Electronic Supporting Information

TBADT Photocatalyst Enabled Radical Induced Cyclization Pathway to Access Functionalized Dihydrobenzofurans

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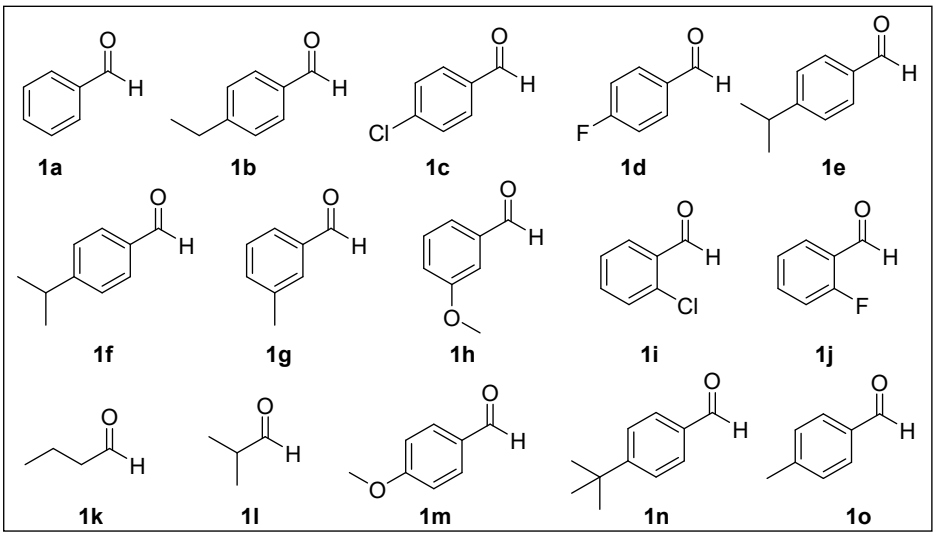
Experimental:

General methods:

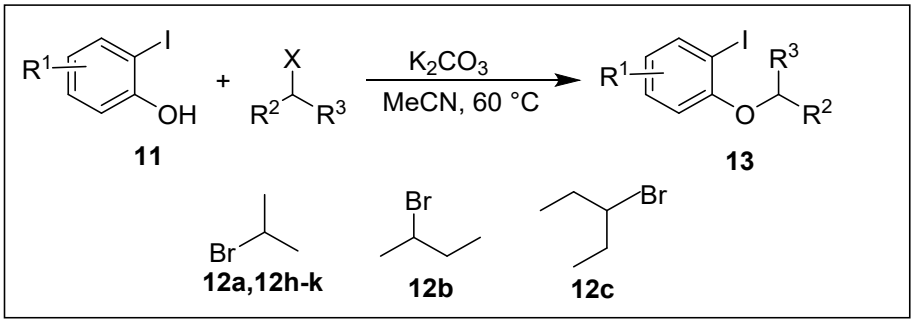
IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Advance 400 (400 MHz) and 600 (600 MHz) spectrometers at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion concerning either internal standard tetramethylsilane (TMS) (δH = 0.00 ppm) or $CDCl_3$ (δH = 7.26 ppm). $^{13}C\{1H\}$ NMR spectra were recorded on Bruker Advance 400 (100 MHz) and 600 (151 MHz) spectrometers at RT in $CDCl_3$. Chemical shifts (δ ppm) are reported relative to $CDCl_3$ [δ = 77.16 ppm (central line of the triplet)]. In the $13C\{^{1}H\}$ 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 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 (HRMS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. A single crystal of **3ag** was selected and mounted on an Oxford SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 298 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using direct methods and refined with the olex2. refinement package using Gauss−Newton minimization. Reactions were conducted using Kessil PR160-390 nm LED Package supply purchased from Bandi technology. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled before use; petroleum ether the boiling range of 60-80 °C was used. Cyclic voltammetry (CV) analysis was performed on autolab 302N potentiostat, using a glassy carbon electrode as working electrode, a platinum electrode as counter electrode and Ag/AgCl electrode as a reference electrode. Cyclic voltammogram was recorded at 200 mV/s scan rate. Alkynes, aliphatic and aromatic aldehydes, and CH_3CN were purchased from Sigma-Aldrich/Avra/BLD/TCI/local sources and used as received, the solvent MeCN was dried and used with purification. Tetrabutylammonium

decatungstate (TBADT) was prepared according to the literature procedure.[1] Acme's silica gel (60-120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

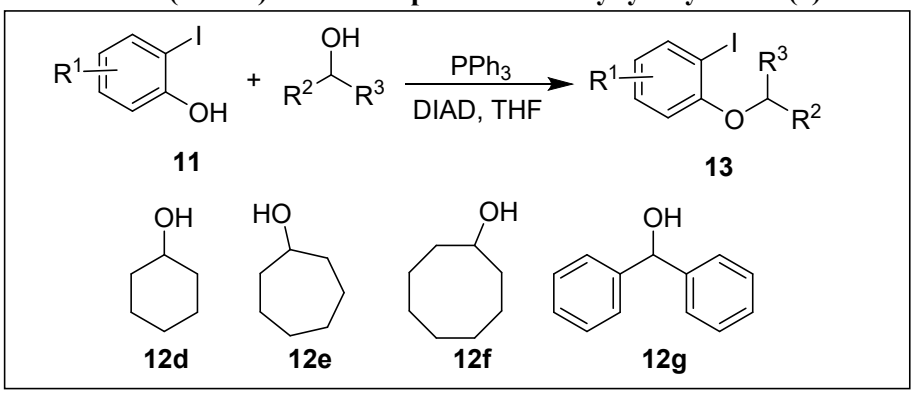
Table-S1. Starting material chart **1**



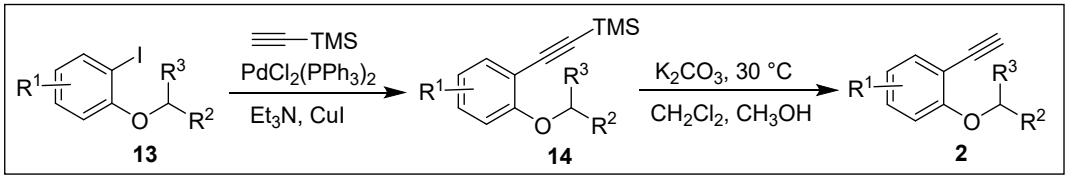
General Procedure – 1a (GP-1a) for the Preparation of alkynyl aryl ether (2):

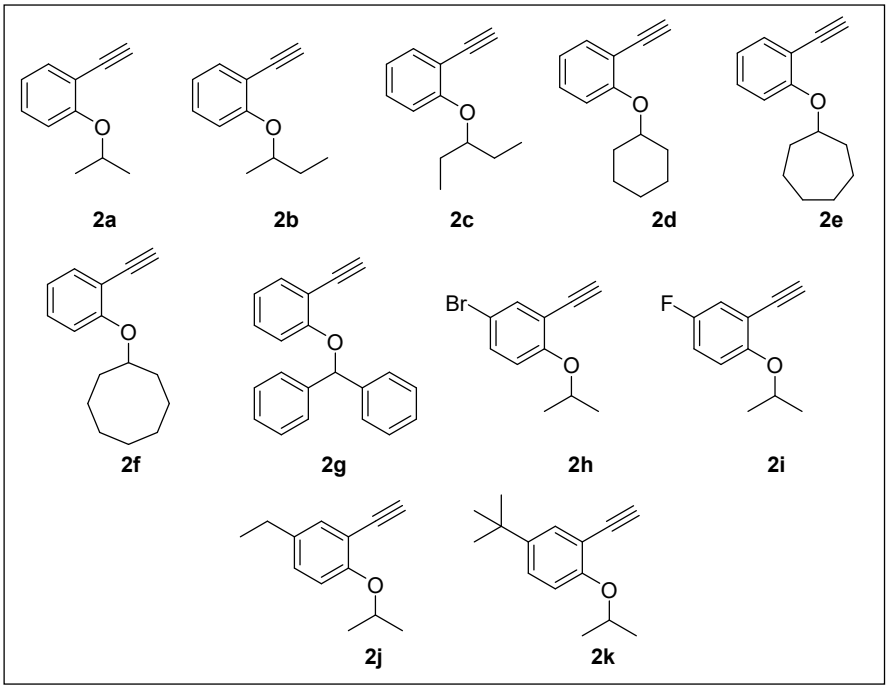


General Procedure – 2a (GP-2a) for the Preparation of alkynyl aryl ether (2):



General Procedure – 3a (GP-3a) for the Preparation of alkynyl aryl ether (2):



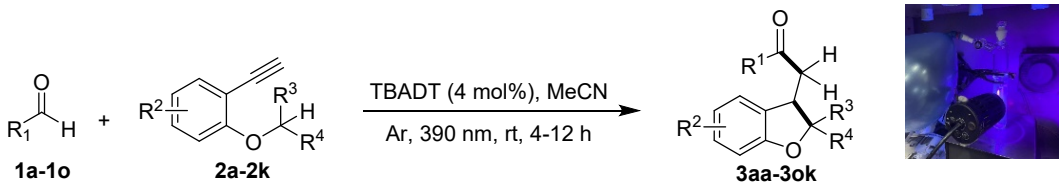


General Procedure – 1a (GP-1a): To an oven-dried round bottom flask was charged with 2-iodophenols **11** (1g, 4.5 mmol, 1.0 equiv), K_2CO_3 (1.25 g, 9 mmol, 2.0 equiv), CH_3CN (20 mL) and 2-bromopropane **12a** (0.83 g, 6.8 mmol, 1.5 equiv). The reaction mixture was stirred at 50 °C in an oil bath for 10 h. The resulting solution was diluted with H_2O (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous $MgSO_4$. The residue was purified by column chromatography to afford 1-iodo-2-isopropoxybenzene **13** as yellow oil.

General Procedure – 2a (GP-2a): To an oven-dried round bottom flask was charged with 2-iodophenol **11** (1 g, 4.5 mmol, 1 equiv), PPh_3 (1.42 g, 5.4 mmol, 1.2 equiv), THF (20 mL), and the mixture was stirred for 5 minutes. Then cyclohexanol (0.9 g, 10 mmol, 2 equiv) and diisopropyl azodicarboxylate (DIAD) (1.1 g, 5.4 mmol, 1.2 equiv) were added and the reaction mixture was stirred at room temperature under argon atmosphere for 12 h. The resulting solution was diluted with H_2O (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous $MgSO_4$. The residue was purified by column chromatography to afford 1-(cyclohexyloxy)-2-iodobenzene **13** as a yellow oil.

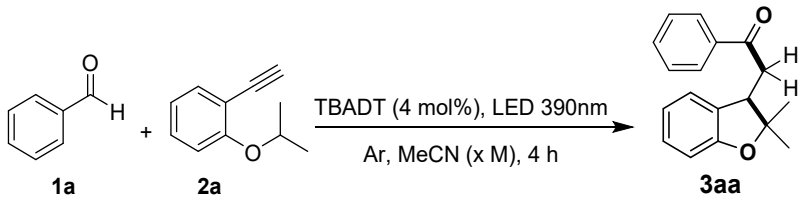
General Procedure – 3a (GP-3a): To an oven-dried round bottom flask was charged with **13** (1.0 equiv), $PdCl_2(PPh_3)_2$ (1 mol%), CuI (2 mol%), Et_3N (20 mL) and trimethylsilylacetylene (1.5 equiv). The reaction mixture was stirred at room temperature under argon atmosphere for 12 h. The resulting solution was diluted with saturated aq. NH_4Cl (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous MgSO4. The residue was purified by column chromatography to give the product **C**. The solution of C and K_2CO_3 (2 equiv) in MeOH/CH_2Cl_2 (1:1, 20 mL) was stirred at 30 °C in an oil bath for 2 h. The reaction mixture was diluted with H_2O (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous $MgSO_4$. The residue was purified by column chromatography to give the product **2** (The above-mentioned procedure for the substituted 2-alkynyl aryl ether **2a-2k** was prepared from previous literature reports).[2]

General Procedure - 2 (GP-2) for the Preparation of Dihidrobenzofurans (3):



To an oven-dried Schlenk tube equipped with a magnetic stir bar, were added with aromatic and aliphatic aldehyde **1** (33 mg, 0.31 mmol) added alkynyl aryl ether **2** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and backfilled with Argon (three times). The Schlenk tube was sealed with Teflon, and the reaction mixture was irradiated (at approximately 5 cm away from the light source) with 30 W blue LEDs under vigorous stirring at room temperature for 4-12 h under Argon conditions. The progress of the reaction was monitored by TLC until the completion of the reaction with visualization under UV fluorescence. The solvent was then removed under a rotary evaporator and purification of the crude product using column chromatography (petroleum ether to 2% ethyl acetate/petroleum ether), furnished dihydrobenzofurans **3** (37 to 76%), as a yellow oil.

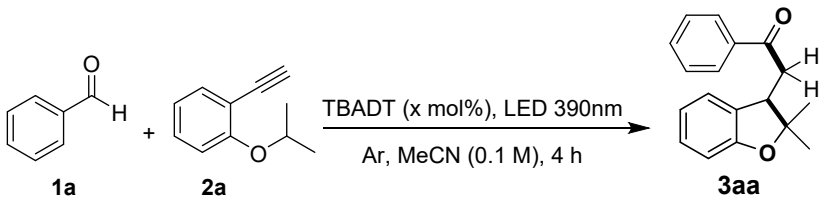
Table S2: Evalutaion of reaction solvent and concentration.[a]



Entry	Deviation from the above	Yield of 3aa (%)[a]
1	MeCN [0.1 M]	74
2	MeCN : H_2O (5 : 1) [0.1 M]	trace
3	Acetone [0.1 M]	28
4	DMF [0.1 M]	42
5	MeCN : Toulene	36
6	MeCN [0.05 M]	trace
7	MeCN [0.075 M]	58
8	MeCN [0.2 M]	65
9	EtOAC [0.1 M]	trace
10	MeCN : DCM (5 : 1) [0.1 M]	46

[a]Yields of the isolated product **3aa** after column chromatography.

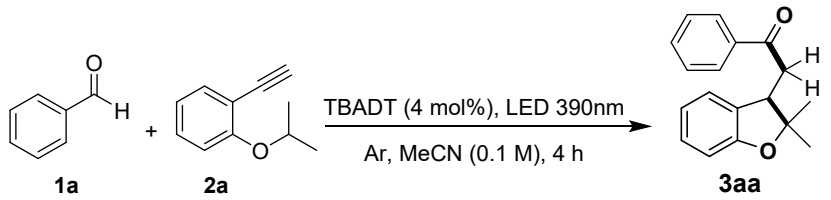
Table S3: Evaluation of PC loading.



Entry	PC loading	Yield[a] of 3aa (%)
1	4 mol%	74
2	3.5 mol%	68
3	2 mol%	47
4	1 mol%	40
5	6 mol%	36

[a]Yield of the isolated product **3aa** after column chromatography.

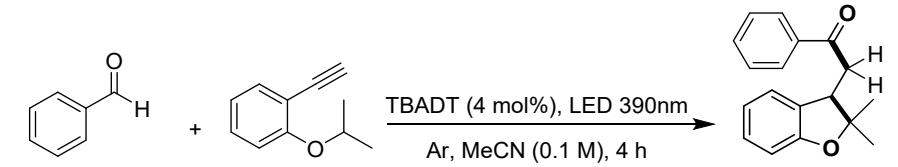
Table S4: Variation from the optimized reaction conditions.[a,b]



Entry	Variation from the optimal conditions	Yield of 3aa (%)[b]
1	None	74
2	w/o TBADT	0
3	w/o light	0
4	dark	0
5	370 nm	60
6	427 nm	0

[a]Unless otherwise specified, reactions were performed using benzaldehyde **1a** (0.31 mmol), 1-ethynyl-2-isopropoxybenzene **2a** (0.31 mmol), TBADT (4 mol%), irradiated by a 34 W LED lamp (390 nm) in (0.1 M) MeCN at room temperature for 4 h. [b]Yield of the isolated product **3aa** after column chromatography.

Scheme S1: Scale-up reaction of **1a** with 1-ethynyl-2-isopropoxybenzene **2a**.



To an oven-dried Schlenk tube equipped with a magnetic stir bar, were added with benzaldehyde **1a** (264 mg, 2.49 mmol) added alkynyl aryl ether **2a** (754 mg, 2.49 mmol), TBADT (4 mol%), and CH_3CN (0.1 M) and backfilled with Argon (three times). The Schlenk tube was sealed with Teflon, and the reaction mixture was irradiated (at approximately 5 cm away from the light source) with 30 W blue LEDs under vigorous stirring at room temperature for 4 h under Argon conditions. The progress of the reaction was monitored by TLC until the completion of the reaction with visualization under UV fluorescence. The solvent was then removed under a rotary evaporator and purification of the crude product using column chromatography (petroleum ether to 2% ethyl acetate/petroleum ether), furnished dihydrobenzofurans **3aa** (58 %), as a yellow oil.

Cyclic Voltammograms:

The cyclic voltammetry (CV) studies were carried out to further investigate the reaction mechanism, and below Figure S1 shows the cyclic voltammetry (CV) curves with 0.01 M $^{n}Bu_4NPF_6$ solution in CH_3CN s as a background. The voltammogram was obtained at a scan rate of 100 mV/s with Pt electrode as a counter electrode, Ag/AgCl as a reference electrode, and glassy carbon electrode as a working electrode. Within the scanning window (-2.0 to 0.5 V), the CV of benzaldehyde **1a** displayed reduction peak at -0.62 V and -0.27 V *vs* Ag/AgCl (curve 1). When testing 1-ethynyl-2-isopropoxybenzene **2a**, a reduction peak was seemed at -1.67 V *vs* Ag/AgCl in (curve 2), signifying that the reduction of alkynyl aryl ether required a strong reduction potential. The mixture of benzaldehyde **1a** and 1-ethynyl-2-isopropoxybenzene **2a** showed reduction peak at -0.39 V *vs* Ag/AgCl, in the reaction (curve 3). The TBADT reduction and oxidation peaks were appeared in the range of -1.44 V and -1.361 V (curve 4). 2-(2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-phenylethan-1-one **3aa** shows reduction peak at -0.20 V. On the basis of above results, we hypothesised that benzaldehyde may produce acyl radicals by cathodic reduction in the presence of TBADT catalyst and further activates alkynes in the reaction process.

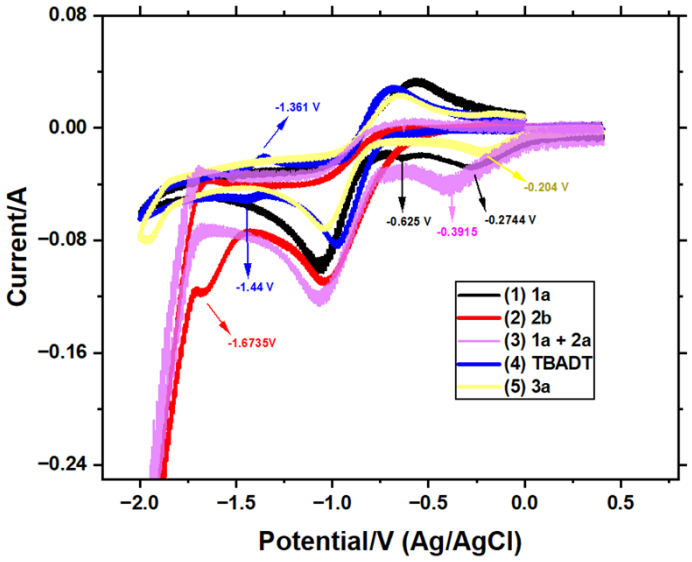
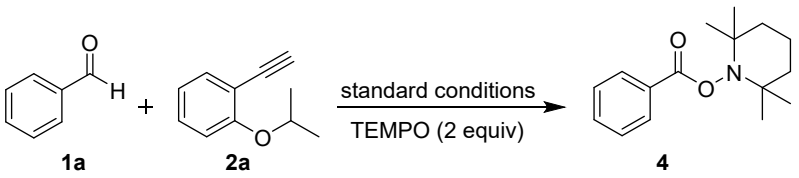


Figure S1: Cyclic voltammograms of reactants and their mixtures in 0.01 M $^{n}Bu_4NPF_6$ solution in CH_3CN at room temperature: 1) benzaldehyde **1a** (0.04 M); 2) alkynyl aryl ether **2a** (0.01 M); 3) benzaldehyde **1a** (0.04 M) + 1-ethynyl-2-isopropoxybenzene **2a** (0.01 M); 4) TBADT (0.01M); 5) 2-(2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-phenylethan-1-one **3aa**. The voltammogram was obtained at a scan rate of 200 mV/s with Pt electrode as a counter electrode, Ag/AgCl as a reference electrode, and glassy carbon electrode as a working electrode.

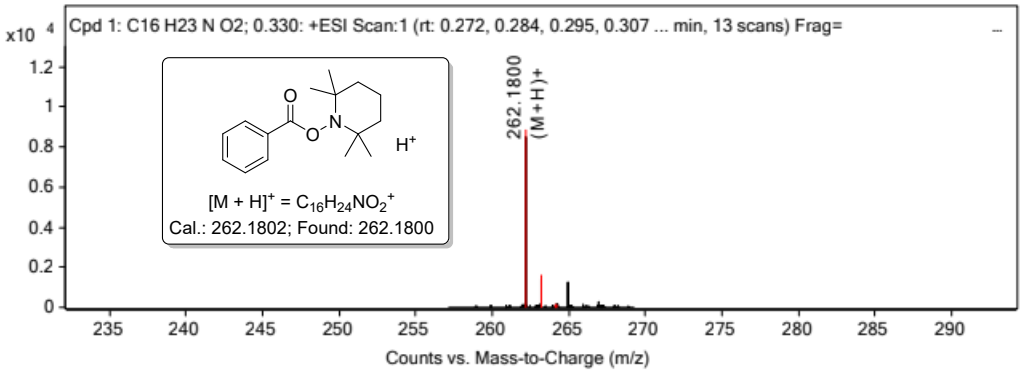
Scheme S2: Control experiments.

a) TEMPO

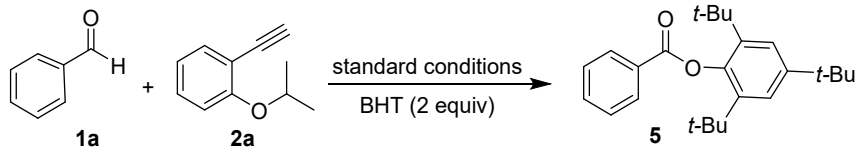


1a **2a** **4**

To an oven-dried Schlenk tube equipped with a magnetic stir bar, were added with benzaldehyde **1a** (66 mg, 0.31 mmol) added 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), CH_3CN (2.5 mL), and TEMPO (96 mg, 0.62 mmol) were added and backfilled with Argon (three times). The Schlenk tube was sealed with Teflon, and the reaction mixture was irradiated (at approximately 5 cm away from the light source) with 30 W blue LEDs under vigorous stirring at room temperature for 4 h under Argon conditions. The progress of the reaction was monitored by TLC until the completion of the reaction with visualization under UV fluorescence, no desired product **3a** was observed detected by LC-MS, indicating that the reaction was completely inhibited. Meanwhile, a trapping product **4** was observed through the LC-MS analysis from the reaction solution.

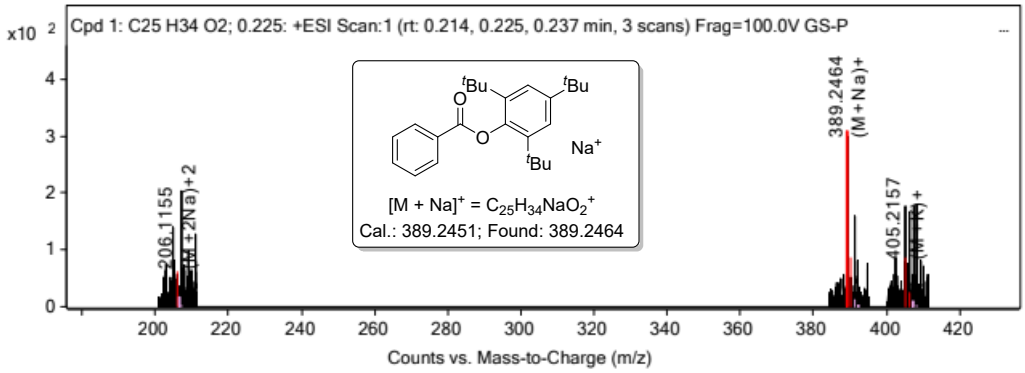


b) BHT

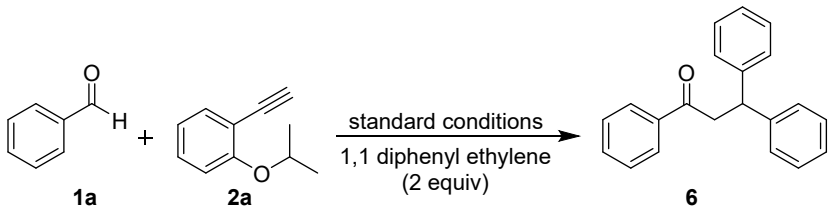


1a **2a** **5**

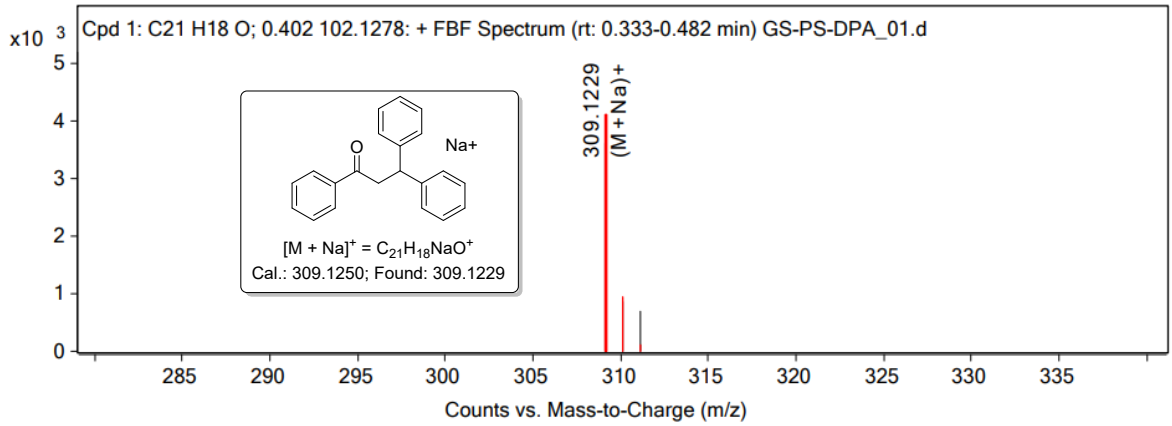
To an oven-dried Schlenk tube equipped with a magnetic stir bar, were added with benzaldehyde **1a** (66 mg, 0.31 mmol) added 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), CH_3CN (2.5 mL), and BHT (136 mg, 0.62 mmol) were added and backfilled with Argon (three times). The Schlenk tube was sealed with Teflon, and the reaction mixture was irradiated (at approximately 5 cm away from the light source) with 30 W blue LEDs under vigorous stirring at room temperature for 4 h under Argon conditions. The progress of the reaction was monitored by TLC until the completion of the reaction with visualization under UV fluorescence, no desired product **3a** was observed detected by LC-MS, indicating that the reaction was completely inhibited. Meanwhile, a trapping product **5** was observed through the LC-MS analysis from the reaction solution.



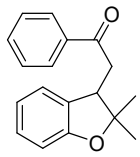
C) 1,1 Diphenyl ethylene



To an oven-dried Schlenk tube (10ml), Benzaldehyde **1a** (0.31 mmol, 66 mg) added 1-ethynyl-2-isopropoxybenzene **2a** (0.31 mmol, 1 equiv), TBADT (4 mol%), and CH_3CN (2.5 mL), 1,1-diphenylethylene (111 mg, 0.62 mmol), were added and backfilled with Argon (three times). The reaction mixture was irradiated (at approximately 5cm away from the light source) with 30 W blue LEDs under vigorous stirring at room temperature for 4-12h under Argon conditions. After the reaction was stopped, no desired product **3** was observed detected by LC-MS, indicating that the reaction was completely inhibited. Meanwhile, a trapping product **5** was observed through the LC-MS analysis from the reaction solution.



Characterization of compounds:



2-(2,2-Dimethyl-2,3-dihydrobenzofuran-3-yl)-1-phenylethan-1-one (3aa):

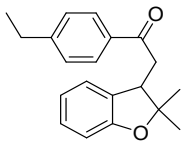
GP - 2 was carried out with benzaldehyde **1a** (33 mg, 0.31 mmol), 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 4 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3aa** (62 mg, 74%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3054, 2967, 1736, 1606, 1485, 1368, 1101, 989, 824 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.63 – 7.55 (m, 1H), 7.52 – 7.43 (m, 2H), 7.16 – 7.08 (m, 2H), 6.82 (td, *J* = 7.4, 0.9 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 3.91 (t, *J* = 6.9 Hz, 1H), 3.38 (dd, *J* = 17.9, 7.7 Hz, 1H), 3.22 (dd, *J* = 17.9, 6.2 Hz, 1H), 1.55 (s, 3H), 1.35 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.6, 158.1, 136.9, 133.5, 131.0, 128.8(2C), 128.6, 128.2(2C), 125.0, 120.3, 109.8, 88.8, 46.0, 40.9, 28.8, 23.0 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{19}O_2^+$ 267.1380; found 267.1384.



2-(2,2-Dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(4-ethylphenyl)ethan-1-one (3ba):

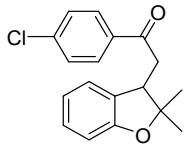
GP - 2 was carried out with 4-ethylbenzaldehyde **1c** (41 mg, 0.31 mmol), 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 8 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ba** (64 mg, 70%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2981, 2252, 1680, 1607, 1439, 1378, 1258, 1038, 752 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 – 7.88 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.08 (m, 2H), 6.81 (ddd, *J* = 7.4, 0.9 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 3.97 – 3.88 (m, 1H), 3.36 (dd, *J* = 17.8, 7.8 Hz, 1H), 3.19 (dd, *J* = 17.8, 6.1 Hz, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.55 (s, 3H), 1.34 (s, 3H), 1.26 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.31, 158.10, 150.54, 134.64, 131.13, 128.52, 128.42(2C), 128.36(2C), 124.99, 120.32, 109.84, 88.91, 46.08, 40.79, 29.09, 28.82, 23.02, 15.32 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{23}O_2^+$ 295.1693; found 295.1707.



1-(4-Chlorophenyl)-2-(2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)ethan-1-one (3ca):

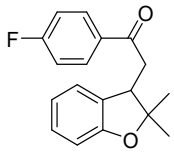
GP - 2 was carried out with 4-chlorobenzaldehyde **1c** (43 mg, 0.31 mmol), 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ca** (66 mg, 71%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3046, 2923, 2857, 1731, 1588, 1256, 1128, 751cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 – 7.88 (m, 2H), 7.48 – 7.41 (m, 2H), 7.05 (t, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.81 (ddd, *J* = 7.6, 0.8 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 3.88 (t, *J* = 6.9 Hz, 1H), 3.33 (dd, *J* = 17.8, 7.6 Hz, 1H), 3.18 (dd, *J* = 17.9, 6.3 Hz, 1H), 1.54 (s, 3H), 1.34 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 197.45, 158.10, 140.03, 135.19, 130.85, 129.61(2C), 129.20(2C), 128.68, 124.98, 120.39, 109.95, 88.74, 46.04, 40.91, 28.78, 23.02 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{17}ClNaO_2^+$ 323.0809; found 323.0806.



2-(2,2-Dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(4-fluorophenyl)ethan-1-one (3da):

GP - 2 was carried out with 4-fluorobenzaldehyde **1d** (38 mg, 0.31 mmol), 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3da** (62 mg, 69%), as a slight yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

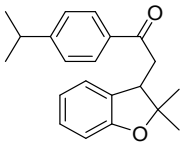
IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3063, 2976, 1736, 1687, 1474, 1370, 1256, 739 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 – 8.06 (m, 2H), 7.29 – 7.20 (m, 4H), 6.93 (ddd, *J* = 7.5, 0.8 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 4.00 (t, *J* = 6.9 Hz, 1H), 3.45 (dd, *J* = 17.8, 7.6 Hz, 1H), 3.31 (dd, *J* = 17.8, 6.3 Hz, 1H), 1.66 (s, 3H), 1.46 (s, 3H) ppm.

^{13}C NMR (151 MHz, CDCl3) δ 197.03 (s), 166.03 (d, $J_{C\text{-}F}$ = 255.1 Hz), 158.10 (s), 133.33 (d, $J_{C\text{-}F}$ = 2.4 Hz), 130.9, 130.9 (d, $J_{C\text{-}F}$ = 9.0 Hz), 128.6, 124.9 (s), 120.4, 115.9 (d, $J_{C\text{-}F}$ = 22.0 Hz), 109.9, 88.7, 46.0, 40.8, 28.8, 23.0 ppm.

^{19}F NMR (565 MHz, $CDCl_3$) δ = −104.63 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{18}FO_2^+$ 285.1285; found 285.1277.



2-(2,2-Dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(4-isopropylphenyl)ethan-1-one (3ea):

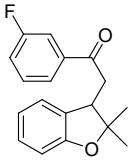
GP - 2 was carried out with 4-isopropylbenzaldehyde **1e** (46 mg, 0.31 mmol), 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ea** (61.6 mg, 64%), as a slight pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3050, 2966, 2347, 1737, 1681, 1470, 1262,734 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 – 7.88 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.20 – 7.05 (m, 2H), 6.81 (ddd, *J* = 7.4, 0.9 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 3.93 – 3.88 (m, 1H), 3.36 (dd, *J* = 17.8, 7.8 Hz, 1H), 3.19 (dd, *J* = 17.8, 6.1 Hz, 1H), 2.97 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.55 (s, 3H), 1.34 (s, 3H), 1.27 (d, *J* = 6.9 Hz, 6H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.3, 158.1, 150.5, 134.6, 131.1, 128.5, 128.4, 128.3, 124.1, 120.3, 109.8, 88.9, 46.1, 40.8, 29.1, 28.8, 23.0, 15.3 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{25}O_2^+$ 309.1849; found 309.1838.



2-(2,2-Dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(3-fluorophenyl)ethan-1-one (3fa):

GP - 2 was carried out with 3-fluorobenzaldehyde **1f** (38 mg, 0.31 mmol), 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3fa** (54 mg, 61%), as a yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

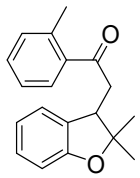
IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3054, 2930, 1684, 1594, 1472, 1365, 1140, 854, 737 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 – 7.72 (m, 1H), 7.66 (ddd, *J* = 9.4, 2.5, 1.6 Hz, 1H), 7.45 (td, *J* = 8.0, 5.5 Hz, 1H), 7.34 – 7.26 (m, 1H), 7.18 – 7.05 (m, 2H), 6.82 (ddd, *J* = 7.4, 0.9 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 3.88 (t, *J* = 6.9 Hz, 1H), 3.34 (dd, *J* = 18.0, 7.6 Hz, 1H), 3.19 (dd, *J* = 18.0, 6.3 Hz, 1H), 1.54 (s, 3H), 1.35 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 197.4, 163.0 (d, $J_{C\text{-}F}$ = 248.5 Hz), 158.1, 138.9 (d, $J_{C\text{-}F}$ = 6.3 Hz), 130.8 , 130.6 (d, $J_{C\text{-}F}$ = 7.7 Hz), 128.7, 124.9, 123.9 (d, $J_{C\text{-}F}$ = 3.1 Hz), 120.6 (d, $J_{C\text{-}F}$ = 21.2 Hz), 120.4 (s, *J* = 14.0 Hz), 114.9 (d, $J_{C\text{-}F}$ = 22.7 Hz), 109.9, 88.7, 46.0, 41.1, 28.8, 23.0. ppm.

^{19}F NMR (565 MHz, $CDCl_3$) δ = −111.46 (s).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{18}FO_2^+$ 285.1285; found 285.1277.



2-(2,2-Dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(o-tolyl)ethan-1-one (3ga):

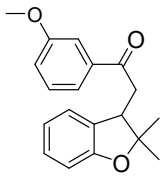
GP - 2 was carried out with 2-methylbenzaldehyde **1g** (37 mg, 0.31 mmol), 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 8 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ga** (55 mg, 63%), as a yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection] yellow oil (yield).

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3059, 2969, 2625, 1685, 1470, 1255, 1125, 748 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (dd, *J* = 7.7, 1.0 Hz 1H), 7.39 (ddd, *J* = 7.5, 7.4, 1.3 Hz, 1H), 7.30−7.28 (m, 1H), 7.24 (dd, *J* = 7.8, 0.5 Hz, 1H), 7.15 – 7.10 (m, 2H), 6.82 (ddd, *J* = 7.5, 7.4, 0.9 Hz, 1H), 6.74 (dd, *J* = 7.7, 1.0 Hz 1H), 3.88 (t, *J* = 7.0 Hz, 1H), 3.28 (dd, *J* = 17.9, 7.5 Hz, 1H), 3.17 (dd, *J* = 17.9, 6.5 Hz, 1H), 2.55 (s, 3H), 1.54 (s, 3H), 1.36 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 202.2, 157.9, 138.3, 137.5, 132.2, 131.7, 130.9, 128.6, 128.4, 125.9, 124.8, 120.2, 109.8, 88.6, 46.1, 43.6, 28.7, 22.9, 21.5 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{21}O_2^+$ 281.1536; found 281.1526.



2-(2,2-Dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(3-methoxyphenyl)ethan-1-one (3ha):

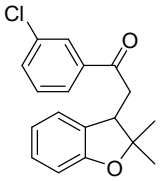
GP - 2 was carried out with 3-methoxybenzaldehyde **1h** (42 mg, 0.31 mmol), 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 8 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ha** (65 mg, 70%), as a yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3055, 1738, 1368, 1263, 1221, 893, 730 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 – 7.49 (m, 2H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.16 – 7.08 (m, 3H), 6.82 (ddd, *J* = 7.4, 1.0 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 3.93 – 3.87 (m, 1H), 3.86 (s, 3H), 3.36 (dd, *J* = 17.9, 7.8 Hz, 1H), 3.20 (dd, *J* = 17.9, 6.2 Hz, 1H), 1.55 (s, 3H), 1.34 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.5, 160.0, 158.1, 138.3, 131.0, 129.8, 128.6, 125.0, 120.8, 120.3, 120.0, 112.4, 109.9, 88.8, 77.1, 55.6, 46.1, 41.0, 28.8, 23.0 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{21}O_3^+$ 297.1485; found 297.1478.



***1-(3-Chlorophenyl)-2-(2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)ethan-1-one (3ia)*:**

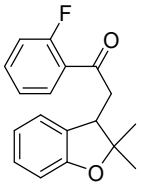
GP - 2 was carried out with 3-chlorobenzaldehyde **1i** (43 mg, 0.31 mmol), 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ia** (49.5 mg, 53%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3061, 2974, 2927, 1734, 1688, 1471, 1297, 791 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (t, *J* = 1.8 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.55 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.16 – 7.07 (m, 2H), 6.82 (td, *J* = 7.4, 0.9 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 3.88 (t, *J* = 6.9 Hz, 1H), 3.34 (dd, *J* = 18.0, 7.6 Hz, 1H), 3.19 (dd, *J* = 18.0, 6.3 Hz, 1H), 1.54 (s, 3H), 1.34 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 197.3, 158.1, 138.3, 135.2, 133.4, 130.7, 130.2, 128.7, 128.3, 126.2, 124.9, 120.4, 109.9, 88.7, 45.9, 41.1, 28.7, 23.0 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{18}H_{17}ClNaO_2^+$ 323.0809; found 323.0805.



2-(2,2-Dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(2-fluorophenyl)ethan-1-one (3ja)

GP - 2 was carried out with 2-fluorobenzaldehyde **1j** (38 mg, 0.31 mmol) 1-ethynyl-2-isopropoxybenzene alkynyl aryl ether **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ja** (58 mg, 65%), as yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

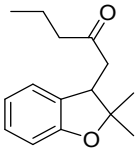
IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2972, 2924, 1686, 1602, 1465, 1259, 988, 752 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (td, *J* = 7.6, 1.9 Hz, 1H), 7.54 (dddd, *J* = 8.3, 7.1, 5.0, 1.9 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.17 – 7.09 (m, 3H), 6.82 (td, *J* = 7.5, 0.9 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 3.87 (t, *J* = 6.9 Hz, 1H), 3.39 (ddd, *J* = 18.4, 7.4, 3.0 Hz, 1H), 3.25 (ddd, *J* = 18.4, 6.5, 2.9 Hz, 1H), 1.54 (s, 3H), 1.35 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 197.0 (d, *J* = 4.1 Hz), 163.2, 160.7, 158.0, 134.9 (d, *J* = 9.2 Hz), 130.8, 130.6 (d, *J* = 2.7 Hz), 128.4, 124.9, 124.6 (d, *J* = 3.4 Hz), 120.2, 116.9, 116.7, 109.7, 88.7, 46.7 (d, *J* = 7.5 Hz), 45.9, 28.7, 22.9 ppm.

^{19}F NMR (565 MHz, $CDCl_3$) δ = –108.81 (s).

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{18}FO_2^+$ 285.1285; found 285.1274.



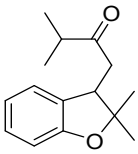
1-(2,2-Dimethyl-2,3-dihydrobenzofuran-3-yl)pentan-2-one (3ka):
GP - 2 was carried out with butaraldehyde **1k** (22 mg, 0.31 mmol), 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 6 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ka** (30 mg, 41%), as yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2966, 2926, 1719, 1597, 1469, 1371, 1023, 735 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.14 – 7.08 (m, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.80 (ddd, *J* = 7.4, 0.9 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 3.68 (t, *J* = 7.1 Hz, 1H), 2.76 (dd, *J* = 17.8, 7.3 Hz, 1H), 2.66 (dd, *J* = 17.8, 7.0 Hz, 1H), 2.42 (td, *J* = 7.2, 1.1 Hz, 2H), 1.64 (dd, *J* = 14.8, 7.4 Hz, 2H), 1.48 (s, 3H), 1.29 (s, 3H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 209.5, 158.0, 130.9, 128.5, 124.8, 120.3, 109.8, 88.6, 45.7, 45.4, 44.9, 28.7, 22.9, 17.4, 13.8 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{15}H_{21}O_2^+$ 233.1536 found 233.1525.



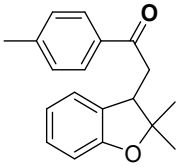
1-(2,2-Dimethyl-2,3-dihydrobenzofuran-3-yl)-3-methylbutan-2-one (3la):
GP - 2 was carried out with isobutaraldehyde **1l** (22 mg, 0.31 mmol), 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 6 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3la** (23 mg, 37%), as yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2969, 2927, 1711, 1470, 1327, 1254, 1023, 751 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10 (ddd, *J* = 11.4, 4.0 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.80 (ddd, *J* = 7.5, 0.8 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 3.68 (t, *J* = 7.1 Hz, 1H), 2.81 (dd, *J* = 18.0, 7.2 Hz, 1H), 2.72 (dd, *J* = 18.0, 6.9 Hz, 1H), 2.62 (dt, *J* = 13.9, 6.9 Hz, 1H), 1.48 (s, 3H), 1.30 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 6H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 213.3, 158.0, 131.8, 128.5, 124.8, 120.3, 109.8, 88.6, 45.6, 42.7, 41.4, 28.7, 22.9, 18.5, 18.4 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{15}H_{21}O_2^+$ 233.1536; found 233.1534.



2-(2,2-Dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(p-tolyl)ethan-1-one (3oa):

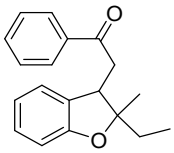
GP - 2 was carried out with 4-methylbenzaldehyde **1o** (22 mg, 0.31 mmol), 1-ethynyl-2-isopropoxybenzene **2a** (50 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 6 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3oa** (46 mg, 76%), as yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) v_{max} = 3049, 2923, 2311, 1680, 1603, 1471, 1414, 1370, 1186 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 – 7.71 (d, *J* =8.2 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.10 – 6.97 (m, 2H), 6.73 (ddd, *J* = 7.4, 0.9 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 3.82 (t, *J* = 7.0 Hz, 1H), 3.27 (dd, *J* = 17.8, 7.8 Hz, 1H), 3.11 (dd, *J* = 17.8, 6.2 Hz, 1H), 2.34 (s, 3H), 1.46 (s, 3H), 1.26 (s, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 198.3, 158.0, 144.4, 134.4, 131.1, 129.5(2C), 128.5, 128.3(2C), 124.9, 120.3, 109.3, 88.9, 77.2, 46.10, 40.7, 28.8, 23.0, 21.8 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{15}H_{21}O_2^+$ 281.1536; found 281.1528.



2-(2-Ethyl-2-methyl-2,3-dihydrobenzofuran-3-yl)-1-phenylethan-1-one (3ab):

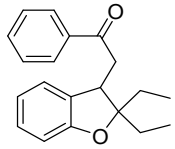
GP - 2 was carried out with benzaldehyde **1a** (33 mg, 0.31 mmol), 1-(sec-butoxy)-2-ethynylbenzene **2b** (54 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ab** (49 mg, 61%), as yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) v_{max} = 3055, 2978, 2345, 1684, 1468, 1369, 730 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 – 7.65(m, 2H), 7.64 – 7.53 (m, 1H), 7.52 – 7.44 (m, 2H), 7.16 – 7.05 (m, 2H), 6.85 – 6.78 (m, 1H), 6.78 – 6.73 (m, 1H), 3.96 (dt, *J* = 18.4, 6.9 Hz, 1H), 3.38 (ddd, *J* = 17.7, 13.8, 7.2 Hz, 1H), 3.23 (ddd, *J* = 17.9, 6.7, 5.3 Hz, 1H), 1.93 – 1.74 (m, 2H), 1.31 (s, 3H), 1.03 (q, *J* = 7.5 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.7, 158.4, 158.2, 137.0, 136.9, 133.5, 131.4, 131.2, 128.9, 128.5, 128.5, 128.2, 128.2, 124.9, 120.2, 120.2, 109.8, 109.7, 91.2, 90.7, 46.7(2C), 43.9(2C), 41.0(2C), 39.9(2C), 34.0(2C), 28.3(2C), 24.7(2C), 20.6(2C), 8.6(2C), 8.3(2C) ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{21}O_2^+$ 281.1536 found 281.1533.



2-(2,2-Diethyl-2,3-dihydrobenzofuran-3-yl)-1-phenylethan-1-one (3ac):

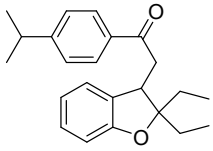
GP - 2 was carried out with benzaldehyde **1a** (33 mg, 0.31 mmol), 1-ethynyl-2-(pentan-3-yloxy)benzene **2c** (58 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ac** (52 mg, 66%), as yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3053, 2962, 2353, 1685, 1595, 1469, 1245, 749 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 – 7.93 (m, 2H), 7.62 – 7.55 (m, 1H), 7.47 (dd, *J* = 10.6, 4.8 Hz, 2H), 7.14 – 7.03 (m, 2H), 6.76 (ddd, *J* = 8.1, 1.3 Hz, 2H), 4.06 (t, *J* = 6.8 Hz, 1H), 3.35 (dd, *J* = 17.7, 6.2 Hz, 1H), 3.23 (dd, *J* = 17.7, 7.5 Hz, 1H), 1.82 (dd, *J* = 7.2, 6.4 Hz, 2H), 1.61 (dd, *J* = 14.2, 7.3 Hz, 2H), 0.99 (q, *J* = 7.4 Hz, 6H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.8, 158.4, 137.0, 133.5, 131.6, 128.8(2C), 128.4, 128.2(2C), 124.9, 120.1, 109.6, 93.0, 43.3, 40.3, 29.2, 26.0, 8.4, 8.1 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{23}O_2^+$ 295.1693; found 295.1678.



2-(2,2-Diethyl-2,3-dihydrobenzofuran-3-yl)-1-(4-isopropylphenyl)ethan-1-one (3ec):

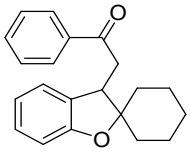
GP - 2 was carried out with 4-isopropylbenzaldehyde **1e** (45 mg, 0.31 mmol), 1-ethynyl-2-(pentan-3-yloxy)benzene **2c** (58 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ec** (52 mg, 59%), as yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2962, 2879, 1686, 1604, 1467, 1283, 833, 744 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 – 7.87 (m, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.13 – 7.01 (m, 2H), 6.81 – 6.71 (m, 2H), 4.06 (t, *J* = 6.9 Hz, 1H), 3.33 (dd, *J* = 17.6, 6.3 Hz, 1H), 3.20 (dd, *J* = 17.6, 7.4 Hz, 1H), 2.97 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.82 – 1.77 (m, 2H), 1.60 (dd, *J* = 14.2, 7.3 Hz, 2H), 1.27 (d, *J* = 6.9 Hz, 6H), 0.98 (td, *J* = 7.4, 5.3 Hz, 6H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.4, 158.4, 155.0, 134.9, 131.8, 128.5(2C), 128.4, 126.9(2C), 124.9, 120.1, 109.5, 93.1, 43.3, 40.2, 34.4, 29.9, 29.3, 26.1, 23.8, 8.4, 8.1 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{29}O_2^+$ 337.2162; found 337.2177.



1-Phenyl-2-(3H-spiro[benzofuran-2,1'-cyclohexan]-3-yl)ethan-1-one (3ad):

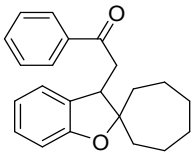
GP - 2 was carried out with benzaldehyde **1a** (33 mg, 0.31 mmol), 1-(cyclohexyloxy)-2-ethynylbenzene **2d** (58 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ad** (50.5 mg, 66%), as yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2930, 2857, 1734, 1684, 1594, 1260, 1140, 737cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 – 7.92 (m, 2H), 7.62 – 7.54 (m, 1H), 7.51 – 7.43 (m, 2H), 7.16 – 7.04 (m, 2H), 6.80 – 6.74 (m, 2H), 3.82 (t, *J* = 6.9 Hz, 1H), 3.37 (dd, *J* = 17.7, 6.9 Hz, 1H), 3.15 (dd, *J* = 17.7, 7.0 Hz, 1H), 1.99 – 1.83 (m, 2H), 1.82 – 1.57 (m, 6H), 1.50 – 1.30 (m, 2H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.9, 158.2, 137.1, 133.4, 131.3, 128.8(2C), 128.4, 128.2(2C), 125.3, 120.2, 110.0, 89.5, 46.0, 40.2, 37.0, 31.8, 25.5, 22.7, 22.7 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{23}O_2^+$ 307.1693; found 307.1684.



1-Phenyl-2-(3H-spiro[benzofuran-2,1'-cycloheptan]-3-yl)ethan-1-one (3ae):

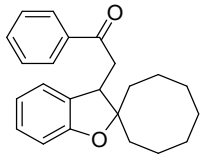
GP - 2 was carried out with benzaldehyde **1a** (33 mg, 0.31 mmol), (2-ethynylphenoxy)cycloheptane **2e** (62 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ae** (42.5 mg, 57%), as yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2925, 2858, 1737, 1685, 1468, 1240, 1005, 750 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.92 (m, 2H), 7.61-7.55 (m, 1H), 7.49 – 7.43 (m, 2H), 7.14 – 7.04 (m, 2H), 6.80 – 6.72 (m, 2H), 3.89 (t, *J* = 6.8 Hz, 1H), 3.38 (dd, *J* = 17.7, 6.8 Hz, 1H), 3.13 (dd, *J* = 17.7, 6.9 Hz, 1H), 2.10 – 1.85 (m, 3H), 1.81 – 1.60 (m, 6H), 1.55 – 1.46 (m, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.7, 144.7, 136.9, 133.3, 131.5, 128.7(2C), 128.3, 128.1(2C), 125.1, 120.1, 109.7, 93.5, 47.0, 40.5, 40.5, 34.7, 29.4, 29.2, 22.3, 22.1 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{25}O_2^+$ 321.1849; found 321.1836.



1-Phenyl-2-(3H-spiro[benzofuran-2,1'-cyclooctan]-3-yl)ethan-1-one (3af):

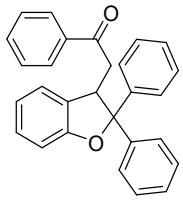
GP - 2 was carried out with benzaldehyde **1a** (33 mg, 0.31 mmol), (2-ethynylphenoxy)cyclooctane **2f** (66 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3af** (40.5 mg, 55%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2919, 2857, 1732, 1594, 1468, 1254, 1089, 159 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.93 (m, 2H), 7.60 – 7.54 (m, 1H), 7.49 – 7.42 (m, *J* = 7.6 Hz, 2H), 7.13 – 7.05 (m, 2H), 6.80 – 6.70 (m, 2H), 3.94 (t, *J* = 6.8 Hz, 1H), 3.36 (dd, *J* = 17.6, 6.5 Hz, 1H), 3.12 (dd, *J* = 17.6, 7.3 Hz, 1H), 2.12 – 1.98 (m, 2H), 1.90 – 1.58 (m, 10H), 1.55 – 1.45 (m, 2H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.8, 157.9, 137.1, 133.4, 131.8, 128.8(2C), 128.5, 128.2(2C), 125.5, 120.2, 109.9, 93.4, 45.3, 40.9, 34.3, 30.9, 29.3, 27.5, 24.6, 22.2, 22.0 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{27}O_2^+$ 335.2006; found 335.2011.



2-(2,2-Diphenyl-2,3-dihydrobenzofuran-3-yl)-1-phenylethan-1-one (3ag):

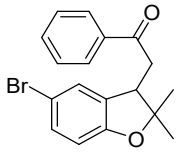
GP - 2 was carried out with benzaldehyde **1a** (33 mg, 0.31 mmol), (2-ethynylphenoxy)methylene)dibenzene **2g** (88 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ag** (38 mg, 55%), as white solid. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2927, 2343, 2019, 1891, 1738, 1598, 1474, 735 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (t, *J* = 7.8 Hz, 2H), 7.58 (dt, *J* = 3.2, 2.4 Hz, 2H), 7.47 (ddd, *J* = 8.6, 7.8, 4.5 Hz, 2H), 7.34 (dt, *J* = 23.6, 7.6 Hz, 6H), 7.15 (td, *J* = 7.4, 4.5 Hz, 4H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.85 – 6.78 (m, 1H), 5.06 (t, *J* = 6.8 Hz, 1H), 3.10 (dd, *J* = 17.7, 6.9 Hz, 1H), 2.81 (dd, *J* = 17.7, 6.7 Hz, 1H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.5, 157.7, 144.6, 141.5, 136.7, 132.9, 132.4, 131.3, 130.1, 128.6, 128.3(2C), 128.3, 128.2, 128.0(2C), 127.8, 127.7(2C), 127.3, 127.0, 126.9, 124.9, 121.1, 110.0, 95.1, 46.0, 43.1 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{28}H_{23}O_2^+$ 391.1693; found 391.1712.



2-(5-Bromo-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-phenylethan-1-one (3ah):

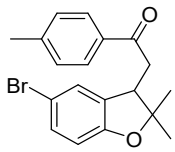
GP - 2 was carried out with benzaldehyde **1a** (33 mg, 0.31 mmol), 4-bromo-2-ethynyl-1-isopropoxybenzene **2h** (74 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ah** (45.5 mg, 63%), as slight yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3064, 2927, 1738, 1683, 1592, 1464, 1096, 750cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 – 7.94 (m, 2H), 7.64 – 7.55 (m, 1H), 7.54 – 7.44 (m, 2H), 7.25 – 7.16 (m, 2H), 6.62 (d, *J* = 9.0 Hz, 1H), 3.89 (t, *J* = 6.9 Hz, 1H), 3.38 (dd, *J* = 18.1, 7.5 Hz, 1H), 3.19 (dd, *J* = 18.1, 6.4 Hz, 1H), 1.53 (s, 3H), 1.34 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.1, 157.3, 136.7, 133.7, 133.6, 131.4, 128.9(2C), 128.1(2C), 128.1, 111.9, 111.5, 89.8, 45.9, 40.7, 28.7, 22.9 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{18}Br^{79}O_2^+$ 345.0485; found 345.0466. $[M+H]^+$ calculated for $C_{18}H_{18}Br^{81}O_2^+$ 347.0464; found 347.0448.



2-(5-Bromo-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(p-tolyl)ethan-1-one (3oh):

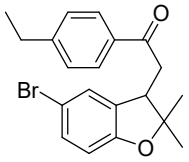
GP - 2 was carried out with 4-ethylbenzaldehyde **1o** (37 mg, 0.31 mmol), 4-bromo-2-ethynyl-1-isopropoxybenzene **2h** (74 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3oh** (46 mg, 61%), as slight yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2926, 2856, 1737, 1468, 1369, 1262, 728cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 – 7.85 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.17 (m, 2H), 6.62 (d, *J* = 9.1 Hz, 1H), 3.88 (t, *J* = 6.9 Hz, 1H), 3.35 (dd, *J* = 17.9, 7.6 Hz, 1H), 3.16 (dd, *J* = 18.0, 6.3 Hz, 1H), 2.42 (s, 3H), 1.53 (s, 3H), 1.32 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 197.7, 157.3, 144.6, 134.2, 133.7, 131.3, 129.6(2C), 128.3(2C), 128.1, 111.9, 111.4, 89.9, 46.0, 40.6, 28.7, 22.9, 21.8 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{20}Br^{79}O_2^+$ 359.0641; found 359.0659. $[M+H]^+$ calculated for $C_{19}H_{20}Br^{81}O_2^+$ 361.0621; found 361.0646.



2-(-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(4-ethylphenyl)ethan-1-one (3bh):

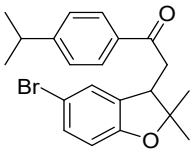
GP - 2 was carried out with benzaldehyde **1b** (41 mg, 0.31 mmol), 4-bromo-2-ethynyl-1-isopropoxybenzene **2h** (74 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3bh** (49 mg, 63%), as slight yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2970, 2928, 1738, 1681, 1468, 1261, 1098, 732cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.98 – 7.86 (m, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.17 (m, 2H), 6.62 (d, *J* = 9.1 Hz, 1H), 3.89 (t, *J* = 6.9 Hz, 1H), 3.35 (dd, *J* = 18.0, 7.6 Hz, 1H), 3.16 (dd, *J* = 18.0, 6.3 Hz, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.53 (s, 3H), 1.33 (s, 3H), 1.26 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 197.7, 157.3, 150.7, 134.4, 133.7, 131.3, 128.4(2C), 128.4(2C), 128.1, 111.9, 111.4, 89.9, 46.0, 40.6, 29.1, 28.7, 22.9, 15.3 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{22}Br^{79}O_2^+$ 373.0798; found 373.0776. $[M+H]^+$ calculated for $C_{20}H_{22}Br^{81}O_2^+$ 375.0777; found 375.0754 ppm.



2-(5-Bromo-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(4-isopropylphenyl)ethan-1-one (3eh):

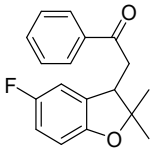
GP - 2 was carried out with 4-isopropylbenzaldehyde **1e** (45 mg, 0.31 mmol), 4-bromo-2-ethynyl-1-isopropoxybenzene **2h** (74 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3eh** (43 mg, 54%), as slight yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2965, 1979, 1602, 1465, 1254, 1140, 810, 724 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.93 – (m, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.19 (m, 2H), 6.62 (d, *J* = 9.1 Hz, 1H), 3.89 (t, *J* = 6.9 Hz, 1H), 3.35 (dd, *J* = 18.0, 7.6 Hz, 1H), 3.16 (dd, *J* = 18.0, 6.3 Hz, 1H), 2.98 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.53 (s, 3H), 1.33 (s, 3H), 1.28 (d, *J* = 6.9 Hz, 6H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 197.7, 157.3, 155.3, 134.6, 133.7, 131.3, 128.5(2C), 128.1, 126.9(2C), 111.9, 111.4, 89.9, 77.2, 46.0, 40.6, 34.4, 28.7, 23.8, 22.9 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{24}Br^{79}O_2^+$ 387.0954; found 387.0941. $[M+H]^+$ calculated for $C_{21}H_{24}Br^{81}O_2^+$ 389.0934; found 389.0922 ppm.



2-(5-Fluoro-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-phenylethan-1-one (3ai):

GP - 2 was carried out with benzaldehyde **1a** (33 mg, 0.31 mmol), 2-ethynyl-4-fluoro-1-isopropoxybenzene **2i** (55 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ai** (47 mg, 59%), as slight yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

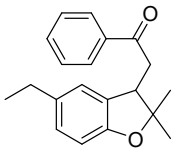
IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2963, 1554, 1482, 1254, 1108, 948, 813, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 – 7.94 (m, 2H), 7.64 – 7.57 (m, 1H), 7.53 – 7.45 (m, 2H), 6.86 – 6.75 (m, 2H), 6.64 (dd, *J* = 8.5, 4.2 Hz, 1H), 3.88 (t, *J* = 6.9 Hz, 1H), 3.36 (dd, *J* = 17.9, 7.2 Hz, 1H), 3.19 (dd, *J* = 17.9, 6.8 Hz, 1H), 1.53 (s, 3H), 1.35 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.2, 158.6, 156.2, 154.1, 136.8, 133.6, 132.5, 128.9, 128.2, 114.6 (d, $J_{C\text{-}F}$ = 24.1 Hz), 112.3 (d, $J_{C\text{-}F}$ = 24.9 Hz), 109.9 (d, $J_{C\text{-}F}$ = 8.6 Hz), 89.5, 46.3, 40.6, 28.6, 23.0 ppm. 198.2, 158.6, 156.2, 154.1, 136.7, 133.6, 132.5, 128.9, 128.2, 114.7, 114.5, 112.4, 112.2, 109.9, 109.9, 89.5, 46.3, 40.6, 28.6, 22.9 ppm.

^{19}F NMR (565 MHz, $CDCl_3$) δ = –124.41 (s).

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{18}FO_2^+$ 285.1285; found 285.1277.



2-(5-Ethyl-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-phenylethan-1-one (3aj):

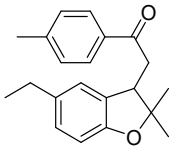
GP - 2 was carried out with benzaldehyde **1a** (33 mg, 0.31 mmol), 4-ethyl-2-ethynyl-1-isopropoxybenzene **2j** (58 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3aj** (47 mg, 56%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2971, 2255, 1684, 1371, 1219, 905, 726 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.0 – 7.95 (m, 2H), 7.63 – 7.55 (m, 1H), 7.52 – 7.44 (m, 2H), 6.98 – 6.90 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 3.91 – 3.84 (m, 1H), 3.37 (dd, *J* = 17.8, 7.8 Hz, 1H), 3.22 (dd, *J* = 17.8, 6.1 Hz, 1H), 2.54 (q, *J* = 7.6 Hz, 2H), 1.54 (s, 3H), 1.34 (s, 3H), 1.16 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.8, 156.2, 136.9, 136.3, 133.5, 130.9, 128.8(2C), 128.2(2C), 127.8, 124.4, 109.4, 88.8, 77.2, 46.2, 40.9, 28.8, 28.5, 23.1, 16.2 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{23}O_2^+$ 295.1693; found 295.1680.



2-(5-Ethyl-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(p-tolyl)ethan-1-one (3oj):

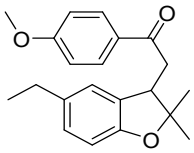
GP - 2 was carried out with 4-methylbenzaldehyde **1o** (37 mg, 0.31 mmol), 4-ethyl-2-ethynyl-1-isopropoxybenzene **2j** (58 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3oj** (46 mg, 56%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2966, 2926, 1679, 1607, 1485, 1255, 1131, 812 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 – 7.85 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.95 – 6.89 (m, 2H), 6.66 (d, *J* = 8.0 Hz, 1H), 3.90 – 3.83 (m, 1H), 3.34 (dd, *J* = 17.7, 7.9 Hz, 1H), 3.19 (dd, *J* = 17.7, 6.1 Hz, 1H), 2.53 (q, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.53 (s, 3H), 1.32 (s, 3H), 1.16 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.4, 156.1, 144.3, 136.2, 134.5, 131.0, 129.5(2C), 128.3(2C), 127.7, 124.3, 109.4, 88.8, 77.2, 46.2, 40.8, 28.8, 28.5, 23.0, 21.8, 16.2 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{25}O_2^+$ 309.1849 found 309.1844.



2-(5-Ethyl-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(4-methoxyphenyl)ethan-1-one (3mj):

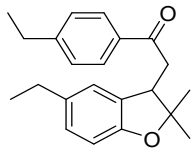
GP - 2 was carried out with 4-methoxybenzaldehyde **1h** (42 mg, 0.31 mmol), 4-ethyl-2-ethynyl-1-isopropoxybenzene **2j** (58 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3mj** (48 mg, 55%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2965, 2925, 1674, 1598, 1481, 1252, 1098, 823 cm^{-1}.

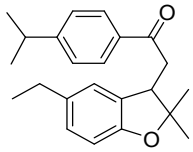
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.92 (m, 2H), 6.98 – 6.89 (m, 4H), 6.66 (d, *J* = 8.0 Hz, 1H), 3.92 – 3.82 (m, 4H), 3.31 (dd, *J* = 17.5, 7.9 Hz, 1H), 3.16 (dd, *J* = 17.6, 6.1 Hz, 1H), 2.53 (q, *J* = 7.6 Hz, 2H), 1.53 (s, 3H), 1.33 (s, 3H), 1.16 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 197.3, 163.8, 156.1, 136.3, 131.1, 130.5(2C), 130.1, 127.7, 124.4, 113.9(2C), 109.4, 88.9, 77.2, 55.7, 46.3, 40.5, 28.8, 28.4, 23.0, 16.2 ppm.

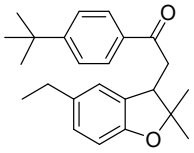
HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{25}O_3^+$ 325.1798; found 325.1794.



2-(5-Ethyl-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(4-ethylphenyl)ethan-1-one (3bj):
GP - 2 was carried out with 4-ethylbenzaldehyde **1b** (41 mg, 0.31 mmol), 4-ethyl-2-ethynyl-1-isopropoxybenzene **2j** (58 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3bj** (51 mg, 60%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].
IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2966, 1681, 1607, 1486, 1370, 1259, 1099, 824 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 – 7.88 (m, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.98 – 6.90 (m, *J* = 4.3 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 3.91 – 3.84 (m, 1H), 3.36 (dd, *J* = 17.7, 7.9 Hz, 1H), 3.20 (dd, *J* = 17.7, 6.1 Hz, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.54 (q, *J* = 7.6 Hz, 2H), 1.54 (s, 3H), 1.33 (s, 3H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.16 (t, *J* = 7.6 Hz, 3H) ppm.
^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.5, 156.1, 150.5, 136.3, 134.7, 131.0, 128.4(2C), 128.3(2C), 127.7, 124.4, 109.4, 88.8, 46.2, 40.8, 29.1, 28.8, 28.45, 23.0, 16.2, 15.3 ppm.
HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{27}O_2^+$ 323.2006; found 323.1996.



2-(5-Ethyl-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(4-isopropylphenyl)ethan-1-one (3ej):
GP - 2 was carried out with 4-isopropylbenzaldehyde **1e** (45 mg, 0.31 mmol), 4-ethyl-2-ethynyl-1-isopropoxybenzene **2j** (58 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ej** (48 mg, 53%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].
IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2925, 2873, 1679, 1567, 1484, 1369, 1134, 819 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 – 7.88 (m, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 6.99 – 6.89 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 3.91 – 3.84 (m, 1H), 3.36 (dd, *J* = 17.7, 7.9 Hz, 1H), 3.20 (dd, *J* = 17.7, 6.1 Hz, 1H), 2.97 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.54 (q, *J* = 7.6 Hz, 2H), 1.54 (s, 3H), 1.33 (s, 3H), 1.28 (d, *J* = 6.9 Hz, 7H), 1.16 (t, *J* = 7.6 Hz, 3H) ppm.
^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.4, 156.2, 155.0, 136.3, 134.9, 131.0, 128.5(2C), 127.7, 126.9(2C), 124.4, 109.4, 88.9, 46.3, 40.8, 34.4, 28.9, 28.5, 23.7(2C), 23.1, 16.2 ppm.
HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{29}O_2^+$ 337.2162; found 337.2161.



1-(4-(tert-Butyl) phenyl)-2-(5-ethyl-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)ethan-1-one (3nj):

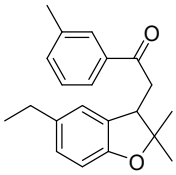
GP - 2 was carried out with 4-tertiarybutylbenzaldehyde **1n** (50 mg, 0.31 mmol), 4-ethyl-2-ethynyl-1-isopropoxybenzene **2j** (58 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3nj** (48 mg, 51%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2960, 1739, 1681, 1608, 1488, 1368, 1261, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 – 7.90 (m, 2H), 7.53 – 7.47 (m, 2H), 6.99 – 6.91 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 3.91 – 3.85 (m, 1H), 3.37 (dd, *J* = 17.7, 7.9 Hz, 1H), 3.21 (dd, *J* = 17.7, 6.1 Hz, 1H), 2.54 (q, *J* = 7.6 Hz, 2H), 1.54 (s, 3H), 1.35 (s, 9H), 1.34 (s, 3H), 1.16 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.4, 157.2, 156.1, 136.2, 134.4, 131.0, 128.2(2C), 127.7, 125.7(2C), 124.4, 109.4, 88.8, 77.2, 46.2, 40.8, 35.3, 31.2(2C), 28.9, 28.5, 23.0, 16.2 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{24}H_{31}O_2^+$ 351.2319 found 351.2306.



2-(5-Ethyl-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(m-tolyl)ethan-1-one (3gj):

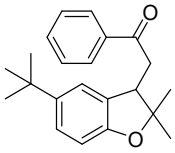
GP - 2 was carried out with 3-methylbenzaldehyde **1g** (45 mg, 0.31 mmol), 4-ethyl-2-ethynyl-1-isopropoxybenzene **2j** (58 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3gj** (46.5 mg, 57%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2964, 1684, 1600, 1485, 1371, 1260, 1098, 728 cm^{-1}.

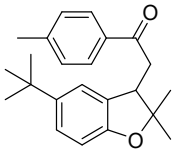
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 – 7.75 (m, 2H), 7.41– 7.31 (m, 2H), 6.97 – 6.90 (m, *J* = 10.3, 2.3 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 3.90 – 3.84 (m, 1H), 3.37 (dd, *J* = 17.8, 7.9 Hz, 1H), 3.21 (dd, *J* = 17.8, 6.0 Hz, 1H), 2.54 (q, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.54 (s, 3H), 1.34 (s, 3H), 1.17 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 199.0, 156.1, 138.7, 137.0, 136.3, 134.2, 131.0, 128.7, 128.7, 127.8, 125.4, 124.4, 109.4, 88.8, 46.2, 41.0, 28.8, 28.5, 23.1, 21.5, 16.2 ppm.

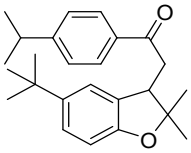
HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{25}O_2^+$ 309.1849; found 309.1845.



2-(5-(tert-Butyl)-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-phenylethan-1-one (3ak):
GP - 2 was carried out with benzaldehyde **1a** (33 mg, 0.31 mmol), 4-(*tert*-butyl)-2-ethynyl-1-isopropoxybenzene **2k** (67 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ak** (41 mg, 55%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].
IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max}= 2962, 1737, 1599, 1376, 1168, 989, 827, 734 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 – (m, 2H), 7.64 – 7.55 (m, 1H), 7.52 – 7.44 (m, 2H), 7.19 – 7.07 (m, 2H), 6.68 (d, *J* = 8.3 Hz, 1H), 3.91 – 3.86 (m, 1H), 3.38 (dd, *J* = 17.5, 8.0 Hz, 1H), 3.23 (dd, *J* = 17.5, 6.0 Hz, 1H), 1.54 (s, 3H), 1.35 (s, 3H), 1.24 (s, 9H) ppm.
^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 199.1, 155.8, 143.3, 137.1, 133.4, 130.4, 128.8(2C), 128.2(2C), 125.3, 121.9, 108.9, 88.8, 46.5, 41.0, 34.4, 31.8(3C), 28.9, 23.1 ppm.
HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{27}O_2^+$ 323.2006; found 323.2009.



2-(5-(tert-Butyl)-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(p-tolyl)ethan-1-one (3ok):
GP - 2 was carried out with 4-methylbenzaldehyde **1o** (37 mg, 0.31 mmol), 4-(*tert*-butyl)-2-ethynyl-1-isopropoxybenzene **2k** (67 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ok** (40 mg, 52%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].
IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2960, 1740, 1679, 1488, 1256, 1096, 987, 812 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 – 7.82 (m, 2H), 7.31 – 7.23 (m, 2H), 7.18 – 7.11 (m, 1H), 7.09 (d, *J* = 1.7 Hz, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 3.92 – 3.83 (m, 1H), 3.34 (dd, *J* = 17.4, 8.1 Hz, 1H), 3.19 (dd, *J* = 17.4, 6.0 Hz, 1H), 2.41 (s, 3H), 1.53 (s, 3H), 1.33 (s, 3H), 1.23 (s, 9H) ppm.
^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.7, 155.8, 144.3, 143.3, 134.6, 130.5, 129.5, 128.4, 125.3, 121.9, 108.9, 88.9, 77.2, 46.6, 40.9, 34.4, 31.8, 28.9, 23.1, 21.8 ppm.
HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{27}O_2^+$ 337.2162; found 337.2157.



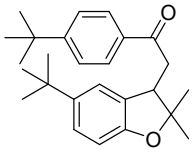
2-(5-(tert-Butyl)-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(4-isopropylphenyl)ethan-1-one (3ek):
GP - 2 was carried out with 4-isopropylbenzaldehyde **1e** (45 mg, 0.31 mmol), 4-(*tert*-butyl)-2-ethynyl-1-isopropoxybenzene **2k** (67 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3ek** (43 mg, 51%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2967, 1679, 1488, 1299, 1097, 865, 730 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 – 7.87 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.18 – 7.12 (m, 1H), 7.08 (d, *J* = 1.5 Hz, 1H), 6.68 (d, *J* = 8.3 Hz, 1H), 3.90 – 3.83 (m, 1H), 3.34 (dd, *J* = 17.3, 8.1 Hz, 1H), 3.20 (dd, *J* = 17.3, 6.1 Hz, 1H), 2.97 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.54 (s, 3H), 1.34 (s, 3H), 1.27 (d, *J* = 6.9 Hz, 6H), 1.23 (s, 9H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.7, 155.8, 155.0, 143.2, 134.9, 130.5, 128.5(2C), 126.9(2C), 125.3, 121.9, 108.9, 88.9, 77.2, 46.7, 40.9, 34.4, 34.4, 31.8(3C), 28.9, 23.8, 23.8, 23.1 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{25}H_{33}O_2^+$ 365.2475; found 365.2474.



2-(5-(tert-Butyl)-2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)-1-(4-(tert-butyl)phenyl)ethan-1-one (3nk):
GP - 2 was carried out with 4-tertiarybutylbenzaldehyde **1n** (50 mg, 0.31 mmol), 4-(*tert*-butyl)-2-ethynyl-1-isopropoxybenzene **2k** (67 mg, 0.31 mmol), TBADT (4 mol%), and CH_3CN (2.5 mL) and the resultant reaction mixture was irradiated for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the product **3nk** (42 mg, 48%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 90:10) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2961, 1681, 1488, 1369, 1264, 986, 906, 727cm^{-1}.

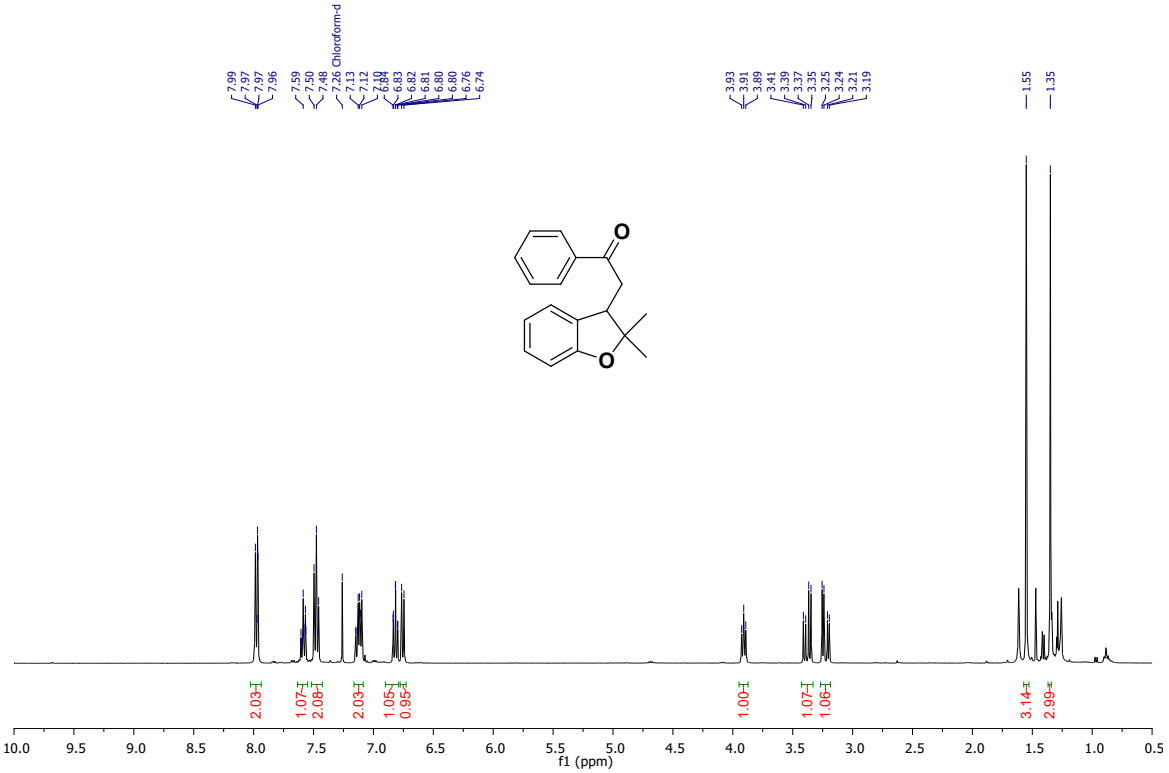
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 – 7.87 (m, 2H), 7.50 – 7.45 (m, 2H), 7.16 – 7.11 (m, 1H), 7.07 (d, *J* = 1.5 Hz, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 3.89 – 3.82 (m, 1H), 3.34 (dd, *J* = 17.3, 8.0 Hz, 1H), 3.20 (dd, *J* = 17.3, 6.1 Hz, 1H), 1.53 (s, 3H), 1.34 (s, 9H), 1.32 (s, 3H), 1.22 (s, 9H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 198.8, 157.2, 155.8, 143.3, 134.5, 130.5, 128.2(2C), 125.8(2C), 125.3, 121.9, 108.9, 88.9, 46.7, 40.9, 35.3, 34.4, 31.8(3C), 31.2(3C), 28.96, 23.1 ppm.

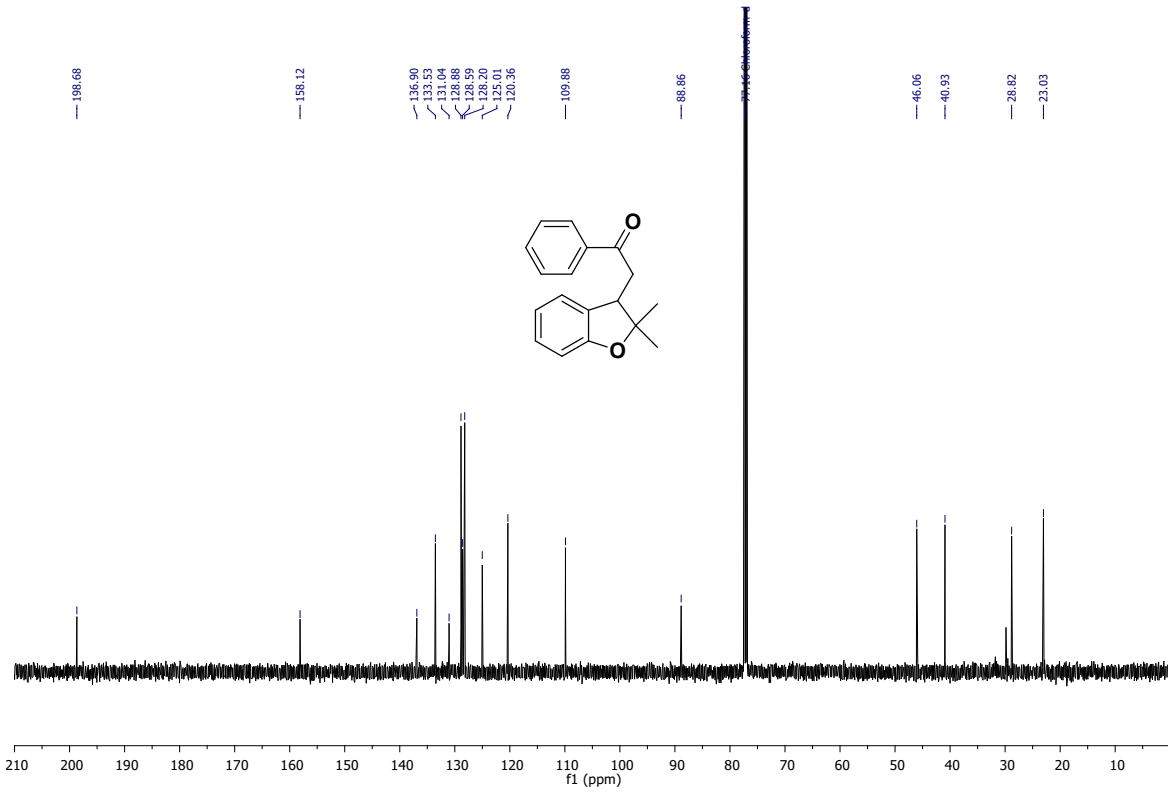
HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{26}H_{35}O_2^+$ 379.2632; found 379.2618.

NMR spectra for the products

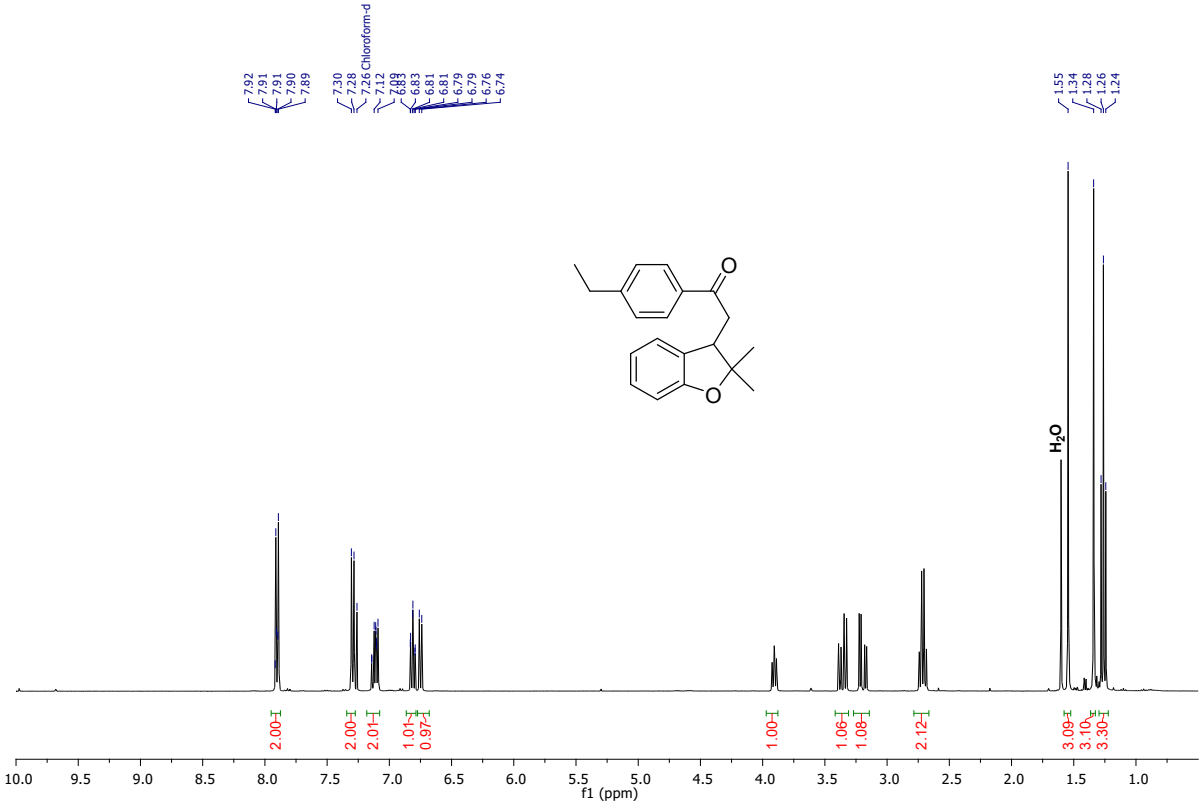
^{1}H NMR (400 MHz) spectrum of **3aa** in $CDCl_3$



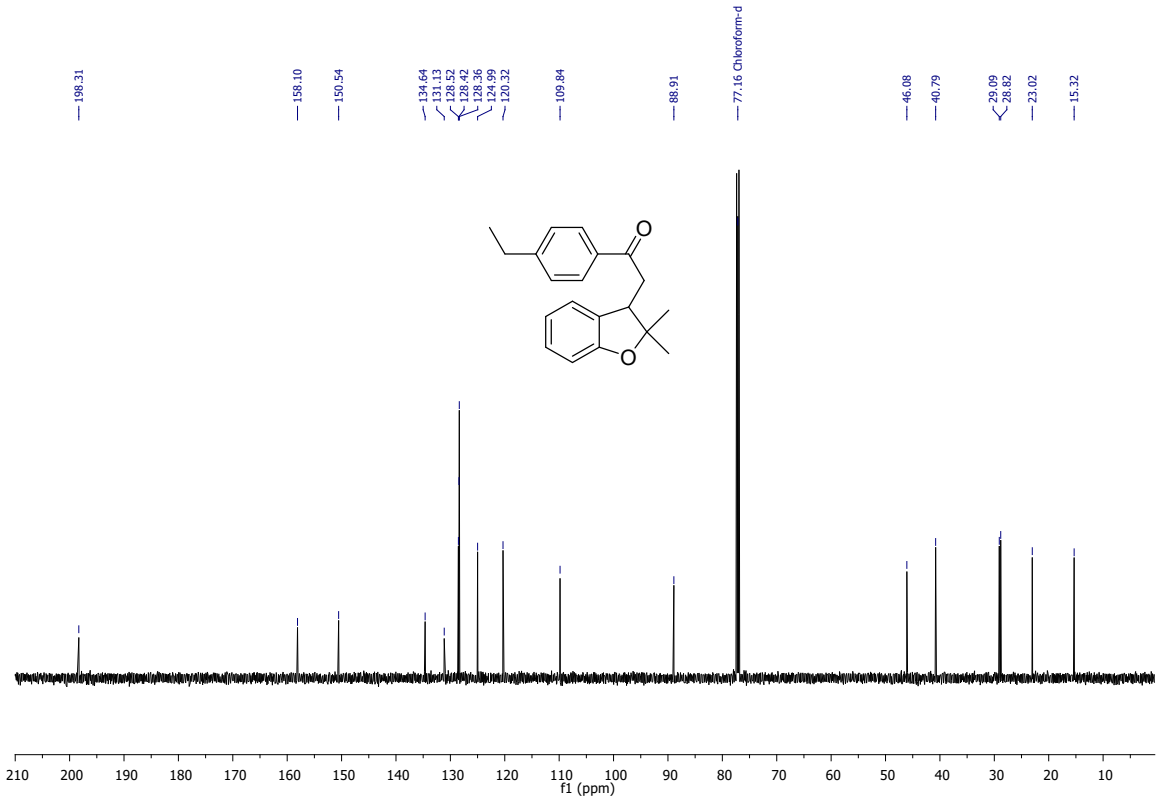
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3aa** in $CDCl_3$



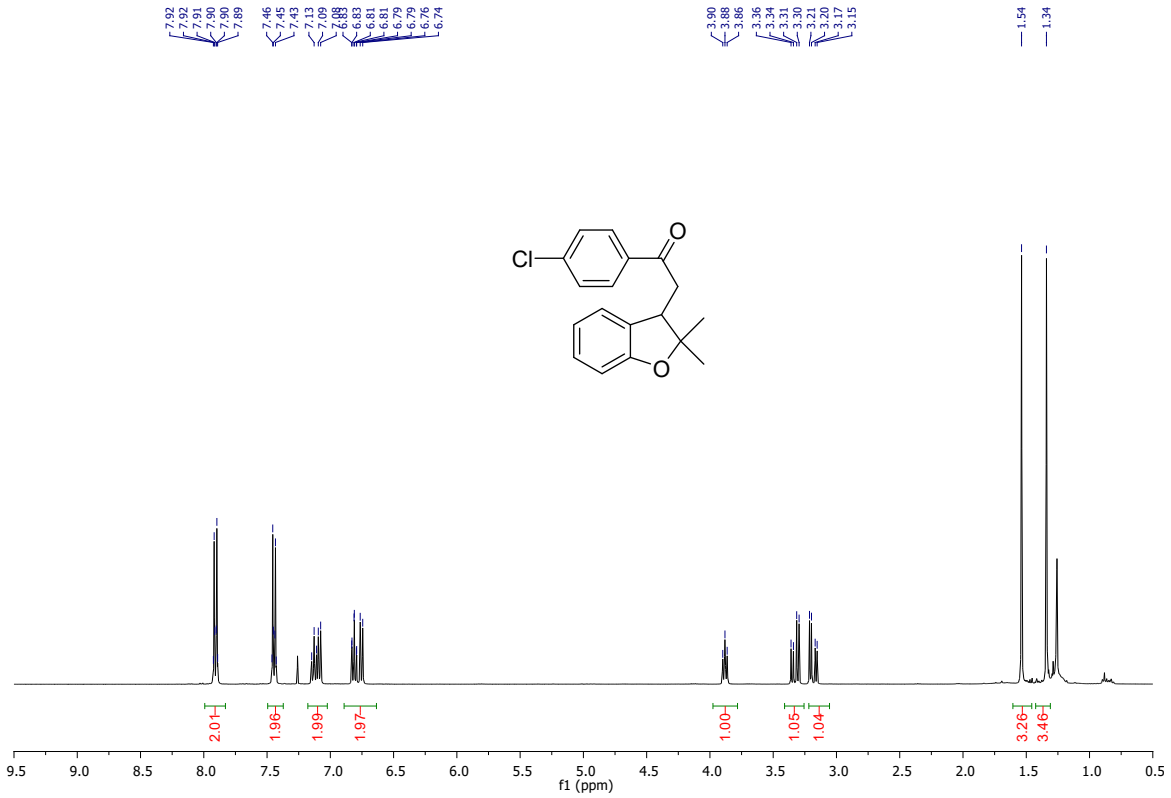
^{1}H NMR (400 MHz) spectrum of **3ba** in $CDCl_3$



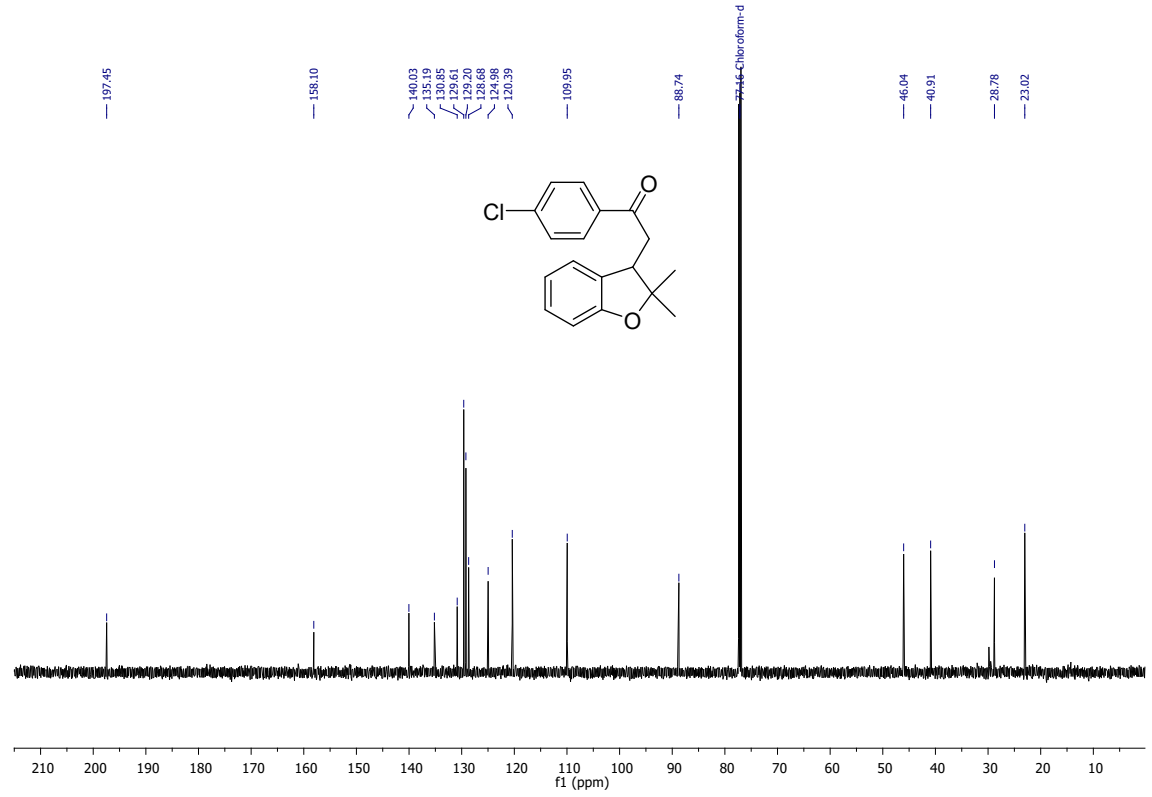
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ba** in $CDCl_3$



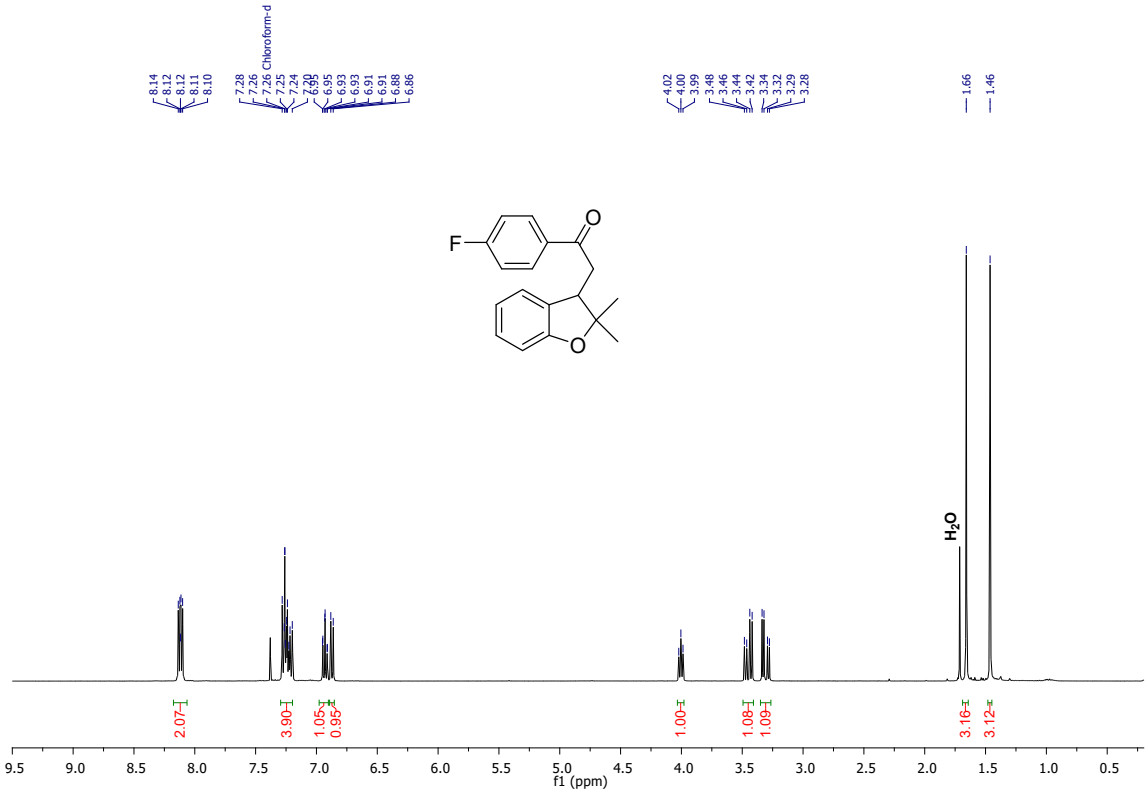
^{1}H NMR (400 MHz) spectrum of **3ca** in $CDCl_3$



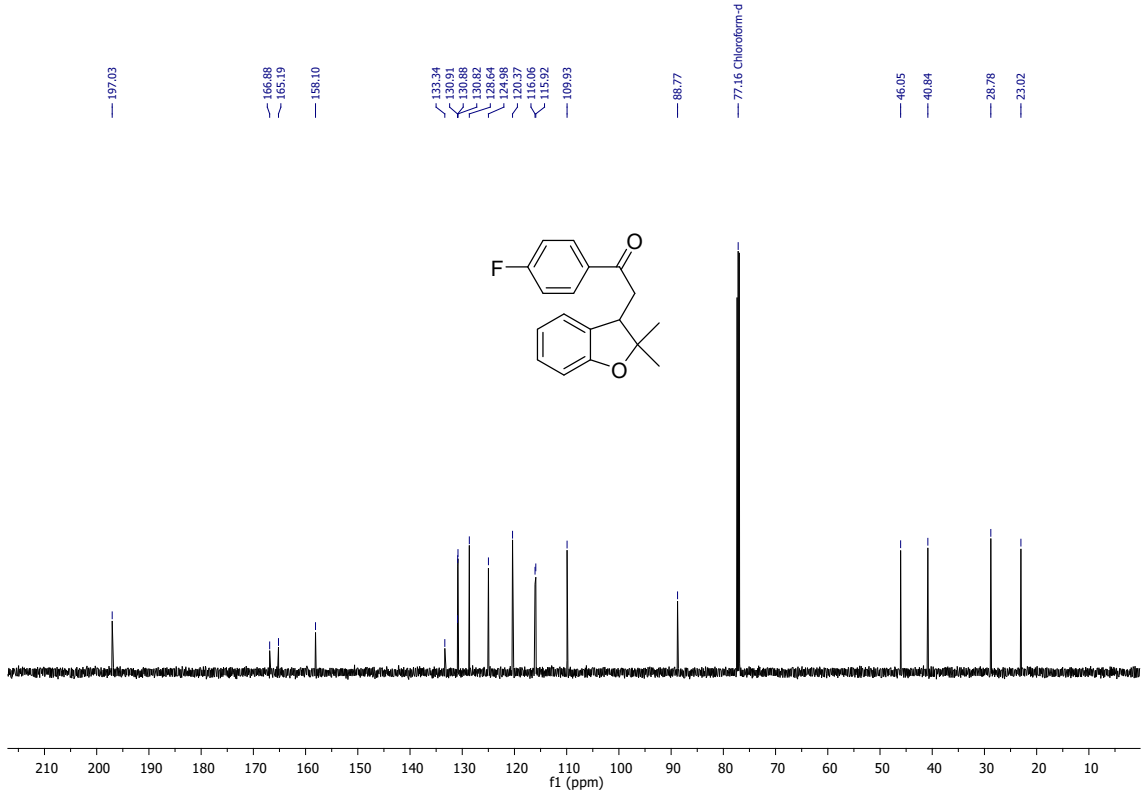
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ca** in $CDCl_3$



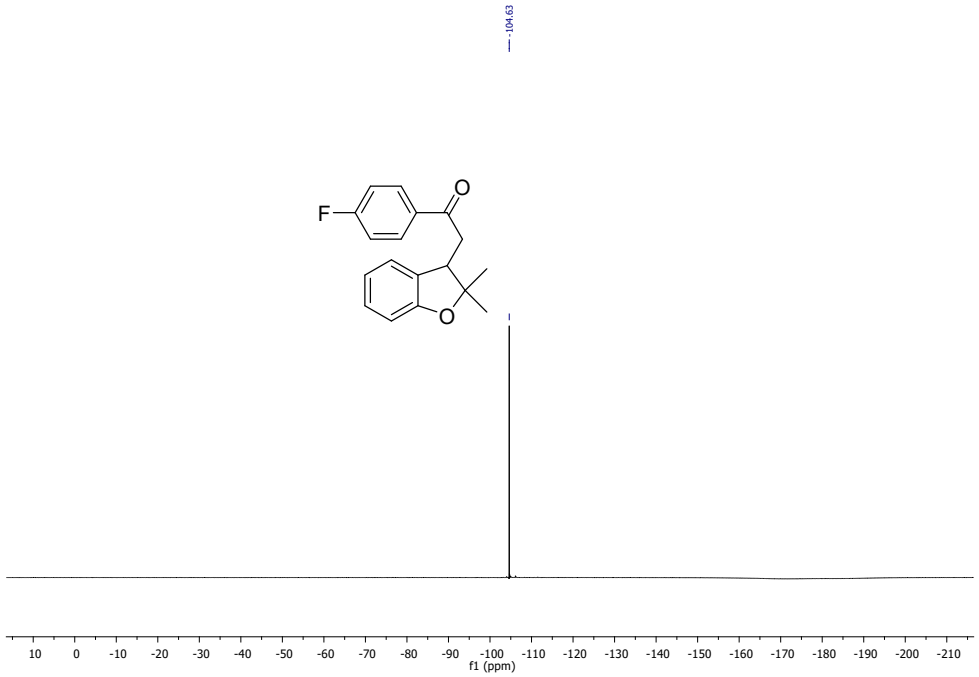
^{1}H NMR (400 MHz) spectrum of **3da** in $CDCl_3$



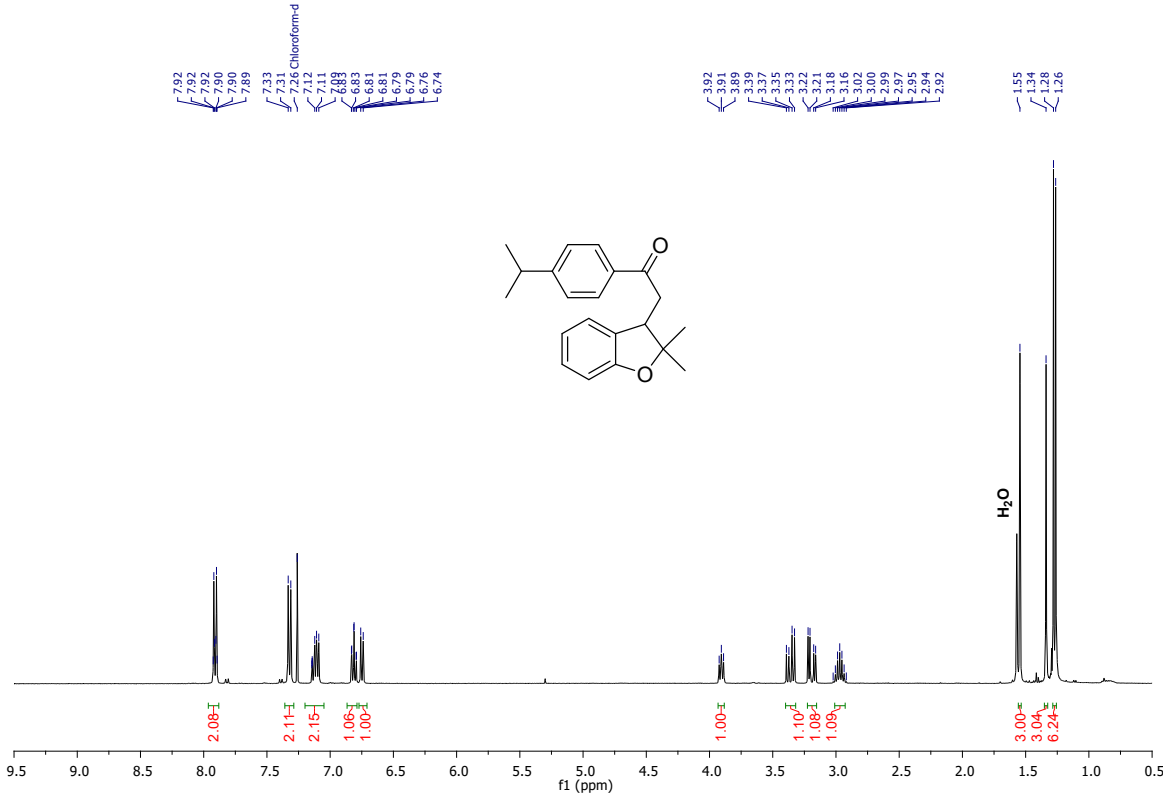
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3da** in $CDCl_3$



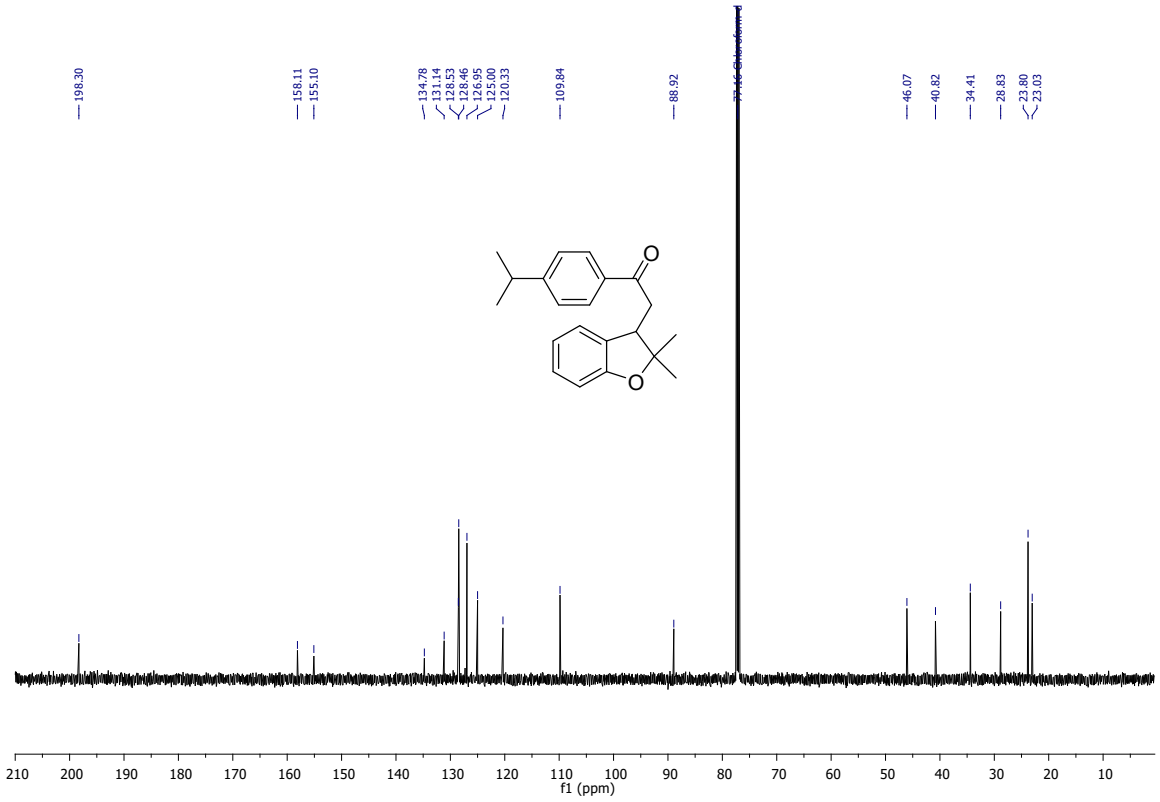
^{19}F-NMR (565 MHz) spectrum of **3da** in $CDCl_3$



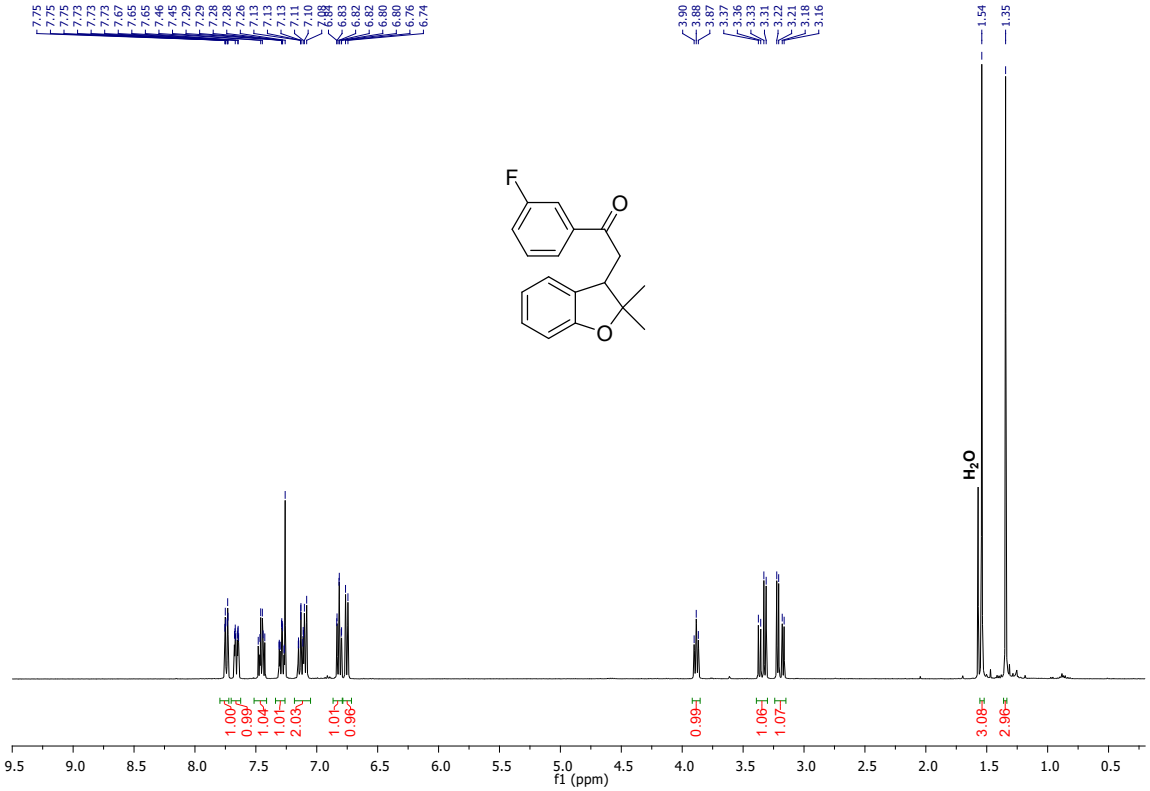
^{1}H NMR (400 MHz) spectrum of **3ea** in $CDCl_3$



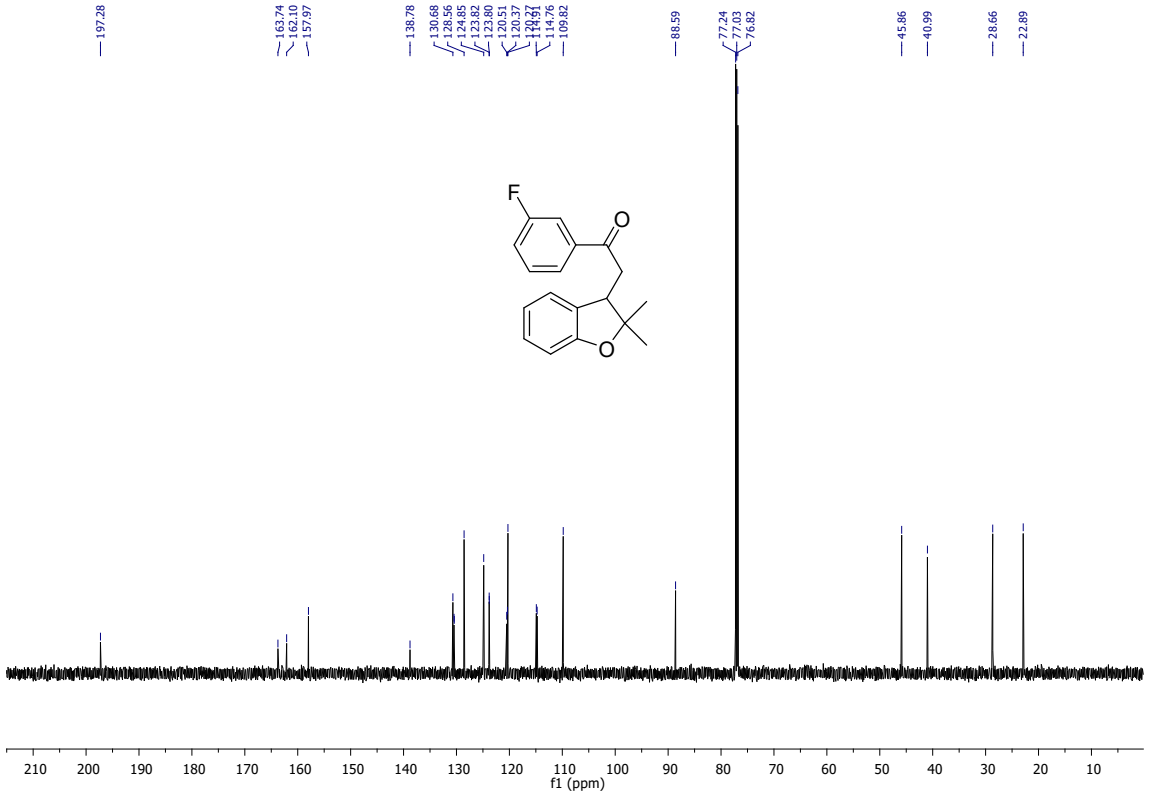
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ea** in $CDCl_3$



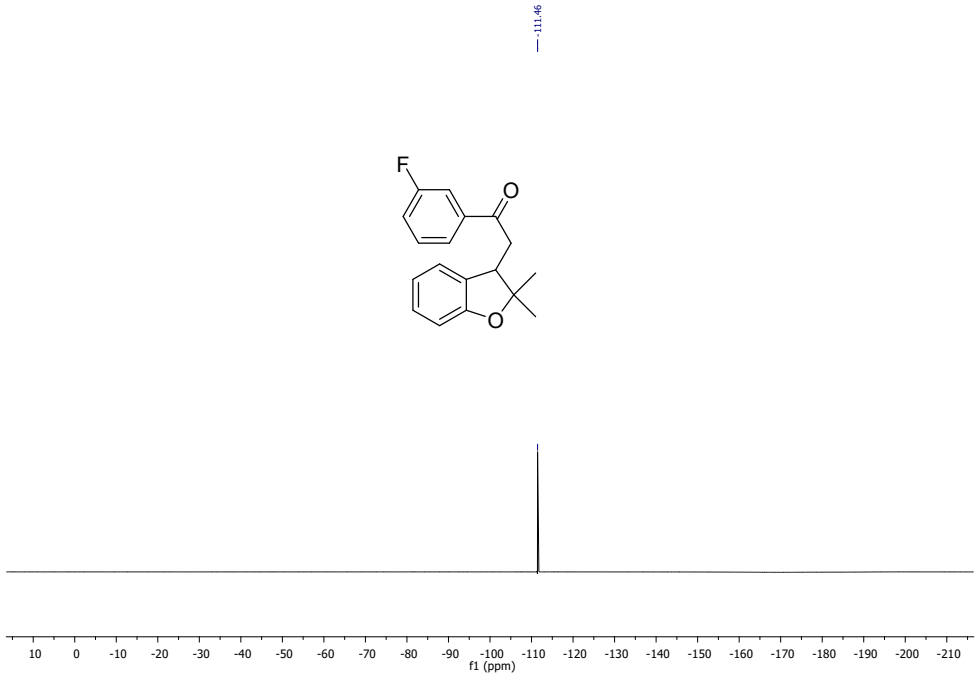
^{1}H NMR (400 MHz) spectrum of **3fa** in $CDCl_3$



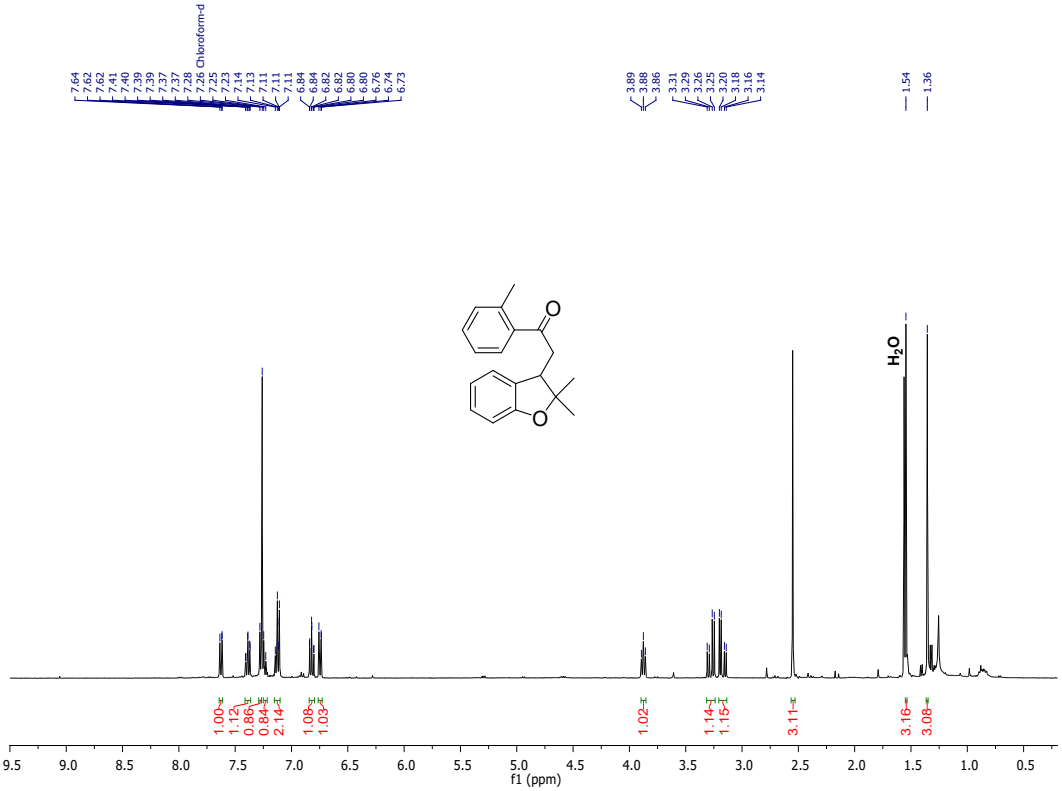
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3fa** in $CDCl_3$



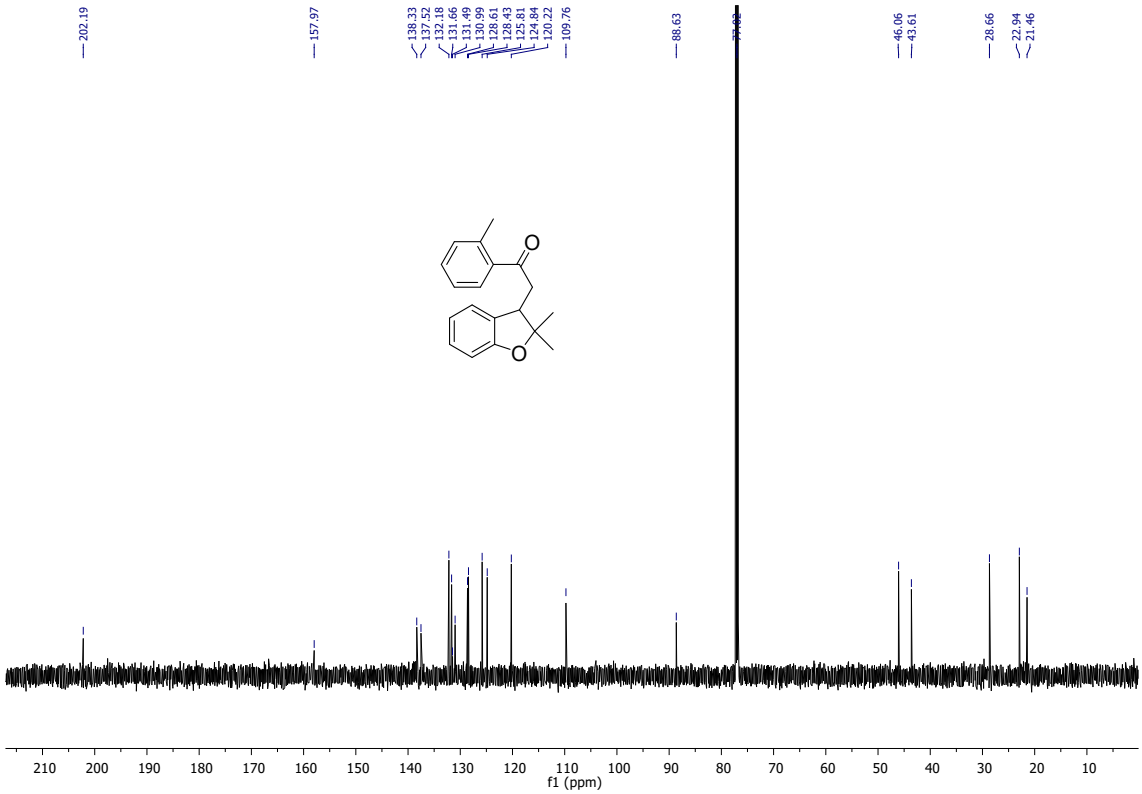
^{19}F-NMR (565 MHz) spectrum of **3fa** in $CDCl_3$



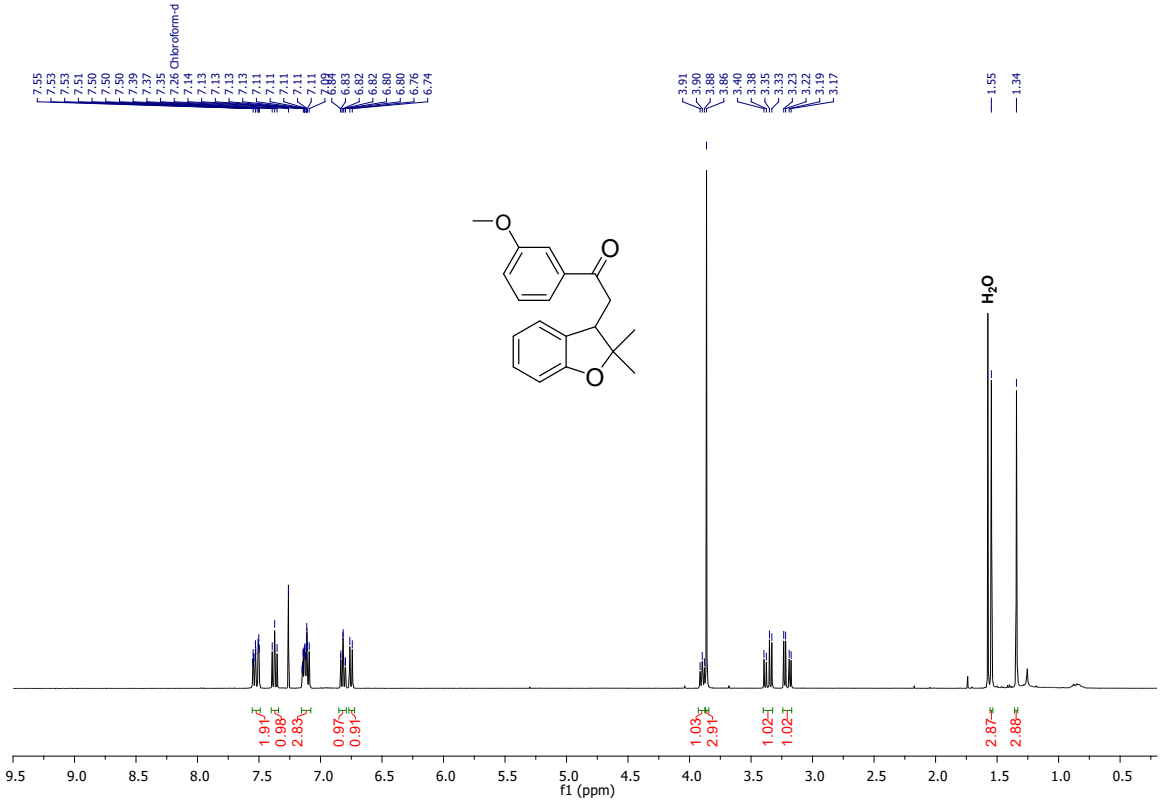
^{1}H NMR (400 MHz) spectrum of **3ga** in $CDCl_3$



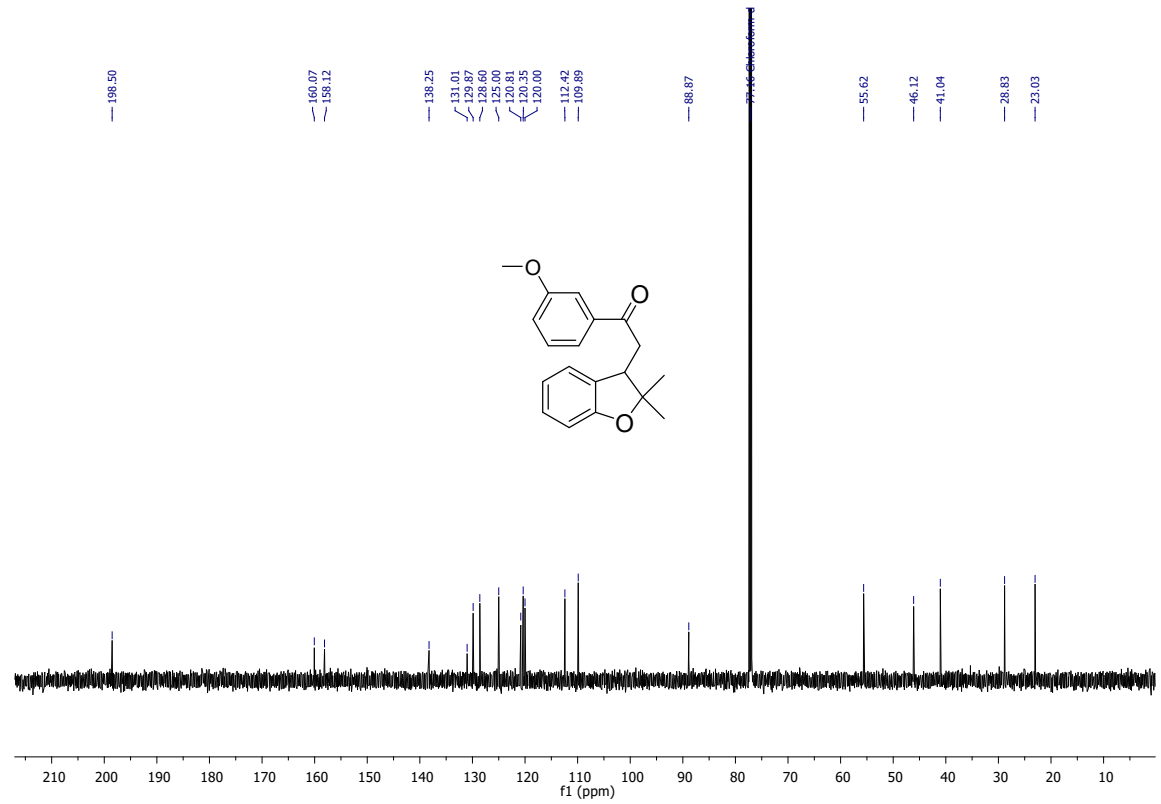
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ga** in $CDCl_3$



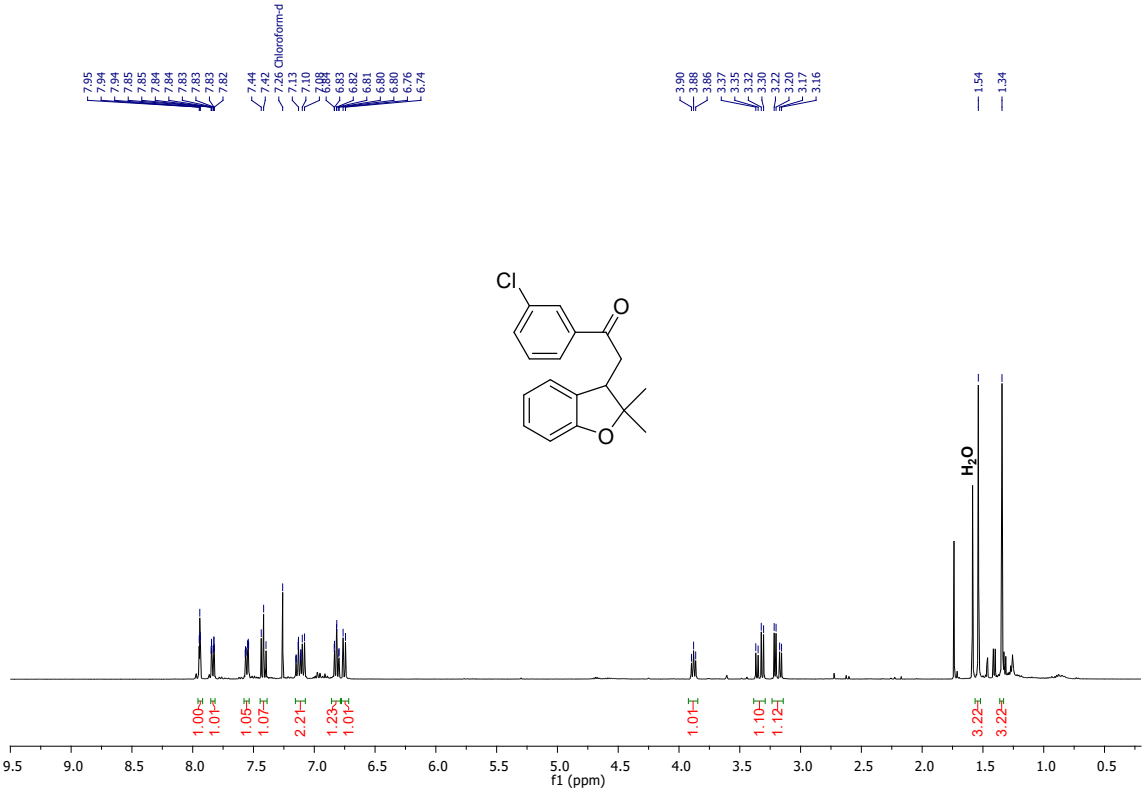
^{1}H NMR (400 MHz) spectrum of **3ha** in $CDCl_3$



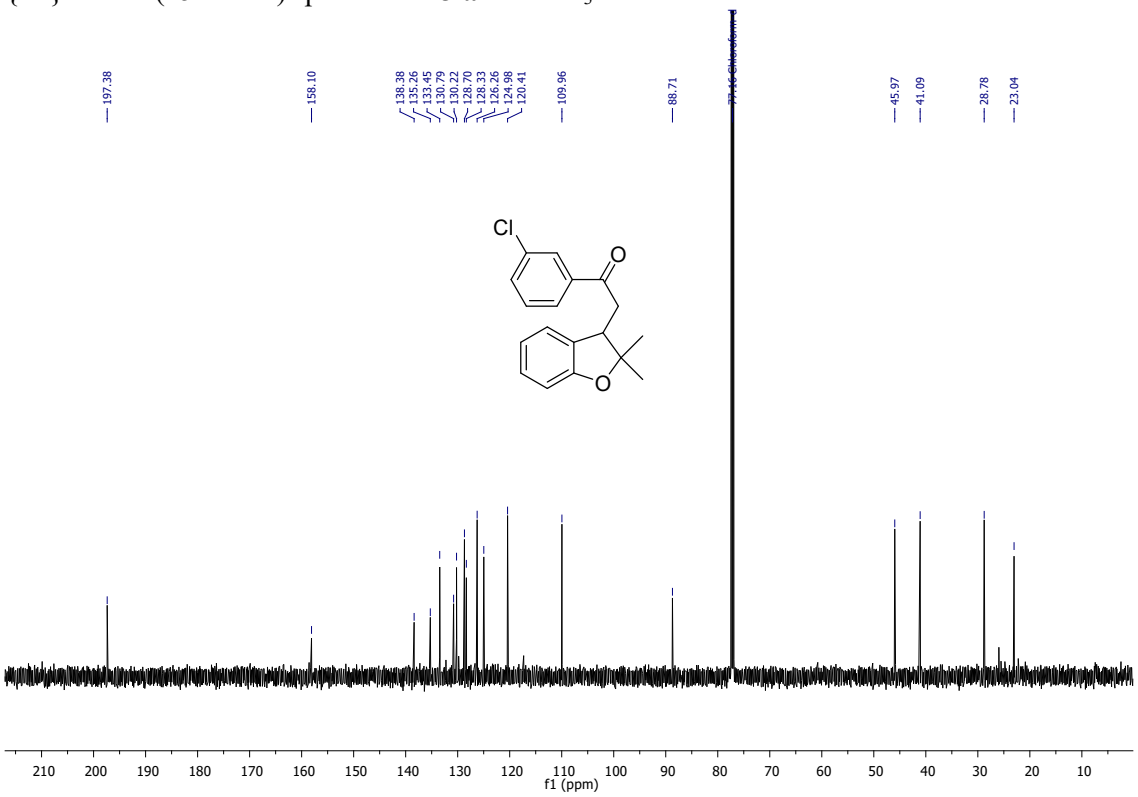
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ha** in $CDCl_3$



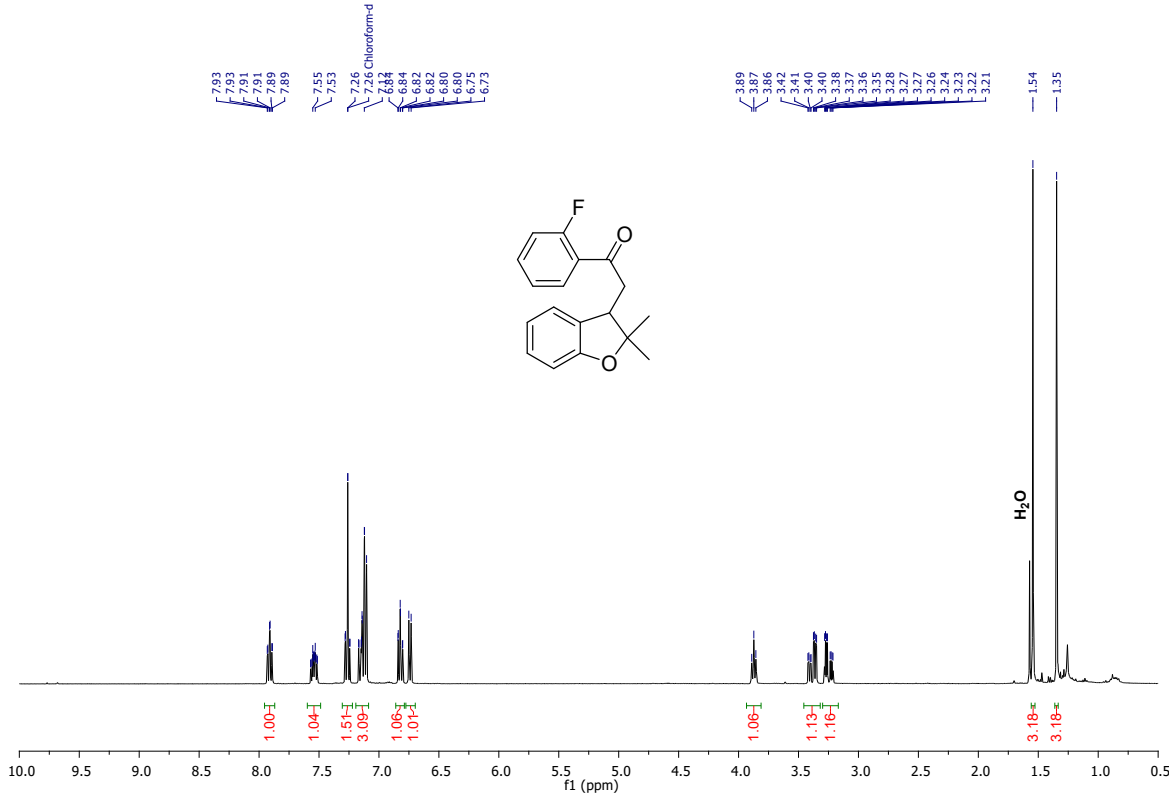
^{1}H NMR (400 MHz) spectrum of **3ia** in $CDCl_3$



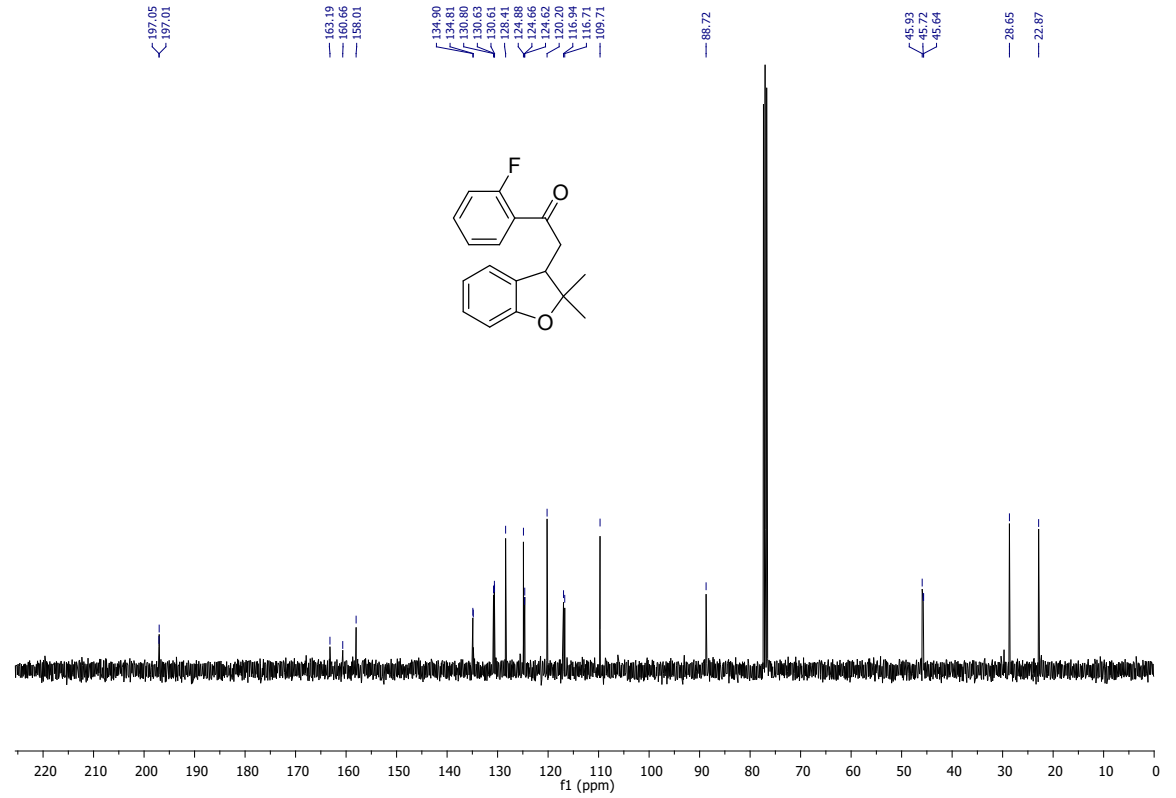
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ia** in $CDCl_3$



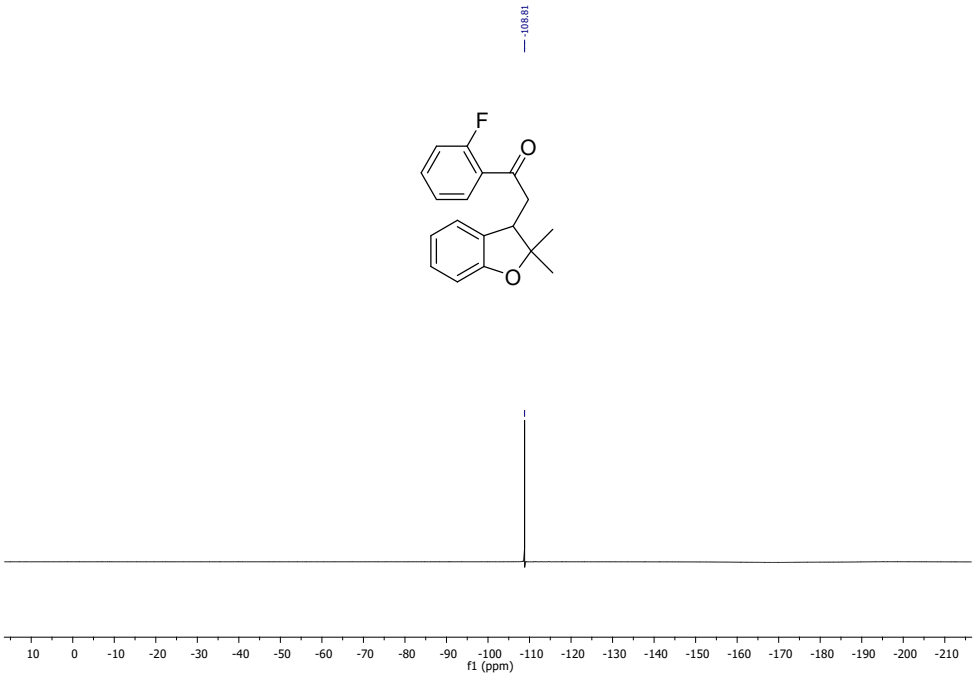
^{1}H NMR (400 MHz) spectrum of **3ja** in $CDCl_3$



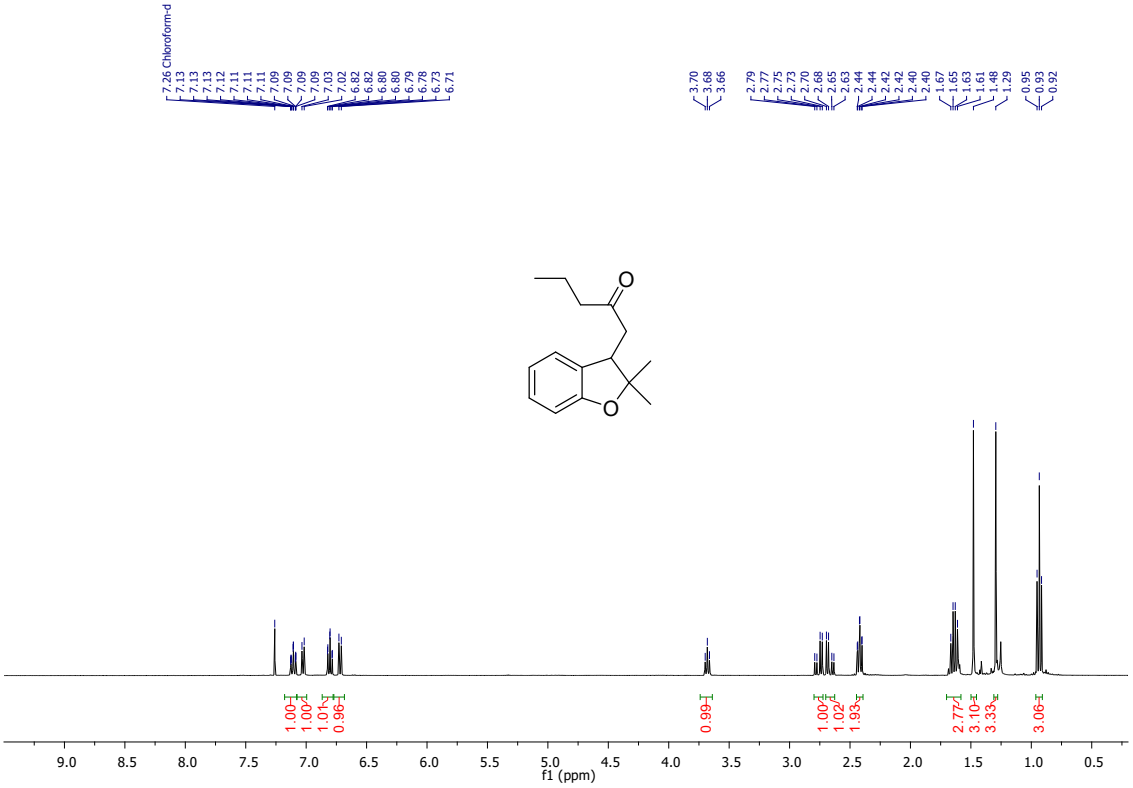
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ja** in $CDCl_3$



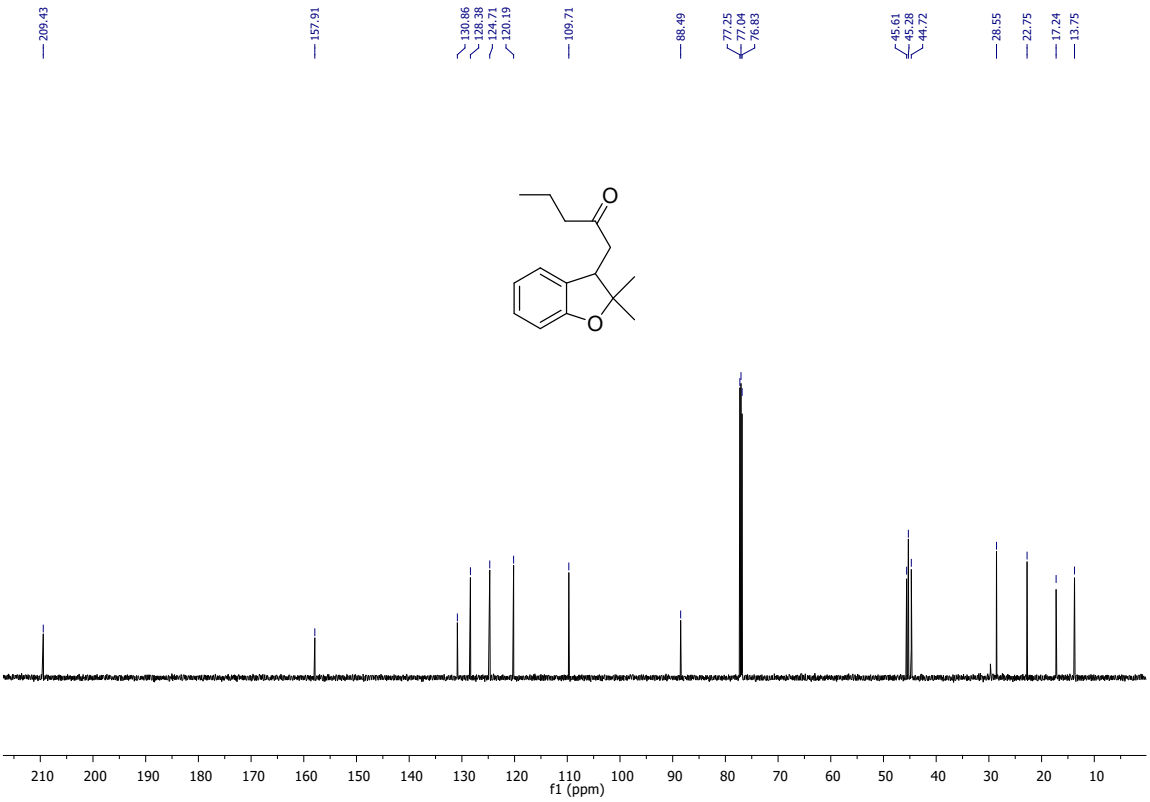
^{19}F-NMR (565 MHz) spectrum of **3ja** in $CDCl_3$



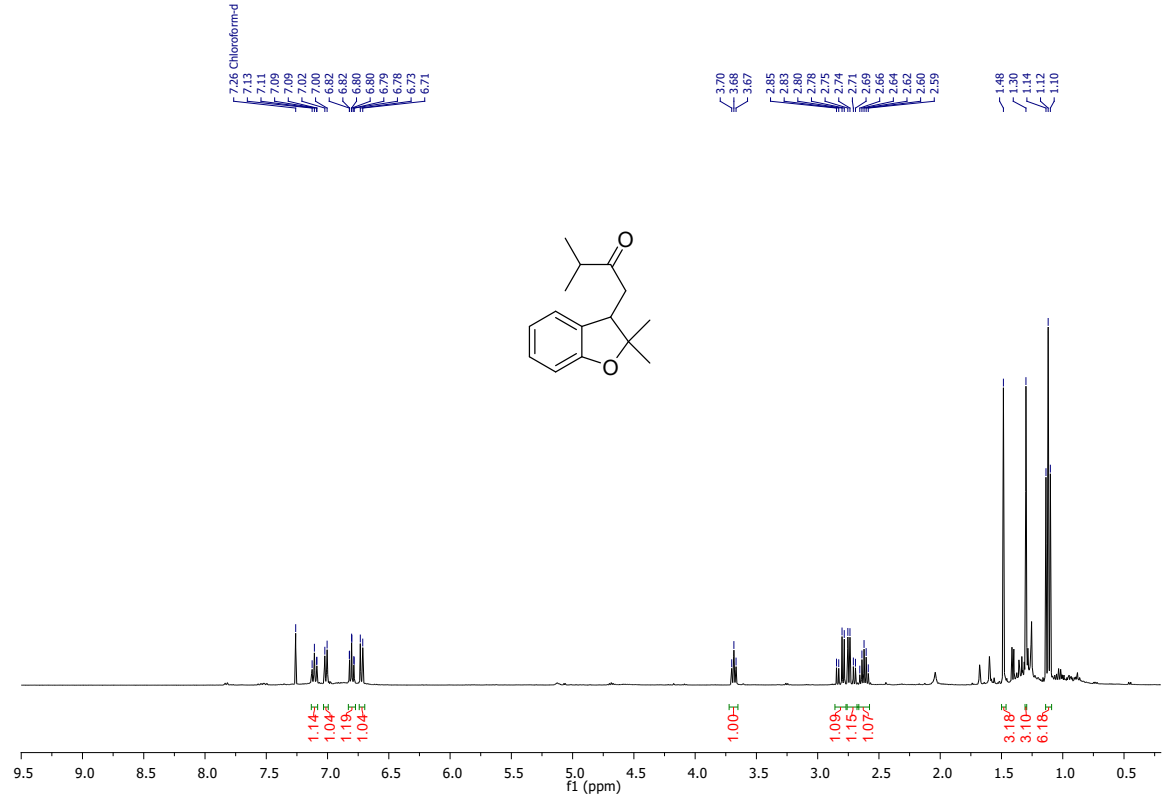
^{1}H NMR (400 MHz) spectrum of **3ka** in $CDCl_3$



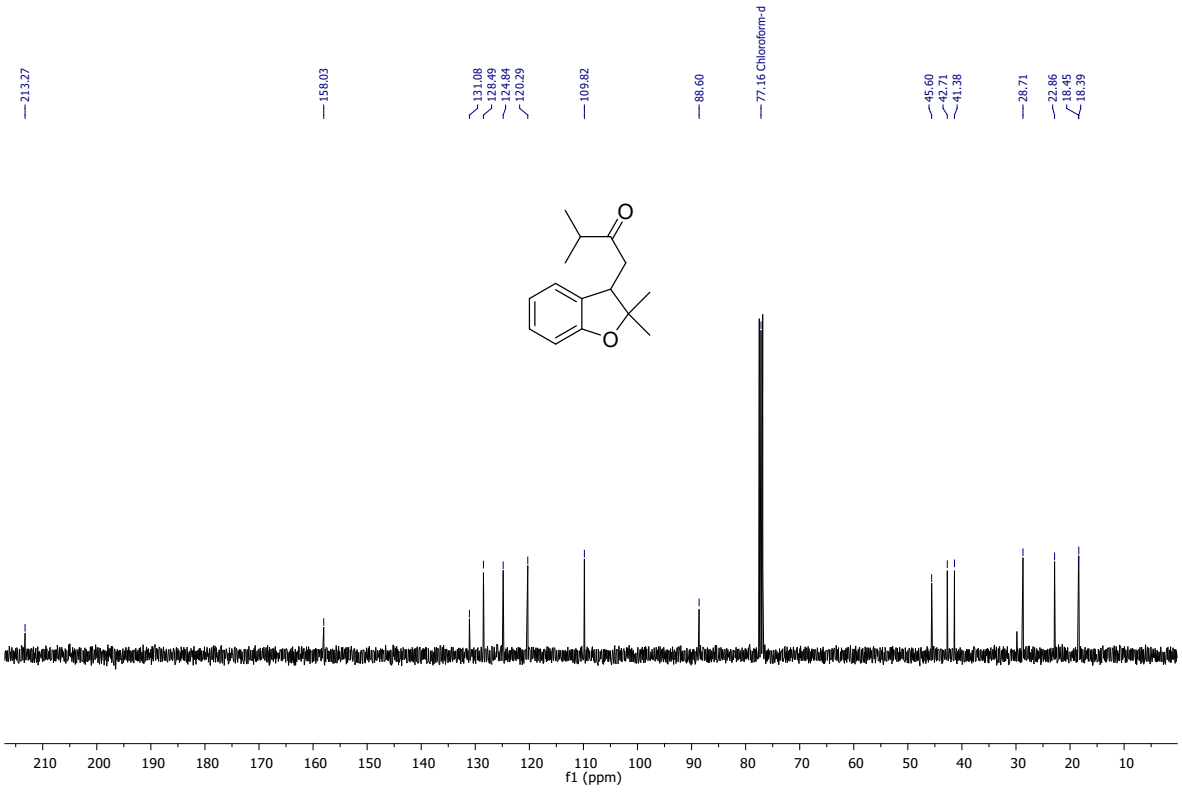
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ka** in $CDCl_3$



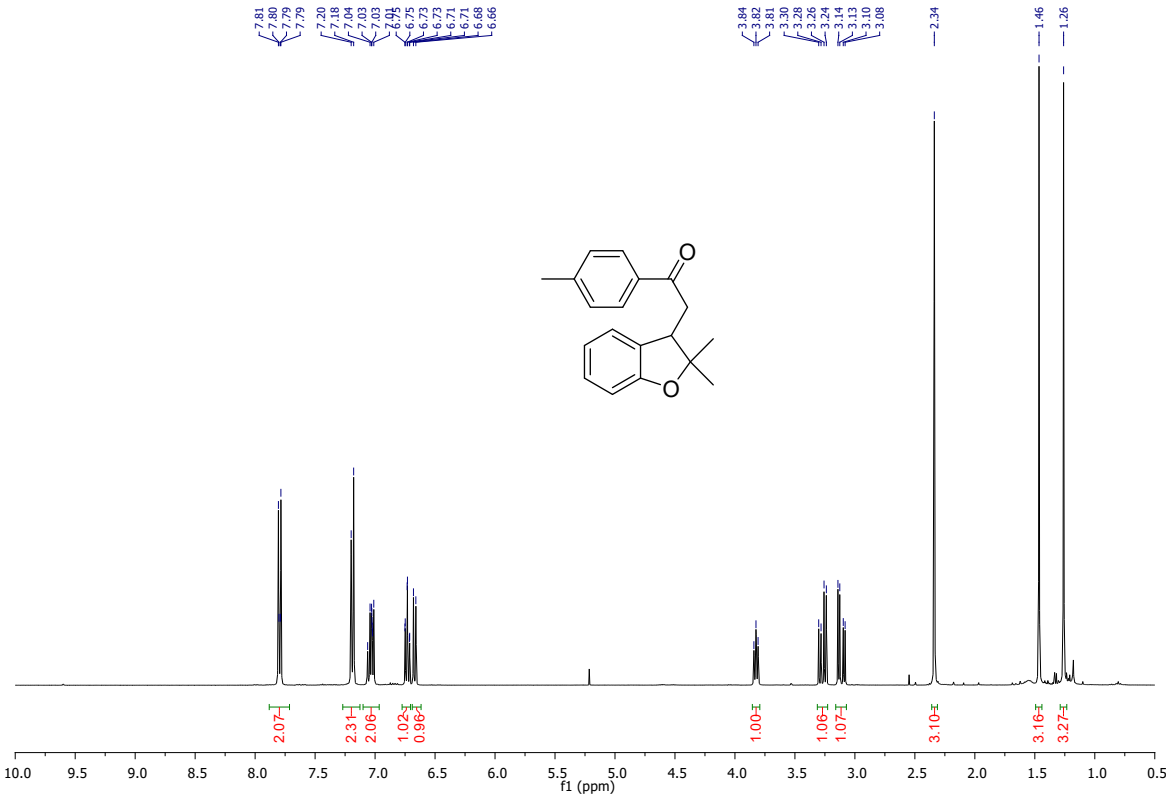
^{1}H NMR (400 MHz) spectrum of **3lj** in $CDCl_3$



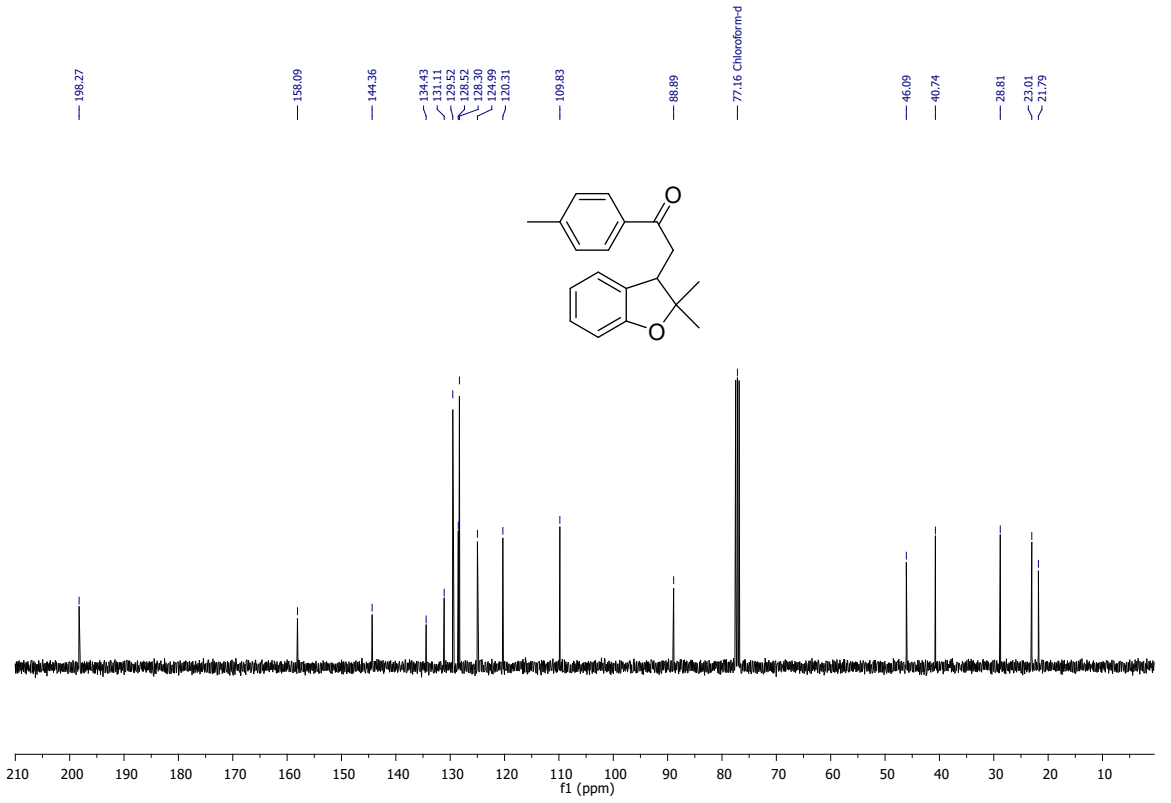
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3lj** in $CDCl_3$



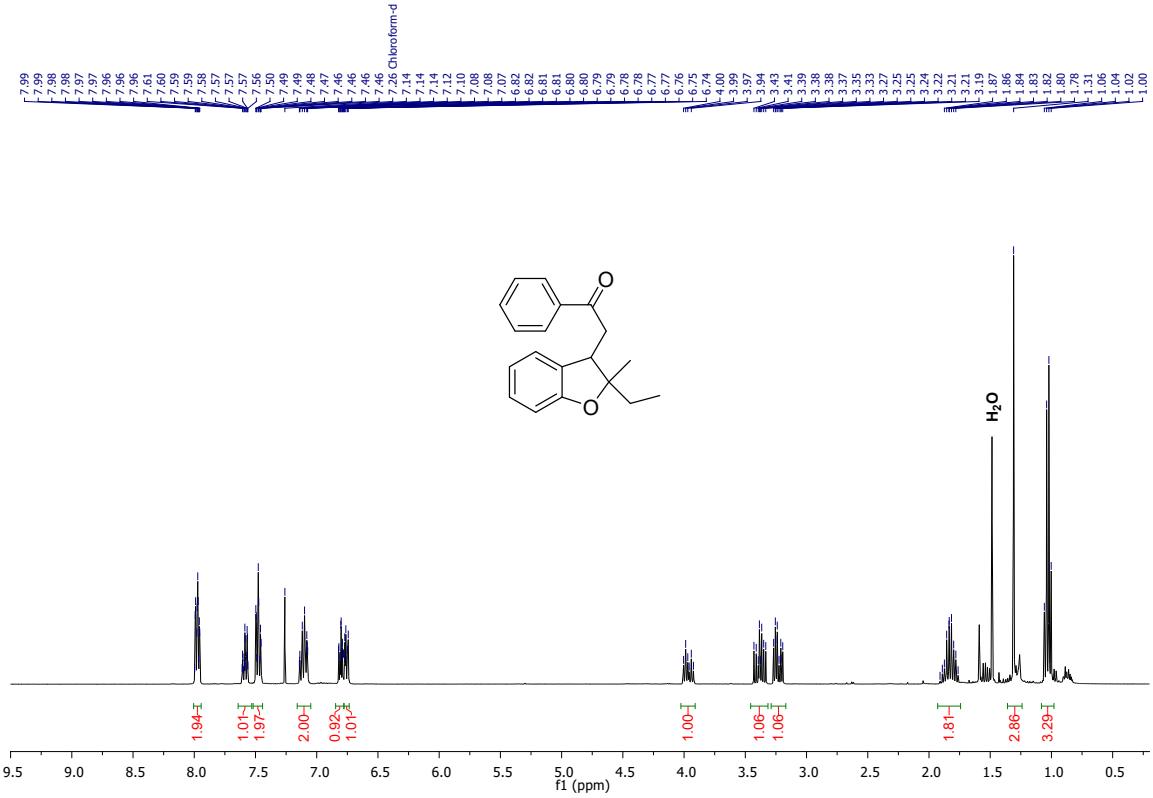
^{1}H NMR (400 MHz) spectrum of **3oa** in $CDCl_3$



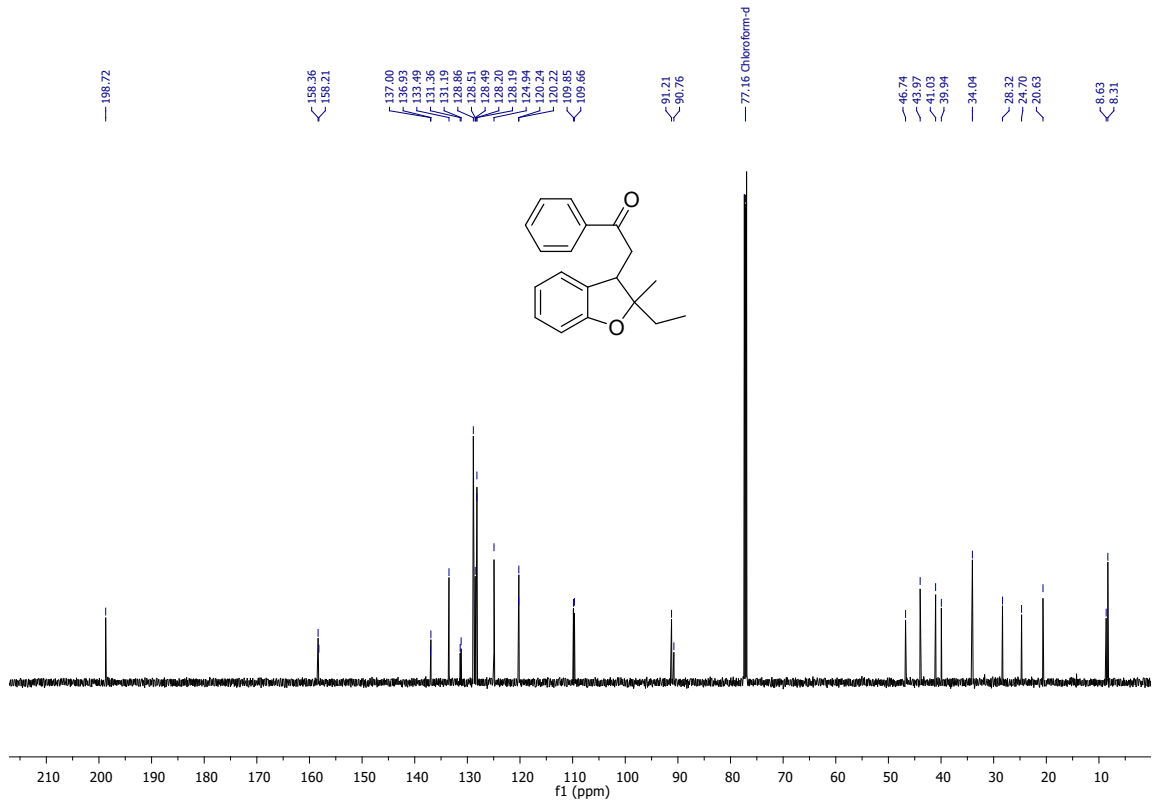
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3oa** in $CDCl_3$



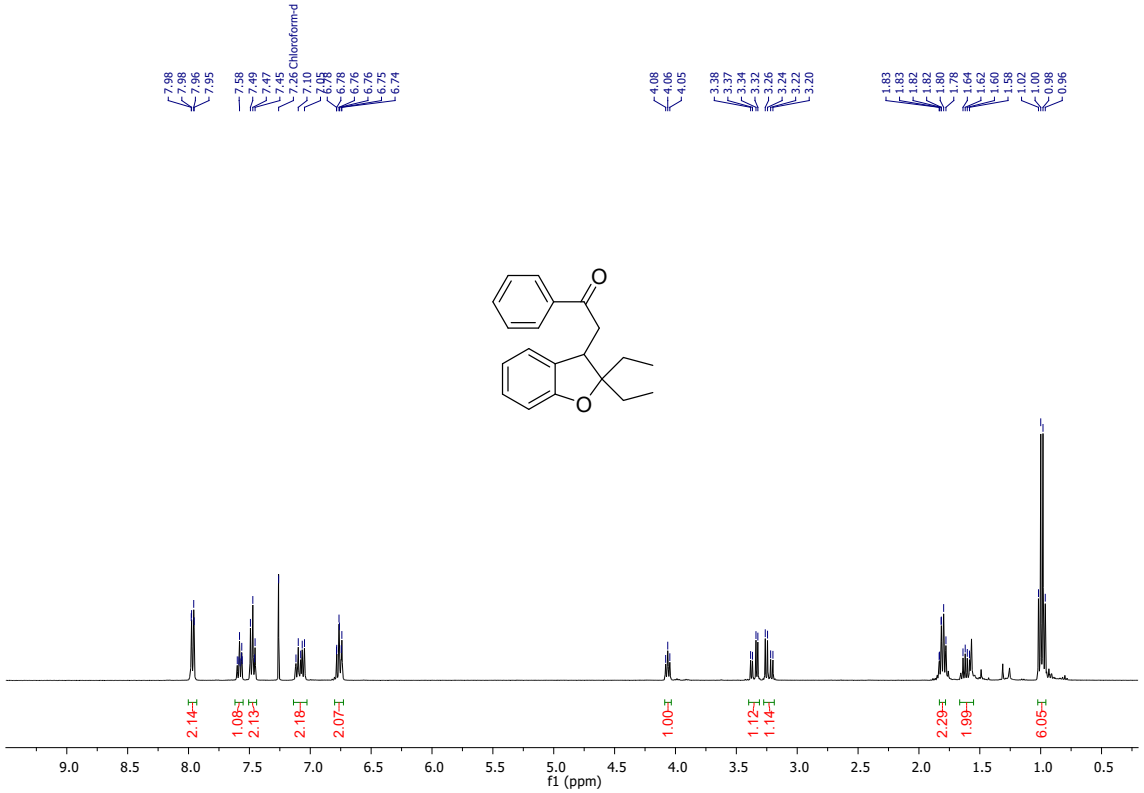
^{1}H NMR (400 MHz) spectrum of **3ab** in $CDCl_3$



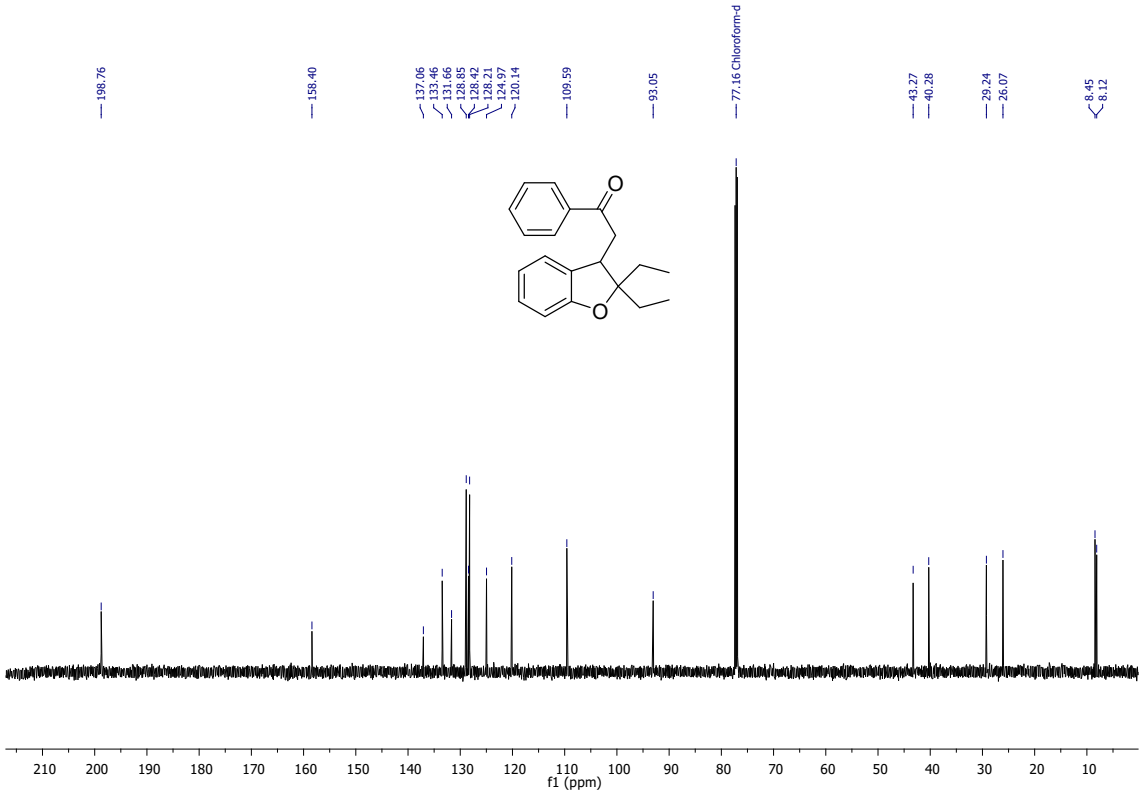
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ab** in $CDCl_3$



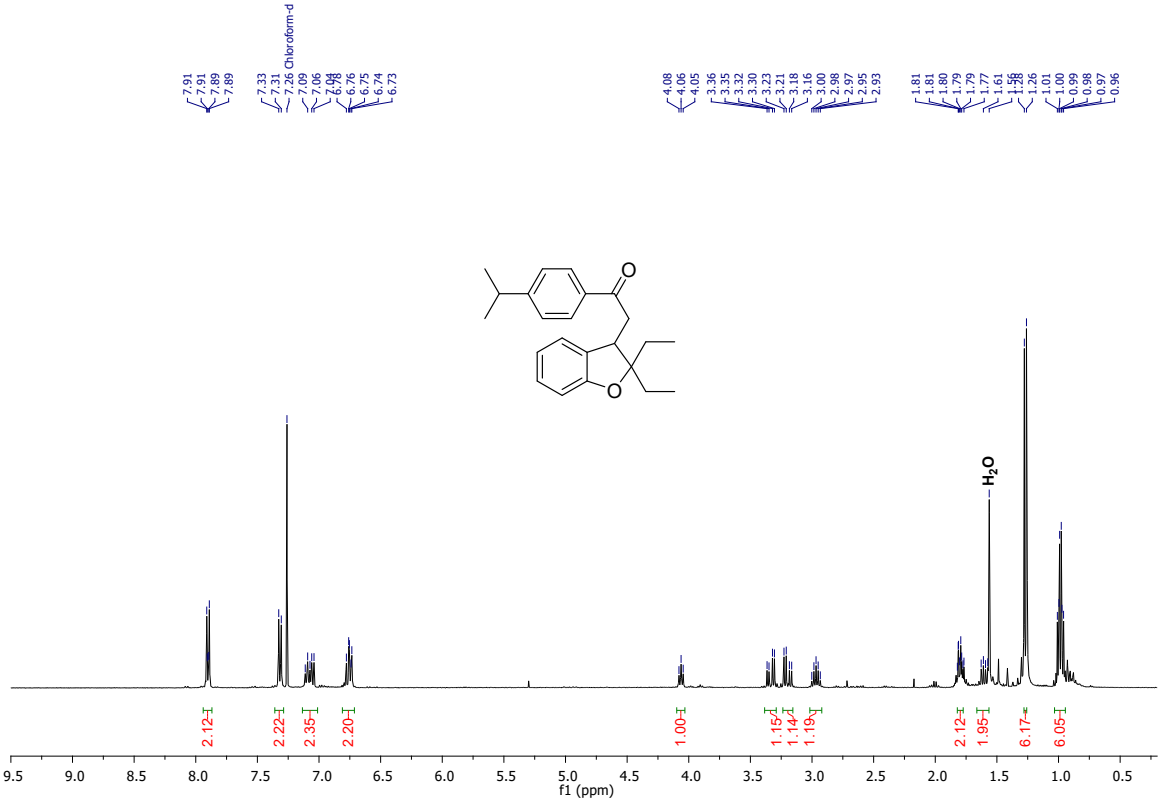
^{1}H NMR (400 MHz) spectrum of **3ac** in $CDCl_3$



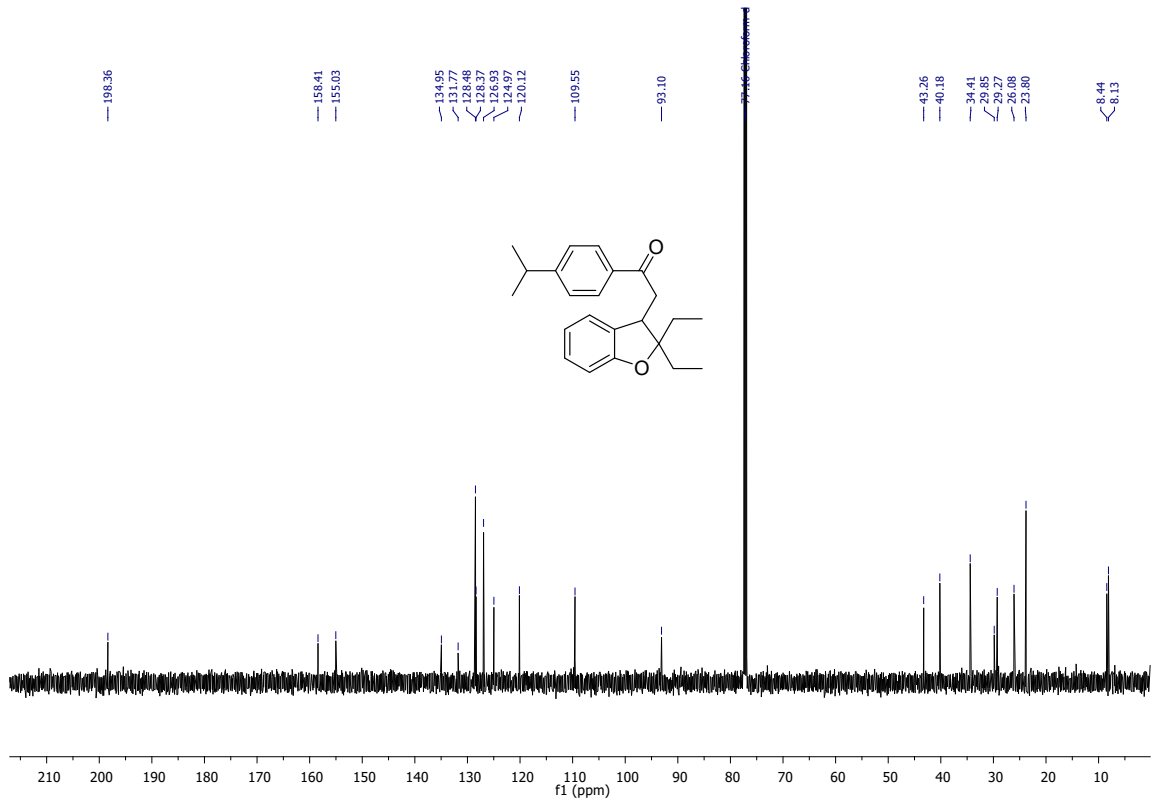
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ac** in $CDCl_3$



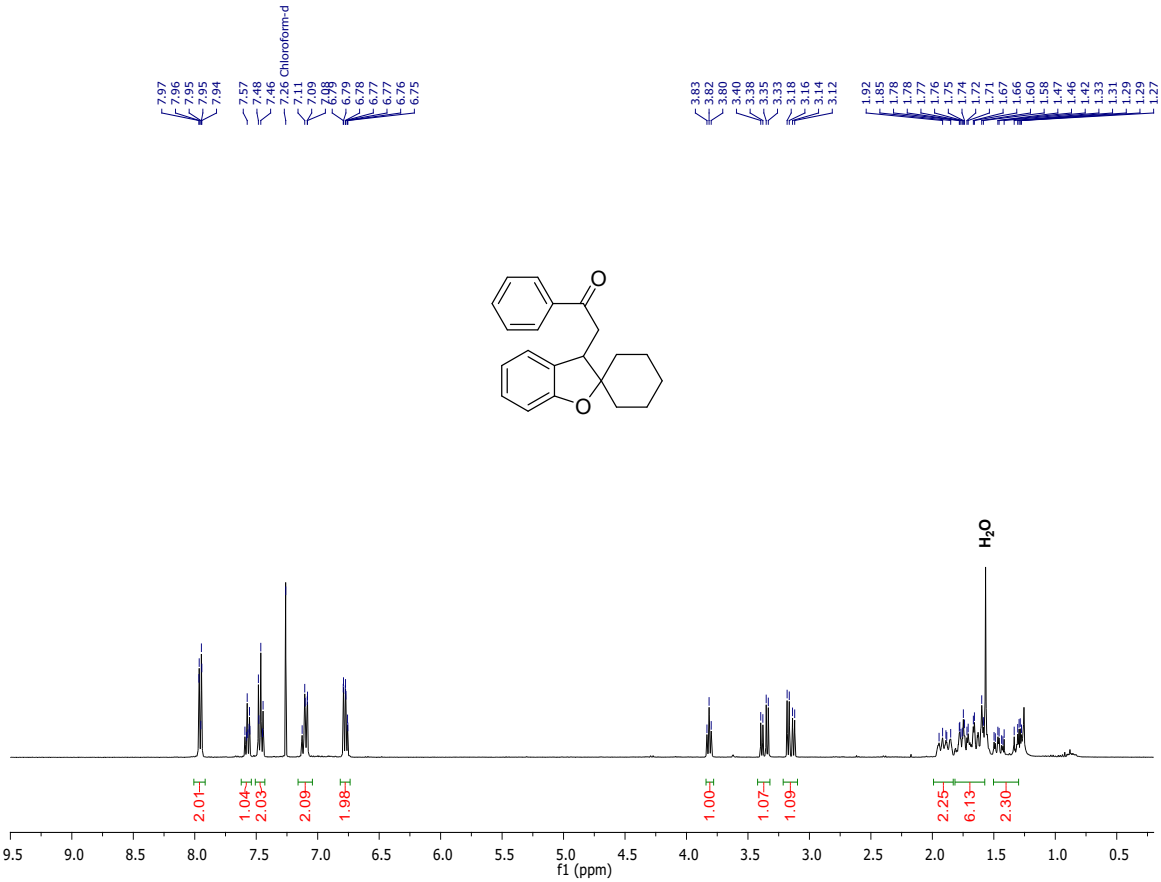
^{1}H NMR (400 MHz) spectrum of **3ec** in $CDCl_3$



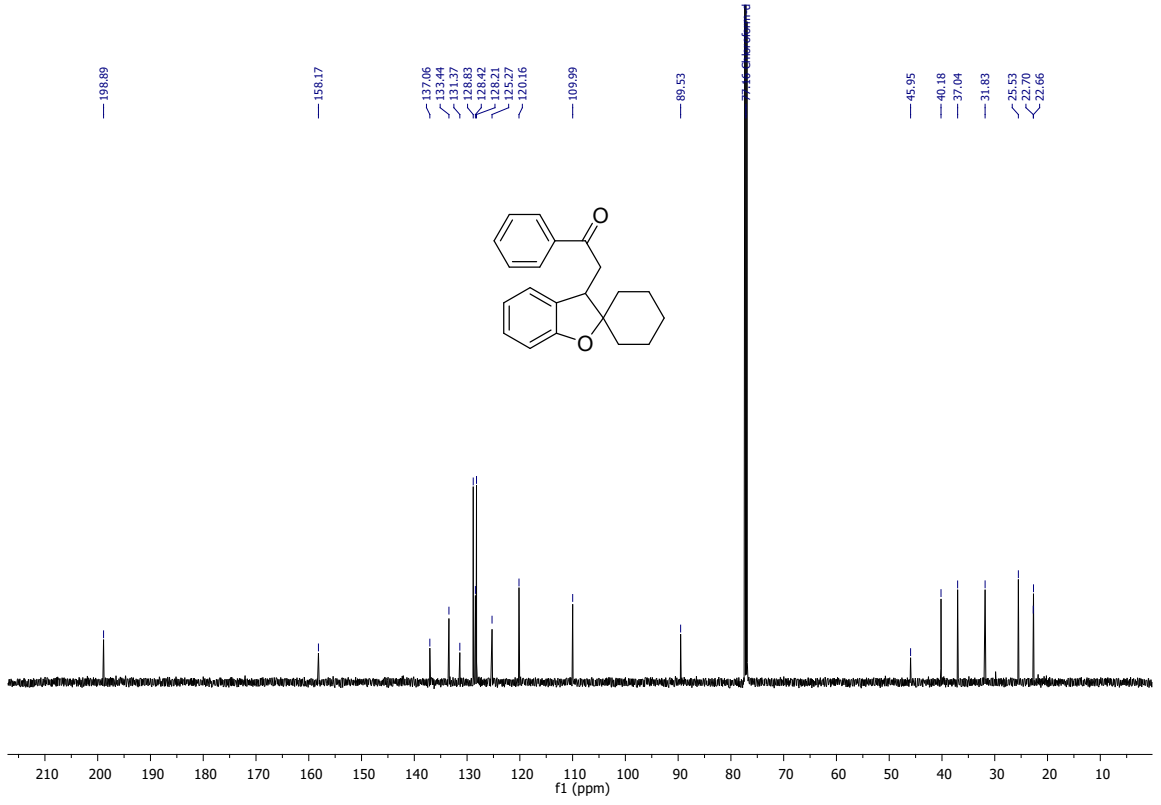
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ec** in $CDCl_3$



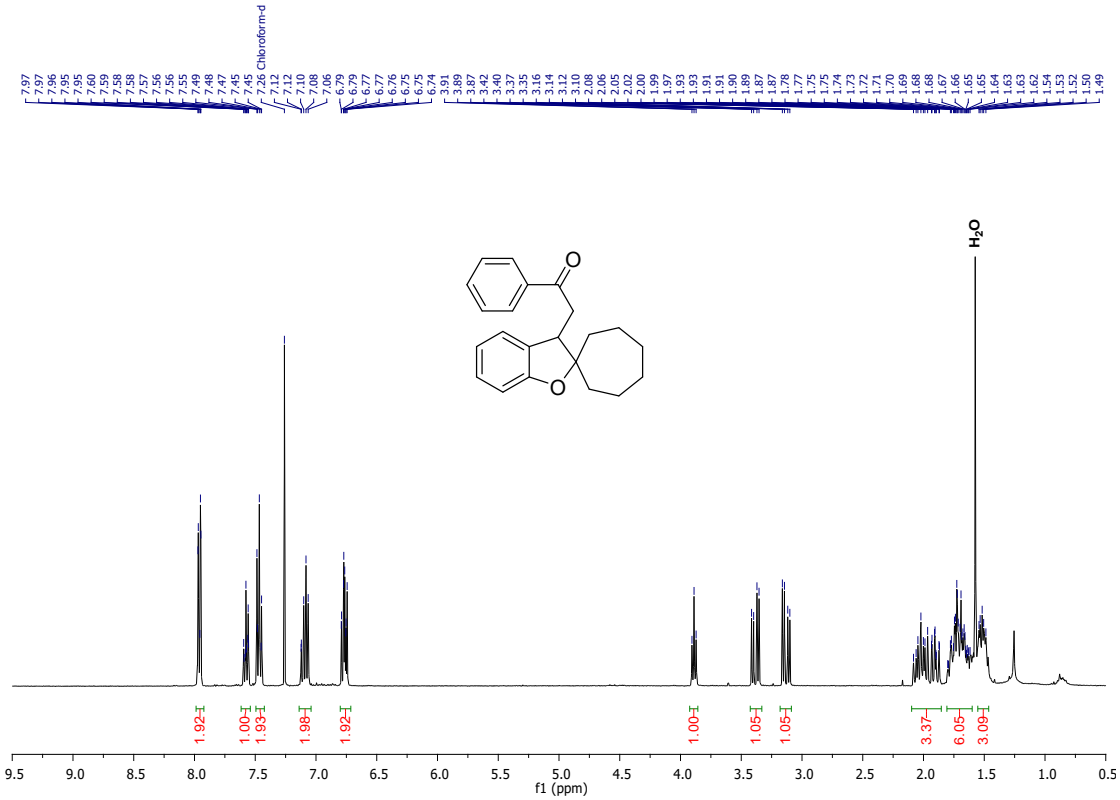
^{1}H NMR (400 MHz) spectrum of **3ad** in $CDCl_3$



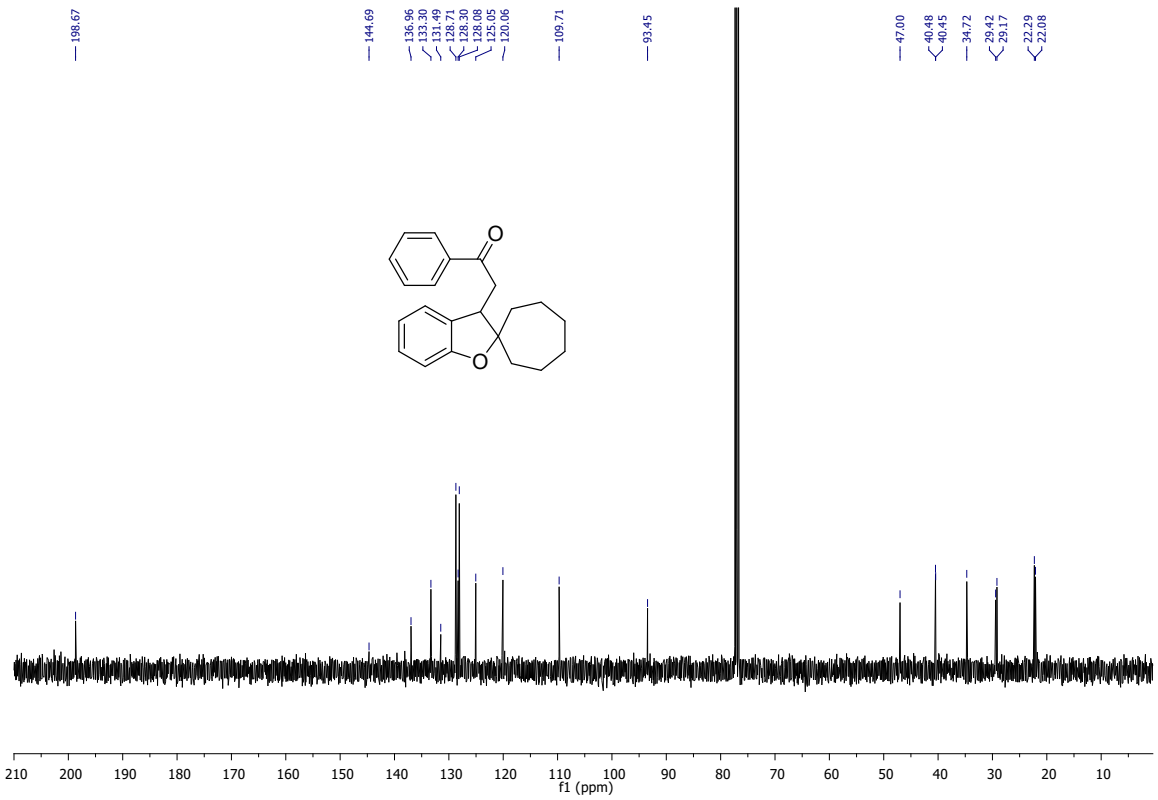
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ad** in $CDCl_3$



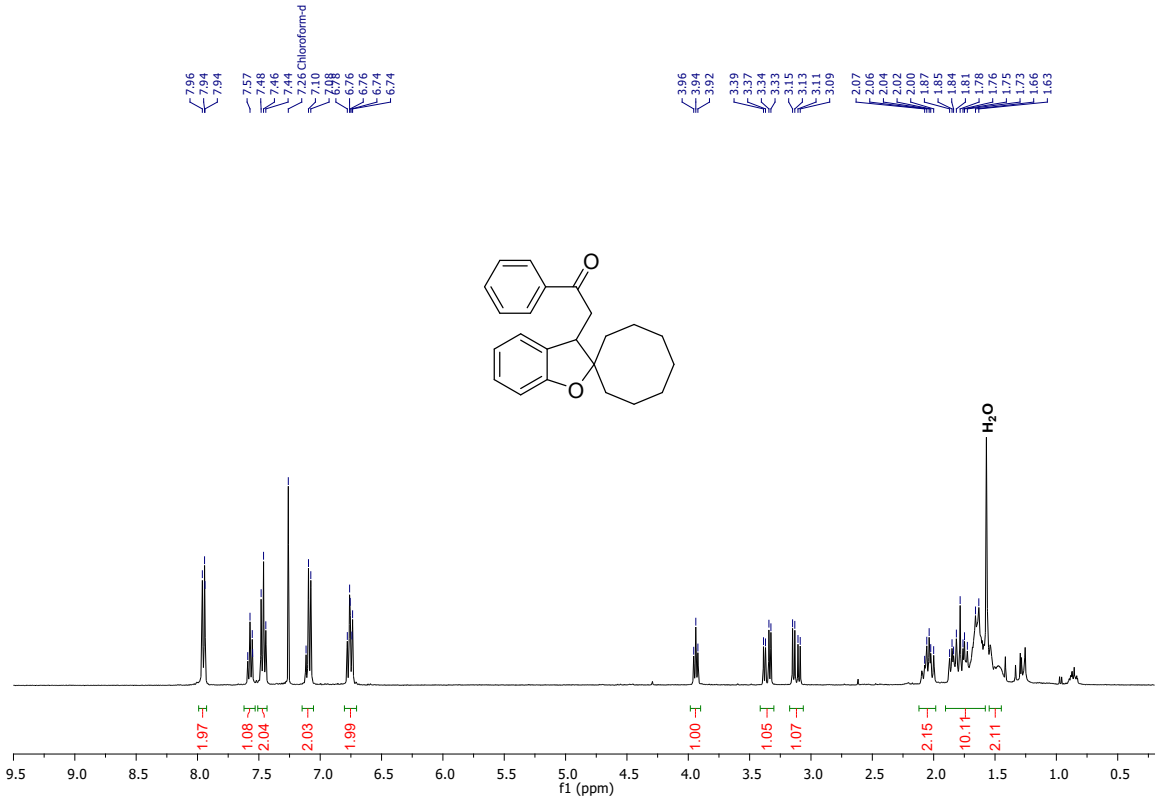
^{1}H NMR (400 MHz) spectrum of **3ae** in $CDCl_3$



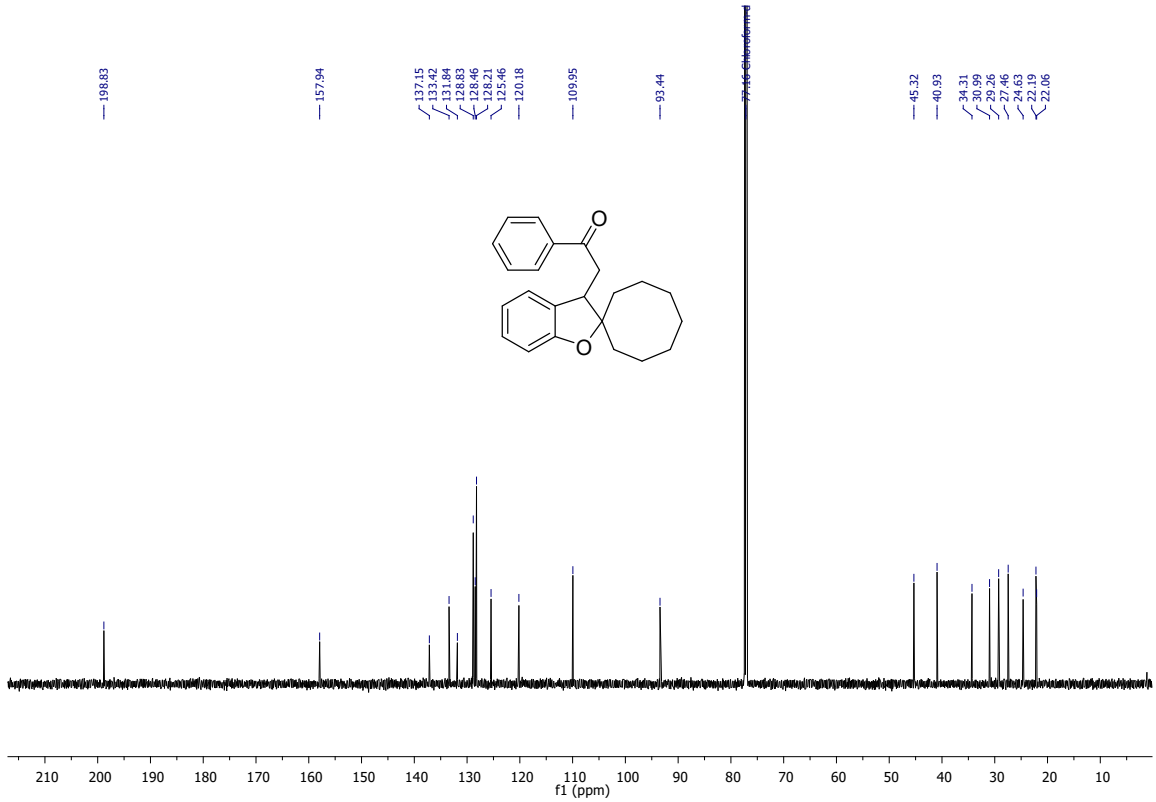
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ae** in $CDCl_3$



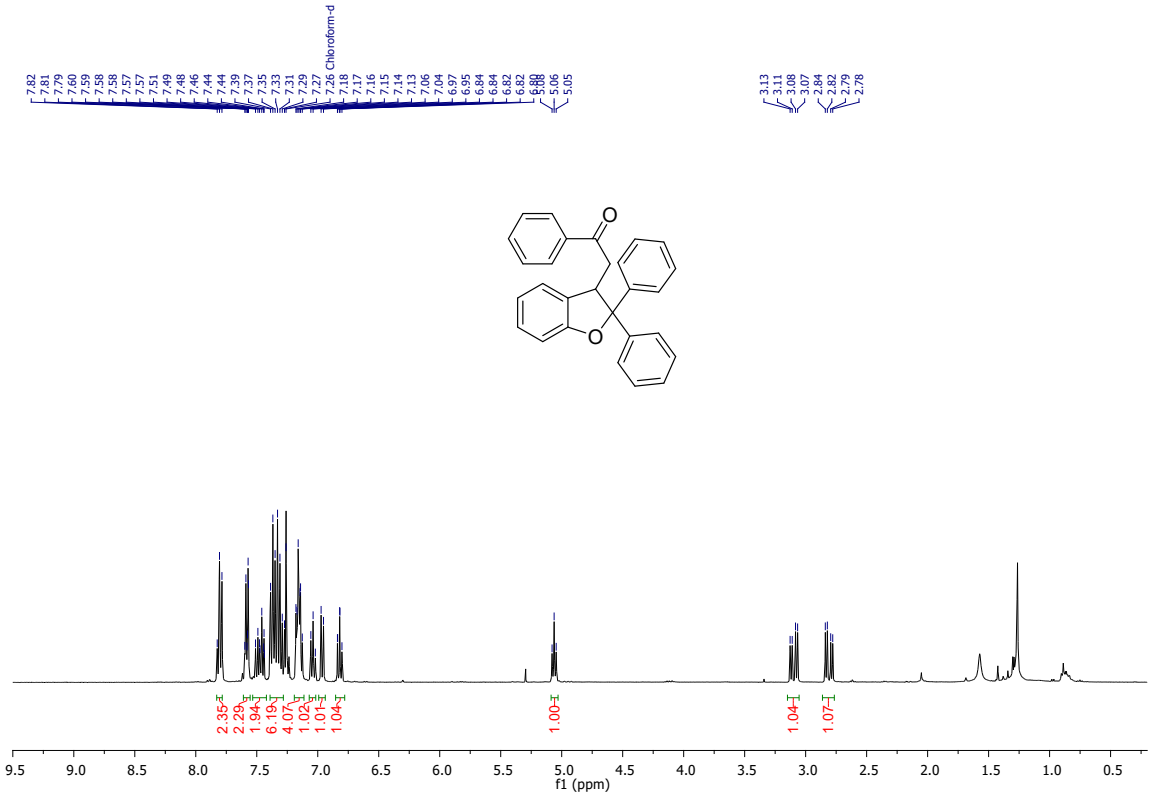
^{1}H NMR (400 MHz) spectrum of **3af** in $CDCl_3$



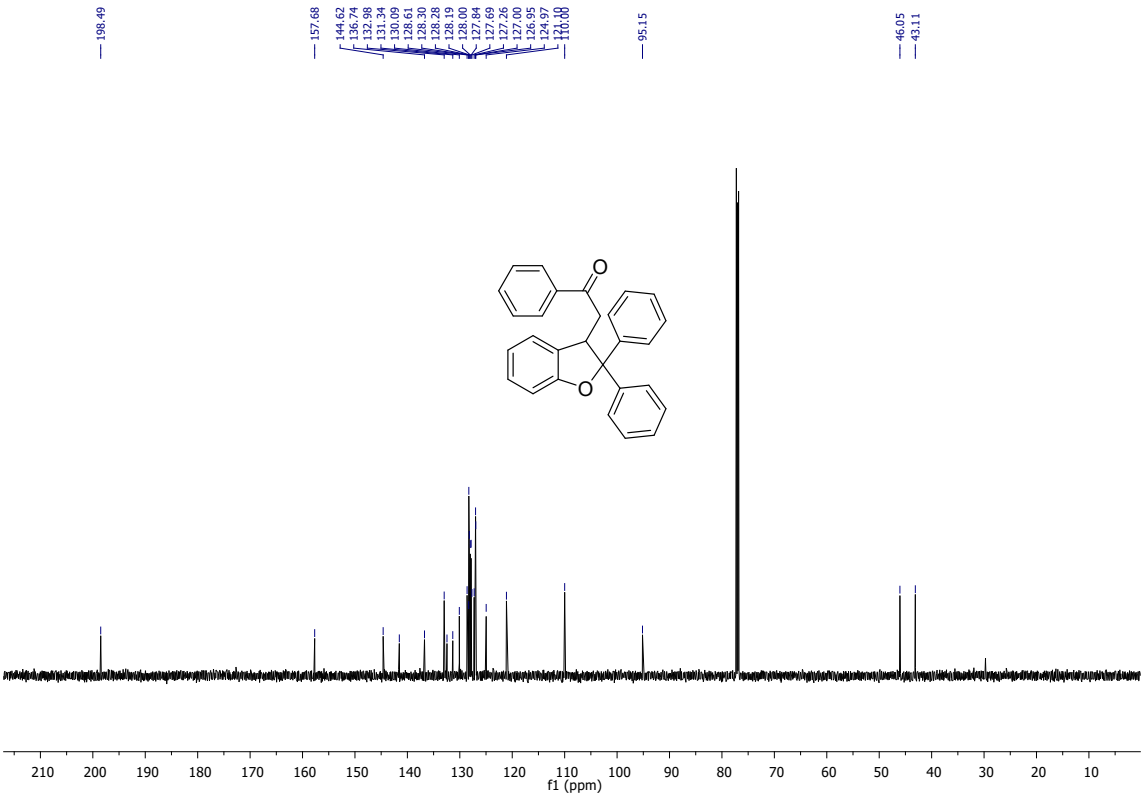
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3af** in $CDCl_3$



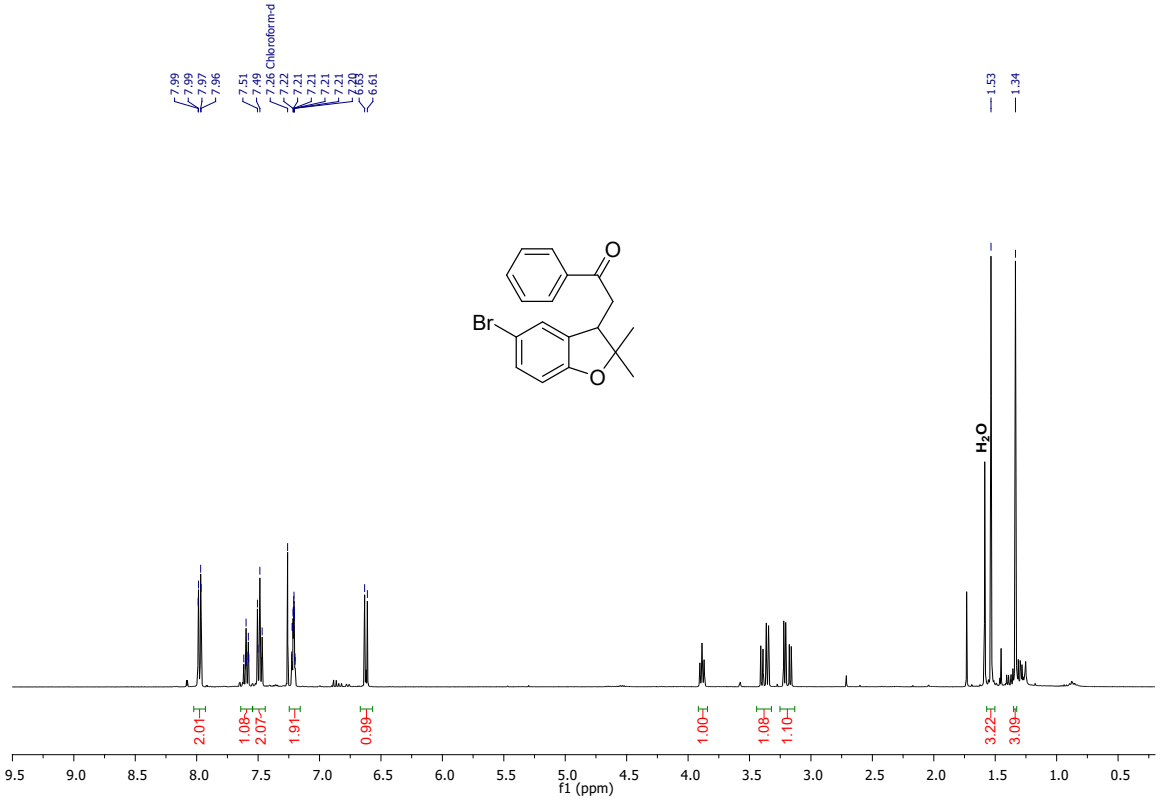
^{1}H NMR (400 MHz) spectrum of **3ag** in $CDCl_3$



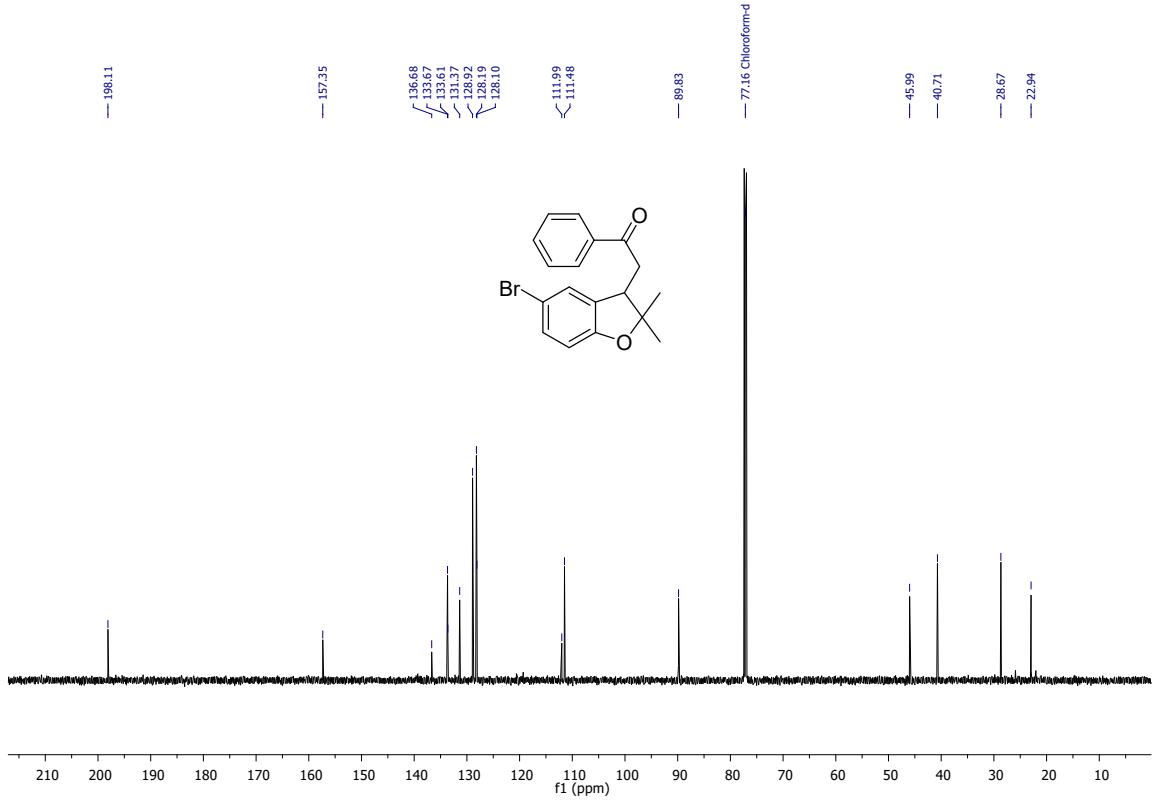
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3ag** in $CDCl_3$



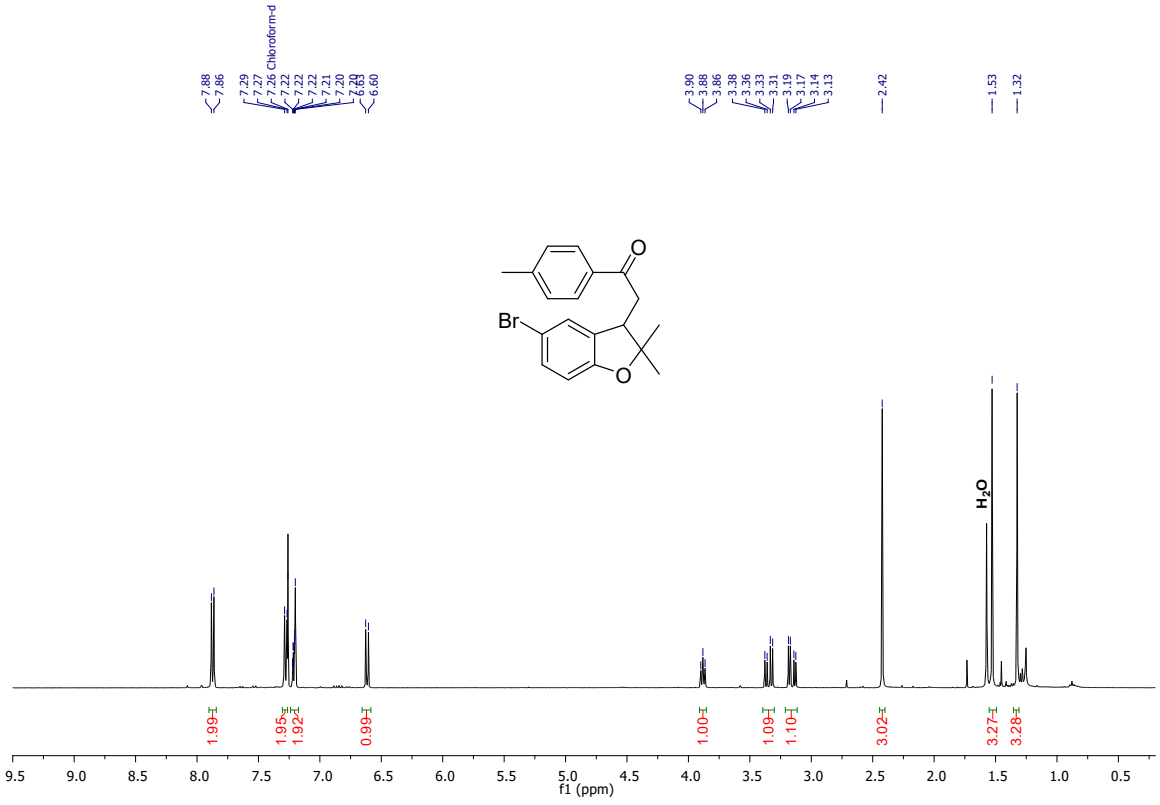
^{1}H NMR (400 MHz) spectrum of **3ah** in $CDCl_3$



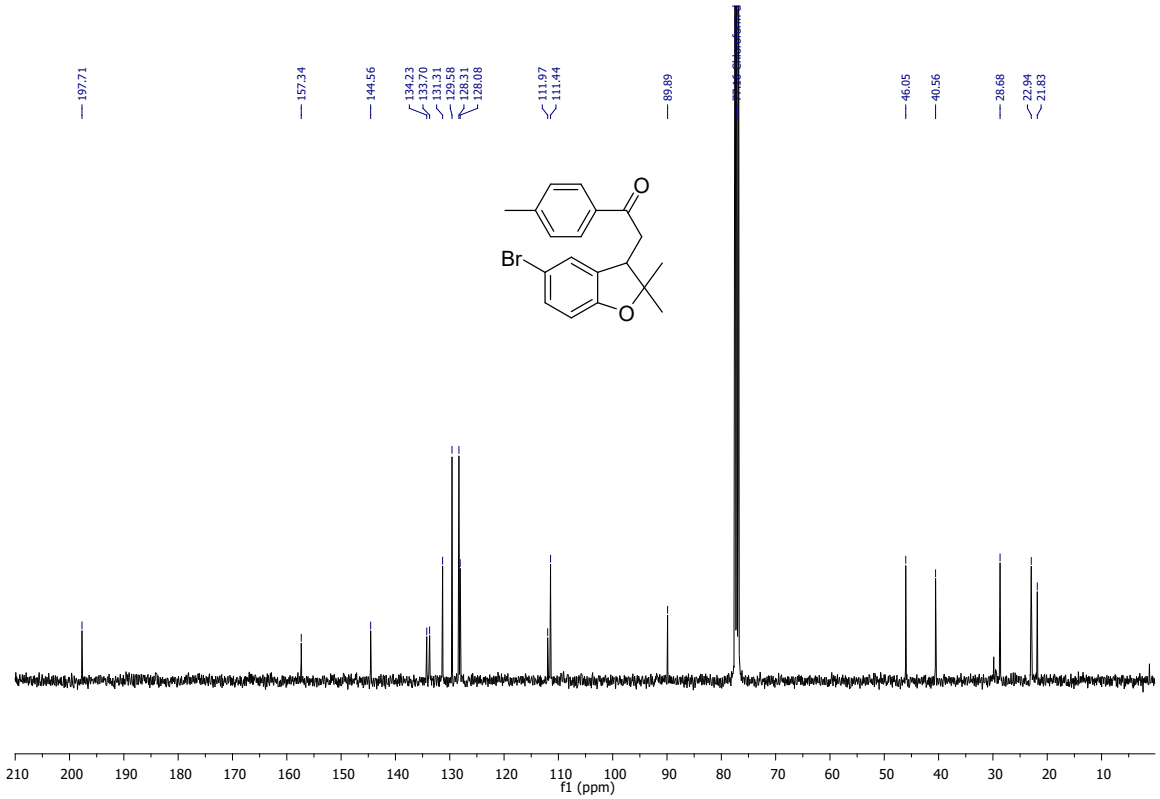
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3ah** in $CDCl_3$



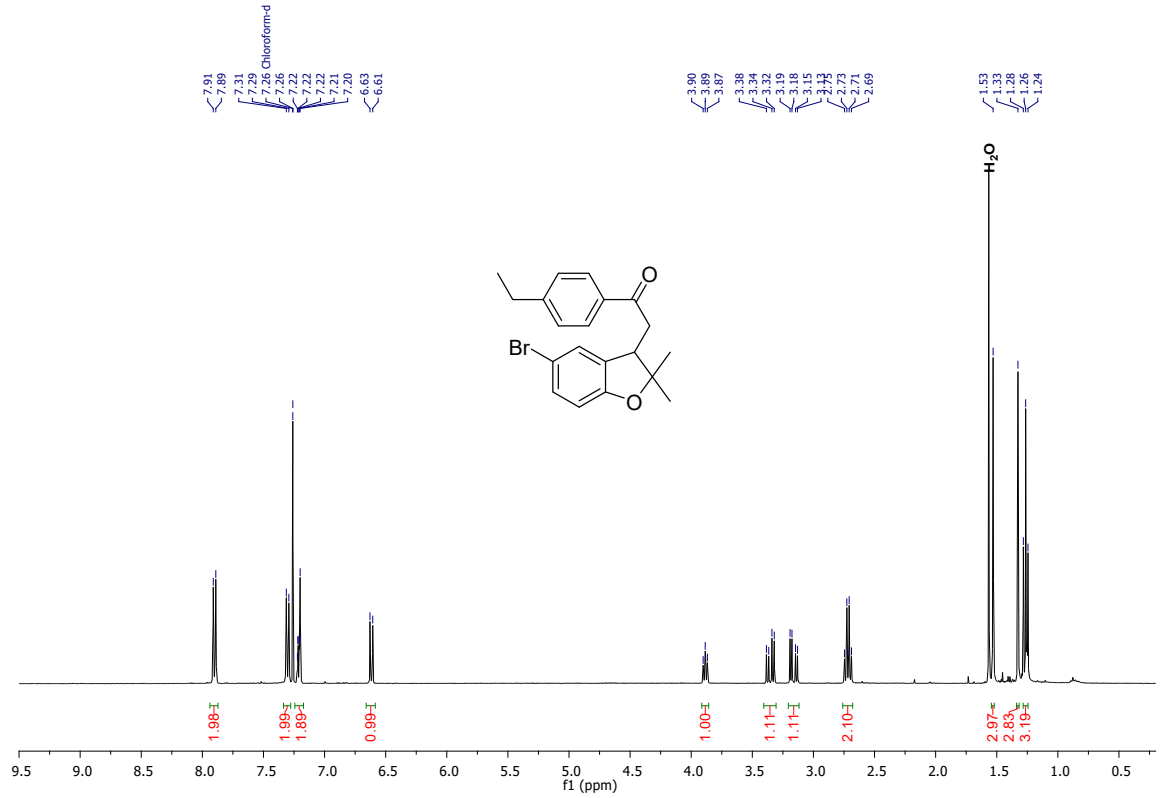
^{1}H NMR (400 MHz) spectrum of **3oh** in $CDCl_3$



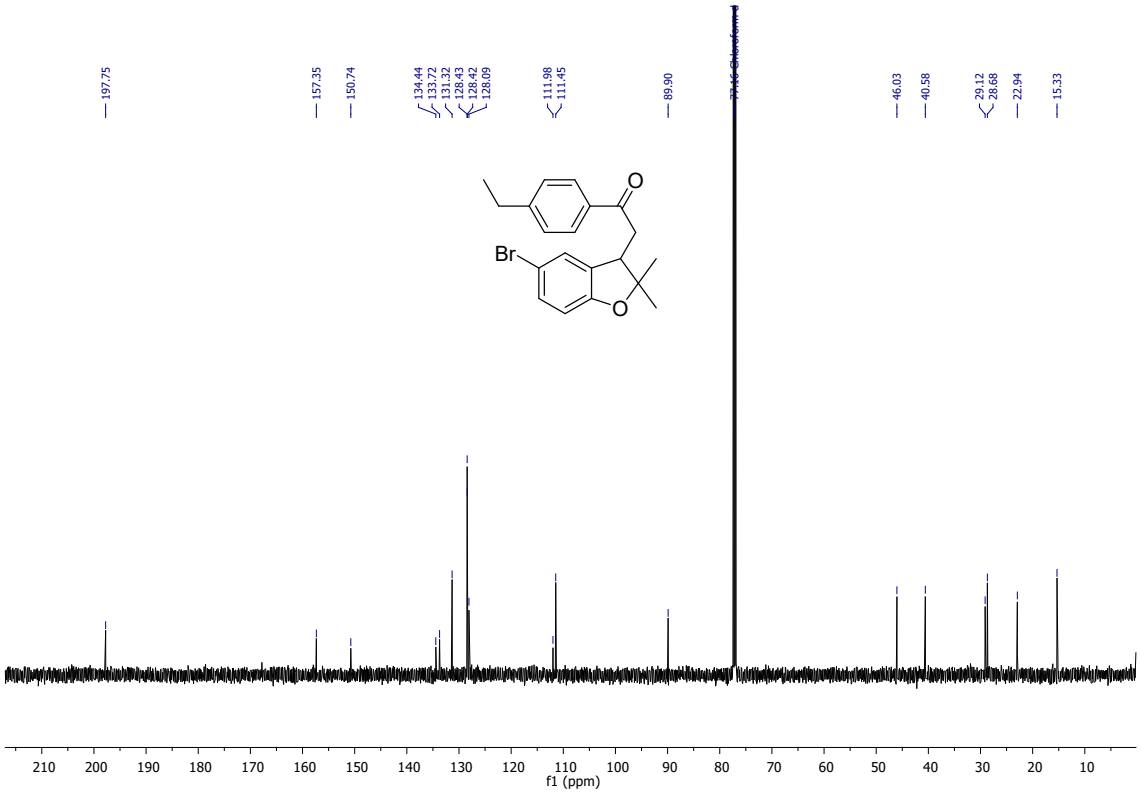
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3oh** in $CDCl_3$



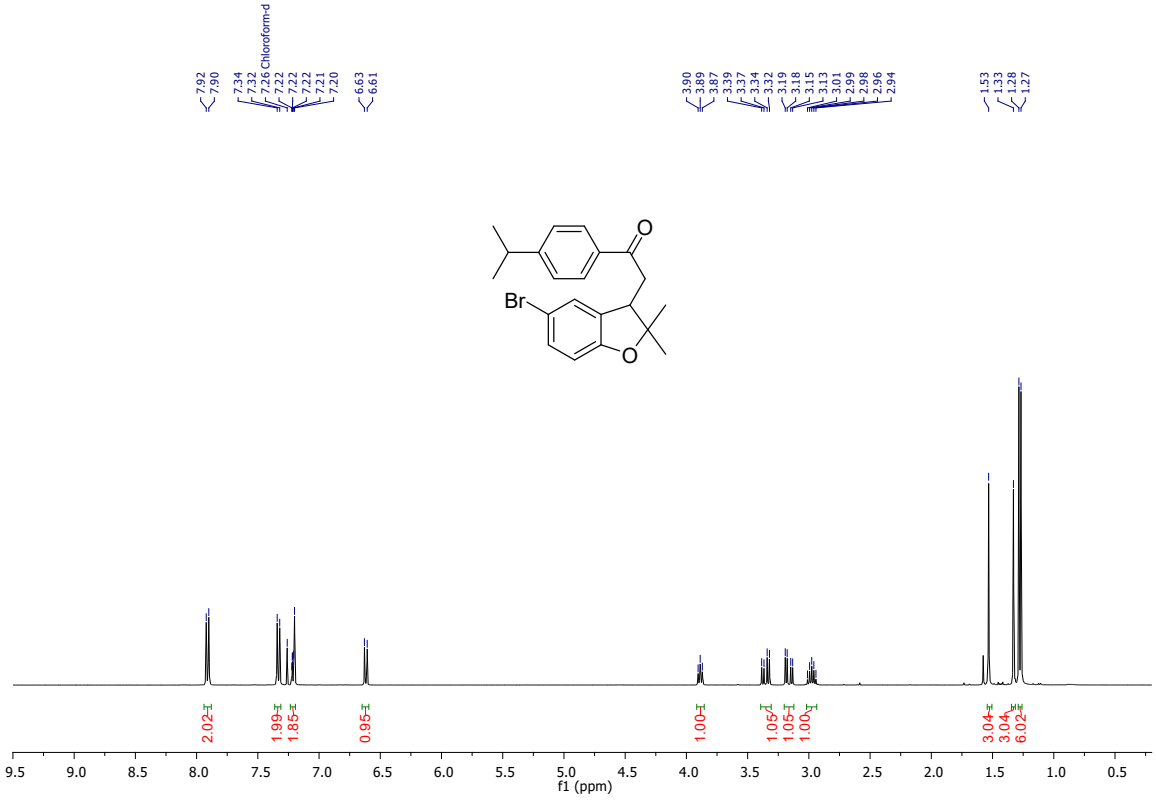
^{1}H NMR (400 MHz) spectrum of **3bh** in $CDCl_3$



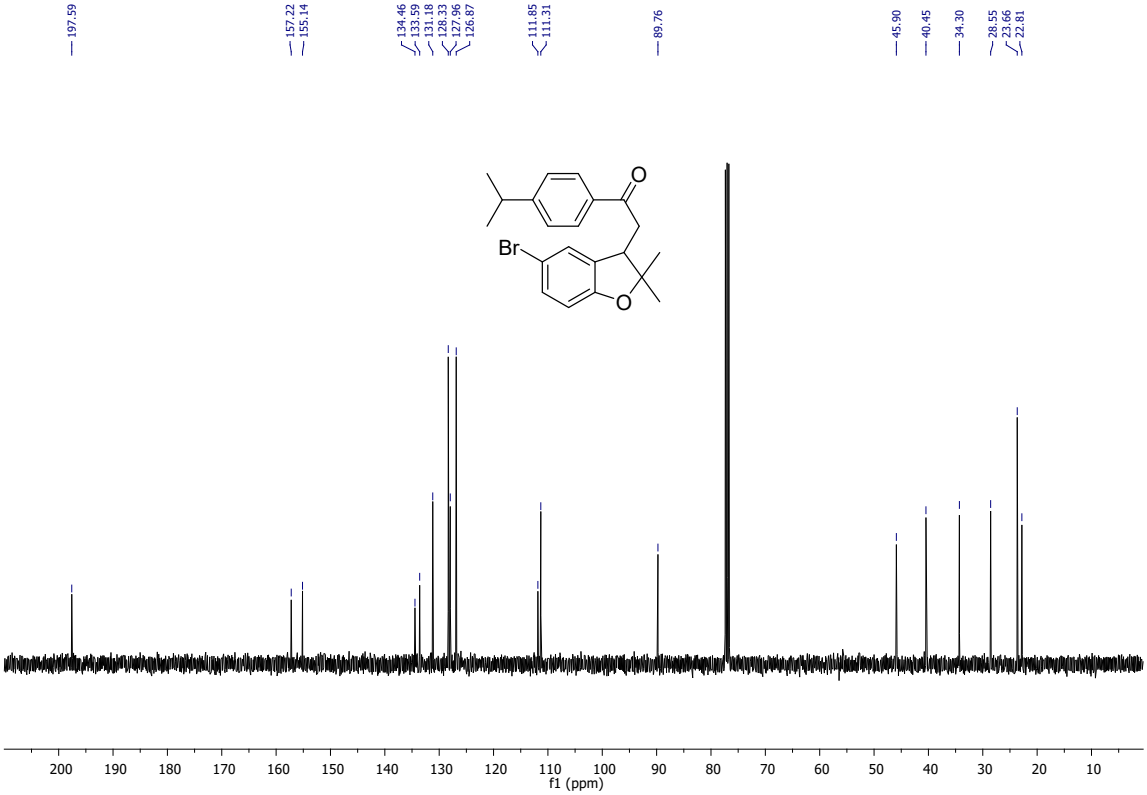
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3bh** in $CDCl_3$



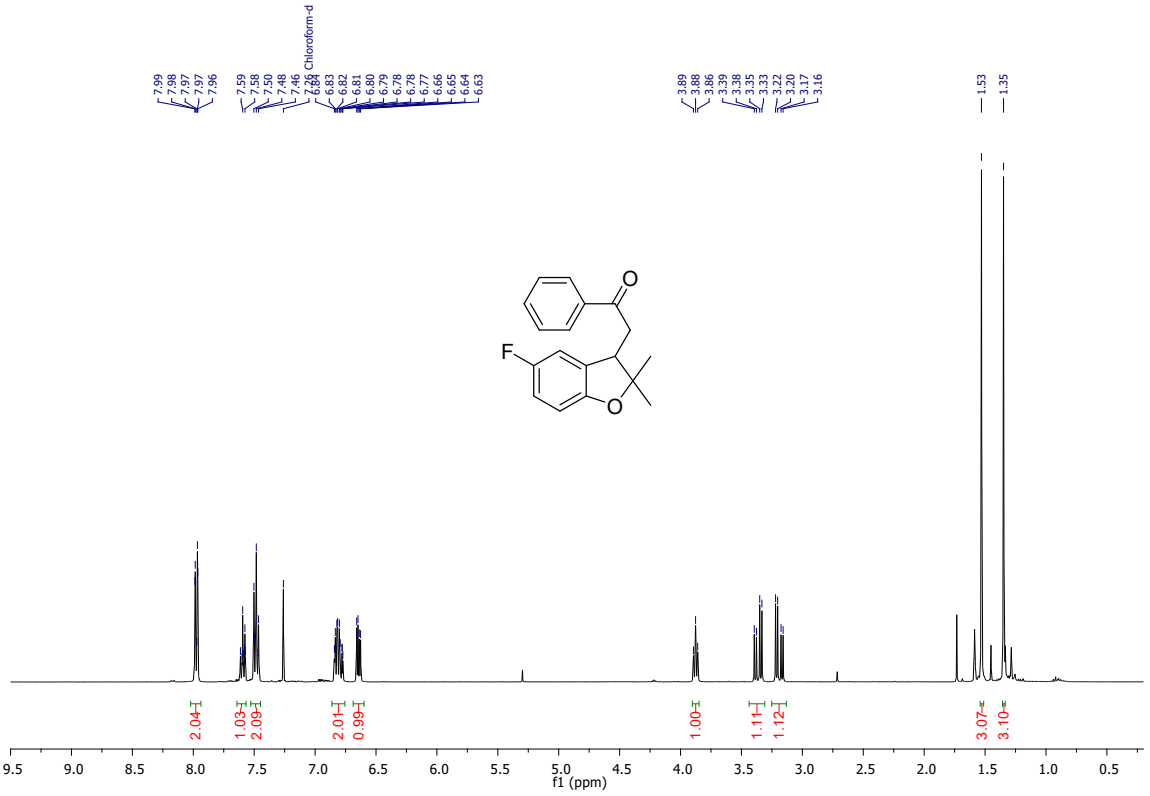
^{1}H NMR (400 MHz) spectrum of **3eh** in $CDCl_3$



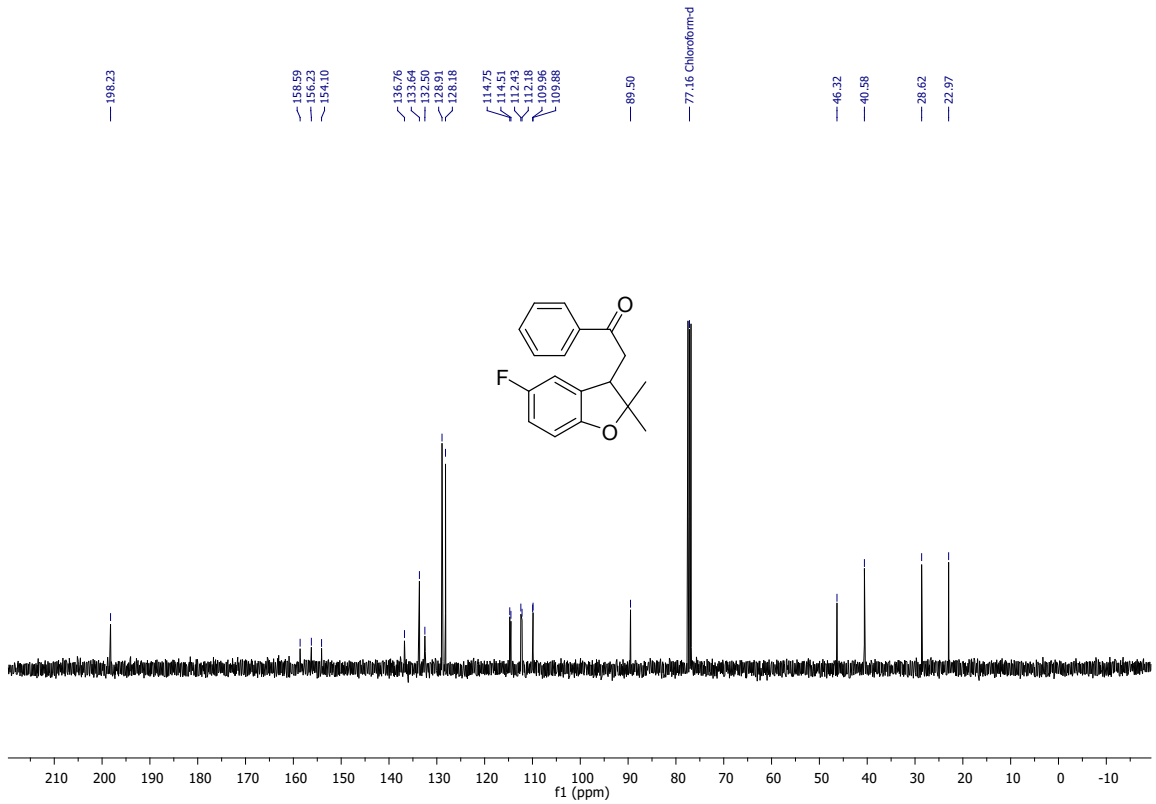
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3eh** in $CDCl_3$



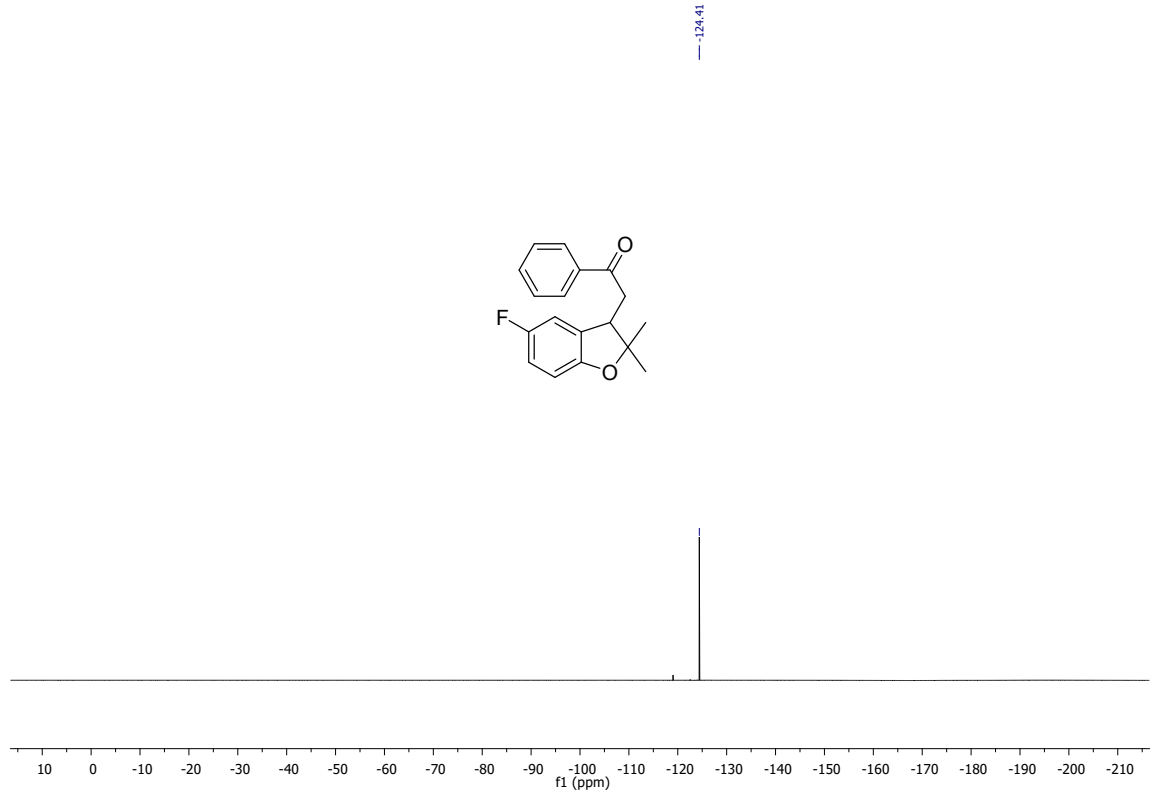
^{1}H NMR (400 MHz) spectrum of **3ai** in $CDCl_3$



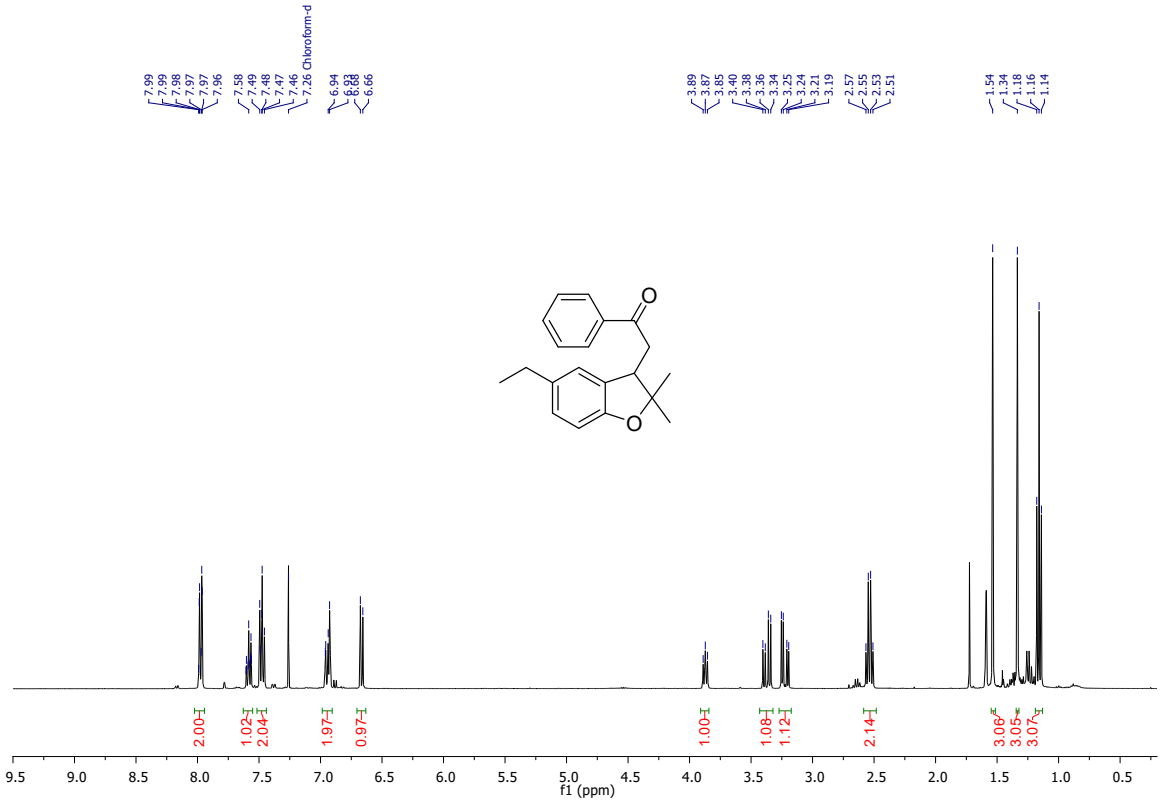
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3ai** in $CDCl_3$



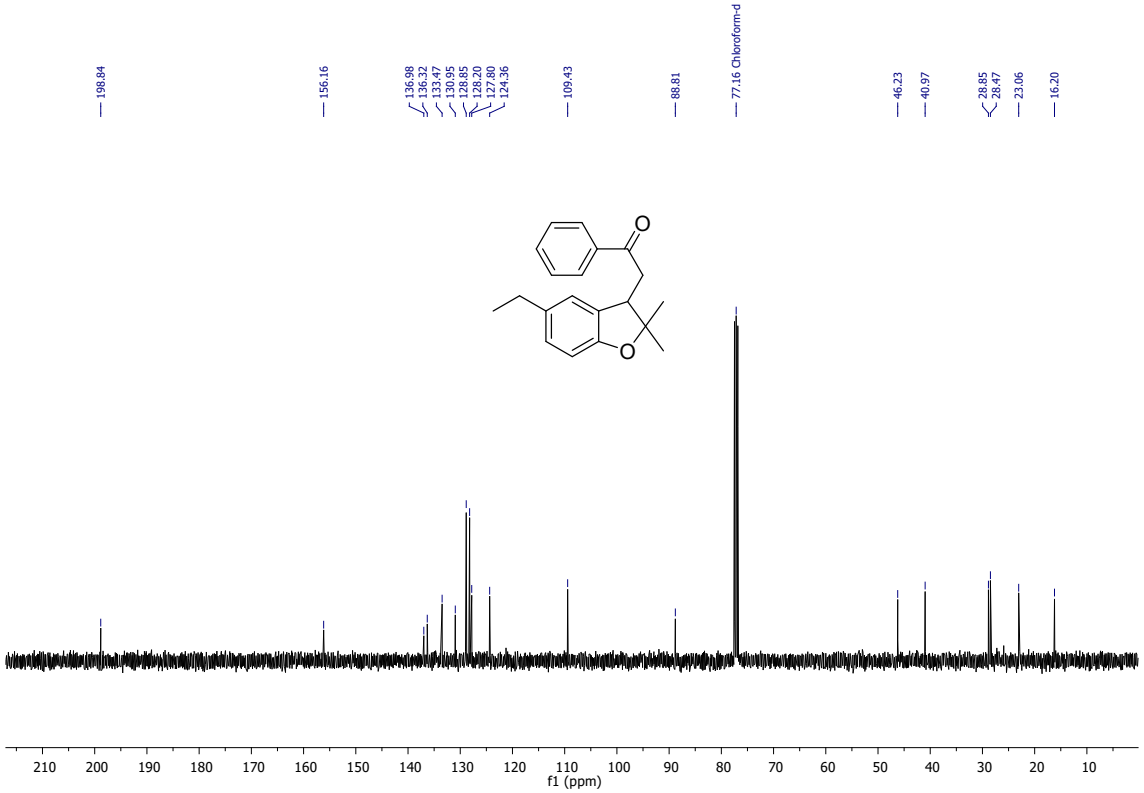
^{19}F-NMR (565 MHz) spectrum of **3ai** in $CDCl_3$



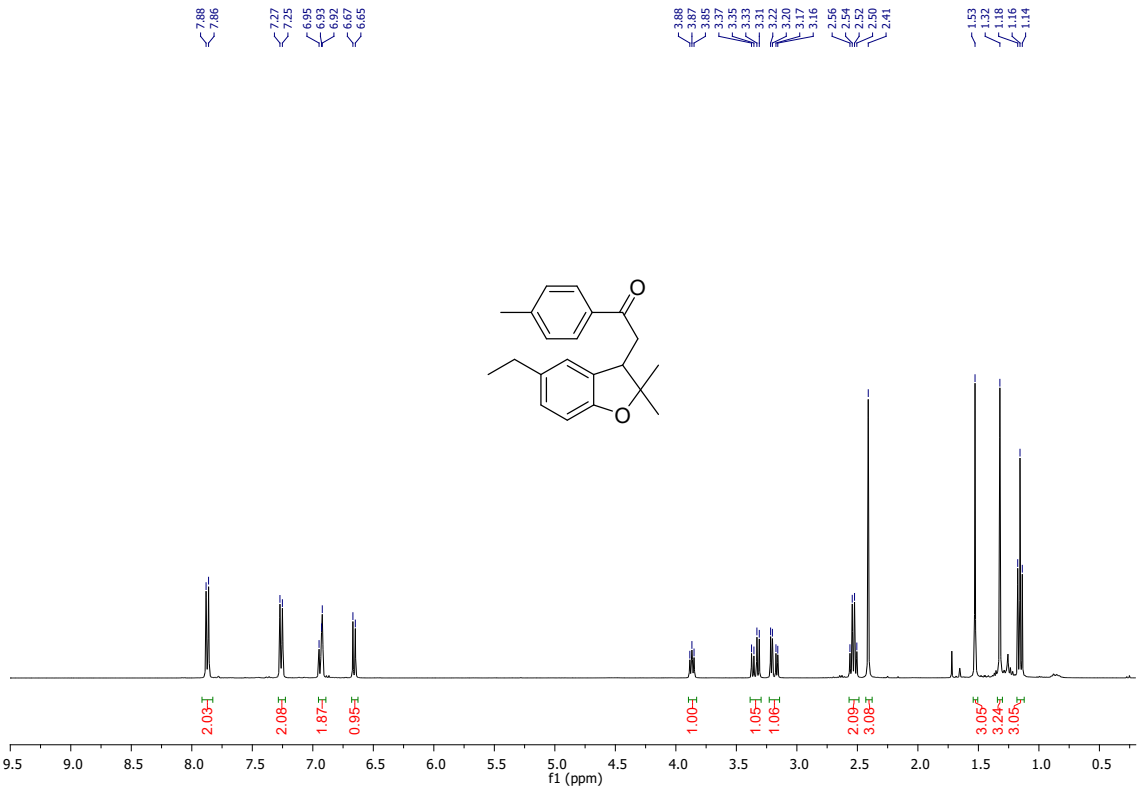
^{1}H NMR (400 MHz) spectrum of **3aj** in $CDCl_3$



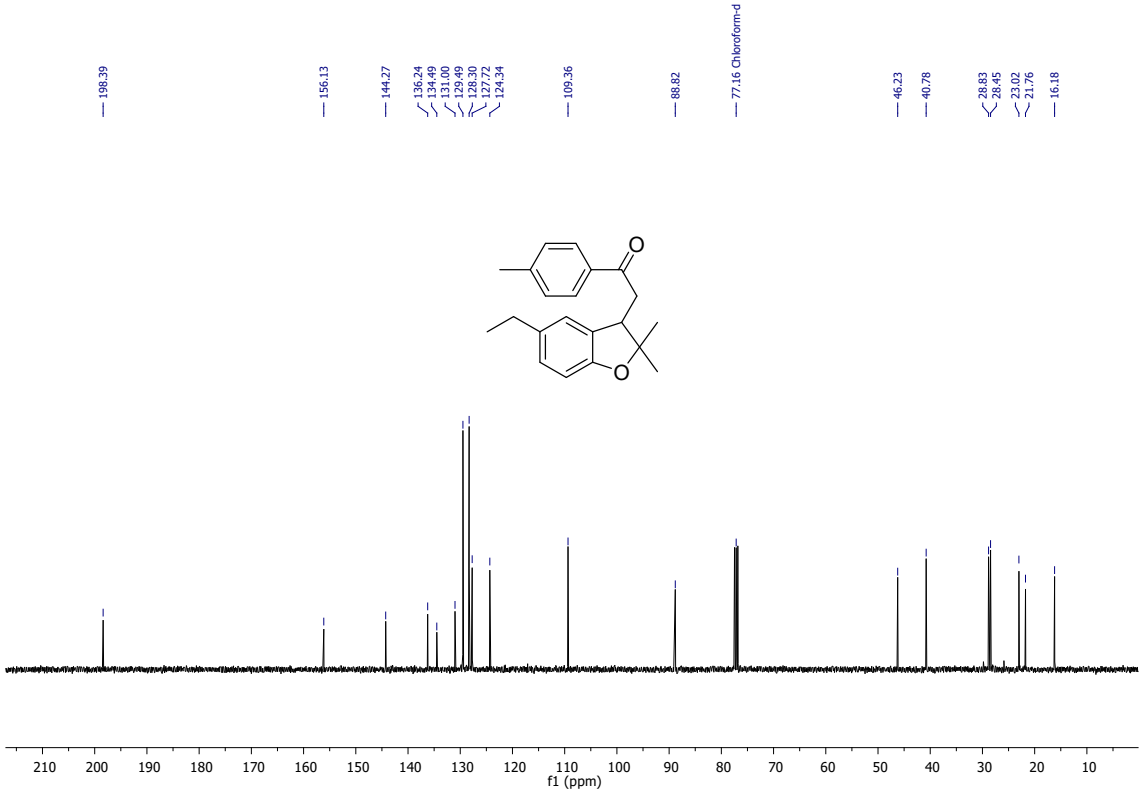
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3aj** in $CDCl_3$



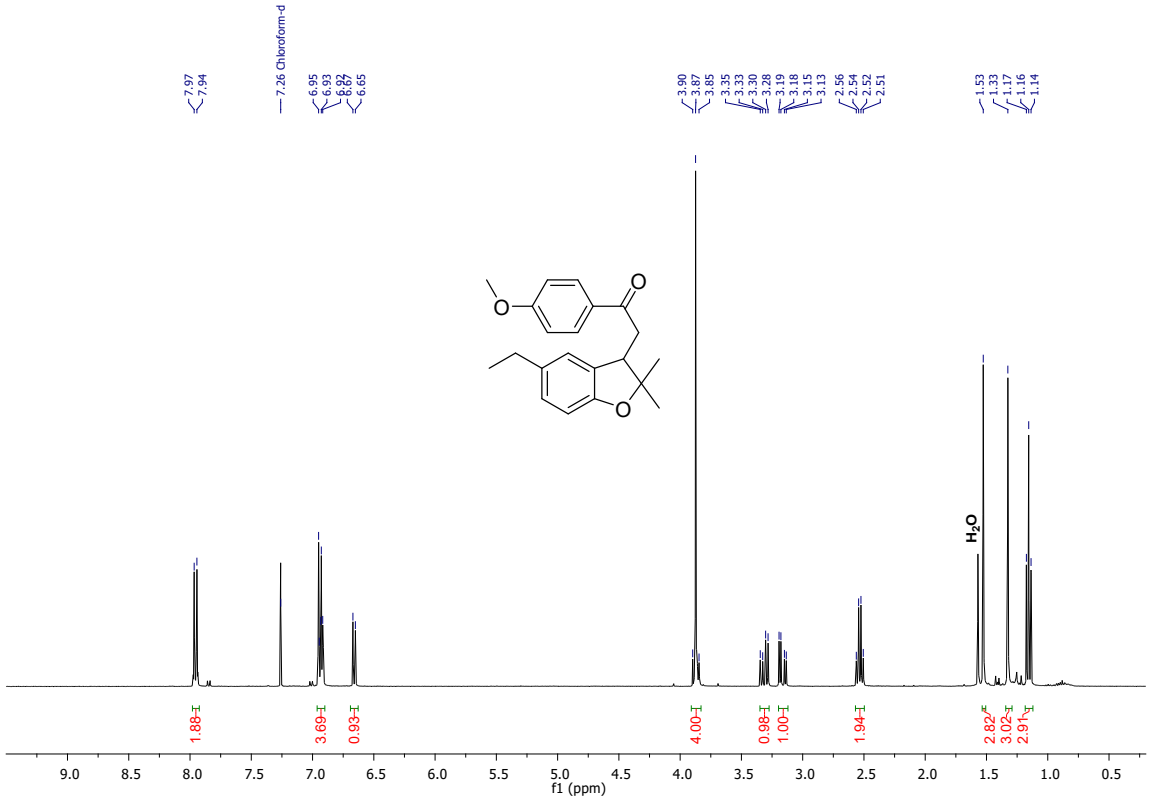
^{1}H NMR (400 MHz) spectrum of **3oj** in $CDCl_3$



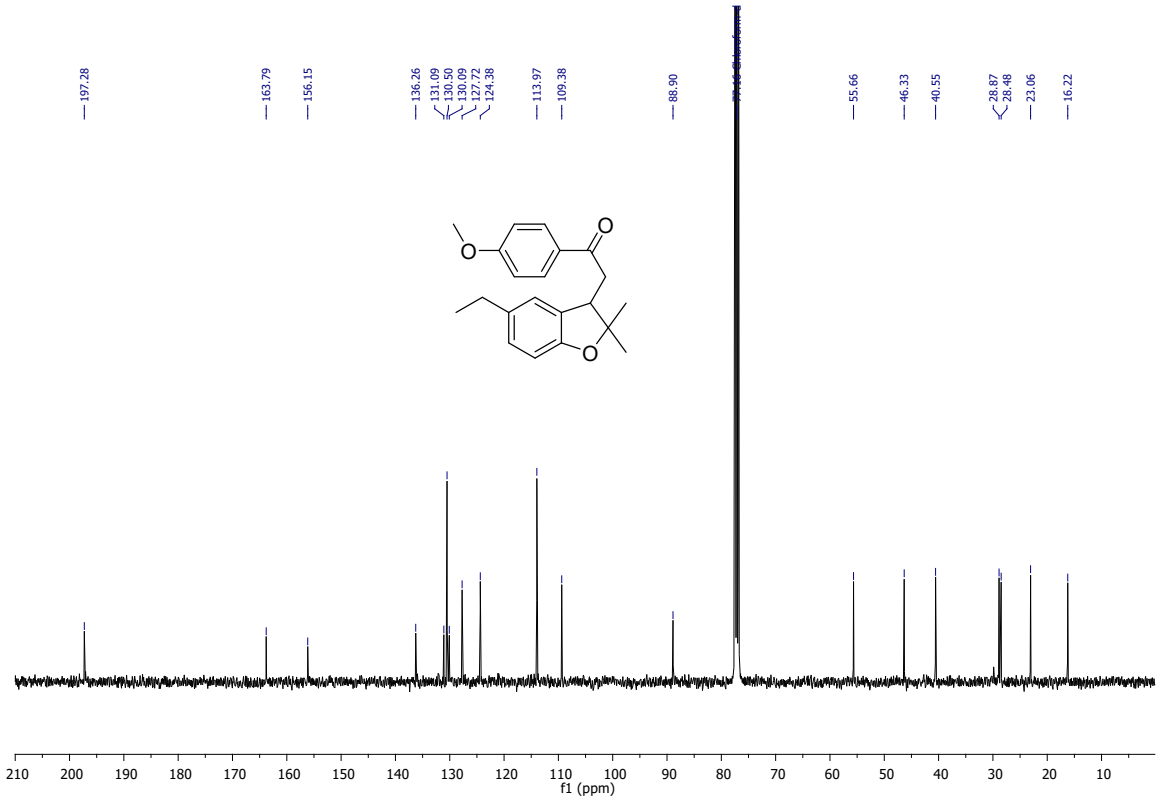
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3oj** in $CDCl_3$



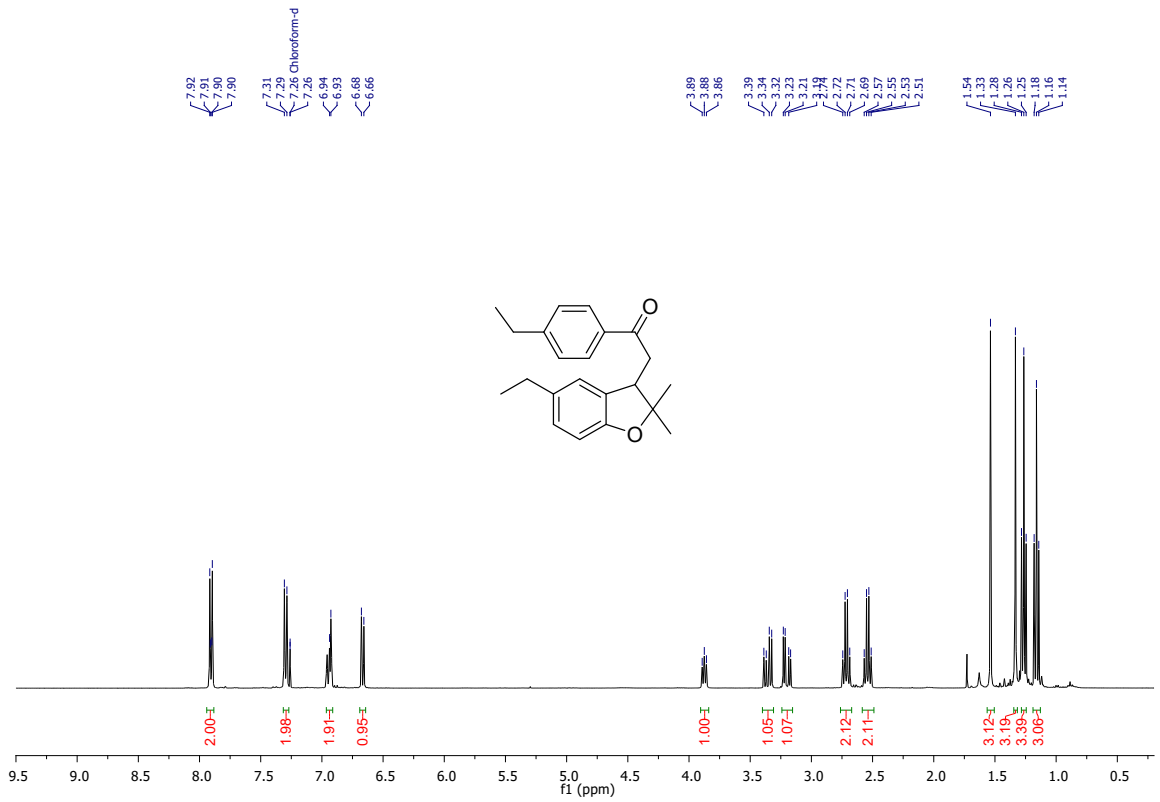
^{1}H NMR (400 MHz) spectrum of **3mj** in $CDCl_3$



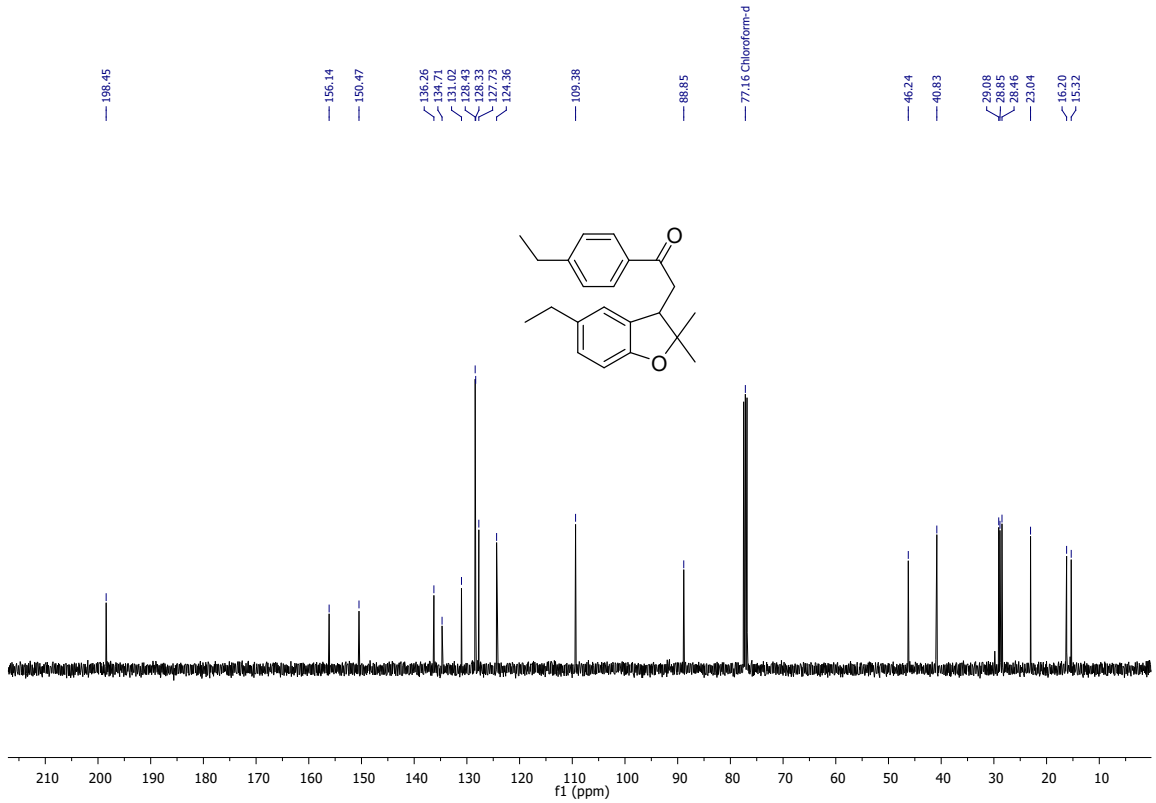
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3mj** in $CDCl_3$



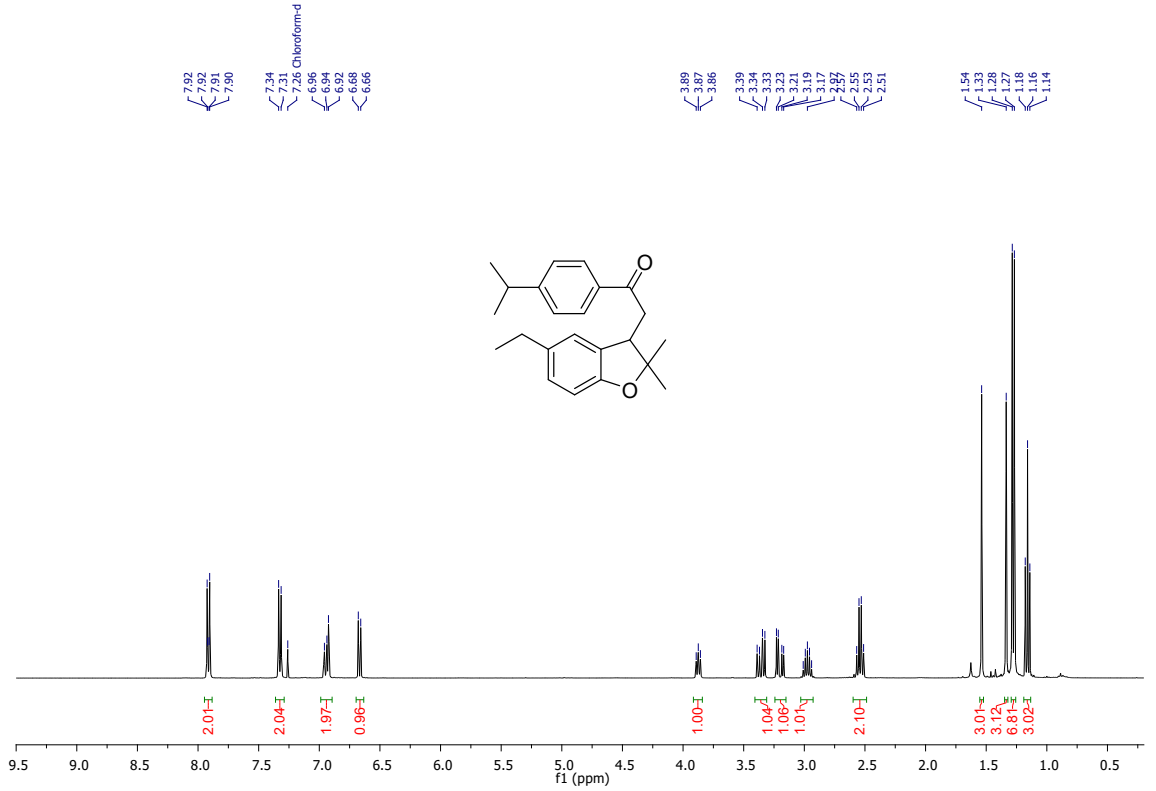
^{1}H NMR (400 MHz) spectrum of **3bj** in $CDCl_3$



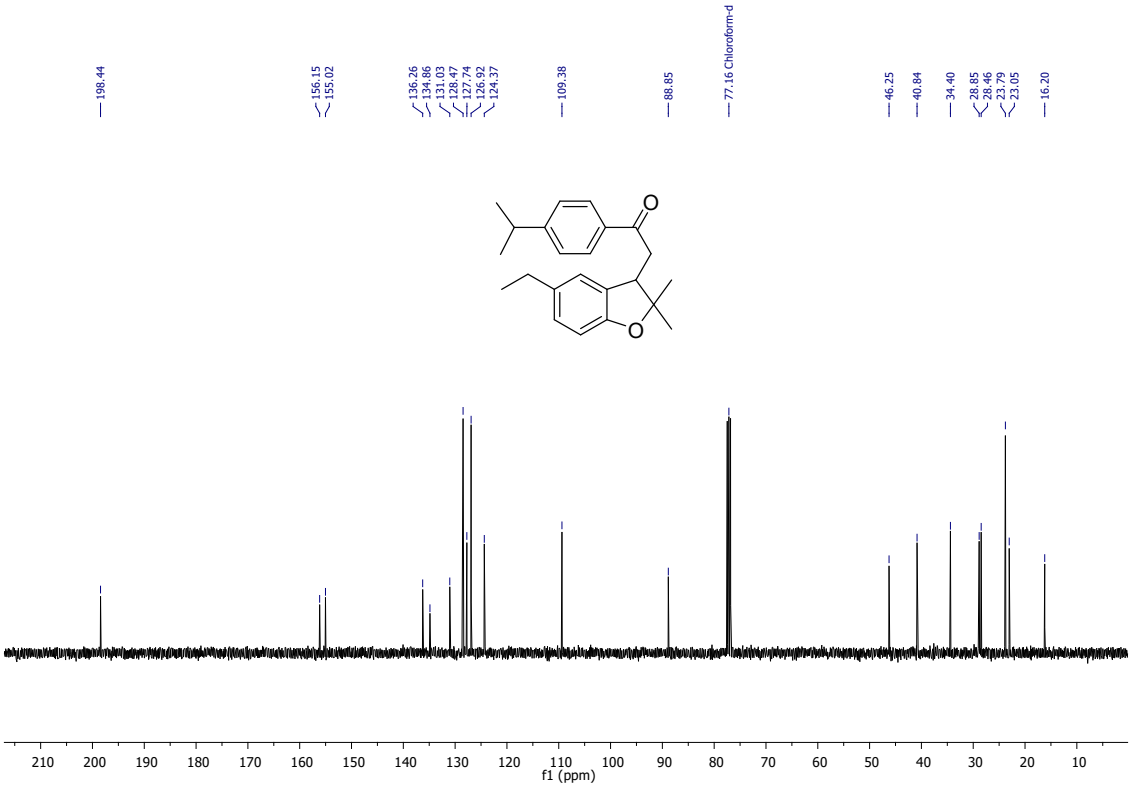
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3bj** in $CDCl_3$



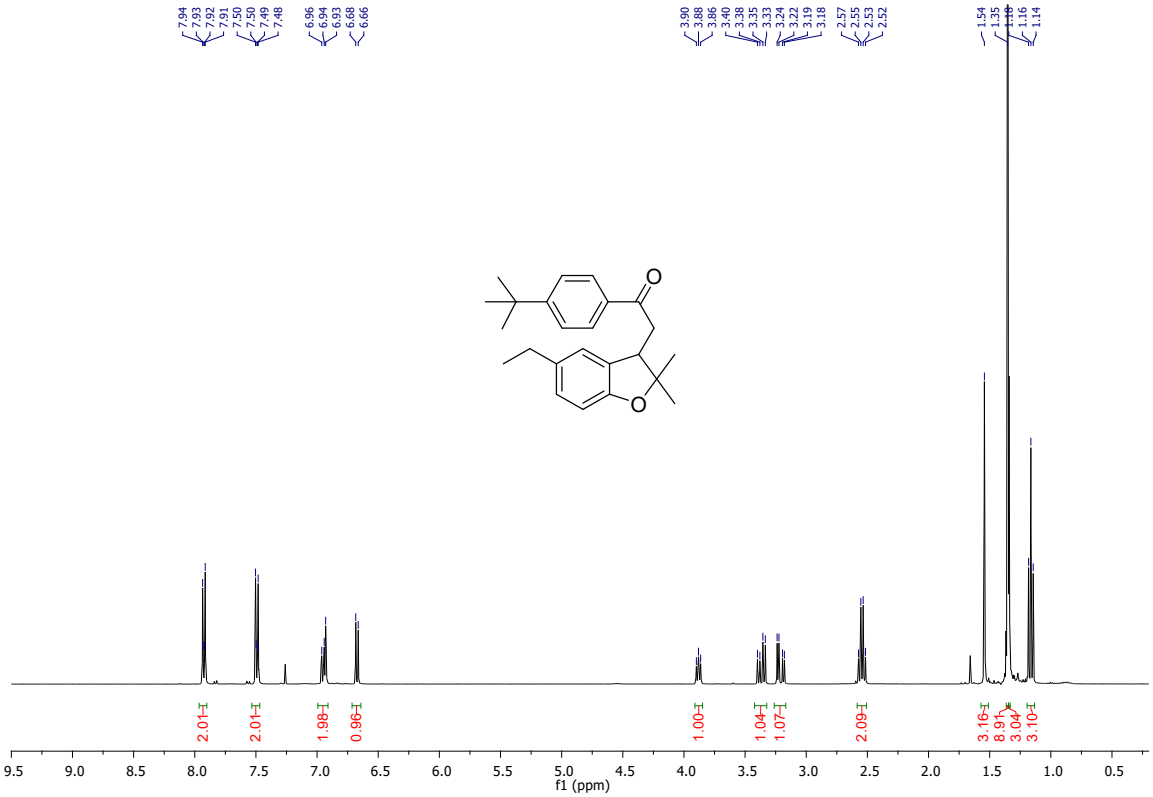
^{1}H NMR (400 MHz) spectrum of **3ej** in $CDCl_3$



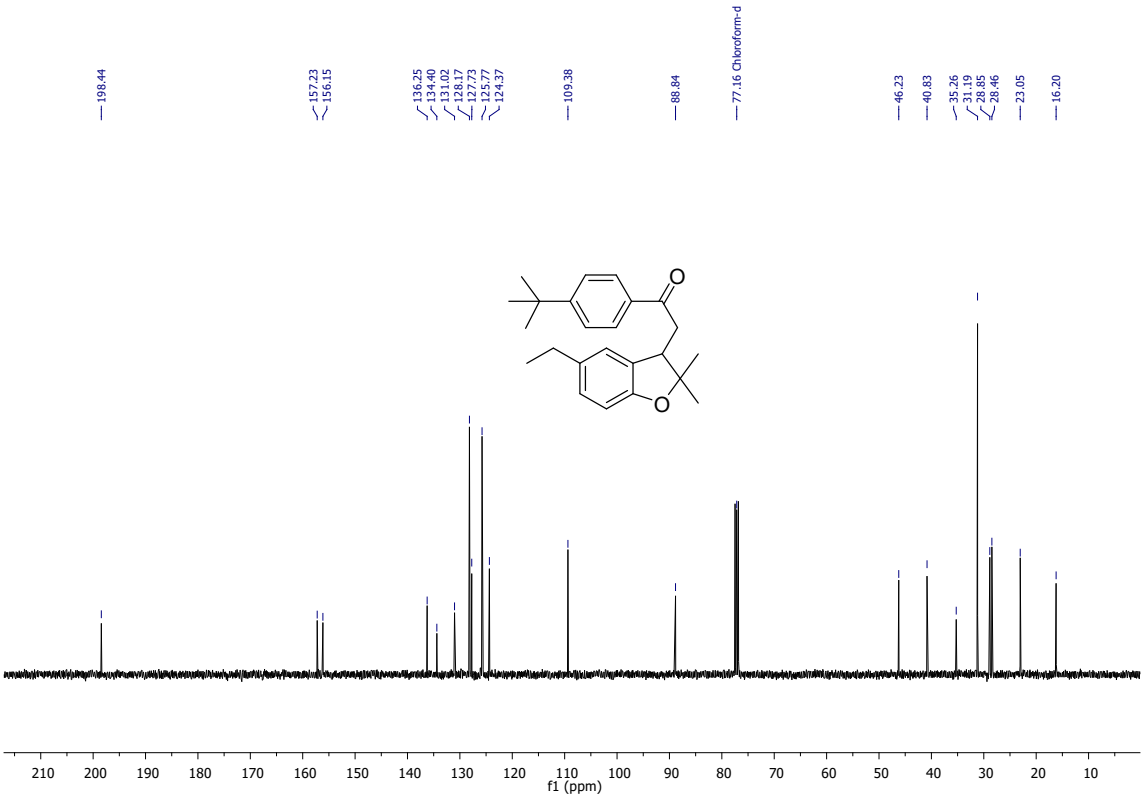
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3ej** in $CDCl_3$



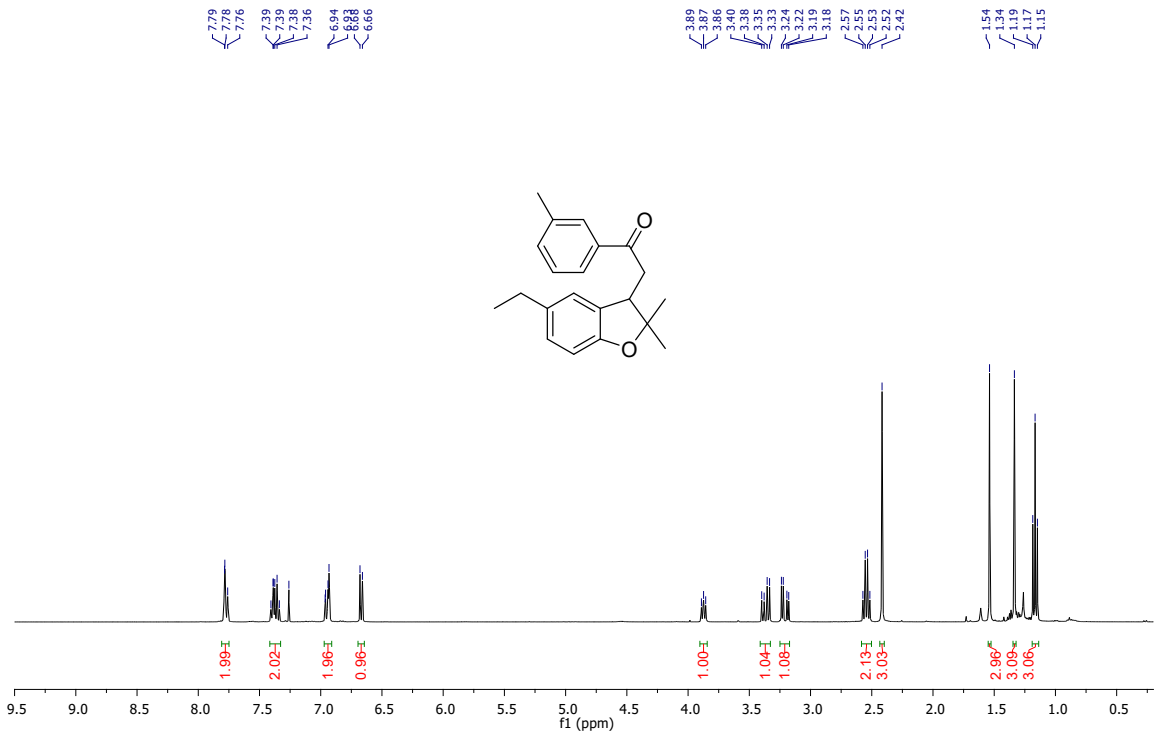
^{1}H NMR (400 MHz) spectrum of **3nj** in $CDCl_3$



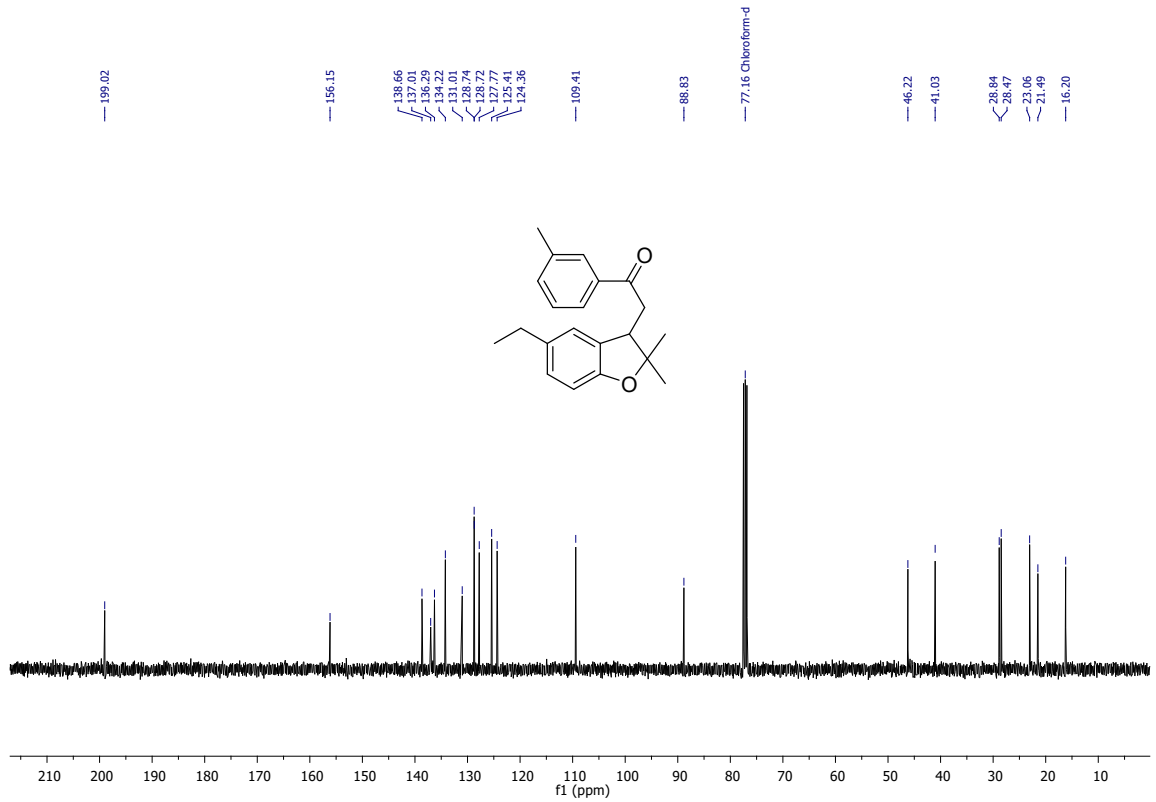
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3nj** in $CDCl_3$



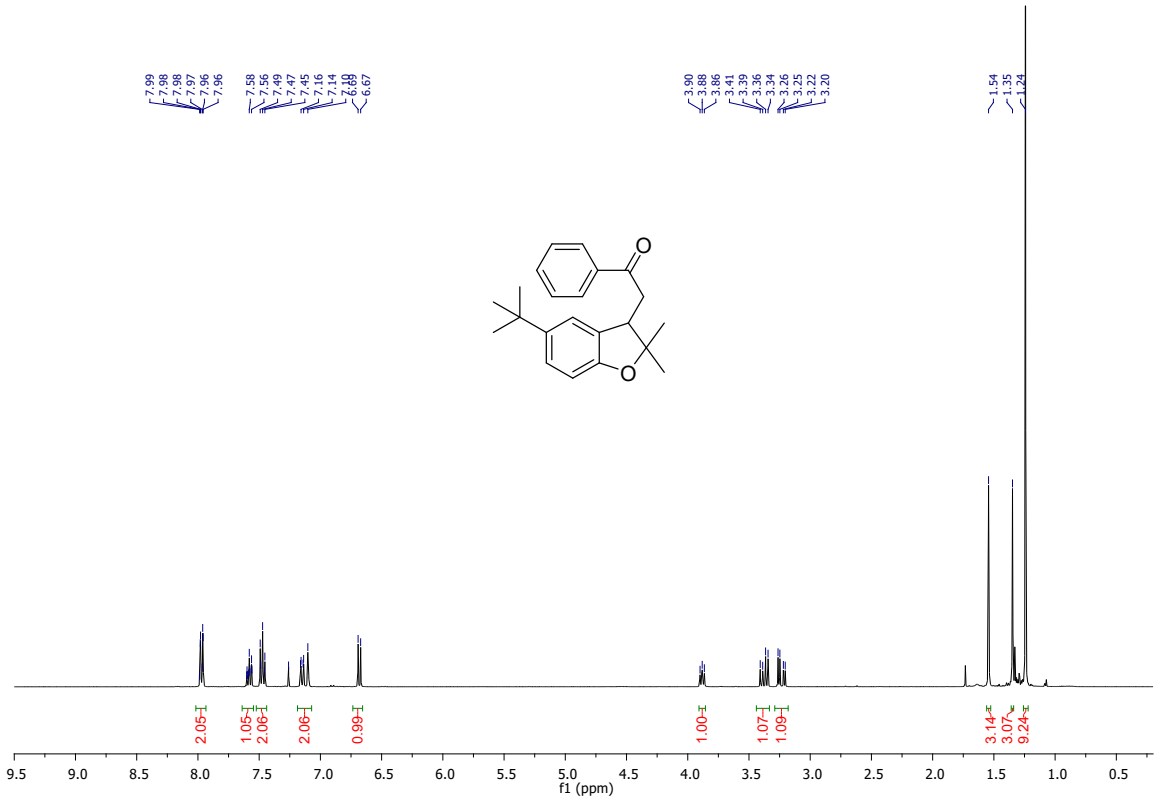
^{1}H NMR (400 MHz) spectrum of **3gj** in $CDCl_3$



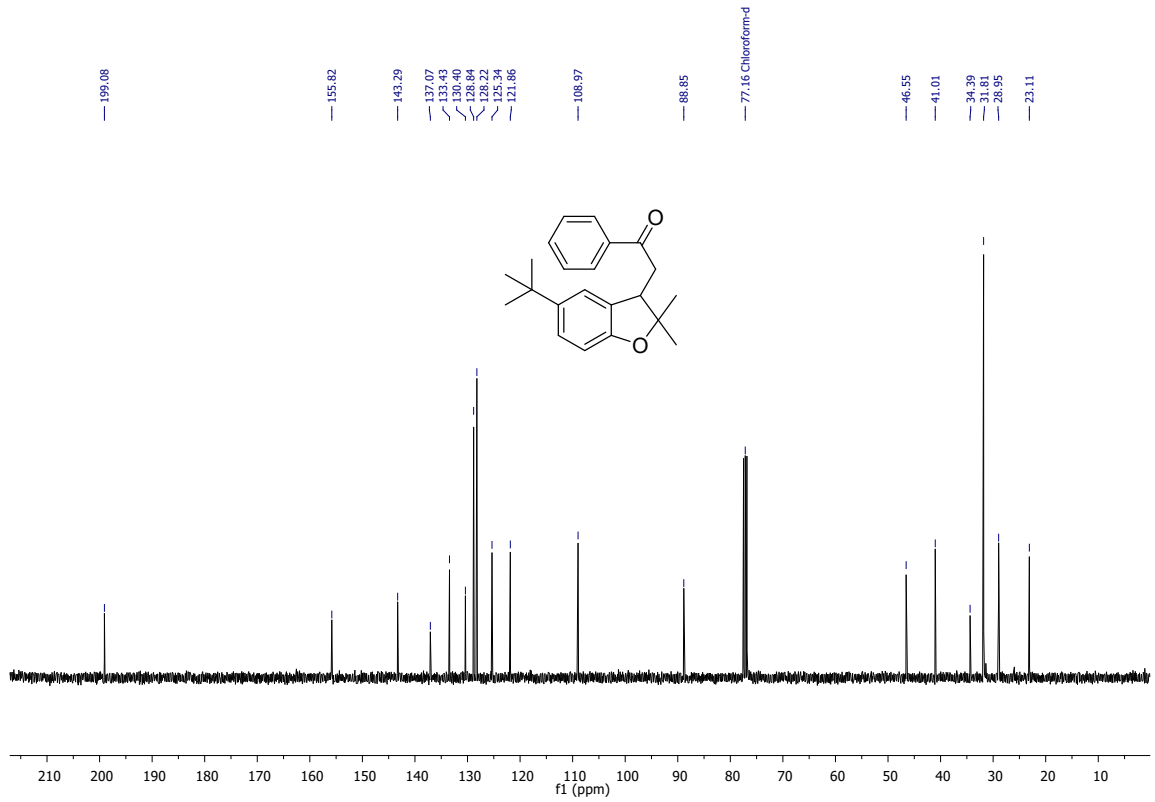
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3gj** in $CDCl_3$



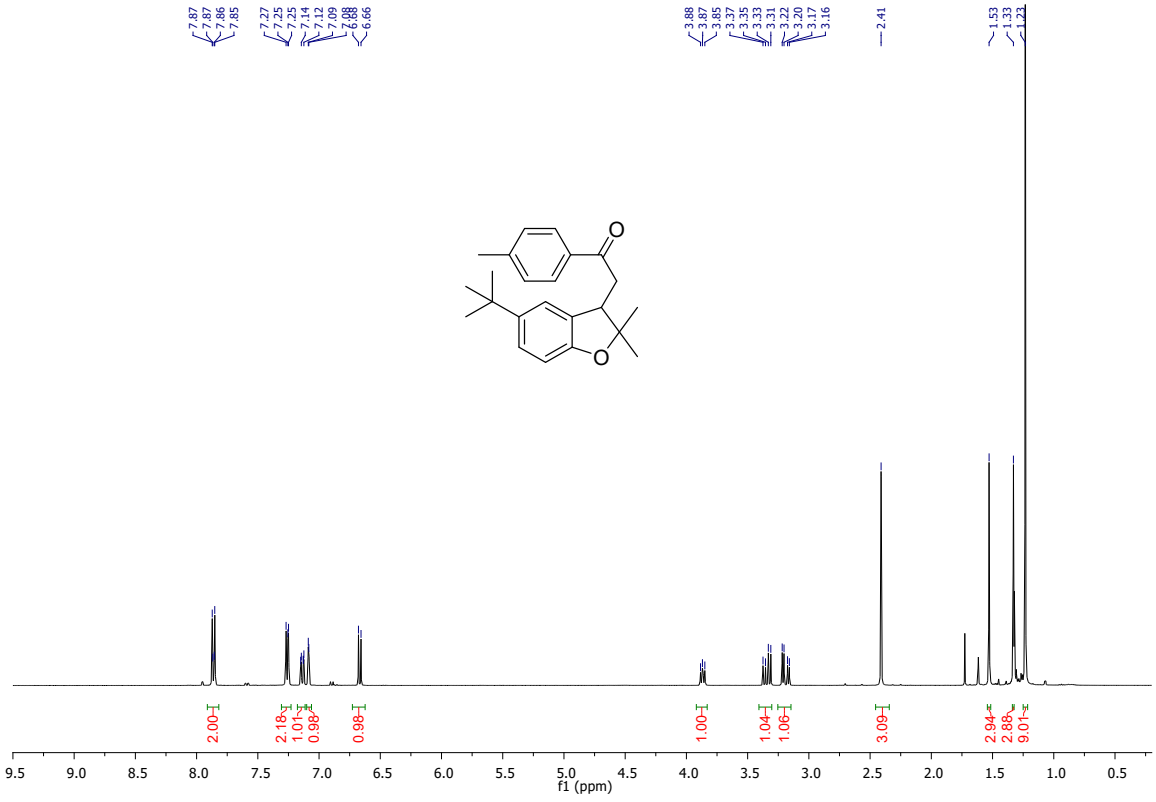
^{1}H NMR (400 MHz) spectrum of **3ak** in $CDCl_3$



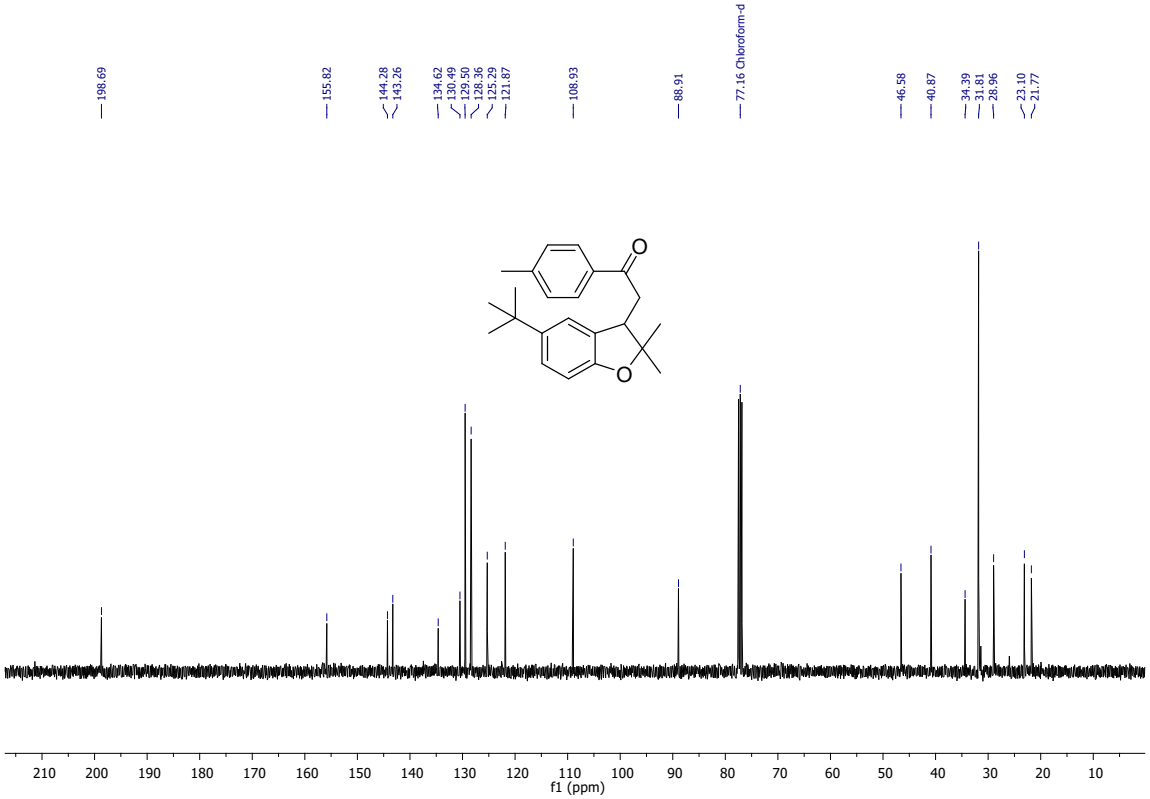
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3ak** in $CDCl_3$



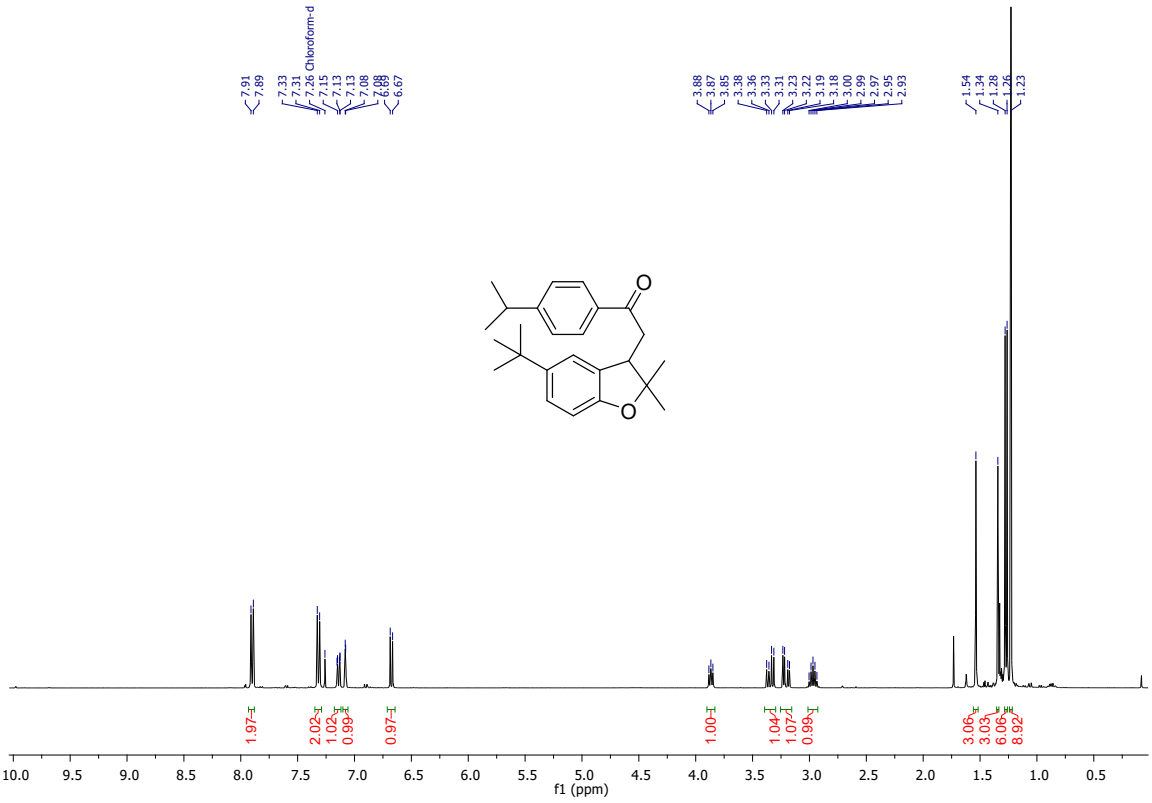
^{1}H NMR (400 MHz) spectrum of **3ok** in $CDCl_3$



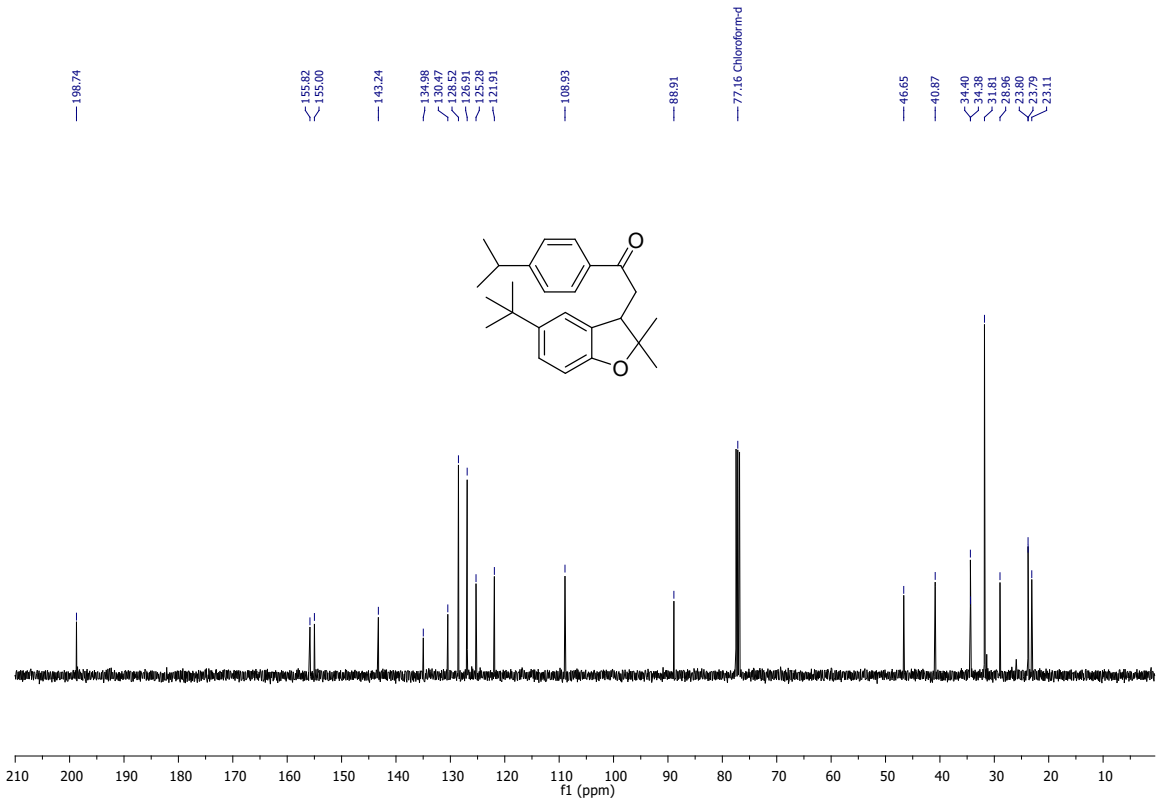
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3ok** in $CDCl_3$



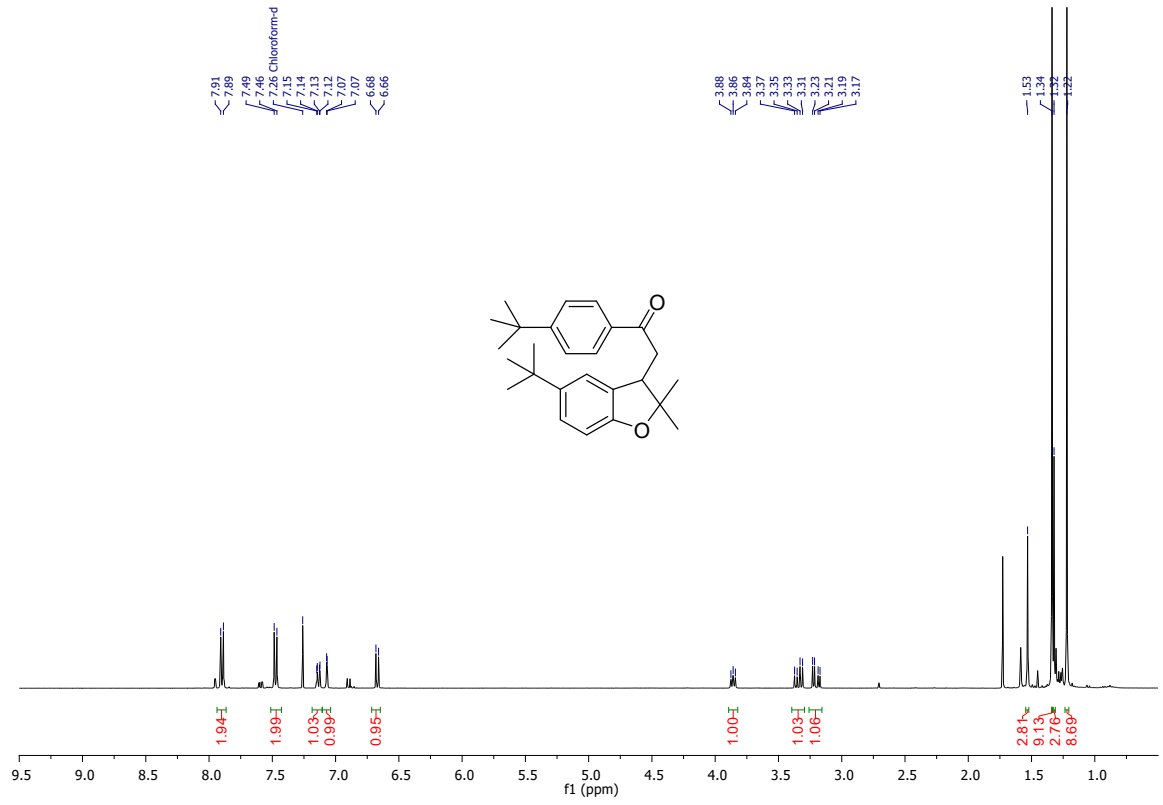
^{1}H NMR (400 MHz) spectrum of **3ek** in $CDCl_3$



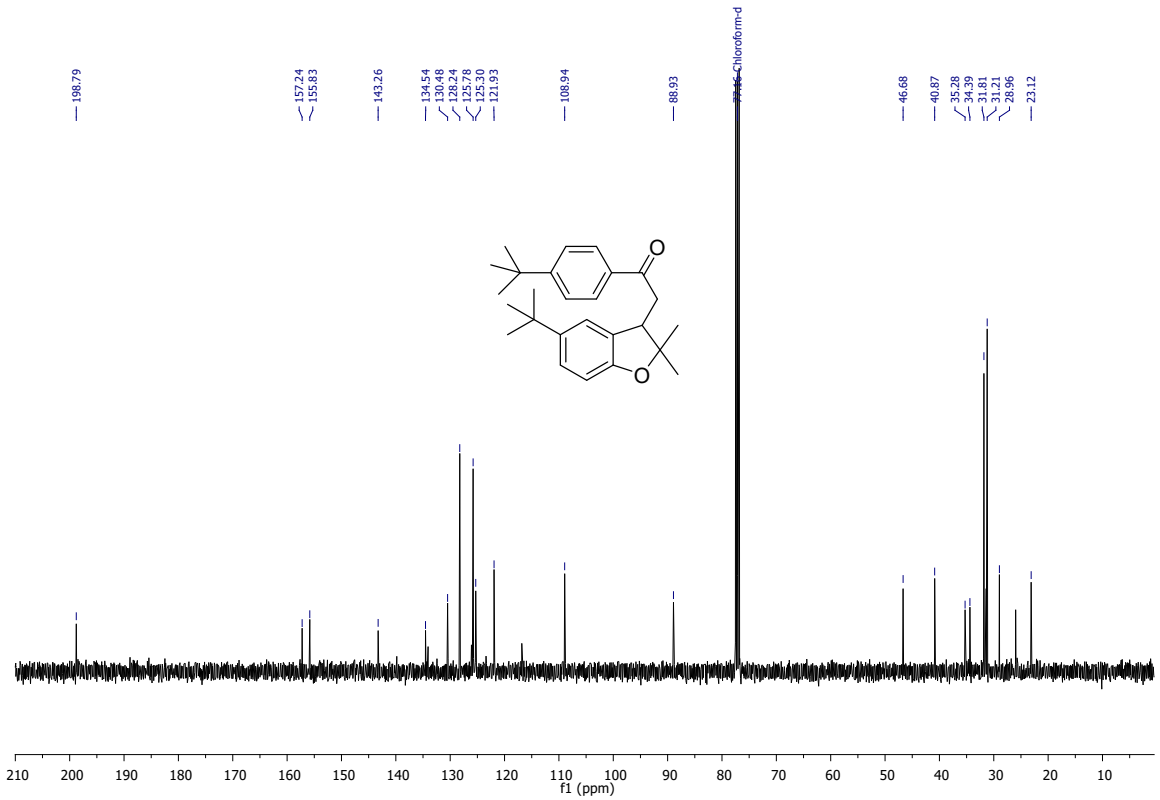
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3ek** in $CDCl_3$



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

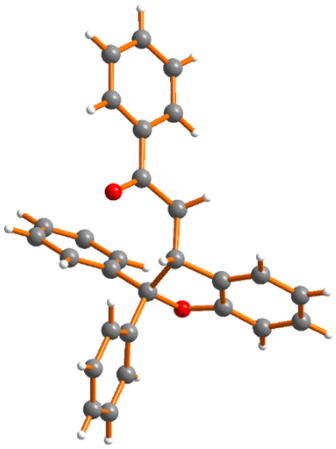


$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3nk** in $CDCl_3$



Crystal structure data:

X-Ray crystal structure of compound **3ag**: Crystal of compound **3ag** were obtained by dissolving the product in an Et_2O mixture 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,[3] the structure was solved with the SHELXT[4] structure solution program using Intrinsic Phasing and refined with the SHELXL[5] refinement package using Least Squares minimisation.[6,7]



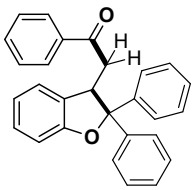


Figure S2: ORTEP diagram of compound **3ag** with ellipsoid shown at the 50% contour percent probability level (**CCDC**-2253565).

Table 3S: Crystal data and structure refinement for **3ag** (**CCDC**-2253565).

Identification code	mo_GS_DSS_PS_P2_80_1_0ma
Empirical formula	$C_{28}H_{22}O_2$
Formula weight	390.45
Temperature/K	299.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.0954(16)
b/Å	15.084(2)
c/Å	13.5172(18)
α/°	90
β/°	93.646(5)
γ/°	90
Volume/Å^3	2054.2(5)
Z	4
ρ_{calc}g/cm^3	1.263
μ/mm^{-1}	0.078
F(000)	824.0
Crystal size/mm^3	0.056 × 0.045 × 0.032
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.05 to 54.452
Index ranges	$-12 \leq h \leq 12$, $-19 \leq k \leq 19$, $-17 \leq l \leq 17$
Reflections collected	51649
Independent reflections	4569 [R_{int} = 0.1255, R_{sigma} = 0.0626]
Data/restraints/parameters	4569/0/272
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0507, wR_2 = 0.1021
Final R indexes [all data]	R_1 = 0.1264, wR_2 = 0.1261
Largest diff. peak/hole / e Å^{-3}	0.15/-0.16

References:

1. I. B. Perry, T. F. Brewer, P. J. Sarver, D. M. Schultz, D. A. DiRocco, D. W. C. MacMillanm *Nature*., 2018, **560** (7716), 70-75.
2. S. Xie, Y. Li, P. Sun, L. Peipei, *Org. Lett*., 2020, **22**, 8774−8779.
3. R. J. Gildea, L. J. Bourhis, O. V. Dolomanov, R. W. Grosse-Kunstleve, H. Puschmann, P. D. Adams and J. a. K. Howard, *J. Appl. Crystallogr.*, 2011, **44**, 1259–1263.
4. 9L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. a. K. Howard and H. Puschmann, *Acta Crystallogr. Sect. Found. Adv*., 2015, **71**, 59–75.
5. G. M. Sheldrick, *Acta Crystallogr. Sect. Found. Adv*., 2015, **71**, 3–8.
6. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. *J. Appl. Cryst*. 2009, **42**, 339-341.
7. Sheldrick, G.M. *Acta Cryst*. 2015, **71**, 3-8.