Supporting Information

Room temperature *Z*-selective hydrogenation of alkynes by hemilabile and non-innocent (*NNN*)Co(II) catalyst

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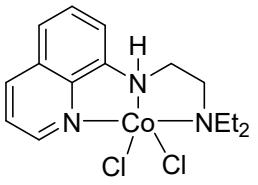
Contents

1. General Experimental

All manipulations were conducted under an argon atmosphere either in a glove box or by using standard Schlenk techniques in pre-dried glassware. The catalytic reactions were performed in oven-dried reaction vessels with Teflon screw caps. Methanol was dried and distilled from Mg-cake. All other liquid reagents were flushed with argon prior to use. The ligands *N1*,*N1*-diethyl-*N2*-(quinolin-8-yl)ethane-1,2-diamine (**1**),[1] 2-(diethylamino)-*N*-(quinolin-8-yl)acetamide (**3**),[2] *N*-methyl-8-aminoquinoline,[3] *N*-acetyl-8-aminoquinoline[4] were prepared according to the literature described procedures. All other chemicals were obtained from commercial sources and were used without further purification. Yields refer to the isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR. High resolution mass spectrometry (HRMS) mass spectra were recorded with a Thermo Scientific Q-Exactive, Accela 1250 pump. ^{1}H and ^{13}C NMR spectra were recorded at 400 or 500 MHz (^{1}H), 100 or 125 MHz, (^{13}C, DEPT) and 377 MHz (^{19}F) with Bruker AV 400 and AV 500 spectrometers in $CDCl_3$ solutions unless otherwise specified. The ^{1}H and ^{13}C NMR spectra were referenced to residual solvent signals ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.2 ppm). Virtual triplets are denoted as "vt".

GC Method. Gas Chromatography analyses were performed using a Shimadzu GC-2010 gas chromatograph equipped with a Shimadzu AOC-20s auto sampler and a Restek RTX-5 capillary column (30 m x 250 μm). The instrument was set to an injection volume of 1 μL, an inlet split ratio of 10:1, and inlet and detector temperatures of 250 and 320 °C, respectively. UHP-grade argon was used as carrier gas with a flow rate of 30 mL/min. The temperature program used for all the analyses is as follows: 80 °C, 1 min; 30 °C/min to 200 °C, 2 min; 30 °C/min to 260 °C, 3 min; 30 °C/min to 300 °C, 3 min.

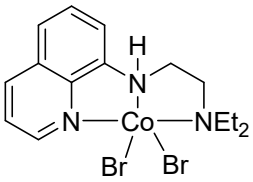
2. Procedure for Synthesis of Cobalt Complexes



(**2a**)

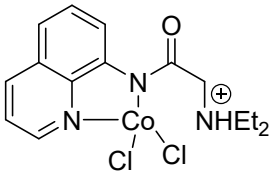
A solution of ligand **1** (0.243 g, 1.0 mmol) in THF (10 mL) was added dropwise to the anhydrous $CoCl_2$ (0.130 g, 1.0 mmol) in THF (10 mL) and the reaction mixture was stirred at room temperature for 12 h. The light pink coloured precipitate obtained was filtered and washed with Et_2O (5 mL x 3). Upon drying under vacuum, the light pink complex **2a** was

obtained. Yield: 0.339 g, 91%. The crystal suitable for a single-crystal X-ray diffraction was obtained from saturated solution of complex **2a** in acetonitrile at -15 ^{o}C. Elemental Analysis Calcd (%) for C, 48.28; H, 5.67; N, 11.26; Found: C, 48.36; H, 5.34; N, 10.95.



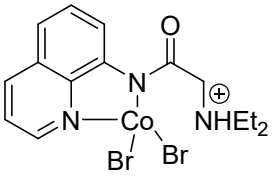
(**2b**)

A solution of ligand **1** (0.243 g, 1.0 mmol) in THF (10 mL) was added dropwise to the anhydrous $CoBr_2$ (0.219 g, 1.0 mmol) in THF (10 mL) and the reaction mixture was stirred at room temperature for 12 h. The light pink coloured precipitate obtained was filtered and washed with Et_2O (5 mL x 3). Upon drying under vacuum, the light pink complex **2b** was obtained. Yield: 0.430 g, 93%. Elemental Analysis Calcd (%) for C, 38.99; H, 4.58; N, 9.09; Found: C, 38.56; H, 4.78; N, 9.47.



(**4a**)

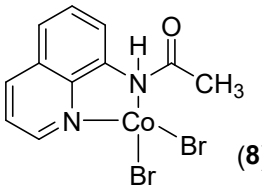
A solution of ligand **3** (0.257 g, 1.0 mmol) in THF (10 mL) was added dropwise to the anhydrous $CoCl_2$ (0.130 g, 1.0 mmol) in THF (10 mL) and the reaction mixture was stirred at room temperature for 12 h. The dark blue coloured precipitate obtained was filtered and washed with Et_2O (5 mL x 3). Upon drying under vacuum, the dark blue complex **4a** was obtained. Yield: 0.364 g, 94%. The crystal suitable for a single-crystal X-ray diffraction was obtained from saturated solution of complex **4a** in acetonitrile at -15 ^{o}C. Elemental Analysis Calcd (%) for C, 46.53; H, 4.95; N, 10.85. Found: C, 46.24; H, 4.74; N, 10.63.



(**4b**)

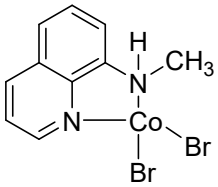
A solution of ligand **3** (0.257 g, 1.0 mmol) in THF (10 mL) was added dropwise to the anhydrous $CoBr_2$ (0.219 g, 1.0 mmol) in THF (10 mL) and the reaction mixture was stirred at room temperature for 12 h. The dark green coloured precipitate obtained was filtered and

washed with Et_2O (5 mL x 3). Upon drying under vacuum, the dark green complex **4b** was obtained. Yield: 0.452 g, 95%. Elemental Analysis Calcd (%) for C, 37.84; H, 4.02; N, 8.83. Found: C, 37.52; H, 3.95; N, 9.09.



(**8**)

A solution of *N*-acetyl-8-aminoquinoline (0.186 g, 1.0 mmol) in THF (10 mL) was added dropwise to the anhydrous $CoBr_2$ (0.219 g, 1.0 mmol) in THF (10 mL) and the reaction mixture was stirred at room temperature for 12 h. The greenish blue solution formed was concentrated under vacuum and Et_2O was added to the concentrated solution to obtain greenish blue precipitate. The decantation of the resulting solution followed by drying under vacuum yielded the greenish blue complex **8**. Yield: 0.296 g, 73%. Elemental Analysis Calcd (%) for C, 32.63; H, 2.49; N, 6.92. Found: C, 32.69; H, 2.97; N, 6.46



(**9**)

A solution of *N*-methyl-8-aminoquinoline (0.158 g, 1.0 mmol) in THF (10 mL) was added dropwise to the anhydrous $CoBr_2$ (0.219 g, 1.0 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature for 12 h. The dark purple solution obtained was concentrated under vacuum and Et_2O was added to precipitate the compound. Filtration of compound followed by washing with Et_2O and drying yielded the dark purple complex **9**. Yield: 0.294 g, 78%. Elemental Analysis Calcd (%) for C, 31.86; H, 2.67; N, 7.43. Found: C, 32.05; H, 2.89; N, 7.58.

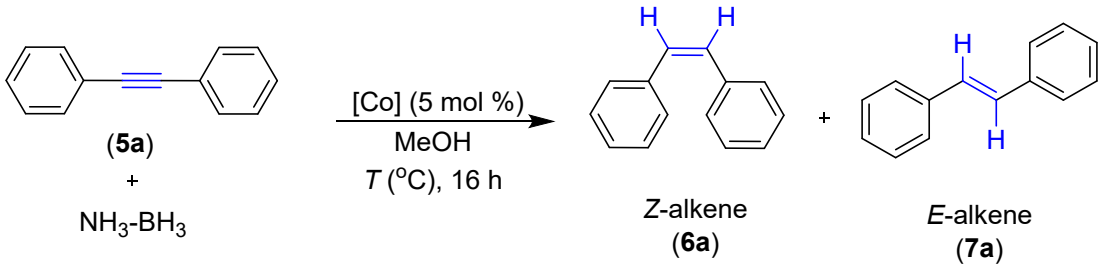
3. Representative Procedure for Hydrogenation

A Teflon screw-cap tube was introduced with catalyst **4b** (0.0048 g, 0.01 mmol), ammonia borane (0.0155 g, 0.5 mmol) and diphenylacetylene (0.089 g, 0.5 mmol) inside the glove box. The solvent MeOH (1.5 mL) was added to the reaction vessel under the argon atmosphere. The reaction mixture was then stirred at room temperature (27 ^{o}C) for 16 h. At ambient temperature, the reaction mixture was diluted with MeOH (5.0 mL) and resulting solution was concentrated under vacuum. The crude reaction mixture was purified by chromatography on silica gel using petroleum ether as eluent to obtain *Z*-stilbene **6a** (0.080 g, 89%).

Gram scale synthesis. Representative procedure for the hydrogenation followed, using 1.069 g (6.0 mmol) of **5a**, catalyst **4b** (0.057 g, 0.12 mmol), NH_3-BH_3 (0.185 g, 6.0 mmol) and MeOH (15 mL). The reaction proceeded smoothly and gave an excellent yield of *Z*-stilbene (0.908 g, 5.04 mmol, 84%) which ensures synthetic applicability of the optimized protocol in the gram-scale production.

4. Detailed Optimization

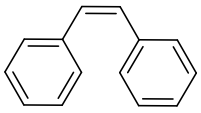
Table S1. Detailed Optimization of Reaction Conditions [a]



entry	[Co]	T (°C)	GC Conv	**6a** (%)	**7a** (%)
1	**2a**	65	100	85	14
2	**2b**	65	100	88	12
4	**4a**	65	100	87	13
5	**4b**	65	100	84	16
6 [b]	**2a**	65	75	61	14
7 [b]	**4a**	65	100	81	19
8	**2a**	27	55	48	7
9	**2b**	27	61	45	16
10	**4a**	27	100	87	7
11	**4b**	27	100	91	8
12 [c]	**4b**	27	100	**94 (89%)** [d]	**6**
13 [e]	**4b**	27	81	73	7
14 [b,c]	**4b**	27	35	24	11
15 [c,f]	**4b**	27	24	18	6
16 [c,g]	**4b**	27	54	50	4
17 [c,h]	**4b**	27	38	31	7
18 [c,i]	**4b**	27	65	42	8
19 [c]	$CoCl_2$	27	15	12	3
20 [c]	$CoBr_2$	27	56	47	9
21	$Co(OAc)_2$	27	52	45	5
22 [c]	**2a**	27	23	18	4
23 [c]	**2b**	27	21	17	4

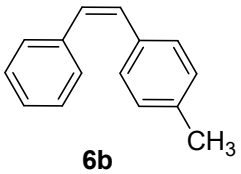
[a]Reaction conditions: Diphenyl acetylene (0.051 g, 0.50 mmol), [H_2]-source (0.50 mmol), solvent (1.5 mL). [b]Me_2NH-BH_3 was used as a hydrogen source. [c]2 mol % loading of catalyst. [d]Isolated yield. [e]1 mol % loading of **4b**. [f]EtOH as solvent. [gi]PrOH as solvent. [h]THF as solvent. [i]Toluene as solvent.

5. Characterization Data of *Z*-Alkenes



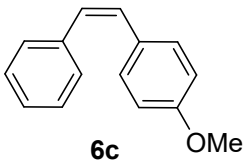
6a

(*Z*)-1,2-diphenylethene (6a):[5] The representative procedure was followed, using 1,2-diphenylethyne (**5a**; 0.089 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0048 g, 0.01 mmol). Purification by column chromatography on silica gel (petroleum ether) yielded **6a** (0.080 g, 89%) as a colourless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.29-7.19 (m, 10H, Ar−H), 6.63 (s, 2H, CH). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 137.4 (2C, C_q), 130.4 (2C, CH), 129.1 (4C, CH), 128.4 (4C, CH), 127.3 (2C, CH). HRMS (ESI): *m/z* Calcd for $C_{14}H_{12}$ + H^+ $[M + H]^+$ 181.1017; Found 181.1012.



6b

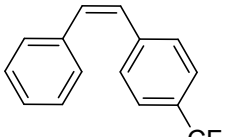
(*Z*)-1-methyl-4-styrylbenzene (6b):[5] The representative procedure was followed, using 1-methyl-4-(phenylethynyl)benzene (**5b**; 0.096 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0095 g, 0.02 mmol). Purification by column chromatography on silica gel (petroleum ether) yielded **6b** (0.084 g, 86%) as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 7.6 Hz, 2H, Ar−H), 7.36 (vt, J = 6.87, 7.63 Hz, 2H, Ar−H), 7.27-7.33 (m, 3H, Ar−H), 7.16 (d, J = 8.0 Hz, 2H, Ar−H), 6.69 (s, 2H, CH), 2.44 (s, 3H, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 137.7 (C_q), 137 (C_q), 134.4 (C_q), 130.4 (CH), 129.7 (CH), 129.1 (2C, CH) 129 (2C, CH), 128.9 (2C, CH), 128.4 (2C, CH), 127.1 (CH), 21.4 (CH_3). HRMS (ESI): *m/z* Calcd for $C_{15}H_{14}$ + H^+ $[M + H]^+$ 195.1174; Found 195.1168.



6c

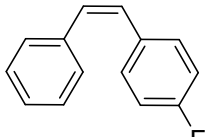
(*Z*)-1-methoxy-4-styrylbenzene (6c):[5] The representative procedure was followed, using 1-methoxy-4-(phenylethynyl)benzene (**5c**; 0.105 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5

mmol) and catalyst **4b** (0.0071 g, 0.015 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 10/1) yielded **6c** (0.091 g, 87%) as a yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.34-7.26 (m, 4H, Ar−H), 7.25-7.21 (m, 3H, Ar−H), 6.82-6.79 (m, 2H, Ar−H), 6.59 (d, J = 12.3 Hz, 1H, CH), 6.56 (d, J = 12.3 Hz, 1H, CH), 3.83 (s, 3H, OCH_3). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 158.9 (C_q), 137.8 (C_q), 130.3 (3C, CH), 129.9 (CH), 129.8 (C_q), 129 (3C, CH) 128.9 (CH), 128.4 (2C, CH), 127.1 (CH), 55.4 (CH_3). HRMS (ESI): *m/z* Calcd for $C_{15}H_{14}O + H^+$ $[M + H]^+$ 211.1123; Found 211.1117.



6d

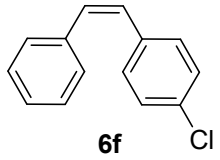
(*Z*)-1-styryl-4-(trifluoromethyl)benzene (6d):[5] The representative procedure was followed, using 1-(phenylethynyl)-4-(trifluoromethyl)benzene (**5d**; 0.074 g, 0.3 mmol), NH_3-BH_3 (0.0093 g, 0.30 mmol) and catalyst **4b** (0.0043 g, 0.009 mmol). Purification by column chromatography on silica gel (petroleum ether) yielded **6d** (0.048 g, 64%) as yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.47 (d, J = 8.4 Hz, 2H, Ar−H), 7.34 (d, J = 8.4 Hz, 2H, Ar−H), 7.27-7.20 (m, 5H, Ar−H), 6.73 (d, J = 12.9 Hz, 1H, CH), 6.60 (d, J = 12.3 Hz, 1H, CH). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 141.1 (C_q), 136.7 (C_q), 132.5 (CH), 129.3 (2C, CH), 129.0 (2C, CH), 128.9 (CH), 128.6 (2C, CH), 128.5 (q, $^{2}J_{C-F}$ = 22.9 Hz, C_q), 127.8 (CH), 125.3 (q, $^{3}J_{C-F}$ = 3.8 Hz, 2C, CH), 124.4 (q, $^{1}J_{C-F}$ = 271.6 Hz, CF_3). ^{19}F-NMR (377 MHz, $CDCl_3$): δ −62.5.



6e

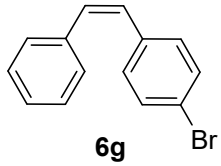
(*Z*)-1-fluoro-4-styrylbenzene (6e):[5] The representative procedure was followed, using 1-fluoro-4-(phenylethynyl)benzene (**5e**; 0.098 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0095 g, 0.02 mmol). Purification by column chromatography on silica gel (petroleum ether) yielded **6e** (0.067 g, 68%) as colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.29-7.24 (m, 7H, Ar−H), 6.95 (t, J = 8.6 Hz, 2H, Ar−H), 6.65 (d, J = 12.3 Hz, 1H, CH), 6.58 (d, J = 12.3 Hz, 1H, CH). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 162 (d, $^{1}J_{C-F}$ = 246.3 Hz, CF), 137.2 (C_q), 133.4 (d, $^{4}J_{C-F}$ = 3.7 Hz, C_q), 130.7 (d, $^{3}J_{C-F}$ = 8.0 Hz, 2C, CH), 130.5 (d, $^{5}J_{C-F}$ =

1.5 Hz, CH), 129.3 (CH), 129 (2C, CH), 128.5 (2C, CH), 127.4 (CH), 115.3 (d, $^2J_{C-F}$ = 21.1 Hz, 2C, CH). ^{19}F-NMR (377 MHz, $CDCl_3$): δ −114.7.



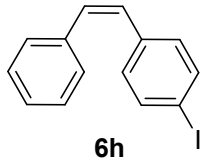
6f

(*Z*)-1-methyl-4-styrylbenzene (6f):[5] The representative procedure was followed, using 1-chloro-4-(phenylethynyl)benzene (**5f**; 0.106 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0071 g, 0.015 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) yielded **6f** (0.091 g, 85%) as a yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.25-7.21 (m, 5H, Ar−H), 7.20-7.16 (m, 4H, Ar−H), 6.64 (d, J = 12.2 Hz, 1H, CH), 6.54 (d, J = 12.2 Hz, 1H, CH). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 137 (C_q), 135.8 (C_q), 132.9 (C_q), 131.1 (CH), 130.4 (2C, CH), 129.1 (CH), 129 (2C, CH), 128.6 (2C,CH), 128.5 (2C, CH), 127.5 (CH). HRMS (ESI): *m/z* Calcd for $C_{14}H_{11}Cl + H^+$ $[M + H]^+$ 215.0628; Found 215.0622.



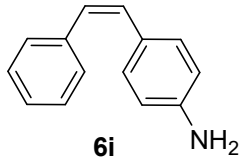
6g

(Z)-1-bromo-4-styrylbenzene (6g):[6] The representative procedure was followed, using 1-bromo-4-(phenylethynyl)benzene (**5g**; 0.077 g, 0.30 mmol), NH_3-BH_3 (0.0093 g, 0.3 mmol) and catalyst **4b** (0.0043 g, 0.009 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) yielded **6g** (0.049 g, 63%) as yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H, Ar−H), 7.28-7.22 (m, 5H, Ar−H), 7.13-7.11 (m, 2H, Ar−H), 6.65 (d, J = 12.3 Hz, 1H, CH), 6.52 (d, J = 12.1 Hz, 1H, CH). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 137 (C_q), 136.3 (C_q), 131.5 (2C, CH), 131.2 (CH), 130.7 (2C, CH), 129.1 (CH), 129 (2C, CH), 128.5 (2C, CH), 127.5 (CH), 121.1 (C_q).



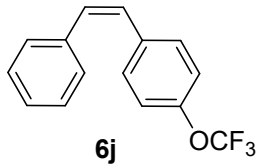
6h

(*Z*)-1-iodo-4-styrylbenzene (6h):[7] The representative procedure was followed, using 1-iodo-4-(phenylethynyl)benzene (**5h**; 0.152 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0071 g, 0.015 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) yielded **6h** (0.127 g, 83%) as white powder. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 2H, Ar−H), 7.29-7.24 (m, 5H, Ar−H), 7.02 (d, J = 8.1 Hz, 2H, Ar-H), 6.68 (d, J = 12.1 Hz, 1H, CH), 6.53 (d, J = 12.1 Hz, 1H, CH). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 137.5 (2C, CH), 137 (C_q), 136.8 (C_q), 131.3 (CH), 130.9 (2C, CH), 129.2 (CH), 128.9 (2C, CH), 128.5 (2C, CH), 127.5 (CH), 92.7 (C_q).



6i

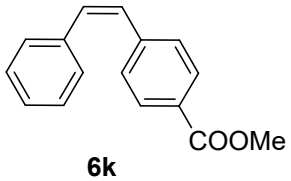
(*Z*)-4-styrylaniline (6i):[5] The representative procedure was followed, using 4-(phenylethynyl)aniline (**5i**; 0.097 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0095 g, 0.02 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 5/1) yielded **6i** (0.084 g, 86%) as a brown oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.34-7.18 (m, 5H, Ar−H), 7.09 (d, J = 8.4 Hz, 2H, Ar−H), 6.55 (d, J = 8.4 Hz, 2H, Ar−H), 6.50 (d, J = 12.2 Hz, 1H, CH), 6.45 (d, J = 12.2 Hz, 1H, CH), 3.69 (s, 2H, NH_2). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 145.6 (C_q), 138.1 (C_q), 130.3 (CH), 130.3 (2C, CH), 129 (2C, CH), 128.3 (2C, CH), 127.8 (CH), 127.7 (C_q), 126.9 (CH), 114.9 (2C, CH). HRMS (ESI): *m/z* Calcd for $C_{14}H_{13}N + H^+$ $[M + H]^+$ 196.1126; Found 196.1121.



6j

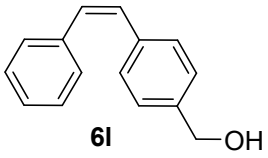
(*Z*)-1-styryl-4-(trifluoromethoxy)benzene (6j): The representative procedure was followed, using 1-(phenylethynyl)-4-(trifluoromethoxy)benzene (**5j**; 0.131 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0095 g, 0.02 mmol). Purification by column chromatography on silica (petroleum ether/EtOAc: 10/1) yielded **6j** (0.103 g, 78%) as a

colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.18-7.14 (m, 7H, Ar−H), 6.98 (d, J = 8.4 Hz, 2H, Ar−H), 6.58 (d, J = 12.3 Hz, 1H, Ar−H), 6.48 (d, J = 12.3 Hz, 1H, Ar−H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 148.3 (C_q), 137 (C_q), 136.1 (C_q), 131.4 (CH), 130.5 (2C, CH), 129 (2C, CH), 128.9 (CH), 128.6 (3C, CH), 127.6 (CH), 120.8 (CH), 120.6 (q, $^{1}J_{C-F}$ = 257.2 Hz, CF_3). ^{19}F-NMR (377 MHz, $CDCl_3$): δ −57.8 (s). HRMS (ESI): *m/z* Calcd for $C_{15}H_{11}OF_3$ + H^+ $[M + H]^+$ 265.0840; Found 265.0835.



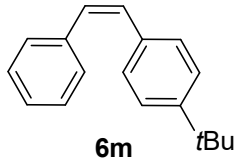
6k

methyl (*Z*)-4-styrylbenzoate (6k):[5] The representative procedure was followed, using methyl 4-(phenylethynyl)benzoate (**5k;** 0.118 g, 0.50 mmol), NH_3-BH_3 (0.015 g, 0.5 mmol) and catalyst **4b** (0.0071 g, 0.015 mmol). Purification by column chromatography on silica (petroleum ether/EtOAc: 10/1) yielded **6k** (0.097 g, 81%) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.4 Hz, 2H, Ar−H), 7.36-7.35 (d, J = 8.4 Hz, 2H, Ar−H), 7.27 (br s, 5H, Ar−H), 6.76 (d, J = 12.6 Hz, 1H, CH), 6.66 (d, J = 12.2 Hz, 1H, CH), 3.95 (s, 3H, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 167.1 (C_q, CO), 142.3 (C_q), 136.8 (C_q), 132.4 (CH), 129.7 (2C, CH), 129.4 (CH), 129 (4C, CH), 128.8 (C_q), 128.5 (2C, CH), 127.7 (CH), 52.2 (CH_3). HRMS (ESI): *m/z* Calcd for $C_{16}H_{14}O_2$ + H^+ $[M + H]^+$ 239.1072; Found 239.1067.



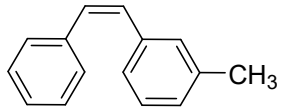
6l

(*Z*)-(4-styrylphenyl)methanol (6l):[8] The representative procedure was followed, using (4-(phenylethynyl)phenyl)methanol (**5l**; 0.104 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0071 g, 0.015 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 10/1) yielded **6l** (0.091 g, 87%) as a brown oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.35-7.22 (m, 9H, Ar−H), 6.67 (d, J = 12.2 Hz, 1H, CH), 6.63 (d, J = 12.2 Hz, 1H, CH), 4.68 (s, 2H, CH_2), 1.88 (s, 1H, OH). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 139.8 (C_q), 137.4 (C_q), 136.8 (C_q), 130.5 (CH), 130 (CH), 129.2 (2C, CH), 129 (2C, CH), 128.4 (2C, CH), 127.3 (CH), 127.1 (2C, CH), 65.3 (CH_2). HRMS (ESI): *m/z* Calcd for $C_{15}H_{14}O$ + H^+ $[M + H]^+$ 211.1123; Found 211.1117.



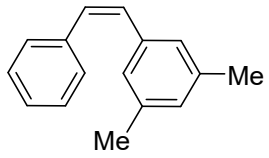
6m

(*Z*)-1-(tert-butyl)-4-styrylbenzene (6m):[9] The representative procedure was followed, using 1-(tert-butyl)-4-(phenylethynyl)benzene (**5m**; 0.117 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0048 g, 0.01 mmol). Purification by column chromatography on silica gel (petroleum ether) yielded **6m** (0.103 g, 87%) as a colourless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.35-7.22 (m, 9H, Ar−H), 6.60 (s, 2H, CH), 1.34 (s, 9H, CH_3). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 150.3 (C_q), 137.8 (C_q), 134.4 (C_q), 130.3 (CH), 129.5 (CH), 129 (2C, CH), 128.8 (2C, CH), 128.4 (2C, CH), 127.1 (CH), 125.3 (2C, CH), 34.7 (C_q), 31.5 (3C, CH_3). HRMS (ESI): *m/z* Calcd for $C_{18}H_{20} + H^+$ $[M + H]^+$ 237.1643; Found 237.1638.



6n

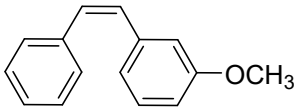
(*Z*)-1-methyl-3-styrylbenzene (6n):[5] The representative procedure was followed, using 1-methyl-3-(phenylethynyl)benzene (**5n**; 0.096 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0071 g, 0.015 mmol). Purification by column chromatography on silica gel (petroleum ether) yielded **6n** (0.081 g, 83%) as a colourless solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.36-7.27 (m, 5H, Ar−H), 7.21-7.13 (m, 3H, Ar−H), 7.10-7.09 (d, J = 6.9 Hz, 1H, Ar−H), 6.66 (s, 2H, CH), 2.35 (s, 3H, CH_3). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 137.9 (C_q), 137.5 (C_q), 137.3 (C_q), 130.5 (CH), 130.2 (CH), 129.8 (CH), 129 (2C, CH), 128.3 (2C, CH), 128.2 (CH), 128 (CH), 127.2 (CH), 126 (CH), 21.5 (CH_3). HRMS (ESI): *m/z* Calcd for $C_{15}H_{14} + H^+$ $[M + H]^+$ 195.1174; Found 195.1168.



6o

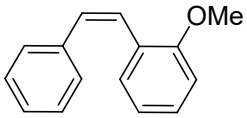
(*Z*)-1,3-dimethyl-5-styrylbenzene (6o): The representative procedure was followed, using 1,3-dimethyl-5-(phenylethynyl)benzene (**5o**; 0.103 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0071 g, 0.015 mmol). Purification by column chromatography on

silica gel (petroleum ether) yielded **6o** (0.079 g, 76%) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.18 (d, J = 7.1 Hz, 2H, Ar−H), 7.15-7.09 (m, 3H, Ar−H), 6.80 (s, 2H, Ar−H), 6.75 (s, 1H, Ar−H), 6.46 (s, 2H, CH), 2.13 (s, 6H, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 137.8 (2C, C_q), 137.6 (C_q), 137.3 (C_q), 130.6 (CH), 130.1 (CH), 129.1 (2C, CH), 128.9 (CH), 128.3 (2C, CH), 127.2 (CH), 126.8 (2C, CH), 21.4 (2C, CH_3). HRMS (ESI): *m/z* Calcd for $C_{16}H_{16} + H^+$ [M + H]$^+$ 209.1330; Found 209.1325.



6p

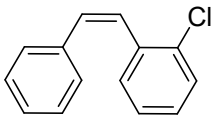
(*Z*)-1-methoxy-3-styrylbenzene (6p):[9] The representative procedure was followed, using 1-methoxy-3-(phenylethynyl)benzene (**5p**; 0.104 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0071 g, 0.015 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 5/1) yielded **6p** (0.078 g, 74%) as a colourless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.30-7.14 (m, 6H, Ar−H), 6.85 (d, J = 7.6 Hz, 1H, Ar−H), 6.80 (vt, J = 2.3 Hz, 1H, Ar−H), 6.76 (dd, J = 8.4, 2.3 Hz, 1H, Ar−H), 6.64 (d, J = 12.2 Hz, 1H, CH), 6.58 (d, J = 12.2 Hz, 1H, CH), 3.66 (s, 3H, CH_3). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 159.5 (C_q), 138.7 (C_q), 137.4 (C_q), 130.7 (CH), 130.3 (CH), 129.4 (CH), 129.1 (2C, CH), 128.4 (2C, CH), 127.3 (CH), 121.7 (CH), 113.9 (CH), 113.5 (CH), 55.2 (CH_3). HRMS (ESI): *m/z* Calcd for $C_{15}H_{14}O + H^+$ [M + H]$^+$ 211.1123; Found 211.1117.



6q

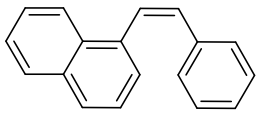
(Z)-1-methoxy-2-styrylbenzene (6q): The representative procedure was followed, using 1-methoxy-2-(phenylethynyl)benzene (**5q**; 0.104 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0071 g, 0.015 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 10:1) yielded **6q** (0.096 g, 91%) as a yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.25-7.15 (m, 7H, Ar−H), 6.89 (d, J = 8.4 Hz, 1H, Ar−H), 6.76 (t, J = 7.6 Hz, 1H, Ar−H), 6.71 (d, J = 12.2 Hz, 1H, CH), 6.64 (d, J = 12.2 Hz, 1H, CH) 3.82 (s, 3H, CH_3). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 157.4 (C_q), 137.5 (C_q), 130.4 (CH), 130.3 (CH), 129 (2C, CH), 128.8 (CH), 128.2 (2C, CH), 127.1 (CH), 126.5 (C_q), 126 (CH), 120.8 (CH),

110.9 (CH), 55.6 (CH_3). HRMS (ESI): *m/z* Calcd for $C_{15}H_{14}O + H^+$ $[M + H]^+$ 211.1123; Found 211.1117.



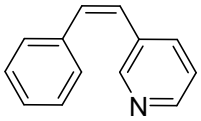
6r

(*Z*)-1-chloro-2-styrylbenzene (6r): The representative procedure was followed, using 1-chloro-2-(phenylethynyl)benzene (**5r**; 0.106 g, 0.50 mmol), NH_3-BH_3 (0.015 g, 0.5 mmol) and catalyst **4b** (0.007 g, 0.015 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded **6r** (0.087 g, 81%) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.0 Hz, 1H, Ar−H), 7.22-7.16 (m, 7H, Ar−H), 7.05 (t, J = 7.5 Hz, 1H, Ar−H), 6.74 (d, J = 12.3 Hz, 1H, CH), 6.69 (d, J = 12.3 Hz, 1H, CH). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 136.6 (C_q), 136.2 (C_q), 133.9 (C_q), 131.9 (CH), 130.9 (CH), 129.7 (CH), 129.2 (2C, CH), 128.7 (CH), 128.4 (2C, CH), 127.5 (CH), 127.4 (CH), 126.5 (CH). HRMS (ESI): *m/z* Calcd for $C_{14}H_{11}Cl + H^+$ $[M + H]^+$ 215.0628; Found 215.0622.



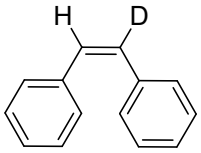
6s

(*Z*)-1-styrylnaphthalene (6s):[6] The representative procedure was followed, using 1-(phenylethynyl)naphthalene (**5s**; 0.114 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0071 g, 0.015 mmol). Purification by column chromatography on silica gel (petroleum ether) yielded **6s** (0.090 g, 78%) as a colourless solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.11-8.09 (m, 1H, Ar−H), 7.91-7.90 (s, 1H, Ar−H), 7.81 (d, J = 7.6 Hz, 1H, Ar−H), 7.54-7.49 (m, 2H, Ar−H), 7.39-7.34 (m, 2H, Ar−H), 7.11 (s, 5H, Ar−H), 7.08 (d, J = 12.2 Hz, 1H, CH), 6.86 (d, J = 12.2 Hz, 1H, CH). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 136.9 (C_q), 135.4 (C_q), 133.8 (C_q), 132.2 (CH), 131.7 (C_q), 129.2 (2C, CH), 128.7 (CH), 128.6 (CH), 128.2 (2C, CH), 127.7 (CH), 127.3 (CH), 126.6 (CH), 126.2 (CH), 126.1 (CH), 125.8 (CH), 125.0 (CH). HRMS (ESI): *m/z* Calcd for $C_{18}H_{14} + H^+$ $[M + H]^+$ 231.1174; Found 231.1168.



6t

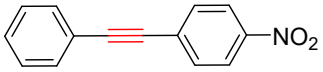
(Z)-3-styrylpyridine (6t): The representative procedure was followed, using 3-(phenylethynyl)pyridine (**5t;** 0.054 g, 0.30 mmol), NH_3-BH_3 (0.0093 g, 0.3 mmol) and catalyst **4b** (0.0043 g, 0.009 mmol). Purification by column chromatography on silica (petroleum ether/EtOAc: 5/1) yielded **6t** (0.046 g, 85%) as a brown oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.54-8.53 (d, J = 1.5 Hz, 1H, Ar−H), 8.47 (dd, J = 5.0, 4.6 Hz, 1H, Ar−H), 7.56 (d, J = 8.0 Hz, 1H, Ar−H), 7.32-7.26 (m, 5H, Ar−H), 7.17 (dd, J = 8.0, 5.0 Hz, 1H, Ar−H), 6.80 (d, J = 12.2 Hz, 1H, CH), 6.60 (d, J = 12.2 Hz, 1H, CH). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 150.3 (CH), 148.2 (CH), 136.7 (C_q), 136 (CH), 133.1 (C_q), 132.9 (CH), 128.8 (2C, CH), 128.7 (2C, CH), 127.7 (CH), 126.6 (CH), 123.2 (CH). HRMS (ESI): *m/z* Calcd for $C_{13}H_{11}N$ + H^+ $[M + H]^+$ 182.0970; Found 182.0964.



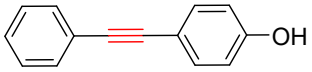
6a-[D]

(*Z*)-(Ethene-1,2-diyl-1-*d*)dibenzene (6a-[D]): The representative procedure was followed, using 1,2-diphenylethyne (**5a**; 0.089 g, 0.50 mmol), NH_3-BH_3 (0.0155 g, 0.5 mmol) and catalyst **4b** (0.0048 g, 0.01 mmol) in CD_3OD. Purification by column chromatography on silica gel (petroleum ether) yielded **6a-[D]** (0.078 g, 86%) as a colourless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.29-7.19 (m, 10H, Ar−H), 6.63 (1H, CH). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 137.4 (C_q), 137.3 (C_q), 130.4 (CH), 130.3 (CH), 129.1 (CH), 128.4 (CH), 127.3 (CH).

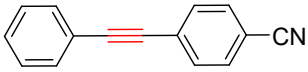
6. Unsuccessful Substrates



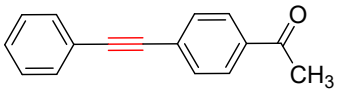
(42 : 28 : 28)
(Z : E : A)



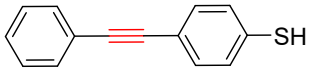
No Reaction



Multiple spots on the TLC



Multiple products



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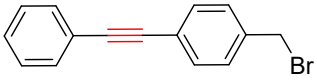

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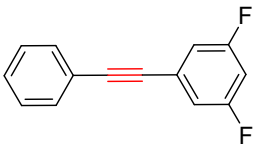

Mixture of products
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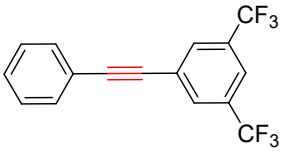

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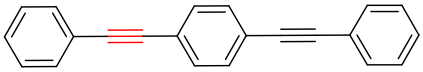
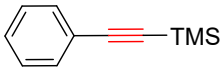
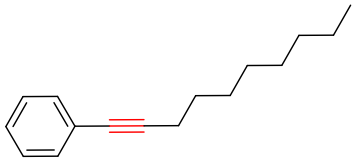


Multiple products



very less conversion at rt
multiple products at 50 °C

No reaction at rt
multiple products at 50 °C



No reaction at rt
multiple products at 50 °C

7. Mechanistic Experiments

Procedure for Rate of Reaction (Electronic Effect). To a flame dried screw-cap tube equipped with magnetic stir bar were introduced 1-methoxy-4-(phenylethynyl)benzene (**5c**, 0.042 g, 0.2 mmol) or 1-(phenylethynyl)-4-(trifluoromethyl)benzene (**5d**, 0.049 g, 0.2 mmol), NH_3-BH_3 (0.006 g, 0.2 mmol), **4b** (0.0029 g, 3 mol %), *n*-dodecane (0.025 mL, 0.11 mmol, internal standard) and MeOH (1.5 mL) inside the glove-box. The reaction mixture was then stirred at room temperature on magnetic stirrer. At regular intervals (2.5, 5, 10, 15, 20, 25, 30, 35 min), the reaction vessel was taken to glove box and an aliquot of sample was withdrawn to the GC vial. The sample was diluted with MeOH and subjected to GC analysis. The concentration of product **6c** or **6d** obtained in each sample was determined with respect to the internal standard *n*-dodecane. The data of the concentration of the product **6c** or **6d** *versus* time (min) plot was drawn (Figure S1) with Origin Pro 8.5, and the rate was determined by initial rate method (up to 35 min). The data were taken from the average of two independent experiments. The initial rate obtained for the transfer hydrogenation of 1-methoxy-4-(phenylethynyl)benzene (**5c**) was 1.02 x 10^{-3} $Mmin^{-1}$. Similarly, the rate for the transfer hydrogenation of 1-(phenylethynyl)-4-(trifluoromethyl)benzene (**5d**) was 0.77 x 10^{-3} $Mmin^{-1}$. Therefore, the rate (4-OMe)/ rate (4-CF_3) = 1.02 x 10^{-3} /0.77 x 10^{-3} = 1.32.

Table S2. Time-dependent formation of product **6c** or **6d** from **5c** and **5d**.

Time (min)	**6c** [M]	**6d** [M]
2.5	0.0240	0.0249
5	0.0319	0.0272
10	0.0345	0.0303
15	0.0396	0.0328
20	0.0442	0.0355
25	0.0499	0.0413
30	0.0538	0.0474
35	0.0603	0.0496

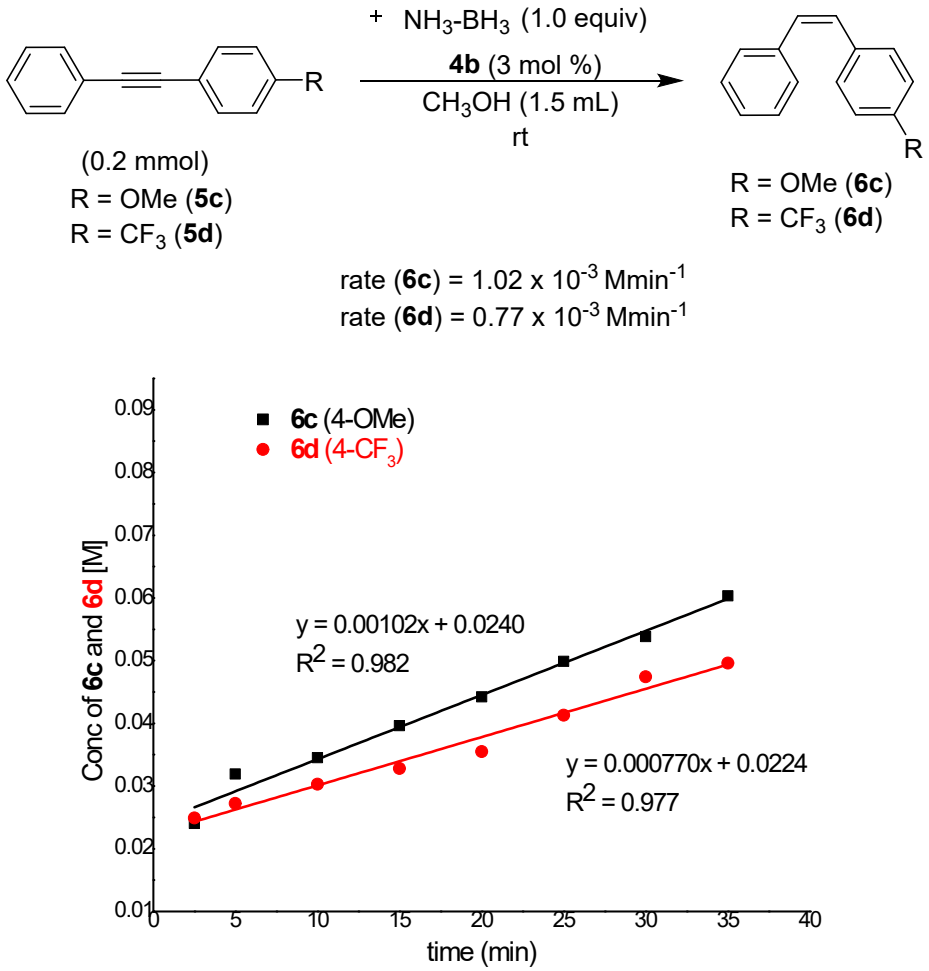


Figure S1. Time dependent formation of product **6c** or **6d** from **5c** and **5d**.

Procedure for Competition Experiment (Electronic Effect). To a flame dried screw-cap tube equipped with magnetic stir bar were introduced 1-methoxy-4-(phenylethynyl)benzene (**5c**, 0.042 g, 0.2 mmol) or 1-(phenylethynyl)-4-(trifluoromethyl)benzene (**5d**, 0.049 g, 0.2 mmol), NH_3-BH_3 (0.006 g, 0.2 mmol), **4b** (0.0029 g, 3 mol %), and MeOH (1 mL) inside the glove-box. The reaction mixture was then stirred at room temperature on magnetic stirrer for 30 min. After that the reaction was quenched with MeOH and purification by column chromatography on silica gel yielded product **6c** (0.068 mmol) and **6d** (0.058 mmol).

Procedure for Deuterium Labelling Experiment. A Teflon screw-cap tube equipped with magnetic bar was introduced the catalyst **4b** (0.0048 g, 0.01 mmol), ammonia borane (0.0155 g, 0.5 mmol) and diphenylacetylene (0.089 g, 0.5 mmol) inside the glove box. The solvent CD_3OD (1.5 mL) was added to the reaction vessel under the argon atmosphere. The reaction mixture was then stirred at room temperature (27 ^oC) for 16 h. At ambient temperature, the reaction mixture was diluted with MeOH (5.0 mL) and resulting solution was concentrated under vacuum. The crude reaction mixture was then purified by flash chromatography using petroleum ether as eluent to obtain deuterated *Z*-stilbene **6a**-[D] (0.078 g, 86%).

Procedure for Attempted Over-Hydrogenation using Excess of H_3NBH_3 (from 5a). A Teflon screw-cap tube equipped with magnetic bar was introduced the catalyst **4b** (0.0048 g, 0.01 mmol), ammonia borane (0.031 g, 1 mmol) and diphenylacetylene (0.089 g, 0.5 mmol) inside the glove box. The solvent MeOH (2 mL) was added to the reaction vessel under the argon atmosphere. The reaction mixture was then stirred at room temperature (27 ^oC) for 16 h. At ambient temperature, the reaction mixture was diluted with MeOH (5.0 mL) and resulting solution was concentrated under vacuum. The crude reaction mixture was then purified by flash chromatography using petroleum ether as eluent to obtain *Z*-stilbene **6a** (0.067 g, 74%).

Procedure for Attempted Isomerization of *Z*-Stilbene. A Teflon screw-cap tube equipped with magnetic bar was introduced the catalyst **4b** (0.0048 g, 0.01 mmol), ammonia borane (0.0155 g, 0.5 mmol) and *Z*-stilbene (0.090 g, 0.5 mmol) inside the glove box. The solvent MeOH (1.5 mL) was added to the reaction vessel under the argon atmosphere. The reaction mixture was then stirred at 60 ^oC for 16 h. At ambient temperature, the reaction mixture was diluted with MeOH (5.0 mL) and resulting solution was concentrated under vacuum. The crude reaction mixture was then purified by flash chromatography using petroleum ether as eluent to obtain *E*-stilbene **7a** (0.050 g, 55%).

Time Course Experiment for Isomerization of *Z*-Stilbene. A Teflon screw-cap tube equipped with magnetic bar was introduced the catalyst **4b** (0.001 g, 0.002 mmol), ammonia borane (0.003 g, 0.1 mmol), *n*-dodecane (0.025 mL, 0.11 mmol, internal standard) and *Z*-stilbene (0.018 g, 0.1 mmol) inside the glove box. The solvent MeOH (1 mL) was added to the reaction vessel under the argon atmosphere. The reaction mixture was then stirred at 60

°C. At regular intervals (5, 10, 20, 20, 30, 60, 120, 180, 300, 420 min), the reaction vessel was taken to the glove box and an aliquot of sample was withdrawn to the GC vial. The sample was diluted with MeOH and subjected to GC analysis. The concentration of **6a** and **7a** in each sample was determined with respect to the internal standard *n*-dodecane (Table S3). The data of the concentration of **6a** and **7a** *versus* time (min) plot was drawn (Figure S2) with Origin Pro 8.5

Table S3. Time-dependent formation of product **7a** from **6a**.

Time (min)	**6a** [M]	**7a** [M]
0	0.1	0
5	0.082	0.018
10	0.076	0.024
20	0.071	0.029
30	0.068	0.032
60	0.066	0.034
120	0.064	0.036
180	0.063	0.037
300	0.061	0.039
420	0.059	0.041

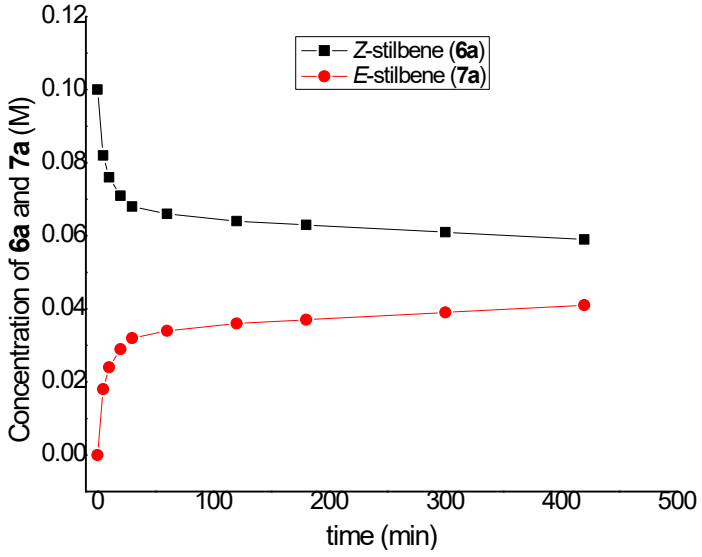


Figure S2. Time-dependent formation of **7a** from **6a**.

8. Crystallographic Data

X-ray intensity data measurements of compounds **2a** and **4a** were carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out with Mo micro-focus sealed tube diffraction source (MoK_{α}= 0.71073 Å) at 100(2) K temperature. The X-ray generator was operated at 50 kV and 1.4 mA. A preliminary set of cell constants and an orientation matrix were calculated from three matrix sets of 36 frames (each matrix run consists of 12 frames). Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 40 secs keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX3 program (Bruker, 2016).[10] All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2016). Using the APEX3 (Bruker) program suite, the structure was solved with the ShelXS-97(Sheldrick, 2008)[11] structure solution program, using direct methods. The model was refined with a version of ShelXL-2018/3 (Sheldrick, 2015)[12] using Least Squares minimization. All the hydrogen atoms were placed in a geometrically idealized position and constrained to ride on its parent atoms. The *ORTEP* III[13] view of the compounds were drawn with 50% probability displacement ellipsoids, and H atoms are shown as small spheres of arbitrary radii.

Table S4. Crystal data of compounds **2a** and **4a**.

Crystal Data	Comp **2a**	Comp **4a**
Formula	$C_{15}H_{21}Cl_2CoN_3$	$C_{15}H_{19}Cl_2CoN_3O$
Molecular weight	373.18 g/mol	387.16 g/mol
Crystal Size, mm	0.060 x 0.110 x 0.230	0.28 x 0.18 x 0.10
Temp. (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal Syst.	monoclinic	tetragonal
Space Group	$P2_1/c$	P-1
a/Å	16.6500(9)	7.3409(3)
b/Å	24.8705(12)	8.2378(3)
c/Å	7.9667(5)	14.1911(6)
α/°	90	77.2420(10)
β/°	90.490(2)	85.133(2)
γ/°	90	77.2610(10)
V/Å^3	3298.8(3)	815.80(6)
Z	8	2
D_{calc}/g cm^{-3}	1.503	1.576
μ/mm^{-1}	1.361	1.383
F(000)	1544	398
Ab. Correct.	multi-scan	multi-scan
T_{min}/T_{max}	0.745/0.9230	0.698/0.874
$2\theta_{max}$	56.00	56.00
Total reflns.	49368	20029
Unique reflns.	6459	3915
Obs. reflns.	5975	3761
h, k, l (min, max)	(-20, 20), (-27, 30), (-9, 0)	(-9, 9), (-10, 10), (-18, 18)
R_{int} / R_{sig}	0.0451 / 0.0254	0.0219 / 0.0172
No. of parameters	384	206
R1 [$I > 2\sigma(I)$]	0.0439	0.0193
wR2[$I > 2\sigma(I)$]	0.0834	0.0518
R1 [all data]	0.0481	0.0526
wR2 [all data]	0.0855	0.0822
goodness-of-fit	1.132	1.072
$\Delta\rho_{max}$, $\Delta\rho_{min}$(eÅ^{-3})	+0.502, -0.703	+0.355, -0.336
CCDC	2119314	2119313

9. References

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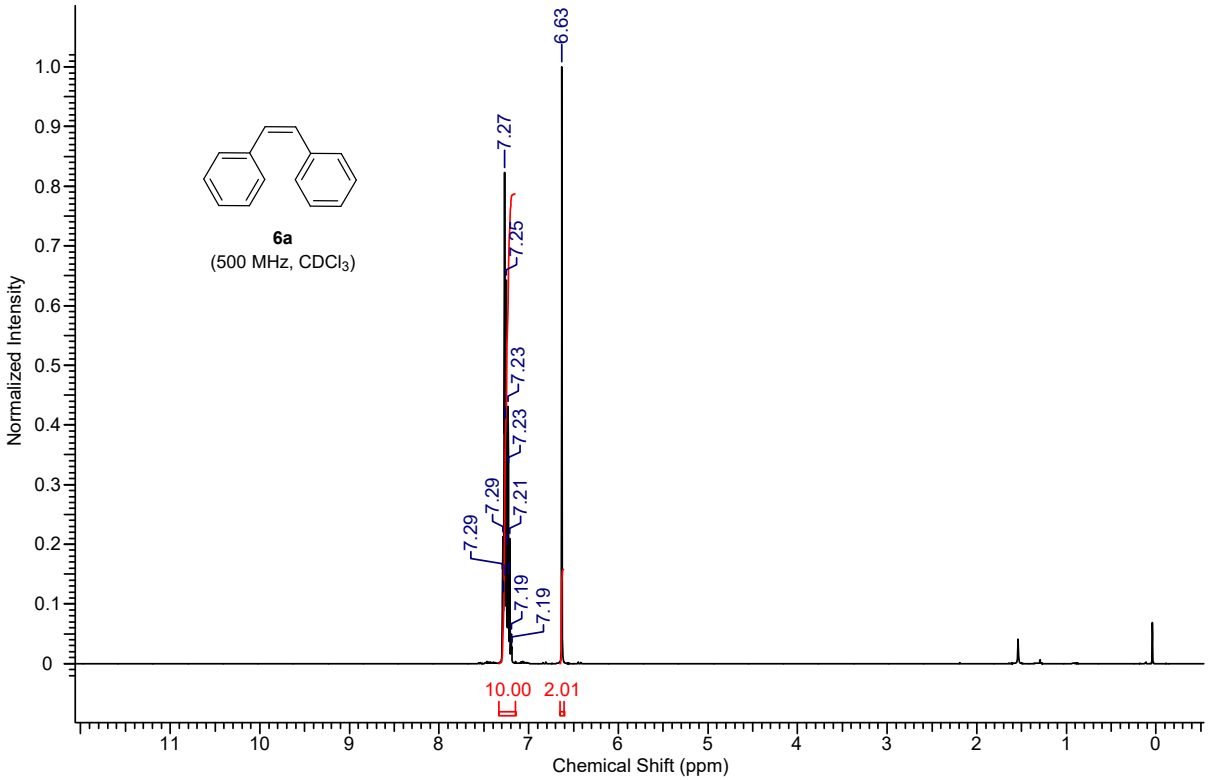
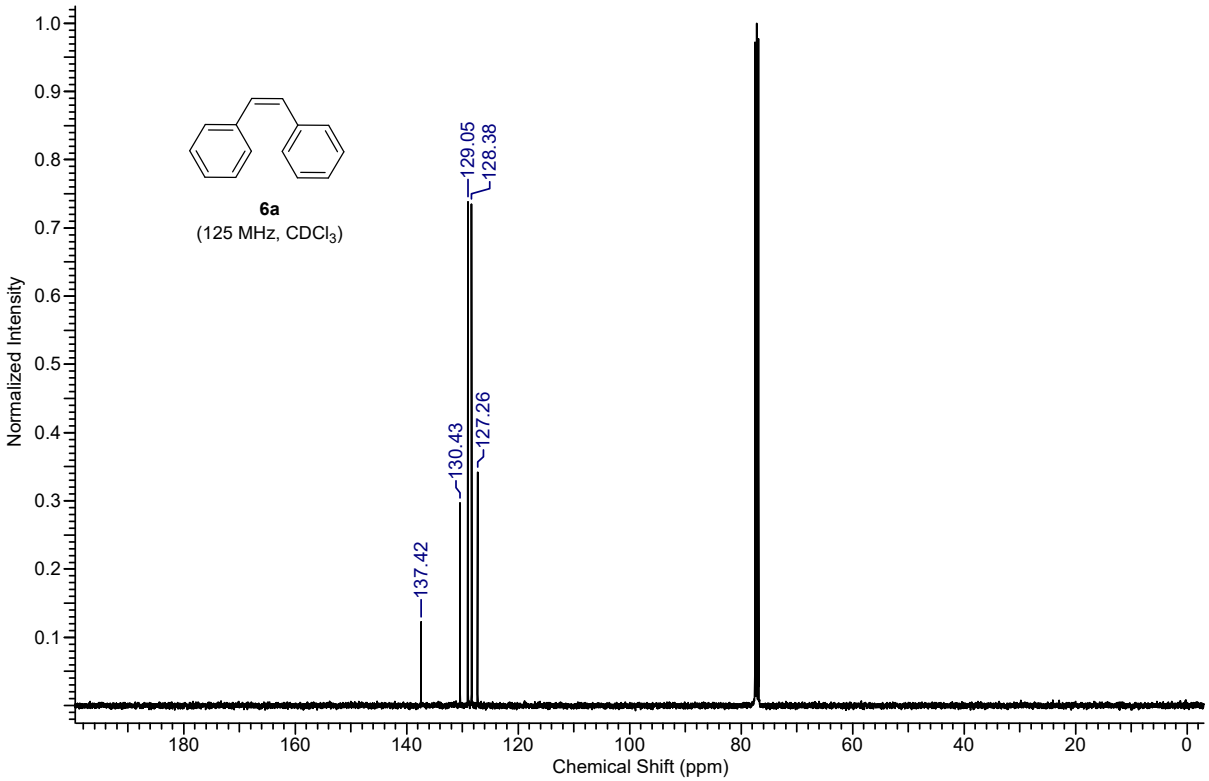
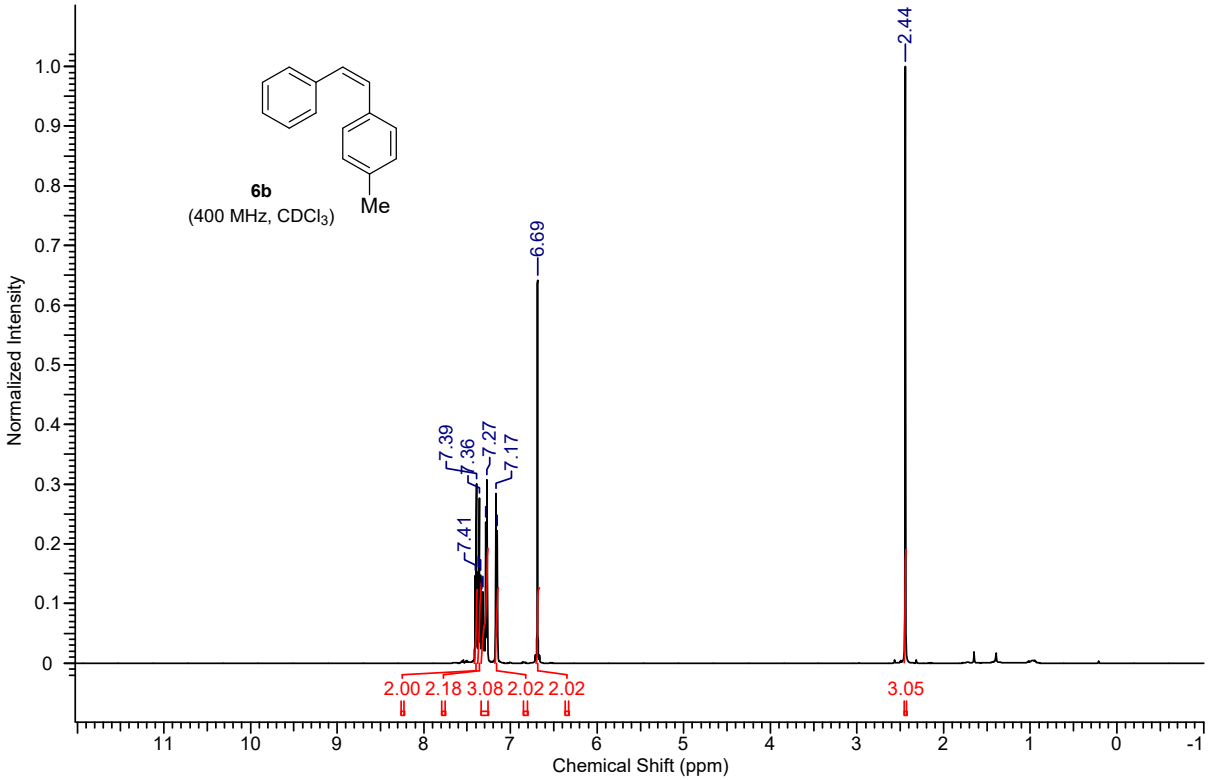
10. NMR Spectra of *Z*-Alkenes



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Chemical Shift (ppm)
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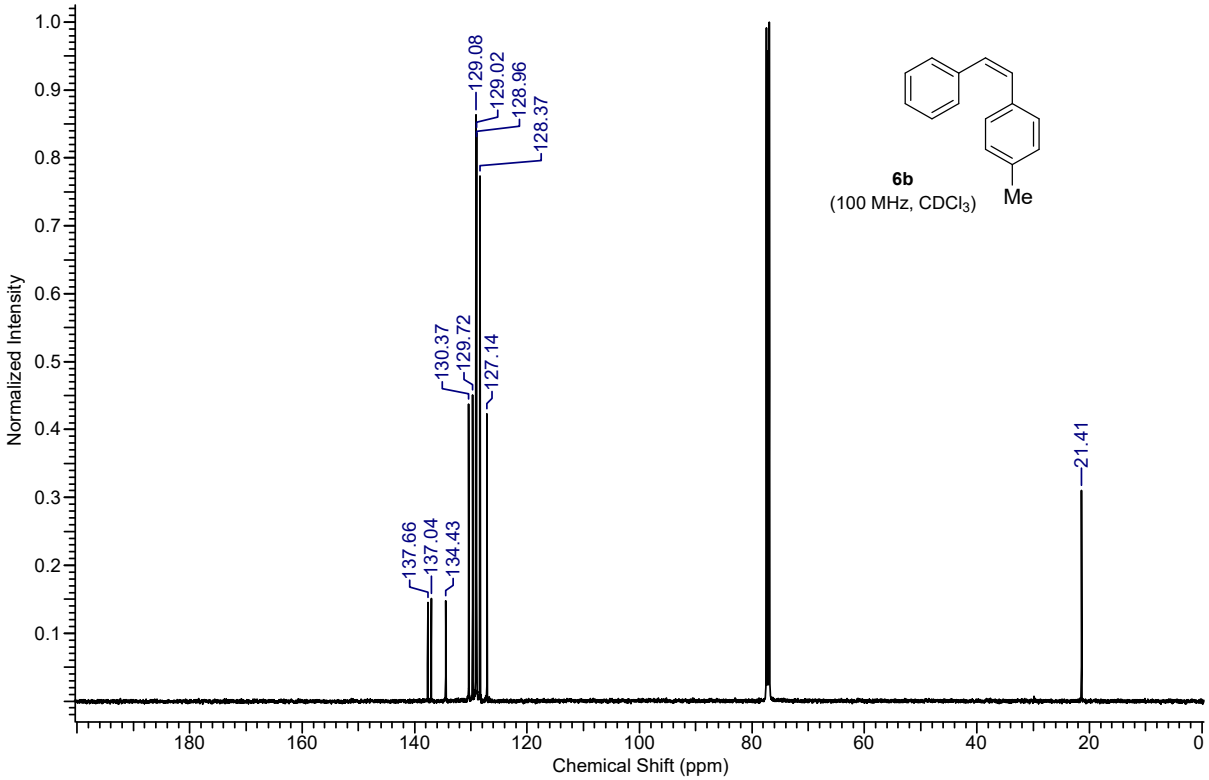
7.41
2.00 2.18 3.08 2.02 2.02
3.05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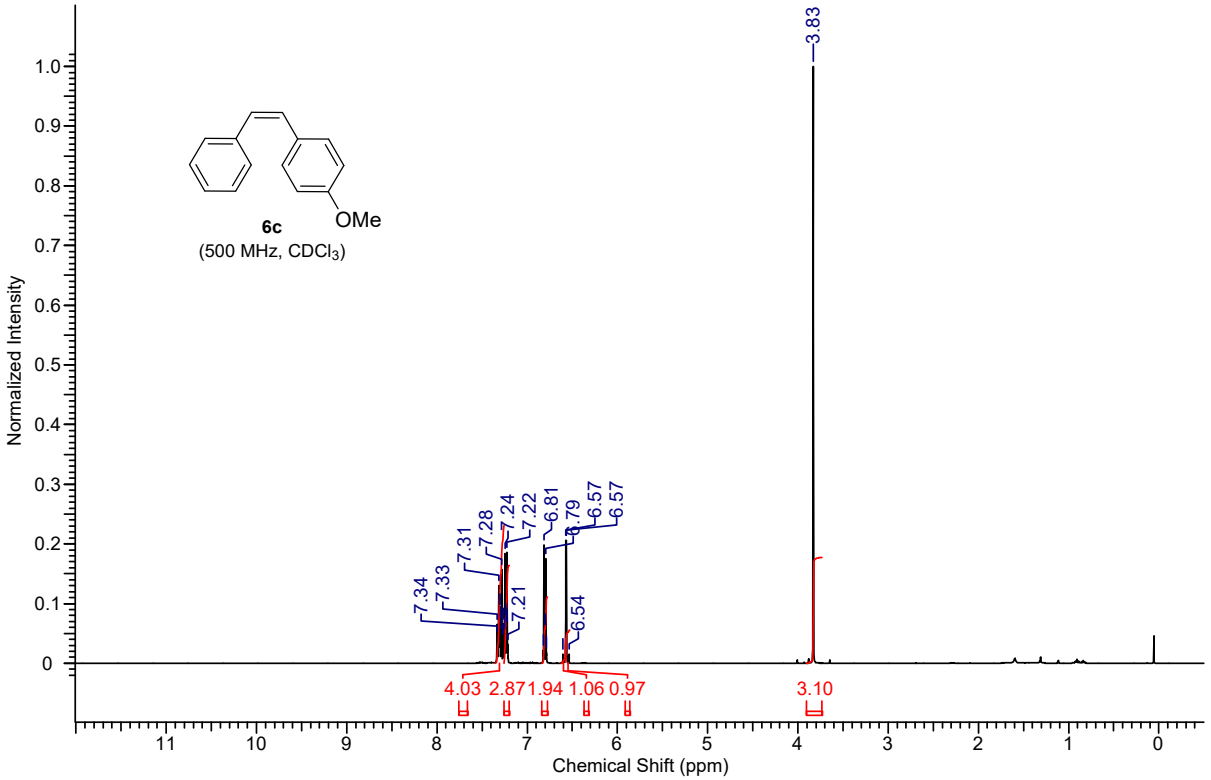
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7.22
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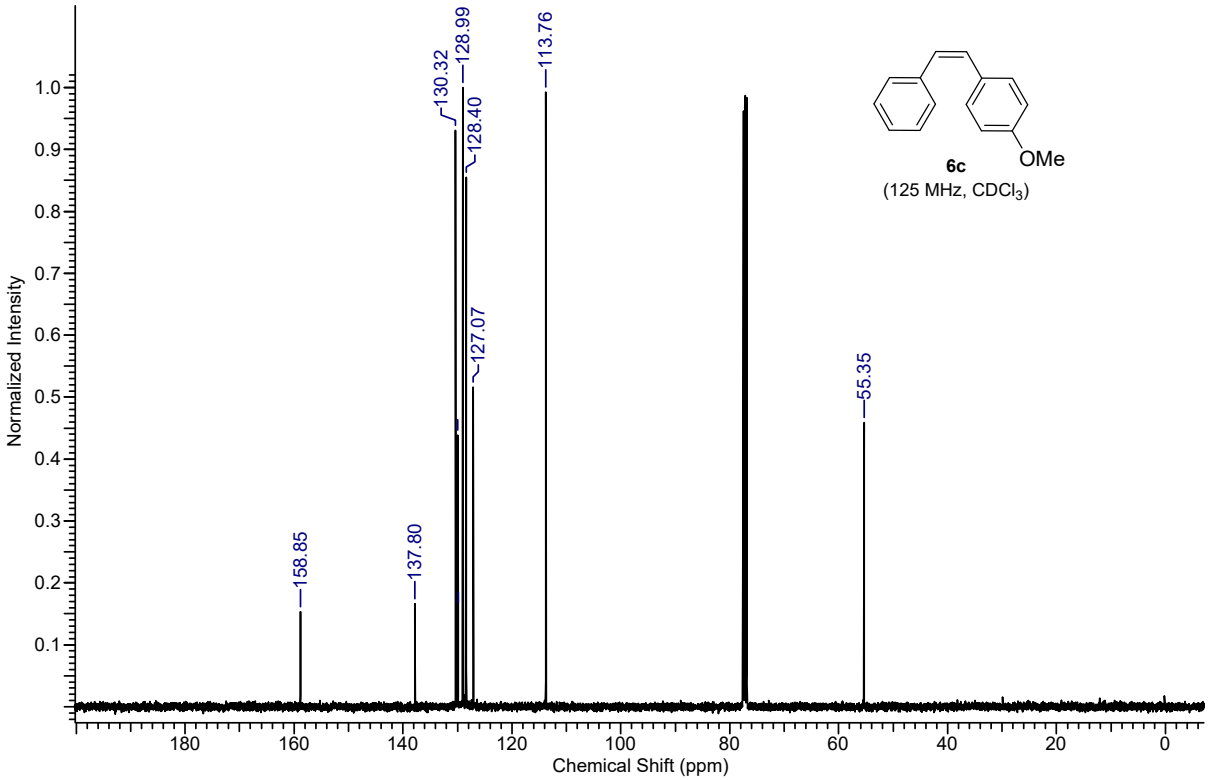
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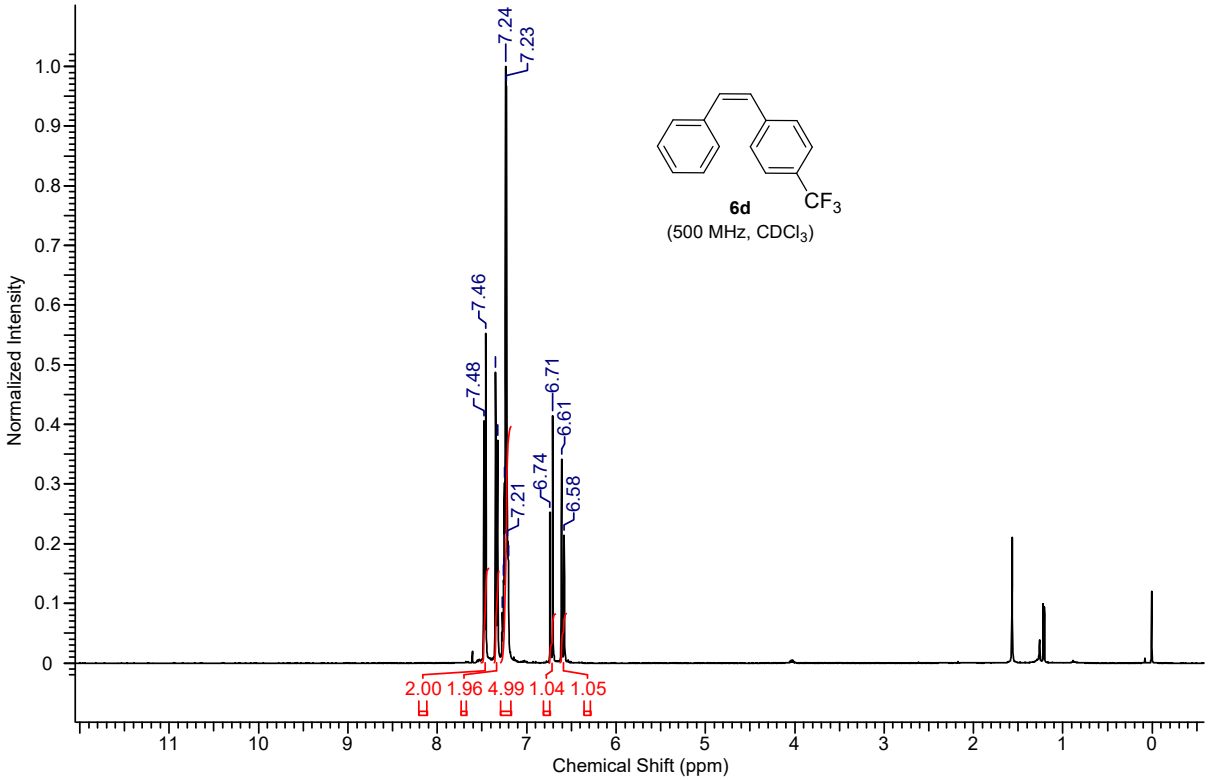
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Chemical Shift (ppm)
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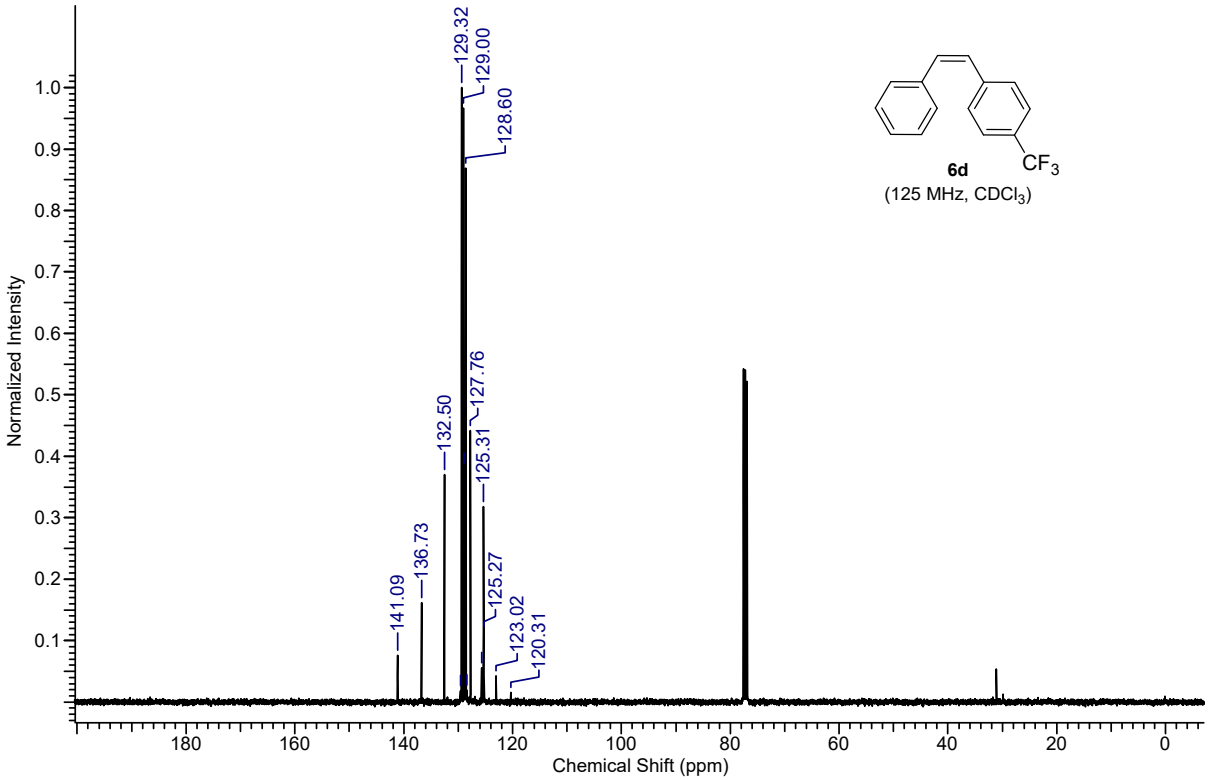
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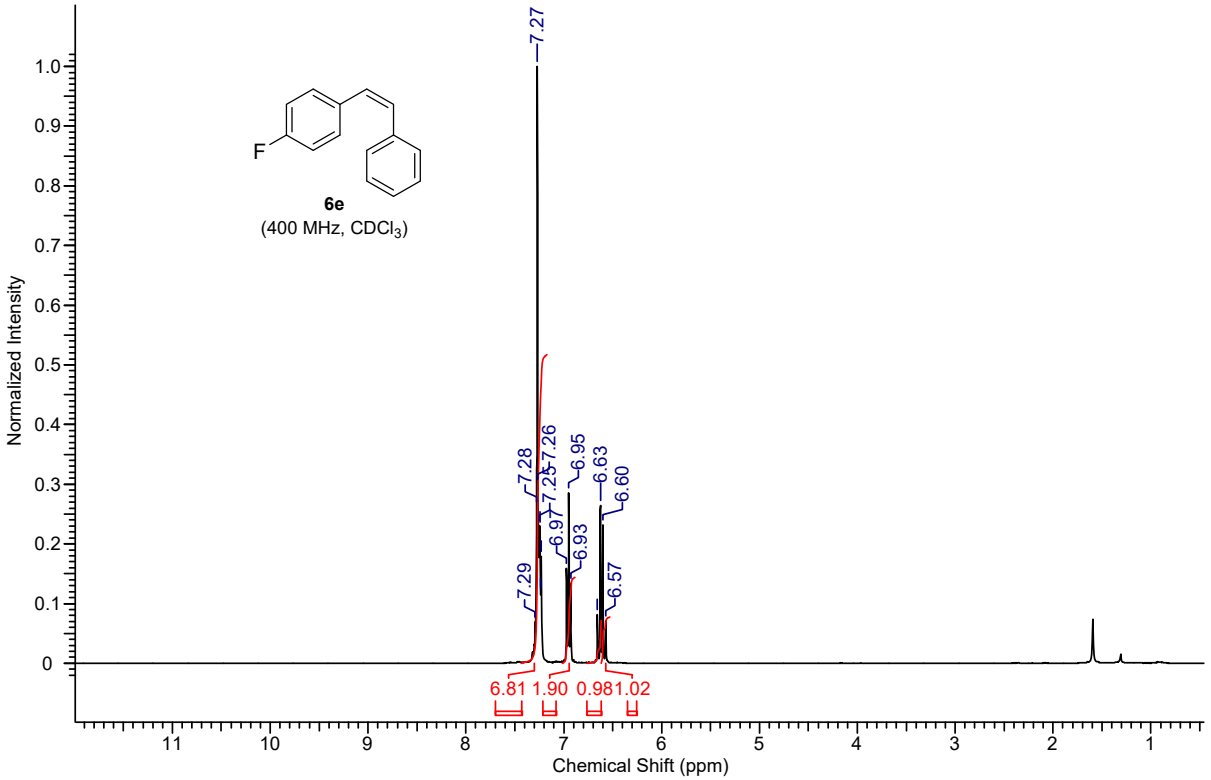
(125 MHz, CDCl3)
CF3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Normalized Intensity
Chemical Shift (ppm)
F
6e
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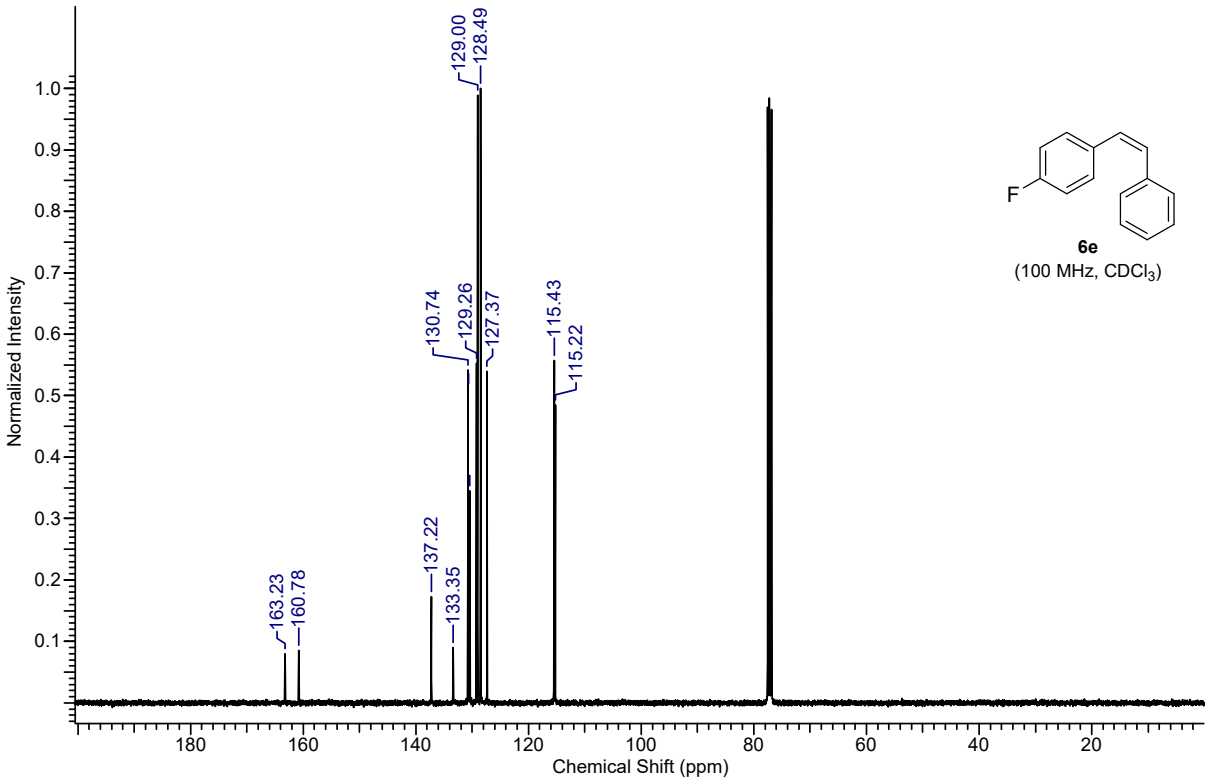
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6e
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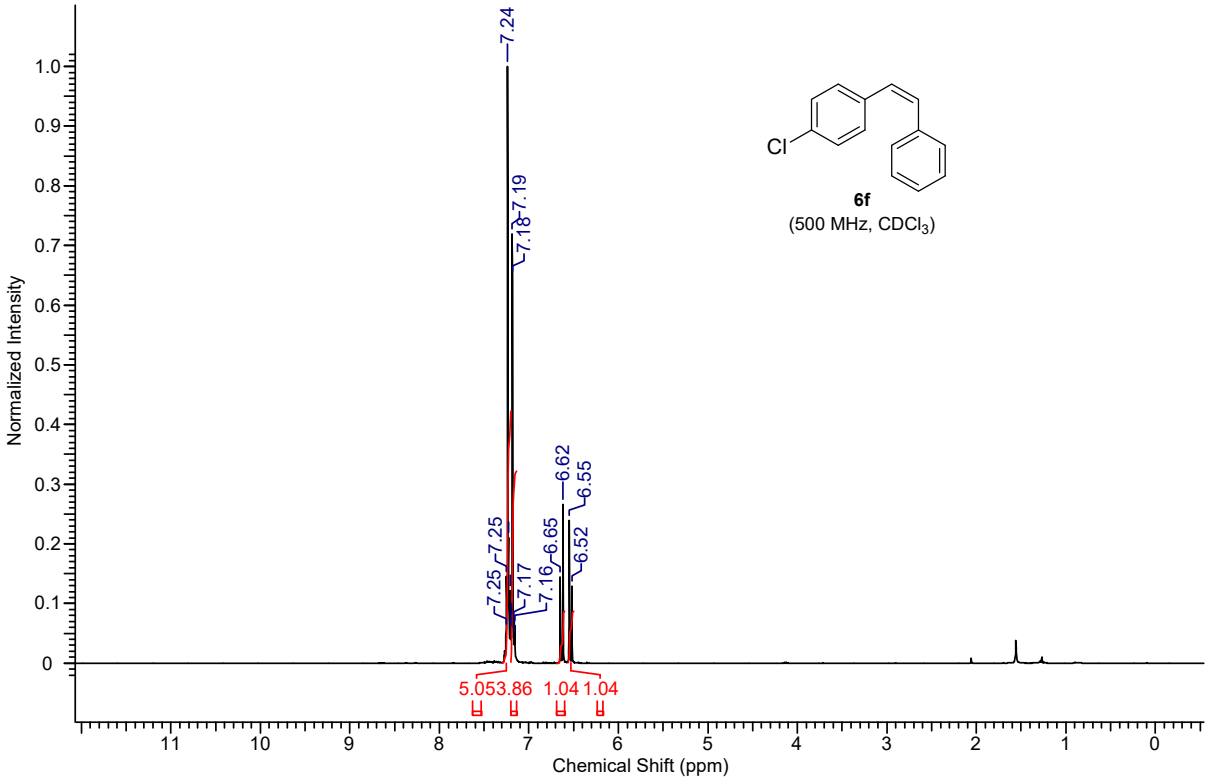
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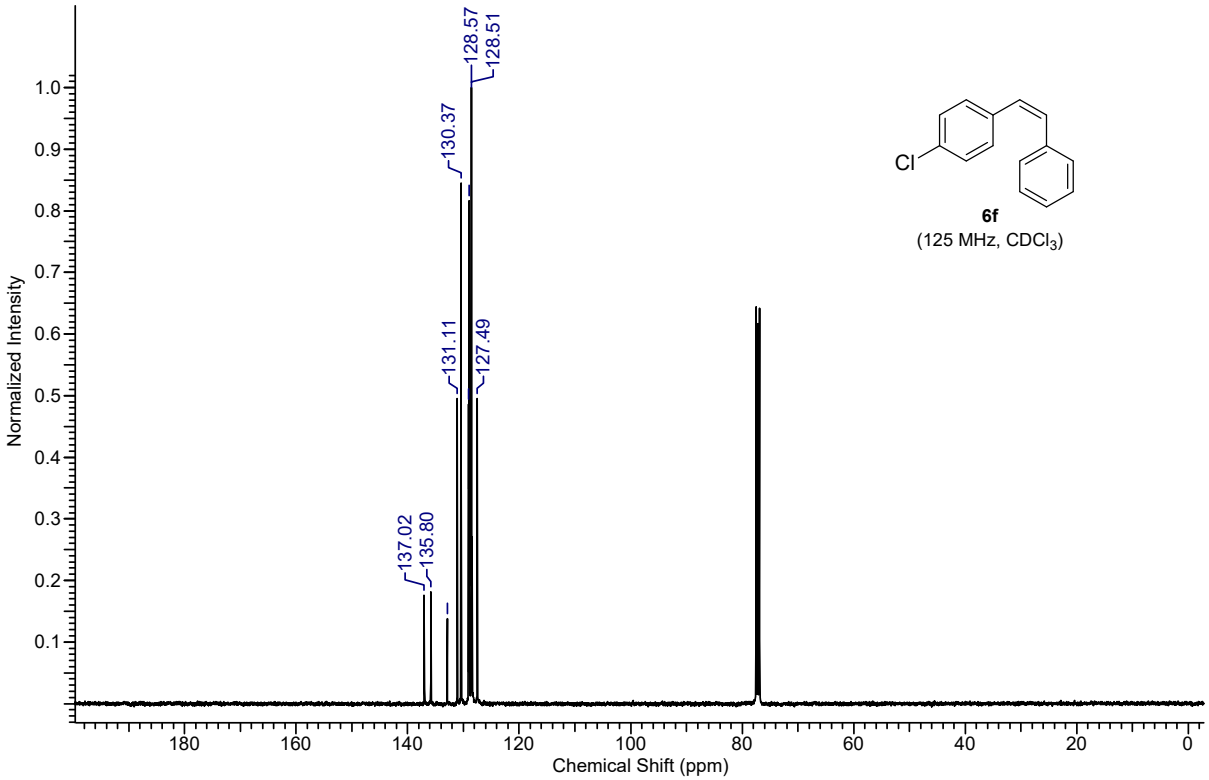
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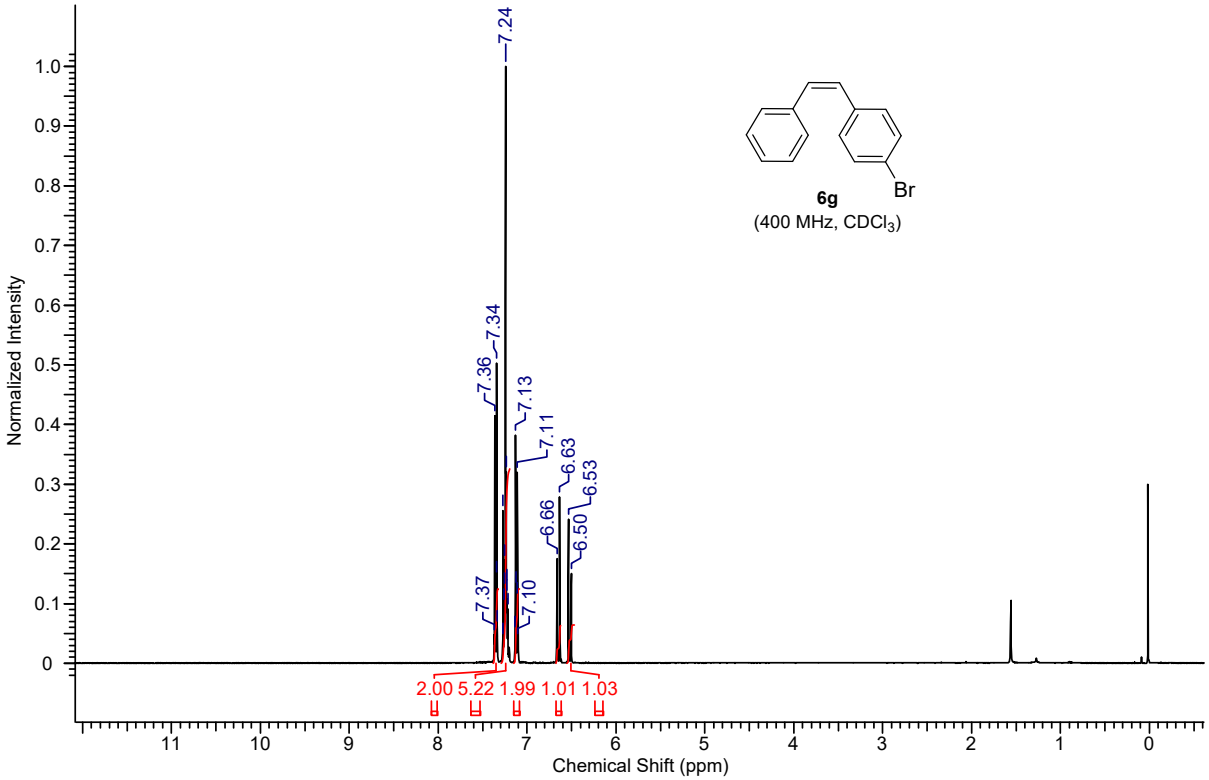
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Chemical Shift (ppm)
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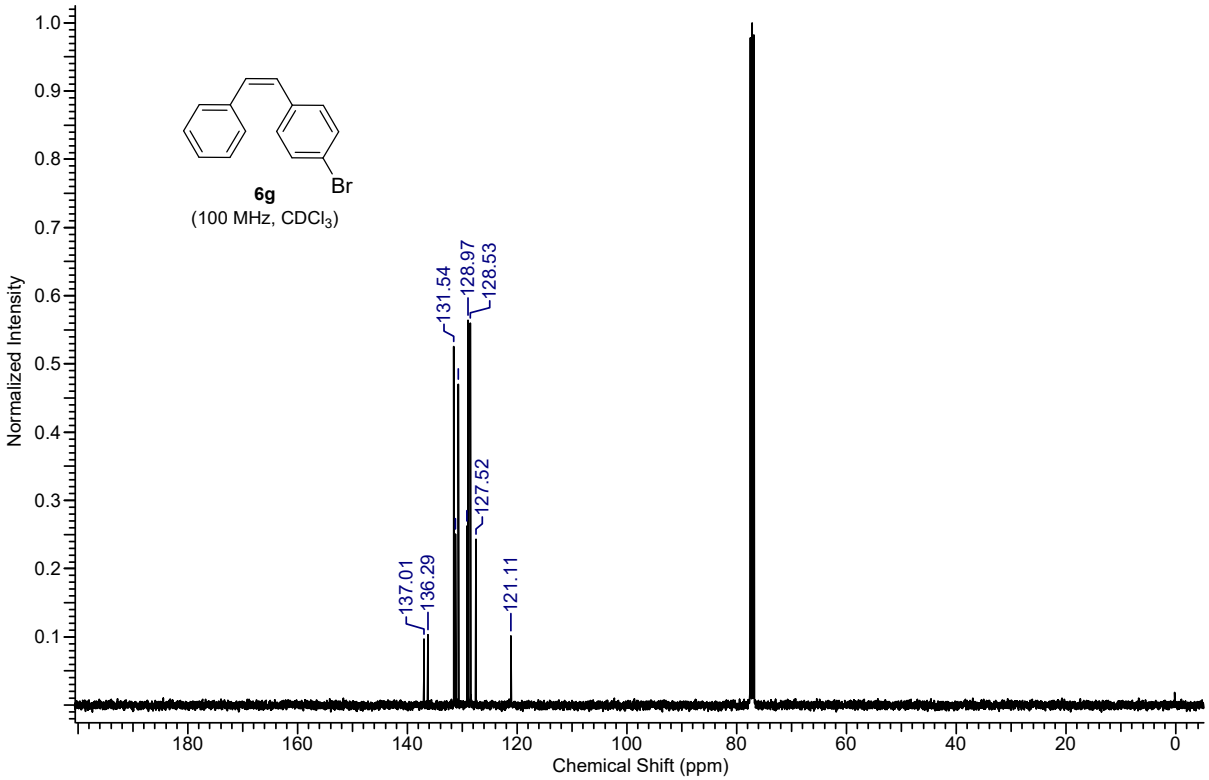
(400 MHz, CDCl3)
Br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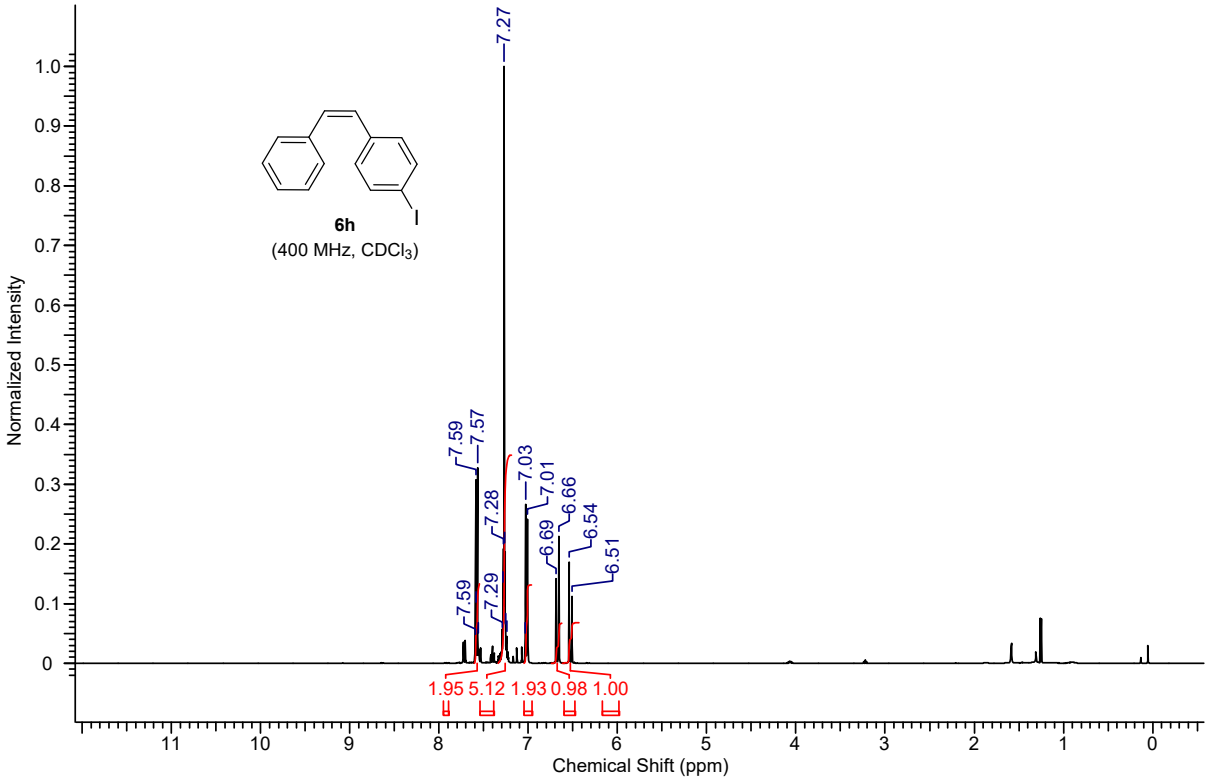
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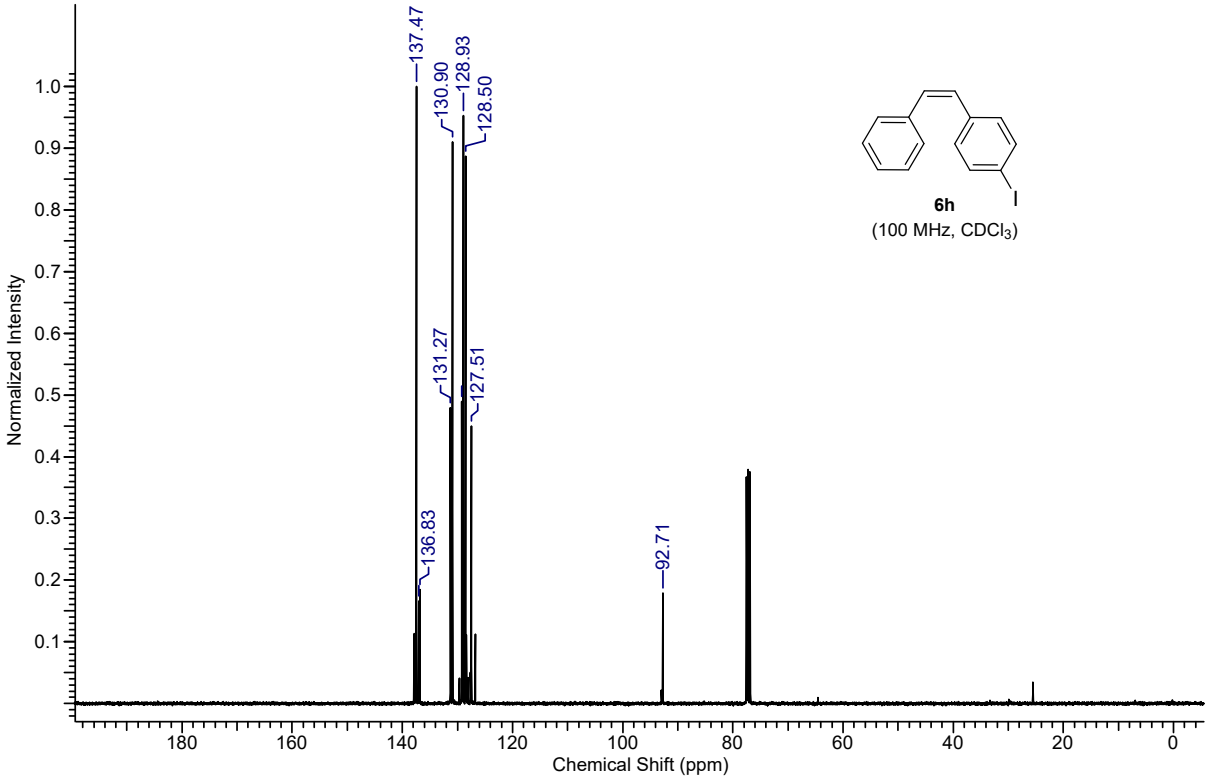
Chemical Shift (ppm)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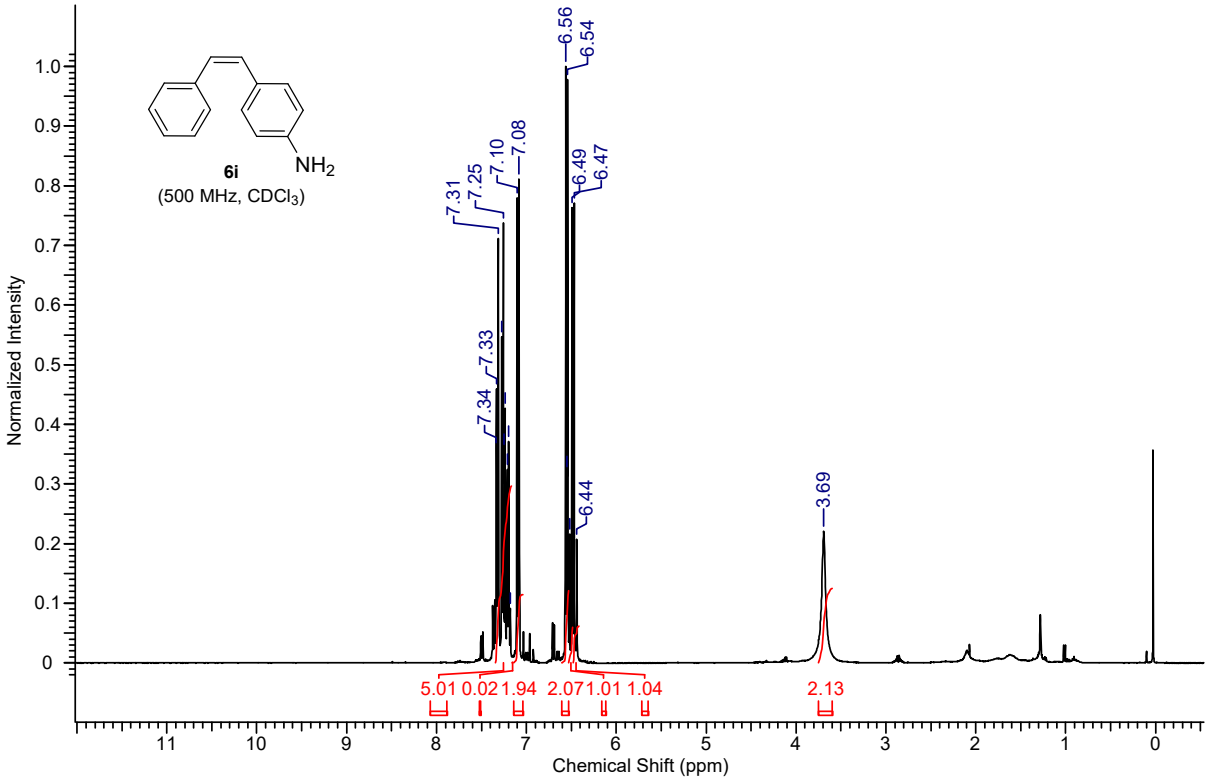
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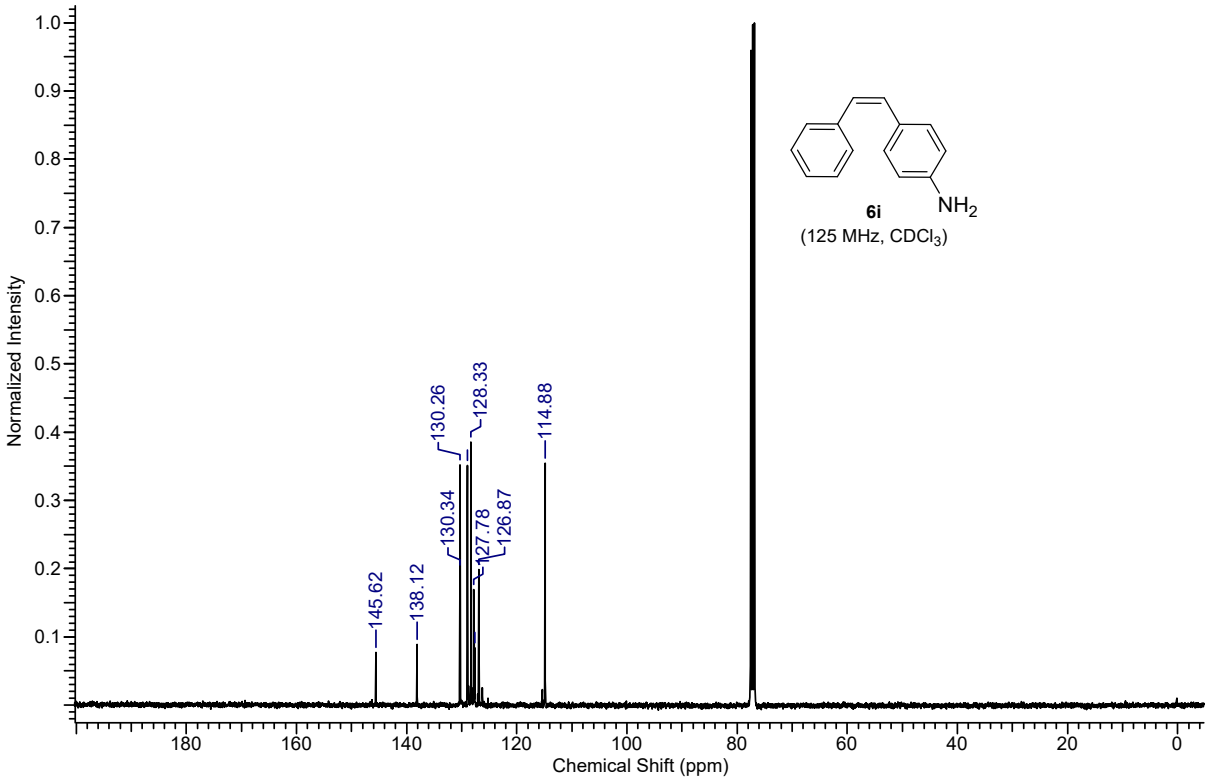
2.13
Normalized Intensity
Chemical Shift (ppm)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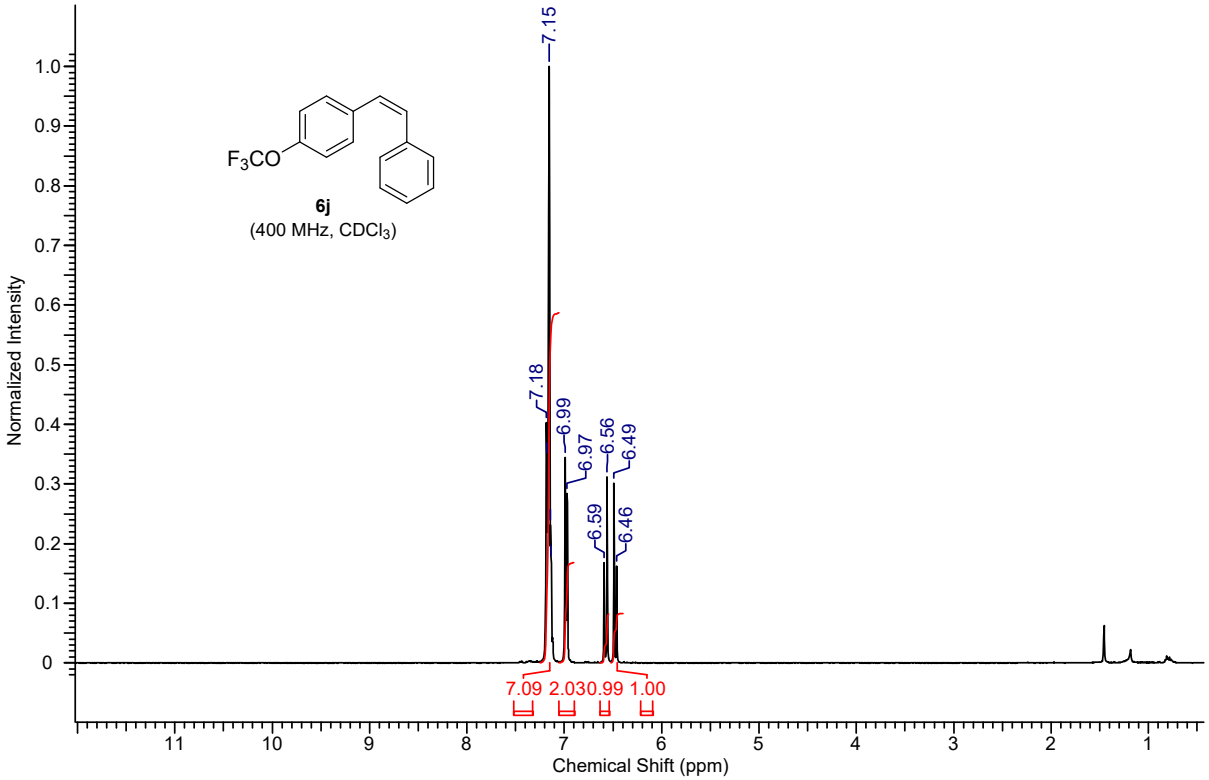
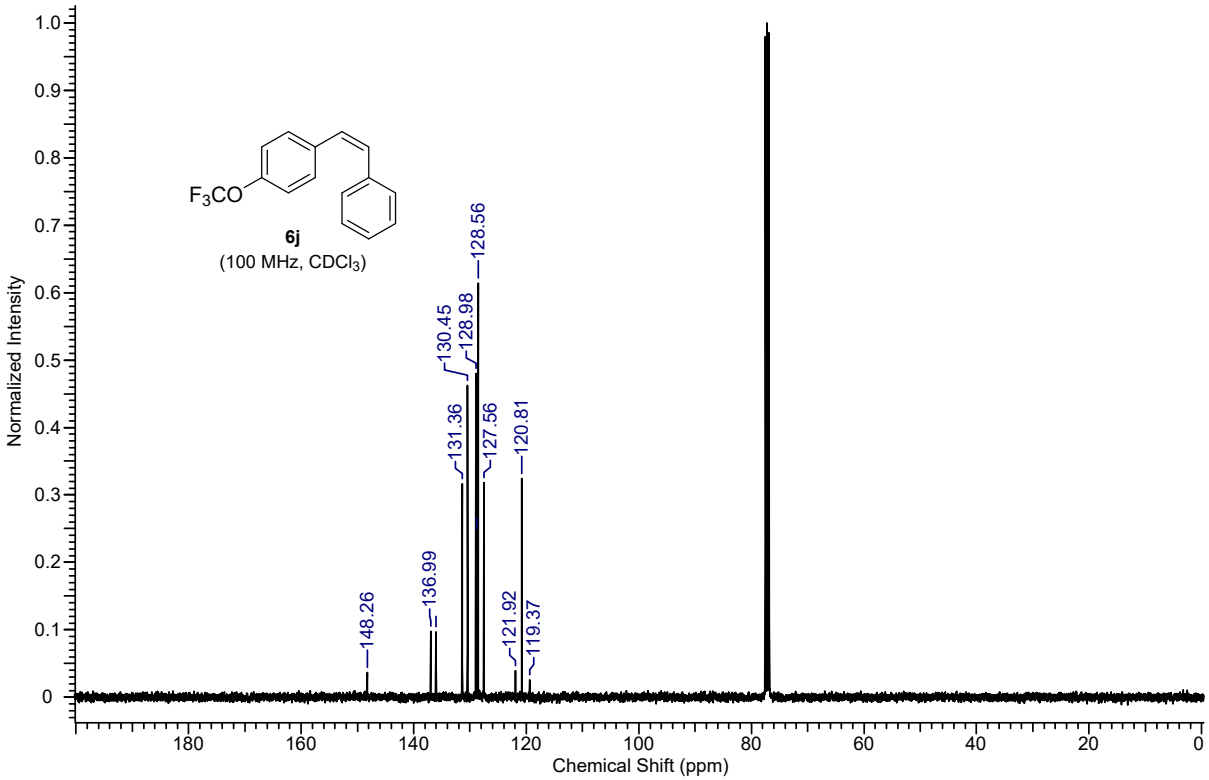
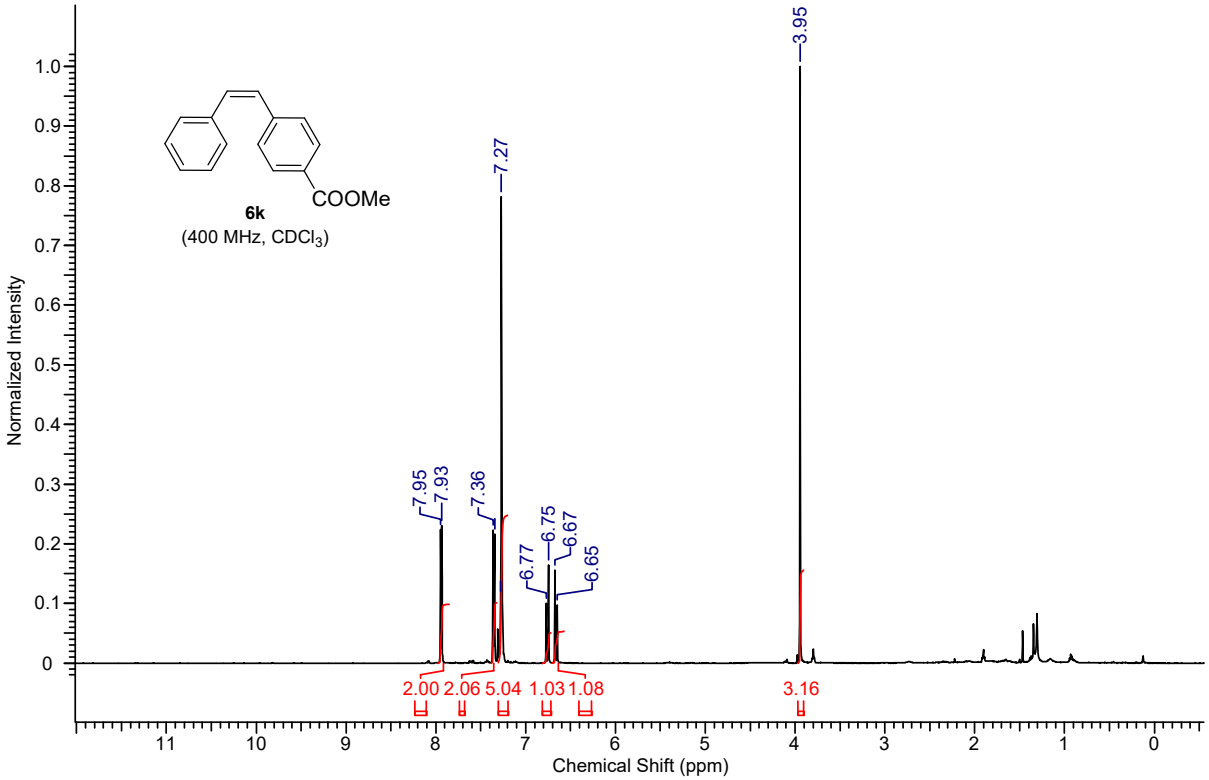
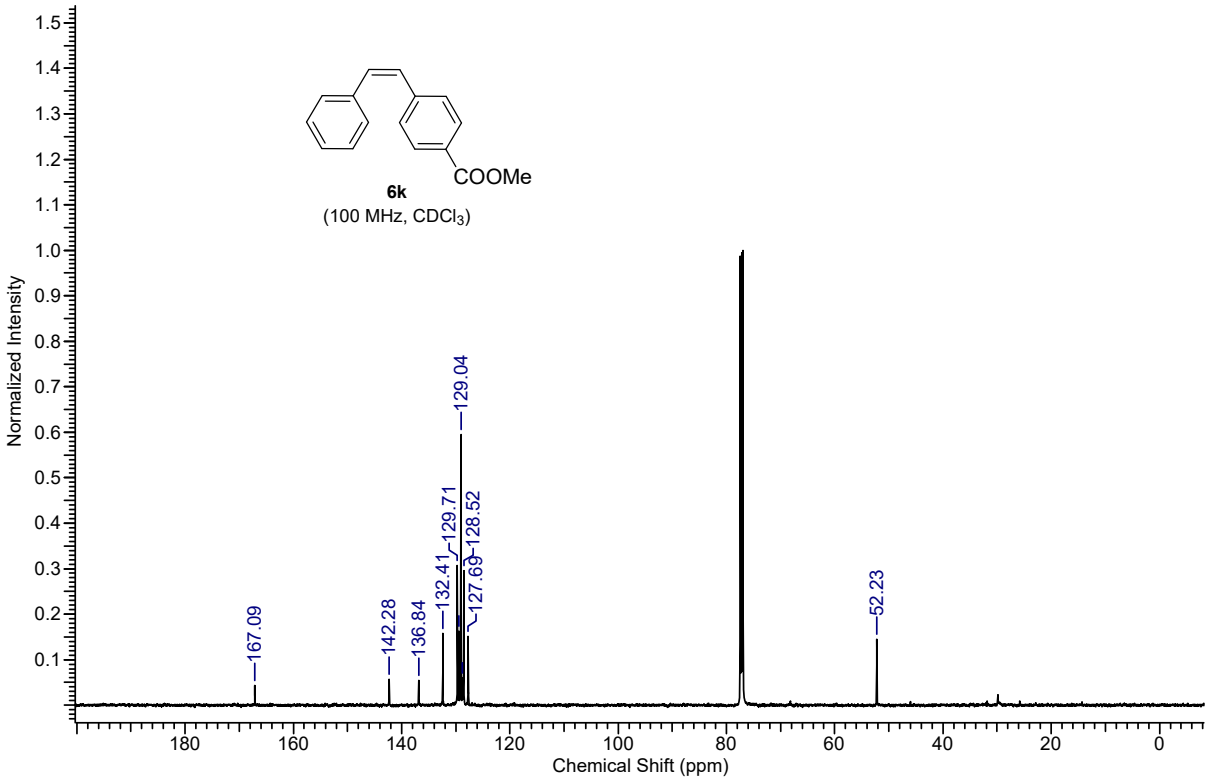
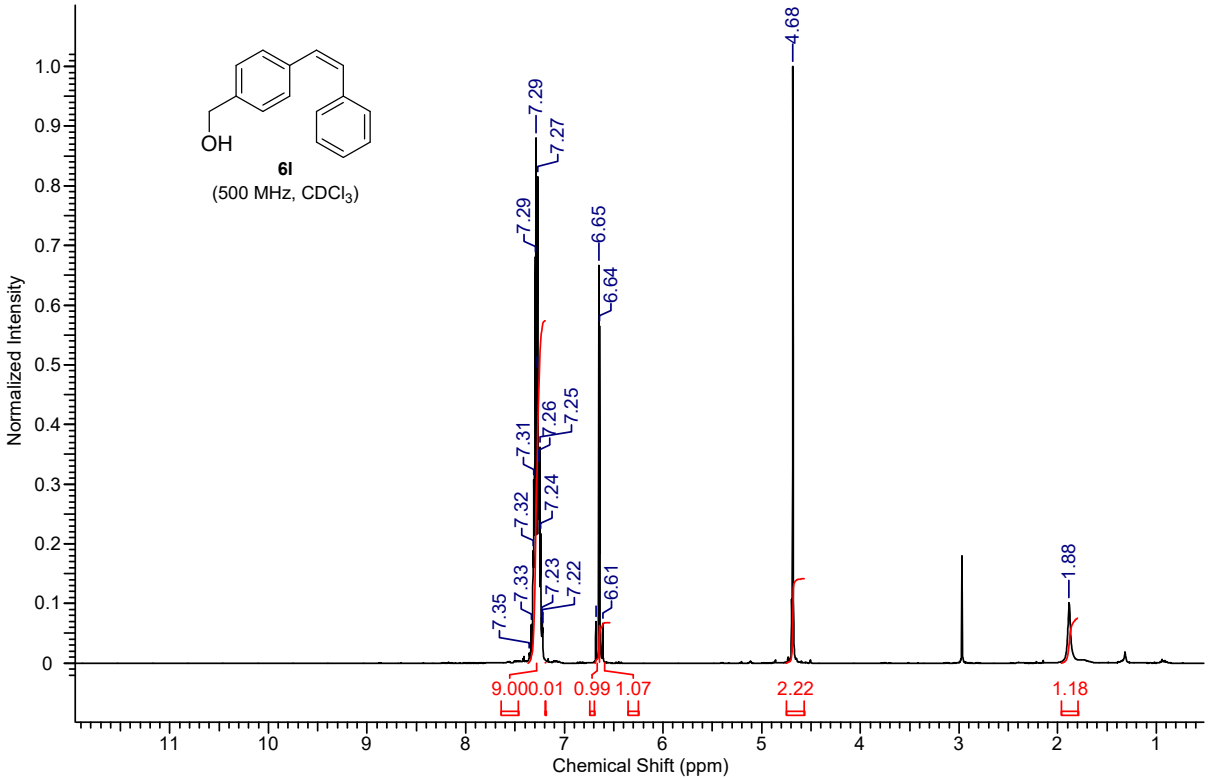
Normalized Intensity
Chemical Shift (ppm)

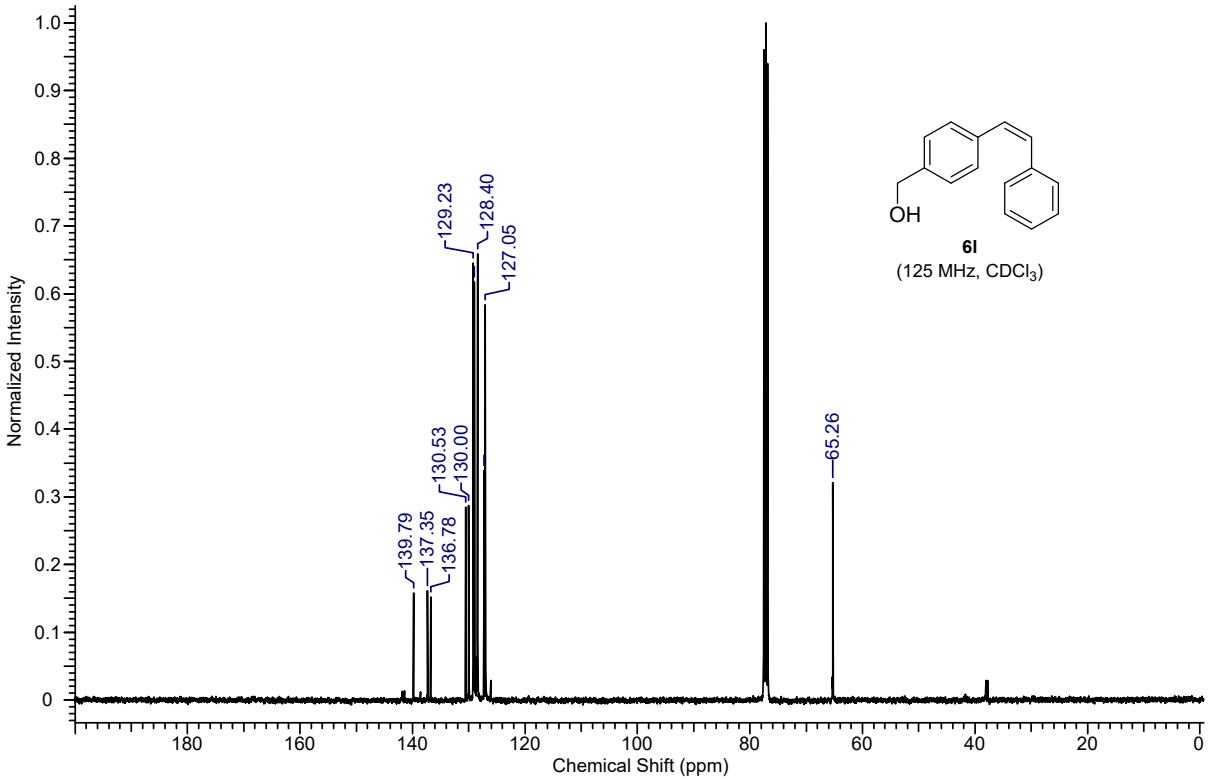

F3CO
6j
(400 MHz, CDCl3)
7.15
7.18
6.99
6.97
6.56
6.49
6.59
6.46
7.09 2.03 0.99 1.00
Normalized Intensity
Chemical Shift (ppm)

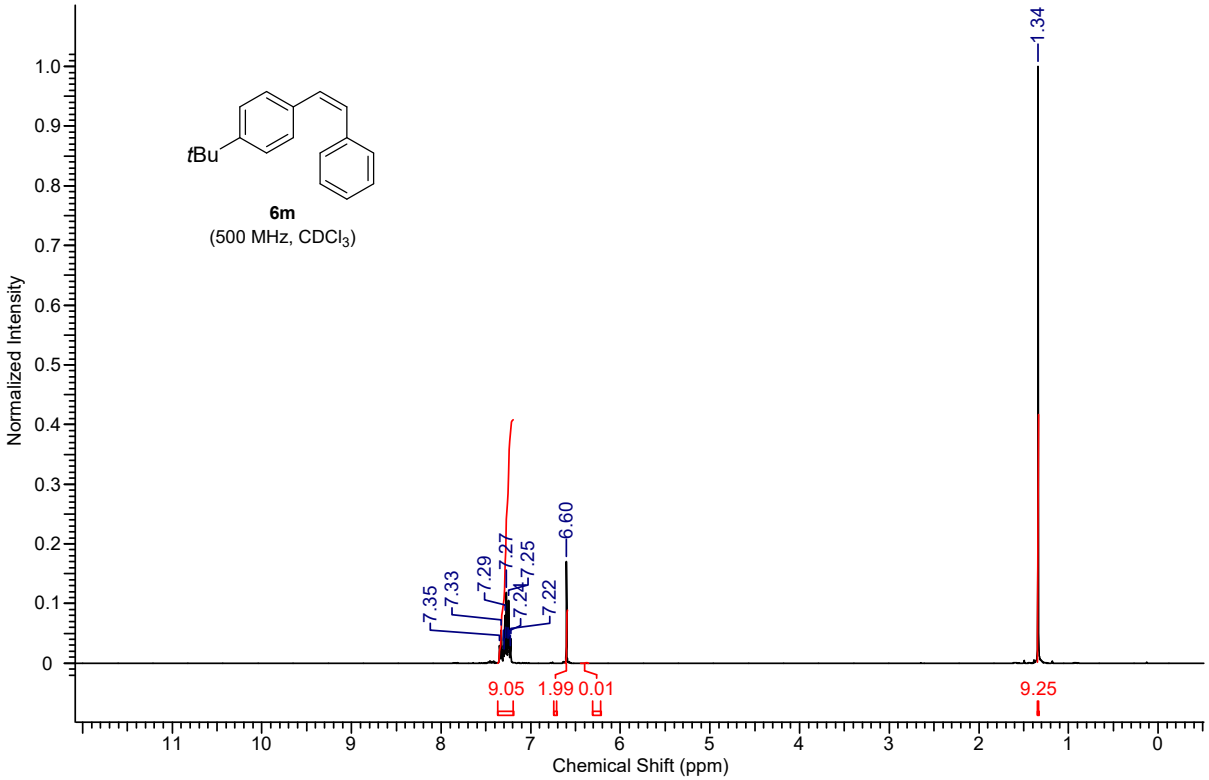

F3CO
6j
(100 MHz, CDCl3)
128.56
130.45
128.98
131.36
127.56
120.81
136.99
148.26
121.92
119.37
Normalized Intensity
Chemical Shift (ppm)

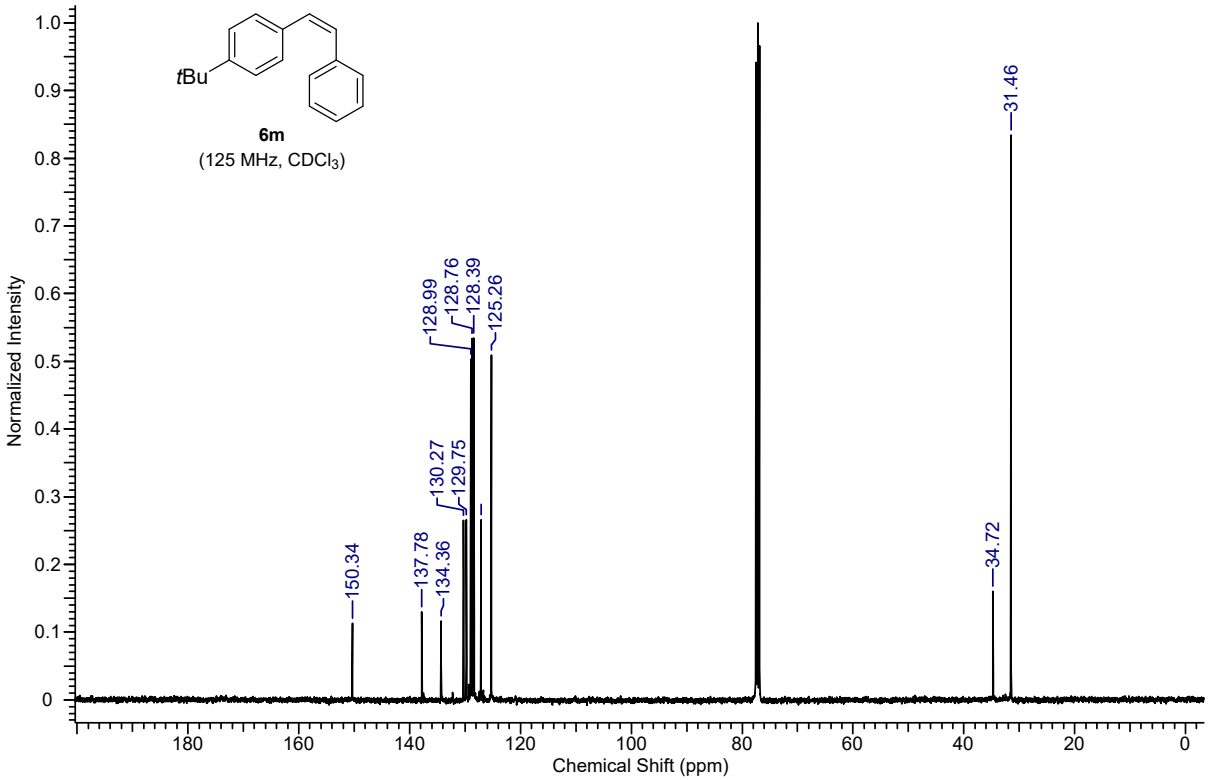

COOMe
6k
(400 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
3.95
7.27
7.95
7.93
7.36
6.75
6.67
6.77
6.65
2.00 2.06 5.04 1.03 1.08
3.16

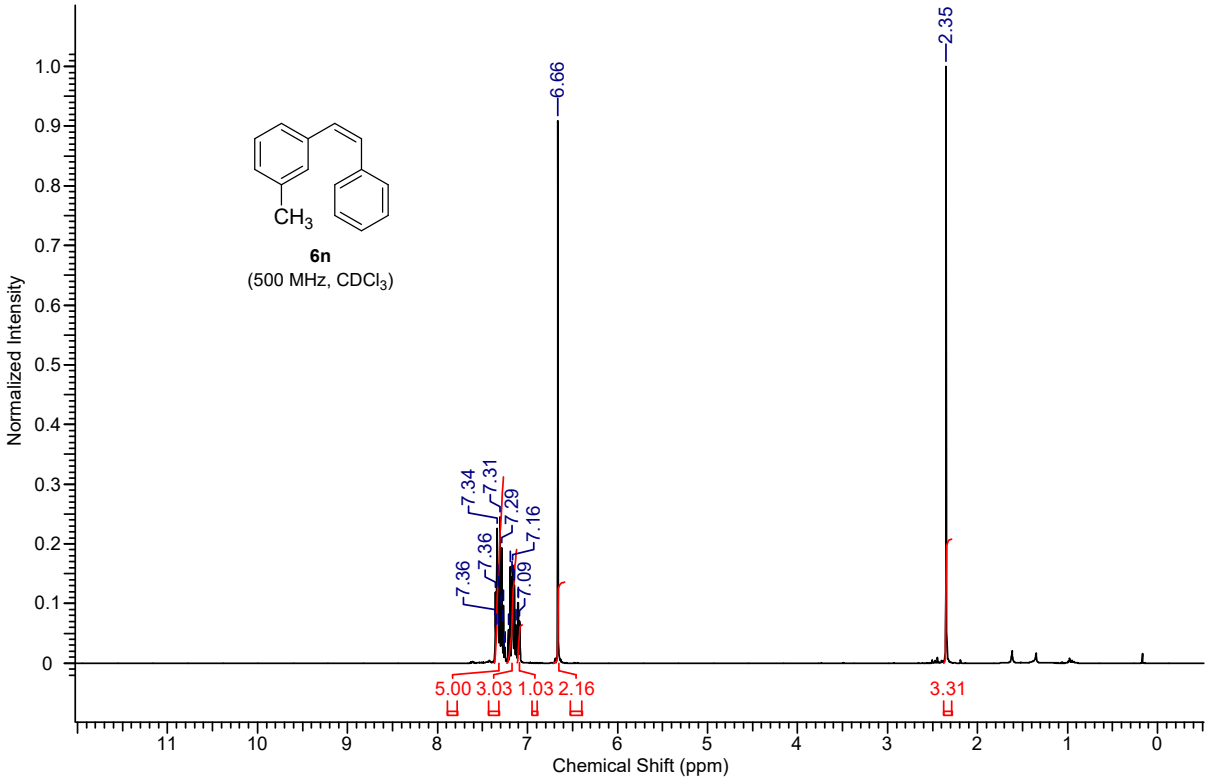

COOMe
6k
(100 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
167.09
142.28
136.84
132.41
129.71
129.04
128.52
127.69
52.23

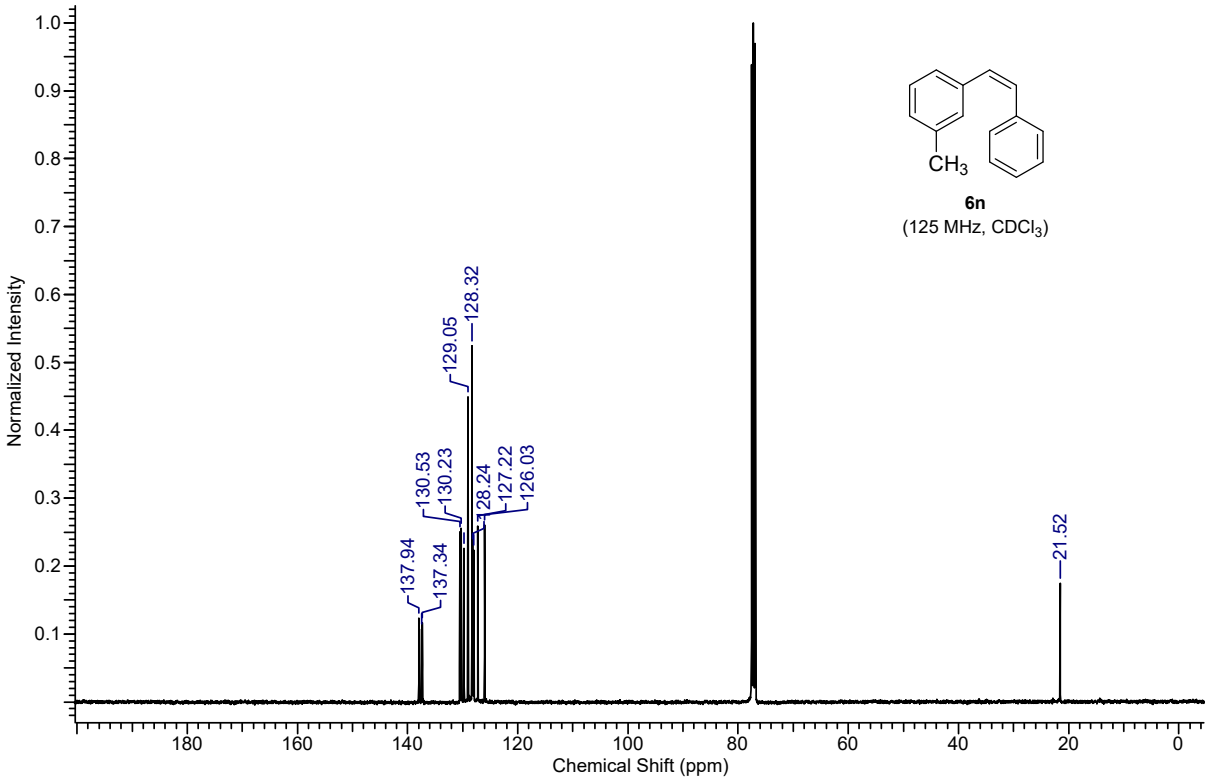

OH
6l
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
4.68
7.29
7.27
7.29
6.65
6.64
7.31
7.26
7.25
7.32
7.24
7.33
7.23
7.22
6.61
7.35
1.88
9.00
0.01
0.99
1.07
2.22
1.18

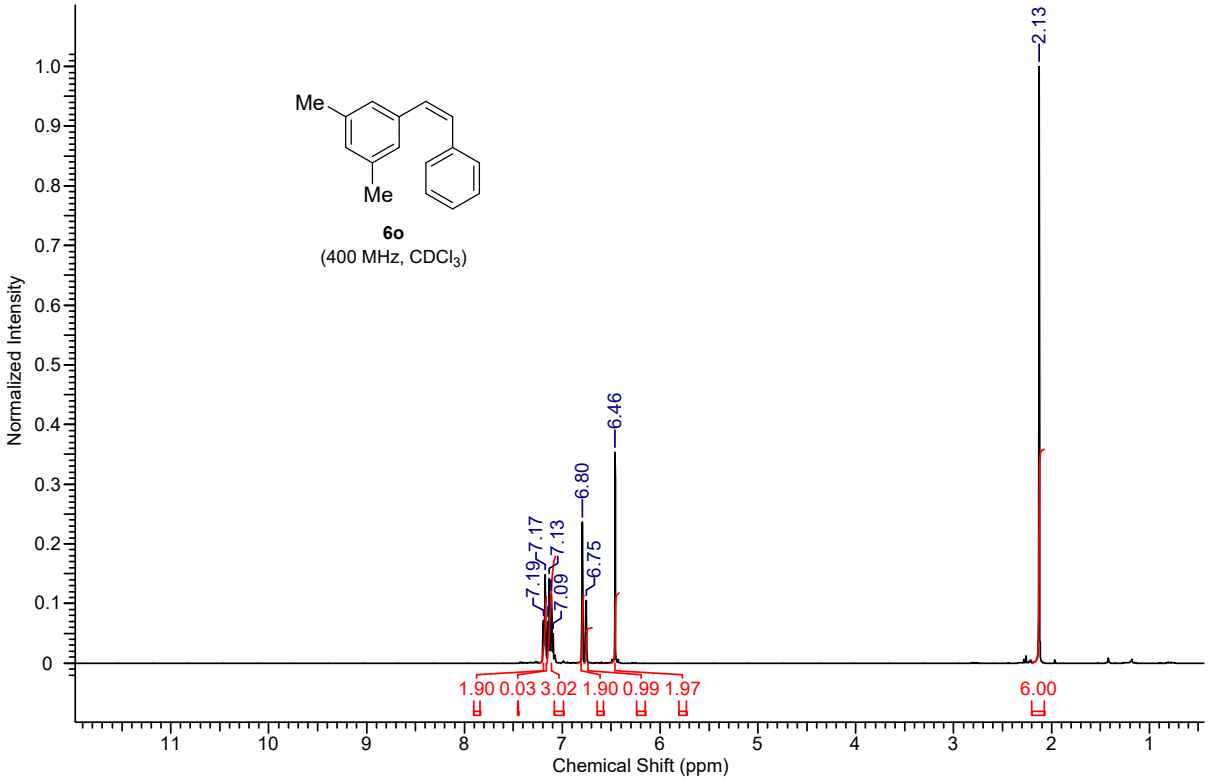

OH
6l
(125 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
129.23
128.40
127.05
130.53
130.00
139.79
137.35
136.78
65.26

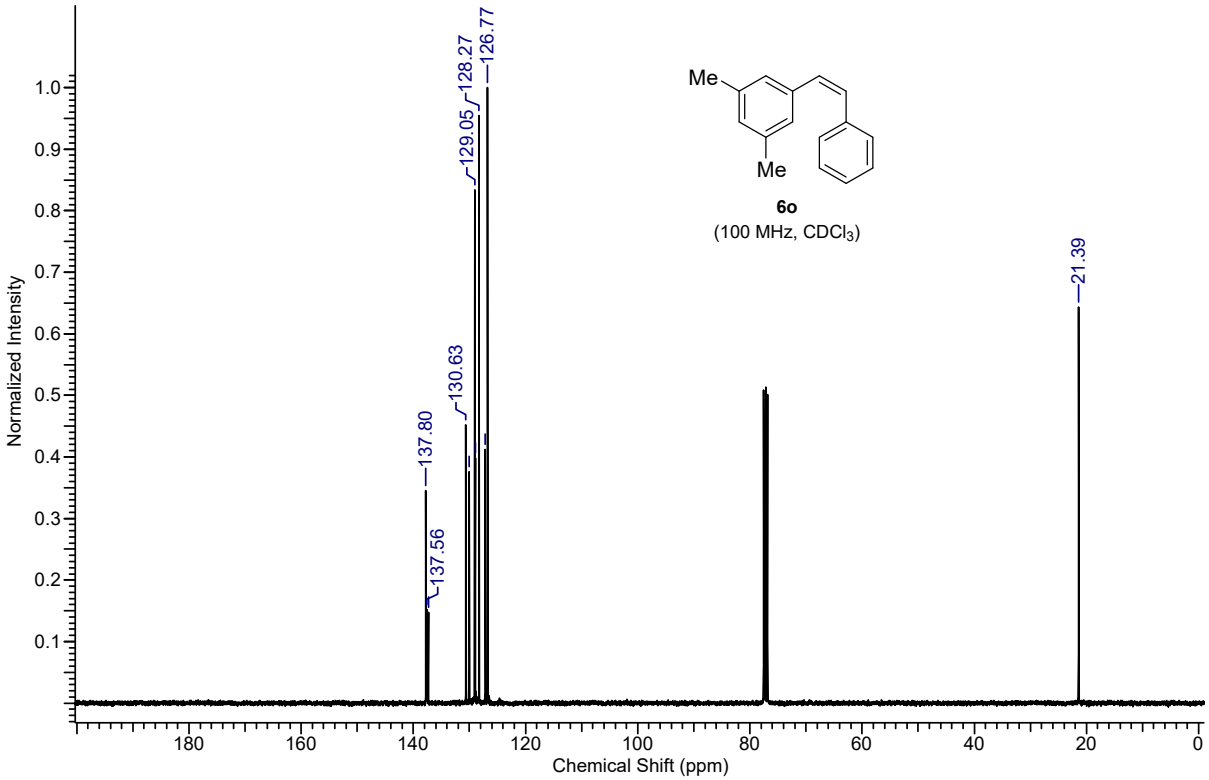

tBu
6m
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
1.34
7.35
7.33
7.29
7.27
7.25
7.24
7.22
6.60
9.05
1.99
0.01
9.25

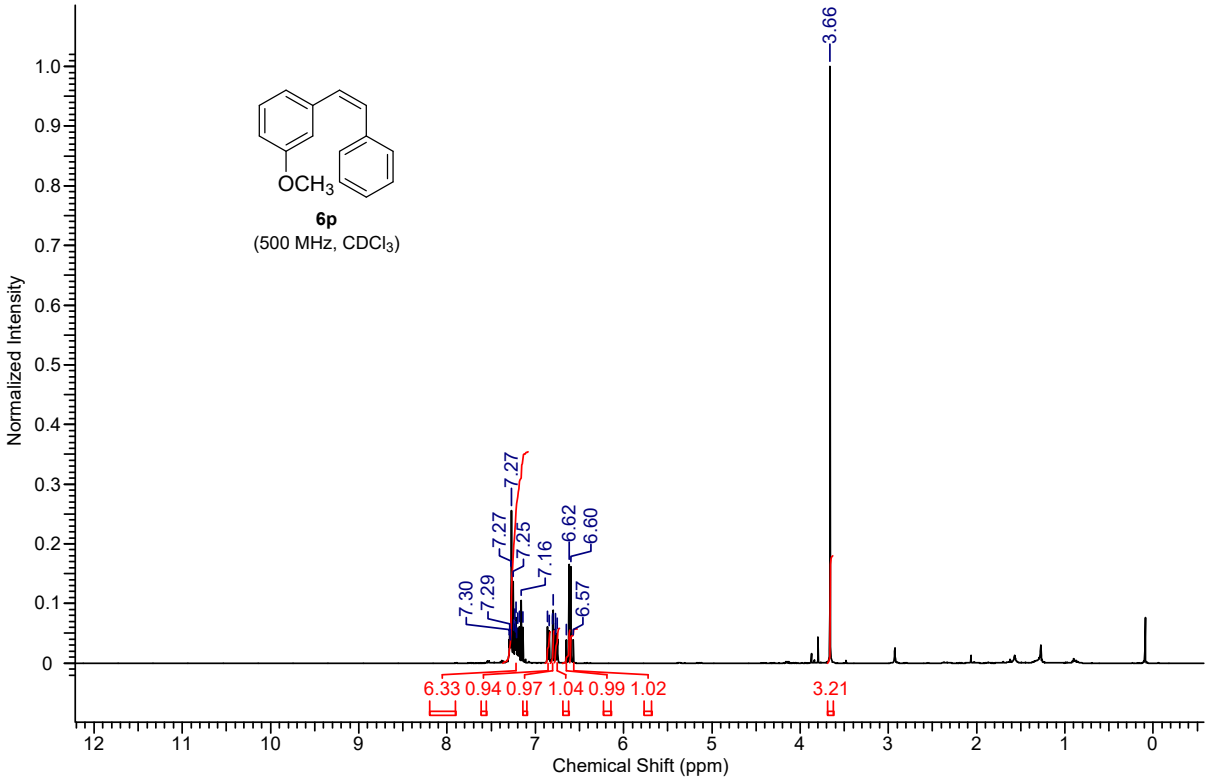

tBu
6m
(125 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
150.34
137.78
134.36
130.27
129.75
128.99
128.76
128.39
125.26
31.46
34.72

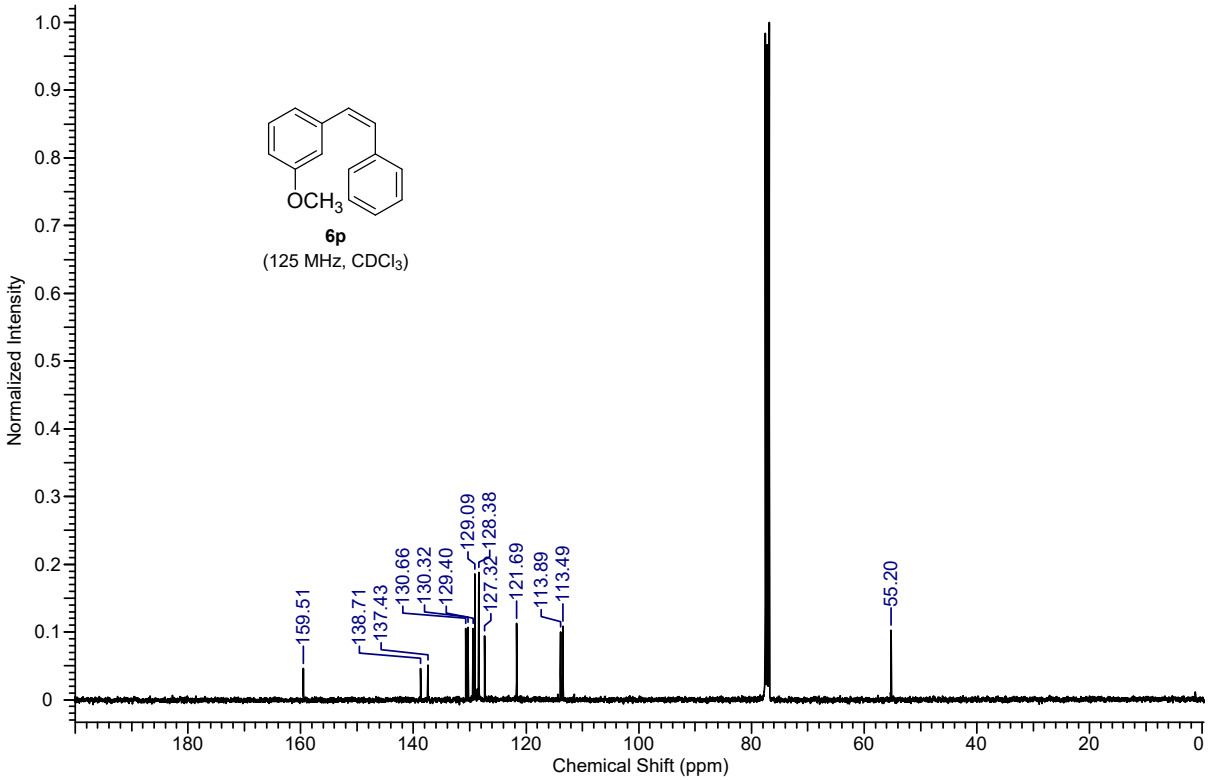

6n
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
6.66
2.35
7.34
7.31
7.29
7.16
7.36
7.36
7.09
5.00 3.03 1.03 2.16
3.31

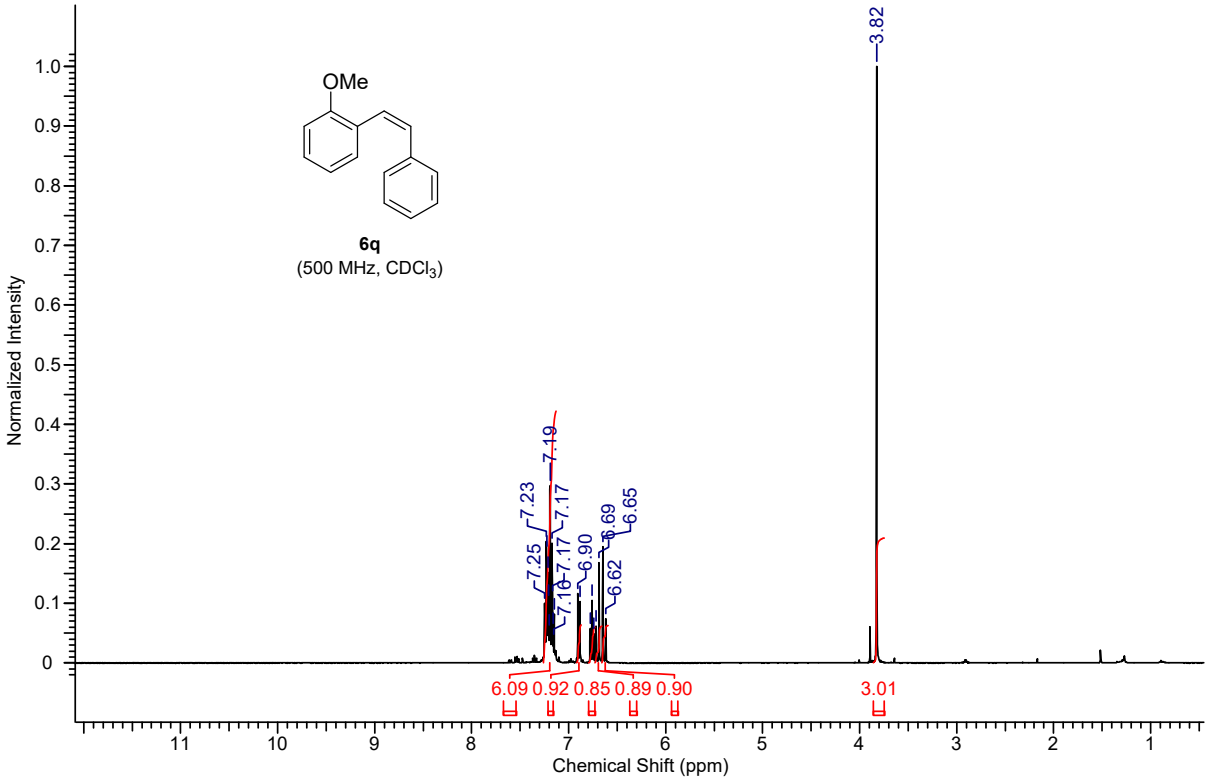

6n
(125 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
128.32
129.05
130.53
130.23
128.24
127.22
126.03
137.94
137.34
21.52

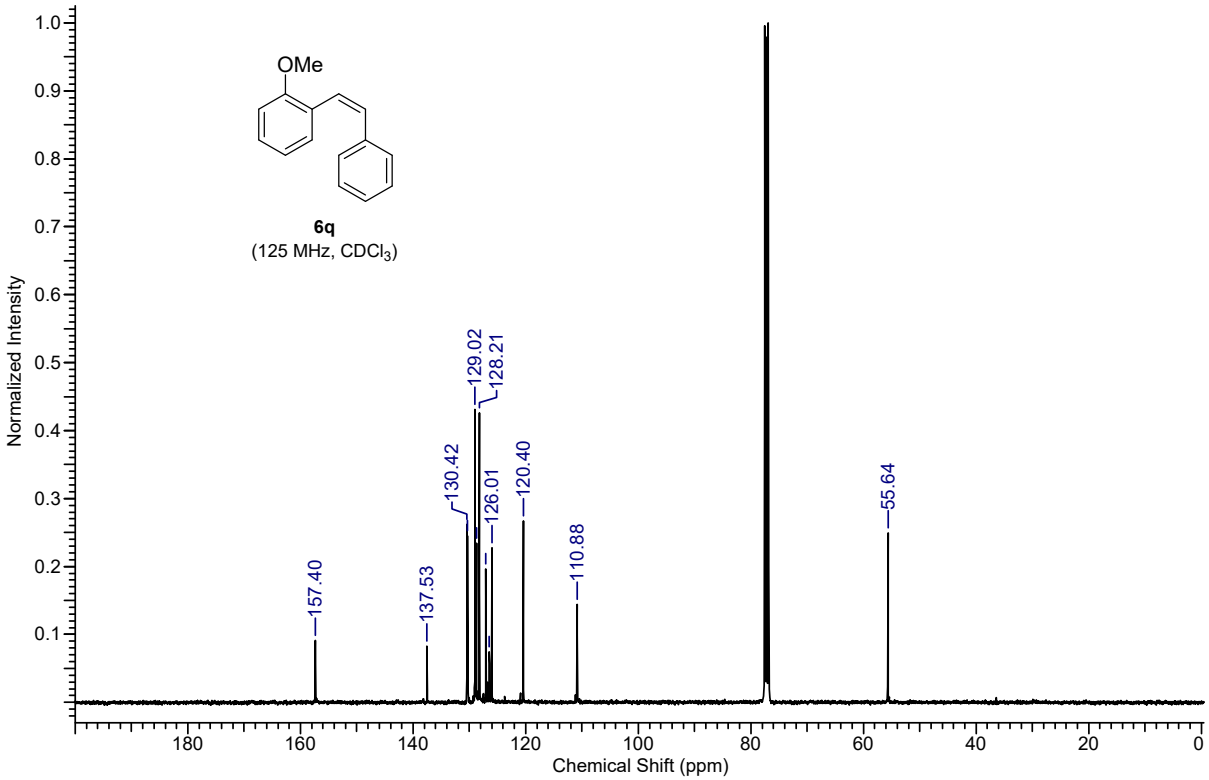

Me
Me
6o
(400 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
2.13
6.46
6.80
6.75
7.19
7.17
7.13
7.09
1.90 0.03 3.02 1.90 0.99 1.97
6.00

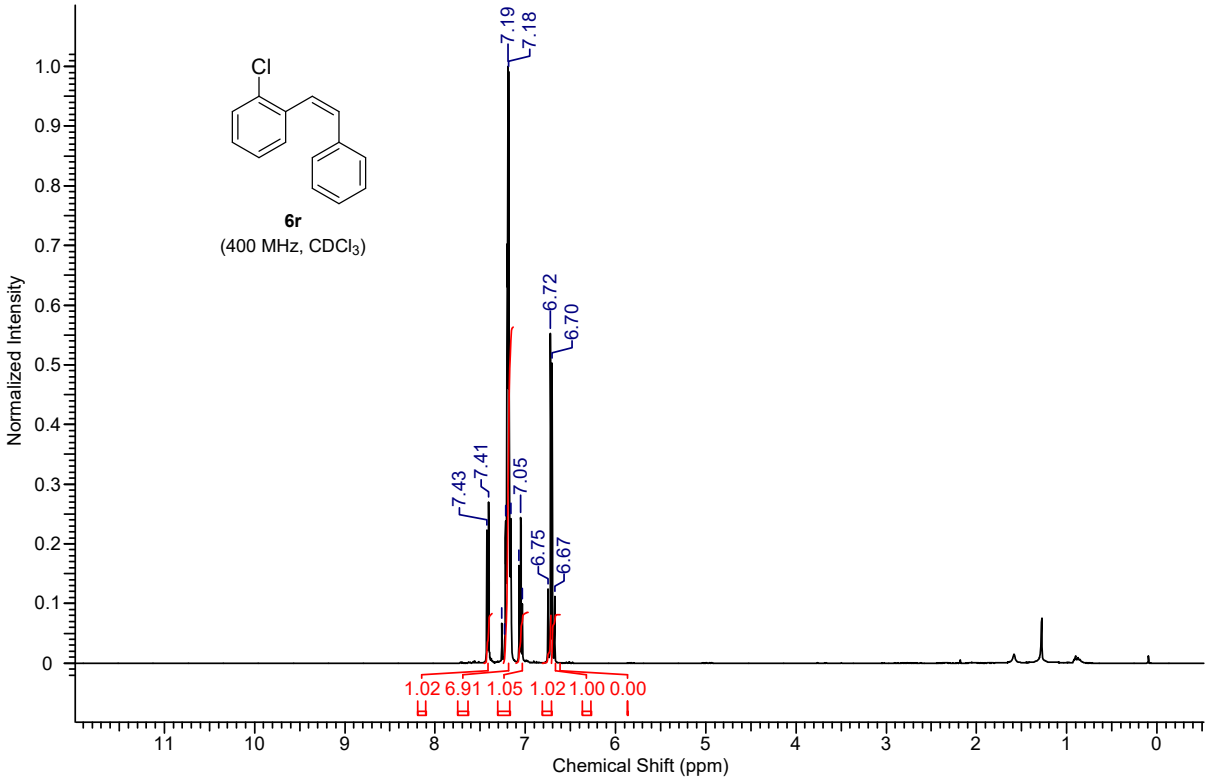

Me
Me
6o
(100 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
126.77
128.27
129.05
130.63
137.80
137.56
21.39

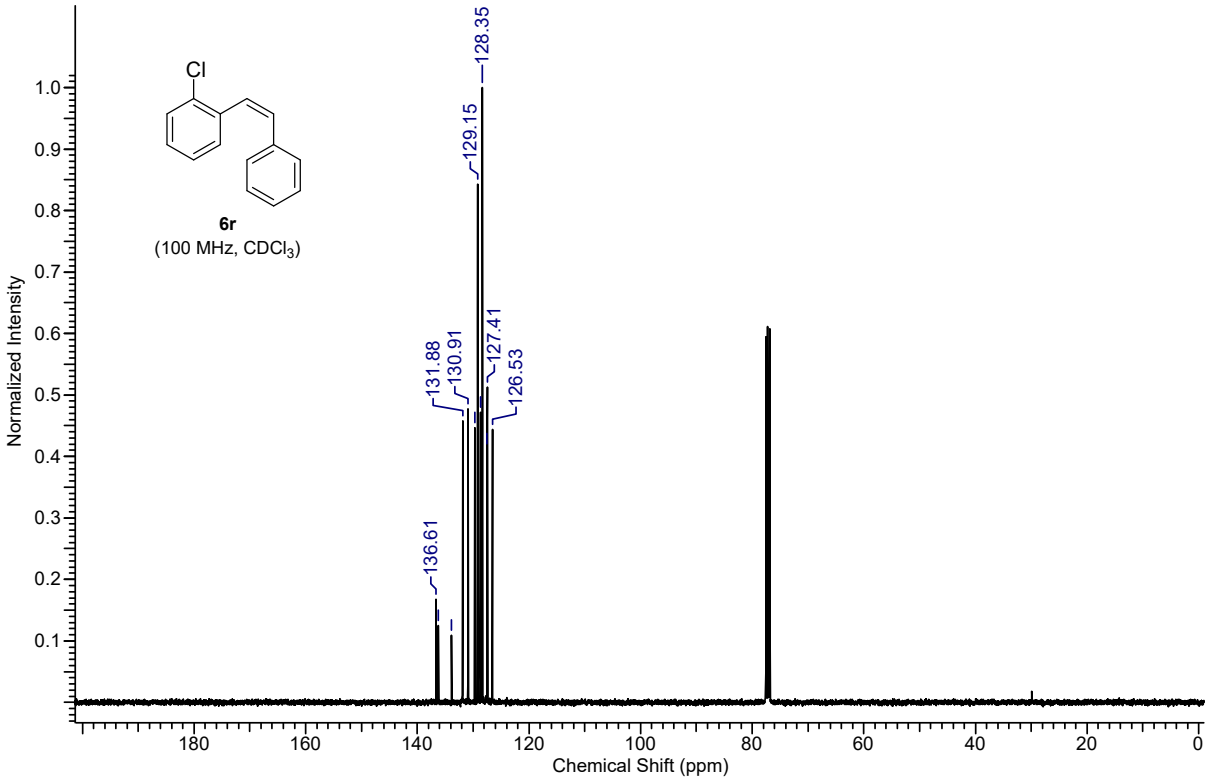

OCH3
6p
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
3.66
7.27
7.27
7.25
7.16
6.62
6.60
7.30
7.29
6.57
6.33 0.94 0.97 1.04 0.99 1.02
3.21

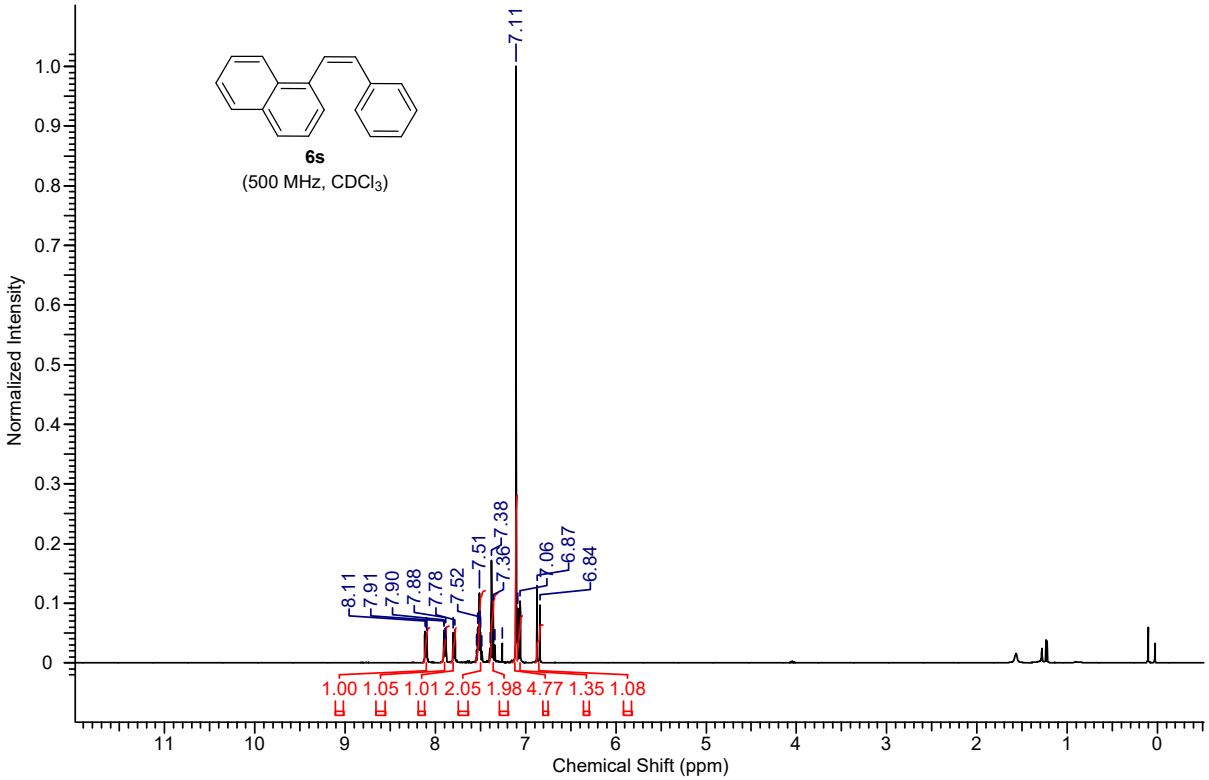

OCH3
6p
(125 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
159.51
138.71
137.43
130.66
130.32
129.40
129.09
128.38
127.32
121.69
113.89
113.49
55.20

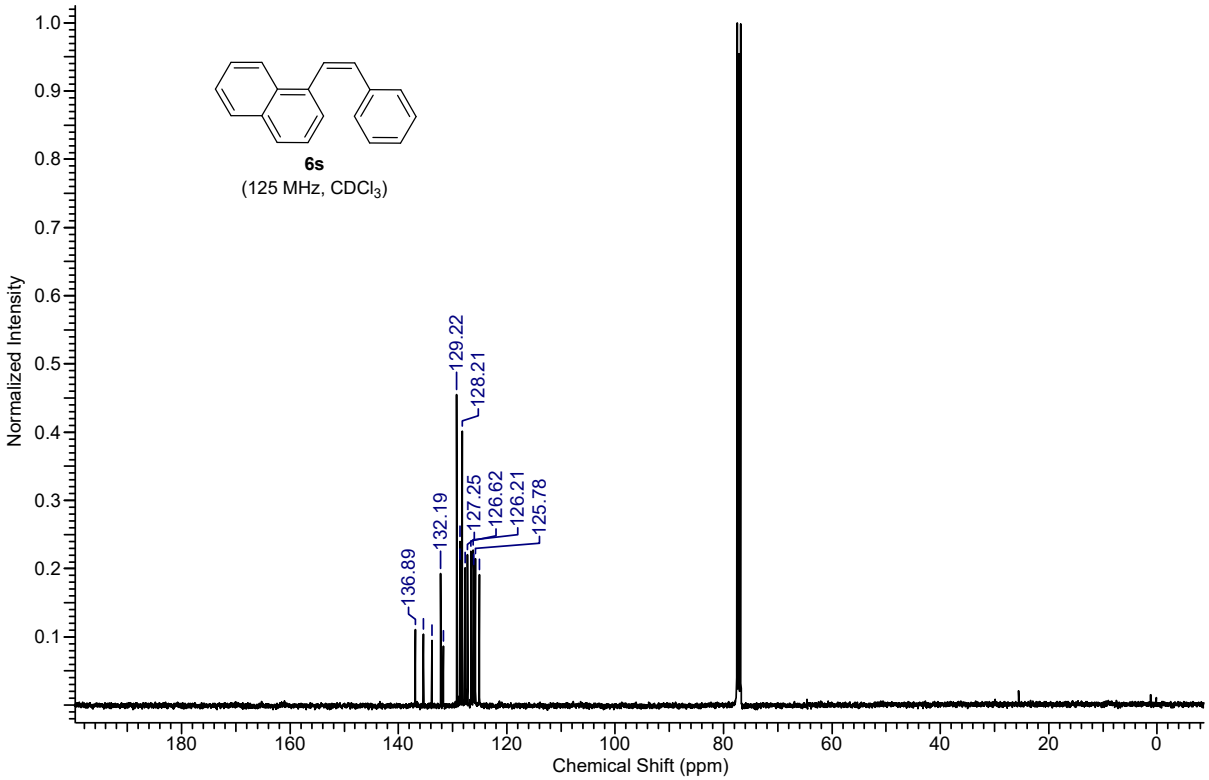

OMe
6q
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
3.82
7.25
7.23
7.19
7.17
7.17
7.10
6.90
6.69
6.65
6.62
6.09 0.92 0.85 0.89 0.90
3.01

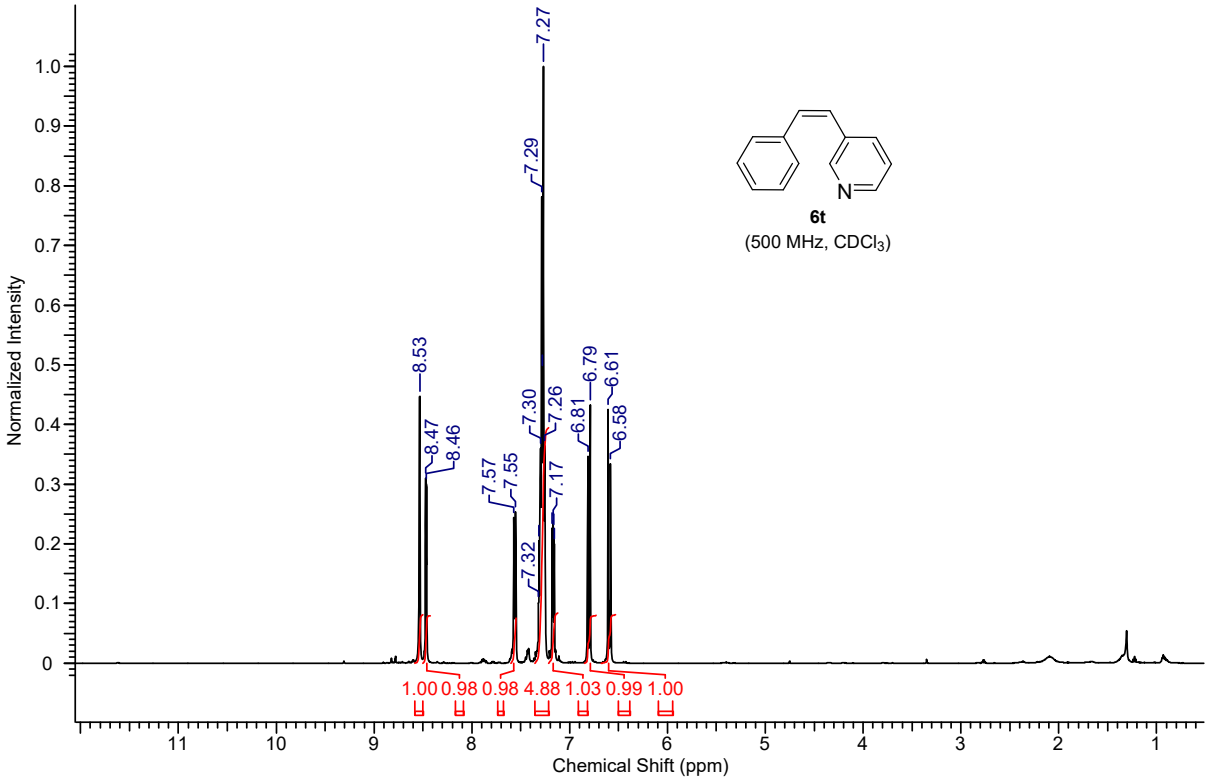

OMe
6q
(125 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
157.40
137.53
130.42
129.02
128.21
126.01
120.40
110.88
55.64

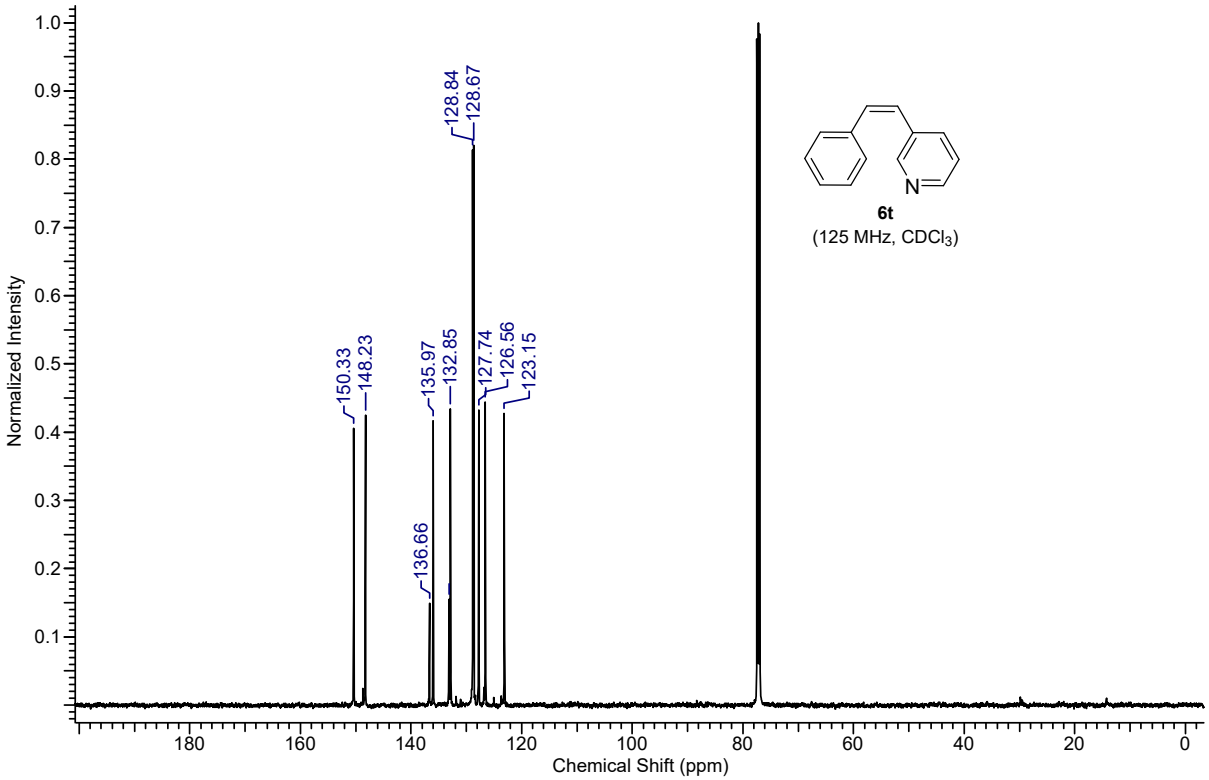

Cl
6r
(400 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
7.19
7.18
6.72
6.70
7.43
7.41
7.05
6.75
6.67
1.02 6.91 1.05 1.02 1.00 0.00

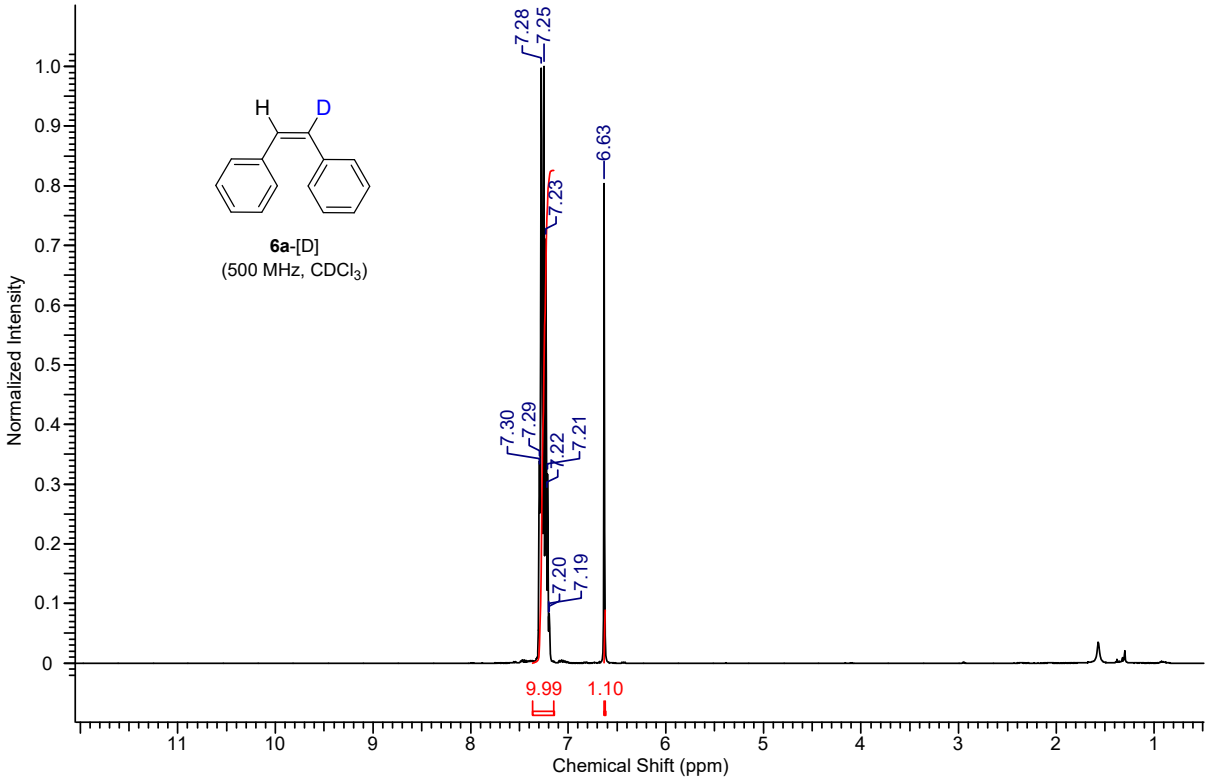

Cl
6r
(100 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
128.35
129.15
131.88
130.91
127.41
126.53
136.61

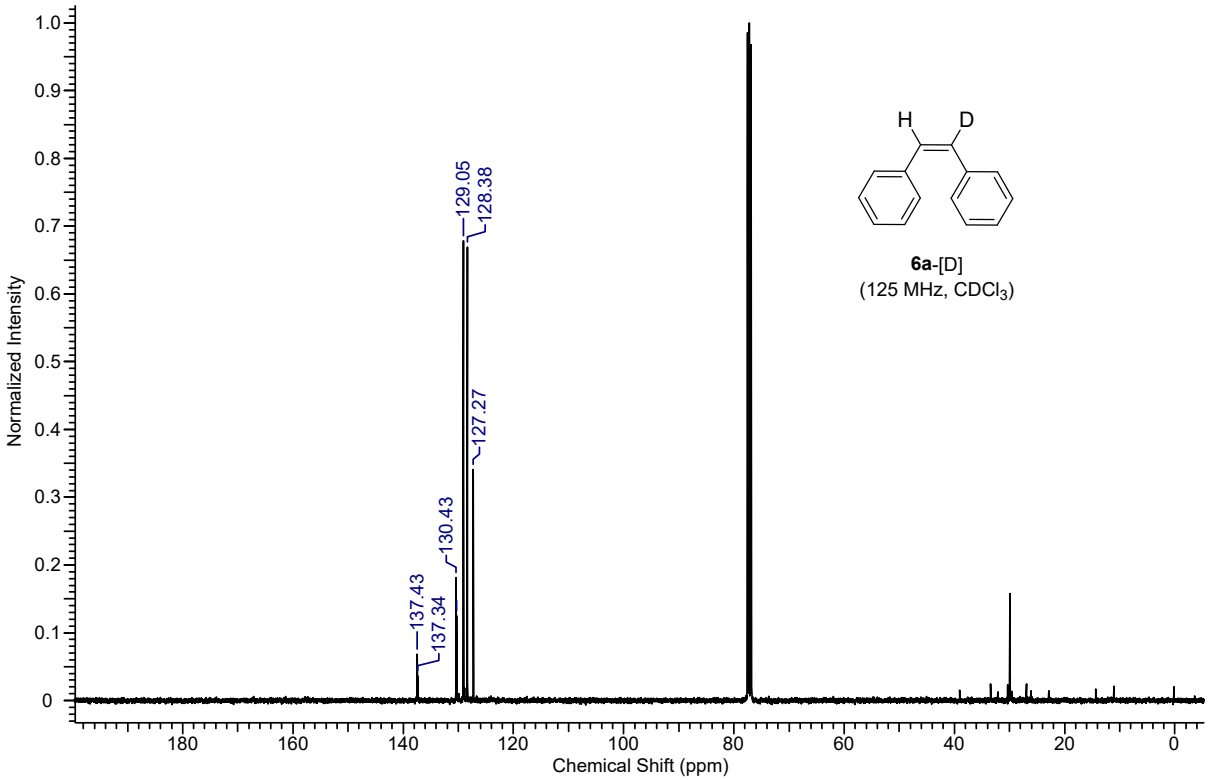

6s
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
7.11
8.11
7.91
7.90
7.88
7.78
7.52
7.51
7.38
7.36
7.06
6.87
6.84
1.00 1.05 1.01 2.05 1.98 4.77 1.35 1.08


6s
(125 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
136.89
132.19
129.22
128.21
127.25
126.62
126.21
125.78


Normalized Intensity
Chemical Shift (ppm)
8.53
8.47
8.46
7.57
7.55
7.32
7.30
7.29
7.27
7.26
7.17
6.81
6.79
6.61
6.58
1.00 0.98 0.98 4.88 1.03 0.99 1.00
N
6t
(500 MHz, CDCl3)


Normalized Intensity
Chemical Shift (ppm)
150.33
148.23
136.66
135.97
132.85
128.84
128.67
127.74
126.56
123.15
N
6t
(125 MHz, CDCl3)


H
D
6a-[D]
(500 MHz, CDCl3)
7.28
7.25
6.63
7.23
7.30
7.29
7.22
7.21
7.20
7.19
9.99
1.10
Normalized Intensity
Chemical Shift (ppm)


H
D
6a-[D]
(125 MHz, CDCl3)
129.05
128.38
127.27
130.43
137.43
137.34
Normalized Intensity
Chemical Shift (ppm)