Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Sequential *Meta*- C–H Olefination of Synthetically Versatile Benzyl Silanes: Effective Synthesis of *meta*-Olefinated Toluene, Benzaldehyde and Benzyl Alcohols

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1. General considerations

Reagent information:

All commercial reagents were purchased from Sigma-Aldrich, Alfa Aesar, TCI, Merck and Spectrochem and used without further purification. Palladium catalysts were obtained from Alfa Aesar. All solvents were bought from Merck and Spectrochem and were used as received. 1, 2-dichloroethane (DCE) and 2,2,2-trifluoroethanol (TFE) was purchased from Spectrochem and used as received. Tetrahydrofuran (THF) and dichloromethane (DCM) were dried using standard procedure and stored over 4 Å molecular sieves before use for preparation of benzyl silyl ether derivatives. Unless otherwise mentioned all reactions were carried out under inert atmosphere using a combination of glovebox and standard Schlenk techniques. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. A gradient elution using petroleum ether and ethyl acetate was performed, based on Merck aluminium TLC sheets (silica gel $60F_{254}$) visualized under UV illumination at 254 nm.

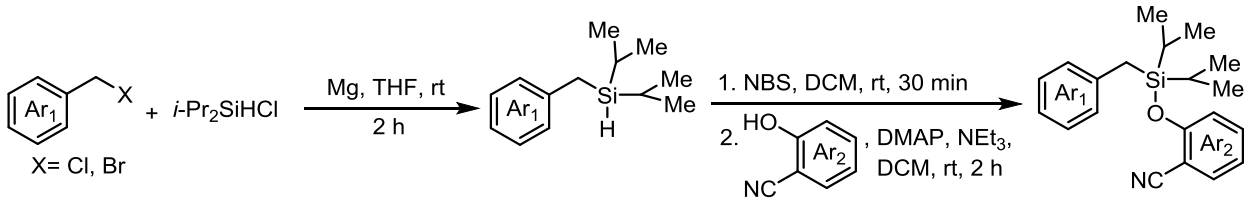
Analytical Information*:*

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III 400 (400 MHz and 100 MHz respectively) and 500 (500 MHz and 125 MHz respectively) instrument. All NMR spectra were reported in parts per million (ppm) downfield of TMS and were internally referenced to TMS (0 ppm) or residual $CHCl_3$ (7.26 ppm for ^{1}H, 77.23 ppm for ^{13}C). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quintet, m = multiplet. Infrared spectra were recorded in chloroform solution on a Perkin-Elmer spectrum one FT-IR spectrometer in transmittance mode (%T, cm^{-1}). High-resolution mass spectra (HRMS) were recorded on Q-TOF micromass (YA-105) and Bruker Maxis Impact system (282001.00081) mass spectrometer in positive ESI mode. Yield and selectivity for optimization was determined form NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene (TMB) as internal standard.

2. Experimental Section

2.1 *Preparation of templates for meta C─H olefination:*

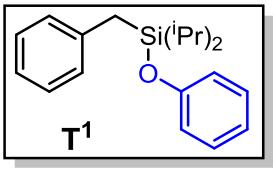
General procedure for preparation of substituted 2-hydroxybenzonitrile: 2-Hydroxybenzonitrile derivatives were prepared from corresponding 2-hydroxybenzaldehyde derivatives using previously reported literature procedure.[1]



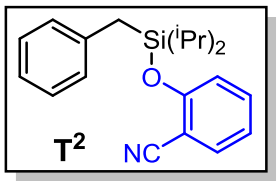
<u>General procedure A</u> for preparation of 2-((benzyldiisopropylsilyl)oxy)benzonitrile derivatives:

To a mixture of magnesium turnings (9 mmol, 218 mg) and a crystal of iodine under nitrogen atmosphere dry THF (8 mL) was added and stirred for 10 min at room temperature. Chlorodiisopropylsilane (3 mmol, 512 µL) was added drop wise, followed by drop wise addition of corresponding benzyl halide (3 mmol) in dry THF (4 mL) at 0 °C. After stirring for 2 h at room temperature, the reaction was quenched by addition of saturated brine solution (15 mL) and was extracted by ethyl acetate (10X3). Combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude benzyldiisopropylsilane derivatives.

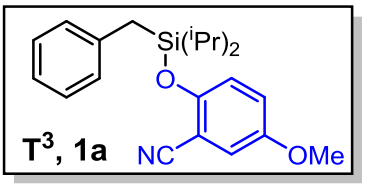
To a suspension of NBS (3.3 mmol, 588 mg) in dry DCM (5 mL) was slowly added crude benzyldiisopropylsilane (3 mmol) in dry DCM (5 mL) at 0 °C under nitrogen atmosphere. After stirring at room temperature for 30 min, the resulting solution was transferred via syringe to a stirred solution of 2-hydroxybenzonitrile derivatives (3 mmol), DMAP (0.3 mmol, 37 mg), and NEt_3 (3.3 mmol, 460 µL) in dry DCM (5 mL) at 0 °C under nitrogen atmosphere. The mixture was stirred at room temperature for 2 h. Finally after removal of DCM, hexane (20X3) was added and filtered through celite. Concentration under reduced pressure afforded crude 2-((benzyldiisopropylsilyl)oxy)benzonitrile derivative product, which was further purified by silica gel column chromatography.



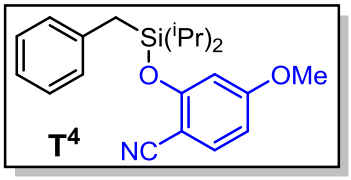
benzyldiisopropyl(phenoxy)silane (Scheme 2, template T^1): General procedure A was followed. Colorless oil. Eluent: petrolium ether/ ethyl acetate (99/1 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 4H), 7.12 (ddd, *J* = 13.0, 7.4, 3.5 Hz, 3H), 6.98 – 6.93 (m, 1H), 6.84 – 6.80 (m, 2H), 2.39 (d, *J* = 2.9 Hz, 2H), 1.20 (tdd, *J* = 11.3, 7.0, 4.1 Hz, 2H), 1.10 – 1.00 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.76, 138.88, 129.61, 129.05, 128.45, 124.58, 121.45, 120.11, 21.18, 17.60, 17.58, 13.04; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{20}H_{26}OSi$: 299.1753, found: 299.1751; **IR** (thin film) 689, 885, 937, 1038, 1157, 1233, 1279, 1499, 1586, 2229, 2869, 2949 cm^{-1}.



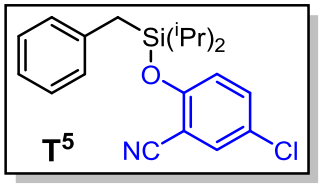
2-((benzyldiisopropylsilyl)oxy)benzonitrile (Scheme 2, template T^2): General procedure A was followed. Colorless oil. Eluent: petrolium ether/ ethyl acetate (98/2 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.32 (ddd, *J* = 8.4, 7.5, 1.8 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.13 – 7.06 (m, 3H), 6.96 (td, *J* = 7.6, 1.0 Hz, 1H), 6.58 (dd, *J* = 8.4, 0.5 Hz, 1H), 2.46 (s, 2H), 1.33 – 1.23 (m, 2H), 1.10 – 1.05 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.16, 137.97, 134.13, 133.76, 129.02, 128.67, 128.53, 124.88, 121.49, 117.19, 105.20, 21.23, 17.53, 17.49, 12.99; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{20}H_{26}OSi$: 324.1784, found: 324.1789.



2-((benzyldiisopropylsilyl)oxy)-5-methoxybenzonitrile (Scheme 2, template T^3): General procedure A was followed. Colorless oil. Eluent: petrolium ether/ ethyl acetate (98/2 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.5 Hz, 2H), 7.14 – 7.06 (m, 3H), 6.97 (d, *J* = 3.2 Hz, 1H), 6.88 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.47 (d, *J* = 9.1 Hz, 1H), 3.76 (s, 3H), 2.43 (s, 2H), 1.29 – 1.22 (m, 2H), 1.09 – 1.04 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.56, 152.29, 138.13, 129.02, 128.64, 124.82, 121.21, 120.68, 117.14, 116.70, 104.93, 56.05, 21.21, 17.54, 17.50, 12.92; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{20}H_{26}OSi$: 354.1889, found: 354.1891.



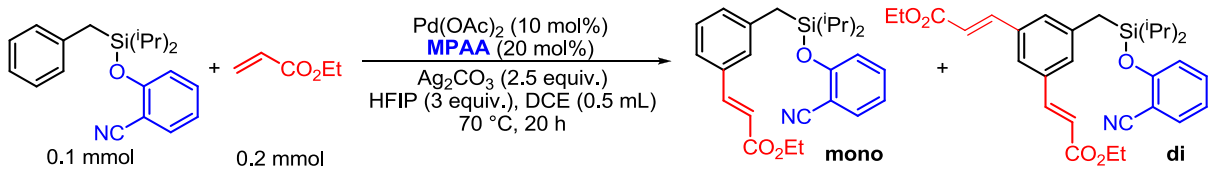
2-((benzyldiisopropylsilyl)oxy)-4-methoxybenzonitrile (Scheme 2, template T^4): General procedure A was followed. Colorless oil. Eluent: petrolium ether/ ethyl acetate (98/2 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.7 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.13 (d, *J* = 6.9 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.50 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.02 (d, *J* = 2.3 Hz, 1H), 3.66 (s, 3H), 2.45 (s, 2H), 1.32 – 1.25 (m, 2H), 1.12 – 1.04 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.21, 159.72, 138.06, 134.50, 129.05, 128.66, 124.87, 117.62, 108.19, 105.34, 97.25, 55.70, 21.14, 17.55, 17.46, 12.89; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{20}H_{26}OSi$: 354.1889, found: 354.1881.



2-((benzyldiisopropylsilyl)oxy)-5-chlorobenzonitrile (Scheme 2, template T[5]): General procedure A was followed. Colorless oil. Eluent: petrolium ether/ ethyl acetate (98/2 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.7 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.11 (d, *J* = 7.1 Hz, 3H), 6.39 (d, *J* = 8.9 Hz, 1H), 2.45 (s, 2H), 1.29 (dd, *J* = 13.2, 5.4 Hz, 2H), 1.12 – 1.05 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.85, 137.68, 134.18, 132.80, 128.96, 128.74, 126.24, 124.98, 120.84, 115.84, 106.37, 21.05, 17.48, 17.41, 12.84; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{20}H_{26}OSi$: 358.1394, found: 358.1388.

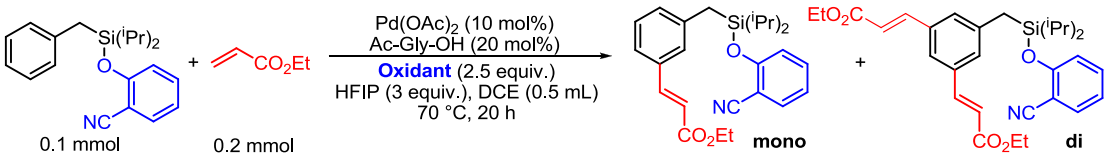
2.2 *Optimization details for meta C–H mono olefination:*

Table S1: Optimization of ligand



Entry	MPAA ligand	Yield (mono: di)	Conv.
1	N-Formylglycine	13 (mono)	29
2	Boc-Gly-OH	40 (5.7:1)	61
3	**Ac-Gly-OH**	**56 (4.8:1)**	**82**
4	Boc-Val-OH	27 (mono)	67
5	Ac-Ala-OH	32 (mono)	70
6	Boc-Pro-OH	22 (mono)	62
7	Ac-Phe-OH	32 (8:1)	69

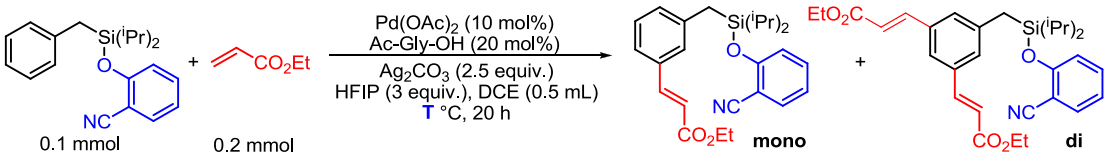
Table S2: Optimization of oxidant



Entry	Oxidant	Yield (mono: di)	Conv.
1	AgOAc	52 (1.5:1)	86
2	**Ag_2CO_3**	**56 (4.8:1)**	**81**

3	Ag_2O	11 (mono)	32
4	$AgNO_3$	24 (mono)	52

Table S3: Optimization of temperature

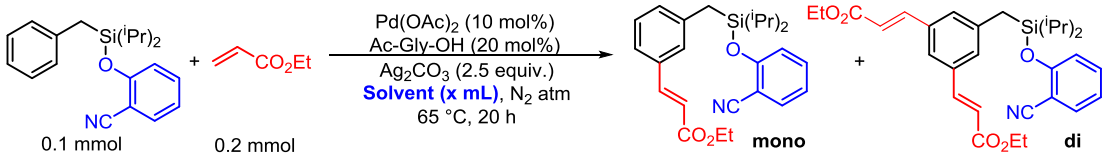


Entry	Temperature	Yield (mono: di)	Conv.
1	90 °C	38 (3:1)	96
2	80 °C	44 (4.2:1)	92
3	70 °C	55 (4.8:1)	81
4	**65 °C**	**58 (5:1)**	**82**
5	60 °C	51 (5.5:1)	76

Table S4: Optimization of atmosphere

Entry	Atmosphere	Yield (mono: di)	Conv.
1	air	58 (5:1)	82
2	**N_2**	**62 (5.2:1)**	**85**
3	O_2	41 (mono)	74

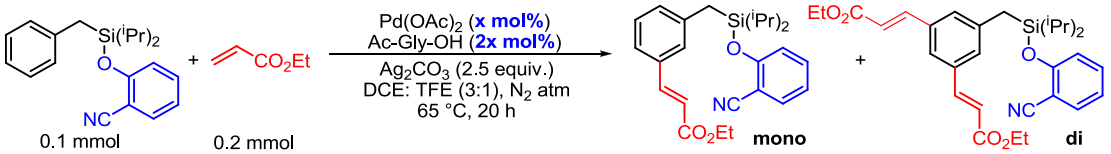
Table S5: Optimization of solvent



Entry	Solvent	Yield (mono: di)	Conv.
1	DCE (0.6 mL)	--	--
2	DCE (0.6 mL), HFIP (3 equiv.)	58 (5:1)	82
3	DCE (0.6 mL), HFIP (5 equiv.)	53 (4:1)	86
4	DCE (0.6 mL), HFIP (10 equiv.)	52 (2.5:1)	94
5	HFIP (0.6 mL)	53 (1:6)	97

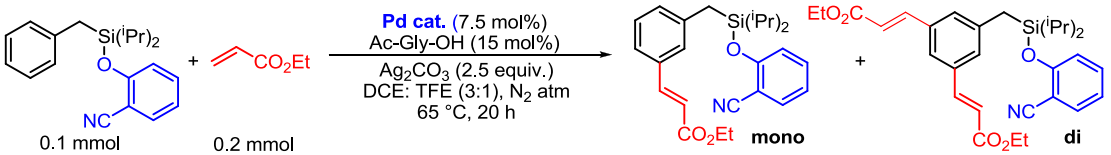
6	DCE (0.7 mL), TFE (0.1 mL)	40 (6:1)	64
7	**DCE (0.6 mL), TFE (0.2 mL)**	**71 (5:1)**	**92**
8	DCE (0.4 mL), TFE (0.4 mL)	70 (3.5:1)	88
9	TFE (0.6 mL)	71 (3.2:1)	94

Table S6: Optimization of catalyst loading



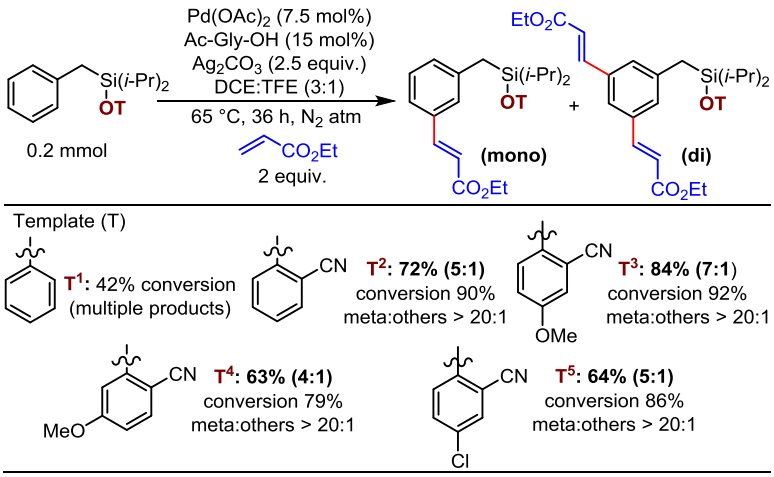
Entry	Catalyst loading (mol%)	Yield (mono: di)	Conv.
1	2.5	14 (mono)	19
2	5.0	57 (5.6:1)	69
3	**7.5**	**72 (5:1)**	**90**
4	10	72 (4:1)	87
5	12.5	73 (3.5:1)	93

Table S7: Optimization of Pd salts



Entry	Pd salt	Yield (mono: di)	Conv.
1	**$Pd(OAc)_2$**	**72 (5:1)**	**90**
2	$PdCl_2$	35 (mono)	52
3	$Pd(OPiv)_2$	64 (5:1)	81
4	$Pd(TFA)_2$	42 (mono)	--
5	$Pd_2(dba)_3$	65 (3.2:1)	91
6	$Pd(acac)_2$	12 (mono)	19
7	$PdSO_4$	21 (mono)	27
8	$Pd(MeCN)_2Cl_2$	67 (2.5:1)	--

Table S8: Optimization of templates*

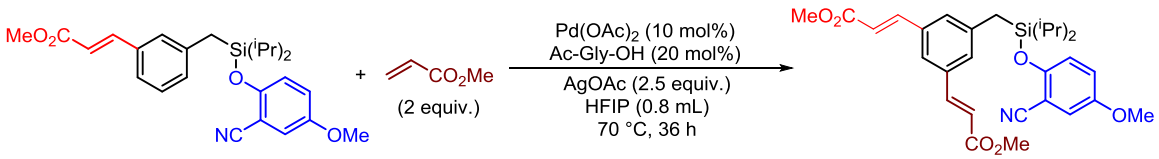


*In parenthesis ratio of mono: di is provided

<u>General procedure B</u> for C−H alkenylation of benzyl silane derivatives through remote *meta* C−H activation:

In a clean, oven–dried screw cap reaction tube containing magnetic stir–bar, substrate (0.2 mmol), $Pd(OAc)_2$ (7.5 mol%), N-Acetyl-glycine (15 mol%), Ag_2CO_3 (2.5 equiv, 0.5 mmol) were weighed and the tube was tightly closed by screw cap fitted with rubber septum. The tube was evacuated and filled with nitrogen through standard Schlenk technique, and this sequence was repeated for three additional times. Then, under positive pressure of nitrogen, olefin (2 equiv, 0.4 mmol), DCE (1.2 mL) and TFE (0.4 mL) were added sequentially by syringes. This reaction tube was placed in a preheated oil bath at 65 °C to stir vigorously for 30 h. Then reaction mixture was cooled to room temperature and filtered through celite with aid of ethyl acetate (10 mL). Regioselectivity was determined from NMR of this crude reaction mixture filtrate. Then, this filtrate was concentrated under reduced pressure and purified by column chromatography through silica gel using petrolium ether/ethyl acetate as eluent.

2.3 *Optimization details for meta C–H sequential bis-olefination:*



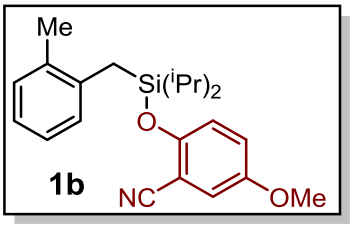
Entry	Deviation from standard condition	Yield	Conv.
1	$Pd(OAc)_2$/ Ac-Gly-OH (7.5 mol%/ 15 mol%)	63	78
2	$Pd(OAc)_2$/ Ac-Gly-OH (15 mol%/ 30 mol%)	77	--
3	Ag_2CO_3 (2.5 equiv.)	63	80
4	TFE (0.8 mL)	71	93
5	DCE (0.4 mL): HFIP (0.4 mL)	69	87

6	**none**	**76**	**94**
7	80 °C	75	98
8	48 h	76	95

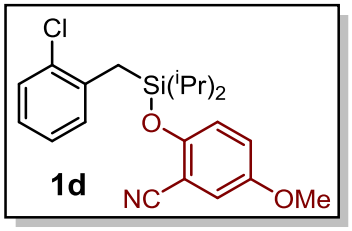
<u>General procedure C</u> for sequential C−H alkenylation of mono olefinated benzyl silane derivatives through remote *meta* C−H activation:

In a clean, oven–dried screw cap reaction tube containing magnetic stir–bar, substrate (0.1 mmol), $Pd(OAc)_2$ (10 mol%), N-Acetyl-glycine (20 mol%), AgOAc (2.5 equiv, 0.25 mmol) were weighed and the tube was tightly closed by screw cap fitted with rubber septum. The tube was evacuated and backfilled with nitrogen through standard Schlenk technique, and this sequence was repeated for three additional times. Then, under positive pressure of nitrogen, olefin (2 equiv, 0.2 mmol) and HFIP (0.8 mL) were added by syringes. This reaction tube was placed in a preheated oil bath at 70 °C to stir vigorously for 36 h. Then reaction mixture was cooled to room temperature and filtered through celite with aid of ethyl acetate (10 mL). Regioselectivity was determined from NMR of this crude reaction mixture filtrate. Then, this filtrate was concentrated under reduced pressure and purified by column chromatography through silica gel using petrolium ether/ethyl acetate as eluent.

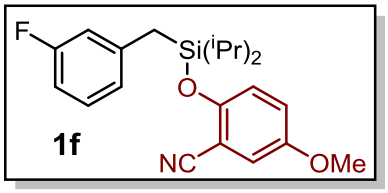
2.4 *Characterization data of benzyldiisopropylsilyl ether derivatives substrates:*



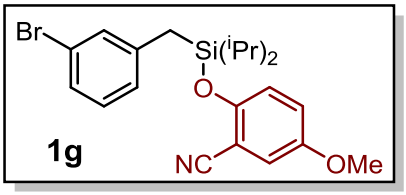
2-((diisopropyl(2-methylbenzyl)silyl)oxy)-5-methoxybenzonitrile (Table 1, entry 1b): General procedure A was followed. Colorless oil. Eluent: petrolium ether/ ethyl acetate (98/2 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 – 7.06 (m, 2H), 7.01 (q, *J* = 6.3 Hz, 2H), 6.93 (dd, *J* = 8.7, 3.2 Hz, 1H), 6.71 (dd, *J* = 9.1, 3.2 Hz, 1H), 5.94 (d, *J*= 8.7 Hz, 1H), 3.72 (s, 3H), 2.40 (s, 2H), 2.23 (s, 3H), 1.32 – 1.26 (m, 2H), 1.12– 1.08 (m, 6H), 1.04 – 1.01 (m, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.38, 151.97, 137.01, 135.81, 130.66, 129.27, 126.20, 125.09, 121.04, 120.32, 117.15, 116.50, 104.59, 56.00, 20.57, 18.12, 17.66, 17.40, 13.00; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{22}H_{30}NO_2Si$: 367.1968, found: 367.1966; **IR** (thin film) 687, 884, 937, 1039, 1154, 1280, 1468, 1591, 1616, 2229, 2869, 2948 cm^{-1}.



2-(((2-chlorobenzyl)diisopropylsilyl)oxy)-5-methoxybenzonitrile (Table 1, entry 1d): General procedure A was followed. Colorless oil. Eluent: petrolium ether/ ethyl acetate (99/1 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 - 7.25 (m, 2H), 7.11 (td, *J* = 7.5, 1.4 Hz, 1H), 7.05 – 6.99 (m, 1H), 6.97 (dd, *J* = 5.8, 2.9 Hz, 1H), 6.86 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.47 (d, *J* = 9.1 Hz, 1H), 3.75 (s, 3H), 2.59 (s, 2H), 1.35-1.29 (m, 2H), 1.09 – 1.04 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.53, 152.11, 136.76, 133.27, 130.88, 129.70, 127.00, 126.32, 121.16, 120.28, 117.13, 116.79, 104.88, 56.06, 18.80, 17.53, 17.40, 13.45; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{21}H_{27}ClNO_2Si$: 388.1550, found: 388.1549; **IR** (thin film) 680, 707, 758, 883, 935, 1036, 1154, 1232, 1280, 1443, 1493, 1572, 2228, 2868, 2947 cm^{-1}.

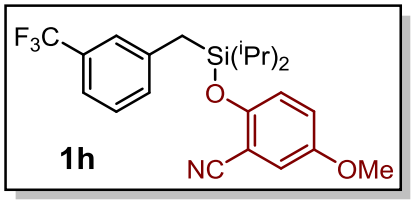


2-(((3-fluorobenzyl)diisopropylsilyl)oxy)-5-methoxybenzonitrile (Table 1, entry 1f): General procedure A was followed. Yellow oil. Eluent: petrolium ether/ ethyl acetate (99/1 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 – 7.10 (m, 1H), 6.98 (d, *J* = 3.2 Hz, 1H), 6.91 (dd, *J* = 9.1, 3.2 Hz, 2H), 6.83 – 6.73 (m, 2H), 6.53 (d, *J* = 9.1 Hz, 1H), 3.76 (s, 3H), 2.43 (s, 2H), 1.31 – 1.22 (m, 2H), 1.09 – 1.04 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.10, 162.15 (d, *J*= 245 Hz), 153.74, 152.10; 140.91, 140.85 (d, *J*= 7.7 Hz); 129.99, 129.92 (d, *J*= 8.7 Hz); 124.76, 124.73 (d, *J*= 2.6 Hz), 121.26, 120.59, 117.05, 116.83; 115.86, 115.69 (d, *J*= 21.4 Hz); 111.79, 111.62 (d, *J*= 21.0 Hz), 105.05, 56.07, 21.32, 17.52, 17.47, 12.99; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{21}H_{27}NO_2FSi$: 372.1795, found: 372.1805; **IR** (thin film) 785, 884, 937, 1039, 1157, 1237, 1280, 1498, 1615, 2229, 2869, 2948 cm^{-1}.

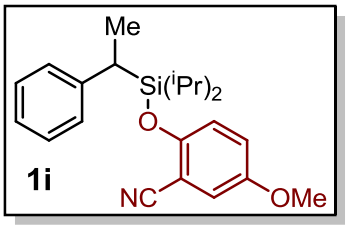


2-(((3-bromobenzyl)diisopropylsilyl)oxy)-5-methoxybenzonitrile (Table 1, entry 1g): General procedure A was followed. Light yellow oil. Eluent: petrolium ether/ ethyl acetate (98/2 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 1H), 7.17 – 7.13 (m, 1H), 7.13 – 7.10 (m, 2H), 6.97 (t, *J* = 3.8 Hz, 1H), 6.88 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.50 (d, *J* = 9.1 Hz, 1H), 3.75 (s, 3H), 2.46 (s, 2H), 1.29-1.25 (m, 2H), 1.07 – 1.02 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ

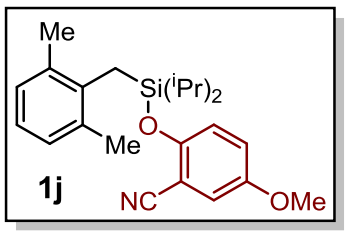
153.57, 152.05, 147.06, 131.51, 131.13, 126.84, 126.27, 121.17, 120.35, 120.27, 117.06, 116.77, 104.87, 56.03, 17.36, 17.28, 14.95, 13.24; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{25}H_{30}BrNO_4Si$: 515.1127, found: 515.1125.



2-((diisopropyl(3-(trifluoromethyl)benzyl)silyl)oxy)-5-methoxybenzonitrile (Table 1, entry 1h): General procedure A was followed. Colorless oil. Eluent: petrolium ether/ ethyl acetate (99/1 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 9.1, 4.5 Hz, 3H), 7.29 (s, 1H), 6.98 (t, *J* = 4.0 Hz, 1H), 6.89 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.52 (d, *J* = 9.1 Hz, 1H), 3.76 (s, 3H), 2.49 (s, 2H), 1.30 – 1.23 (m, 2H), 1.09 – 1.05 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.80, 151.96, 139.39, 132.35; 130. 97, 130.71 (q, *J*= 31.9 Hz); 127.61, 125.46, 123.28, 121.11 (q, *J*= 274 Hz); 125.52, 125.49 (q, *J*= 3.7 Hz); 121.70, 121.67 (*J*= 3.7 Hz), 129.03, 123. 54, 121.25, 120.49, 117.01, 116.88, 105.03, 56.05, 21.36, 17.52, 17.46, 13.05; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{22}H_{26}F_3NO_3NaSi$: 421.1683, found: 421.1685.

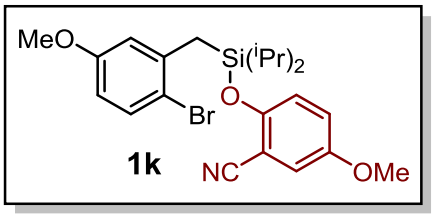


2-((diisopropyl(1-phenylethyl)silyl)oxy)-5-methoxybenzonitrile (Table 1, entry 1i): General procedure A was followed. Colorless oil. Eluent: petrolium ether/ ethyl acetate (98/2 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 4H), 7.14 – 7.08 (m, 1H), 6.99 (d, *J* = 3.2 Hz, 1H), 6.88 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.48 (d, *J* = 9.1 Hz, 1H), 3.77 (s, 3H), 2.71 – 2.61 (m, 1H), 1.57 (d, *J* = 7.6 Hz, 3H), 1.41 – 1.32 (m, 1H), 1.29-1.23 (m, 1H), 1.09-0.98 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.39, 152.46, 144.35, 128.52, 128.27, 125.24, 121.18, 120.41, 117.23, 116.70, 104.65, 56.03, 27.73, 18.04, 17.97, 17.81, 17.70, 16.30, 13.19, 13.01; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{22}H_{30}NO_2Si$: 368.2046, found: 368.2043.



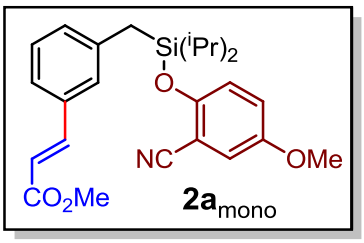
2-(((2,6-dimethylbenzyl)diisopropylsilyl)oxy)-5-methoxybenzonitrile (Table 1, entry 1j): General procedure A was followed. Colorless oil. Eluent: petrolium ether/ ethyl acetate (98/2

v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.94 – 6.88 (m, 4H), 6.68 (dd, *J* = 9.1, 3.2 Hz, 1H), 5.93 (d, *J* = 9.1 Hz, 1H), 3.72 (s, 3H), 2.42 (s, 2H), 2.28 (s, 6H), 1.29-1.23 (m, 2H), 1.18 – 1.00 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.26, 151.84, 136.13, 135.65, 128.38, 128.22, 124.70, 120.98, 119.95, 117.15, 116.48, 104.37, 55.99, 21.55, 17.65, 17.41, 15.71, 13.95; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{23}H_{32}NO_2Si$: 382.2124, found: 382.2123; **IR** (thin film) 687, 784, 883, 939, 1037, 1157, 1232, 1277, 1464, 1498, 1588, 1614, 2228, 2869, 2948 cm^{-1}.

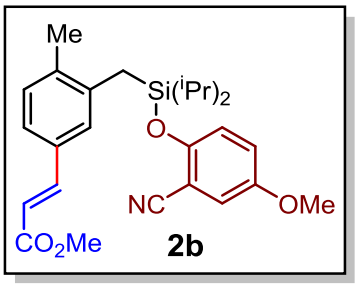


2-(((2-bromo-5-methoxybenzyl)diisopropylsilyl)oxy)-5-methoxybenzonitrile (Table 1, entry 1k): General procedure A was followed. Colorless oil. Eluent: petrolium ether/ ethyl acetate (97/3 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 3.2 Hz, 1H), 6.87 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.80 (d, *J* = 3.0 Hz, 1H), 6.54 – 6.49 (m, 2H), 3.75 (s, 3H), 3.71 (s, 3H), 2.60 (s, 2H), 1.39 – 1.31 (m, 2H), 1.11 – 1.05 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.04, 153.54, 152.10, 139.59, 133.49, 121.19, 120.30, 117.15, 116.74, 115.67, 114.92, 112.96, 104.83, 56.07, 55.62, 22.00, 17.58, 17.45, 13.47; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{22}H_{29}BrNO_3Si$: 462.1100, found: 462.1096.

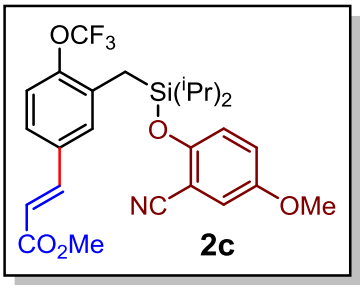
2.5 *Characterization data of meta mono-olefinated product:*



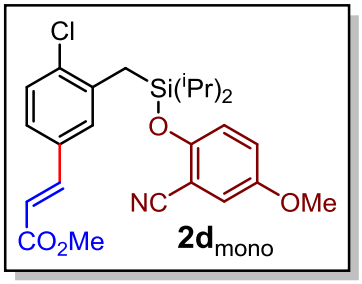
(E)-methyl-3-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)phenyl)acrylate (Table 1, entry $2a_{mono}$): Colorless oil. Mono/di= 7:1. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 16.0 Hz, 1H), 7.25 – 7.18 (m, 3H), 7.16 (s, 1H), 6.97 (d, *J* = 3.2 Hz, 1H), 6.88 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.52 (d, *J* = 9.1 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 2.44 (s, 2H), 1.30 – 1.20 (m, 2H), 1.09-1.04 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.75, 153.78, 152.21, 145.44, 139.17, 134.67, 130.99, 129.16, 128.65, 124.73, 121.35, 120.69, 117.70, 117.04, 116.94, 105.14, 56.09, 51.88, 21.17, 17.62, 17.51, 13.04; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{25}H_{33}NO_4Si$: 438.2107, found: 438.2094; **IR** (thin film) 687, 883, 1173, 1232, 1279, 1498, 1639, 1717, 2227, 2868, 2949 cm^{-1}.



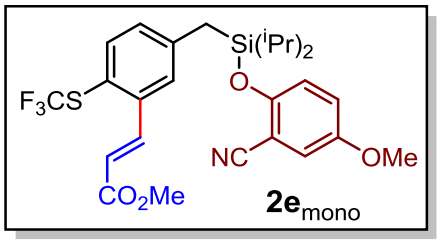
(E)-methyl-3-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-4-methylphenyl) acrylate (Table 1, entry 2b): Colorless oil. Exclusive mono. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 16.0 Hz, 1H), 7.23 (d, *J* = 1.5 Hz, 1H), 7.18 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 3.2 Hz, 1H), 6.73 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 6.07 (d, *J* = 9.1 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 2.41 (s, 2H), 2.26 (s, 3H), 1.31-1.27 (m, 2H), 1.18 – 1.00 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.90, 153.50, 151.79, 145.22, 138.76, 137.86, 132.31, 131.21, 129.13, 124.72, 121.05, 120.17, 117.05, 116.76, 116.66, 104.69, 56.00, 51.87, 20.68, 18.28, 17.65, 17.40, 13.15. **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{27}H_{36}NO_4Si$: 451.6300, found: 451.6298; **IR** (thin film) 678, 758, 882, 935, 1037, 1163, 1279, 1465, 1498, 1630, 1716, 2227, 2869, 2948 cm^{-1}.



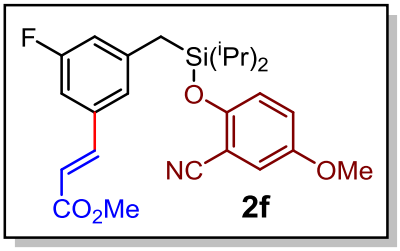
(E)-methyl 3-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-4-(trifluoro methoxy) phenyl)acrylate (Table 1, entry 2c): Colorless oil. Exclusive mono. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 1H), 7.23 – 7.18 (m, 2H), 7.17 – 7.13 (m, 1H), 6.99 – 6.95 (m, 1H), 6.90 – 6.85 (m, 1H), 6.53 – 6.50 (m, 1H), 6.36 – 6.31 (m, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 2.44 (s, 2H), 1.26 – 1.25 (m, 2H), 1.11 – 1.04 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.71, 153.73, 152.14, 145.21, 139.54, 139.05, 134.66, 131.07, 129.17, 128.69, 124.70, 121.28, 120.59, 117.79, 117.06, 116.79, 105.05, 56.07, 51.88, 29.91, 21.24, 17.52, 13.07; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{25}H_{30}ClNO_4Si$: $C_{26}H_{31}F_3NO_5Si$: 522.1924, found: 522.1934; **IR** (thin film) 626, 735, 824, 883, 1036, 1176, 1232, 1278, 1499, 1640, 1720, 2228, 2869, 2930 cm^{-1}.



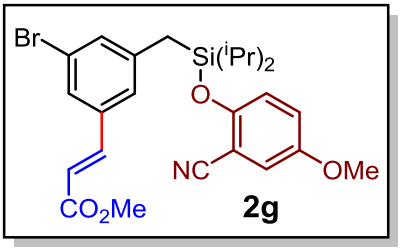
(E)-ethyl 3-(4-chloro-3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)phenyl) acrylate (Table 1, entry 2d$_{mono}$): Light yellow oil. Mono/di= 5.2. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 16.0 Hz, 1H), 7.36-7.34 (m, 2H), 7.18 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.97 (d, *J* = 3.2 Hz, 1H), 6.86 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.50 (d, *J* = 9.1 Hz, 1H), 6.33 – 6.28 (m, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 2.60 (s, 2H), 1.35 – 1.34 (m, 2H), 1.09-1.03 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.05, 153.66, 143.58, 141.77, 137.58, 135.12, 133.33, 132.22, 130.47, 126.84, 125.53, 121.22, 120.22, 118.91, 116.83, 104.98, 60.78, 56.06, 17.54, 17.42, 14.53, 13.55; **HRMS (*m/z*):** $[M + Na]^+$ calcd for $C_{25}H_{30}ClNO_4SiNa$: 494.1530, found: 494.1524; **IR** (thin film) 692, 758, 883, 1039, 1180, 1232, 1279, 1498, 1638, 1714, 2228, 2868, 2929 cm^{-1}.



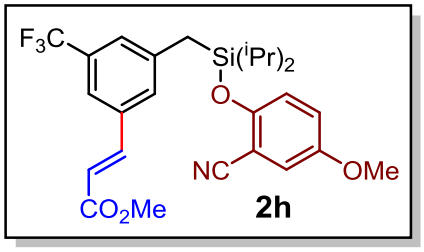
(E)-methyl 3-(5-(((2-cyano-4-methoxyphenoxy) diisopropylsilyl) methyl)-2-((trifluoro methyl)thio)phenyl)acrylate (Table 1, entry 2e$_{mono}$): Colorless oil. Mono/di= 12.5. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 16.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 1.6 Hz, 1H), 7.22 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.96 (d, *J* = 3.2 Hz, 1H), 6.85 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.45 (d, *J* = 9.1 Hz, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 2.49 (s, 2H), 1.29–1.24 (m, 2H), 1.11-1.09 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.01, 153.84, 151.78, 143.41, 141.98, 139.88, 139.20, 131.38, 130.95, 127.92, 121.20, 121.10, 120.33, 116.98, 116.84, 104.99, 55.98, 52.09, 21.66, 17.55, 17.44, 13.07; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{26}H_{31}F_3NO_4SSi$: 538.1695, found: 538.1701; **IR** (thin film) 760, 883, 935, 1040, 1112, 1154, 1223, 1278, 1322, 1496, 1640, 1721, 2228, 2869, 2949 cm^{-1}.



(E)-methyl 3-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-5-fluorophenyl) acrylate (Table 1, entry 2f): Light yellow oil. Exclusive mono. Eluent: petrolium ether/ ethyl acetate (94/6 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 16.0 Hz, 1H), 6.98 (d, *J* = 3.3 Hz, 2H), 6.95 – 6.87 (m, 2H), 6.84 (d, *J* = 9.6 Hz, 1H), 6.57 (d, *J* = 9.1 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 2.44 (s, 2H), 1.26 (m, 2H), 1.11-1.04 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.34; 164.44, 161.99 (*J* = 247 Hz), 153.85, 151.95, 143.91; 141.71, 141.63 (*J* = 8.1 Hz); 136.52, 136.44 (*J* = 8.1 Hz), 124.91, 124.89 (*J* = 2.0 Hz), 121.33, 120.51, 119.16; 117.72, 117.50 (*J* = 22.2 Hz), 117.00, 116.81; 110.85, 110.63 (*J* = 22.2 Hz), 105.11, 56.05, 52.00, 21.40, 17.55, 17.48, 13.08; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{25}H_{31}FNO_4Si$: 456.2006, found: 456.2017; **IR** (thin film) 673, 734, 883, 1037, 1174, 1232, 1280, 1498, 1640, 1716, 2228, 2868, 2950 cm^{-1}.

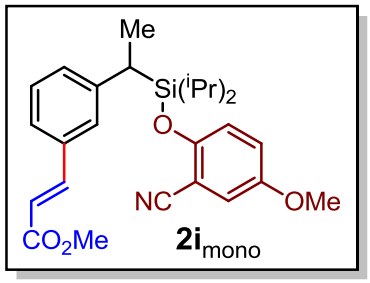


(E)-methyl 3-(3-bromo-5-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)phenyl) acrylate (Table 1, entry 2g): Yellow oil. Exclusive mono. Eluent: petrolium ether/ ethyl acetate (94/6 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 16.0 Hz, 1H), 7.36 (d, *J* = 2.1 Hz, 1H), 7.27-7.25 (m, 1H), 7.16 (dd, *J* = 8.5, 1.6 Hz, 1H), 6.97 (d, *J* = 3.2 Hz, 1H), 6.88 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.53 (d, *J* = 9.1 Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 3.80 (d, *J* = 8.5 Hz, 3H), 3.74 (s, 3H), 2.46 (s, 2H), 1.30-1.24 (m, 2H), 1.09 – 1.03 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.40, 153.70, 151.90, 148.15, 143.52, 132.83, 131.77, 131.11, 125.92, 121.27, 120.33, 120.19, 118.68, 116.97, 116.76, 104.96, 56.01, 51.97, 17.37, 17.29, 15.19, 13.35; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{25}H_{30}BrNO_4Si$: 515.1127, found: 515.1135; **IR** (thin film) 671,762, 884, 1038, 1172, 1252, 1278, 1499, 1641, 1720, 2228, 2870, 2950 cm^{-1}.

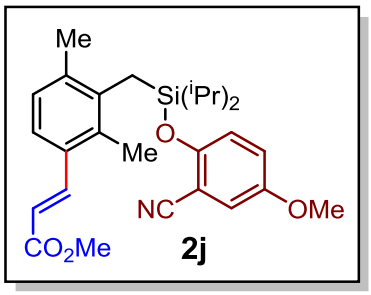


(E)-methyl 3-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-5-(trifluoromethyl) phenyl)acrylate (Table 1, entry 2h): Yellowish oil. Exclusive mono. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 16.1 Hz, 1H), 7.46 (s, 1H), 7.40 (s, 1H), 7.31 (s, 1H), 6.97 (d, *J* = 3.2 Hz, 1H), 6.89 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.55 (d, *J* = 9.1 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 2.50 (s, 2H), 1.29 – 1.22 (m, 2H), 1.10-1.04 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.18, 153.87, 151.79, 143.43,

140.50, 135.36; 132.07, 131.75, 131.63, 131.43 (J = 32.3 Hz); 131.11; 127.06, 127.03, 126.99, 126.96 (J = 32.3 Hz); 128.00, 125.29, 122.58, 119.87 (J = 273.7 Hz); 121.18, 121.14, 121.10, 121.07 (J = 4.0 Hz), 121.32, 120.41, 119.71, 116.95, 116.79, 105.06, 77.55, 77.23, 76.91, 56.01, 52.07, 21.38, 17.53, 17.46, 13.10; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{26}H_{31}F_3NO_4Si$: 506.1974, found: 506.1987; **IR** (thin film) 670, 755, 883, 1036, 1169, 1233, 1270, 1499, 1634, 1720, 2228, 2863, 2946 cm^{-1}.

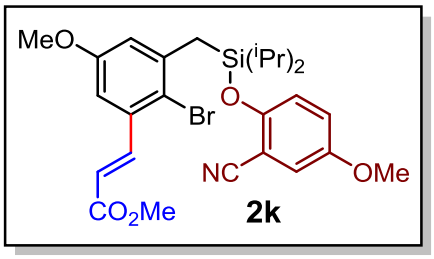


(E)-methyl 3-(3-(1-((2-cyano-4-methoxyphenoxy)diisopropylsilyl)ethyl)phenyl)acrylate (Table 1, entry 2i$_{mono}$): Colorless oil. Mono/di= 9.3. Eluent: petrolium ether/ ethyl acetate (94/6 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, J = 16.0 Hz, 1H), 7.32-7.24 (m, 4H), 6.98 (d, J = 3.2 Hz, 1H), 6.86 (dd, J = 9.1, 3.2 Hz, 1H), 6.50 (d, J = 9.1 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 2.66 (m, 1H), 1.57 (d, J = 7.6 Hz, 3H), 1.42 – 1.33 (m, 1H), 1.30-1.24 (m, 1H), 1.13 – 1.01 (m, 9H), 0.97 (m, J = 7.5 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.66, 153.53, 152.19, 145.20, 145.18, 134.45, 130.40, 129.06, 128.11, 125.00, 121.40, 120.24, 117.64, 117.06, 116.78, 104.67, 55.93, 51.86, 27.58, 18.03, 17.95, 17.76, 17.63, 16.14, 13.19, 13.07; **HRMS** (ESI): calcd. for $C_{26}H_{34}NO_4Si$: 452.2257, found: 452.2254; **IR** (thin film) 687, 823, 883, 935, 1038, 1174, 1231, 1280, 1320, 1464, 1498, 1638, 1718, 2227, 2870, 2950 cm^{-1}.

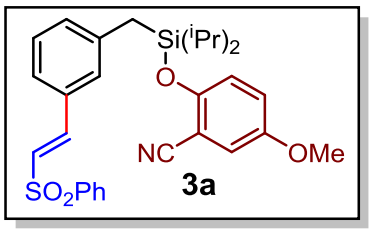


(E)-methyl 3-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-2,4-dimethyl phenyl) acrylate (Table 1, entry 2j): Colorless oil. Exclusive mono. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 15.8 Hz, 1H), 7.18 (d, J = 7.9 Hz, 1H), 6.92 (dd, J = 10.1, 5.5 Hz, 2H), 6.66 (dd, J = 9.1, 3.2 Hz, 1H), 6.21 (d, J = 15.7 Hz, 1H), 5.99 (d, J = 9.1 Hz, 1H), 3.79 (s, 3H), 3.71 (d, J = 3.1 Hz, 3H), 2.47 (d, J = 10.0 Hz, 2H), 2.36 – 2.29 (m, 6H), 1.27 – 1.23 (m, 2H), 1.16 (d, J = 7.2 Hz, 6H), 1.03 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.80, 153.39, 151.69, 144.32, 138.11, 137.06, 135.03, 132.36, 128.49, 123.47,

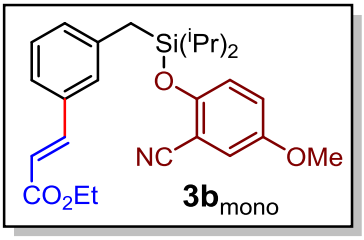
120.99, 119.72, 118.65, 117.05, 116.54, 104.41, 56.00, 51.81, 22.18, 17.64, 17.43, 17.13, 16.22, 14.09; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{27}H_{36}NO_4Si$: 466.2414, found: 466.2437; **IR** (thin film) 678, 758, 882, 935, 1037, 1163, 1279, 1465, 1498, 1630, 1716, 2227, 2869, 2948 cm^{-1}.



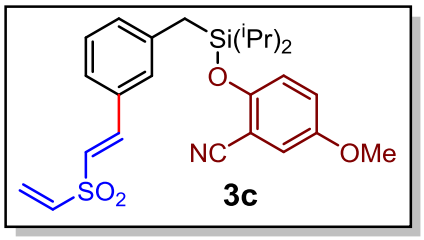
methyl (E)-3-(2-bromo-3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-5-methoxyphenyl)acrylate (Table 1, entry 2k): Colorless oil. Exclusive mono. Eluent: petrolium ether/ ethyl acetate (93/7v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 15.9 Hz, 1H), 6.94 (d, *J* = 3.2 Hz, 1H), 6.87 (d, *J* = 3.0 Hz, 1H), 6.85 – 6.80 (m, 2H), 6.49 (d, *J* = 9.1 Hz, 1H), 6.25 (d, *J* = 15.8 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 2.68 (s, 2H), 1.40 – 1.31 (m, 2H), 1.11 – 1.05 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.05, 158.54, 153.54, 151.90, 144.92, 141.09, 136.28, 121.04, 120.81, 120.13, 117.81, 117.38, 117.12, 116.68, 110.50, 104.82, 77.48, 77.23, 76.98, 56.02, 55.71, 52.03, 22.69, 17.58, 17.43, 13.57; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{26}H_{33}BrNO_5Si$: 546.1311, found: 546.1317.



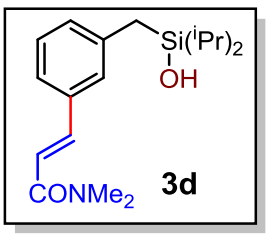
(E)-2-((diisopropyl(3-(2-(phenylsulfonyl)vinyl)benzyl)silyl)oxy)-5-methoxybenzonitrile (Table 2, entry 3a): Yellowish oil. Mono/di= 18.5. Eluent: petrolium ether/ ethyl acetate (90/10 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.55 (s, 4H), 7.20 (s, 4H), 6.94 (s, 1H), 6.90 – 6.85 (m, 1H), 6.79 (d, *J* = 15.4 Hz, 1H), 6.55 (s, 1H), 3.76 (s, 3H), 2.42 (s, 2H), 1.28 – 1.21 (m, 2H), 1.10-1.03 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.71, 152.03, 142.83, 140.96, 139.45, 133.53, 132.61, 131.93, 129.51, 129.30, 129.15, 127.85, 127.14, 125.19, 121.26, 120.38, 117.08, 116.81, 104.92, 56.09, 21.07, 17.57, 17.49, 13.07; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{29}H_{34}NO_4SSi$: 520.1978, found: 520.1987; **IR** (thin film) 624, 800, 893, 933, 1022, 1146, 1234, 1261, 1278, 1497, 1646, 2322, 2866, 2918 cm^{-1}.



(E)-ethyl 3-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)phenyl)acrylate (Table 2, entry 3b$_{mono}$): Colorless oil. Mono: di= 7:1. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 16.0 Hz, 1H), 7.28 (d, *J* = 4.2 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.17 (d, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 3.0 Hz, 1H), 6.90 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.54 (d, *J* = 9.1 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 2.46 (s, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.31 – 1.26 (m, 2H), 1.11-1.07 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.24, 153.71, 152.11, 144.89, 139.00, 134.72, 130.96, 129.13, 128.67, 124.63, 121.23, 120.57, 118.24, 117.03, 116.80, 105.03, 60.65, 56.02, 21.18, 17.56, 17.50, 14.53, 13.04; **HRMS (*m*/*z*):** $[M + Na]^+$ calcd for $C_{26}H_{33}NO_4SiNa$: 474.2077, found: 474.2064; **IR** (thin film) 670, 757, 884, 1037, 1209, 1232, 1280, 1499, 1640, 1720, 2227, 2870, 2946 cm^{-1}.

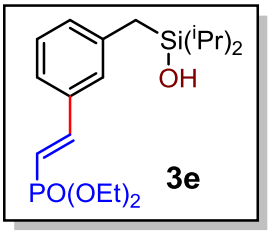


(E)-2-((diisopropyl(3-(2-(vinylsulfonyl)vinyl)benzyl)silyl)oxy)-5-methoxybenzonitrile (Table 2, entry 3c): Yellowish oil. Mono/di= 14.2. Eluent: petrolium ether/ ethyl acetate (90/10 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.48 (m, 1H), 7.26 (m, 4H), 7.08 – 6.88 (m, 2H), 6.80 – 6.66 (m, 2H), 6.61 (s, 1H), 6.51 (d, *J* = 8.5 Hz, 1H), 6.14 (d, *J* = 9.4 Hz, 1H), 3.80 (s, 3H), 2.49 (s, 2H), 1.33-1.27 (m, 2H), 1.11-1.07 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.79, 152.06, 144.82, 139.53, 137.97, 132.61, 132.16, 129.37, 129.11, 128.73, 125.34, 125.30, 121.33, 120.42, 116.86, 115.65, 104.97, 56.11, 21.11, 17.57, 17.52, 13.13; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{25}H_{32}NO_4SSi$: 470.1821, found: 470.1832; **IR** (thin film) 541, 691, 757, 848, 883, 1036, 1129, 1154, 1232, 1281, 1308, 1498, 1598, 1615, 2228, 2868, 2946 cm^{-1}.

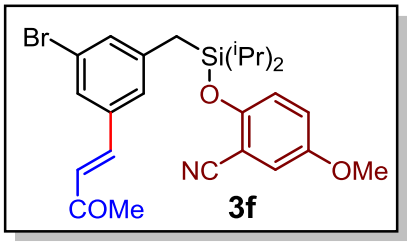


(E)-3-(3-((hydroxydiisopropylsilyl)methyl)phenyl)-N,N-dimethylacrylamide (Table 2, entry 3d): Colorless oil. Exclusive mono. Eluent: petrolium ether/ ethyl acetate (75/25 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 15.4 Hz, 1H), 7.28 (s, 1H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.10 (d, *J* =

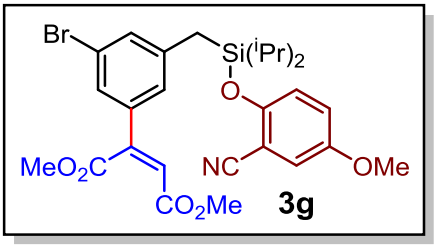
7.4 Hz, 1H), 6.85 (d, *J* = 15.4 Hz, 1H), 3.11 (d, *J* = 45.6 Hz, 6H), 2.22 (s, 2H), 1.28-1.21 (m, 2H), 1.02-10.96 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.07, 142.89, 140.28, 135.63, 129.99, 128.97, 128.37, 123.79, 117.37, 29.90, 21.67, 17.49, 17.44, 12.93; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{18}H_{30}NO_2Si$: 320.2046, found: 320.2051; **IR** (thin film) 685, 760, 861, 883, 1146, 1226, 1258, 1399, 1463, 1489, 1611, 1648, 2864, 2926 cm^{-1}.



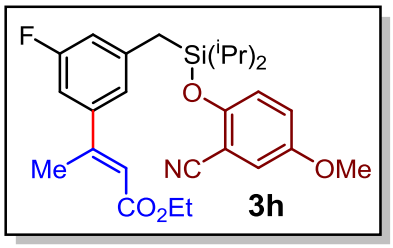
(E)-diethyl 3-((hydroxydiisopropylsilyl)methyl)styrylphosphonate (Table 2, entry 3e): Colorless oil. Exclusive mono. Eluent: petrolium ether/ ethyl acetate (80/20 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 17.5 Hz, 1H), 7.42 (d, *J* = 17.5 Hz, 1H), 7.24 (d, *J* = 4.8 Hz, 2H), 7.13 (d, *J* = 2.1 Hz, 1H), 6.21 (t, *J* = 17.7 Hz, 1H), 4.18 – 4.07 (m, 4H), 2.21 (s, 2H), 1.35 (t, *J* = 7.1 Hz, 6H), 1.03 – 0.96 (m, 14H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.39, 149.33, 140.49, 135.21, 134.98, 130.72, 129.03, 128.19, 123.82, 114.61, 112.70, 62.10, 62.04, 21.65, 17.48, 17.43, 16.64, 16.57, 12.92; **HRMS** (ESI): calcd. for $C_{19}H_{34}O_4PSi$: 385.1886, found: 385.1888; **IR** (thin film) 527, 571, 607, 691, 853, 929, 1020, 1112, 1292, 1375, 1636, 1708, 1781 cm^{-1}.



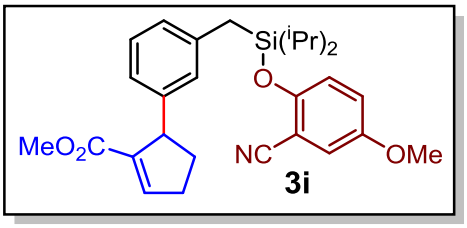
(E)-2-(((3-bromo-5-(3-oxobut-1-en-1-yl)benzyl)diisopropylsilyl)oxy)-5-methoxybenzonitrile (Table 2, entry 3f) : Light yellow oil. Exclusive mono. Eluent: petrolium ether/ ethyl acetate (94/6 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 2.2 Hz, 1H), 7.42 (d, *J* = 16.3 Hz, 1H), 7.30 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.18 (dt, *J* = 8.6, 1.8 Hz, 1H), 6.97 (d, *J* = 3.1 Hz, 1H), 6.90 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.60 (d, *J* = 5.3 Hz, 1H), 6.57 (d, *J* = 1.8 Hz, 1H), 3.76 (s, 3H), 2.46 (s, 2H), 2.37 (s, 3H), 1.31-1.25 (m, 2H), 1.09-1.04 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.67, 153.70, 151.96, 142.24, 132.94, 131.79, 131.69, 127.87, 125.87, 121.33, 120.37, 120.11, 117.14, 116.81, 115.40, 104.84, 56.06, 27.77, 17.40, 17.28, 14.92, 13.41; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{25}H_{31}BrNO_3Si$: 500.1257, found: 500.1269; **IR** (thin film) 760, 825, 884, 1037, 1174, 1251, 1278, 1499, 1614, 1671, 2228, 2870, 2947 cm^{-1}.



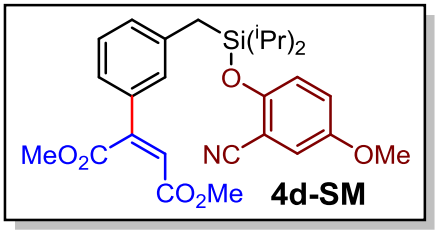
Dimethyl 2-(3-bromo-5-(((2-cyano-4 methoxyphenoxy)diisopropylsilyl)methyl)phenyl)maleate (Table 2, entry 3g): Colorless oil. Exclusive mono. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 2.2 Hz, 1H), 7.19 (dd, *J* = 10.1, 1.9 Hz, 2H), 6.97 (d, *J* = 3.2 Hz, 1H), 6.88 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.49 (d, *J* = 9.1 Hz, 1H), 6.19 (s, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.75 (s, 3H), 2.47 (s, 2H), 1.26 – 1.24 (m, 2H), 1.09 – 1.03 (m, 12H); **^{13}C NMR** (126 MHz, CDCl3) δ 168.17, 165.47, 153.75, 151.80, 148.516, 147.64, 132.690, 132.15, 131.60, 129.77, 124.94, 121.21, 120.37, 120.22, 117.96, 116.92, 104.99, 56.03, 52.96, 52.33, 17.37, 17.31, 15.47, 13.33; **HRMS (*m/z*):** $[M + Na]^+$ calcd for $C_{27}H_{32}BrNNaO_6Si$: 596.1080, found: 596.1091; **IR** (thin film) 737, 885, 912, 1036, 1156, 1156, 1255, 1499, 1628, 1738, 2227, 2872, 2953 cm^{-1}.



methyl (E)-3-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-5-fluorophenyl)but-2-enoate (Table 2, entry 3h): Colorless oil. Exclusive mono. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.97 (d, *J* = 3.0 Hz, 1H), 6.93 (s, 1H), 6.91 – 6.85 (m, 2H), 6.81 (d, *J* = 9.5 Hz, 1H), 6.53 (d, *J* = 9.1 Hz, 1H), 6.00 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 2.45 (d, *J* = 3.4 Hz, 5H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.26 – 1.22 (m, 2H), 1.10-1.06 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.83, 153.80, 141.12, 122.76, 122.75, 121.26, 120.47, 119.06, 118.01, 116.98, 116.81, 116.24, 116.07, 109.98, 109.80, 105.07, 60.18, 56.05, 21.55, 18.02, 17.56, 17.49, 14.53, 13.05; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{27}H_{35}FNO_4Si$: 484.2319, found: 484.2324; **IR** (thin film) 757, 883, 1037, 1170, 1233, 1274, 1499, 1640, 1720, 2228, 2870, 2946 cm^{-1}.

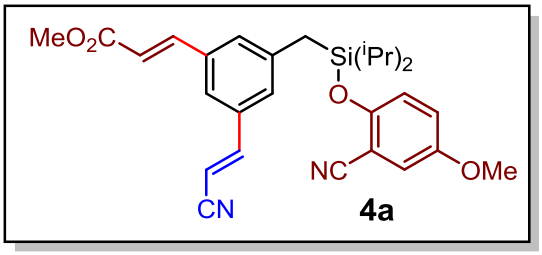


(R)-methyl 5-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)phenyl)cyclopent-1-enecarboxylate (Table 2, entry 3i): Light yellow oil. Exclusive mono. Eluent: petrolium ether/ ethyl acetate (94/6 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 (t, *J* = 7.6 Hz, 1H), 6.97 – 6.85 (m, 6H), 6.38 (d, *J* = 9.1 Hz, 1H), 4.08 – 4.01 (m, 1H), 3.75 (s, 3H), 3.56 (s, 3H), 2.55 – 2.43 (m, 2H), 2.39 (s, 2H), 1.80 (dd, *J* = 10.5, 6.5 Hz, 1H), 1.28 – 1.17 (m, 3H), 1.07 – 1.00 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.35, 153.50, 152.29, 145.50, 145.13, 139.27, 138.13, 128.79, 127.33, 126.98, 123.77, 121.26, 120.73, 117.15, 116.65, 104.81, 56.04, 51.47, 50.13, 34.27, 32.37, 21.23, 17.52, 17.49, 17.44, 12.84, 12.79; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{28}H_{36}NO_3Si$: 462.2464, found: 462.2471; **IR** (thin film) 710, 765, 883, 1036, 1095, 1232, 1281, 1498, 1598, 1718, 2227, 2868, 2946 cm^{-1}.



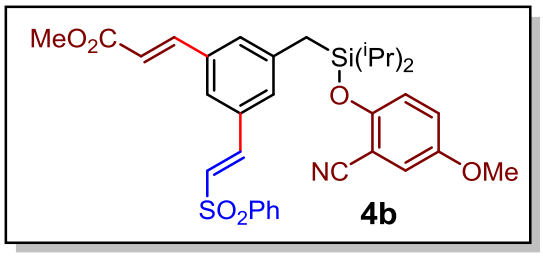
Dimethyl 2-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)phenyl)maleate (Table 3, entry 4d-SM): Colorless oil. Mono: di= 8.5. Eluent: petrolium ether/ ethyl acetate (94/6 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (ddd, *J* = 5.4, 2.9, 1.5 Hz, 3H), 7.18 (s, 1H), 6.97 (d, *J* = 3.2 Hz, 1H), 6.88 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.49 (d, *J* = 9.1 Hz, 1H), 6.20 (s, 1H), 3.90 (s, 3H), 3.78 (s, 3H), 3.75 (s, 3H), 2.45 (s, 2H), 1.27-1.23 (m, 2H), 1.08 – 1.04 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.68, 153.72, 152.02, 149.23, 139.38, 133.41, 131.39, 129.34, 129.24, 127.17, 123.42, 121.22, 120.54, 117.04, 116.95, 116.88, 104.99, 56.02, 52.83, 52.22, 21.36, 17.55, 17.49, 13.00; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{27}H_{33}NNaO_6Si$:518.1975, found: 518.1987; **IR** (thin film) 668, 758, 824, 883, 1035, 1167, 1230, 1280, 1351, 1496, 1623, 1738, 2228, 2869, 2950 cm^{-1}.

2.6 *Characterization data of sequential meta bis-olefinated product:*

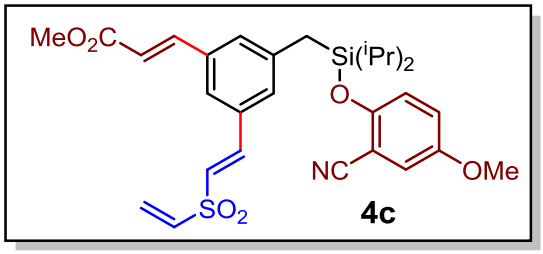


(E)-methyl 3-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-5-((E)-2-cyanovinyl)phenyl)acrylate (Table 3, entry 4a): Yellowish oil. Eluent: petrolium ether/ ethyl acetate (90/10 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (t, *J* = 9.9 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 6.98 (d, *J* = 3.1 Hz, 1H), 6.91 (dt, *J* = 9.1, 5.0 Hz, 1H), 6.60 (d, *J* = 9.1

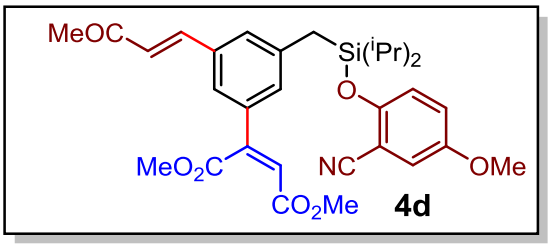
Hz, 1H), 6.39 (t, *J* = 11.5 Hz, 1H), 5.89 – 5.83 (m, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 2.45 (s, 2H), 1.29 – 1.23 (m, 2H), 1.09-1.04 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.34, 153.86, 151.95, 150.07, 143.87, 140.42, 135.46, 134.44, 130.93, 129.36, 123.73, 121.46, 120.37, 119.20, 118.16, 117.08, 116.68, 104.95, 97.47, 56.06, 52.08, 21.08, 17.60, 17.51, 13.20; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{28}H_{33}N_2O_4Si$: 489.2210 found: 489.2219; **IR** (thin film) 758, 884, 1037, 1170, 1233, 1280, 1498, 1640, 1718, 2219, 2868, 2949 cm^{-1}.



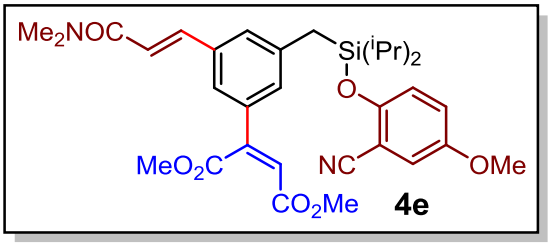
(E)-methyl 3-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-5-((E)-2-(phenylsulfonyl)vinyl)phenyl)acrylate (Table 3, entry 4b): Colorless oil. Eluent: petrolium ether/ ethyl acetate (85/15 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (dt, *J* = 3.5, 2.4 Hz, 2H), 7.65 – 7.52 (m, 5H), 7.32 (s, 1H), 7.27 (s, 1H), 7.24 (s, 1H), 6.95 – 6.82 (m, 3H), 6.57 (d, *J* = 9.1 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.43 (s, 2H), 1.28–1.19 (m, 2H), 1.07-1.03 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.25, 153.81, 151.87, 143.81, 141.78, 140.72, 140.36, 135.44, 133.64, 133.33, 130.95, 130.59, 129.55, 128.34, 127.91, 124.65, 121.30, 120.30, 119.16, 117.01, 116.81, 104.96, 56.05, 51.99, 21.08, 17.57, 17.48, 13.14; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{33}H_{38}NO_6SSi$: 604.2189, found: 604.2191; **IR** (thin film) 539, 756, 883, 1036, 1147, 1233, 1280, 1498, 1589, 1715, 2228, 2868, 2949 cm^{-1}.



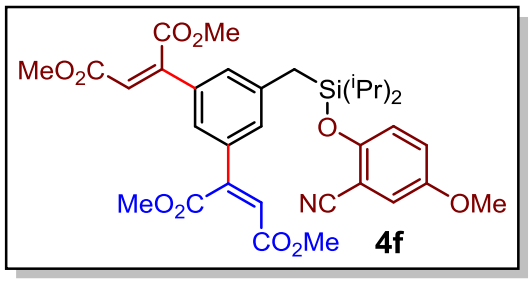
(E)-methyl 3-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-5-((E)-2-(vinylsulfonyl)vinyl)phenyl)acrylate (Table 3, entry 4c): Light yellow oil. Eluent: petrolium ether/ ethyl acetate (85/15 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 29.3, 15.8 Hz, 2H), 7.36 – 7.27 (m, 2H), 6.98 (d, *J* = 3.2 Hz, 1H), 6.90 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.76 (d, *J* = 15.5 Hz, 1H), 6.67 (dd, *J* = 16.6, 9.8 Hz, 1H), 6.60 (d, *J* = 9.1 Hz, 1H), 6.47 (d, *J* = 16.6 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.11 (d, *J* = 9.8 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 2.46 (s, 2H), 1.28-1.24 (m, 2H), 1.09-1.05 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.27, 153.88, 151.93, 150.63, 143.80, 140.47, 137.82, 135.56, 133.34, 131.15, 130.52, 129.13, 126.58, 124.83, 121.39, 120.36, 119.29, 117.05, 116.85, 105.03, 56.08, 52.04, 21.14, 17.61, 17.52, 13.22; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{29}H_{36}NO_6SSi$: 554.2033, found: 554.2040; **IR** (thin film) 671, 755, 884, 1037, 1170, 1233, 1278, 1499, 1639, 1715, 2228, 2860, 2946, 3747 cm^{-1}.



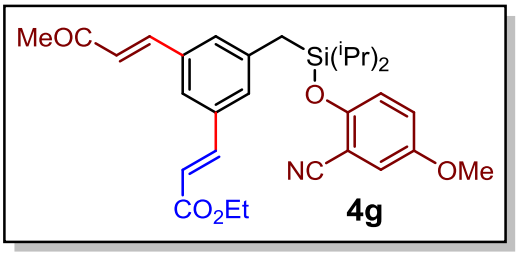
Dimethyl 2-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-5-((E)-3-oxobut-1-en-1-yl)phenyl)maleate (Table 3, entry 4d): Yellowish oil. Eluent: petrolium ether/ ethyl acetate (90/10 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 16.0 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.20 (s, 1H), 6.96 (d, *J* = 3.1 Hz, 1H), 6.88 (ddd, *J* = 9.1, 3.2, 0.9 Hz, 1H), 6.53 (d, *J* = 9.0 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.22 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.74 (s, 3H), 2.46 (s, 2H), 1.28-1.25 (m, 2H), 1.09 – 1.06 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.20, 167.30, 165.46, 153.80, 151.85, 148.35, 143.95, 140.29, 135.48, 134.17, 130.34, 128.76, 123.10, 121.28, 120.46, 119.17, 118.06, 116.98, 116.80, 105.03, 55.98, 52.99, 52.33, 52.02, 21.36, 17.56, 17.49, 13.05; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{31}H_{38}NO_7Si$: 563.2339, found: 563.2334.



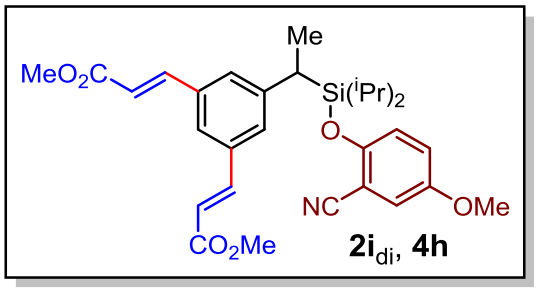
Dimethyl 2-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-5-((E)-3-(dimethylamino)-3-oxoprop-1-en-1-yl)phenyl)maleate (Table 3, entry 4e): Colorless oil. Eluent: petrolium ether/ ethyl acetate (70/30 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 1H), 7.33 (s, 2H), 7.20 (s, 1H), 7.03 – 6.99 (m, 1H), 6.94 (t, *J* = 6.1 Hz, 2H), 6.89 – 6.82 (m, 1H), 6.30 (s, 1H), 3.93 (s, 3H), 3.79 (s, 3H), 3.75 (s, 3H), 3.19 (s, 3H), 3.08 (s, 3H), 2.23 (s, 2H), 1.30-1.23 (m, 2H), 1.01 – 0.97 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 182.88, 168.47, 165.57, 150.69, 148.82, 136.25, 133.97, 128.15, 125.55, 123.23, 122.66, 122.31, 122.12, 118.06, 117.91, 117.89, 116.78, 116.54, 115.69, 104.49, 56.14, 53.04, 52.34, 32.94, 29.91, 21.92, 17.51, 17.46, 12.94; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{32}H_{41}N_2O_7Si$: 593.2683, found: 593.2691; **IR** (thin film) 671, 757, 883, 1037, 1169, 1235, 1278, 1499, 1639, 1715, 2228, 2860, 2947 cm^{-1}.



tetramethyl 2,2'-(5-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-1,3-phenylene)dimaleate (Table 3, entry 4f): Yellowish oil. Eluent: petrolium ether/ ethyl acetate (90/10 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H), 7.23 (d, *J* = 1.6 Hz, 2H), 6.96 (d, *J* = 3.2 Hz, 1H), 6.88 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.50 (d, *J* = 9.1 Hz, 1H), 6.21 (s, 2H), 3.90 (s, 6H), 3.79 (s, 6H), 3.75 (s, 3H), 2.47 (s, 2H), 1.29-1.24 (m, 2H), 1.09-1.04 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.02, 165.42, 153.87, 151.76, 150.34, 148.11, 140.61, 134.48, 129.12, 121.68, 121.23, 120.47, 118.60, 116.95, 107.54, 105.06, 102.75, 55.99, 52.98, 52.35, 21.59, 17.54, 17.48, 13.01; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{33}H_{40}NO_{10}Si$: 638.2421, found: 838.2430; **IR** (thin film) 715, 758, 884, 1037, 1170, 1232, 1280, 1499, 1650, 1730, 2228, 2869, 2946 cm^{-1}.

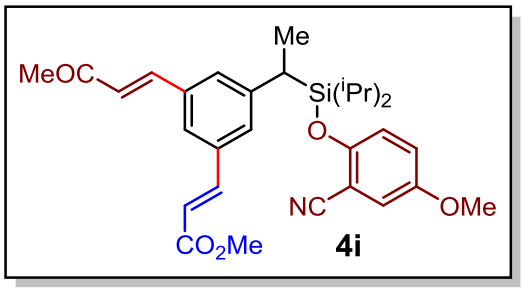


(E)-ethyl 3-(3-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-5-((E)-3-oxobut-1-en-1-yl)phenyl)acrylate (Table 3, entry 4g): Colorless oil. Eluent: petrolium ether/ ethyl acetate (90/10 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 1H), 7.45 – 7.38 (m, 2H), 7.31 – 7.29 (m, 1H), 7.25 – 7.23 (m, 1H), 6.99 – 6.96 (m, 1H), 6.91 – 6.85 (m, 1H), 6.67 – 6.61 (m, 1H), 6.60 – 6.55 (m, 1H), 6.41 – 6.33 (m, 1H), 4.31 – 4.22 (q, *J*= 7.4 Hz, 2H), 3.75 (s, 3H), 2.46 (s, 2H), 2.38 (s, 3H), 1.33 (t, *J*= 7.4 Hz, 3H), 1.29 – 1.23 (m, 2H), 1.10-1,05 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.55, 167.00, 153.82, 152.01, 143.95, 142.88, 140.04, 135.44, 130.48, 130.37, 127.91, 124.75, 124.43, 121.35, 120.44, 119.36, 117.09, 116.82, 105.04, 60.87, 56.06, 27.88, 21.11, 17.63, 17.56, 14.55, 13.20; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{30}H_{38}NO_5Si$: 520.2519, found: 520.2524; **IR** (thin film) 668, 757, 883, 1037, 1180, 1233, 1279, 1498, 1592, 1669, 1709, 2228, 2868, 2948 cm^{-1}.

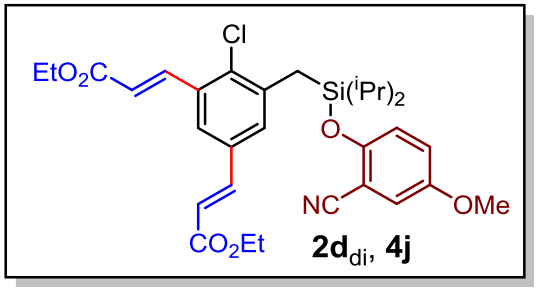


(2E,2'E)-dimethyl 3,3'-(5-(1-((2-cyano-4-methoxyphenoxy)diisopropylsilyl)ethyl)-1,3-phenylene)diacrylate (Table 3, entry 4h): Yellowish oil. Eluent: petrolium ether/ ethyl acetate (90/10 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 12.2 Hz, 2H), 7.39 (s, 1H), 7.34 (s, 2H), 7.00 – 6.94 (m, 1H), 6.85 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.51 (d, *J* = 7.9 Hz, 1H), 6.38 (d, *J* = 10.5 Hz, 2H), 3.80 (s, 6H), 3.74 (s, 3H), 2.68 (q, *J* = 7.5 Hz, 1H), 1.58 (d, *J* = 7.5 Hz, 3H), 1.40 – 1.32

(m, 1H), 1.28 – 1.22 (m, 1H), 1.11 – 1.06 (m, 6H), 1.04 (d, *J* = 7.4 Hz, 3H), 0.97 (d, *J* = 7.5 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.42, 153.59, 152.10, 146.14, 144.35, 135.14, 129.52, 124.69, 121.27, 120.10, 118.73, 117.08, 116.73, 104.73, 55.96, 51.96, 27.68, 18.09, 18.00, 17.80, 17.65, 16.08, 13.25, 13.18; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{30}H_{38}NO_6Si$: 535.2468, found: 535.2471; **IR** (thin film) 683, 757, 884, 983, 1037, 1168, 1233, 1281, 1498, 1638, 1719, 2228, 2870, 2950 cm^{-1}.

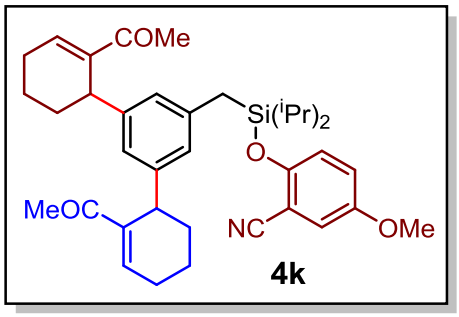


(E)-methyl 3-(3-(1-((2-cyano-4-methoxyphenoxy)diisopropylsilyl)ethyl)-5-((E)-3-oxobut-1-en-1-yl)phenyl)acrylate (Table 3, entry 4i): Colorless oil. Eluent: petrolium ether/ ethyl acetate (90/10 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 16.0 Hz, 1H), 7.45 (dd, *J* = 11.9, 8.9 Hz, 3H), 7.36 (s, 1H), 6.99 (d, *J* = 3.2 Hz, 1H), 6.87 (s, 1H), 6.68 (d, *J* = 16.3 Hz, 1H), 6.55 (d, *J* = 9.1 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 2.73 – 2.63 (m, 1H), 2.39 (s, 3H), 1.56 (d, *J* = 7.4 Hz, 3H), 1.40-1.33 (m, 1H), 1.29-1.23 (m, 1H), 1.10 (m, 6H), 1.03 (d, *J* = 7.4 Hz, 3H), 0.95 (d, *J* = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.59, 167.46, 153.64, 152.19, 146.30, 144.36, 142.97, 135.34, 135.23, 129.92, 129.74, 127.93, 124.81, 121.35, 120.09, 118.84, 117.20, 116.83, 104.72, 56.04, 52.02, 27.86, 27.67, 18.16, 18.05, 17.84, 17.67, 16.20, 13.37, 13.30; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{30}H_{38}NO_5Si$: 520.2519, found: 520.2530; **IR** (thin film) 672, 737, 912, 1037, 1167, 1233, 1280, 1498, 1639, 1719, 2225, 2871, 2955 cm^{-1}.



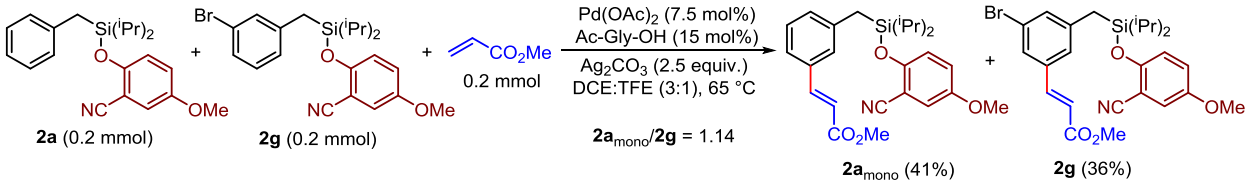
(2E,2'E)-diethyl 3,3'-(4-chloro-5-(((2-cyano-4-methoxyphenoxy)diisopropylsilyl)methyl)-1,3-phenylene)diacrylate (Table 3, entry 4j): Colorless oil. Eluent: petrolium ether/ ethyl acetate (90/10 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 16.0 Hz, 2H), 7.37 (s, 1H), 7.22 (d, *J* = 0.9 Hz, 1H), 6.96 (t, *J* = 4.3 Hz, 1H), 6.87 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.54 (d, *J* = 9.1 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 4H), 3.74 (s, 3H), 2.45 (s, 2H), 1.34 (t, *J* = 7.1 Hz, 6H), 1.29-1.25 (m, 2H), 1.12 – 1.05 (m, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.81, 166.52, 153.63, 151.79, 142.95, 141.12, 138.96, 135.19, 134.26, 133.06, 131.03, 123.83, 121.88, 121.14, 120.06, 119.73, 117.02, 116.68, 104.95, 60.99, 60.89, 56.01, 29.91, 19.64, 17.56, 17.41,

14.51, 13.63; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{31}H_{39}ClNO_6Si$: 584.2235, found: 584.2241; **IR** (thin film) 632, 757, 884, 1033, 1170, 1232, 1280, 1499, 1640, 1720, 2228, 2869, 2947 cm^{-1}.



2-(((((1R,1''R)-6,6''-diacetyl-1,1'',2,2'',3,3'',4,4''-octahydro-[1,1':3',1''-terphenyl]-5'-yl) methyl)diisopropylsilyl)oxy)-5-methoxybenzonitrile (Table 3, entry 4k): Colorless oil. Eluent: petrolium ether/ ethyl acetate (90/10 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06 (dd, *J* = 6.7, 3.4 Hz, 2H), 6.94 (d, *J* = 3.2 Hz, 1H), 6.88 (ddd, *J* = 9.1, 3.2, 1.9 Hz, 1H), 6.68 – 6.57 (m, 3H), 6.12 (t, *J* = 8.7 Hz, 1H), 3.88-3.86 (m, 2H), 3.74 (s, 3H), 2.32-2.33 (m, 2H), 2.26-2.24 (m, 2H), 2.13 (s, 3H), 2.12 (s, 3H), 1.78 – 1.72 (m, 3H), 1.60-1.58 (m, 2H), 1.44 – 1.41 (m, 3H), 1.20-1.15 (m, 2H), 1.20- 0.98 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.79, 198.71, 153.47, 152.19, 145.27, 145.24, 141.59, 141.52, 141.19, 137.52, 137.39, 126.25, 126.15, 124.63, 124.36, 121.35, 120.79, 116.66, 104.53, 56.02, 38.64, 38.52, 31.41, 31.31, 26.29, 26.07, 21.16, 17.52, 17.48, 17.45, 17.40, 17.10, 16.97, 12.77, 12.70, 12.65; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{37}H_{48}NO_4Si$: 598.3353, found: 598.3361; **IR** (thin film) 671, 755, 884, 1036, 1169, 1232, 1280, 1499, 1530, 1640, 1734, 2228, 2869, 2946 cm^{-1}.

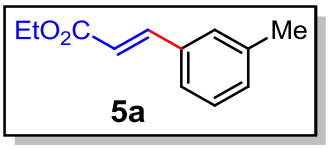
2.8 *Intermolecular control experiment:*



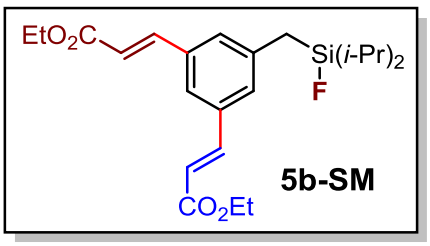
In a clean, oven–dried screw cap reaction tube containing magnetic stir–bar, **2a** (0.2 mmol), **2g** (0.2 mmol), $Pd(OAc)_2$ (0.03 mmol), N-Acetyl-glycine (0.06 mmol), Ag_2CO_3 (0.8 mmol) were weighed and the tube was tightly closed by screw cap fitted with rubber septum. The tube was evacuated and filled with nitrogen through standard Schlenk technique, and this sequence was repeated for three additional times. Then, under positive pressure of nitrogen, olefin (1 equiv, 0.2 mmol), DCE (2.4 mL) and TFE (0.8 mL) were added sequentially by syringes. The reaction tube was placed in a preheated oil bath at 65 °C to stir vigorously for 20 h. Then reaction mixture was cooled to room temperature and filtered through celite with aid of ethyl acetate (10 mL). Then, this filtrate was concentrated under reduced pressure and purified by column chromatography through silica gel using petrolium ether/ethyl acetate as eluent to obtain pure **2a**$_{mono}$ (36 mg) as

colorless liquid and **2g** (37 mg) as light yellow liquid. Characterization data were identical with previously observed data for individual cases.

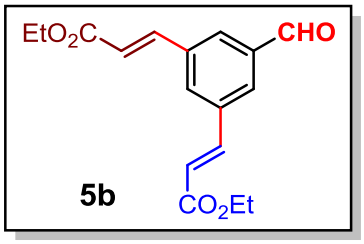
2.9 ***Applicability of meta C-H olefination:***



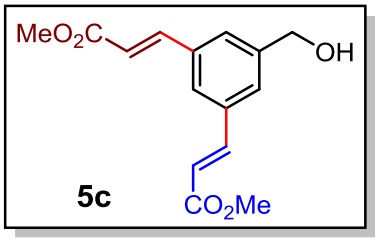
(E)-ethyl 3-(3-((hydroxydiisopropylsilyl)methyl)phenyl)acrylate (Scheme 5, entry 5a):
n-tetrabutylammonium fluoride (TBAF) in THF (1 M, 2 equiv.) was added to a solution of **3c**$_{mono}$ in THF (0.4 mmol in 3 mL) and stirred at room temperature for 2 h. This solution was concentrated and purified by column chromatography. Yellowish oil. Eluent: ether/ ethyl acetate (96/4 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.33 (d, *J* = 6.9 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.33, 145.00, 138.77, 134.68, 131.29, 129.00, 128.96, 125.48, 118.30, 60.70, 21.56, 14.57; **HRMS (*m/z*):** [M + H]$^{+}$ calcd for $C_{12}H_{15}O_2$: 191.1072, found: 191.1065; **IR** (thin film) 529, 571, 691, 853, 929, 1020, 1296, 1377, 1632, 1708, 1783 cm^{-1}.



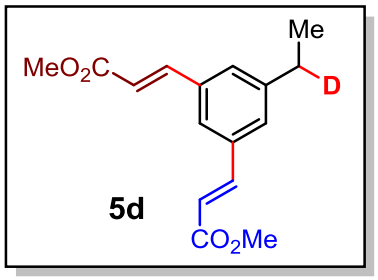
diethyl 3,3'-(5-((fluorodiisopropylsilyl)methyl)-1,3-phenylene)(2E,2'E)-diacrylate (Scheme 5, entry 5b-SM):
Trimethyloxonium tetrafluoroborate ($Me_3O^+BF_4^-$, 2 equiv.) was added to a solution of **3c**$_{di}$ in DCE (0.4 mmol in 2 mL) under inert atmosphere and stirred at 50 °C for 48 h. After completion, the reaction mixture was diluted with 10 mL DCM and treated with saturated aqueous $NaHCO_3$ solution (10 mL). The mixture was stirred for additional 30 min at room temperature. Aqueous work up followed by concentration of combined organic portions and purification by column chromatography led to desire product. Colorless oil. Eluent: ether/ ethyl acetate (92/8 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 2H), 7.42 (s, 1H), 7.29 (s, 2H), 6.44 (d, *J* = 16.0 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 4H), 2.30 (d, *J* = 8.0 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 6H), 1.06 – 0.99 (m, 14H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.02, 144.09, 139.78, 135.40, 130.00, 124.30, 119.28, 60.82, 16.93, 14.52, 12.39, 12.27; **HRMS (*m/z*):** [M + H]$^{+}$ calcd for $C_{23}H_{34}FO_4Si$: 421.2210, found: 421.2214.



diethyl 3,3'-(5-formyl-1,3-phenylene)(2E,2'E)-diacrylate (Scheme 5, entry 5b):
A screw cap reaction tube containing stirring bar was charged with compound **5b** (0.2 mmol), CsF (2 equiv.) and PhNO (3 equiv.). Commercial DMF (1mL) was added via syringe and the reaction mixture was heated at 65 °C for 2 h. After aqueous work up combined organic layer was concentrated and purified by column chromatography. Light yellow solid. Eluent: ether/ ethyl acetate (88/12 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.02 (s, 2H), 7.86 (s, 1H), 7.72 (d, *J* = 16.0 Hz, 2H), 6.56 (d, *J* = 16.0 Hz, 2H), 4.29 (d, *J* = 7.2 Hz, 4H), 1.35 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.24, 166.48, 142.29, 137.67, 136.51, 132.78, 129.89, 121.31, 61.11, 14.48; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{17}H_{19}O_5$: 303.1232, found: 303.1228.

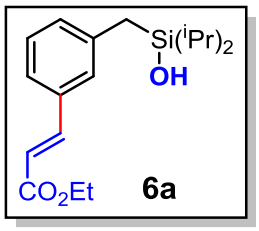


dimethyl 3,3'-(5-(hydroxymethyl)-1,3-phenylene)(2E,2'E)-diacrylate (Scheme 5, entry 5c):
A screw cap reaction tube containing stirring bar was charged with compound **4a** (0.2 mmol), KF (2 equiv.) and $KHCO_3$ (10 equiv.). THF (0.5 mL), MeOH (0.5 mL) and 30% H_2O_2 (200 µL) were added via syringes and the reaction mixture was heated at 60 °C for 36 h. After aqueous work up combined organic layer was concentrated and purified by column chromatography. Light yellow oil. Eluent: ether/ ethyl acetate (80/20 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.0 Hz, 2H), 7.54 (s, 3H), 6.48 (d, *J* = 16.0 Hz, 2H), 4.75 (s, 2H), 3.82 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.38, 143.98, 142.61, 135.56, 127.90, 127.16, 119.25, 64.65, 52.07; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{15}H_{17}O_5$: 277.1076, found: 277.1074; **IR** (thin film) 671, 759, 852, 982, 1038, 1176, 1199, 1294, 1313, 1438, 1639, 1720, 2853, 2925 cm^{-1}.

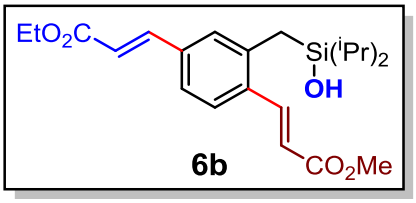


dimethyl 3,3'-(5-(ethyl-1-d)-1,3-phenylene)(2E,2'E)-diacrylate (Scheme 5, entry 5d):

n-tetrabutylammonium fluoride (TBAF) in THF (1 M, 2 equiv.) was added to a solution of **4j** in CD_3OD (0.2 mmol in 1 mL) and stirred at room temperature for 2 h. This solution was concentrated and purified by column chromatography. Light yellow oil. Eluent: ether/ ethyl acetate (80/20 v/v) mixture as eluent. Deuterium incorporation ~70%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 16.0 Hz, 2H), 7.46 (s, 1H), 7.36 (s, 2H), 6.46 (d, *J* = 16.0 Hz, 2H), 3.81 (s, 6H), 2.68 (d, *J* = 7.7 Hz, 1H), 1.25 (d, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.47, 145.79, 144.41, 135.26, 129.44, 125.43, 118.71, 51.99, 28.79, 28.61, 28.45, 28.30, 15.55, 15.47; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{16}H_{18}DO_4$: 275.1268, found: 275.1273.



ethyl (E)-3-(3-((hydroxydiisopropylsilyl)methyl)phenyl)acrylate (Scheme 6, entry 6a):
A screw cap reaction tube containing stirring bar was charged with compound **3c**$_{mono}$ (0.4 mmol) and *p*-toluenesulfonic acid (0.04 mmol). 3 mL wet ethanol (EtOH: H_2O; 3:1) was added at room temperature and the reaction mixture was heated at 100 °C for 16 h. After work up with ethyl acetate combined organic layer was concentrated and purified by column chromatography. Colorless oil. Eluent: ether/ ethyl acetate (93/7 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.14 (dt, *J* = 6.5, 1.9 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.22 (s, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.03 – 0.97 (m, 14H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.35, 145.15, 140.40, 134.71, 130.70, 129.07, 128.39, 124.29, 118.17, 60.68, 21.63, 17.47, 17.42, 14.53, 12.91; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{18}H_{29}O_3Si$: 321.1886, found: 321.1883.



ethyl (E)-3-(3-((hydroxydiisopropylsilyl)methyl)-4-((E)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)acrylate (Scheme 6, entry 6b):
A screw cap reaction tube containing stirring bar was charged with $Pd(OAc)_2$ (20 mol%), compound **4a** (0.1 mmol), AgOAc (2 equiv.), KH_2PO_4 (2 equiv.), methyl acrylate (2 equiv.) and $CHCl_3$ (1 mL). The reaction tube was sealed and heated at 100 °C for 16 h with vigorous stirring. The reaction mixture was cooled and filtered through celite with the aid of ethyl acetate. This filtrate was concentrated and purified by column chromatography. Yelloish oil. Eluent: ether/ ethyl acetate (88/12 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 15.8 Hz, 1H), 7.57 (d, *J* = 16.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.19 (m, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 2.33 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.99

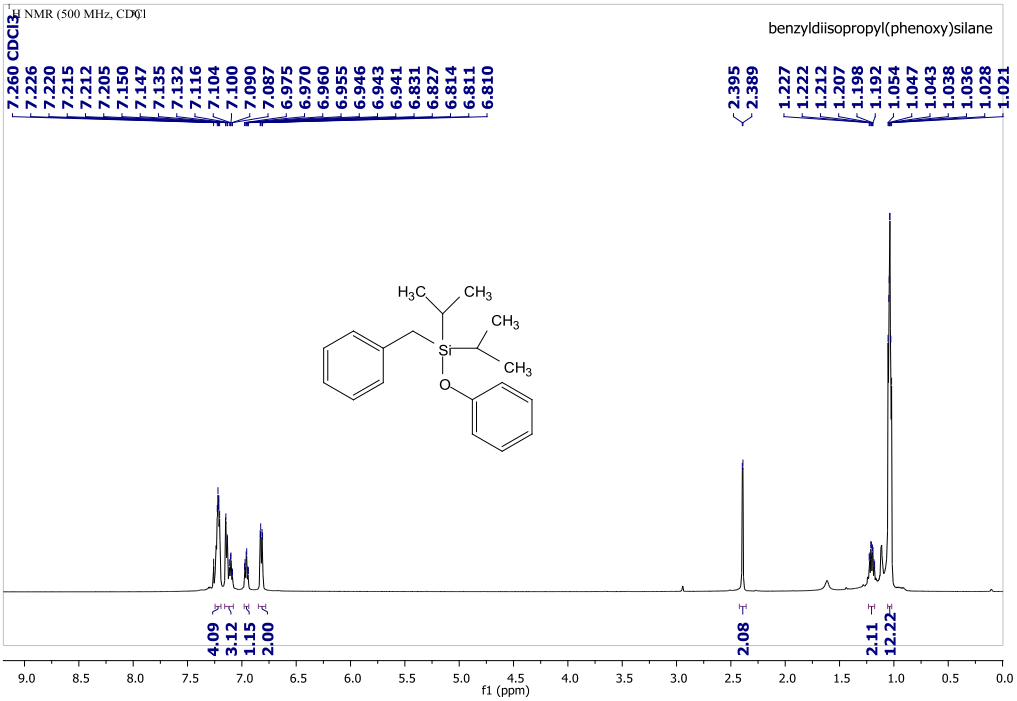
– 0.95 (m, 14H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.67, 167.09, 144.03, 142.59, 140.99, 136.03, 134.13, 130.39, 127.27, 124.46, 119.22, 60.82, 51.99, 19.78, 17.45, 17.36, 14.52, 13.13; **HRMS (*m*/*z*):** $[M + Na]^+$ calcd for $C_{12}H_{32}O_5NaSi$: 427.1917, found: 427.1919.

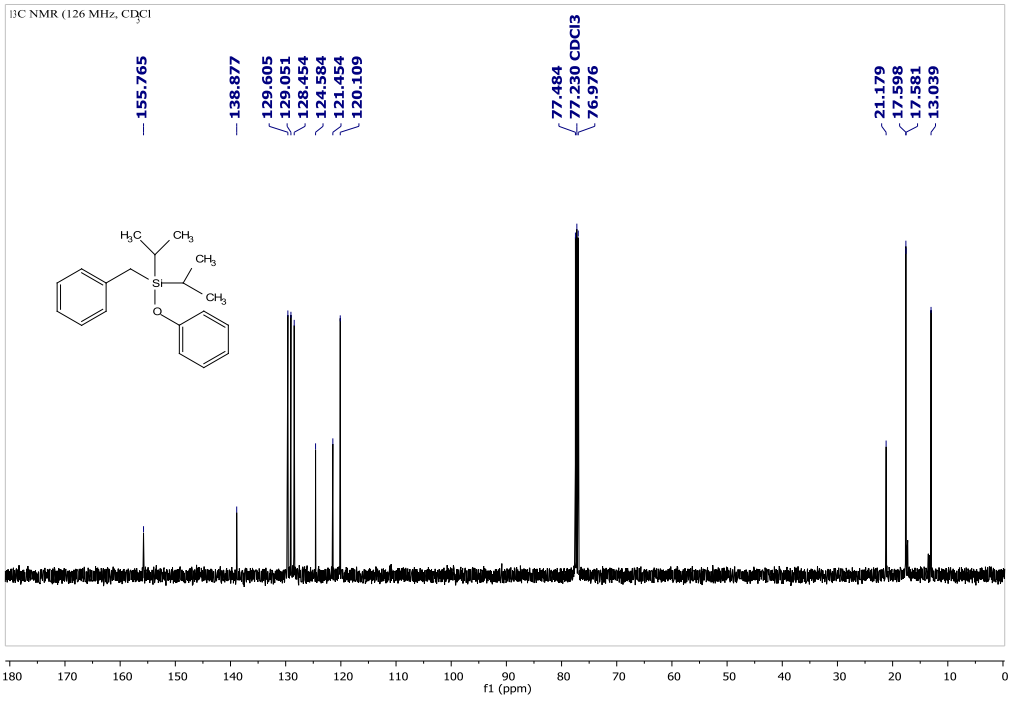
Reference:

1. Whiting, E.; Lanning, M. E.; Scheenstra, J. A.; Fletcher, S. *J. Org. Chem.* **2015**, *80*, 1229−1234.

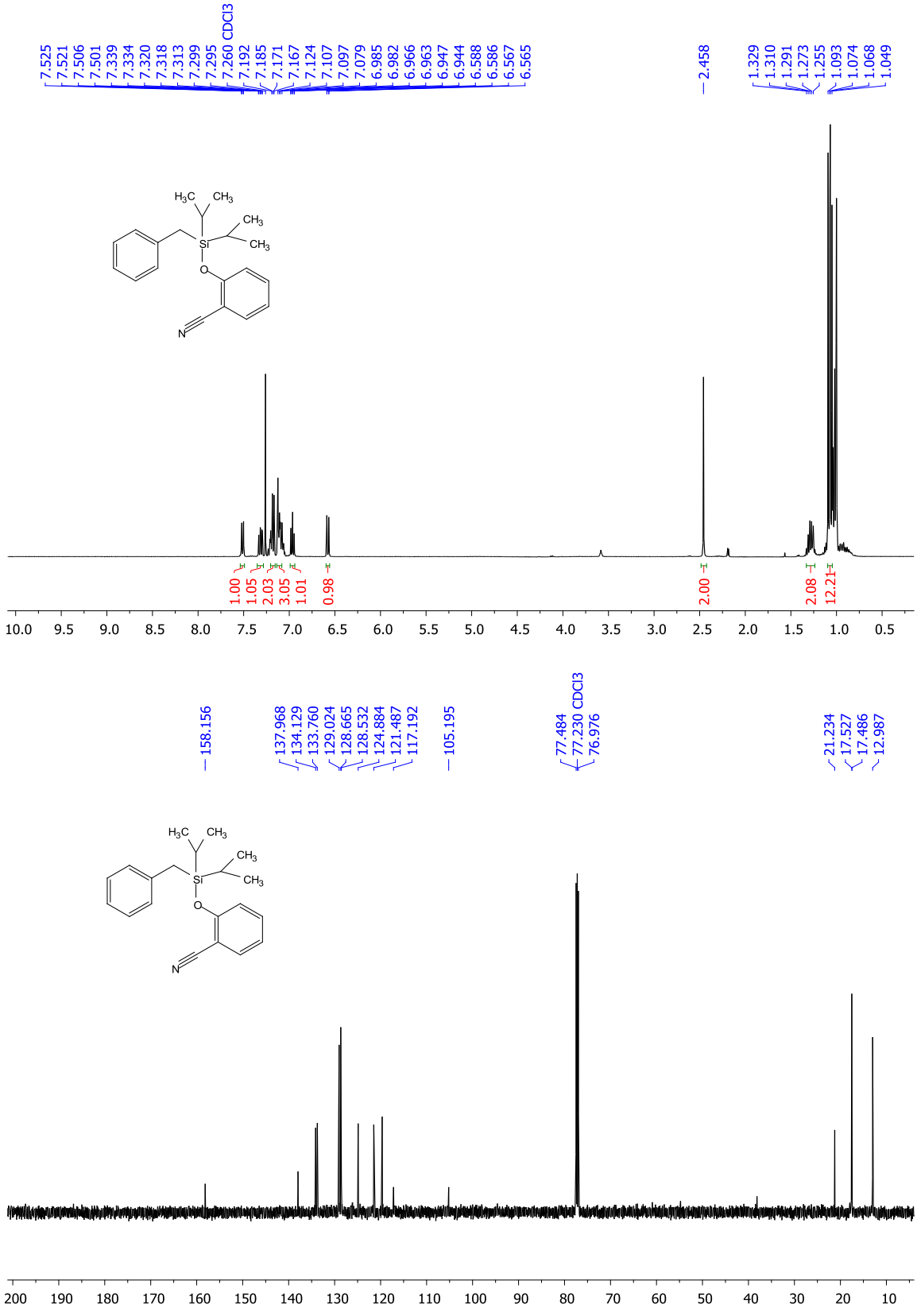
NMR Data

Scheme 2, template T[1]:

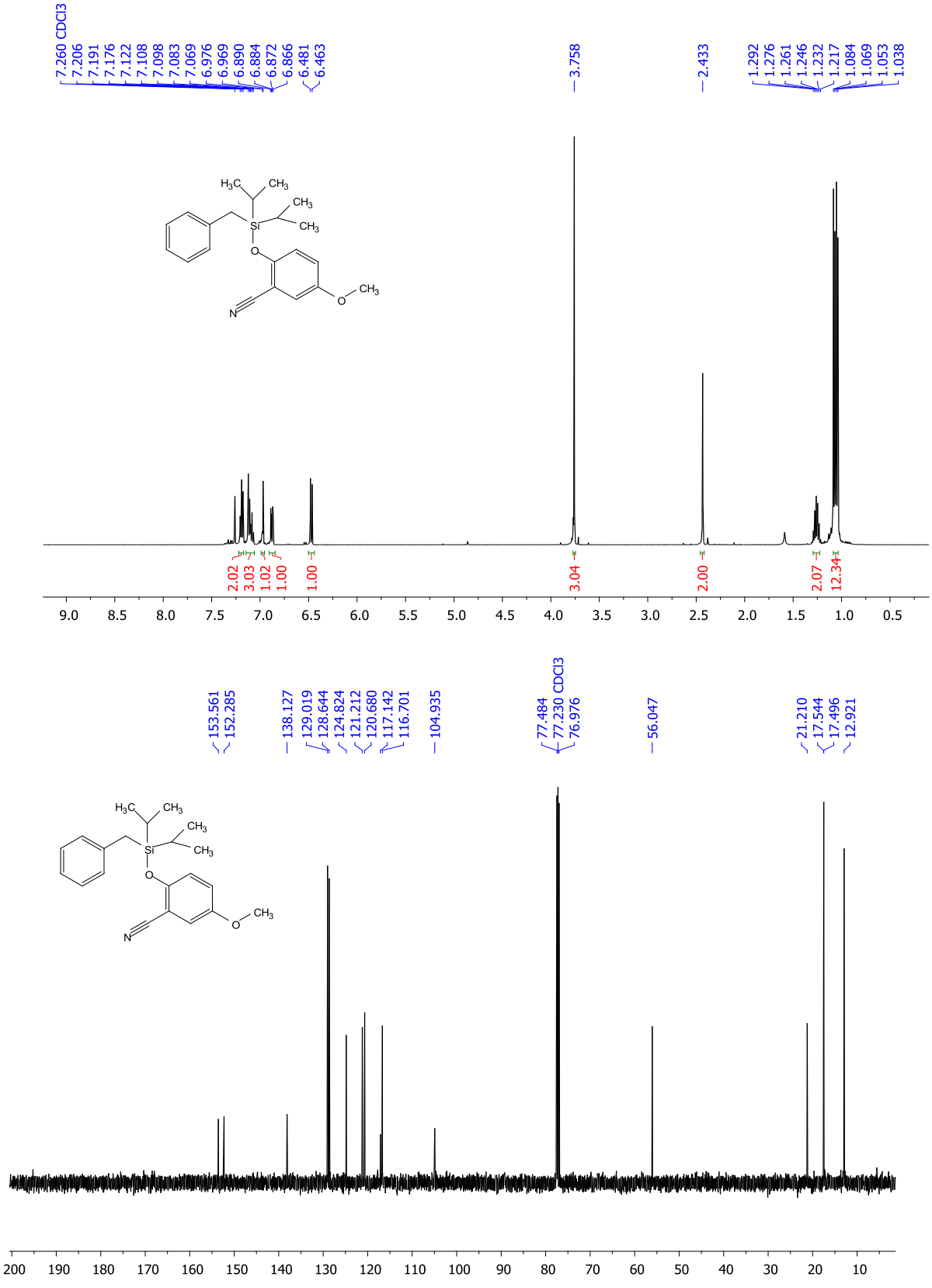




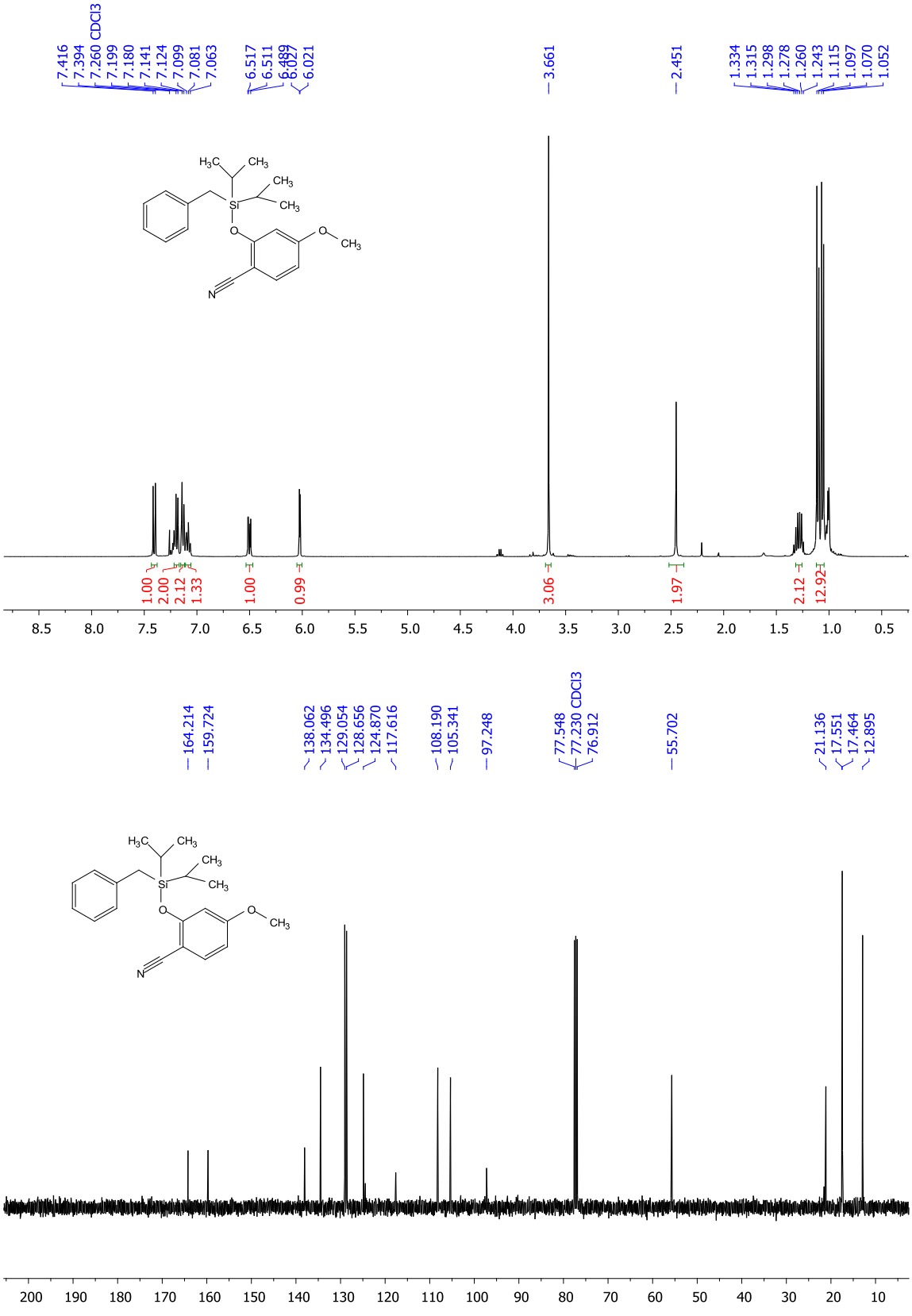
Scheme 2, template T^2:



Scheme 2, template T^3 (1a):



Scheme 2, template T^4:



Scheme 2, template T^5:

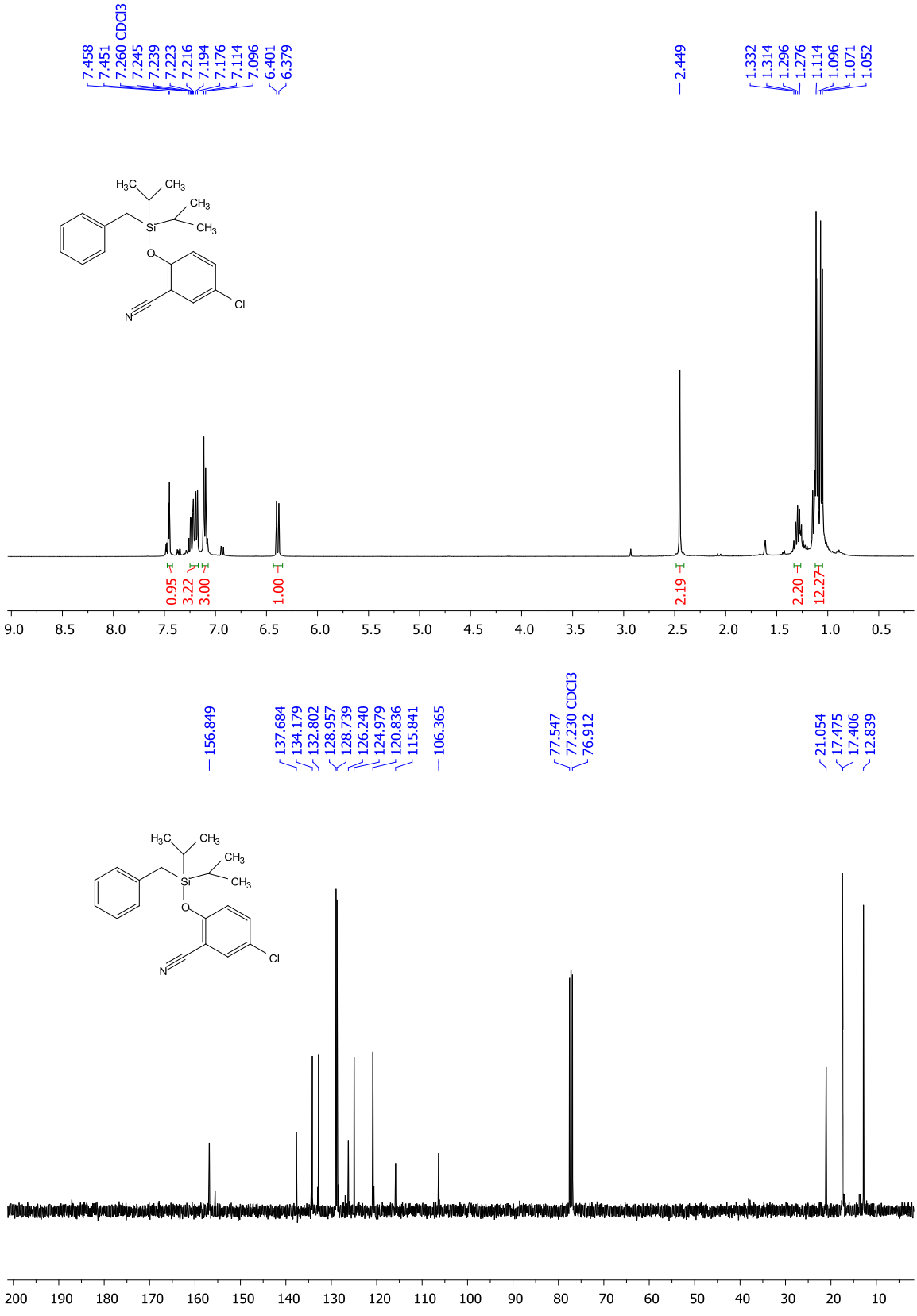
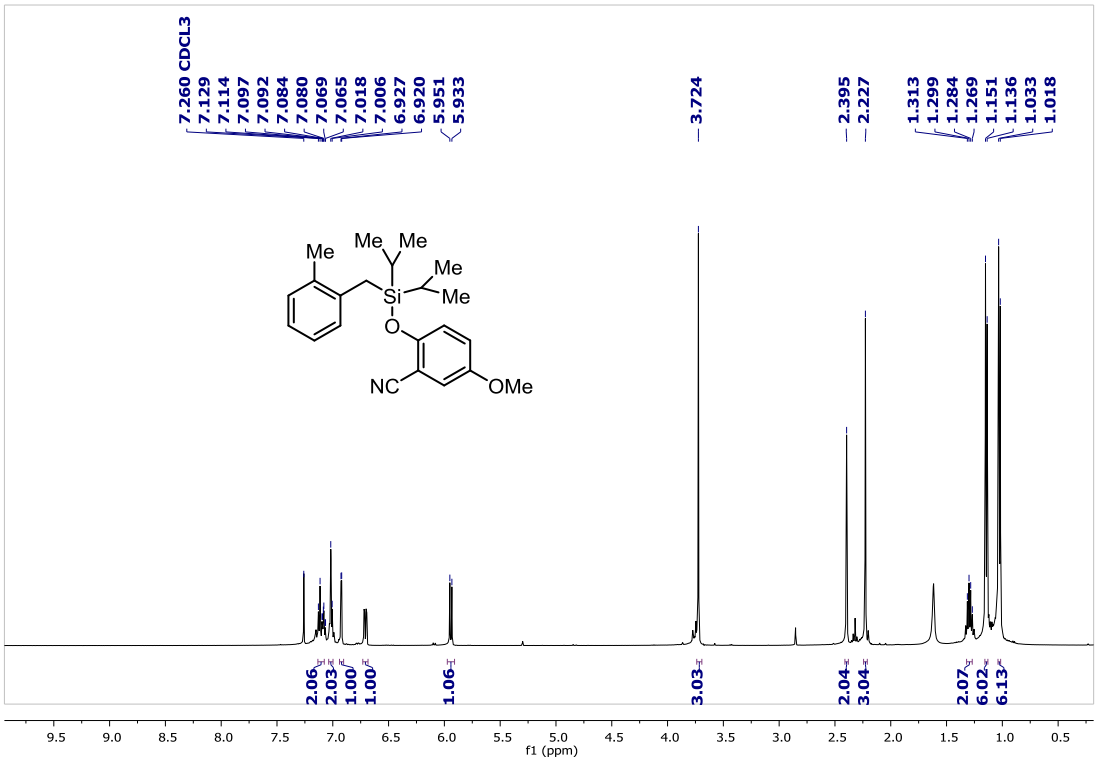
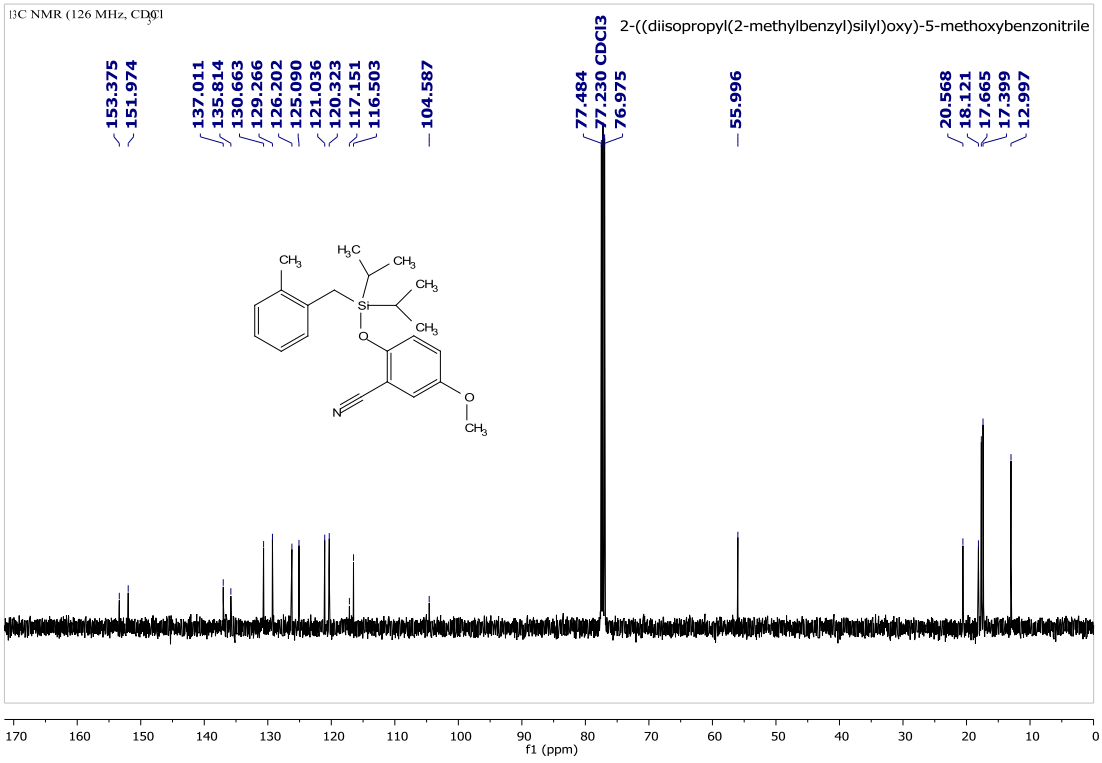


Table 1, entry 1b:





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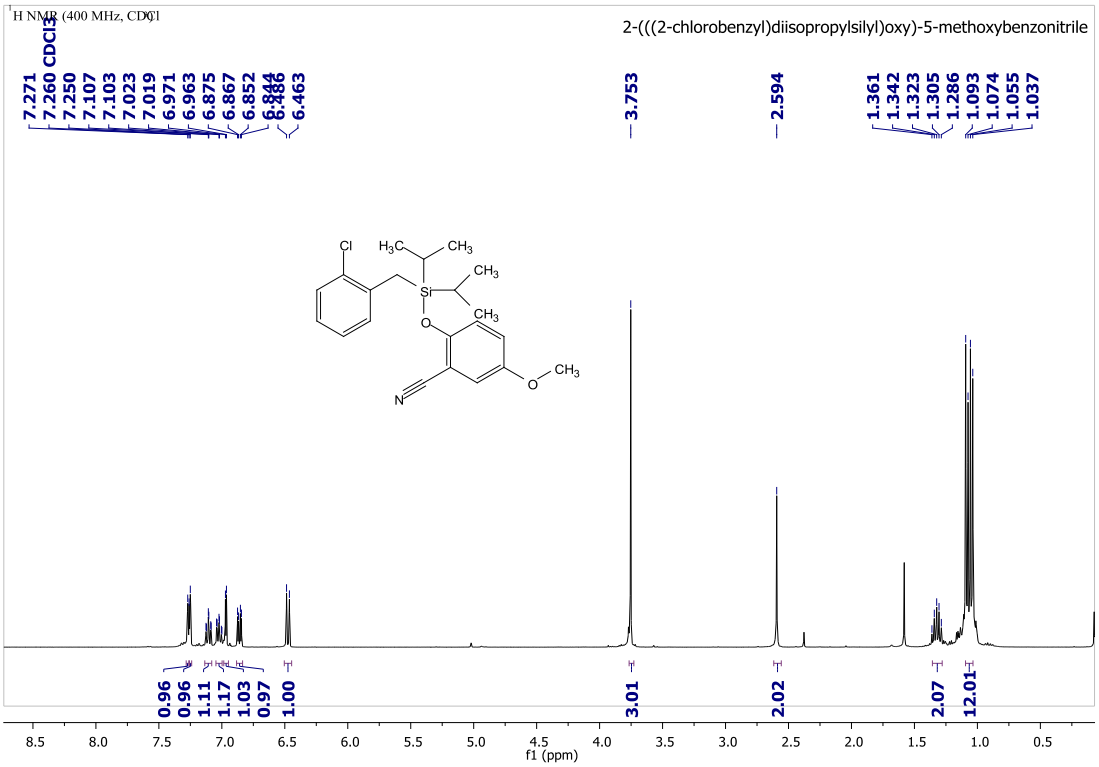

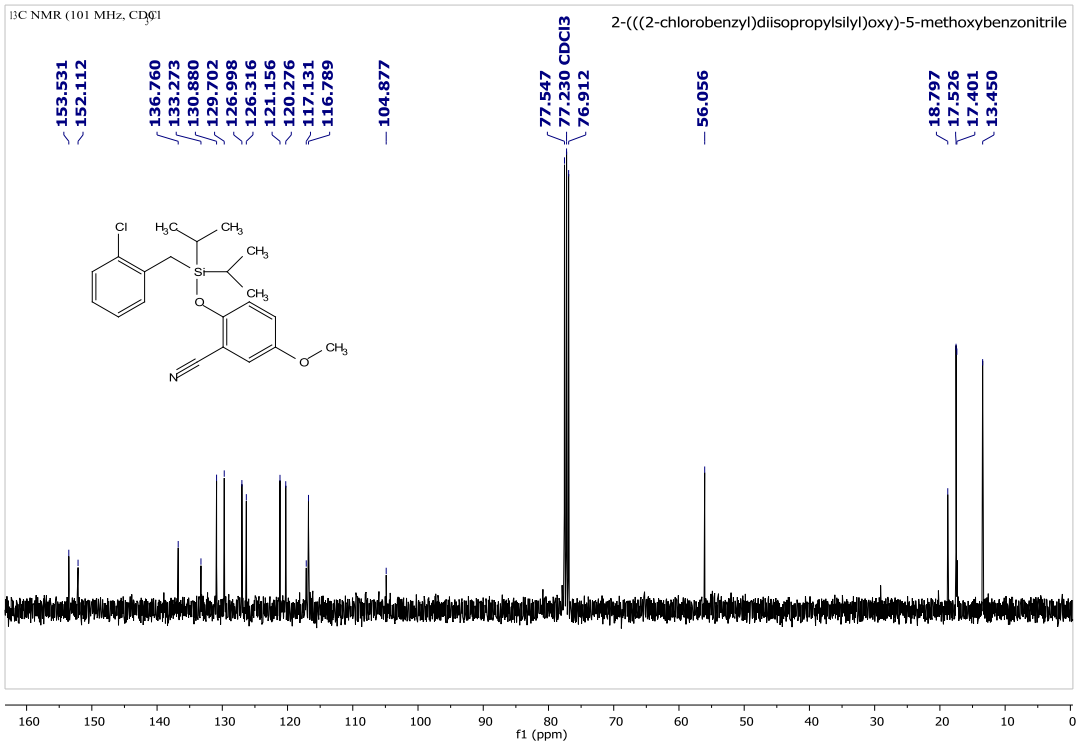

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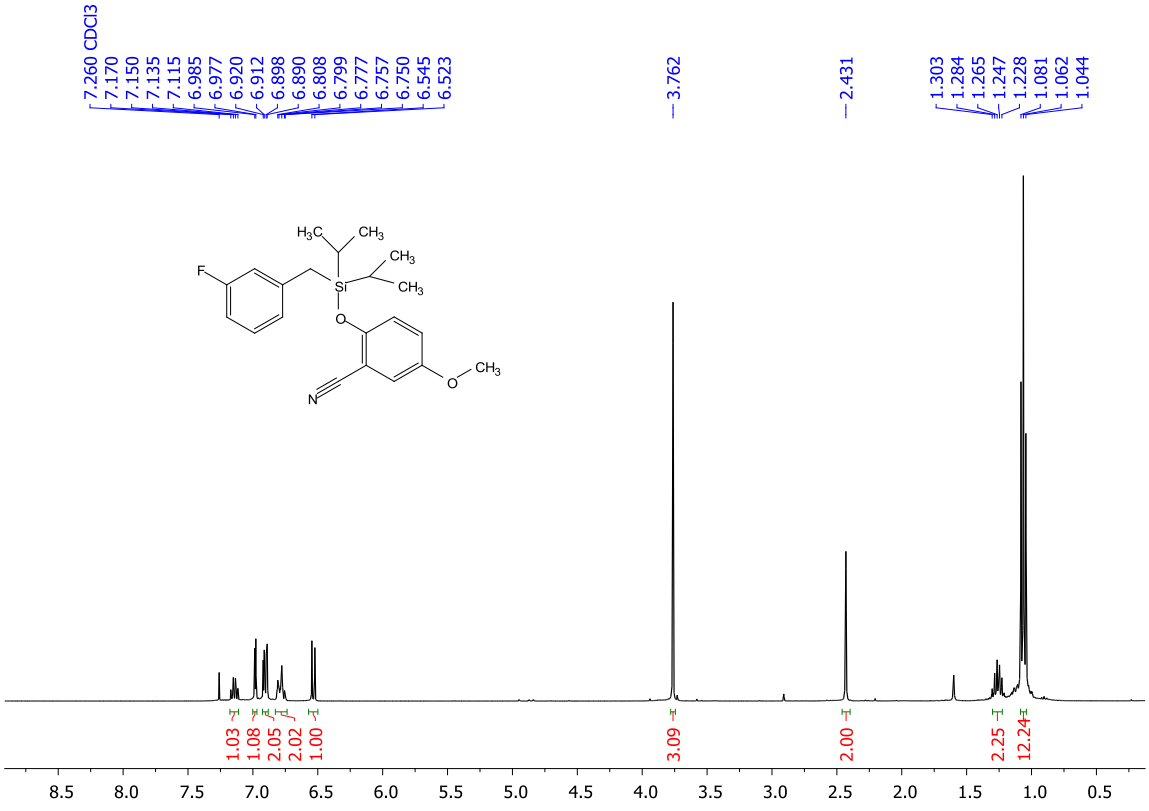


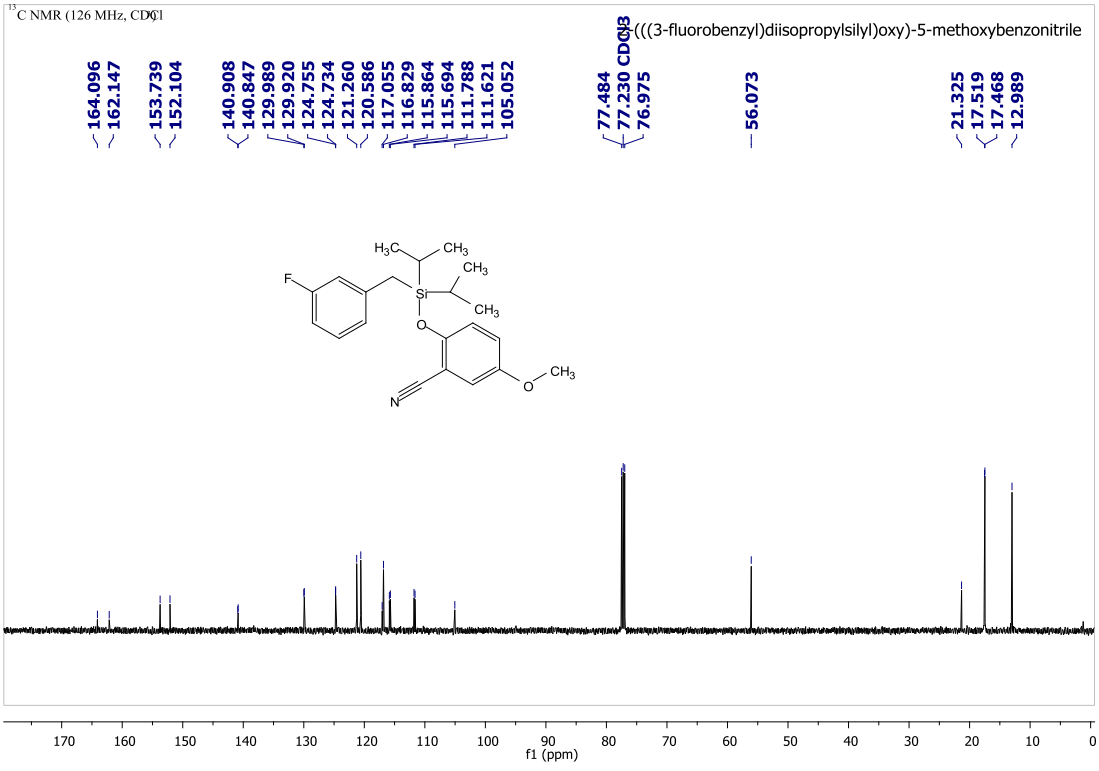
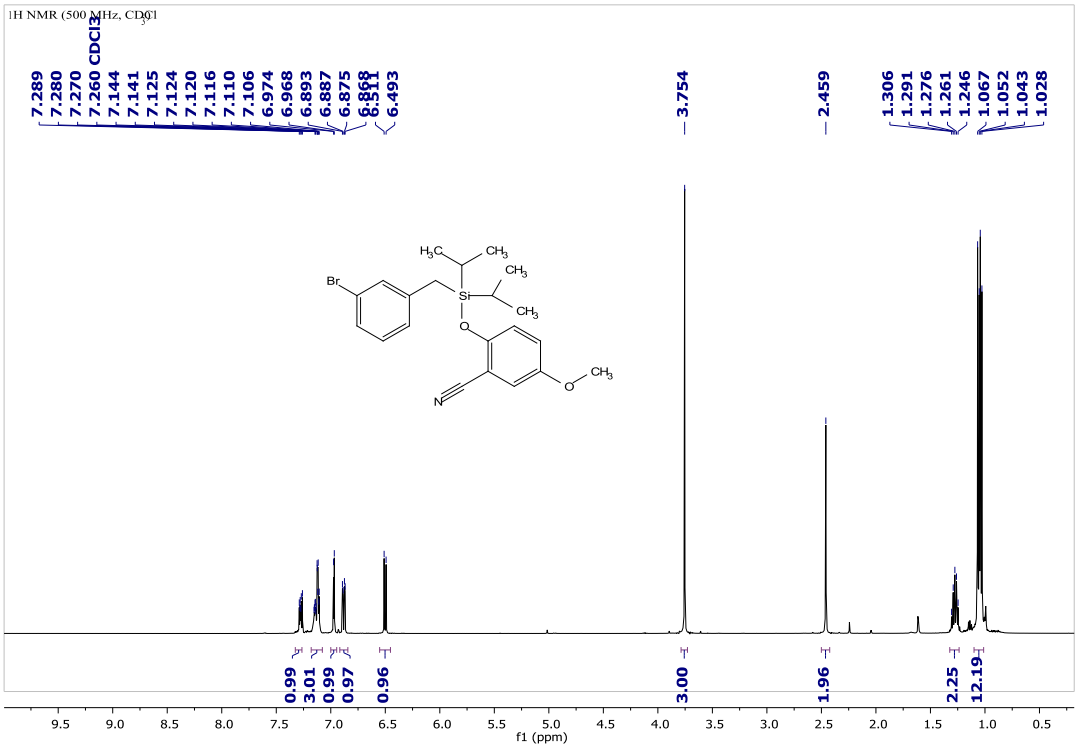


Table 1, entry 1g:



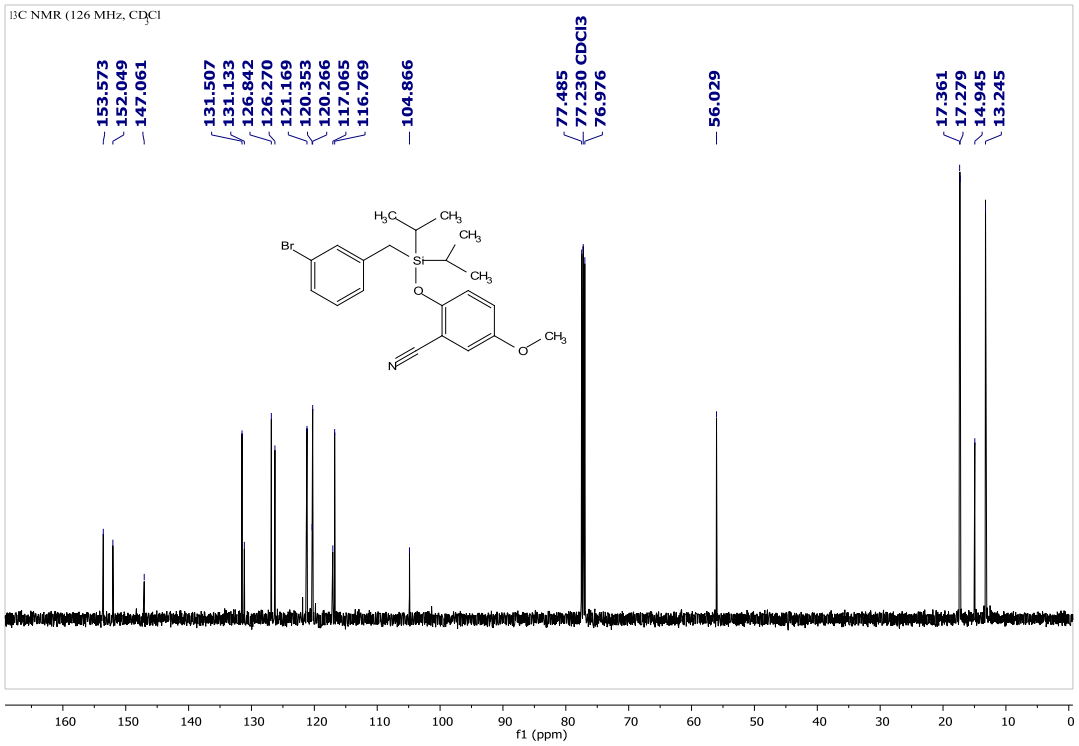
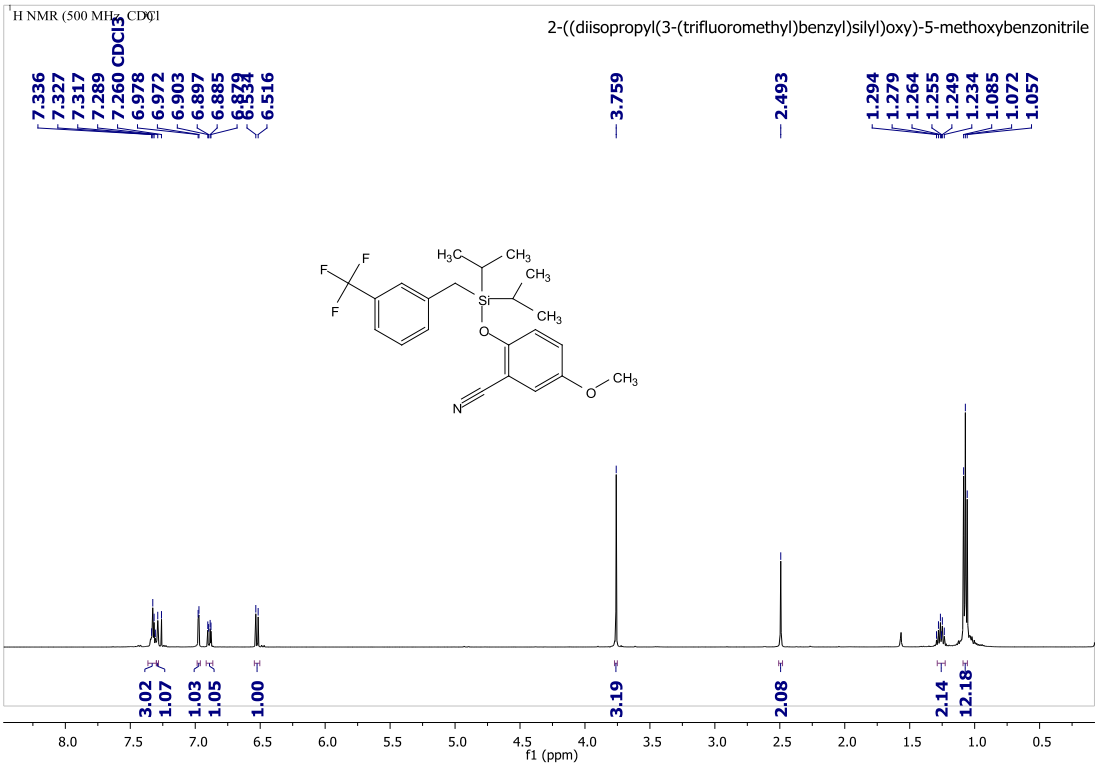


Table 1, entry 1h:



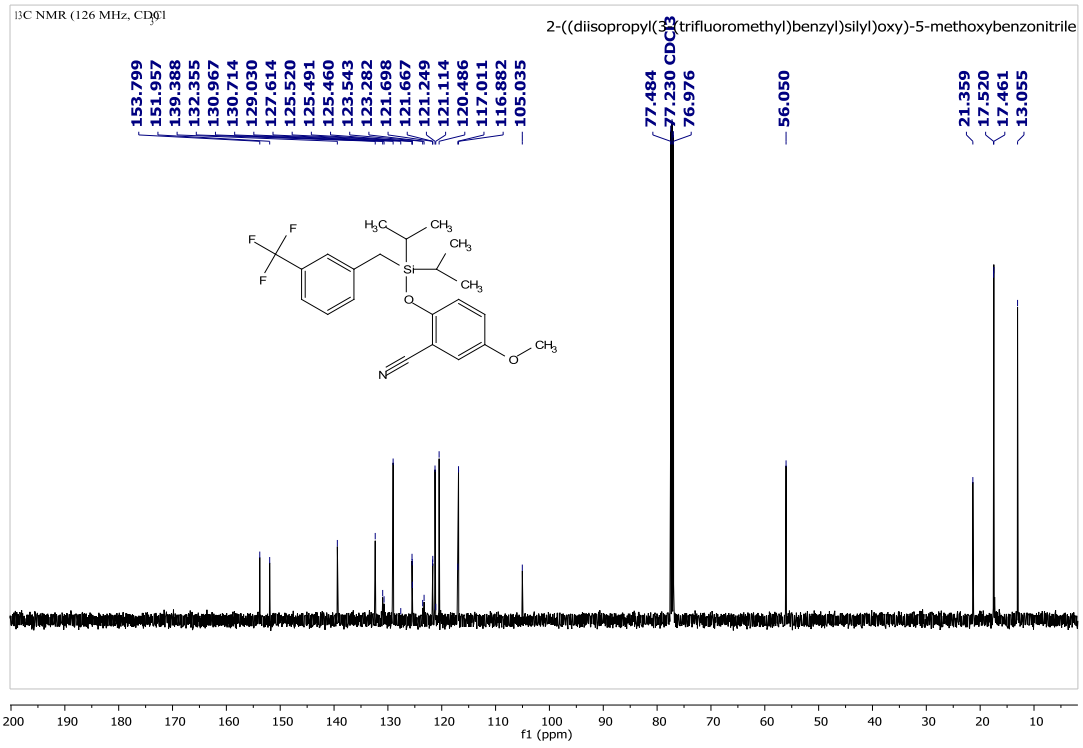
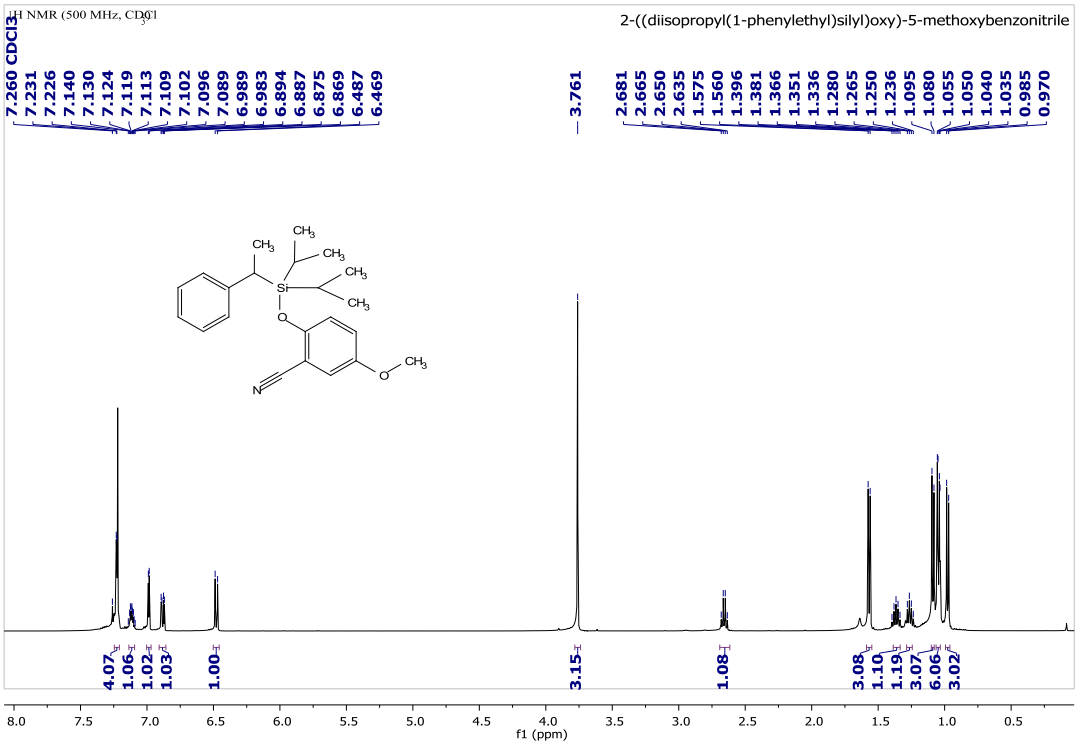
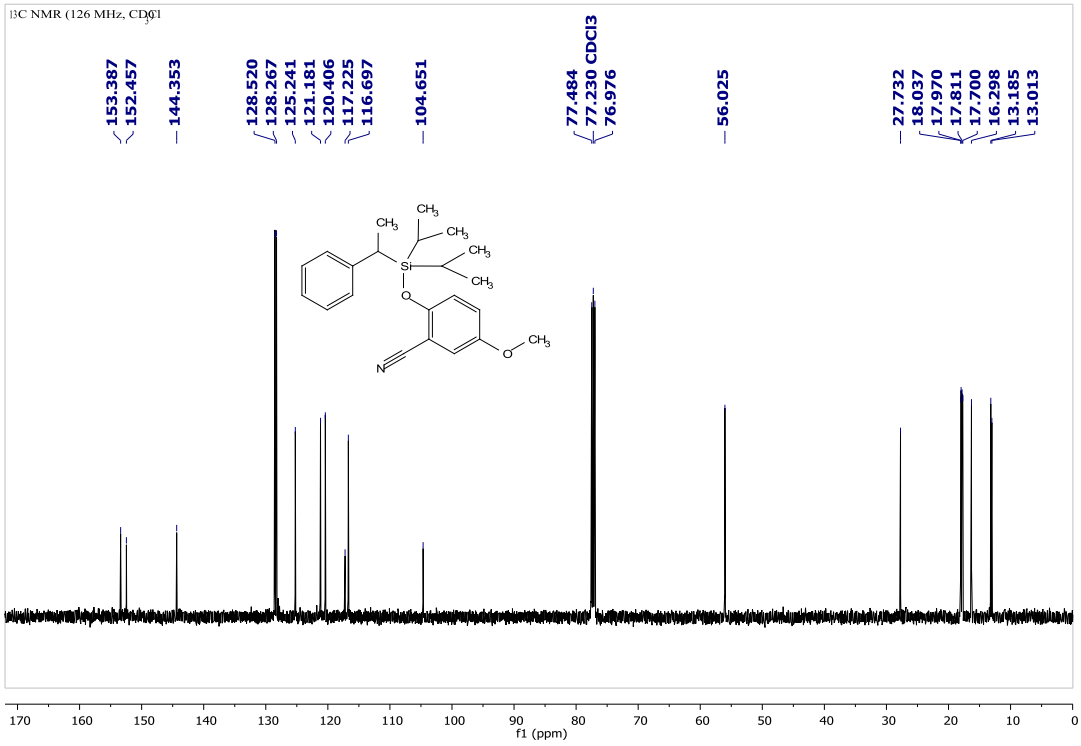


Table 1, entry 1i:





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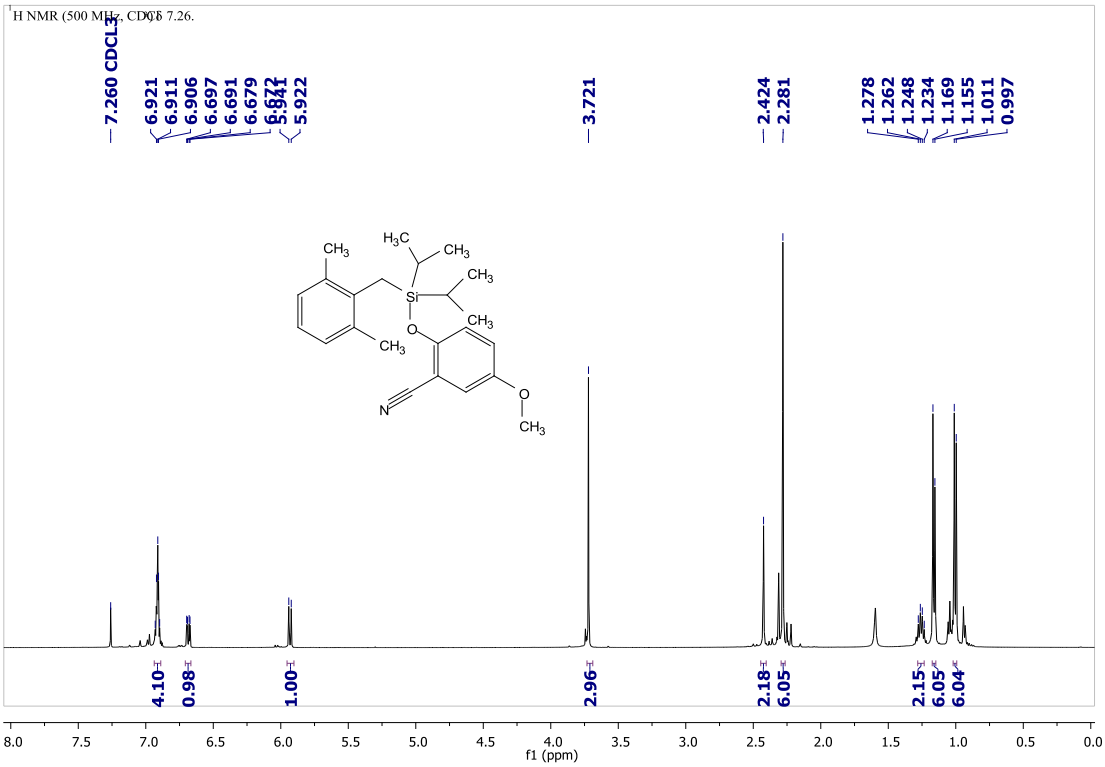

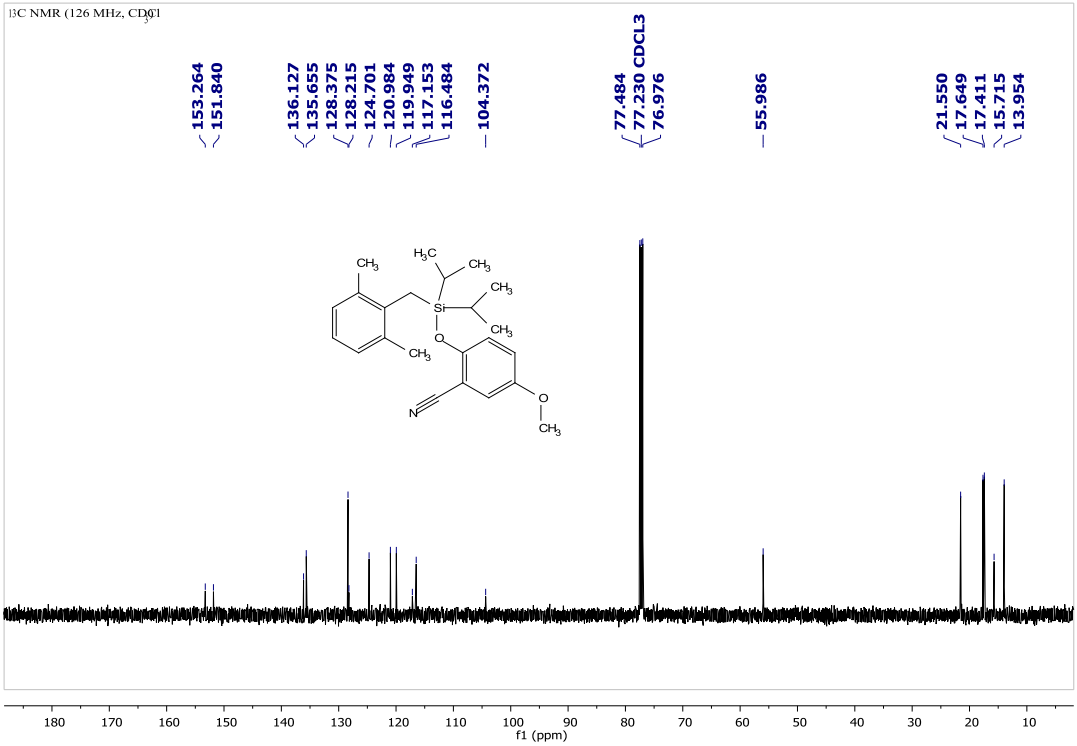

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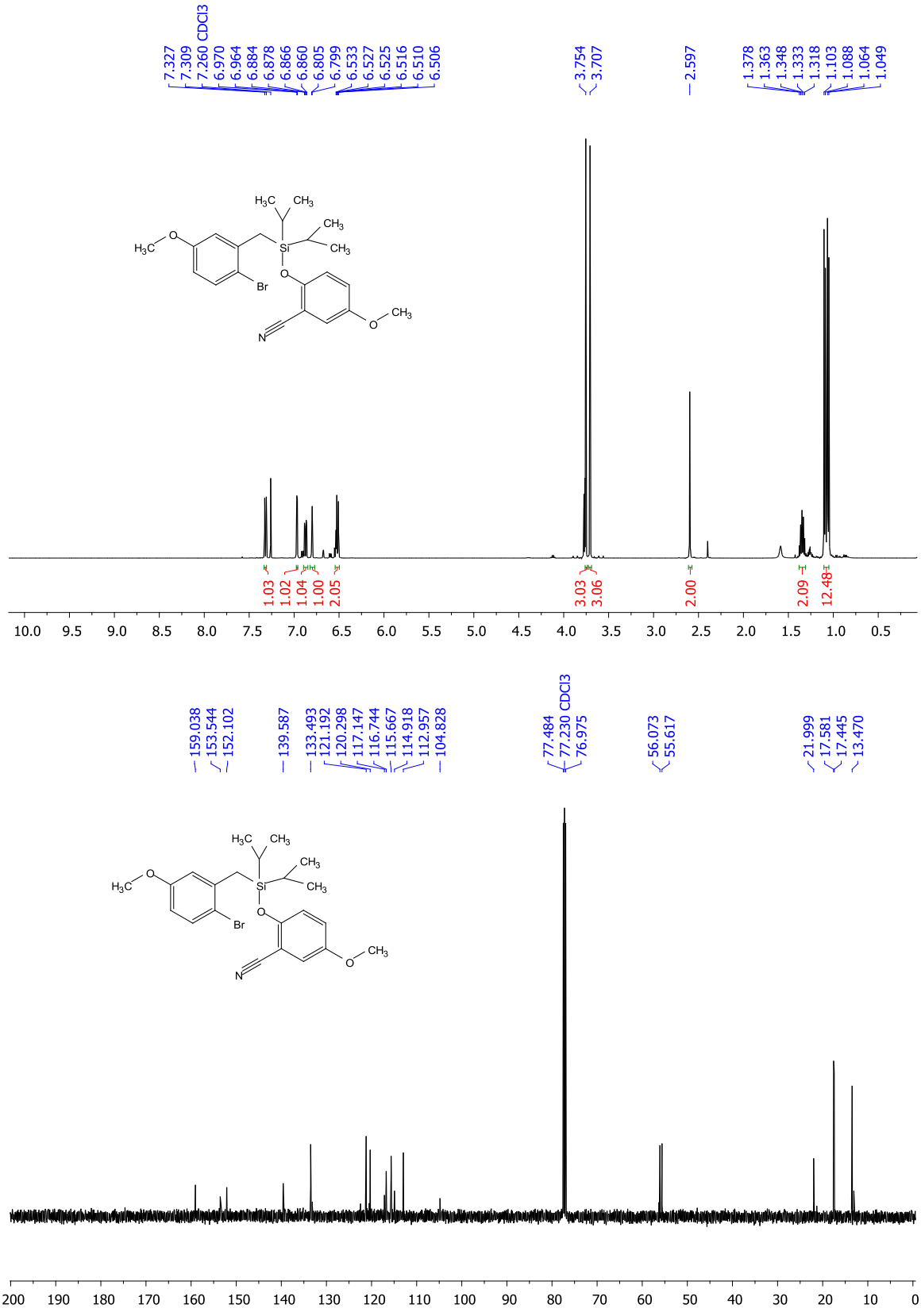
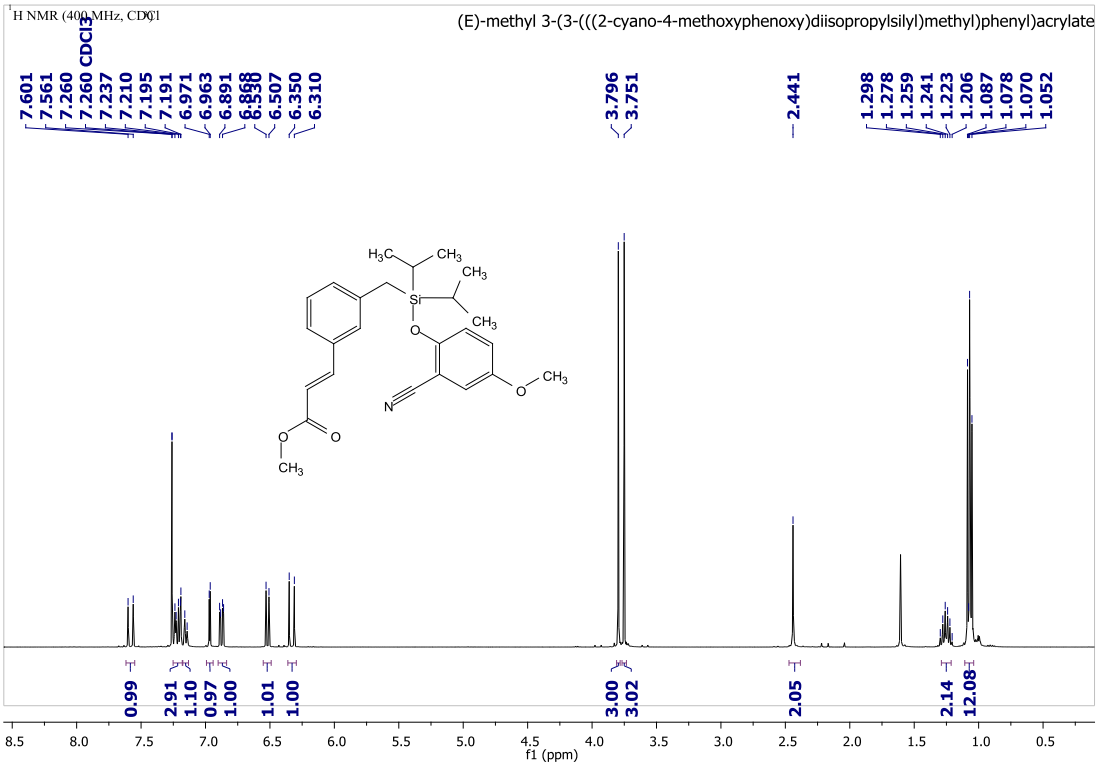


Table 1, entry 2a$_{mono}$:



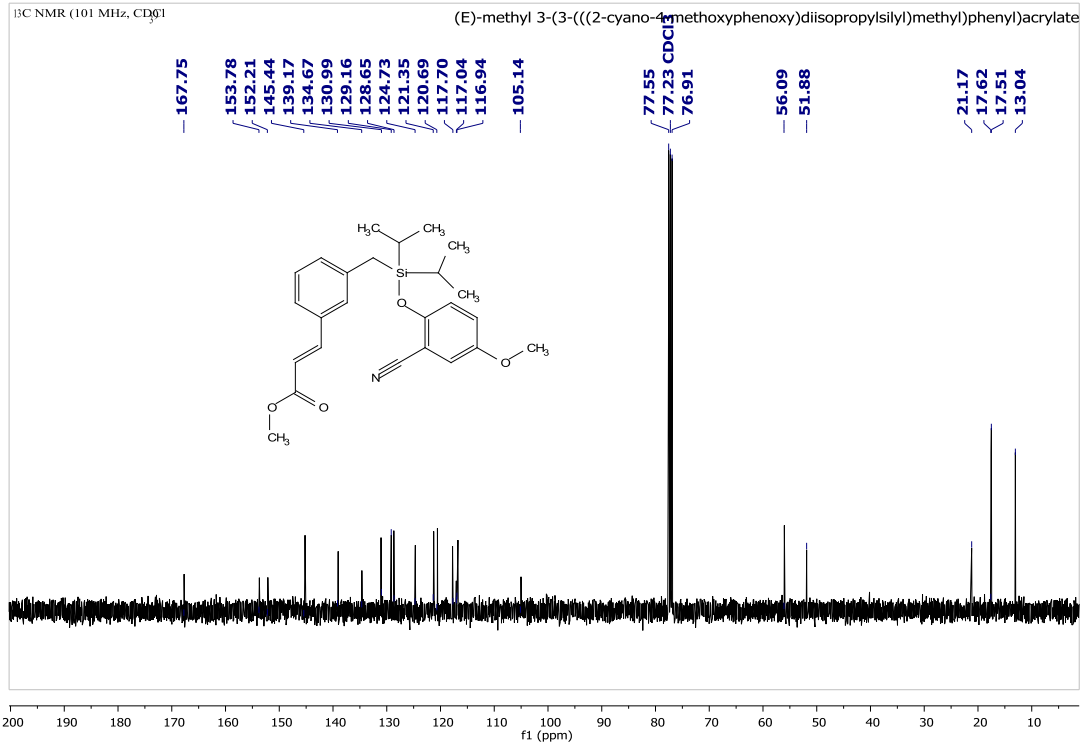
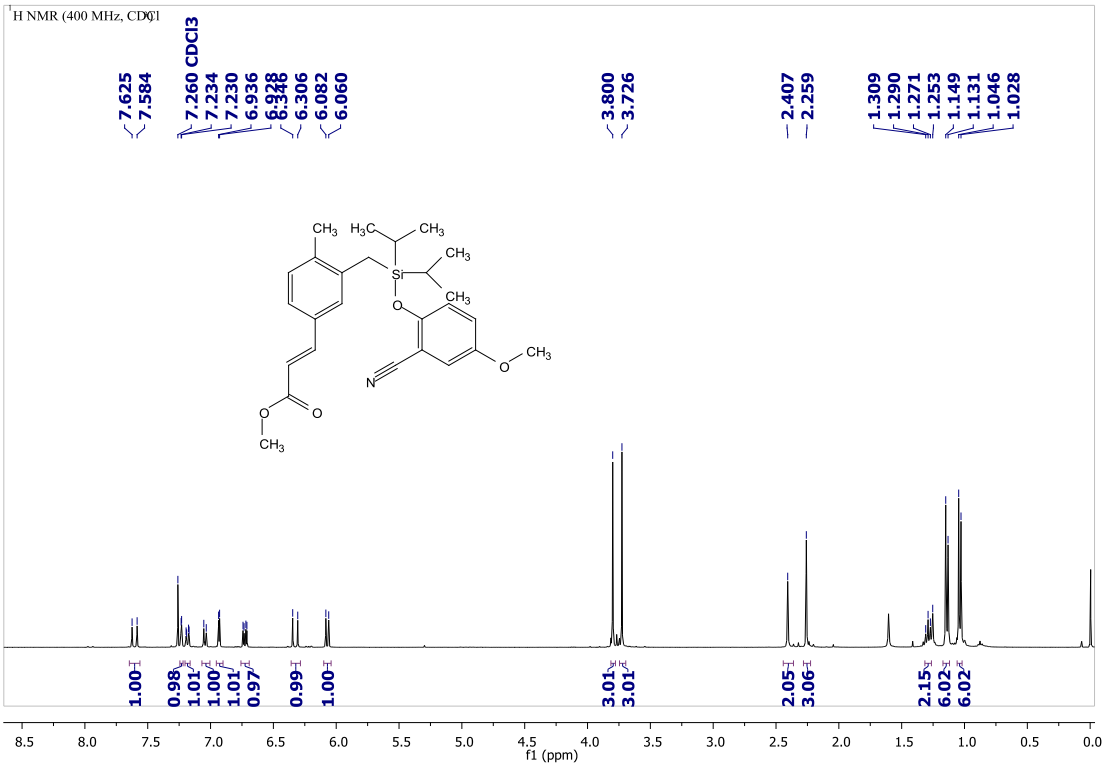
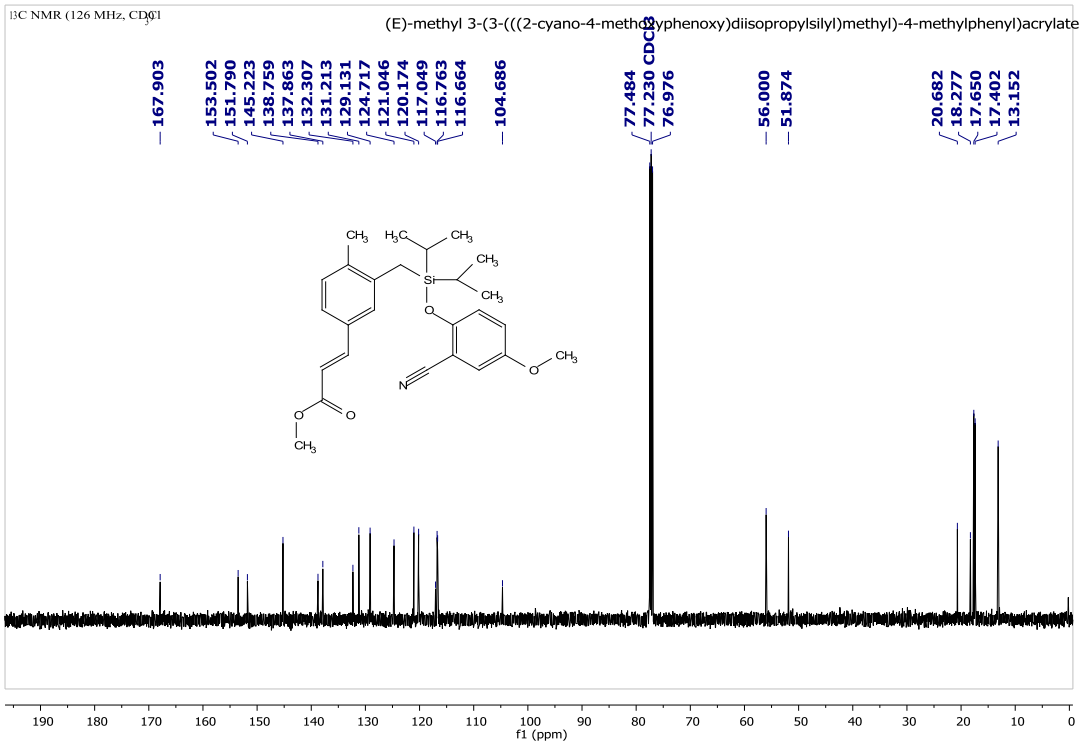


Table 1, entry 2b:





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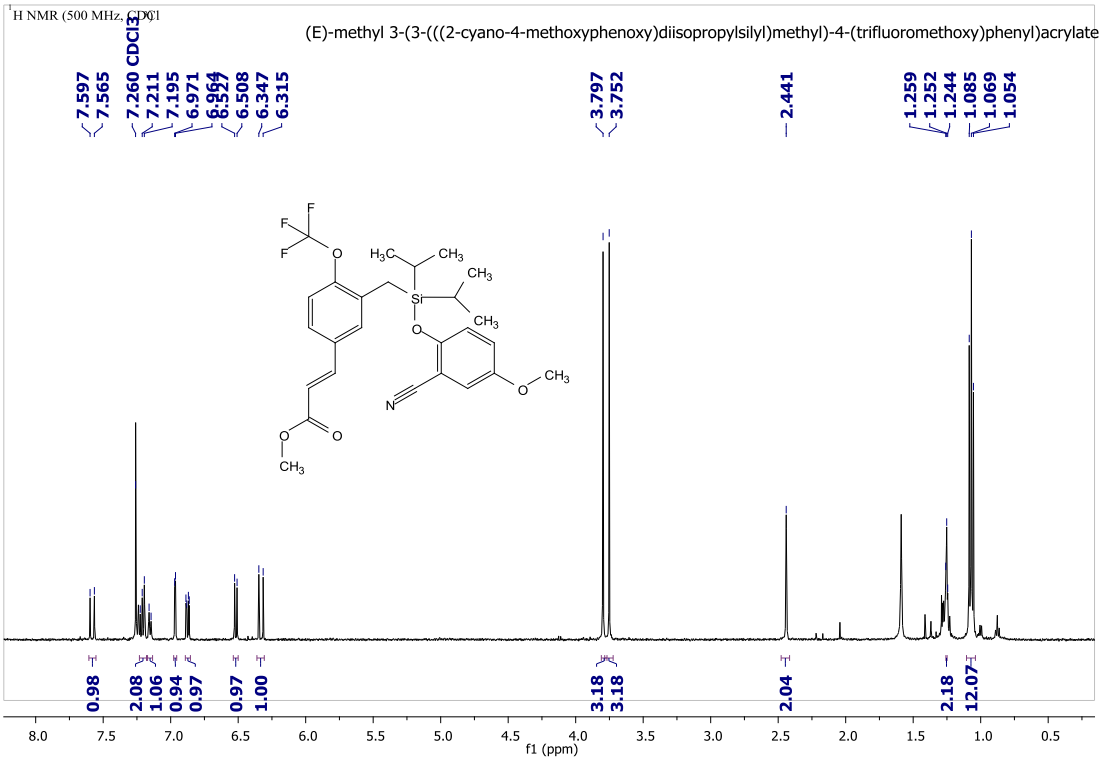


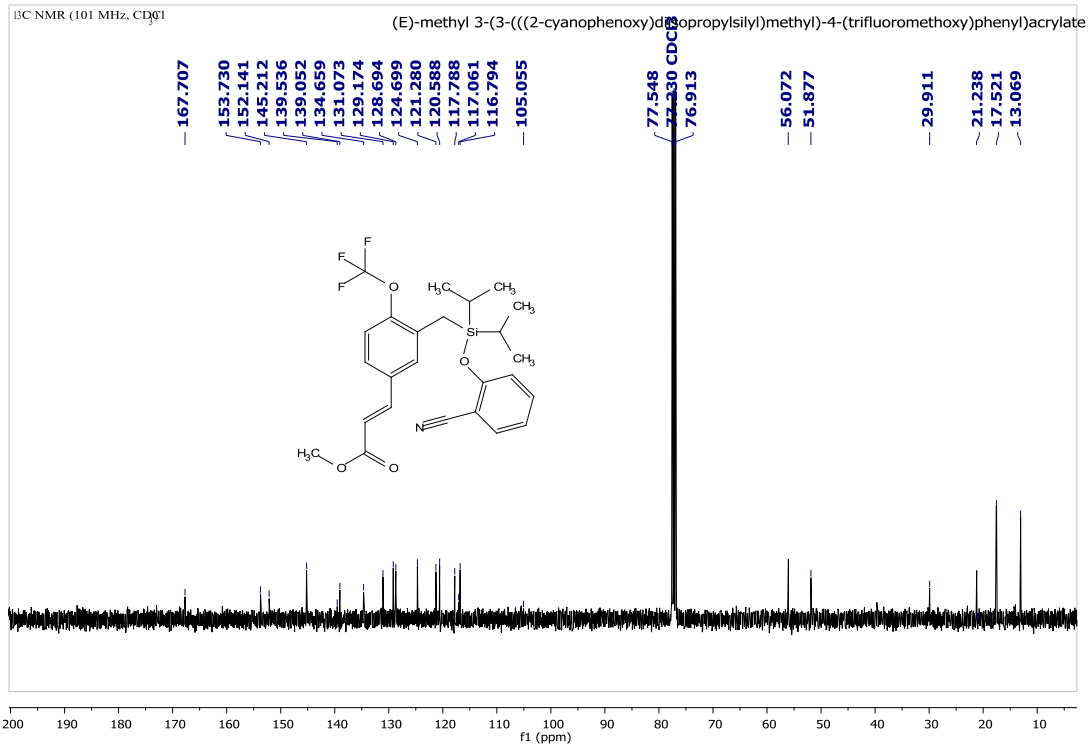
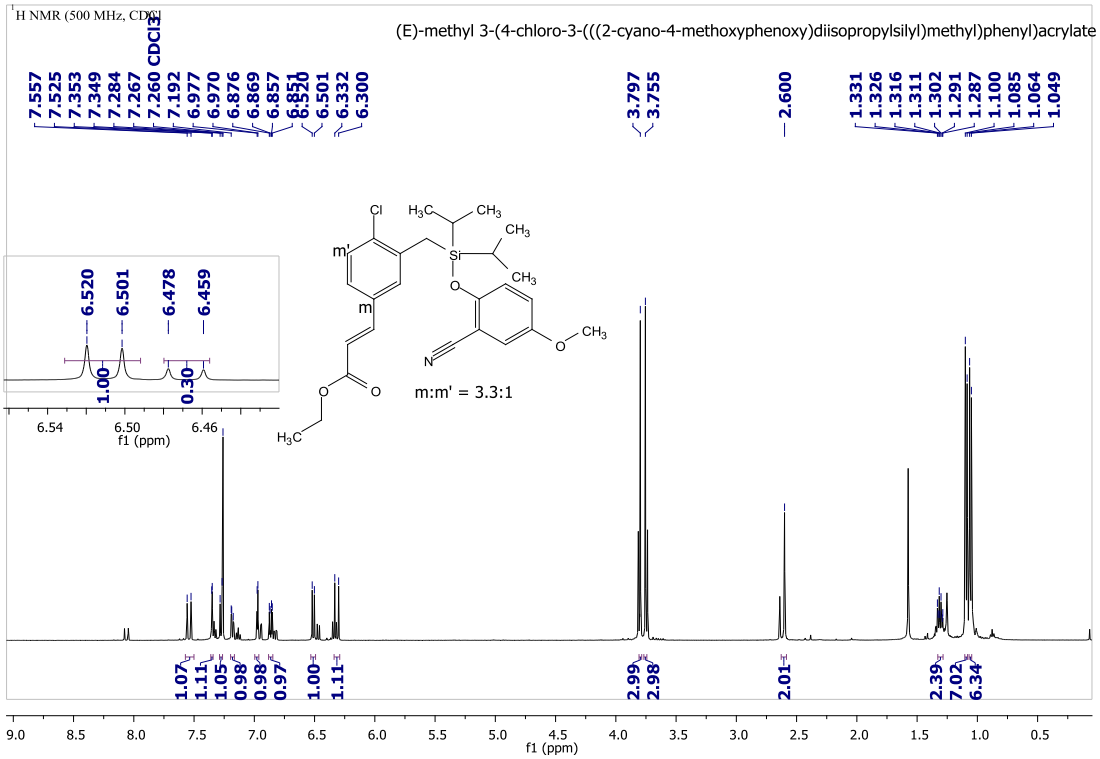


Table 1, entry 2d$_{mono}$:



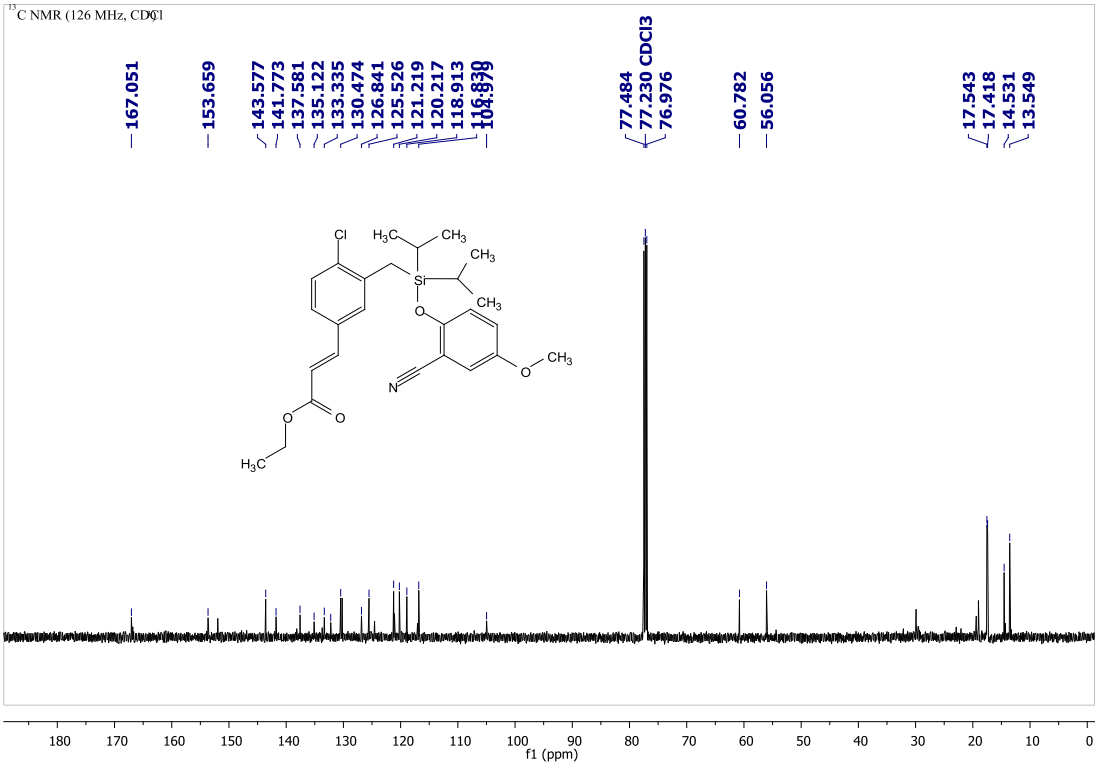
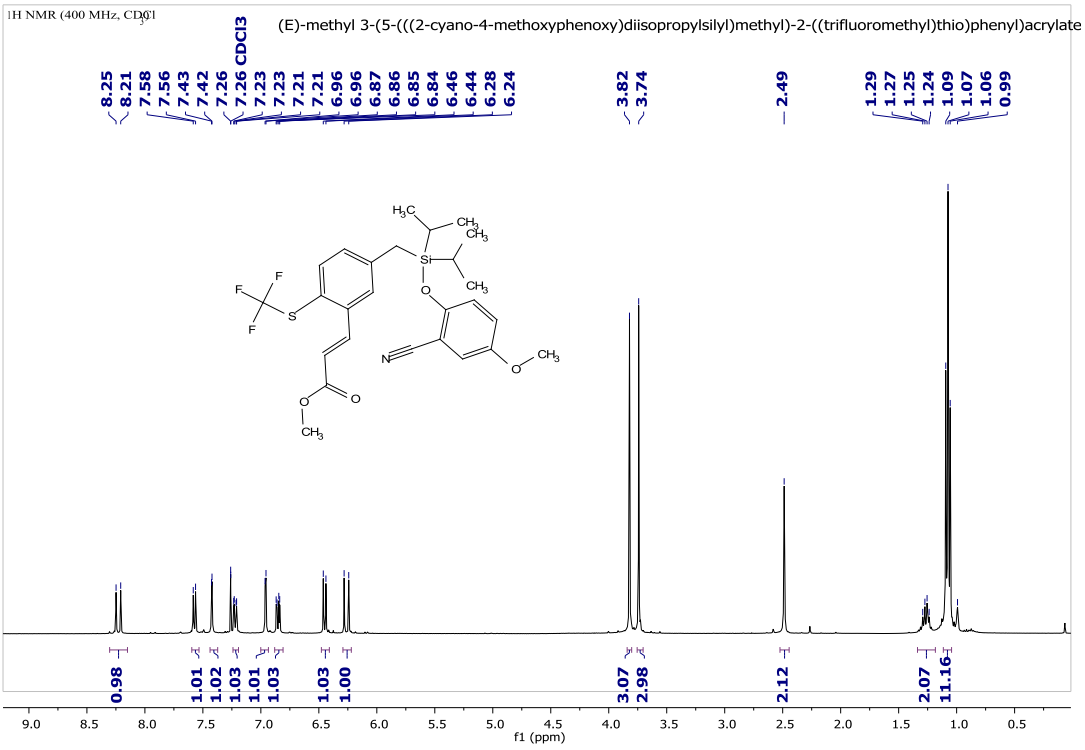


Table 1, entry 2e$_{mono}$:



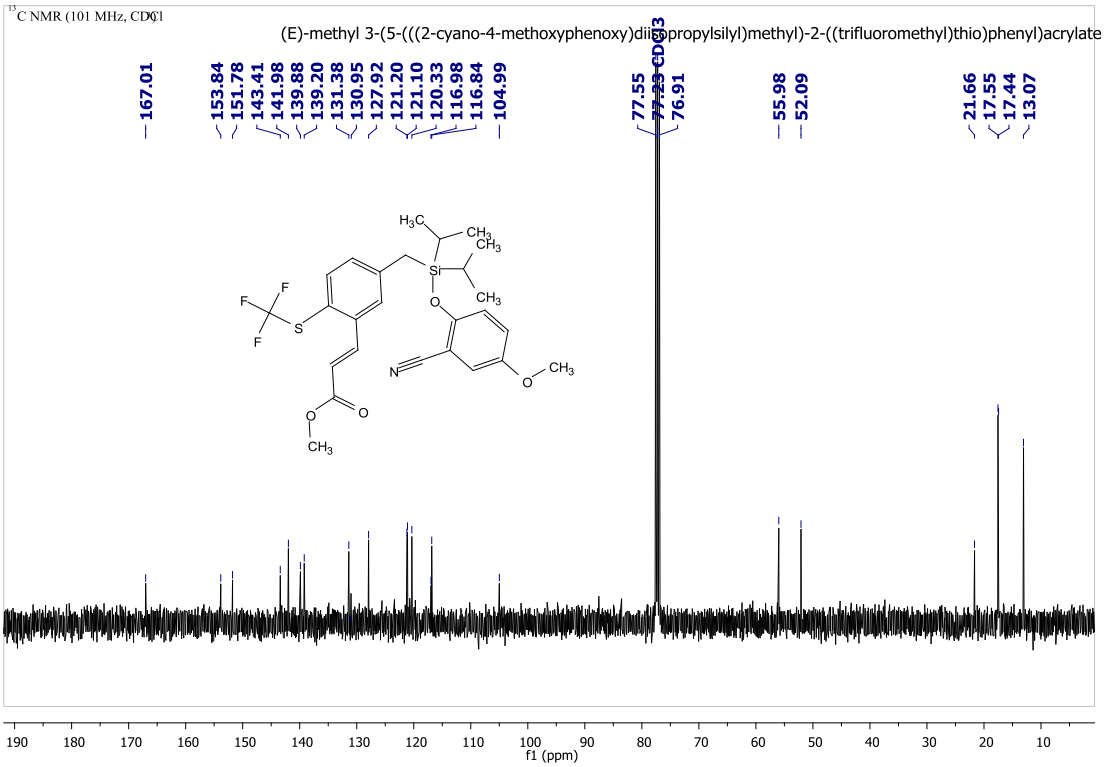
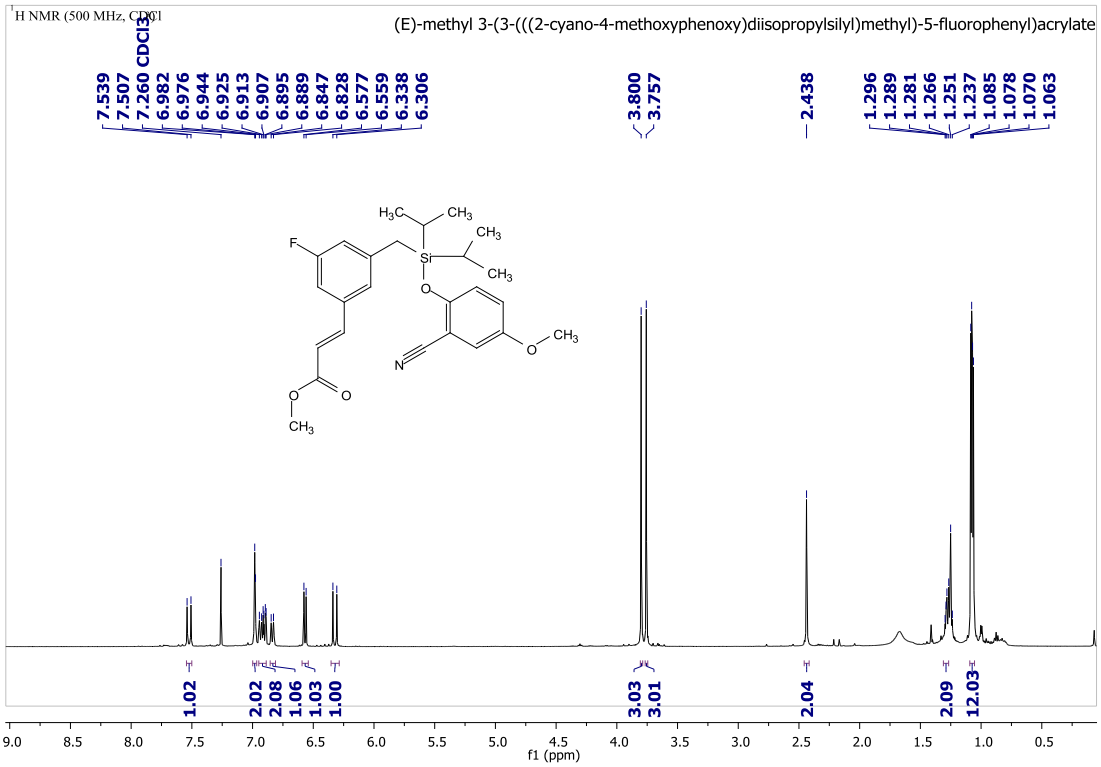


Table 1, entry 2f:



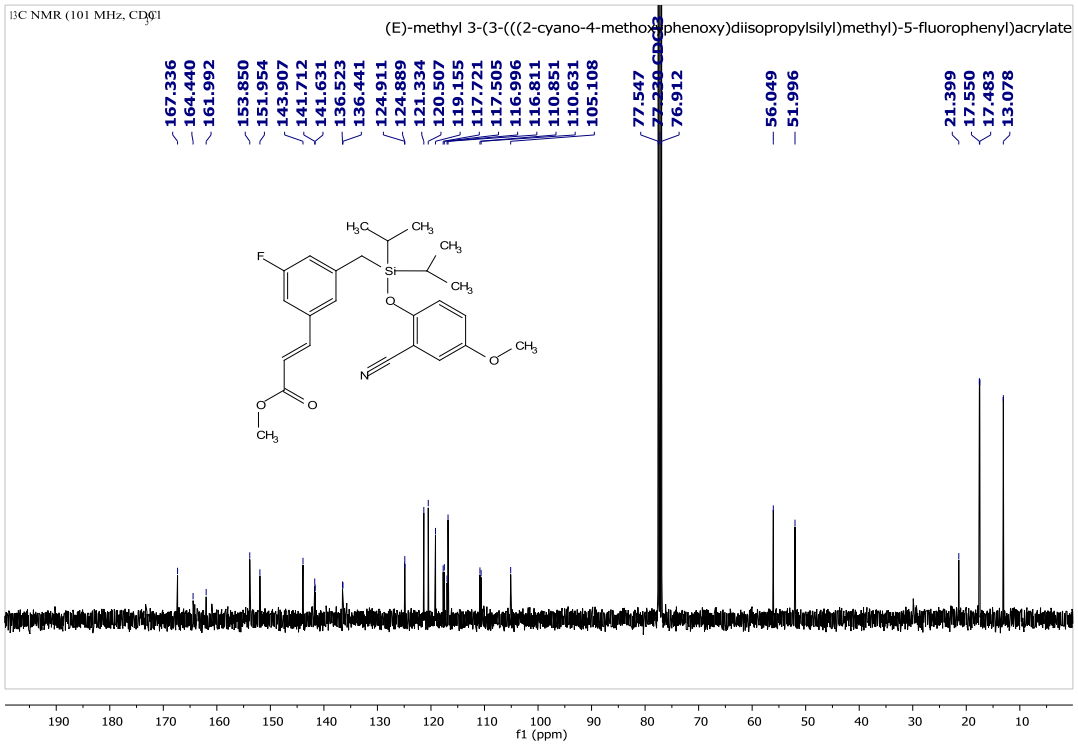
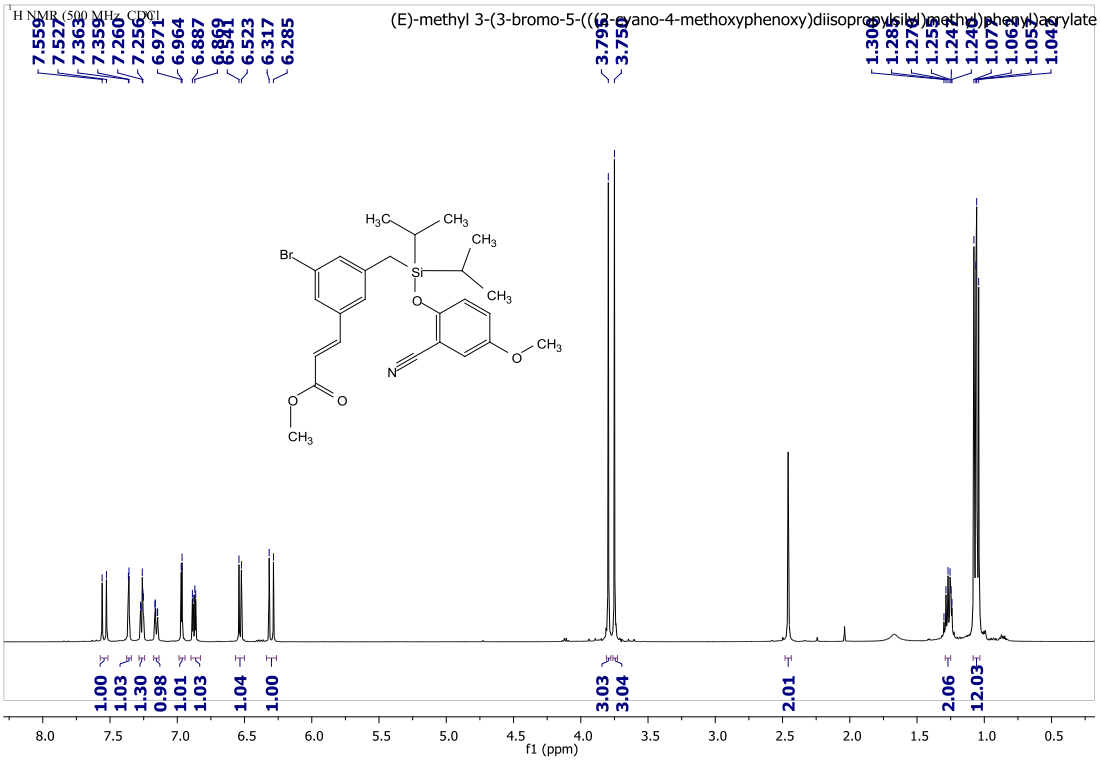


Table 1, entry 2g:



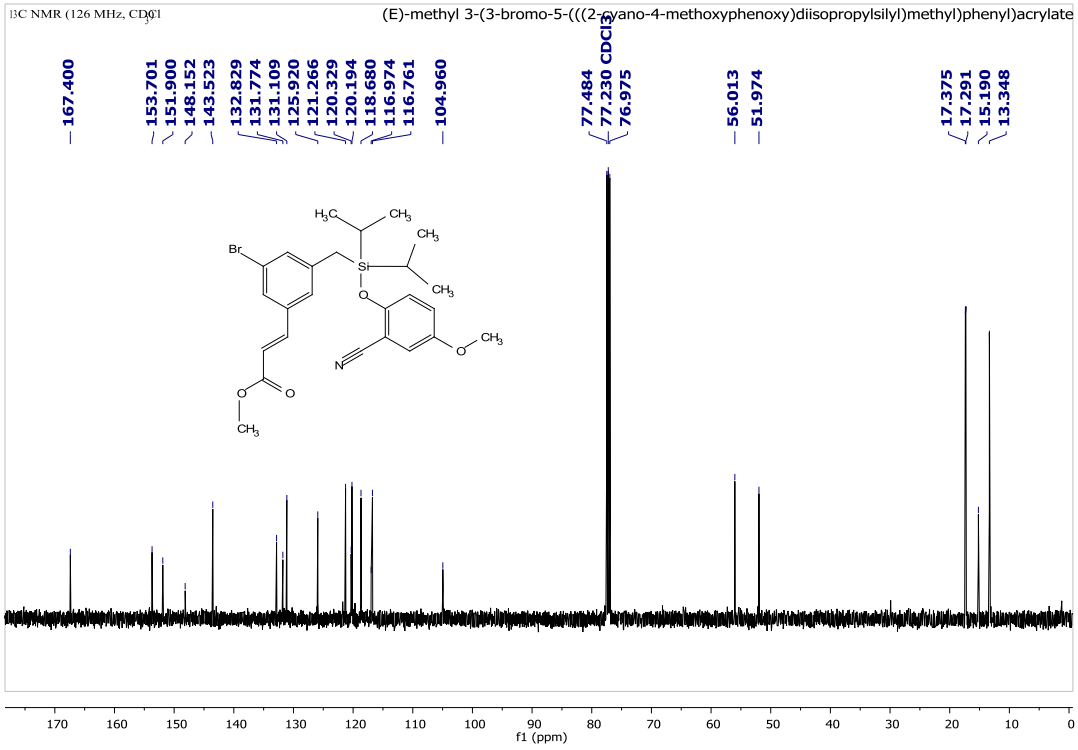
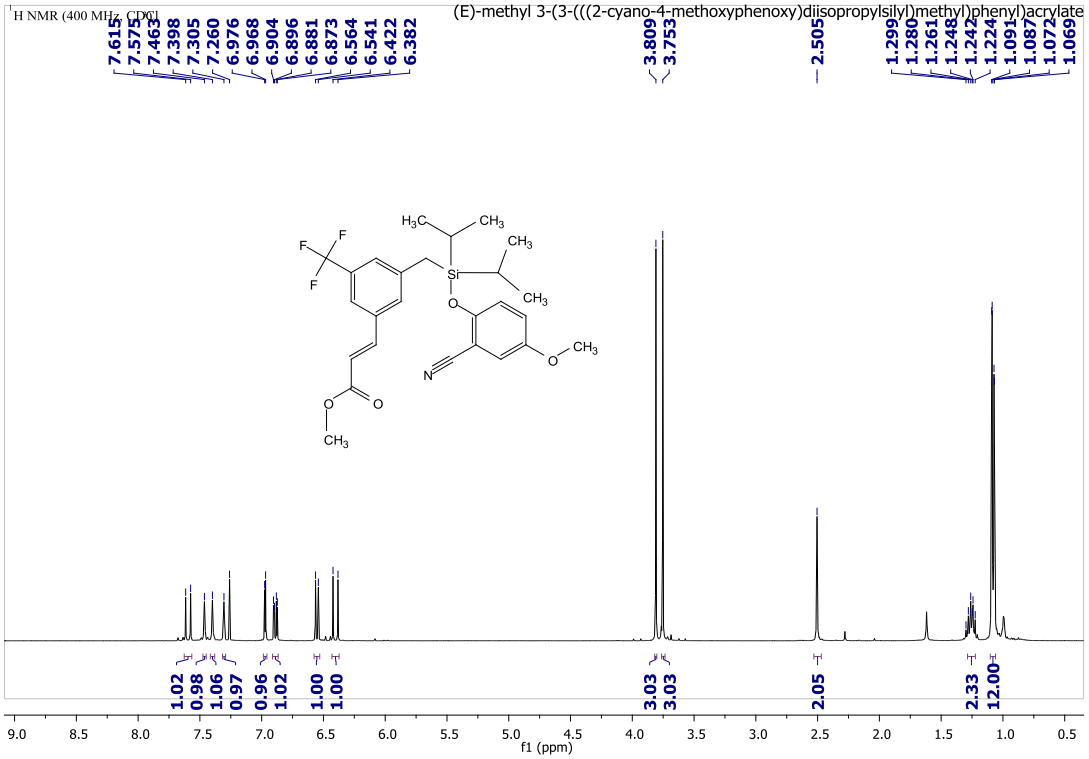


Table 1, entry 2h:



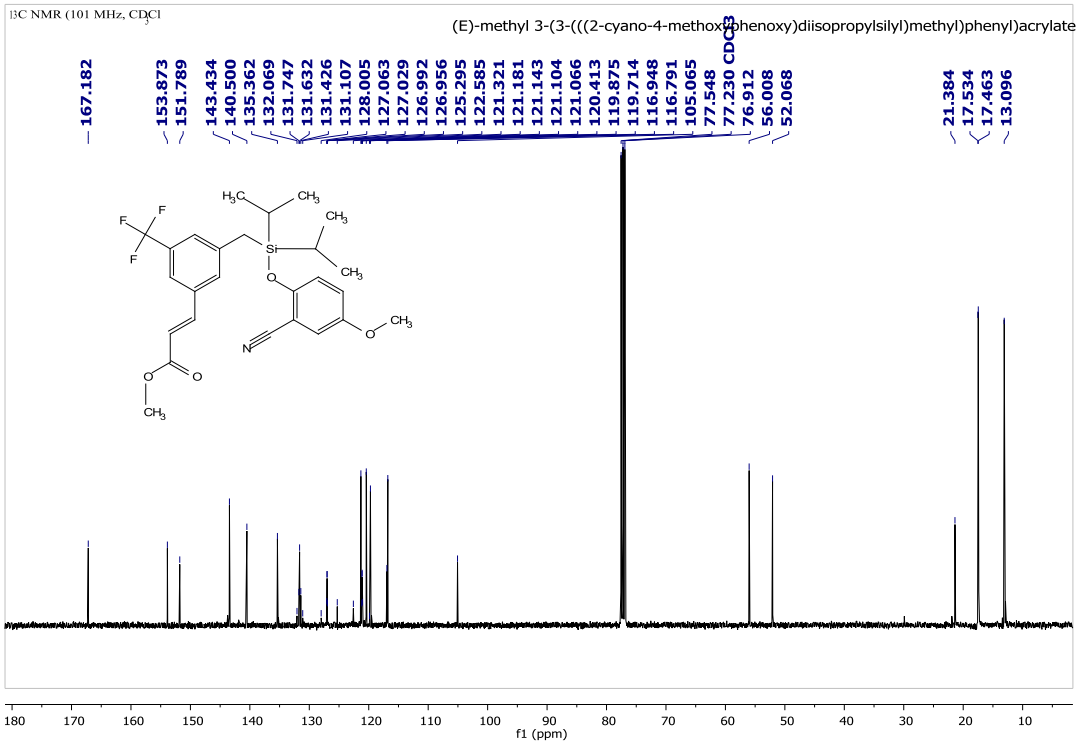
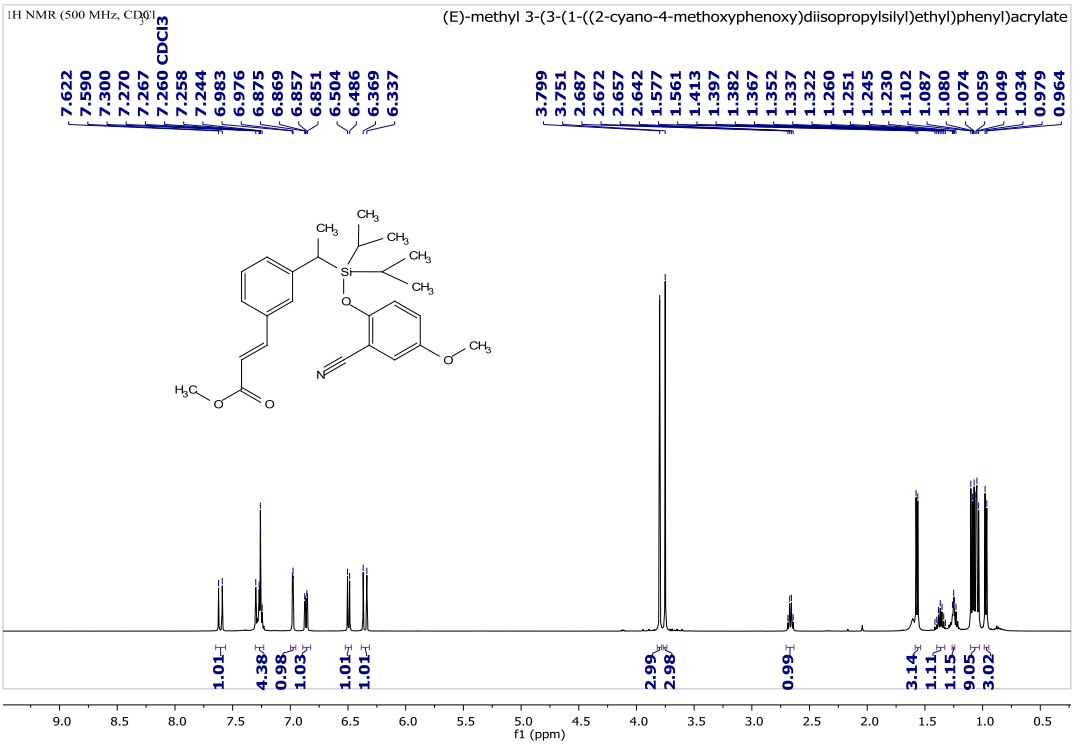


Table 1, entry 2i$_{mono}$:



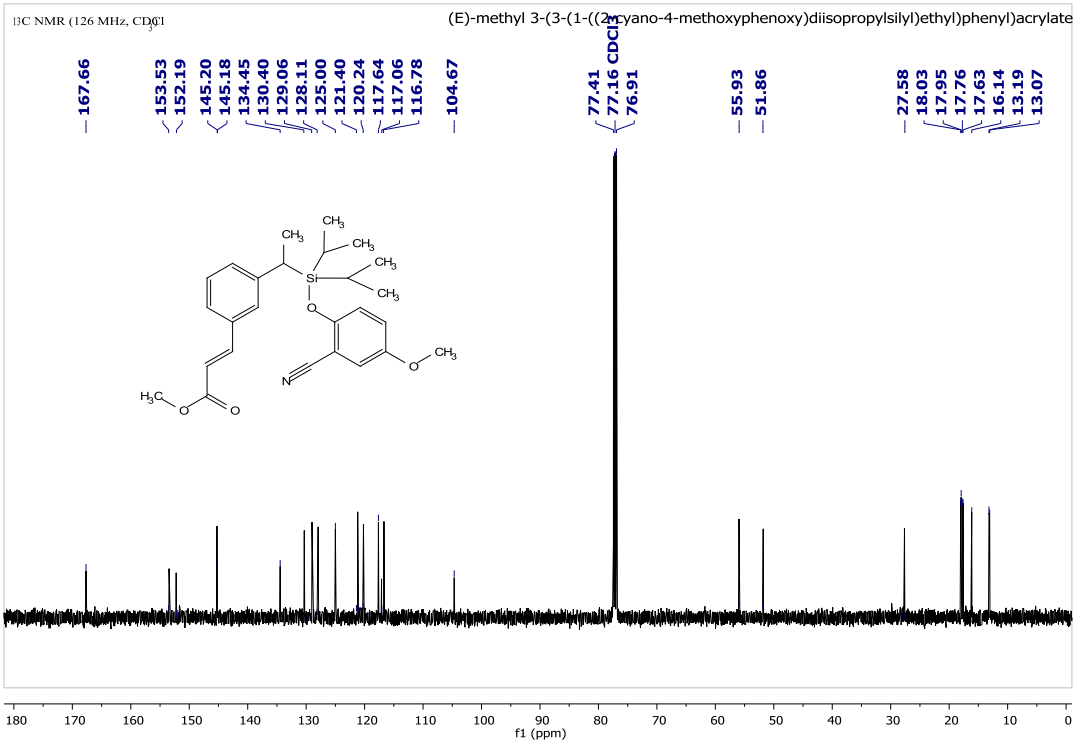
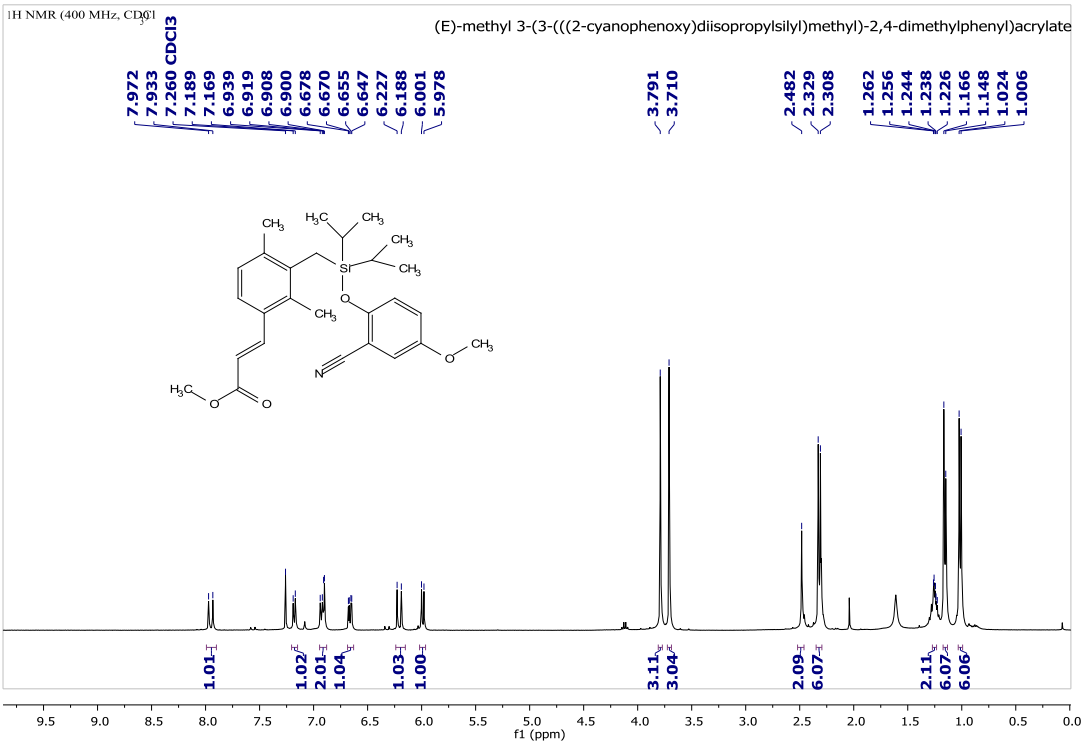
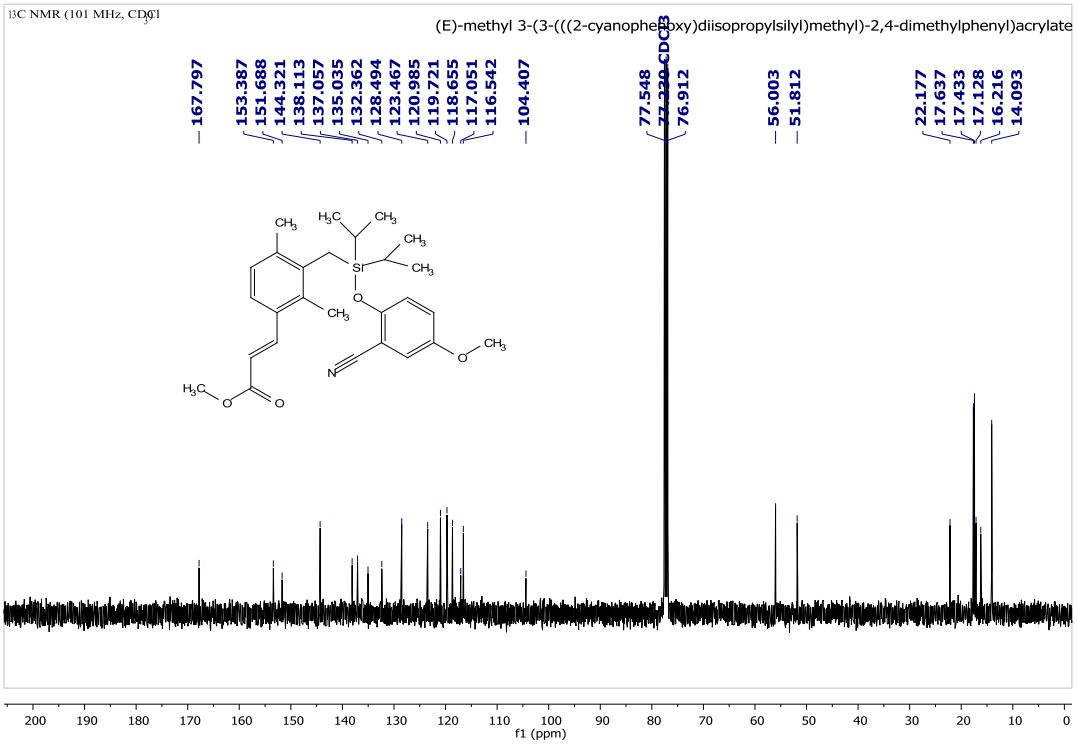


Table 1, entry 2j:





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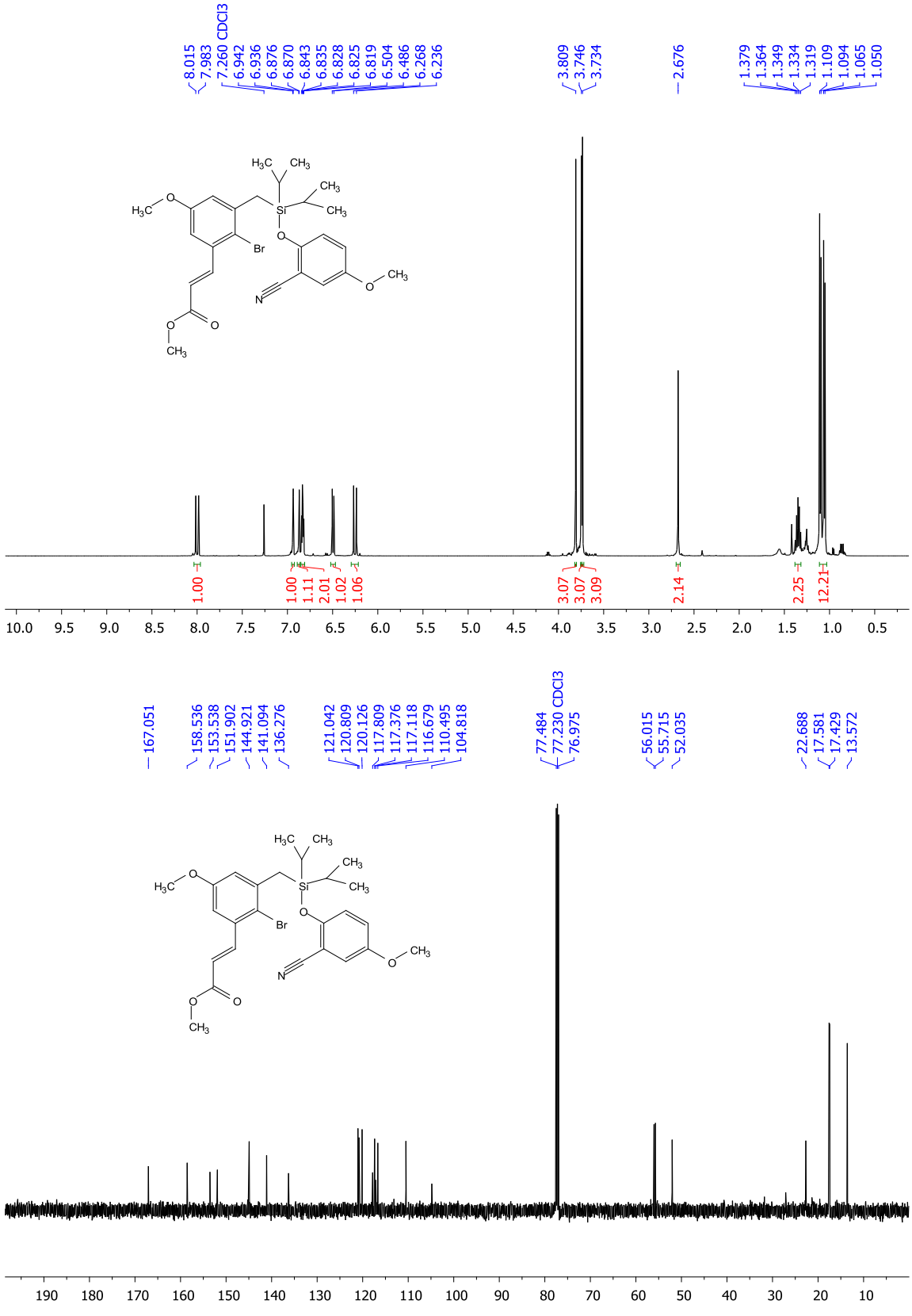
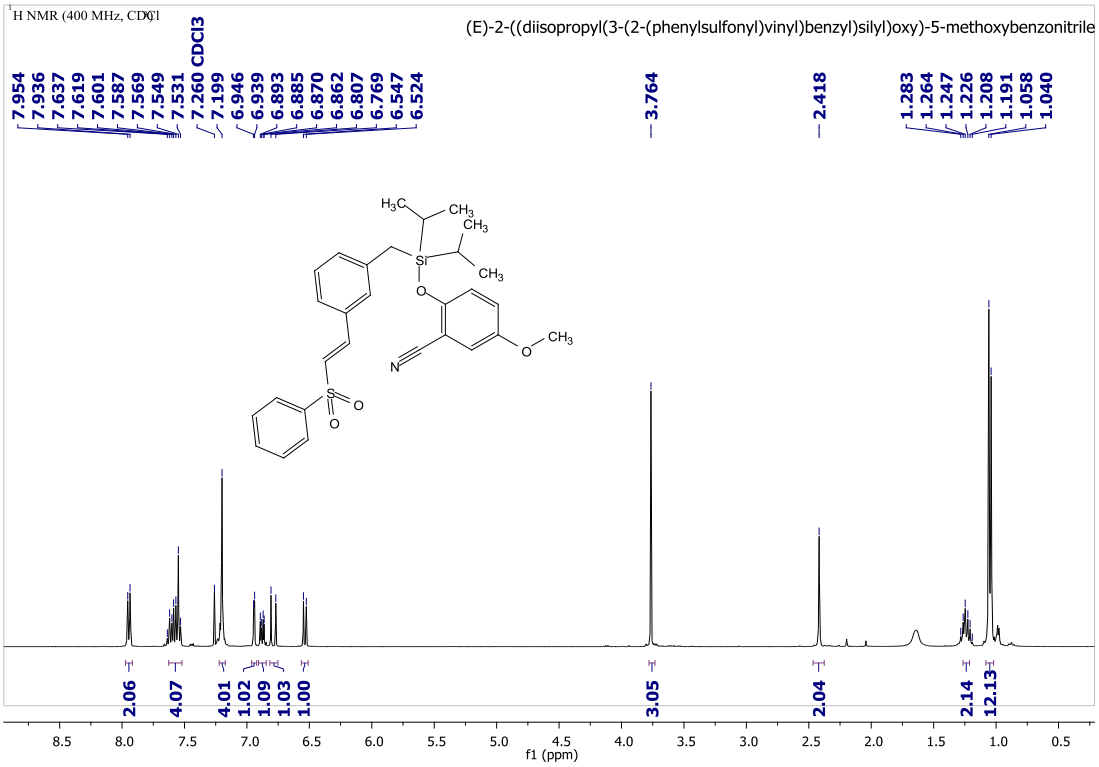


Table 2, entry 3a:



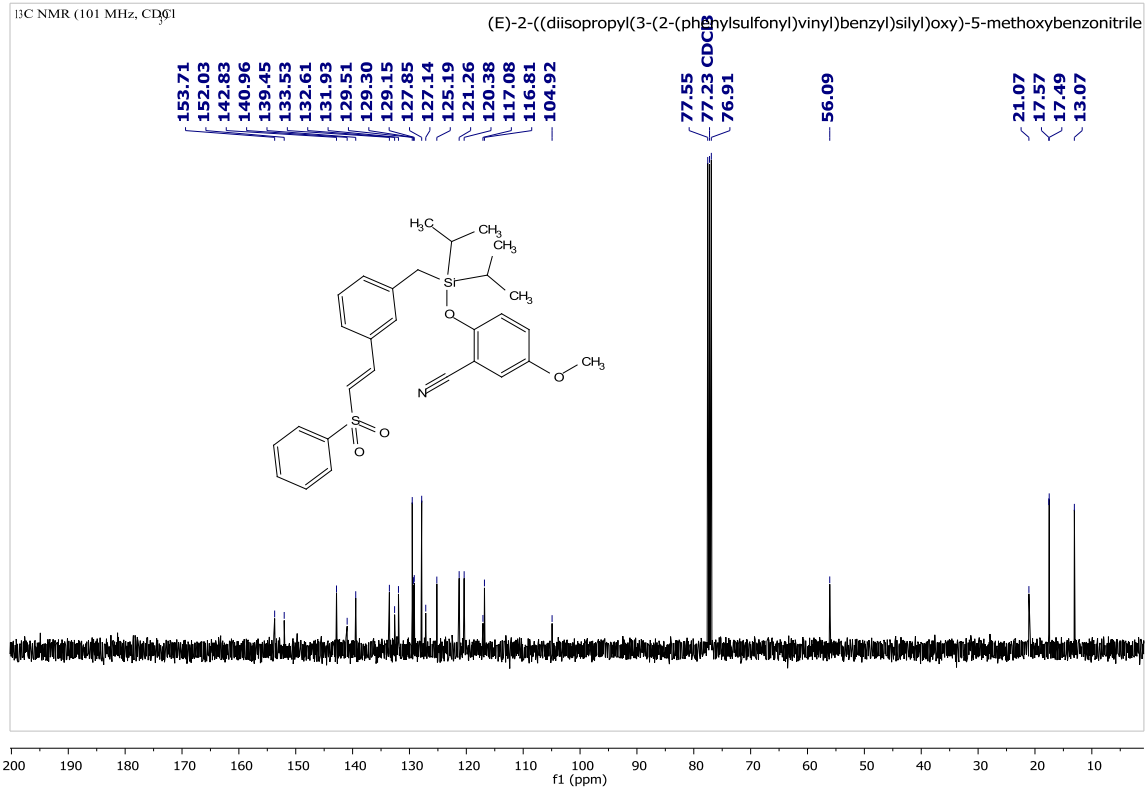
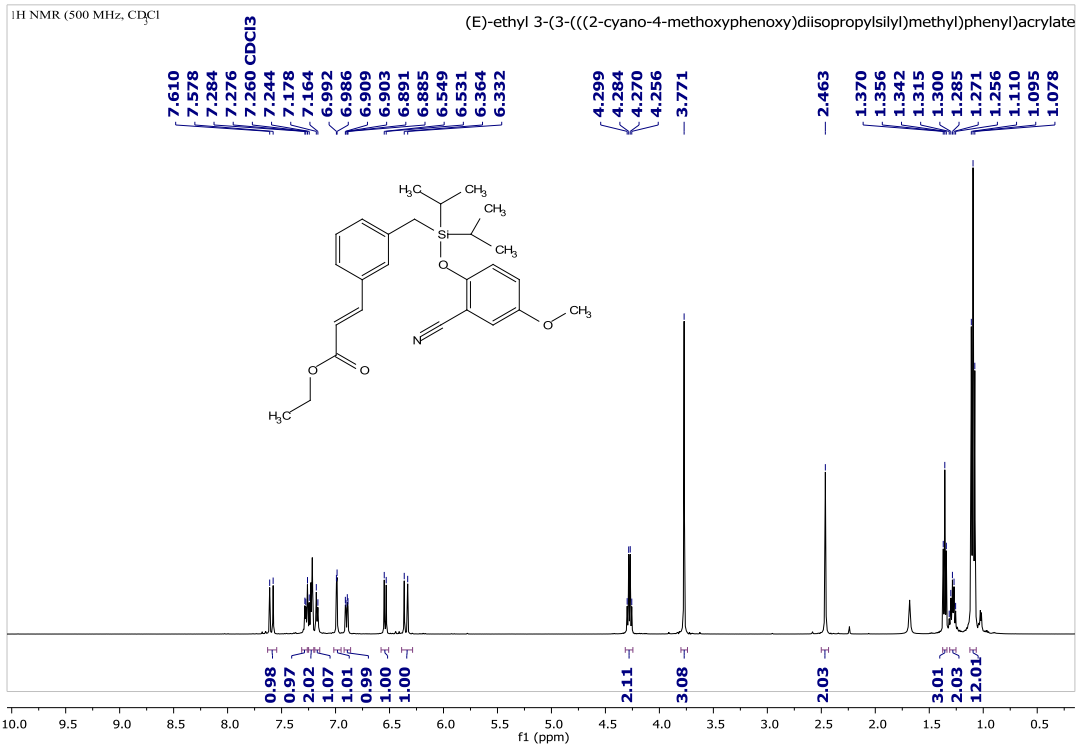


Table 2, entry 3b$_{mono}$:



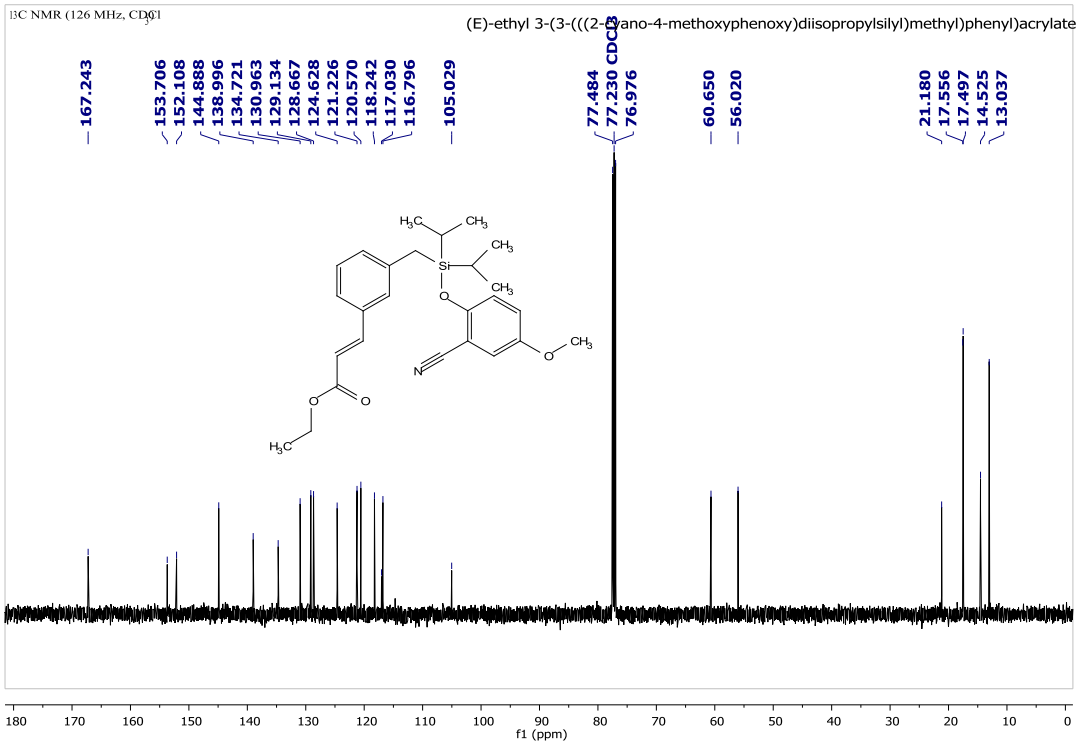
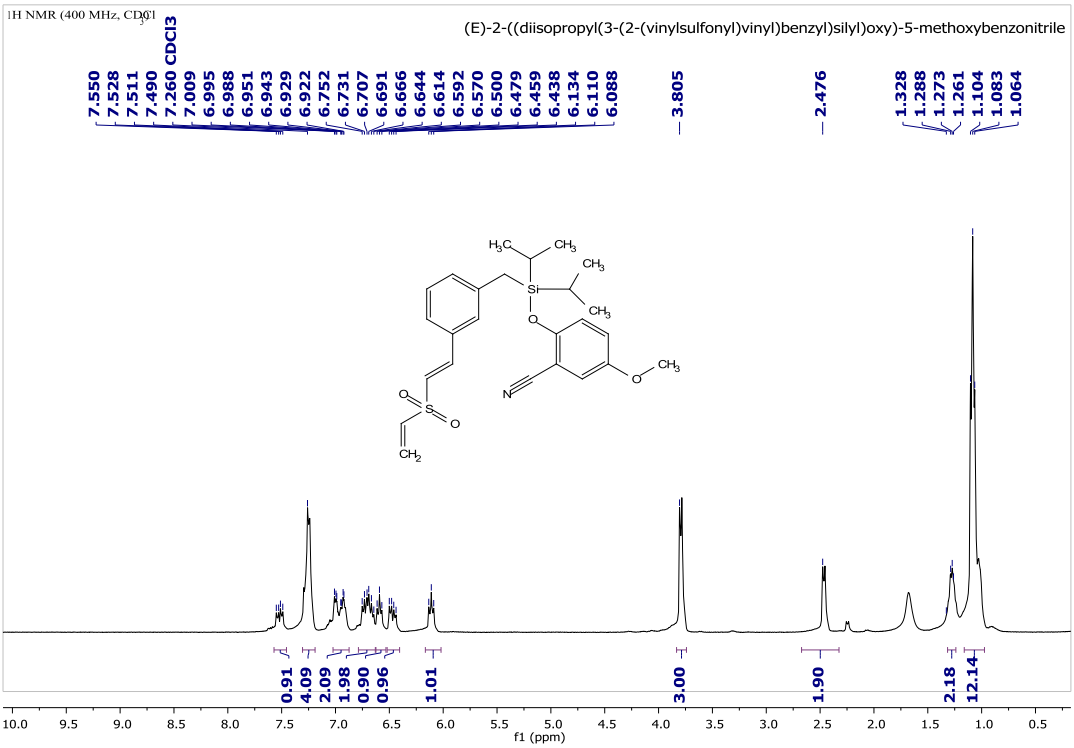
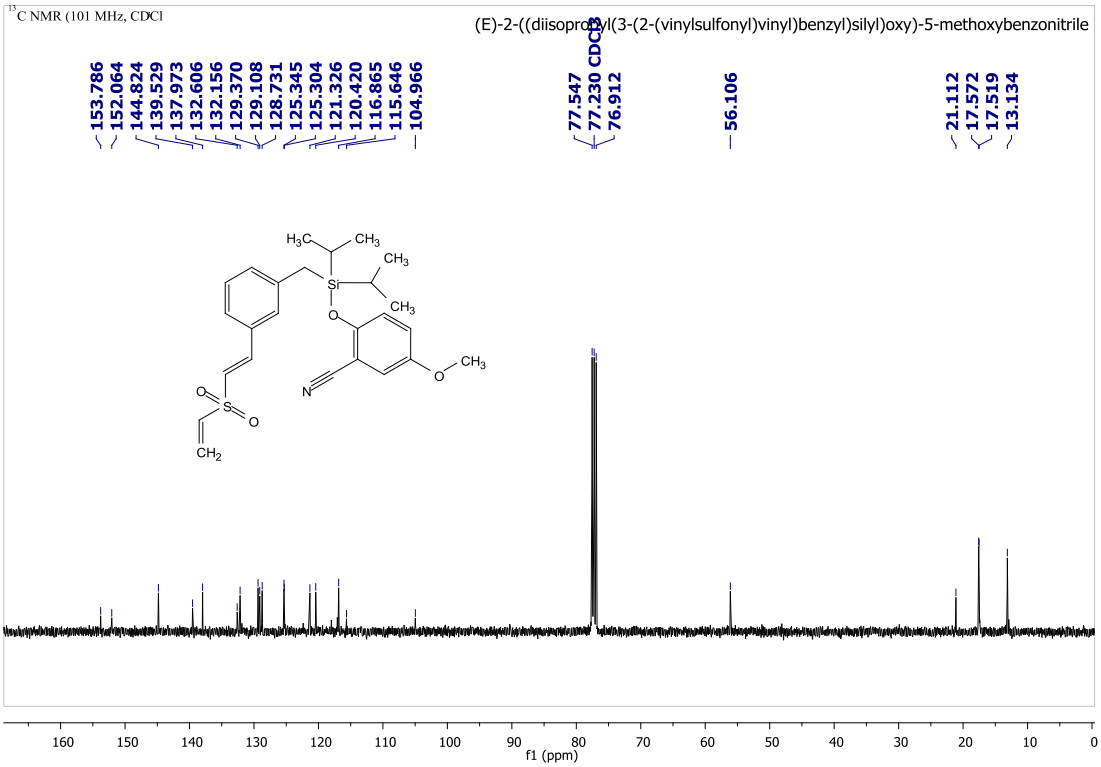


Table 2, entry 3c:





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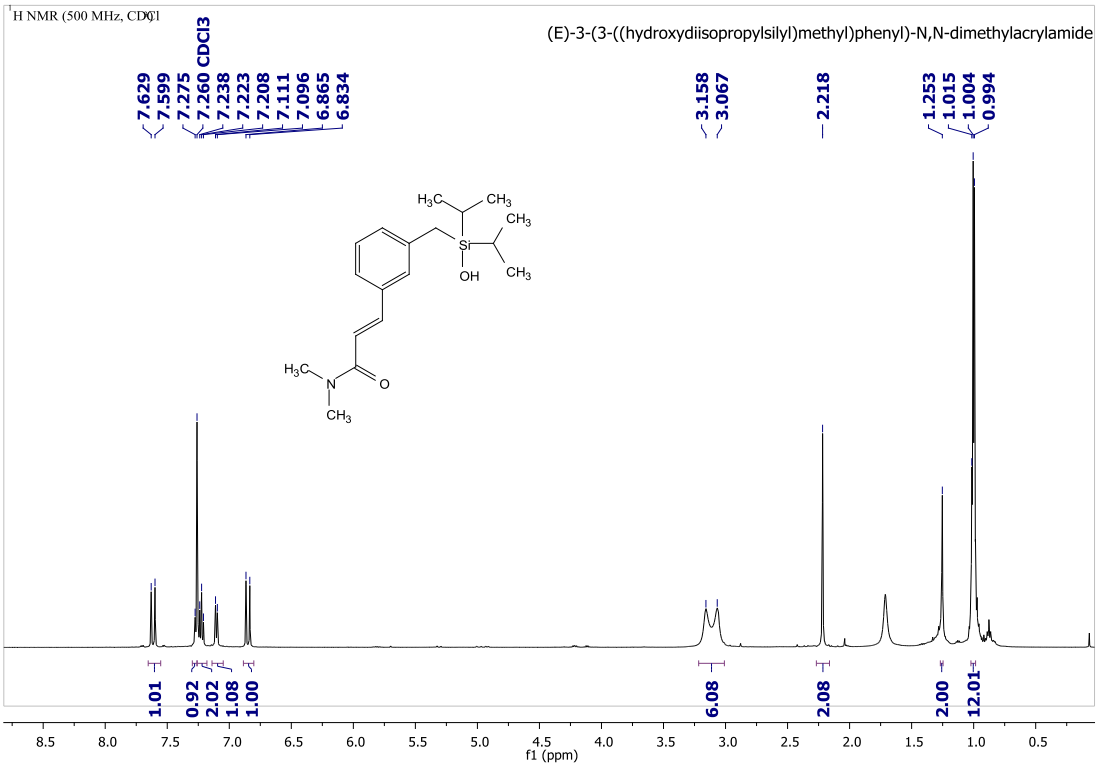


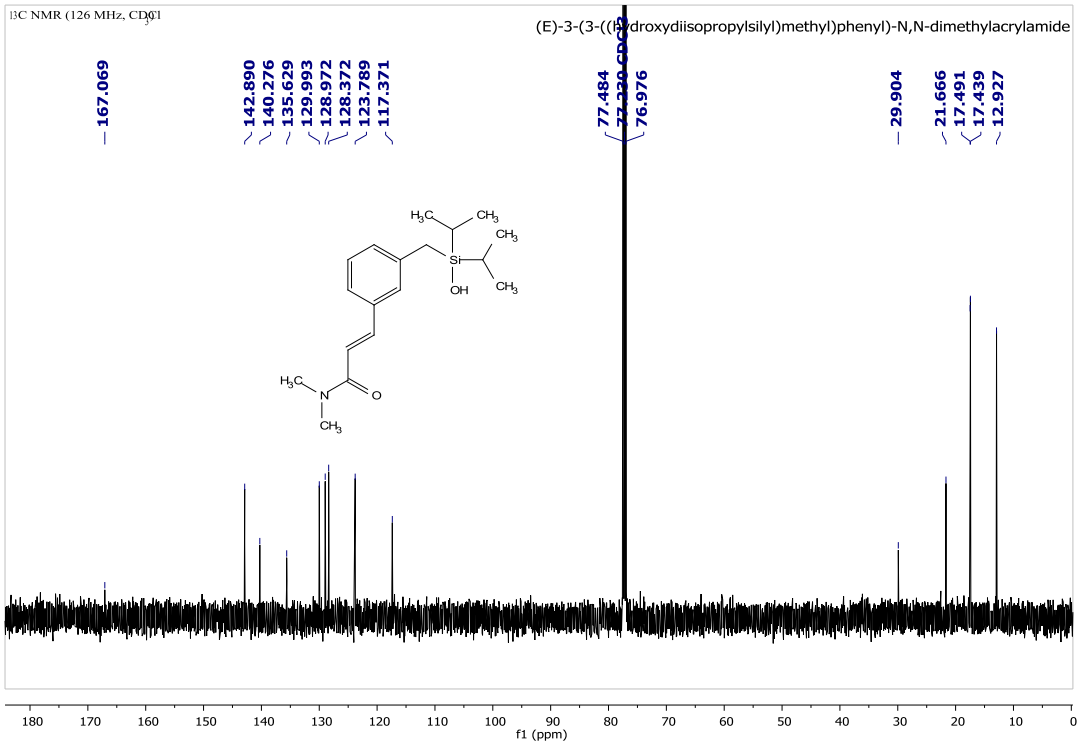
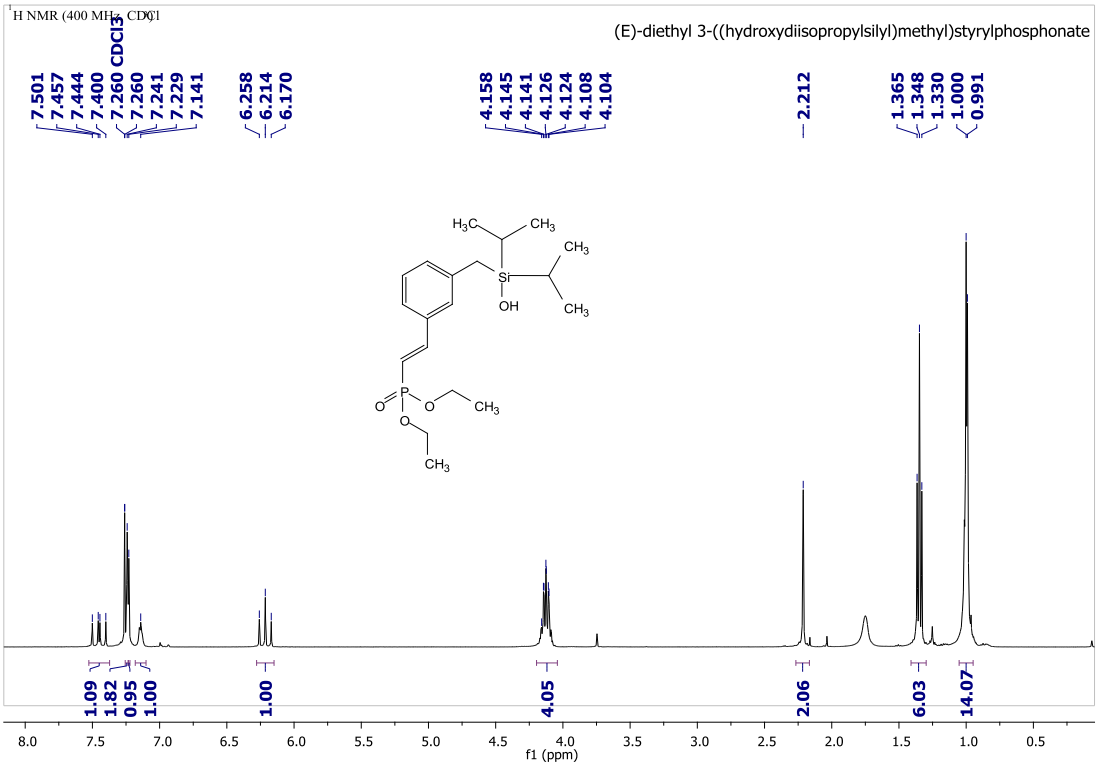


Table 2, entry 3e:



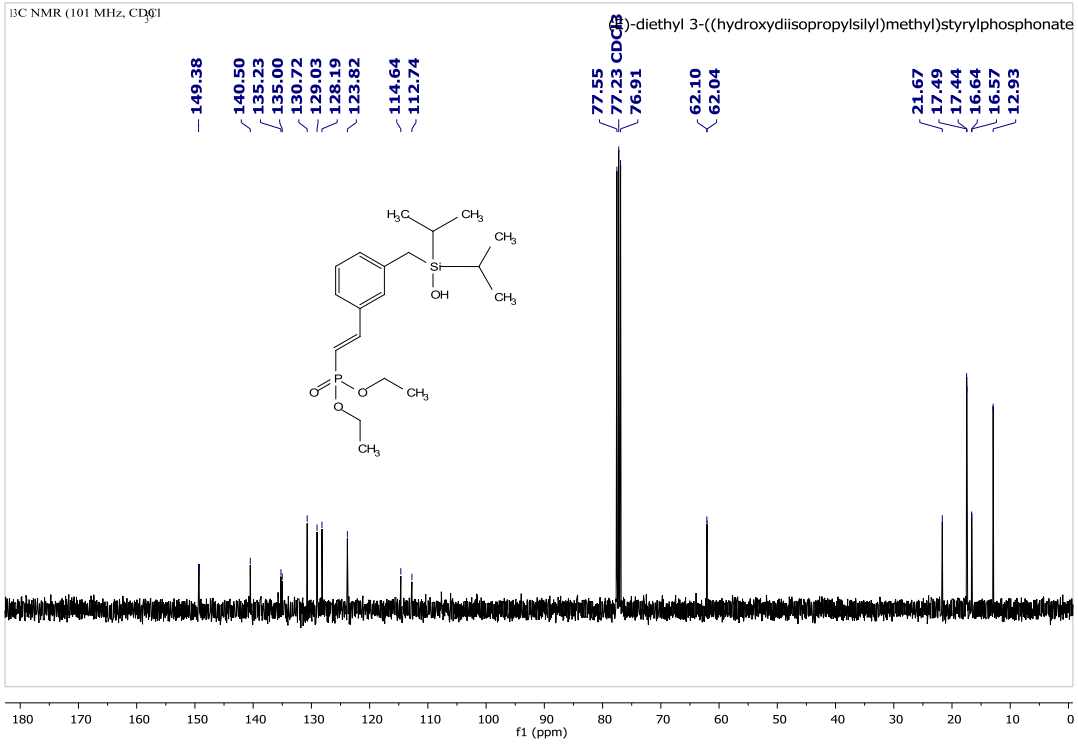
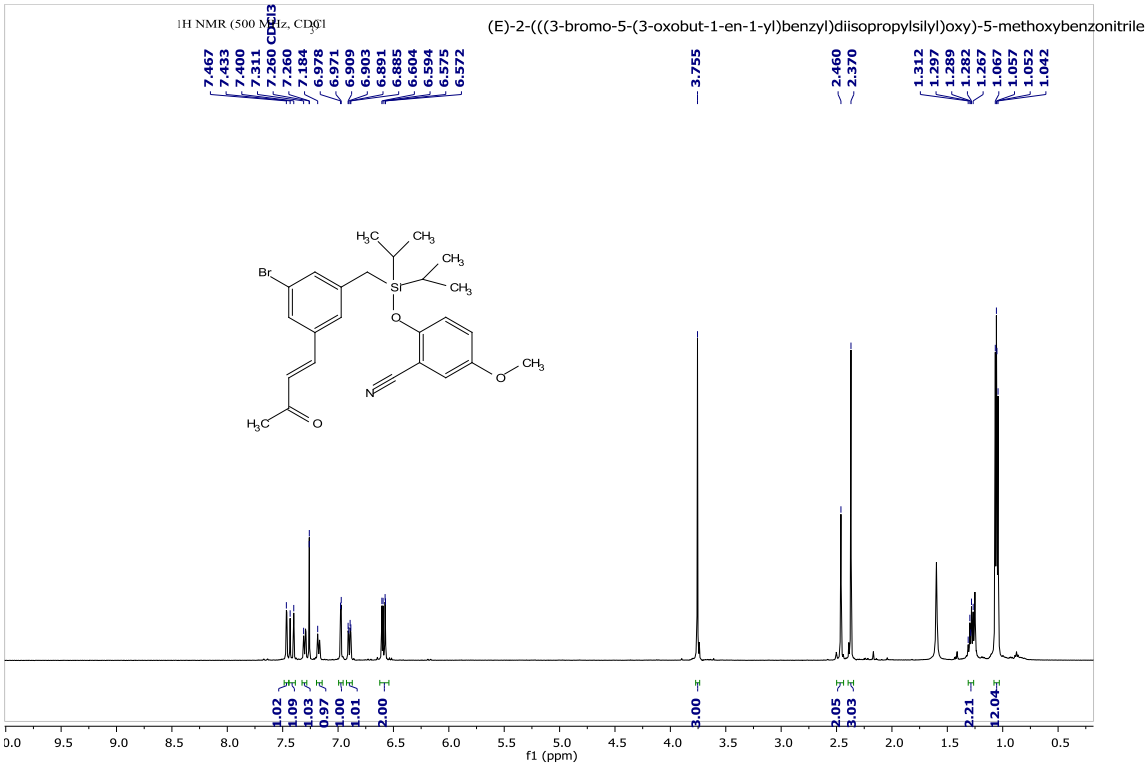


Table 2, entry 3f:



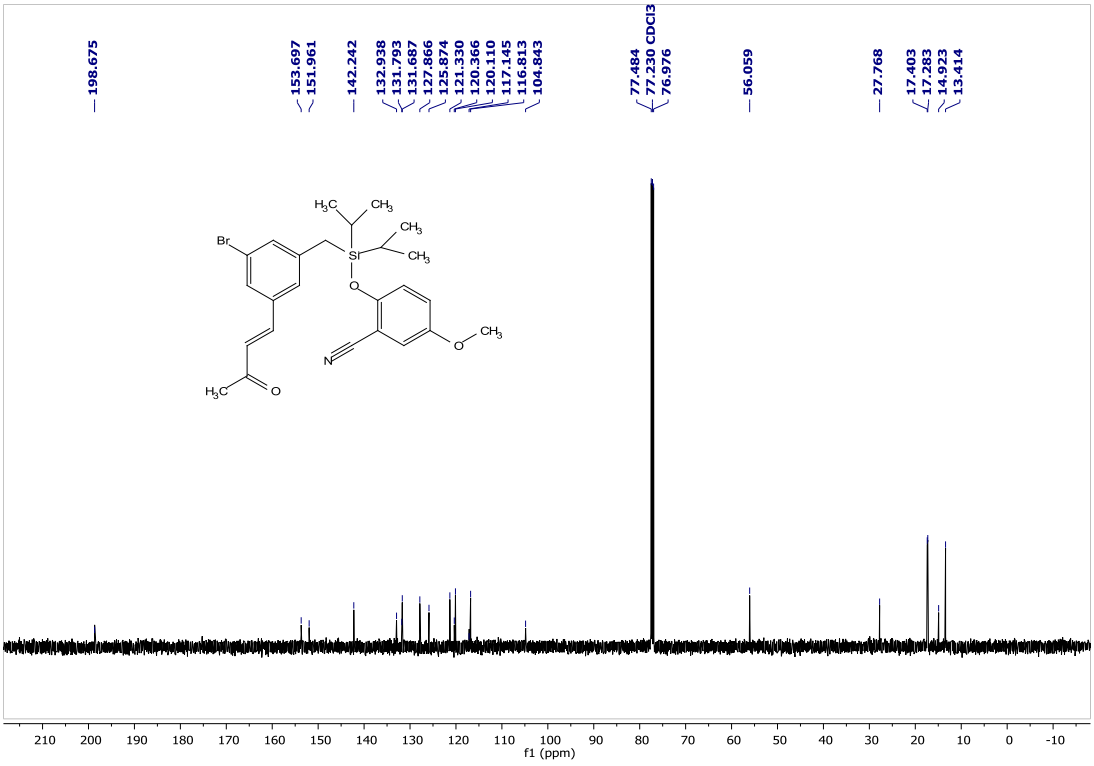
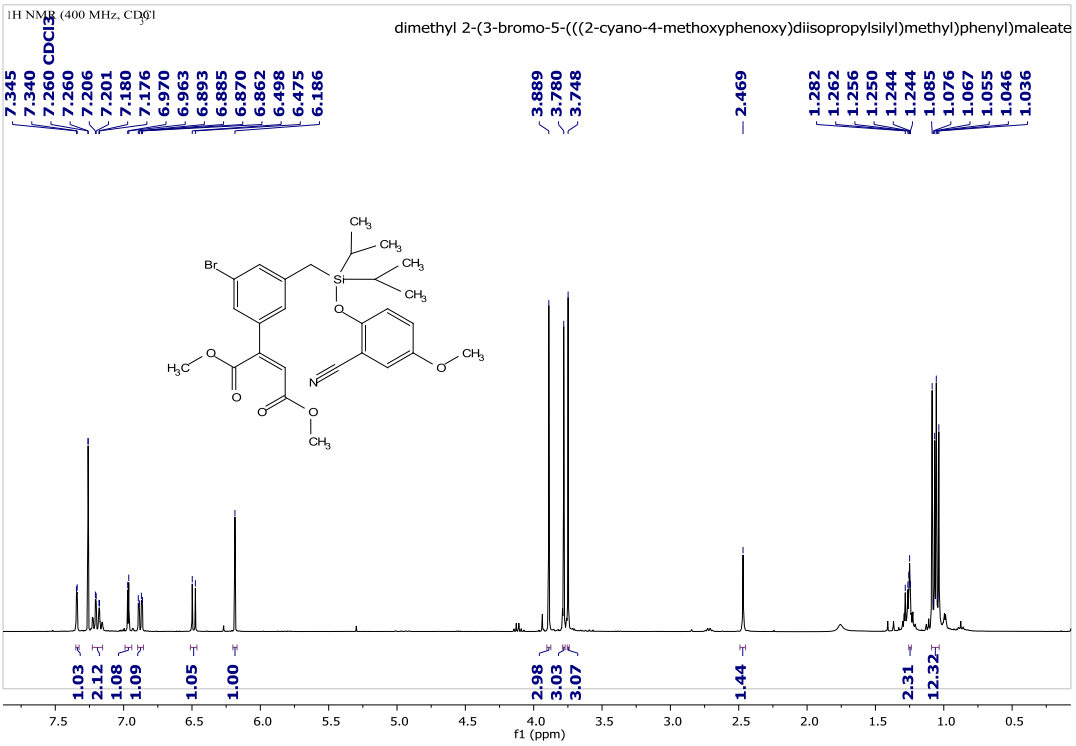


Table 2, entry 3g:



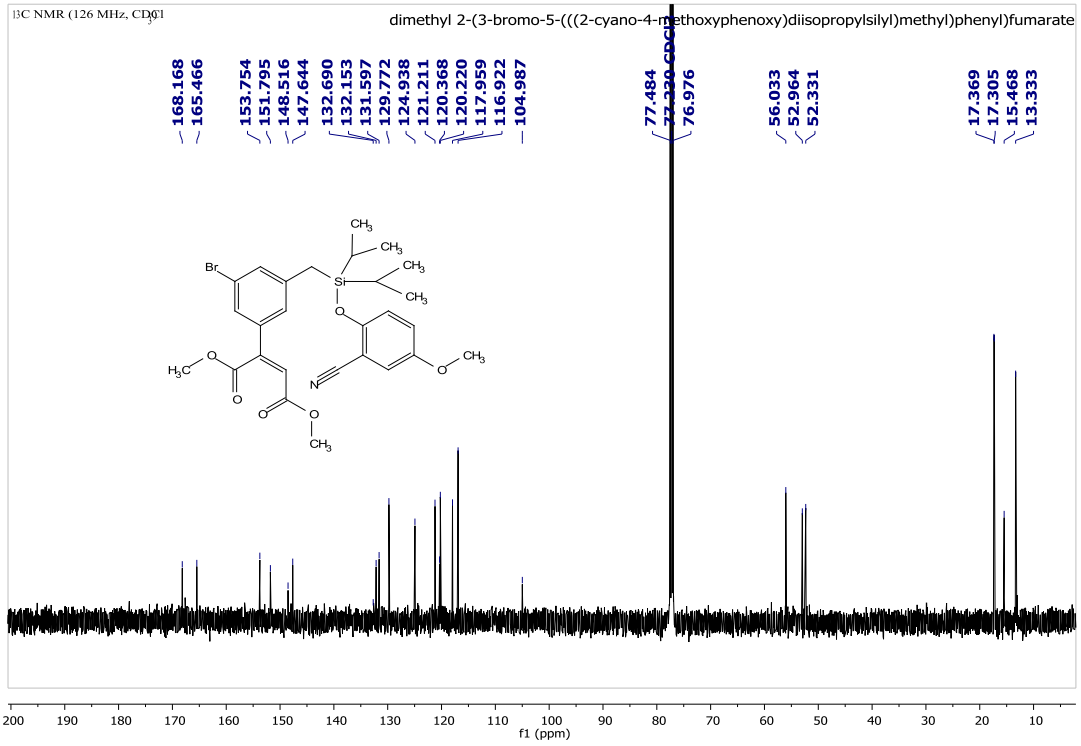
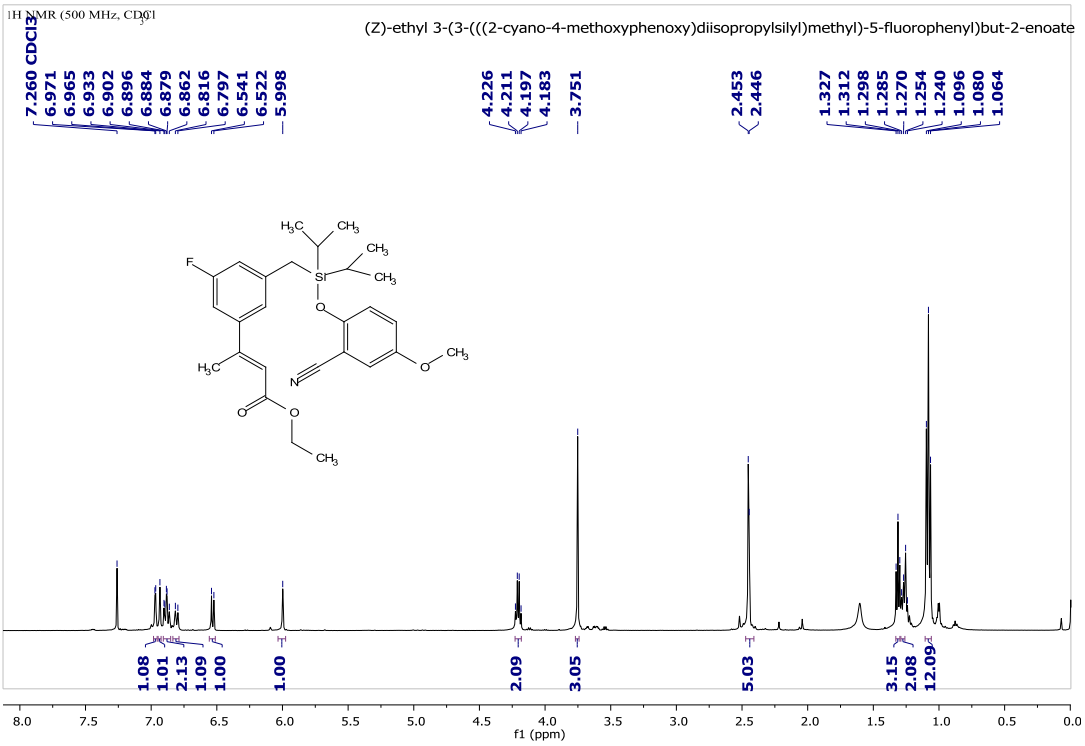


Table 2, entry 3h:



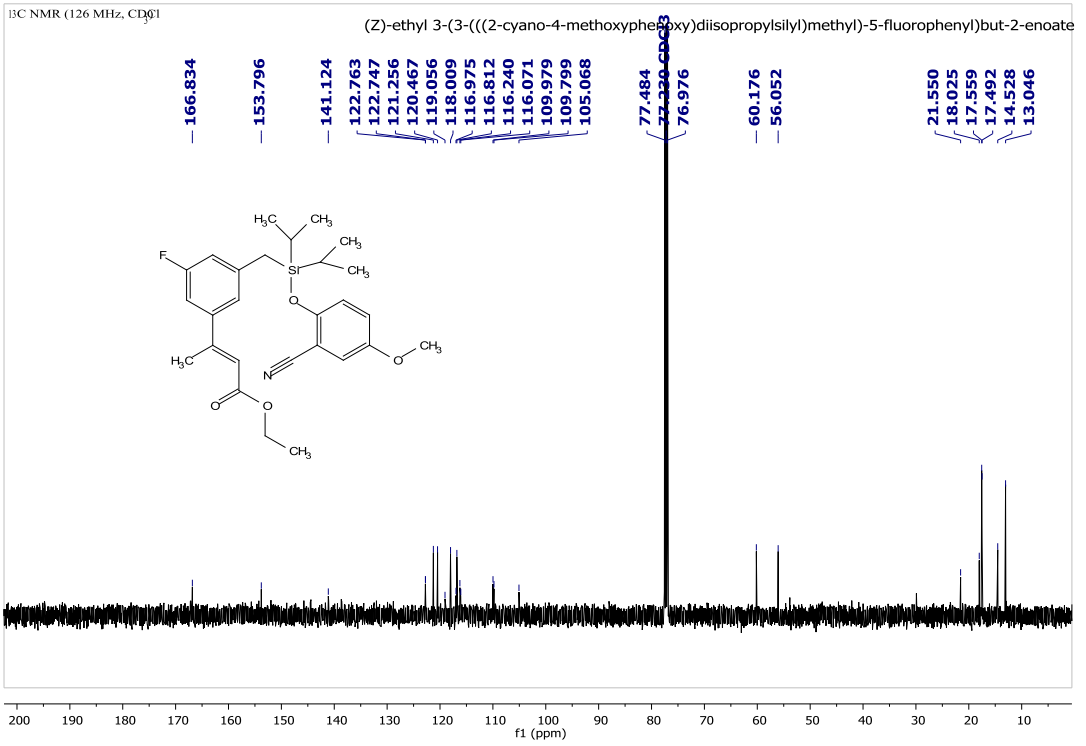
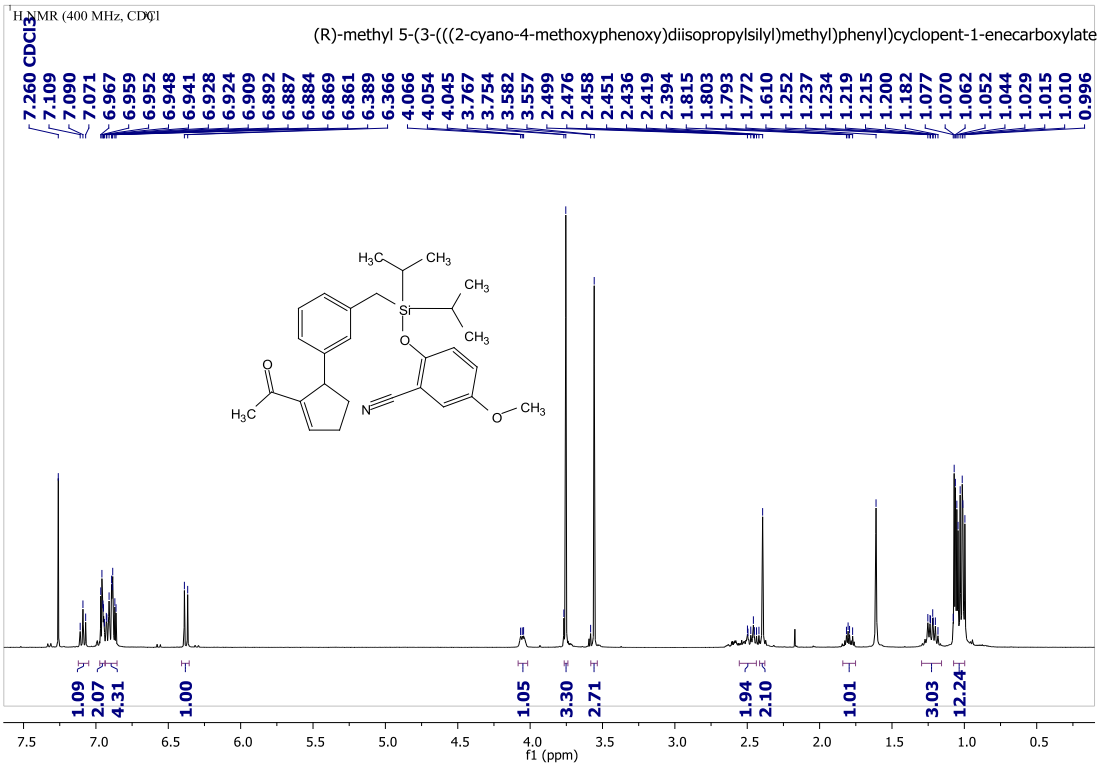


Table 2, entry 3i:



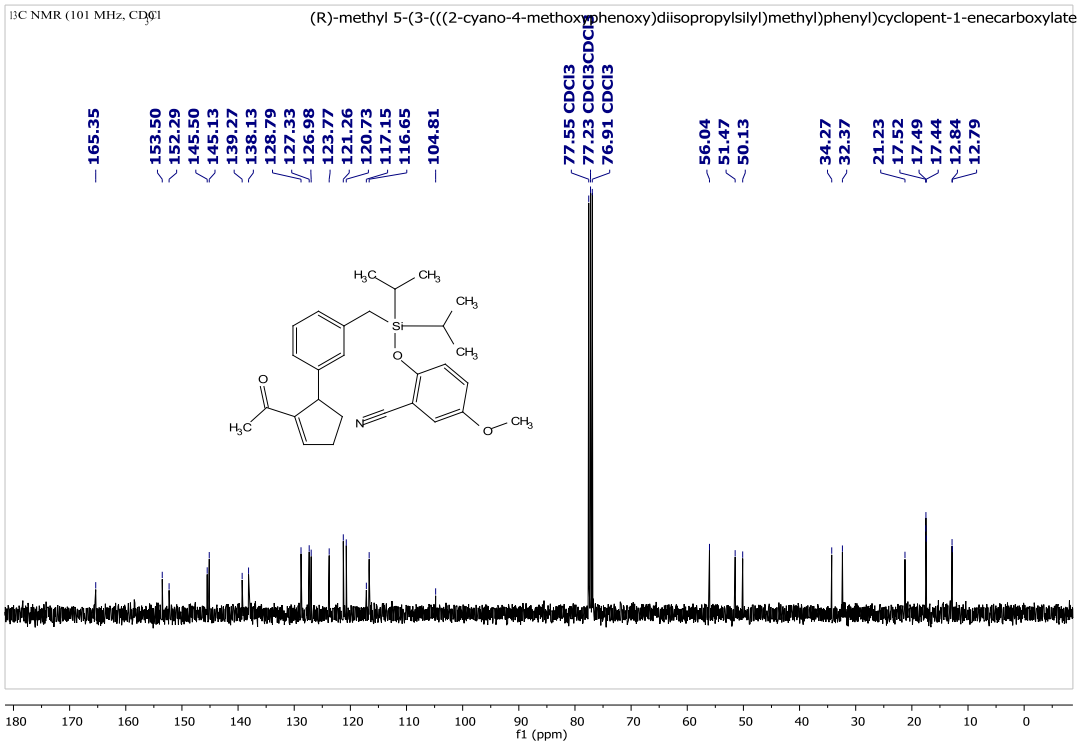
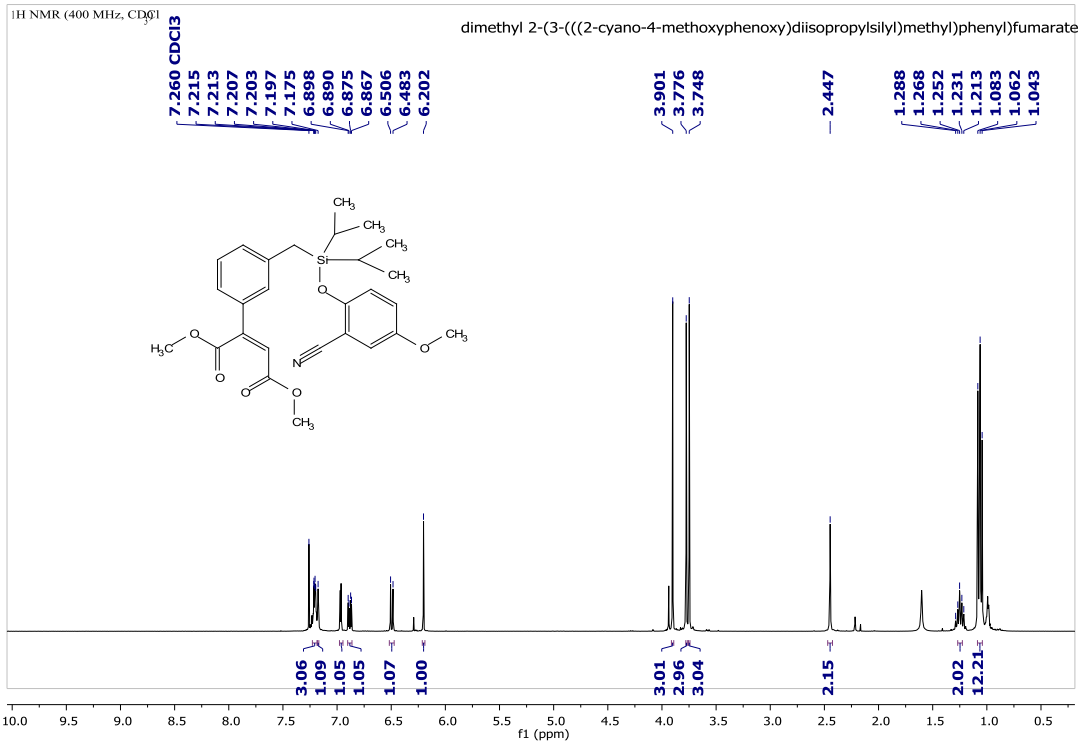


Table 3, entry 4d-SM:



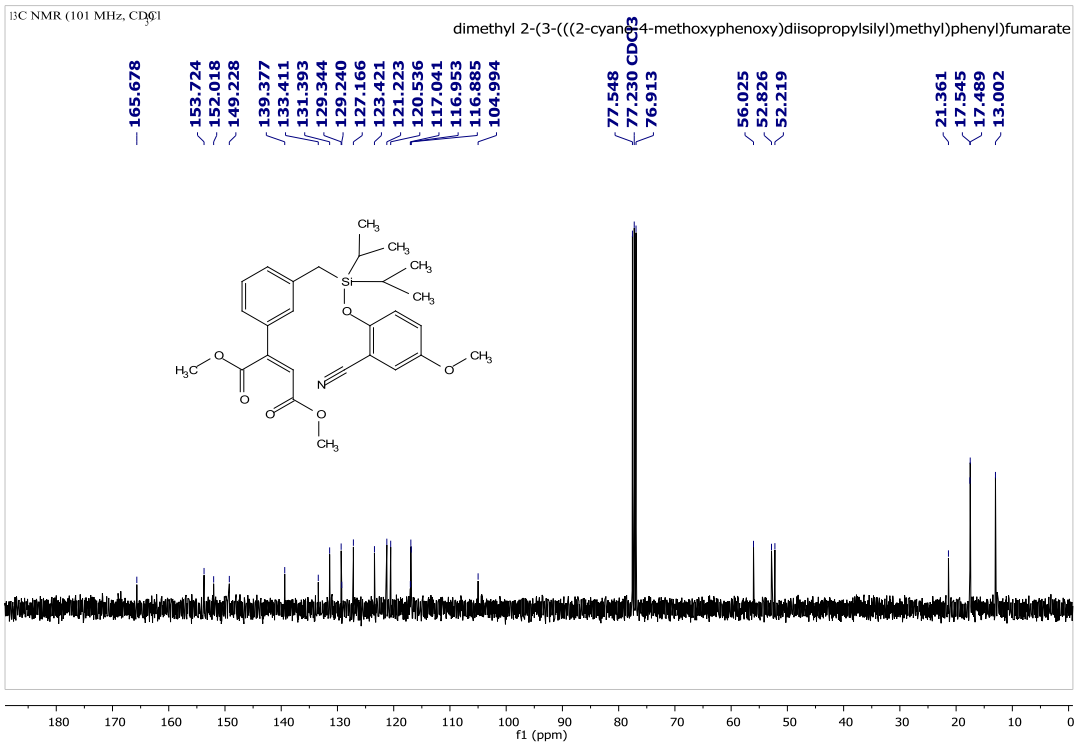
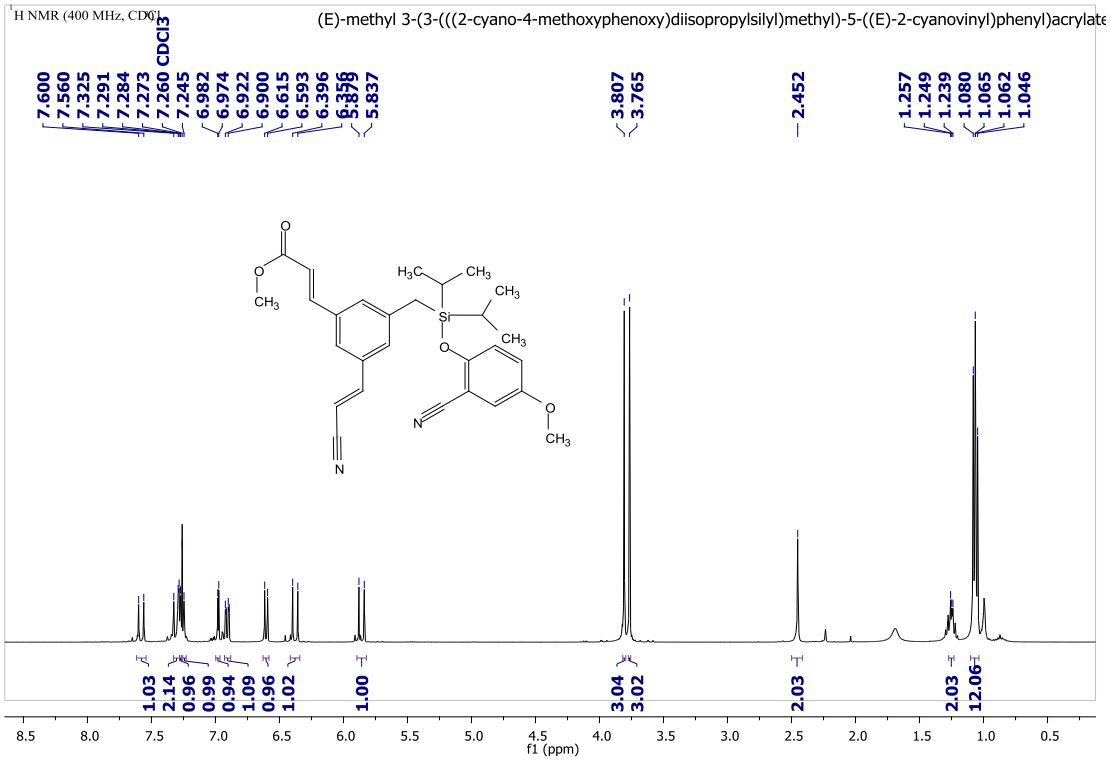


Table 3, entry 4a:



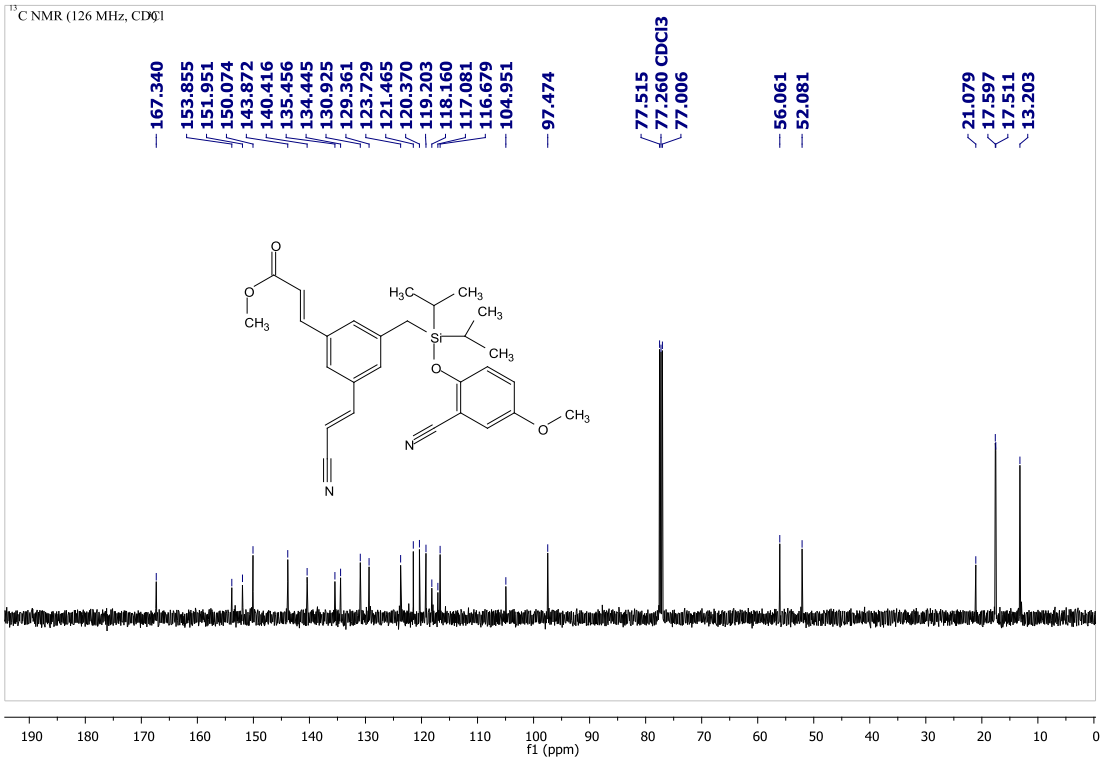
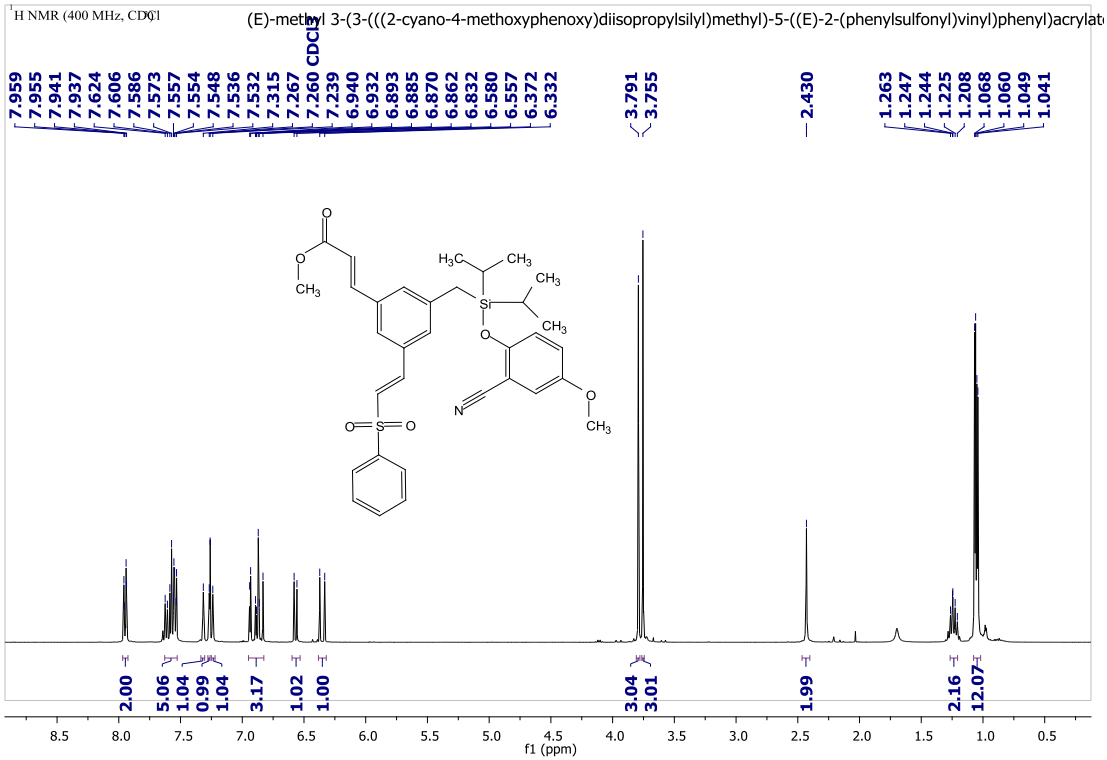


Table 3, entry 4b:



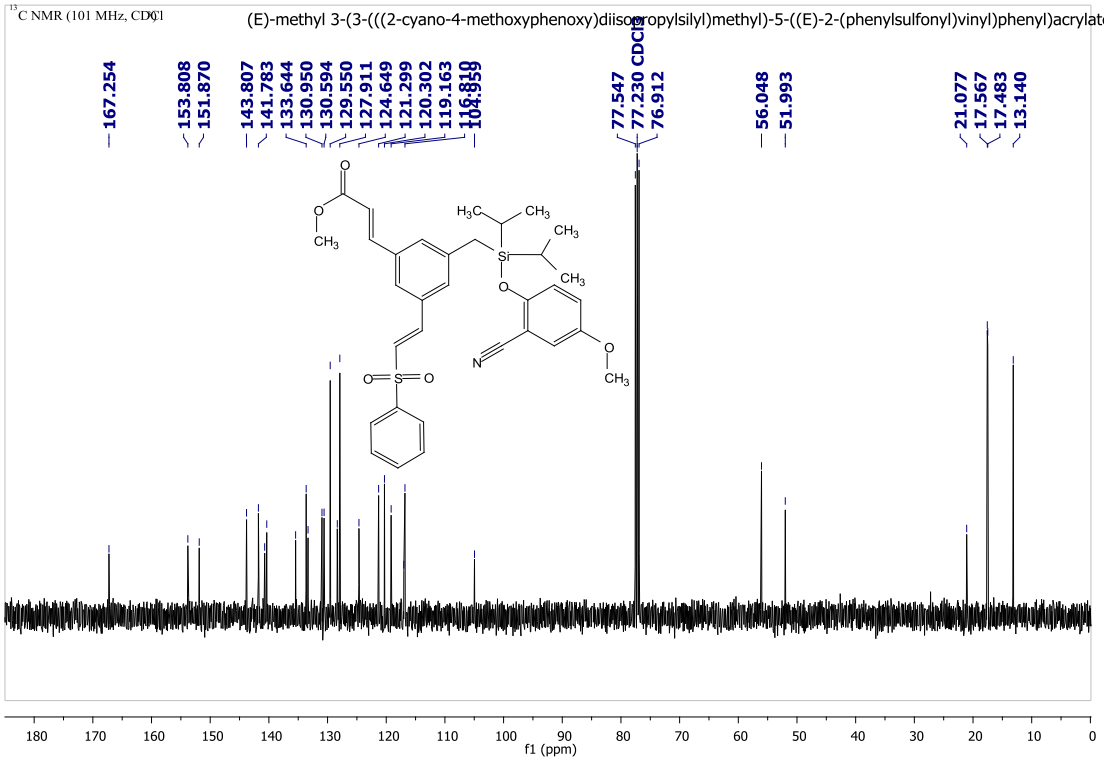
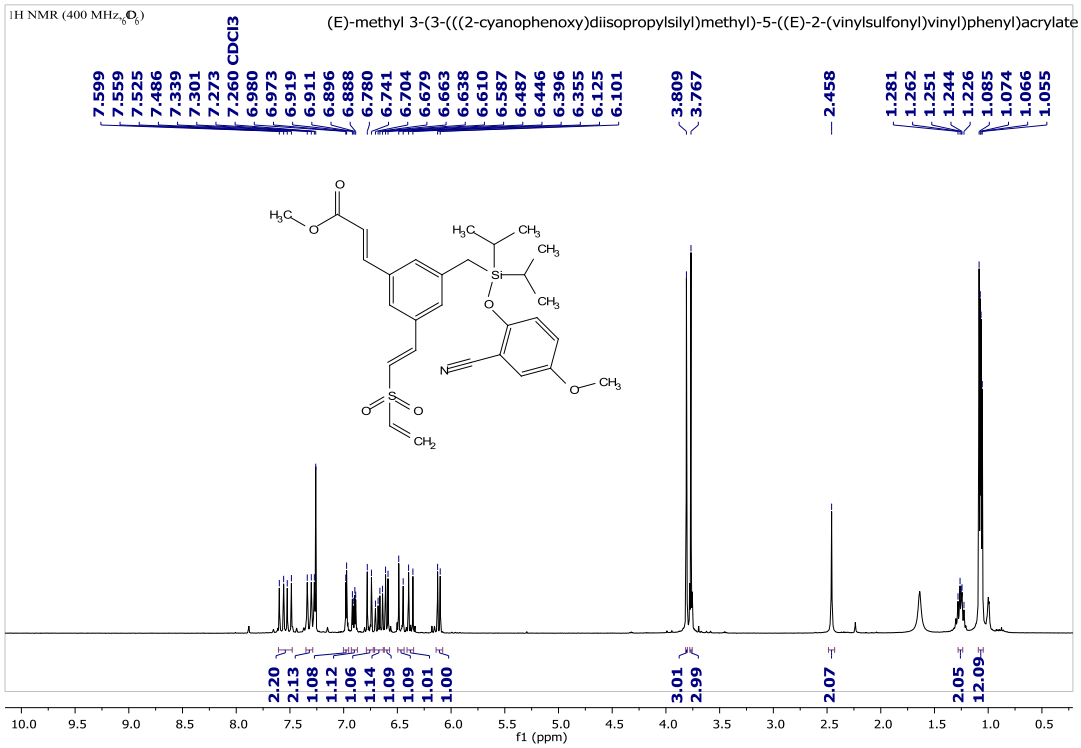


Table 3, entry 4c:



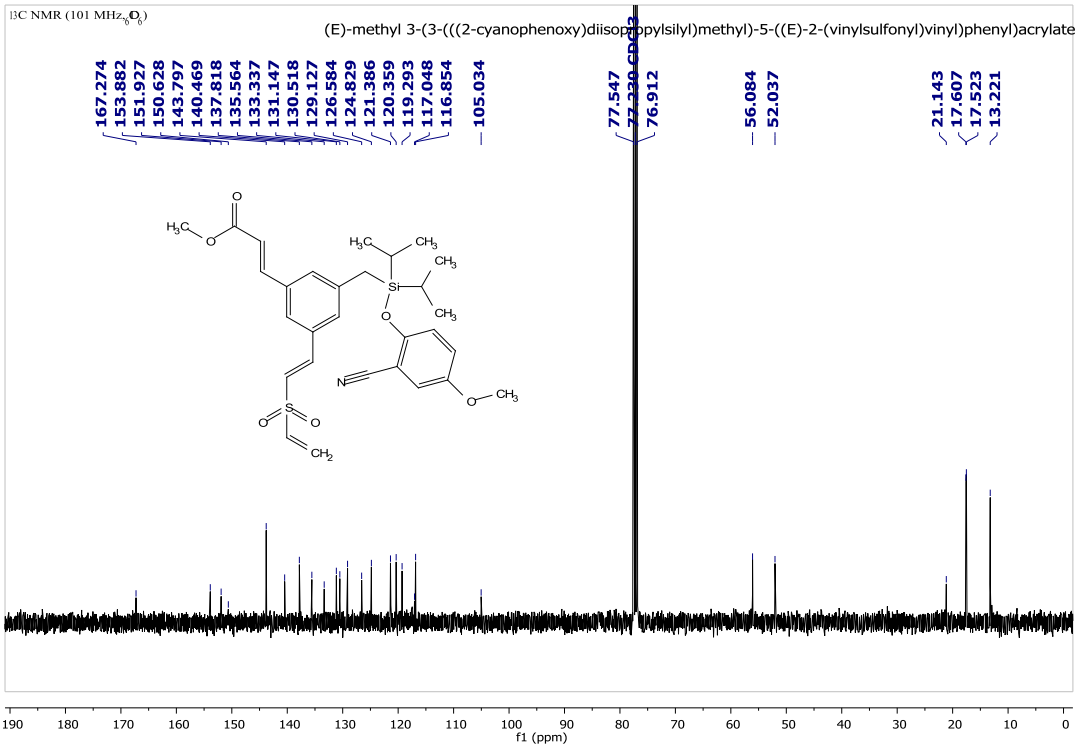
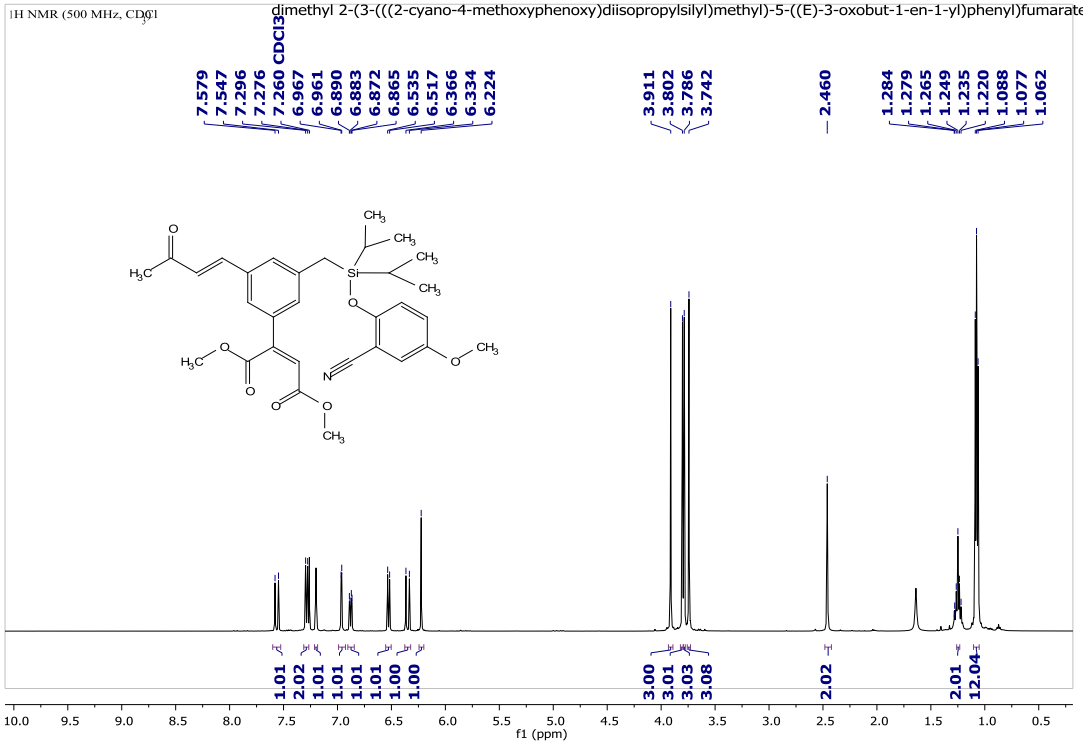


Table 3, entry 4d:



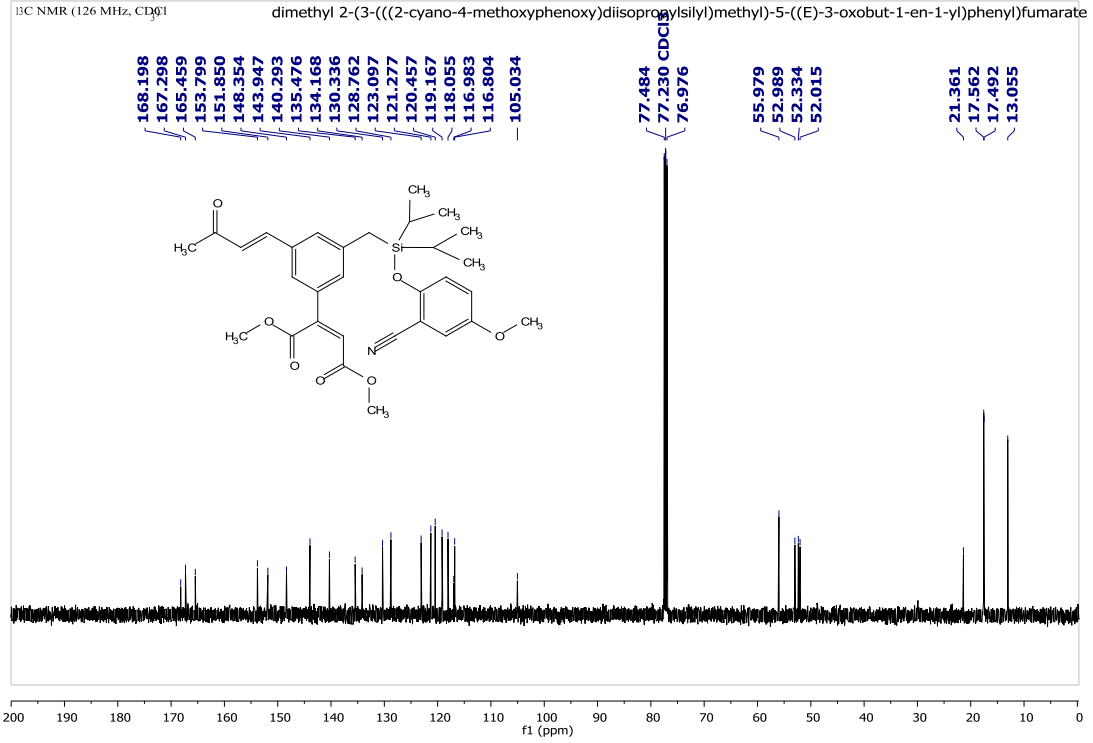
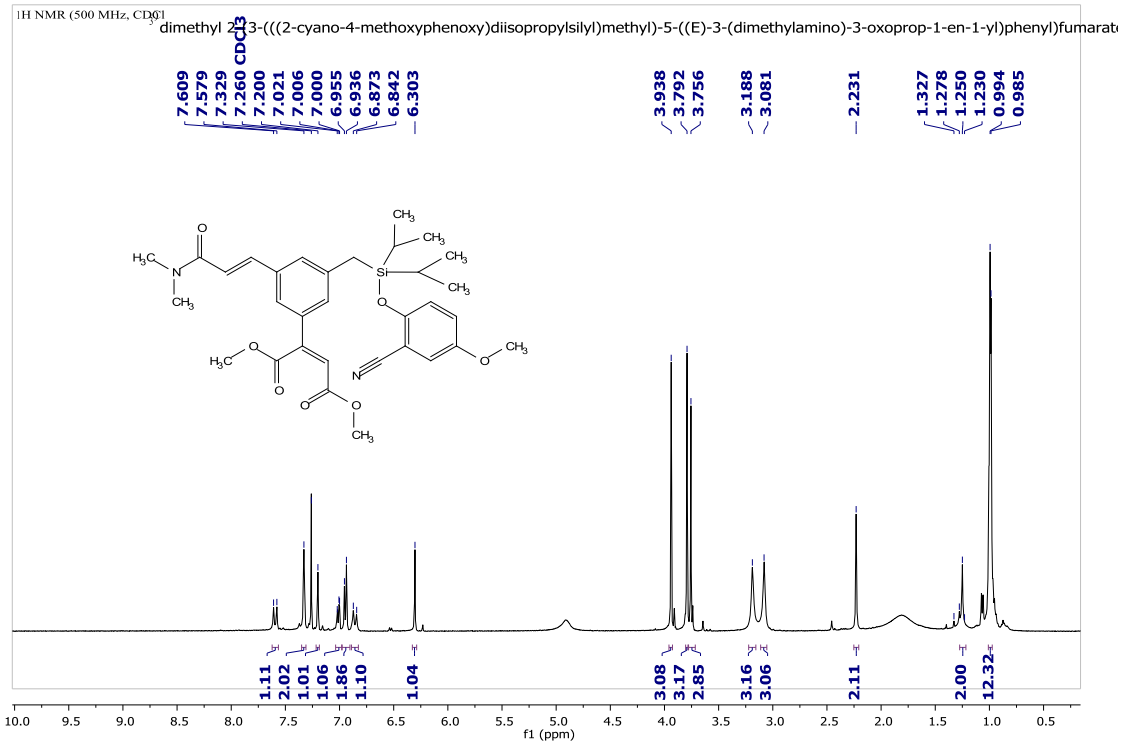


Table 3, entry 4e:



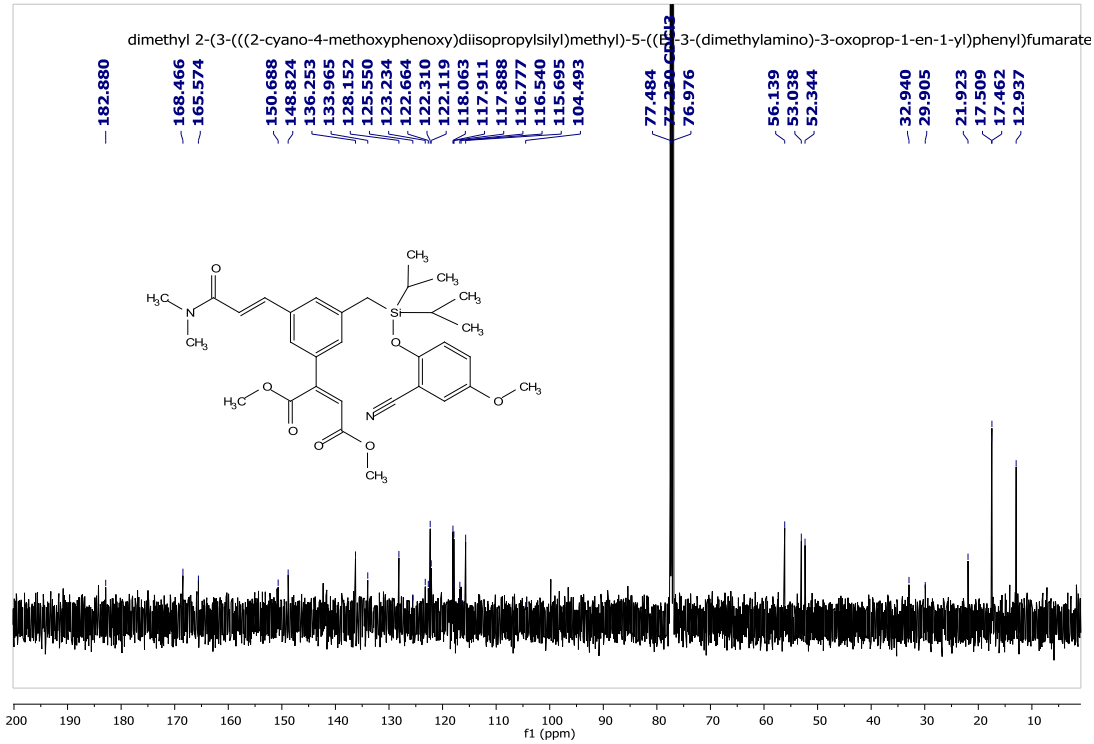
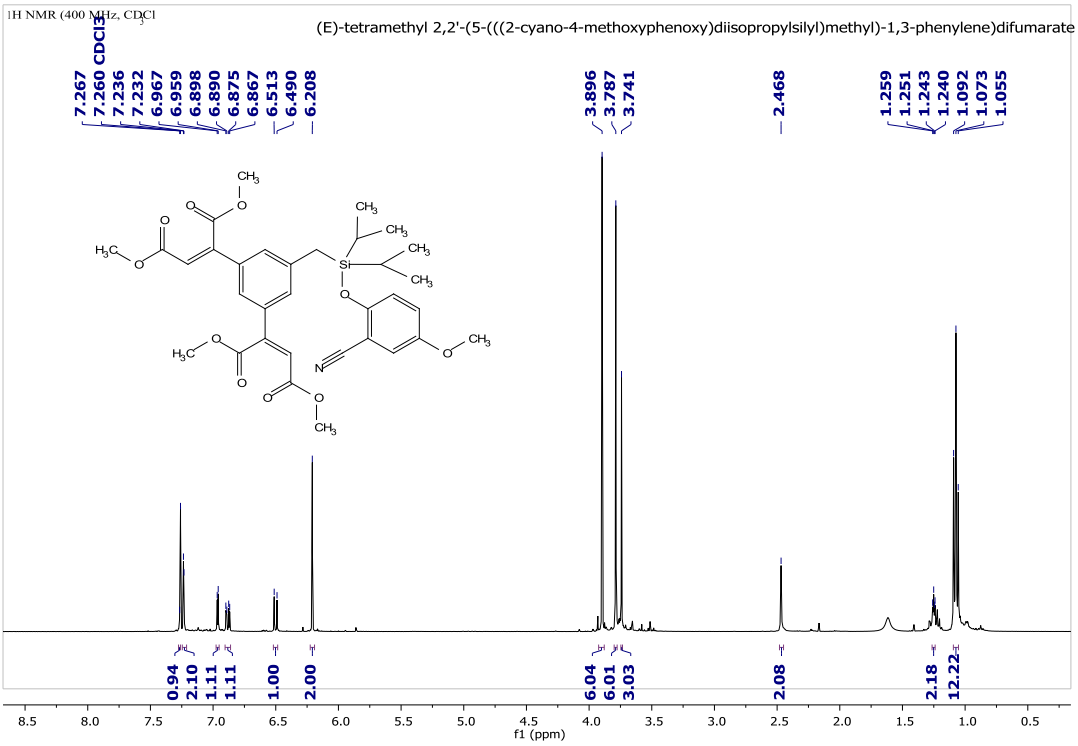


Table 3, entry 4f:



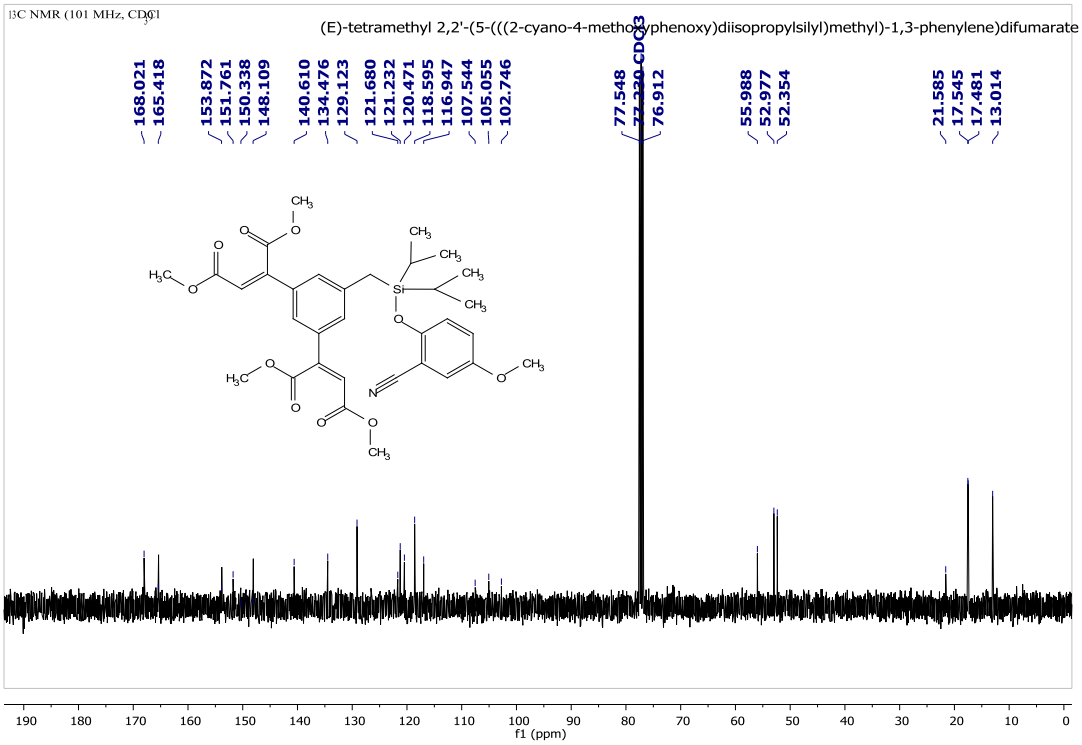
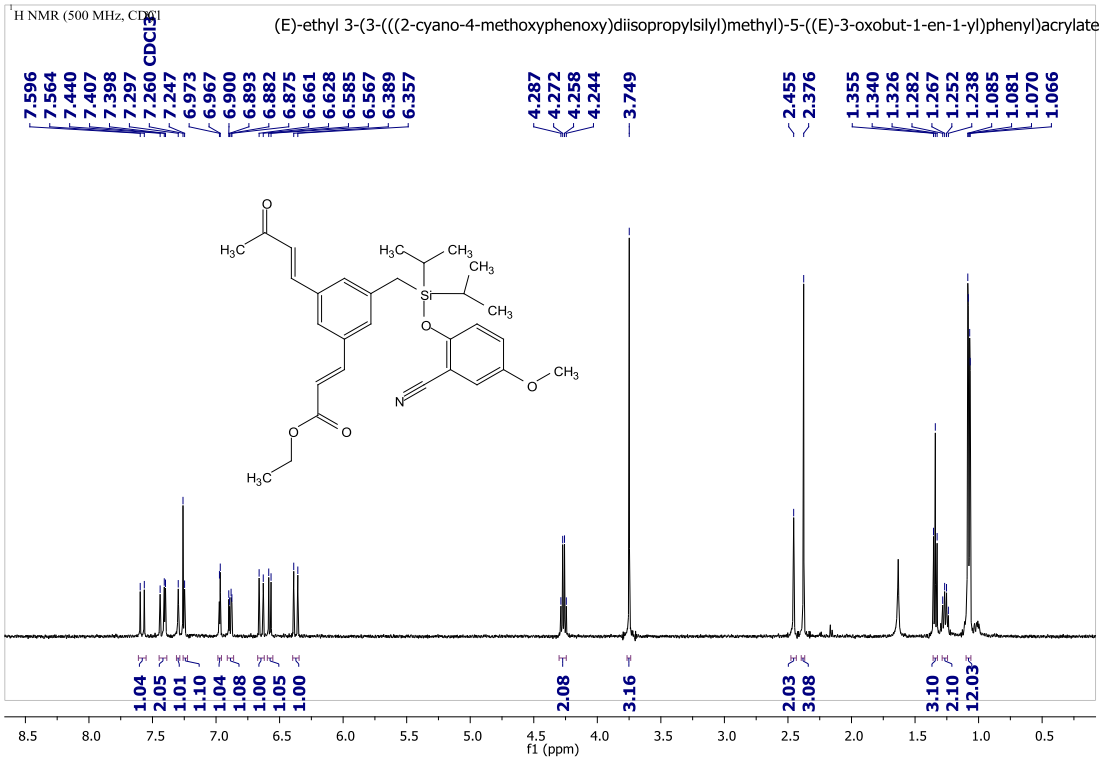


Table 3, entry 4g:



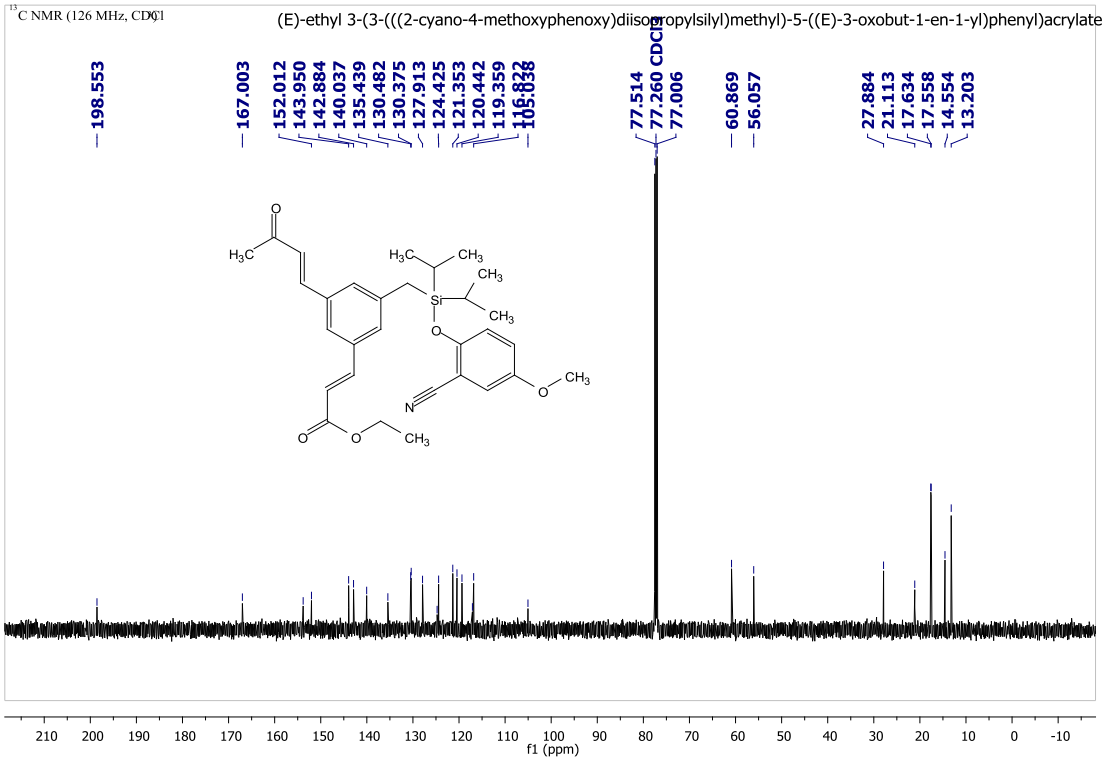
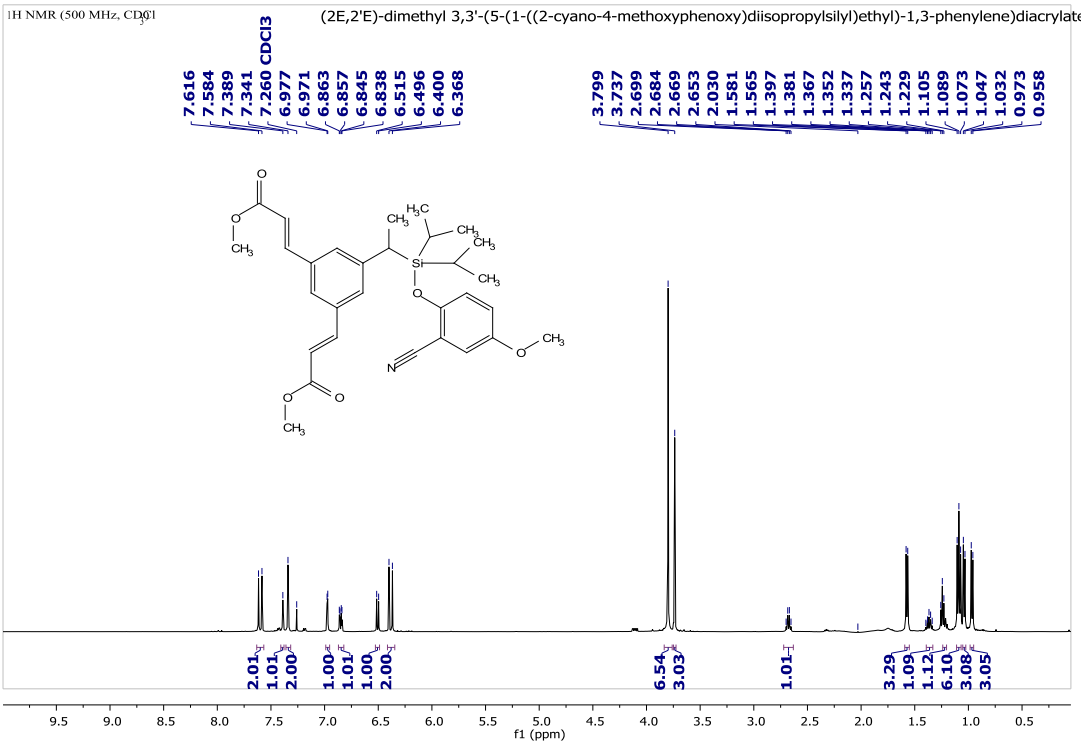


Table 3, entry 4h, $2i_{di}$:



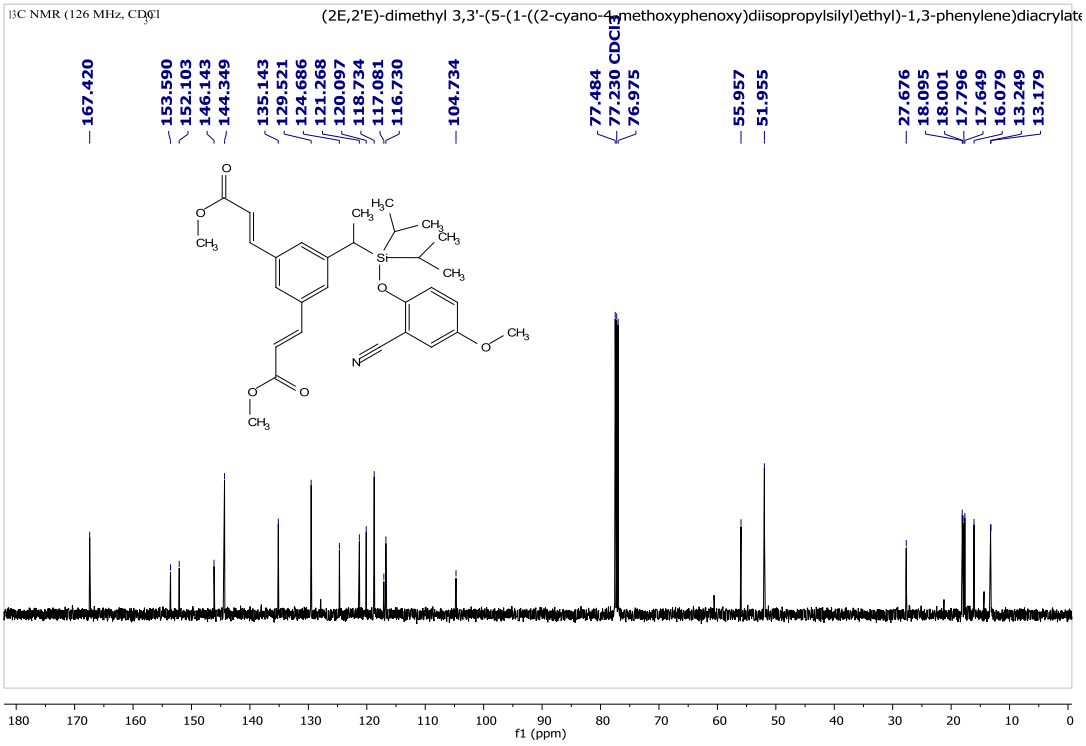
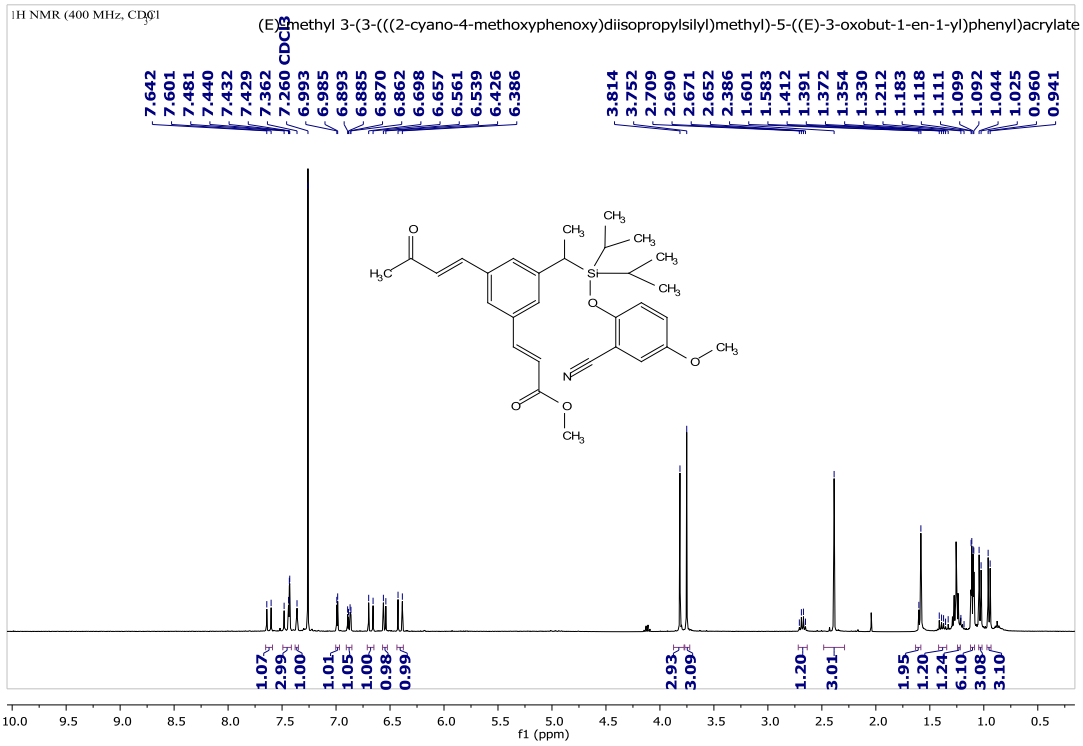


Table 3, entry 4i:



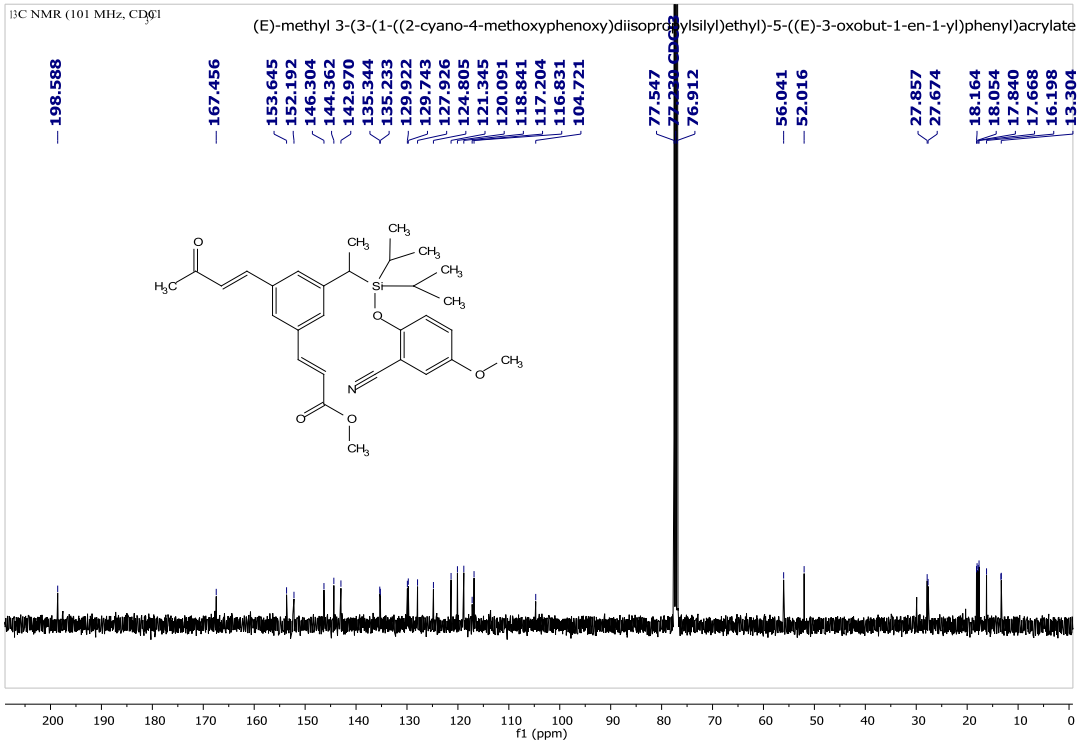
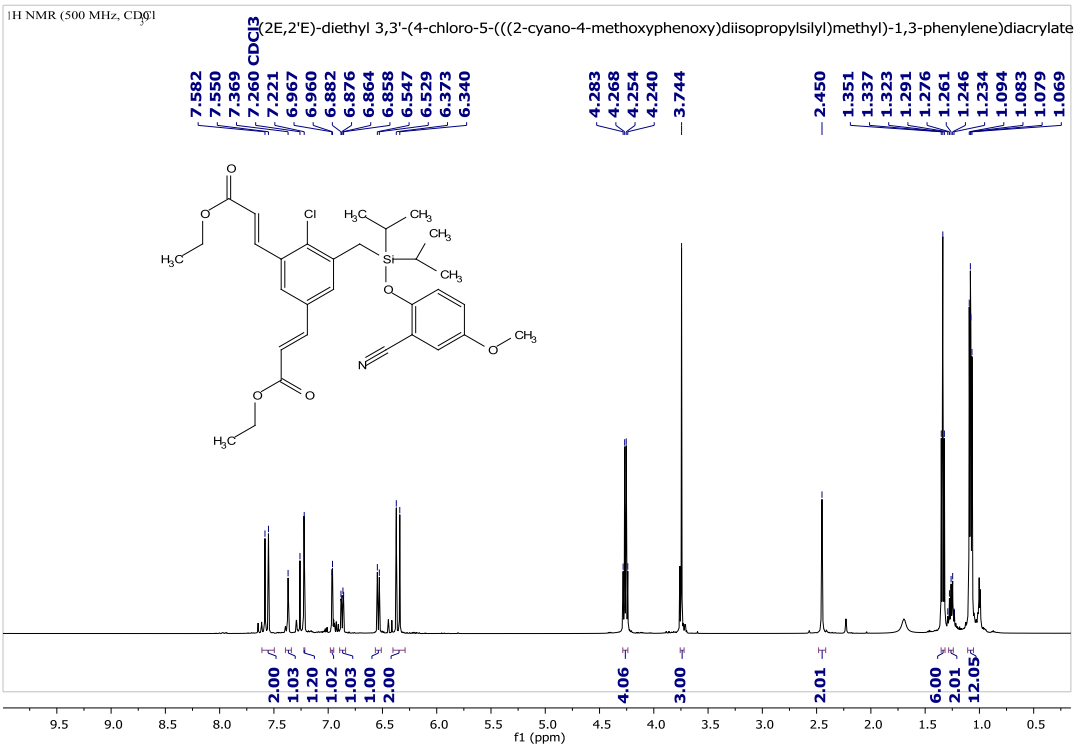


Table 3, entry 4j, $2d_{di}$:



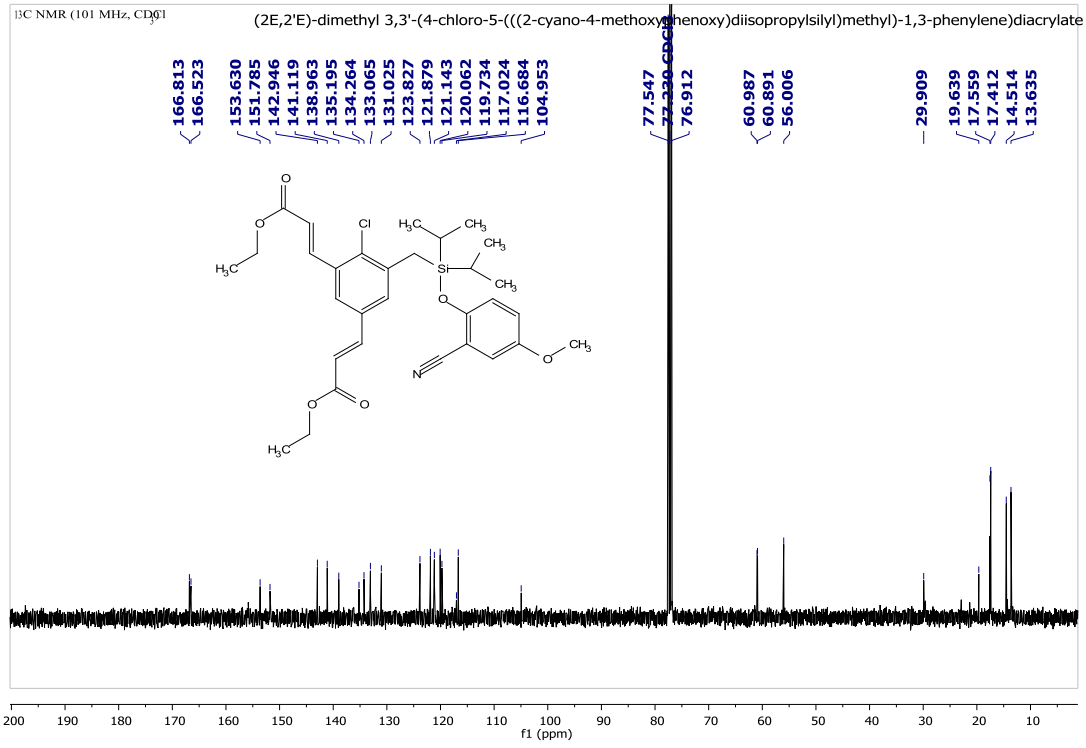
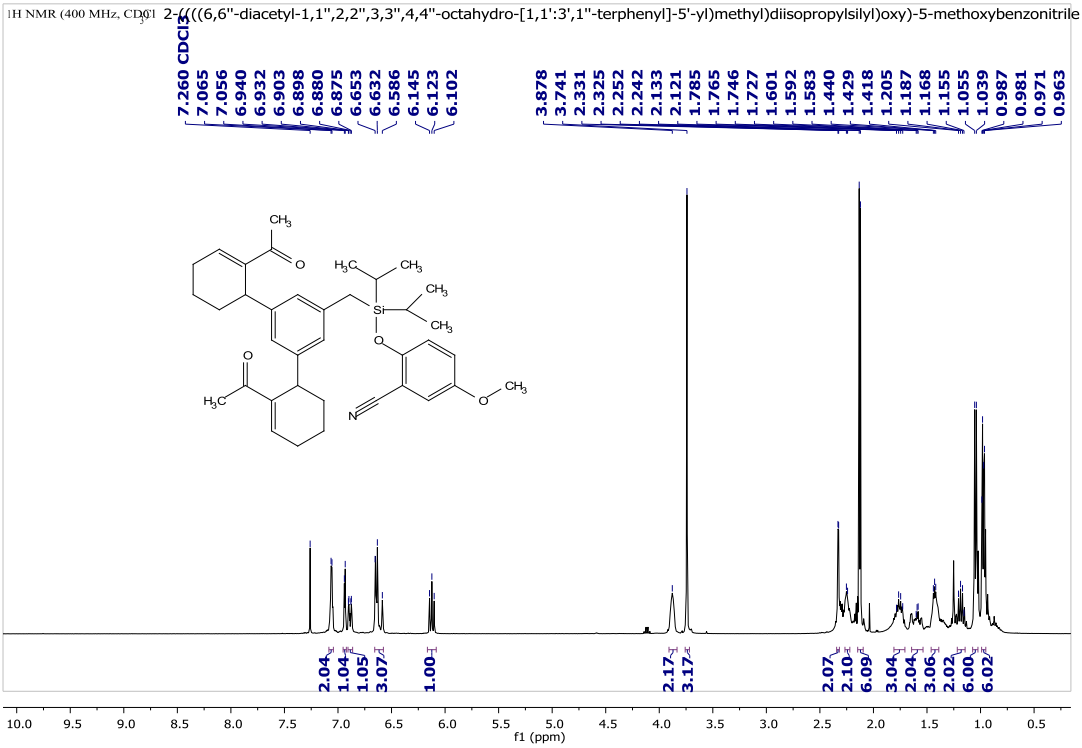
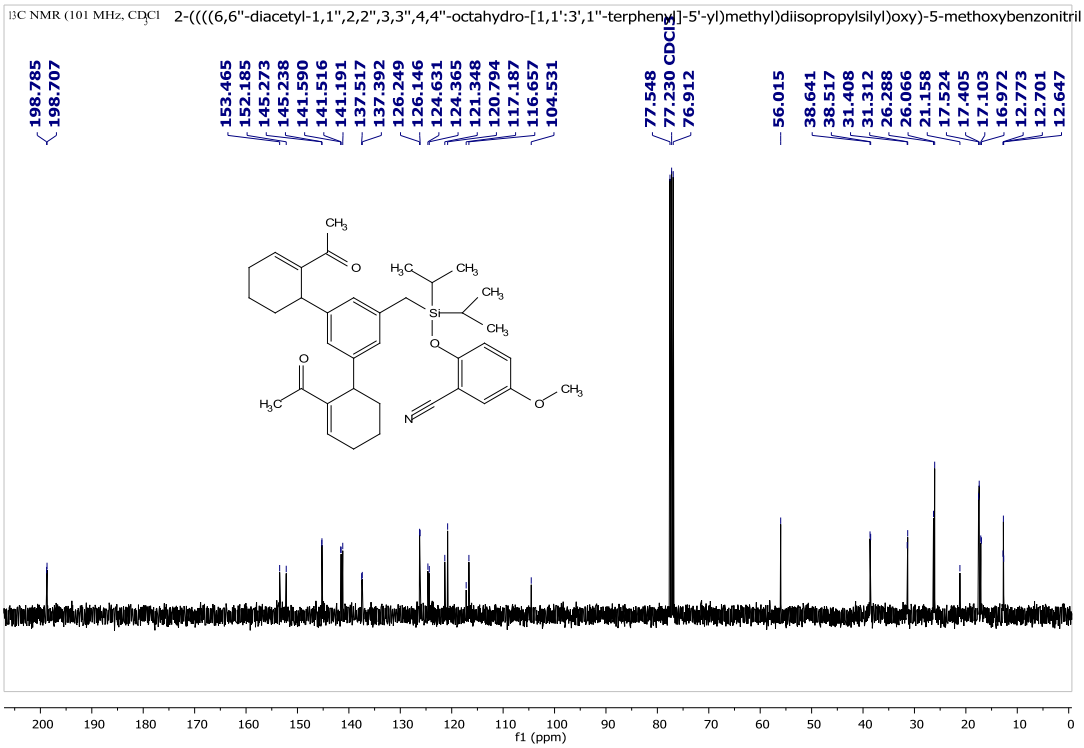
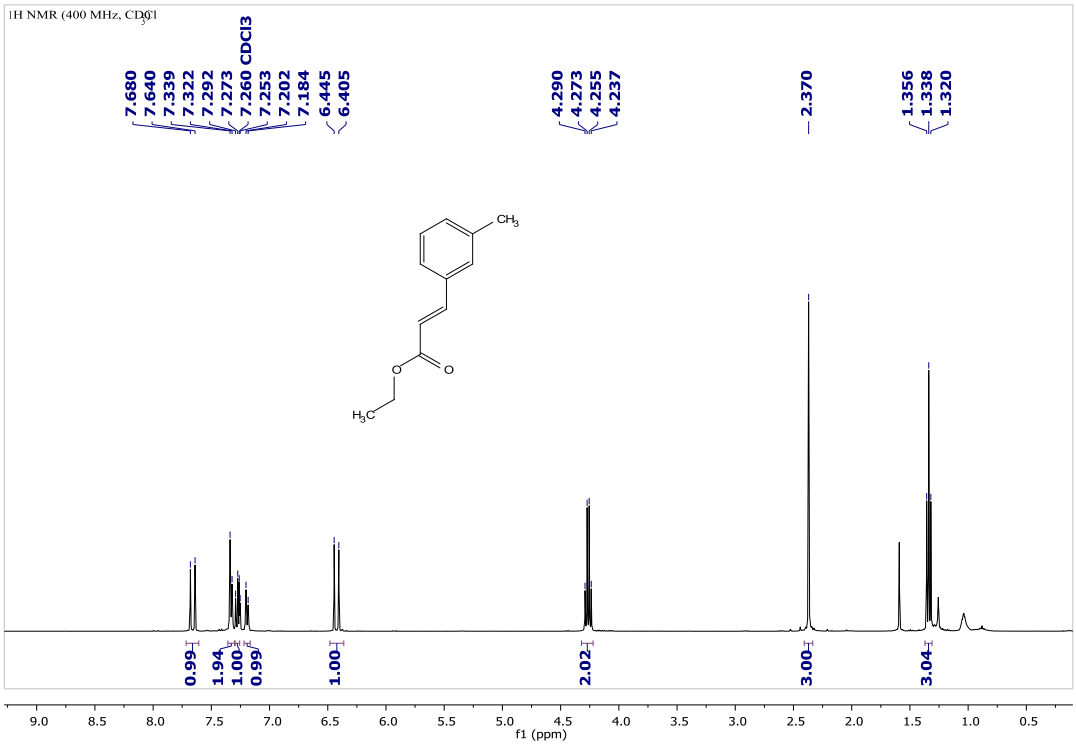


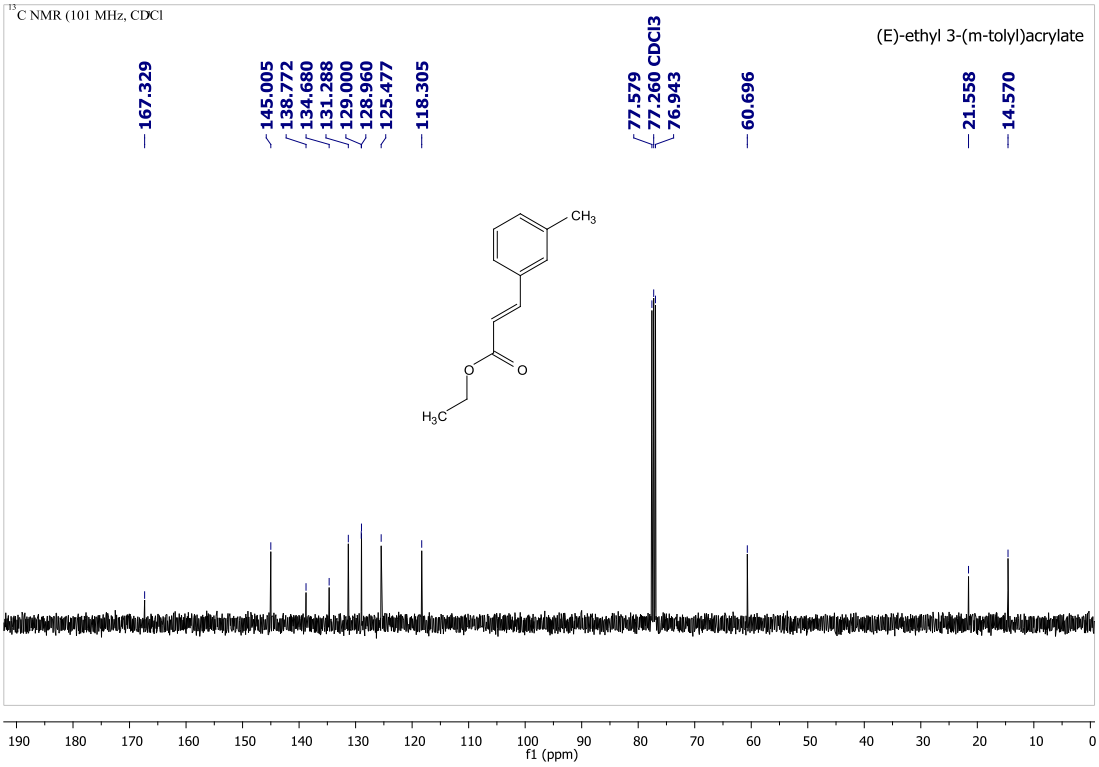
Table 3, entry 4k:



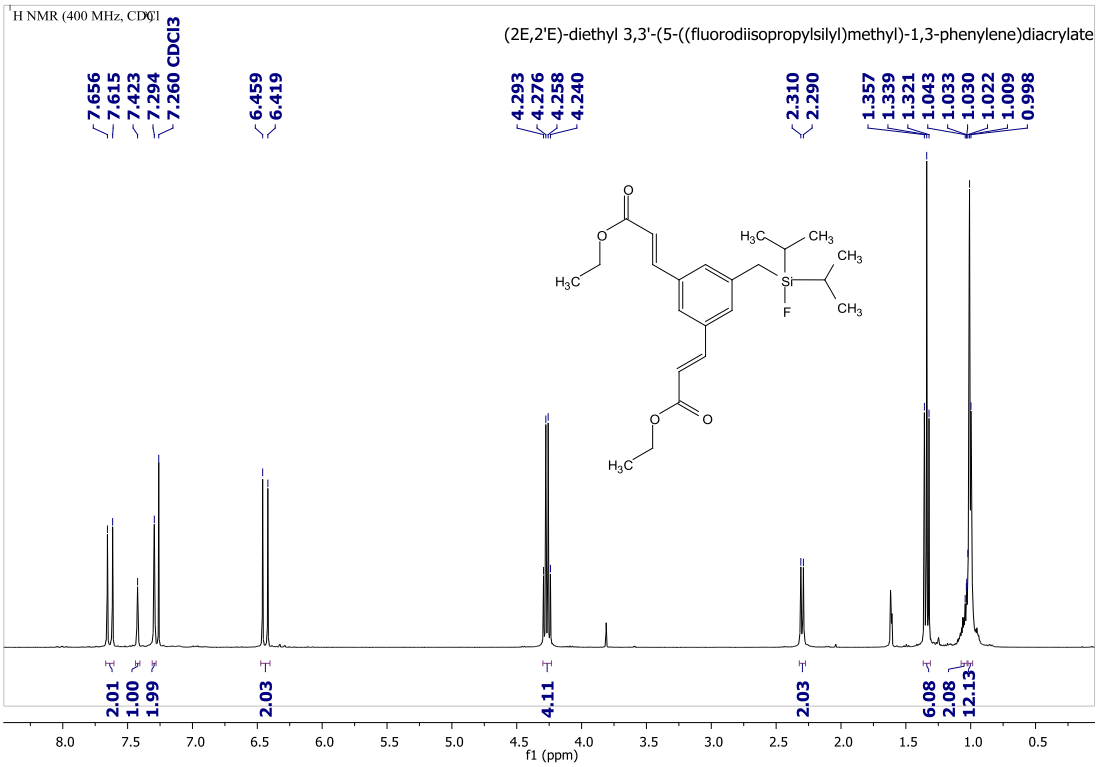


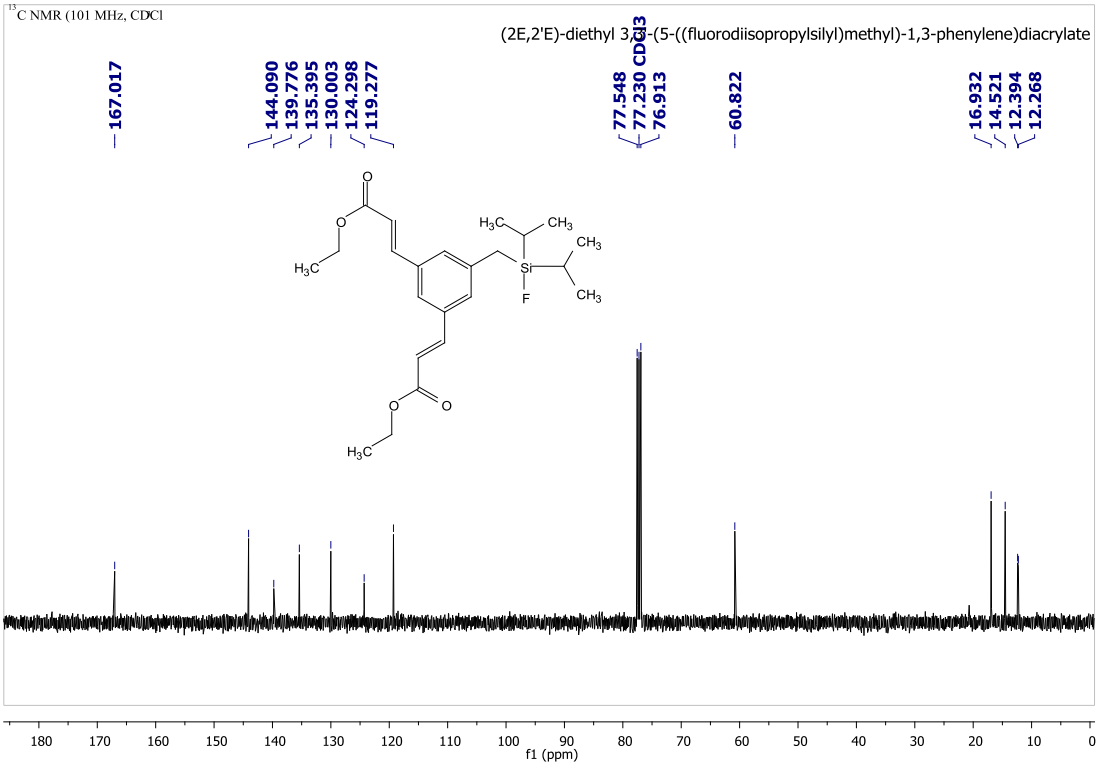
Scheme 5, entry 5a:



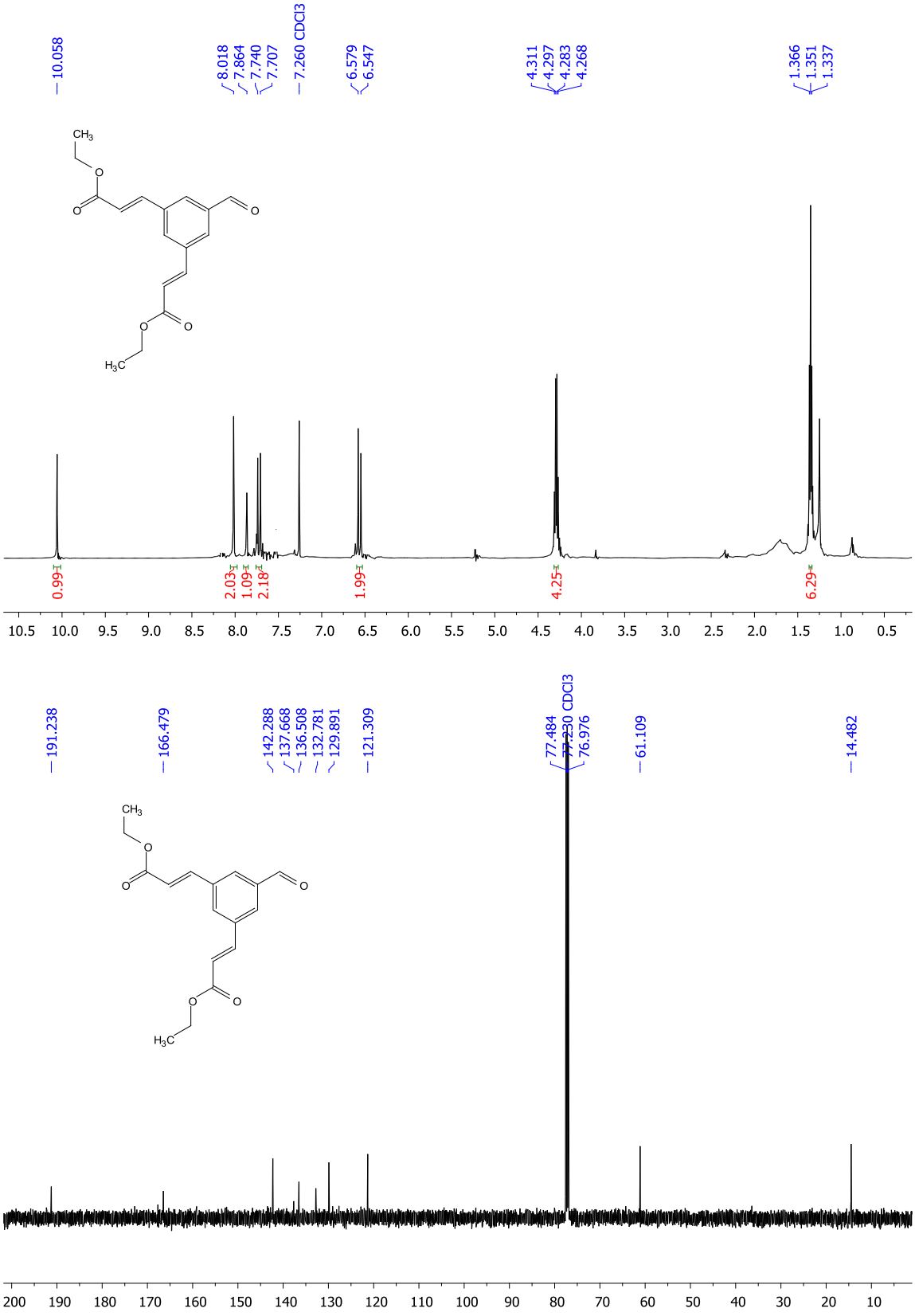


Scheme 5, entry 5b-SM:

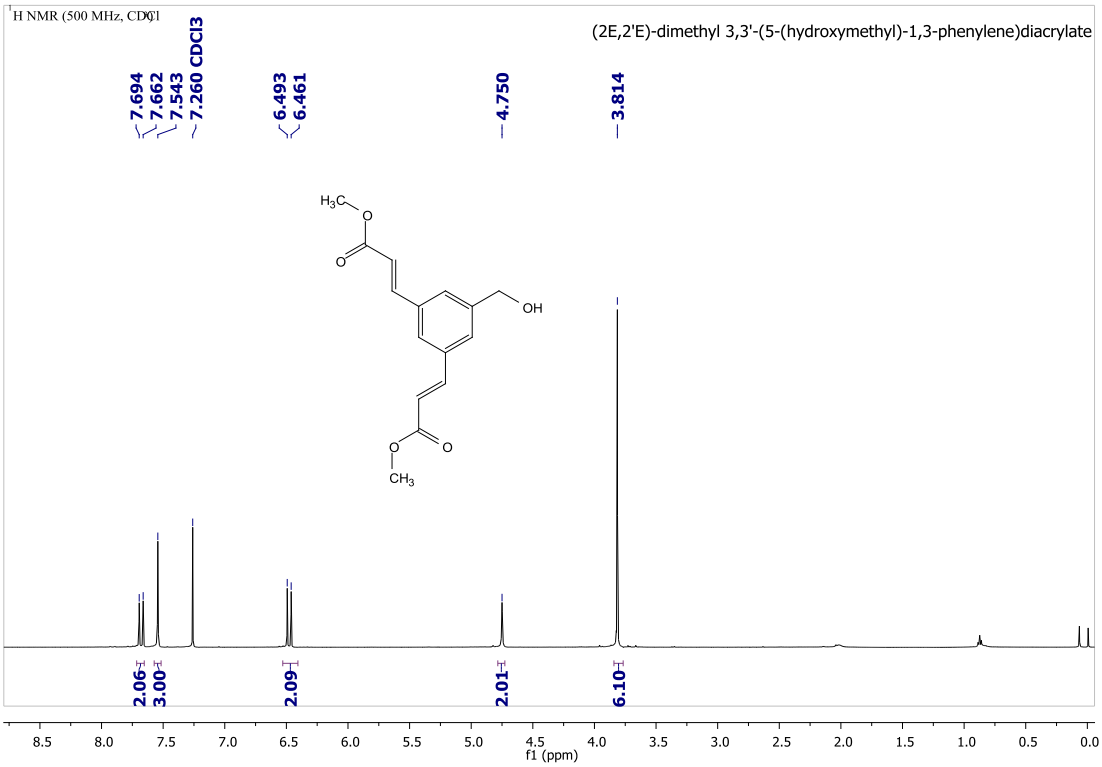


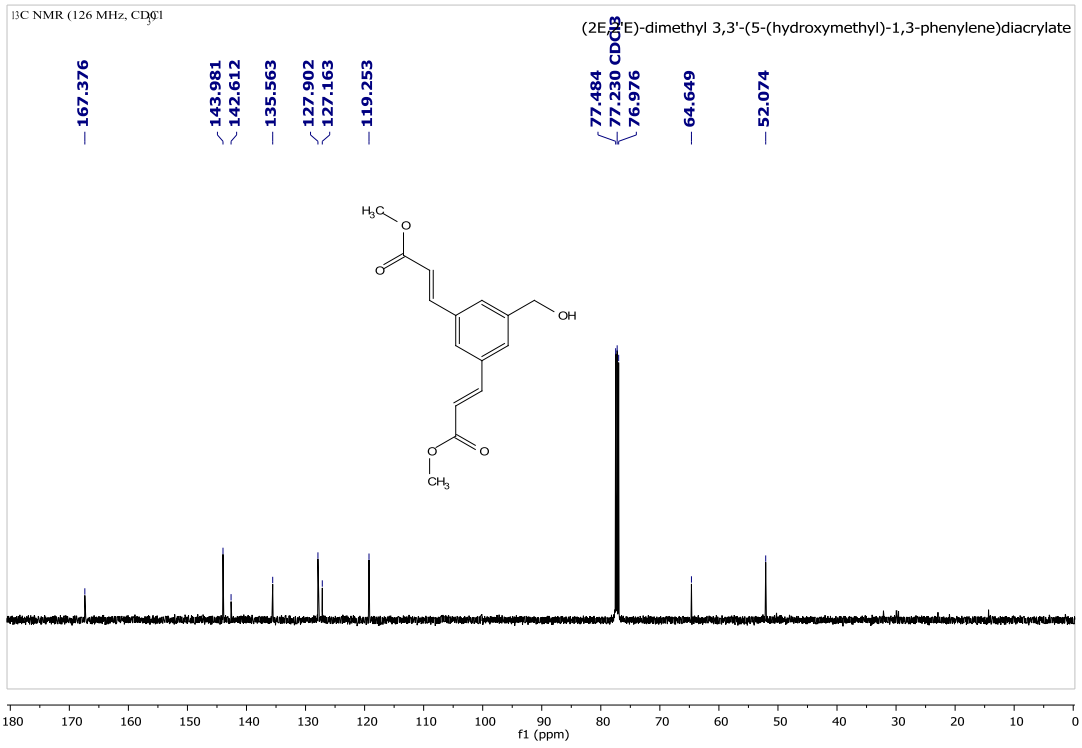


Scheme 5, entry 5b:

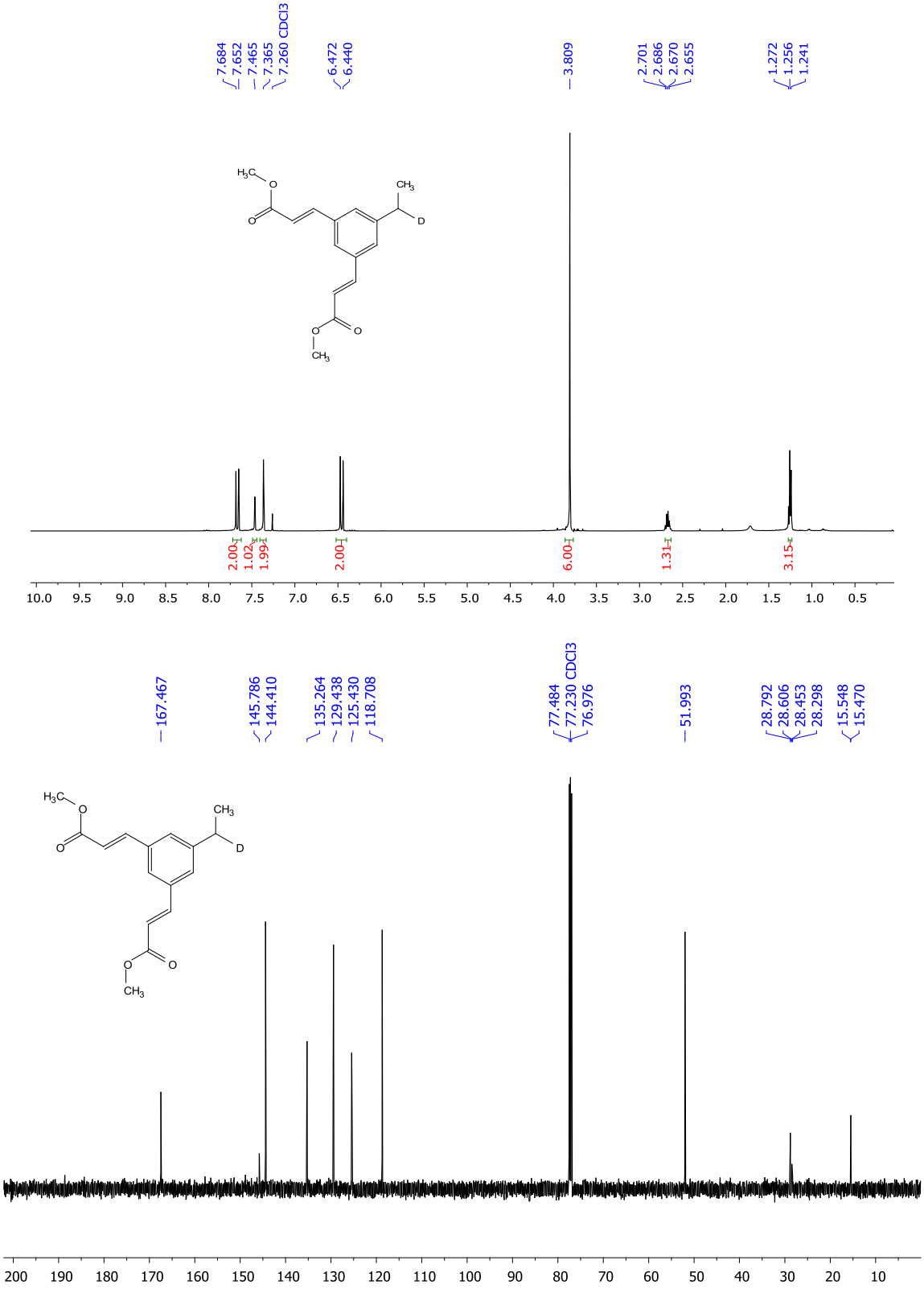


Scheme 5, entry 5c:

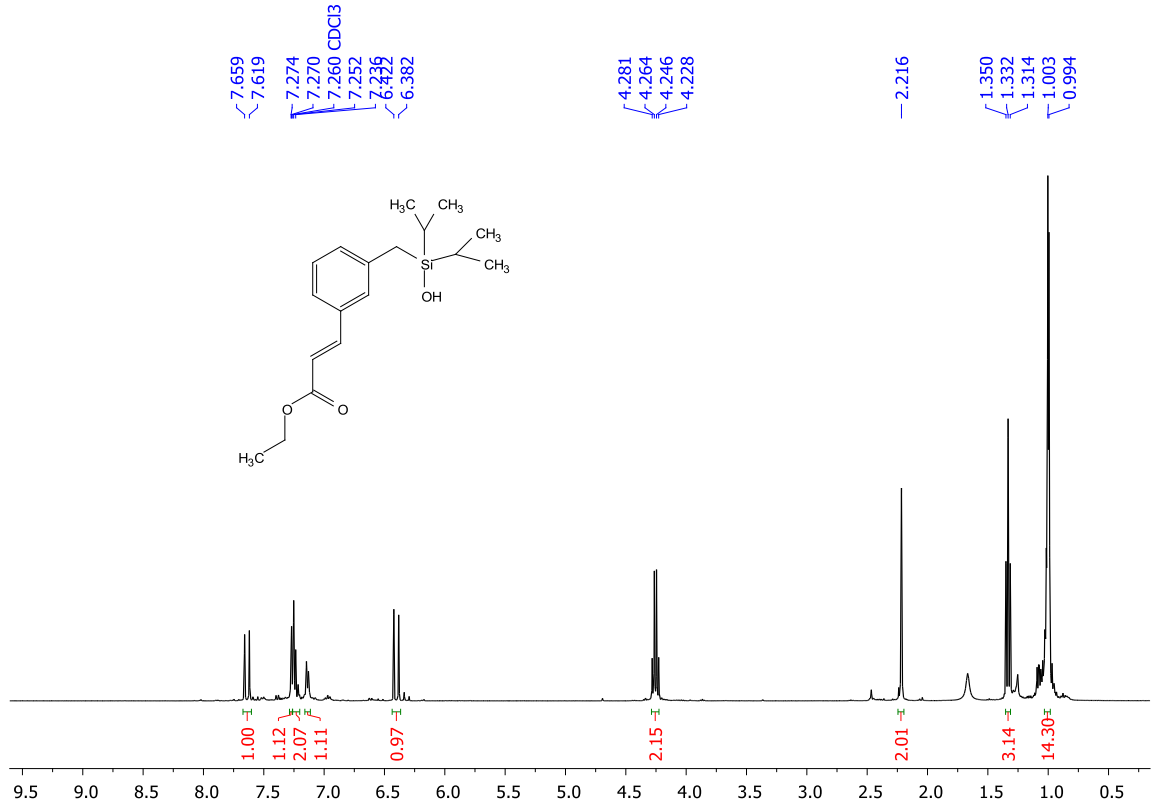


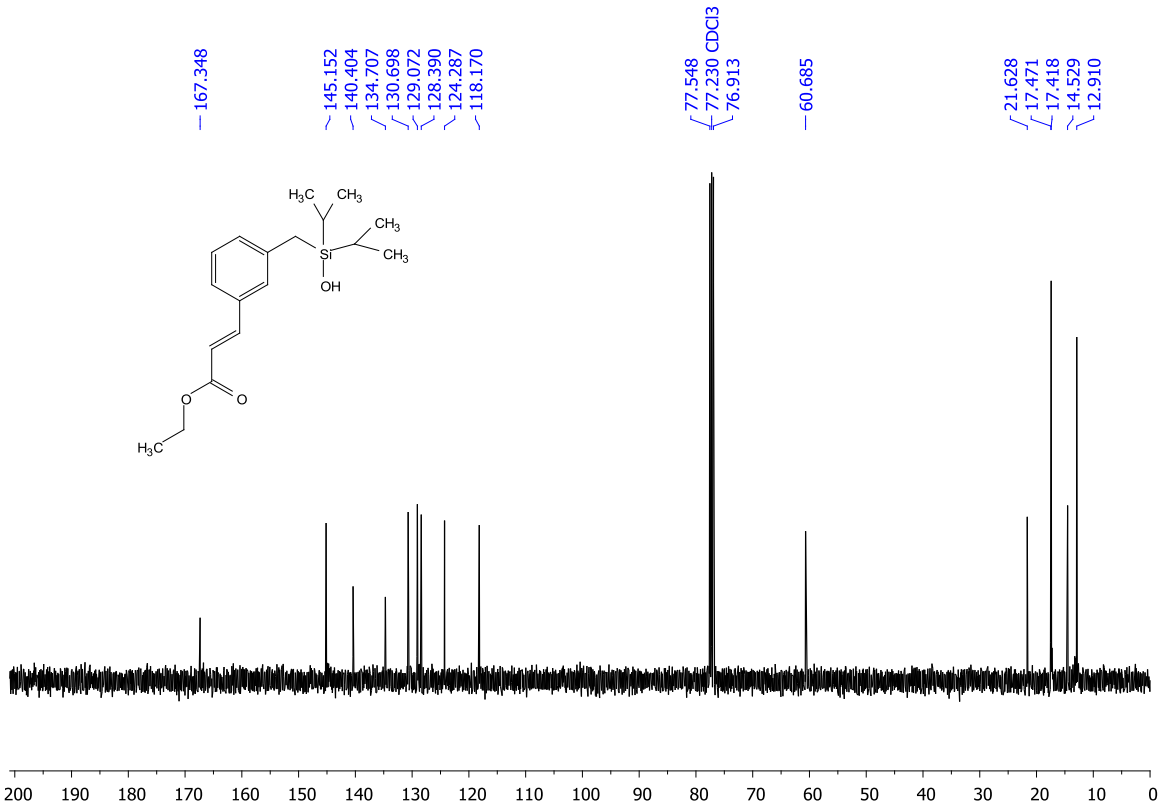


Scheme 5, entry 5d:



Scheme 6, entry 6a:





Scheme 6, entry 6b: