Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

A meta-Selective-C-H Alkenylation of Phenol-derivatives Employing a Traceless Organosilicon Template

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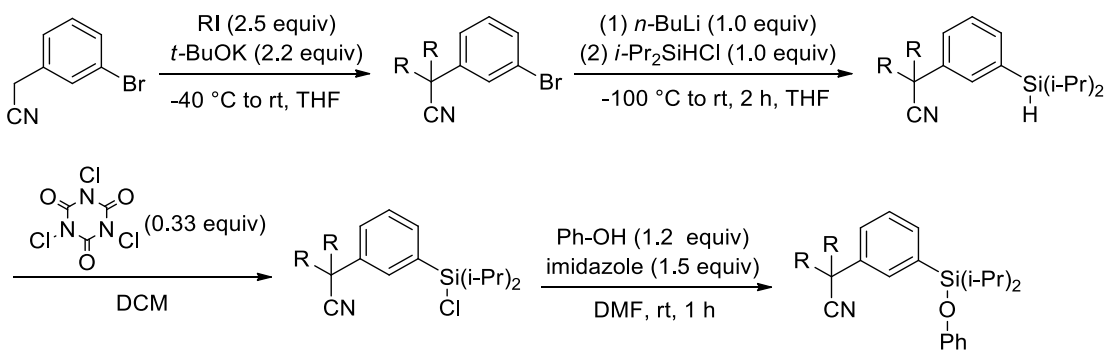
1. General Information

All commercial reagents of analytical grade were used without further purification. Tetrahydrofuran (THF), dichloromethane (DCM), dichloroethane (DCE), and hexafluoroisopropanol (HFIP) were dried with standard procedures and stored over 4 Å molecular sieves. Unless otherwise mentioned, all reactions were carried out under inert atmosphere using standard Schlenk techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Ascend 500 (500 MHz and 125 MHz respectively) instrument. High-resolution mass spectra (HRMS) were recorded on a Q-TOF micromass (YA-105) and Bruker Maxis Impact system (282001.00081) mass spectrometer in positive ESI mode.

2. Experimental Section

2.1 Typical procedure for the preparation of phenol substrates with organosilicon template.



Step 1:To a solution of 2-(3-bromophenyl)-acetonitrile (392.1 mg, 2.0 mmol) in THF (6.0 mL) was added potassium tert-butoxide (493.7 mg, 4.4 mmol) portionwise at -40 °C under stirring. After15 min, alkyl iodide (5.0 mmol) was added, and the mixture was warmed to room temperature and further stirred for 1h. The resulting mixture was then filtered off and the filtrate was concentrated in vacuo. A column chromatography on silica gel (petrolium ether/ethyl acetate = 30/1) afforded the α,α'-dialkyl substituted 2-(3-bromophenyl)-acetonitrile as colorless oil.

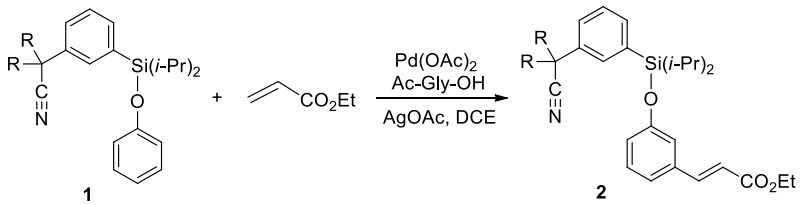
Step 2: To a solution of arylbromide (2.0 mmol) in tetrahydrofuran (6 mL) was added n-BuLi (0.8 mL, 2.5 M, 2.0 mmol) at -100 °C in a liquid nitrogen/ ethanol bath. After stirring for 30min at -100 °C, chlorodiisopropylsilane (341.0 µL, 2.0 mmol)was added and the mixture was allowed to warm to room temperature and further stirred for 2h. The resulting mixture was added with silica gel to quench the reaction, and a column chromatography on silica gel (petrolium ether/ethyl acetate = 30/1) afforded the silane product as colorless oil.

Step 3: To a suspension of trichloroisocyanuric acid (153.4 mg, 0.66 mmol) in dichloromethane (0.3 M) was added previously synthesized silane (2.0 mmol) in dichloromethane (4.0 mL) at 0°C. After being stirred for 1h at room temperature, the mixture was filtered off and the filtrate was concentrated in vacuo to give the corresponding chlorosilane product.

Step 4: Phenol (2.4 mmol, 1.2 equiv) and imidazole (204.2 mg, 3.0 mmol) was dissolved in 3 mL dry DMF. After being stirred for 30min, a solution of chlorosilane (2.0 mmol) in 3 mL DMF was added, and the mixture was further stirred for 1 h. When the reaction was completed, the mixture was added with water and then extracted with diethyl ether for three times (10 mL×3). The combined organic layer was further washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, filtered, and finally concentrated in vacuo. Finally, a column chromatography on silica gel (petrolium ether/ethyl acetate =15/1) afforded the desired phenol substrate as colorless oil.

2.2 Optimization of reaction conditions.

Table S1**.** Modification of the directing group [a]



entry	R	Yield (%) [b]	meta:others [c]
1	Me(**1aa**)	17	70:30 (**2aa**)
2	Et(**1a**)	31	88:12 (**2a**)
3	i-Pr(**1ac**)	22	65:35 (**2ac**)
4	Cy(**1ad**)	25	57:43 (**2ad**)

[a] The reactions were carried out using **1** (0.1 mmol), ethyl acrylate (0.15 mmol), AgOAc (3equiv), $Pd(OAc)_2$ (20 mol%), Ac-Gly-OH (40 mol%) in DCE(1 mL) at 60 ºC for 24 h. [b] Isolate yields. [c] Determined by ^1H NMR.

***Analysis of the Crude ^{1}H NMR for* 2a**

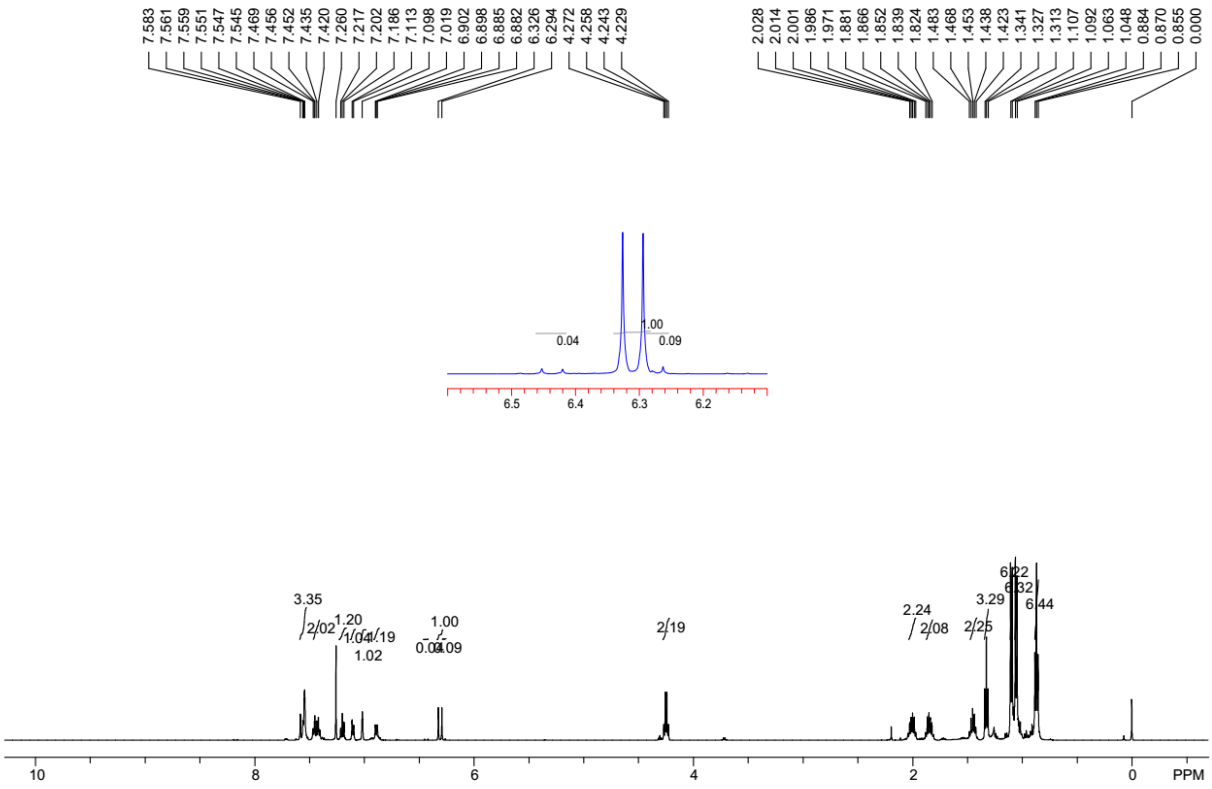
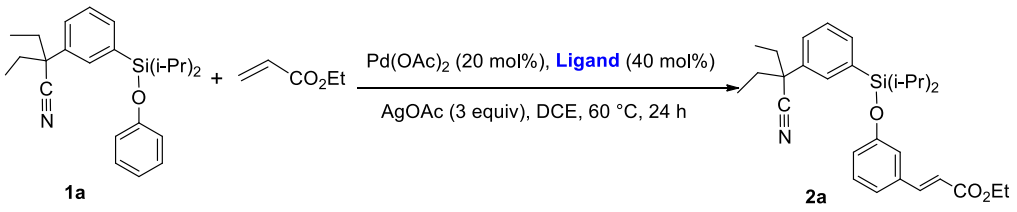


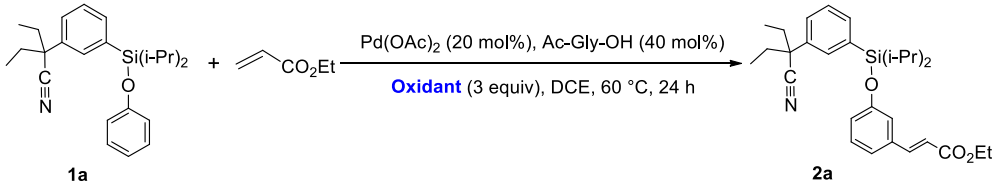
Table S2. Ligand screening [a]



Entry	Ligand	Yield (%) [b]	meta:others [c]
1	Ac-Gly-OH	31	88:12
2	Ac-Ala-OH	26	70:30
3	Ac-Val-OH	30	63:37
4	Ac-Phe-OH	28	75:25
5	Ac-Leu-OH	26	77:23
6	Ac-Ile-OH	27	69:31

[a] The reactions were carried out using **1a** (0.1 mmol), ethyl acrylate (0.15 mmol), AgOAc (3 equiv), DCE (1 mL), $Pd(OAc)_2$ (20 mol%), Ligand (40 mol%) at 60 ºC for 24 h. [b] Isolate yields. [c] Determined by ^{1}H NMR.

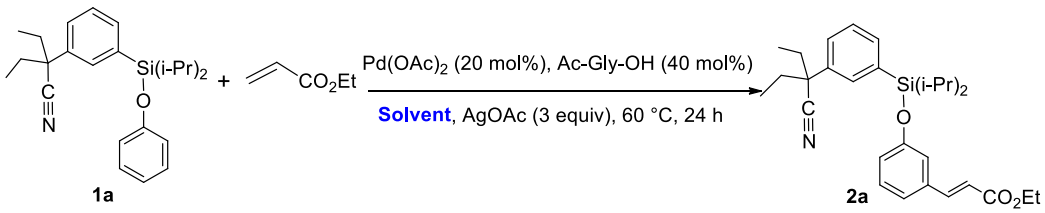
Table S3. Oxidant screening [a]



Entry	Oxidant	Yield (%) [b]	meta:others [c]
1	AgOAc	31	88:12
2	CuOAc	20	83:17
3	Ag_2O	0	-
4	$AgNO_3$	19	75:25
5	Ag_2CO_3	24	77:23

[a] The reactions were carried out using **1a** (0.1 mmol), ethyl acrylate (0.15 mmol), oxidant (3 equiv), DCE (1 mL), $Pd(OAc)_2$ (20 mol%), Ac-Gly-OH (40 mol%) at 60 ºC for 24 h. [b] Isolate yields. [c] Determined by ^1H NMR.

Table S4. Solvent screening and further modifications [a]

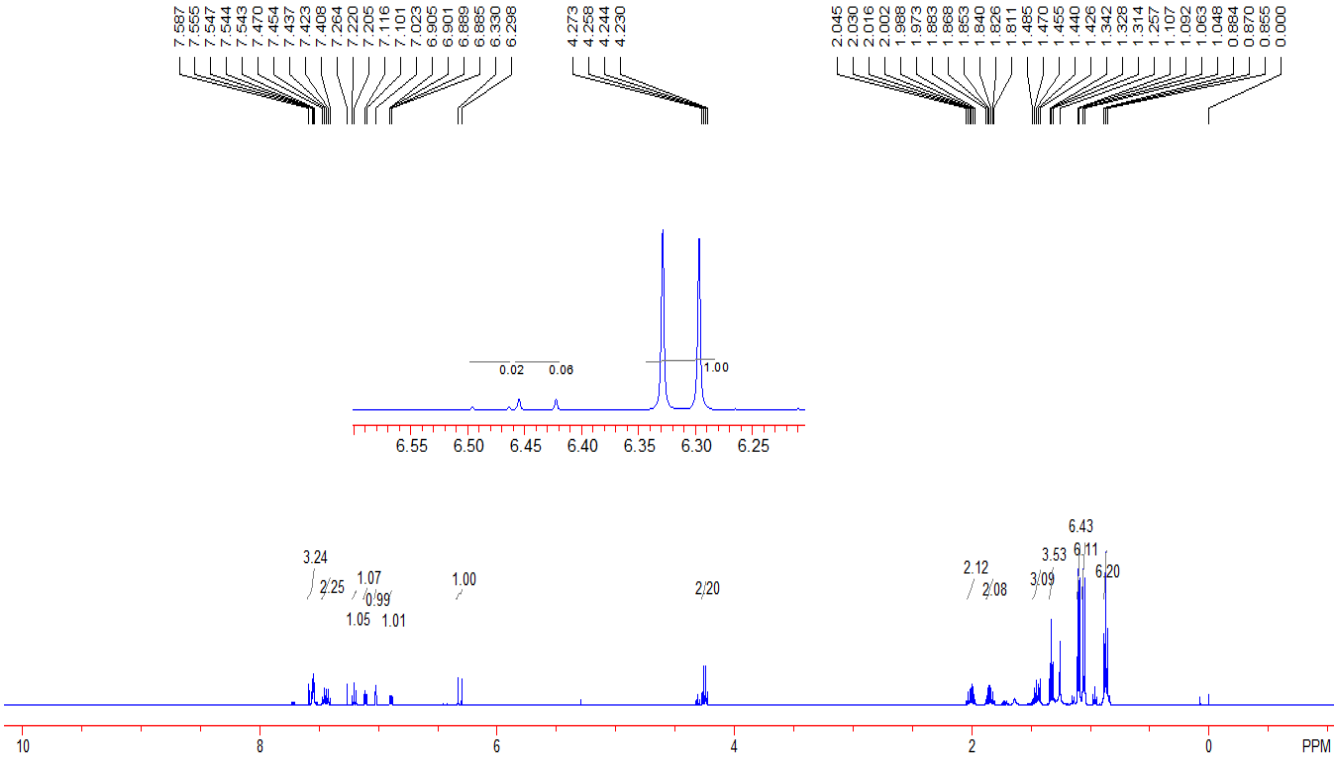


Entry	Solvent (mL)	AgOAc (equiv)	$Pd(OAc)_2$ (mol%)	Yield (%) [b] m:others [c]
1	DCE	3	20	31(88:12)
2	HFIP	3	20	25(90:10)
3	Toluene	3	20	0
4	TFA	3	20	16(86:14)
5	tert-Butylbenzene	3	20	22(84:16)
6	DCE/HFIP (0.9:0.1)	3	20	59(80:20)
7	DCE/HFIP (0.8:0.2)	3	20	64(82:18)
8	DCE/HFIP (0.7:0.3)	3	20	73(80:20)
9	DCE/HFIP (0.6:0.4)	3	20	66(85:15)
10	DCE/HFIP (0.5:0.5)	3	20	55(85:15)
11	DCE/HFIP (1:0.1)	3	20	75(86:14)
12	DCE/HFIP (1:0.3)	3	20	80(88:12)

13	DCE/HFIP (1:0.3) [d]	3	20	0
14	DCE/HFIP (1:0.3) [e]	3	20	79(81:19)
15	DCE/HFIP (1:0.3) [f]	3	20	77(80:20)
16	DCE/HFIP (1:0.3)	3	10	80(90:10)
17	DCE/HFIP (1:0.3)	3	5	65(85:15)
18	DCE/HFIP (1:0.3)	2	10	82(92:8)

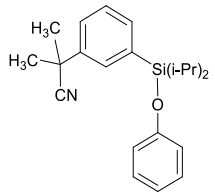
[a] The reactions were carried out using **1a** (0.1 mmol), ethyl acrylate (0.15 mmol), AgOAc, $Pd(OAc)_2$, Ac-Gly-OH, 24 h. [b] Isolate yields. [c] Determined by ^1H NMR. [d] rt. [e] 90 ºC. [f] 120 ºC.

Analysis of the Crude ^1H NMR for* 2a *under the optimal conditions:



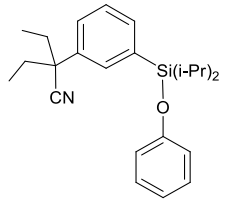
2.3 Characteristic data of phenol substrates with organosilicon template

2-(3-(diisopropyl(phenoxy)silyl)phenyl)-2-methylpropanenitrile (1aa)



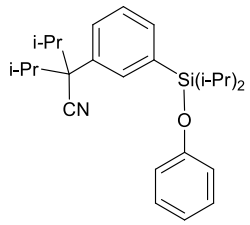
Colorless oil; yield: 0.60 g (85 %); ^{1}HNMR ($CDCl_3$, 500 MHz) δ7.67 (s, 1H), 7.57 (d, *J*=7.0 Hz, 1H), 7.53 (d, *J*=8.0 Hz, 1H), 7.41 (t, *J*=7.5 Hz, 1H),7.20 (t, *J*=8.5 Hz, 2H), 6.94 (t, *J*=7.5 Hz, 1H), 6.90 (d, *J*=8.5 Hz, 2H), 1.69 (s, 6H), 1.48-1.40 (m, 2H), 1.09 (d, *J*=7.5 Hz, 6H), 1.05 (d, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.51, 140.49, 134.98, 133.90, 131.03, 129.38, 128.16, 126.25, 124.47, 121.34, 119.82, 37.10, 29.03, 17.30, 17.10, 12.56; HRMS (ESI): $[M+Na]^+$calcd for $C_{22}H_{29}NNaOSi$: 374.1911, found: 374.1913.

2-(3-(diisopropyl(phenoxy)silyl)phenyl)-2-ethylbutanenitrile (1a)



Colorless oil; yield: 0.68 g (89 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.59-7.54 (m, 2H), 7.48-7.44 (m, 1H), 7.43-7.35 (m, 1H), 7.19 (t, *J*=8.5 Hz, 2H), 6.95-6.86 (m, 3H), 2.07-1.95 (m,2H), 1.88-1.79 (m, 2H), 1.50-1.40 (m, 2H), 1.09 (d, *J*=7.0 Hz, 6H), 1.05 (d, *J*=7.0 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.46, 136.98, 134.52, 133.62, 131.91, 129.28, 128.06, 127.52, 125.98, 121.24, 119.72, 49.66, 33.64, 17.25, 17.05, 12.48, 9.53; HRMS (ESI):$[M+Na]^+$calcd for $C_{24}H_{33}NNaOSi$: 402.2224, found: 402.2240.

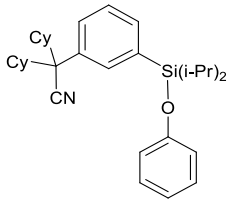
2-(3-(diisopropyl(phenoxy)silyl)phenyl)-2-isopropyl-3-methylbutanenitrile (1ac)



Colorless oil; yield: 0.66 g (81 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.60-7.53 (m, 2H), 7.49-7.43 (m, 1H), 7.39 (t, *J*=7.5 Hz, 1H), 7.21-7.17 (m, 2H), 6.93 (t, *J*=7.5 Hz, 1H), 6.88 (d, *J*=8.5 Hz, 2H), 2.48-2.38 (m, 2H), 1.50-1.40 (m, 2H), 1.09 (d, *J*=7.5 Hz, 6H), 1.05 (d, *J*=7.5 Hz, 6H), 1.01 (d, *J*=7.5 Hz, 6H), 0.83 (d, *J*=6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.59, 133.86, 133.81, 133.77, 131.03, 130.49, 129.39,

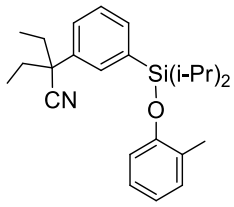
127.51, 121.82, 121.29, 119.80, 57.90, 32.46, 18.79, 17.54, 17.37, 17.20, 12.71; HRMS (ESI): $[M+Na]^+$calcd for $C_{26}H_{37}NNaOSi$: 430.2537, found: 430.2543.

2,2-dicyclohexyl-2-(3-(diisopropyl(phenoxy)silyl)phenyl)acetonitrile (1ad)



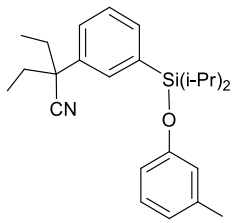
Colorless oil; yield: 0.74 g (75 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58-7.46 (m, 2H), 7.40-7.28 (m, 3H), 7.24-7.14 (m, 2H), 6.95-6.85 (m, 2H), 1.97-1.87 (m, 3H), 1.76-1.74 (m, 3H), 1.70-1.58 (m, 6H), 1.52-1.42 (m, 3H), 1.32-1.22 (m, 7H), 1.09 (d, *J*=7.0 Hz, 6H), 1.04 (d, *J*=7.0 Hz, 6H), 0.83 (t, *J*=7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.58, 140.80, 134.54, 133.55, 130.63, 130.13, 129.35, 127.54, 122.31, 121.27, 119.75, 47.09, 41.64, 36.86, 28.95, 28.67, 27.61, 27.45, 26.43, 26.37, 26.24, 26.14, 26.08, 25.83, 25.59, 17.37, 17.18, 13.71, 12.86; HRMS (ESI):$[M+Na]^+$ calcd for $C_{32}H_{45}NNaOSi$: 510.3163, found: 510.3185.

2-(3-(diisopropyl(o-tolyloxy)silyl)phenyl)-2-ethylbutanenitrile (1b)



Colorless oil; yield: 0.62 g (79 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.59-7.54 (m, 2H), 7.50-7.45 (m, 1H), 7.40 (t, *J*=8.0 Hz, 1H), 7.14 (d, *J*=6.5 Hz, 1H), 6.95 (t, *J*=7.5 Hz, 1H), 6.83 (t, *J*=7.0 Hz, 1H), 6.69 (d, *J*=8.0 Hz, 1H), 2.29 (s, 3H), 2.06-1.94 (m, 2H), 1.89-1.79 (m, 2H), 1.53-1.42 (m, 2H), 1.11 (d, *J*=7.5 Hz, 6H), 1.05 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ153.83, 137.09, 135.00, 133.58, 131.86, 130.93, 128.44, 128.09, 127.68, 126.44, 122.18, 121.02, 118.18, 49.73, 33.71, 17.47, 17.26, 16.92, 12.97, 9.57; HRMS (EI): calcd for $C_{25}H_{35}NOSi$: 393.2488, found:393.2484.

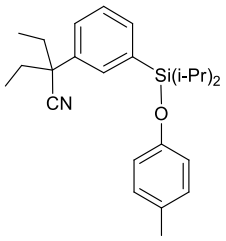
2-(3-(diisopropyl(m-tolyloxy)silyl)phenyl)-2-ethylbutanenitrile (1c)



Colorless oil; yield: 0.67 g (85 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.58-7.52 (m, 2H), 7.48-7.44 (m, 1H), 7.43-7.38 (m, 1H), 7.06 (t, *J*=7.5 Hz, 1H), 6.77-6.71 (m, 2H), 6.67 (d, *J*=8.0 Hz, 1H), 2.26 (s, 3H), 2.05-1.96 (m, 2H),1.90-1.80 (m, 2H), 1.47-1.39 (m, 2H), 1.09 (d, *J*=7.5 Hz, 6H), 1.04 (d, *J*=7.5 Hz, 6H), 0.87

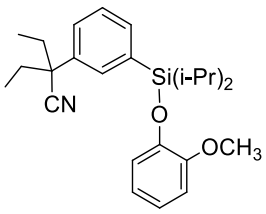
(t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 155.47, 139.35, 137.00, 134.77, 133.68, 131.93, 129.00, 128.07, 127.59, 122.19, 122.09, 120.55, 116.68, 49.74, 33.71, 21.29, 17.34, 17.15, 12.59, 9.59; HRMS(EI): calcd for $C_{25}H_{35}NOSi$: 393.2488, found: 393.2476.

2-(3-(diisopropyl(p-tolyloxy)silyl)phenyl)-2-ethylbutanenitrile (1d)



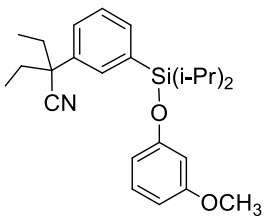
Colorless oil; yield: 0.65 g (82 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.59-7.52 (m, 2H), 7.48-7.43 (m, 1H), 7.42-7.35 (m, 1H), 6.98 (d, *J*=8.0 Hz, 2H), 6.78 (d, *J*=8.0 Hz, 2H), 2.24 (s, 3H), 2.05-1.95 (m, 2H),1.90-1.80 (m, 2H),1.48-1.39 (m, 2H), 1.09 (d, *J*=7.5 Hz, 6H), 1.05 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.18, 136.94, 134.69, 133.62, 131.93, 130.34, 129.71, 128.01, 127.46, 122.05, 119.41, 49.66, 33.62, 20.38, 17.26, 17.06, 12.49, 9.49; HRMS(EI): calcd for $C_{25}H_{35}NOSi$: 393.2488, found: 393.2477.

2-(3-(diisopropyl(2-methoxyphenoxy)silyl)phenyl)-2-ethylbutanenitrile (1e)



Colorless oil; yield: 0.66 g (80 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.63-7.59 (m, 2H), 7.45-7.42 (m, 1H), 7.40-7.35 (m, 1H), 6.90-6.86 (m, 2H), 6.85-6.82 (m, 1H),6.79-6.75 (m, 1H), 3.72 (s, 3H), 2.03-1.94 (m, 2H), 1.89-1.80 (m, 2H),1.49-1.41 (m, 2H), 1.10-1.04 (m, 12H), 0.86 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.50, 144.75, 136.68, 135.16, 133.39, 131.69, 127.72, 127.23, 122.05, 121.63, 120.59, 120.23, 111.98, 55.09, 49.58, 33.57, 17.24, 17.06, 12.75, 9.46; HRMS (ESI): $[M+Na]^+$calcd for $C_{25}H_{35}NNaO_2Si$: 432.2329, found: 432.2333.

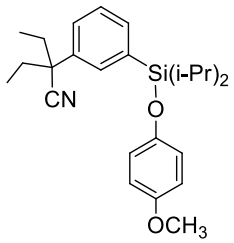
2-(3-(diisopropyl(3-methoxyphenoxy)silyl)phenyl)-2-ethylbutanenitrile (1f)



Colorless oil; yield: 0.72 g (88 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.59-7.55 (m, 2H), 7.48-7.44 (m, 1H), 7.43-7.38 (m, 1H), 7.11-7.05 (m, 1H), 6.53-6.45 (m, 3H), 3.71 (s, 3H), 2.06-1.96 (m, 2H), 1.89-1.80 (m, 2H), 1.49-1.41 (m, 2H), 1.10 (d, *J*=7.5 Hz, 6H), 1.05 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C

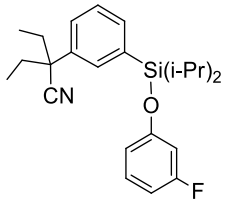
NMR ($CDCl_3$, 125 MHz)δ 160.59, 156.61, 137.01, 134.47, 133.61, 131.94, 129.58, 128.07, 127.50, 122.08, 112.17, 106.81, 105.96, 54.99, 49.67, 33.64, 17.26, 17.06, 12.49, 9.51; HRMS(EI): calcd for $C_{25}H_{35}NO_2Si$: 409.2437, found: 409.2428.

2-(3-(diisopropyl(4-methoxyphenoxy)silyl)phenyl)-2-ethylbutanenitrile (1g)



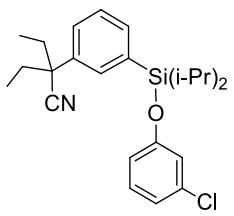
Colorless oil; yield: 0.66 g (80 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.60-7.55 (m, 2H), 7.48-7.44 (m, 1H), 7.43-7.38 (m, 1H), 6.84-6.79 (m, 2H), 6.75-6.71 (m, 2H), 3.72 (s, 3H), 2.06-1.97 (m, 2H),1.90-1.81 (m, 2H),1.46-1.37 (m, 2H), 1.08 (d, *J*=7.0 Hz, 6H), 1.04 (d, *J*=8.0 Hz, 6H), 0.88 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.96, 149.22, 136.95, 134.67, 133.63, 131.96, 128.03, 127.43, 122.08, 120.20, 114.30, 55.41, 49.66, 33.63, 17.25, 17.05, 12.42, 9.51. HRMS (EI): calcd for $C_{25}H_{35}NO_2Si$:409.2437, found: 409.2438.

2-ethyl-2-(3-((3-fluorophenoxy)diisopropylsilyl)phenyl)butanenitrile (1h)



Colorless oil; yield: 0.57 g (72 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.57-7.53 (m, 2H), 7.48-7.45 (m, 1H), 7.44-7.37 (m, 1H), 7.16-7.09 (m, 1H), 6.69-6.62 (m, 2H), 6.61-6.56 (m, 1H), 2.06-1.97 (m, 2H),1.90-1.81 (m, 2H),1.50-1.40 (m, 2H), 1.10 (d, *J*=7.5 Hz, 6H), 1.05 (d, *J*=7.5 Hz, 6H), 0.88 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ164.27, 162.32, 156.84 (d, *J*=11.0 Hz), 137.19, 134.04, 133.61, 131.97, 129.94 (d, *J*=11.0 Hz), 128.24, 127.67, 122.05, 115.59 (d, *J*=3.8 Hz), 108.22 (d, *J*=23.0 Hz), 107.42 (d, *J*=22.6 Hz), 49.73, 33.69, 17.23, 17.04, 12.48, 9.53; HRMS (EI): calcd for$C_{24}H_{32}NOFSi$: 397.2237, found: 397.2230.

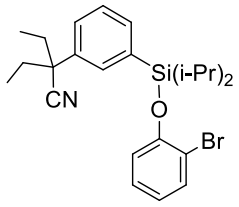
2-(3-((3-chlorophenoxy)diisopropylsilyl)phenyl)-2-ethylbutanenitrile (1i)



Colorless oil; yield: 0.69 g (83 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.57-7.53 (m, 2H), 7.48-7.45 (m, 1H), 7.44-7.39 (m, 1H), 7.12-7.07 (m, 1H), 6.92-6.87 (m, 2H), 6.79-6.75 (m, 1H), 2.06-1.97 (m, 2H), 1.90-

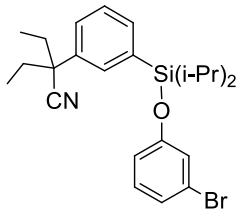
1.81 (m, 2H),1.50-1.41 (m, 2H), 1.10 (d, *J*=7.5 Hz, 6H), 1.06 (d, *J*=7.5 Hz, 6H), 0.88 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.27, 137.19, 134.43, 133.94, 133.53, 131.91, 129.98, 128.22, 127.63, 121.95, 121.48, 120.19, 118.02, 49.67, 33.64, 17.20, 17.01, 12.45, 9.50; HRMS(EI): calcd for$C_{24}H_{32}NOClSi$: 413.1942, found: 413.1935.

2-(3-((2-bromophenoxy)diisopropylsilyl)phenyl)-2-ethylbutanenitrile (1j)



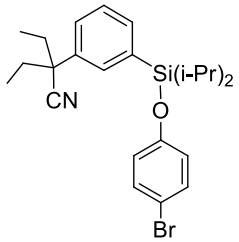
Colorless oil; yield: 0.73 g (80 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.63-7.59 (m, 2H), 7.54-7.48 (m, 2H), 7.44-7.36 (m, 1H), 7.08-7.03 (m, 1H), 6.80-6.76 (m, 2H), 2.07-1.97 (m, 2H), 1.94-1.83 (m, 2H), 1.56-1.47 (m, 2H), 1.14 (d, *J*=7.5 Hz, 6H), 1.09 (d, *J*=7.5 Hz, 6H), 0.86 (t, *J*=8.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.37, 137.13, 134.06, 133.58, 131.83, 128.66, 128.08, 127.46, 125.98, 122.27, 122.09, 119.69, 114.82, 49.68, 33.65, 17.35, 17.20, 12.88, 9.53; HRMS(ESI): $[M+Na]^+$ calcd for$C_{24}H_{32}BrNNaOSi$: 480.1329, found: 480.1330.

2-(3-((3-bromophenoxy)diisopropylsilyl)phenyl)-2-ethylbutanenitrile (1k)



Colorless oil; yield: 0.75 g (82 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.56-7.51 (m, 2H), 7.49-7.45 (m, 1H), 7.44-7.37 (m, 1H), 7.09-7.02 (m, 3H), 6.81-6.77 (m, 1H), 2.07-1.97 (m, 2H), 1.90-1.81 (m, 2H),1.48-1.39 (m, 2H), 1.09 (d, *J*=7.5 Hz, 6H), 1.05 (d, *J*=7.5 Hz, 6H), 0.88 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 156.40, 137.26, 134.03, 133.63, 131.92, 130.38, 128.29, 127.79, 124.48, 123.20, 122.44, 122.11, 118.53, 49.76, 33.73, 17.30, 17.11, 12.54, 9.62; HRMS (EI): calcd for$C_{24}H_{32}NOSiBr$: 457.1437, found: 457.1433.

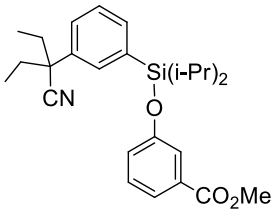
2-(3-((4-bromophenoxy)diisopropylsilyl)phenyl)-2-ethylbutanenitrile (1l)



Colorless oil; yield: 0.78 g (85 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.56-7.50 (m, 2H), 7.47-7.44 (m, 1H), 7.44-7.39 (m, 1H), 7.30-7.25 (m, 2H), 6.77-6.73 (m, 2H), 2.06-1.97 (m, 2H),1.89-1.80 (m, 2H),1.48-

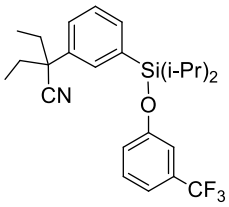
1.39 (m, 2H), 1.09 (d, *J*=7.5 Hz, 6H), 1.04 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 154.73, 137.18, 134.04, 133.62, 132.20, 132.01, 128.24, 127.61, 122.05, 121.56, 113.54, 49.71, 33.68, 17.26, 17.08, 12.47, 9.56; HRMS (EI): calcd for$C_{24}H_{32}NOSiBr$:457.1437, found: 457.1444.

Methyl 3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)benzoate (1m)



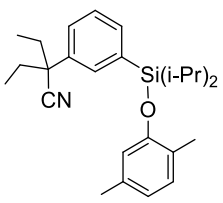
Colorless oil; yield: 0.59 g (68 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.65-7.61 (m, 1H), 7.58-7.53 (m, 3H), 7.48-7.45 (m, 1H), 7.44-7.40 (m, 1H), 6.28-6.24 (m, 1H), 6.08-6.05 (m, 1H), 3.87 (s, 3H), 2.04-1.97 (m, 2H),1.89-1.80 (m, 2H), 1.50-1.43 (m, 2H), 1.10 (d, *J*=7.5 Hz, 6H), 1.05 (d, *J*=8.0 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 166.74, 155.60, 137.20, 134.18, 133.67, 131.92, 131.47, 129.34, 128.26, 127.72, 124.41, 122.57, 122.12, 120.73, 52.06, 49.75, 33.71, 17.31, 17.13, 12.56, 9.56; HRMS(ESI): $[M+H]^+$calcd for$C_{26}H_{36}NO_3Si$: 438.2459, found: 438.2464.

2-(3-(diisopropyl(3-(trifluoromethyl)phenoxy)silyl)phenyl)-2-ethylbutanenitrile (1n)



Colorless oil; yield: 0.67 g (75 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.58-7.54 (m, 2H), 7.50-7.46 (m, 1H), 7.46-7.40 (m, 1H), 7.32-7.26 (m, 1H), 7.21-7.17 (m, 1H), 7.13-7.10 (m, 1H), 7.06-7.02 (m, 1H), 2.06-1.97 (m, 2H), 1.90-1.80 (m, 2H),1.51-1.43 (m, 2H), 1.11 (d, *J*=7.5 Hz, 6H), 1.07 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 155.83, 137.33, 133.86, 133.62, 131.77 (q, *J*=32.5 Hz), 131.97, 129.90, 128.34, 127.74, 123.76 (q, *J*=270.0 Hz), 123.09, 122.04, 117.95 (q, *J*=3.8 Hz), 116.63 (q, *J*=3.8 Hz), 49.76, 33.69, 17.23, 17.03, 12.50, 9.48; HRMS(ESI): $[M+Na]^+$calcd for$C_{25}H_{32}F_3NNaOSi$: 470.2097, found: 470.2104.

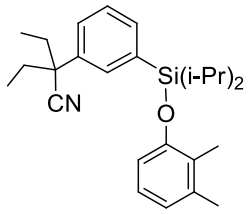
2-(3-((2,5-dimethylphenoxy)diisopropylsilyl)phenyl)-2-ethylbutanenitrile (1o)



White solid; yield: 0.69 g (85 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.59-7.55 (m, 2H), 7.50-7.45 (m, 1H), 7.43-7.36 (m, 1H), 7.03-6.90 (m, 1H), 6.68-6.63 (m, 1H), 6.54-6.50 (m, 1H), 2.24 (s, 3H), 2.15 (s, 3H),

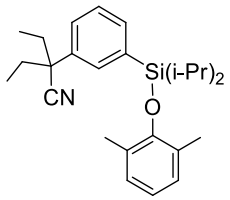
2.05-1.95 (m, 2H), 1.91-1.80 (m, 2H),1.52-1.41 (m, 2H), 1.11 (d, *J*=7.5 Hz, 6H), 1.05 (d, *J*=7.0 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 153.61, 136.98, 136.10, 135.10, 133.49, 131.80, 130.56, 128.02, 127.64, 125.11, 122.13, 121.66, 118.96, 49.70, 33.69, 20.91, 17.44, 17.24, 16.48, 12.95, 9.55; HRMS(ESI): $[M+Na]^+$calcd for$C_{26}H_{37}NNaOSi$: 430.2537, found: 430.2542.

2-(3-((2,3-dimethylphenoxy)diisopropylsilyl)phenyl)-2-ethylbutanenitrile (1p)



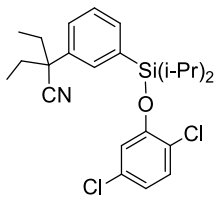
White solid; yield: 0.67 g (82 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.58-7.53 (m, 2H), 7.48-7.44 (m, 1H), 7.42-7.37 (m, 1H), 6.86-6.80 (m, 1H), 6.75-6.72 (m, 1H), 6.59-6.54 (m, 1H), 2.26 (s, 3H), 2.21 (s, 3H), 2.04-1.94 (m, 2H), 1.90-1.80 (m, 2H), 1.53-1.42 (m, 2H), 1.10 (d, *J*=7.5 Hz, 6H), 1.05 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 153.60, 138.20, 137.09, 135.11, 133.63, 131.90, 128.06, 127.66, 116.94, 125.39, 122.68, 122.20, 115.90, 49.74, 33.71, 20.25, 17.49, 17.29, 12.96, 12.46, 9.58; HRMS(ESI): $[M+Na]^+$calcd for$C_{26}H_{37}NNaOSi$: 430.2537, found: 430.2544.

2-(3-((2,6-dimethylphenoxy)diisopropylsilyl)phenyl)-2-ethylbutanenitrile (1q)



White solid; yield: 0.67 mg (82 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.55-7.52 (m, 1H), 7.48-7.46 (m, 1H), 7.41-7.38 (m, 1H), 7.34-7.30 (m, 1H), 6.86-6.83 (m, 2H), 6.72-6.68 (m, 1H), 2.06 (s, 6H), 1.98-1.90 (m, 2H), 1.84-1.77 (m, 2H), 1.46-1.39 (m, 2H), 0.98 (d, *J*=6.0 Hz, 6H), 0.89 (d, *J*=6.5 Hz, 6H), 0.80 (t, *J*=6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 152.95, 136.86, 134.86, 133.46, 131.85, 128.66, 128.20, 127.84, 127.62, 122.20, 121.43, 49.83, 33.80, 18.12, 17.08, 16.92, 12.96, 9.60; HRMS(ESI): $[M+Na]^+$calcd for$C_{26}H_{37}NNaOSi$: 430.2537, found: 430.2546.

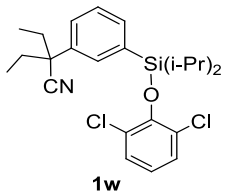
2-(3-((2,5-dichlorophenoxy)diisopropylsilyl)phenyl)-2-ethylbutanenitrile (1r)



White solid; yield: 0.59g (66 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ 7.62-7.59 (m, 1H), 7.59-1.56 (m, 1H), 7.52-7.48 (m, 1H), 7.46-7.41 (m, 1H), 7.29-7.25 (m, 1H), 6.88-6.84 (m, 1H), 6.78-6.76 (m, 1H), 2.07-1.98 (m, 2H), 1.92-1.83 (m, 2H), 1.55-1.46 (m, 2H), 1.13 (d, *J*=7.5 Hz, 6H), 1.09 (d, *J*=7.5 Hz,

6H), 0.88 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 152.04, 137.44, 133.68, 133.56, 132.43, 131.90, 130.76, 128.34, 128.14, 123.82, 122.13, 122.10, 120.37, 49.81, 33.79, 17.32, 17.17, 12.86, 9.61; HRMS(ESI):$[M+Na]^+$ calcd for $C_{24}H_{31}Cl_2NNaOSi$: 470.1444, found: 470.1451.

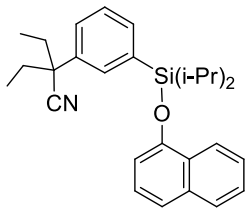
2-(3-((2,6-dichlorophenoxy)diisopropylsilyl)phenyl)-2-ethylbutanenitrile (1s)



1w

White solid; yield: 0.63 g (70 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ 7.64 (s, 1H), 7.58-7.54 (m, 1H), 7.48-7.44 (m, 1H), 7.39-7.34 (m, 1H), 7.19 (d, *J*=8.0 Hz, 2H), 6.82-6.77 (m, 1H), 2.06-1.98 (m, 2H), 1.93-1.84 (m, 2H), 1.73-1.64 (m, 2H), 1.13-1.05 (m, 12H), 0.85 (t, *J*=7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 148.86, 136.75, 133.75, 133.46, 131.91, 128.55, 128.23, 127.80, 127.71, 126.79, 122.19, 49.83, 33.78, 17.17, 17.11, 13.25, 9.60; HRMS(ESI):$[M+Na]^+$ calcd for $C_{24}H_{31}Cl_2NNaOSi$: 470.1444, found: 470.1455.

2-(3-(diisopropyl(naphthalen-1-yloxy)silyl)phenyl)-2-ethylbutanenitrile (1t)



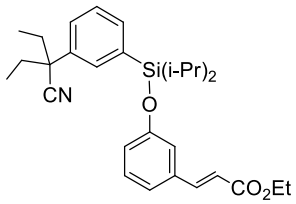
Colorless oil; yield: 0.69 g (80 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ8.35-8.30 (m, 1H), 7.82-7.70 (m, 1H), 7.64-7.59 (m, 2H), 7.51-7.45 (m, 3H), 7.45-7.38 (m, 2H), 7.23-7.16 (m, 1H), 6.79-6.75 (m, 1H), 1.98-1.87 (m, 2H), 1.80-1.71(m, 2H),1.62-1.54 (m, 2H), 1.16 (d, *J*=7.5 Hz, 6H), 1.09 (d, *J*=7.5 Hz, 6H), 0.85 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 151.52, 137.21, 134.93, 134.55, 133.65, 131.78, 128.19, 127.93, 127.59, 127.43, 126.18, 125.64, 125.21, 122.47, 122.16, 120.94, 112.36, 49.67, 33.59, 17.52, 17.35, 12.93, 9.54; HRMS(EI): calcd for$C_{28}H_{35}NOSi$: 429.2488, found: 429.2482.

2.4 General procedure for Pd(II)-catalyzed meta-alkenylation of phenols

In a typical procedure, phenol substrate (0.5mmol), $Pd(OAc)_2$ (11 mg, 10 mol%), *N*-acetyl glycine (Ac-Gly-OH, 11mg, 20 mol%), AgOAc (167 mg, 2 equiv) were mixed in DCE (5.0 mL). The alkenylation reagent (0.75mmol, 1.5 equiv) dissolved in HFIP (1.5 mL) were added sequentially by syringes. The reaction was then allowed to performed at 60 °C with vigorous stirring for 24 h. After the reaction, the mixture was cooled to room temperature and filtered through celite with aid of ethyl acetate (10 mL). The filtrate was then concentrated under the reduced pressure and purified by column chromatography through silica gel using petrolium ether/ethyl acetate as eluent (15/1).

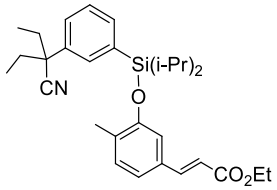
2.5 Characteristic data of meta-alkenylated products

(*E*)-ethyl3-(3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)phenyl)acrylate (2a)



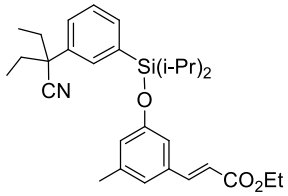
Colorless oil; yield: 196.5 mg (82 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.62-7.54 (m, 3H), 7.49-7.45 (m, 1H), 7.45-7.40 (m, 1H), 7.23-7.18 (m, 1H), 7.14-7.10 (m, 1H), 7.05 (s, 1H), 6.94-6.90 (m, 1H), 6.33 (d, *J*=16.0 Hz, 1H), 4.28-4.22 (m, 2H), 2.06-1.97 (m, 2H), 1.90-1.81 (m, 2H), 1.51-1.42 (m, 2H), 1.32 (t, *J*=7.0 Hz, 3H), 1.11 (d, *J*=7.0 Hz, 6H), 1.06 (d, *J*=7.5 Hz, 6H), 0.86 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 166.84, 155.98, 144.28, 137.24, 135.84, 134.29, 133.67, 132.00, 129.80, 128.27, 127.67, 122.08, 121.76, 121.31, 119.01, 118.40, 60.42, 49.76, 33.71, 17.33, 17.14, 14.25, 12.60, 9.59; HRMS(EI): calcd for $C_{29}H_{40}NO_3Si$: 478.2772, found: 478.2774.

(*E*)-ethyl3-(3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)-4-methylphenyl)acrylate (2b)



Colorless oil; yield: 182.6 mg (74 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.60-7.54 (m, 2H), 7.50-7.40 (m, 3H), 7.15 (d, *J*=7.5 Hz, 1H), 7.03 (d,*J*=7.5 Hz, 1H), 6.83 (s, 1H), 6.14 (d, *J*=15.5 Hz, 1H), 4.28-4.18 (m, 2H), 2.31 (s, 3H), 2.05-1.97 (m, 2H), 1.90-1.80 (m, 2H), 1.52-1.46 (m, 2H), 1.35-1.28 (m, 3H), 1.13 (d, *J*=7.5 Hz, 6H), 1.07 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.92, 154.09, 144.41, 137.21, 134.47, 133.48, 132.98, 131.89, 131.26, 128.24, 127.62, 126.89, 121.98, 121.09, 118.40, 117.22, 116.93, 115.55, 60.35, 49.74, 33.69, 21.17, 17.32, 17.13, 14.22, 12.58, 9.58; HRMS(ESI):$[M+Na]^+$ calcd for $C_{30}H_{41}NNaO_3Si$: 514.2748, found: 514.2766.

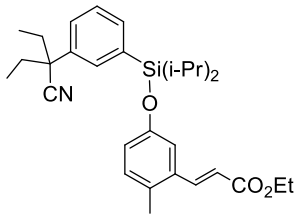
(*E*)-ethyl3-(3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)-5-methylphenyl)acrylate (2c)



Colorless oil; yield: 187.6 mg (76 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.59-7.50 (m, 3H), 7.49-7.37 (m, 2H), 6.94 (s, 1H), 6.83 (s, 1H), 6.75 (s, 1H), 6.30 (d, *J*=16.0 Hz, 1H), 4.29-4.20 (m, 2H), 2.27 (s, 3H), 2.07-1.96 (m, 2H), 1.90-1.80 (m, 2H), 1.51-1.40 (m, 2H), 1.32 (t, *J*=7.0 Hz, 3H), 1.10 (d, *J*=7.5 Hz, 6H), 1.06 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 166.89, 155.84, 144.48,

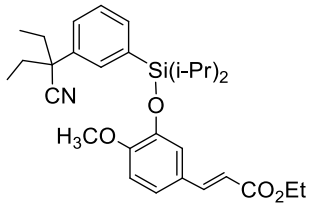
139.85, 137.15, 135.45, 134.38, 133.63, 131.96, 128.22, 127.61, 122.59, 122.17, 122.07, 118.08, 116.08, 60.35, 49.74, 33.69, 21.17, 17.32, 17.13, 14.22, 12.58, 9.58; HRMS(ESI): $[M+H]^+$calcd for$C_{30}H_{42}NO_3Si$: 492.2928, found: 492.2932.

(*E*)-ethyl3-(5-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)-2-methylphenyl)acrylate (2d)



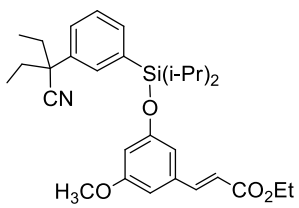
Colorless oil; yield: 170.3 mg (69 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.90-7.83 (m, 1H), 7.58-7.53 (m, 2H), 7.48-7.39 (m, 2H),7.07-7.04 (m, 1H),7.03-6.99 (m, 1H), 6.82-6.77 (m, 1H), 6.16 (d, *J*=15.5 Hz, 1H), 4.29-4.20 (m, 2H), 2.34 (s, 3H), 2.06-1.96 (m, 2H), 1.90-1.80 (m, 2H), 1.51-1.40 (m, 2H), 1.33 (t, *J*=7.0 Hz, 3H), 1.09 (d, *J*=7.5 Hz, 6H), 1.05 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 166.96, 153.87, 142.14, 137.17, 134.48, 134.13, 133.73, 131.95, 131.62, 130.56, 128.23, 127.66, 122.15, 121.61, 119.16, 117.18, 60.46, 49.77, 33.74, 18.86, 17.36, 17.18, 14.29, 12.58, 9.61; HRMS(ESI): $[M+H]^+$calcd for$C_{30}H_{42}NO_3Si$: 492.2928, found: 492.2934.

(*E*)-ethyl3-(3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)-4-methoxyphenyl)acrylate (2e)



Colorless oil; yield: 186.0 mg (73 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.60-7.56 (m, 2H), 7.56-7.53 (m, 1H), 7.53-7.50 (m, 1H),7.47-7.38 (m, 1H),7.12-7.07 (m, 1H), 7.07-7.03 (m, 1H), 6.85-6.78 (m, 1H), 6.17 (d, *J*=16.0 Hz, 1H), 4.29-4.20 (m, 2H), 3.78 (s, 3H), 2.06-1.96 (m, 2H), 1.90-1.80 (m, 2H), 1.51-1.40 (m, 2H), 1.32 (t, *J*=7.0 Hz, 3H), 1.08 (d, *J*=7.0 Hz, 6H), 1.06 (d, *J*=7.5 Hz, 6H), 0.86 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 167.26, 152.70, 145.22, 144.33, 136.96, 134.97, 133.55, 131.83, 128.02, 127.48, 127.36, 123.01, 122.05, 119.09, 115.75, 111.78, 60.30, 55.39, 49.76, 33.76, 17.39, 17.23, 14.32, 12.92, 9.64; HRMS(ESI): $[M+H]^+$calcd for$C_{30}H_{42}NO_4Si$: 508.2878, found: 508.2884.

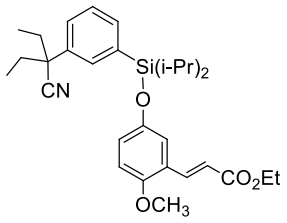
(*E*)-ethyl3-(3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)-5-methoxyphenyl)acrylate (2f)



Colorless oil; yield: 191.1 mg (75 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.50-7.42 (m, 3H), 7.40-7.31 (m, 2H), 6.60-6.54 (m, 2H), 6. 40 (s, 1H), 6.22 (d, *J*=13.5 Hz, 1H), 4.20-4.10 (m, 2H), 3.65 (s, 3H), 1.97-

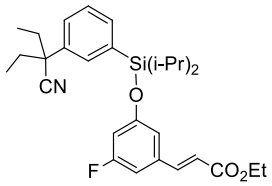
1.89 (m, 2H), 1.81-1.73 (m, 2H), 1.41-1.34 (m, 2H), 1.24 (t, *J*=6.0 Hz, 3H), 1.02 (d, *J*=6.5 Hz, 6H), 0.97 (d, *J*=6.5 Hz, 6H), 0.79 (t, *J*=6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 166.75, 160.77, 156.87, 144.33, 137.16, 136.10, 134.15, 133.61, 131.96, 128.23, 127.59, 122.05, 118.52, 112.03, 107.99, 106.42, 60.41, 55.21, 49.72, 33.68, 17.28, 17.10, 14.20, 12.51, 9.55; HRMS(ESI): $[M+H]^+$calcd for$C_{30}H_{42}NO_4Si$: 508.2878, found: 508.2879.

(*E*)-ethyl3-(5-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)-2-methoxyphenyl)acrylate (2g)



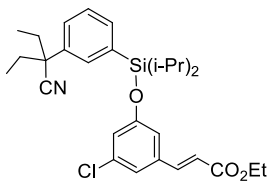
Colorless oil; yield: 168.2 mg (66 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.93-7.85 (m, 1H), 7.58-7.53 (m, 2H), 7.48-7.39 (m, 2H),7.04-7.00 (m, 1H), 6.90-6.84 (m, 1H), 6.77-6.72 (m, 1H), 6.36 (d, *J*=16.5 Hz, 1H), 4.29-4.20 (m, 2H), 3.82 (s, 3H), 2.06-1.96 (m, 2H), 1.91-1.82 (m, 2H), 1.47-1.39 (m, 2H), 1.33 (t, *J*=7.0 Hz, 3H), 1.09 (d, *J*=7.0 Hz, 6H), 1.06 (d, *J*=7.5 Hz, 6H), 0.88 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 167.39, 153.04, 149.12, 139.66, 137.13, 134.47, 133.68, 132.00, 128.22, 127.54, 123.83, 122.37, 122.10, 119.23, 118.73, 112.04, 60.32, 55.81, 49.74, 33.69, 17.31, 17.12, 14.25, 12.50, 9.56; HRMS(ESI): $[M+H]^+$calcd for$C_{30}H_{42}NO_4Si$: 508.2878, found:508.2879.

(*E*)-ethyl3-(3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)-5-fluorophenyl)acrylate (2h)



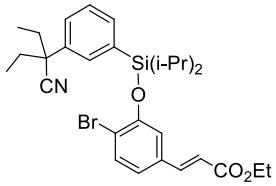
Colorless oil; yield: 159.2 mg (64 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.57-7.51 (m, 2H),7.50-7.40 (m, 3H), 6.85-6.78 (m, 2H), 6.62-6.56 (m, 1H), 6. 30 (d, *J*=16.0 Hz, 1H), 4.30-4.20 (m, 2H), 2.08-1.97 (m, 2H), 1.90-1.82 (m, 2H), 1.51-1.41 (m, 2H), 1.33 (t, *J*=7.0 Hz, 3H), 1.11 (d, *J*=7.5 Hz, 6H), 1,06 (d, *J*=7.5 Hz, 6H), 0.88 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ166.49, 157.18, 143.10 (d, *J*=2.8 Hz), 137.38, 136.78 (d, *J*=9.9 Hz), 133.68 (d, *J*=13.5 Hz), 132.01, 128.42, 127.78, 122.01, 119.68,115.49 (d, *J*=2.8 Hz), 109.16, 108.97, 107.61, 107.43, 60.61, 49.78, 33.74, 17.28, 17.10, 14.22, 12.53, 9.58; HRMS(ESI): $[M+H]^+$calcd for$C_{29}H_{39}FNO_3Si$: 496.2678, found: 496.2687.

(*E*)-ethyl3-(3-chloro-5-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)phenyl)acrylate (2i)



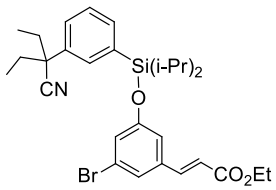
Colorless oil; yield: 192.6 mg (75 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.57-7.51 (m, 2H), 7.50-7.40 (m, 3H), 7.11 (s, 1H), 6.90-6.85 (m, 2H), 6.30 (d, *J*=16.0 Hz, 1H), 4.30-4.20 (m, 2H), 2.07-1.97 (m, 2H), 1.92-1.80 (m, 2H), 1.51-1.41 (m, 2H), 1.32 (t, *J*=7.0 Hz, 3H), 1.11 (d, *J*=7.5 Hz, 6H), 1.06 (d, *J*=7.5 Hz, 6H), 0.88 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 166.43, 156.61, 142.80, 137.40, 136.80, 135.11, 133.71, 133.60, 131.97, 128.42, 127.81, 122.01, 121.70, 121.00, 119.77, 117.58, 60.61, 49.78, 33.74, 17.29, 17.11, 14.21, 12.54, 9.60; HRMS(ESI): $[M+H]^+$calcd for$C_{29}H_{39}ClNO_3Si$: 512.2382, found: 512.2383.

(*E*)-ethyl3-(4-bromo-3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)phenyl)acrylate (2j)



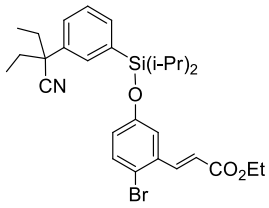
Colorless oil; yield: 215.0 mg (77 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ 8.12 (d, *J*=16.0 Hz, 1H), 7.63-7.54 (m, 2H), 7.53-7.47 (m, 1H), 7.47-7.38 (m, 1H), 7.21-7.15 (m, 1H), 7.07 (t, *J*=8.0 Hz, 1H), 6.82-6.75 (m, 1H), 6.37 (d, *J*=16.0 Hz, 1H), 4.33-4.25 (m, 2H), 2.07-1.95 (m, 2H), 1.92-1.80 (m, 2H), 1.57-1.48 (m, 2H), 1.35 (t, *J*=7.0 Hz, 3H), 1.14 (d, *J*=7.5 Hz, 6H), 1.09 (d, *J*=7.5 Hz, 6H), 0.86 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 166.39, 153.05, 143.53, 137.28, 136.40, 133.86, 133.60, 131.90, 128.22, 128.03, 127.61, 122.11, 121.14, 120.39, 120.21, 118.12, 60.60, 49.72, 33.68, 17.39, 17.26, 14.24, 12.92, 9.58; HRMS(ESI): $[M+Na]^+$calcd for$C_{29}H_{38}BrNNaO_3Si$: 578.1697, found: 578.1702.

(*E*)-ethyl3-(3-bromo-5-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)phenyl)acrylate (2k)



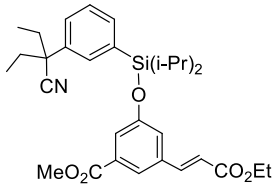
Colorless oil; yield: 217.8 mg (78 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.57-7.50 (m, 2H),7.50-7.41 (m, 3H), 7.27-7.24 (m, 1H), 7.03 (s, 1H), 6.91 (s, 1H), 6. 29 (d, *J*=16.0 Hz, 1H), 4.29-4.20 (m, 2H), 2.07-1.97 (m, 2H), 1.92-1.80 (m, 2H), 1.51-1.41 (m, 2H), 1.32 (t, *J*=7.0 Hz, 3H), 1.11 (d, *J*=7.5 Hz, 6H), 1.06 (d, *J*=7.5 Hz, 6H), 0.88 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 166.46, 156.68, 142.72, 137.45, 137.14, 133.74, 133.65, 131.96, 128.46, 127.88, 124.64, 123.95, 122.95, 122.07, 119.82, 118.03, 60.66, 49.81, 33.77, 17.34, 17.15, 14.25, 12.58, 9.66; HRMS(ESI): $[M+H]^+$calcd for$C_{29}H_{39}BrNO_3Si$: 556.1877, found: 556.1878.

(*E*)-ethyl3-(2-bromo-5-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)phenyl)acrylate (2l)



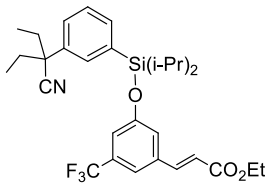
Colorless oil; yield: 206.6 mg (74 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ 7.94 (d, *J*=15.5 Hz, 1H), 7.57-7.51 (m, 2H),7.49-7.41 (m, 2H), 7.41-7.35 (m, 1H), 7.11-7.06 (m, 1H), 6.79-6.71 (m, 1H), 6. 17 (d, *J*=16.0Hz, 1H), 4.29-4.20 (m, 2H), 2.07-1.97 (m, 2H), 1.92-1.80 (m, 2H), 1.51-1.41 (m, 2H), 1.34 (t, *J*=7.0 Hz, 3H), 1.11 (d, *J*=7.5 Hz, 6H), 1.06 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 166.24, 155.14, 142.75, 137.37, 135.16, 133.93, 133.83, 133.67, 132.06, 128.40, 127.70, 123.04, 122.02, 120.96, 118.70, 116.61, 60.64, 49.76, 33.72, 17.31, 17.13, 14.24, 12.53, 9.59; HRMS(ESI): $[M+H]^+$calcd for$C_{29}H_{39}BrNO_3Si$: 556.1877, found: 556.1879.

(*E*)-methyl3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)-5-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (2m)



Colorless oil; yield: 174.5 mg (65 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ 7.81 (s, 1H), 7.62-7.51 (m, 4H),7.50-7.42 (m, 2H), 7.18 (s, 1H), 6.39 (d, *J*=16.0 Hz, 1H), 4.29-4.23 (m, 2H), 3.89 (s, 3H), 2.06-1.98 (m, 2H), 1.90-1.83 (m, 2H), 1.52 - 1.43 (m, 2H), 1.33 (t, *J*=7.0 Hz, 3H), 1.11 (d, *J*=7.5 Hz, 6H), 1.07 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 166.52, 166.10, 156.03, 143.13, 137.30, 135.97, 133.78, 133.63, 132.01, 131.91, 128.39, 127.73, 123.23, 122.24, 122.13, 122.02, 119.58, 60.57, 52.26, 49.75, 33.71, 17.28, 17.11, 14.20, 12.51, 9.56; HRMS(ESI): $[M+H]^+$calcd for$C_{31}H_{42}NO_5Si$: 536.2827, found: 536.2838.

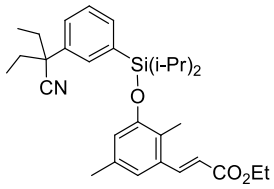
(*E*)-ethyl3-(3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)-5-(trifluoromethyl)phenyl)-acrylate (2n)



Colorless oil; yield: 161.5 mg (59 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.58-7.53 (m, 3H), 7.49-7.43 (m, 2H), 7.35 (s, 1H), 7.15 (s, 1H), 7.09 (s, 1H), 6.36 (d, *J*=16.0 Hz, 1H), 4.29-4.23 (m, 2H), 2.07-1.98 (m, 2H), 1.09-1.81 (m, 2H), 1.52-1.45 (m, 2H), 1.33 (t, *J*=7.0 Hz, 3H), 1.12 (d, *J*=7.5 Hz, 6H), 1.07 (d, *J*=8.0 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 166.34, 156.35, 142.60, 137.48, 136.62, 133.63, 133.52, 132.42 (q, *J*=32.5 Hz), 131.99, 128.51, 127.83, 123.38 (q, *J*=271.3Hz), 122.04,

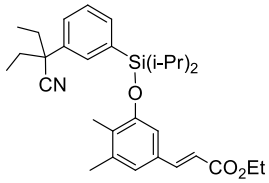
120.22, 118.09 (q, *J*=3.8 Hz), 117.50 (q, *J*=3.8 Hz), 60.71, 49.79, 33.74, 17.29, 17.10, 14.21, 12.52, 9.56; HRMS(ESI): $[M+H]^+$calcd for$C_{30}H_{39}F_3NO_3Si$: 546.2646, found: 546.2653.

(*E*)-ethyl3-(3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)-2,5-dimethylphenyl)acrylate (2o)



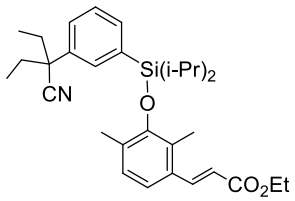
Colorless oil; yield: 172.6 mg (68 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.91 (d, *J*=13.0Hz, 1H),7.48-7.45 (m, 2H), 7.40-7.37 (m, 1H), 7.35-7.31 (m, 1H), 6.90 (s, 1H), 6.47 (s, 1H), 6.24 (d, *J*=13.0 Hz, 1H), 4.20-4.15 (m, 2H), 2.24 (s, 3H), 2.07 (s, 3H), 1.95-1.89 (m, 2H), 1.80-1.73 (m, 2H), 1.43-1.37 (m, 2H), 1.25 (t, *J*=6.0 Hz, 3H), 1.03 (d, *J*=6.0 Hz, 6H), 0.97 (d, *J*=6.0 Hz, 6H), 0.78 (t, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 167.01, 153.92, 142.82, 137.11, 135.65, 134.68, 134.65, 133.49, 131.87, 128.14, 127.65, 125.26, 122.05, 120.52, 120.00, 119.32, 60.31, 49.70, 33.68, 20.92, 17.40, 17.22, 14.23, 12.86, 12.05, 9.54; HRMS(ESI): $[M+Na]^+$calcd for$C_{31}H_{43}NNaO_3Si$: 528.2904, found: 528.2912.

(*E*)-ethyl3-(3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)-4,5-dimethylphenyl)acrylate (2p)



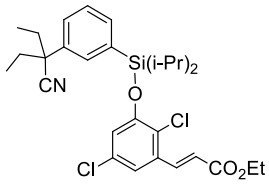
Colorless oil; yield: 180.2 mg (71 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.51-7.49 (m, 1H), 7.48-7.45 (m, 1H), 7.39-7.30 (m, 3H), 6.86 (s, 1H), 6.63 (s, 1H), 6.05 (d, *J*=13.0 Hz, 1H), 4.15-4.10 (m, 2H), 2.19 (s, 3H), 2.14 (s, 3H), 1.95-1.87 (m, 2H), 1.80-1.73 (m, 2H), 1.43-1.37 (m, 2H), 1.21 (t, *J*=6.0 Hz, 3H), 1.03 (d, *J*=6.0 Hz, 6H), 0.97 (d, *J*=6.5 Hz, 6H), 0.78 (t, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 167.00, 153.87, 144.63, 138.59, 137.16, 134.54, 133.50, 131.92, 131.74, 130.02, 128.20, 127.57, 122.71, 122.01, 116.70, 115.07, 60.21, 49.70, 33.69, 20.24, 17.40, 17.20, 14.19, 12.86, 12.70, 9.54; HRMS(ESI): $[M+H]^+$calcd for$C_{31}H_{44}NO_3Si$: 506.3085, found: 506.3090.

(*E*)-ethyl3-(3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)-2,4-dimethylphenyl)acrylate (2q)



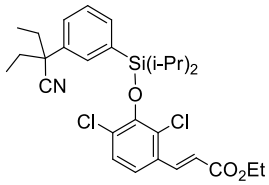
Colorless oil; yield: 210.6 mg (83 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.94(d, *J*=15.5 Hz, 1H), 7.62 (s, 1H),7.57-7.51 (m, 1H), 7.49-7.45 (m, 1H), 7.43-7.39 (m, 1H),7.15 (d, *J*=8.0 Hz, 1H), 6.97 (d, *J*=8.0 Hz,1H), 6.32 (d, *J*=16.0 Hz, 1H), 4.27-4.22 (m, 2H), 2.22 (s, 3H), 2.14 (s, 3H), 2.07-1.98 (m, 2H), 1.92-1.84 (m, 2H), 1.55-1.47 (m, 2H), 1.33 (t, *J*=7.0 Hz, 3H), 1.05 (d, *J*=7.5 Hz, 6H), 0.96 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 167.20, 153.26, 142,84, 137.02, 134.46, 133.47, 132.70, 131.98, 130.50, 128.45, 128.20, 127.99, 127.64, 122.12, 119.90, 118.62, 60.35, 49.84, 33.80, 18.55, 17.02, 16.88, 14.29, 13.74, 12.87, 9.61; HRMS(ESI): $[M+H]^+$calcd for$C_{31}H_{44}NO_3Si$: 506.3085, found: 506.3100.

(*E*)-ethyl3-(2,5-dichloro-3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)phenyl)acrylate (2r)



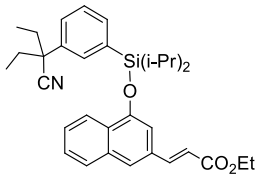
Colorless oil; yield: 178.3 mg (65 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.97 (d, *J*=13.0 Hz, 1H), 7.54-7.51 (m, 1H), 7.50-7.47 (m, 1H), 7.43-7.40 (m, 1H), 7.38-7.34 (m, 1H),7.14-7.10 (m, 1H), 6.71-6.68 (m, 1H), 6.32 (d, *J*=13.0 Hz, 1H), 4.23-4.15 (m, 2H), 2.00-1.90 (m, 2H), 1.84-1.76 (m, 2H), 1.47-1.40 (m, 2H), 1.26 (t, *J*=6.0 Hz, 3H), 1.05 (d, *J*=6.0 Hz, 6H), 1.01 (d, *J*=6.5 Hz, 6H), 0.80 (t, *J*=6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 166.05, 152.61, 139.55, 137.46, 135.15, 133.49, 133.32, 132.31, 131.90, 128.39, 128.09, 124.77, 122.14, 122.00, 120.74, 119.87, 60.74, 49.76, 33.74, 17.27, 17.14, 14.18, 12.78, 9.58; HRMS(ESI): $[M+H]^+$calcd for$C_{29}H_{38}Cl_2NO_3Si$: 546.1993, found: 546.1987.

(*E*)-ethyl3-(2,4-dichloro-3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)phenyl)acrylate (2s)



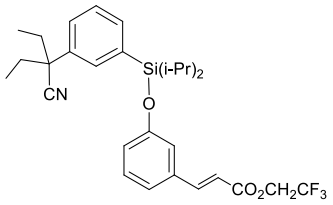
Colorless oil; yield: 194.04 mg (71 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.98 (d, *J*=16.0 Hz, 1H),7.64-7.60 (m, 1H), 7.57-7.52 (m, 1H), 7.48-7.43 (m, 1H), 7.40-7.35 (m, 1H), 7.24-7.20 (m, 1H), 7.19-7.14 (m, 1H), 6. 37 (d, *J*=16.0 Hz, 1H), 4.30-4.20 (m, 2H), 2.07-1.97 (m, 2H), 1.92-1.83 (m, 2H), 1.75-1.65 (m, 2H), 1.33 (t, *J*=7.0 Hz, 3H), 1.11 (d, *J*=7.0 Hz, 6H), 1.08 (d, *J*=3 Hz, 6H), 0.84 (t, *J*=7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ166.23, 149.41, 139.98, 136.79, 133.38, 133.42, 132.71, 131.90, 128.06, 127.88, 127.77, 127.64, 127.23, 122.08, 121.23, 120.18, 60.66, 49.79, 33.76, 17.13, 17.08, 14.19, 13.22, 9.58; HRMS(ESI): $[M+H]^+$calcd for$C_{29}H_{38}Cl_2NO_3Si$: 546.1993, found: 546.1989.

(*E*)-ethyl3-(4-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)naphthalen-2-yl)acrylate (2t)



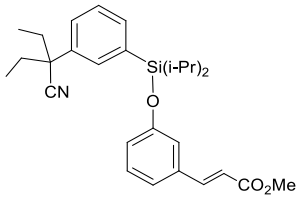
Colorless oil; yield: 219.0 mg (83 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ 8.37 (s,1H), 7.89-7.82 (m, 1H),7.82-7.76 (m, 1H), 7.72-7.65 (m, 1H), 7.65-7.58 (m, 1H), 7.57 (s, 1H), 7.54-7.48 (m, 1H), 7.48-7.37 (m, 2H), 7.28-7.20 (m, 1H), 6.78 (d, *J*=7.5 Hz, 1H), 6.53 (d, *J*=16.0 Hz, 1H), 4.32-4.27 (m, 2H), 2.01-1.92 (m, 2H), 1.83-1.74 (m, 2H), 1.64-1.57 (m, 2H), 1.36 (t, *J*=7.0 Hz, 3H), 1.17 (d, *J*=7.5 Hz, 6H), 1.10 (d, *J*=7.5 Hz, 6H), 0.86 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 167.19, 152.22, 145.04, 137.37, 135.68, 134.25, 133.68, 131.75, 131.33, 128.50, 128.34, 128.07, 127.28, 125.01, 123.62, 122.17, 120.78, 117.95, 113.30, 60.48, 49.73, 33.67, 17.55, 17.37, 14.34, 12.92, 9.59; HRMS(ESI): $[M+H]^+$calcd for$C_{33}H_{42}NO_3Si$: 528.2928, found: 528.2932.

(*E*)-trifluoromethyl3-(3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)phenyl)acrylate (3a)



Colorless oil; yield: 148.8 mg (56 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ 9.67 (d, *J*=7.5 Hz, 1H), 7.63-7.50 (m, 2H), 7.50-7.33 (m, 3H), 7.32-7.21 (m, 1H), 7.19-7.12 (m, 1H), 7.10-7.05 (m, 1H), 7.02-6.91 (m, 1H), 6.64-6.54 (m, 1H), 2.07-1.95 (m, 2H), 1.93-1.79 (m, 2H),1.56-1.34 (m, 2H), 1.11 (d, *J*=7.5 Hz, 6H), 1.07 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 165.06, 156.07, 146.89, 137.27, 135.19, 134.17, 133.67, 132.09, 129.94, 128.32, 127.62, 126.34, 124.13, 122.45, 122.08, 121.93, 121.64, 119.73, 119.24, 115.98, 60.30 (q, *J*=36.13 Hz), 49.76, 33.72, 17.31, 17.13, 17.09, 12.56, 9.58; HRMS(EI): calcd for$C_{29}H_{36}F_3NO_3Si$: 531.2417, found: 531.2425.

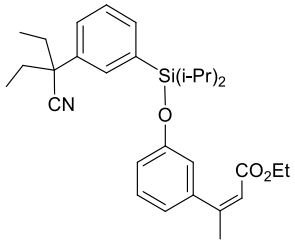
(*E*)-methyl3-(3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)phenyl)acrylate (3b)



Colorless oil; yield: 169.1 mg (73 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.61-7.54 (m, 3H), 7.48-7.39 (m, 2H), 7.23-7.18 (m, 1H), 7.12-7.09(m, 1H), 7.04-7.00 (m, 1H), 6.92-6.88 (m, 1H), 6.32 (d, *J*=16.0 Hz, 1H), 3.79 (s, 3H), 2.05-1.95 (m, 2H),1.89-1.80 (m, 2H),1.49-1.40 (m, 2H), 1.10 (d, *J*=7.0 Hz, 6H), 1.06 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 167.27, 155.99, 144.57, 137.24, 135.74, 134.26, 133.66, 132.03, 129.83, 128.27, 127.66, 122.08, 121.84, 121.33, 119.03, 117.92,

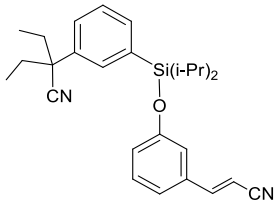
51.62, 49.76, 33.70, 17.33, 17.13, 12.59, 9.59; HRMS(ESI):[M+Na]$^+$ calcd for $C_{28}H_{37}NNaO_3Si$: 486.2435, found: 486.2450.

(*Z*)-ethyl 3-(3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)phenyl)but-2-enoate (3c)



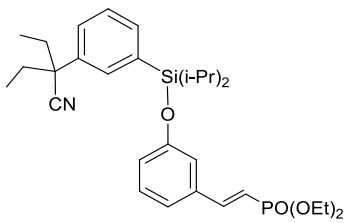
Colorless oil; yield: 177.5 mg (72 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.58-7.51 (m, 2H), 7.48-7.39 (m, 2H), 7.18 (t, *J*=8.0 Hz, 1H), 7.08-7.03 (m, 1H), 6.99-6.95(m, 1H), 6.88-6.83(m, 1H),6.05-6.02(m,1H), 2.50-2.45(m, 2H), 2.05-1.96 (m, 2H),1.89-1.80 (m, 2H),1.49-1.40 (m, 2H), 1.31 (t, *J*=7.5 Hz, 3H), 1.14-1.03(m, 12H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 166.77, 155.65, 155.01, 143.64, 137.21, 134.41, 133.72, 131.98, 129.36, 128.23, 127.66, 122.11, 120.26, 119.31, 117.81, 117.09, 59.78, 49.75, 33.71, 17.82, 17.35, 17.15, 14.29, 12.58, 9.58; HRMS(ESI):[M+Na]$^+$ calcd for $C_{30}H_{41}NNaO_3Si$: 514.2748, found: 514.2766.

(*E*)-2-(3-((3-(2-cyanovinyl)phenoxy)diisopropylsilyl)phenyl)-2-ethylbutanenitrile (3d)



Colorless oil; yield: 152.8 mg (71 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.60-7.56 (m, 1H), 7.56-7.52 (m, 1H), 7.46-7.41 (m, 2H), 7.32-7.25 (m, 1H), 7.25-7.20 (m, 1H), 7.05-7.00 (m, 1H), 6.97-6.91 (m, 2H), 5.78 (d, *J*=17.0 Hz, 1H), 2.07-1.98 (m, 2H), 1.90-1.80 (m, 2H),1.49-1.41 (m, 2H), 1.10 (d, *J*=7.5 Hz, 6H), 1.05 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 156.14, 150.30, 137.29, 134.86, 134.03, 133.64, 132.31, 130.08, 128.37, 127.46, 122.65, 122.08, 120.66, 118.27, 118.05, 96.49, 49.79, 43.72, 17.31, 17.13, 12.52, 9.63; HRMS(ESI):[M+Na]$^+$ calcd for $C_{27}H_{34}N_2NaOSi$: 453.2333, found: 453.2347.

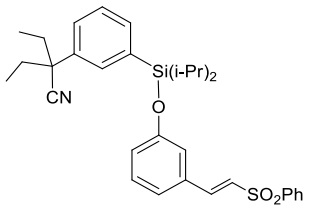
(*E*)-diethyl3-(((3-(3-cyanopentan-3-yl)phenyl)diisopropylsilyl)oxy)styrylphosphonate (3e)



Colorless oil; yield: 165.1 mg (61 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.49-7.45 (m, 2H), 7.39-7.34 (m, 2H), 7.33-7.30 (m, 1H), 7.16-7.10 (m, 1H), 7.04-6.99 (m, 1H), 6.94-6.91 (m, 1H), 6.84-6.80 (m, 1H),

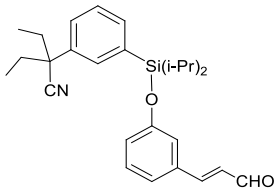
6.16 (t, *J*=15.0 Hz, 1H), 4.08-3.99 (m, 4H), 1.97-1.89 (m, 2H),1.80-1.73 (m, 2H),1.41-1.33 (m, 2H), 1.27 (t, *J*=6.0 Hz, 6H), 1.02 (d, *J*=6.5 Hz, 6H), 0.97 (d, *J*=6.5 Hz, 6H), 0.79 (t, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ155.911, 148.40 (d, *J*=5.5 Hz), 137.14, 136.2 (d, *J*=19.3 Hz), 134.15, 133.59, 131.96, 129.73, 128.22, 127.55, 122.03, 121.66, 120.79, 118.74, 113.98 (d, *J*=158.5 Hz), 49.69, 33.65, 17.25, 17.07, 16.31, 16.26, 12.49, 9.55; HRMS(ESI):$[M+Na]^+$ calcd for $C_{30}H_{44}NNaO_4PSi$: 564.2669, found: 564.2697.

(*E*)-2-(3-(diisopropyl(3-(2-(phenylsulfonyl)vinyl)phenoxy)silyl)phenyl)-2-ethylbutanenitrile (3f)



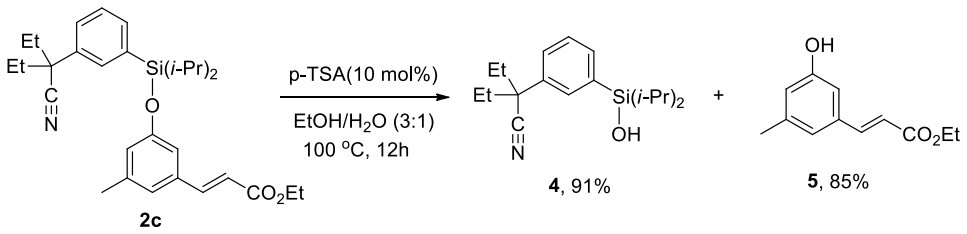
Colorless oil; yield: 180.0 mg (66 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.87-7.83 (m, 2H), 7.55-7.49 (m, 2H), 7.48-7.43 (m, 4H), 7.35-7.31 (m, 2H), 7.14-7.10 (m, 1H), 7.00-6.97 (m, 1H), 6.91-6.89 (m, 1H), 6.85-6.81 (m, 1H), 6.69 (d, *J*=12.5 Hz, 1H), 1.96-1.86 (m, 2H),1.78-1.70 (m, 2H),1.39-1.34 (m, 2H), 1.00 (d, *J*=6.0 Hz, 6H), 0.96 (d, *J*=6.0 Hz, 6H), 0.75 (t, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ156.01, 142.09, 140.51, 137.19, 133.97, 133.60, 133.55, 133.31, 132.06, 129.98, 129.23, 128.27, 127.52, 127.47, 127.30, 122.59, 121.98, 121.68, 119.52, 49.67, 33.60, 17.24, 17.06, 12.43, 9.53; HRMS(ESI): $[M+Na]^+$ calcd for $C_{32}H_{39}NNaO_3SSi$: 568.2312, found: 568.2334.

(*E*)-2-(3-(diisopropyl(3-(3-oxoprop-1-en-1-yl)phenoxy)silyl)phenyl)-2-ethylbutanenitrile (3g)

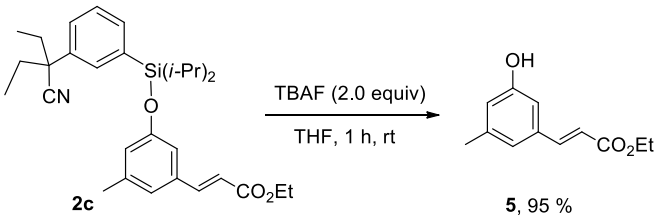


Colorless oil; yield: 162.5 mg (75 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ 9.67 (d, *J*=7.5 Hz, 1H), 7.63-7.50 (m, 2H), 7.50-7.33 (m, 3H), 7.32-7.21 (m, 1H), 7.19-7.12 (m, 1H), 7.10-7.05 (m, 1H), 7.02-6.91 (m, 1H), 6.64-6.54 (m, 1H), 2.07-1.95 (m, 2H), 1.93-1.79 (m, 2H),1.56-1.34 (m, 2H), 1.11 (d, *J*=7.5 Hz, 6H), 1.07 (d, *J*=7.5 Hz, 6H), 0.87 (t, *J*=7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 193.51, 156.12, 152.43, 137.28, 135.36, 134.09, 133.62, 132.18, 130.04, 128.66, 128.32, 127.51, 122.78, 122.03, 121.82, 119.23, 49.74, 33.67, 17.30, 17.11, 12.55, 9.57; HRMS(ESI):$[M+Na]^+$ calcd for $C_{27}H_{35}NNaO_2Si$: 456.2329, found: 456.2333.

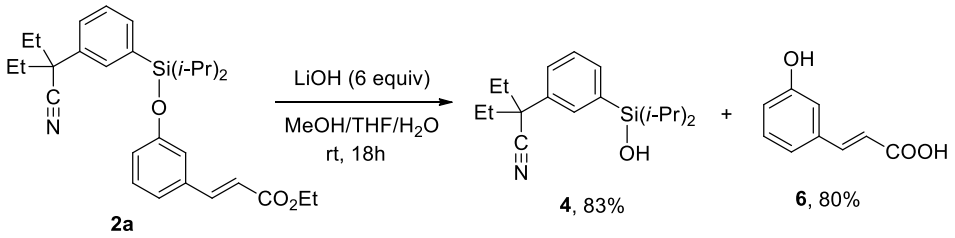
2.6 General procedure for the removal and reinstallation of organosilicon group.



To a clean, oven-dried screw cap reaction tube with previously placed magnetic stir-bar, compound **2c** (98.4 mg, 0.2 mmol) and *p*-toluenesulfonic acid (2.3 mg, 0.02 mmol) were dissolved in 3 mL of EtOH and 1 mL H_2O (EtOH/H_2O : 3/1). The solution was stirred at 100 °C for 12 h. The reaction mixture was cooled and 10 mL of brine solution was added. Ethanol was removed under reduced pressure and aqueous part was extracted by EtOAc (10 mL × 3). Organic phase was concentrated and was purified by column chromatography (petroleum ether/ethyl acetate = 3/1) to afford pure product **4** and **5** as colorless oil.

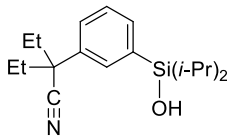


Compound **2c** (491.8 mg, 1.0 mmol,) was dissolved in 15 mL THF in a clean and oven-dried screw cap reaction tube, then a solution of TBAF (1M inTHF, 3.0 mL) was added dropwisely at room temperature and the solution was kept stirring for 3 h at room temperature. After the reaction, the solvent was evaporated off and the residue was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (3/1 v/v) to afford pure **5** as colorless oil.



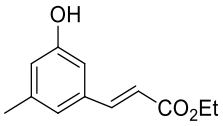
To a 25 mL vial equipped with a magnetic stir bar was charged **2a** (95.6 mg, 0.2 mmol) and LiOH monohydrate (28.8 mg, 1.2 mmol). To this mixture was then added MeOH (2.4 mL), THF (1.2 mL), and H_2O (0.6 mL). The reaction was then stirred for 18 h when TLC indicated the completion of hydrolysis. The MeOH and THF was then removed in vacuo, and the resulting residue was diluted with H_2O (20 mL) and EtOAc (30 mL). After acidification with 2 M HCl (3 mL), the solution was extracted with EtOAc for three times. The combined organic extract was washed with brine, dried over Mg_2SO_4. The organic layer was further concentrated and purified by column chromatography on a silica gel column (petroleum ether/ethyl acetate = 3/1 to 1/1) to give the product **6** as white solid.

2-ethyl-2-(3-(hydroxydiisopropylsilyl)phenyl)butanenitrile (4)



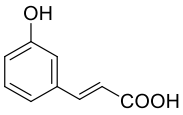
Colorless oil; yield: 55.2 mg (91 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ 7.55-7.53 (m, 1H), 7.52-7.48 (m, 1H), 7.43-7.36 (m, 2H), 2.09-2.00 (m, 2H), 1.97-1.89 (m, 2H), 1.27-1.20 (m, 2H), 1.05 (d, *J*=7.0 Hz, 6H), 0.97 (d, *J*=7.5 Hz, 6H), 0.90 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 136.98, 136.30, 133.27, 131.42, 128.01, 127.13, 122.32, 49.79, 33.72, 17.08, 16.82, 12.34, 9.60; HRMS (ESI):$[M+Na]^+$ calcd for $C_{18}H_{29}NNaOSi$: 326.1911, found: 326.1913.

(*E*)-ethyl 3-(3-hydroxy-5-methylphenyl)acrylate (5)

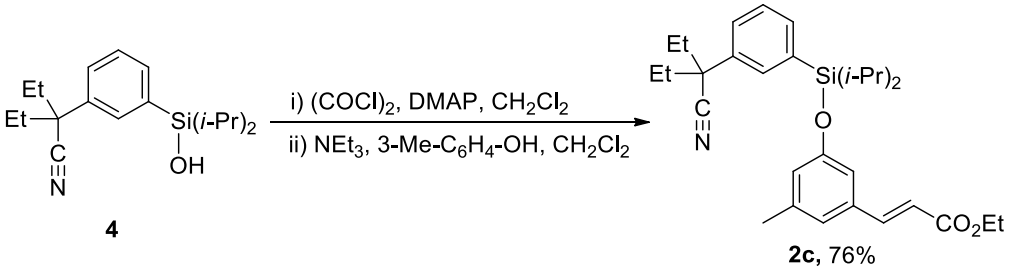


Colorless oil; yield: 195.9 mg (95 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ 7.61 (d, *J*=16.0 Hz, 1H), 6.91 (s, 1H), 6.86 (s, 1H), 6.73 (s, 1H), 6.39 (d, *J*=15.5 Hz, 1H), 4.33-4.23 (m, 2H), 2.31 (s, 3H), 1.34 (t, *J*=7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz)δ 167.67, 156.13, 145.05, 140.23, 135.46, 121.50, 118.38, 117.94, 111.77, 60.82, 21.25, 14.22; HRMS(ESI):$[M+Na]^+$ calcd for $C_{12}H_{14}NaO_3$: 229.0835, found: 229.0839.

(*E*)-3-(3-hydroxyphenyl)acrylic acid (6)



White solid; yield: 26.3 mg (70 %); ^{1}H NMR (DMSO-d_6, 500 MHz)δ 12.39 (s, 1H), 9.62 (s, 1H), 7.54 (d, *J*=16.0 Hz, 1H), 7.26-7.20 (m, 1H), 7.15-7.09 (m, 1H), 7.07-7.02 (m, 1H), 6.88-6.83 (m, 1H), 6.44 (d, *J*=16.0 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz)δ 172.16, 162.30, 148.76, 140.08, 134.50, 123.73, 123.54, 122.02, 119.10.

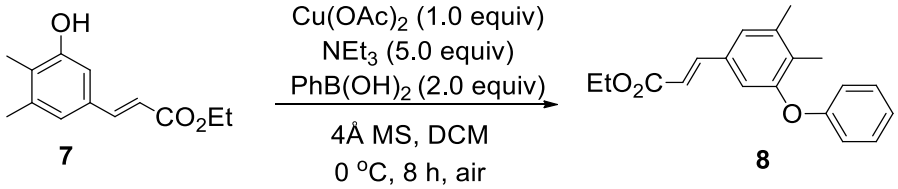


4 **2c**, 76%

To a stirred solution of the silanol (60.7 mg, 0.2 mmol) and DMAP (36.8 mg, 0.3 mmol) in dry DCM (3 mL), oxalyl chloride (71 µL, 0.8 mmol) was added dropwise under inert atmosphere at 0 °C slowly to maintain a gentle exotherm. After addition, the reaction mixture was stirred overnight at room temperature. DCM was removed by evaporation; diethyl ether (5 mL) was added and filtered through celite. Then diethyl ether was removed to get crude chlorosilane. DCM solution of this crude chlorosilane was added dropwise to a stirred solution of 3-methylphenol (21.6 mg, 0.2 mmol) and

trimethylamine in dry DCM at 0 °C under inert atmosphere. After stirring for 5 h at room temperature, DCM was removed and hexane (10 mL x 3) was added and filtered through celite. Concentration under reduced pressure followed by purification by column chromatography (petrolium ether/ ethyl acetate = 15:1) afforded **2c** as colorless oil.

2.7 Synthetic applications of the meta-alkenylation products



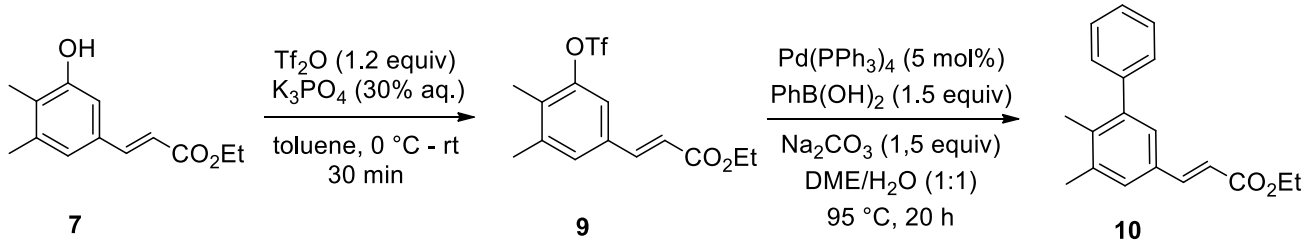
$Cu(OAc)_2$ (99.8 mg, 0.5 mmol), triethylamine(2.5 mmol), compound **7** (110.0 mg, 0.5 mmol), $PhB(OH)_2$ (121.9 mg, 1.0 mmol), 4Å molecular sieve (5.0 g) were added to a screw cap reaction tube containing a stirring bar. Dichloromethane (20 mL) was then injected via syringe and the reaction mixture was kept stirring at 0°C. After 8 hours, 4Å molecular sieves was filtered off, and the filtrate was concentrated under the reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (2:1 to 1:1) to afford the desired product **8** as colorless oil.

(*E*)-ethyl 3-(3-hydroxy-4,5-dimethylphenyl)acrylate (7)

Colorless oil; yield: 404.8 mg (92 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.59 (d, *J*=15.5 Hz , 1H), 6.92 (s, 1H), 6.87 (s, 1H), 6.35 (d, *J*=16.0 Hz , 1H), 4.26 (q, *J*=7.0 Hz, 2H), 2.72 (s, 3H), 2.18 (s, 3H), 1.33 (t, *J*=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.66, 154.21, 145.07, 138.70, 132.17, 125.96, 122.24, 116.96, 111.91, 60.62, 20.08, 14.25, 11.80; HRMS(ESI):$[M+Na]^+$ calcd for $C_{13}H_{16}NaO_3$: 243.0992, found: 243.0997.

(*E*)-ethyl 3-(5,6-dimethyl-[1,1'-biphenyl]-3-yl)acrylate (8)

Colorless oil; yield: 111.1 mg (75 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ 7.55 (d, *J*=16 Hz, 1H), 7.35-7.28 (m, 2H), 7.14 (s, 1H), 7.09-7.04 (m, 1H), 6.94 (s, 1H), 6.92-6.89 (m, 2H), 6.30 (d, *J*=16 Hz, 1H), 4.26-4.20 (m, 2H), 2.34 (s, 3H), 2.18 (s, 3H), 1.31 (t, *J*=7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.01, 157.71, 154.74, 144.11, 139.32, 132.75, 131.33, 129.75, 125.31, 122.63, 117.69, 117.41, 116.44, 60.41, 20.16, 14.28, 12.43; HRMS(ESI):$[M+Na]^+$ calcd for $C_{19}H_{20}NaO_3$: 319.1305, found: 319.1313.



Step 1: Compound **7** (440.2 mg, 2 mmol) was added to a cooled biphasic solution (0 °C) containing 4 mL toluene and 4 mL K_3PO_4 aqueous solution (30% w/v), thenTf_2O (2.4 mmol) was added dropwisely at a rate to maintain the reaction temperature lower than 10 °C.The reaction was then allowed to warm to room temperature and stirred for 30 min. After the reaction, the two layers were separated, and the toluene layer was washed with water (10 mL) and concentrated under the reduced pressure. The product **8** was directly used for next step without further purifications.

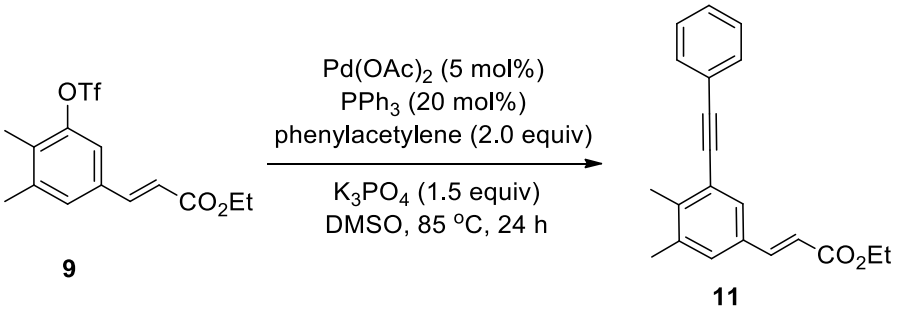
(*E*)-ethyl 3-(3,4-dimethyl-5-(((trifluoromethyl)sulfonyl)oxy)phenyl)acrylate (9)

Colorless oil; yield: 675.8 mg (96 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ7.58 (d, *J*=16.0 Hz , 1H), 733 (s, 1H), 7.24 (s, 1H), 6.41 (d, *J*=16.0 Hz , 1H), 4.27 (q, *J*=7.0 Hz, 2H), 2.35 (s, 3H), 2.29 (s, 3H), 1.34 (t, *J*=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ166.55, 148.66, 142.47, 140.43, 133.45, 131.71, 128.94, 119.51, 118.00, 60.71, 20.27, 14.27, 13.15.

Step 2: $Pd(PPh_3)_4$ (11.6mg, 0.01mmol), compound **9** (70.4 mg, 0.2 mmol), $PhB(OH)_2$ (36.6 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.3 mmol) were added to a Schlenk tube, DME/H_2O (2 mL, 1:1 v/v) was then injected via syringe and the reaction mixture was heated with vigorous stirring at 95 °C for 20 h. After the reaction was completed, the mixture was cooled to room temperature, followed by the addition of 10 mL brine solution. The mixture was then extracted with ethyl acetate (10 mL × 3), and the combined organic layer was dried over anhydrous $MgSO_4$. The organic layer was further concentrated and purified by column chromatography on a silica gel column(petroleum ether/ethyl acetate = 3/1) to give the product **9** as colorless oil.

(*E*)-ethyl 3-(5,6-dimethyl-[1,1'-biphenyl]-3-yl)acrylate (10)

Yield: 49.3 mg (88 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.66 (d, *J*=16.0 Hz, 1H), 7.43-7.38 (m, 2H), 7.36-7.31 (m, 2H), 7.30-7.26 (m, 3H), 6.41 (d, *J*=16.0 Hz, 1H), 4.25 (q, *J*=7.5 Hz, 2H), 2.36 (s, 3H), 2.16 (s, 3H), 1.32 (t, *J*=7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.19, 144.46, 142.86, 141.79, 137.85, 136.89, 131.49, 129.24, 128.33, 128.14, 127.40, 126.97, 117.41, 60.35, 20.70, 17.15, 14.30.HRMS(ESI):$[M+Na]^+$ calcd for $C_{19}H_{20}NaO_2$: 303.1356, found: 303.1367.



9 **11**

$Pd(OAc)_2$ (2.3 mg, 0.01mmol), PPh_3 (10.5 mg, 0.04mmol), compound **9** (70.4 mg, 0.2 mmol), phenylacetylene (40.9 mg, 0.4 mmol) and K_3PO_4 (63.7 mg, 0.3 mmol) were added to a screw cap reaction tube which was sealed with a screw cap fitted with a septum. Then DMSO (2 mL) was added via syringe and the reaction mixture was heated with vigorous stirring at 85 °C for 24 h. The obtained reaction mixture was cooled to room temperature and concentrated in vacuo, followed by addition of 10 mL brine solution. The resulting mixture was further extracted with ethyl acetate for three times (10 mL×3) and the combined organic layer was dried over anhydrous $MgSO_4$. The organic layer was concentrated in vacuo and purified by column chromatography (petrolium ether/ethyl acetate = 15/1).

(*E*)-ethyl 3-(3,4-dimethyl-5-(phenylethynyl)phenyl)acrylate (11)

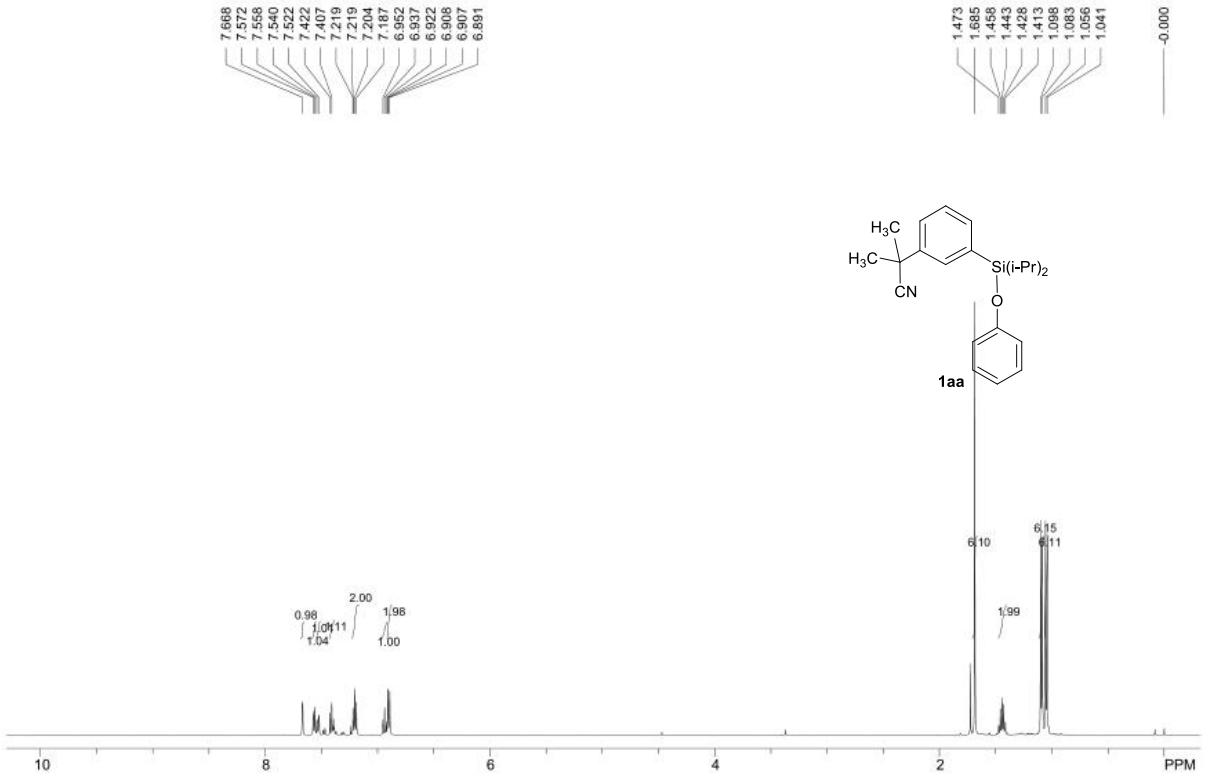
Colorless oil; yield: 47.5 mg (78 %); ^{1}H NMR ($CDCl_3$, 500 MHz)δ 7.61 (d, *J*=16 Hz, 1H), 7.58-7.51 (m, 3H), 7.40-7.34 (m, 3H), 7.28 (s, 1H), 6.43 (d, *J*=16 Hz, 1H) ,4.26 (q, *J*=14.5 Hz, 2H), 2.48 (s, 3H), 2.32 (s, 3H), 1.34 (t, *J*=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ167.04, 143.88, 140.98, 137.44, 131.71, 131.51, 129.36, 129.26, 128.37, 128.32, 123.87, 123.25, 117.82, 93.24, 88.18, 60.43, 20.42, 17.65, 14.29; HRMS(ESI):$[M+Na]^+$ calcd for $C_{21}H_{20}NaO_2$: 327.1356, found: 327.1350.

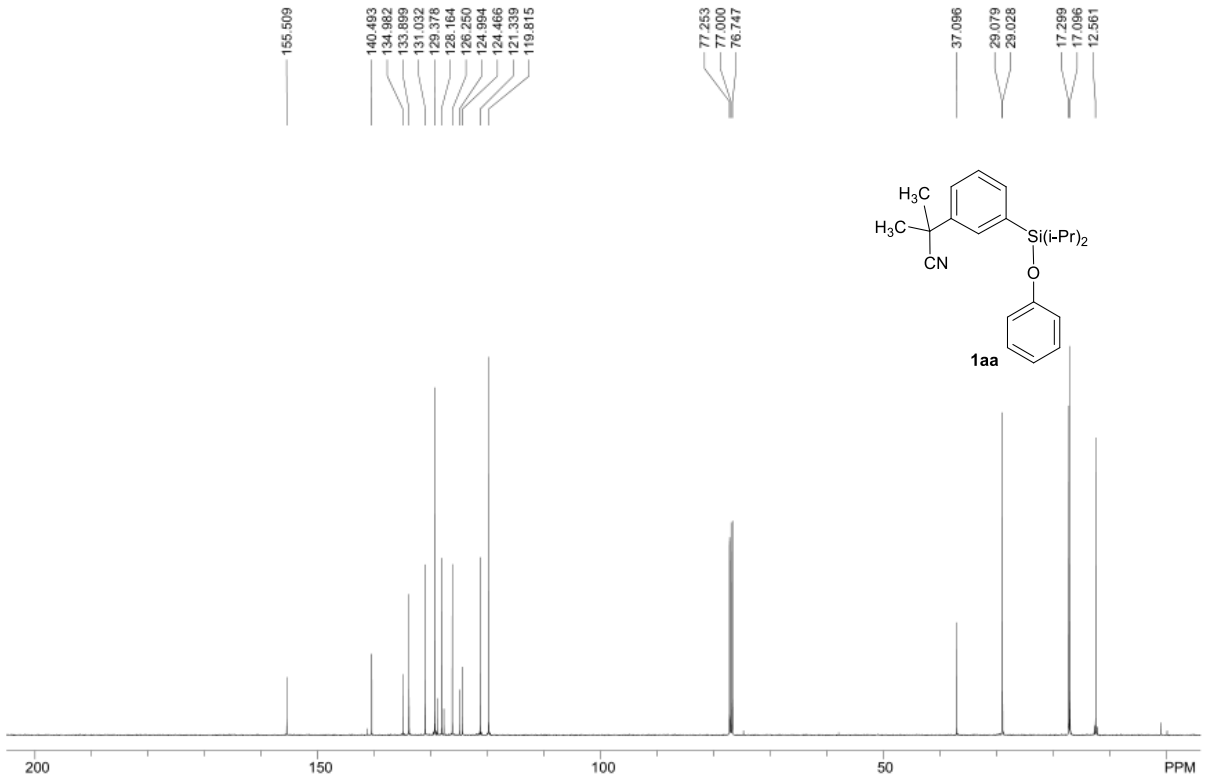
3. References

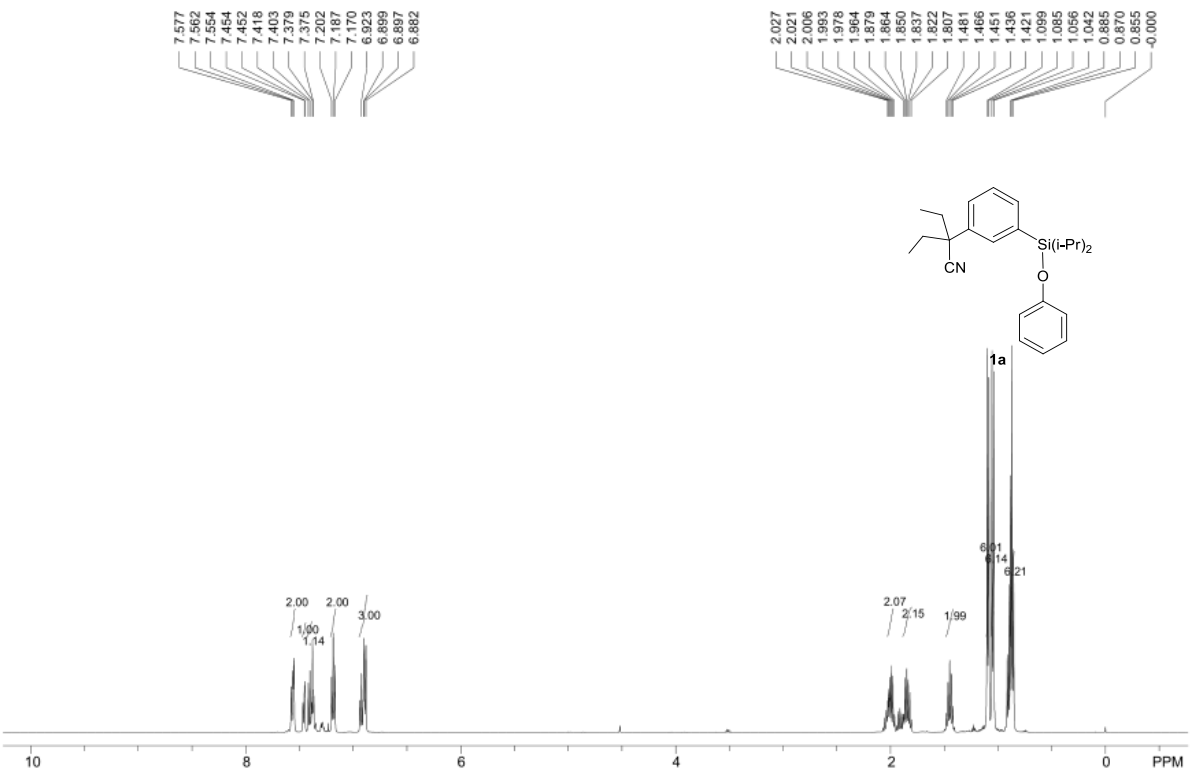
(1) S. Lee, H. Lee and K. L. Tan, *J. Am. Chem. Soc.* 2013, **135**, 18778-18781.

(2) T. Patra, S. Bag, R. Kancherla, A. Mondal, A. Dey, S. Pimparkar, S. Agasti, A. Modak and D. Maiti, *Angew .Chem. Int. Ed.* **2016**, *55*,7751-7755; *Angew .Chem.* 2016, **128**, 7882-7886.

4. NMR spectra



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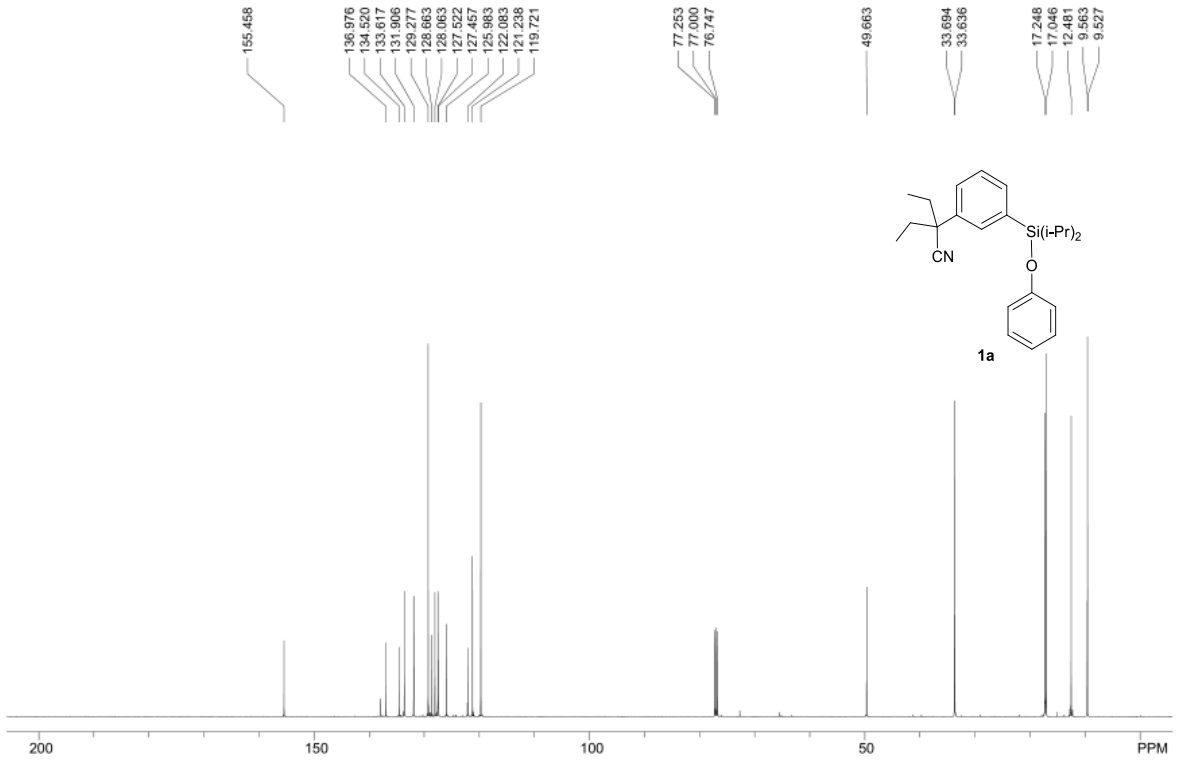
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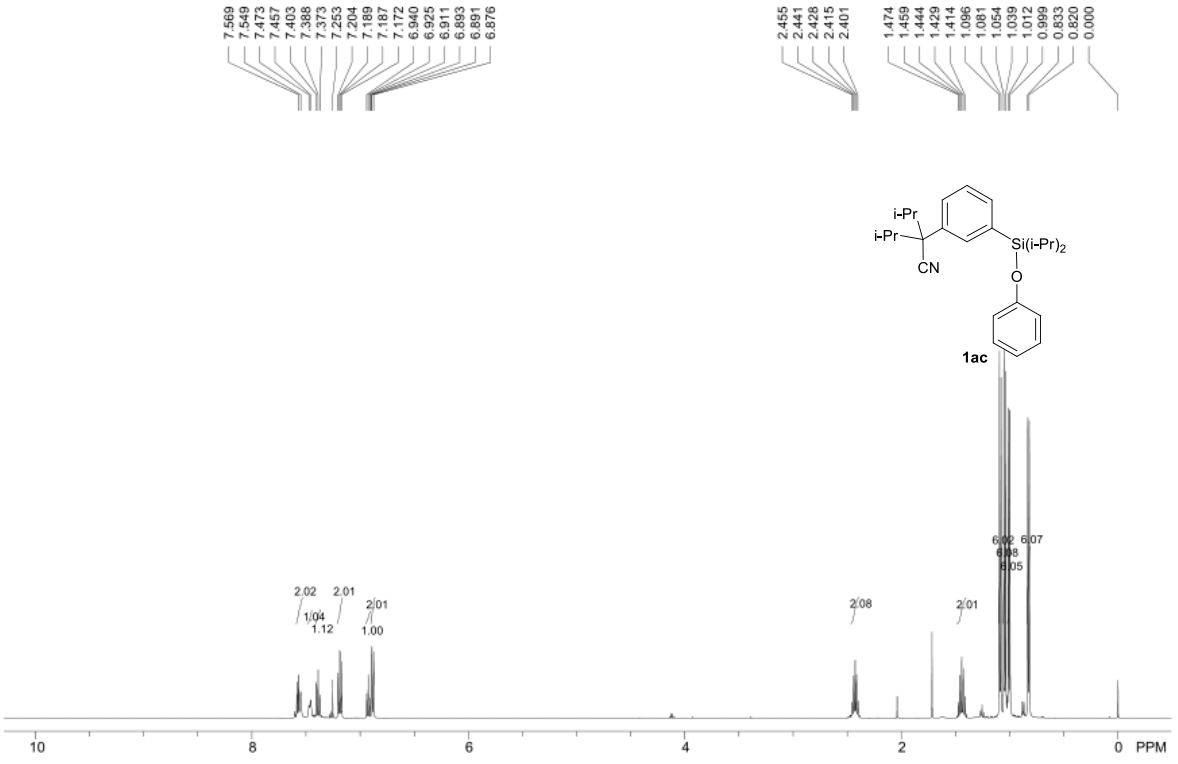
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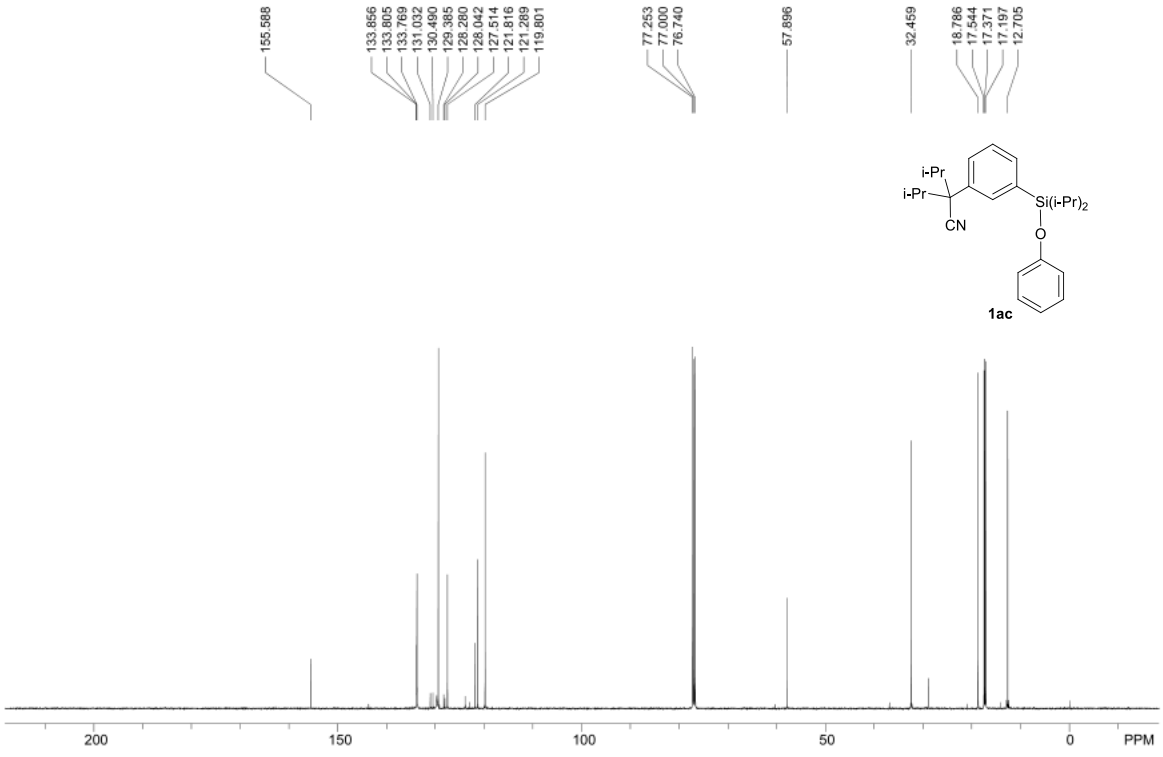
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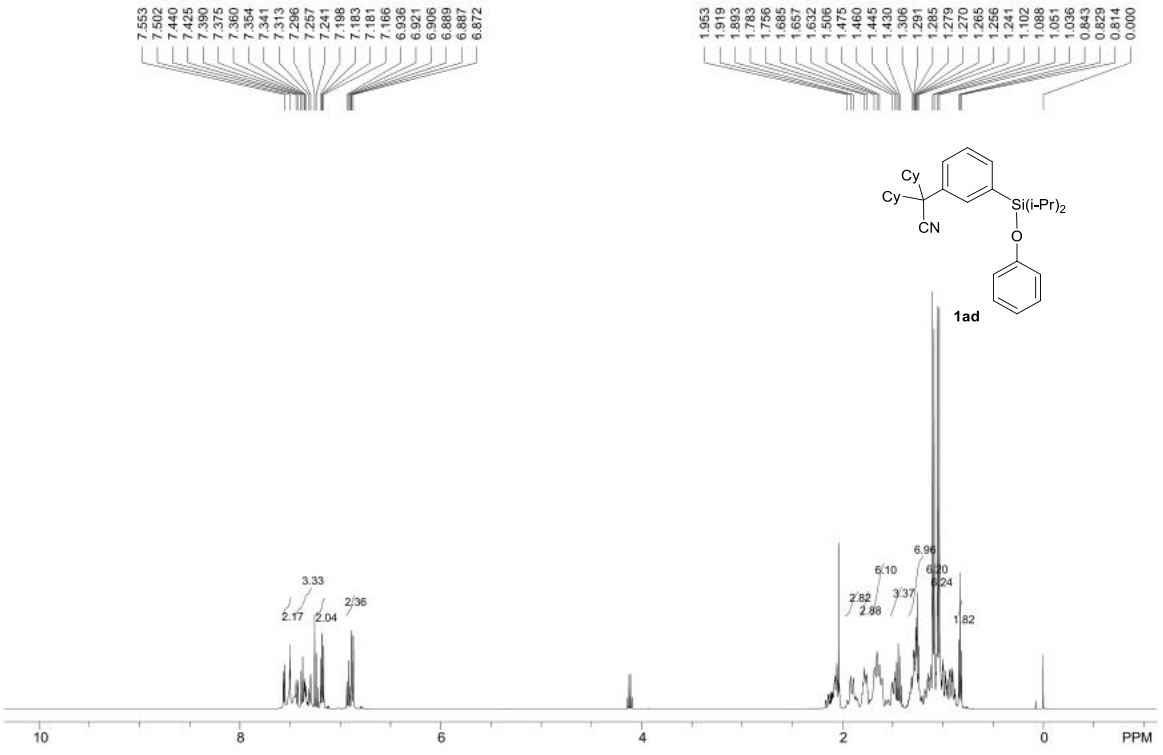
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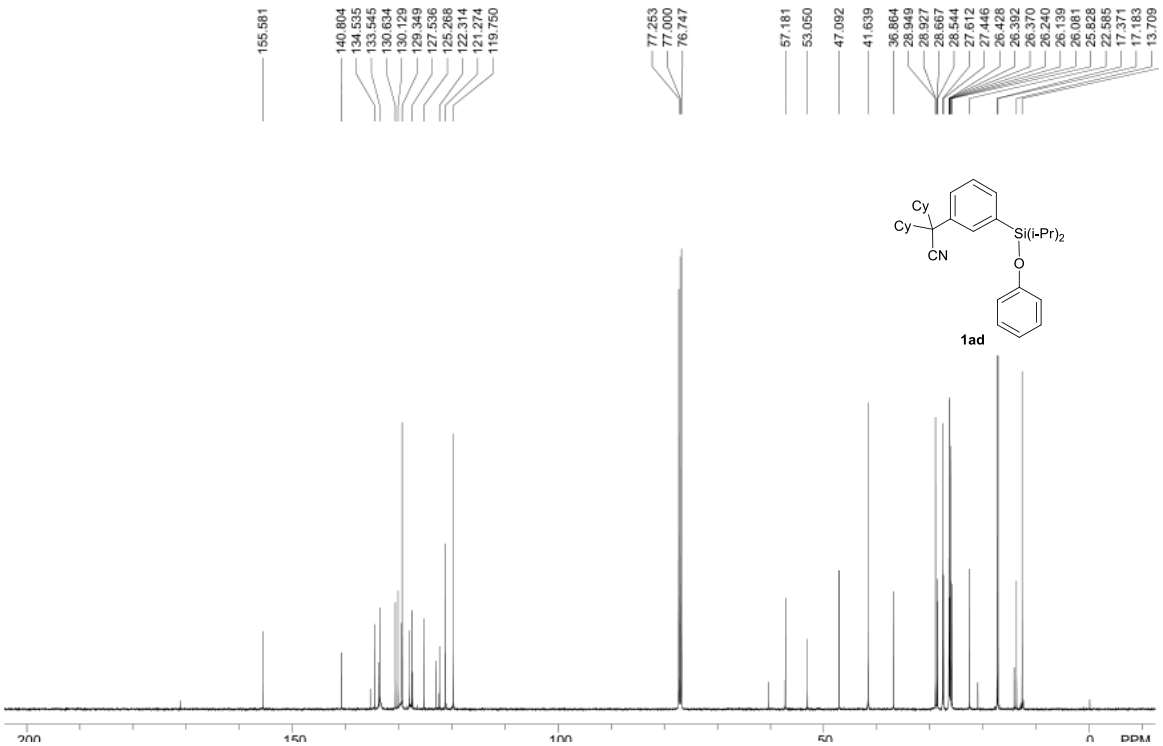
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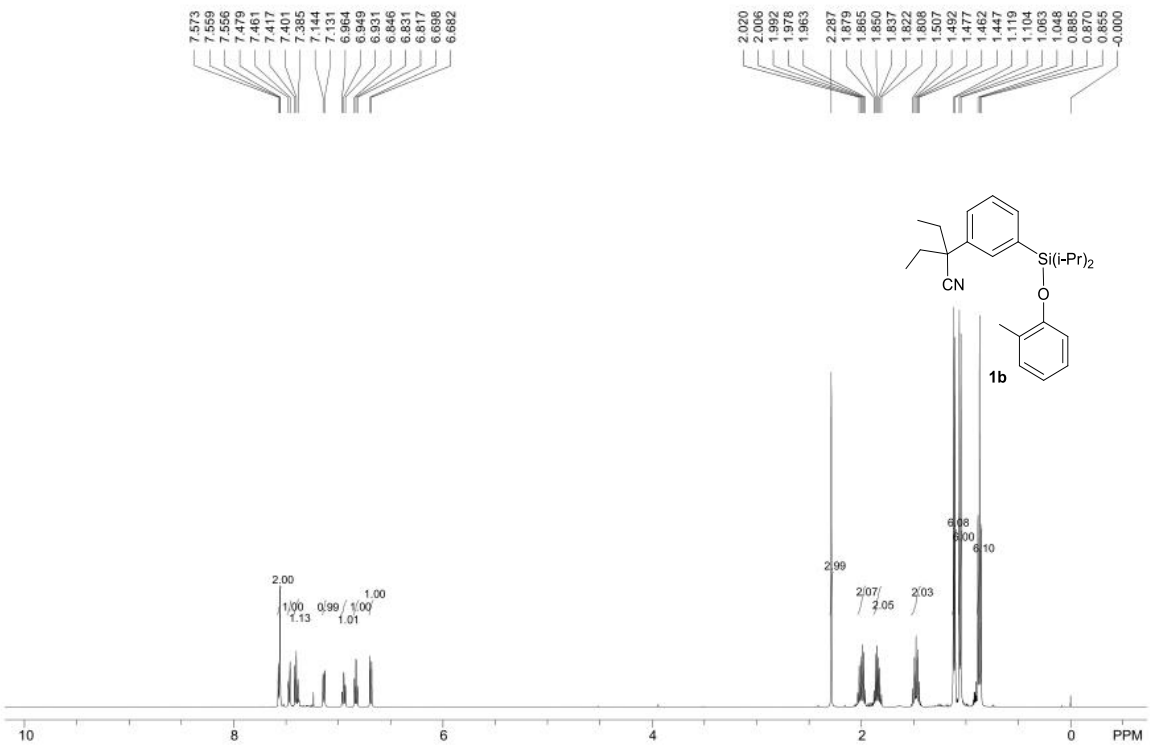
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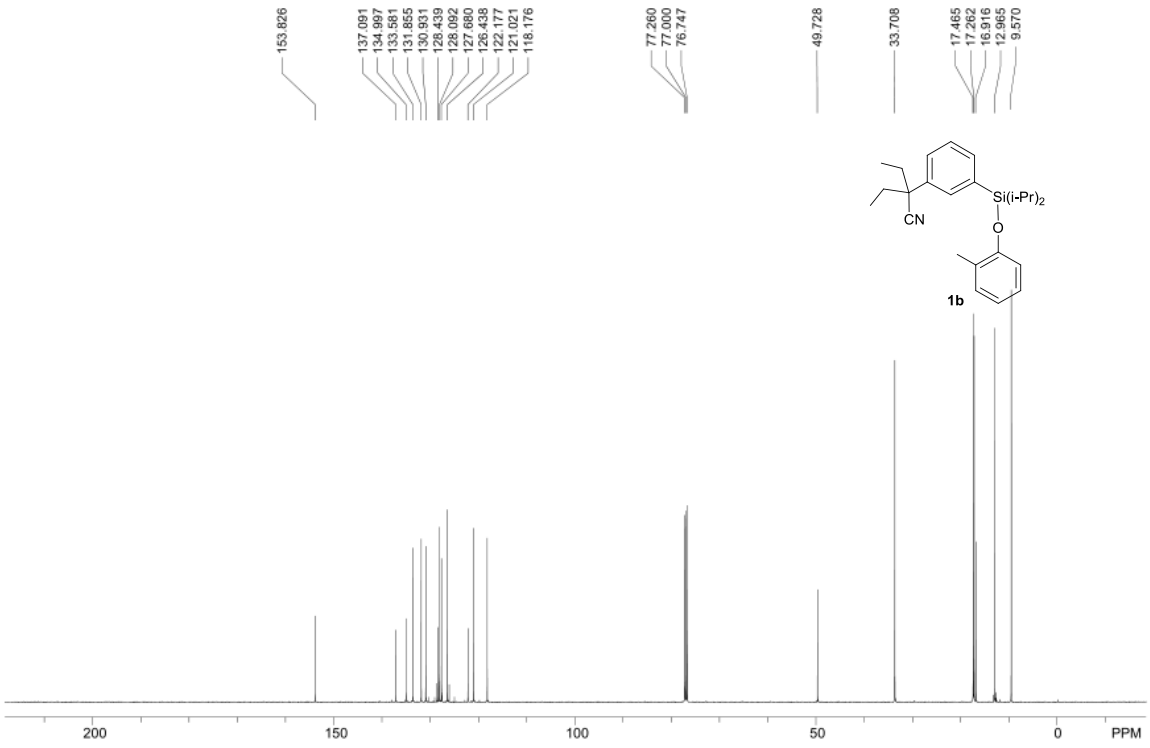
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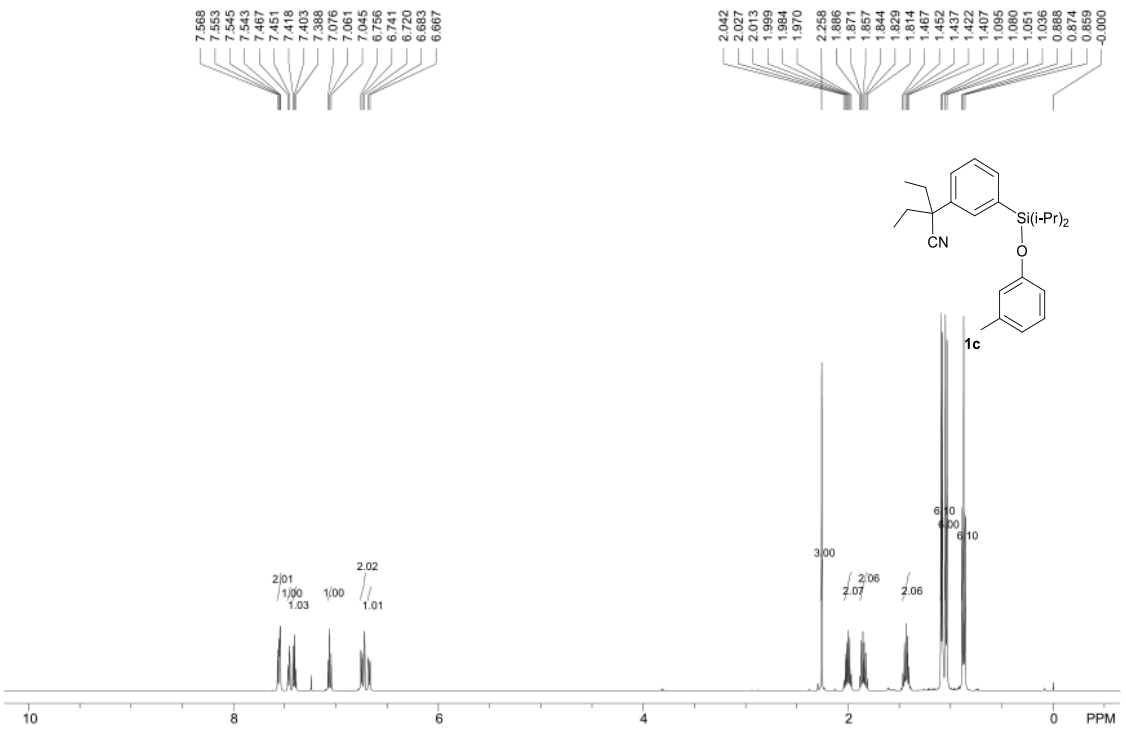
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1.036
0.888
0.874
0.859
-0.000
Si(i-Pr)2
CN
O
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1.03
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2.02
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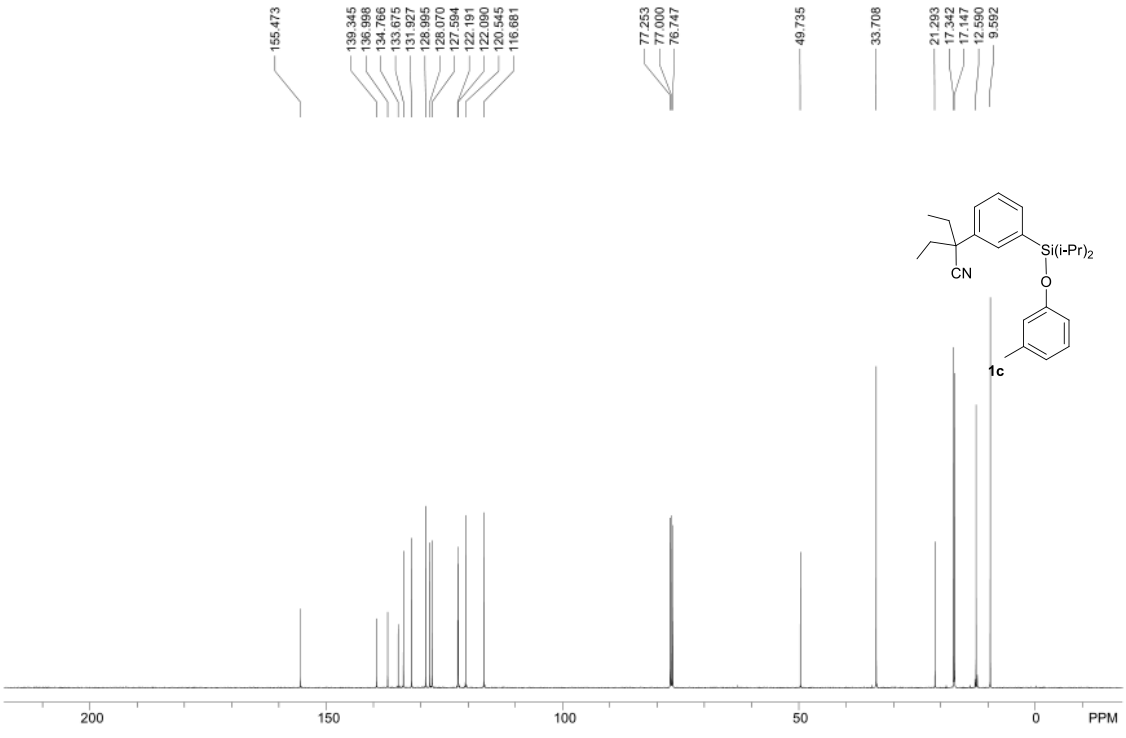
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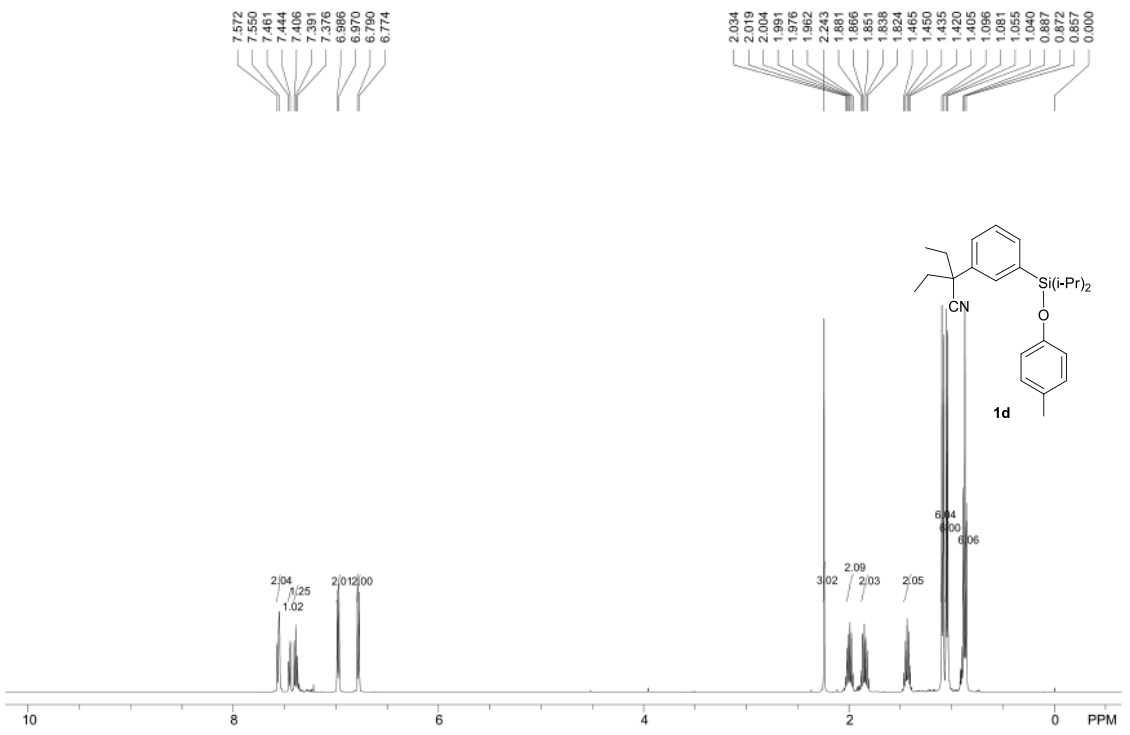
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CN
O
1d
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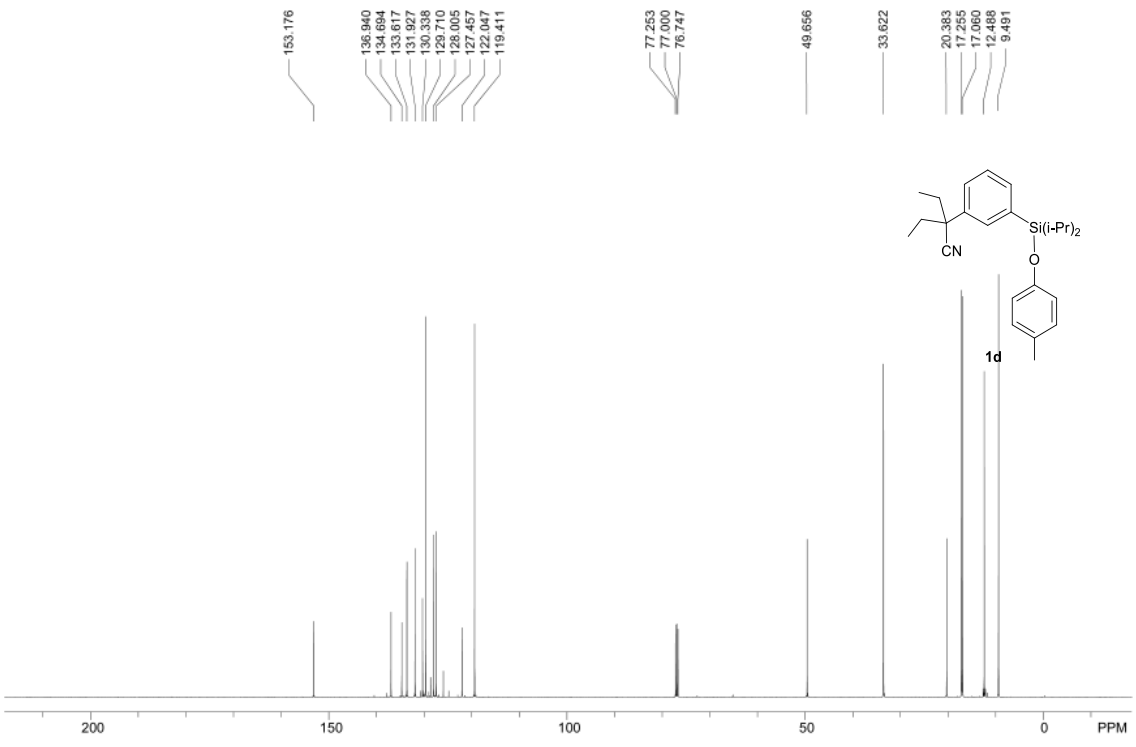
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O
1d
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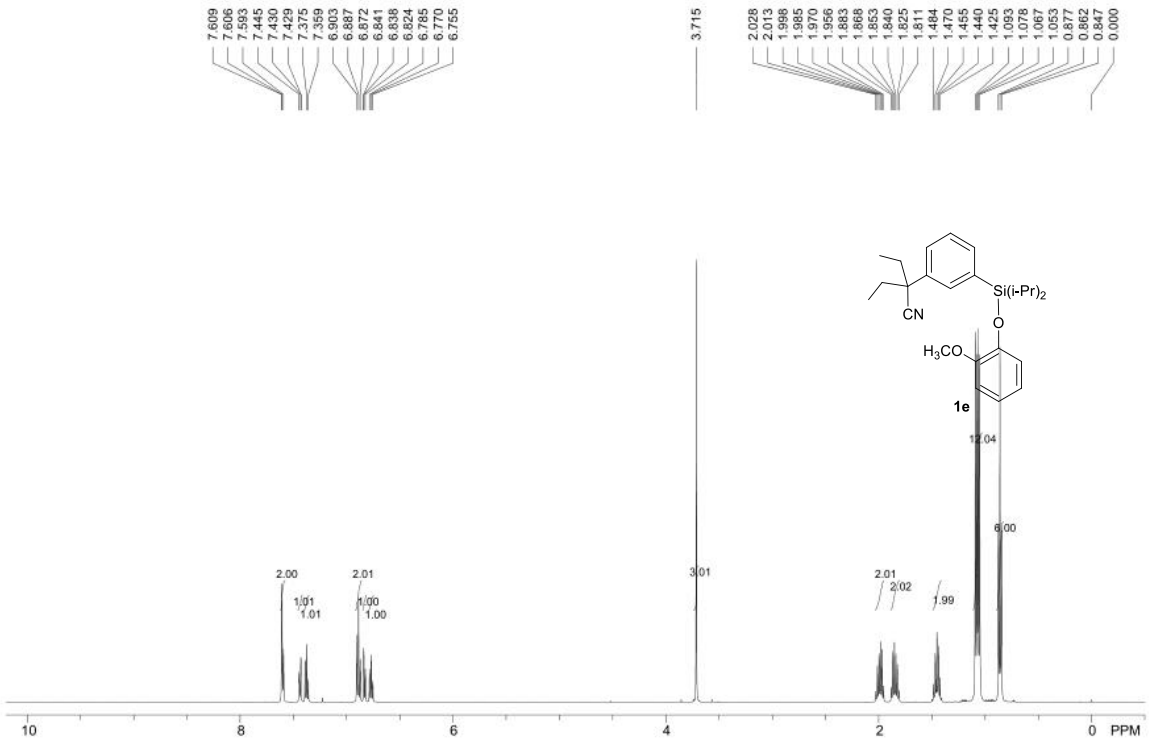
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Si(i-Pr)2
CN
O
H3CO
1e
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1.01
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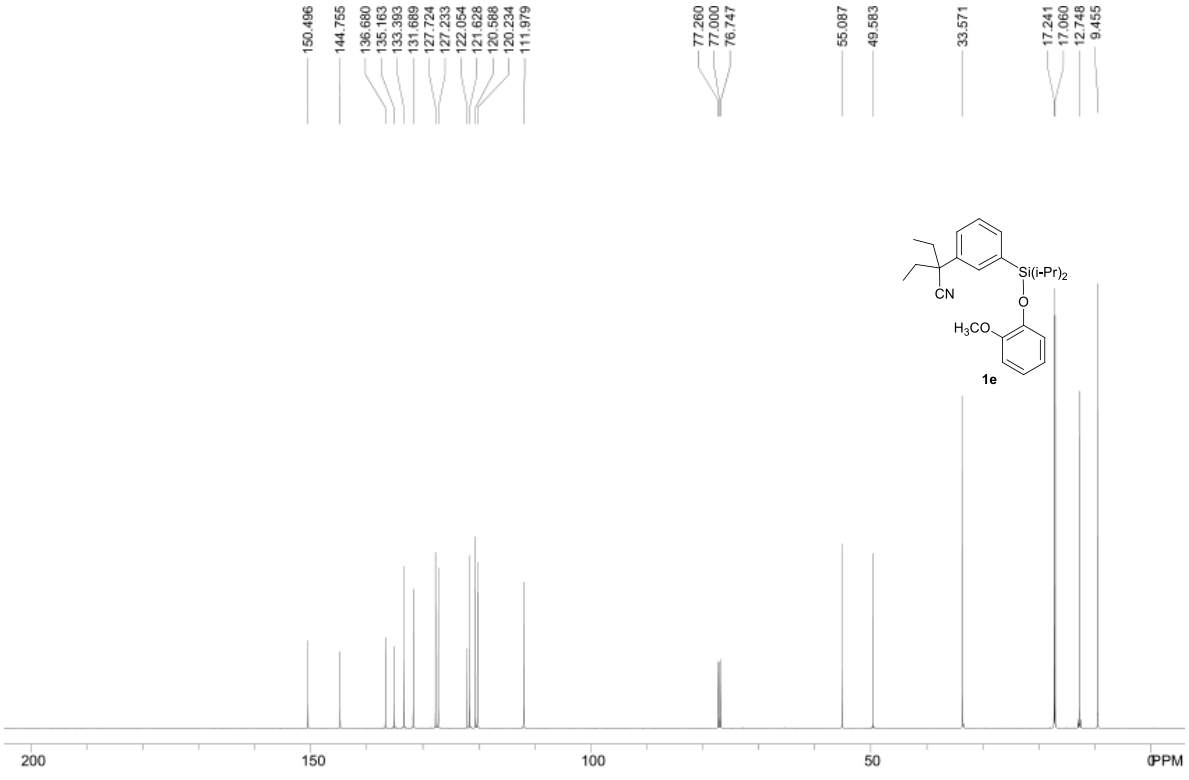
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Si(i-Pr)2
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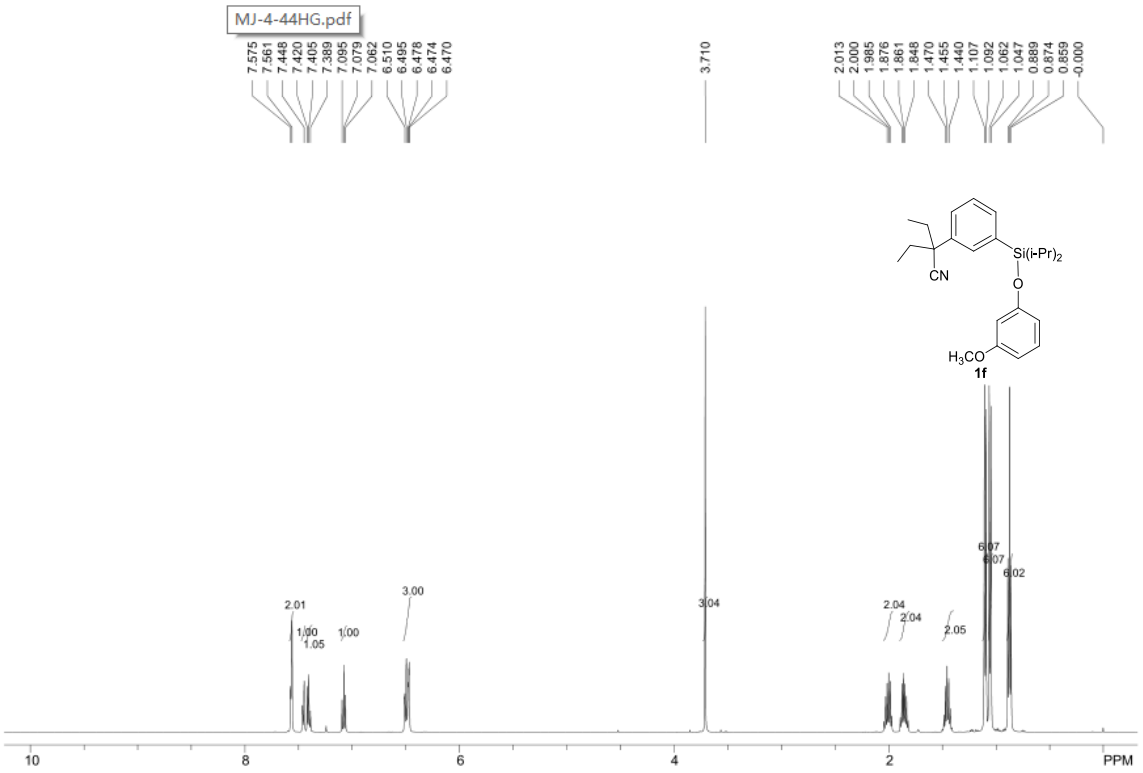
O
H3CO
1e
200
150
100
50
0 PPM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Si(i-Pr)2
O
CN
H3CO
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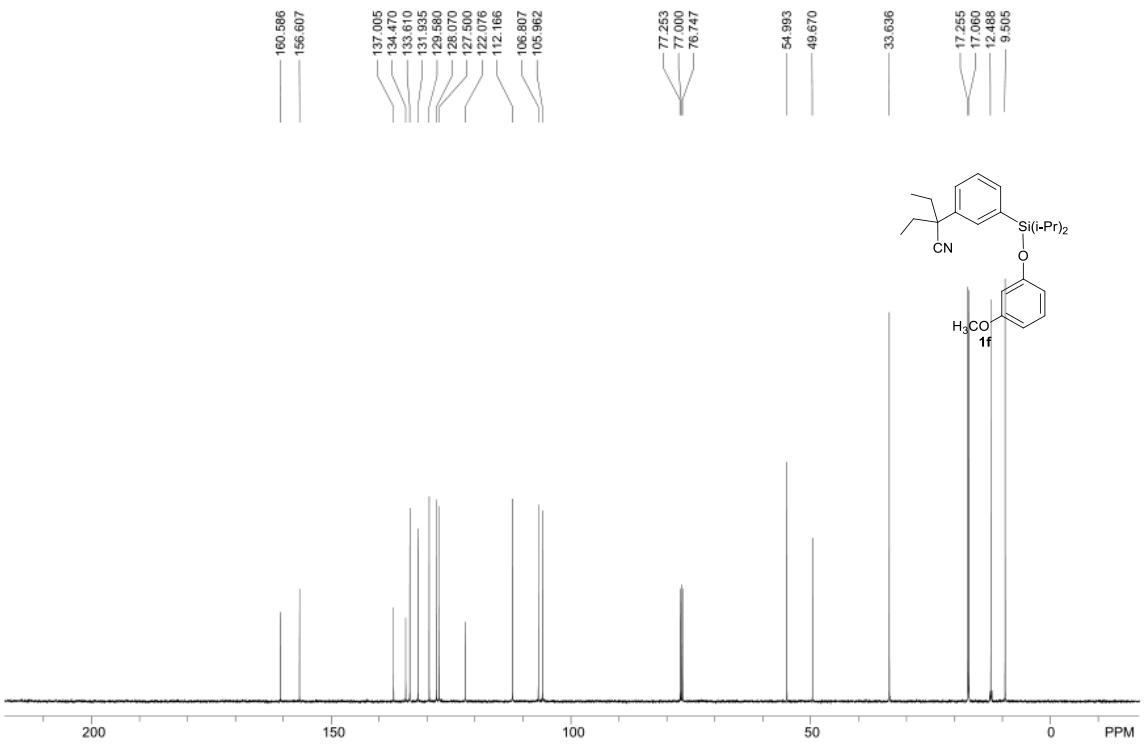
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33.636
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Si(i-Pr)2
O
CN
H3CO
1f
200
150
100
50
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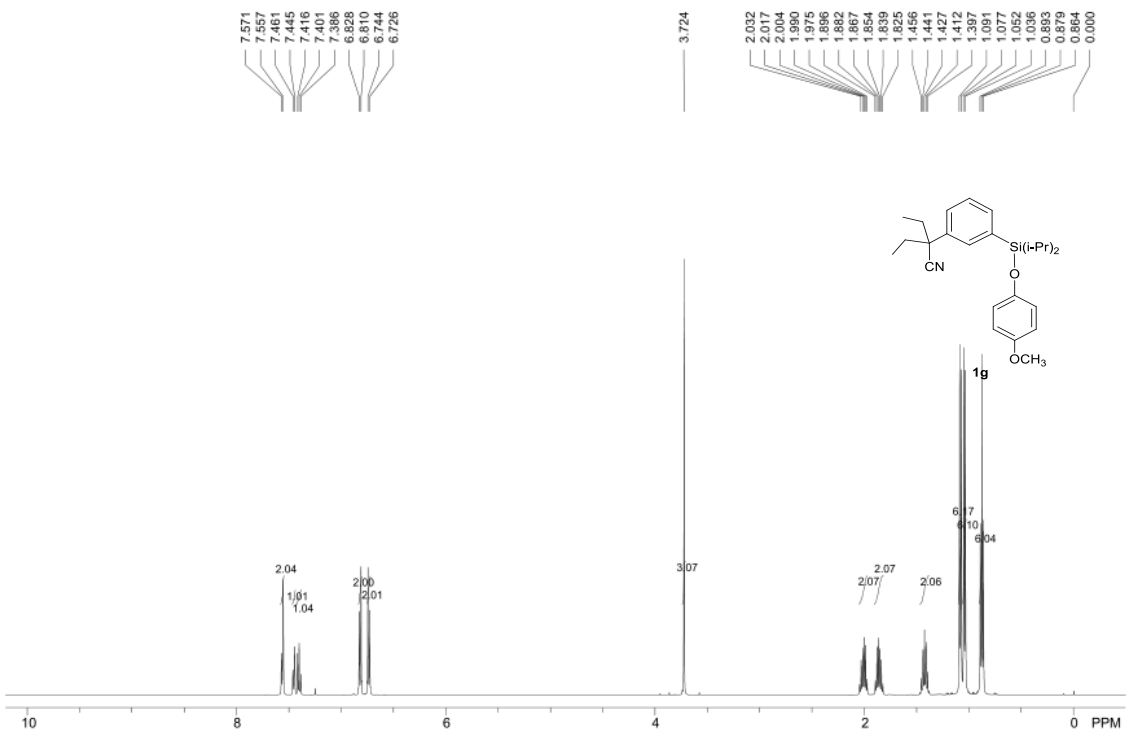
PPM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0.879
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CN
O
OCH3
1g
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1.04
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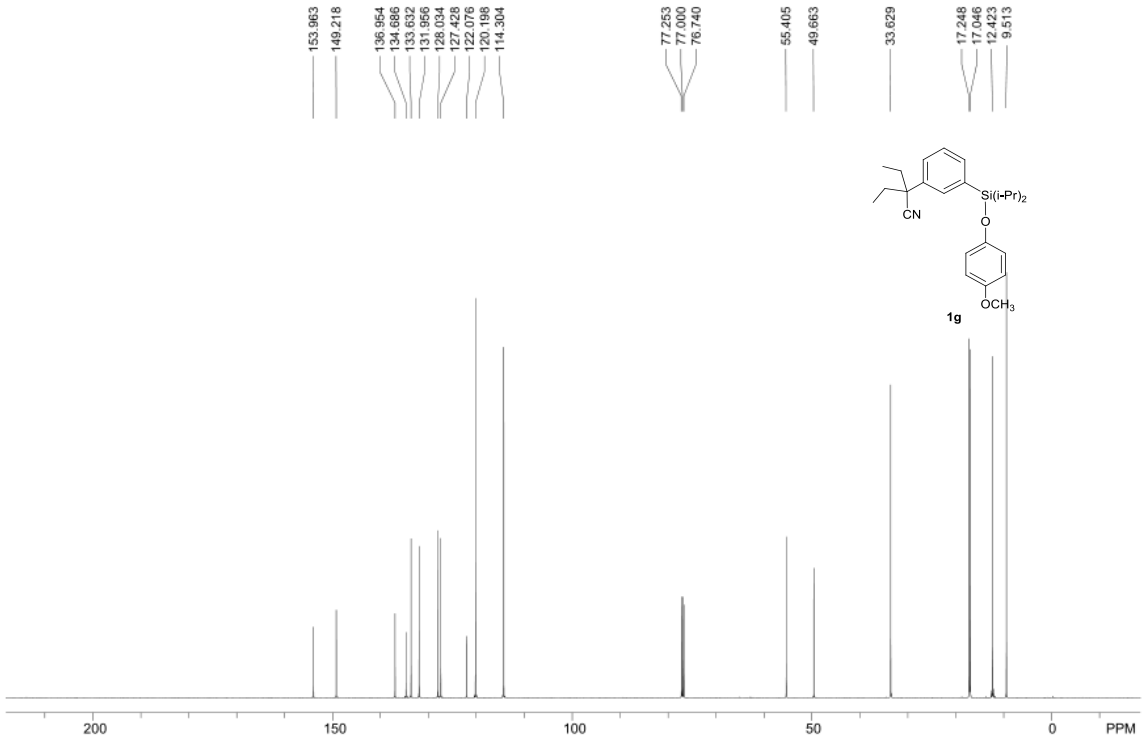
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1g
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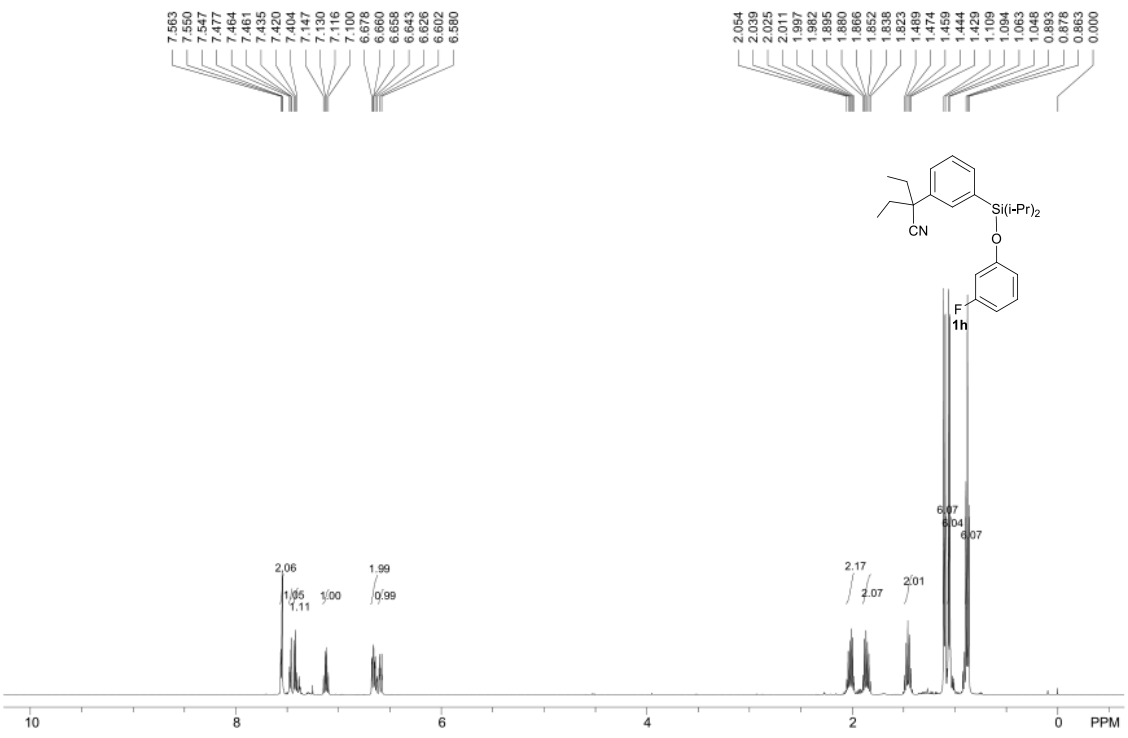
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O
F
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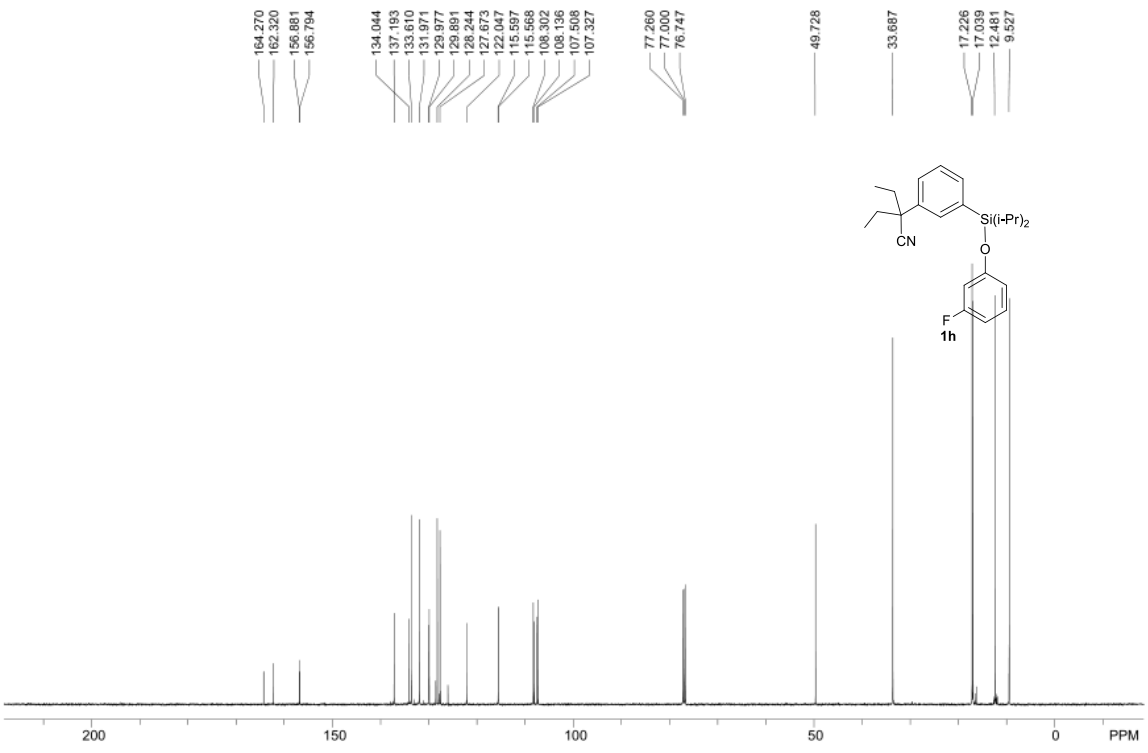
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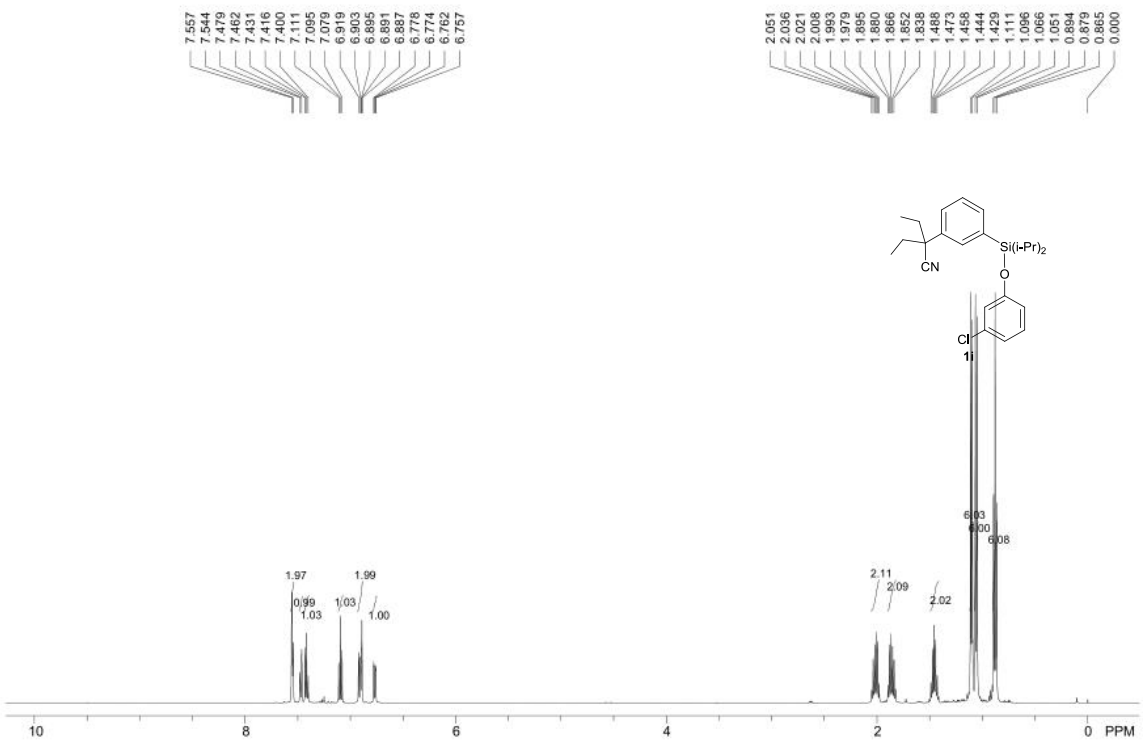
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O
Cl
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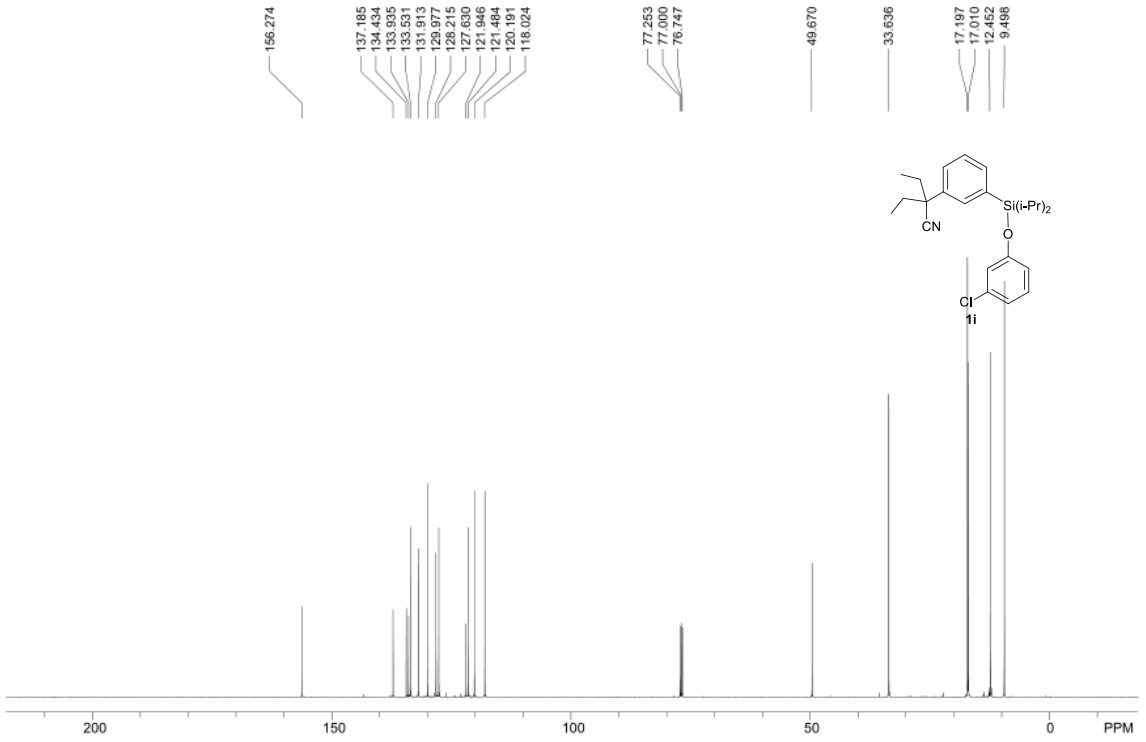
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Cl
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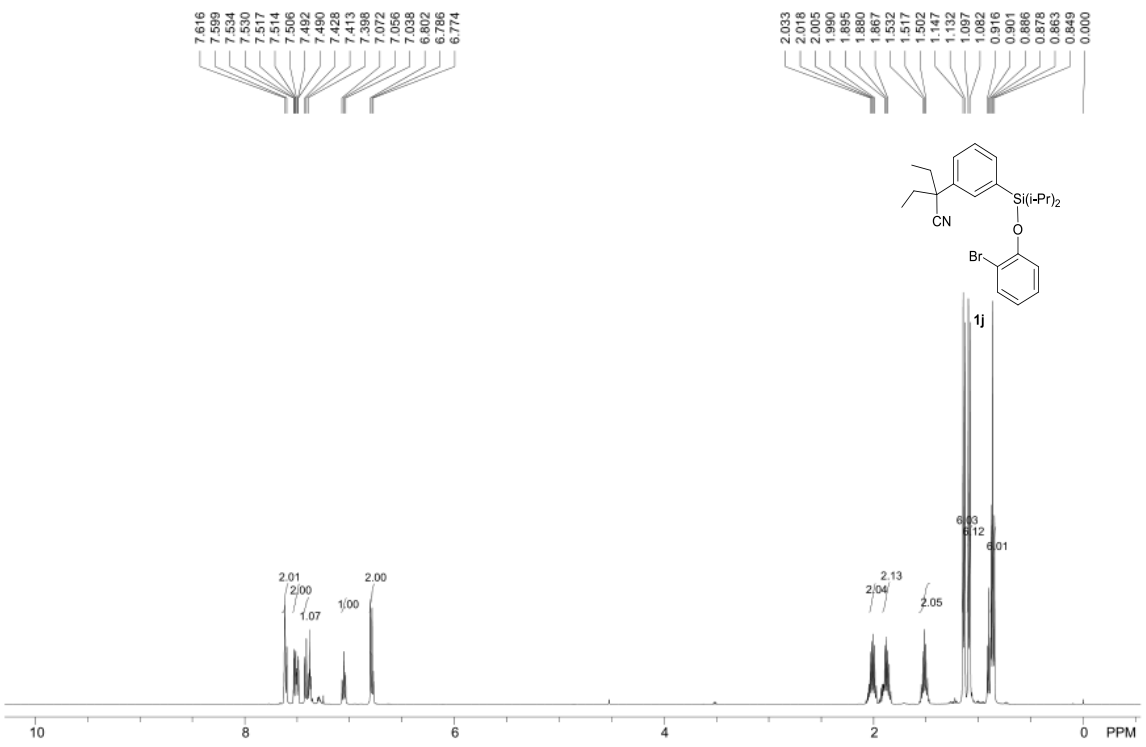
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Si(i-Pr)2
CN
O
Br
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2.00
1.07
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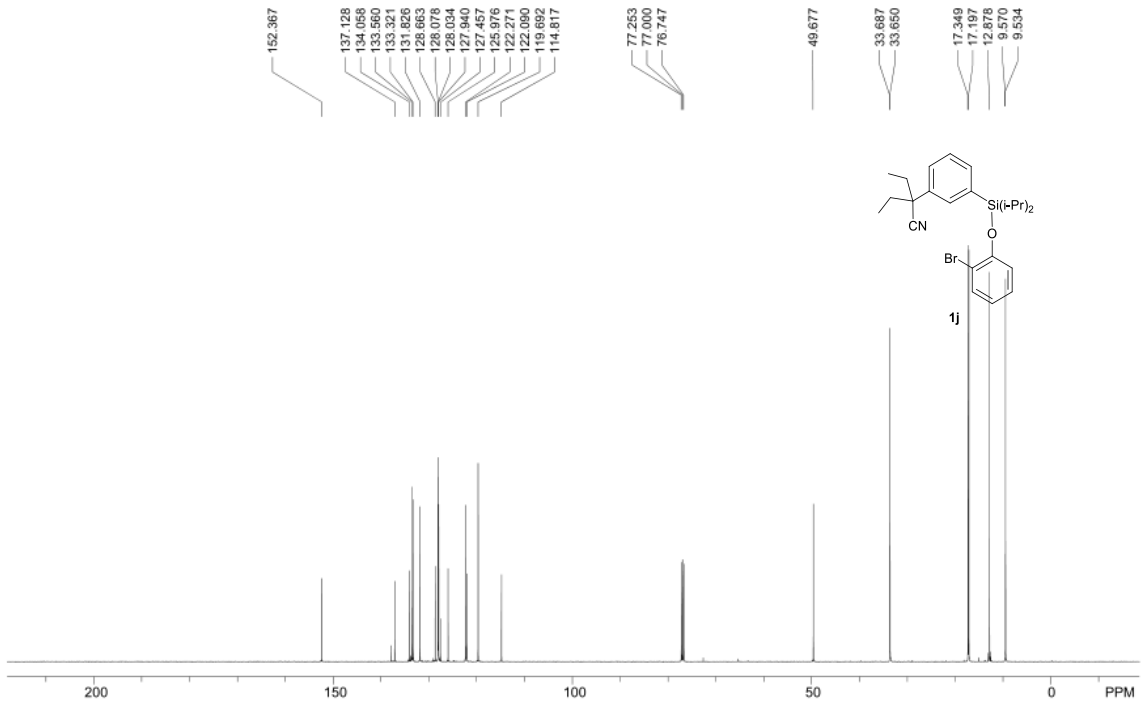
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Si(i-Pr)2
CN
O
Br
1j
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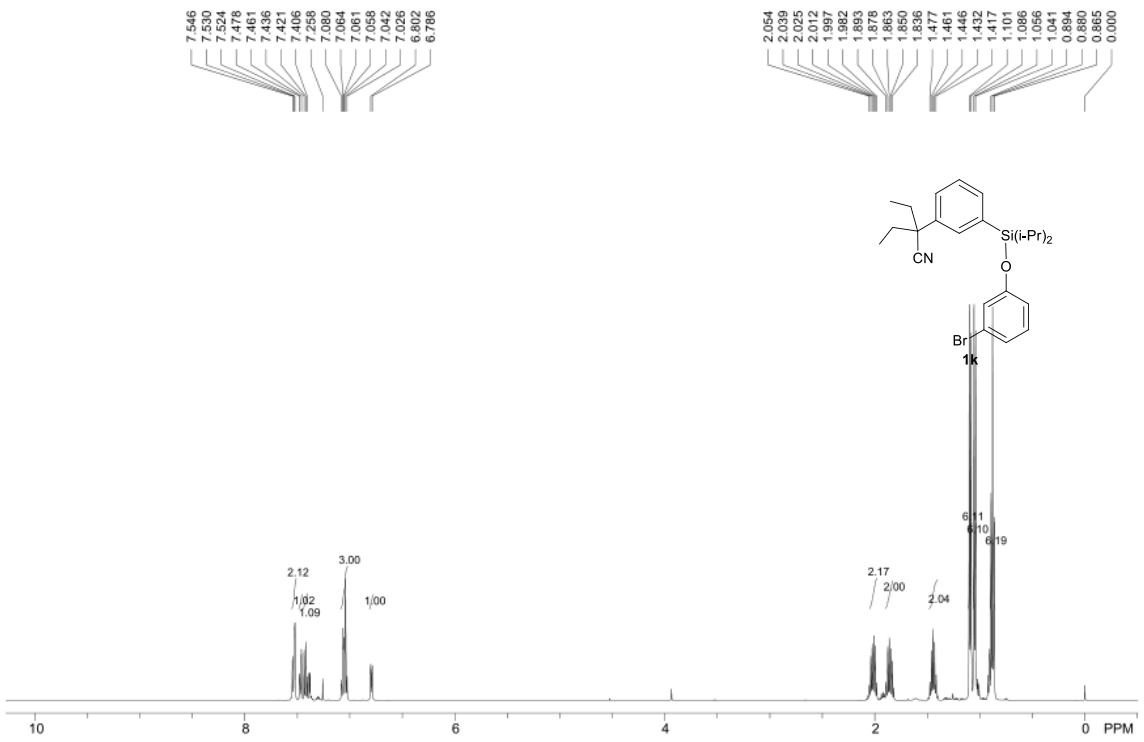
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O
Br
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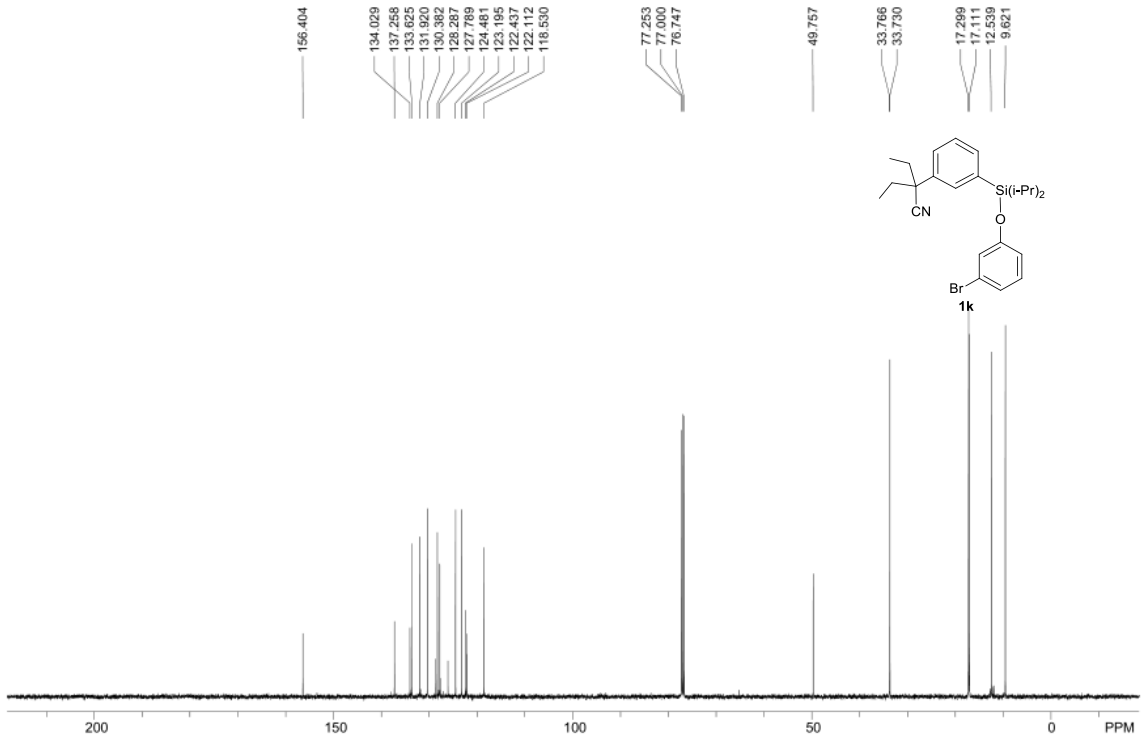
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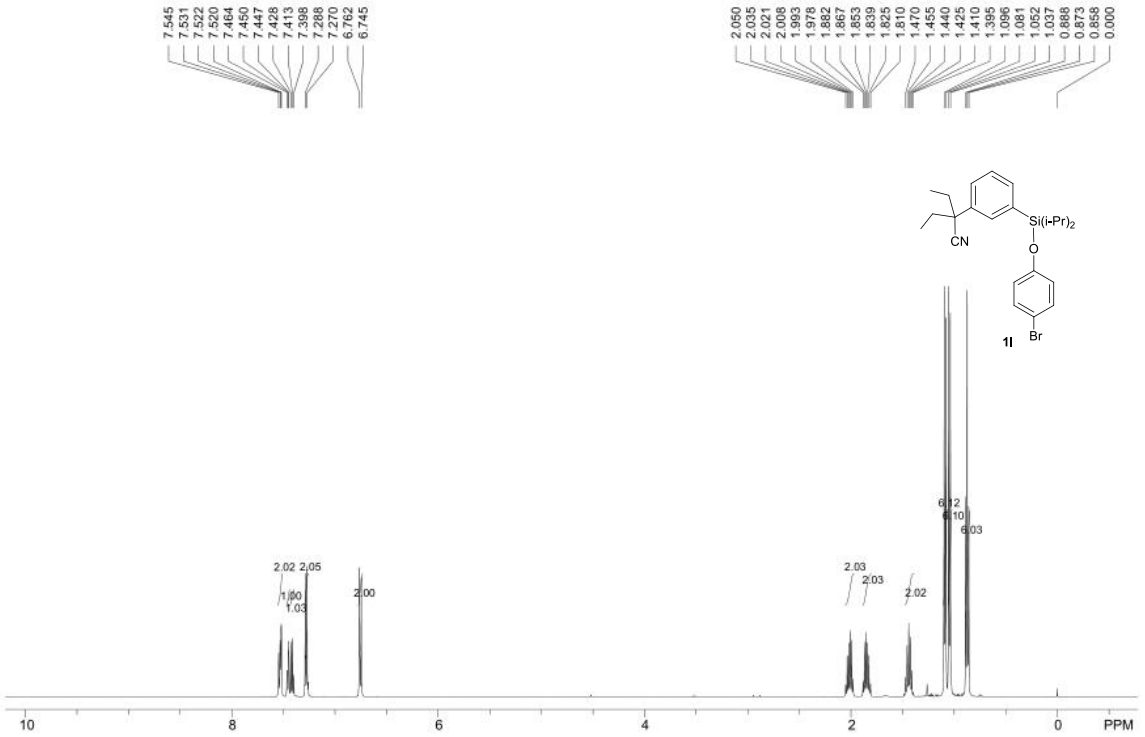
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Si(i-Pr)2
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O
Br
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1.00
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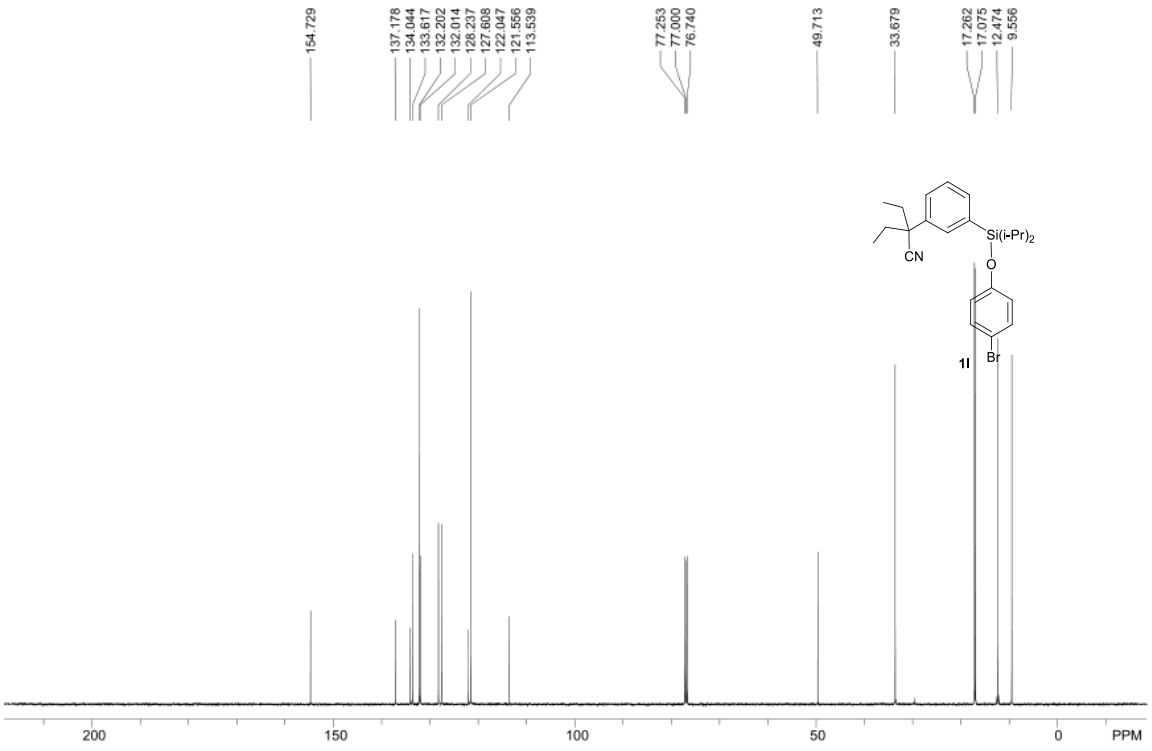
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Si(i-Pr)2
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O
Br
1l
200
150
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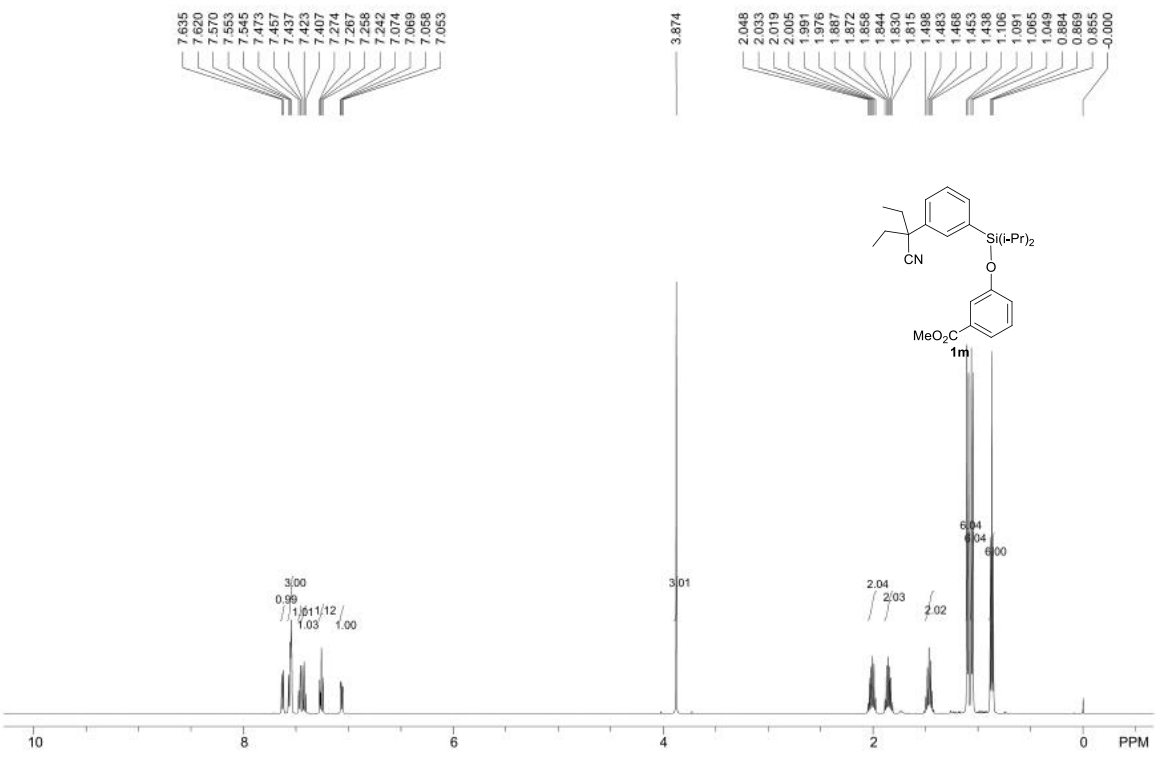
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6
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2
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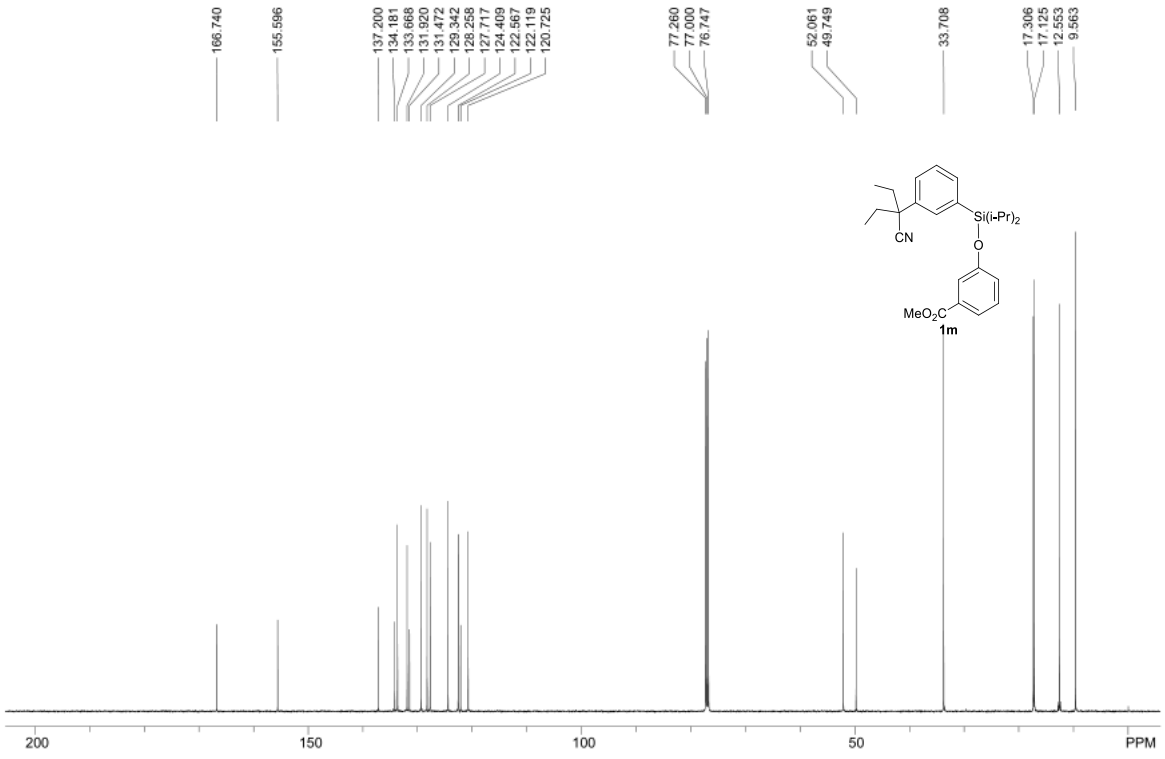
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77.000
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33.708
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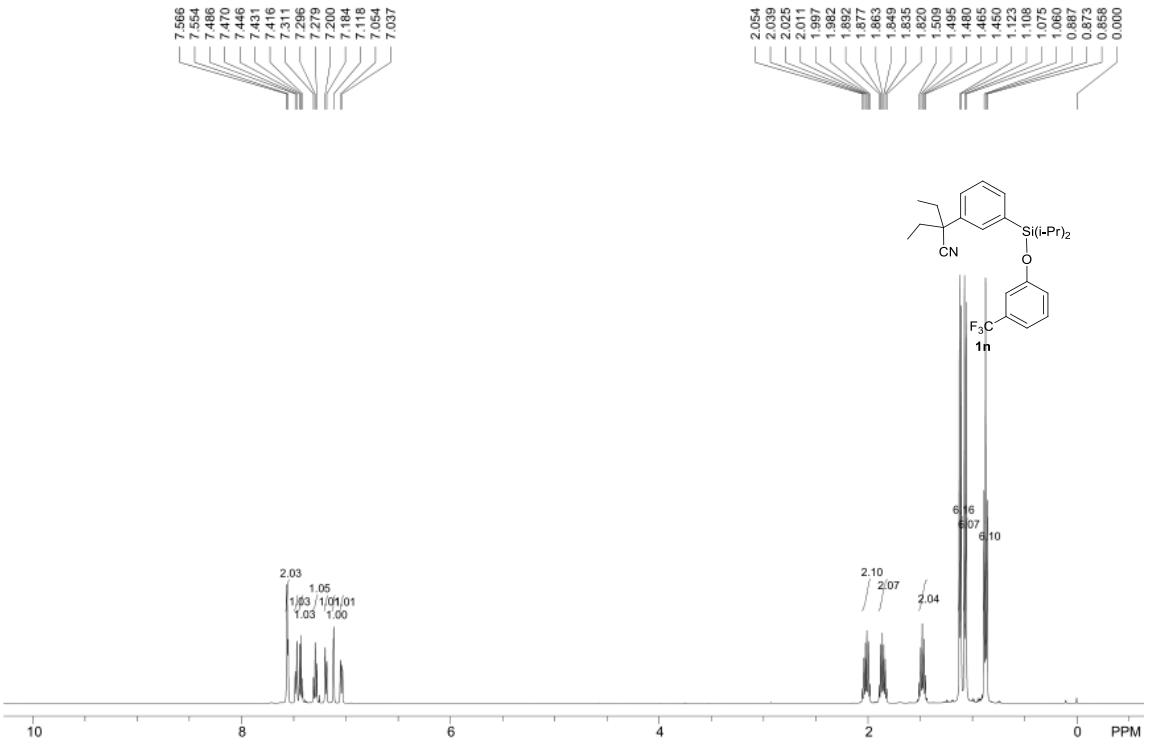
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2.054
2.039
2.025
2.011
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1.892
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1.863
1.849
1.835
1.820
1.509
1.495
1.480
1.465
1.450
1.123
1.108
1.075
1.060
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0.873
0.858
0.000
Si(i-Pr)2
CN
O
F3C
1n
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1.05
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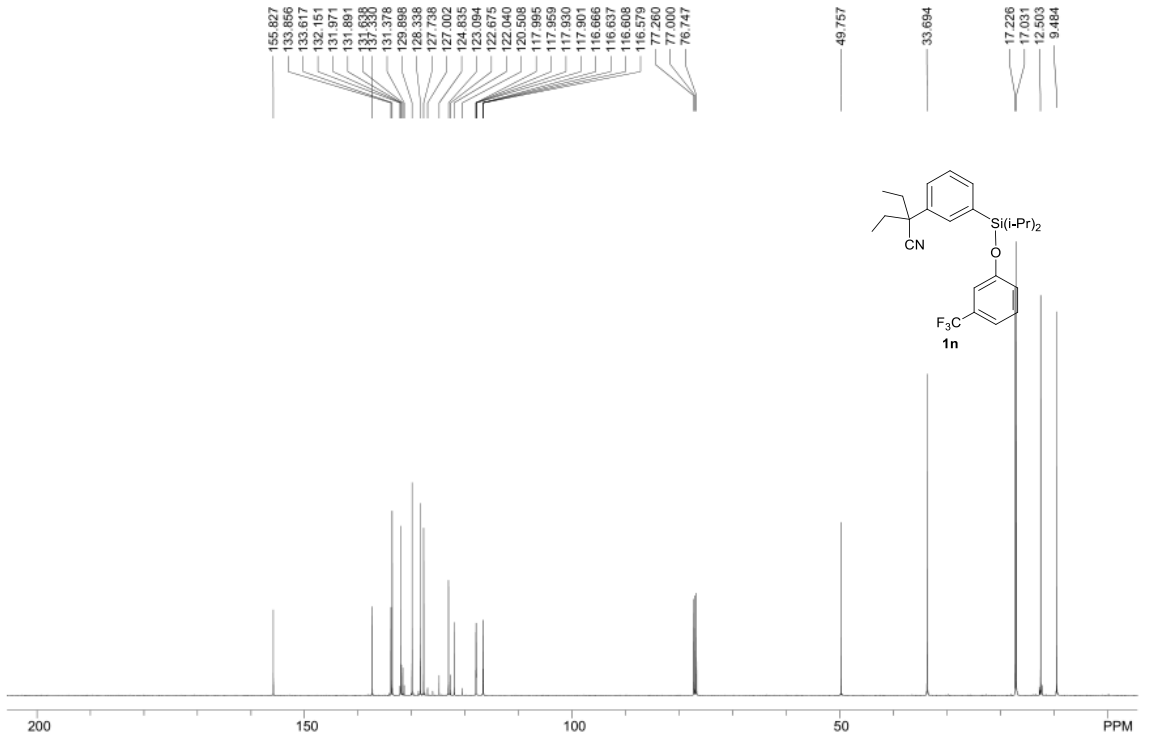
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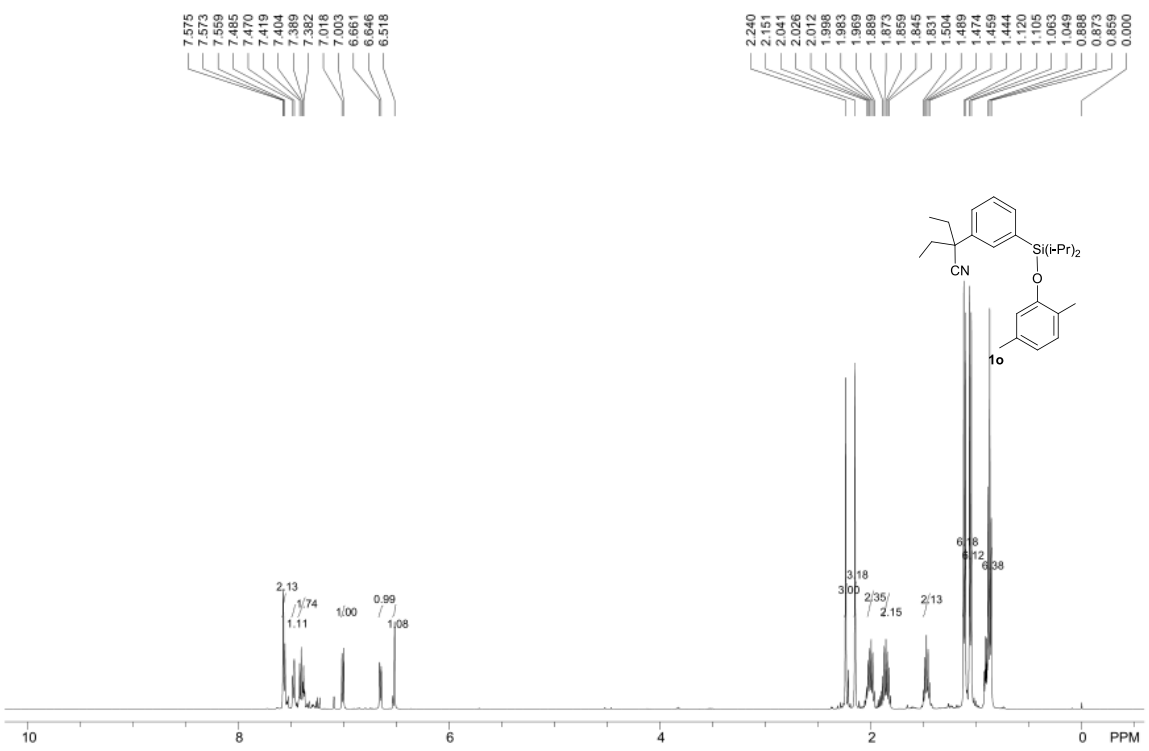
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2.026
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1.889
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1.859
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1.831
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1.474
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1.444
1.120
1.105
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1.049
0.888
0.873
0.859
0.000
Si(i-Pr)2
CN
O
1o
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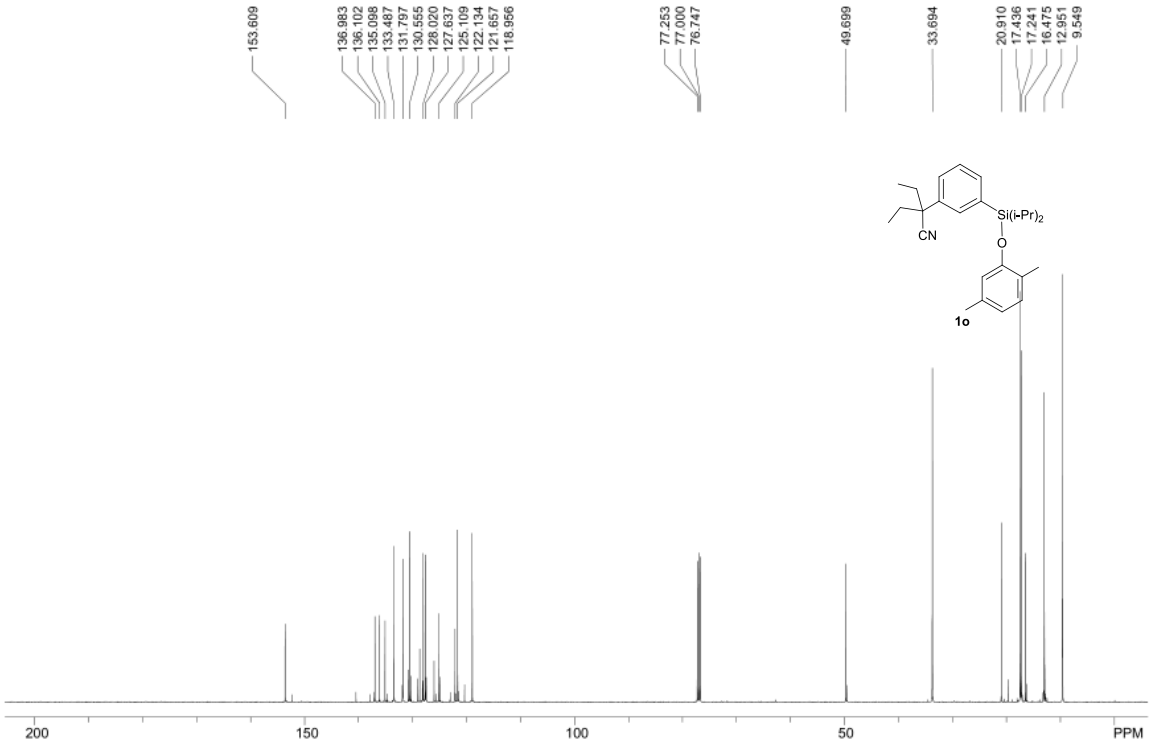
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CN
O
1o
200
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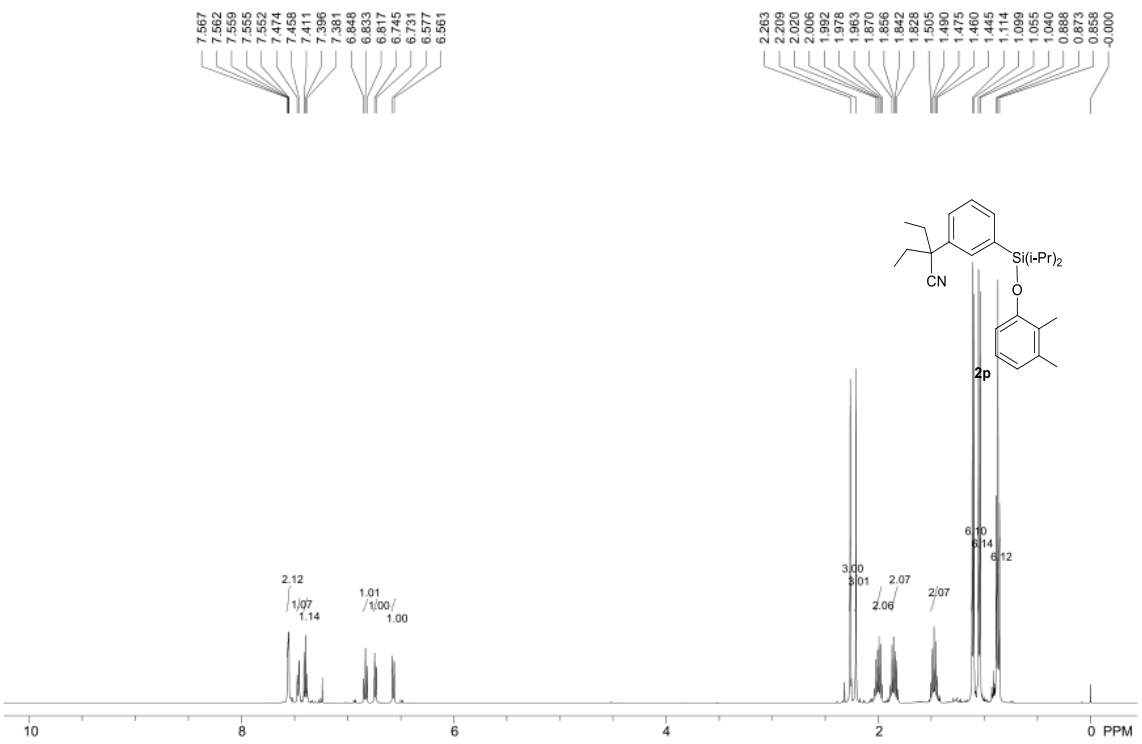
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6.833
6.817
6.745
6.731
6.577
6.561
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2.020
2.006
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1.978
1.963
1.870
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1.505
1.490
1.475
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1.445
1.114
1.099
1.055
1.040
0.888
0.873
0.858
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Si(i-Pr)2
CN
O
2p
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1.14
1.01
1.00
1.00
3.00
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6.14
6.12
10
8
6
4
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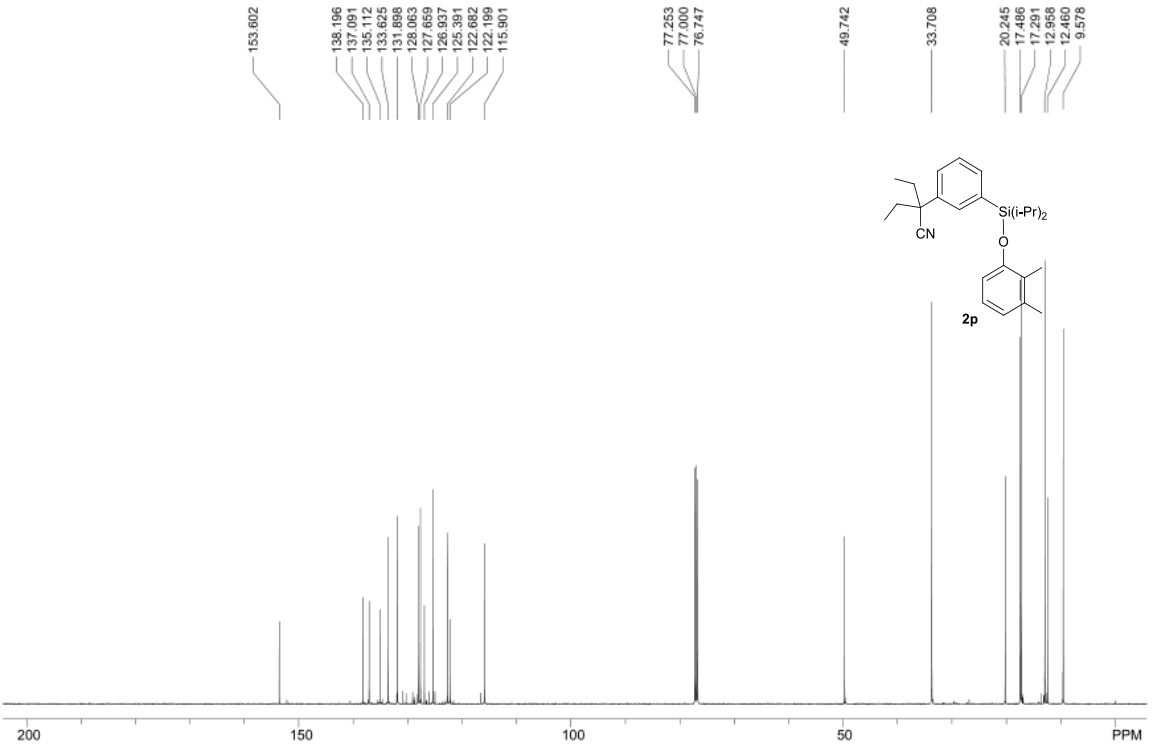
0 PPM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77.253
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76.747
49.742
33.708
20.245
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Si(i-Pr)2
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O
2p
200
150
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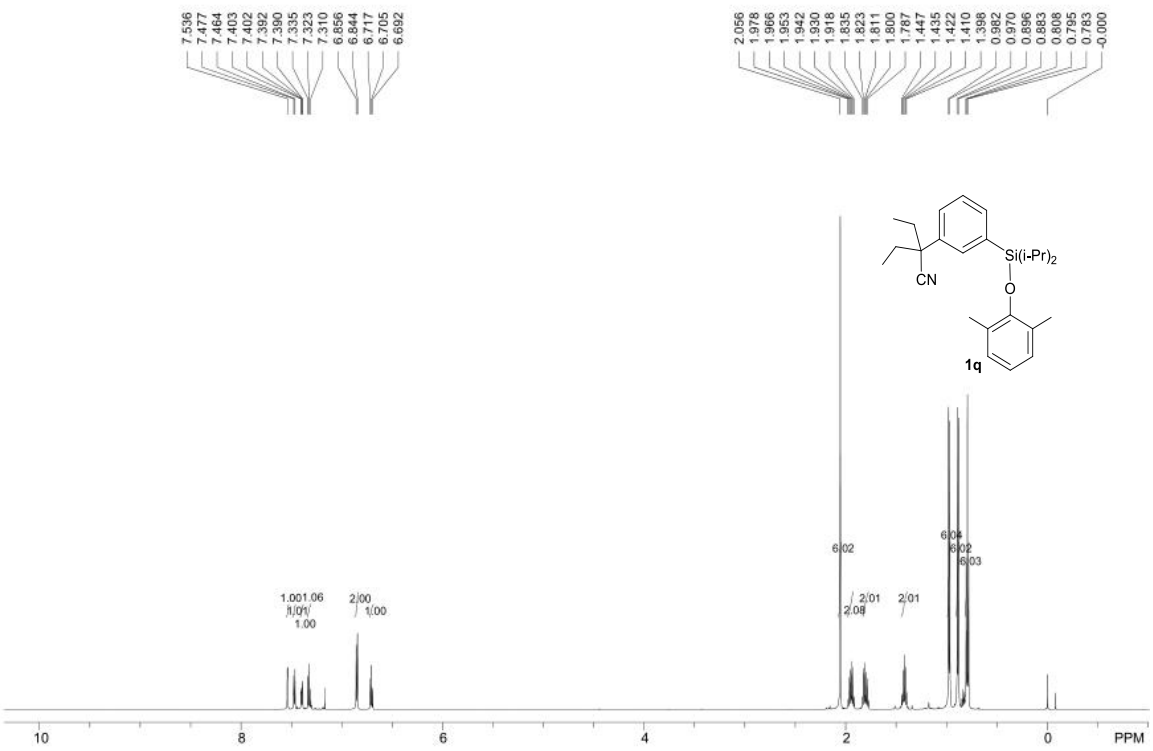
50
PPM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6.705
6.692
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0.883
0.808
0.795
0.783
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Si(i-Pr)2
CN
O
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2.00
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6.02
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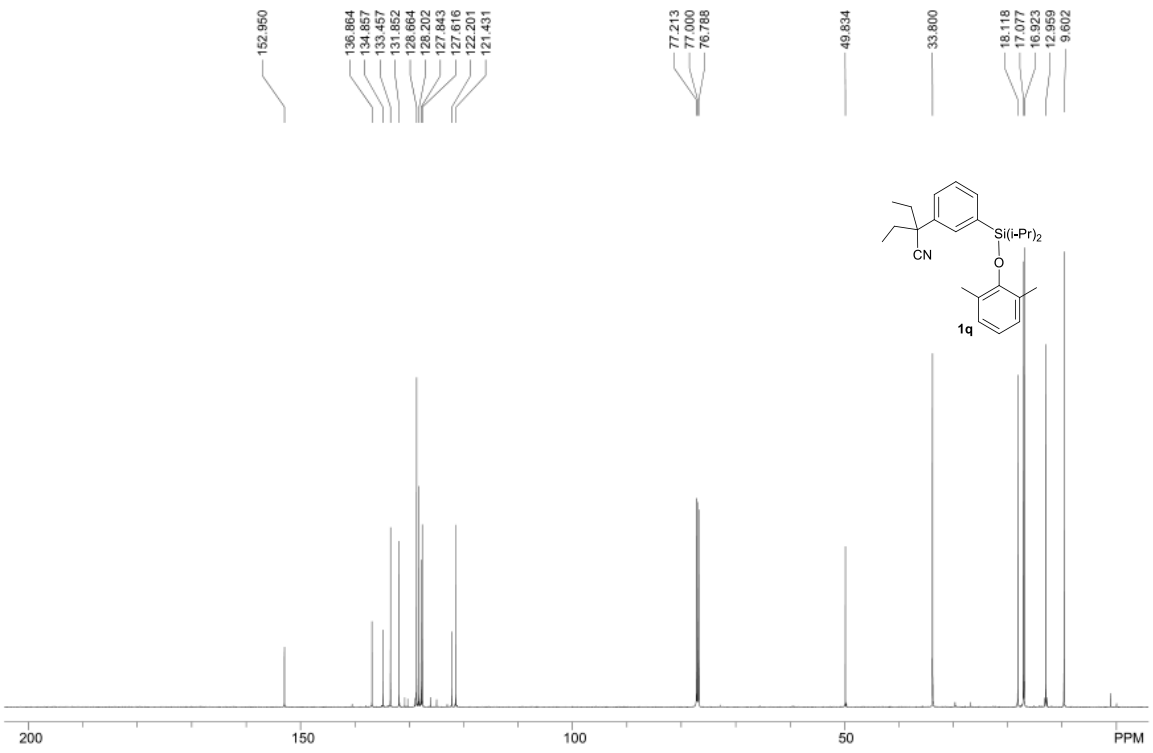
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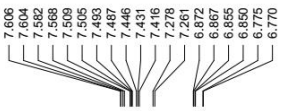
Si(i-Pr)2
CN
O
1q
200
150
100
50
PPM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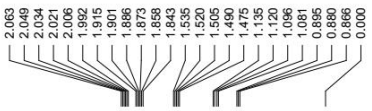
6.770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1.858
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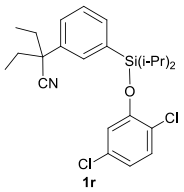
0.000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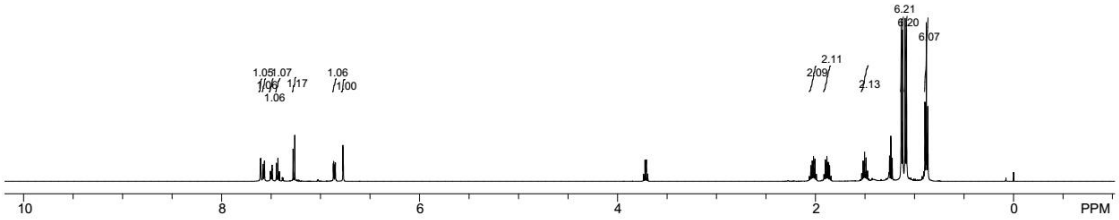
CN
O
Cl
Cl

1r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1.06
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1.00
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10
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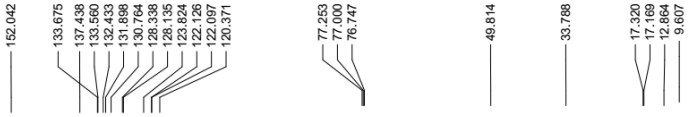
PPM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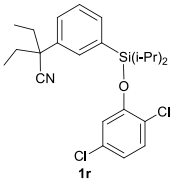
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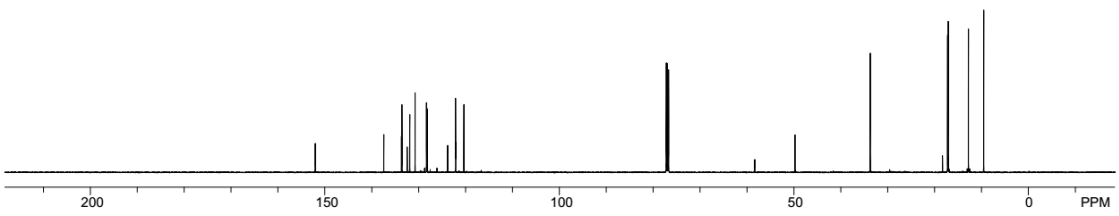
CN
O
Cl
Cl

1r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100
50
0
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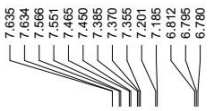
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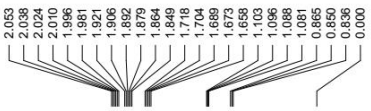
6.780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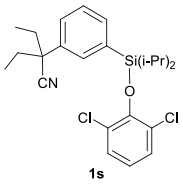
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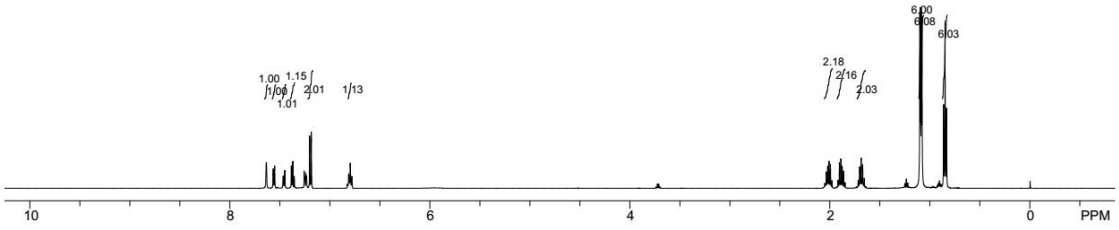
O
Cl
Cl

1s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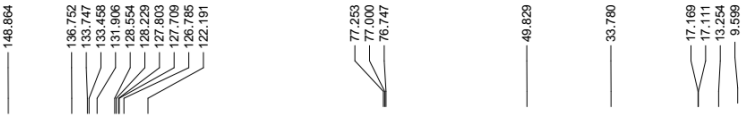
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33.780
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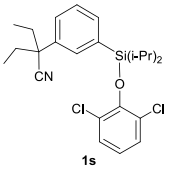
9.599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CN
O
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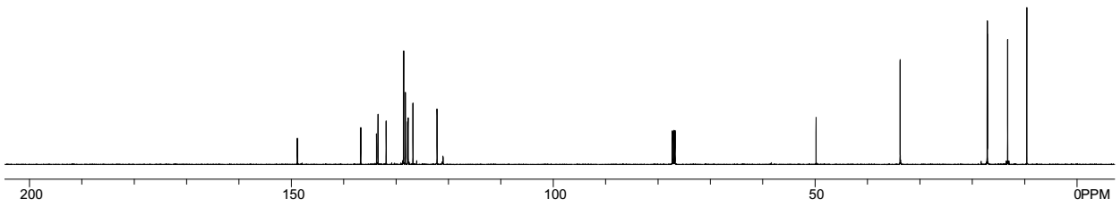
Cl

1s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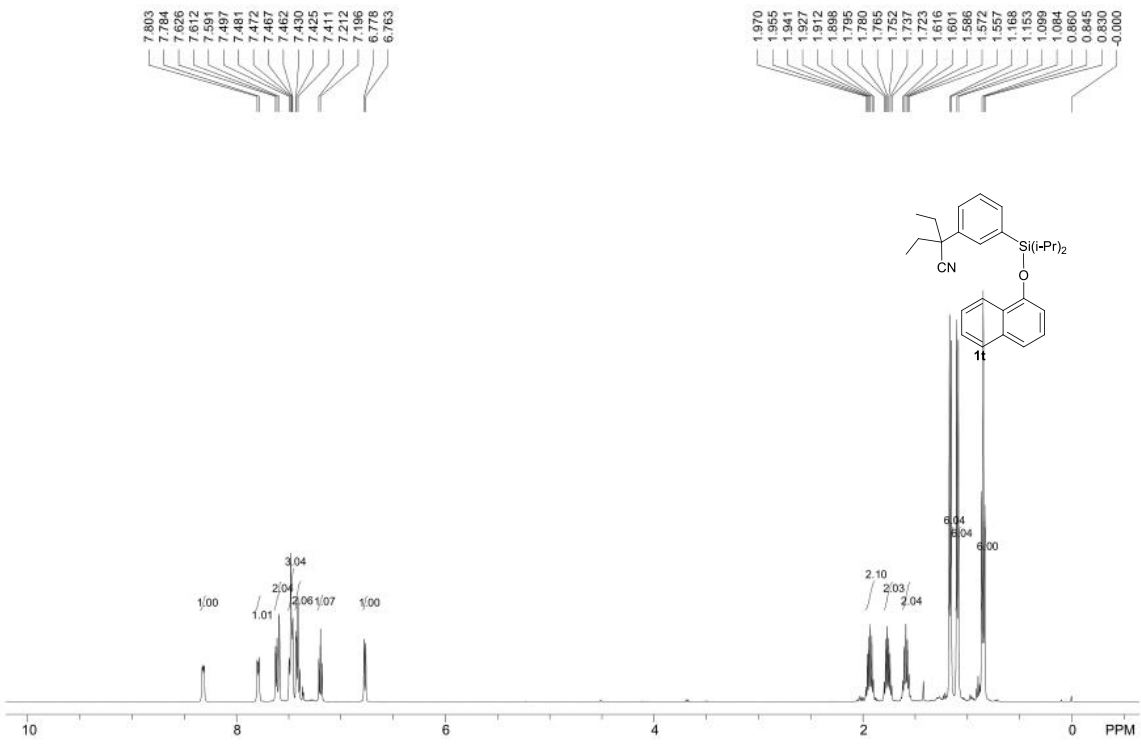
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0.845
0.830
-0.000
Si(i-Pr)2
CN
O
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2.04
3.04
2.06
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10
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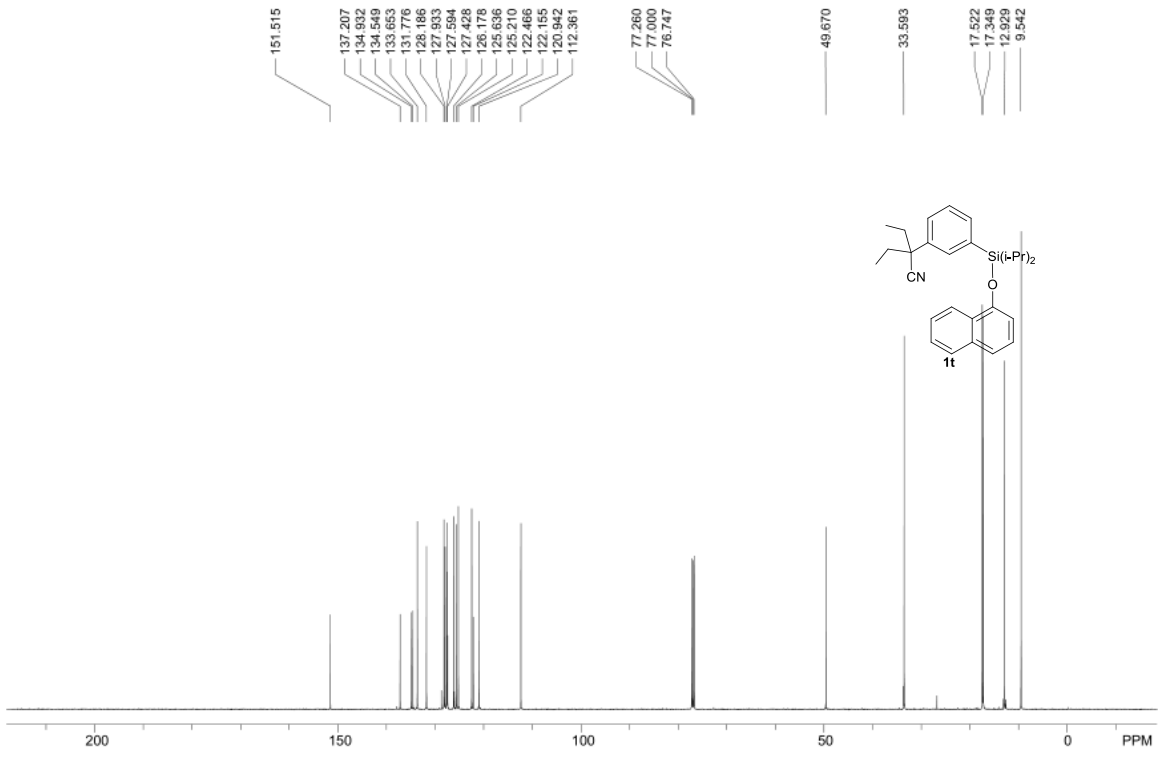
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49.670
33.593
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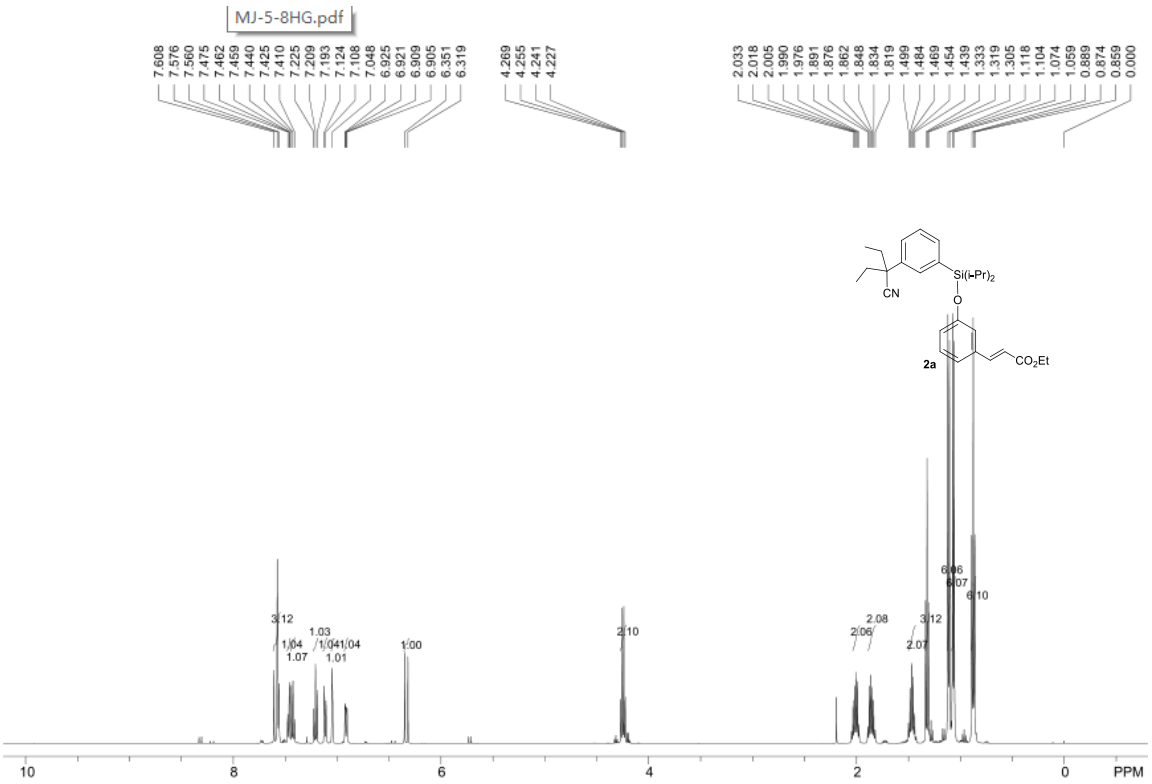
12.929
9.542
Si(i-Pr)2
CN
O
1t
200
150
100
50
0
PPM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4.269 4.255 4.241 4.227
2.033 2.018 2.005 1.990 1.976 1.891 1.876 1.862 1.848 1.834 1.819 1.499 1.484 1.469 1.454 1.439 1.333 1.319 1.305 1.118 1.104 1.074 1.059 0.889 0.874 0.859 0.000
Si(i-Pr)2
CN
O
2a
CO2Et
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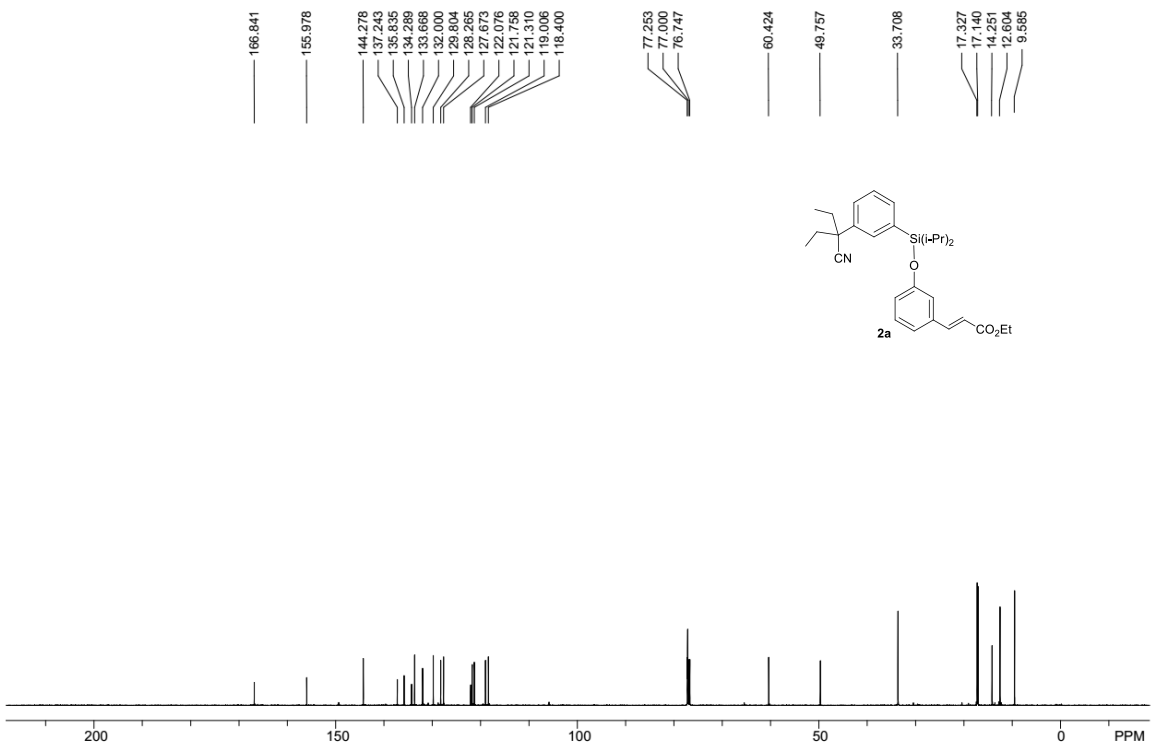
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77.253 77.000 76.747
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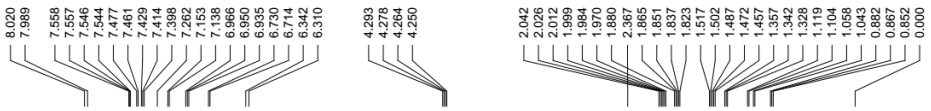
Si(i-Pr)2
CN
O
2a
CO2Et
200 150 100 50 0 PPM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4.250
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2.012
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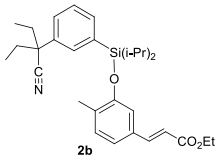
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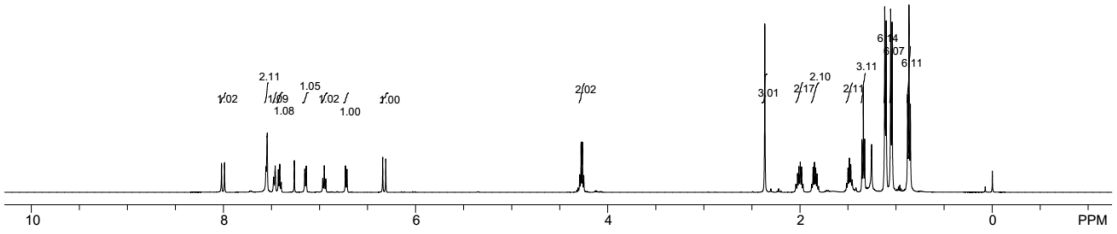
N
O
CO2Et
2b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10
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6
4
2
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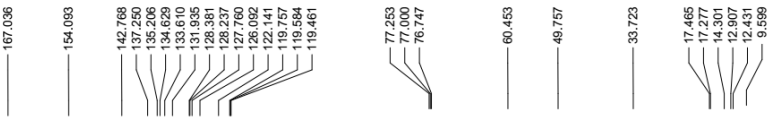
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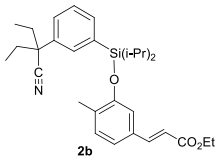
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O
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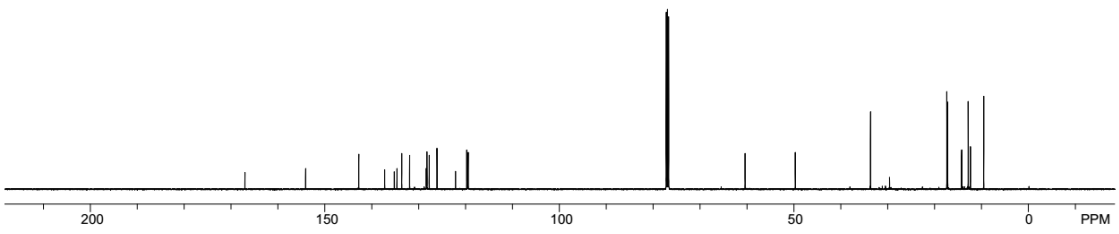
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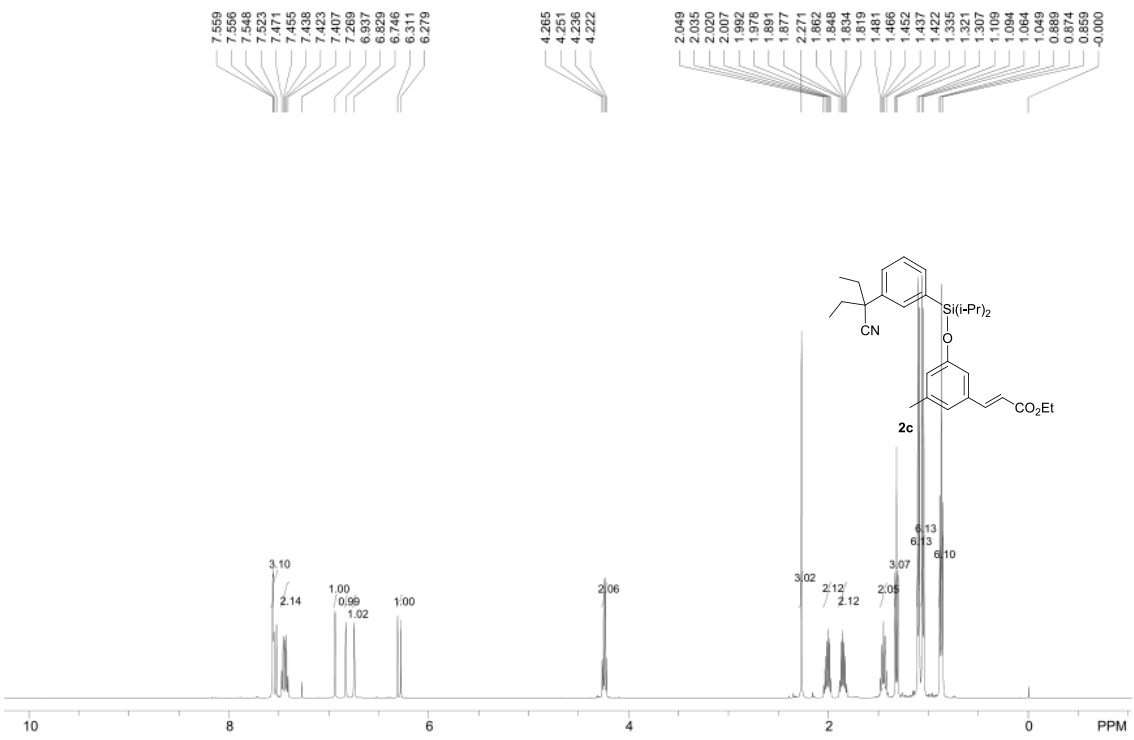
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CN
O
CO2Et
2c
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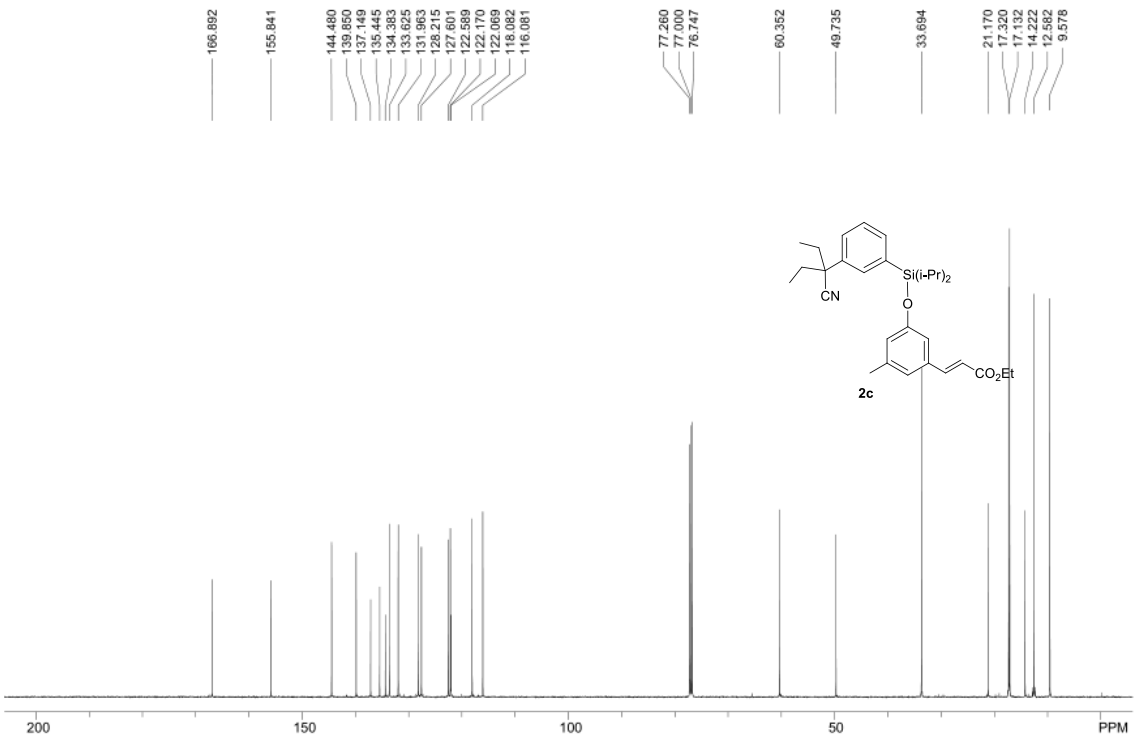
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CO2Et
2c
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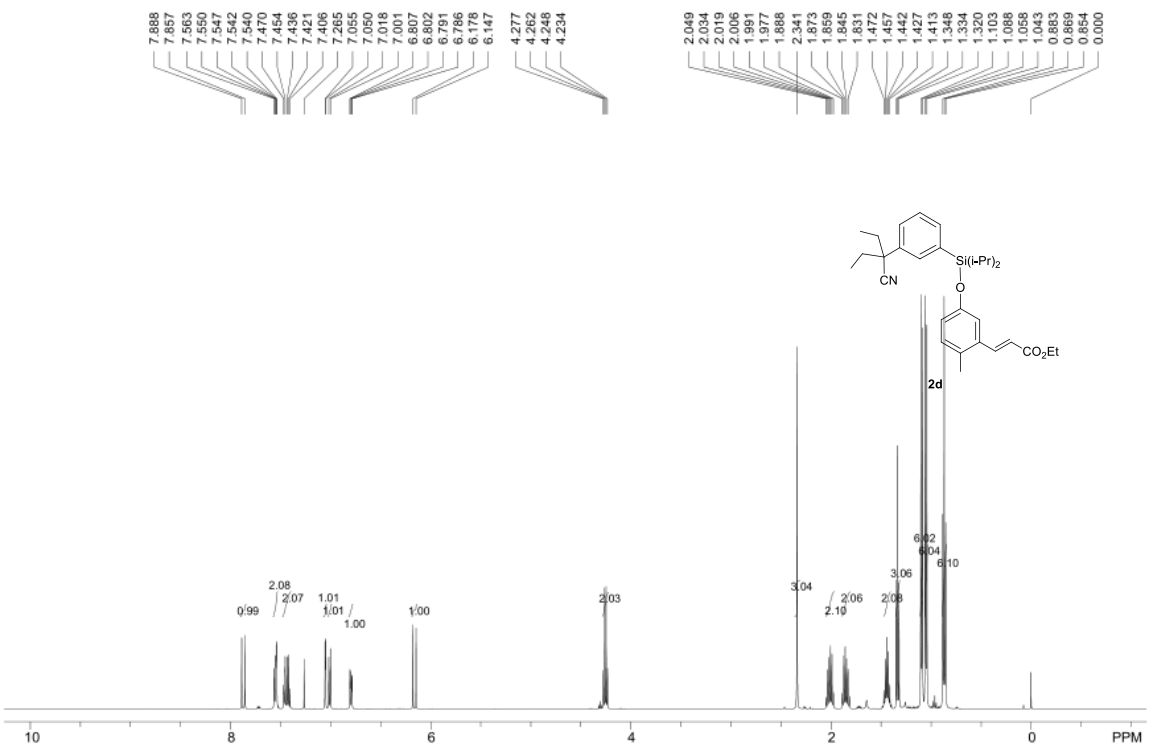
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CN
O
CO2Et
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1.00
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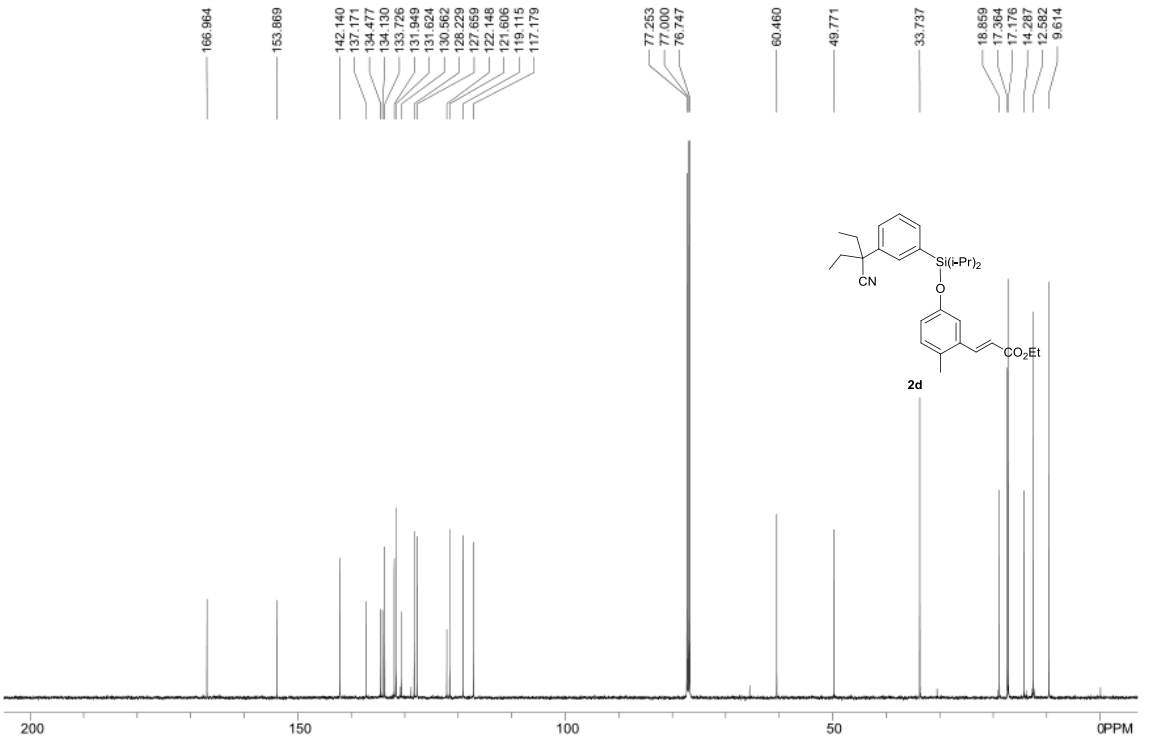
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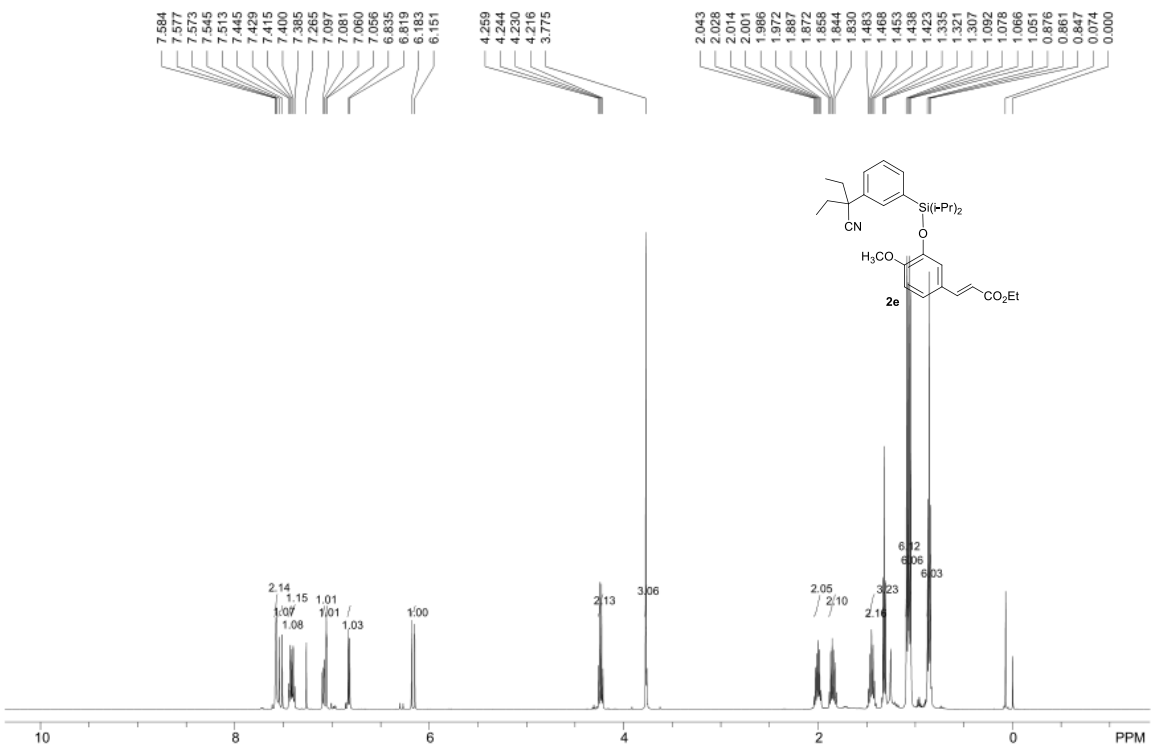
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CO2Et
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1.07
1.01
1.08
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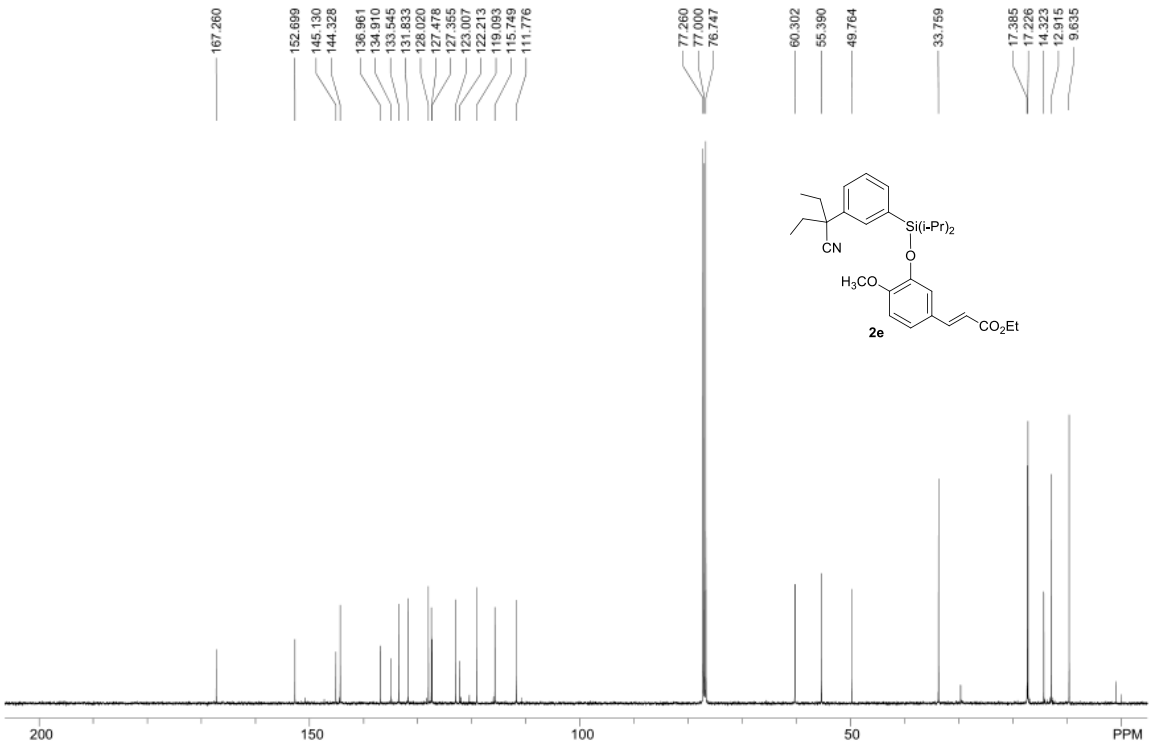
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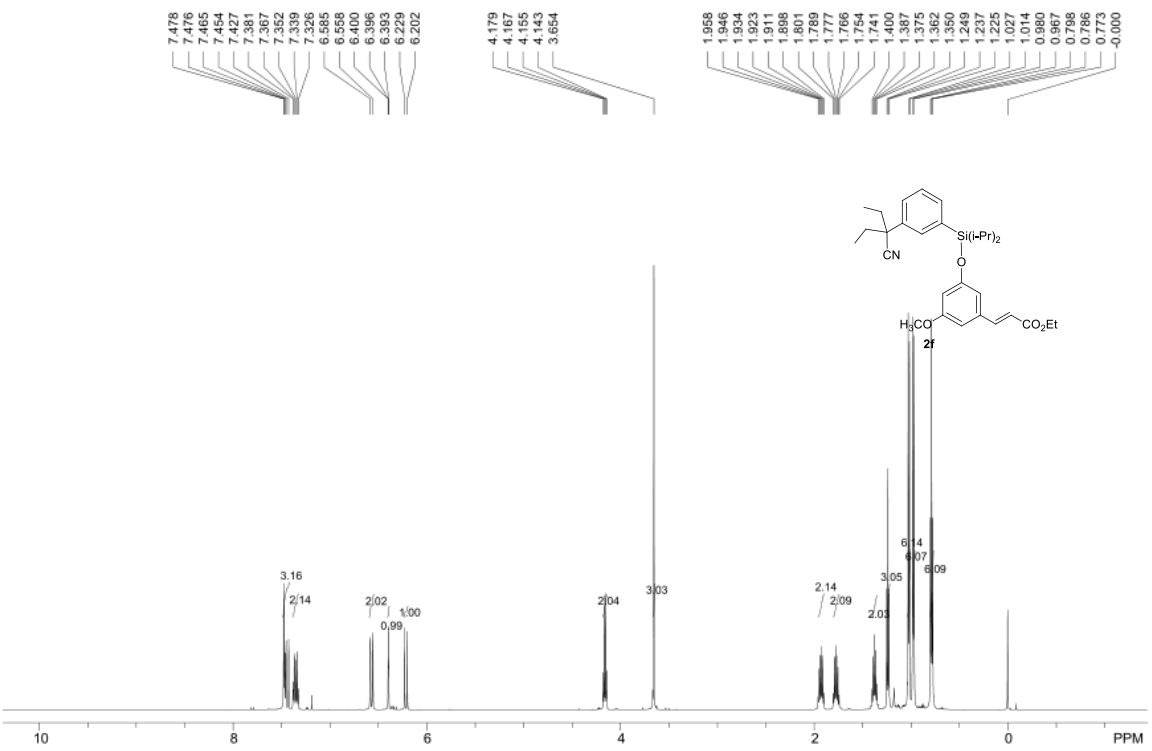
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CO2Et
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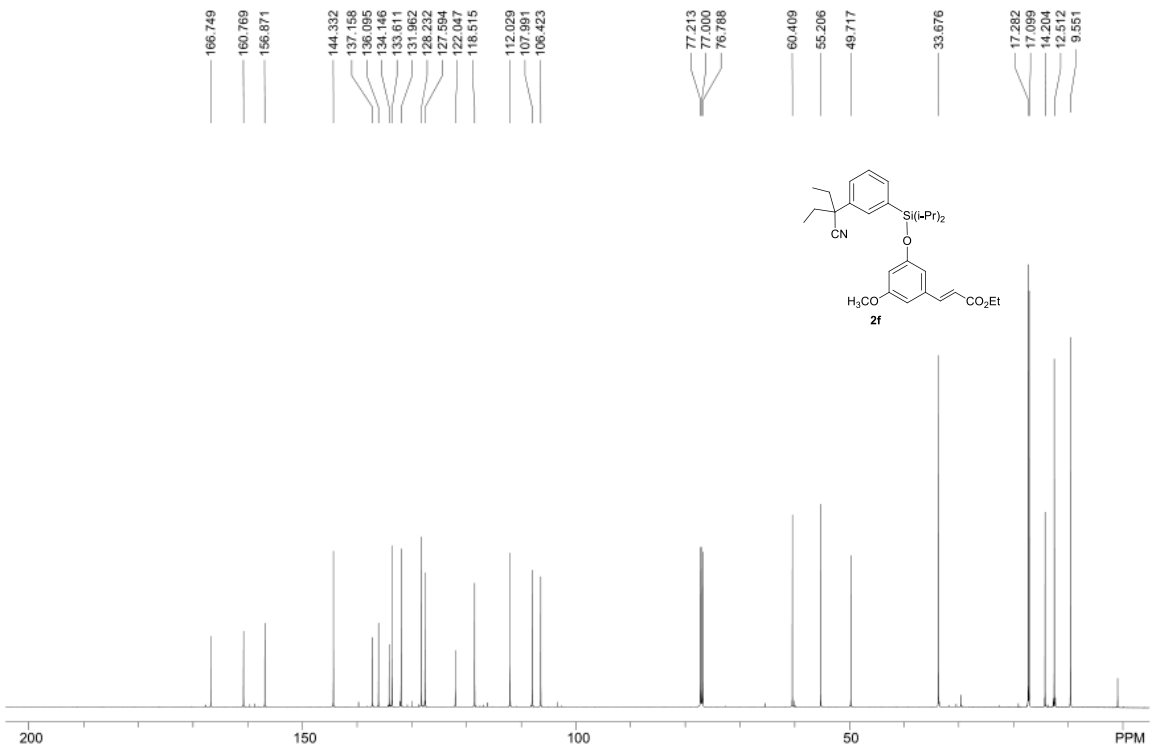
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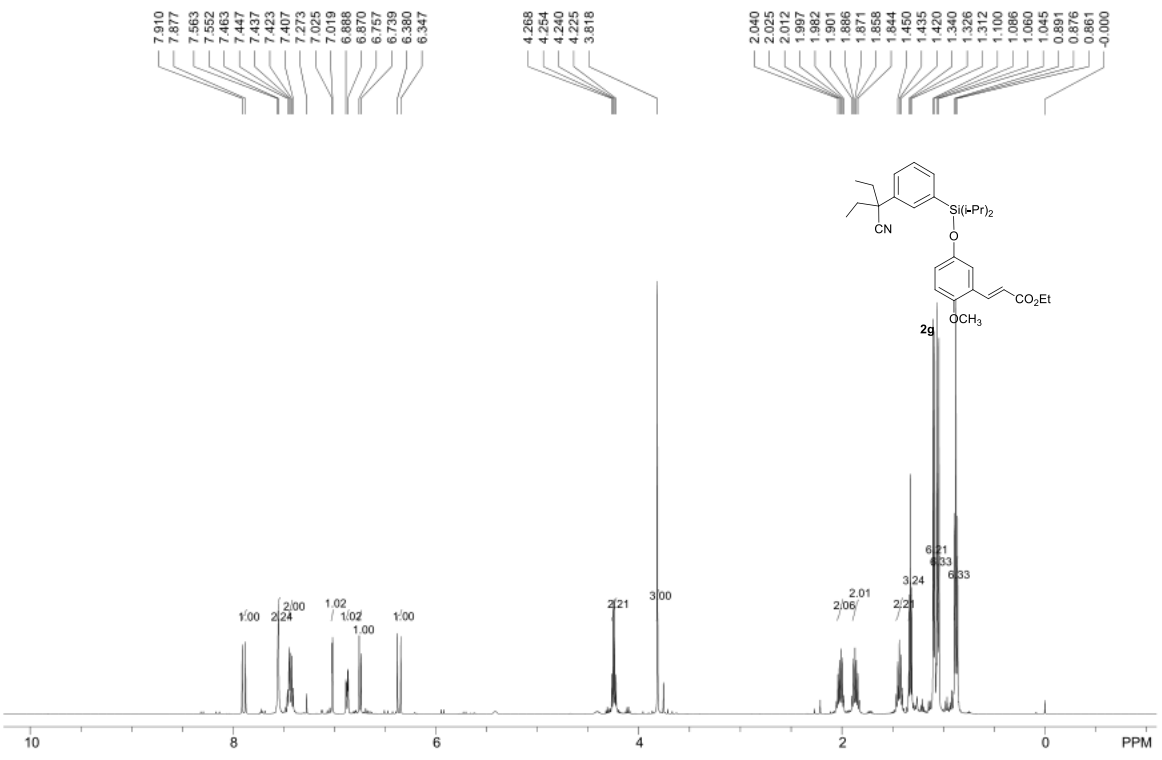
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CO2Et
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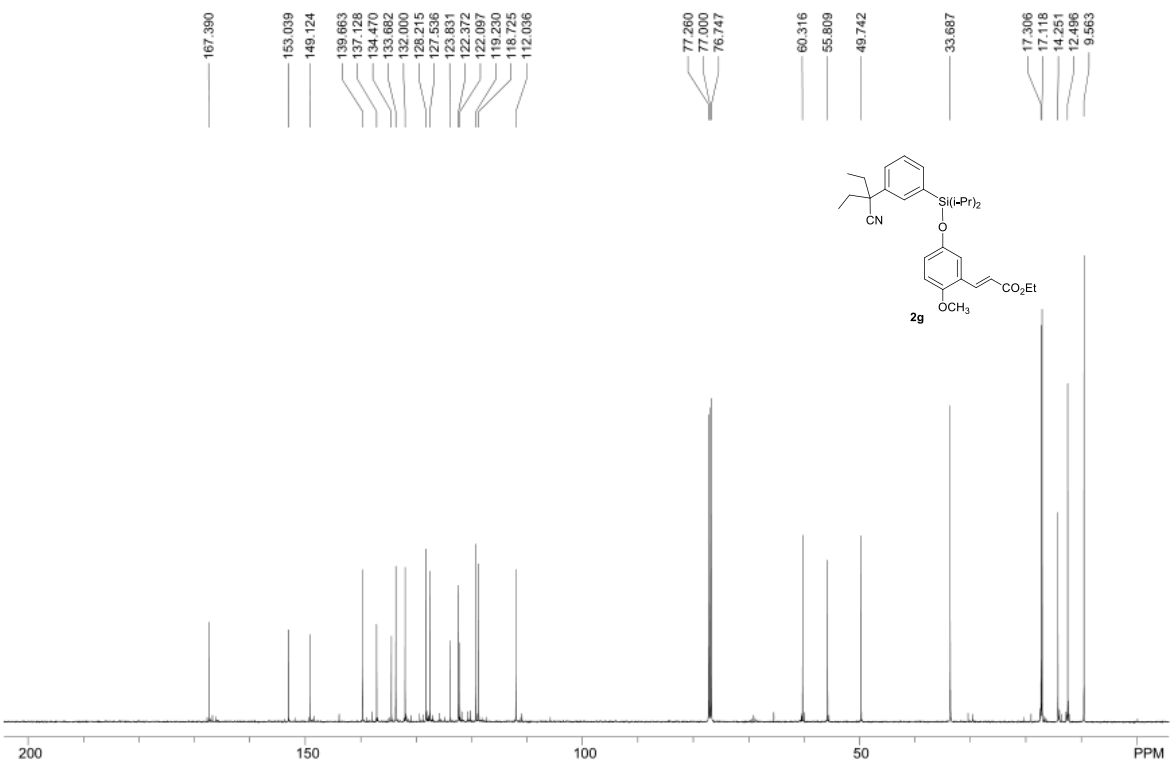
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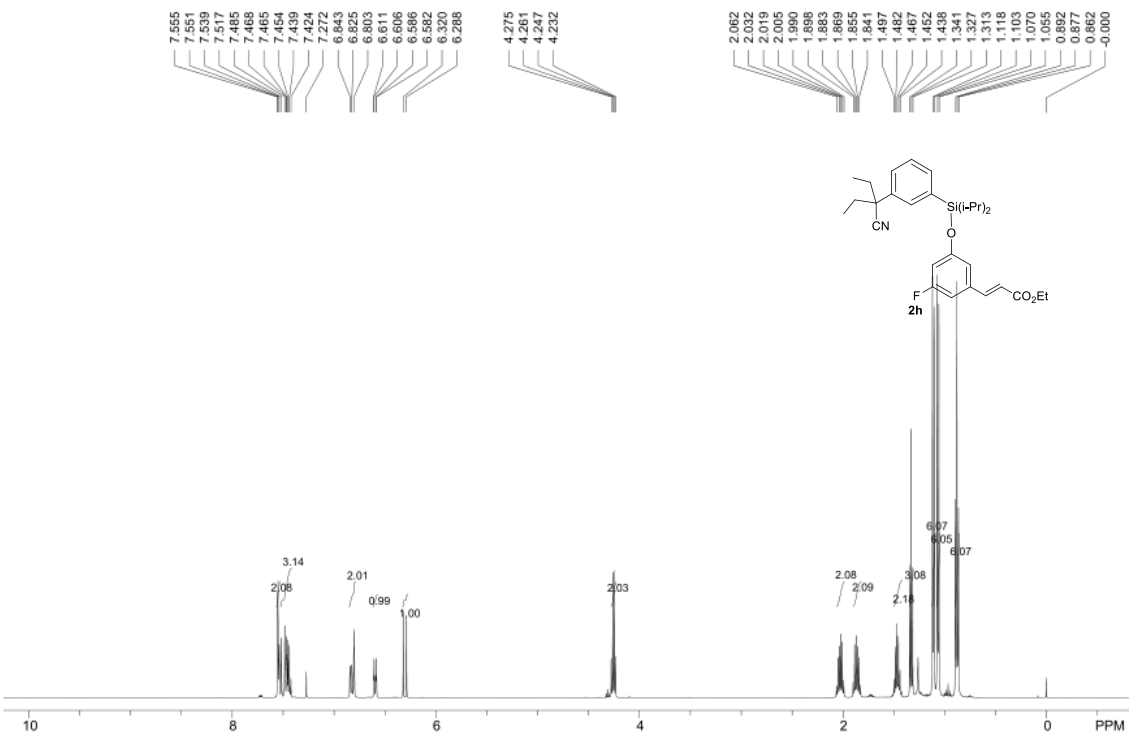
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F
CO2Et
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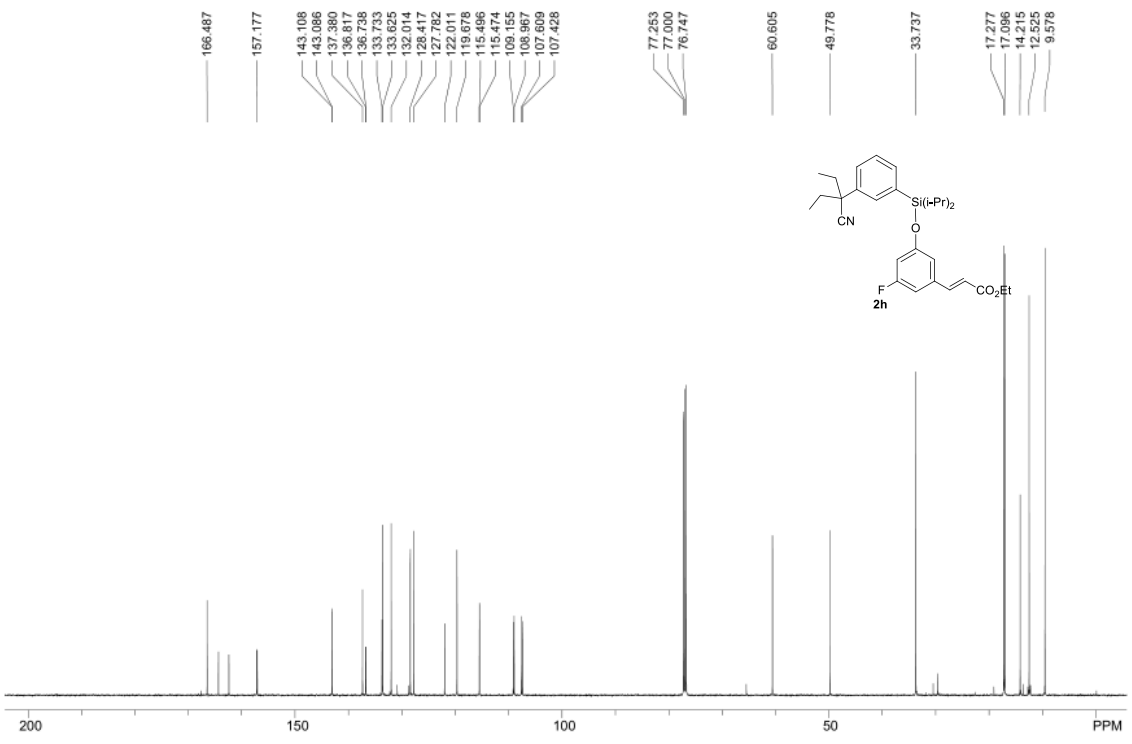
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CO2Et
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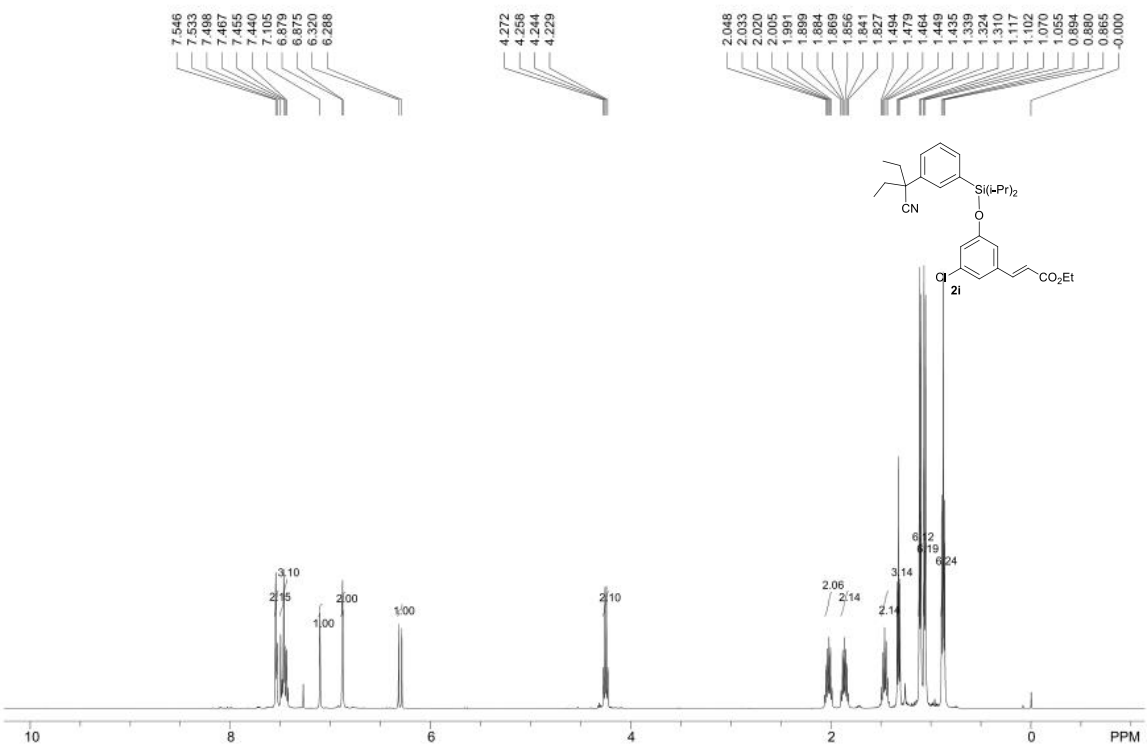
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Cl
CO2Et
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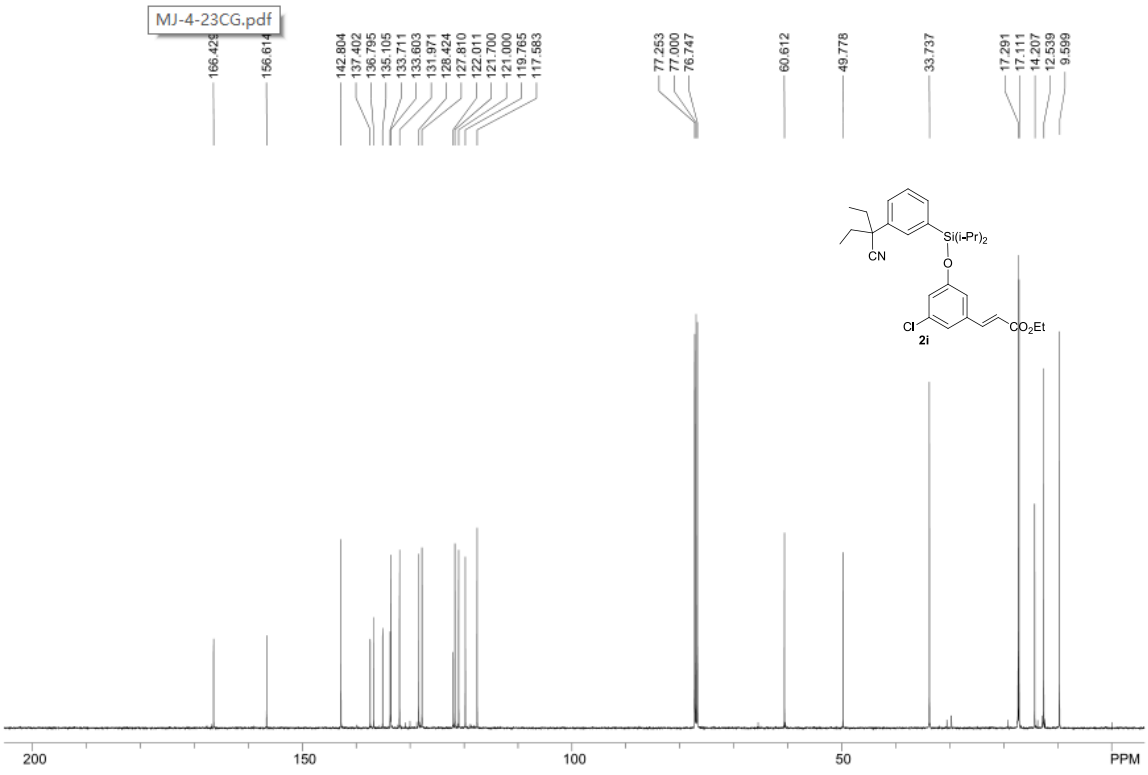
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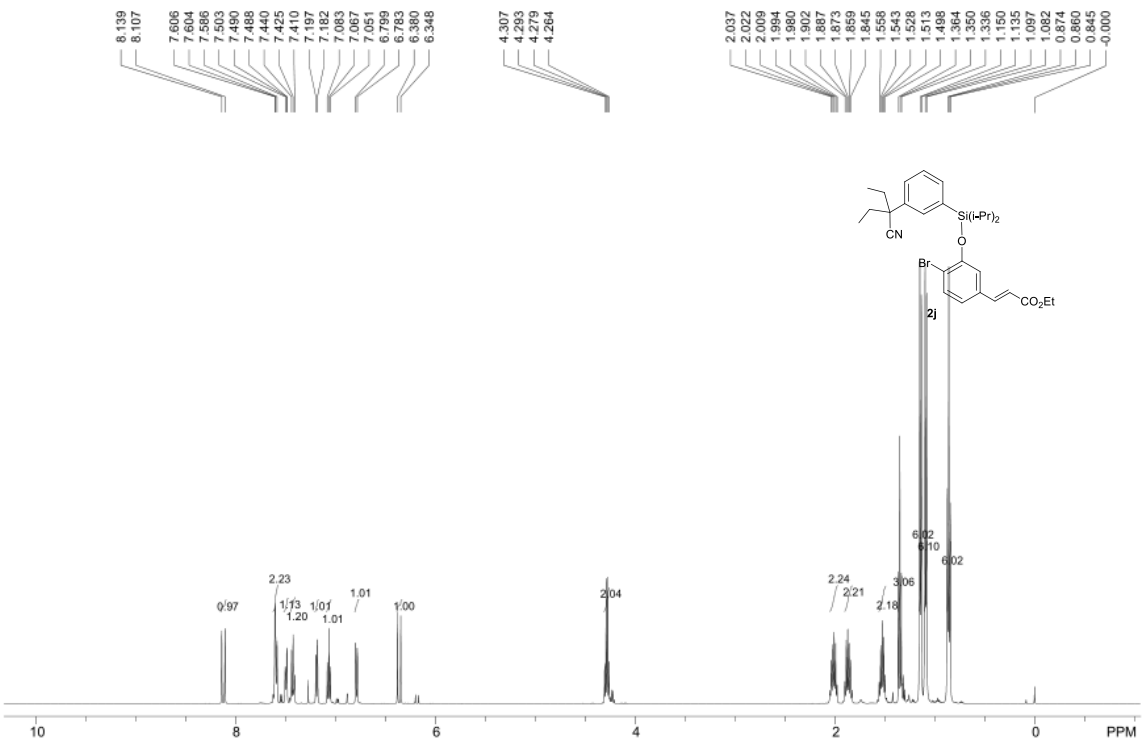
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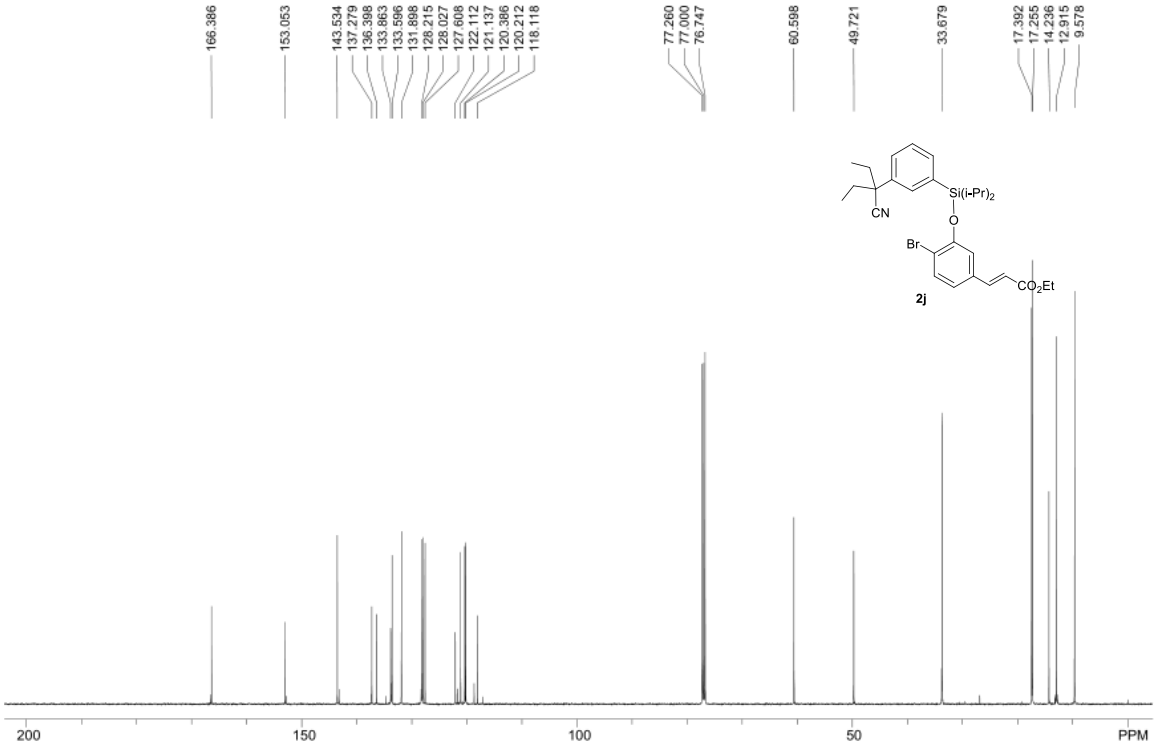
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CO2Et
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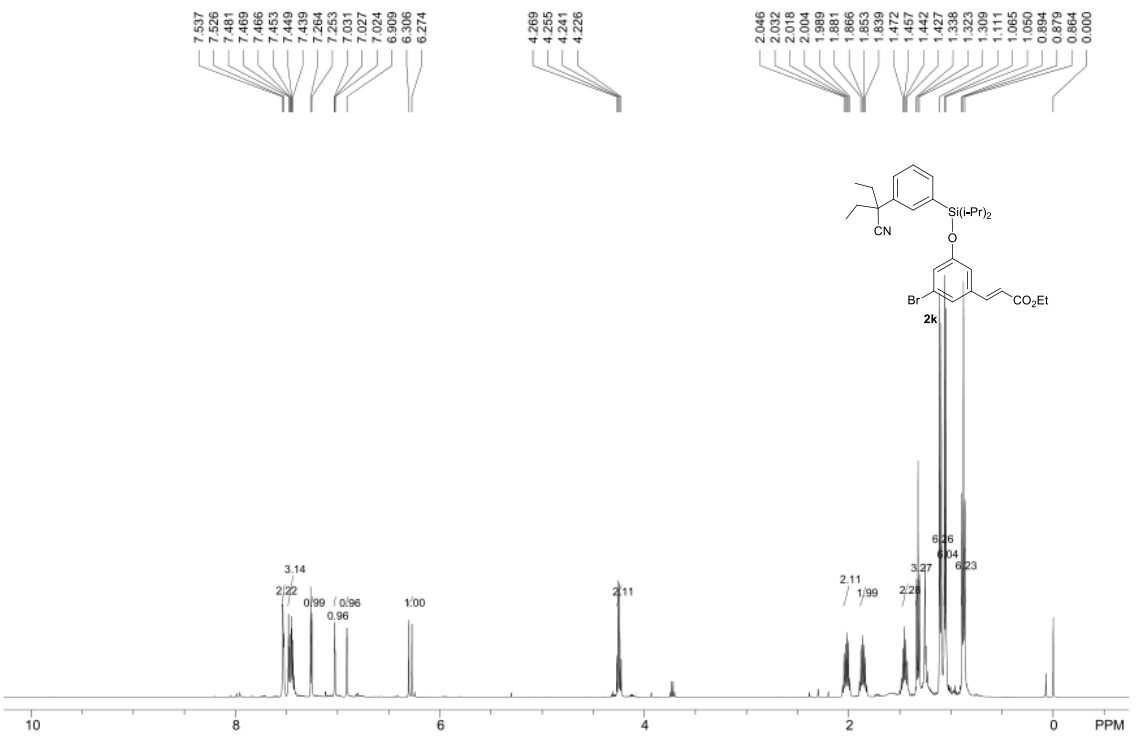
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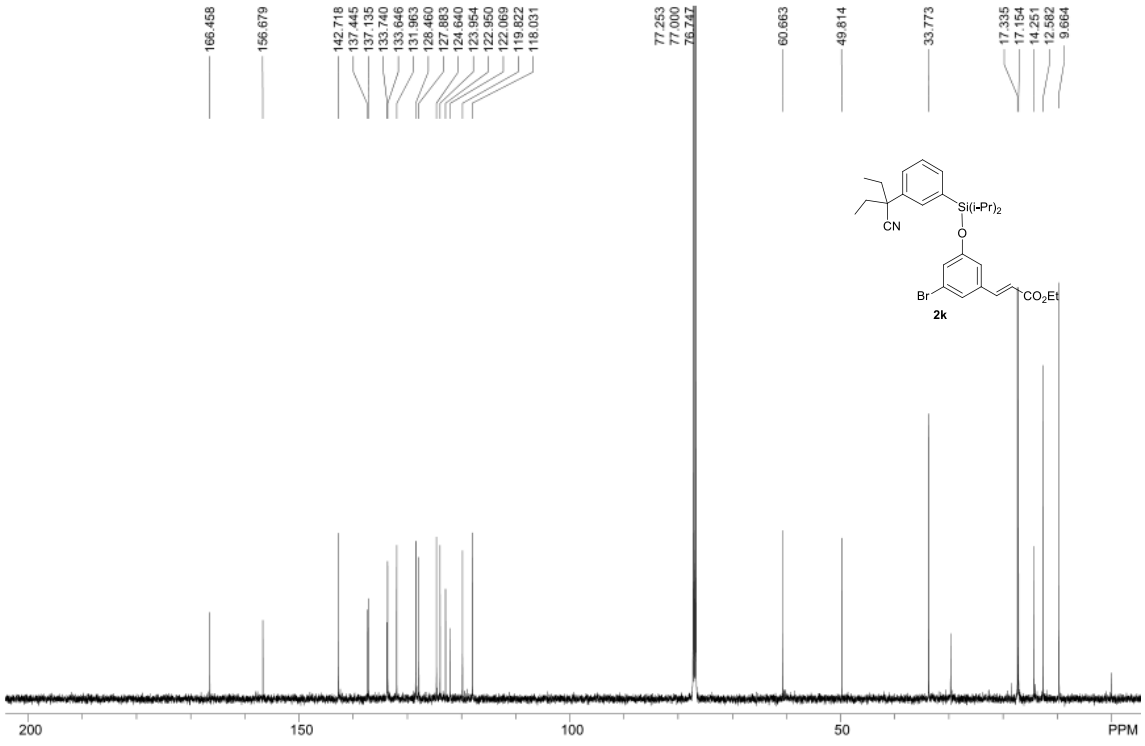
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CO2Et
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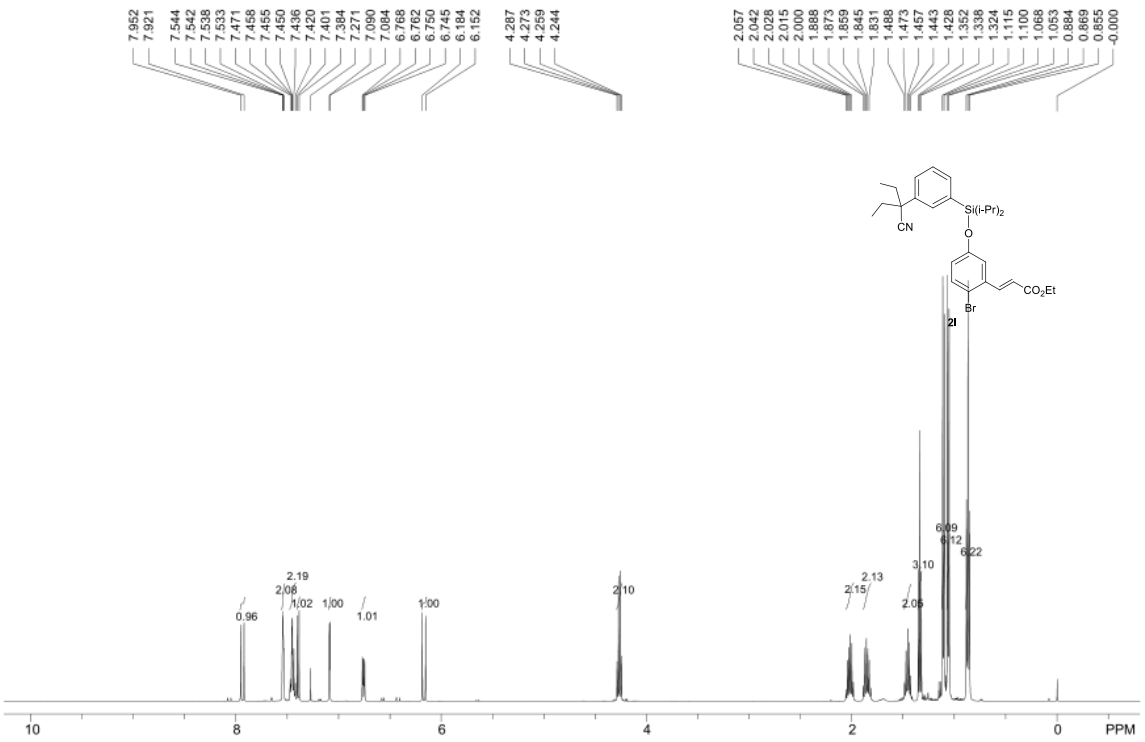
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O
CO2Et
Br
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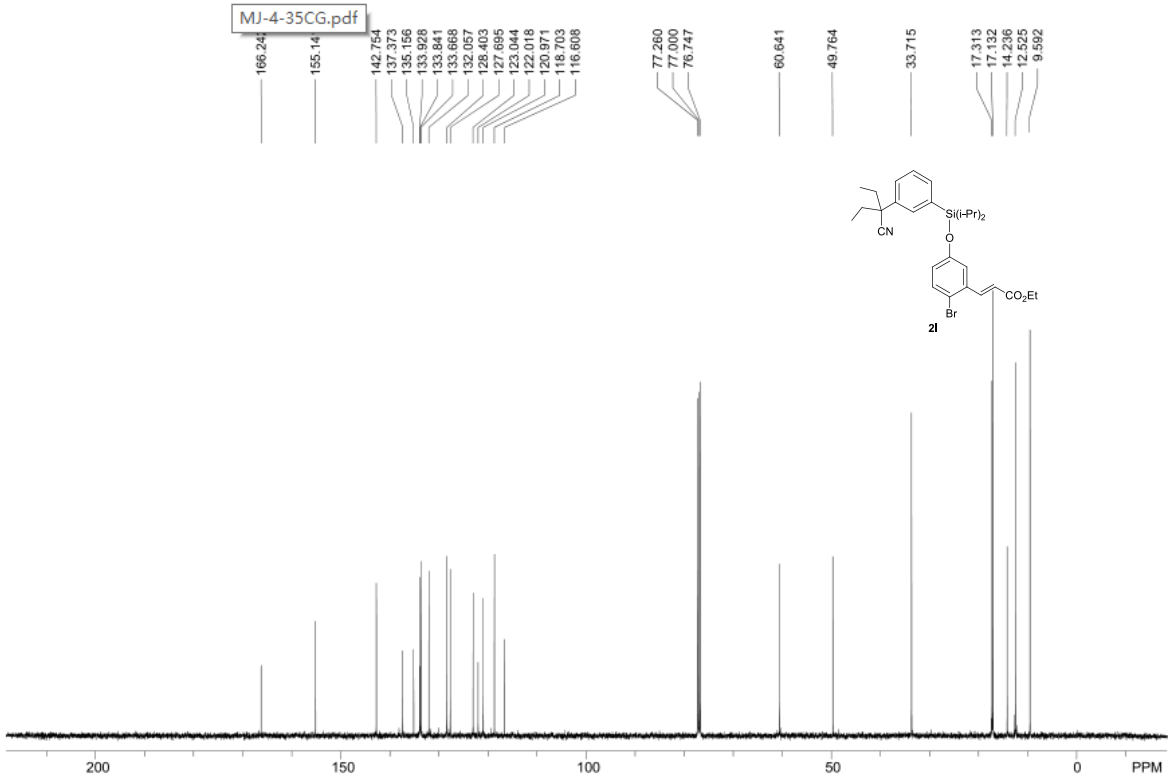
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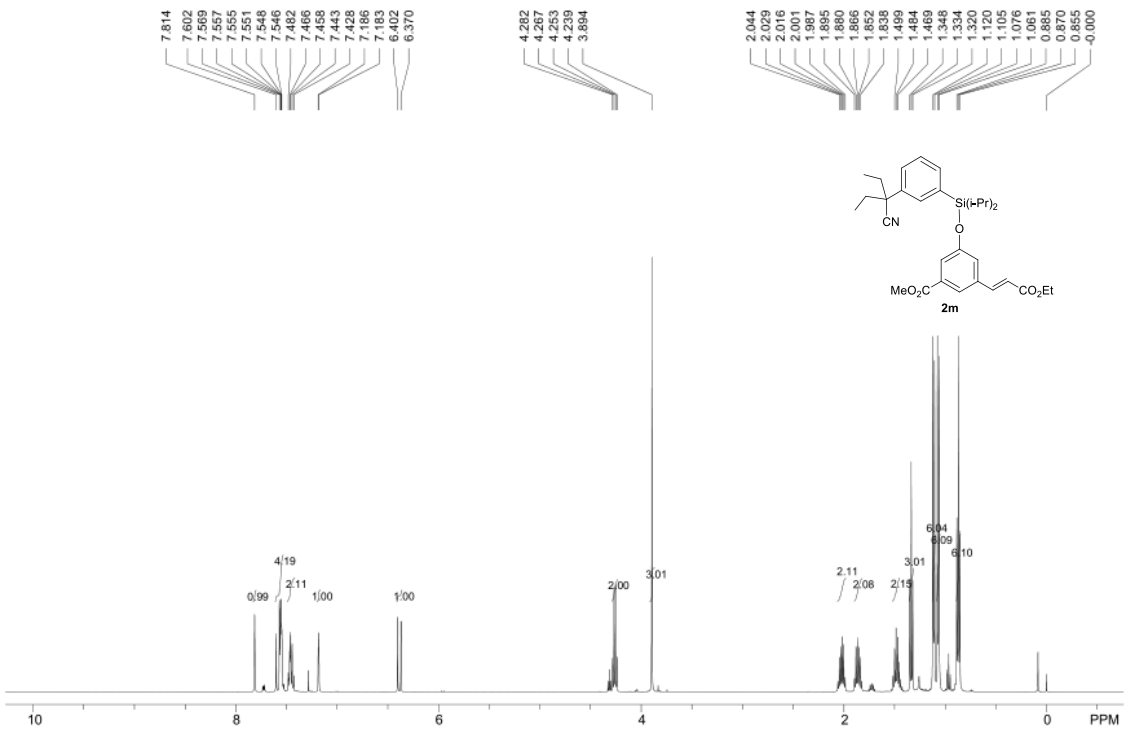
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CO2Et
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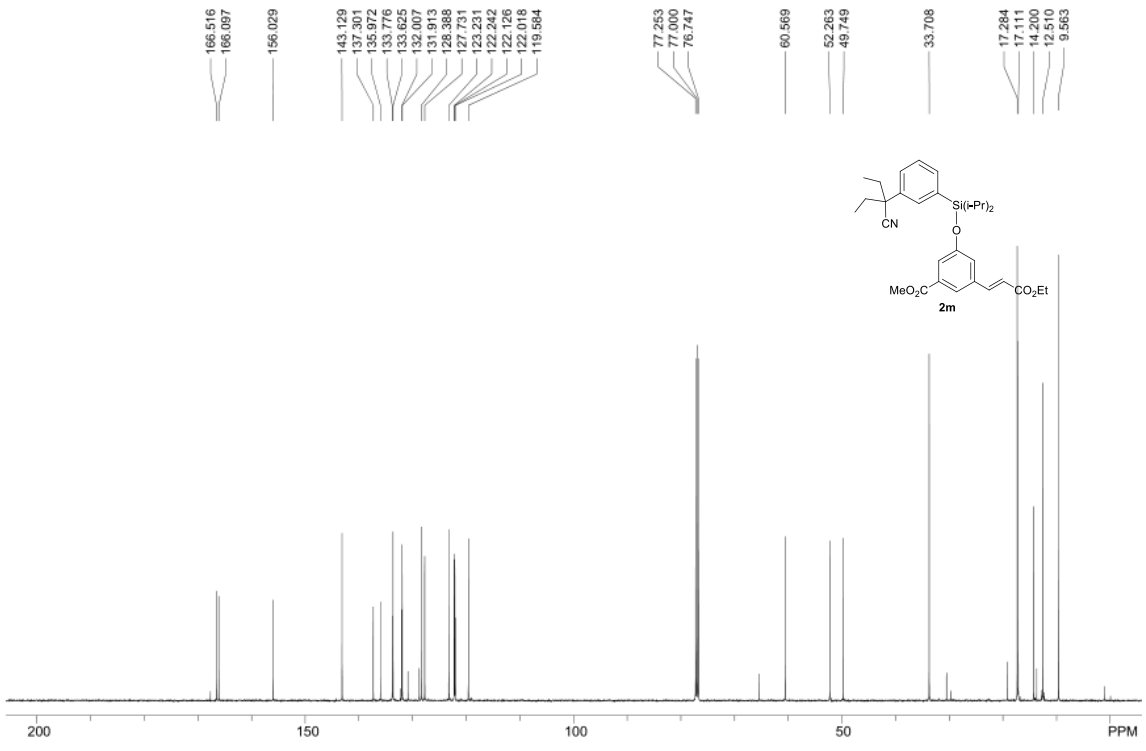
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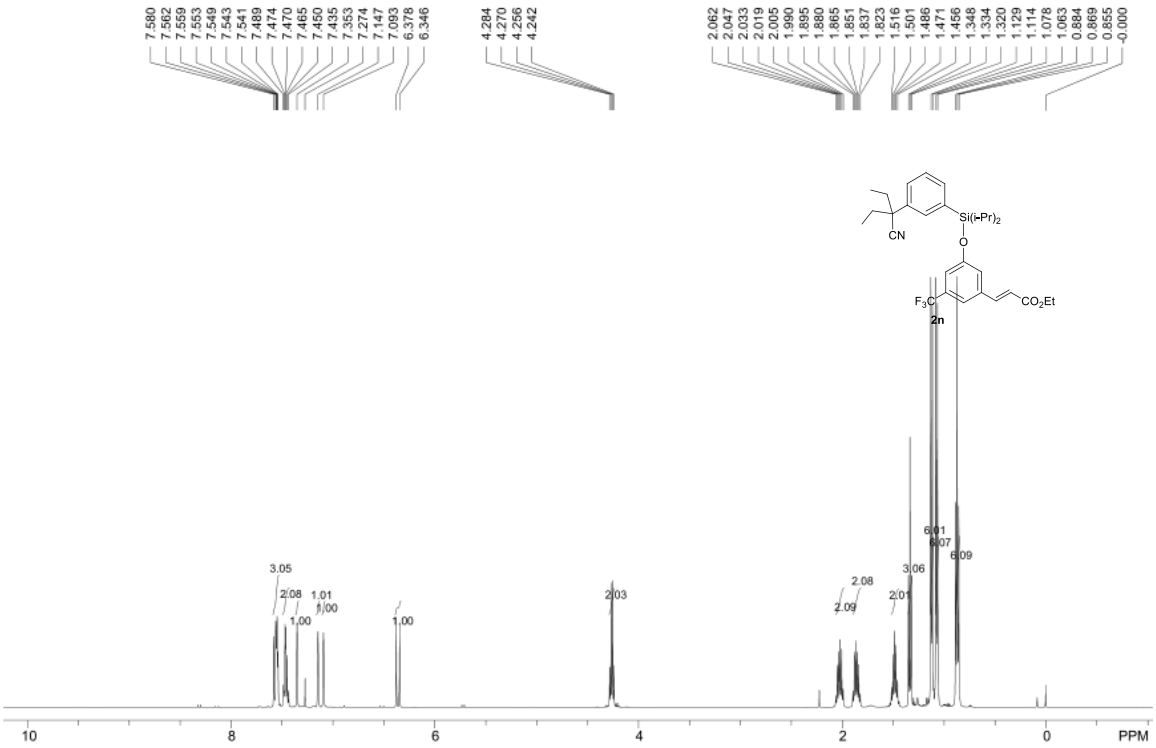
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Si(i-Pr)2
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O
F3C
CO2Et
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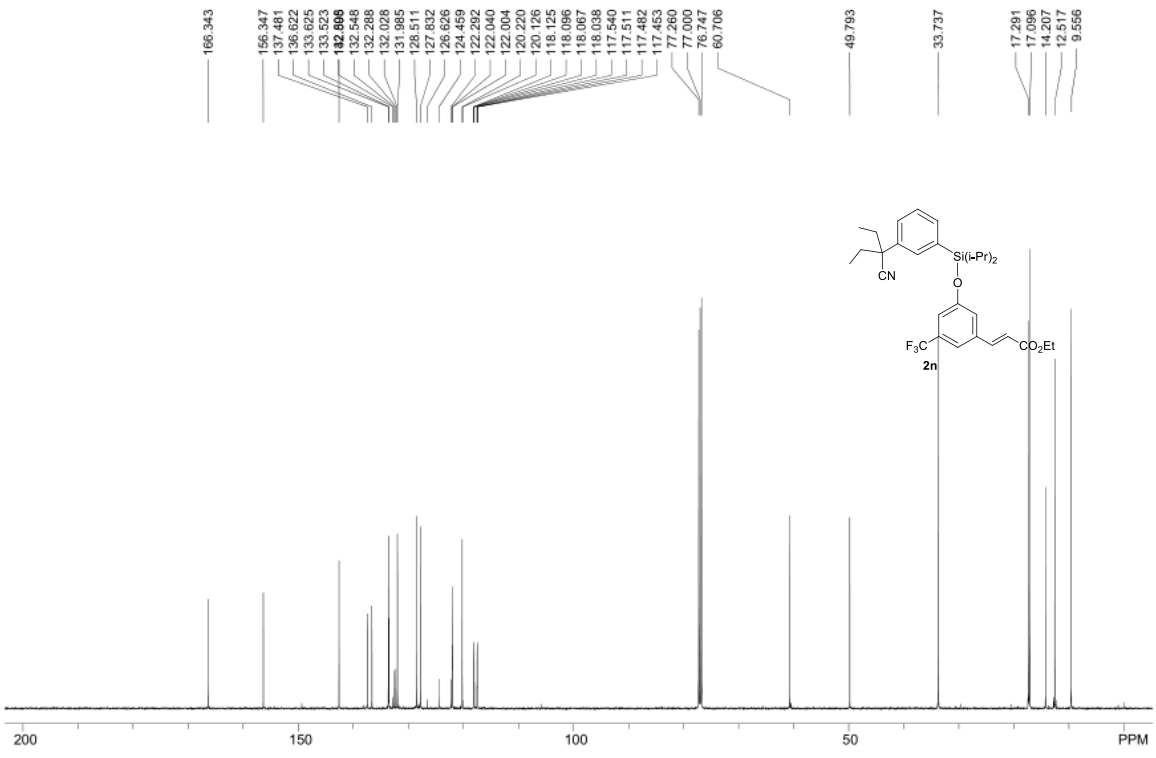
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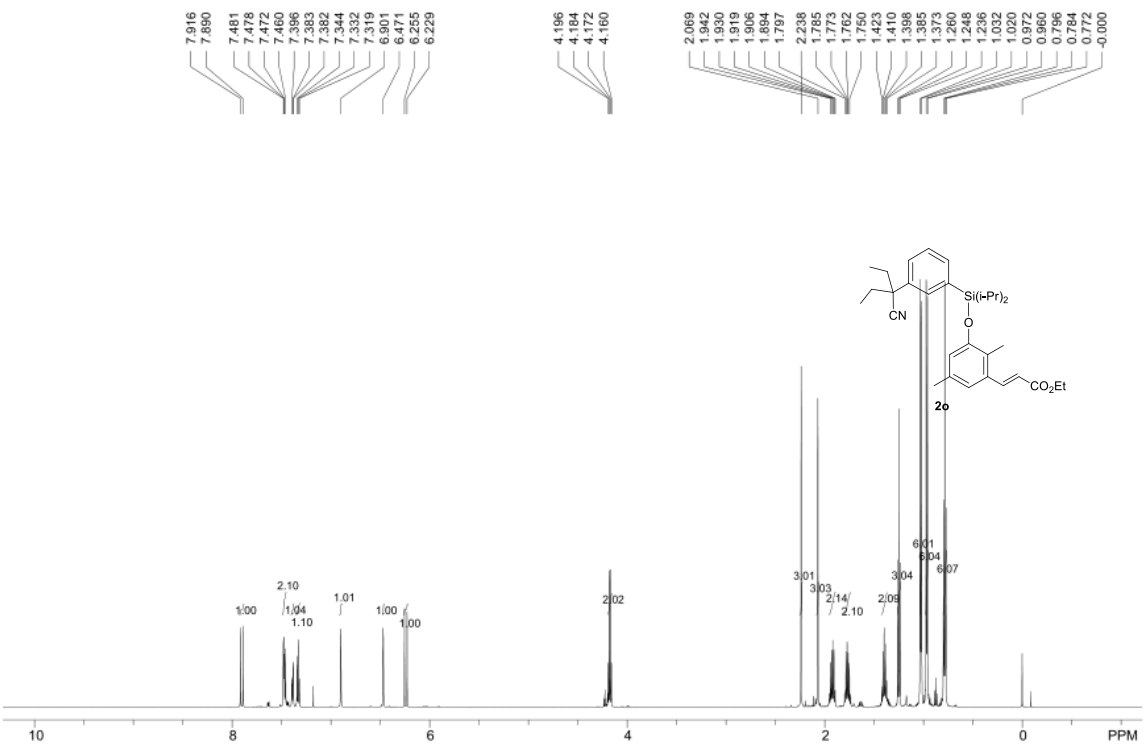
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CN
O
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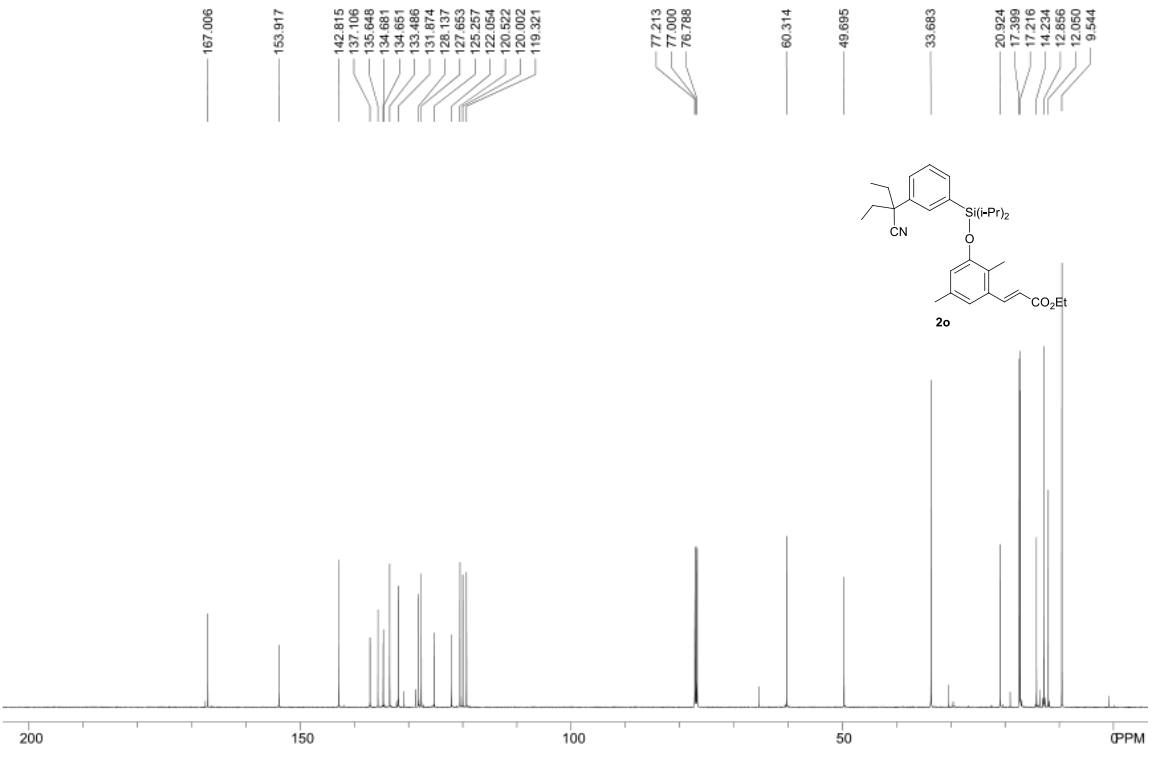
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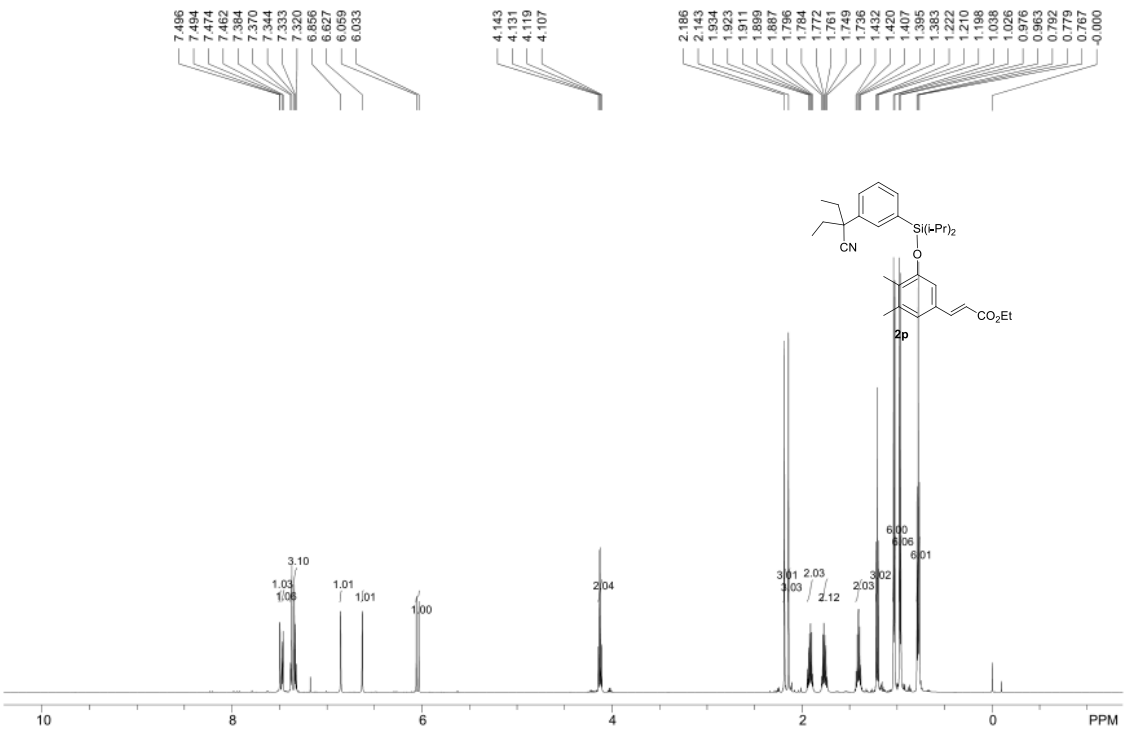
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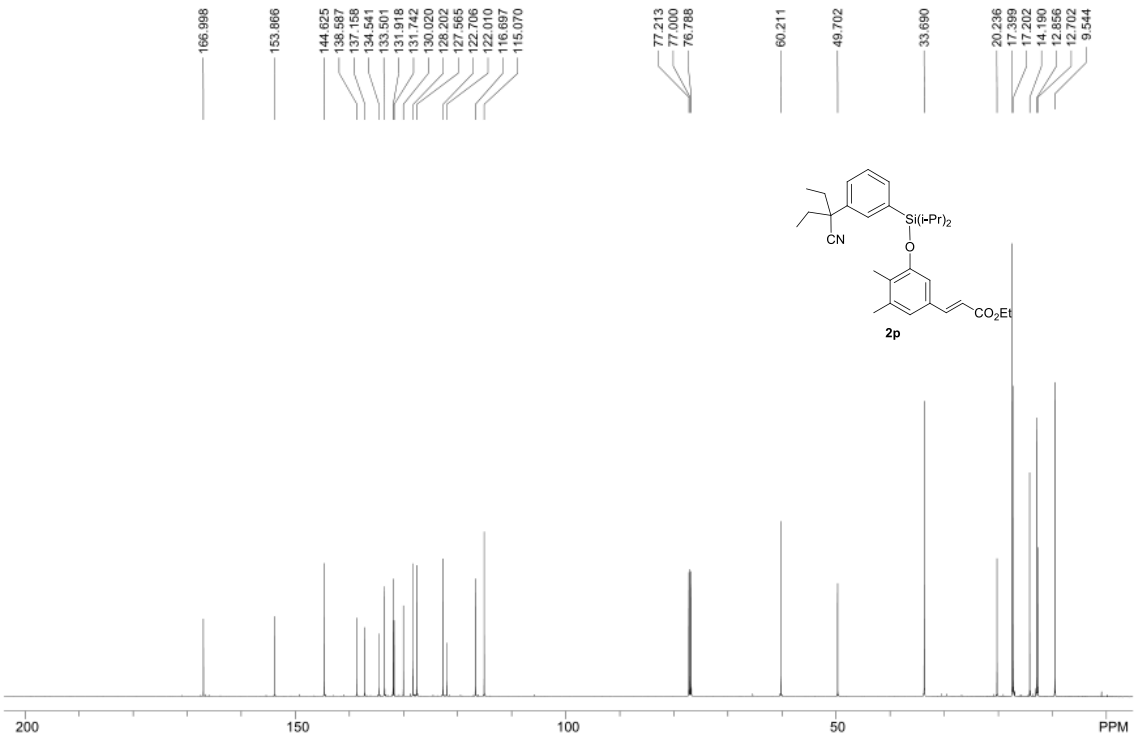
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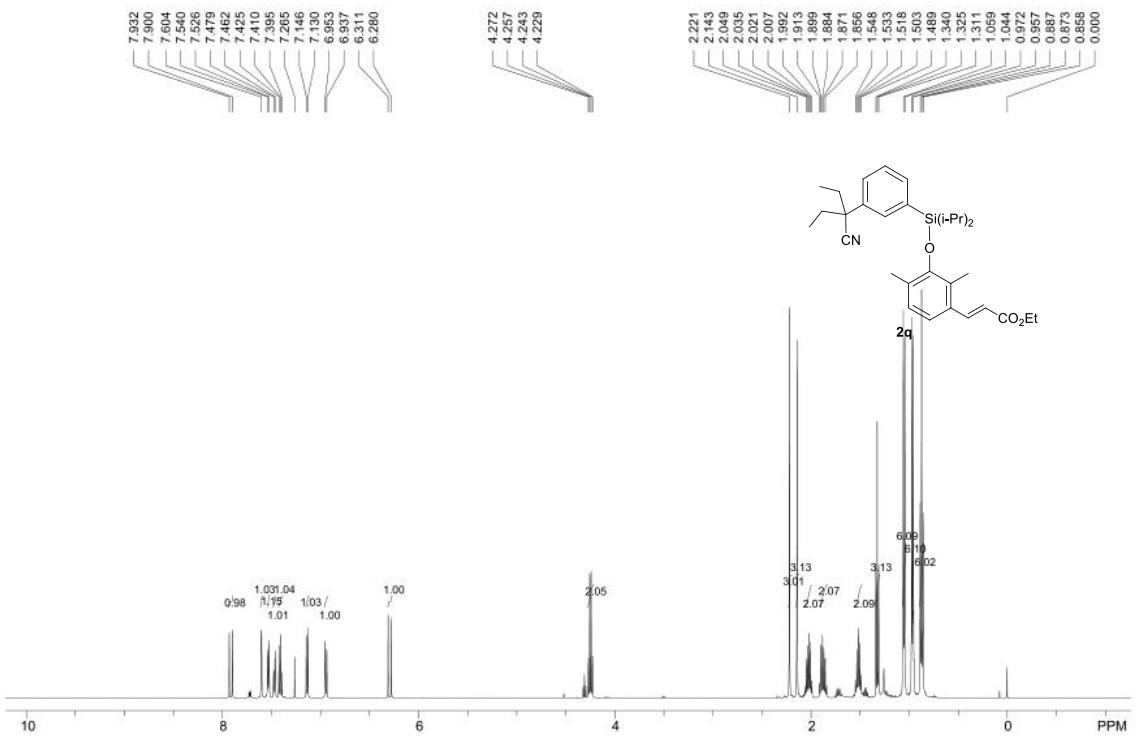
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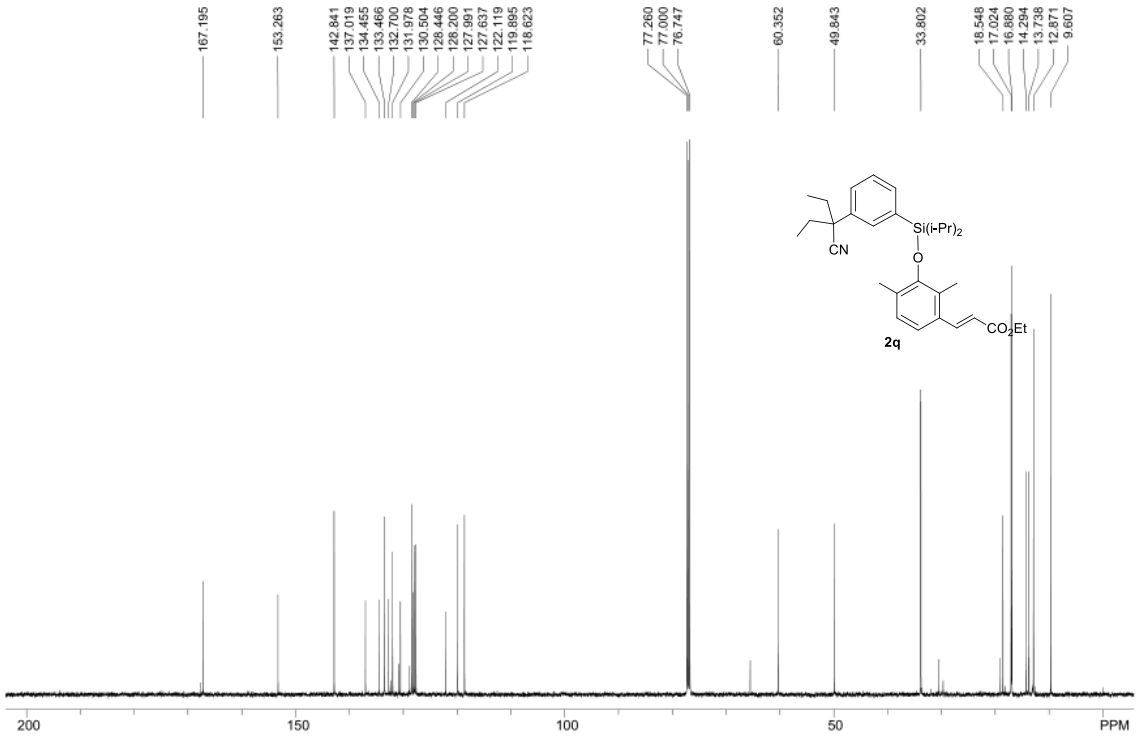
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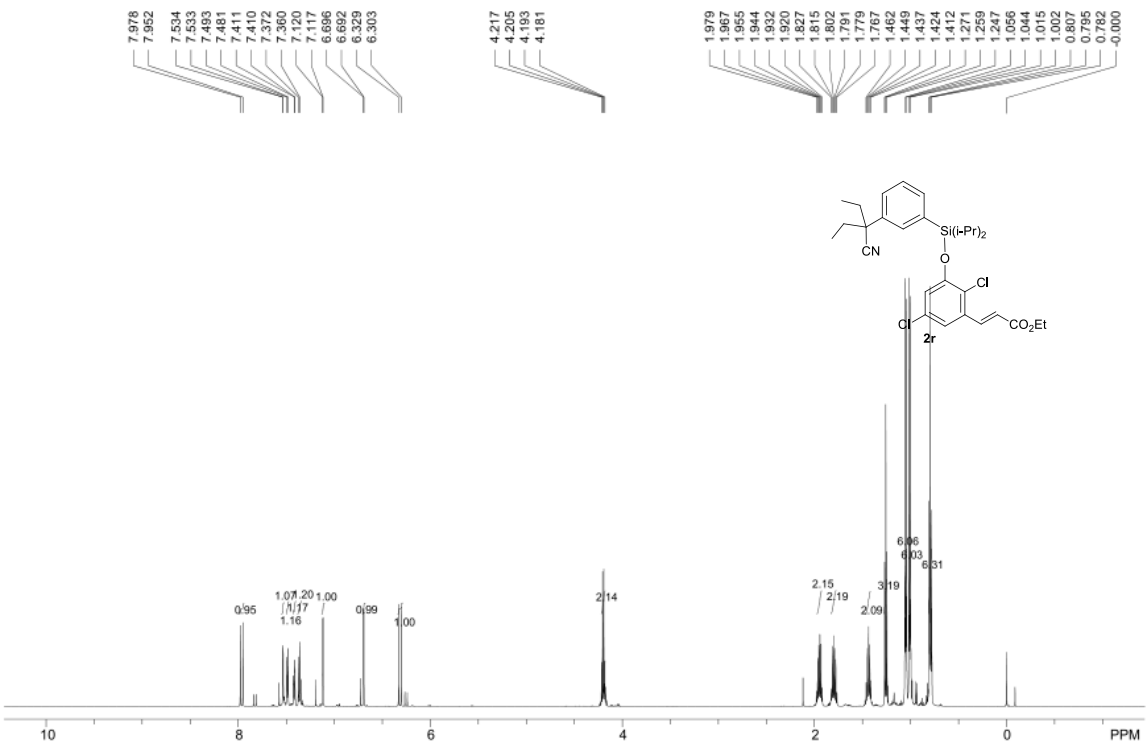
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Cl
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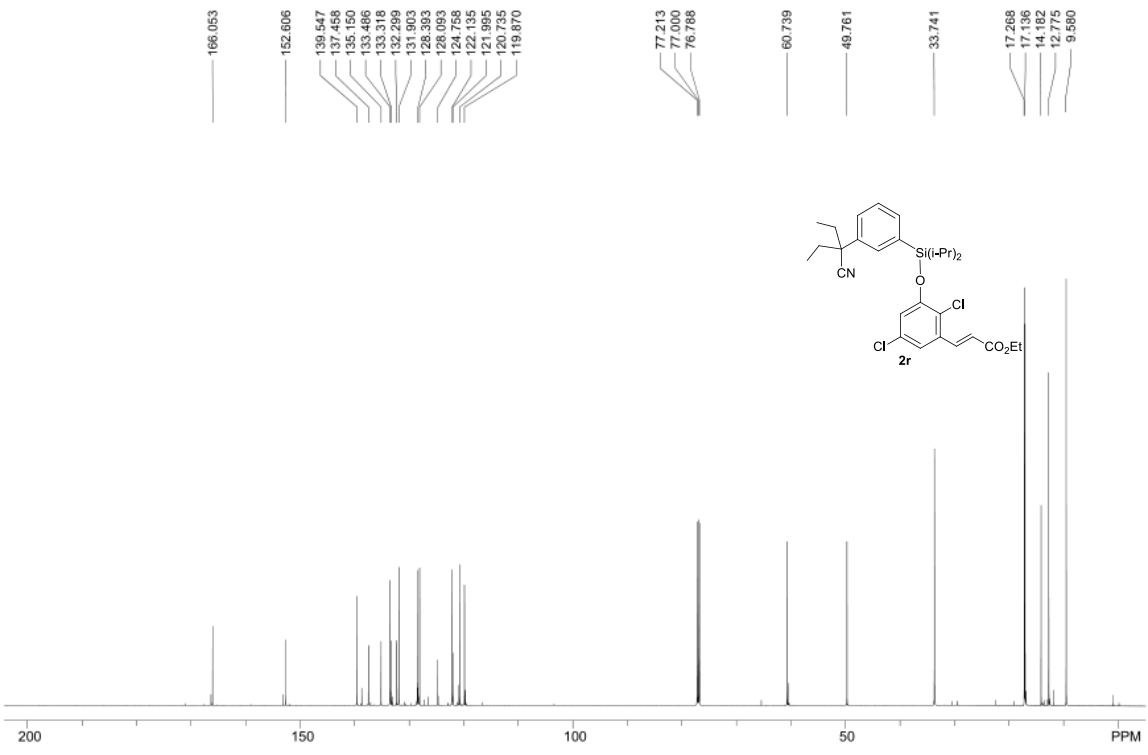
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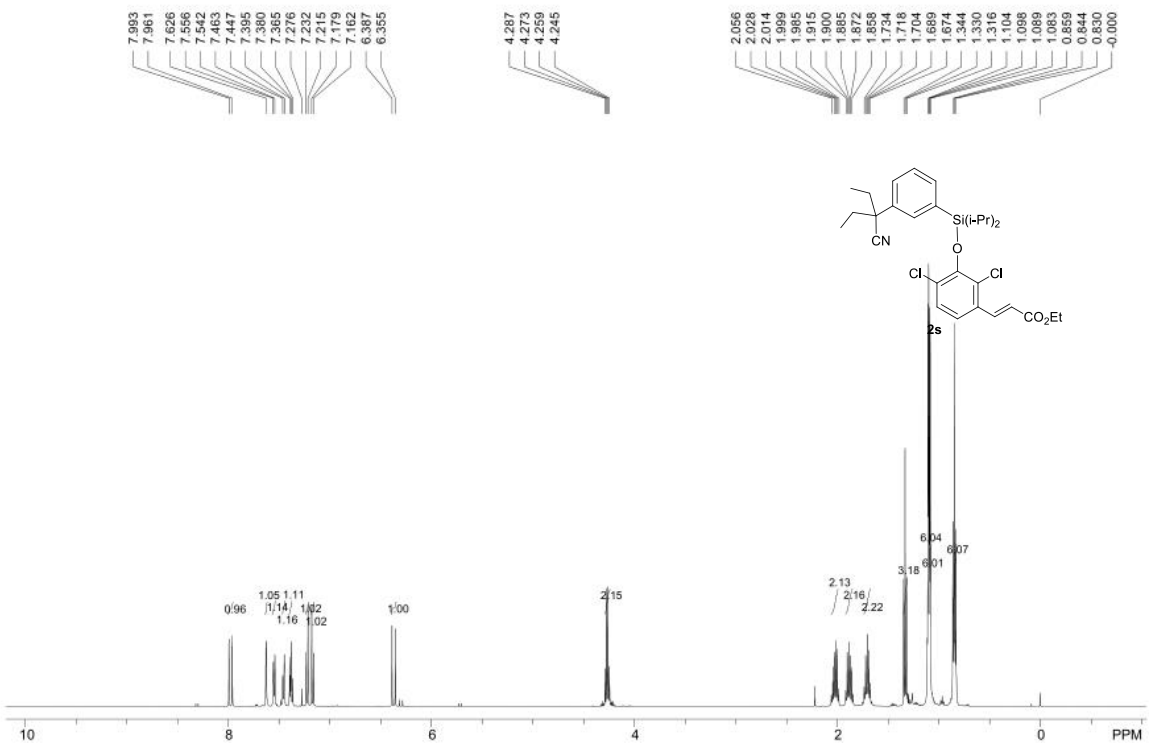
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Cl
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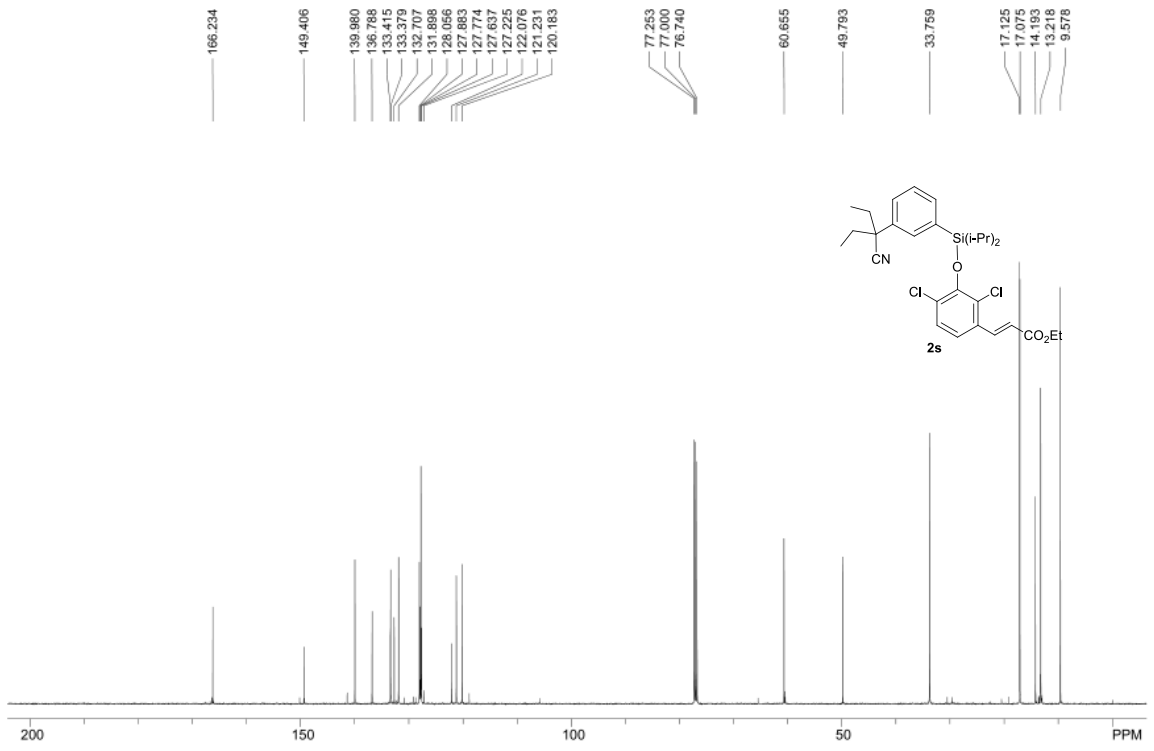
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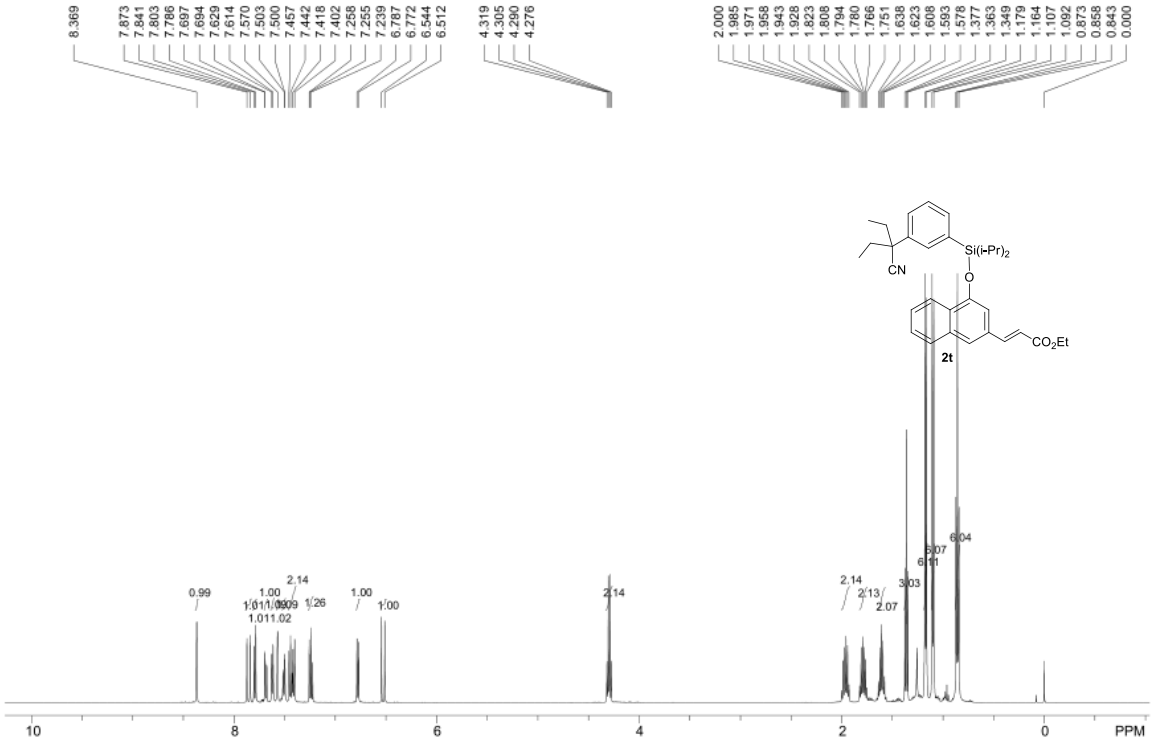
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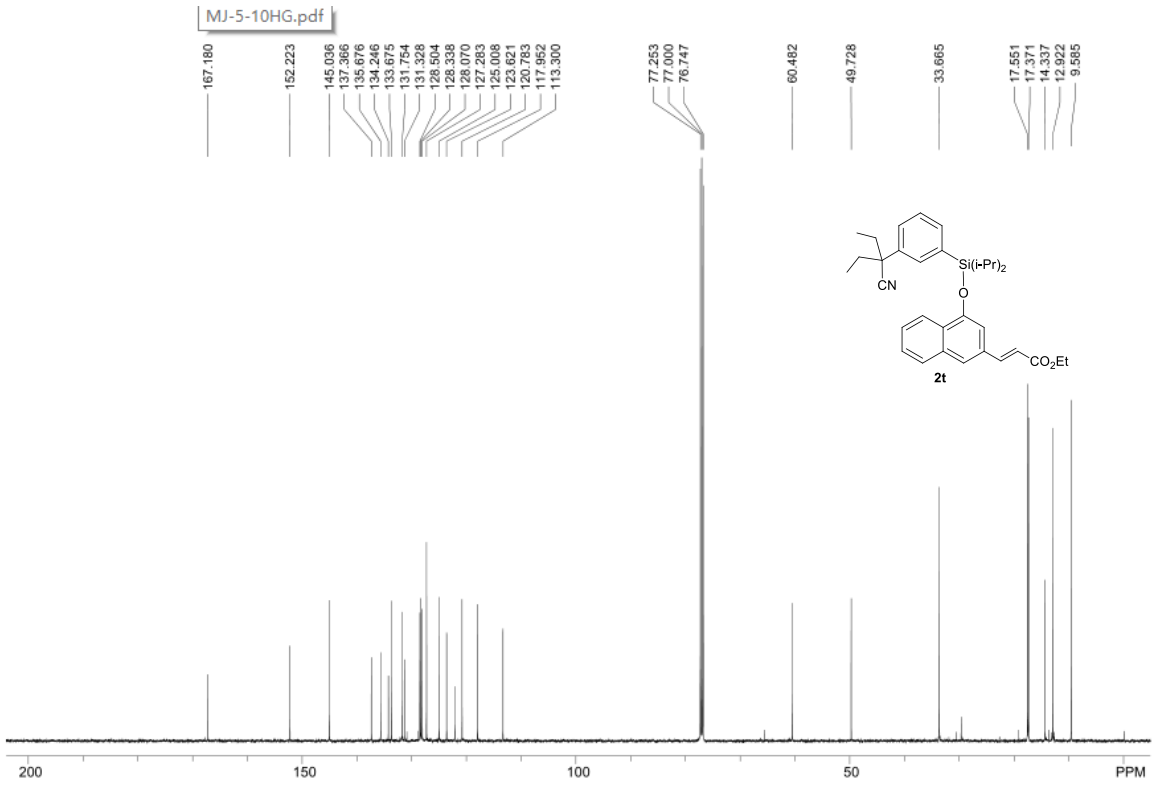
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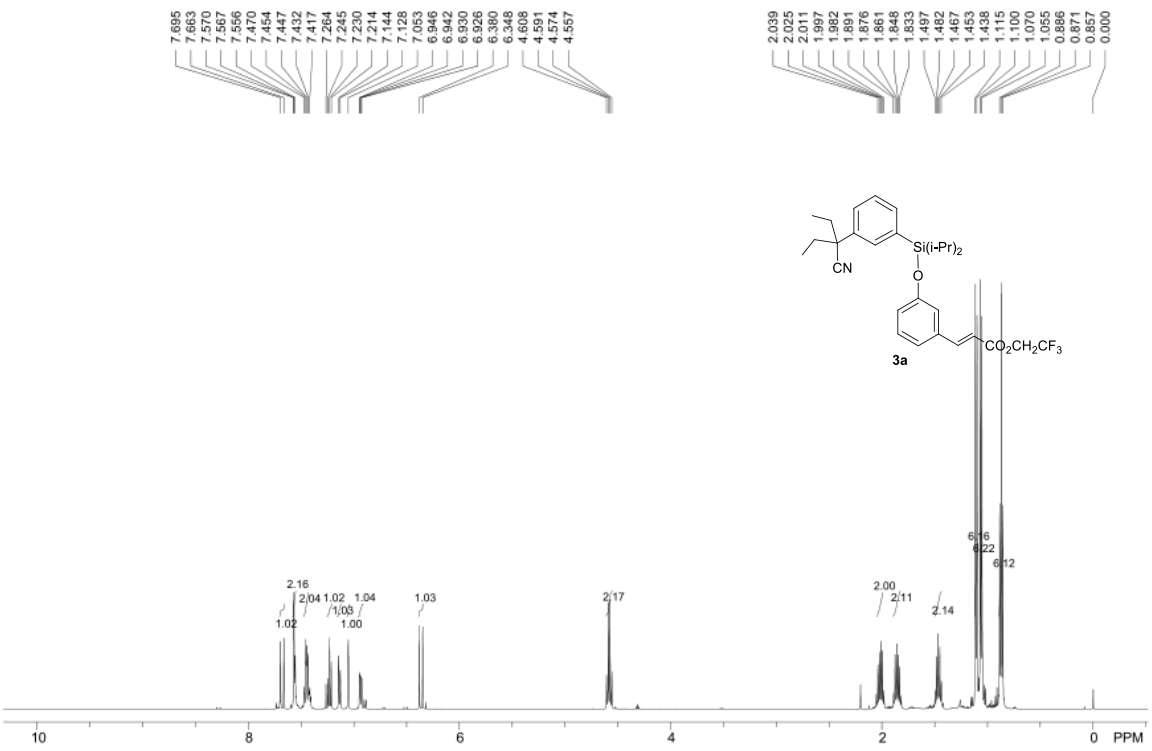
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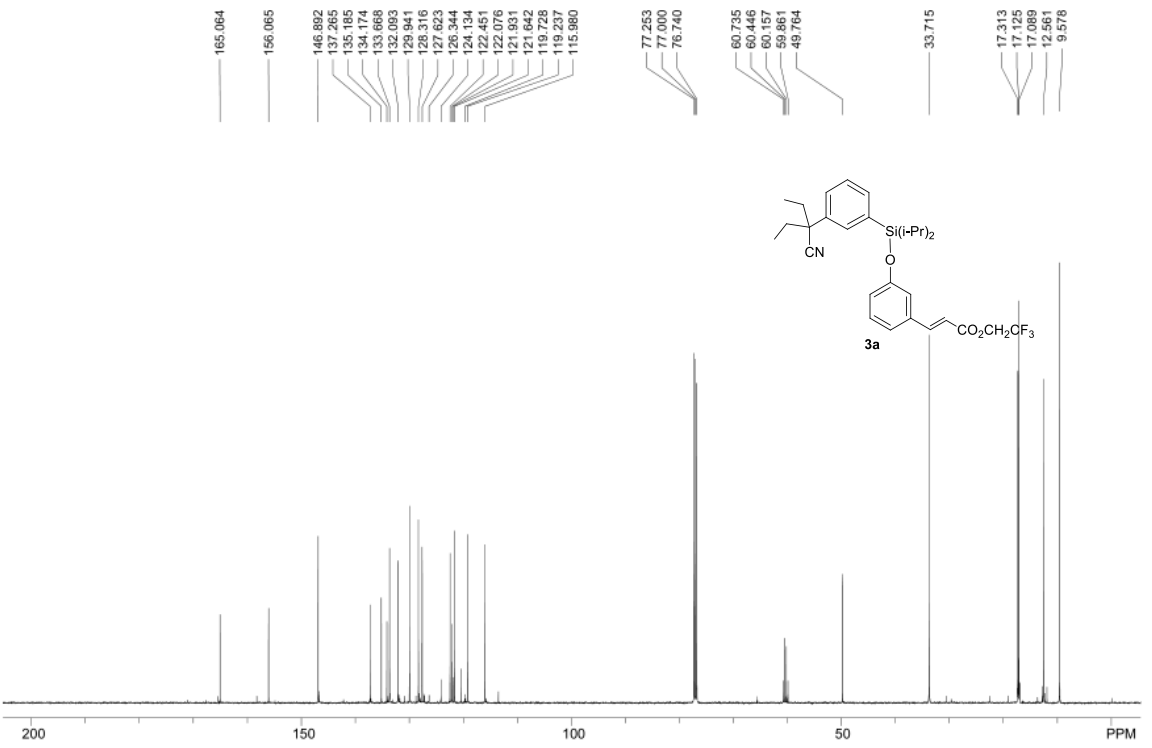
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Si(i-Pr)2
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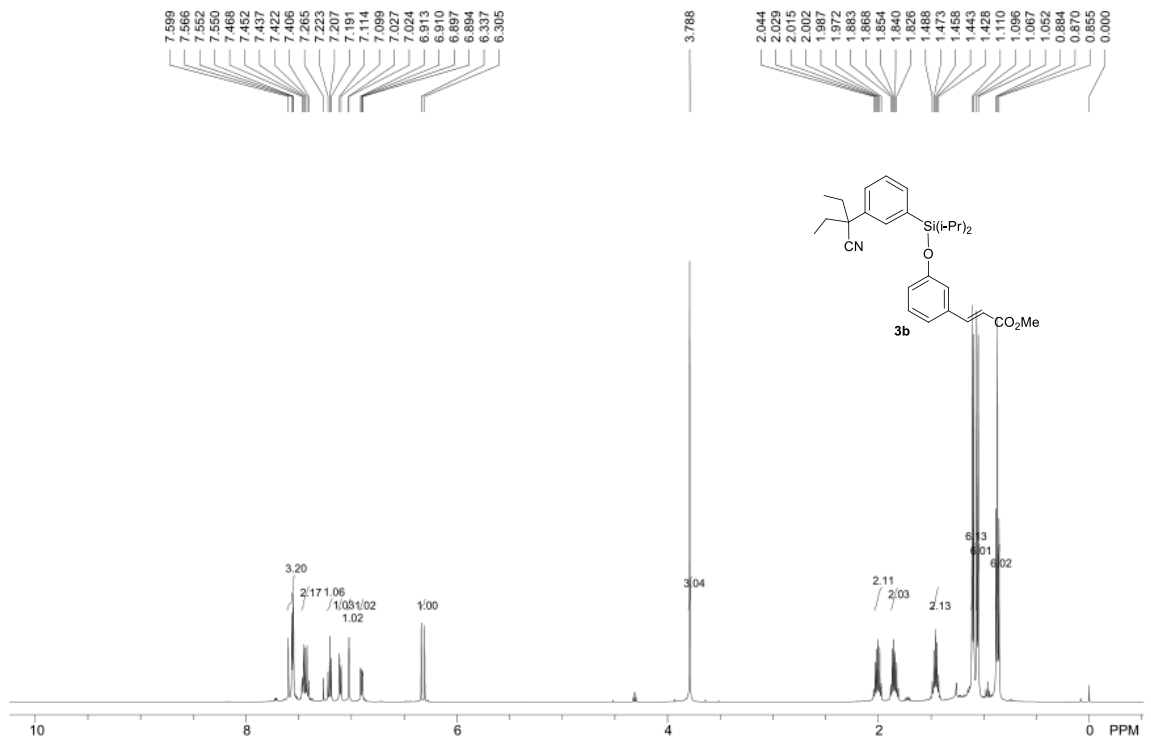
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1.067
1.052
0.884
0.870
0.855
0.000
Si(i-Pr)2
CN
O
CO2Me
3b
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1.03
1.02
1.02
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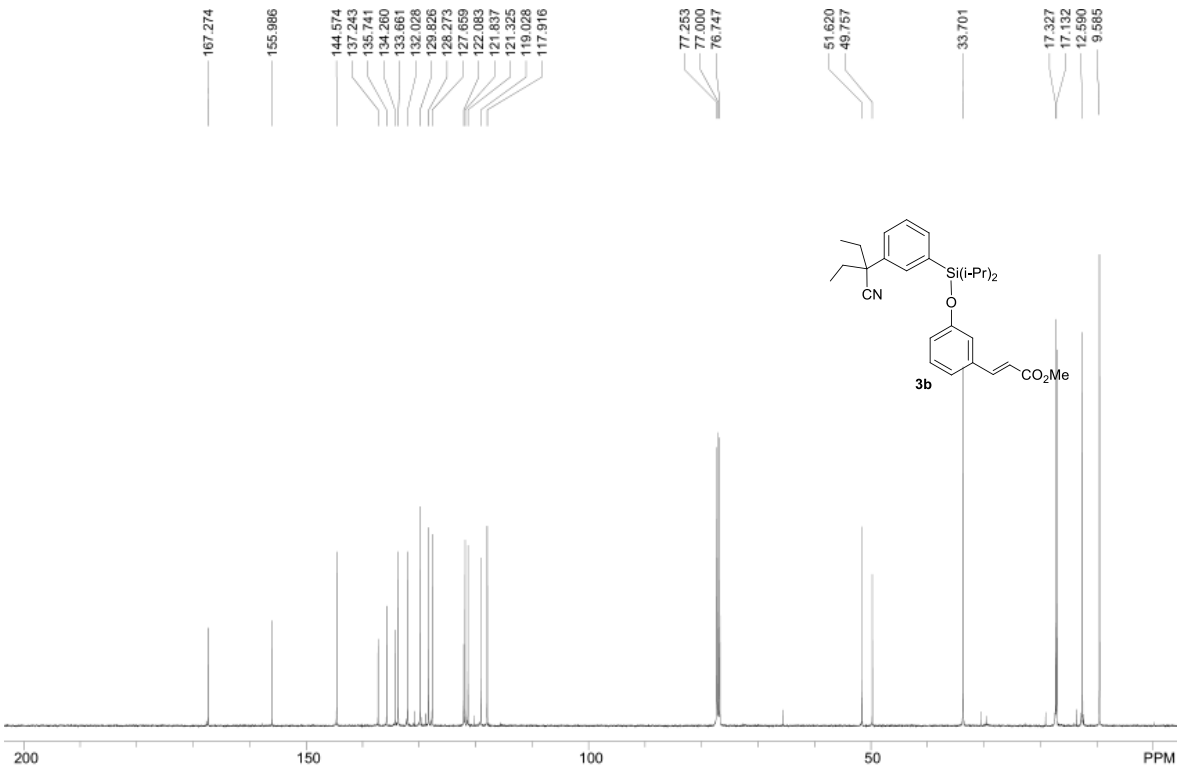
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49.757
33.701
17.327
17.132
12.590
9.585
Si(i-Pr)2
CN
O
CO2Me
3b
200
150
100
50
PPM


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7.469
7.453
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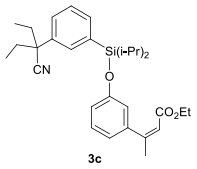
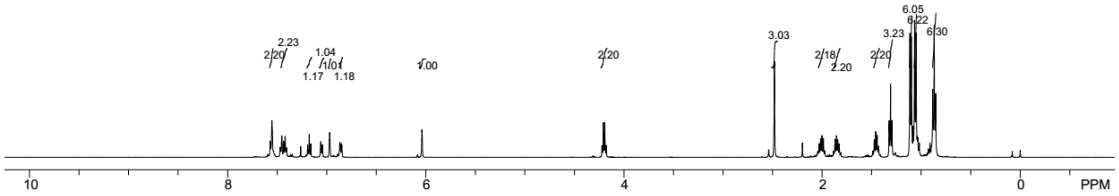

Si(i-Pr)2
CN
O
CO2Et

3c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2.20
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10
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4
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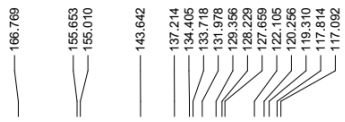
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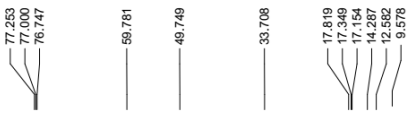
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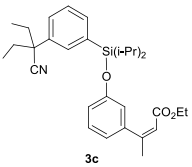
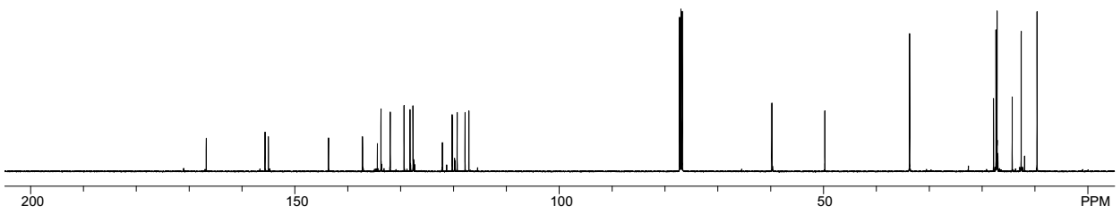

Si(i-Pr)2
CN
O
CO2Et

3c


200
150
100
50
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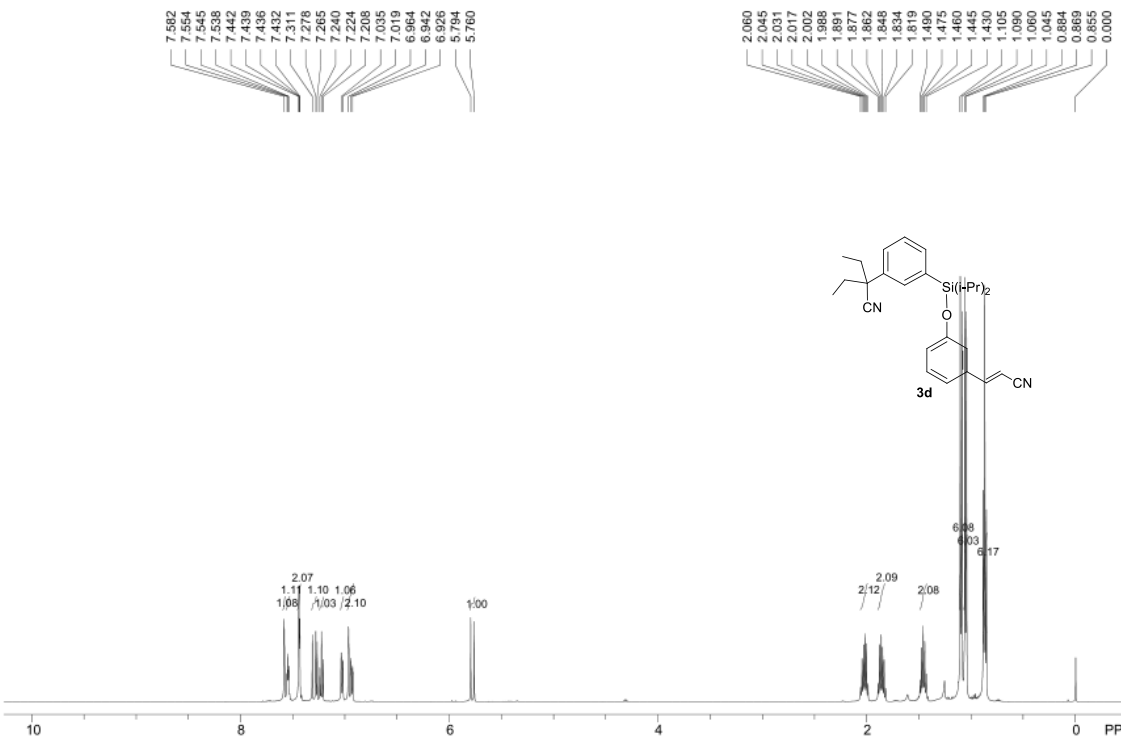
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0.884
0.869
0.855
0.000
Si(i-Pr)2
CN
O
CN
3d
2.07
1.11
1.08
1.10
1.03
1.06
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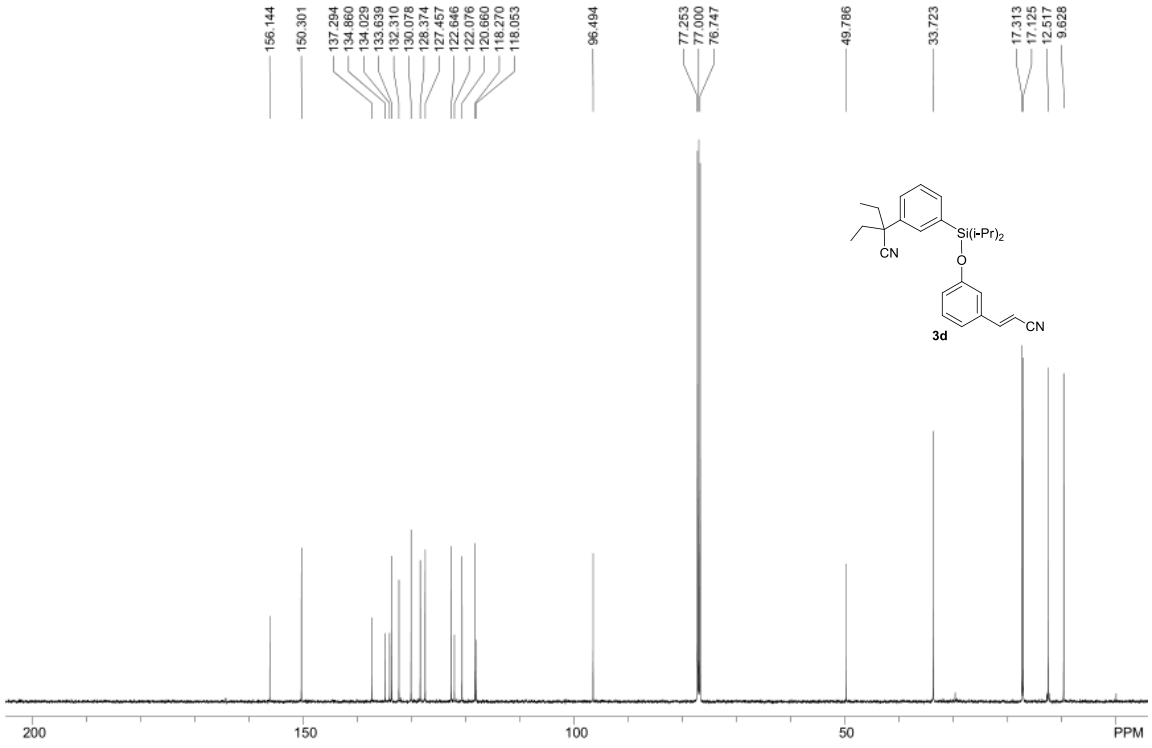
PPM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118.053
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77.253
77.000
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33.723
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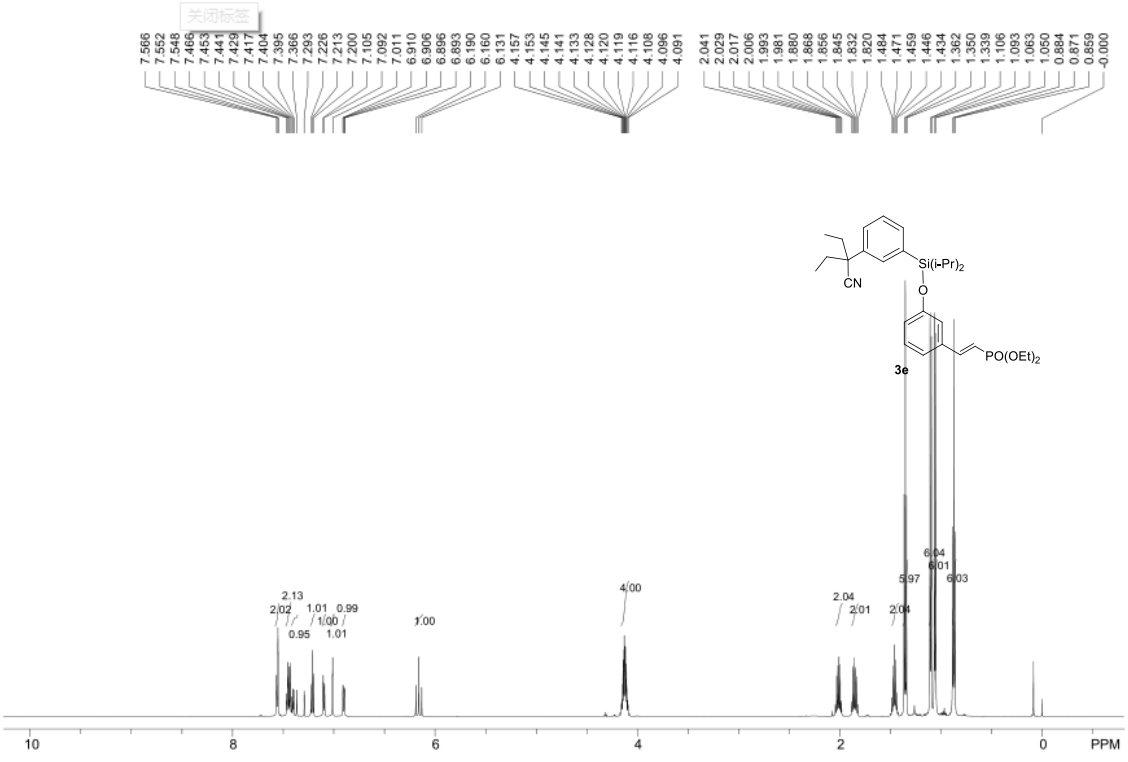
12.517
9.628
Si(i-Pr)2
CN
O
CN
3d
200
150
100
50
PPM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2.041 2.029 2.017 2.006 1.993 1.981 1.880 1.868 1.856 1.845 1.832 1.820 1.484 1.471 1.459 1.446 1.434 1.362 1.350 1.339 1.106 1.093 1.063 1.050 0.884 0.871 0.859 0.000
Si(i-Pr)2
CN
O
PO(OEt)2
3e
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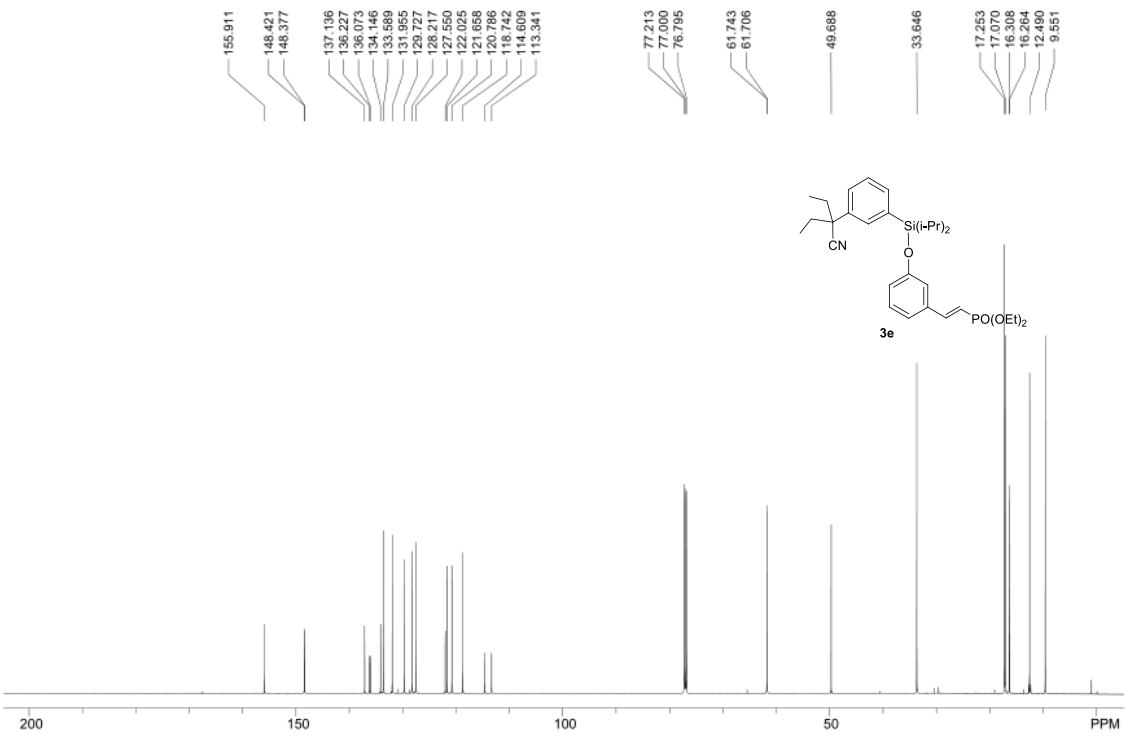
10 8 6 4 2 0 PPM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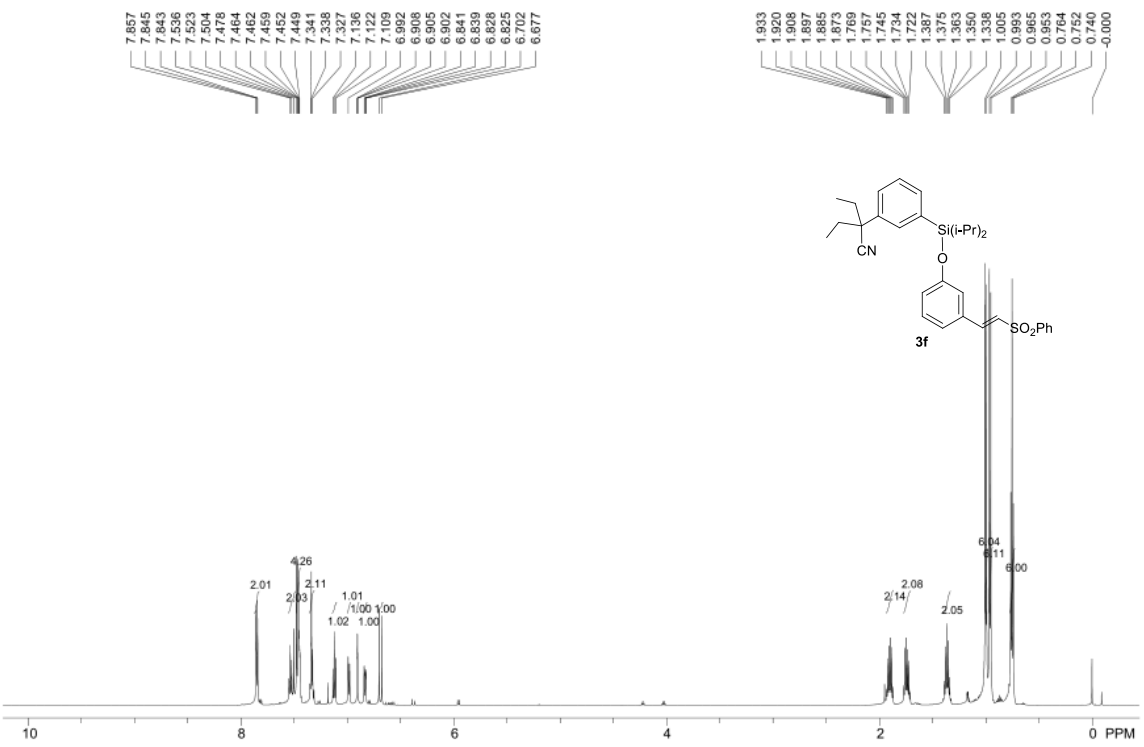
77.213 77.000 76.795 61.743 61.706 49.688 33.646 17.253 17.070 16.308 16.264 12.490 9.551
Si(i-Pr)2
CN
O
PO(OEt)2
3e
200 150 100 50 PPM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-0.000
Si(i-Pr)2
CN
O
SO2Ph
3f
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4.26
2.03
2.11
1.01
1.02
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4
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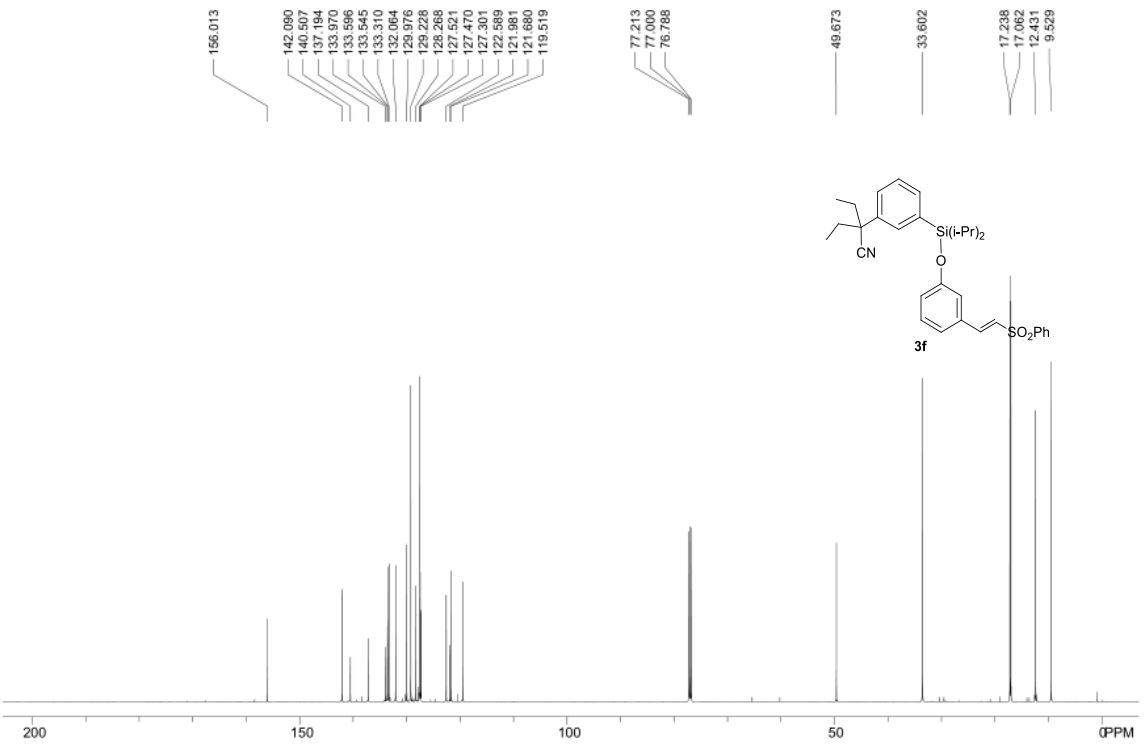
0 PPM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76.788
49.673
33.602
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9.529
Si(i-Pr)2
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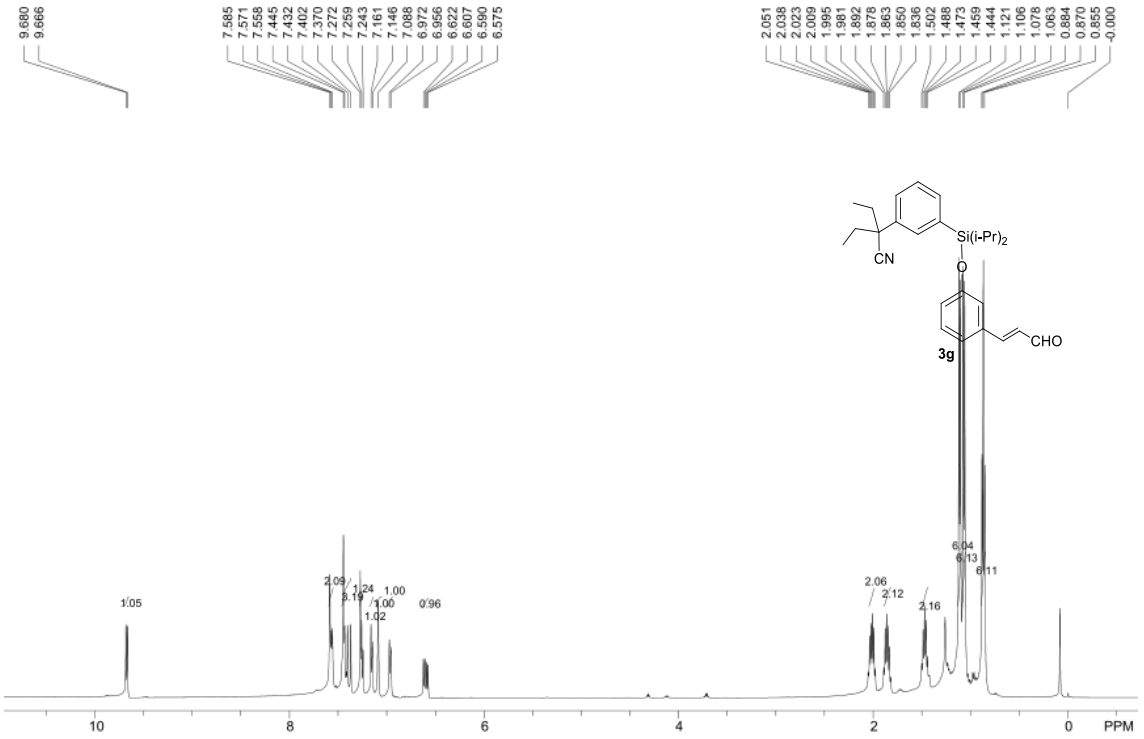
O
SO2Ph
3f
200
150
100
50
0PPM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1.078
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Si(i-Pr)2
CN
O
CHO
3g
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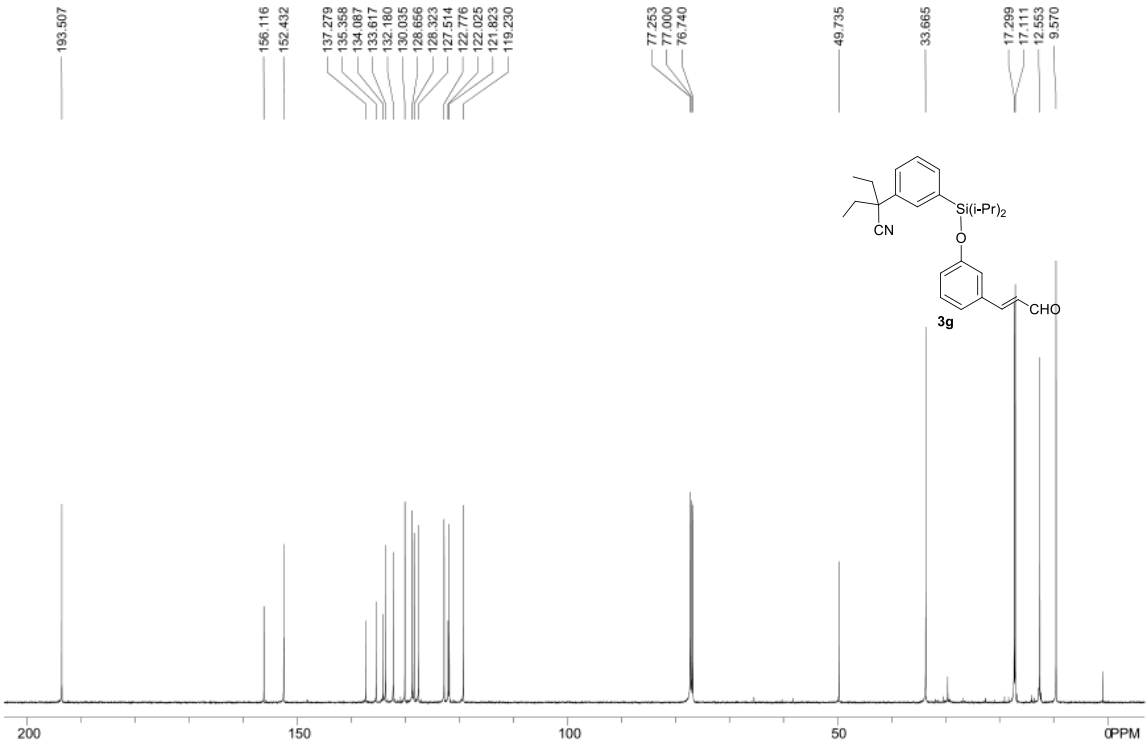
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Si(i-Pr)2
CN
O
CHO
3g
200
150
100
50
0PPM


ANGEW对位苯酚.pdf
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Et
C
N
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OH
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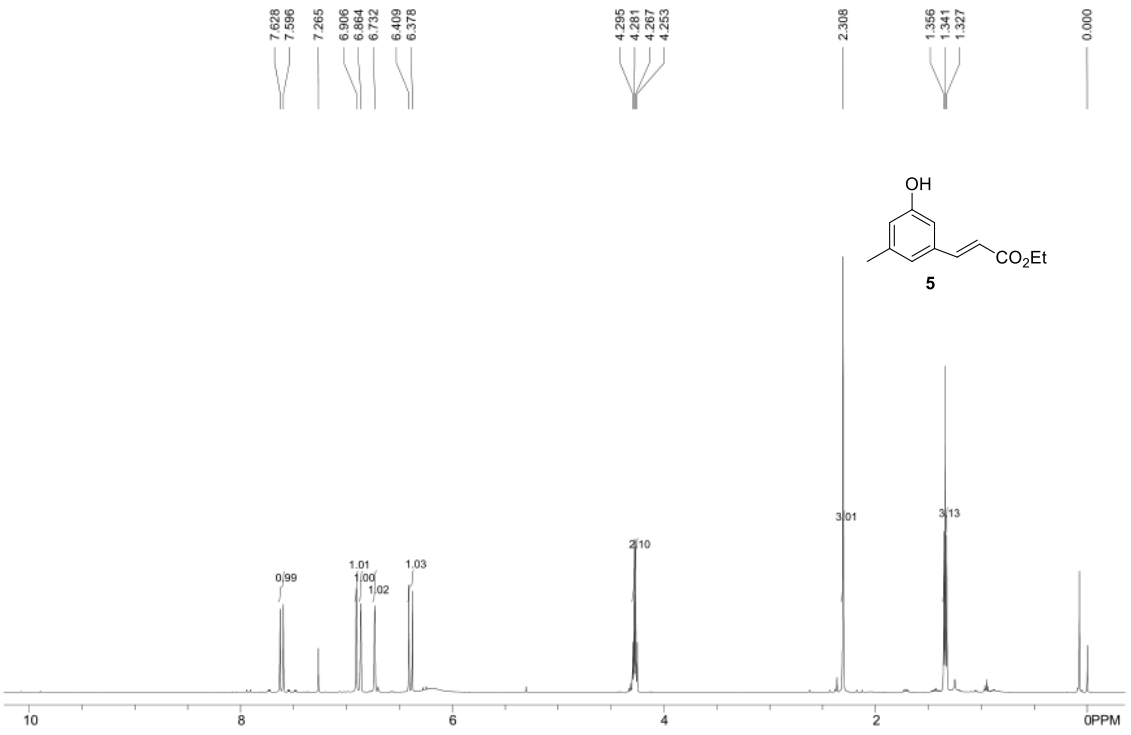
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CO2Et
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3.01
3.13
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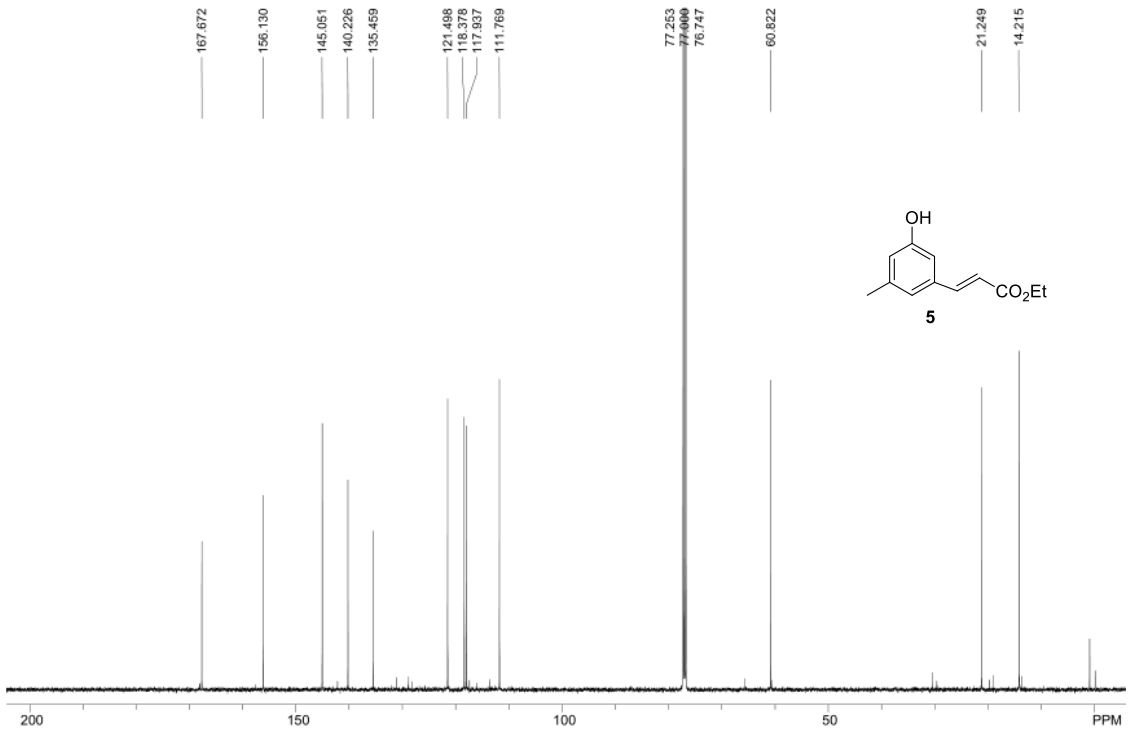
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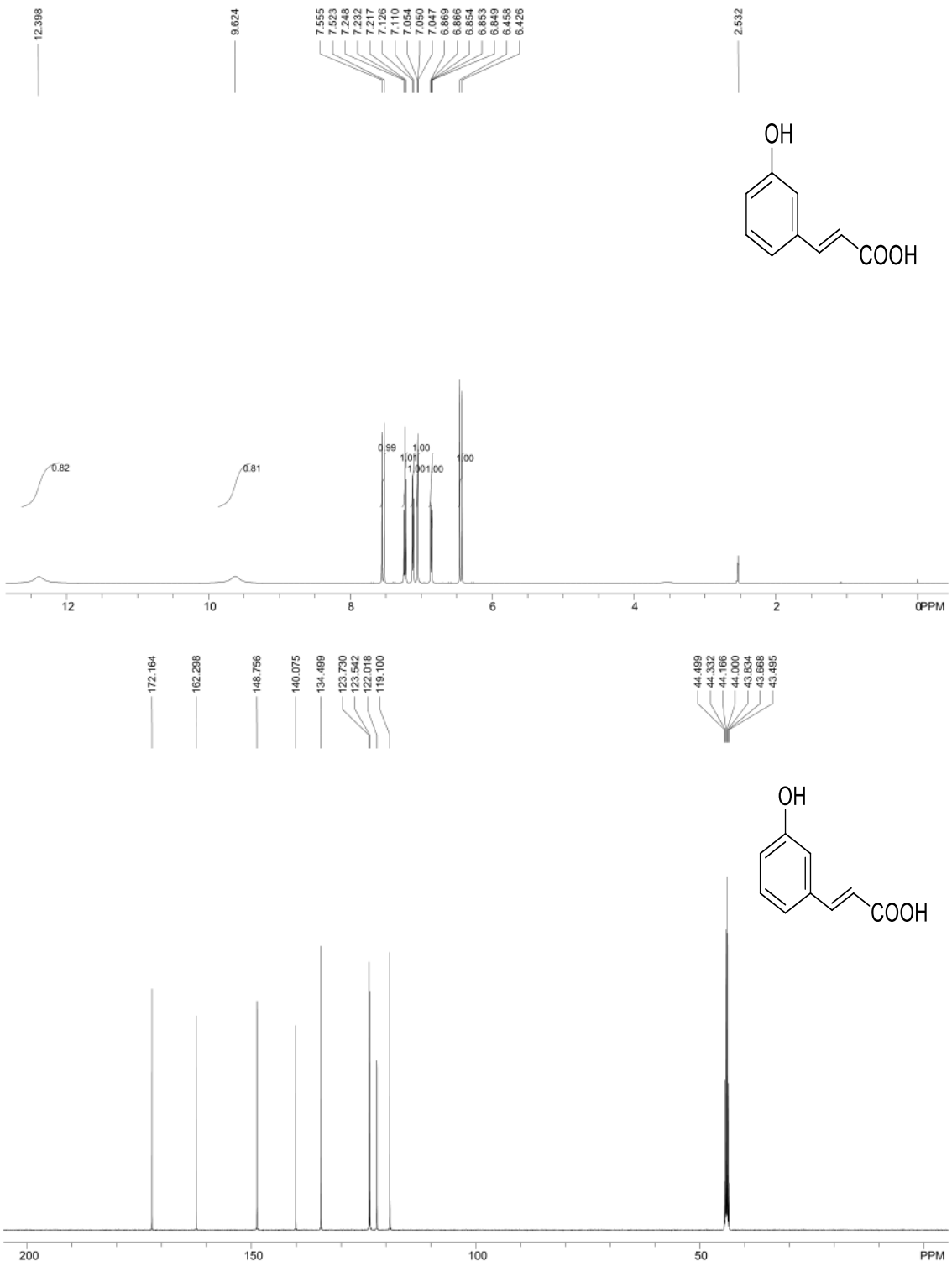
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1.00
1.00
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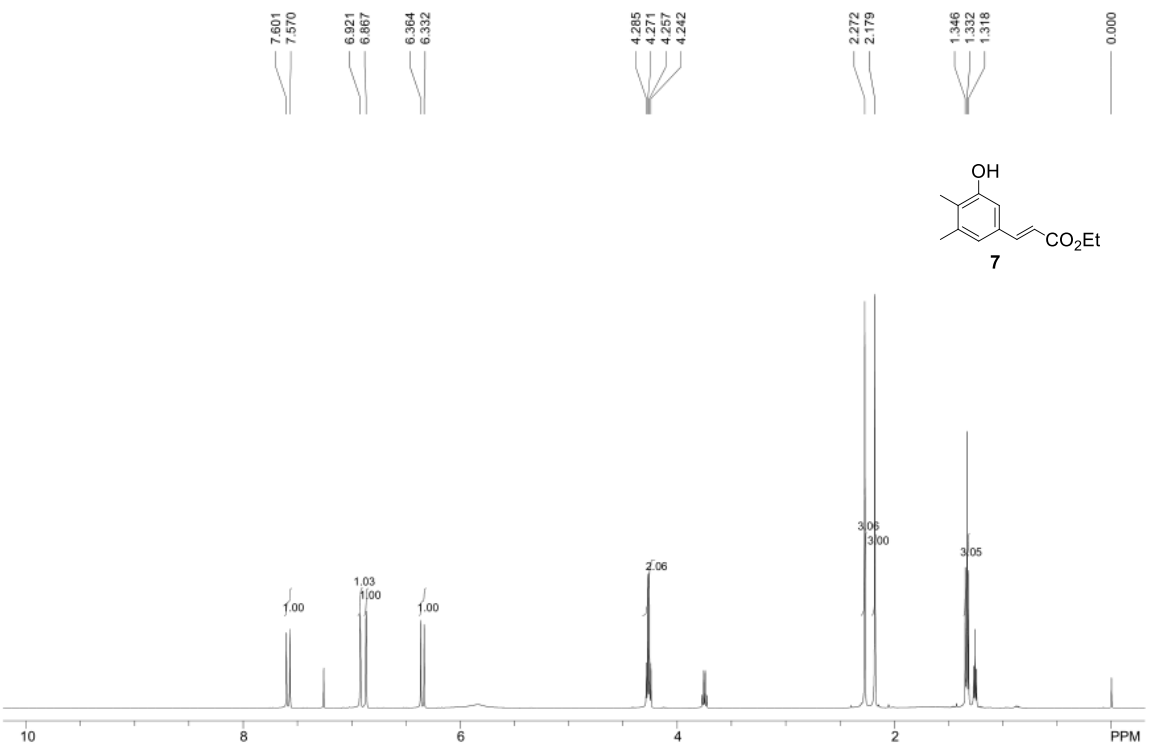
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CO2Et
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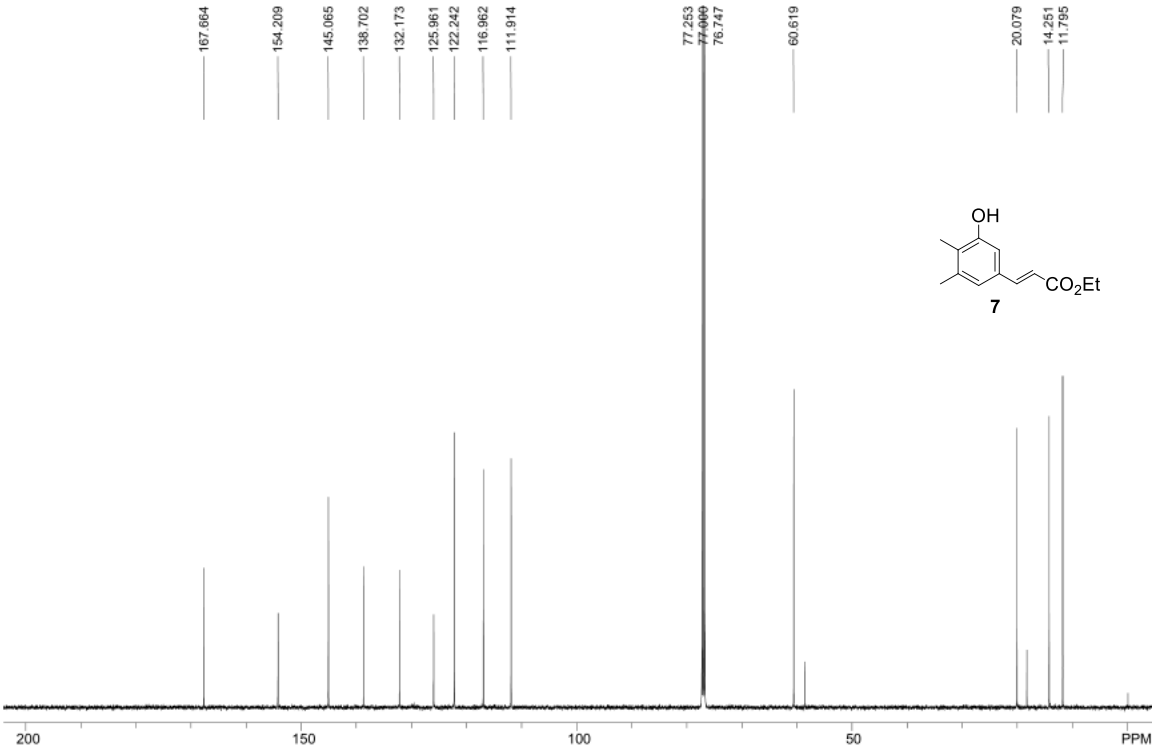
2
PPM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CO2Et
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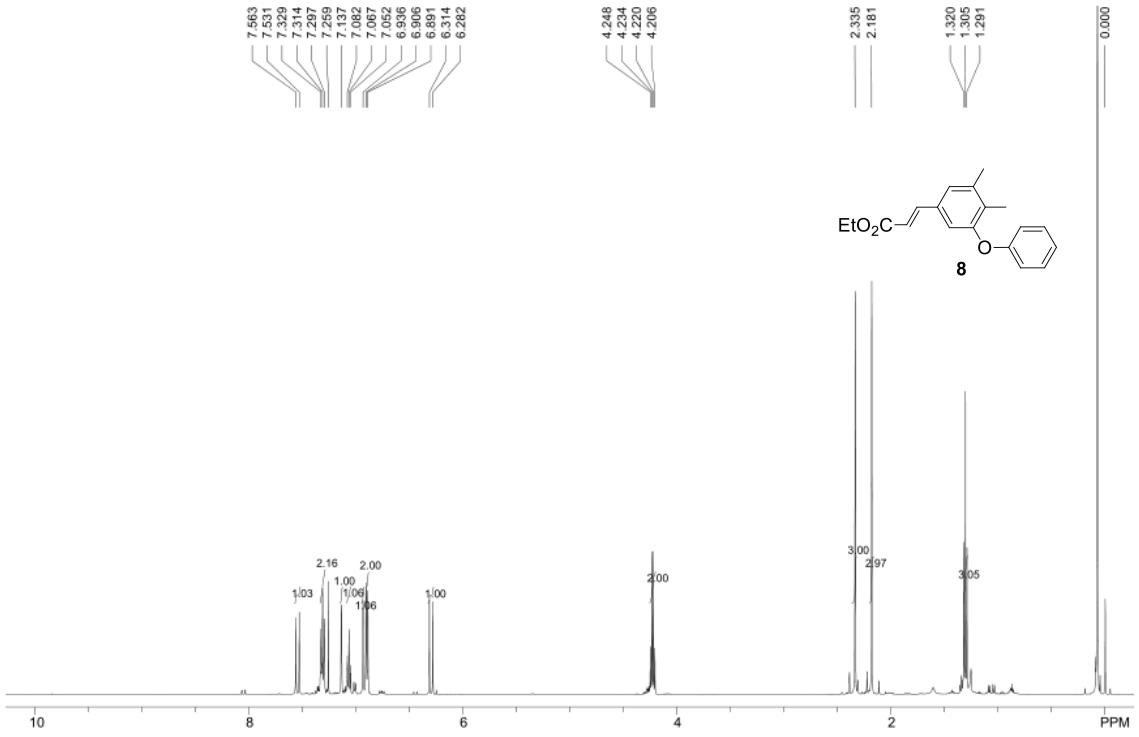
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O
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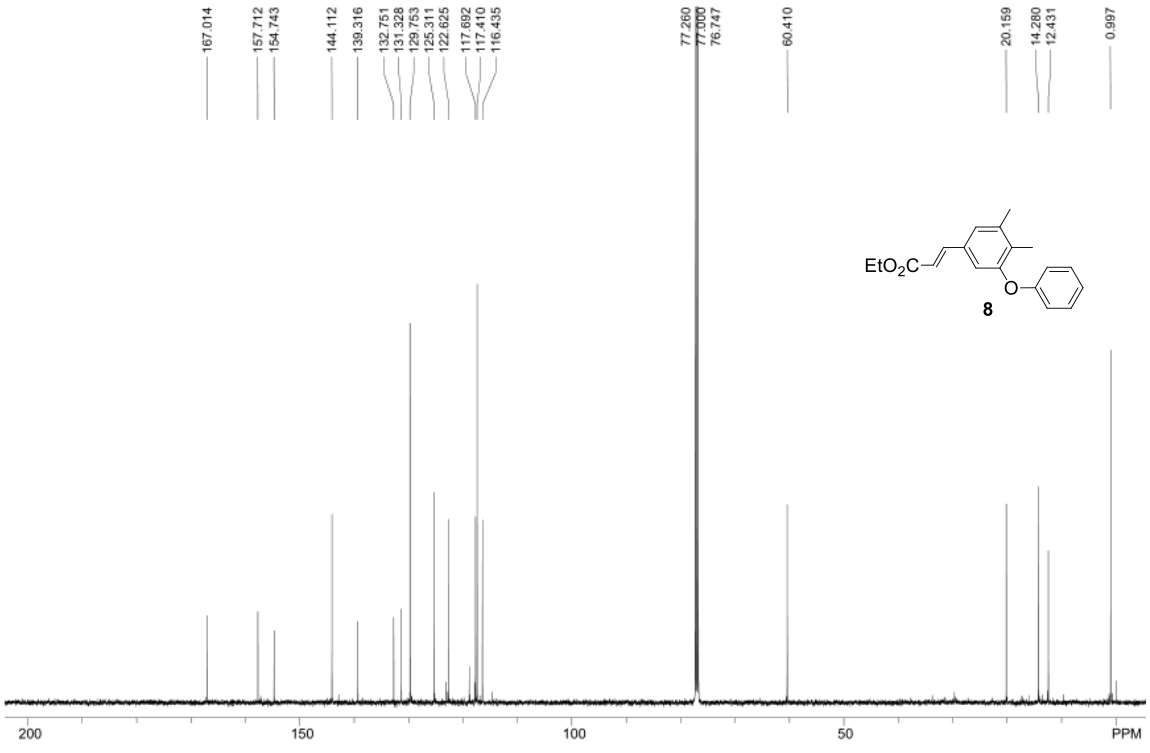
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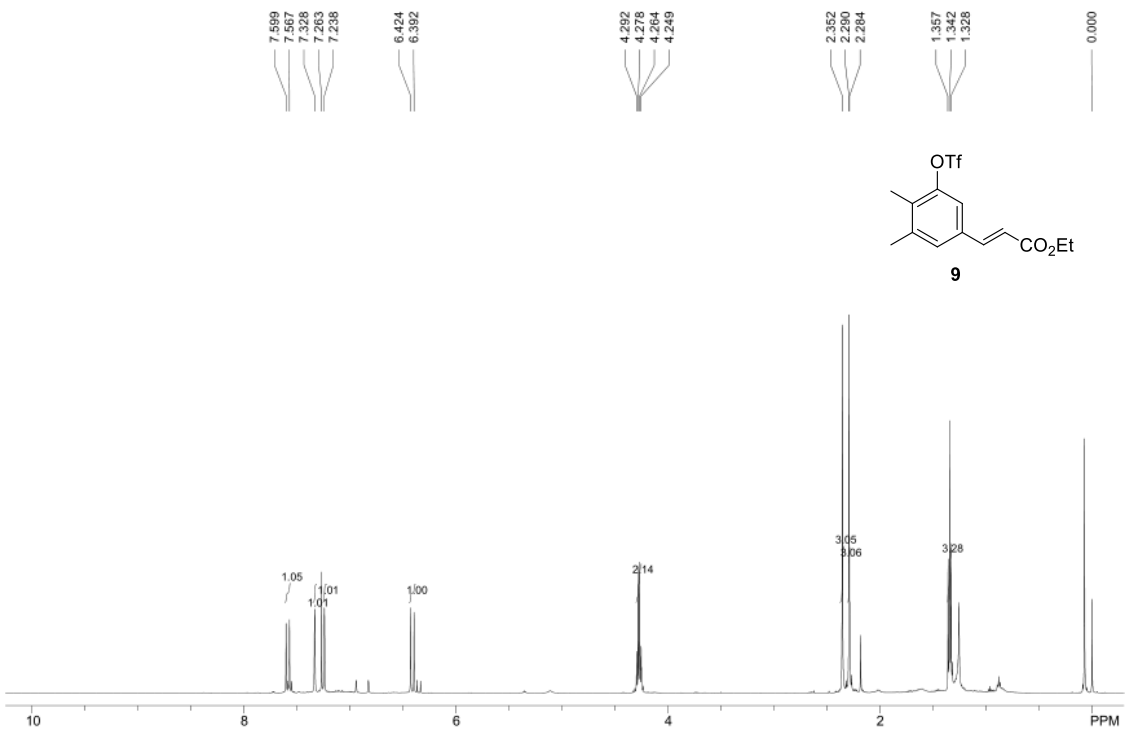
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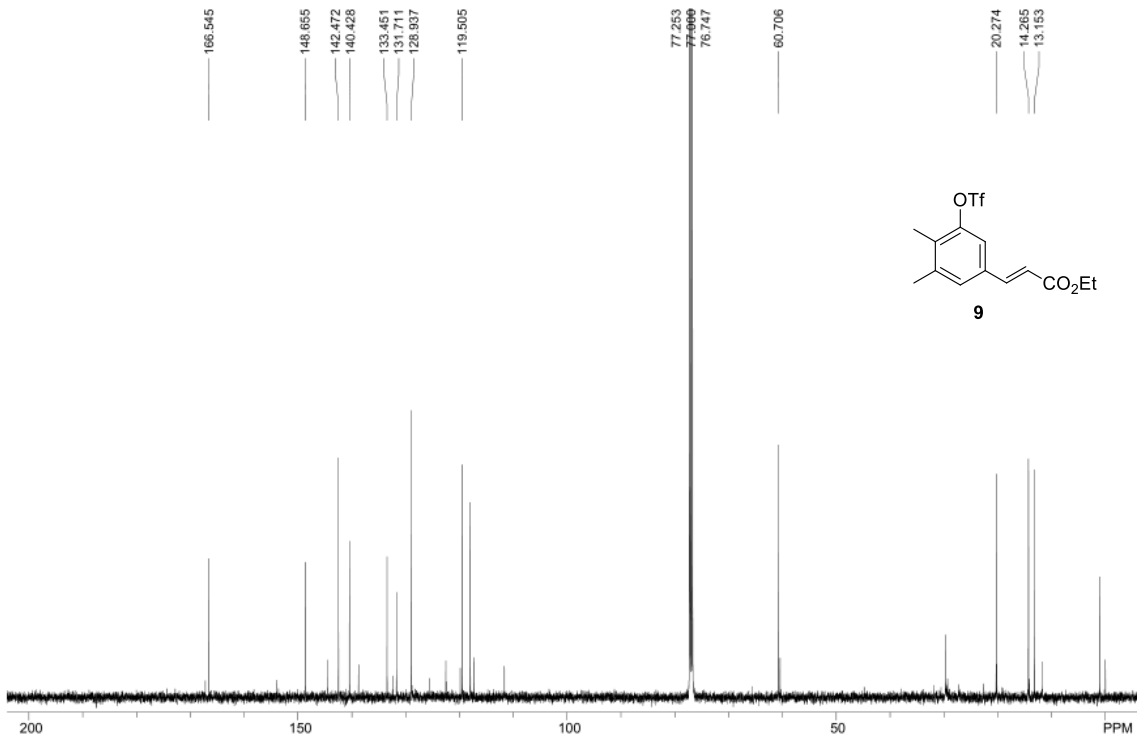
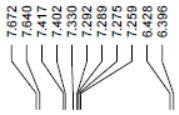
8
6
4
2
PPM


166.545
148.655
142.472
140.428
133.451
131.711
128.937
119.505
77.253
77.000
76.747
60.706
20.274
14.265
13.153
OTf
CO2Et
9
200
150
100
50
PPM

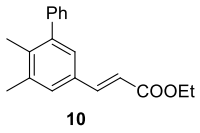

7.672
7.640
7.417
7.402
7.330
7.292
7.289
7.275
7.259
6.428
6.396


4.269
4.254
4.240
4.226

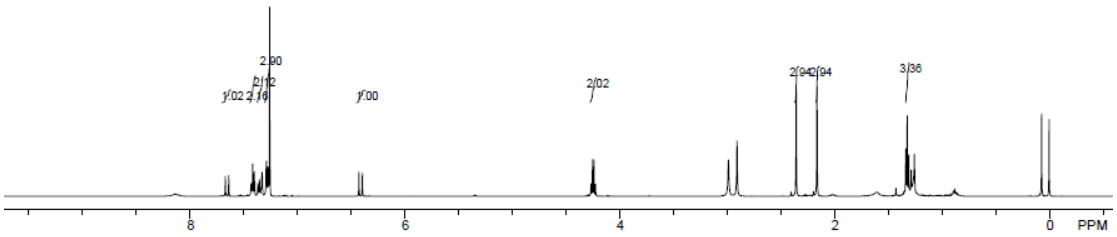

2.357
2.163

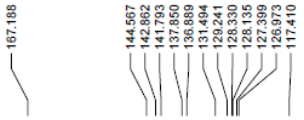

1.336
1.322
1.308

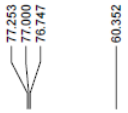

0.000

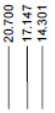

Ph
COOEt

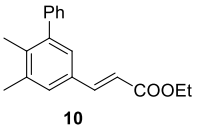
10


2.90
2.02
2.02
2.16
1.00
2.02
2.94
2.94
3.36
8
6
4
2
0
PPM


167.188
144.567
142.862
141.793
137.850
136.889
131.494
129.241
128.330
128.135
127.399
126.973
117.410

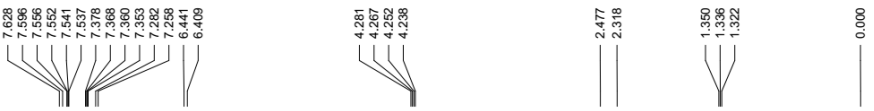

77.253
77.000
76.747
60.352


20.700
17.147
14.301


Ph
COOEt

10

200
150
100
50
PPM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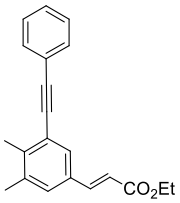
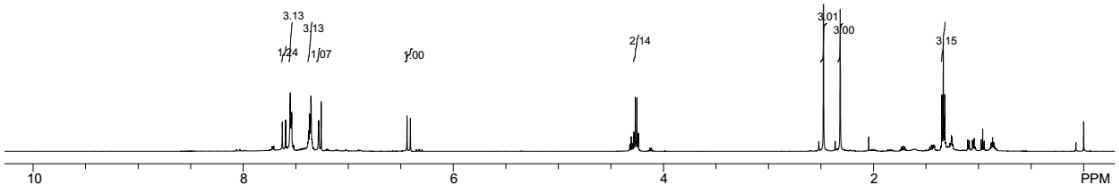
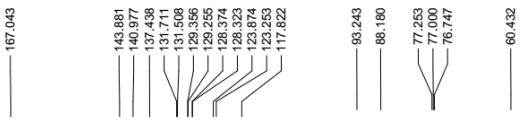
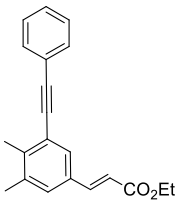
7.596
7.566
7.562
7.541
7.537
7.378
7.368
7.360
7.353
7.282
7.258
6.441
6.409
4.281
4.267
4.252
4.238
2.477
2.318
1.350
1.336
1.322
0.000


CO2Et

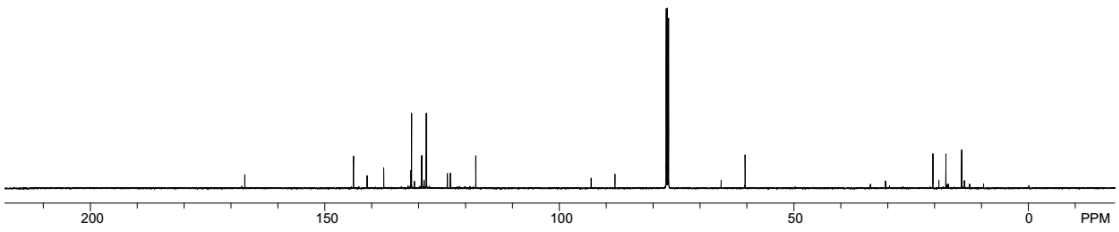
11


3.13
3.13
1.44
1.07
1.00
2.14
3.01
3.00
3.15
10
8
6
4
2
PPM


167.043
143.881
140.977
137.438
131.711
131.508
129.356
129.255
128.374
128.323
123.874
123.253
117.822
93.243
88.180
77.253
77.000
76.747
60.432
20.419
17.652
14.294


CO2Et

11


200
150
100
50
0
PPM