Supporting Information For:

Nickel-catalyzed allyl-allyl coupling reactions between 1,3-dienes and allylboronates

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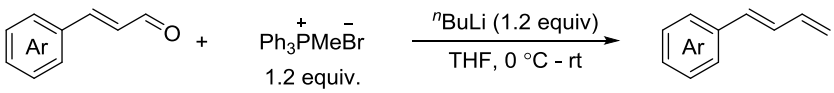
1. General experimental details: All the reagents were commercially available and were used without further purification unless otherwise stated. Solvents were treated prior to use according to the standard methods. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on 400 MHz instrument with tetramethylsilane (TMS) as internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Flash column chromatography was performed on commercially available silica gel (200-300 mesh). All reactions were monitored by TLC, GC-FID, GC-MS or NMR analysis. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI) or Agilent 6540 Accurate-MS spectrometer (Q-TOF).

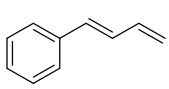
2. Typical procedure for the preparation of substrates

Substrates **1a-1o** were synthesized according to the following procedure[1].

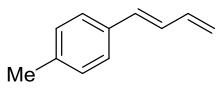


To a flame-dried round-bottom flask, methyltriphenylphosphonium bromide (6.0 mmol) in THF (40 mL) was added ^{n}BuLi (2.4 mL, 2.5 M in THF, 6.0 mmol) slowly at 0 °C under N_2. After stirring for 20 min, a cinnamaldehyde (5.0 mmol) was added. The reaction mixture was then

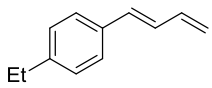
warmed to room temperature and stirred for another 5-10 hours. After the starting material was consumed completely which was detected by TLC, the reaction mixture was quenched with sat. NH_4Cl aq. (15 mL) and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over $MgSO_4$, concentrated in vacuo and purified by flash chromatography on silica gel with *n*-pentene or *n*-hexane to afford the diene products **1a-1o**.



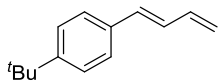
(*E*)-Buta-1,3-dien-1-ylbenzene (1a)[1]: Prepared according to the general procedure, 85% yield, yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.7 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 6.78 (dd, J = 15.6, 10.5 Hz, 1H), 6.55 (d, J = 15.6 Hz, 1H), 6.49 (dt, J = 16.9, 10.3 Hz, 1H), 5.32 (d, J = 16.9 Hz, 1H), 5.16 (d, J = 10.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.23, 137.16, 132.90, 129.66, 128.65, 127.67, 126.49, 117.66.



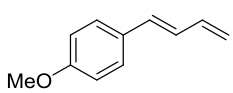
(*E*)-1-(buta-1,3-dien-1-yl)-4-methylbenzene (1b)[1]: Prepared according to the general procedure, 86% yield, yellow oil. **^{1}H NMR** δ 7.28 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.73 (dd, J = 15.6, 10.5 Hz, 1H), 6.52 (d, J = 15.5 Hz, 1H), 6.48 (dt, J = 16.9, 10.3 Hz, 1H), 5.31 – 5.26 (m, 1H), 5.14 – 5.10 (m, 1H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.55, 137.38, 134.39, 132.88, 129.38, 128.74, 126.42, 117.05, 21.29.



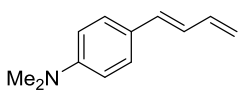
(*E*)-1-(buta-1,3-dien-1-yl)-4-ethylbenzene (1c)[2]: Prepared according to the general procedure, 89% yield, yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 6.74 (dd, J = 15.6, 10.5 Hz, 1H), 6.52 (d, J = 16.6 Hz, 1H), 6.48 (dt, J = 16.9, 10.0 Hz, 1H), 5.32 – 5.26 (m, 1H), 5.14 – 5.10 (m, 1H), 2.61 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.96, 137.41, 134.66, 132.91, 128.81, 128.19, 126.51, 117.05, 28.70, 15.57.



(*E*)-1-(buta-1,3-dien-1-yl)-4-(tert-butyl)benzene (1d)[1]: Prepared according to the general procedure, 96% yield, yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (s, 4H), 6.75 (dd, J = 15.6, 10.5 Hz, 1H), 6.54 (d, J = 15.6 Hz, 1H), 6.49 (dt, J = 16.9, 10.2 Hz, 1H), 5.32 – 5.28 (m, 1H), 5.15 – 5.12 (m, 1H), 1.31 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.80, 137.39, 134.38, 132.73, 128.93, 126.21, 125.57, 117.06, 34.64, 31.31.

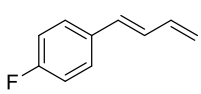


(*E*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene (1e)[1]: Prepared according to the general procedure, 71% yield, white solid, melting point: 43 – 44 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.3 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.67 (dd, J = 15.5, 10.4 Hz, 1H), 6.55 – 6.42 (m, 2H), 5.31 – 5.25 (m, 1H), 5.13 – 5.07 (m, 1H), 3.81 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.28, 137.37, 132.40, 129.93, 127.65, 127.65, 116.44, 114.07, 55.30.

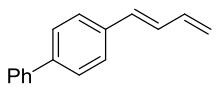


(*E*)-4-(buta-1,3-dien-1-yl)-*N*,*N*-dimethylaniline (1f)[3]: Prepared according to the general procedure, 67% yield, yellow solid, melting point: 57 – 58 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.5 Hz, 2H), 6.69 –

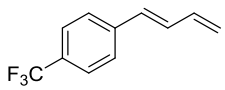
6.58 (m, 3H), 6.54 – 6.42 (m, 2H), 5.22 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.04 (dd, *J* = 9.8, 1.7 Hz, 1H), 2.96 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.11, 137.80, 133.12, 127.52, 125.61, 125.55, 115.00, 112.38, 40.46.



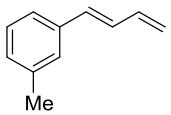
(*E*)-1-(buta-1,3-dien-1-yl)-4-fluorobenzene (1g)[1]: Prepared according to the general procedure, 80% yield, colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 2H), 7.03 – 6.95 (m, 2H), 6.69 (dd, *J* = 15.5, 10.5 Hz, 1H), 6.54 – 6.41 (m, 2H), 5.35 – 5.29 (m, 1H), 5.20 – 5.13 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.33 (d, *J* = 247.2 Hz), 136.99 , 133.31 (d, *J* = 3.5 Hz), 131.58 , 129.39 (d, *J* = 2.4 Hz), 127.91 (d, *J* = 8.0 Hz), 117.68 (d, *J* = 1.3 Hz), 115.56 (d, *J* = 21.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.19



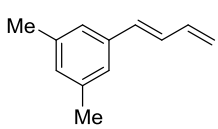
(*E*)-4-(buta-1,3-dien-1-yl)-1,1'-biphenyl (1h)[1]: Prepared according to the general procedure, 86% yield, white solid, melting point: 112 – 114 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 4H), 7.48 – 7.41 (m, 4H), 7.36 – 7.31 (m, 1H), 6.83 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.63 – 6.48 (m, 2H), 5.35 (d, *J* = 16.9 Hz, 1H), 5.19 (d, *J* = 9.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.66, 140.34, 137.21, 136.18, 132.39, 129.71, 128.80, 127.33, 127.29, 126.91, 126.87, 117.72.



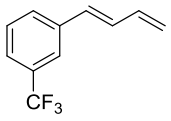
(*E*)-1-(buta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (1i)[4]: Prepared according to the general procedure, 87% yield, yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 6.85 (dd, *J* = 15.7, 10.5 Hz, 1H), 6.56 (d, *J* = 15.7 Hz, 1H), 6.51 (dt, *J* = 16.9, 10.3 Hz, 1H), 5.40 (dd, *J* = 16.9, 1.2 Hz, 1H), 5.26 (dd, *J* = 10.0, 1.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.59, 136.66, 131.97, 131.21, 129.26 (q, *J* = 32.4 Hz), 126.48, 125.54 (q, *J* = 3.8 Hz), 124.21 (q, *J* = 271.1 Hz), 119.40. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.50.



(*E*)-1-(buta-1,3-dien-1-yl)-3-methylbenzene (1j)[5]: Prepared according to the general procedure, 92% yield, yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 3H), 7.05 – 7.02 (m, 1H), 6.77 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.55 – 6.45 (m, 2H), 5.34 – 5.29 (m, 1H), 5.17 – 5.14 (m, 1H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.14, 137.27, 137.07, 132.99, 129.46, 128.52, 128.48, 127.16, 123.65, 117.42, 21.42.

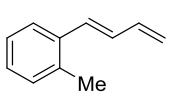


(*E*)-1-(buta-1,3-dien-1-yl)-3,5-dimethylbenzene (1k)[1]: Prepared according to the general procedure, 83% yield, yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 (s, 2H), 6.86 (s, 1H), 6.79 – 6.72 (m, 1H), 6.53 – 6.42 (m, 2H), 5.32 – 5.27 (m, 1H), 5.15 – 5.11 (m, 1H), 2.23 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.04, 137.37, 137.05, 133.12, 129.47, 129.31, 124.39, 117.22, 21.30.

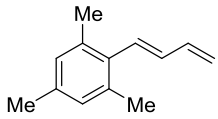


(*E*)-1-(buta-1,3-dien-1-yl)-3-(trifluoromethyl)benzene(1l)[4]: Prepared according to the general procedure, 51% yield, yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 1.4 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.38 (m, 2H), 6.83 (dd, *J* = 15.7, 10.5 Hz, 1H), 6.59 – 6.45 (m, 2H), 5.42 – 5.37 (m, 1H), 5.26 –

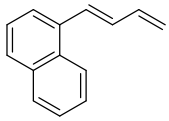
5.23 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.91, 136.63, 131.33, 131.16, 131.05 (q, J = 31.9 Hz), 129.46, 129.03, 124.12 (q, J = 270.7), 124.04 (q, J = 3.9 Hz), 122.97 (q, J = 3.9 Hz), 119.08. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.84.



(*E*)-1-(buta-1,3-dien-1-yl)-2-methylbenzene (1m)[5]: Prepared according to the general procedure, 99% yield, yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 1H), 7.17 – 7.10 (m, 3H), 6.79 – 6.64 (m, 2H), 6.52 (dt, J = 16.8, 10.0 Hz, 1H), 5.31 (dd, J = 16.8, 1.5 Hz, 1H), 5.15 (dd, J = 10.0, 1.5 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.59, 136.06, 135.70, 130.84, 130.58, 130.48, 127.61, 126.19, 125.26, 117.54, 19.89.

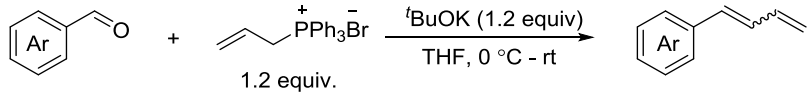


(*E*)-2-(buta-1,3-dien-1-yl)-1,3,5-trimethylbenzene (1n)[6]: Prepared according to the general procedure, 75% yield, yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.85 (s, 2H), 6.56 (d, J = 16.0 Hz, 1H), 6.27 (dd, J = 16.0, 10.3 Hz, 1H), 6.52 (dt, J = 17.0, 10.2 Hz, 1H), 5.23 (d, J = 16.9 Hz, 1H), 5.12 (d, J = 10.0 Hz, 1H), 2.28 (s, 6H), 2.26 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.74, 136.33, 136.06, 134.75, 133.60, 131.06, 128.77, 116.60, 21.08, 21.00.

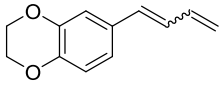


(*E*)-1-(buta-1,3-dien-1-yl)naphthalene (1o)[1]: Prepared according to the general procedure, 50% yield, yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.1 Hz, 1H), 7.82 (dd, J = 7.5, 1.9 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 7.2 Hz, 1H), 7.52 – 7.40 (m, 3H), 7.33 (d, J = 15.3 Hz, 1H), 6.84 (dd, J = 15.3, 10.6 Hz, 1H), 6.65 (dt, J = 16.8, 10.2 Hz, 1H), 5.38 (d, J = 16.8 Hz, 1H), 5.22 (d, J = 10.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.47, 134.54, 133.76, 132.50, 131.21, 129.66, 128.64, 128.07, 126.10, 125.82, 125.64, 123.65, 123.44, 117.99.

Substrates **1p-1r** were synthesized according to the following procedures.[1]

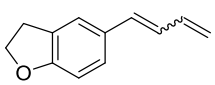


To a flame-dried round-bottom flask, allyltriphenylphosphonium bromide (6.0 mmol) in THF (40 mL) was added potassium *tert*-butoxide (6.0 mmol) at 0 °C under N_2. After stirring for 20 min, an aldehyde (5.0 mmol) was added. The reaction mixture was then warmed to room temperature and stirred for another 10-18 hours. After the starting material was consumed completely which was detected by TLC, the reaction mixture was quenched with sat. NH_4Cl aq. (15 mL) and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over $MgSO_4$, concentrated in vacuo and purified by flash chromatography on silica gel with *n*-hexane to afford the diene products **1p-1r**.

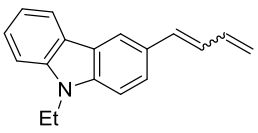


6-(buta-1,3-dien-1-yl)-2,3-dihydrobenzo[b][1,4]dioxine (1p): Prepared according to the general procedure, 57% yield (Z/*E* = 1.7/1), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94 – 6.78 (m, *Z*/*E*), 6.63 (dd, J = 15.6, 10.3 Hz,

E), 6.51 – 6.41 (m, 1H, *E*), 6.32 (d, *J* = 11.5 Hz, 1H, *Z*), 6.16 (t, *J* = 11.3 Hz, 1H, *Z*), 5.33 (d, *J* = 16.8 Hz, 1H, *Z*), 5.30 – 5.24 (m, 1H, *E*), 5.19 (d, *J* = 10.2 Hz, 1H, *Z*), 5.11 (d, *J* = 10.0 Hz, 1H, *E*), 4.24 (s, 4H, *Z*), 4.23 (s, 4H, *E*). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 143.57, 143.40, 143.18, 142.82, 137.25, 133.30, 132.31, 130.98, 129.75, 128.21, 122.50, 120.00, 119.18, 117.74, 117.38, 117.02, 116.77, 114.92, 64.47, 64.37. C signals could not be located likely due to overlapping. **HRMS** Calculated for $C_{12}H_{13}O_2$ $[M+H]^+$ 189.0910, found 189.0913.



5-(buta-1,3-dien-1-yl)-2,3-dihydrobenzofuran (1q): Prepared according to the general procedure, 49% yield (*Z*/*E* = 1.7/1), yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.28 – 6.72 (m, *Z*/*E*), 6.64 (dd, *J* = 15.3, 10.6 Hz, 1H, *E*), 6.53 – 6.42 (m, 2H, *E*), 6.38 (d, *J* = 11.5 Hz, 1H, *Z*), 6.19 – 6.12 (m, 1H, *Z*), 5.36 – 5.31 (m, 1H, *Z*), 5.28 – 5.23 (m, 1H, *E*), 5.20 – 5.16 (m, 1H, *Z*), 5.10 – 5.07 (m, 1H, *E*), 4.58 (t, *J* = 8.7, 2H, *Z*), 4.57 (t, *J* = 8.7, 2H, *E*), 3.20 (t, *J* = 8.7, 2H, *Z*), 3.18 (t, *J* = 8.7, 2H, *E*). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 159.99, 159.31, 137.45, 133.42, 132.85, 130.39, 130.01, 129.19, 128.96, 127.54, 127.09, 127.05, 125.58, 122.63, 118.70, 116.10, 109.34, 109.01, 71.40, 29.65. C signals could not be located likely due to overlapping. **HRMS** Calculated for $C_{12}H_{13}O$ $[M+H]^+$ 173.0961, found 173.0962.

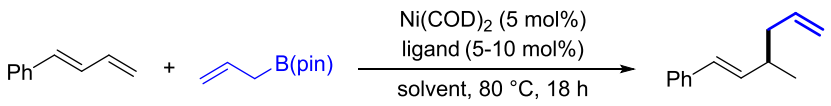


3-(buta-1,3-dien-1-yl)-9-ethyl-9H-carbazole (1r): Prepared according to the general procedure, 51% yield (*Z*/*E* = 2.5/1), yellow solid, melting point: 85 – 87 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.12 – 8.07 (m, 2H, *Z*/*E*), 7.58 – 7.33 (m, 4H, *Z*/*E*), 7.26 – 7.21 (m, 1H, *Z*/*E*), 7.05 (dt, *J* = 16.9, 10.7 Hz, 1H, *Z*), 6.89 – 6.74 (m, 2H, *E*), 6.66 (d, *J* = 11.4 Hz, 1H, *Z*), 6.57 (dt, *J* = 16.7, 9.9 Hz, 1H. *E*), 6.28 (t, *J* = 11.3 Hz, 1H, *Z*), 5.40 (d, *J* = 16.9 Hz, 1H, *Z*), 5.32 (d, *J* = 17.1 Hz, 1H, *E*), 5.23 (d, *J* = 10.1 Hz, 1H, *Z*), 5.13 (d, *J* = 10.0 Hz, 1H, *E*), 4.40 – 4.32 (m, 2H, *Z*/*E*), 1.44 (td, *J* = 7.2, 3.4 Hz, 3H, *Z*/*E*). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 140.38, 140.34, 139.76, 139.14, 137.73, 133.99, 133.80, 131.43, 129.00, 128.39, 128.35, 127.17, 125.84, 124.43, 123.29, 122.98, 121.00, 120.53, 119.06, 119.01, 118.74, 115.91, 108.66, 108.63, 108.19, 37.64, 13.88. C signals could not be located likely due to overlapping. **HRMS** Calculated for $C_{18}H_{18}N$ $[M+H]^+$ 248.1434, found 248.1433.

Substrates **2b-2d** were synthesized according to reported procedures.[7]

3. Screening of reaction conditions

Table S1. Screening of the conditions for 3a[a]



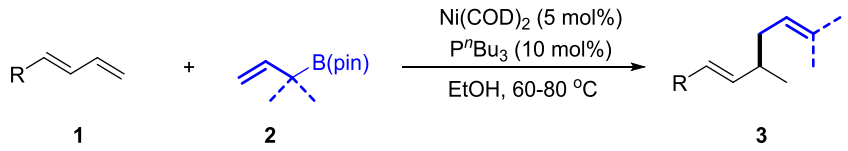
1a **2a** **3a**

Entry	Ligand (x mol%)	Additive (2.0 equiv)	Solvent	T (°C)	Yield(%) [b]
1	PPh_3 (10)	-	MeOH	80	50

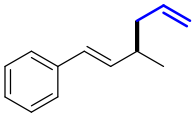
2	PPh_3 (10)	-	EtOH	80	58
3	PPh_3 (10)	-	^{n}PrOH	80	51
4	PPh_3 (10)	-	^{i}PrOH	80	55
5	PPh_3 (10)	-	^{t}BuOH	80	45
6	PCy_3 (10)	-	EtOH	80	22
7	P(^{t}Bu)$_3$ (10)	-	EtOH	80	trace
8	P(^{n}Bu)$_3$ (10)	-	EtOH	80	83
9	dppp (5)	-	EtOH	80	2
10	dppb (5)	-	EtOH	80	50
11	dppf (5)		EtOH	80	5
12	P(^{n}Bu)$_3$ (10)	EtOH	THF	80	8
13	P(^{n}Bu)$_3$ (10)	EtOH	Dioxane	80	28
14	P(^{n}Bu)$_3$ (10)	EtOH	DMF	80	73
15	P(^{n}Bu)$_3$ (10)	EtOH	MeCN	80	17
16	P(^{n}Bu)$_3$ (10)	EtOH	DME	80	23
17	P(^{n}Bu)$_3$ (10)	-	EtOH	60	42
18	P(^{n}Bu)$_3$ (10)	-	EtOH	100	74
19[c]	P(^{n}Bu)$_3$ (10)	-	EtOH	80	93 (85)[e]
20[d]	P(^{n}Bu)$_3$ (10)	-	EtOH	80	75
21[c]	P(^{n}Bu)$_3$ (10)	-	MeOH	80	71
22[c]	P(^{n}Bu)$_3$ (10)	-	^{i}PrOH	80	56
23[c]	P(^{n}Bu)$_3$ (10)	-	^{t}BuOH	80	32

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), $Ni(COD)_2$ (5 mol%), ligand (5 -10 mol%), additive (2.0 equiv), solvent (0.5 mL), 80 °C, 18 h. [b]Determined by GC-FID using 1,3,5-trimethoxybenzene as internal standard. [c]0.25 mL EtOH. [d]1.0 mL EtOH. [e]Isolated yield.

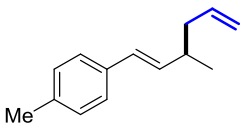
4. Typical procedure for nickel-catalyzed allyl-allyl coupling reaction



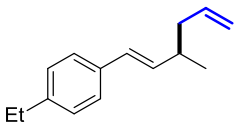
In glove box, a sealed tube was charged with $Ni(COD)_2$ (0.01 mmol, 5 mol%), P^{n}Bu$_3$ (0.02 mmol, 10 mol%) and EtOH (0.25 mL) at room temperature. After stirring for 20 min, 1,4-diene **1** (0.20 mmol, 1.0 equiv) and allylboronate **2** (0.40 mmol, 2.0 equiv) were added. Then the reaction tube was sealed with a teflon screw cap, removed from the glove box and stirred at 60-80 °C for 6-72 h. After cooling to room temperature, the reaction mixture was directly purified by column chromatography on silica gel using *n*-pentene or *n*-hexane to afford the corresponding product **3**.



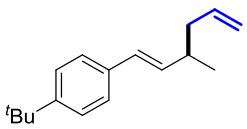
(*E*)-(3-methylhexa-1,5-dien-1-yl)benzene (3a): Prepared according to the general procedure, 80 °C, 18 h, 85% yield, known compound,[8] colorless oil, R_f = 0.85 (Petroleum ether), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 7.30 – 7.26 (m, 2H), 7.21 – 7.16 (m, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 6.15 (dd, *J* = 15.9, 7.5 Hz, 1H), 5.81 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.07 – 4.99 (m, 2H), 2.45 – 2.34 (m, 1H), 2.24 – 2.08 (m, 2H), 1.09 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.82, 136.98, 136.06, 128.48, 128.19, 126.87, 126.02, 115.98, 41.41, 36.93, 19.95.



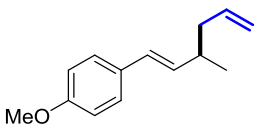
(*E*)-1-methyl-4-(3-methylhexa-1,5-dien-1-yl)benzene (3b): Prepared according to the general procedure, 80 °C, 22 h, 90% yield, known compound,[9] colorless oil, R_f = 0.82 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.32 (dd, *J* = 15.9, 1.0 Hz, 1H), 6.09 (dd, *J* = 15.9, 7.5 Hz, 1H), 5.81 (ddt, *J* = 17.1, 10.2, 7.1 Hz, 1H), 5.05 – 4.98 (m, 2H) 2.44 – 2.28 (m, 1H), 2.32 (s, 3H), 2.23 – 2.07 (m, 2H), 1.08 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.07, 136.56, 135.05, 135.04, 129.18, 128.00, 125.91, 115.91, 41.48, 36.92, 21.15, 19.99.



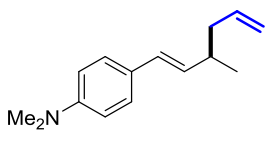
(*E*)-1-ethyl-4-(3-methylhexa-1,5-dien-1-yl)benzene (3c): Prepared according to the general procedure, 80 °C, 18 h, 83% yield, colorless oil, R_f = 0.85 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.33 (dd, *J* = 16.0, 1.0 Hz, 1H), 6.09 (dd, *J* = 15.9, 7.5 Hz, 1H), 5.80 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.06 – 4.98 (m, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.43 – 2.32 (m, 1H), 2.23 – 2.07 (m, 2H), 1.22 (t, *J* = 7.6 Hz, 3H), 1.08 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.04, 137.07, 135.30, 135.14, 128.02, 128.00, 125.99, 115.90, 41.48, 36.94, 28.59, 20.01, 15.67. **HRMS** Calculated for $C_{15}H_{20}$ $[M]^+$ 200.1565, found 200.1560.



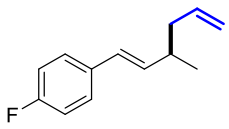
(*E*)-1-(tert-butyl)-4-(3-methylhexa-1,5-dien-1-yl)benzene (3d): Prepared according to the general procedure, 80 °C, 36 h, 85% yield, colorless oil, R_f = 0.72 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 77.34 – 7.27 (m, 4H), 6.33 (d, *J* = 15.9 Hz, 1H), 6.10 (dd, *J* = 15.9, 7.5 Hz, 1H), 5.80 (ddt, *J* = 17.2, 10.1, 7.0 Hz, 1H), 5.05 – 4.97 (m, 2H), 2.38 (hept, *J* = 7.1 Hz, 1H), 2.23 – 2.07 (m, 2H), 1.30 (s, 9H), 1.08 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.91, 137.08, 135.33, 135.06, 127.91, 125.73, 125.41, 115.91, 41.50, 36.98, 34.52, 31.36, 20.05. **HRMS** Calculated for $C_{17}H_{24}$ $[M]^+$ 228.1878, found 228.1872.



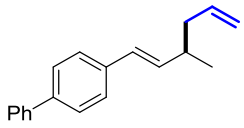
(*E*)-1-methoxy-4-(3-methylhexa-1,5-dien-1-yl)benzene (3e): Prepared according to the general procedure, 80 °C, 72 h, 62% yield, known compound,[8] colorless oil, R_f = 0.35 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.30 (d, *J* = 15.9 Hz, 1H), 6.00 (dd, *J* = 15.9, 7.5 Hz, 1H), 5.81 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.05 – 4.98 (m, 2H), 3.79 (s, 3H), 2.37 (hept, *J* = 6.8 Hz, 1H), 2.22 – 2.07 (m, 2H), 1.08 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.69, 137.11, 133.97, 130.65, 127.50, 127.08, 115.87, 113.91, 55.30, 41.52, 36.89, 20.04.



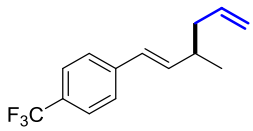
(*E*)-*N*,*N*-dimethyl-4-(3-methylhexa-1,5-dien-1-yl)aniline (3f): Prepared according to the general procedure, 80 °C, 24 h, 33% yield, colorless oil, R_f = 0.75 (PE/EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 9.0 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 6.27 (d, *J* = 15.9 Hz, 1H), 5.94 (dd, *J* = 15.9, 7.5 Hz, 1H), 5.81 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.05 – 4.97 (m, 2H), 2.93 (s, 6H), 2.42 – 2.29 (m, 1H), 2.22 – 2.05 (m, 2H), 1.07 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.75, 137.33, 132.04, 127.83, 126.82, 126.59, 115.69, 112.68, 41.69, 40.69, 36.93, 20.17. **HRMS** Calculated for $C_{15}H_{22}N$ $[M+H]^+$ 216.1747, found 216.1749.



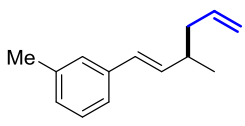
(*E*)-1-fluoro-4-(3-methylhexa-1,5-dien-1-yl)benzene (3g): Prepared according to the general procedure, 80 °C, 18 h, 80% yield, known compound,[8] colorless oil, R_f = 0.80 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.00 – 6.94 (m, 2H), 6.31 (dd, *J* = 15.9, 1.1 Hz, 1H), 6.05 (dd, *J* = 15.9, 7.4 Hz, 1H), 5.80 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.07 – 4.99 (m, 2H), 2.44 – 2.33 (m, 1H), 2.23 – 2.08 (m, 2H), 1.09 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.92 (d, *J* = 246.5 Hz), 136.89, 135.79 (d, *J* = 2.3 Hz), 133.94 (d, *J* = 3.3 Hz), 127.40 (d, *J* = 8.0 Hz), 127.04, 116.03, 115.29 (d, *J* = 21.5 Hz), 41.37, 36.87, 19.92; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.78.



(*E*)-4-(3-methylhexa-1,5-dien-1-yl)-1,1'-biphenyl (3h): Prepared according to the general procedure, 70 °C, 14 h, 87% yield, known compound,[8] colorless oil, R_f = 0.80 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.40 (m, 4H), 7.34 – 7.30 (m, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.19 (dd, *J* = 15.9, 7.4 Hz, 1H), 5.82 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.08 – 5.00 (m, 2H), 2.42 (hept, *J* = 6.9 Hz, 1H), 2.28 – 2.08 (m, 2H), 1.11 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.90, 139.67, 136.98, 136.90, 136.28, 128.78, 127.79, 127.22, 127.18, 126.93, 126.45, 116.05, 41.44, 37.03, 19.99.

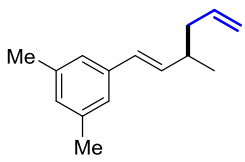


(*E*)-1-(3-methylhexa-1,5-dien-1-yl)-4-(trifluoromethyl)benzene (3i): Prepared according to the general procedure, 70 °C, 6 h, 71% yield, known compound,[8] colorless oil, R_f = 0.75 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 16.0, 7.3 Hz, 1H), 5.80 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.08 – 5.00 (m, 2H), 2.43 (hept, *J* = 6.9 Hz, 1H), 2.18 (qt, *J* = 13.9, 6.9 Hz, 2H), 1.11 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.29, 138.81, 136.61, 128.70 (q, *J* = 32.7 Hz), 127.09, 126.12, 125.41 (q, *J* = 3.8 Hz), 121.60 (q, *J* = 272.7 Hz), 116.24, 41.19, 36.96, 19.74. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.40.

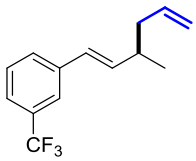


(*E*)-1-methyl-3-(3-methylhexa-1,5-dien-1-yl)benzene (3j): Prepared according to the general procedure, 80 °C, 24 h, 93% yield, colorless oil, R_f = 0.75 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 3H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.32 (d, *J* = 15.9 Hz, 1H), 6.13 (dd, *J* = 15.9, 7.5 Hz, 1H), 5.81 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.06 – 4.98 (m, 2H), 2.43 – 2.32 (m, 4H), 2.23 – 2.07 (m, 2H), 1.09 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.99, 137.76, 137.02,

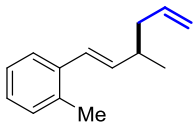
135.86, 128.40, 128.26, 127.67, 126.73, 123.20, 115.95, 41.43, 36.97, 21.43, 19.99. **HRMS** Calculated for $C_{14}H_{18}$ $[M]^+$ 186.1409, found 186.1405.



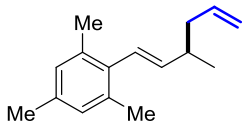
(*E*)-1,3-dimethyl-5-(3-methylhexa-1,5-dien-1-yl)benzene (3k): Prepared according to the general procedure, 80 °C, 18 h, 82% yield, known compound,[8] colorless oil, R_f = 0.73 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.97 (s, 2H), 6.84 (s, 1H), 6.29 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 15.9, 7.5 Hz, 1H), 5.80 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.06 – 4.98 (m, 2H), 2.37 (hept, *J* = 7.0 Hz, 1H), 2.29 (s, 6H), 2.23 – 2.07 (m, 2H), 1.08 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.91, 137.73, 137.06, 135.68, 128.61, 128.31, 123.93, 115.91, 41.45, 37.00, 21.30, 20.02.



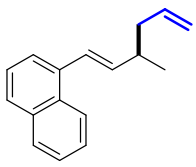
(*E*)-1-(3-methylhexa-1,5-dien-1-yl)-3-(trifluoromethyl)benzene (3l): Prepared according to the general procedure, 70 °C, 6 h, 86% yield, known compound,[8] colorless oil, R_f = 0.60 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 2.1 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.45 – 7.37 (m, 2H), 6.38 (dd, *J* = 15.9, 1.0 Hz, 1H), 6.22 (dd, *J* = 15.9, 7.4 Hz, 1H), 5.80 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H), 5.08 – 5.00 (m, 2H), 2.42 (tdd, *J* = 13.6, 6.8, 1.1 Hz, 1H), 2.25 – 2.10 (m, 2H), 1.11 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.56, 138.04, 136.66, 130.86 (q, *J* = 32.1 Hz), 129.17, 128.87, 127.03, 124.21 (q, *J* = 273.3 Hz), 123.39 (q, *J* = 3.8 Hz), 122.65 (q, *J* = 3.9 Hz), 116.21, 41.20, 36.95, 19.80. **^{9}F NMR** (376 MHz, $CDCl_3$) δ -62.75.



(*E*)-1-methyl-2-(3-methylhexa-1,5-dien-1-yl)benzene (3m): Prepared according to the general procedure, 80 °C, 18 h, 83% yield, colorless oil, R_f = 0.78 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.9 Hz, 1H), 7.15 –7.10 (m,3H), 6.54 (d, *J* = 15.7 Hz, 1H), 5.99 (dd, *J* = 15.8, 7.6 Hz, 1H), 5.82 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.09 – 4.97 (m, 2H), 2.42 (hept, *J* = 7.0 Hz, 1H), 2.32 (s, 3H), 2.23 – 2.10 (m, 2H), 1.10 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.51, 137.04, 137.02, 135.02, 130.14, 126.83, 126.13, 126.01, 125.53, 115.96, 41.49, 37.24, 20.15, 19.87. **HRMS** Calculated for $C_{14}H_{18}$ $[M]^+$ 186.1409, found 186.1403.

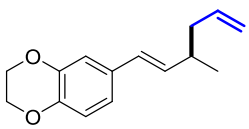


(*E*)-1,3,5-trimethyl-2-(3-methylhexa-1,5-dien-1-yl)benzene (3n): Prepared according to the general procedure, 60 °C, 30 h, 85% yield, colorless oil, R_f = 0.75 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.91 (s, 2H), 6.30 (d, *J* = 16.2 Hz, 1H), 5.89 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H), 5.59 (dd, *J* = 16.2, 7.7 Hz, 1H), 5.12 – 5.05 (m, 2H), 2.53 – 2.42 (m, 1H), 2.31 (s, 3H), 2.30 (s, 6H), 2.22 (tdt, *J* = 6.8, 2.8, 1.3 Hz, 2H), 1.16 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.70, 137.24, 135.85, 135.63, 134.75, 128.41, 125.61, 115.89, 41.54, 37.63, 20.95, 20.93, 20.37. **HRMS** Calculated for $C_{16}H_{22}$ $[M]^+$ 214.1722, found 214.1718.

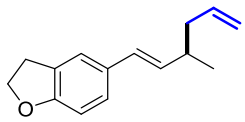


(*E*)-1-(3-methylhexa-1,5-dien-1-yl)naphthalene (3o): Prepared according to the general procedure, 70 °C, 12 h, 92% yield, colorless oil, R_f = 0.70 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 8.09 (m, 1H), 7.81 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.38 (m, 4H), 7.07 (d,

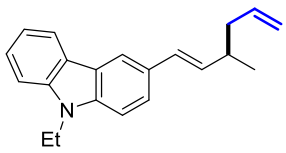
J = 15.6 Hz, 1H), 6.14 (dd, *J* = 15.6, 7.5 Hz, 1H), 5.87 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.11 – 5.03 (m, 2H), 2.52 (hept, *J* = 6.9 Hz, 1H), 2.23 (qt, *J* = 14.0, 7.0 Hz, 2H), 1.17 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 139.46, 137.05, 135.76, 133.67, 131.25, 128.50, 127.33, 125.82, 125.69, 125.67, 125.52, 124.03, 123.64, 116.13, 41.51, 37.35, 20.12. **HRMS** Calculated for $C_{17}H_{18}$ $[M]^+$ 222.1409, found 222.1404.



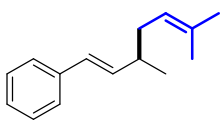
(*E*)-6-(3-methylhexa-1,5-dien-1-yl)-2,3-dihydrobenzo[b][1,4]dioxine (3p): Prepared according to the general procedure, 60 °C, 72 h, 60% yield, colorless oil, R_f = 0.50 (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 6.87 (d, *J* = 2.1 Hz, 1H), 6.83 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 6.23 (dd, *J* = 15.8, 1.1 Hz, 1H), 5.99 (dd, *J* = 15.8, 7.5 Hz, 1H), 5.79 (ddt, *J* = 17.1, 10.2, 7.1 Hz, 1H), 4.98 – 5.04 (m, 2H), 4.24 (s, 4H), 2.39 – 2.33 (m, 1H), 2.19 – 2.08 (m, 2H), 1.07 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 143.46, 142.67, 137.05, 134.57, 131.71, 127.40, 119.39, 117.18, 115.90, 114.46, 64.44, 64.40, 41.47, 36.83, 20.00. **HRMS** Calculated for $C_{15}H_{19}O_2$ $[M+H]^+$ 231.1380, found 231.1390.



(*E*)-5-(3-methylhexa-1,5-dien-1-yl)-2,3-dihydrobenzofuran (3q): Prepared according to the general procedure, 70 °C, 72 h, 23% yield, colorless oil, R_f = 0.45 (PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.23 (s, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.29 (d, *J* = 15.9 Hz, 1H), 5.96 (dd, *J* = 15.9, 7.5 Hz, 1H), 5.81 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.05 – 4.97 (m, 2H), 4.56 (q, *J* = 8.6 Hz, 2H), 3.18 (q, *J* = 8.7 Hz, 2H), 2.43 – 2.28 (m, 1H), 2.22 – 2.06 (m, 2H), 1.07 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 159.27, 137.14, 133.35, 130.70, 127.89, 127.28, 126.29, 122.17, 115.83, 109.11, 71.33, 41.57, 36.89, 29.68, 20.11. **HRMS** Calculated for $C_{15}H_{19}O$ $[M+H]^+$ 215.1430, found 215.1428.

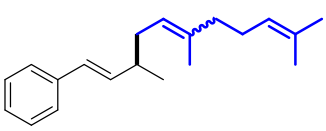


(*E*)-9-ethyl-3-(3-methylhexa-1,5-dien-1-yl)-9H-carbazole (3r): Prepared according to the general procedure, 60 °C, 72 h, 21% yield, known compound,[8] colorless oil, R_f = 0.55 (PE/EA = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.17 – 8.01 (m, 2H), 7.51 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.40 – 7.37 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.23 – 7.20 (m, 1H), 6.55 (d, *J* = 15.7 Hz, 1H), 6.17 (dd, *J* = 15.8, 7.5 Hz, 1H), 5.87 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.11 – 4.99 (m, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.48 – 2.42 (m, 1H), 2.28 – 2.23 (m, 1H), 2.20 – 2.14 (m, 1H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.14 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 140.29, 139.29, 137.29, 133.43, 129.04, 128.78, 125.61, 123.99, 123.16, 123.02, 120.44, 118.77, 118.00, 115.84, 108.51, 108.40, 41.67, 37.07, 29.72, 20.19, 13.83.



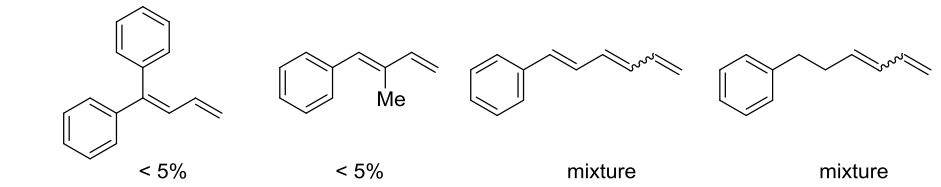
(*E*)-(3,6-dimethylhepta-1,5-dien-1-yl)benzene (3s): Prepared according to the general procedure, 80 °C, 18 h, 43% yield, colorless oil, R_f = 0.74 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.35 (d, *J* = 8.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 6.16 (dd, *J* = 15.9, 7.4 Hz, 1H), 5.16 (t, *J* = 7.1 Hz, 1H), 2.38 – 2.28 (m, 1H), 2.16 – 2.02 (m, 2H), 1.70 (s, 3H), 1.61 (s, 3H), 1.08 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 137.99, 136.64, 132.46, 128.46, 127.82, 126.75, 125.98, 122.60, 37.59, 35.47, 25.83, 19.95, 17.93. **HRMS**

Calculated for $C_{15}H_{20}$ $[M]^+$ 200.1565, found 200.1561.

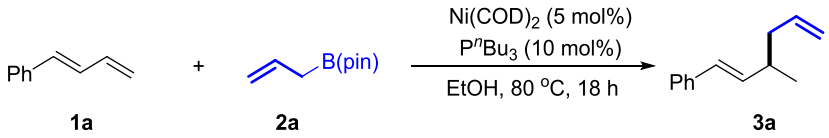


((1*E*)-3,6,10-trimethylundeca-1,5,9-trien-1-yl)benzene (3t): Prepared according to the general procedure, 80 °C, 18 h, 42% yield, Z/E mixture, colorless oil, R_f = 0.75 (Petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 6.16 (ddd, *J* = 15.9, 7.4, 2.1 Hz, 1H), 5.18 (t, *J* = 6.6 Hz, 1H), 5.09 (t, *J* = 6.9 Hz, 1H), 2.40 – 2.27 (m, 1H), 2.16 – 1.98 (m, 6H), 1.71 – 1.65 (m, 4H), 1.60 (d, *J* = 5.9 Hz, 5H), 1.08 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ138.00, 136.64, 136.17, 136.09, 131.55, 131.30, 128.45, 127.87, 127.79, 126.76, 126.74, 125.99, 125.98, 124.37, 123.31, 122.58, 39.86, 37.65, 37.59, 35.35, 35.18, 32.12, 26.74, 26.58, 25.73, 25.71, 23.50, 20.03, 19.84, 17.70, 17.65, 16.20. **HRMS** Calculated for $C_{20}H_{28}$ $[M]^+$ 268.2191, found 268.2186.

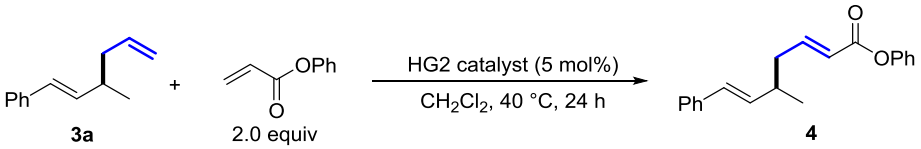
Unsuccessful substrates:



5. Scale-up synthesis and further transformation of 3a

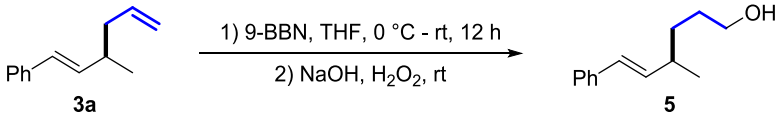


In glove box, a sealed tube was charged with $Ni(COD)_2$ (0.25 mmol, 5 mol%), P^nBu_3 (0.50 mmol, 10 mol%) and EtOH (6.25 mL) at room temperature. After stirring for 20 min, 1,4-diene **1a** (5.0 mmol, 1.0 equiv) and allylboronate **2a** (10.0 mmol, 2.0 equiv) were added. Then the reaction tube was sealed with a Teflon screw cap, removed from the glove box and stirred at 80 °C for 18 h. After cooling to room temperature, the reaction mixture was directly purified by column chromatography on silica gel using *n*-pentene to afford product **3a** as colorless oil (762 mg, 88%).



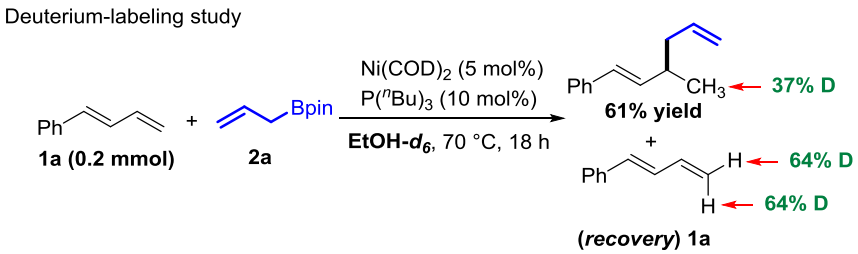
phenyl (*2E,6E*)-5-methyl-7-phenylhepta-2,6-dienoate (4). In a glove box, Hoveyda-Grubbs Catalyst 2nd (6.3 mg, 0.01 mmol), phenyl acrylate (40.0 mg, 0.4 mmol) were weighed out into a flame-dried flask equipped with a magnetic stirring bar flame. Then, a solution of **3a** (34.5 mg, 0.2 mmol) dissolved in DCM (3.0 mL) was added through a syringe and the resulting mixture was

allowed to stir at 40 ℃ for 24 h. The mixture was allowed to cool to rt and the volatiles were removed in vacuo and the crude product was purified by flash column chromatography (using 2% EA/PE) to give the corresponding product **4** as colorless oil (21.4 mg, 37%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 4H), 7.30 (t, J = 7.5 Hz, 2H), 7.23 – 7.20 (m, 2H), 7.18 – 7.10 (m, 3H), 6.42 (d, J = 15.9 Hz, 1H), 6.15 (dd, J = 15.8, 7.3 Hz, 1H), 6.06 (d, J = 15.6 Hz, 1H), 2.58 (hept, J = 6.2 Hz, 1H), 2.48 – 2.32 (m, 2H), 1.17 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.78, 150.74, 149.62, 137.38, 134.71, 129.36, 129.10, 128.54, 127.17, 126.12, 125.68, 122.04, 121.64, 39.87, 36.42, 20.27. **HRMS** Calculated for $C_{20}H_{21}O_2$ $[M+H]^+$ 293.1536, found 293.1536.



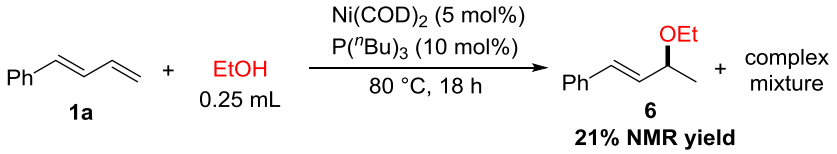
(*E*)-4-methyl-6-phenylhex-5-en-1-ol (5). To a flame-dried flask equipped with a magnetic stirring bar were added **3a** (34.5 mg, 0.2 mmol) and dry THF (2.0 mL) and then a solution of 9-BBN (0.5 M solution in THF, 0.4 mL) at 0 ℃ under N_2. Then the reaction flask was stirred for 12 h at rt. NaOH (80 mg) and H_2O_2 (30%, 1.2 mL) were then added to the reaction. After 3 h, the reaction mixture was quenched with sat. NH_4Cl aq. (15 mL) and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over $MgSO_4$, concentrated in vacuo and purified by flash chromatography on silica gel (using 5% EtOAc/PE) to afford **5** as colorless oil (31.0 mg, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.4 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.21 – 7.16 (m, 1H), 6.35 (d, J = 15.9 Hz, 1H), 6.08 (dd, J = 15.9, 8.0 Hz, 1H), 3.64 (t, J = 6.5 Hz, 2H), 2.31 (hept, J = 6.9 Hz, 1H), 1.64– 1.56 (m, 2H), 1.50 – 1.41 (m, 2H), 1.37 (s, 1H), 1.10 (d, J = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.76, 136.40, 128.49, 128.43, 126.88, 125.98, 63.11, 37.18, 33.09, 30.67, 20.77. **HRMS** Calculated for $C_{13}H_{19}O$ $[M+H]^+$ 191.1430, found 191.1425.

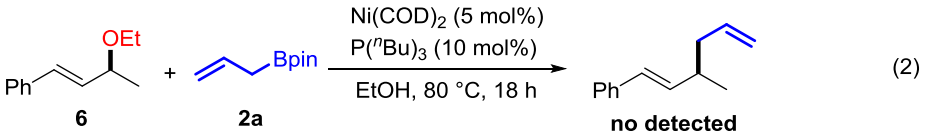
6. Control and deuterium labeling experiments



In glove box, a sealed tube was charged with $Ni(COD)_2$ (0.01 mmol, 5 mol%), P^nBu_3 (0.02 mmol, 10 mol%) and EtOH-d_6 (0.25 mL) at room temperature. After stirring for 20 min, 1,4-diene **1a** (0.2 mmol, 1.0 equiv) and allylboronate **2a** (0.4 mmol, 2.0 equiv) were added. Then the reaction tube was sealed with a Teflon screw cap, removed from the glove box and stirred at 70 °C for 18 h. After cooling to room temperature, the reaction mixture was directly purified by column chromatography on silica gel using *n*-pentene to afford the product **3a-d_n**. Accompanied by small amount of recovery diene **1a**.

Controlled experiments





(1) In glove box, a sealed tube was charged with $Ni(COD)_2$ (0.01 mmol, 5 mol%), P^nBu_3 (0.02 mmol, 10 mol%) and EtOH (0.25 mL) at room temperature. After stirring for 20 min, 1,4-diene **1a** (0.2 mmol, 1.0 equiv) were added. Then the reaction tube was sealed with a Teflon screw cap, removed from the glove box and stirred at 80 °C for 18 h. The mixture was then allowed to cool to room temperature and 1,3,5-trimethoxybenzene was added as the internal standard to determine the NMR yield.

(2) In glove box, a sealed tube was charged with $Ni(COD)_2$ (0.01 mmol, 5 mol%), P^nBu_3 (0.02 mmol, 10 mol%) and EtOH-d_6 (0.25 mL) at room temperature. After stirring for 20 min, **6** (0.2 mmol, 1.0 equiv) and allylboronate **2a** (0.4 mmol, 2.0 equiv) were added. Then the reaction tube was sealed with a Teflon screw cap, removed from the glove box and stirred at 80 °C. The reaction mixture was monitored by TLC and GC-MS and no product were detected after 18 hours.

7. References

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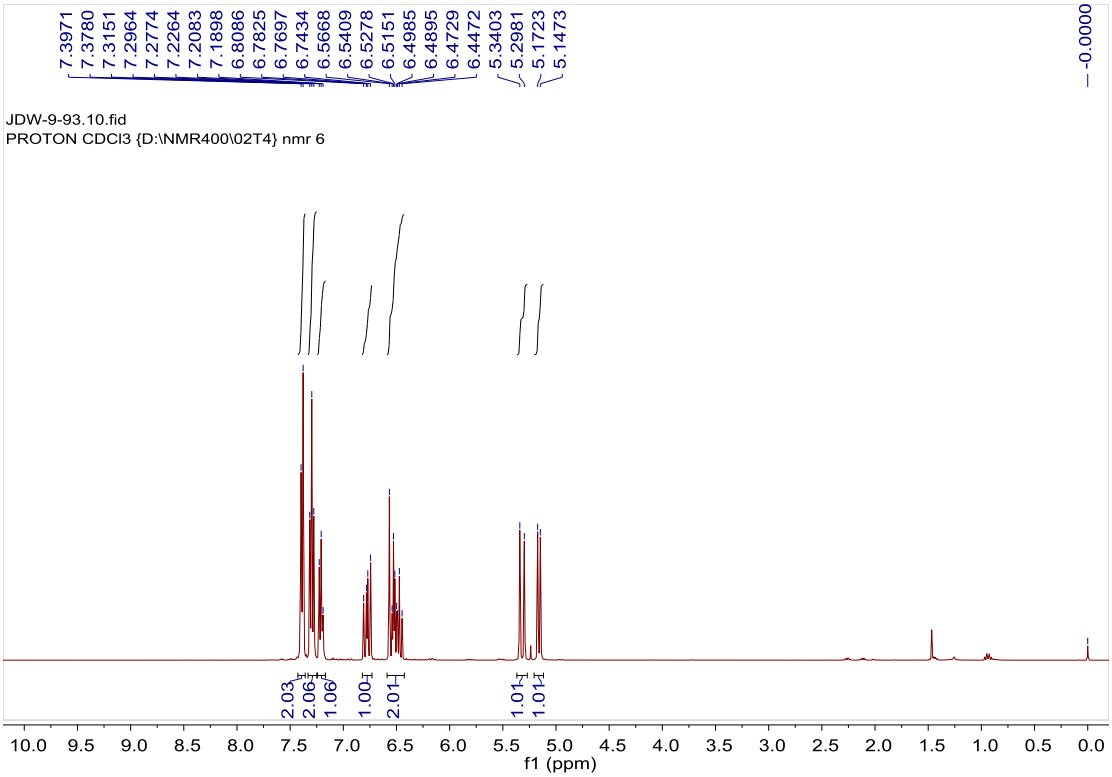
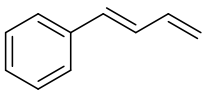
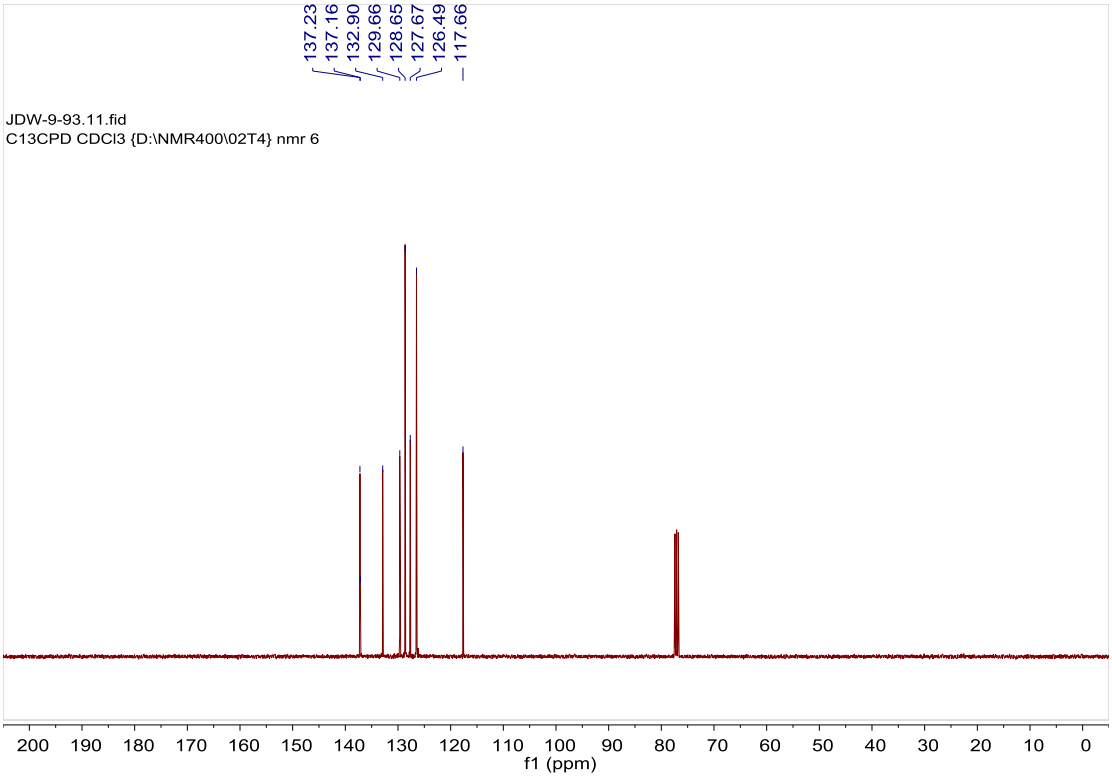
8. Copy of NMR for products

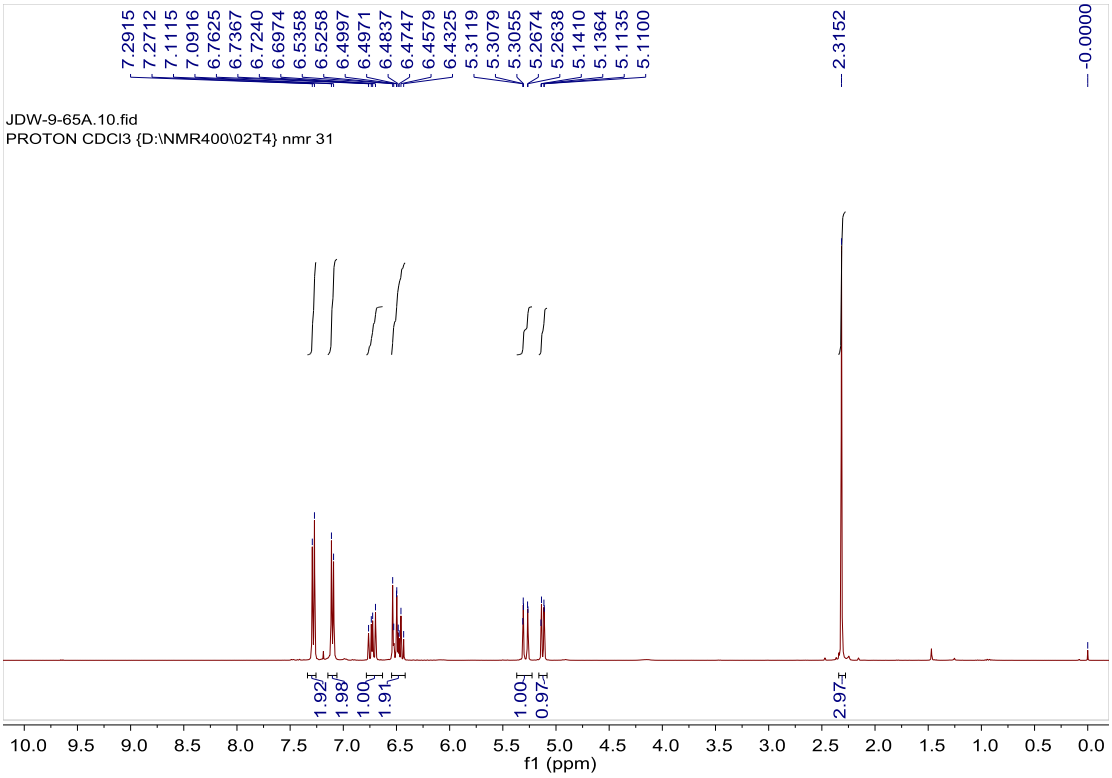


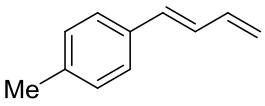


1a ^{1}H NMR (400 MHz, $CDCl_3$)

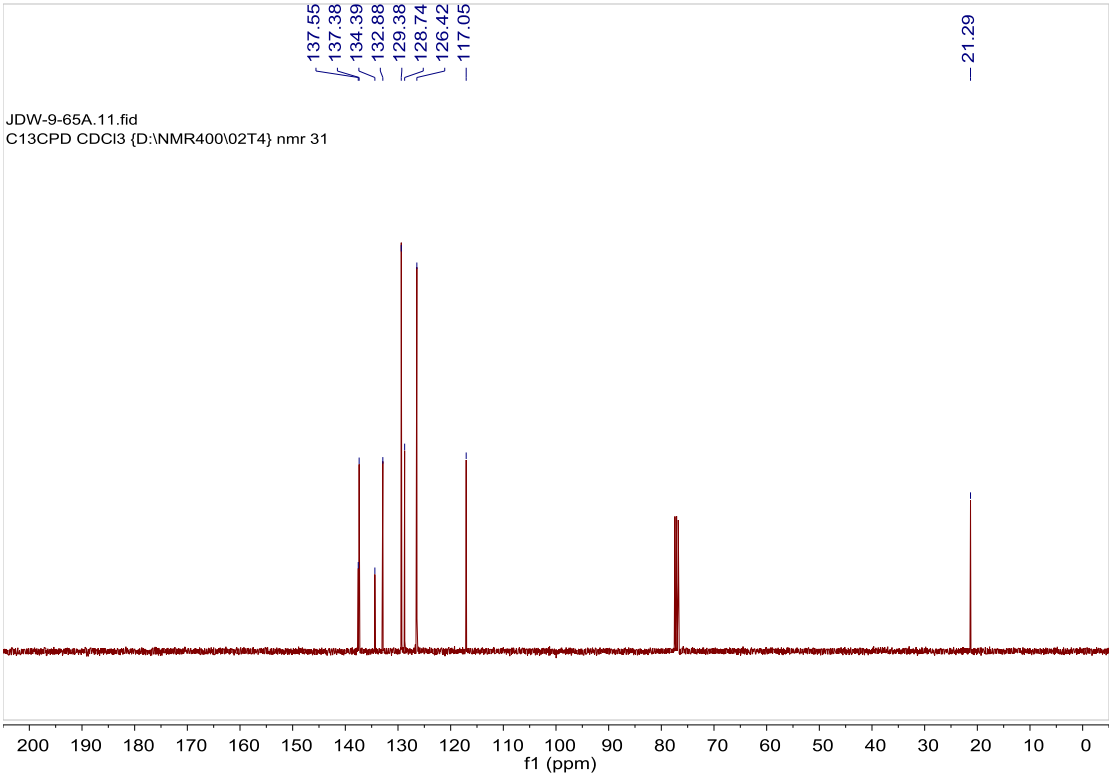
^{13}C NMR (100 MHz, $CDCl_3$)

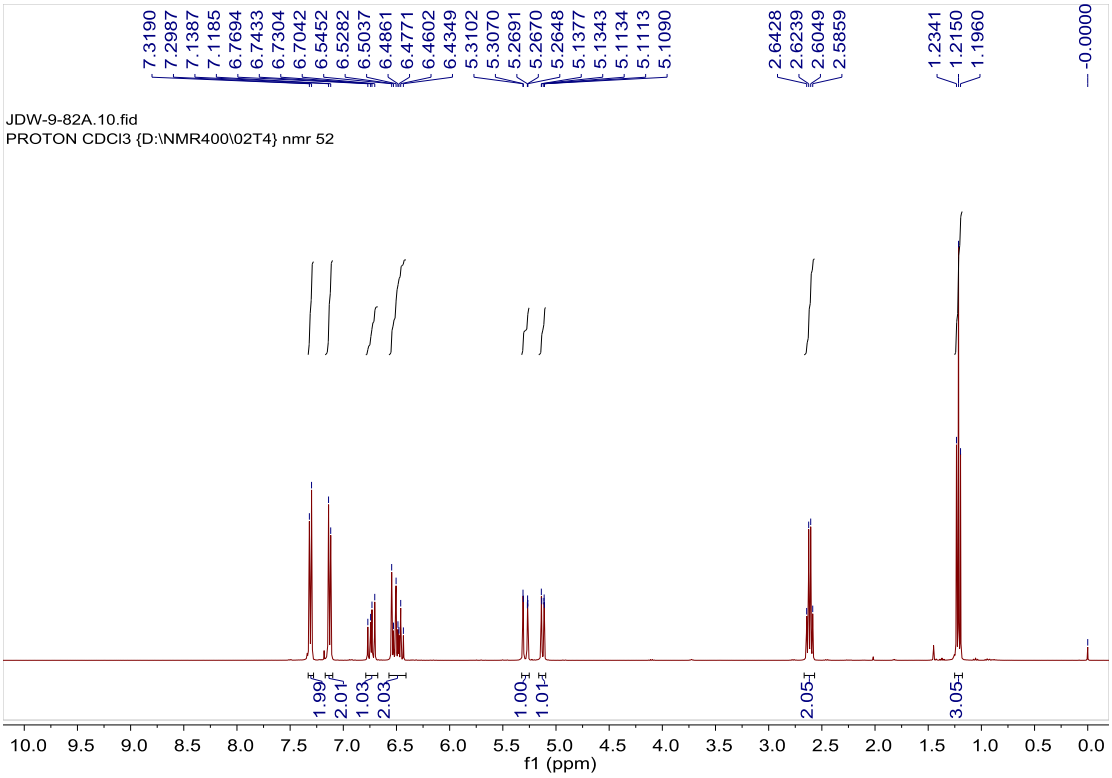


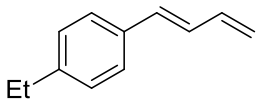




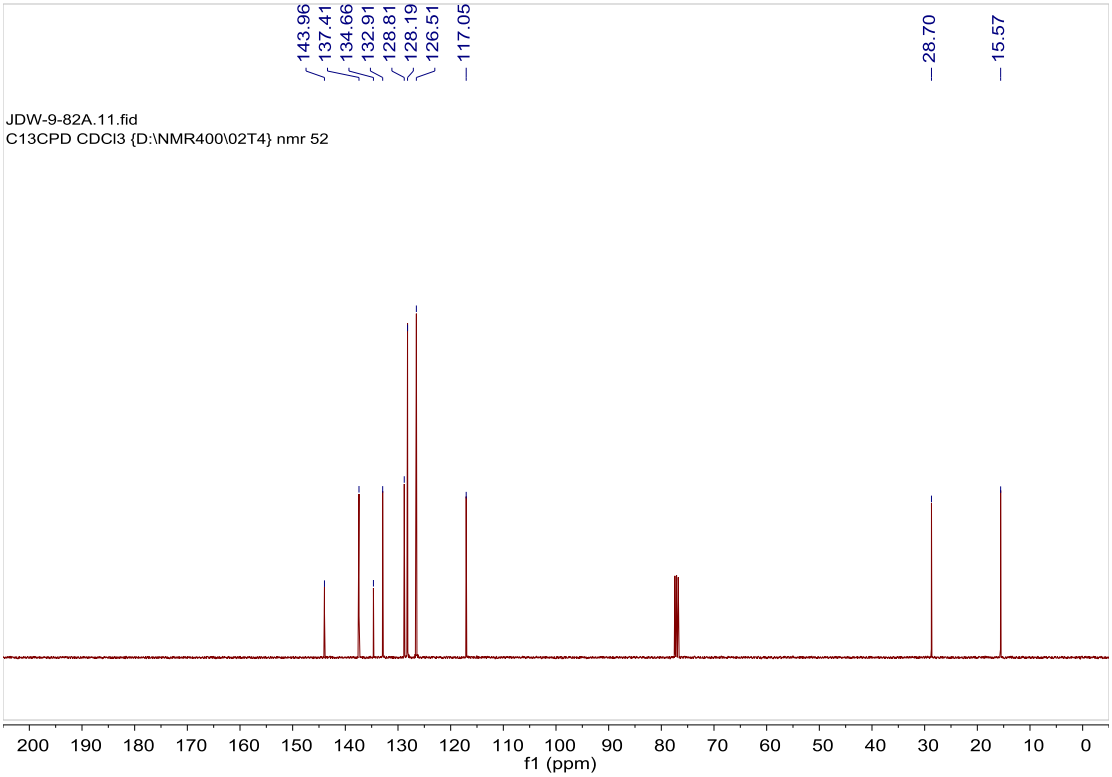
1b ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

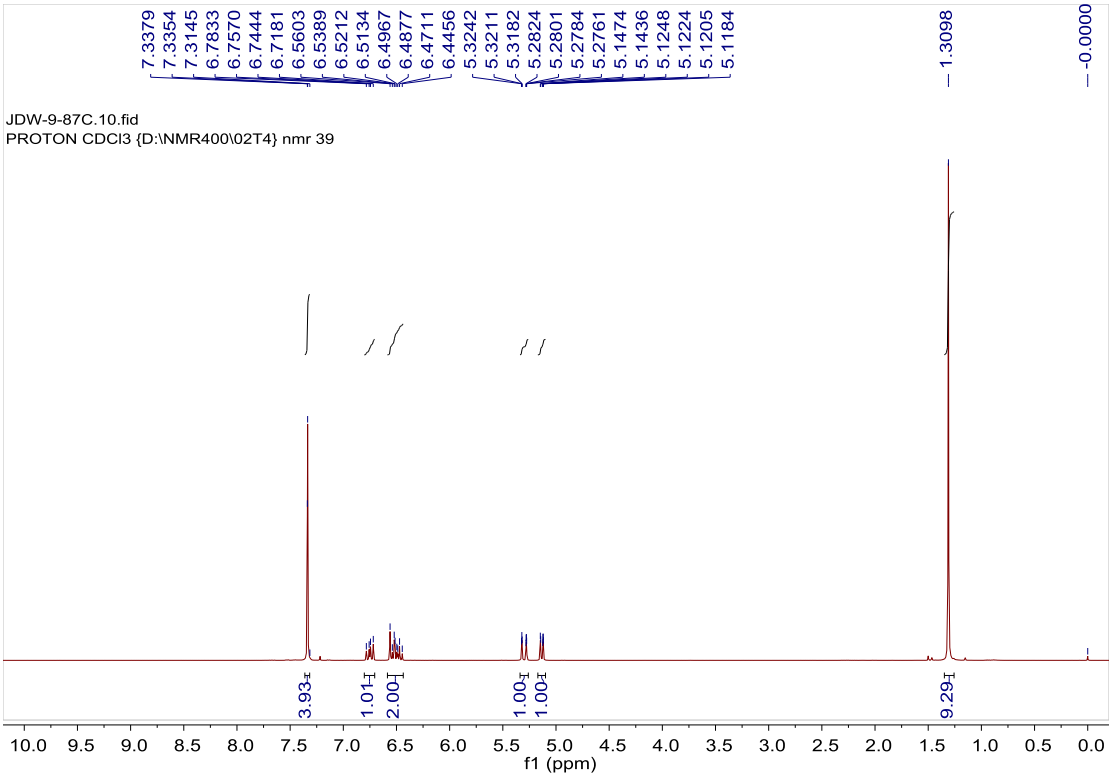


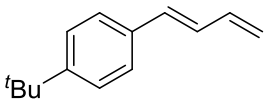




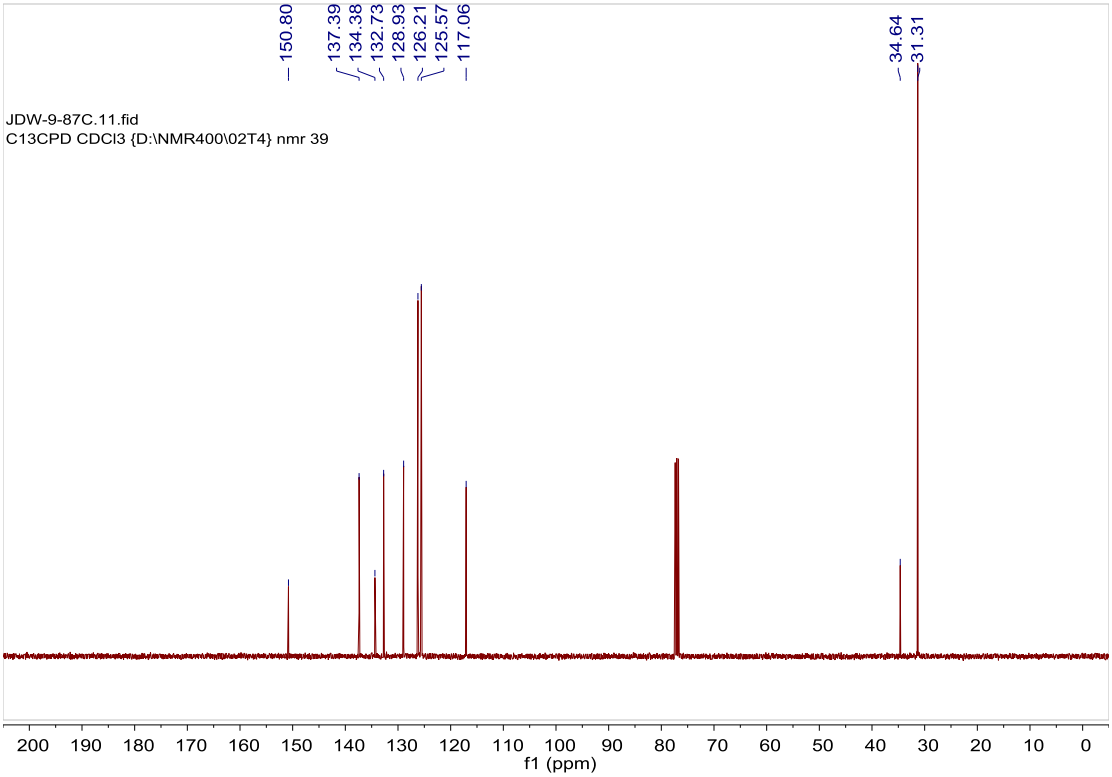
1c ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

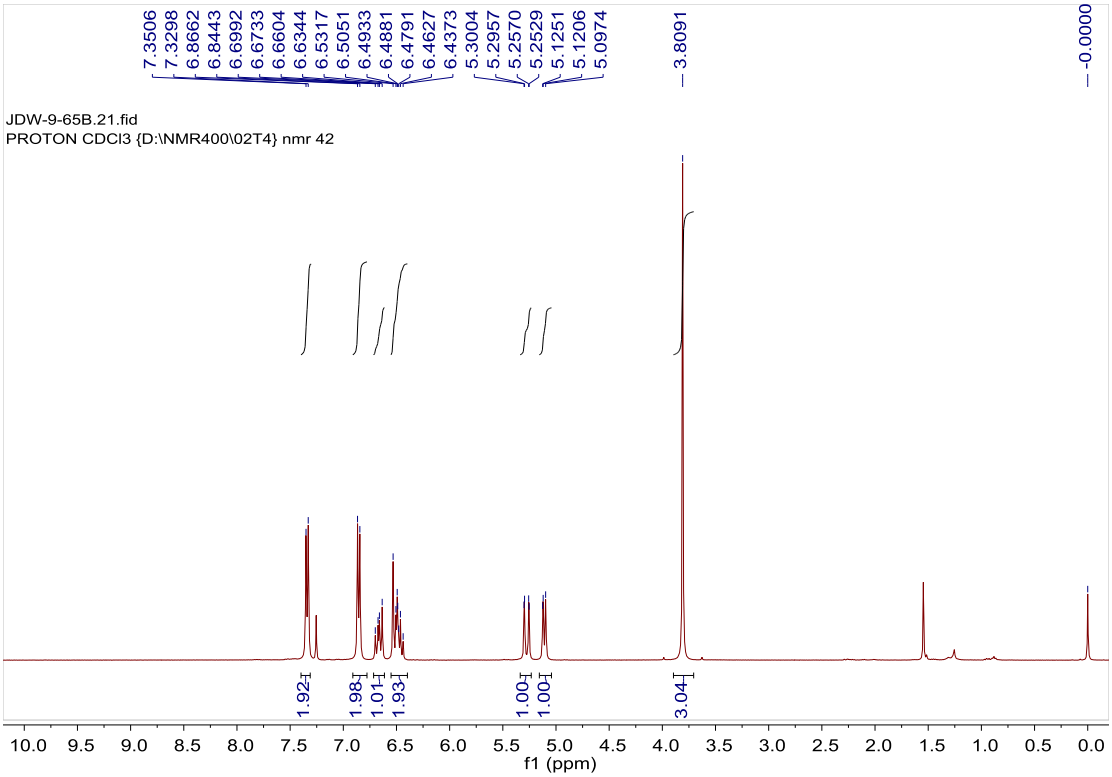


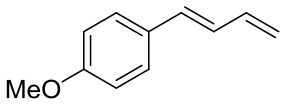




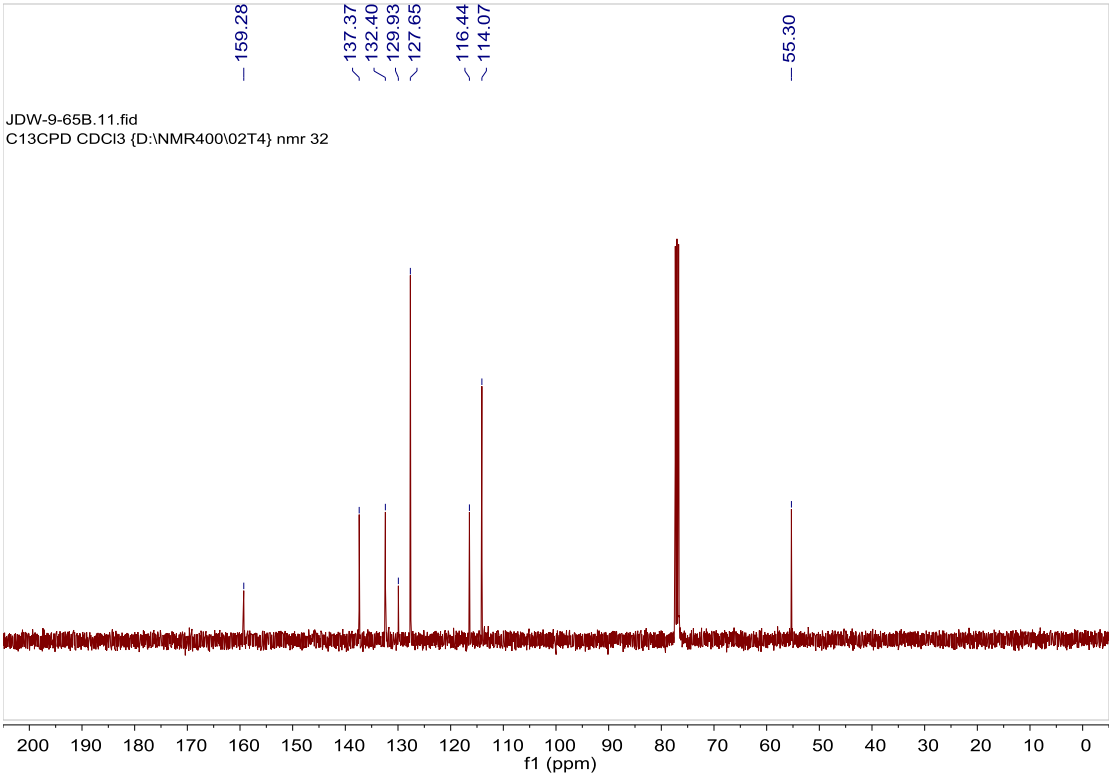
1d ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

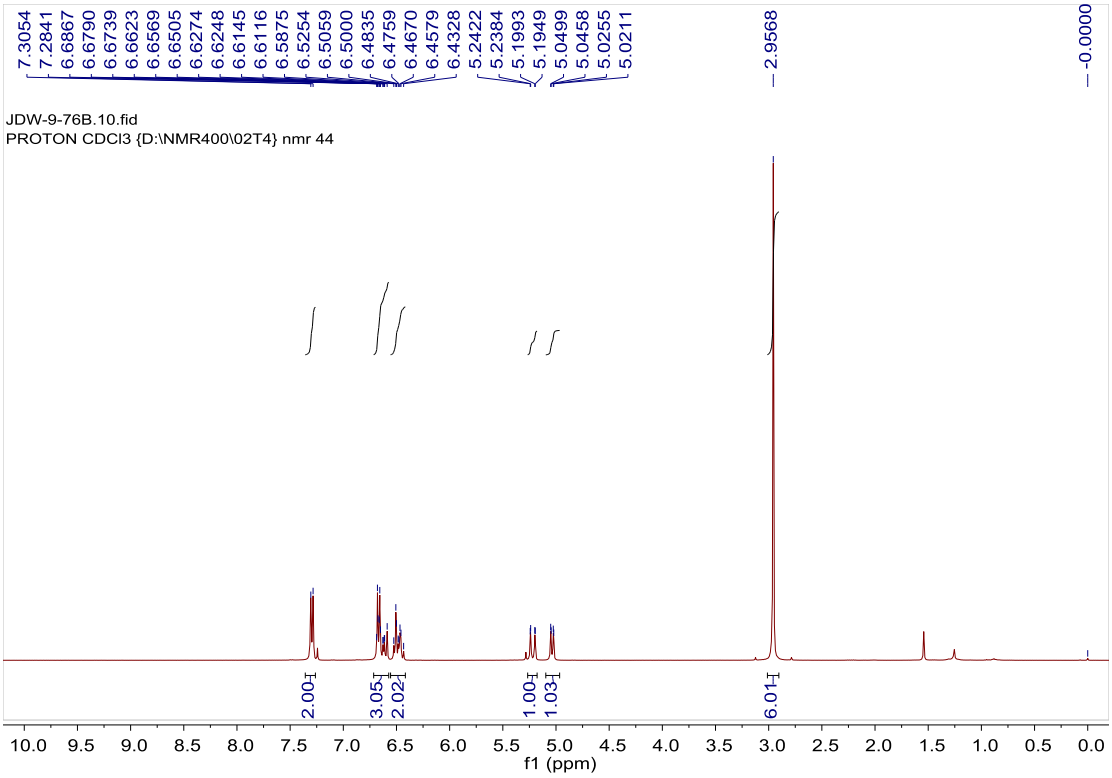


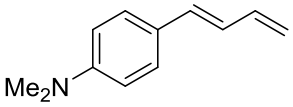




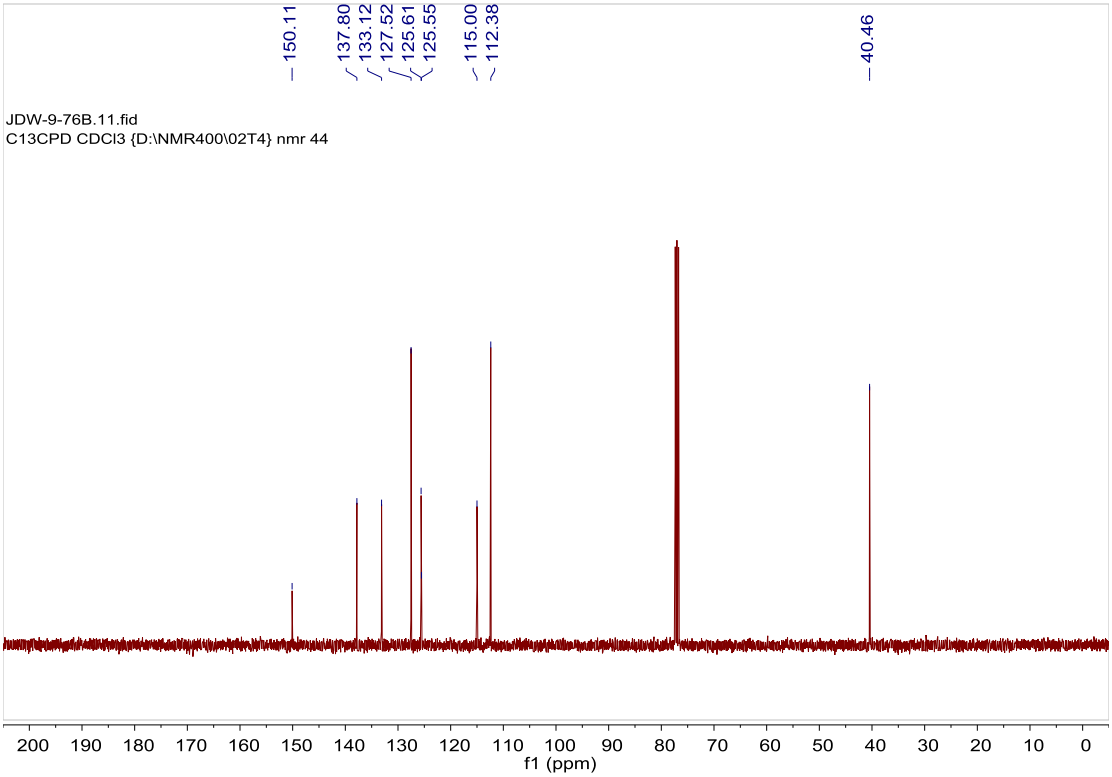
1e ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

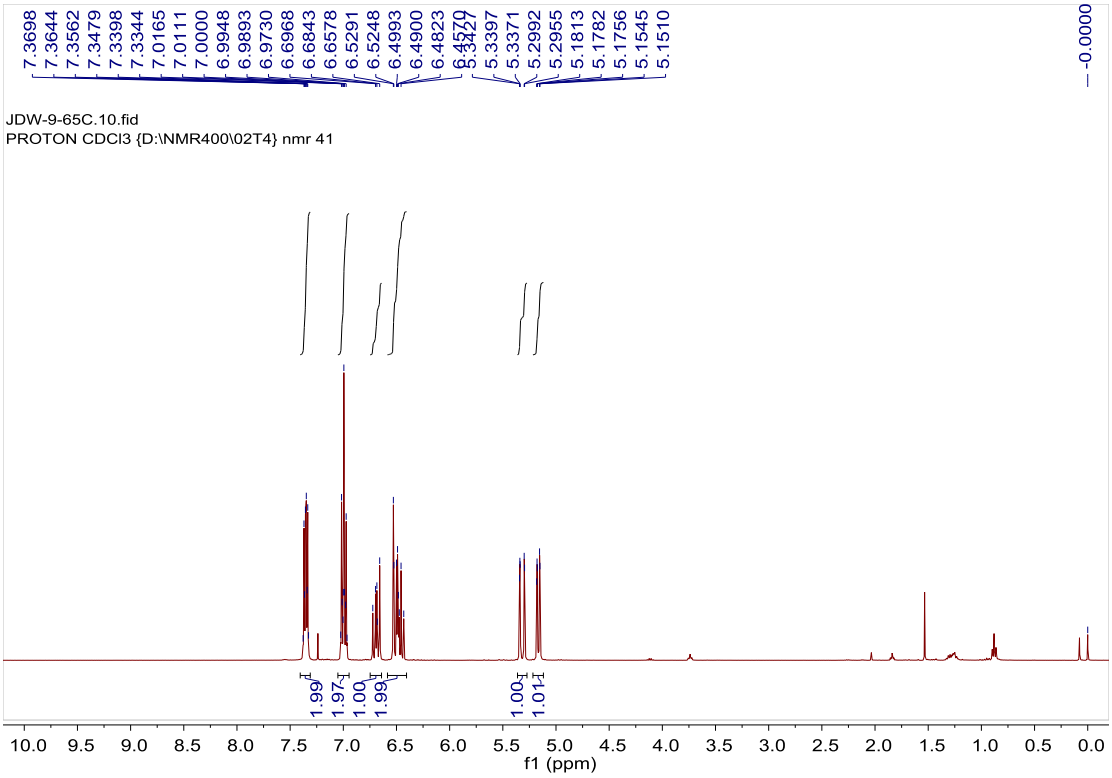


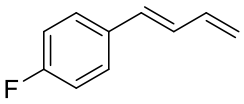




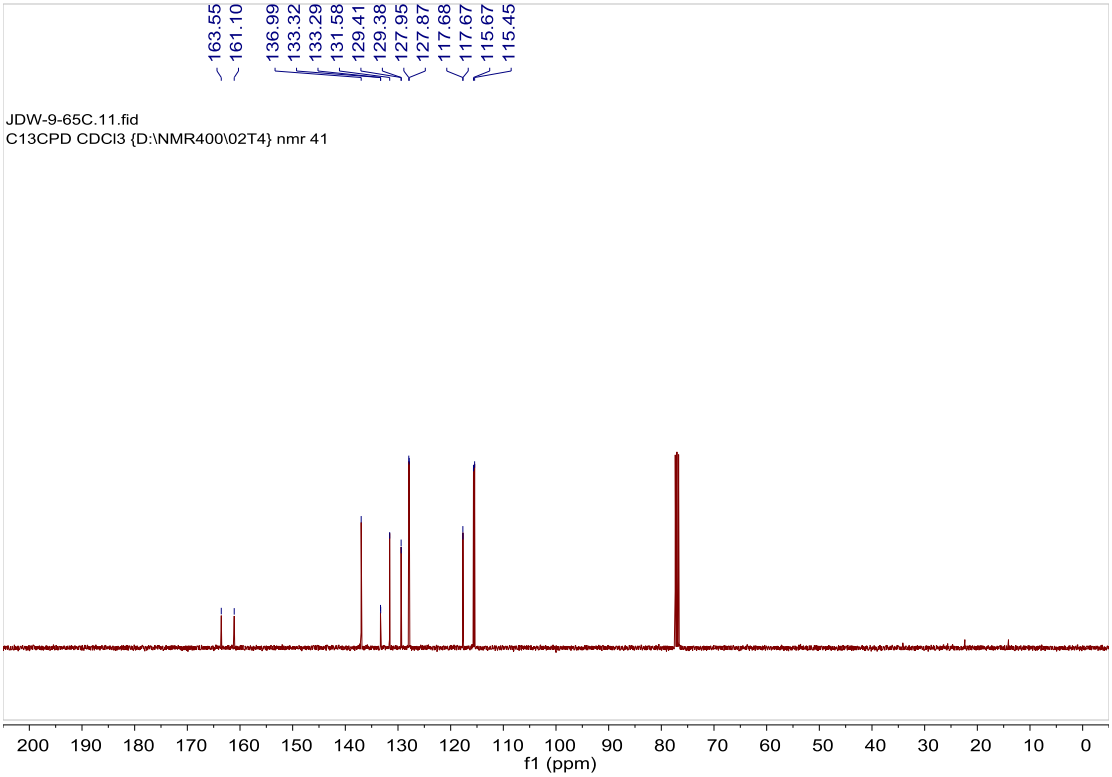
1f ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

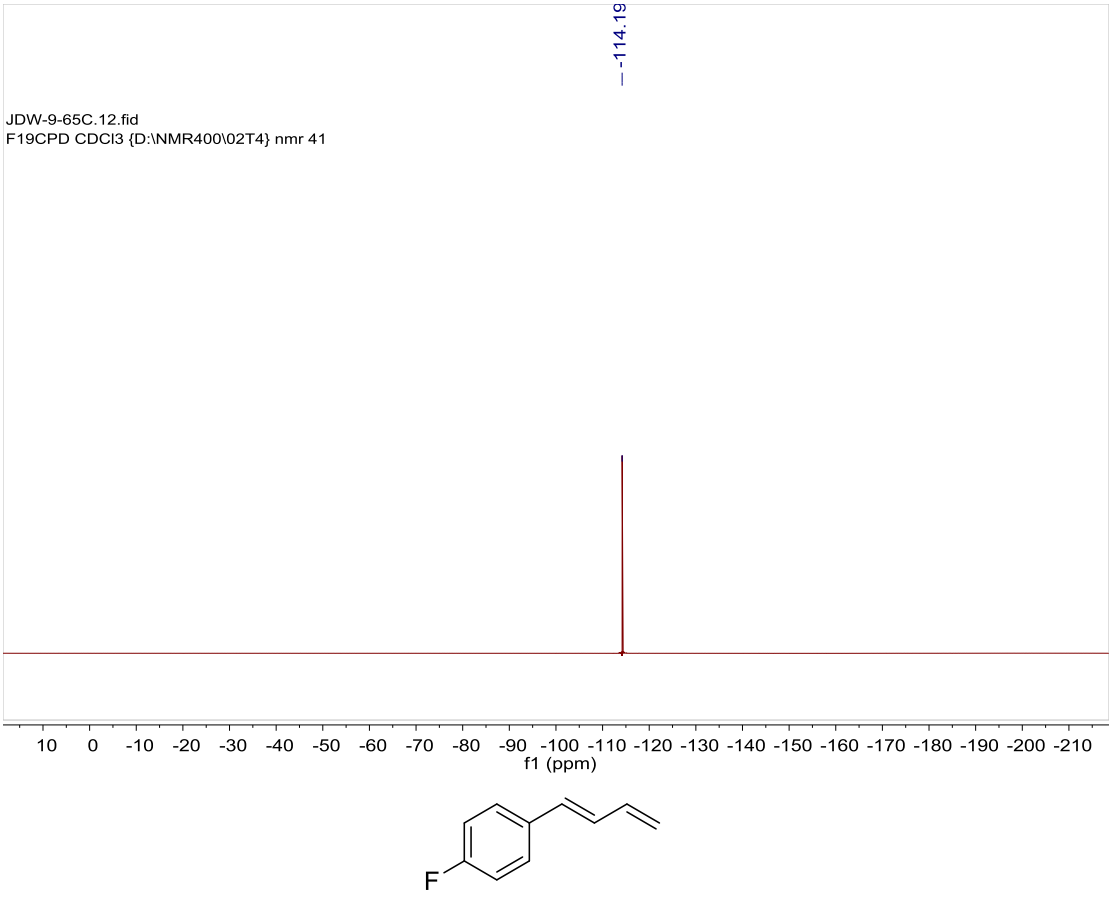




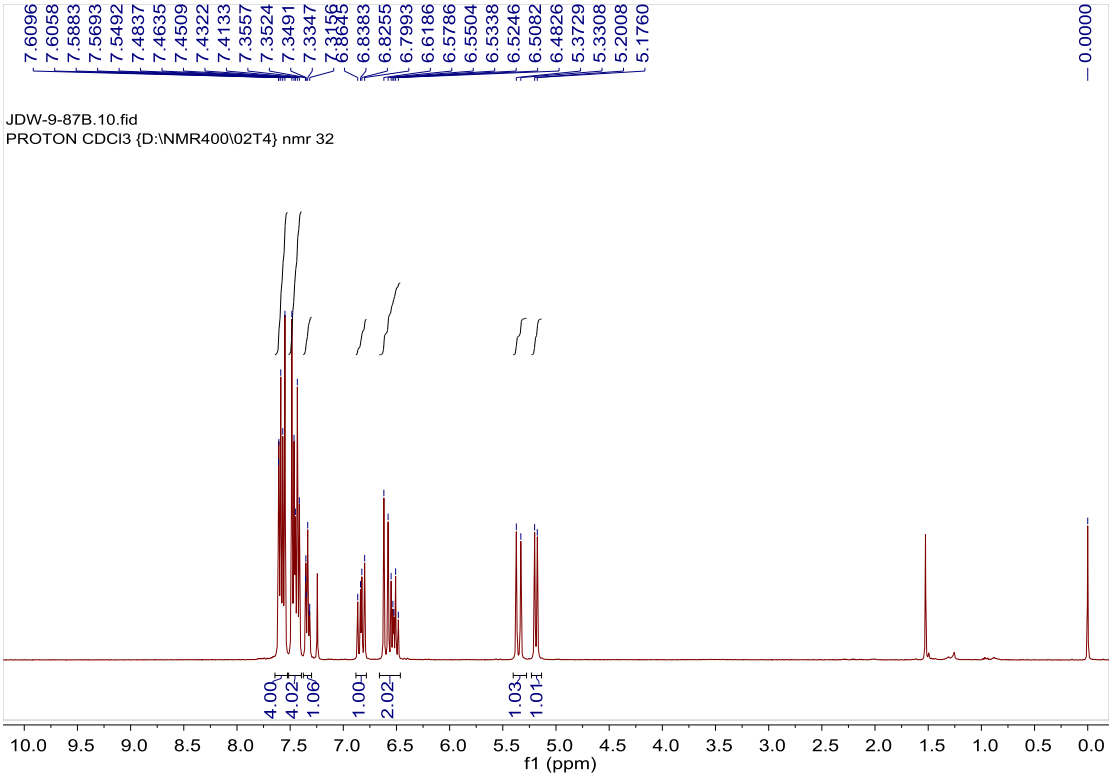


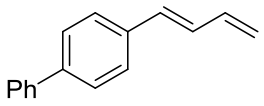
1g ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)



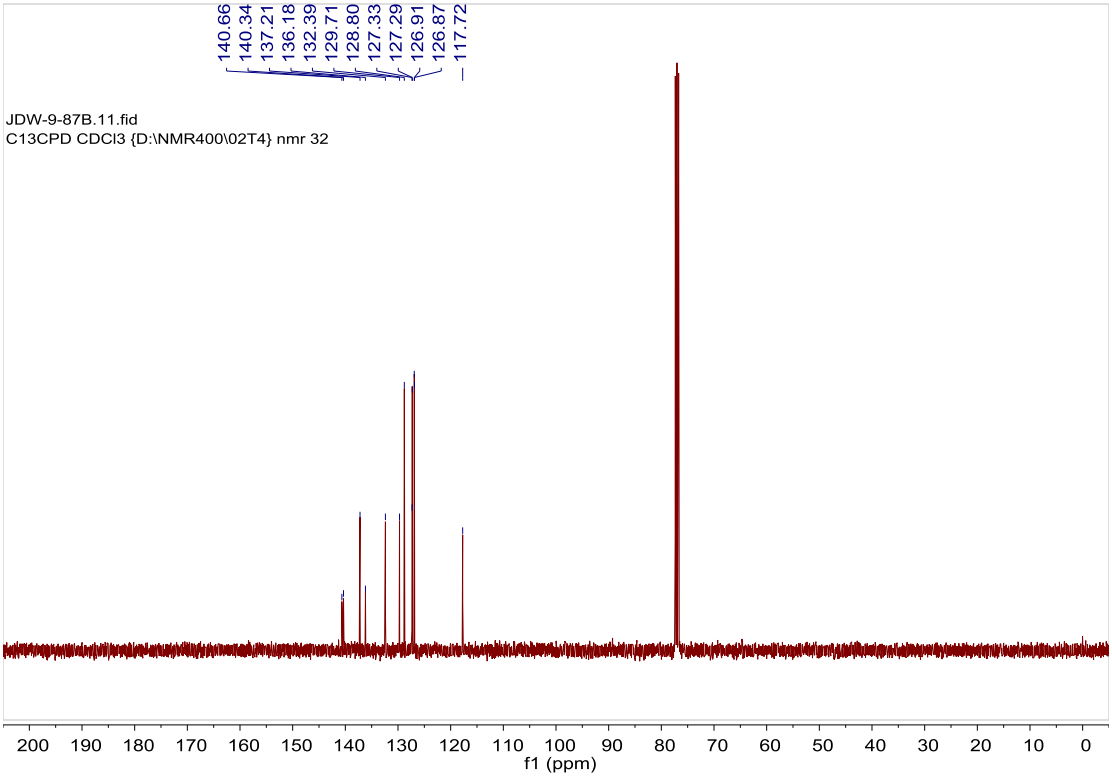


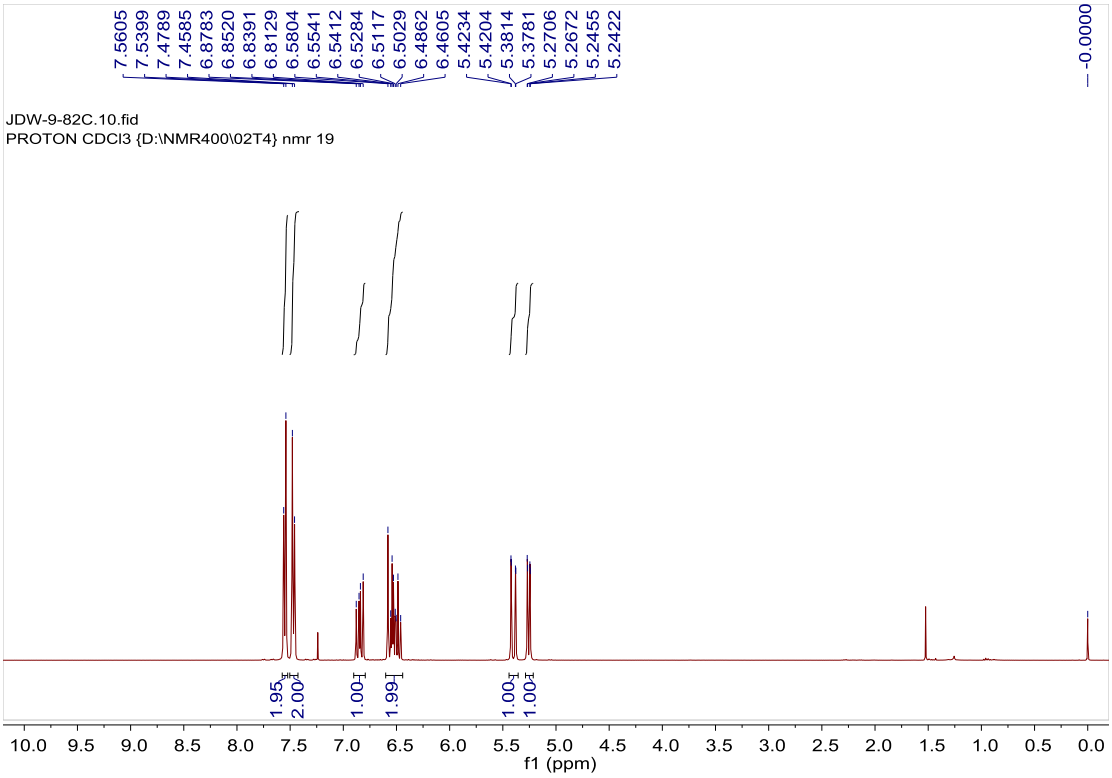
1g ^{19}F NMR (376 MHz, $CDCl_3$)

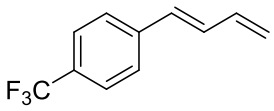




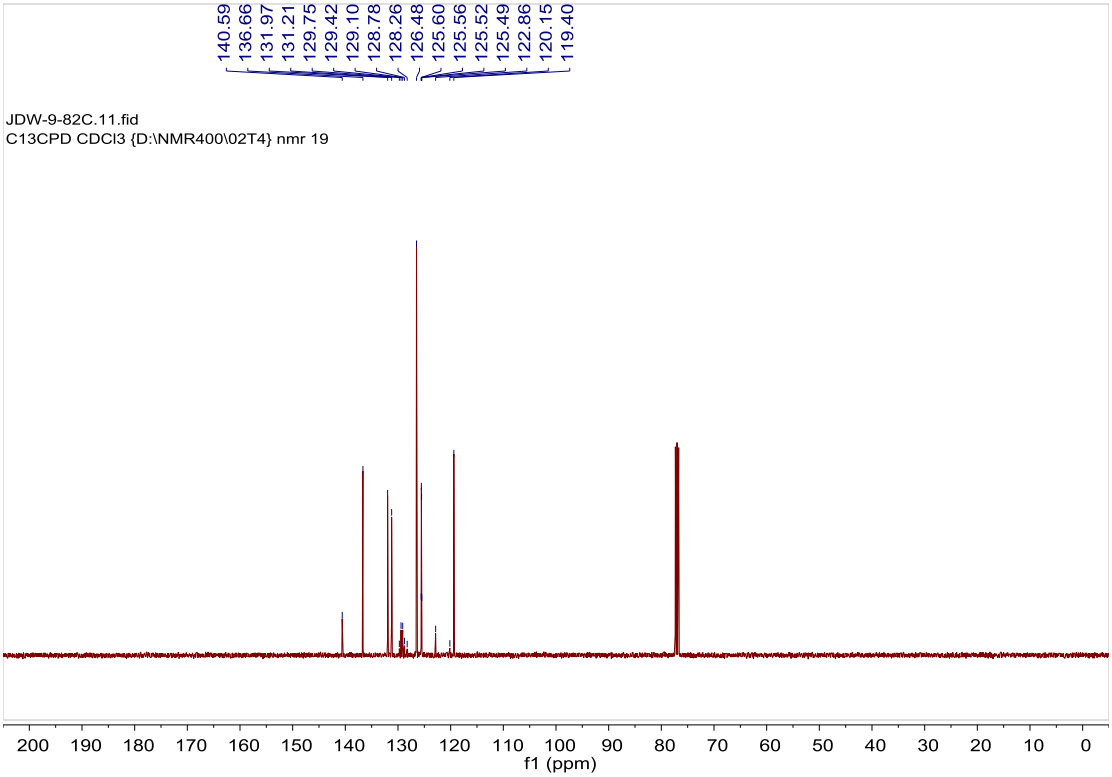
1h ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

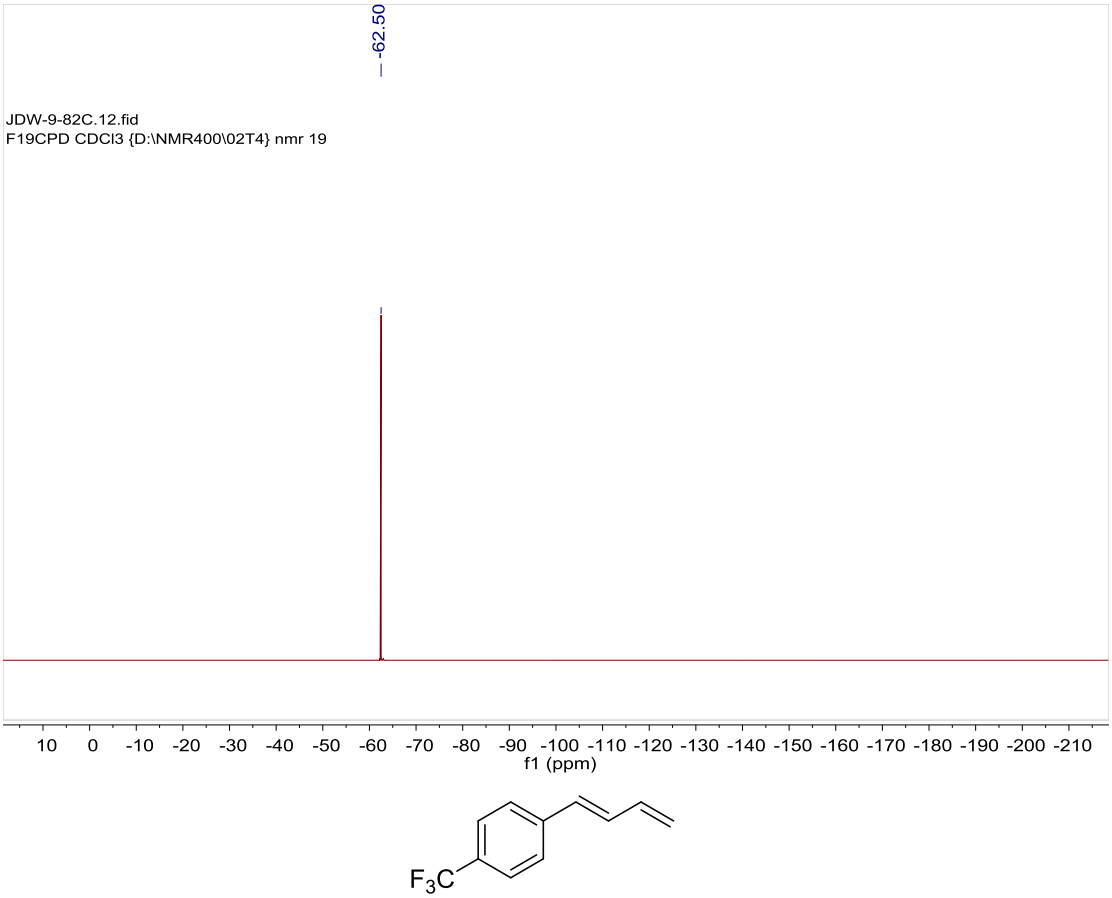




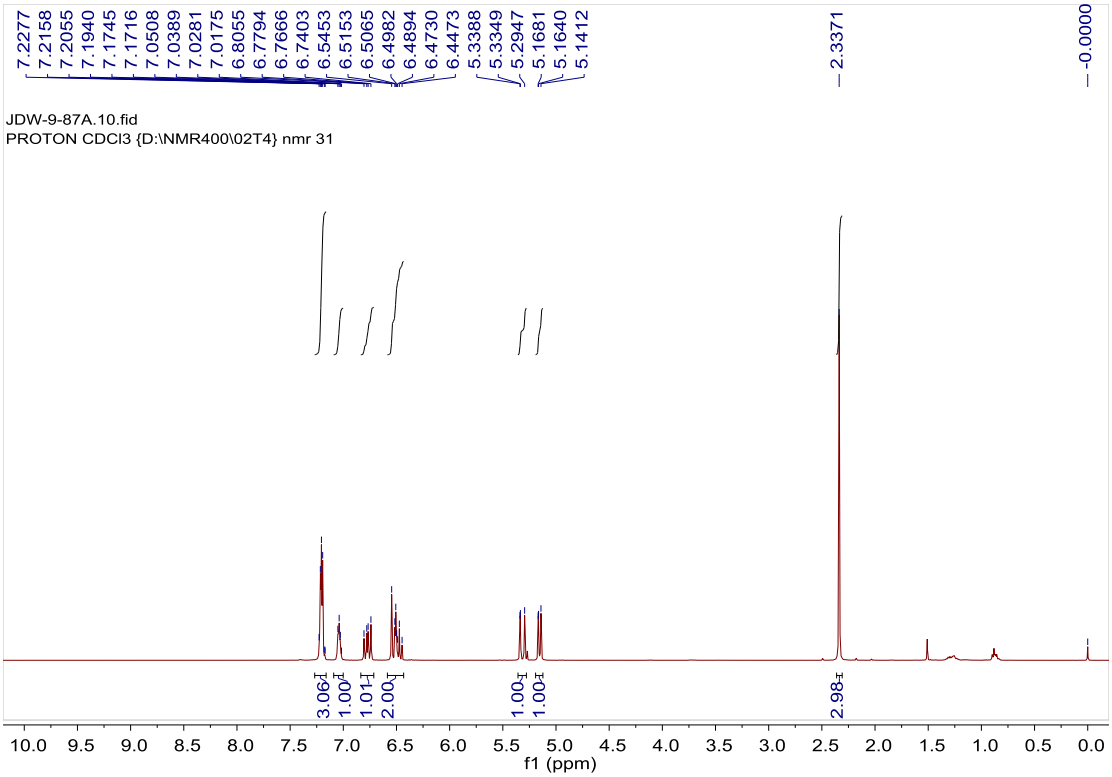


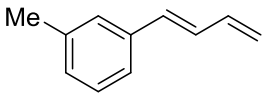
1i ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)



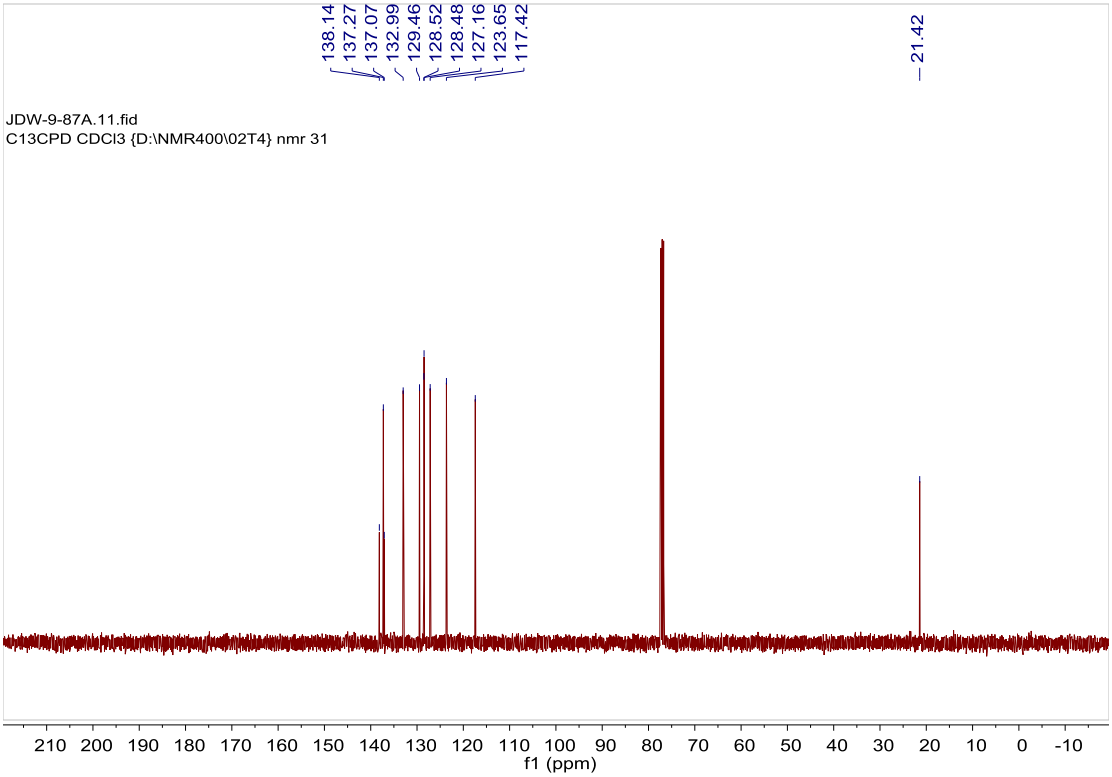


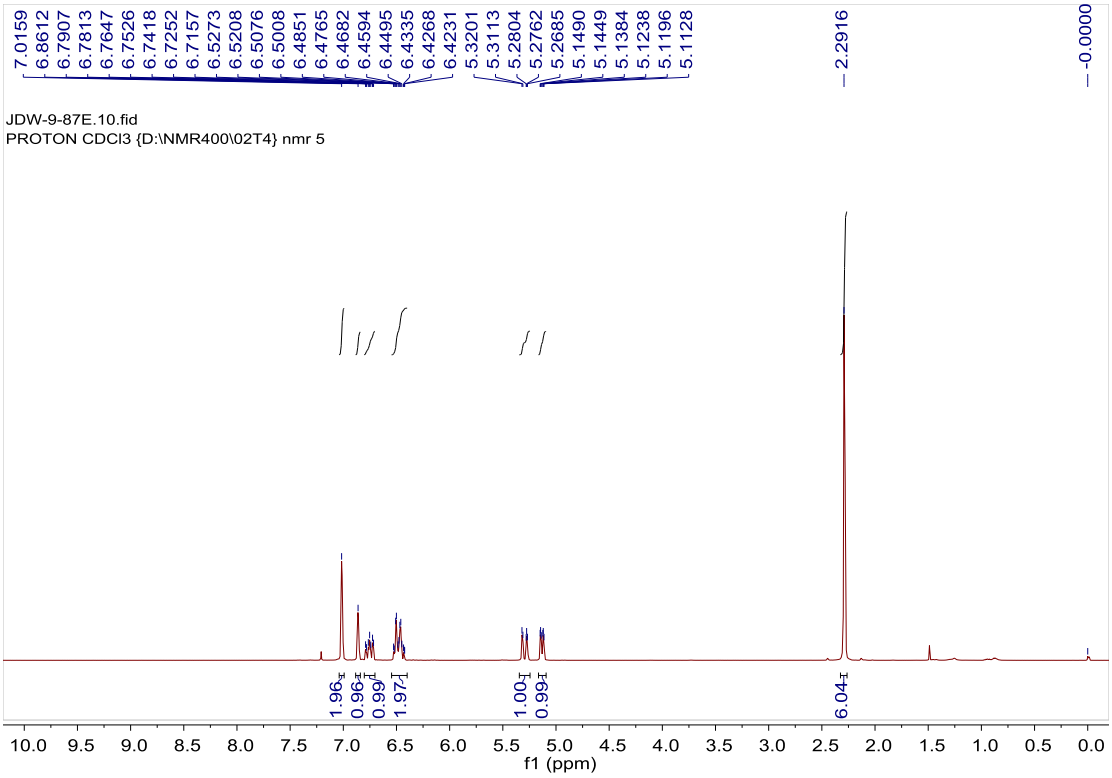
1i ^{19}F NMR (376 MHz, $CDCl_3$)

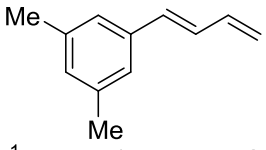




1j ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

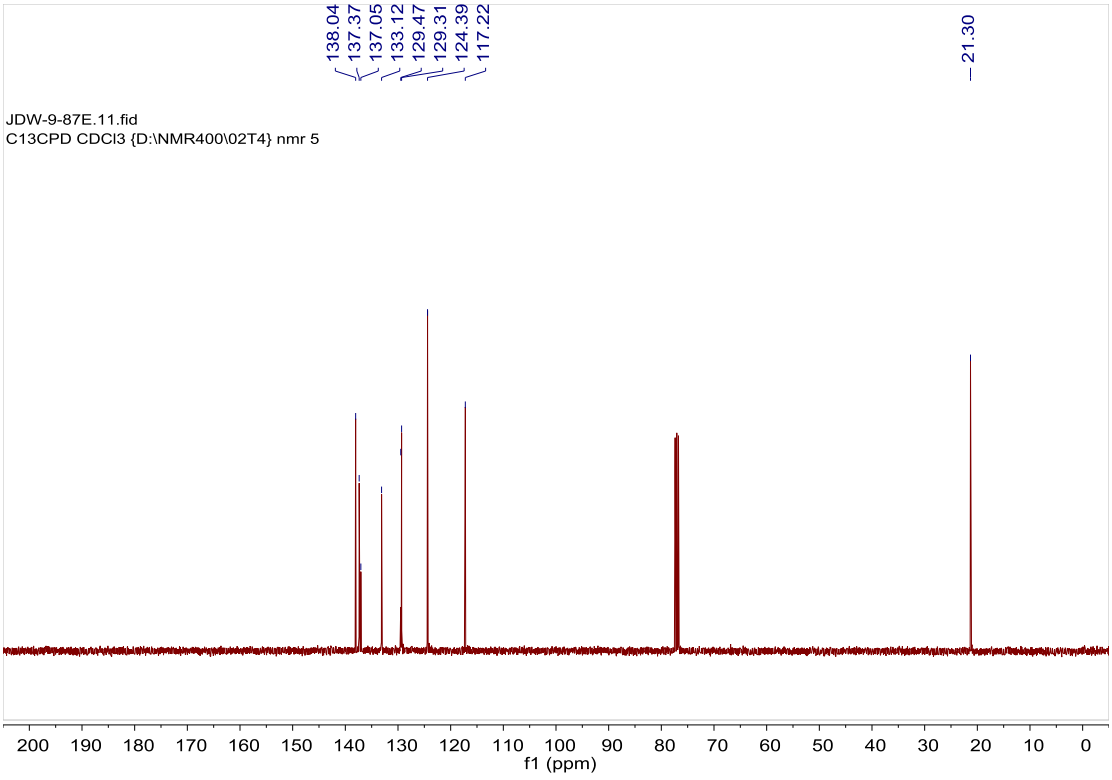


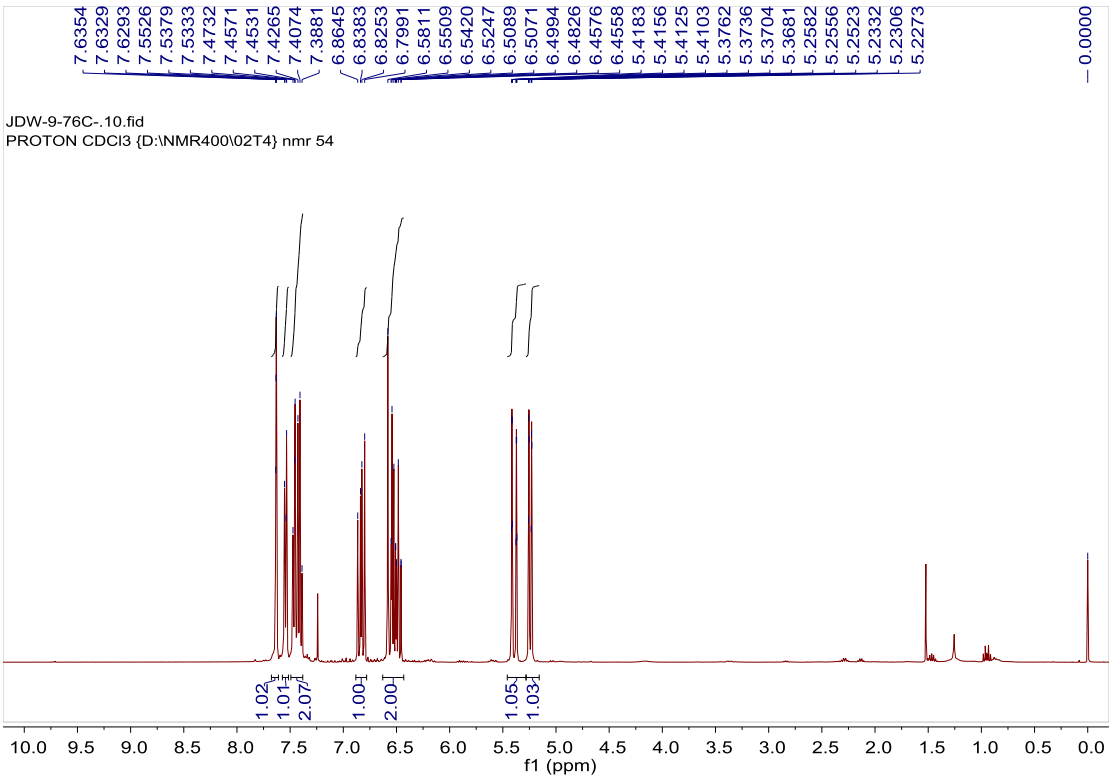


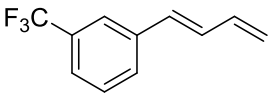


1k ^{1}H NMR (400 MHz, $CDCl_3$)

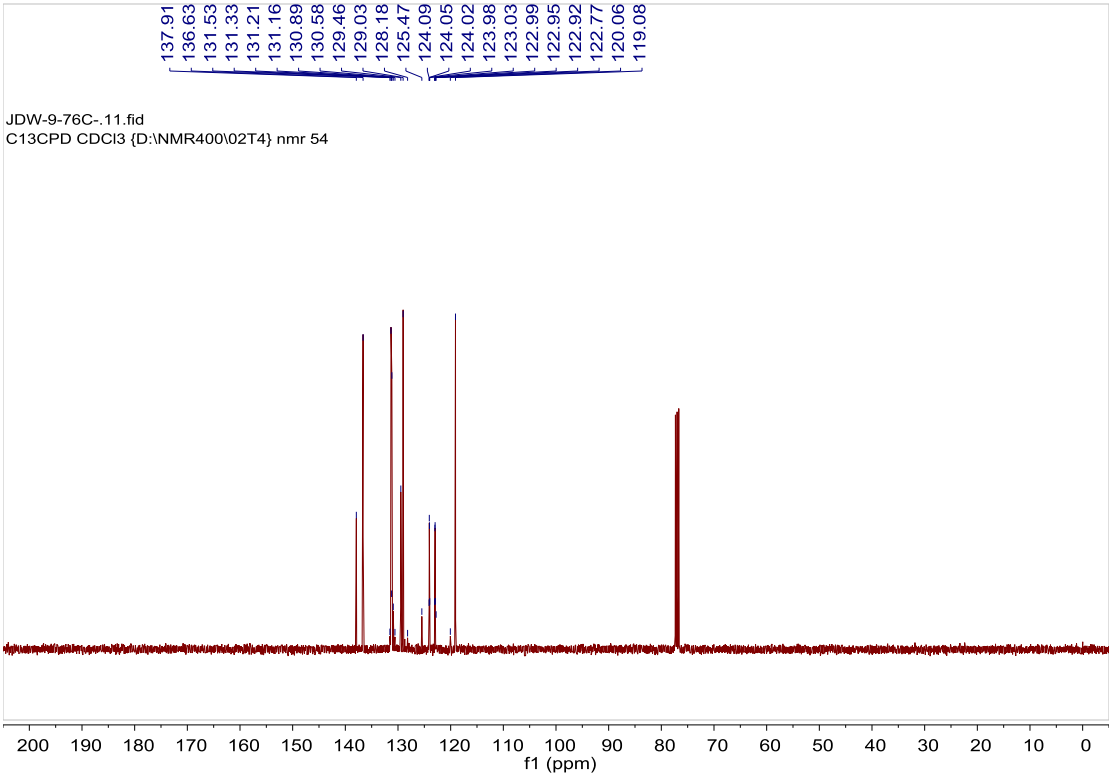
^{13}C NMR (100 MHz, $CDCl_3$)

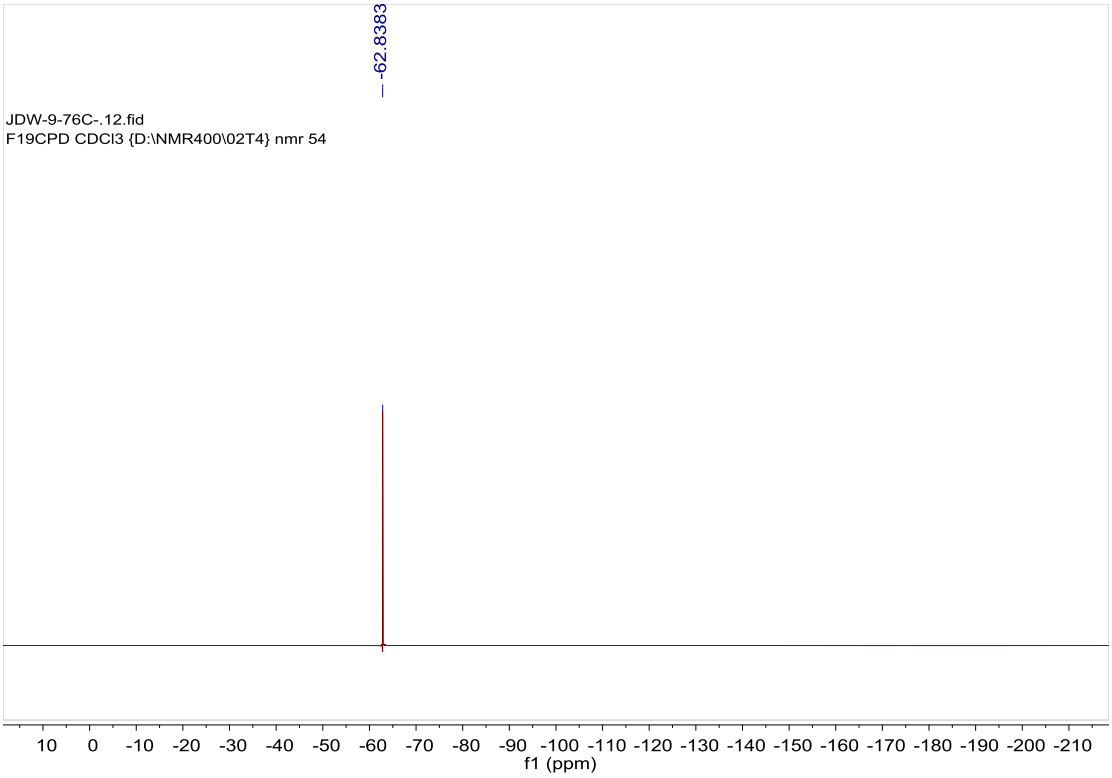


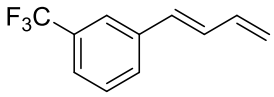




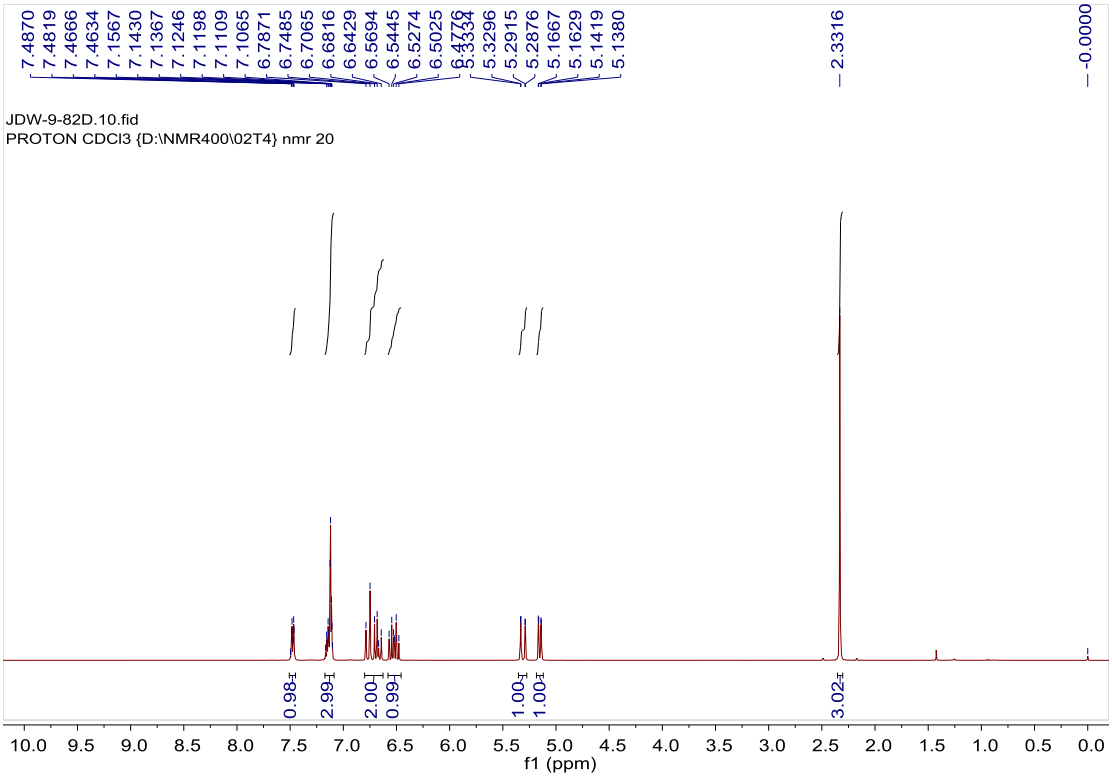
1l ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

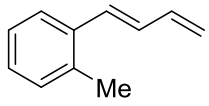




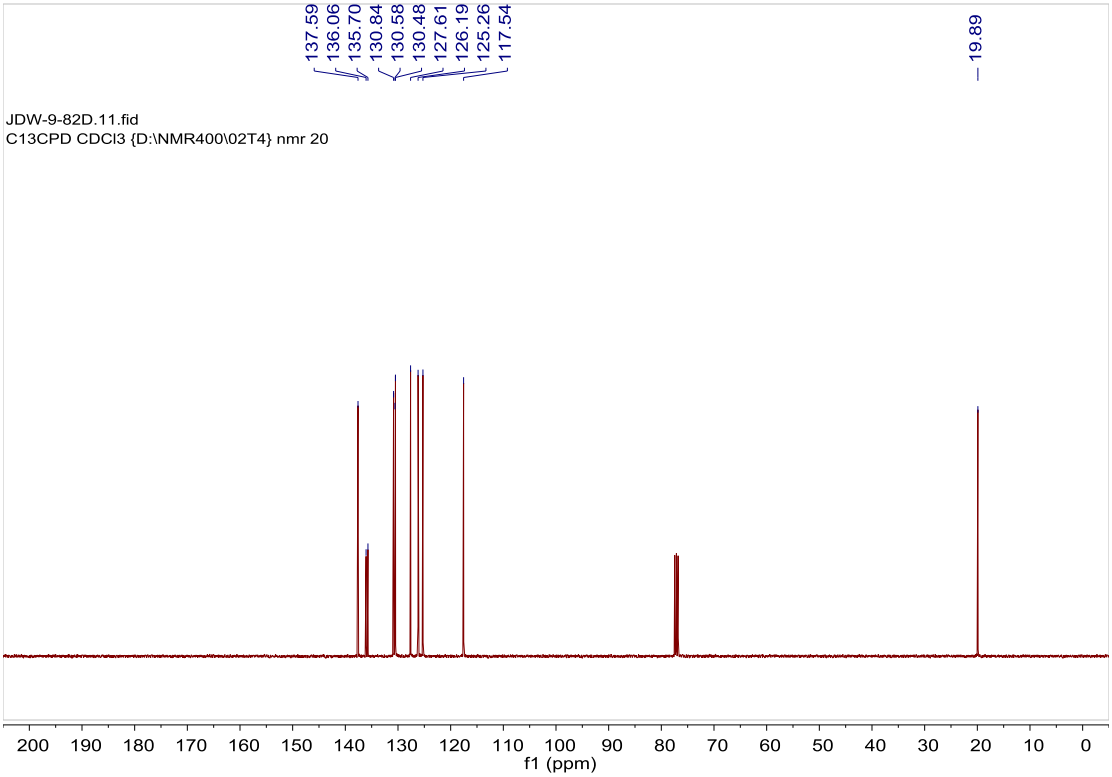


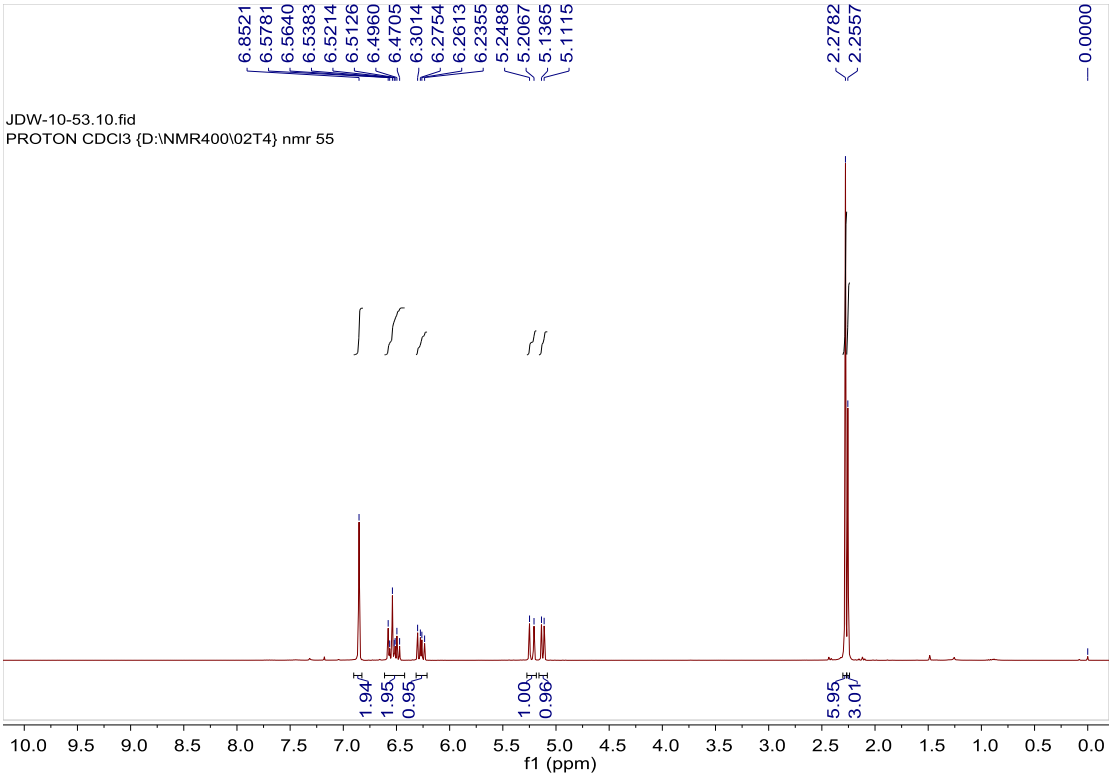
1l ^{19}F NMR (376 MHz, $CDCl_3$)

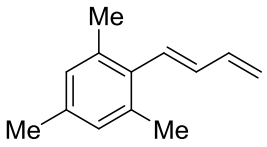




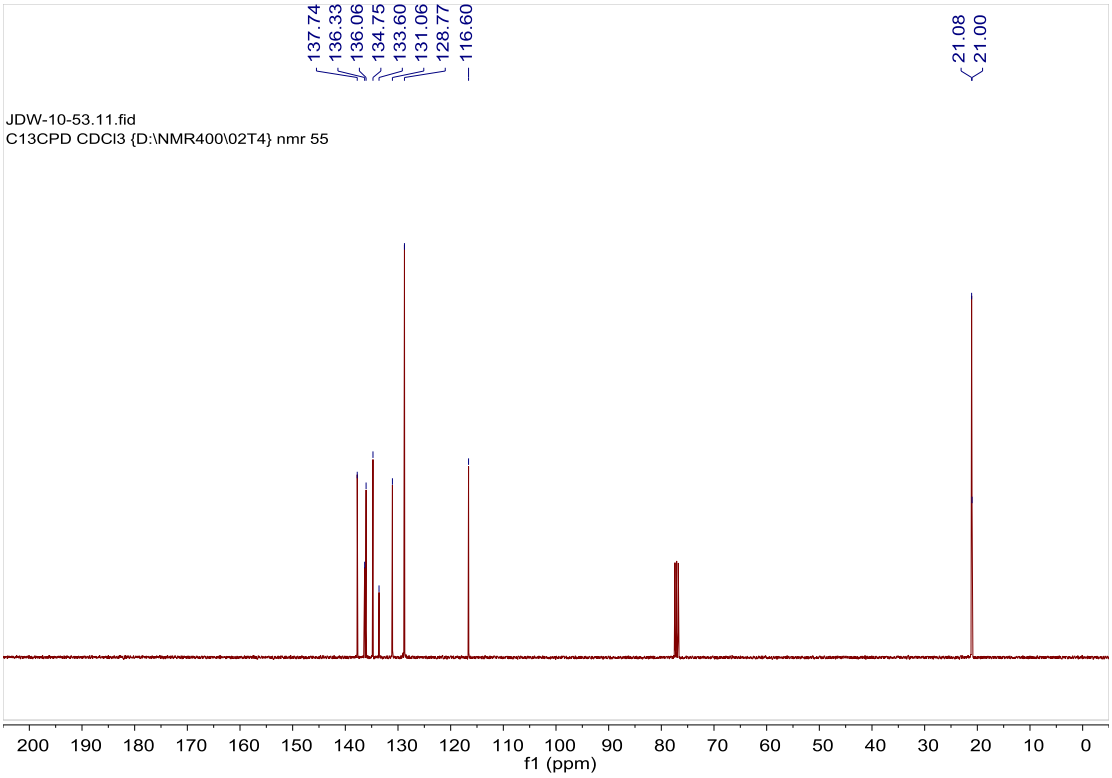
1m ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

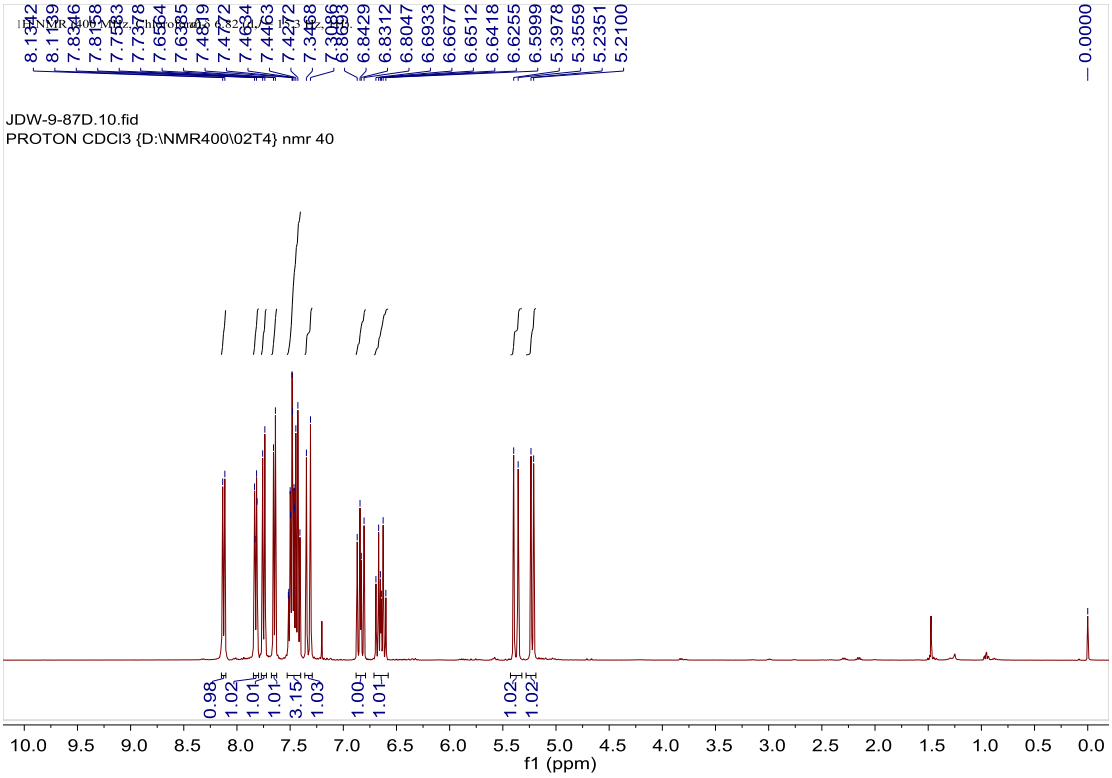


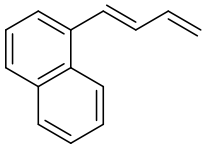




1n ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

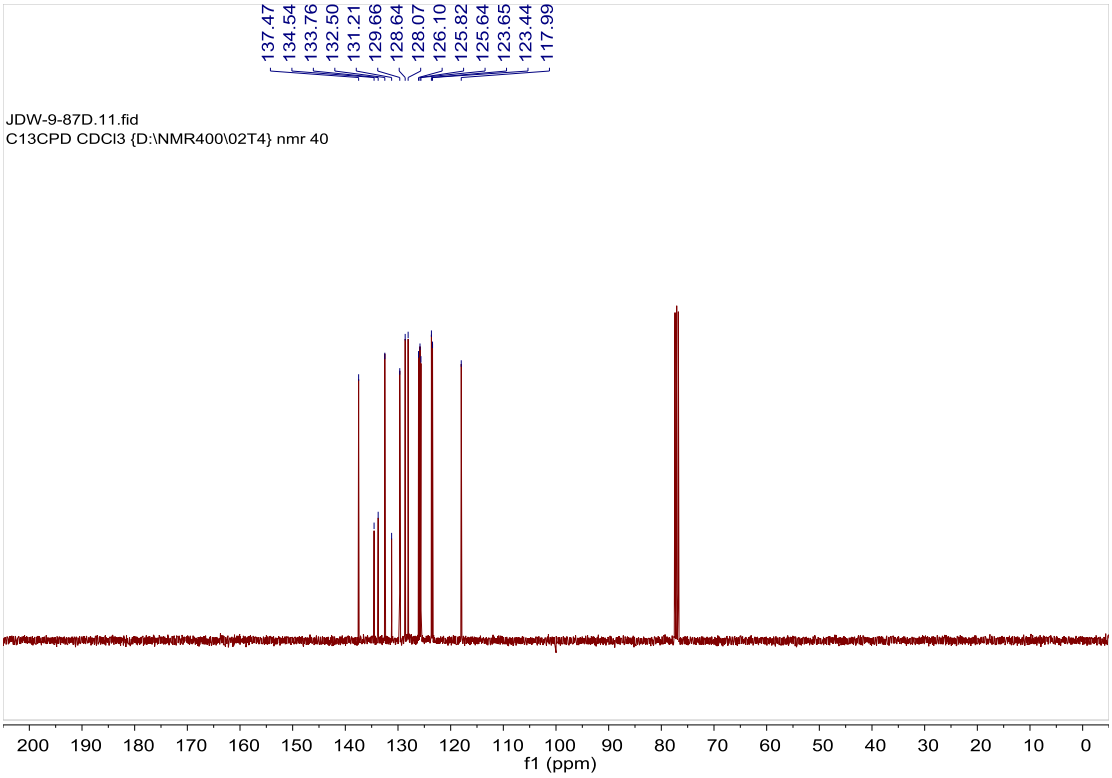


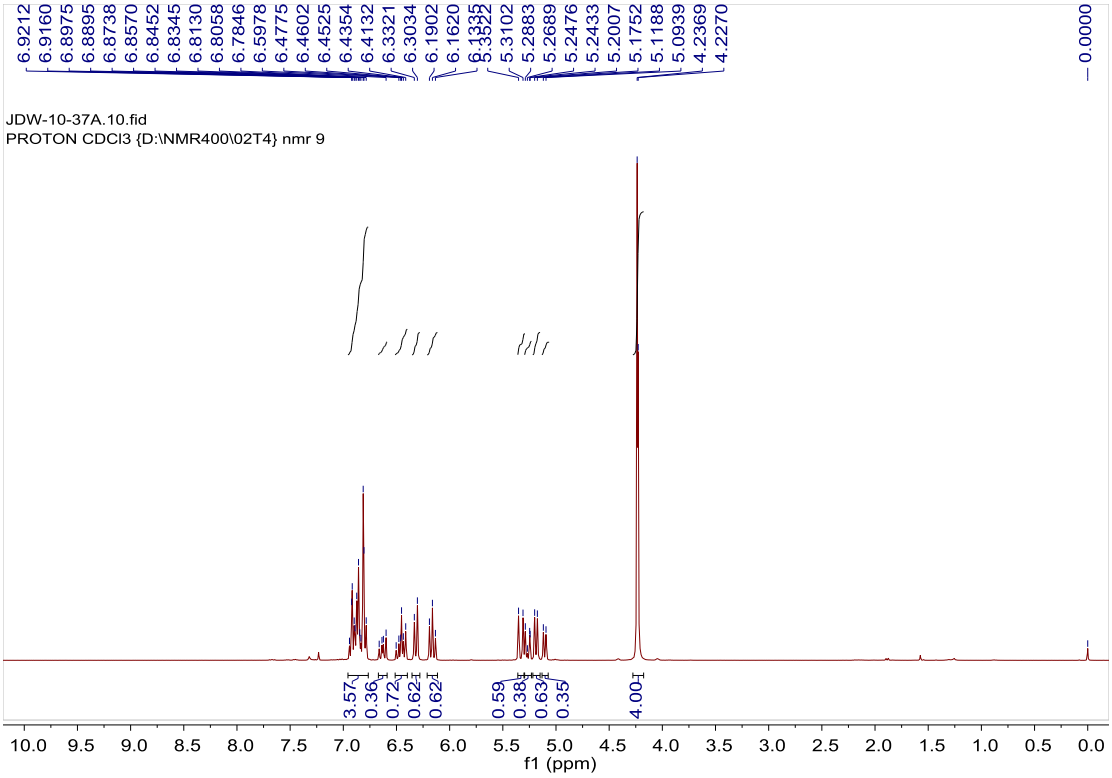


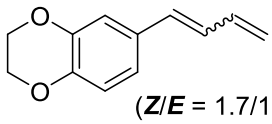


1o ^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (100 MHz, $CDCl_3$)



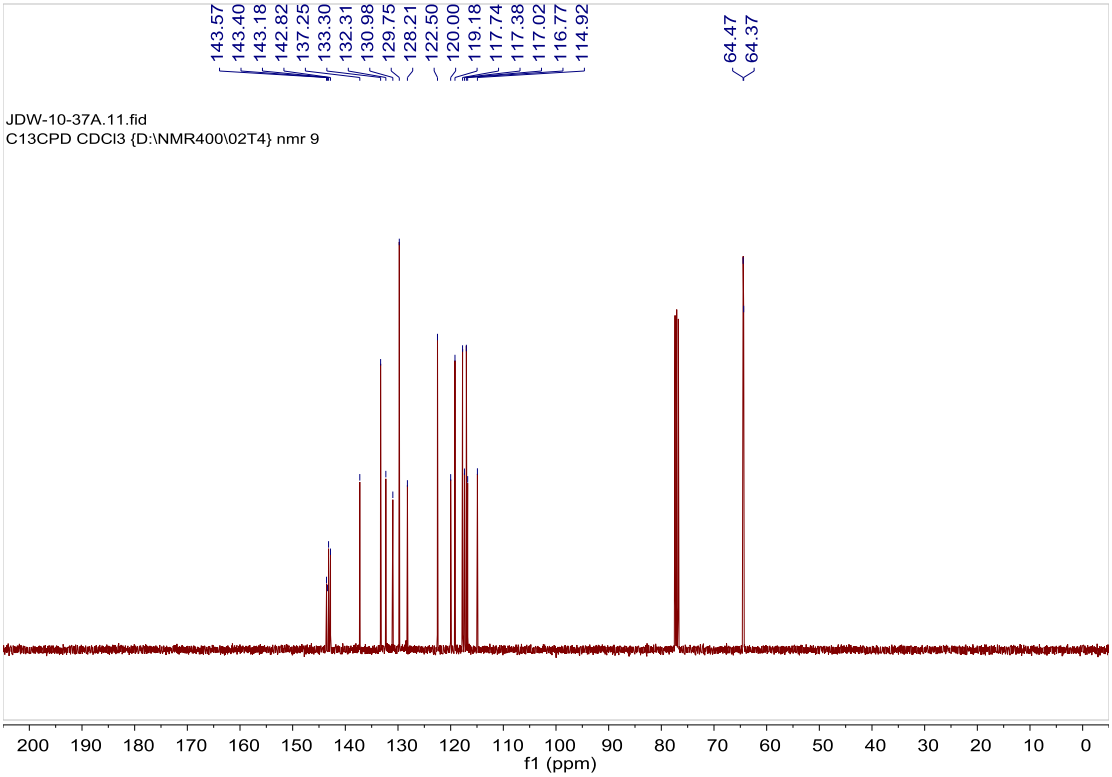


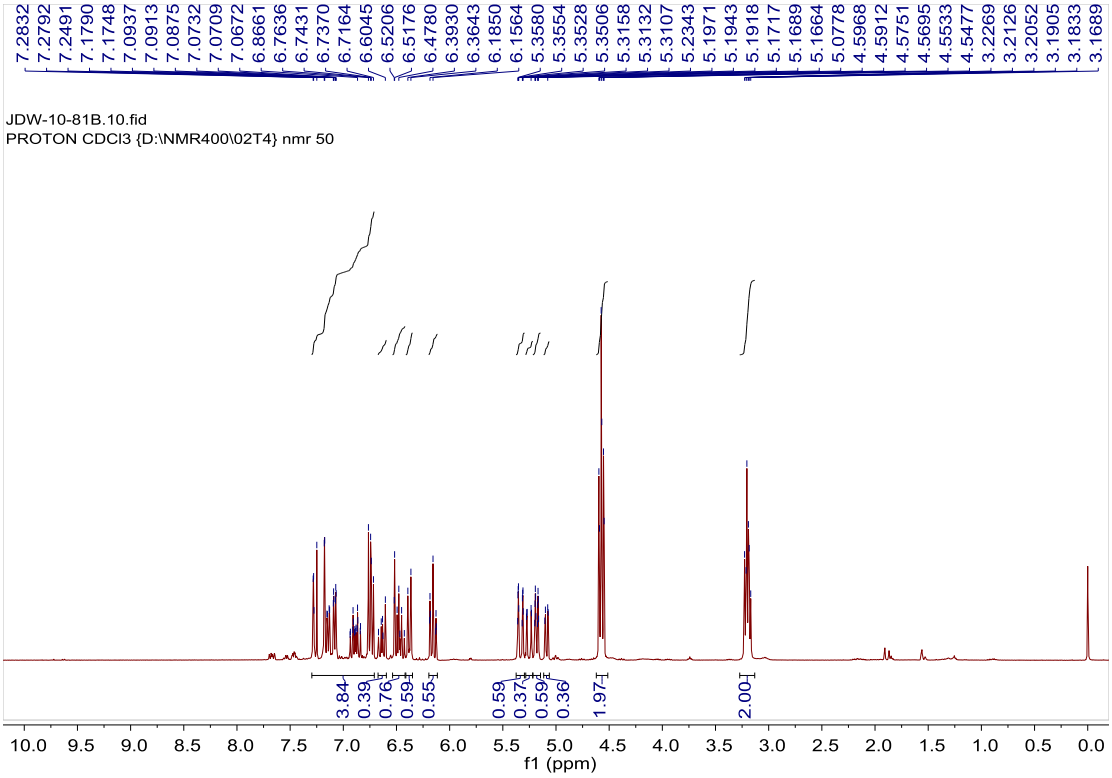


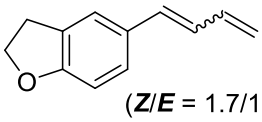
(***Z***/***E*** = 1.7/1)

1p ^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (100 MHz, $CDCl_3$)



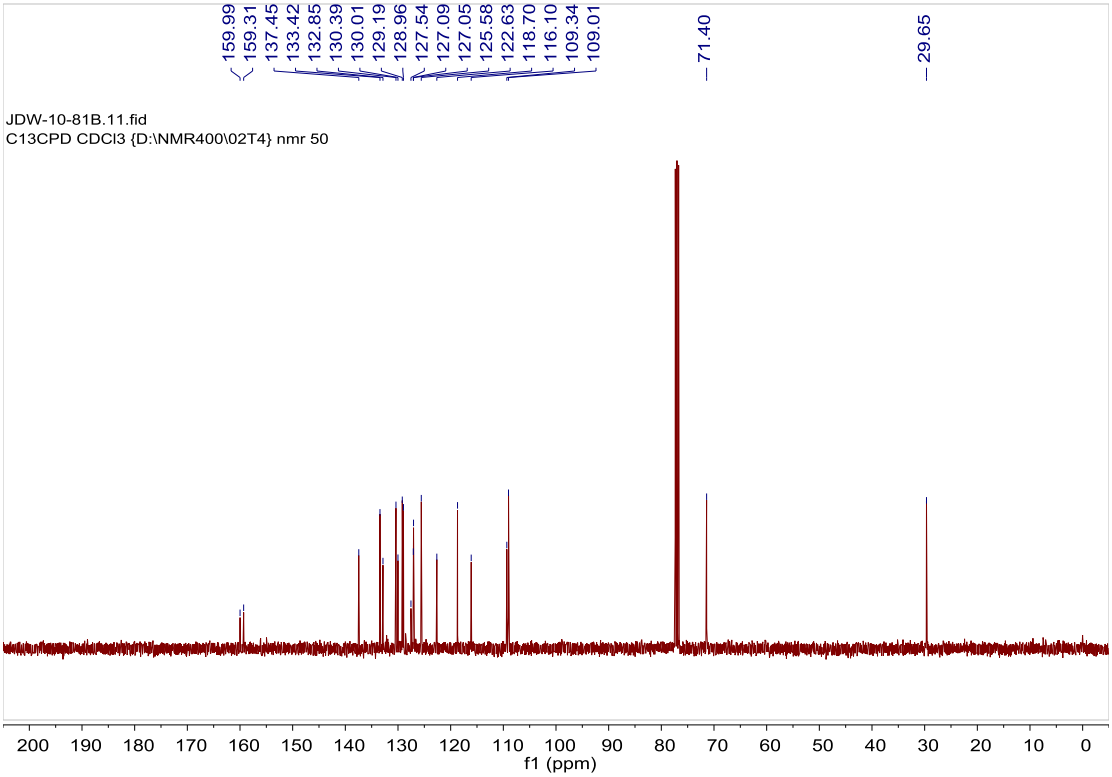


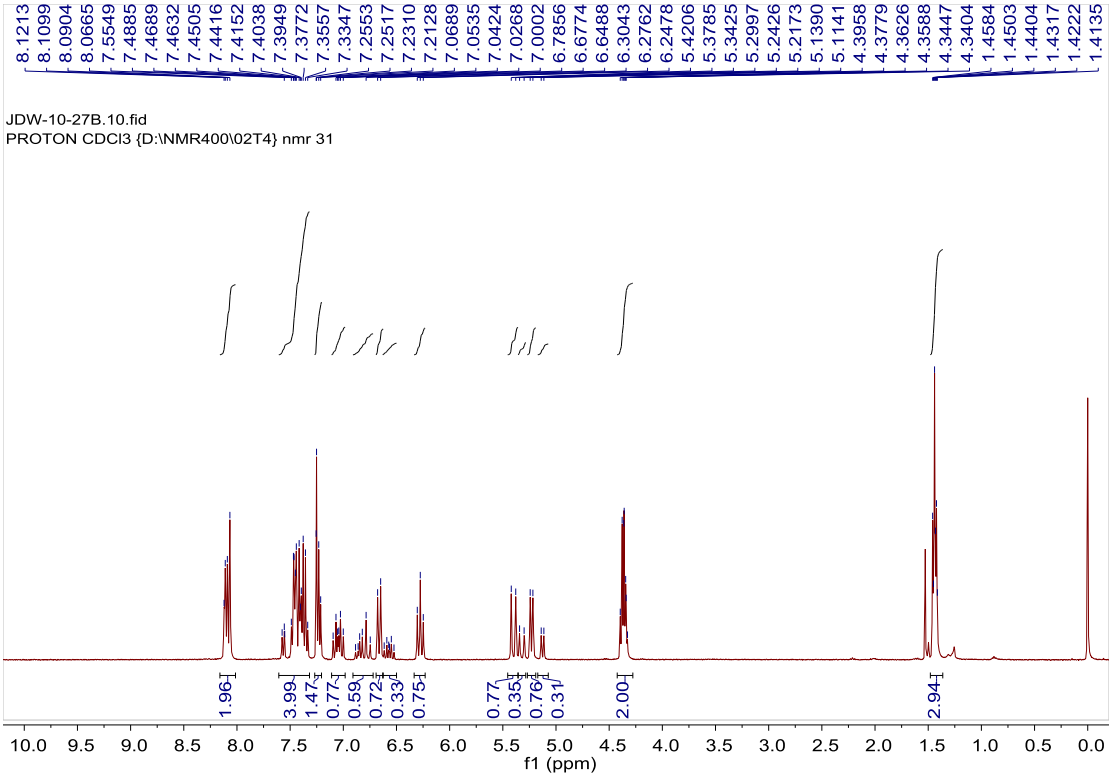


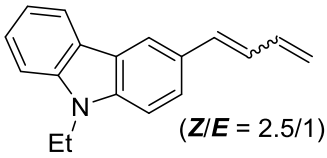
(***Z***/***E*** = 1.7/1)

1q ^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (100 MHz, $CDCl_3$)



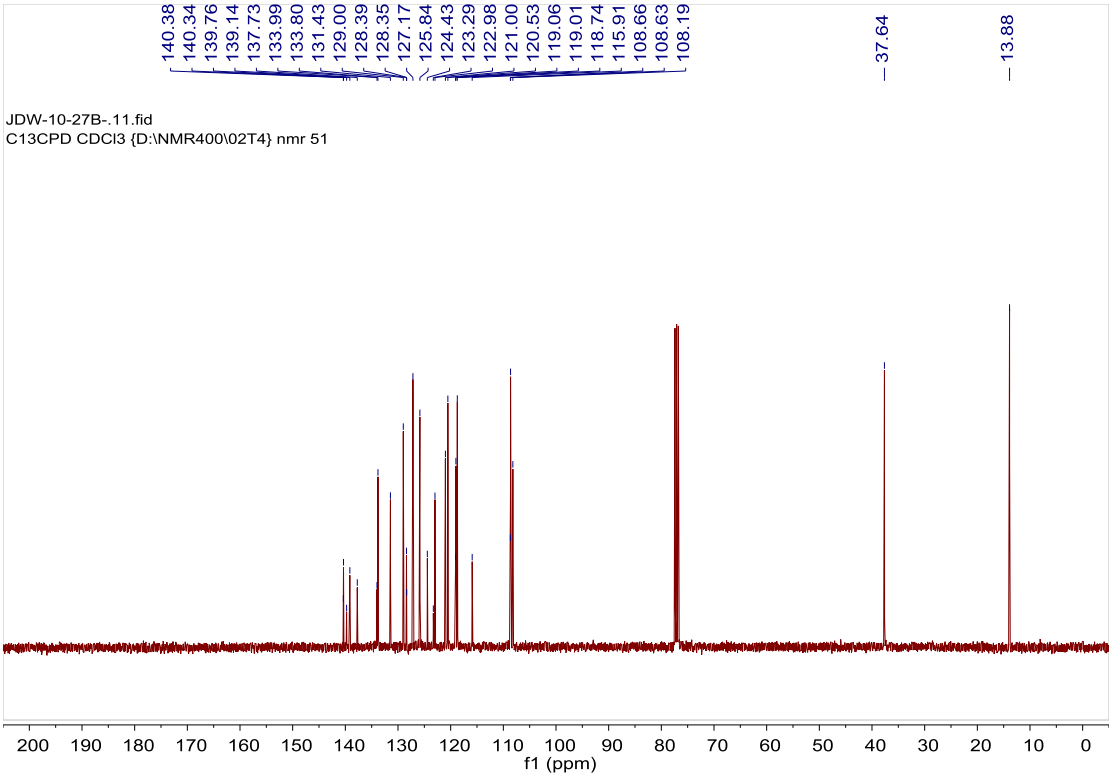


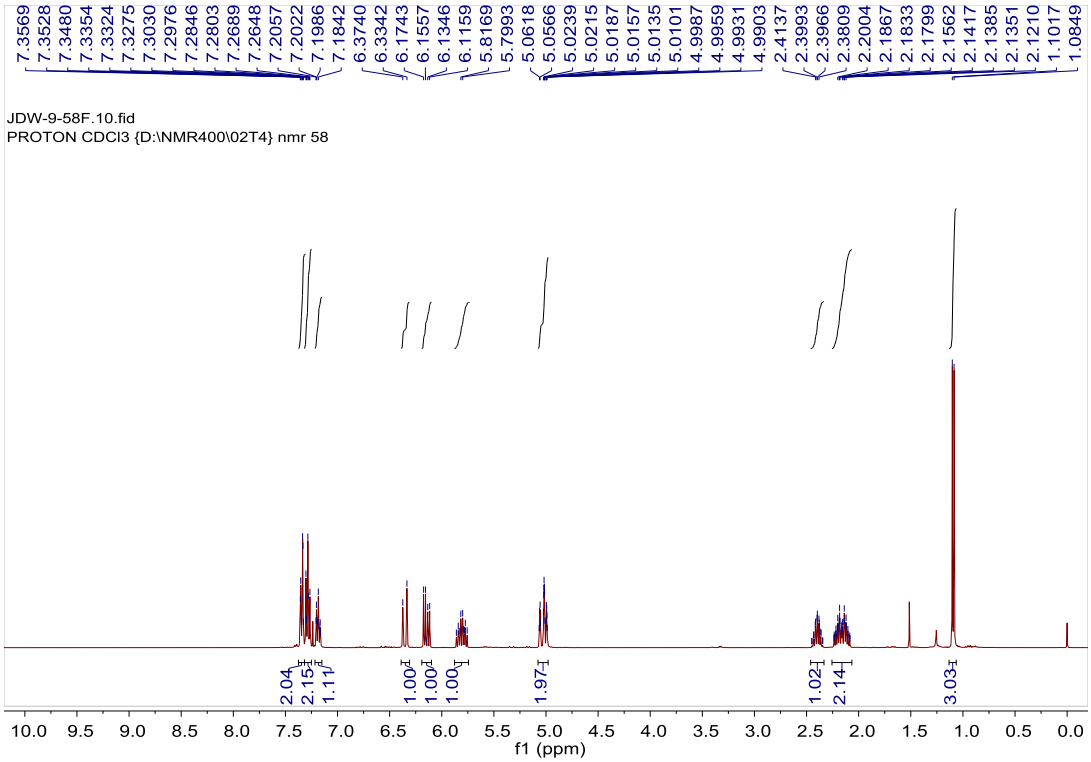


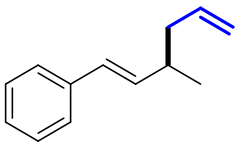
(***Z***/***E*** = 2.5/1)

1r ^{1}H NMR (400 MHz, $CDCl_3$)

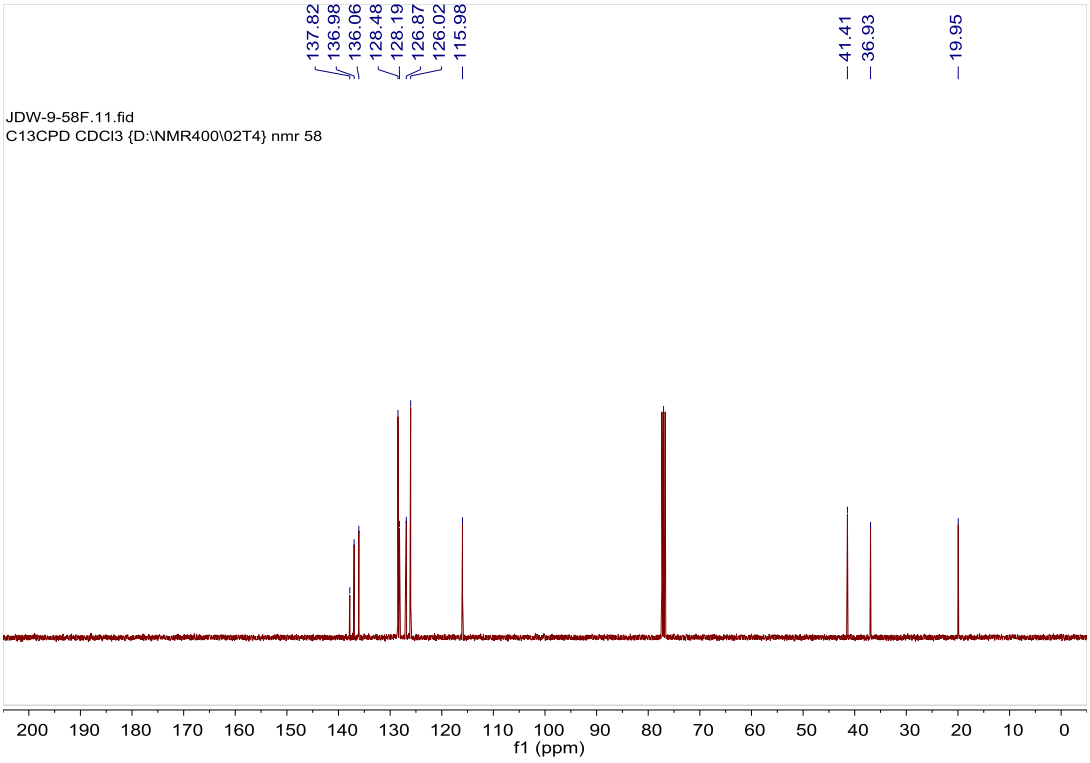
^{13}C NMR (100 MHz, $CDCl_3$)

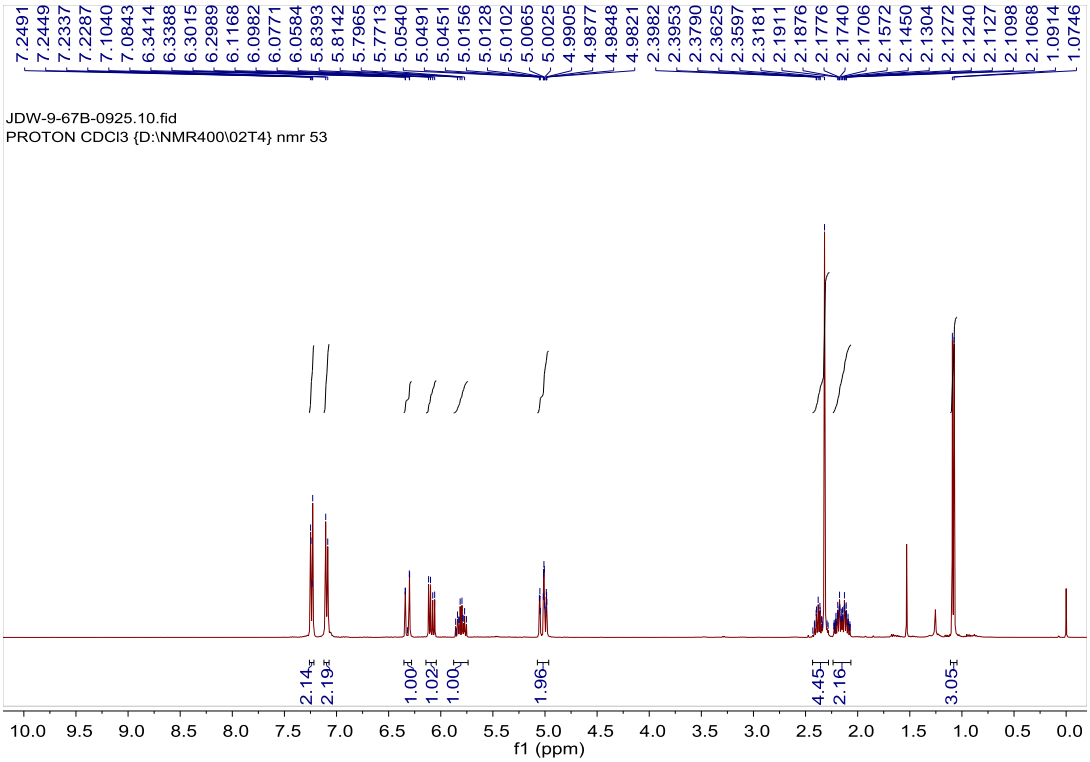


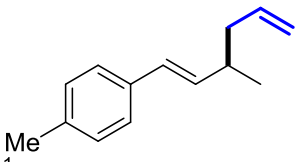




3a ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

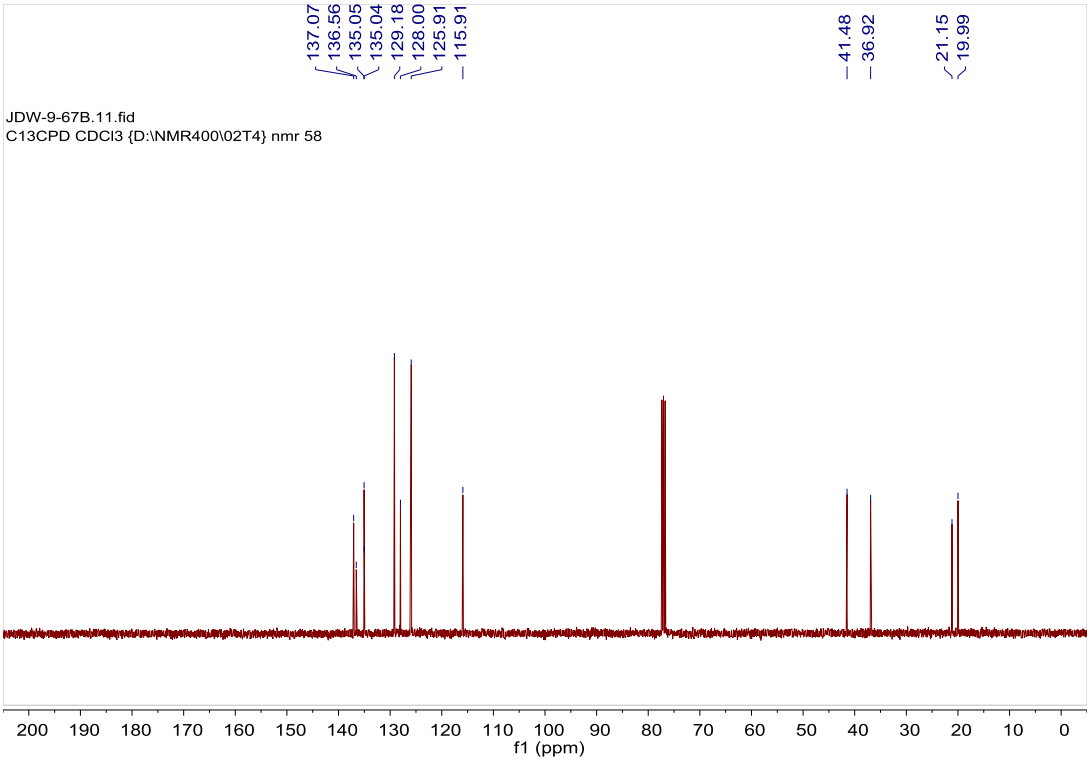


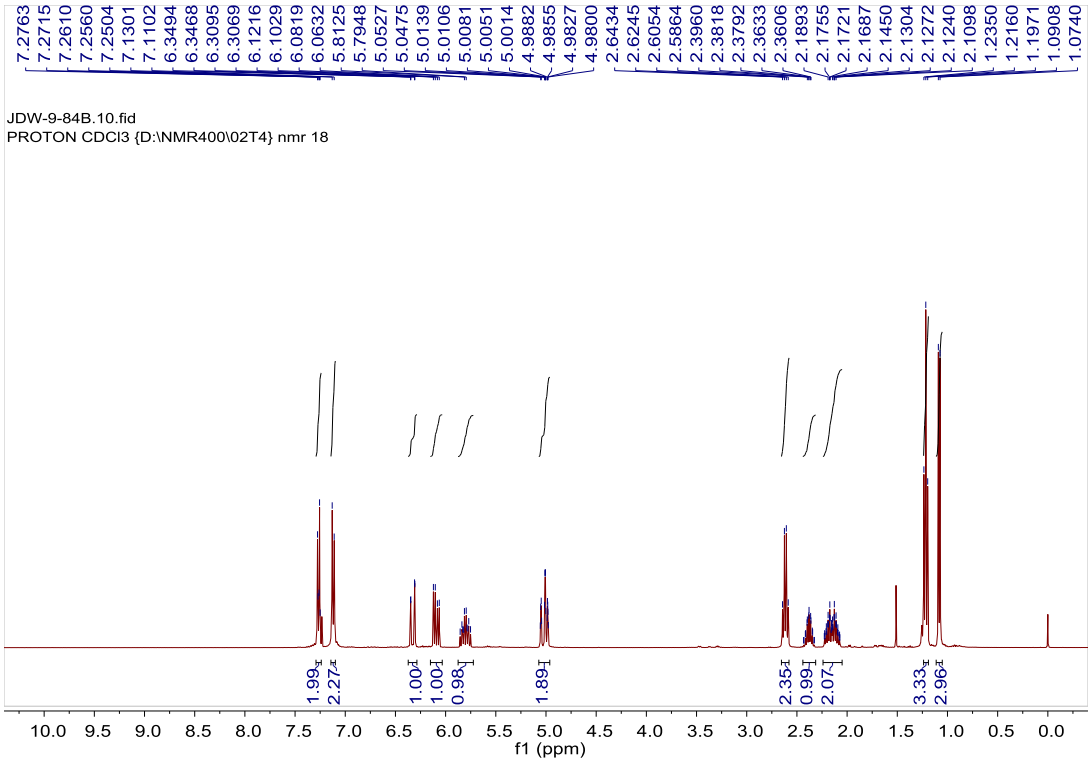


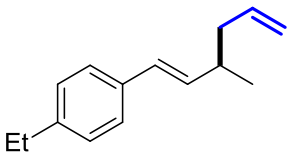


3b ^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (100 MHz, $CDCl_3$)

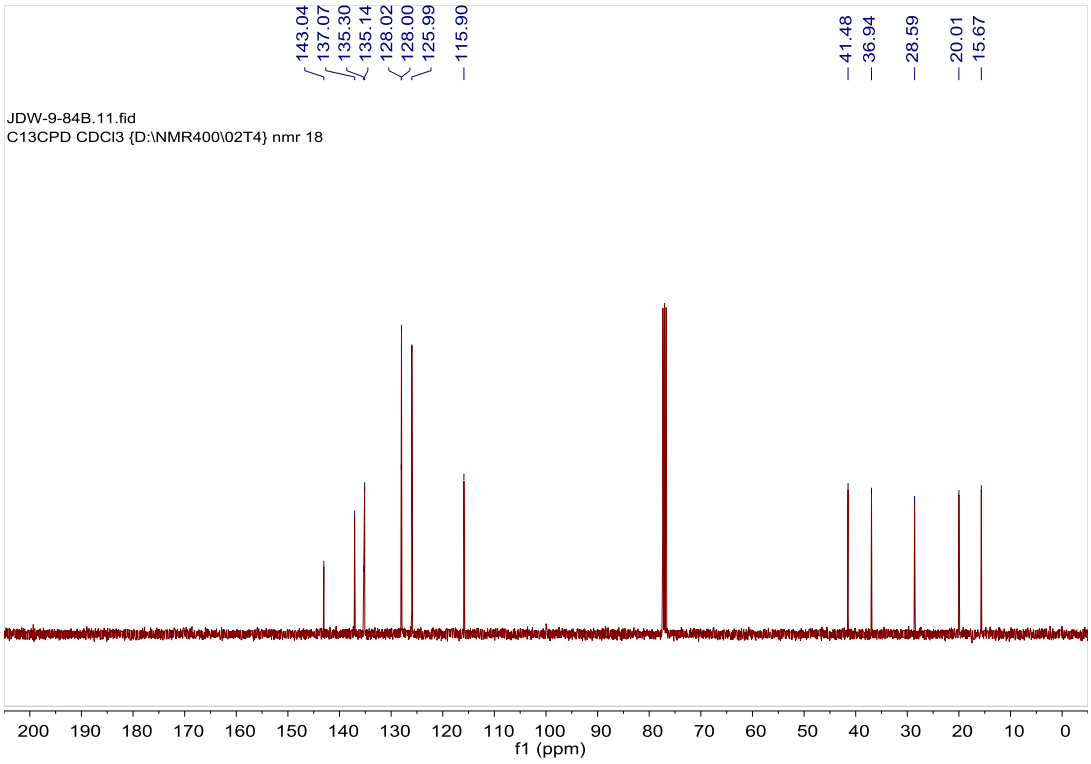


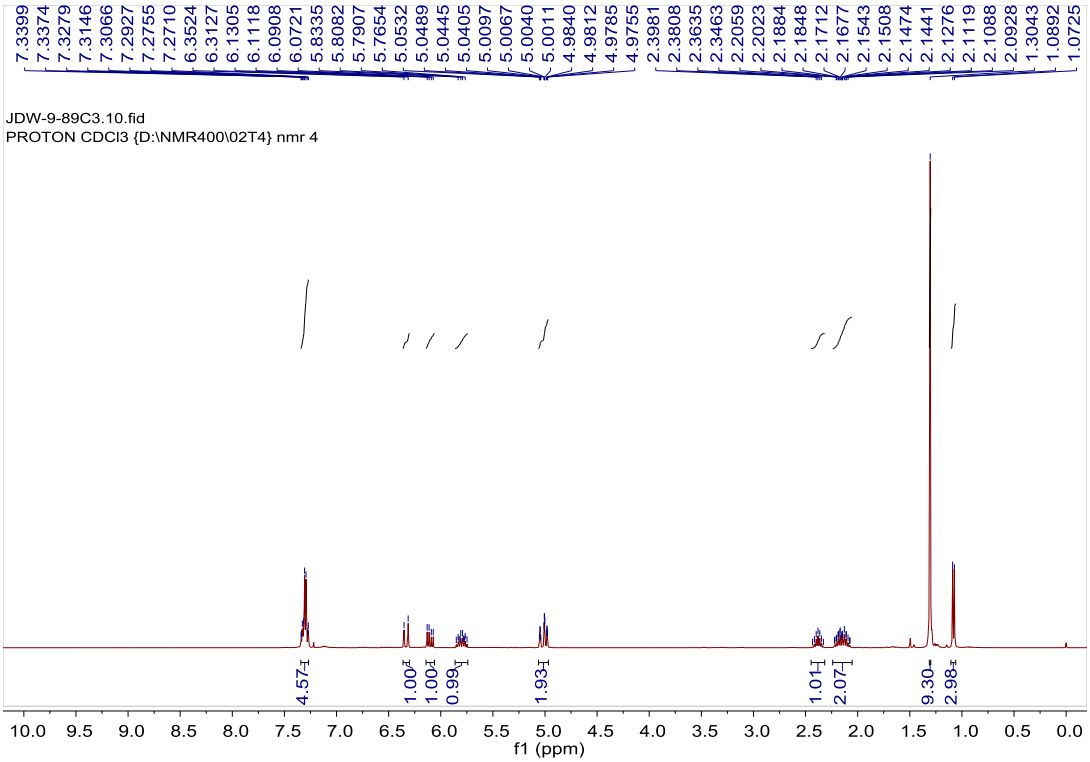


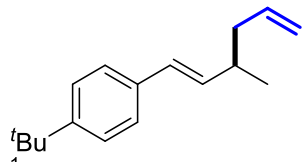


3c ^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (100 MHz, $CDCl_3$)

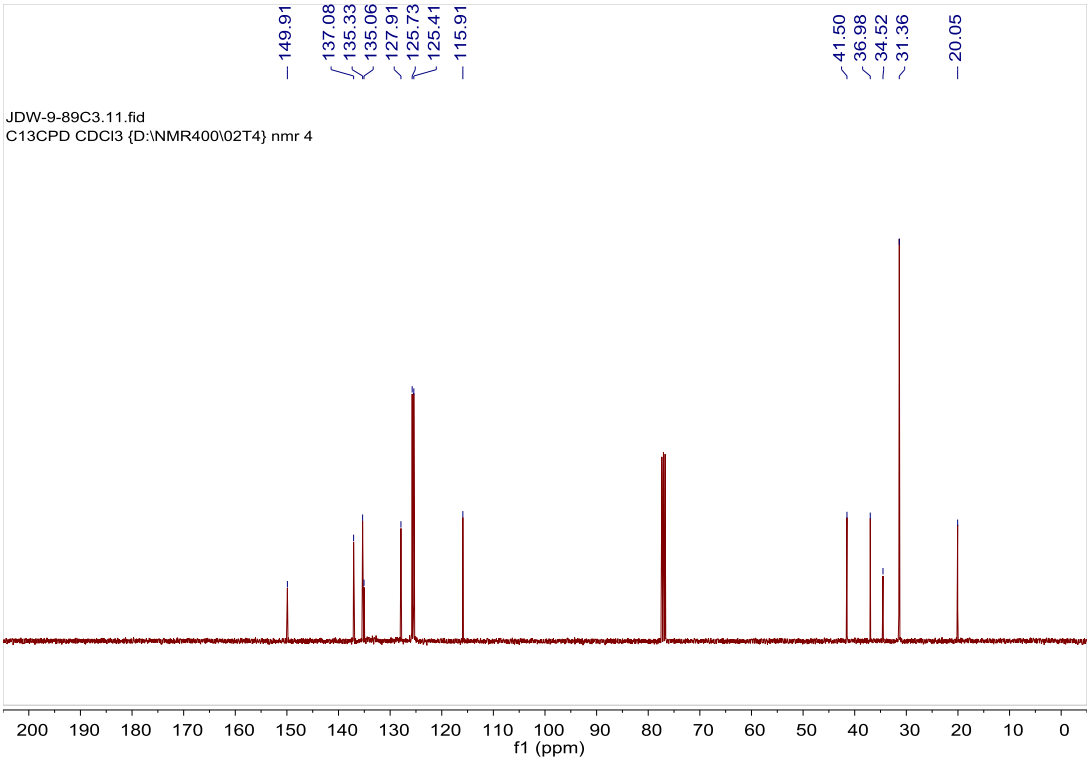


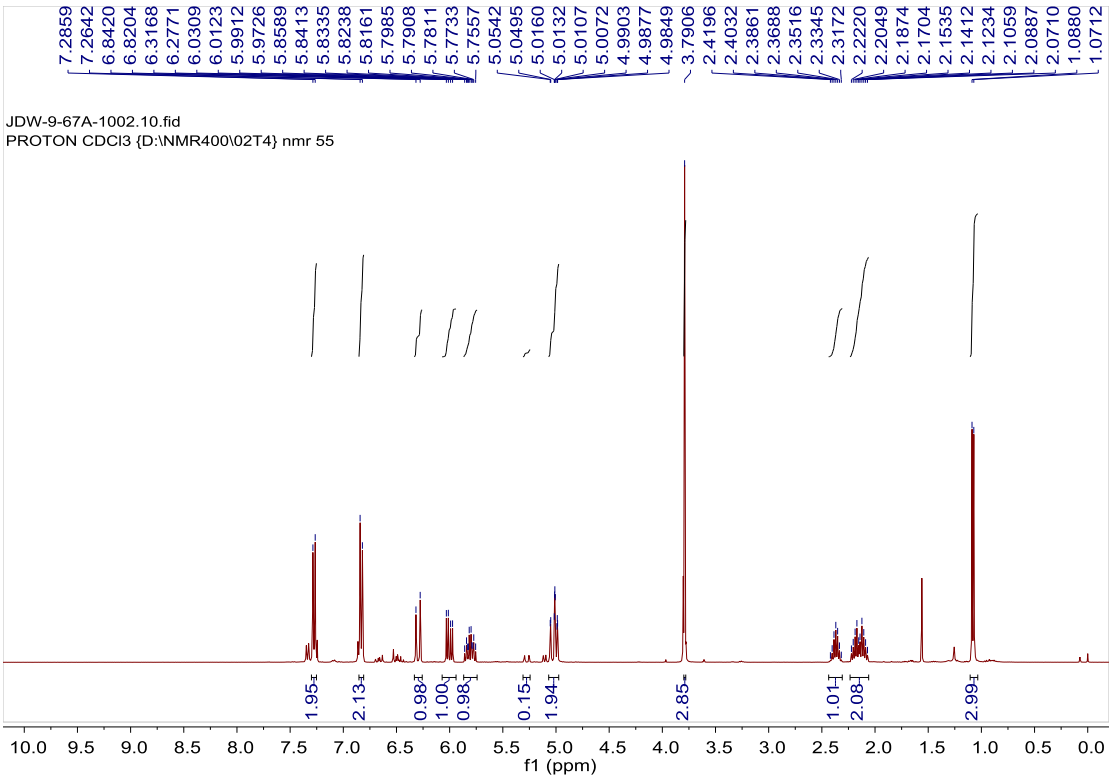


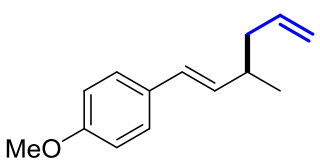


3d ^{1}H NMR (400 MHz, $CDCl_3$)

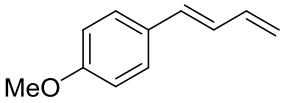
^{13}C NMR (100 MHz, $CDCl_3$)





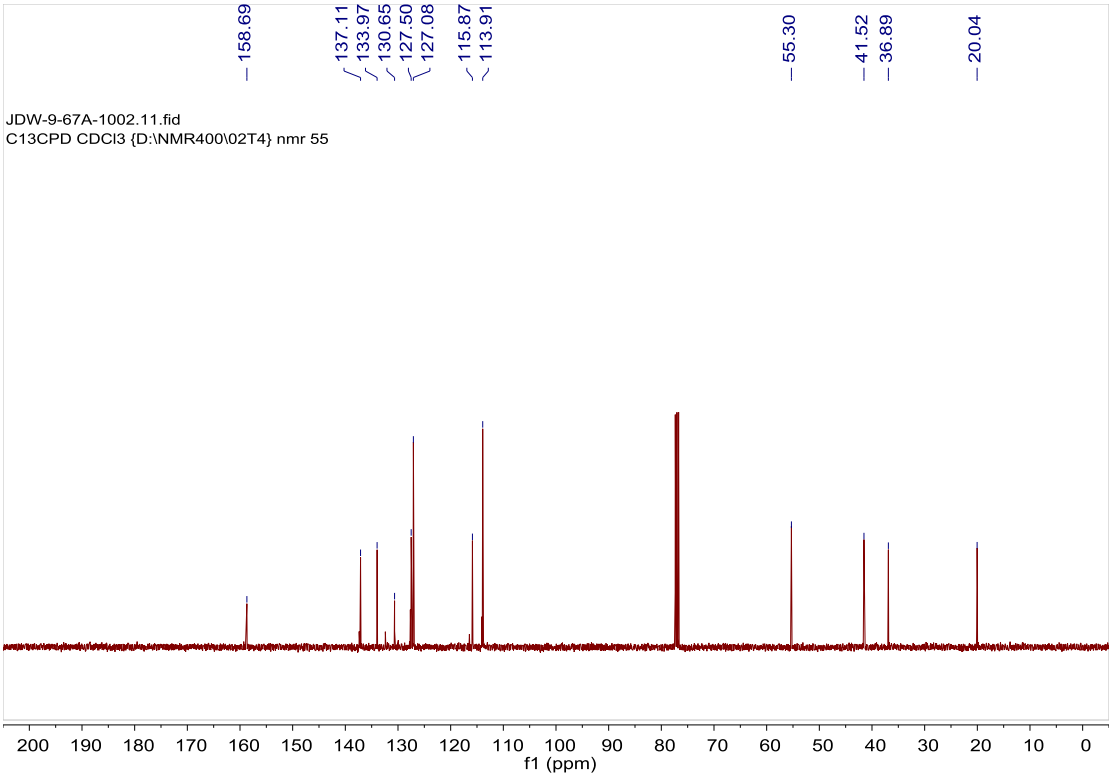


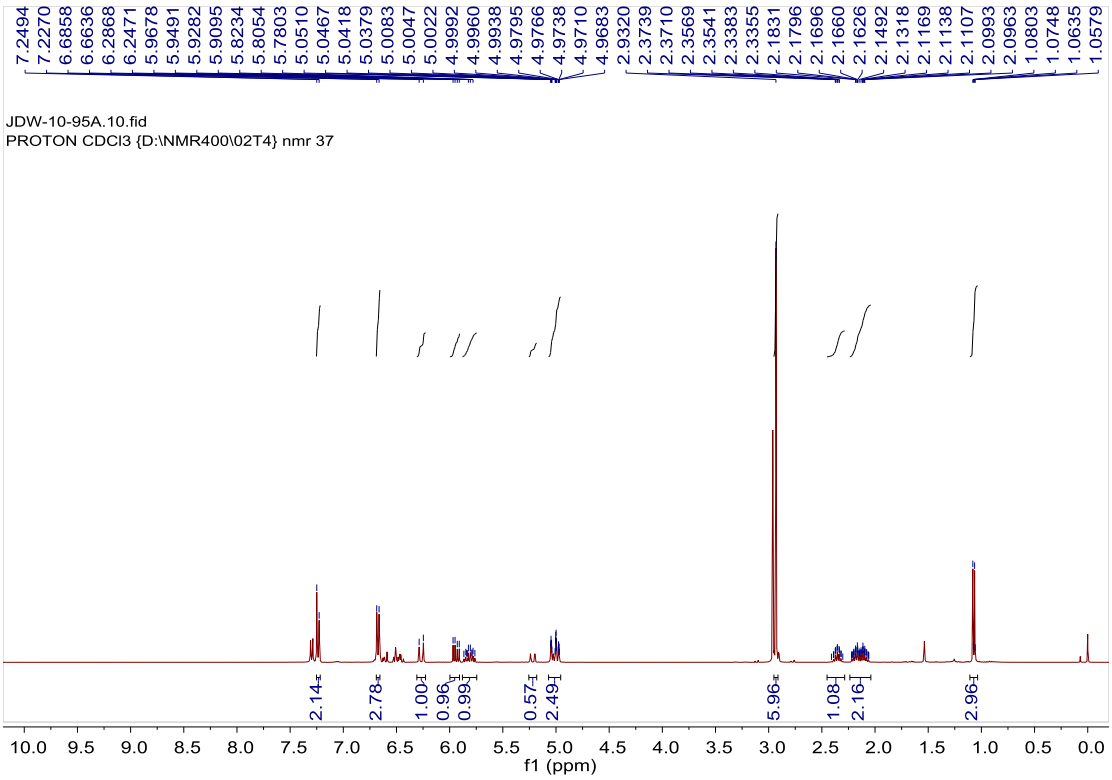
3e ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

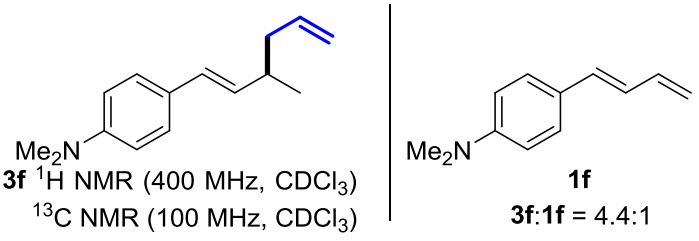


1e

3e:**1e** = 6.7:1



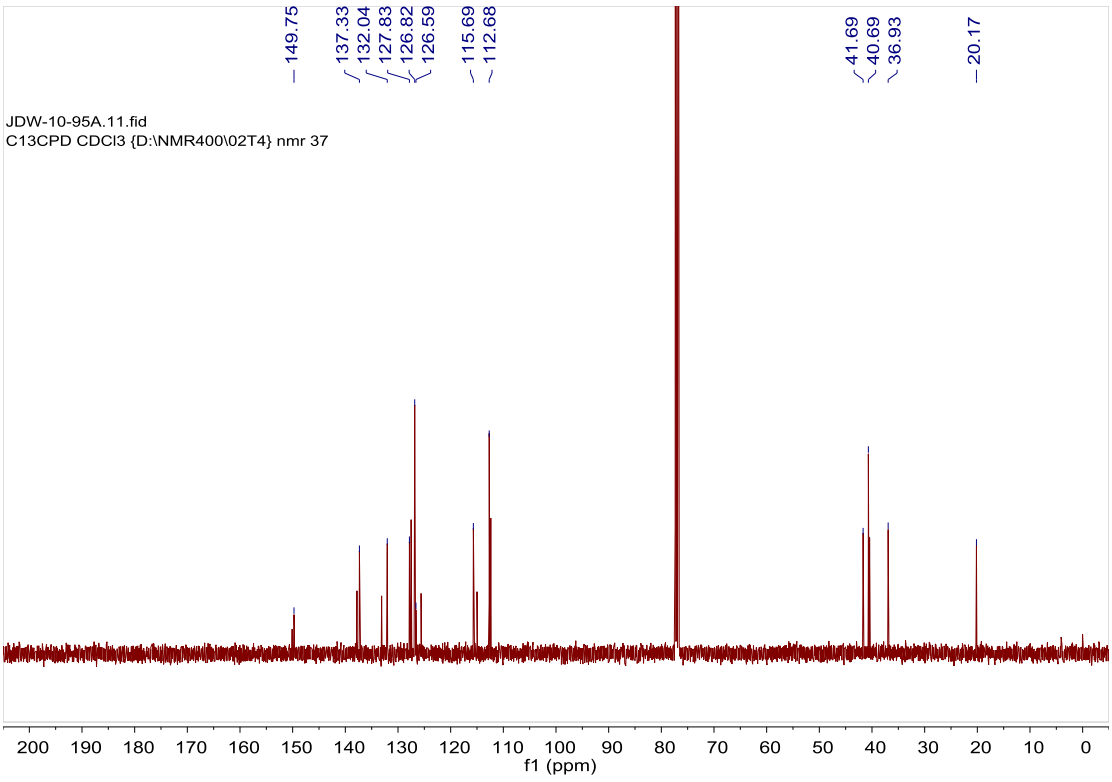


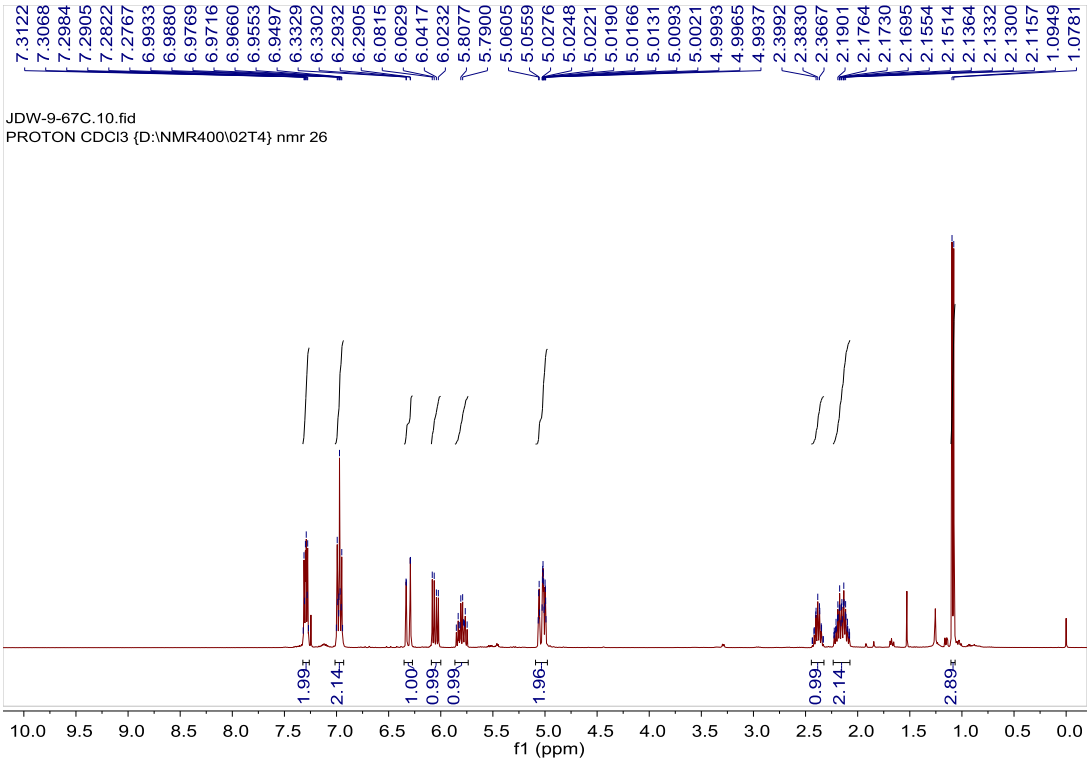


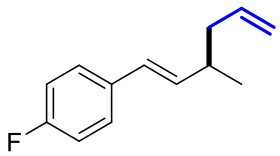
3f ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

1f

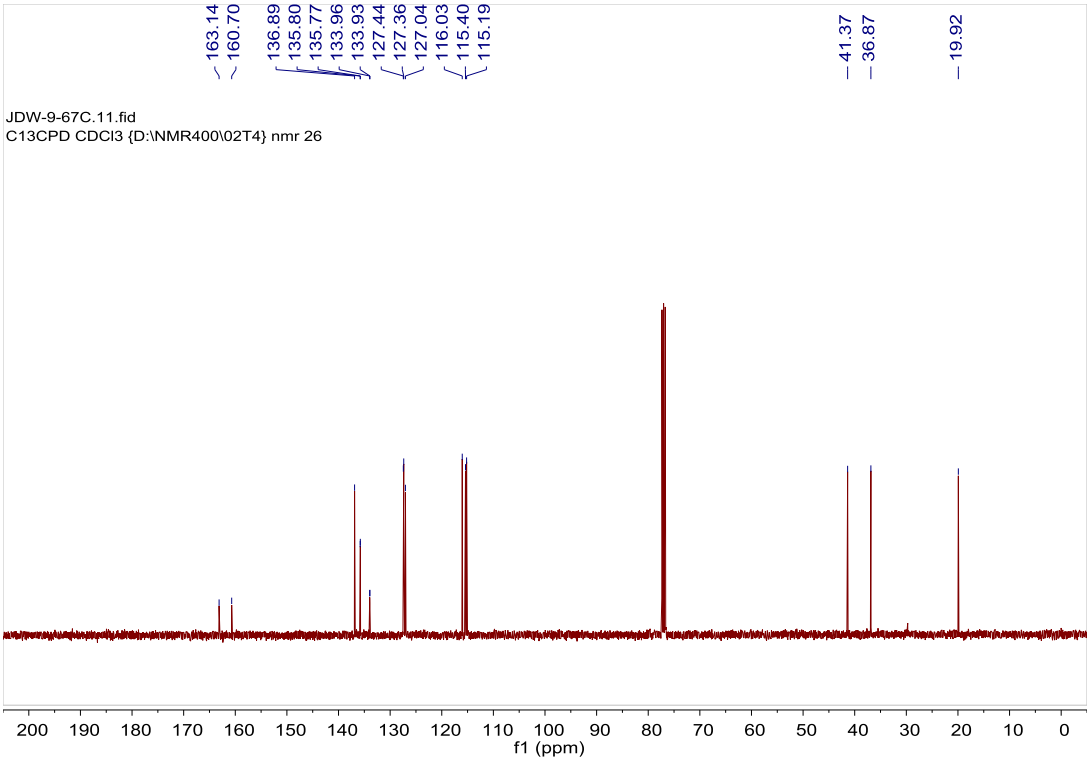
3f:**1f** = 4.4:1

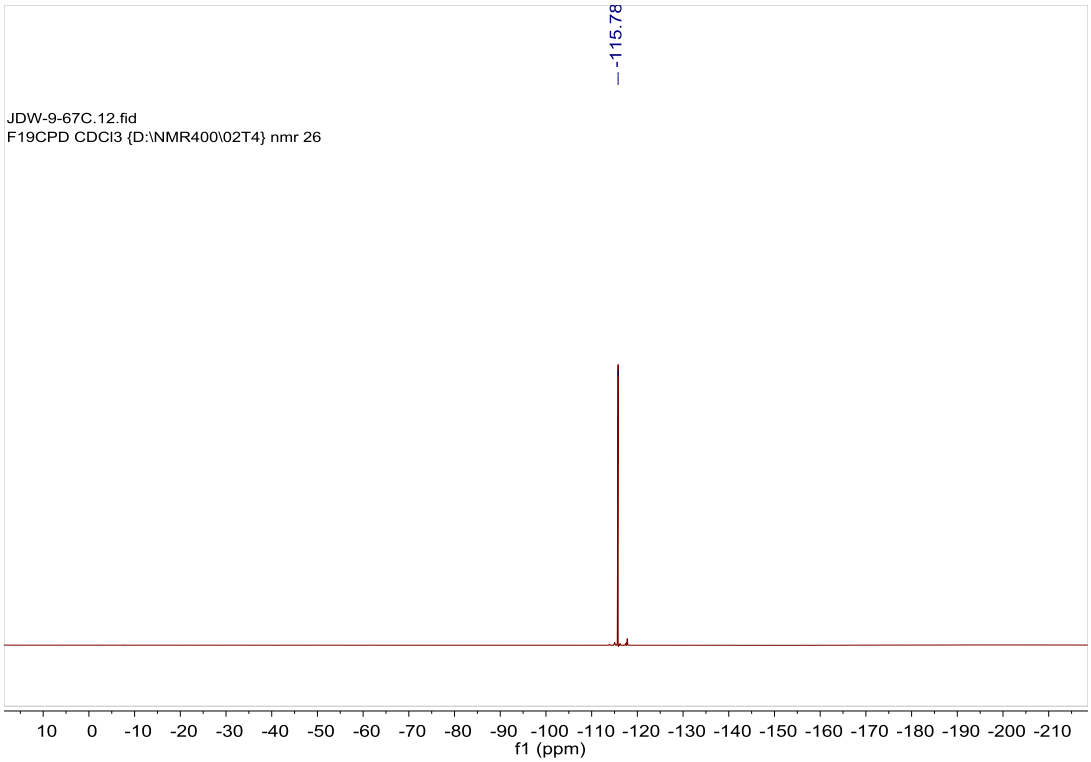


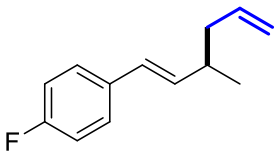




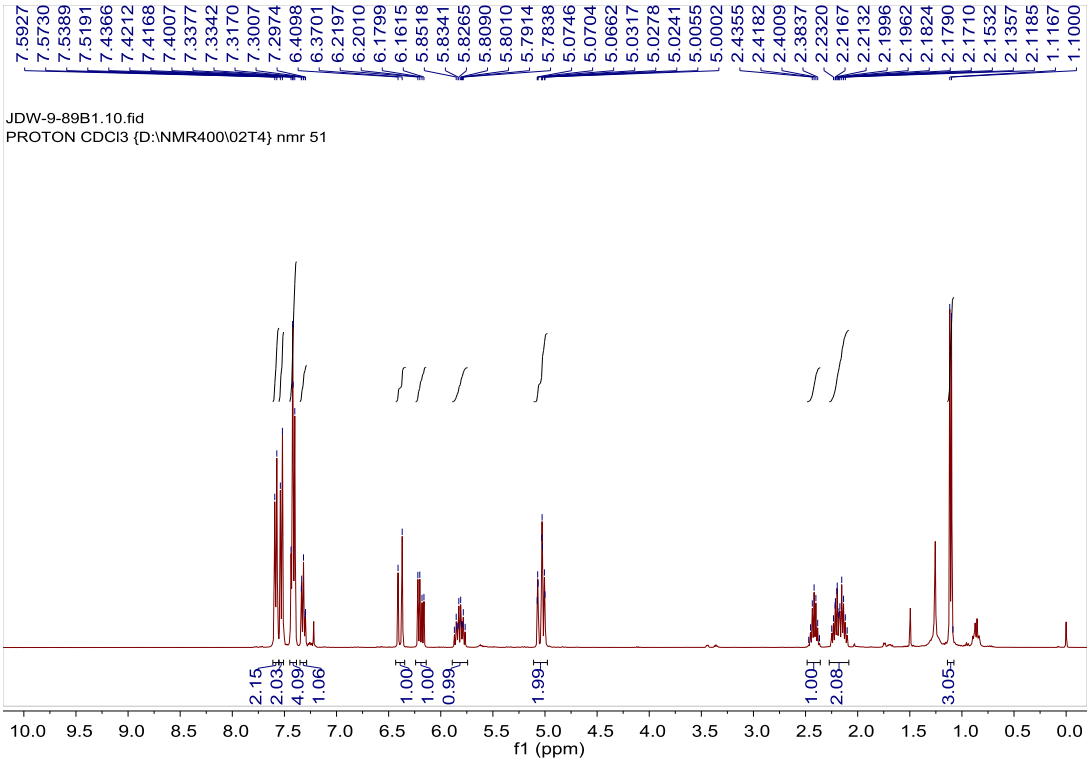
3g ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

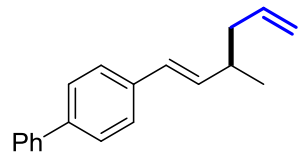






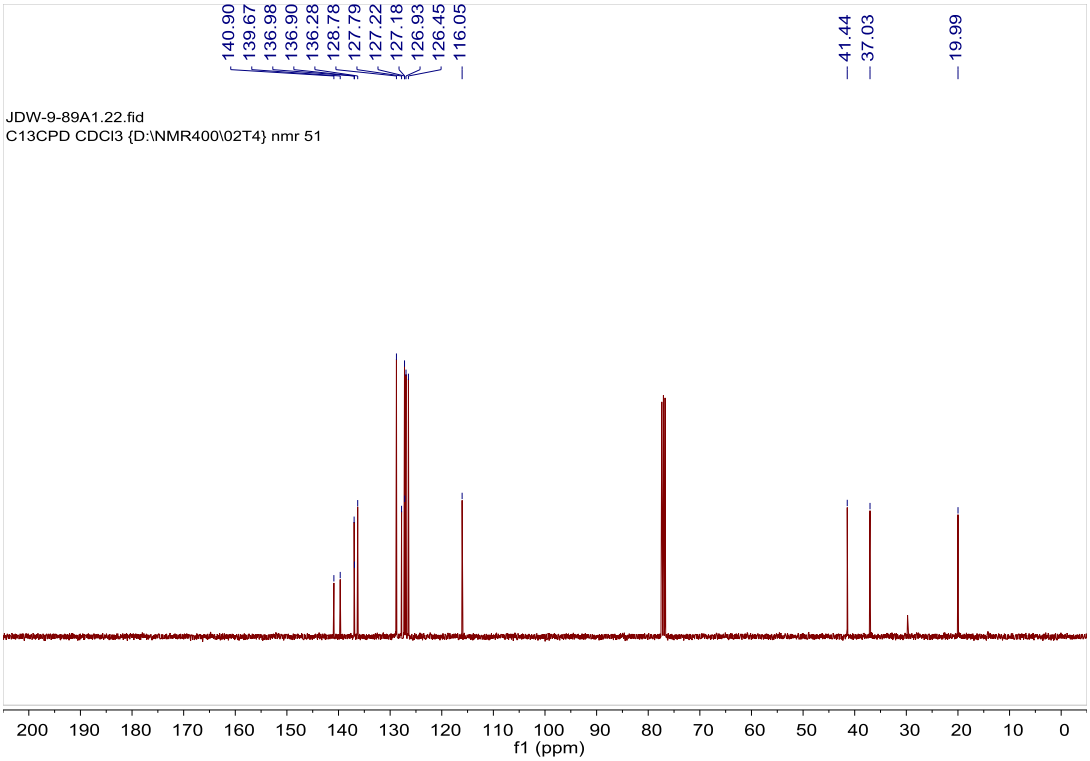
3g ^{19}F NMR (376 MHz, $CDCl_3$)

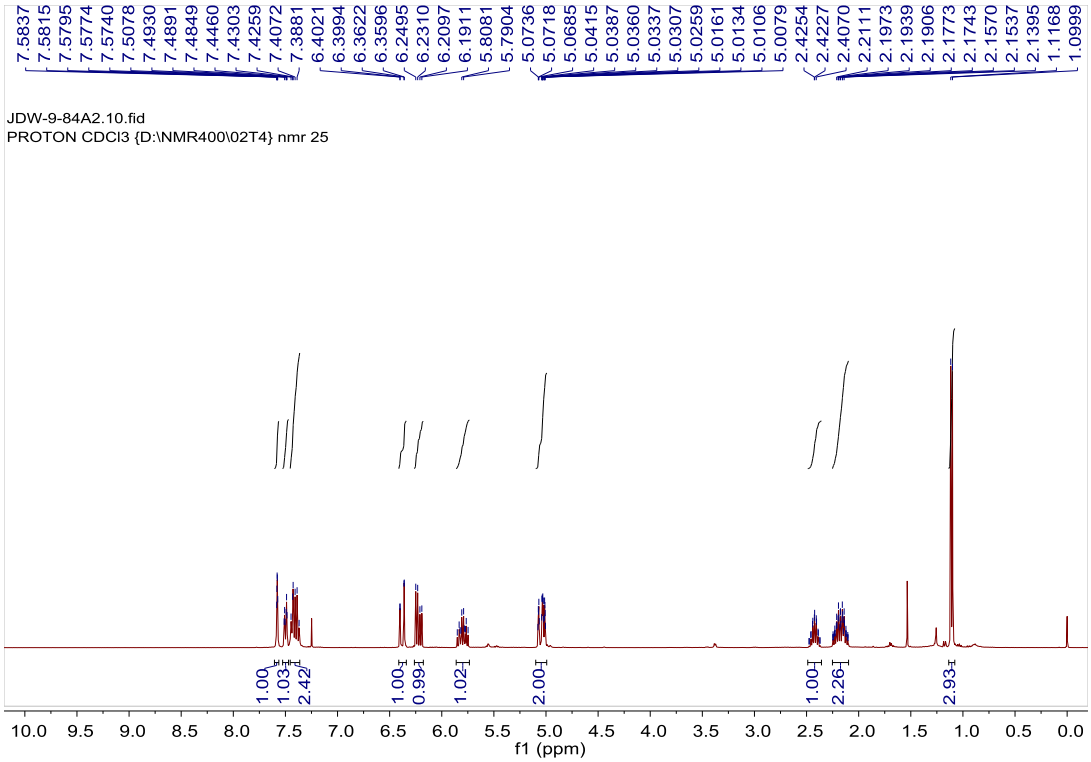


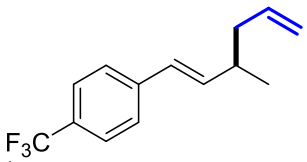


3h ^{1}H NMR (400 MHz, $CDCl_3$)

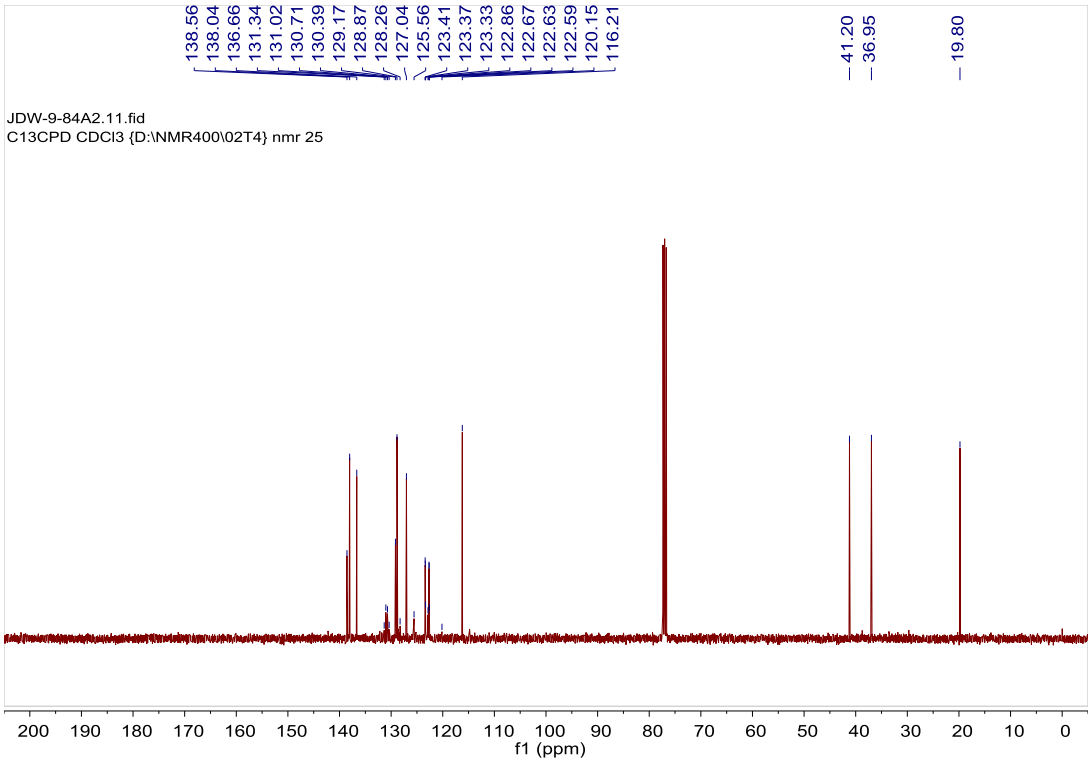
^{13}C NMR (100 MHz, $CDCl_3$)

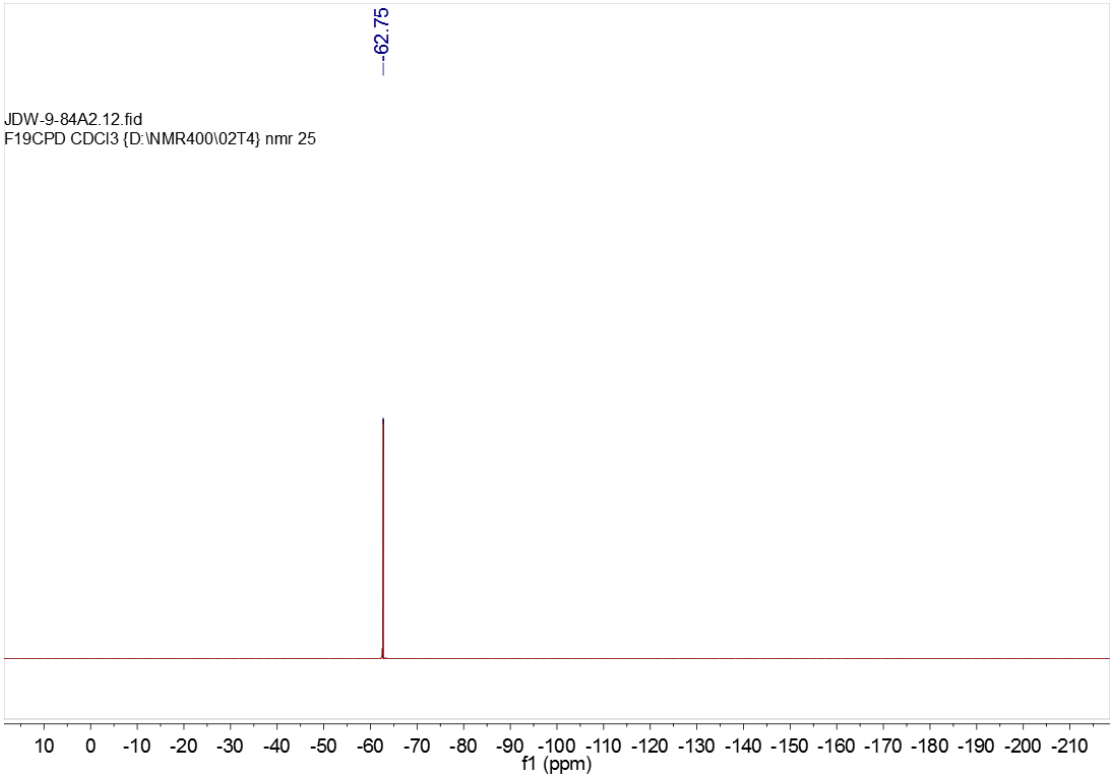


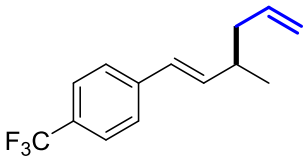




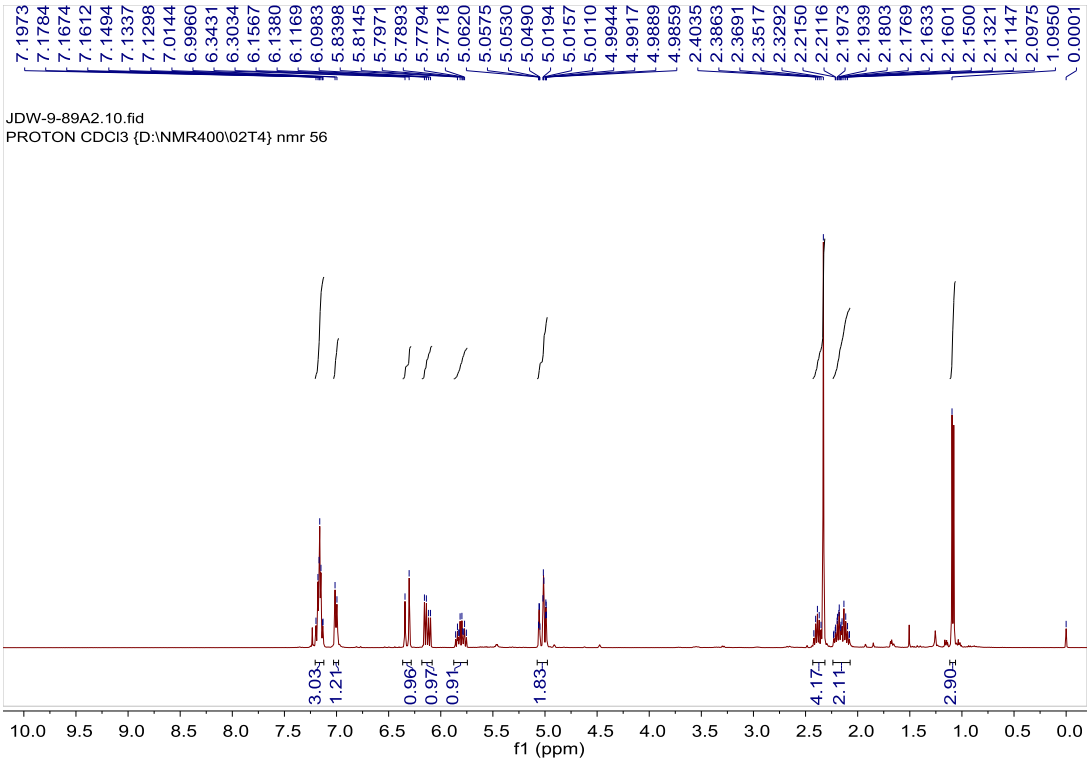
3i ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

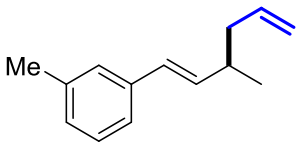




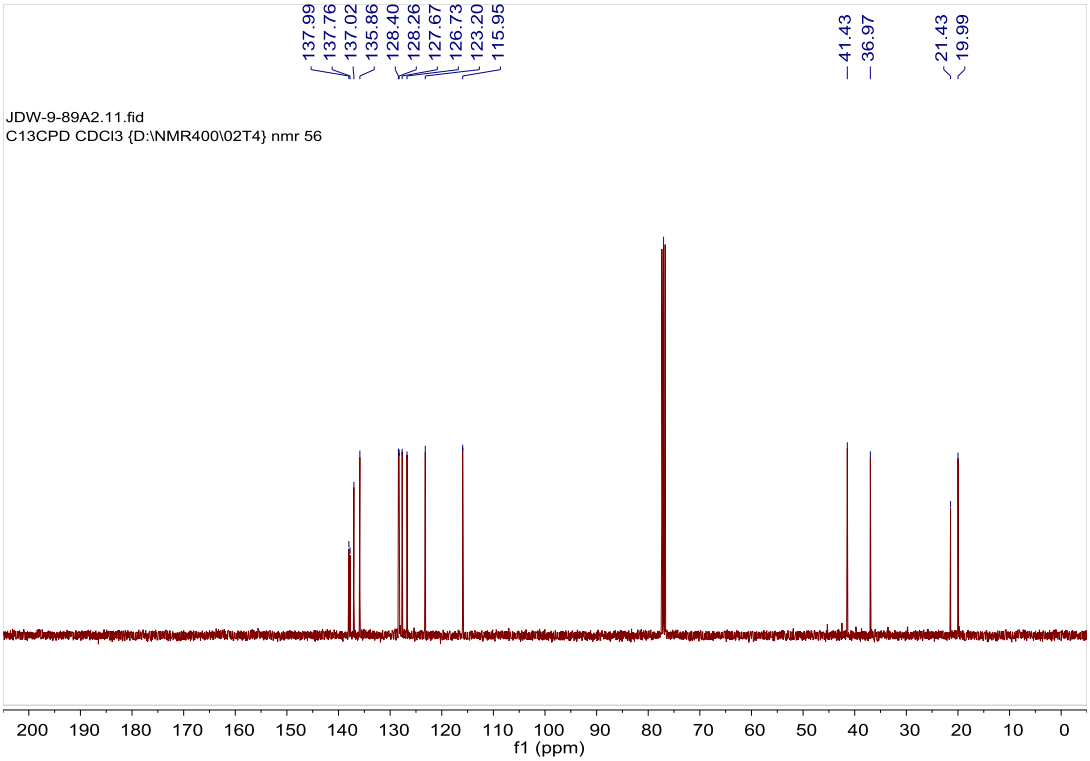


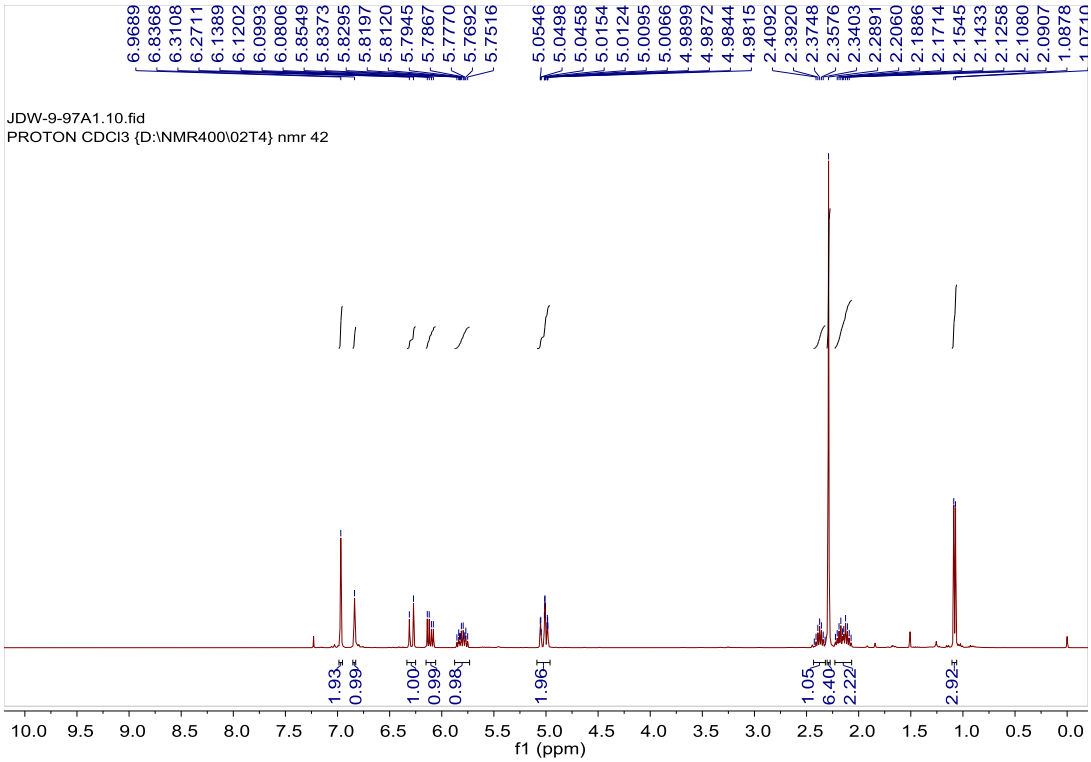
3i ^{19}F NMR (376 MHz, $CDCl_3$)

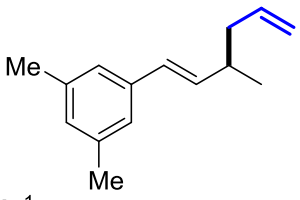




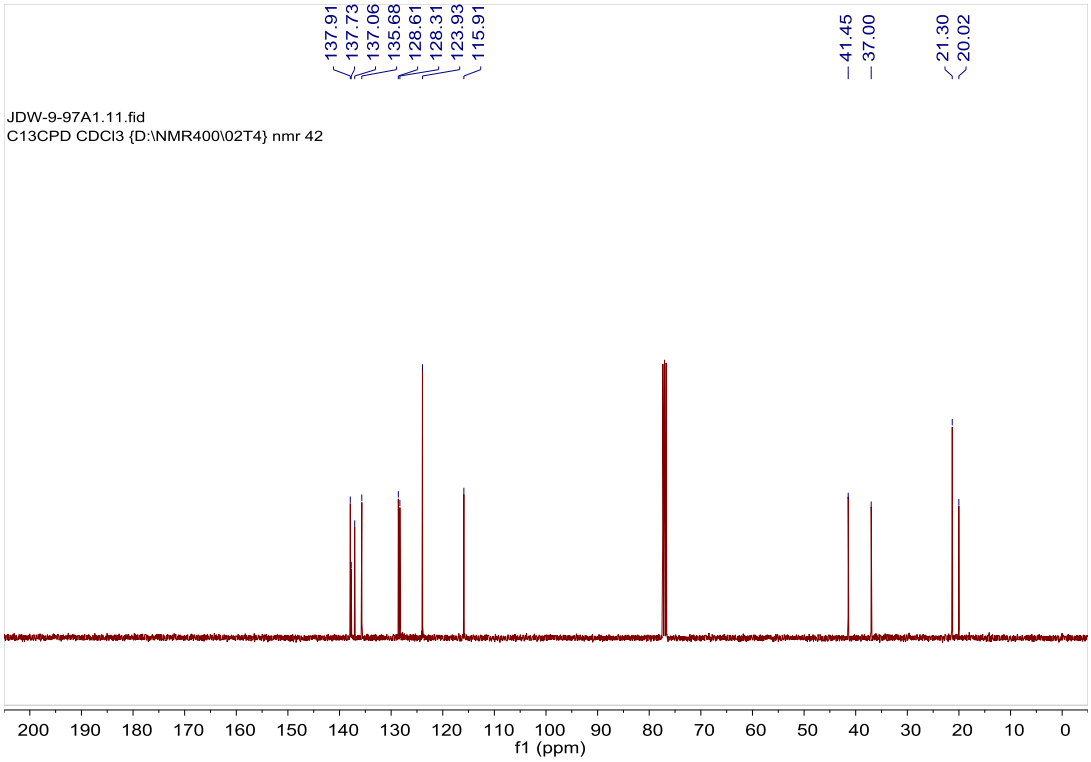
3j ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

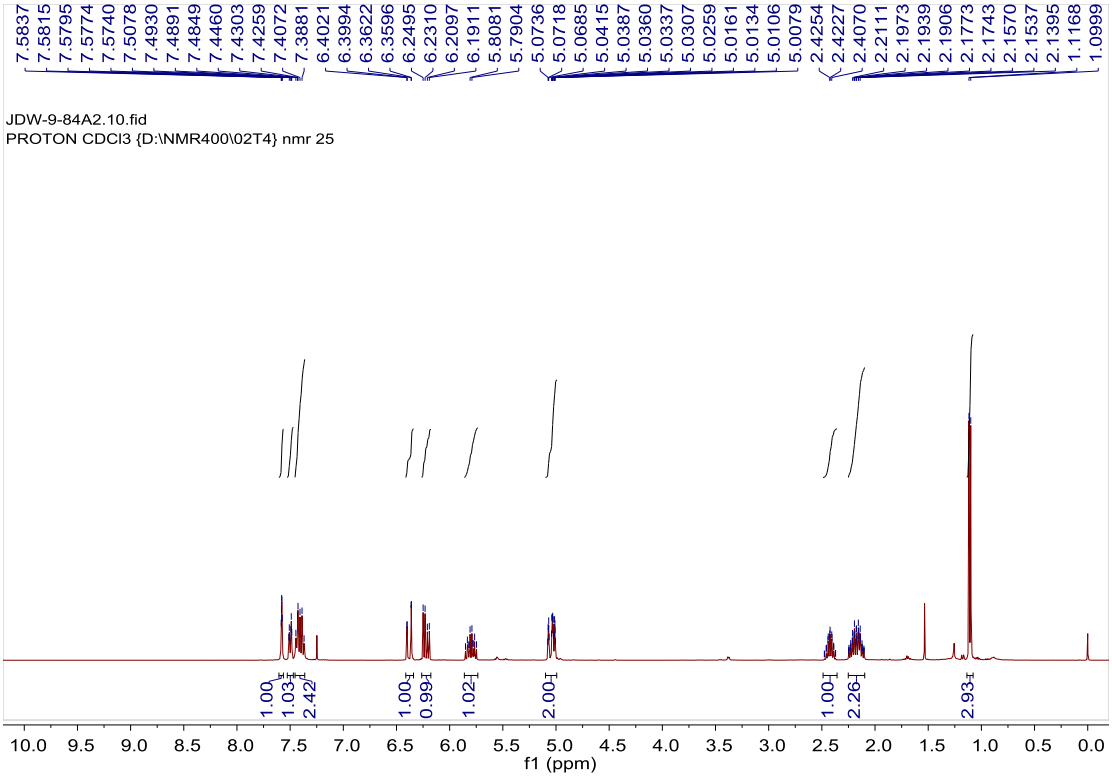


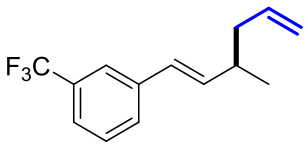




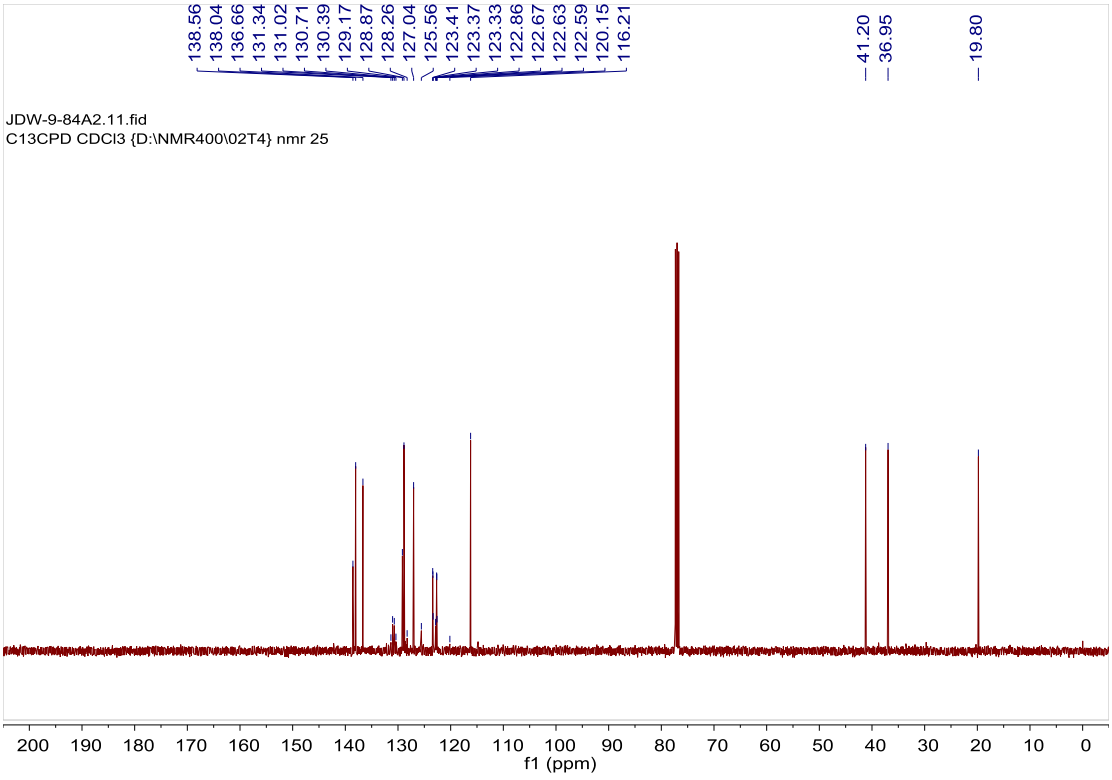
3k ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

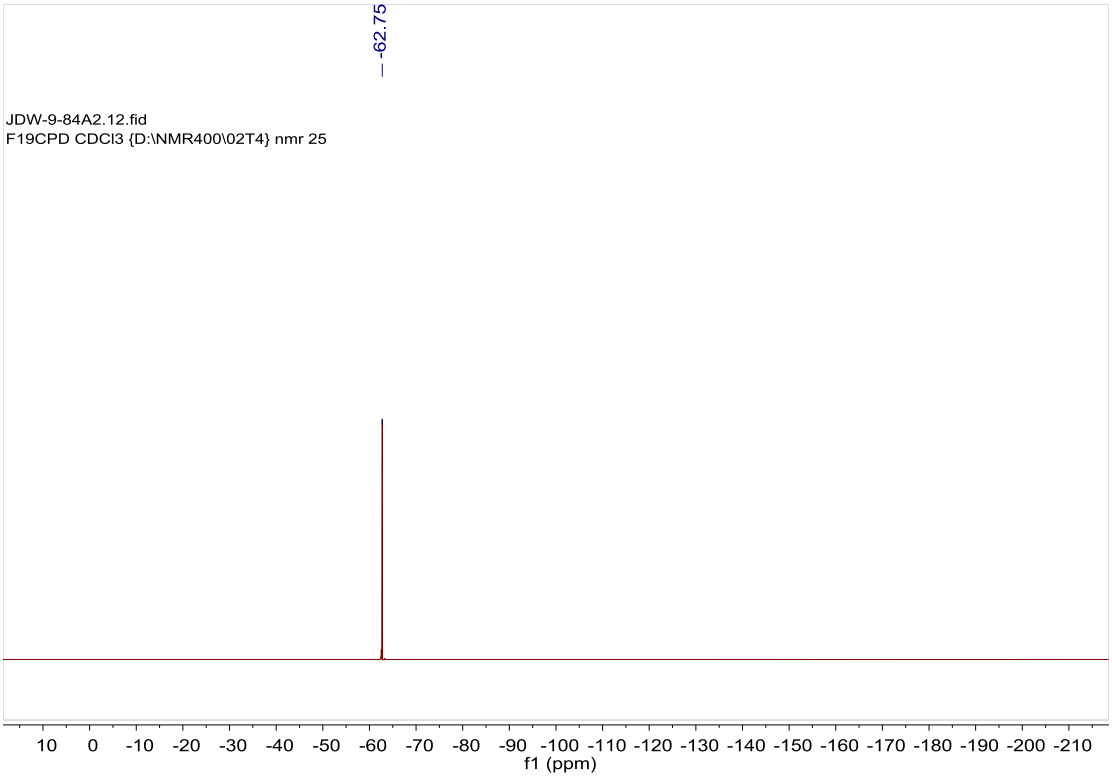


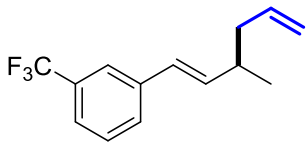




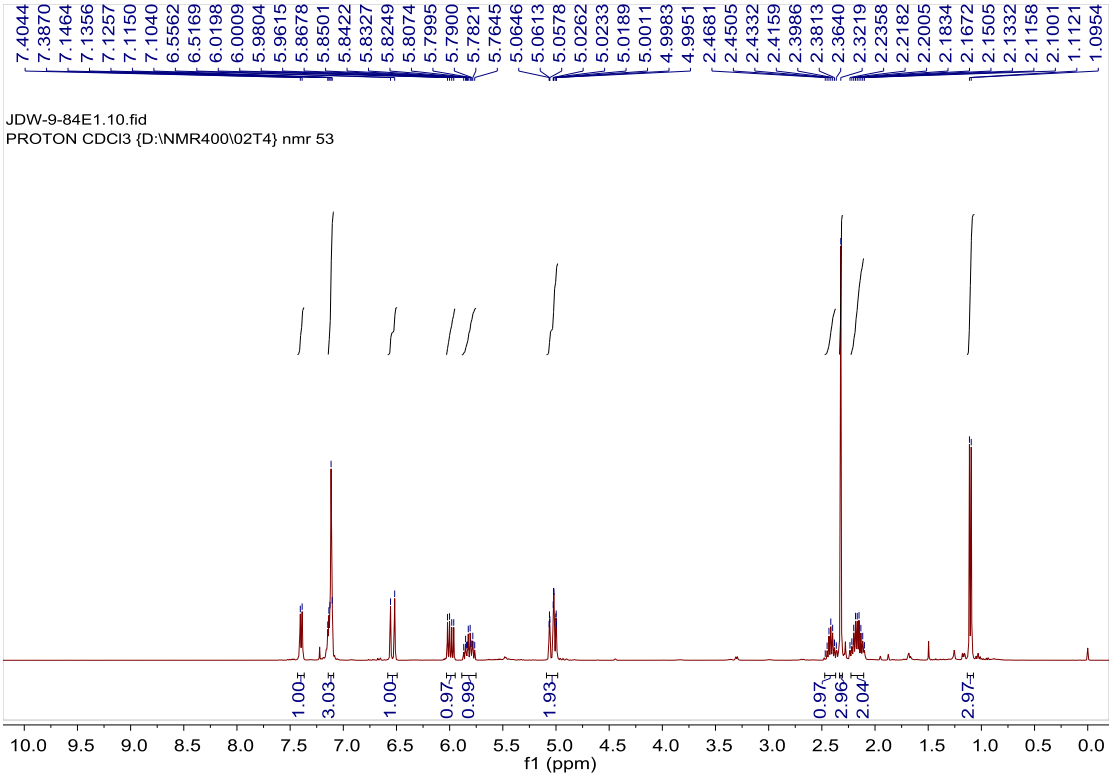
3l ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

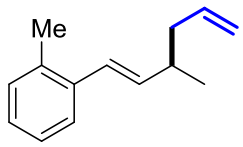




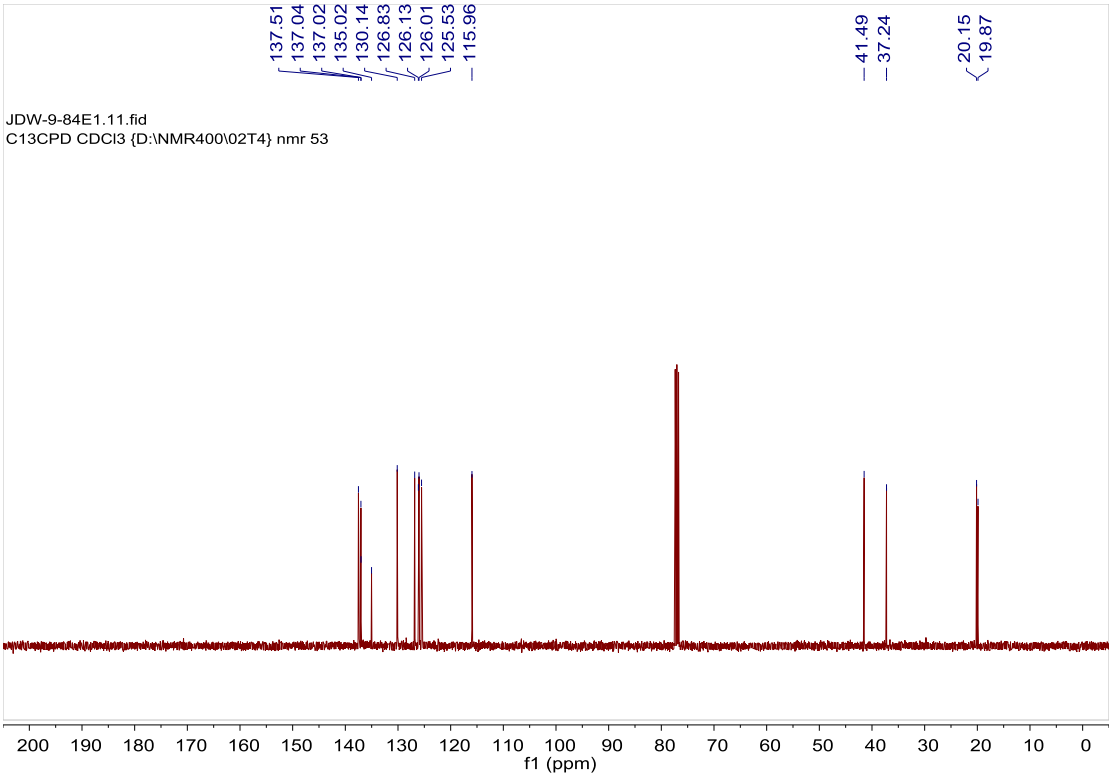


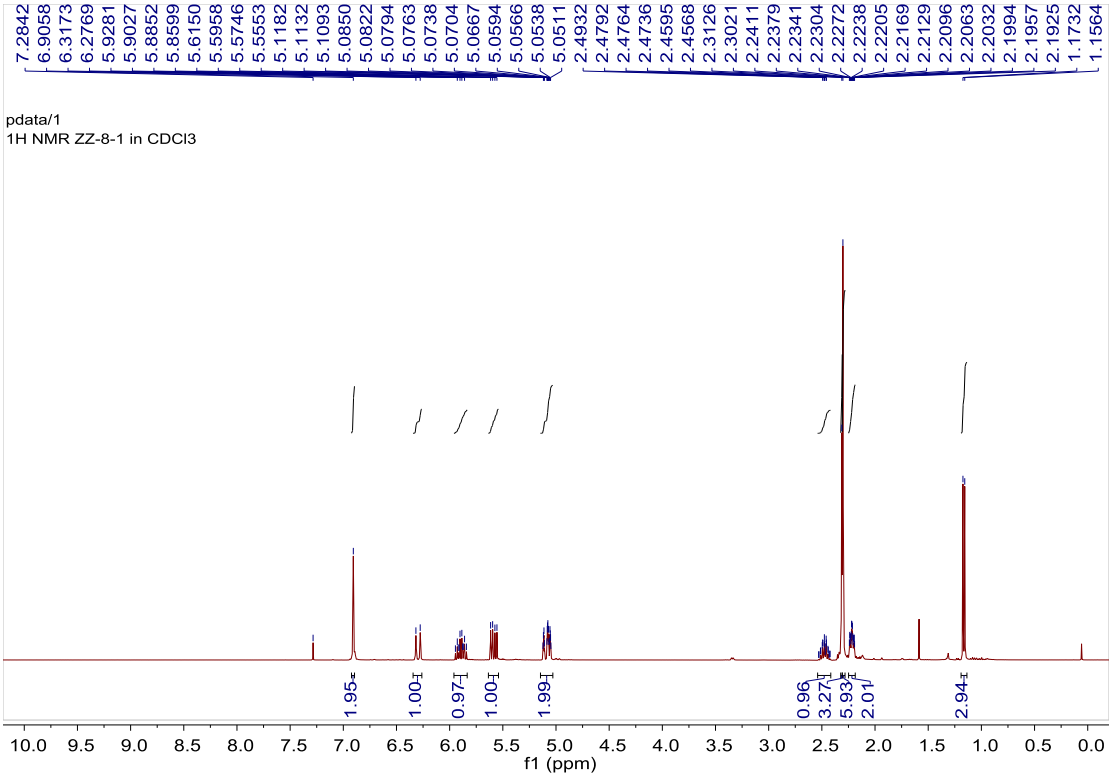
3l ^{19}F NMR (376 MHz, $CDCl_3$)

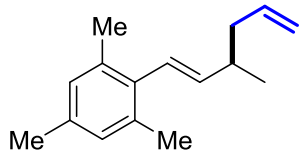




3m ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

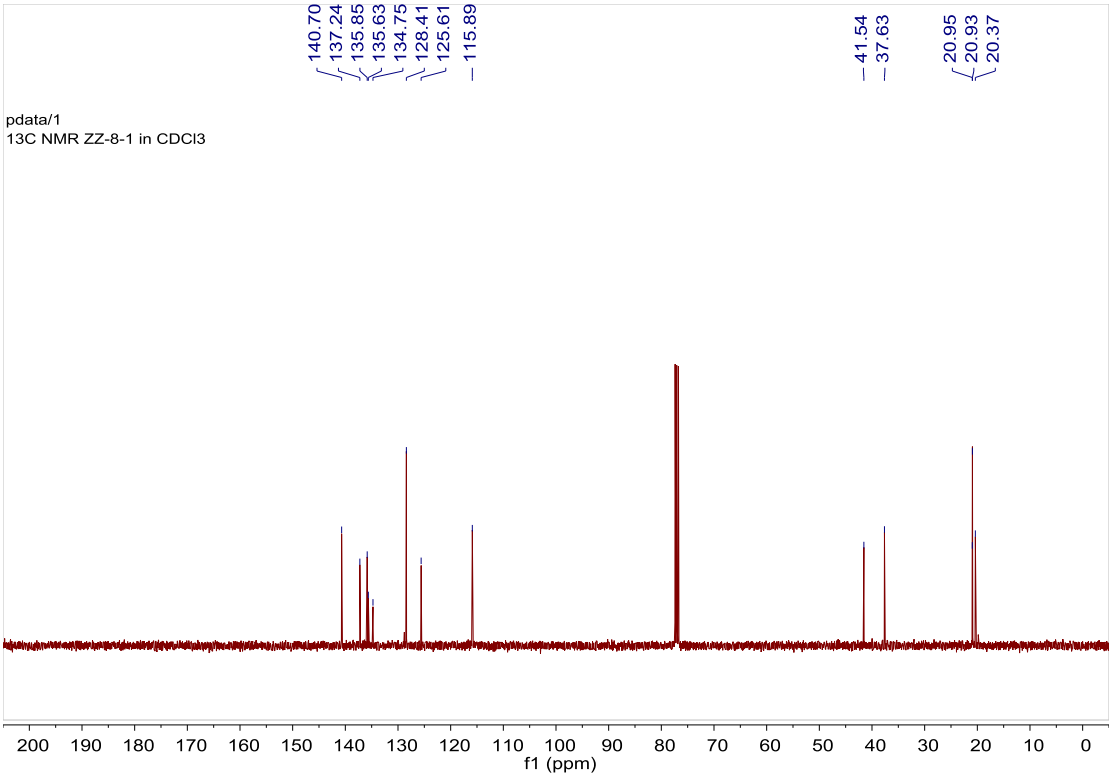


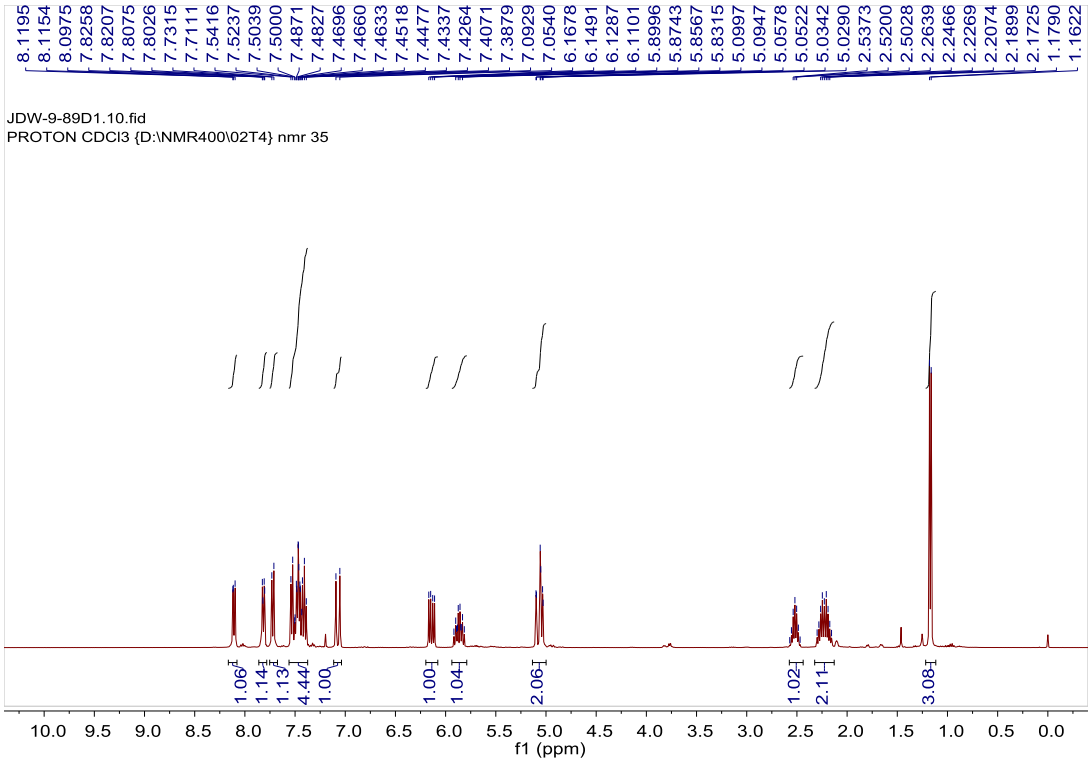


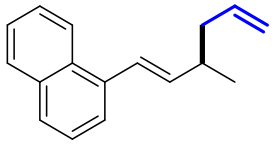


3n ^{1}H NMR (400 MHz, $CDCl_3$)

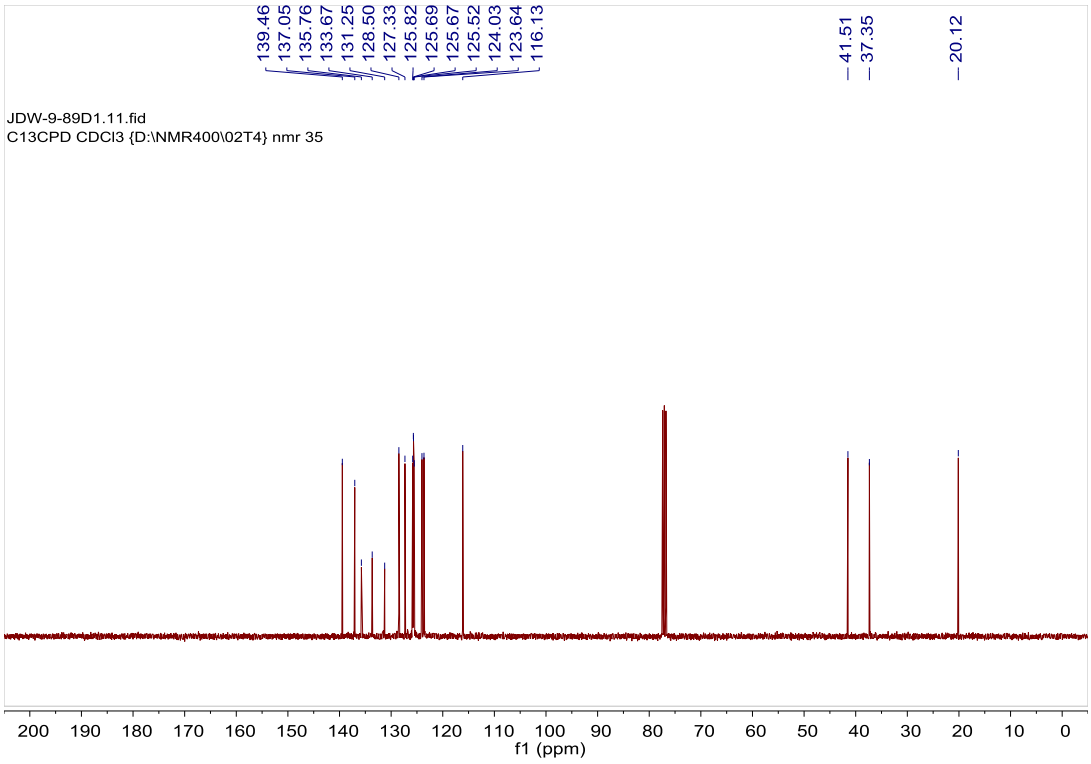
^{13}C NMR (100 MHz, $CDCl_3$)

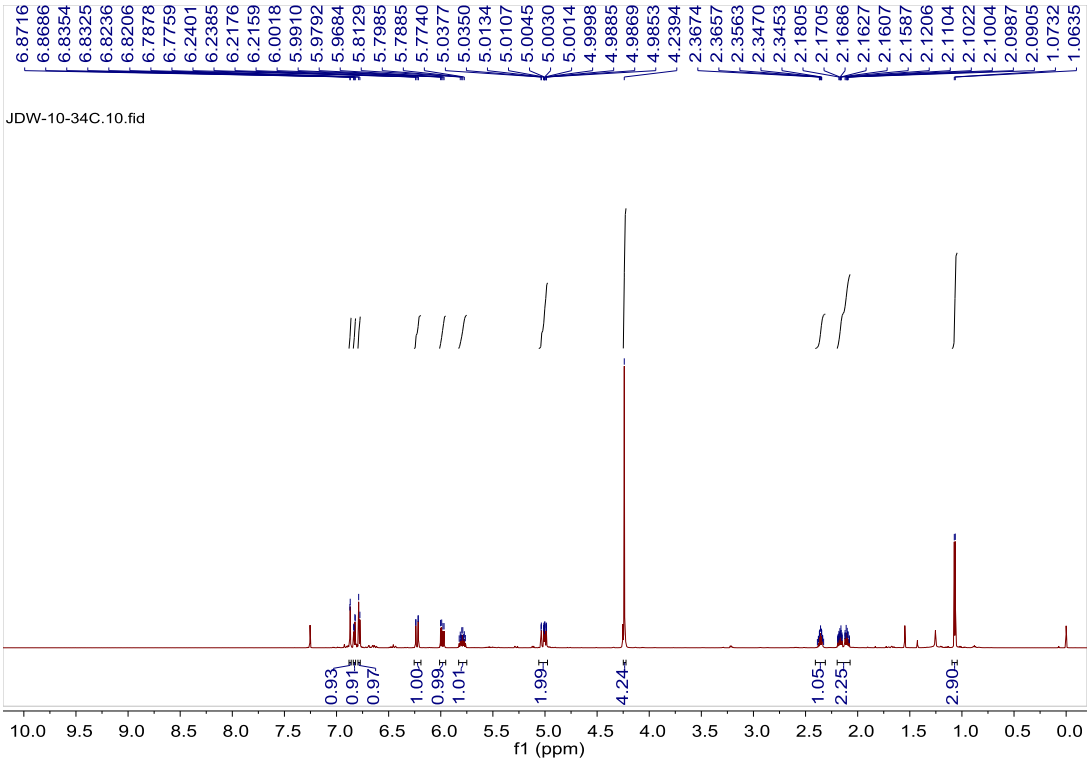


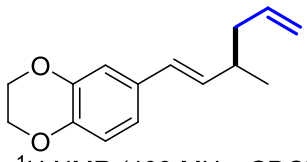




3o ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

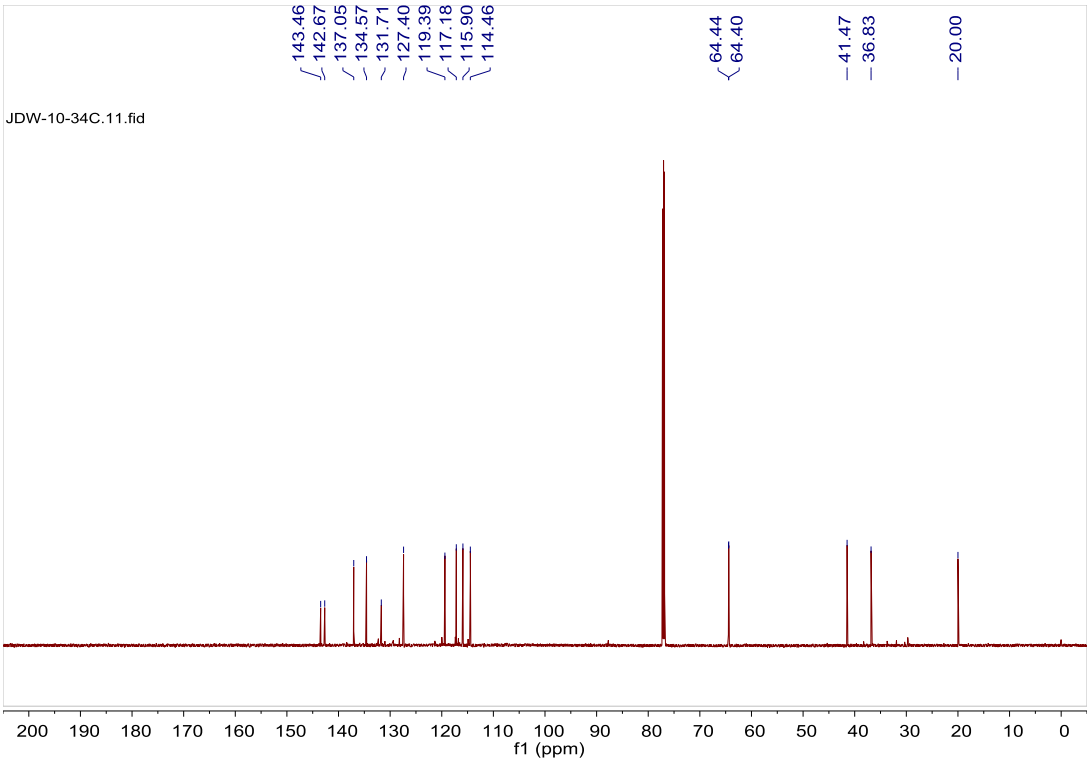


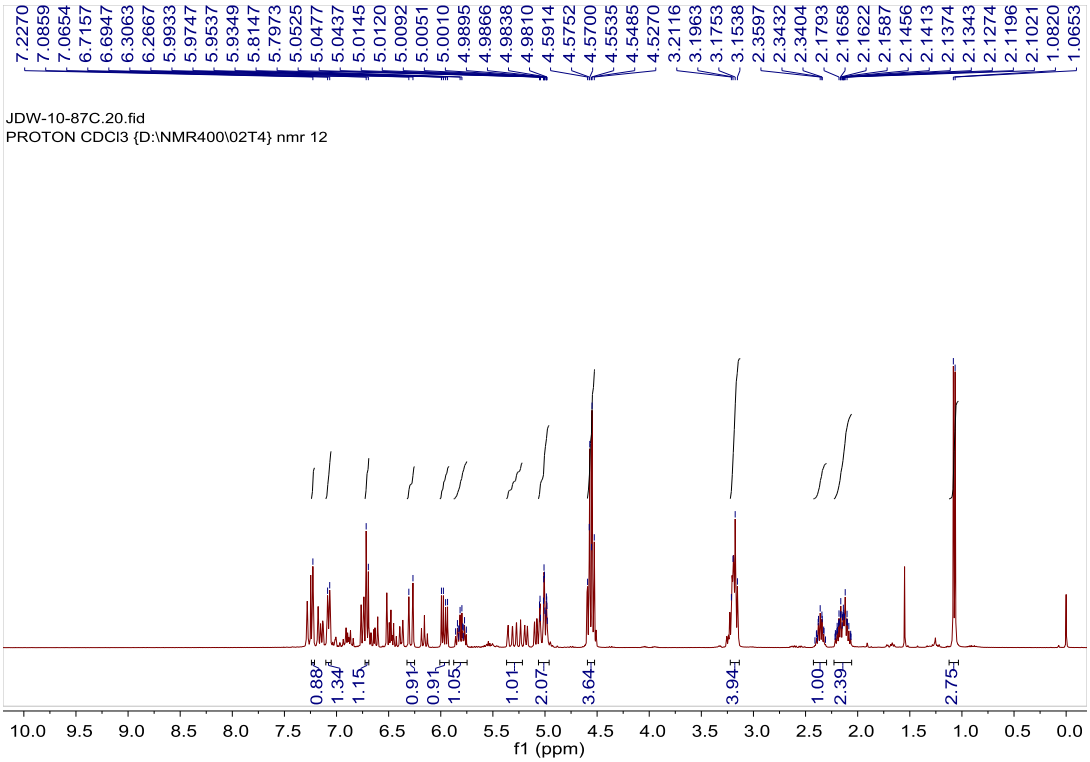


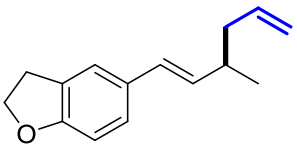


3p ^{1}H NMR (400 MHz, $CDCl_3$)

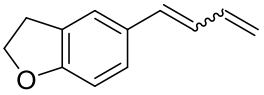
^{13}C NMR (100 MHz, $CDCl_3$)



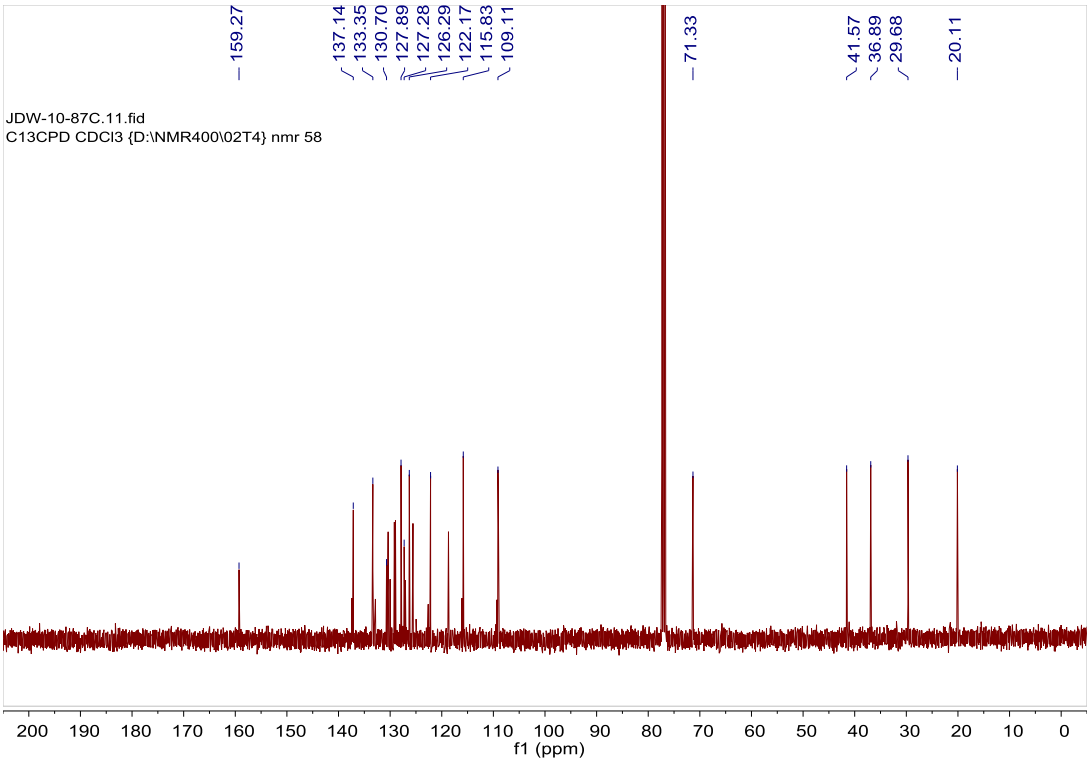


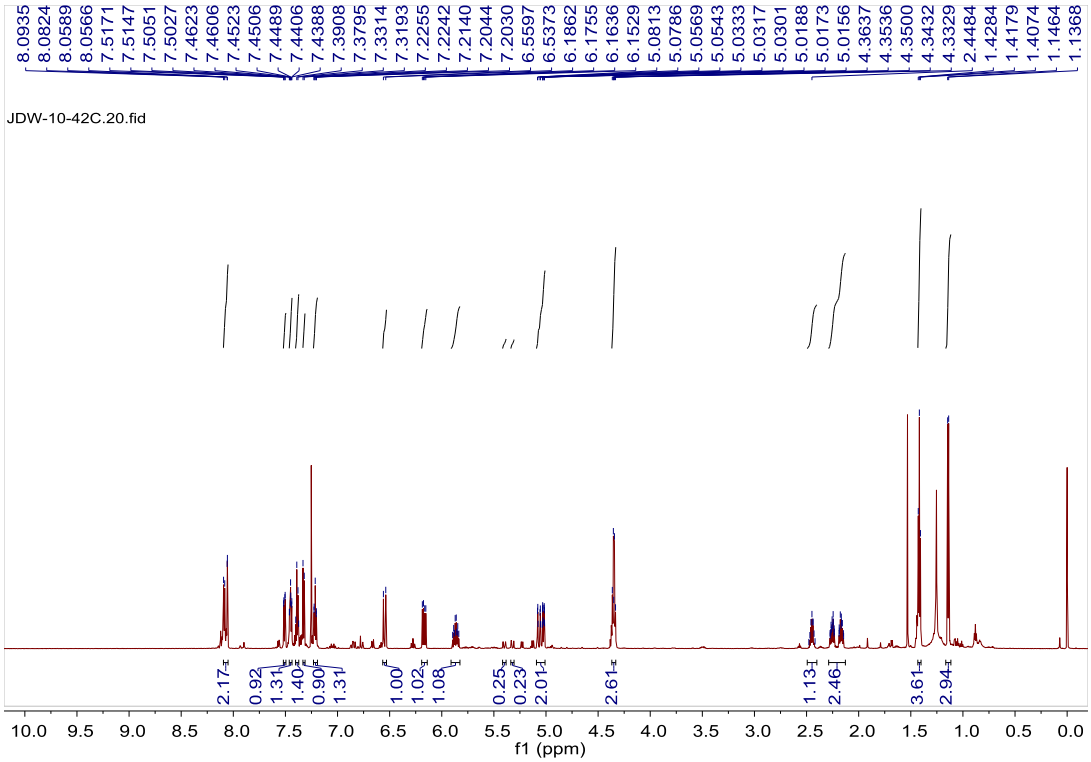


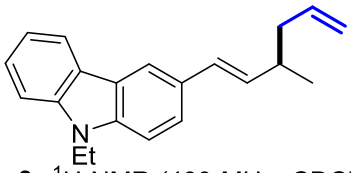
3q ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)



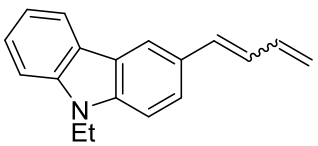
1q
(**3q**:**1q** = 2.0:1)





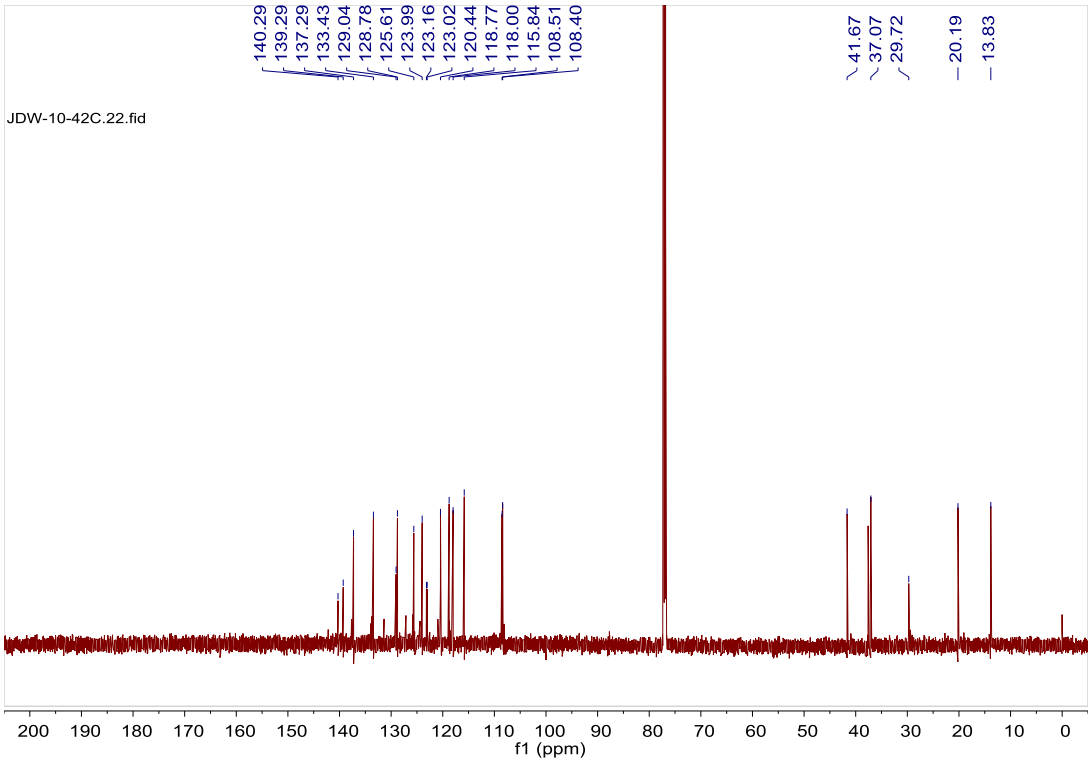


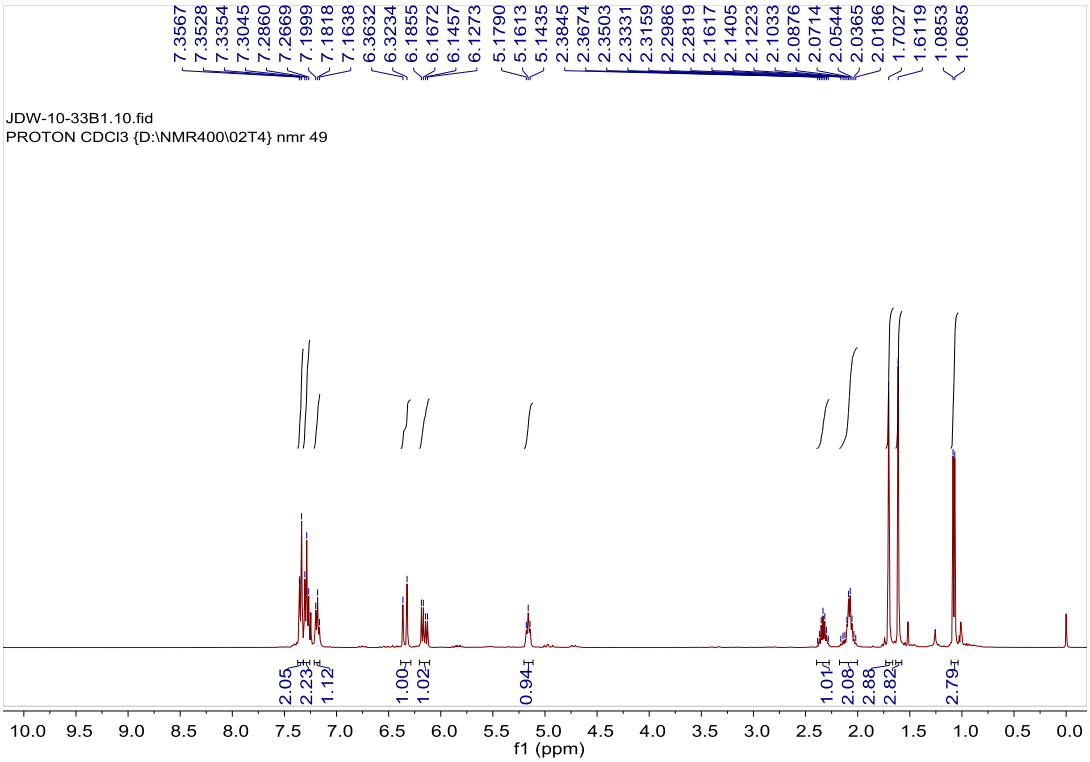
3r ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

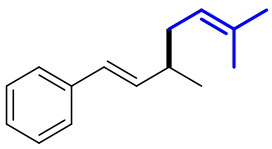


1r

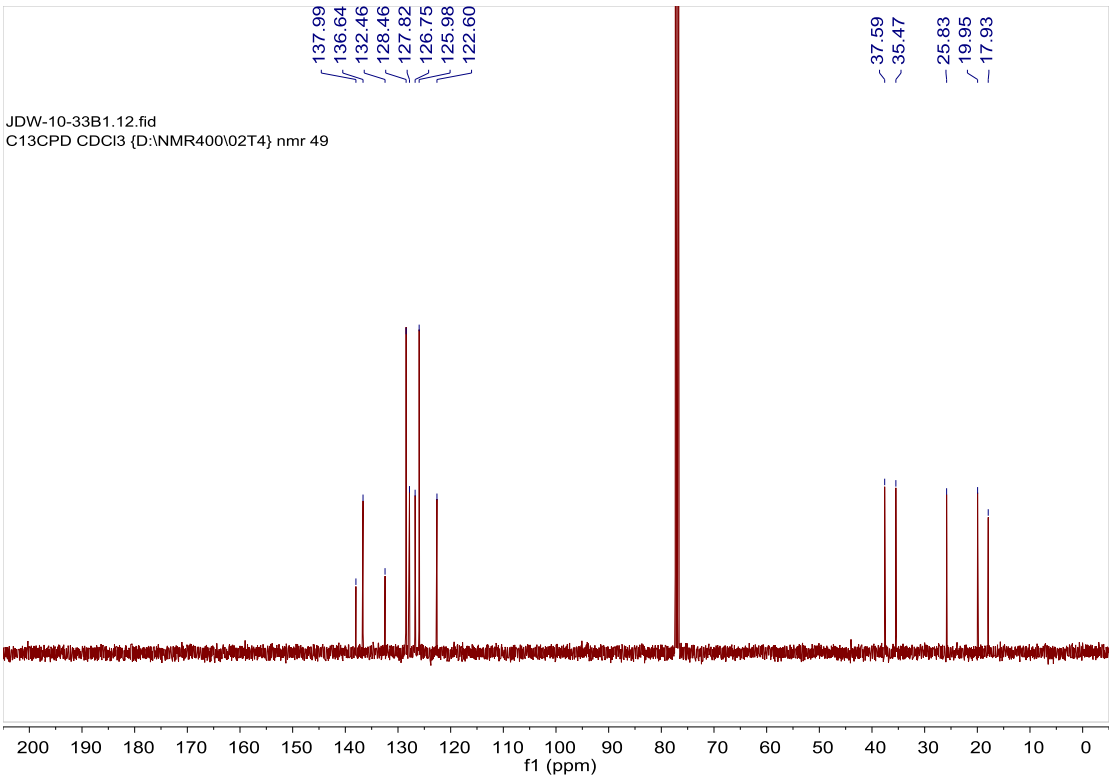
(**3r**:**1r** = 2.1:1)

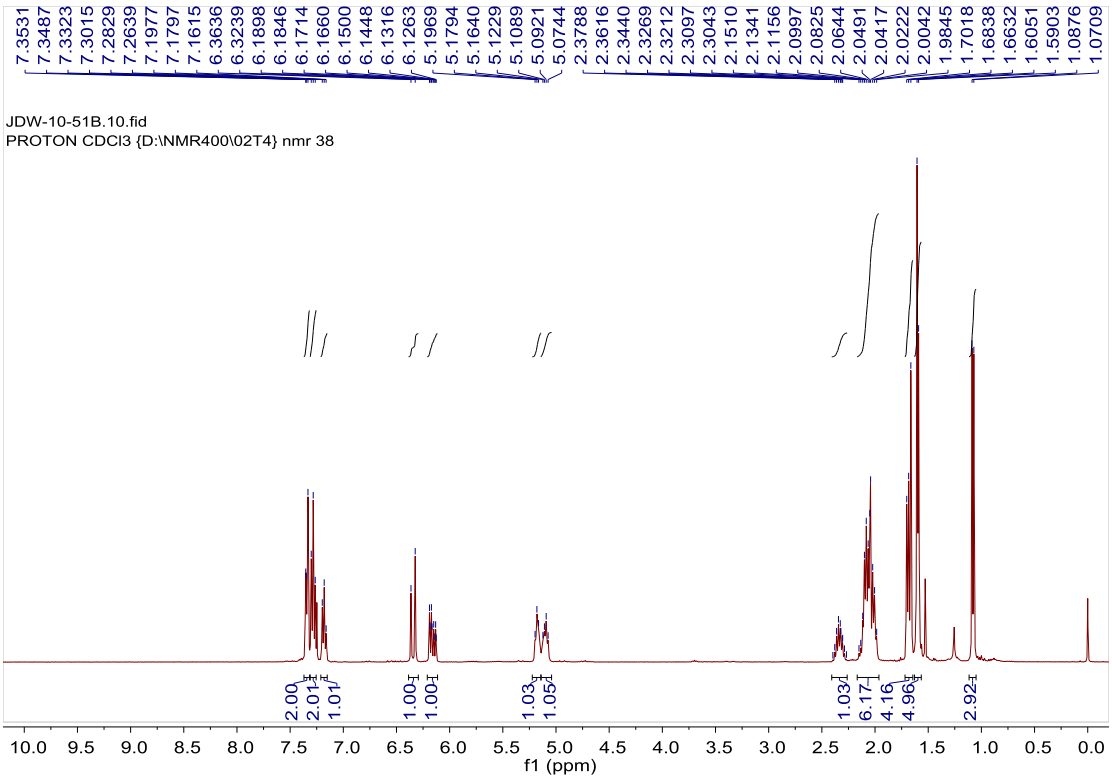


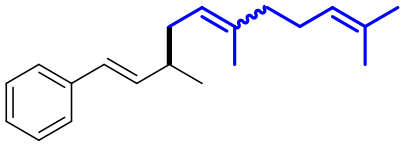




3s ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

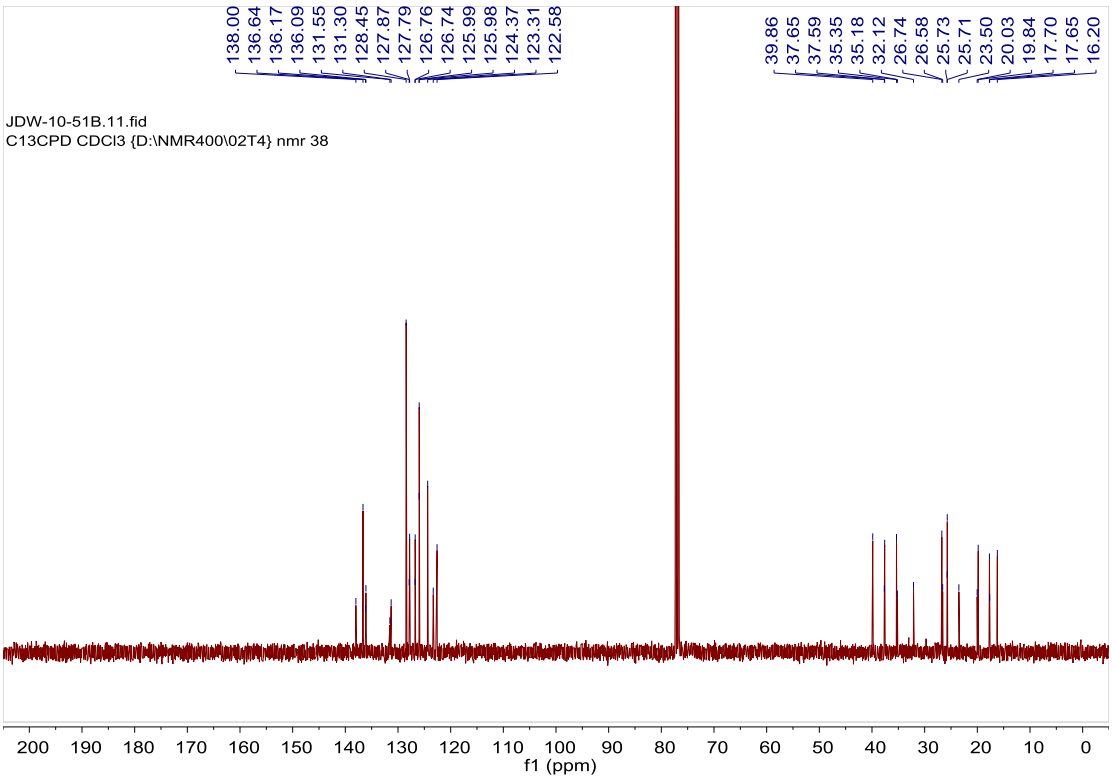


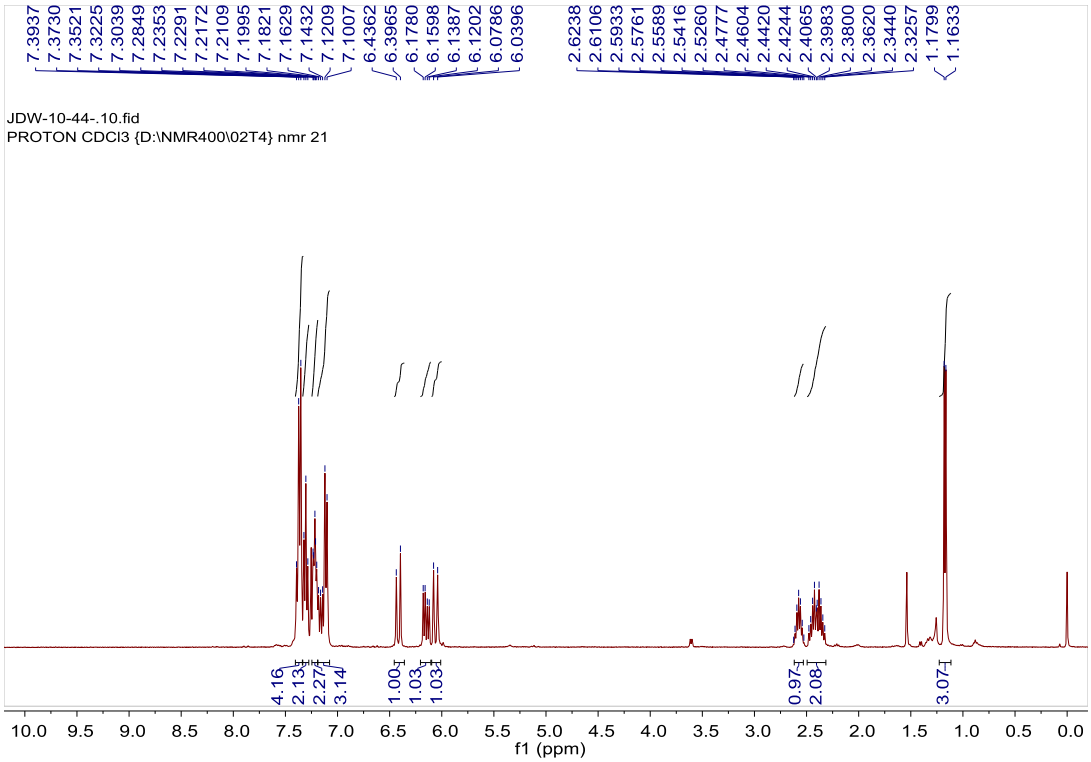


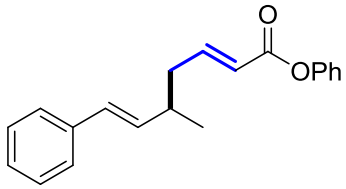


3t ^{1}H NMR (400 MHz, $CDCl_3$)

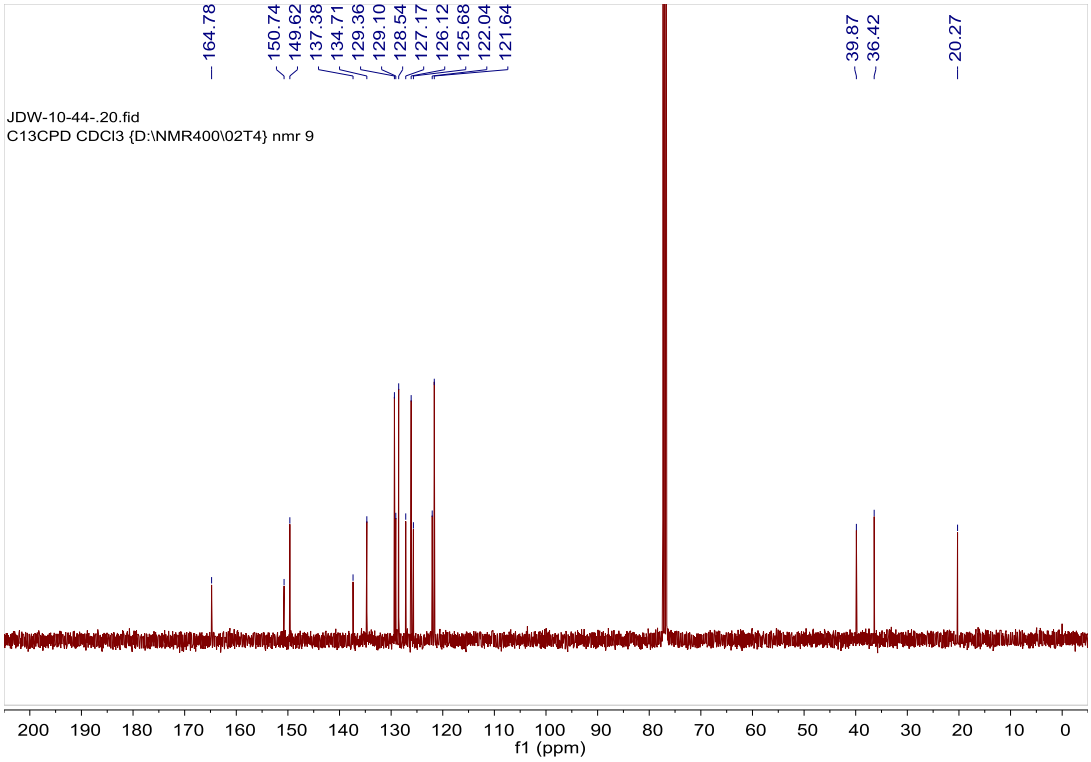
^{13}C NMR (100 MHz, $CDCl_3$)

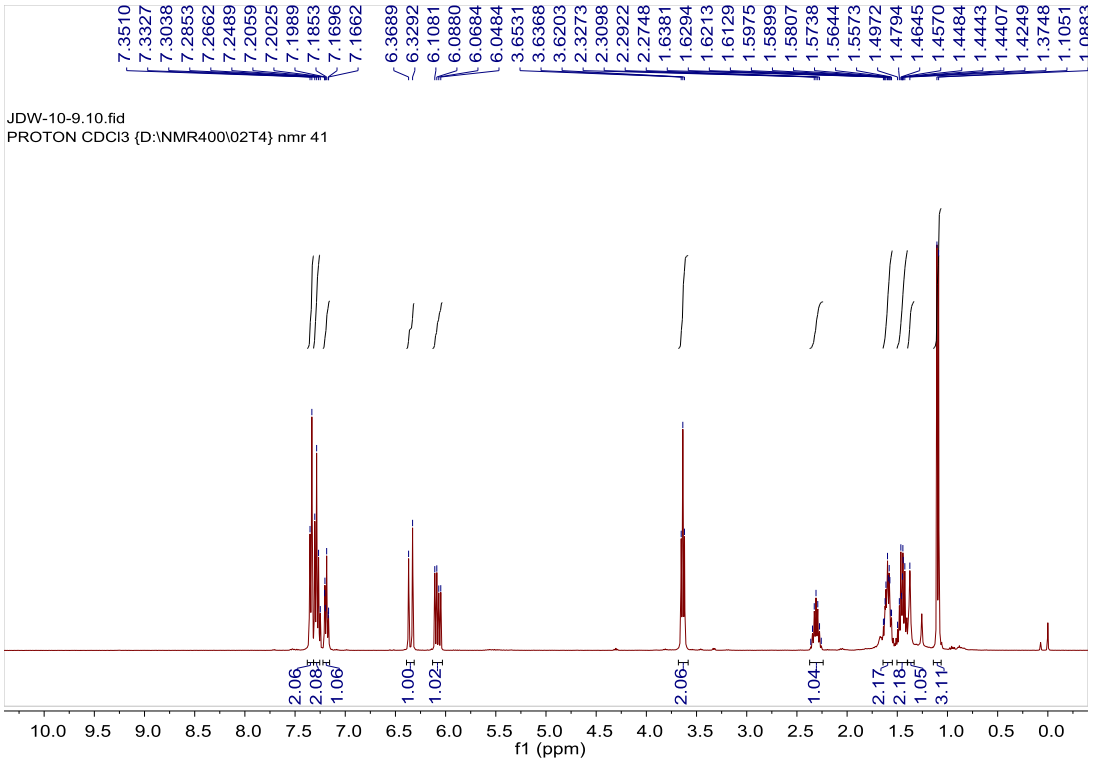


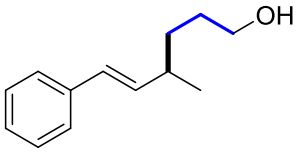




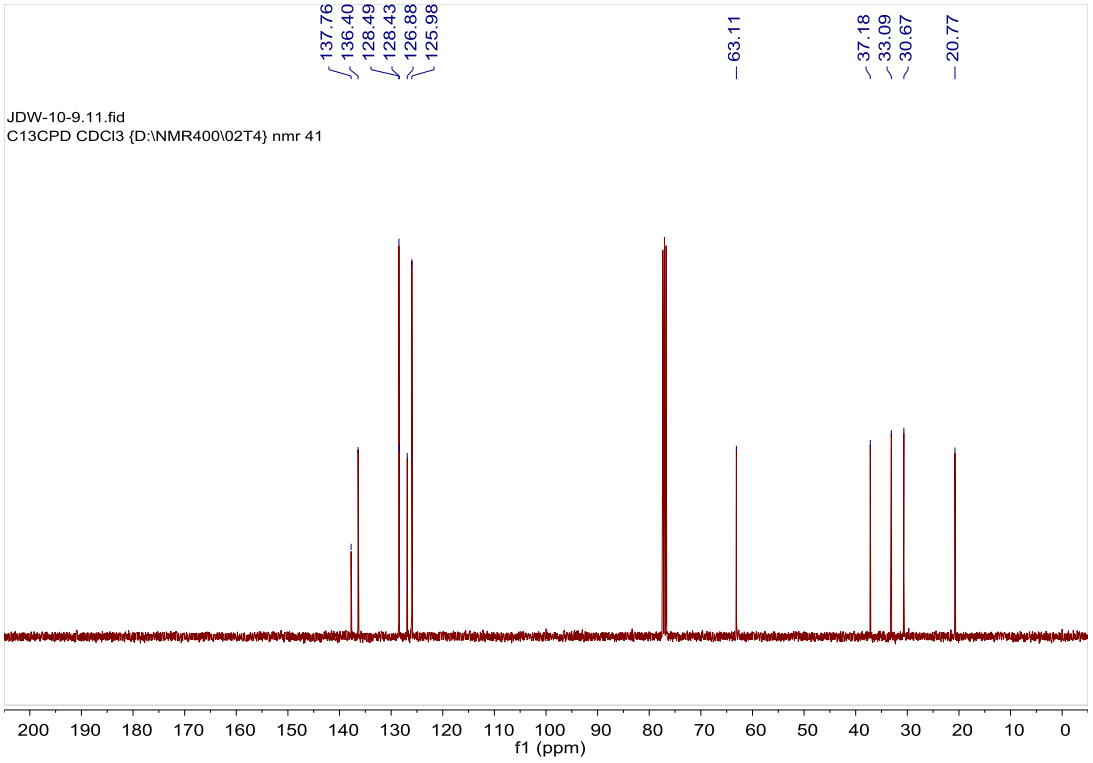
4 ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

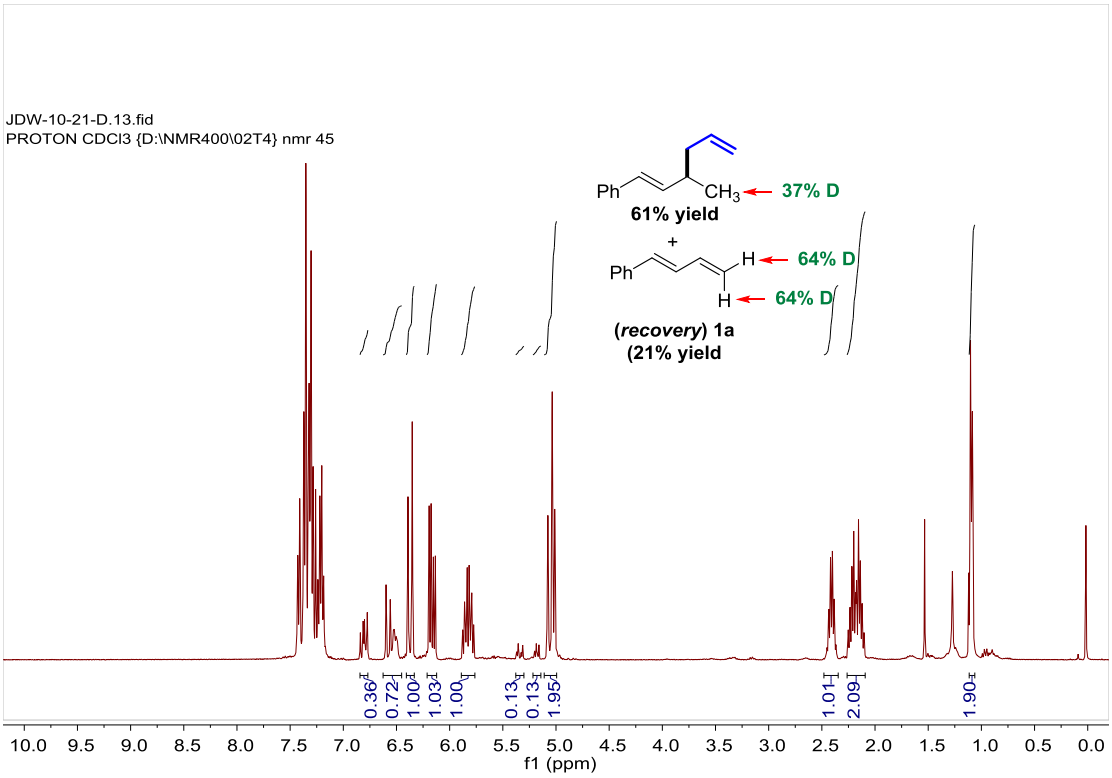


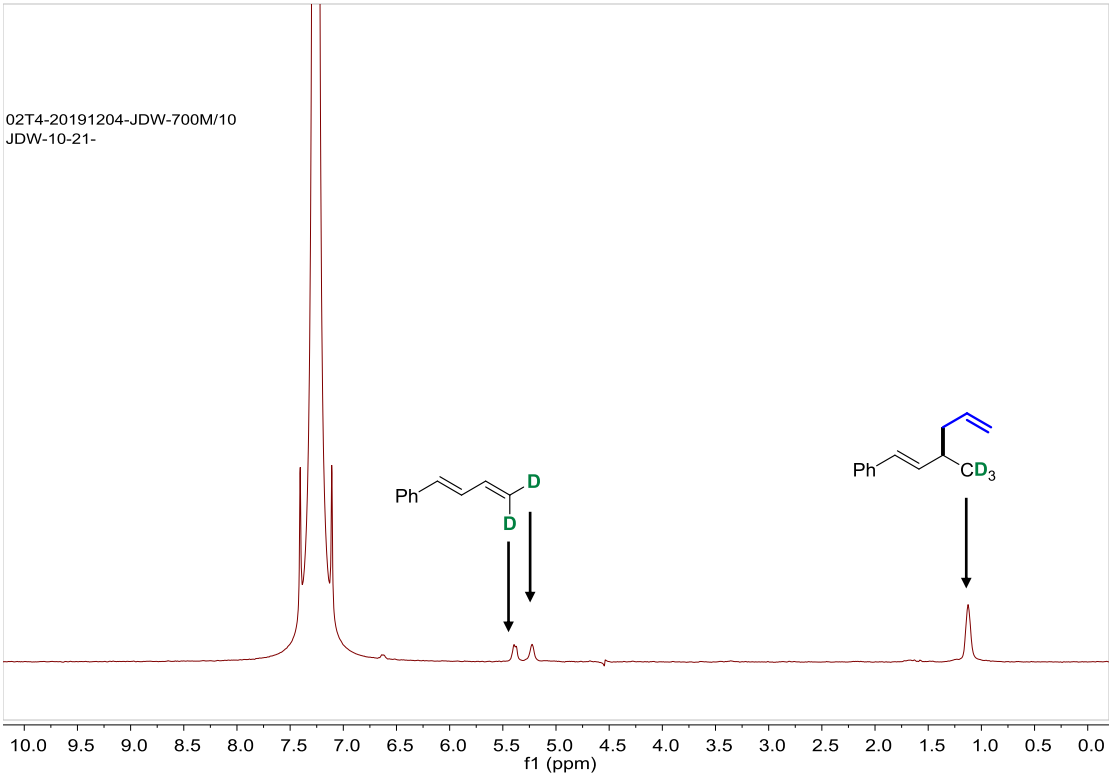




5 ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)




JDW-10-21-D.13.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr 45
Ph
CH3
37% D
61% yield
+
Ph
H
64% D
H
64% D
(recovery) 1a
(21% yield
0.36
0.72
1.00
1.03
1.00
0.13
0.13
1.95
1.01
2.09
1.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


02T4-20191204-JDW-700M/10
JDW-10-21-
Ph
D
D
Ph
CD3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)