Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Palladium-Catalyzed α-Arylation/β-Elimination of Sulfones

*Mengzhao Yu,‡ Luqiong Duan,‡ Xinwei Zhang, Qian Zhang, Hongzhen Wang and Xiaolei Huang**

Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Materials Science, Zhejiang Normal University, Jinhua, Zhejiang 321004, China. E-mails: huangxl@zjnu.edu.cn

Table of Contents

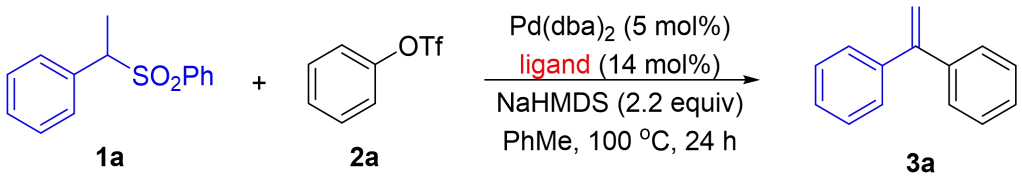
I. General remarks

NMR spectra were obtained on a Bruker BBF-400 MHz, AV-400 MHz and AV-600 MHz spectrometer. The ^{1}H NMR chemical shifts were measured relative to $CDCl_3$ as the internal reference ($CDCl_3$: δ = 7.26 ppm). The ^{13}C NMR chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.16 ppm). High resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). GC-MS measurements were performed on a 7890B GC system with an Agilent 5975 MSD detector. Gas chromatography (GC) analysis was performed on a Shimadzu GC-2010 instrument with Agilent J & W GC column DB-5MS-UI. Substrates **1** were prepared according to the literature.[1] Aryl triflates **2** were synthesized from phenols according to the literature procedures.[2] Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Ultra dry solvents including *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide (DMA), *N*-Methylpyrrolidone (NMP), acetonitrile, toluene and 1,4-dioxane were purchased from J&K Scientific. Tetrahydrofuran (THF), benzene, (trifluoromethyl)benzene, xylenes and mesitylene were dried by refluxing over Na and freshly distilled prior to use.

II. Detailed optimization information

In a nitrogen-filled glove box, a 10-mL Schlenk tube with a magnetic stir bar was charged with sulfone **1a** (30 mg, 0.12 mmol, 1.2 equiv), phenyl triflate **2a** (22.6 mg, 0.1 mmol, 1 equiv), Pd catalyst (5 mol%), ligand (14 mol%), base (0.22 mmol, 2.2 equiv) and solvent (0.8 mL). *n*-$C_{12}H_{26}$ (10 μL) were added as GC standard. The reaction mixture was stirred at 100 °C for 24 h. Aliquots were taken from the organic phase, and passed through a short plug of silica gel with EtOAc washing (about 1.5 mL). The filtrate was subjected to GC analysis to determine the yield of the product.

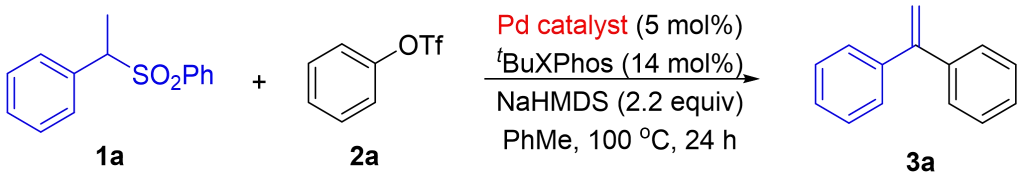
Table S1 The effect of ligands



1a + **2a** → **3a**

Entry	ligand	Yield **2a** (%)
1	PPh_3	32
2	PCy_3	12
3	XPhos	25
4	SPhos	36
5	**^{t}BuXPhos**	**87**
6	BINAP	75
7	dppe	10
8	dppf	trace

Table S2 The effect of palladium catalysts

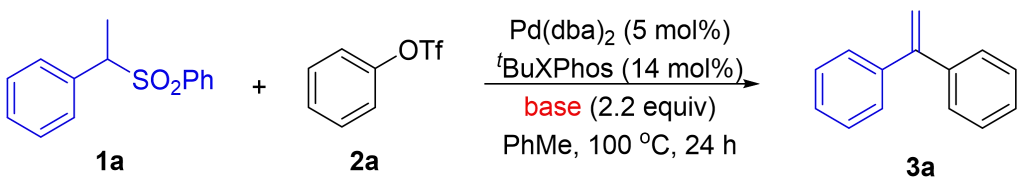


1a + **2a** → **3a**

Entry	[Pd]	Yield **2a** (%)
1	$Pd(OAc)_2$	71
2	**$Pd(dba)_2$**	**87**
3[a]	$Pd_2(dba)_3$	84
4	$Pd(PPh_3)_4$	76
5	$PdCl_2$	65
6	$Pd(TMEDA)Cl_2$	74
7	$Pd(TMEDA)Me_2$	78
8	$Pd(TFA)_2$	85

[a] 2.5 mol% of $Pd_2(dba)_3$ was used.

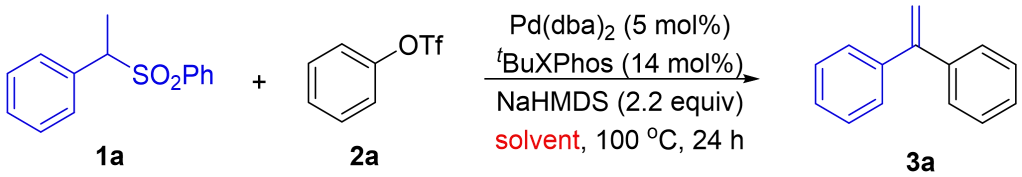
Table S3 The effect of base



1a + **2a** → **3a**

Entry	Base	Yield **3a** (%)
1	NaH	32
2	KHMDS	65
3	**NaHMDS**	**87**
4	LiHMDS	71
5	KO^{t}Bu	15
6	NaO^{t}Bu	12
7	KOH	0
8	Cs_2CO_3	0
9	K_3PO_4	0

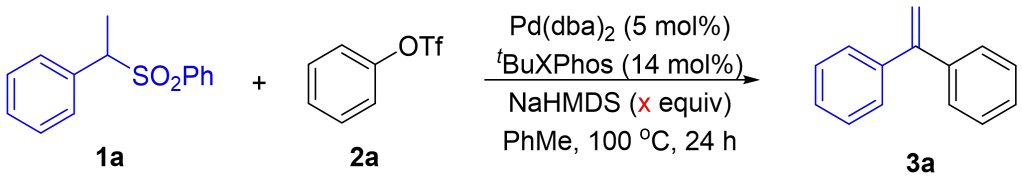
Table S4. The effect of solvents



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

Entry	Solvent	Yield **2a** (%)
1	THF	19
2	1,4-dioxane	14
3	**toluene**	**87**
4	$PhCF_3$	56
5	benzene	84
6	xylene	80
7	mesitylene	83
8	DMF	75
9	DMSO	21
10	DMA	70
11	NMP	12
12	MeCN	trace

Table S5. The effect of base loadings.

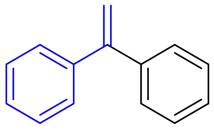


1a **2a** **3a**

Entry	x	Yield **2a** (%)
1	1.0	40
2	2.0	75
3	3.0	62
4	2.1	80
5	2.2	87
6	2.3	82
7	2.5	70

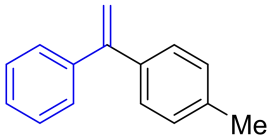
III. General procedure for for α-arylation/β-elimination of sulfones

In a nitrogen-filled glove box, a 10-mL Schlenk tube with a magnetic stir bar was charged with sulfone **1** (0.24 mmol, 1.2 equiv), phenyl triflate **2a** (0.2 mmol, 1 equiv), $Pd(dba)_2$ (5.8 mg, 5 mol%), ^{t}BuXPhos (12 mg, 14 mol%), NaHMDS (80.7 mg, 0.44 mmol, 2.2 equiv) and toluene (1.6 mL). The reaction mixture was stirred at 100 °C for 24 h. The solution was filtered through a celite pad and washed with 10 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product.



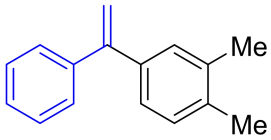
Ethene-1,1-diyldibenzene (3a)[3]

Following the general procedure, product was obtained as colorless oil (30.3 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 10H), 5.48 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 141.6, 128.4, 128.3, 127.9, 114.5. GC-MS (EI): Calcd for $C_{14}H_{12}$: 180.3. Found: 180.2.



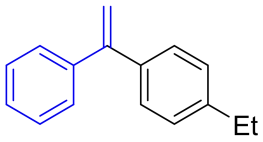
1-Methyl-4-(1-phenylvinyl)benzene (3b)[3]

Following the general procedure, product was obtained as colorless oil (35.8 mg, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35-7.29 (m, 5H), 7.25-7.22 (m, 2H), 7.14-7.12 (m, 2H), 5.43 (d, J = 1.2 Hz, 1H), 5.40 (d, J = 1.2 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 141.9, 138.8, 137.7, 129.0, 128.4, 128.30, 128.26, 127.8, 113.8, 21.31. GC-MS (EI): Calcd for $C_{15}H_{14}$: 194.3. Found: 194.1.



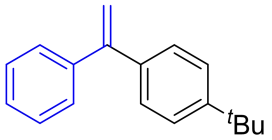
1,2-Ddimethyl-4-(1-phenylvinyl)benzene (3c)[4]

Following the general procedure, product was obtained as colorless oil (36.6 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 5H), 7.12-7.05 (m, 3H), 5.42 (s, 1H), 5.39 (s, 1H), 2.27 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 141.9, 139.3, 136.4, 136.3, 129.6, 128.5, 128.2, 127.7, 125.9, 113.7, 19.9, 19.6. GC-MS (EI): Calcd for $C_{16}H_{16}$: 208.3. Found: 208.0.



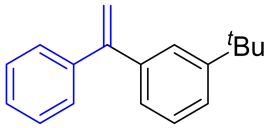
1-Ethyl-4-(1-phenylvinyl)benzene (3d)[5]

Following the general procedure, product was obtained as colorless oil (34.2 mg, 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42-7.35 (m, 5H), 7.32 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 5.49 (s, 1H), 5.46 (s, 1H), 2.72 (q, J = 7.6 Hz, 2H), 1.31 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 144.0, 141.9, 139.0, 128.5, 128.34, 128.25, 127.79, 127.77, 113.8, 28.7, 15.7. GC-MS (EI): Calcd for $C_{16}H_{16}$: 208.3. Found: 208.1.



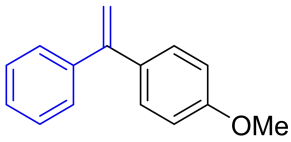
1-(*tert*-Butyl)-4-(1-phenylvinyl)benzene (3e)[6]

Following the general procedure, product was obtained as colorless oil (31.2 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 7H), 7.29-7.25 (m, 2H), 5.46 (d, J = 1.6 Hz, 1H), 5.40 (d, J = 1.6 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 150.0, 141.9, 138.6, 128.5, 128.3, 128.0, 127.8, 125.2, 113.8, 34.7, 31.5. GC-MS (EI): Calcd for $C_{18}H_{20}$: 236.4. Found: 236.2.



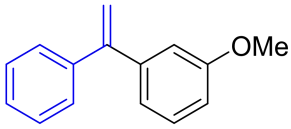
1-(*tert*-Butyl)-3-(1-phenylvinyl)benzene (3f)[3]

Following the general procedure, product was obtained as colorless oil (34.0 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.30 (m, 7H), 7.28-7.24 (m, 1H), 7.14-7.12 (m, 1H), 5.46 (d, J = 1.2 Hz, 1H), 5.45 (d, J = 1.6 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 150.7, 141.8, 141.3, 128.4, 128.3, 127.9, 127.8, 125.7, 125.5, 124.8, 114.1, 34.9, 31.5. GC-MS (EI): Calcd for $C_{18}H_{20}$: 236.4. Found: 236.1.



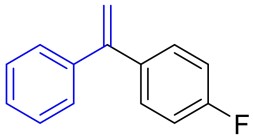
1-Methoxy-4-(1-phenylvinyl)benzene (3g)[3]

Following the general procedure, product was obtained as colorless oil (34.5 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (m, 7H), 6.89-6.84 (m, 2H), 5.39 (d, J = 1.6 Hz, 1H), 5.35 (d, J = 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 149.7, 142.0, 134.2, 129.5, 128.5, 128.3, 127.8, 113.7, 113.1, 55.4. GC-MS (EI): Calcd for $C_{15}H_{14}O$: 210.3. Found: 210.2.



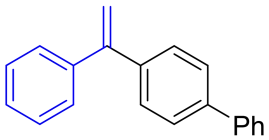
1-Methoxy-3-(1-phenylvinyl)benzene (3h)[3]

Following the general procedure, product was obtained as colorless oil (33.6 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 4H), 7.28-7.22 (m, 2H), 6.94-6.91 (m, 1H), 6.90-6.85 (m, 2H), 5.46 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 150.1, 143.2, 141.5, 129.3, 128.4, 128.3, 127.9, 121.1, 114.6, 114.1, 113.4, 55.4. GC-MS (EI): Calcd for $C_{15}H_{14}O$: 210.3. Found: 210.0.



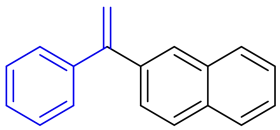
1-Fluoro-4-(1-phenylvinyl)benzene (3i)[6]

Following the general procedure, product was obtained as colorless oil (26.6 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 7H), 7.06-7.00 (m, 2H), 5.45 (s, 1H), 5.43 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.65 (d, $J_{C\text{-}F}$ = 246.7 Hz), 149.2, 141.4, 137.7 (d, $J_{C\text{-}F}$ = 3.3 Hz),130.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.4 (d, $J_{C\text{-}F}$ = 5.1 Hz), 128.0, 115.3, 115.1, 114.4 (d, $J_{C\text{-}F}$ = 1.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.8. GC-MS (EI): Calcd for $C_{14}H_{11}F$: 198.2. Found: 198.2.



4-(1-Phenylvinyl)-1,1'-biphenyl (3j)[7]

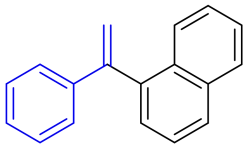
Following the general procedure, product was obtained as colorless oil (42.5 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72-7.70 (m, 2H), 7.68-7.64 (m, 2H), 7.55-7.41 (m, 10H), 5.62 (d, J = 1.2 Hz, 1H), 5.57 (d, J = 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 141.6, 140.8, 140.7, 140.5, 128.9, 128.8, 128.5, 128.3, 127.9, 127.5, 127.1, 127.0, 114.5. GC-MS (EI): Calcd for $C_{20}H_{16}$: 256.3. Found: 256.1.



2-(1-Phenylvinyl)naphthalene (3k)[3]

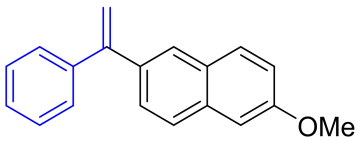
Following the general procedure, product was obtained as colorless oil (38.7 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.81 (m, 4H), 7.53-7.48 (m, 3H), 7.43-7.37

(m, 5H), 5.62 (d, J = 0.8 Hz, 1H), 5.58 (d, J = 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 141.6, 139.0, 133.4, 133.1, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.4, 126.5, 126.3, 126.1, 115.0. GC-MS (EI): Calcd for $C_{18}H_{14}$: 230.3. Found: 230.2.



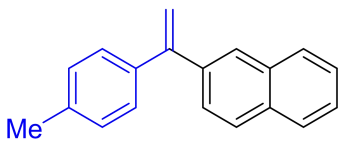
1-(1-Phenylvinyl)naphthalene (3l)[3]

Following the general procedure, product was obtained as colorless oil (34.5 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.0, 3.6 Hz, 2H), 7.87 (d, J = 8.4 Hz, 1H), 7.60-7.49 (m, 3H), 7.43-7.39 (m, 3H), 7.35-7.31 (m, 3H), 6.07 (d, J = 1.6 Hz, 1H), 5.49 (d, J = 1.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 141.2, 139.9, 133.8, 132.0, 128.5, 128.3, 128.1, 127.8, 127.4, 126.8, 126.6, 126.0, 125.8, 125.6, 116.4. GC-MS (EI): Calcd for $C_{18}H_{14}$: 230.3. Found: 230.2.



2-Methoxy-6-(1-phenylvinyl)naphthalene (3m)[6]

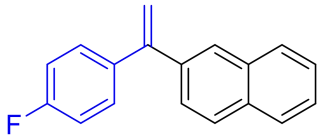
Following the general procedure, product was obtained as colorless oil (46.3 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.68 (m, 3H), 7.46 (dd, J = 8.4, 1.6 Hz, 1H), 7.41-7.34 (m, 5H), 7.16-7.13 (m, 2H), 5.57 (d, J = 1.2 Hz, 1H), 5.51 (d, J = 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 150.2, 141.9, 136.9, 134.3, 129.9, 128.9, 128.6, 128.4, 127.9, 127.3, 127.0, 126.7, 119.1, 114.3, 105.8, 55.5. GC-MS (EI): Calcd for $C_{19}H_{16}O$: 260.3. Found: 260.1.



2-(1-(*p*-Tolyl)vinyl)naphthalene (4a)[3]

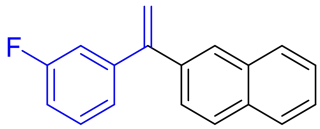
Following the general procedure, product was obtained as colorless oil (31.8 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.92 (m, 4H), 7.51-7.46 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 5.55 (s, 1H), 5.54 (s, 1H), 2.40 (s, 3H); ^{13}C

NMR (101 MHz, $CDCl_3$) δ 150.1, 139.3, 138.8, 137.8, 133.5, 133.1, 129.1, 128.4, 128.3, 127.8, 127.7, 127.4, 126.7, 126.3, 126.1, 114.3, 21.35. GC-MS (EI): Calcd for $C_{19}H_{16}$: 244.3. Found: 244.2.



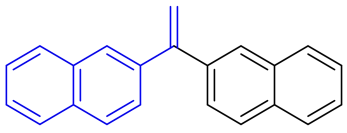
2-(1-(4-Fluorophenyl)vinyl)naphthalene (4b)[8]

Following the general procedure, product was obtained as colorless oil (33.8 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.76 (m, 4H), 7.51-7.45 (m, 3H), 7.38-7.32 (m, 2H), 7.08-7.02 (m, 2H), 5.57 (s, 1H), 5.51 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, $J_{C\text{-}F}$ = 246.9 Hz), 149.2, 138.9, 137.7 (d, $J_{C\text{-}F}$ = 3.3 Hz), 133.4, 133.2, 130.1 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.3, 128.0, 127.8, 127.4, 126.40 (d, $J_{C\text{-}F}$ = 1.4 Hz), 126.3, 115.4, 115.1, 114.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.6. GC-MS (EI): Calcd for $C_{18}H_{13}F$: 248.3. Found: 248.2.



2-(1-(3-Fluorophenyl)vinyl)naphthalene (4c)

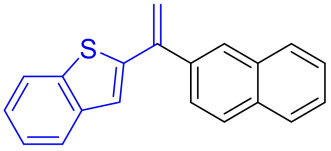
Following the general procedure, product was obtained as colorless oil (30.8 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.75 (m, 3H), 7.72-7.70 (m, 1H), 7.54 (dd, J = 8.8, 2.0 Hz, 1H), 7.48-7.45 (m, 2H), 7.37-7.33 (m, 2H), 7.21-7.10 (m, 2H), 5.91 (s, 1H), 5.54 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4 (d, $J_{C\text{-}F}$ = 248.5 Hz), 144.3, 138.1, 133.5, 133.2, 131.8 (d, $J_{C\text{-}F}$ = 3.7 Hz), 129.6 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.4, 128.0, 127.7, 126.3, 126.2, 125.0, 124.2 (d, $J_{C\text{-}F}$ = 3.7 Hz), 117.7 (d, $J_{C\text{-}F}$ = 2.2 Hz), 116.1, 115.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2. HRMS (ESI): calcd for $C_{18}H_{14}F$ $[M+H]^+$ 249.1080, found 249.1071.



2,2'-(Ethene-1,1-diyl)dinaphthalene (4d)[9]

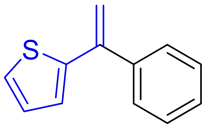
Following the general procedure, product was obtained as a white solid (47.7 mg,

85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.75 (m, 8H), 7.54-7.43 (m, 6H), 5.67 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 139.1, 133.5, 133.2, 128.4, 127.9, 127.8, 127.6, 126.6, 126.4, 126.2, 115.5. HRMS (ESI): calcd for $C_{22}H_{17}$ $[M+H]^+$ 281.1330, found 281.1334.



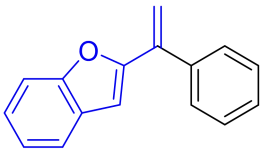
2-(1-(Naphthalen-2-yl)vinyl)benzo[*b*]thiophene (4e)

Following the general procedure, product was obtained as colorless oil (49.3 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.90-7.85 (m, 3H), 7.82-7.80 (m, 1H), 7.66-7.64 (m, 1H), 7.60 (dd, J = 8.4, 1.6 Hz, 1H), 7.54-7.50 (m, 2H), 7.35-7.30 (m, 2H), 7.12 (s, 1H), 5.80 (s, 1H), 5.51 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 144.0, 140.3, 139.7, 138.1, 133.4, 133.3, 128.4, 128.0, 127.8, 127.6, 126.7, 126.5, 126.4, 124.9, 124.6, 123.9, 122.3, 116.5. HRMS (ESI): calcd for $C_{20}H_{15}S$ $[M+H]^+$ 287.0894, found 287.0891.



2-(1-Phenylvinyl)thiophene (4f)[7]

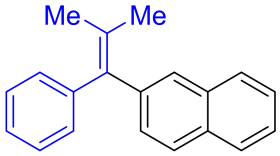
Following the general procedure, product was obtained as colorless oil (31.3 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.45 (m, 2H), 7.42-7.37 (m, 3H), 7.27-7.25 (m, 1H), 7.02-7.00 (m, 1H), 6.94 (dd, J = 3.6, 1.2 Hz, 1H), 5.62 (s, 1H), 5.28 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 143.5, 141.2, 128.4, 128.3, 128.2, 127.4, 126.6, 125.2, 113.8. GC-MS (EI): Calcd for $C_{12}H_{10}S$: 186.3. Found: 186.2.



2-(1-Phenylvinyl)benzofuran (4g)

Following the general procedure, product was obtained as colorless oil (33.0 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 4H), 7.45-7.41 (m, 3H), 7.34-7.30 (m, 1H), 7.22 (td, J = 7.6, 0.8 Hz, 1H), 6.56 (s, 1H), 6.08 (d, J = 1.6 Hz, 1H), 5.46 (d,

J = 1.2 Hz, 1H); ^{13}C NMR (101 MHz, CDC_{l3}) δ 156.0, 155.1, 139.6, 139.4, 129.0, 128.6, 128.5, 128.4, 124.9, 123.0, 121.3, 115.2, 111.2, 106.0. HRMS (ESI): calcd for $C_{16}H_{13}O$ $[M+H]^+$ 221.0966, found 221.0971.



2-(2-Methyl-1-phenylprop-1-en-1-yl)naphthalene (4h)

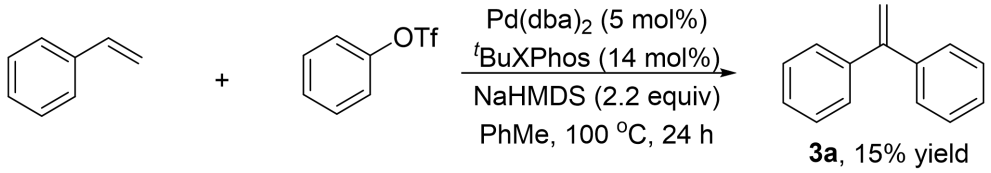
Following the general procedure, product was obtained as colorless oil (38.8 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.76 (m, 2H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.44-7.41 (m, 2H), 7.28-7.17 (m, 6H), 1.86 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 141.0, 137.2, 133.4, 132.1, 131.7, 130.2, 128.6, 128.5, 128.04, 128.02, 127.7, 127.5, 126.3, 126.0, 125.7, 22.8, 22.7. HRMS (ESI): calcd for $C_{20}H_{19}$ $[M+H]^+$ 259.1487, found 259.1481.

IV. Procedure for the gram-scale reaction

In a nitrogen-filled glove box, a 100-mL thick-walled Schlenk tube with a magnetic stir bar was charged with sulfone **1a** (1 g, 4.1 mmol, 1.2 equiv), phenyl triflate **2a** (0.77 g, 3.4 mmol, 1 equiv), $Pd(dba)_2$ (96 mg, 5 mol%), ^{t}BuXPhos (202 mg, 14 mol%), NaHMDS (1.37 g, 6.8 mmol, 2.2 equiv) and toluene (20 mL). The reaction mixture was stirred at 100 °C for 24 h. The solution was filtered through a celite pad and washed with 30 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product (0.45 g, 73%).

V. General procedures for parallel control experiments

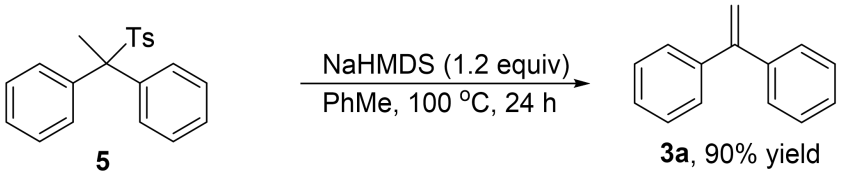
1. The coupling of styrene with phenyl triflate **2a**



In a nitrogen-filled glove box, a 10-mL Schlenk tube with a magnetic stir bar was charged with styrene (28 μL, 0.24 mmol, 1.2 equiv), phenyl triflate **2a** (45.2 mg, 0.2 mmol, 1 equiv), $Pd(dba)_2$ (5.8 mg, 5 mol%), ^{t}BuXPhos (12 mg, 14 mol%), NaHMDS

(80.7 mg, 0.44 mmol, 2.2 equiv) and toluene (1.6 mL). The reaction mixture was stirred at 100 °C for 24 h. The solution was filtered through a celite pad and washed with 10 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product in 15% yield.

2. The coupling of (1-tosylethane-1,1-diyl)dibenzene **5** with phenyl triflate **2a**



In a nitrogen-filled glove box, a 10-mL Schlenk tube with a magnetic stir bar was charged with **5** (67 mg, 0.2 mmol), NaHMDS (44 mg, 0.24 mmol, 1.2 equiv) and toluene (1.6 mL). The reaction mixture was stirred at 100 °C for 24 h. The solution was filtered through a celite pad and washed with 10 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product in 90% yield.

*Compound **5** was synthesized according to the literature procedure.*[10] The NMR data of compound **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 4H), 7.32-7.25 (m, 6H), 7.17 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 139.5, 133.8, 130.5, 129.7, 128.7, 128.11, 128.07, 75.1, 26.1, 21.7. HRMS (ESI): calcd for $C_{21}H_{24}NO_2S$ $[M+NH_4]^+$ 354.1528, found 354.1536.

VI. References

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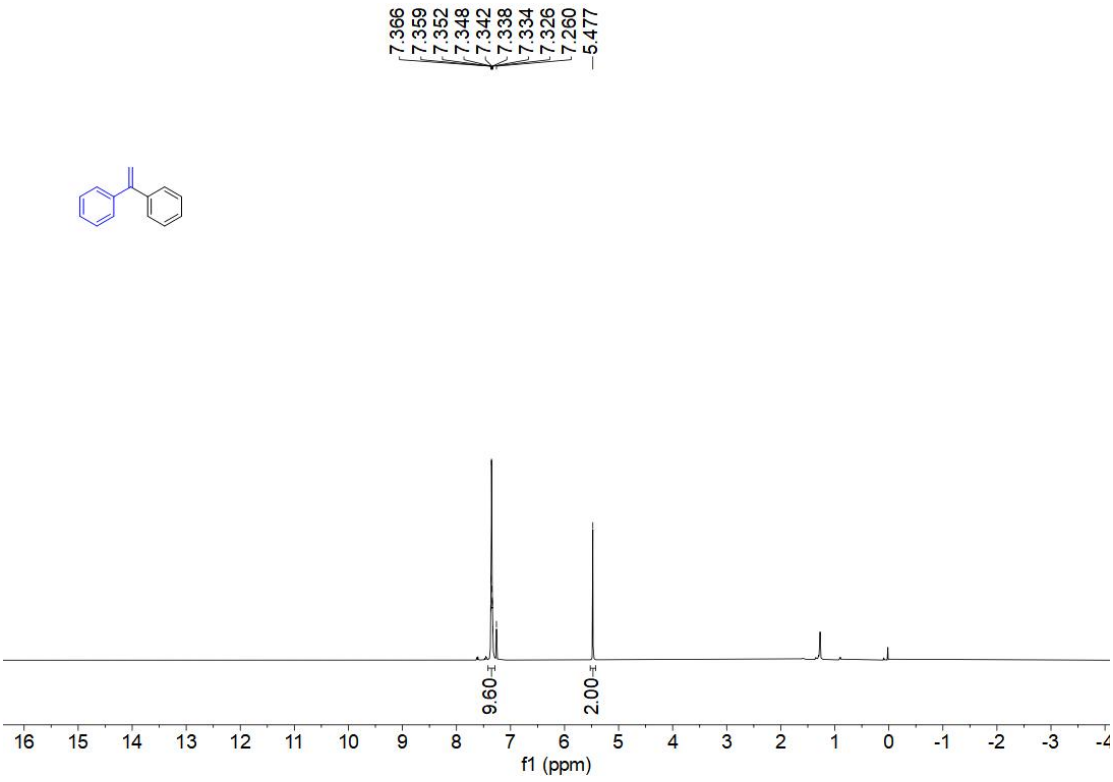
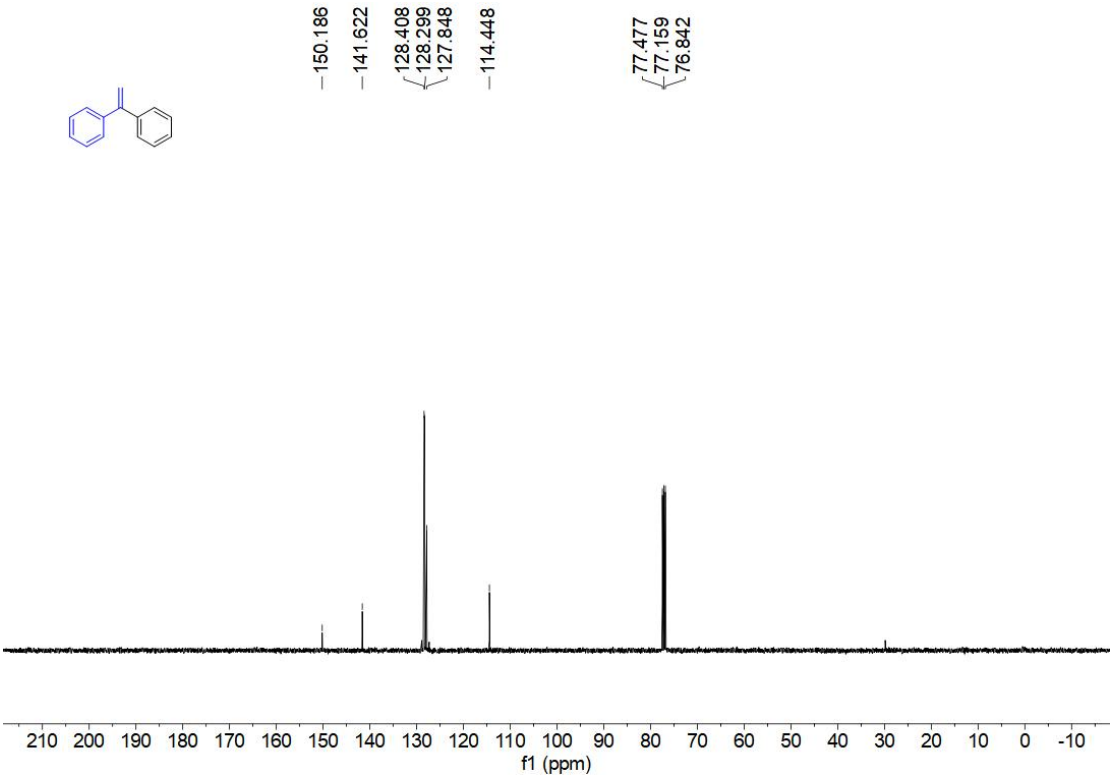
VII. Copies of ^{1}H and ^{13}C NMR spectra

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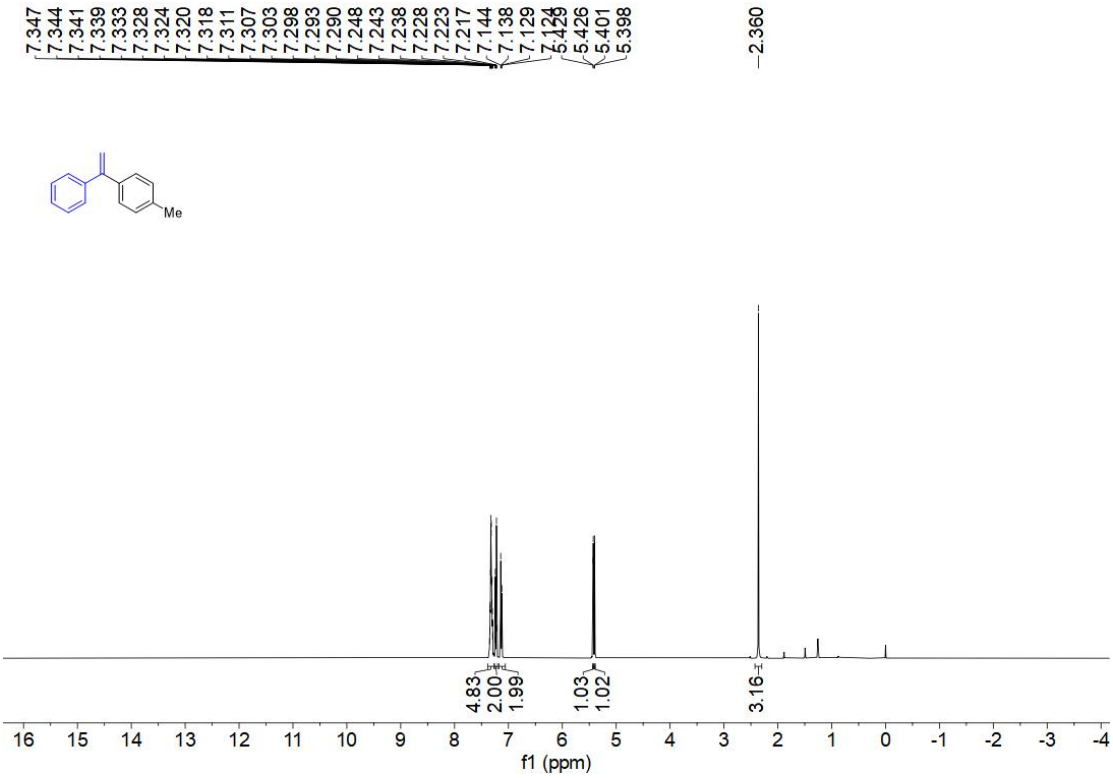
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1.02
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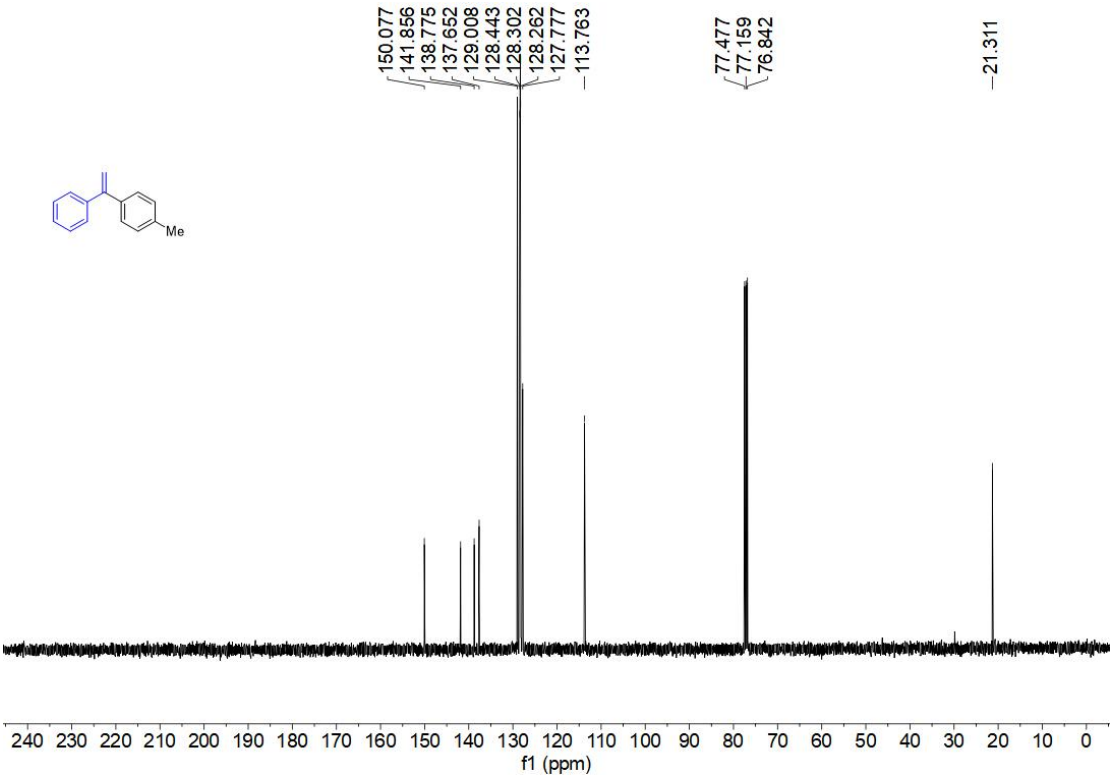
f1 (ppm)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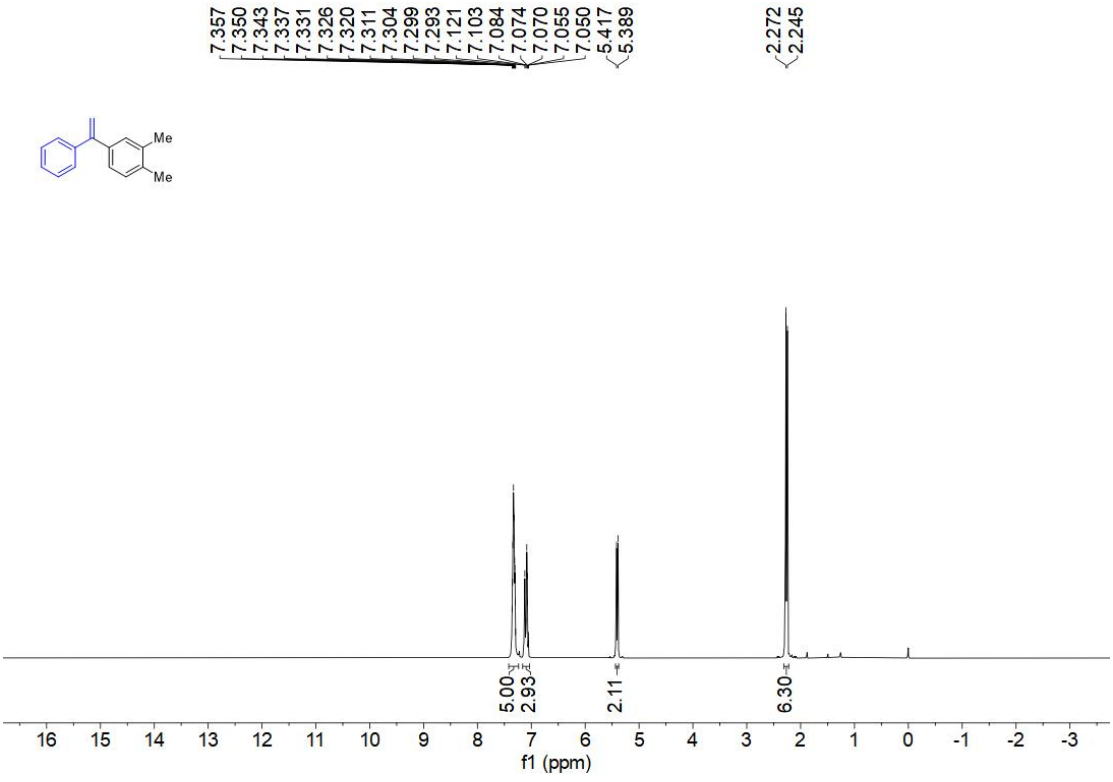
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6.30
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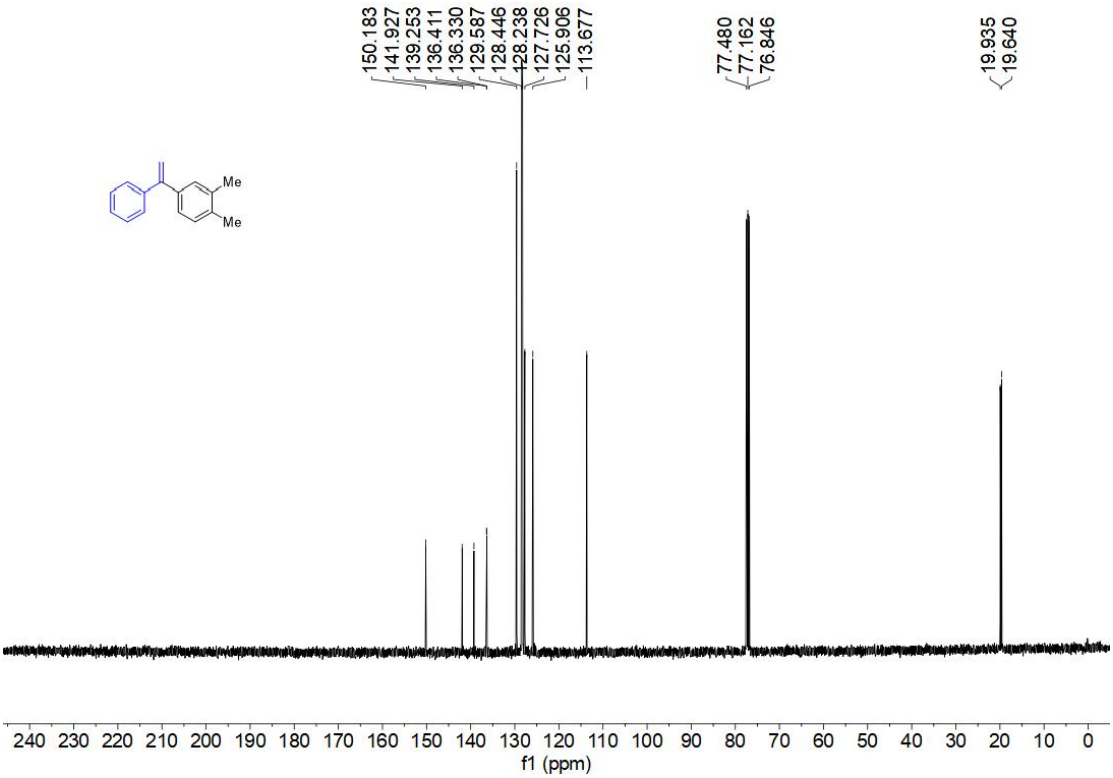
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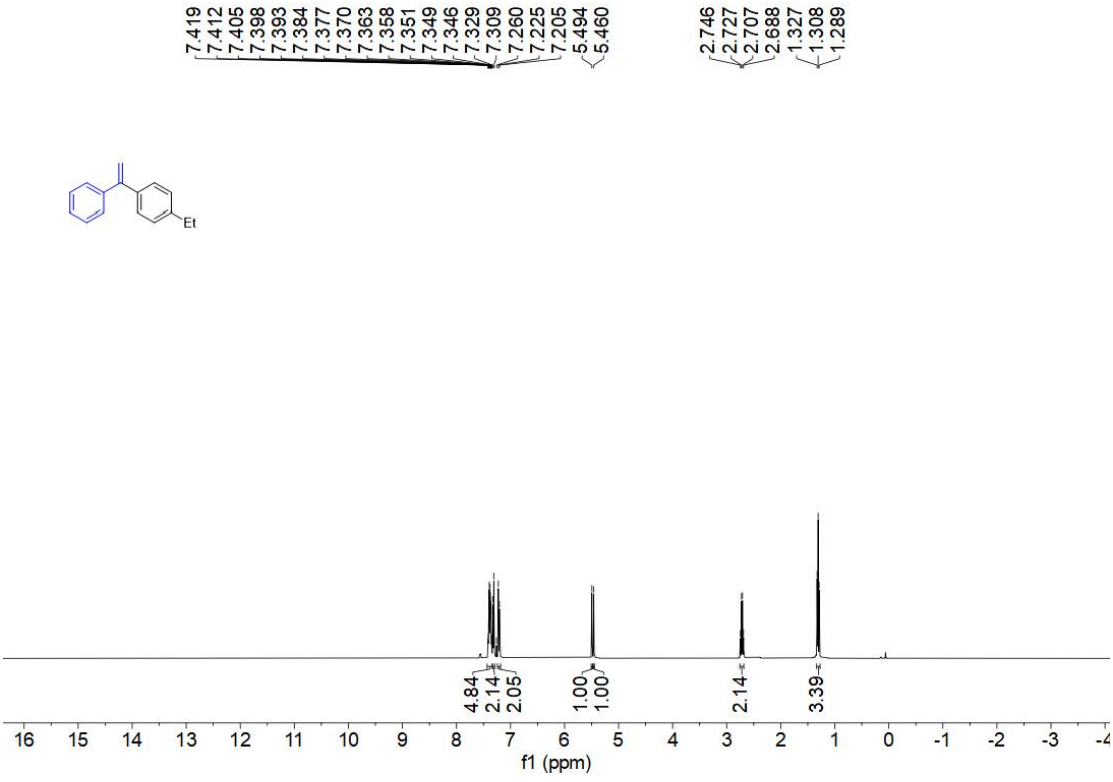
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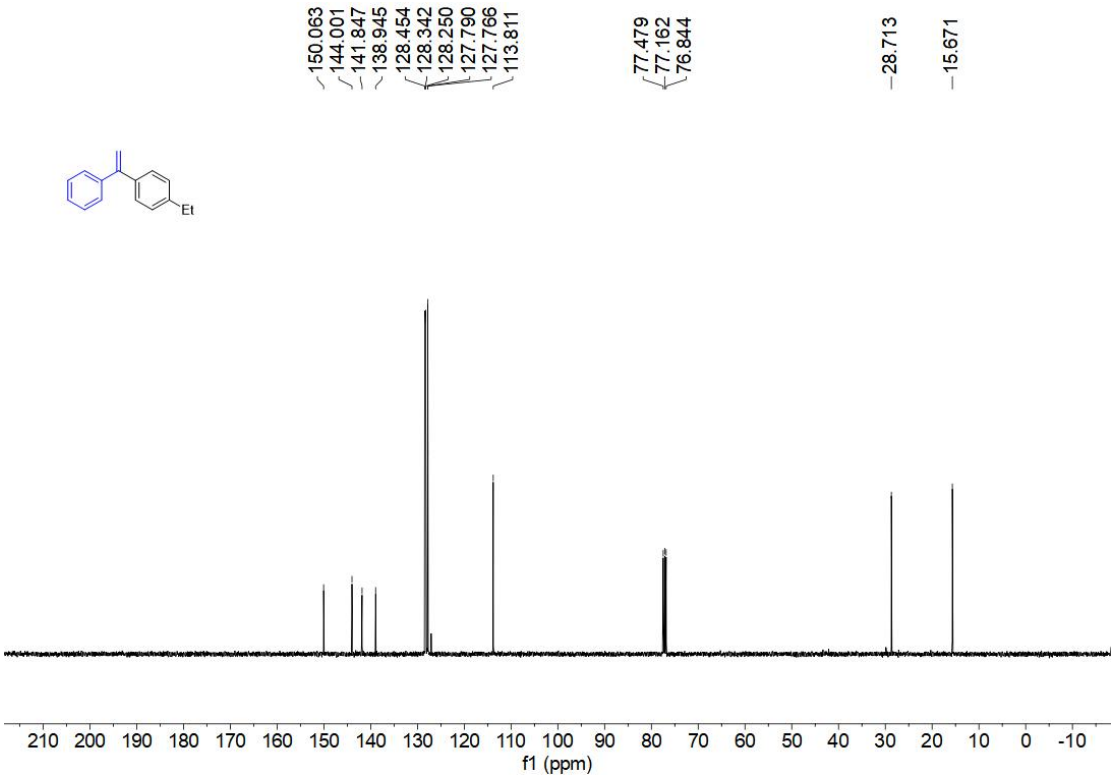
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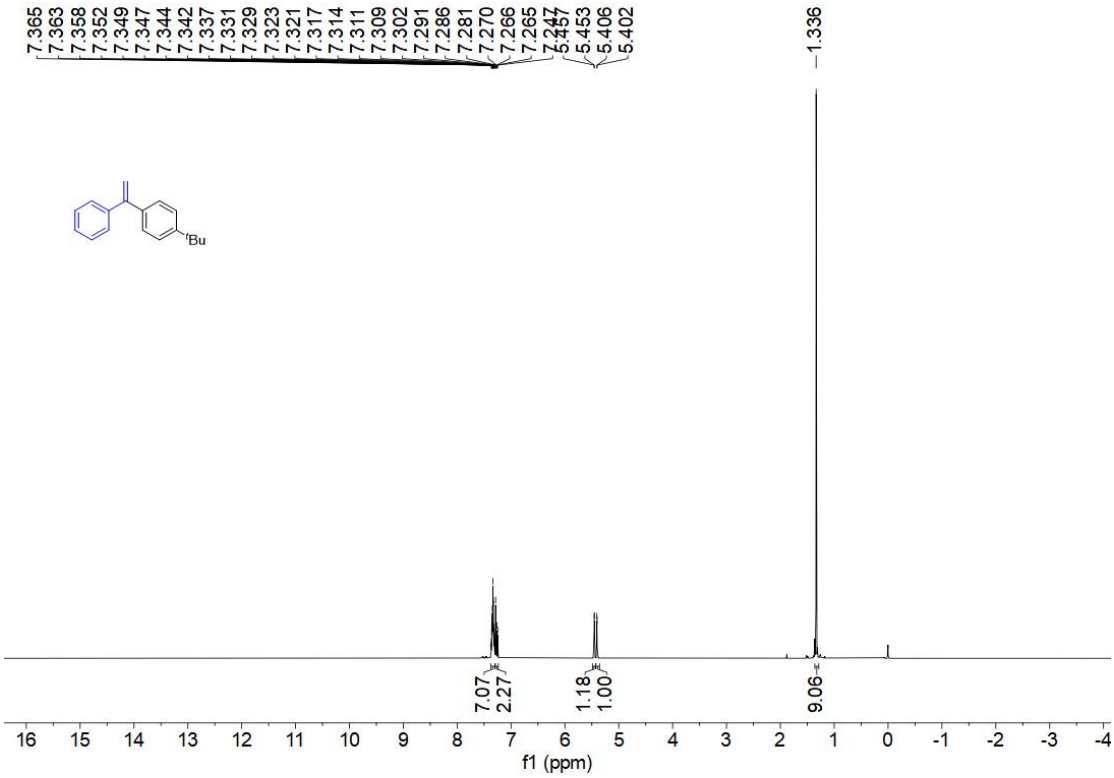
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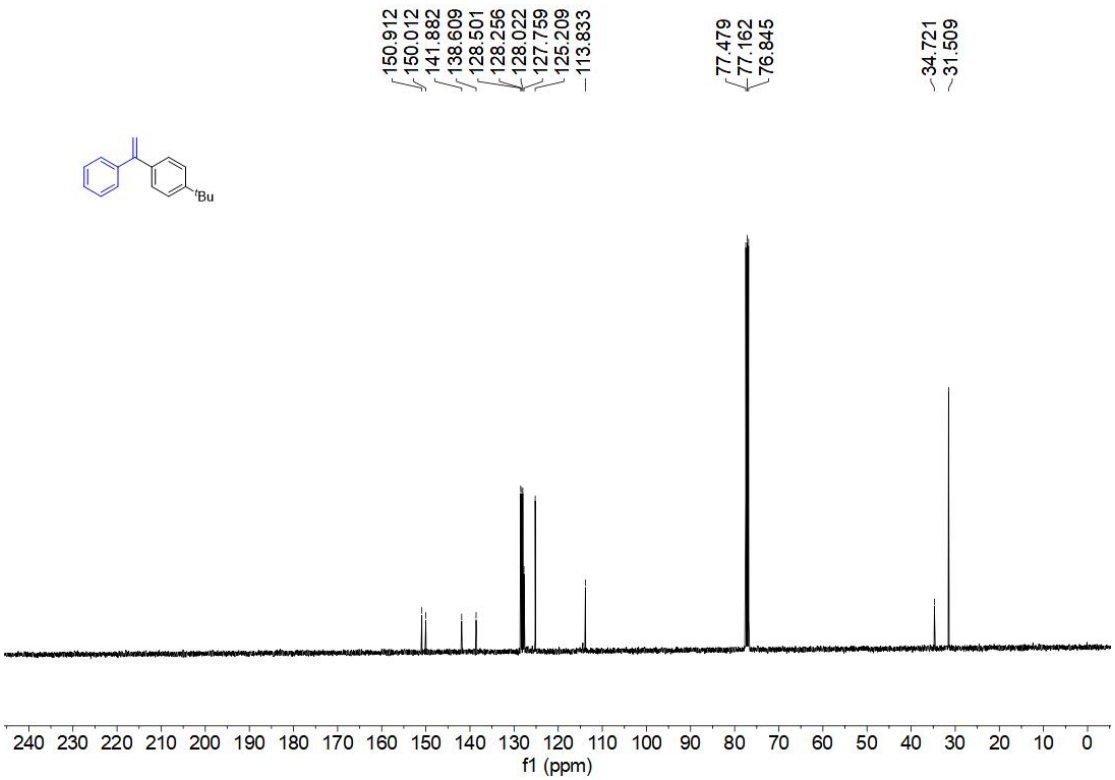
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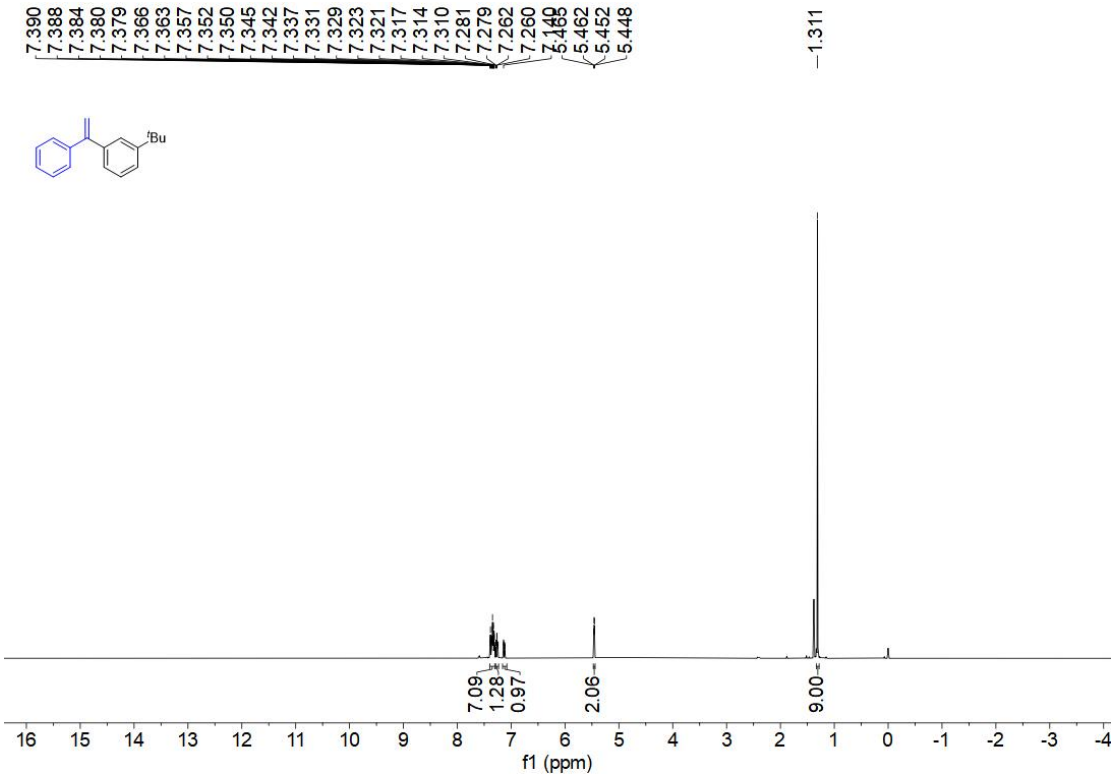
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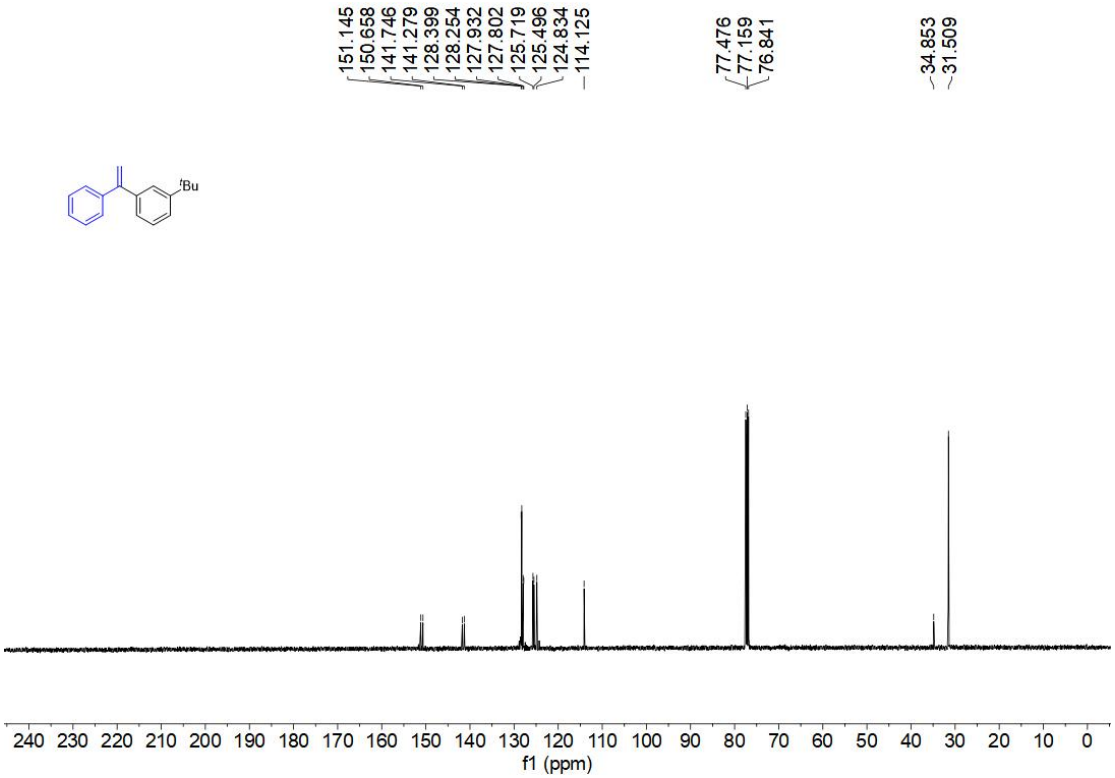
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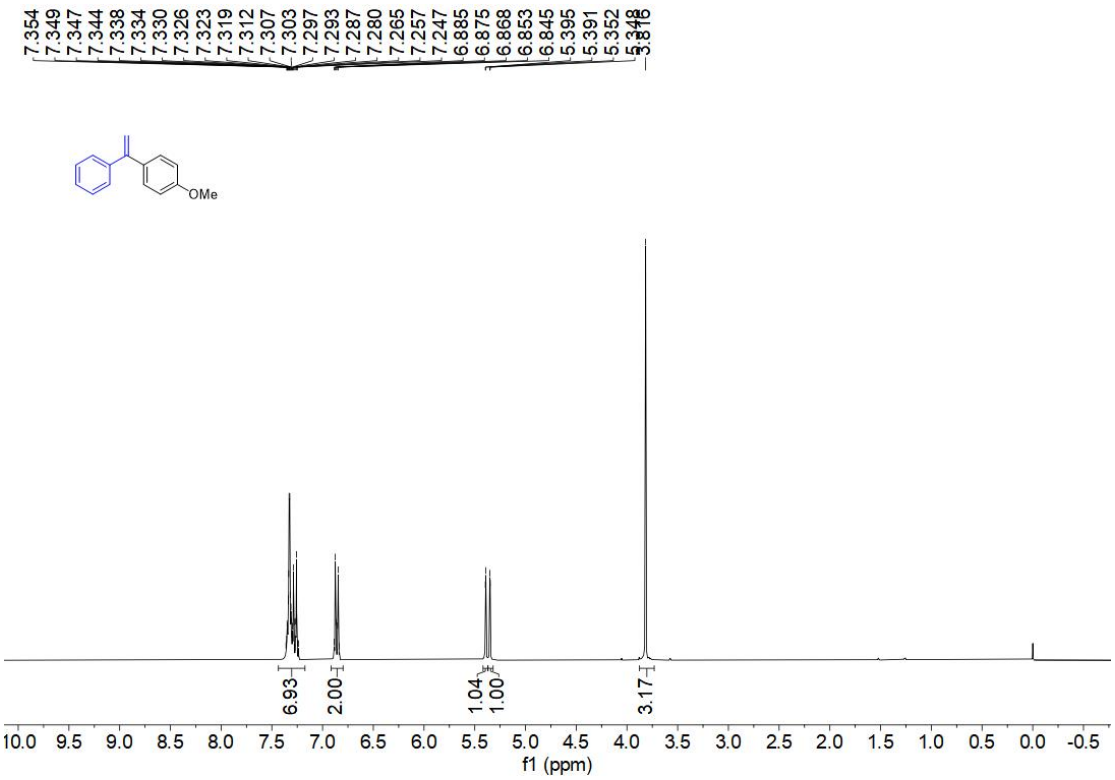
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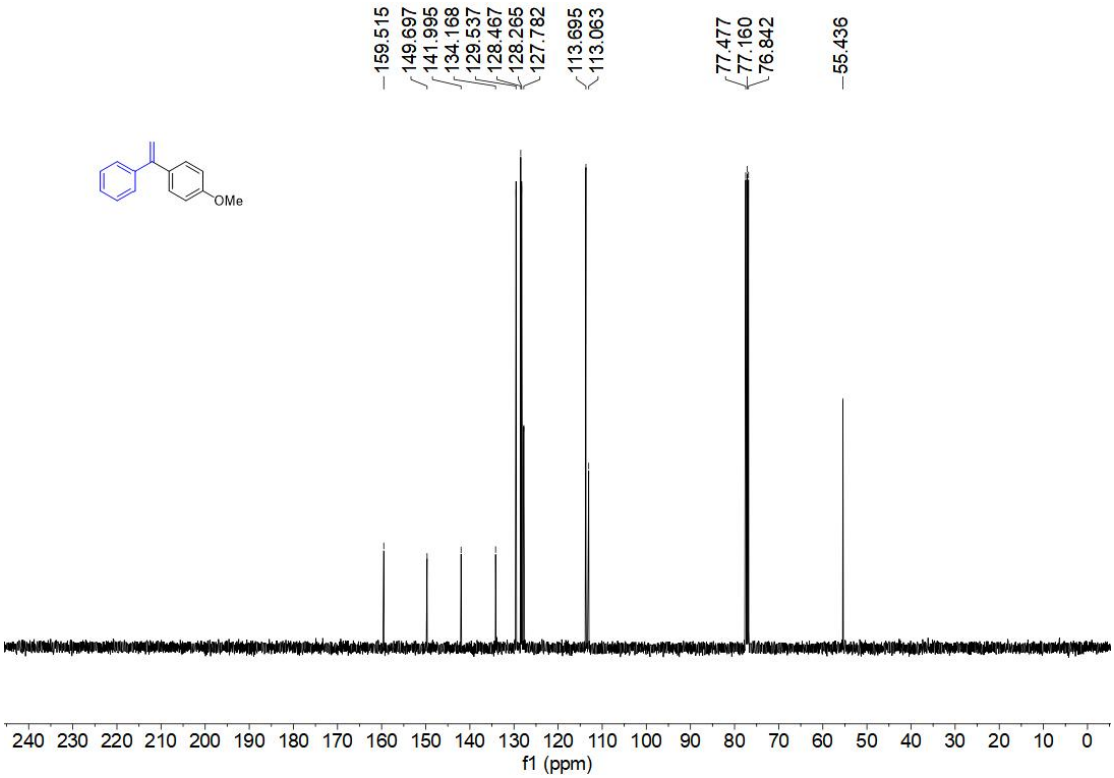
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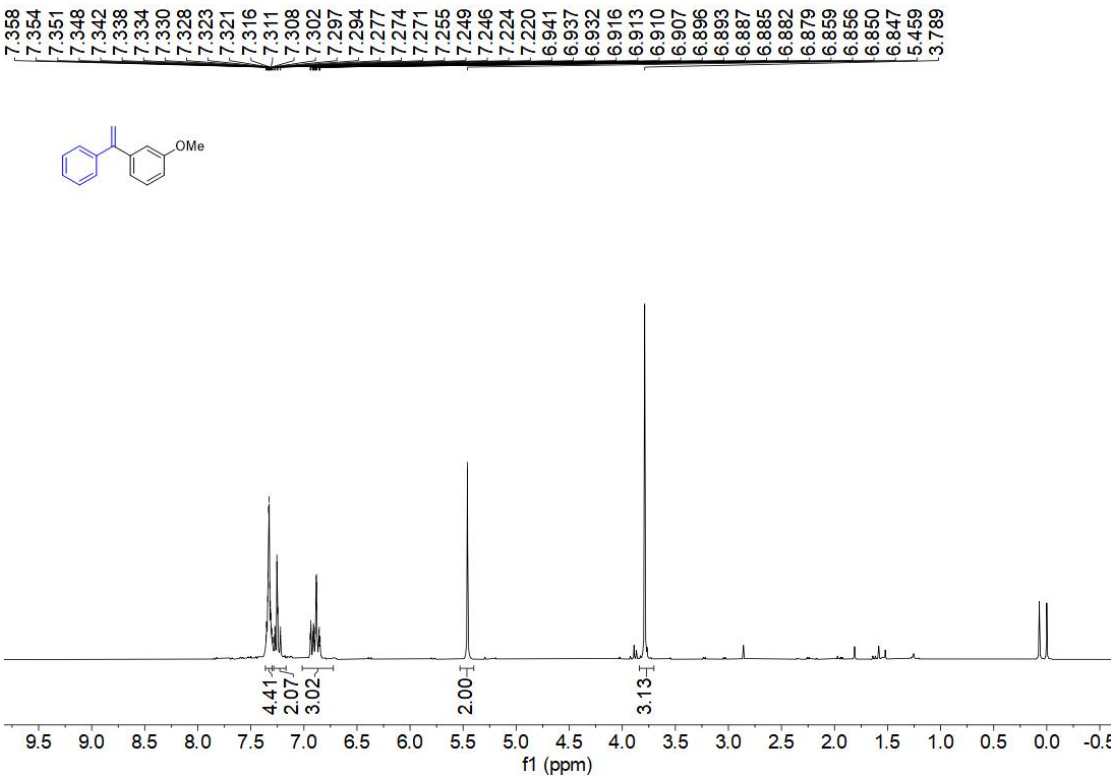
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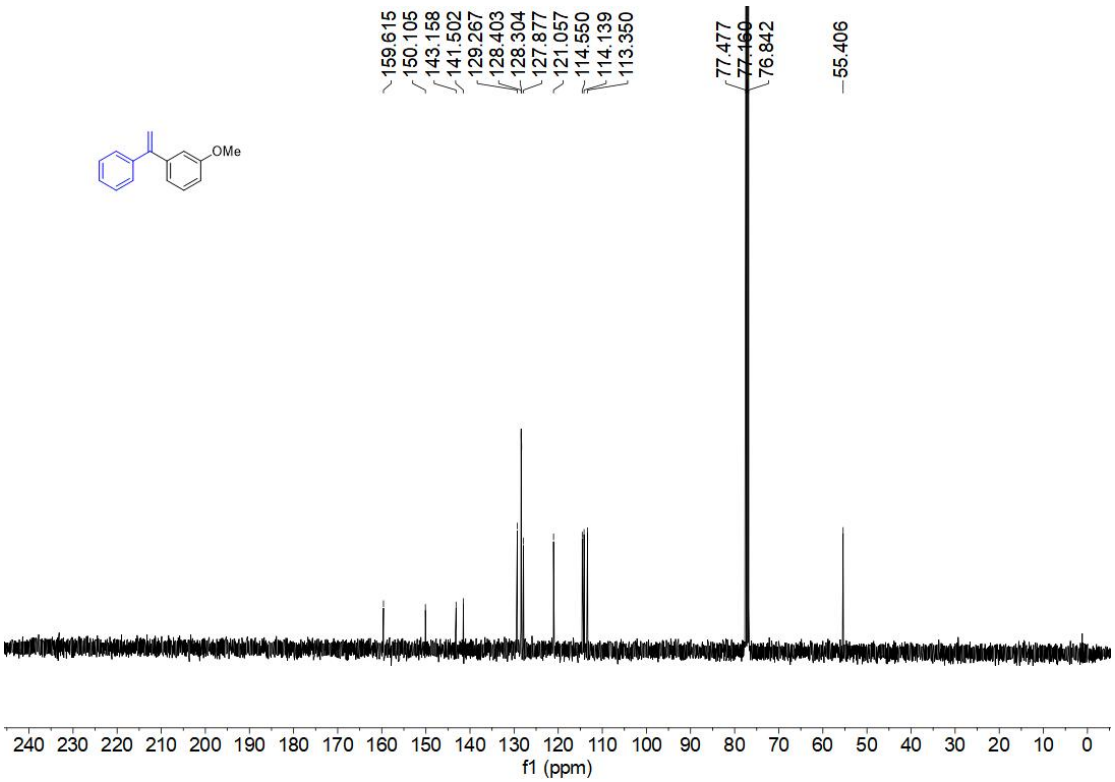
6.885
6.882
6.879
6.859
6.856
6.850
6.847
5.459
3.789
OMe
4.41
2.07
3.02
2.00
3.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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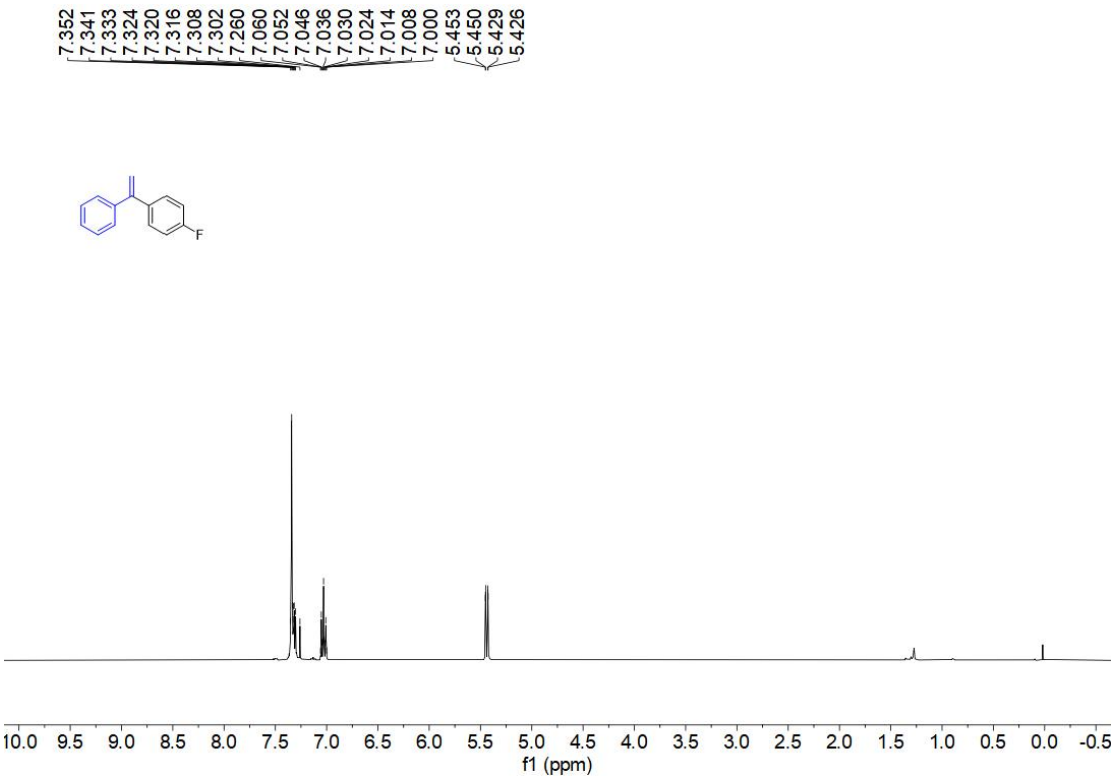
150.105
143.158
141.502
129.267
128.403
128.304
127.877
121.057
114.550
114.139
113.350
77.477
77.160
76.842
55.406
OMe
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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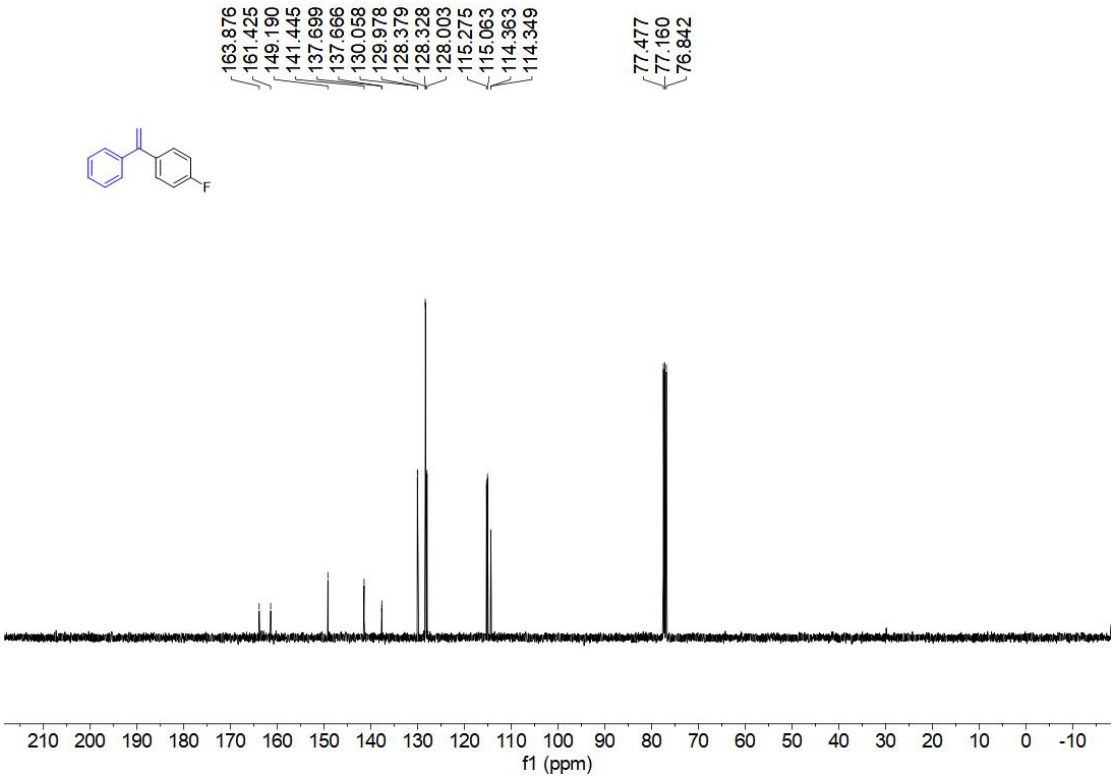
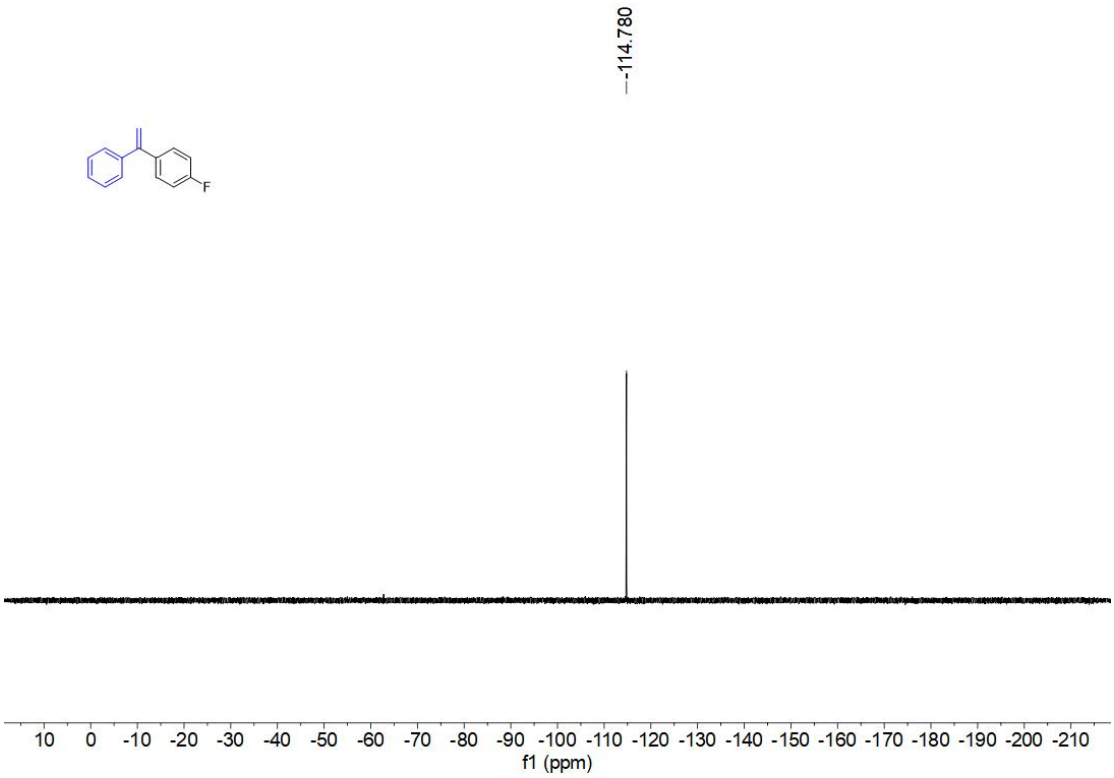
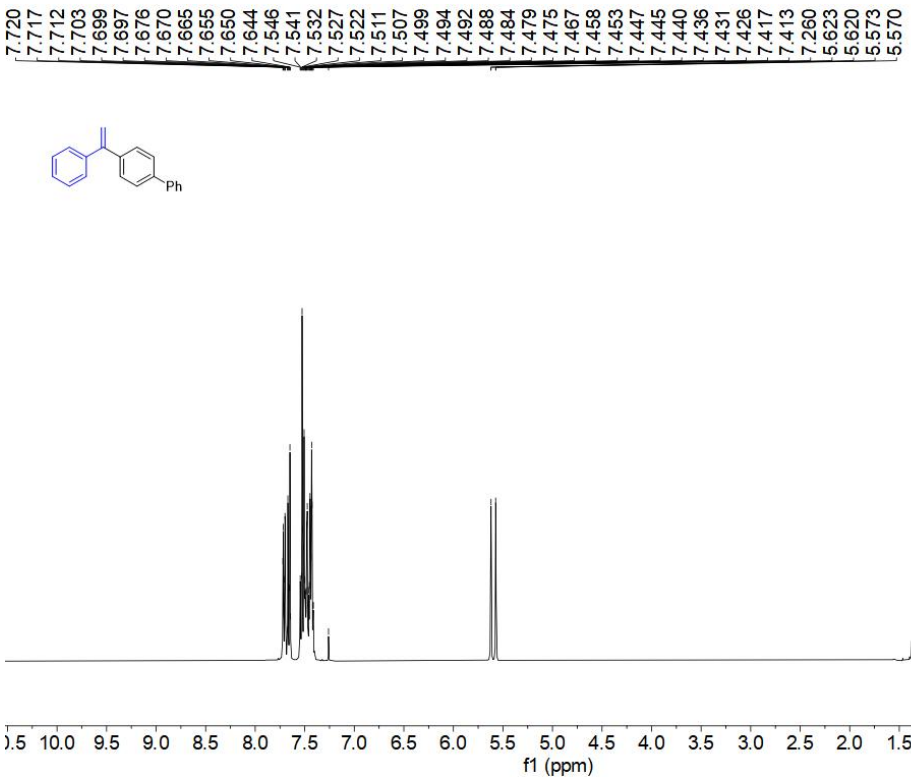
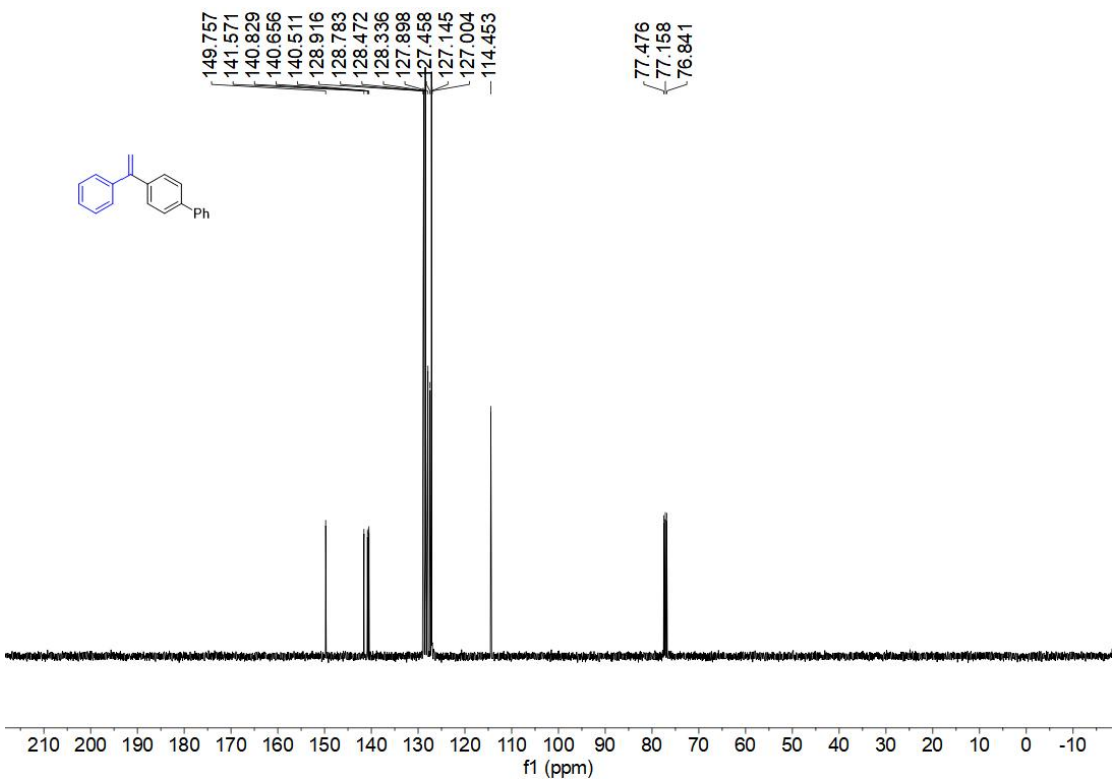
7.341
7.333
7.324
7.320
7.316
7.308
7.302
7.260
7.060
7.052
7.046
7.036
7.030
7.024
7.014
7.008
7.000
5.453
5.450
5.429
5.426
F
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


163.876
161.425
149.190
141.445
137.699
137.666
130.058
129.978
128.379
128.328
128.003
115.275
115.063
114.363
114.349
77.477
77.160
76.842
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-114.780
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.720
7.717
7.712
7.703
7.699
7.697
7.676
7.670
7.665
7.655
7.650
7.644
7.546
7.541
7.532
7.527
7.522
7.511
7.507
7.499
7.494
7.492
7.488
7.484
7.479
7.475
7.467
7.458
7.453
7.447
7.445
7.440
7.436
7.431
7.426
7.417
7.413
7.260
5.623
5.620
5.573
5.570
Ph
f1 (ppm)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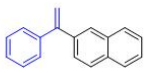
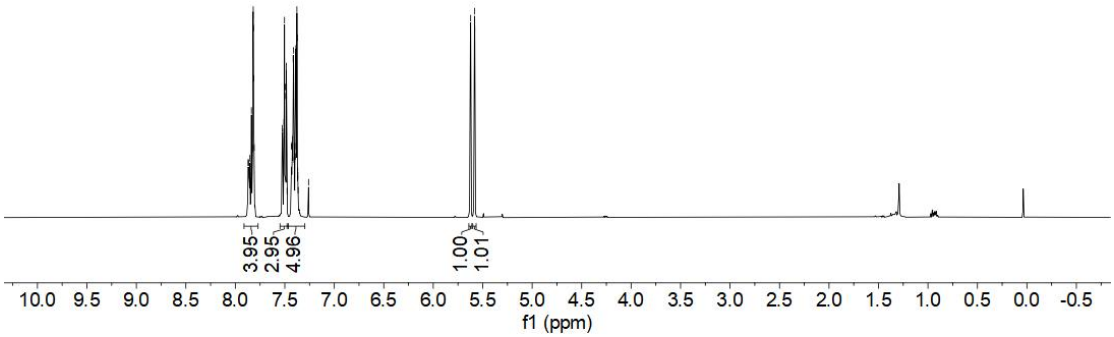
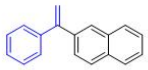
141.571
140.829
140.656
140.511
128.916
128.783
128.472
128.336
127.898
127.458
127.145
127.004
114.453
77.476
77.158
76.841
Ph
f1 (ppm)

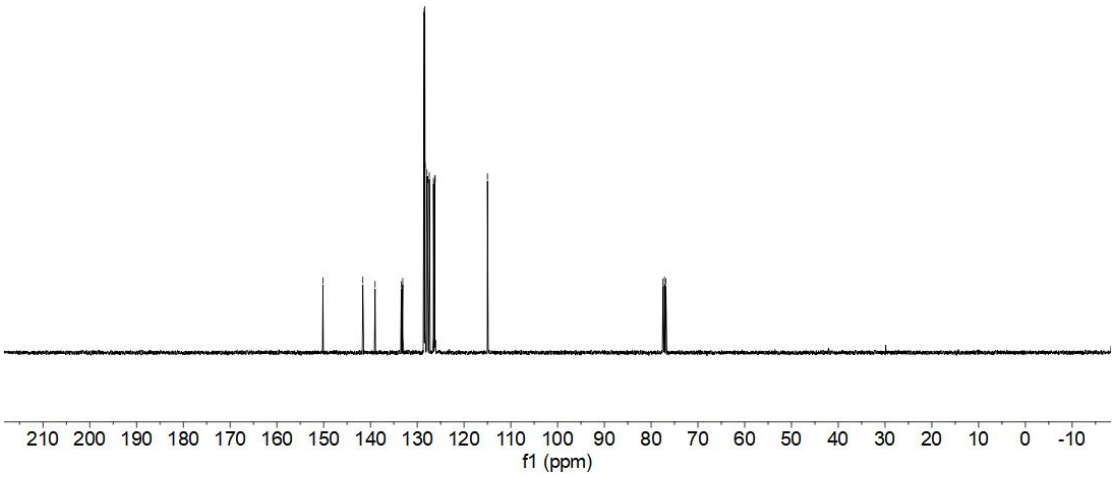

7.872
7.865
7.861
7.860
7.857
7.853
7.846
7.837
7.828
7.821
7.819
7.816
7.814
7.810
7.525
7.522
7.509
7.505
7.503
7.497
7.491
7.484
7.477
7.432
7.427
7.425
7.422
7.416
7.412
7.406
7.404
7.401
7.397
7.394
7.390
7.388
7.384
7.378
7.374
7.369
7.368
7.365
7.260
5.624
5.622
5.583
5.580

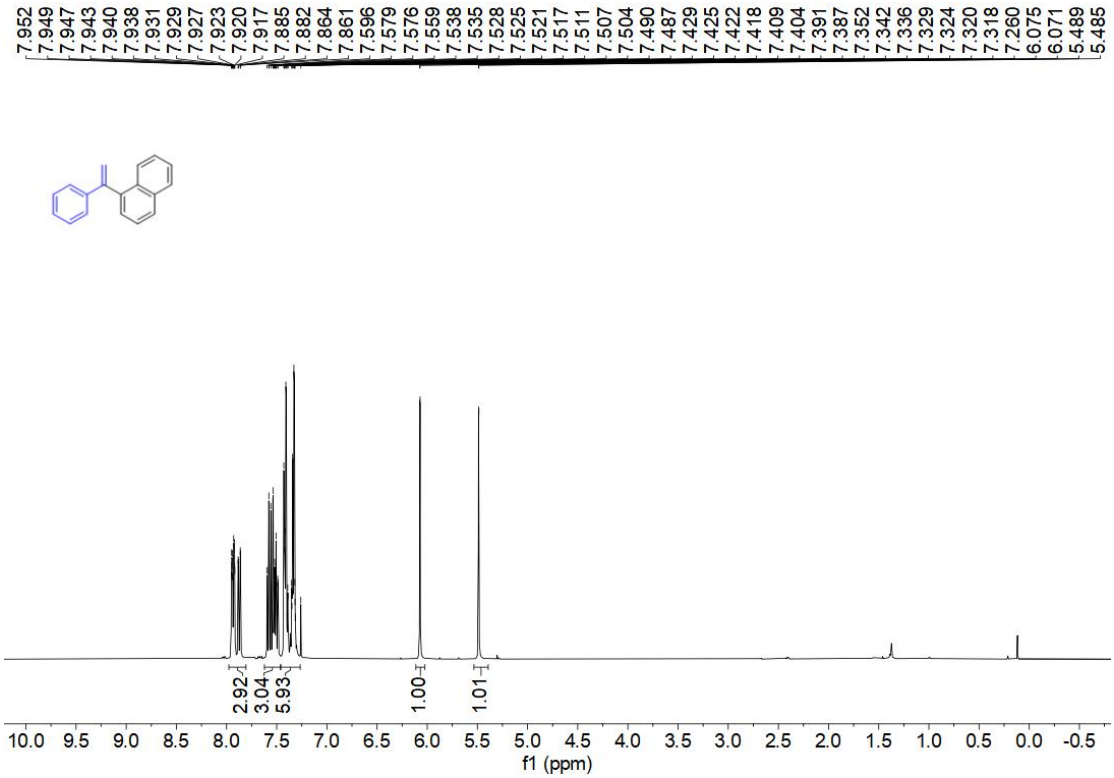



3.95
2.95
4.96
1.00
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


150.151
141.626
139.003
133.414
133.086
128.510
128.366
128.310
127.931
127.825
127.719
127.415
126.527
126.284
126.144
114.984
77.476
77.159
76.841




210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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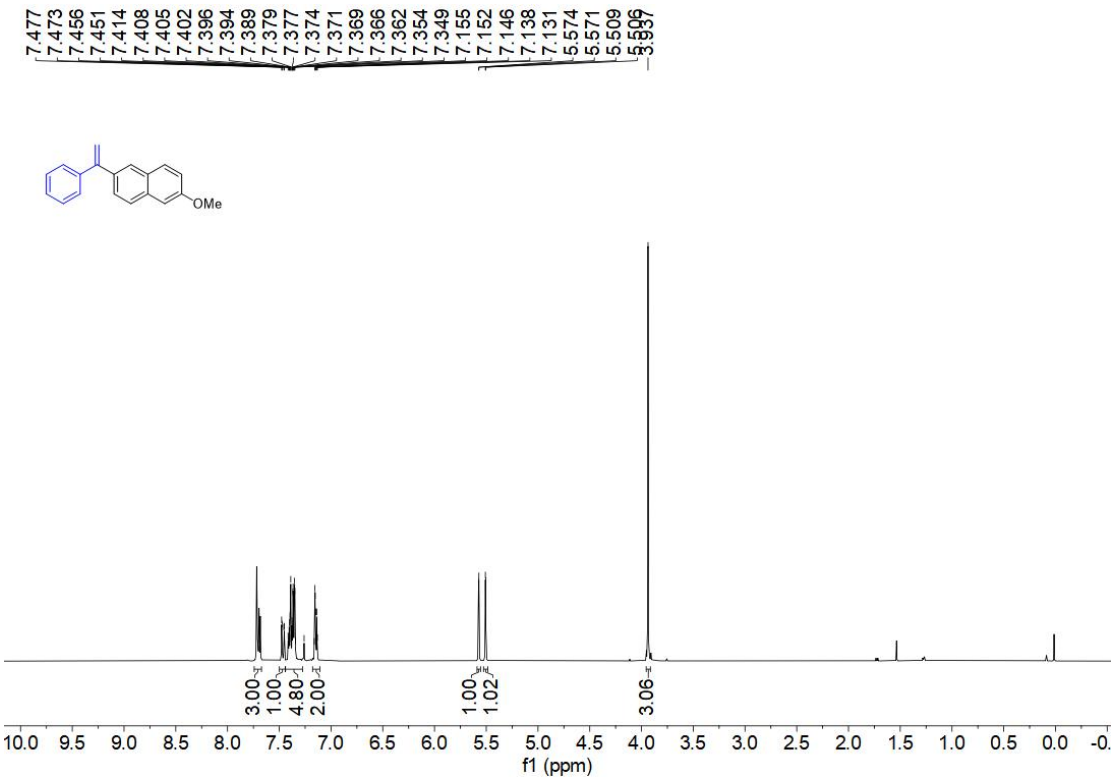
7.949
7.947
7.943
7.940
7.938
7.931
7.929
7.927
7.923
7.920
7.917
7.885
7.882
7.864
7.861
7.596
7.579
7.576
7.559
7.538
7.535
7.528
7.525
7.521
7.517
7.511
7.507
7.504
7.490
7.487
7.429
7.425
7.422
7.418
7.409
7.404
7.391
7.387
7.352
7.342
7.336
7.329
7.324
7.320
7.318
7.260
6.075
6.071
5.489
5.485
2.92
3.04
5.93
1.00
1.01
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 -0.5
f1 (ppm)
148.384
141.164
139.920
133.816
131.983
128.506
128.306
128.081
127.825
127.360
126.746
126.557
126.005
125.808
125.559
116.373
77.478
77.160
76.842
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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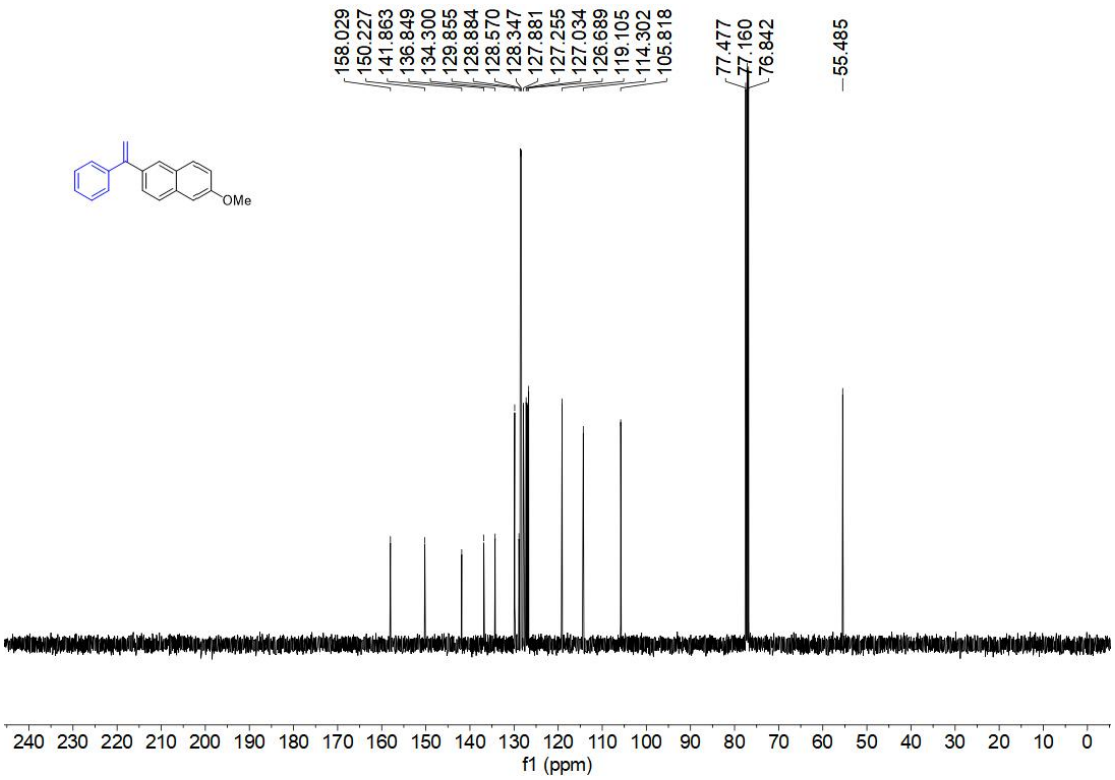
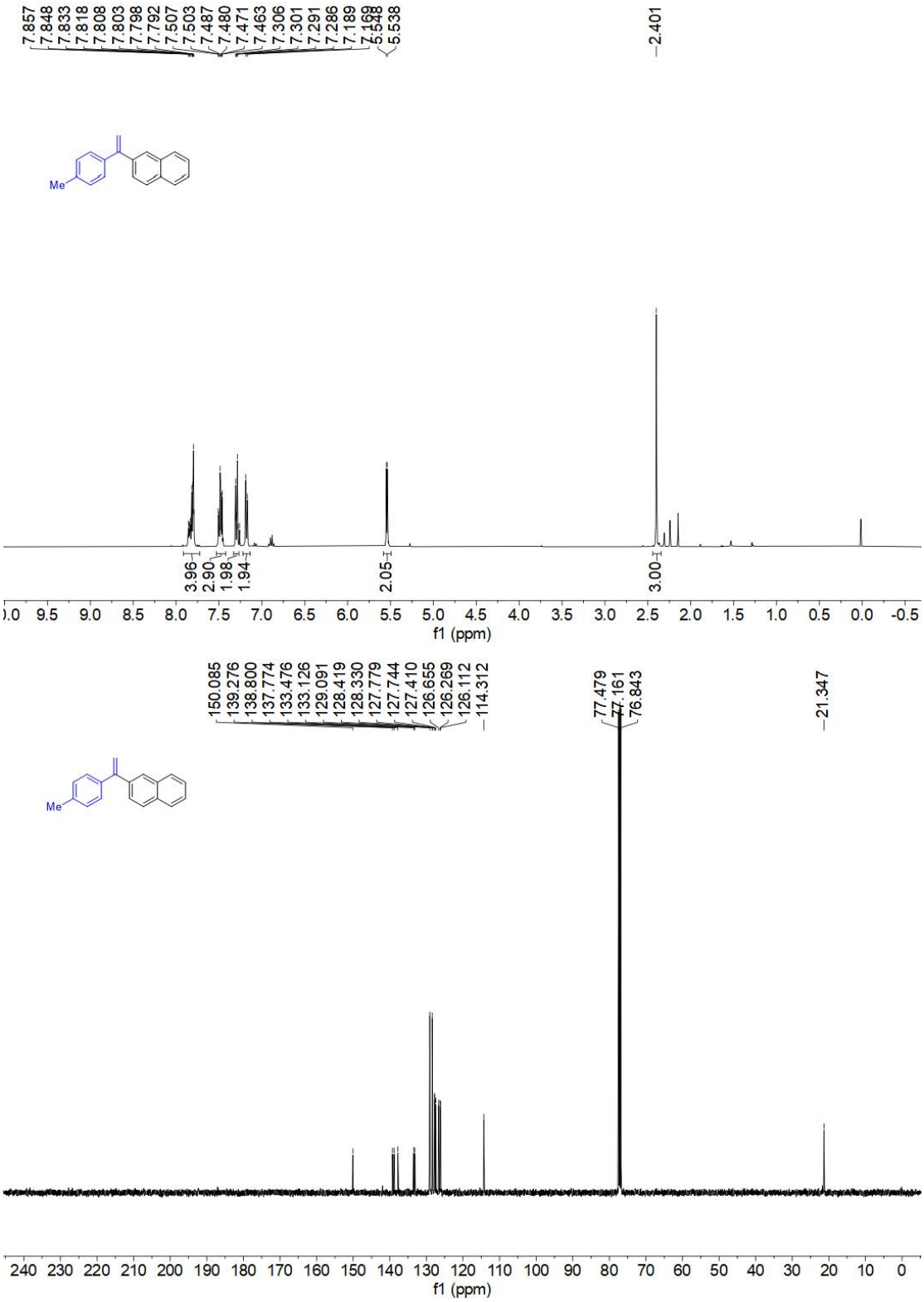
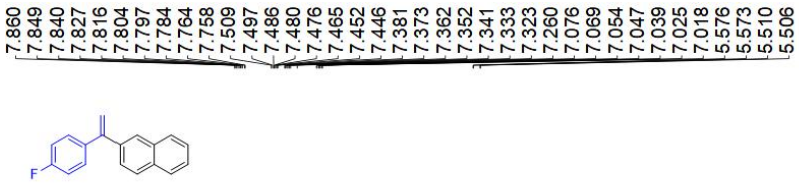
7.473
7.456
7.451
7.414
7.408
7.405
7.402
7.396
7.394
7.389
7.379
7.377
7.374
7.371
7.369
7.366
7.362
7.354
7.349
7.155
7.152
7.146
7.138
7.131
5.574
5.571
5.509
3.937
OMe
3.00
1.00
4.80
2.00
1.00
1.02
3.06
f1 (ppm)


158.029
150.227
141.863
136.849
134.300
129.855
128.884
128.570
128.347
127.881
127.255
127.034
126.689
119.105
114.302
105.818
77.477
77.160
76.842
55.485
OMe
f1 (ppm)


7.857
7.848
7.833
7.818
7.808
7.803
7.798
7.792
7.507
7.503
7.487
7.480
7.471
7.463
7.306
7.301
7.291
7.286
7.189
7.169
5.548
5.538
2.401
Me
3.96
2.90
1.98
1.94
2.05
3.00
f1 (ppm)
150.085
139.276
138.800
137.774
133.476
133.126
129.091
128.419
128.330
127.779
127.744
127.410
126.655
126.269
126.112
114.312
77.479
77.161
76.843
21.347
Me
f1 (ppm)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7.840
7.827
7.816
7.804
7.797
7.784
7.764
7.758
7.509
7.497
7.486
7.480
7.476
7.465
7.452
7.446
7.381
7.373
7.362
7.352
7.341
7.333
7.323
7.260
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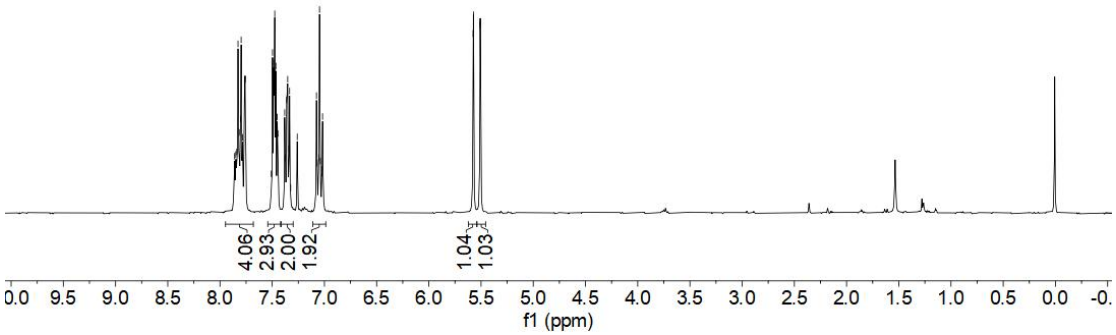
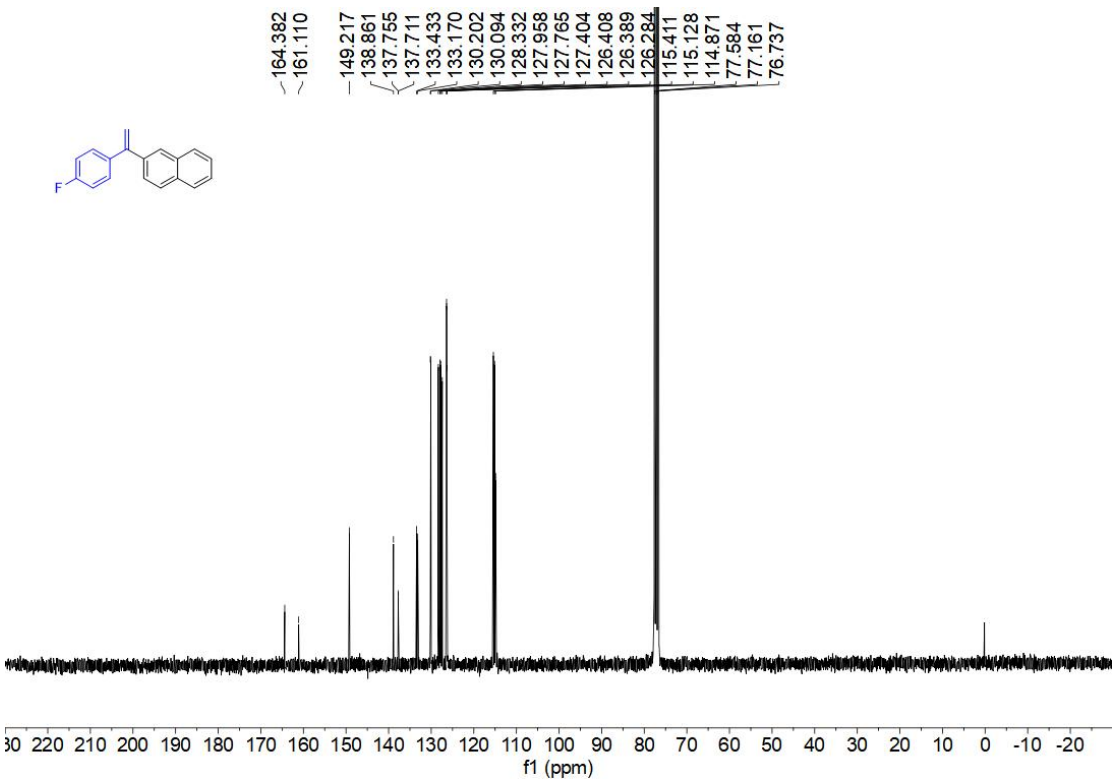
7.018
5.576
5.573
5.510
5.506


4.06
2.93
2.00
1.92
1.04
1.03
f1 (ppm)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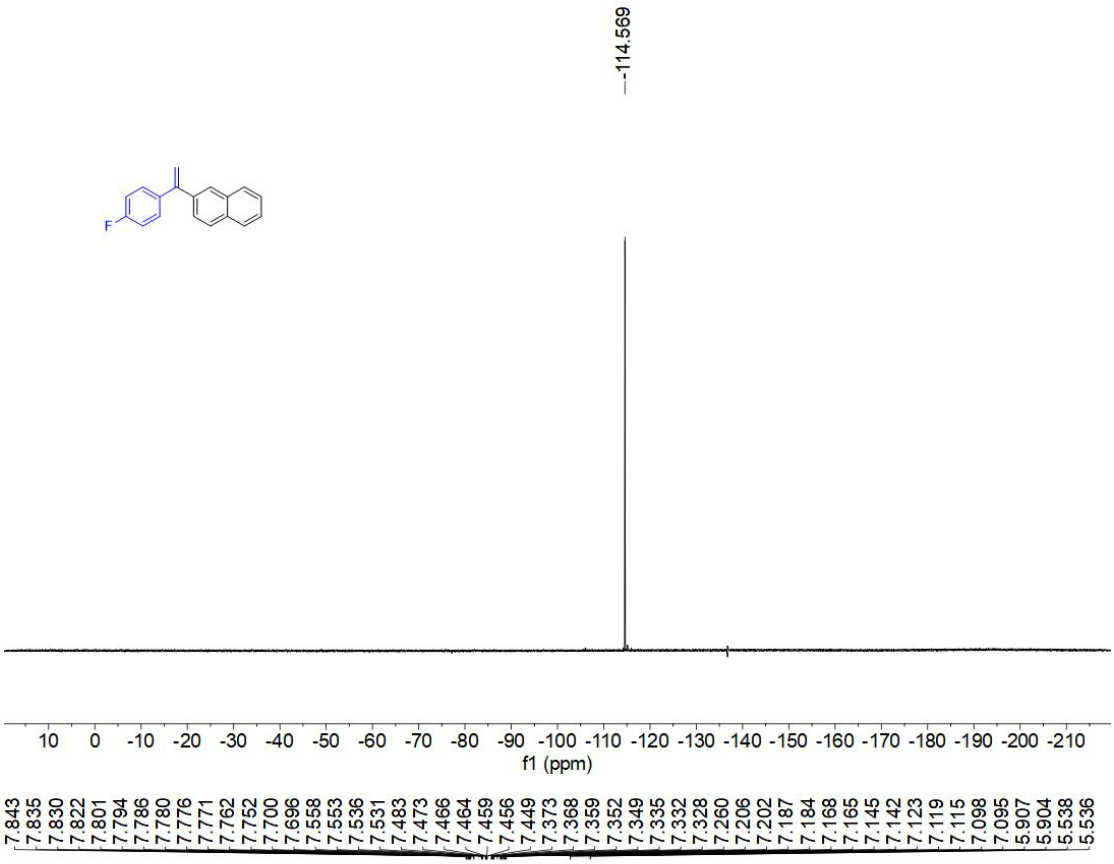
137.711
133.433
133.170
130.202
130.094
128.332
127.958
127.765
127.404
126.408
126.389
126.284
115.411
115.128
114.871
77.584
77.161
76.737
f1 (ppm)


-114.569
F
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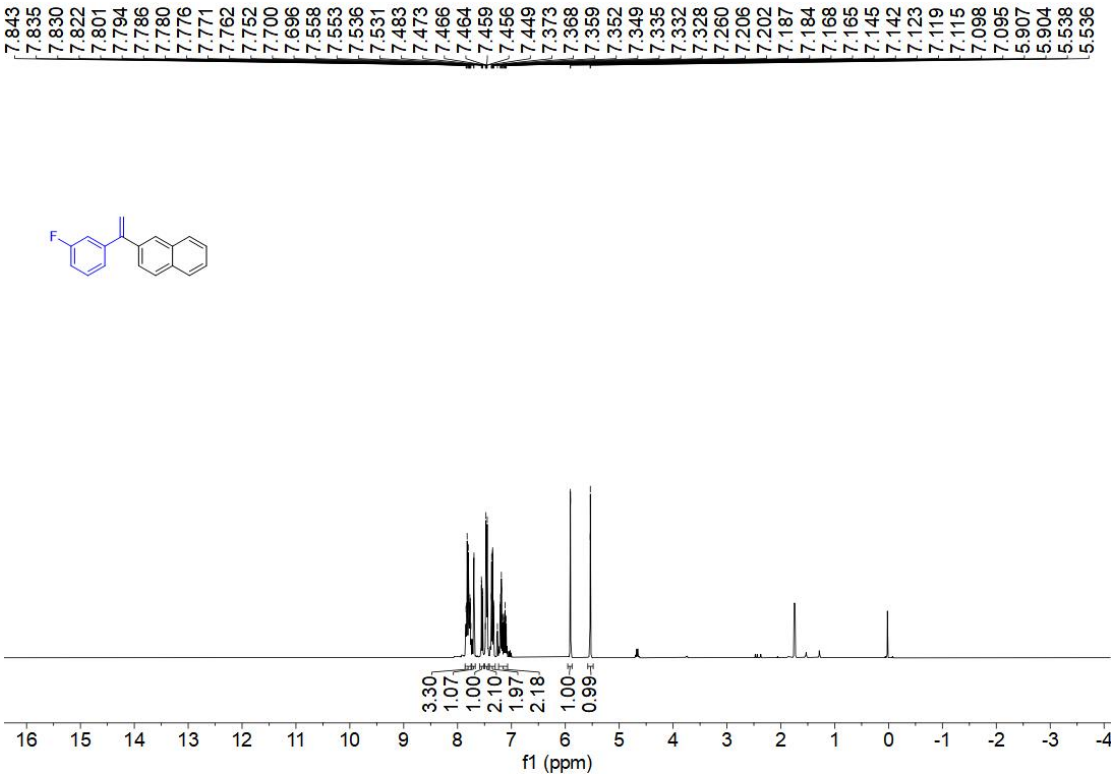
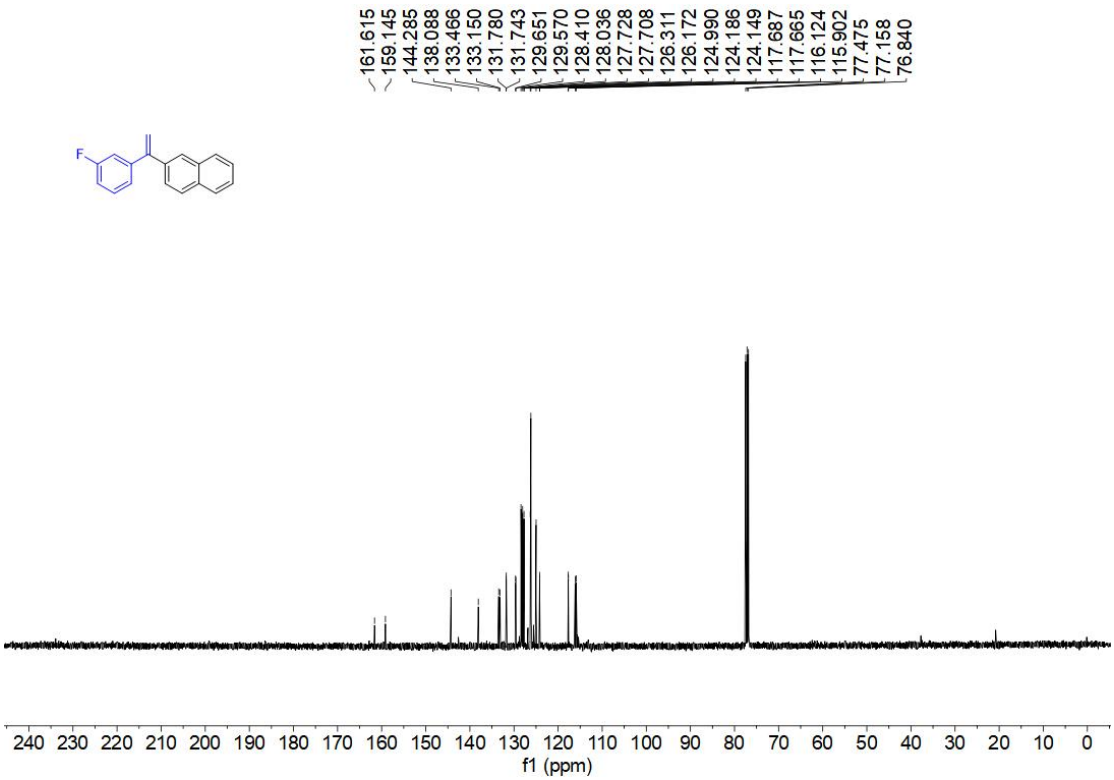
f1 (ppm)


F
3.30
1.07
1.00
2.10
1.97
2.18
1.00
0.99
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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159.145
144.285
138.088
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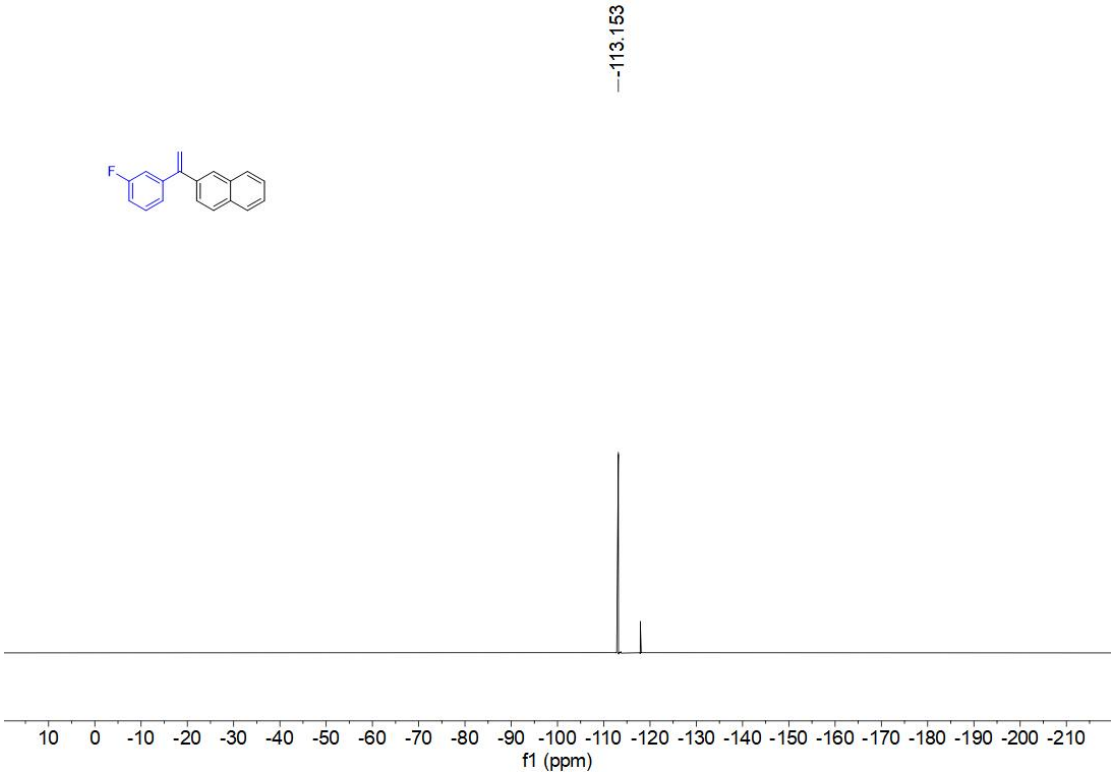
133.150
131.780
131.743
129.651
129.570
128.410
128.036
127.728
127.708
126.311
126.172
124.990
124.186
124.149
117.687
117.665
116.124
115.902
77.475
77.158
76.840
F
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-113.153
F
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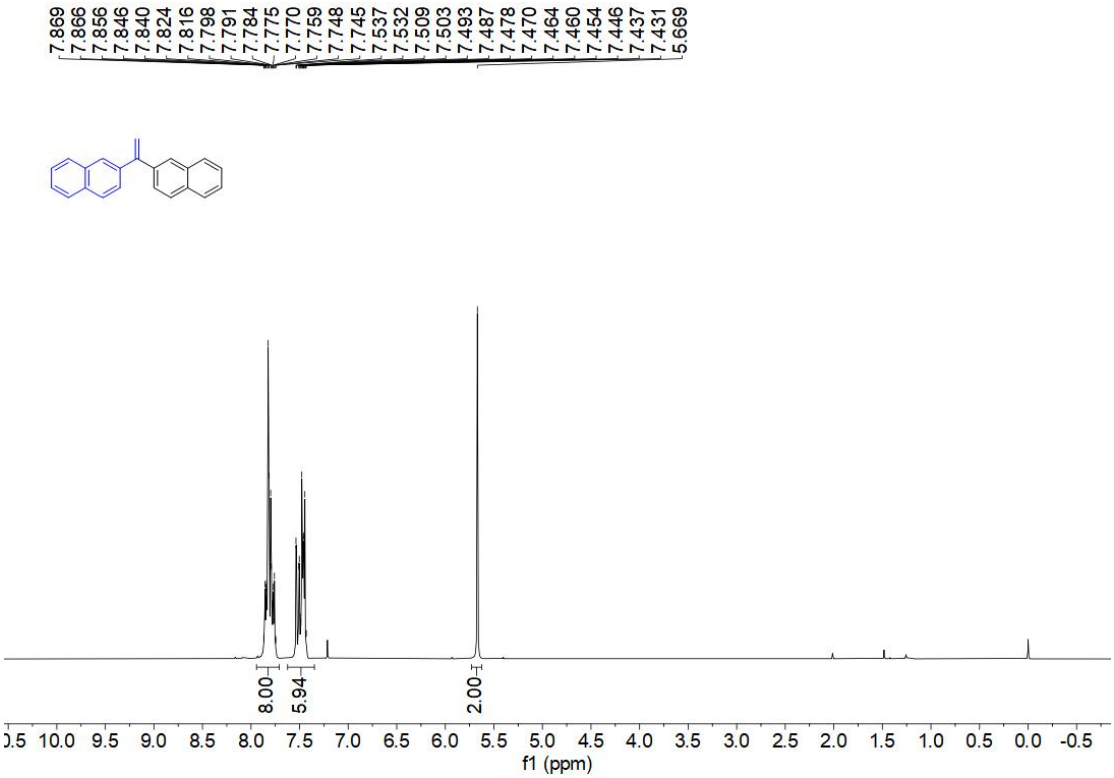
f1 (ppm)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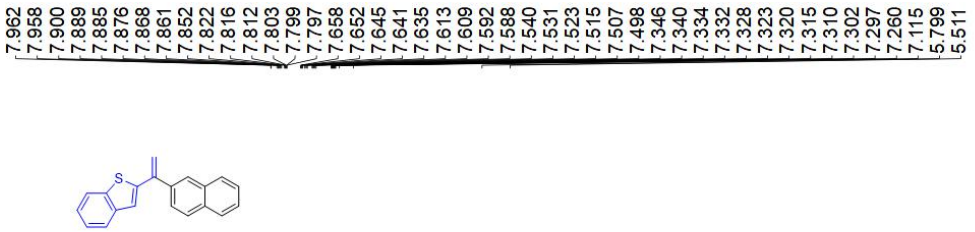
7.798
7.791
7.784
7.775
7.770
7.759
7.748
7.745
7.537
7.532
7.509
7.503
7.493
7.487
7.478
7.470
7.464
7.460
7.454
7.446
7.437
7.431
5.669
8.00
5.94
2.00
f1 (ppm)
150.211
139.096
133.496
133.184
128.375
127.922
127.775
127.583
126.633
126.349
126.223
115.475
77.477
77.160
76.842
f1 (ppm)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7.812
7.803
7.799
7.797
7.658
7.652
7.645
7.641
7.635
7.613
7.609
7.592
7.588
7.540
7.531
7.523
7.515
7.507
7.498
7.346
7.340
7.334
7.332
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7.320
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7.310
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7.297
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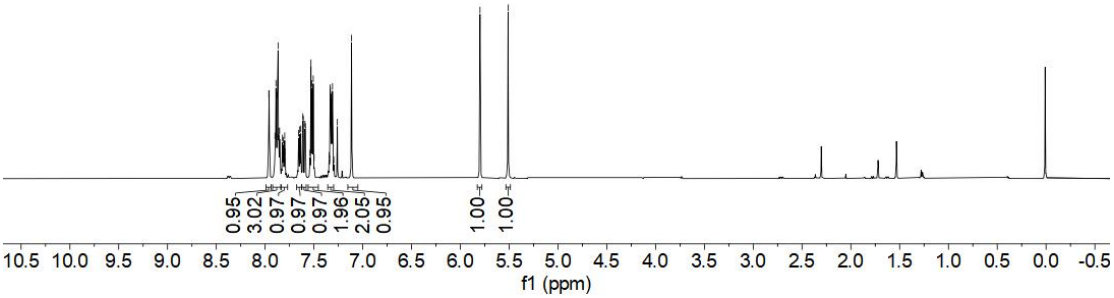
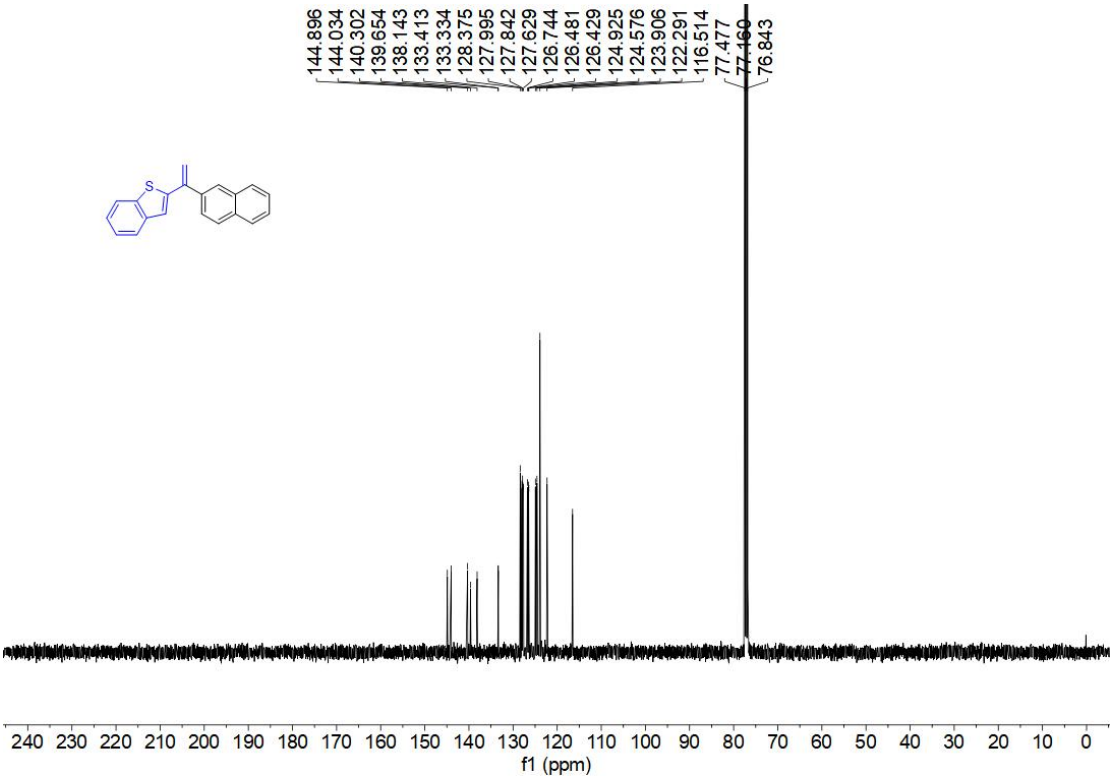
7.115
5.799
5.511


0.95
3.02
0.97
0.97
0.97
1.96
2.05
0.95
1.00
1.00
10.5 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 -0.5
f1 (ppm)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139.654
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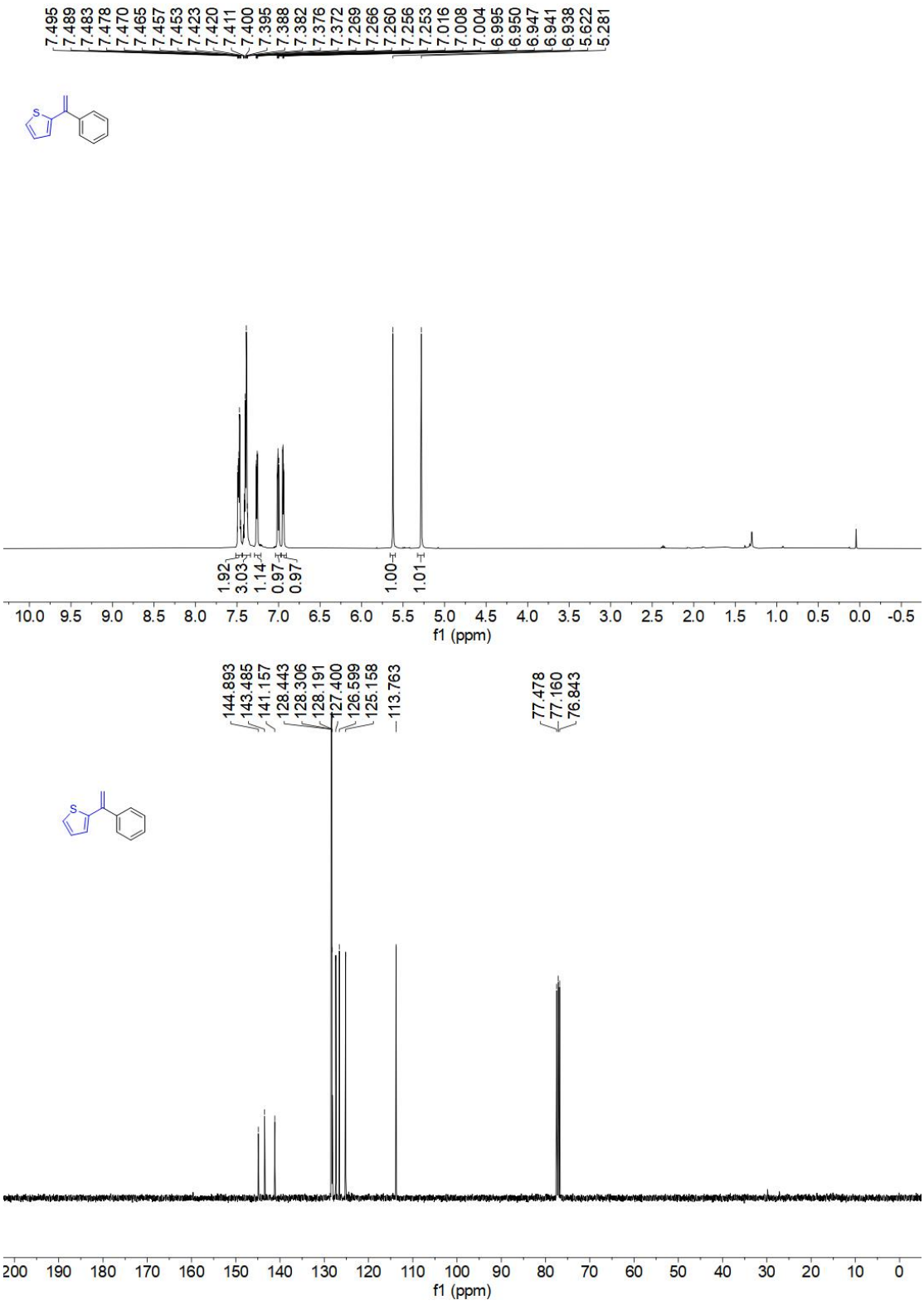
133.413
133.334
128.375
127.995
127.842
127.629
126.744
126.481
126.429
124.925
124.576
123.906
122.291
116.514
77.477
77.160
76.843
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.478
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7.465
7.457
7.453
7.423
7.420
7.411
7.400
7.395
7.388
7.382
7.376
7.372
7.269
7.266
7.260
7.256
7.253
7.016
7.008
7.004
6.995
6.950
6.947
6.941
6.938
5.622
5.281
1.92
3.03
1.14
0.97
0.97
1.00
1.01
f1 (ppm)
144.893
143.485
141.157
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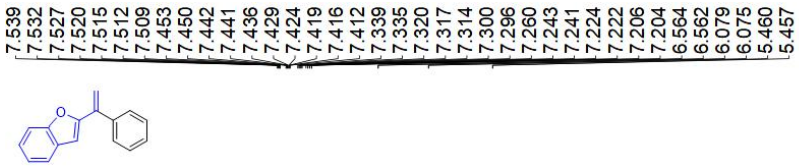
128.191
127.400
126.599
125.158
113.763
77.478
77.160
76.843
f1 (ppm)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7.532
7.527
7.520
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7.512
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7.453
7.450
7.442
7.441
7.436
7.429
7.424
7.419
7.416
7.412
7.339
7.335
7.320
7.317
7.314
7.300
7.296
7.260
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6.562
6.079
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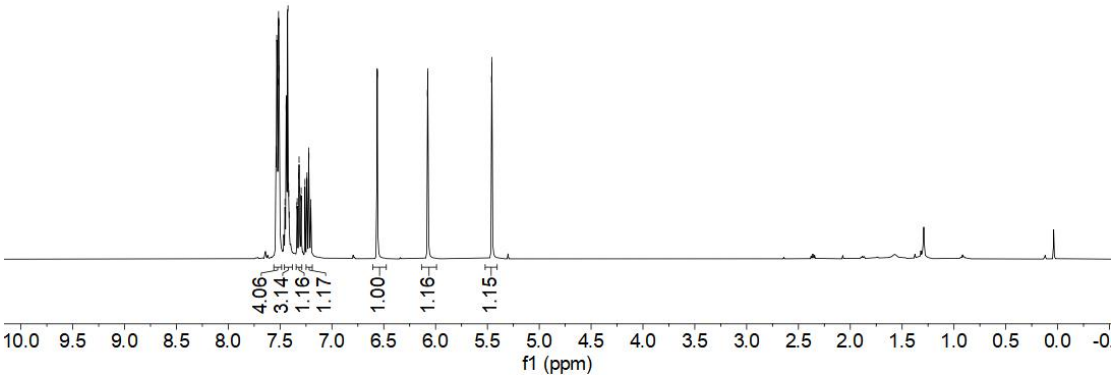
5.460
5.457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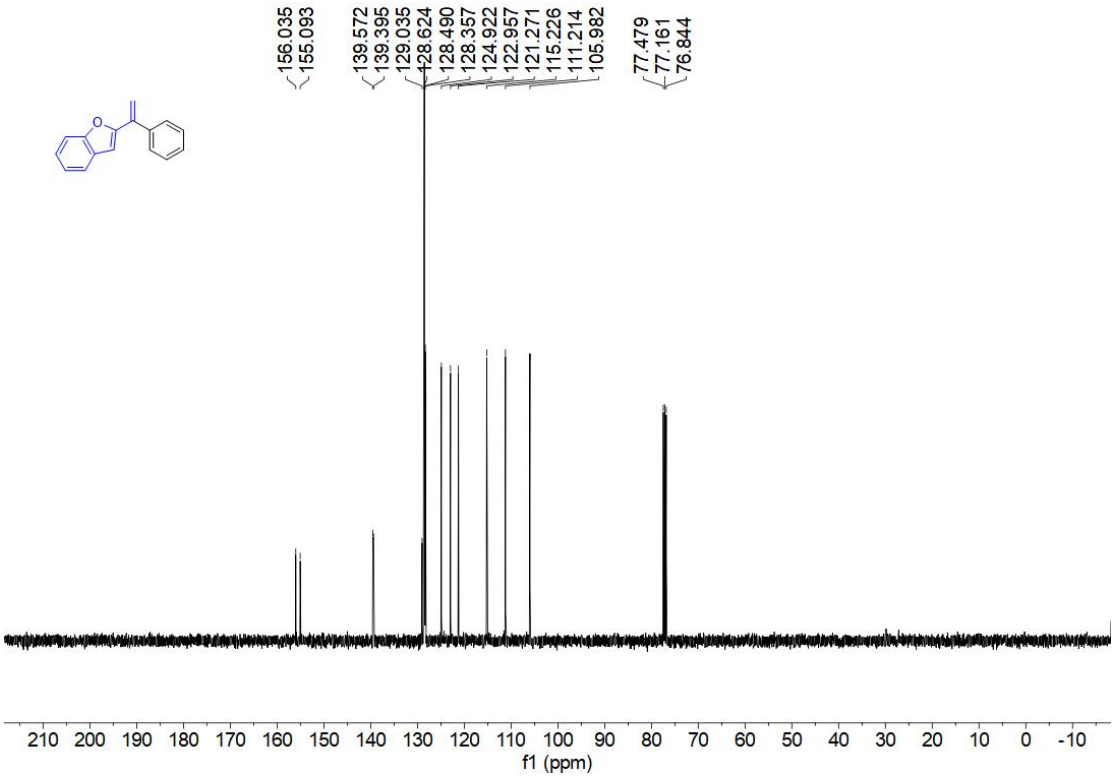
3.14
1.16
1.17
1.00
1.16
1.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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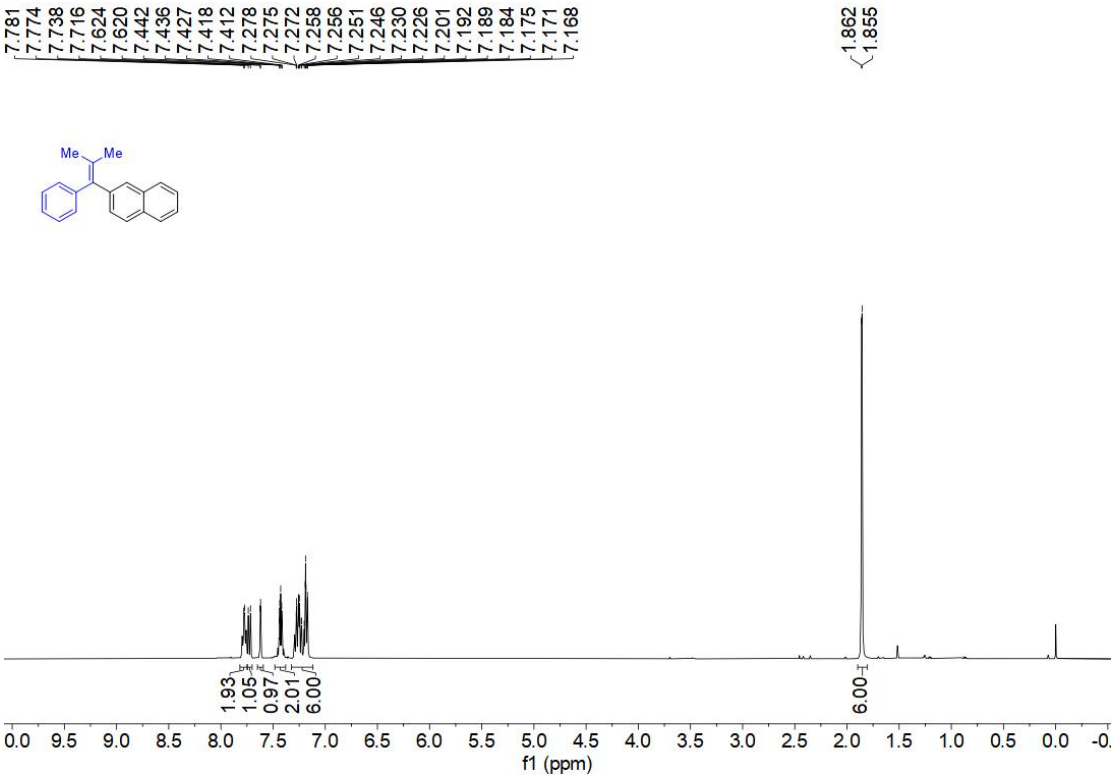
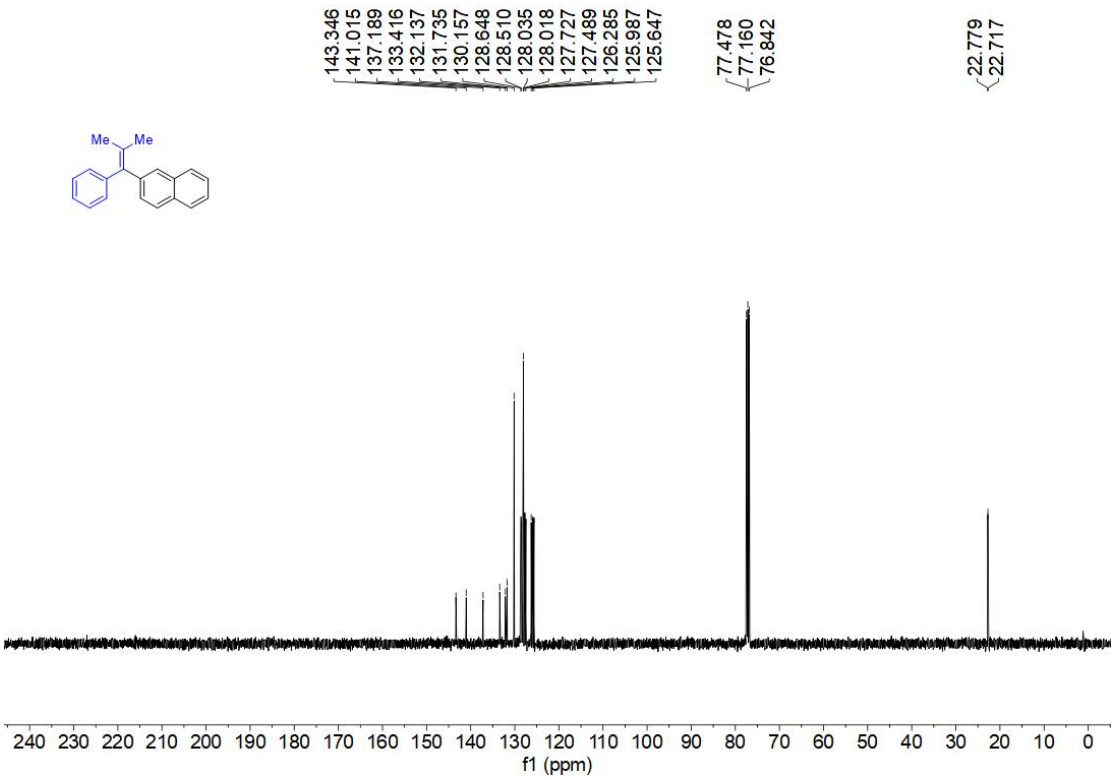
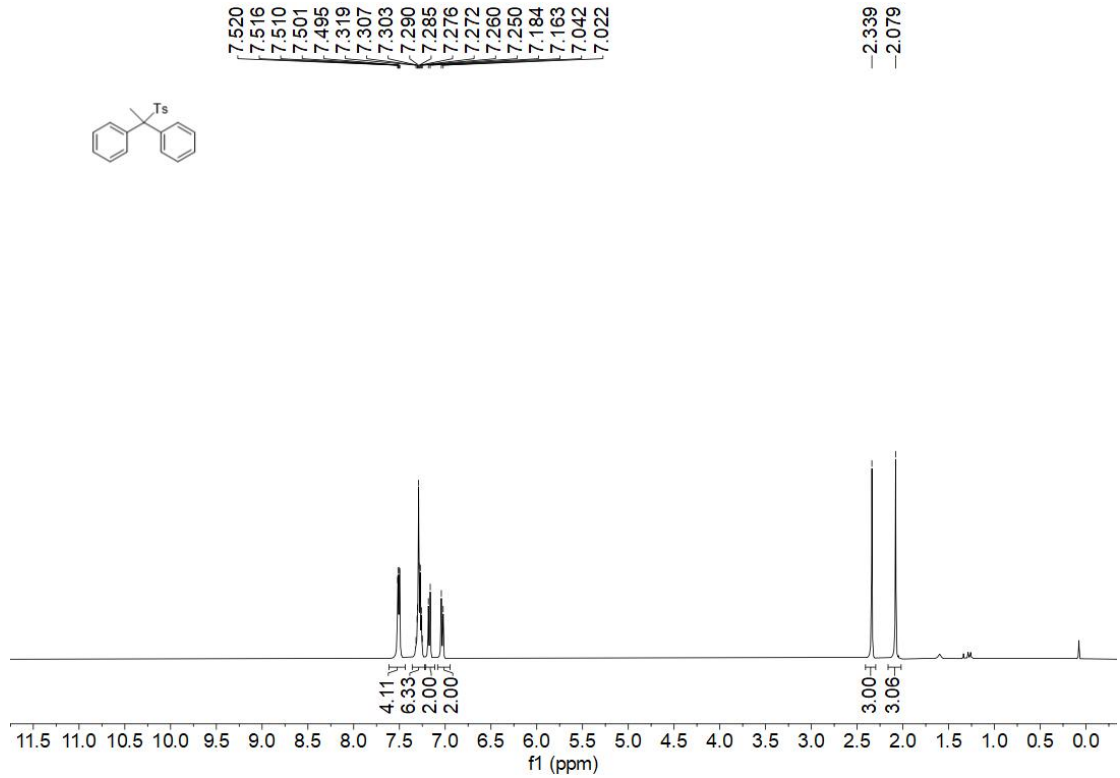
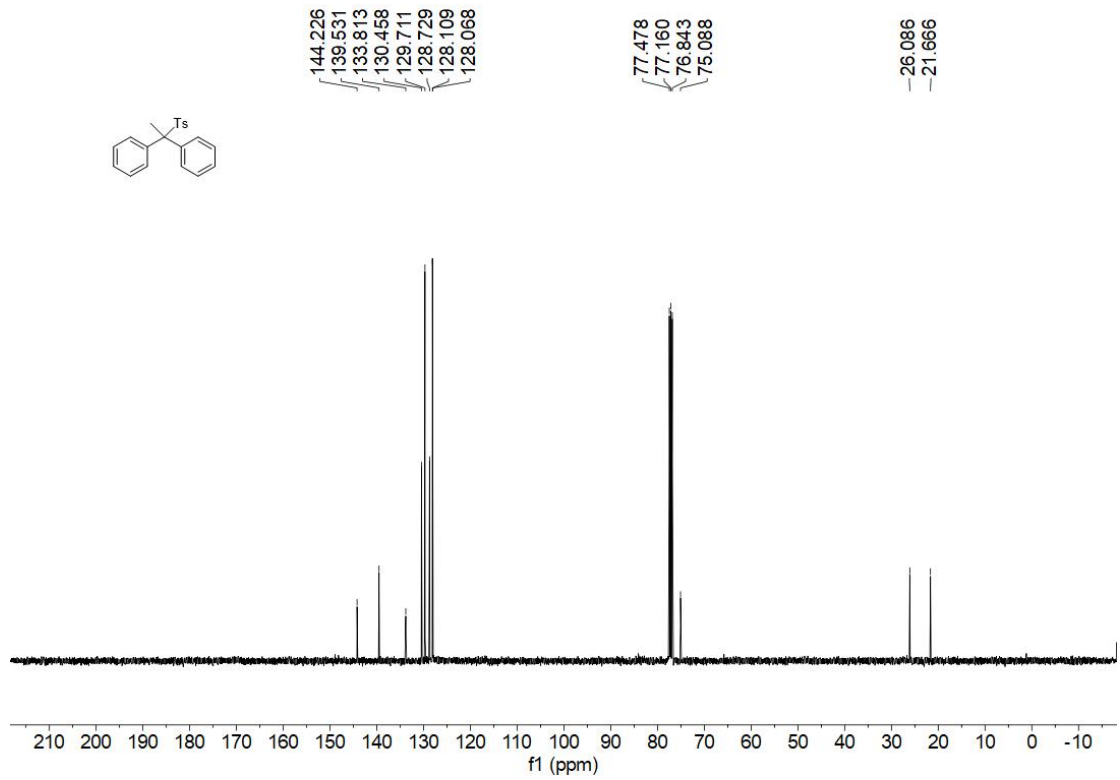
155.093
139.572
139.395
129.035
128.624
128.490
128.357
124.922
122.957
121.271
115.226
111.214
105.982
77.479
77.161
76.844
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.781
7.774
7.738
7.716
7.624
7.620
7.442
7.436
7.427
7.418
7.412
7.278
7.275
7.272
7.258
7.256
7.251
7.246
7.230
7.226
7.201
7.192
7.189
7.184
7.175
7.171
7.168
1.862
1.855
Me
Me
1.93
1.05
0.97
2.01
6.00
6.00
f1 (ppm)


143.346
141.015
137.189
133.416
132.137
131.735
130.157
128.648
128.510
128.035
128.018
127.727
127.489
126.285
125.987
125.647
77.478
77.160
76.842
22.779
22.717
Me
Me
f1 (ppm)


7.520
7.516
7.510
7.501
7.495
7.319
7.307
7.303
7.290
7.285
7.276
7.272
7.260
7.250
7.184
7.163
7.042
7.022
2.339
2.079
Ts
4.11
6.33
2.00
2.00
3.00
3.06
f1 (ppm)


144.226
139.531
133.813
130.458
129.711
128.729
128.109
128.068
77.478
77.160
76.843
75.088
26.086
21.666
Ts
f1 (ppm)