Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

A Two Step Access to Fused-/Spiro-Polycyclic Frameworks *via* Double Heck Cascade and Acid-Driven Processes

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Supporting Information

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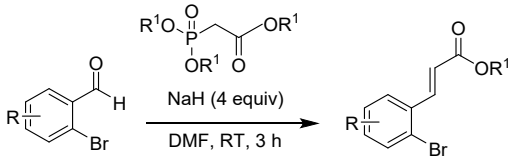
Supporting Information

Experimental Section

General Methods:

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion concerning either internal standard tetramethylsilane (TMS) (δH = 0.00 ppm) or $CDCl_3$ (δH = 7.25 ppm). $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CDCl_3$ [δC = 77.00 ppm (central line of the triplet)]. In the $^{13}C\{^{1}H\}$ NMR, the nature of carbons (C, CH, CH_2, and CH_3) was determined by recording the DEPT-135 spectra and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^{1}H NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, dd = doublet of the doublet, m = multiplet, and br. s = broad singlet. The assignment of signals was confirmed by ^{1}H, $^{13}C\{^{1}H\}$ CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. All small-scale reactions were carried out by using a Schlenk tube. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled before use; for petroleum ether, the boiling range of 60−80 °C was used. $Pd(OAc)_2$, K_3CO_3, DPEPhos, TEBAC, and TfOH were purchased from Sigma-Aldrich and used as received. Diphenylacetylene was purchased from BLD. Toluene was dried over sodium metal, whereas DCE was dried over calcium hydride. Acme's silica gel (60−120 mesh) was used for column chromatography (approximately 20 g per 1 g of crude material).



Scheme 1S: Preparation of ethyl 2-bromocinnamate esters **1**.

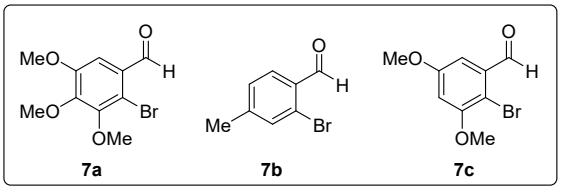


Table-1S: 2-Bromobenzaldehydes **7a-7c**.

The following starting materials, ethyl 2-bromocinnamate esters **1a-1o** (Table-2S) are known in the literature except **1l**, **1n,** and, **1o**, and were prepared according to the previous literature reports.[1–6]

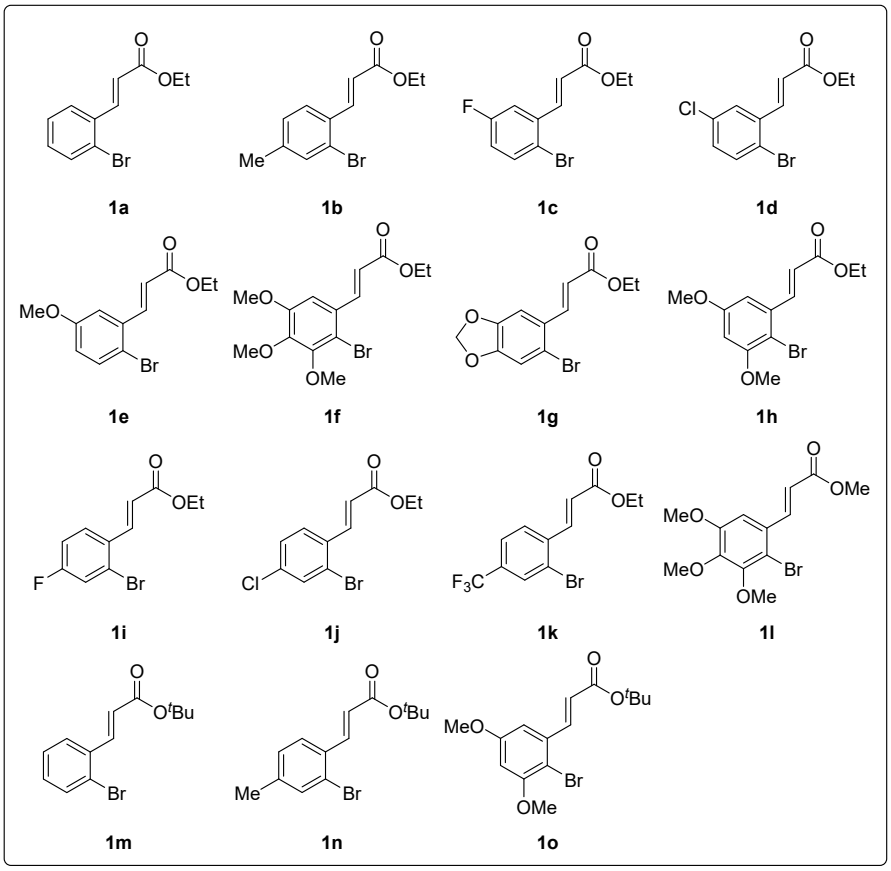


Table-2S: Ethyl 2-bromocinnamate esters **1a-1o**.

The following diarylacetylenes **2a-2n** (Table-3S) are known in the literature and were prepared according to the previous literature reports.[7–10]

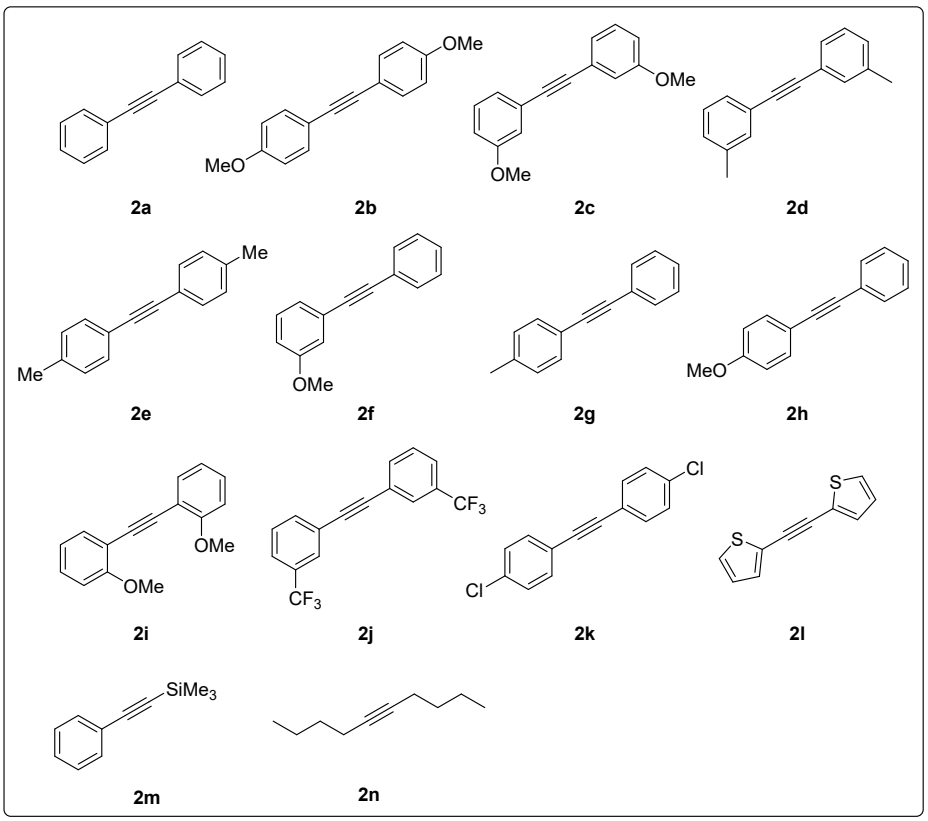


Table-3S: Diaryl acetylenes **2a-2n**.

The following *para*-substituted phenols were purchased and used as received as shown in Table-4S.

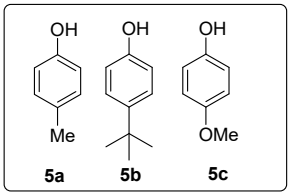


Table-4S: *para*-substituted Phenols **5a-5c**.

Experimental:

General Procedure - 1 (GP-1) for the Preparation of ethyl 2-bromocinnamate esters (1l, 1n and 1o):

To an oven-dried round-bottomed flask equipped with a magnetic stir bar under nitrogen atmosphere, were added NaH (34.7 mg, 1.4 mmol) and anhydrous THF (1 mL) at 0 ℃ and stirred for 2 min. To the resultant solution at 0 ℃, was added the phosphonate reagent (294-362, 1.4 mmol) dropwise until the effervescence is stopped and golden-coloured clear ylide solution is generated, the solution was continued to stir for 10 min at the same temperature. To the ylide reagent at 0 ℃, was added the solution of benzaldehyde **7a**/**7b**/**7c** (71.6-100 mg, 0.36 mmol) in dry THF (0.5 mL) under nitrogen atmosphere and the reaction mixture was warmed to room temperature and stirred for 3 h. Completion of the reaction was monitored by TLC. The reaction mixture was quenched with aqueous ammonium chloride and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine solution, dried (Na_2SO_4), and evaporated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the ethyl 2-bromocinnamate ester **1l/1n/1o** (95-96%), as colorless oil/white solid.

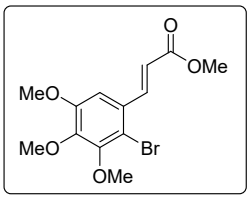
General Procedure - 2 (GP-2) for the Preparation of 2,3-diarylindene enoate ester (3aa-3an):

To an oven-dried Schlenk tube charged with a stirring base, were added ethyl 2-bromocinnamate ester **1a-o** (99–134 mg, 0.39 mmol), diarylacetylene **2a-n** (41–94 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol), and toluene (1 mL) at room temperature under open air atmosphere. The resultant reaction mixture as stirred at 120 ℃ for 9 to 16 h. Completion of the reaction was monitored by TLC (5:95 to 15:85 ethyl acetate and hexane). The reaction mixture was cooled to room temperature, quenched with aqueous ammonium chloride, and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine solution, dried (Na_2SO_4), and evaporated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the 2,3-diarylindene enoate ester **3aa-3an** (52–96%), as orange/yellow/red/maroon solid or yellow oil.

General Procedure - 3 (GP-3) for the Preparation of benzo[*a*]fluorene (4a-4i): To a solution of 2,3-diarylindene enoate ester **3aa-3jc** (35-49 mg, 0.1 mmol) in a Schlenk tube in

dichloroethane solvent (1 mL), was added TfOH (15 mg, 0.1 mmol) under open air atmosphere and allowed the reaction mixture to stir at 100 ℃ for 4 to 13 h. Completion of the reaction was monitored by TLC (5:95 to 15:85 ethyl acetate and hexane). The reaction mixture was quenched with aqueous ammonium chloride and extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine solution, dried (Na_2SO_4), and evaporated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the benzo[*a*]fluorene **4a-i** (48-96%), as maroon/purple solid.

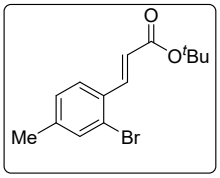
General Procedure - 4 (GP-4) for the Preparation of spiro-chromenone indene (6a-6j): To a solution of 2,3-diarylindene enoate ester **3aa-3ak** (35-44 mg, 0.1 mmol) in a Schlenk tube in dichloroethane solvent (1 mL), was added phenol **5a-c** (32-45 mg, 0.3 mmol) and TfOH (7.5 mg, 0.5 mmol) under open air atmosphere and allowed the reaction mixture to stir at 80 ℃ for 1 to 3 h. Completion of the reaction was monitored by TLC (5:95 to 15:85 ethyl acetate and hexane). The reaction mixture was quenched with aqueous ammonium chloride and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine solution, dried (Na_2SO_4), and evaporated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the spiro-chromenone indene **6a-6j** (75-92%) as red/pink/yellow oil or white solid.



Methyl (*E*)-3-(2-bromo-3,4,5-trimethoxyphenyl)acrylate (1l):

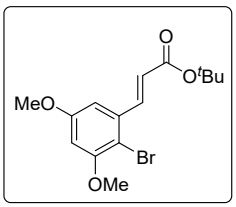
GP-1 was carried out with 2-bromo-3,4,5-trimethoxybenzaldehyde **7a** (100 mg, 0.36 mmol), NaH (34.7 mg, 1.4 mmol), methyl 2-(diethoxyphosphoryl)acetate (294 mg, 1.4 mmol) and DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 97:3), furnished the methyl 2-bromocinnamate ester **1l** (112.9 mg, 95%), as white solid; mp = 80-82 ℃ [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**7a**) = 0.3, R_f(**1l**) = 0.2 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2943, 1714, 1476, 1437, 1279, 1172, 1107, 1003, 826 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.03 (d, J = 15.9 Hz, 1H), 6.92 (s, 1H), 6.29 (d, J = 15.9 Hz, 1H), 3.90 (s, 3H), 3.89 – 3.86 (m, 6H), 3.81 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.8, 152.8, 151.1, 144.8, 143.2, 129.7,

119.7, 112.9, 105.9, 61.1, 60.9, 56.1, 51.8 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{13}H_{16}Br^{79}O_5]^+$ 331.0176; found 331.0169; calcd for $[C_{13}H_{16}Br^{81}O_5]^+$ 333.0155; found 333.0150.



***tert*-Butyl (*E*)-3-(2-bromo-4-methylphenyl)acrylate (1n):**

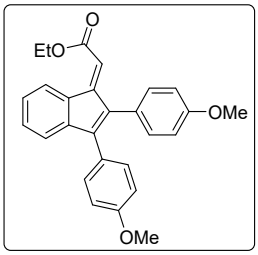
GP-1 was carried out with 2-bromo-4-methylbenzaldehyde **7b** (71.6 mg, 0.36 mmol), NaH (34.7 mg, 1.4 mmol), *tert*-butyl 2-(diethoxyphosphoryl)acetate (362 mg, 1.4 mmol) and DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the *tert*-butyl 2-bromocinnamate ester **1n** (102 mg, 96%), as colorless oil [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**7b**) = 0.6, R_f(**1n**) = 0.5 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2976, 1705, 1631, 1314, 1262, 1144, 976, 812, 762 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.93 (d, J = 15.9 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.41 (s, 1H), 7.08 (d, J = 8.0 Hz, 1H), 6.27 (d, J = 15.9 Hz, 1H), 2.31 (s, 3H), 1.53 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 165.8, 141.7, 141.6, 133.7, 131.6, 128.5, 127.2, 125.1, 121.7, 80.5, 28.1, 20.9 (3C) ppm. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{14}H_{17}Br^{79}NaO_2]^+$ 319.0304; found 319.0307; calcd for $[C_{14}H_{17}Br^{81}NaO_2]^+$ 321.0284; found 321.0288.



***tert*-Butyl (*E*)-3-(2-bromo-3,5-dimethoxyphenyl)acrylate (1o):**

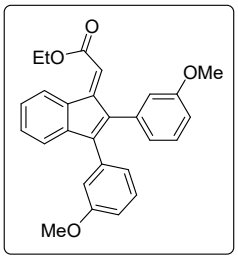
GP-1 was carried out with 2-bromo-3,5-dimethoxybenzaldehyde **7c** (88.2 mg, 0.36 mmol), NaH (34.7 mg, 1.4 mmol), tert-butyl 2-(diethoxyphosphoryl)acetate (362 mg, 1.4 mmol) and DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 97:3), furnished the *tert*-butyl 2-bromocinnamate ester **1o** (118 mg, 96%), as colorless oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**7c**) = 0.2, R_f(**1o**) = 0.4 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2972, 1705, 1580, 1457, 1280, 1151, 1080, 975, 838 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, J = 15.9 Hz,

1H), 6.68 (d, J = 2.7 Hz, 1H), 6.46 (d, J = 2.7 Hz, 1H), 6.26 (d, J = 15.9 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 1.52 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 165.7, 159.6, 157.0, 142.5, 136.1, 123.2, 106.3, 103.2, 101.1, 80.8, 56.4, 55.6, 28.2 ppm. HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{15}H_{19}Br^{79}KO_4]^+$ 381.0098; found 381.0082; calcd for $[C_{15}H_{19}Br^{81}KO_4]^+$ 383.0078; found 383.0064.



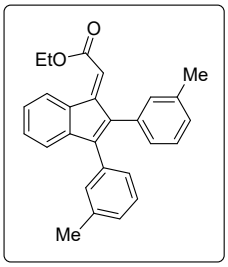
Ethyl (*E*)-2-(2,3-bis(4-methoxyphenyl)-1*H*-inden-1-ylidene)acetate (3ab):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1a** (99 mg, 0.39 mmol), diaryl acetylene **2b** (71 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 97:3), furnished the 2,3-diarylindene enoate ester **3ab** (109 mg, 88%), as orange solid; mp = 136-138 °C [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1a**) = 0.8, R_f(**3ab**) = 0.4, R_f(**2b**) = 0.6 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2356, 1715, 1607, 1501, 1292, 1249, 1175, 1035, 773 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.69 (d, J = 7.0 Hz, 1H), 7.35 – 7.23 (m, 3H), 7.22 – 7.16 (m, 2H), 7.11 – 7.03 (m, 2H), 6.90 – 6.77 (m, 4H), 6.17 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.6, 159.0, 158.7, 152.5, 144.5, 144.1, 138.4, 133.3, 132.1 (2C), 130.6 (2C), 129.7, 127.2, 126.8, 126.3, 126.2, 120.2, 119.4, 113.7 (2C), 113.6 (2C), 60.7, 55.2, 55.1, 14.2 ppm. HRMS (ESI) *m/z*: $[M]^+$ calcd for $[C_{27}H_{24}O_4]^+$ 412.1669; found 412.1665.



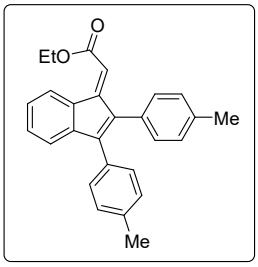
Ethyl (*E*)-2-(2,3-bis(3-methoxyphenyl)-1*H*-inden-1-ylidene)acetate (3ac):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1a** (99 mg, 0.39 mmol), diaryl acetylene **2c** (71 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:2 to 99:3), furnished the 2,3-diarylindene enoate ester **3ac** (105 mg, 85%), as red solid; mp = 90-92 °C [TLC control (petroleum ether/ethyl acetate 100:2), R_f(**1a**) = 0.8, R_f(**3ac**) = 0.4, R_f(**2c**) = 0.6 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2945, 1716, 1577, 1461, 1188, 1149, 1047, 769, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.68 (d, J = 6.8 Hz, 1H), 7.36 – 7.15 (m, 5H), 6.94 – 6.60 (m, 6H), 6.21 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.69 (s, 3H), 3.63 (s, 3H) 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.4, 159.2, 159.2, 151.9, 144.7, 144.1, 139.3, 135.3, 134.9, 133.1, 129.8, 129.2, 129.1, 127.3, 127.1, 123.4, 121.6, 120.5, 120.3, 116.4, 114.3, 113.9, 113.1, 60.7, 55.1, 55.1, 14.2 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{27}H_{25}O_4]^+$ 413.1747; found 413.1746.



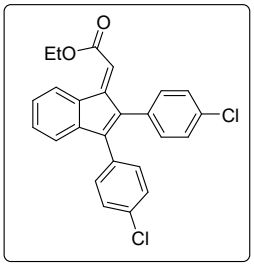
Ethyl (*E*)-2-(2,3-di-*m*-tolyl-1*H*-inden-1-ylidene)acetate (3ad):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1a** (99 mg, 0.39 mmol), diaryl acetylene **2d** (62 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the 2,3-diarylindene enoate ester **3ad** (98 mg, 86%), as orange solid; mp = 98-100 °C [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1a**) = 0.5, R_f(**3ad**) = 0.6, R_f(**2d**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3436, 1716, 1456, 1377, 1201, 1178, 1034, 796, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.61 – 8.59 (m, 1H), 7.23 – 6.80 (m, 11H), 6.08 (d, J = 2.8 Hz, 1H), 4.26 – 4.07 (q, J = 7.1 Hz, 2H), 2.19 (s, 3H), 2.17 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.6, 152.4, 144.8, 144.5, 139.5, 137.7, 137.6, 133.9, 133.8, 133.3, 131.6, 129.8, 129.8, 128.6, 128.2, 128.2, 128.1, 128.0, 127.4, 126.9, 126.5, 120.5, 120.1, 60.8, 21.5 (2C), 14.3. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{27}H_{25}O_2]^+$ 381.1849; found 381.1857.



Ethyl (*E*)-2-(2,3-di-*p*-tolyl-1*H*-inden-1-ylidene)acetate (3ae):

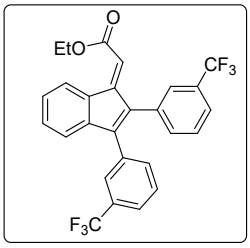
GP-2 was carried out with ethyl 2-bromocinnamate ester **1a** (99 mg, 0.39 mmol), diaryl acetylene **2e** (62 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the 2,3-diarylindene enoate ester **3ae** (99 mg, 87%), as red solid; mp = 160-162 °C [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1a**) = 0.5, R_f(**3ae**) = 0.6, R_f(**2e**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3433, 1712, 1454, 1377, 1188, 1164, 1036, 813, 770 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.76 – 8.58 (m, 1H), 7.30 – 7.25 (m, 3H), 7.15 – 7.08 (m, 6H), 7.05 – 7.01 (m, 2H), 6.16 (s, 1H), 4.27 (q, J = 7.1 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.6, 152.4, 144.5, 139.0, 137.6, 136.9, 136.5, 133.3, 130.9, 130.9, 130.8 (2C), 129.7, 129.2 (2C), 128.9 (2C), 128.8 (2C), 127.3, 126.9, 120.4, 119.8, 60.7, 21.3, 21.3, 14.2 ppm. HRMS (ESI) *m/z*: $[M]^+$ calcd for $[C_{27}H_{24}O_2]^+$ 380.1771; found 380.1754.



Ethyl (*E*)-2-(2,3-bis(4-chlorophenyl)-1*H*-inden-1-ylidene)acetate (3ak):

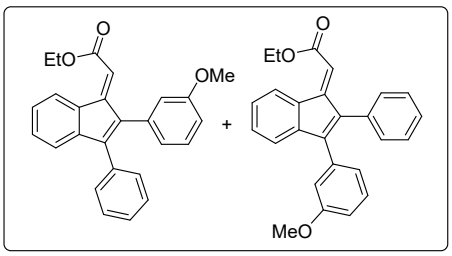
GP-2 was carried out with ethyl 2-bromocinnamate ester **1a** (99 mg, 0.39 mmol), diaryl acetylene **2k** (74 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:2), furnished the 2,3-diarylindene enoate ester **3ak** (113 mg, 90%), as red solid; mp = 148-150 °C [TLC control (petroleum ether/ethyl acetate 100:2), R_f(**1a**) = 0.5,

R_f(**3ak**) = 0.6, R_f(**2k**) = 0.7 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2977, 1714, 1454, 1377, 1194, 1165, 1093, 771, 515 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.72 – 8.70 (m, 1H), 7.32 – 7.25 (m, 6H), 7.23 – 7.19 (m, 1H), 7.17 – 7.12 (m, 2H), 7.08 – 7.03 (m, 2H), 6.13 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.1, 151.5, 144.1, 143.6, 138.4, 133.9, 133.7, 132.9, 132.1 (2C), 132.0, 131.9, 130.5 (2C), 129.9, 128.7 (2C), 128.6 (2C), 127.5, 127.4, 120.5, 120.3, 60.9, 14.2 ppm. HRMS (ESI) *m/z*: $[M+2K]^{+2}$ calcd for $[C_{25}H_{18}Cl_2K_2O_2]^{+2}$ 248.9974; found 248.9957.



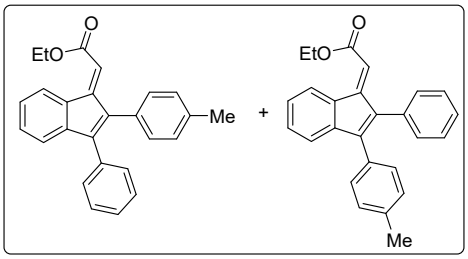
Ethyl (*E*)-2-(2,3-bis(3-(trifluoromethyl)phenyl)-1*H*-inden-1-ylidene)acetate (3aj):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1a** (99 mg, 0.39 mmol), diaryl acetylene **2j** (94 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:2), furnished the 2,3-diarylindene enoate ester **3aj** (88 mg, 60%), as orange solid; mp = 140-142 °C [TLC control (petroleum ether/ethyl acetate 100:2), R_f(**1a**) = 0.4, R_f(**3aj**) = 0.5, R_f(**2j**) = 0.8 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3427, 2343, 1714, 1620, 1365, 1307, 1167, 1120, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.66 – 8.64 (m, 1H), 7.50 – 7.42 (m, 2H), 7.40 – 7.28 (m, 5H), 7.27 – 7.21 (m, 3H), 7.13 (m, 1H), 6.16 – 5.91 (m, 1H), 4.21 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.0, 151.0, 144.4, 143.2, 138.8, 134.2, 134.2, 134.0, 132.9, 132.4, 130.9 (q, J = 32.4 Hz), 130.8 (q, J = 32.6 Hz), 130.2, 128.9, 128.9, 127.8, 127.7, 127.5 (q, J = 3.7 Hz), 125.9 (q, J = 3.9 Hz), 124.8 (q, J = 3.6 Hz), 124.5 (q, J = 3.8 Hz), 123.8 (q, J = 273.5 Hz), 123.7 (q, J = 273.6 Hz), 121.0, 120.3, 101.7, 61.0, 14.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.84 (s), -62.98 (s) ppm. HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{27}H_{22}F_6NO_2]^+$ 506.1549; found 506.1561.



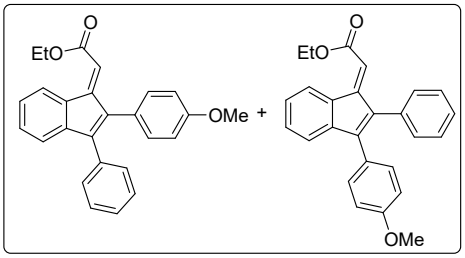
Ethyl (*E*)-2-(2-(3-methoxyphenyl)-3-phenyl-1*H*-inden-1-ylidene)acetate & Ethyl (*E*)-2-(3-(3-methoxyphenyl)-2-phenyl-1*H*-inden-1-ylidene)acetate (1:1) (3af+3af'):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1a** (99 mg, 0.39 mmol), diaryl acetylene **2f** (62 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 97:3), furnished the 2,3-diarylindene enoate ester **3af+3af'** as orange solid (88 mg, 77%), as orange solid; mp = 80-82 °C [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1a**) = 0.8, R_f(**3af+3af'**) = 0.6, R_f(**2f**) = 0.7 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2355, 1716, 1459, 1377, 1286, 1190, 1034, 770, 701 cm^{-1}. ^1H NMR [400 MHz, $CDCl_3$; inseparable regioisomeric mixture of **3af** and **3af'** in (1:1)] δ = 8.81 – 8.57 (m, 1H), 7.44 – 7.05 (m, 9H), 6.95 – 6.59 (m, 3H), 6.24 and 6.19 (2×s, 1H), 4.29 and 4.29 (2×q, J = 7.1 Hz, 2H), 3.69 and 3.62 (2×s, 3H), 1.33 and 1.32 (2×t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR [100 MHz, $CDCl_3$; inseparable regioisomeric mixture of **3af** and **3af'** in (1:1)] δ = 166.5, 166.4, 159.2, 159.1, 152.1, 151.9, 144.8, 144.7, 144.2, 144.1, 139.5, 139.2, 135.2, 134.98, 133.8, 133.7, 133.1 (2C), 130.9 (2C), 129.8, 129.8, 129.2 (2C), 129.2, 129.1, 128.2 (2C), 128.2 (2C), 127.8, 127.4, 127.4, 127.3, 127.0 (2C), 123.5, 121.6, 120.4, 120.5, 120.2, 120.2, 116.4, 114.3, 113.9, 113.1, 60.7 (2C), 55.1, 55.0, 14.2 (2C) ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{23}O_3]^+$ 383.1642; found 383.1650.



Ethyl (*E*)-2-(3-phenyl-2-(p-tolyl)-1*H*-inden-1-ylidene)acetate & Ethyl (*E*)-2-(2-phenyl-3-(*p*-tolyl)-1*H*-inden-1-ylidene)acetate (1:1) (3ag+3ag'):

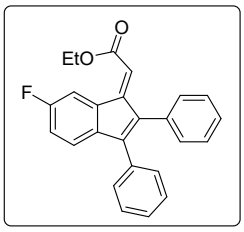
GP-2 was carried out with ethyl 2-bromocinnamate ester **1a** (99 mg, 0.39 mmol), diaryl acetylene **2g** (58 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 97:3), furnished the 2,3-diarylindene enoate ester **3ag+3ag'** (83 mg, 76%), as orange solid; mp = 130-132 °C [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1a**) = 0.8, R_f(**3ag+3ag'**) = 0.6, R_f(**2g**) = 0.7 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2860, 1716, 1619, 1453, 1379, 1176, 1094, 1031, 701 cm^{-1}. ^1H NMR [400 MHz, $CDCl_3$; inseparable regioisomeric mixture of **3ag** and **3ag'** in (1:1)] δ = 8.76 – 8.60 (m, 1H), 7.32 – 7.23 (m, 7H), 7.18 – 7.07 (m, 4H), 7.05 – 7.00 (m, 1H), 6.20 and 6.16 (2×s, 1H), 4.29 and 4.29 (2×q, J = 7.1 Hz, 2H), 2.34 and 2.33 (2×s, 3H), 1.32 and 1.32 (2×t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR [100 MHz, $CDCl_3$; inseparable regioisomeric mixture of **3ag** and **3ag'** in (1:1)] δ = 166.5 (2C), 152.2, 152.2, 144.9, 144.5, 144.4, 144.4, 139.4, 139.0, 137.7, 137.0, 134.1, 133.9, 133.2, 133.2, 130.9 (2C), 130.8 (2C), 130.8, 130.7, 129.8, 129.8, 129.3 (2C), 129.1 (2C), 128.9, (2C) 128.9 (2C), 128.2 (2C), 128.1 (2C), 127.7, 127.3 (2C), 127.3, 126.9, 126.9, 120.5, 120.3, 120.1, 119.8, 60.7 (2C), 21.3, 21.3, 14.2 (2C) ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{23}O_2]^+$ 367.1693; found 367.1689.



Ethyl (*E*)-2-(2-(4-methoxyphenyl)-3-phenyl-1*H*-inden-1-ylidene)acetate & Ethyl(*E*)-2-(3-(4-methoxyphenyl)-2-phenyl-1*H*-inden-1-ylidene)acetate (1:1) (3ah+3ah′):

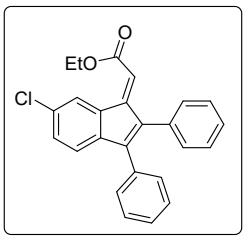
GP-2 was carried out with ethyl 2-bromocinnamate ester **1a** (99 mg, 0.39 mmol), diaryl acetylene **2h** (62 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 97:3), furnished the 2,3-diarylindene enoate ester **3ah+3ah'** (90 mg, 79%), as orange solid; mp = 110-112 °C [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1a**) = 0.8, R_f(**3ah+3ah'**) = 0.6, R_f(**2h**) = 0.7 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2975, 1711, 1606, 1451, 1377, 1243, 1164, 1027, 697 cm^{-1}. ^1H NMR [400 MHz, $CDCl_3$; inseparable

regioisomeric mixture of **3ah** and **3ah'** in (1:1)] δ = 8.74 – 8.71 (m, 1H), 7.33 – 7.22 (m, 7H), 7.19 – 7.15 (m, 2H), 7.08 and 7.05 (2×s, 1H), 6.84 – 6.79 (m, 2H), 6.21 and 6.17 (2×s, 1H), 4.28 and 4.28 (2×q, J = 7.1 Hz, 2H), 3.77 and 3.75 (2×s, 3H), 1.32 and 1.31 (2×t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$; inseparable regioisomeric mixture of **3ah** and **3ah'** in (1:1)) δ = 166.4, 166.4, 159.1, 158.8, 152.3, 152.2, 144.5, 144.4, 144.3, 144.3, 139.1, 138.6, 134.2, 133.9, 133.3, 133.1, 132.0 (2C), 130.9 (2C), 130.5 (2C), 129.8, 129.7, 129.2 (2C), 128.1 (2C), 128.1 (2C), 127.7, 127.3 (2C), 127.2, 126.9, 126.8, 125.9, 125.9, 120.4, 120.2, 120.0, 119.5, 113.6 (4C), 60.7, 60.63, 55.0 (2C), 14.2 (2C) ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{23}O_3]^+$ 383.1642; found 383.1631.



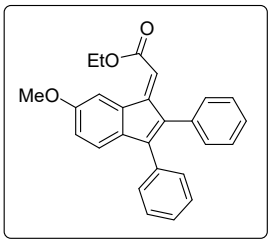
Ethyl (*E*)-2-(6-fluoro-2,3-diphenyl-1*H*-inden-1-ylidene)acetate (3ca):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1c** (106 mg, 0.39 mmol), diaryl acetylene **2a** (53 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the 2,3-diarylindene enoate ester **3ca** (63 mg, 57%), as red solid; mp = 122-124 °C [TLC control (petroleum ether/ethyl acetate 100:1), R_f(**1c**) = 0.4, R_f(**3ca**) = 0.5, R_f(**2a**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3108, 1706, 1462, 1442, 1369, 1267, 1198, 1164, 701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57 (dd, J = 10.2 and 2.4 Hz, 1H), 7.33 – 7.24 (m, 6H), 7.23 – 7.17 (m, 3H), 7.15 – 7.11 (m, 2H), 6.98 (td, J = 8.5, and 2.5 Hz, 1H), 6.22 (s, 1H), 4.29 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.1, 162.6 (d, J = 243.7 Hz), 151.4 (d, J = 2.0 Hz), 144.4, 140.1 (d, J = 2.7 Hz), 139.1 (d, J = 4.0 Hz), 134.9 (d, J = 9.7 Hz), 133.6, 133.5, 130.9 (2C), 129.1 (2C), 128.2 (2C), 128.2 (2C), 127.9, 127.4, 121.0, 120.9 (d, J = 8.5 Hz), 115.9 (d, J = 12.6 Hz), 115.6 (d, J = 8.7 Hz), 60.9, 14.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.99 (s) ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{20}FO_2]^+$ 371.1442; found 371.1442.



Ethyl (*E*)-2-(6-chloro-2,3-diphenyl-1*H*-inden-1-ylidene)acetate (3da):

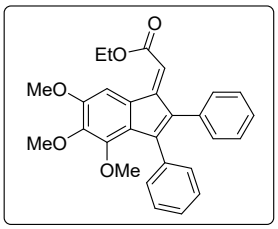
GP-2 was carried out with ethyl 2-bromocinnamate ester **1d** (112 mg, 0.39 mmol), diaryl acetylene **2a** (53 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the 2,3-diarylindene enoate ester **3da** (71 mg, 61%), as orange solid; mp = 110-112 °C [TLC control (petroleum ether/ethyl acetate 100:1), R_f(**1d**) = 0.5, R_f(**3da**) = 0.6, R_f(**2a**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3429, 1715, 1451, 1423, 1193, 1166, 1094, 1032, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.76 (d, J = 1.9 Hz, 1H), 7.33 – 7.25 (m, 7H), 7.23 – 7.17 (m, 3H), 7.16 – 7.12 (m, 2H), 6.22 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.1, 151.1, 144.2, 142.6, 139.6, 134.7, 133.5, 133.3, 132.9, 130.9 (2C), 129.4, 129.2 (2C), 128.3 (2C), 128.2 (2C), 128.0, 127.9, 127.6, 121.3, 121.1, 61.0, 14.2 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{20}ClO_2]^+$ 387.1146; found 387.1136.



Ethyl (*E*)-2-(6-methoxy-2,3-diphenyl-1*H*-inden-1-ylidene)acetate (3ea):

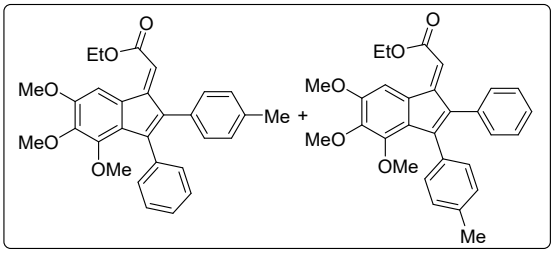
GP-2 was carried out with ethyl 2-bromocinnamate ester **1e** (111 mg, 0.39 mmol), diaryl acetylene **2a** (53 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the 2,3-diarylindene enoate ester **3ea** (100 mg, 88%), as dark red solid; mp = 96-98 °C [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1e**) = 0.6, R_f(**3ea**) = 0.4, R_f(**2a**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3441, 2928, 1713, 1607, 1464, 1368, 1179, 1033, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = ^1H NMR (400

MHz, $CDCl_3$) δ = 8.51 (d, J = 2.4 Hz, 1H), 7.31 – 7.22 (m, 8H), 7.19 – 7.10 (m, 3H), 6.82 (dd, J = 8.3 and 2.5 Hz, 1H), 6.17 (s, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.5, 159.7, 152.5, 145.1, 137.8, 137.1, 135.0, 134.2, 134.0, 131.1 (2C), 129.3 (2C), 128.2 (2C), 128.2 (2C), 127.9, 127.3, 120.9, 119.9, 114.9, 114.3, 60.8, 55.7, 14.3 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{23}O_3]^+$ 383.1642; found 383.1643.



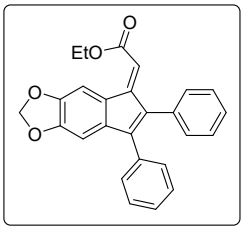
Ethyl (*E*)-2-(6-methoxy-2,3-diphenyl-1*H*-inden-1-ylidene)acetate (3fa):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1f** (134 mg, 0.39 mmol), diaryl acetylene **2a** (53 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the 2,3-diarylindene enoate ester **3fa** (119 mg, 90%), as red solid; mp = 172-174 °C [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1f**) = 0.3, R_f(**3fa**) = 0.5, R_f(**2a**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2932, 1713, 1587, 1464, 1414, 1172, 1126, 889, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.53 (s, 1H), 7.25 – 7.18 (m, 8H), 7.07 (dd, J = 7.7 and 1.7 Hz, 2H), 6.11 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.98 (s, 3H), 3.89 (s, 3H), 3.30 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.6, 152.8, 152.6, 148.2, 145.2, 144.5, 138.9, 135.4, 133.9, 131.2 (2C), 129.7, 129.5 (2C), 129.3, 127.9 (2C), 127.2, 127.2, 127.1 (2C), 119.6, 109.6, 61.2, 61.1, 60.7, 56.5, 14.3 ppm. HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{28}H_{26}KO_5]^+$ 481.1412; found 481.1410.



Ethyl (*E*)-2-(4,5,6-trimethoxy-3-phenyl-2-(p-tolyl)-1*H*-inden-1-ylidene)acetate & Ethyl (*E*)-2-(4,5,6-trimethoxy-2-phenyl-3-(*p*-tolyl)-1*H*-inden-1-ylidene)acetate (1:1) (3fg+3fg'):

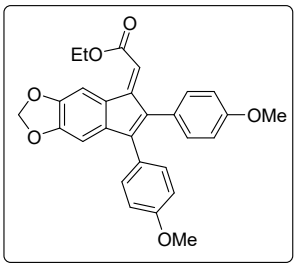
GP-2 was carried out with ethyl 2-bromocinnamate ester **1f** (134 mg, 0.39 mmol), diaryl acetylene **2g** (58 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the 2,3-diarylindene enoate ester **3fg+3fg'** (128 mg, 94%), as dark red solid; mp = 157-159 °C [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1f**) = 0.3, R_f(**3fg+3fg'**) = 0.5, R_f(**2g**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2939, 1713, 1465, 1414, 1383, 1290, 1195, 1174, 1126, 887 cm^{-1}. ^1H NMR [400 MHz, $CDCl_3$; inseparable regioisomeric mixture of **3fg** and **3fg'** in (1:1)] δ = 8.44 (d, J = 2.6 Hz, 1H), 7.17 – 7.12 (m, 4H), 7.04 – 6.86 (m, 5H), 6.04 and 6.00 (2×s, 1H), 4.17 and 4.16 (2×q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 3.80 (s, 3H), 3.24 and 3.20 (2×s, 3H), 2.21 and 2.21 (2×s, 3H), 1.22 and 1.21 (2×t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR [100 MHz, $CDCl_3$; inseparable regioisomeric mixture of **3fg** and **3fg'** in (1:1)] δ = 166.5 (2C), 152.7, 152.7, 152.6, 152.6, 148.1, 147.9, 145.2, 144.8, 144.4 (2C), 138.8, 138.6, 136.7, 136.6, 135.5, 134.0, 132.2, 131.1 (2C), 130.9 (2C), 130.65, 129.8, 129.6, 129.4 (2C), 129.3, 129.3 (2C), 129.2, 128.6 (2C), 127.8 (2C), 127.8 (2C), 127.1 (2C), 127.0 (2C), 126.9, 119.5, 119.2, 109.5, 109.5, 61.2, 61.1, 61.0, 61.0, 60.6 (2C), 56.4 (2C), 21.3, 21.2, 14.2 (2C) ppm. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{29}H_{28}NaO_5]^+$ 479.1829; found 479.1835.



Ethyl (*E*)-2-(6,7-diphenyl-5H-indeno[5,6-*d*][1,3]dioxol-5-ylidene)acetate (3ga):

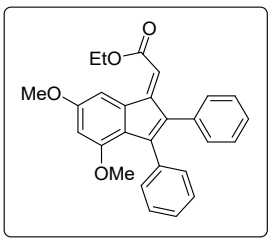
GP-2 was carried out with ethyl 2-bromocinnamate ester **1g** (116 mg, 0.39 mmol) and diaryl acetylene **2a** (53 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and Toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 97:3), furnished the 2,3-diaryl indene ester **3ga** as dark maroon solid (101 mg, 85%); mp = 130-132 °C [TLC control (petroleum ether/ethyl acetate 100:3), R_f(**1g**) = 0.4, R_f(**3ga**) = 0.5, R_f(**2a**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2891, 1713, 1589, 1468, 1444, 1294, 1186, 1135, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, J = 1.4 Hz, 1H), 7.29 – 7.23 (m, 6H), 7.21 – 7.17 (m, 2H), 7.12 – 7.08 (m, 2H), 6.74 (s, 1H), 6.09

(s, 1H), 5.94 (s, 2H), 4.25 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.4, 151.8, 148.7, 146.6, 144.1, 140.1, 138.4, 133.8, 133.7, 130.9 (2C), 129.1 (2C), 128.2 (2C), 128.0 (2C), 127.8, 127.2, 126.7, 119.5, 109.5, 102.2, 101.4, 60.7, 14.2 ppm. HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{26}H_{24}NO_4]^+$ 414.1700; found 414.1681.



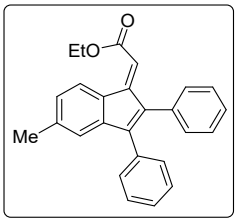
Ethyl (*E*)-2-(6,7-bis(4-methoxyphenyl)-5*H*-indeno[5,6-*d*][1,3]dioxol-5-ylidene)acetate (3gb):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1g** (116 mg, 0.39 mmol), diaryl acetylene **2b** (71 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the 2,3-diarylindene enoate ester **3gb** (109 mg, 80%), as dark brown solid; mp = 148-150 °C [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1g**) = 0.4, R_f(**3gb**) = 0.5, R_f(**2b**) = 0.7 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2926, 1607, 1503, 1468, 1377, 1243, 1249, 1177, 768 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.39 (s, 1H), 7.19 – 7.12 (m, 2H), 7.08 – 7.02 (m, 2H), 6.89 – 6.77 (m, 5H), 6.09 (s, 1H), 5.99 (s, 2H), 4.28 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.5, 159.0, 158.6, 152.3, 148.6, 146.4, 143.3, 140.3, 137.4, 132.1 (2C), 130.5 (2C), 126.9, 126.3, 126.1, 118.8, 113.7 (2C), 113.6 (2C), 109.5, 102.1, 101.4, 60.6, 55.1 (2C), 14.2 ppm. HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{28}H_{28}NO_6]^+$ 474.1911; found 474.1920.



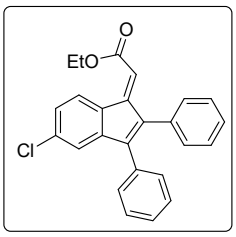
Ethyl (*E*)-2-(4,6-dimethoxy-2,3-diphenyl-1*H*-inden-1-ylidene) acetate (3ha):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1h** (123 mg, 0.39 mmol), diaryl acetylene **2a** (53 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 99:1 to 97:3), furnished the 2,3-diarylindene enoate ester **3ha** (95 mg, 77%), as maroon solid; mp = 140-142 °C [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**1h**) = 0.5, R_f(**3ha**) = 0.6, R_f(**2a**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3436, 1713, 1592, 1460, 1290, 1202, 1039, 738, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, J = 2.0 Hz, 1H), 7.24 – 7.14 (m, 8H), 7.08 – 7.02 (m, 2H), 6.45 (d, J = 2.1 Hz, 1H), 6.14 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 3.53 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.4, 160.9, 154.2, 152.5, 145.7, 137.2, 136.0, 135.8, 134.1, 131.2 (2C), 129.6 (2C), 127.8 (2C), 126.9, 126.8, 126.7 (2C), 123.9, 119.9, 106.6, 101.2, 60.6, 55.7, 55.4, 14.2 ppm. HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{27}H_{24}KO_4]^+$ 451.1306; found 451.1314.



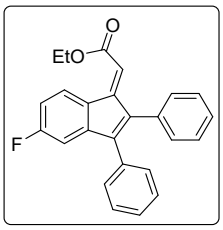
Ethyl (*E*)-2-(5-methyl-2,3-diphenyl-1*H*-inden-1-ylidene)acetate (3ba):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1b** (105 mg, 0.39 mmol), diaryl acetylene **2a** (53 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the 2,3-diarylindene enoate ester **3ba** (105 mg, 96%), as orange solid; mp = 136-138 °C [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1b**) = 0.5, R_f(**3ba**) = 0.6, R_f(**2a**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2983, 1709, 1622, 1379, 1186, 1163, 1095, 1032, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.59 (d, J = 7.7 Hz, 1H), 7.31 – 7.24 (m, 6H), 7.24 – 7.20 (m, 2H), 7.15 – 7.07 (m, 4H), 6.12 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 2.34 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.5, 152.2, 144.8, 144.6, 140.2, 139.8, 133.9, 133.9, 130.9 (2C), 130.5, 129.3 (2C), 128.2 (2C), 128.1 (2C), 127.7, 127.4, 127.4, 127.3, 121.4, 119.3, 60.6, 21.8, 14.2. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{26}H_{22}NaO_2]^+$ 389.1512; found 389.1496.



Ethyl (*E*)-2-(5-chloro-2,3-diphenyl-1*H*-inden-1-ylidene)acetate (3ja):

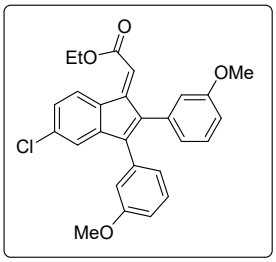
GP-2 was carried out with ethyl 2-bromocinnamate ester **1j** (113 mg, 0.39 mmol), diaryl acetylene **2a** (53 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the 2,3-diarylindene enoate ester **3ja** (90 mg, 78%), as orange solid; mp = 134-136 °C [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1j**) = 0.4, R_f(3**ja**) = 0.5, R_f(**2a**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2983, 1710, 1450, 1376, 1192, 1164, 876, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.69 (d, J = 8.8 Hz, 1H), 7.31 – 7.22 (m, 8H), 7.22 – 7.19 (m, 2H), 7.16 – 7.11 (m, 2H), 6.21 (s, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.2, 151.1, 146.1, 143.9, 140.8, 135.9, 133.4, 133.1, 131.3, 130.8 (2C), 129.1 (2C), 128.5, 128.3 (2C), 128.2 (2C), 128.0, 127.6, 126.5, 120.9, 120.7, 60.8, 14.2. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{20}ClO_2]^+$ 387.1146; found 387.1140.



Ethyl (*E*)-2-(5-fluoro-2,3-diphenyl-1*H*-inden-1-ylidene)acetate (3ia):

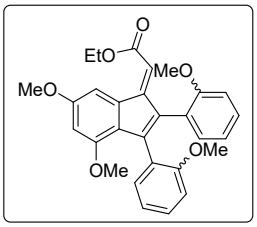
GP-2 was carried out with ethyl 2-bromocinnamate ester **1i** (106 mg, 0.39 mmol), diaryl acetylene **2a** (53 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the 2,3-diarylindene enoate ester **3ia** (82 mg, 74%), as orange solid; mp = 114-116 °C [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1i**) = 0.5, R_f(**3ia**) = 0.6, R_f(**2a**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2983, 1710, 1594, 1465, 1378, 1207, 1186, 734, 868 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.74 (dd, J = 8.4 and

5.4 Hz, 1H), 7.31 – 7.23 (m, 6H), 7.22 – 7.19 (m, 2H), 7.16 – 7.10 (m, 2H), 6.98 – 6.91 (m, 2H), 6.16 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.3, 164.1 (d, J = 249.4 Hz), 151.1, 147.1 (d, J = 8.9 Hz), 143.7 (d, J = 2.3 Hz), 141.1, 133.5, 133.2, 130.8 (2C), 129.2, 129.1 (2C), 128.9 (d, J = 3.0 Hz), 128.3 (2C), 128.1, 128.0 (2C), 127.6, 120.2 (d, J = 1.9 Hz), 112.8 (d, J = 22.1 Hz), 108.3 (d, J = 24.6 Hz), 60.8, 14.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -110.20 (s) ppm. HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{25}H_{19}FKO_2]^+$ 409.1001; found 409.1007.



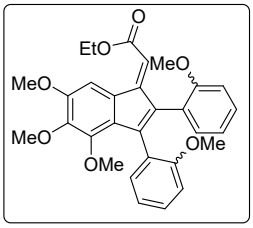
Ethyl (*E*)-2-(5-chloro-2,3-bis(3-methoxyphenyl)-1*H*-inden-1-ylidene)acetate (3jc):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1j** (112 mg, 0.39 mmol), diaryl acetylene **2c** (71 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:2), furnished the 2,3-diarylindene enoate ester **3jc** (111 mg, 83%), as orange solid; mp = 121-123 °C [TLC control (petroleum ether/ethyl acetate 100:2), R_f(**1j**) = 0.7, R_f(**3jc**) = 0.5, R_f(**2c**) = 0.8 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2937, 1714, 1591, 1454, 1377, 1286, 1188, 1045, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.66 (d, J = 8.1 Hz, 1H), 7.30 – 7.16 (m, 4H), 6.88 – 6.65 (m, 6H), 6.23 (s, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.69 (s, 3H), 3.65 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.2, 159.3, 159.2, 150.9, 146.0, 143.7, 140.7, 135.9, 134.8, 134.4, 131.3, 129.4, 129.2, 128.5, 126.6, 123.3, 121.4, 121.0, 120.9, 116.3, 114.3, 114.0, 113.3, 60.9, 55.1, 55.1, 14.2 ppm. HRMS (ESI) *m/z*: $[M]^{+2}$ calcd for $[C_{27}H_{23}ClO_4]^{+2}$ 223.0637; found 223.0616.



Ethyl(*E*)-2-(4,6-dimethoxy-2,3-bis(2-methoxyphenyl)-1*H*-inden-1-ylidene)acetate (1:1) (3hi+3hi'):

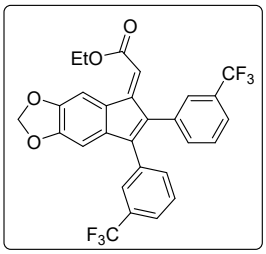
GP-2 was carried out with ethyl 2-bromocinnamate ester **1h** (122 mg, 0.39 mmol), diaryl acetylene **2i** (71 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5), furnished the 2,3-diarylindene enoate ester **3hi** (127 mg, 90%), as dark maroon solid; mp = 146-148 °C [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**1h**) = 0.6, R_f(**3hi**) = 0.4, R_f(**2i**) = 0.7 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2933, 1710, 1595, 1462, 1431, 1292, 1149, 1028, 754 cm^{-1}. ^1H NMR [400 MHz, $CDCl_3$; inseparable diastereomeric mixture of **3hi** in (1:1)] δ = 8.16 and 8.16 (2×d, J = 3.1 Hz, 1H), 7.20 – 7.08 (m, 2H), 6.96 – 6.82 (m, 3H), 6.80 – 6.66 (m, 3H), 6.34 and 6.33 (2×d, J = 3.3Hz, 1H), 5.99 and 5.81 (2×s, 1H), 4.16 and 4.15 (2×q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 3.65 and 3.61 (2×s, 3H), 3.58 and 3.44 (2×s, 3H), 3.41 and 3.35 (2×s, 3H), 1.28 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR [100 MHz, $CDCl_3$; inseparable diastereomeric mixture of **3hi** in (1:1)] δ = 166.7, 166.6, 160.6, 160.6, 158.2, 158.0, 157.8, 157.59, 154.1, 154.0, 152.6, 152.5, 143.9, 143.8, 136.1, 135.9, 135.2, 133.8, 132.7, 132.4, 129.7, 129.6, 128.8, 128.6, 128.4, 128.3, 126.4, 126.3, 125.6, 125.2, 123.5, 123.3, 120.3, 119.9, 119.5, 119.2, 119.1, 118.8, 111.1, 110.6, 109.6, 109.6, 106.8, 106.7, 101.3, 101.2, 60.5, 60.5, 55.8, 55.8, 55.7 (2C), 55.4, 55.36, 55.3, 55.1, 14.3 (2C) ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{29}H_{29}O_6]^+$ 473.1959; found 473.1957.



Ethyl(*E*)-2-(4,5,6-trimethoxy-2,3-bis(2-methoxyphenyl)-1*H*-inden-1-ylidene)acetate (1:1) (3fi+3fi'):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1f** (134 mg, 0.39 mmol), diaryl acetylene **2i** (71 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5), furnished the 2,3-diarylindene enoate ester **3fi** (102 mg, 68%), as maroon solid; mp = 104-106 °C [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**1f**) = 0.5,

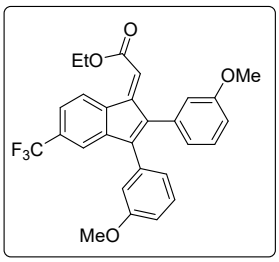
R_f(**3fi**) = 0.2, R_f(**2i**) = 0.6 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2934, 1709, 1466, 1244, 1194, 1124, 1111, 1027, 753 cm^{-1}. ^1H NMR [400 MHz, $CDCl_3$; inseparable diastereomeric mixture of **3fi** in (1:1)] δ = 8.51 and 8.50 (2×s, 1H), 7.24 – 7.12 (m, 2H), 7.12 – 6.97 (m, 1H), 6.97 – 6.90 (m, 1H), 6.91 – 6.70 (m, 4H), 6.02 and 5.85 (2×s, 1H), 4.24 and 4.23 (2×q, J = 7.1 Hz, 2H), 3.96 (s, 3H), 3.85 (s, 3H), 3.74 and 3.72 (2×s, 3H), 3.69 and 3.47 (2×s, 3H), 3.30 and 3.30 (2×s, 3H), 1.27 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR [100 MHz, $CDCl_3$; inseparable diastereomeric mixture of **3fi** in (1:1)] δ =166.6, 166.6, 157.9, 157.8, 157.8, 157.6, 152.5, 152.4, 152.3, 152.3, 147.9, 147.8, 144.2, 144.1, 143.3, 143.1, 136.8, 135.5, 132.6, 132.6, 132.1, 130.9, 130.4, 129.7, 129.5, 129.3, 129.2, 128.9, 128.7, 128.5, 128.5, 125.7, 125.7, 123.2, 122.9, 120.2, 119.8, 119.6, 119.2, 118.4, 118.1, 111.0, 110.5, 109.7, 109.7, 109.6, 61.2, 61.1, 60.9, 60.9, 60.3, 60.4, 56.43, 56.4, 55.3, 55.3, 55.1, 21.0, 14.2, 14.1 ppm. HRMS (ESI) *m/z*: $[M]^+$ calcd for $[C_{30}H_{30}O_7]^+$ 502.1986; found 502.1957.



Ethyl (*E*)-2-(6,7-bis(3-(trifluoromethyl)phenyl)-5*H*-indeno[5,6-*d*][1,3]dioxol-5-ylidene)acetate (3gj):

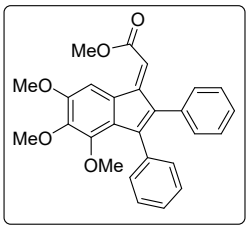
GP-2 was carried out with ethyl 2-bromocinnamate ester **1g** (117 mg, 0.39 mmol), diaryl acetylene **2j** (94 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:3), furnished the 2,3-diarylindene enoate ester **3gj** (108 mg, 68%), as maroon solid; mp = 126-128 °C [TLC control (petroleum ether/ethyl acetate 100:3), R_f(**1g**) = 0.4, R_f(**3gj**) = 0.5, R_f(**2j**) = 0.8 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2912, 1716, 1471, 1327, 1186, 1122, 1040, 929, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.41 (s, 1H), 7.55 (dd, J = 6.6 and 5.7 Hz, 2H), 7.46 – 7.30 (m, 6H), 6.70 (s, 1H), 6.07 (s, 1H), 6.00 (s, 2H), 4.29 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.0, 150.8, 149.0, 147.2, 143.7, 138.9, 137.8, 134.2 (2C), 134.0, 132.3, 130.9 (q, J = 32.6 Hz), 130.5 (q, J = 32.5 Hz), 129.0, 128.8, 127.6 (q, J = 3.8 Hz), 126.6, 125.9 (q, J = 3.8 Hz), 124.8 (q, J = 3.8 Hz), 124.4 (q, J = 3.8 Hz), 123.8 (q, J = 273.5 Hz), 123.7 (q, J = 273.5 Hz),

120.3, 109.8, 102.0, 101.7, 60.9, 14.1 ppm. ^{19}F NMR (565 MHz, $CDCl_3$) δ = -62.86 (s), -62.99 (s) ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{28}H_{19}F_6O_4]^+$ 533.1182; found 533.1214



Ethyl (*E*)-2-(2,3-bis(3-methoxyphenyl)-5-(trifluoromethyl)-1*H*-inden-1-ylidene)acetate (3kc):

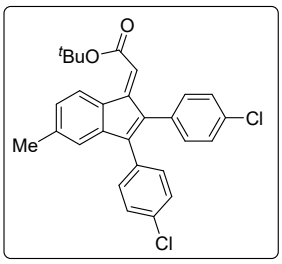
GP-2 was carried out with ethyl 2-bromocinnamate ester **1k** (125 mg, 0.39 mmol), diaryl acetylene **2c** (71 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:2), furnished the 2,3-diarylindene enoate ester **3kc** (98 mg, 68%), as yellow solid; mp = 110-112 °C [TLC control (petroleum ether/ethyl acetate 100:2), R_f(**1k**) = 0.7, R_f(**3kc**) = 0.5, R_f(**2c**) = 0.4 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3456, 2343, 1718, 1593, 1462, 1313, 1161, 1043, 704 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.79 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.42 (m, 2H), 7.26 – 7.22 (m, 2H), 6.94 – 6.80 (m, 3H), 6.80 – 6.70 (m, 2H), 6.67 (dd, *J* = 2.5 and 1.5 Hz, 1H), 6.31 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 3H), 3.65 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.1, 159.4, 159.3, 150.5, 144.7, 143.8, 140.7, 136.2, 134.6, 134.2, 131.5 (q, *J* = 32.1 Hz), 129.5, 129.3, 127.3, 124.0 (q, *J* = 3.8 Hz), 123.3, 122.5, 121.4, 116.9 (q, *J* = 3.6 Hz), 116.8 (q, *J* = 253.6 Hz), 116.3, 114.3 (2C), 113.4, 61.1, 55.2, 55.1, 14.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.50 (s) ppm. HRMS (ESI) *m/z*: $[M]^{+2}$ calcd for $[C_{28}H_{23}F_3O_4]^{+2}$= 240.0769; found 240.0801.



Methyl (*E*)-2-(4,5,6-trimethoxy-2,3-diphenyl-1*H*-inden-1-ylidene)acetate (3la):

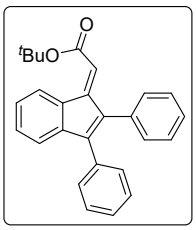
GP-2 was carried out with methyl 2-bromocinnamate ester **1l** (134 mg, 0.39 mmol), diaryl acetylene **2a** (53 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL).

Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the 2,3-diarylindene enoate ester **3la** (101 mg, 79%), as red solid; mp = 168-170 °C [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1l**) = 0.4, R_f(**3la**) = 0.5, R_f(**2a**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2935, 1712, 1466, 1381, 1290, 1200, 1124, 1038, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.55 (s, 1H), 7.27 – 7.15 (m, 8H), 7.05 (dd, J = 7.6 and 1.7 Hz, 2H), 6.11 (s, 1H), 3.98 (s, 3H), 3.88 (s, 3H), 3.77 (s, 3H), 3.29 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.8, 153.0, 152.7, 148.1, 145.3, 144.5, 138.8, 135.3, 133.7, 131.0 (2C), 129.6, 129.3 (2C), 129.1, 127.8 (2C), 127.1, 127.0 (2C), 127.0, 118.9, 109.6, 61.1, 61.0, 56.3, 51.7 ppm. HRMS (ESI) *m/z*: $[M+2Na]^{+2}$ calcd for $[C_{27}H_{24}Na_2O_5]^{+2}$ 237.0704; found 237.0695.



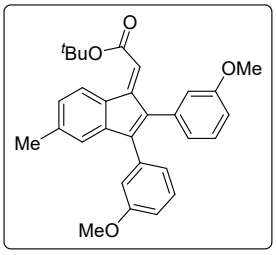
***tert*-Butyl (*E*)-2-(2,3-bis(4-chlorophenyl)-5-methyl-1*H*-inden-1-ylidene)acetate (3nk):**

GP-2 was carried out with *tert*-butyl 2-bromocinnamate ester **1n** (116 mg, 0.39 mmol), diaryl acetylene **2k** (74 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the 2,3-diarylindene enoate ester **3nk** (118 mg, 85%), as orange solid; mp = 200-202 °C [TLC control (petroleum ether/ethyl acetate 100:1), R_f(**1n**) = 0.5, R_f(**3nk**) = 0.6, R_f(**2k**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2979, 1710, 1487, 1381, 1216, 1143, 1089, 1014, 835 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.54 (d, J = 7.8 Hz, 1H), 7.31 – 7.25 (m, 4H), 7.17 – 6.99 (m, 6H), 6.03 (s, 1H), 2.35 (s, 3H), 1.54 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 165.7, 149.9, 143.9, 143.5, 140.1, 138.8, 133.7, 133.5, 132.3, 132.2 (2C), 132.1, 130.5 (2C), 130.4, 128.6 (2C), 128.5 (2C), 127.7, 127.2, 121.8, 121.1, 81.3, 28.1 (3C), 21.8 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{28}H_{25}Cl_2O_2]^+$ 463.1226; found 463.1240.



***tert*-Butyl (*E*)-2-(2,3-diphenyl-1*H*-inden-1-ylidene)acetate (3ma):**

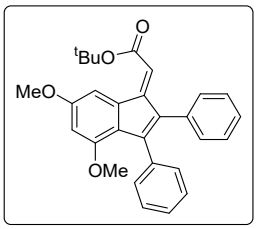
GP-2 was carried out with *tert*-butyl 2-bromocinnamate ester **1m** (110 mg, 0.39 mmol), diaryl acetylene **2a** (53 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the 2,3-diarylindene enoate ester **3ma** (77 mg, 68%), as orange solid; mp = 148-150 °C [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1m**) = 0.5, R_f(**3ma**) = 0.6, R_f(**2a**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2977, 1710, 1628, 1454, 1381, 1211, 1145, 756, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.57 – 8.52 (m, 1H), 7.29 – 7.16 (m, 11H), 7.11 (dd, J = 7.5 and 1.7 Hz, 2H), 6.10 (s, 1H), 1.50 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 165.9, 150.3, 144.3, 144.2, 139.4, 134.0, 133.9, 133.3, 130.9 (2C), 129.5, 129.3 (2C), 128.1 (2C), 128.1 (2C), 127.7, 127.3, 126.9, 126.8, 122.4, 120.3, 81.3, 28.2 (3C) ppm. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{27}H_{24}NaO_2]^+$ 403.1669; found 403.1685.



***tert*-Butyl (*E*)-2-(2,3-bis(3-methoxyphenyl)-5-methyl-1*H*-inden-1-ylidene)acetate (3nc):**

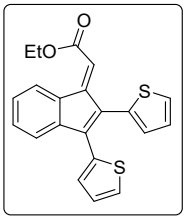
GP-2 was carried out with *tert*-butyl 2-bromocinnamate ester **1n** (116 mg, 0.39 mmol), diaryl acetylene **2c** (71 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:2), furnished the 2,3-diarylindene enoate ester **3nc** (95 mg, 70%), as orange solid; mp = 123-125 °C [TLC control (petroleum ether/ethyl acetate 100:2), R_f(**1n**) = 0.7, R_f(**3nc**) = 0.5, R_f(**2c**) = 0.8 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2976, 1710, 1466, 1373, 1286, 1224, 1145, 1099, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.43 (d, J =

7.7 Hz, 1H), 7.16 – 7.12 (m, 2H), 7.03 – 6.98 (m, 2H), 6.81 – 6.66 (m, 5H), 6.60 (dd, J = 2.5 and 1.5 Hz, 1H), 6.03 (s, 1H), 3.61 (s, 3H), 3.56 (s, 3H), 2.28 (s, 3H), 1.46 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.1, 159.3, 159.2, 150.3, 144.4, 144.2, 139.9, 139.7, 135.62, 135.4, 130.6, 129.3, 129.1, 127.4, 127.0, 123.5, 121.6 (2C), 121.4, 116.4, 114.5, 113.7, 113.0, 81.2, 55.2, 55.1, 28.2 (3C), 21.9 ppm. HRMS (ESI) *m/z*: $[M+2NH_4]^{+2}$ calcd for $[C_{30}H_{38}N_2O_4]^{+2}$ 245.1410; found 245.1416.



***tert*-Butyl (*E*)-2-(4,6-dimethoxy-2,3-diphenyl-1*H*-inden-1-ylidene)acetate (3oa):**

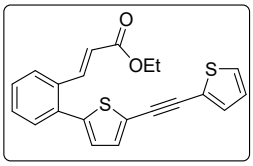
GP-2 was carried out with *tert*-butyl 2-bromocinnamate ester **1o** (134 mg, 0.39 mmol), diaryl acetylene **2a** (53 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:3), furnished the 2,3-diarylindene enoate ester **3oa** (79 mg, 60%), as dark maroon solid; mp = 130-132 °C [TLC control (petroleum ether/ethyl acetate 100:3), R_f(**1o**) = 0.4, R_f(**3oa**) = 0.5, R_f(**2a**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2960, 1705, 1595, 1460, 1294, 1143, 1107, 740, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.15 – 8.00 (m, 1H), 7.30 – 7.22 (m, 3H), 7.22 – 7.15 (m, 5H), 7.12 – 7.05 (m, 2H), 6.47 (d, J = 2.1 Hz, 1H), 6.13 (d, J = 0.9 Hz, 1H), 3.91 (s, 3H), 3.57 (s, 3H), 1.56 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.1, 160.7, 154.2, 150.2, 144.8, 137.1, 136.2, 135.9, 134.3, 131.2 (2C), 129.6 (2C), 127.8 (2C), 126.8, 126.7 (2C), 126.7, 123.9, 122.2, 106.1, 100.8, 81.2, 55.7, 55.5, 28.1 (3C) ppm. HRMS (ESI) *m/z*: $[M]^+$ calcd for $[C_{29}H_{28}O_4]^+$ 440.1982; found 440.1968.



Ethyl (*E*)-2-(2,3-di(thiophen-2-yl)-1*H*-inden-1-ylidene)acetate (3al):

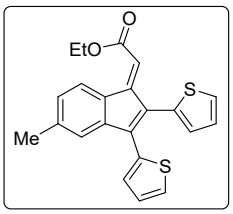
GP-2 was carried out with ethyl 2-bromocinnamate ester **1a** (99 mg, 0.39 mmol), diaryl acetylene **2l** (57 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03

mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5), furnished the 2,3-diarylindene enoate ester **3al** (57 mg, 52%), as orange solid; mp = 106-108 °C [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**1a**) = 0.5, R_f(**3al**) = 0.6, R_f(**2l**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3434, 1714, 1455, 1376, 1210. 1178, 768, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.83 – 8.44 (m, 1H), 7.56 (dd, J = 7.4 and 1 Hz, 1H), 7.36 (dd, J = 5.1 and 1.1 Hz, 1H), 7.34 – 7.23 (m, 3H), 7.21 – 7.16 (m, 1H), 7.05 (dd, J = 5.1 and 3.5 Hz, 1H), 6.98 (dd, J = 5.1 and 3.7 Hz, 1H), 6.93 (dd, J = 3.5 and 1.2 Hz, 1H), 6.18 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.4, 152.2, 142.9, 140.2, 135.0, 134.2, 133.3, 131.8, 130.1, 129.9, 128.7, 127.7, 127.6, 127.5, 127.4, 127.3, 127.0, 120.9, 120.2, 60.9, 14.3 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{21}H_{17}O_2S_2]^+$ 365.0664; found 365.0665.



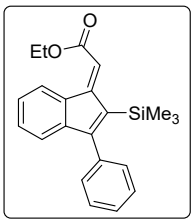
Ethyl (*E*)-3-(2-(5-(thiophen-2-ylethynyl)thiophen-2-yl)phenyl)acrylate (3al'):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1a** (99 mg, 0.39 mmol), diaryl acetylene **2l** (57 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:5), furnished the 2,3-diarylindene enoate ester **3al'** (44 mg, 40%), as brown solid; mp = 68-70 °C [TLC control (petroleum ether/ethyl acetate 100:5), R_f(**1a**) = 0.5, R_f(**3al'**) = 0.4, R_f(**2l**) = 0.8 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3426, 1710, 1632, 1314, 1177, 1030, 808, 763, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.98 (d, J = 15.9 Hz, 1H), 7.66 (dd, J = 7.3 and 1.8 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.45 – 7.36 (m, 2H), 7.35 – 7.27 (m, 3H), 7.03 (dd, J = 5.1 and 3.7 Hz, 1H), 6.93 (d, J = 3.7 Hz, 1H), 6.42 (d, J = 15.9 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.7, 143.2, 134.0, 133.3, 132.7, 132.2, 130.7, 129.9, 128.4, 128.3, 127.8, 127.5, 127.2 (2C), 123.9, 122.7, 120.3, 87.3, 86.0, 60.5, 14.3 ppm. HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{21}H_{16}KO_2S_2]^+$ 403.0223; found 403.0212.



Ethyl (*E*)-2-(5-methyl-2,3-di(thiophen-2-yl)-1*H*-inden-1-ylidene)acetate (3bl):

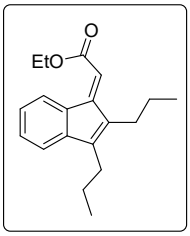
GP-2 was carried out with ethyl 2-bromocinnamate ester **1b** (105 mg, 0.39 mmol), diaryl acetylene **2l** (57 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the 2,3-diarylindene enoate ester **3bl** (68 mg, 60%), as orange solid; mp = 94-96 °C [TLC control (petroleum ether/ethyl acetate 100:1), R_f(**1b**) = 0.4, R_f(**3bl**) = 0.5, R_f(**2l**) = 0.7 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2921, 1714, 1633, 1378, 1313, 1265, 1174, 1035, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.63 (d, J = 7.8 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.36 (dd, J = 5.1 and 1.1 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.13 – 7.09 (m, 2H), 7.06 (dd, J = 5.1 and 3.7 Hz, 1H), 6.99 (dd, J = 3.5 and 1.2 Hz, 1H), 6.21 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.4, 152.2, 143.3, 140.3, 140.0, 135.0, 134.3, 132.2, 130.6, 130.0, 128.6, 128.0, 127.5, 127.4 (2C), 127.2, 126.9, 121.9, 119.3, 77.0, 60.7, 21.9, 14.2 ppm. HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{22}H_{18}KO_2S_2]^+$ 417.0380; found 417.0367.



Ethyl (*E*)-2-(3-phenyl-2-(trimethylsilyl)-1*H*-inden-1-ylidene)acetate (3am):

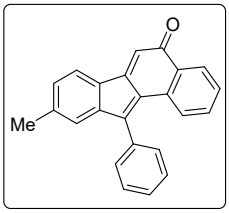
GP-2 was carried out with ethyl 2-bromocinnamate ester **1a** (99 mg, 0.39 mmol), alkylaryl acetylene **2m** (52 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the 2,3-alkylarylindene enoate ester **3am** (88 mg, 84%), as yellow oil. [TLC control (petroleum ether/ethyl acetate 100:1), R_f(**1a**) = 0.5, R_f(**3am**) = 0.6, R_f(**2m**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2960, 1716, 1619, 1451, 1373, 1184, 1029, 842, 690 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.65 – 8.47 (m, 1H), 7.45 –

7.34 (m, 3H), 7.27 – 7.23 (m, 2H), 7.22 – 7.15 (m, 2H), 6.90 – 6.76 (m, 1H), 6.52 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H), 0.03 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 166.6, 159.8, 155.7, 147.1, 138.2, 136.8, 135.1, 129.8, 128.9 (2C), 128.3 (2C), 128.2, 127.3, 126.9, 120.5, 120.3, 60.9, 14.4, 1.6 (3C) ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{22}H_{25}O_2Si]^+$ 349.1618; found 349.1618.



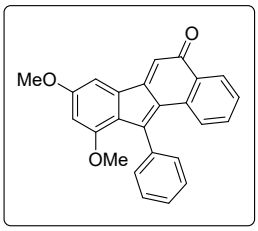
Ethyl (*Z*)-2-(2,3-dipropyl-1*H*-inden-1-ylidene)acetate (3an):

GP-2 was carried out with ethyl 2-bromocinnamate ester **1a** (99 mg, 0.39 mmol), dialkyl acetylene **2n** (41 mg, 0.3 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), DPEPhos (16.14 mg, 0.03 mmol), TEBAC (68 mg, 0.3 mmol), K_2CO_3 (165 mg, 1.2 mmol) and toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the 2,3-dialkylindene enoate ester **3an** (69 mg, 81%), as yellow oil. [TLC control (petroleum ether/ethyl acetate 100:1), R_f(**1a**) = 0.5, R_f(**3an**) = 0.6, R_f(**2n**) = 0.9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2957, 1714, 1629, 1455, 1267, 1164, 1031, 871, 754 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 8.55 (d, J = 7.6 Hz, 1H), 7.24 (dt, J = 7.5, 3.7 Hz, 1H), 7.14 (td, J = 7.6, 1.1 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 6.20 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.49 (dd, J = 8.5, 7.0 Hz, 2H), 2.44 – 2.36 (m, 2H), 1.60 (dd, J = 15.2, 7.6 Hz, 2H), 1.52 (dd, J = 15.4, 7.6 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 4.7 Hz, 3H), 0.98 (t, J = 4.7 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 166.6, 152.1, 145.4, 145.3, 137.5, 133.5, 129.7, 126.9, 126.2, 118.4, 115.3, 60.7, 27.9, 26.7, 24.1, 22.0, 14.5, 14.4, 14.4 ppm. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{19}H_{24}NaO_2]^+$ 307.1669; found 307.1662.



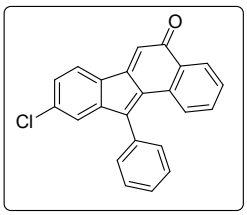
9-Methyl-11-phenyl-5*H*-benzo[*a*]fluoren-5-one (4b):

GP-3 was carried out with 2,3-diarylindene enoate ester **3ba** (36.7 mg, 0.1 mmol), TfOH (15 mg, 0.1 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the benzo[*a*]fluorene **4b** (29 mg, 91%), as maroon solid; mp = 127-129 °C [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**4b**) = 0.4., R_f(**3ba**) = 0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2923, 1961, 1639, 1549, 1463, 1281, 889, 759 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.27 – 8.00 (m, 1H), 7.62 – 7.51 (m, 3H), 7.54 – 7.48 (m, 2H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.17 (m, 3H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.80 (s, 1H), 6.71 (s, 1H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 186.4, 152.9, 148.9, 146.24, 141.3, 134.4, 133.4, 132.9, 132.2, 130.4, 129.3 (2C), 129.0, 128.5, 128.1 (2C), 128.0, 127.7, 127.4, 125.1, 123.4, 121.9, 120.6, 21.7 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{24}H_{17}O]^+$ 321.1274; found 321.1275.



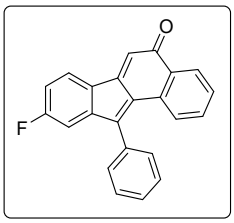
8,10-Dimethoxy-11-phenyl-5*H*-benzo[*a*]fluoren-5-one (4c):

GP-3 was carried out with 2,3-diarylindene enoate ester **3ha** (41.2 mg, 0.1 mmol), TfOH (15 mg, 0.1 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5), furnished the benzo[*a*]fluorene **4c** (35 mg, 95%), as purple solid; mp = 178-180 °C **[**TLC control (petroleum ether/ethyl acetate 99:5), R_f(**4c**) = 0.5, R_f(**3ha**) = 0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2923, 2854, 1599, 1470, 1287, 1209, 1057, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.06 (dd, *J* = 7.9 and 1.2 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.43 – 7.38 (m, 2H), 7.18 (td, *J* = 7.6 and 1.2 Hz, 1H), 7.10 (ddd, *J* = 8.8, 7.3 and 1.6 Hz, 1H), 6.89 (dd, *J* = 8.1 and 1 Hz, 1H), 6.83 (s, 1H), 6.79 (d, *J* = 2.0 Hz, 1H), 6.21 (d, *J* = 2.0 Hz, 1H), 3.86 (s, 3H), 3.47 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 186.5, 162.5, 156.6, 152.8, 151.1, 139.5, 136.9, 133.9, 132.1, 130.1, 128.4 (2C), 128.1, 127.5 (2C), 127.3, 126.8, 125.3, 124.6, 124.5, 121.1, 102.4, 100.5, 55.7, 55.4 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{19}O_3]^+$ 367.1329; found 367.1330.



9-Chloro-11-phenyl-5*H*-benzo[*a*]fluoren-5-one (4d):

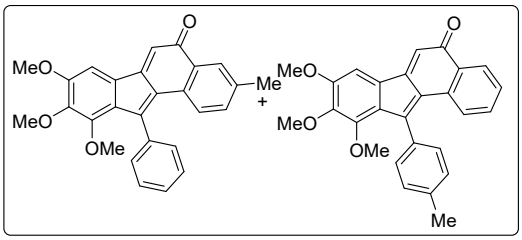
GP-3 was carried out with 2,3-diarylindene enoate ester **3ja** (38.7 mg, 0.1 mmol), TfOH (15 mg, 0.1 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the benzo[*a*]fluorene **4d** (28 mg, 81%), as maroon solid; mp = 194-196 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**4d**) = 0.5, R_f(**3ja**) = 0.3, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3060, 2291, 2096, 1640, 1450, 1280, 1073, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.06 (dd, *J* = 7.8 and 1.1 Hz, 1H), 7.60 – 7.49 (m, 3H), 7.3d – 7.30 (m, 3H), 7.31 – 7.20 (m, 2H), 7.21 – 7.14 (m, 1H), 7.11 (dd, *J* = 7.8 and 1.8 Hz, 1H), 6.88 – 6.72 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 186.0, 151.6, 151.7, 147.5, 147.3, 136.8, 133.7, 133.6, 132.9, 132.4, 130.2, 129.4 (2C), 129.4, 128.8, 128.2, 128.1 (2C), 127.6, 127.5, 125.2, 122.6, 121.7 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{23}H_{14}ClO]^+$ 341.0728; found 341.0732.



9-Fluoro-11-phenyl-5*H*-benzo[*a*]fluoren-5-one (4e):

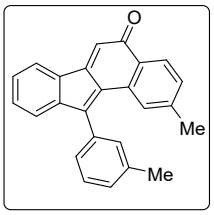
GP-3 was carried out with 2,3-diarylindene enoate ester **3ia** (37 mg, 0.1 mmol), TfOH (15 mg, 0.1 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the benzo[*a*]fluorene **4e** (25 mg, 77%), as maroon solid; mp = 207-209 °C [TLC control (petroleum ether/ethyl acetate 99:2), R_f(**4e**) = 0.6, R_f(**3ia**) = 0.3, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3062, 2396, 1981, 1640, 1462, 1277, 878, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.10 (dd, *J* = 7.7 and 1.1 Hz, 1H), 7.66 – 7.53 (m, 3H), 7.52 – 7.42 (m, 3H), 7.33 – 7.24 (m, 2H), 7.23 – 7.16 (m, 1H), 6.92 – 6.76 (m, 2H), 6.60 (dd, *J* = 8.6 and 2.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 186.2, 165.0 (d, *J* = 250.3 Hz), 151.8, 148.4 (d, *J* = 8.7 Hz), 147.1, 133.7, 133.0, 132.3, 131.2 (d, *J* = 3.0 Hz), 130.2, 129.4 (2C), 129.3 (2C), 129.2, 128.1, 128.1, 127.6, 125.2, 123.1 (d, *J* = 9.1 Hz), 121.2, 113.9 (d, *J* = 23.5 Hz), 110.5 (d, *J* = 25.2 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -109.10 (s) ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{23}H_{14}FO]^+$ 325.1023; found 325.1024.



8,9,10-Trimethoxy-3-methyl-11-phenyl-5*H*-benzo[*a*]fluoren-5-one & 8,9,10-trimethoxy-11-(*p*-tolyl)-5H-benzo[*a*]fluoren-5-one (1:1) (4f+4f'):

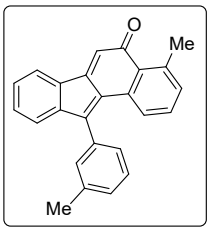
GP-3 was carried out with 2,3-diarylindene enoate ester **3fg** (45.6 mg, 0.1 mmol), TfOH (15 mg, 0.1 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the benzo[*a*]fluorene **4f+4f'** (39 mg, 96%), as purple solid; mp = 196-198 °C [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**4f+4f'**) = 0.5, R_f(**3fg**) = 0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3737, 2935, 1637, 1466, 1379, 1276, 1121, 755 cm^{-1}. ^1H NMR [400 MHz, $CDCl_3$; inseparable regioisomeric mixture of **4f** and **4f'** in (1:1)] δ = 8.11 – 7.80 (m, 1H), 7.52 – 7.42 (m, 2H), 7.33 (s, 2H), 7.16 (m, 1H), 7.02 – 6.64 (m, 4H), 3.92 and 3.92 (2×s, 3H), 3.81 and 3.81 (2×s, 3H), 3.32 and 3.29 (2×s, 3H), 2.47 and 2.29 (2×s, 3H). $^{13}C\{^1H\}$ NMR [151 MHz, $CDCl_3$; inseparable regioisomeric mixture of **4f** and **4f'** in (1:1)] δ = 186.6, 186.4, 154.4, 154.2, 152.8, 152.8, 150.7, 150.5, 149.9, 148.5, 145.1, 145.0, 138.2, 137.2 (2C), 136.6, 136.5, 133.8, 133.3, 132.3, 132.2, 131.1, 130.7, 130.5, 130.0, 129.9, 129.4 (2C), 128.7 (2C), 128.2, 127.5, 127.5 (2C), 127.4 (2C), 127.3, 127.1, 126.9, 126.6, 124.9, 124.8, 120.7, 120.5, 103.6, 103.5, 61.1, 60.9, 60.9 (2C), 56.5, 56.5, 21.5, 21.1 ppm. HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{27}H_{22}KO_4]^+$ 449.1150; found 449.1154.



2-Methyl-11-(*m*-tolyl)-5*H*-benzo[*a*]fluoren-5-one (4g):

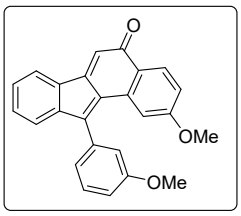
GP-3 was carried out with 2,3-diarylindene enoate ester **3ad** (38 mg, 0.1 mmol), TfOH (15 mg, 0.1 mmol), and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the benzo[*a*]fluorene

4g (16 mg, 48%) as maroon solid; mp = 117-118 °C [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**4g**) = 0.3, R_f(**3ad**) = 0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3741, 2208, 1999, 1833, 1537, 1270, 909, 755 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, J = 8.0 Hz, 1H), 7.53 – 7.32 (m, 2H), 7.30 – 7.19 (m, 3H), 7.14 – 7.07 (m, 2H), 7.05 – 6.97 (m, 2H), 6.88 – 6.80 (m, 1H), 6.77 (s, 1H), 2.39 (s, 3H), 2.04 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 186.4, 152.8, 149.01, 145.9, 142.7, 138.9, 135.8, 134.2, 133.4, 130.7, 129.8, 129.0, 128.8, 128.6, 128.3, 128.1, 127.7, 127.5, 125.7, 125.2, 122.4, 121.8, 121.2, 21.7, 21.5 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{19}O]^+$= 335.1430; found 335.1421.



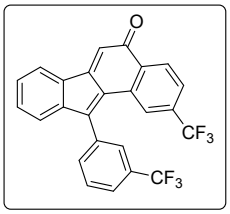
4-Methyl-11-(*m*-tolyl)-5*H*-benzo[*a*]fluoren-5-one (4g'):

GP-3 was carried out with 2,3-diarylindene enoate ester **3ad** (38 mg, 0.1 mmol), TfOH (15 mg, 0.1 mmol), and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the benzo[*a*]fluorene **4g'** (16 mg, 48%), as maroon solid; mp = 176-178 °C [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**4g'**) = 0.4, R_f(**3ad**) = 0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3740, 2748, 1843, 1633, 1539, 1267, 902, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.58 – 7.49 (m, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.31 (d, J = 7.7 Hz, 1H), 7.29 – 7.21 (m, 3H), 7.19 – 7.14 (m, 2H), 7.09 – 7.01 (m, 2H), 6.90 – 6.84 (m, 1H), 6.79 (s, 1H), 2.73 (s, 3H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 188.9, 150.8, 147.8, 146.3, 141.9, 139.1, 135.5, 134.9, 134.6, 132.0, 131.3, 130.5, 129.6, 129.2, 128.5, 128.5, 128.3, 127.8, 125.2, 124.1, 122.8, 122.2, 121.7, 23.9, 21.5 ppm. HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{25}H_{18}KO]^+$ 373.0989; found 373.0991.



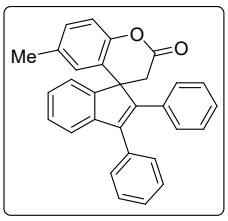
2-Methoxy-11-(3-methoxyphenyl)-5*H*-benzo[*a*]fluoren-5-one (4h):

GP-3 was carried out with 2,3-diarylindene enoate ester **3ac** (41 mg, 0.1 mmol), TfOH (15 mg, 0.1 mmol), and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5), furnished the benzo[*a*]fluorene **4h** (30 mg, 83%), as maroon solid; mp = 117-119 °C [TLC control (petroleum ether/ethyl acetate 99:4), R_f(**4h**) = 0.4, R_f(**3ac**) = 0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2942, 2118, 2028, 1636, 1590, 1465, 1270, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 8.2 Hz, 1H), 7.41 (dd, *J* = 9.6 and 6.0 Hz, 2H), 7.09 (dd, *J* = 5.3 and 3.0 Hz, 2H), 7.04 – 6.90 (m, 3H), 6.84 (dd, *J* = 5.2 and 3.2 Hz, 1H), 6.70 (dd, *J* = 10.2 and 2.2 Hz, 3H), 3.77 (s, 3H), 3.38 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 185.6, 162.5, 160.3, 152.2, 148.7, 145.6, 135.7, 135.5, 135.1, 130.6, 130.5, 129.5, 128.2, 127.9, 124.2, 122.3, 121.8, 121.5, 120.2, 115.4, 114.8, 113.1, 108.4, 55.4, 54.8 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{19}O_3]^+$ 367.1329; found 367.1337.



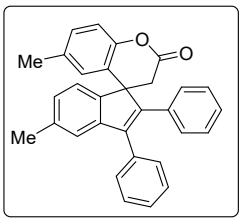
2-(Trifluoromethyl)-11-(3-(trifluoromethyl)phenyl)-5*H*-benzo[*a*]fluoren-5-one (4i):

GP-3 was carried out with 2,3-diarylindene enoate ester **3aj** (48.8 mg, 0.1 mmol) and TfOH (15 mg, 0.1 mmol) DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the benzo[*a*]fluorene **4i** (30 mg, 67%), as maroon solid; mp = 173-175 °C [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**4i**) = 0.5, R_f(**3aj**) = 0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2399, 2185, 1735, 1645, 1324, 1132, 903, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 1 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.51 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.39 (s, 1H), 7.27 – 7.24 (m, 2H), 6.95 – 6.91 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 185.0, 152.9, 148.3, 144.8, 135.3, 134.3, 133.8 (q, *J* = 32.7 Hz), 133.2, 132.3, 132.2 (q, *J* = 33.2 Hz), 131.5, 131.3, 130.2, 129.0, 128.4, 127.4, 126.3 (q, *J* = 3.4 Hz), 125.2 (q, *J* = 3.9 Hz), 124.4 (q, *J* = 3.6 Hz), 123.6 (q, *J* = 272.5 Hz), 123.2 (q, *J* = 272.7 Hz), 122.6, 122.5, 121.8 (q, *J* = 3.6 Hz), 121.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.91 (s), -64.09 (s) ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{13}F_6O]^+$ 443.0865; found 443.0884.



6-Methyl-2',3'-diphenylspiro[chromane-4,1'-inden]-2-one (6a):

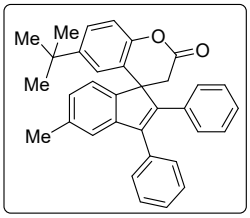
GP-4 was carried out with 2,3-diarylindene enoate ester **3aa** (35 mg, 0.1 mmol), phenol **5a** (32 mg, 0.3 mmol), TfOH (7.5 mg, 0.05 mmol), and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the spiro-chromenone indene **6a** (37 mg, 90%), as red oil. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**3aa**) = 0.5, R_f(**5a**) = 0.2, R_f(**6a**) = 0.3 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3050, 2925, 1771, 1603, 1268, 1198, 1027, 756, 703 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.42 – 7.28 (m, 8H), 7.27 – 7.21 (m, 1H), 7.16 (d, J = 7.3 Hz, 1H), 7.10 (ddd, J = 7.1, 4.9 and 2.2 Hz, 3H), 7.03 (d, J = 8.3 Hz, 1H), 6.86 (dd, J = 8.3 and 1.2 Hz, 2H), 6.82 (d, J = 1.7 Hz, 1H), 3.02 (d, J = 16.2 Hz, 1H), 2.87 (d, J = 16.2 Hz, 1H), 2.23 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 167.5, 150.2, 149.5, 146.1, 142.8, 141.6, 134.6, 134.3, 133.8, 129.9, 129.7 (2C), 129.4 (2C), 128.5 (2C), 128.1 (2C), 128.0, 127.8, 127.78, 126.88, 126.2, 123.5, 122.4, 121.4, 117.5, 56.2, 37.4, 20.9 ppm. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{30}H_{22}NaO_2]^+$ 437.1512; found 437.1497.



5',6-Dimethyl-2',3'-diphenylspiro[chromane-4,1'-inden]-2-one (6b):

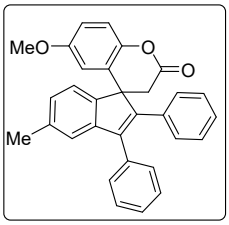
GP-4 was carried out with 2,3-diarylindene enoate ester **3ba** (37 mg, 0.1 mmol), phenol **5a** (32 mg, 0.3 mmol), TfOH (7.5 mg, 0.05 mmol), and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the spiro-chromenone indene **6b** (39 mg, 91%), as white solid; mp = 169-171 °C [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**3ba**) = 0.5, R_f(**5a**) = 0.2, R_f(**6b**) = 0.3 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3397, 3031, 1753, 1606, 1496, 1350. 1200, 816, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 7.31 (m, 5H), 7.23 – 7.14 (m, 3H), 7.14 – 6.99 (m, 5H), 6.86 (ddd, J = 9.6, 5.7, 2.0 Hz, 3H), 3.01 (d, J = 16.2 Hz, 1H), 2.85 (d, J = 16.2 Hz, 1H), 2.38 (s, 3H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 167.5, 150.5, 146.7,

146.3, 143.0, 141.6, 137.9, 134.6, 134.5, 133.9, 129.8, 129.7 (2C), 129.4 (2C), 128.5 (2C), 128.1 (2C), 127.8, 127.7, 127.6, 126.2, 123.8, 122.1, 122.1, 117.4, 55.8, 37.6, 21.5, 20.9 ppm. HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{31}H_{28}NO_2]^+$ 446.2115 found 446.2116.



6-(*tert*-Butyl)-5'-methyl-2',3'-diphenylspiro[chromane-4,1'-inden]-2-one (6c):

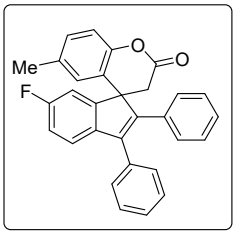
GP-4 was carried out with 2,3-diarylindene enoate ester **3ba** (37 mg, 0.1 mmol), phenol **5b** (45 mg, 0.3 mmol), TfOH (7.5 mg, 0.05 mmol), and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the spiro-chromenone indene **6c** (38 mg, 80%), as white solid; mp = 189-191 °C [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**3ba**) = 0.5, R_f(**5b**) = 0.2, R_f(**6c**) = 0.3 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2959, 1767, 1604, 1484, 1265, 1028, 1198, 815, 726 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.40 (d, J = 4.4 Hz, 4H), 7.38 – 7.32 (m, 2H), 7.23 (d, J = 7.8 Hz, 2H), 7.16 (dd, J = 5.0 and 3.7 Hz, 1H), 7.14 – 7.04 (m, 5H), 6.92 – 6.87 (m, 2H), 3.06 (d, J = 16.1 Hz, 1H), 2.84 (d, J = 16.1 Hz, 1H), 2.39 (s, 3H), 1.23 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 167.7, 150.3, 147.8, 146.8, 146.1, 142.8, 142.1, 137.8, 134.6, 134.0, 129.8 (2C), 129.4 (2C), 128.6 (2C), 128.1 (2C), 127.7, 127.7, 127.5, 126.1, 123.5, 122.9, 122.1, 122.0, 117.1, 55.9, 37.6, 34.4, 31.3 (3C), 21.5 ppm. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{34}H_{30}NaO_2]^+$ 493. 2138 found 493. 2126.



6-Methoxy-5'-methyl-2',3'-diphenylspiro[chromane-4,1'-inden]-2-one (6d):

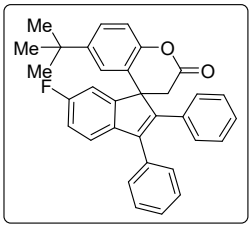
GP-4 was carried out with 2,3-diarylindene enoate ester **3ba** (37 mg, 0.1 mmol), phenol **5c** (37 mg, 0.3 mmol), TfOH (7.5 mg, 0.05 mmol), and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the spiro-chromenone indene **6d** as yellow oil (41 mg, 92%), as yellow oil **[**TLC control (petroleum ether/ethyl acetate 97:3), R_f(**3ba**) = 0.5, R_f(**5c**) = 0.3, R_f(**6d**) = 0.4 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2931, 1766, 1601, 1486, 1269, 1194, 1036, 755, 705 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.31 (m, 5H), 7.22 – 7.04 (m, 7H), 6.92 – 6.82 (m, 3H), 6.58 (d, *J* = 3.0 Hz, 1H), 3.69 (s, 3H), 3.02 (d, *J* = 16.3 Hz, 1H), 2.86 (d, *J* = 16.2 Hz, 1H), 2.37 (s, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ = 167.5, 156.4, 146.5, 146.0, 142.9, 141.9, 138.0, 134.4, 133.8, 129.7 (2C), 129.4 (2C), 128.6 (2C), 128.1 (3C), 127.8, 127.7, 127.63, 125.3, 122.2, 122.1, 118.4, 114.1, 111.0, 55.9, 55.5, 37.3, 21.5 ppm. HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{31}H_{24}KO_3]^+$ 483.1357 found 483.1369.



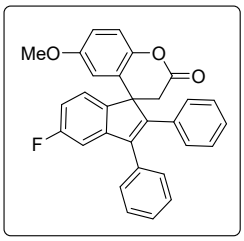
6'-Fluoro-6-methyl-2',3'-diphenylspiro[chromane-4,1'-inden]-2-one (6e):

GP-4 was carried out with 2,3-diarylindene enoate ester **3ca** (37 mg, 0.1 mmol), phenol **5a** (32 mg, 0.3 mmol), TfOH (7.5 mg, 0.05 mmol), and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the spiro-chromenone indene **6e** (30 mg, 70%), as white solid; mp = 183-185 °C [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**3ca**)=0.5, R_f(**5a**) = 0.2, R_f(**6e**) = 0.3 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2925, 1770, 1597, 1481, 1265, 1194, 917, 750, 706 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 – 7.27 (m, 6H), 7.21 – 7.08 (m, 4H), 7.07 – 6.99 (m, 3H), 6.87 – 6.79 (m, 3H), 3.02 (d, *J* = 16.3 Hz, 1H), 2.87 (d, *J* = 16.3 Hz, 1H), 2.26 (s, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ = 166.9, 162.1 (d, *J* = 247.1 Hz), 151.4 (d, *J* = 7.6 Hz), 150.5, 145.9 (d, *J* = 4.2 Hz), 140.6, 138.7 (d, *J* = 1.8 Hz), 134.8, 134.1, 133.6, 130.2, 129.7 (2C), 129.3 (2C), 128.6 (2C), 128.2 (2C), 127.9, 127.9, 126.2, 122.9, 122.4 (d, *J* = 8.6 Hz), 117.63, 114.95 (d, *J* = 22.6 Hz), 110.4 (d, *J* = 23.8 Hz), 56.11, 37.37, 20.87 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.20 (s) ppm. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{30}H_{21}FNaO_2]^+$ 455.1418 found 455.1427.



6-(*tert*-Butyl)-6'-fluoro-2',3'-diphenylspiro[chromane-4,1'-inden]-2-one (6f):

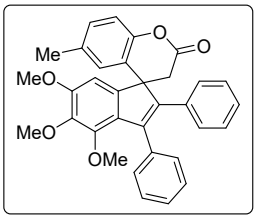
GP-4 was carried out with 2,3-diarylindene enoate ester **3ca** (37 mg, 0.1 mmol), phenol **5b** (45 mg, 0.3 mmol), TfOH (7.5 mg, 0.05 mmol), and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the spiro-chromenone indene **6f** (35 mg, 75%), as pink oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**3ca**) = 0.5, R_f(**5b**) = 0.2, R_f(**6f**) = 0.3 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2959, 1773, 1598, 1353, 1268, 1196, 1130, 917, 756, 705 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.30 (m, 7H), 7.15 (dd, J = 5.0 and 3.6 Hz, 1H), 7.12 – 7.06 (m, 4H), 7.07 – 6.98 (m, 2H), 6.85 (dd, J = 5.3 and 3.3 Hz, 2H), 3.06 (d, J = 16.2 Hz, 1H), 2.82 (d, J = 16.2 Hz, 1H), 1.22 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 167.2, 162.1 (d, J = 253.6 Hz), 151.5 (d, J = 7.7 Hz), 150.2, 148.1, 145.6 (d, J = 4.2 Hz), 141.2, 138.5 (d, J = 2.0 Hz), 134.2, 133.7, 129.7 (2C), 129.3 (2C), 128.7 (2C), 128.2 (2C), 127.9, 127.9, 126.5, 122.7 , 122.6, 122.4 (d, J = 8.6 Hz), 117.3, 114.9 (d, J = 22.5 Hz), 110.3 (d, J = 23.8 Hz), 56.2, 37.3, 34.4, 31.25 (3C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.28 (s) ppm. HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{33}H_{31}FNO_2]^+$ 492.2333 found 492.2350.



5'-Fluoro-6-methoxy-2',3'-diphenylspiro[chromane-4,1'-inden]-2-one (6g):

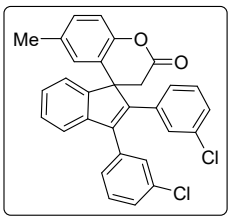
GP-4 was carried out with 2,3-diarylindene enoate ester **3ia** (37 mg, 0.1 mmol), phenol **5c** (37 mg, 0.3 mmol), TfOH (7.5 mg, 0.05 mmol), and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the spiro-chromenone indene **6g** (35 mg, 78%), as yellow solid; mp = 175-177 °C [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**3ia**) = 0.7, R_f(**5c**) = 0.2, R_f(**6g**) = 0.3 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2932, 1766, 1600, 1483, 1268, 1196, 1035, 755, 704 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.38 – 7.32 (m, 4H), 7.25 – 7.01 (m, 6H), 6.97 – 6.85 (m, 4H), 6.79 – 6.70 (m, 1H), 6.56 (d, J = 3.0 Hz, 1H), 3.71 (s, 3H), 3.02 (d, J = 16.3 Hz, 1H), 2.87 (d, J = 16.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 167.2, 163.1 (d, J = 245.5 Hz), 156.5, 147.9, 146.5, 145.1 (d, J = 8.6 Hz), 144.6 (d, J = 2.0 Hz), 141.0 (d, J = 2.9 Hz), 133.7, 133.3, 129.6 (2C), 129.2 (2C), 128.7 (2C), 128.2 (2C), 128.1, 128.1, 124.6, 123.4 (d, J = 9.4 Hz), 118.6, 114.3, 113.5 (d, J = 23.4 Hz), 110.9, 108.9 (d, J = 24.0 Hz), 55.8, 55.5, 37.2 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -113.64 (s) ppm. HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{30}H_{21}FKO_3]^+$ 487.1106 found 487.1121.



4',5',6'-Trimethoxy-6-methyl-2',3'-diphenylspiro[chromane-4,1'-inden]-2-one (6h):

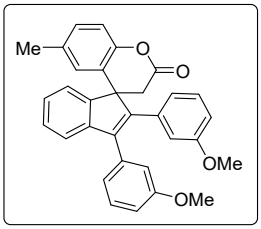
GP-4 was carried out with 2,3-diarylindene enoate ester **3fa** (44 mg, 0.1 mmol), phenol **5a** (32 mg, 0.3 mmol), TfOH (7.5 mg, 0.05 mmol), and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5), furnished the spiro-chromenone indene **6h** (43 mg, 85%), as yellow oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**3fa**) = 0.2, R_f(**5a**) = 0.5, R_f(**6h**) = 0.3 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2937, 1766, 1589, 1468, 1344, 1261, 1117, 1035, 752 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.39 – 7.33 (m, 2H), 7.30 – 7.23 (m, 3H), 7.14 – 7.00 (m, 5H), 6.85 (d, J = 1.6 Hz, 1H), 6.81 – 6.73 (m, 2H), 6.62 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.40 (s, 3H), 2.99 (d, J = 16.2 Hz, 1H), 2.85 (d, J = 16.2 Hz, 1H), 2.28 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 167.3, 153.3, 150.4, 148.8, 145.6, 145.0, 142.6, 141.1, 135.8, 134.7, 133.8, 129.9, 129.8 (2C), 129.7 (2C), 128.1, 127.9 (2C), 127.5 (3C), 127.1, 126.4, 123.8, 117.4, 102.4, 61.1, 61.0, 56.4, 56.2, 37.9, 31.1, 20.9 ppm. HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{33}H_{28}KO_5]^+$ 543.1568 found 543.1586.



2',3'-Bis(3-chlorophenyl)-6-methylspiro[chromane-4,1'-inden]-2-one (6i):

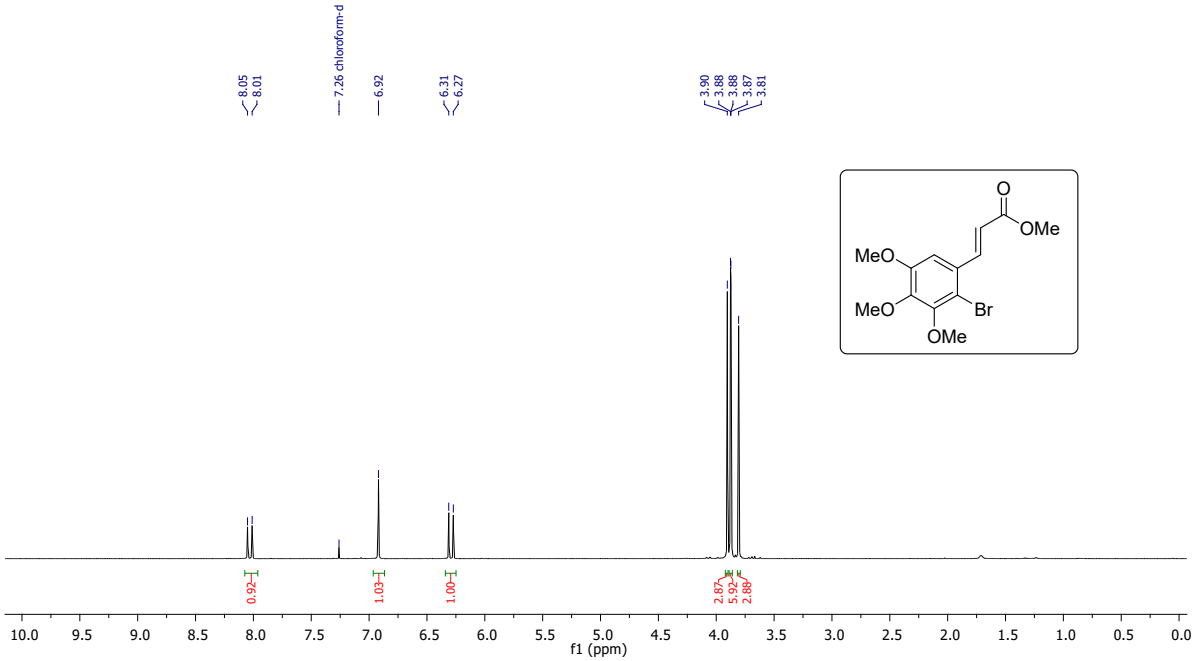
GP-4 was carried out with 2,3-diarylindene enoate ester **3ak** (42 mg, 0.1 mmol), phenol **5a** (32 mg, 0.3 mmol), TfOH (7.5 mg, 0.05 mmol), and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the spiro-chromenone indene **6i** (35 mg, 72%), as yellow oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**3ak**) = 0.5, R_f(**5a**) = 0.2, R_f(**6i**) = 0.3 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3055, 1765, 1595, 1484, 1263, 1197, 1014, 822, 726 cm^{-1}. ^1H NMR

(400 MHz, $CDCl_3$) δ = 7.37 – 7.22 (m, 8H), 7.17 – 7.05 (m, 3H), 7.01 (d, J = 8.3 Hz, 1H), 6.77 – 6.66 (m, 3H), 2.90 (s, 2H), 2.21 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 166.9, 150.6, 149.2, 145.7, 142.3, 140.8, 134.8, 134.2, 133.9, 132.4, 131.9, 130.9 (2C), 130.7 (2C), 130.2, 128.9 (2C), 128.6 (2C), 128.2, 127.3, 126.1, 122.9, 122.6, 121.3, 117.6, 56.2, 37.5, 20.8 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{30}H_{21}Cl_2O_2]^+$ 483.0913 found 483.0935.

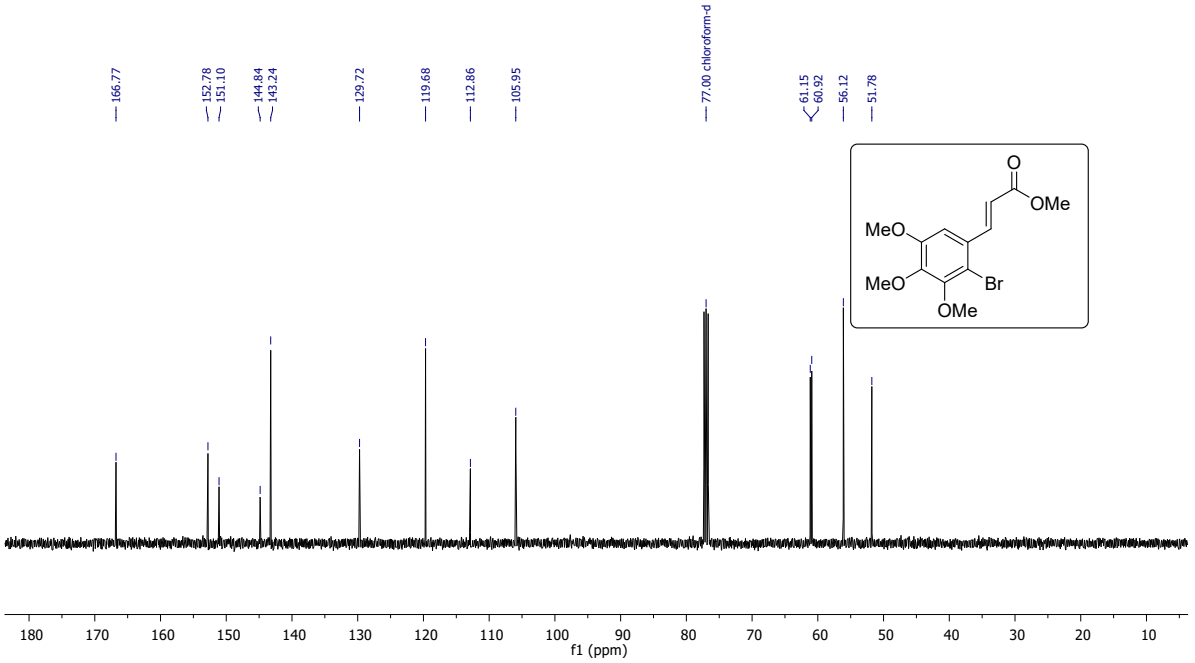


2',3'-Bis(3-methoxyphenyl)-6-methylspiro[chromane-4,1'-inden]-2-one (6j):

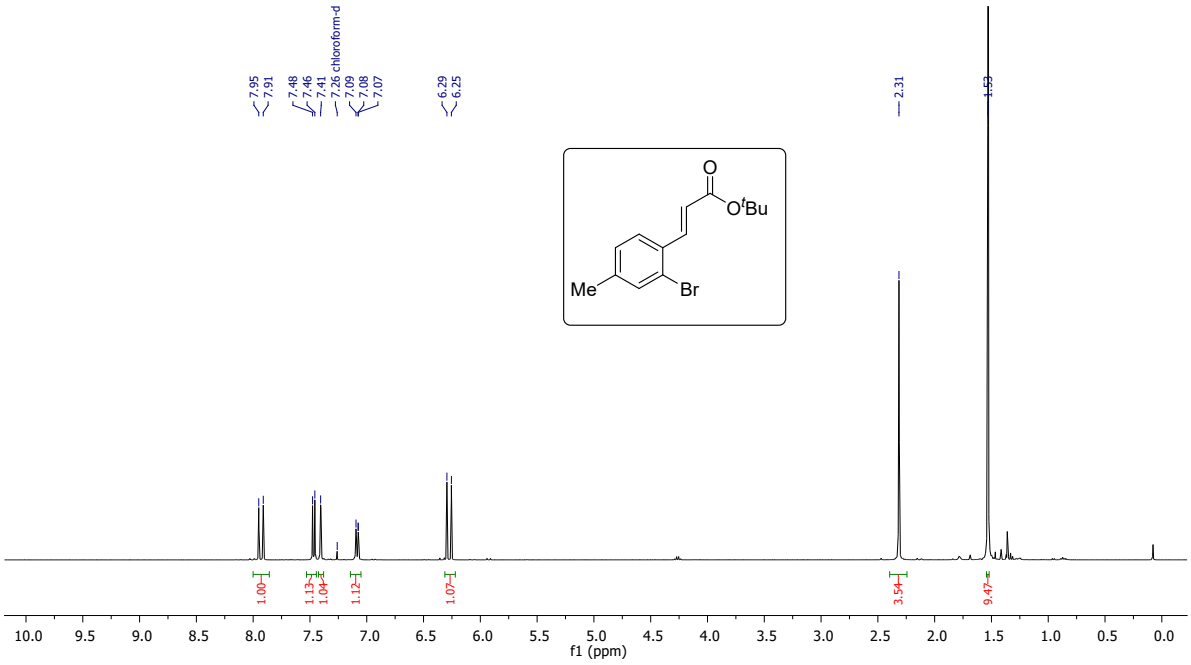
GP-4 was carried out with 2,3-diarylindene enoate ester **3ac** (41 mg, 0.1 mmol), phenol **5a** (32 mg, 0.3 mmol), TfOH (7.5 mg, 0.05 mmol) in DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5), furnished the spiro-chromenone indene **6j** (40 mg, 85%), as yellow oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**3ac**) = 0.4, R_f(**5a**) = 0.6, R_f(**6j**) = 0.7 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2942, 1764, 1587, 1475, 1260, 1200, 1040, 892, 724 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, J = 7.5 Hz, 1H), 7.33 – 7.16 (m, 4H), 7.09 – 7.02 (m, 1H), 7.02 – 6.93 (m, 3H), 6.91 – 6.86 (m, 1H), 6.84 (d, J = 1.1 Hz, 1H), 6.75 (d, J = 1.7 Hz, 1H), 6.68 (dd, J = 4.6 and 3.7 Hz, 1H), 6.46 – 6.40 (m, 1H), 6.40 – 6.34 (m, 1H), 3.69 (d, J = 5.1 Hz, 3H), 3.44 (s, 3H), 3.00 (d, J = 16.2 Hz, 1H), 2.82 (d, J = 16.2 Hz, 1H), 2.18 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 166.4, 158.6, 158.0, 149.5, 148.5, 144.9, 141.7, 140.5, 134.7, 134.0, 133.6, 128.9, 128.6, 128.2, 127.1, 125.9, 125.3, 122.5, 121.4, 121.2, 120.8, 120.5, 116.5, 113.8, 113.7, 113.1, 112.4, 55.1, 54.2, 53.8, 36.4, 19.8 ppm. HRMS (ESI) *m/z*: $[M]^+$ calcd for $[C_{32}H_{26}O_4]^+$ 474.1826 found 474.1843.



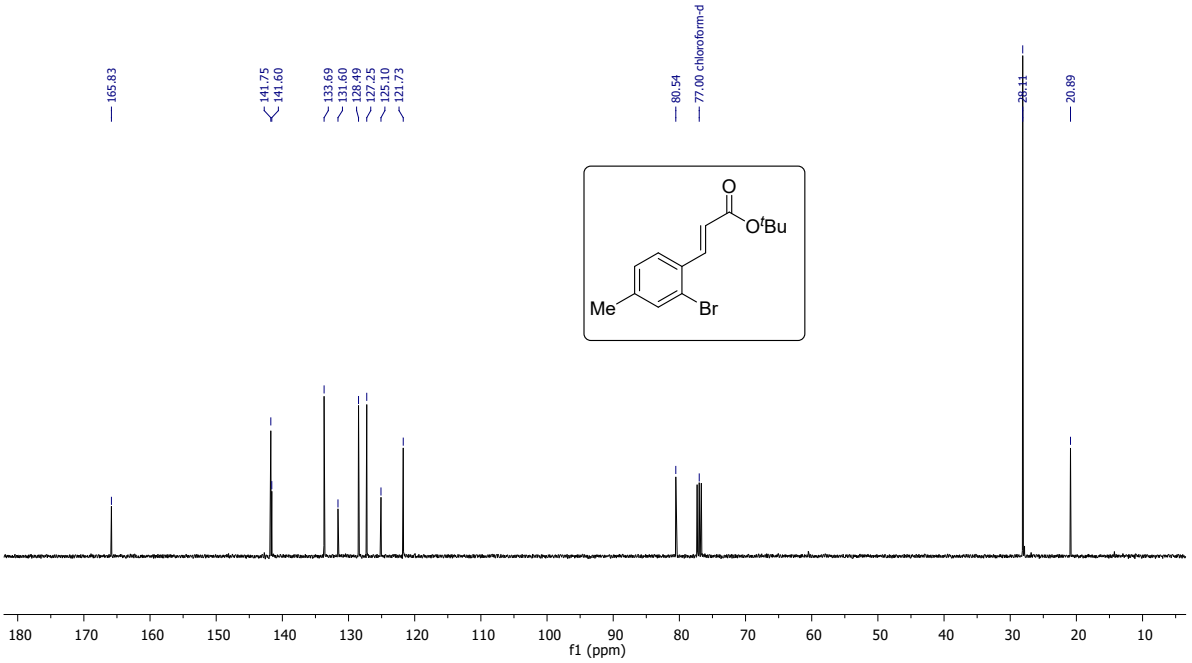
^{1}H NMR (400 MHz) spectrum of **1l** in $CDCl_3$



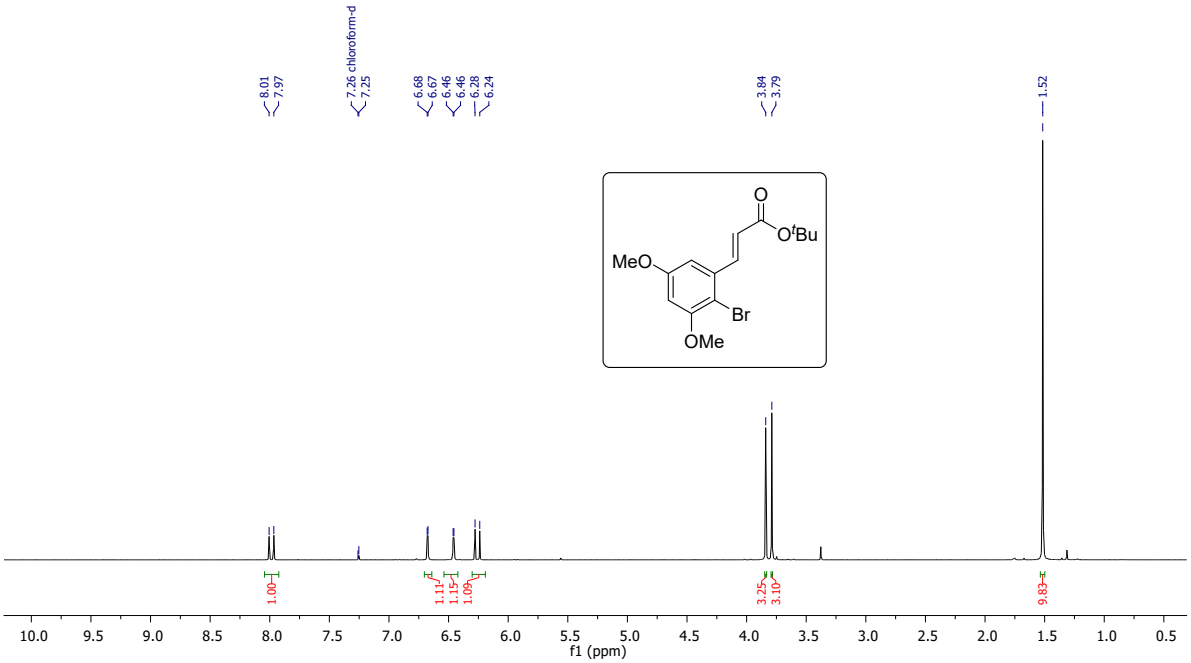
^{13}C{H} NMR (100 MHz) spectrum of **1l** in $CDCl_3$



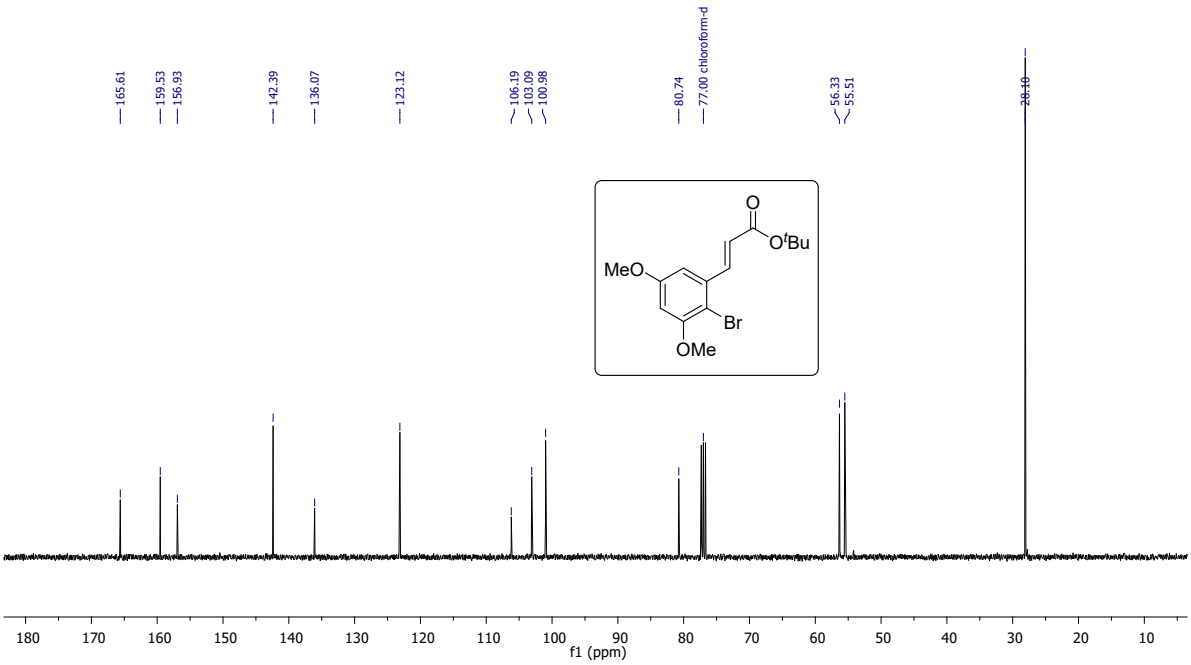
^{1}H NMR (400 MHz) spectrum of **1n** in $CDCl_3$



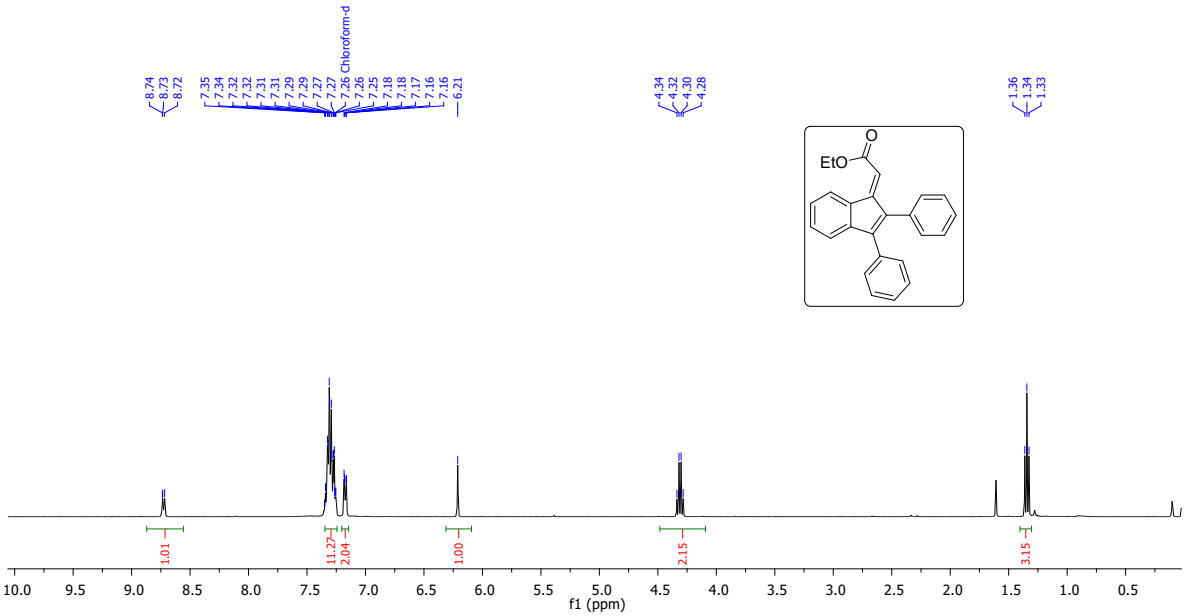
^{13}C{H} NMR (100 MHz) spectrum of **1n** in $CDCl_3$



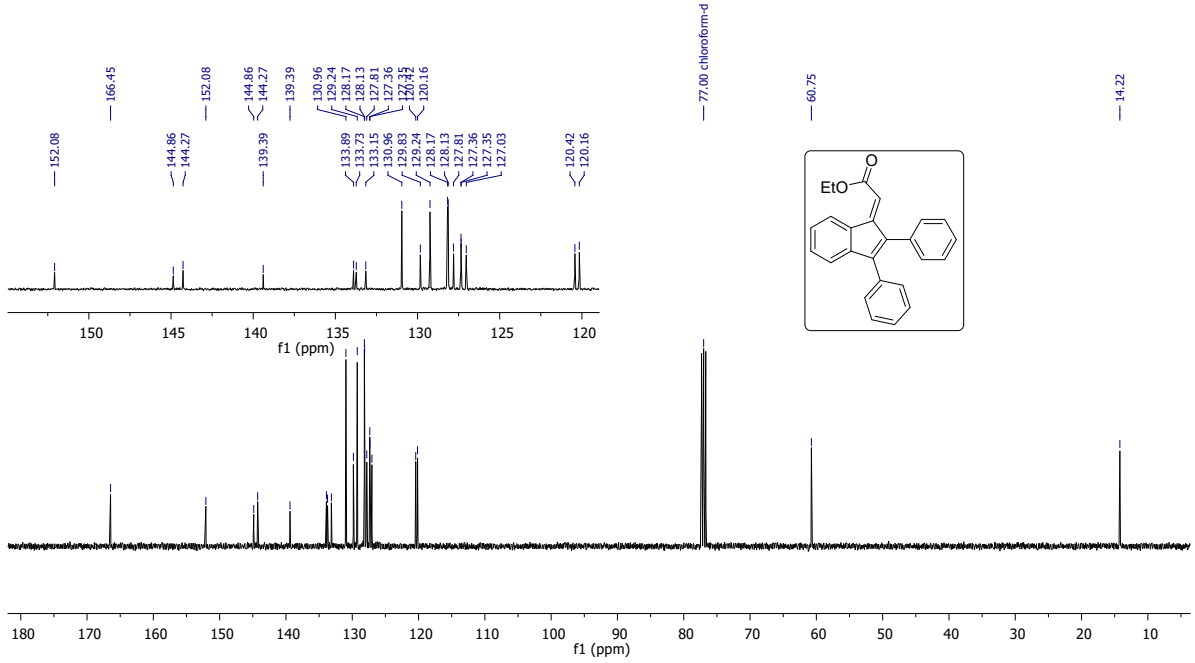
^{1}H NMR (400 MHz) spectrum of **1o** in $CDCl_3$



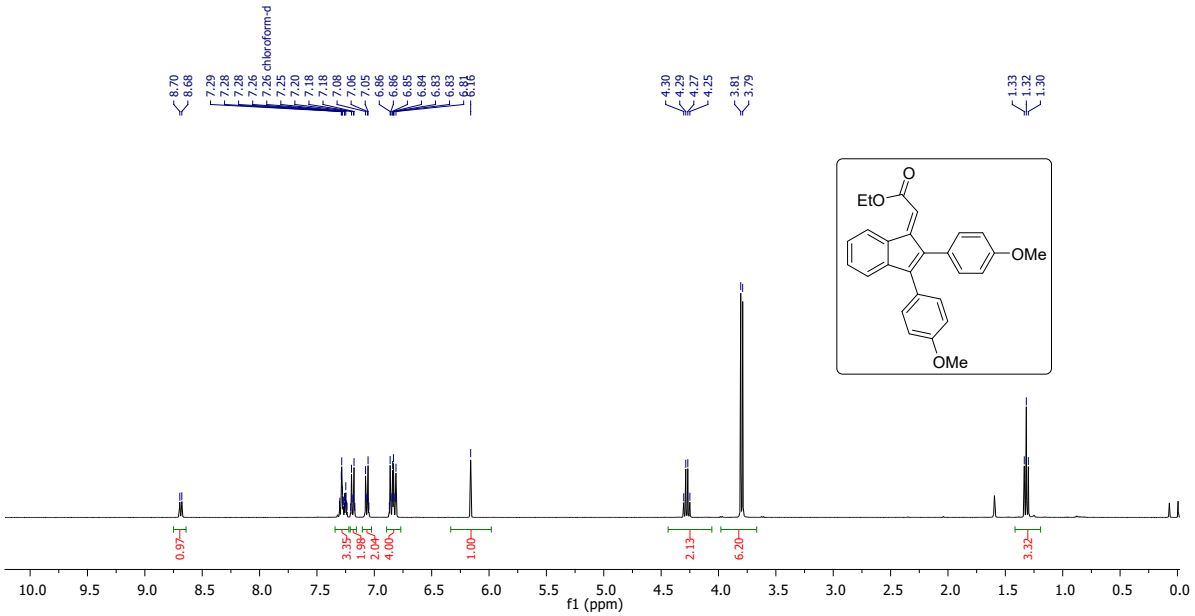
^{13}C{H} NMR (100 MHz) spectrum of **1o** in $CDCl_3$



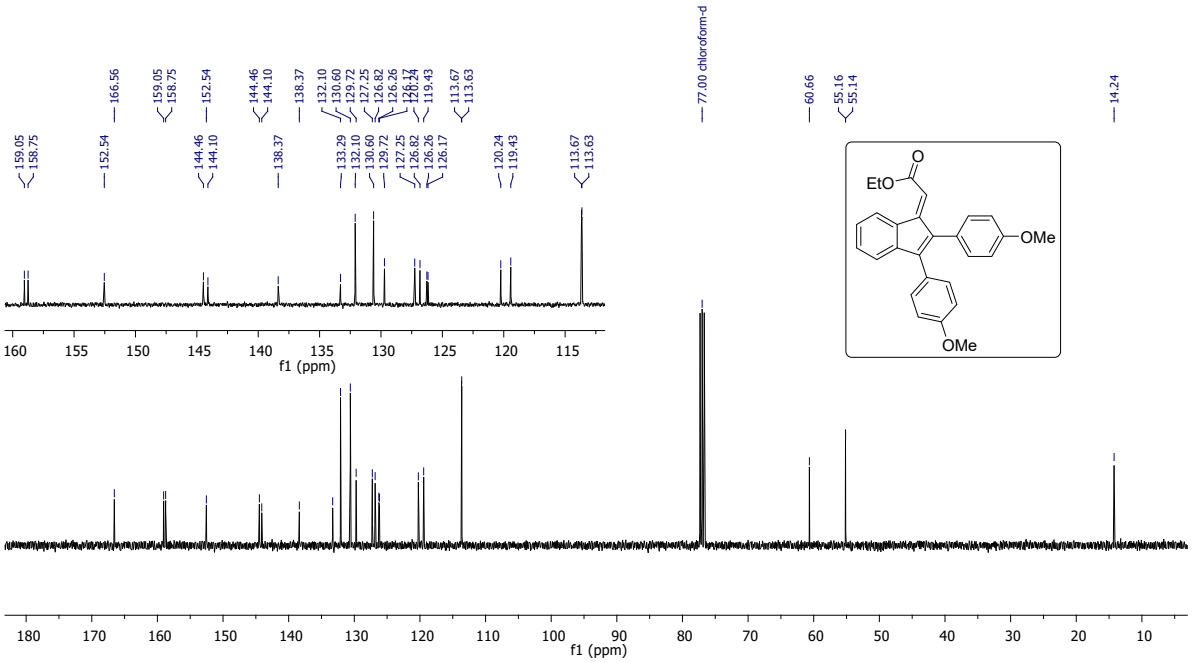
^{1}H NMR (400 MHz) spectrum of **3aa** in $CDCl_3$



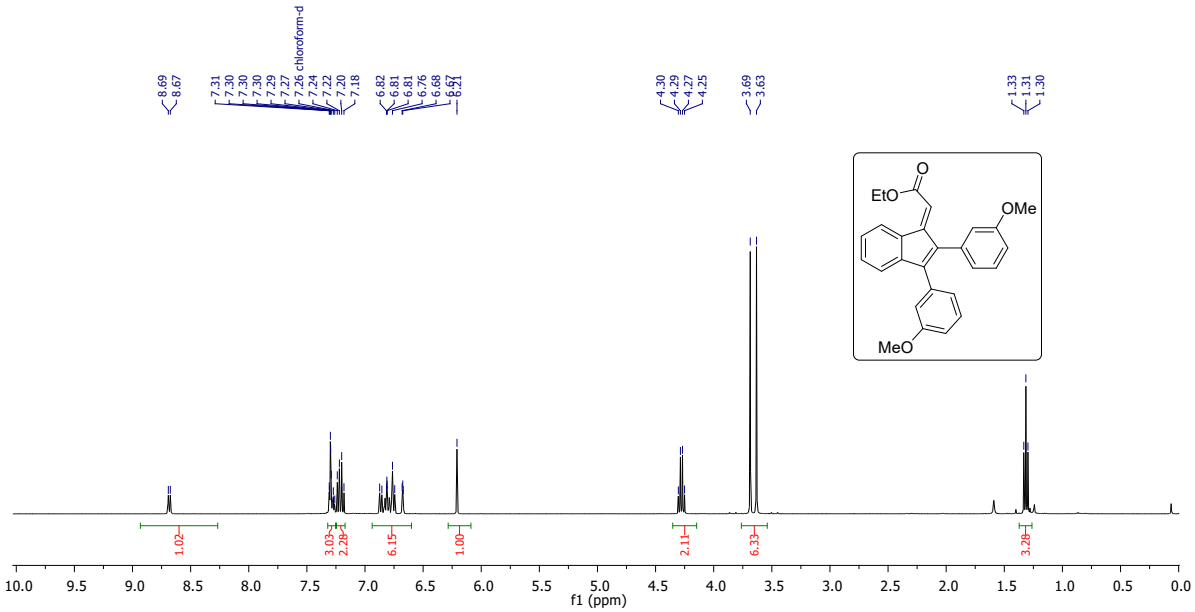
^{13}C{H} NMR (100 MHz) spectrum of **3aa** in $CDCl_3$



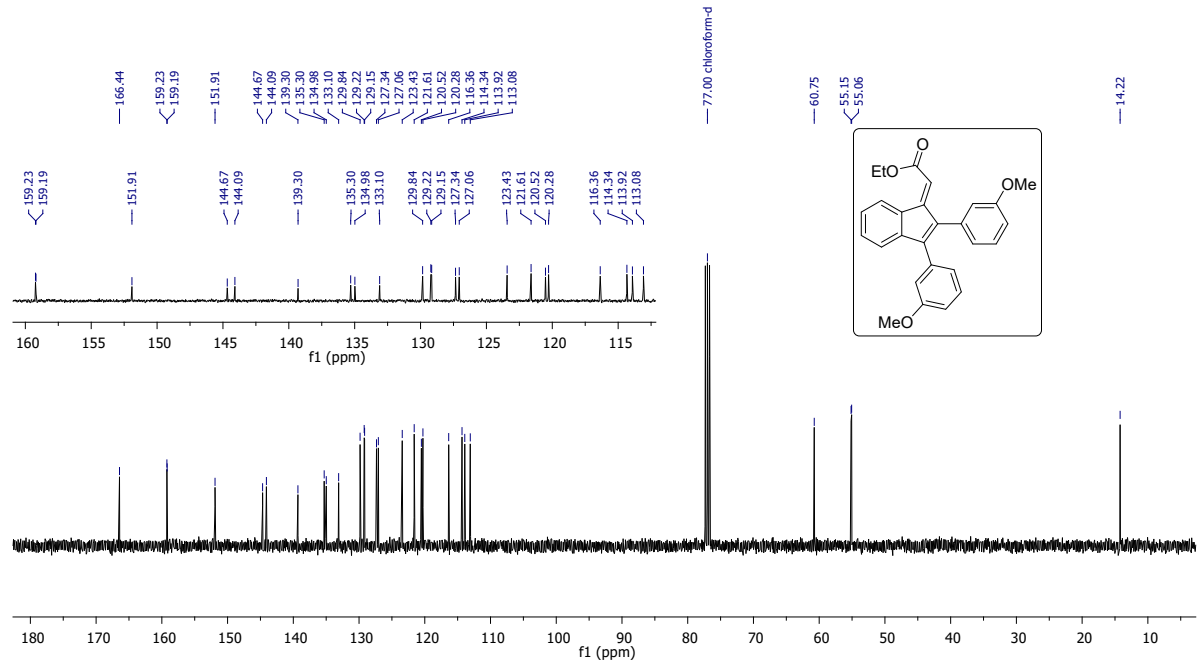
^{1}H NMR (400 MHz) spectrum of **3ab** in $CDCl_3$



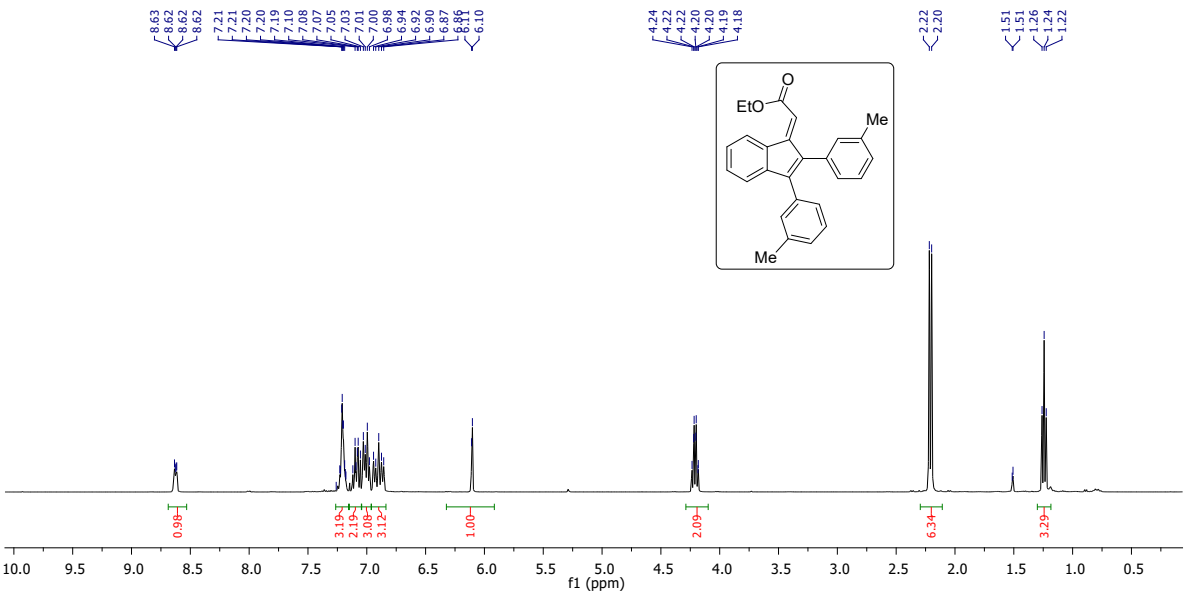
^{13}C{H} NMR (100 MHz) spectrum of **3ab** in $CDCl_3$



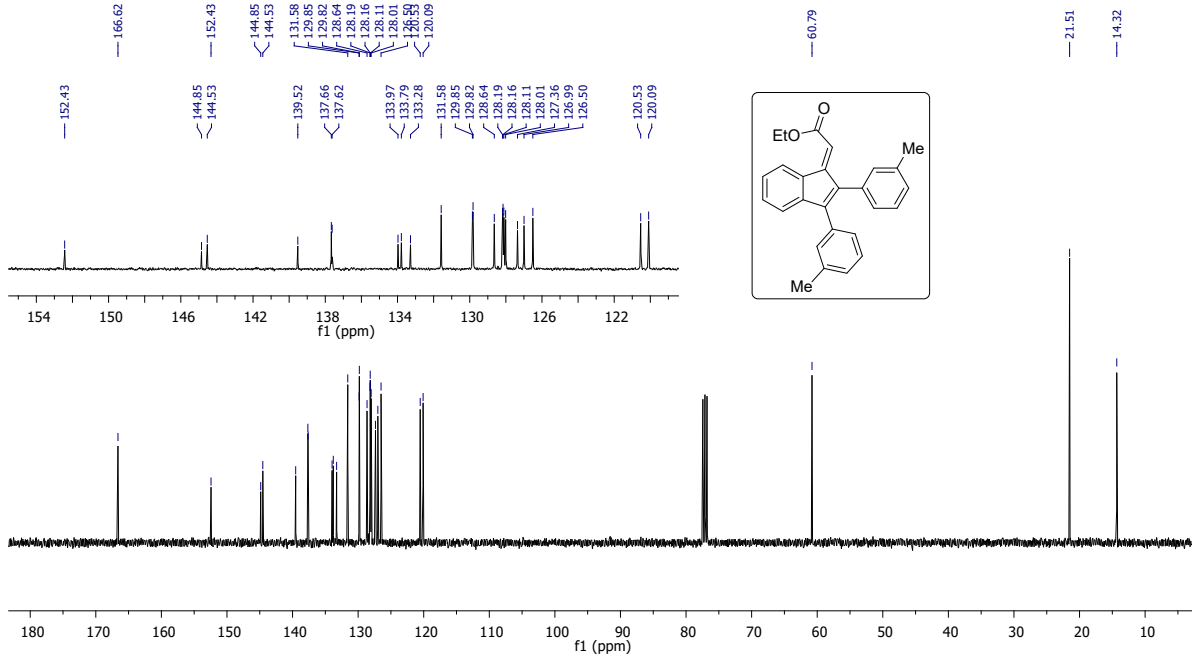
^{1}H NMR (400 MHz) spectrum of **3ac** in $CDCl_3$



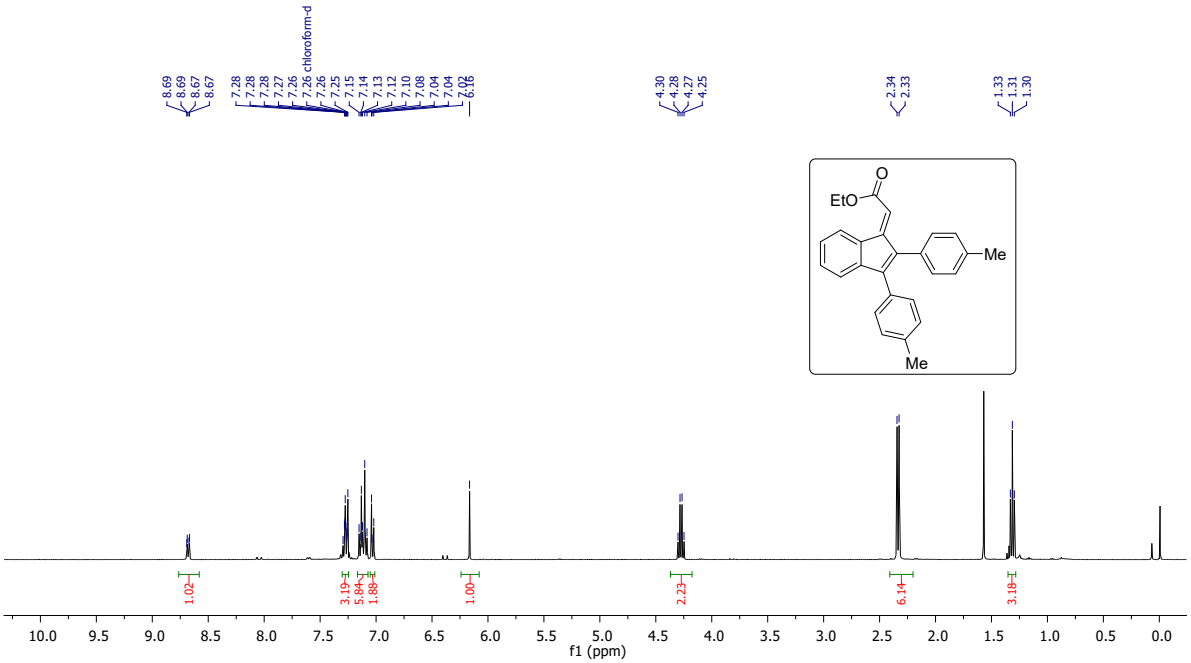
^{13}C{H} NMR (100 MHz) spectrum of **3ac** in $CDCl_3$



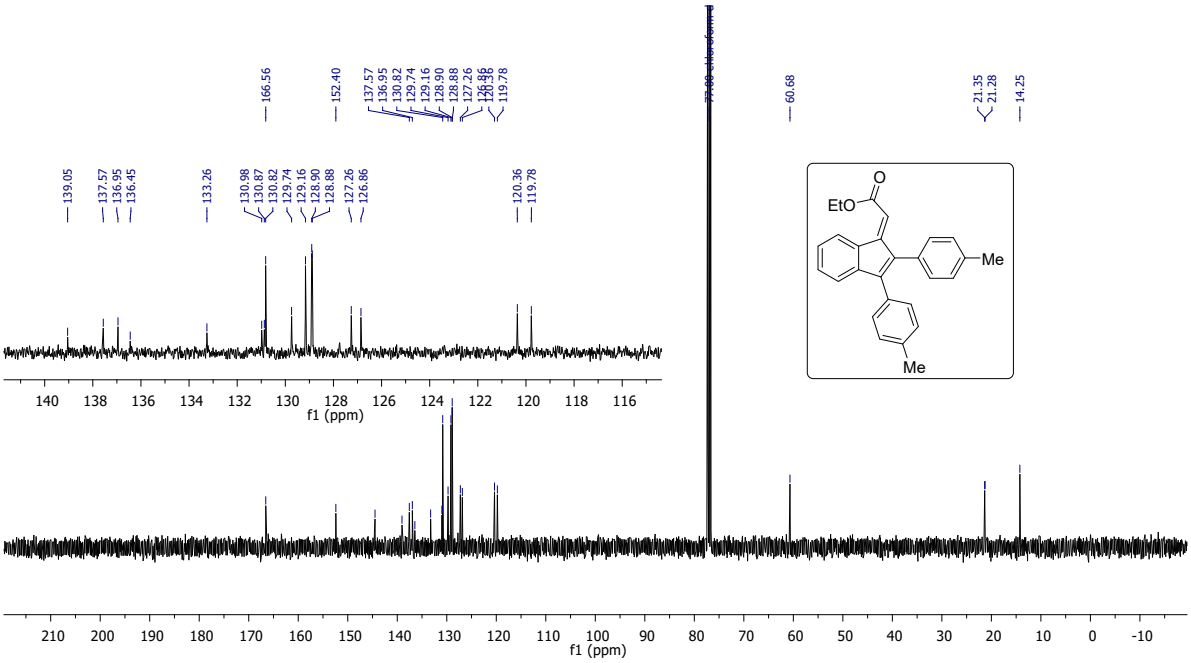
^{1}H NMR (400 MHz) spectrum of **3ad** in $CDCl_3$



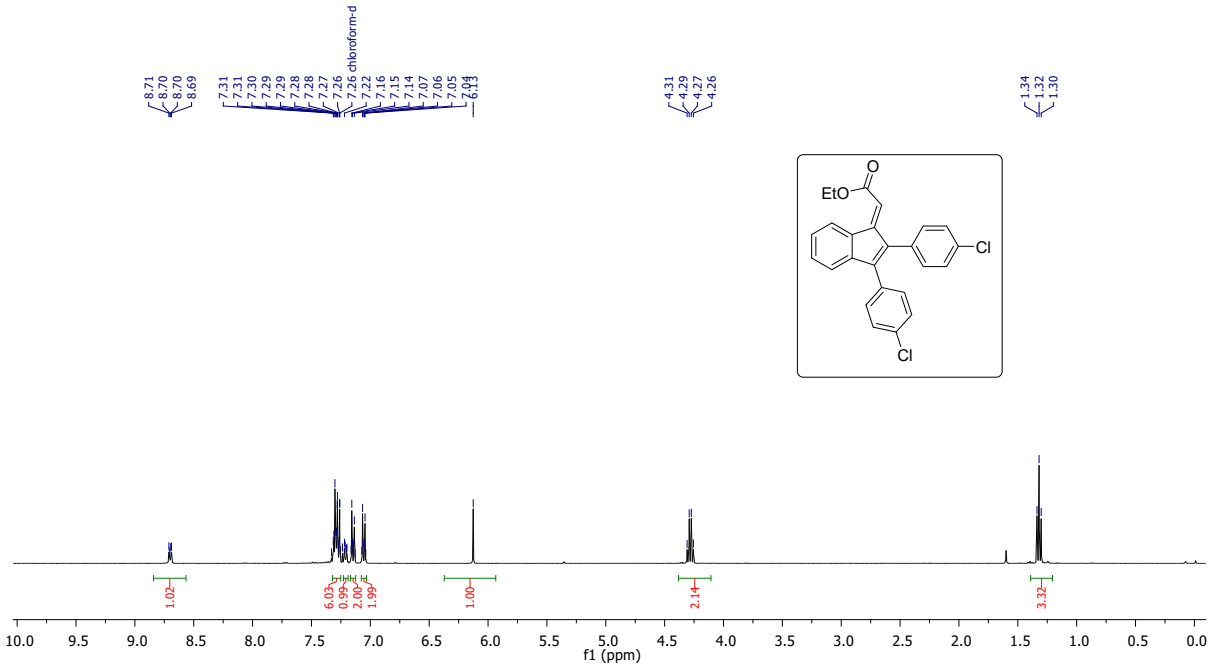
^{13}C{H} NMR (100 MHz) spectrum of **3ad** in $CDCl_3$



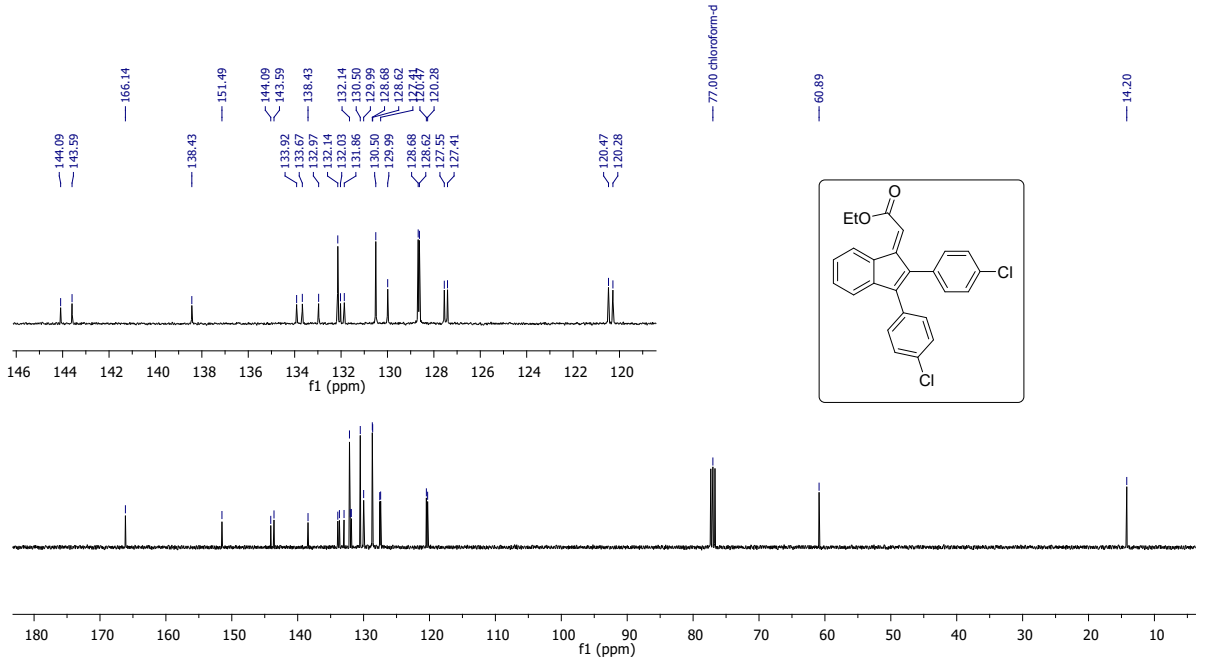
^{1}H NMR (400 MHz) spectrum of **3ae** in $CDCl_3$



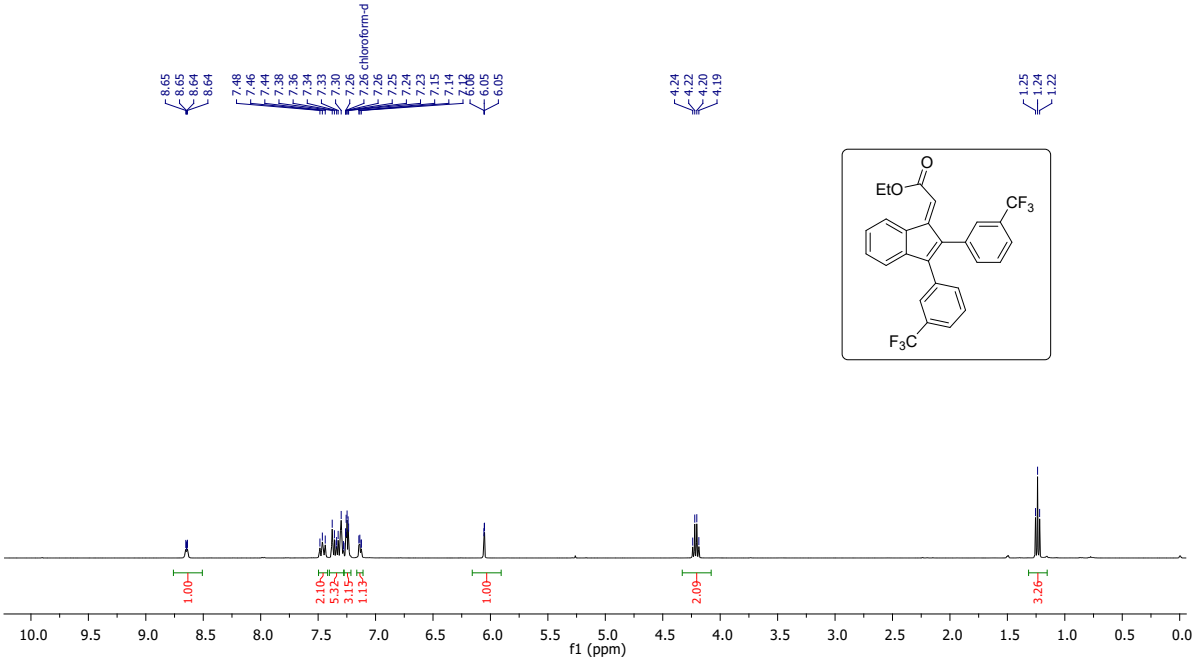
^{13}C{H} NMR (100 MHz) spectrum of **3ae** in $CDCl_3$



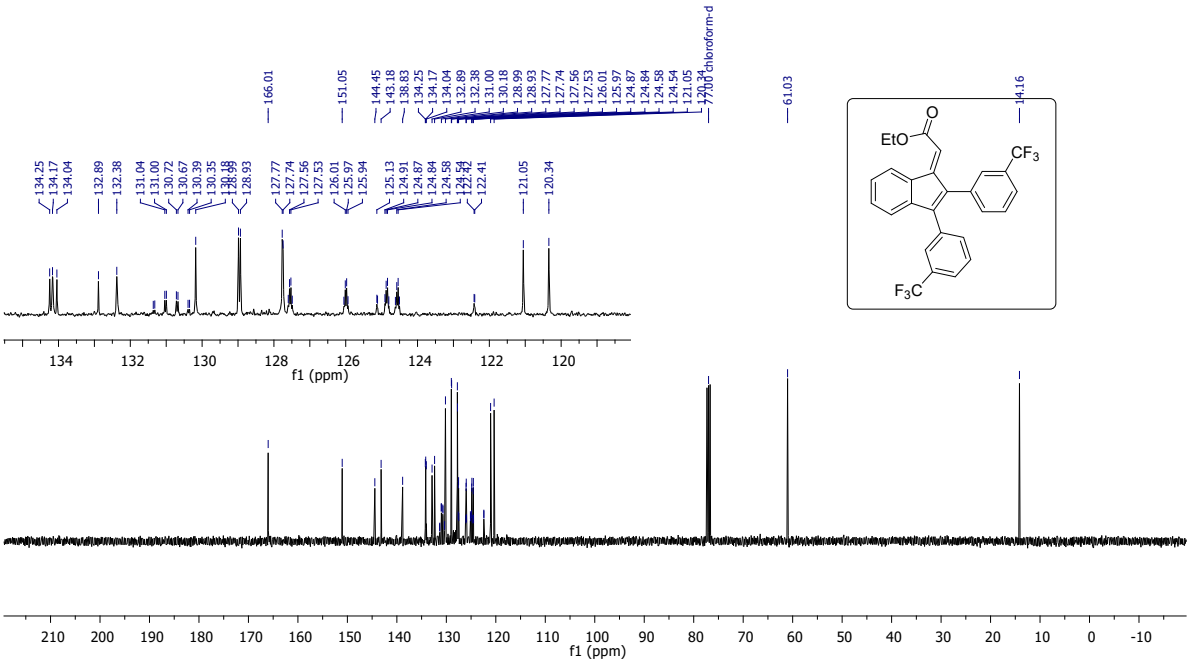
^{1}H NMR (400 MHz) spectrum of **3ak** in $CDCl_3$



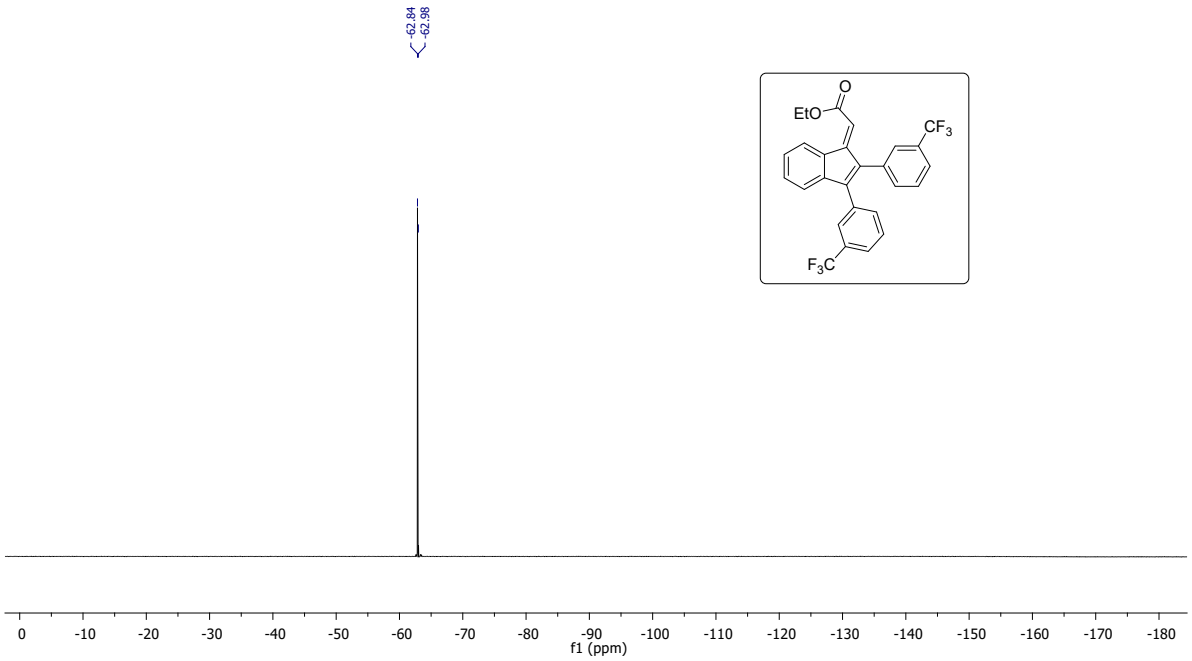
^{13}C{H} NMR (100 MHz) spectrum of **3ak** in $CDCl_3$



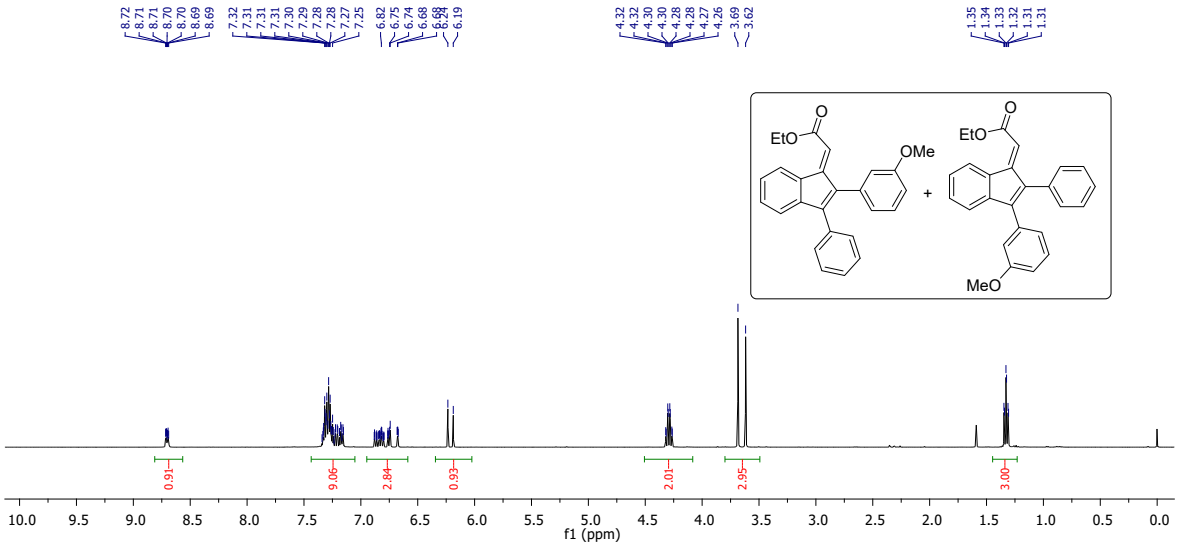
^{1}H NMR (400 MHz) spectrum of **3aj** in $CDCl_3$



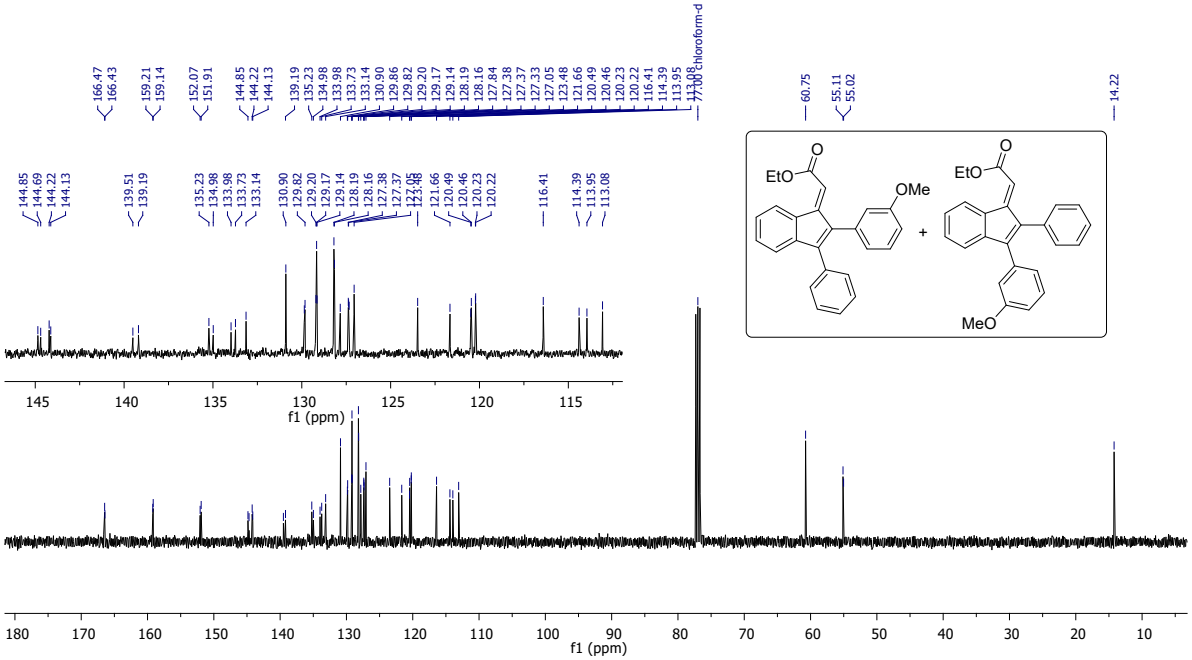
^{13}C{H} NMR (100 MHz) spectrum of **3aj** in $CDCl_3$



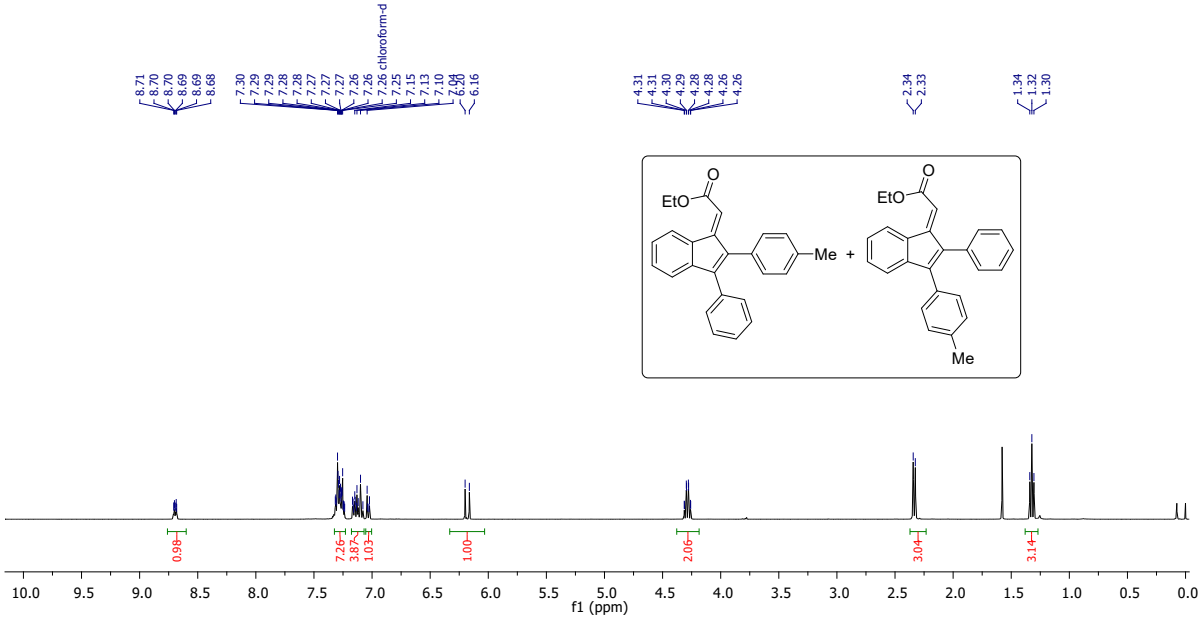
^{19}F NMR (376 MHz) spectrum of **3aj** in $CDCl_3$



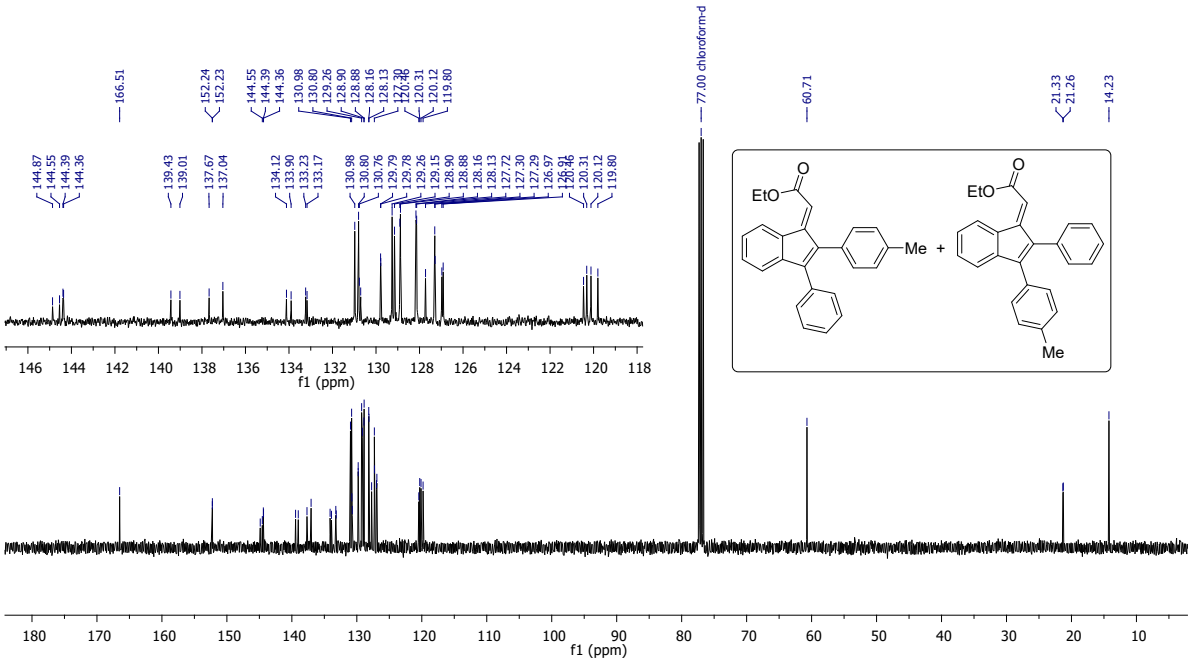
^{1}H NMR (400 MHz) spectrum of **3af+3af'** in $CDCl_3$



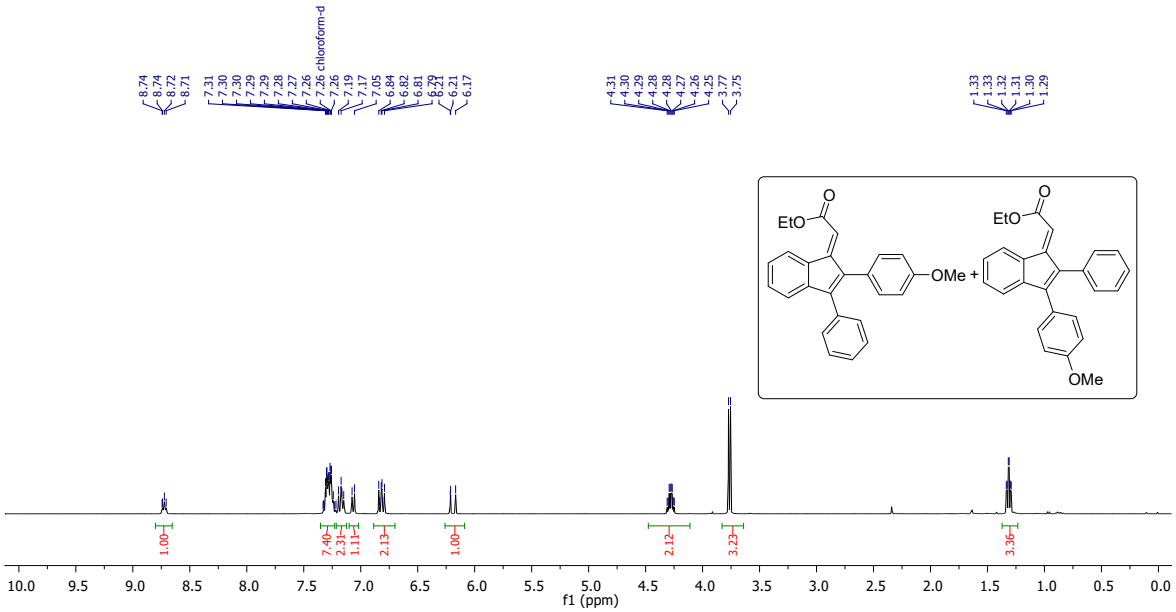
^{13}C{H} NMR (100 MHz) spectrum of **3af+3af'** in $CDCl_3$



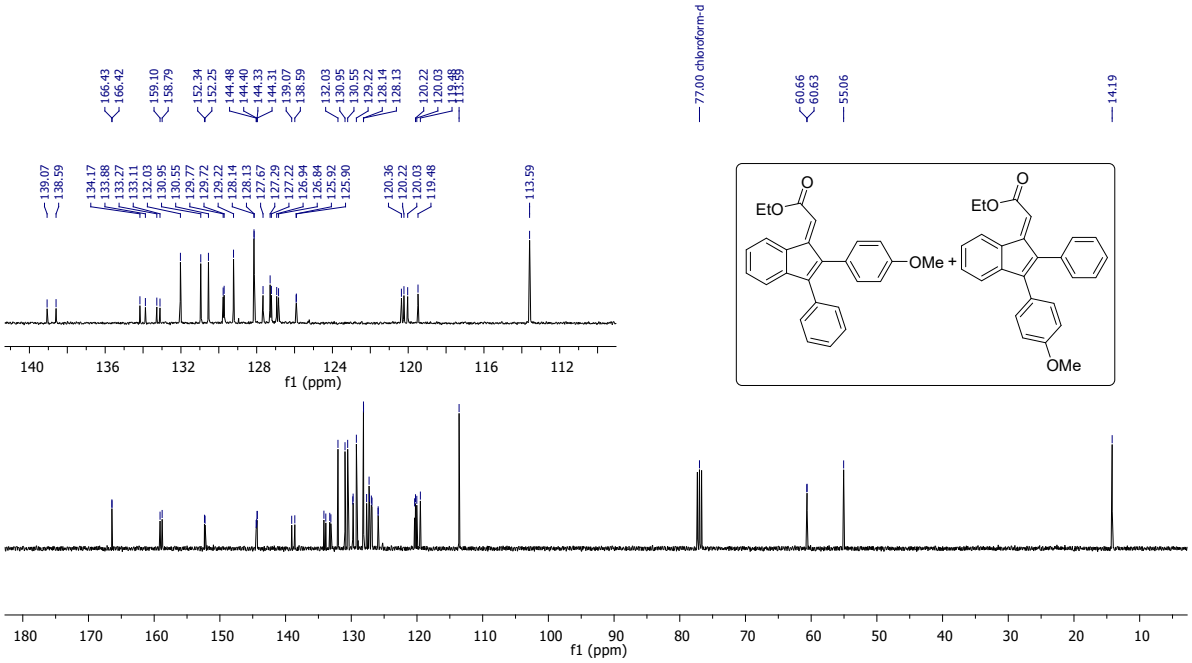
^{1}H NMR (400 MHz) spectrum of **3ag+3ag'** in $CDCl_3$



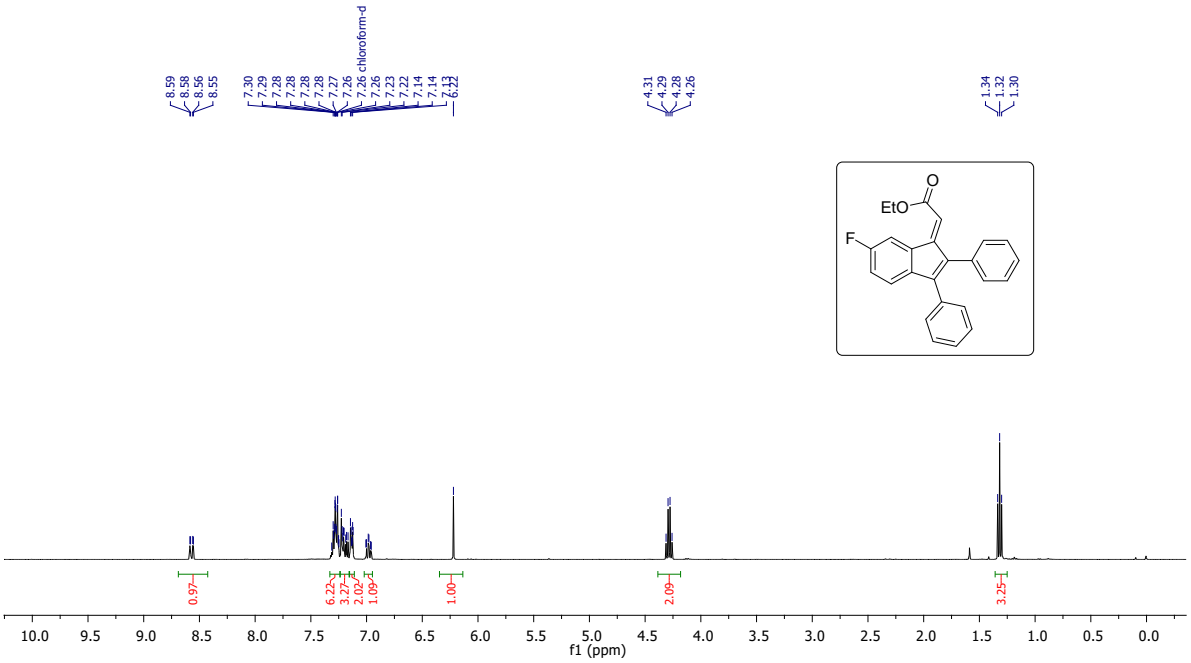
^{13}C{H} NMR (100 MHz) spectrum of **3ag+3ag'** in $CDCl_3$



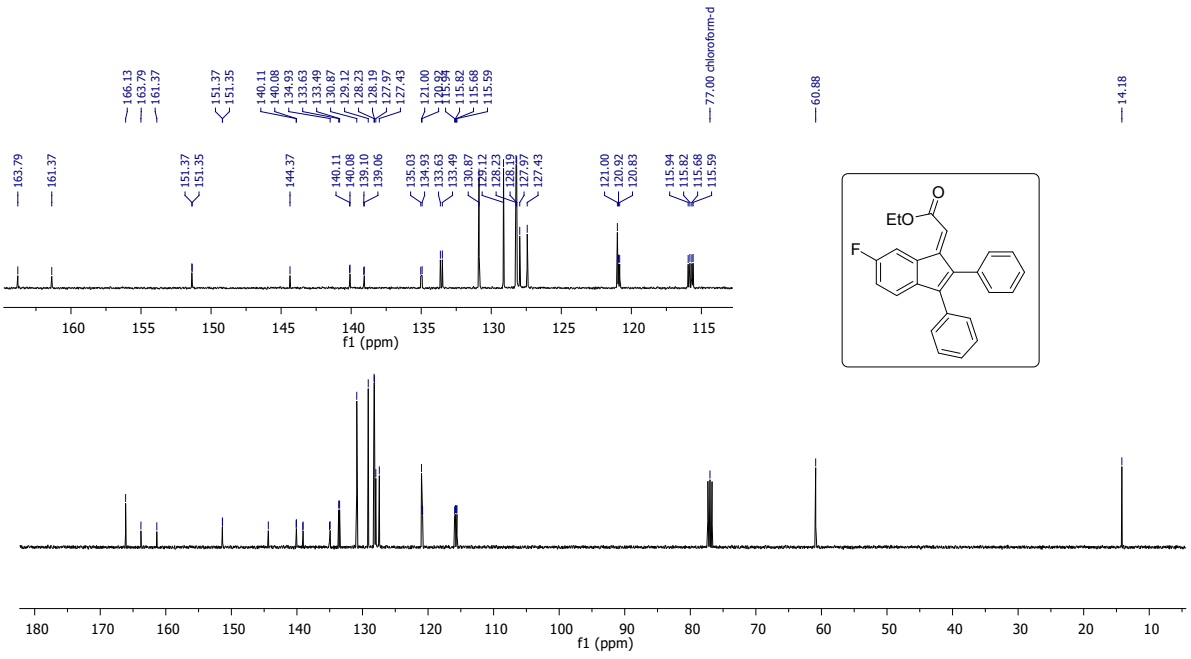
^{1}H NMR (400 MHz) spectrum of **3ah+3ah'** in $CDCl_3$



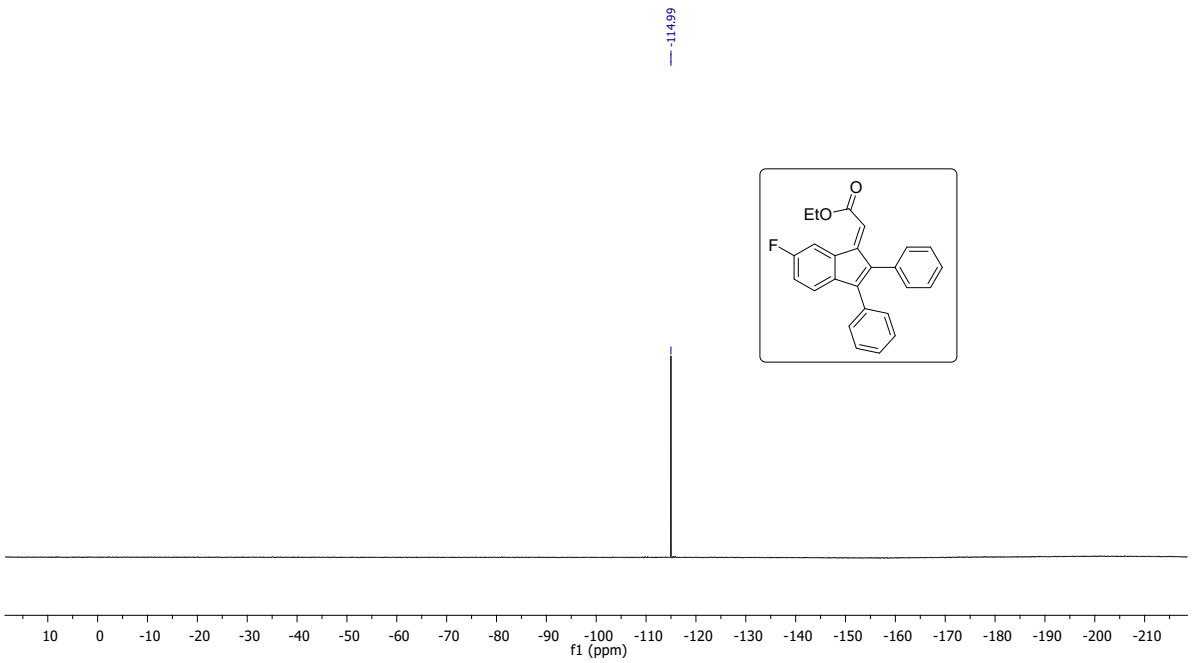
^{13}C{H} NMR (100 MHz) spectrum of **3ah+3ah'** in $CDCl_3$



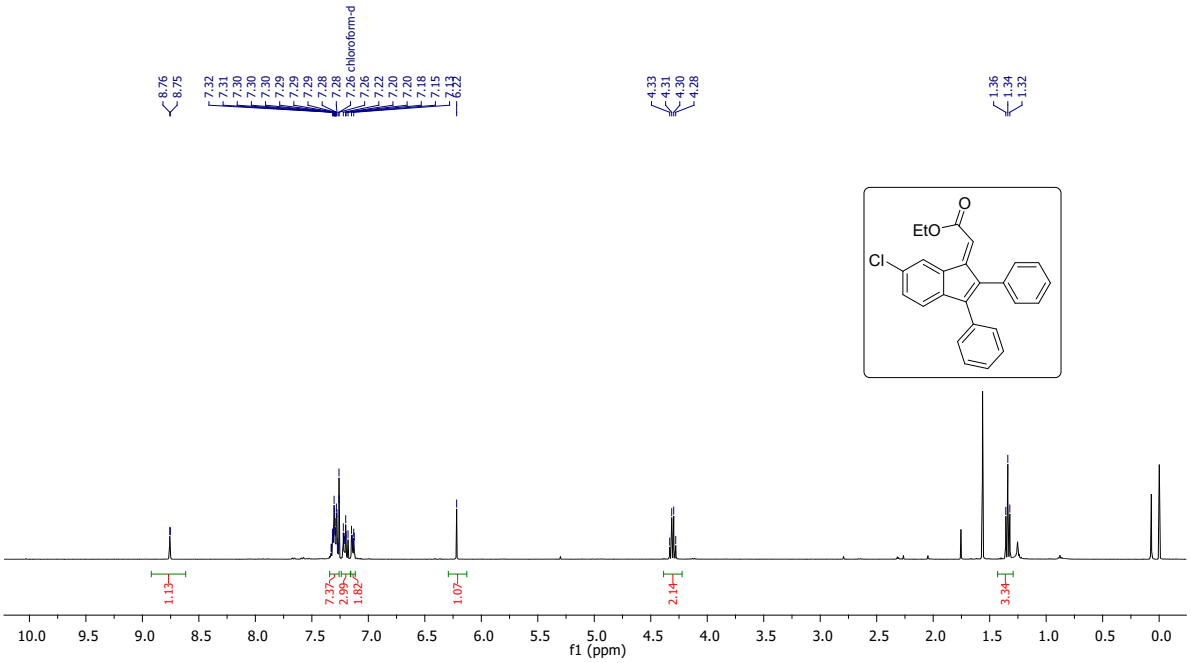
^{1}H NMR (400 MHz) spectrum of **3ca** in $CDCl_3$



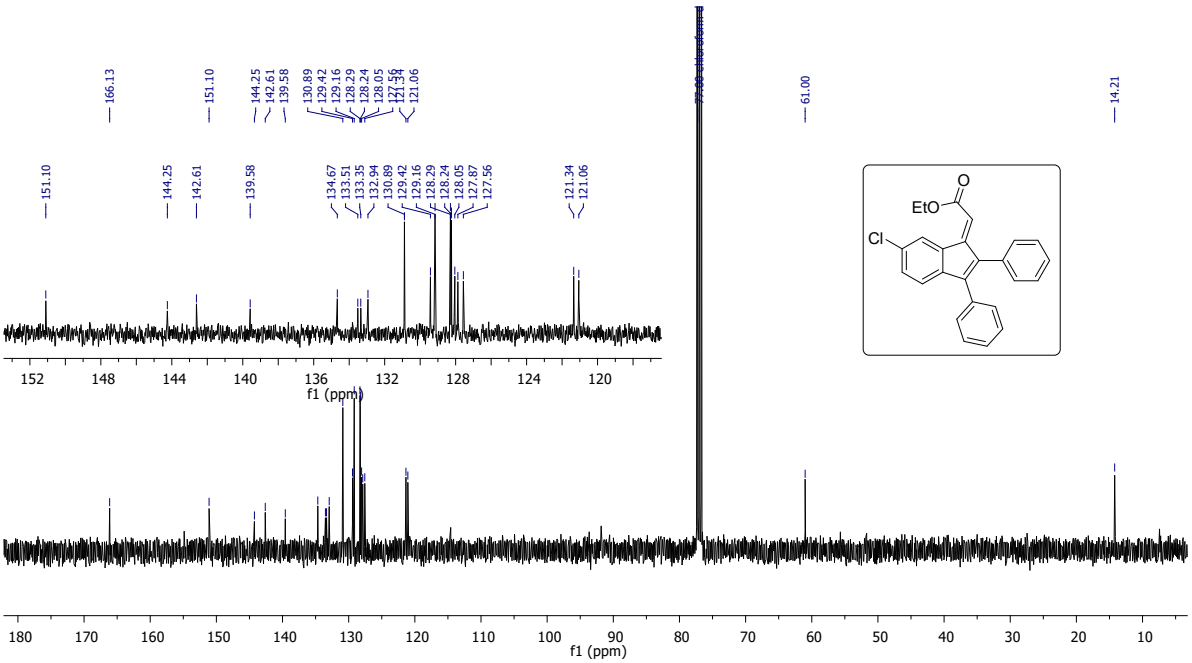
^{13}C{H} NMR (100 MHz) spectrum of **3ca** in $CDCl_3$



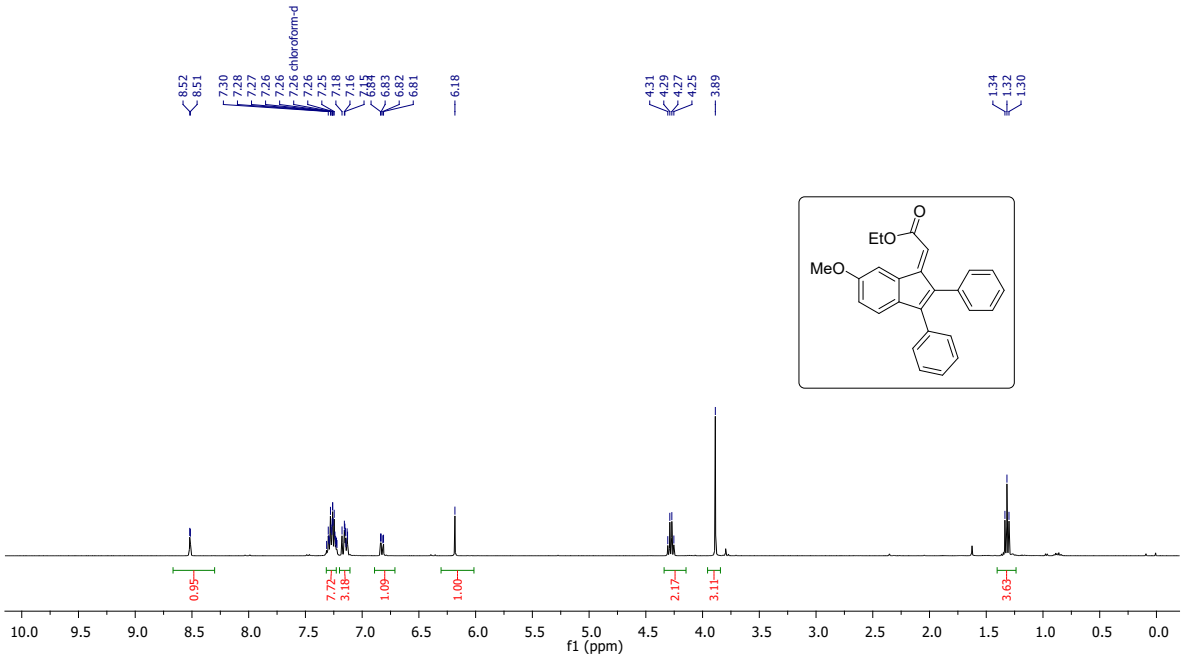
^{19}F NMR (376 MHz) spectrum of **3ca** in $CDCl_3$



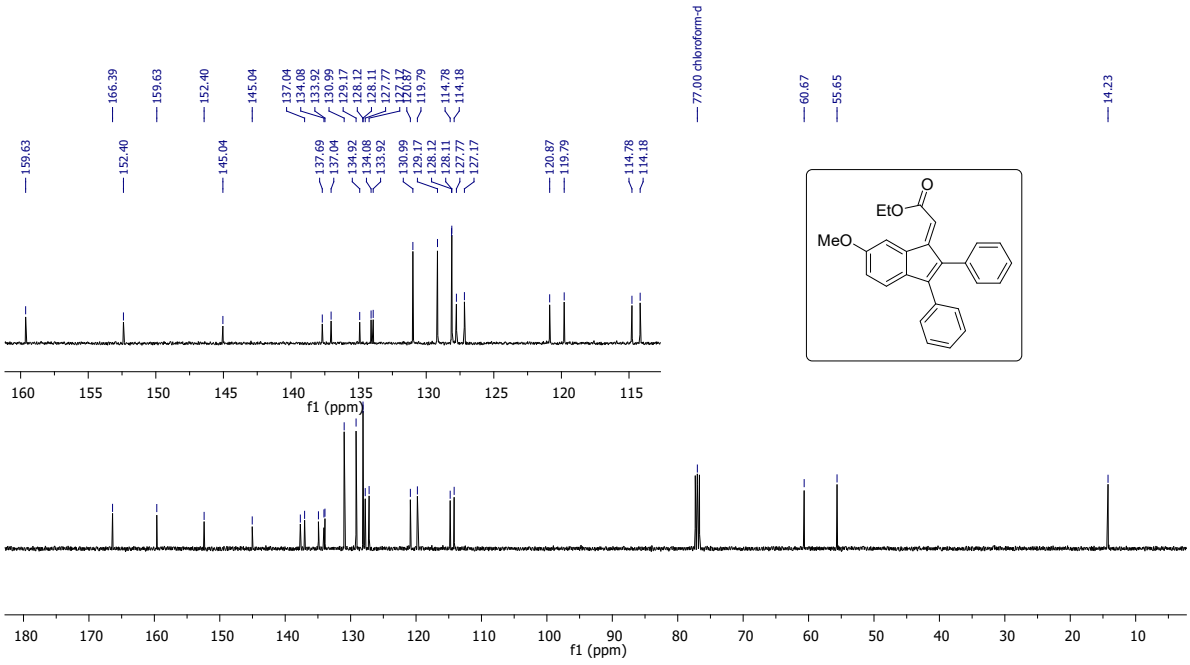
^{1}H NMR (400 MHz) spectrum of **3da** in $CDCl_3$



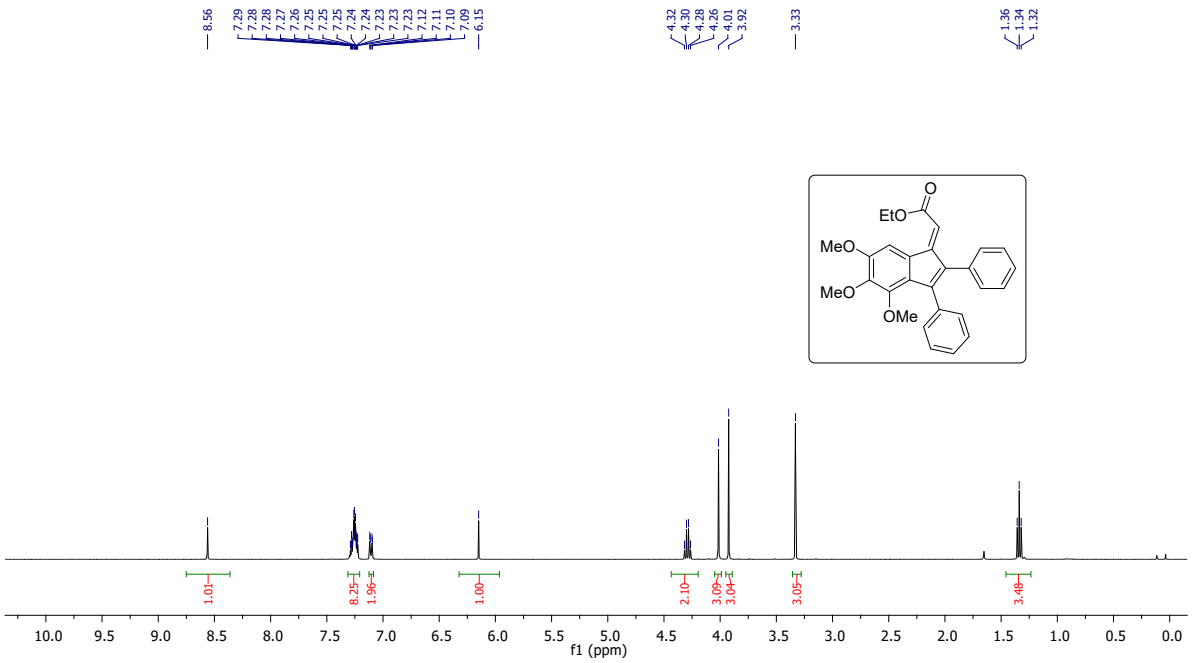
^{13}C{H} NMR (100 MHz) spectrum of **3da** in $CDCl_3$



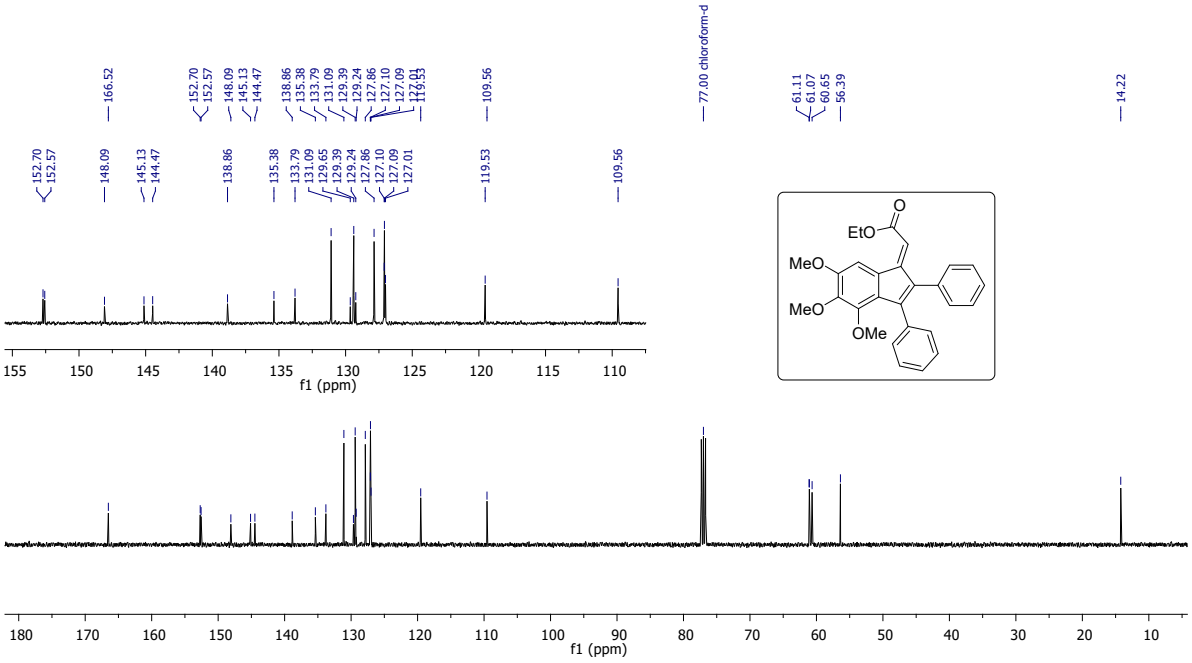
^{1}H NMR (400 MHz) spectrum of **3ea** in $CDCl_3$



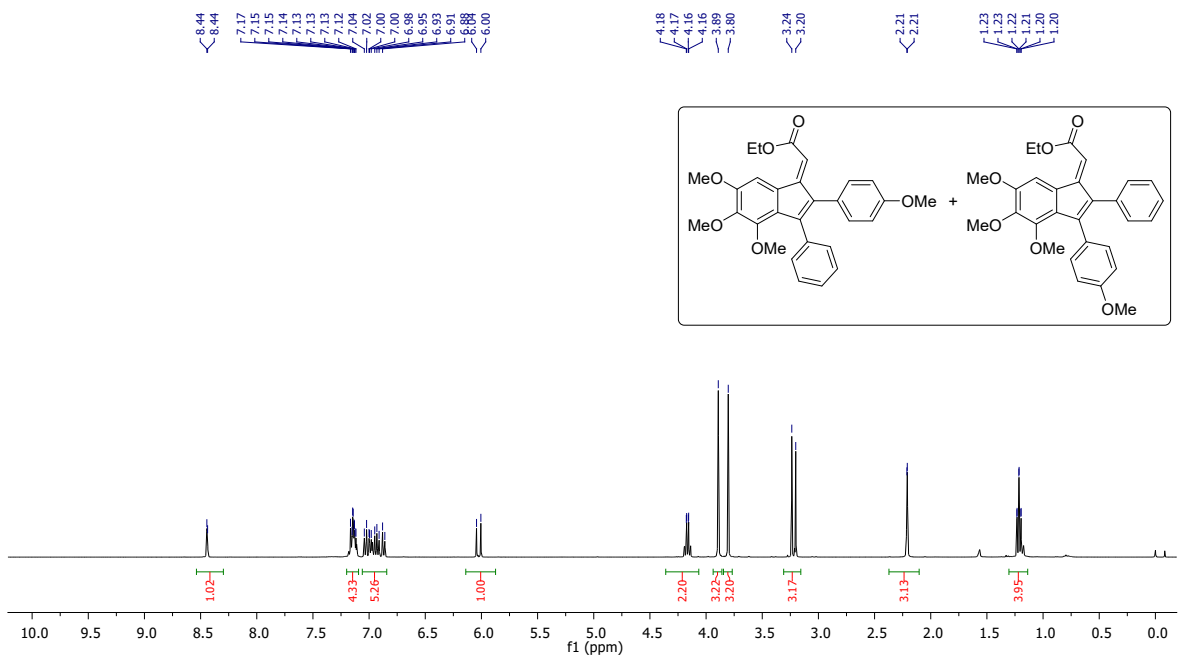
^{13}C{H} NMR (100 MHz) spectrum of **3ea** in $CDCl_3$



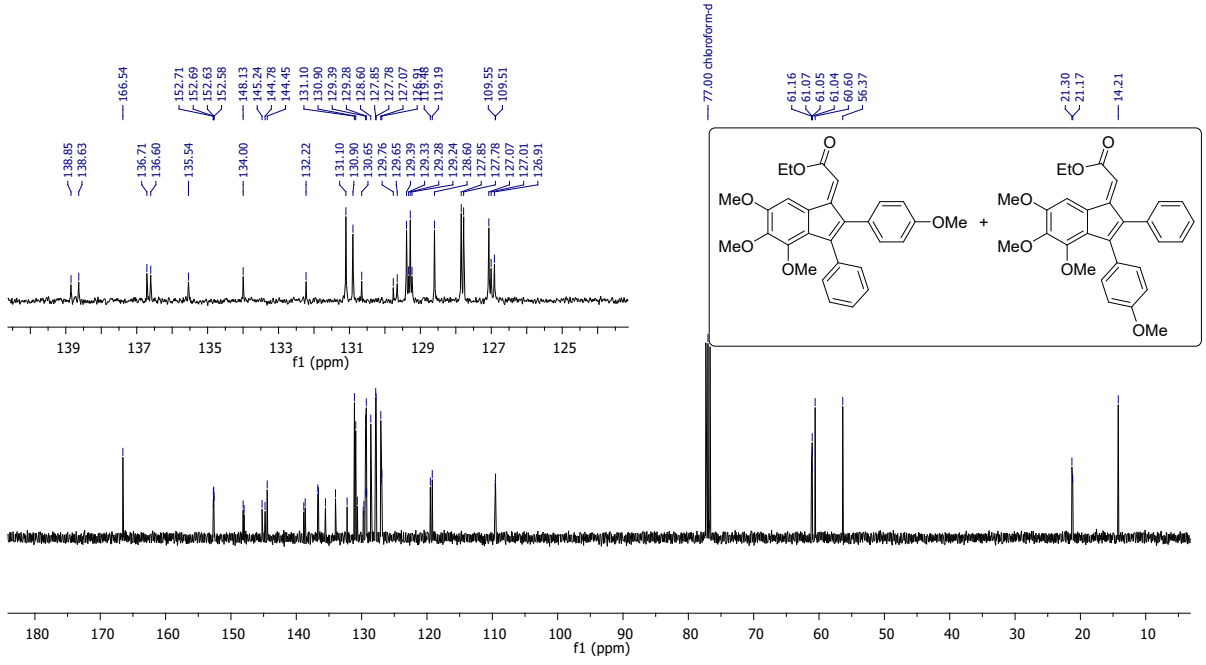
^{1}H NMR (400 MHz) spectrum of **3fa** in $CDCl_3$



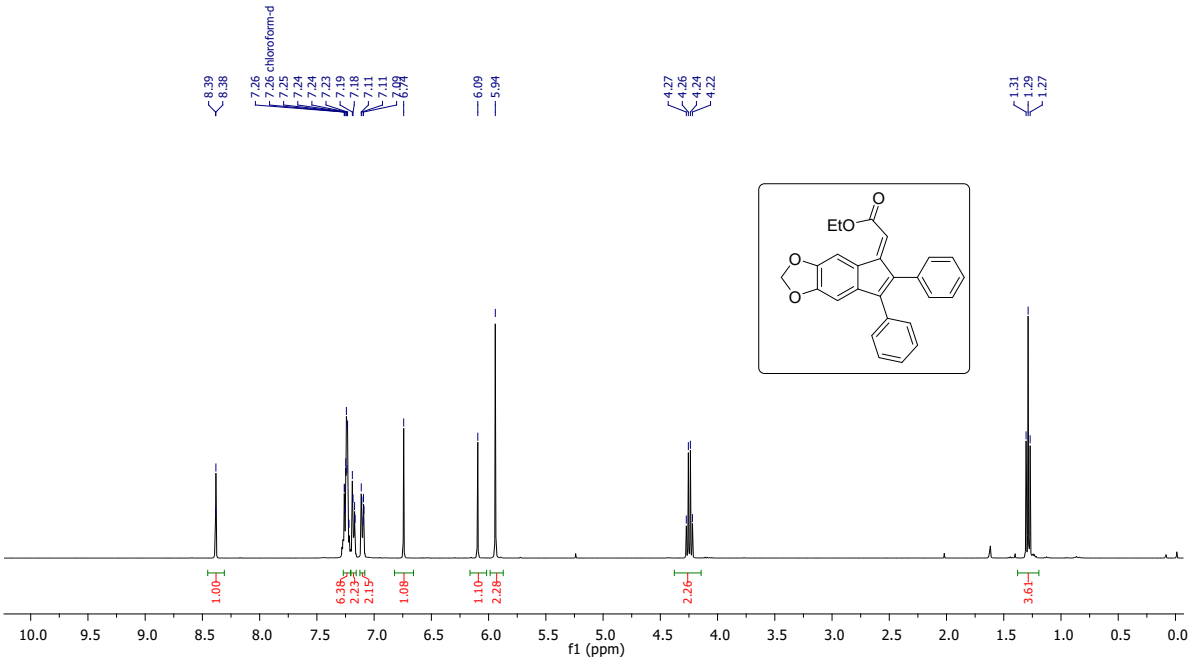
^{13}C{H} NMR (100 MHz) spectrum of **3fa** in $CDCl_3$



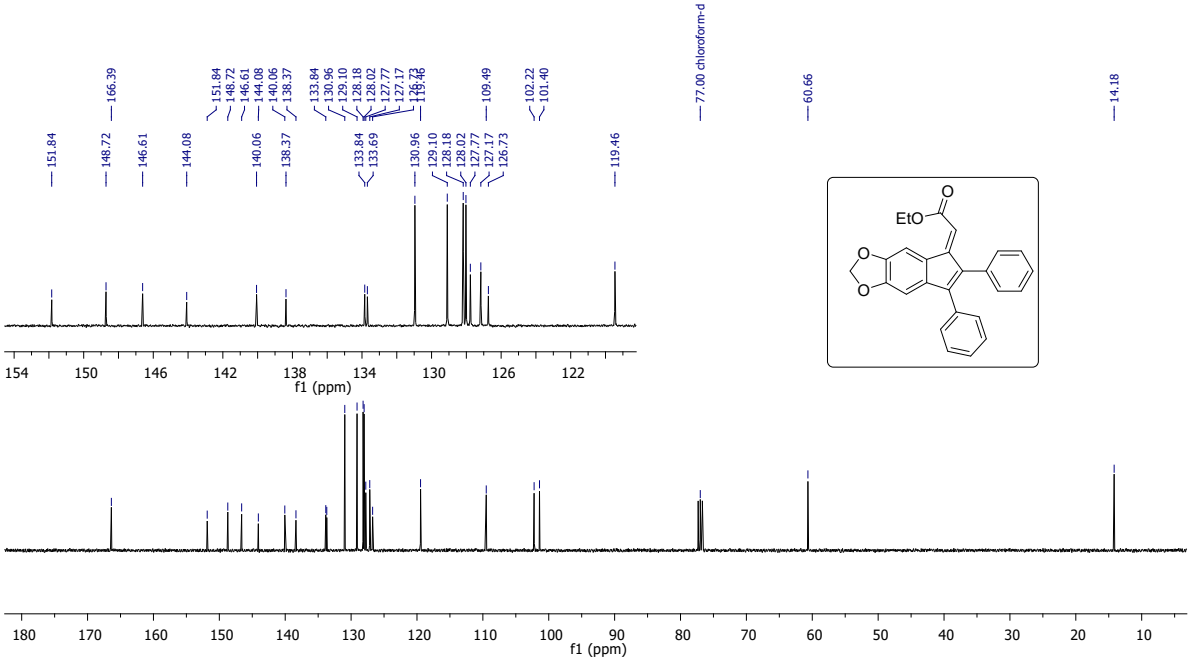
^{1}H NMR (400 MHz) spectrum of **3fg+3fg'** in $CDCl_3$



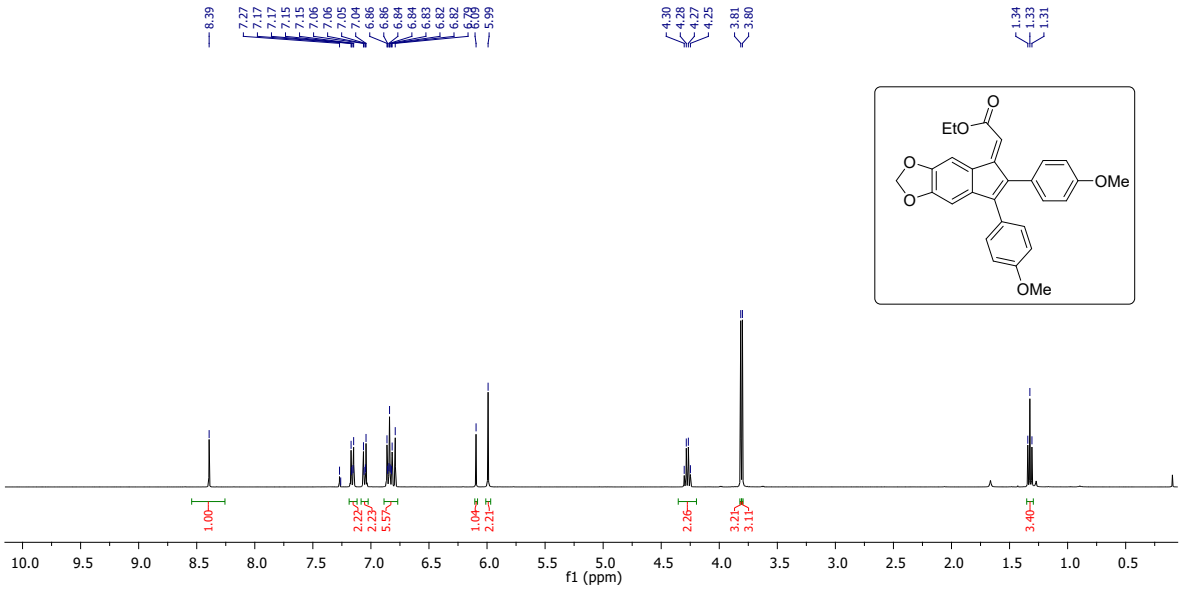
^{13}C{H} NMR (100 MHz) spectrum of **3fg+3fg'** in $CDCl_3$



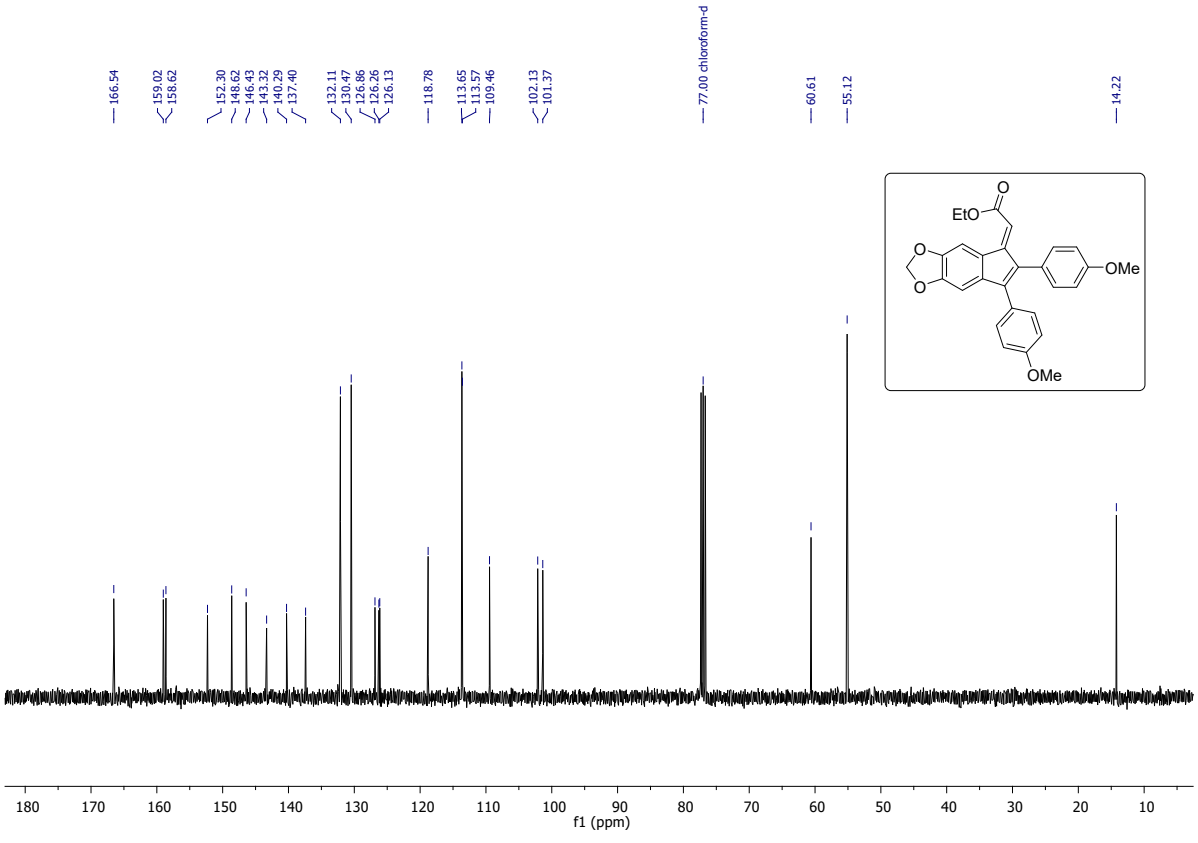
^{1}H NMR (400 MHz) spectrum of **3ga** in $CDCl_3$



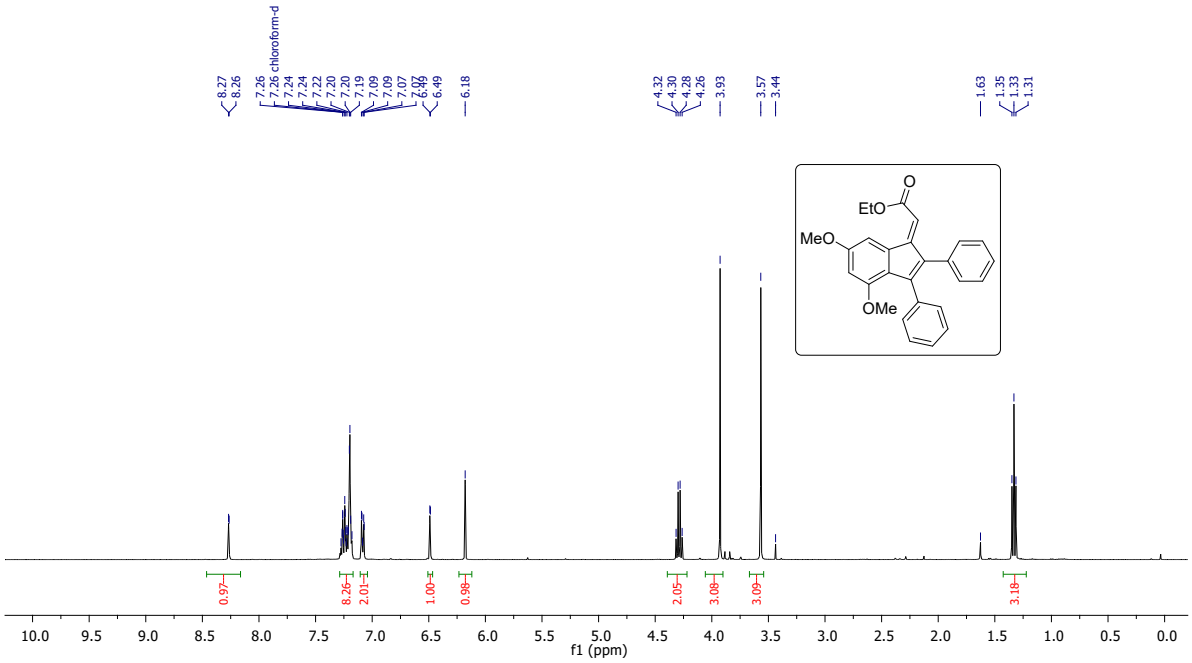
^{13}C{H} NMR (100 MHz) spectrum of **3ga** in $CDCl_3$



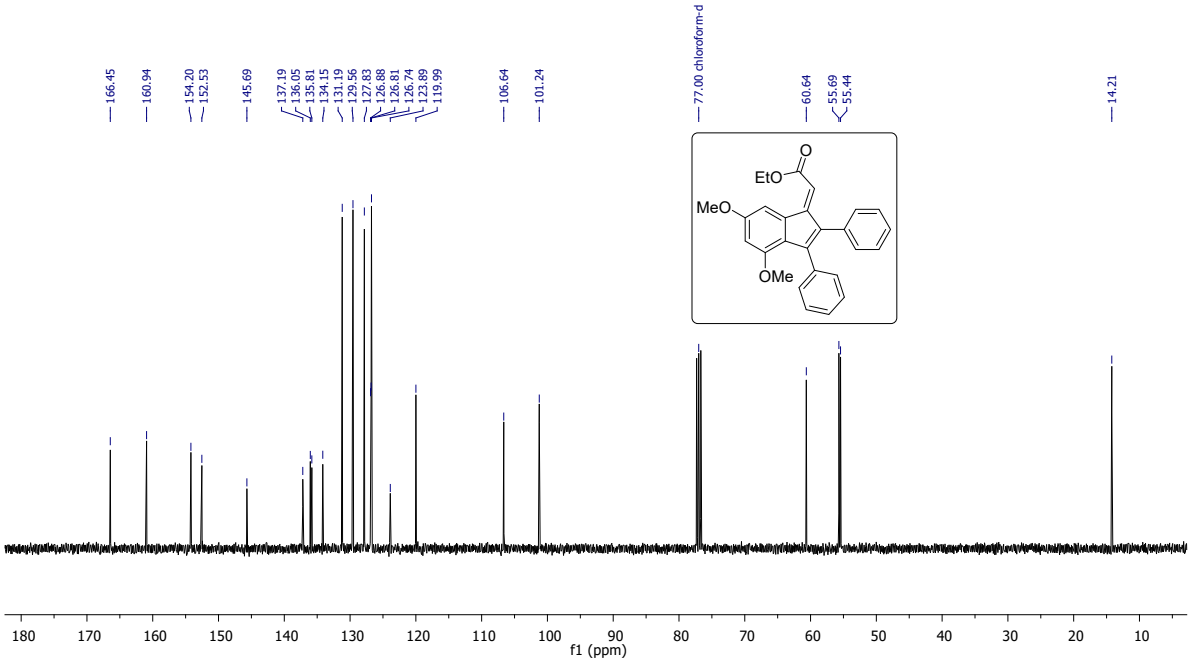
^{1}H NMR (400 MHz) spectrum of **3gb** in $CDCl_3$



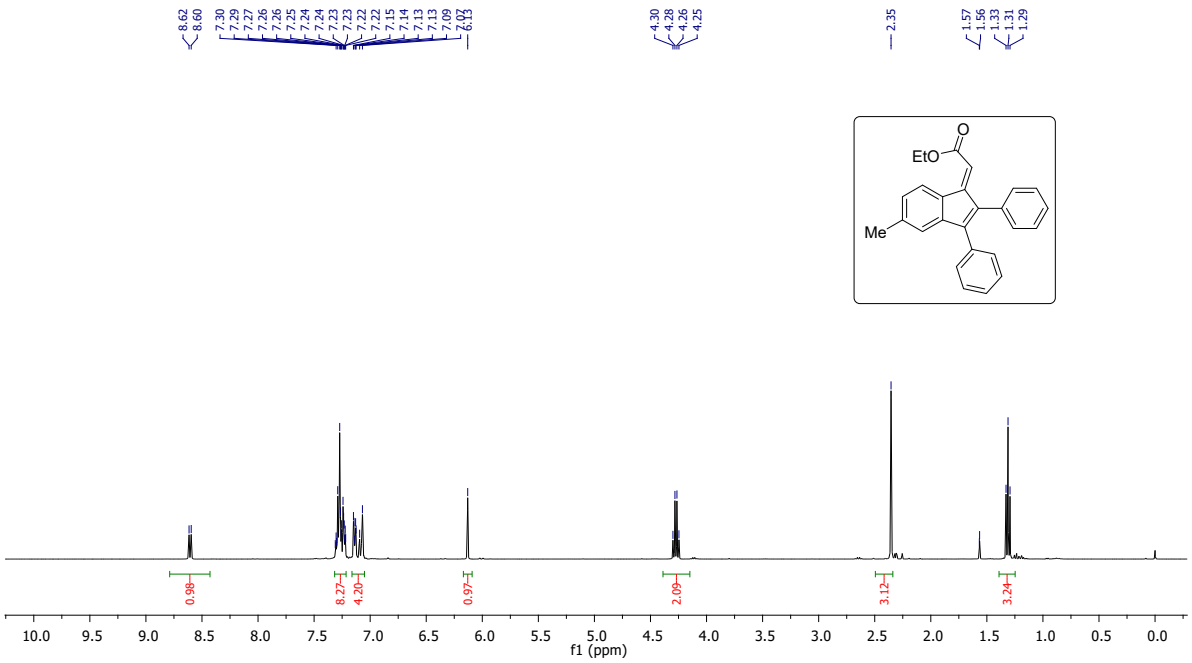
^{13}C{H} NMR (100 MHz) spectrum of **3gb** in $CDCl_3$



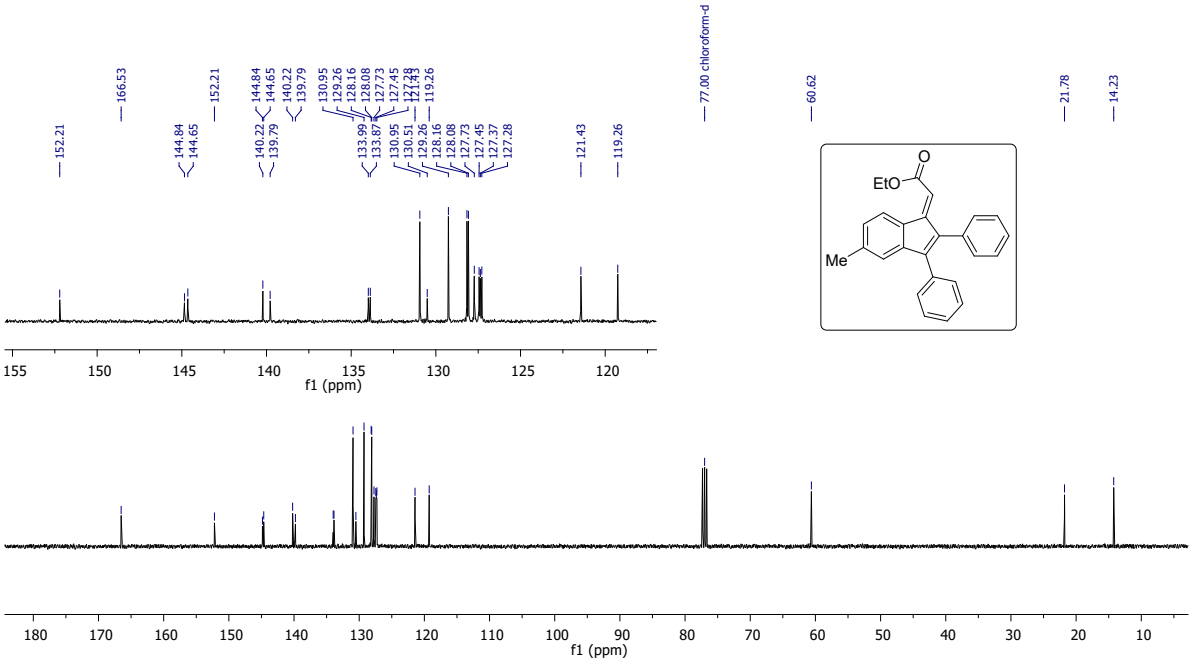
^{1}H NMR (400 MHz) spectrum of **3ha** in $CDCl_3$



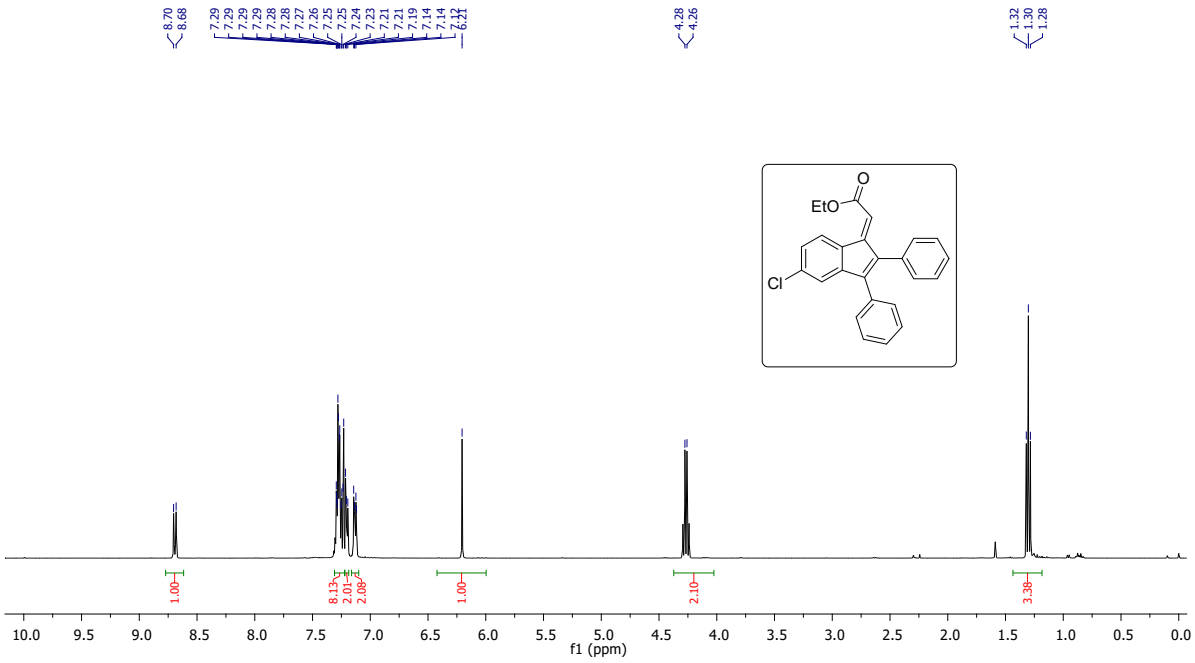
^{13}C{H} NMR (100 MHz) spectrum of **3ha** in $CDCl_3$



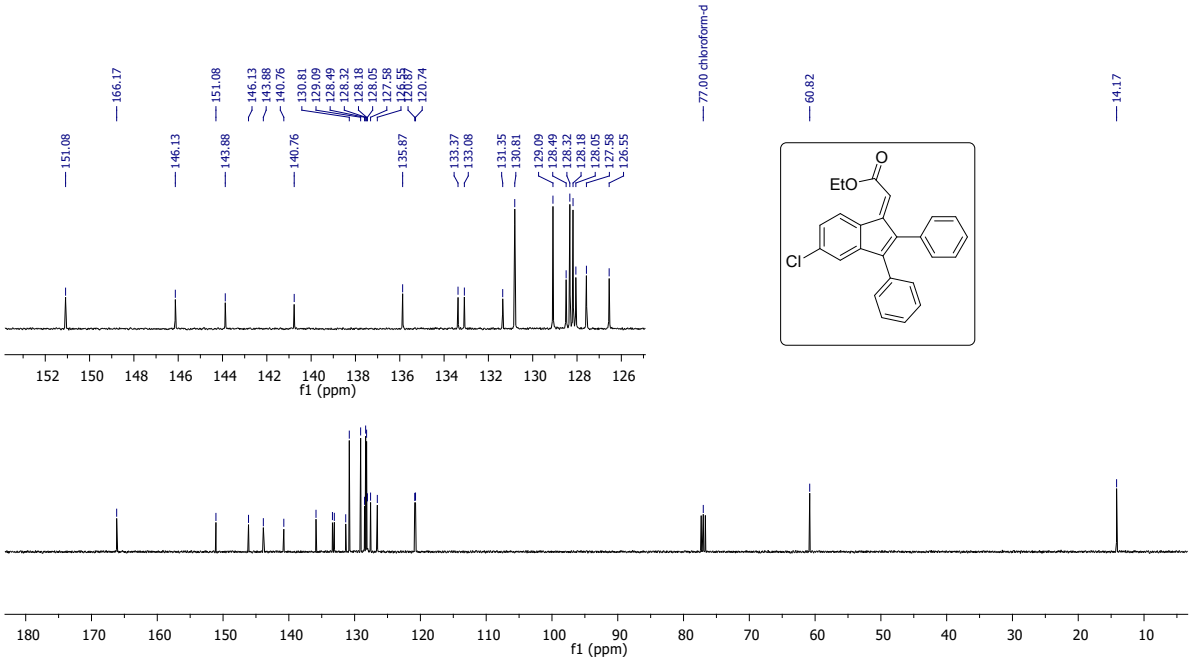
^{1}H NMR (400 MHz) spectrum of **3ba** in $CDCl_3$



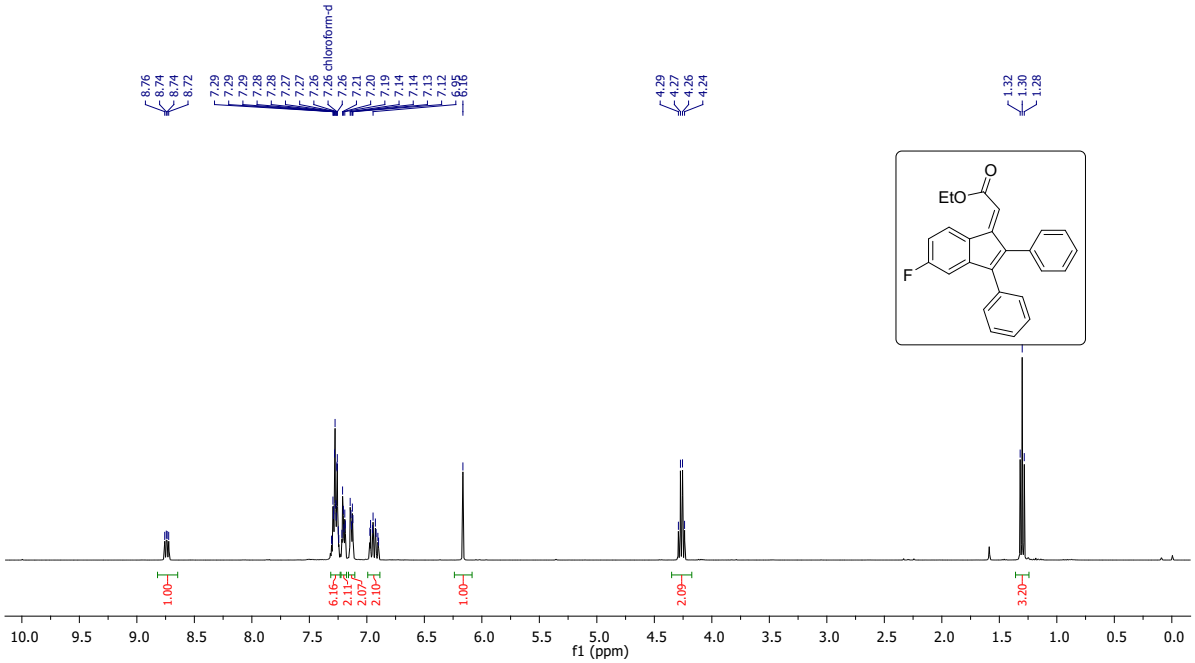
^{13}C{H} NMR (100 MHz) spectrum of **3ba** in $CDCl_3$



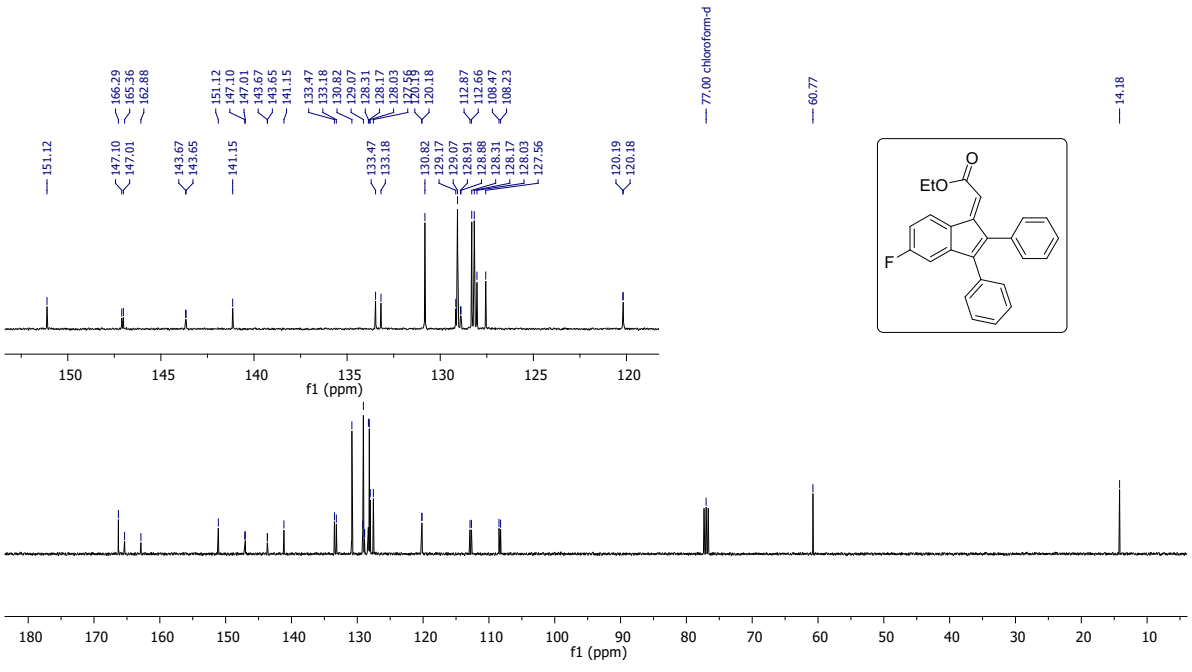
^{1}H NMR (400 MHz) spectrum of **3ja** in $CDCl_3$



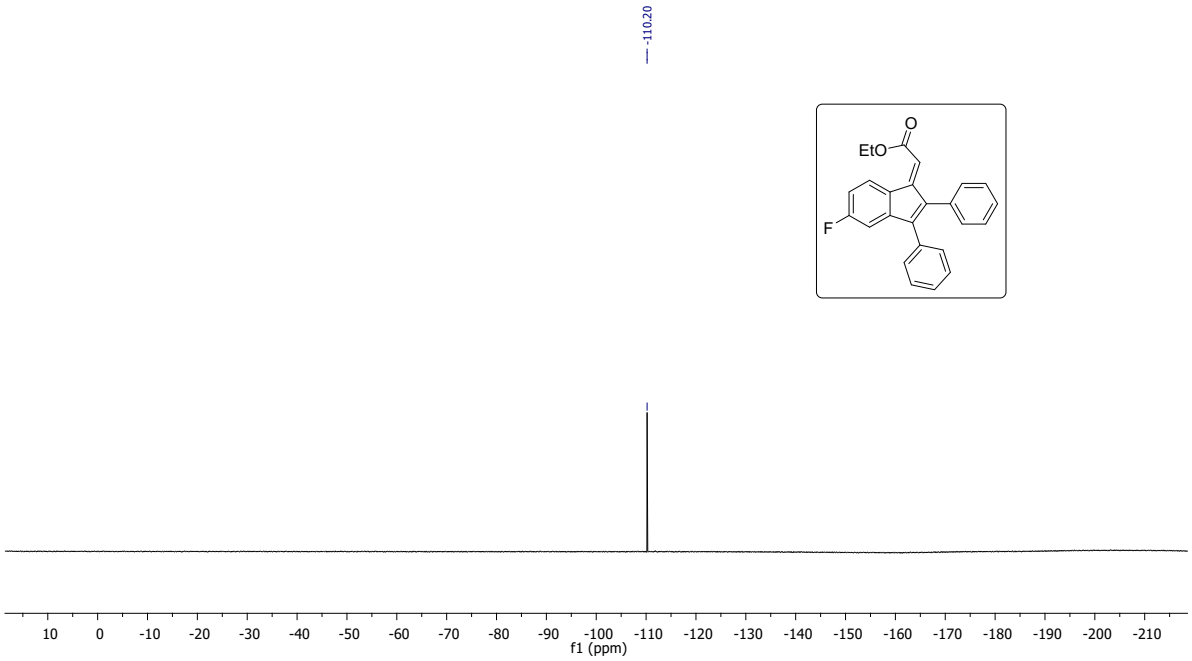
^{13}C{H} NMR (100 MHz) spectrum of **3ja** in $CDCl_3$



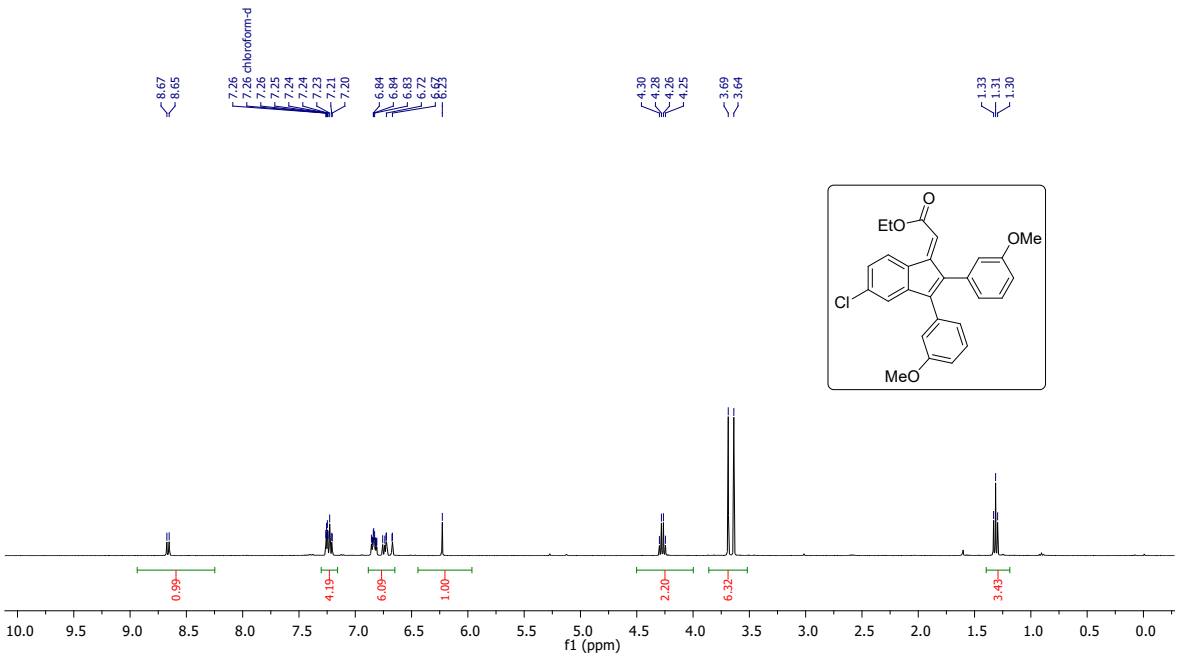
^{1}H NMR (400 MHz) spectrum of **3ia** in $CDCl_3$



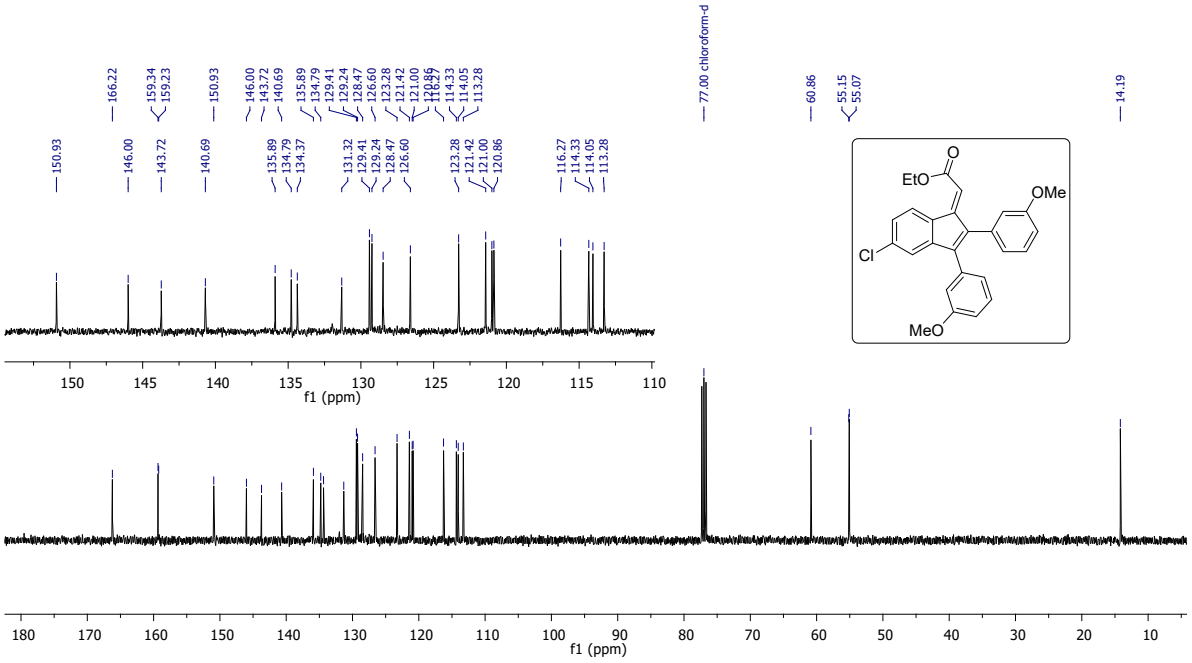
^{13}C{H} NMR (100 MHz) spectrum of **3ia** in $CDCl_3$



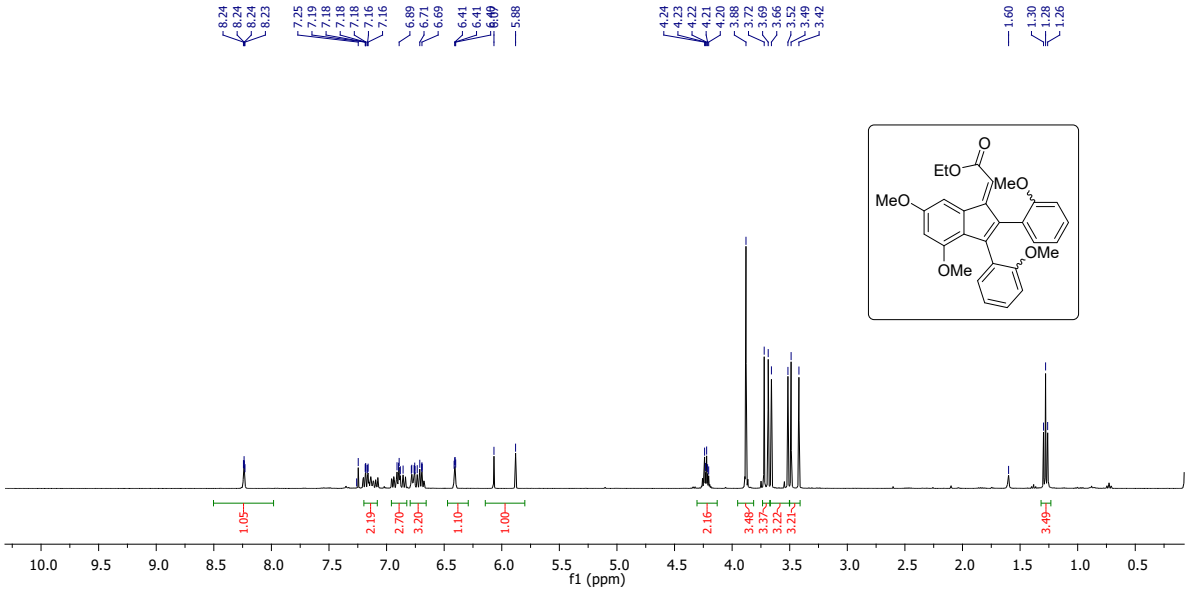
^{19}F NMR (376 MHz) spectrum of **3ia** in $CDCl_3$



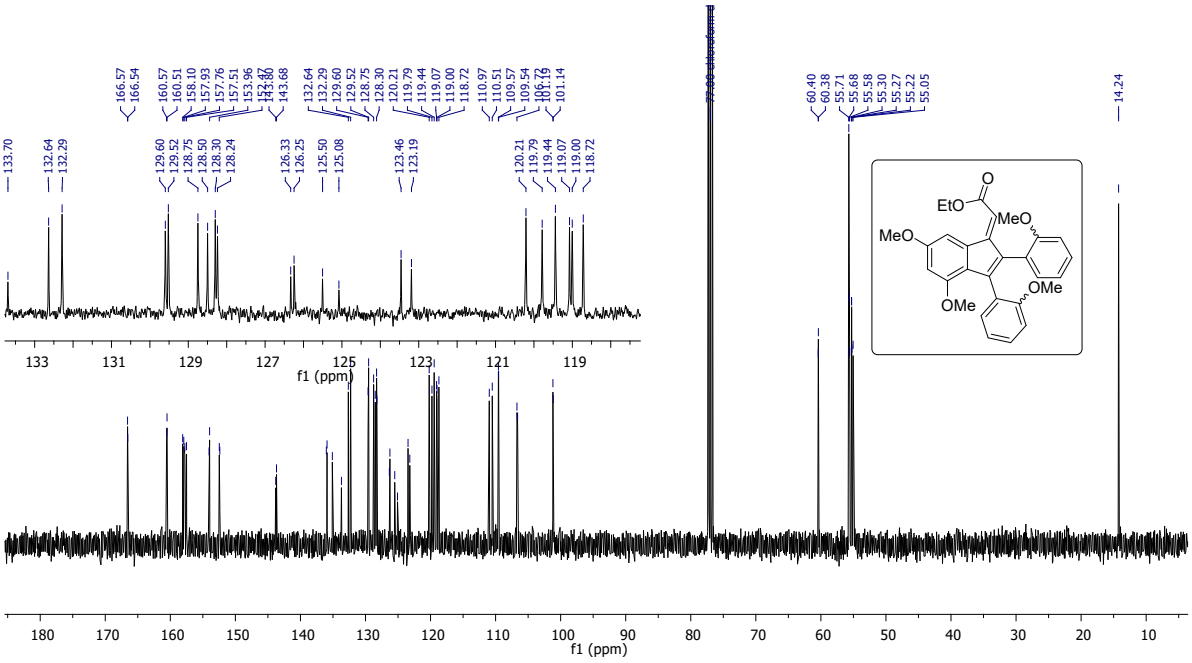
^{1}H NMR (400 MHz) spectrum of **3jc** in $CDCl_3$



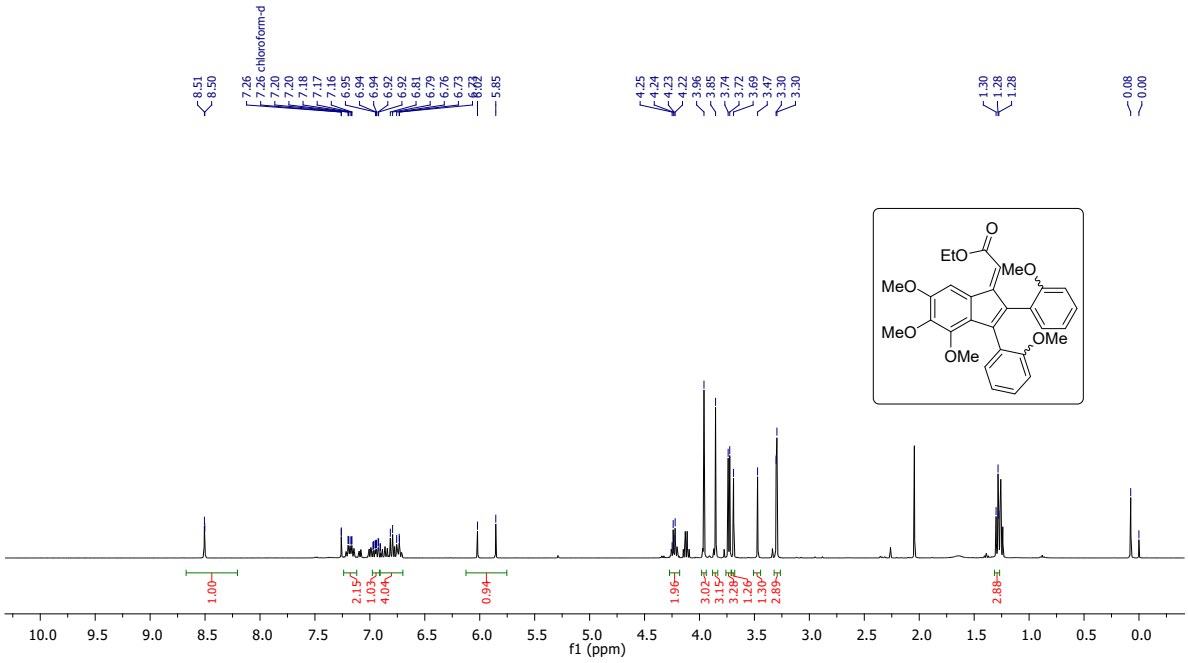
^{13}C{H} NMR (100 MHz) spectrum of **3jc** in $CDCl_3$



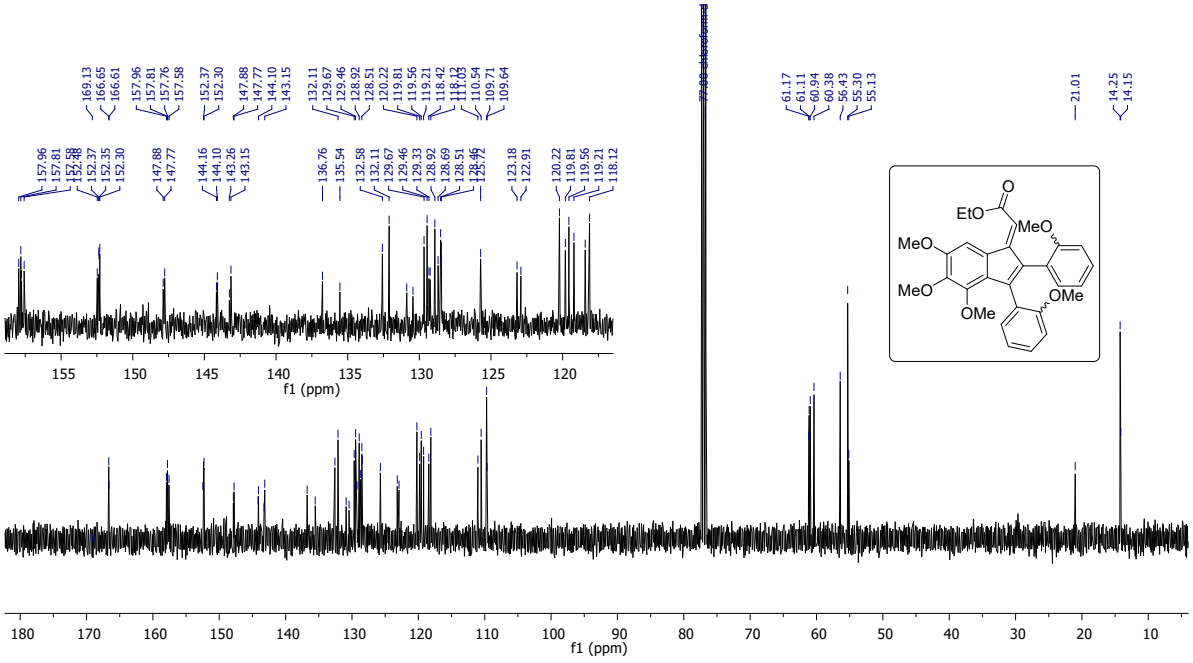
^{1}H NMR (400 MHz) spectrum of **3hi+3hi'** in $CDCl_3$



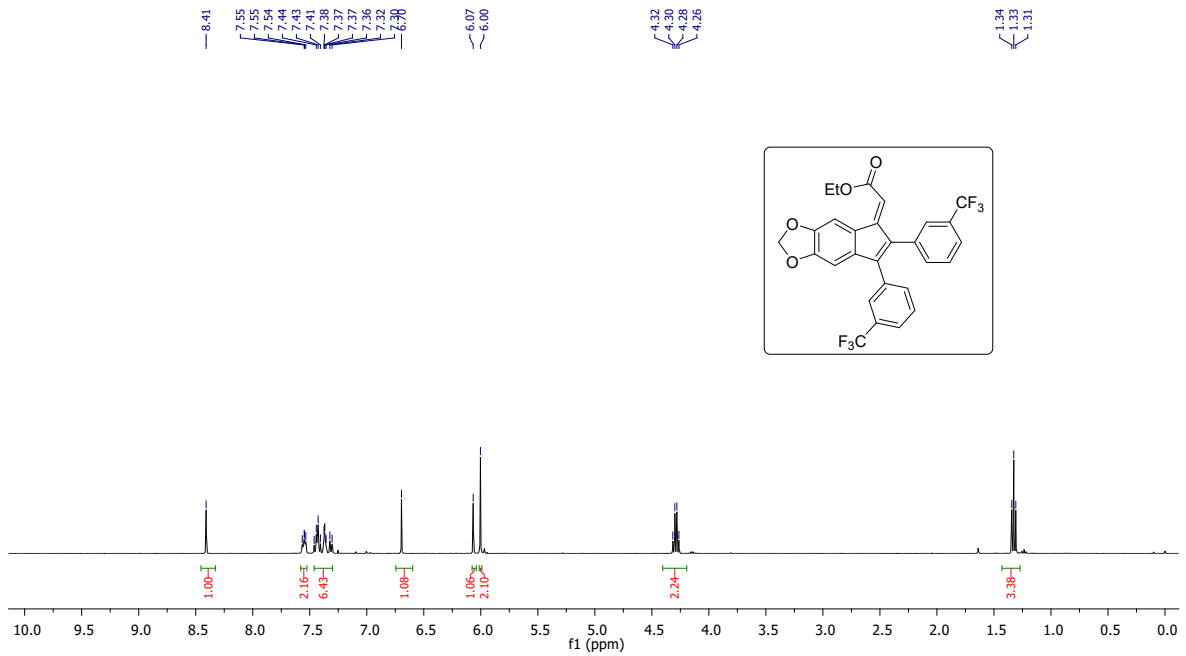
^{13}C{H} NMR (100 MHz) spectrum of **3hi+3hi'** in $CDCl_3$



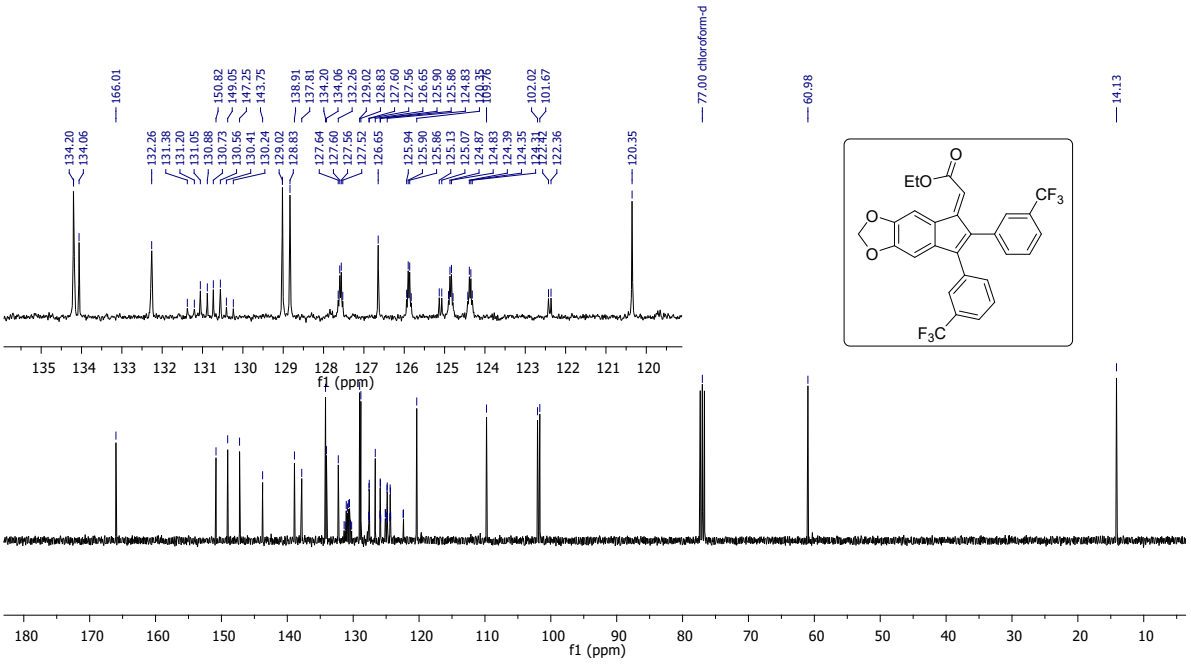
^{1}H NMR (400 MHz) spectrum of **3fi+3fi'** in $CDCl_3$



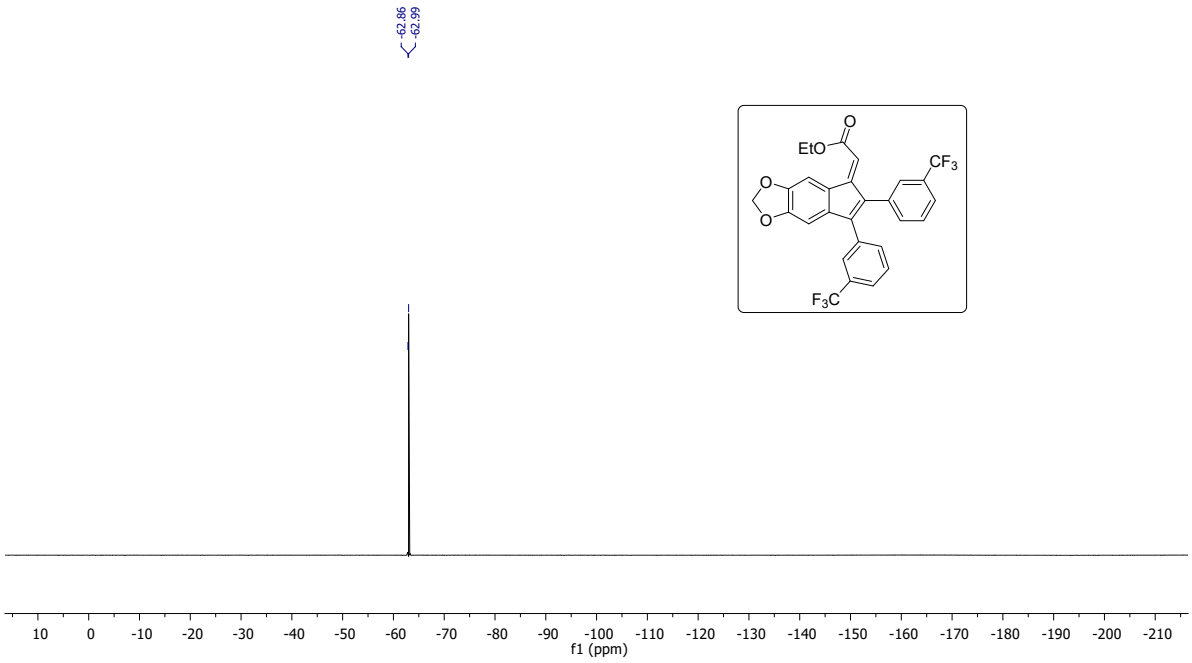
^{13}C{H} NMR (100 MHz) spectrum of **3fi+3fi'** in $CDCl_3$



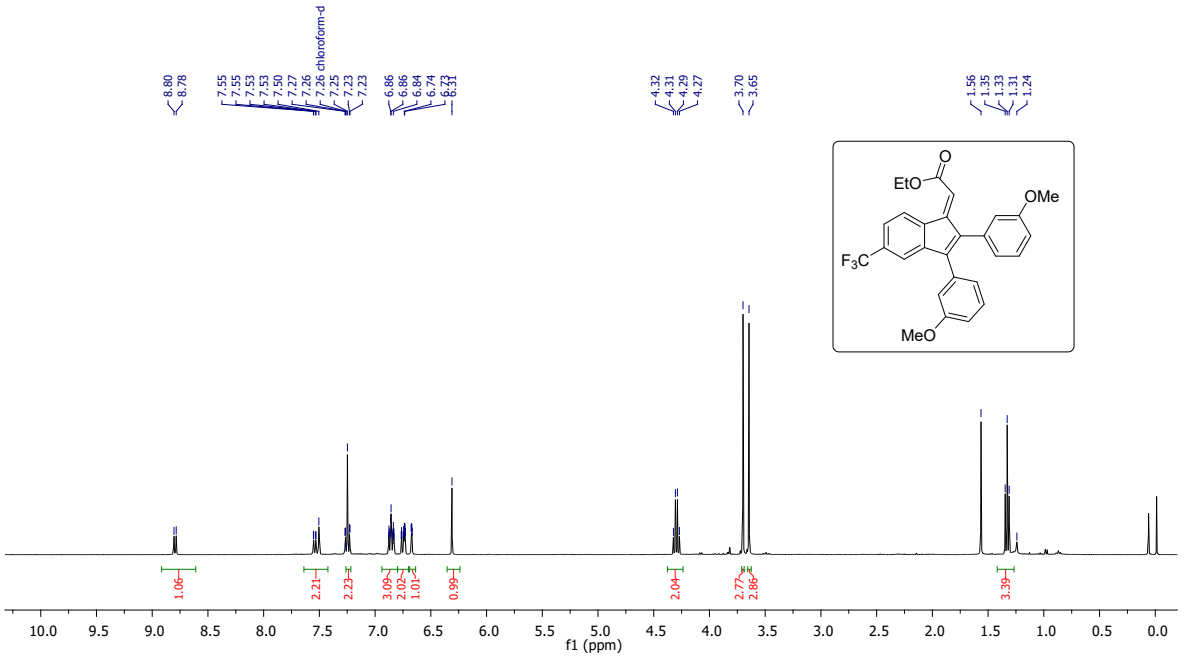
^{1}H NMR (400 MHz) spectrum of **3gj** in $CDCl_3$



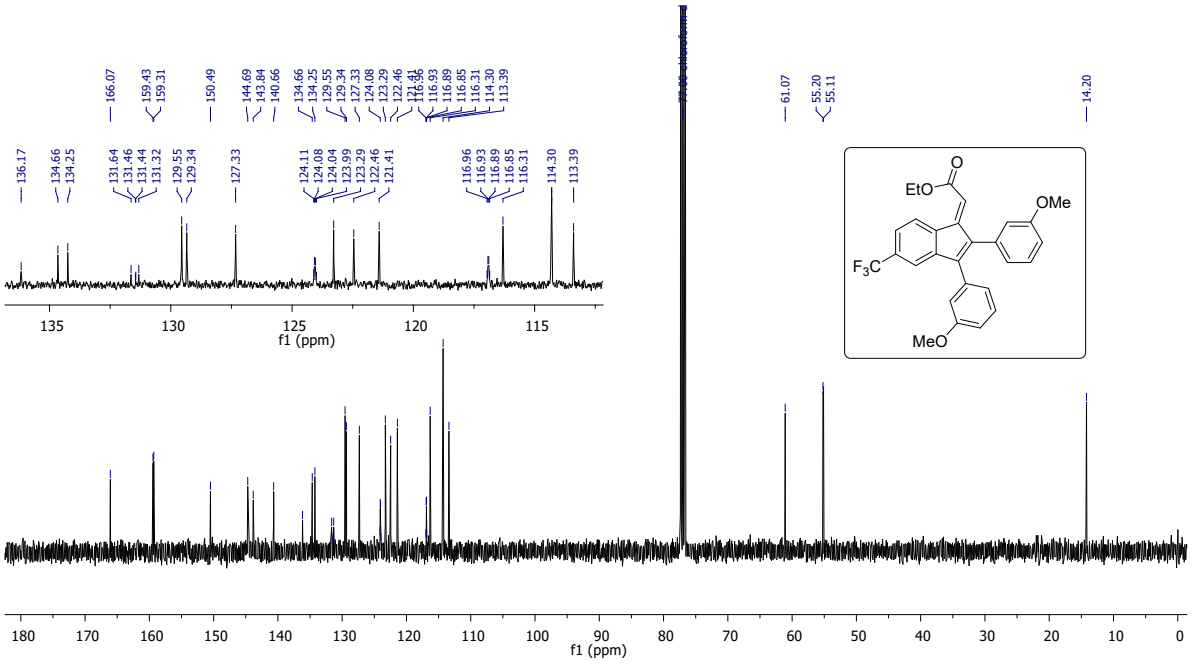
^{13}C{H} NMR (100 MHz) spectrum of **3gj** in $CDCl_3$



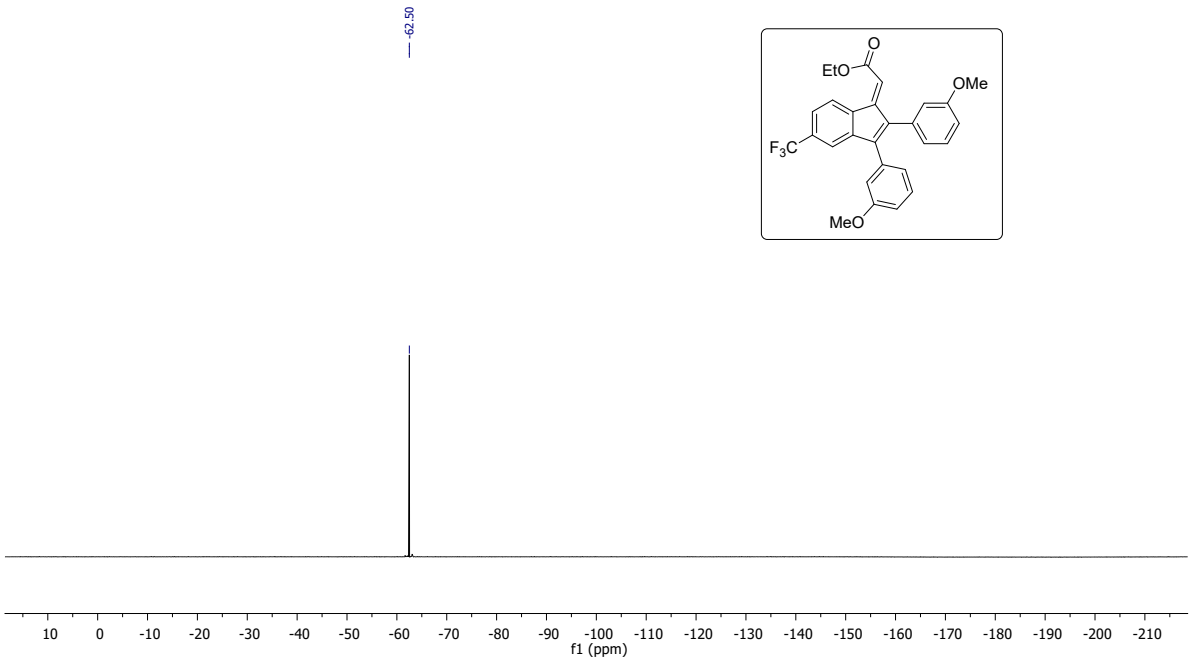
^{19}F NMR (565 MHz) spectrum of **3gj** in $CDCl_3$



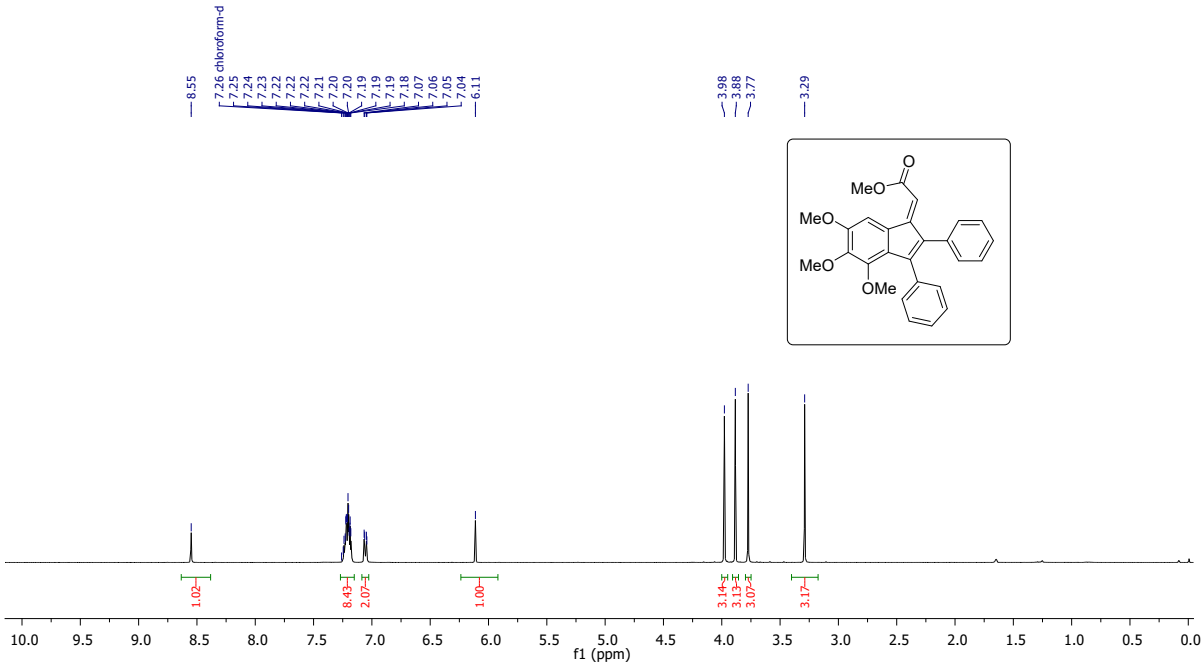
^{1}H NMR (400 MHz) spectrum of **3kc** in $CDCl_3$



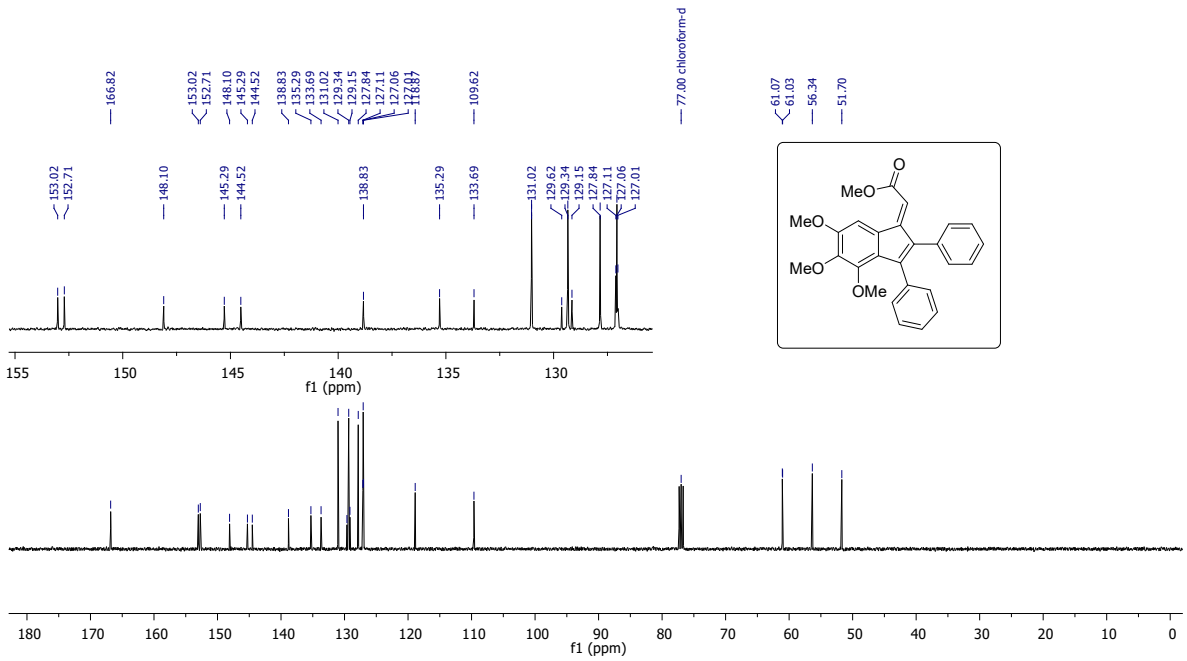
^{13}C{H} NMR (100 MHz) spectrum of **3kc** in $CDCl_3$



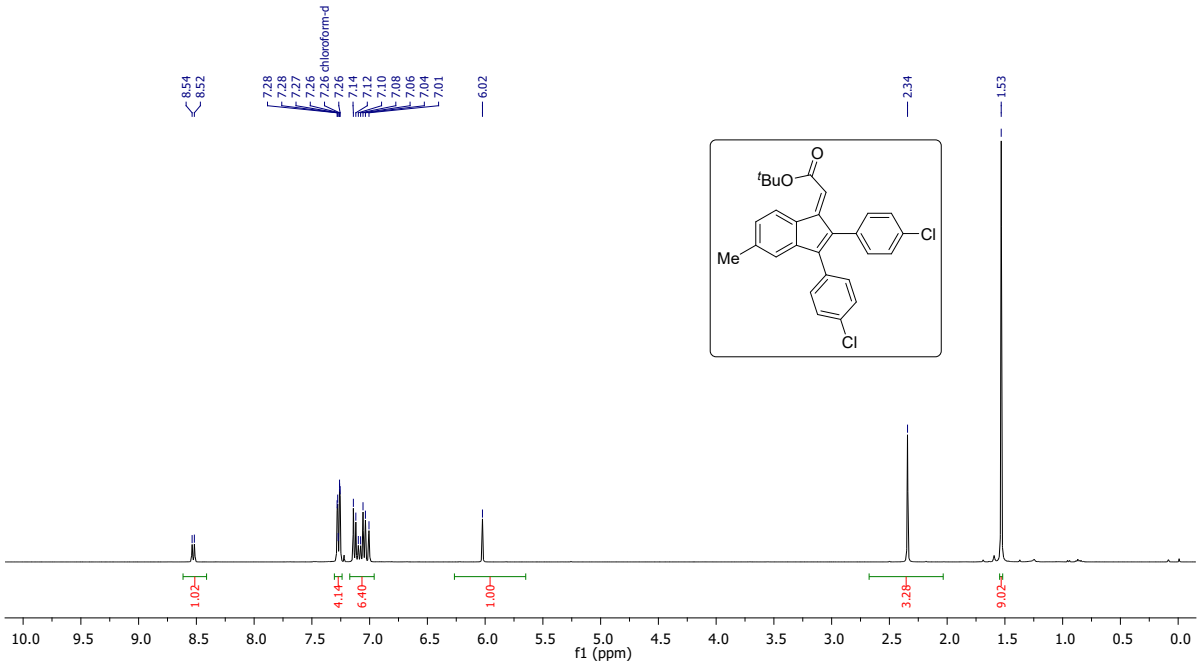
^{19}F NMR (376 MHz) spectrum of **3kc** in $CDCl_3$



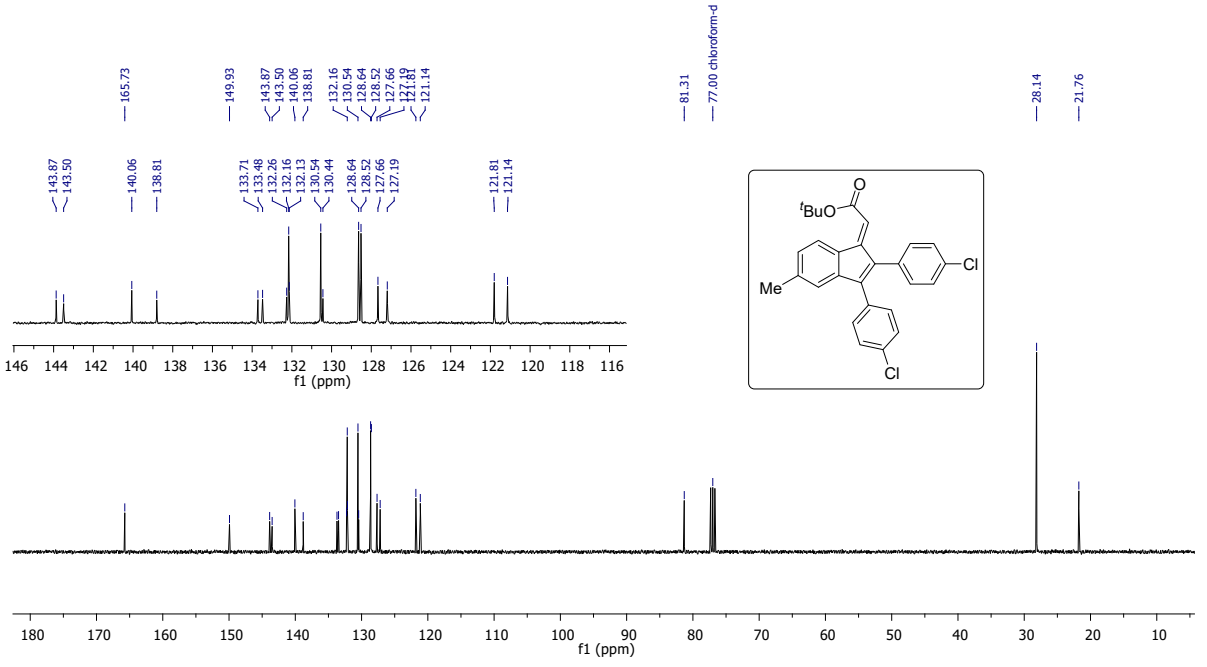
^{1}H NMR (400 MHz) spectrum of **3la** in $CDCl_3$



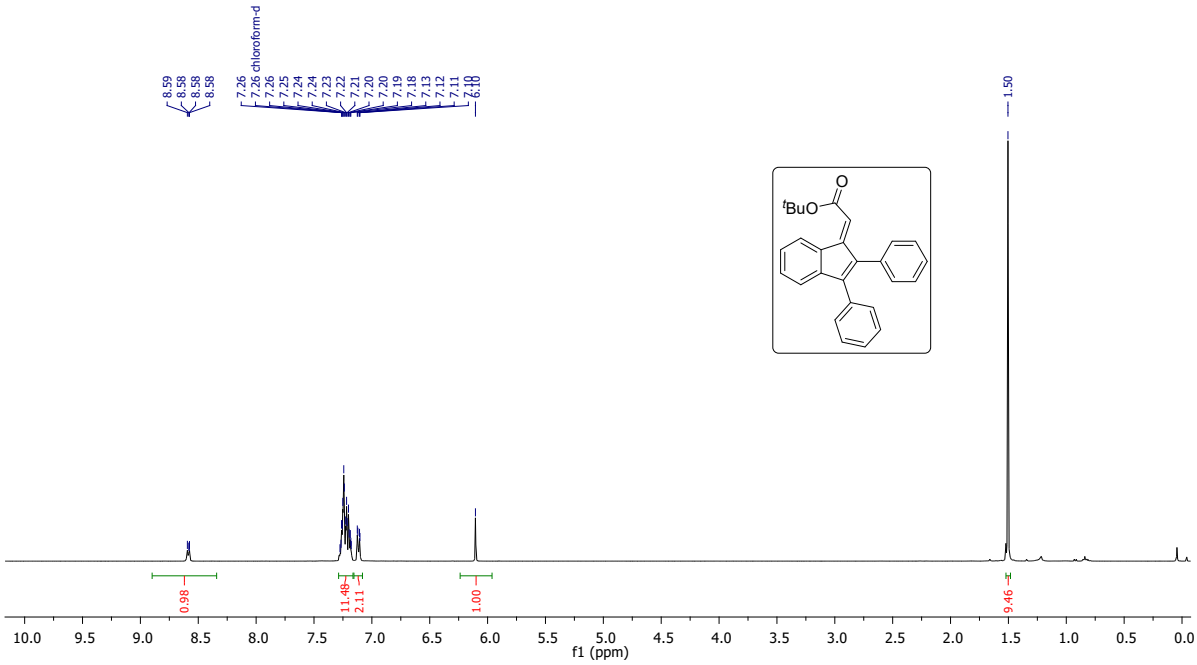
^{13}C{H} NMR (100 MHz) spectrum of **3la** in $CDCl_3$



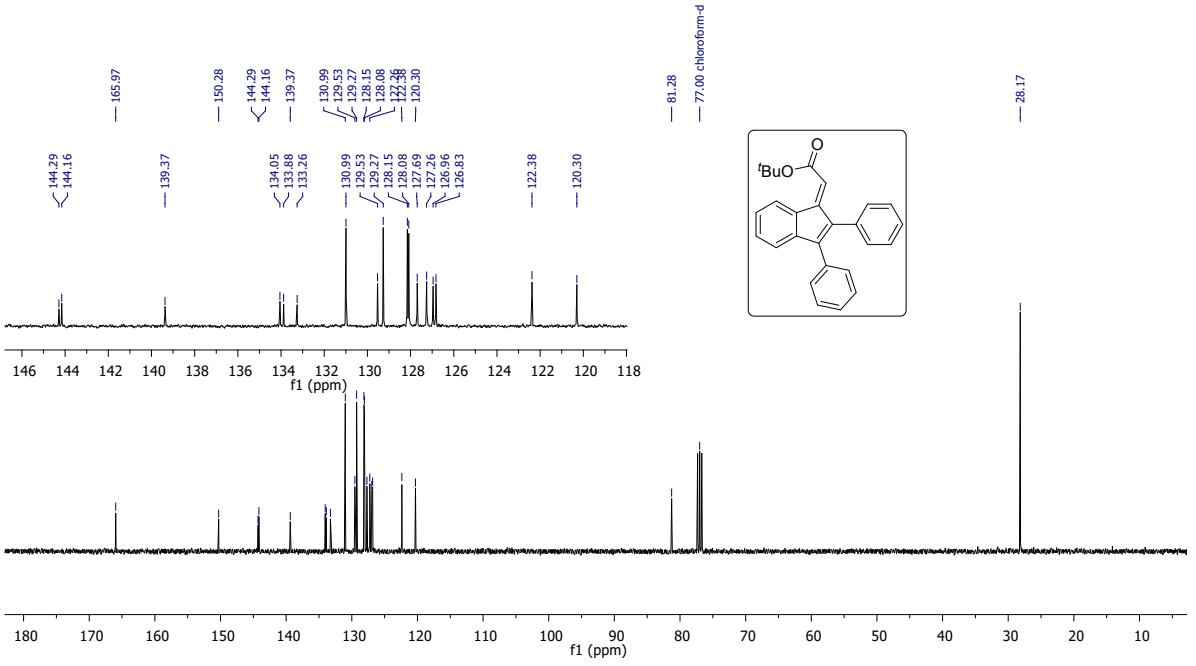
^{1}H NMR (400 MHz) spectrum of **3nk** in $CDCl_3$



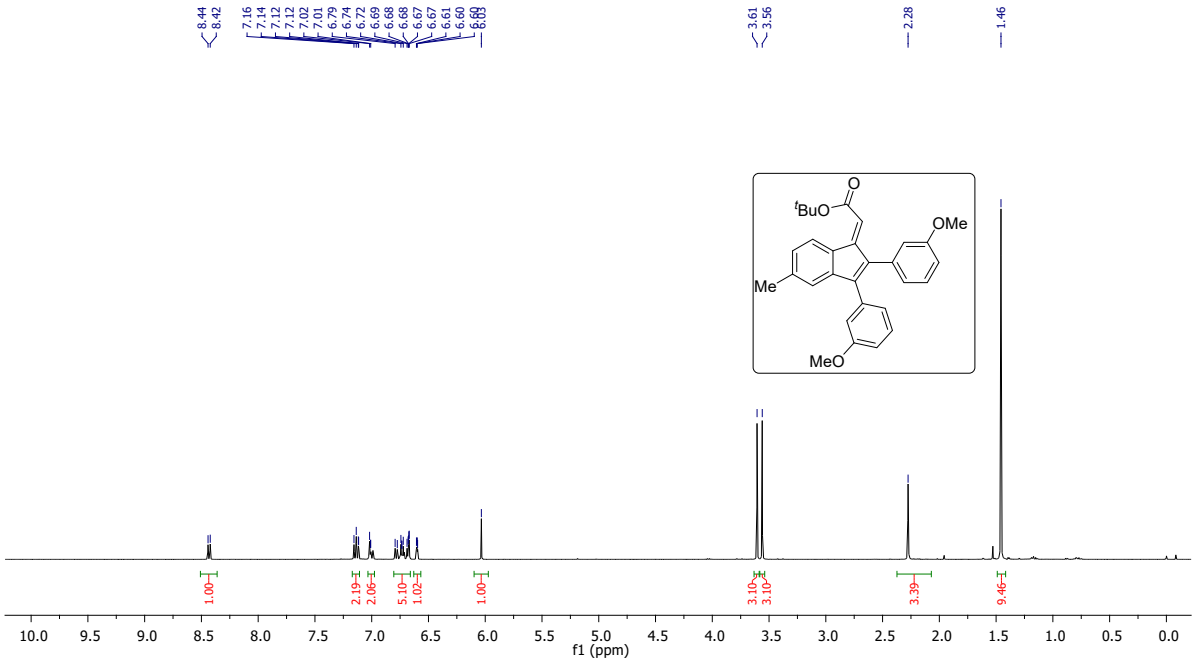
^{13}C{H} NMR (100 MHz) spectrum of **3nk** in $CDCl_3$



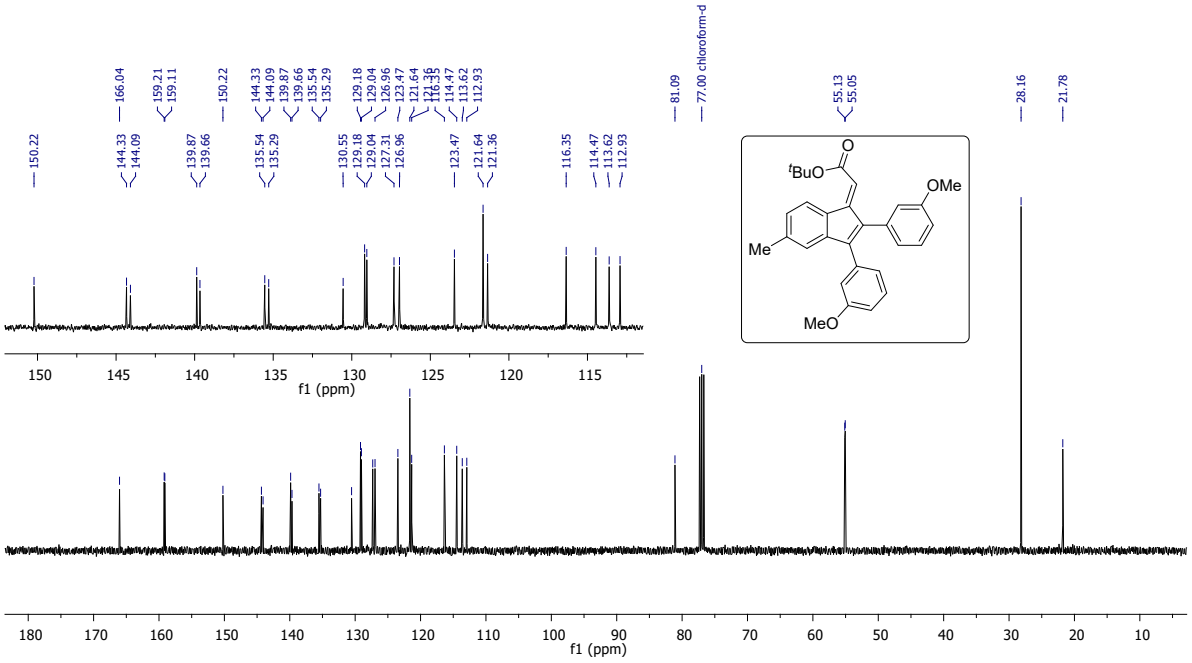
^{1}H NMR (400 MHz) spectrum of **3ma** in $CDCl_3$



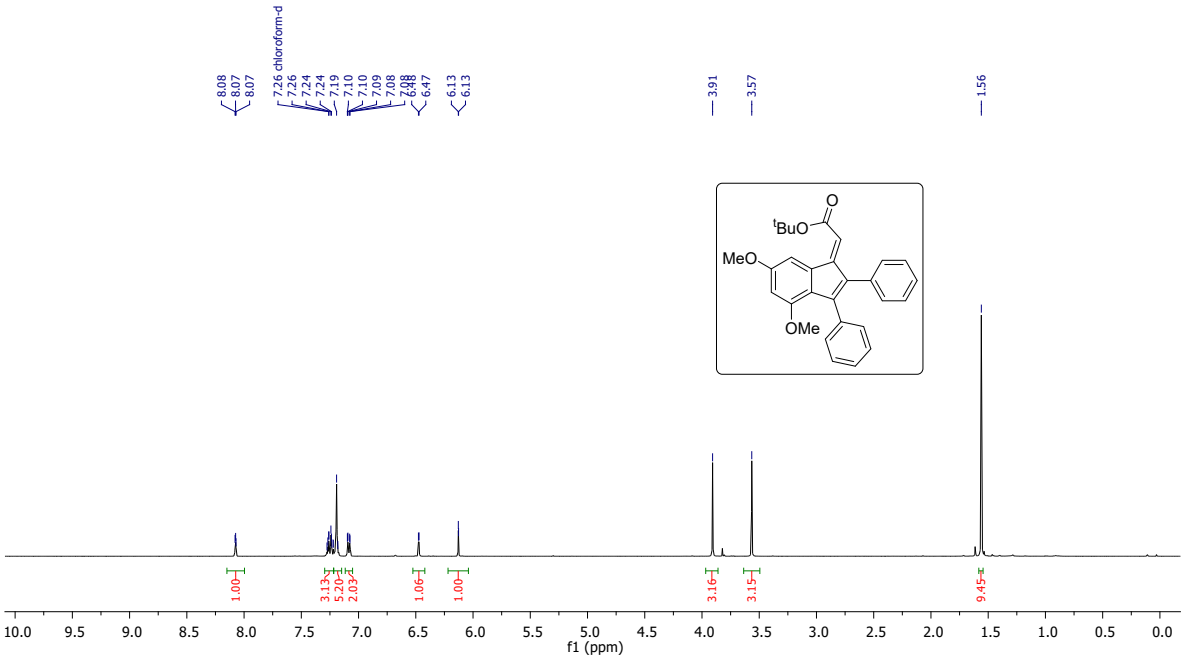
^{13}C{H} NMR (100 MHz) spectrum of **3ma** in $CDCl_3$



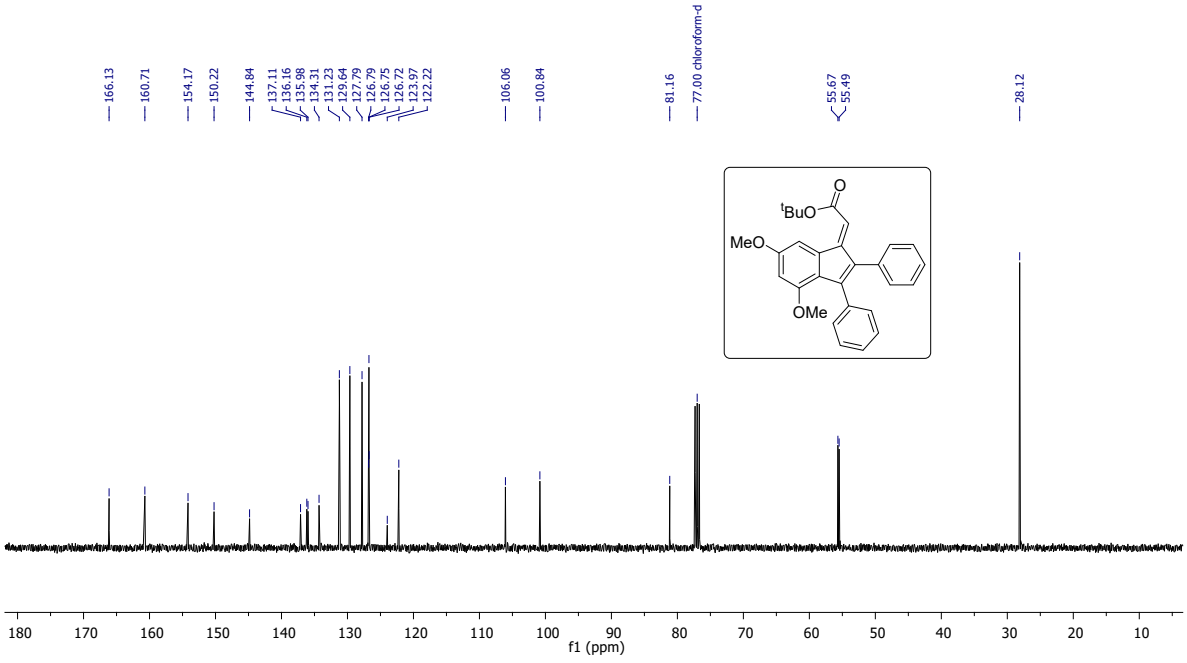
^{1}H NMR (400 MHz) spectrum of **3nc** in $CDCl_3$



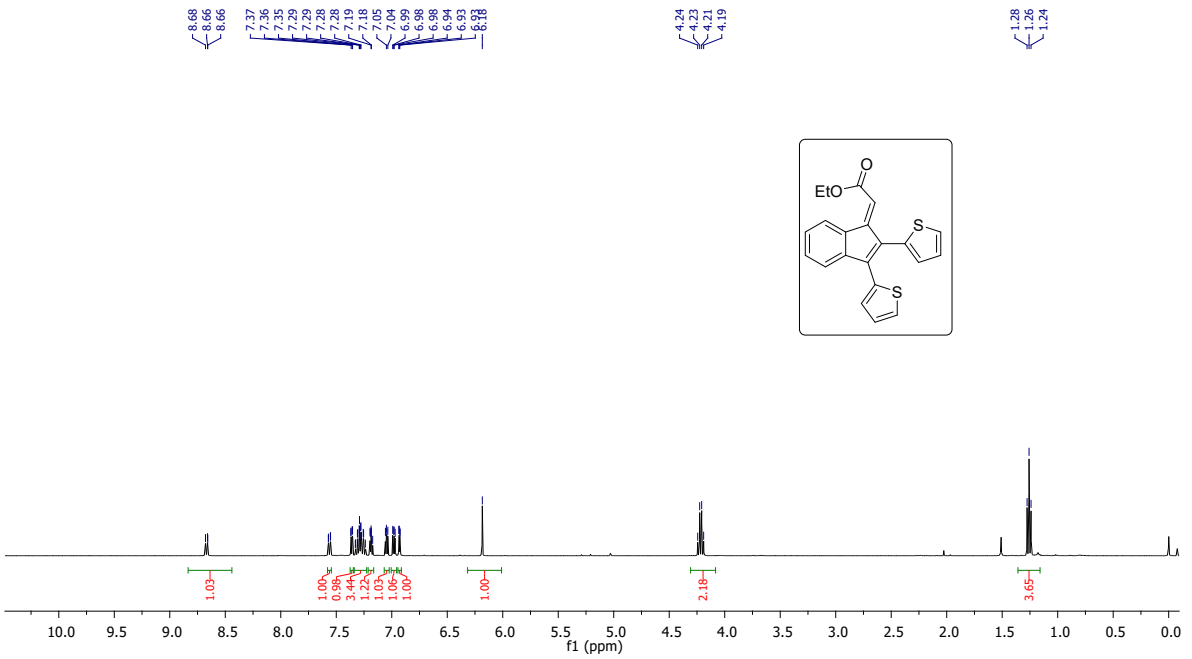
^{13}C{H} NMR (100 MHz) spectrum of **3nc** in $CDCl_3$



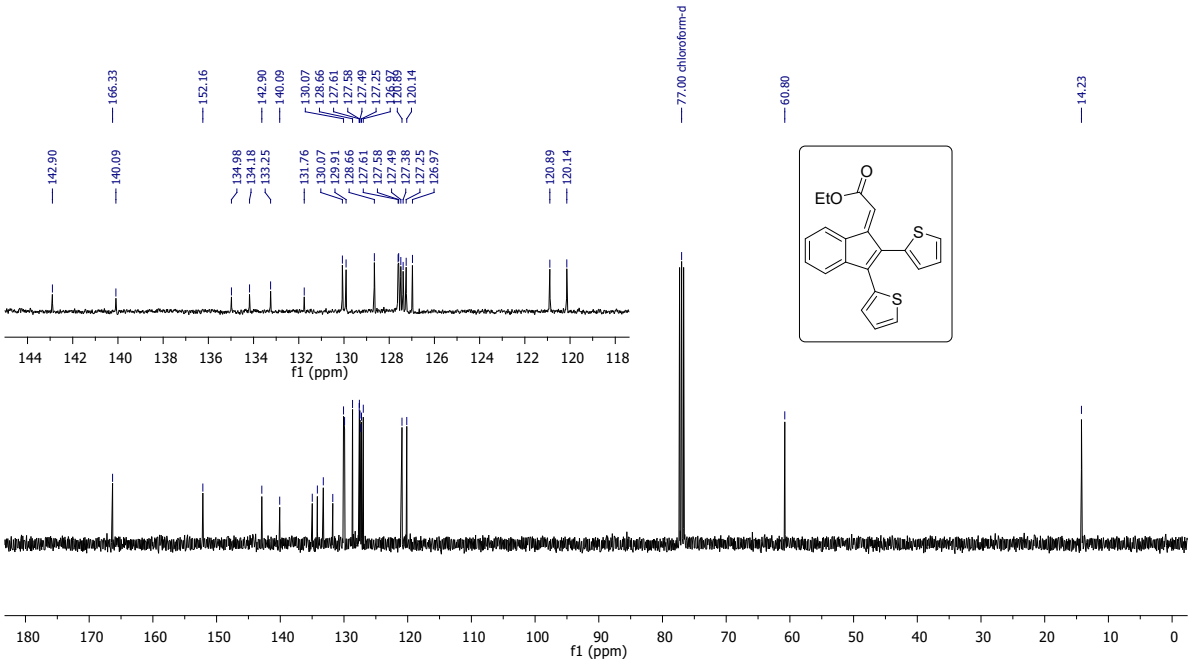
^{1}H NMR (400 MHz) spectrum of **3oa** in $CDCl_3$



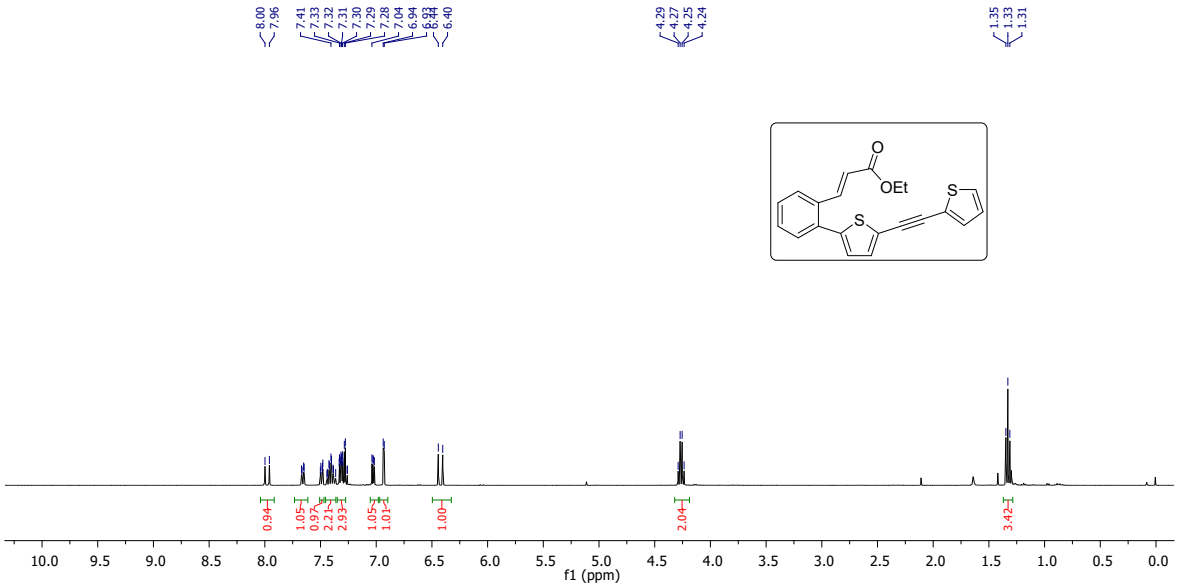
^{13}C{H} NMR (100 MHz) spectrum of **3oa** in $CDCl_3$



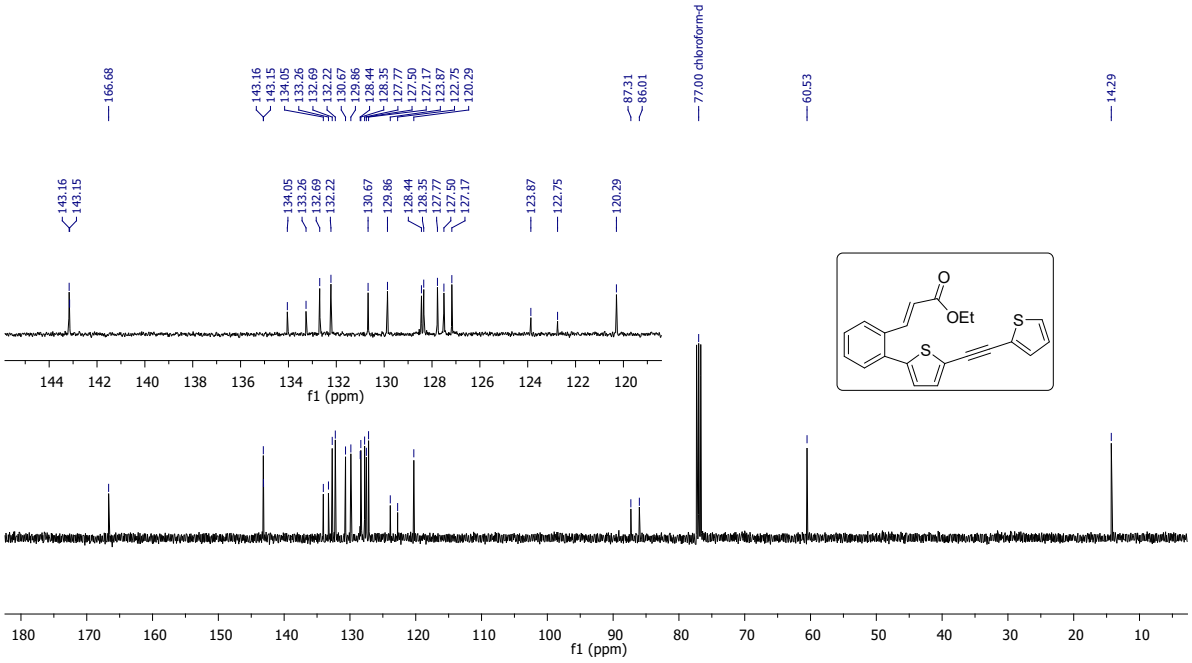
^{1}H NMR (400 MHz) spectrum of **3al** in $CDCl_3$



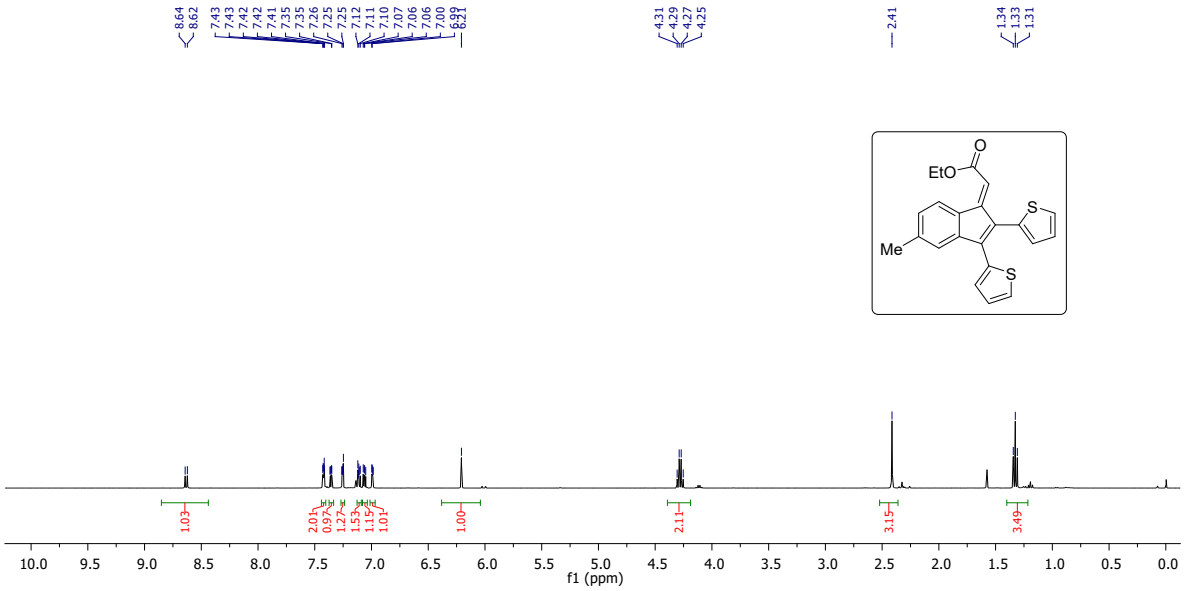
^{13}C{H} NMR (100 MHz) spectrum of **3al** in $CDCl_3$



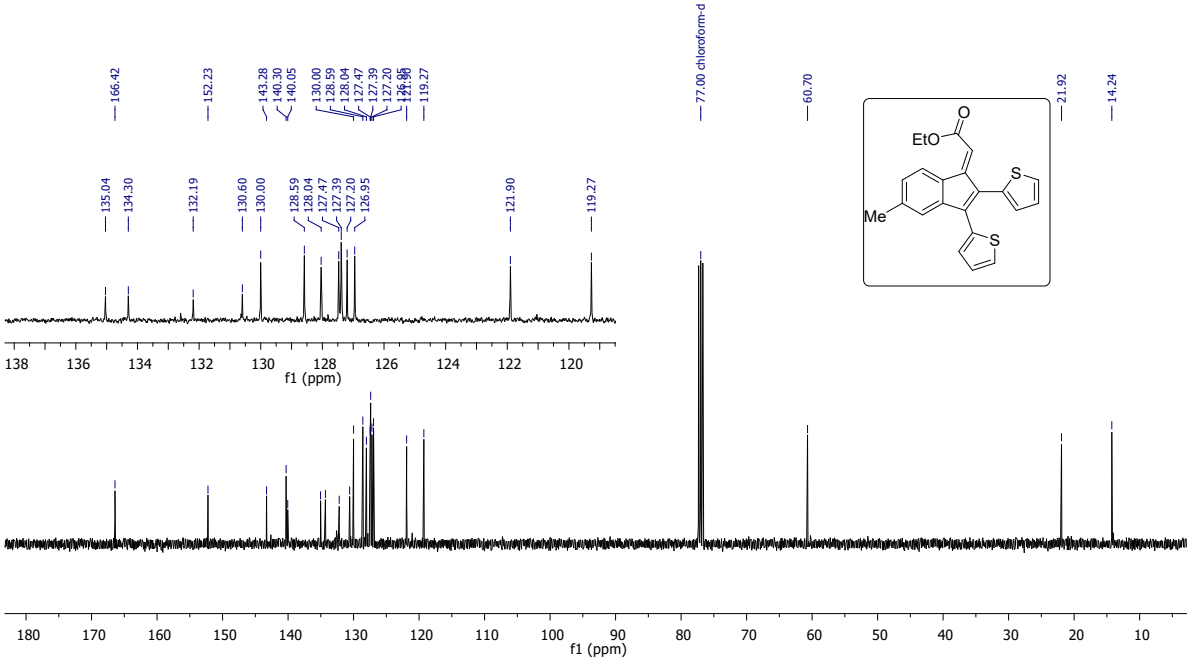
^{1}H NMR (400 MHz) spectrum of **3al'** in $CDCl_3$



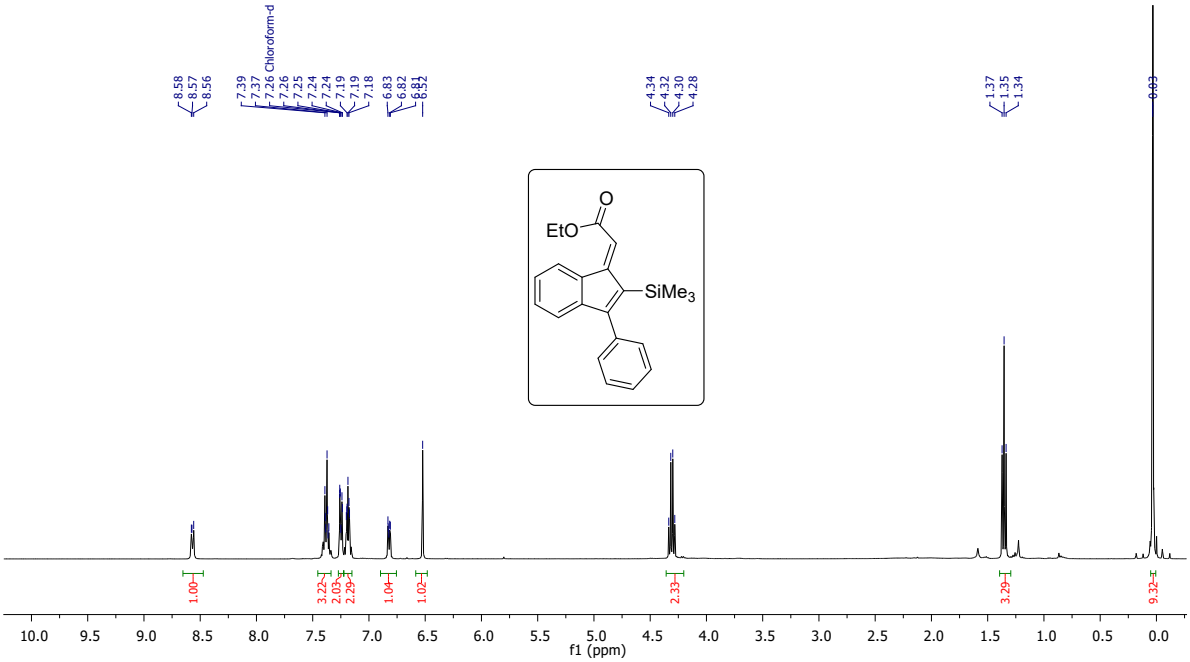
^{13}C{H} NMR (100 MHz) spectrum of **3al'** in $CDCl_3$



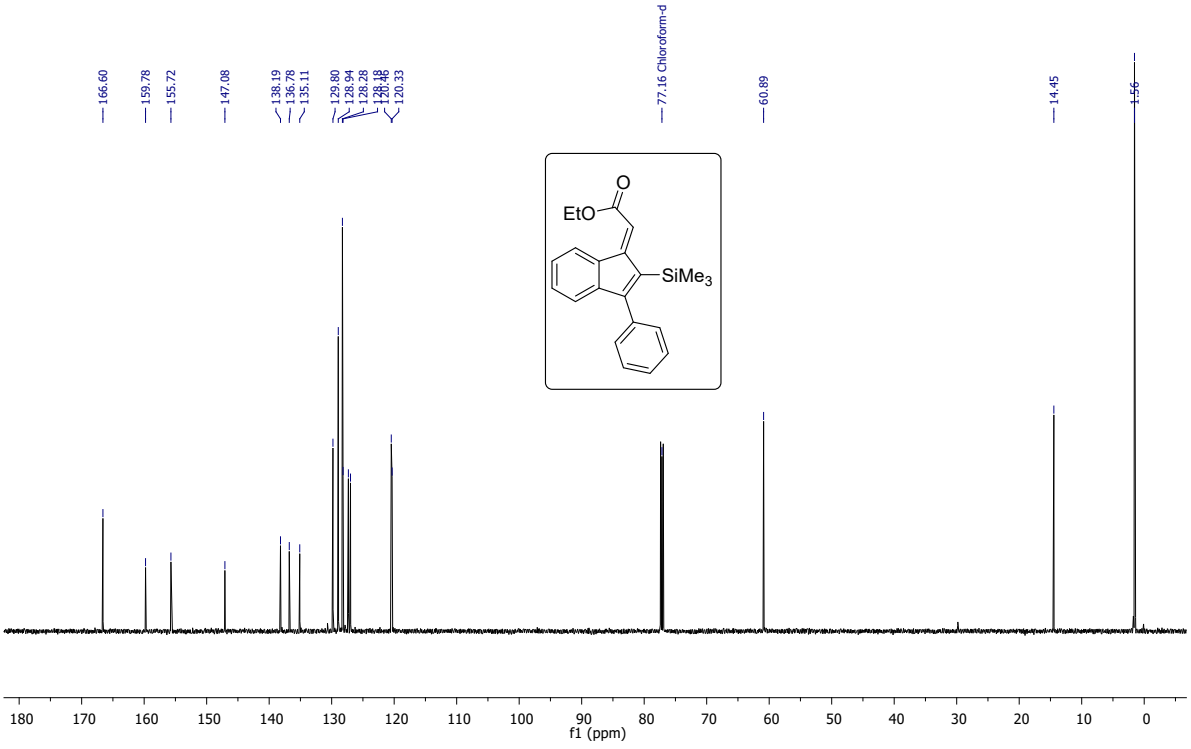
^{1}H NMR (400 MHz) spectrum of **3bl** in $CDCl_3$



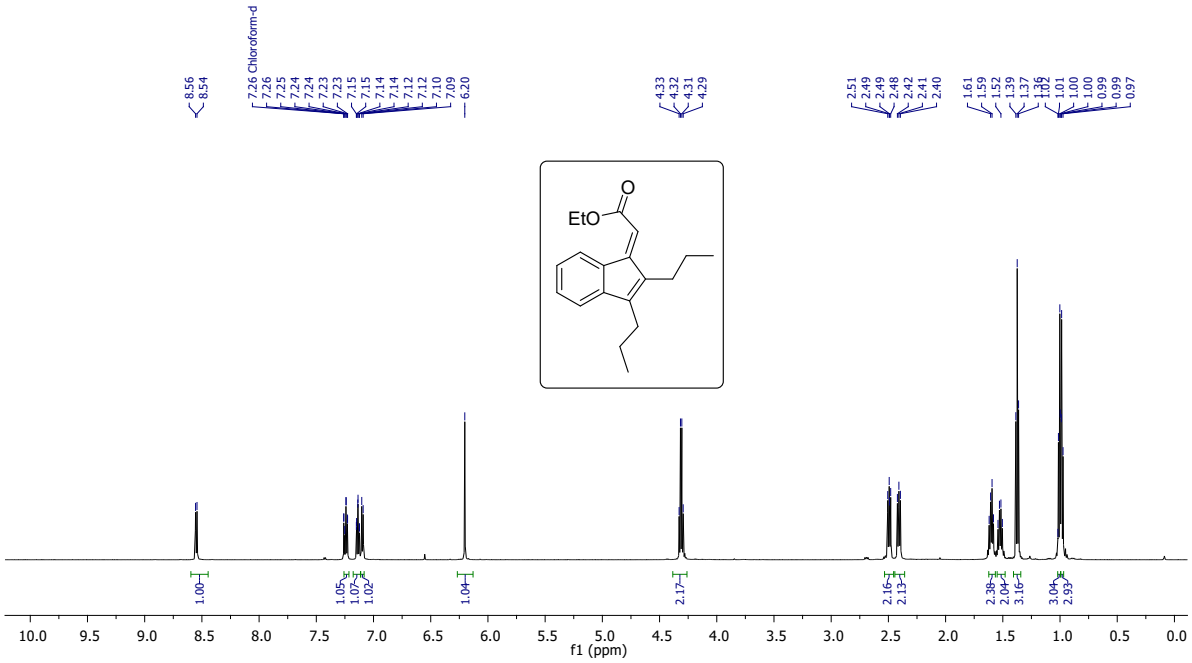
^{13}C{H} NMR (100 MHz) spectrum of **3bl** in $CDCl_3$



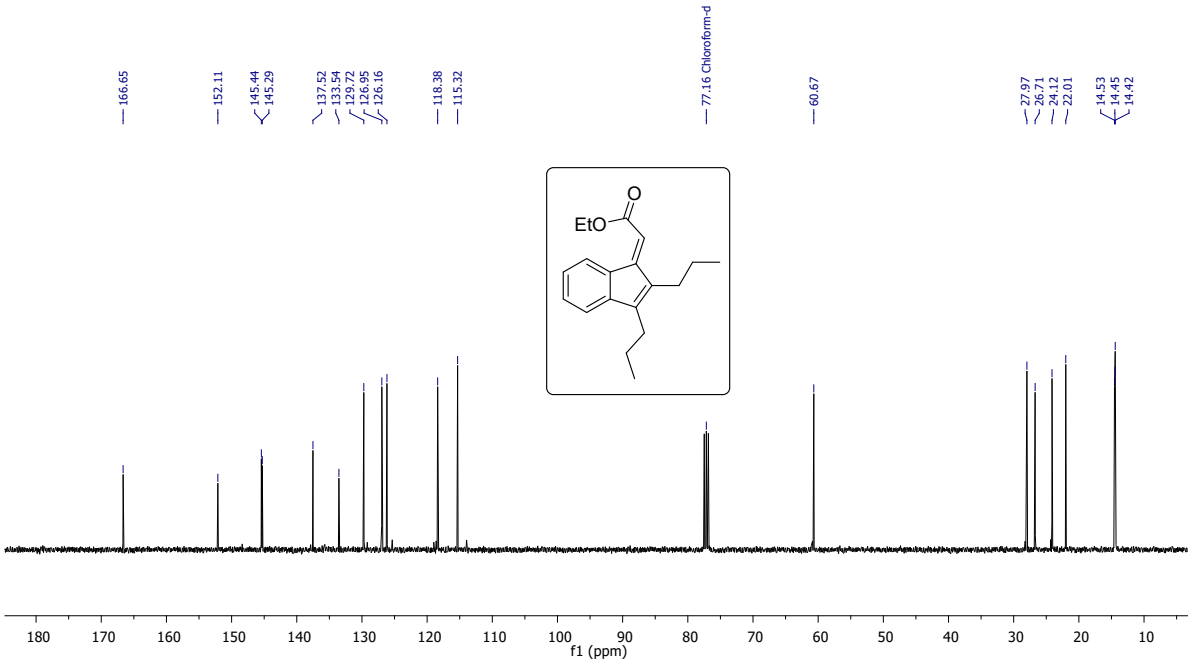
^{1}H NMR (400 MHz) spectrum of **3am** in $CDCl_3$



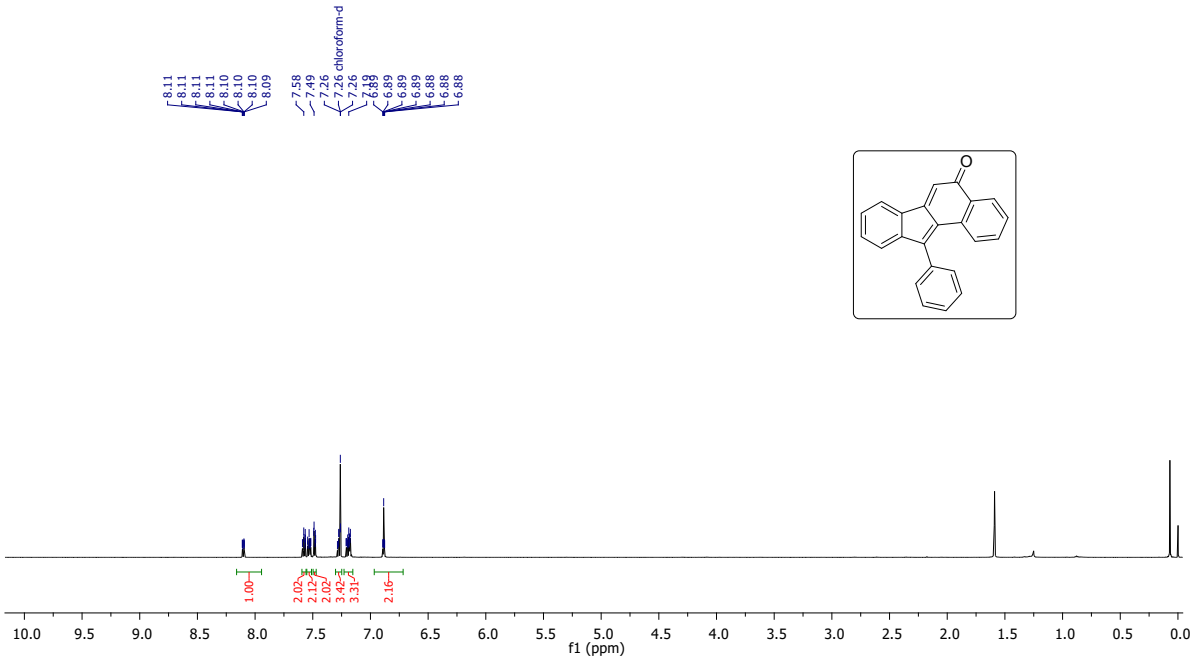
^{13}C{H} NMR (151 MHz) spectrum of **3am** in $CDCl_3$



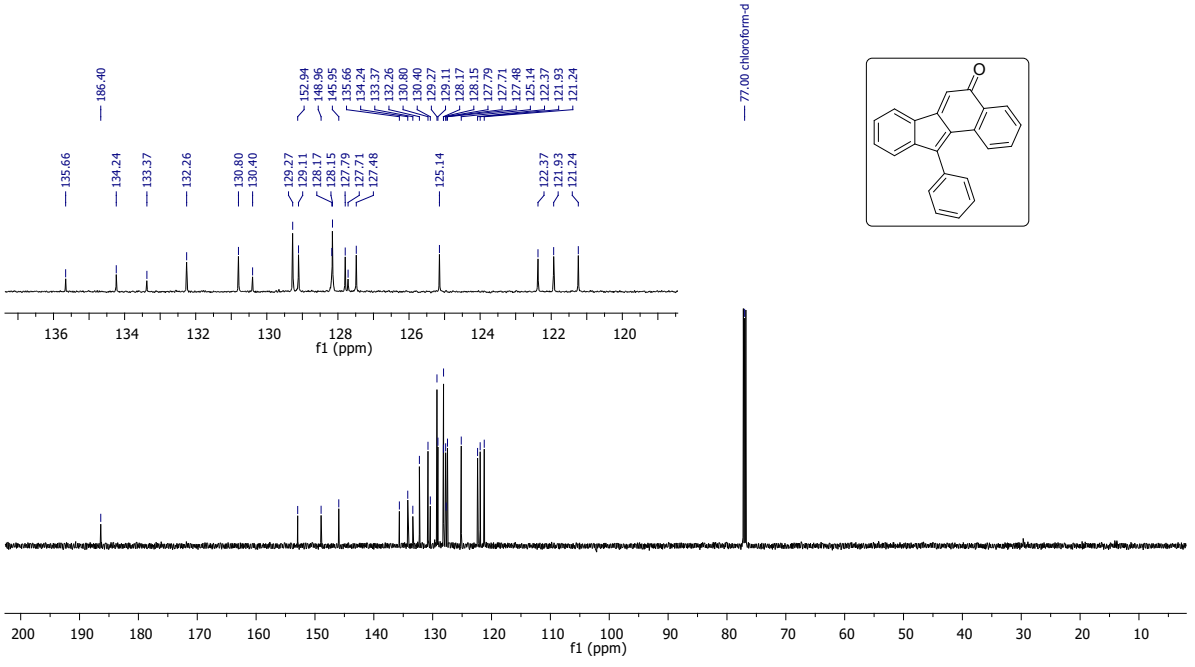
^{1}H NMR (600 MHz) spectrum of **3an** in $CDCl_3$



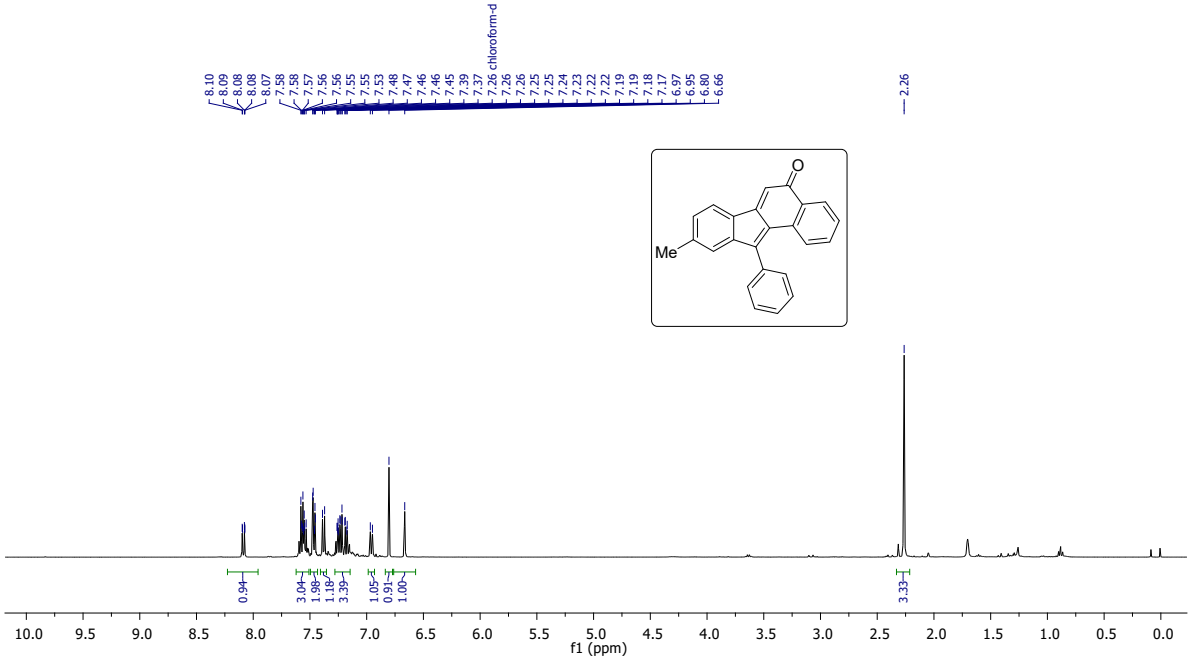
^{13}C{H} NMR (151 MHz) spectrum of **3an** in $CDCl_3$



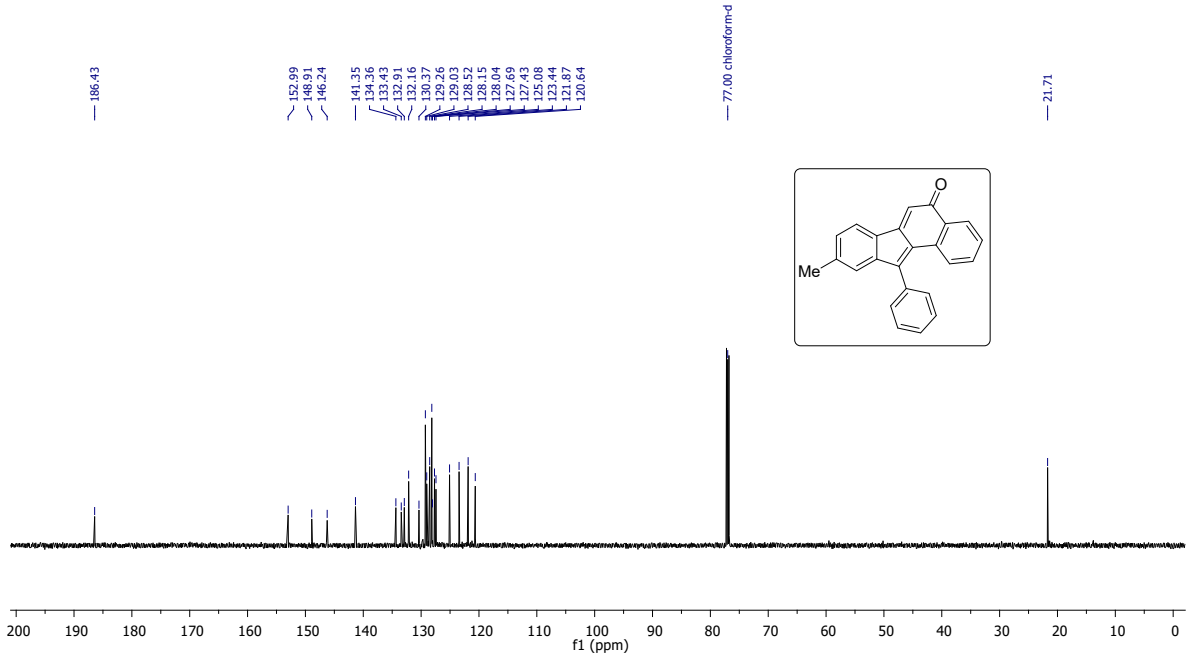
^{1}H NMR (400 MHz) spectrum of **4a** in $CDCl_3$



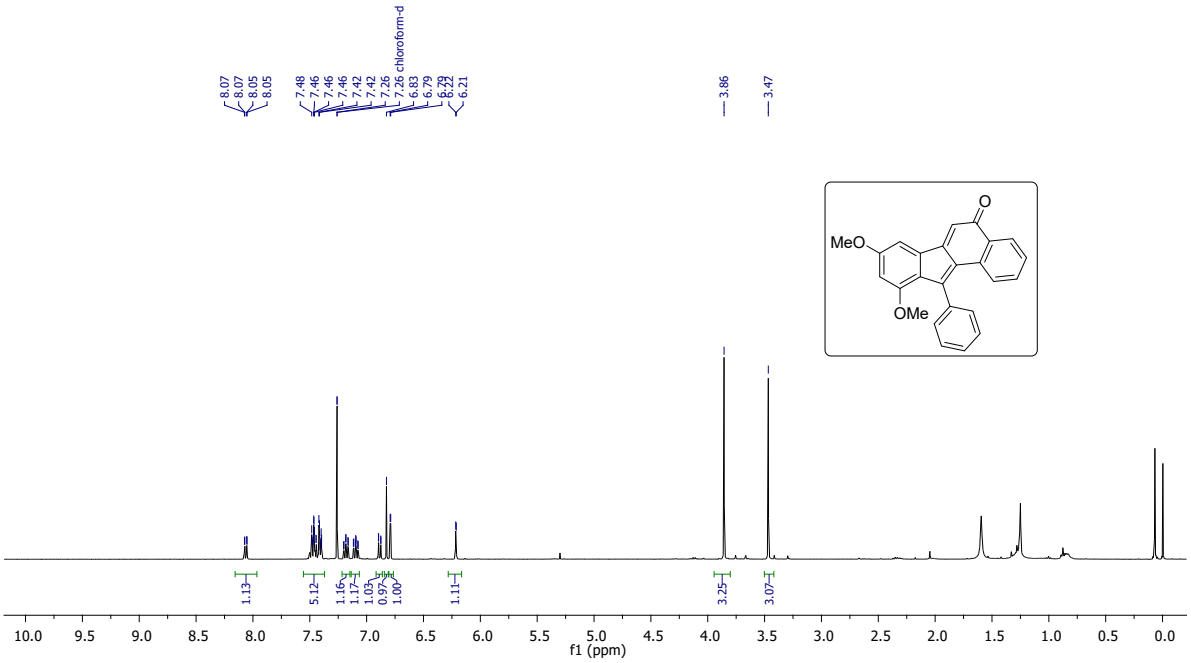
^{13}C{H} NMR (151 MHz) spectrum of **4a** in $CDCl_3$



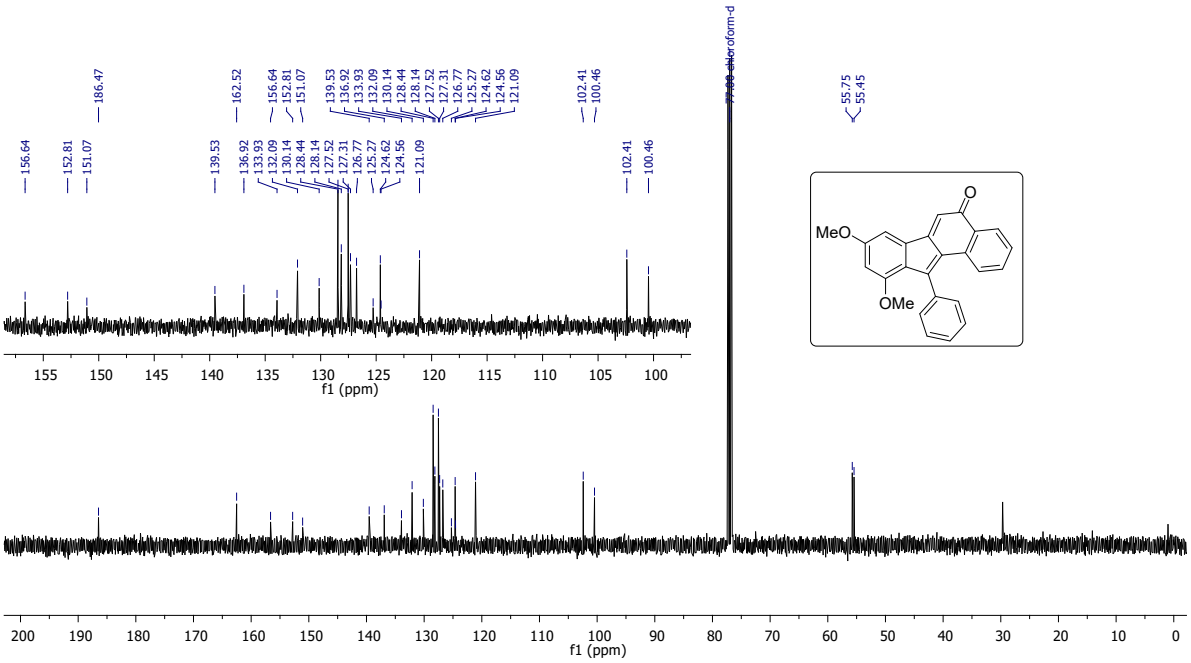
^{1}H NMR (400 MHz) spectrum of **4b** in $CDCl_3$



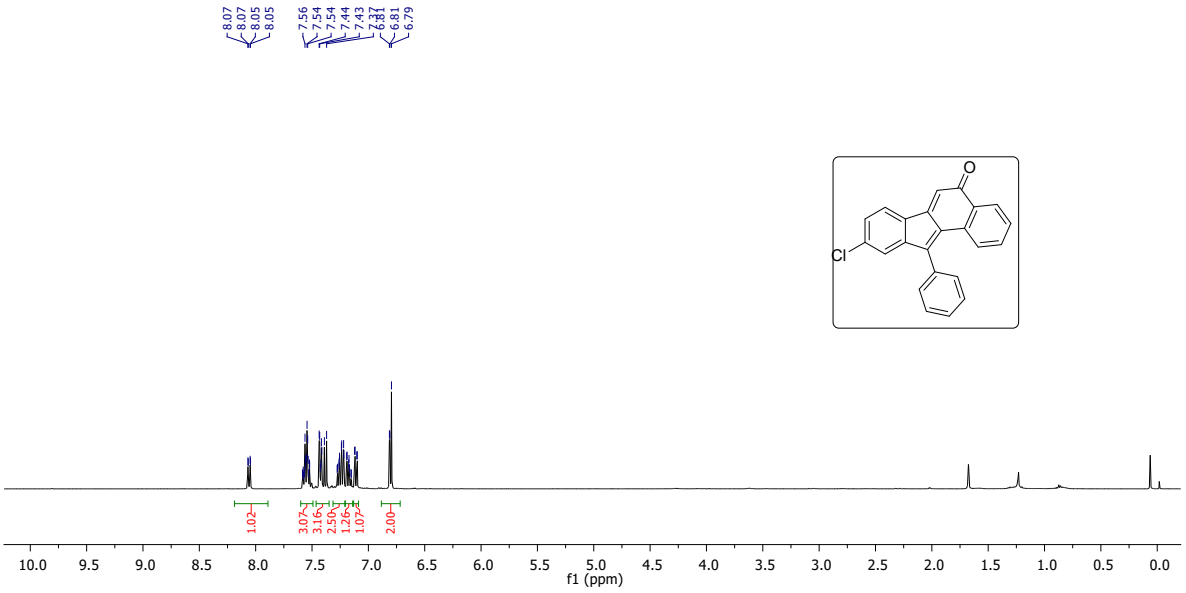
^{13}C{H} NMR (151 MHz) spectrum of **4b** in $CDCl_3$



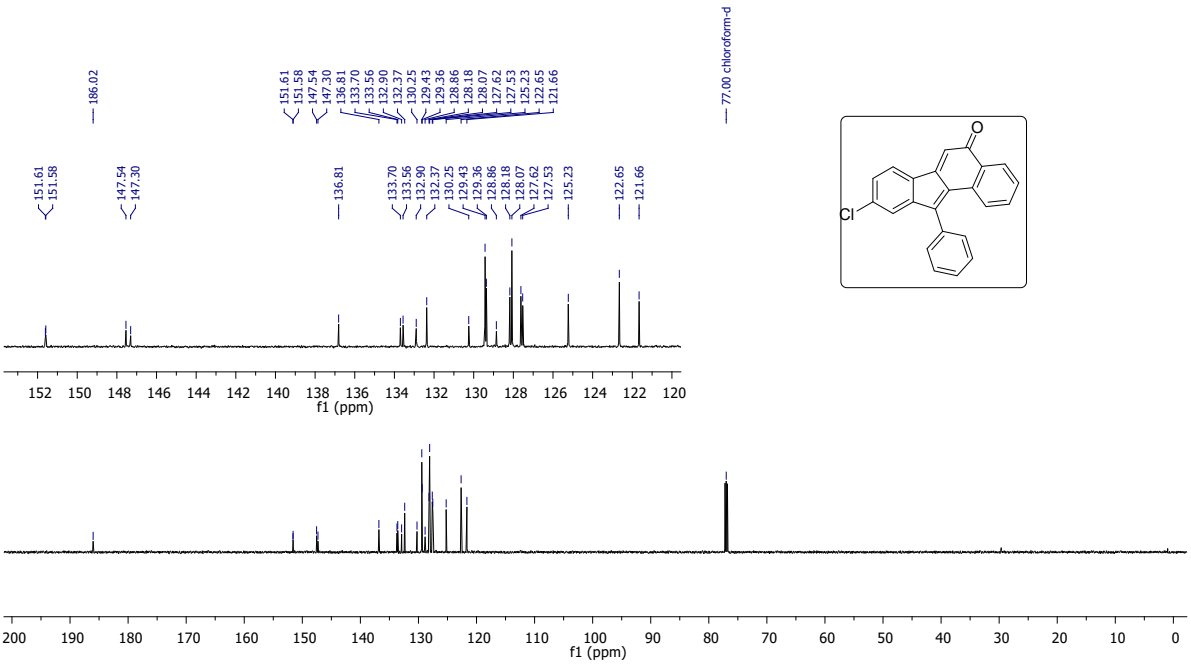
^{1}H NMR (400 MHz) spectrum of **4c** in $CDCl_3$



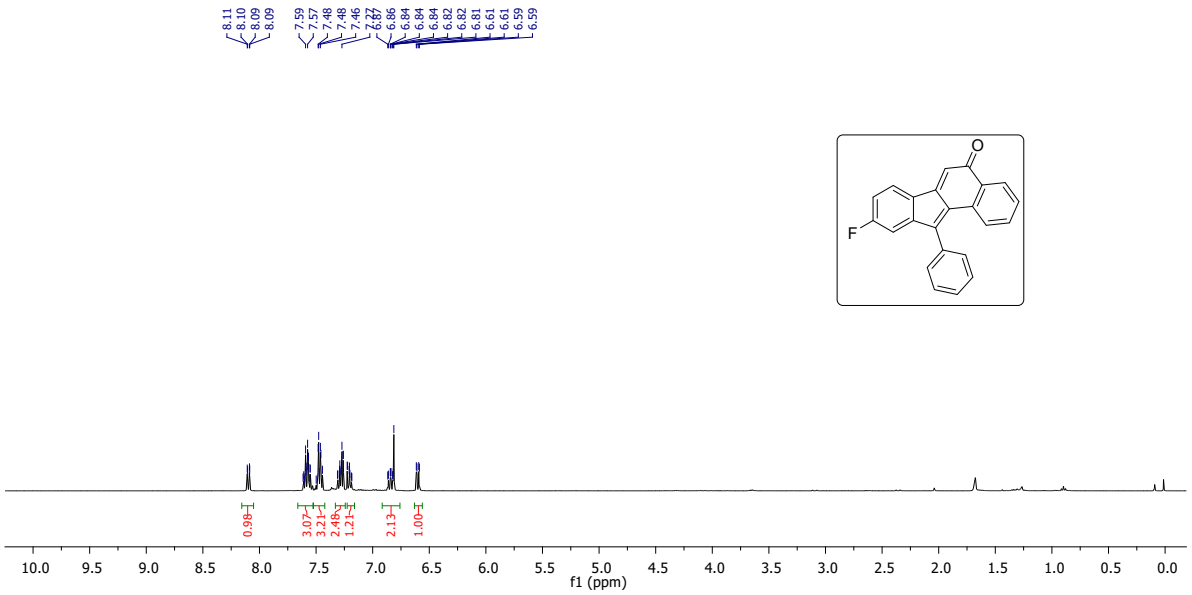
^{13}C{H} NMR (100 MHz) spectrum of **4c** in $CDCl_3$



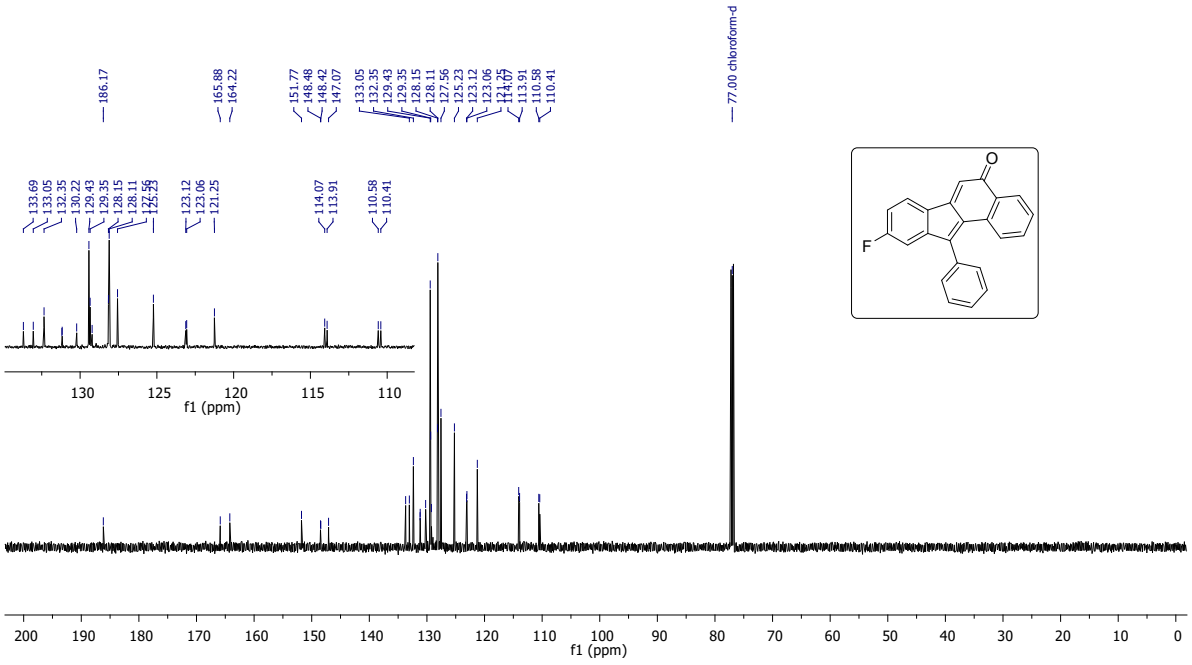
^{1}H NMR (400 MHz) spectrum of **4d** in $CDCl_3$



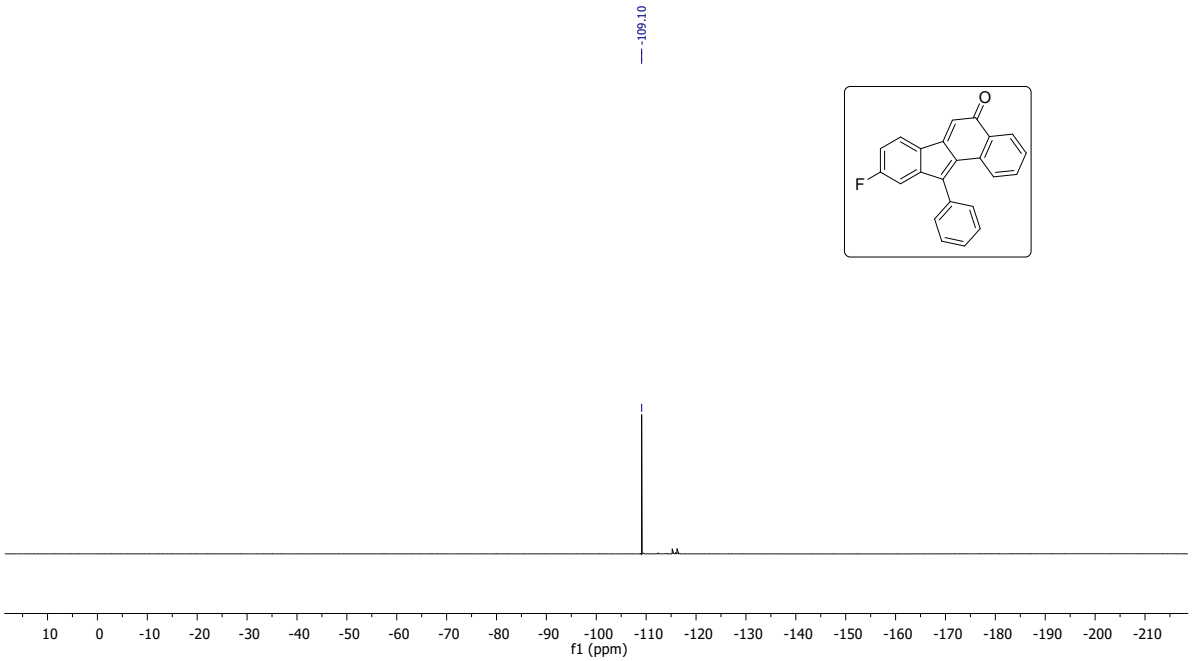
^{13}C{H} NMR (151 MHz) spectrum of **4d** in $CDCl_3$



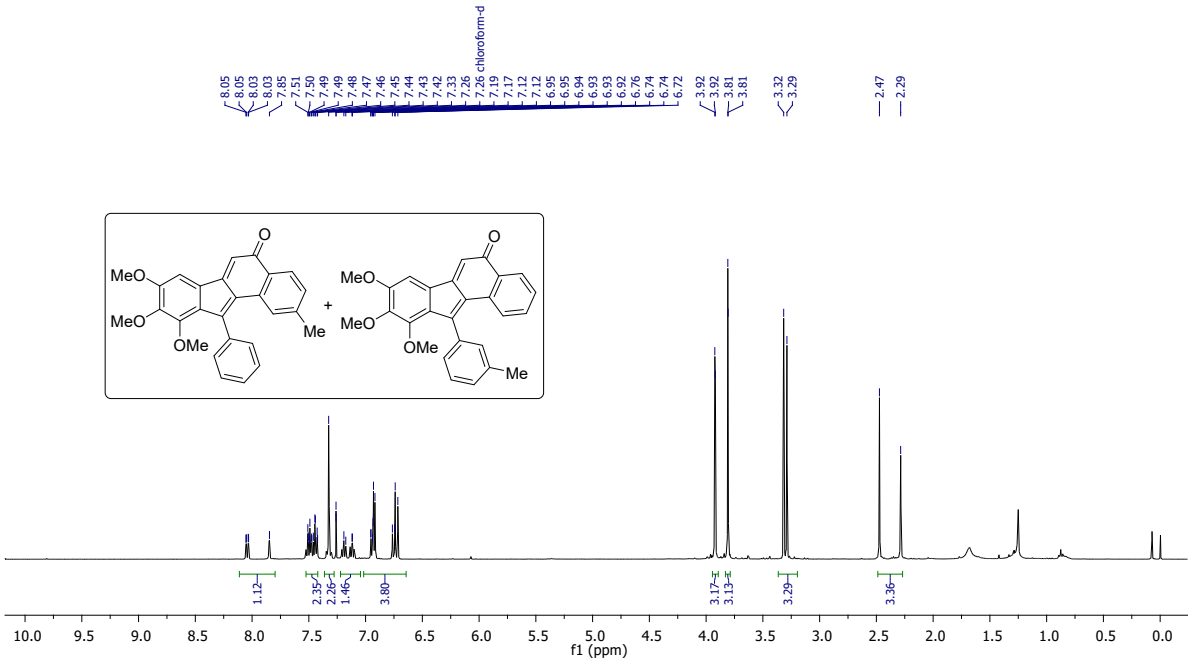
^{1}H NMR (400 MHz) spectrum of **4e** in $CDCl_3$



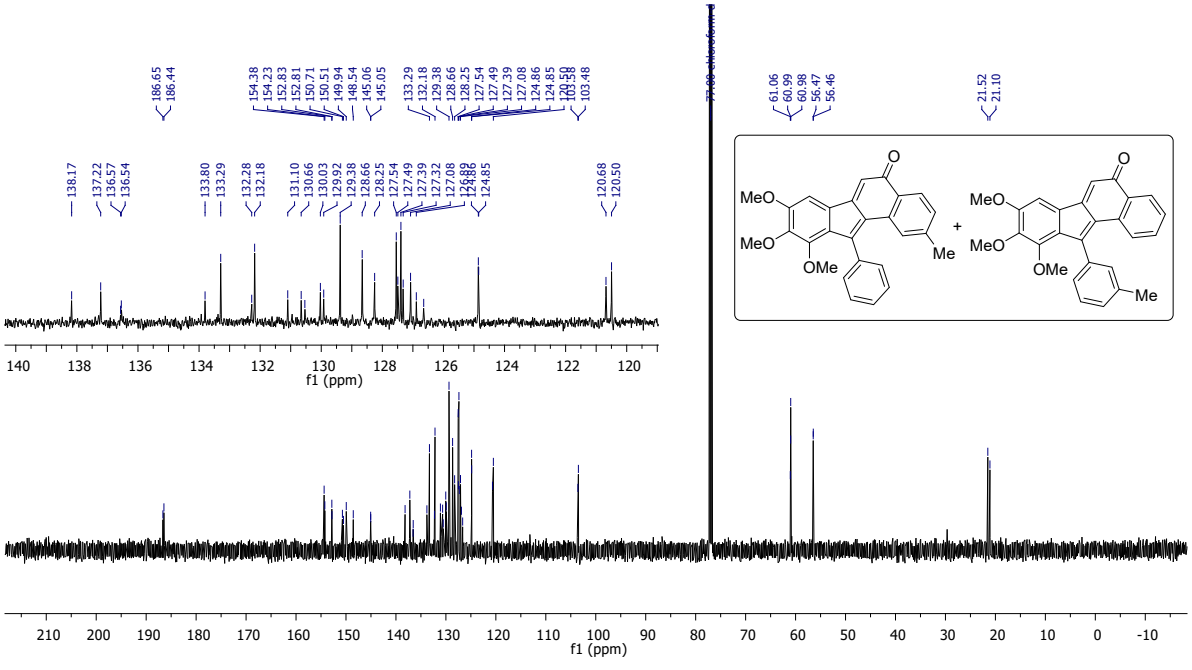
^{13}C{H} NMR (151 MHz) spectrum of **4e** in $CDCl_3$



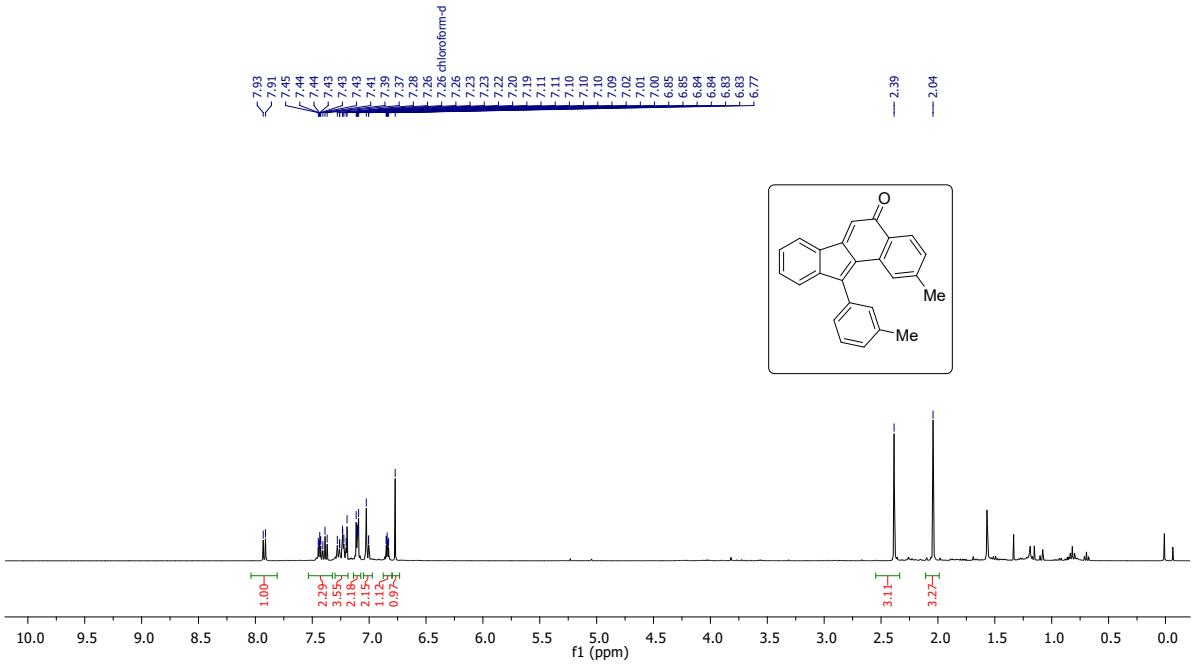
^{19}F NMR (376 MHz) spectrum of **4e** in $CDCl_3$



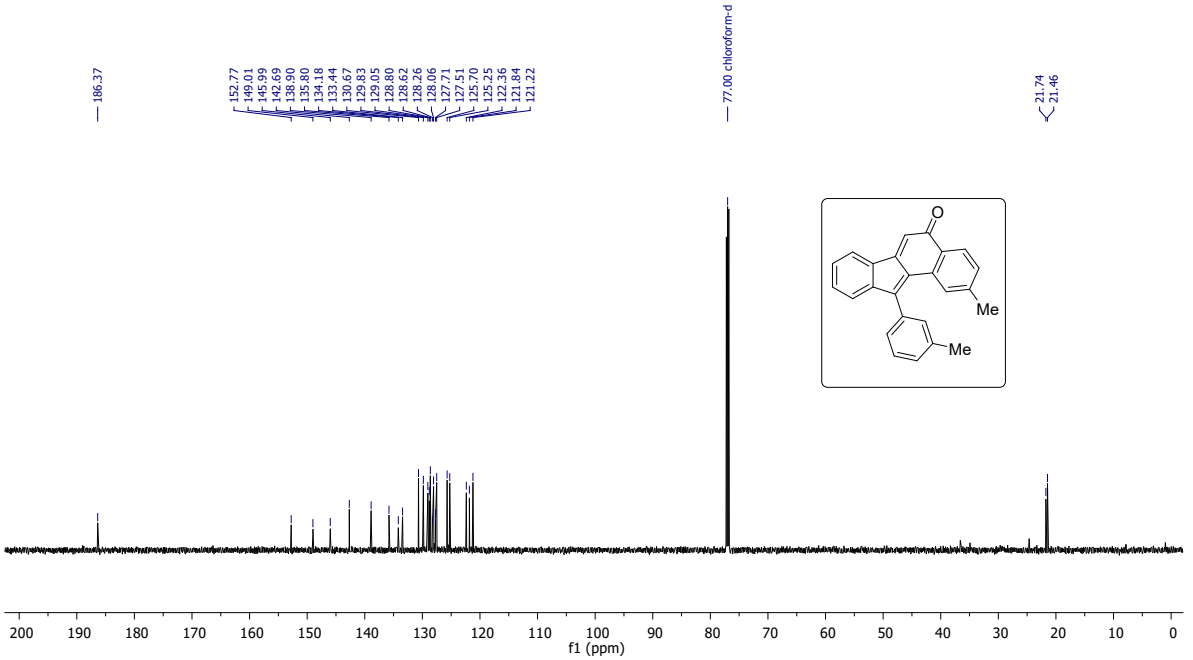
^{1}H NMR (400 MHz) spectrum of **(4f+4f')** in $CDCl_3$



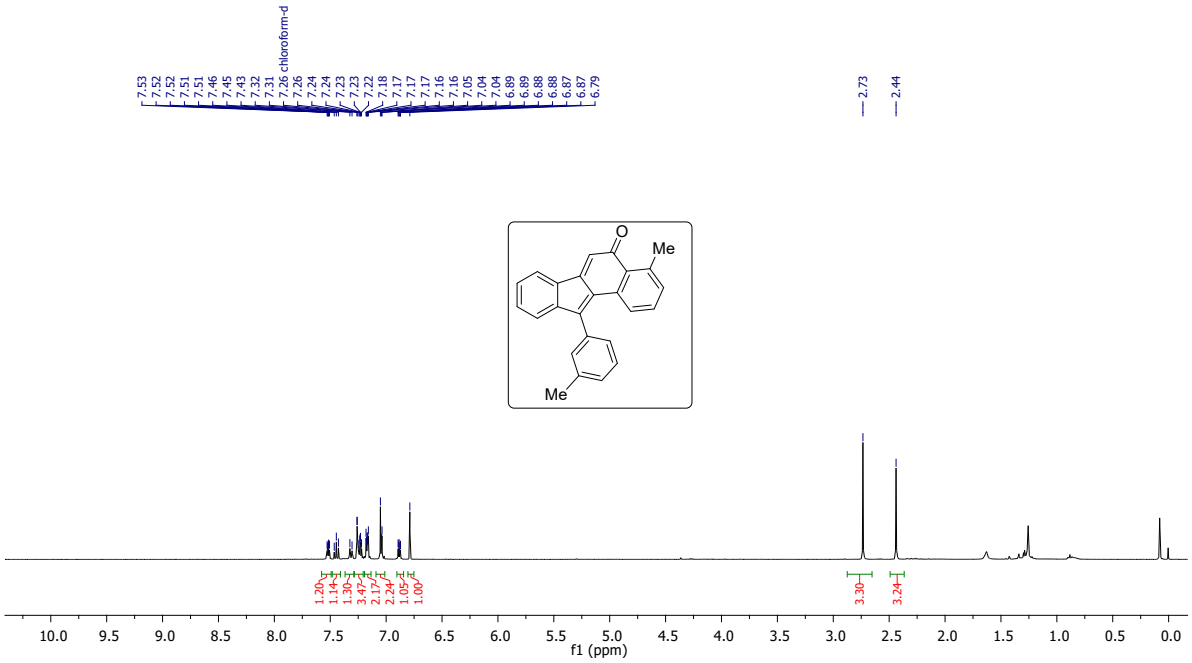
^{13}C{H} NMR (151 MHz) spectrum of **(4f+4f')** in $CDCl_3$



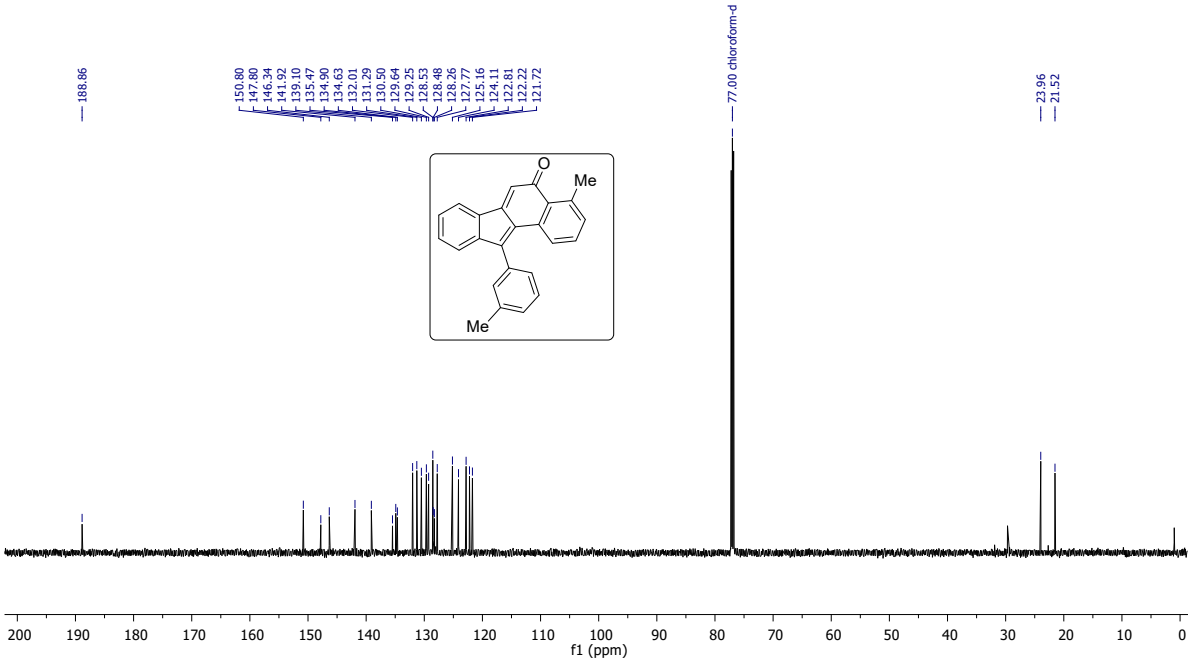
^{1}H NMR (400 MHz) spectrum of **4g** in $CDCl_3$



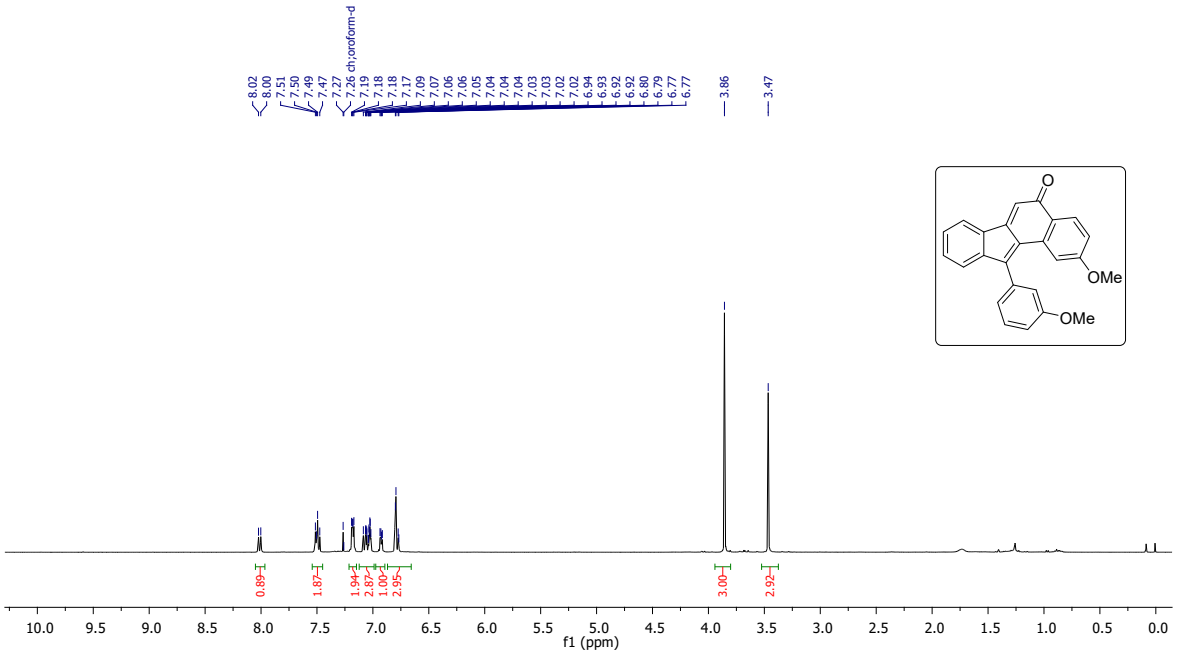
^{13}C{H} NMR (151 MHz) spectrum of **4g** in $CDCl_3$



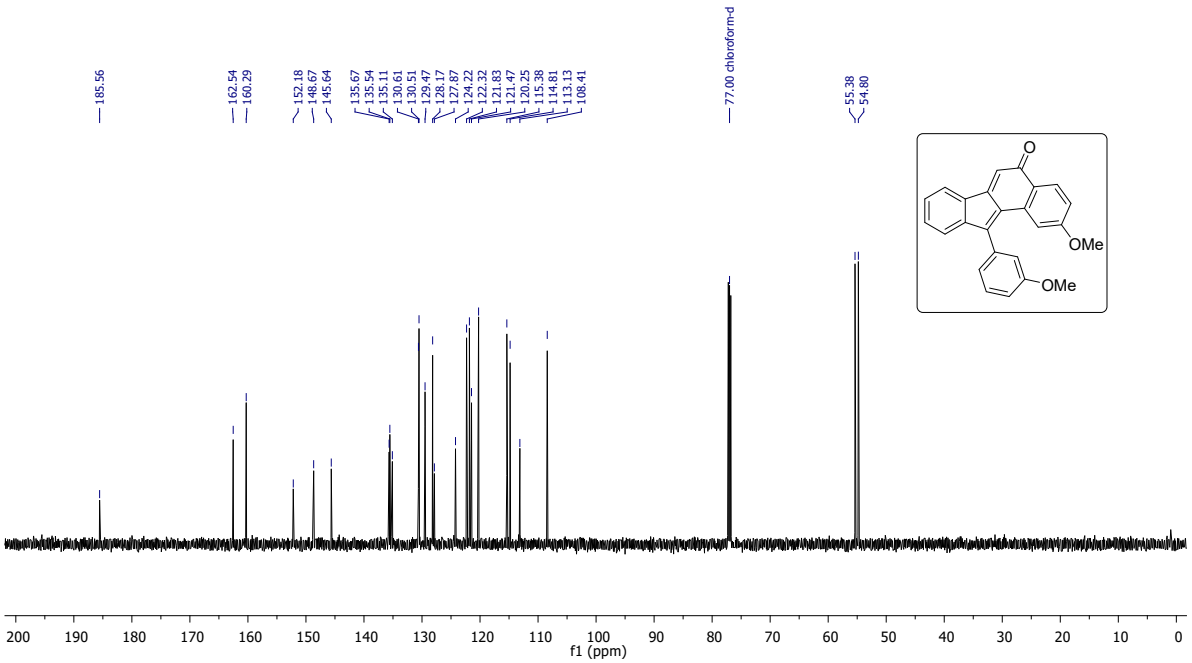
^{1}H NMR (400 MHz) spectrum of **4g'** in $CDCl_3$



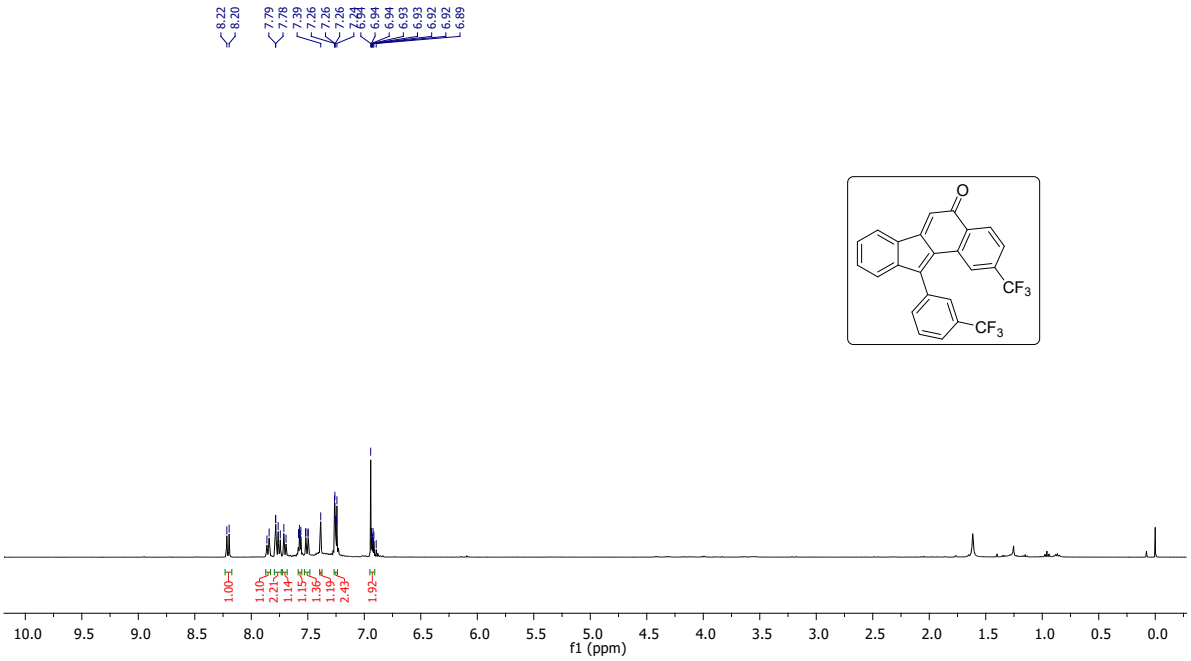
^{13}C{H} NMR (151 MHz) spectrum of **4g'** in $CDCl_3$



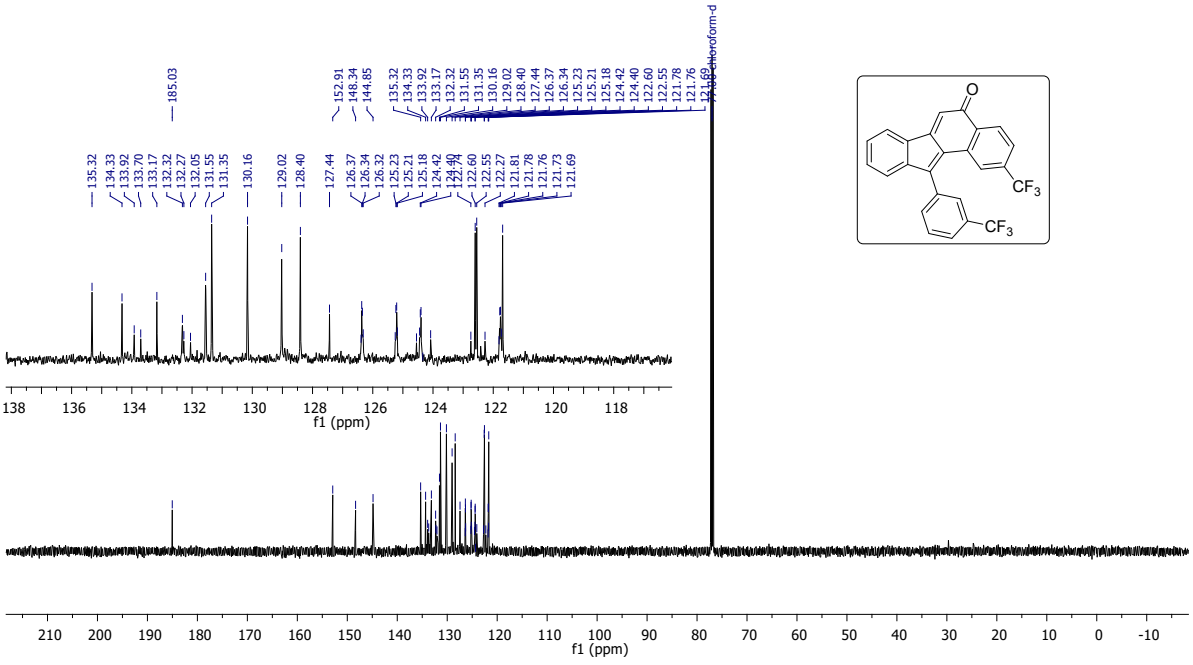
^{1}H NMR (400 MHz) spectrum of **4h** in $CDCl_3$



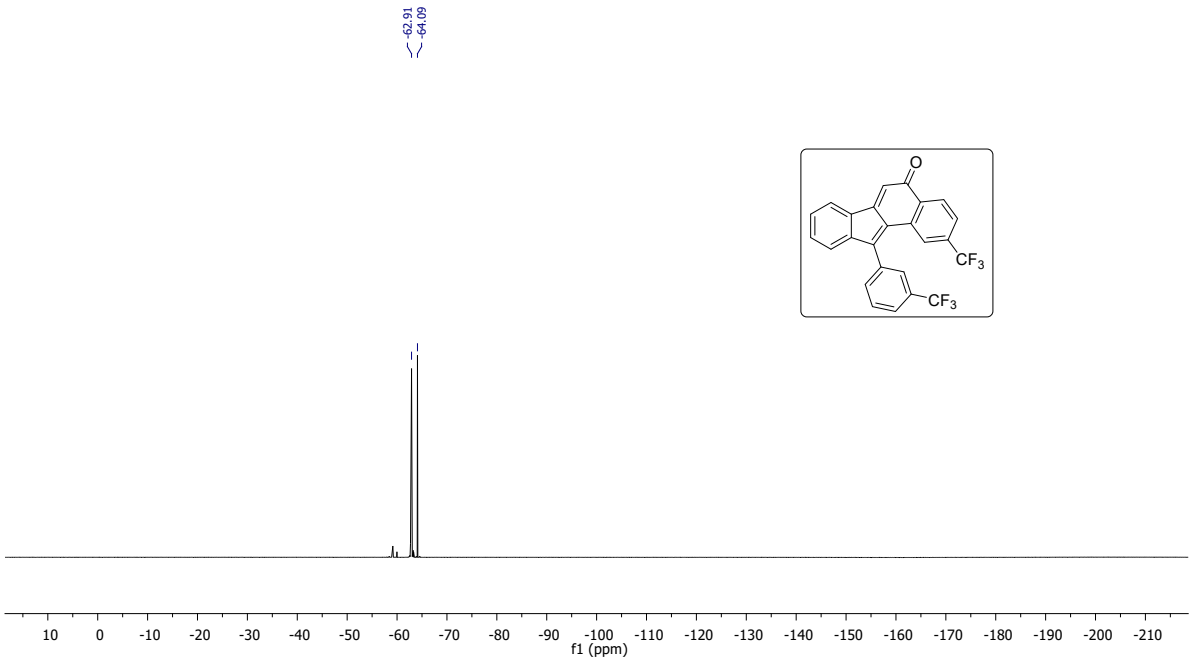
^{13}C{H} NMR (151 MHz) spectrum of **4h** in $CDCl_3$



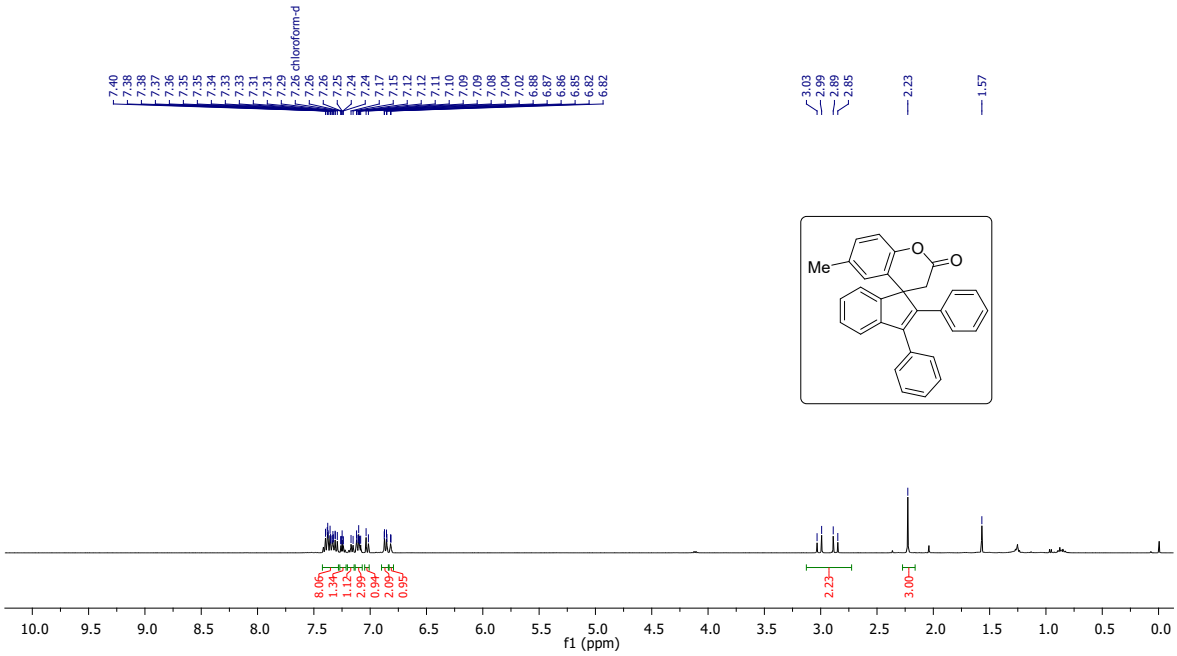
^{1}H NMR (400 MHz) spectrum of **4i** in $CDCl_3$



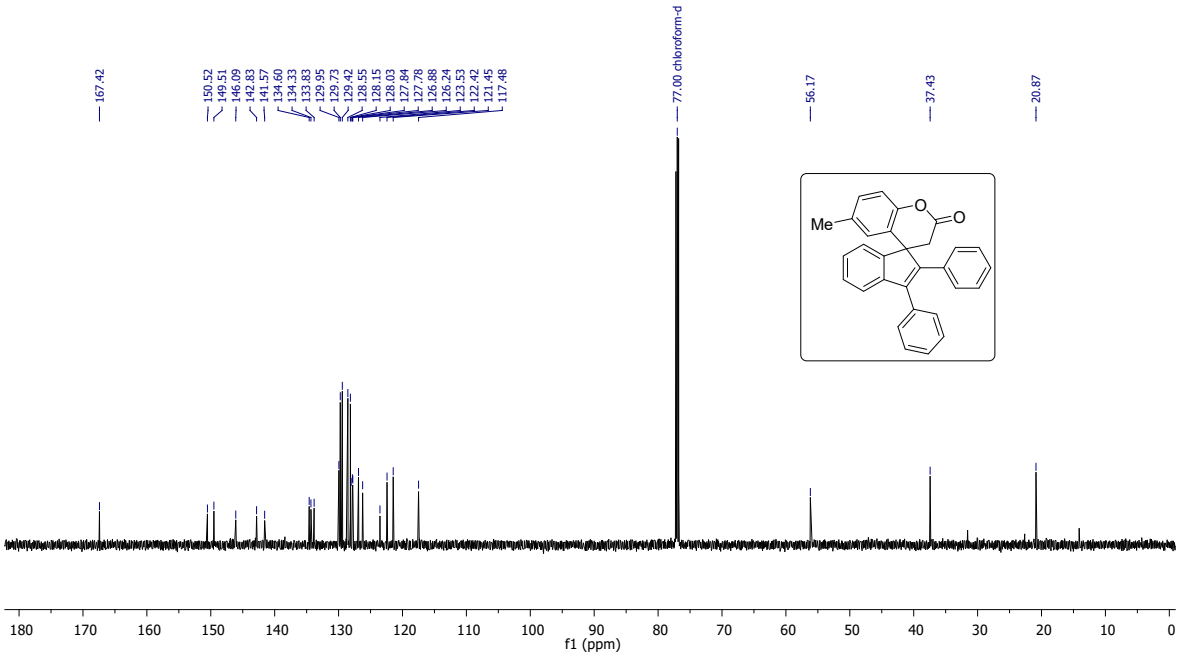
^{13}C{H} NMR (151 MHz) spectrum of **4i** in $CDCl_3$



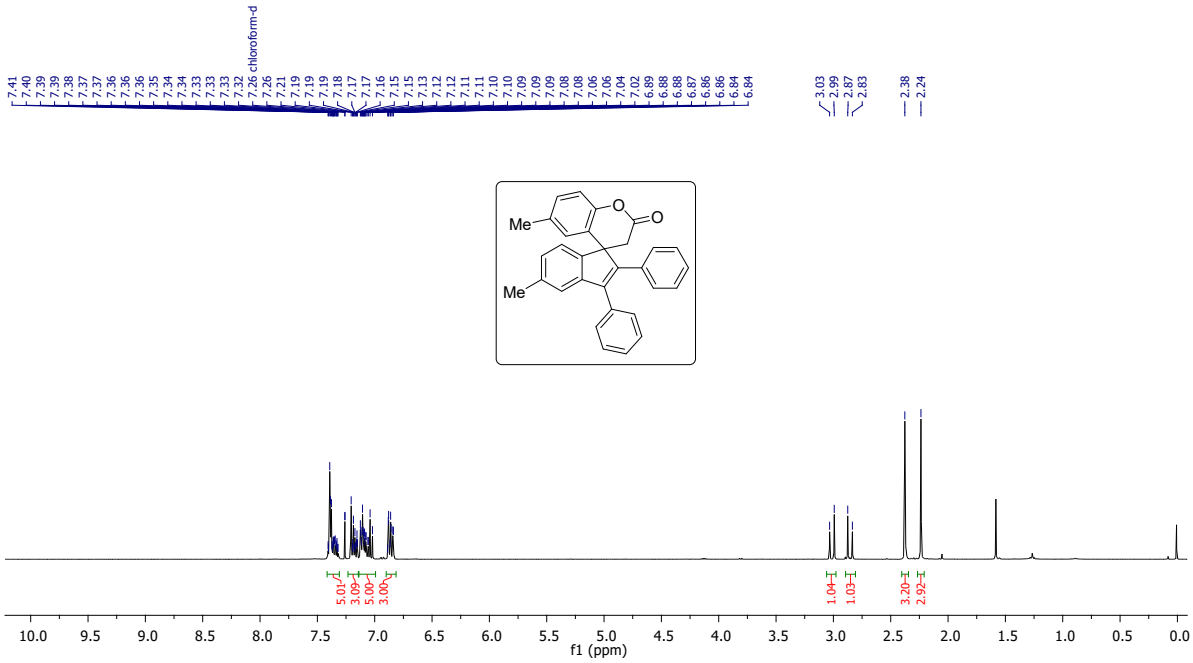
^{19}F NMR (376 MHz) spectrum of **4i** in $CDCl_3$



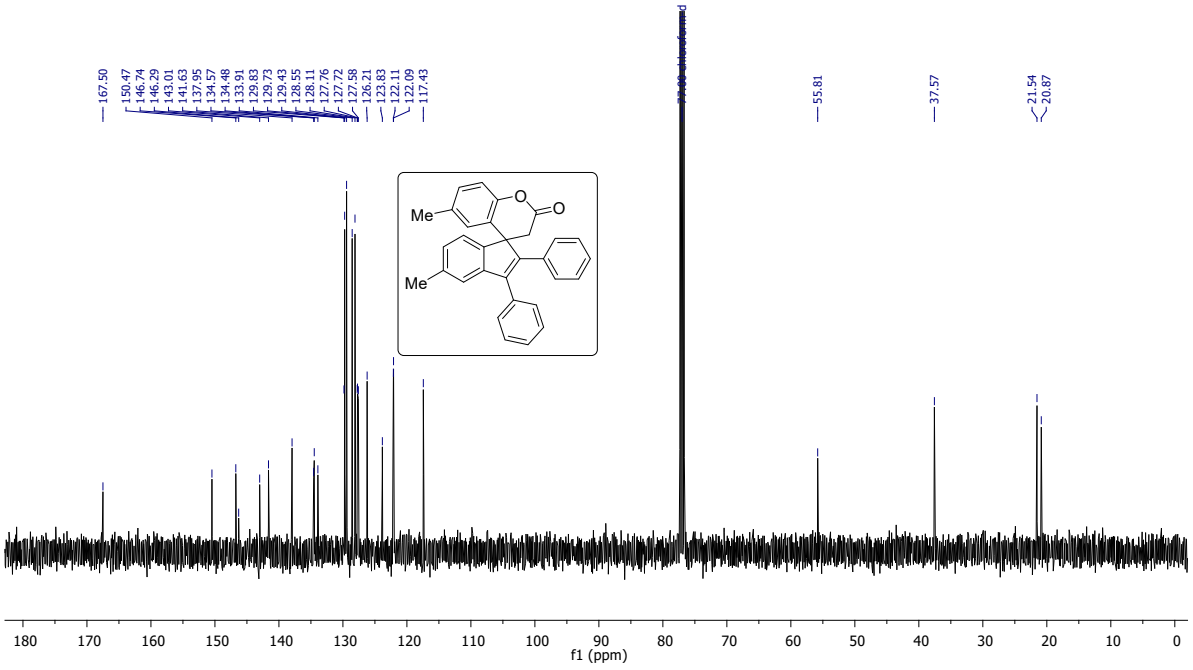
^{1}H NMR (400 MHz) spectrum of in **6a** $CDCl_3$



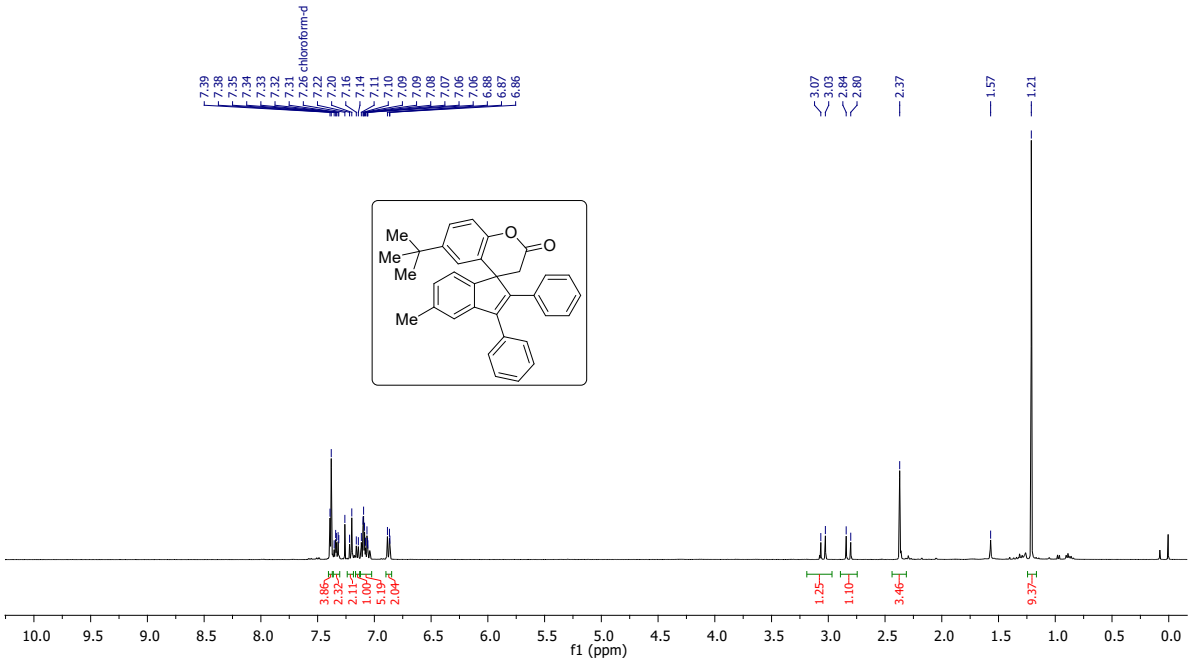
^{13}C{H} NMR (151 MHz) spectrum of **6a** in $CDCl_3$



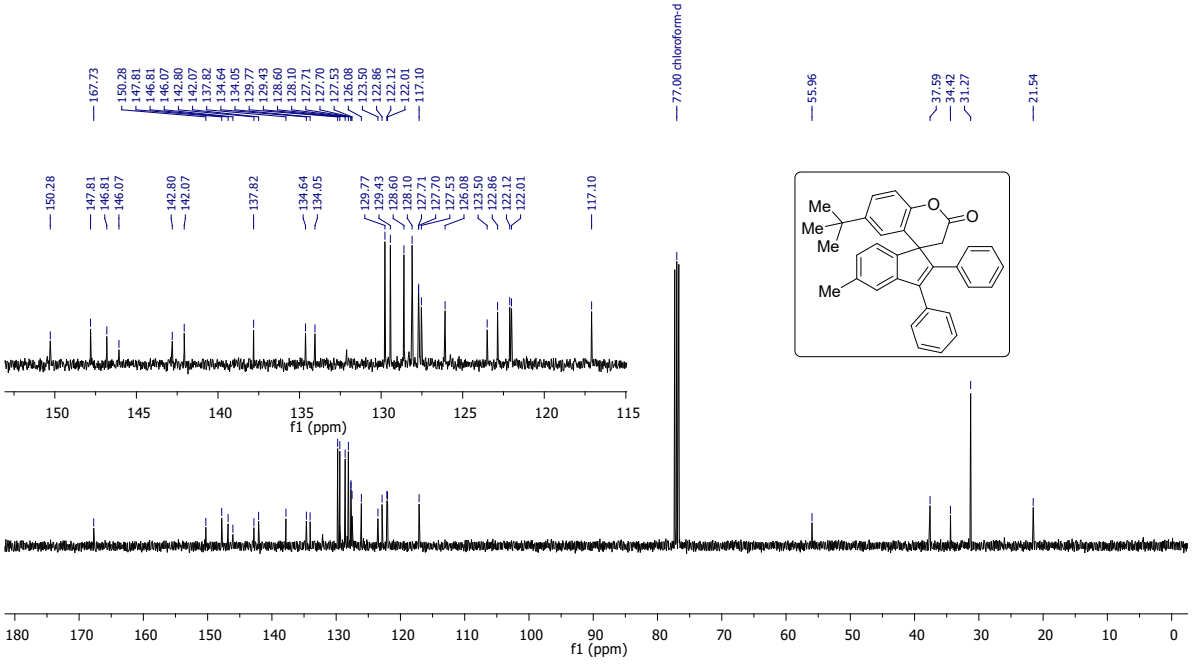
^{1}H NMR (400 MHz) spectrum of **6b** in $CDCl_3$



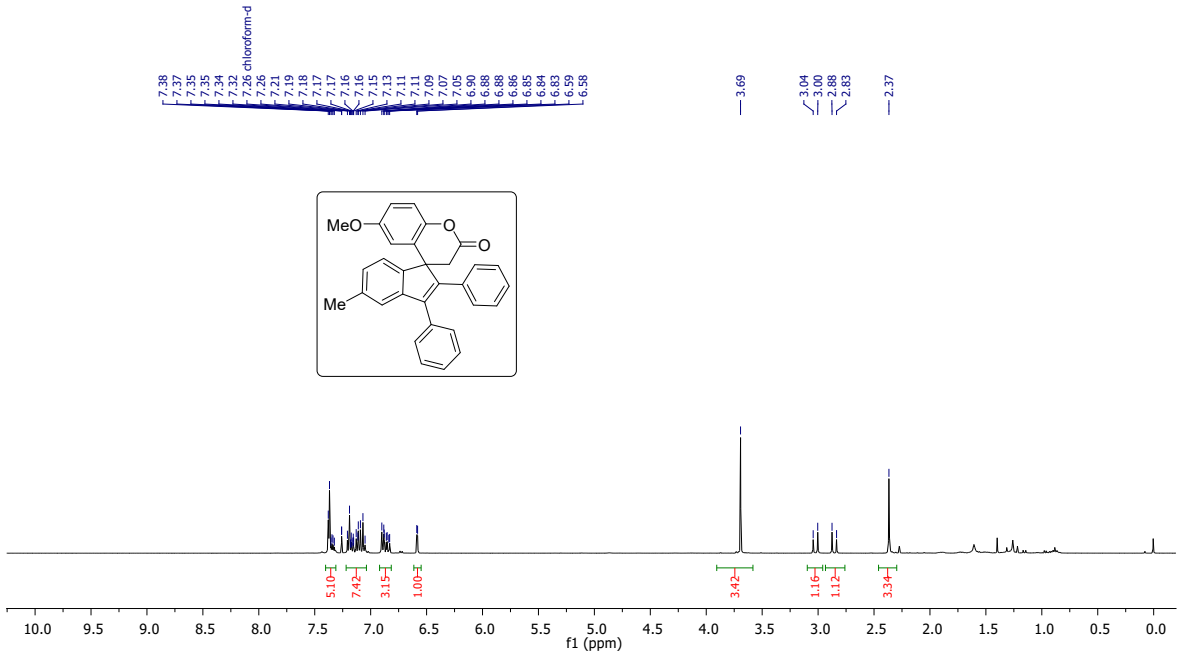
^{13}C{H} NMR (100 MHz) spectrum of **6b** in $CDCl_3$



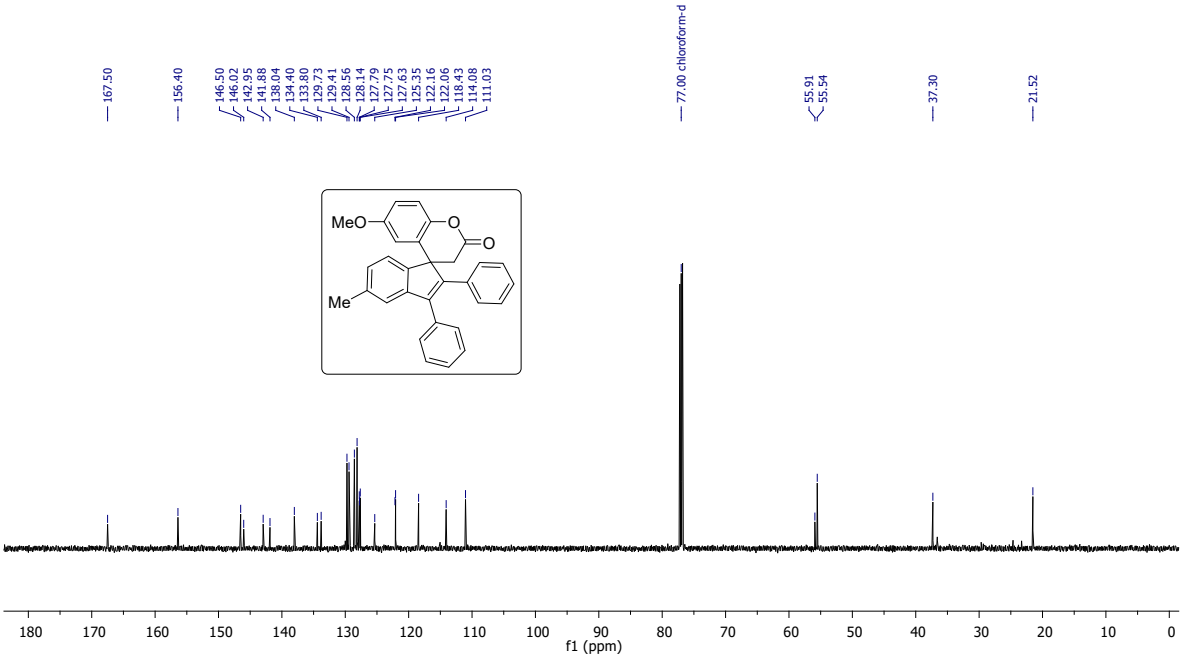
^{1}H NMR (400 MHz) spectrum of **6c** in $CDCl_3$



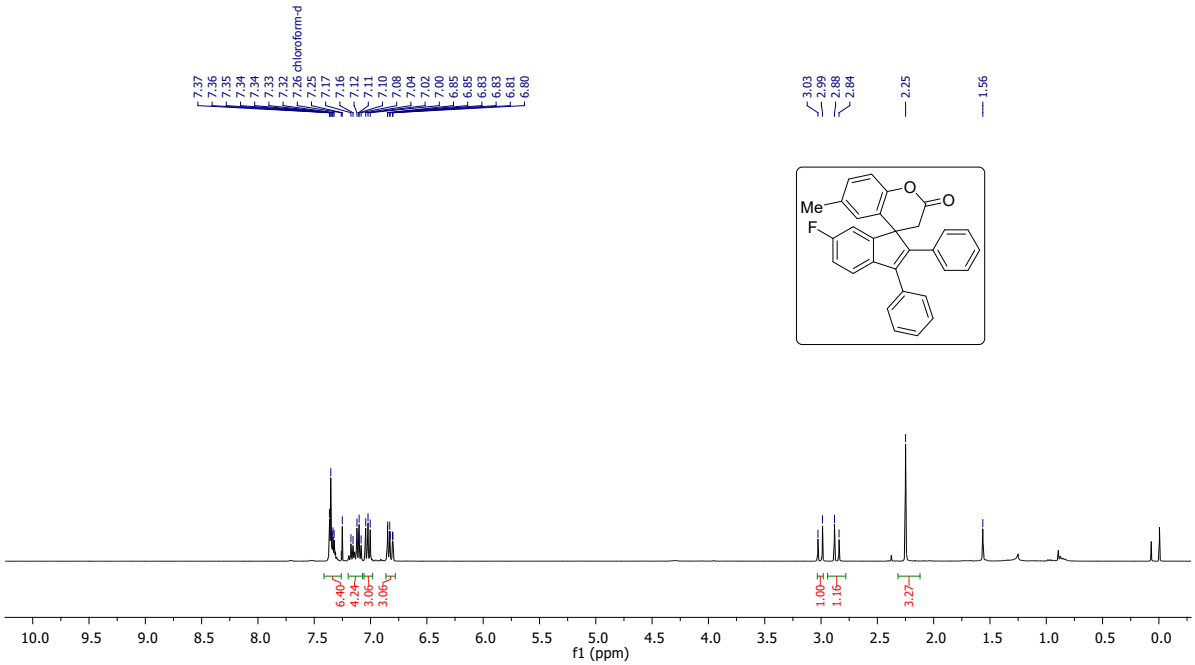
^{13}C{H} NMR (100 MHz) spectrum of **6c** in $CDCl_3$



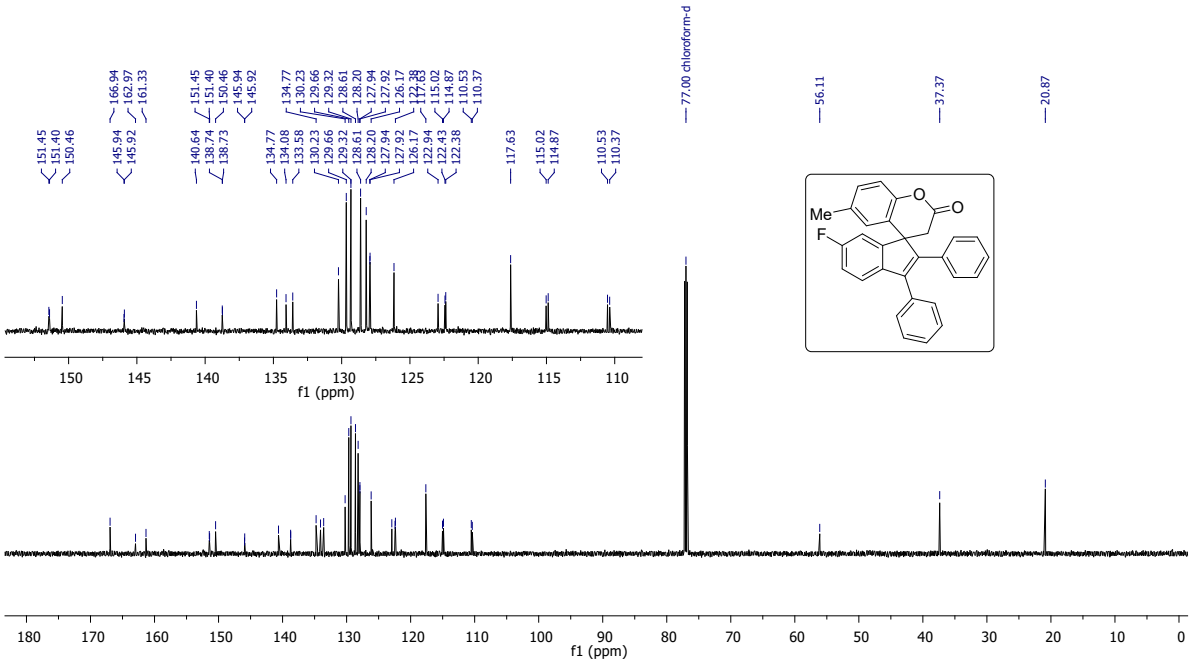
^{1}H NMR (400 MHz) spectrum of **6d** in $CDCl_3$



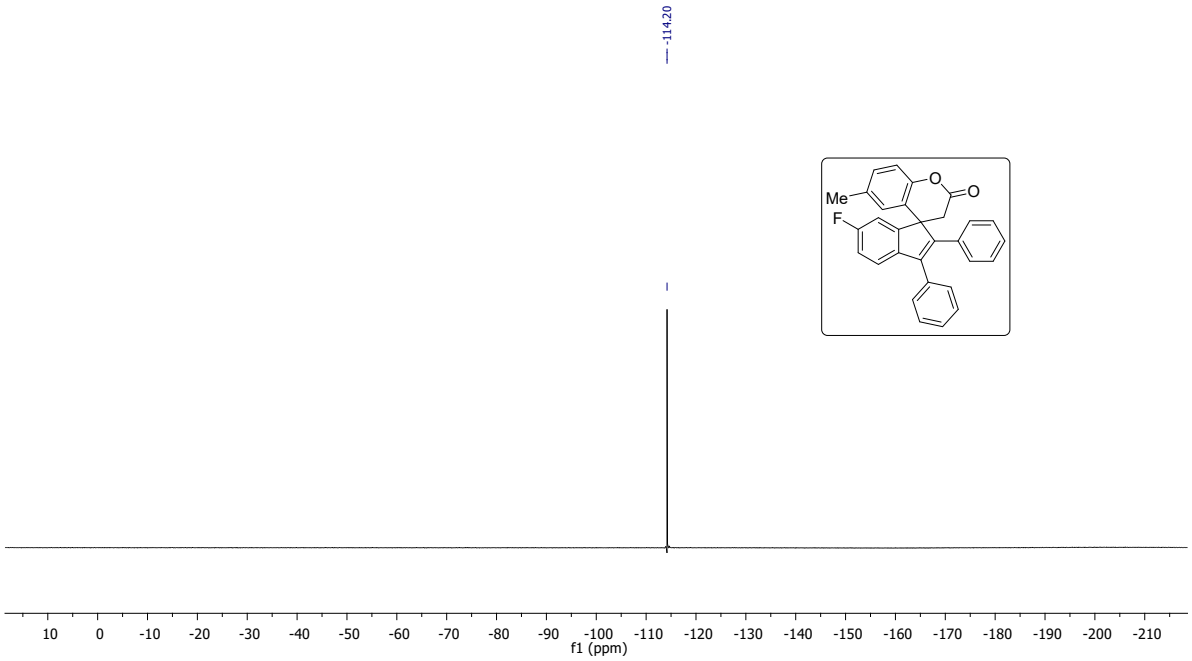
^{13}C{H} NMR (151 MHz) spectrum of **6d** in $CDCl_3$



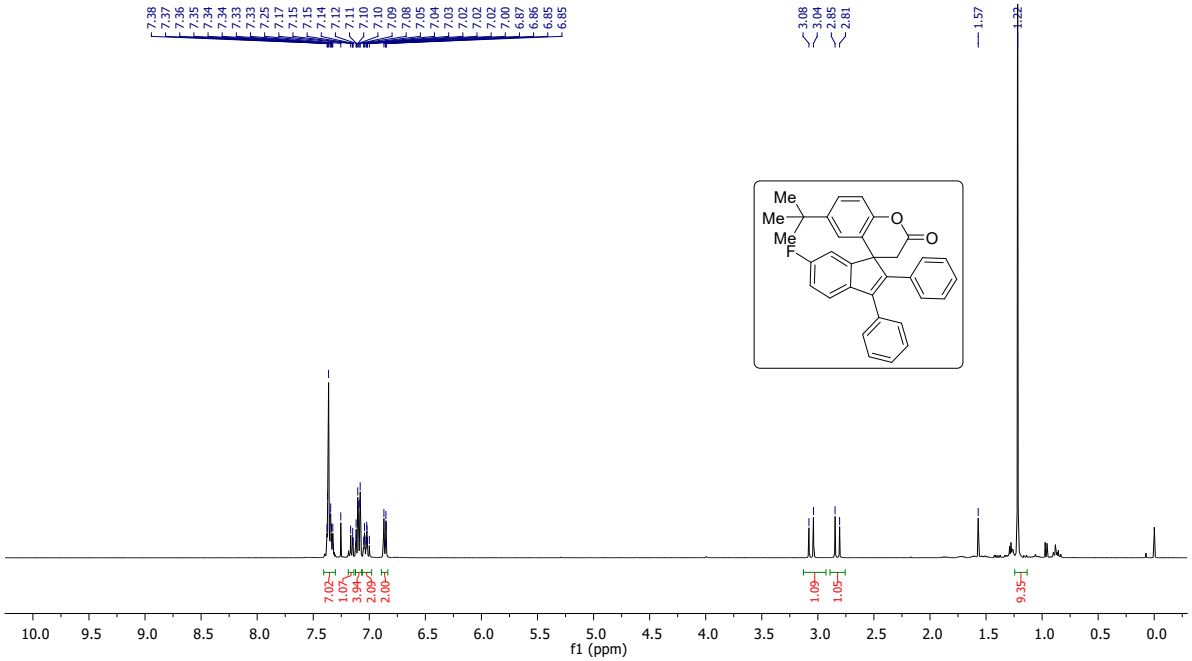
^{1}H NMR (400 MHz) spectrum of **6e** in $CDCl_3$



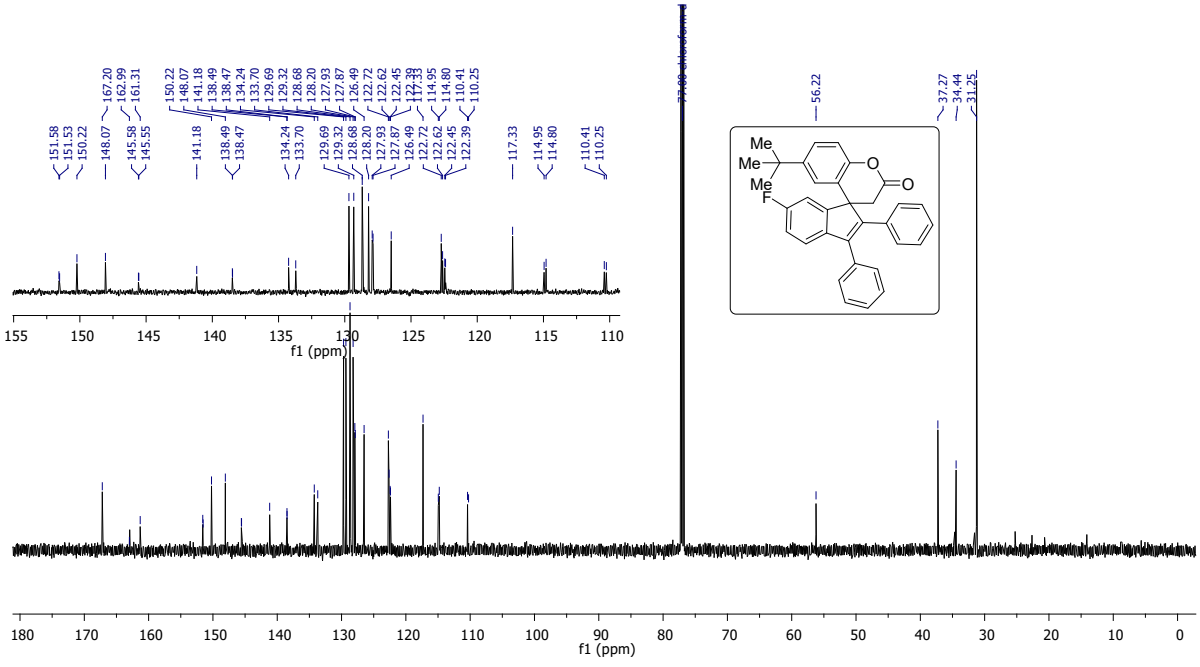
^{13}C{H} NMR (151 MHz) spectrum of **6e** in $CDCl_3$



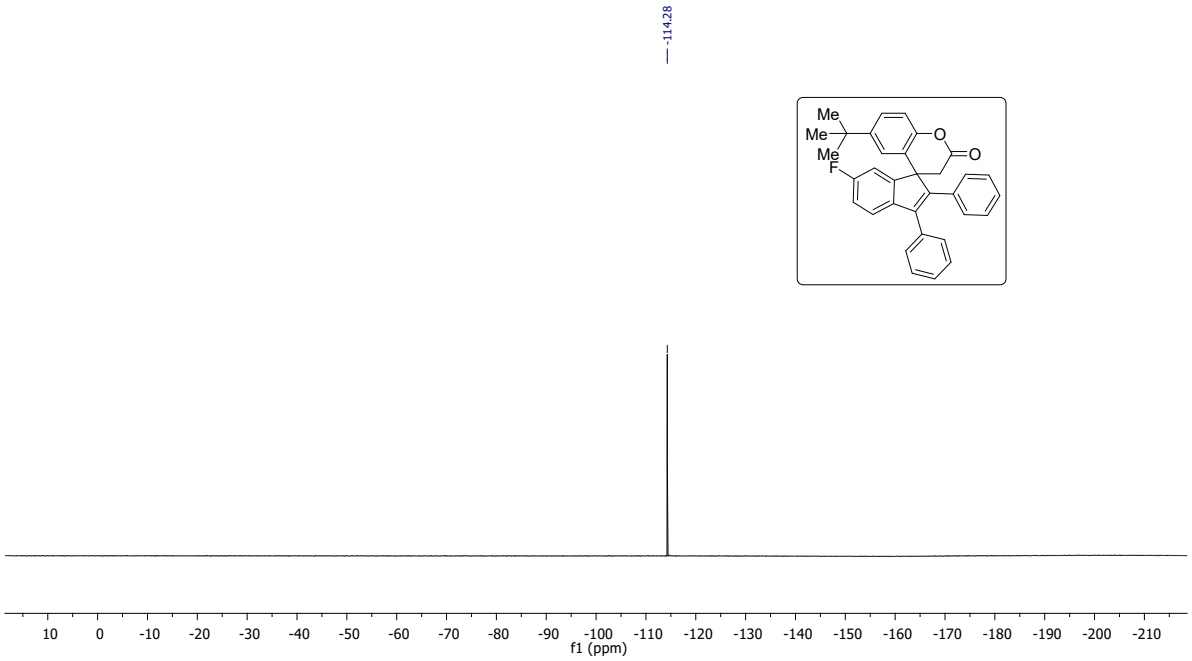
^{19}F NMR (376 MHz) spectrum of **6e** in $CDCl_3$



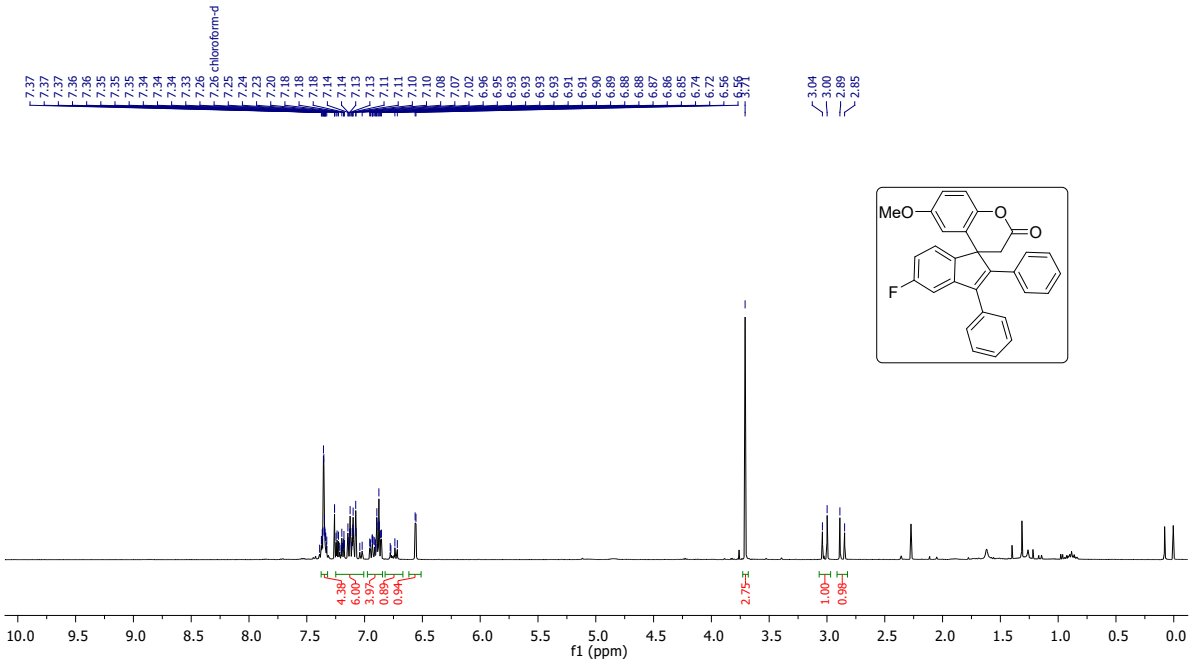
^{1}H NMR (400 MHz) spectrum of **6f** in $CDCl_3$



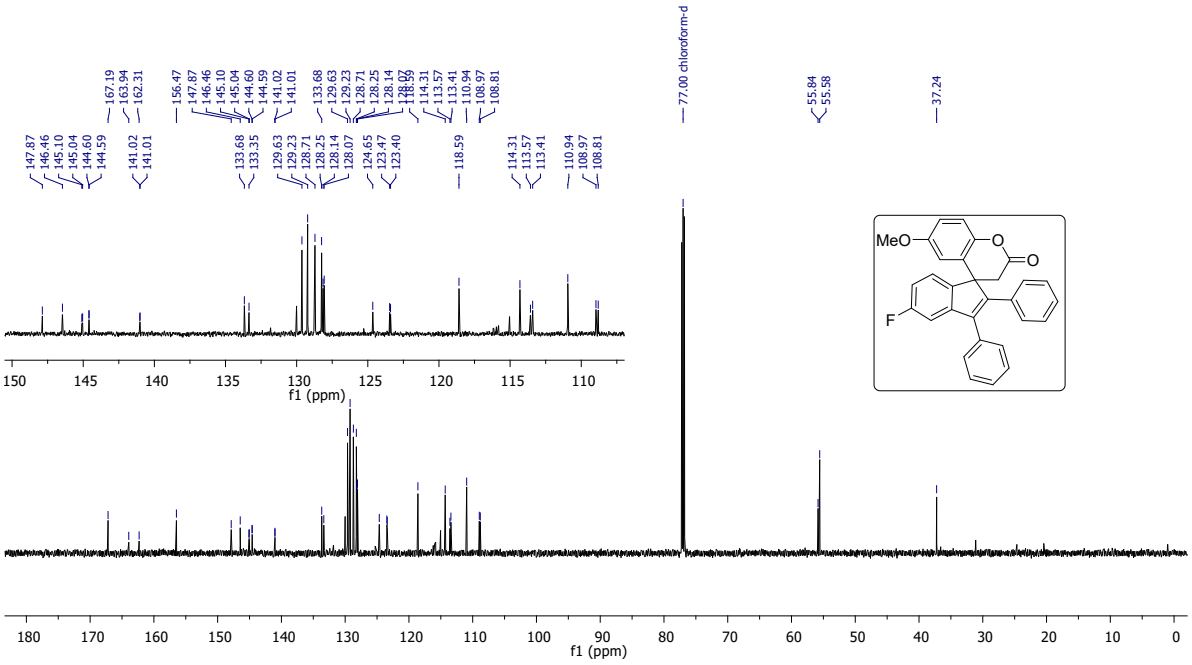
^{13}C{H} NMR (151 MHz) spectrum of **6f** in $CDCl_3$



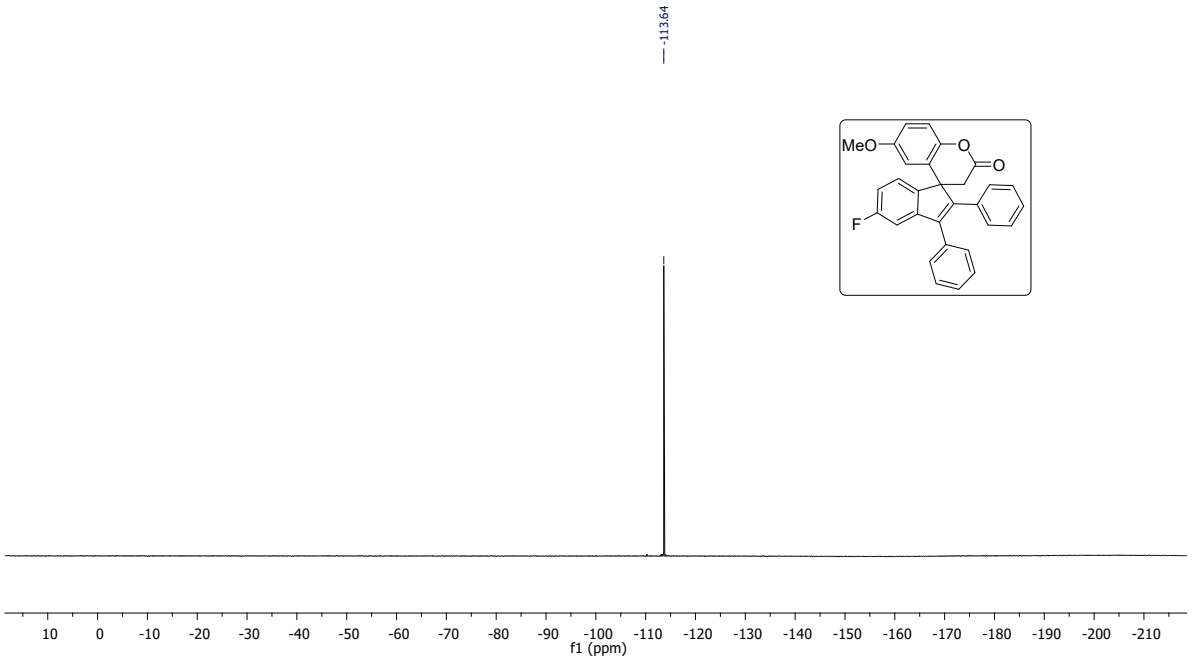
^{19}F NMR (376 MHz) spectrum of **6f** in $CDCl_3$



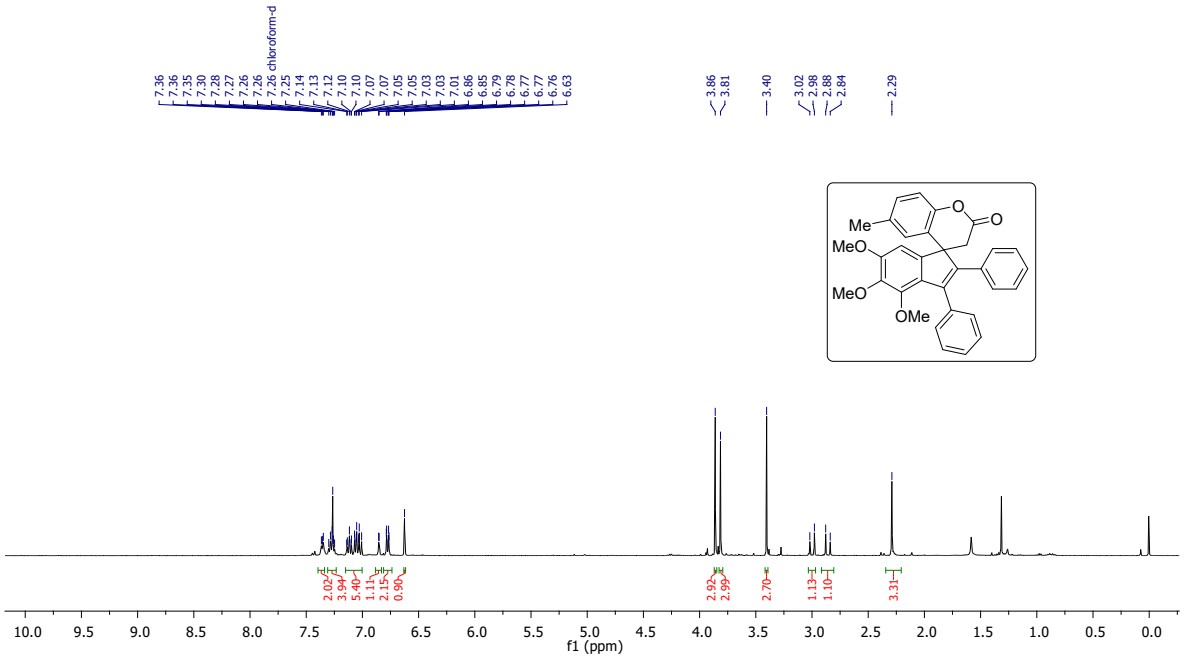
^{1}H NMR (400 MHz) spectrum of **6g** in $CDCl_3$



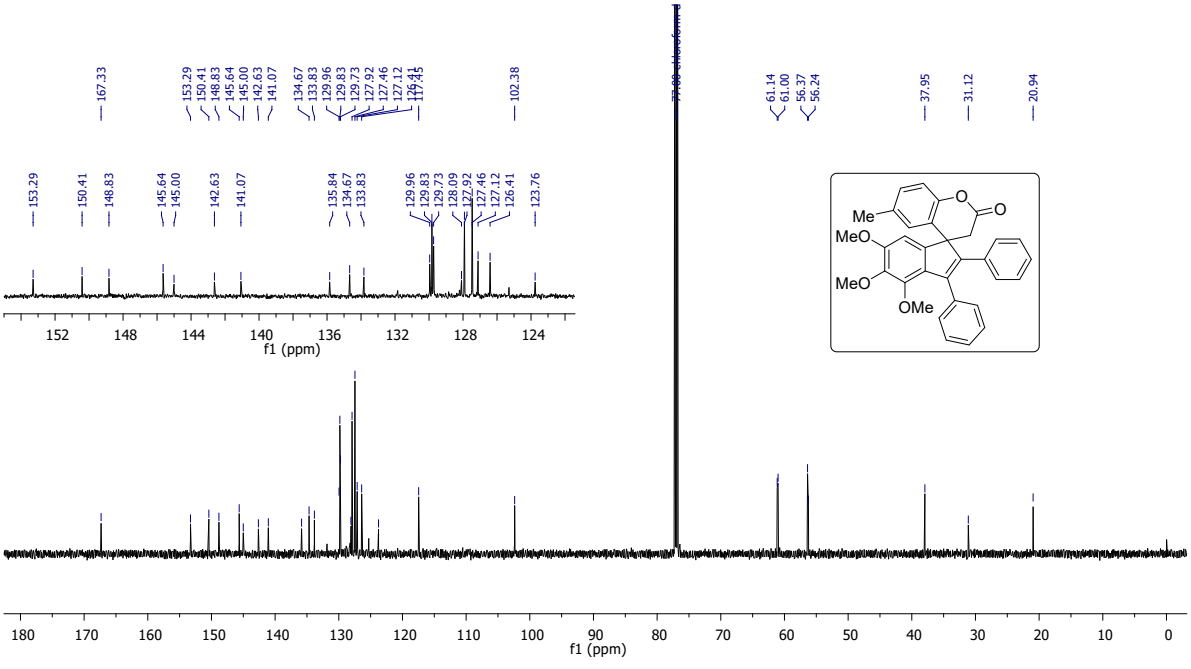
^{13}C{H} NMR (151 MHz) spectrum of **6g** in $CDCl_3$



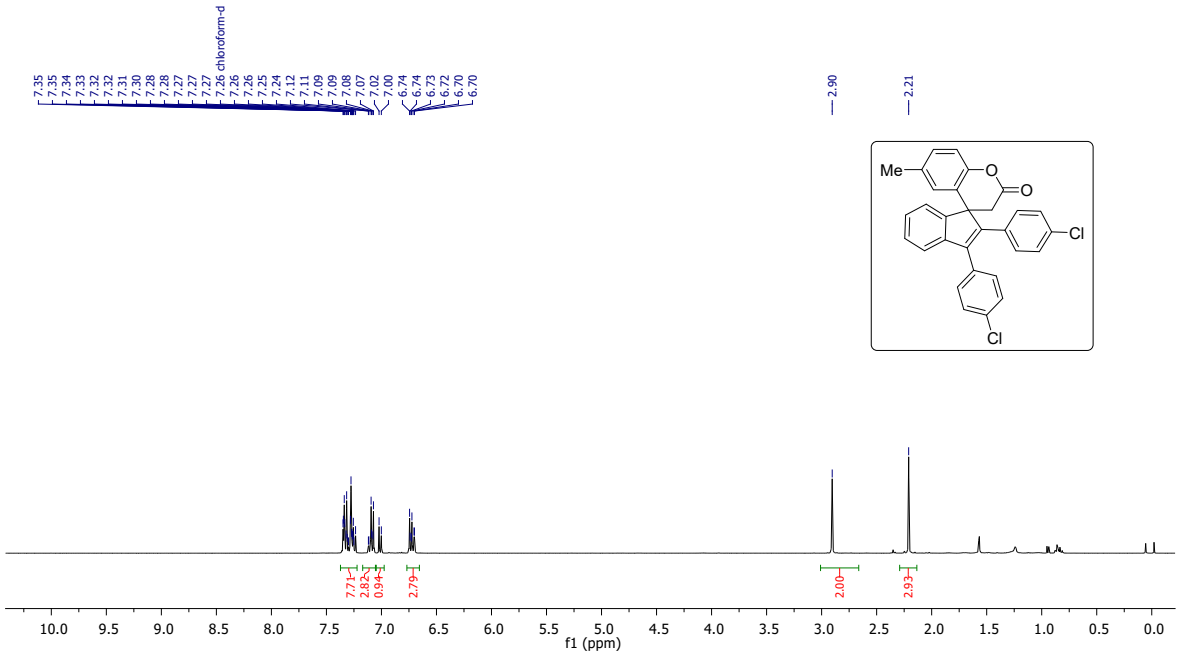
^{19}F NMR (376 MHz) spectrum of **6g** in $CDCl_3$



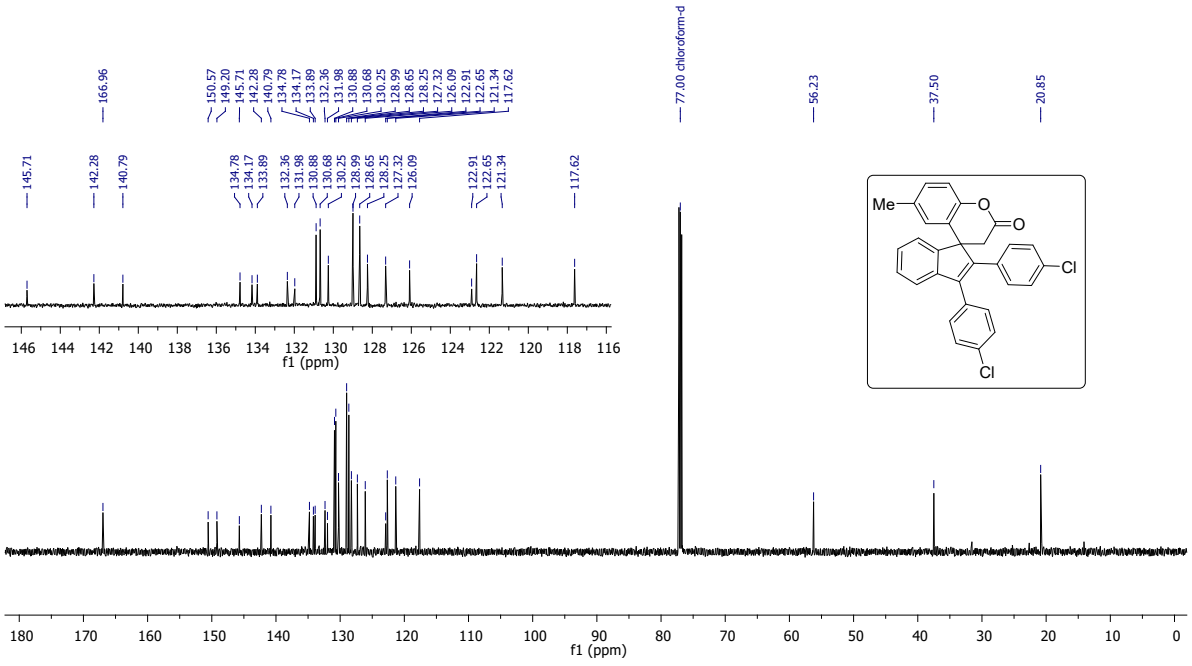
^{1}H NMR (400 MHz) spectrum of **6h** in $CDCl_3$



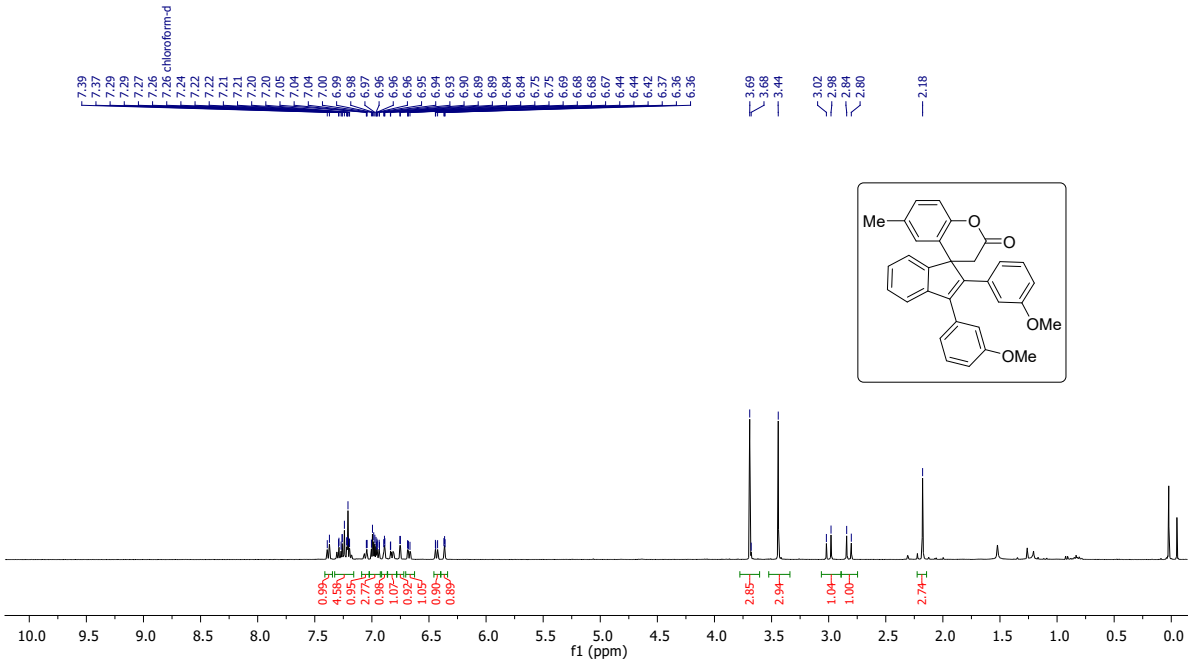
^{13}C{H} NMR (151 MHz) spectrum of **6h** in $CDCl_3$



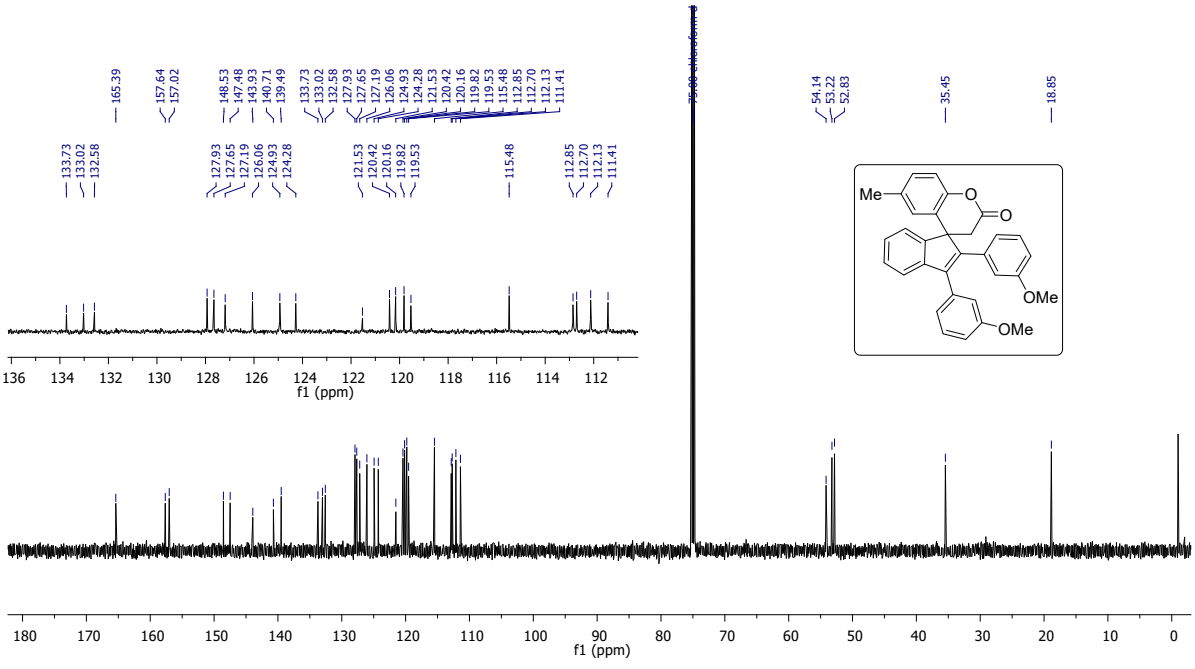
^{1}H NMR (400 MHz) spectrum of **6i** in $CDCl_3$



^{13}C{H} NMR (151 MHz) spectrum of **6i** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of **6j** in $CDCl_3$



^{13}C{H} NMR (151 MHz) spectrum of **6j** in $CDCl_3$

2. X-Ray crystal structure of compound 3ae, 4c and 6c:

Crystal of compounds **3ae** & **4c** were obtained by dissolving the product in Hexane/CH_2Cl_2 mixture and the crystal of compound **6c** was obtained by dissolving it in acetonitrile solvent and allowing the solvent to slowly evaporate at room temperature. A suitable crystal was selected and mounted onto the cryoloop on a Bruker APEX-II CCD diffractometer. The crystal was kept at 273.15 K during data collection. Using Olex2,8 the structure was solved with the SHELXT9 structure solution program using Intrinsic Phasing and refined with the SHELXL10 refinement package using Least Squares minimization.

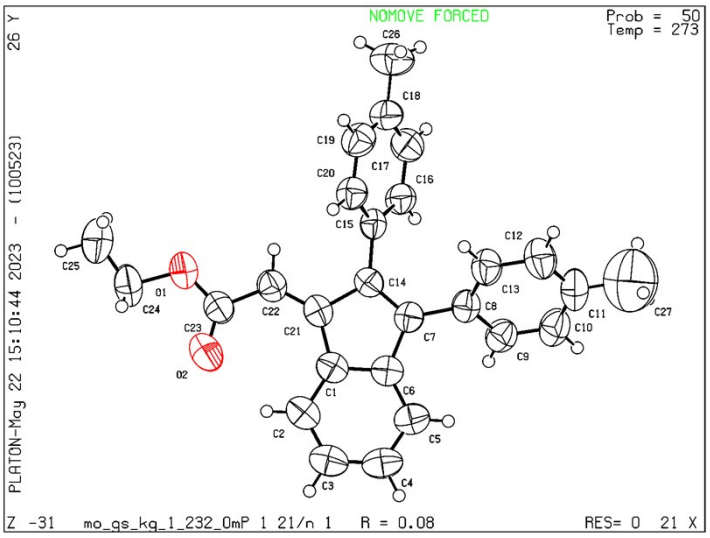


Figure S1: X-ray diagram of compound **3ae** with ellipsoid shown at the 50% contour percent probability level (CCDC-2269423).

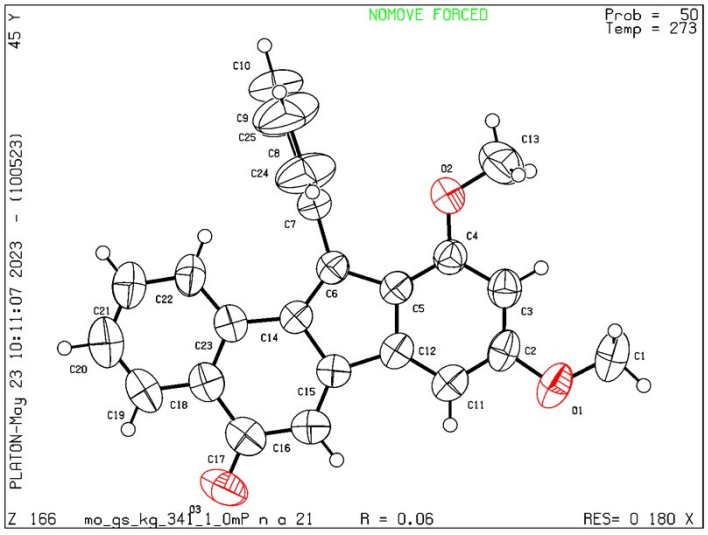


Figure S2: X-ray diagram of compound **4c** with ellipsoid shown at the 50% contour percent probability level (CCDC-2269424).

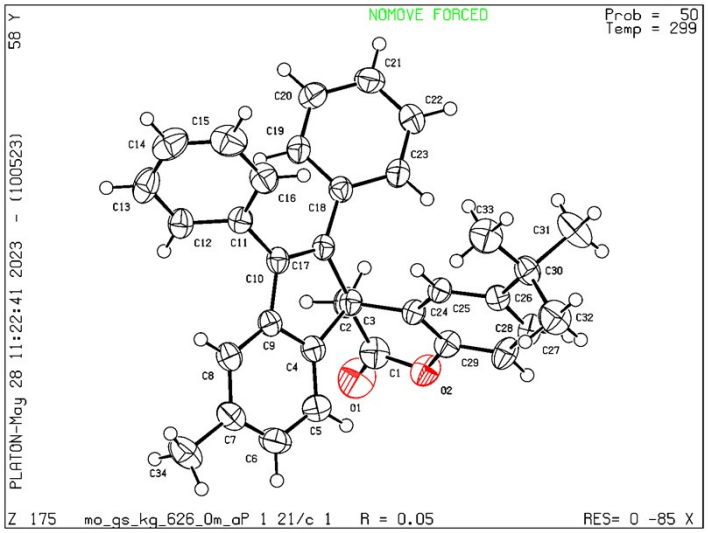


Figure S3: X-ray diagram of compound **6c** with ellipsoid shown at the 50% contour percent probability level (CCDC-2269426).

Table 5S: Crystal data and structure refinement for **3ae** (CCDC-2269423).

Table 5S Crystal data and structure refinement for 3ae.	
Identification code	**3ae**
Empirical formula	$C_{26.57}H_{22.71}O_2$
Formula weight	373.99
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.9007(14)
b/Å	8.9383(8)
c/Å	16.3695(16)
α/°	90
β/°	100.127(3)
γ/°	90
Volume/Å^3	2002.2(3)
Z	4
ρ_{calc}g/cm^3	1.241
μ/mm^{-1}	0.077
F(000)	793.0
Crystal size/mm^3	0.08 × 0.07 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.23 to 54.142
Index ranges	$-17 \leq h \leq 16$, $-11 \leq k \leq 11$, $-19 \leq l \leq 20$
Reflections collected	19402

Independent reflections	4376 [R_{int} = 0.0580, R_{sigma} = 0.0524]
Data/restraints/parameters	4376/0/266
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0771, wR_2 = 0.2323
Final R indexes [all data]	R_1 = 0.1456, wR_2 = 0.2790
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.43

Table 6S: Crystal data and structure refinement for **4c** (CCDC-2269424).

Table 6S Crystal data and structure refinement for 4c.	
Identification code	**4c**
Empirical formula	$C_{25}H_{18}O_3$
Formula weight	366.39
Temperature/K	273.15
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	9.722(5)
b/Å	12.020(6)
c/Å	16.073(6)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1878.3(15)
Z	4
ρ_{calc}g/cm^3	1.296
μ/mm^{-1}	0.084
F(000)	768.0
Crystal size/mm^3	0.08 × 0.07 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.232 to 55.002
Index ranges	-11 ≤ h ≤ 12, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20
Reflections collected	16411
Independent reflections	4171 [R_{int} = 0.1120, R_{sigma} = 0.1215]
Data/restraints/parameters	4171/1/255
Goodness-of-fit on F^2	0.960
Final R indexes [I>=2σ (I)]	R_1 = 0.0596, wR_2 = 0.1217
Final R indexes [all data]	R_1 = 0.1723, wR_2 = 0.1623
Largest diff. peak/hole / e $Å^{-3}$	0.15/-0.23
Flack parameter	0.1(10)

Table 7S: Crystal data and structure refinement for **6c** (CCDC-2269426).

Table 7S Crystal data and structure refinement for 6c.	
Identification code	**6c**

Empirical formula	$C_{34}H_{30}O_2$
Formula weight	470.58
Temperature/K	299.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.118(3)
b/Å	10.404(3)
c/Å	18.151(4)
α/°	90
β/°	101.378(9)
γ/°	90
Volume/Å^3	2613.9(11)
Z	4
ρ_{calc}g/cm^3	1.196
μ/mm^{-1}	0.073
F(000)	1000.0
Crystal size/mm^3	0.08 × 0.07 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.536 to 54.29
Index ranges	$-18 \leq h \leq 17$, $-13 \leq k \leq 13$, $-20 \leq l \leq 23$
Reflections collected	42000
Independent reflections	5799 [R_{int} = 0.0585, R_{sigma} = 0.0370]
Data/restraints/parameters	5799/0/329
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0454, wR_2 = 0.1049
Final R indexes [all data]	R_1 = 0.0690, wR_2 = 0.1173
Largest diff. peak/hole / e Å^{-3}	0.17/-0.18

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