Supporting Information for

Gold-catalyzed Direct Amination of Arenes with Azodicarboxylates

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General Information: All solvents are anhydrous and purchased from Sigma-Aldrich (99.8%) without further treatment. d_5-Bromobenzene (99.5%) is purchased from Sigma-Aldrich. Metal catalysts are from Sigma-Aldrich or Strem Chemicals. All reagents were used without purification from commercial suppliers, unless otherwise indicated. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-400 (400 MHz) instrument. The mass spectra were recorded on Shimadzu GC-2010 (QP–2010 gas chromatograph) or Shimadzu LCMS-2010EV (Liquid chromatograph). Reaction yields are determined by purification of crude products using preparation TLC or flash column chromatography. Hydrazide **3d** [1] is known compound and other hydrazides (**3a** – **3c**, **3e** - **3k**) are unknown compounds.

General procedure for Table 1:

In glovebox, to dry reaction tube (10 mL) were added gold (III) chloride (6 mg 0.02 mmol), DCM (1 mL), and then mesitylene **1a** (280 μL, 2 mmol). The capped mixture was moved out from the glovebox and stirred at room temperature for 5 min before injection of diisopropyl azodicarboxylate **2** (206 μL, 1 mmol). The reaction mixture was stirred for 2 h to 1 d at room temperature and then directly purified by preparation TLC or flash column chromatography affording pure mono-aminated product **3a** (183 mg, 57%) and bisaminated product **3aa** (88 mg, 34%).

General procedure for Scheme 1:

Condition A: In glovebox, to dry reaction tube (10 mL) were added gold (III) chloride (6 mg 0.02 mmol or 3 mg 0.01 mmol, 1 mol% or 2 mol%), DCM (1 mL or 0.5 mL), and then arene **1** (2 mmol or 1 mmol). The capped mixture was moved out from the glovebox and stirred at room temperature for 5 min before injection of diisopropyl azodicarboxylate **2** (206 μL, 1 mmol or 103 μL, 0.5 mmol). The reaction mixture was stirred for 10 min to 1 d at room temperature and then directly purified by preparation TLC or flash column chromatography affording pure aminated product **3a – 3f**. The yields were calculated based on diisopropyl azodicarboxylate **2.**

Condition B: In glovebox, to dry reaction tube (10 mL) were added gold (III) chloride (6 mg 0.02 mmol, 5 mol%), DCM or DCE (0.7 mL), and then arene **1** (0.3 mL, 7.0 ~ 8.4 equiv.). The reaction mixture was stirred at room temperature for 5 min before addition of bis (2, 2, 2-trichlororethyl) azodicarboxylate **4** (152 mg, 0.4 mmol, 1equiv.). The capped mixture was moved out from the glovebox and stirred for 1 d to 2 d at room temperature to 60 ^{o}C. The reaction mixture was directly purified by preparation TLC or flash column chromatography affording pure aminated product **3g – 3k**. The yields were calculated based on bis (2, 2, 2-trichlororethyl) azodicarboxylate **4.**

General procedure for control reactions without arenes:

In glovebox, to dry reaction tube (10 mL) were added gold (III) chloride (15 mg 0.05 mmol) and d_2-DCM (0.5 mL), the reaction mixture was stirred for 5 min before injection of diisopropyl azodicarboxylate **2** (10.3 μL, 0.05 mmol) or addition of bis (2, 2, 2-trichlororethyl) azodicarboxylate **4** (19.0 mg, 0.05 mmol). The capped mixture was stirred for another 10 min before it was transferred into a dry NMR tube. The NMR sample was moved out from the glovebox for analysis. The NMR shifts remained unchanged, which indicated that there is no obvious coordination between gold (III) chloride and azodicarboxylates (very small amount of unknown product was also detected in both NMR experiments).

Procedure for control reaction after $AuCl_3$ metalation of arene:

In glovebox, to dry reaction tube (10 mL) were added gold (III) chloride (30 mg 0.10 mmol), d_2-DCM (0.5 mL), and then fluorobenzene (20 μL, 0.2 mmol). The reaction mixture was stirred for 5 min. Then half of which was transferred into NMR tubes (number **1**) and bis (2, 2, 2-trichlororethyl) azodicarboxylate **4** (38.0 mg, 0.10 mmol, 1 equiv based on fluorobezene in the residual mixture) was added into the residual mixture. The capped mixture was stirred at room temperature for another 10 min before it was transferred into another dry NMR tube (number **2**). The NMR samples were moved out from the glovebox for analysis. Change on NMR shifts of fluorobenzene was difficult to identify due to the overlap. Meanwhile, the NMR shifts of azodicarboxylate ($C\underline{H}_2CO_2CCl_3$) changed obviously (2/3 of which changed from 5.12 ppm to 4.85 ppm, details of spectra see **S19**), which indicated that there might be strong interaction between aryl gold (III) complexe and the azodicarboxylate.

General procedure for kinetic isotope experiments:

In glovebox, to dry reaction tube (10 mL) were added gold (III) chloride (6 mg 0.02 mmol, 5 mol%), DCE (0.7 mL), and then bromobenzene/deuterated bromobenzene (V/V = 1/1, 0.3 mL). The reaction mixture was stirred at room temperature for 5 min before addition of bis (2, 2, 2-trichlororethyl) azodicarboxylate **4** (152 mg, 0.4 mmol, 1 equiv.). Then the capped mixture was moved out from the glovebox and stirred for 1 d at 60 ^{o}C.

Then the mixture was purified by preparation TLC affording pure aminated product **3j** (100 mg, Yield: 46.1%). ^{1}H NMR (details of spectra see **S19)** results indicated that the value of $k_H/k_D = 1$.

NMR data and MS data of 3a – 3k, bisaminated product 3gg and KIE see below:

1-(2,4,6-Trimethylphenyl)-1,2-hydrazinedicarboxylic acid diisopropyl ester 3a:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.09 (brs, 1H), 6.89 (s, 2H), 5.00 (m, 2H), 2.30 (m, 2H), 1.16 – 1.32 (m, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.1, 155.7, 137.9, 137.7, 136.5, 135.9, 129.4, 129.1, 70.5, 70.3, 22.1, 22.0, 21.9, 20.9, 20.9, 18.2 ppm.

GC - MS *m/z* (%): 322 (35), 236 (52), 194 (100), 149 (77), 134 (52), 133 (51). 122 (52), 107 (10).

1-(2,3,5,6-Tetramethylphenyl)-1,2-hydrazinedicarboxylic acid diisopropyl ester 3b:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.97 (s, 1H), 6.79 (brs, 1H), 5.02 (m, 2H), 2.23 (m, 12H), 1.35-1.16 (m, 12 H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.9, 139.0, 134.4, 131.6, 131.3, 70.6, 70.4, 22.1, 22.0, 21.9, 20.1, 16.6, 14.7 ppm.

GC - MS *m/z* (%): 336 (32), 250 (32), 235 (26), 208 (42), 191 (41), 175 (13), 163 (50), 148 (100), 147 (81), 136 (32), 119 (13).

1-(2,4,6-Trimethoxyphenyl)-1,2-hydrazinedicarboxylic acid diisopropyl ester 3c:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.94 (brs, 1H), 6.10 (s, 1H), 6.08 (s, 1H), 4.92 (m, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 1.28 – 1.12 (m, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.8, 160.5, 156.6, 155.0, 112.9, 90.7, 70.1, 69.2, 55.9, 55.5, 55.4, 22.0 ppm.

GC - MS *m/z* (%): 370 (10), 283 (68), 242 (38), 197 (100), 182 (44), 166 (13). 140 (15).

1-(4-Hdroxyphenyl)-1,2-hydrazinedicarboxylic acid diisopropyl ester 3d [1]:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 (s, 2H), 7.05 (brs, 1H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.52 (brs, 1H), 5.00 (m, 2H), 1.27 (m, 12H) ppm.

GC - MS *m/z* (%): 296 (10), 210 (32), 195 (10), 168 (100), 123 (65), 107 (25). 77 (10).

The data is consistent with that in reported lit. [1]

1-(4-Methoxynaphthyl)-1,2-hydrazinedicarboxylic acid diisopropyl ester 3e:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.30 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 7.2 Hz, 1H), 7.69 (brs, 1H), 7.50 (m, 3H), 6.75 (d, *J* = 8.4 Hz, 1H), 5.00 (s, 2H), 3.98 (s, 3H), 1.36 – 1.02 (m, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.4, 155.3, 131.0, 127.2, 126.3, 125.9, 125.4, 122.4, 103.2, 70.8, 69.8, 55.6, 22.0 ppm.

GC - MS *m/z* (%): 360 (44), 274 (53), 273 (54), 232 (88), 187 (100), 172 (56). 158 (25), 144 (15).

1-(4-N,N-Dimethylaminonaphthyl)-1,2-hydrazinedicarboxylic acid diisopropyl ester 3f:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 (m, 1H), 7.93 (s, 1H), 7.64 (brs, 1H), 7.50 (m, 3H), 7.03 (d, *J* = 6.0 Hz, 1H), 5.00 (m, 2H), 2.91 (s, 6H), 1.36 – 1.04 (m, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.3, 151.2, 132.9, 131.2, 129.2, 126.5, 126.0, 125.3, 124.7, 123.0, 113.5, 70.8, 69.8, 45.2, 22.0 ppm.

GC - MS m/z (%): 373 (62), 286 (43), 271 (24), 200 (56), 185 (100), 171 (15). 170 (15).

3g (*p*/*m* = 7/3):

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (brs, 1H), 7.54 (t, *J* = 7.6 Hz, 0.33H, *m*-isomer), 7.36 (d, *J* = 7.6 Hz, 1.4H, *p*-isomer), 7.28 (m, 1H, *m*-isomer), 7.19 (d, *J* = 8.0 Hz, 1.4H, *p*-isomer), 4.83 (m, 4H), 2.37 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.4, 154.0, 153.0, 138.0, 135.7, 131.1, 130.9, 129.7, 129.2, 128.4, 127.0, 125.8, 123.9, 94.7, 75.8, 75.2, 21.1, 17.8 ppm.

LC - MS *m/z* (%): [M – H^+] = 471 (100).

3gg (*m*, *p*/*m*, *m* = 1/1):

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (m, 2H), 7.45 (s, 1H), 7.37 (brs, 1H), 4.84 (m, 8H), 2.36 (s, 1.5H) 2.34 (s, 1.4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.3, 154.0, 136.7, 129.0, 100.0, 94.5, 75.8, 75.3, 18.0 ppm.

LC - MS *m/z* (%): [M – $2H^+$] = 851 (100).

1-[4-[1,2-bis(2,2,2-trichloroethyloxy)carbonylhyrazino]phenyl]-1,2-hydrazine-dicarboxylic acid bis(2,2,2-trichloroethyl) ester 3h:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (brs, 1H), 7.50 (s, 4H), 4.83 (d, *J* = 10.8 Hz, 8H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 100.0, 94.5, 75.9, 75.3 ppm.

LC - MS *m/z* (%): [M – $2H^+$] = 837 (100), 839 (93).

1-(4-Chlorophenyl)-1,2-hydrazinedicarboxylic acid bis(2,2,2-trichloroethyl) ester 3i:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (brs, 1H), 7.44 (s, 2H), 7.36 (dd, *J* = 6.4, 2.0 Hz, 2H), 4.83 (d, *J* = 8.8 Hz, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 129.2, 94.5, 75.9, 75.3 ppm.

LC - MS *m/z* (%): [M – H^+] = 491 (100), 493 (95).

1-(4-Bromophenyl)-1,2-hydrazinedicarboxylic acid bis(2,2,2-trichloroethyl) ester 3j:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (brs, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.39 (s, 2H), 4.82 (d, *J* = 10.0 Hz, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 132.1, 94.5, 75.9, 75.3 ppm.

LC - MS *m/z* (%): [M – H^+] = 537 (100), 539 (72).

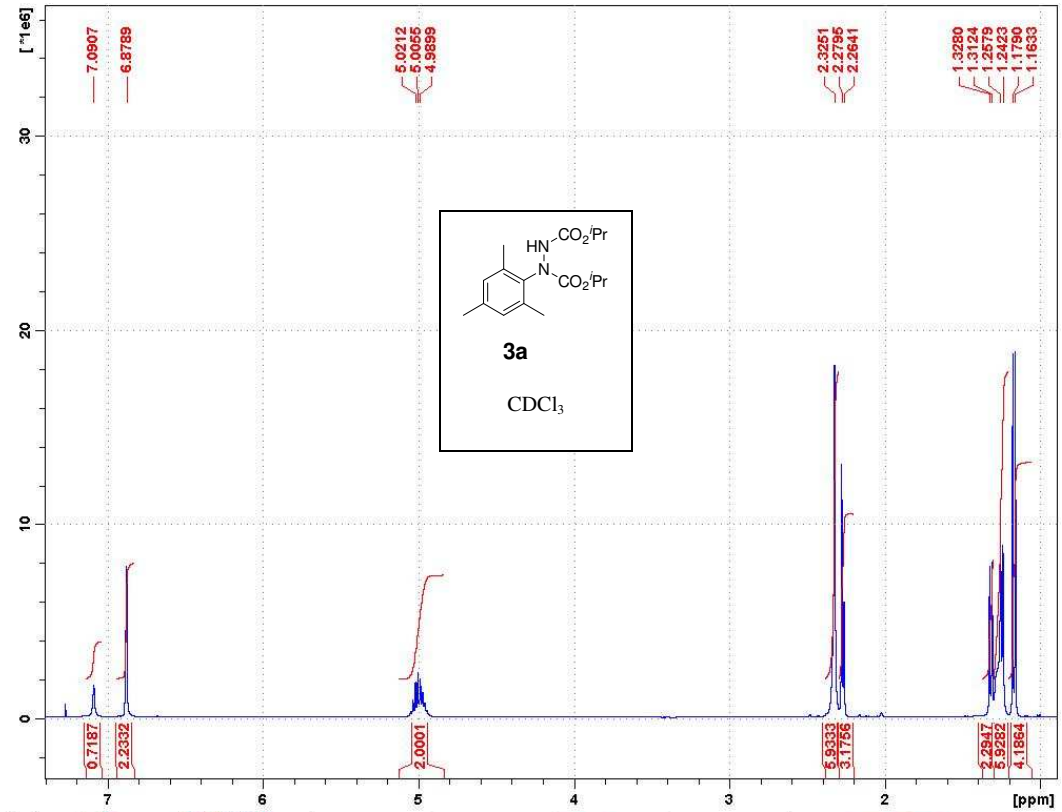
1-(4-Fluorophenyl)-1,2-hydrazinedicarboxylic acid bis(2,2,2-trichloroethyl) ester 3k:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (brs, 1H), 7.47 (s, 2H), 7.08 (t, *J* = 8.8 Hz, 2H), 4.00 (d, *J* = 6.0 Hz, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 116.1, 115.8, 94.6, 75.9, 75.3 ppm.

LC - MS *m/z* (%): [M – H^+] = 475 (100), 477 (95).

The spectra of acids of ^{1}H and ^{13}C NMR see below: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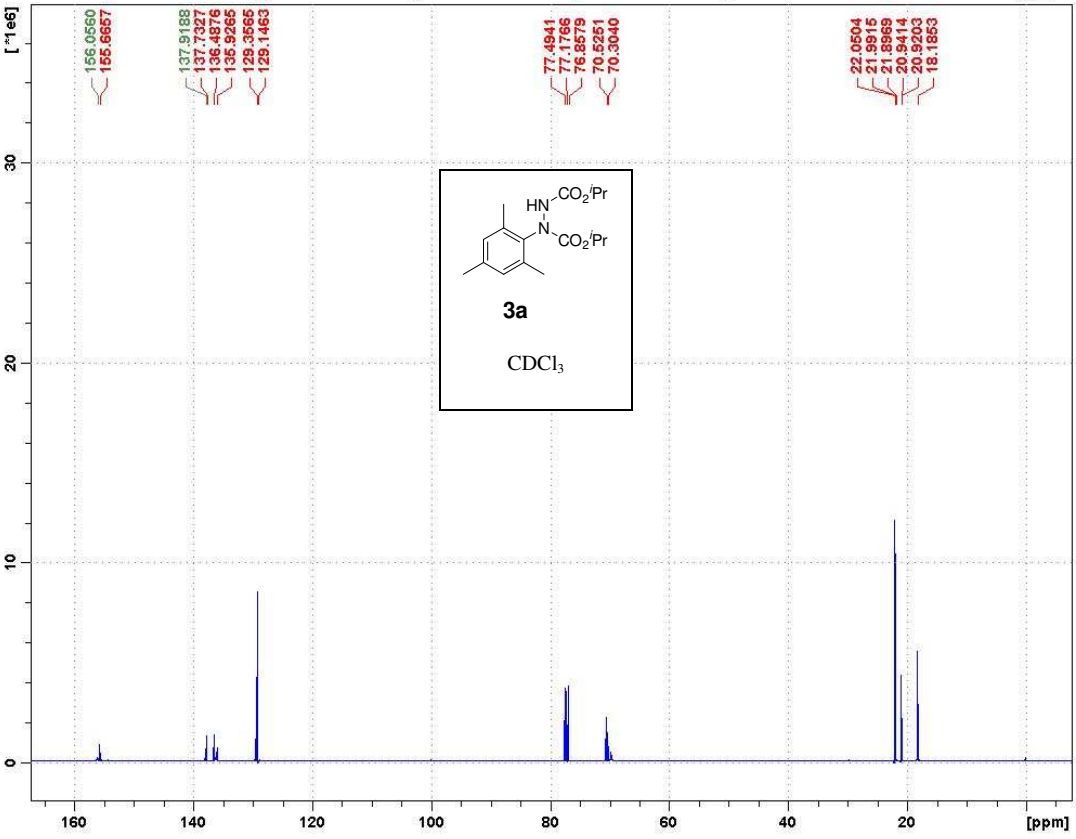
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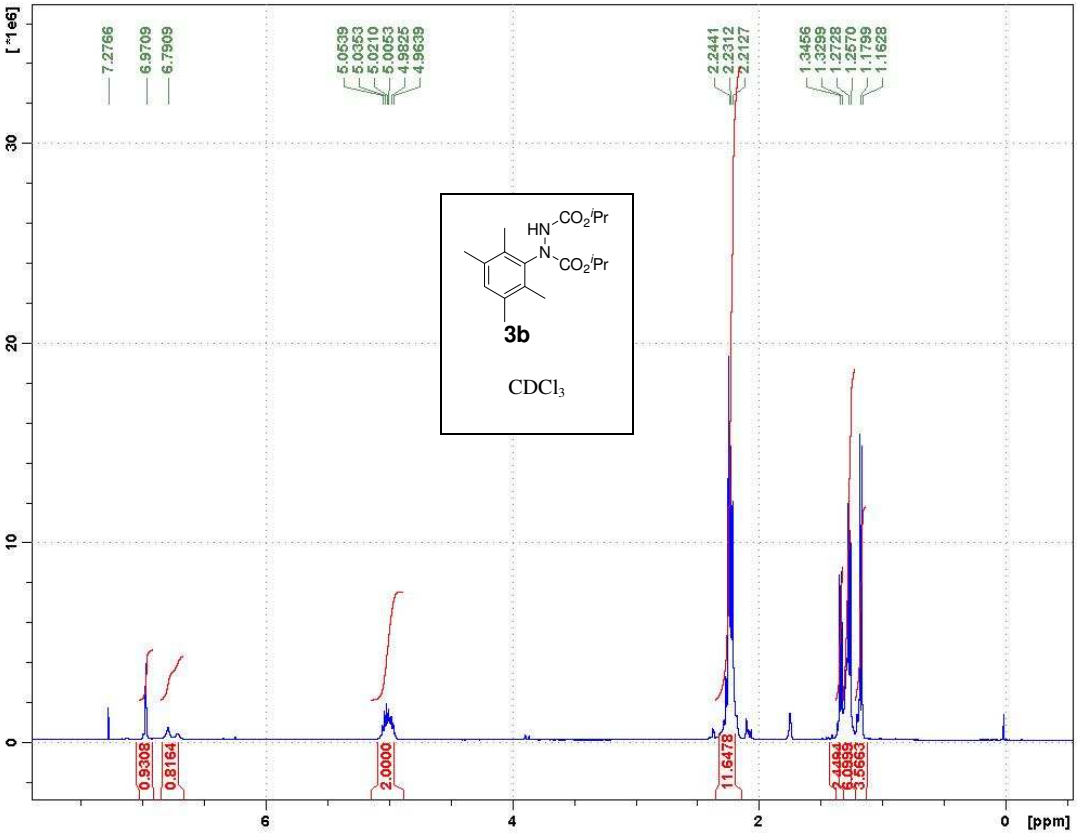
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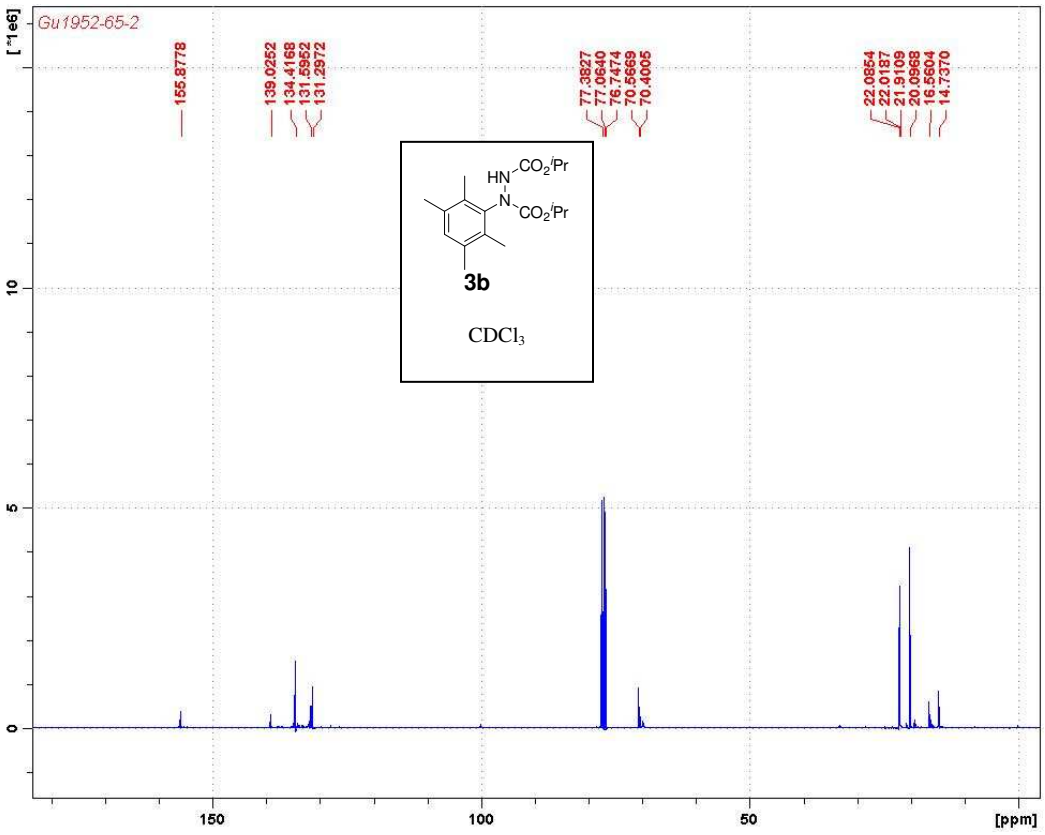
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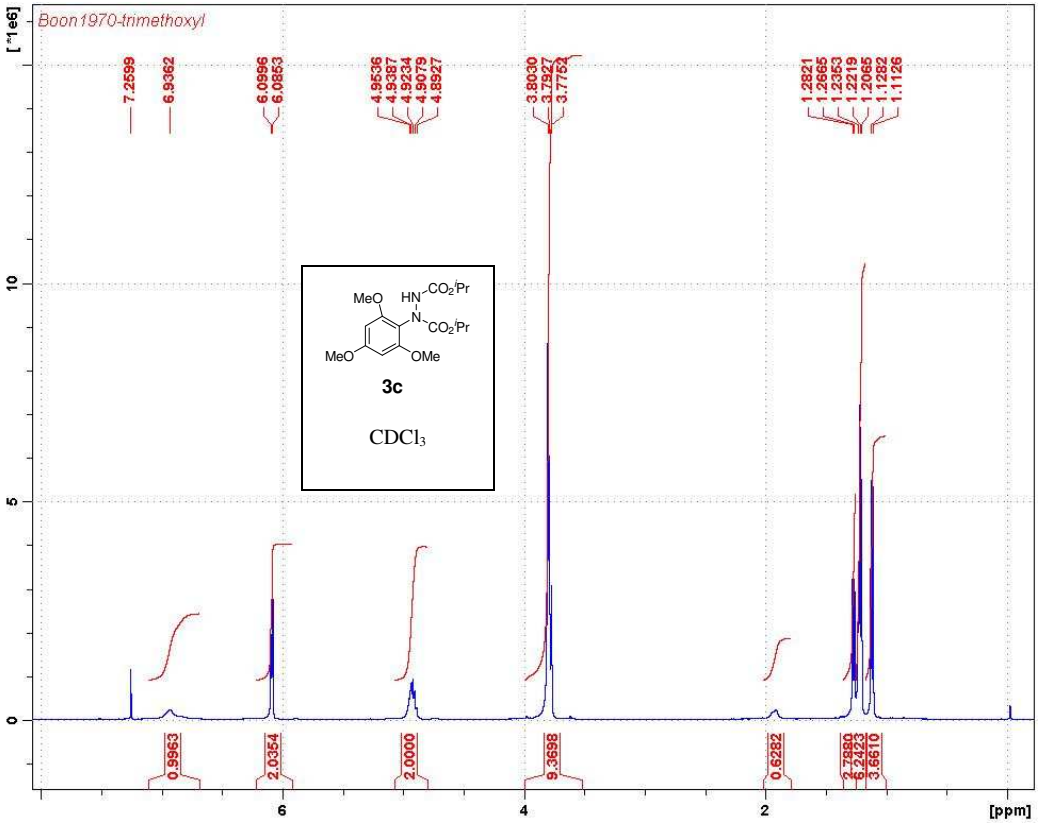
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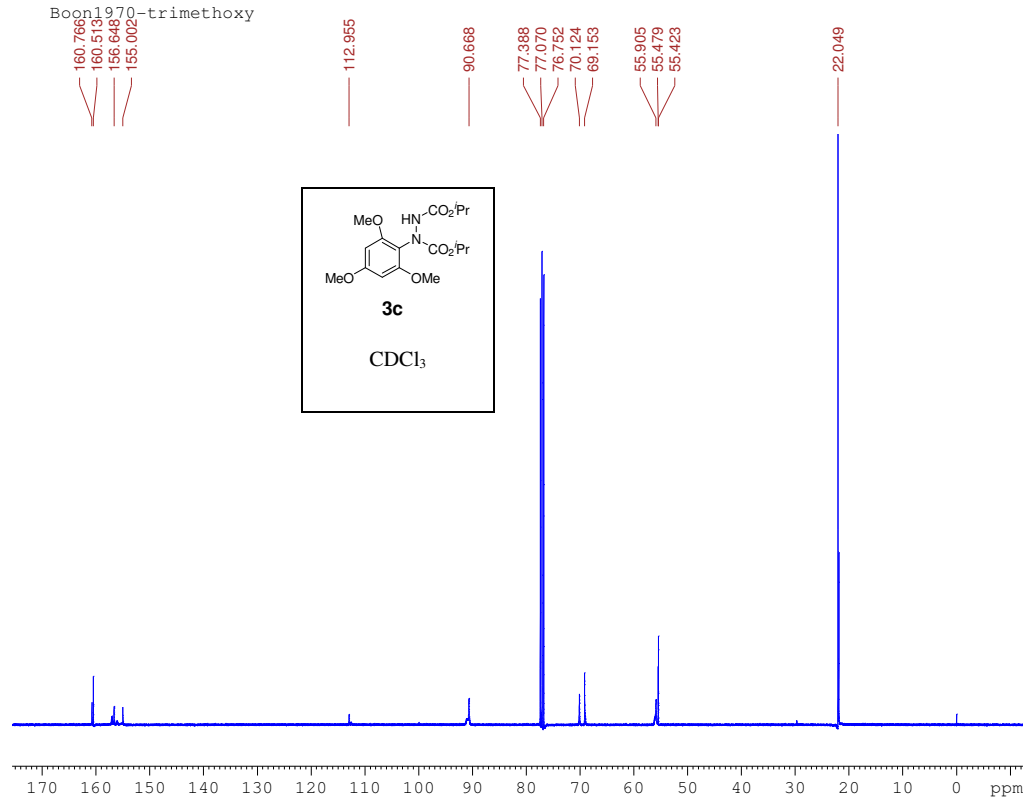
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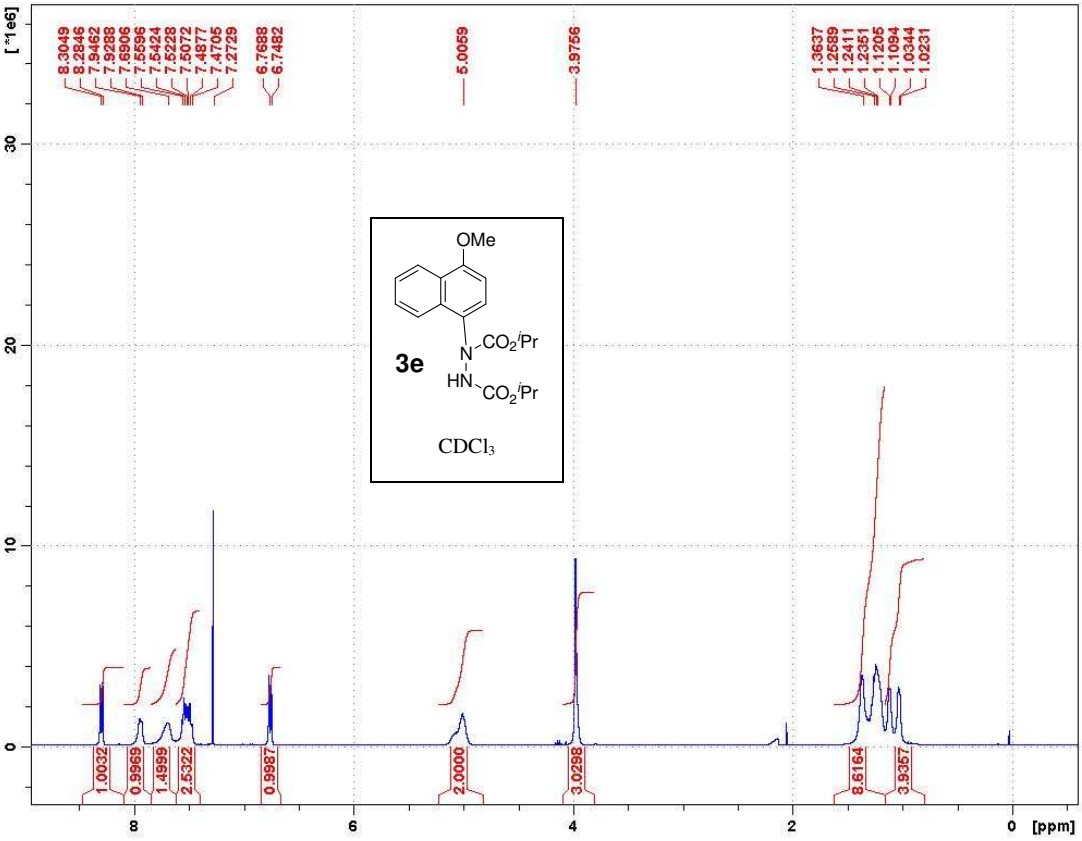
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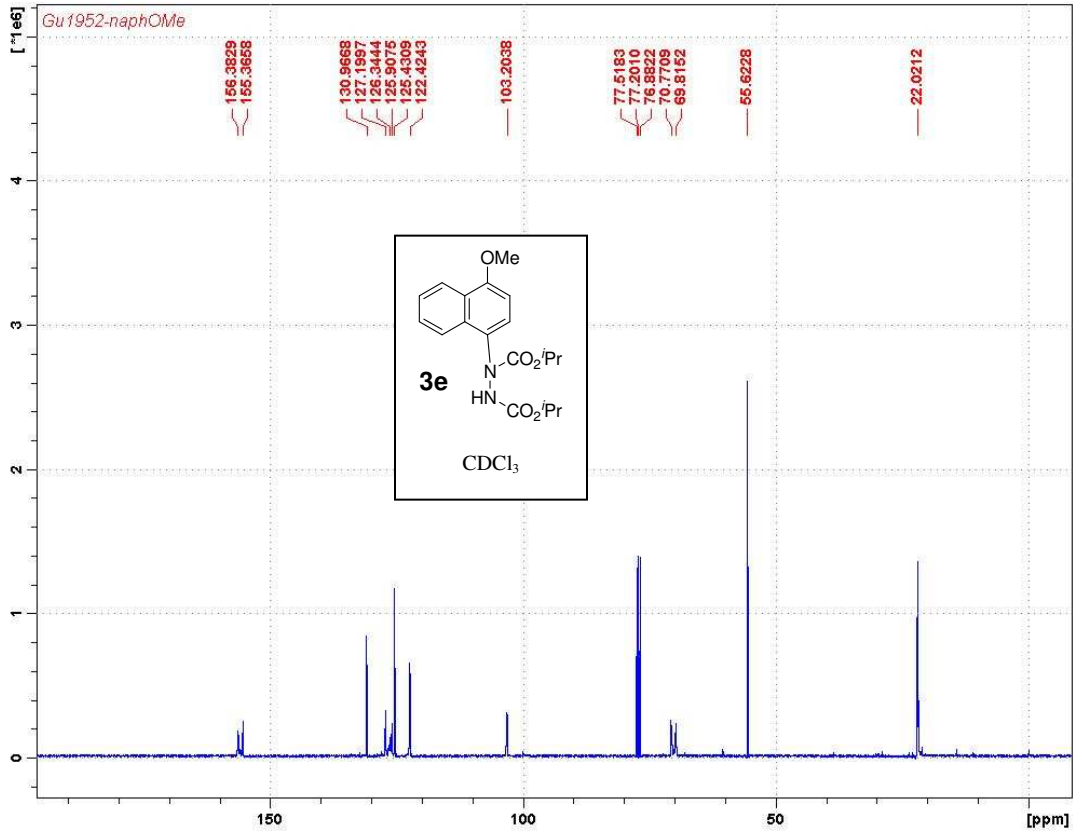
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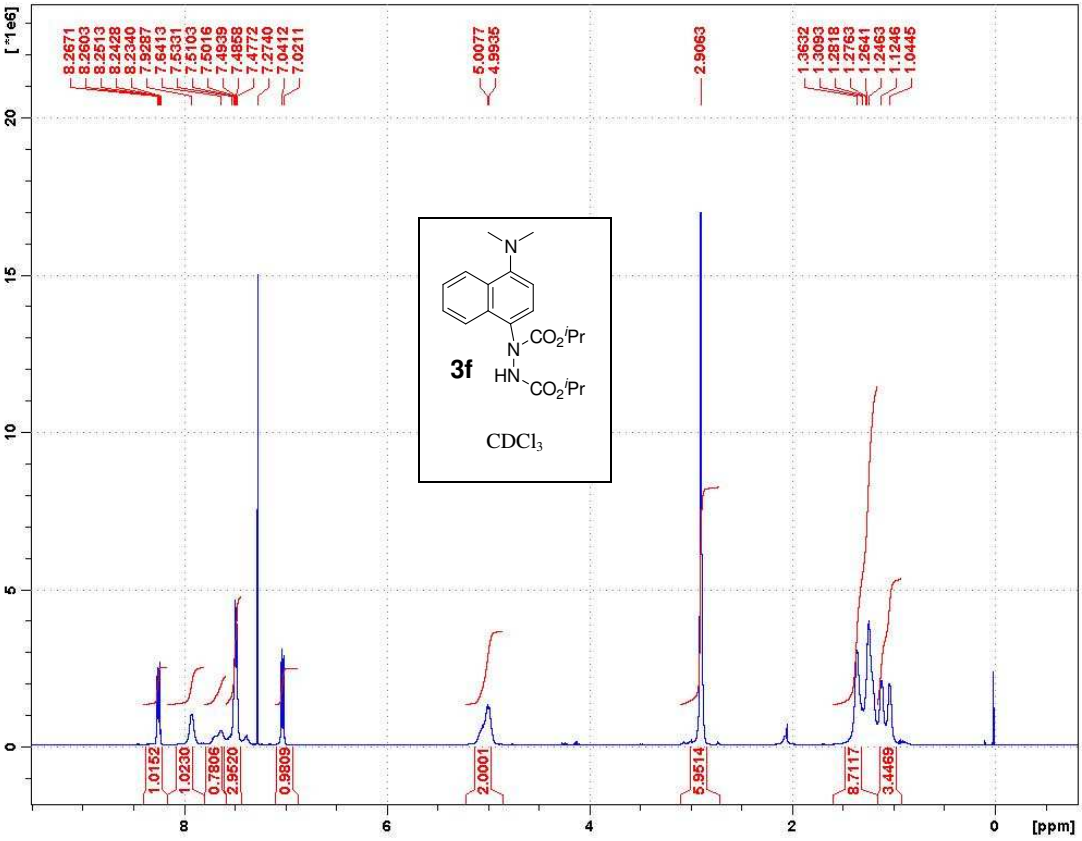
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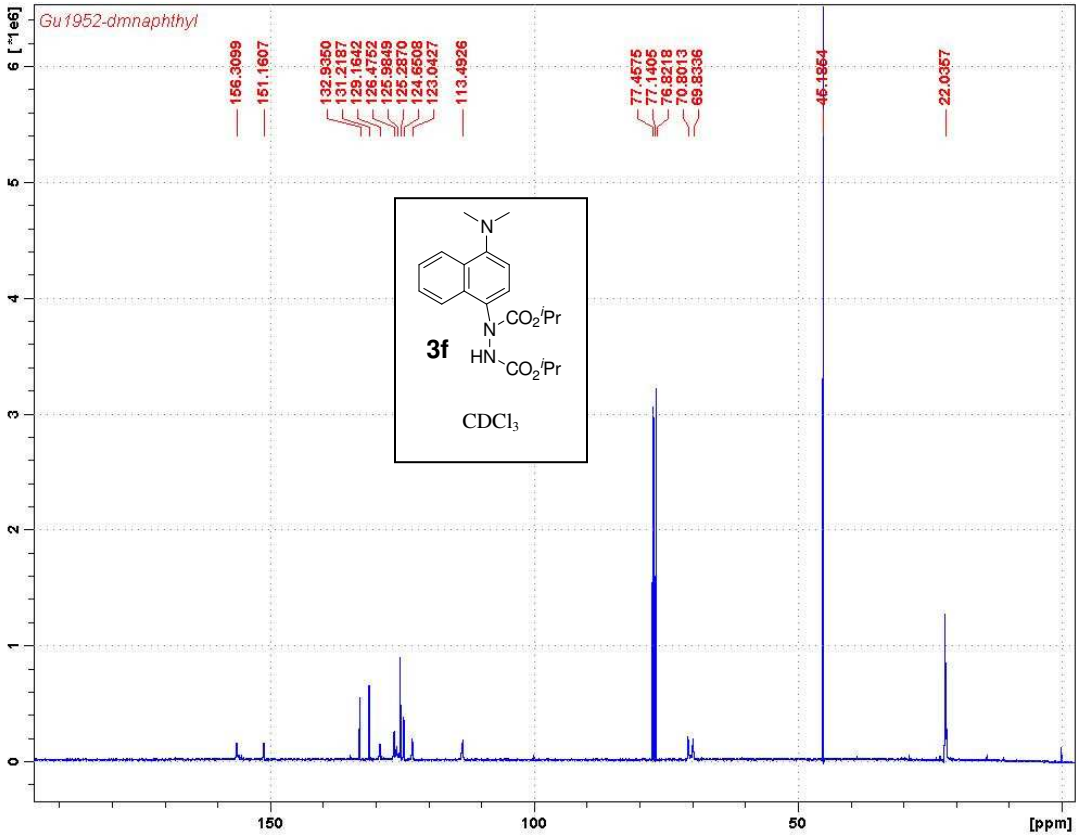
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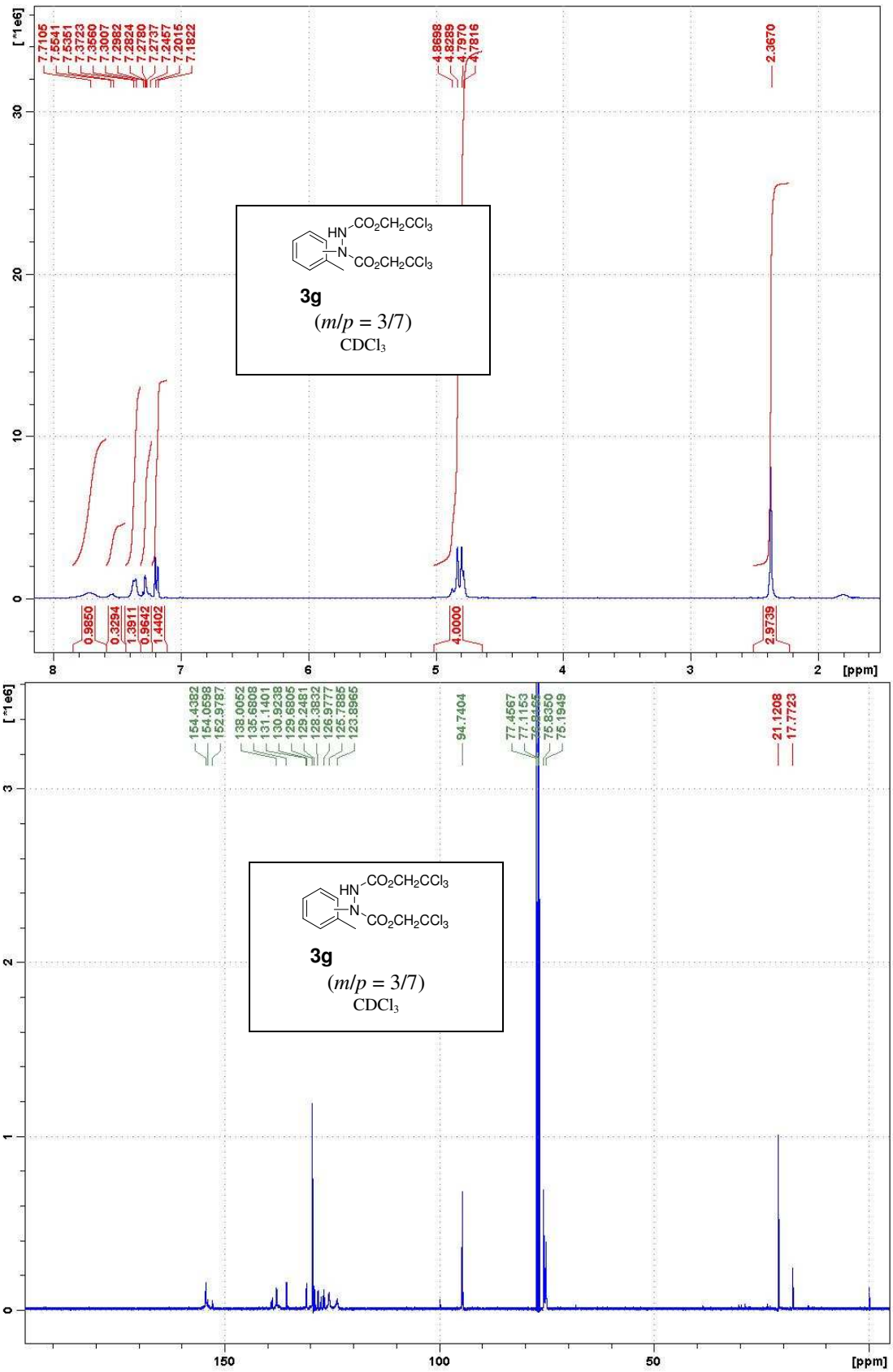
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(m/p = 3/7)
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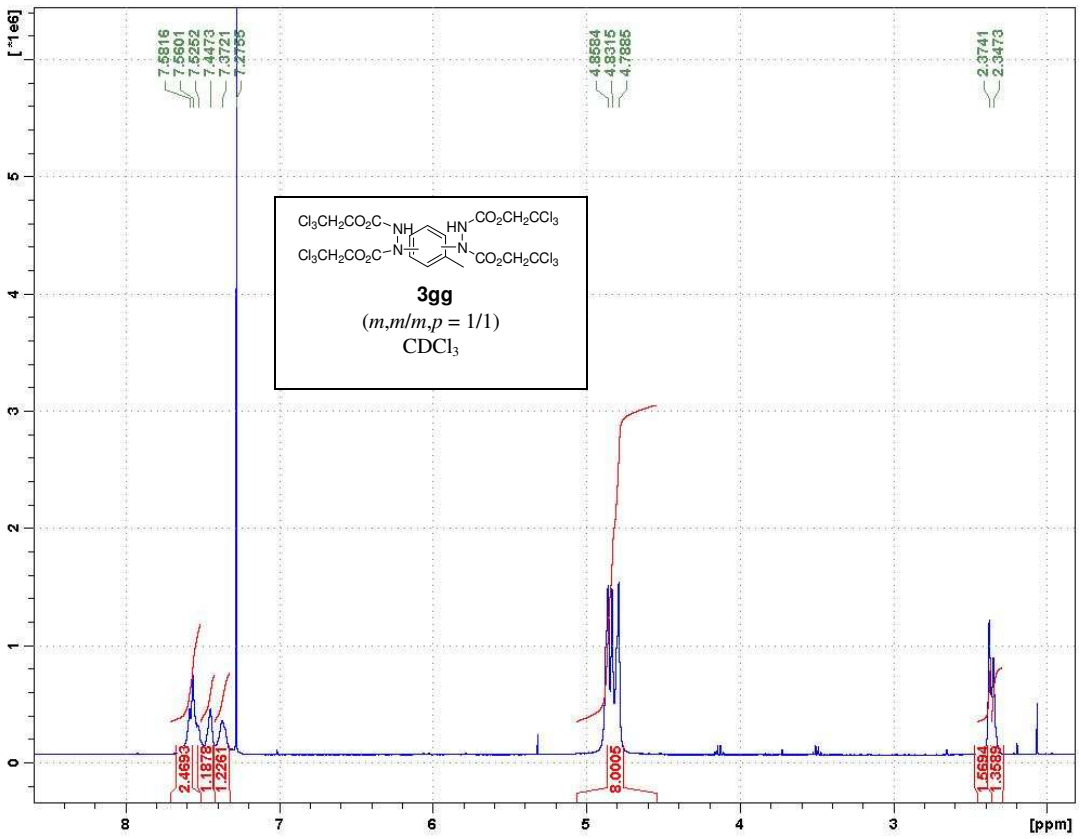
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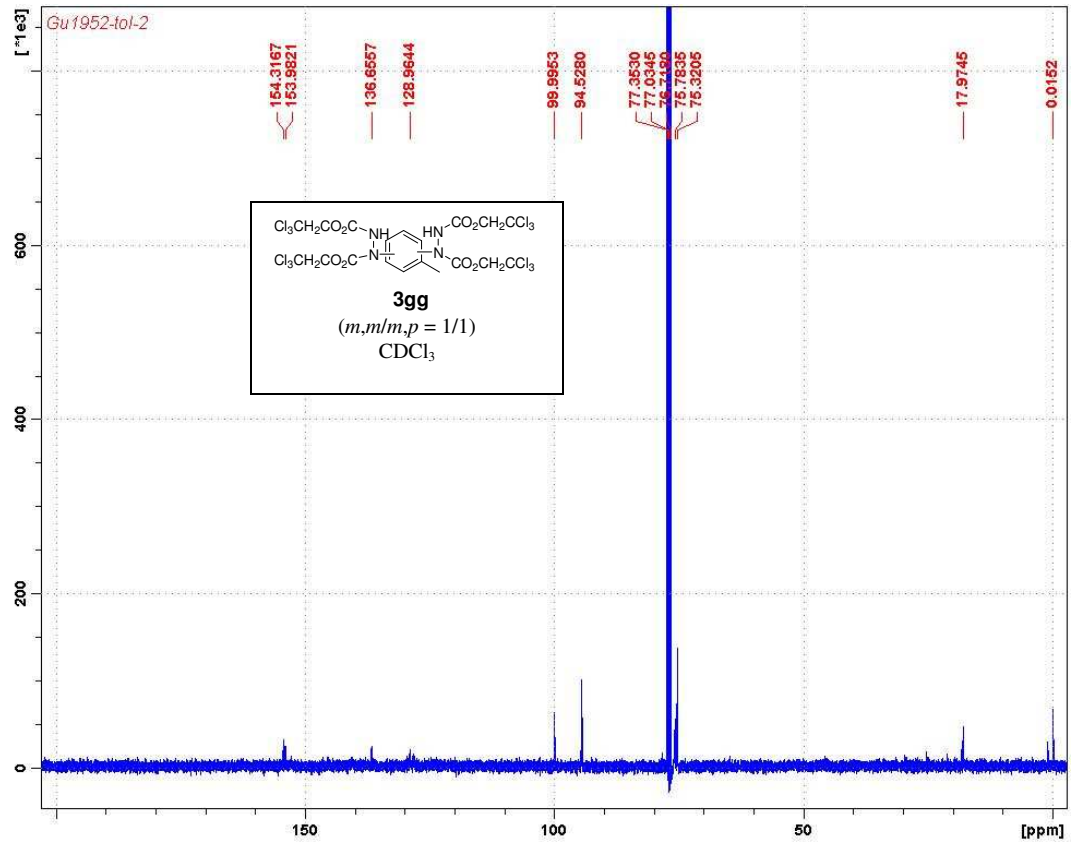
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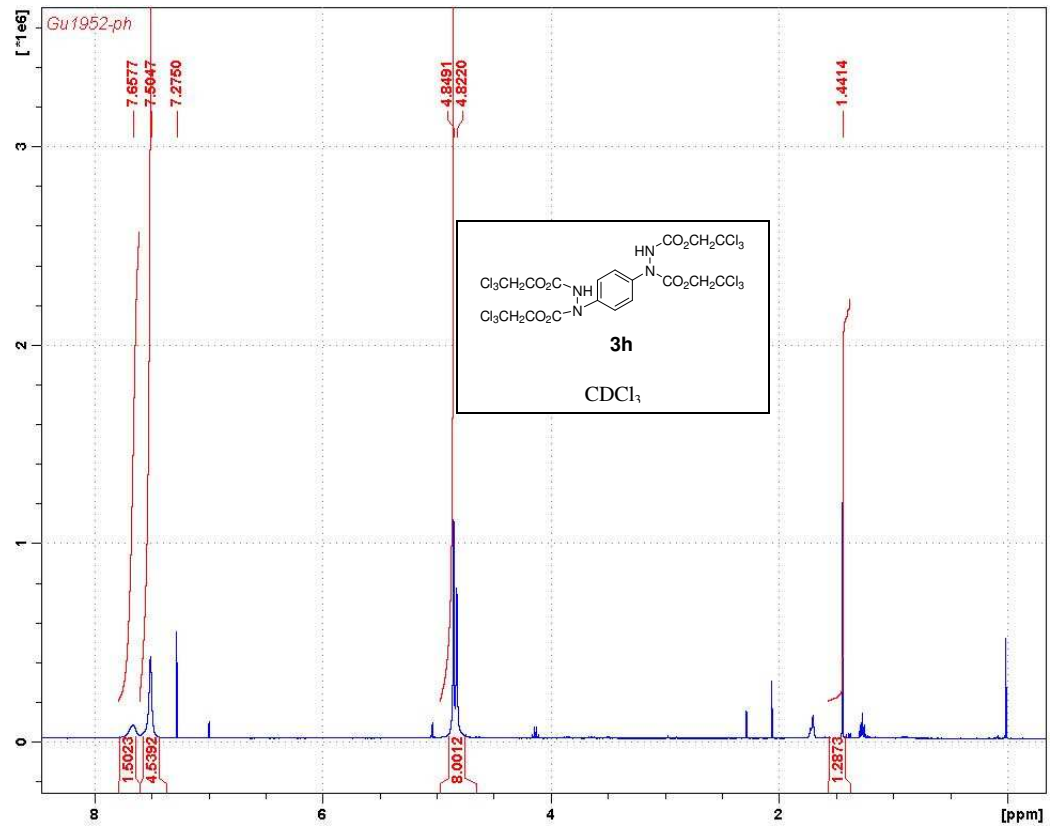
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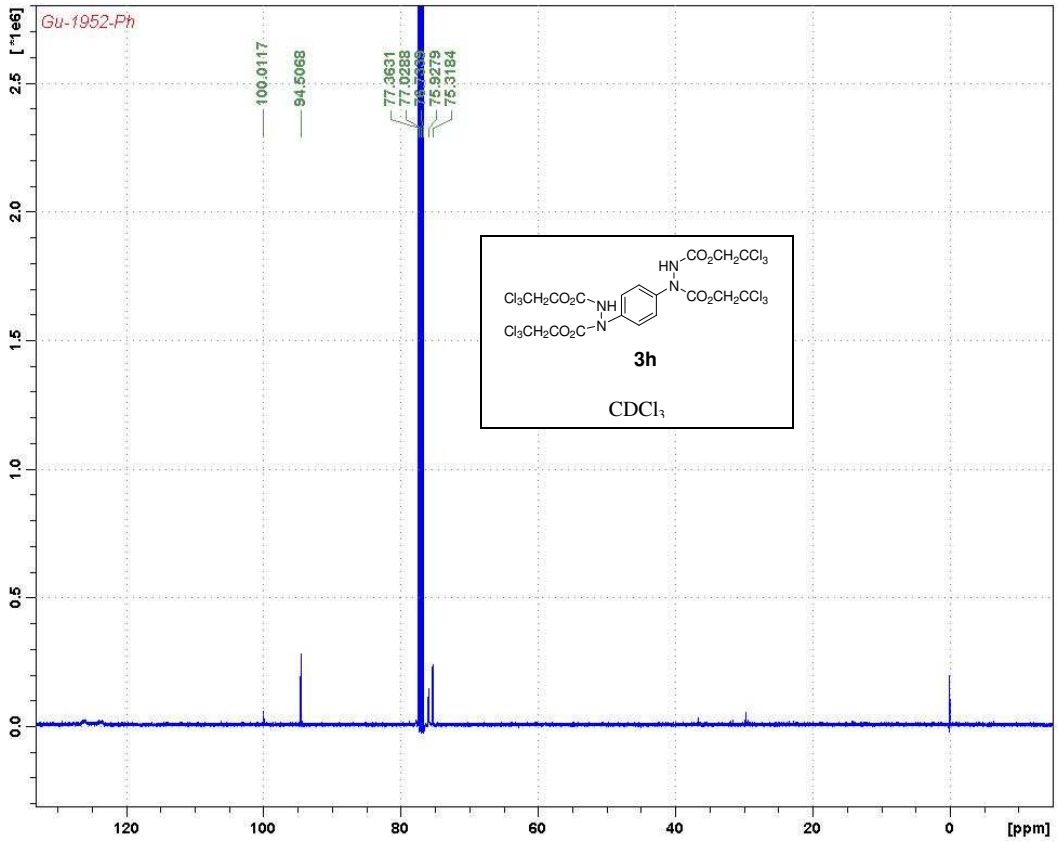
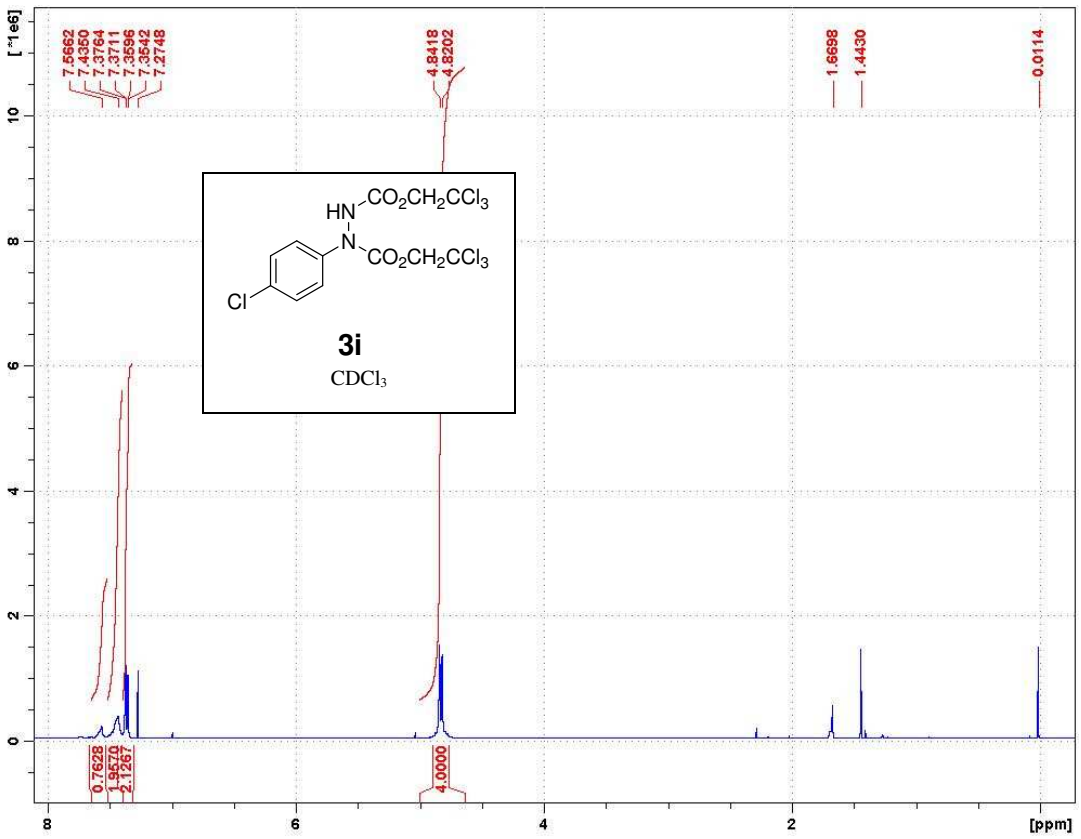
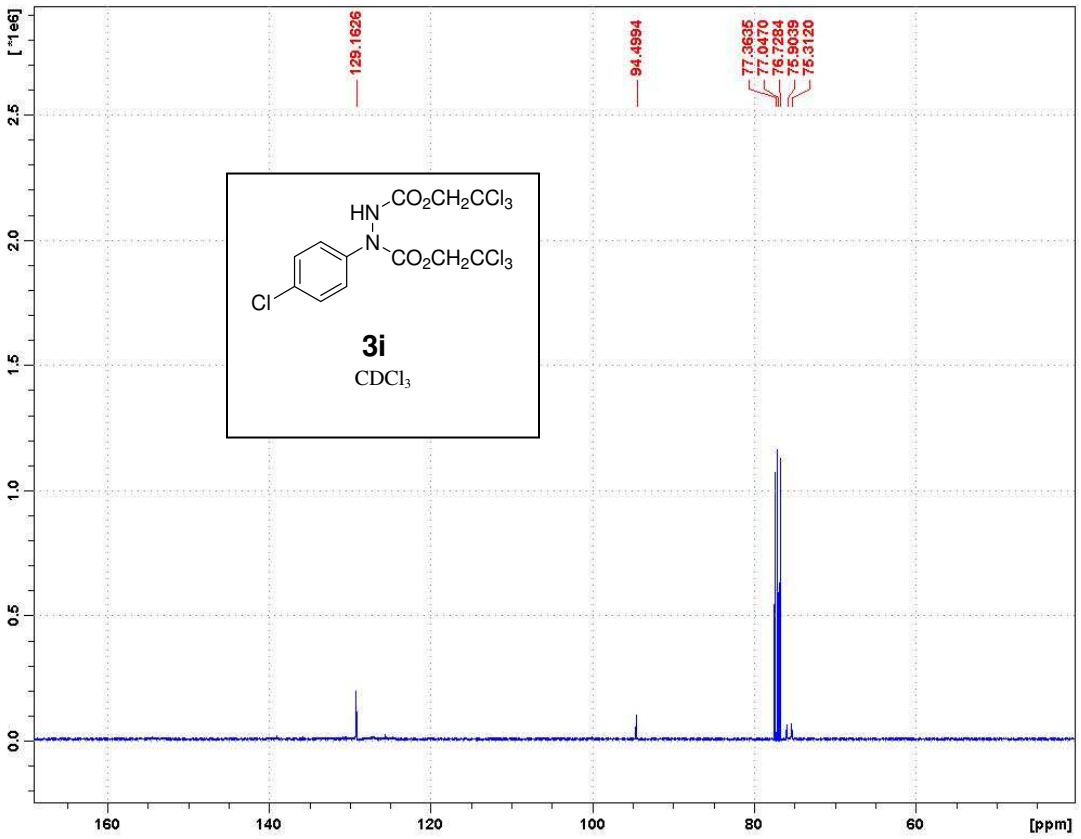
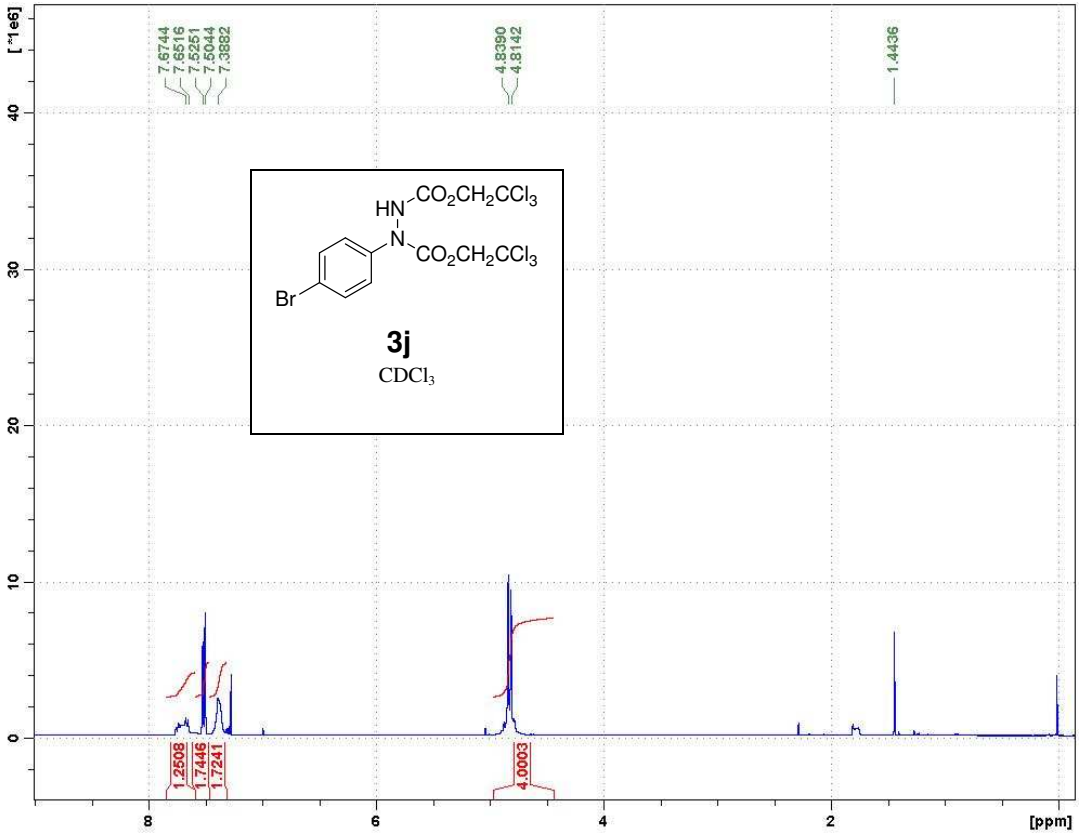
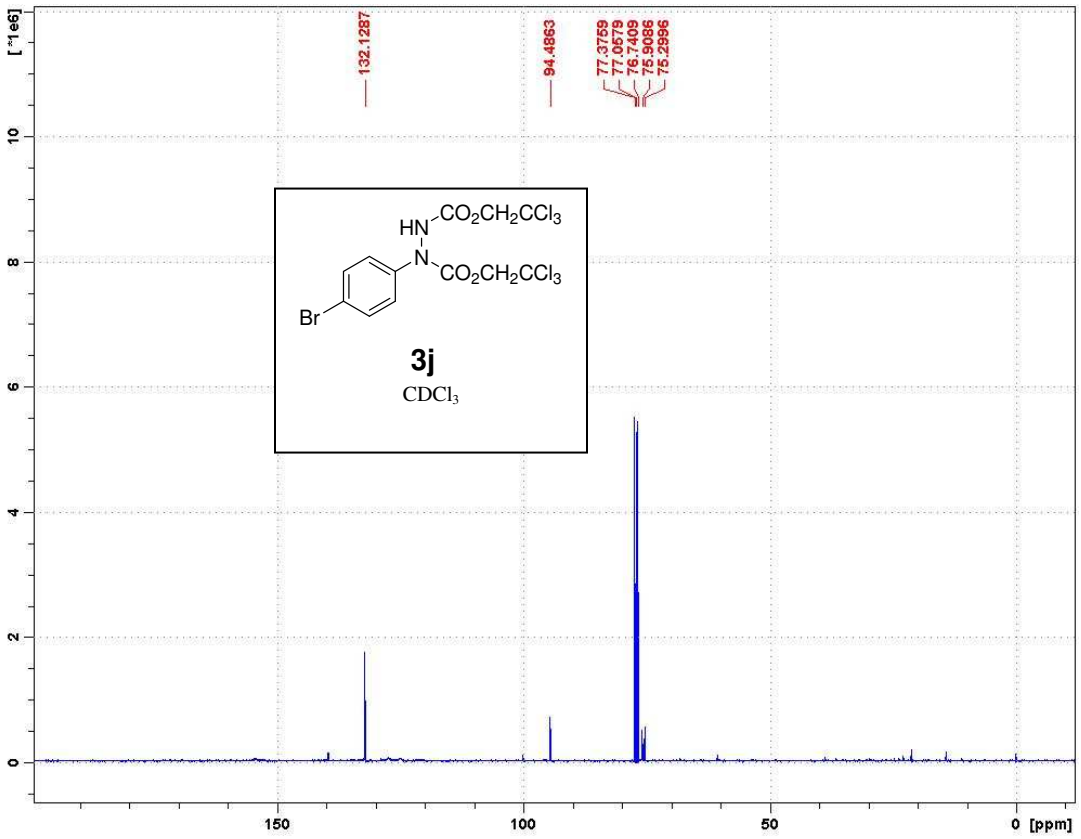
3h
CDCl3

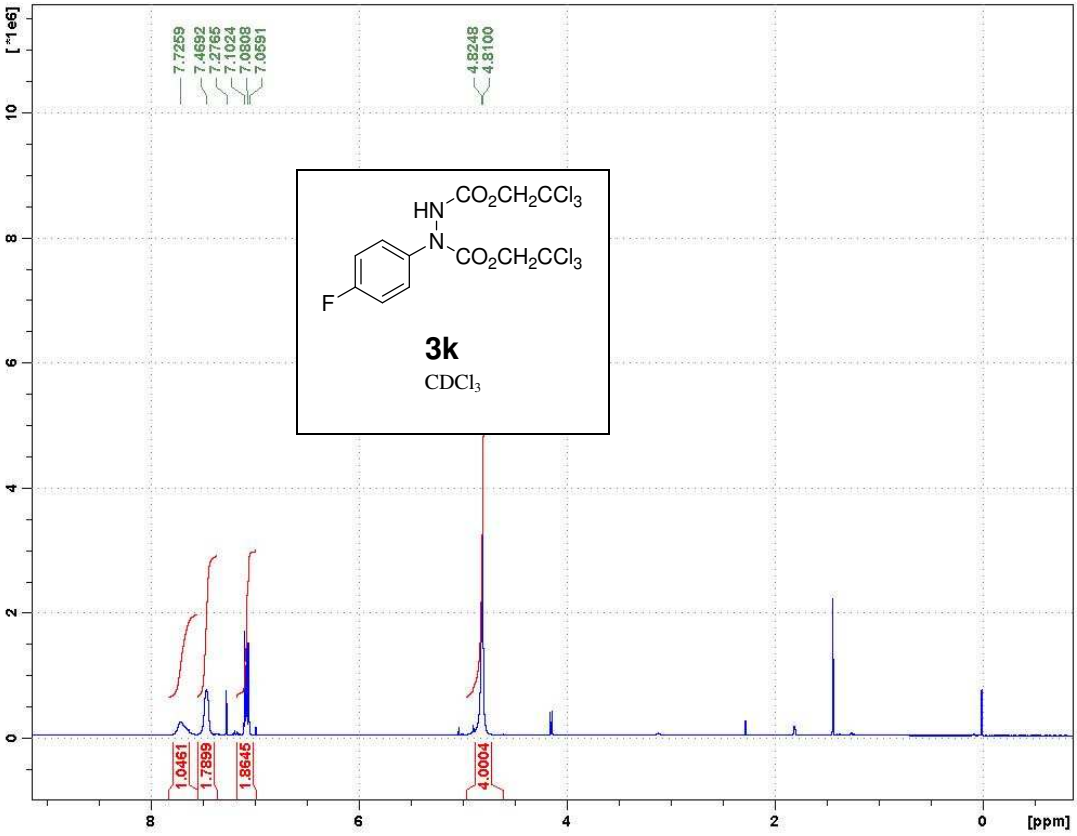

Gu-1952-Ph
[*1e6]
100.0117
94.5068
77.3631
77.0288
75.9279
75.3184
[ppm]
3h
CDCl3

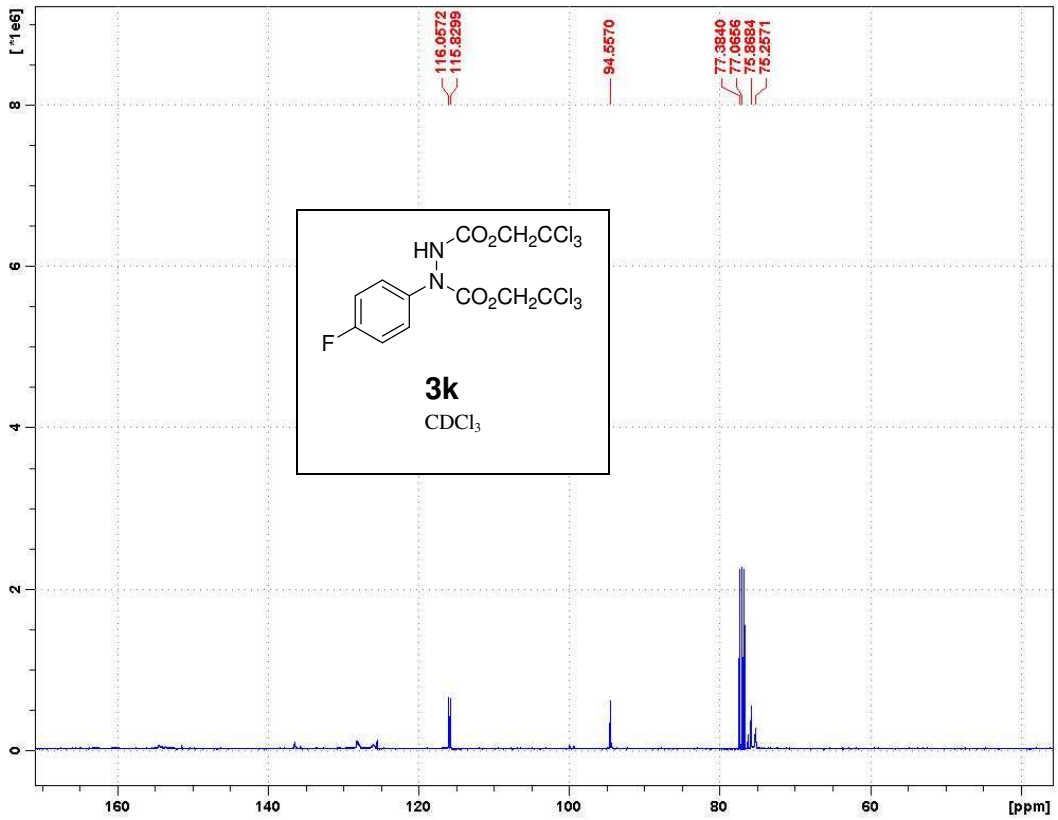

7.5662
7.4350
7.3764
7.3711
7.3596
7.3542
7.2748
4.8418
4.8202
1.6698
1.4430
0.0114
HN
CO2CH2CCl3
N
CO2CH2CCl3
Cl
3i
CDCl3
0.7628
1.9570
2.1267
4.0000
[*1e6]
[ppm]

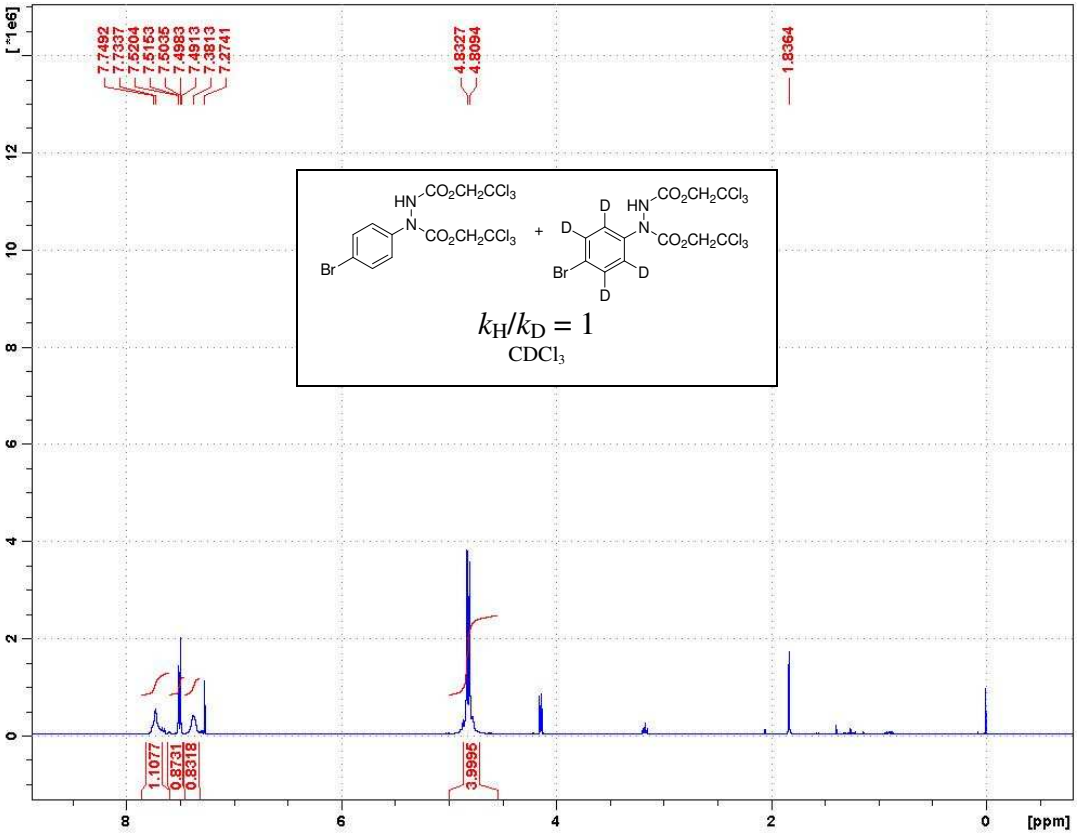

129.1626
94.4994
77.3635
77.0470
76.7284
75.9039
75.3120
HN
CO2CH2CCl3
N
CO2CH2CCl3
Cl
3i
CDCl3
[*1e6]
[ppm]

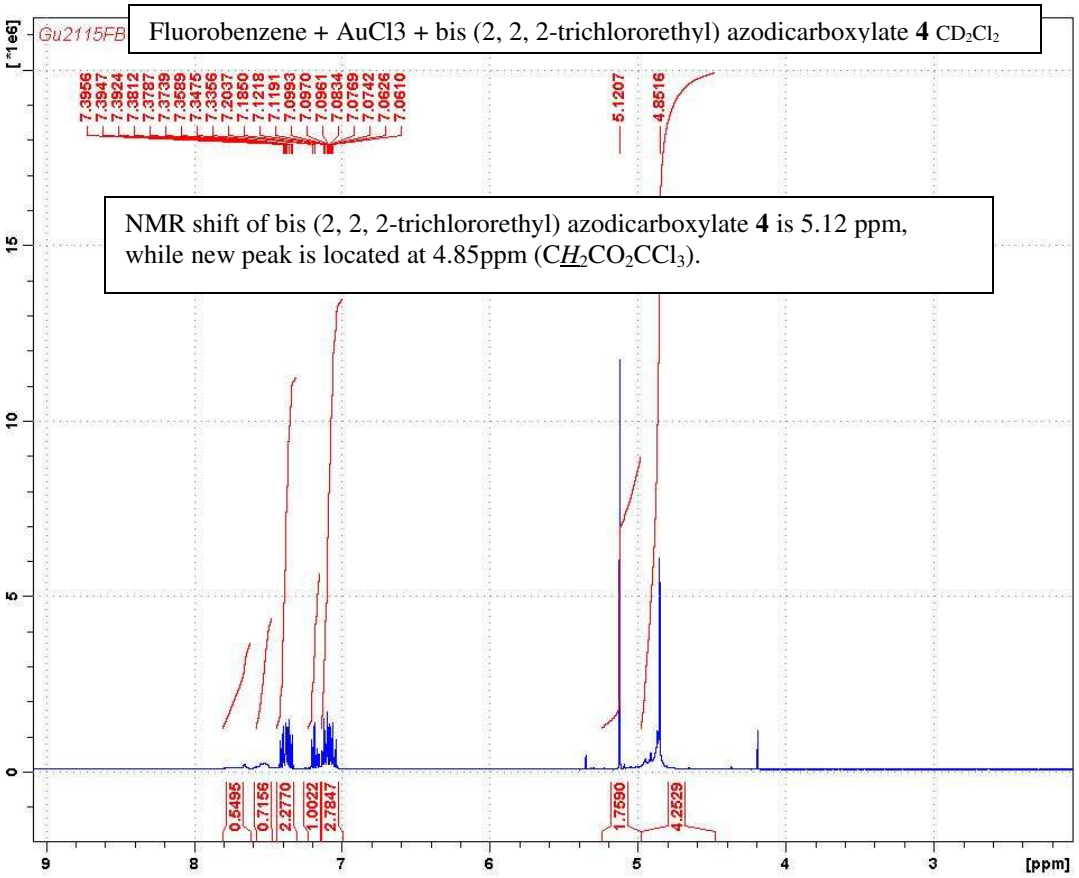

7.6744
7.6516
7.5251
7.5044
7.3882
4.8390
4.8142
1.4436
HN
CO2CH2CCl3
N
CO2CH2CCl3
Br
3j
CDCl3
1.2508
1.7446
1.7241
4.0003
[*1e6]
[ppm]


132.1287
94.4863
77.3759
77.0579
76.7409
75.9086
75.2996
HN
CO2CH2CCl3
N
CO2CH2CCl3
Br
3j
CDCl3
[*1e6]
[ppm]


7.7259
7.4692
7.2765
7.1024
7.0808
7.0591
4.8248
4.8100
HN
CO2CH2CCl3
N
CO2CH2CCl3
F
3k
CDCl3
1.0461
1.7899
1.8645
4.0004
[ppm]


116.0572
115.8299
94.5570
77.3840
77.0656
75.8684
75.2571
HN
CO2CH2CCl3
N
CO2CH2CCl3
F
3k
CDCl3
[ppm]


7.7492
7.7337
7.5204
7.5153
7.5035
7.4983
7.4913
7.3813
7.2741
4.8327
4.8094
1.8364
HN
CO2CH2CCl3
N
CO2CH2CCl3
Br
+
D
HN
CO2CH2CCl3
N
CO2CH2CCl3
Br
kH/kD = 1
CDCl3
1.1077
0.8731
0.8318
3.9995
[*1e6]
[ppm]


Gu2115FB
Fluorobenzene + AuCl3 + bis (2, 2, 2-trichlororethyl) azodicarboxylate 4 CD2Cl2
7.3956
7.3947
7.3924
7.3812
7.3787
7.3739
7.3589
7.3475
7.3356
7.2037
7.1850
7.1218
7.1191
7.0993
7.0970
7.0961
7.0834
7.0769
7.0742
7.0626
7.0610
5.1207
4.8516
NMR shift of bis (2, 2, 2-trichlororethyl) azodicarboxylate 4 is 5.12 ppm,
while new peak is located at 4.85ppm (CH2CO2CCl3).
0.5495
0.7156
2.2770
1.0022
2.7847
1.7590
4.2529
[*1e6]
[ppm]

References

(1). Bombek, S.; Lenarsic, R.; Kocevar, M.; Jalmes, L-S.; Desmurs, J.–R. and Polanc, S. *Chem. Commun.* **2002**, 1494.