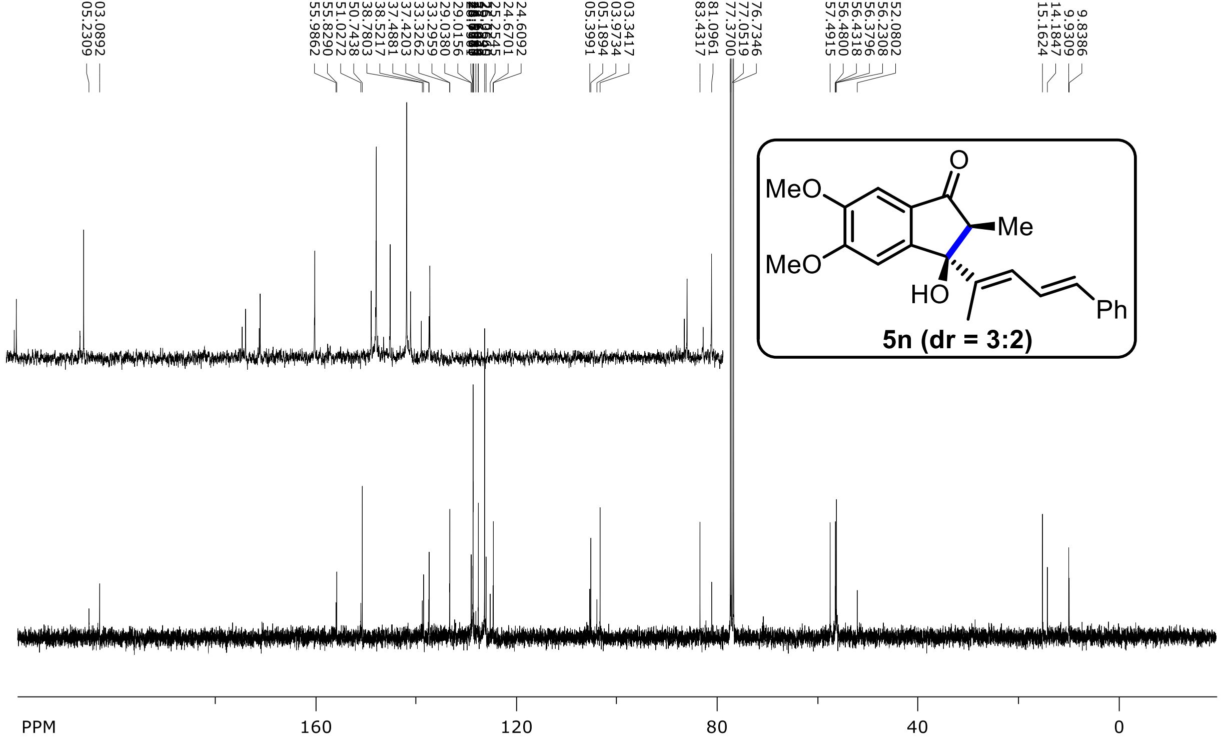
SpinWorks 4: BS 09 25
C13CPD256 CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 51



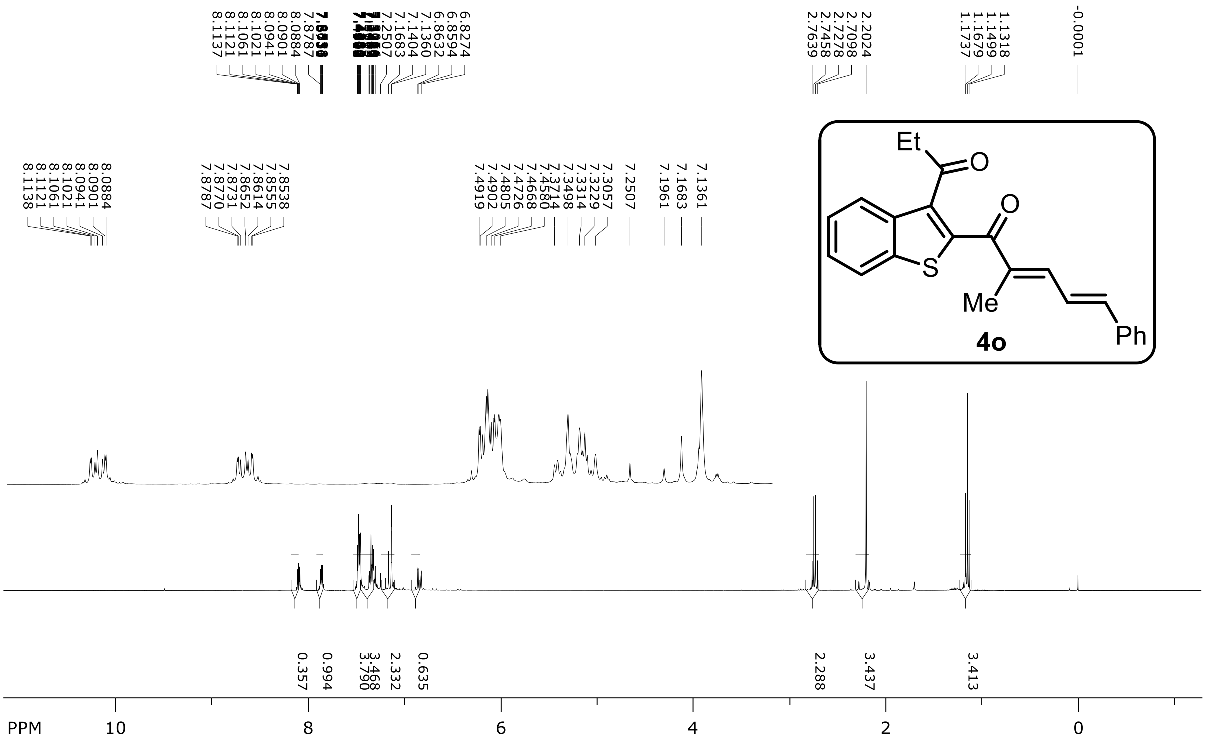
SpinWorks 4: BS-09-26



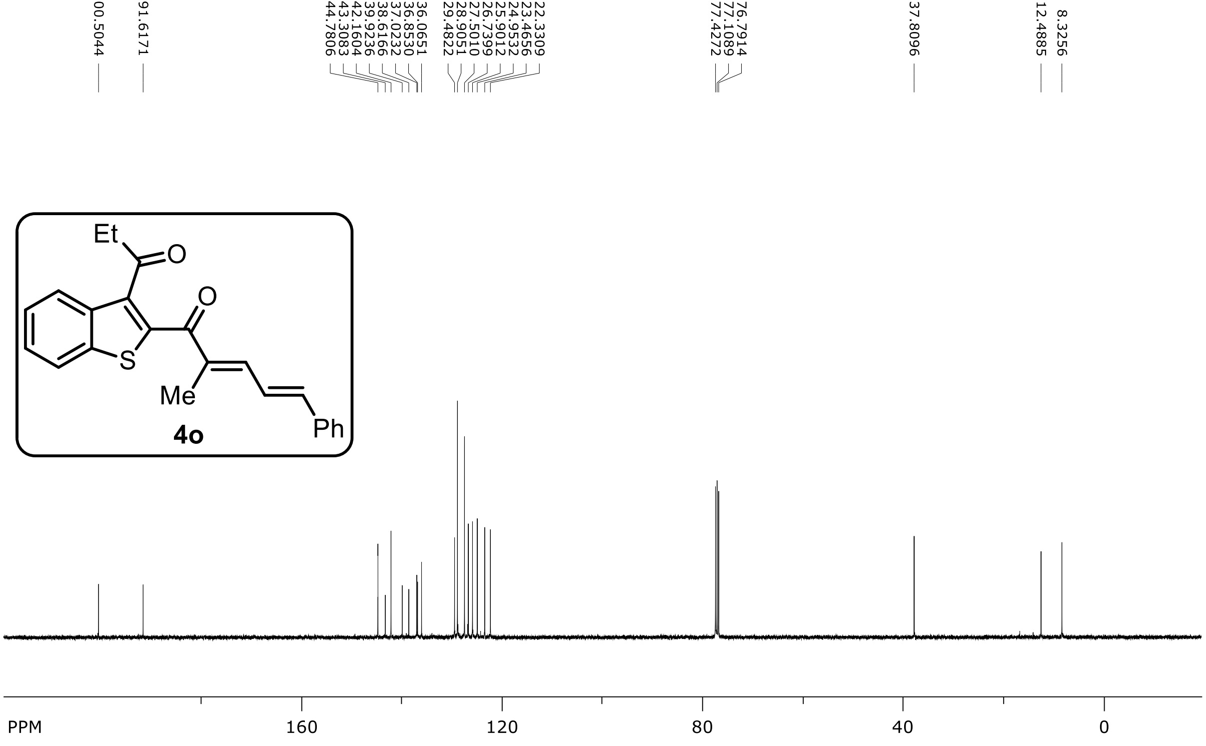
SpinWorks 4: BS 09 26
C13CPD256 CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 12



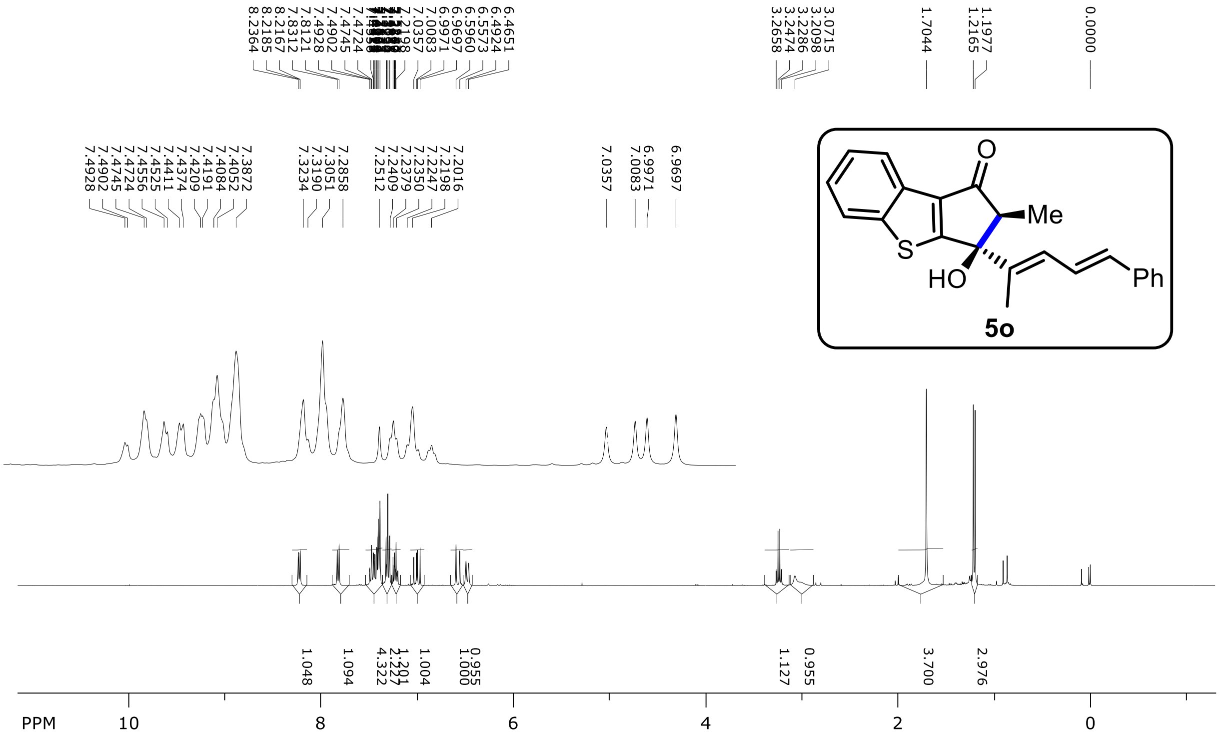
SpinWorks 4: BS-09-24



SpinWorks 4: BS 09 24
C13CPD256 CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 49



SpinWorks 4: BS-09-27



SpinWorks 4: BS 09 27
C13CPD256 CDCl3 /opt/topspin3.5pl2/nmrdata nmrsu 13