Supporting Information

MCF-supported boronic acids as efficient catalysts for direct amide condensations of carboxylic acids and amines

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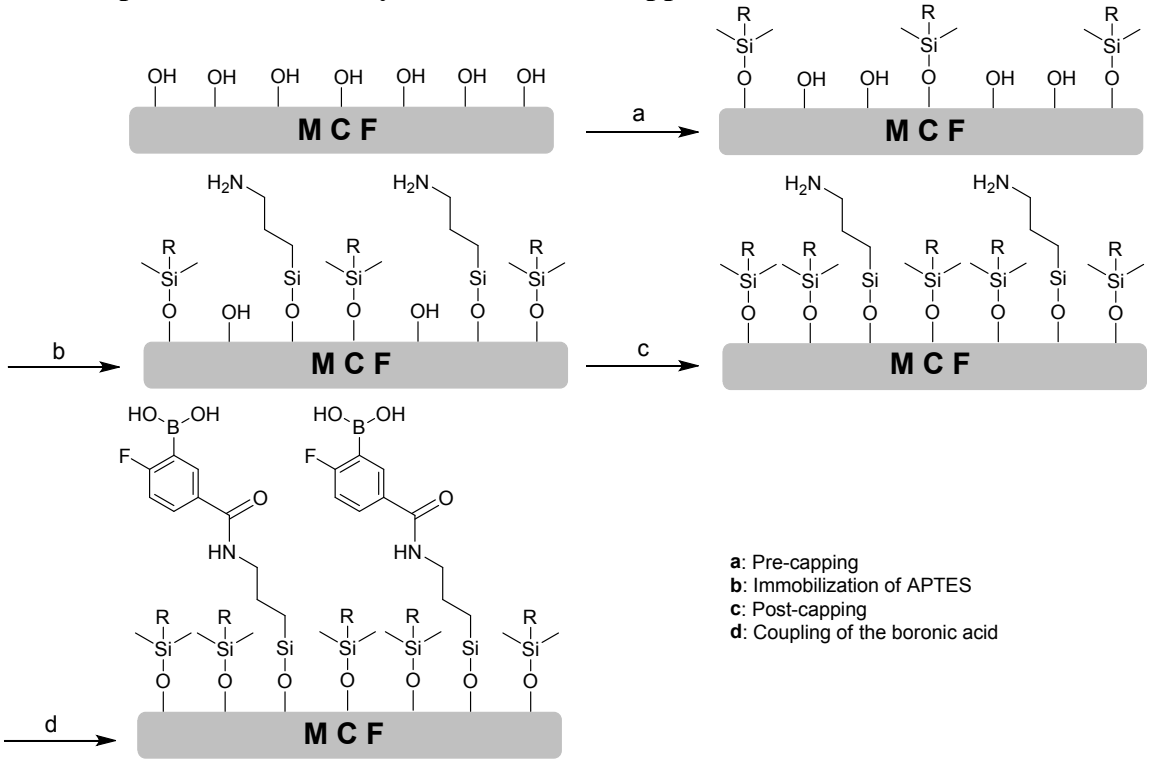
General Information: All anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. All silanes including dialkyltetramethyldisilazanes were purchased from Gelest, Inc. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-400 (400 MHz) instrument. ^{13}C CP-MAS and ^{29}Si CP-MAS NMR spectra were recorded on a 400 MHz Bruker spectrometer for the MCF-supported compounds. The mass spectra were recorded on Shimadzu GC-2010 (QP–2010 gas chromatograph). Reaction yields were determined by purification of crude products using preparative TLC or flash column chromatography. Amides **11a**,[1] **11d**,[2] **11e**,[3] **11f**,[1] **11g**,[4] **11h**,[5] and **11i**[6] were known and their NMR spectra were consistent with those reported in literature. The NMR data of boronic acid **2**, amides **11b** and **11c** has been not reported although they have been known in the literature.

General procedure for the synthesis of MCF-supported boronic acid



Scheme S1 Preparation of MCF-supported boronic acid catalysts

MCF (8.0 g) was degassed at 120 °C overnight under vacuum before reaction. HMDS (675 μl, 3.2 mmol) was added to a suspension of MCF in anhydrous toluene (50 ml). The mixture was stirred at room temperature under argon for 3 h, and then heated at 60 °C overnight. The resulting suspension was filtered, washed with toluene and methanol, and then dried under vacuum. The resulting TMS-capped MCF (5.0 g) was degassed at 120 °C overnight under vacuum before reaction and then dispersed in anhydrous toluene (30 ml). 3-aminopropyltriethoxysilane (APTES) (232 mg, 1.05 mmol) was added to the mixture. The mixture was stirred at room temperature under argon for 3 h, and then

heated at 100 °C overnight. The mixture was cooled down, filtered and washed with toluene, CH_2Cl_2, and methanol. The collected particles were dried under vacuum. The ^1H NMR spectrum of the collected filtrate after solvent evaporation did not show any organic compounds confirming the immobilization of all APTES. The weight gain also confirmed the complete anchoring of all APTES. The particles were post-capped with TMS by the vapor-phase reaction with HMDS. The amine-functionalized MCF was used for the immobilization of boronic acid. This amine-functionalized MCF could be prepared in one pot without recovering the MCF particles at each step. 5-Carboxy-2-fluorophenylboronic acid (232 mg, 1.26 mmol) in anhydrous N-methyl-2-pyrrolidone (NMP) was added to 5.0 g of the amine-functionalized MCF dispersed in anhydrous NMP. 2-(1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium tetrafluoroborate (TBTU) (405 mg, 1.26 mmol) in anhydrous NMP was added to the mixture and then N,N-diisopropylethylamine (DIEA) (658 μL, 3.78 mmol) was added. The resulting mixture was stirred overnight at room temperature, filtered, and washed with NMP (4 × 15 ml), CH_2Cl_2 (4 × 15 ml) and methanol (4 × 15 ml). The final MCF-supported boronic acid was dried under vacuum. A Kaiser test confirmed that most of amine groups were coupled to the boronic acid. Considering overall weight increase by both post-capping and the coupling of the boronic acid, the loading of the boronic acid was calculated to give 0.2 mmol/g. For fluoroalkyl capping, bis(trifluoropropyl)tetramethyldisilazane (Gelest, Inc.) was used. For propyl and octyl capping, di-n-propyltetramethylsilazane and di-n-octylteteramethylsilazance were used, respectively. With these disilazane compounds, the pre-capping was done at 80 °C and the post-capping was done in anhydrous toluene at 90 °C overnight and then further post-capping with HMDS under the vapor-phase condition.

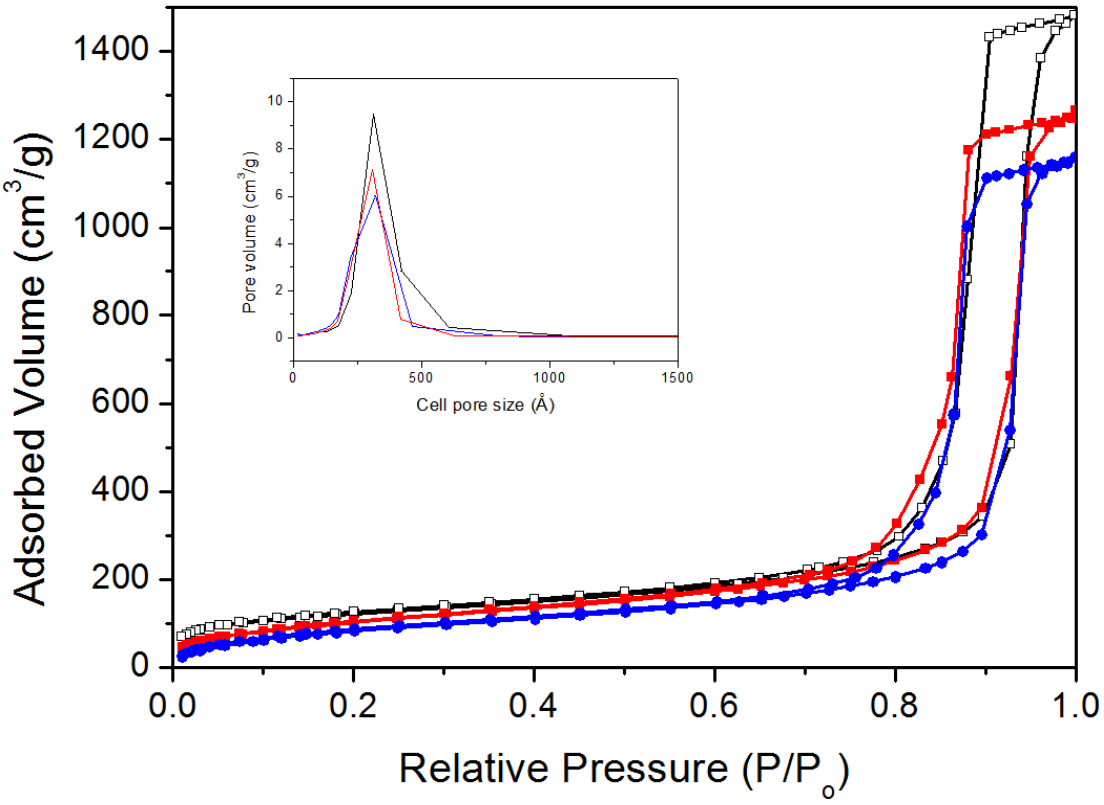


Fig. S1. Nitrogen adsorption –desorption isotherms for the bare support MCF (□), amine-functionalized MCF with fluoroalkyl capping (■) and MCF-supported boronic acid with fluoroalkyl capping **8a** (●)

Table S1. Characteristics of bare MCF, amine-functionalized MCF and the catalyst **8a**

Support materials	Surface area[a] (m^2/g)	Pore volume[b] (cm^3/g)
Bare MCF	421.5	2.29
Amine-functionalized MCF	382.8	1.96
8a	320.3	1.80

[a]BET surface area; [b]Estimated at the relative pressure of P/P_0=0.99.

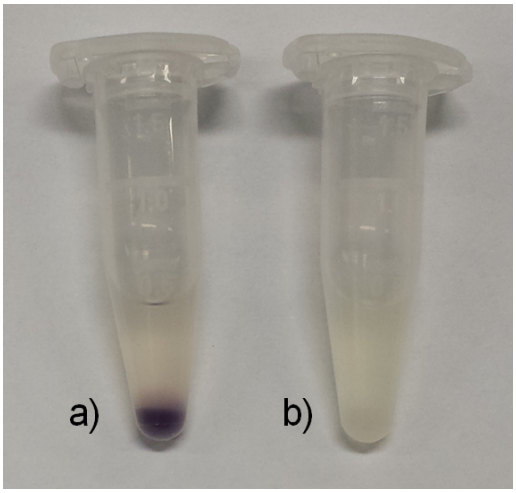
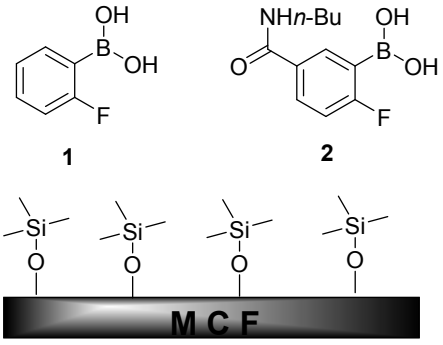
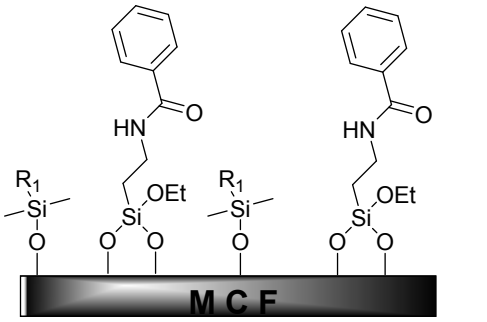


Fig. S2. A Kaiser test of a) amine-functionalized MCF and b) MCF-supported boronic acid

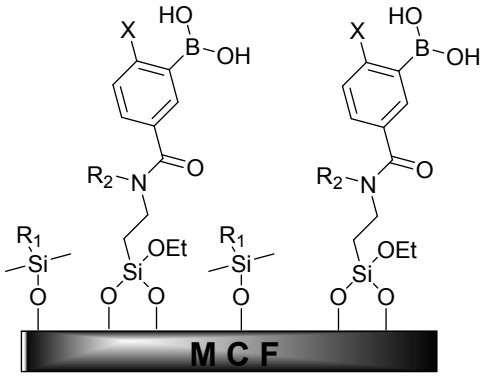
General procedure for the direct amide condensation of carboxylic acids and amines (Table 1)

To a 10 ml headspace vial was added phenylacetic acid (68mg, 0.5 mmol), catalyst (5 mol%) and toluene (2 ml), then benzylamine (55 µl, 0.5 mmol) was added. After the reaction vial was sealed with PTFE/silicone septa, it was placed in a heating block on a magnetic stirrer at 120 °C for 1-2 h. After reaction was completed, 5 ml of EtOAc was added to fully dissolve the crude products following with filtration through a fritted glass funnel. And then the catalyst was washed with EtOAc (3 × 5 ml). The filtrate was concentrated to afford crude products. The crude products were purified with preparative TLC or flash column chromatography to give a pure amide product.

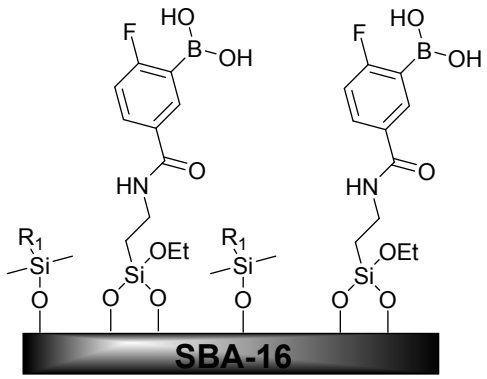




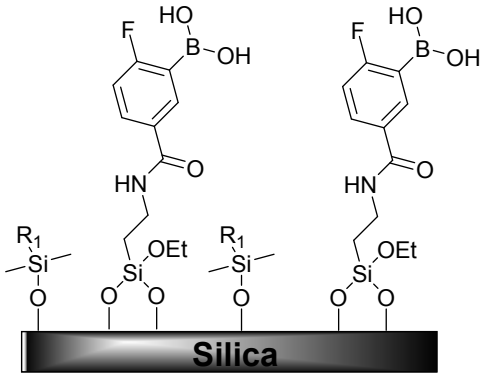
4 : $R_1 = (CH_2)_2CF_3$, (Loading: 0.2 mmol/g)



5a :$R_1 = CH_3$, R_2 = H, X = F (Loading: 1.0 mmol/g)
5b : $R_1 = CH_3$, R_2 = H, X = F (Loading: 0.2 mmol/g)
5c : $R_1 = CH_3$, R_2 = Me, X = F (Loading: 0.2 mmol/g)
6 : $R_1 = (CH_2)_2CH_3$, R_2 = H, X = F (Loading: 0.2 mmol/g)
7 : $R_1 = (CH_2)_7CH_3$, R_2 = H, X = F (Loading: 0.2 mmol/g)
8a: $R_1 = (CH_2)_2CF_3$, R_2 = H, X = F (Loading: 0.2 mmol/g)
8b: $R_1 = (CH_2)_2CF_3$, R_2 = H, X = F (Loading: 0.2 mmol/g)
Pre-capping = 0.5 mmol/g, No post-capping
8c: $R_1 = (CH_2)_2CF_3$, R_2 = H, X = F (Loading: 0.5 mmol/g)
8d : $R_1 = (CH_2)_2CF_3$, R_2 = H, X = H (Loading: 0.2 mmol/g)



9 : $R_1 = (CH_2)_2CF_3$, (Loading: 0.2 mmol/g)



10 : $R_1 = (CH_2)_2CF_3$, (Loading: 0.2 mmol/g)

Fig. S3. Catalysts tested. Silica: Silica gel 60 (0.040-0.063 mm), Merck KGaA

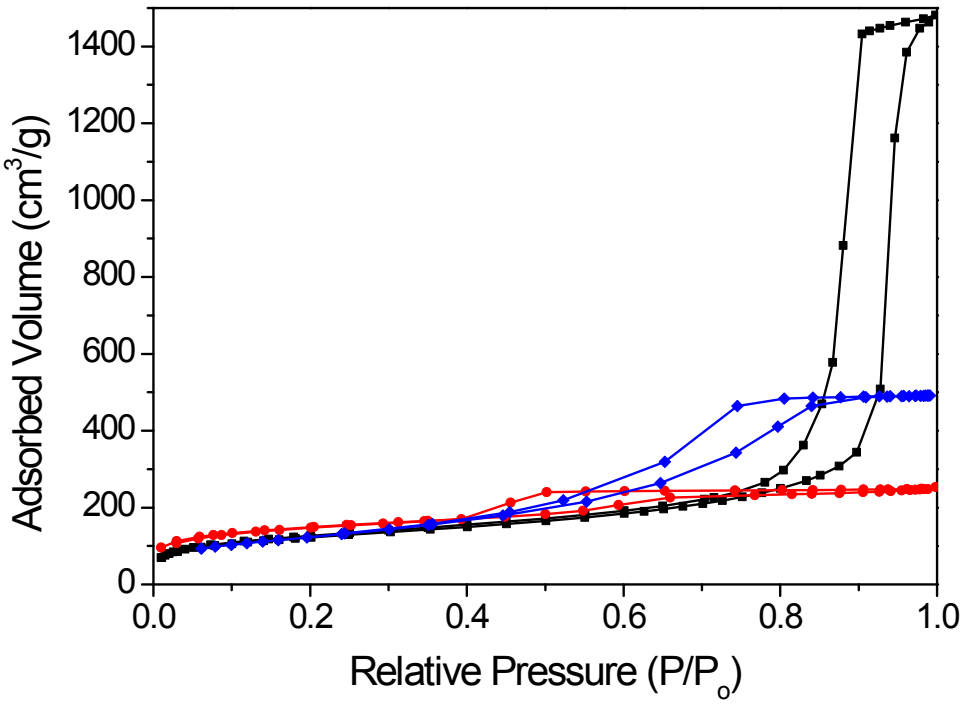


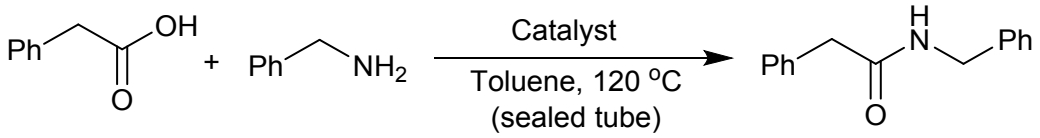
Fig. S4. Nitrogen adsorption–desorption isotherms for MCF (■), SBA-16 (●) and the commercial silica (♦)

Table S2. Characteristics of the support materials

Support materials	Surface area[a] (m^2/g)	Pore volume[b] (cm^3/g)	Pore size[c] (nm)
MCF	421.5	2.29	23.8
SBA-16	527.4	0.38	3.7
Silica	448.7	0.76	4.7

[a]BET surface area; [b]Estimated at the relative pressure of P/P_0=0.99; [c]The pore size was derived from the N_2 adsorption branch using the BJH method.

Table S3. Direct amide condensations of phenylacetic acid and benzylamine by various catalysts under sealed conditions[a]



Entry	Catalyst (mol%)	Time (hr)	Yield (%)[b]
1	bare MCF[c]	2	23
2	**1** (10)	2	74
3	**2** (10)	2	78
4	**3**[d]	2	20
5	**3**[d] + **1** (10)	2	27
6	**4** (5)	2	11[e]
7	**5a** (10)	2	44
8	**5b** (10)	2	71
9	**5c** (10)	2	79
10	**6** (10)	2	98
11	**7** (10)	2	88
12	**8a** (10)	2	>98
13	**8d** (10)	2	84
14	**6** (5)	1	55
15	**8a** (5)	1	82
16	**8b** (5)	1	26
17	**8c** (5)	1	40
18	**9** (5)	1	28
19	**10** (5)	1	42

[a]Conditions: catalyst (10 or 5 mol%), phenylacetic acid (0.5 mmol), benzylamine (0.5 mmol), toluene (2 ml), 120 °C, 1 or 2 hr; [b]Isolated yield; [c]250 mg, dried under high vacuum at 120 °C for 15 hr; [d]250 mg; [e]Azeotropic removal of water.

General procedure for the direct amide condensation of carboxylic acids and amines (Table 2)

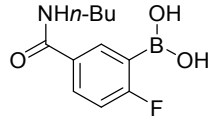
To a 10 ml headspace vial was added carboxylic acid (75mg, 0.55 mmol), catalyst **8a** (5 mmol%, 125 mg) and toluene (or *o*-xylene) (2 ml), and then amine (0.5 mmol or other amounts as shown in Table 1) were added. After the reaction vial was sealed with PTFE/silicone septa, it was placed in a heating block on a stirrer for 2-16 h at 120 °C (or 155 °C). After the reaction was completed, 5 ml of EtOAc was added to fully dissolve the crude products, followed by filtration with celite. And then the catalyst was washed with EtOAc (3 × 5 ml). The filtrate was concentrated to afford crude products. The crude products were purified with preparative TLC afforded to give a pure product. For azeotropic removal of water, a Dean-Stark trap was used under reflux conditions.

Recycling of the catalyst 8a (Table 3)

To a 10 ml round-bottomed flask containing phenylacetic acid (340 mg, 2.5 mmol), MCF-supported catalyst **8a** (625 mg, 5 mol%) and toluene (5 ml), was added benzylamine (265 µl, 2.5 mmol). After the reaction mixture was stirred under azeotropic removal of *in situ* generated water for 2 h (oil bath temperature: 130 °C), it was cooled to room temperature. 5 ml of EtOAc was added to fully dissolve the crude products, followed by filtration through a fritted glass funnel. And then the catalyst was thoroughly washed with EtOAc (3 × 5 ml). The filtrate was concentrated to afford crude products and the recovered catalyst was dried under high vacuum for the next round of run. The crude products were purified by flash column chromatography to give a pure amide product.

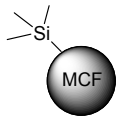
^{1}H and ^{13}C NMR Data for 2, the supported catalysts and intermediates

Cat **2**

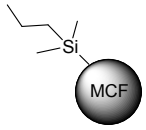


^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.44 (t, *J* = 5.6 Hz, 1H), 8.36 (s, 2H), 8.05 (dd, *J* = 2.4, 5.6 Hz, 1H), 7.87 (m, 1H), 7.16 (t, *J* = 8.8 Hz, 1H), 3.23 (dd, *J* = 6.8, 12.4 Hz, 2H), 1.48 (m, 2H), 1.31 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H).

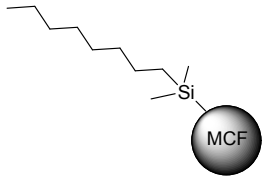
^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.5, 166.1, 165.8, 135.2, 135.1, 131.3, 131.2, 130.7, 130.7, 115.3, 115.0, 100.0, 31.7, 20.1, 14.2.
Mol. Wt.: 239.1
GC - MS *m/z* (%): 195 (6) (M-HBO2), 153 (16), 152 (12), 124 (7), 123 (100), 95 (33), 75 (11).



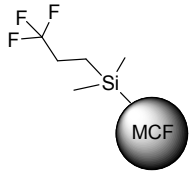
^{13}C NMR (100 MHz): δ 0.9.



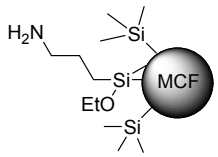
^{13}C NMR (100 MHz): δ 23.5, 19.8, 1.0.



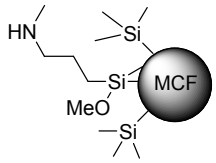
^{13}C NMR (100 MHz): δ 36.4, 35.2, 32.4, 25.8, 20.4, 15.4, 0.8.



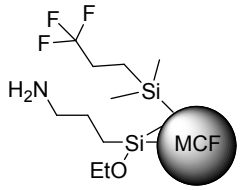
^{13}C NMR (100 MHz): δ 31.8, 13.0, 0.9.



^{13}C NMR (100 MHz): δ 59.9, 43.9, 25.6, 17.0, 10.5, 0.9.

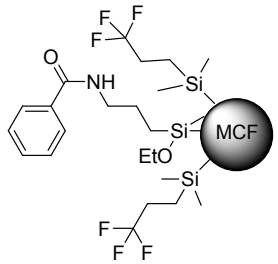


^{13}C NMR (100 MHz): δ 60.2, 54.8, 35.0, 23.5, 17.6, 11.0, 1.0.



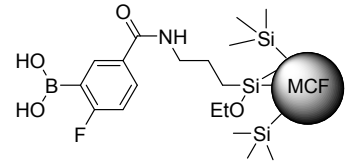
^{13}C NMR (100 MHz): δ 60.3, 44.1, 29.0, 17.2, 10.3, 0.9 .
^{29}Si NMR: δ 13.8, -57.7, -64.9, -100.5, -108.8.

Cat **4**



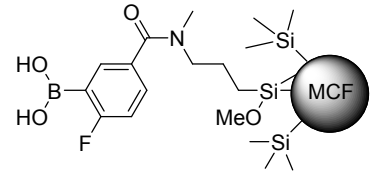
^{13}C NMR (100 MHz): δ 170.0, 135.9, 128.7, 60.7, 51.3, 43.8, 29.4, 24.5, 17.8, 10.8, 1.0.
^{29}Si NMR: δ 14.4, -55.0, -63.6, -99.8, -108.4.

Cat **5b**



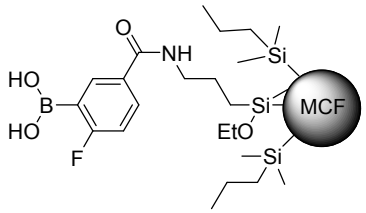
^{13}C NMR (100 MHz): δ 169.5, 134.5, 114.6, 60.0, 43.1, 31.3, 23.9, 17.0, 10.5, 0.9.
^{29}Si NMR: δ 13.9, -56.4, -63.2, -100.0, -108.5.

Cat **5c**



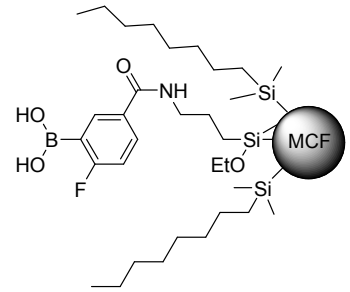
^{13}C NMR (100 MHz): δ 170.6, 133.3, 114.3, 59.9, 51.3, 33.9, 21.2, 10.1, 0.9.
^{29}Si NMR: δ 13.7, -56.8, -65.3, -99.9, -108.6.

Cat **6**



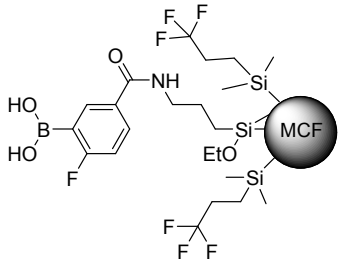
^{13}C NMR (100 MHz): δ 169.9, 134.3, 115.1, 60.5, 51.5, 43.3, 21.5, 17.6, 11.0, 1.0.
^{29}Si NMR: δ 13.8, -56.5, -64.9, -100.5, -109.2.

Cat **7**



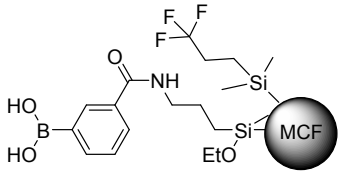
^{13}C NMR (100 MHz): δ 169.5, 133.8, 115.1, 60.2, 51.5, 42.8, 34.2, 32.9, 30.2, 23.7, 18.6, 12.8, 1.0.
^{29}Si NMR: δ 13.7, -56.8, -64.0, -100.8, -109.3.

Cat **8a**



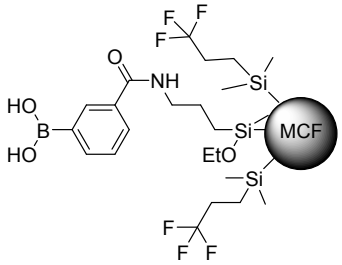
^{13}C NMR (100 MHz): δ 170.3, 130.4, 115.6, 60.9, 51.3, 43.7, 29.5, 24.5, 17.7, 10.8, 1.0.
^{29}Si NMR δ = 13.7, -56.9, -64.3, -100.9, -108.6.

Cat **8b**



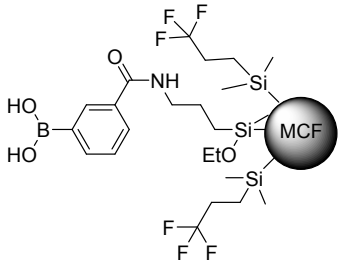
^{13}C NMR (100 MHz): δ 172.7, 151.9, 133.2, 118.51, 63.5, 52.7, 46.14, 31.5, 26.2, 19.6, 0.8.
^{29}Si NMR δ = 14.2, -54.9, -64.7, -99.9, -108.4.

Cat **8c**



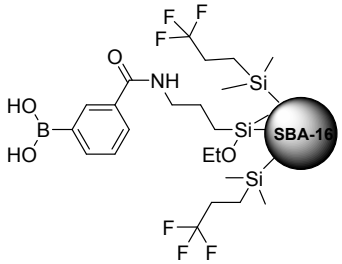
^{13}C NMR (100 MHz): δ 169.6, 131.6, 115.4, 60.4, 50.3, 43.3, 29.1, 24.3, 17.6, 10.5, 0.9.
^{29}Si NMR δ = 15.0, -56.5, -63.8, -100.3, -107.4.

Cat **8d**



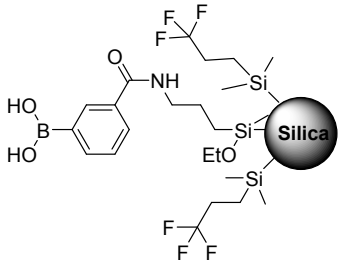
^{13}C NMR (100 MHz): δ 170.1, 135.7, 129.8, 127.0, 60.2, 50.9, 43.1, 28.8, 17.2, 10.2, 0.8.
^{29}Si NMR δ = 13.7, -56.3, -64.2, -100.1, -108.1.

Cat **9**



^{13}C NMR (100 MHz): δ 178.3, 130.5, 128.1, 60.8, 51.6, 44.2, 29.2, 18.8, 10.6, 0.7.
^{29}Si NMR δ = 15.0, -55.7, -61.8, -99.9, -107.1.

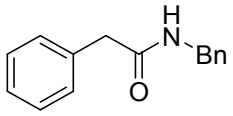
Cat **10**



^{13}C NMR (100 MHz): δ 169.4, 129.9, 127.2, 115.1, 60.3, 51.3, 42.7, 28.8, 17.58, 10.3, 0.8.
^{29}Si NMR δ = 15.2, -54.9, -62.2, -99.9, -108.2.

^{1}H and ^{13}C NMR data for amides

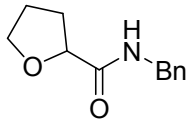
11a



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31-7.18 (m, 10H), 5.92 (brs, 1H), 4.41 (d, *J* = 5.8 Hz, 2H), 3.62 (s, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.0, 134.8, 129.4, 129.0, 128.7, 127.5, 127.4, 127.3, 43.8, 43.6.
Mol. Wt.: 225.29
GC - MS *m/z* (%):225 (32), 91.5 (100).

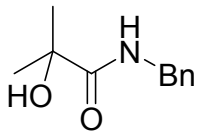
11b



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32-7.24 (m, 5H), 7.05 (brs, 1H), 4.44 (t, *J* = 2.8 Hz, 2H), 4.39 (dd, *J* = 6 Hz, 8.4 Hz, 1H), 3.91-3.83 (m, 2H), 2.29 (m, 1H), 2.09 (m, 1H), 1.88 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.2, 138.2, 128.7, 127.6, 127.5, 78.5, 69.4, 42.8, 30.3, 25.6.
Mol. Wt.: 205.25
GC - MS *m/z* (%):205 (9), 177 (13), 106 (15), 91 (43), 71 (100).

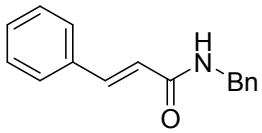
11c



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33-7.25 (m, 5H), 4.41 (d, *J* = 6.0 Hz, 2H), 3.19 (brs, 1H), 1.47 (s, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.6, 138.1, 128.7, 127.6, 127.5, 73.5, 43.2, 27.9.
Mol. Wt.: 193.24.
GC - MS *m/z* (%): 193 (16), 175 (22), 107 (24), 92 (25), 134 (33), 106 (53), 135 (63), 91 (100).

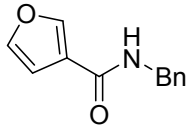
11d



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, *J* = 15.6 Hz, 1H), 7.47 (t, *J* = 3.6 Hz, 2H), 7.36 (m, 8H), 6.48 (d, *J* = 15.6 Hz, 1H), 6.39 (brs, 1H), 4.55 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.0, 141.3, 138.2, 134.8, 129.7, 128.8, 128.7, 127.9, 127.8, 127.6, 120.5, 43.8.
Mol. Wt.: 237.3.
GC - MS *m/z* (%):237 (72), 131 (100).

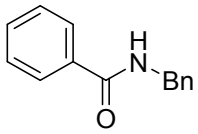
11e



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (s, 1H), 7.43 (s, 1H) 7.33(m, 5H), 6.65 (s, 1H), 6.36 (brs, 1H), 4.56 (d, *J* = 5.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.6, 144.9, 143.8, 143.8, 138.1, 138.1, 128.8, 127.9, 127.6, 122.4, 108.3, 43.5.
Mol. Wt.: 201.22
GC - MS *m/z* (%):201 (29), 95 (100).

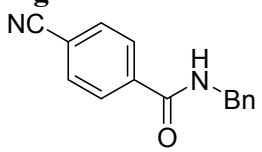
11f



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, *J* = 0.8 Hz, 2H), 7.79 (m, 1H), 7.43 (m, 2H), 7.27 (m, 5H), 6.77 (brs, 1H), 4.62 (d, *J* = 7.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.5, 138.2, 134.3, 131.6, 128.8, 128.6, 127.9, 127.6, 127.0, 44.1.
Mol. Wt.: 211.26
GC - MS *m/z* (%): 211 (66), 105 (100).

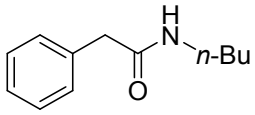
11g



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (dd, *J* = 0.8 Hz, 8.4 Hz, 1H), 7.71 (dd, *J* = 0.4 Hz, 8.4 Hz, 1H), 7.35 (m, 5H), 6.78 (brs, 1H), 4.62 (d, *J* = 5.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.7, 138.2, 137.5, 132.4, 128.9, 127.9, 127.9, 127.8, 118.0, 115.1, 44.3.
Mol. Wt.: 236.27
GC - MS *m/z* (%): 77 (17), 91 (25), 79 (28), 106 (46), 235 (50), 102 (66), 130 (94), 236 (100).

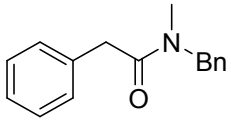
11h



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.25 (m, 5H), 5.68 (brs, 1H), 3.56 (s, 2H), 3.19 (m, 2H), 1.43 (m, 2H), 1.26 (m, 2H), 0.87 (t, *J* = 9.6 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.0, 135.1, 129.4, 128.9, 128.4, 127.4, 127.3, 43.8, 39.4, 31.5, 19.9, 13.7.
Mol. Wt.: 191.27
GC - MS *m/z* (%):191 (9), 100 (13), 91 (58), 92 (100).

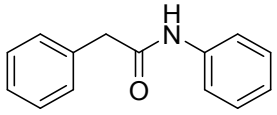
11i



^{1}H NMR ($CDCl_3$, 400 MHz), a mixture of two rotamers: δ 7.30-7.23 (m, 10H), 7.13 (m, 1H), 4.63 (s, 1.3H, major rotamer), 4.55 (s, 1H, minor rotamer), 3.81 (s, 1.3H, major rotamer), 3.78 (s, 1H, minor rotamer), 2.98 (s, 1.5H, minor rotamer), 2.92 (s, 2H, major rotamer).

^{13}C NMR ($CDCl_3$, 100 MHz), a mixture of two rotamers: δ 171.6 (minor rotamer), 171.2 (major rotamer), 137.3, 136.5, 135.1, 135.0, 129.0, 128.9, 128.8, 128.7, 128.6, 128.1, 127.7, 127.4, 126.9, 126.8, 126.4, 53.7 (minor rotamer), 51.0 (major rotamer), 41.2 (major rotamer), 40.9 (minor rotamer), 35.3 (major rotamer), 34.1 (minor rotamer).
Mol. Wt.: 239.13.
GC - MS *m/z* (%): 239 (57), 91 (100).

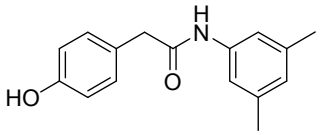
11j



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.27 (m, 9H), 7.05 (m, 1H), 3.71 (brs, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.3, 137.7, 134.5, 129.6, 129.3, 129.0, 127.7, 124.5, 120.0, 44.8.
Mol. Wt.: 211.26
GC - MS *m/z* (%): 211 (35), 91 (59), 93 (100).

11k



^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.91 (brs, 1H), 9.28 (brs, 1H), 7.21 (s, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.70 (dd, *J* = 1.6 Hz, 6.8 Hz, 2H), 6.66 (s, 1H), 3.46 (s, 2H) 2.21 (s, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.0, 156.5, 139.6, 138.1, 130.4, 126.7, 125.1, 117.3, 115.5, 43.1, 21.6.
Mol. Wt.: 255.31
GC - MS *m/z* (%): 255 (53), 121 (100), 108 (56).

References

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3. N. Zanatta, D. Faoro, S. C. Silva, H. G. Bonacorso, M. A.P. Martins *Tetrahedron Lett.*, 2004, **45**, 5689.
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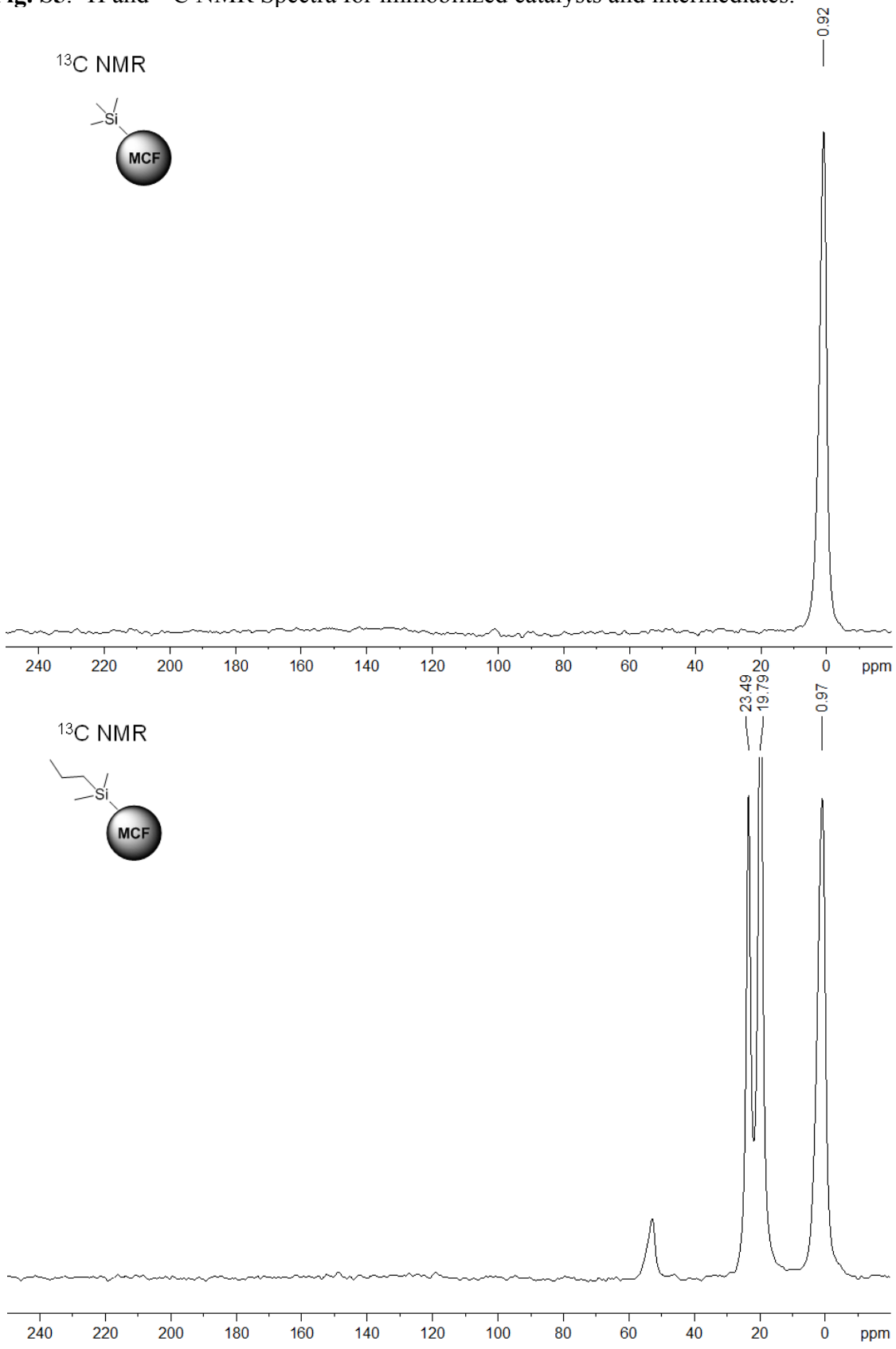
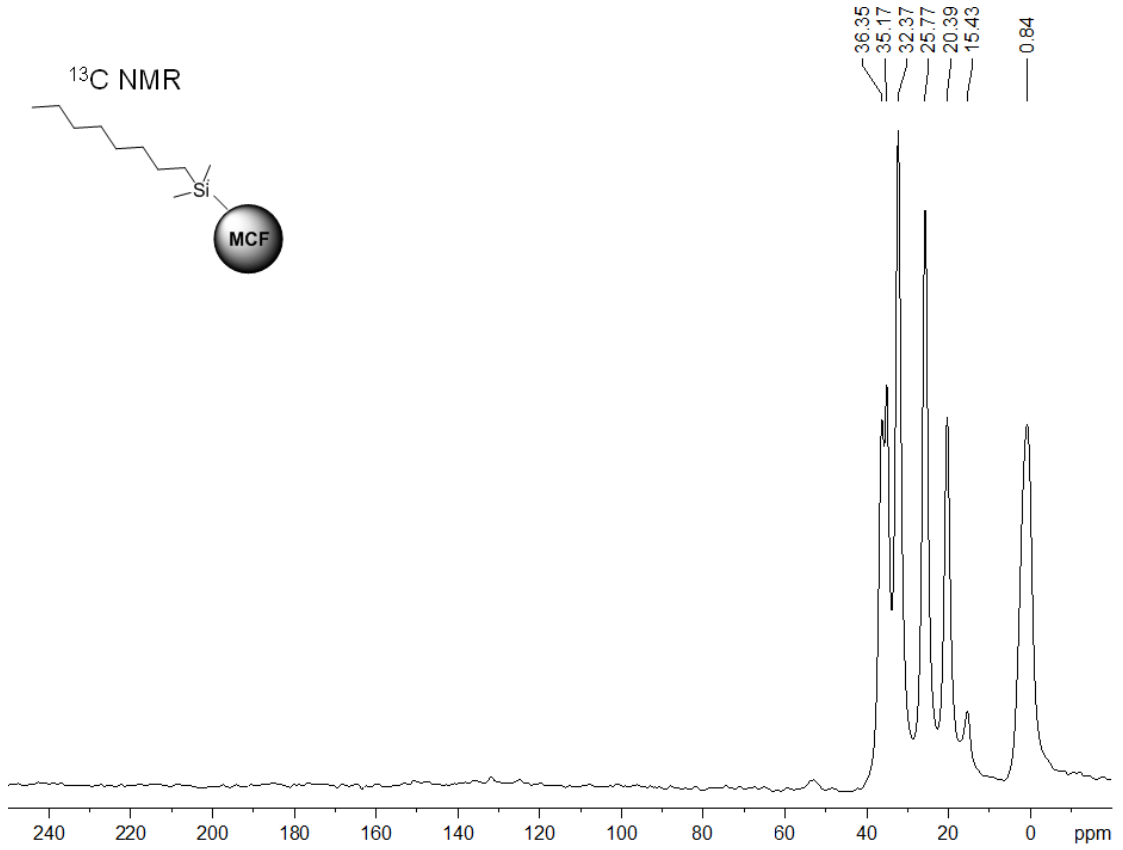
5. G. Pelletier, W. S. Bechara, and A. B. Charette *J. Am. Chem.Soc.*, 2010, **132**, 121817.
6. Z.-W. Chen, H.-F. Jiang, X.-Y. Pan, Z.-J. He *Tetrahedron*, 2011, **61**, 1431.

Fig. S5. ^{1}H and ^{13}C NMR Spectra for immobilized catalysts and intermediates.

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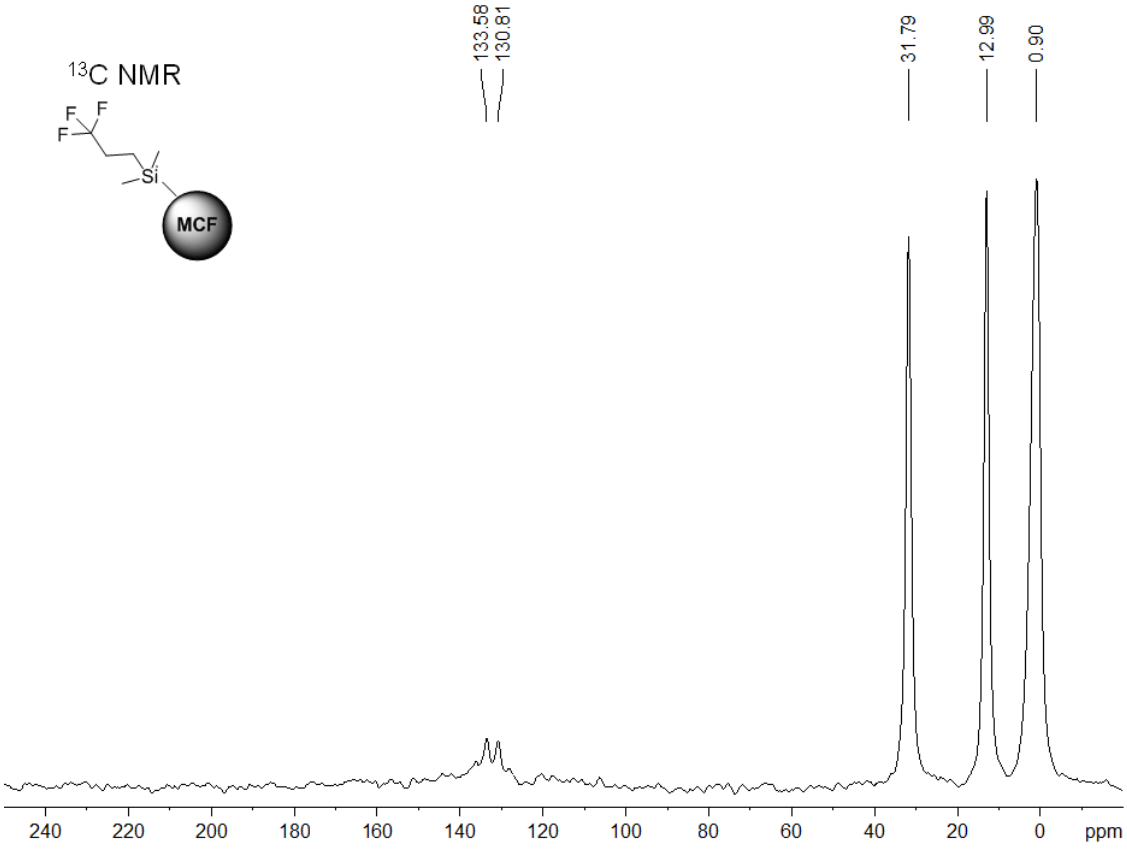
Si
MCF
36.35
35.17
32.37
25.77
20.39
15.43
0.84
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


^{13}C NMR
F
F
F
Si
MCF
133.58
130.81
31.79
12.99
0.90
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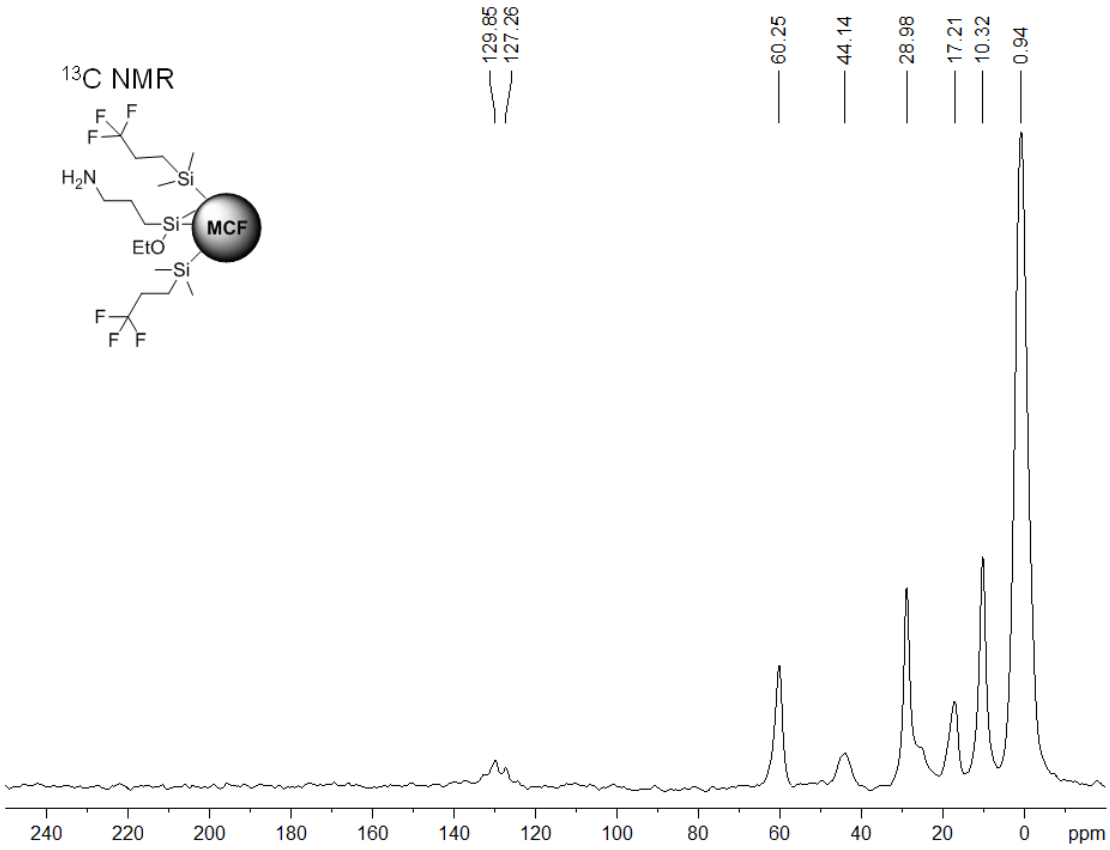
220
200
180
160
140
120
100
80
60
40
20
0
ppm


^{13}C NMR
MCF
129.85
127.26
60.25
44.14
28.98
17.21
10.32
0.94
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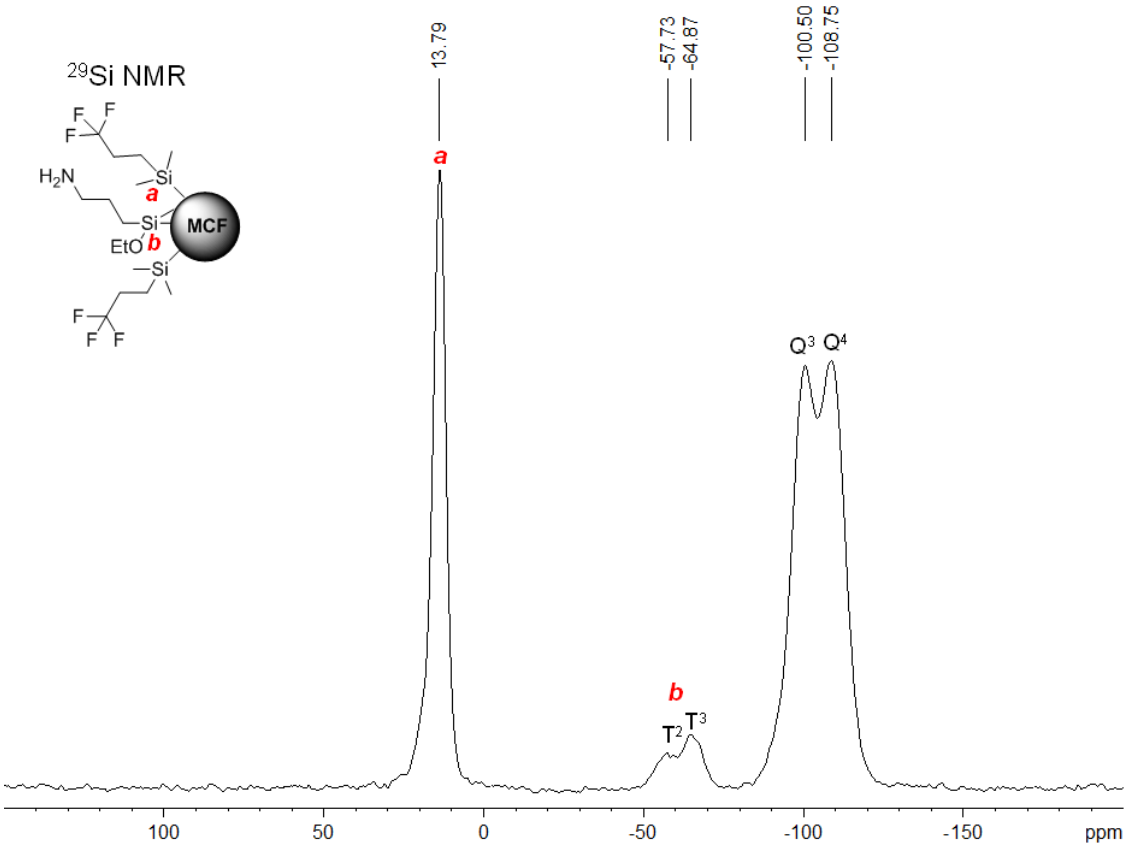
220
200
180
160
140
120
100
80
60
40
20
0
ppm


^{29}Si NMR
MCF
a
b
13.79
-57.73
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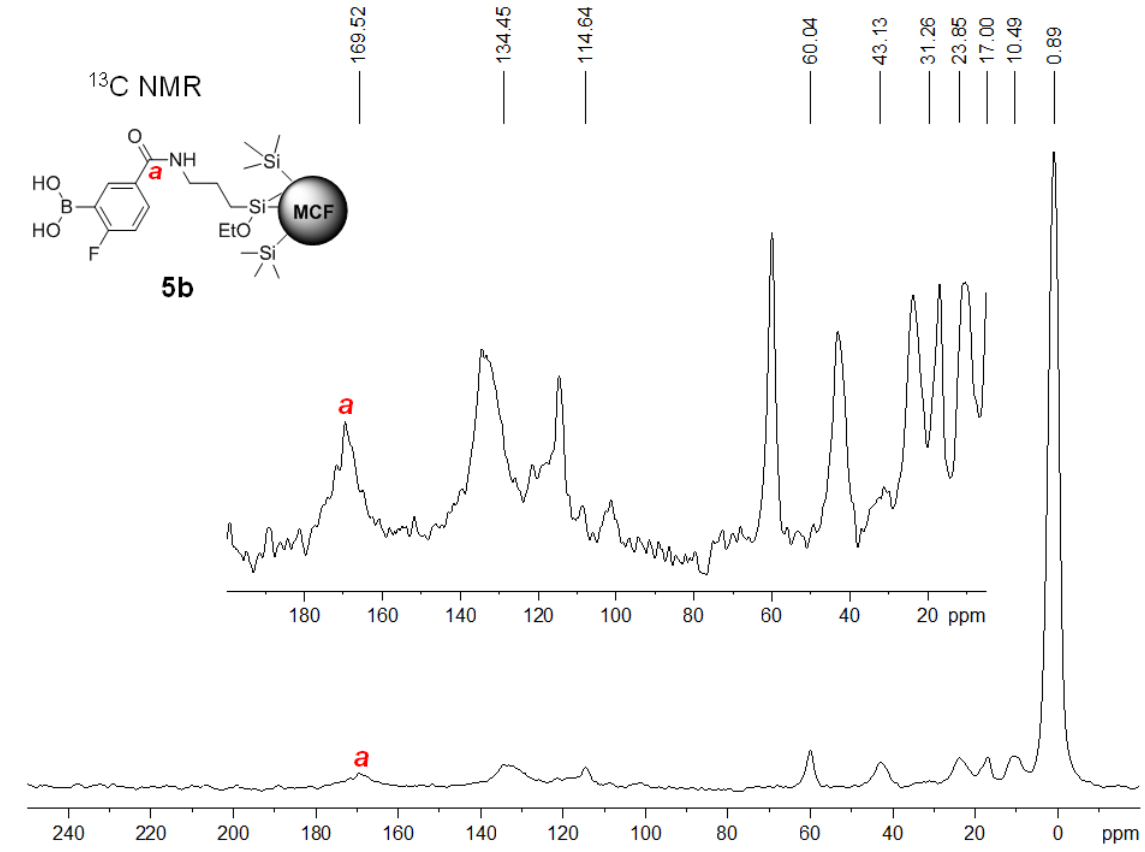
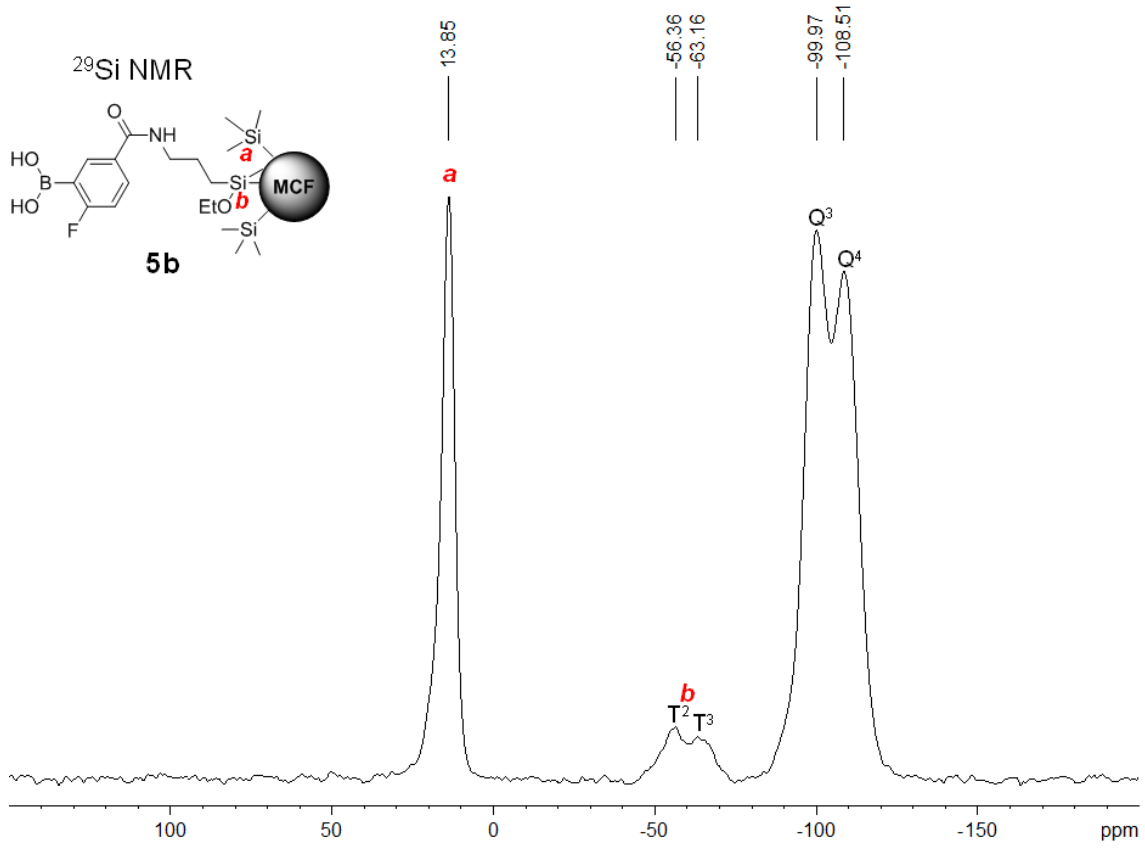
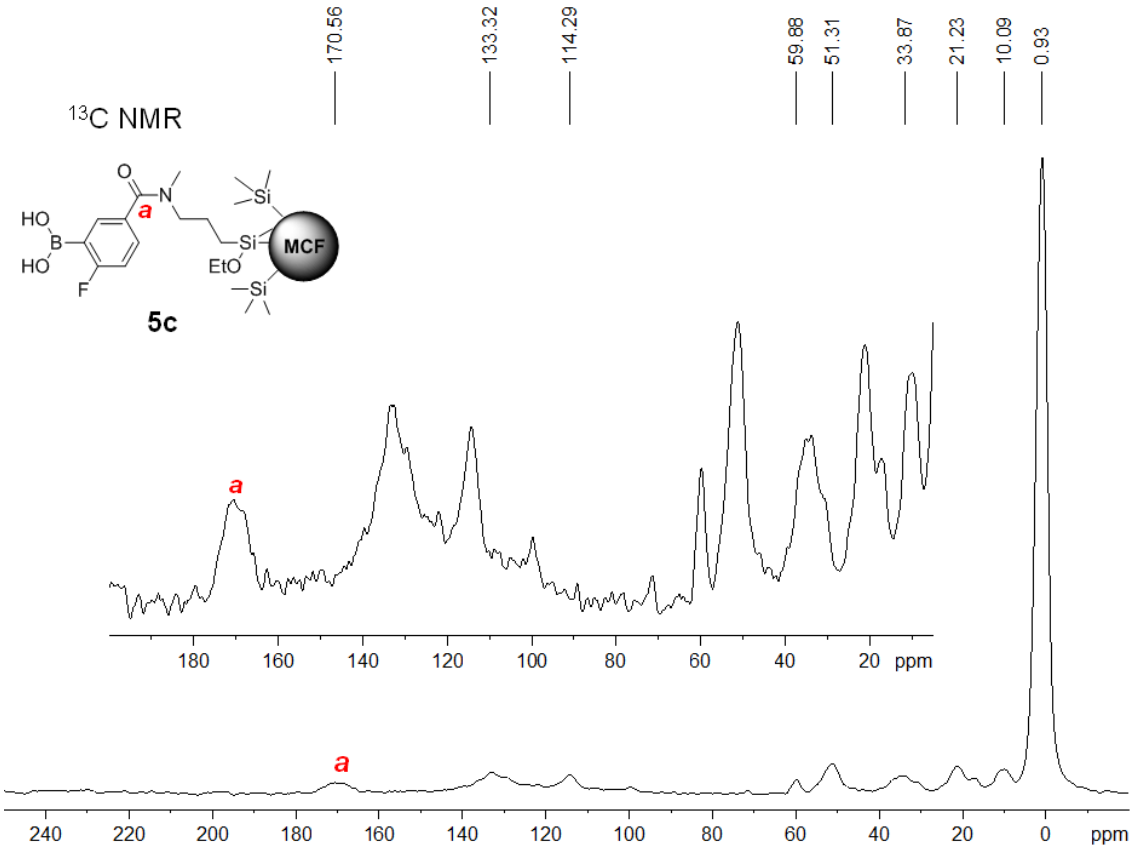
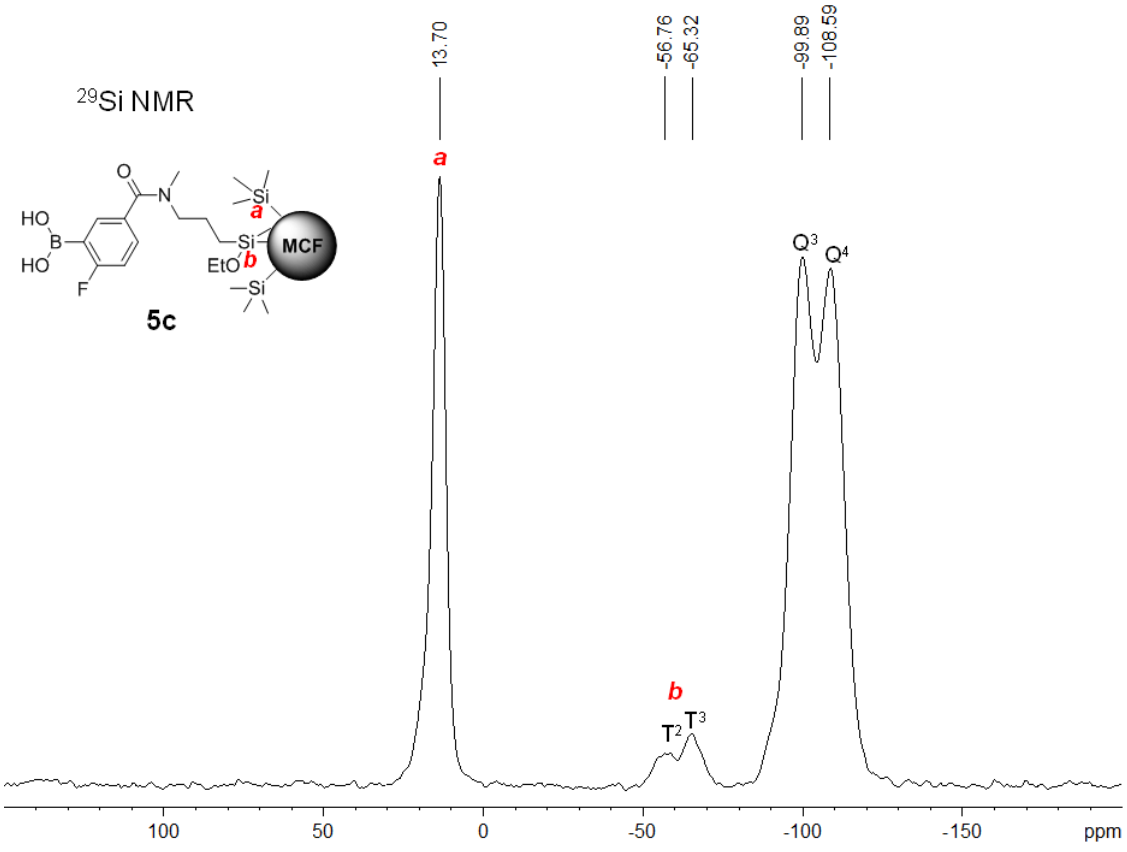
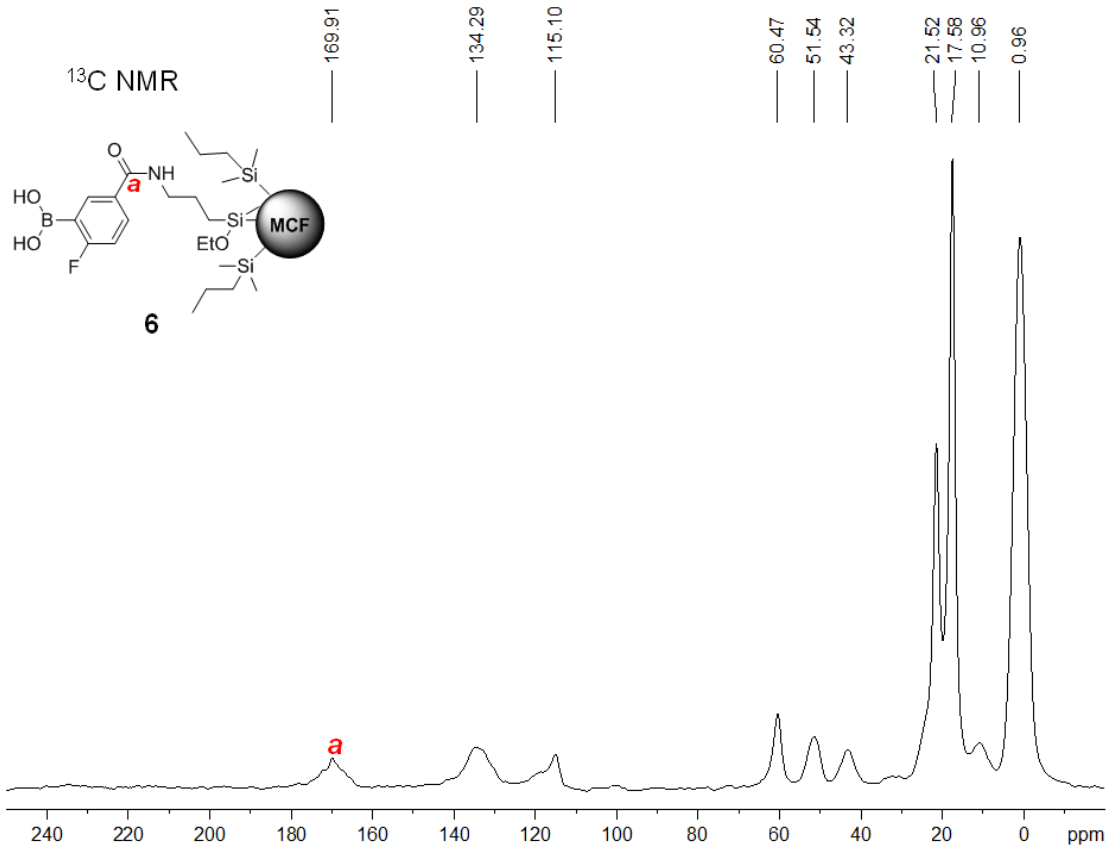
-100.50
-108.75
Q^3
Q^4
T^2
T^3
100
50
0
-50
-100
-150
ppm


169.52
134.45
114.64
60.04
43.13
31.26
23.85
17.00
10.49
0.89
13C NMR
5b
a
MCF
240 220 200 180 160 140 120 100 80 60 40 20 0 ppm
180 160 140 120 100 80 60 40 20 ppm


13.85
-56.36
-63.16
-99.97
-108.51
29Si NMR
5b
a
b
MCF
Q3
Q4
T2
T3
100 50 0 -50 -100 -150 ppm


170.56
133.32
114.29
59.88
51.31
33.87
21.23
10.09
0.93
13C NMR
5c
a
180 160 140 120 100 80 60 40 20 ppm
240 220 200 180 160 140 120 100 80 60 40 20 0 ppm


13.70
-56.76
-65.32
-99.89
-108.59
29Si NMR
5c
a
b
Q3
Q4
T2
T3
100 50 0 -50 -100 -150 ppm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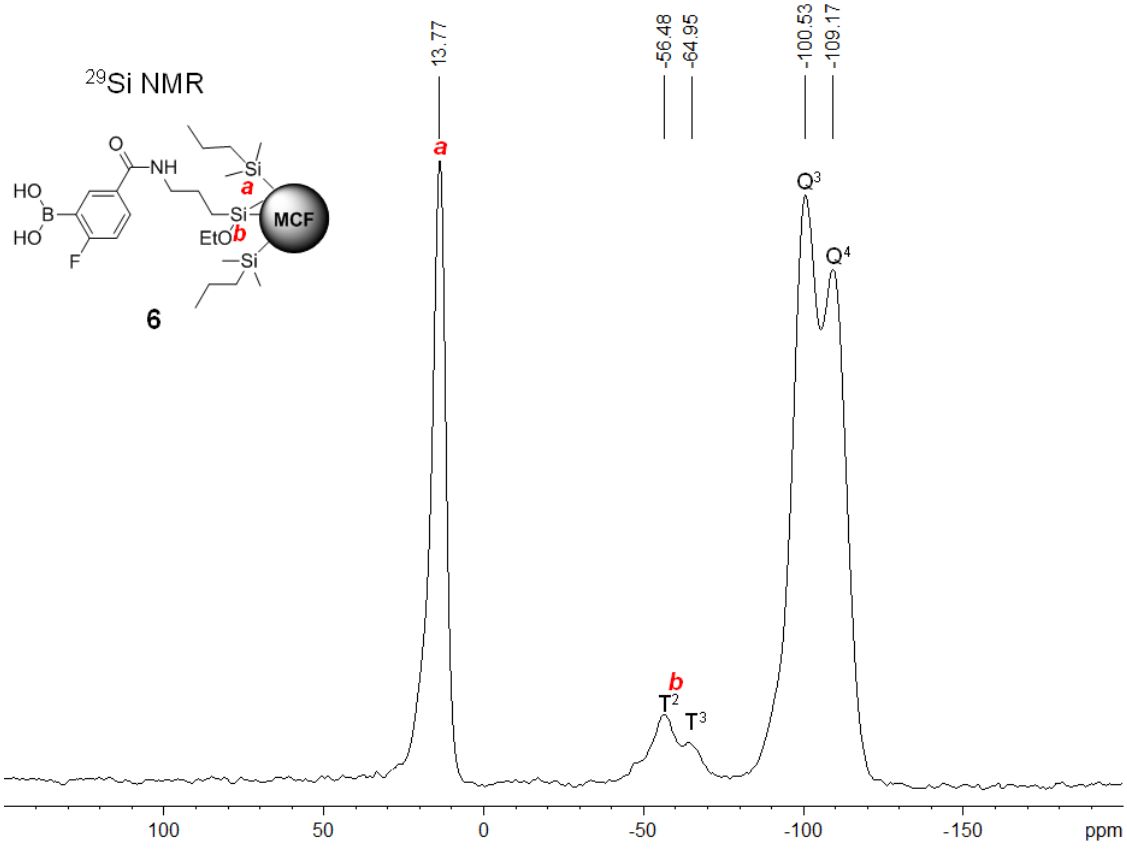
169.91
134.29
115.10
60.47
51.54
43.32
21.52
17.58
10.96
0.96
a
6
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm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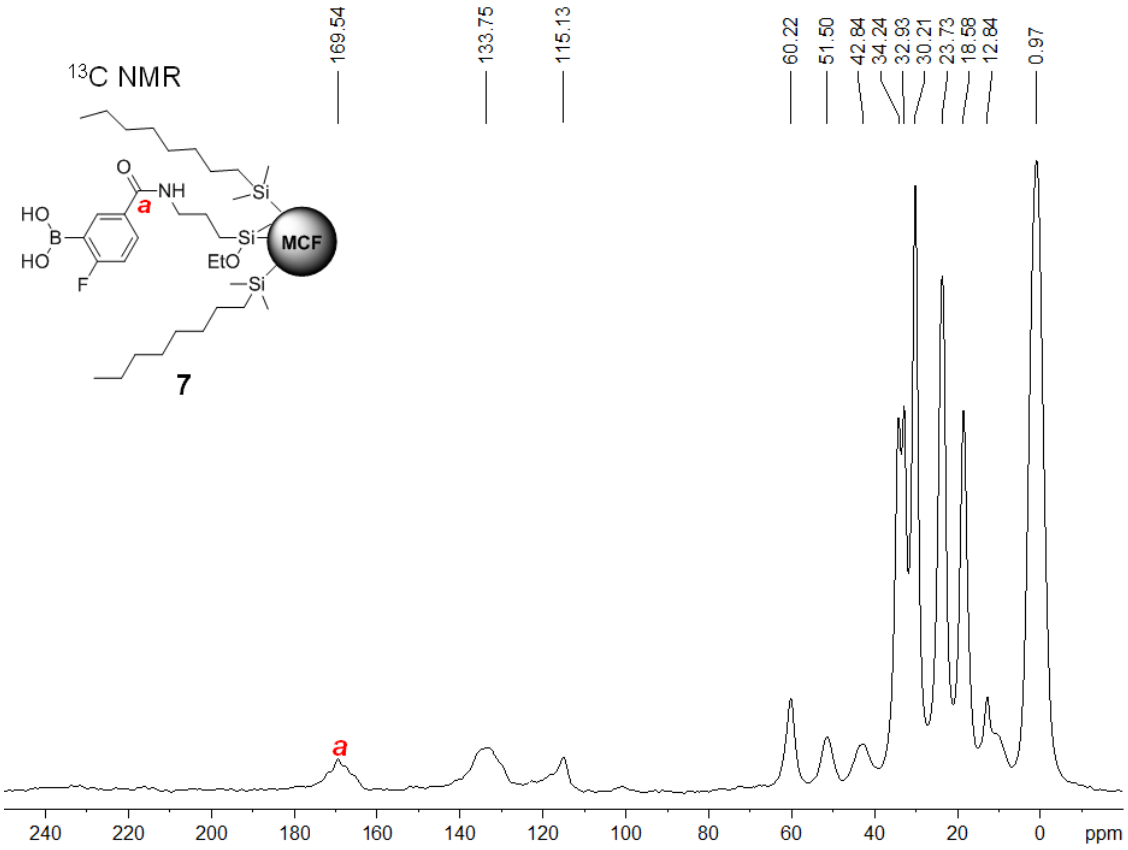
13.77
-56.48
-64.95
-100.53
-109.17
a
b
T^2
T^3
Q^3
Q^4
6
100
50
0
-50
-100
-150
ppm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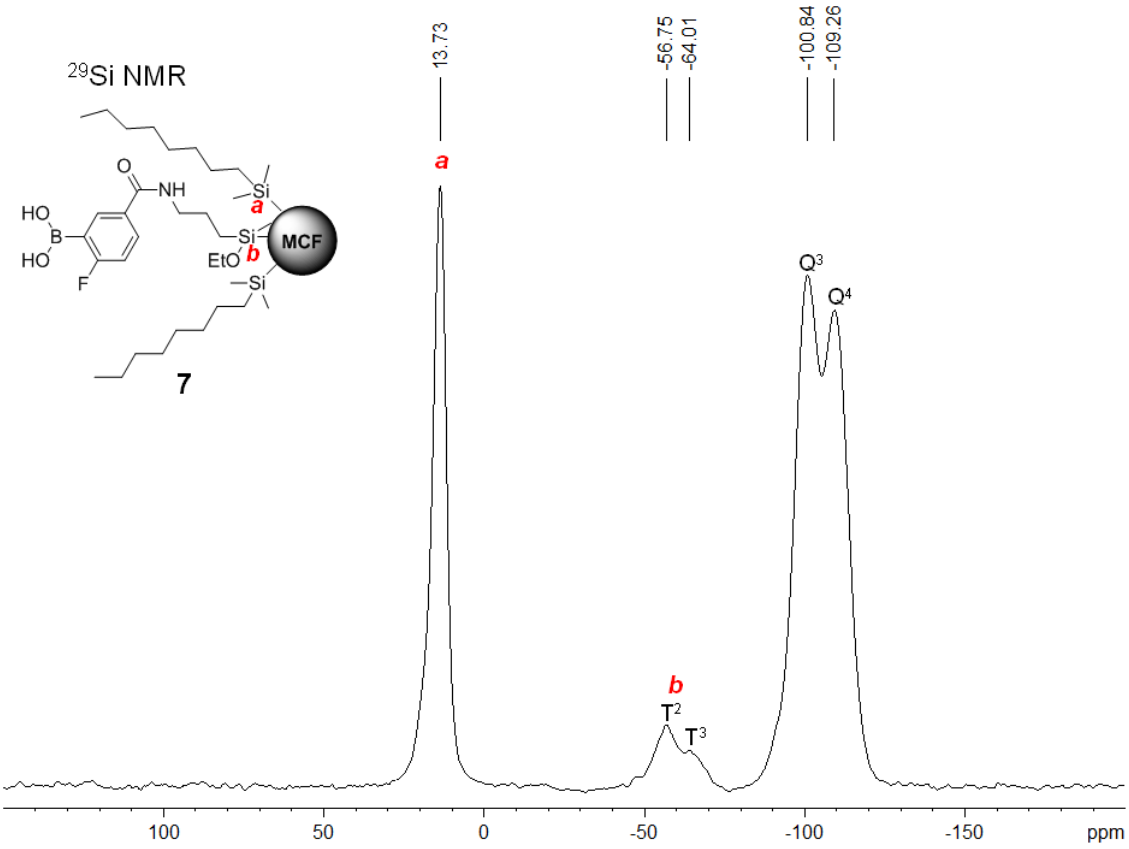
133.75
115.13
60.22
51.50
42.84
34.24
32.93
30.21
23.73
18.58
12.84
0.97
HO
B
HO
F
O
NH
a
Si
Si
EtO
MCF
Si
7
a
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm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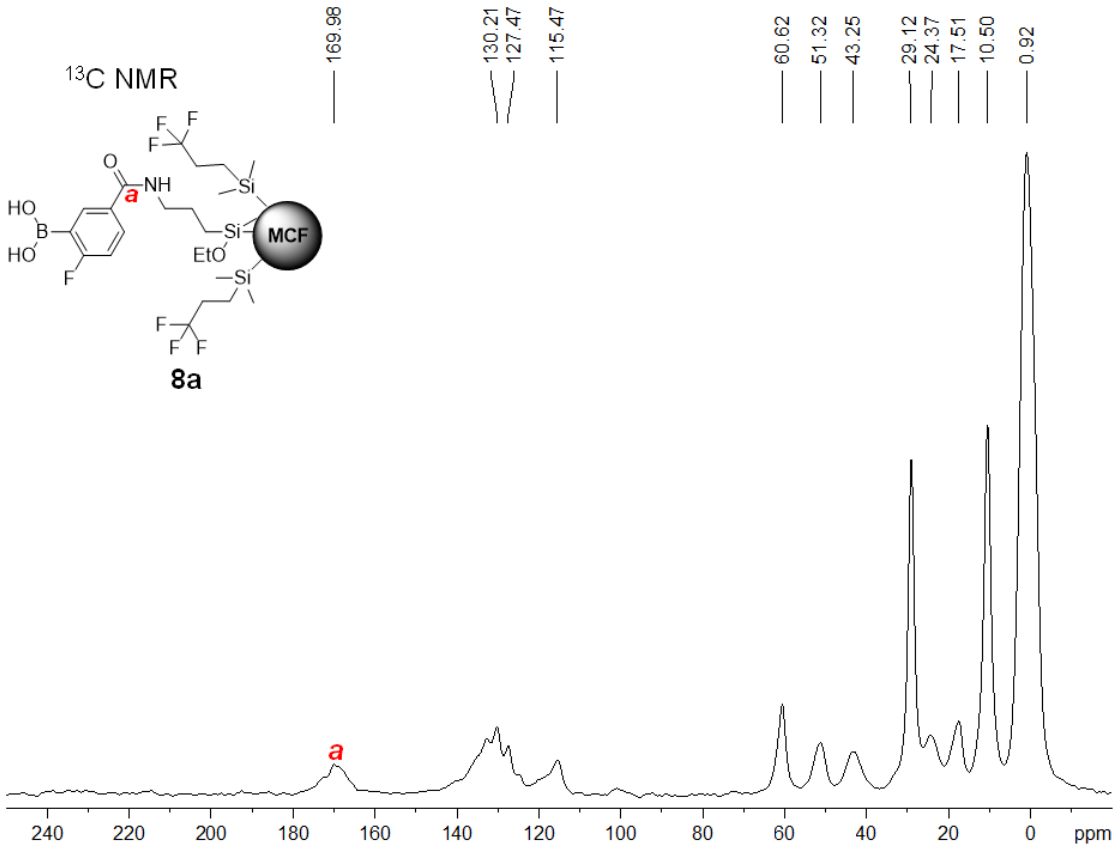
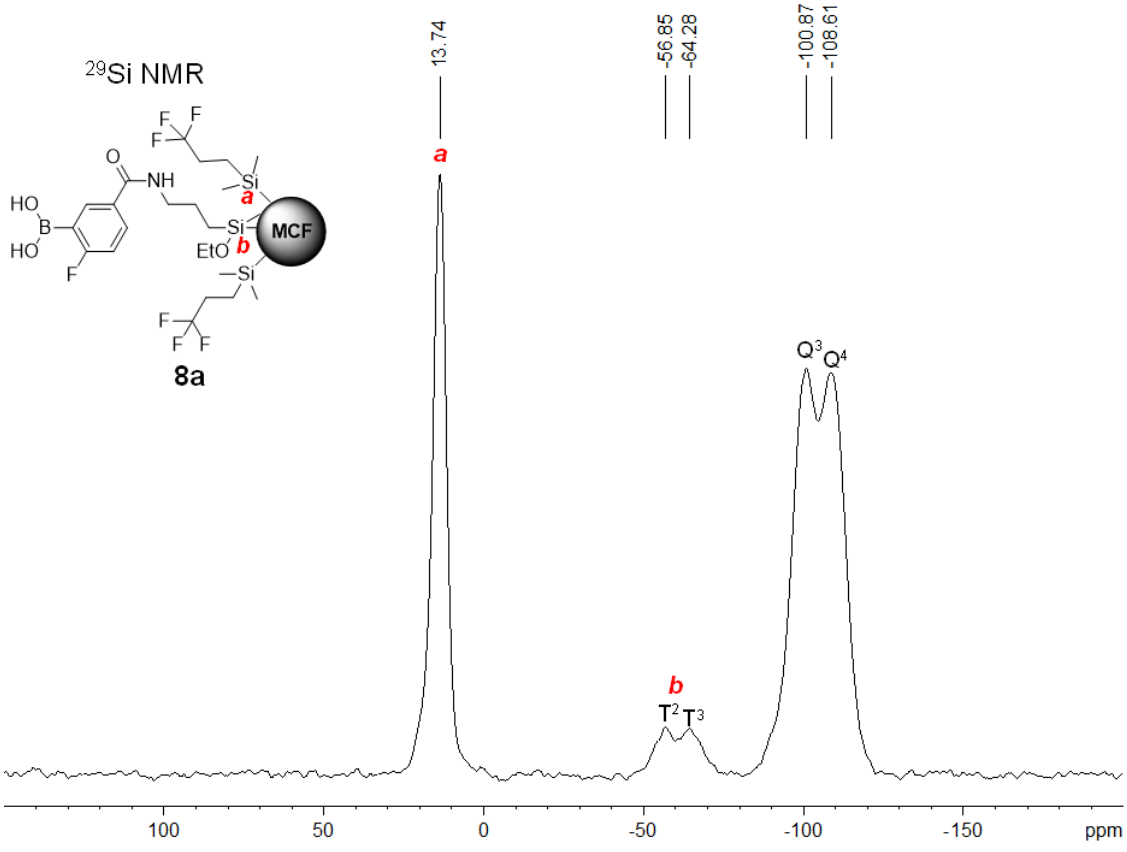
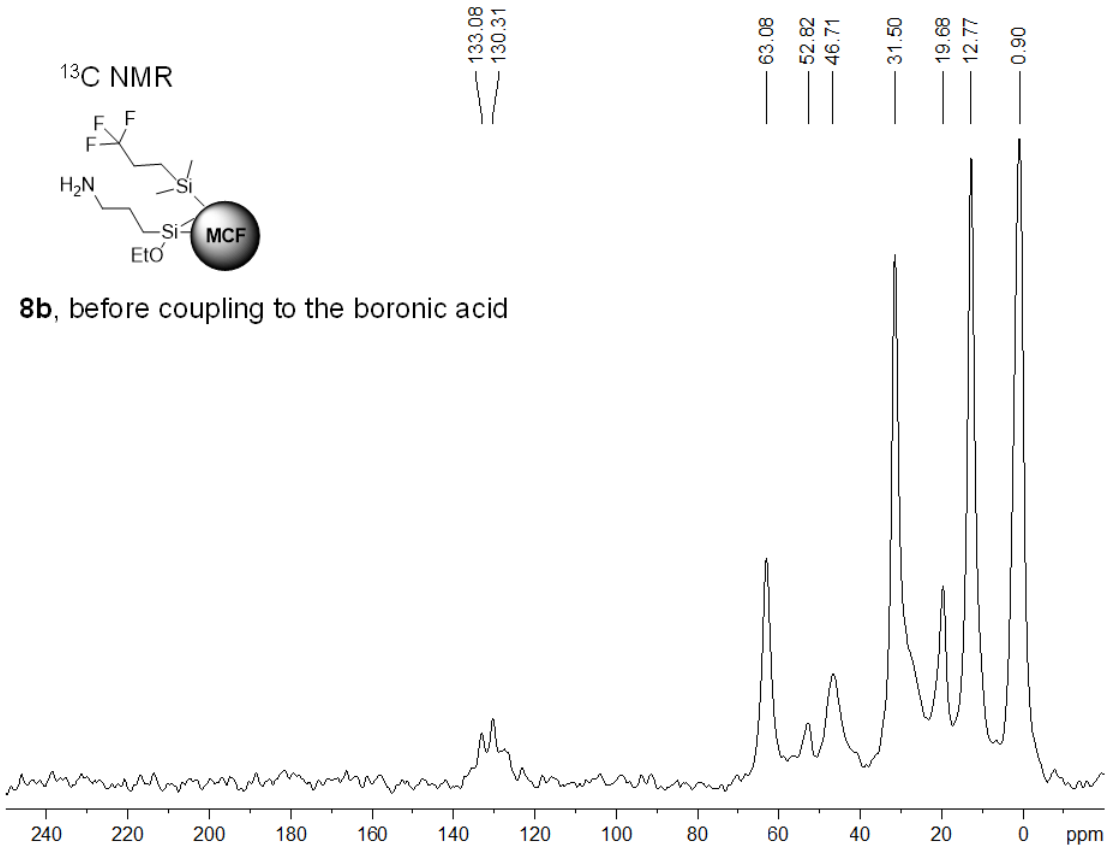
-100.84
-109.26
HO
B
HO
F
O
NH
a
Si
a
Si
EtO
b
MCF
Si
7
a
Q3
Q4
b
T2
T3
100
50
0
-50
-100
-150
ppm


^{13}C NMR
169.98
130.21
127.47
115.47
60.62
51.32
43.25
29.12
24.37
17.51
10.50
0.92
a
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

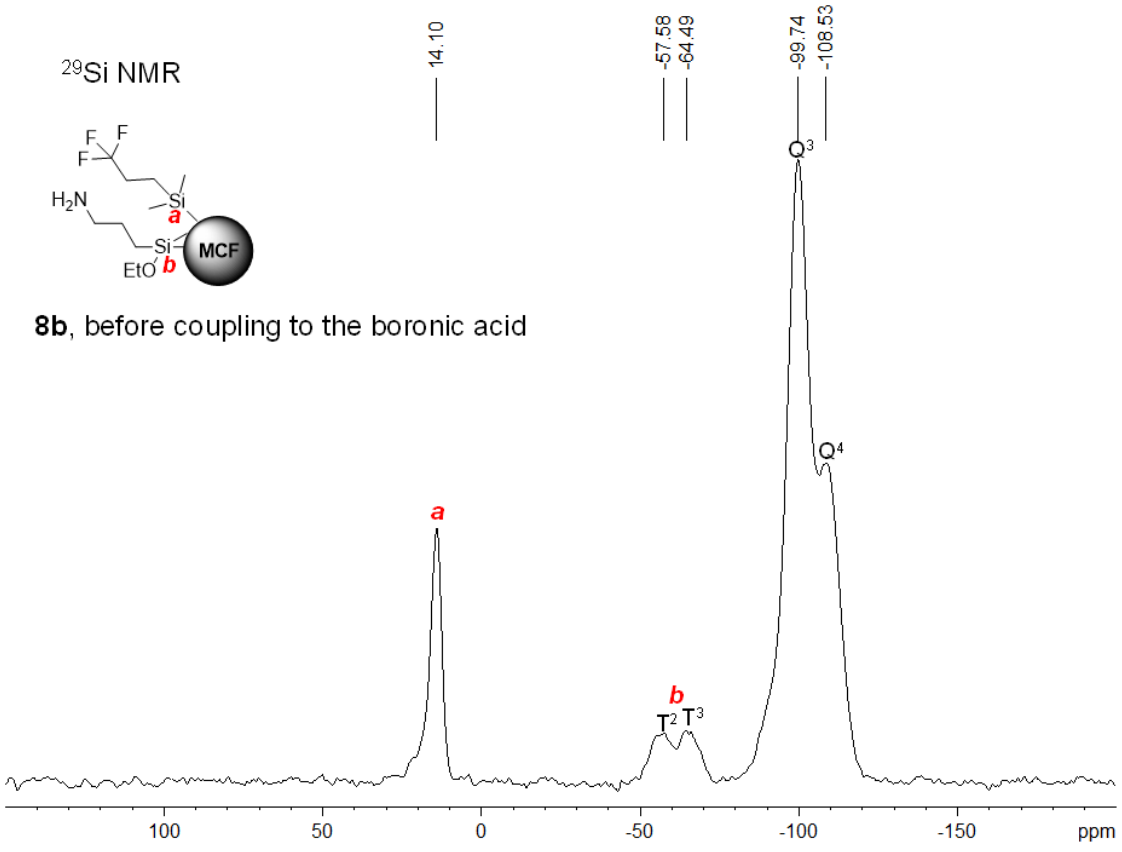
8a


^{29}Si NMR
13.74
-56.85
-64.28
-100.87
-108.61
a
b
T^2 T^3
Q^3 Q^4
100
50
0
-50
-100
-150
ppm

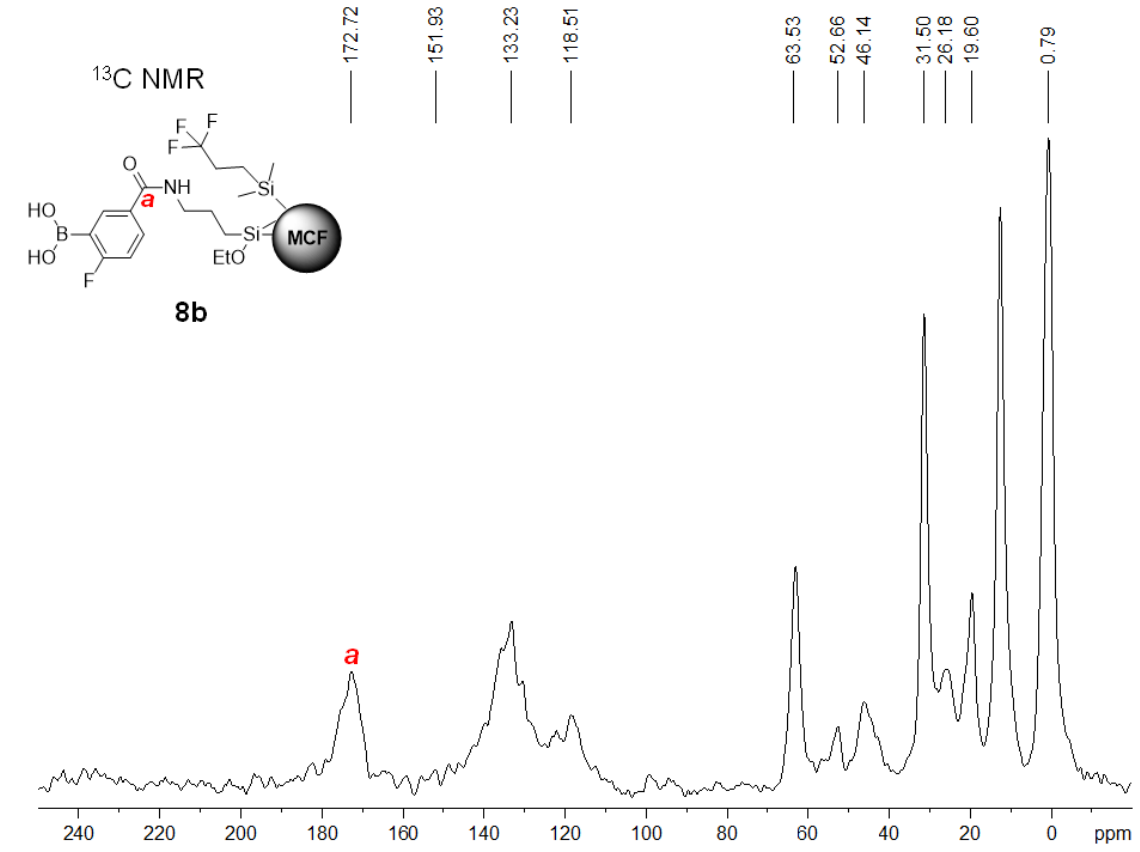
8a



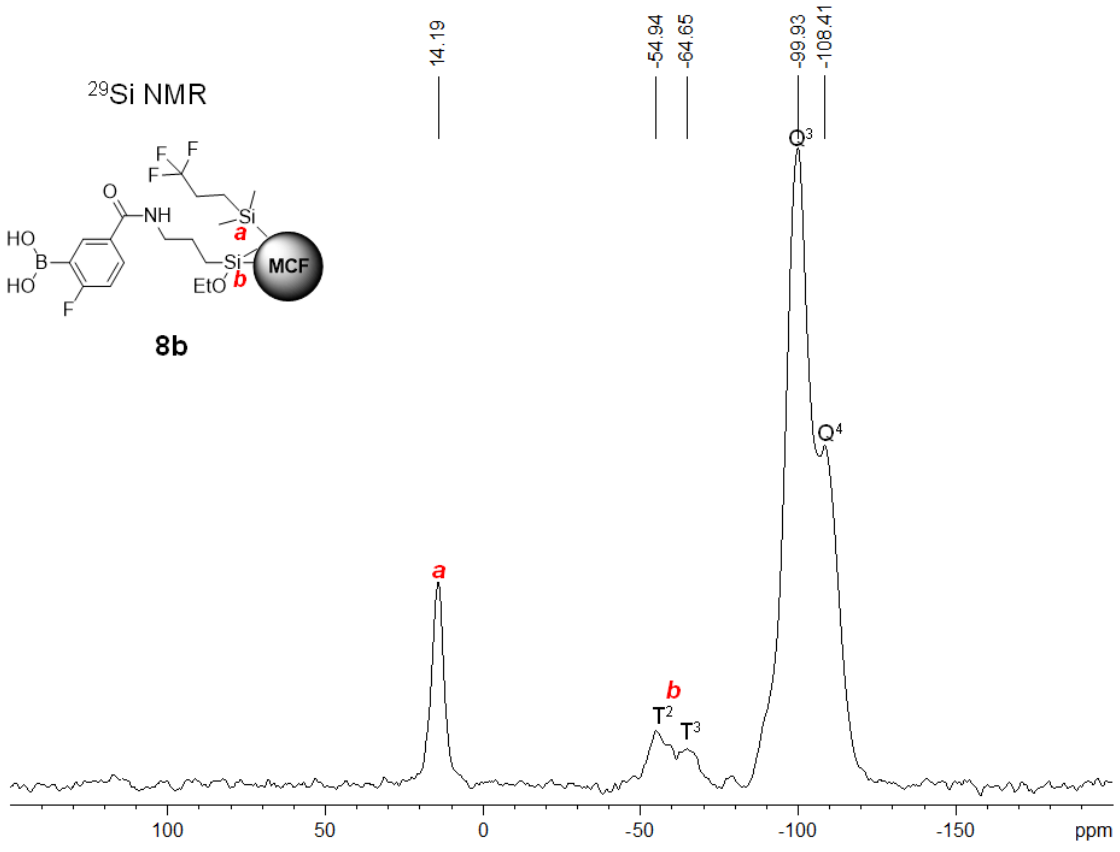
8b, before coupling to the boronic acid



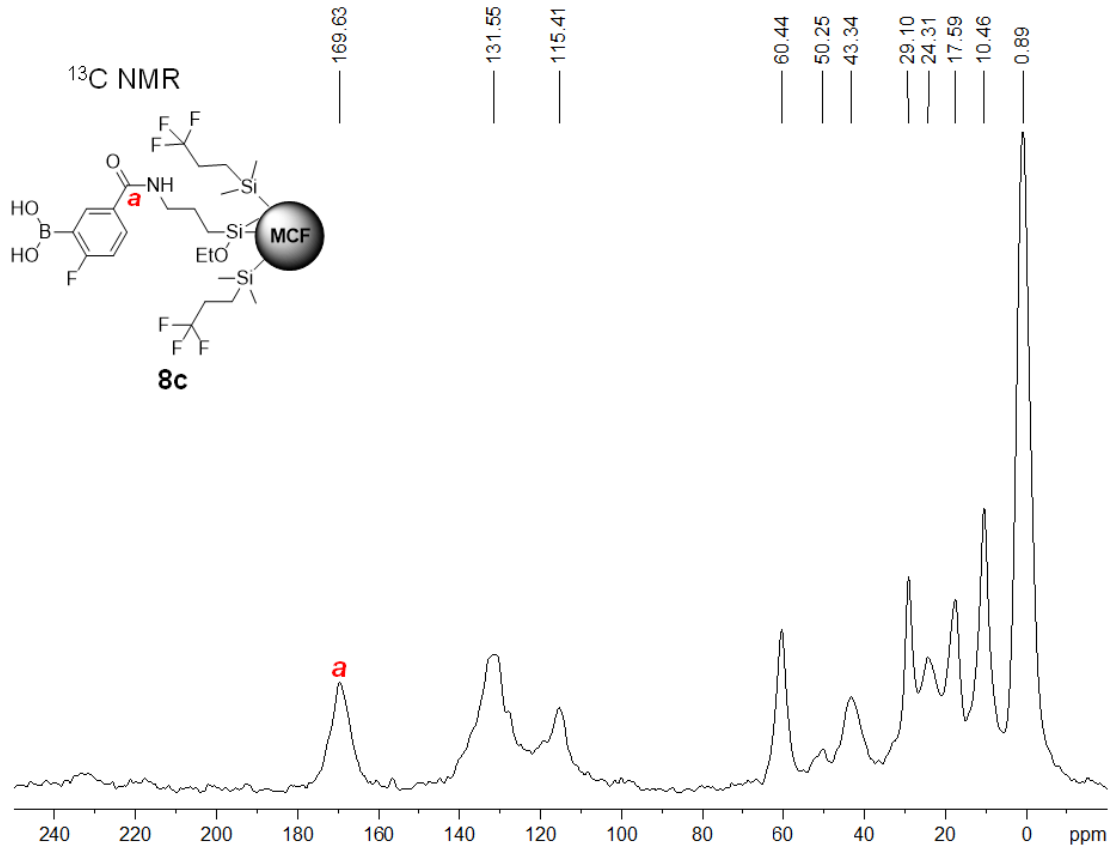
8b, before coupling to the boronic acid

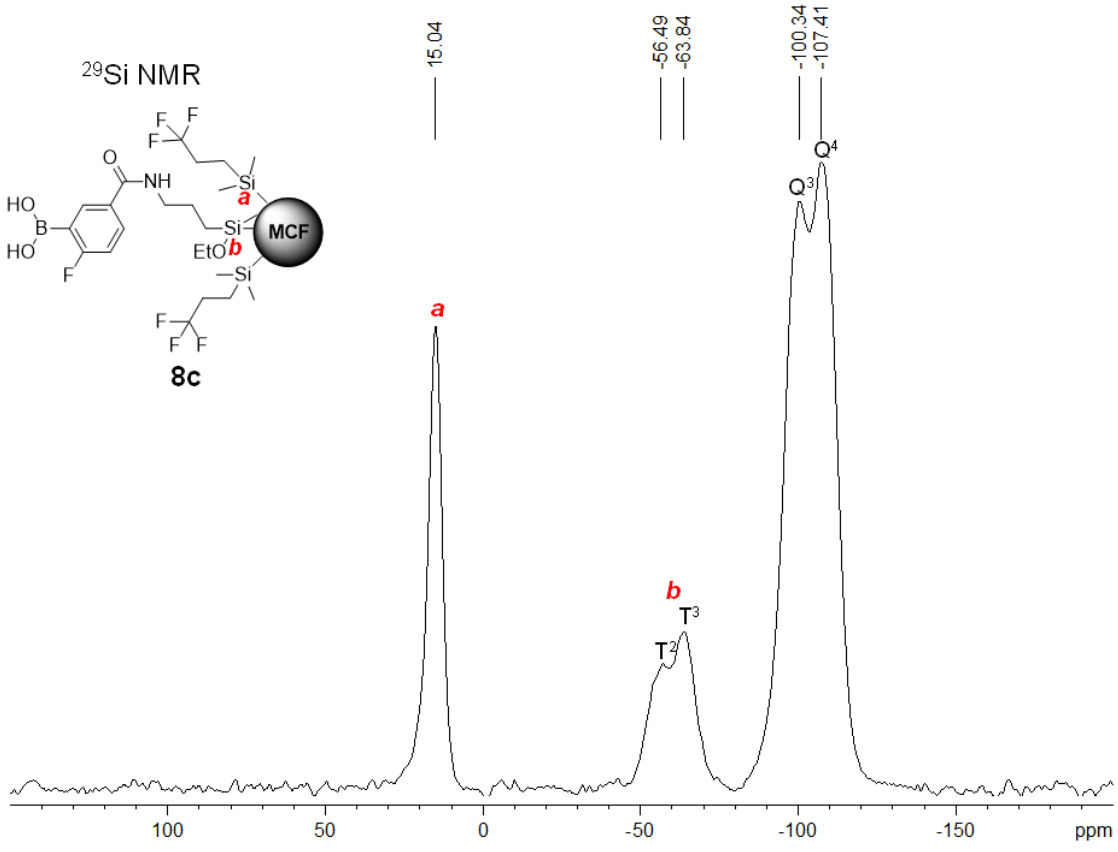

^{13}C NMR
172.72
151.93
133.23
118.51
63.53
52.66
46.14
31.50
26.18
19.60
0.79
a
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

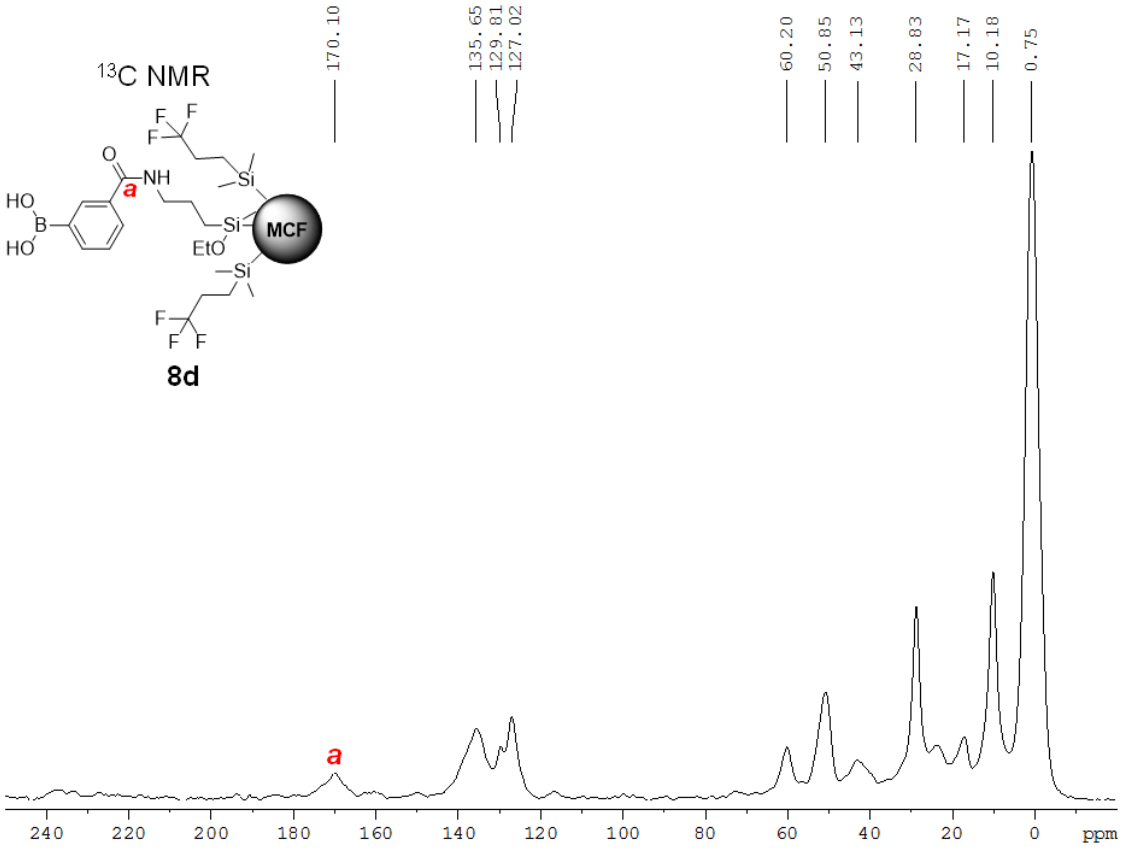
8b

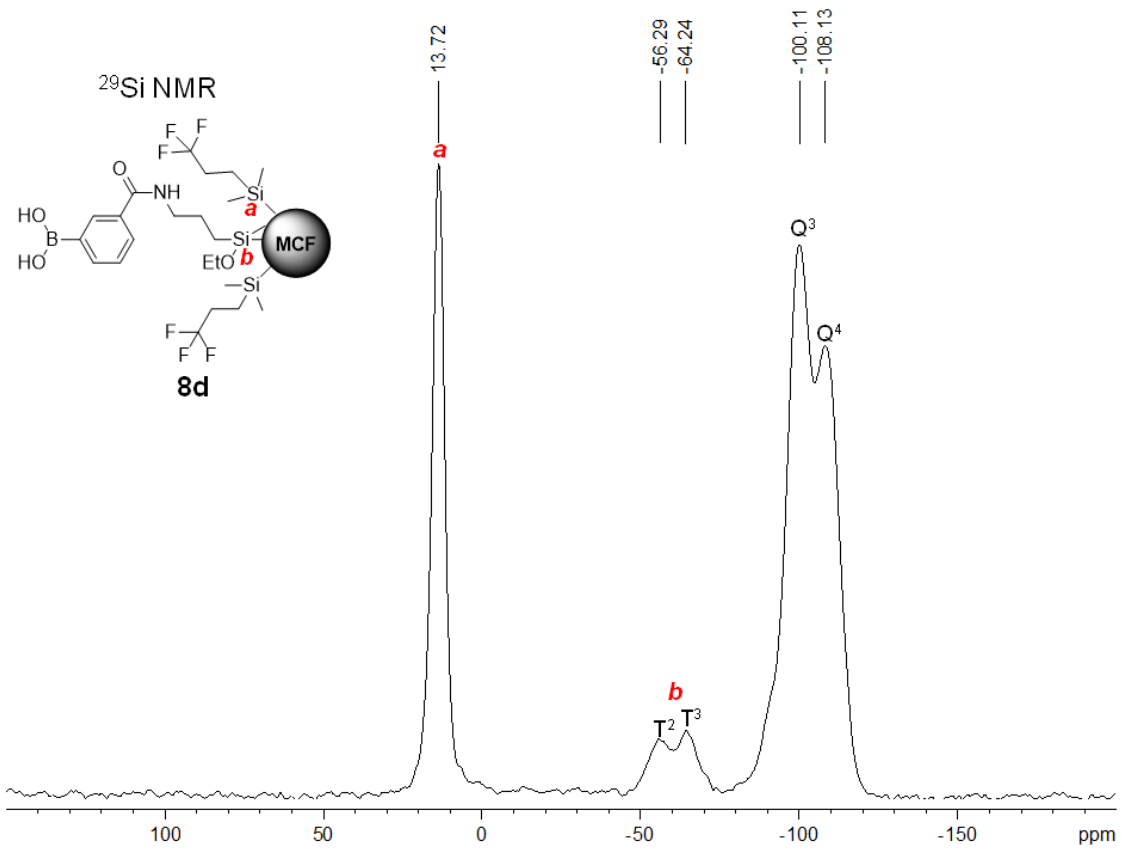

^{29}Si NMR
14.19
-54.94
-64.65
-99.93
-108.41
a
b
T^2
T^3
Q^3
Q^4
100
50
0
-50
-100
-150
ppm

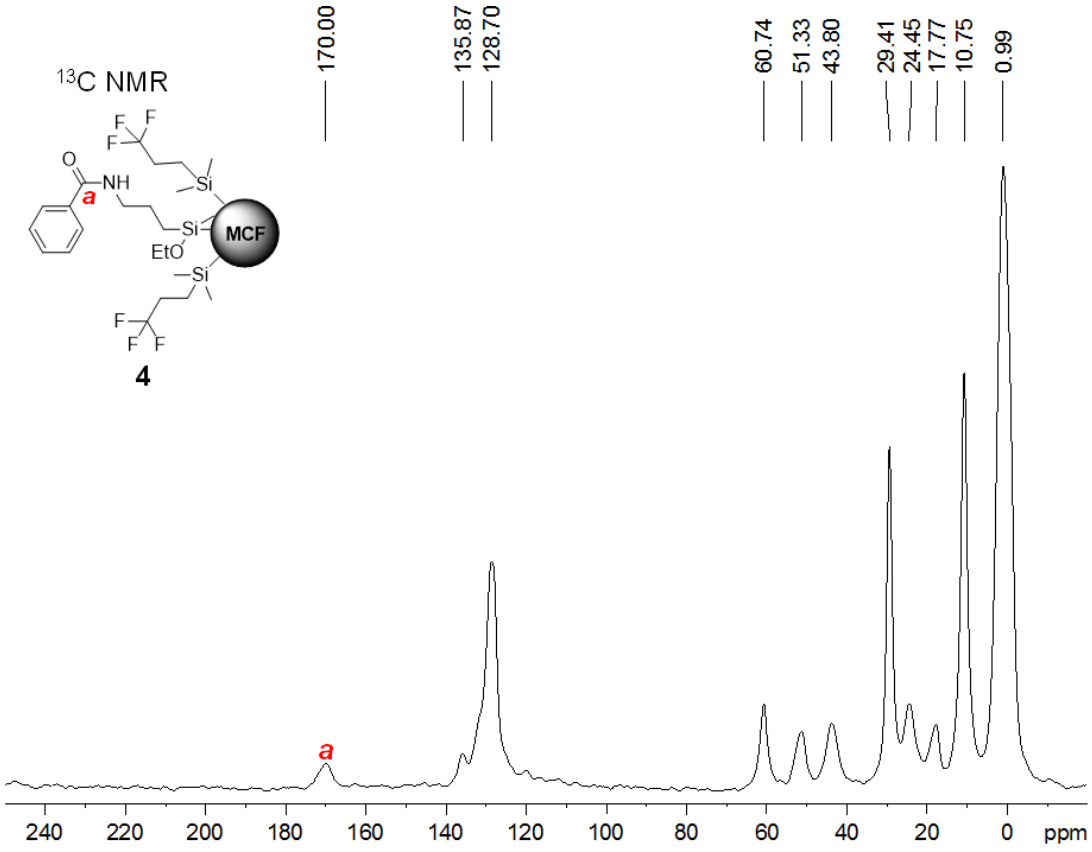
8b

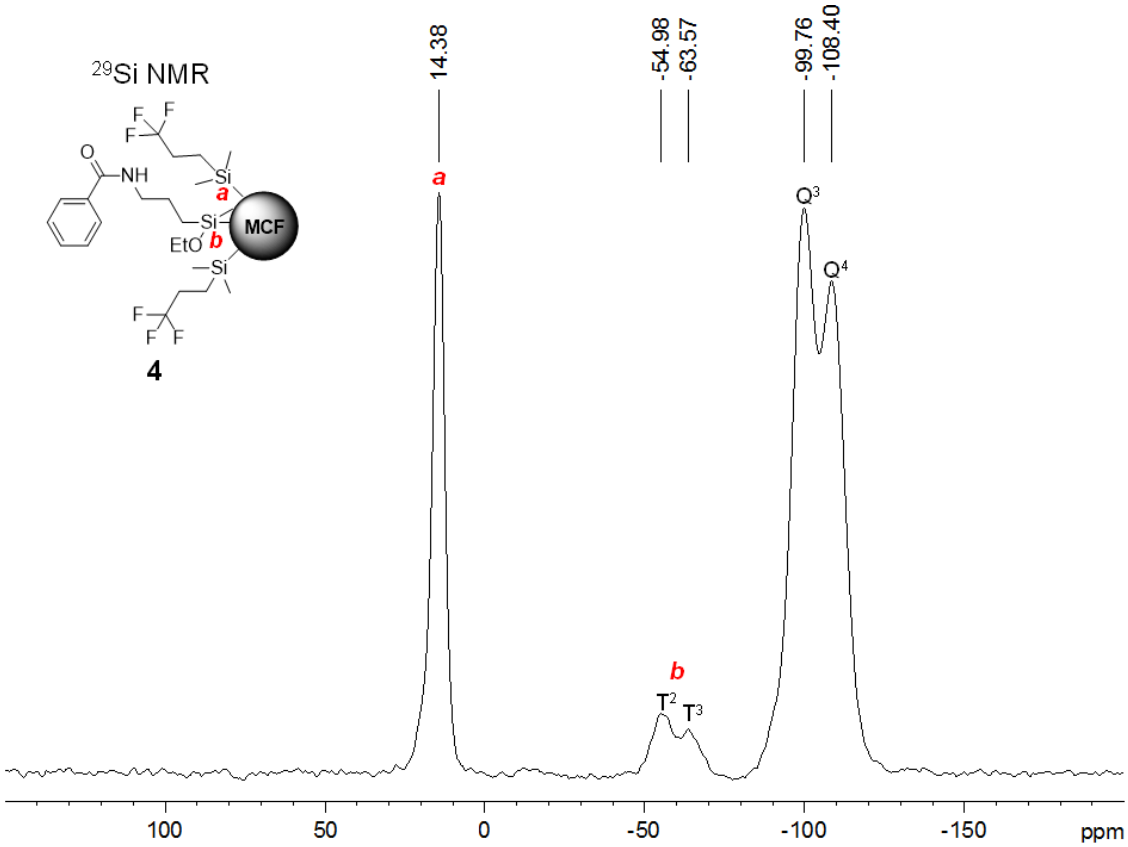

^{13}C NMR
169.63
131.55
115.41
60.44
50.25
43.34
29.10
24.31
17.59
10.46
0.89
a
MCF
8c
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

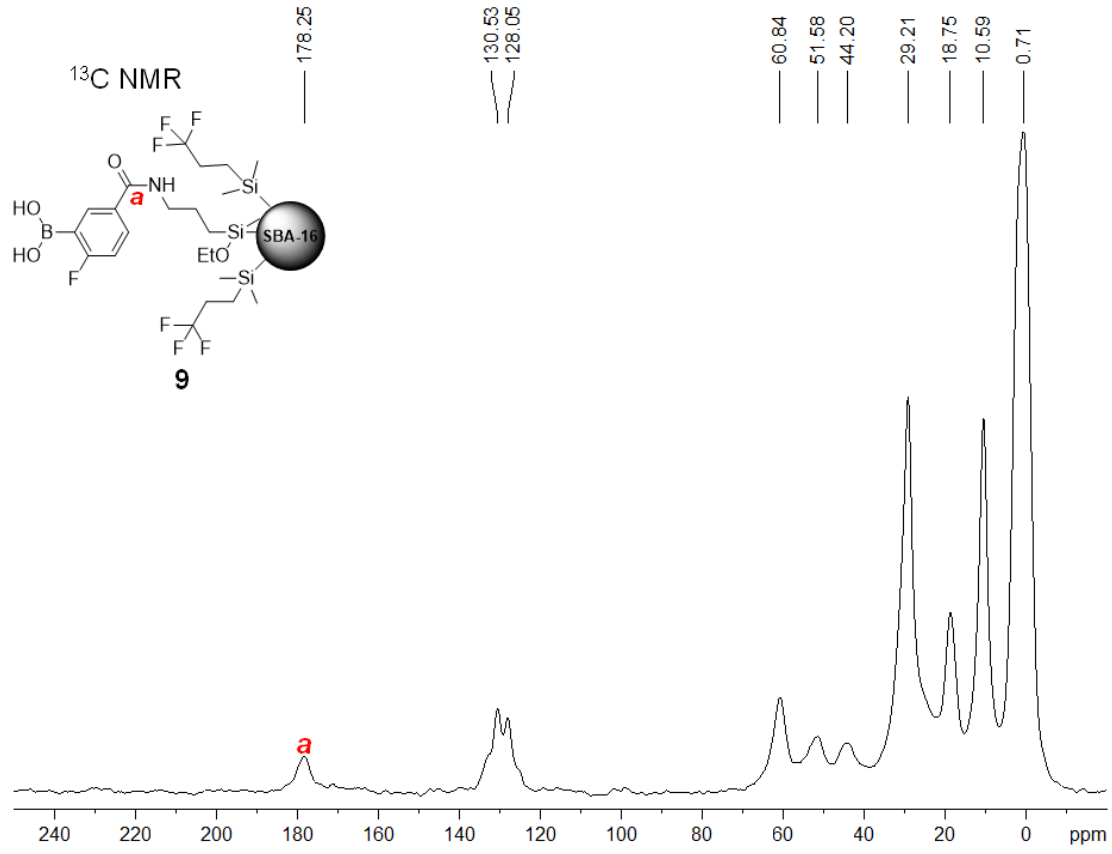

^{29}Si NMR
15.04
-56.49
-63.84
-100.34
-107.41
Q^4
Q^3
a
b
T^3
T^2
MCF
8c
100
50
0
-50
-100
-150
ppm

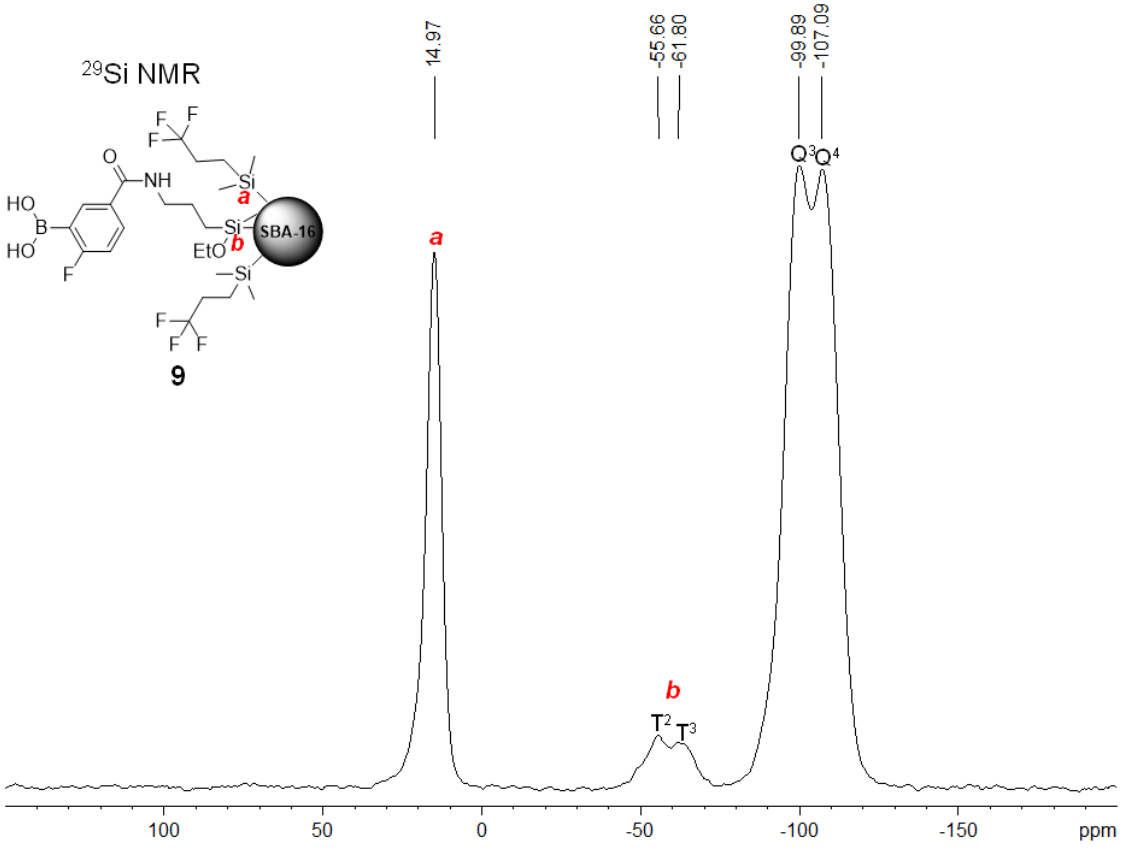

^{13}C NMR
170.10
135.65
129.81
127.02
60.20
50.85
43.13
28.83
17.17
10.18
0.75
a
MCF
8d
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

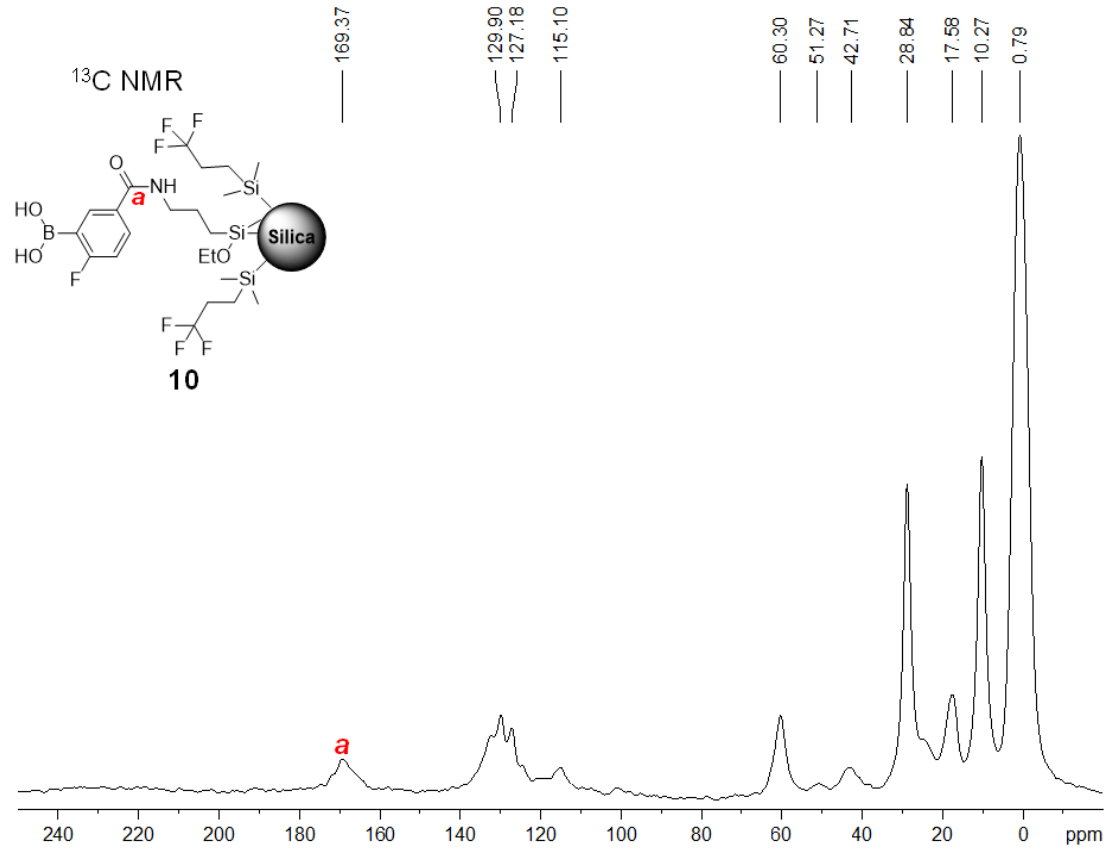

^{29}Si NMR
13.72
-56.29
-64.24
-100.11
-108.13
a
b
MCF
8d
Q^3
Q^4
T^2
T^3
100
50
0
-50
-100
-150
ppm


^{13}C NMR
170.00
135.87
128.70
60.74
51.33
43.80
29.41
24.45
17.77
10.75
0.99
a
MCF
EtO
4
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


^{29}Si NMR
14.38
-54.98
-63.57
-99.76
-108.40
a
b
MCF
EtO
4
Q^3
Q^4
T^2
T^3
100
50
0
-50
-100
-150
ppm


^{13}C NMR
178.25
130.53
128.05
60.84
51.58
44.20
29.21
18.75
10.59
0.71
a
SBA-16
9
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


^{29}Si NMR
14.97
-55.66
-61.80
-99.89
-107.09
a
b
SBA-16
9
Q^3
Q^4
T^2
T^3
100
50
0
-50
-100
-150
ppm


^{13}C NMR
169.37
129.90
127.18
115.10
60.30
51.27
42.71
28.84
17.58
10.27
0.79
Silica
10
a
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

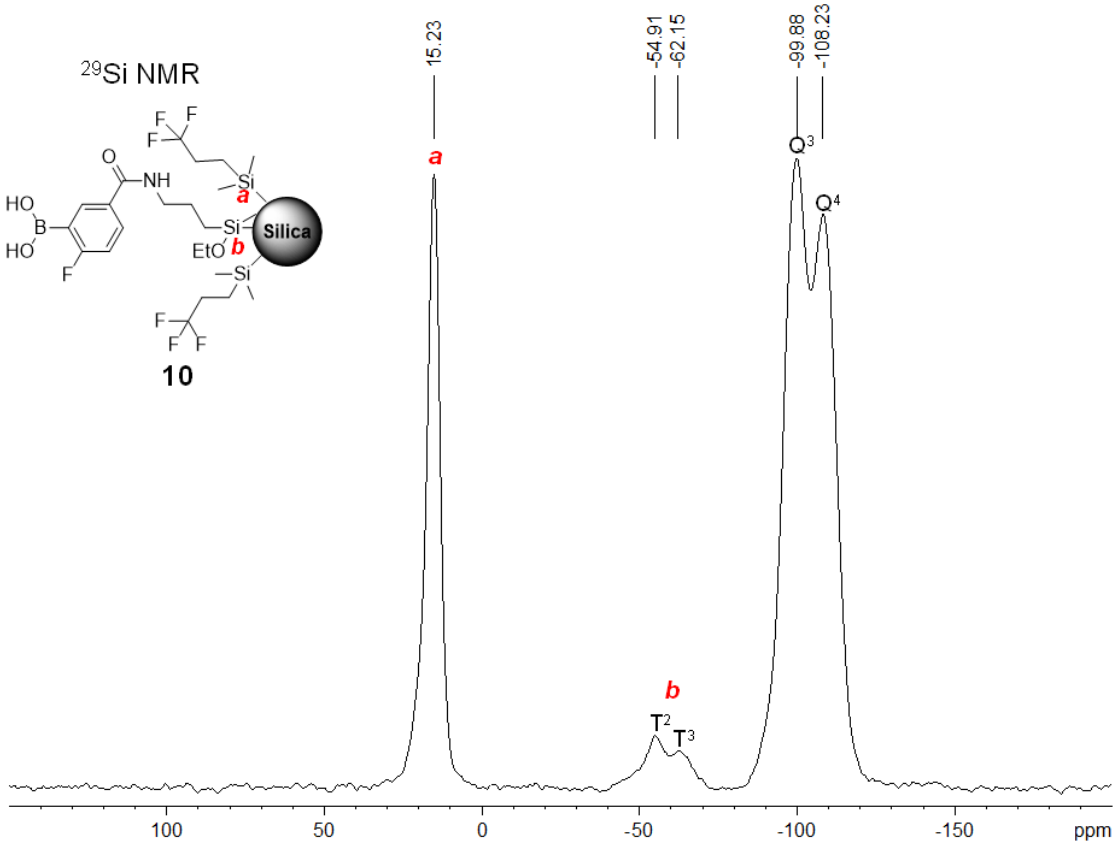
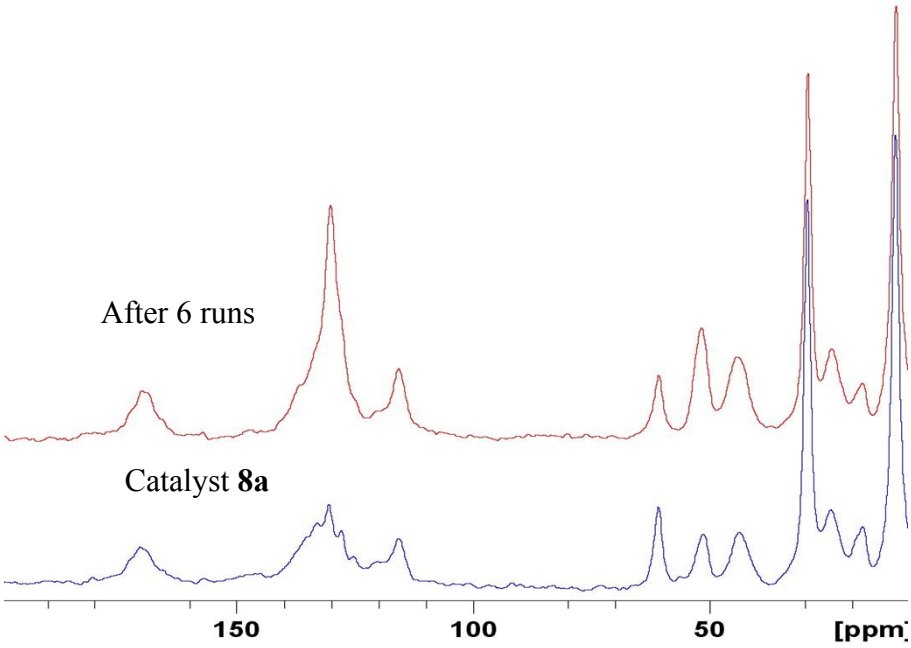

^{29}Si NMR
15.23
-54.91
-62.15
-99.88
-108.23
Silica
10
a
b
Q^3
Q^4
T^2
T^3
100
50
0
-50
-100
-150
ppm

Fig. S6. CPMAS ^{13}C and ^{29}Si NMR spectra of catalyst **8a** after 6 runs



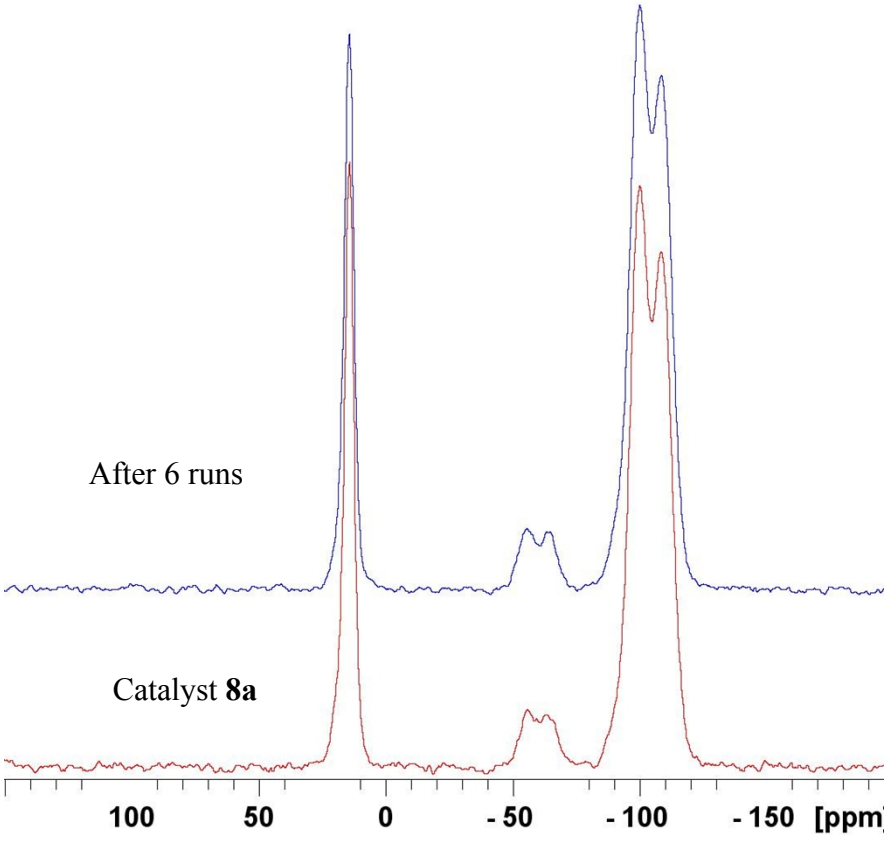
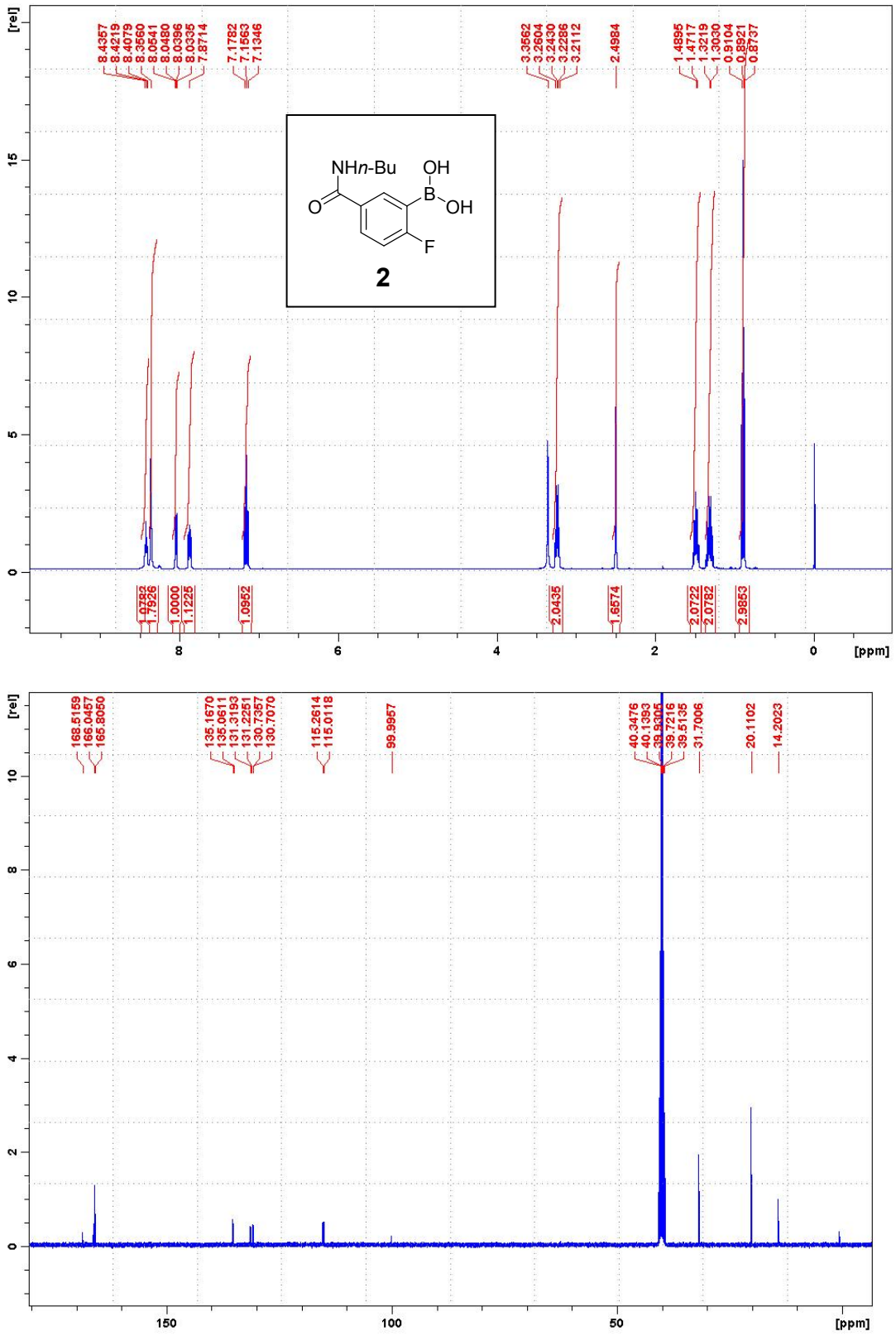
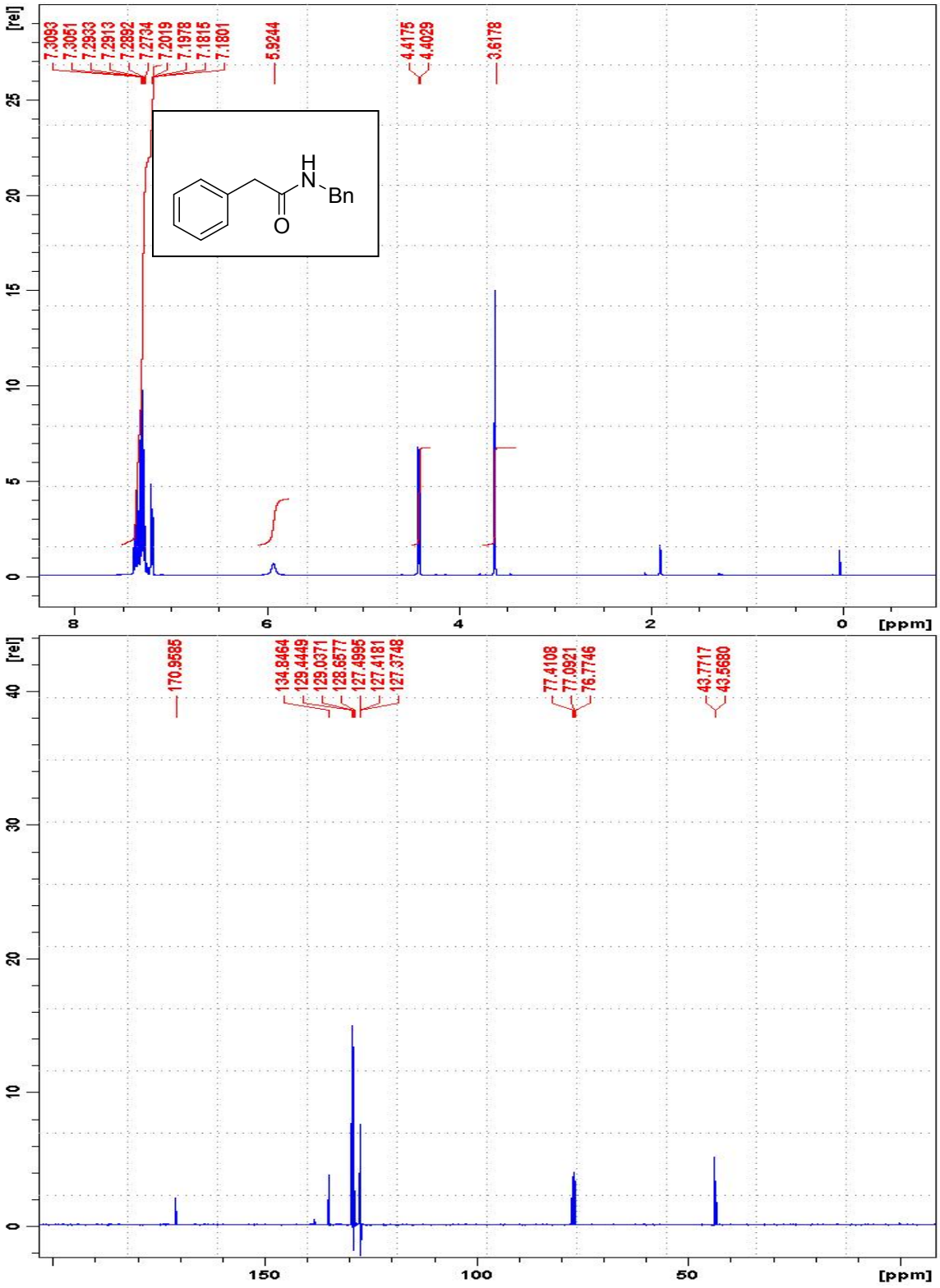


Fig. S7. ^{1}H and ^{13}C NMR Spectra of **2** and amides

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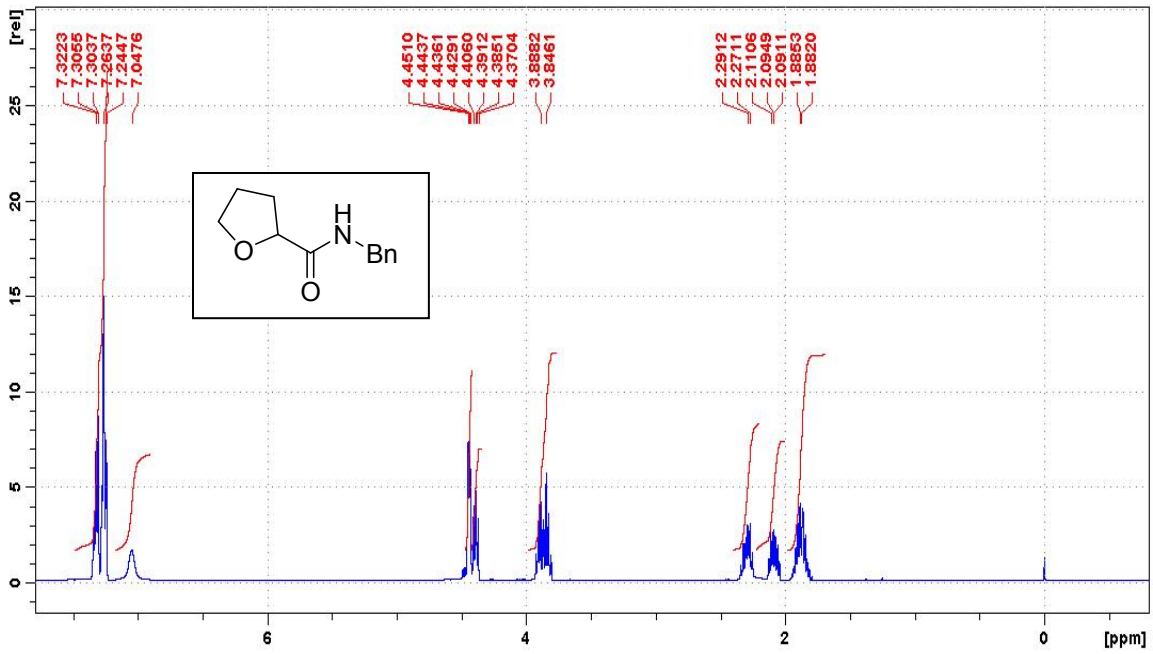
7.3051
7.2933
7.2913
7.2892
7.2734
7.2019
7.1978
7.1815
7.1801
5.9244
4.4175
4.4029
3.6178
H
N
Bn
O
[ppm]
[rel]
170.9585
134.8464
129.4449
129.0371
128.6577
127.4995
127.4181
127.3748
77.4108
77.0921
76.7746
43.7717
43.5680
[ppm]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7.3037
7.2637
7.2447
7.0476
4.4510
4.4437
4.4361
4.4291
4.4060
4.3912
4.3851
4.3704
3.8882
3.8461
2.2912
2.2711
2.1106
2.0949
2.0911
1.8853
1.8820
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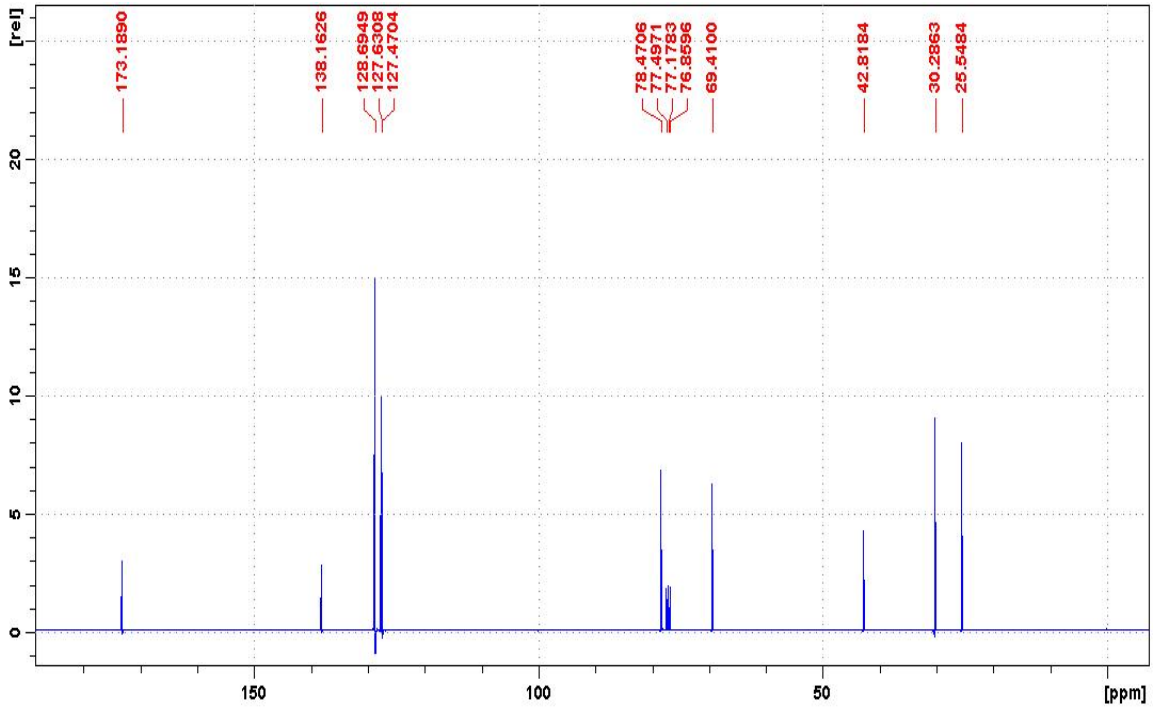
N
Bn
O
O
[ppm]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128.6949
127.6308
127.4704
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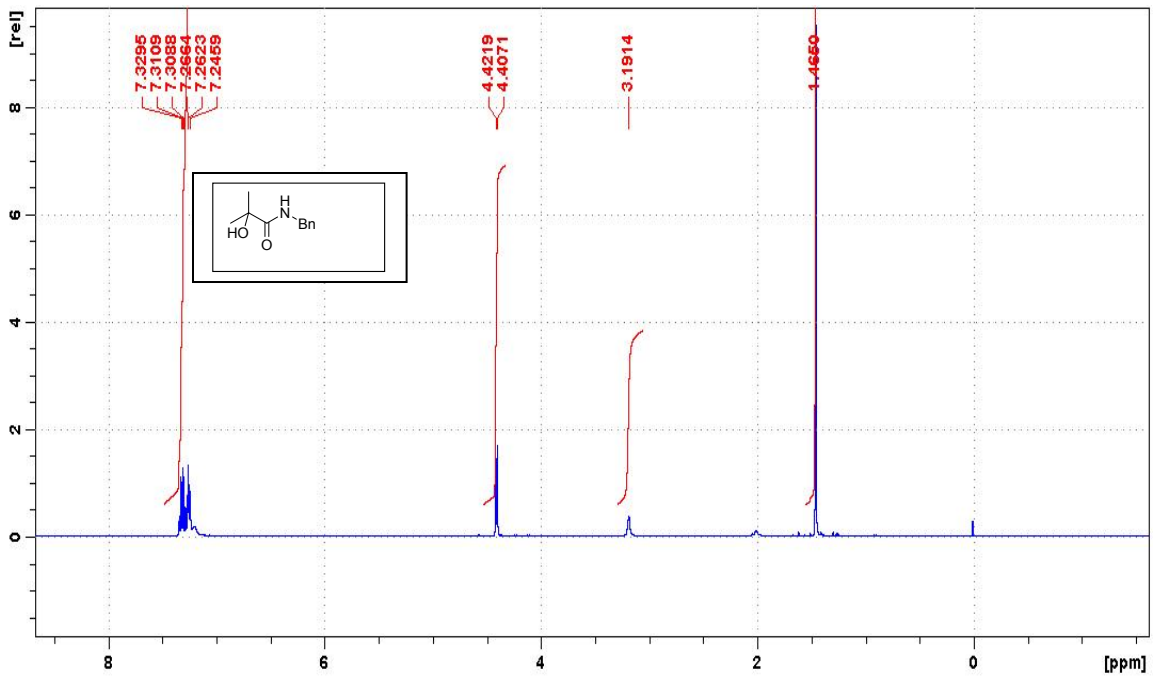
77.4971
77.1783
76.8596
69.4100
42.8184
30.2863
25.5484
[ppm]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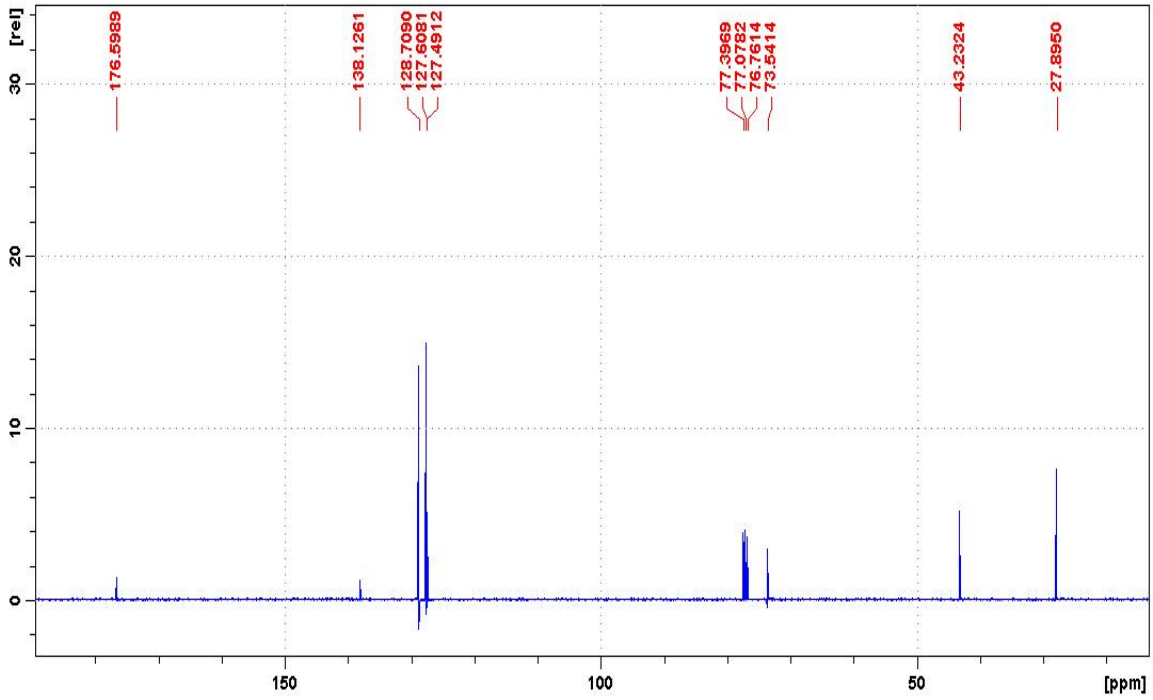
7.3295
7.3109
7.3088
7.2664
7.2623
7.2459
4.4219
4.4071
3.1914
1.4650
HO
O
H
N
Bn
[ppm]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127.4912
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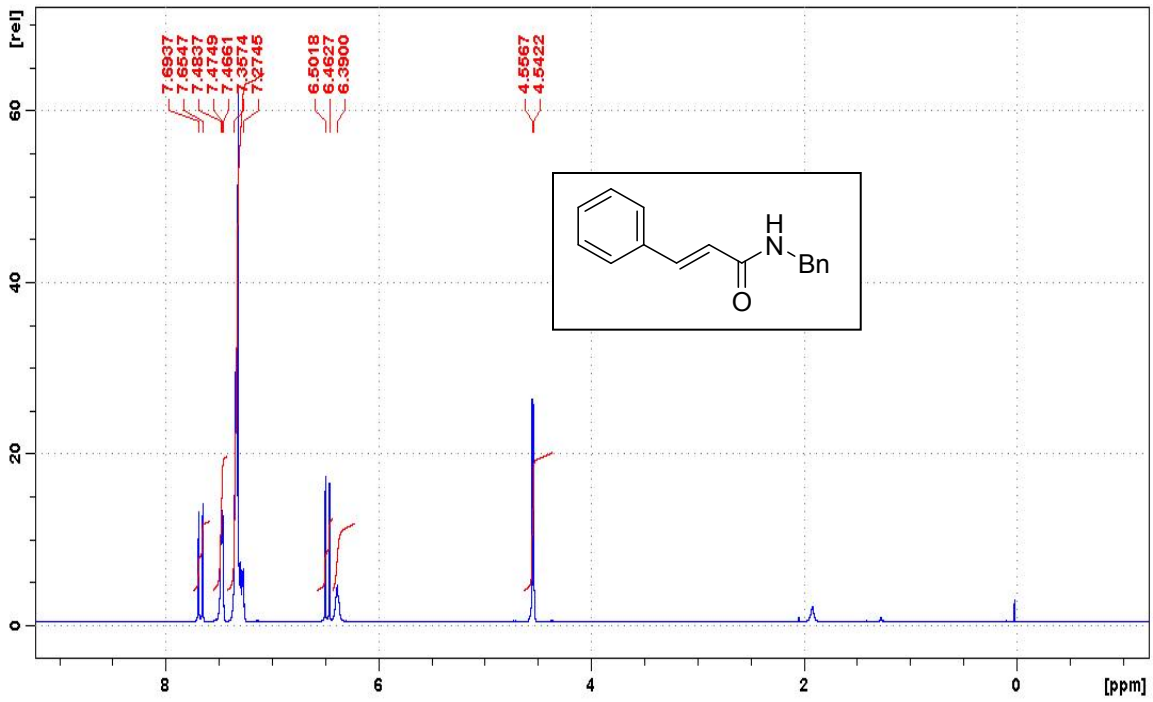
73.5414
43.2324
27.8950
[ppm]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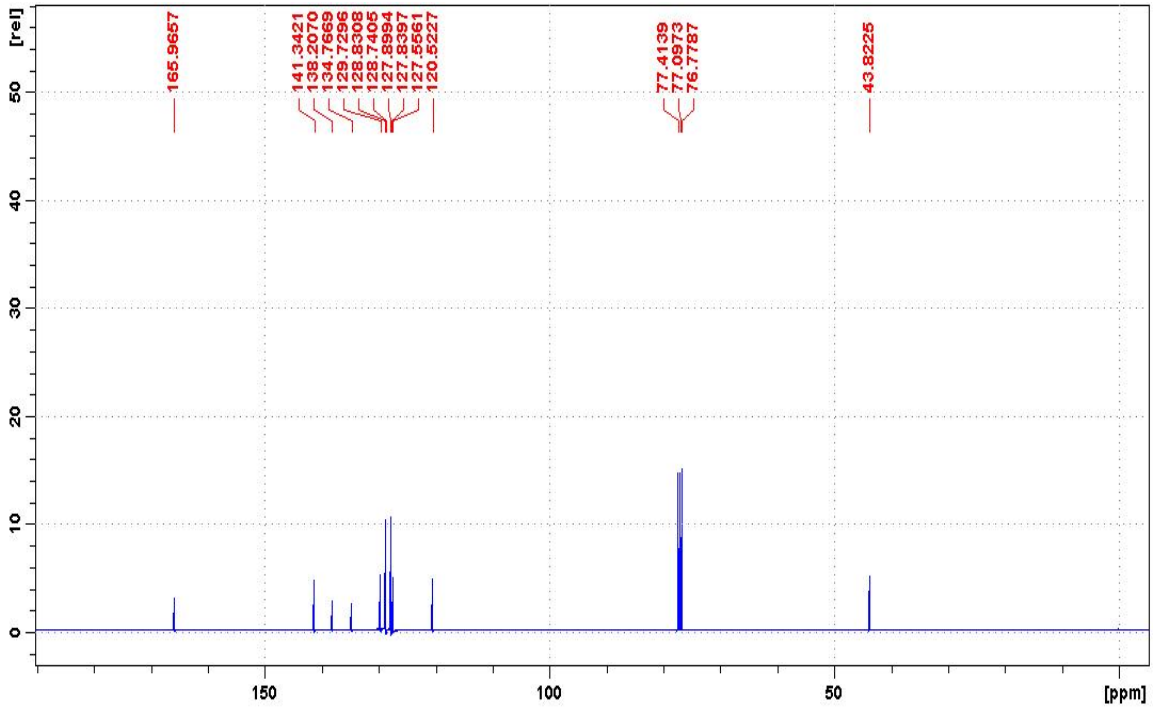
4.5422
H
N
Bn
O
[ppm]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77.0973
76.7787
43.8225
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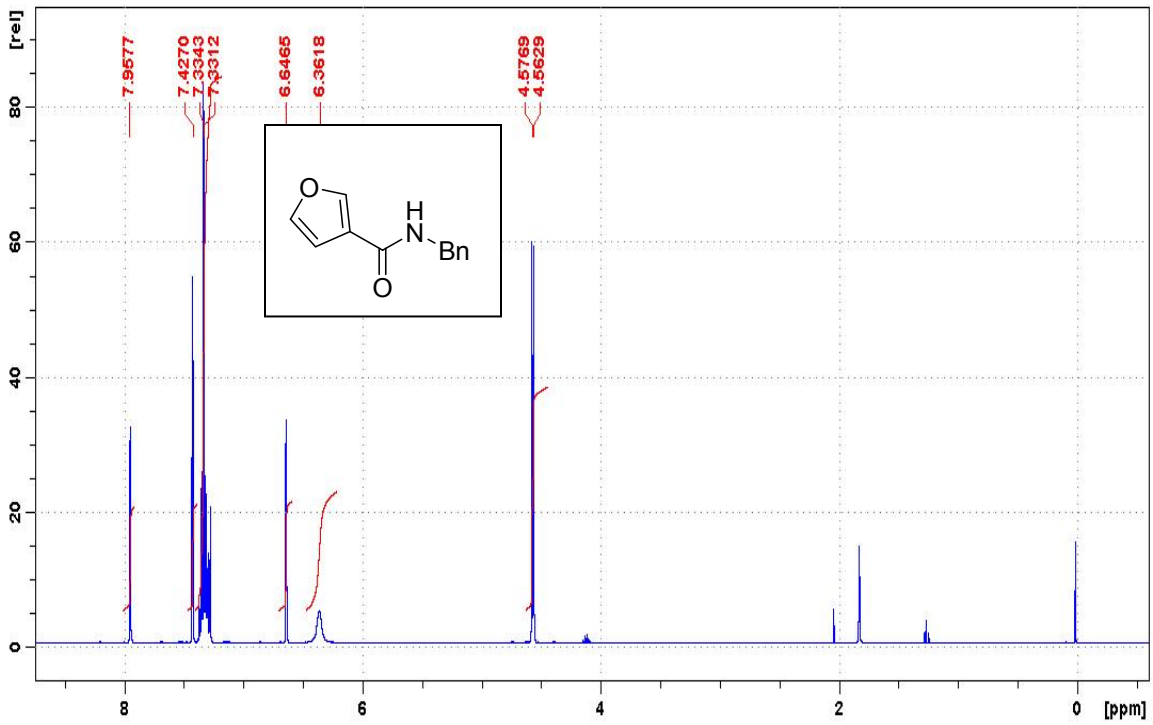
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4.5629
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H
N
Bn
O
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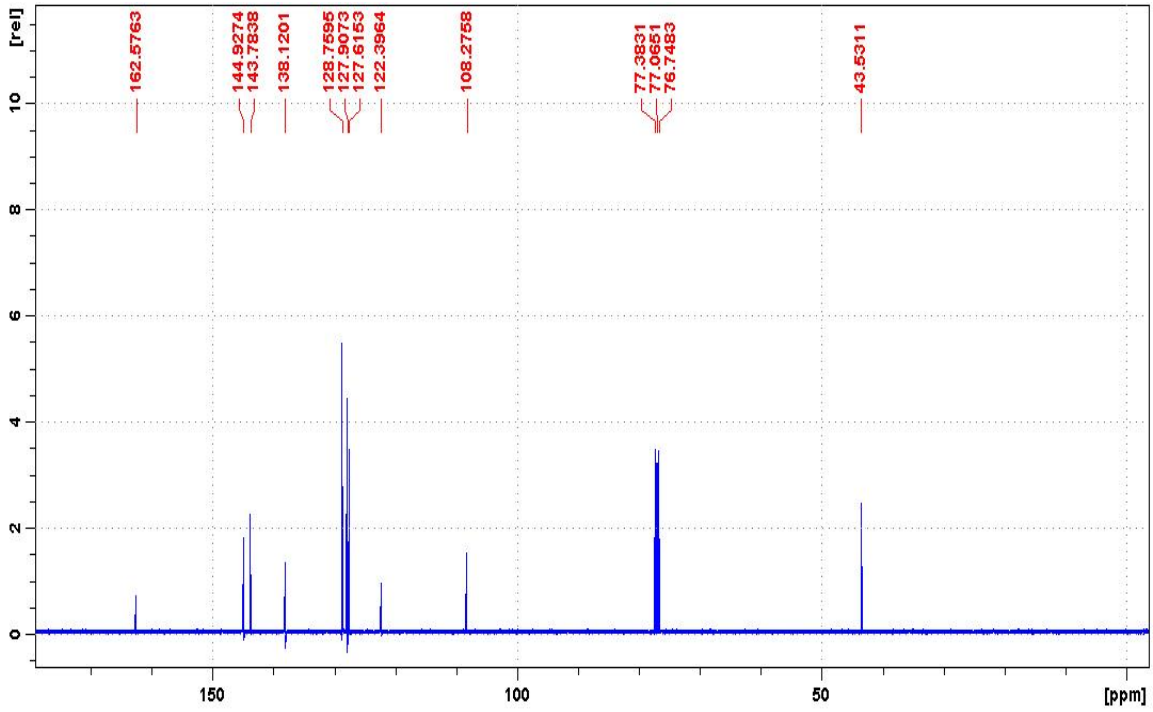
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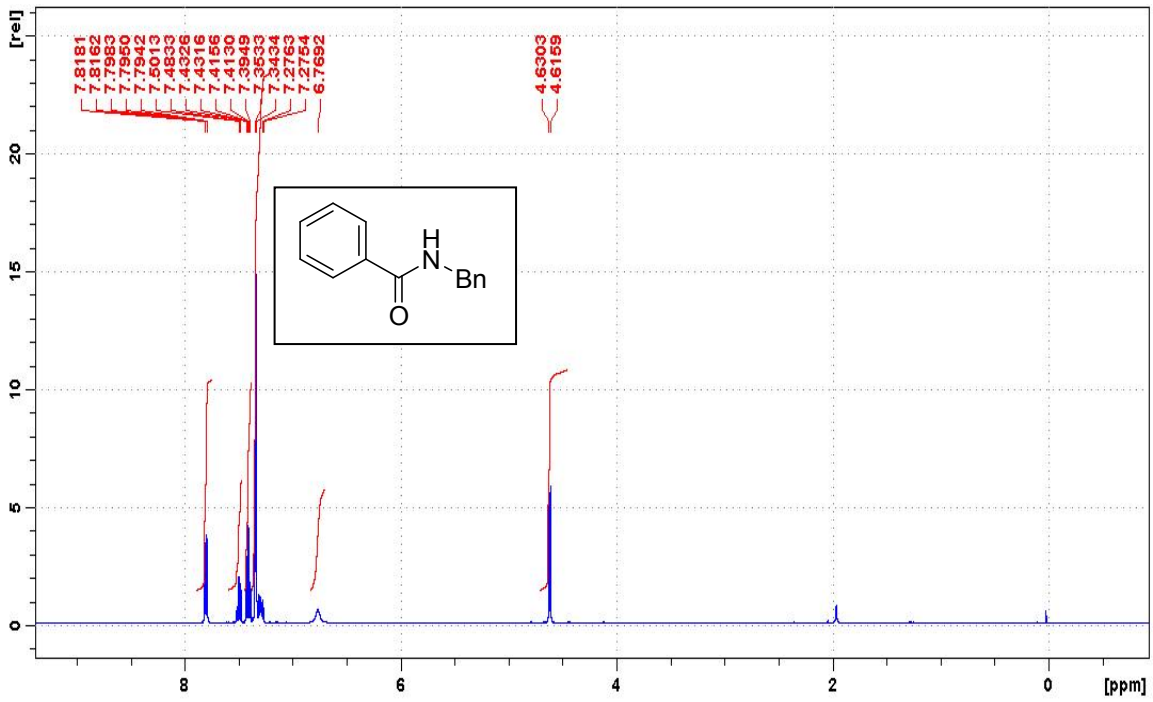
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7.3949
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7.2763
7.2754
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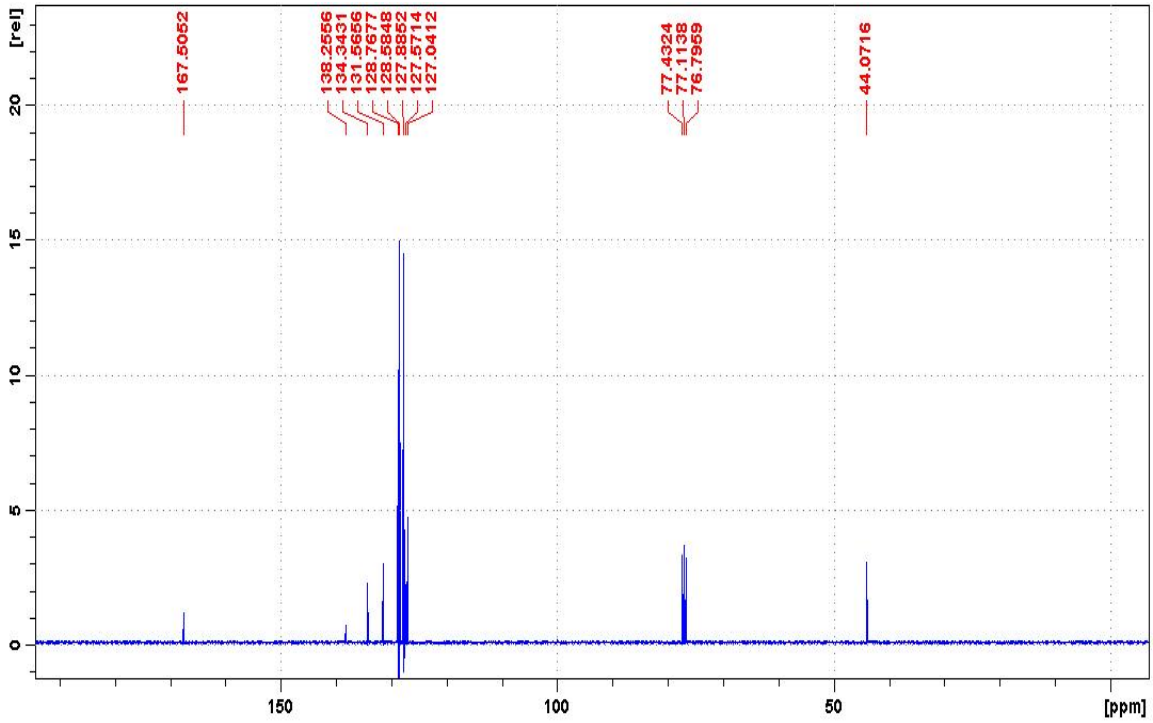
4.6159
H
N
Bn
O
[ppm]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44.0716
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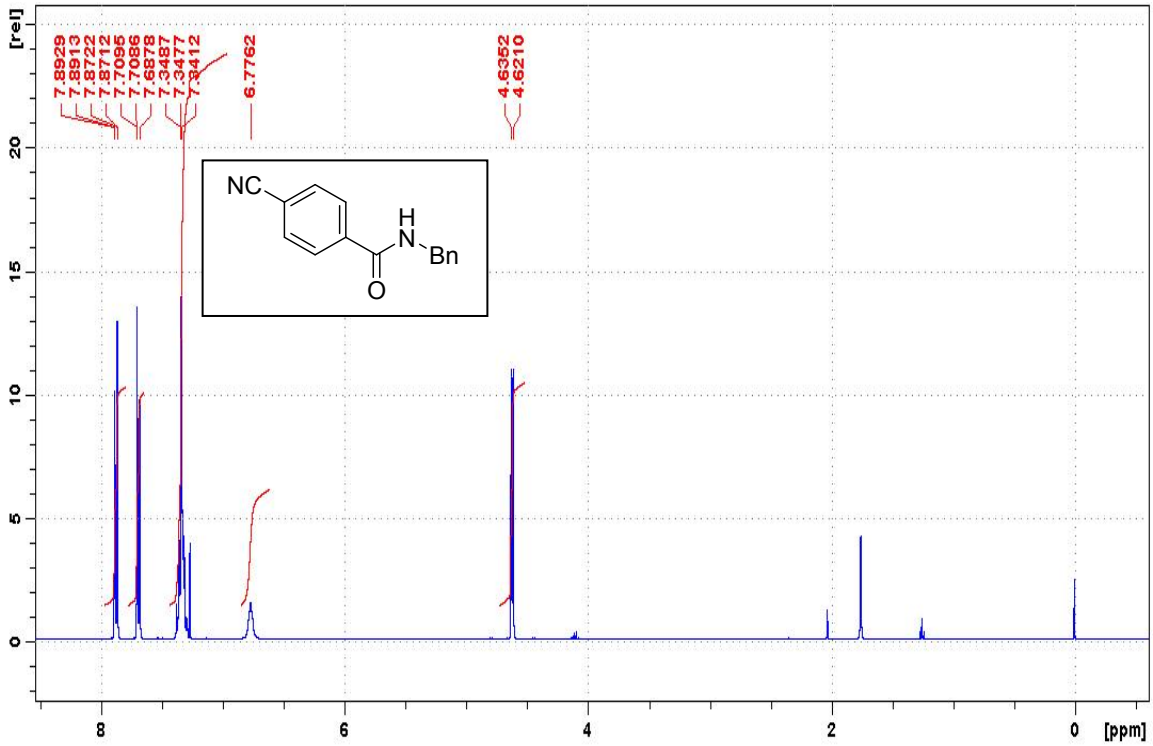
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NC
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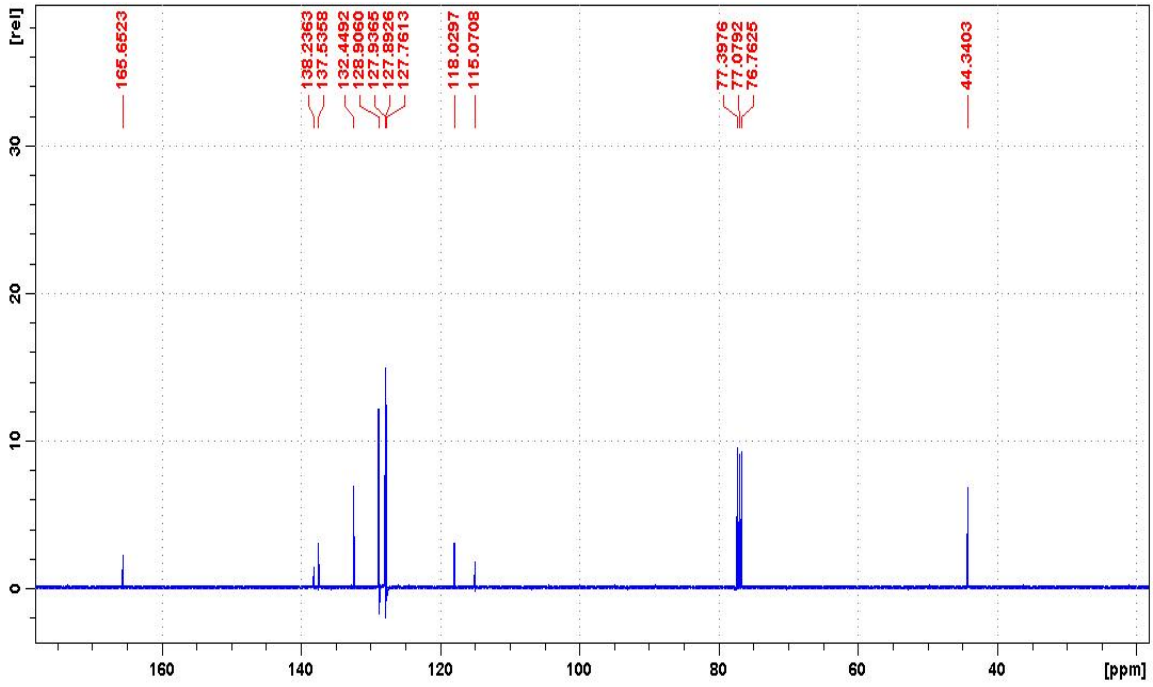
N
Bn
O
[ppm]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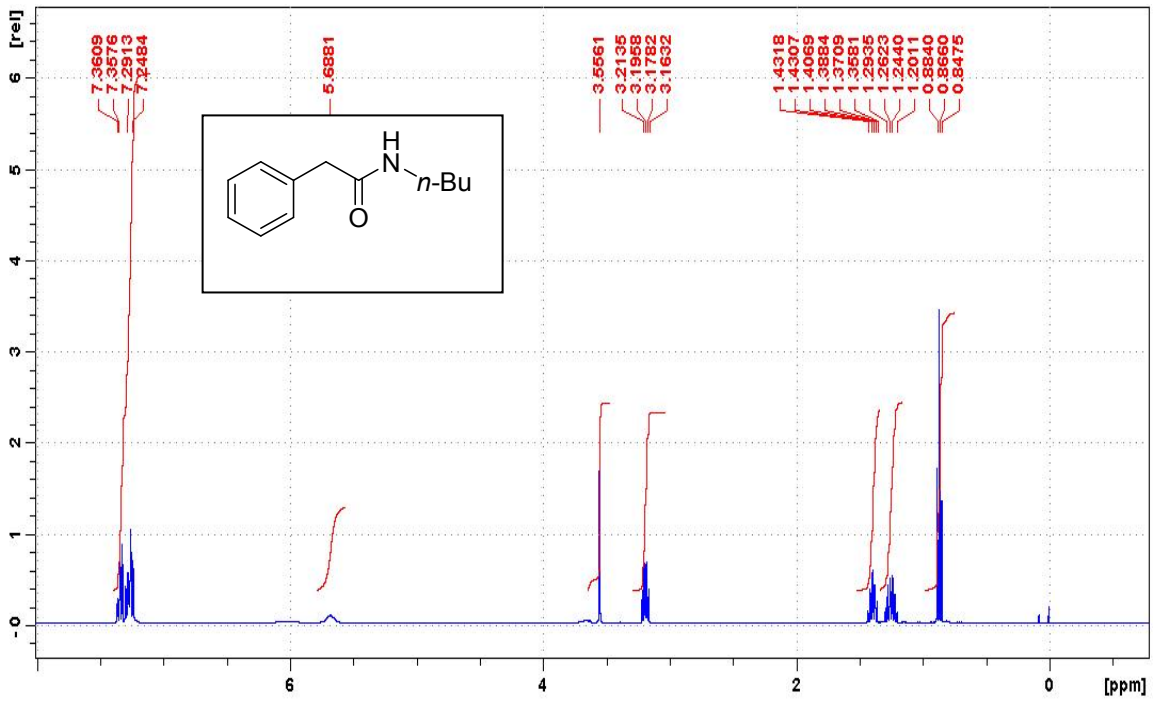
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1.4069
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1.3709
1.3581
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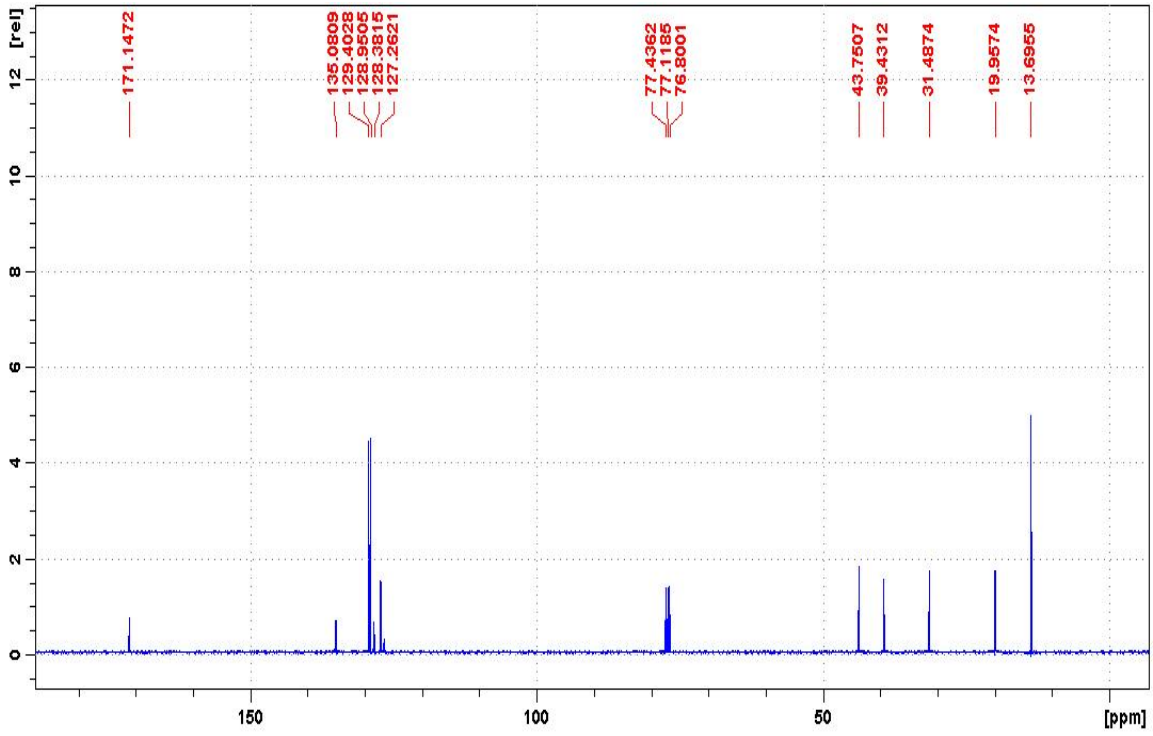
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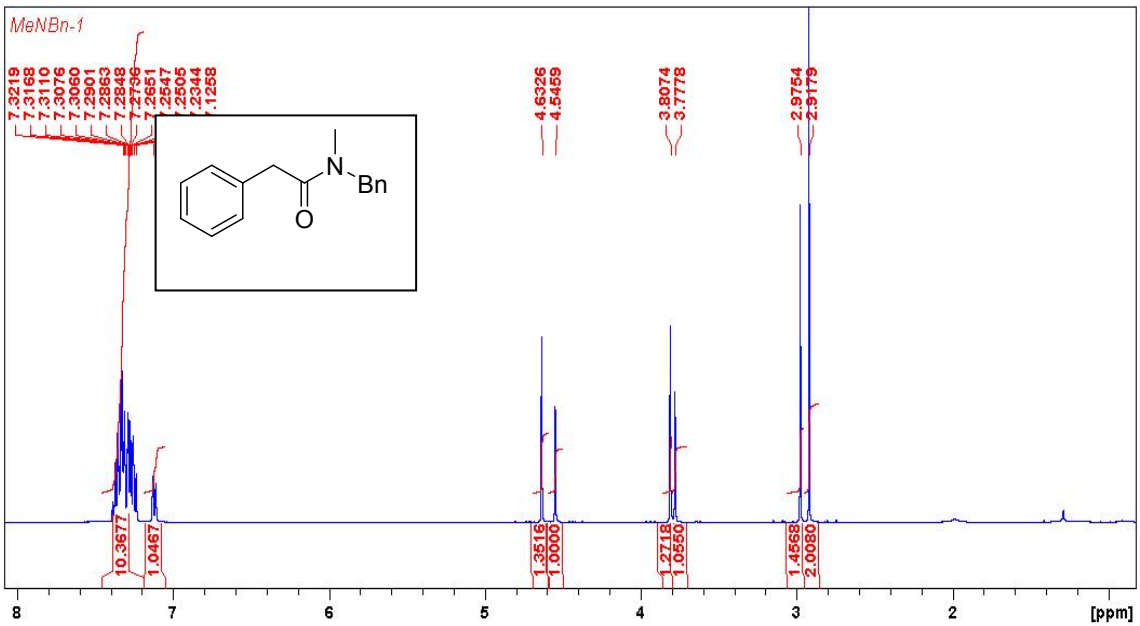
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7.3076
7.3060
7.2901
7.2863
7.2848
7.2736
7.2651
7.2547
7.2505
7.2344
7.1258
4.6326
4.5459
3.8074
3.7778
2.9754
2.9179
N
Bn
O
10.3677
1.0467
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1.2718
1.0550
1.4568
2.0080
8
7
6
5
4
3
2
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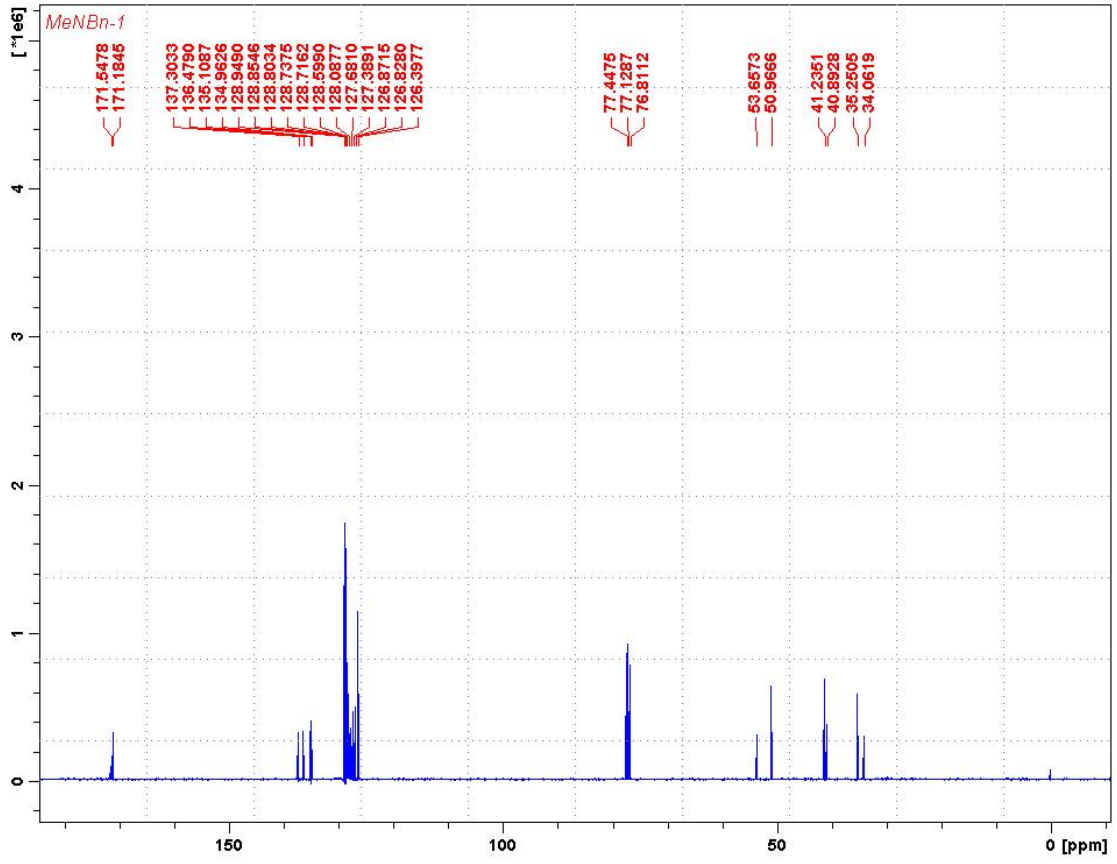
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128.5990
128.0877
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126.8715
126.8280
126.3977
77.4475
77.1287
76.8112
53.6573
50.9666
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34.0619
4
3
2
1
0
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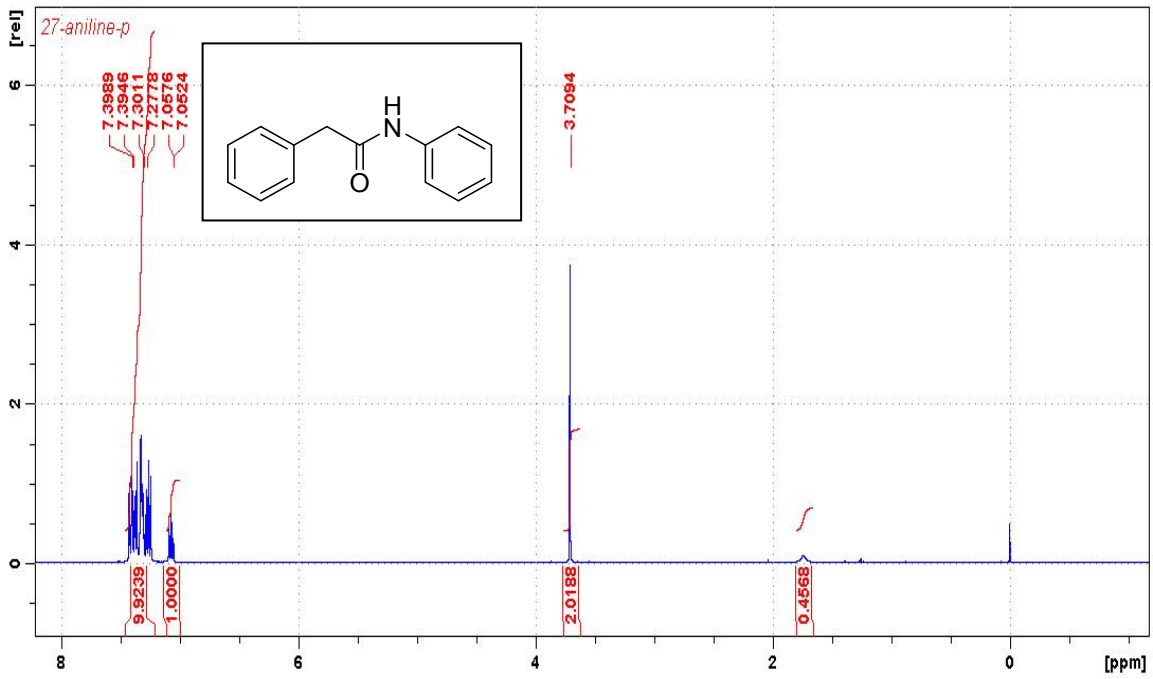
100
50
0 [ppm]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2.0188
0.4568
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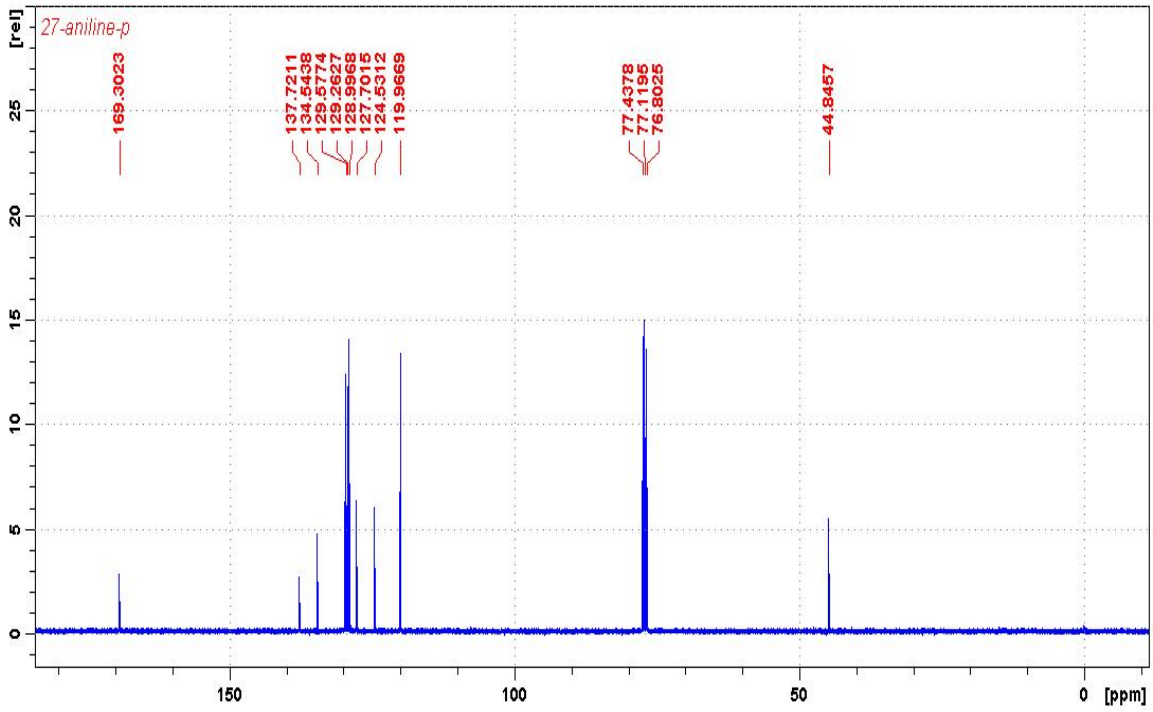
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77.1195
76.8025
44.8457
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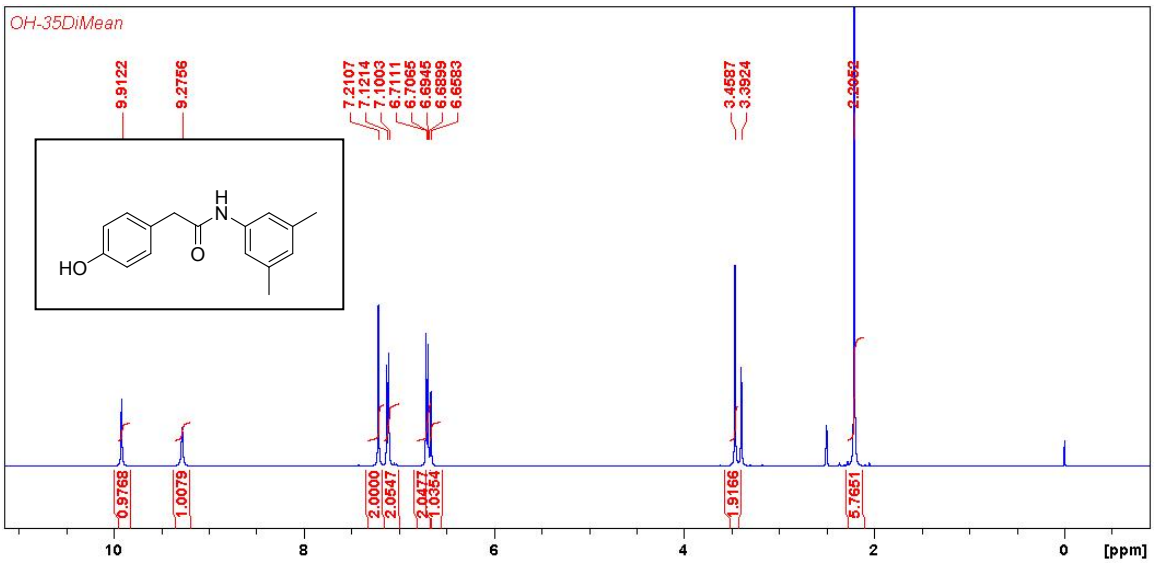
OH-35DiMean
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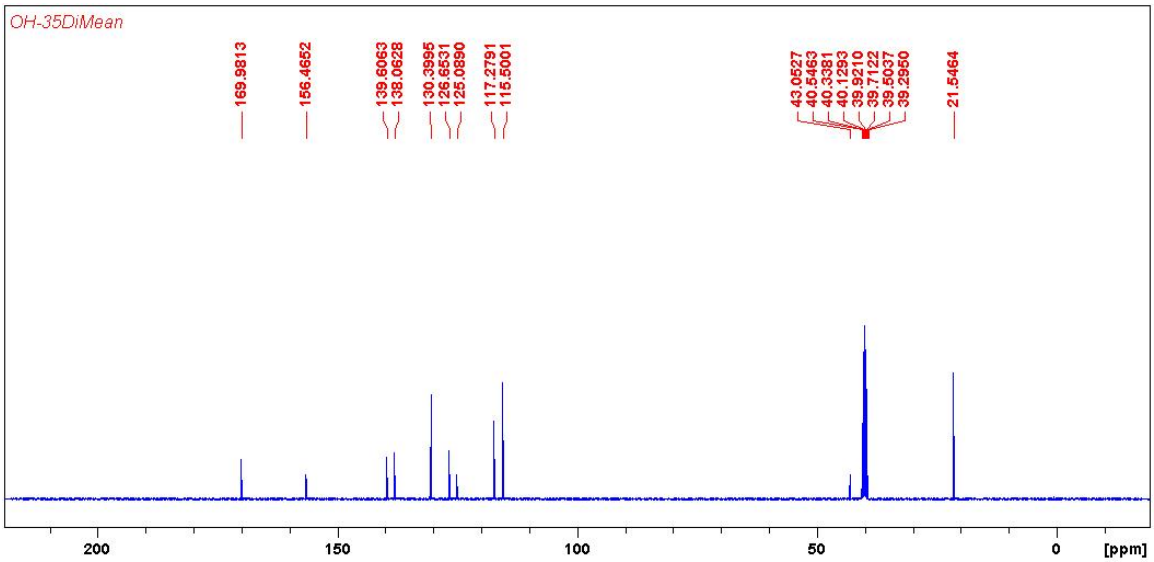
9.2756
7.2107
7.1214
7.1003
6.7111
6.7065
6.6945
6.6899
6.6583
3.4587
3.3924
2.2052
HO
H
N
O
0.9768
1.0079
2.0000
2.0547
2.0477
1.0354
1.9166
6.7651
10
8
6
4
2
0
[ppm]


OH-35DiMean
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138.0628
130.3995
126.6531
125.0890
117.2791
115.5001
43.0527
40.5463
40.3381
40.1293
39.9210
39.7122
39.5037
39.2950
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150
100
50
0
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