

Photoinduced 1,2-Dicarbofunctionalization of Alkenes with Organotrifluoroborate Nucleophiles via Radical/Polar Crossover

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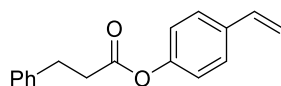
1. General Considerations

1.1 General: All chemical transformations requiring inert atmospheric conditions were carried out using Schlenk line techniques with a 4- or 5-port dual-bank manifold. For blue light irradiation, blue LED strips (light-emitting diode, $\lambda_{\text{max}} = 456 \text{ nm}$) were employed at a distance of $\sim 3\text{-}5 \text{ cm}$ from the reaction vials. A fan was used to ensure reactions remained near room temperature.¹ NMR spectra (^1H , ^{13}C , ^{19}F , ^{11}B) were obtained at 298 °K using 300, 400, or 500 MHz spectrometers. ^1H NMR spectra were referenced to residual, CHCl_3 (δ 7.26) in CDCl_3 , acetone (δ 1.96) in acetone- d_6 , or DMSO- d_6 (δ 2.50). ^{13}C NMR spectra were referenced to CDCl_3 (δ 77.16), acetone- d_6 (δ 30.9), or DMSO- d_6 (δ 39.5). ^{19}F NMR spectra were referenced to hexafluorobenzene (δ -161.64 in CDCl_3). Reactions were monitored by GC/MS, LC/MS, ^1H NMR, and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc or hexanes/acetone as the eluents and visualized using ninhydrin, *p*-anisaldehyde, or KMnO_4 stain as well as UV light. Flash chromatography was accomplished using an automated system (CombiFlash®, UV detector, $\lambda = 254 \text{ nm}$ and 280 nm) with RediSep® R_f silica gel disposable flash columns (60 Å porosity, 40–60 μm) or RediSep R_f Gold® silica gel disposable flash columns (60 Å porosity, 20–40 μm). Accurate mass measurement analyses were conducted using electron ionization (EI) or electrospray ionization (ESI). The signals were mass measured against an internal lock mass reference of perfluorotributylamine (PFTBA) for EI-GCMS and leucine enkephalin for ESI-LCMS. The utilized software calibrates the instruments and reports measurements by use of neutral atomic masses. The mass of the electron is not included. IR spectra were recorded on an FT-IR using either neat oil or solid products. Solvents were purchased and used as is or purified with drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected. UV-vis absorption spectra for the quantum yield reaction were recorded on a Perkin-Elmer Lambda 365 UV-Vis spectrophotometer. Quartz fluorometric cells (1 cm optical path length, Starna) were used in all optical experiments. The quantum yield reaction was conducted on a FS920 spectrofluorometer (Edinburgh Instruments, UK), equipped with R2658P red-sensitive PMT (Hamamatsu), a temperature and stir controller.

1.2 Chemicals: Deuterated NMR solvents were purchased from commercial suppliers and stored over 4 Å molecular sieves. CH_2Cl_2 , EtOAc, hexanes, Et_2O , and toluene were obtained commercially and used as received. When used as dry solvents, THF and CH_2Cl_2 were dried *via* a solvent delivery system. Anhydrous MeCN was obtained from commercial sources and stored over molecular sieves. The photocatalyst $\text{Ir}(\text{ppy})_3$ was synthesized following a reported literature procedure.² All reagents were purchased from commercial suppliers and used without further manipulation. Redox-active esters, organotrifluoroborates, and vinyl(hetero)arenes were prepared according to the literature.³⁻⁶ The synthesis of all new redox-active esters, styrene derivatives, and organotrifluoroborates is reported here. Photoredox-catalyzed reactions were performed using 4 mL vials (1-dram, 15 x 45 mm, 13–425 Green Open Top Cap, TFE septa) or 8 mL vials (2-dram, 17 x 60 mm, 15–425 Green Open Top Cap, TFE Septa).

2. Synthesis of Styrene Derivatives

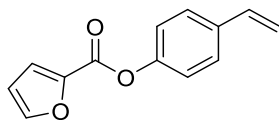
4-Vinylphenyl 3-Phenylpropanoate (1aj)



4-Vinylphenyl 3-phenylpropanoate (**1aj**) was prepared according to the literature.^{6d} To a round-bottom flask was added 4-hydroxybenzaldehyde (200 mg, 1.66 mmol, 1 equiv, 10% in ethylene glycol) and Et_3N (0.7 mL, 5.0 mmol, 3 equiv) in dry CH_2Cl_2 (5.6 mL). The soln was cooled to 0 °C using an ice/water bath. To this mixture was added 3-phenylpropanoyl chloride (0.75 mL, 4.99 mmol, 3 equiv) dropwise, and the reaction was stirred at rt overnight. Upon completion, the mixture was quenched with NaHCO_3 and extracted with CH_2Cl_2 . The combined organic phases were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure to dryness. The resulting oil was purified using an automated system (UV detector, $\lambda = 254 \text{ nm}$ and 280 nm) with RediSep R_f Gold® silica gel disposable flash columns (60 Å porosity, 20–40 μm) and hexanes/EtOAc as eluent to obtain the title compound as a white solid (88 mg, 0.35 mmol, 21%). ^1H NMR (400 MHz, CDCl_3), δ (ppm) = 7.40 (d, $J = 8.6 \text{ Hz}$, 2H), 7.32 (d, $J = 7.5 \text{ Hz}$, 2H), 7.30 – 7.24 (m, 3H), 6.98 (d, $J = 8.6 \text{ Hz}$, 2H), 6.70 (dd, $J = 17.6, 10.9 \text{ Hz}$, 1H), 5.70 (dd, $J =$

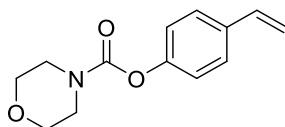
17.5, 0.9 Hz, 1H), 5.24 (dd, $J = 10.9, 0.9$ Hz, 1H), 3.09 (t, $J = 7.7$ Hz, 2H), 2.89 (t, $J = 7.6$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ (ppm) = 171.5, 150.3, 140.2, 136.0, 135.5, 128.7 (2C), 128.6 (2C), 127.3 (2C), 126.6, 121.7 (2C), 114.2, 36.1, 31.1. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu} = 1756, 1602, 1454, 1367, 1287, 1208, 1197, 1166, 1127, 1077, 1015$. **HRMS** (EI) calcd for $\text{C}_{17}\text{H}_{17}\text{O}_2$ [$\text{M}+\text{H}$] $^+$: 252.1150, found 252.1158. **mp** = 34 – 35 °C.

4-Vinylphenyl Furan-2-carboxylate (1ak)



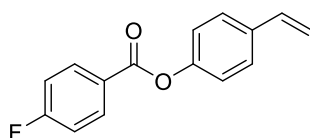
4-Vinylphenyl furan-2-carboxylate (**1ak**) was prepared according to the literature.^{6d} To a round-bottom flask was added 4-hydroxybenzaldehyde (200 mg, 1.66 mmol, 1 equiv, 10% in ethylene glycol) and Et_3N (0.7 mL, 5.0 mmol, 3 equiv) in dry CH_2Cl_2 (5.6 mL). The soln was cooled to 0 °C using an ice/water bath. To this mixture was added furan-2-carbonyl chloride (0.5 mL, 5.0 mmol, 3 equiv) dropwise, and the reaction mixture was stirred at rt overnight. Upon completion, the mixture was quenched with NaHCO_3 and extracted with CH_2Cl_2 . The combined organic phases were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure to dryness. The resulting oil was purified using an automated system (UV detector, $\lambda = 254$ nm and 280 nm) with RediSep R_f Gold[®] silica gel disposable flash columns (60 Å porosity, 20–40 μm) and hexanes/ EtOAc as eluent to obtain the title compound as a white solid (99 mg, 0.46 mmol, 28%). $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm) = 7.68 (s, 1H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 3.6$ Hz, 1H), 7.18 (d, $J = 8.1$ Hz, 2H), 6.72 (dd, $J = 17.6, 10.9$ Hz, 1H), 6.60 (s, 1H), 5.73 (d, $J = 17.6$ Hz, 1H), 5.26 (d, $J = 10.9$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ (ppm) = 157.0, 149.9, 147.3, 144.1, 134.0, 135.8, 127.4 (2C), 121.8 (2C), 119.6, 114.3, 112.3. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu} = 1731, 1506, 1469, 1392, 1291, 1231, 1206, 1195, 1168, 1084, 1069, 1013$. **HRMS** (EI) calcd for $\text{C}_{13}\text{H}_{11}\text{O}_3$ [$\text{M}+\text{H}$] $^+$: 214.0630, found 214.0616. **mp** = 42 – 44 °C.

4-Vinylphenyl Morpholine-4-carboxylate (1al)



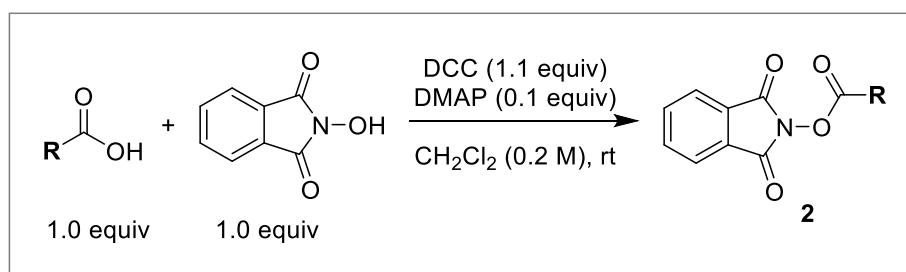
4-Vinylphenyl morpholine-4-carboxylate (**1al**) was prepared according to the literature.^{6d} To a round-bottom flask was added 4-hydroxybenzaldehyde (200 mg, 1.66 mmol, 1 equiv, 10% in ethylene glycol) and Et_3N (0.7 mL, 5.0 mmol, 3 equiv) in dry CH_2Cl_2 (5.6 mL). The soln was cooled to 0 °C using an ice/water bath. To this mixture was added morpholine-4-carbonyl chloride (0.6 mL, 5.0 mmol, 3 equiv) dropwise, and the reaction mixture was stirred at rt overnight. The mixture was quenched with NaHCO_3 and extracted with CH_2Cl_2 . The combined organic phases were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure to dryness. The resulting oil was purified using an automated system (UV detector, $\lambda = 254$ nm and 280 nm) with RediSep R_f Gold[®] silica gel disposable flash columns (60 Å porosity, 20–40 μm) and hexanes/ EtOAc as eluent to obtain the title compound as a white solid (92.3 mg, 0.40 mmol, 24%). $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm) = 7.40 (d, $J = 8.7$ Hz, 2H), 7.07 (d, $J = 8.6$ Hz, 2H), 6.70 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.69 (dd, $J = 17.5, 0.9$ Hz, 1H), 5.23 (dd, $J = 10.9, 0.9$ Hz, 1H), 3.77 – 3.71 (m, 4H), 3.67 (bs, 2H), 3.57 (bs, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ (ppm) = 153.8, 150.9, 136.1, 135.1, 127.2 (2C), 121.8 (2C), 113.9, 66.7 (2C), 45.0, 44.3. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu} = 2859, 1718, 1508, 1454, 1419, 1365, 1277, 1241, 1210, 1198, 1168, 1116, 1064, 1024, 1015$. **HRMS** (EI) calcd for $\text{C}_{13}\text{H}_{16}\text{NO}_3$ [$\text{M}+\text{H}$] $^+$: 233.1052, found 233.1041. **mp** = 55 – 57 °C.

4-Vinylphenyl 4-Fluorobenzoate (1am)



4-Vinylphenyl 4-fluorobenzoate (**1am**) was prepared according to the literature.^{6d} To a round-bottom flask was added 4-hydroxybenzaldehyde (200 mg, 1.66 mmol, 1 equiv, 10% in ethylene glycol) and Et₃N (0.7 mL, 5.0 mmol, 3 equiv) in dry CH₂Cl₂ (5.6 mL). The soln was cooled to 0 °C using an ice/water bath. To this mixture was added 4-fluorobenzoyl chloride (0.6 mL, 5.0 mmol, 3 equiv) dropwise, and the reaction mixture was stirred at rt overnight. The mixture was quenched with NaHCO₃ and extracted with CH₂Cl₂. The combined organic phases were washed with brine, dried (Na₂SO₄), and concentrated under reduced pressure to dryness. The resulting oil was purified using an automated system (UV detector, λ = 254 nm and 280 nm) with RediSep R_f Gold[®] silica gel disposable flash columns (60 Å porosity, 20–40 μm) and hexanes/EtOAc as eluent to obtain the title compound as a white solid (90 mg, 0.37 mmol, 22%). ¹H NMR (400 MHz, CDCl₃), δ (ppm) = 8.23 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.23 – 7.14 (m, 4H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 5.27 (d, *J* = 10.9 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃), δ (ppm) = -104.38. ¹³C NMR (101 MHz, CDCl₃), δ (ppm) = 166.3 (d, *J*_{C-F} = 255.1 Hz), 164.3, 150.5, 136.0, 135.7, 133.0 (d, *J*_{C-F} = 9.4 Hz, 2C), 127.4 (2C), 125.9 (d, *J*_{C-F} = 2.9 Hz), 121.9 (2C), 115.8, 115.2 (d, *J*_{C-F} = 22.0 Hz, 2C). FT-IR (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 1732, 1602, 1508, 1264, 1219, 1207, 1197, 1167, 1155, 1075, 1015. HRMS (EI) calcd for C₁₅H₁₂O₂ [M+H]⁺: 242.0743, found 242.0740. mp = 94 – 95 °C.

3. Synthesis of Redox-Active Esters

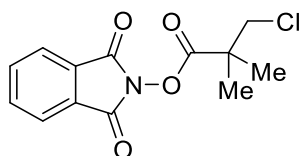


Redox-active esters were prepared according to the literature.³

General Procedure A

To a round-bottom flask equipped with a stir bar was added the corresponding carboxylic acid (if solid) (1.0 equiv), *N*-hydroxyphthalimide (1.0 equiv), and DMAP (0.1 equiv). The flask was then charged with CH₂Cl₂ or EtOAc (0.2 M). At this point, carboxylic acid (1.0 equiv) was added via syringe (if liquid). DCC (1.1 equiv) was added, and the reaction was allowed to stir at rt until full consumption of the starting material. The mixture was then filtered over Celite and rinsed with additional CH₂Cl₂. The solvent was removed under reduced pressure, and the crude material was purified via flash chromatography (UV detector, λ = 254 nm and 280 nm) with RediSep R_f Gold[®] silica gel disposable flash columns (60 Å porosity, 20–40 μm).

1,3-Dioxoisindolin-2-yl 4-Chloro-2,2-dimethylbutanoate (**2g**)

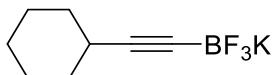


Prepared using carboxylic acid (2.0 g, 15 mmol, 1.0 equiv). After chromatographic purification (0–10% EtOAc in hexanes), the title compound was obtained as a white solid (2.8 g, 9.9 mmol, 68%). ¹H NMR (400 MHz, CDCl₃), δ (ppm) = 7.93 – 7.84 (m, 2H), 7.84 – 7.75 (m, 2H), 3.77 (s, 2H), 1.53 (s, 6H). ¹³C NMR (101 MHz, CDCl₃), δ (ppm) = 171.6, 161.9 (2C), 134.9 (2C), 129.1 (2C), 124.1 (2C), 50.9, 44.5, 23.3 (2C). FT-IR (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 1810, 1786, 1741, 1468, 1370, 1290, 1187, 1160, 1056, 1019. HRMS (EI) calcd for C₁₃H₁₃ClNO₄ [M+H]⁺: 282.0533, found 282.0525. m.p. = 54 – 56 °C

4. Synthesis of Potassium Organotrifluoroborates

Potassium organotrifluoroborate salts **3a**, **3k-o** were prepared from the corresponding acetylene derivatives according to the literature.⁴ Organotrifluoroborates **3p-ad** were synthesized from the corresponding boronic acids following a reported literature procedure.⁵

(Cyclohexylethynyl)trifluoro- λ^4 -borane, Potassium Salt (**3n**)

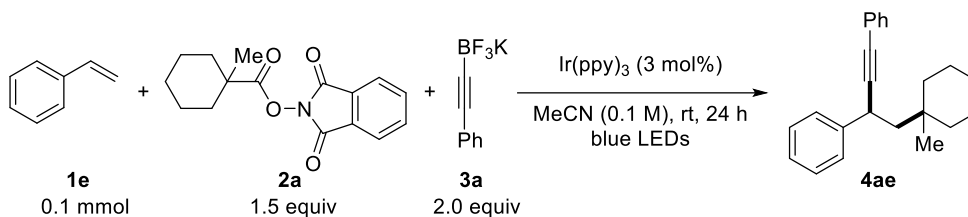


(Cyclohexylethynyl)trifluoro- λ^4 -borane, potassium salt (**3n**) was prepared according to the literature.⁴ To a round-bottom flask was added 2-cyclohexylacetylene (1.0 mL, 7.65 mmol, 1 equiv) in dry THF (19.0 mL, 0.4 M), and the temperature was maintained at -78 °C using a dry ice/acetone bath under inert atmosphere. To this soln was added *n*-BuLi (3.1 mL, 7.6 mmol, 1 equiv, 2.5 M in hexanes) dropwise, and the mixture was stirred for 30 min at -78 °C. Trimethylborate (1.3 mL, 11 mmol, 1.5 equiv) was then added dropwise at -78 °C, and the soln was stirred at this temperature for 30 min. The reaction was then allowed to warm to -30 °C and stirred for 30 min. An aq soln of KHF₂ (5.0 g, 46 mmol, 6 equiv, 4.5 M) was added to the vigorously stirred soln at -30 °C. The resulting mixture was allowed to warm to rt and stirred for 2 h. The solvents were removed under reduced pressure, and the resulting white solid was dried under high vacuum to remove all the water. The solid was dissolved in hot acetone, and the non-soluble solids were filtered off. The acetone solution was removed under reduced pressure to afford a fluffy white solid. This solid was then dissolved in hot acetone and precipitated with Et₂O, after which the soln was cooled to -20 °C to allow complete precipitation of the solid. The title product was collected as a white crystalline solid (819 mg, 3.82 mmol, 50%). ¹H NMR (400 MHz, DMSO), δ (ppm) = 2.19 – 2.08 (m, 1H), 1.72 – 1.56 (m, 4H), 1.53 – 1.39 (m, 1H), 1.31 – 1.15 (m, 5H). ¹⁹F NMR (376 MHz, DMSO), δ (ppm) = -130.79. ¹¹B NMR (128 MHz, DMSO), δ (ppm) = -1.9. ¹³C NMR (101 MHz, DMSO), δ (ppm) = 33.14 (2C), 29.13 (2C), 25.57 (2C), 24.66 (2C). FT-IR (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2931, 1115, 1005. HRMS (ESI) calcd for C₈H₁₁BF₃ [M-K⁺]: 175.0906, found 175.0899.

5. Reaction Optimization

To an 8 mL reaction vial (2-dram, 17 x 60 mm) equipped with a magnetic stir bar was added the corresponding amounts of 1-methylcyclohexyl redox active ester, phenylethynyltrifluoroborate, and Ir(ppy)₃. The vial was sealed with a cap containing a TFE-lined silicone septum and then evacuated and backfilled with nitrogen three times. Corresponding amounts of solvent and styrene were then added via syringe. The reaction was irradiated for 24 h with blue LEDs for 16 h (as described in the Reaction Workflow section) whereby the temperature was maintained at approximately 27 °C via cooling with a fan. Upon completion, the reaction mixture was concentrated to dryness and then analyzed by crude ¹NMR using equimolar (0.1 mmol) trimethoxybenzene as internal standard.

Table S1. Supplementary optimization of loadings and reaction concentration. ^aYields determined by ¹H NMR using 0.1 mmol trimethoxybenzene as internal standard.



Entry	Deviation from Std. Conditions	Yield ^a	Entry	Deviation from Std. Conditions	Yield ^a
1	none	59 %	6	0.05 M MeCN	n. r.
2	3 equiv RBF ₃ K	n. r.	7	DSMO instead of MeCN	22 %
3	1 mol % Ir (ppy) ₃	32 %	8	CHCl ₃ instead of MeCN	n.r.
4	10 mol % Ir (ppy) ₃	36 %	9	THF instead of MeCN	44 %
5	0.2 M MeCN	n. r.			

6. Photoinduced Dicarbofunctionalization of Alkenes

6.1 Reaction Workflow

All photoredox reactions were performed using blue LED strips (light-emitting diode, $\lambda_{\text{max}} = 456 \text{ nm}$) at a distance of ~ 3-5 cm from the reaction vials. A fan was used to ensure reactions remained near rt. A typical reaction setup is shown below:

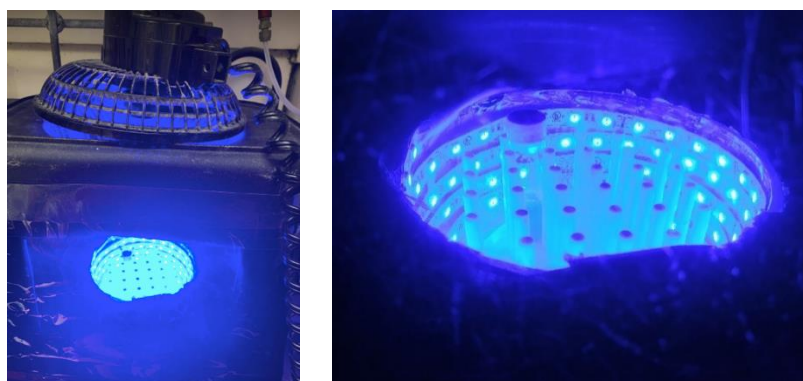
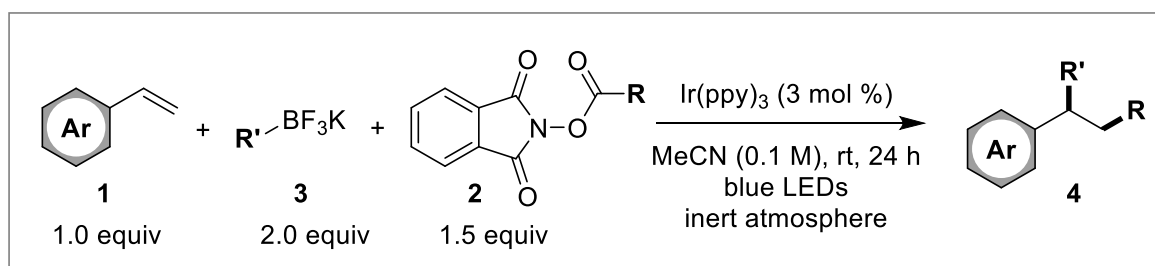


Figure 1. Reaction setup for photoinduced dicarbofunctionalization reactions.

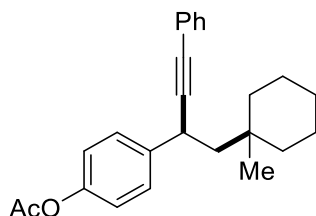
6.2 General Procedure B:



To an 8 mL reaction vial (2-dram, 17 x 60 mm) equipped with a magnetic stir bar was added styrene derivative (0.3 mmol, 1.0 equiv, if solid or non-volatile liquid), redox-active ester (0.45 mmol, 1.5 equiv), potassium organotrifluoroborate salt (0.6 mmol, 2.0 equiv), and Ir(ppy)₃ (6 mg, 0.009 mmol, 3.0 mol %, 0.03 equiv) under

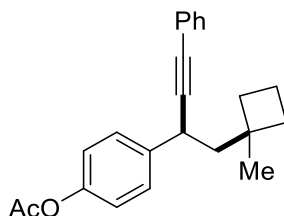
air. The vial was sealed with a cap containing a TFE-lined silicone septum, evacuated, and back-filled with nitrogen. After this process was repeated 3 times, anhyd MeCN (3 mL, 0.1 M) was added followed by styrene via syringe (0.3 mmol, 1.0 equiv, if volatile liquid). The reaction was irradiated for 24 h using blue LED strips ($\lambda_{\max} = 456$ nm, distance lamp–vial ~ 3 -5 cm), whereby the temperature was maintained at approximately 25 °C via cooling with a fan. Upon completion, the mixture was taken to dryness and then purified using an automated system (UV detector, $\lambda = 254$ nm and 280 nm) with RediSep Rf Gold[®] silica gel disposable flash columns (60 Å porosity, 20–40 μm) with hexanes/EtOAc as eluent.

4-(1-(1-Methylcyclohexyl)-4-phenylbut-3-yn-2-yl)phenyl Acetate (4a)



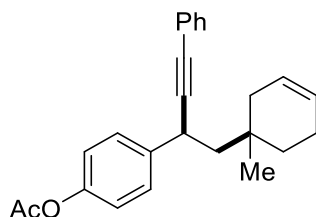
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (89 mg, 0.25 mmol, 82%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.46 – 7.39 (m, 4H), 7.33 – 7.27 (m, 3H), 7.06 (d, $J = 8.6$ Hz, 2H), 3.91 (dd, $J = 10.2, 3.2$ Hz, 1H), 2.31 (s, 3H), 2.03 (dd, $J = 13.9, 10.1$ Hz, 1H), 1.63 (dd, $J = 14.0, 3.3$ Hz, 1H), 1.62 – 1.53 (m, 2H), 1.53 – 1.32 (m, 8H), 1.12 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 169.7, 149.3, 142.0, 131.5 (2C), 128.5 (2C), 128.3 (2C), 127.8, 124.0, 121.7 (2C), 93.2, 83.3, 51.1, 38.5, 38.1, 33.9, 33.4, 26.5, 25.9, 22.2 (2C), 21.3. FT-IR (cm⁻¹, neat, ATR): $\tilde{\nu} = 2924, 2860, 1761, 1691, 1599, 1504, 1491, 1443, 1369, 1198, 1166, 1102, 1018$. HRMS (EI) calcd for C₂₅H₂₉O₂ [M+H]⁺: 361.2168, found 361.2160.

4-(1-(1-Methylcyclobutyl)-4-phenylbut-3-yn-2-yl)phenyl Acetate (4b)



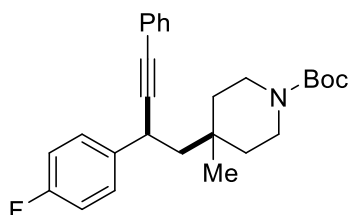
Prepared according to *General Procedure B* using the corresponding redox-active ester (117 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–10% EtOAc in hexanes), the title compound was obtained as a colorless oil (59 mg, 0.180 mmol, 59%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.47 – 7.39 (m, 4H), 7.33 – 7.26 (m, 3H), 7.10 – 7.03 (m, 2H), 3.87 (dd, $J = 10.3, 4.7$ Hz, 1H), 2.30 (s, 3H), 2.25 – 2.15 (m, 1H), 2.07 (dd, $J = 13.5, 10.3$ Hz, 1H), 1.97 (dddd, $J = 15.8, 10.5, 5.0, 2.5$ Hz, 1H), 1.89 – 1.75 (m, 4H), 1.73 – 1.61 (m, 1H), 1.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.7, 149.3, 141.0, 131.5 (2C), 128.5 (2C), 128.3 (2C), 127.8, 124.0, 121.6 (2C), 91.9, 83.6, 51.7, 38.9, 34.6, 34.6, 34.4, 25.6, 21.3, 15.8. FT-IR (cm⁻¹, neat, ATR): $\tilde{\nu} = 2950, 2923, 1759, 1503, 1489, 1368, 1196, 1017, 754$. HRMS (ESI) calcd for C₂₃H₂₅O₂ [M+H]⁺: 333.1855, found 333.1852.

4-(1-(1-Methylcyclohex-3-en-1-yl)-4-phenylbut-3-yn-2-yl)phenyl Acetate (4c)



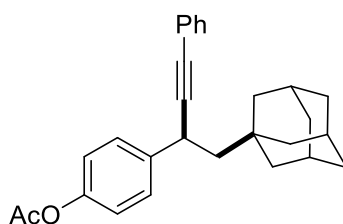
Prepared according to *General Procedure B* using the corresponding redox-active ester (128 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–15% acetone in hexanes), the title compound was obtained as a colorless oil (50 mg, 0.14 mmol, 46%, isolated as an inseparable 1:1 diastereomeric mixture). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.41 (ddt, J = 6.6, 4.0, 2.1 Hz, 4H), 7.29 (dd, J = 5.1, 2.0 Hz, 3H), 7.07 – 7.02 (m, 2H), 5.72 – 5.55 (m, 2H), 3.96 – 3.88 (m, 1H), 2.30 (s, 3H), 2.24 – 2.12 (m, 1H), 2.10 – 1.80 (m, 4H), 1.72 – 1.64 (m, 1H), 1.64 – 1.57 (m, 1H), 1.57 – 1.45 (m, 1H), 1.13 (d, J = 7.4 Hz, 3H). **Diastereomer 1** $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.7, 149.3, 141.8, 131.5 (2C), 128.5 (2C), 128.4 (2C), 127.9, 125.8, 125.5, 124.0, 121.7 (2C), 93.1, 83.4, 50.5, 38.2, 33.8, 33.7, 32.4, 25.3, 22.9, 21.3. **Diastereomer 2** $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.7, 149.3, 141.8, 131.5 (2C), 128.5 (2C), 128.4 (2C), 127.9, 126.3, 125.9, 124.0, 121.7 (2C), 93.1, 83.6, 50.4, 37.9, 34.1, 33.6, 32.3, 25.3, 22.8, 21.3. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2915, 1759, 1503, 1490, 1368, 1197, 1165, 1017. **HRMS** (ESI) calcd for $\text{C}_{25}\text{H}_{27}\text{O}_2$ $[\text{M}+\text{H}]^+$: 359.2011, found 359.2008.

tert-Butyl 4-(2-(4-Fluorophenyl)-4-phenylbut-3-yn-1-yl)-4-methylpiperidine-1-carboxylate (4d)



Prepared according to *General Procedure B* using the corresponding redox-active ester (175 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (36.6 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–20% EtOAc in hexanes), the title compound was obtained as a colorless oil (75.2 mg, 0.178 mmol, 60%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.42 – 7.34 (m, 4H), 7.33 – 7.27 (m, 3H), 7.08 – 6.96 (m, 2H), 3.91 (dd, J = 10.1, 3.5 Hz, 1H), 3.62 (dd, J = 13.2, 6.3 Hz, 1H), 3.56 – 3.46 (m, 1H), 3.35 – 3.23 (m, 2H), 2.06 (dd, J = 14.0, 10.1 Hz, 1H), 1.76 – 1.67 (m, 1H), 1.61 (dd, J = 14.0, 3.5 Hz, 1H), 1.55 – 1.33 (m, 12H), 1.17 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.0, 160.5, 155.1, 139.5 (2C), 131.5, 128.9 (2C), 128.4, 128.1, 123.6, 115.7, 115.5, 92.5, 83.8, 79.4, 50.7, 39.9, 37.6, 37.0, 33.2, 32.5, 29.8, 28.6 (3C), 24.2. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -116.34. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2925, 1684, 1506, 1422, 1364, 1248, 1222, 1156, 755. **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{25}\text{FN}$ $[\text{M}-\text{Boc}+2\text{H}]^+$: 322.1971, found 322.1971.

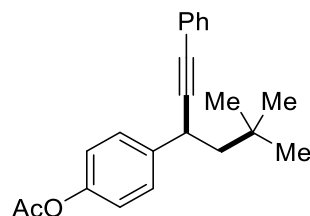
4-(1-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-4-phenylbut-3-yn-2-yl)phenyl Acetate (4e)



Prepared according to *General Procedure B* using the corresponding redox-active ester (146 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv)

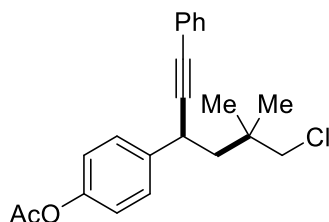
with an irradiation time of 24 h. After chromatographic purification (0–15% acetone in hexanes), the title compound was obtained as a colorless oil (84 mg, 0.21 mmol, 70%). **¹H NMR** (400 MHz, CDCl₃) δ (ppm) = 7.42 (dt, *J* = 6.6, 2.3 Hz, 4H), 7.33 – 7.26 (m, 3H), 7.05 (d, *J* = 8.2 Hz, 2H), 3.93 (dd, *J* = 10.2, 3.1 Hz, 1H), 2.30 (s, 3H), 2.03 – 1.97 (m, 3H), 1.83 (dd, *J* = 14.0, 10.1 Hz, 1H), 1.78 – 1.62 (m, 12H), 1.50 (dd, *J* = 13.9, 3.1 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 169.7, 149.2, 142.0, 131.5 (2C), 128.5 (2C), 128.3 (2C), 127.8, 124.1, 121.6 (2C), 93.4, 83.4, 54.2, 42.8 (3C), 37.2 (3C), 33.4, 32.5, 28.9 (3C), 21.3. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2899, 2845, 1760, 1502, 1489, 1199, 1166, 755. **HRMS** (ESI) calcd for C₂₈H₃₁O₂ [M+H]⁺: 399.2324, found 399.2318.

4-(5,5-Dimethyl-1-phenylhex-1-yn-3-yl)phenyl Acetate (4f)



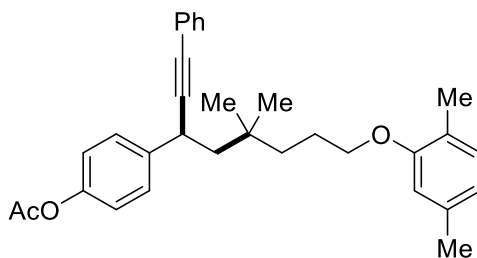
Prepared according to *General Procedure B* using the corresponding redox-active ester (111 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (64 mg, 0.20 mmol, 66%). **¹H NMR** (400 MHz, CDCl₃) δ (ppm) = 7.46 – 7.38 (m, 4H), 7.33 – 7.26 (m, 3H), 7.06 (d, *J* = 8.5 Hz, 2H), 3.89 (dd, *J* = 10.2, 3.4 Hz, 1H), 2.30 (s, 3H), 1.93 (dd, *J* = 13.8, 10.2 Hz, 1H), 1.65 (dd, *J* = 13.8, 3.4 Hz, 1H), 1.08 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ (ppm) = 169.7, 149.3, 141.8, 131.5 (2C), 128.5 (2C), 128.3 (2C), 127.8, 124.0, 121.7 (2C), 93.1, 83.6, 53.1, 34.5, 31.5, 30.0 (3C), 21.3. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2954, 2866, 1762, 1692, 1599, 1504, 1490, 1476, 1367, 1199, 1166, 1103, 1018. **HRMS** (EI) calcd for C₂₂H₂₅O₂ [M+H]⁺: 321.1855, found 321.1854.

4-(6-Chloro-5,5-dimethyl-1-phenylhex-1-yn-3-yl)phenyl Acetate (4g)



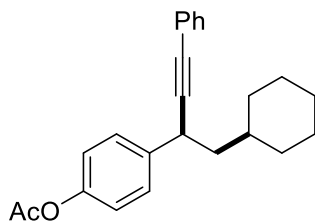
Prepared according to *General Procedure B* using the corresponding redox-active ester (127 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (64 mg, 0.18 mmol, 60%). **¹H NMR** (400 MHz, CDCl₃) δ (ppm) = 7.48 – 7.41 (m, 4H), 7.35 – 7.28 (m, 3H), 7.07 (d, *J* = 8.5 Hz, 2H), 3.92 (dd, *J* = 10.8, 3.5 Hz, 1H), 3.65 – 3.53 (m, 2H), 2.31 (s, 3H), 2.02 (dd, *J* = 14.1, 10.8 Hz, 1H), 1.79 (dd, *J* = 14.1, 3.5 Hz, 1H), 1.19 (d, *J* = 1.9 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ (ppm) = 169.6, 149.5, 140.9, 131.6 (2C), 128.5 (2C), 128.4 (2C), 128.1, 123.6, 121.8 (2C), 91.9, 84.1, 55.3, 47.9, 36.2, 34.0, 26.1, 25.9, 21.3. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2963, 1760, 1598, 1504, 1490, 1470, 1443, 1387, 1368, 1200, 1167, 1018. **HRMS** (EI) calcd for C₂₂H₂₄ClO₂ [M+H]⁺: 354.1387, found 354.1404.

4-(8-(2,5-Dimethylphenoxy)-5,5-dimethyl-1-phenyloct-1-yn-3-yl)phenyl Acetate (4h)



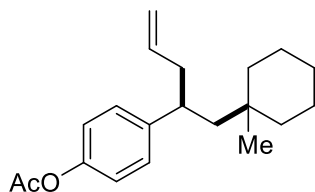
Prepared according to *General Procedure B* using the corresponding redox-active ester (178 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (108 mg, 0.23 mmol, 77%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = 7.50 – 7.40 (m, 4H), 7.28 (dd, J = 5.2, 2.0 Hz, 3H), 7.09 (d, J = 8.6 Hz, 2H), 7.04 (d, J = 7.4 Hz, 1H), 6.69 (d, J = 6.8 Hz, 1H), 6.62 (s, 1H), 4.00 – 3.88 (m, 3H), 2.33 (d, J = 3.7 Hz, 6H), 2.23 (s, 3H), 2.02 (dd, J = 13.9, 10.3 Hz, 1H), 1.96 – 1.74 (m, 2H), 1.70 (dd, J = 14.0, 3.3 Hz, 1H), 1.65 – 1.57 (m, 2H), 1.14 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 169.7, 157.2, 149.3, 141.7, 136.5, 131.5 (2C), 130.4, 128.5 (2C), 128.3 (2C), 127.9, 123.9, 123.7, 121.7 (2C), 120.7, 112.1, 92.9, 83.5, 68.6, 50.8, 38.4, 34.0, 33.7, 27.9, 27.9, 24.5, 21.5, 21.3, 16.0. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2954, 2869, 1762, 1585, 1507, 1490, 1471, 1443, 1415, 1389, 1368, 1265, 1200, 1166, 1130, 1018. **HRMS** (EI) calcd for C₃₂H₃₇O₃ [M+H]⁺: 496.2743, found 496.2751.

4-(1-Cyclohexyl-4-phenylbut-3-yn-2-yl)phenyl Acetate (4i)



Prepared according to *General Procedure B* using the corresponding redox-active ester (123 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–15% EtOAc in hexanes), the title compound was obtained as a colorless oil (42 mg, 0.120 mmol, 40%). **¹H NMR** (400 MHz, CDCl₃) δ (ppm) = 7.49 – 7.41 (m, 4H), 7.32 (dd, J = 5.2, 2.0 Hz, 3H), 7.11 – 7.04 (m, 2H), 3.95 (dd, J = 9.8, 5.2 Hz, 1H), 2.33 (s, 3H), 1.92 (d, J = 12.8 Hz, 1H), 1.84 – 1.57 (m, 7H), 1.37 – 1.17 (m, 3H), 1.06 – 0.91 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 169.7, 149.4, 140.5, 131.8 (2C), 128.5 (2C), 128.3 (2C), 127.9, 123.9, 121.6 (2C), 91.7, 83.3, 46.7, 35.7, 35.3, 33.9, 32.7, 26.8, 26.4, 26.3, 21.3. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2921, 2849, 1759, 1503, 1490, 1447, 1368, 1196, 1165. **HRMS** (EI) calcd for C₂₄H₂₆O₂ [M]⁺: 346.1933, found 346.1917.

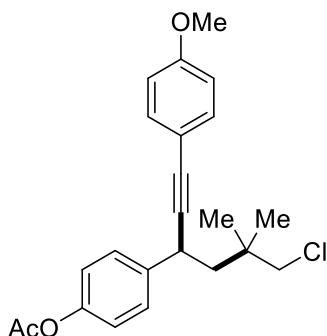
4-(1-(1-Methylcyclohexyl)pent-4-en-2-yl)phenyl Acetate (4j)



Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (89 mg, 0.60 mmol, 2.0 equiv), Ir(dtbbpy)(ppy)₂ (8 mg, 0.009 mmol, 3.0 mol %, 0.03 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a yellow oil (47 mg, 0.16 mmol, 53%).

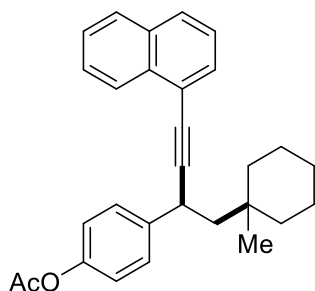
$^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm) = 7.17 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 5.60 (ddt, J = 17.1, 10.1, 7.0 Hz, 1H), 4.98 – 4.87 (m, 2H), 2.74 (qd, J = 7.5, 3.3 Hz, 1H), 2.27 (s, 3H), 1.69 (dd, J = 14.2, 8.6 Hz, 1H), 1.60 (dd, J = 14.2, 3.4 Hz, 1H), 1.49 – 1.32 (m, 4H), 1.32 – 1.18 (m, 6H), 1.06 – 1.01 (m, 2H), 0.74 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ (ppm) = 169.6, 148.7, 145.2, 137.3, 128.7 (2C), 121.2 (2C), 116.1, 48.1, 44.4, 41.2, 38.6, 38.5, 33.8, 26.5, 25.5, 22.2, 22.0, 21.3. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2923, 2849, 1766, 1640, 1606, 1507, 1446, 1368, 1198, 1166, 1100, 1017. **HRMS** (EI) calcd for $\text{C}_{20}\text{H}_{28}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 323.1982, found 323.1978.

4-(6-Chloro-1-(4-methoxyphenyl)-5,5-dimethylhex-1-yn-3-yl)phenyl Acetate (4k)



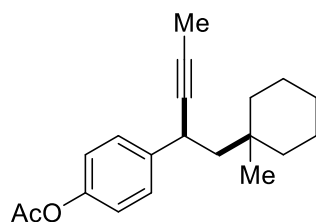
Prepared according to *General Procedure B* using the corresponding redox-active ester (127 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (143 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–10% EtOAc in hexanes), the title compound was obtained as a colorless oil (94 mg, 0.24 mmol, 81%). $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm) = 7.44 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.89 (dd, J = 10.8, 3.5 Hz, 1H), 3.80 (s, 3H), 3.67 – 3.53 (m, 2H), 2.30 (s, 3H), 1.99 (dd, J = 14.1, 10.8 Hz, 1H), 1.77 (dd, J = 14.1, 3.5 Hz, 1H), 1.17 (d, J = 3.1 Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ (ppm) = 169.7, 159.5, 149.4, 141.2, 132.9 (2C), 128.5 (2C), 121.7 (2C), 115.8, 114.0 (2C), 90.3, 83.9, 55.4, 55.4, 47.9, 36.2, 34.0, 26.2, 25.9, 21.3. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2961, 1758, 1605, 1508, 1466, 1442, 1368, 1290, 1246, 1195, 1165, 1105, 1030, 1018. **HRMS** (EI) calcd for $\text{C}_{23}\text{H}_{26}\text{ClO}_3$ $[\text{M}+\text{H}]^+$: 385.1570, found 385.1555.

4-(1-(1-Methylcyclohexyl)-4-(naphthalen-1-yl)but-3-yn-2-yl)phenyl Acetate (4l)



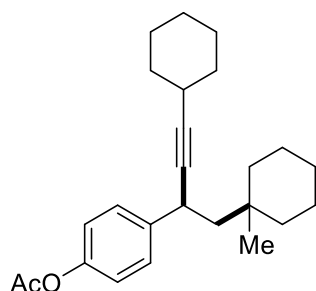
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (155 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (56 mg, 0.14 mmol, 45%). $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm) = 8.32 (d, J = 8.0 Hz, 1H), 7.84 (dd, J = 7.9, 1.6 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.64 (dd, J = 7.2, 1.2 Hz, 1H), 7.57 – 7.48 (m, 4H), 7.41 (dd, J = 8.3, 7.1 Hz, 1H), 7.09 (d, J = 8.5 Hz, 2H), 4.07 (dd, J = 10.1, 3.2 Hz, 1H), 2.31 (s, 3H), 2.13 (dd, J = 14.0, 10.1 Hz, 1H), 1.73 (dd, J = 14.0, 3.2 Hz, 1H), 1.69 – 1.54 (m, 2H), 1.52 – 1.37 (m, 8H), 1.17 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ (ppm) = 169.7, 149.3, 142.2, 133.6, 133.3, 130.2, 128.5 (2C), 128.3, 128.2, 126.7, 126.4, 126.4, 125.4, 121.8 (2C), 121.7, 98.2, 81.6, 51.5, 38.5, 38.3, 33.9, 33.8, 26.5, 25.8, 22.2 (2C), 21.3. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2923, 2850, 1760, 1504, 1454, 1396, 1368, 1265, 1196, 1165, 1017. **HRMS** (EI) calcd for $\text{C}_{29}\text{H}_{31}\text{O}_2$ $[\text{M}+\text{H}]^+$: 411.2324, found 411.2325.

4-(1-(1-Methylcyclohexyl)pent-3-yn-2-yl)phenyl Acetate (4m)



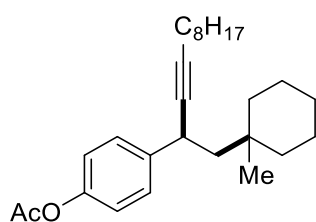
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (87.6 mg 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–15% acetone in hexanes), the title compound was obtained as a colorless oil (49.3 mg, 0.165 mmol, 55%). **¹H NMR** (400 MHz, CDCl₃) δ (ppm) = 7.38 – 7.29 (m, 2H), 7.05 – 6.96 (m, 2H), 3.62 (dt, J = 9.5, 3.0 Hz, 1H), 2.29 (s, 3H), 1.89 – 1.83 (m, 1H), 1.81 (d, J = 2.4 Hz, 3H), 1.56 – 1.38 (m, 7H), 1.38 – 1.22 (m, 4H), 1.01 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 169.7, 149.1, 142.8, 128.4 (2C), 121.5 (2C), 82.6, 78.4, 51.1, 38.4, 38.2, 33.8, 32.9, 26.6, 25.7, 22.2, 22.1, 21.3, 3.8. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2922, 2858, 1762, 1504, 1368, 1200, 1165, 1018, 911. **HRMS** (ESI) calcd for C₂₀H₂₇O₂ [M+H]⁺: 299.2011, found 299.2010.

4-(4-Cyclohexyl-1-(1-methylcyclohexyl)but-3-yn-2-yl)phenyl Acetate (4n)



Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (128 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (52 mg, 0.14 mmol, 48%). **¹H NMR** (400 MHz, CDCl₃) δ (ppm) = 7.35 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H), 3.66 (dt, J = 10.2, 2.6 Hz, 1H), 2.43 – 2.32 (m, 1H), 2.29 (s, 3H), 1.89 – 1.76 (m, 3H), 1.74 – 1.66 (m, 2H), 1.59 – 1.48 (m, 3H), 1.48 – 1.27 (m, 14H), 1.05 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ (ppm) = 169.7, 149.0, 143.0, 128.4 (2C), 121.4 (2C), 87.5, 83.1, 51.4, 38.5, 38.1, 33.8, 33.0 (2C), 32.8, 29.4, 26.6, 26.1, 25.9, 25.1, 22.2 (3C), 21.3. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2925, 2854, 1762, 1675, 1599, 1504, 1449, 1368, 1194, 1164, 1103, 1045, 1011. **HRMS** (EI) calcd for C₂₅H₃₅O₂ [M+H]⁺: 367.2637, found 367.2655.

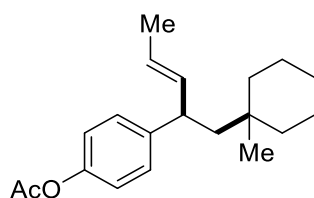
4-(1-(1-Methylcyclohexyl)dodec-3-yn-2-yl)phenyl Acetate (4o)



Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (146 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (56 mg, 0.14 mmol, 47%). **¹H NMR** (400 MHz, CDCl₃) δ (ppm) = 7.34 (d, J = 8.5 Hz,

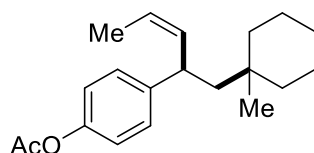
2H), 7.01 (d, $J = 8.6$ Hz, 2H), 3.64 (dd, $J = 10.1, 2.8$ Hz, 1H), 2.29 (s, 3H), 2.18 (td, $J = 7.0, 2.2$ Hz, 2H), 1.85 (dd, $J = 13.9, 10.0$ Hz, 1H), 1.56 – 1.47 (m, 5H), 1.45 – 1.26 (m, 18H), 1.03 (s, 3H), 0.92 – 0.85 (m, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ (ppm) = 169.7, 149.1, 142.9, 128.4 (2C), 121.5 (2C), 83.3 (2C), 51.3, 38.4, 38.2, 33.8, 32.9, 32.0, 29.4, 29.3, 29.1, 29.0, 26.6, 25.8, 22.8, 22.2, 22.2, 21.3, 19.0, 14.3. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu} = 2924, 2855, 1763, 1675, 1599, 1504, 1454, 1369, 1277, 1194, 1164, 1103, 1044, 1011$. **HRMS** (EI) calcd for $\text{C}_{27}\text{H}_{41}\text{O}_2$ [$\text{M}+\text{H}$] $^+$: 397.3107, found 397.3094.

(E)-4-(1-(1-Methylcyclohexyl)pent-3-en-2-yl)phenyl Acetate (4p)



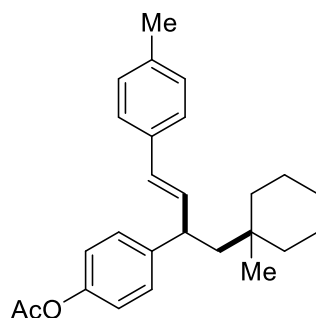
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (89 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (33 mg, 0.11 mmol, 36%). $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm) = 7.18 (d, $J = 8.5$ Hz, 2H), 6.99 (d, $J = 8.5$ Hz, 2H), 5.56 (ddd, $J = 15.2, 8.2, 1.6$ Hz, 1H), 5.41 – 5.29 (m, 1H), 3.40 (q, $J = 6.9$ Hz, 1H), 2.28 (s, 3H), 1.67 (d, $J = 6.4$ Hz, 2H), 1.62 (dd, $J = 6.4, 1.6$ Hz, 3H), 1.45 – 1.32 (m, 5H), 1.31 – 1.22 (m, 3H), 1.21 – 1.08 (m, 2H), 0.84 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ (ppm) = 169.7, 148.6, 145.1, 137.5, 128.5 (2C), 123.8, 121.4 (2C), 48.6, 44.6, 38.7, 38.6, 33.9, 26.6, 25.6, 22.1 (2C), 21.3, 18.0. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu} = 2922, 2853, 1766, 1605, 1505, 1451, 1368, 1197, 1166, 1100, 1044, 1017$. **HRMS** (EI) calcd for $\text{C}_{20}\text{H}_{29}\text{O}_2$ [$\text{M}+\text{H}$] $^+$: 301.2168, found 301.2177.

(Z)-4-(1-(1-Methylcyclohexyl)pent-3-en-2-yl)phenyl Acetate (4q)



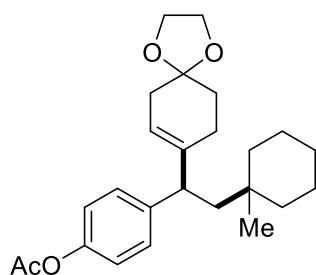
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (89 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (31 mg, 0.10 mmol, 34%). $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm) = 7.21 (d, $J = 8.5$ Hz, 2H), 6.98 (d, $J = 8.6$ Hz, 2H), 5.62 – 5.53 (m, 1H), 5.41 – 5.30 (m, 1H), 3.76 (dt, $J = 9.7, 6.4$ Hz, 1H), 2.28 (s, 3H), 1.69 – 1.64 (m, 5H), 1.45 – 1.36 (m, 5H), 1.31 – 1.19 (m, 5H), 0.89 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ (ppm) = 169.7, 148.6, 145.4, 136.9, 128.2 (2C), 122.0, 121.5 (2C), 49.8, 38.7, 38.6, 38.5, 33.9, 26.6, 25.6, 22.2 (2C), 21.3, 13.2. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu} = 2923, 2858, 1765, 1505, 1449, 1399, 1368, 1196, 1166, 1100, 1017$. **HRMS** (EI) calcd for $\text{C}_{20}\text{H}_{29}\text{O}_2$ [$\text{M}+\text{H}$] $^+$: 301.2168, found 301.2174.

(E)-4-(1-(1-Methylcyclohexyl)-4-(p-tolyl)but-3-en-2-yl)phenyl Acetate (4r)



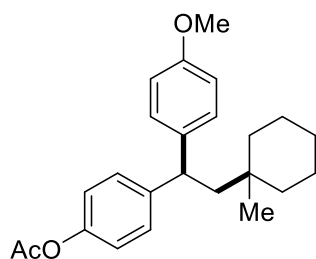
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (134 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–15% acetone in hexanes), the title compound was obtained as a colorless oil (73 mg, 0.194 mmol, 65%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.32 – 7.27 (m, 2H), 7.26 – 7.22 (m, 2H), 7.12 (d, J = 7.9 Hz, 2H), 7.07 – 7.02 (m, 2H), 6.37 – 6.24 (m, 2H), 3.65 (q, J = 6.4 Hz, 1H), 2.34 (s, 3H), 2.31 (s, 3H), 1.90 – 1.77 (m, 2H), 1.54 – 1.18 (m, 10H), 0.93 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.7, 148.8, 144.4, 136.8, 135.3, 135.0, 129.3 (2C), 128.6 (3C), 126.1 (2C), 121.5 (2C), 48.7, 44.8, 38.7, 38.6, 34.0, 26.5, 25.7, 22.2 (2C), 21.3 (2C). **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2922, 2853, 1765, 1504, 1452, 1367, 1199. **HRMS** (EI) calcd for $\text{C}_{26}\text{H}_{32}\text{O}_2$ $[\text{M}]^+$: 376.2402, found 376.2385.

4-(2-(1-Methylcyclohexyl)-1-(1,4-dioxaspiro[4.5]dec-7-en-8-yl)ethyl)phenyl Acetate (4s)



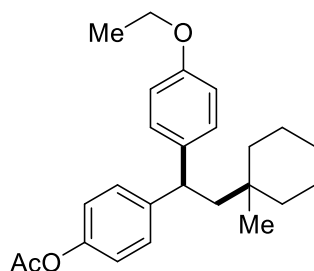
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (148 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (45 mg, 0.11 mmol, 38%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.20 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 5.58 (s, 1H), 3.96 – 3.83 (m, 4H), 3.35 (t, J = 6.4 Hz, 1H), 2.27 (s, 3H), 2.22 (s, 2H), 2.09 (q, J = 16.8 Hz, 2H), 1.77 (d, J = 6.3 Hz, 1H), 1.63 (t, J = 6.6 Hz, 2H), 1.42 – 1.21 (m, 10H), 1.11 (t, J = 5.9 Hz, 1H), 0.79 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm) = 169.6, 148.8, 142.9, 139.8, 129.0 (2C), 121.1 (2C), 120.0, 108.7, 64.4 (2C), 47.6, 44.9, 38.7, 38.4, 37.0, 33.8, 30.9, 26.6, 25.0, 24.3, 22.2, 22.1, 21.3. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2923, 1761, 1504, 1448, 1367, 1310, 1199, 1166, 1100, 1059, 1042, 1017. **HRMS** (EI) calcd for $\text{C}_{25}\text{H}_{35}\text{O}_4$ $[\text{M}+\text{H}]^+$: 399.2535, found 399.2551.

4-(1-(4-Methoxyphenyl)-2-(1-methylcyclohexyl)ethyl)phenyl Acetate (4t)



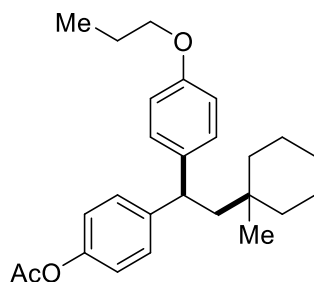
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (128 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–10% EtOAc in hexanes), the title compound was obtained as a colorless oil (53 mg, 0.14 mmol, 48%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = 7.27 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 1H), 3.77 (s, 3H), 2.26 (s, 3H), 2.07 (qd, *J* = 14.2, 6.6 Hz, 2H), 1.44 – 1.32 (m, 5H), 1.27 – 1.15 (m, 5H), 0.79 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 169.6, 157.9, 148.7, 145.2, 138.8, 128.8 (2C), 128.6 (2C), 121.4 (2C), 113.9 (2C), 55.3, 48.6, 46.0, 38.6 (2C), 34.0, 26.5, 25.4, 22.1, 22.1, 21.3. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2923, 2848, 1761, 1609, 1504, 1462, 1368, 1301, 1247, 1198, 1166, 1110, 1037, 1017. **HRMS** (EI) calcd for C₂₄H₃₁O₃ [M+H]⁺: 367.2273, found 367.2280.

4-(1-(4-Ethoxyphenyl)-2-(1-methylcyclohexyl)ethyl)phenyl Acetate (4u)



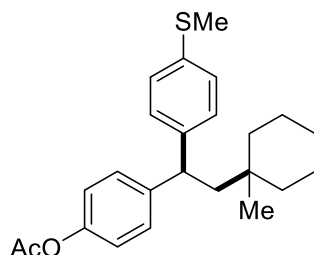
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (137 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–10% EtOAc in hexanes), the title compound was obtained as a colorless oil (70 mg, 0.18 mmol, 61%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = 7.26 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 1H), 3.99 (q, *J* = 7.0 Hz, 2H), 2.26 (s, 3H), 2.15 – 1.97 (m, 2H), 1.45 – 1.30 (m, 8H), 1.29 – 1.16 (m, 5H), 0.78 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 169.6, 157.3, 148.7, 145.2, 138.7, 128.8 (2C), 128.7 (2C), 121.4 (2C), 114.5 (2C), 63.5, 48.7, 46.0, 38.7 (2C), 34.0, 26.5, 25.4, 22.2, 22.1, 21.3, 15.0. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2923, 1761, 1610, 1504, 1478, 1445, 1368, 1244, 1197, 1166, 1116, 1047, 1017. **HRMS** (EI) calcd for C₂₅H₃₃O₃ [M+H]⁺: 381.2430, found 381.2421.

4-(2-(1-Methylcyclohexyl)-1-(4-propoxyphenyl)ethyl)phenyl Acetate (4v)



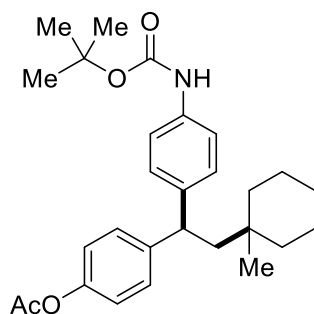
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (145 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–10% EtOAc in hexanes), the title compound was obtained as a colorless oil (59 mg, 0.15 mmol, 50%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = 7.27 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 1H), 3.88 (t, *J* = 6.5 Hz, 2H), 2.27 (s, 3H), 2.15 – 1.98 (m, 2H), 1.84 – 1.72 (m, 2H), 1.46 – 1.31 (m, 5H), 1.29 – 1.16 (m, 5H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.79 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 169.6, 157.4, 148.6, 145.2, 138.6, 128.8 (2C), 128.6 (2C), 121.4 (2C), 114.5 (2C), 69.6, 48.7, 46.0, 38.6 (2C), 34.0, 26.5, 25.4, 22.8, 22.1 (2C), 21.3, 10.7. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2924, 1761, 1504, 1455, 1368, 1243, 1197, 1166, 1112, 1068, 1048, 1017. **HRMS** (EI) calcd for C₂₆H₃₅O₃ [M+H]⁺: 395.2586, found 395.2570.

4-(2-(1-Methylcyclohexyl)-1-(4-(methylthio)phenyl)ethyl)phenyl Acetate (4w)



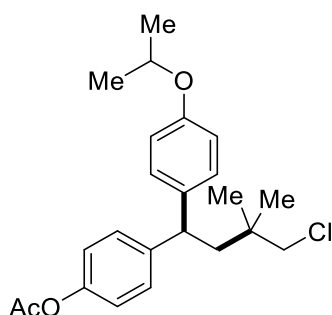
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (138 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–10% EtOAc in hexanes), the title compound was obtained as a colorless oil (56 mg, 0.15 mmol, 49%). $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm) = 7.27 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.5 Hz, 2H), 4.05 (t, J = 6.5 Hz, 1H), 2.44 (s, 3H), 2.26 (s, 3H), 2.14 – 1.99 (m, 2H), 1.45 – 1.30 (m, 5H), 1.27 – 1.16 (m, 5H), 0.79 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ (ppm) = 169.6, 148.8, 144.6, 143.8, 135.6, 128.7 (2C), 128.5 (2C), 127.2 (2C), 121.5 (2C), 48.4, 46.4, 38.6 (2C), 34.0, 26.5, 25.4, 22.1 (2C), 21.3, 16.3. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2921, 2847, 1757, 1504, 1492, 1441, 1406, 1367, 1195, 1166, 1094, 1015. **HRMS** (EI) calcd for $\text{C}_{24}\text{H}_{31}\text{O}_2\text{S}$ [$\text{M}+\text{H}$] $^+$: 383.2045, found 383.2044.

4-(1-(4-((*tert*-Butoxycarbonyl)amino)phenyl)-2-(1-methylcyclohexyl)ethyl)phenyl Acetate (4x)



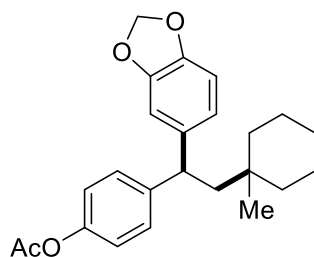
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (179 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–15% EtOAc in hexanes), the title compound was obtained as a white solid (80 mg, 0.18 mmol, 59%). $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm) = 7.25 (d, J = 8.8 Hz, 4H), 7.20 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 6.44 (bs, 1H), 4.04 (dd, J = 7.3, 5.8 Hz, 1H), 2.26 (s, 3H), 2.14 – 1.98 (m, 2H), 1.50 (s, 9H), 1.44 – 1.31 (m, 5H), 1.26 – 1.13 (m, 5H), 0.78 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ (ppm) = 169.6 (2C), 152.9, 148.7, 144.9, 141.3, 136.4, 128.6 (2C), 128.5 (2C), 121.4 (2C), 118.8, 80.5, 48.5, 46.2, 38.6, 38.6, 34.0, 28.5 (3C), 26.5, 25.4, 22.1, 22.1, 21.3. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2925, 1756, 1725, 1594, 1521, 1504, 1454, 1412, 1392, 1367, 1314, 1218, 1199, 1157, 1052, 1016. **HRMS** (ESI) calcd for $\text{C}_{28}\text{H}_{37}\text{NO}_4\text{Na}$ [$\text{M}+\text{Na}$] $^+$: 474.2620, found 474.2609. **mp** = 142 – 144 $^{\circ}\text{C}$

4-(4-Chloro-1-(4-isopropoxyphenyl)-3,3-dimethylbutyl)phenyl Acetate (4y)



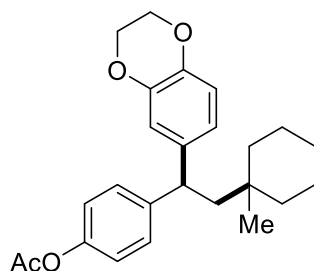
Prepared according to *General Procedure B* using the corresponding redox-active ester (127 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (145 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–10% EtOAc in hexanes), the title compound was obtained as a colorless oil (57 mg, 0.15 mmol, 49%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = 7.28 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 4.53 – 4.44 (m, 1H), 4.00 (t, J = 7.0 Hz, 1H), 3.24 (d, J = 2.5 Hz, 2H), 2.27 (s, 3H), 2.17 (qd, J = 14.4, 7.0 Hz, 2H), 1.31 (d, J = 6.0 Hz, 6H), 0.91 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 169.6, 156.4, 148.9, 144.0, 137.3, 128.8 (2C), 128.6 (2C), 121.5 (2C), 116.0 (2C), 70.0, 56.1, 46.5, 44.9, 36.3, 26.2, 26.0, 22.2 (2C), 21.3. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2975, 2933, 1759, 1609, 1505, 1468, 1384, 1369, 1297, 1243, 1198, 1167, 1118, 1017. **HRMS** (EI) calcd for C₂₃H₃₀ClO₃ [M+H]⁺: 389.1883, found 389.1885.

4-(1-(Benzo[d][1,3]dioxol-5-yl)-2-(1-methylcyclohexyl)ethyl)phenyl Acetate (4z)



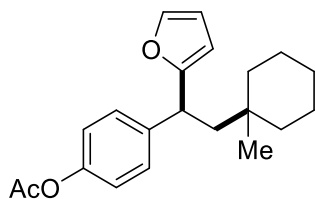
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (137 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–10% EtOAc in hexanes), the title compound was obtained as a colorless oil (58 mg, 0.15 mmol, 50%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = 7.27 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.2 Hz, 2H), 6.83 – 6.66 (m, 3H), 5.90 (d, J = 3.6 Hz, 2H), 4.01 (t, J = 6.5 Hz, 1H), 2.27 (s, 3H), 2.11 – 1.98 (m, 2H), 1.47 – 1.29 (m, 5H), 1.29 – 1.13 (m, 5H), 0.80 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 169.6, 148.8, 147.7, 145.8, 144.8, 140.8, 128.6 (2C), 121.4 (2C), 120.8, 108.3, 108.2, 100.9, 48.5, 46.5, 38.6 (2C), 34.0, 26.5, 25.3, 22.1 (2C), 21.3. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2923, 2859, 1761, 1503, 1487, 1440, 1368, 1244, 1197, 1166, 1120, 1097, 1038, 1017. **HRMS** (EI) calcd for C₂₄H₂₉O₄ [M+H]⁺: 381.2066, found 381.2078.

4-(1-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-2-(1-methylcyclohexyl)ethyl)phenyl Acetate (4aa)



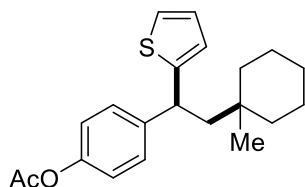
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (145 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–10% EtOAc in hexanes), the title compound was obtained as a white solid (61 mg, 0.15 mmol, 52%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = 7.26 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 6.79 (s, 1H), 6.74 (s, 2H), 4.21 (s, 4H), 3.97 (t, J = 6.5 Hz, 1H), 2.26 (s, 3H), 2.11 – 1.95 (m, 2H), 1.45 – 1.31 (m, 5H), 1.27 – 1.17 (m, 5H), 0.78 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 169.6, 148.7, 144.9, 143.4, 141.8, 140.2, 128.6 (2C), 121.4 (2C), 120.8, 117.2, 116.5, 64.5, 64.4, 48.5, 46.2, 38.6, 38.6, 34.0, 26.5, 25.3, 22.1 (2C), 21.3. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2925, 1764, 1589, 1504, 1459, 1431, 1369, 1308, 1286, 1258, 1200, 1167, 1126, 1069, 1017. **HRMS** (EI) calcd for C₂₅H₃₁O₄ [M+H]⁺: 395.2222, found 395.2231. **mp** = 95 – 96 °C.

4-(1-(Furan-2-yl)-2-(1-methylcyclohexyl)ethyl)phenyl Acetate (4ab)



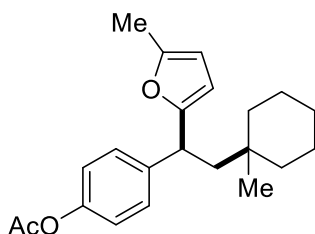
Prepared according to *General Procedure B* using the corresponding redox-active ester (219 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (104 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (115 mg, 0.44 mmol, 87%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = 7.31 – 7.26 (m, 3H), 7.00 (d, J = 8.6 Hz, 2H), 6.26 (d, J = 2.0 Hz, 1H), 6.02 (d, J = 3.2 Hz, 1H), 4.11 (dd, J = 7.9, 5.4 Hz, 1H), 2.28 (s, 3H), 2.20 (dd, J = 14.1, 7.9 Hz, 1H), 1.82 (dd, J = 14.1, 5.4 Hz, 1H), 1.41 – 1.36 (m, 5H), 1.25 – 1.17 (m, 5H), 0.79 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 169.7, 156.6, 150.6, 149.0, 143.0, 128.8 (2C), 121.4 (2C), 106.0, 105.9, 47.1, 40.6, 38.4, 38.2, 33.7, 26.5, 25.1, 22.1, 21.3, 13.7. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2924, 2849, 1765, 1505, 1449, 1368, 1196, 1166, 1072, 1010. **HRMS** (EI) calcd for C₂₁H₂₇O₃ [M+H]⁺: 327.1960, found 327.1959.

4-(2-(1-Methylcyclohexyl)-1-(thiophen-2-yl)ethyl)phenyl Acetate (4ac)



Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (114 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (40 mg, 0.12 mmol, 39%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = 7.30 – 7.24 (m, 2H), 7.22 (dd, J = 5.0, 3.0 Hz, 1H), 7.03 – 6.95 (m, 4H), 4.18 (t, J = 6.5 Hz, 1H), 2.28 (s, 3H), 2.15 – 2.01 (m, 2H), 1.46 – 1.32 (m, 5H), 1.29 – 1.16 (m, 5H), 0.80 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 169.6, 148.8, 147.6, 144.3, 128.8 (2C), 127.9, 125.5, 121.4 (2C), 120.0, 49.0, 42.3, 38.6, 38.5, 33.9, 26.5, 25.3, 22.1, 22.1, 21.3. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2922, 2851, 1763, 1504, 1450, 1368, 1196, 1166, 1103, 1017. **HRMS** (ESI) calcd for C₂₁H₂₇O₂S [M+H]⁺: 343.1732, found 343.1735.

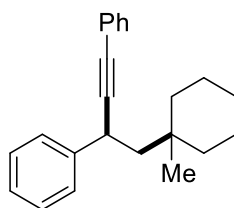
4-(2-(1-Methylcyclohexyl)-1-(5-methylfuran-2-yl)ethyl)phenyl Acetate (4ad)



Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (113 mg, 0.60 mmol, 2.0 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (50 mg, 0.15 mmol, 49%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = 7.28 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 5.88 (d, J = 3.1 Hz, 1H), 5.82 (dd, J = 3.0, 1.2 Hz, 1H), 4.03 (dd, J = 7.8, 5.5 Hz, 1H), 2.28 (s, 3H), 2.24 (s, 3H), 2.17 (dd, J = 14.1, 7.8 Hz, 1H), 1.78 (dd, J = 14.1, 5.5 Hz, 1H), 1.42 – 1.36 (m, 5H), 1.26 – 1.17 (m, 5H), 0.80 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 169.7, 156.7, 150.6, 149.0, 143.0, 128.8 (2C), 121.4

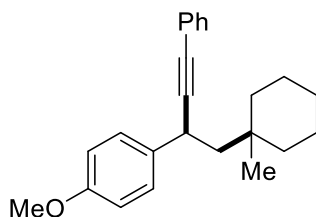
(2C), 106.0, 105.9, 49.2, 40.6, 38.4, 38.2, 33.7, 26.5, 24.3, 22.1 (2C), 21.3, 13.7. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2924, 2854, 1762, 1605, 1505, 1450, 1369, 1196, 1166, 1102, 1044, 1017. **HRMS** (EI) calcd for $\text{C}_{22}\text{H}_{29}\text{O}_3$ $[\text{M}+\text{H}]^+$: 341.2117, found 341.2108.

(4-(1-Methylcyclohexyl)but-1-yne-1,3-diyl)dibenzene (4ae)



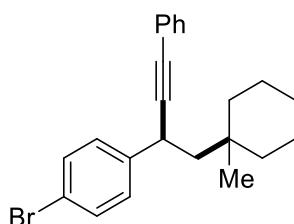
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (31.2 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (hexanes), the title compound was obtained as a colorless oil (45 mg, 0.15 mmol, 50%). **$^1\text{H NMR}$** (400 MHz, CDCl_3), δ (ppm) = 7.43 (td, J = 7.1, 1.8 Hz, 4H), 7.34 (t, J = 7.6 Hz, 2H), 7.31 – 7.22 (m, 4H), 3.91 (dd, J = 10.1, 3.3 Hz, 1H), 2.04 (dd, J = 14.0, 10.1 Hz, 1H), 1.64 (dd, J = 14.0, 3.3 Hz, 1H), 1.63 – 1.52 (m, 2H), 1.50 – 1.33 (m, 8H), 1.12 (s, 3H). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3), δ (ppm) = 144.5, 131.6 (2C), 128.7 (2C), 128.3 (2C), 127.7, 127.5 (2C), 126.6, 124.2, 93.6, 83.1, 51.1, 38.5, 38.2, 34.0, 33.9, 26.6, 25.9, 22.2 (2C). **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2923, 2849, 1692, 1673, 1598, 1490, 1450, 1377, 1350, 1318, 1262, 1177, 1071, 1025. **HRMS** (EI) calcd for $\text{C}_{23}\text{H}_{27}$ $[\text{M}+\text{H}]^+$: 303.2113, found 303.2100.

1-Methoxy-4-(1-(1-methylcyclohexyl)-4-phenylbut-3-yn-2-yl)benzene (4af)



Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (40.3 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (hexanes), the title compound was obtained as a colorless oil (55 mg, 0.16 mmol, 55%). **$^1\text{H NMR}$** (400 MHz, CDCl_3), δ (ppm) = 7.42 – 7.38 (m, 2H), 7.33 (d, J = 8.7 Hz, 2H), 7.32 – 7.24 (m, 3H), 6.87 (d, J = 8.7 Hz, 2H), 3.85 (dd, J = 9.5, 2.9 Hz, 1H), 3.80 (s, 3H), 2.00 (dd, J = 13.9, 10.0 Hz, 1H), 1.61 (dd, J = 14.0, 3.5 Hz, 1H), 1.60 – 1.51 (m, 2H), 1.49 – 1.32 (m, 8H), 1.09 (s, 3H). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3), δ (ppm) = 158.3, 136.7, 131.5 (2C), 128.5 (2C), 128.3 (2C), 127.7, 124.3, 114.1 (2C), 93.9, 83.0, 55.5, 44.5, 38.5, 38.2, 33.8, 33.1, 26.6, 25.9, 22.2 (2C). **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2925, 2860, 1749, 1726, 1610, 1510, 1490, 1462, 1301, 1250, 1211, 1175, 1118, 1037. **HRMS** (EI) calcd for $\text{C}_{24}\text{H}_{29}\text{O}$ $[\text{M}+\text{H}]^+$: 332.2140, found 332.2144.

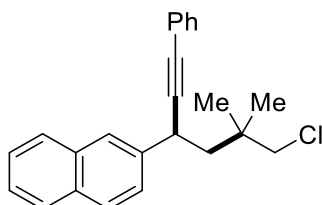
1-Bromo-4-(1-(1-methylcyclohexyl)-4-phenylbut-3-yn-2-yl)benzene (4ag)



Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5

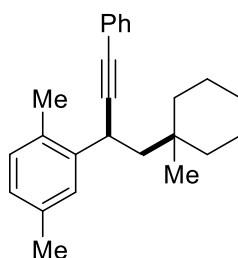
equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (54.9 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–10% EtOAc in hexanes), the title compound was obtained as a colorless oil (41.4 mg, 0.135 mmol, 45%). **¹H NMR** (400 MHz, CDCl₃), δ 7.49 – 7.43 (m, 2H), 7.41 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.34 – 7.27 (m, 5H), 3.87 (dd, *J* = 10.0, 3.4 Hz, 1H), 2.01 (dd, *J* = 13.9, 10.0 Hz, 1H), 1.64 – 1.30 (m, 11H), 1.10 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.5, 131.8 (2C), 131.5 (2C), 129.3 (2C), 128.4 (2C), 127.9, 123.9, 120.3, 92.8, 83.5, 51.0, 38.5, 38.2, 33.9, 33.5, 26.5, 25.8, 22.2 (2C). **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2923, 2848, 1597, 1486, 1071, 1011, 754. **HRMS** (EI) calcd for C₂₃H₂₅Br [M]⁺: 380.1140, found 380.1144.

2-(6-Chloro-5,5-dimethyl-1-phenylhex-1-yn-3-yl)naphthalene (4ah)



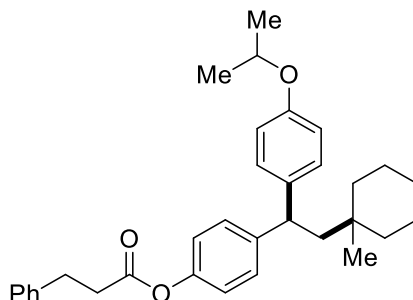
Prepared according to *General Procedure B* using the corresponding redox-active ester (127 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (46 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (49 mg, 0.14 mmol, 47%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = δ 7.92 – 7.80 (m, 4H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.53 – 7.42 (m, 4H), 7.37 – 7.29 (m, 3H), 4.09 (dd, *J* = 10.5, 3.7 Hz, 1H), 3.62 (q, *J* = 10.8 Hz, 2H), 2.13 (dd, *J* = 14.1, 10.5 Hz, 1H), 1.91 (dd, *J* = 14.1, 3.7 Hz, 1H), 1.22 (d, *J* = 5.0 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 140.7, 133.7, 132.6, 131.6 (2C), 128.6, 128.4 (2), 128.1, 127.9, 127.8, 126.3, 126.0, 125.8, 125.8, 123.8, 92.2, 84.2, 55.5, 47.7, 36.3, 34.7, 26.2, 25.9. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2961, 1598, 1507, 1490, 1468, 1442, 1387, 1367, 1265. **HRMS** (EI) calcd for C₂₄H₂₄Cl [M+H]⁺: 347.1567, found 347.1557.

1,4-Dimethyl-2-(1-(1-methylcyclohexyl)-4-phenylbut-3-yn-2-yl)benzene (4ai)



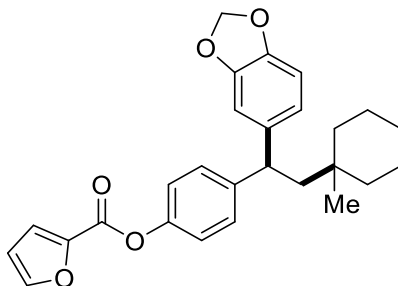
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and styrene (39.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (hexanes), the title compound was obtained as a colorless oil (55 mg, 0.17 mmol, 55%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = 7.46 – 7.39 (m, 3H), 7.34 – 7.26 (m, 3H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.98 (dd, *J* = 7.7, 1.9 Hz, 1H), 4.10 (dd, *J* = 10.7, 2.8 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 2.34 (d, *J* = 5.6 Hz, 1H), 2.04 (dd, *J* = 13.9, 10.7 Hz, 1H), 1.71 – 1.59 (m, 2H), 1.54 – 1.45 (m, 6H), 1.45 – 1.37 (m, 2H), 1.17 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 142.3, 136.0, 131.5 (2C), 131.2, 130.6, 128.7, 128.3 (2C), 127.6, 127.3, 124.4, 94.1, 82.4, 49.6, 38.8, 38.1, 34.0, 30.3, 26.6, 25.7, 22.3 (2C), 21.3, 19.2. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2924, 2861, 1598, 1502, 1490, 1443, 1378, 1156, 1069. **HRMS** (EI) calcd for C₂₅H₃₁ [M+H]⁺: 330.2348, found 330.2349.

4-(1-(4-Isopropoxyphenyl)-2-(1-methylcyclohexyl)ethyl)phenyl 3-Phenylpropanoate (4aj)



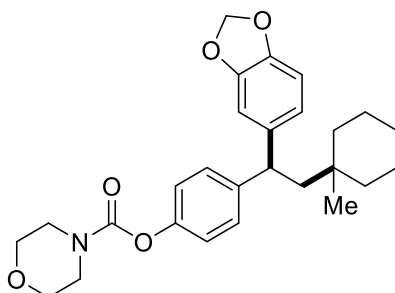
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (145 mg, 0.60 mmol, 2.0 equiv), and styrene (76 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (65 mg, 0.13 mmol, 45%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = 7.36 – 7.30 (m, 2H), 7.31 – 7.20 (m, 5H), 7.17 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 4.54 – 4.44 (m, 1H), 4.03 (t, J = 6.5 Hz, 1H), 3.07 (t, J = 7.7 Hz, 2H), 2.87 (t, J = 7.7 Hz, 2H), 2.13 – 1.99 (m, 2H), 1.47 – 1.33 (m, 5H), 1.32 (dd, J = 6.0, 1.3 Hz, 6H), 1.26 – 1.14 (m, 5H), 0.79 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 171.6, 156.2, 148.6, 145.2, 140.3, 138.7, 128.8 (2C), 128.7(4C), 128.5 (2C), 126.5, 121.3 (2C), 115.9 (2C), 70.0, 48.6, 46.0, 44.6, 38.6, 36.1, 34.0, 31.1, 29.9, 26.5, 25.4, 22.3, 22.2, 22.1. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 3029, 2974, 2924, 2860, 1758, 1608, 1504, 1454, 1372, 1297, 1243, 1203, 1167, 1129, 1077, 1017. **HRMS** (ESI) calcd for C₃₃H₄₀O₃Na [M+Na]⁺: 507.2875, found 507.2886.

4-(1-(Benzo[d][1,3]dioxol-5-yl)-2-(1-methylcyclohexyl)ethyl)phenyl furan-2-carboxylate (4ak)



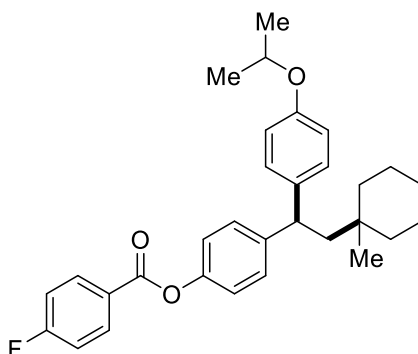
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (137 mg, 0.60 mmol, 2.0 equiv), and styrene (64 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–10% EtOAc in hexanes), the title compound was obtained as a white solid (63 mg, 0.15 mmol, 48%). **¹H NMR** (400 MHz, CDCl₃), δ (ppm) = 7.68 – 7.63 (m, 1H), 7.37 – 7.29 (m, 3H), 7.11 (d, J = 8.6 Hz, 2H), 6.82 – 6.68 (m, 3H), 6.57 (dd, J = 3.5, 1.8 Hz, 1H), 5.90 (d, J = 2.4 Hz, 2H), 4.03 (t, J = 6.5 Hz, 1H), 2.11 – 2.01 (m, 2H), 1.46 – 1.34 (m, 5H), 1.29 – 1.18 (m, 5H), 0.80 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃), δ (ppm) = 157.1, 148.3, 147.8, 147.2, 145.8, 145.1, 144.2, 140.7, 128.7 (2C), 121.5 (2C), 120.8, 119.4, 112.3, 108.4, 108.3, 101.0, 48.5, 46.6, 38.6 (2C), 34.0, 26.5, 25.3, 22.1 (2C). **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2924, 2859, 1740, 1503, 1486, 1471, 1441, 1392, 1293, 1245, 1231, 1203, 1174, 1089, 1070, 1040, 1015. **HRMS** (ESI) calcd for C₂₇H₂₈O₅Na [M+Na]⁺: 455.1834, found 455.1835. **mp** = 75 – 77 °C.

4-(1-(Benzo[d][1,3]dioxol-5-yl)-2-(1-methylcyclohexyl)ethyl)phenyl Morpholine-4-carboxylate (4al)



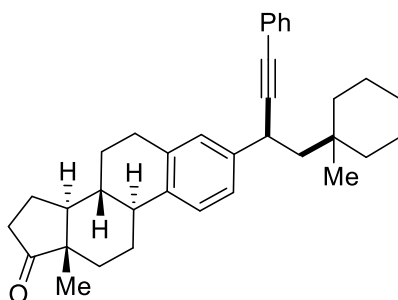
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (137 mg, 0.60 mmol, 2.0 equiv), and styrene (70 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–30% EtOAc in hexanes), the title compound was obtained as a white solid (92 mg, 0.20 mmol, 68%) with 5% of isoindoline-1,3-dione as impurity. $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm) = 7.28 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.2 Hz, 2H), 6.81 – 6.68 (m, 3H), 5.91 (d, J = 3.7 Hz, 2H), 4.02 (t, J = 6.5 Hz, 1H), 3.75 (t, J = 4.7 Hz, 4H), 3.66 (bs, 2H), 3.58 (bs, 2H), 2.05 (d, J = 6.5 Hz, 2H), 1.45 – 1.34 (m, 5H), 1.29 – 1.18 (m, 5H), 0.81 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ (ppm) = 153.9, 149.3, 147.7, 145.7, 144.4, 141.0, 128.5 (2C), 121.5 (2C), 120.8, 108.4, 108.2, 100.9, 66.7 (2C), 48.5, 46.5, 45.0, 44.6, 38.6 (2C), 34.0, 26.5, 25.4, 22.1 (2C). **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2922, 2858, 1719, 1503, 1487, 1454, 1439, 1420, 1366, 1278, 1241, 1208, 1169, 1117, 1066, 1040, 1017. **HRMS** (EI) calcd for $\text{C}_{27}\text{H}_{34}\text{NO}_5$ [$\text{M}+\text{H}$] $^+$: 474.2256, found 474.2259. **mp** = 103 – 105 °C

4-(1-(4-Isopropoxyphenyl)-2-(1-methylcyclohexyl)ethyl)phenyl 4-Fluorobenzoate (4am)



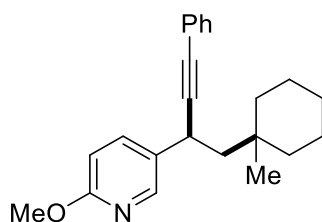
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (145 mg, 0.60 mmol, 2.0 equiv), and styrene (73 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a white solid (65 mg, 0.14 mmol, 46%). $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm) = 8.20 (dd, J = 8.7, 5.6 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 7.22 – 7.14 (m, 4H), 7.10 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.5 Hz, 2H), 4.54 – 4.44 (m, 1H), 4.07 (t, J = 6.5 Hz, 1H), 2.13 – 2.05 (m, 2H), 1.44 – 1.35 (m, 5H), 1.31 (d, J = 6.1 Hz, 6H), 1.28 – 1.17 (m, 5H), 0.81 (s, 3H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3), δ (ppm) = -104.62. $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ (ppm) = 166.1 (d, $J_{\text{C-F}}$ = 255.0 Hz), 164.3, 156.1, 148.7, 145.3, 138.6, 132.8 (d, $J_{\text{C-F}}$ = 9.4 Hz, 2C), 128.7 (4C), 126.0 (d, $J_{\text{C-F}}$ = 2.9 Hz), 121.3 (2C), 115.83 (2C), 115.76 (d, $J_{\text{C-F}}$ = 22.1 Hz, 2C), 69.9, 48.5, 46.0, 38.6 (2C), 33.9, 26.4, 25.3, 22.2, 22.1, 22.0 (2C). **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2975, 2924, 2860, 1739, 1604, 1507, 1452, 1297, 1262, 1242, 1202, 1168, 1154, 1120, 1071, 1015. **HRMS** (ESI) calcd for $\text{C}_{31}\text{H}_{35}\text{FO}_3\text{Na}$ [$\text{M}+\text{Na}$] $^+$: 492.2468, found 492.2463. **mp** = 67 – 68 °C

(8R,9S,13S,14S)-13-Methyl-3-(1-(1-methylcyclohexyl)-4-phenylbut-3-yn-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4an)



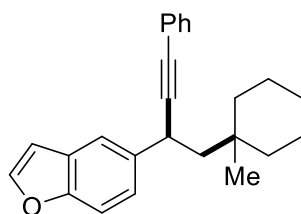
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and alkene (84.1 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–15% acetone in hexanes), the title compound was obtained as a colorless oil (112 mg, 0.234 mmol, 78%, isolated as 1:1 diastereomeric mixture). **¹H NMR** (400 MHz, CDCl₃) δ 7.40 (ddd, *J* = 6.3, 3.1, 1.4 Hz, 2H), 7.31 – 7.25 (m, 4H), 7.20 (ddd, *J* = 8.2, 3.8, 2.1 Hz, 1H), 7.15 (d, *J* = 2.2 Hz, 1H), 3.84 (dd, *J* = 10.4, 3.0 Hz, 1H), 2.94 (dd, *J* = 9.2, 4.2 Hz, 2H), 2.51 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.31 (td, *J* = 11.1, 4.1 Hz, 1H), 2.21 – 1.90 (m, 5H), 1.71 – 1.27 (m, 17H), 1.11 (s, 3H), 0.91 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 142.1, 138.1, 138.0, 136.8 (2C), 131.5, 128.3, 128.0, 127.7, 125.8, 124.9, 124.3, 93.7 (2C), 83.0 (2C), 50.7, 48.2, 44.5, 38.6, 38.3, 38.2, 36.0, 33.9, 33.5 (2C), 31.8, 29.7, 29.6, 26.7, 26.6, 25.9, 22.3, 21.8, 14.0. **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2923, 2856, 1739, 1489, 1453, 755. **HRMS** (ESI) calcd for C₃₅H₄₃O [M+H]⁺: 479.3314, found 479.3308.

2-Methoxy-5-(1-(1-methylcyclohexyl)-4-phenylbut-3-yn-2-yl)pyridine (4ao)



Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and alkene (40.6 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–15% acetone in hexanes), the title compound was obtained as a colorless oil (58.3 mg, 0.175 mmol, 58%). **¹H NMR** (400 MHz, CDCl₃) δ 8.18 (d, *J* = 2.6 Hz, 1H), 7.65 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.28 (dt, *J* = 4.7, 2.8 Hz, 3H), 6.73 (d, *J* = 8.5 Hz, 1H), 3.93 (s, 3H), 3.86 (dd, *J* = 9.8, 3.6 Hz, 1H), 2.01 (dd, *J* = 14.0, 9.8 Hz, 1H), 1.63 – 1.50 (m, 3H), 1.49 – 1.31 (m, 8H), 1.09 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 163.1, 145.4, 138.1, 132.7, 131.5 (2C), 128.4 (2C), 127.9, 123.9, 110.9, 92.8, 83.3, 53.6, 50.9, 38.5, 38.2, 33.9, 30.7, 26.5, 25.8, 22.2 (2C). **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2924, 2847, 1605, 1490, 1391, 1288, 1027, 755. **HRMS** (ESI) calcd for C₂₃H₂₈NO [M+H]⁺: 334.2171, found 334.2175.

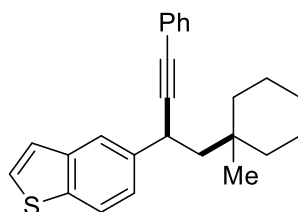
5-(1-(1-Methylcyclohexyl)-4-phenylbut-3-yn-2-yl)benzofuran (4ap)



Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5

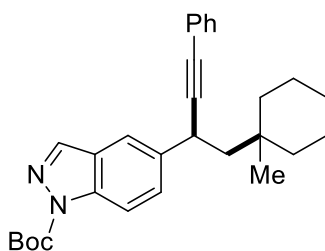
equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and alkene (43.3 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–15% acetone in hexanes), the title compound was obtained as a colorless oil (65.4 mg, 0.191 mmol, 64%). **¹H NMR** (400 MHz, CDCl₃) δ 7.64 (dd, *J* = 16.8, 2.0 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.41 (dq, *J* = 5.0, 2.9 Hz, 2H), 7.34 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.31–7.22 (m, 3H), 6.75 (d, *J* = 2.1 Hz, 1H), 4.00 (dd, *J* = 10.0, 3.4 Hz, 1H), 2.08 (dd, *J* = 13.9, 10.0 Hz, 1H), 1.68 (dd, *J* = 14.0, 3.4 Hz, 1H), 1.63–1.54 (m, 2H), 1.51–1.30 (m, 8H), 1.12 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 154.0, 145.5, 139.2, 131.8, 131.6 (2C), 128.3 (2C), 127.7, 124.2, 124.1, 119.8, 111.5, 106.8, 94.0, 83.1, 51.6, 38.5, 38.2, 33.9 (2C), 26.6, 25.9, 22.3 (2C). **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2924, 2849, 1490, 1466, 1442, 1262, 1109, 1031, 755. **HRMS** (EI) calcd for C₂₅H₂₆O [M]⁺: 342.1984, found 342.1974.

5-(1-(1-Methylcyclohexyl)-4-phenylbut-3-yn-2-yl)benzo[b]thiophene (4aq)



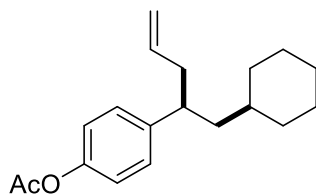
Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and alkene (48.1 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–15% acetone in hexanes), the title compound was obtained as a colorless oil (78 mg, 0.22 mmol, 73%). **¹H NMR** (400 MHz, CDCl₃) δ 7.89 (d, *J* = 1.7 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.42 (ddd, *J* = 8.2, 7.1, 3.6 Hz, 4H), 7.35–7.27 (m, 4H), 4.03 (dd, *J* = 10.0, 3.3 Hz, 1H), 2.10 (dd, *J* = 13.9, 10.0 Hz, 1H), 1.70 (dd, *J* = 14.0, 3.3 Hz, 1H), 1.65–1.53 (m, 2H), 1.52–1.31 (m, 8H), 1.13 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 140.8, 140.1, 138.1, 131.6 (2C), 128.3 (2C), 127.8, 126.9, 124.4, 124.2, 124.0, 122.7, 122.2, 93.7, 83.2, 51.4, 38.5, 38.2, 33.9 (2C), 26.6, 25.9, 22.3 (2C). **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2921, 2845, 1597, 1489, 1441, 754, 690. **HRMS** (ESI) calcd for C₂₅H₂₇S [M+H]⁺: 359.1833, found 359.1826.

tert-Butyl 5-(1-(1-methylcyclohexyl)-4-phenylbut-3-yn-2-yl)-1H-indazole-1-carboxylate (4ar)



Prepared according to *General Procedure B* using the corresponding redox-active ester (129 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (125 mg, 0.60 mmol, 2.0 equiv), and alkene (73.3 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–15% acetone in hexanes), the title compound was obtained as a colorless oil (86.4 mg, 0.195 mmol, 65%). **¹H NMR** (400 MHz, CDCl₃) δ 8.14 (d, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 1.7 Hz, 1H), 7.59 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.42 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.33–7.27 (m, 3H), 4.04 (dd, *J* = 9.9, 3.4 Hz, 1H), 2.08 (dd, *J* = 14.0, 9.9 Hz, 1H), 1.73 (s, 9H), 1.67 (dd, *J* = 14.0, 3.5 Hz, 1H), 1.63–1.53 (m, 2H), 1.51–1.32 (m, 8H), 1.12 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 149.3, 140.2, 139.7, 138.8, 131.5 (2C), 129.1, 128.4 (2C), 127.9, 126.3, 123.9, 119.2, 114.9, 93.2, 84.9, 83.5, 51.3, 38.5, 38.2, 33.9, 33.7, 28.3 (3C), 26.5, 25.9, 22.2 (2C). **FT-IR** (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2923, 1758, 1734, 1384, 1369, 1350, 1290, 1249, 1162, 1149, 1029. **HRMS** (EI) calcd for C₂₄H₂₅N₂ [M-Boc]: 341.2018, found 341.2032.

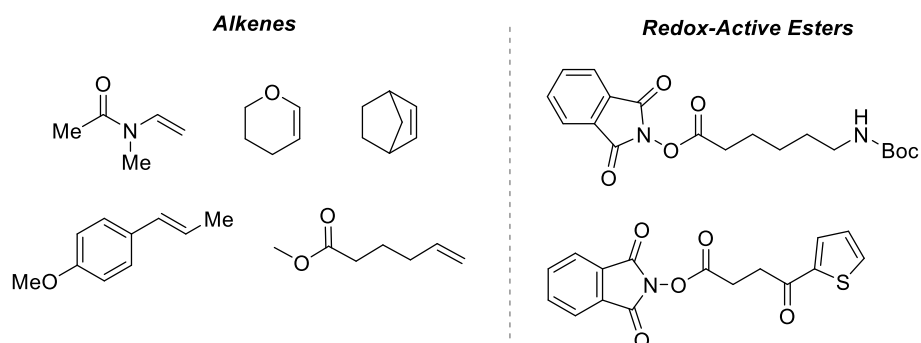
4-(1-Cyclohexylpent-4-en-2-yl)phenyl Acetate (4as)



Prepared according to *General Procedure B* using the corresponding redox-active ester (123 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate salt (89 mg, 0.60 mmol, 2.0 equiv), Ir(dtbbpy)(ppy)₂ (8 mg, 0.009 mmol, 3.0 mol %, 0.03 equiv), and styrene (48.7 mg, 0.300 mmol, 1.0 equiv) with an irradiation time of 24 h. After chromatographic purification (0–5% EtOAc in hexanes), the title compound was obtained as a colorless oil (43 mg, 0.15 mmol, 50%). ¹H NMR (400 MHz, CDCl₃), δ (ppm) = 7.14 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 5.63 (ddt, *J* = 17.2, 10.1, 7.0 Hz, 1H), 4.97 – 4.88 (m, 2H), 2.74 (m, 1H), 2.78 – 2.70 (m, 2H), 2.32 – 2.25 (s, 3H), 1.77 (d, *J* = 13.0 Hz, 1H), 1.65 – 1.53 (m, 4H), 1.48 (t, *J* = 7.2 Hz, 2H), 1.17 – 1.04 (m, 4H), 0.94 – 0.78 (m, 2H). ¹³C NMR (101 MHz, CDCl₃), δ (ppm) = 169.7, 148.9, 143.3, 137.1, 128.6 (2C), 121.3 (2C), 116.0, 44.0, 42.2, 42.2, 34.8, 34.3, 32.9, 26.8, 26.3, 26.2, 21.3. FT-IR (cm⁻¹, neat, ATR): $\tilde{\nu}$ = 2920, 2850, 1765, 1639, 1506, 1448, 1368, 1193, 1166, 1102, 1017. HRMS (EI) calcd for C₁₉H₂₆O₂ [M]⁺: 286.1933, found 286.1942.

6.3 Unsuccessful Substrates:

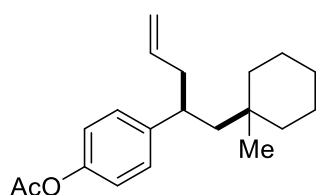
Table S2. Unsuccessful redox-active esters and alkene systems under this RPC difunctionalization conditions.



6.4 Gram Scale Synthesis: 4-(1-(1-Methylcyclohexyl)pent-4-en-2-yl)phenyl Acetate (4j)



Figure 2. Gram scale synthesis reaction setup of 4j.

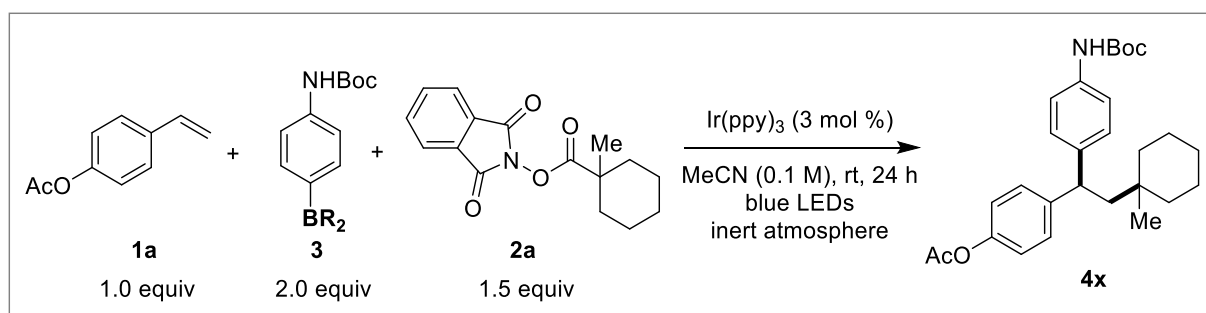


To an 40 mL reaction vial (28 x 95 mm) equipped with a magnetic stir bar was added 1,3-dioxoisindolin-2-yl 1-methylcyclohexane-1-carboxylate (2.7 g, 9.25 mmol, 1.5 equiv), allyltrifluoro- λ^4 -borane, potassium salt (1.8 g, 12.33 mmol, 2.0 equiv), and Ir(dtbbpy)(ppy)₂ (170.0 mg, 0.19 mmol, 3.0 mol %, 0.03 equiv) under air. The vial was sealed with a cap containing a TFE-lined silicone septum, evacuated, and back-filled with nitrogen. After this process was repeated 3 times, MeCN (6.2 mL, 0.1 M) was added followed by 4-vinylphenyl acetate (1.0 g, 6.2 mmol, 1.0 equiv) via syringe. The reaction was irradiated for 24 h using blue LED strips ($\lambda_{\text{max}} = 456$ nm, distance lamp–vial ~ 8-10 cm), whereby the temperature was maintained at approximately 25 °C via cooling with a fan. Upon completion, the mixture was taken to dryness and then purified using an automated system (UV detector, $\lambda = 254$ nm and 280 nm) with RediSep R_f Gold[®] silica gel disposable flash columns (60 Å porosity, 20–40 μm) with hexanes/EtOAc (0–10% EtOAc in hexanes) as eluent. The title compound was obtained as a yellow oil (0.9 g, 2.96 mmol, 48%). ¹H NMR (400 MHz, CDCl₃), δ (ppm) = 7.17 (d, $J = 8.6$ Hz, 2H), 6.99 (d, $J = 8.5$ Hz, 2H), 5.60 (ddt, $J = 17.1, 10.1, 7.0$ Hz, 1H), 4.98 – 4.87 (m, 2H), 2.74 (qd, $J = 7.5, 3.3$ Hz, 1H), 2.27 (s, 3H), 1.69 (dd, $J = 14.2, 8.6$ Hz, 1H), 1.60 (dd, $J = 14.2, 3.4$ Hz, 1H), 1.49 – 1.32 (m, 4H), 1.32 – 1.18 (m, 6H), 1.06 – 1.01 (m, 2H), 0.74 (s, 3H). ¹³C NMR (101 MHz, CDCl₃), δ (ppm) = 169.6, 148.7, 145.2, 137.3, 128.7 (2C), 121.2 (2C), 116.1, 48.1, 44.4, 41.2, 38.6, 38.5, 33.8, 26.5, 25.5, 22.2, 22.0, 21.3. FT-IR (cm⁻¹, neat, ATR): $\tilde{\nu} = 2923, 2849, 1766, 1640, 1606, 1507, 1446, 1368, 1198, 1166, 1100, 1017$. HRMS (EI) calcd for C₂₀H₂₈O₂Na [M+Na]⁺: 323.1982, found 323.1978.

7. Mechanistic Studies

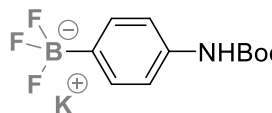
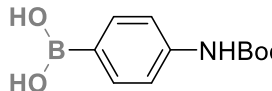
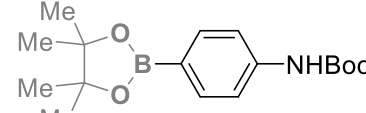
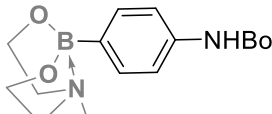
7.1 Reactivity Studies of Organoboron Compounds:

(4-((*tert*-Butoxycarbonyl)amino)phenyl)boronic acid (**3a**) was purchased commercially and use as received. *tert*-Butyl (4-(trifluoro- λ^4 -boranyl)phenyl)carbamate, potassium salt (**3x**),⁵ *tert*-butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate (**3xb**)⁷ and *tert*-butyl (4-(4-methyltetrahydro-2H-4 $\lambda^4,8\lambda^4$ -[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborol-8-yl)phenyl)carbamate (**3xc**)⁸ were synthesized following reported literature protocols.

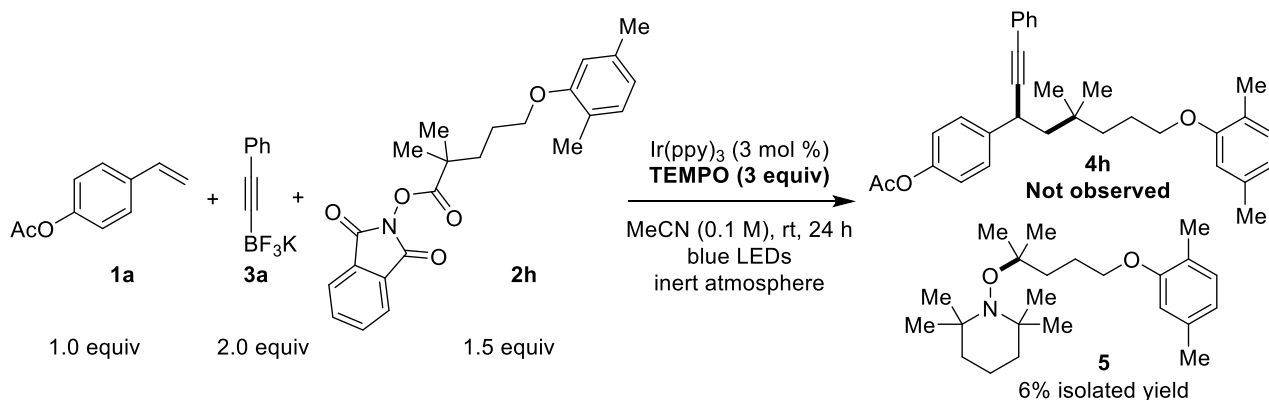


To an 8 mL reaction vial (17 x 60 mm) equipped with a magnetic stir bar was added 1,3-dioxoisindolin-2-yl 1-methylcyclohexane-1-carboxylate (86 mg, 0.30 mmol, 1.5 equiv), boron substrate (0.20 mmol, 2.0 equiv), and Ir(ppy)₃ (4 mg, 0.006 mmol, 3.0 mol %, 0.03 equiv) under air. The vial was sealed with a cap containing a TFE-lined silicone septum, evacuated, and back-filled with nitrogen. After this process was repeated 3 times, MeCN (3.0 mL, 0.1 M) was added followed by 4-vinylphenyl acetate (32.4 mg, 0.2 mmol, 1.0 equiv) via syringe. The reaction was irradiated for 24 h using blue LED strips ($\lambda_{\text{max}} = 456$ nm, distance lamp–vial ~3-5 cm), whereby the temperature was maintained at approximately 25 °C via cooling with a fan. Upon completion, the mixture was taken to dryness and then purified using an automated system (UV detector, $\lambda = 254$ nm and 280 nm) with RediSep R_f Gold[®] silica gel disposable flash columns (60 Å porosity, 20–40 μm) with hexanes/EtOAc (0–15% EtOAc in hexanes) as eluent. The yield of the title compound was determined by ¹H NMR analysis using trimethoxybenzene (34 mg, 0.20 mmol, 1.0 equiv) as internal standard in MeCN-*d*₃ (δ 2.13).

Table S3. Reactivity studies with different boron compounds. ^aYields determined by ¹H NMR using 0.1 mmol trimethoxybenzene as internal standard. n.r. = no reaction.

Boron Substrates	Yield of 4x^a
 <p>3x</p>	71%
 <p>3xa</p>	n.r.
 <p>3xb</p>	traces
 <p>3xc</p>	n.r.

7.2 Radical Trapping Experiment

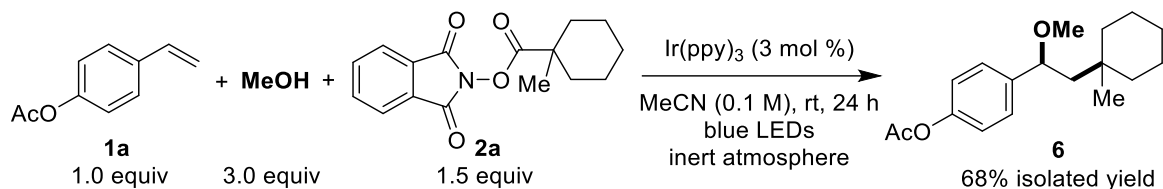


To an 8 mL reaction vial (17 x 60 mm) equipped with a magnetic stir bar was added 1,3-dioxoisindolin-2-yl 1-methylcyclohexane-1-carboxylate (129 mg, 0.45 mmol, 1.5 equiv), TEMPO (141 mg, 0.90 mmol, 3.0 equiv), trifluoro(phenylethynyl)- λ^4 -borane, potassium salt (125 mg, 0.60 mmol, 2.0 equiv), and $\text{Ir}(\text{ppy})_3$ (6 mg, 0.009 mmol, 3.0 mol %, 0.03 equiv) under air. The vial was sealed with a cap containing a TFE-lined silicone septum, evacuated, and back-filled with nitrogen. After this process was repeated 3 times, MeCN (3.0 mL, 0.1 M) was added followed by 4-vinylphenyl acetate (48.7 mg, 0.3 mmol, 1.0 equiv) via syringe. The reaction was irradiated for 24 h using blue LED strips ($\lambda_{\text{max}} = 456 \text{ nm}$, distance lamp–vial $\sim 3\text{--}5 \text{ cm}$), whereby the temperature was maintained at approximately 25 °C via cooling with a fan. Upon completion, the mixture was taken to dryness and then purified using an automated system (UV detector, $\lambda = 254 \text{ nm}$ and 280 nm) with RediSep R_f Gold[®] silica gel disposable flash columns (60 Å porosity, 20–40 μm) with hexanes/EtOAc (0–10% EtOAc in hexanes) as eluent. The TEMPO derivative was isolated as a colorless oil (6 mg, 0.02 mmol, 6%). ¹H NMR (400 MHz, CDCl₃), δ (ppm) 7.00 (d, $J = 7.4 \text{ Hz}$, 1H), 6.68–6.61 (m, 2H), 3.96 (t, $J = 6.3 \text{ Hz}$, 2H), 2.31 (s, 3H), 2.18 (s, 3H), 2.01–1.91 (m, 2H), 1.80–1.72 (m, 2H), 1.52–1.42 (m, 4H), 1.30 (s, 6H), 1.30–1.23 (m, 2H), 1.13 (s, 6H), 1.09 (s, 6H). ¹³C NMR (101 MHz, CDCl₃), δ (ppm) = 157.2, 136.4, 130.3, 123.6, 120.5, 111.9, 78.3, 68.4, 59.2 (2C), 40.9 (2C), 40.1, 34.8 (2C), 27.0

(2C), 24.4, 21.4, 20.7 (2C), 17.2, 15.9. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 3007, 2971, 2928, 2869, 1586, 1509, 1467, 1414, 1375, 1361, 1285, 1265, 1209, 1180, 1157, 1130, 1046. **HRMS** (ESI) calcd for $\text{C}_{23}\text{H}_{40}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 361.2981, found 361.2993.

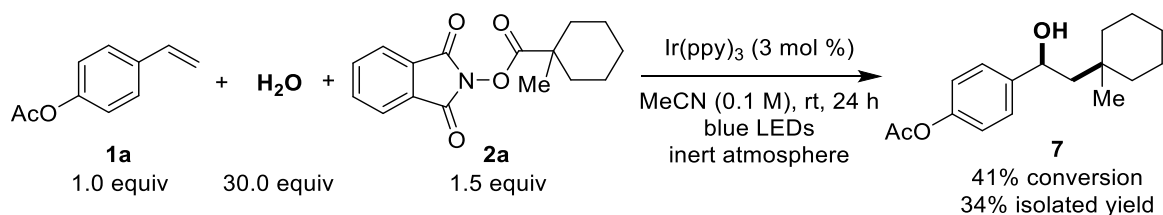
7.3 Carbocation Trapping Experiments

Formation of 4-(1-methoxy-2-(1-methylcyclohexyl)ethyl)phenyl Acetate (6)



To an 8 mL reaction vial (17 x 60 mm) equipped with a magnetic stir bar was added 1,3-dioxoisindolin-2-yl 1-methylcyclohexane-1-carboxylate (129 mg, 0.45 mmol, 1.5 equiv) and $\text{Ir}(\text{ppy})_3$ (6 mg, 0.009 mmol, 3.0 mol %, 0.03 equiv) under air. The vial was sealed with a cap containing a TFE-lined silicone septum, evacuated, and back-filled with nitrogen. After this process was repeated 3 times, MeCN (3.0 mL, 0.1 M) and MeOH (36 μL , 0.9 mmol, 3.0 equiv) were added. This was followed by addition of 4-vinylphenyl acetate (48.7 mg, 0.3 mmol, 1.0 equiv) via syringe. The reaction was irradiated for 24 h using blue LED strips ($\lambda_{\text{max}} = 456$ nm, distance lamp–vial \sim 3–5 cm), whereby the temperature was maintained at approximately 25 $^\circ\text{C}$ via cooling with a fan. Upon completion, the mixture was taken to dryness and then purified using an automated system (UV detector, $\lambda = 254$ nm and 280 nm) with RediSep R_f Gold[®] silica gel disposable flash columns (60 Å porosity, 20–40 μm) and hexanes/EtOAc (0–10% EtOAc in hexanes) as eluent. The title compound was obtained as a colorless oil (59 mg, 0.20 mmol, 68%). **¹H NMR** (400 MHz, CDCl_3), δ (ppm) = 7.28 (d, $J = 8.3$ Hz, 2H), 7.05 (d, $J = 8.4$ Hz, 2H), 4.22 (dd, $J = 8.7, 2.9$ Hz, 1H), 3.14 (s, 3H), 2.29 (s, 3H), 1.78 (dd, $J = 14.7, 8.7$ Hz, 1H), 1.51 – 1.39 (m, 6H), 1.38 – 1.23 (m, 5H), 0.97 (s, 3H). **¹³C NMR** (101 MHz, CDCl_3), δ (ppm) = 169.6, 149.8, 141.8, 127.5 (2C), 121.5 (2C), 80.8, 56.4, 50.6, 38.7, 38.4, 33.1, 26.5, 25.8, 22.2, 22.1, 21.3. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu}$ = 2923, 2861, 1759, 1504, 1450, 1369, 1212, 1196, 1163, 1097, 1048, 1016. **HRMS** (ESI) calcd for $\text{C}_{18}\text{H}_{26}\text{O}_3$ $\text{Na}[\text{M}+\text{Na}]^+$: 313.1780, found 313.1782.

Formation of 4-(1-hydroxy-2-(1-methylcyclohexyl)ethyl)phenyl Acetate (7)



To an 8 mL reaction vial (17 x 60 mm) equipped with a magnetic stir bar was added 1,3-dioxoisindolin-2-yl 1-methylcyclohexane-1-carboxylate (129 mg, 0.45 mmol, 1.5 equiv) and $\text{Ir}(\text{ppy})_3$ (6 mg, 0.009 mmol, 3.0 mol %, 0.03 equiv) under air. The vial was sealed with a cap containing a TFE-lined silicone septum, evacuated, and back-filled with nitrogen. After this process was repeated 3 times, MeCN (3.0 mL, 0.1 M) and H_2O (162 μL , 9.0 mmol, 30.0 equiv) were added. This was followed by addition of 4-vinylphenyl acetate (48.7 mg, 0.3 mmol, 1.0 equiv) via syringe. The reaction was irradiated for 24 h using blue LED strips ($\lambda_{\text{max}} = 456$ nm, distance lamp–vial \sim 3–5 cm), whereby the temperature was maintained at approximately 25 $^\circ\text{C}$ via cooling with a fan. Upon completion, the mixture was taken to dryness and then purified using an automated system (UV detector, $\lambda = 254$ nm and 280 nm) with RediSep R_f Gold[®] silica gel disposable flash columns (60 Å porosity, 20–40 μm) and hexanes/EtOAc (0–10% EtOAc in hexanes) as eluent. The title compound was obtained as a colorless oil (30 mg, 0.10 mmol, 34%). **¹H NMR** (400 MHz, CDCl_3), δ (ppm) = 7.35 (d, $J = 8.1$ Hz, 2H), 7.05 (d, $J = 8.1$ Hz, 2H), 4.87 (dd, $J = 8.6, 3.2$ Hz, 1H), 2.29 (s, 3H), 1.82 – 1.67 (m, 2H), 1.60 (dd, $J = 14.8, 3.3$ Hz, 1H), 1.49 – 1.26 (m, 10H), 1.01 (s, 3H). **¹³C NMR** (101 MHz, CDCl_3), δ (ppm) = 169.7, 149.8, 144.5, 126.9 (2C), 121.7 (2C), 71.4, 51.5, 38.8, 38.4, 33.1, 26.5, 25.7, 22.1

(2C), 21.3. **FT-IR** (cm^{-1} , neat, ATR): $\tilde{\nu} = 3431, 2923, 2859, 1758, 1606, 1505, 1451, 1369, 1196, 1165, 1061, 1016$. **HRMS** (ESI) calcd for $\text{C}_{17}\text{H}_{24}\text{O}_3\text{Na}$ [$\text{M}+\text{Na}$] $^+$: 299.1623, found 299.1632.

7.4 Stern-Volmer Quenching Studies

Fluorescence measurements were obtained using septa-capped UV-Quartz cuvettes (10 mm pathlength) obtained from Starna Cells (Cat#: 29F—Q—10). Excitation was performed at 375 nm; fluorescence spectra were obtained from 400-700 nm. In a nitrogen filled glovebox, the following stock solutions were prepared:

- Photocatalyst solution (0.0002 M):** To an oven dried scintillation vial equipped with a stir bar was added $\text{Ir}(\text{ppy})_3$ (1.46 mg, 2.23×10^{-3} mmol). This was diluted with 10.8 mL of MeCN and stirred until completely dissolved, producing a 2.06×10^{-4} M solution of $\text{Ir}(\text{ppy})_3$.
- Phthalimide ester solution (0.004 M):** To an oven dried scintillation vial equipped with a stir bar, was added 1,3-dioxoisindolin-2-yl 1-methylcyclohexane-1-carboxylate **2a** (12.4 mg, 4.32×10^{-2} mmol). This was diluted in 10.8 mL of MeCN and stirred until completely dissolved, producing a colorless, 4.00×10^{-3} M solution of phthalimide ester **2a**.
- Organotrifluoroborate solution (0.004 M):** To an oven dried scintillation vial equipped with a stir bar was added (trifluoro(phenylethynyl)- λ^4 -borane, potassium salt **3a** (8.99 mg, 4.32×10^{-2} mmol). This was diluted in 10.8 mL of MeCN and stirred until completely dissolved, producing a colorless, 4.00×10^{-3} M solution of organotrifluoroborate **3a**.
- Styrene solution (0.004 M):** To an oven dried scintillation vial equipped with a stir bar, was added 10.8 mL of MeCN followed by styrene derivative **1a** (6.6 μL , 4.32×10^{-2} mmol). The solution was stirred until completely dissolved, producing a 4.00×10^{-3} M solution of styrene derivative **1a**.

Following preparation, the solutions were allocated to the cuvettes and fluorescence quenching was determined with individual quenchers (phthalimide ester, styrene, and organotrifluoroborate). The I_0/I values of each sample were calculated from the average of three scans per data point. Linear regression of I_0/I against concentration was carried out to yield the Stern-Volmer quenching rate constant (K_{SV}). The following Stern-Volmer plots for luminescence quenching of $\text{Ir}(\text{ppy})_3$ (1.9×10^{-5} M in degassed MeCN) by quenchers were obtained. The excited catalyst is quenched most efficiently by the aliphatic phthalimide ester with a Stern-Volmer quenching rate constant of $1.4 \times 10^4 \text{ M}^{-1}$.

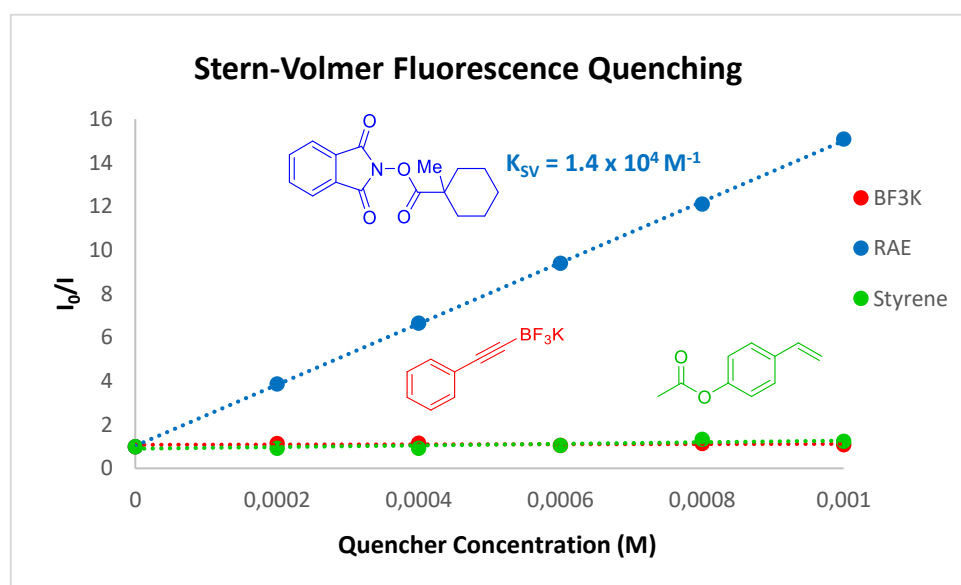
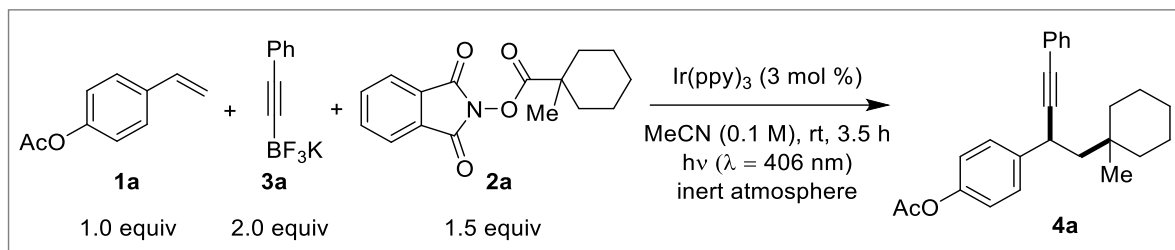


Figure 3. Stern-Volmer plots for luminescence quenching of $\text{Ir}(\text{ppy})_3$ (1.9×10^{-5} M in degassed MeCN) by redox-active ester **2a** (blue), organotrifluoroborate **3a** (red), styrene **1a** (green), $\lambda_{\text{exc.}} = 375 \text{ nm}$, $\lambda_{\text{em.}} = 534 \text{ nm}$, $K_{SV} =$ Stern-Volmer constant.

7.5 Determination of Quantum Yield: A Closed Catalytic Loop ($\Phi \leq 1$) or Radical Chain Process ($\Phi > 1$)?

The quantum yield of the reaction was determined using the procedure reported previously:⁹⁻¹⁰ 4-Vinylphenyl acetate **1a**, *N*-hydroxyphthalamide ester **2a** and potassium (2-phenylethynyl)trifluoroborate **3a** were used as a model substrates to determine the quantum yield, using trimethoxybenzene as internal standard in a proportion 1:1 with **1a**.



The quantum yield of the reaction is defined as:

$$\Phi = \frac{\text{mol of product formed}}{\text{mol of photon flux} \times t \times f} \quad (1)$$

where Φ is the quantum yield of the reaction, t is the time of the reaction (s), f is the incident light absorbed by the Ir catalyst at 406 nm and the photon flux is calculated by standard ferrioxalate actinometry¹¹ (section C).

A) Incident light absorbed by the $\text{Ir}(\text{ppy})_3$ (f)

The fraction of light, f , absorbed was determined according to equation 2:

$$f = 1 - 10^{-A} \quad (2)$$

where A is the absorbance of the fully soluble Ir in acetonitrile at 406 nm. The wavelength of 406 nm was chosen based on two criteria: the wavelength at which the (i) absolute $\Phi(\text{Fe}^{2+})$ had been established,¹¹ and (ii) reaction was going to be irradiated where the Ir catalyst absorbs most. The absorbance of Ir catalyst was measured by adding $\text{Ir}(\text{ppy})_3$ (4 mg, 0.003 mmol) in acetonitrile (2 mL) to a cuvette equipped with a Teflon-coated magnetic stir bar and stirred for 10 minutes. The absorbance of the suspension was recorded. To accurately determine the fraction of light absorbed, another identical solution of Ir in acetonitrile was prepared and then filtered. The absorbance of the solvated Ir solution in acetonitrile was measured. The absorbance (A) at 406 nm was determined to be 1.94888 (Figure 4), and thus indicating the fraction of light absorbed is > 0.98875 according to equation 2.

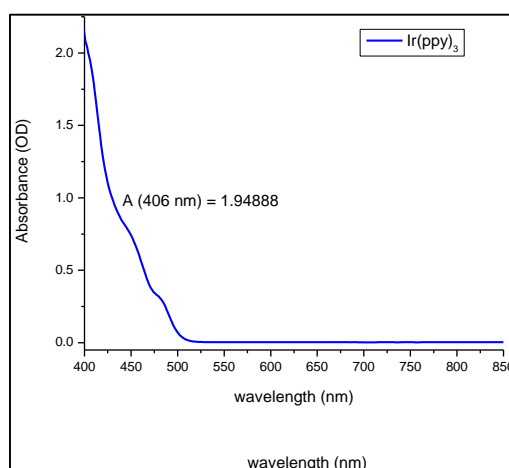


Figure 4. Absorption spectrum for filtered solution of $\text{Ir}(\text{ppy})_3$ in acetonitrile.

B) The photoredox reaction

To the cuvette in section A containing Ir(ppy)₃ (4 mg, 0.003 mmol) in acetonitrile (2 mL) was added 4-vinylphenyl acetate (32.4 mg, 0.2 mmol), potassium trifluoro(phenylethynyl)borate (83.2 mg, 0.4 mmol, 2 equiv) and 1,3-dioxoisindolin-2-yl 1-methylcyclohexane-1-carboxylate (86.2 mg, 0.3 mmol, 1.5 equiv) in a dark room (laboratory lights were shut off). The cuvette was then capped with a PTFE stopper, and Ar(g) was bubbled through for 300 s. Initial emission quenching experiments were performed on the Ir catalyst to determine the time it takes for the system to deoxygenate, and this was found to be 200 s. Under an Ar (g) atm., the sample was stirred (1200 rpm, temp maintained at 23 °C using a temperature controller) and irradiated ($\lambda = 406$ nm, excitation slit width = 10.0 nm, step = 1.0 nm, Iris = 100) for 12600 s (3.5 h) (Figure 5). Note: the reaction is heterogeneous and light scattering due to solids has not been accounted for.

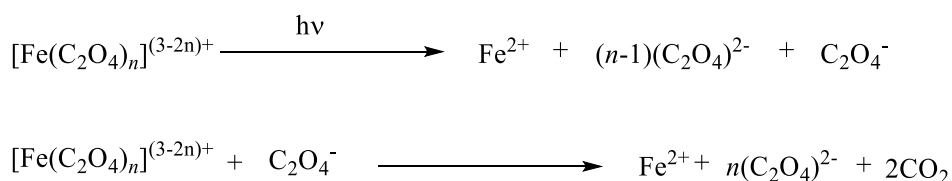


Figure 5. The photoredox reaction set-up. The reaction mixture was irradiated at 406 nm under an atmosphere of Ar (g) at 23 °C.

After irradiation, the crude mixture was passed through a silica plug using EtOAc and the filtrate concentrated under reduced pressure to give a yellow residue. The reaction was repeated twice for reproducibility. The yield of product (0.01 mmol after 12,600 s) obtained after irradiating at 406 nm was determined by ¹H NMR based on a 1,3,5-trimethoxybenzene internal standard (internal standard added was 1:1 with **1a**, the limiting reagent).

C) Photon flux at 406 nm.

Standard ferrioxalate actinometry was used to determine the photon flux of the spectrophotometer using equations 3 and 4.⁹⁻¹¹ For the ferrioxalate actinometer the production of iron(II) ions proceeds by the following reactions:¹¹



The moles of Fe²⁺ formed are determined spectrophotometrically by development with 1,10-phenanthroline (phen) to form the red [Fe(phen)₃]²⁺ moiety ($\lambda = 510$ nm).⁹⁻¹¹ The photon flux is defined as:

$$\text{Photon flux} = \frac{\text{mol}(\text{Fe}^{2+})}{\Phi(\text{Fe}^{2+}) \times t \times f} \quad (3)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.188 at $\lambda = 406$ nm),¹¹ t is the time (s), and $f > 0.999$, and the mol of Fe²⁺ are calculated according to equation 4.

$$\text{mol}(\text{Fe}^{2+}) = \frac{V \times \Delta A}{l \times \epsilon} \quad (4)$$

Where V is the total volume of the solution, ΔA is the difference in absorbance between irradiated and non-irradiated solutions, l is the path length (1.0 cm), ϵ is the molar absorptivity at 510 nm ($11,110 \text{ L mol}^{-1}\text{cm}^{-1}$).¹¹

D) Experimental.

The following solutions were prepared in the dark (flasks were wrapped in aluminum foil) and stored in the dark at room temperature:

- *Ferrioxalate solution (0.15 M)*: Potassium ferrioxalate hydrate (2.21 g) was added to a flask wrapped in aluminum foil containing H_2SO_4 (30 mL, 0.05 M). The flask was stirred for complete solvation of the green solid in complete darkness. It is noteworthy that the solution should not be exposed to any incident light.
- *Developer solution*: 1,10-Phenanthroline (50 mg) and sodium acetate (11.25 g) was added to a flask containing H_2SO_4 (50 mL, 0.5 M) and sonicated until completely solvated.

The absorbance of the non-irradiated sample. The buffered solution of phen (0.35 mL) was added to a ferrioxalate (2.0 mL) in a vial that had been covered with aluminum foil {lights of the laboratory were switched off}. The vial was capped and allowed to rest for 1 h and then transferred to a cuvette. The absorbance of the non-irradiated was measured at 510 nm to be 0.3534 (Figure 6).

The absorbance of the irradiated sample. In a cuvette equipped with a stir bar was added the ferrioxalate solution (2.0 mL), and the stirred solution was irradiated for 90.0 s at $\lambda = 406 \text{ nm}$ with an excitation slit width = 10.0 nm (step = 1.0 nm, Iris = 100). After irradiation, the buffered phen solution (0.35 mL) was added to the cuvette and allowed to rest for 1 h in the dark to allow the ferrous ions to coordinate completely to phen. The absorbance was measured at 510 nm to be 1.93858 (Figure 6).

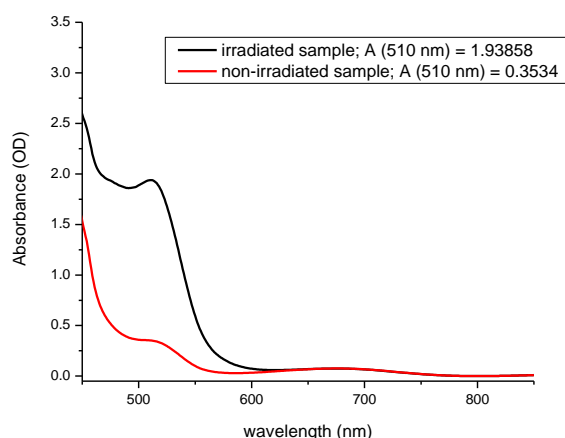


Figure 6. Absorption spectra for irradiated and non-irradiated samples of red $[\text{Fe}(\text{phen})_3]^{2+}$.

Photon flux sample calculation. Sample calculation:

$$\text{mol}(\text{Fe}^{2+}) = \frac{V \times \Delta A}{l \times \epsilon} \quad (4)$$

$$\text{mol}(\text{Fe}^{2+}) = \frac{0.00235 \text{ L} \times 1.58518}{1.00 \text{ cm} \times 11.110 \text{ L mol}^{-1}\text{cm}^{-1}} = 3.3530 \times 10^{-7} \text{ mol}$$

$$\text{Photon flux} = \frac{\text{mol}(\text{Fe}^{2+})}{\Phi(\text{Fe}^{2+}) \times t \times f} \quad (3)$$

$$\text{Photon flux} = \frac{3.3530 \times 10^{-7} \text{ mol}}{1.188 \times 90.0 \text{ s} \times 1.00} = 3.13598 \times 10^{-9} \text{ einstein s}^{-1}$$

E) Quantum yield of the reaction.

Therefore, the quantum yield of the reaction is determined to be:

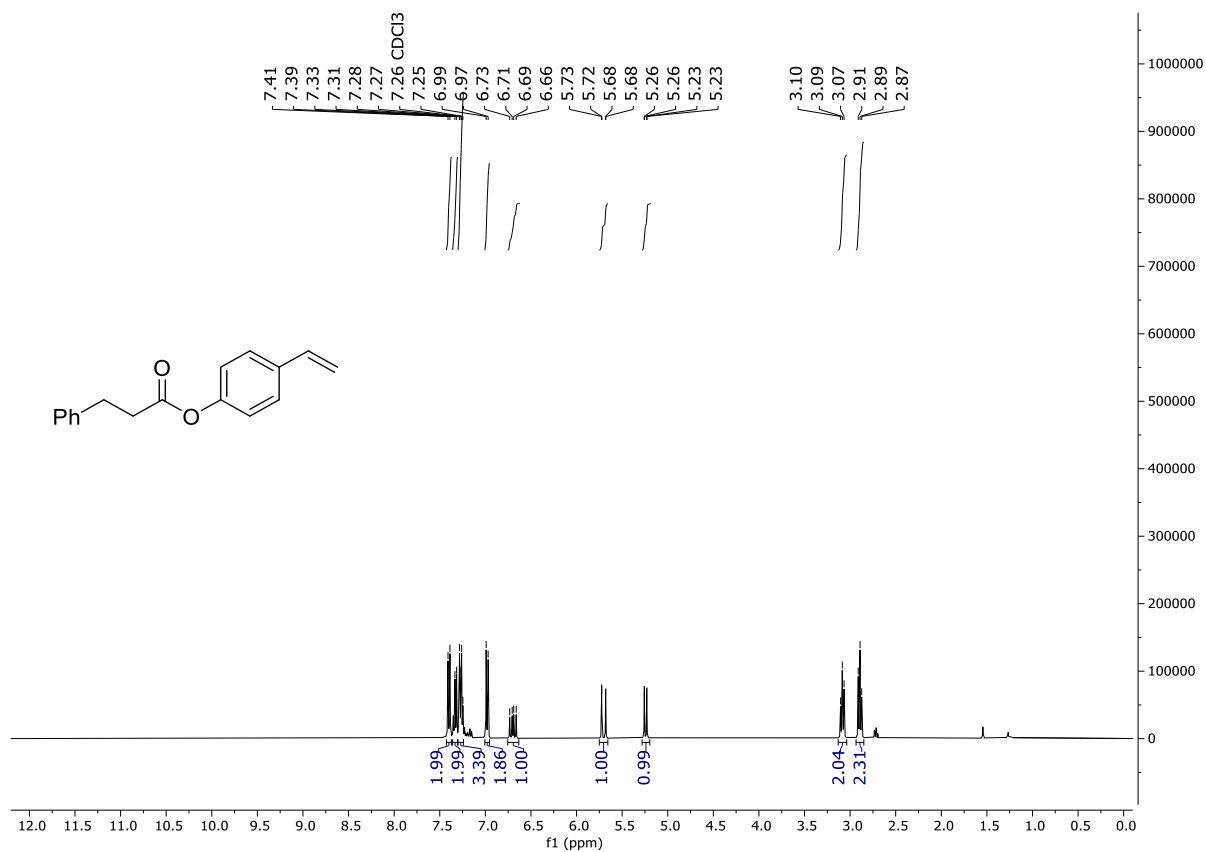
$$\Phi = \frac{\text{mol of product formed}}{\text{mol of photon flux} \times t \times f} \quad (1)$$

$$\Phi = \frac{0.1 \times 10^{-3} \text{ mol}}{3.13598 \times 10^{-9} \text{ einstein s}^{-1} \times 12600 \text{ s} \times 0.98875} = 0.256$$

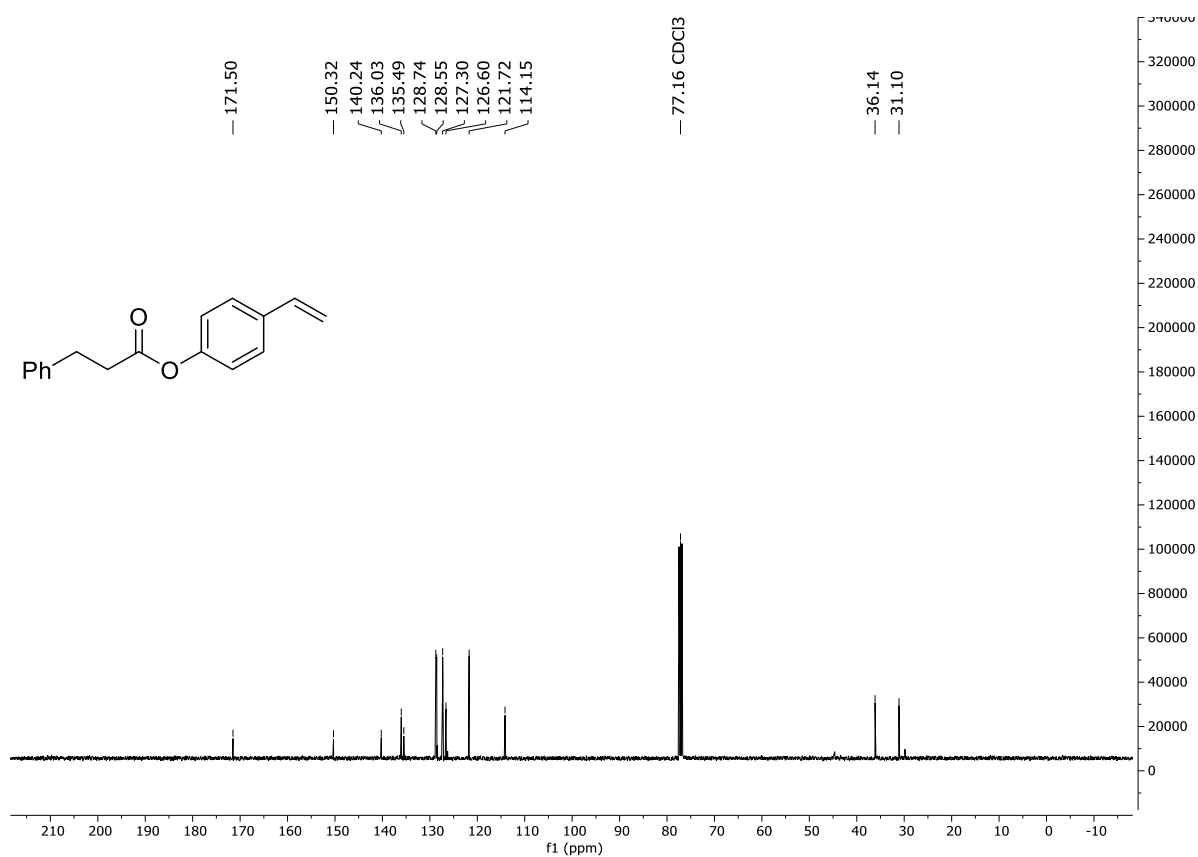
$\Phi > 1$ would mean that the chain propagation; $\Phi \leq 1$ would mean closed photocatalytic pathway

The quantum yield studies indicate that this is not a radical-chain process as evidenced by the Φ .

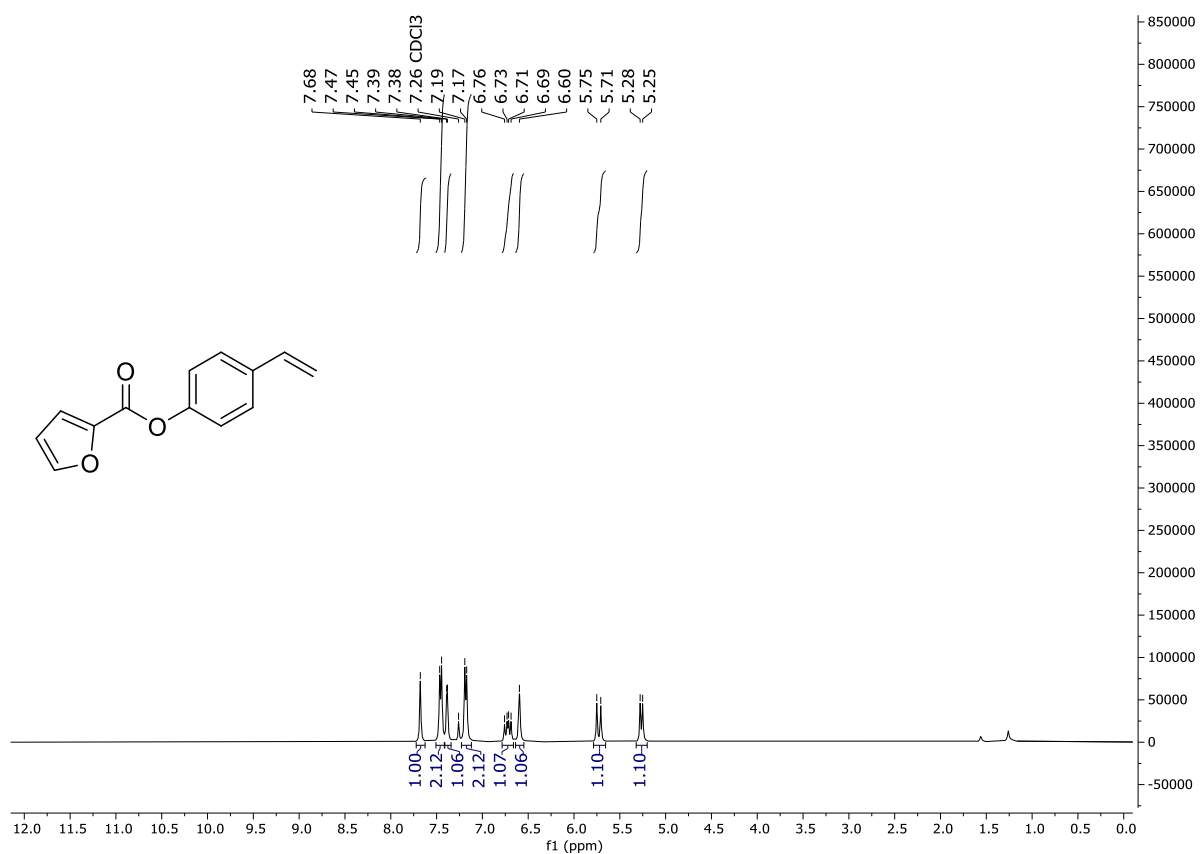
8. NMR Spectra of Synthesized Compounds



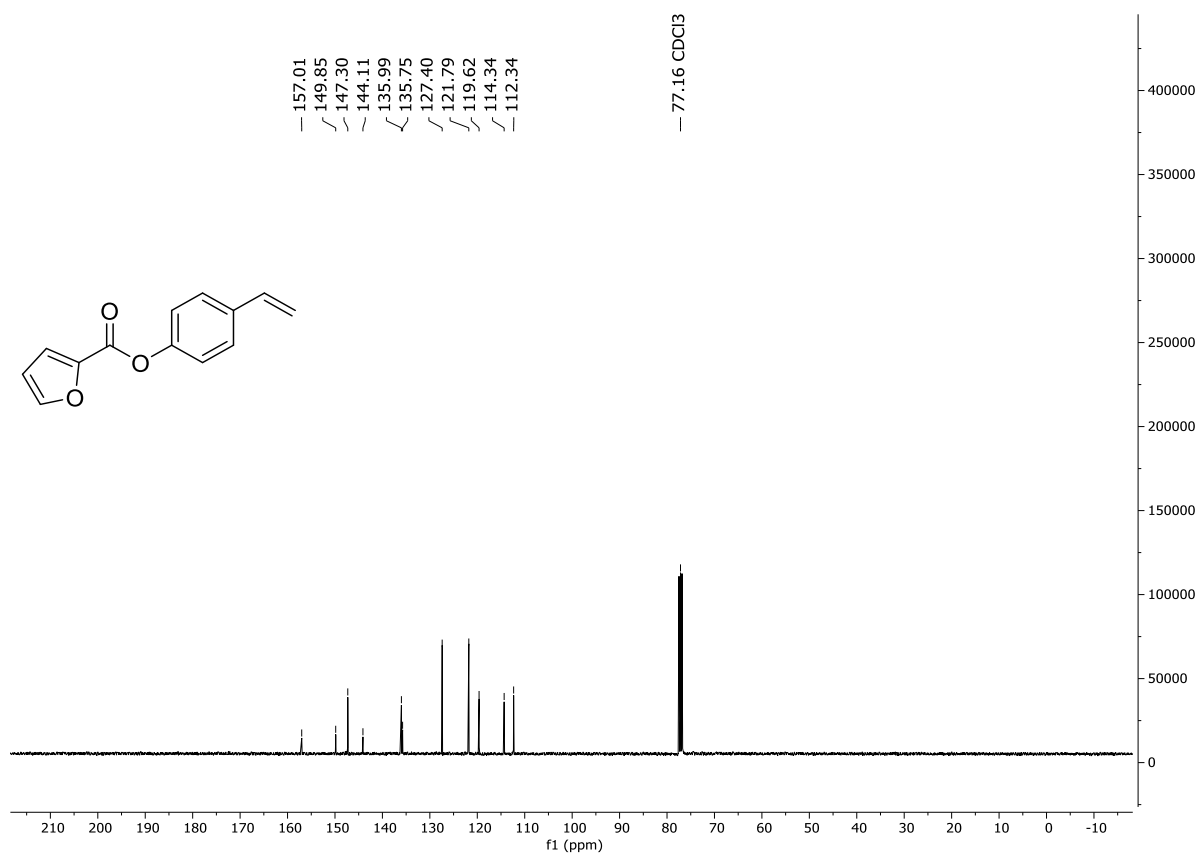
¹H NMR (400 MHz, CDCl₃) spectrum of **1aj**



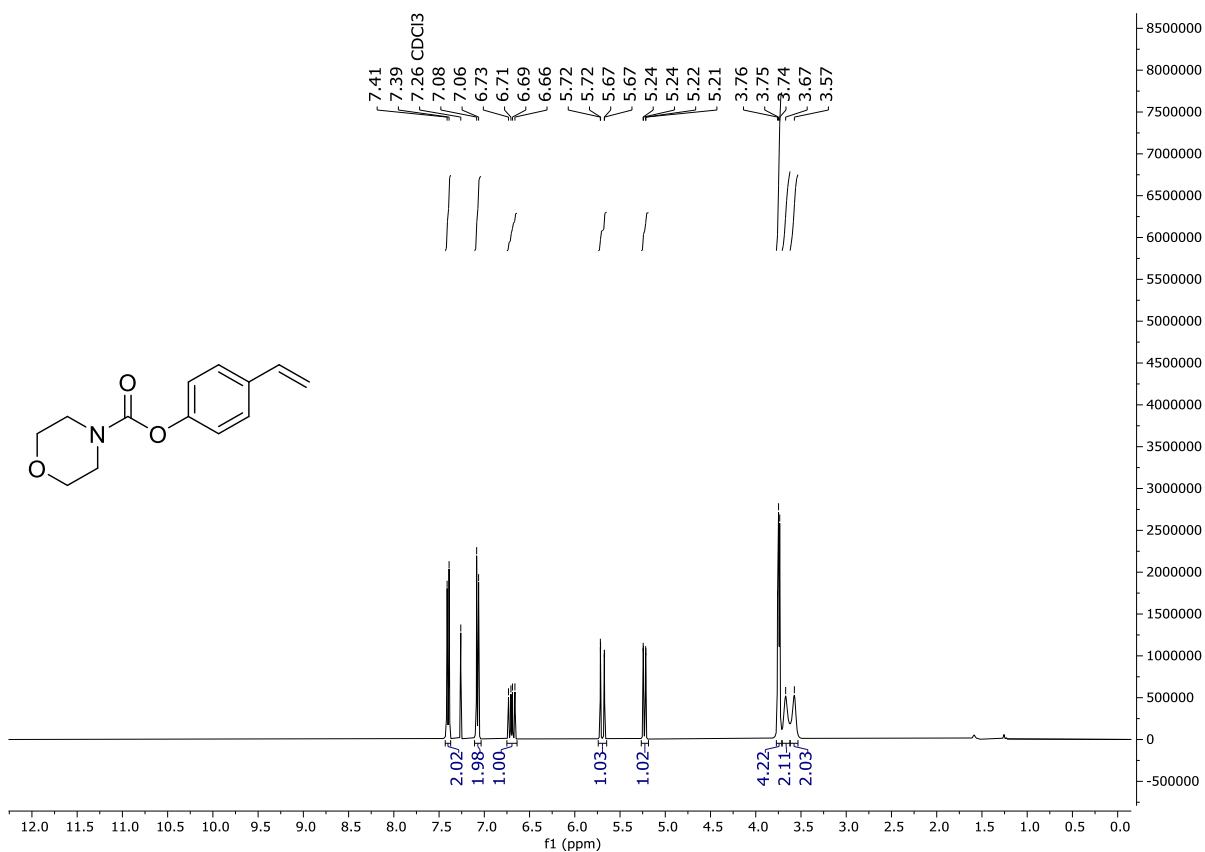
¹³C NMR (101 MHz, CDCl₃) spectrum of **1aj**



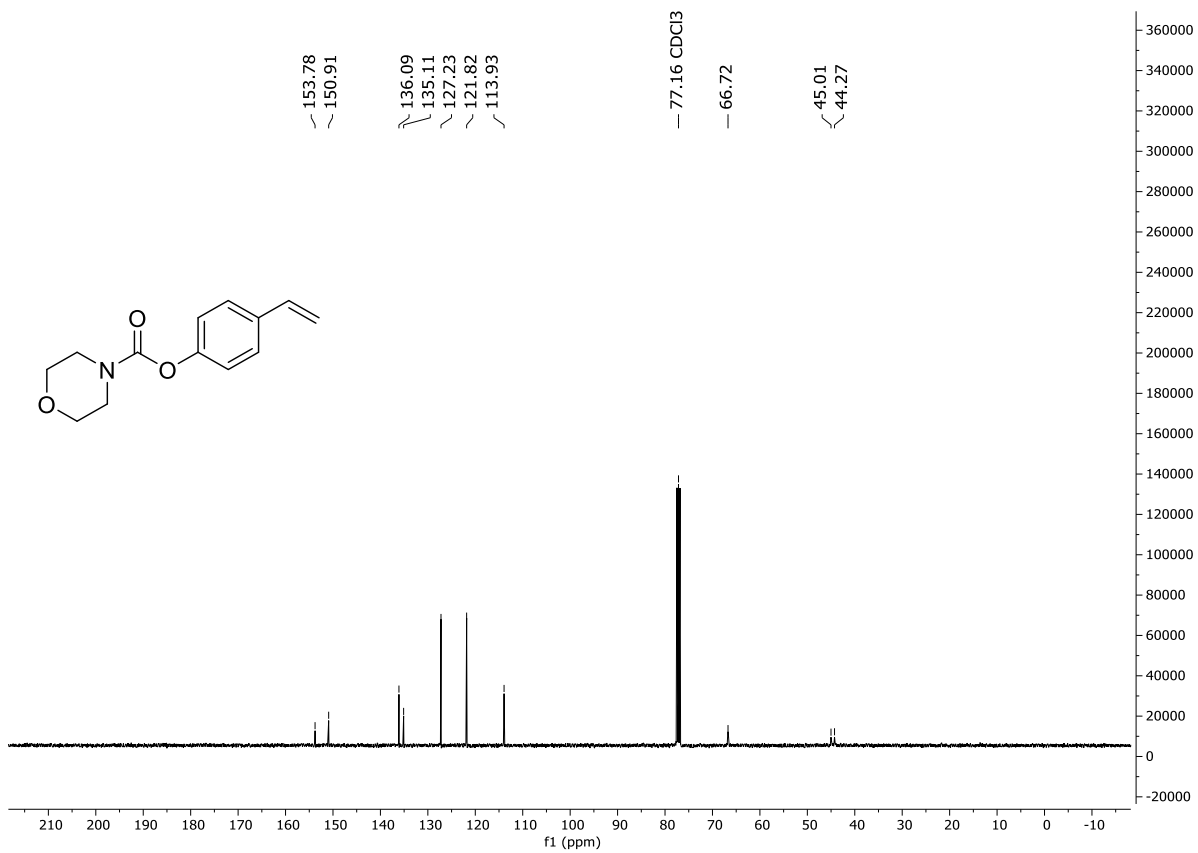
¹H NMR (400 MHz, CDCl₃) spectrum of 1ak



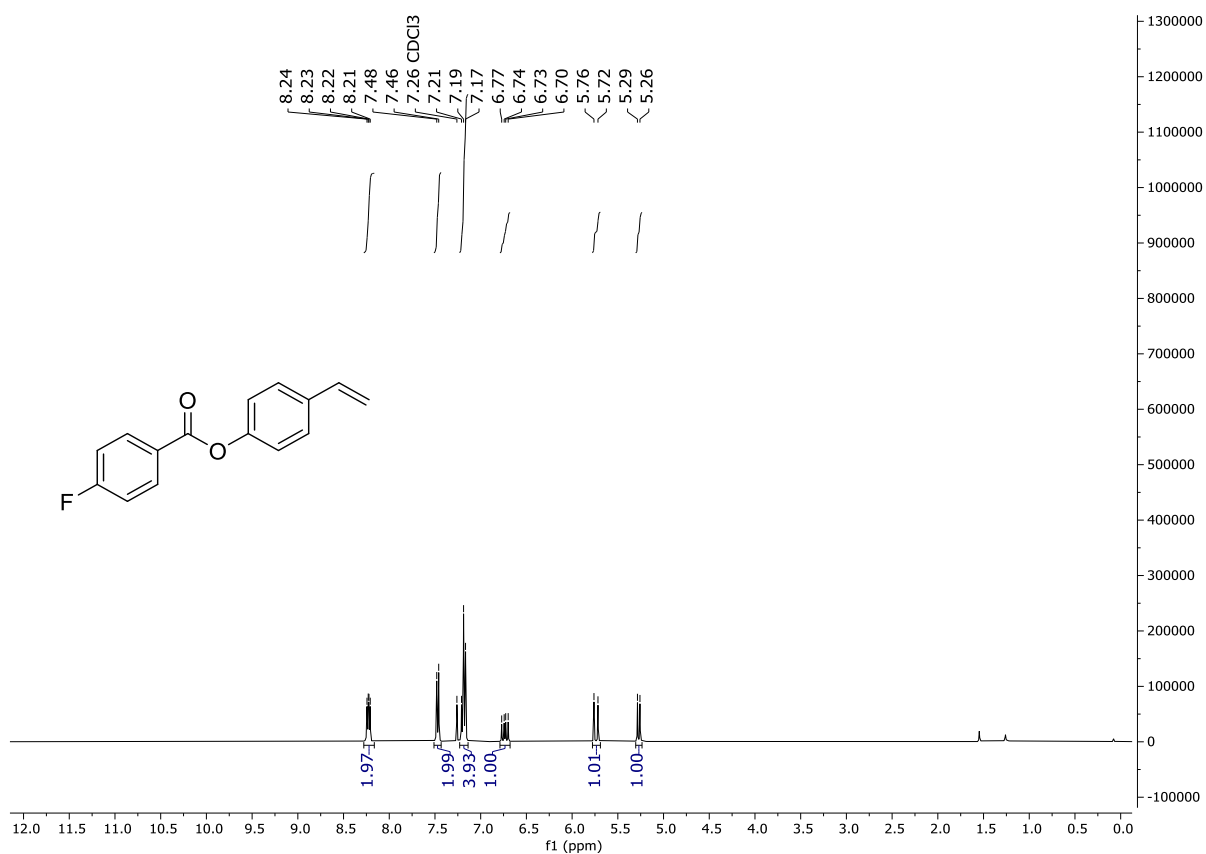
¹³C NMR (101 MHz, CDCl₃) spectrum of 1ak



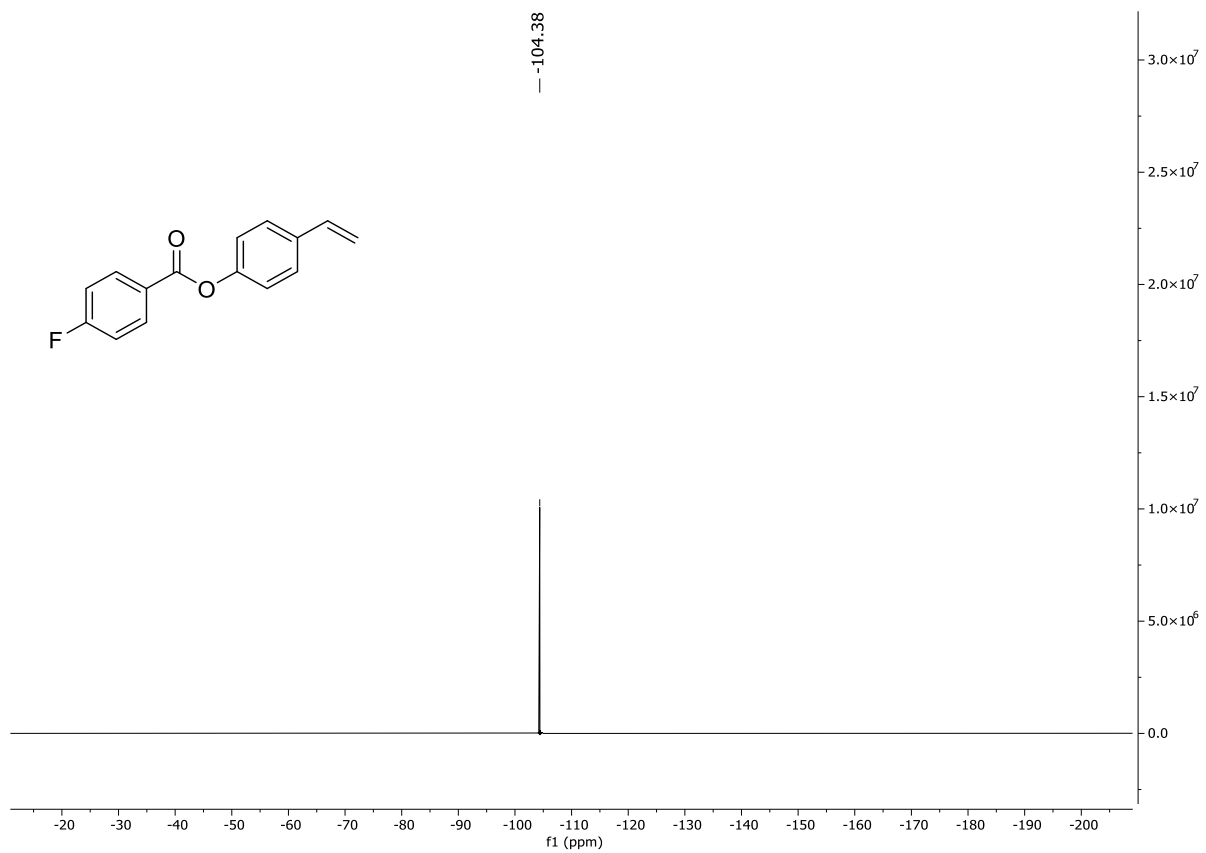
¹H NMR (400 MHz, CDCl₃) spectrum of **1a**



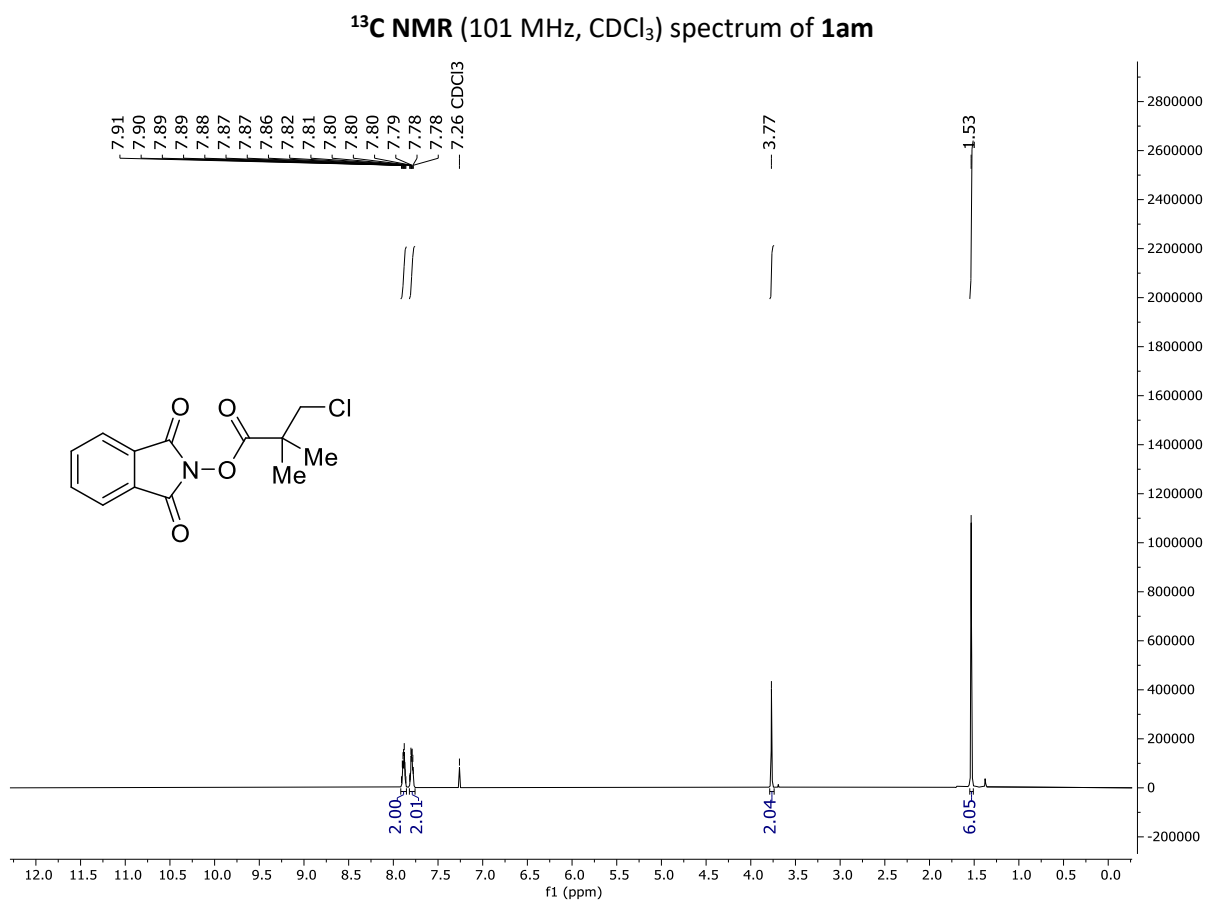
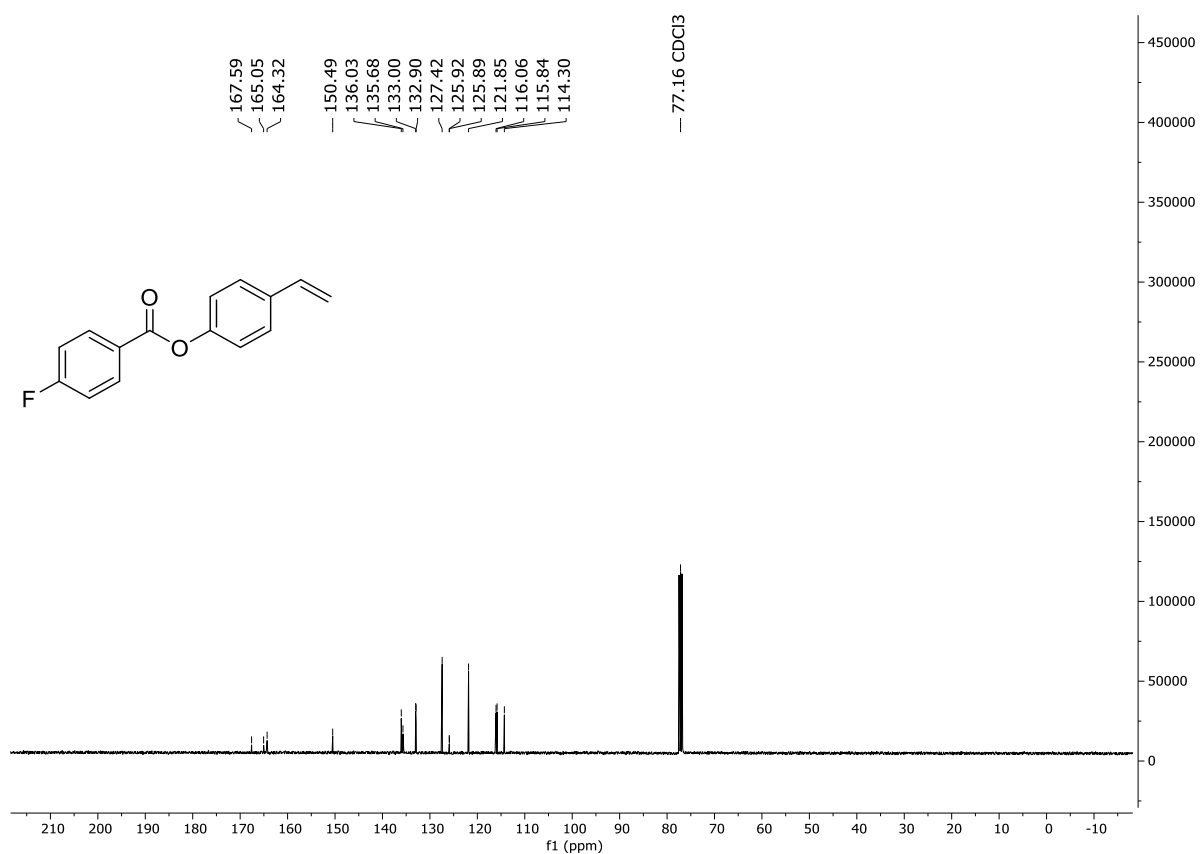
¹³C NMR (101 MHz, CDCl₃) spectrum of **1a**

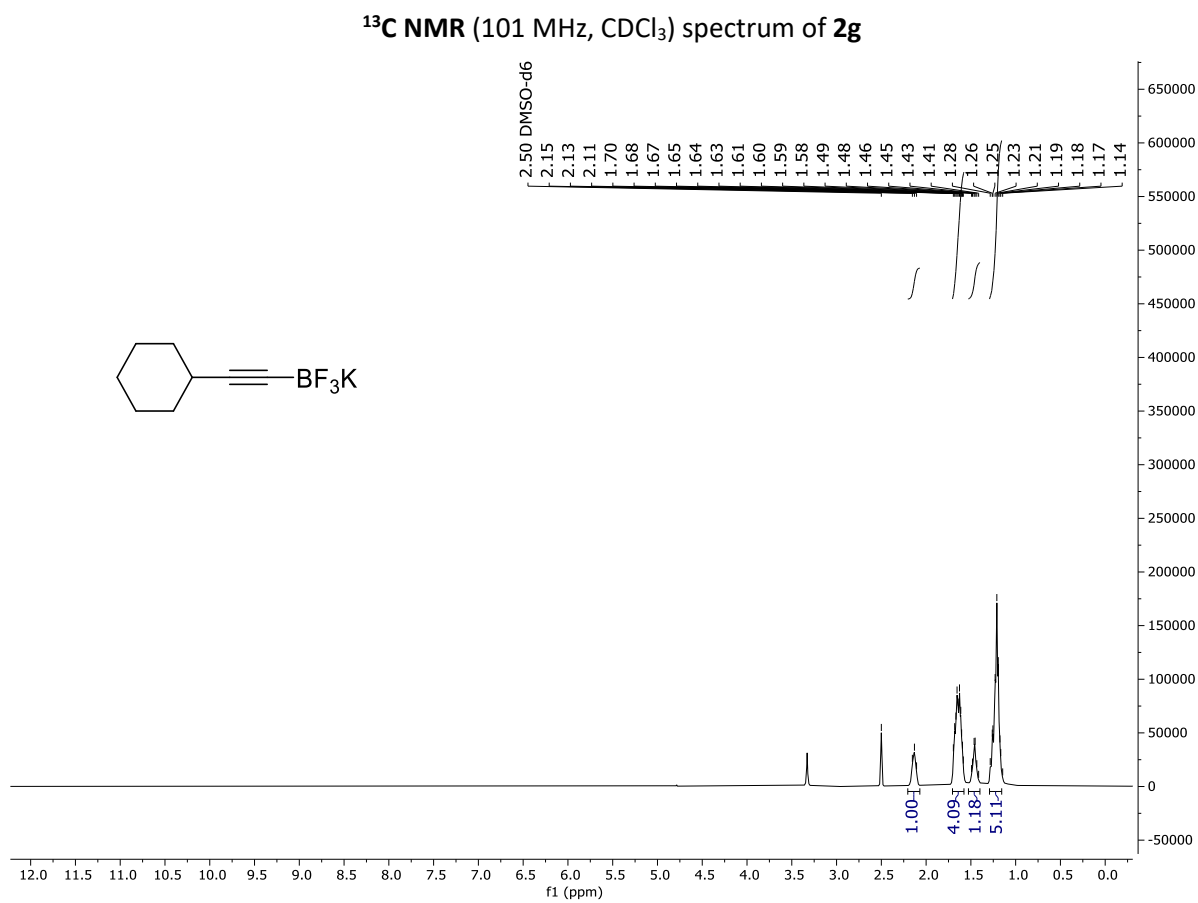
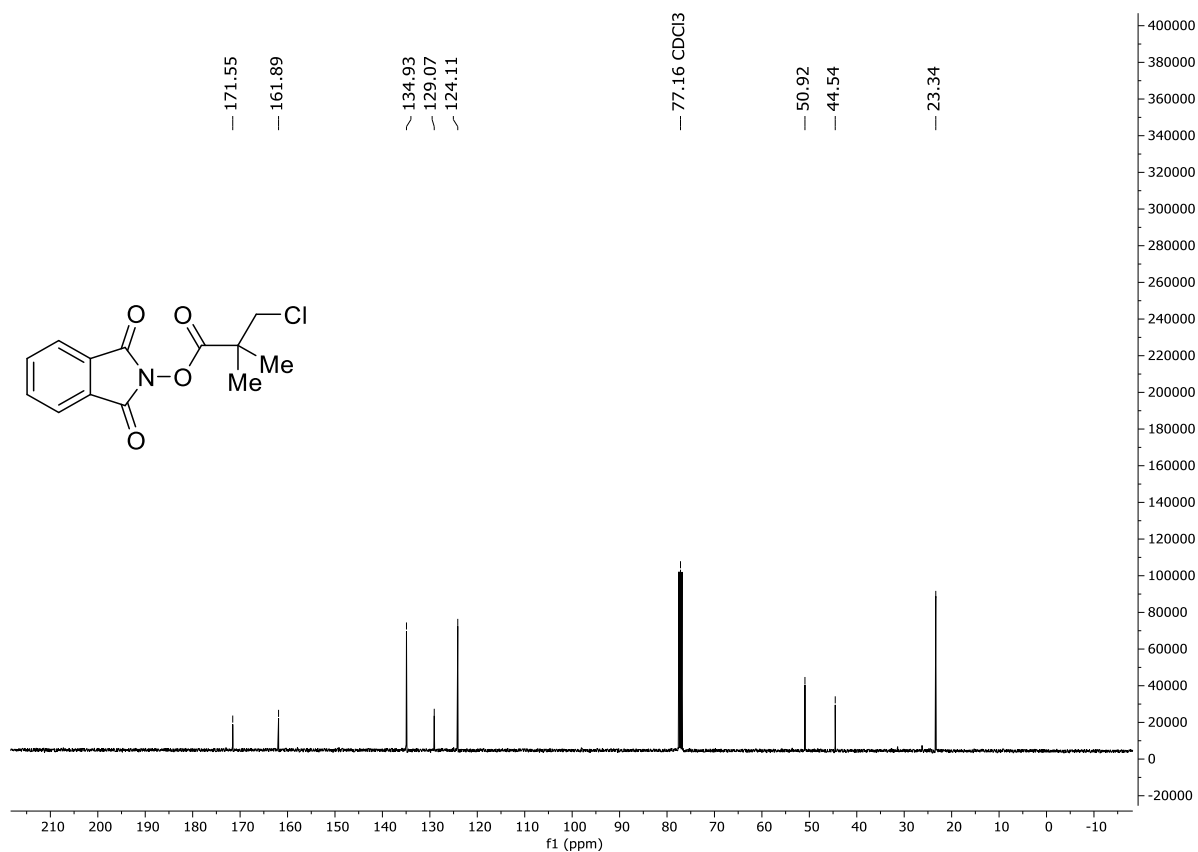


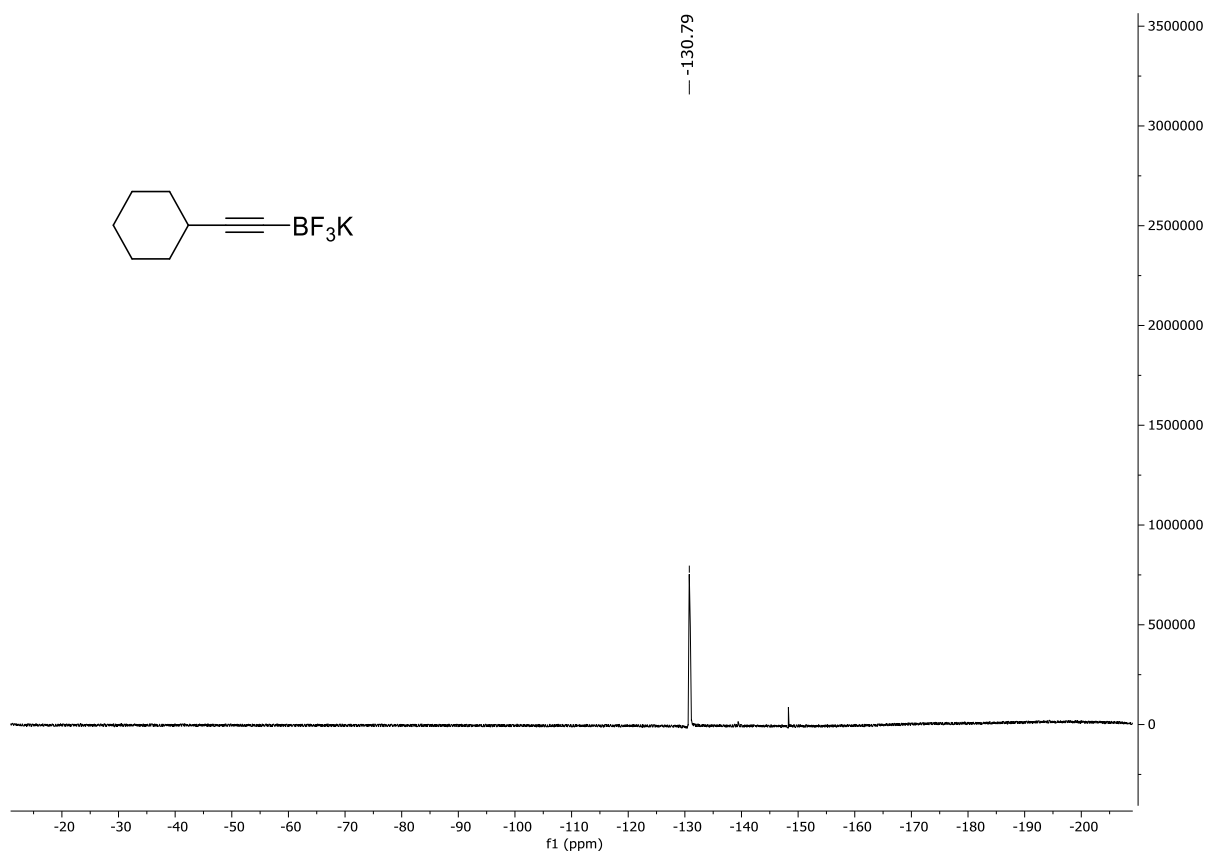
¹H NMR (400 MHz, CDCl₃) spectrum of **1am**



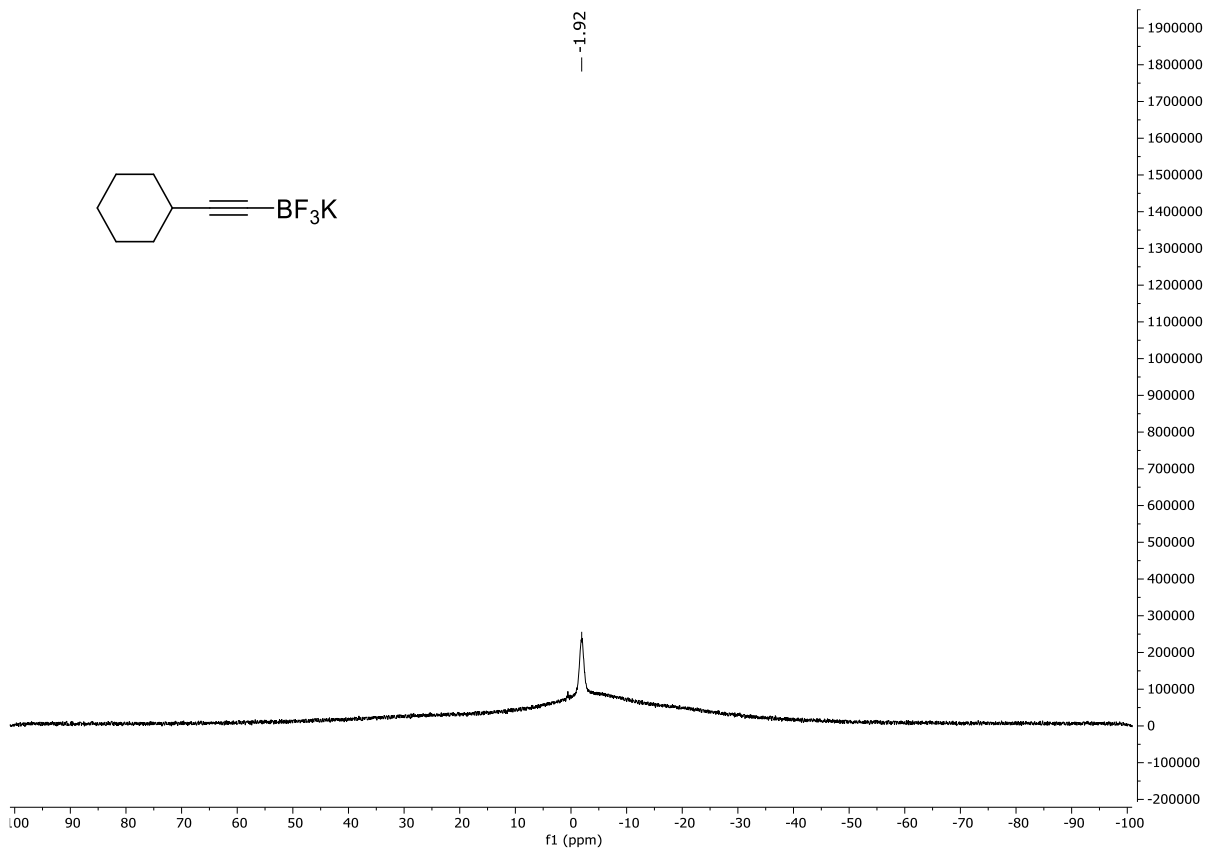
¹⁹F NMR (376 MHz, CDCl₃) spectrum of **1am**



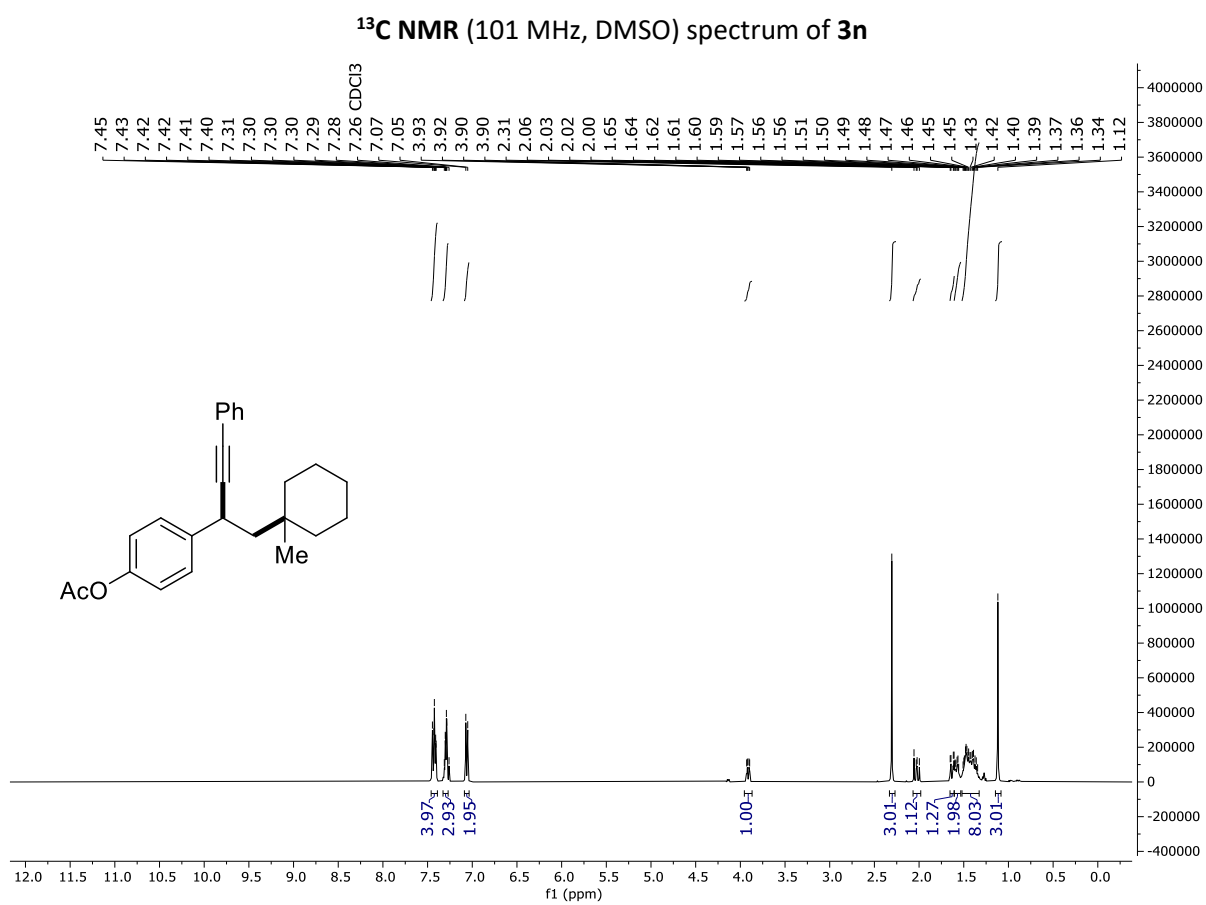
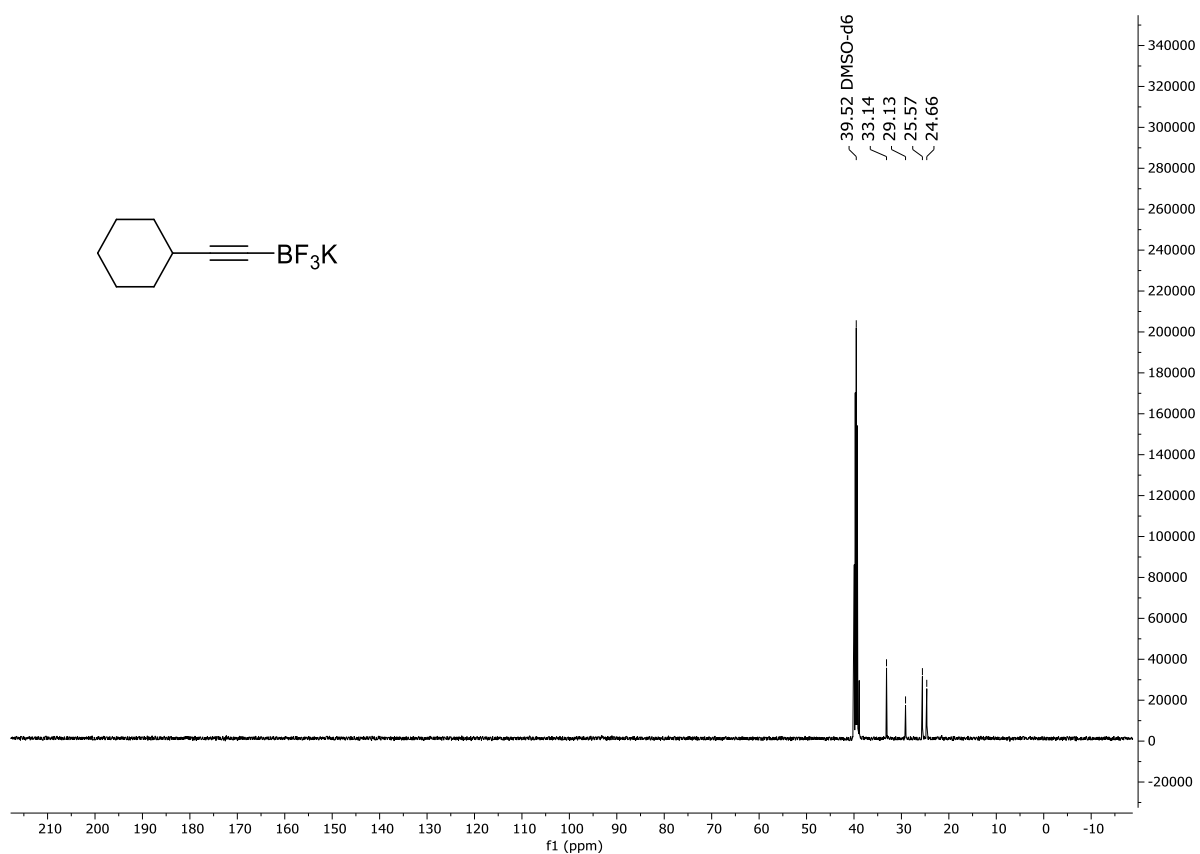


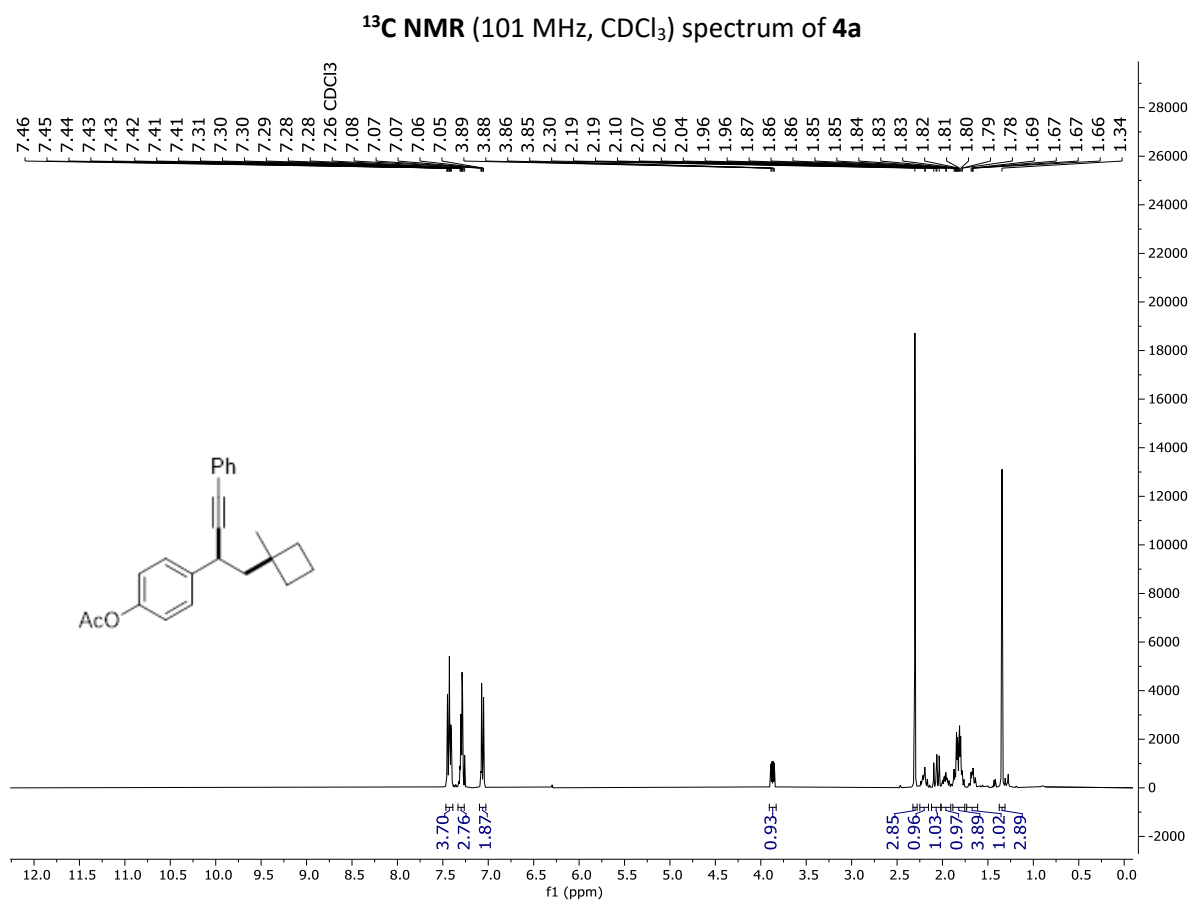
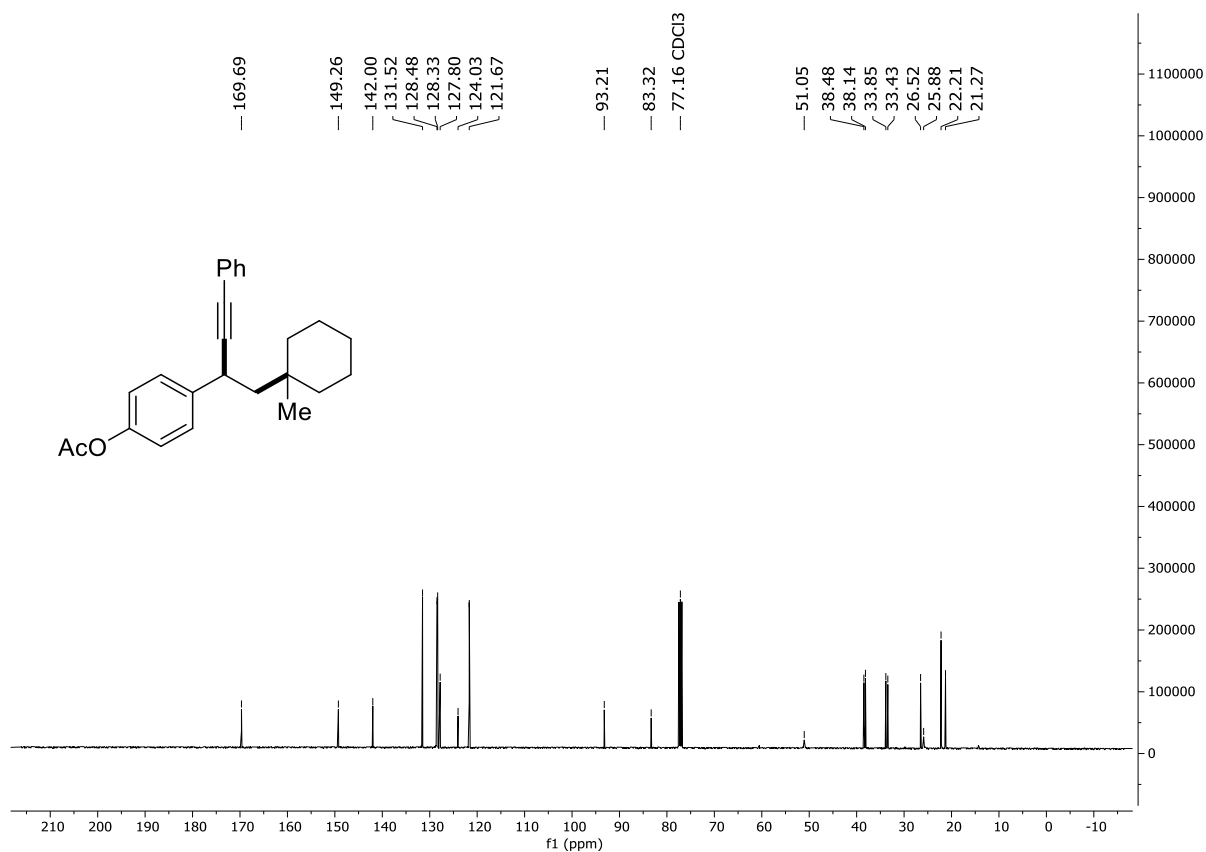


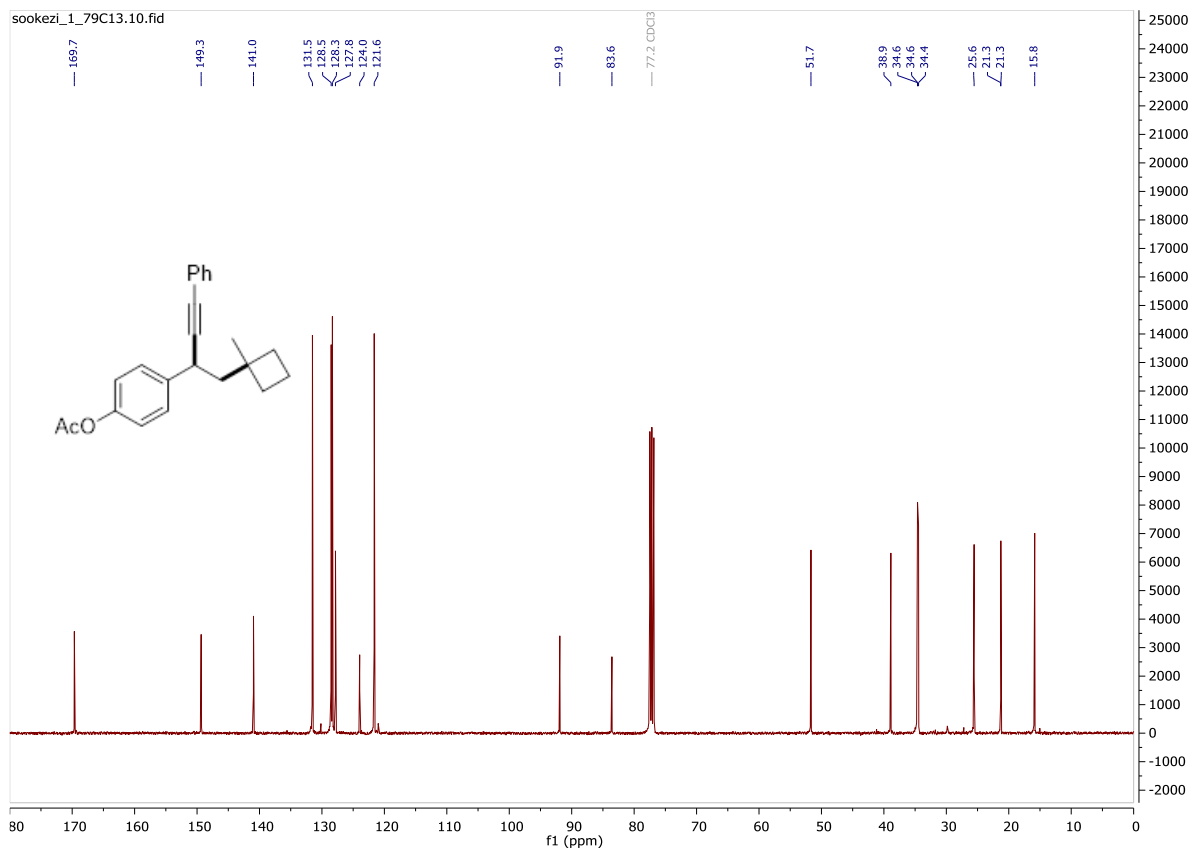
^{19}F NMR (376 MHz, DMSO) spectrum of **3n**



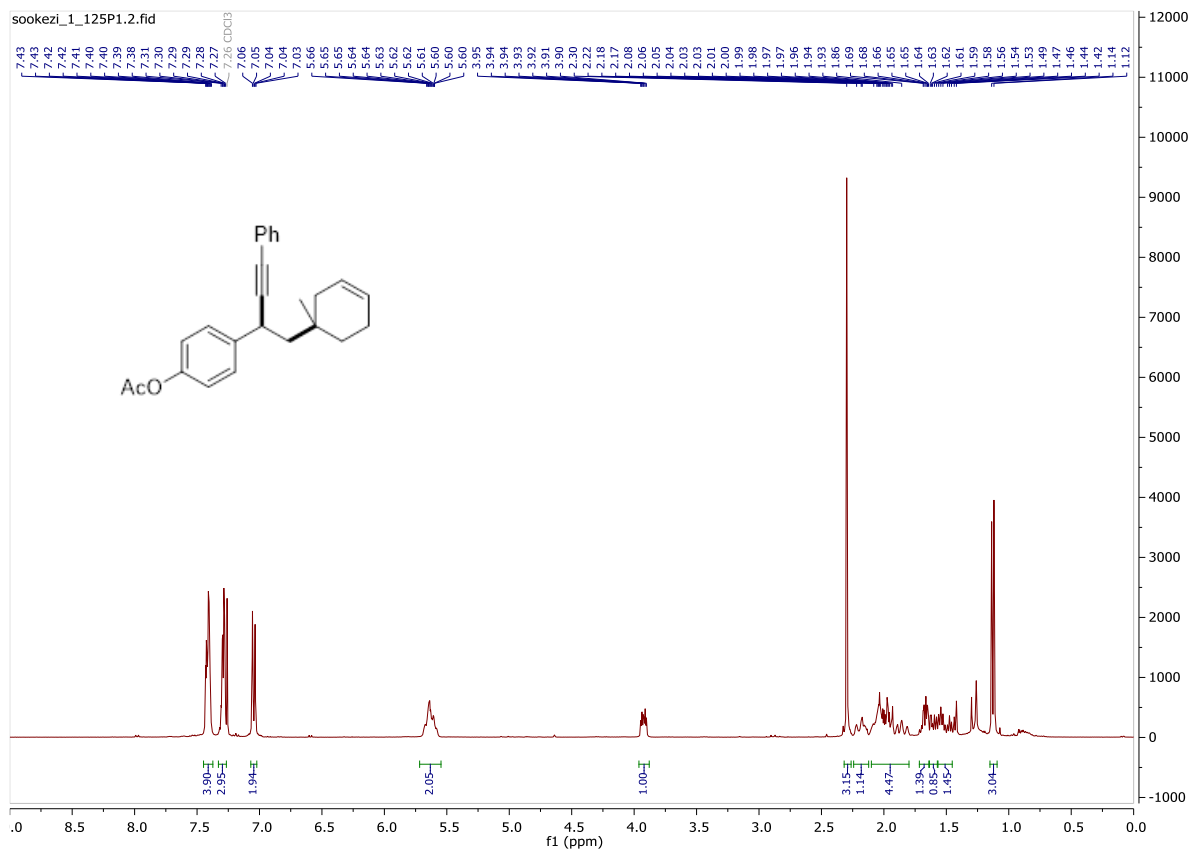
^{11}B NMR (128 MHz, DMSO) spectrum of **3n**



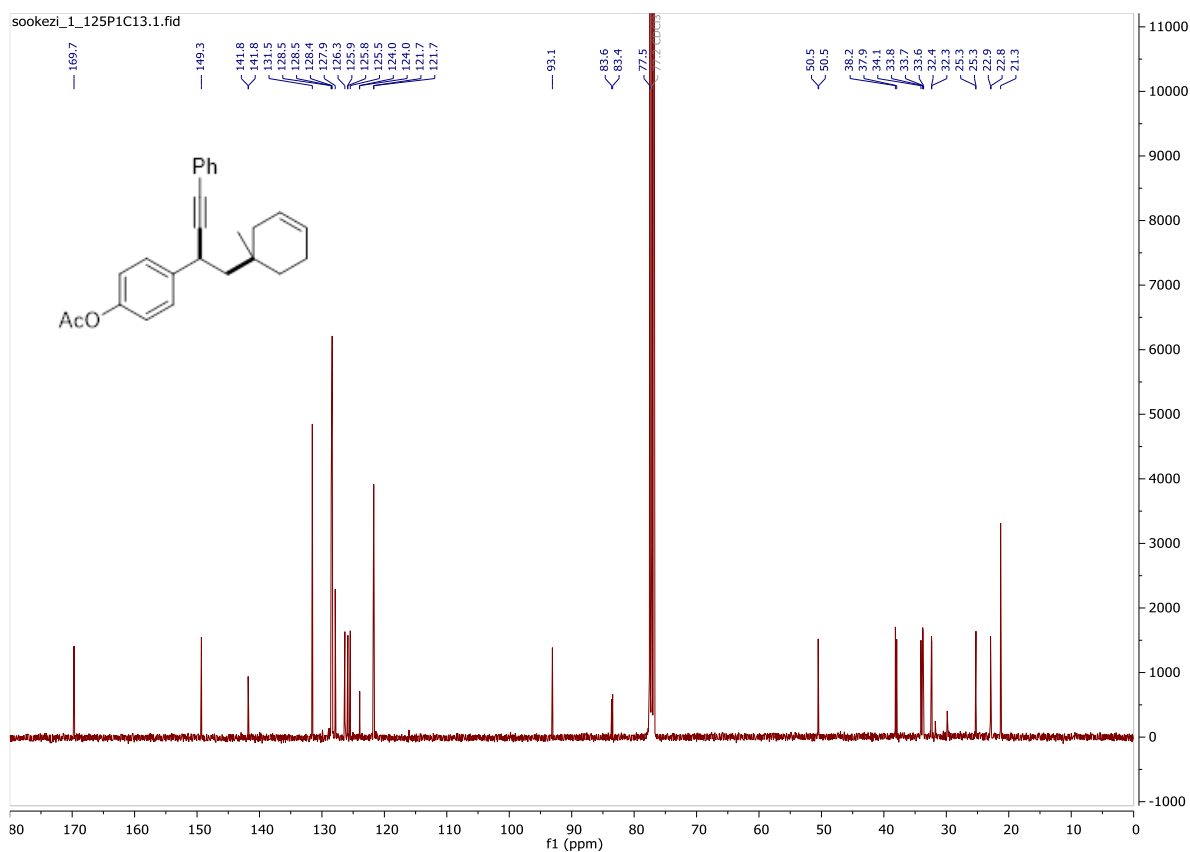




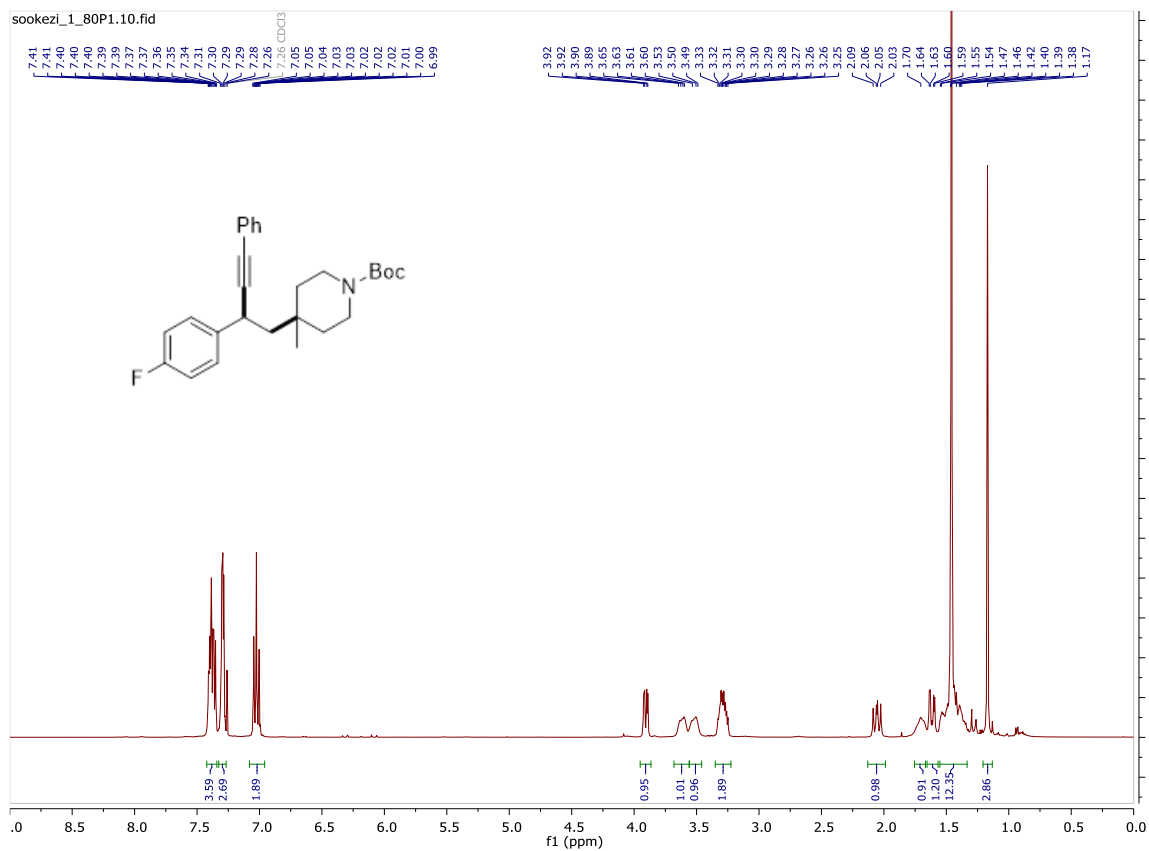
¹³C NMR (101 MHz, CDCl₃) spectrum of **4b**



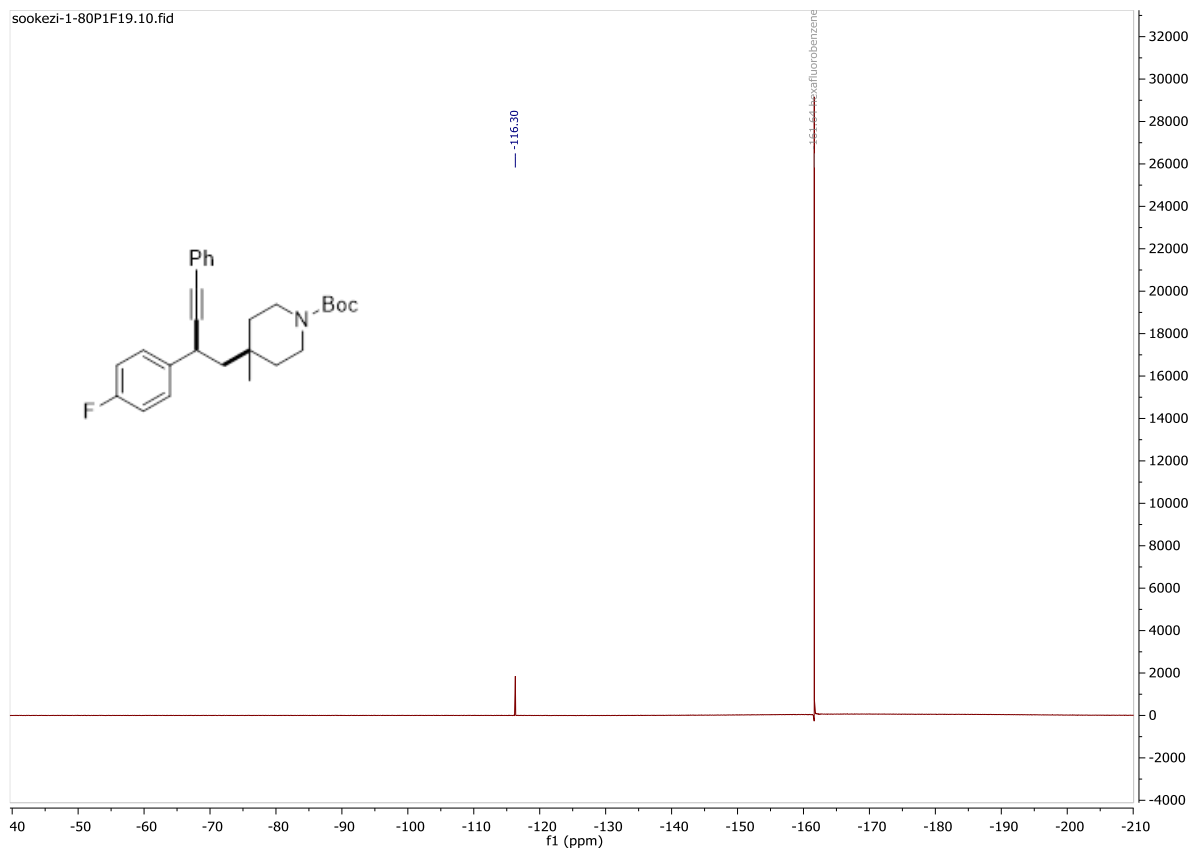
¹H NMR (400 MHz, CDCl₃) spectrum of **4c**



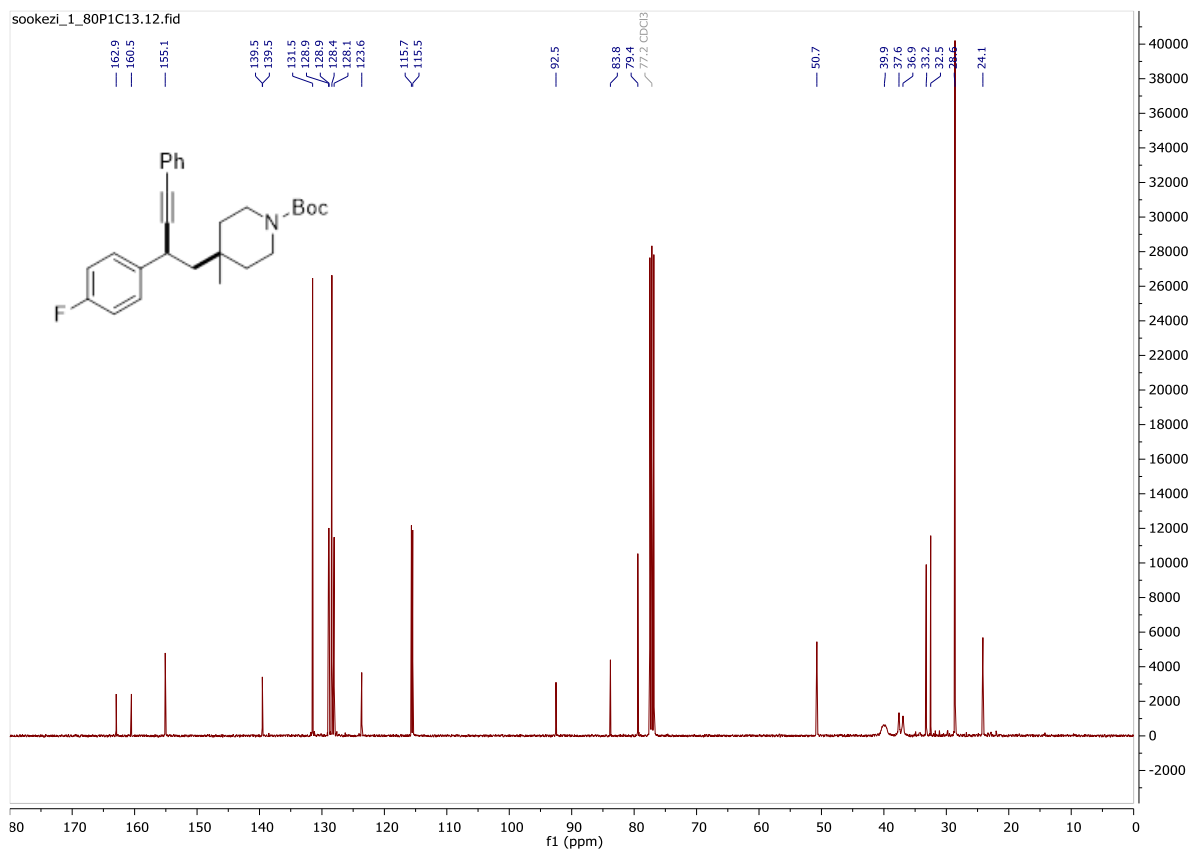
^{13}C NMR (101 MHz, CDCl_3) spectrum of **4c**



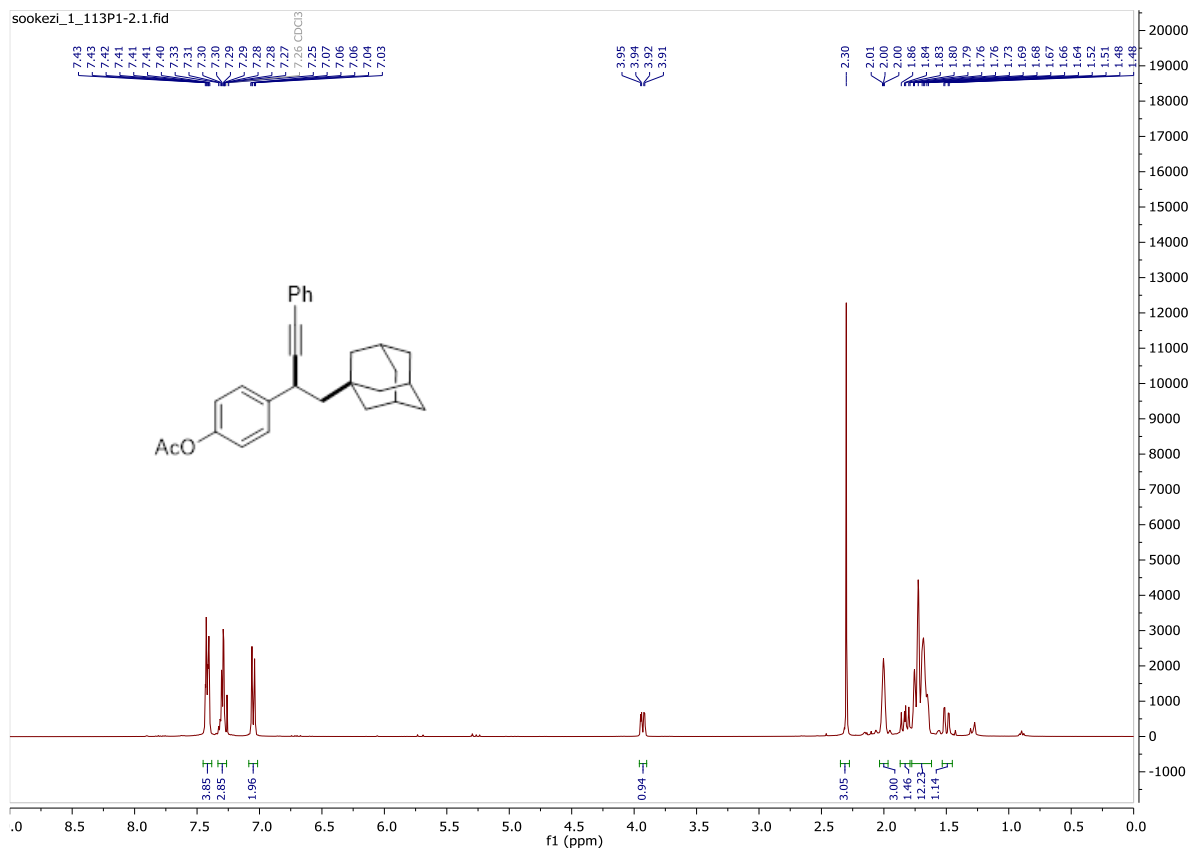
^1H NMR (400 MHz, CDCl_3) spectrum of **4d**



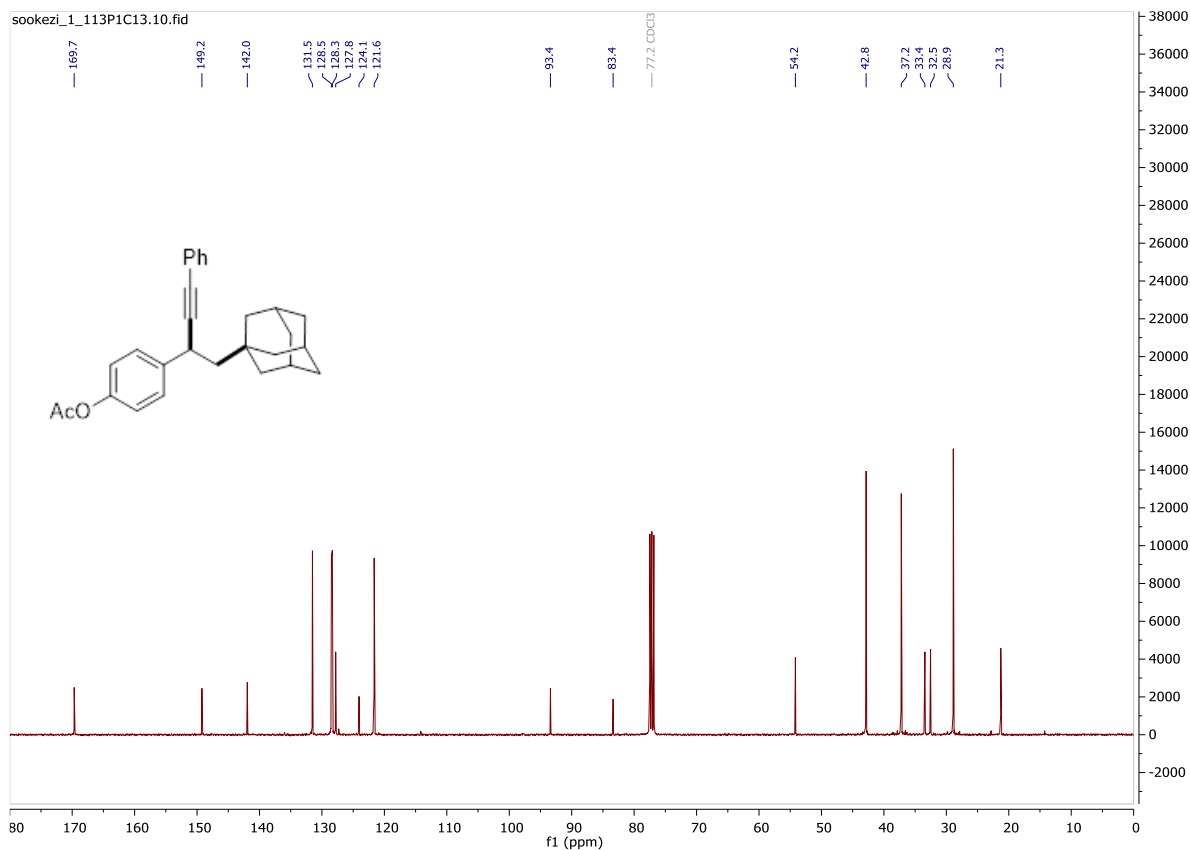
¹⁹F NMR (376 MHz, DMSO) spectrum of 4d



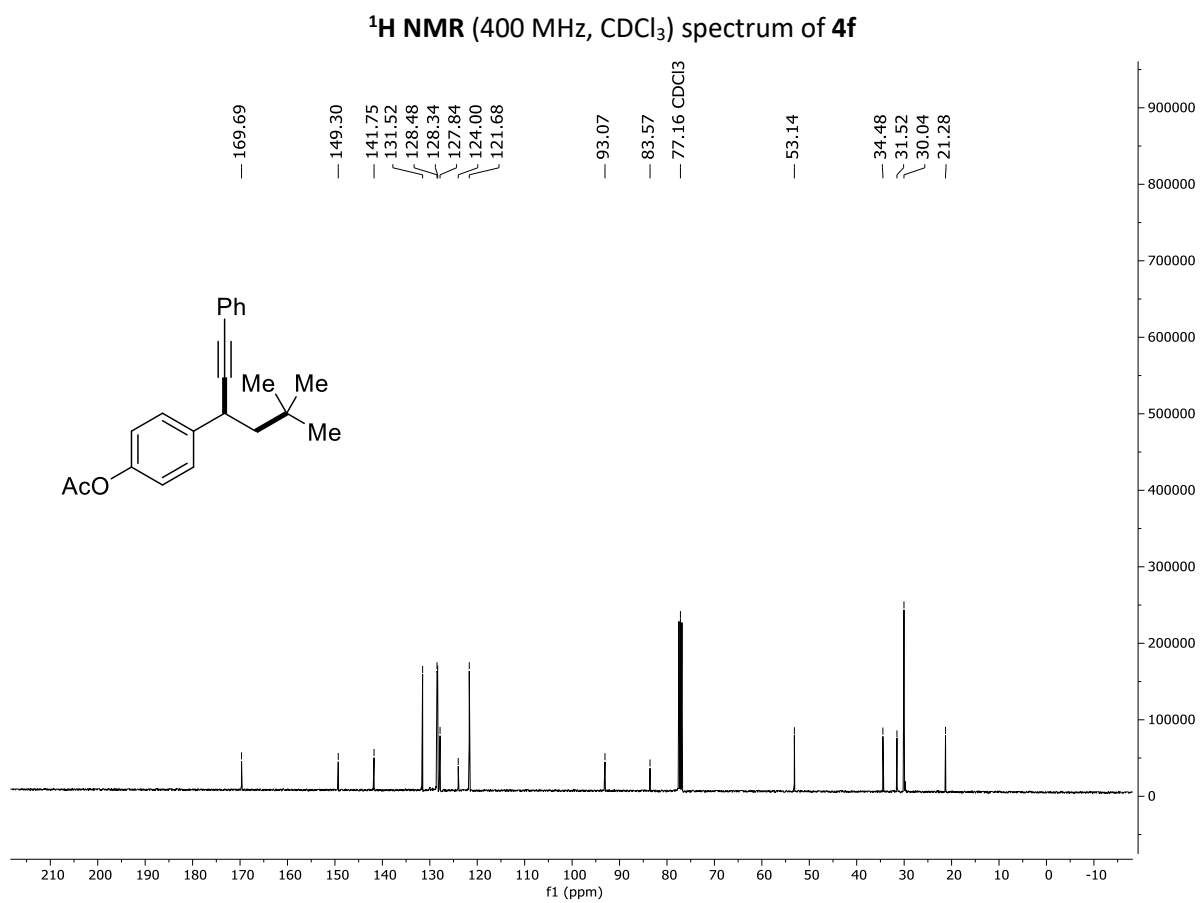
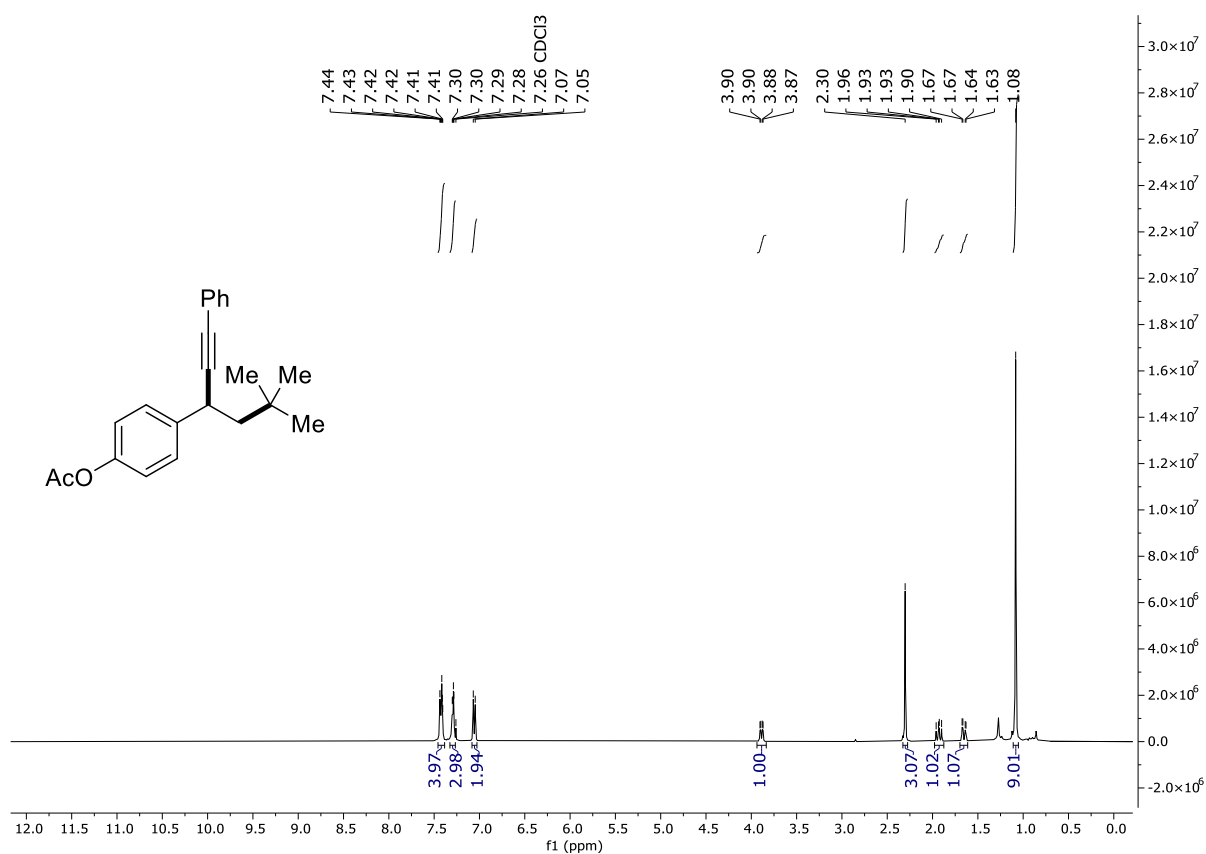
¹³C NMR (101 MHz, CDCl₃) spectrum of 4d

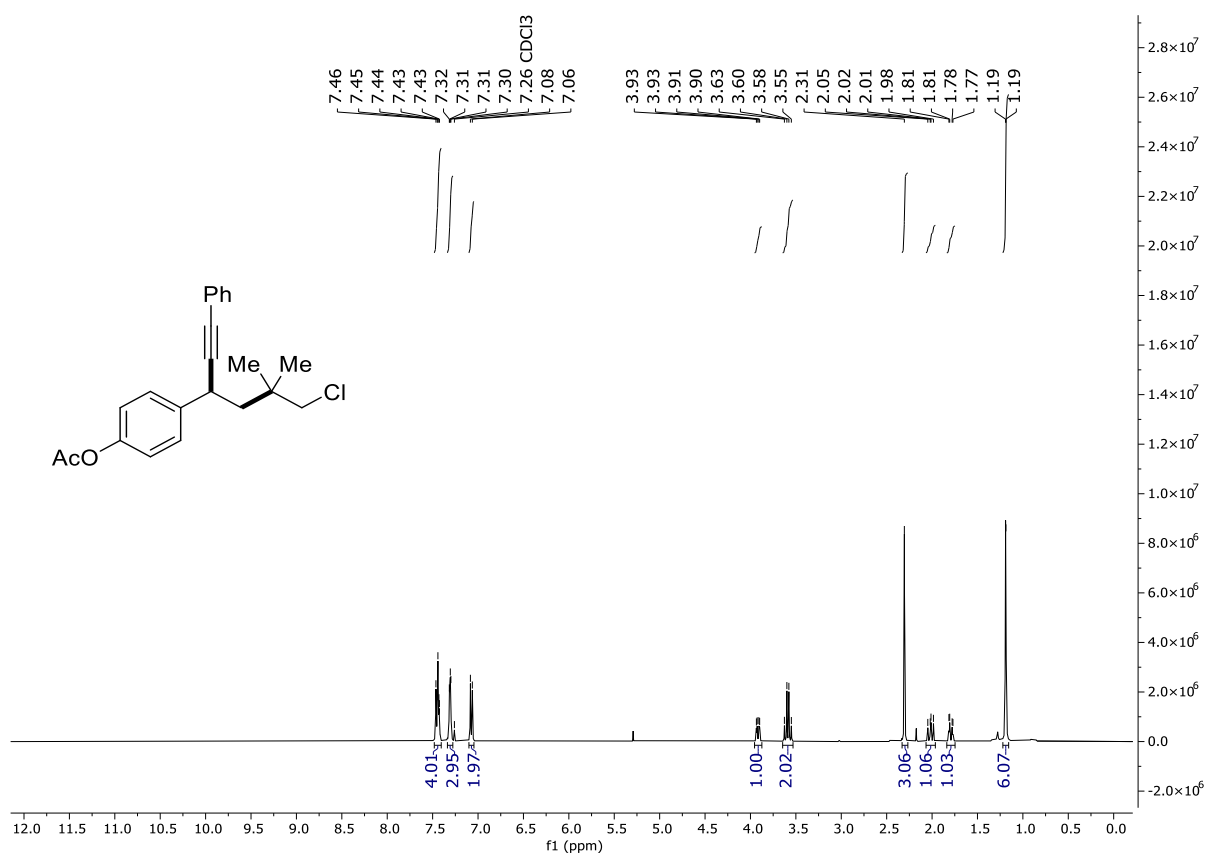


¹H NMR (400 MHz, CDCl₃) spectrum of **4e**

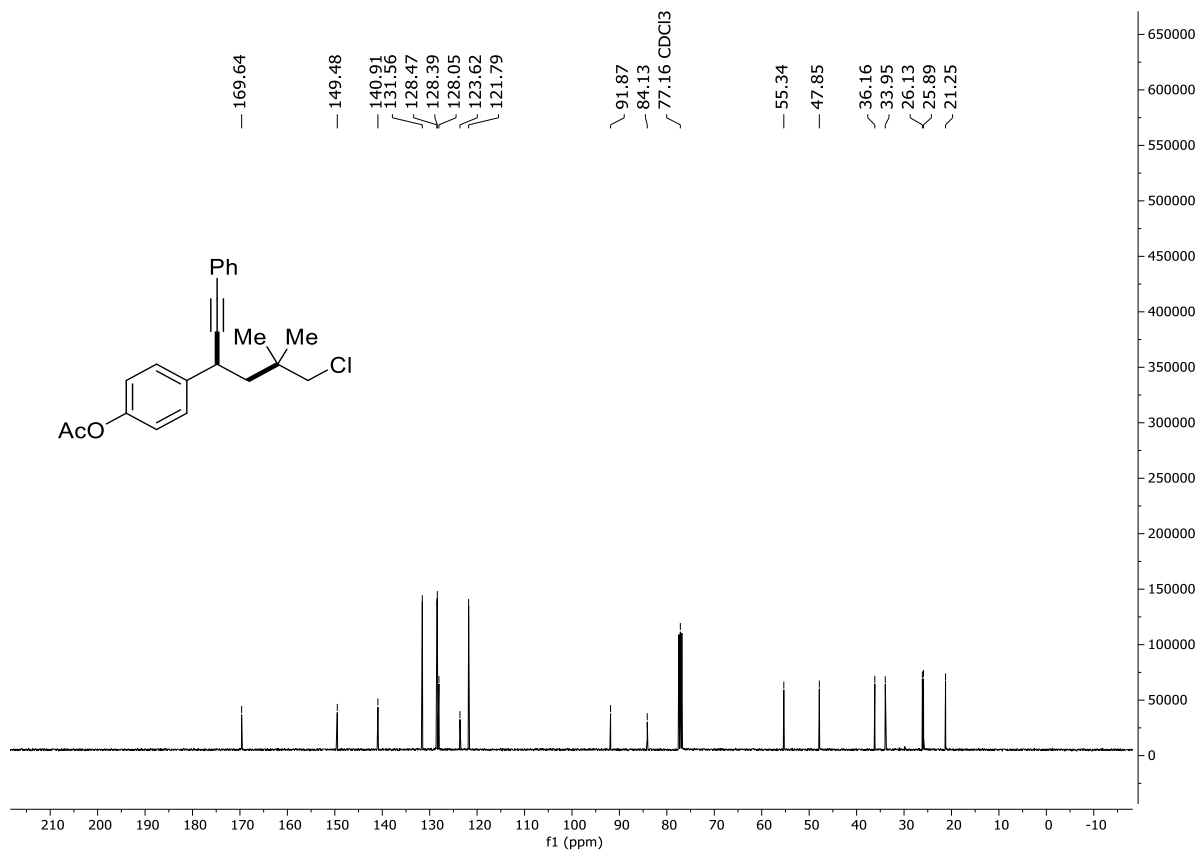


¹³C NMR (101 MHz, CDCl₃) spectrum of **4e**

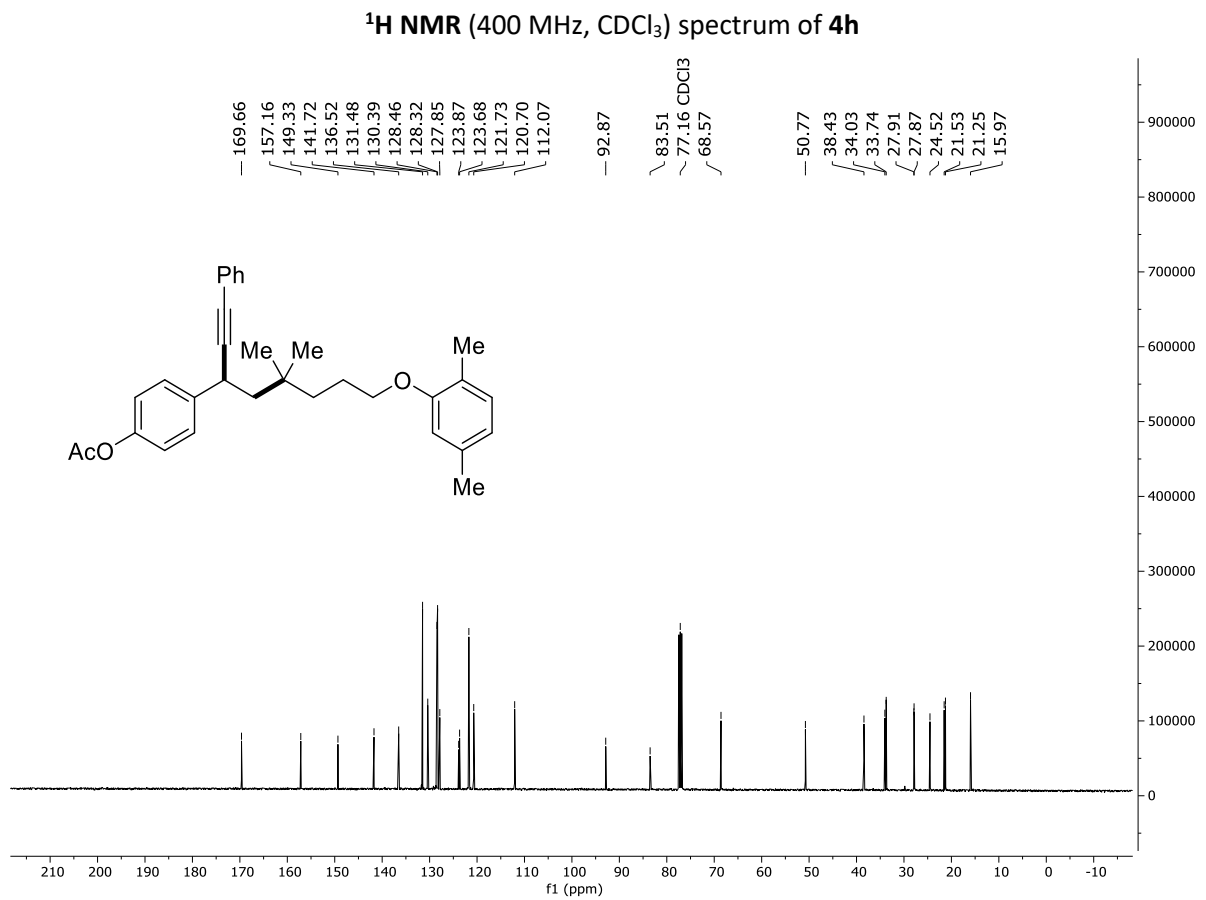
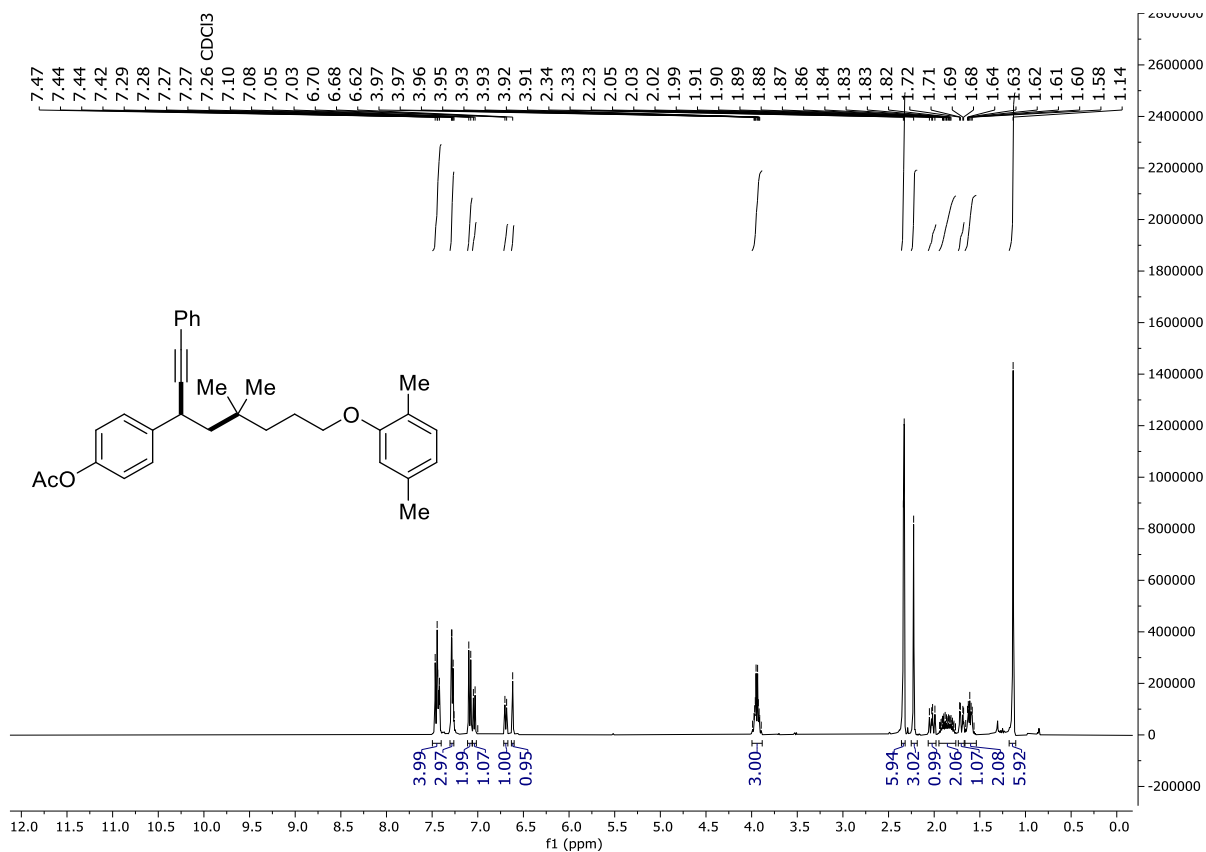


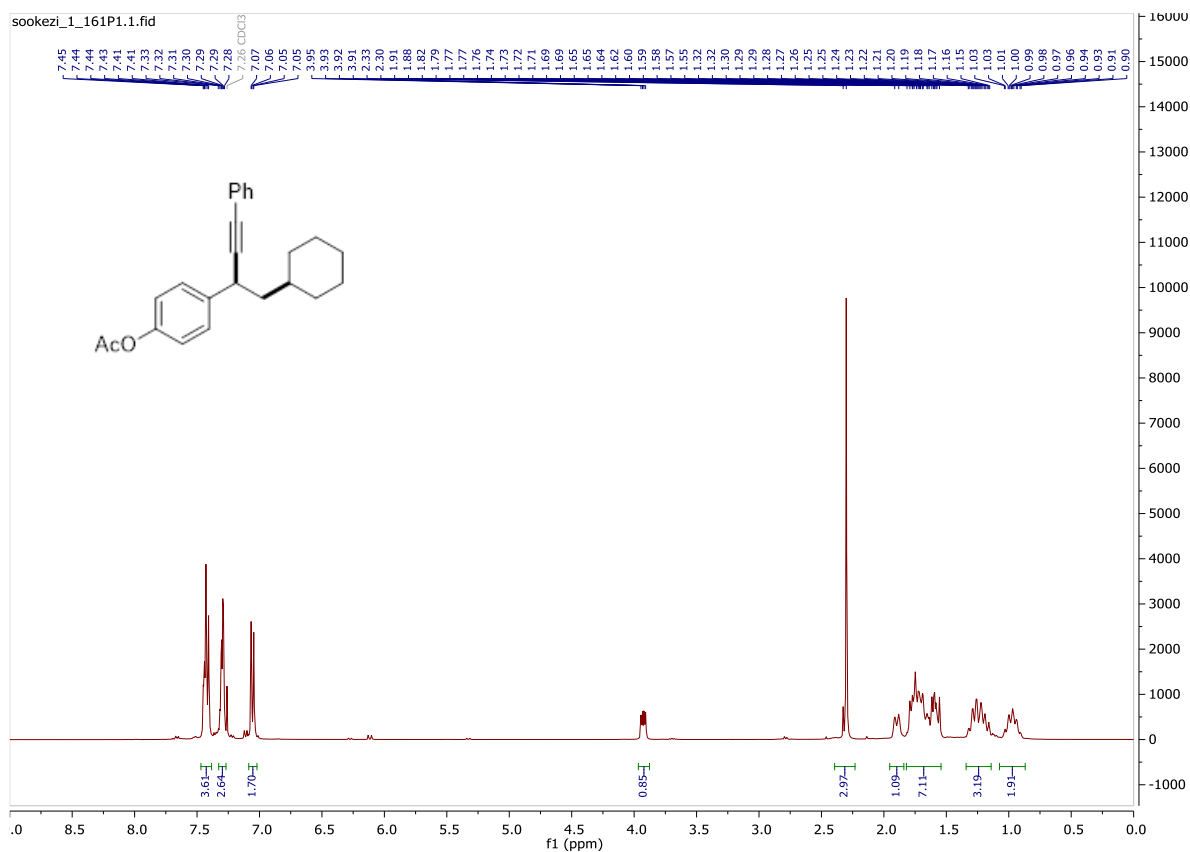


¹H NMR (400 MHz, CDCl₃) spectrum of 4g

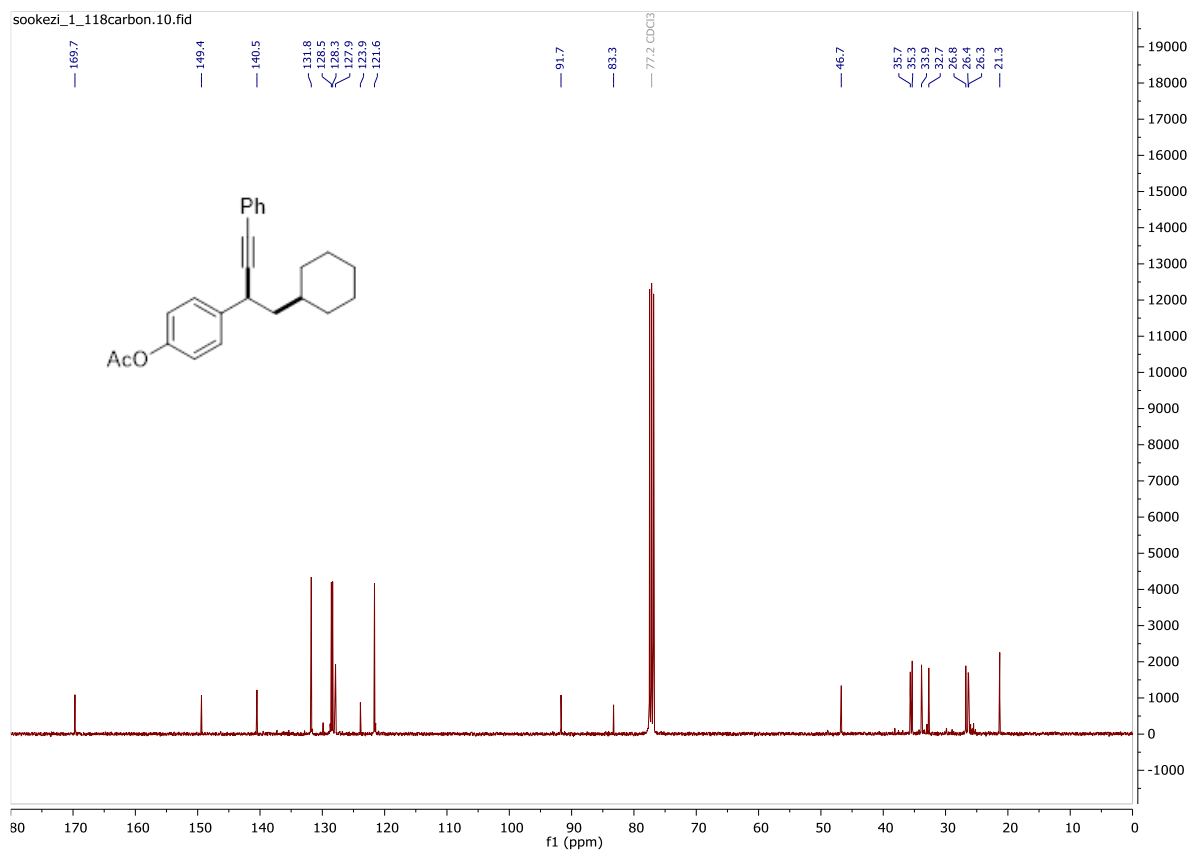


¹³C NMR (101 MHz, CDCl₃) spectrum of 4g

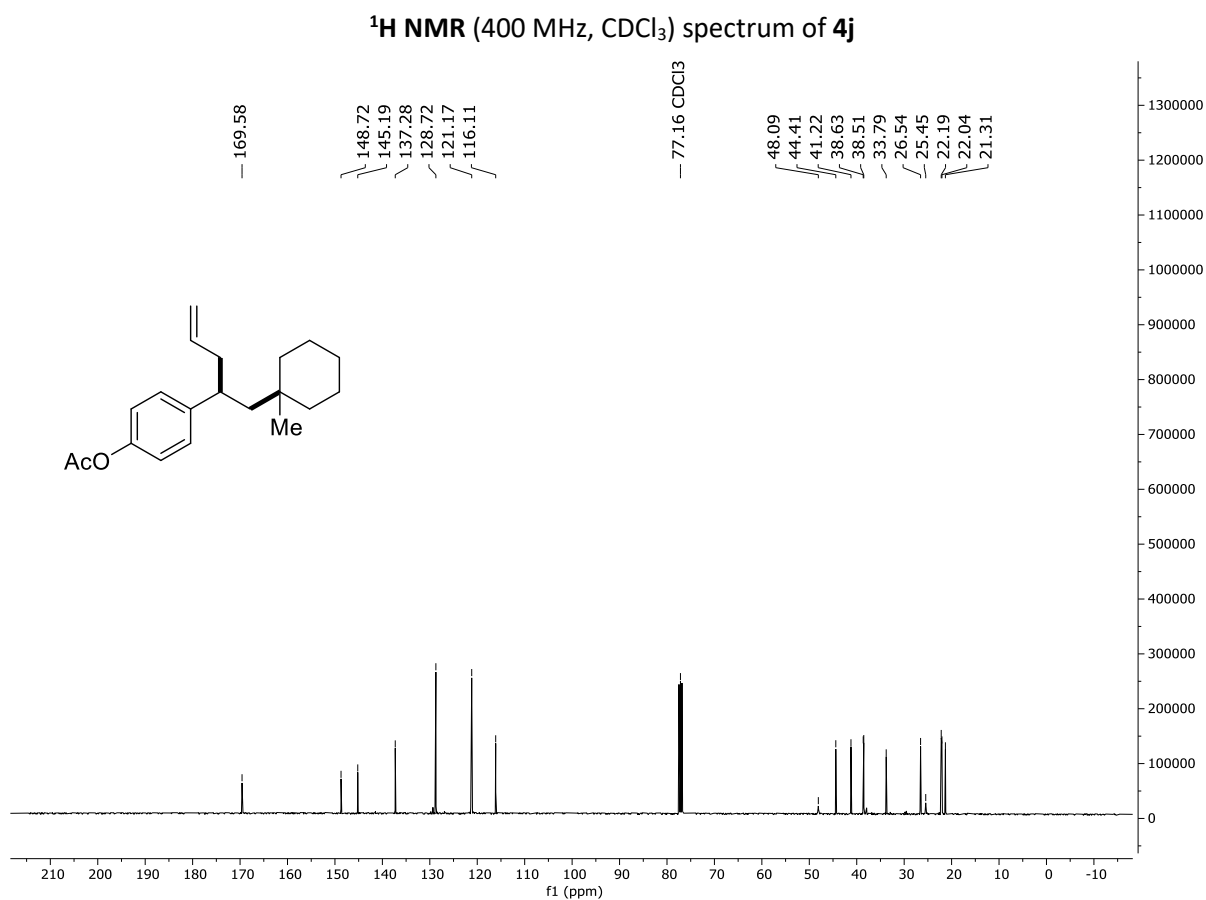
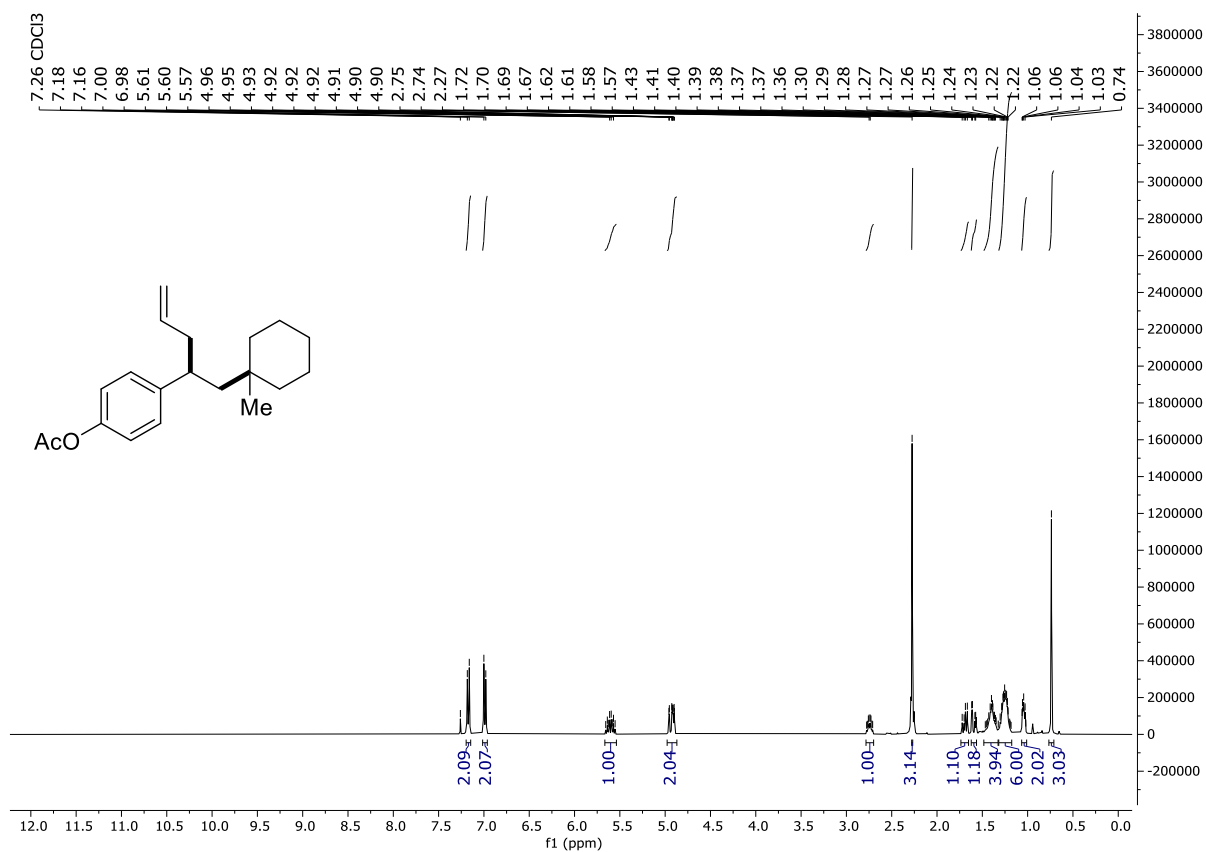


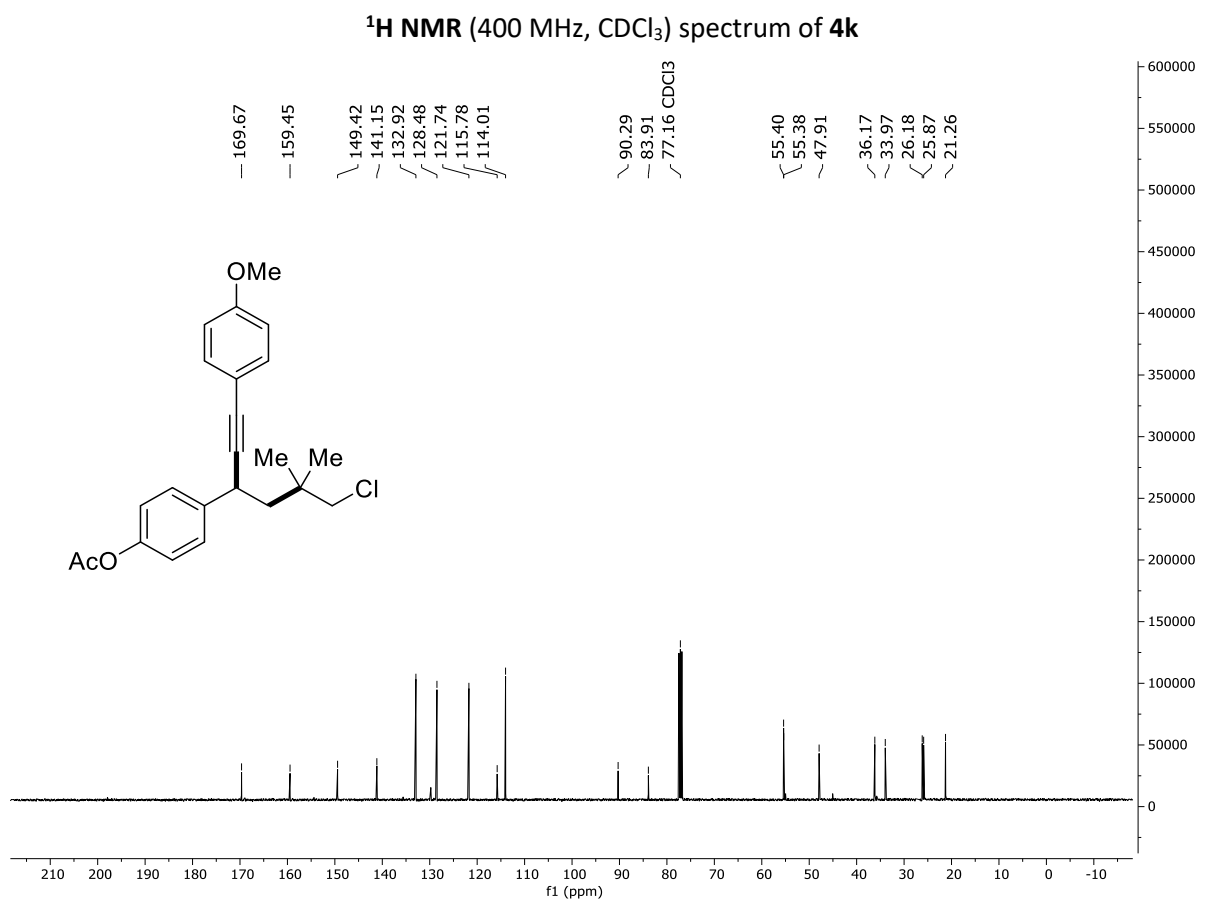
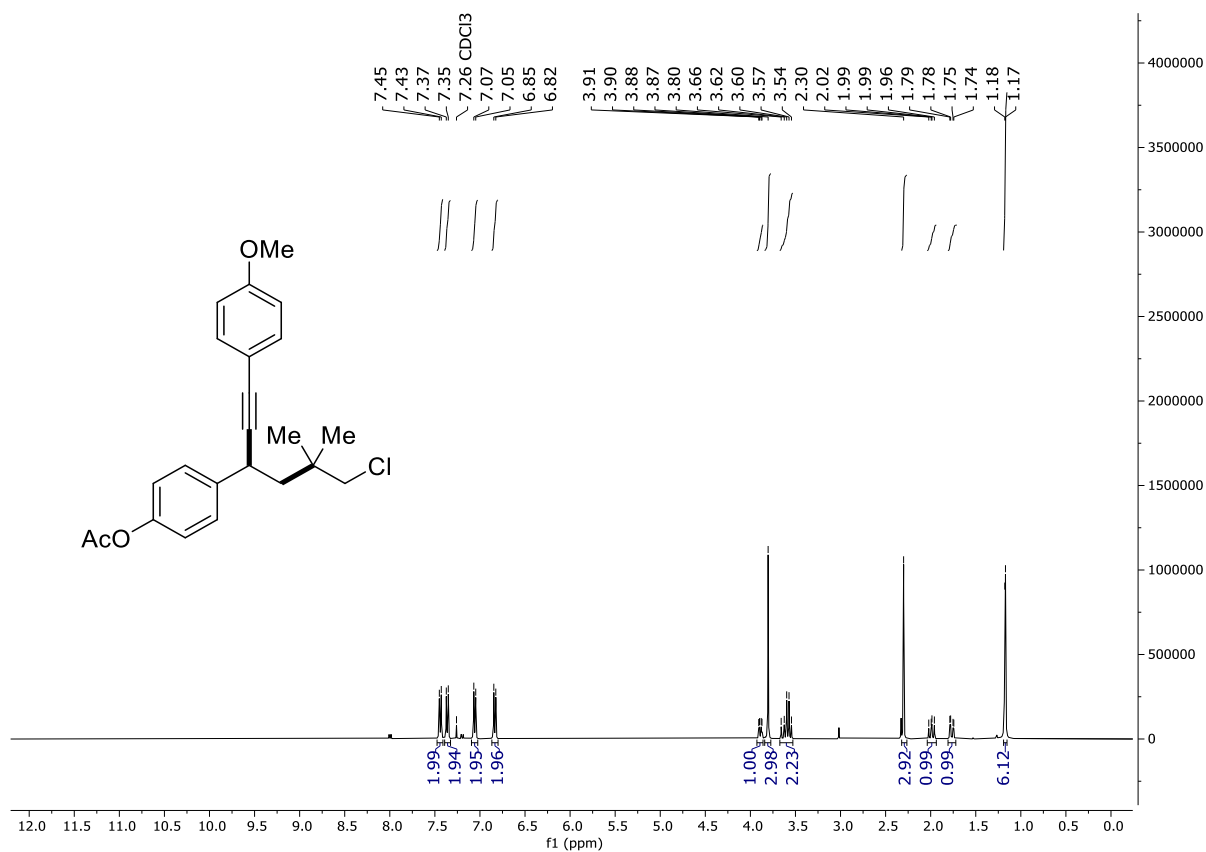


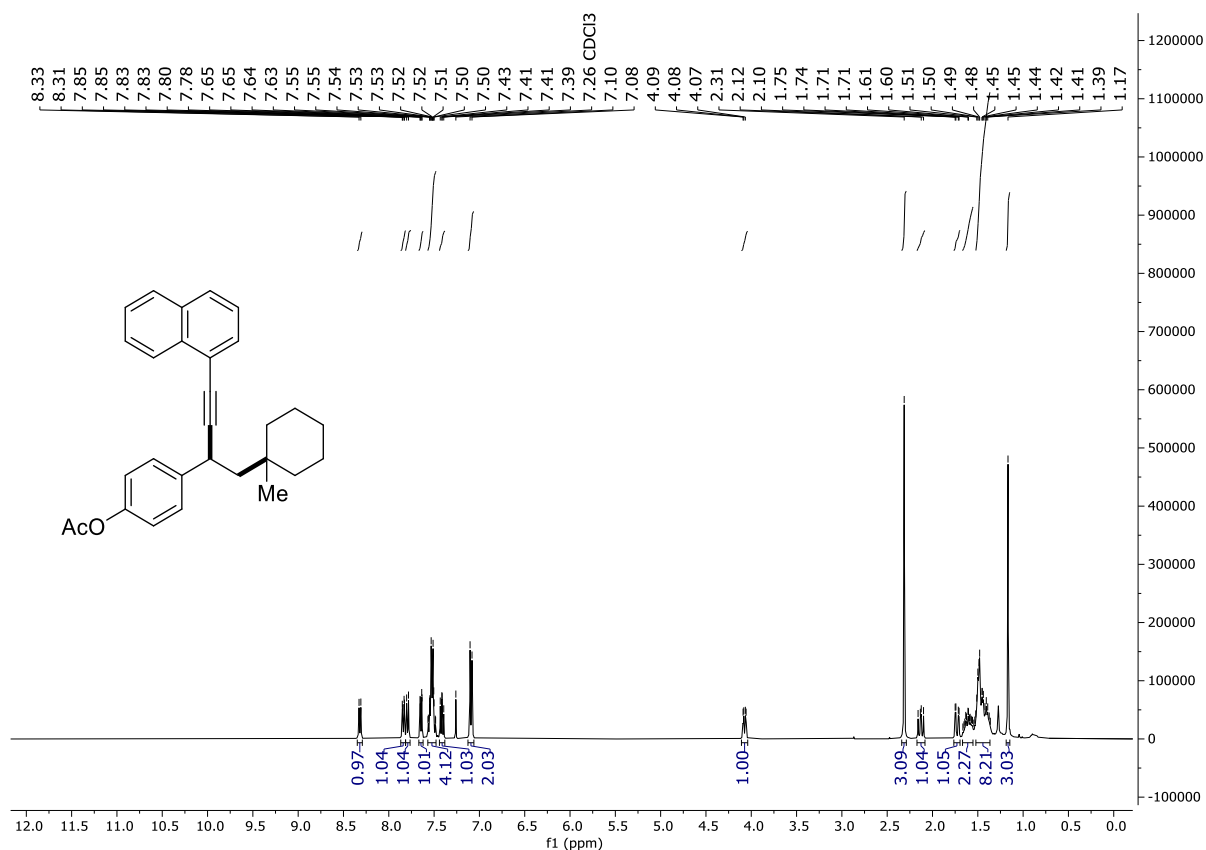
¹H NMR (400 MHz, CDCl₃) spectrum of **4i**



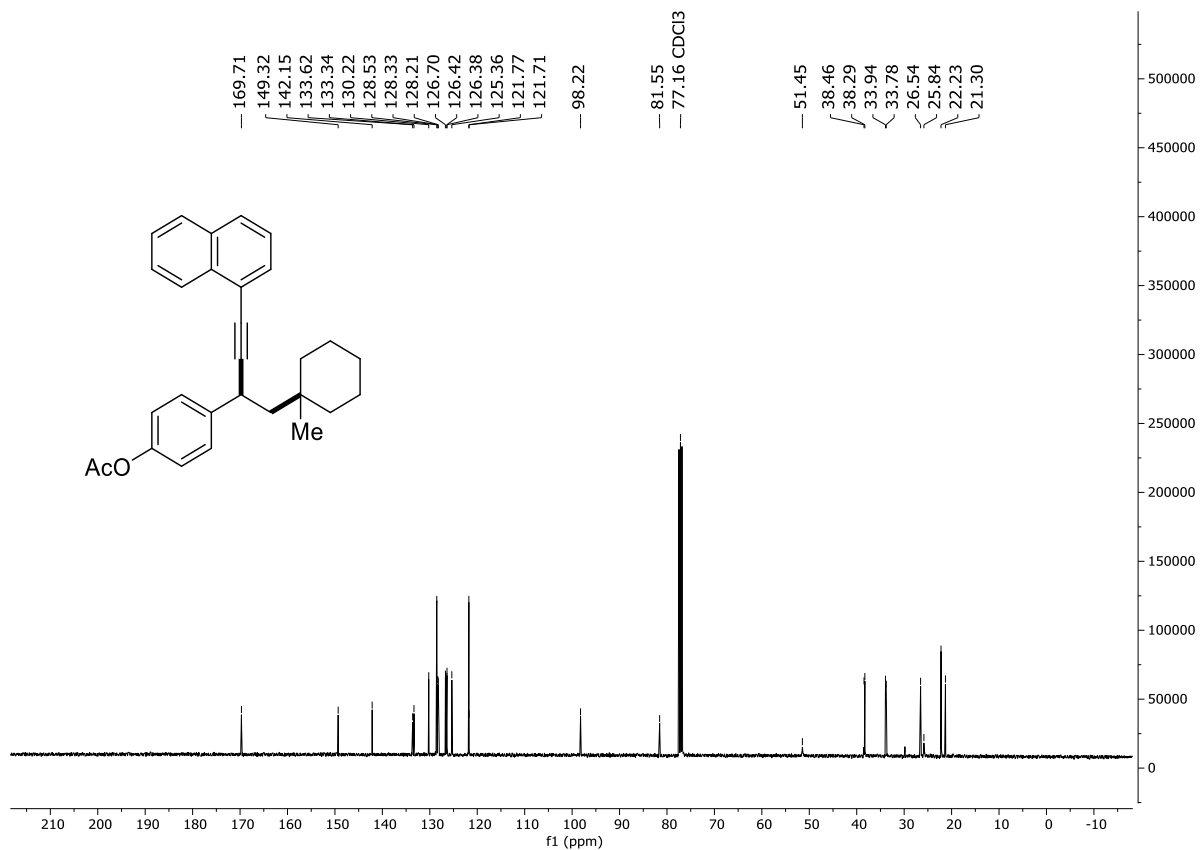
¹³C NMR (101 MHz, CDCl₃) spectrum of **4i**



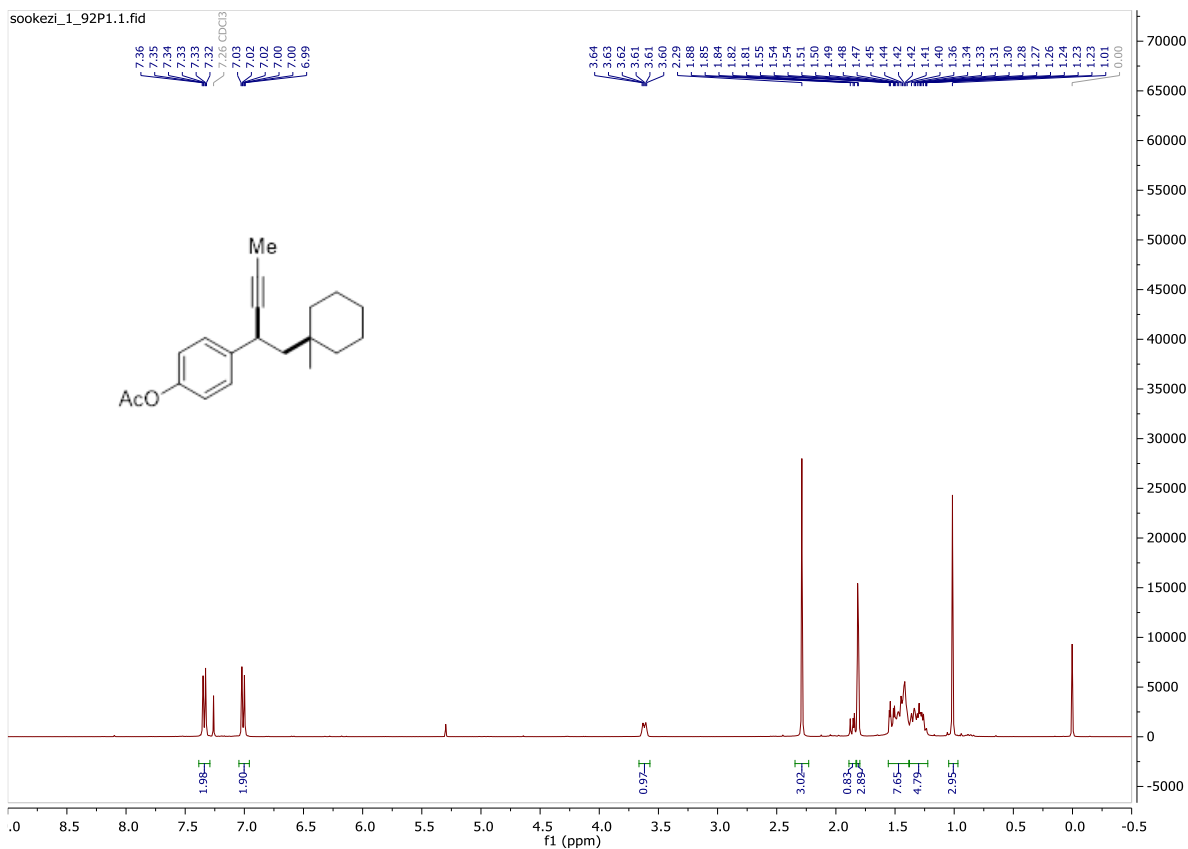




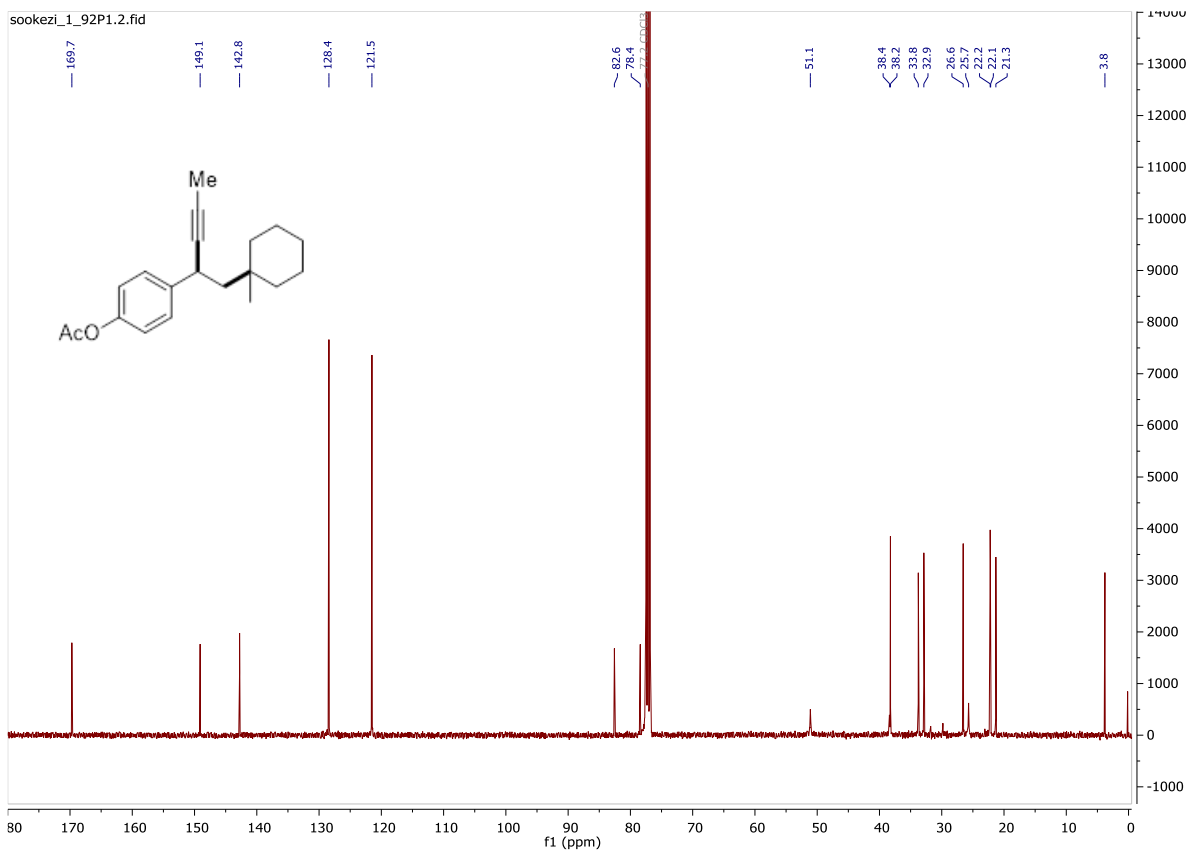
¹H NMR (400 MHz, CDCl₃) spectrum of 4I



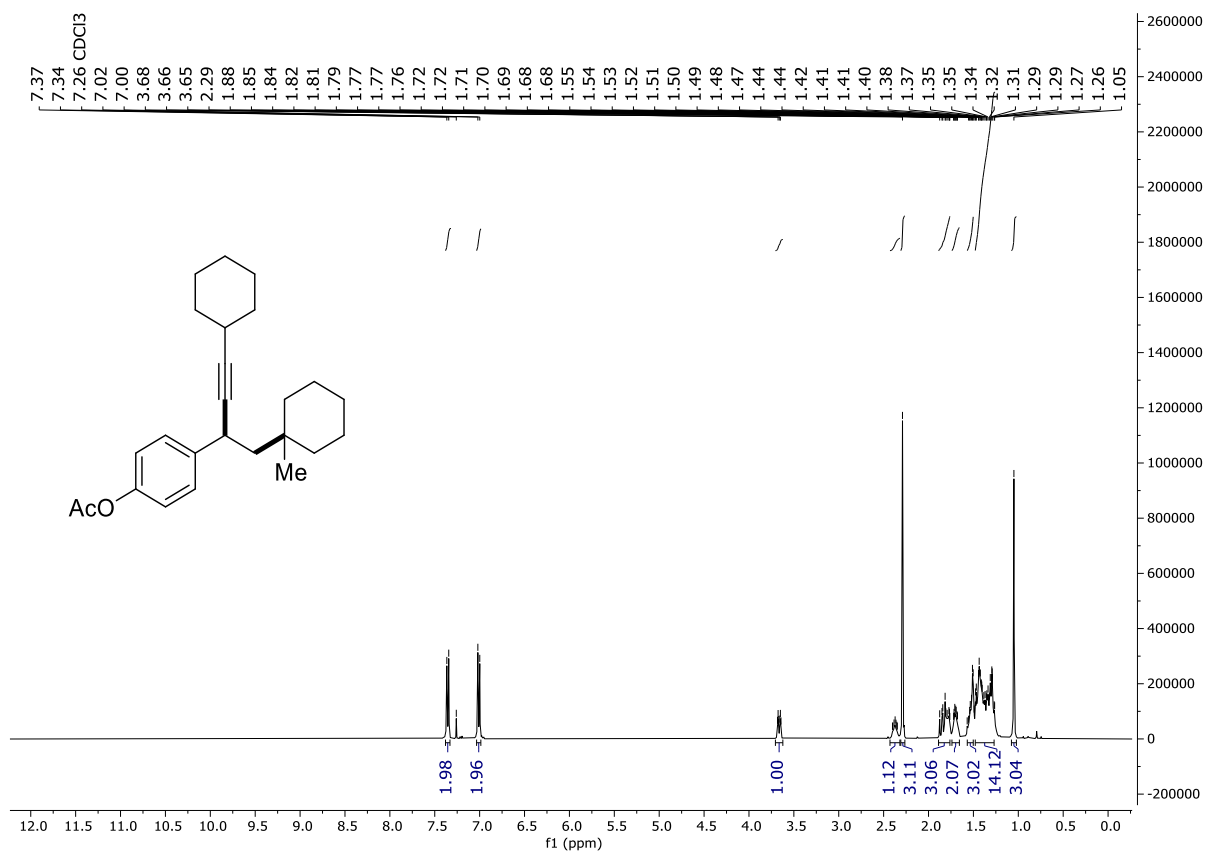
¹³C NMR (101 MHz, CDCl₃) spectrum of 4I



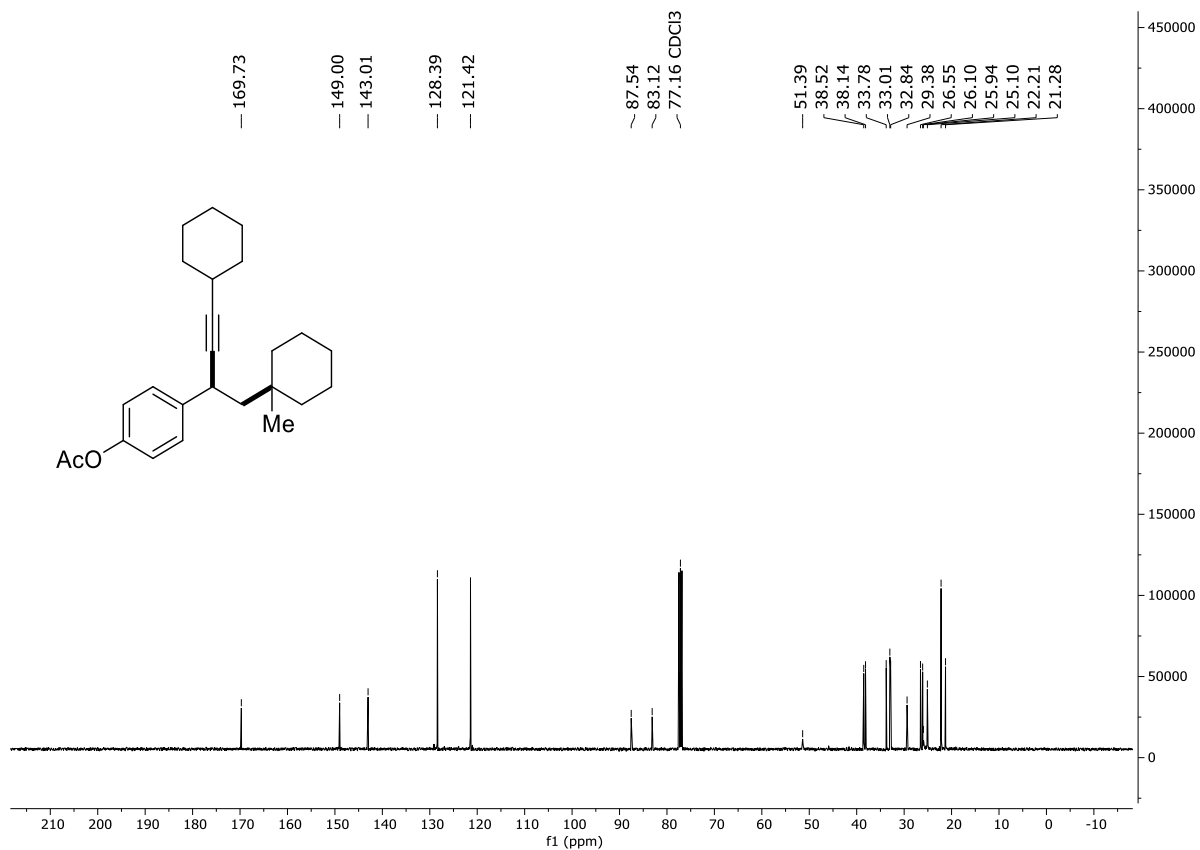
¹H NMR (400 MHz, CDCl₃) spectrum of **4m**



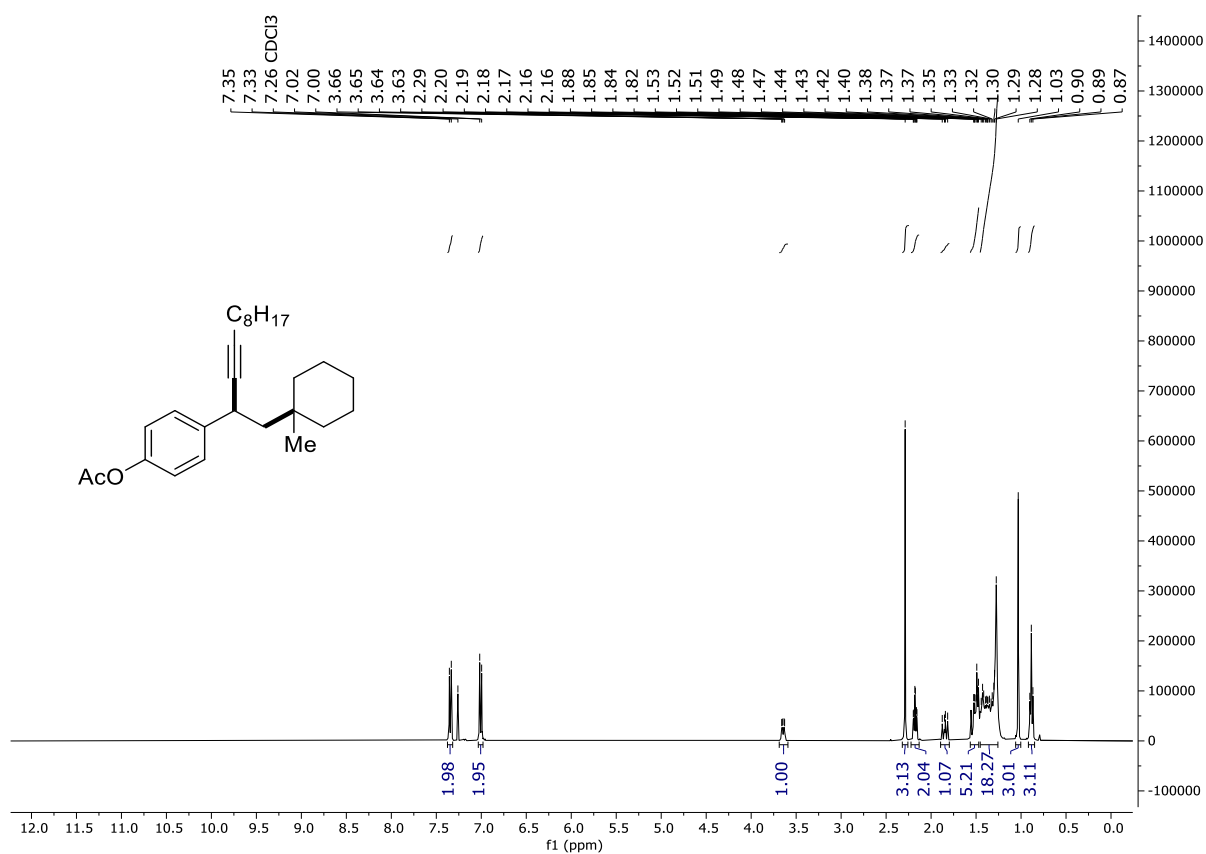
¹³C NMR (101 MHz, CDCl₃) spectrum of **4m**



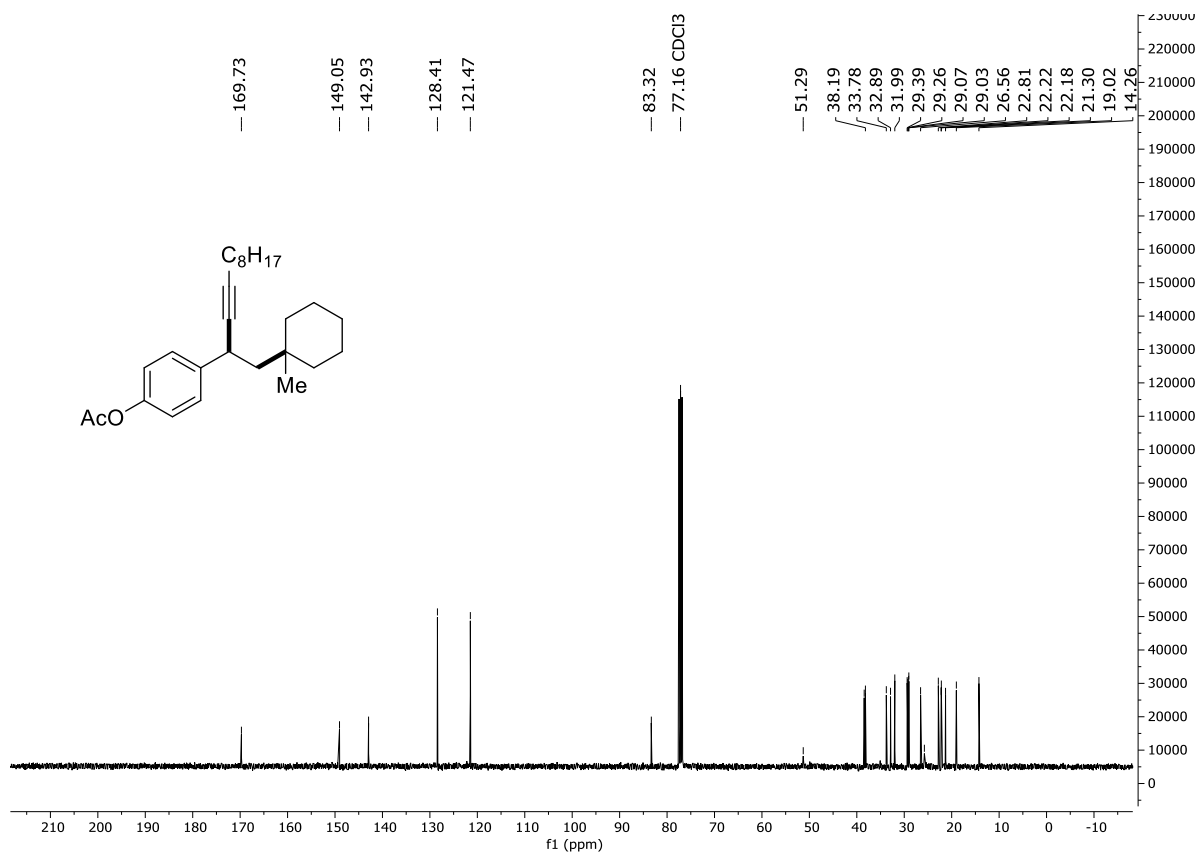
¹H NMR (400 MHz, CDCl₃) spectrum of **4n**



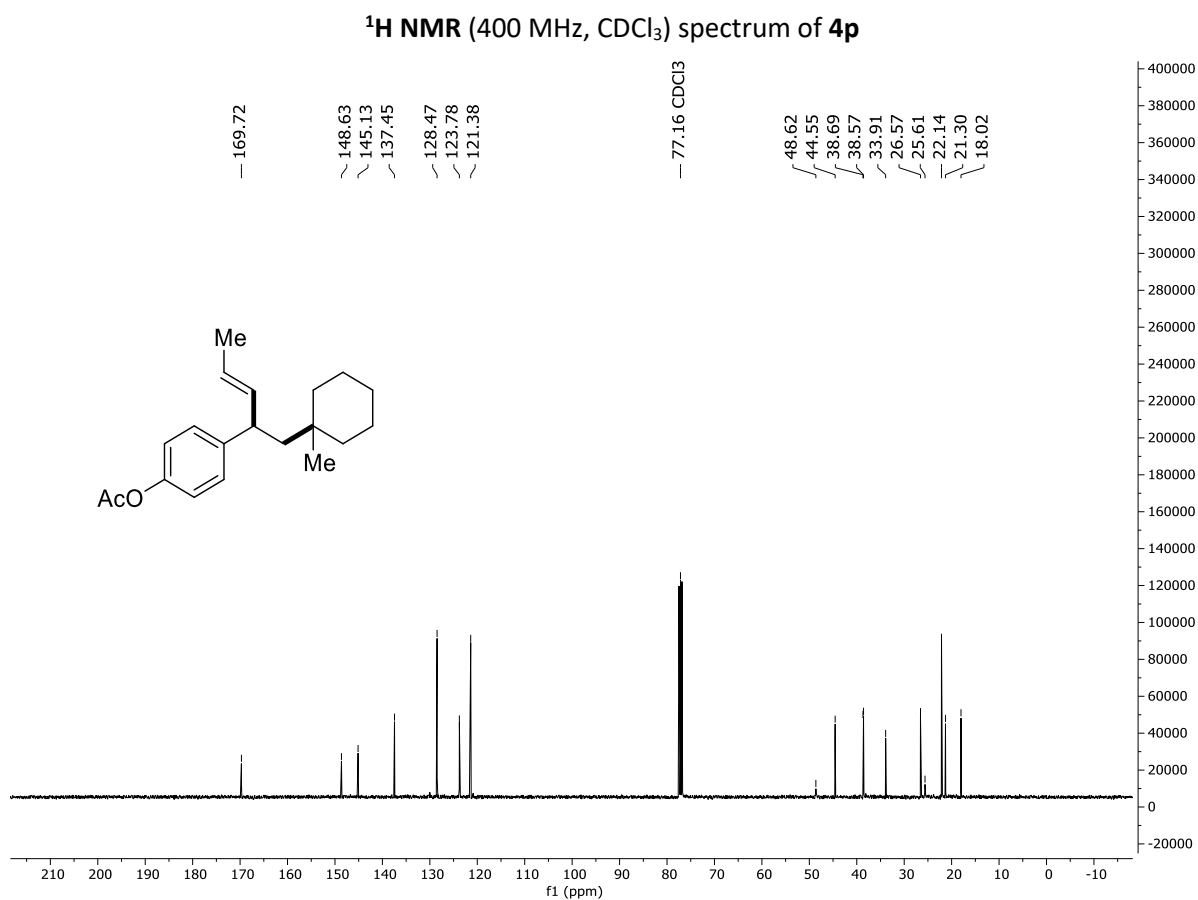
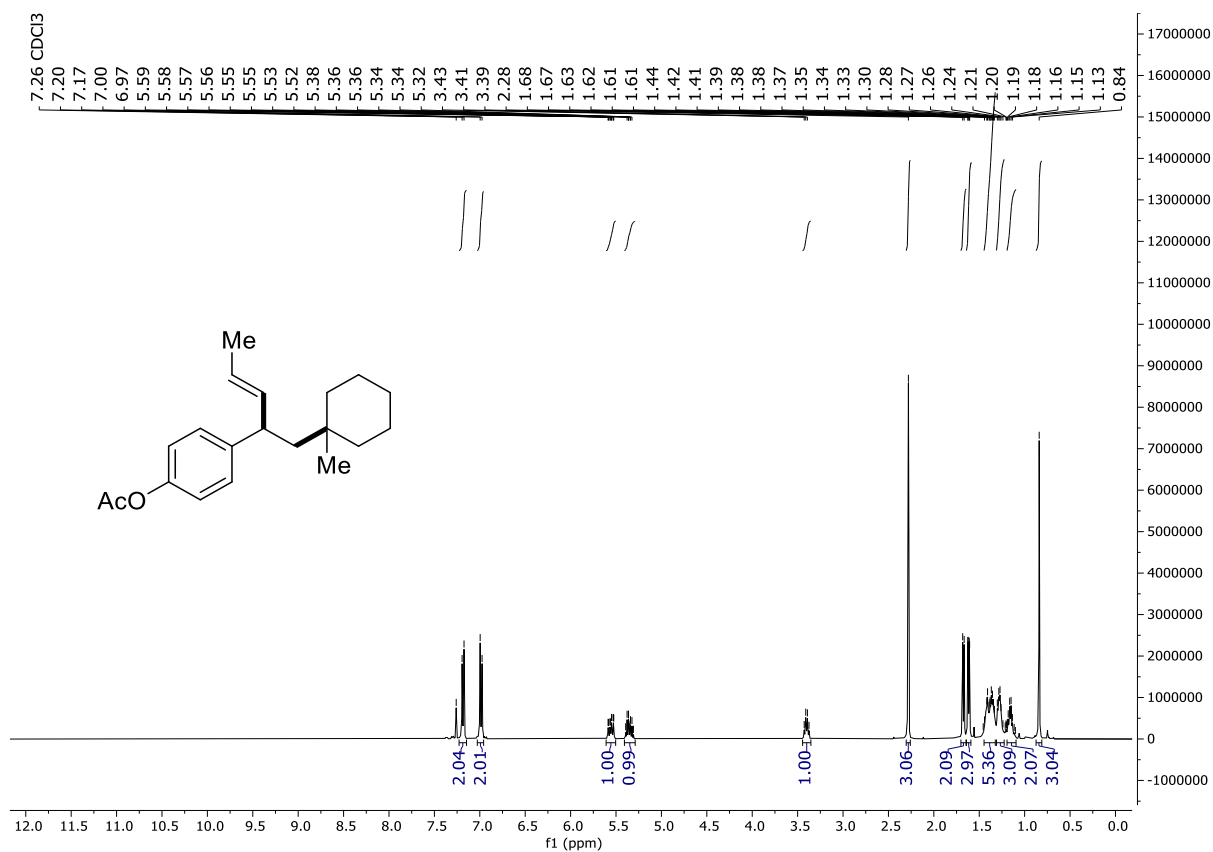
¹³C NMR (101 MHz, CDCl₃) spectrum of **4n**

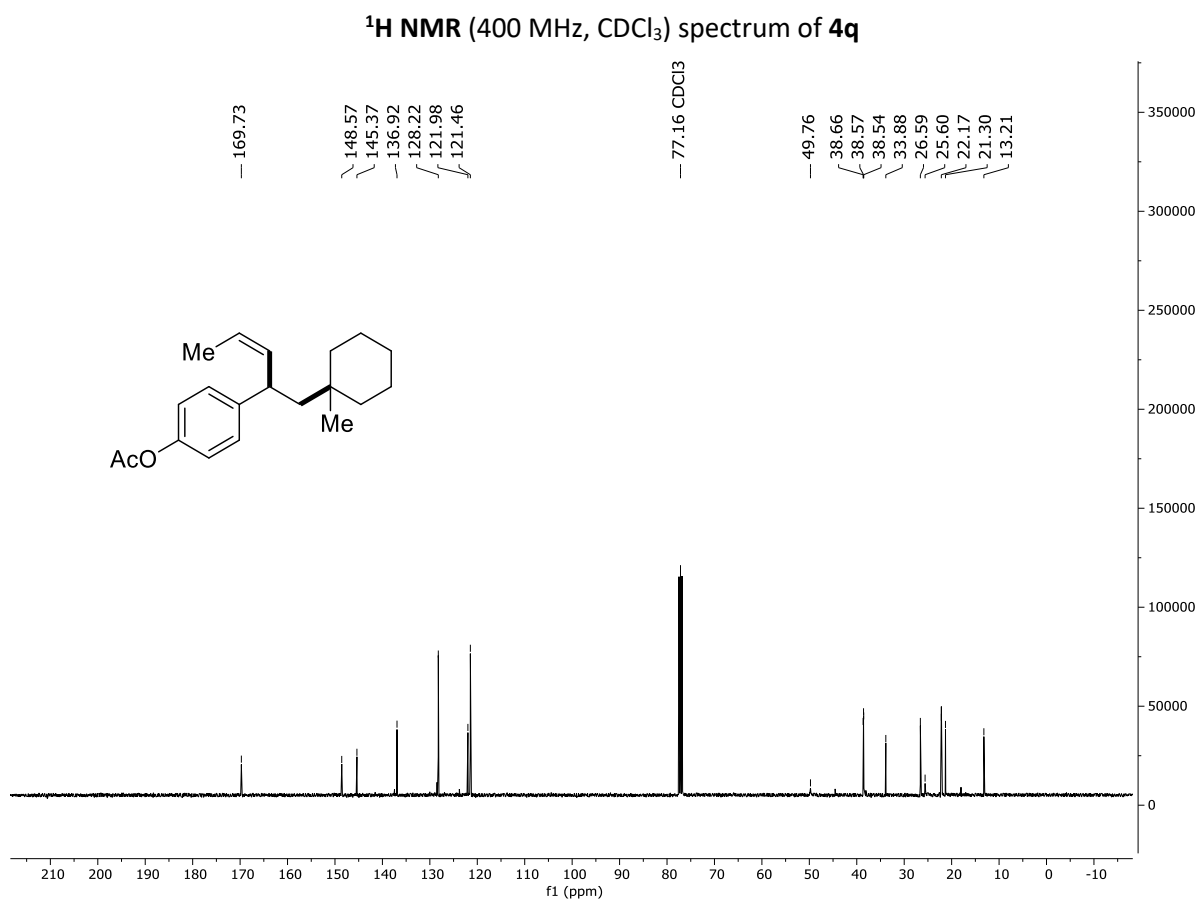
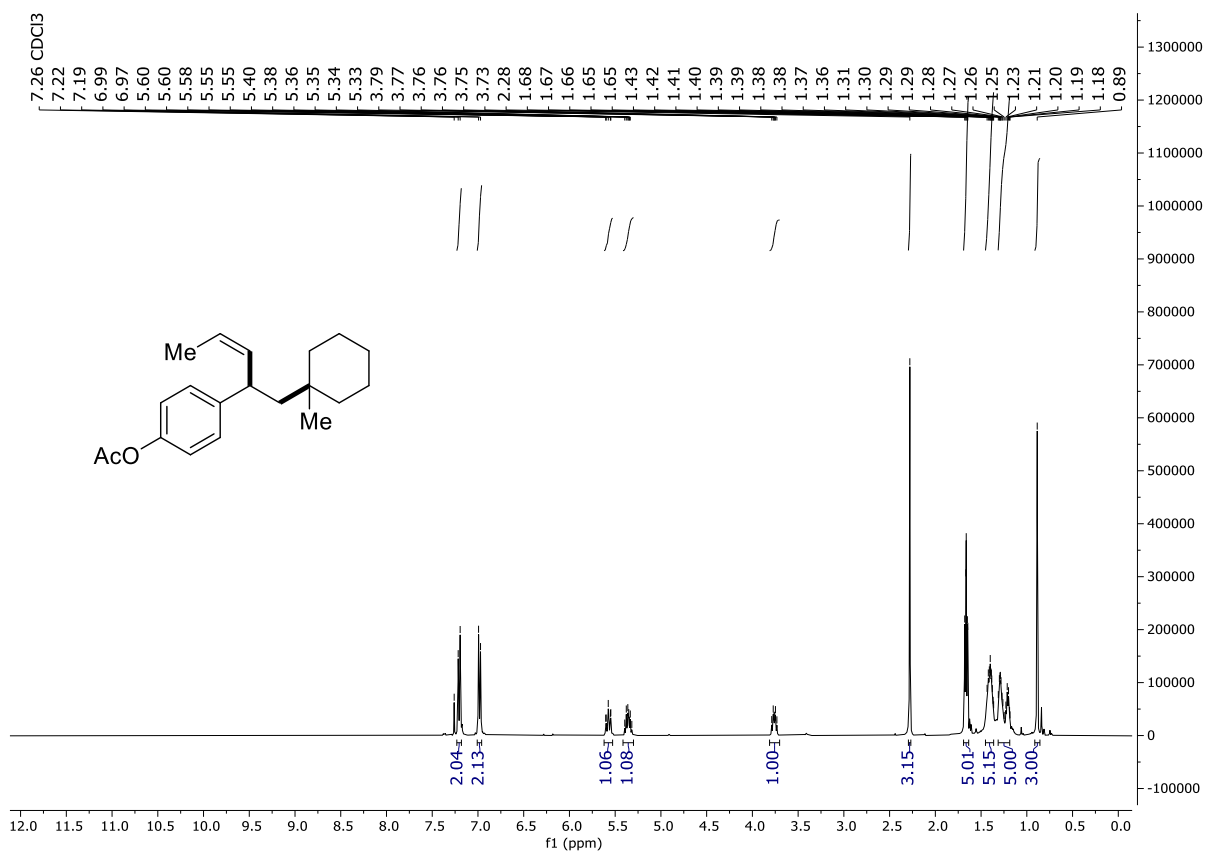


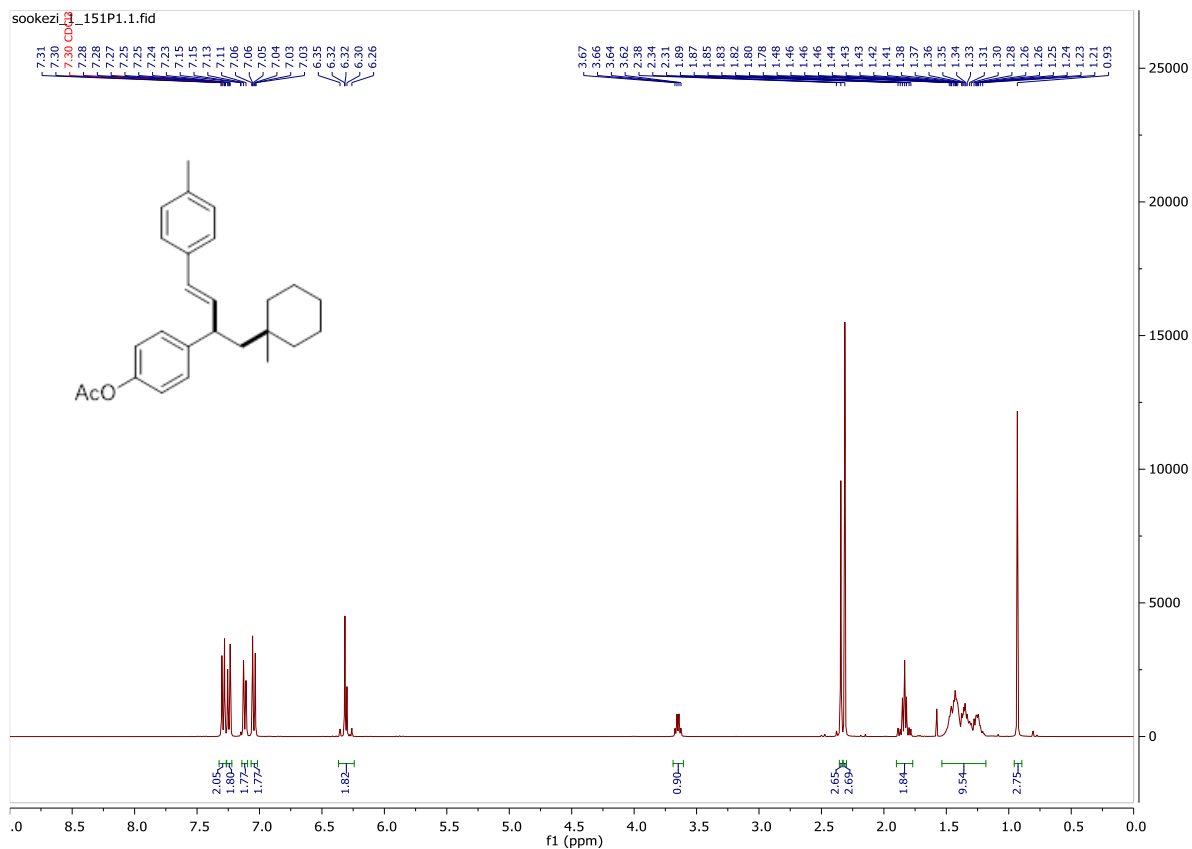
¹H NMR (400 MHz, CDCl₃) spectrum of **4o**



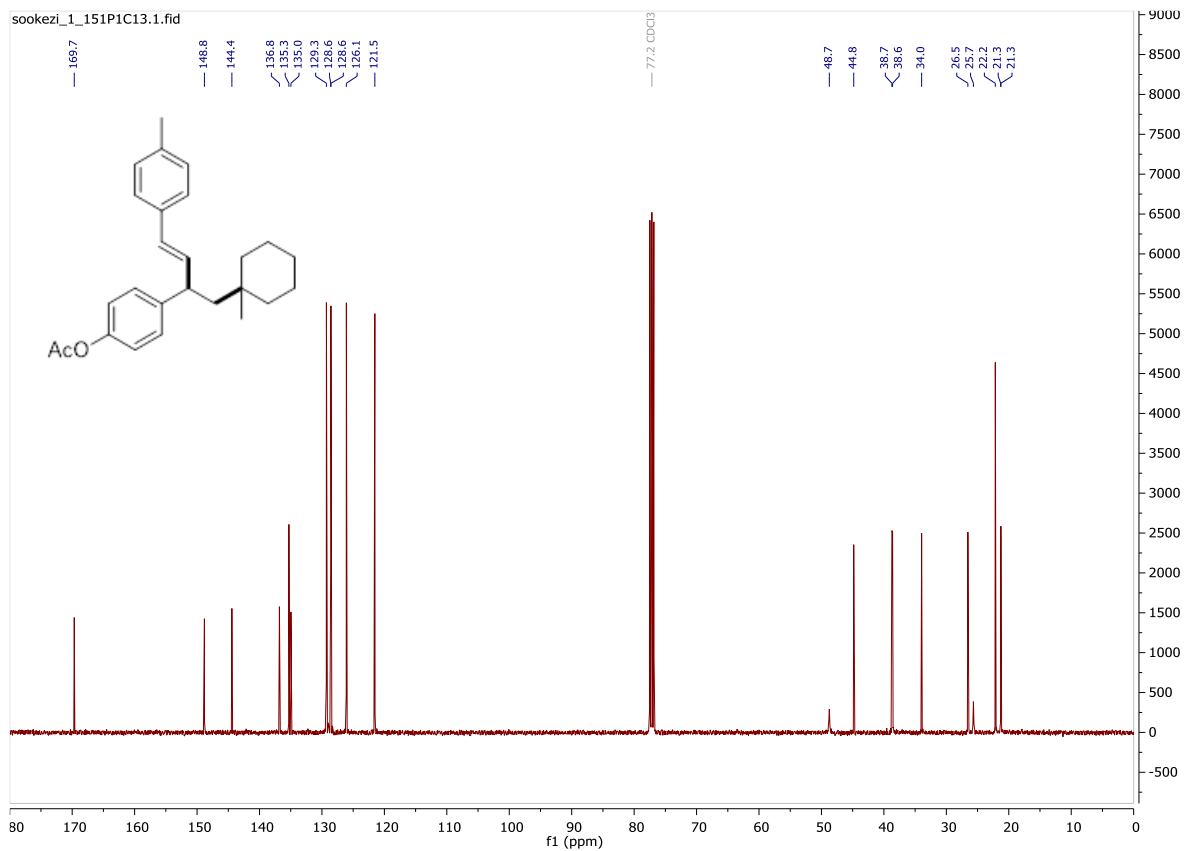
¹³C NMR (101 MHz, CDCl₃) spectrum of **4o**



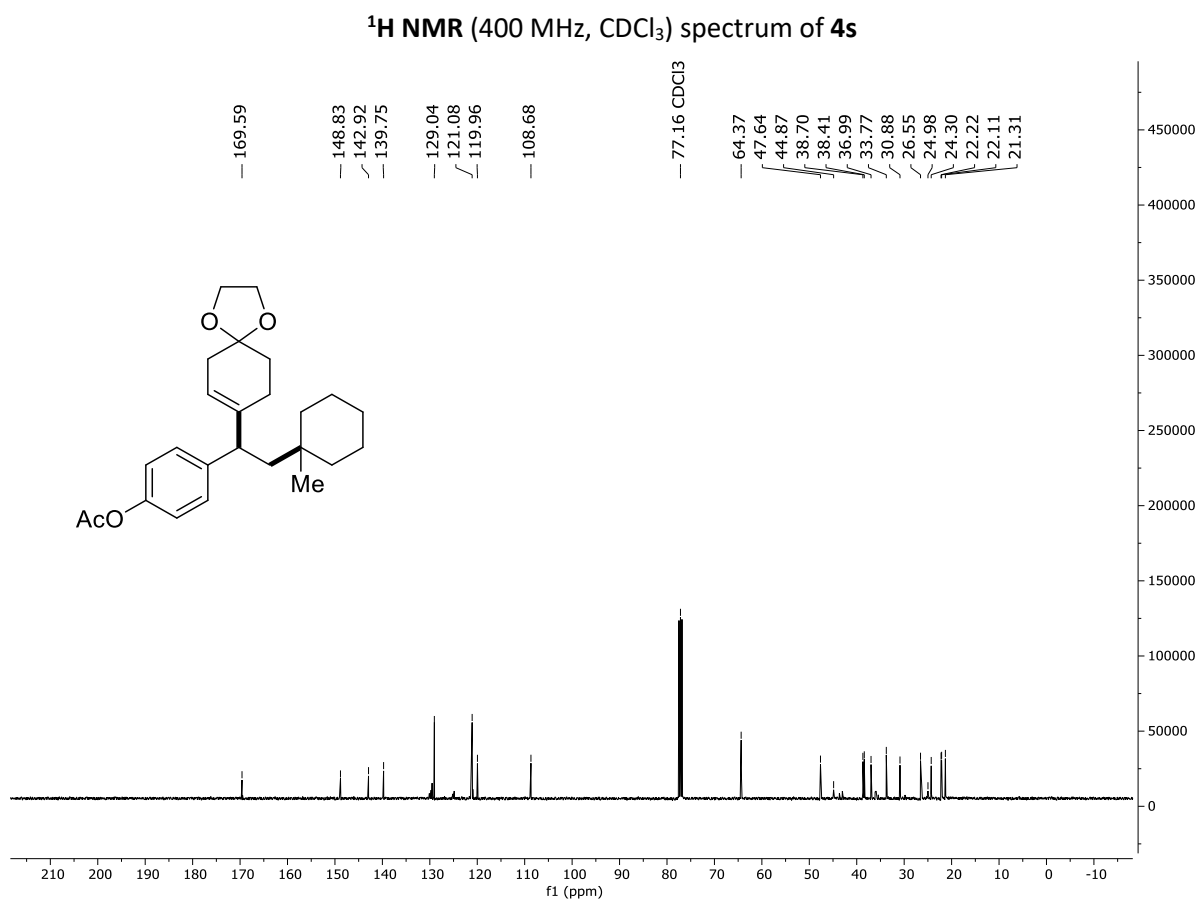
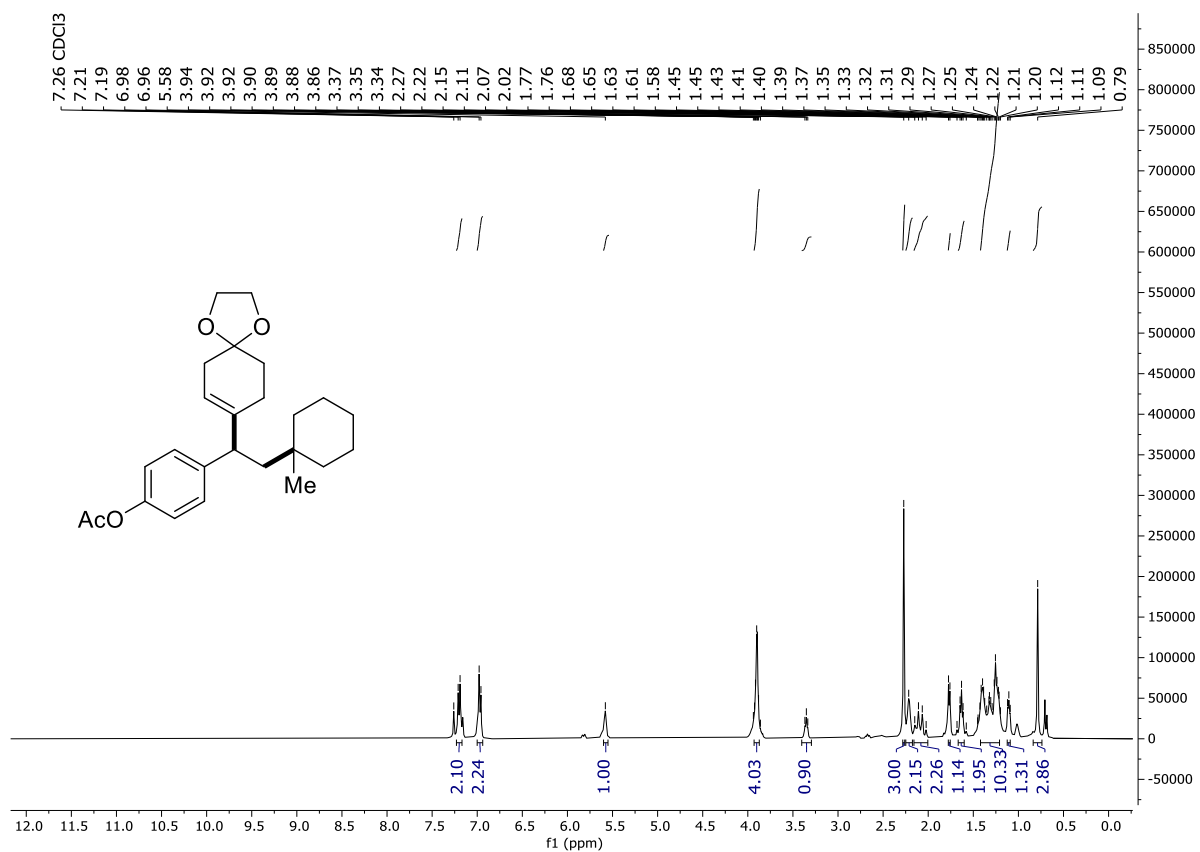


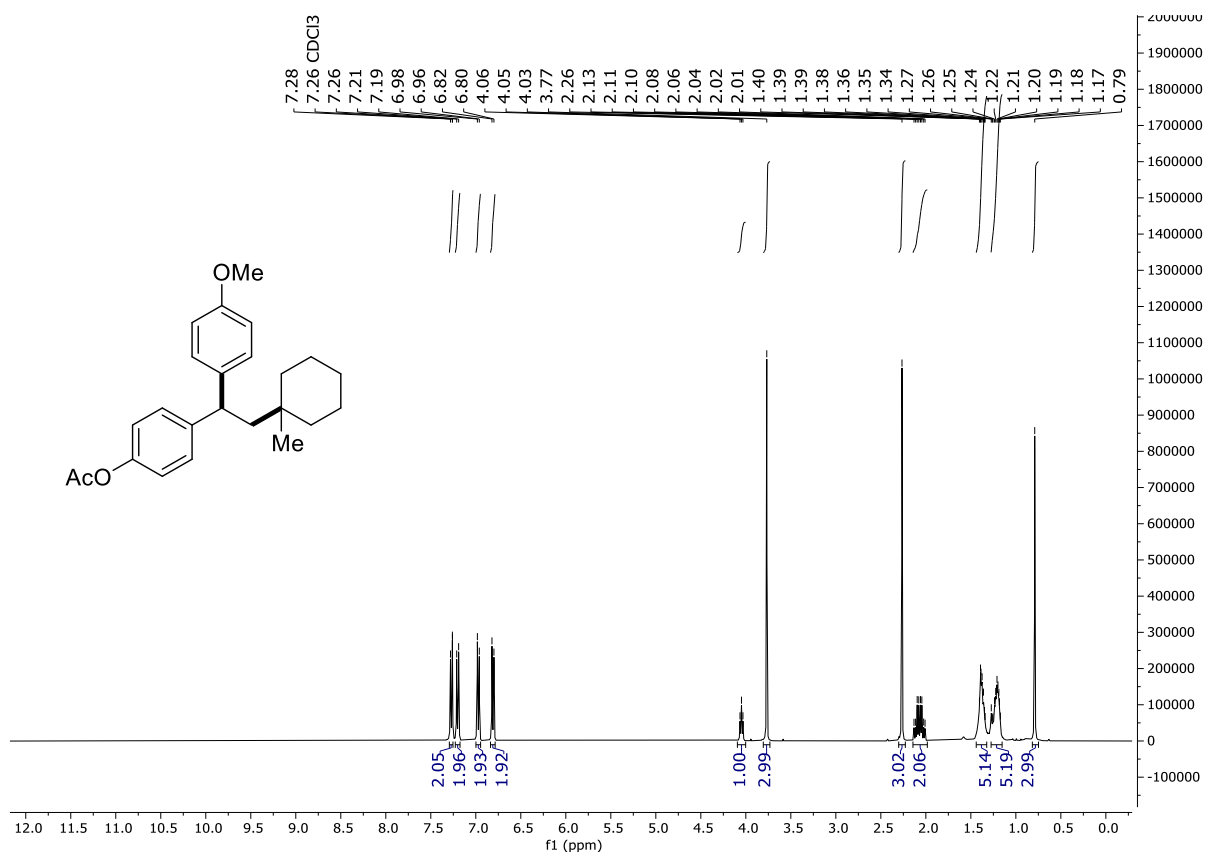


¹H NMR (400 MHz, CDCl₃) spectrum of **4r**

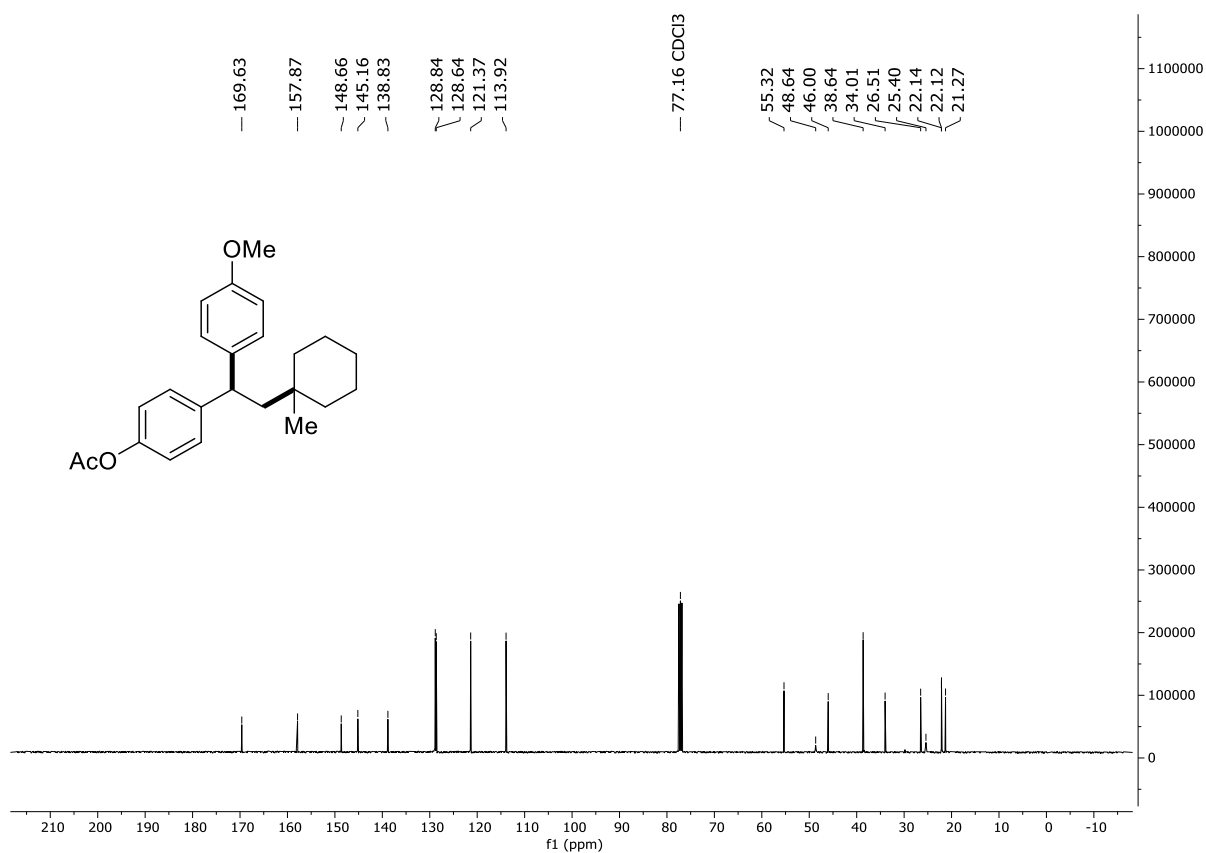


¹³C NMR (101 MHz, CDCl₃) spectrum of **4r**

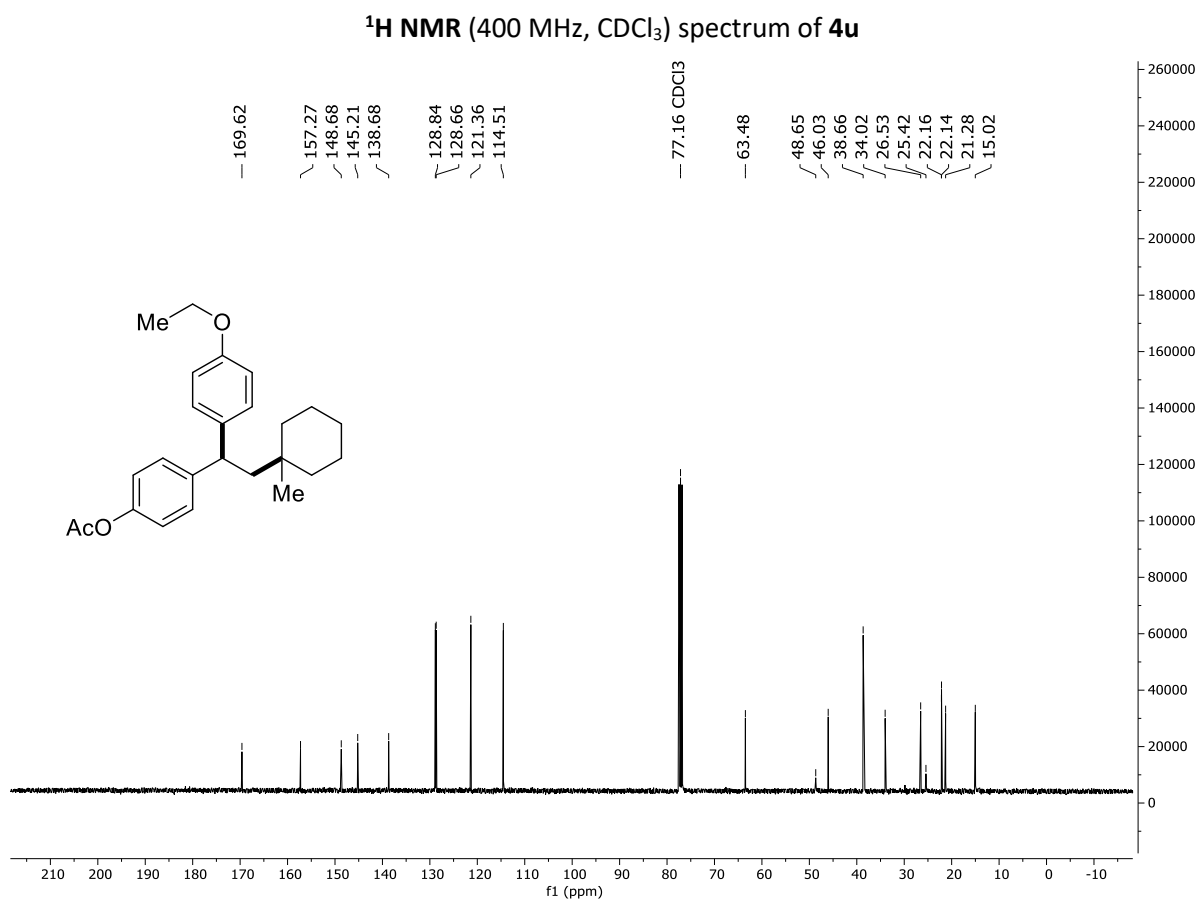
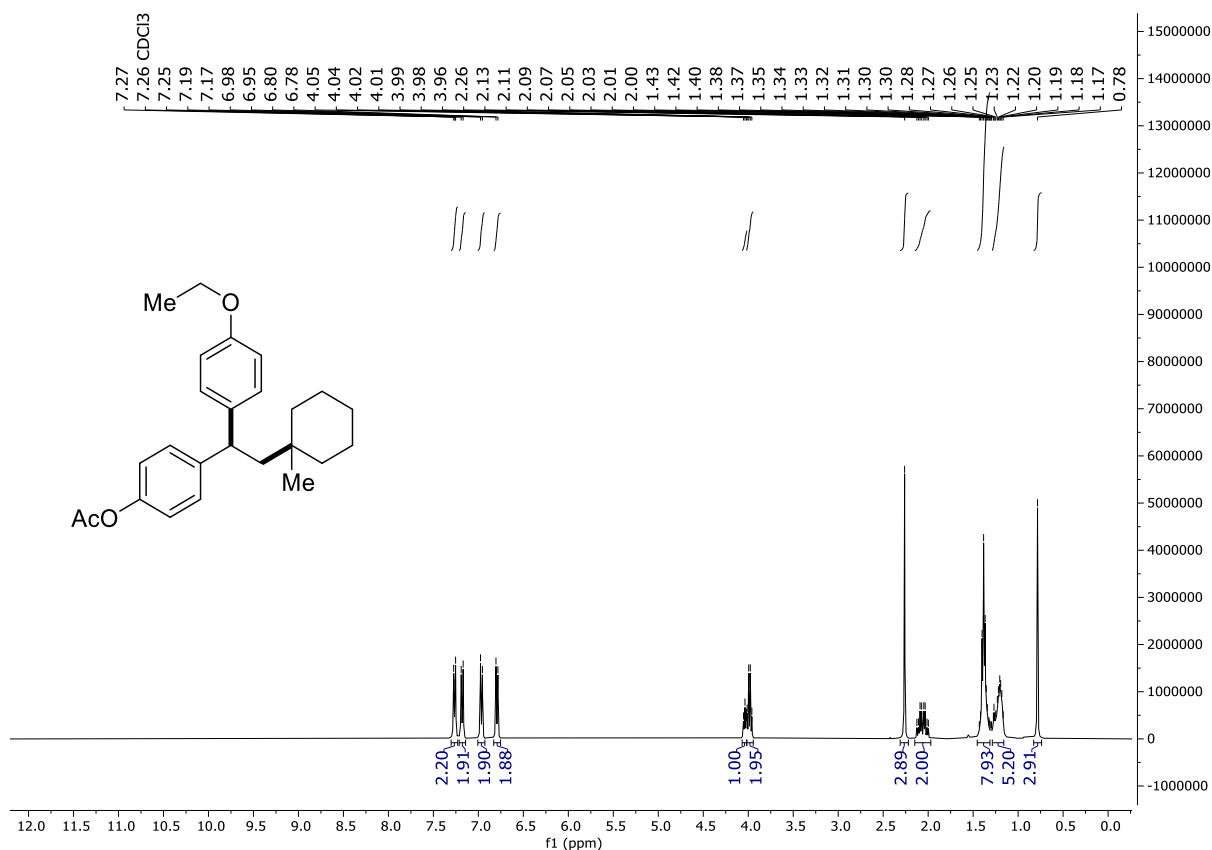


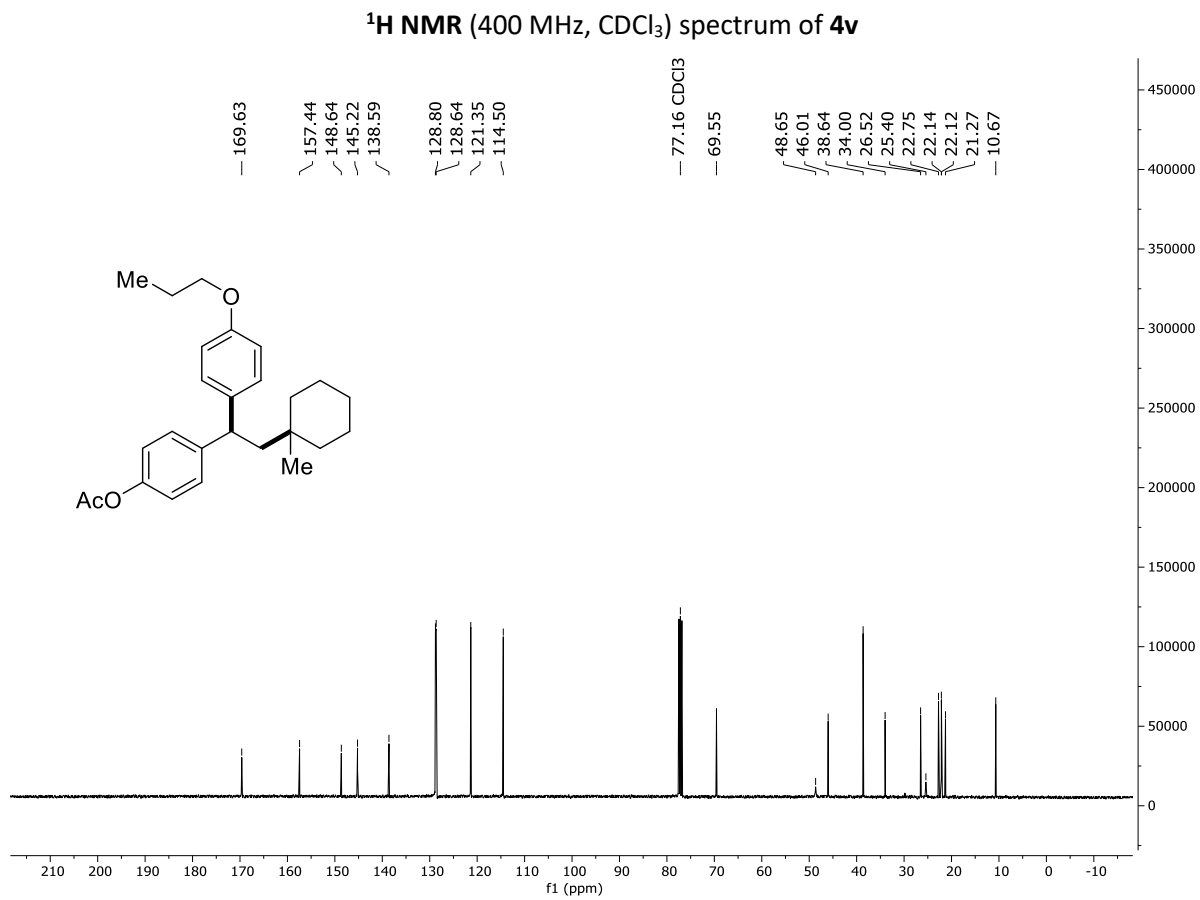
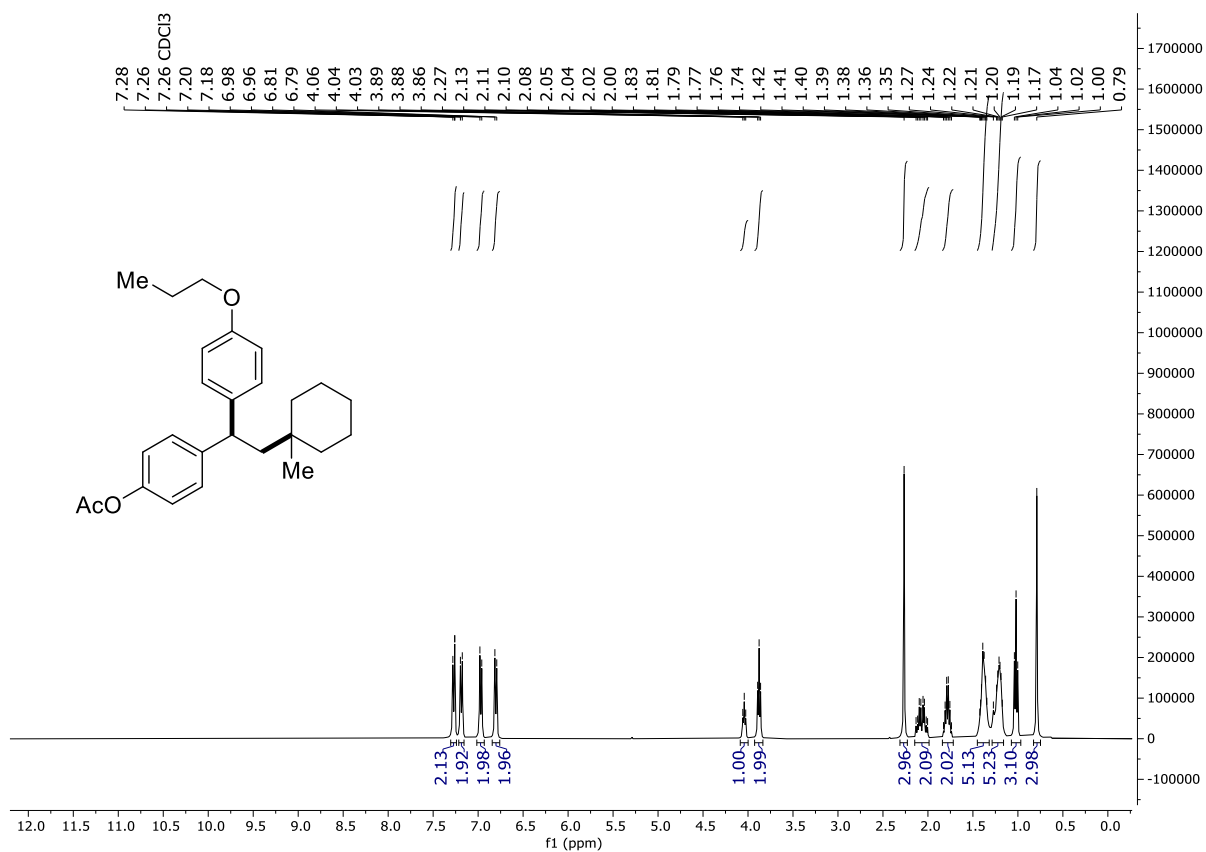


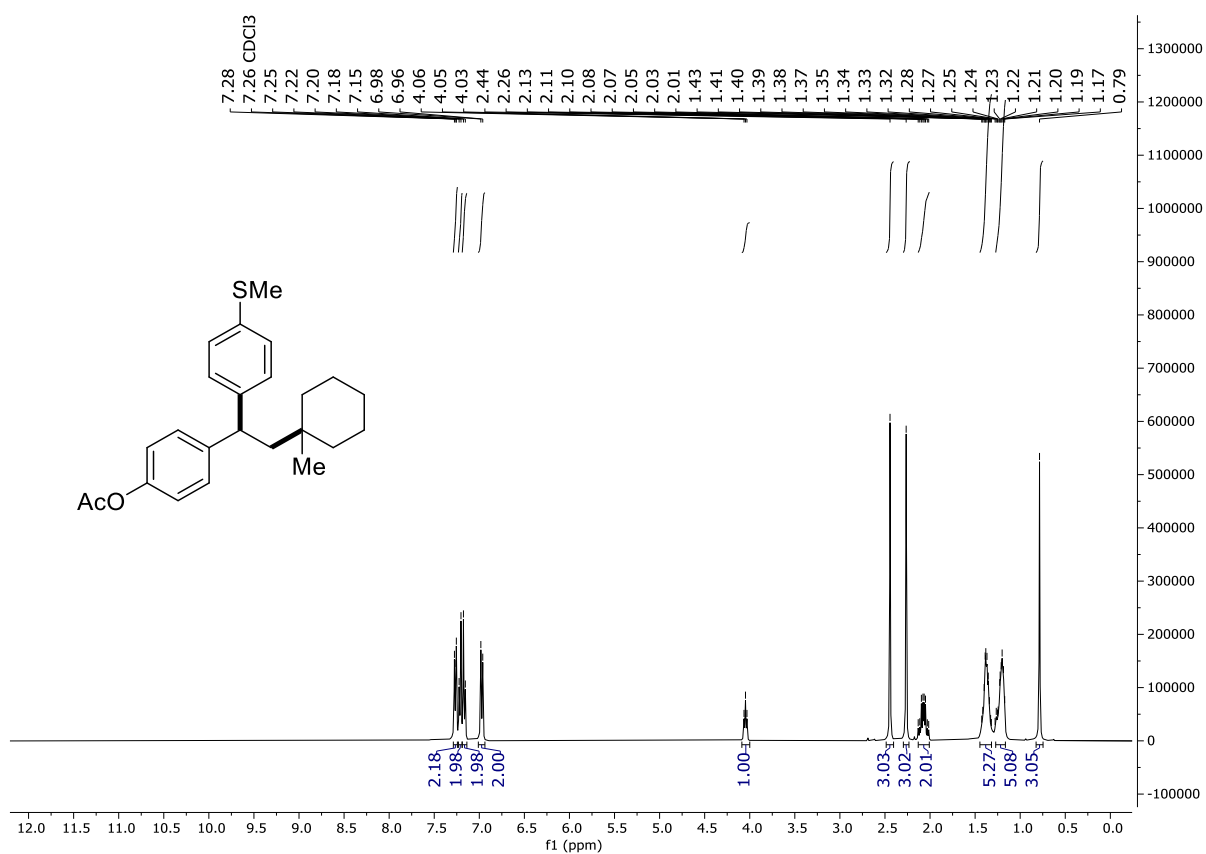
¹H NMR (400 MHz, CDCl₃) spectrum of 4t



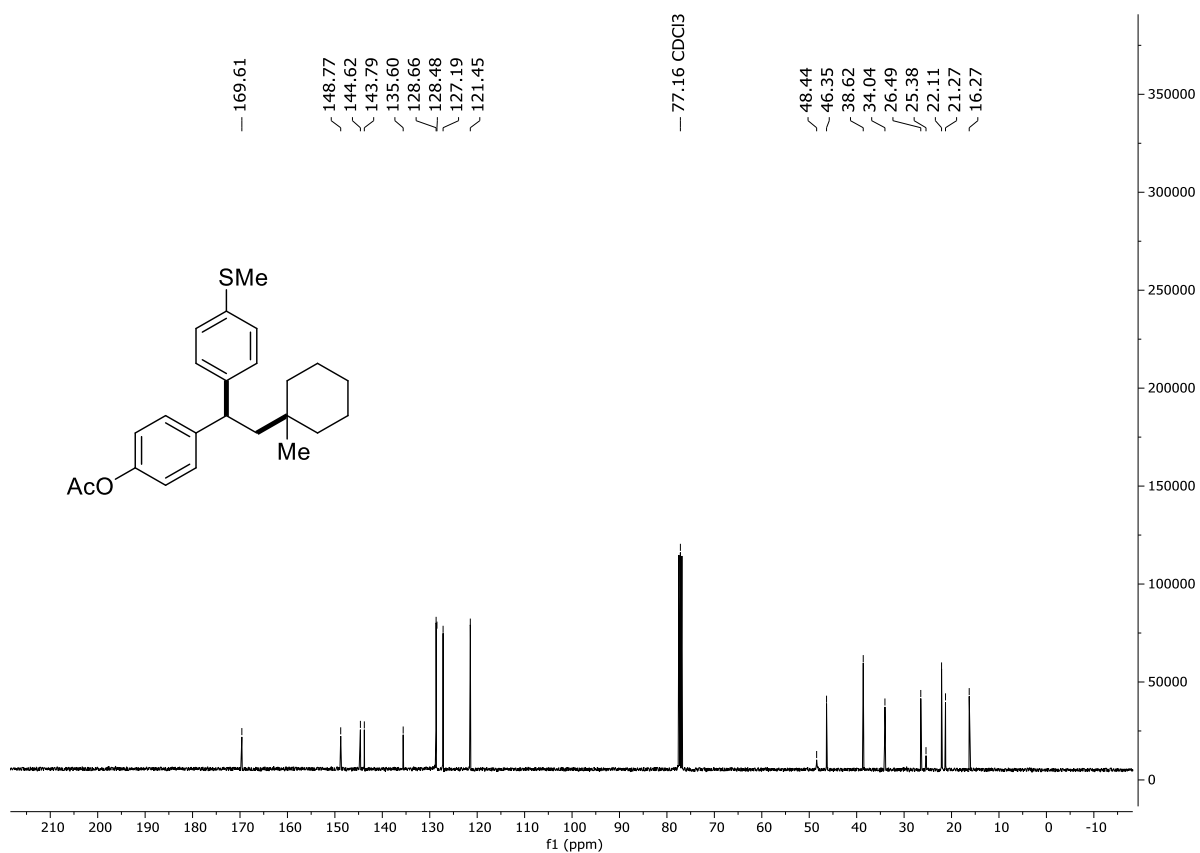
¹³C NMR (101 MHz, CDCl₃) spectrum of 4t



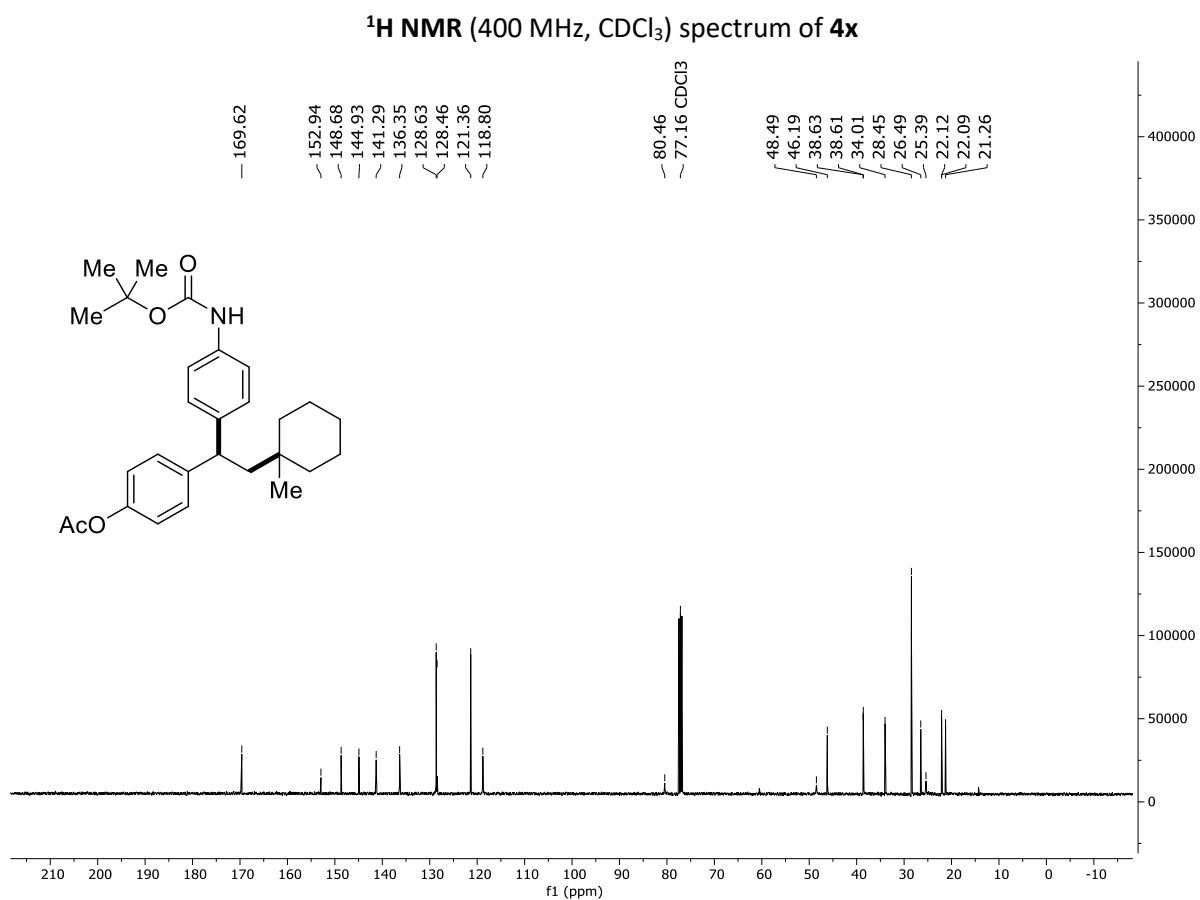
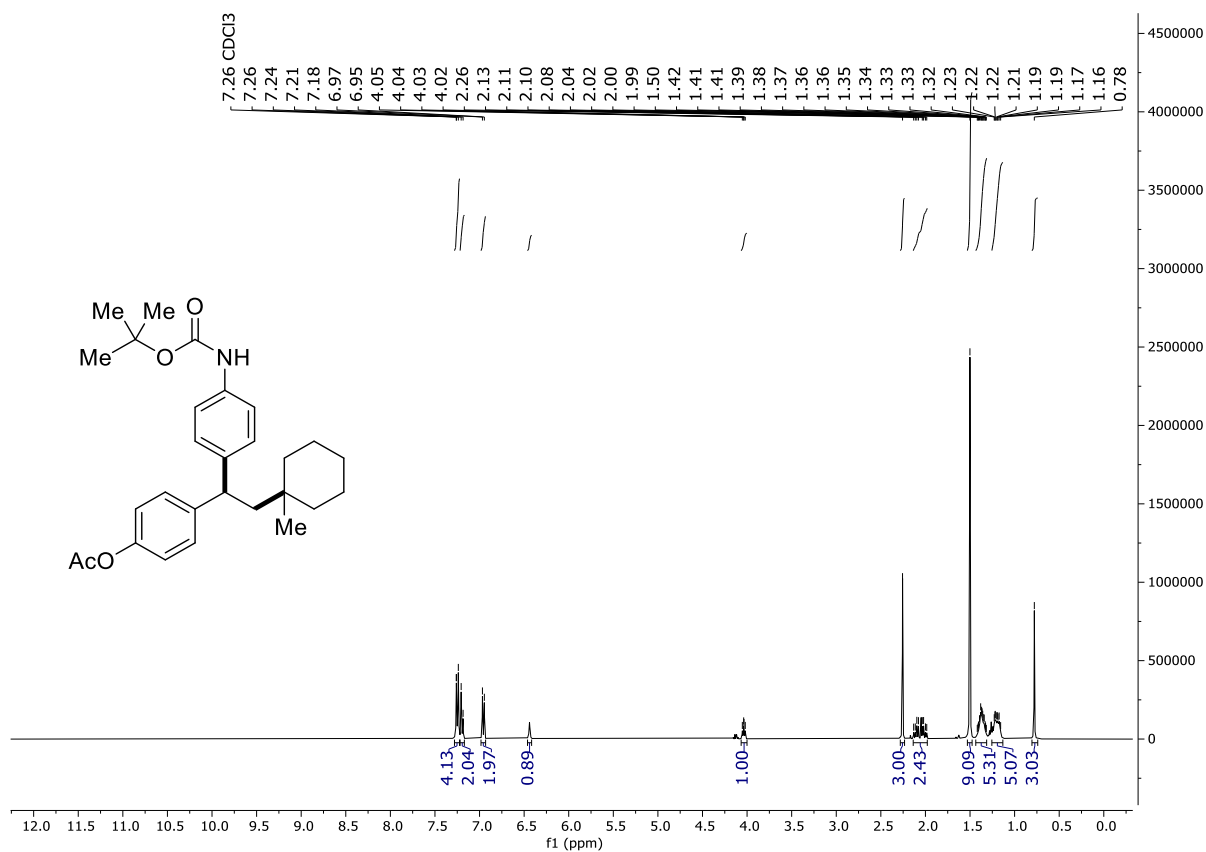


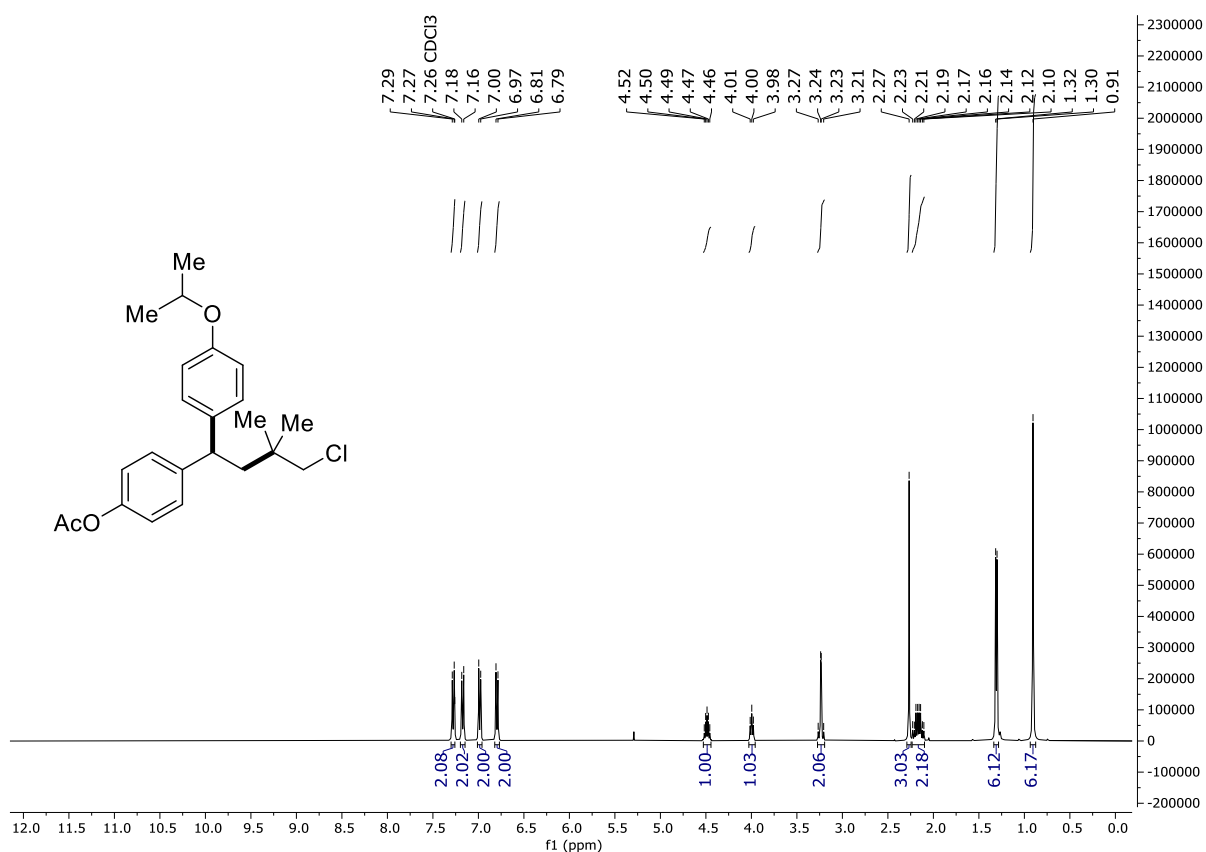


¹H NMR (400 MHz, CDCl₃) spectrum of 4w

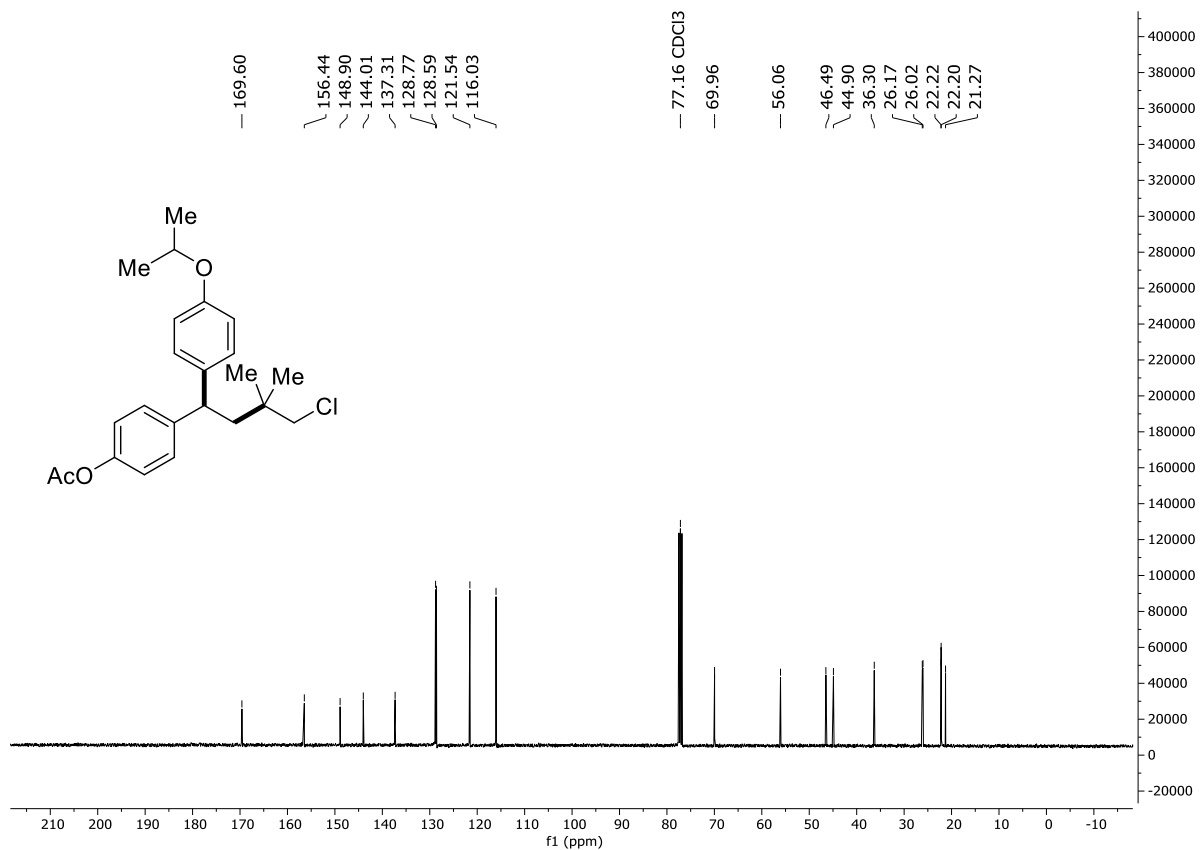


¹³C NMR (101 MHz, CDCl₃) spectrum of 4w

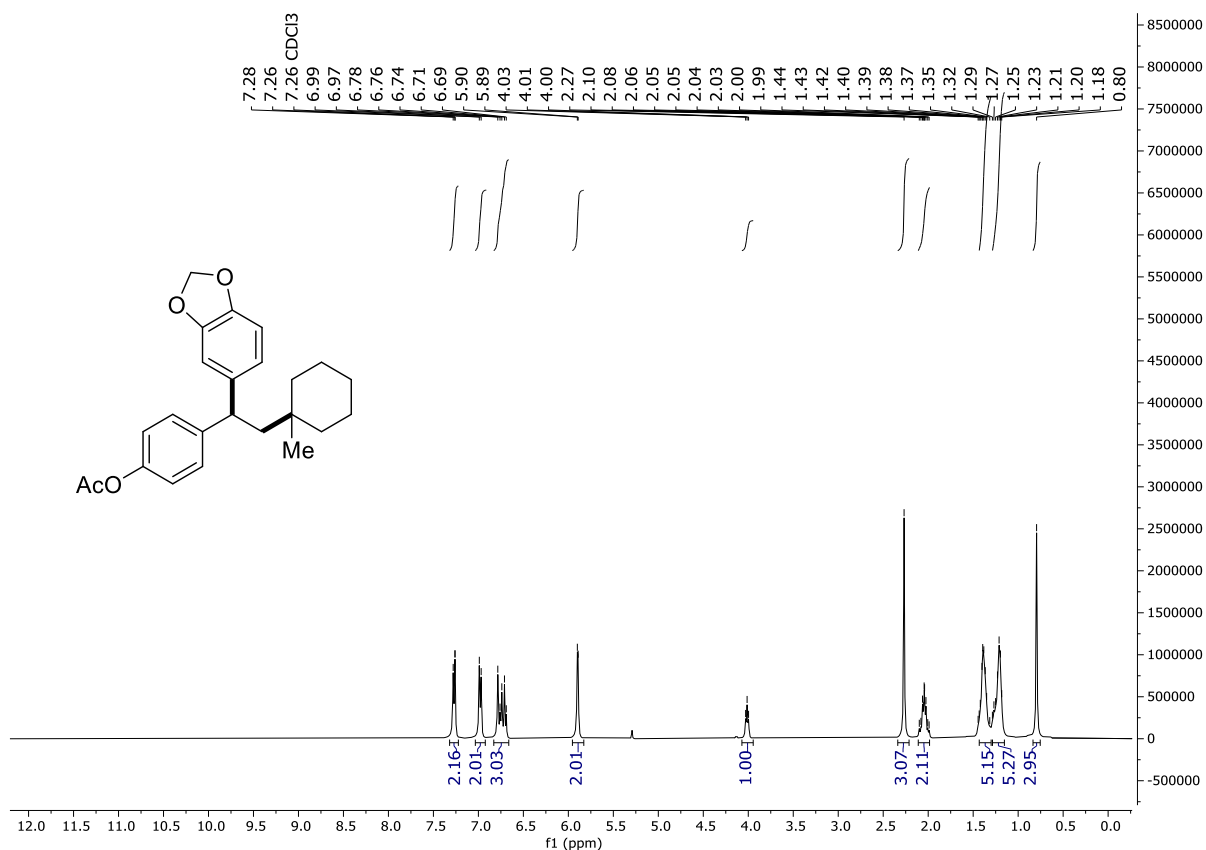




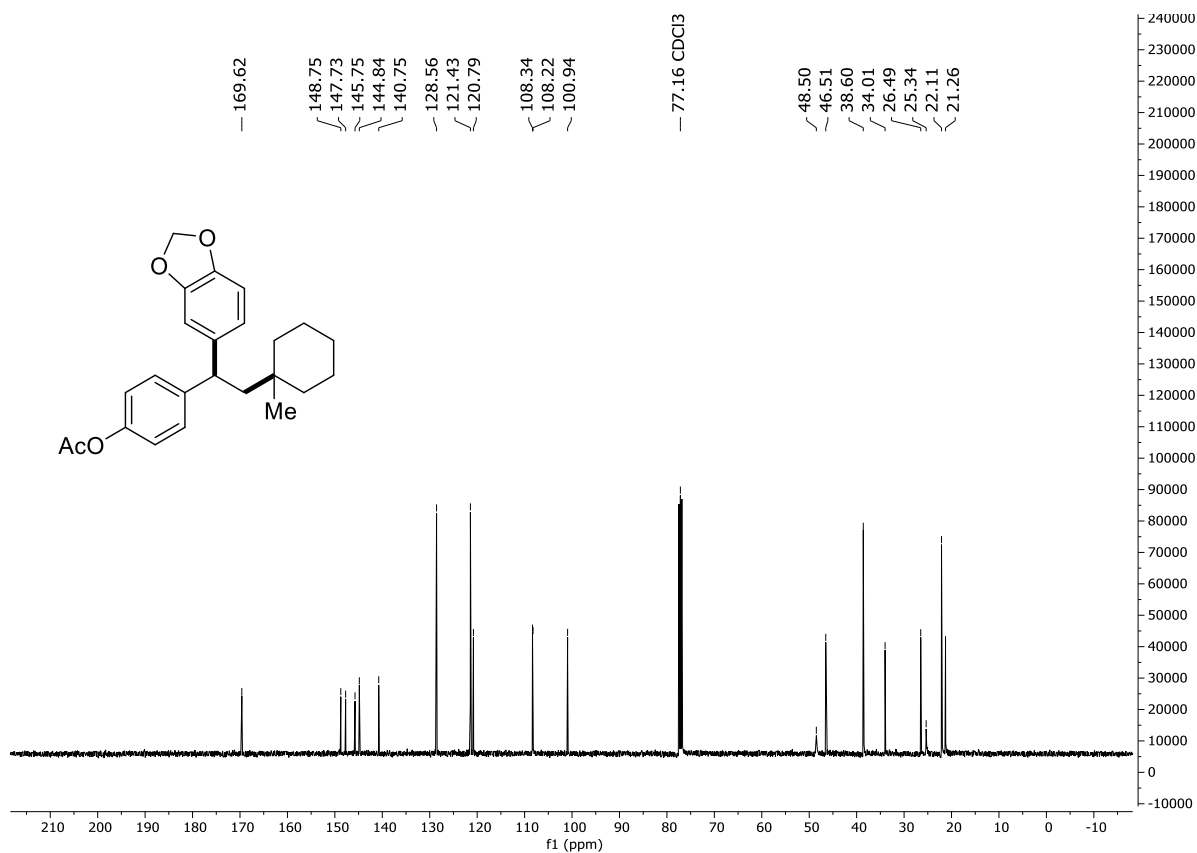
¹H NMR (400 MHz, CDCl₃) spectrum of **4y**



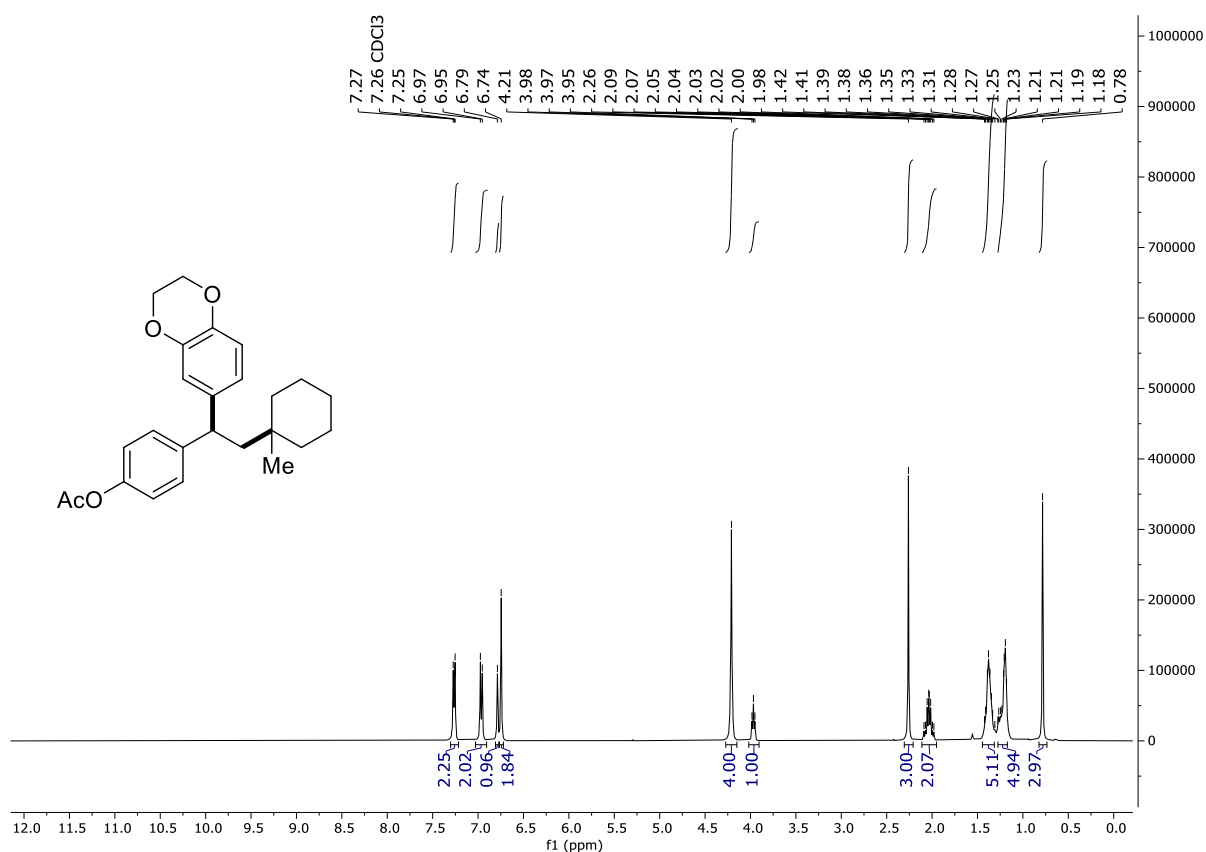
¹³C NMR (101 MHz, CDCl₃) spectrum of **4y**



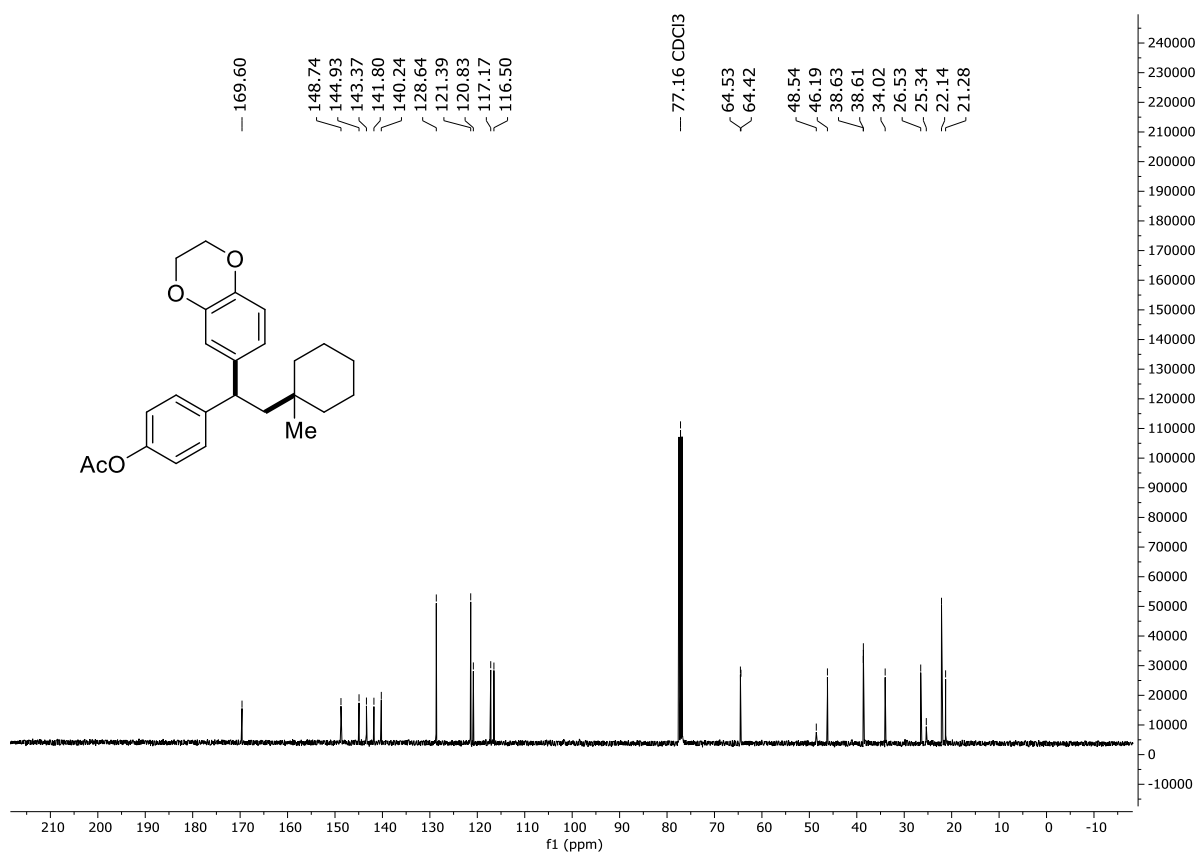
¹H NMR (400 MHz, CDCl₃) spectrum of 4z



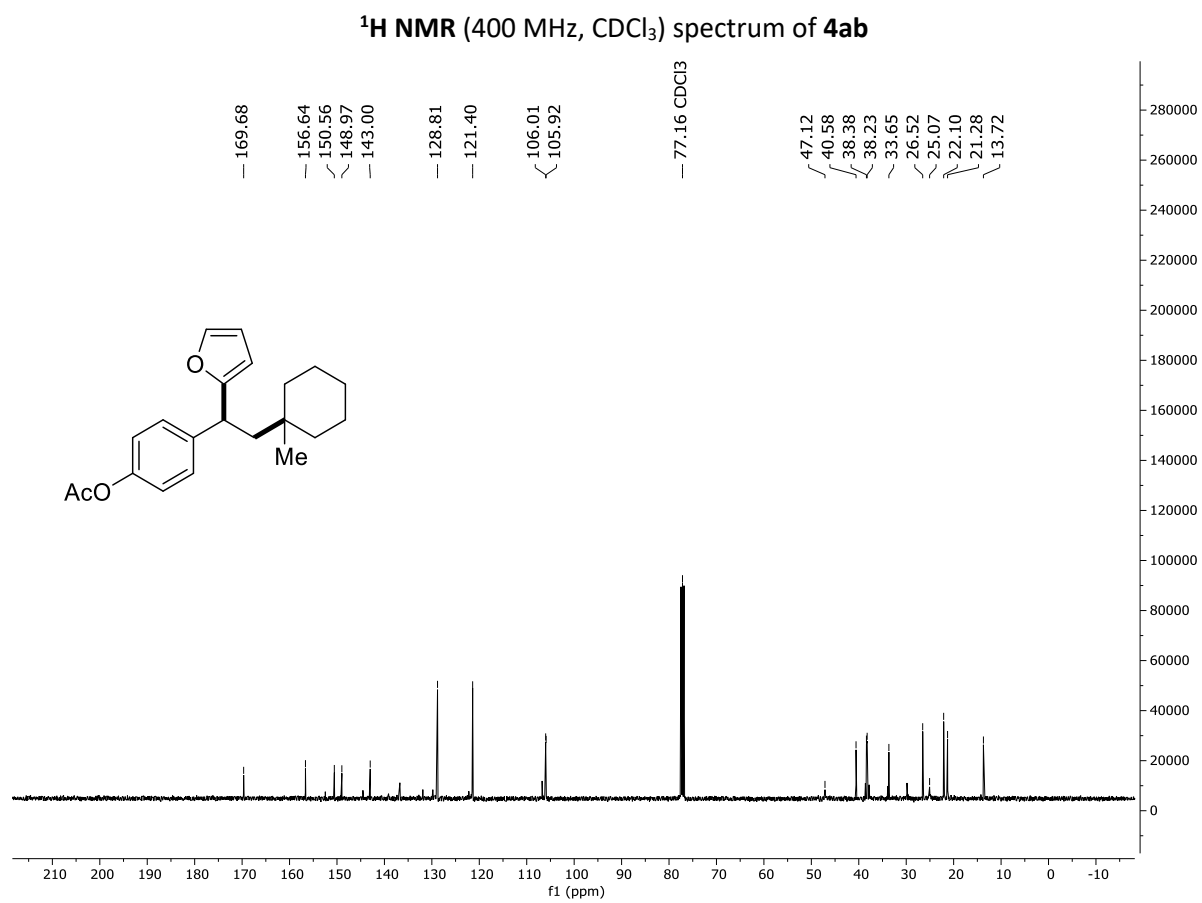
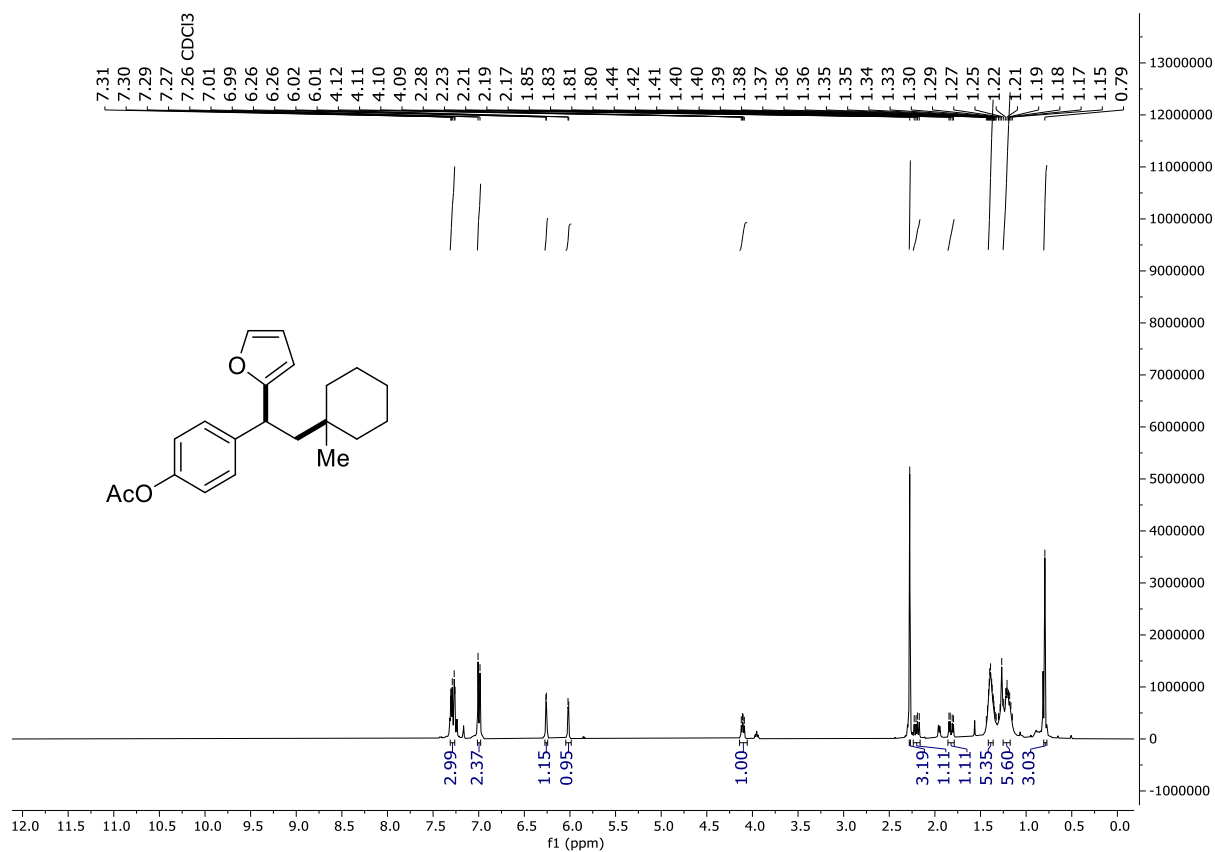
¹³C NMR (101 MHz, CDCl₃) spectrum of 4z

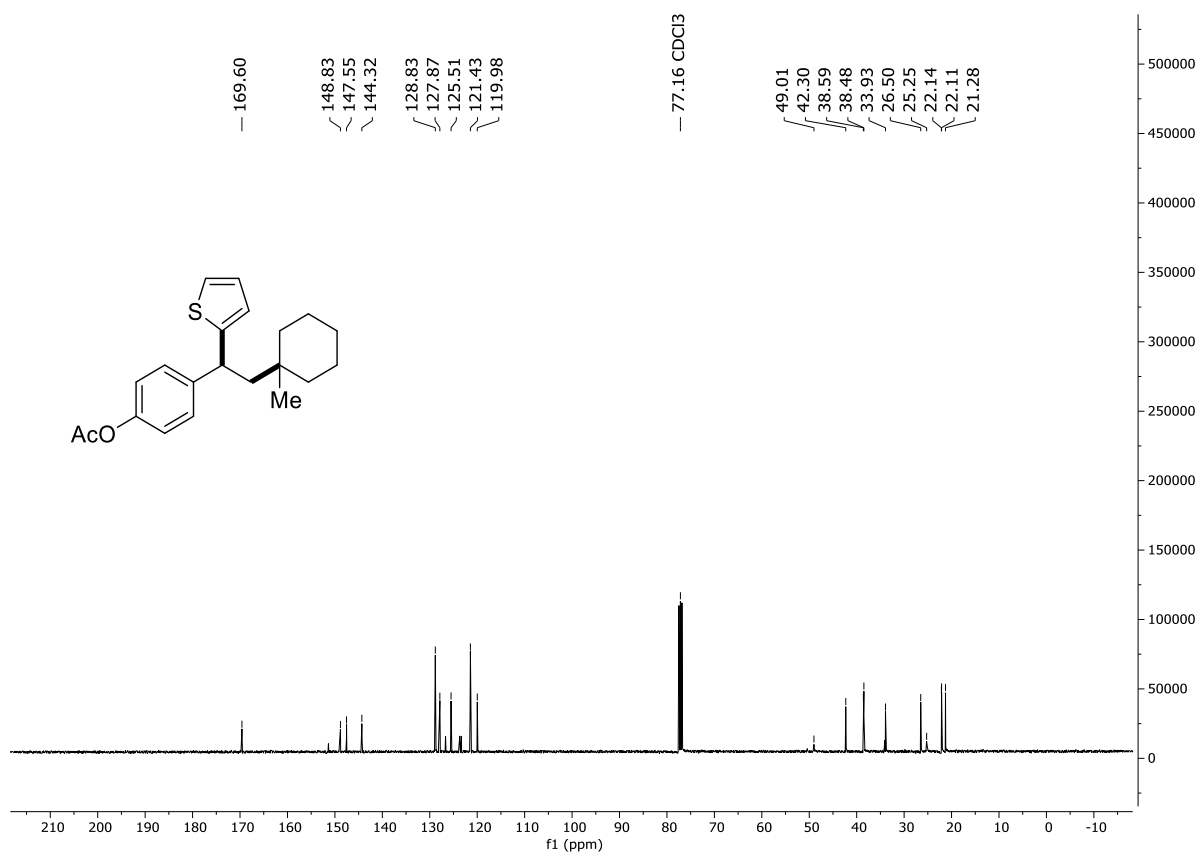
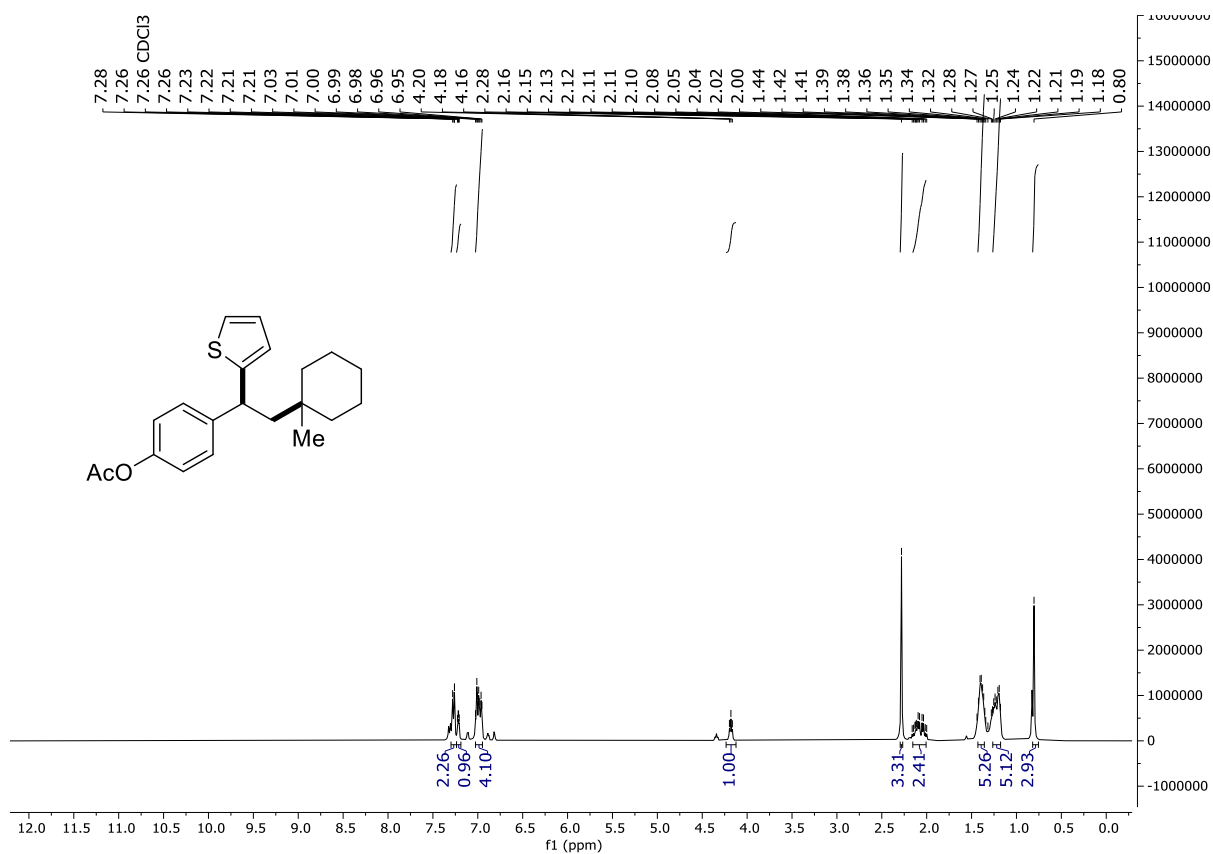


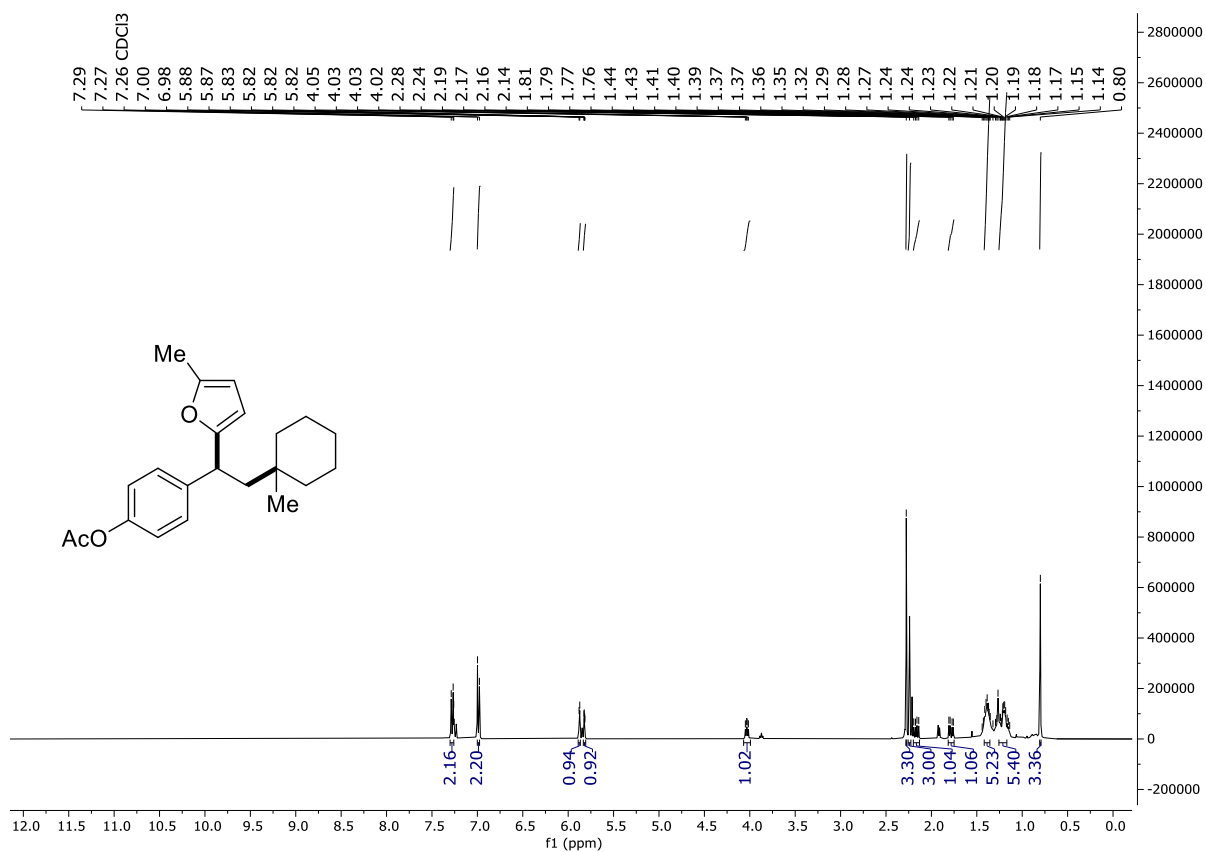
¹H NMR (400 MHz, CDCl₃) spectrum of 4aa



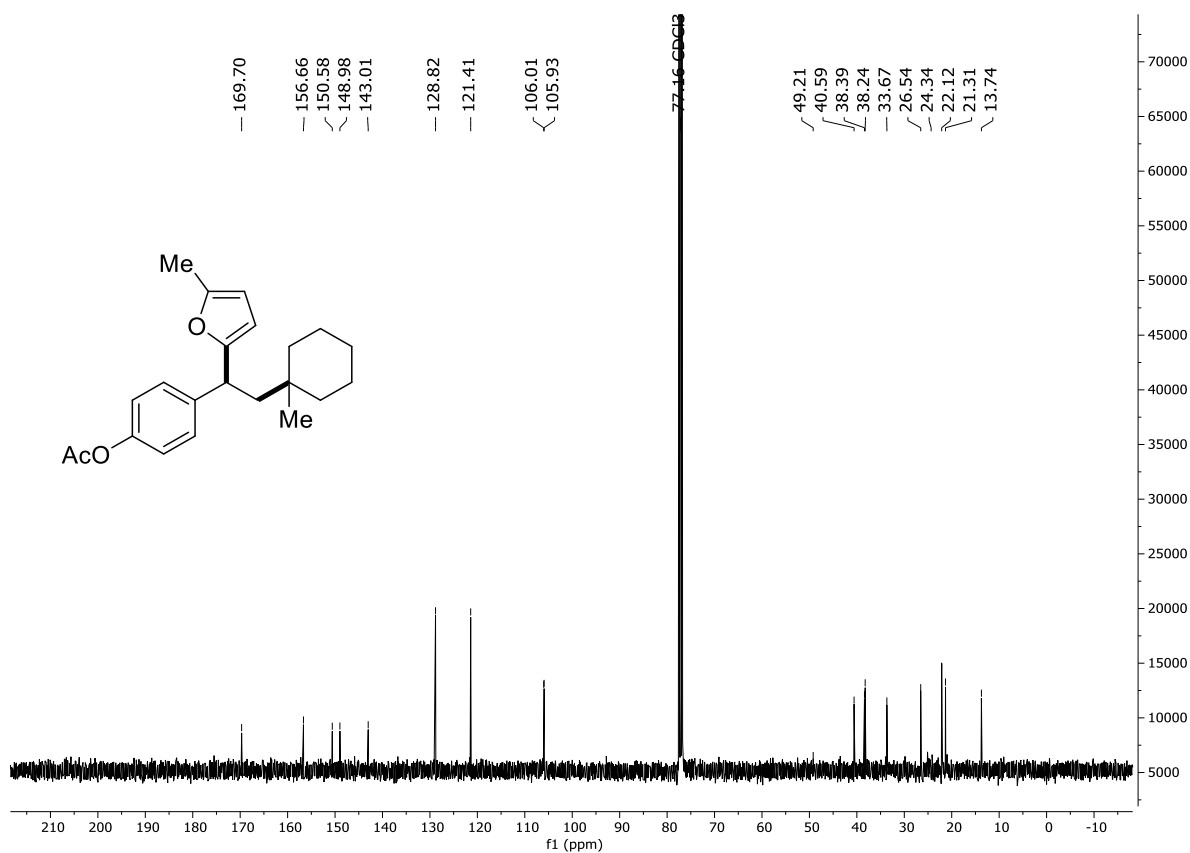
¹³C NMR (101 MHz, CDCl₃) spectrum of 4aa



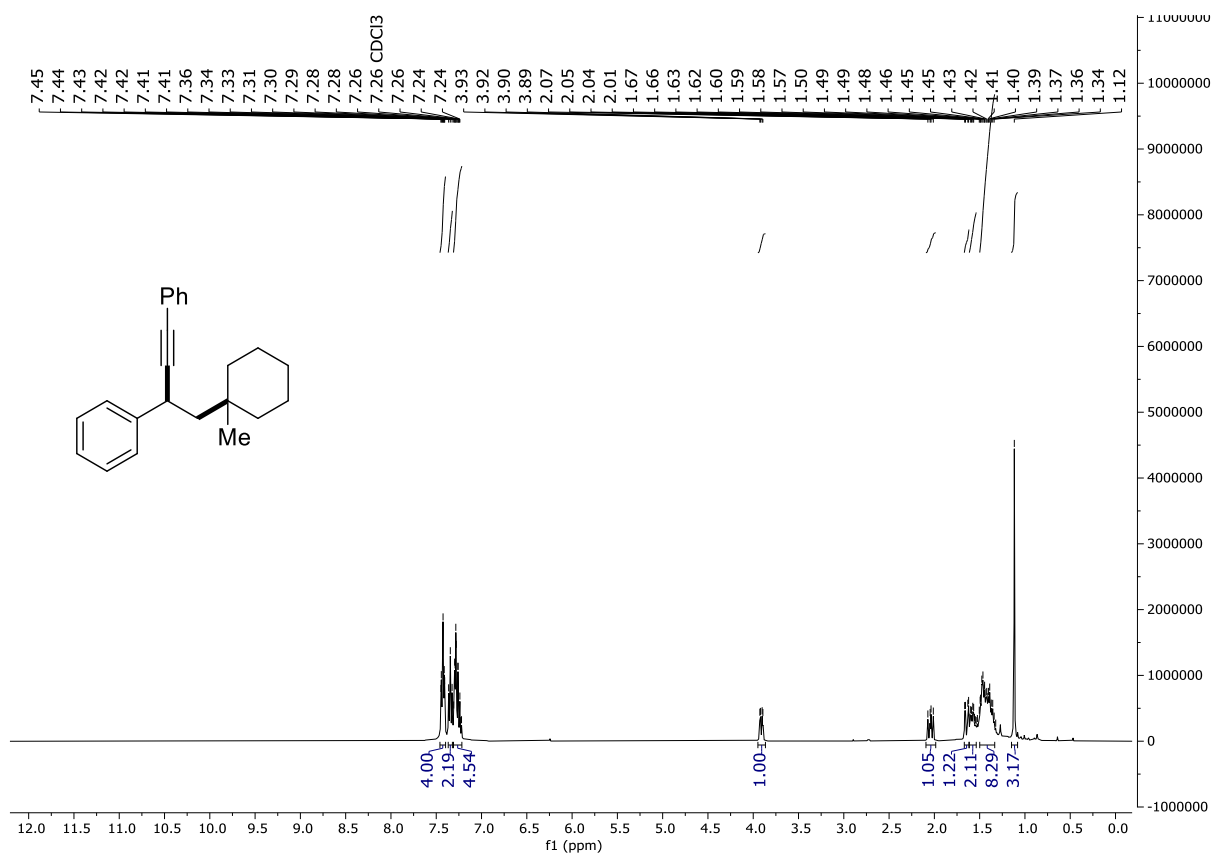




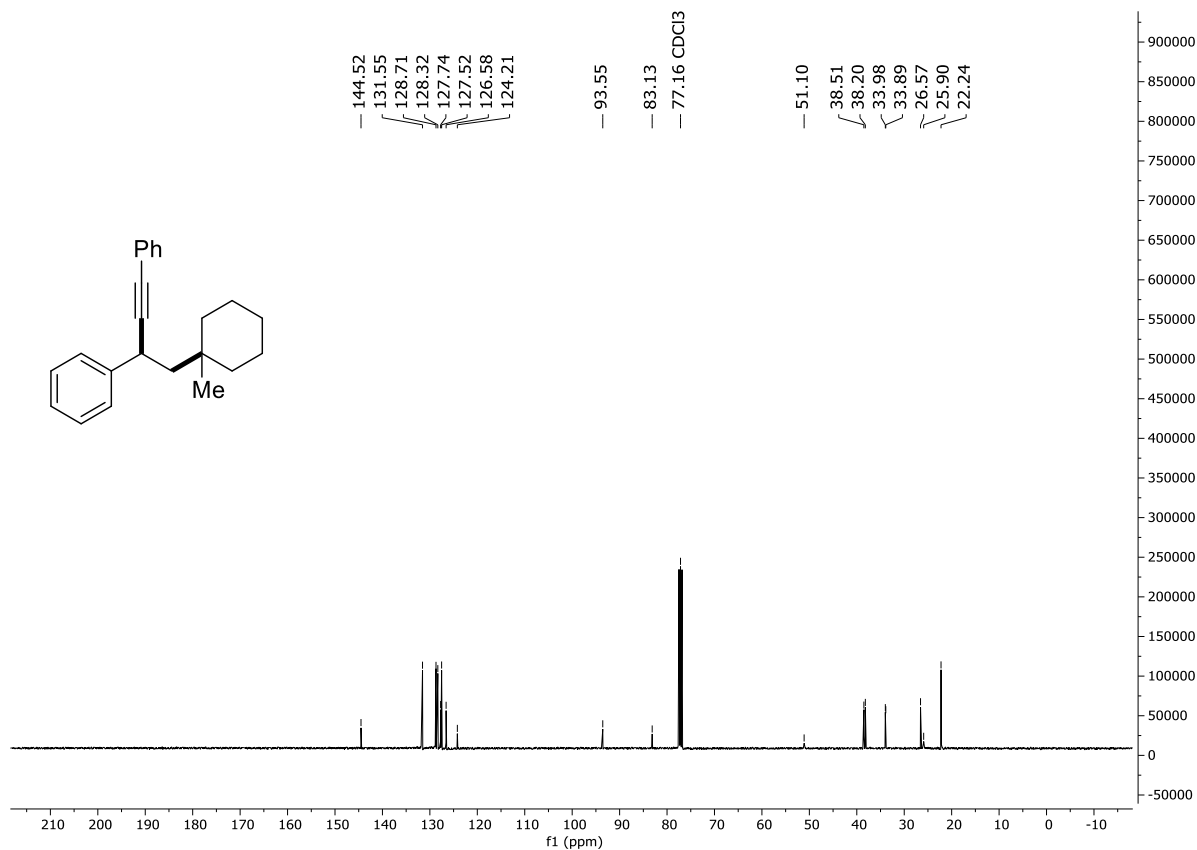
¹H NMR (400 MHz, CDCl₃) spectrum of 4ad



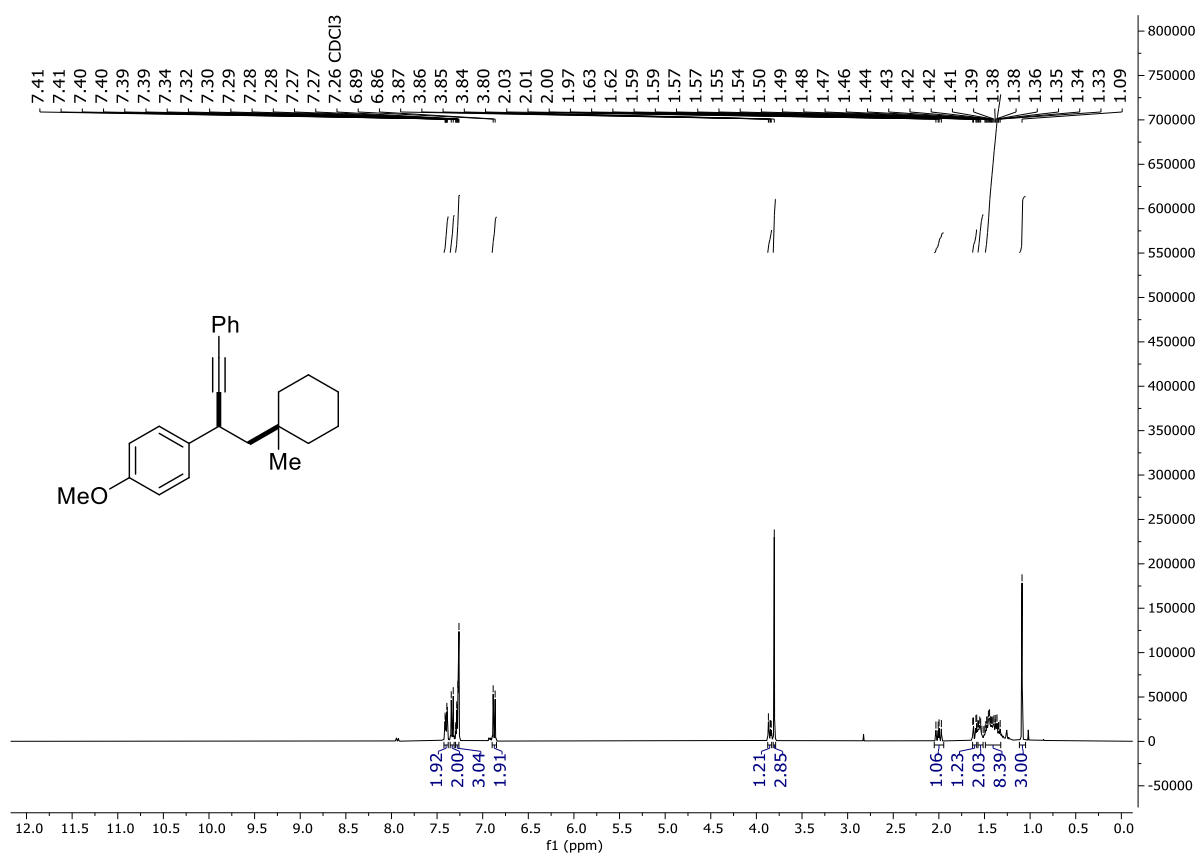
¹³C NMR (101 MHz, CDCl₃) spectrum of 4ad



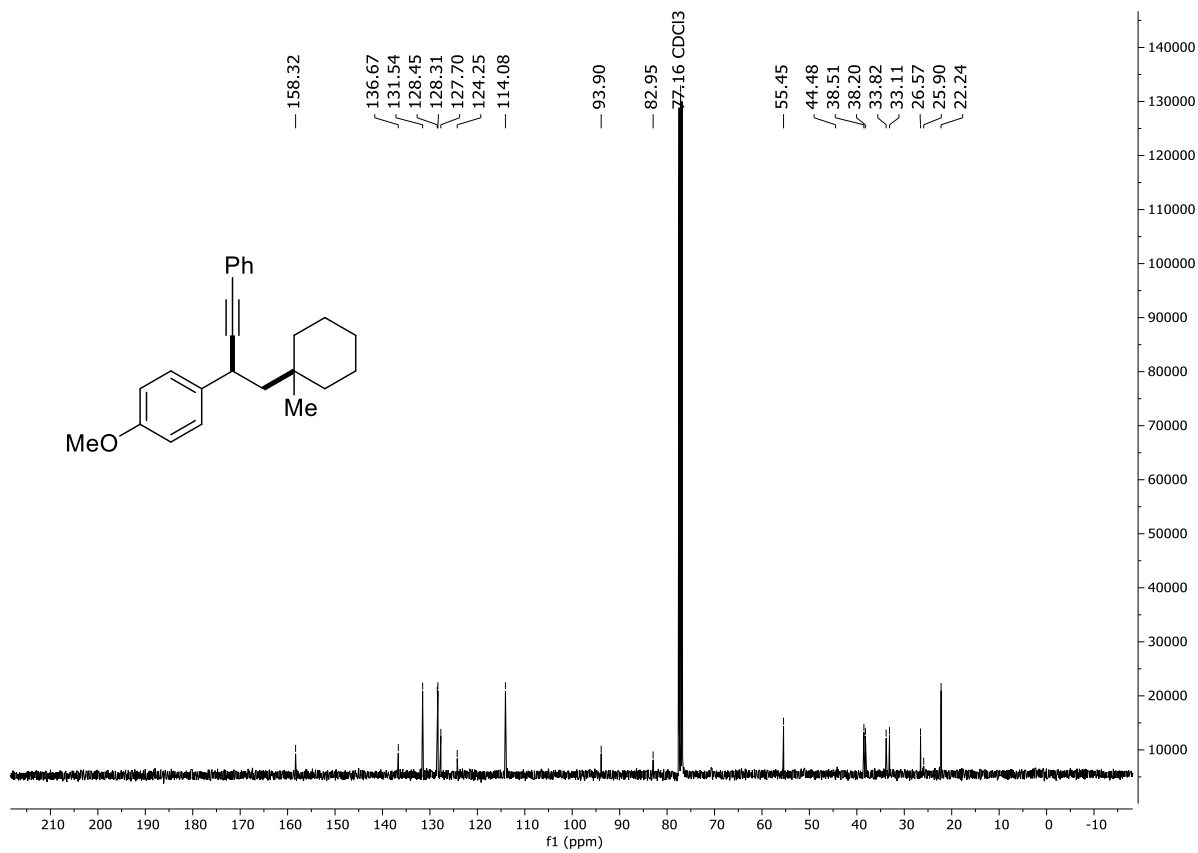
¹H NMR (400 MHz, CDCl₃) spectrum of 4ae



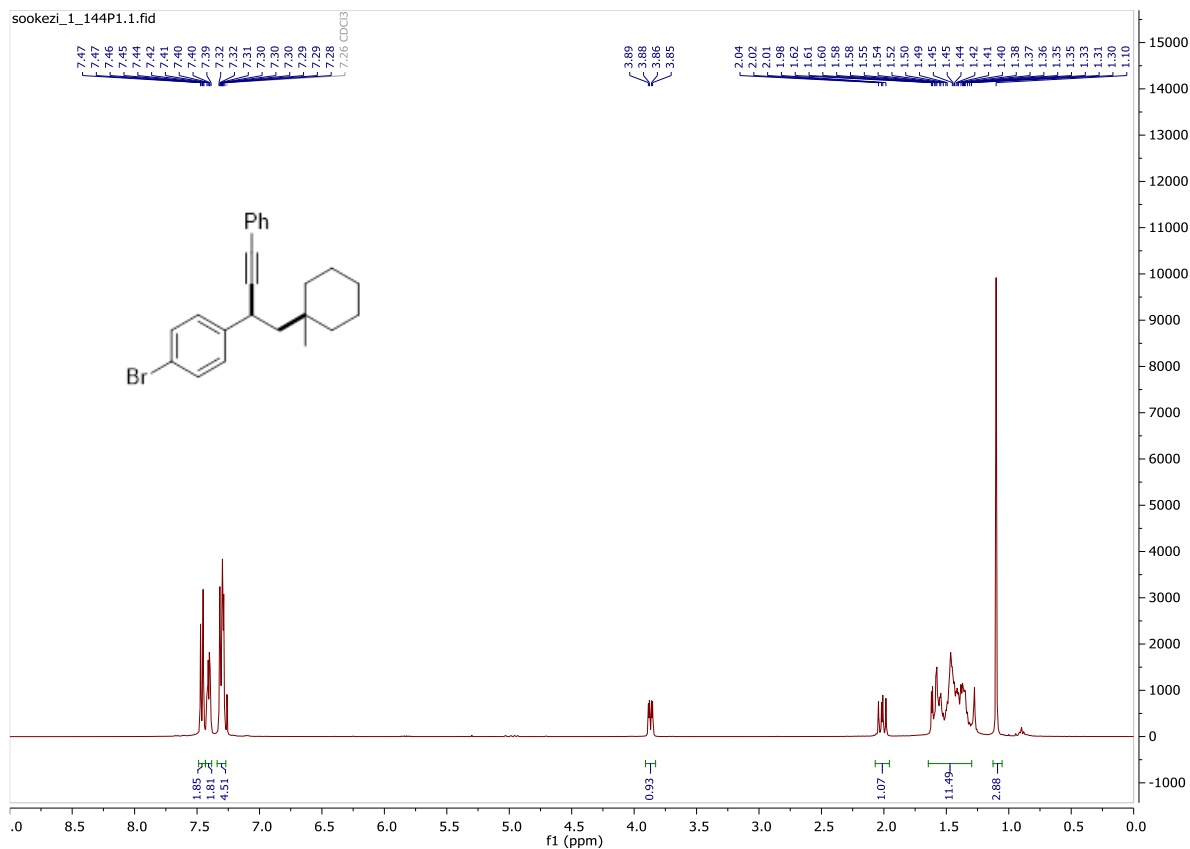
¹³C NMR (101 MHz, CDCl₃) spectrum of 4ae



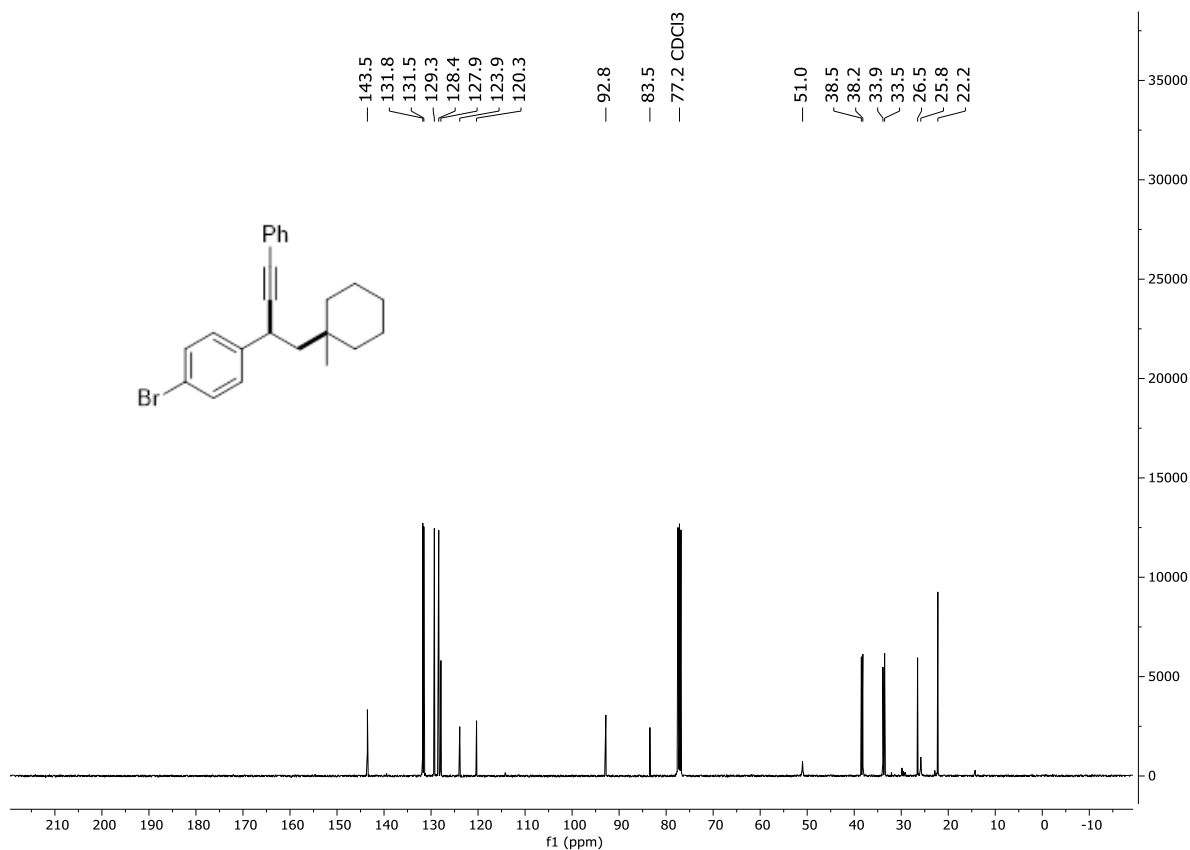
¹H NMR (400 MHz, CDCl₃) spectrum of 4af



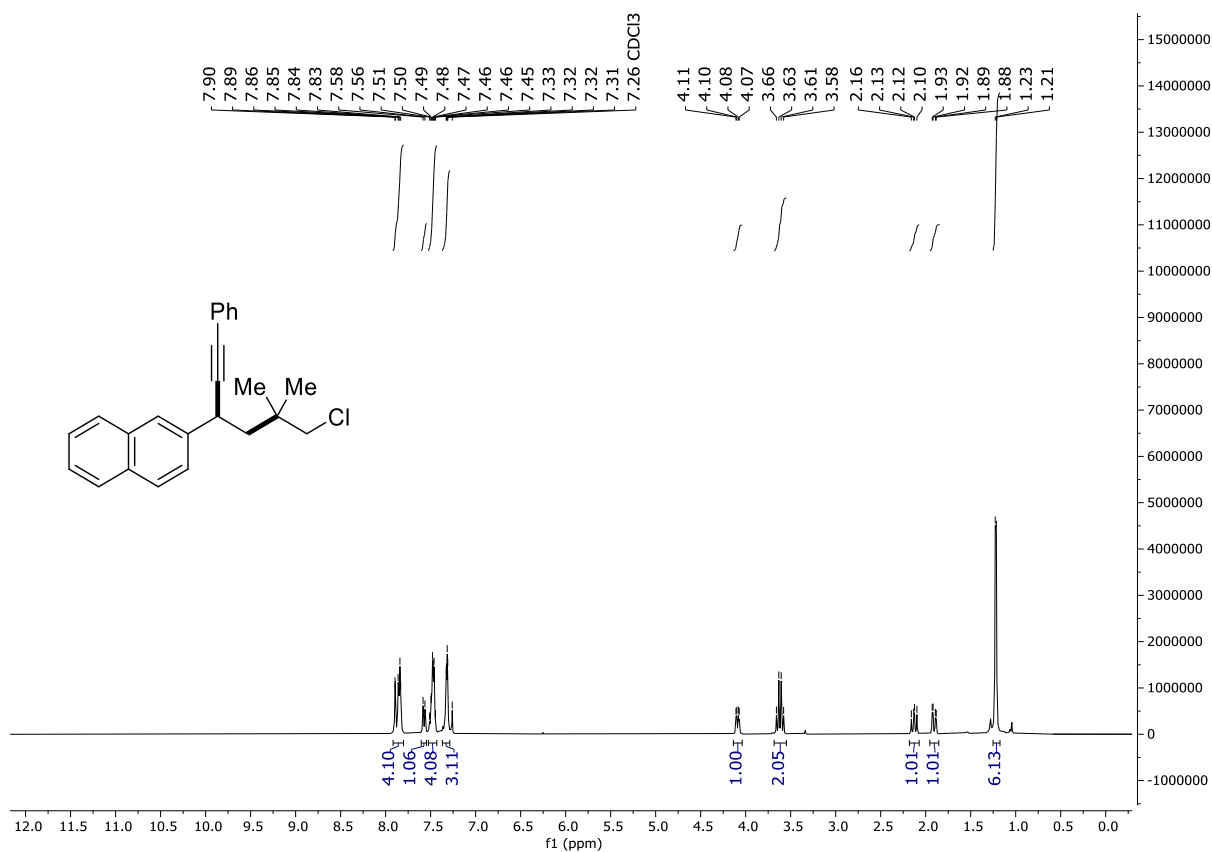
¹³C NMR (101 MHz, CDCl₃) spectrum of 4af



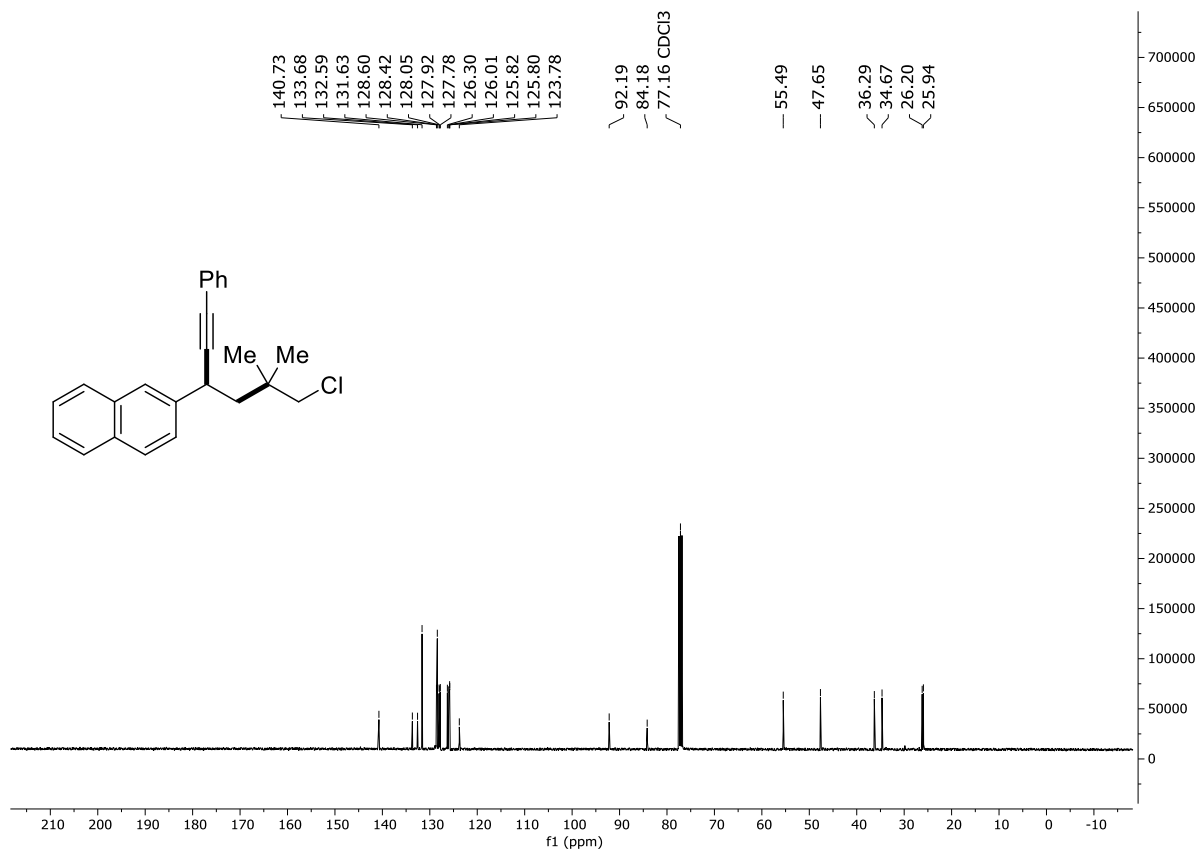
¹H NMR (400 MHz, CDCl₃) spectrum of **4ag**



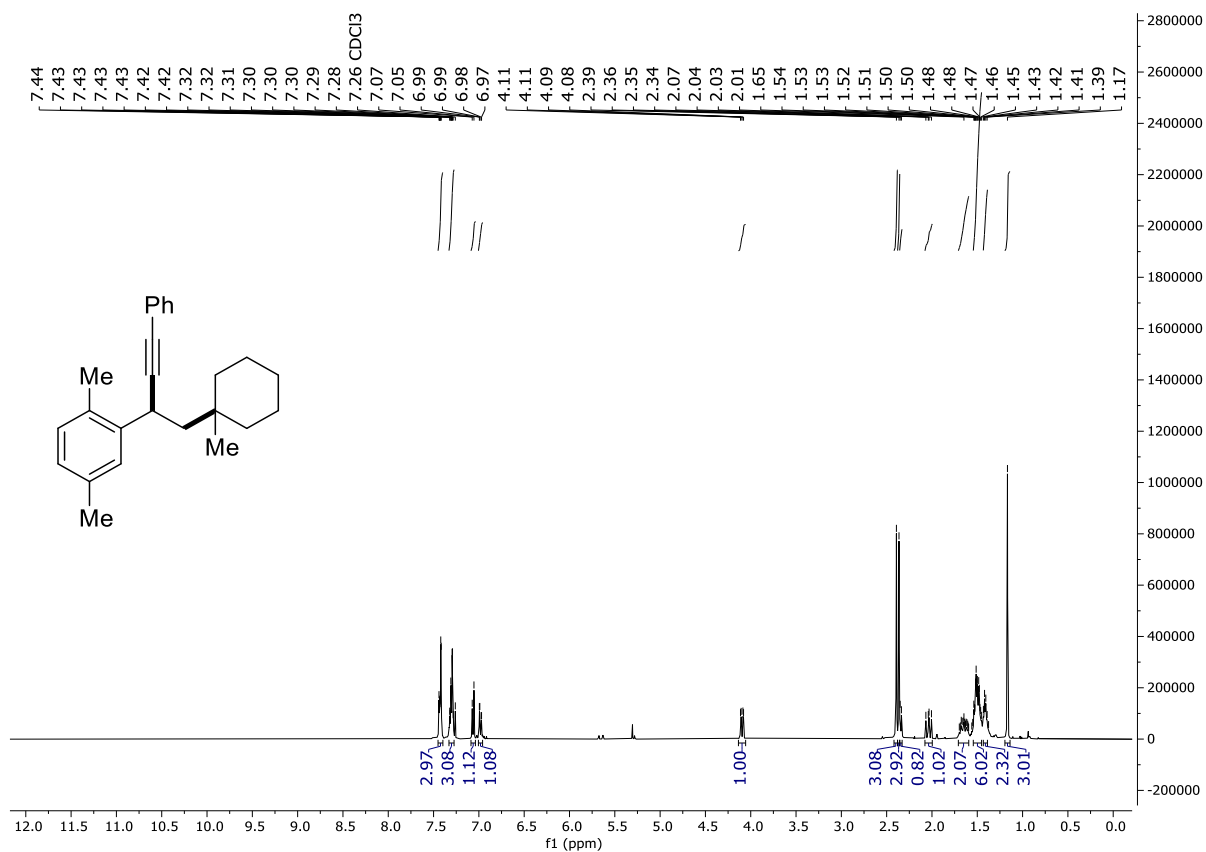
¹³C NMR (101 MHz, CDCl₃) spectrum of **4ag**



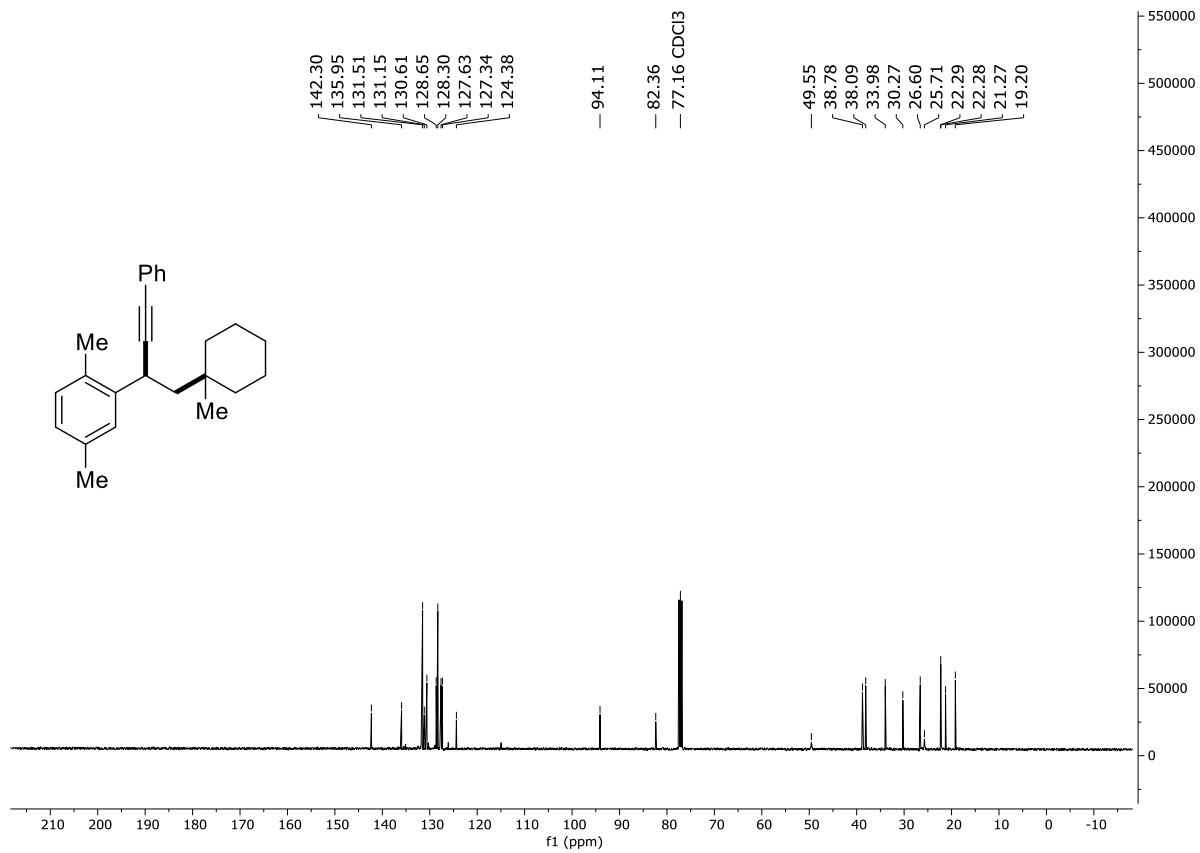
¹H NMR (400 MHz, CDCl₃) spectrum of 4ah



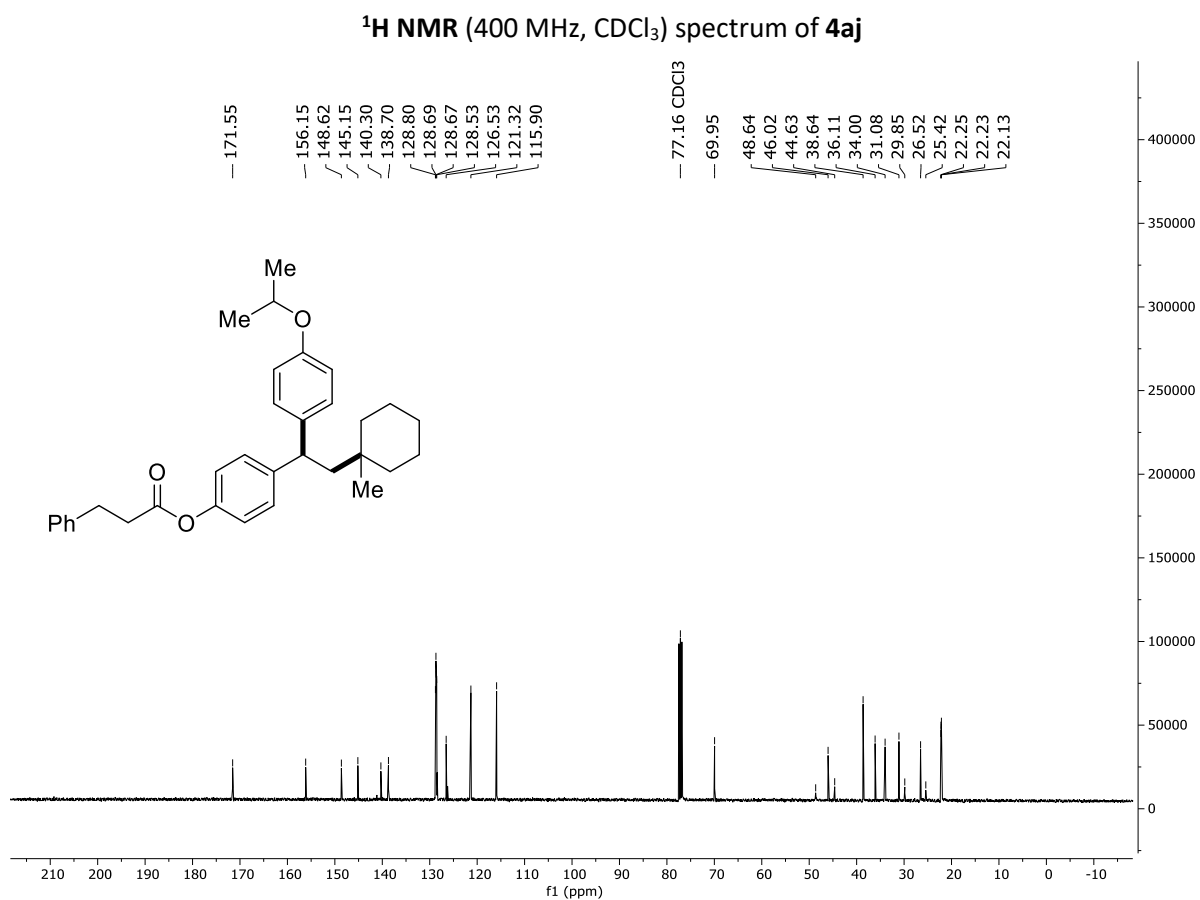
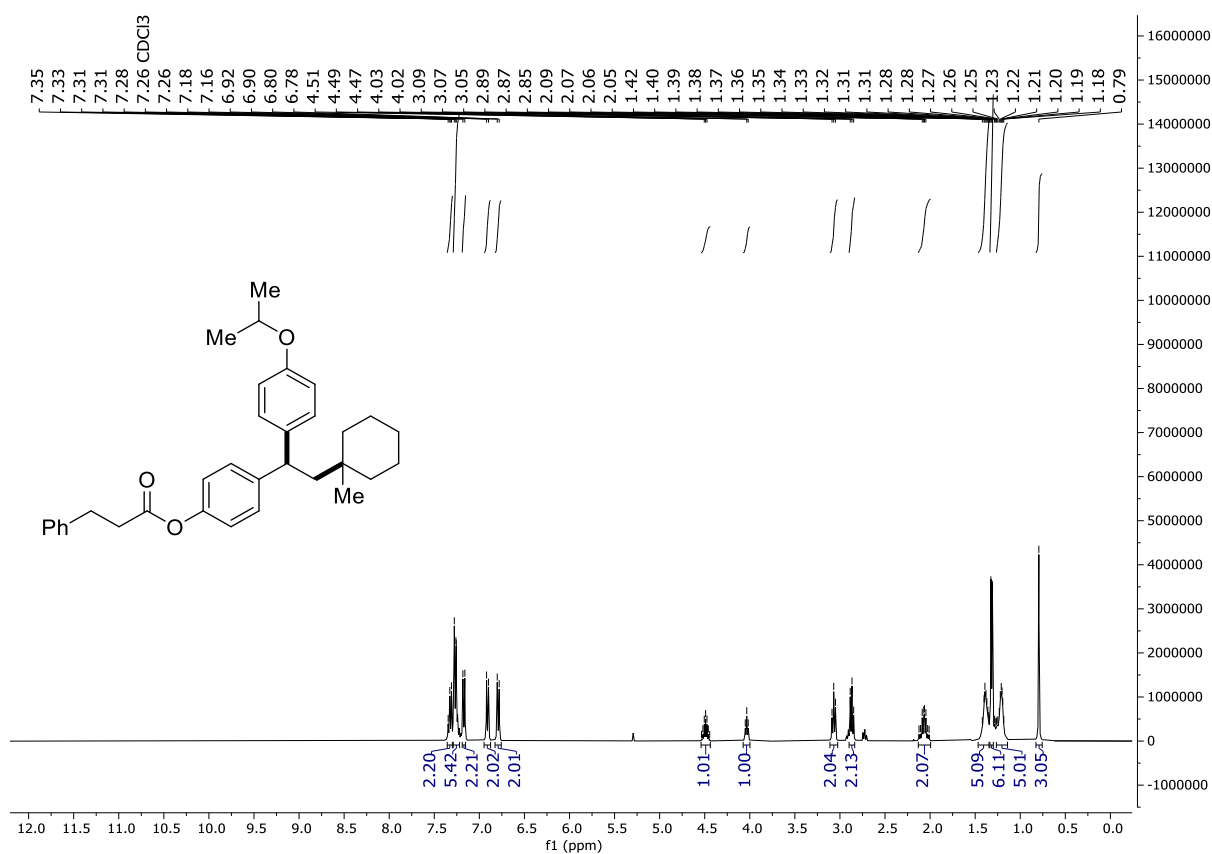
¹³C NMR (101 MHz, CDCl₃) spectrum of 4ah

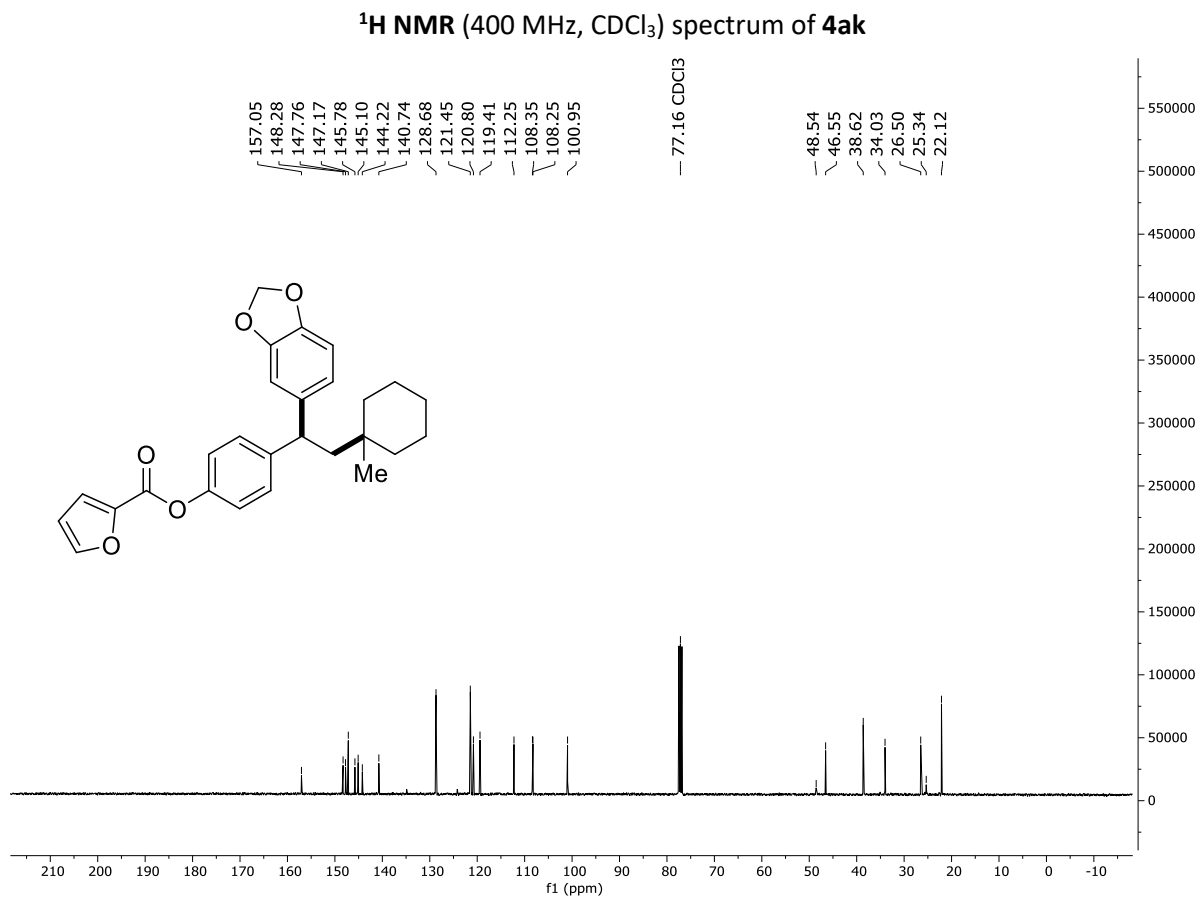
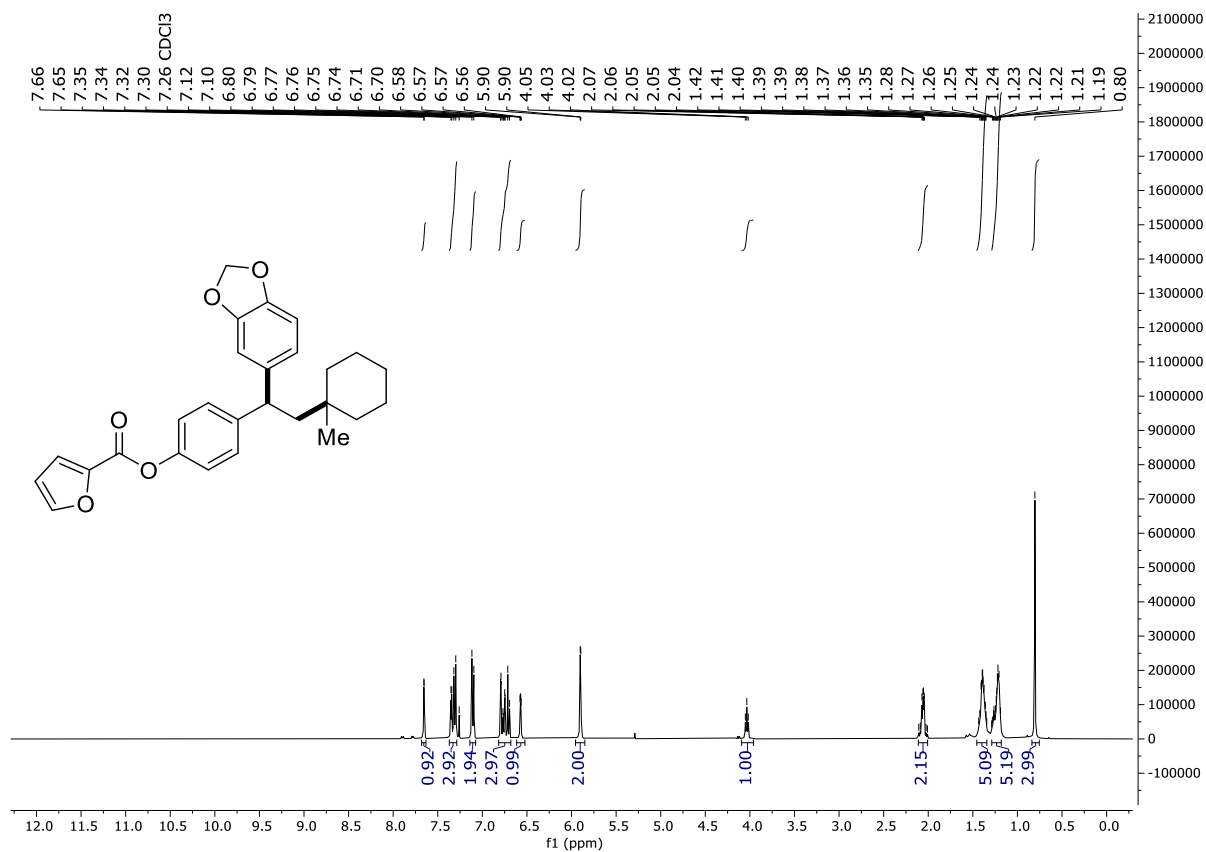


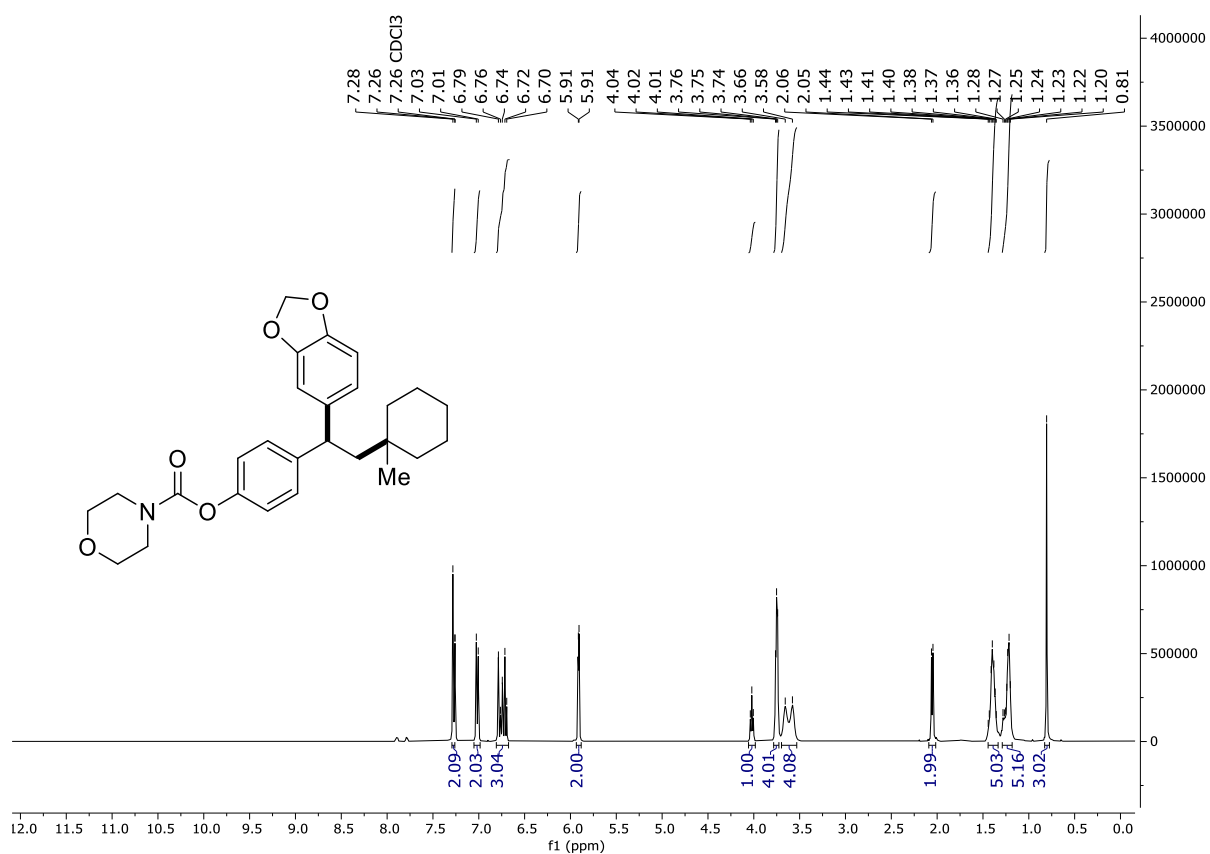
¹H NMR (400 MHz, CDCl₃) spectrum of **4ai**



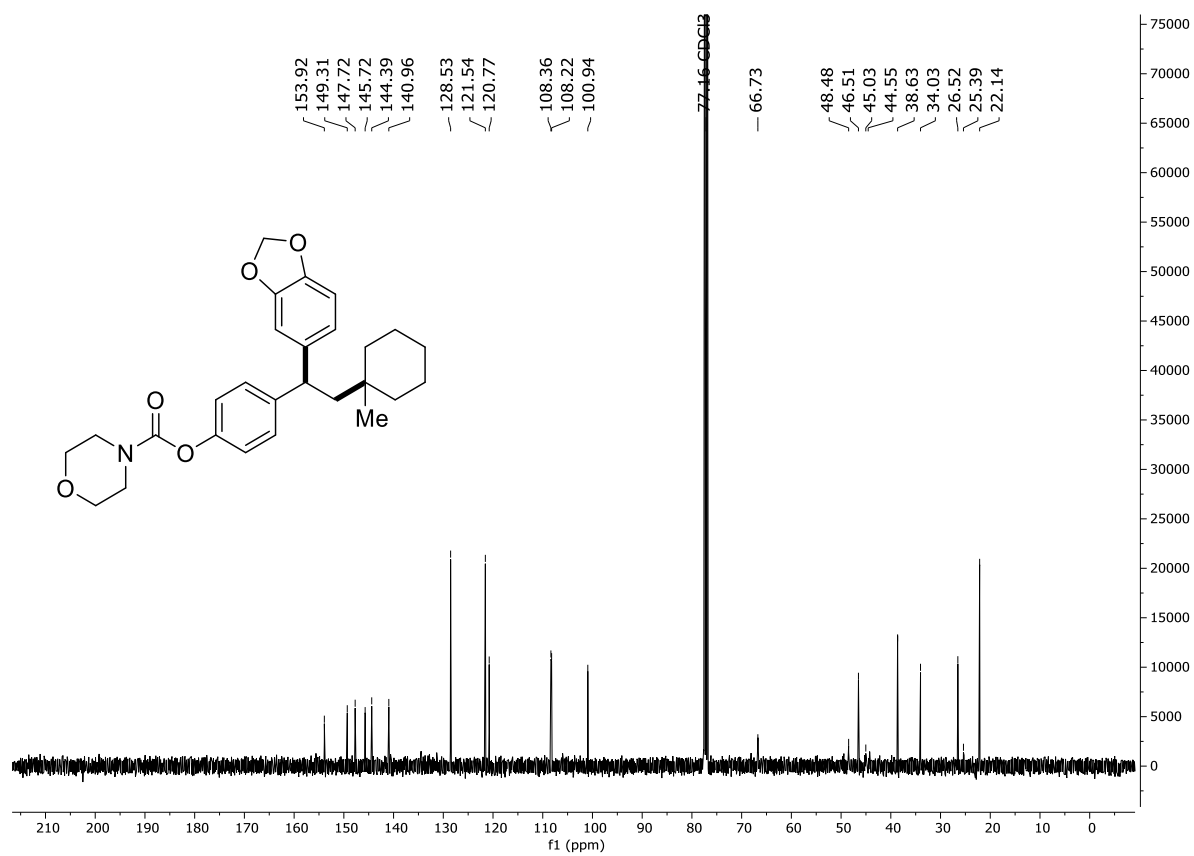
¹³C NMR (101 MHz, CDCl₃) spectrum of **4ai**



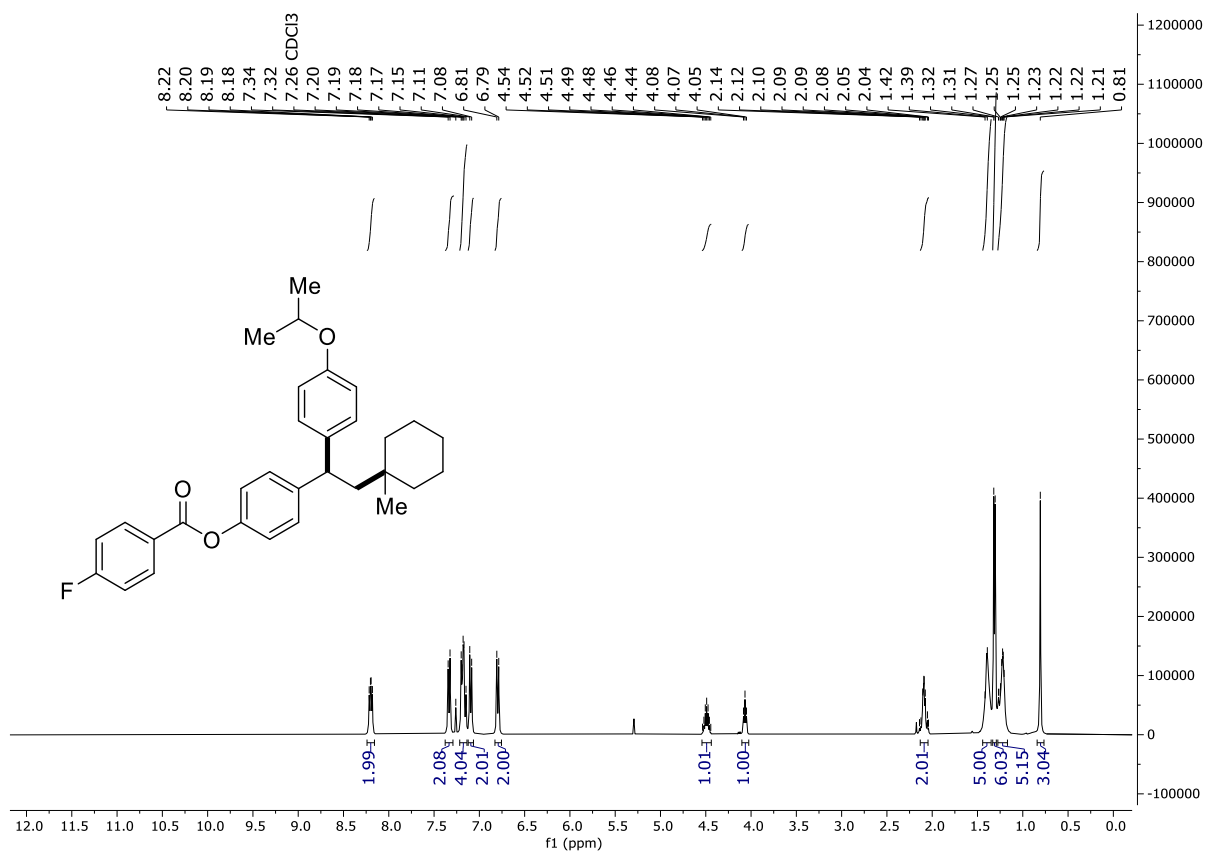




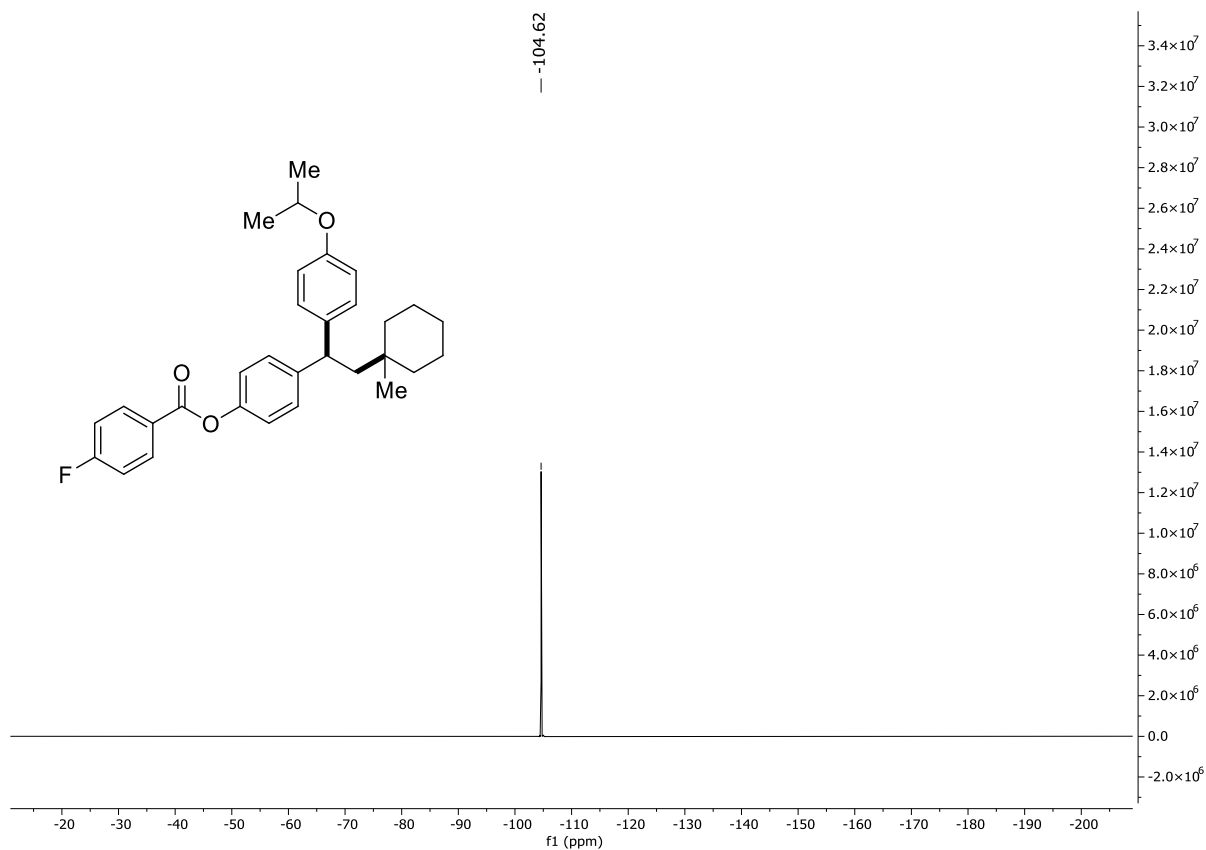
¹H NMR (400 MHz, CDCl₃) spectrum of 4aI



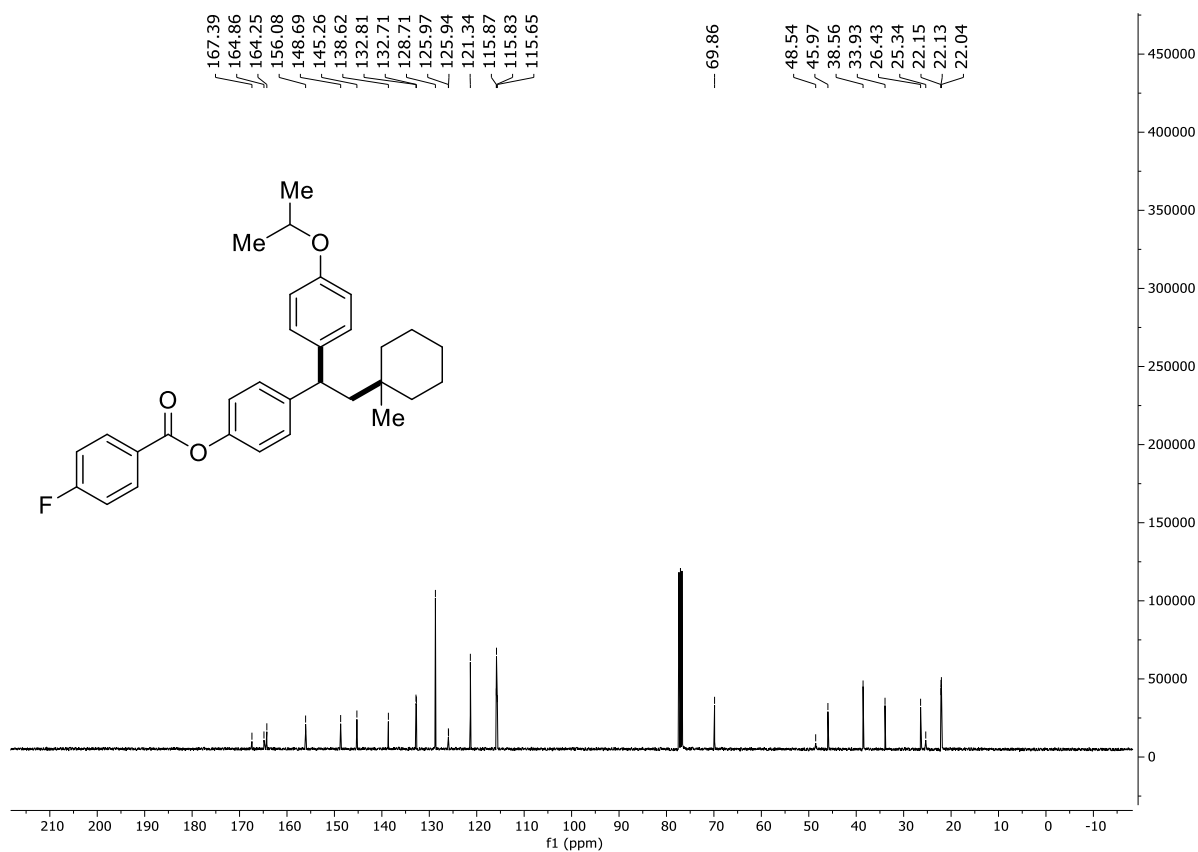
¹³C NMR (101 MHz, CDCl₃) spectrum of 4aI



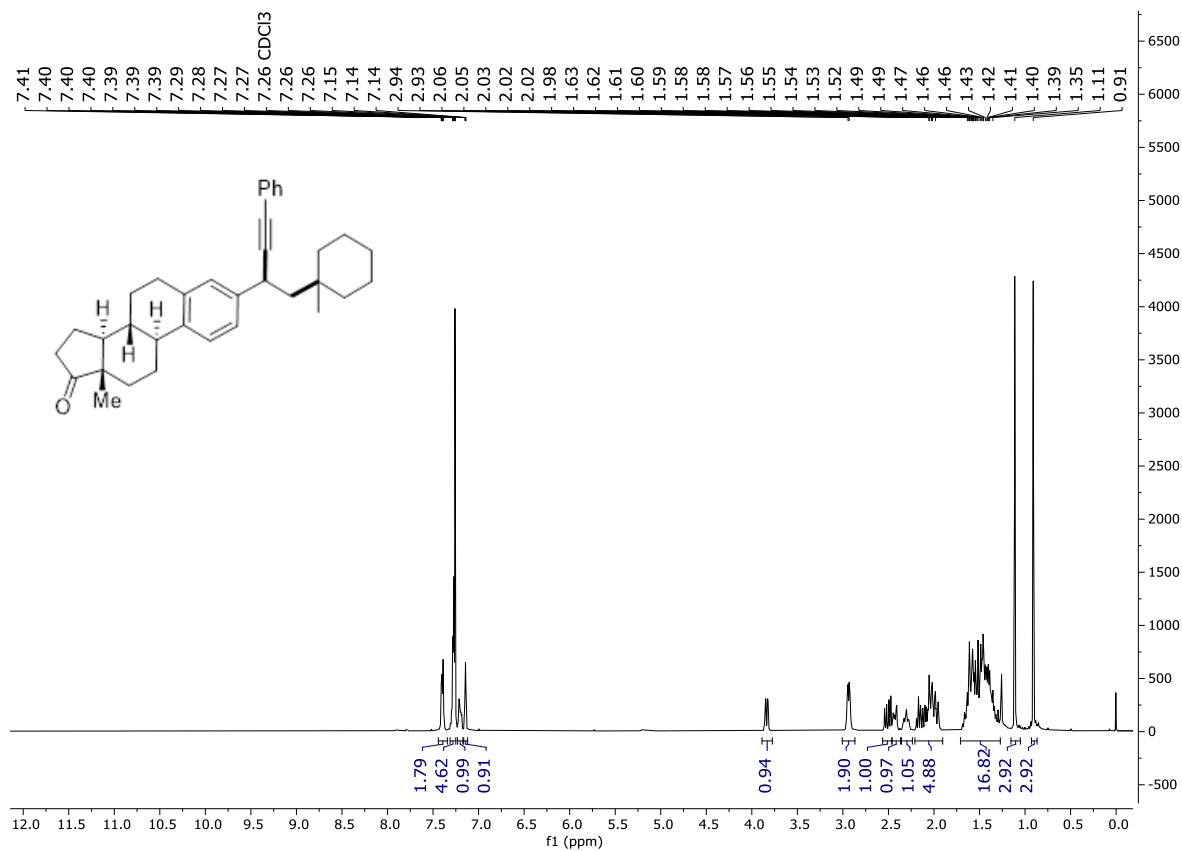
¹H NMR (400 MHz, CDCl₃) spectrum of 4am



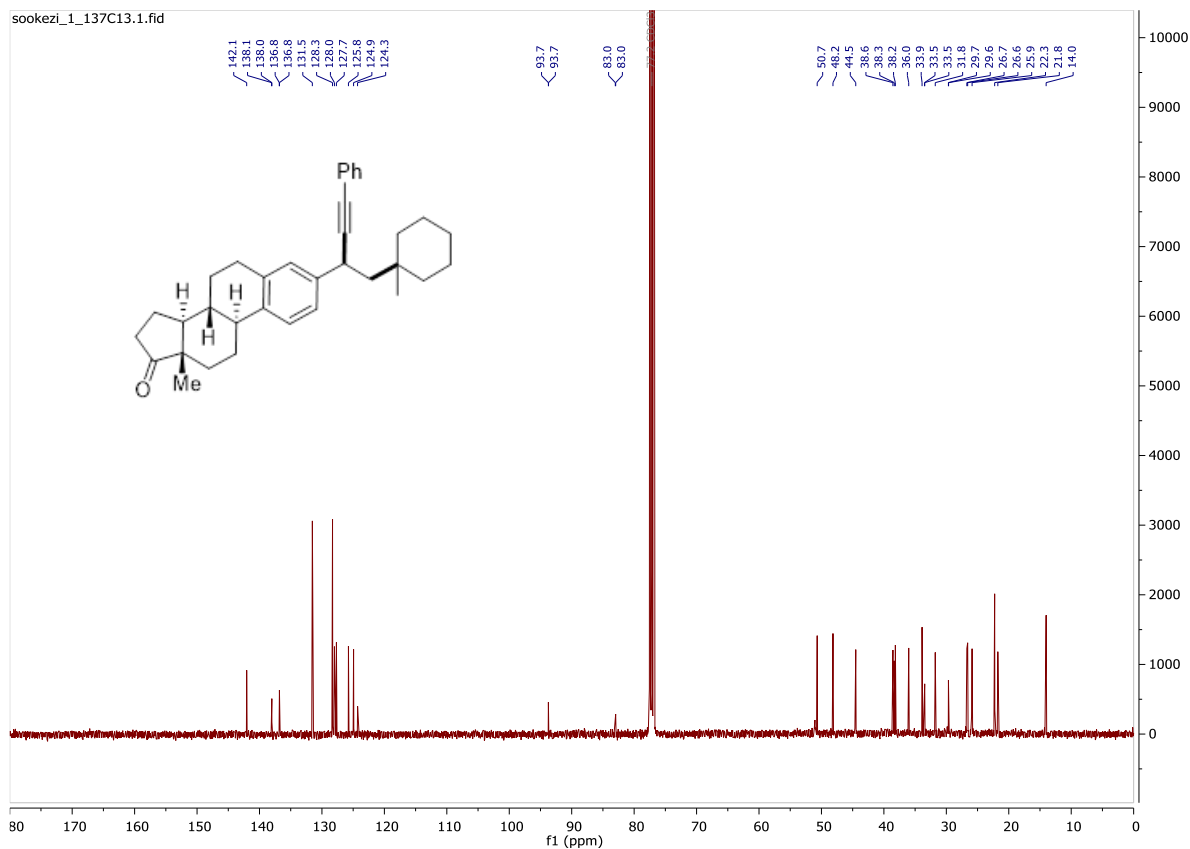
¹⁹F NMR (376 MHz, DMSO) spectrum of 4am



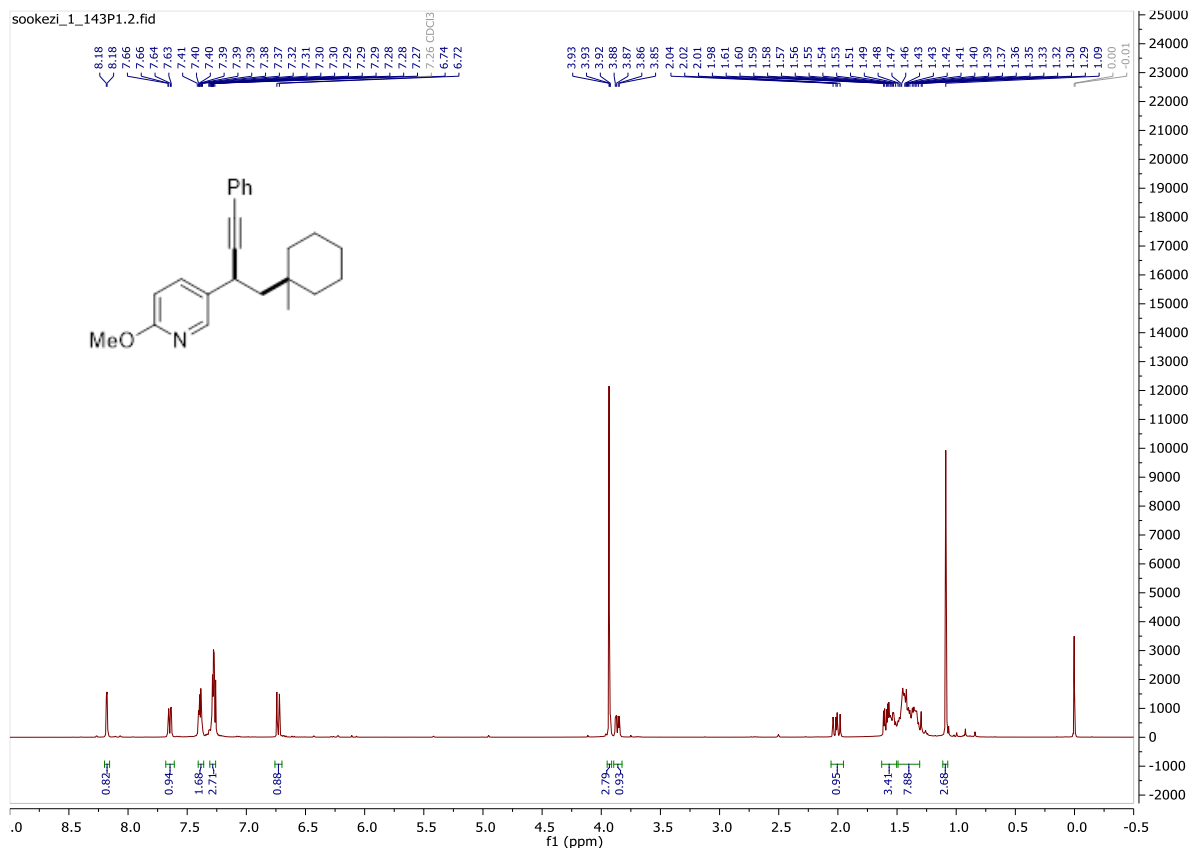
¹³C NMR (101 MHz, CDCl₃) spectrum of 4am



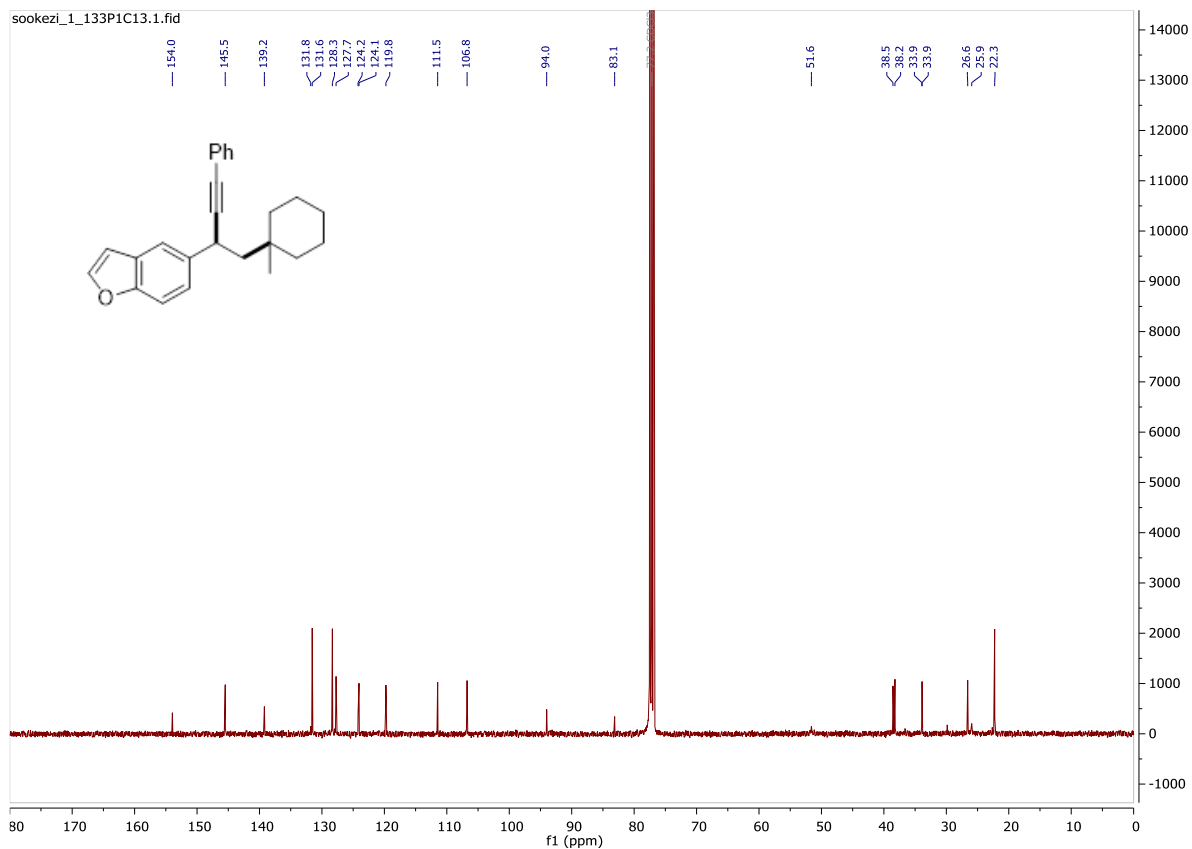
¹H NMR (400 MHz, CDCl₃) spectrum of 4an



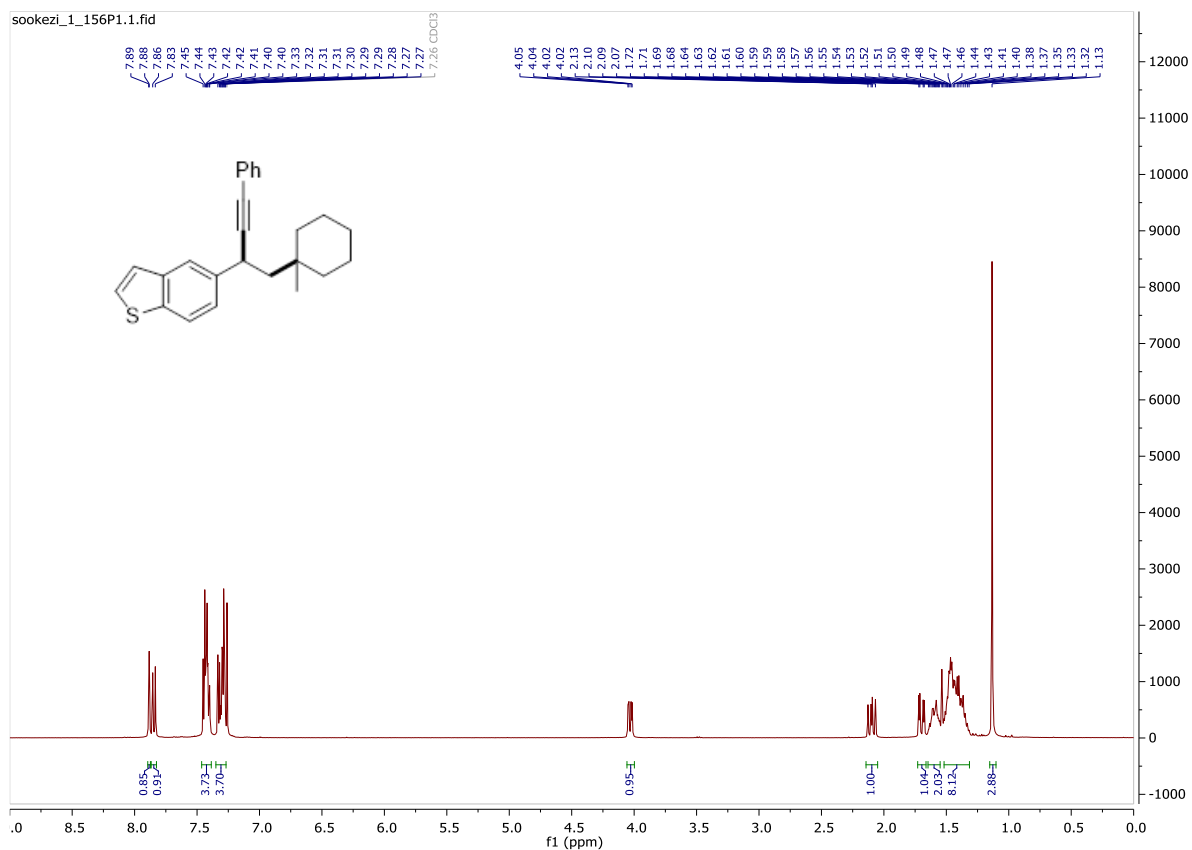
¹³C NMR (101 MHz, CDCl₃) spectrum of 4an



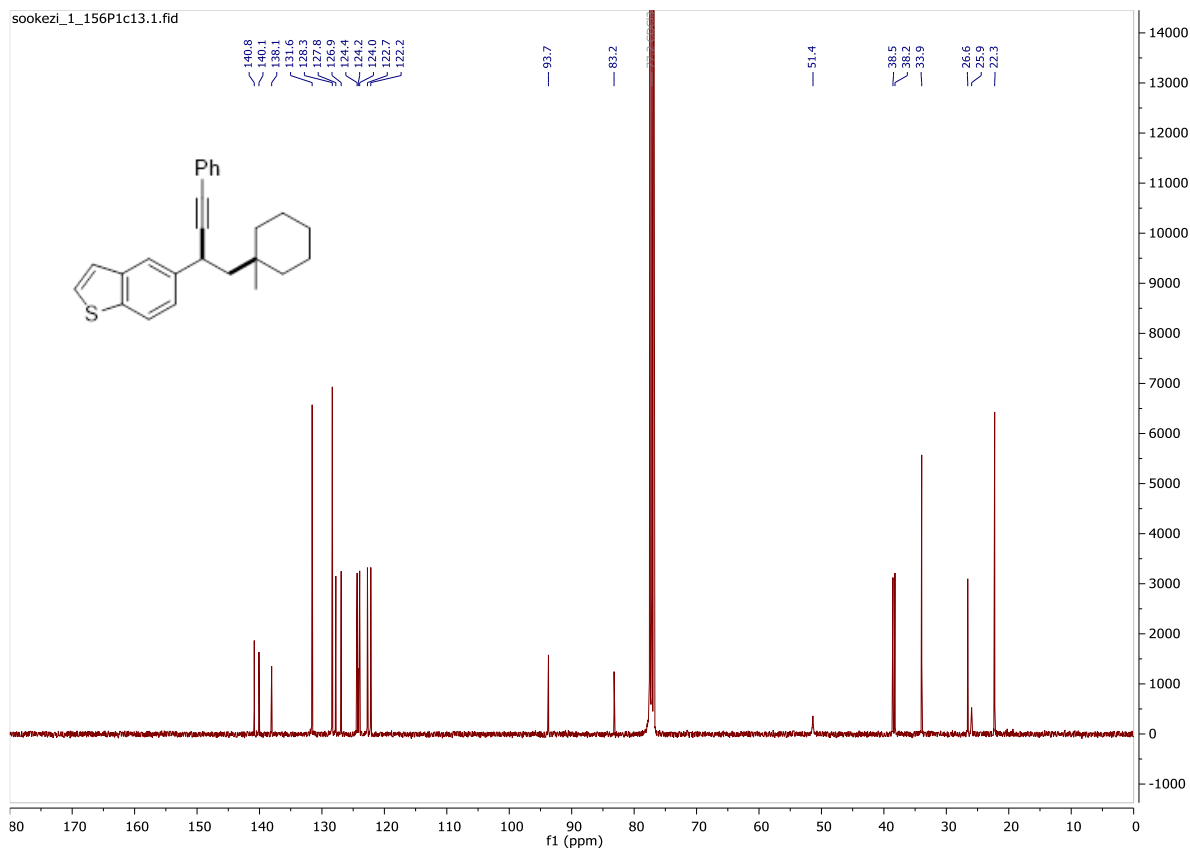
¹H NMR (400 MHz, CDCl₃) spectrum of 4ao



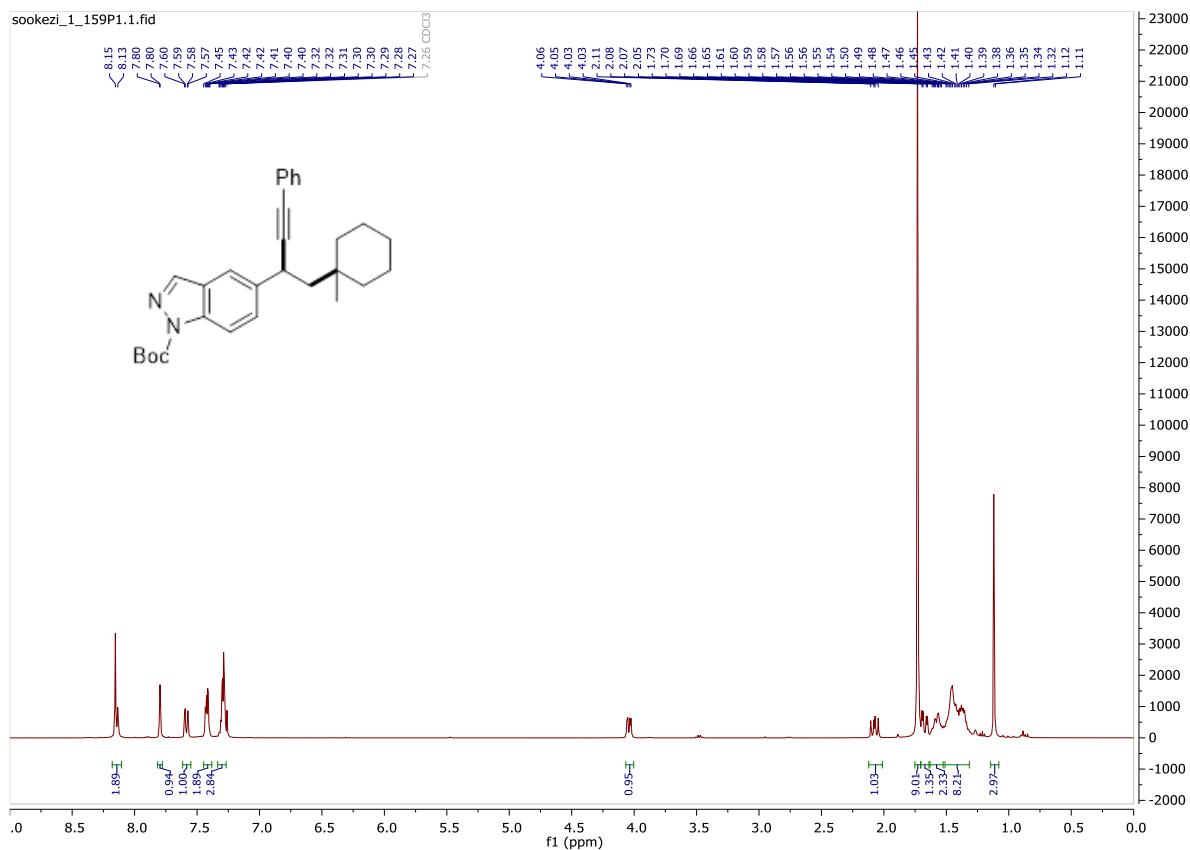
¹³C NMR (101 MHz, CDCl₃) spectrum of 4ap



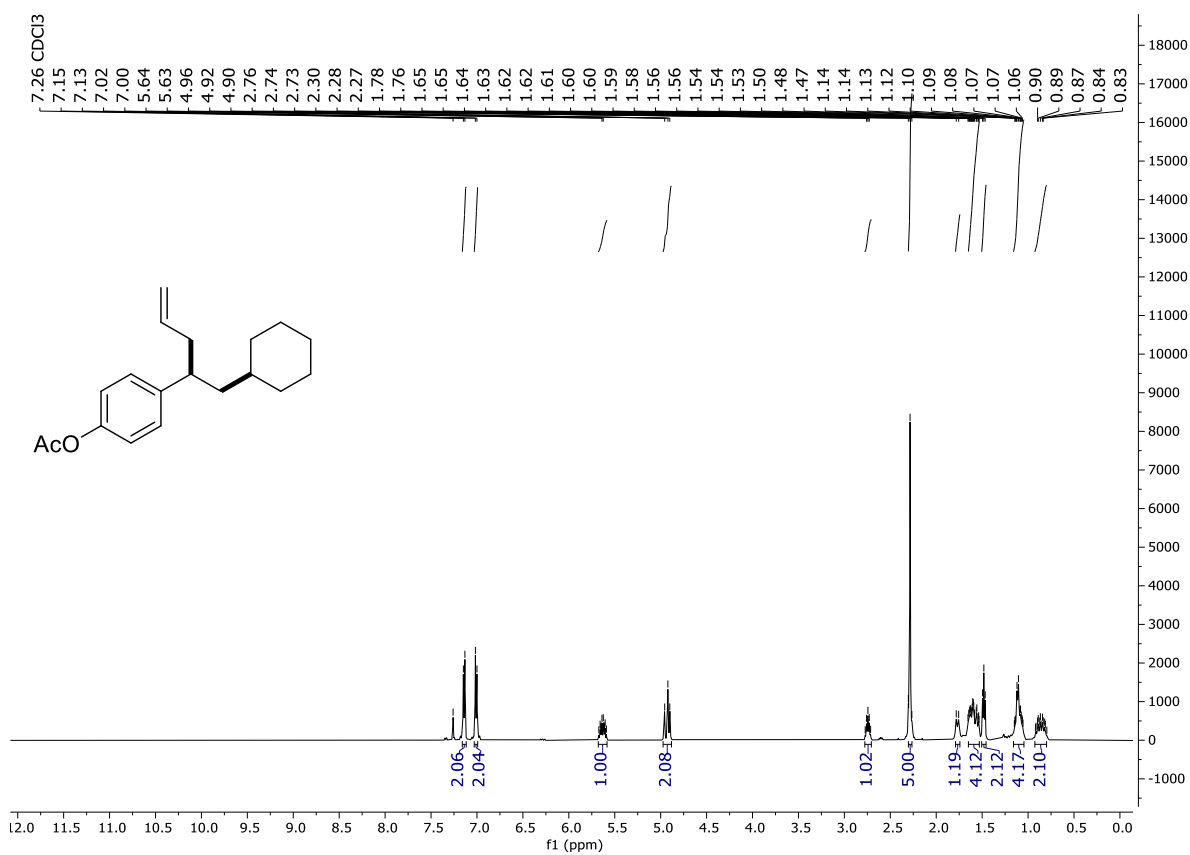
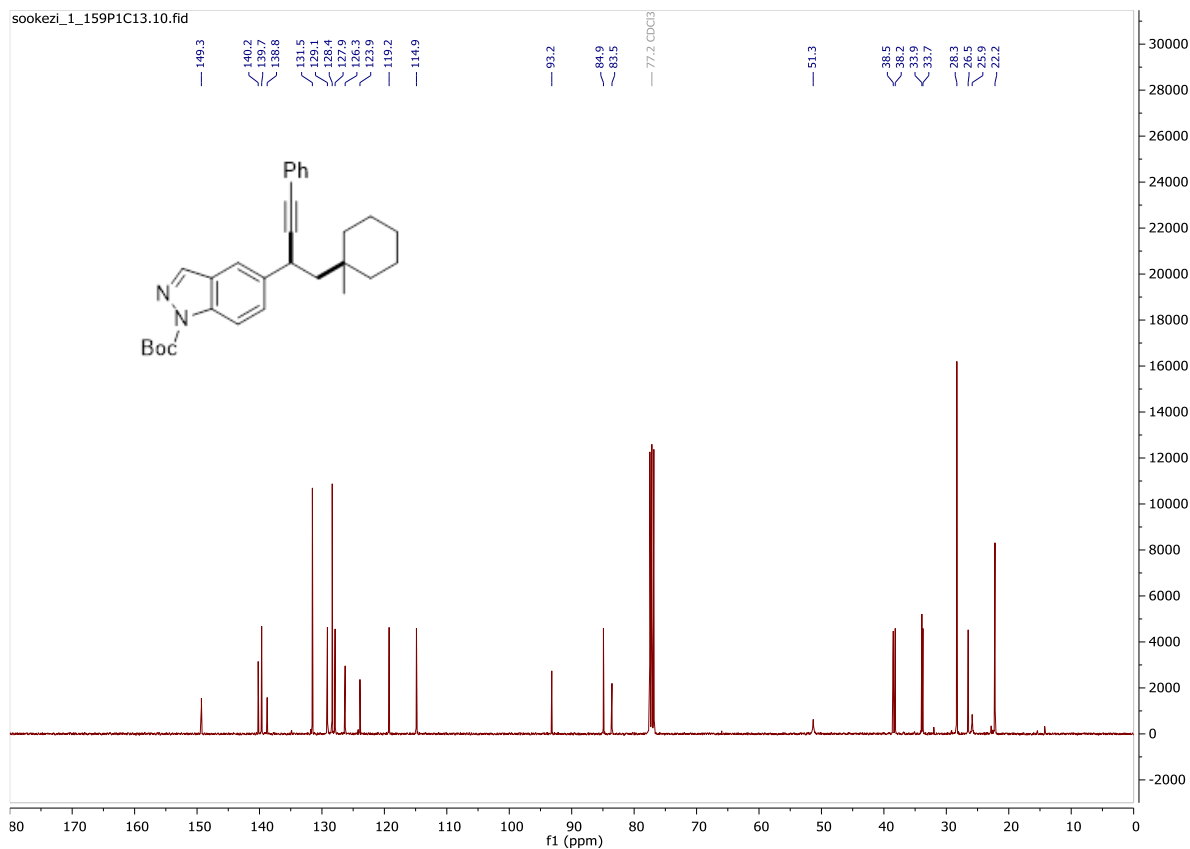
¹H NMR (400 MHz, CDCl₃) spectrum of 4aq

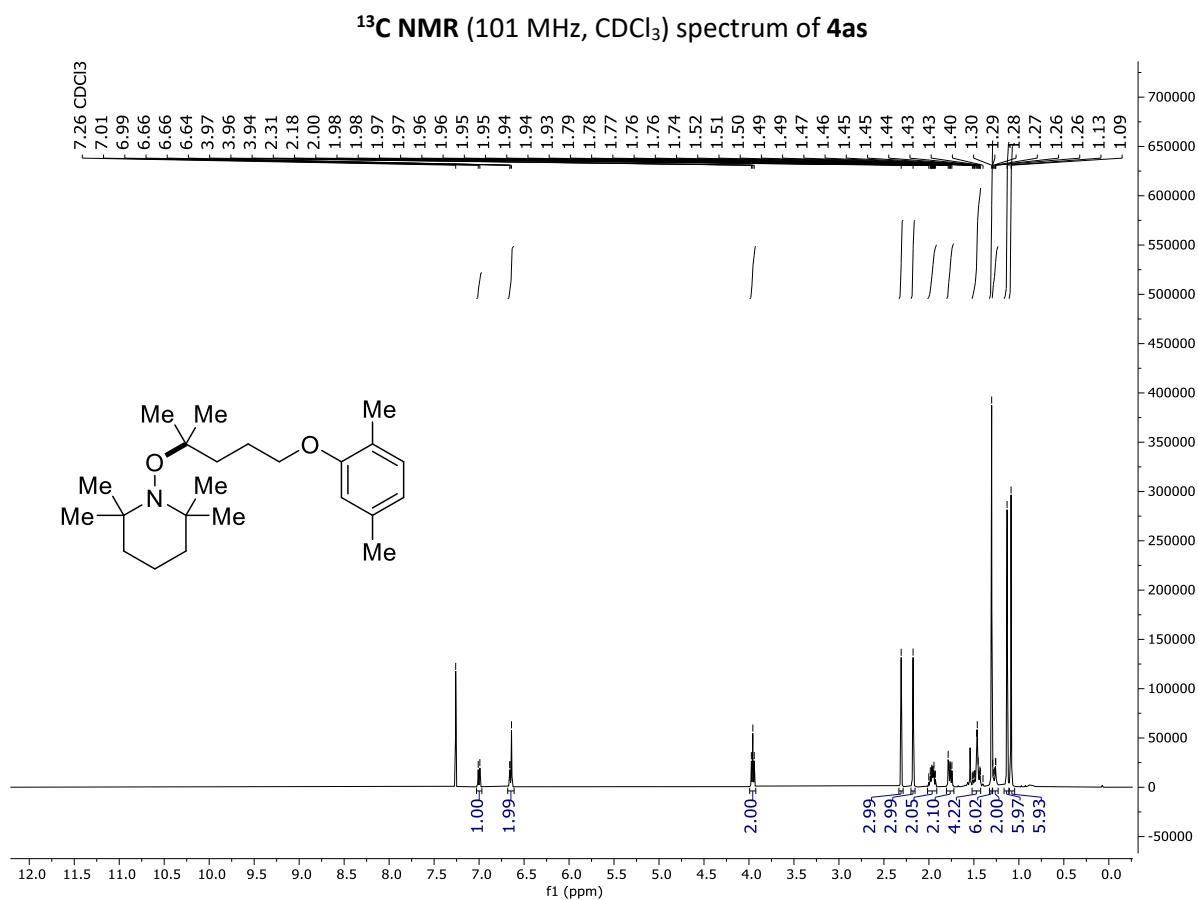
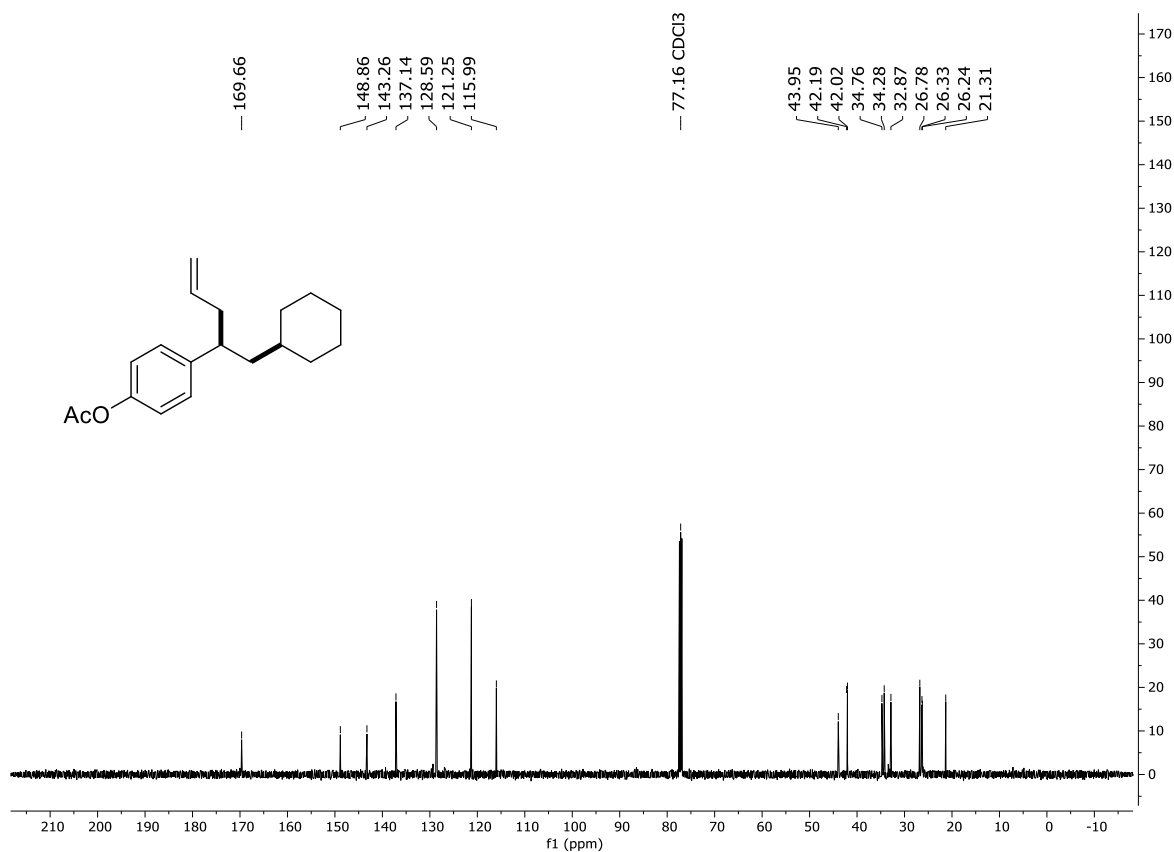


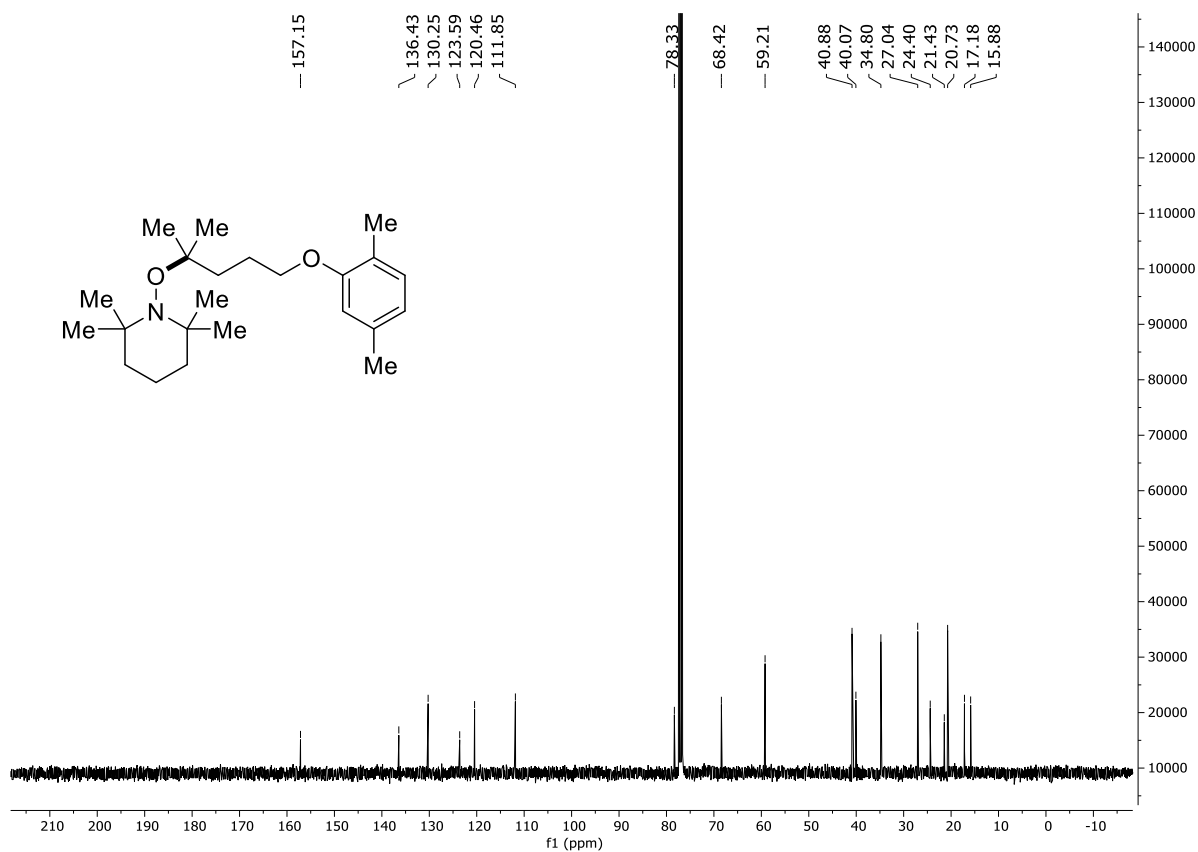
¹³C NMR (101 MHz, CDCl₃) spectrum of **4aq**



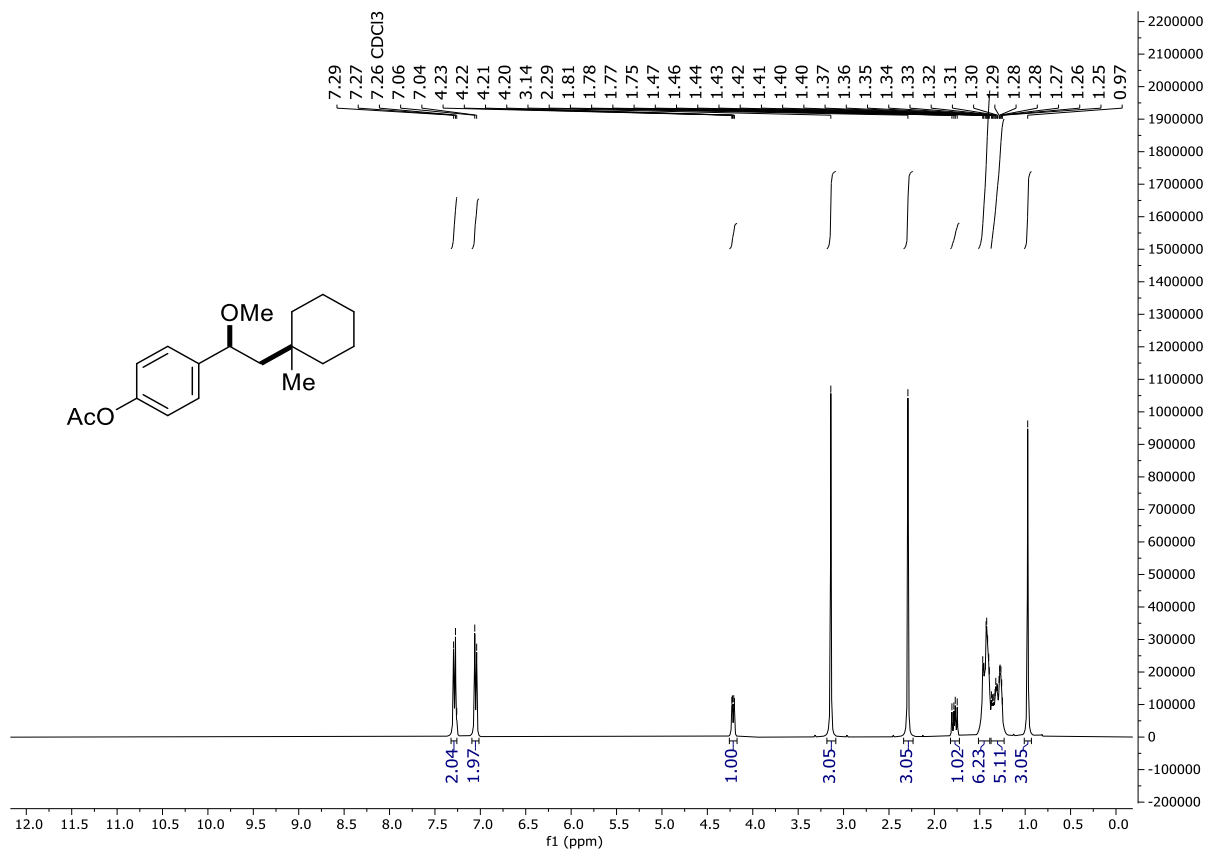
¹H NMR (400 MHz, CDCl₃) spectrum of **4ar**



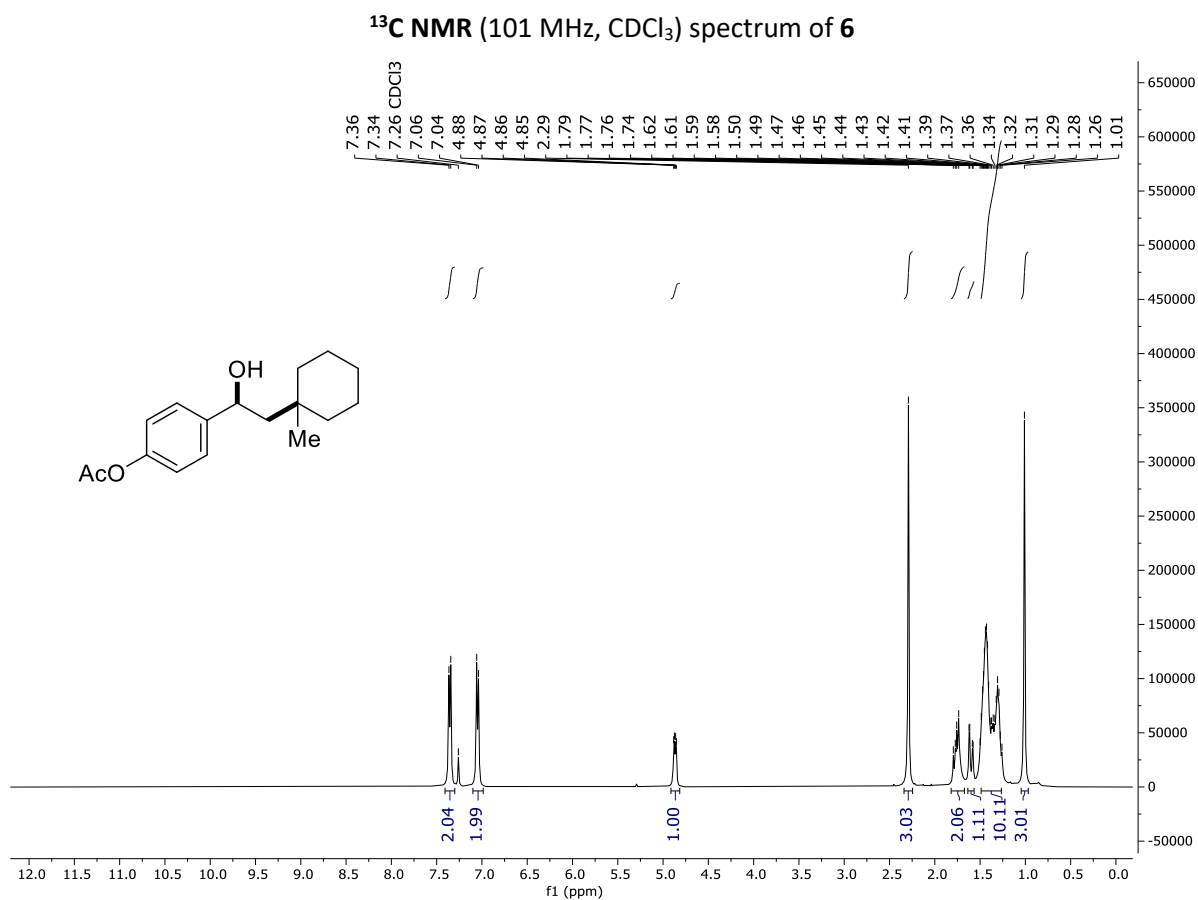
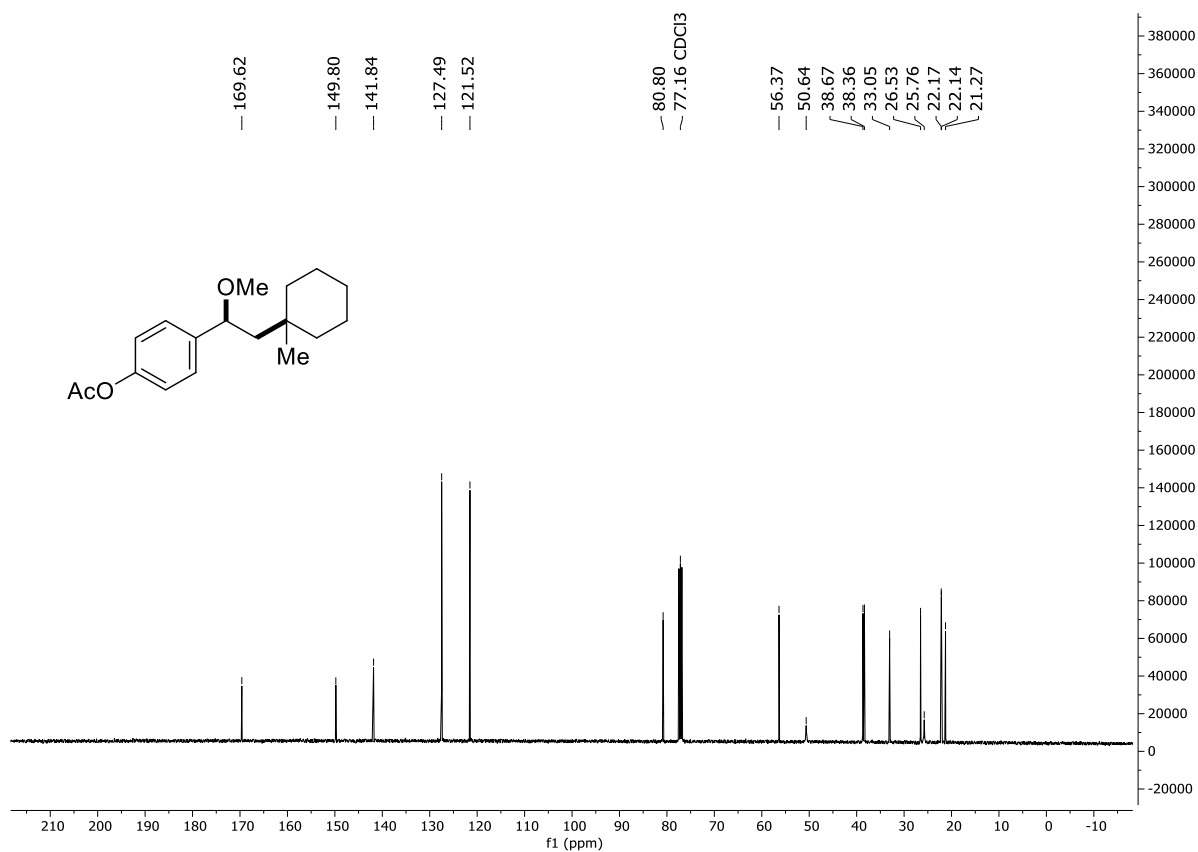


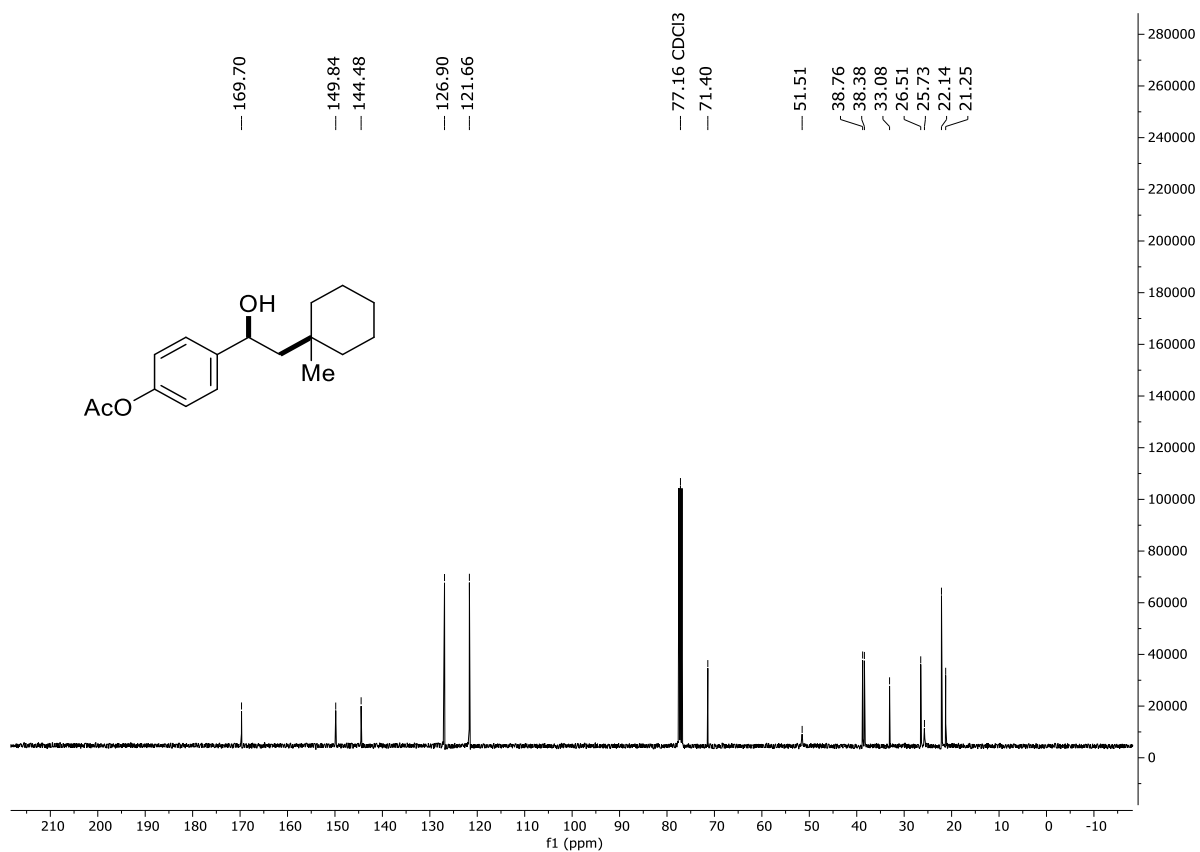


¹³C NMR (101 MHz, CDCl₃) spectrum of 5



¹H NMR (400 MHz, CDCl₃) spectrum of 6





^{13}C NMR (101 MHz, CDCl_3) spectrum of 7

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10. Author Contributions

The project was conceived by Shorouk O. Badir. María Jesús Cabrera-Afonso and Shorouk O. Badir performed Stern-Volmer quenching studies. Mirna El Khatib conducted quantum yield experiments. María Jesús Cabrera-Afonso and Anasheh Sookezian contributed equally. María Jesús Cabrera-Afonso, Anasheh Sookezian, and Shorouk O. Badir carried out extensive optimization studies and performed experiments with input from Gary A. Molander. Shorouk O. Badir, María Jesús Cabrera-Afonso, and Anasheh Sookezian wrote the manuscript with input from Gary A. Molander.