

Supporting Information

For

CO₂ Promoted Photoredox/Ni-Catalyzed Semi-reduction of Alkynes with H₂O

Shenhao Chen^a, Chanjuan Xi^{*a,b}

^aMOE Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology,
Department of Chemistry, Tsinghua University, Beijing 100084, China

^bState Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin
300071, China

Email: cjxi@tsinghua.edu.cn

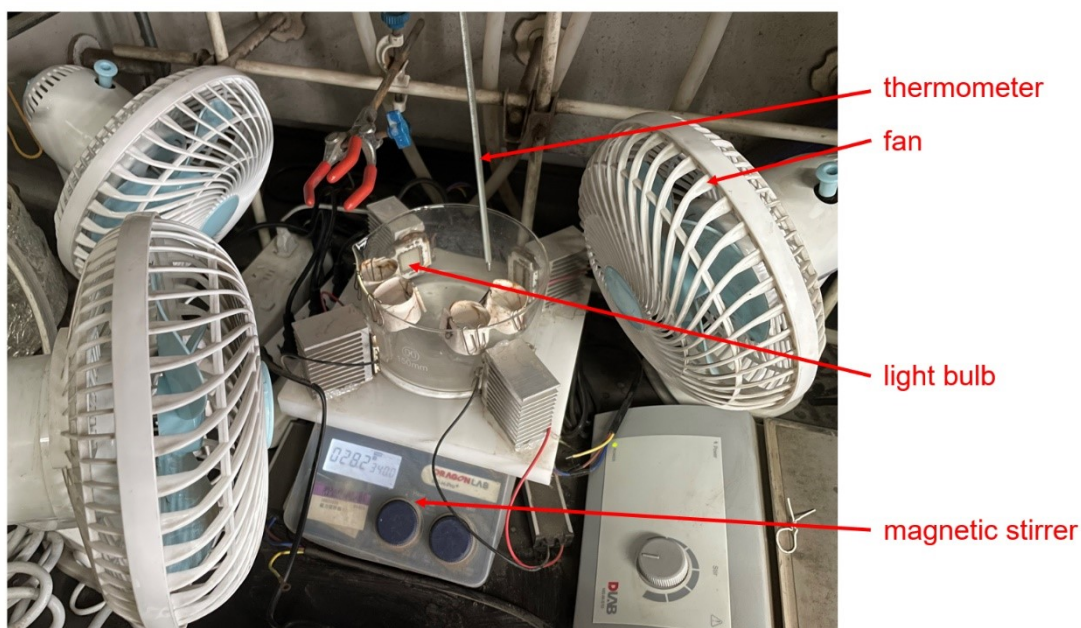
List of the Contents

1. General Information.....	S2
2. General Procedures for Synthesis of Substrates 1.....	S4
3. General Procedures for Synthesis of Products 2.....	S6
4. General Procedures for Mechanism Studies.....	S7
5. Spectral Data for Synthesized Substrates.....	S10
6. Spectral Data for All Products.....	S12
7. References	S18
8. Copies of ¹ H, ¹³ C{ ¹ H}, ¹⁹ F NMR Spectra for Synthesized Compounds	S19

1. General Information

Unless otherwise noted, all the reactions were carried out in oven-dried sealed tube with Teflon-lined-septum under CO₂ atmosphere. Materials were obtained from commercial sources and used as received, or synthesized according to previous literatures. Super dry acetonitrile with molecular sieves was use in the reaction. ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra were recorded on 400 MHz at ambient temperature with CDCl₃ as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of CDCl₃ (7.26), to the carbon resonance of CDCl₃ (77.16). Coupling constants (*J*) were given in Hertz (Hz). The term m, q, t, d, and s referred to multiplet, quartet, triplet, doublet, and singlet. The reaction progress was monitored by GC-MS if applicable. Column chromatography was performed with silica gel (200-300 meshes). Thin layer chromatography (TLC) was visualized using UV light. HRMS analysis was performed on a Shimadzu LCMS-IT/TOF spectrometer.

The photoreactor used in this research was built by our group, which was made up of 4 blue LED bulbs (30 W for each) with 3 cooler fans to keep room temperature. Spectral distribution: 425 nm. In the reaction, each Schlenk tube is mainly irradiated by one of the light bulbs. The approximate distance of the tube to the closest light bulb is 2 cm. A magnetic stirrer is placed under the photoreactor to keep the reaction being stirred.



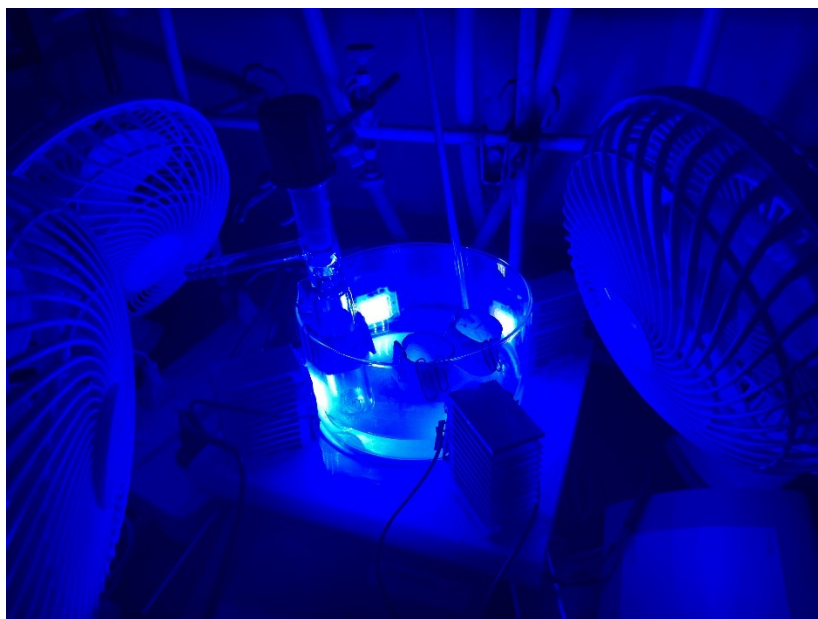
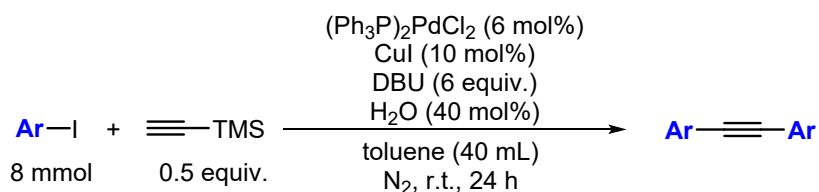
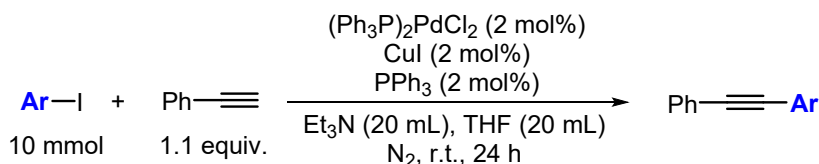


Figure S1 Photos of the photoreactor

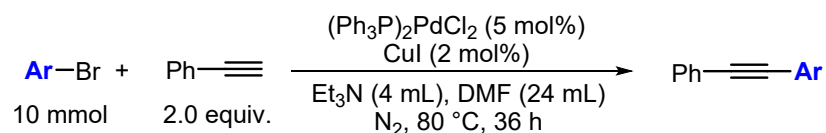
2. General Procedures for Synthesis of Substrates 1:



General procedures for synthesis of substrates 2c, 2f: A sealed tube equipped with a stirrer bar was charged with aryl iodide (8 mmol, 1.0 equiv.), $(\text{PPh}_3)_2\text{PdCl}_2$ (0.168 g, 6.0 mol%), CuI (0.152 mg, 10 mol%), then degassed and refilled with N_2 for 3 times. Subsequently, toluene (40 mL), trimethylsilylacetylene (0.393 g, 0.5 equiv.), DBU (7.307 g, 6.0 equiv.), H_2O (58.0 mg, 40 mol%) were added under N_2 . The reaction mixture was stirred at room temperature for 24 hours. After removing toluene in vacuo, the mixture was quenched with 50 mL H_2O and the aqueous layer was extracted with 30 mL trichloromethane (CHCl_3) for three times. The combined organic layer was successively washed with 20 mL 10% HCl for 3 times, and 20 mL brine for 1 time, then dried by Na_2SO_4 and concentrated in vacuo. The residue was purified by chromatography on silica gel to give products **2c** and **2f**, which were identified by ^1H and ^{13}C NMR.

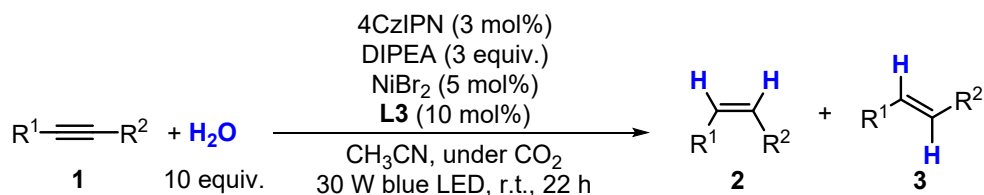


General procedures for synthesis of substrates 2d, 2j: A sealed tube equipped with a stirrer bar was charged with aryl iodide (10 mmol, 1.0 equiv.), $(\text{PPh}_3)_2\text{PdCl}_2$ (140.4 mg, 2.0 mol%), CuI (38.1 mg, 2 mol%), PPh_3 (52.5 mg, 2 mol%), then degassed and refilled with N_2 for 3 times. Subsequently, dry THF (20 mL), Et_3N (20 mL) and phenylacetylene (1.123 g, 1.1 equiv.) were added under N_2 . The reaction mixture was stirred at room temperature for 36 hours, then quenched with 50 mL H_2O , and the aqueous layer was extracted with 30 mL trichloromethane (CHCl_3) for three times. The combined organic layer was dried by Na_2SO_4 and concentrated in vacuo. The residue was purified by chromatography on silica gel to give products **2d** and **2j**, which were identified by ^1H and ^{13}C NMR.



General procedures for synthesis of substrate 2h: A sealed tube equipped with a stirrer bar was charged with aryl bromine (10 mmol, 1.0 equiv.), (PPh₃)₂PdCl₂ (351.0 mg, 5.0 mol%), CuI (38.1 mg, 2 mol%), then degassed and refilled with N₂ for 3 times. Subsequently, dry DMF (24 mL), Et₃N (4 mL) and phenylacetylene (2.042 g, 2.0 equiv.) were added under N₂. The reaction mixture was stirred at 80 °C for 36 hours, then quenched with 50 mL H₂O, and the aqueous layer was extracted with 30 mL trichloromethane (CHCl₃) for three times. The combined organic layer was dried by Na₂SO₄ and concentrated in vacuo. The residue was purified by chromatography on silica gel to give products **2h**, which was identified by ¹H and ¹³C NMR.

3. General Procedures for Synthesis of Products 2:

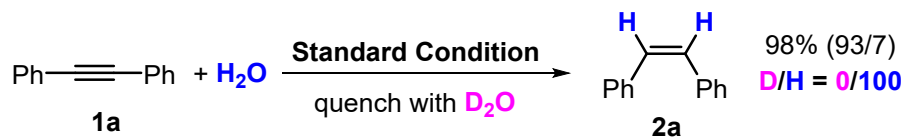


General procedures for synthesis of products 2a-2p (internal alkenes): A sealed tube equipped with a stirrer bar was charged with 4CzIPN (4.7 mg, 3.0 mol%), 4,4'-*tert*-butyl-2,2'-bipyridine **L3** (5.4 mg, 10 mol%), NiBr₂ (from the glove box, 2.2 mg, 5 mol%), then degassed and refilled with CO₂ for 3 times. After that, anhydrous CH₃CN (3 mL) was added under CO₂. The mixture was bubbled with CO₂ for 5 minutes, then DIPEA (25.8 mg, 1.0 equiv.), H₂O (36.0 mg, 10 equiv.) and alkyne **1** (0.2 mmol) were added under CO₂. The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 22 hours, then cooled down to 10 °C and irradiated for another 30 minutes. The reaction was quenched with 10 mL H₂O and the aqueous layer was extracted with 6 mL dichloromethane (CH₂Cl₂) for three times. The combined organic layer was dried by Na₂SO₄ and concentrated in vacuo. The residue was purified by chromatography on silica gel to give products **2a-2q**, which were identified by ¹H, ¹³C, and ¹⁹F NMR.

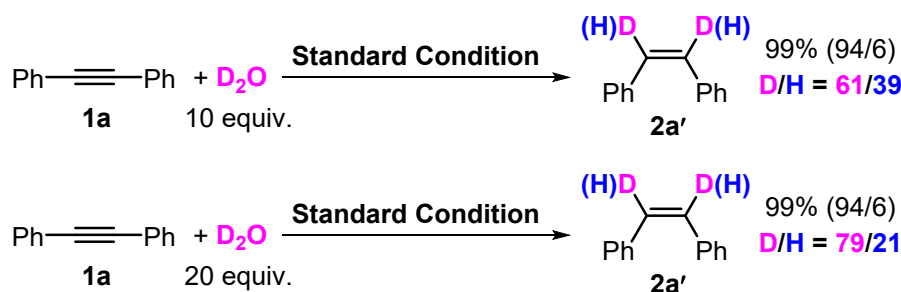
General procedures for synthesis of products 2q-2s (terminal alkenes): A sealed tube equipped with a stirrer bar was charged with 4CzIPN (4.7 mg, 3.0 mol%), 4,4'-*tert*-butyl-2,2'-bipyridine **L3** (5.4 mg, 10 mol%), NiBr₂ (from the glove box, 2.2 mg, 5 mol%), then degassed and refilled with CO₂ for 3 times. After that, anhydrous CH₃CN (3 mL) was added under CO₂. The mixture was bubbled with CO₂ for 5 minutes, then DIPEA (25.8 mg, 1.0 equiv.), H₂O (36.0 mg, 10 equiv.) and alkyne **1** (0.2 mmol) were added under CO₂. The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 22 hours, then quenched with 10 mL H₂O. The aqueous layer was extracted with 6 mL dichloromethane (CH₂Cl₂) for three times. The combined organic layer was dried by Na₂SO₄ and concentrated in vacuo. The residue was purified by chromatography on silica gel to give products **2q-2s** which were identified by ¹H and ¹³C NMR.

4. General Procedures for Mechanism Studies

4.1 Deuterium-labelled experiments



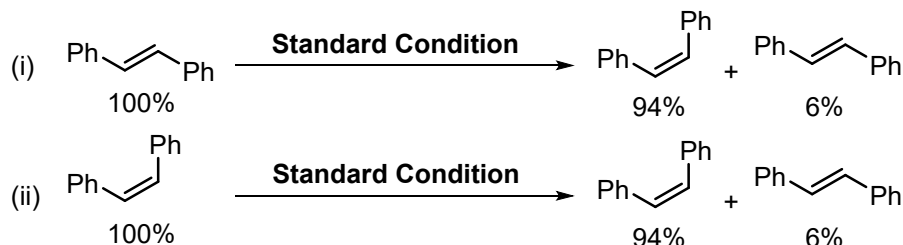
A sealed tube equipped with a stirrer bar was charged with 4CzIPN (4.7 mg, 3.0 mol%), 4,4'-di-*tert*-butyl-2,2'-bipyridine **L3** (5.4 mg, 10 mol%), NiBr₂ (from the glove box, 2.2 mg, 5 mol%), then degassed and refilled with CO₂ for 3 times. After that, anhydrous CH₃CN (3 mL) was added under CO₂. The mixture was bubbled with CO₂ for 5 minutes, then DIPEA (25.8 mg, 1.0 equiv.), H₂O (36.0 mg, 10 equiv.) and alkyne **1a** (0.2 mmol) were added under CO₂. The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 22 hours, then cooled down to 10 °C and irradiated for another 30 minutes. The reaction was quenched with 10 mL D₂O and the aqueous layer was extracted with 6 mL dichloromethane (CH₂Cl₂) for three times. The combined organic layer was dried by Na₂SO₄ and concentrated in vacuo. The residue was tested by ¹H NMR to determine the deuterium ratio.



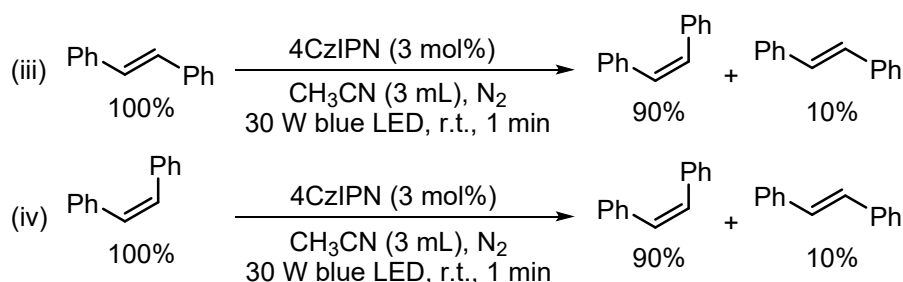
A sealed tube equipped with a stirrer bar was charged with 4CzIPN (4.7 mg, 3.0 mol%), 4,4'-di-*tert*-butyl-2,2'-bipyridine **L3** (5.4 mg, 10 mol%), NiBr₂ (from the glove box, 2.2 mg, 5 mol%), then degassed and refilled with CO₂ for 3 times. After that, anhydrous CH₃CN (3 mL) was added under CO₂. The mixture was bubbled with CO₂ for 5 minutes, then DIPEA (25.8 mg, 1.0 equiv.), D₂O (36.0 mg / 72.0 mg, 10 equiv. / 20 equiv.) and alkyne **1a** (0.2 mmol) were added under CO₂. The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 22 hours, then cooled down to 10 °C and irradiated for another 30 minutes. The reaction was quenched with 10 mL H₂O and the aqueous layer was extracted with 6 mL dichloromethane (CH₂Cl₂) for

three times. The combined organic layer was dried by Na₂SO₄ and concentrated in vacuo. The residue was tested by ¹H NMR to determine the deuterium ratio.

4.2 Isomerization experiments



A sealed tube equipped with a stirrer bar was charged with 4CzIPN (4.7 mg, 3.0 mol%), 4,4'-di-*tert*-butyl-2,2'-bipyridine **L3** (5.4 mg, 10 mol%), NiBr₂ (from the glove box, 2.2 mg, 5 mol%), then degassed and refilled with CO₂ for 3 times. After that, anhydrous CH₃CN (3 mL) was added under CO₂. The mixture was bubbled with CO₂ for 5 minutes, then DIPEA (25.8 mg, 1.0 equiv.), H₂O (36.0 mg, 10 equiv.) and alkene **2a** or **3a** (0.2 mmol) were added under CO₂. The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 22 hours, then quenched with 10 mL H₂O. The aqueous layer was extracted with 6 mL dichloromethane (CH₂Cl₂) for three times. The combined organic layer was dried by Na₂SO₄ and concentrated in vacuo. The residue was tested by ¹H NMR to determine the *Z/E* ratio.

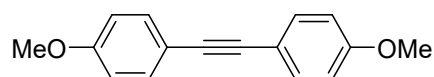


A sealed tube equipped with a stirrer bar was charged with 4CzIPN (4.7 mg, 3.0 mol%), then degassed and refilled with N₂ for 3 times. After that, anhydrous CH₃CN (3 mL) was added under N₂. Subsequently, alkene **2a** or **3a** (0.2 mmol) was added under N₂. The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 1 minute, then concentrated in vacuo. The residue was tested by ¹H NMR to determine the *Z/E* ratio.

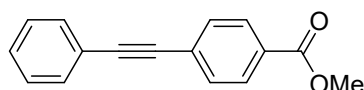


A sealed tube equipped with a stirrer bar was degassed and refilled with N_2 for 3 times. After that, anhydrous CH_3CN (3 mL) was added under N_2 . Subsequently, alkene **2a** or **3a** (0.2 mmol) was added under N_2 . The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 22 hours, then concentrated in vacuo. The residue was tested by 1H NMR to determine the *Z/E* ratio.

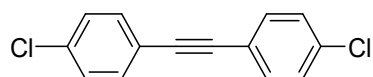
5. Spectra Data for Synthesized Substrates



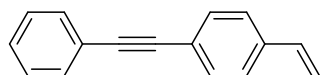
1,2-Bis(4-methoxyphenyl)ethyne (1c): ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.48 – 7.41 (m, 4H), 6.90 – 6.83 (m, 4H), 3.81 (s, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 159.5, 133.0, 115.8, 114.1, 88.1, 55.4. The spectroscopic data corresponds to the reported data.¹



Methyl 4-(phenylethynyl)benzoate (1d): ^1H NMR (400 MHz, CHLOROFORM-D) δ 8.01 (d, J = 8.4 Hz, 2H), 7.60 – 7.51 (m, 4H), 7.38 – 7.32 (m, 3H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 166.5, 131.8, 131.5, 129.6, 129.5, 128.8, 128.5, 128.0, 122.8, 92.4, 88.7, 52.2. The spectroscopic data corresponds to the reported data.²

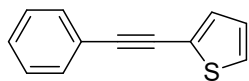


1,2-Bis(4-chlorophenyl)ethyne (1f): ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.44 (d, J = 8.4 Hz, 4H), 7.32 (d, J = 8.4 Hz, 4H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 134.7, 133.0, 128.9, 121.6, 89.3. The spectroscopic data corresponds to the reported data.¹



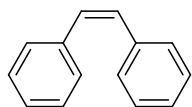
1-(Phenylethynyl)-4-vinylbenzene (1h): ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.57 – 7.52 (m, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 7.37 – 7.32 (m, 3H), 6.72 (dd, J = 17.6, 10.9 Hz, 1H), 5.79 (d, J = 17.6 Hz, 1H), 5.30 (d, J = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 137.6, 136.4, 131.9, 131.7, 128.5,

128.4, 126.3, 123.4, 122.7, 114.9, 90.2, 89.6. The spectroscopic data corresponds to the reported data.³

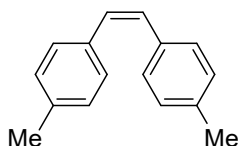


2-(Phenylethynyl)thiophene (1j): ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.52 – 7.50 (m, 2H), 7.36 – 7.32 (m, 3H), 7.28 – 7.27 (m, 2H), 7.02 – 6.98 (m, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 132.6, 132.0, 131.5, 129.3, 128.5, 128.5, 127.4, 127.2, 123.4, 123.1, 93.2, 82.7. The spectroscopic data corresponds to the reported data.⁴

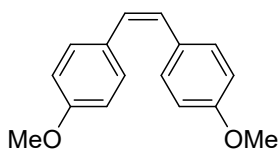
6. Spectral Data for All Products



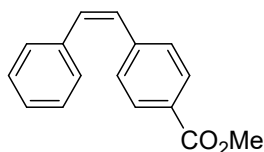
(Z)-1,2-Diphenylethene (2a): colorless liquid (33.5 mg, 99%, *Z/E*: 94/6). Eluent for the flash chromatography with silica gel: hexane. ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.27 – 7.20 (m, 10H), 6.62 (s, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 137.4, 130.4, 129.0, 128.4, 127.2. The spectroscopic data corresponds to the reported data.⁵



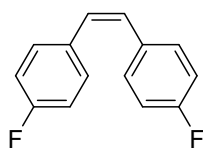
(Z)-4,4'-Dimethylstilbene (2b): colorless liquid (33.9 mg, 97%, *Z/E*: 84/16). Eluent for the flash chromatography with silica gel: hexane. ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.21 (d, $J = 8.0$ Hz, 4H), 7.08 (d, $J = 7.9$ Hz, 4H), 6.56 (s, 2H), 2.36 (s, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 136.8, 134.7, 129.7, 129.0, 128.9, 21.4. The spectroscopic data corresponds to the reported data.⁵



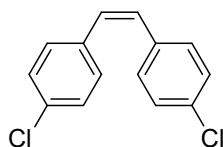
(Z)-4,4'-Dimethoxystilbene (2c): colorless liquid (25.2 mg, 99%, *Z/E*: 53/47). Eluent for the flash chromatography with silica gel: hexane / ethyl acetate (EA): 40/1. ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.24 – 7.18 (m, 4H), 6.80 – 6.75 (m, 4H), 6.45 (s, 2H), 3.79 (s, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 158.6, 130.2, 130.1, 128.5, 113.7, 55.3. The spectroscopic data corresponds to the reported data.⁵



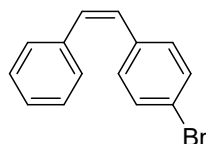
(Z)-4-Carbomethoxystilbene (2d): colorless liquid (40.2 mg, 98%, *Z/E*: 86/14). Eluent for the flash chromatography with silica gel: hexane/EA: 60/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.20 (m, 5H), 6.73 – 6.57 (m, 2H), 3.89 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 167.0, 142.2, 136.8, 132.3, 129.6, 129.3, 129.0, 128.7, 128.4, 127.6, 52.1. The spectroscopic data corresponds to the reported data.⁵



(Z)-4,4'-Difluorostilbene (2e): colorless liquid (40.3 mg, 97%, *Z/E*: 96/4). Eluent for the flash chromatography with silica gel: hexane. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.21 – 7.16 (m, 4H), 6.97 – 6.88 (m, 4H), 6.54 (s, 2H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 162.0 (d, *J* = 247.4 Hz), 133.1 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 7.1 Hz), 129.2, 115.4 (d, *J* = 22.2 Hz). ¹⁹F NMR (376 MHz, CHLOROFORM-D) δ -114.4 – -114.3 (m). The spectroscopic data corresponds to the reported data.⁵

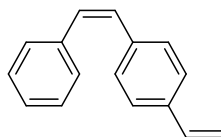


(Z)-4,4'-Dichlorostilbene (2f): colorless liquid (38.5 mg, 85%, *Z/E*: 91/9). Eluent for the flash chromatography with silica gel: hexane. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.21 – 7.19 (m, 4H), 7.15 – 7.13 (m, 4H), 6.55 (s, 2H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 135.4, 133.1, 130.2, 129.7, 128.7. The spectroscopic data corresponds to the reported data.⁶

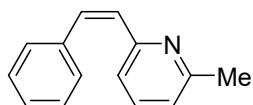


(Z)-1-(4-Bromidephenyl)-2-phenylethene (2g): colorless liquid (21.2 mg, 43%, *Z/E*: 95/5). Eluent for the flash chromatography with silica gel: hexane. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.36 – 7.32 (m, 2H), 7.24 – 7.21 (m, 5H), 7.12 – 7.09 (m, 2H),

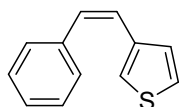
6.64 (d, $J = 12.4$ Hz, 1H), 6.50 (d, $J = 12.4$ Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 137.0, 136.2, 131.5, 131.2, 130.7, 129.1, 128.9, 128.5, 127.2, 121.1. The spectroscopic data corresponds to the reported data.⁷



1-Ethenyl-4-[(1Z)-2-phenylethenyl]benzene (2h): colorless liquid (30.0 mg, 97%, *Z/E*: 75/25). Eluent for the flash chromatography with silica gel: hexane. ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.33 – 7.21 (m, 9H), 6.70 (dd, $J = 17.6, 10.9$ Hz, 1H), 6.66 – 6.57 (m, 2H), 5.75 (d, $J = 17.5$ Hz, 1H), 5.25 (d, $J = 10.9$ Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 137.4, 136.9, 136.6, 136.5, 130.5, 130.0, 129.2, 129.0, 128.4, 127.3, 126.2, 113.8. The spectroscopic data corresponds to the reported data.⁸

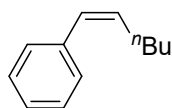


2-Methyl-6-[(1Z)-2-phenylethenyl]pyridine (2i): colorless liquid (34.4 mg, 88%, *Z/E*: 99/1). Eluent for the flash chromatography with silica gel: hexane/EA/Et₃N: 100/3.3/1. ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.61 – 7.56 (m, 3H), 7.52 (t, $J = 7.7$ Hz, 1H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.28 (t, $J = 7.3$ Hz, 1H), 7.22 (d, $J = 7.8$ Hz, 1H), 7.17 (d, $J = 16.2$ Hz, 1H), 7.00 (d, $J = 7.6$ Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 158.4, 155.2, 136.9, 136.7, 132.4, 128.8, 128.5, 128.2, 127.2, 121.8, 118.9, 24.8. The spectroscopic data corresponds to the reported data.⁹

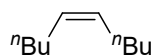


1-Ethenyl-4-[(1Z)-2-phenylethenyl]benzene (2j): colorless liquid (24.8 mg, 90%, *Z/E*: 74/26). Eluent for the flash chromatography with silica gel: hexane. ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.39 – 7.28 (m, 5H), 7.09 (d, $J = 5.1$ Hz, 1H), 6.97 (d, $J = 3.5$ Hz, 1H), 6.89 (dd, $J = 5.0, 3.7$ Hz, 1H), 6.70 (d, $J = 12.2$, 1H), 6.58 (d, $J = 12.1$,

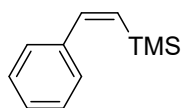
1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 139.9, 137.5, 129.0, 129.0, 128.7, 128.3, 127.7, 126.6, 125.6, 123.5. The spectroscopic data corresponds to the reported data.⁵



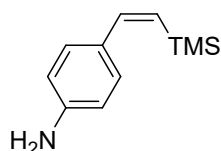
(Z)-1-Hexen-1-ylbenzene (2k): colorless liquid (27.2 mg, 85%, *Z/E*: 99/1). Eluent for the flash chromatography with silica gel: hexane. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.38 – 7.29 (m, 4H), 7.26 – 7.21 (m, 1H), 6.43 (d, *J* = 11.7 Hz, 1H), 5.69 (dt, *J* = 11.7, 7.3 Hz, 1H), 2.36 (qd, *J* = 7.4, 1.8 Hz, 2H), 1.49 – 1.35 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 138.0, 133.4, 128.9, 128.8, 128.2, 126.5, 32.3, 28.5, 22.6, 14.1. The spectroscopic data corresponds to the reported data.¹⁰



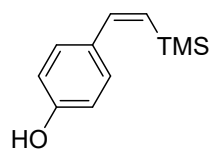
(Z)-5-Decene (2l): colorless liquid (3.4 mg, 12%, *Z/E*: 99/1). Eluent for the flash chromatography with silica gel: hexane. ¹H NMR (400 MHz, CHLOROFORM-D) δ 5.35 – 5.33 (m, 2H), 2.04 – 1.99 (m, 4H), 1.33 – 1.29 (m, 8H), 0.90 – 0.87 (m, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 130.0, 32.1, 27.0, 22.5, 14.1. The spectroscopic data corresponds to the reported data.¹¹



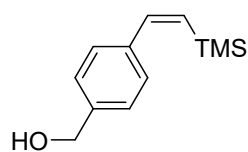
(Z)-β-(Trimethylsilyl)styrene (2m): colorless liquid (24.9 mg, 86%, *Z/E*: 82/18). Eluent for the flash chromatography with silica gel: hexane. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.37 (d, *J* = 15.1 Hz, 1H), 7.34 – 7.23 (m, 5H), 5.83 (d, *J* = 15.1 Hz, 1H), 0.05 (s, 9H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 146.7, 140.3, 133.0, 128.3, 128.0, 127.5, 0.3. The spectroscopic data corresponds to the reported data.¹²



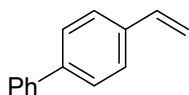
4-[(Z)-2-(Trimethylsilyl)ethenyl]benzenamine (2n): yellow liquid (17.2 mg, 75%, *Z/E*: 60/40). Eluent for the flash chromatography with silica gel: hexane/EA = 15/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.26 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 18.8 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 2H), 6.22 (d, *J* = 18.8 Hz, 1H), 3.69 (s, 2H), 0.13 (s, 9H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 146.5, 143.6, 129.5, 127.8, 124.8, 115.1, -1.0. The spectroscopic data corresponds to the reported data.¹³



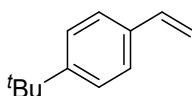
4-[(Z)-2-(Trimethylsilyl)ethenyl]phenol (2o): yellow liquid (26.8 mg, 93%, *Z/E*: 75/25). Eluent for the flash chromatography with silica gel: hexane/EA = 20/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.33 (d, *J* = 8.7 Hz, 2H), 6.83 – 6.76 (m, 3H), 6.29 (d, *J* = 18.8 Hz, 1H), 4.86 (s, 1H), 0.14 (s, 9H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 155.6, 143.0, 131.8, 128.0, 127.0, 115.5, -1.0. HRMS (ESI-) calculated *m/z* for C₁₁H₁₅OSi⁻ [M-H]⁻: 191.0898, found 191.0899.



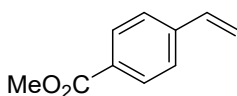
4-[(Z)-2-(Trimethylsilyl)ethenyl]benzenemethanol (2p): colorless liquid (29.8 mg, 95%, *Z/E*: 76/24). Eluent for the flash chromatography with silica gel: hexane/EA = 7/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.34 (d, *J* = 15.1 Hz, 1H), 7.32 – 7.25 (m, 4H), 5.83 (d, *J* = 15.1 Hz, 1H), 4.67 (s, 2H), 1.82 (s, 1H), 0.06 (s, 9H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 146.3, 140.1, 139.6, 133.1, 128.5, 126.7, 65.3, 0.3. The spectroscopic data corresponds to the reported data.¹⁴



4-Ethenyl-1,1'-biphenyl (2q): white solid (22.0 mg, 61%). Eluent for the flash chromatography with silica gel: hexane. ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.66 – 7.58 (m, 4H), 7.51 (d, J = 8.3 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 6.79 (dd, J = 17.6, 10.9 Hz, 1H), 5.82 (d, J = 17.5 Hz, 1H), 5.30 (d, J = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 140.8, 140.7, 136.7, 136.5, 128.9, 127.4, 127.4, 127.1, 126.8, 114.0. The spectroscopic data corresponds to the reported data.⁵



4-tert-Butylstyrene (2r): colorless liquid (19.9 mg, 62%). Eluent for the flash chromatography with silica gel: hexane. ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.37 (s, 4H), 6.72 (dd, J = 17.6, 10.9 Hz, 1H), 5.73 (d, J = 17.5 Hz, 1H), 5.21 (d, J = 10.7 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 151.0, 136.7, 135.0, 126.1, 125.6, 113.2, 34.7, 31.4. The spectroscopic data corresponds to the reported data.¹⁵



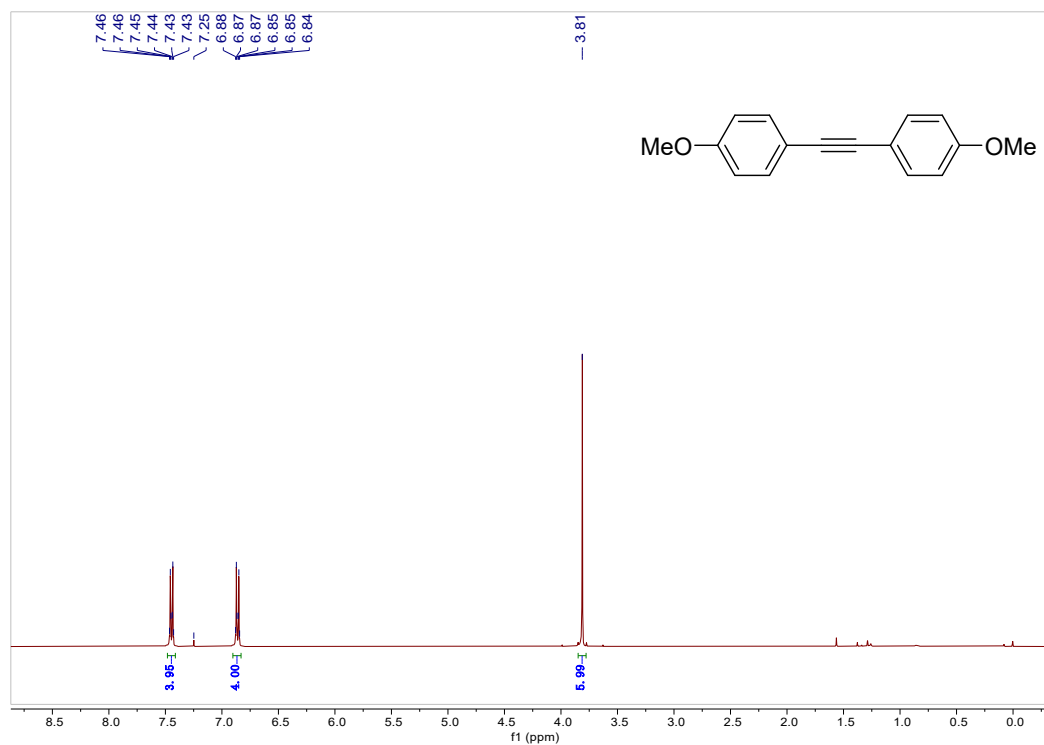
Methyl 4-vinylbenzoate (2s): white solid (17.8 mg, 55%). Eluent for the flash chromatography with silica gel: hexane/EA: 60/1. ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.98 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 6.74 (dd, J = 17.4, 11.0 Hz, 1H), 5.85 (d, J = 17.9 Hz, 1H), 5.37 (d, J = 11.0 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 167.0, 142.1, 136.2, 130.0, 129.4, 126.3, 116.6, 52.2. The spectroscopic data corresponds to the reported data.¹⁶

7. References

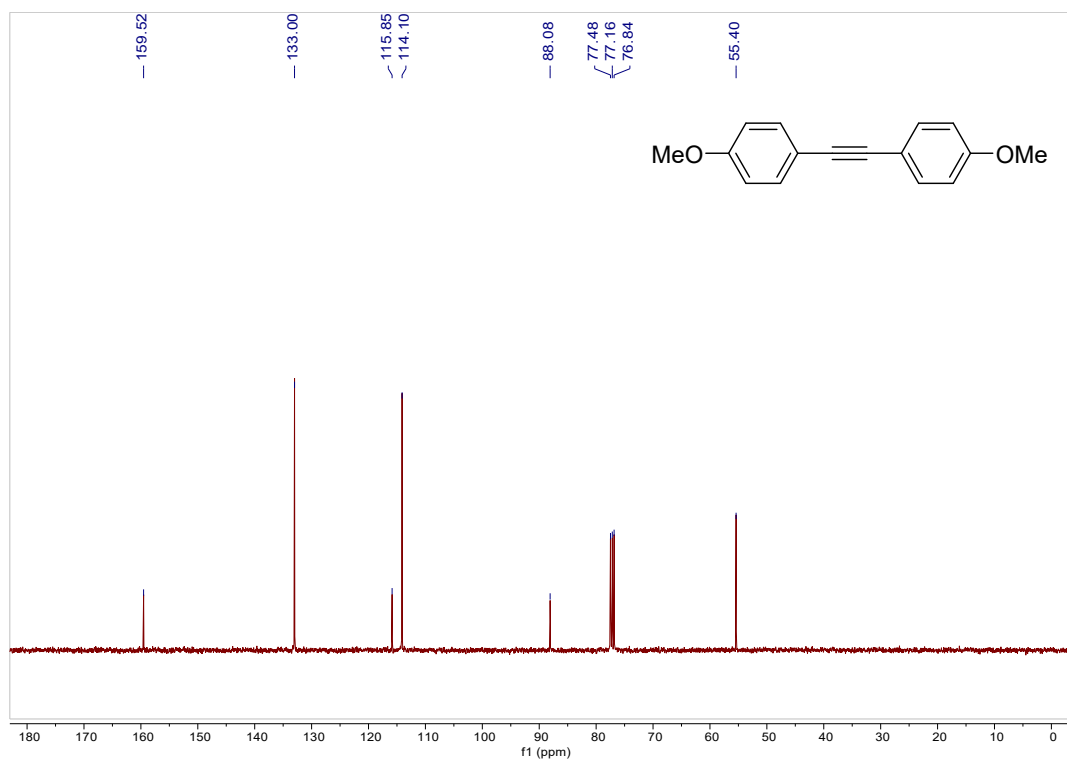
1. M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth and P. A. Grieco, *Org. Lett.*, 2002, **4**, 3199-3202.
2. X. Li, F. Yang and Y. Wu, *J. Org. Chem.*, 2013, **78**, 4543-4550.
3. A. Dasgupta, K. Stefkova, R. Babaahmadi, B. F. Yates, N. J. Buurma, A. Ariafard, E. Richards and R. L. Melen, *J. Am. Chem. Soc.*, 2021, **143**, 4451-4464.
4. C. W. D. Gallop, M.-T. Chen and O. Navarro, *Org. Lett.*, 2014, **16**, 3724-3727.
5. Y. Wu, Y. Ao, Z. Li, C. Liu, J. Zhao, W. Gao, X. Li, H. Wang, Y. Liu and Y. Liu, *Nat. Commun.*, 2023, **14**, 1655.
6. C.-C. Tai, M.-S. Yu, Y.-L. Chen, W.-H. Chuang, T.-H. Lin, G. P. A. Yap and T.-G. Ong, *Chem. Commun.*, 2014, **50**, 4344-4346.
7. L. Ilies, T. Yoshida and E. Nakamura, *J. Am. Chem. Soc.*, 2012, **134**, 16951-16954.
8. M. Gaydou, T. Moragas, F. Juliá-Hernández and R. Martin, *J. Am. Chem. Soc.*, 2017, **139**, 12161-12164.
9. D. Srimani, G. Leitus, Y. Ben-David and D. Milstein, *Angew. Chem. Int. Ed.*, 2014, **53**, 11092-11095.
10. G.-p. Lu, K. R. Voigtritter, C. Cai and B. H. Lipshutz, *Chem. Commun.*, 2012, **48**, 8661-8663.
11. G. Cahiez, G. Lefèvre, A. Moyeux, O. Guerret, E. Gayon, L. Guillonnet, N. Lefèvre, Q. Gu and E. Zhou, *Org. Lett.*, 2019, **21**, 2679-2683.
12. S. I. Faßbender, J. J. Molloy, C. Mück-Lichtenfeld and R. Gilmour, *Angew. Chem. Int. Ed.*, 2019, **58**, 18619-18626.
13. M. Espinal-Viguri, S. E. Neale, N. T. Coles, S. A. Macgregor and R. L. Webster, *J. Am. Chem. Soc.*, 2019, **141**, 572-582.
14. N. Gorgas, J. Brünig, B. Stöger, S. Vanicek, M. Tilset, L. F. Veiros and K. Kirchner, *J. Am. Chem. Soc.*, 2019, **141**, 17452-17458.
15. R. Kusy, M. Lindner, J. Wagner and K. Grela, *Chem Catal.*, 2022, **2**, 1346-1361.
16. G. Wienhöfer, F. A. Westerhaus, R. V. Jagadeesh, K. Junge, H. Junge and M. Beller, *Chem. Commun.*, 2012, **48**, 4827-4829.

8. Copies of ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{19}F NMR Spectra for Synthesized Compounds

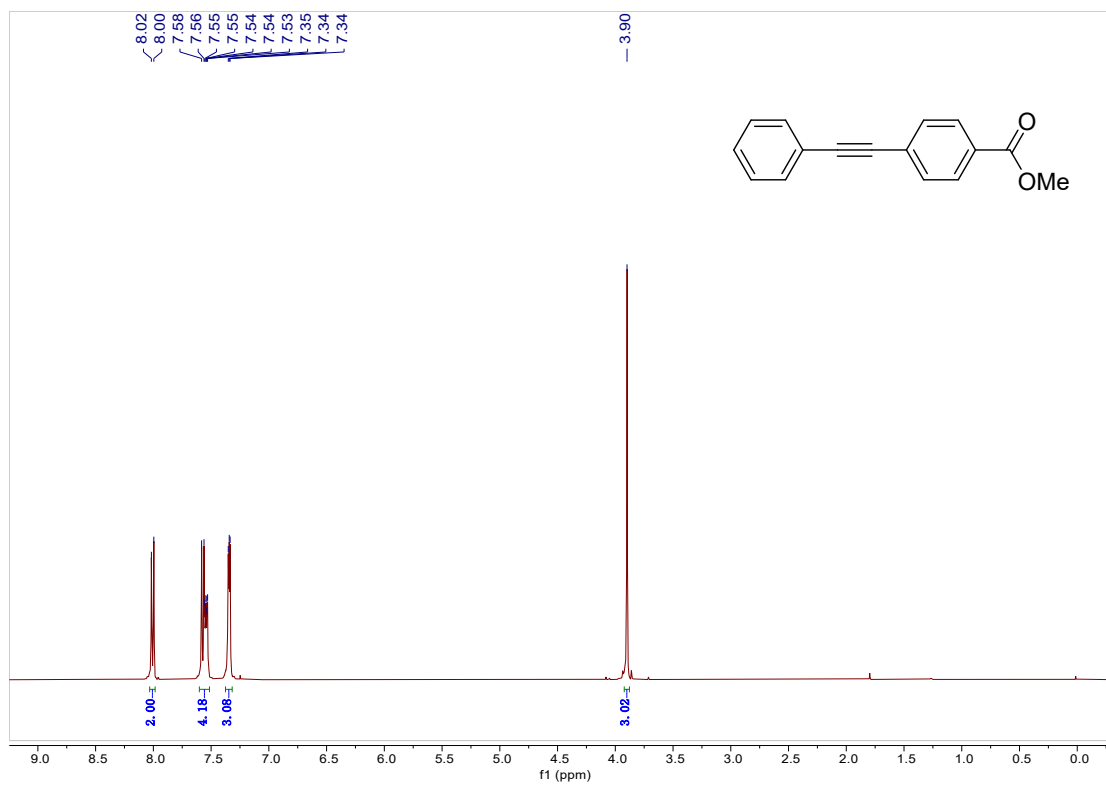
8.1 Copies of ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{19}F NMR Spectra for Substrates 1



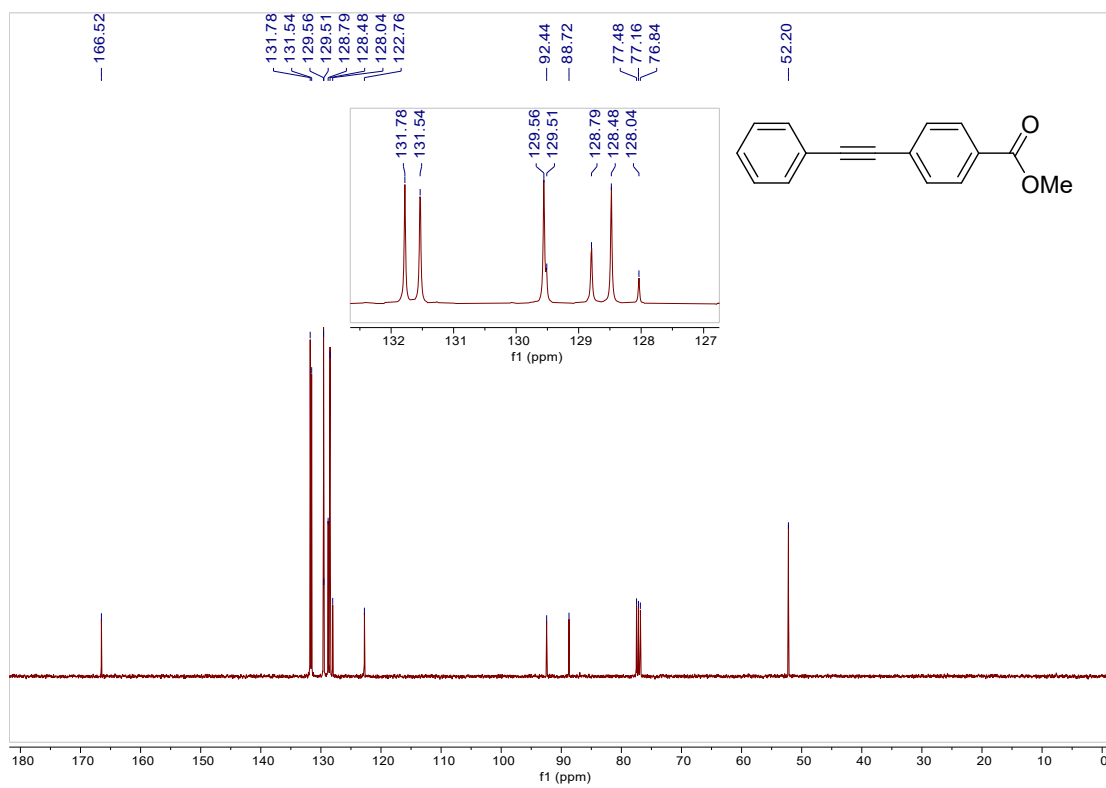
^1H NMR for compound **1c**



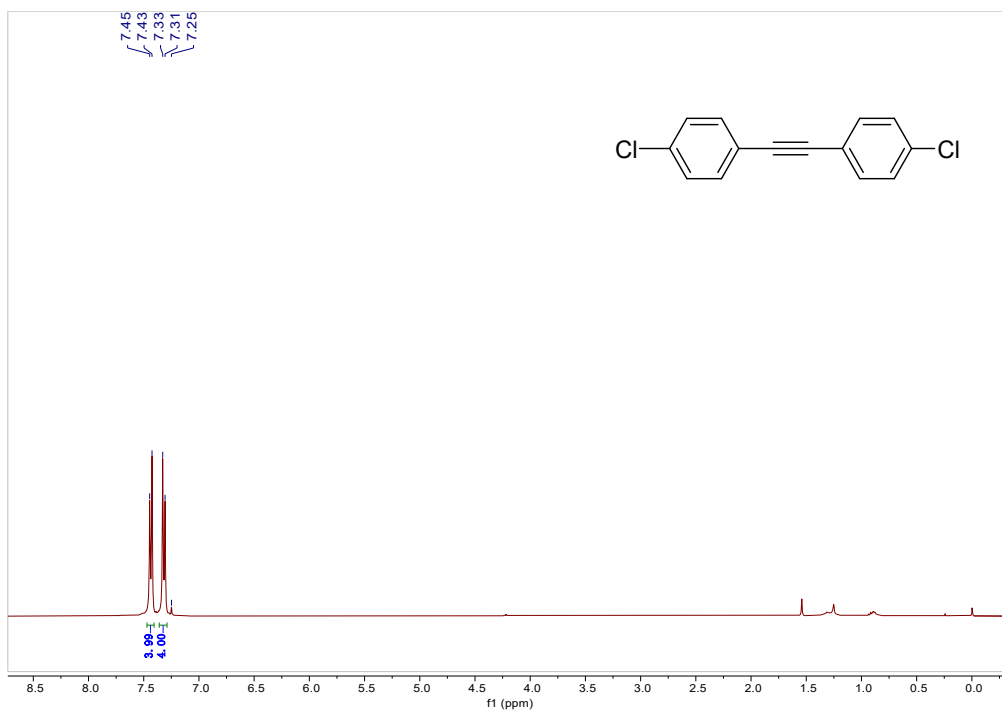
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **1c**



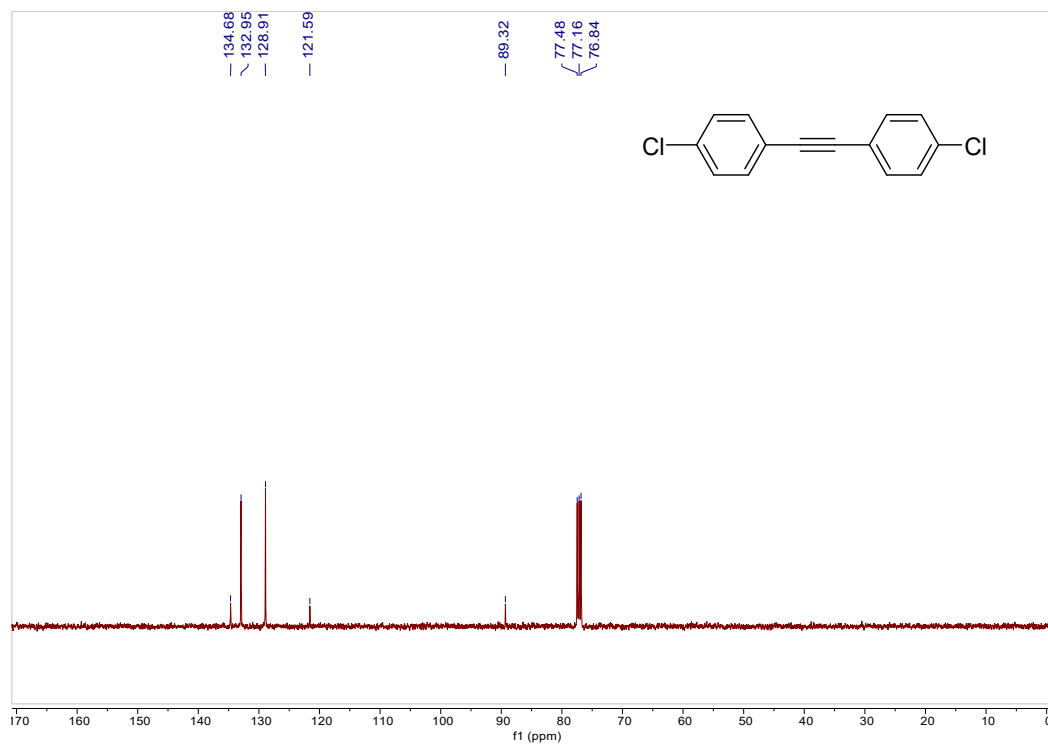
$^1\text{H NMR}$ for compound **1d**



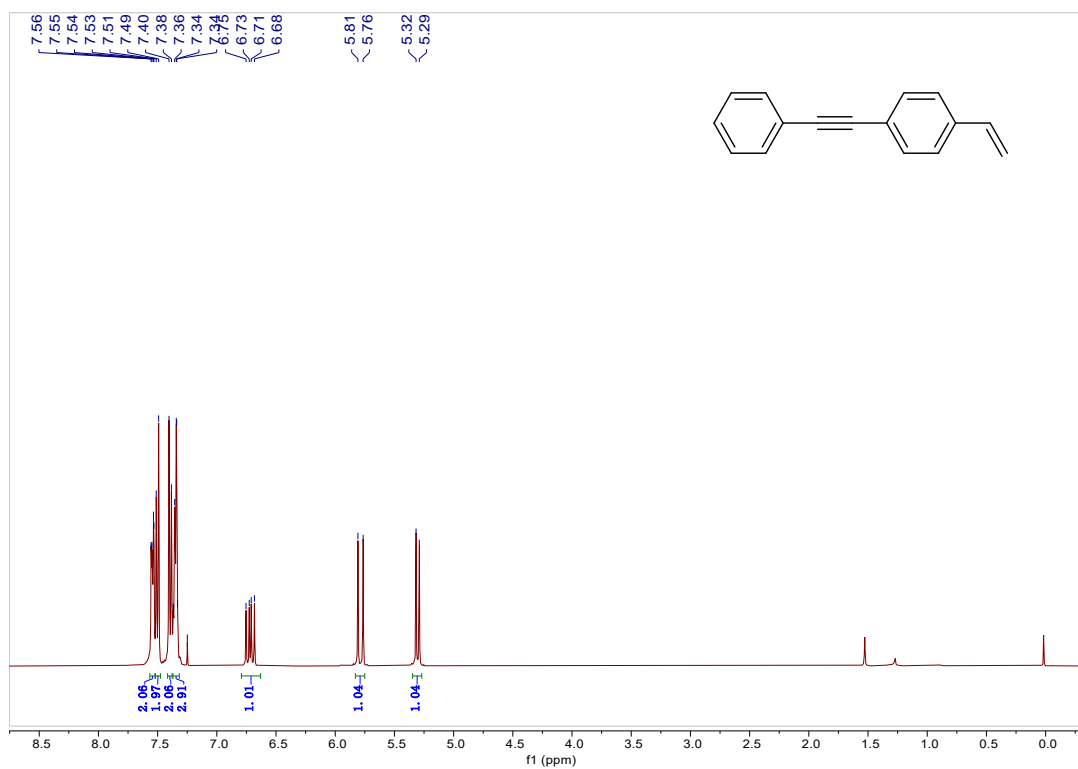
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **1d**



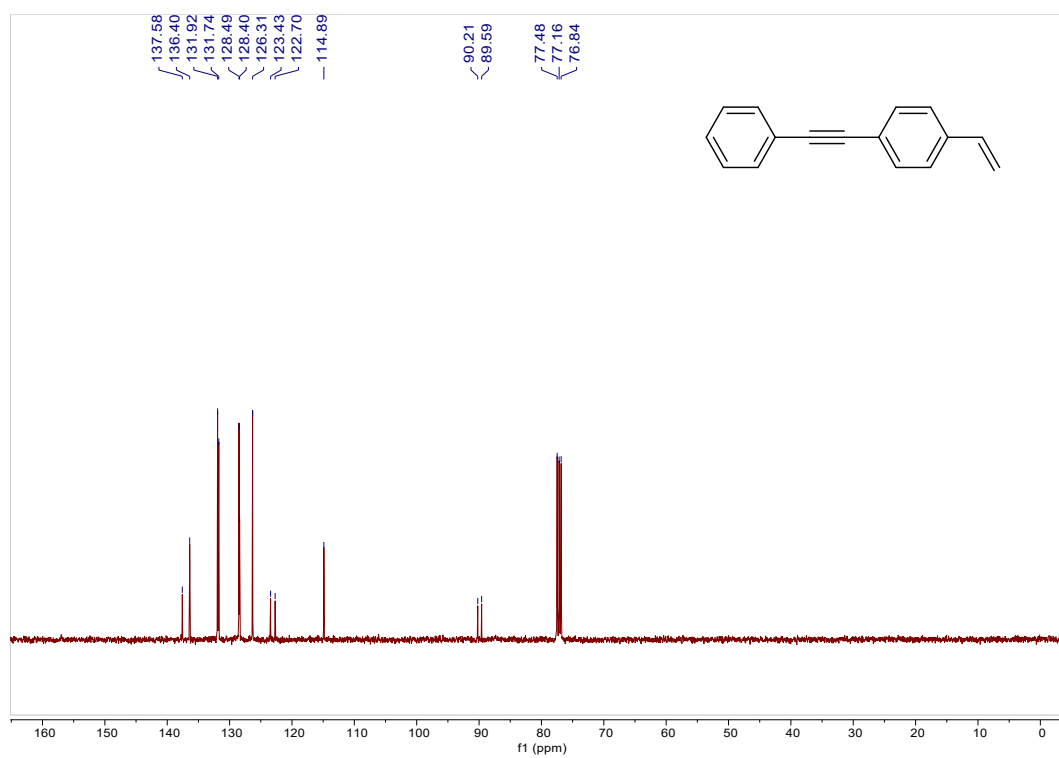
^1H NMR for compound **1f**



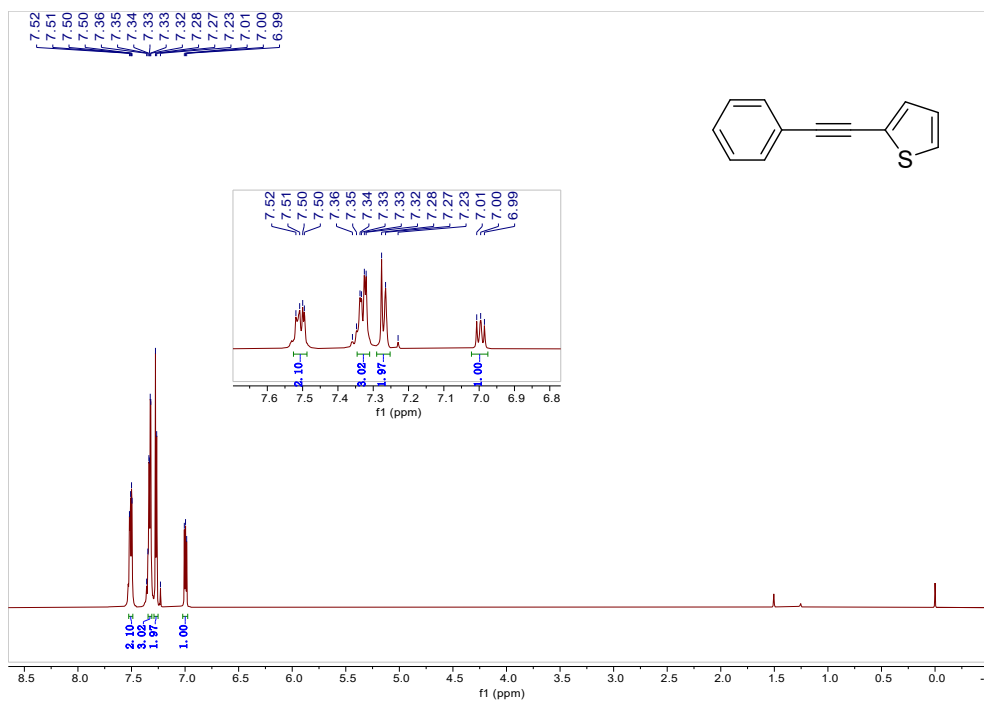
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **1f**



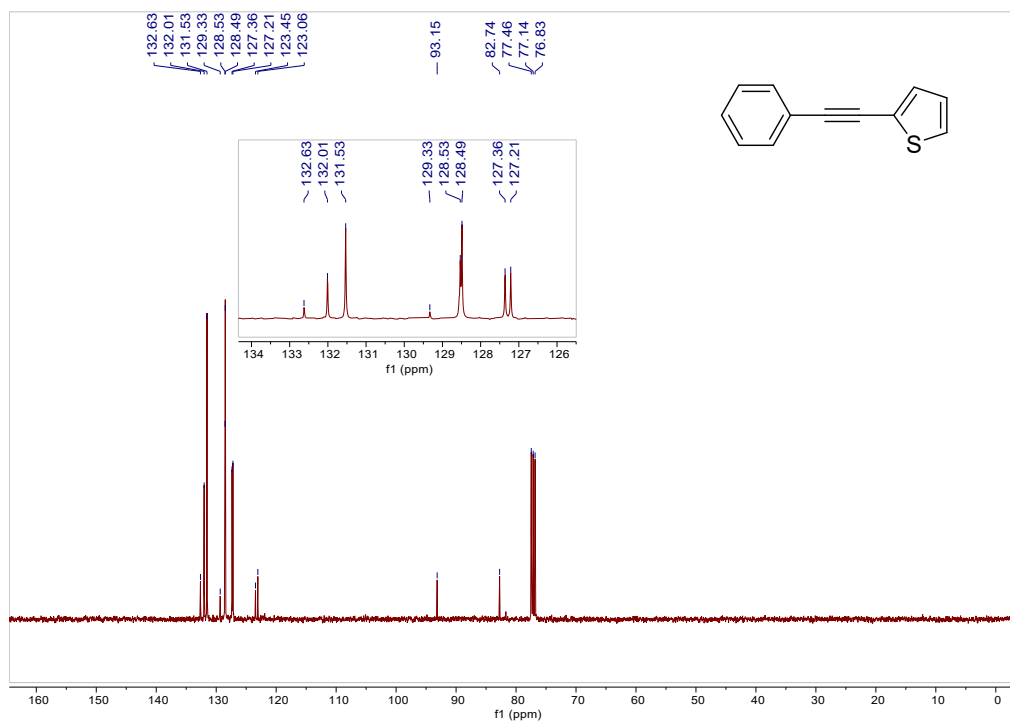
^1H NMR for compound **1h**



$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **1h**

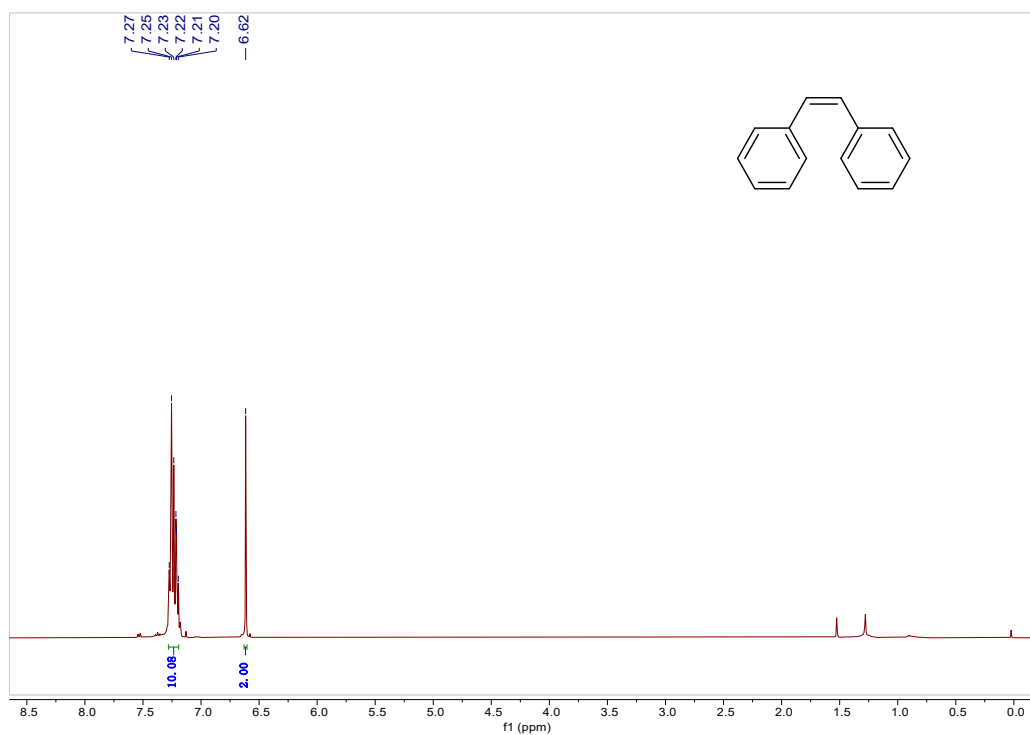


¹H NMR for compound 1j

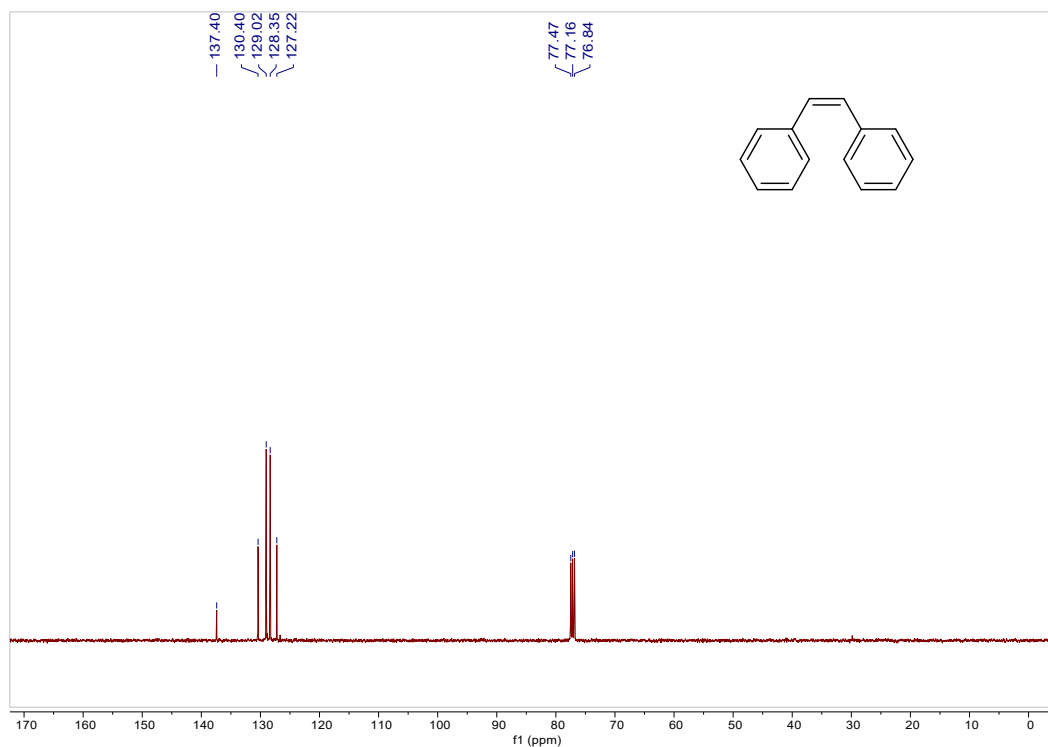


¹³C {¹H} NMR for compound 1j

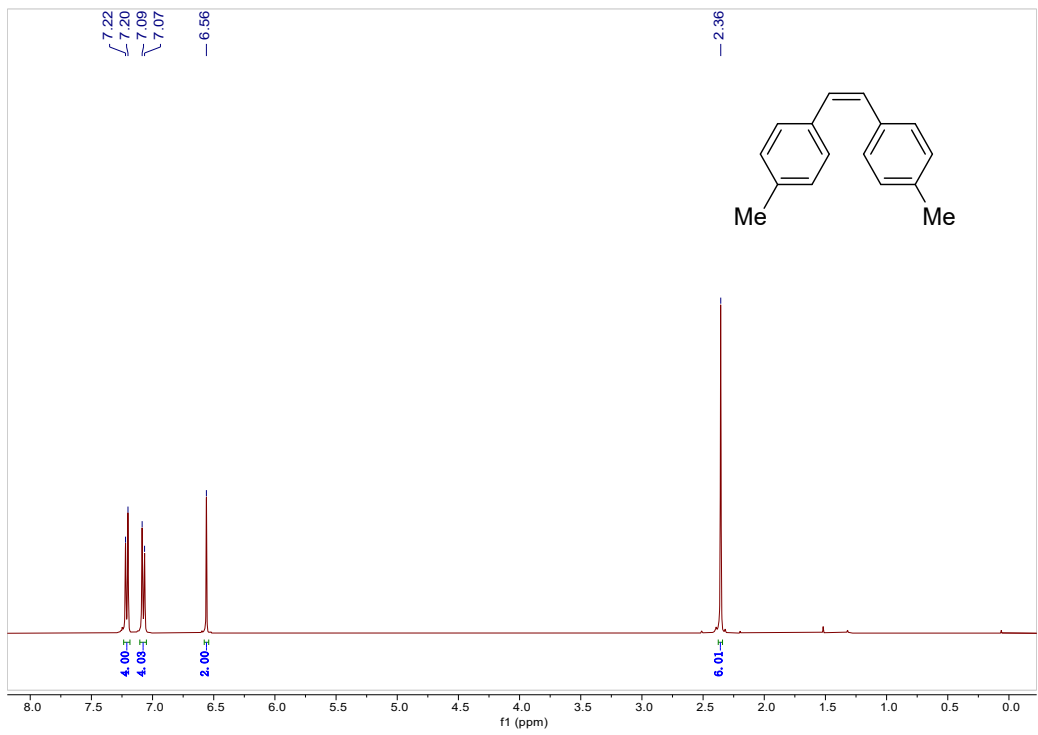
8.2 Copies of ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{19}F NMR Spectra for Products 2 and 3



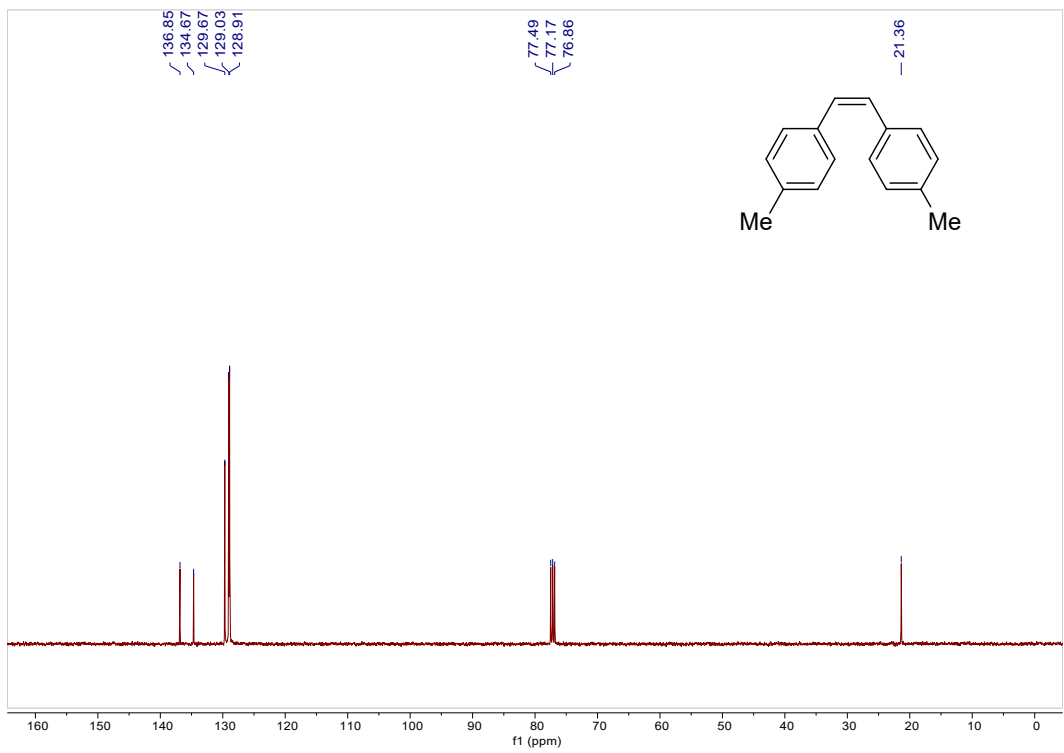
^1H NMR for compound **2a**



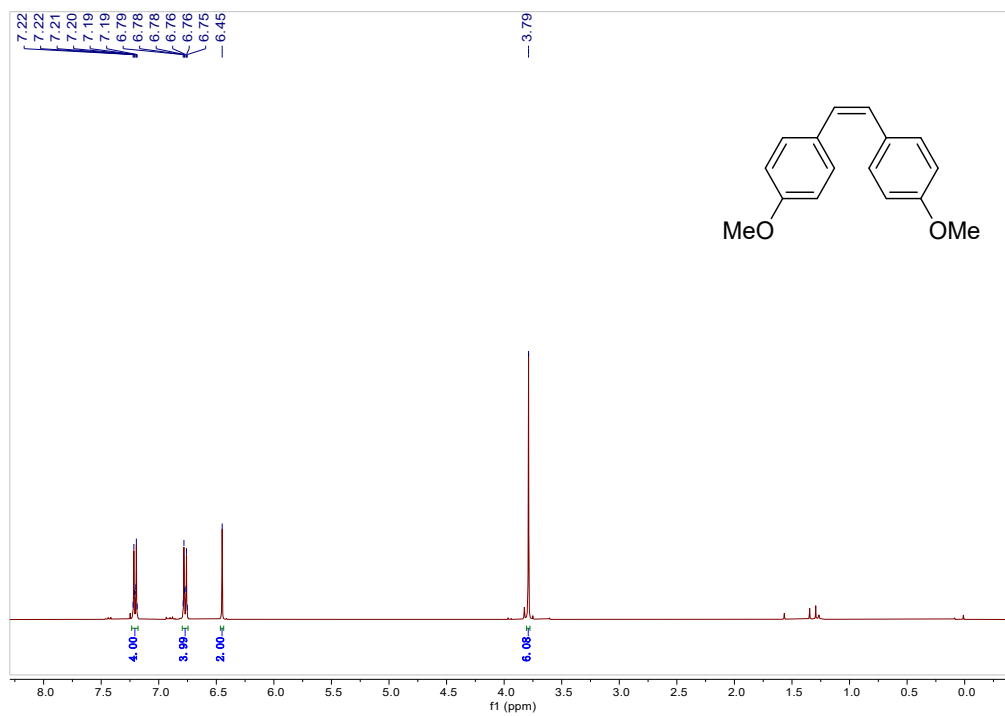
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2a**



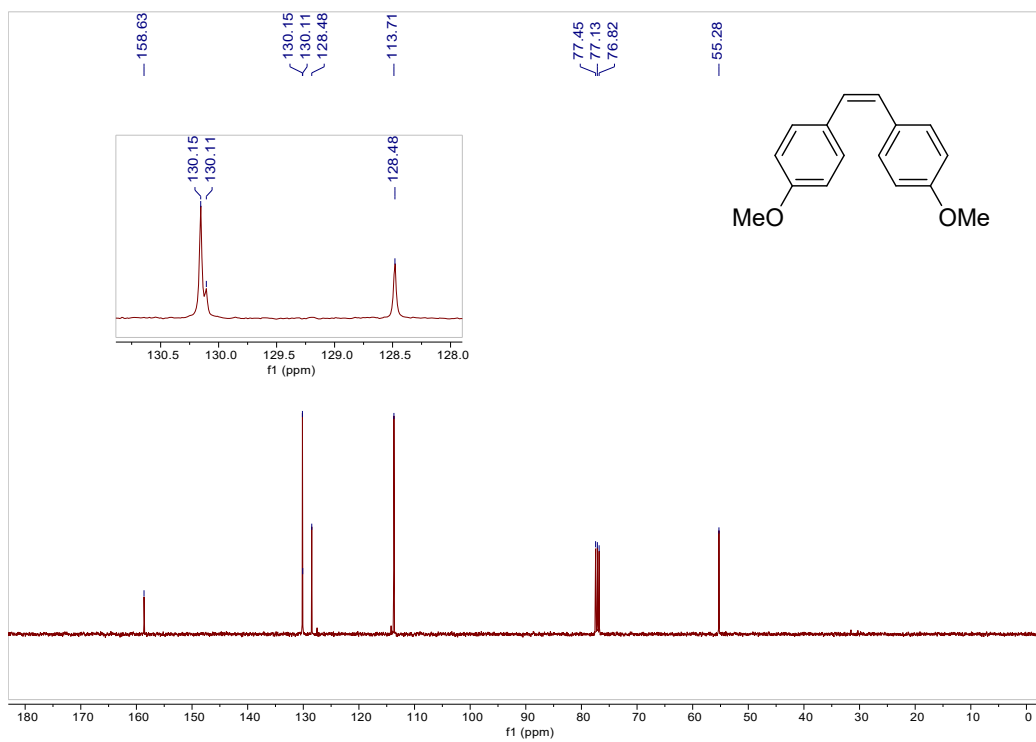
^1H NMR for compound **2b**



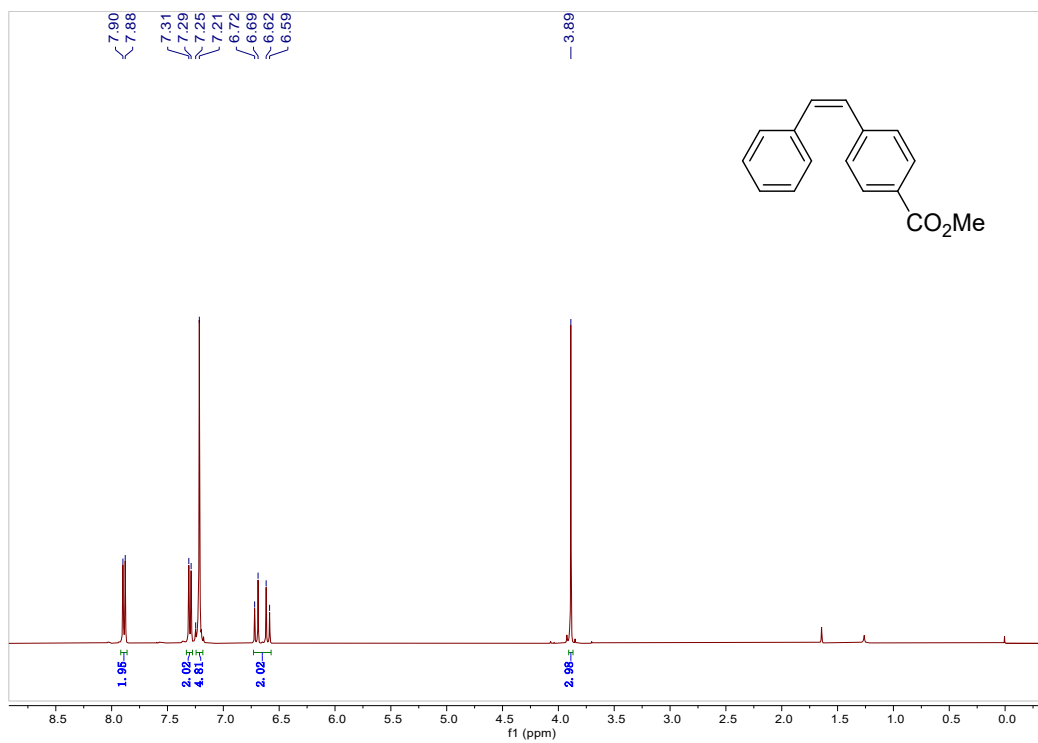
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2b**



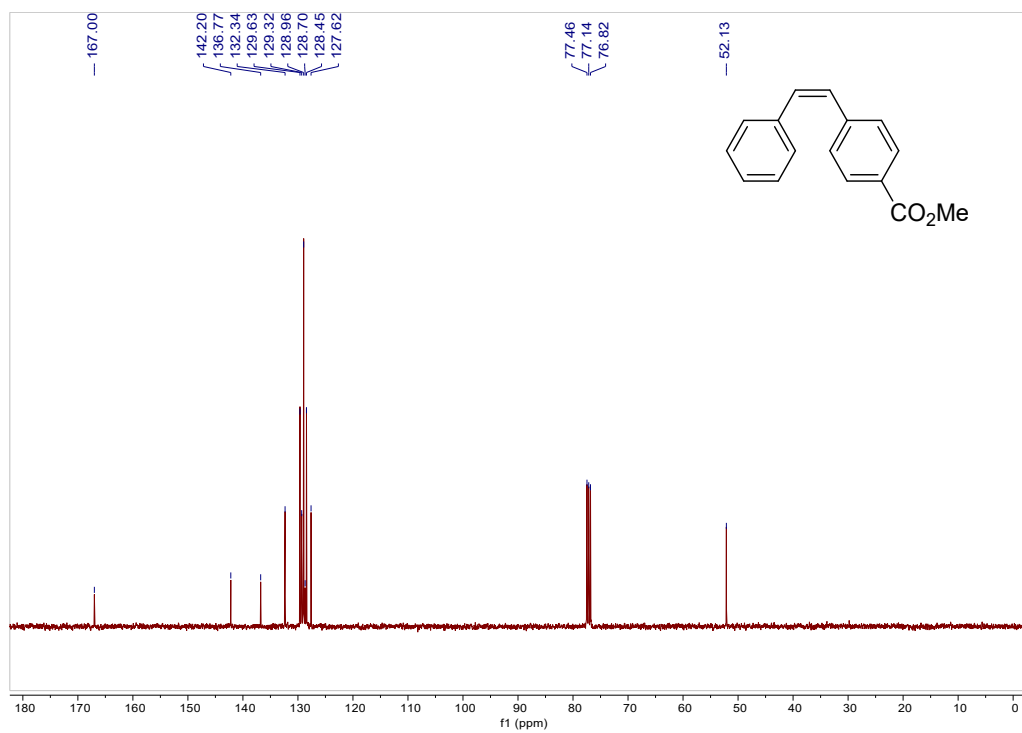
^1H NMR for compound **2c**



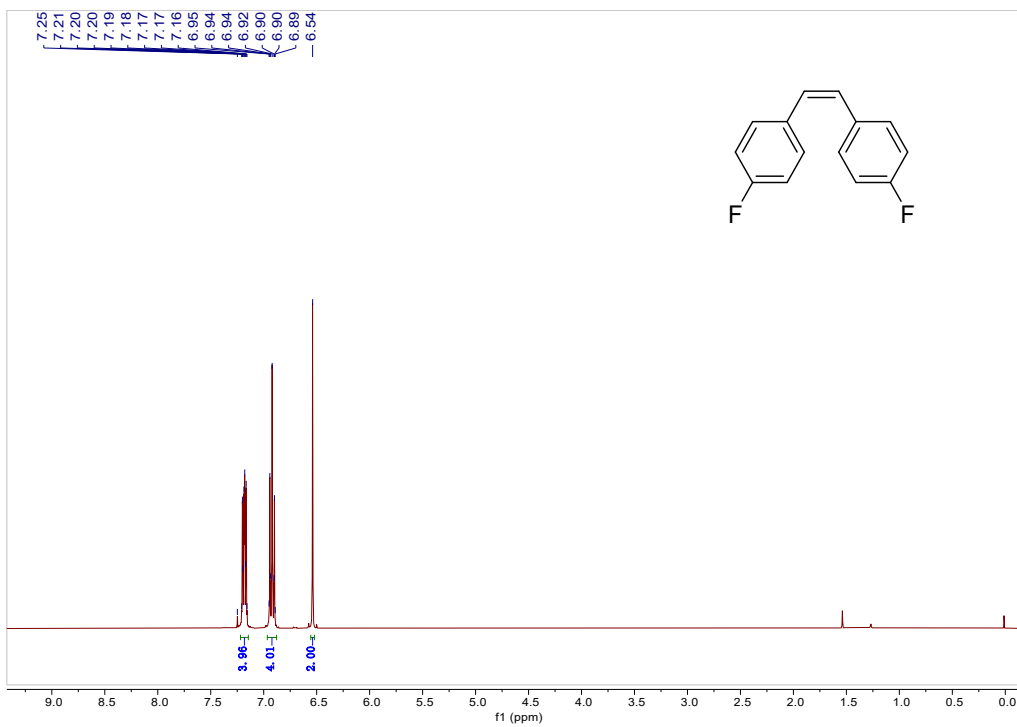
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2c**



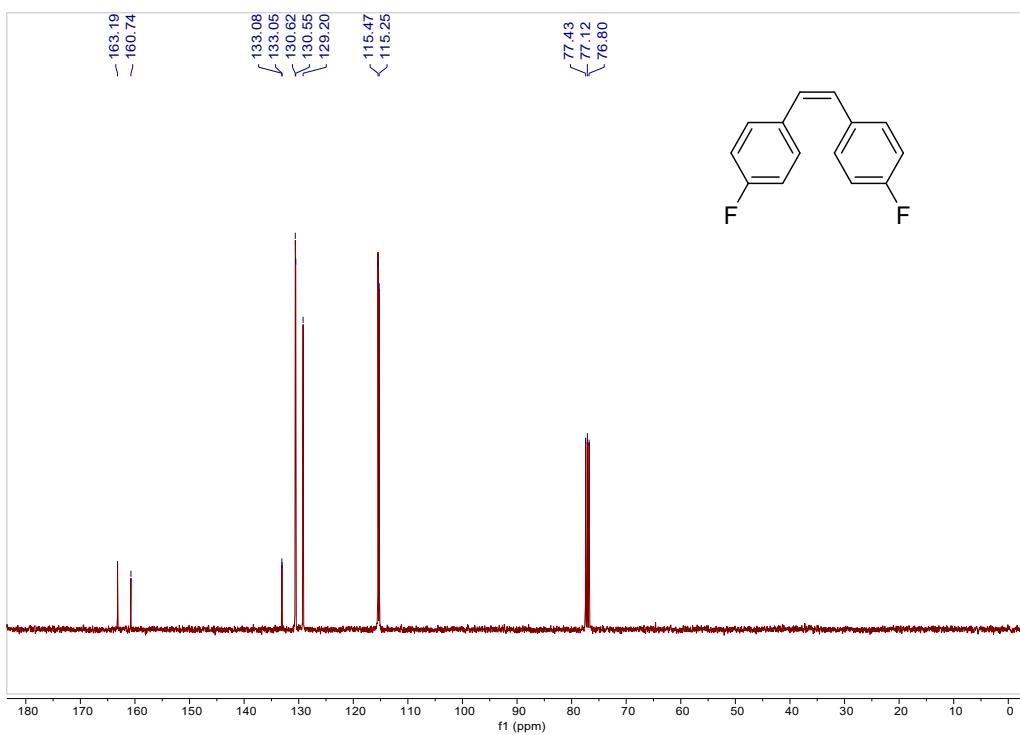
^1H NMR for compound **2d**



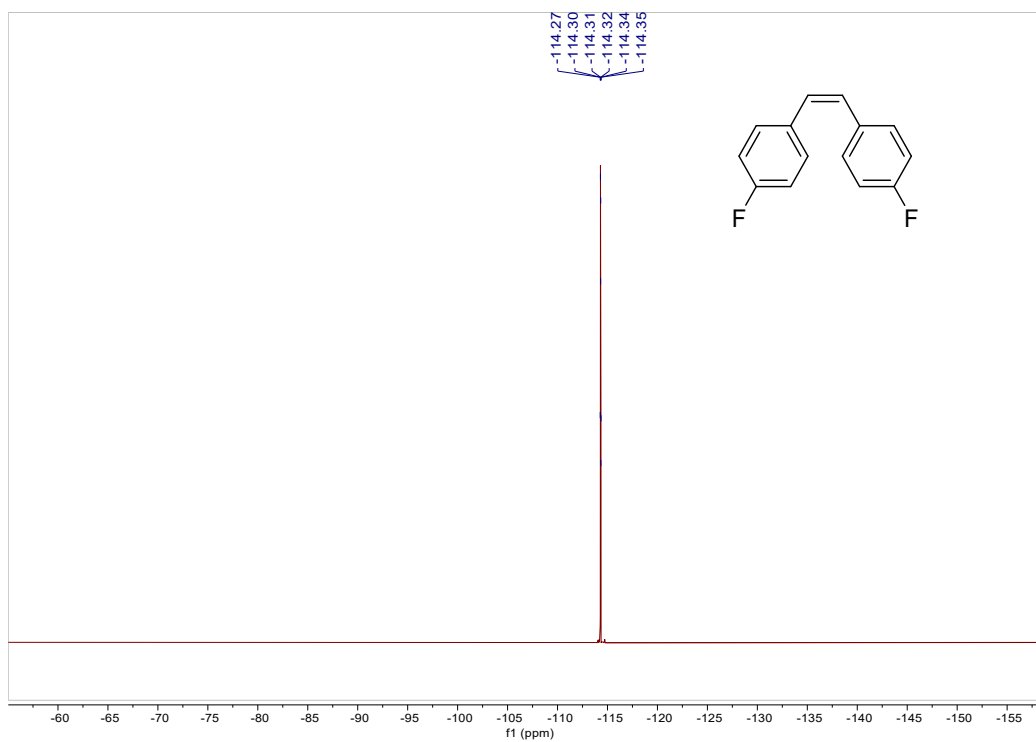
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2d**



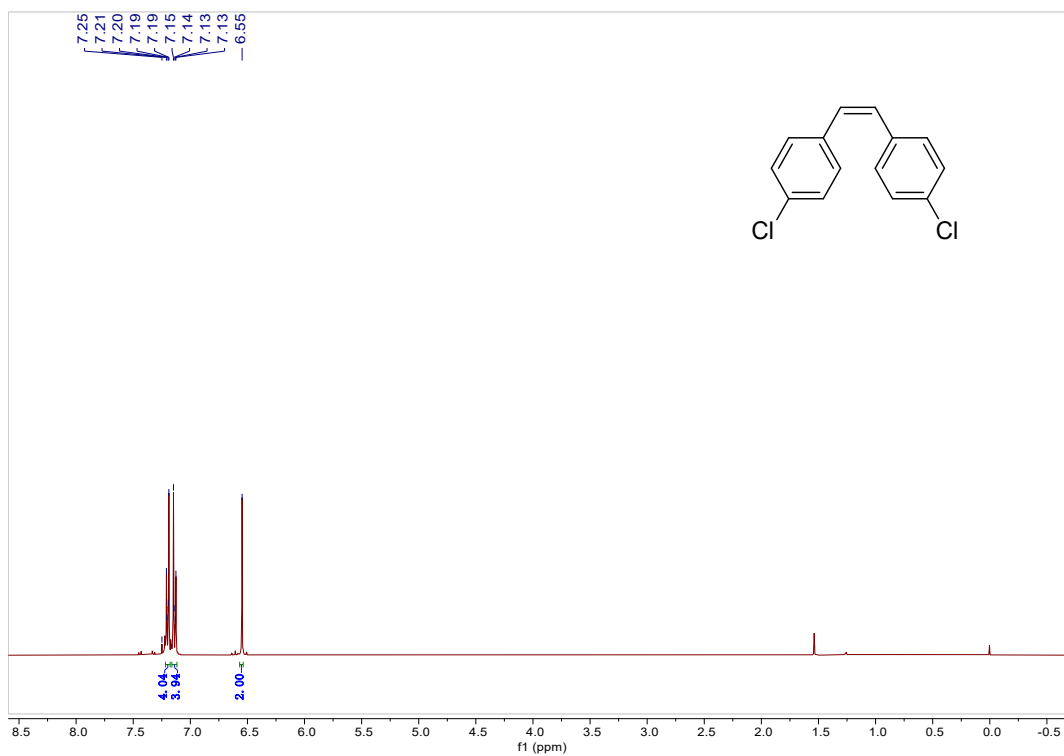
^1H NMR for compound **2e**



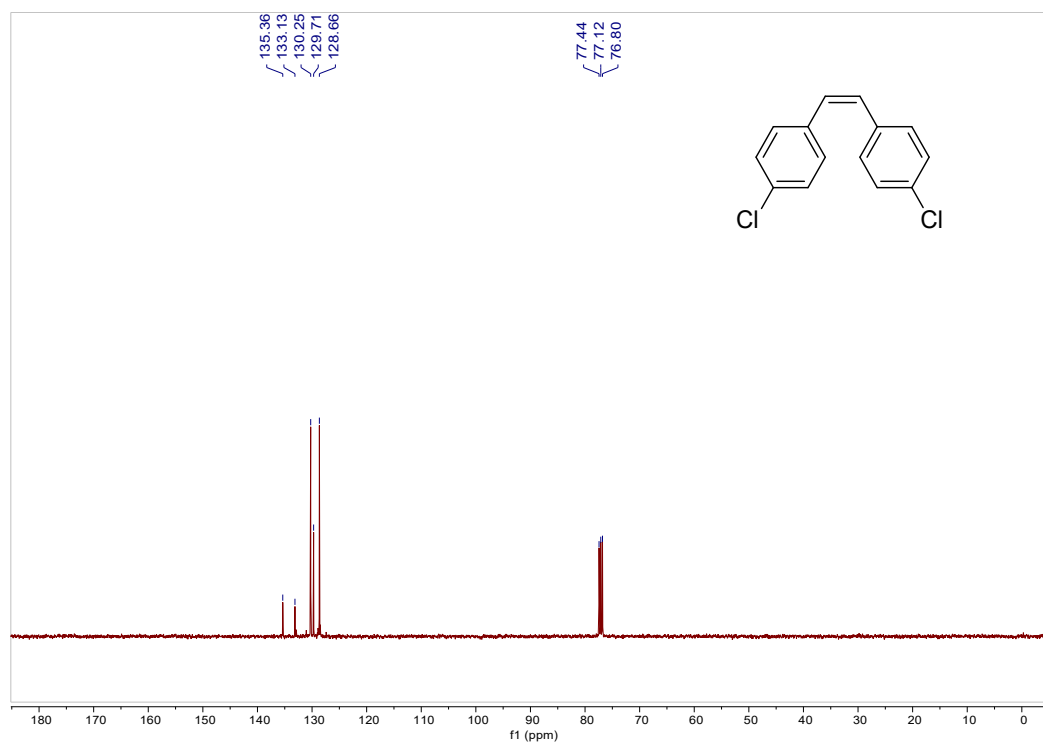
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2e**



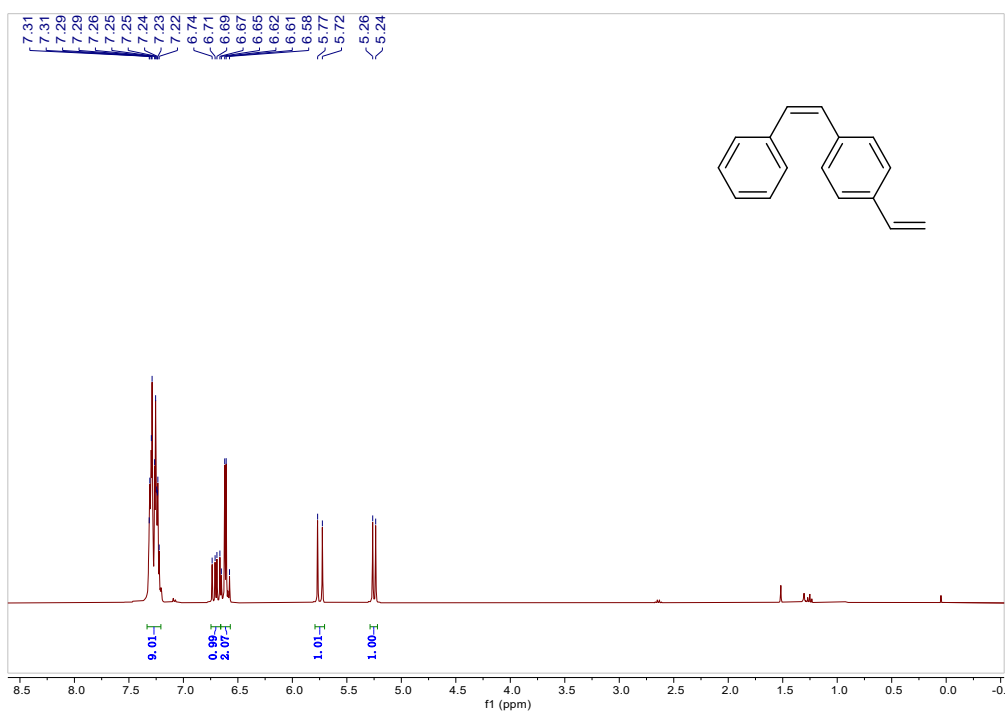
^{19}F NMR for compound **2e**



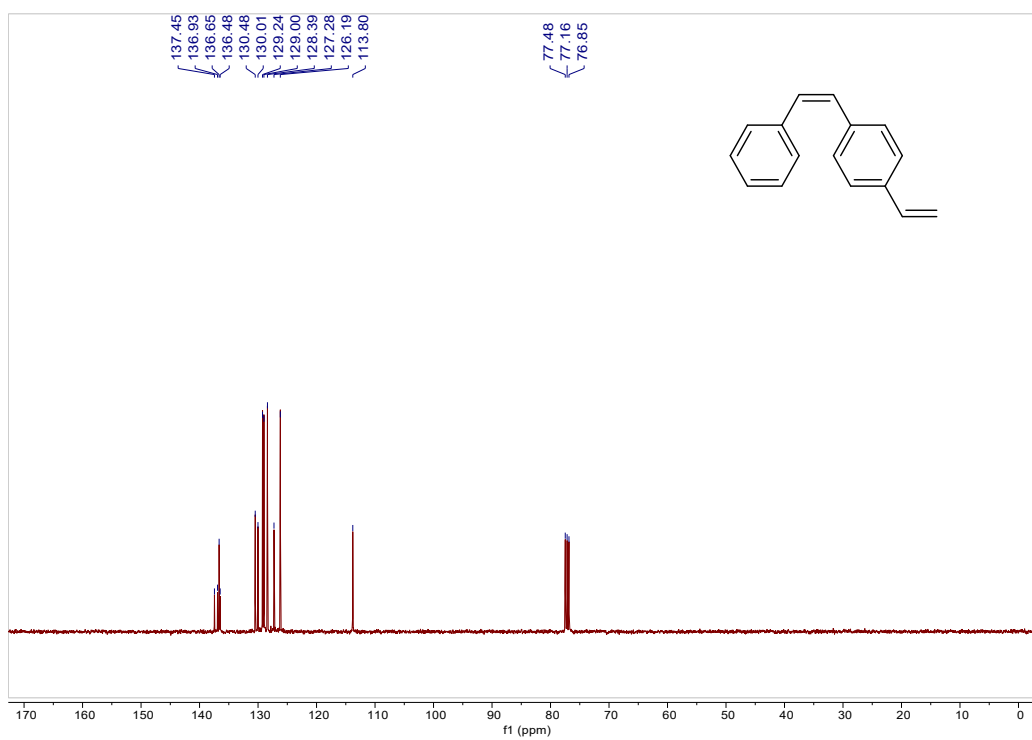
¹H NMR for compound 2f



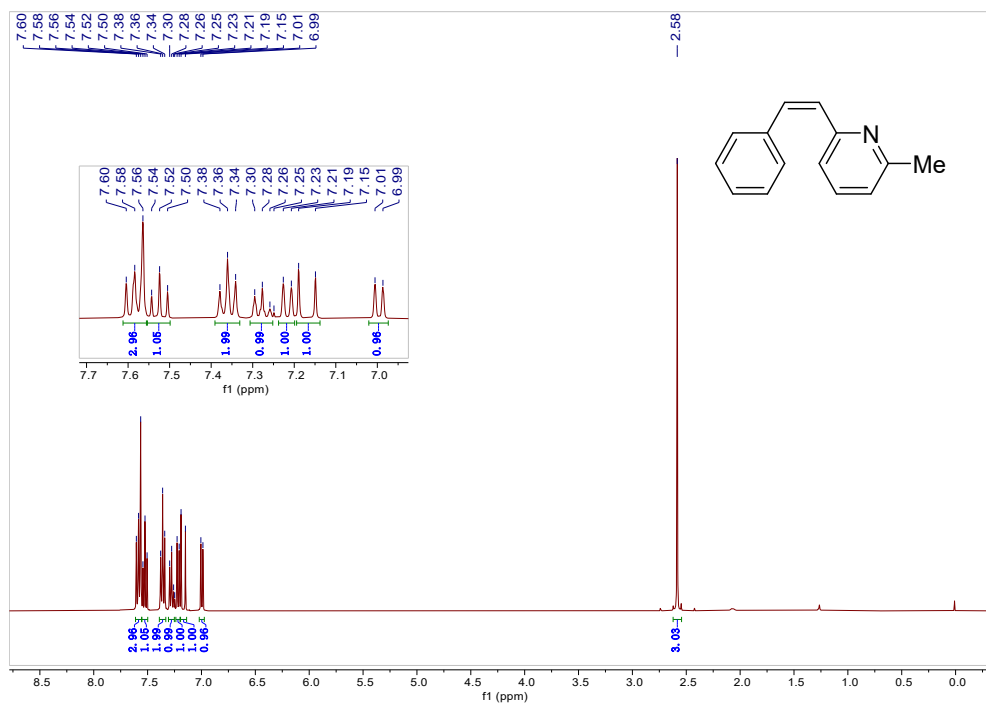
¹³C{¹H} NMR for compound 2f



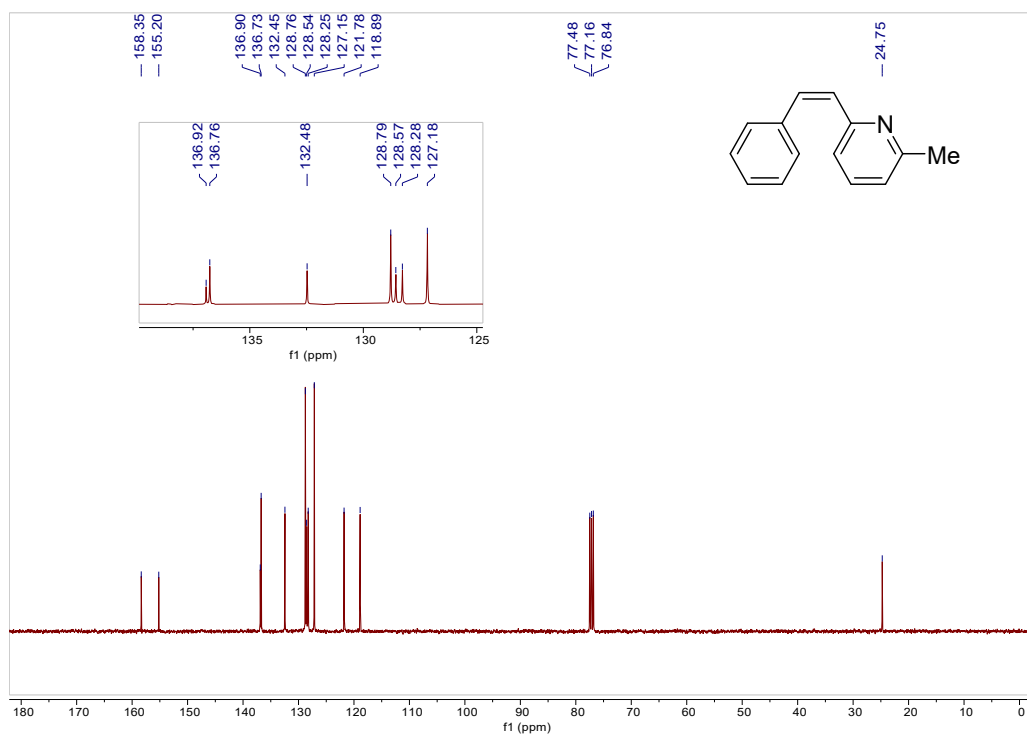
^1H NMR for compound **2h**



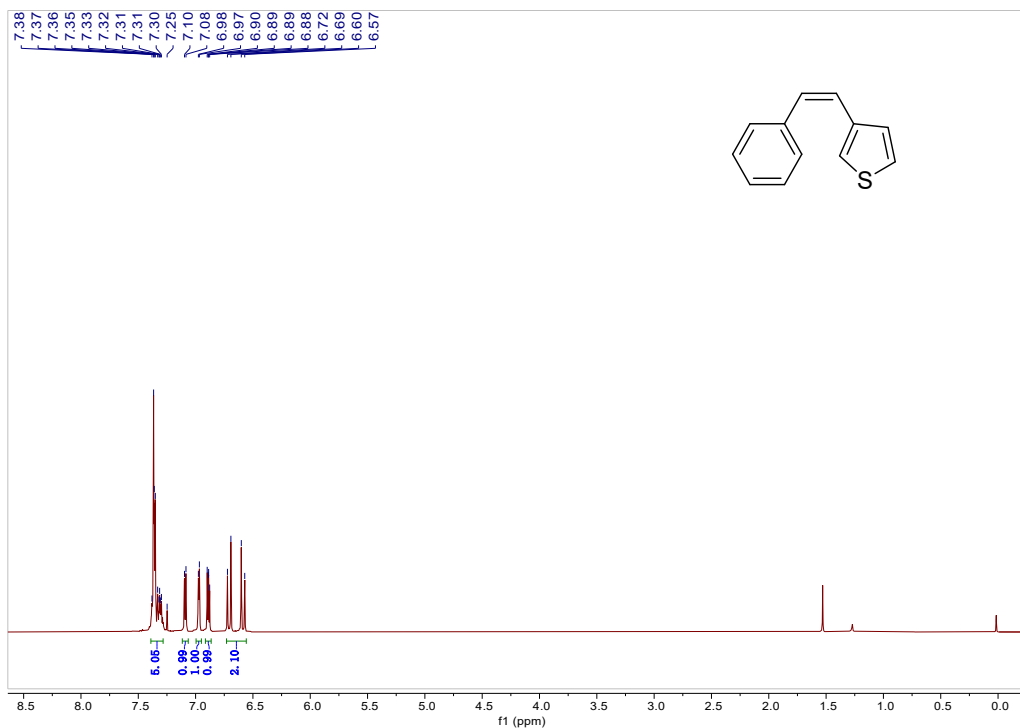
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2h**



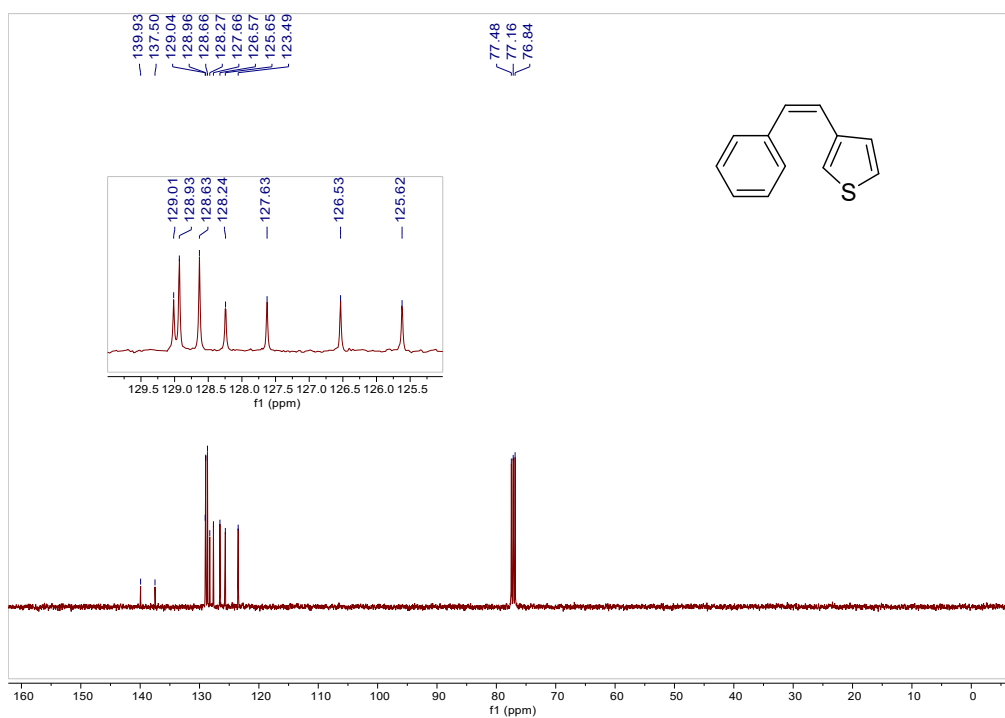
¹H NMR for compound 2i



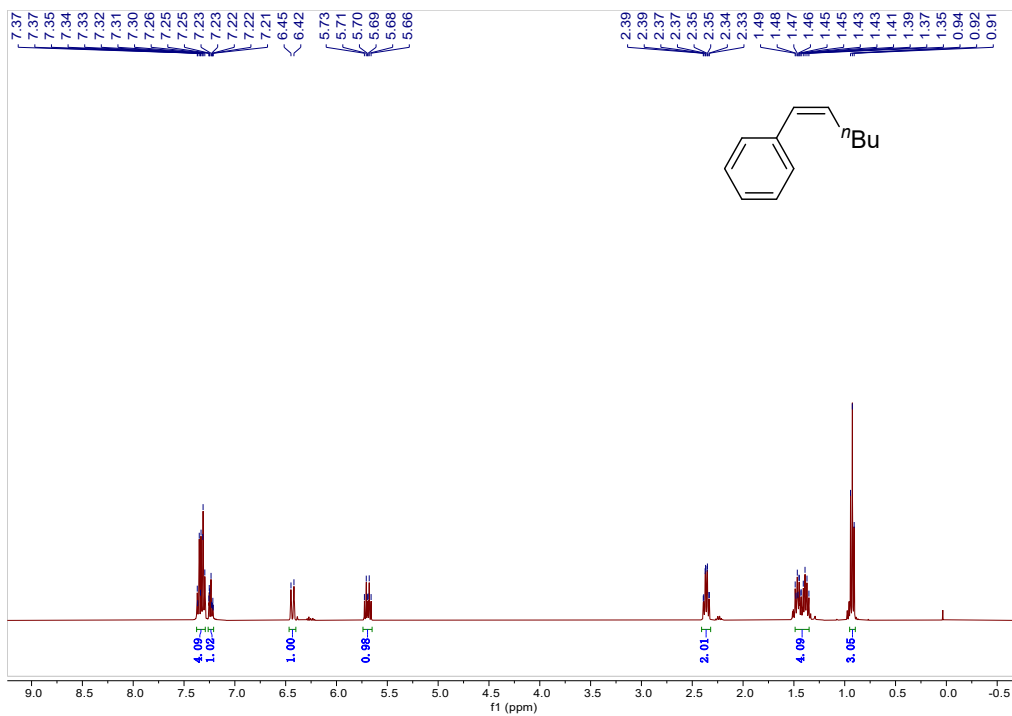
¹³C {¹H} NMR for compound 2i



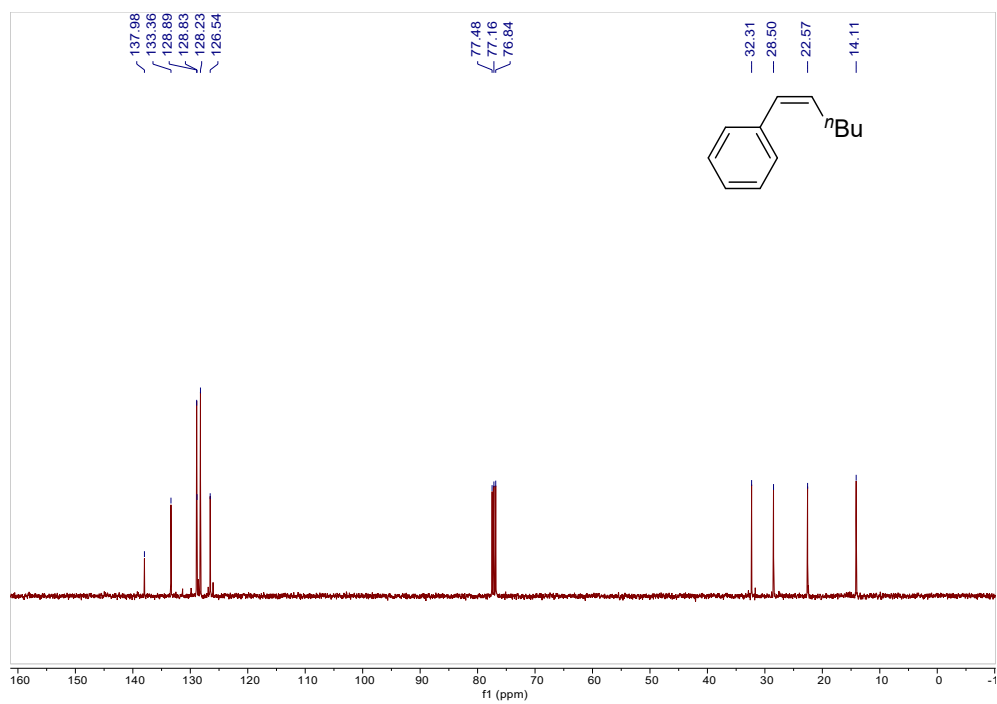
^1H NMR for compound **2j**



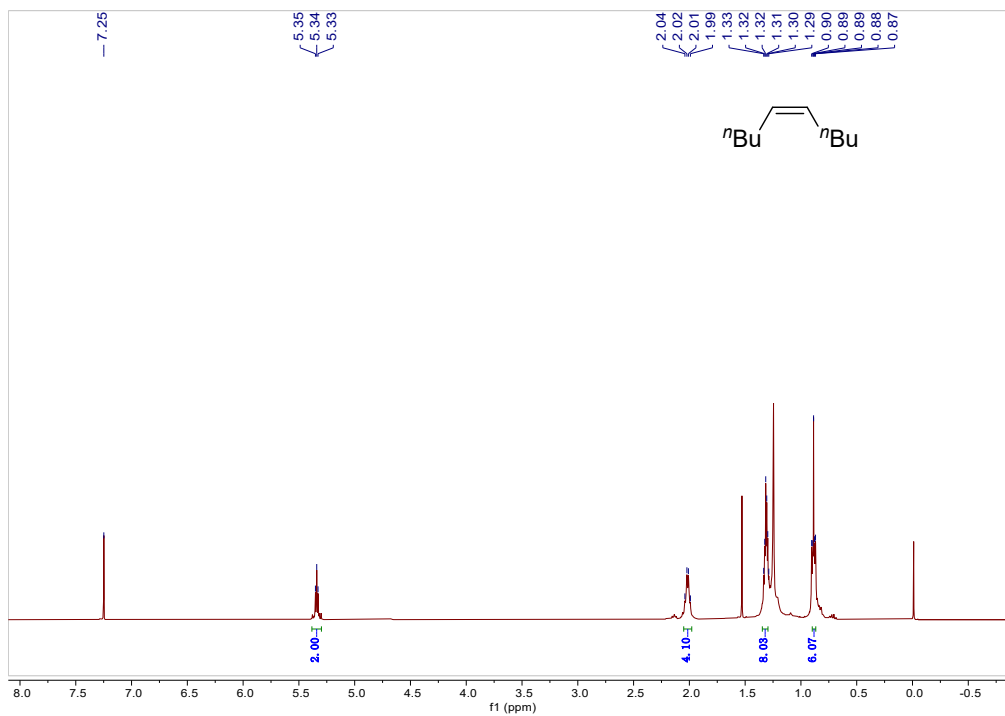
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2j**



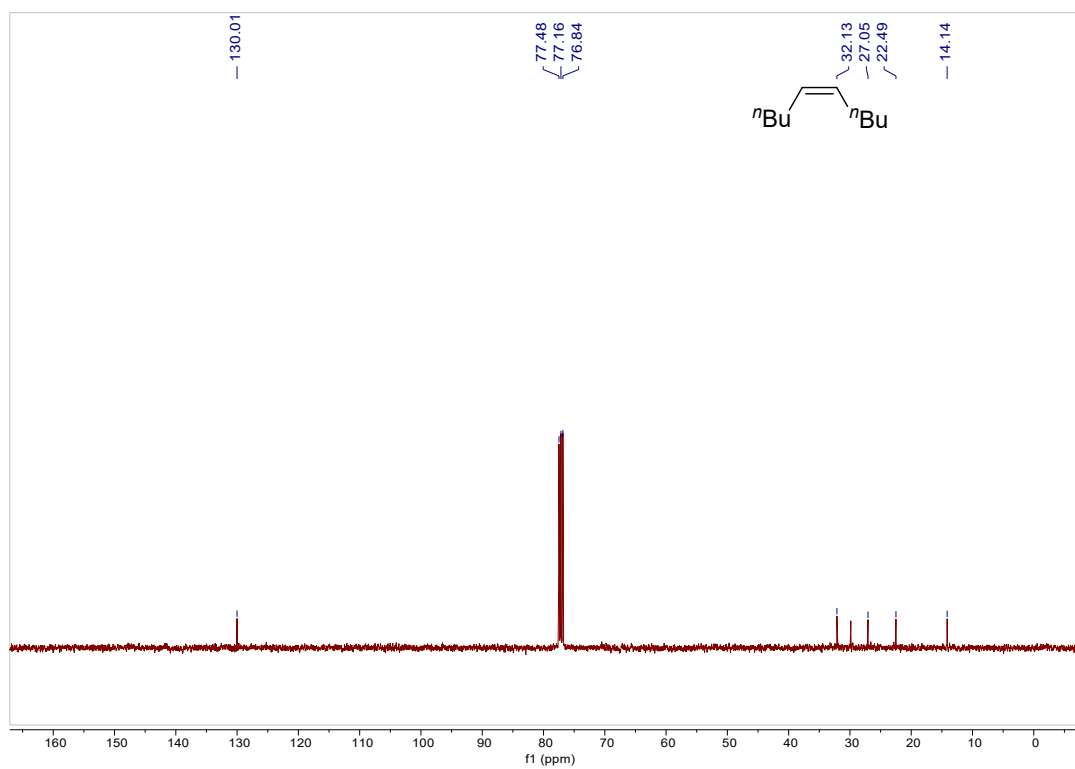
^1H NMR for compound **2k**



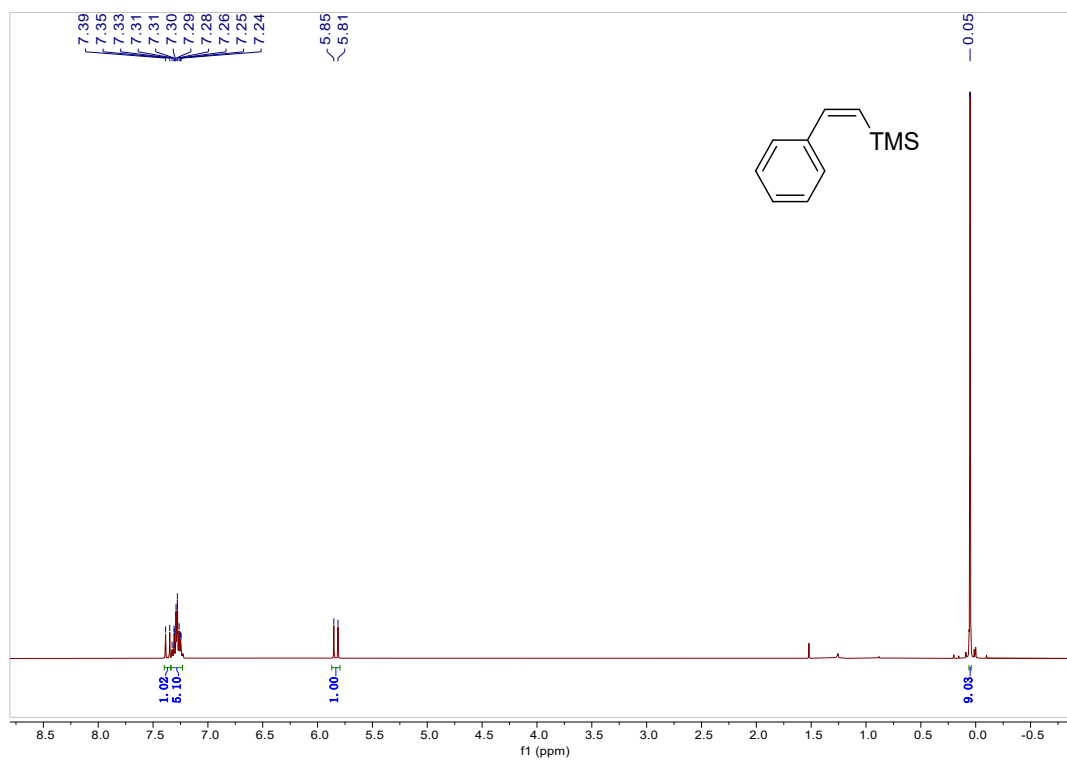
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2k**



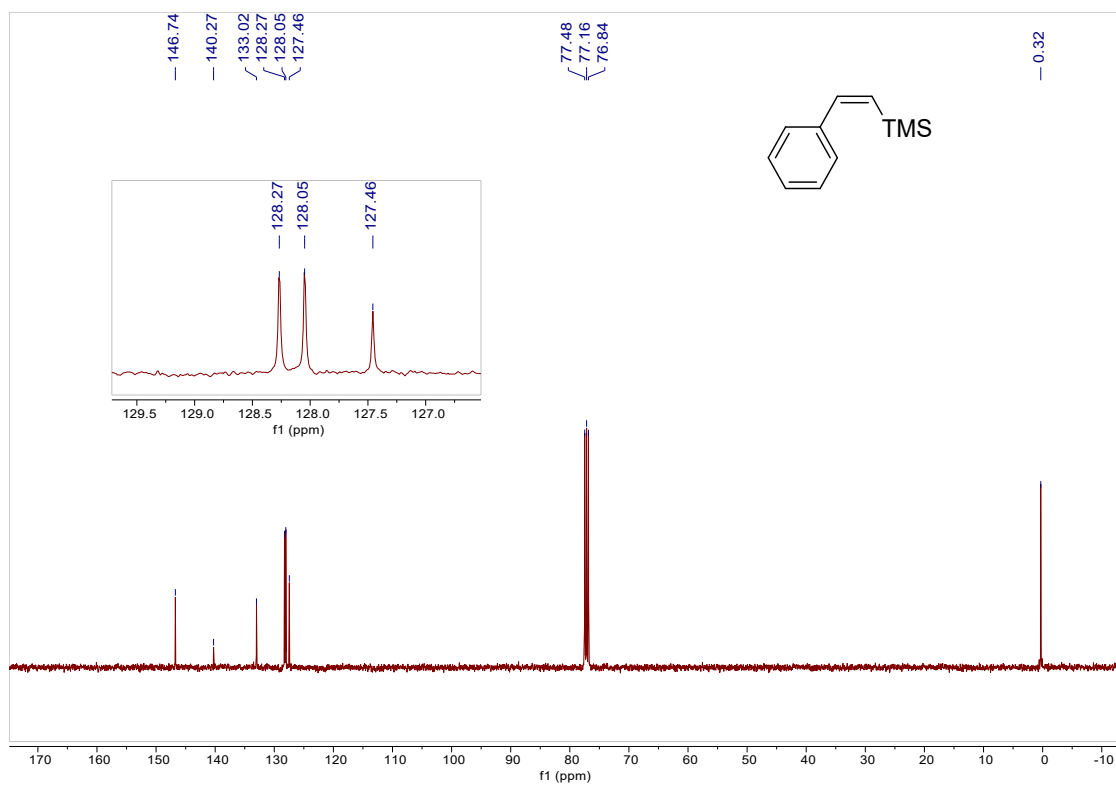
^1H NMR for compound **2I**



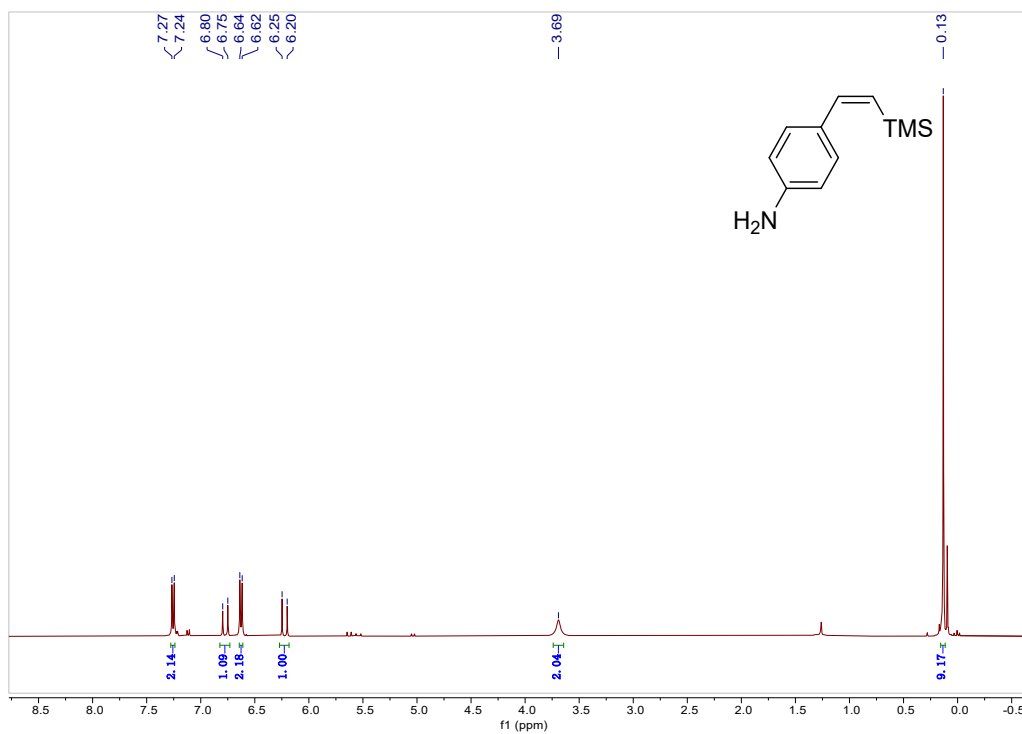
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2I**



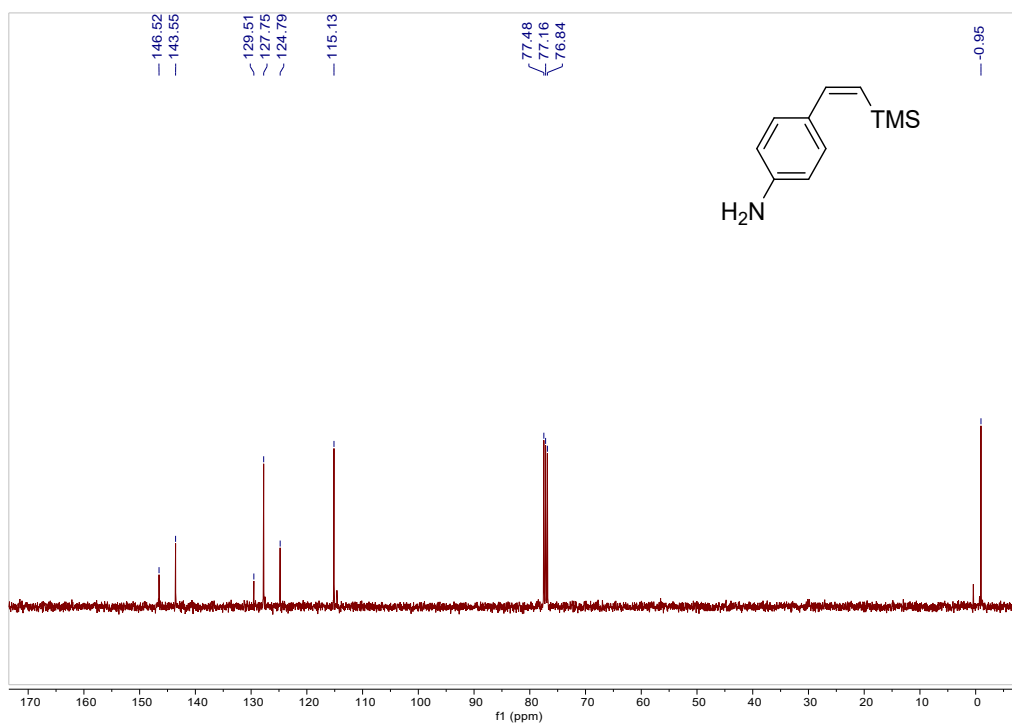
^1H NMR for compound **2m**



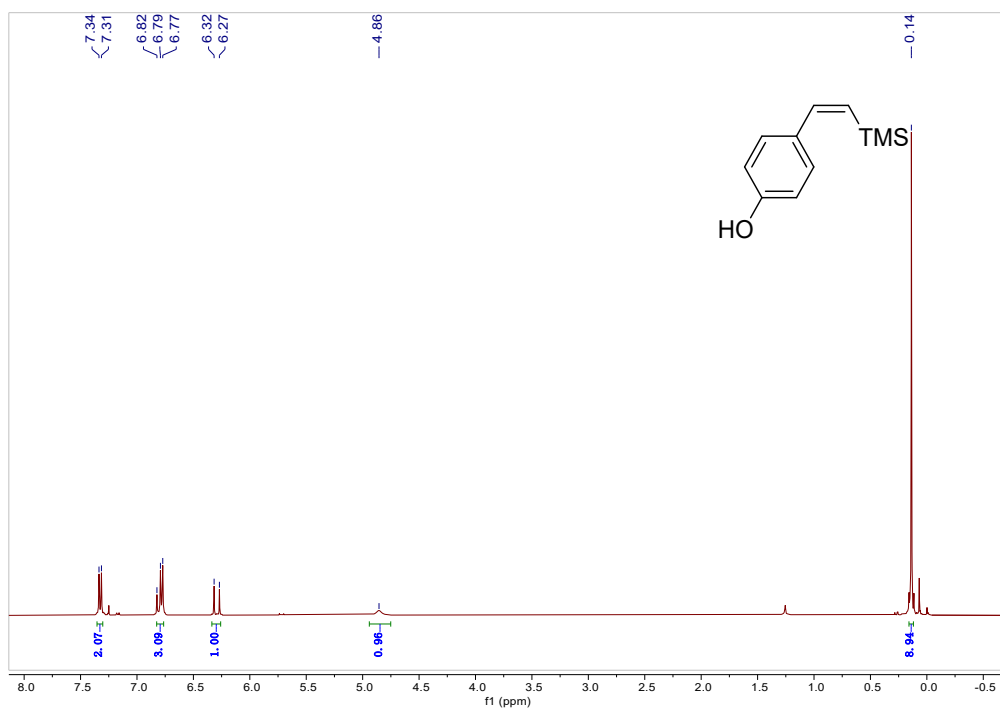
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2m**



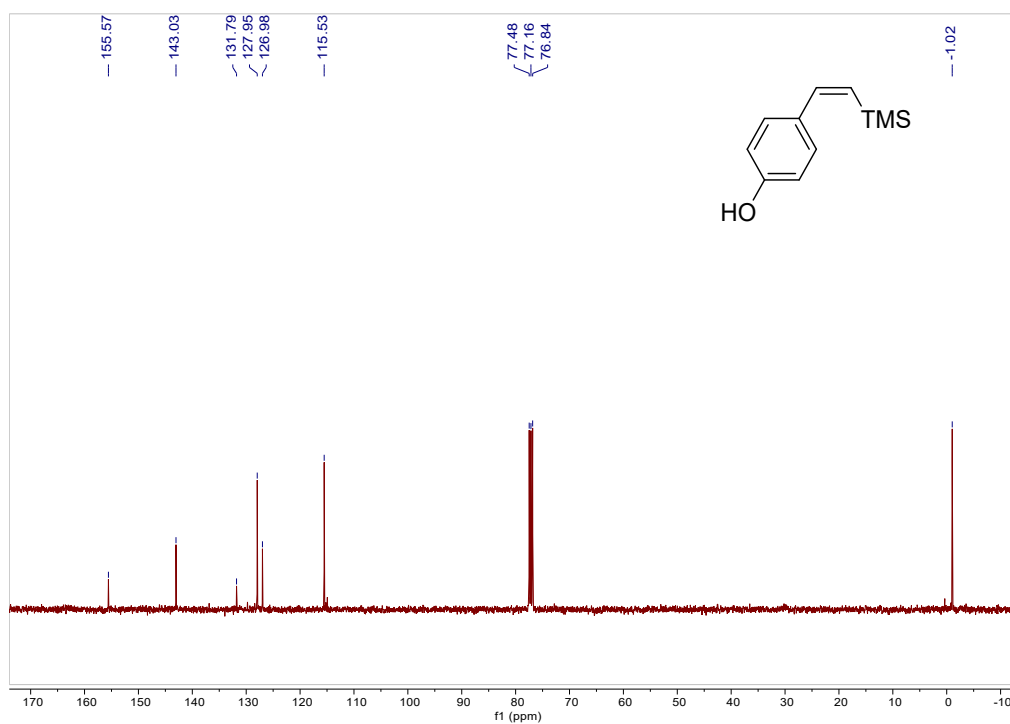
^1H NMR for compound **2n**



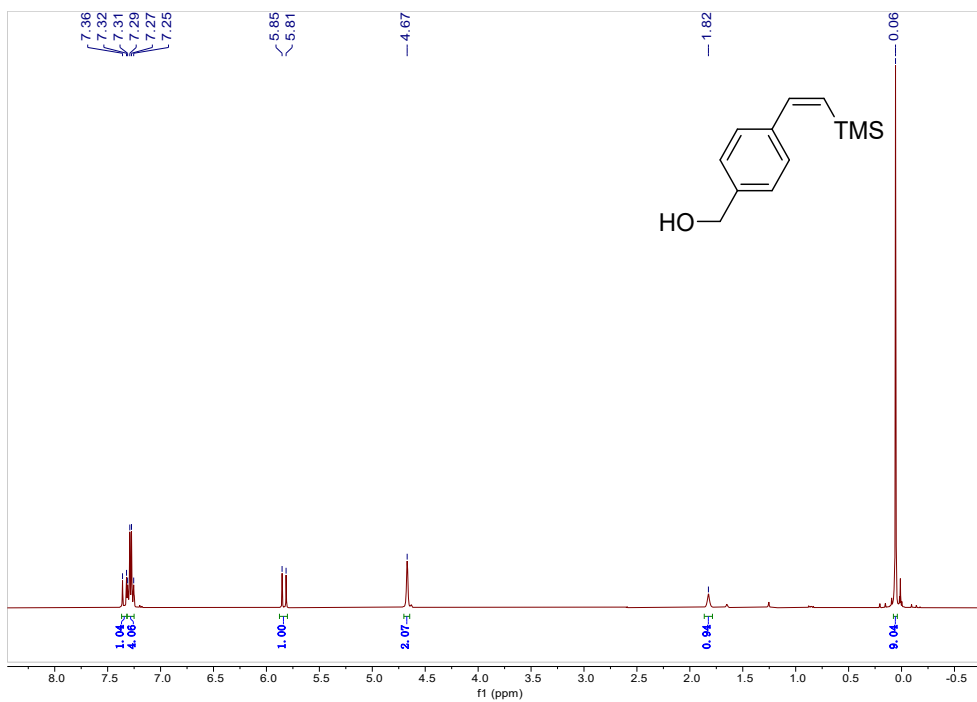
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2n**



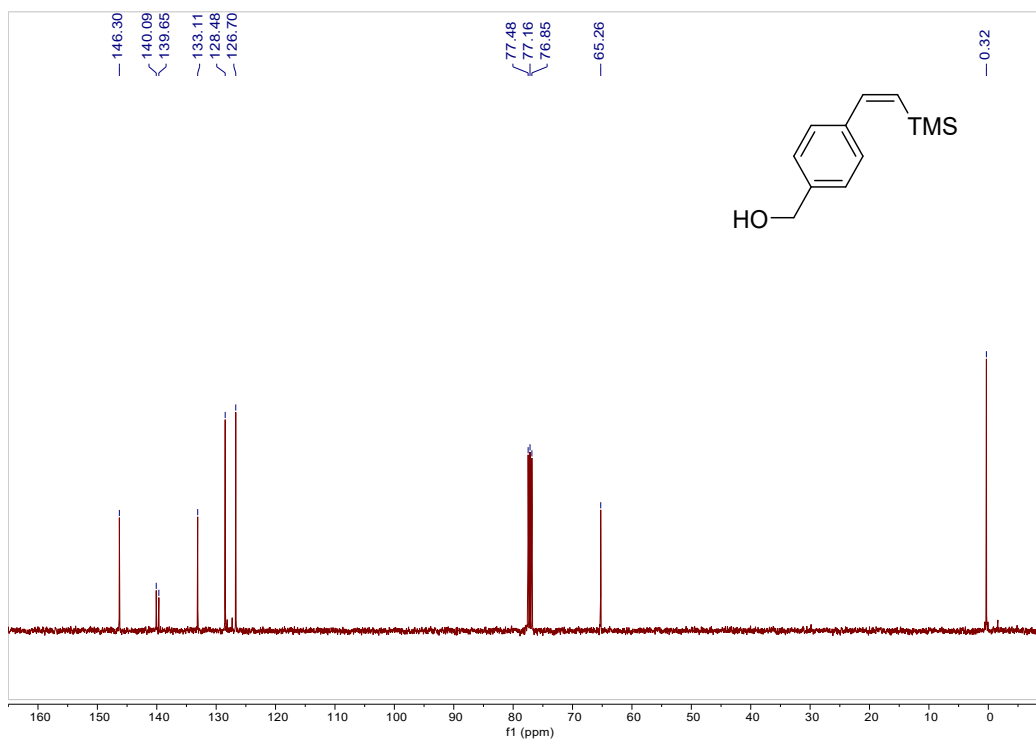
^1H NMR for compound **2o**



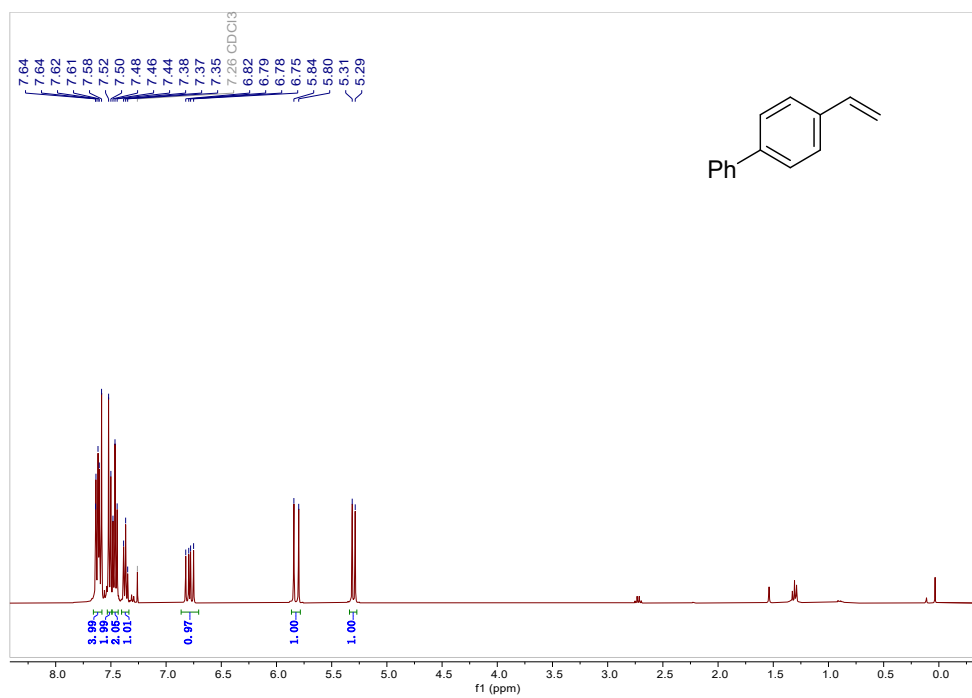
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2o**



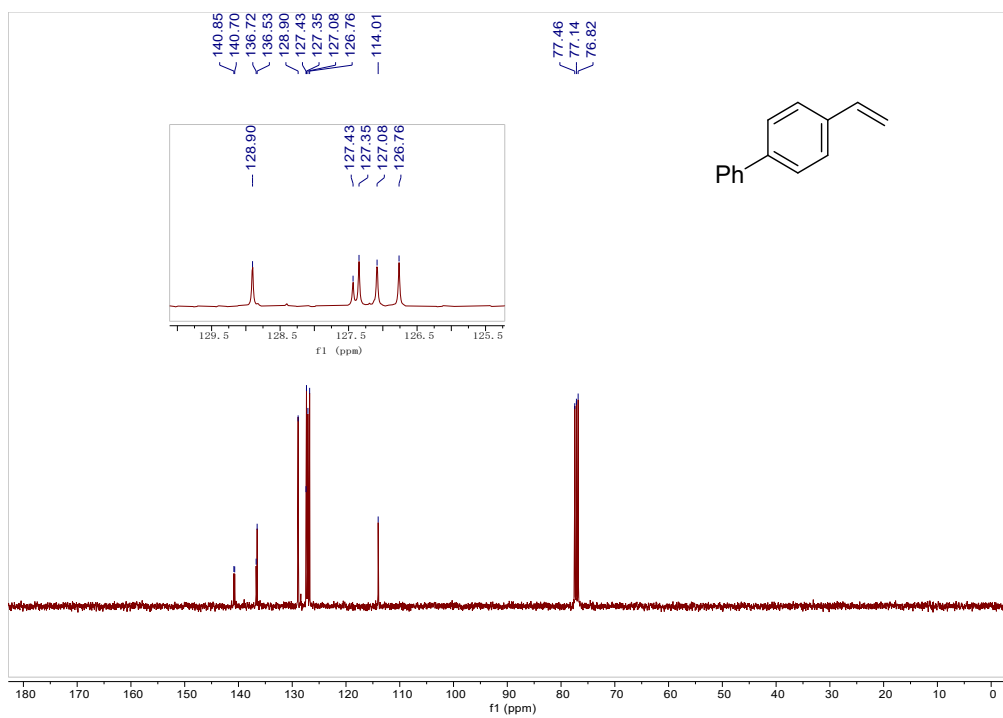
^1H NMR for compound **2p**



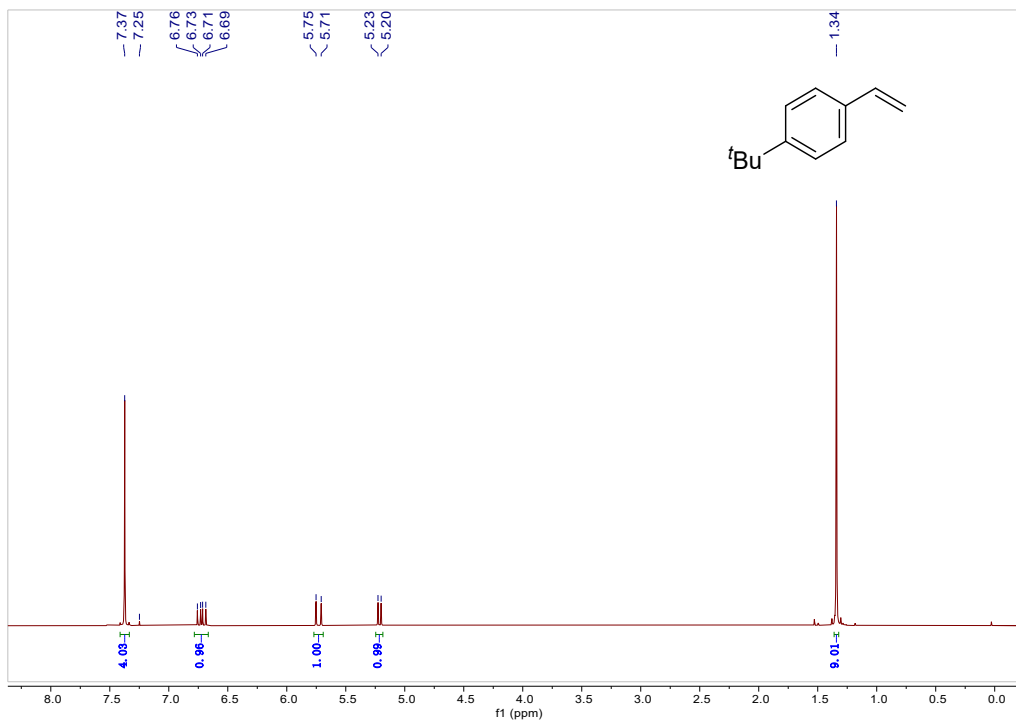
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2p**



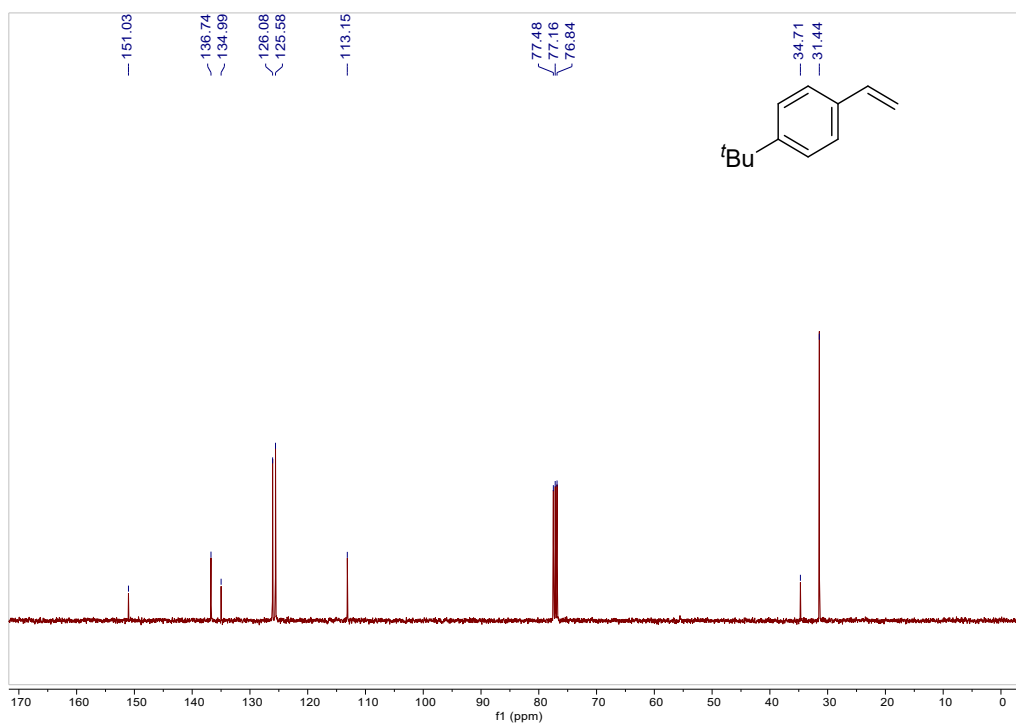
^1H NMR for compound **2q**



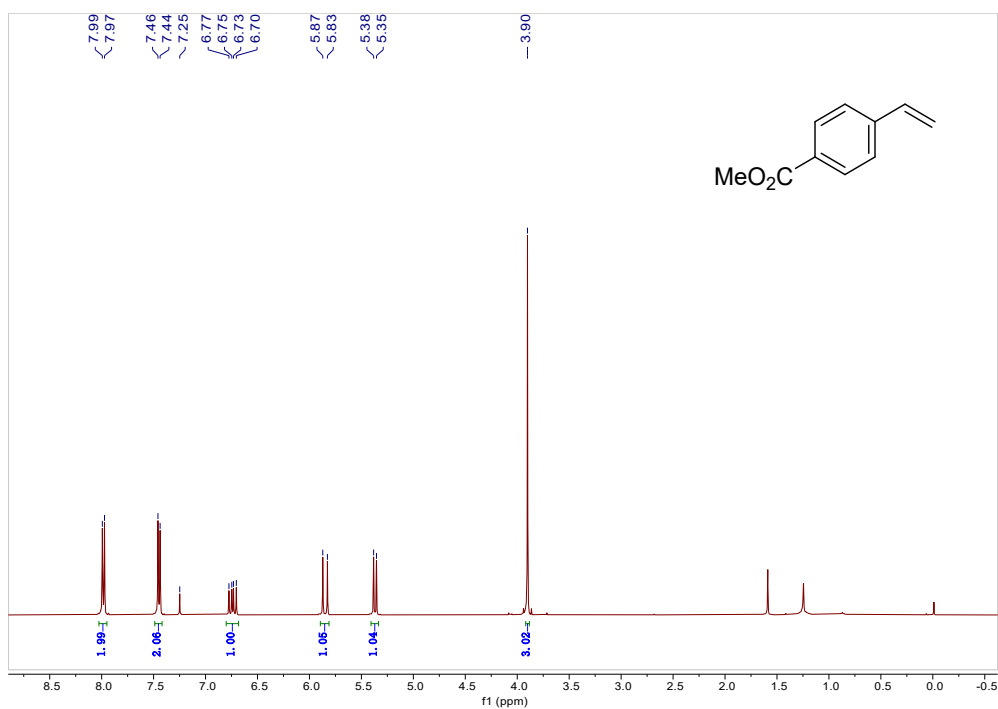
$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2q**



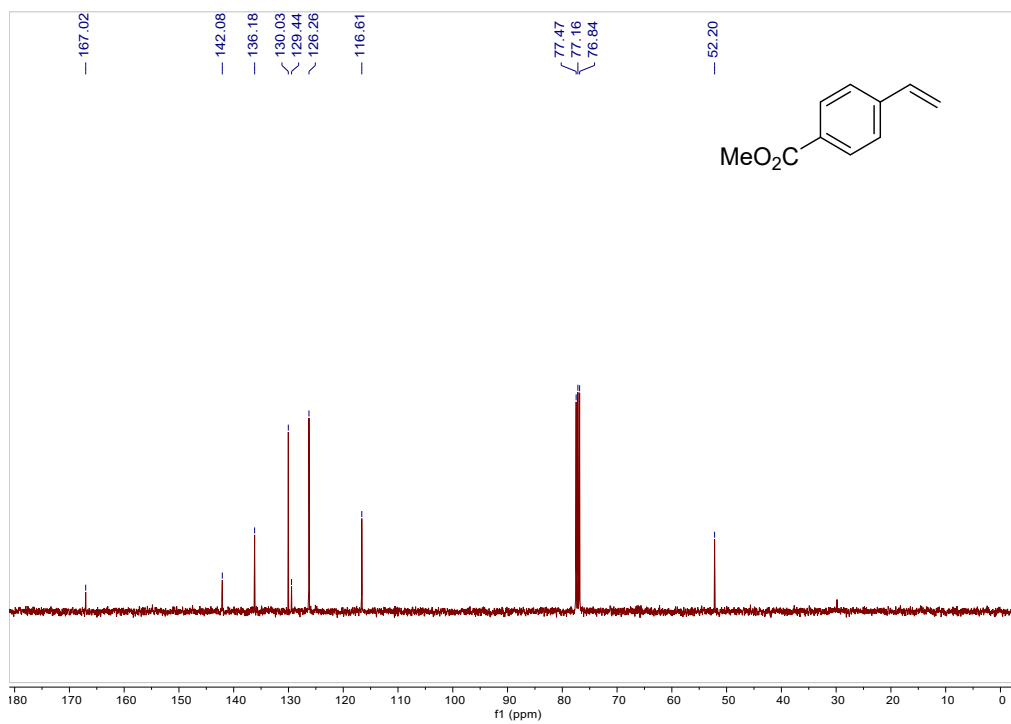
^1H NMR for compound **2r**



$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2r**



^1H NMR for compound **2s**



$^{13}\text{C}\{^1\text{H}\}$ NMR for compound **2s**