Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Potassium Methoxide/Disilane-Mediated Formylation of Aryl Iodides with DMF at Room Temperature

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1. General Information

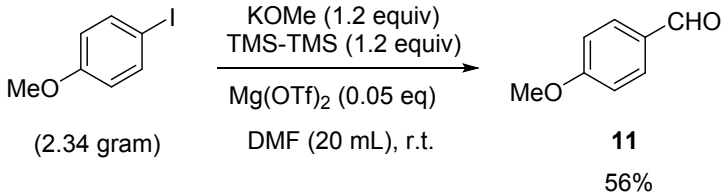
All reactions were performed under argon atmosphere using flame-dried glassware unless otherwise noted. DMF was distilled over CaH_2 and rigorously degassed by freeze/pump/thaw. All reagents were commercially available and used without further purification unless indicated otherwise. Thin layer chromatographies were carried out on GF254 plates. Flash chromatography was performed with 200-300 mesh silica gels. Visualization of the developed chromatogram was performed by fluorescence quenching or by ceric ammonium molybdate, or $KMnO_4$ stain. Yields reported were for isolated, spectroscopically pure compounds.

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer . Chemical shifts (δ) are expressed in ppm., and *J*-values are given in Hz. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards. ESIMS and HRESIMS were taken on Agilent 6540 Q-TOF spectrometer.

2. General Procedure for Formylation of Aryl Halides

To an oven dried 10 mL glass tube with a magnetic stirring bar was added aryl halides (0.5 mmol, 1 equiv), KOMe (0.6 mmol, 1.2 equiv) and $Mg(OTf)_2$ (0.025 mmol, 0.05 eq). Then the reaction tube was allowed to be vacuumed and purged with argon for three times. DMF (2.0 mL) were carefully added under argon and TMS-TMS (0.6 mmol, 1.2 equiv) were added dropwise at room temperature. The reaction mixture was stirred for 4 to 12 hours. The reaction was quenched by water (5 mL), extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was subjected to column chromatography (ethyl acetate/petroleum ether) on silica gel to afford the product.

3. Gram-Scale reaction



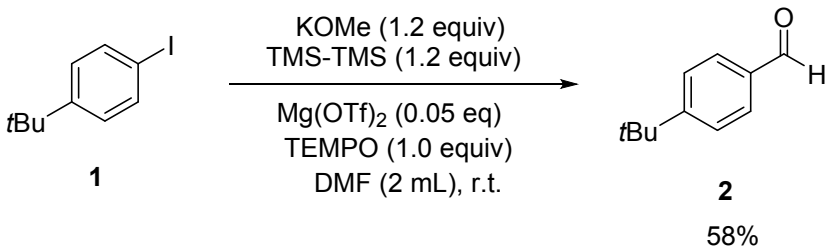
(2.34 gram) **11** 56%

To an oven dried 50 mL round-bottom flask with a magnetic stirring bar was added 1-iodo-4-methoxybenzene (2.34g, 10 mmol), KOMe (0.84g, 12 mmol,) and $Mg(OTf)_2$ (0.16g, 0.5 mmol). Then

the reaction tube was allowed to be vacuumed and purged with argon for three times. DMF (20.0 mL) were carefully added under argon and TMS-TMS (1.2 mL, 12 mmol) were added dropwise at room temperature. The reaction mixture was stirred for 8 hours. The reaction was quenched by water (20 mL), extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was subjected to column chromatography (ethyl acetate/petroleum ether = 1:30) on silica gel to afford 0.76 g of product **11** in 56% yield.

4. Procedures for Mechanistic Experiments

Radical trapping experiment with TEMPO

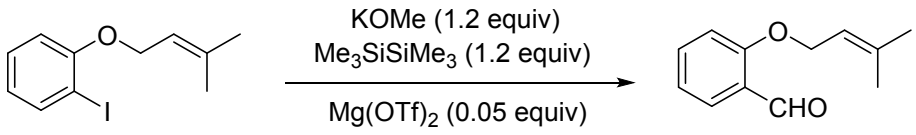


1 **2**

58%

To an oven dried 10 mL glass tube with a magnetic stirring bar was added 1-tert-butyl-4-iodobenzene **1** (130.0 mg, 0.5 mmol), TEMPO (78.2 mg, 0.5 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq) and KOMe (42.1 mg, 0.6 mmol). Then the reaction tube was allowed to be vacuumed and purged with argon for three times. DMF (2.0 mL) were carefully added under Argon and TMS-TMS (122.8 μL, 0.6 mmol) were added dropwise at room temperature. The reaction mixture was stirred for 4 hours. The reaction was quenched by water (5 mL), extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was subjected to column chromatography (ethyl acetate/petroleum ether=1:50) on silica gel to afford **2** as a colorless oil (47.0 mg, 58% yield).

Intramolecular Radical Cyclization Experiment

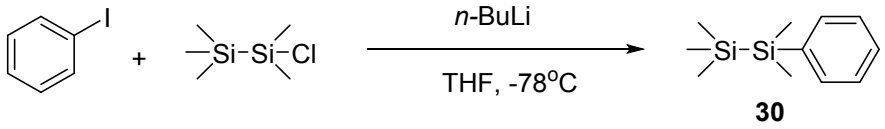


27 **28**

63%

To an oven dried 10 mL glass tube with a magnetic stirring bar was added **27** (144.0 mg, 0.5 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq) and KOMe (42.1 mg, 0.6 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. DMF (2.0 mL) were carefully added under argon and TMS-TMS (122.8 μL, 0.6 mmol) were added dropwise at room temperature. The reaction mixture was stirred for 4 hours. The reaction was quenched by water (5 mL), extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was subjected to column chromatography (ethyl acetate/petroleum ether=1:150) on silica gel to afford **28** as a colorless oil (59.8 mg, 63% yield).

Preparation of unsymmetrical disilane



30

To an oven dried 100 mL round-bottom flask with a magnetic stirring bar was added Iodobenzene (204 mg, 1 mmol). Then the reaction tube was allowed to be vacuumed and purged with argon for three times.THF (30.0 mL) were carefully added under argon. The *n*-BuLi (2.5 M in in hexanes, 0.6 mL, 1.5 mmol) were added dropwise at -78°C. Then chloropentamethyldisilane (166.8 mg, 1 mmol) were added dropwise after 30 min. The reaction mixture was warmed up to room temperature and stirred for 12 hours. The reaction was quenched by water (10 mL), extracted with Et_2O (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was subjected to column chromatography using hexanes on silica gel to afford 187.2 mg of product **30** in 90% yield[1]. ^{1}H NMR (600 MHz, DMF) δ 7.51 (d, J = 6.5 Hz, 2H), 7.44 – 7.32 (m, 3H), 0.36 (s, 6H), 0.07 (s, 9H). ^{13}C NMR (151 MHz, DMF) δ134.8, 129.6, 129.0, -1.7, -3.4. ^{29}Si NMR (119 MHz, DMF) δ -19.42, -21.68.

^{1}H, ^{13}C, and ^{29}Si NMR Spectroscopic Studies

The ^{1}H NMR spectra of TMS-TMS (14.6 mg, 0.1 mmol) in 0.5 mL of dried DMF-d7 in NMR tube was recorded using a Bruker AM-600NMR spectrometer at room temperature. The ^{1}H NMR spectra of KO*t*Bu (11.2 mg, 0.1 mmol) and $Me_3SiSiMe_2Ph$ (10.4 mg, 0.05 mmol) were also recorded by the same method.

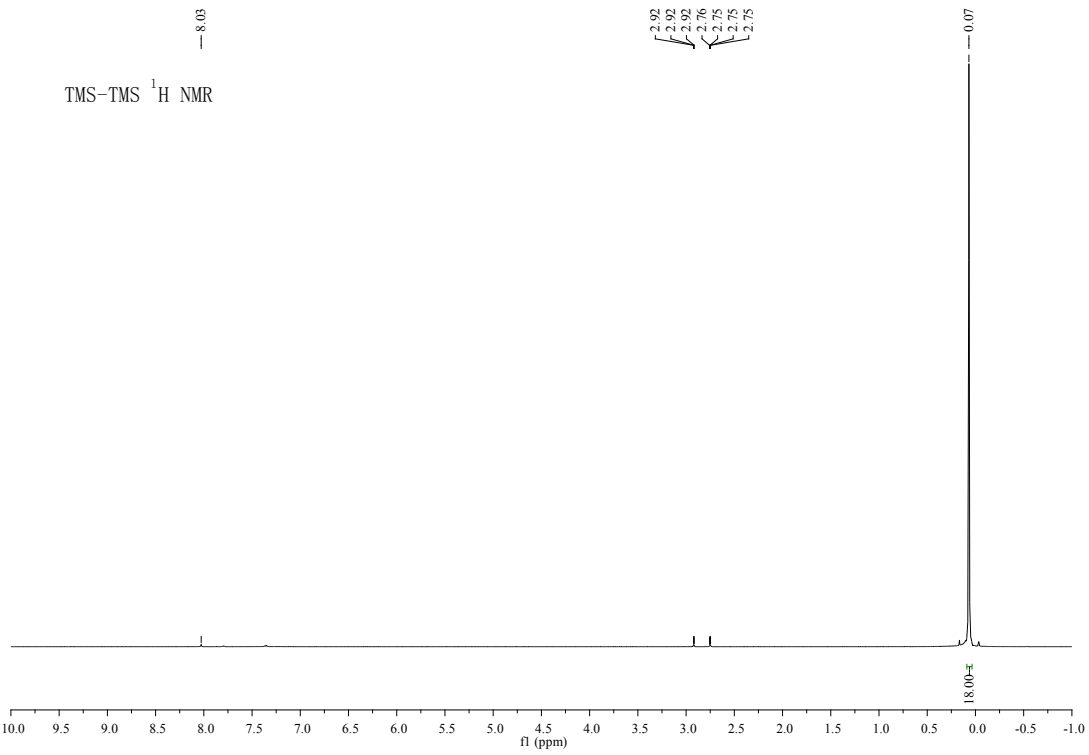
The ^{1}H NMR analysis of silane intermediate was conducted as following: To a NMR tube containing 0.5 mL of dried DMF-d7 were added TMS-TMS (14.6 mg, 0.1 mmol) and KOMe (7.0 mg, 0.1 mmol) under argon. Then the ^{1}H NMR spectra was recorded after 10 min, 30 min, 1 h and 4 h.

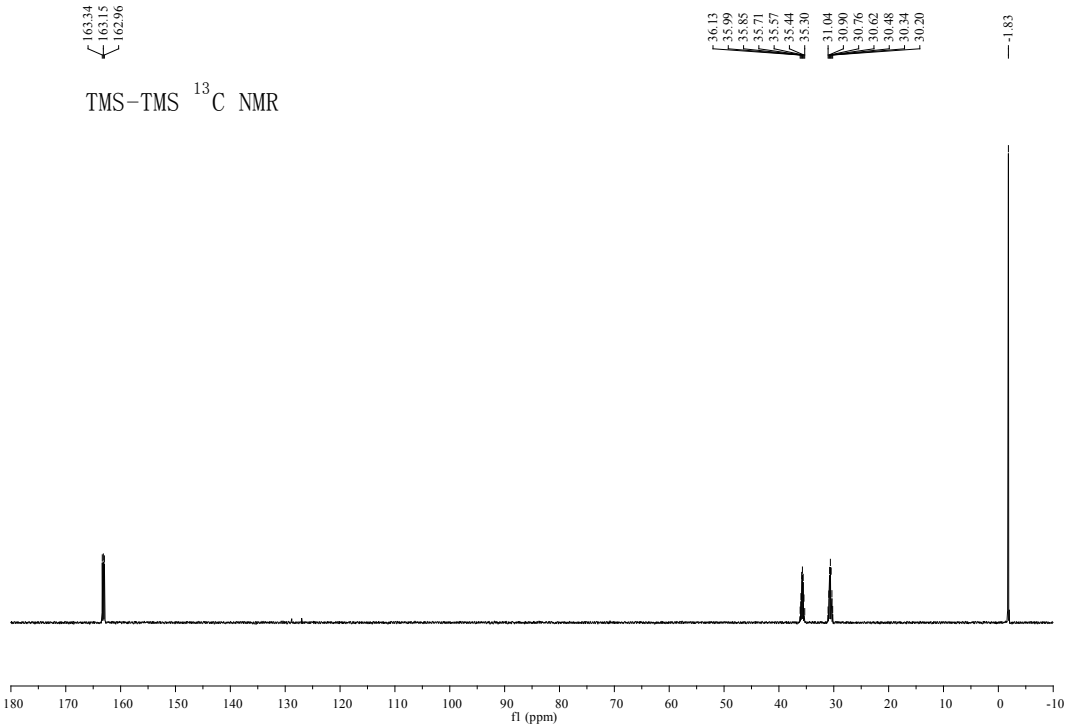
The^{13}C NMR spectra of *t*-butoxytrimethylsilane (14.6 mg, 0.1 mmol) in 0.5 mL of dried DMF-d7 in NMR tube was recorded using a Bruker AM-600NMR spectrometer at room temperature. The ^{13}C NMR spectra of ethoxytrimethylsilane (11.8 mg, 0.1 mmol), trimethylmethoxysilane (10.4 mg, 0.1 mmol), and TMS-TMS(14.6 mg, 0.1 mmol) were also recorded by the same method.

The ^{13}C NMR analysis of silane intermediate was conducted as following: To a NMR tube containing 0.5 mL of dried DMF-d7 were added TMS-TMS (14.6 mg, 0.1 mmol) and KO*t*Bu (11.2 mg, 0.1 mmol) under argon. Then the ^{13}C NMR spectra was recorded after 10 min, 30 min, 1 h and 4 h. Other alkali alkoxides KOEt, KOMe, LiOMe and NaOMe (0.1 mmol) were also recorded by the ^{13}C NMR under the same conditions.

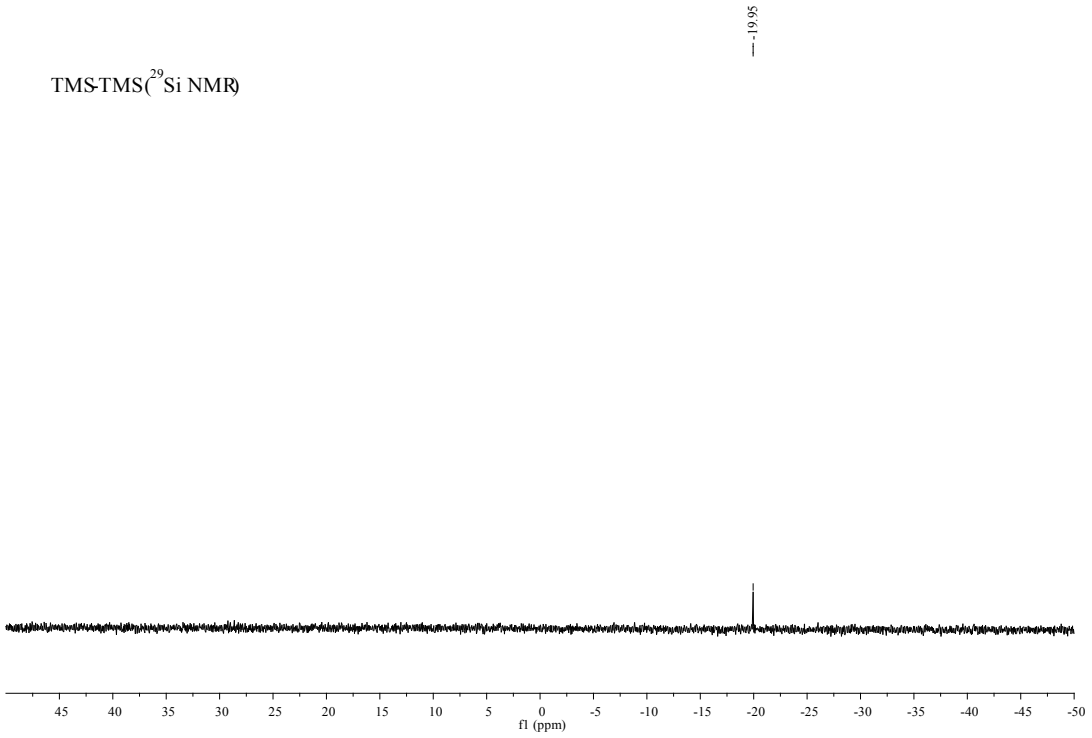
The ^{29}Si NMR spectra of TMS-TMS (14.6 mg, 0.1 mmol) in 0.5 mL of dried DMF-d7 in Teflon NMR tube was recorded using a Bruker AM-600NMR spectrometer at room temperature. The ^{29}Si NMR spectra of $Me_3SiSiMe_2Ph$ (10.4 mg, 0.05 mmol) were also recorded by the same method.

The ^{29}Si NMR analysis of silane intermediate was conducted as following: To a Teflon NMR tube containing 0.5 mL of dried DMF-d7 were added TMS-TMS (14.6 mg, 0.1 mmol) and KOMe (7.0 mg, 0.1 mmol) under argon. Then the ^{29}Si NMR spectra was recorded after 1 h using a Bruker AM-600NMR spectrometer at room temperature. $Me_3SiSiMe_2Ph$ (10.4 mg, 0.05 mmol) were also recorded by the ^{29}Si NMR under the same conditions.

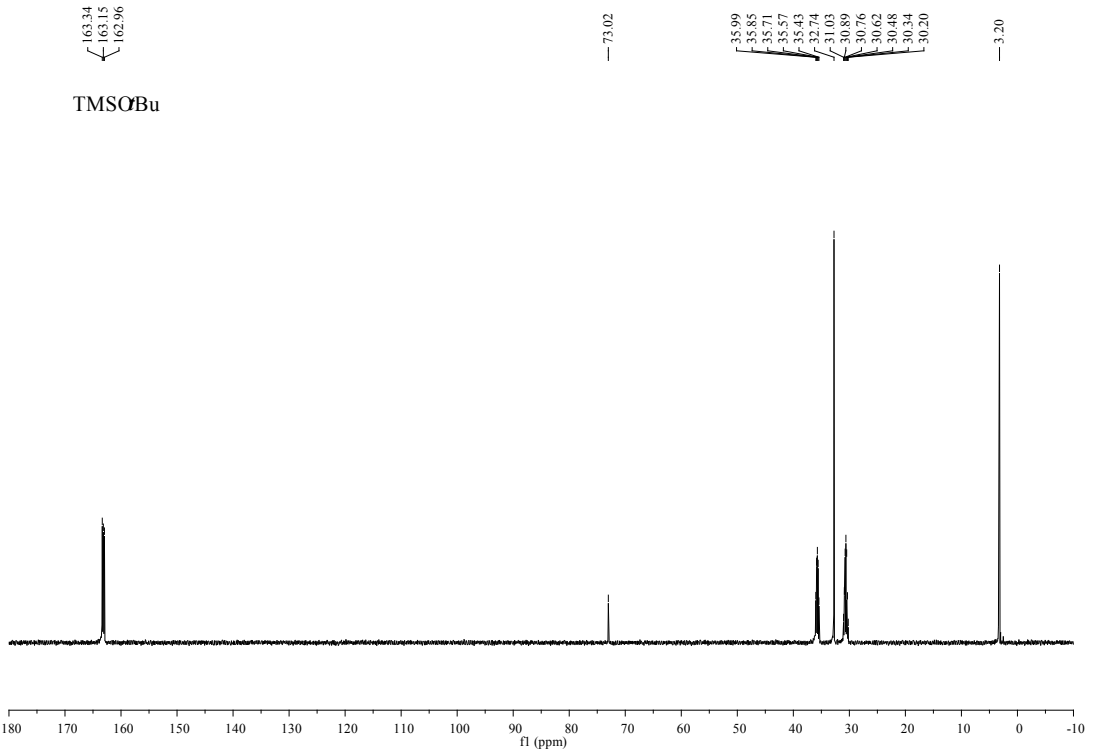

TMS-TMS ^{1}H NMR
8.03
2.92
2.92
2.92
2.76
2.75
2.75
2.75
0.07
18.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


TMS-TMS ^{13}C NMR
163.34
163.15
162.96
36.13
35.99
35.85
35.71
35.57
35.44
35.30
31.04
30.90
30.76
30.62
30.48
30.34
30.20
1.83
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

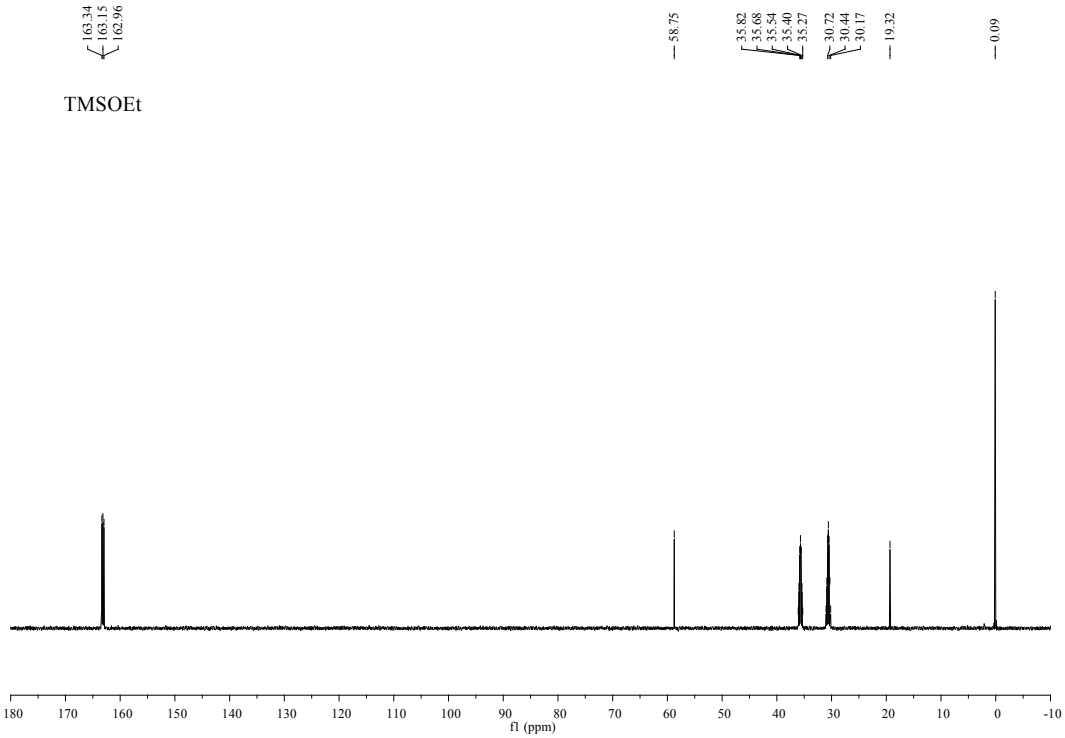
TMS-TMS(^{29}Si NMR)



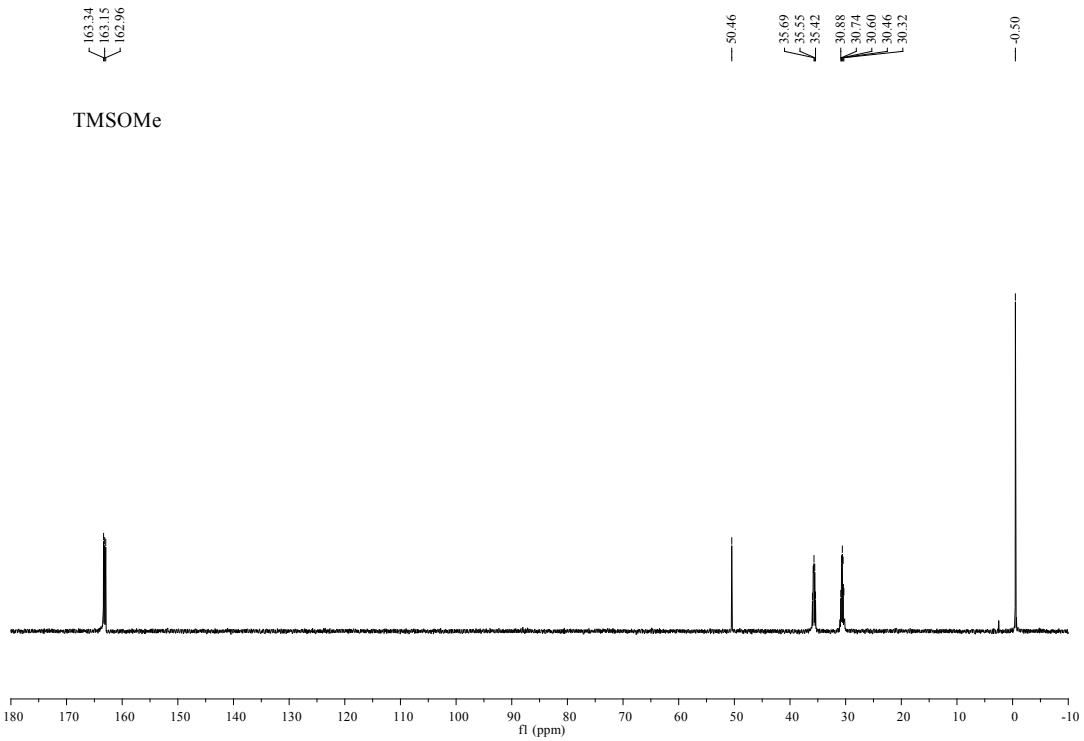
TMSO^{t}Bu



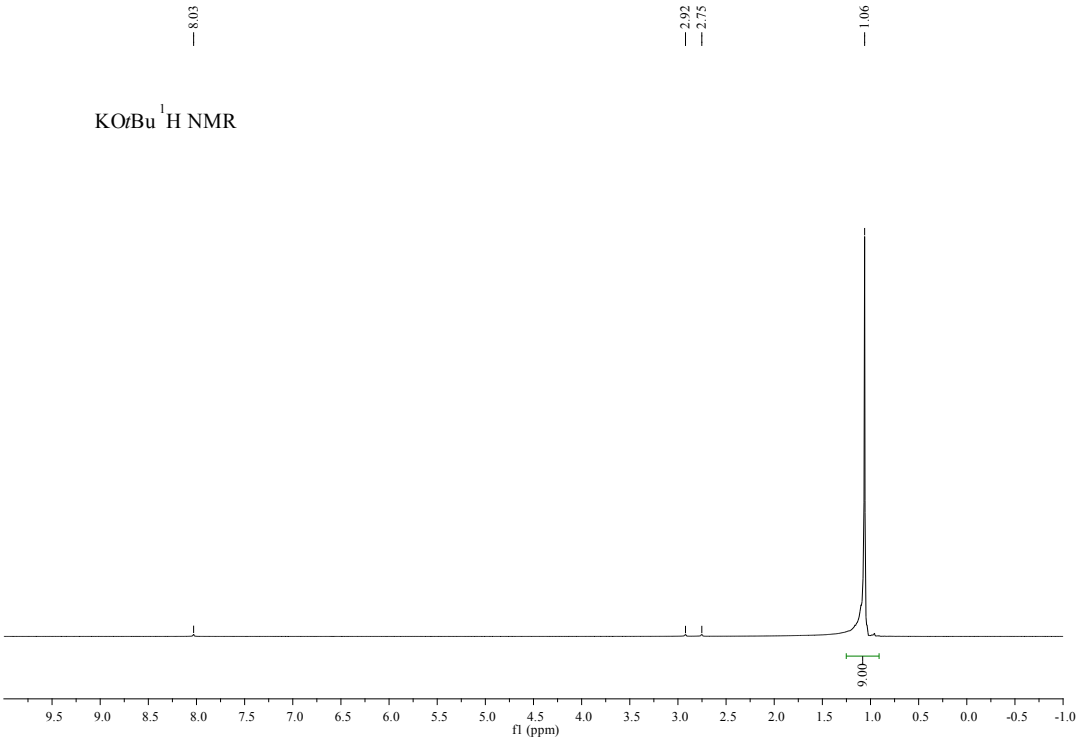
TMSOEt



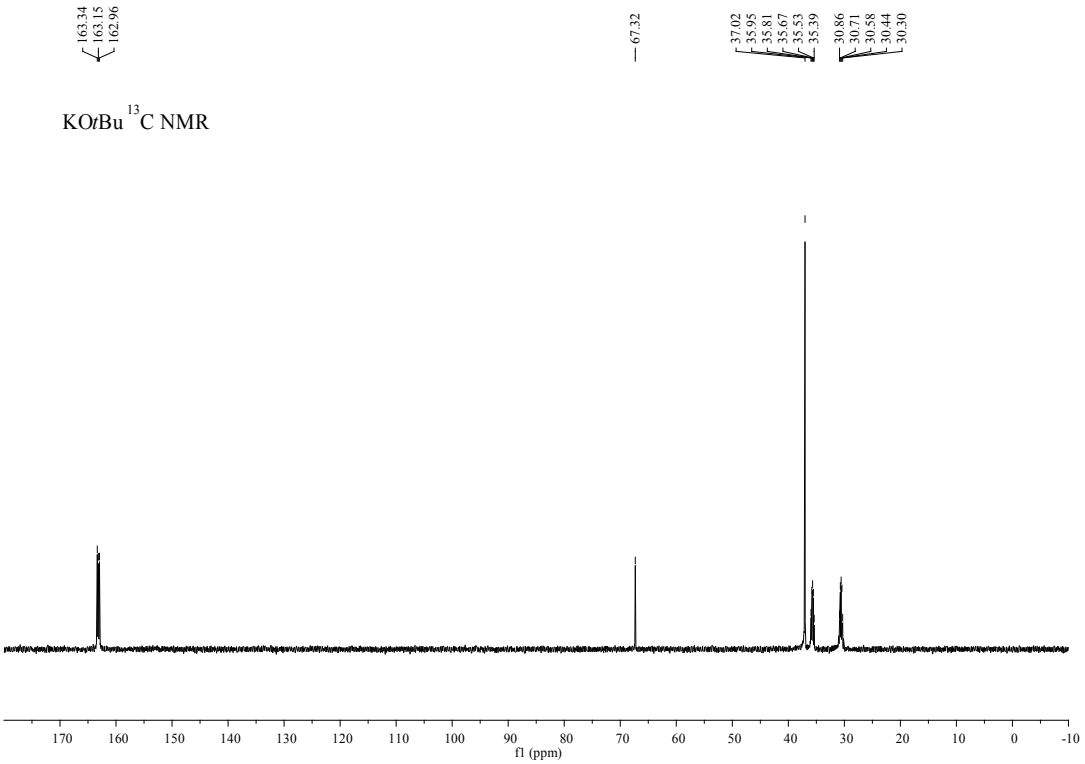
TMSOMe



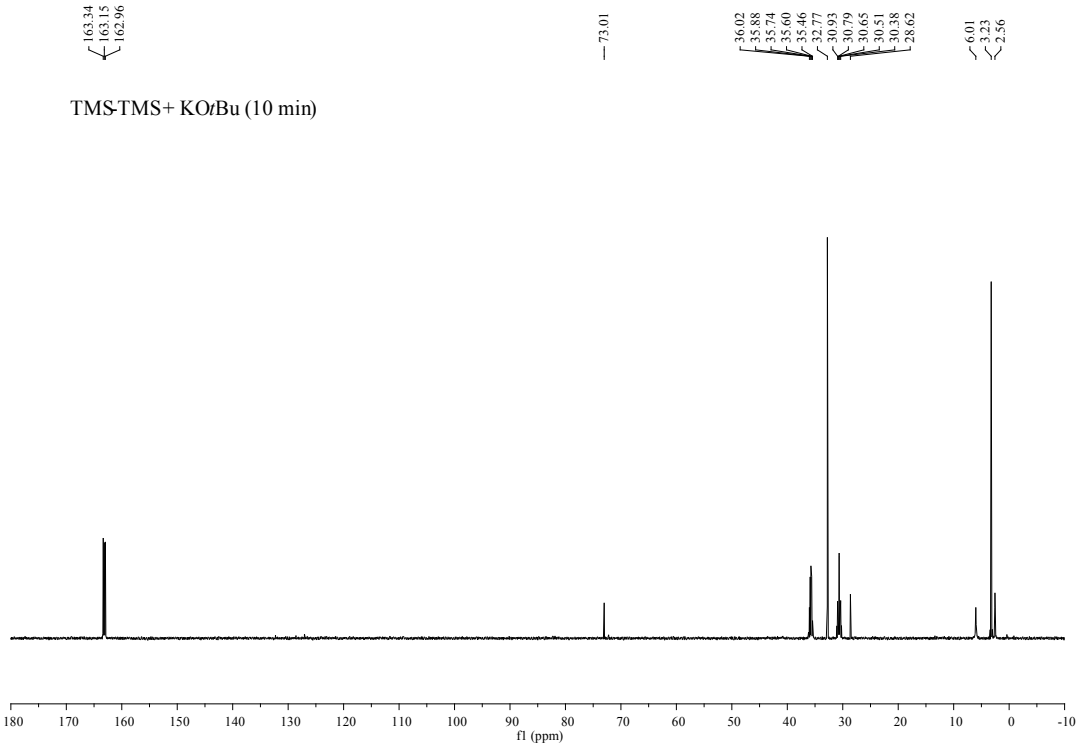
KO*t*Bu ^{1}H NMR



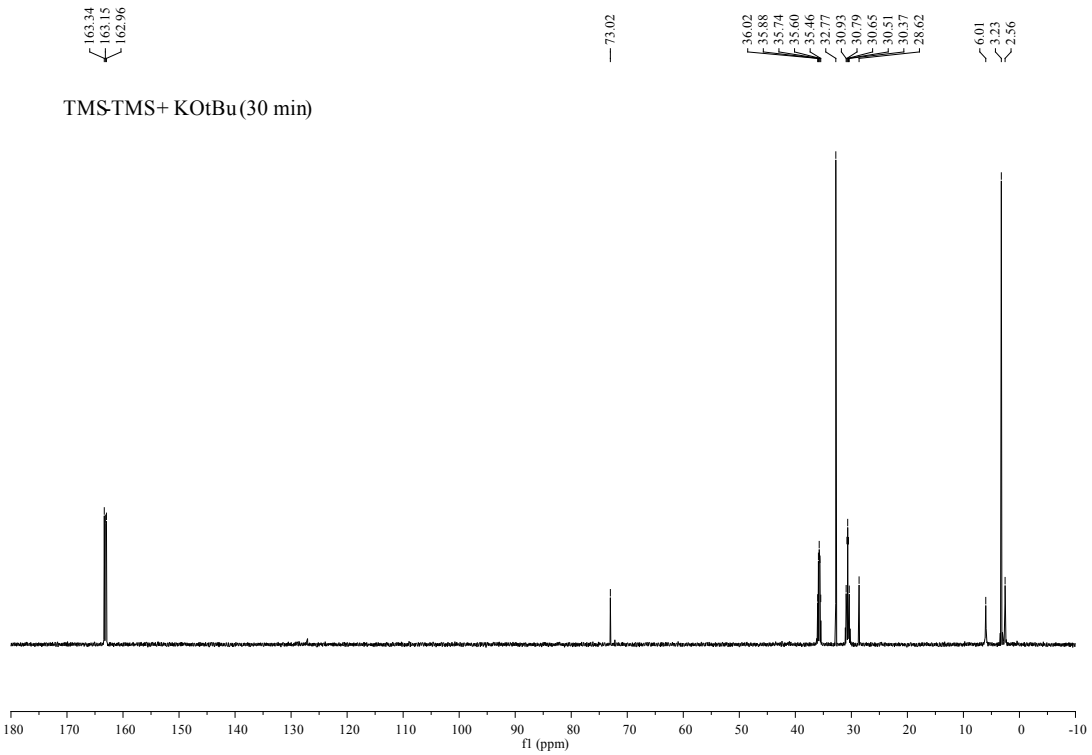
KO*t*Bu ^{13}C NMR

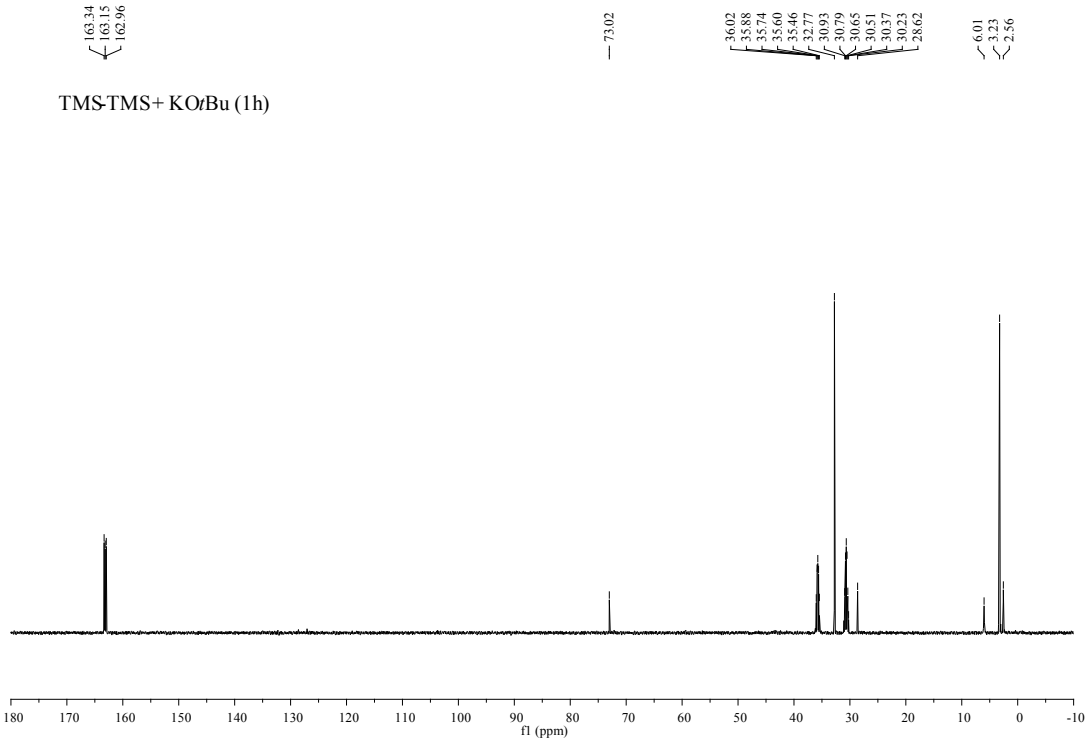


TMS-TMS+ KO*t*Bu (10 min)

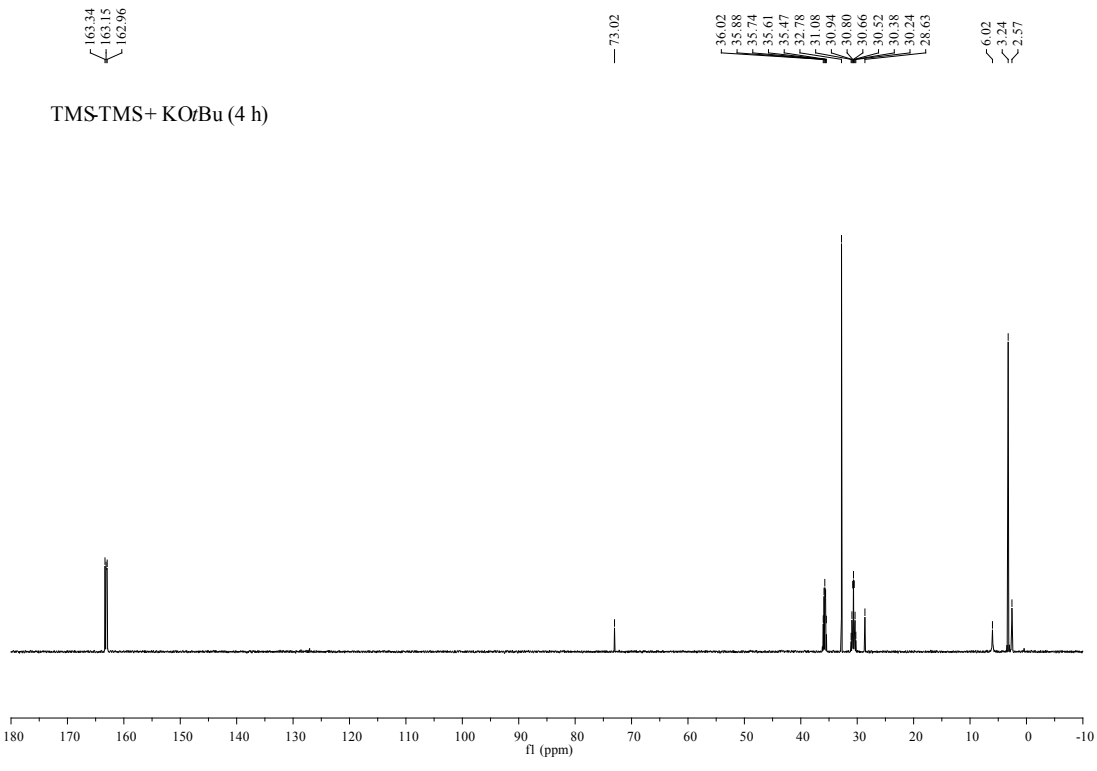


TMS-TMS+ KOtBu (30 min)

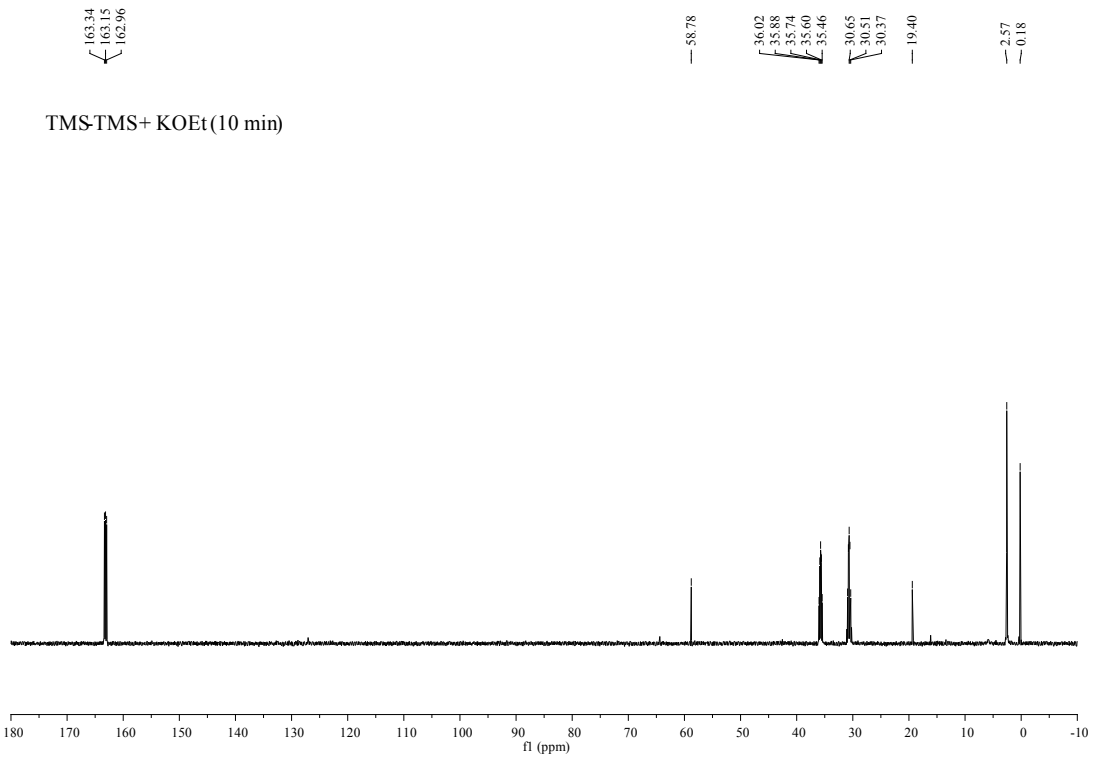




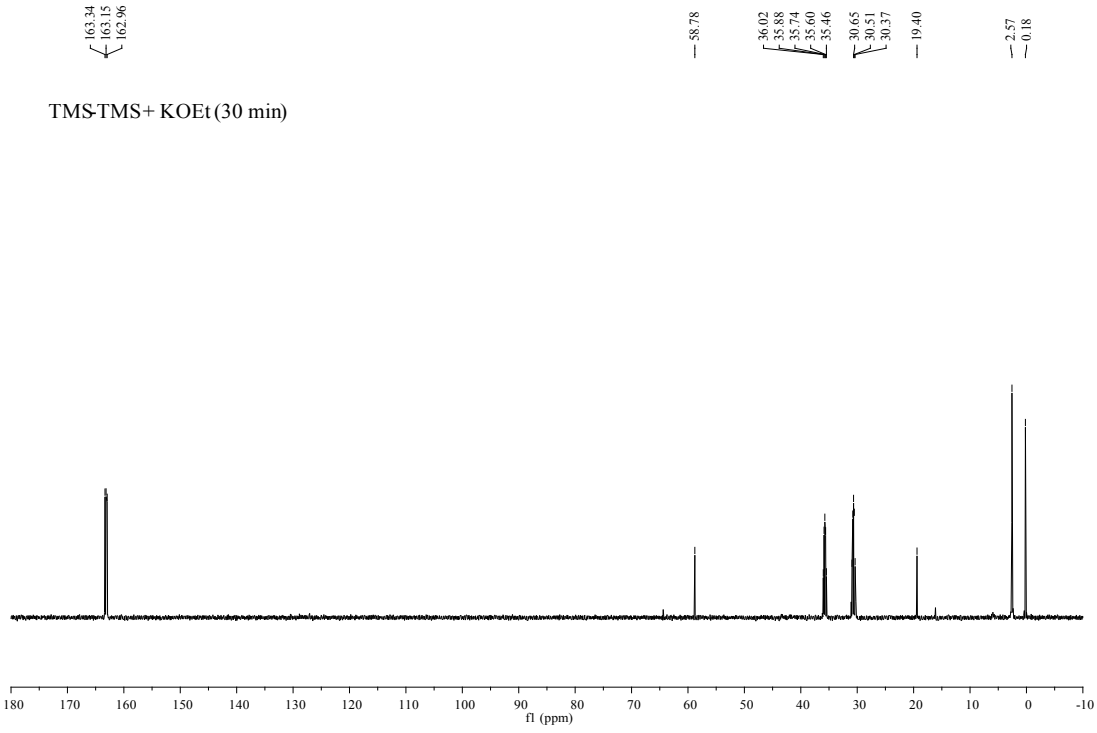
TMS-TMS+ KO*t*Bu (1h)



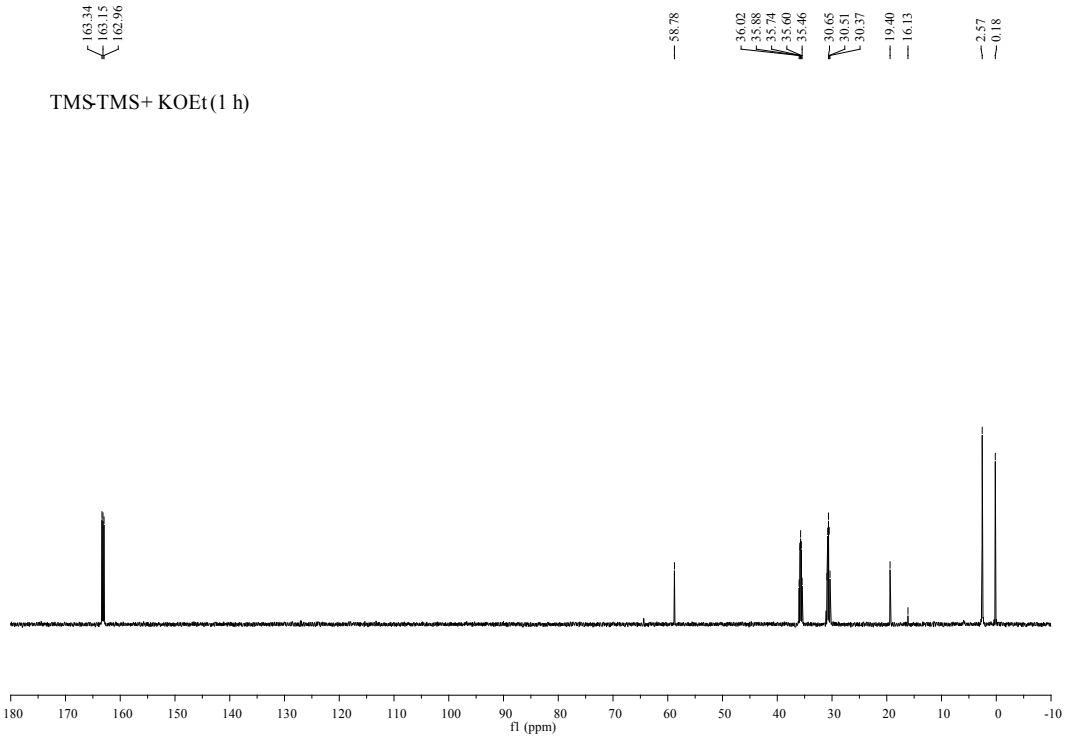
TMS-TMS+ KO*t*Bu (4 h)



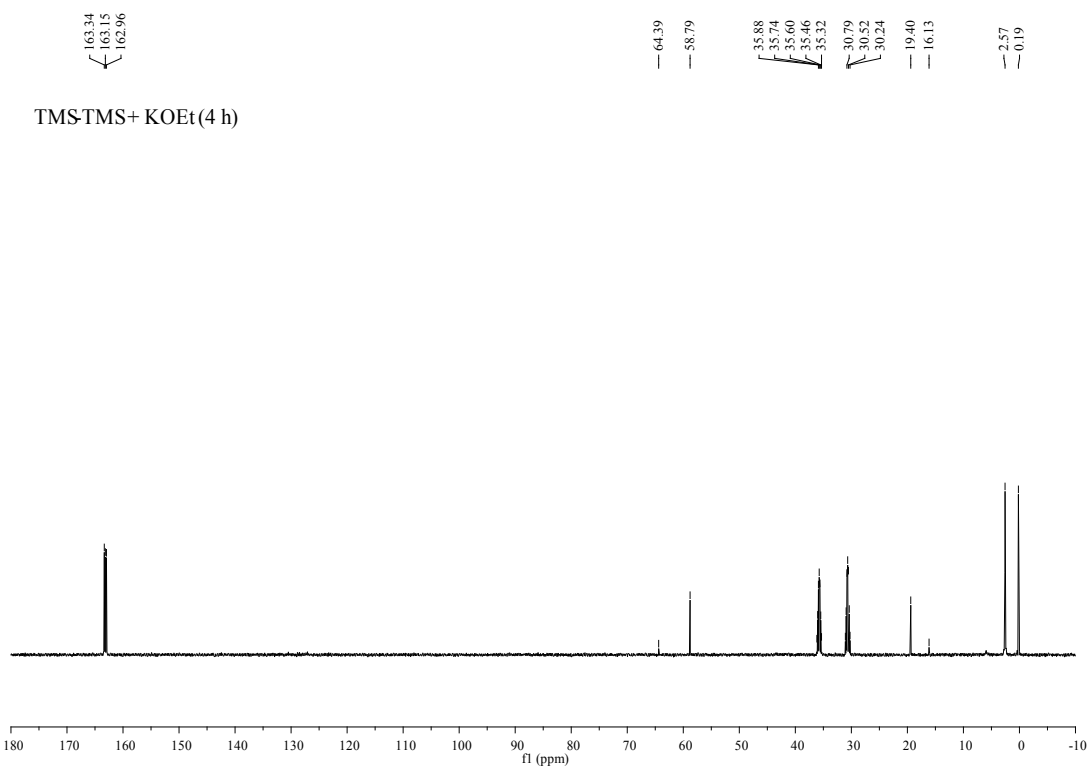
TMS-TMS+ KOEt (10 min)



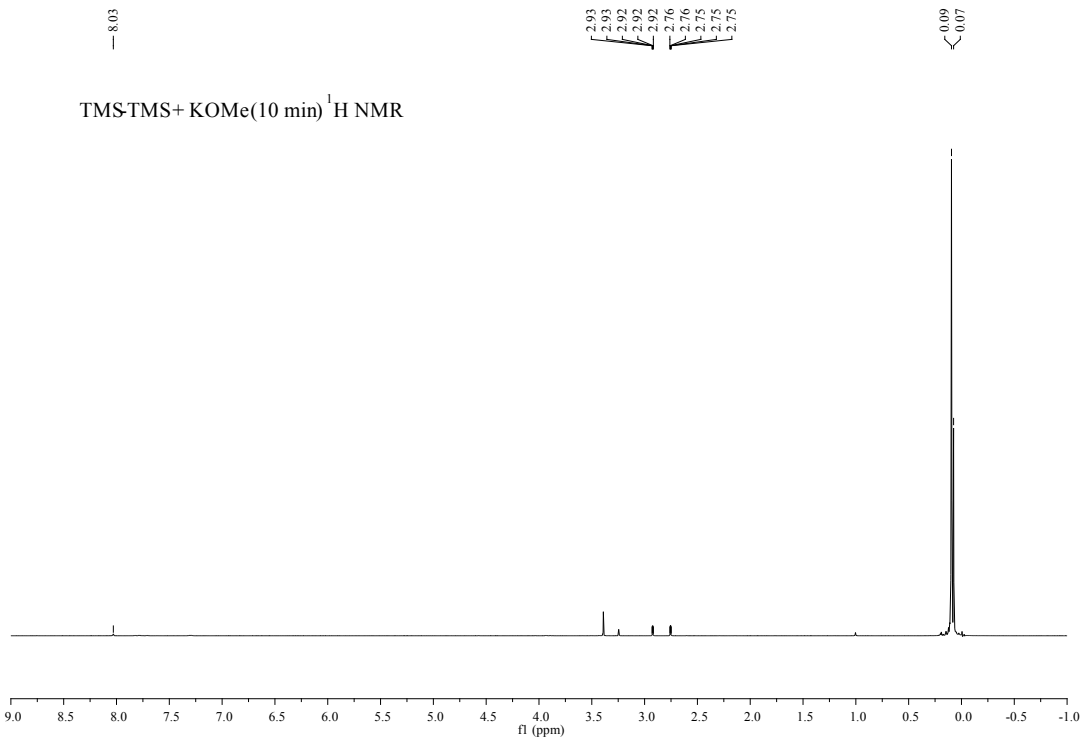
TMS-TMS+ KOEt (30 min)



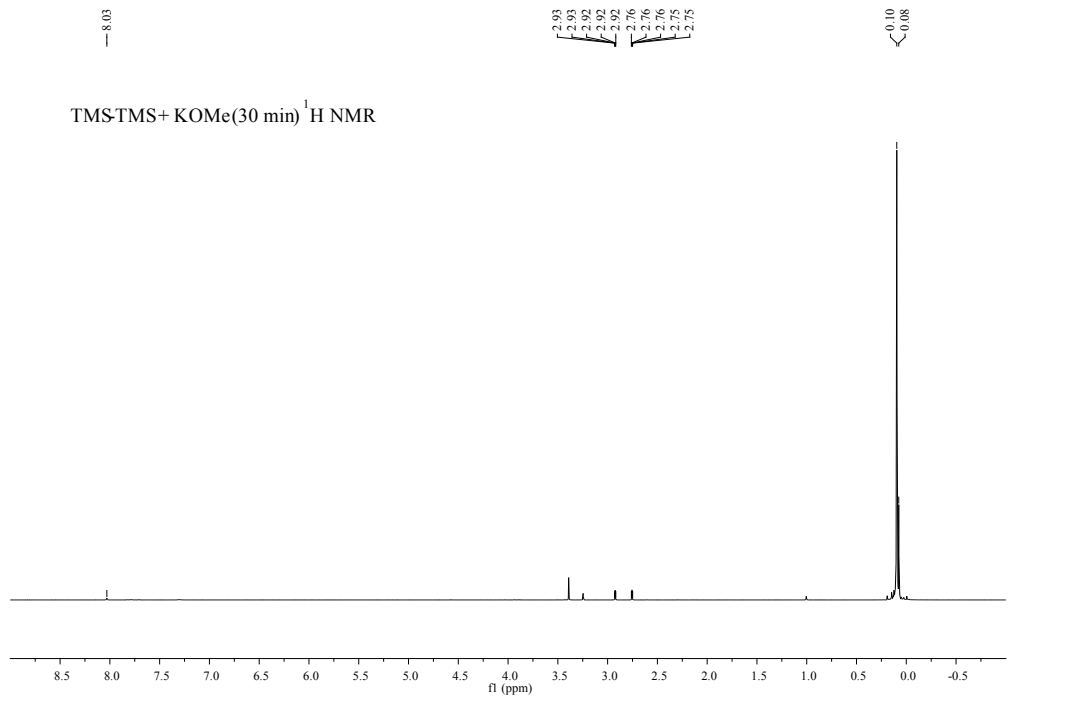
TMS-TMS+ KOEt (1 h)



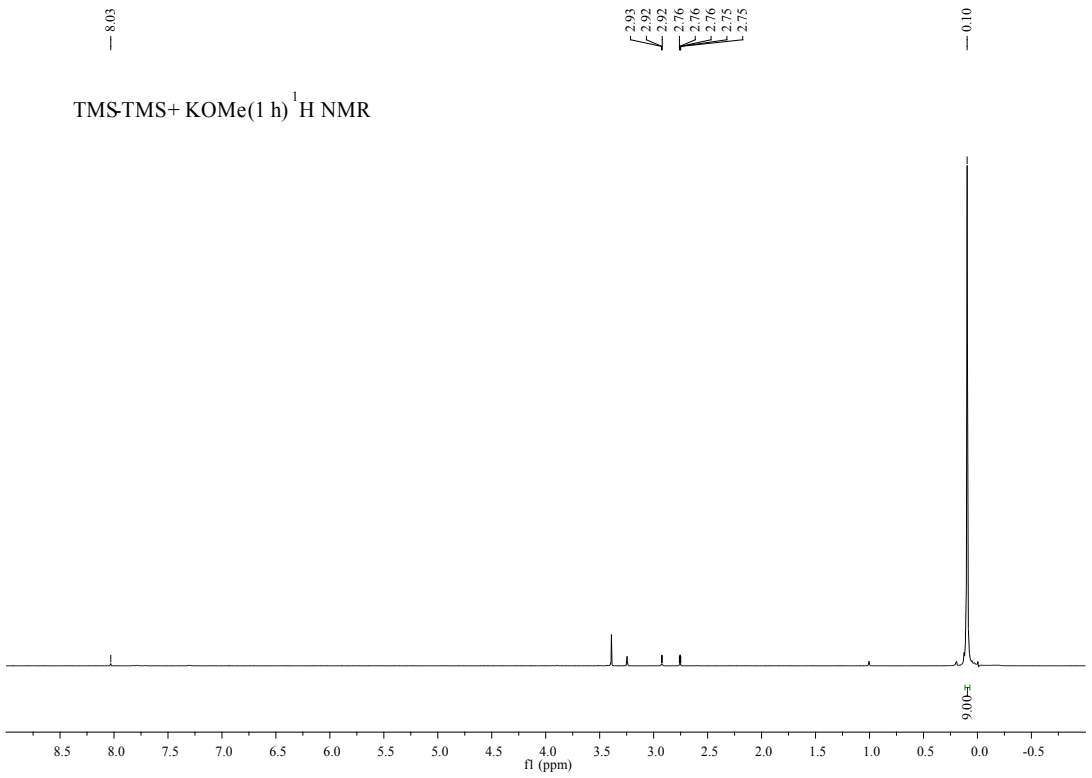
TMS-TMS+ KOEt (4 h)



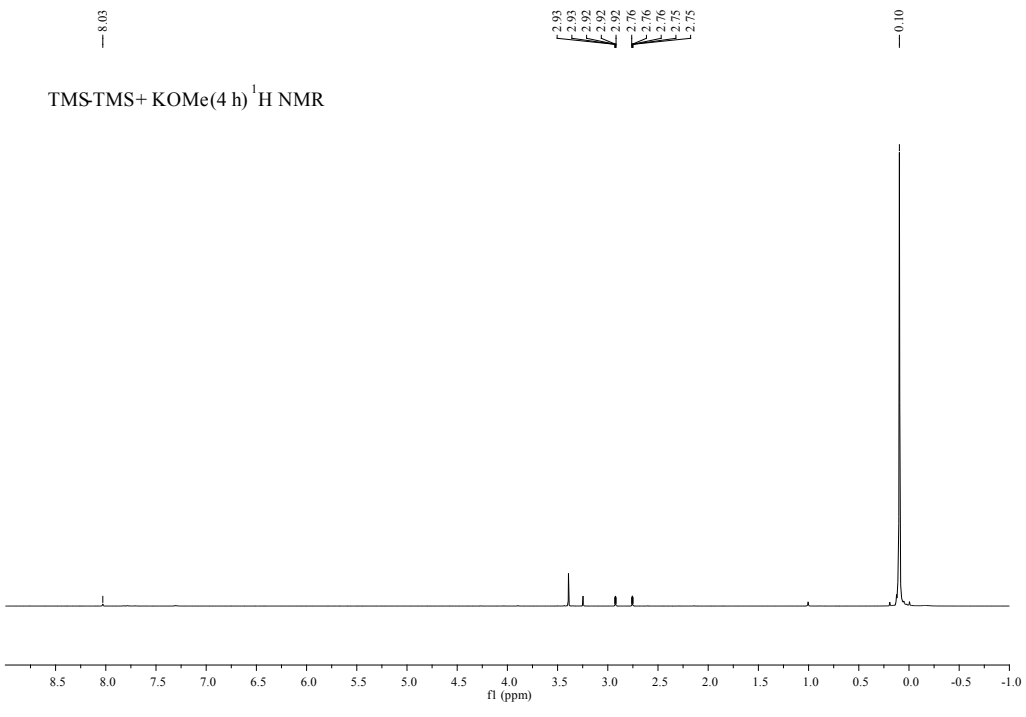
TMS-TMS+ KOMe(10 min) ^{1}H NMR



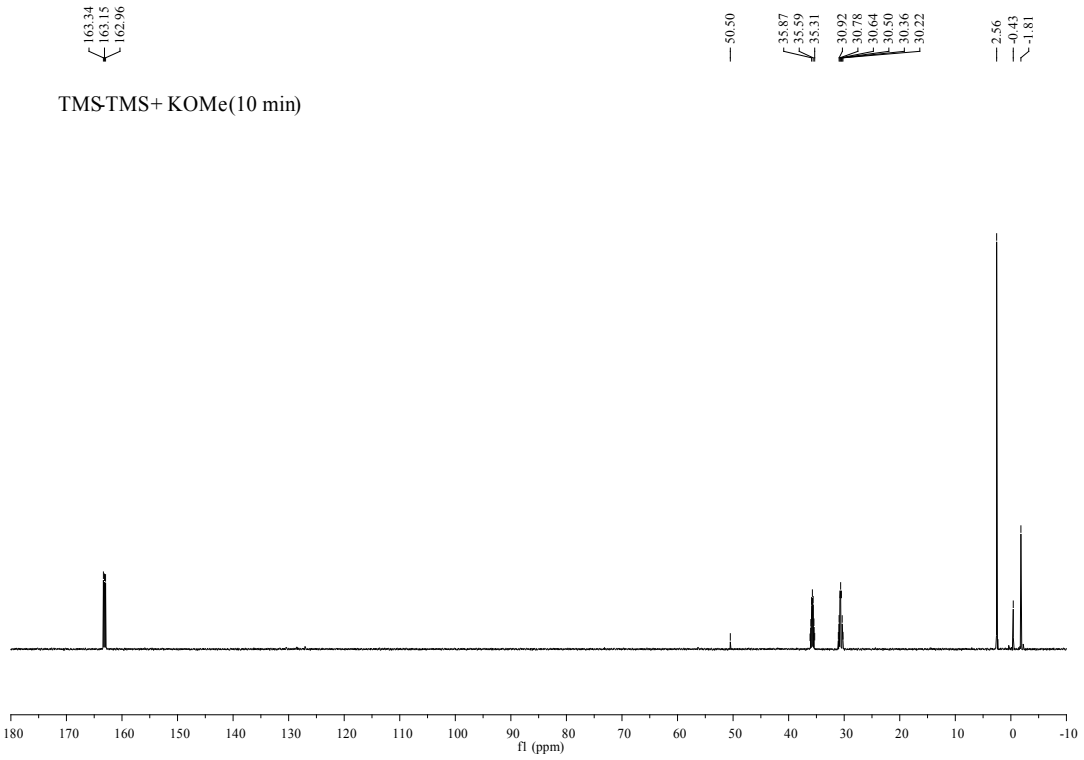
TMS-TMS+ KOMe(30 min) ^{1}H NMR



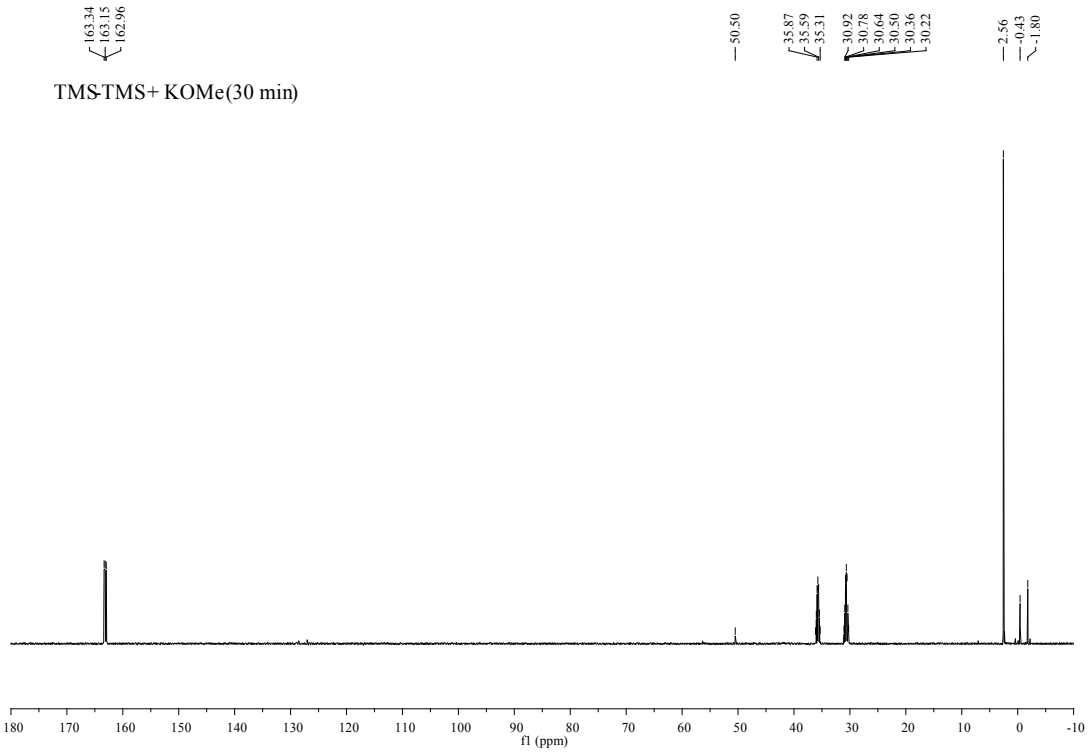
TMS-TMS+ KOMe(1 h) ^{1}H NMR



TMS-TMS+ KOMe(4 h) ^{1}H NMR



TMS-TMS+ KOMe(10 min)



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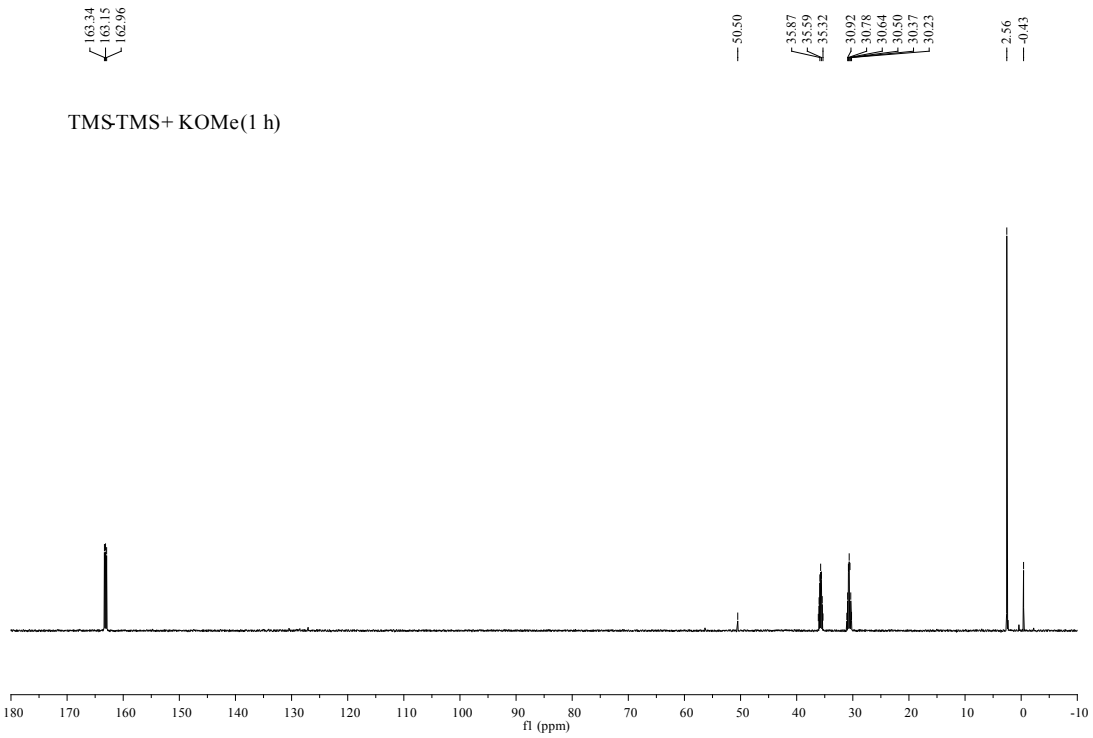

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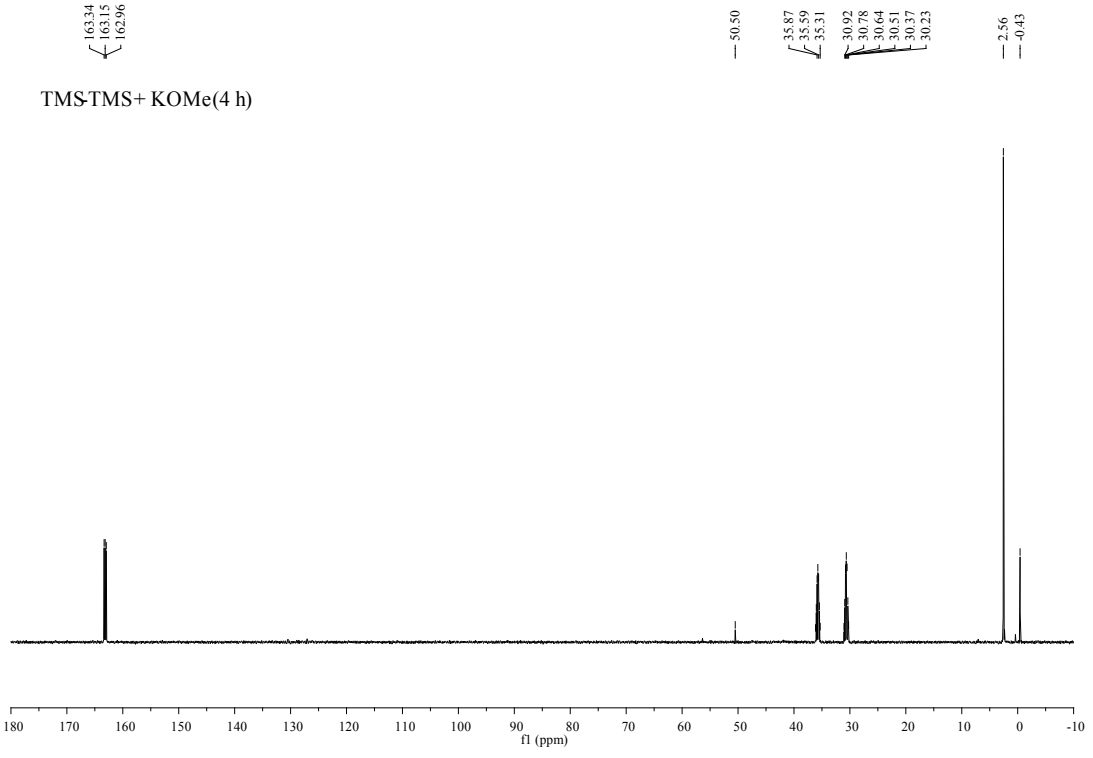
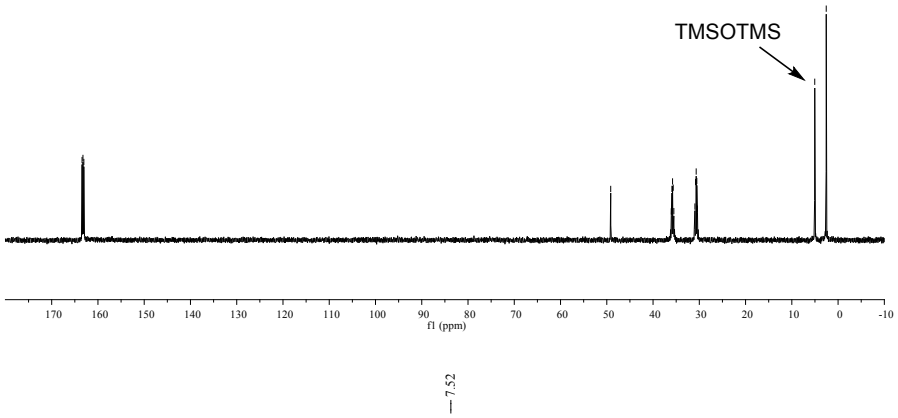
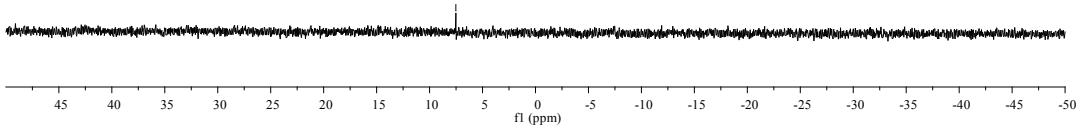


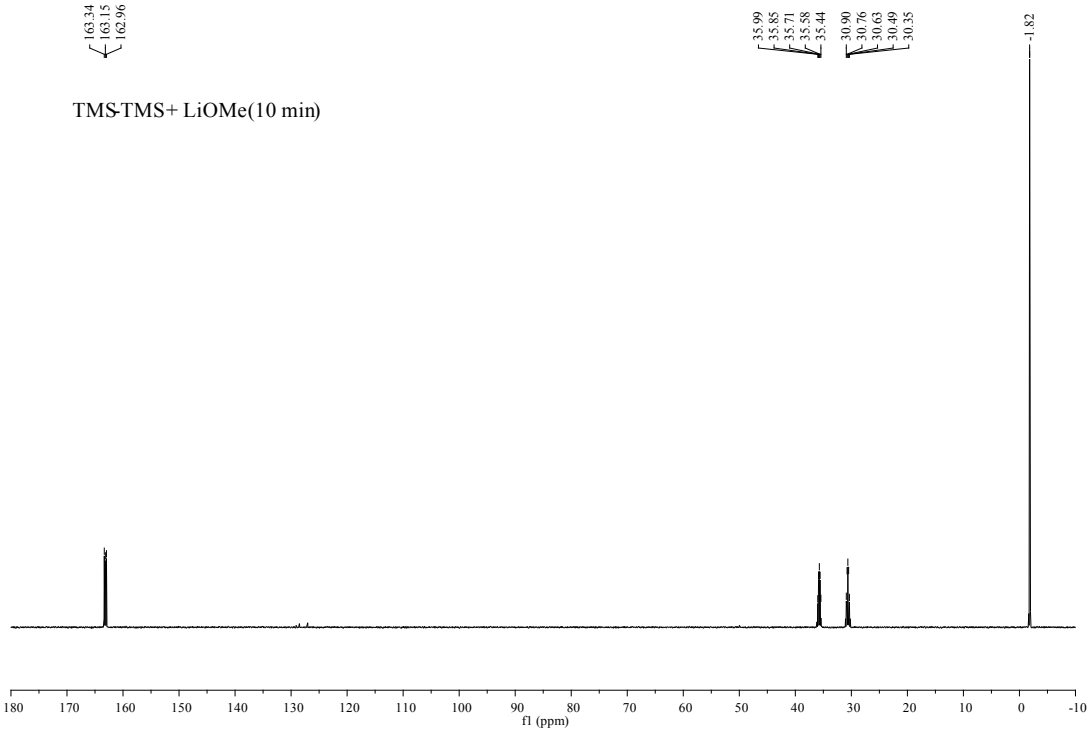
TMS-TMS+ KOMe(4 h)

TMS-TMS + TMSOTMS + KOMe (10 min)

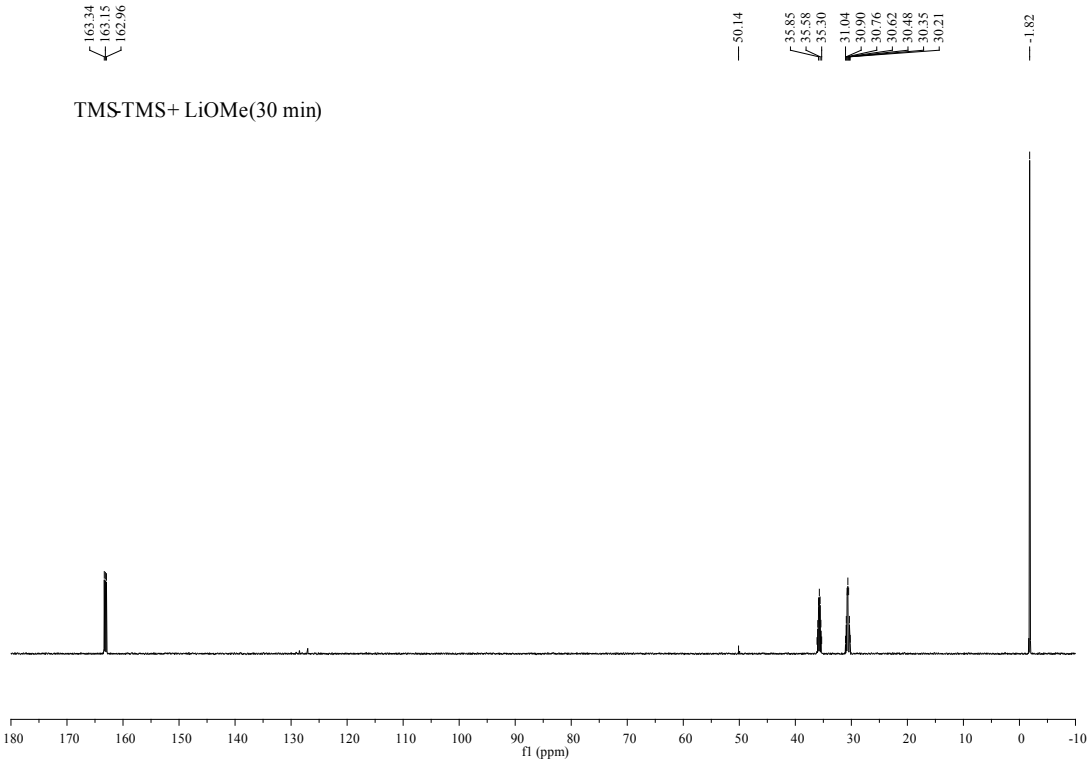


TMS-TMS + KOMe (^{29}Si NMR)





TMS-TMS+ LiOMe(10 min)



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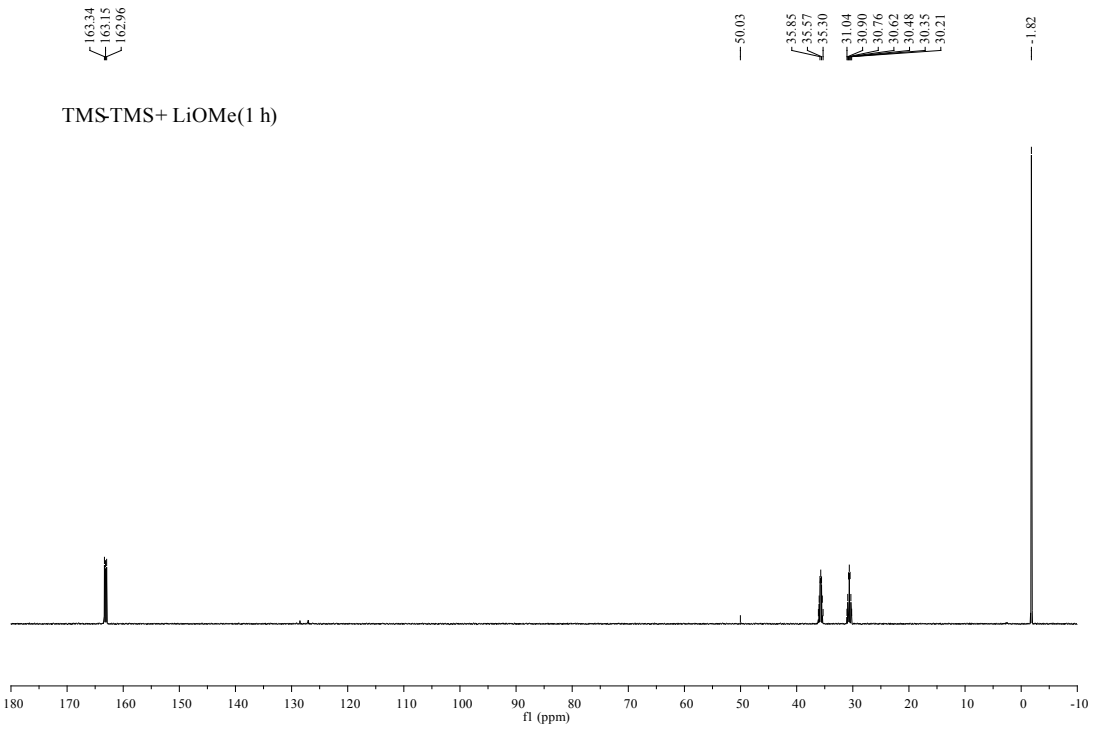
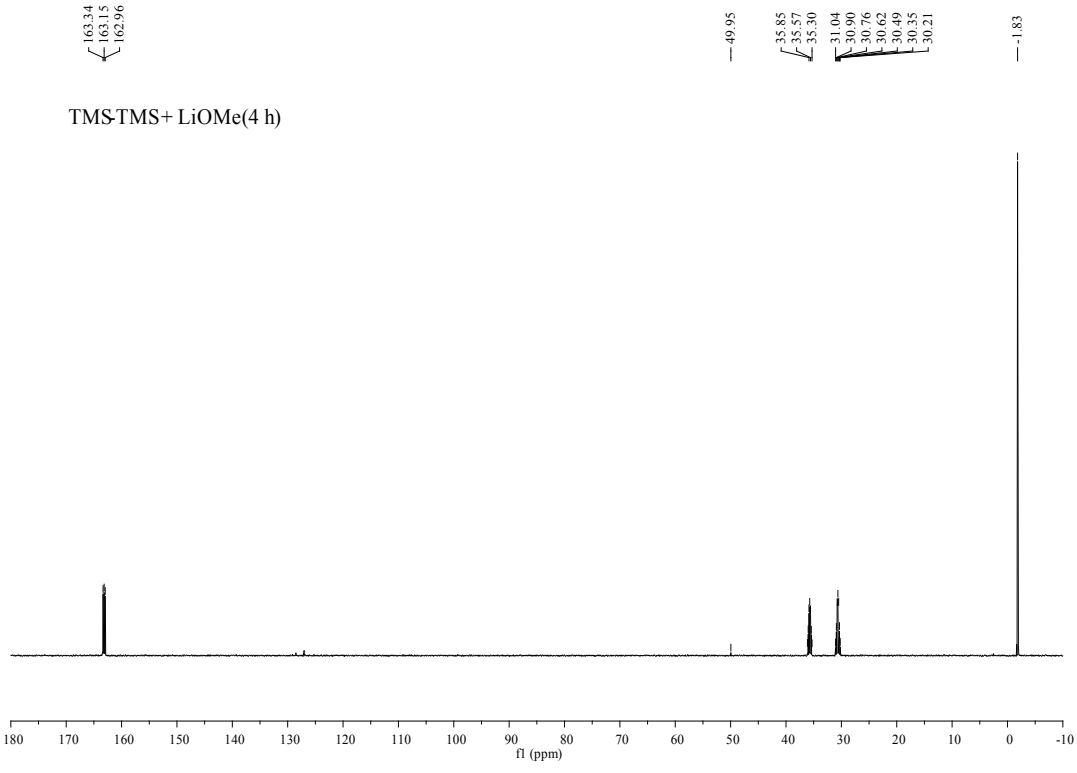
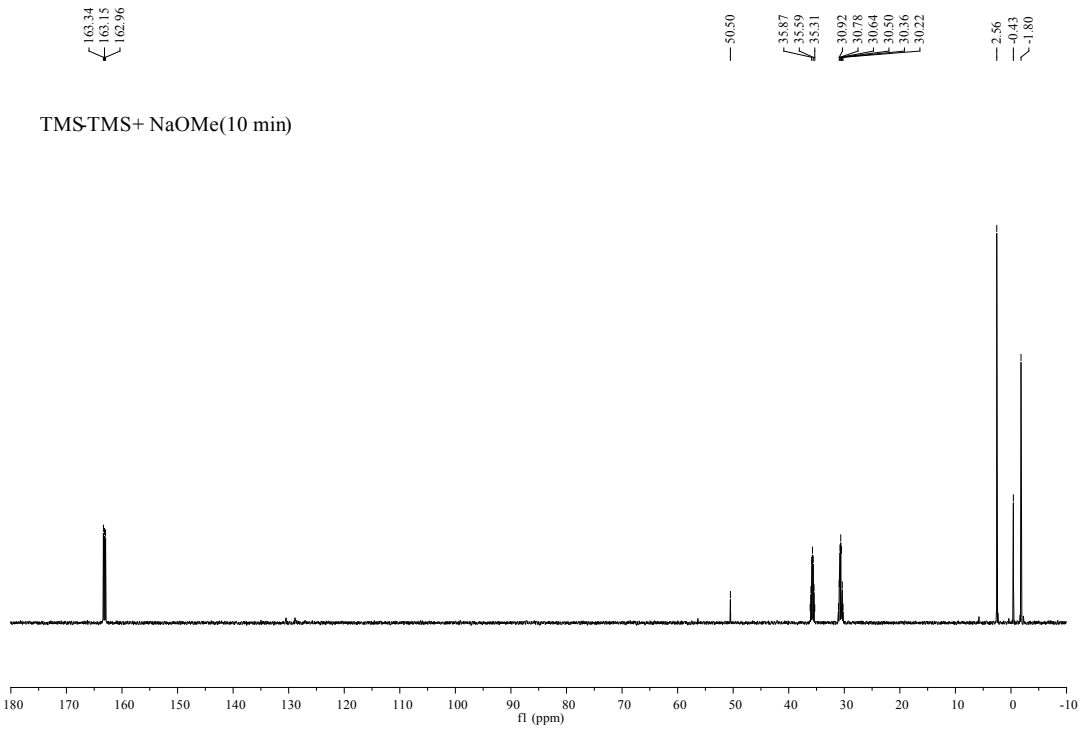


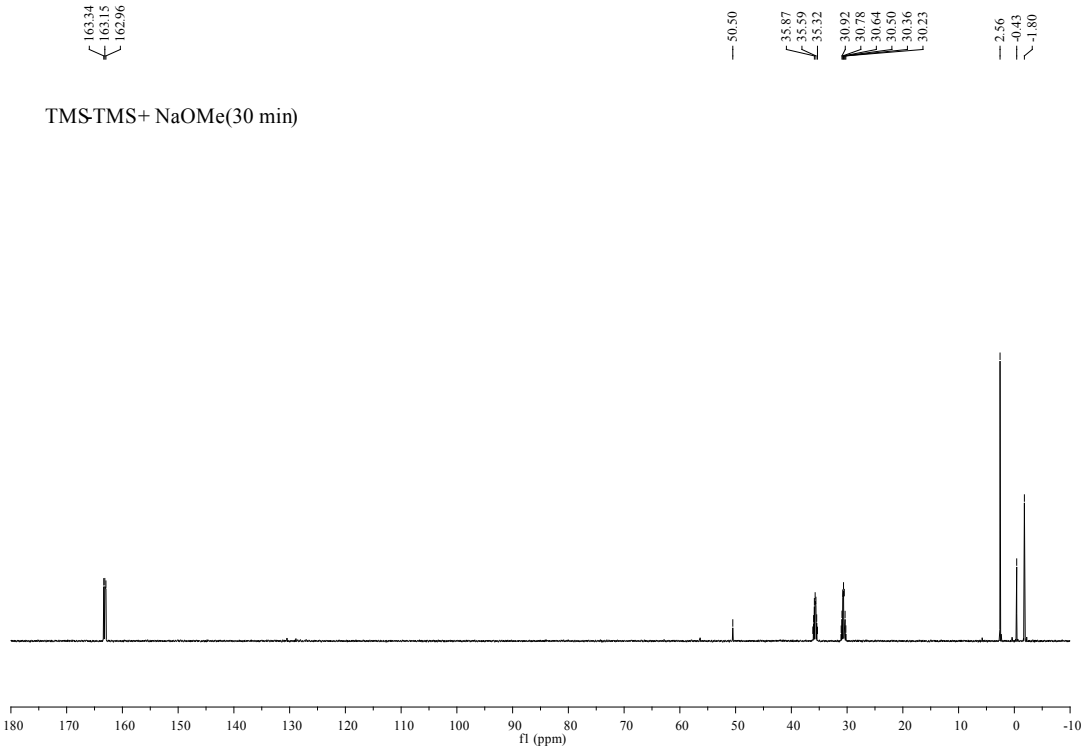
TMS-TMS+ LiOMe(1 h)



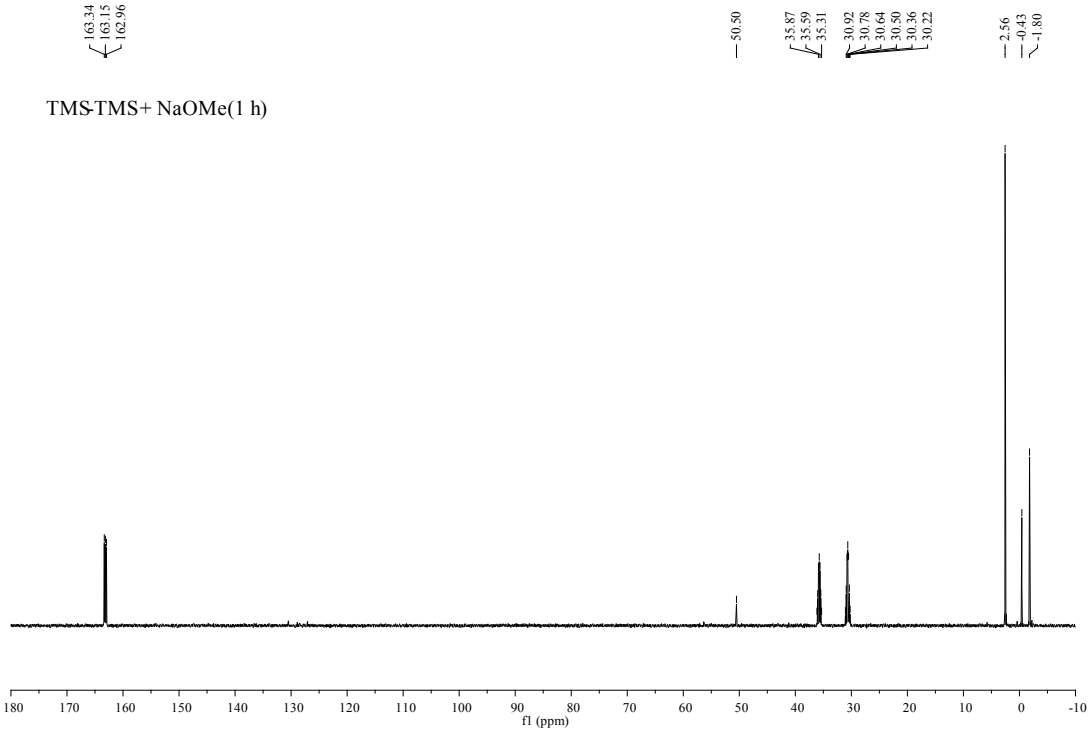
TMS-TMS+ LiOMe(4 h)



TMS-TMS+ NaOMe(10 min)



TMS-TMS+ NaOMe(30 min)



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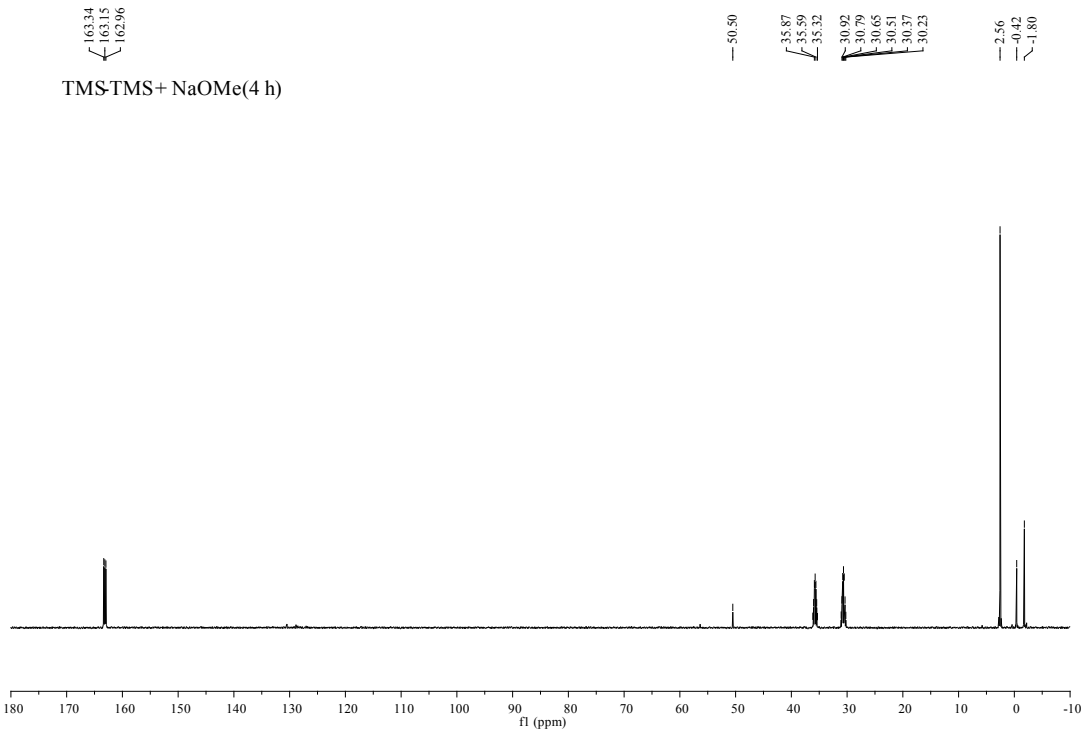
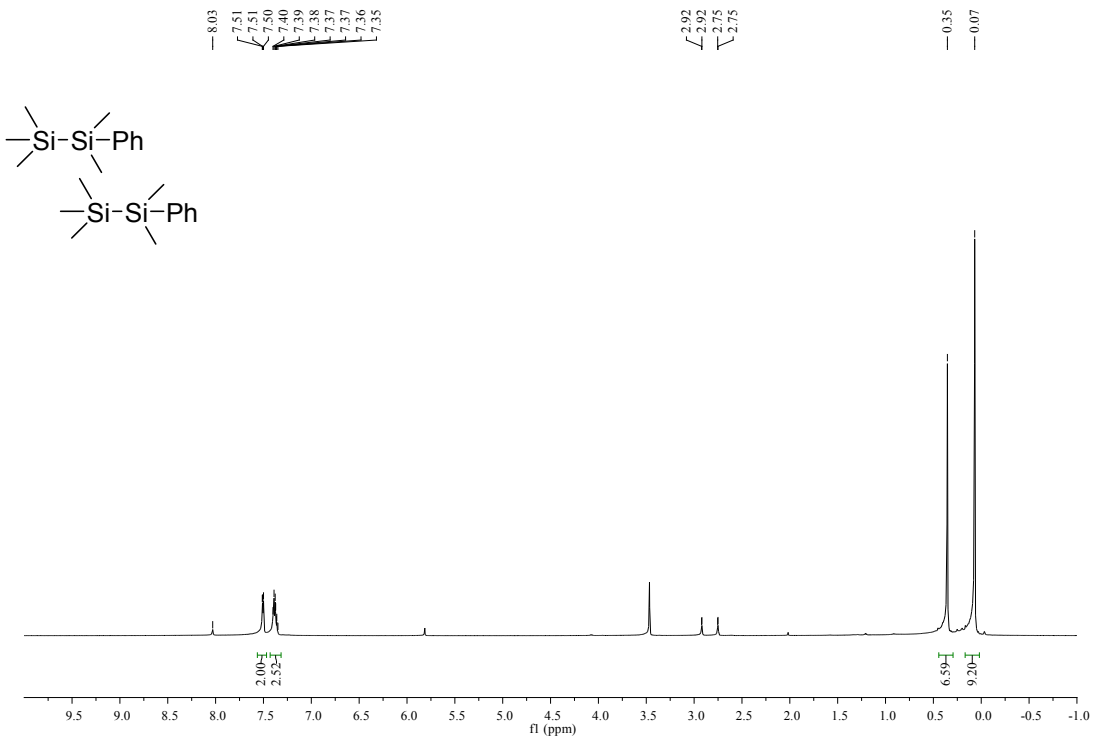
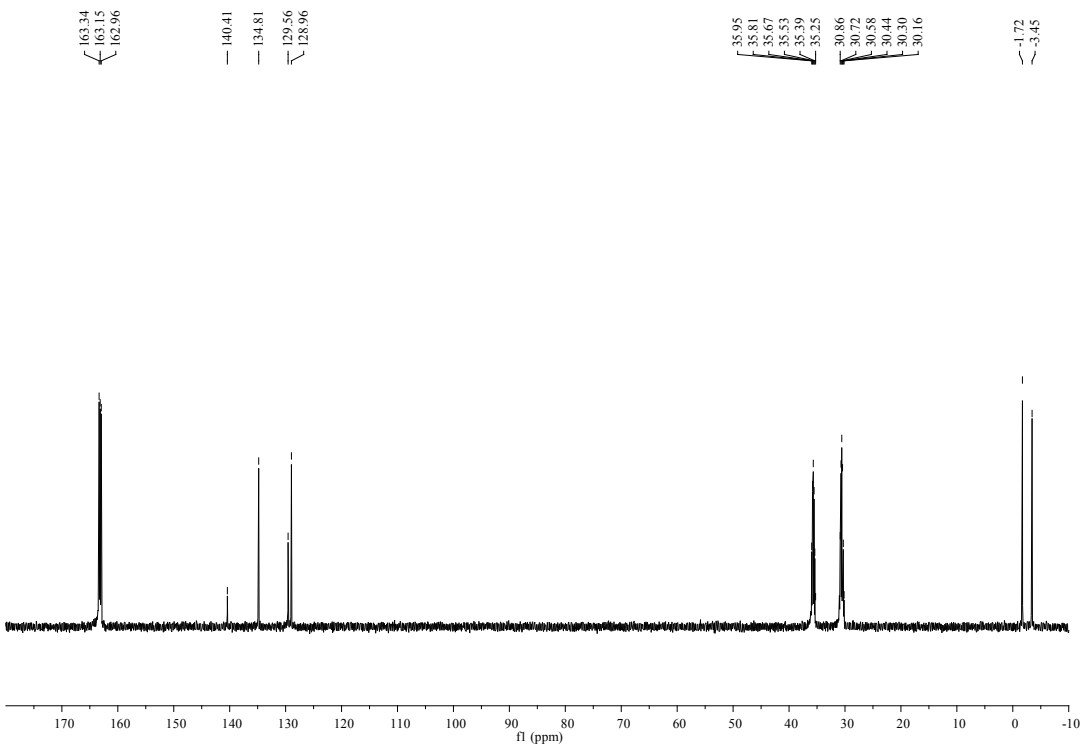


TMS-TMS+ NaOMe(4 h)


8.03
7.51
7.51
7.50
7.40
7.39
7.38
7.37
7.37
7.36
7.35
2.92
2.92
2.75
2.75
0.35
0.07
Si-Si-Ph
Si-Si-Ph
2.00
2.52
6.59
9.20
fl (ppm)


163.34
163.15
162.96
140.41
134.81
129.56
128.96
35.95
35.81
35.67
35.53
35.39
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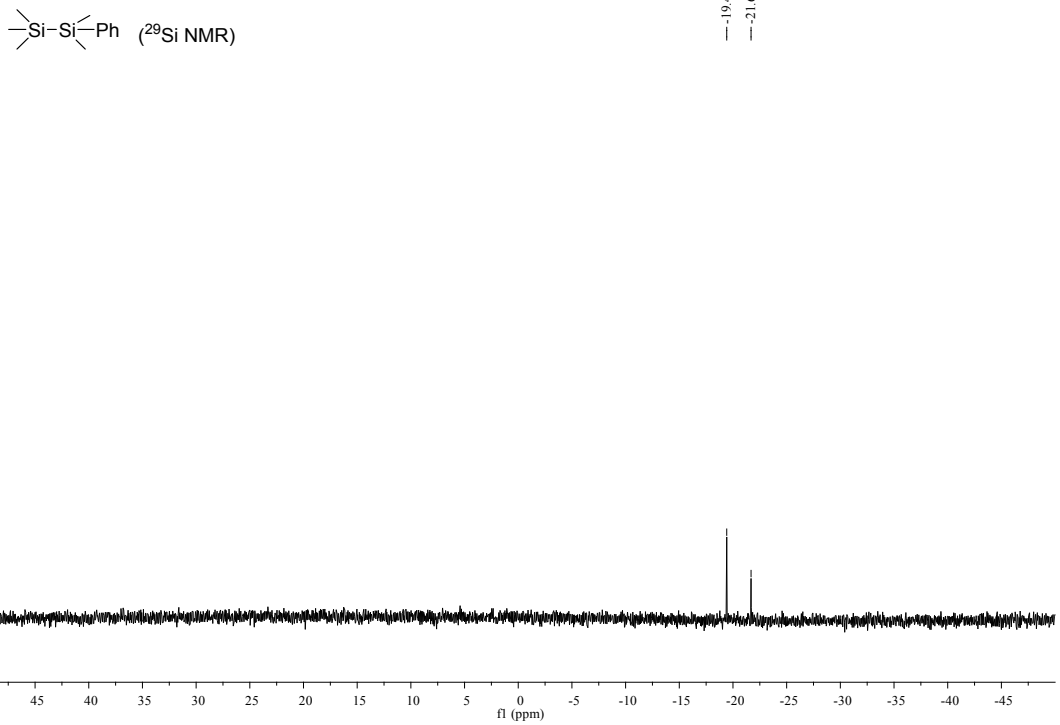
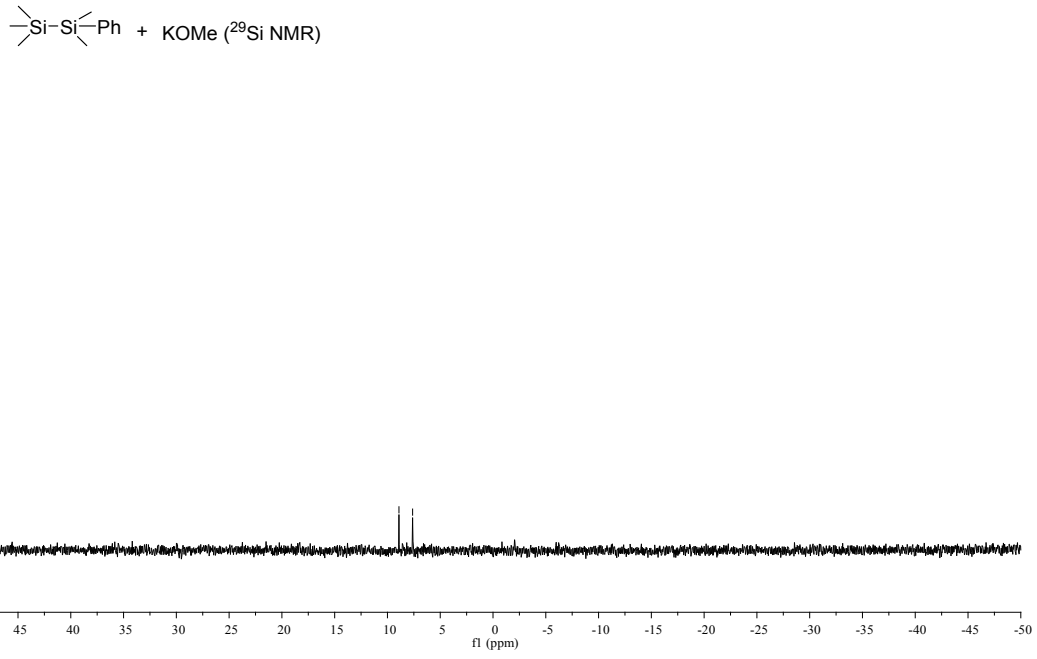
30.72
30.58
30.44
30.30
30.16
-1.72
-3.45
fl (ppm)

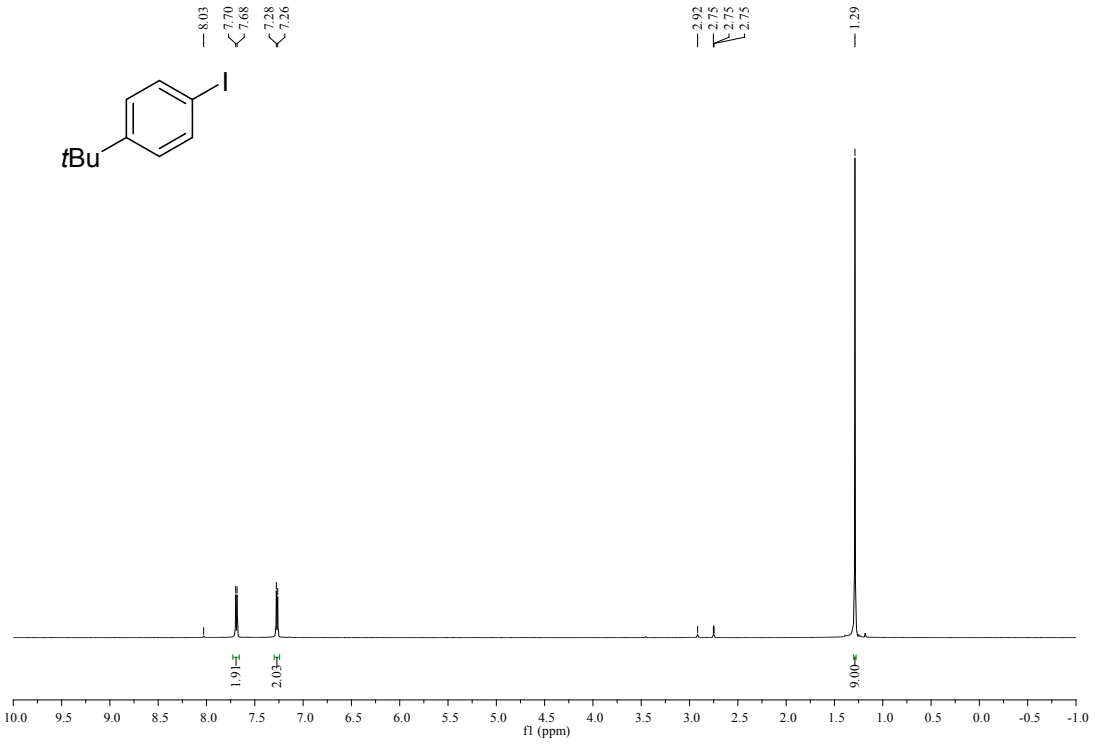

Si–Si–Ph
(^{29}Si NMR)
-19.42
-21.68
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

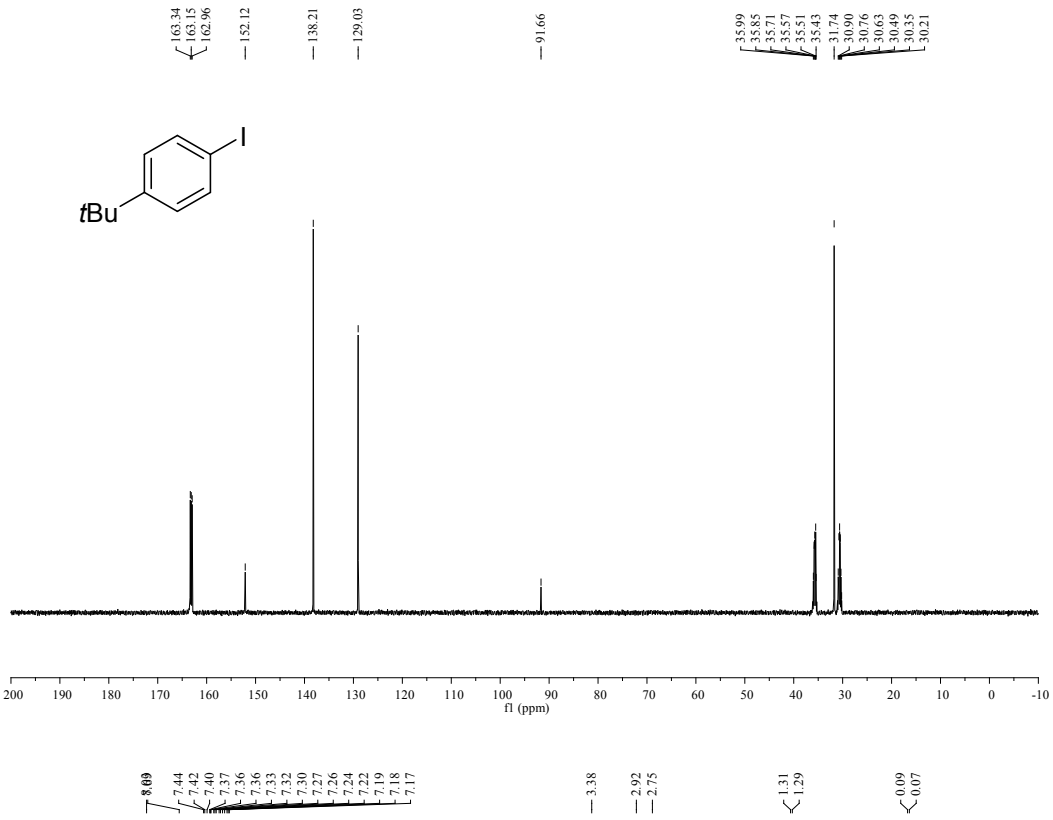

8.91
7.62
Si–Si–Ph + KOMe (^{29}Si NMR)
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

The ^{1}H and ^{13}C NMR NMR spectra of 4-tert-Butyliodobenzene (13.0 mg, 0.05 mmol) in 0.5 mL of dried DMF-d7 in NMR tube was recorded using a Bruker AM-600NMR spectrometer at room temperature.

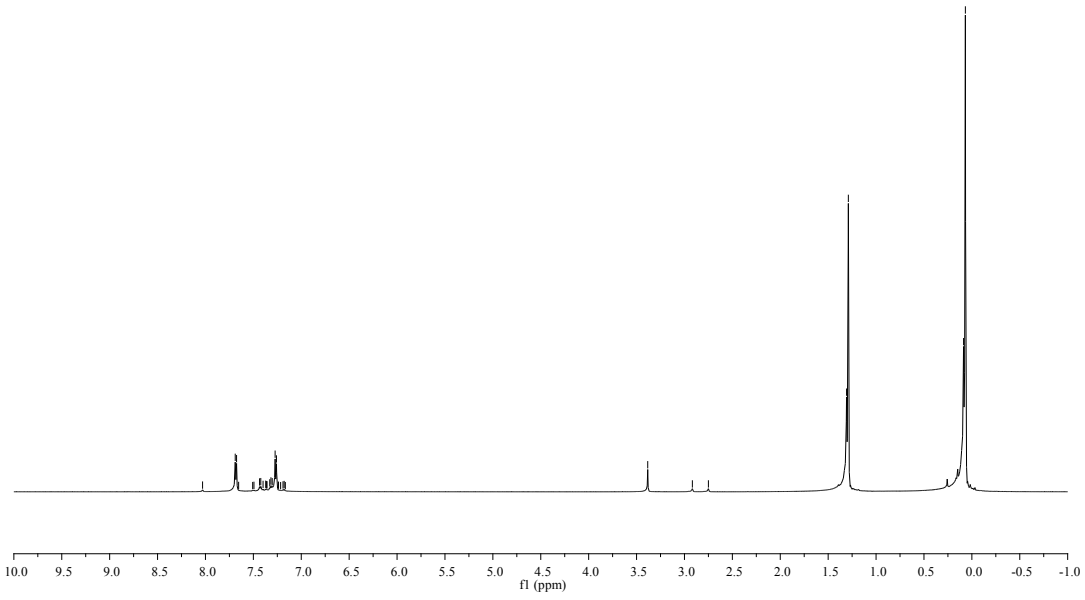
The ^{1}H NMR and ^{13}C NMR analysis of silane intermediate was conducted as following: To a NMR tube containing 0.5 mL of dried DMF-d7 were added TMS-TMS (14.6 mg, 0.1 mmol), KOMe (7.0 mg, 0.1 mmol) and 4-tert-Butyliodobenzene (26.0 mg, 0.1 mmol) under argon. Then the ^{1}H NMR and ^{13}C NMR spectra was recorded after 10 min.

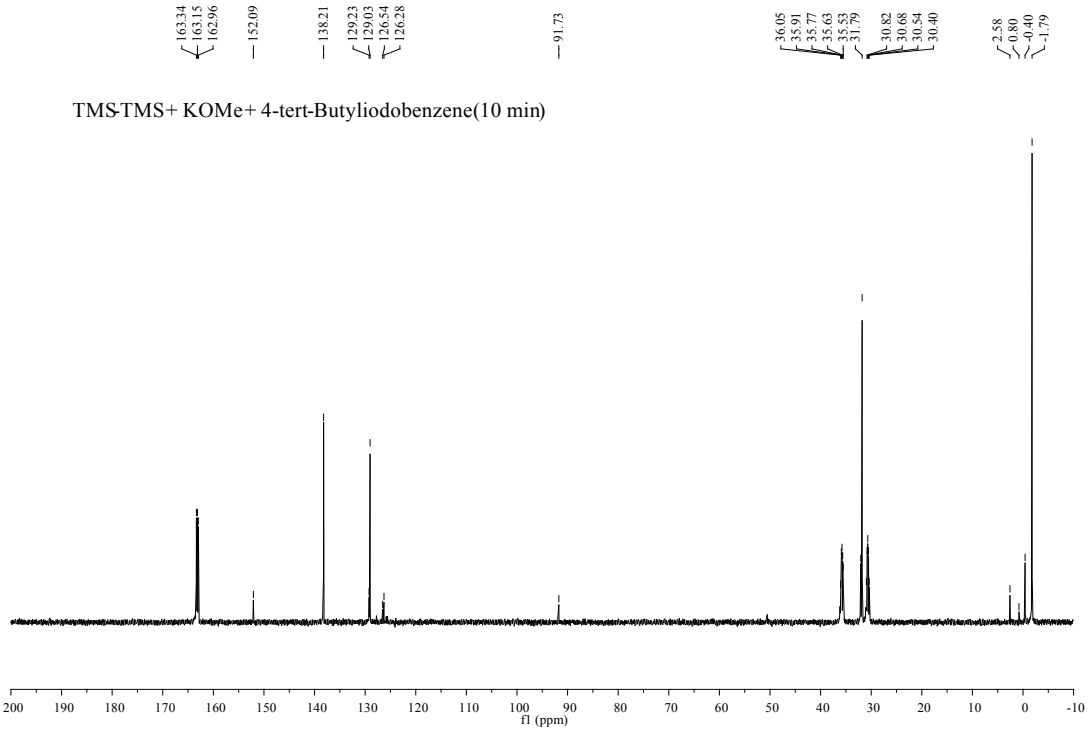
In situ NMR studies with the addition of substrates were helpful to provide information about the nature of the peak (2.56 ppm) which was significantly less.



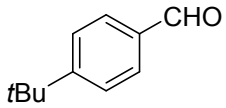


TMS-TMS+ KOMe+ 4-tert-Butyliodobenzene(10 min)



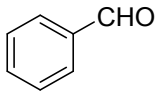

163.34
163.15
162.96
152.09
138.21
129.23
129.03
126.54
126.28
91.73
36.05
35.91
35.77
35.63
35.53
31.79
30.82
30.68
30.54
30.40
2.58
0.80
-0.40
-1.79
TMS-TMS+ KOMe+ 4-tert-Butyliodobenzene(10 min)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5. Identification of compounds



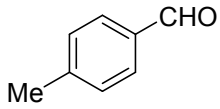
4-tert-Butylbenzaldehyde (2)[2]

Prepared according to the general procedure using 1-*tert*-butyl-4-iodobenzene **1** (130.1 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:50) to afford the product **2** as a colorless oil (56.7mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 158.6, 134.2, 129.8, 126.1, 35.5, 31.2.



Benzaldehyde (3)[3]

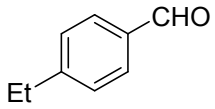
Prepared according to the general procedure using iodobenzene (102.1 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:100) to afford the product **3** as a colorless oil (25.4 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.88 (d, J = 6.7 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 136.6, 134.6, 129.9, 129.1.



4-Methylbenzaldehyde (4)[3]

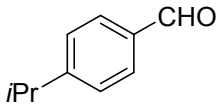
Prepared according to the general procedure using 1-iodo-4-methylbenzene (109.5 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:60) to afford the product **4** as a colorless oil (37.9 mg, 63% yield). ^{1}H NMR

(400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 145.7, 134.3, 130.0, 129.9, 22.0.



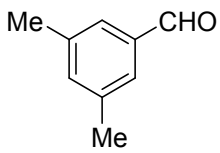
4-Ethylbenzaldehyde (5)[4]

Prepared according to the general procedure using 1-iodo-4-ethylbenzene (116.0 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:50) to afford the product **5** as a colorless oil (45.5 mg, 67% yield). ^1H NMR (600 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.06, 151.79, 134.62, 130.08, 128.66, 29.27, 15.21.



4-Isopropylbenzaldehyde (6)[5]

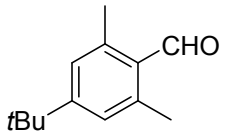
Prepared according to the general procedure using 1-iodo-4-isopropylbenzene (123.2 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:40) to afford the product **6** as a colorless oil (40.8 mg, 55% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 2.99 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 156.4, 134.7, 130.2, 127.3, 34.6, 23.8.



3,5-Dimethylbenzaldehyde (7)[6]

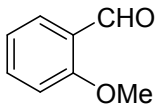
Prepared according to the general procedure using 3,5-Dimethyliodobenzene (116.0 mg, 0.5 mmol),

KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:40) to afford the product **7** as a colorless oil (41.5 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.53 (s, 2H), 7.31 (s, 1H), 2.44 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 138.8, 136.7, 136.3, 127.6, 21.2.



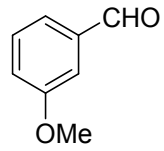
2,6-Dimethyl-4-tert-butylbenzaldehyde (8)[7]

Prepared according to the general procedure using 5-tert-butyl-2-iodo-1,3-dimethylbenzene (144.1 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:80) to afford the product **8** as a colorless oil (43.7 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.09 (s, 2H), 2.62 (s, 6H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 156.8, 141.3, 130.2, 127.0, 35.0, 31.1, 21.0; HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{19}O$ $[M + H]^+$, 191.1430, found 191.1434.



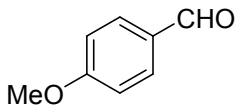
2-Methoxybenzaldehyd (9)[8]

Prepared according to the general procedure using 1-iodo-2-methoxybenzene (117.1 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:40) to afford the product **9** as a colorless oil (36.0 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.82 (dd, *J*=7.7, 1.9, 1H), 7.55 (m, 1H), 7.06 – 6.95 (m, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 162.0, 136.1, 128.7, 125.0, 120.8, 111.8, 55.7.



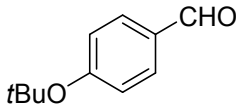
3-Methoxybenzaldehyde (10)[9]

Prepared according to the general procedure using 1-iodo-3-methoxybenzene (117.1 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:40) to afford the product **10** as a colorless oil (40.1 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.48 – 7.42 (m, 2H), 7.38 (s, 1H), 7.17 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 160.3, 138.0, 130.2, 123.6, 121.6, 112.2, 55.6.



4-Methoxybenzaldehyde (11)[10]

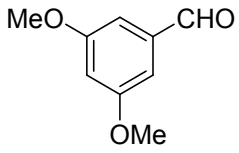
Prepared according to the general procedure using 1-iodo-4-methoxybenzene (117.1 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:40) to afford the product **11** as a colorless oil (X=I, 46.2 mg, 68% yield; X=Br, 31.3 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.89 – 7.78 (m, 2H), 7.06 – 6.94 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 164.8, 132.1, 130.1, 114.5, 55.7.



4-tert-Butyloxybenzaldehyde (12)[11]

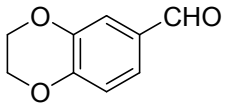
Prepared according to the general procedure using 4-tert-Butoxybromobenzene (114.5 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:50) to afford the product **12** as a colorless oil (53.4 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.80 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H), 1.44 (s, 9H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 191.2, 161.9, 131.4, 122.5, 80.1, 29.0; HR-ESI-MS (*m/z*): calcd. for $C_{11}H_{14}O_2Na$ $[M + Na]^+$, 201.0886, found 201.0888.



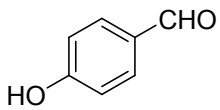
3,5-Dimethoxybenzaldehyde (13)[12]

Prepared according to the general procedure using 1-iodo-3,5-dimethoxybenzene (132.1 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:40) to afford the product **13** as a colorless oil (50.2 mg, 60% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.00 (d, *J* = 2.4 Hz, 2H), 6.69 (s, 1H), 3.83 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 161.4, 138.5, 107.3, 107.3, 55.7.



1,4-Benzodioxane-6-aldehyde (14)[13]

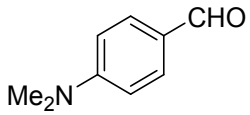
Prepared according to the general procedure using 6-iodo-2,3-dihydrobenzo[b][1,4]dioxine (131.1 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:10) to afford the product **14** as a colorless oil (52.0 mg, 63% yield). ^{1}H NMR (400 MHz,$CDCl_3$) δ 9.81 (s, 1H), 7.39 (m, *J* = 2.0 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 1H), 4.32 (d, *J* = 4.5 Hz, 2H), 4.29 (d, *J* = 4.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 149.4, 144.1, 130.8, 124.3, 118.5, 117.9, 64.8, 64.2; HR-ESI-MS (*m/z*): calcd. for $C_9H_9O_3$ $[M + H]^+$, 165.0546, found 165.0547.



4-Hydroxybenzaldehyde (15)[14]

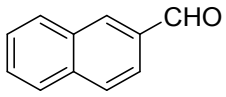
Prepared according to the general procedure using 1-Iodo-4-hydroxybenzene (110.0 mg, 0.5 mmol),

KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:3) to afford the product **15** as a colorless oil (25.2 mg, 41% yield). ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.85 (s, 1H), 9.40 (s, 1H), 7.80 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 206.30, 191.01, 163.86, 132.80, 130.47, 116.68.



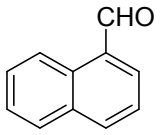
4-(Dimethylamino)benzaldehyde (16)[15]

Prepared according to the general procedure using 4-iodo-N,N-dimethylaniline (123.5 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 12 hours. temperature: -10 °C. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:20) to afford the product **16** as a colorless oil (36.5 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.73 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 3.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 154.5, 132.1, 125.3, 111.1, 40.2.



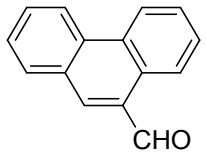
2-Naphthaldehyde (17)[16]

Prepared according to the general procedure using 2-iodonaphthalene (127.0 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:40) to afford the product **17** as a colorless oil (51.5 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.32 (s, 1H), 8.01 – 7.87 (m, 4H), 7.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 136.6, 134.6, 134.3, 132.8, 129.6, 129.2, 129.2, 128.2, 127.2, 122.9; HR-ESI-MS (*m/z*): calcd. for $C_{11}H_9O$ $[M + H]^+$, 157.0648, found 157.0650.



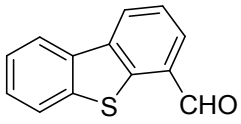
1-Naphthaldehyde (18)[17]

Prepared according to the general procedure using 1-iodonaphthalene (127.0 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:40) to afford the product **18** as a colorless oil (51.5 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 9.26 (d, *J* = 8.6 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 7.0 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.61 (dd, *J* = 16.8, 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.62, 136.75, 135.38, 133.83, 131.52, 130.64, 129.17, 128.58, 127.06, 124.98; HR-ESI-MS (*m/z*): calcd. for $C_{11}H_9O$ $[M + H]^+$, 157.0648, found 157.0652.



9-Phenanthrenecarboxaldehyde (19)

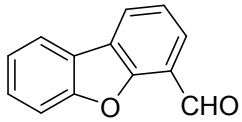
Prepared according to the general procedure using 9-Iodophenanthrene (152.0 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:40) to afford the product **19** as a colorless oil (64.9 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 9.37 (dd, *J* = 6.3, 3.3 Hz, 1H), 8.69 (dd, *J* = 12.9, 6.3 Hz, 2H), 8.24 (s, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.73 (dd, *J* = 6.2, 3.4 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.71, 141.35, 133.12, 130.78, 130.64, 130.50, 130.35, 130.27, 128.40, 128.36, 127.76, 127.42, 126.09, 123.05, 122.86; HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{11}O$ $[M + H]^+$, 207.0804, found 207.0806; for $C_{15}H_{10}NaO$ $[M + Na]^+$, 229.0624, found 229.0619.



Dibenzothiophene-4-carbaldehyde (20)[18]

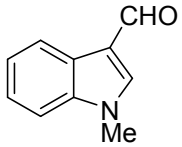
Prepared according to the general procedure using 4-Iododibenzothiophene (155.0 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl

acetate/petroleum ether 1:40) to afford the product **20** as a colorless oil (72.0 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 8.37 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 6.8 Hz, 1H), 7.94 (d, *J* = 7.4 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.57 – 7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.37, 141.72, 138.24, 137.41, 133.63, 132.98, 130.75, 127.50, 127.03, 124.89, 124.47, 123.12, 121.60; HR-ESI-MS (*m/z*): calcd. for $C_{13}H_9OS$ $[M + H]^+$, 213.0369, found 213.0369.



4-Dibenzofurancarboxaldehyde (21)[19]

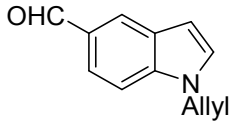
Prepared according to the general procedure using 4-Iododibenzofuran (147.0 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:50) to afford the product **21** as a colorless oil (59.2 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 8.17 (d, *J* = 7.6 Hz, 1H), 7.96 (dd, *J* = 11.8, 7.7 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.55, 156.73, 156.04, 128.24, 127.58, 126.77, 126.14, 123.65, 123.04, 122.94, 121.39, 120.92, 112.28; HR-ESI-MS (*m/z*): calcd. for $C_{13}H_9O_2$ $[M + H]^+$, 197.0597, found 197.0602; for $C_{13}H_8NaO_2$ $[M + Na]^+$, 219.0417, found 219.0417.



1-Methylindole-3-carbaldehyde (22)[20]

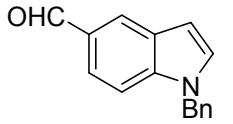
Prepared according to the general procedure using 3-iodo-1-methyl-1H-indole (128.5 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:15) to afford the product **22** as a colorless oil (48.5 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.35 – 8.24 (m, 1H), 7.57 (t, *J* = 3.6 Hz, 1H), 7.31 (dd, *J* = 4.4, 2.1

Hz, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4, 139.4, 137.9, 125.2, 124.0, 122.9, 122.0, 118.0, 109.9, 33.6; HR-ESI-MS (*m/z*): calcd. for $C_{10}H_{10}NO$ $[M + H]^+$, 160.0757, found 160.0756.



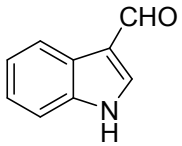
1-Allyl-1H-indole-5-carbaldehyde (23)

Prepared according to the general procedure using 1-allyl-5-iodo-1H-indole (141.5 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:10) to afford the product **23** as a colorless oil (51.8 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.16 (s, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.19 (d, *J* = 3.2 Hz, 1H), 6.68 (d, *J* = 3.2 Hz, 1H), 6.00 (m, 1H), 5.24 (d, *J* = 10.3 Hz, 1H), 5.08 (d, *J* = 17.0 Hz, 1H), 4.77 (d, *J* = 5.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 139.5, 132.8, 129.9, 129.6, 128.6, 126.6, 122.0, 118.0, 110.3, 103.8, 49.2; HR-ESI-MS (*m/z*): calcd. for $C_{12}H_{12}NO$ $[M + H]^+$, 186.0913, found 186.0916.



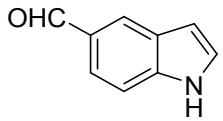
1-Benzylindole-5-carboxaldehyde (24)[21]

Prepared according to the general procedure using 1-benzyl-5-iodo-1H-indole (166.5 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:10) to afford the product **24** as a colorless oil (61.1 mg, 52% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.03 (s, 1H), 8.18 (s, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 3H), 7.23 (d, *J* = 3.2 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.72 (d, *J* = 3.2 Hz, 1H), 5.36 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 139.7, 136.7, 130.3, 129.7, 129.1, 128.6, 128.1, 126.9, 126.6, 122.2, 110.4, 104.0, 50.5; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{13}NONa$ $[M + Na]^+$, 258.0889, found 258.0888.



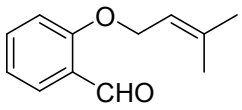
Indole-3-carboxaldehyde (25)[22]

Prepared according to the general procedure using 3-iodo-1H-indole (121.5 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 12 hours. temperature: -10 °C. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:2) to afford the product **25** as a colorless oil (38.2 mg, 53% yield). ^{1}H NMR (400 MHz, DMSO-d6) δ 12.16 (s, 1H), 9.94 (s, 1H), 8.29 (s, 1H), 8.10 (d, J = 7.5 Hz, 1H), 7.59 – 7.43 (m, 1H), 7.24 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d6) δ 185.0, 138.5, 137.1, 124.2, 123.5, 122.2, 120.9, 118.2, 112.5.



1H-Indole-5-carboxaldehyde (26)[23]

Prepared according to the general procedure using 5-iodo-1H-indole (121.5 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 12 hours. temperature: -10 °C. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:4) to afford the product **26** as a colorless oil (36.2 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.81 (s, 1H), 8.19 (s, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 8.5 Hz, 1H), 7.33 (s, 1H), 6.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 139.5, 129.8, 127.9, 126.5, 126.3, 122.4, 111.9, 104.6.



2-(3-Methylbut-2-enoxy)benzaldehyde (28)[24]

Prepared according to the general procedure using 1-Iodo-2-(prenyloxy)benzene **27** (144.0 mg, 0.5 mmol), KOMe (42.1 mg, 0.6 mmol), $Mg(OTf)_2$ (8.0 mg, 0.05 eq), TMS-TMS (122.8 μL, 0.6 mmol), and DMF (2.0 mL). Time of reaction: 4 hours. The crude mixture was purified by silica gel chromatography

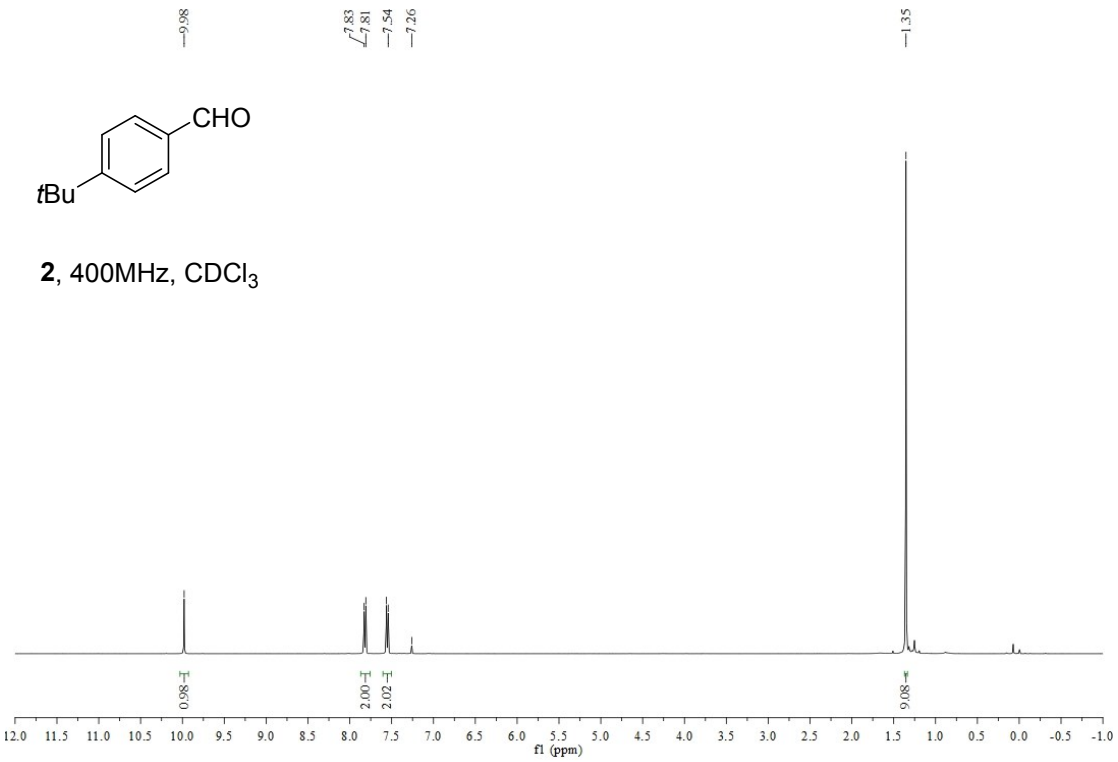
(ethyl acetate/petroleum ether 1:150) to afford the product **28** as a colorless oil (59.8 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 7.83 (d, *J* = 6.6 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.05 – 6.95 (m, 2H), 5.50 (t, *J* = 6.5 Hz, 1H), 4.63 (d, *J* = 6.6 Hz, 2H), 1.80 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.11, 161.51, 138.83, 135.90, 128.43, 125.34, 120.70, 119.14, 113.13, 65.64, 25.88, 18.41; HR-ESI-MS (*m/z*): calcd. for $C_{12}H_{14}O_2Na$ $[M + Na]^+$, 213.0886, found 213.0883.

6. References:

1. M. Ahmad, A.-C. Gaumont, M. Durandetti and J. Maddaluno, Direct Syn Addition of Two Silicon Atoms to a C≡C Triple Bond by Si−Si Bond Activation: Access to Reactive Disilylated Olefins, *Angew. Chem. Int. Ed.*, 2017, **56**, 2464.
2. K. Lee and R. E. Maleczka, Pd(0)-Catalyzed PMHS Reductions of Aromatic Acid Chlorides to Aldehydes, *Org. Lett.*, 2006, **8**, 1887.
3. N. Jiang and A. J. Ragauskas, Copper(II)-Catalyzed Aerobic Oxidation of Primary Alcohols to Aldehydes in Ionic Liquid [bmpy]PF6, *Org. Lett.*, 2005, **7**, 3689.
4. A. Schmidt, T. Habeck, B. Snovydovych and W. Eisfeld, Addition Reactions and Redox Esterifications of Carbonyl Compounds by N-Heterocyclic Carbenes of Indazole, *Org. Lett.*, 2007, **9**, 3515.
5. C. Han and S. L. Buchwald, Negishi Coupling of Secondary Alkylzinc Halides with Aryl Bromides and Chlorides, *J. Am. Chem. Soc.*, 2009, **131**, 7532.
6. R. Hilgraf and A. Pfaltz, Chiral Bis(N-sulfonylamino)phosphine- and TADDOL-Phosphite-Oxazoline Ligands: Synthesis and Application in Asymmetric Catalysis, *Adv. Synth. Catal.*, 2005, **347**, 61.
7. M. Tashiro and T. Yamato, Metacyclophanes and related compounds. 8. Preparation and reactions of 8,16-diformyl[2.2]metacyclophanes, *J. Org. Chem.*, 1983, **48**, 1461.
8. M. Maddani and K. R. Prabhu, A chemoselective aerobic oxidation of benzylic azides catalyzed by molybdenum xanthate in an aqueous medium, *Tetrahedron Lett.*, 2008, **49**, 4526.
9. M. Dabrowski, P. Kurach, S. Lulinski and J. Serwatowski, An ortho-lithiated derivative of protected phenylboronic acid: an approach to ortho-functionalized arylboronic acids and 1,3-dihydro-1-hydroxybenzo[c][2,1]oxaboroles, *Appl. Organomet. Chem.*, 2007, **21**, 234.
10. S. Velusamy, M. Ahamed and T. Punniyamurthy, Novel Polyaniline-Supported Molybdenum-Catalyzed Aerobic Oxidation of Alcohols to Aldehydes and Ketones, *Org. Lett.*, 2004, **6**, 4821.
11. M. Paventi and A. S. Hay, Synthesis, structure and stability of E/Z-isomers of novel conjugated enamines prepared from 9-arylmethyl- or 9-arylpropenyl-9H-carbazole with arylmethyleneanilines, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1059.
12. A. Takada, Y. Hashimoto, H. Takikawa, K. Hikita and K. Suzuki, Total Synthesis and Absolute Stereochemistry of Seragakinone A, *Angew. Chem., Int. Ed.*, 2011, **50**, 2297.
13. C. Huang, Y. Li, Y. Song, Y. Li, H. Liu and D. Zhu, Ordered Nanosphere Alignment of Porphyrin for the Improvement of Nonlinear Optical Properties, *Adv. Mater. (Weinheim, Ger.)*, 2010, **22**, 3532.
14. H. Kim, J. Ralph, F. Lu, S. A. Ralph, A.-M. Boudet, J. J. MacKay, R. R. Sederoff, T. Ito, S. Kawai, H. Ohashi and T. Higuchi, NMR analysis of lignins in CAD-deficient plants. Part 1. Incorporation of hydroxycinnamaldehydes and hydroxybenzaldehydes into lignins, *Org. Biomol. Chem.*, 2003, **1**, 268.
15. B. Jiang, S.-J. Tu, P. Kaur, W. Wever and G. Li, Four-Component Domino Reaction Leading to Multifunctionalized Quinazolines, *J. Am. Chem. Soc.*, 2009, **131**, 11660.
16. B. Guan, D. Xing, G. Cai, X. Wan, N. Yu, Z. Fang, L. Yang and Z. Shi, Highly Selective Aerobic Oxidation of Alcohol Catalyzed by a Gold(I) Complex with an Anionic Ligand, *J. Am. Chem. Soc.*, 2005, **127**, 18004.
17. K. Lee and R. E. Maleczka, Jr., Pd(0)-Catalyzed PMHS reductions of aromatic acid chlorides to aldehydes, *Org. Lett.*, 2006, **8**, 1887.

18. L. V. Dunkerton, B. C. Barot and A. Nigam, Synthesis of multisulfur containing substituted dibenzothiophenes, *J. Heterocycl. Chem.*, 1987, **24**, 749.
19. N. Lakshminarayana, Y. R. Prasad, L. Gharat, A. Thomas, S. Narayanan, A. Raghuram, C. V. Srinivasan and B. Gopalan, Synthesis and evaluation of some novel dibenzo[b,d]furan carboxylic acids as potential anti-diabetic agents, *Eur. J. Med. Chem.*, 2010, **45**, 3709.
20. T. Kurihara, T. Fujimoto, S. Harusawa and R. Yoneda, Simple N-alkylation and N-acylation of 3-acetylindole and 3-indolecarboxaldehyde, *Synthesis*, 1987, DOI: 10.1055/s-1987-27960, 396.
21. L. Poszavacz, G. Simig, J. Fetter and F. Bertha, New synthesis of naratriptan, *Heterocycles*, 2006, **68**, 713.
22. N. Duarte and M.-J. U. Ferreira, Lagaspholones A and B: Two New Jatropholane-Type Diterpenes from Euphorbia lagascae, *Org. Lett.*, 2007, **9**, 489.
23. J. Fetter, F. Bertha, L. Poszavacz and G. Simig, New practical synthesis of 5-formylindole, *J. Heterocycl. Chem.*, 2005, **42**, 137.
24. E. Tyrrell, K. H. Tesfa, J. Millet and C. Muller, Enantioselective alkynylation reactions to aldehydes: the effects of aromatic substituents upon the enantioselectivity, *Synthesis*, 2006, 3099.

7. ^{1}H-NMR and ^{13}C-NMR Spectral Data



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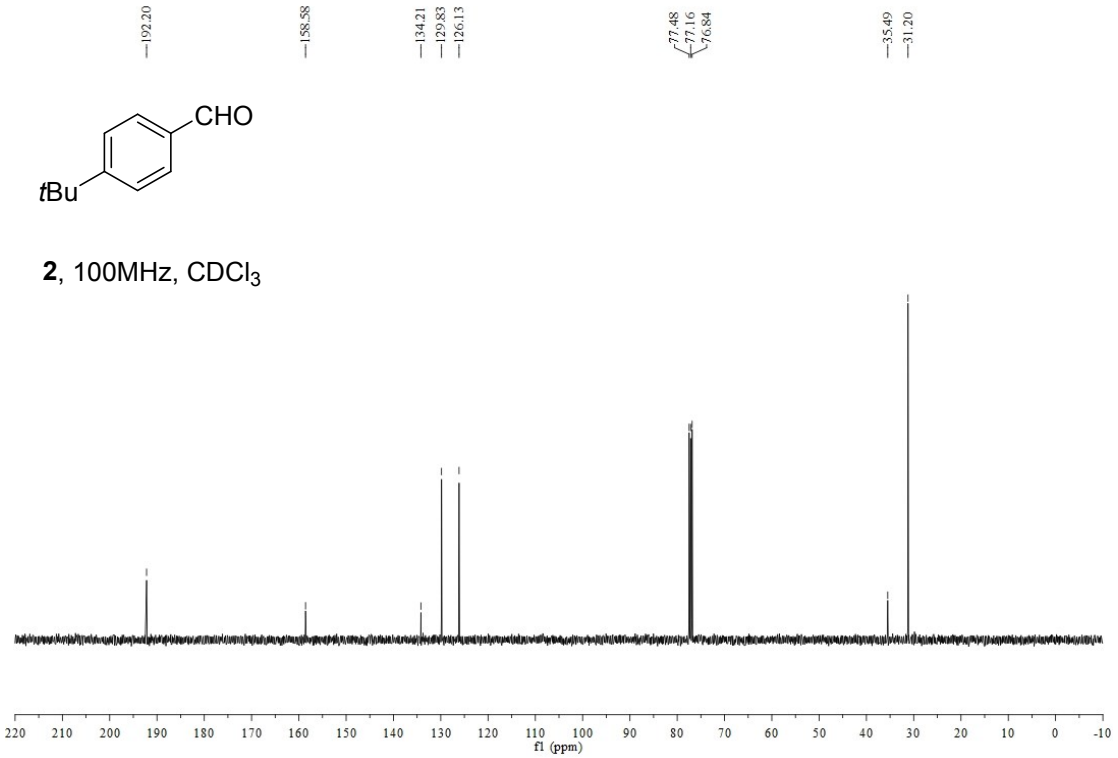

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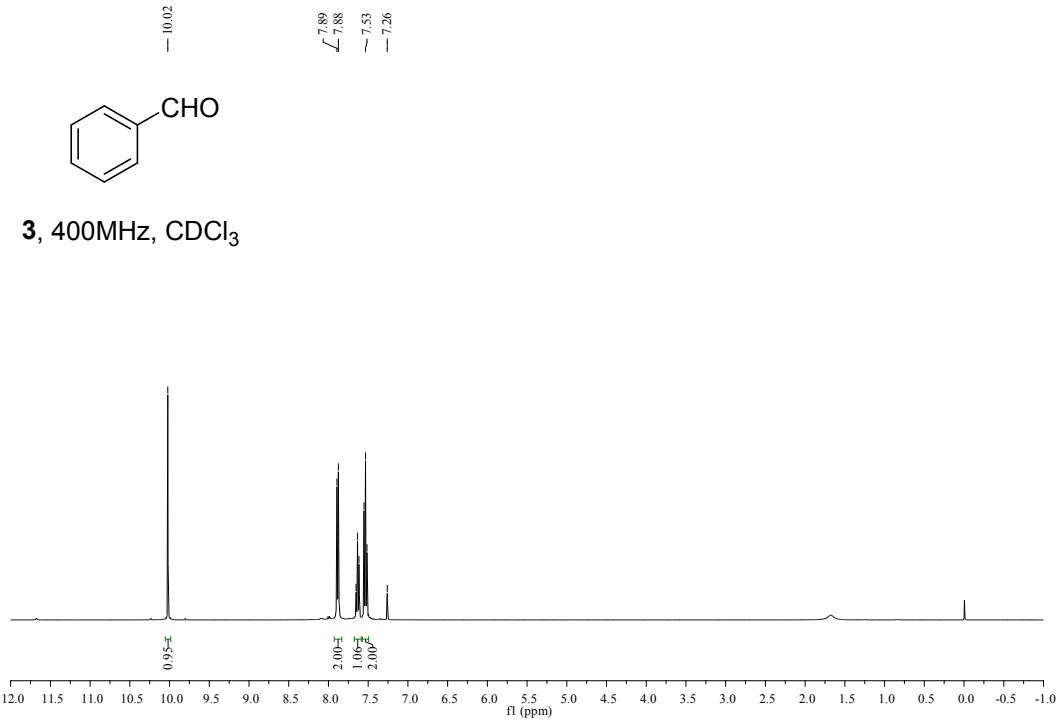

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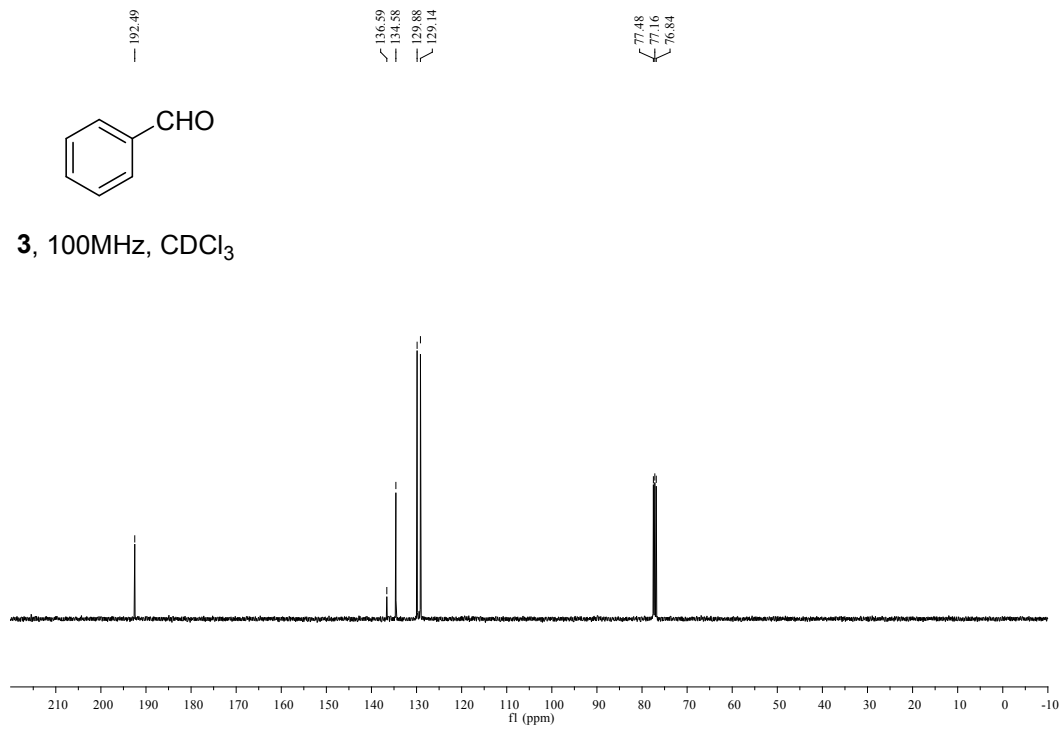
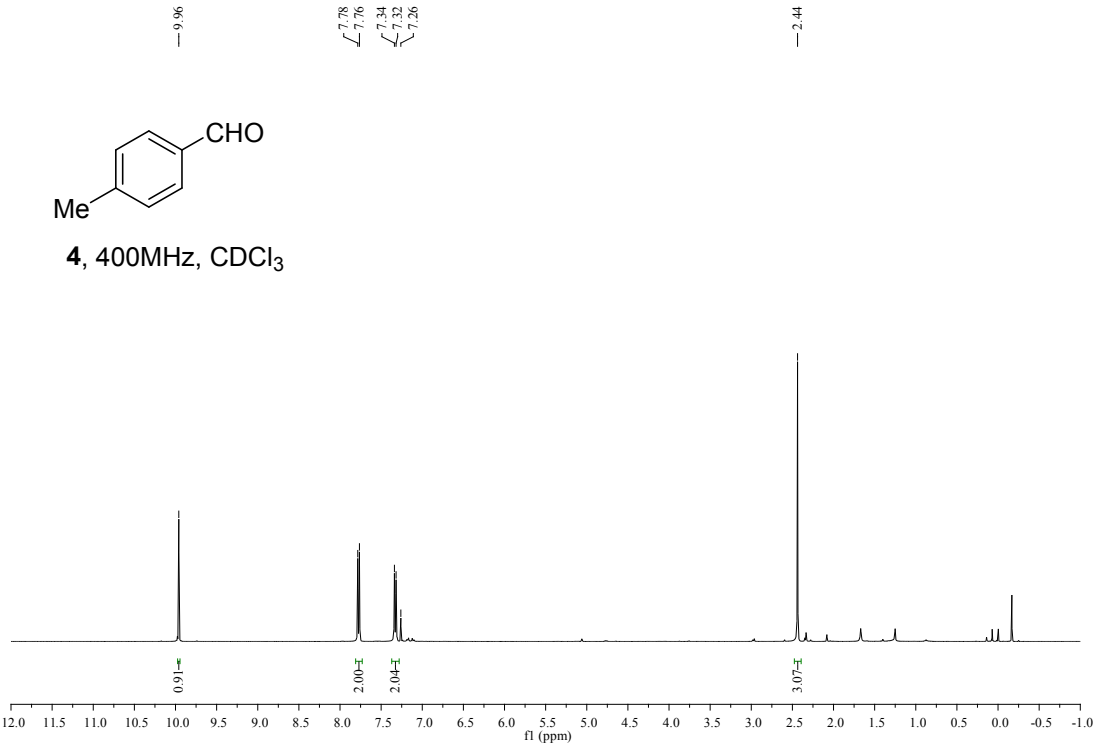
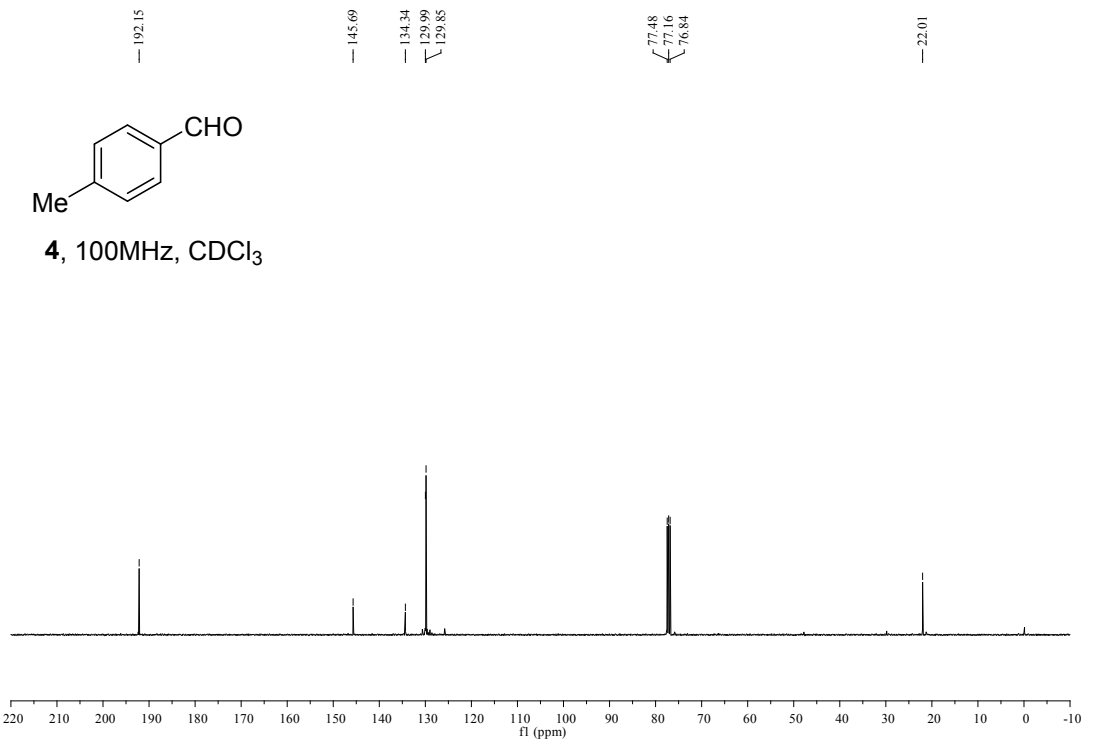


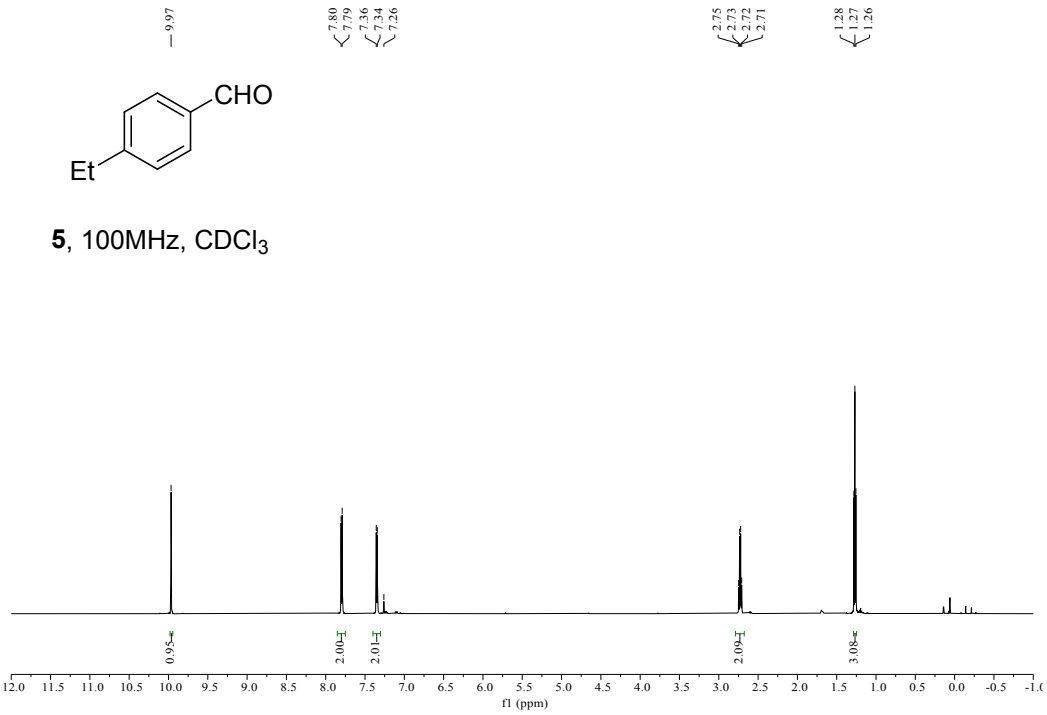
3, 100MHz, $CDCl_3$



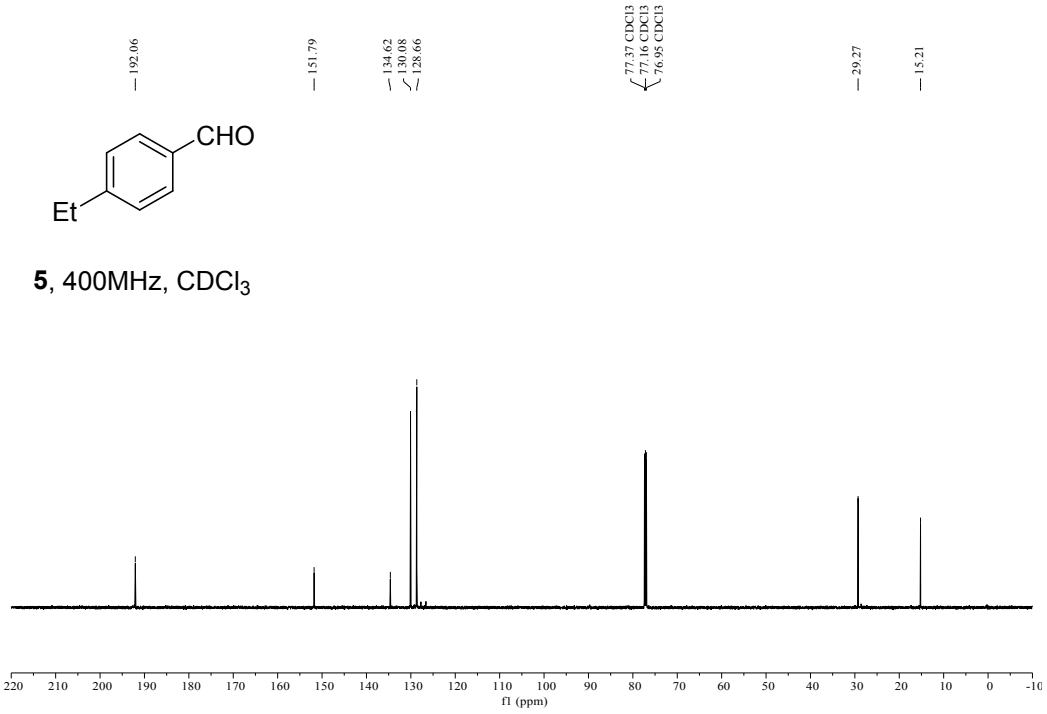
4, 400MHz, $CDCl_3$



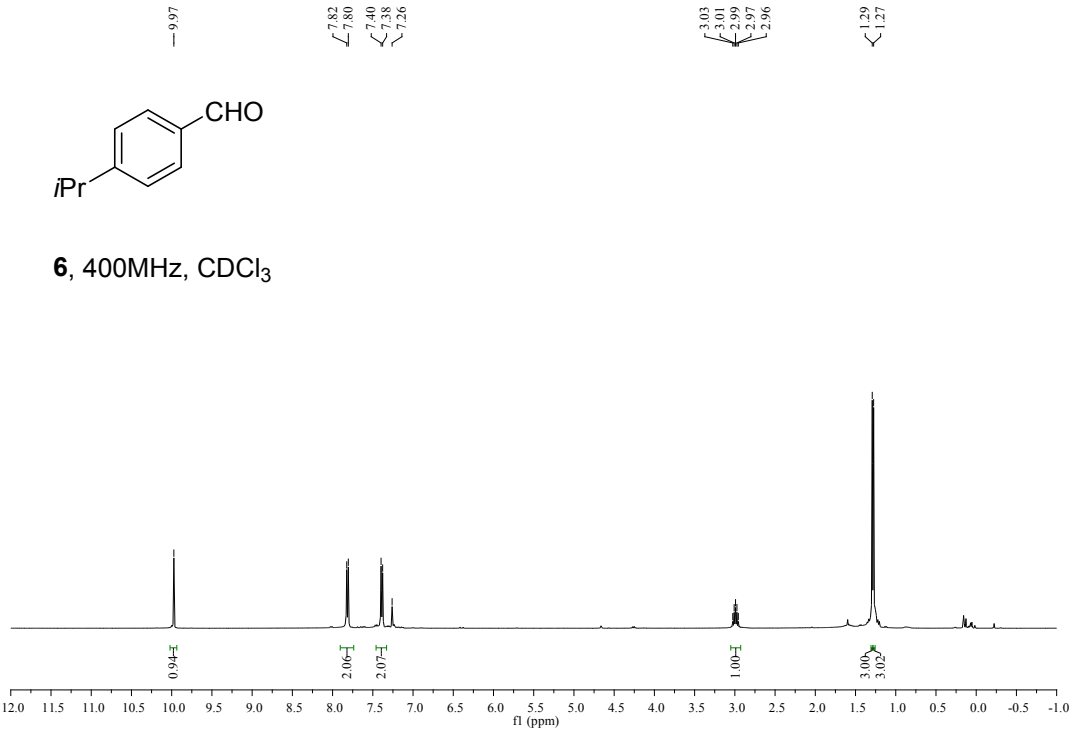
4, 100MHz, $CDCl_3$



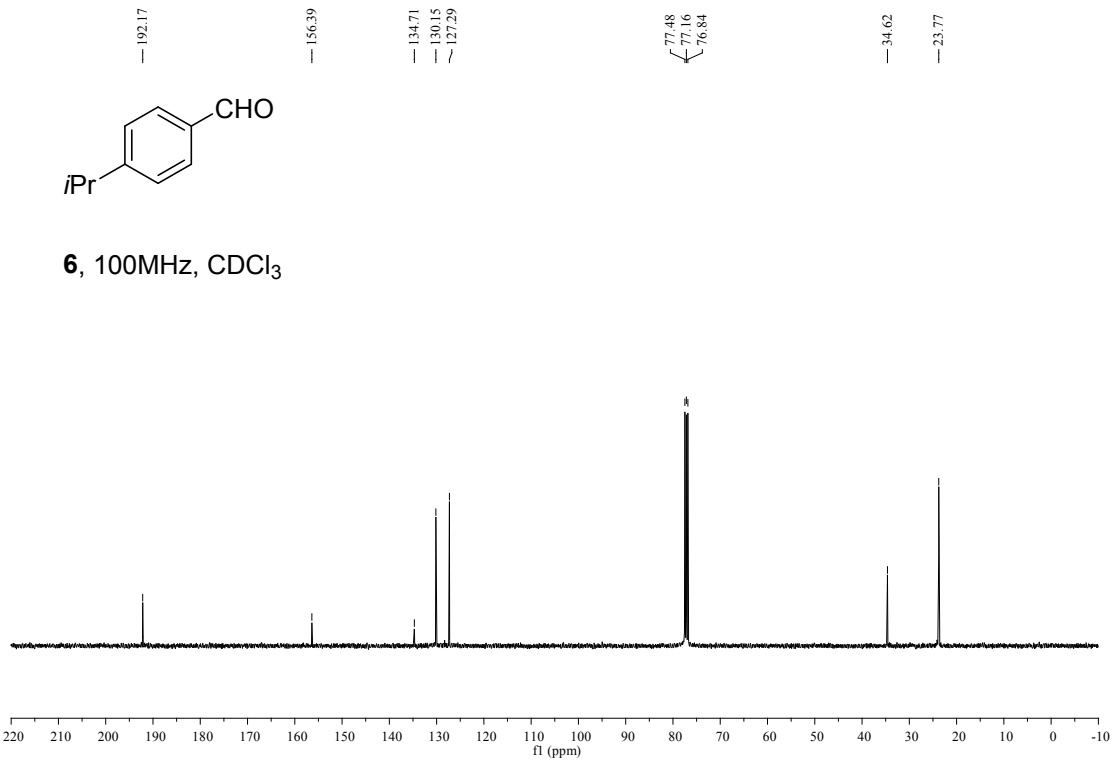
5, 100MHz, $CDCl_3$



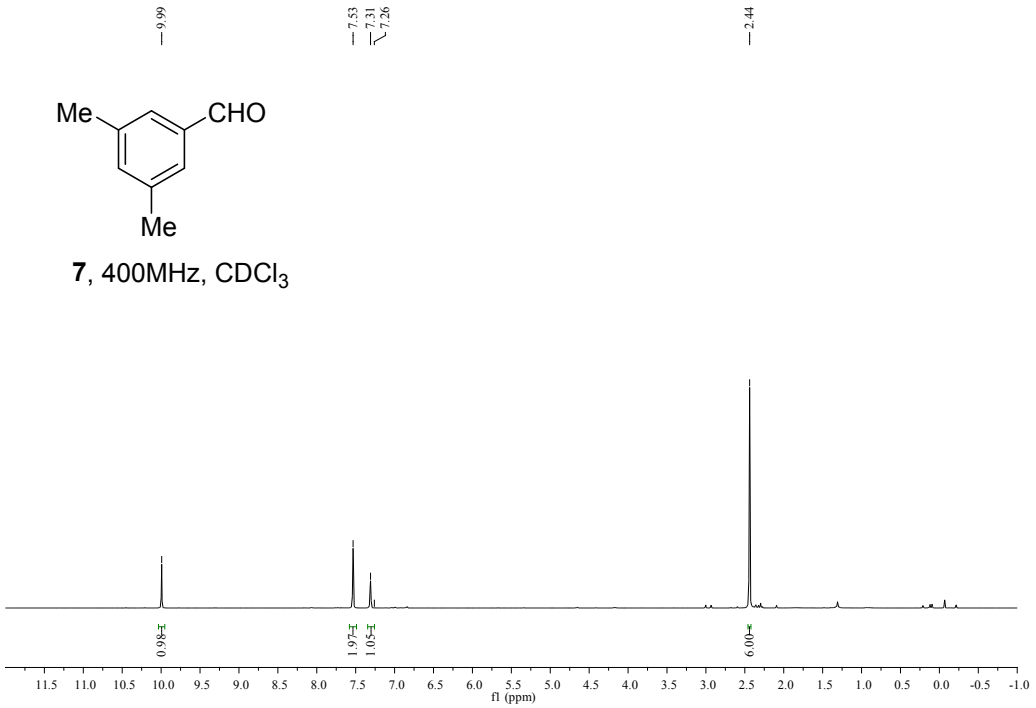
5, 400MHz, $CDCl_3$



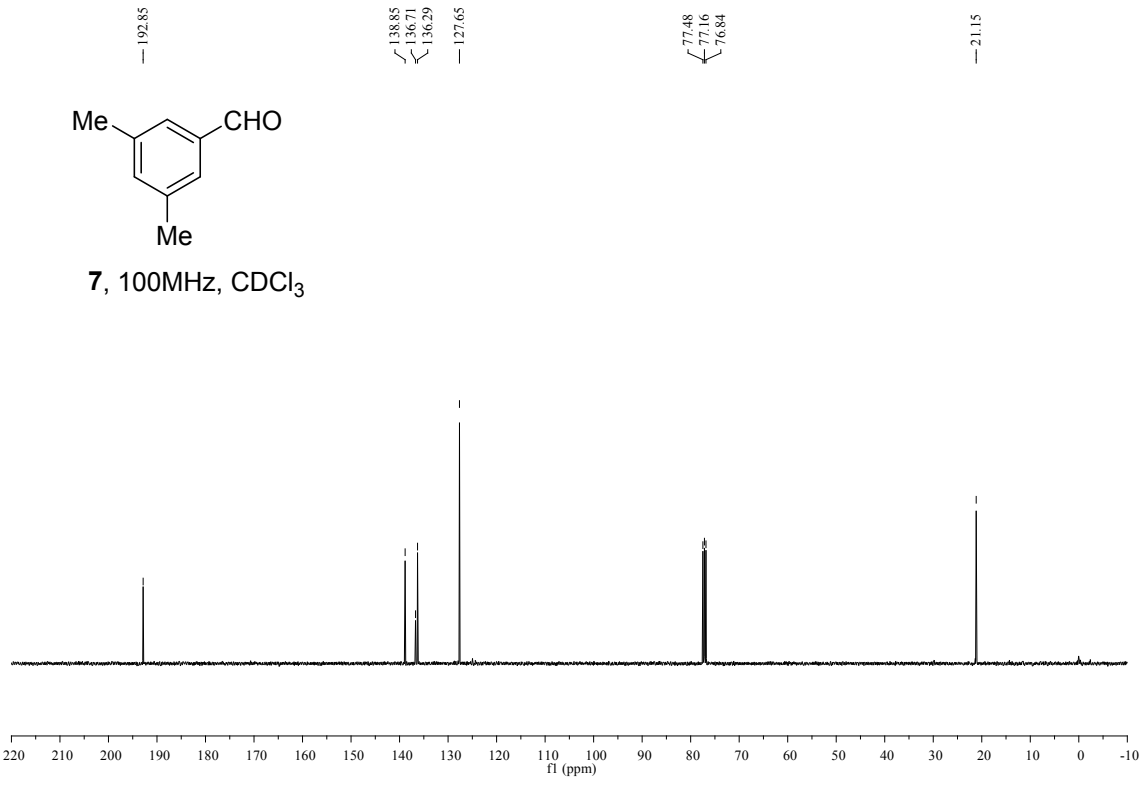
6, 400MHz, $CDCl_3$



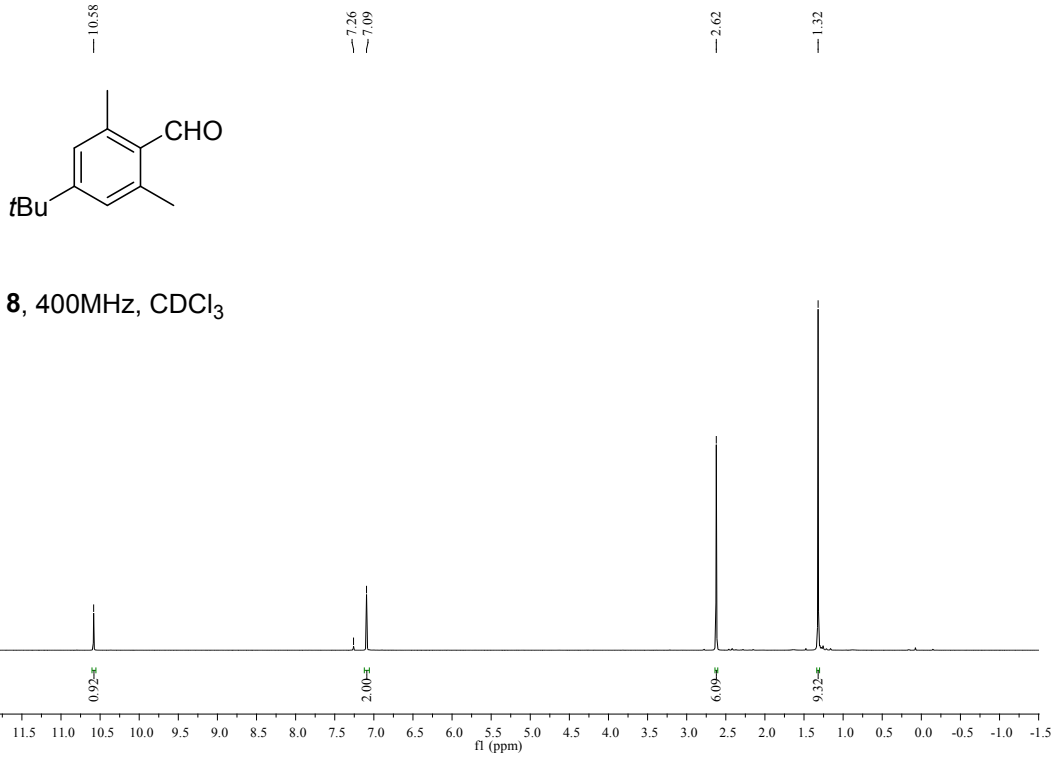
6, 100MHz, $CDCl_3$



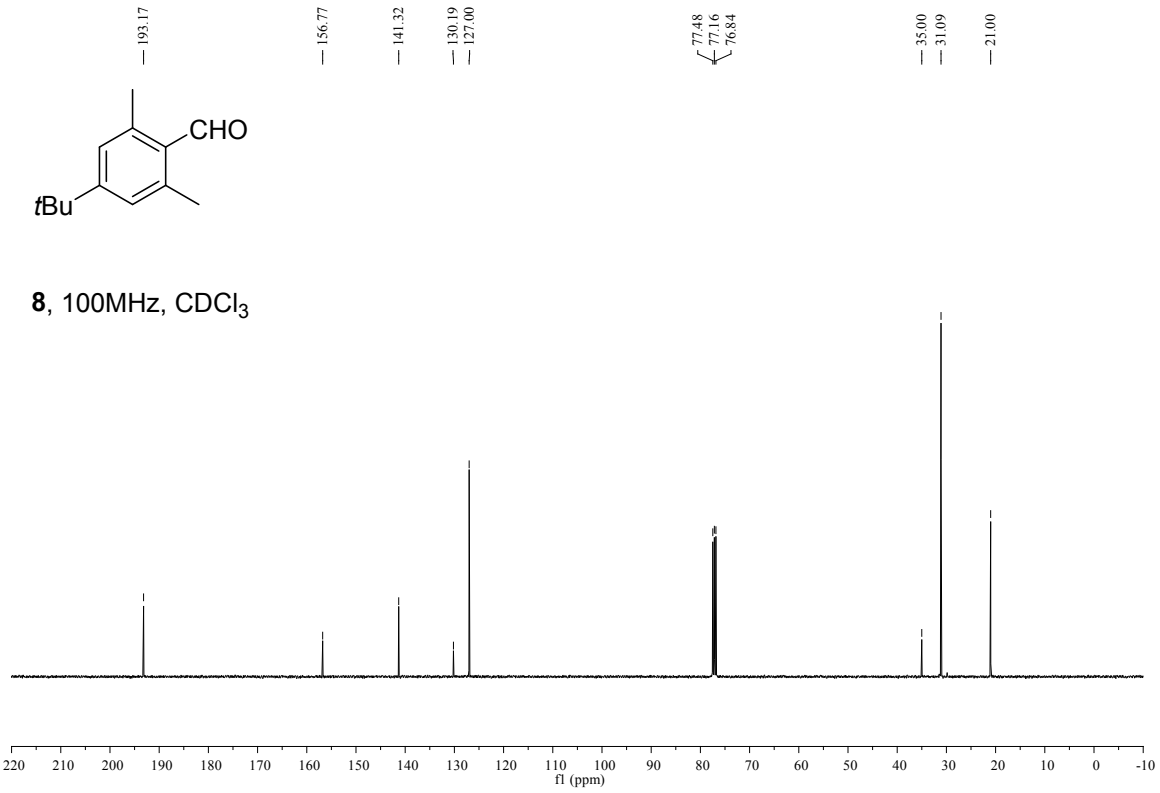
7, 400MHz, $CDCl_3$



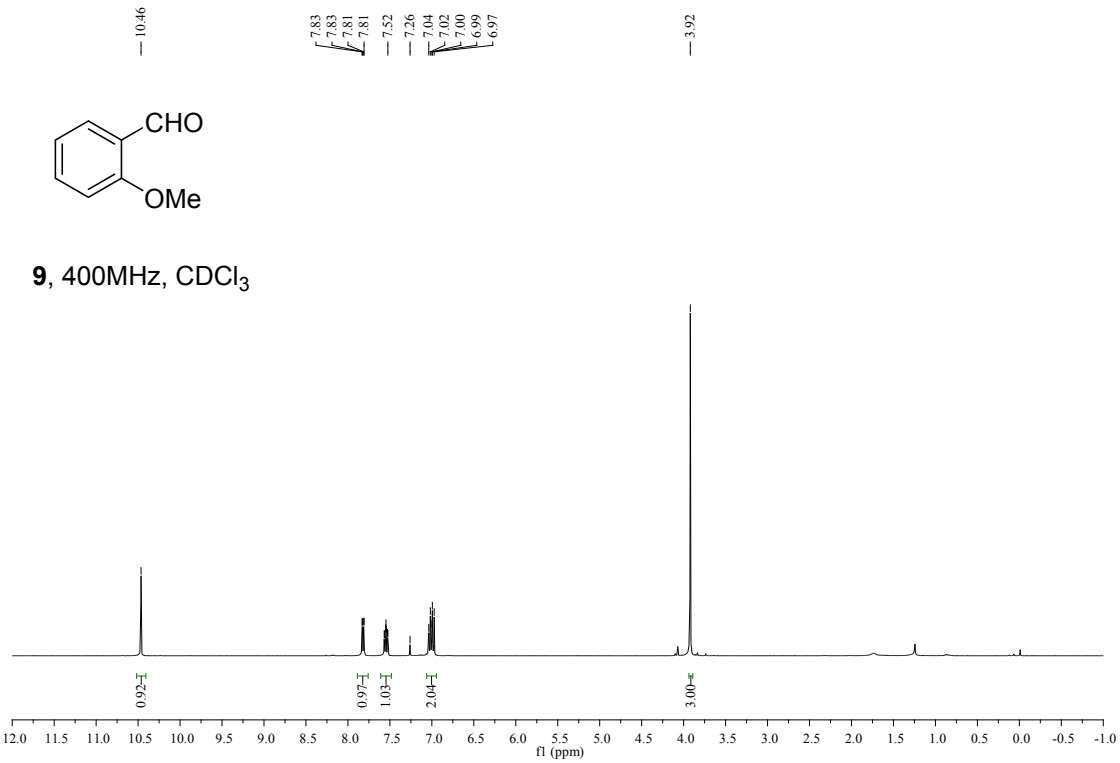
7, 100MHz, $CDCl_3$



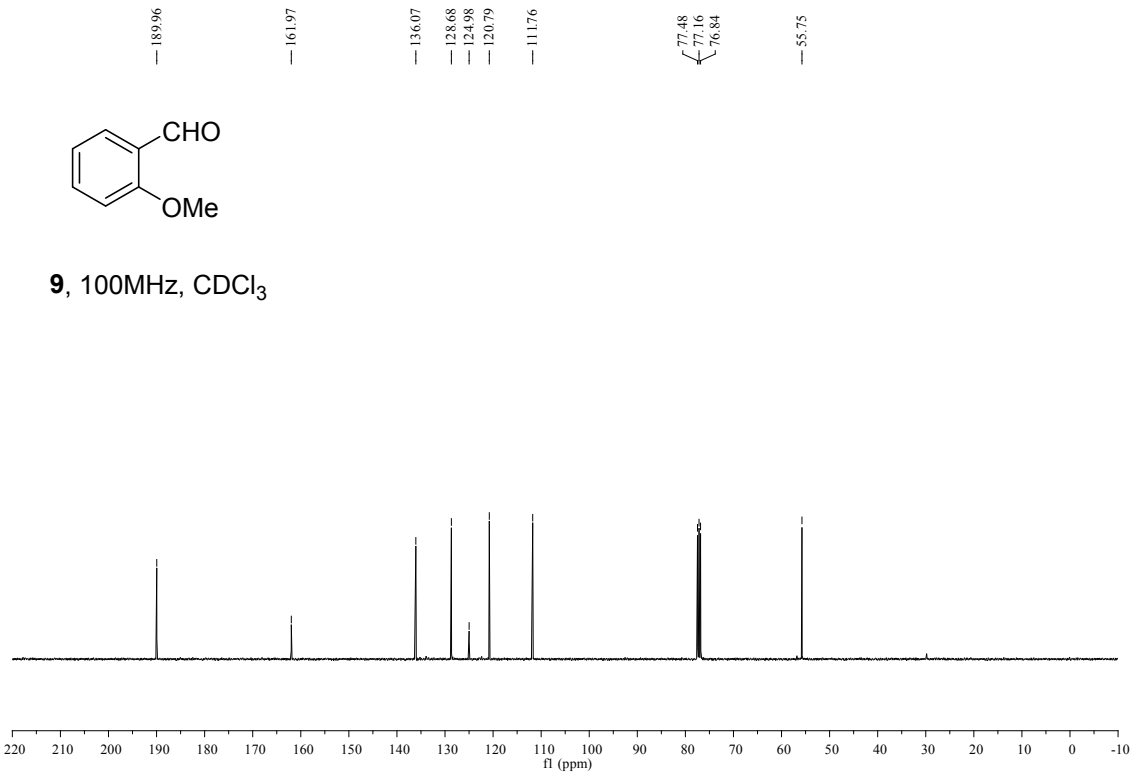
8, 400MHz, $CDCl_3$



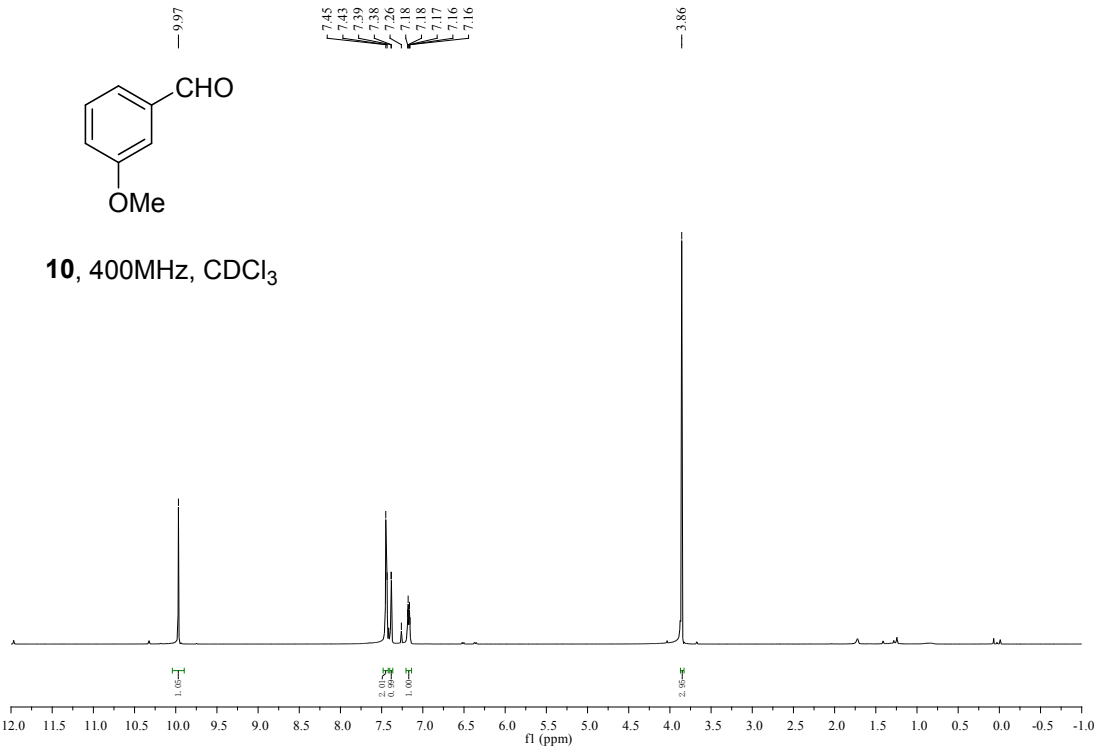
8, 100MHz, $CDCl_3$



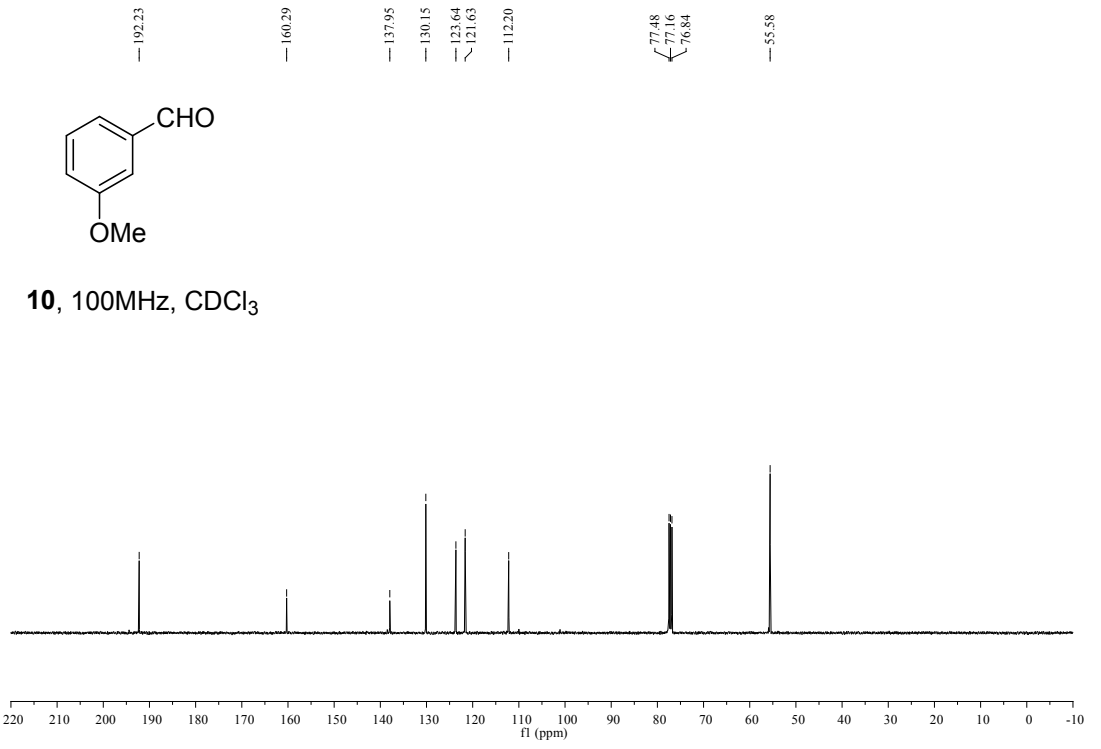
9, 400MHz, $CDCl_3$



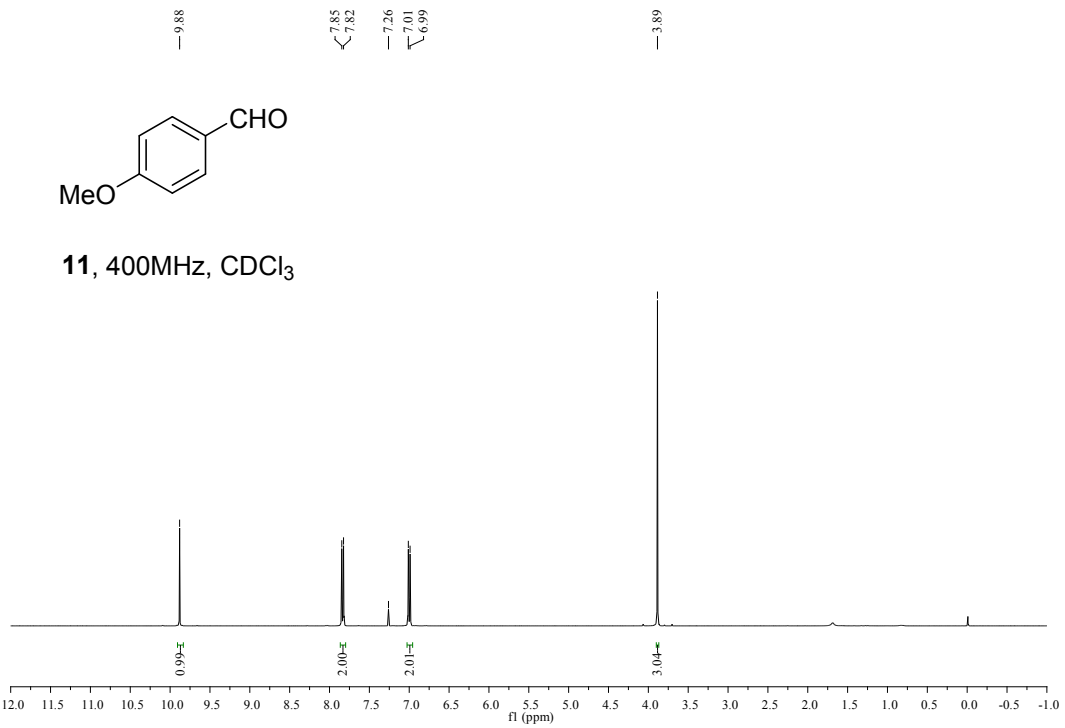
9, 100MHz, $CDCl_3$



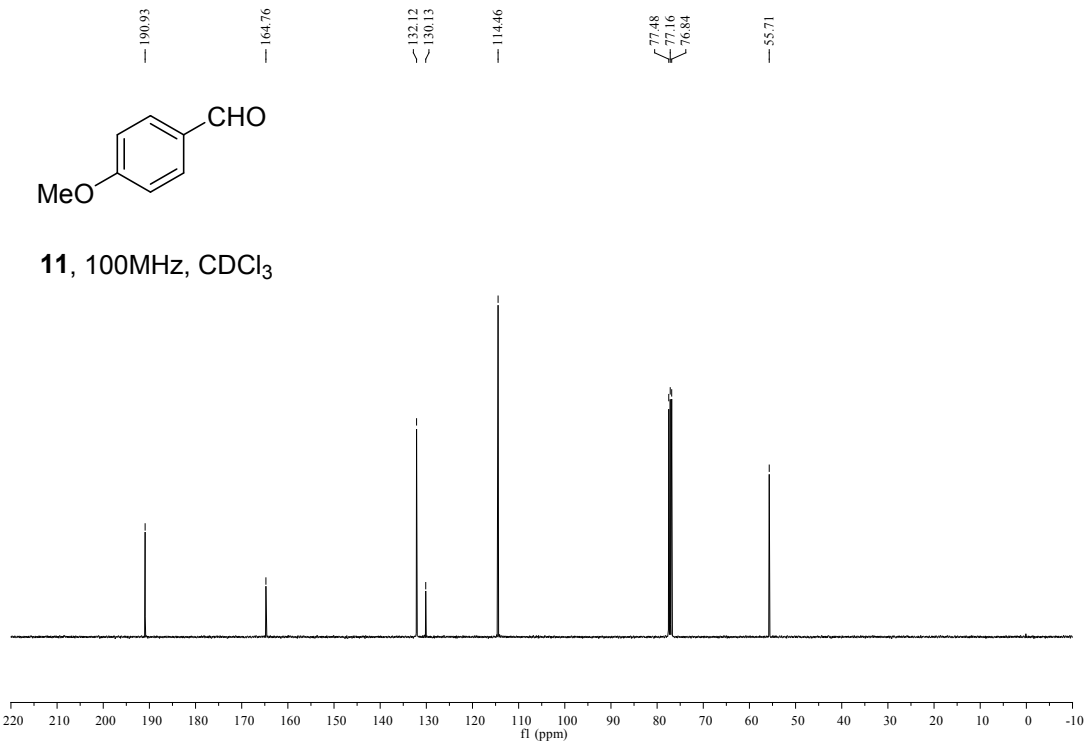
10, 400MHz, $CDCl_3$



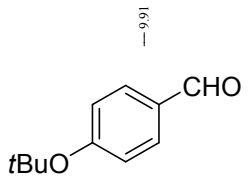
10, 100MHz, $CDCl_3$



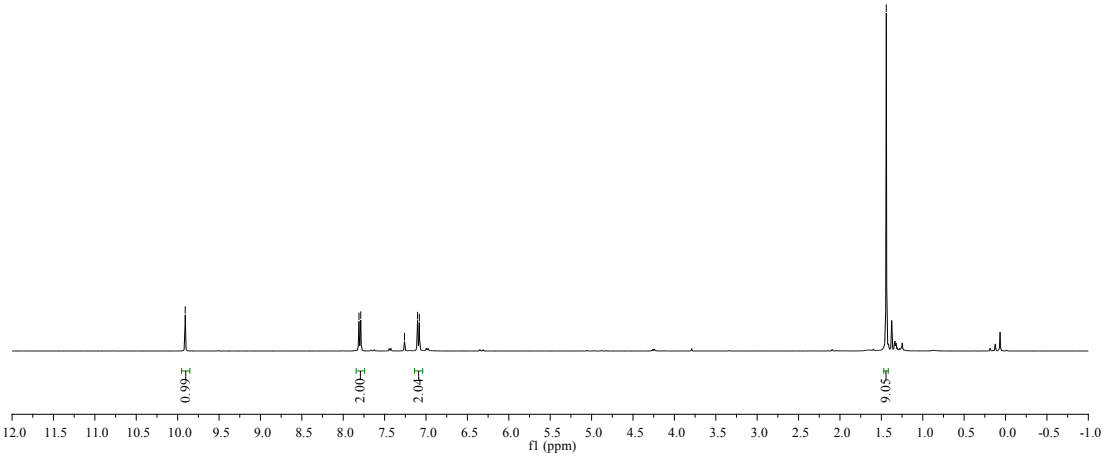
11, 400MHz, $CDCl_3$

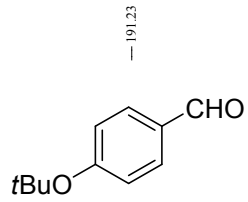


11, 100MHz, $CDCl_3$

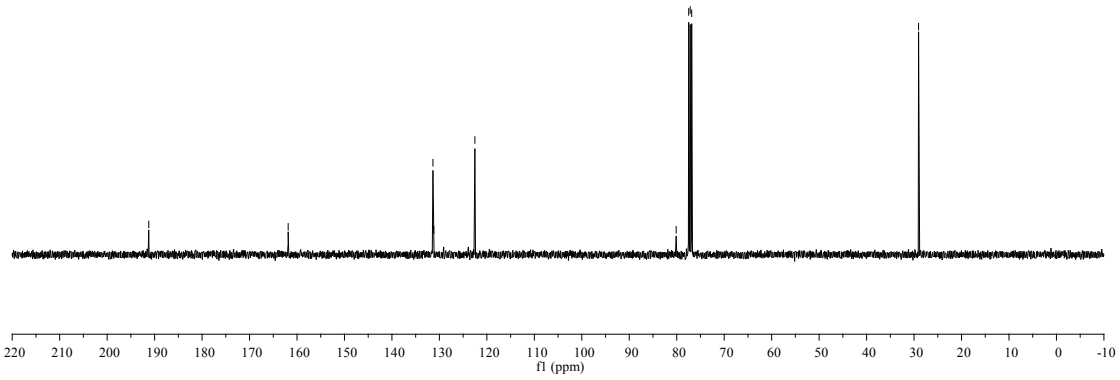


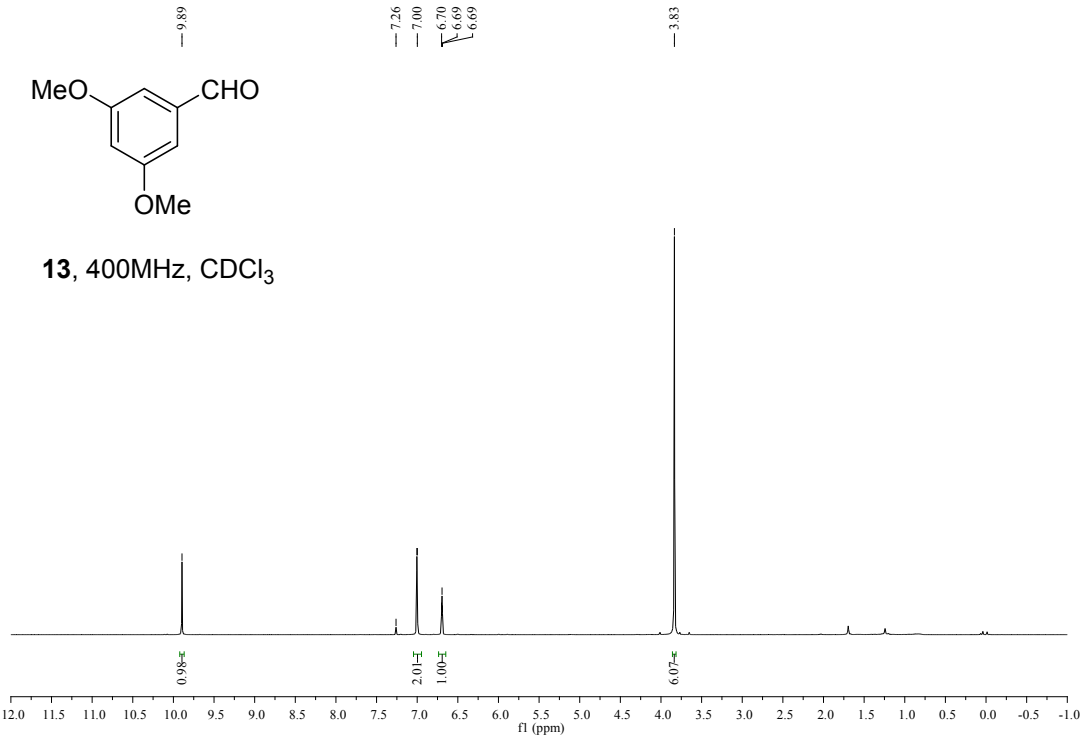
12, 400MHz, $CDCl_3$



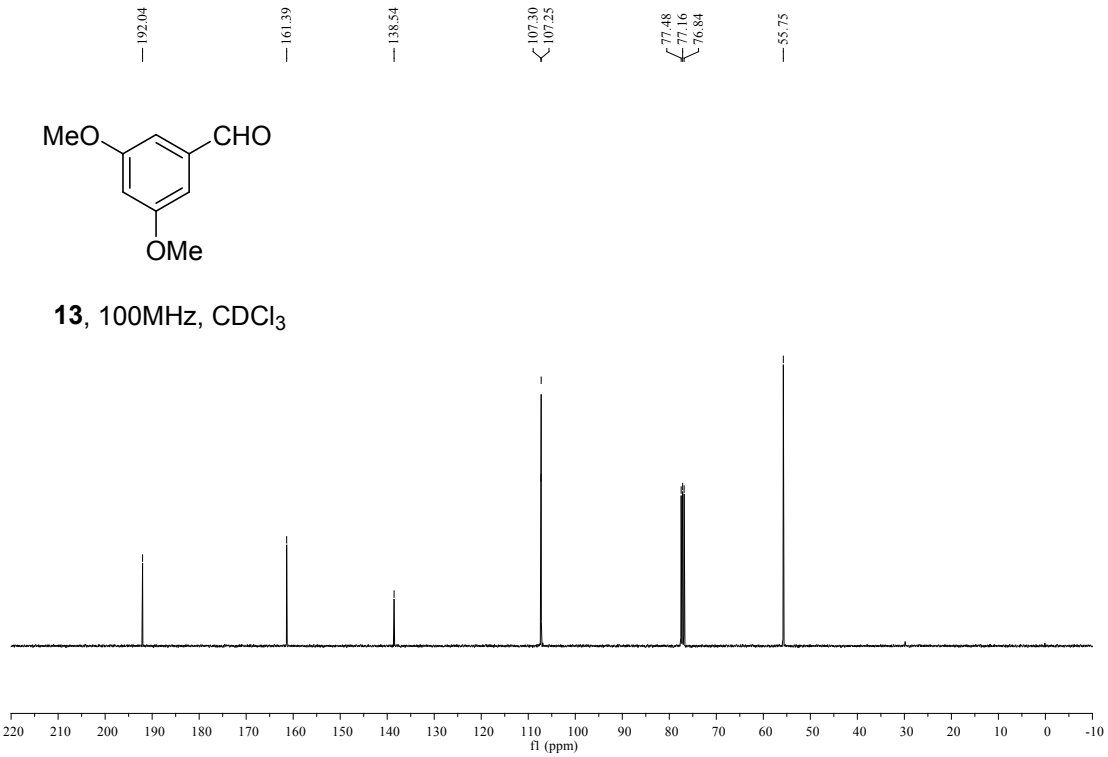


12, 100MHz, $CDCl_3$

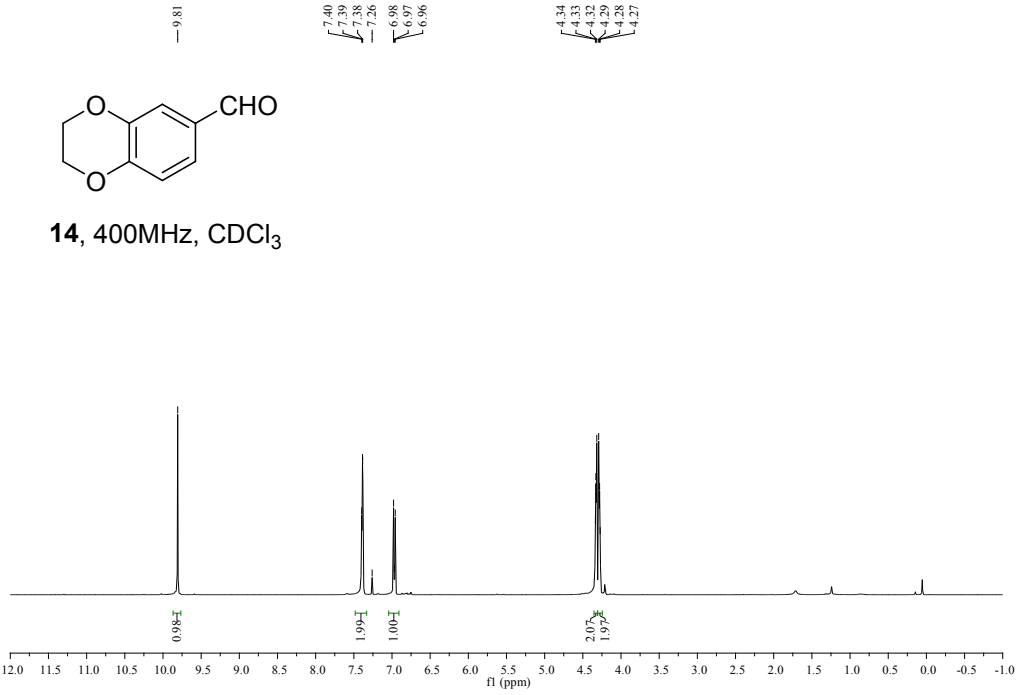




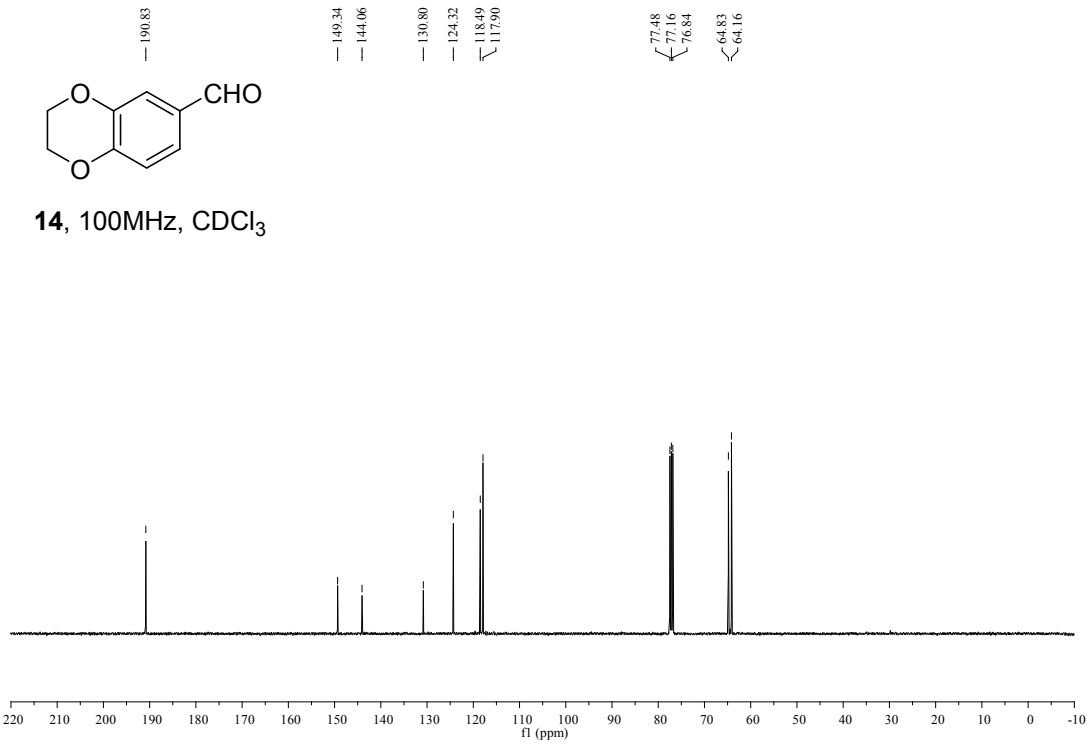
13, 400MHz, $CDCl_3$



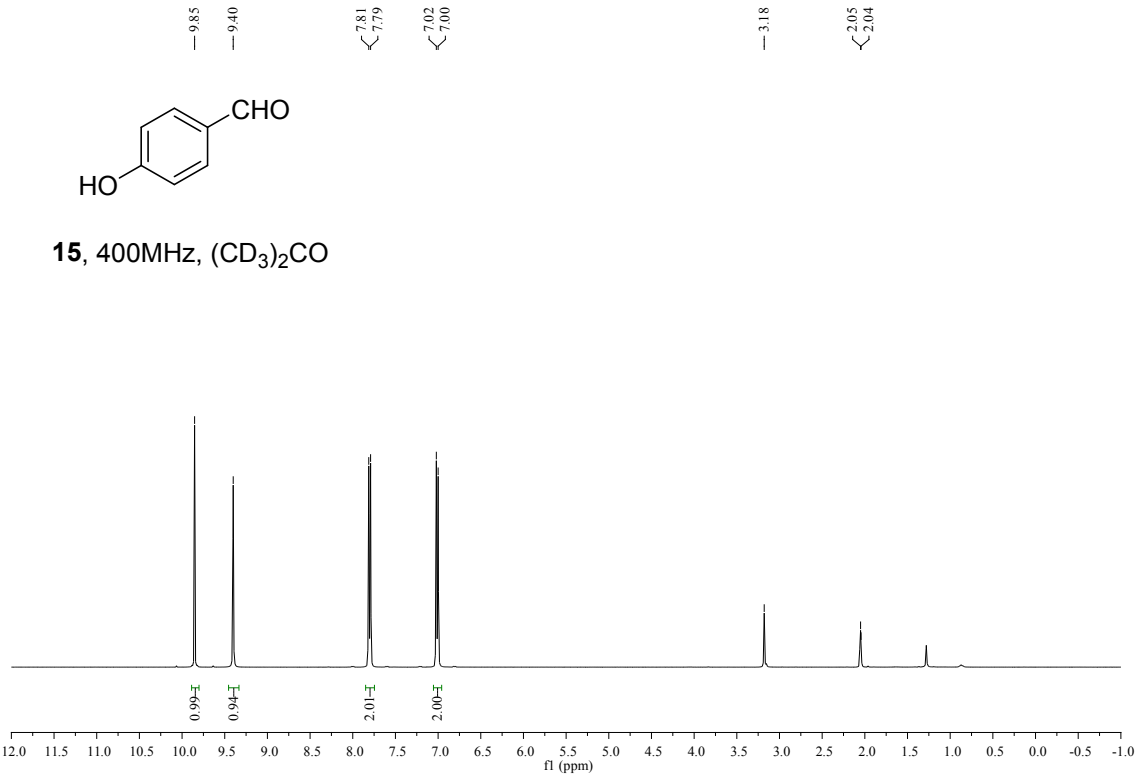
13, 100MHz, $CDCl_3$



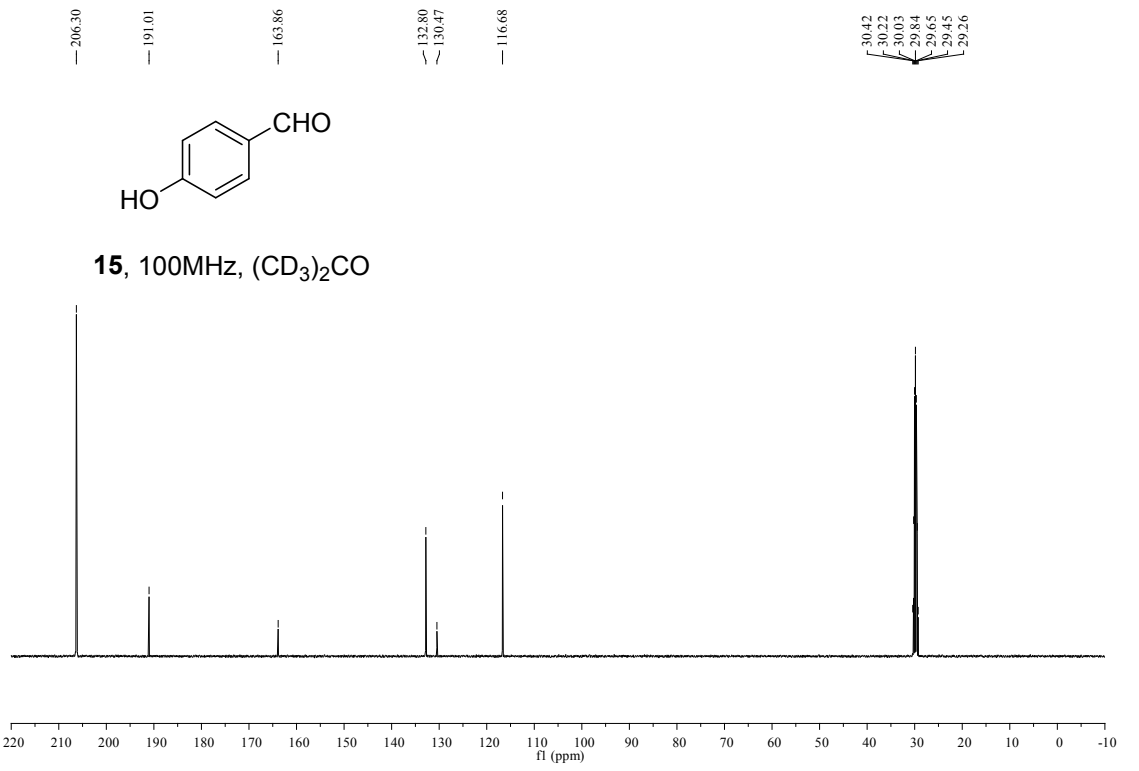
14, 400MHz, $CDCl_3$



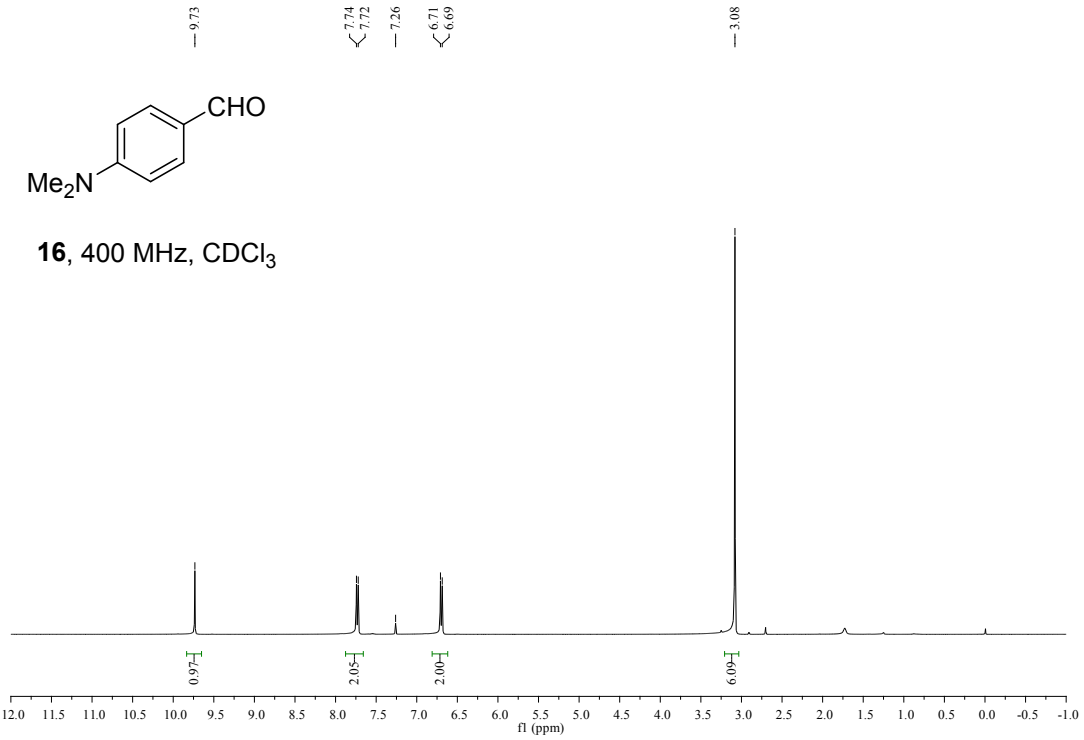
14, 100MHz, $CDCl_3$



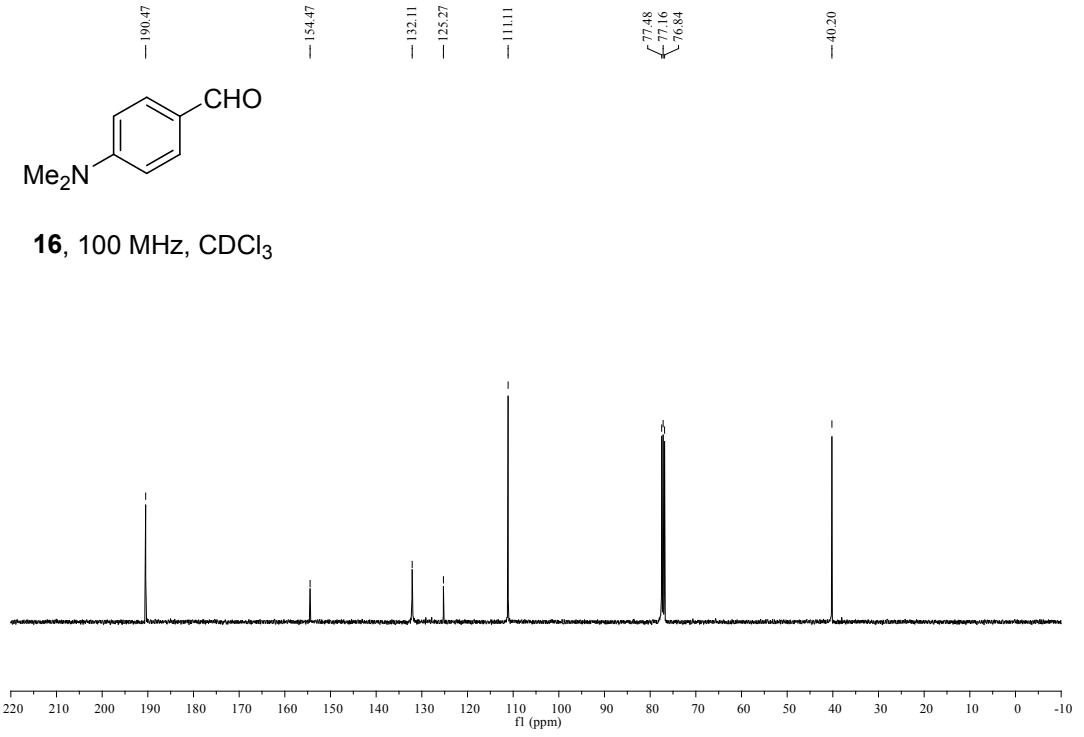
15, 400MHz, $(CD_3)_2CO$



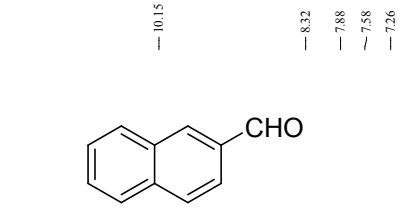
15, 100MHz, $(CD_3)_2CO$



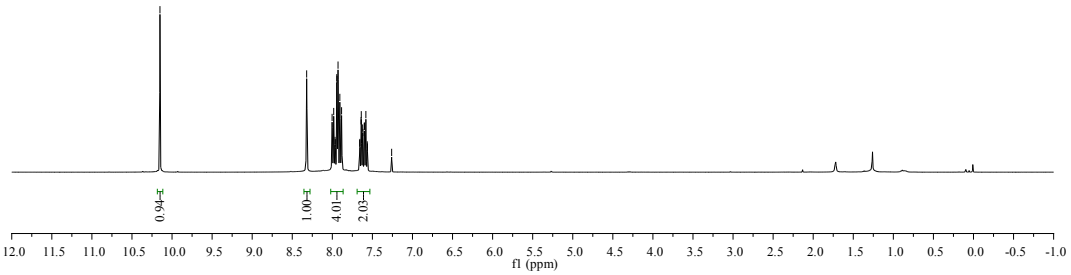
16, 400 MHz, $CDCl_3$

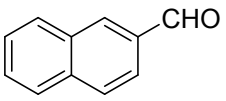


16, 100 MHz, $CDCl_3$

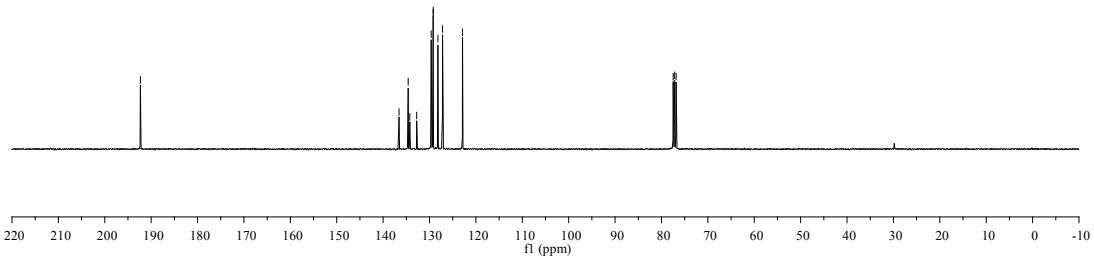


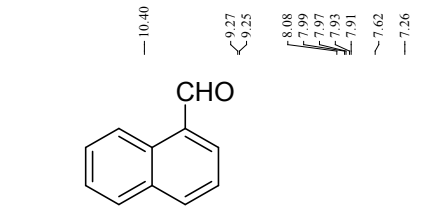
17, 400 MHz, $CDCl_3$



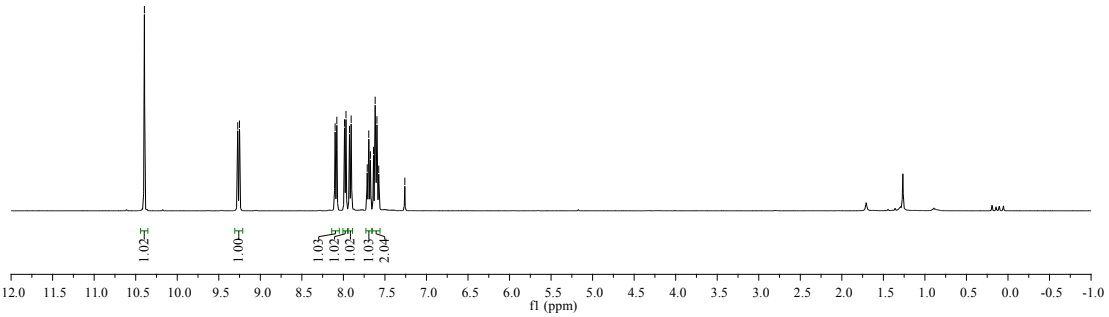


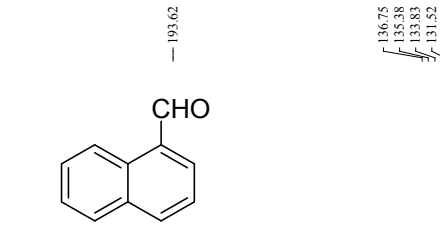
17, 100 MHz, $CDCl_3$



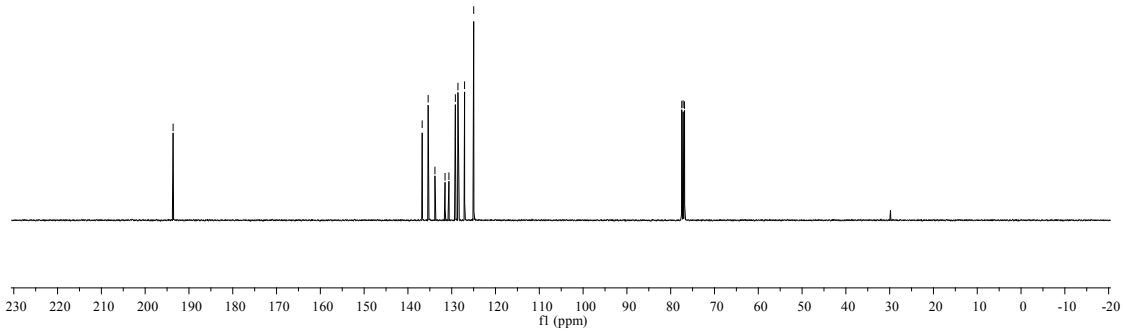


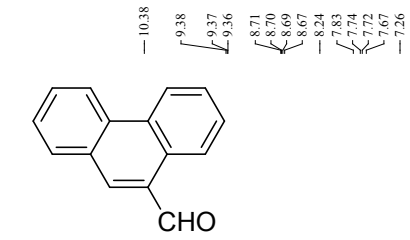
18, 400 MHz, $CDCl_3$



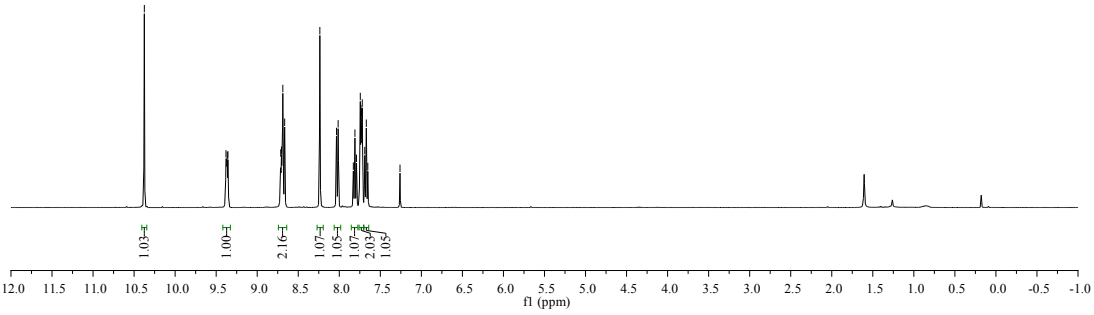


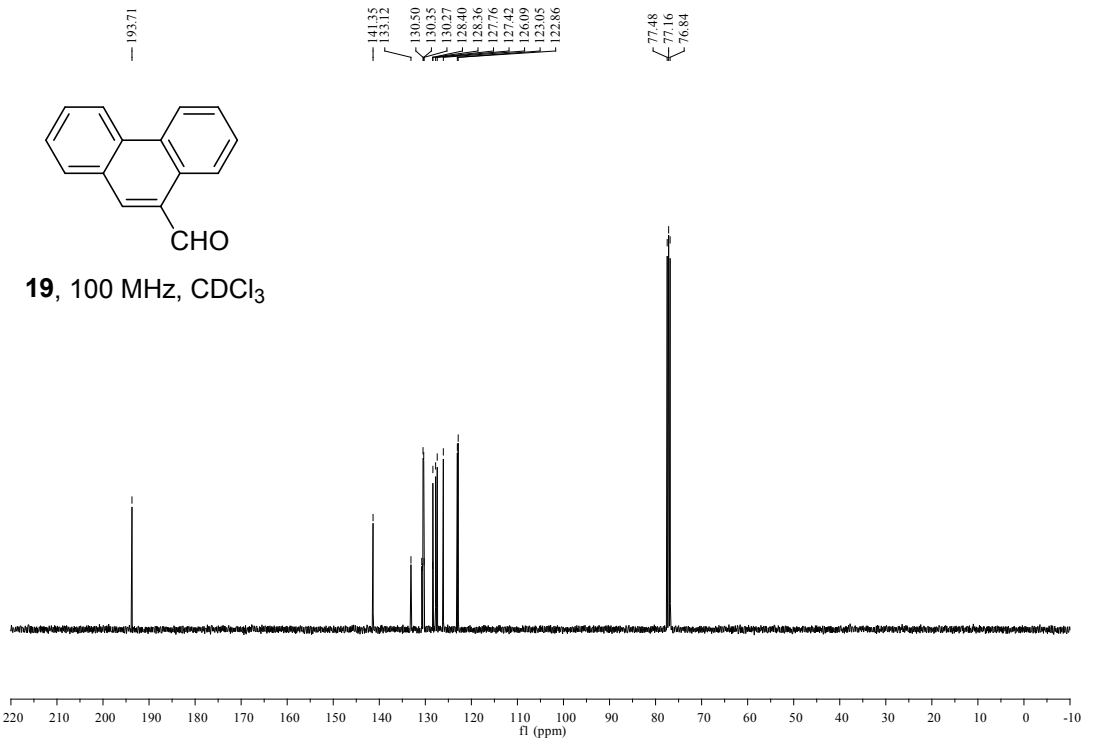
18, 100 MHz, $CDCl_3$



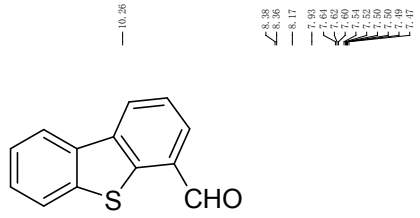


19, 400 MHz, $CDCl_3$

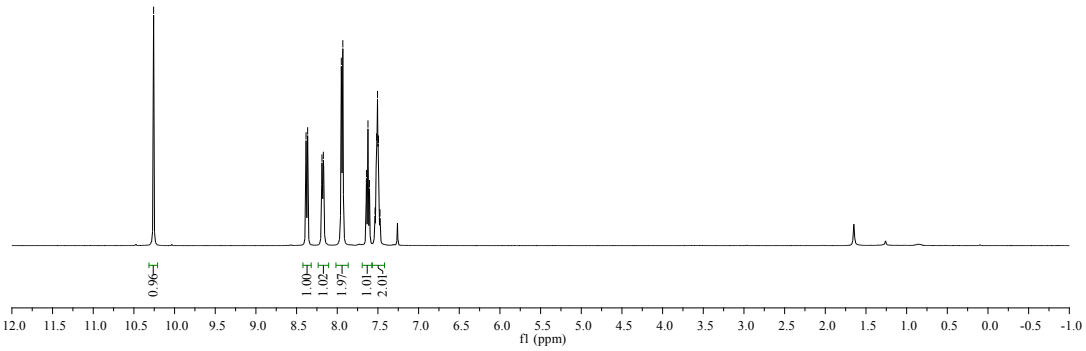


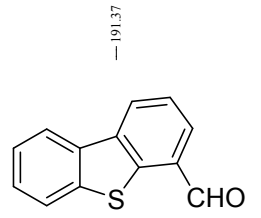


19, 100 MHz, $CDCl_3$

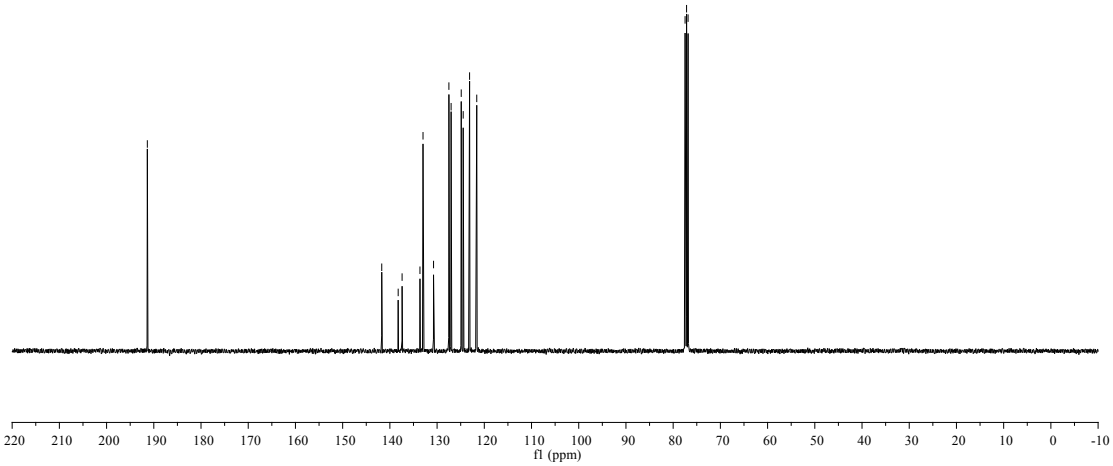


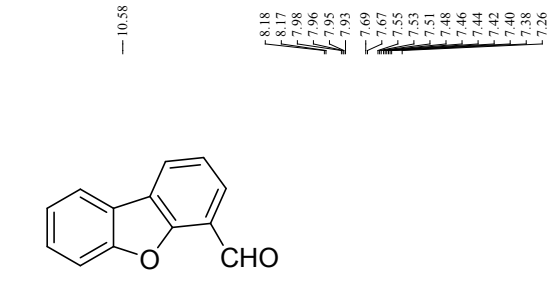
20, 400 MHz, $CDCl_3$



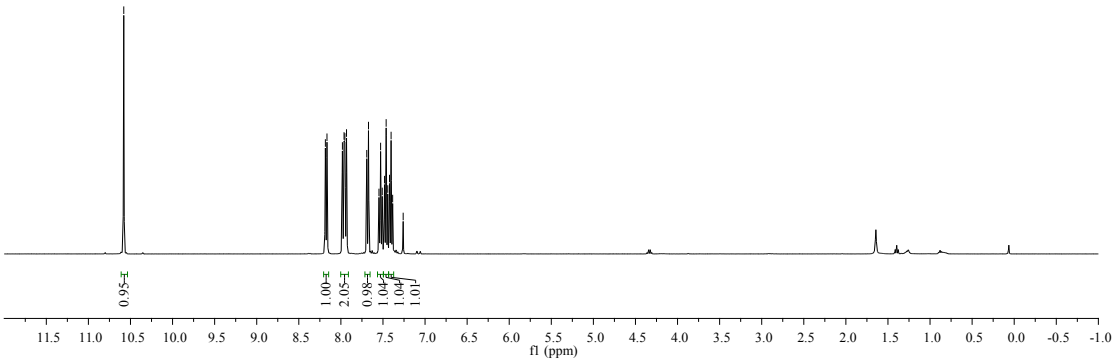


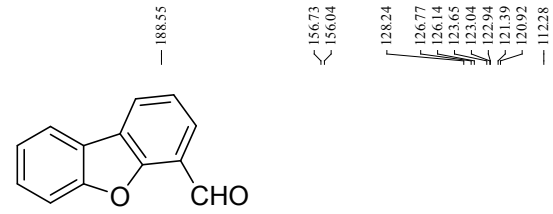
20, 100 MHz, $CDCl_3$



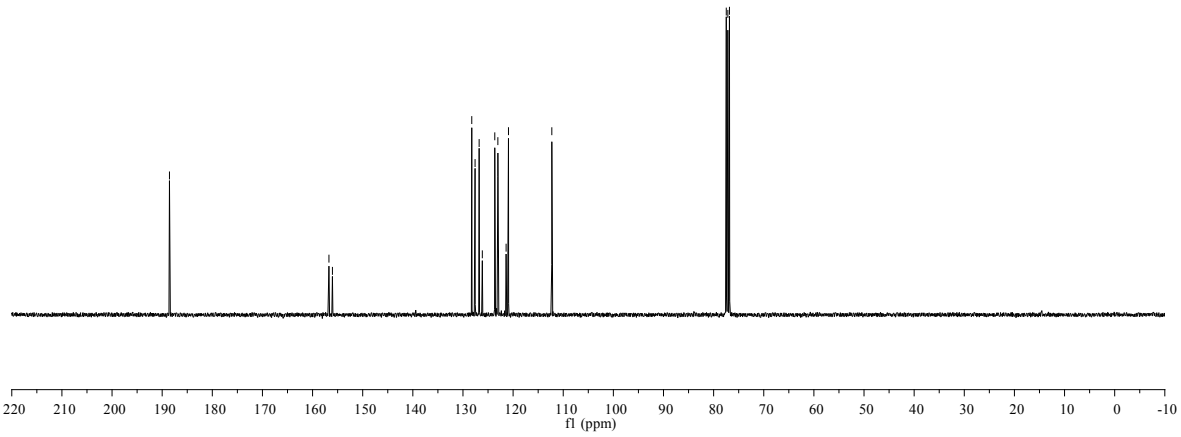


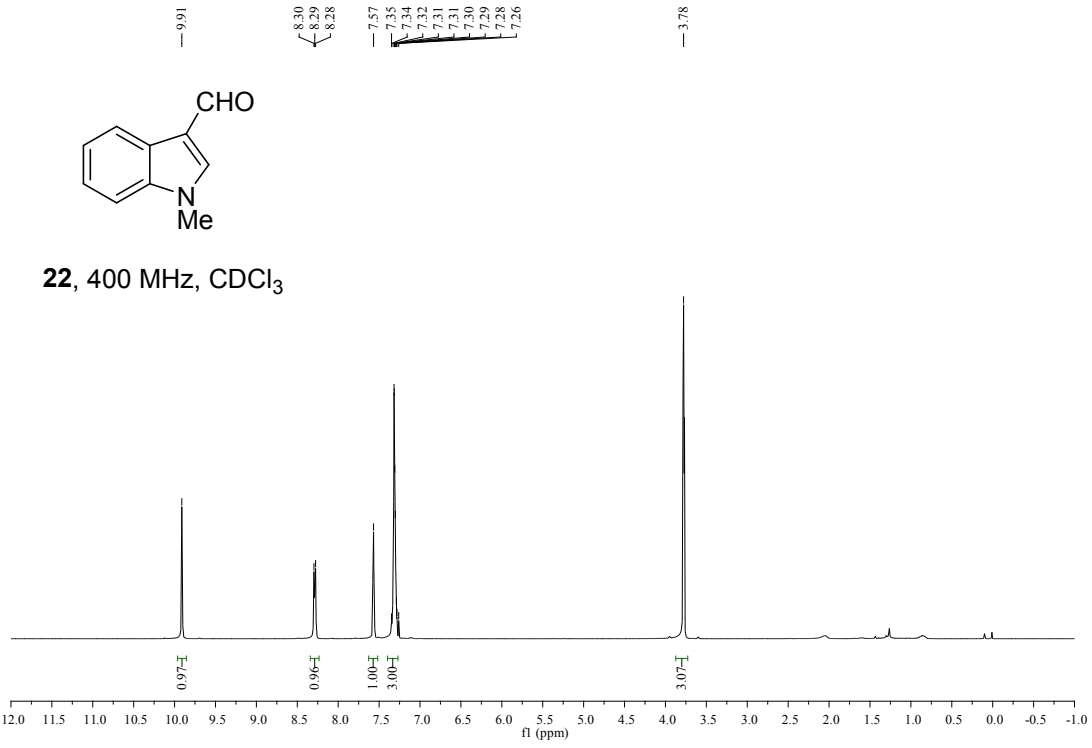
21, 400 MHz, $CDCl_3$



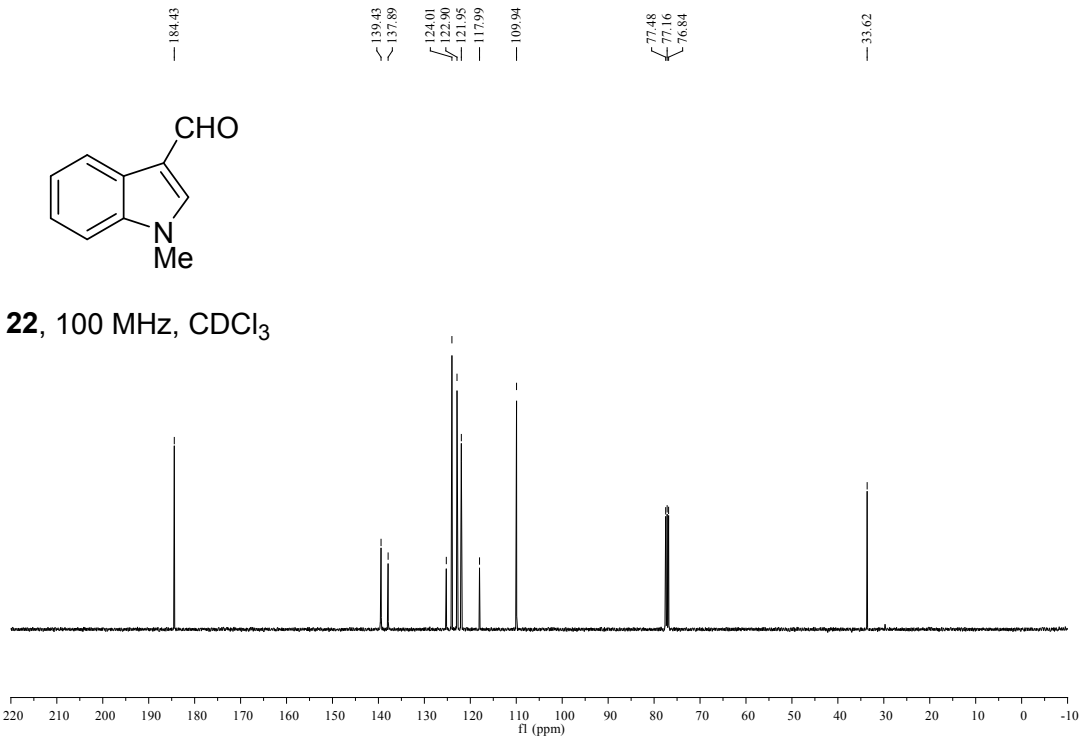


21, 100 MHz, $CDCl_3$

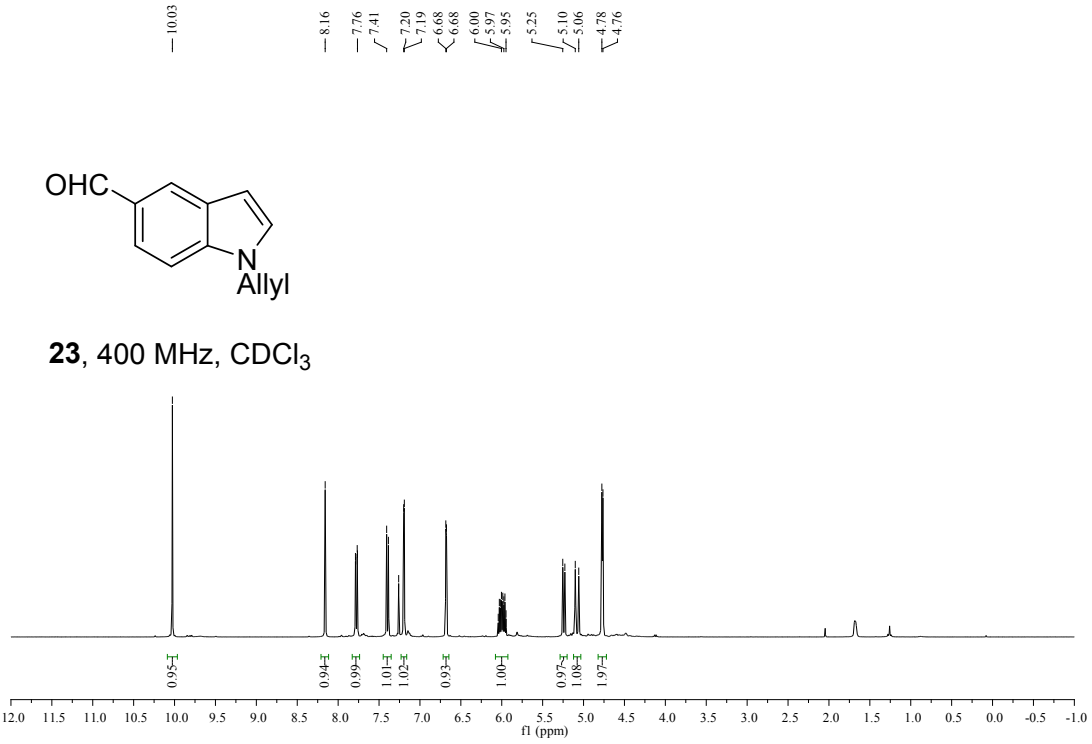




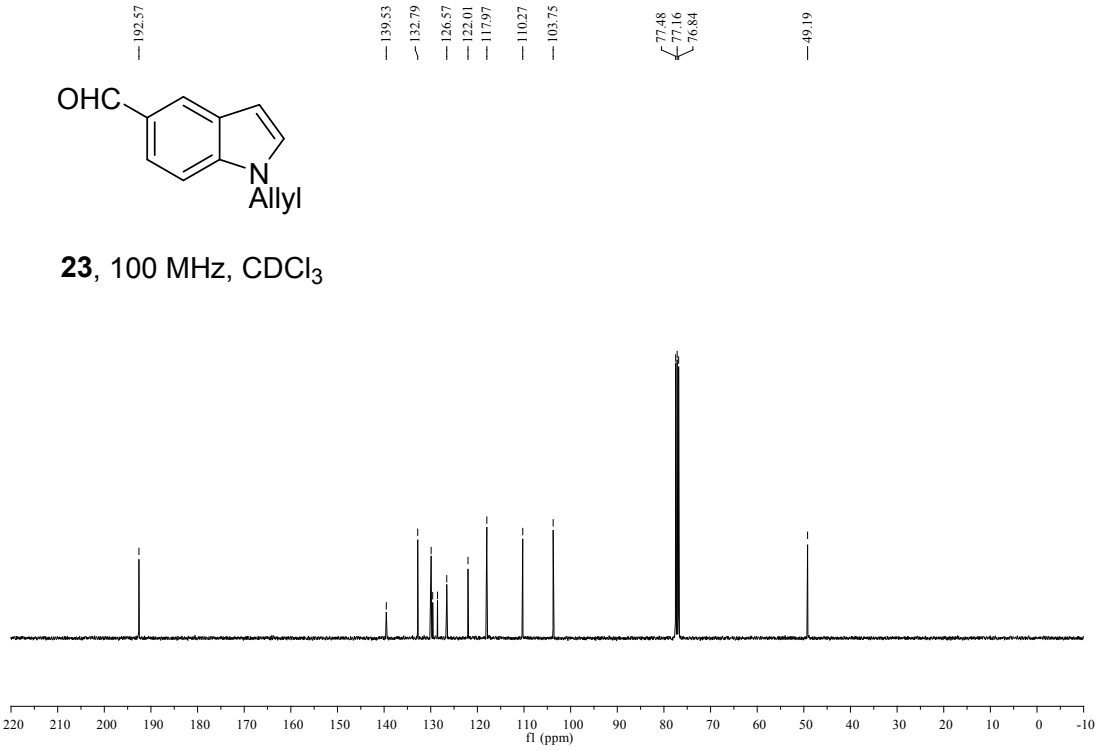
22, 400 MHz, $CDCl_3$



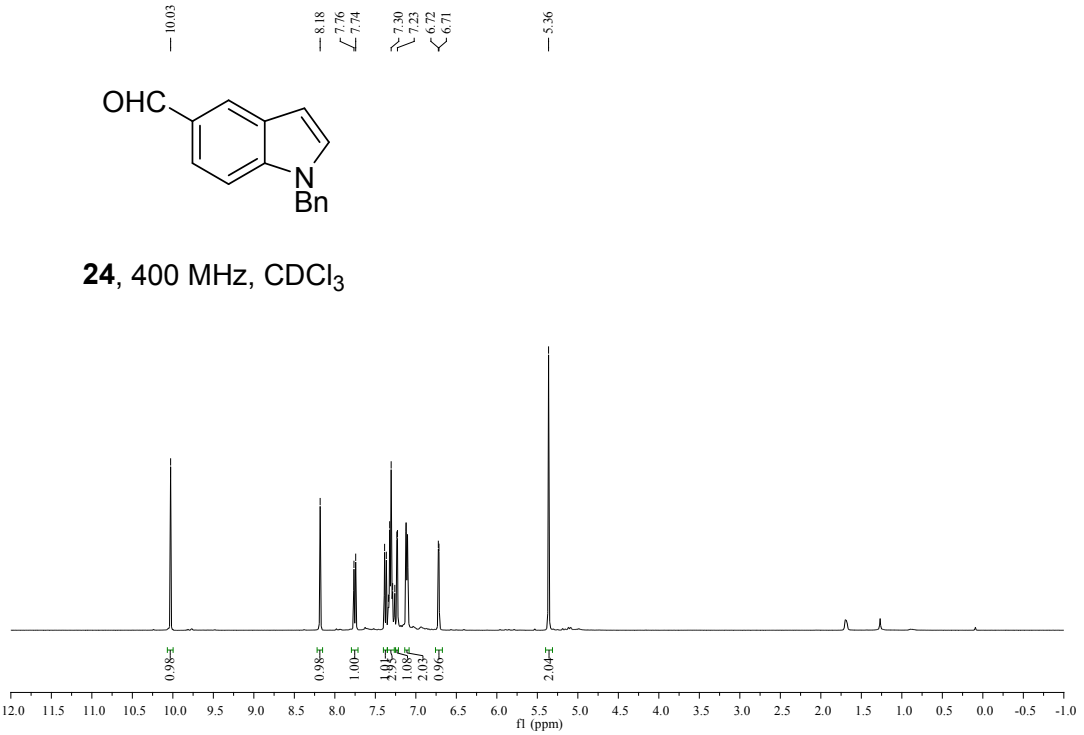
22, 100 MHz, $CDCl_3$



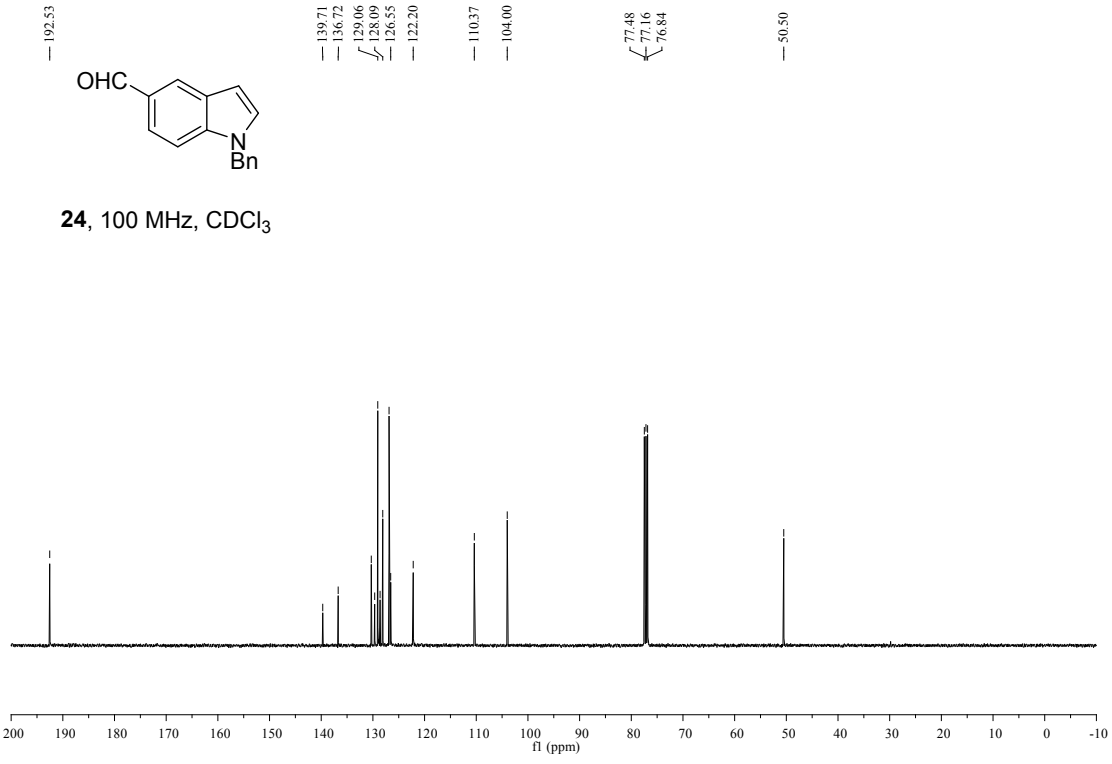
23, 400 MHz, $CDCl_3$



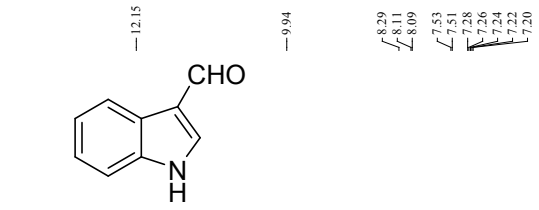
23, 100 MHz, $CDCl_3$



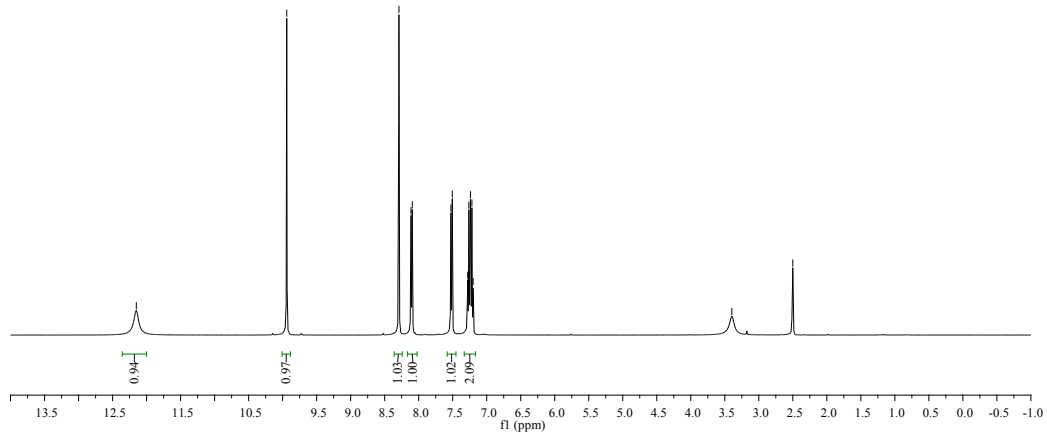
24, 400 MHz, $CDCl_3$

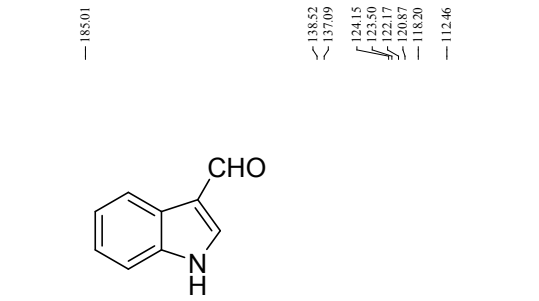


24, 100 MHz, $CDCl_3$

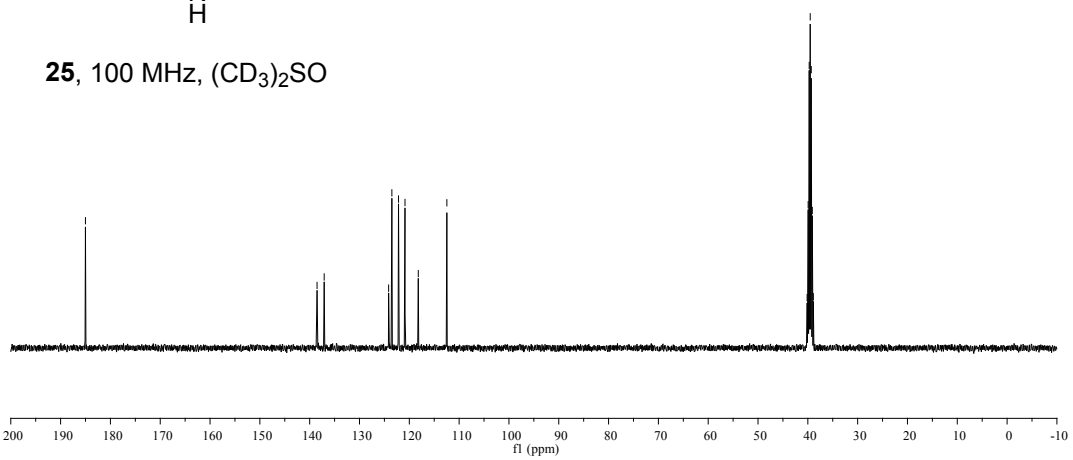


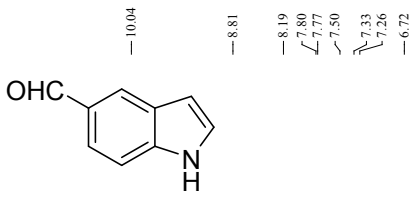
25, 400 MHz, $(CD_3)_2SO$



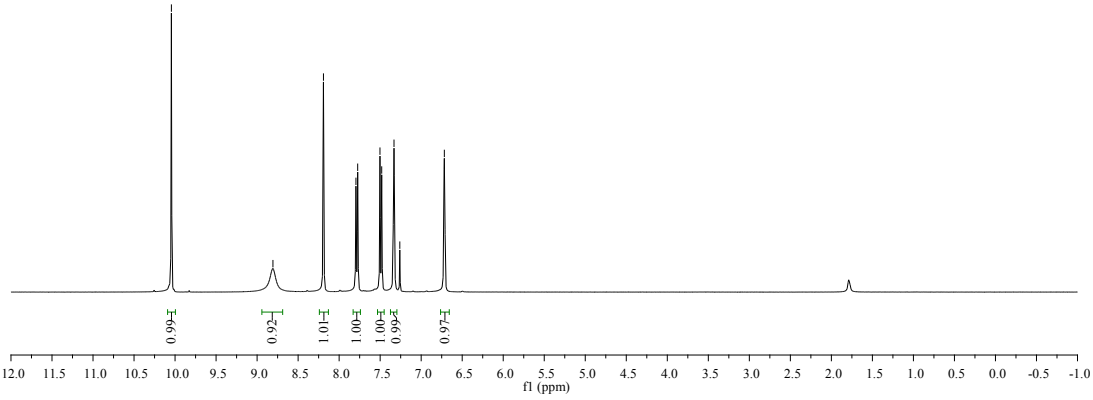


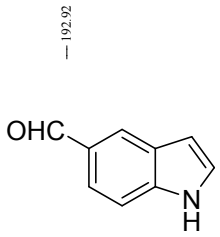
25, 100 MHz, $(CD_3)_2SO$



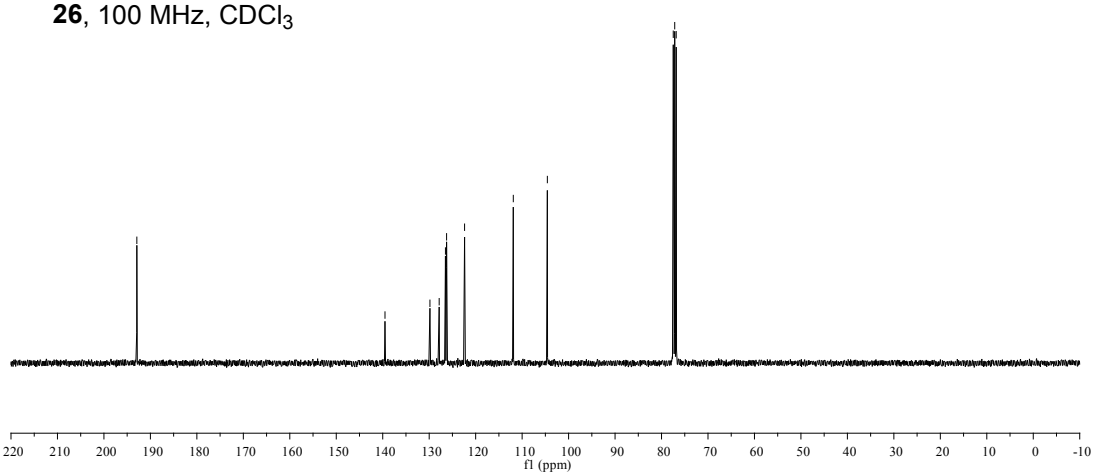


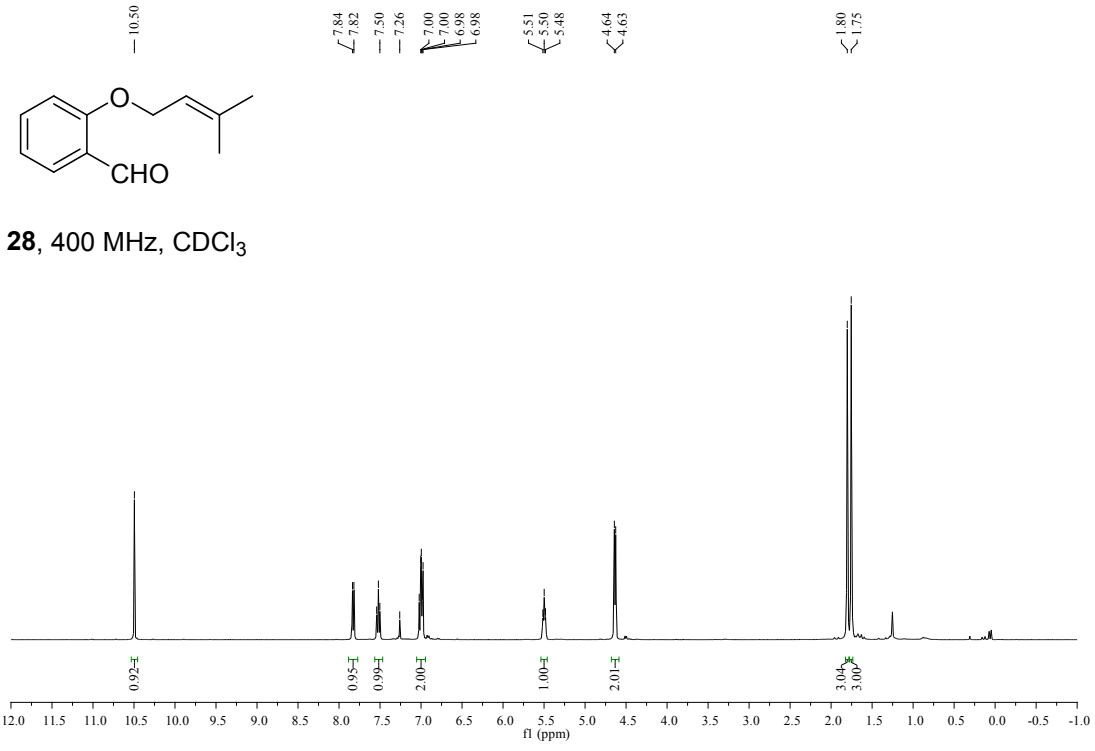
26, 400 MHz, $CDCl_3$



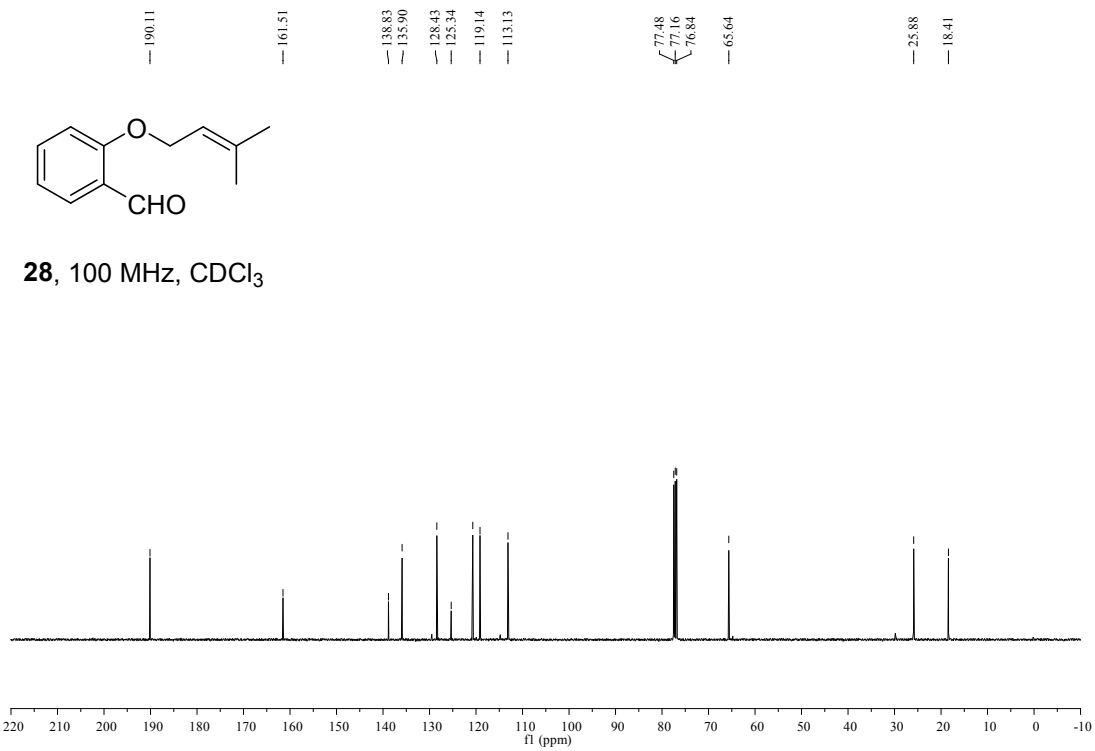


26, 100 MHz, $CDCl_3$





28, 400 MHz, $CDCl_3$



28, 100 MHz, $CDCl_3$