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Base-promoted transformation of 2-C(O)R-1,8-bis(dimethylamino)naphthalenes into benzo[*g*]indole derivatives

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8: Colorless crystals, mp 116–117 °C. Yield 0.07 g (7%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.72 (s, 6H), 4.09 (s, 3H), 7.18 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.38–7.41 (m, 1H), 7.44 (q, *J* = 1.3 Hz, 1H), 7.55–7.59 (m, 2H), 7.74 (dq, *J* = 8.6, 1.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 40.3, 43.3, 107.5 (q, *J* = 36.4 Hz), 114.6, 118.1, 118.7, 122.6 (q, *J* = 2.0 Hz), 123.2, 123.3, 124.7, 124.4 (q, *J* = 266.1 Hz), 129.9 (q, *J* = 5.1 Hz), 132.8, 134.1, 148.5. EI–MS, *m/z* (I, %): 292 (100) $[M]^+$.

9: Yellow crystals, mp 119–120 °C. Yield 0.08 g (6%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.87 (s, 6H), 3.85 (s, 3H), 7.06 (d, *J* = 8.6 Hz, 1H), 7.45 (q, *J* = 1.2 Hz, 1H), 7.95 (dq, *J* = 9.1, 1.0 Hz, 1H), 8.11 (dq, *J* = 8.5, 2.1 Hz, 1H), 8.94 (d, *J* = 9.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 38.6. 42.2, 108.0 (q, *J* = 36.9 Hz), 110.2, 117.8 (m), 119.5, 122.47, 122.5 (d, *J* = 1.7 Hz), 124.0 (q, *J* = 266.3 Hz), 133.3 (dd, *J* = 9.9, 5.0 Hz), 132.8 (q, *J* = 4.1 Hz), 133.3, 133.6, 155.1, 179.8 (q, *J* = 32.0 Hz). EI–MS, *m/z* (I, %): 388 (39), $[M]^+$, 319 (100) $[M–CF_3]^+$.

10: Beige crystals, mp 73–75 °C (*n*-hexane). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.73 (s, 6H), 4.07 (s, 3H), 6.63 (d, *J* = 3.0 Hz, 1H), 7.12 (d, *J* = 3.0 Hz, 1H), 7.13 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.31–7.34 (m, 1H), 7.45 (dd, *J* = 8.4, 0.5 Hz, 1H), 7.56 (ddd, *J* = 7.9, 1.2, 0.5 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 39.6, 43.2, 103.0, 113.6, 118.4, 121.1, 121.4, 123.0, 123.6, 127.0, 130.7, 132.3, 133.8, 148.4. EI–MS, *m/z* (I, %): 224 (68) $[M^+]$.

*Procedure S1: Trifluoroacetylation of indole derivative **8**.*

Trifluoroacetic anhydride (0.05 mL, 0.36 mmol) as a solution in dry Et_2O (0.5 mL) was added portionwise to a solution of compound **8** (100 mg, 0.34 mmol) in dry Et_2O (10 mL) under argon atmosphere at –20 °C. Then the temperature was raised to ambient, the red colored reaction mixture was kept for 4.5 h and treated with 10% aqueous Na_2CO_3 till pH 11–12. The organic layer was separated and the water layer was extracted with Et_2O (4 × 5 mL). The combined organic layers were evaporated to dryness and chromatographed by TLC (Al_2O_3, Et_2O–petroleum ether, 1:2). Four fractions were collected (see SI-1, Figure S1): yellow (R_f = 0.1), pale orange (R_f = 0.2), yellow (R_f = 0.4), yellow (R_f = 0.7). The first one represented a mixture of indoles **11** and **14**, which were not separated and identified by their rather distinct NMR spectra (SI-2, p. S-10). Compound **11** was later obtained in pure state in another reaction (see procedure S2). The other fractions contained individual indoles **12**, **9** and **13**, respectively. The starting indole **8** was also recovered in a yield 19 mg (19%).

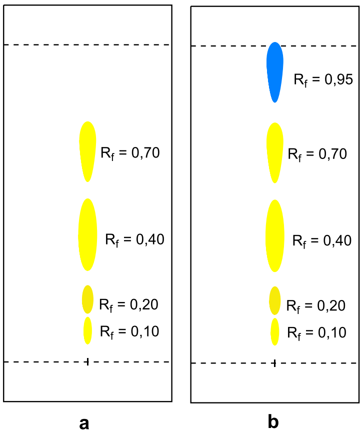


Figure S1 TLC of the reaction mixture before (a) and after (b) iodine vapor exposition.

12: Yellow crystals, mp 184–189 °C. Yield 14 mg (6%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.88 (s, 6H), 3.98 (s, 3H), 7.09 (d, J = 8.6 Hz, 1H), 7.95 (q, J = 1.7 Hz, 1H), 8.14 (dq, J = 8.6, 2.0 Hz, 1H), 8.64 (d, J = 9.1 Hz, 1H), 9.03 (d, J = 9.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 39.6, 42.4, 110.6, 110.7, 115.0, 116.9 (q, J = 291.2 Hz), 117.3 (q, J = 293.3 Hz), 118.1, 121.8, 124.4, 125.4, 133.1 (dd, J = 8.3, 4.1 Hz), 133.8, 134.2, 139.2 (dd, J = 9.6, 4.8 Hz), 155.0, 175.2 (q, J = 35.2 Hz), 179.9 (q, J = 32.7 Hz).

13: Yellow oil. Yield 14 mg (13%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.87 (s, 6H), 3.81 (s, 3H), 6.67 (d, J = 3.0 Hz, 1H), 7.00 (d, J = 8.6 Hz, 1H), 7.13 (d, J = 3.1 Hz, 1H), 7.27 (s, 1H), 7.86 (d, J = 8.9 Hz, 1H), 8.07 (dq, J = 8.6, 2.2 Hz, 1H), 8.85 (d, J = 8.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 38.0, 42.1, 103.4, 109.3, 115.4, 117.6, 117.6 (q, J = 293.6 Hz), 124.7, 127.0, 131.2, 132.3 (q, J = 4.4 Hz), 133.0, 133.1 (dd, J = 1.3, 0.7 Hz), 155.2, 179.8 (dd, J = 64.2, 32.0 Hz).

*Procedure S2: Trifluoroacetylation of compound **9**.*

Trifluoroacetic anhydride (0.08 mL, 0.34 mmol) dissolved in dry Et_2O (0.4 mL) was added by portions to a solution of indole derivative **9** (100 mg, 0.26 mmol) in dry Et_2O (10 mL) under argon atmosphere at room temperature. The bright-yellow reaction mass was then refluxed for 13 h and treated with water (20 mL) and 5% aq. Na_2CO_3 till pH 7–8. The organic layer was separated and the water layer was extracted with Et_2O (5 × 5 mL). The combined organic layers were evaporated to dryness and chromatographed by TLC (Al_2O_3, EtOAc–petroleum ether, 1:5). The yellow-colored fraction (R_f = 0.2) representing product **11** was isolated. The starting compound **9** was also recovered: 63 mg (63%).

11: yellow crystals, mp 189–191 °C, yield 32 mg (26%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 3.22 (s, 6H), 3.62 (s, 3H), 7.47 (q, J = 1.3 Hz, 1H), 8.02 (dq, J = 9.0, 1.0 Hz, 1H), 8.60–8.61 (m, 1H), 8.85 (d, J = 9.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 36.1, 46.1, 105.4, 107.9, 109.1 (q, J = 37.4 Hz), 112.6, 117.3 (q, J = 290.9 Hz), 117.5 (q, J = 293.0 Hz), 118.3, 122.4, 123.6 (q, J = 266.5 Hz), 124.1, 130.3 (dd, J = 9.8, 4.8 Hz), 132.6, 132.7, 135.3–135.9 (m), 162.8, 173.1 (q, J = 34.0 Hz), 177.3 (q, J = 32.5 Hz).

*Procedure S3: Preparation of **5** by deacetylation of **7**.*

Trifluoroacetic acid (0.9 mL, 12.32 mmol) was added to a solution of 2,4-bis(trifluoroacetyl)-1,8-bis(dimethylamino)naphthalene (**7**) (500 mg, 1.23 mmol) in a mixture of MeCN (3.7 mL) and water (1.1 mL). The reaction mixture was refluxed for 26 h and after cooling to the room temperature was neutralized with 5% aq. Na_2CO_3 (~20 mL). After separation of organic and water phases, the latter was extracted with chloroform (4 × 5 mL), the combined organic layers were evaporated to dryness and purified by TLC (Al_2O_3, Et_2O–petroleum ether, 1:1). An orange fraction with R_f = 0.7 was collected. Yield of practically pure monoketone **5** – 295 mg (77%). After recrystallization from *n*-heptane product **5** was obtained as orange needles with mp 103–104 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 2.73 (s, 6H), 3.13 (s, 6H), 6.71 (d, *J* = 8.8 Hz, 1H), 6.79 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.08 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.30–7.42 (m, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ: 43.6. 46.0, 107.5, 112.2, 114.7, 114.9, 118.2, 118.5 (q, *J* = 291.6 Hz), 124.8 (q, *J* = 3.6 Hz), 129.9, 139.5, 151.6, 162.4, 172.9 (q, *J* = 32.2 Hz). EI–MS *m/z* (*I*, %): 310 (42) $[M]^+$.

15: Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.47 (br s, 1H, OH), 2.80 (br s, 6H), 3.06 (s, 3H), 3.52 (dq, *J* = 12.7, 1.5 Hz, 1H), 3.96 (d, *J* = 12.6 Hz, 1H), 6.95 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.34–7.36 (m, 2H), 7.38–7.40 (m, 1H), 7.41 (dq, *J* = 8.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 43.5, 44.7, 45.2, 65.0, 81.1 (q, *J* = 30.6 Hz), 113.2, 117.9, 120.4, 121.9, 122.1, 124.6, 126.9, 122.5–128.3 (m), 139.0, 150.2, 152.7.

16: Colorless crystals, mp 197–198 °C. ^{1}H NMR (600 MHz, $CDCl_3$, –58 °C) δ: 1.87 (s, 3H). 2.40 (s, 3H), 2.49–2.75 (m, 15H), 3.04 (s, 3H), 6.82 (s, 1H), 7.32–7.51 (m, 6H), 7.70 (dd, *J* = 57.7, 7.0 Hz, 2H), 8.07 (s, 1H), 12.52 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, –58 °C) δ: 42.2, 44.1, 44.8, 45.6, 46.7, 48.0, 50.0, 83.2 (dd, *J* = 51.2, 24.9 Hz), 117.6, 117.9, 125.1, 125.4, 125.7, 125.8, 126.1, 126.4, 127.0, 127.2, 129.1, 129.7, 135.2, 135.7, 137.3, 141.6, 144.6, 149.1, 151.4, 153.0. ESI–HRMS m/z: 525.2819 $[M + H]^+$ (calc. for $C_{30}H_{35}F_3N_4O$ 525.2836).

Procedure S4: *Dehydration of alcohol* ***15***.

A solution of alcohol **15** (16 mg, 0.052 mmol) in CH_2Cl_2 (6 mL) was poured into chromatographic column (6 × 1.3 cm) filled with silica gel. After the solvent stacked, the column was closed and allowed to stand overnight. The column was then eluted with acetone to give benzo[*g*]indole **8** as a single product. Yield 12 mg (80%).

Procedure S5: Reaction of diketone ***7*** *with 2-lithio-1,8-bis(dimethylamino)naphthalene (**4**).*

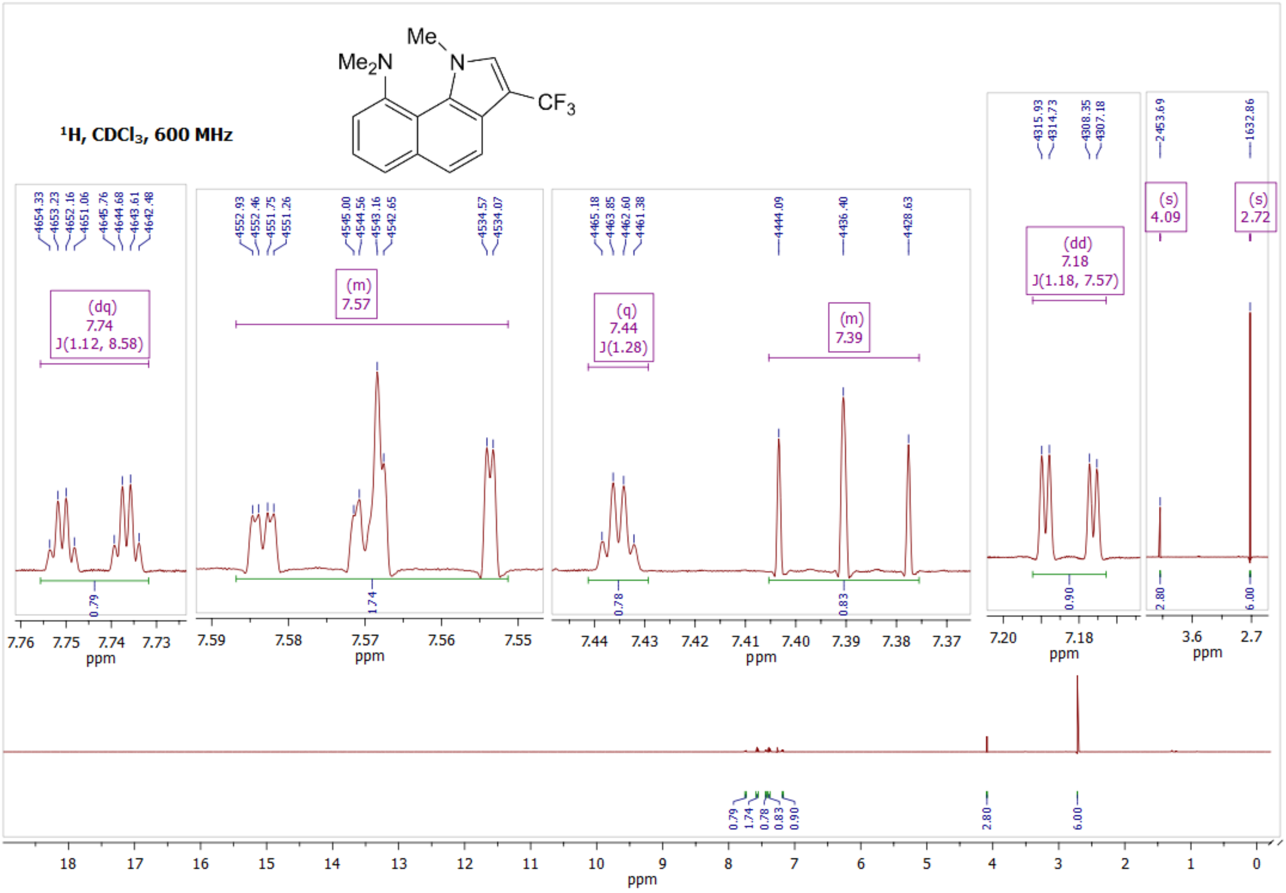
A solution of diketone **7** (230 mg, 0.57 mmol) in dry Et_2O (10 mL) was added portionwise (during 1.5 h) to a solution of **4** obtained from 2-bromo-1,8-bis(dimethylamino)naphthalene (340 mg, 0.12 mmol; see procedure 1) in dry Et_2O (5 mL) under argon atmosphere at –20 °C. The red colored reaction mixture was treated with water (10 mL). The organic layer was separated and the water layer was extracted with Et_2O (4 × 5 mL). The combined organic layers were evaporated to dryness and chromatographed by TLC (Al_2O_3, CH_2Cl_2–hexane, 1:1). The dominating brown fraction (R_f = 0.1) was isolated and crystallized from hexane to give product **19** as colorless crystals with mp 166–167 °C. Yield 157 mg (43%).

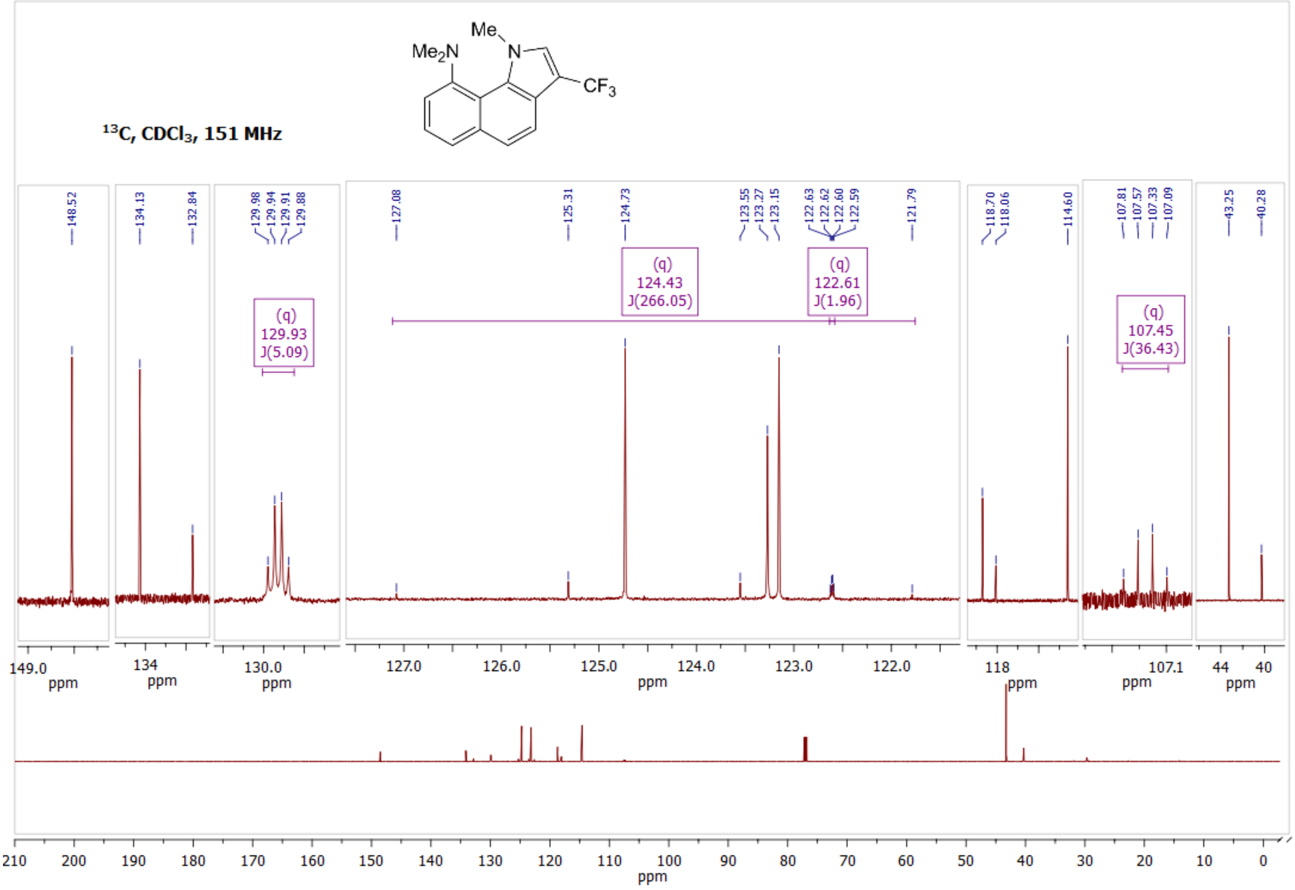
^{1}H NMR (250 MHz, DMSO-d_6, 70 °C) δ: 2.61–2.87 (m, 18H), 2.99 (s, 3H), 3.57 (d, *J* = 12.5 Hz, 1H), 3.93 (d, *J* = 12.5 Hz, 1H), 6.72 (s, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 8.1 Hz, 1H), 7.43–7.72 (m, 4H), 7.18 (d, *J* = 6.4 Hz, 1H), 7.78 (s, 1H), 11.25 (brs, 1H). ^{13}C NMR (63 MHz, DMSO) δ: 44.1, 44.6, 45.3, 47.1, 49.7, 55.7, 65.4, 80.1 (q, *J* = 28.9 Hz), 79.3–80.9 (m), 112.7, 118.2, 120.2, 120.7, 120.7, 121.0, 122.0, 124.5, 125.0, 126.1, 126.7, 127.7, 128.3, 129.0, 129.6, 134.8, 136.2, 137.6, 147.4, 147.5, 150.7, 152.7, 153.1. ESI–HRMS *m/z*: 621.2636 [M + H]$^+$ (calc. for $C_{32}H_{35}F_3N_4O$ 621.2659).

22: ^{1}H NMR (250 MHz, $CDCl_3$) *δ*: 2.85 (s, 12H), 2.95 (s, 12H), 6.96 (d, *J* = 6.8 Hz, 2H), 7.18–7.41 (m, 6H), 7.46 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) *δ*: 44.9, 45.3, 87.5, 113.1, 113.6, 120.4, 121.5, 122.1, 122.4, 125.9, 127.7, 128.4, 128.6, 140.1, 152.3, 153.1, 197.4. IR (nujol): 1647 cm^{-1} (C=O). ESI–HRMS m/z: 455.2775 [M + H]$^+$ (calc. for $C_{29}H_{35}N_4O$ 455.2805).

23: ^{1}H NMR (250 MHz, $CDCl_3$) *δ*: 2.78 (s, 6H), 2.92 (s, 6H), 2.93 (s, 6H), 4.32 (s, 3H), 7.14 (s, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.23–7.33 (m, 1H), 7.38–7.75 (m, 8H). ^{13}C NMR (63 MHz, $CDCl_3$), *δ*: 40.1, 43.7, 45.1, 45.7, 114.1, 114.2, 118.8, 119.2, 120.7, 121.7, 122.8, 123.1, 123.5, 124.2, 124.7, 125.6, 127.3, 128.1, 130.0, 131.5, 132.8, 134.4, 137.7, 148.5, 148.9, 152.1. ESI–HRMS m/z: 437.2658 [M + H]$^+$ (calc. for $C_{29}H_{33}N_4$ 437.2700).

^{1}H and ^{13}C NMR spectra for products

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N
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J(5.09)
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125.31
124.73
123.55
123.27
123.15
122.63
122.62
122.60
122.59
121.79
(q)
124.43
J(266.05)
(q)
122.61
J(1.96)
118.70
118.06
114.60
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107.57
107.33
107.09
(q)
107.45
J(36.43)
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134
ppm
130.0
ppm
127.0
126.0
125.0
124.0
123.0
122.0
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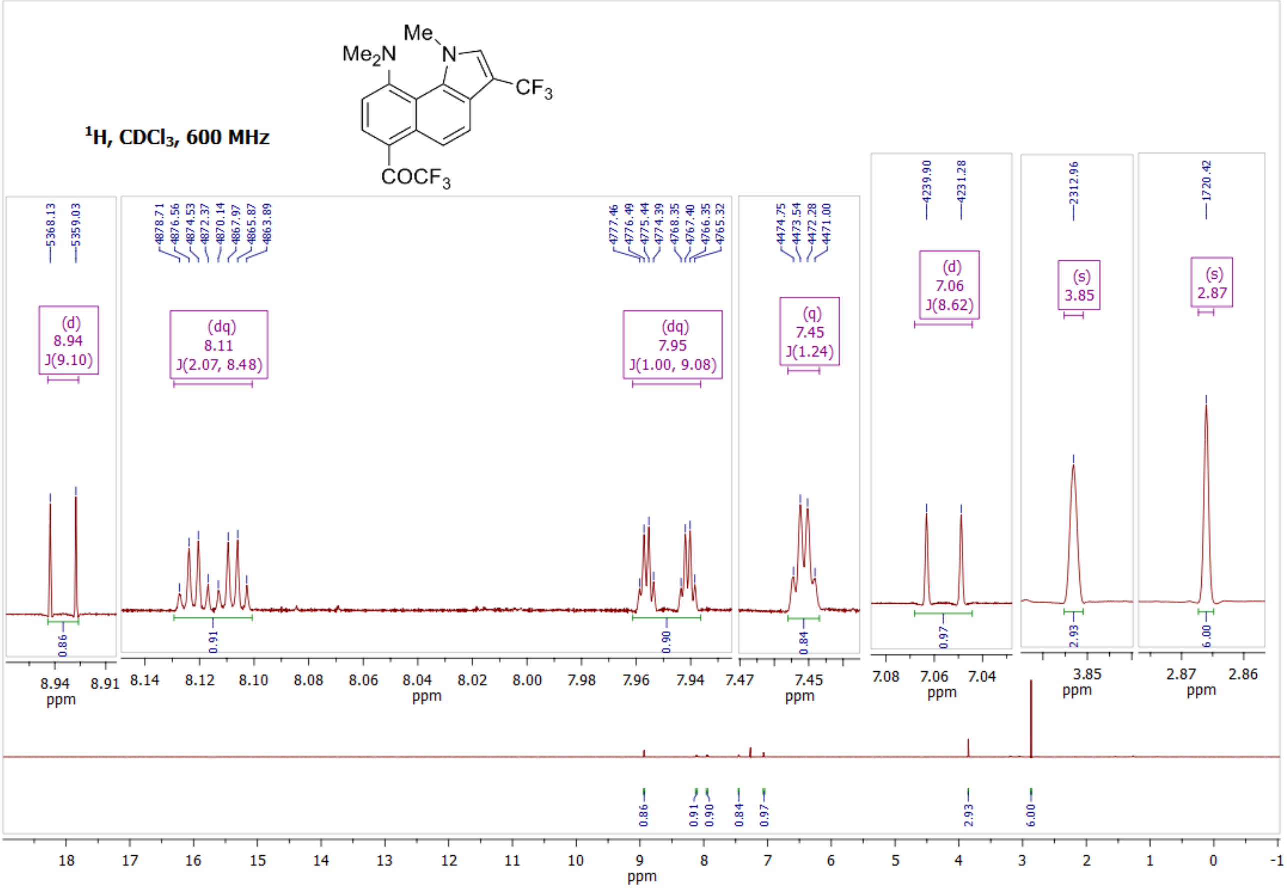
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N
CF3
COCF3
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J(9.10)
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4876.56
4874.53
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4870.14
4867.97
4865.87
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(dq)
8.11
J(2.07, 8.48)
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4776.49
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4765.32
(dq)
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J(1.00, 9.08)
4474.75
4473.54
4472.28
4471.00
(q)
7.45
J(1.24)
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4231.28
(d)
7.06
J(8.62)
2312.96
(s)
3.85
1720.42
(s)
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0.86
0.91
0.90
0.84
0.97
2.93
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8.94
8.91
ppm
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8.10
8.08
8.06
8.04
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ppm
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7.45
ppm
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7.06
7.04
ppm
3.85
ppm
2.87
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ppm
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0.97
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6.00
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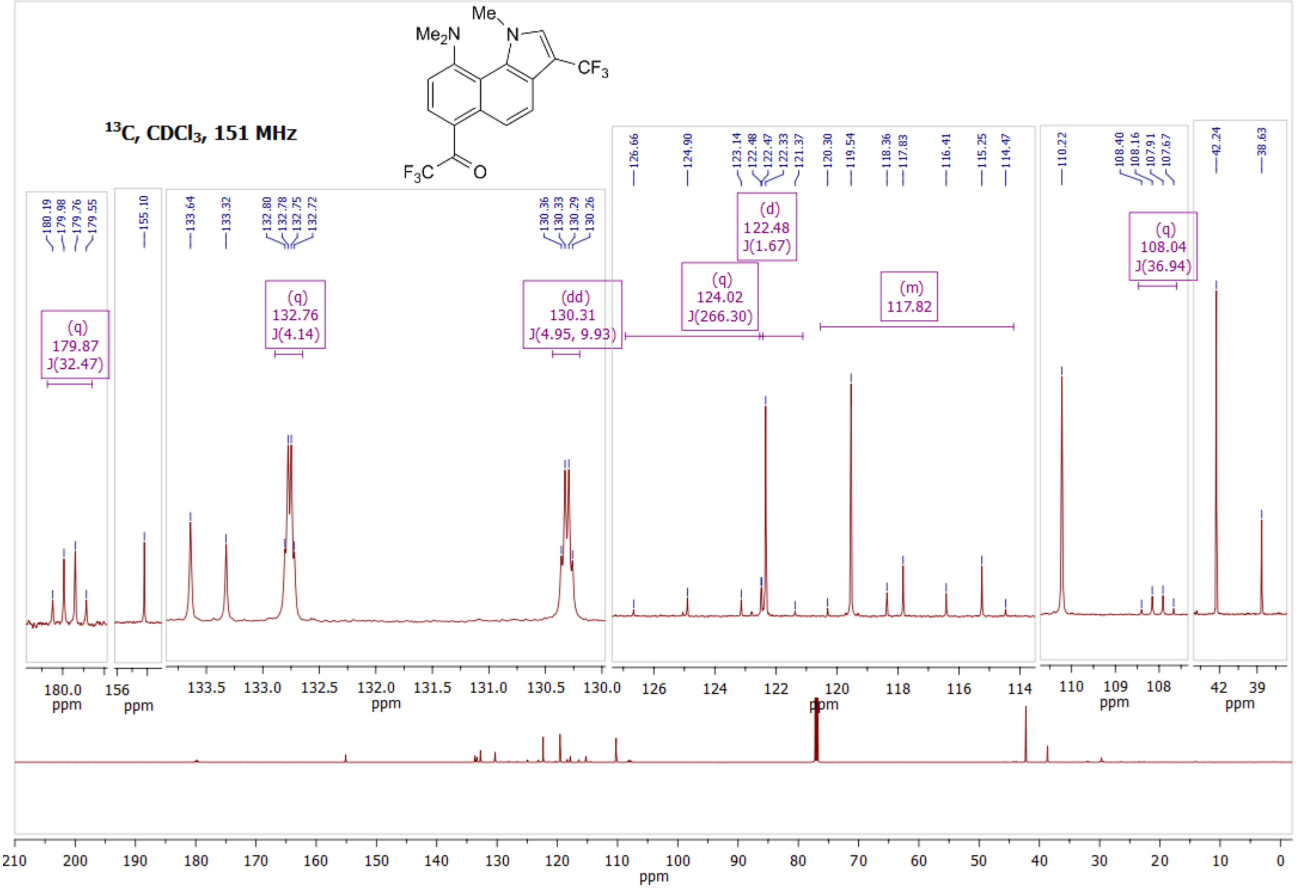
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CF$_3$
F$_3$C
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179.55
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133.64
133.32
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124.90
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121.37
120.30
119.54
118.36
117.83
116.41
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114.47
110.22
108.40
108.16
107.91
107.67
42.24
38.63
(q) 179.87 J(32.47)
(q) 132.76 J(4.14)
(dd) 130.31 J(4.95, 9.93)
(d) 122.48 J(1.67)
(q) 124.02 J(266.30)
(m) 117.82
(q) 108.04 J(36.94)
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131.5
131.0
130.5
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126
124
122
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118
116
114
110
109
108
42
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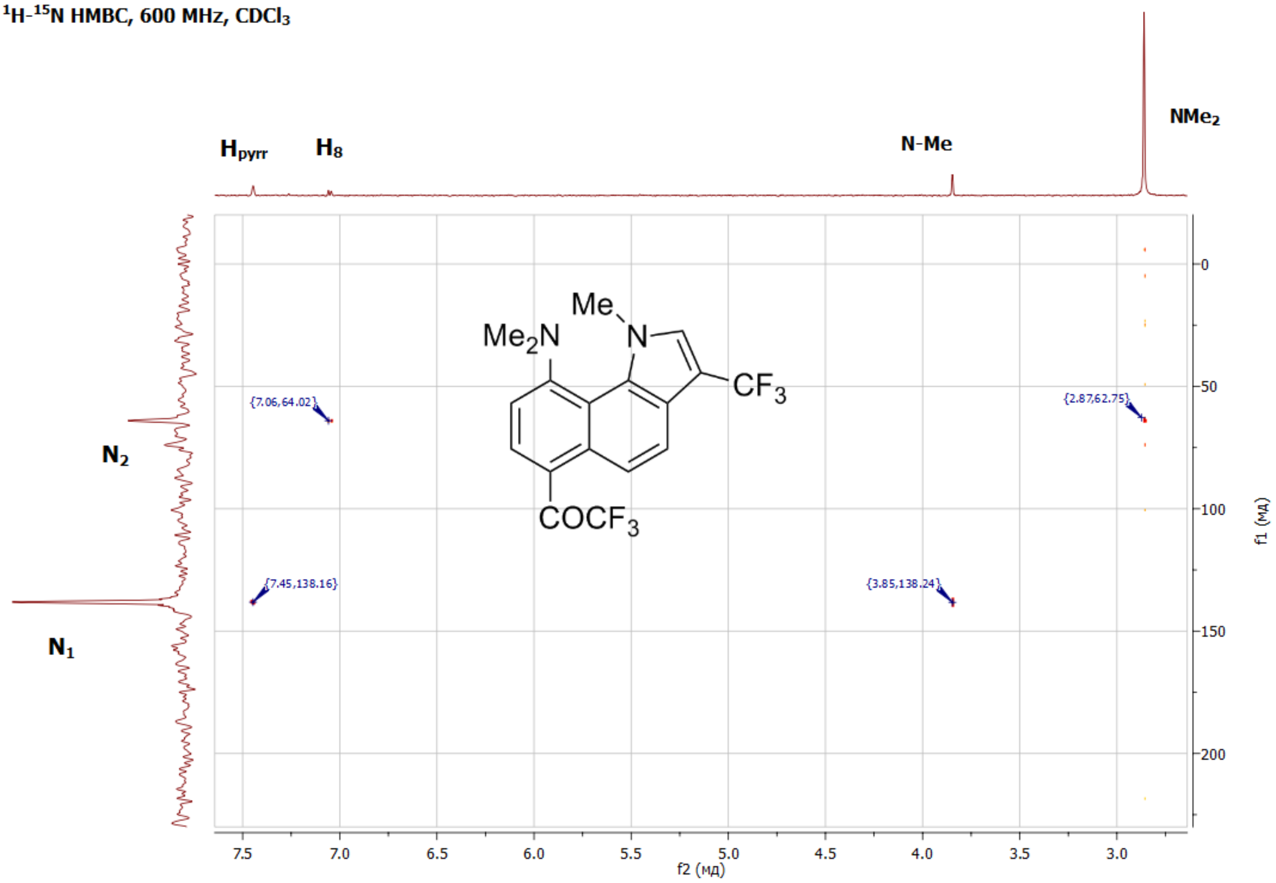
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H$_8$
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Me
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N
CF$_3$
COCF$_3$
{7.06,64.02}
{2.87,62.75}
{7.45,138.16}
{3.85,138.24}
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100
150
200
f1 (мд)
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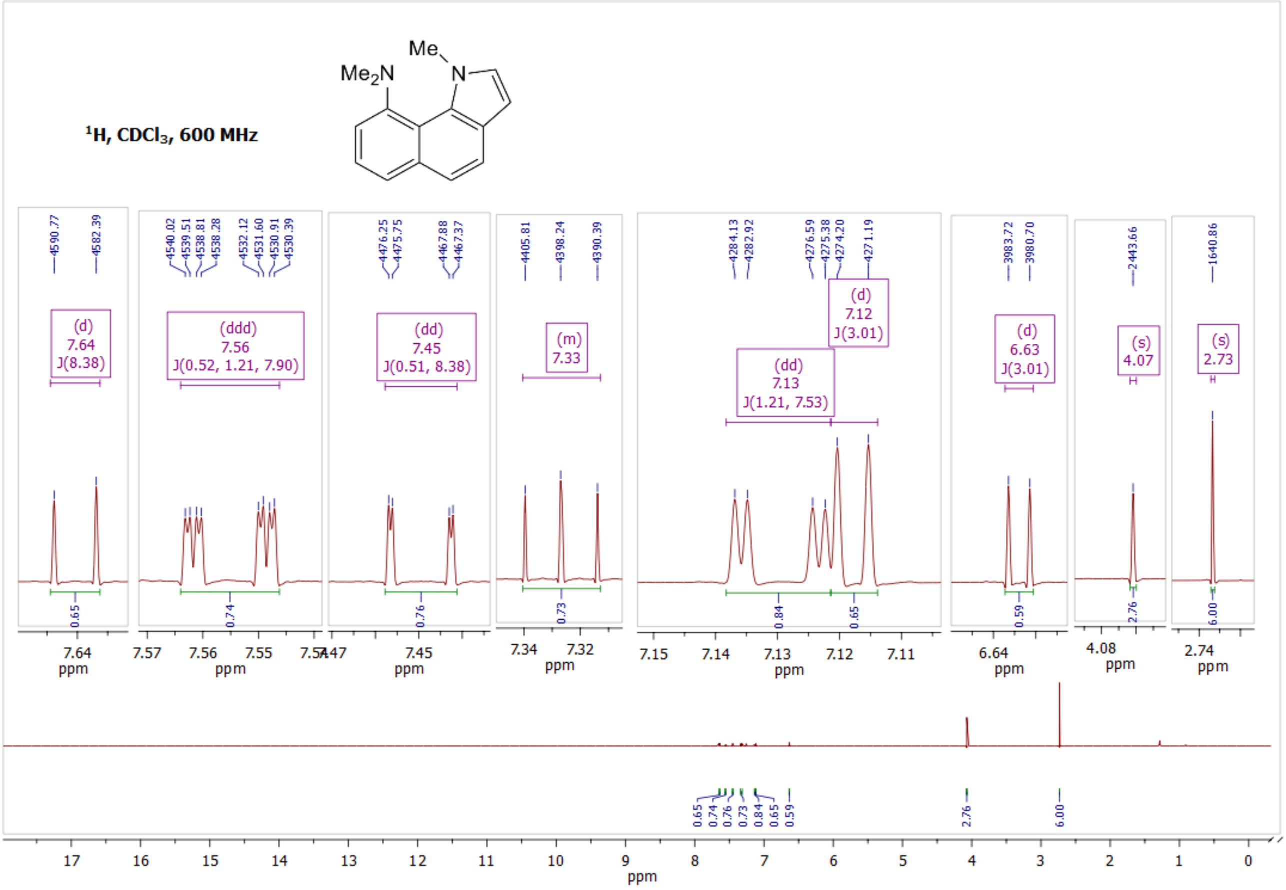
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f2 (мд)



^{1}H, CDCl$_3$, 600 MHz
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Me$_2$N
N
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4582.39
(d) 7.64 J(8.38)
4540.02
4539.51
4538.81
4538.28
4532.12
4531.60
4530.91
4530.39
(ddd) 7.56 J(0.52, 1.21, 7.90)
4476.25
4475.75
4467.88
4467.37
(dd) 7.45 J(0.51, 8.38)
4405.81
4398.24
4390.39
(m) 7.33
4284.13
4282.92
4276.59
4275.38
4274.20
4271.19
(d) 7.12 J(3.01)
(dd) 7.13 J(1.21, 7.53)
3983.72
3980.70
(d) 6.63 J(3.01)
2443.66
(s) 4.07
1640.86
(s) 2.73
0.65
0.74
0.76
0.73
0.84
0.65
0.59
2.76
6.00
7.64
7.57
7.56
7.55
7.54
7.47
7.45
7.34
7.32
7.15
7.14
7.13
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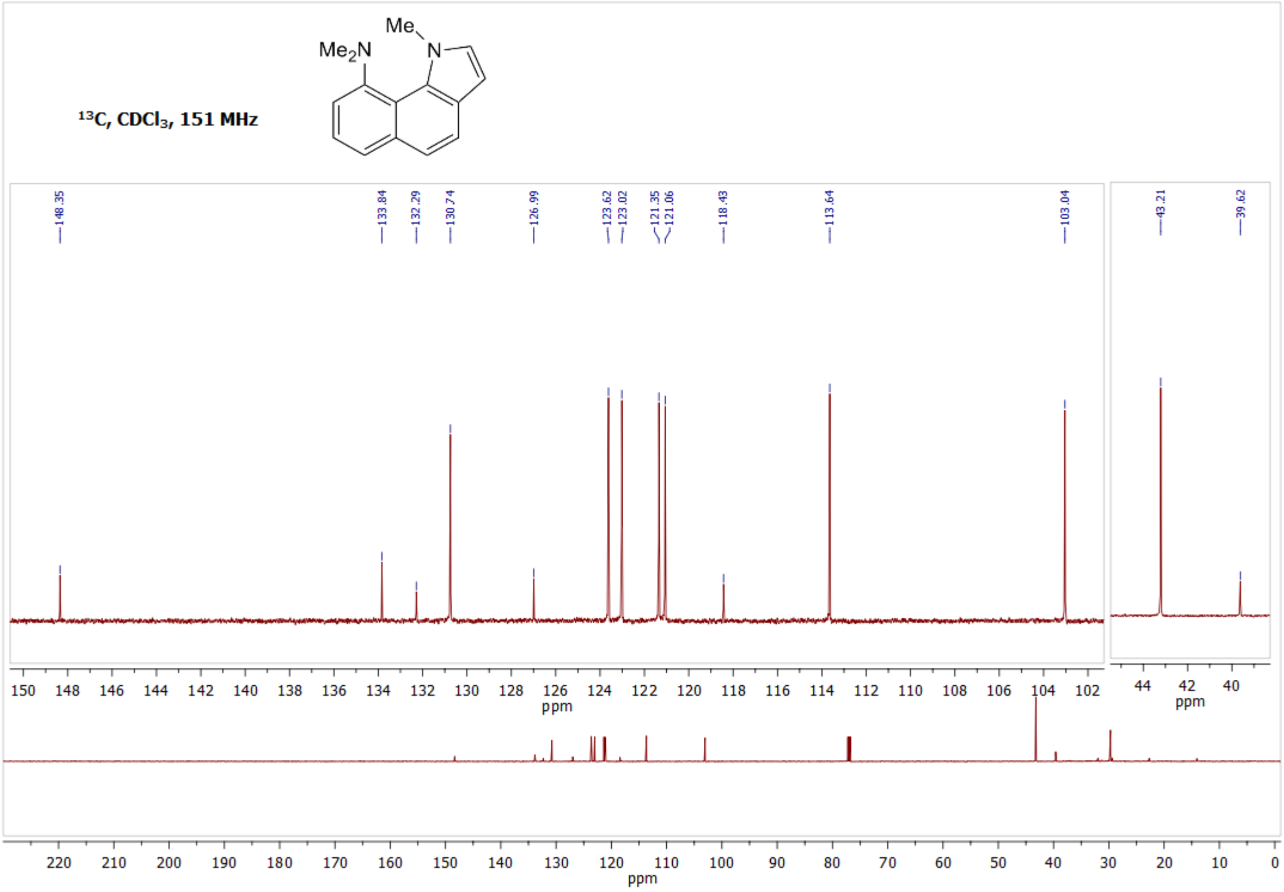

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Me
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N
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130.74
126.99
123.62
123.02
121.35
121.06
118.43
113.64
103.04
43.21
39.62
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
110
108
106
104
102
ppm
44
42
40
ppm
220
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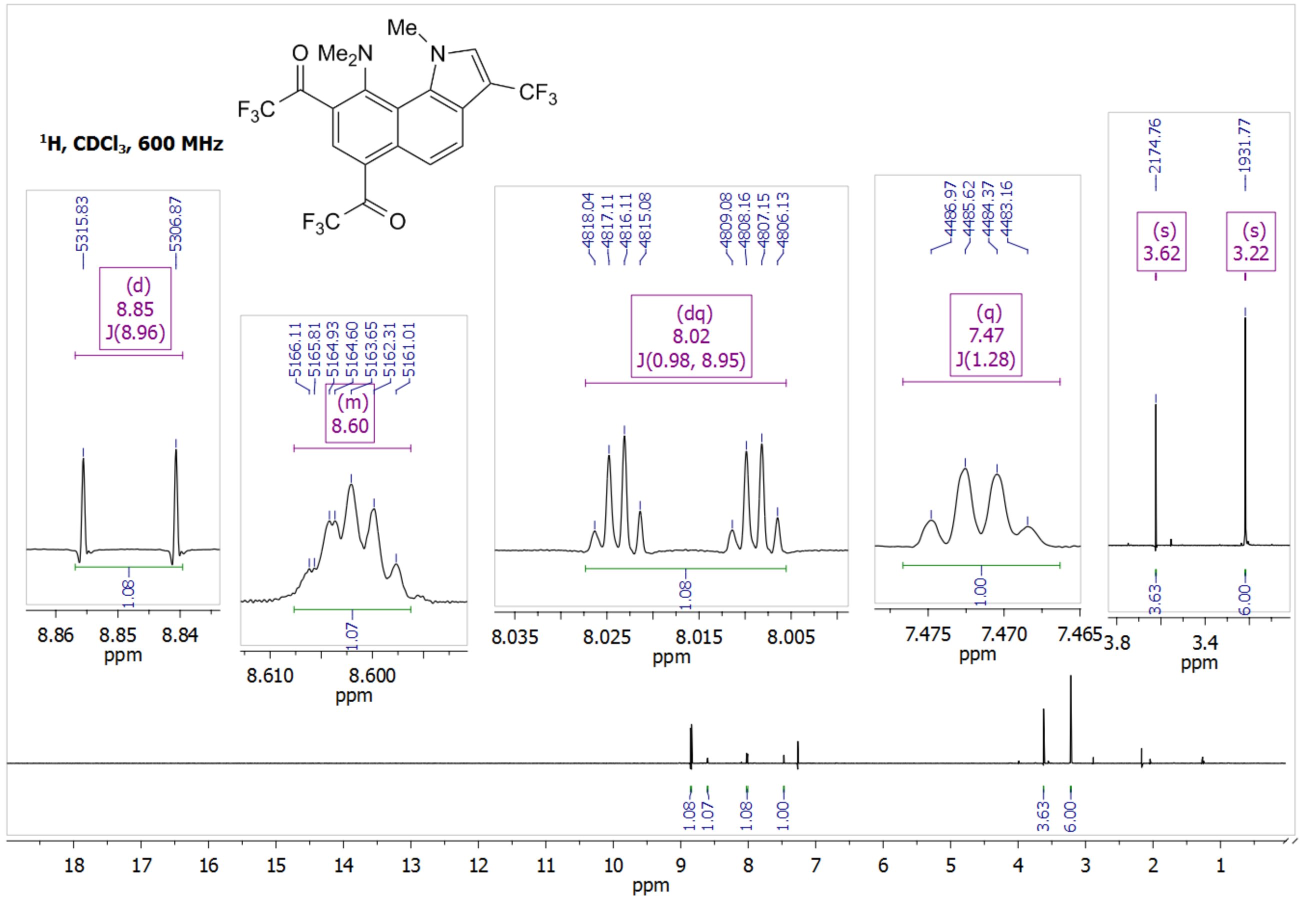
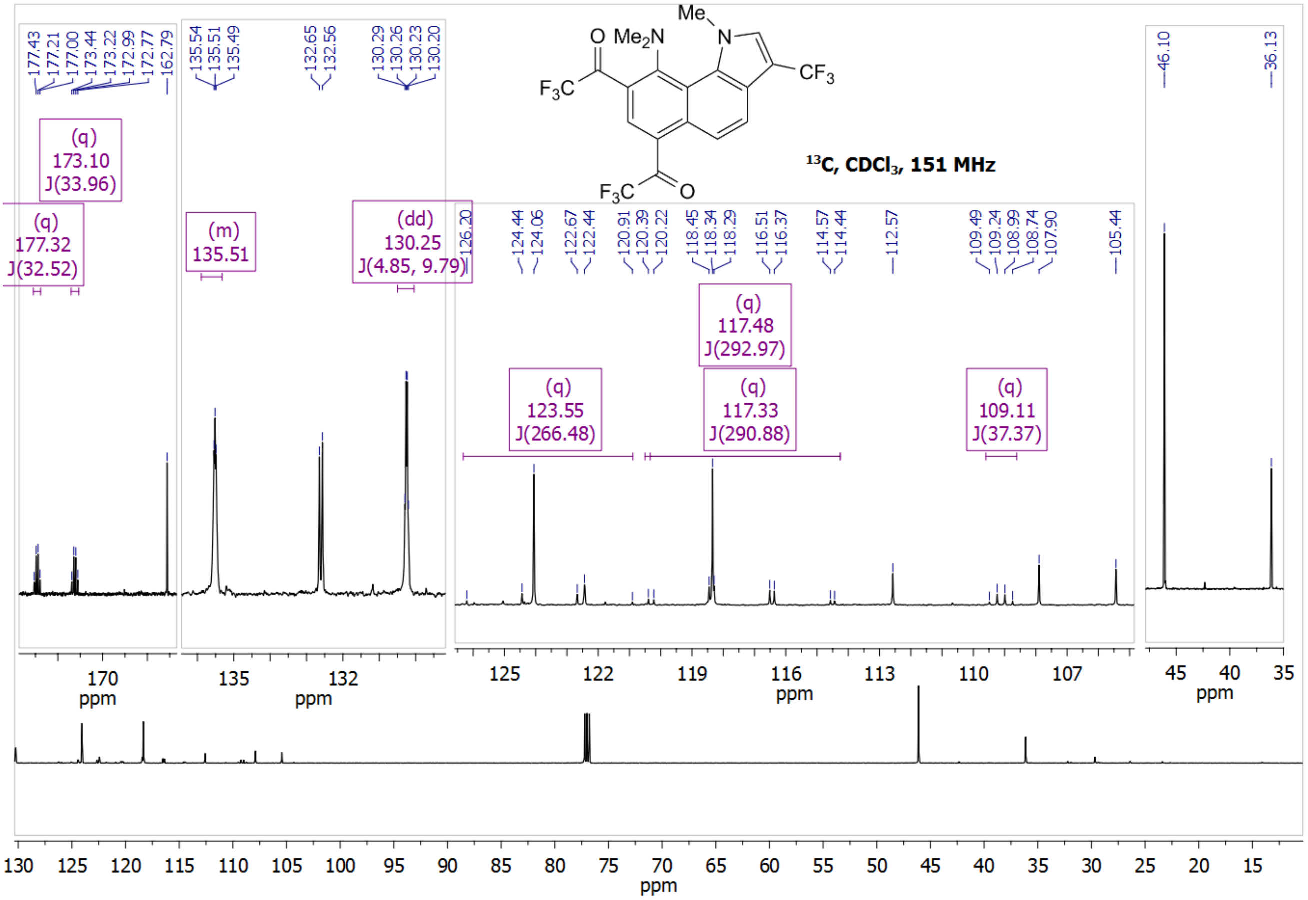
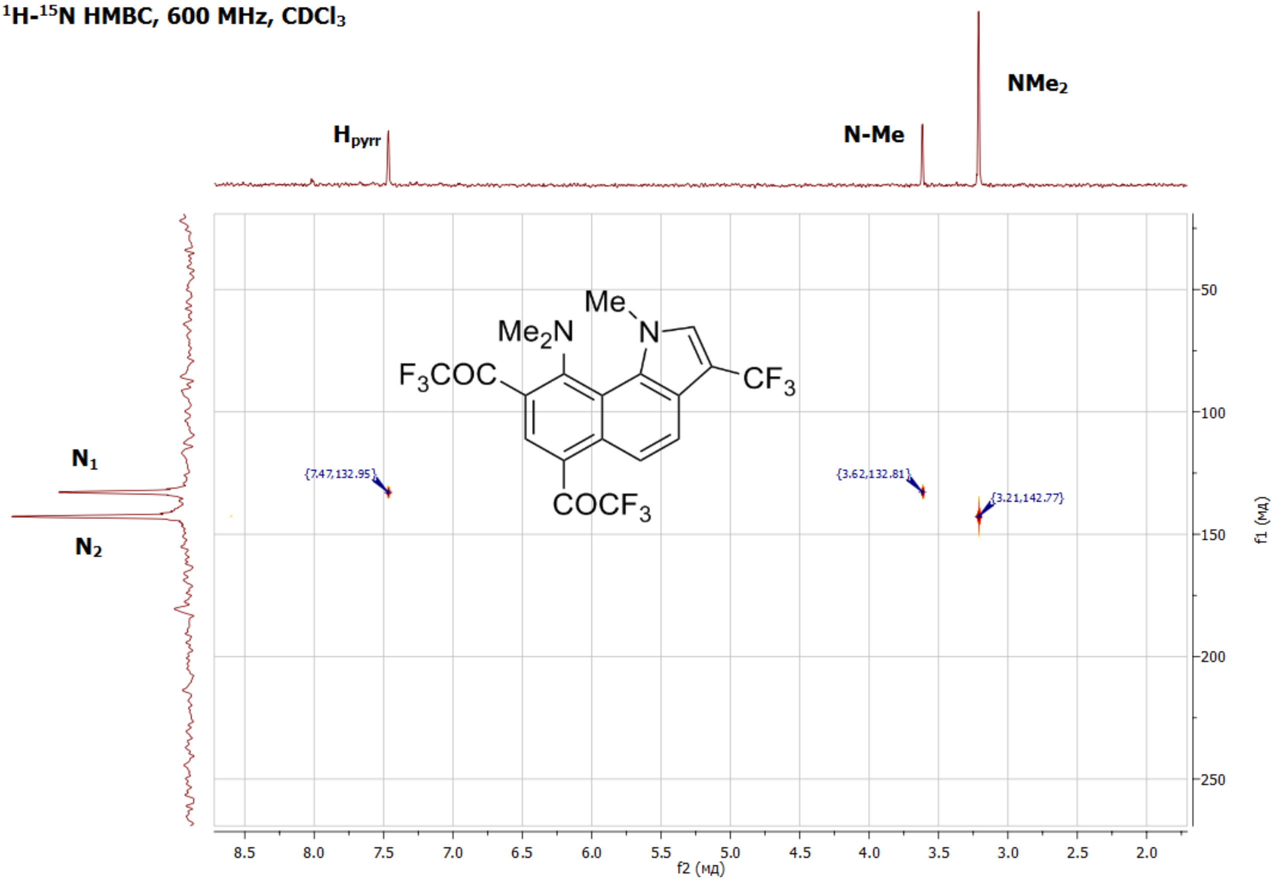
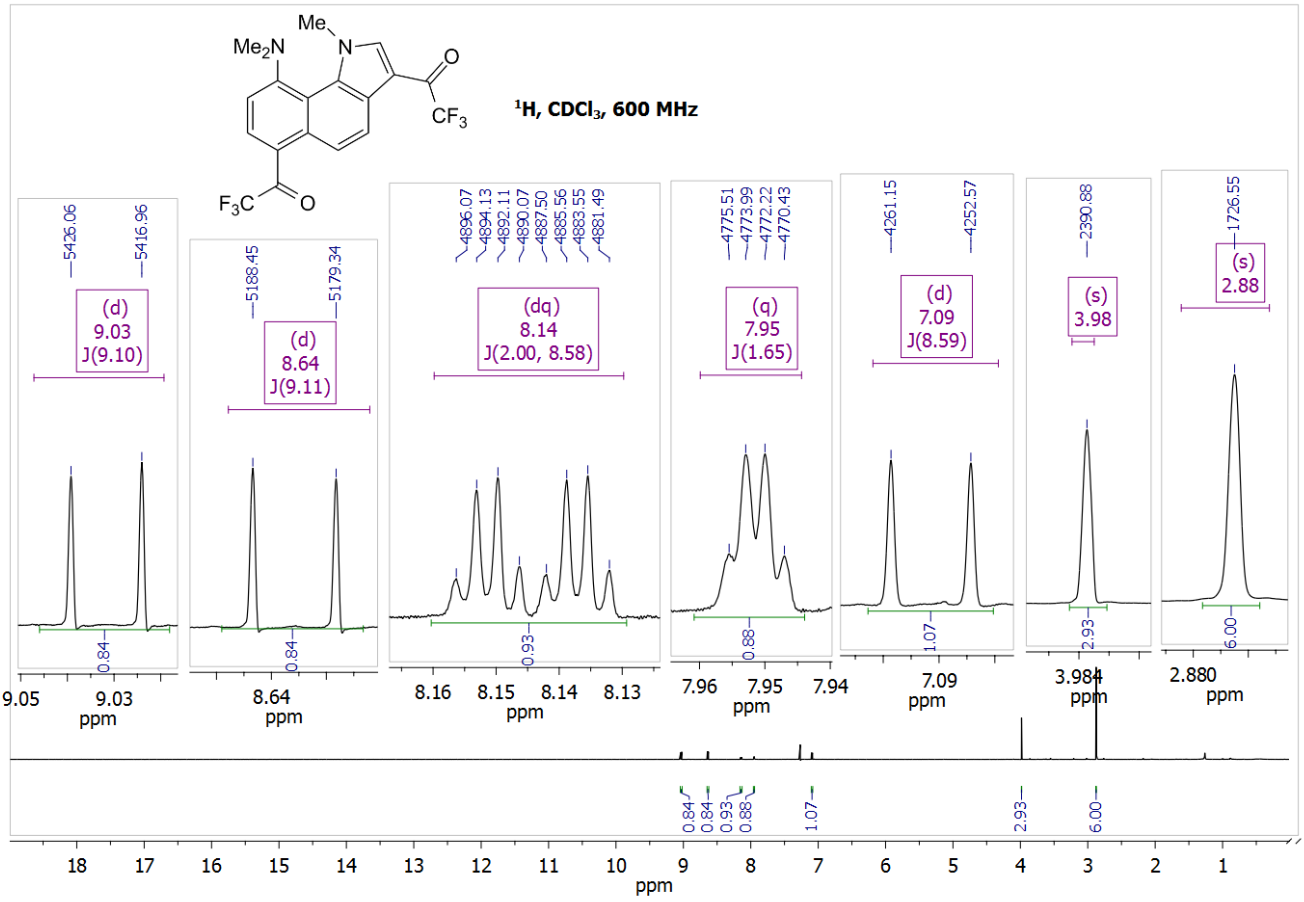
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

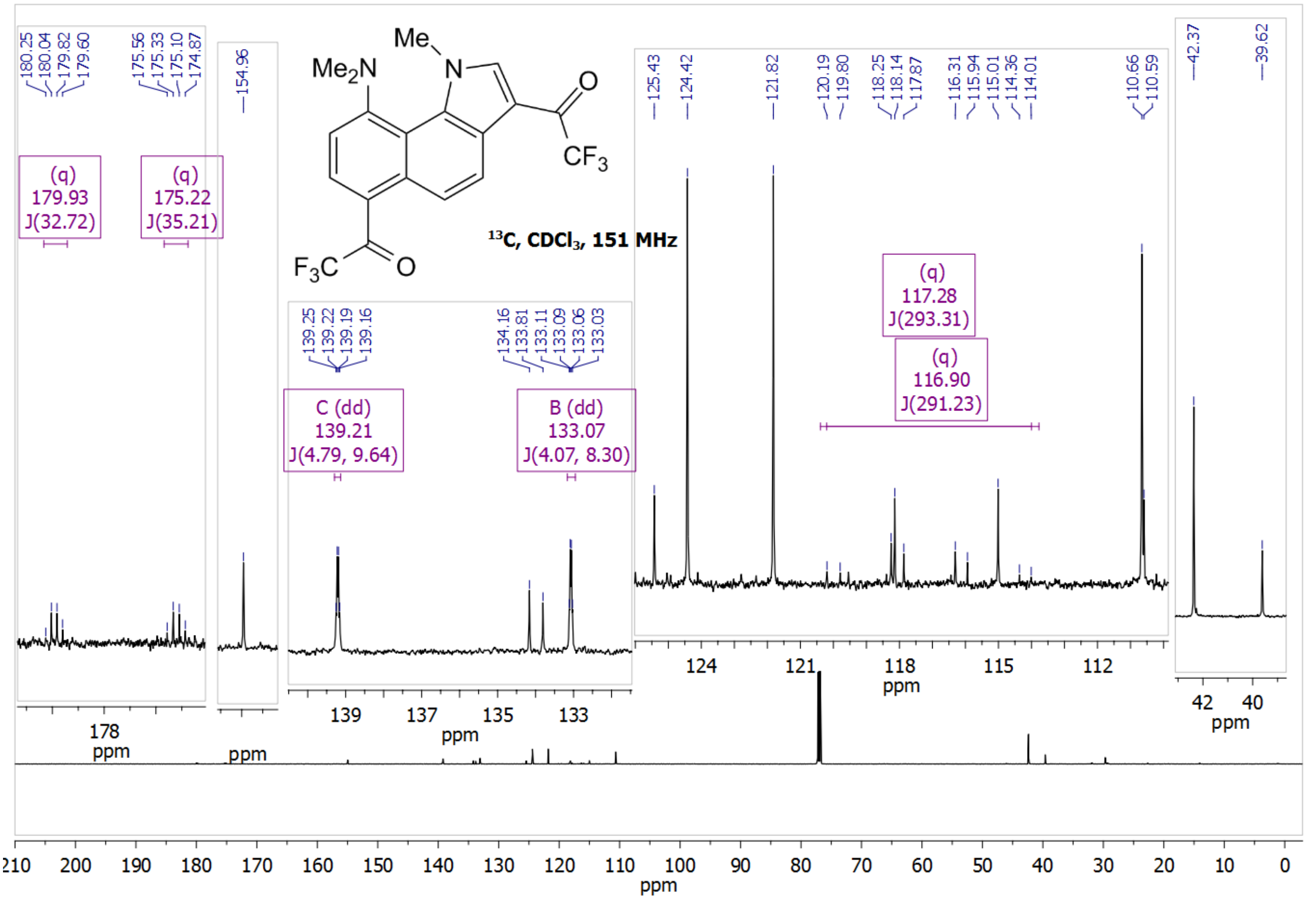

¹H, CDCl₃, 600 MHz
Me
N
Me₂N
O
F₃C
CF₃
F₃C
O
5315.83
5306.87
(d)
8.85
J(8.96)
1.08
8.86
8.85
8.84
ppm
5166.11
5165.81
5164.93
5164.60
5163.65
5162.31
5161.01
(m)
8.60
1.07
8.610
8.600
ppm
4818.04
4817.11
4816.11
4815.08
4809.08
4808.16
4807.15
4806.13
(dq)
8.02
J(0.98, 8.95)
1.08
8.035
8.025
8.015
8.005
ppm
4486.97
4485.62
4484.37
4483.16
(q)
7.47
J(1.28)
1.00
7.475
7.470
7.465
ppm
2174.76
1931.77
(s)
3.62
(s)
3.22
3.63
6.00
3.8
3.4
ppm
1.08
1.07
1.08
1.00
3.63
6.00
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

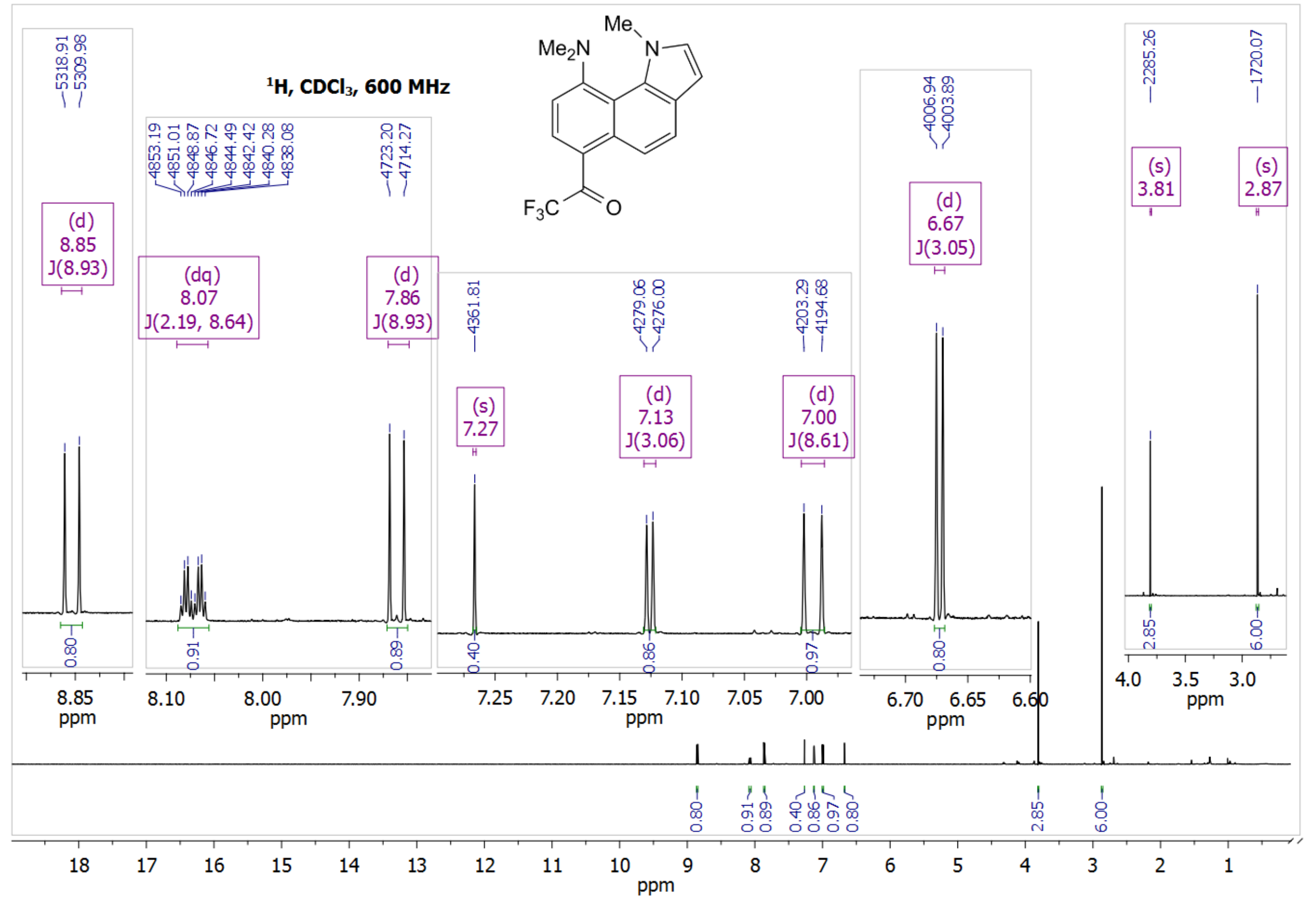

177.43
177.21
177.00
173.44
173.22
172.99
172.77
162.79
(q)
173.10
J(33.96)
(q)
177.32
J(32.52)
170
ppm
135.54
135.51
135.49
132.65
132.56
130.29
130.26
130.23
130.20
(m)
135.51
(dd)
130.25
J(4.85, 9.79)
135
132
ppm
Me
N
O
Me₂N
F₃C
CF₃
F₃C
O
¹³C, CDCl₃, 151 MHz
126.20
124.44
124.06
122.67
122.44
120.91
120.39
120.22
118.45
118.34
118.29
116.51
116.37
114.57
114.44
112.57
109.49
109.24
108.99
108.74
107.90
105.44
(q)
117.48
J(292.97)
(q)
123.55
J(266.48)
(q)
117.33
J(290.88)
(q)
109.11
J(37.37)
125
122
119
116
113
110
107
ppm
46.10
36.13
45
40
35
ppm
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
ppm

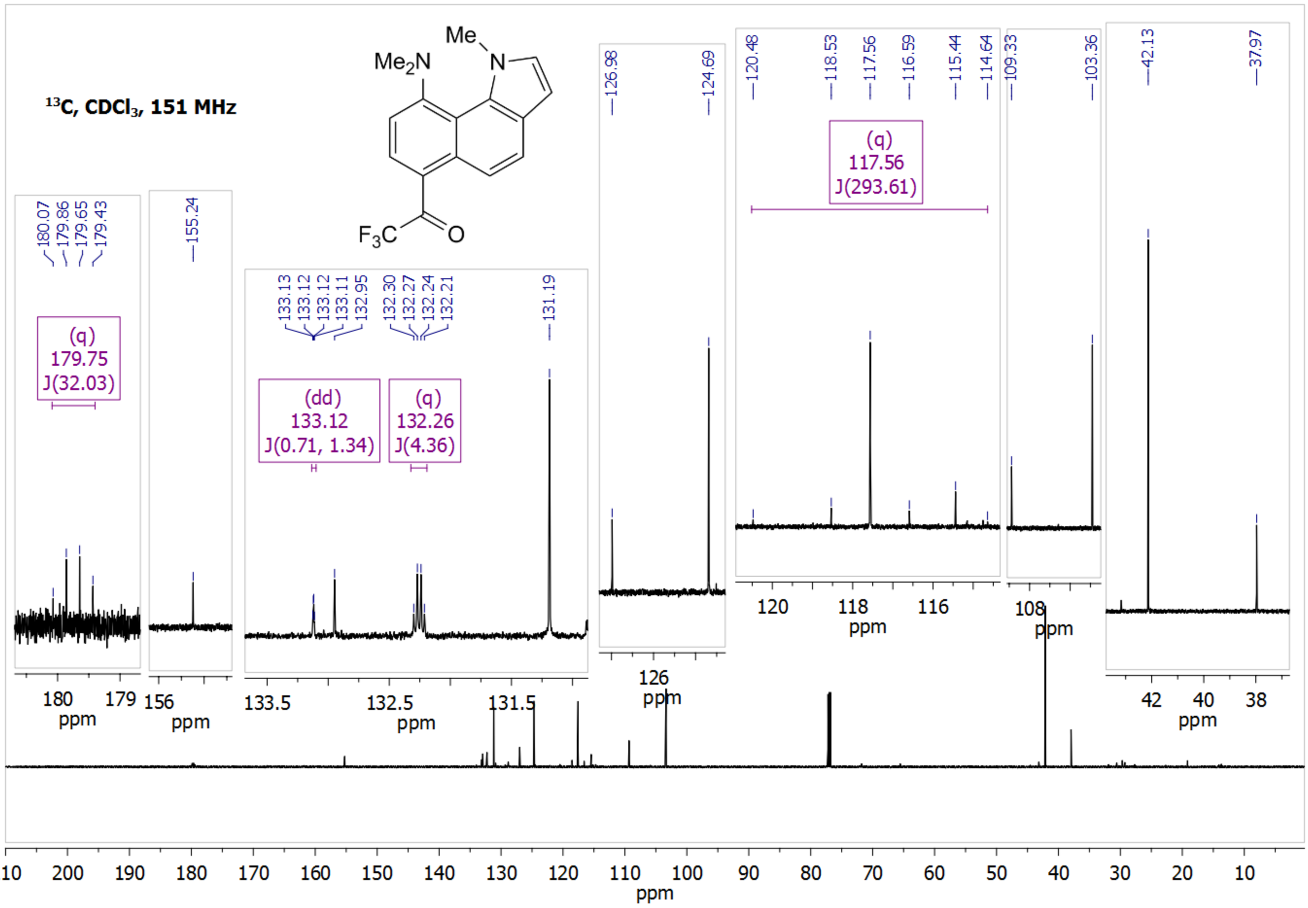
^{1}H-^{15}N HMBC, 600 MHz, CDCl$_3$

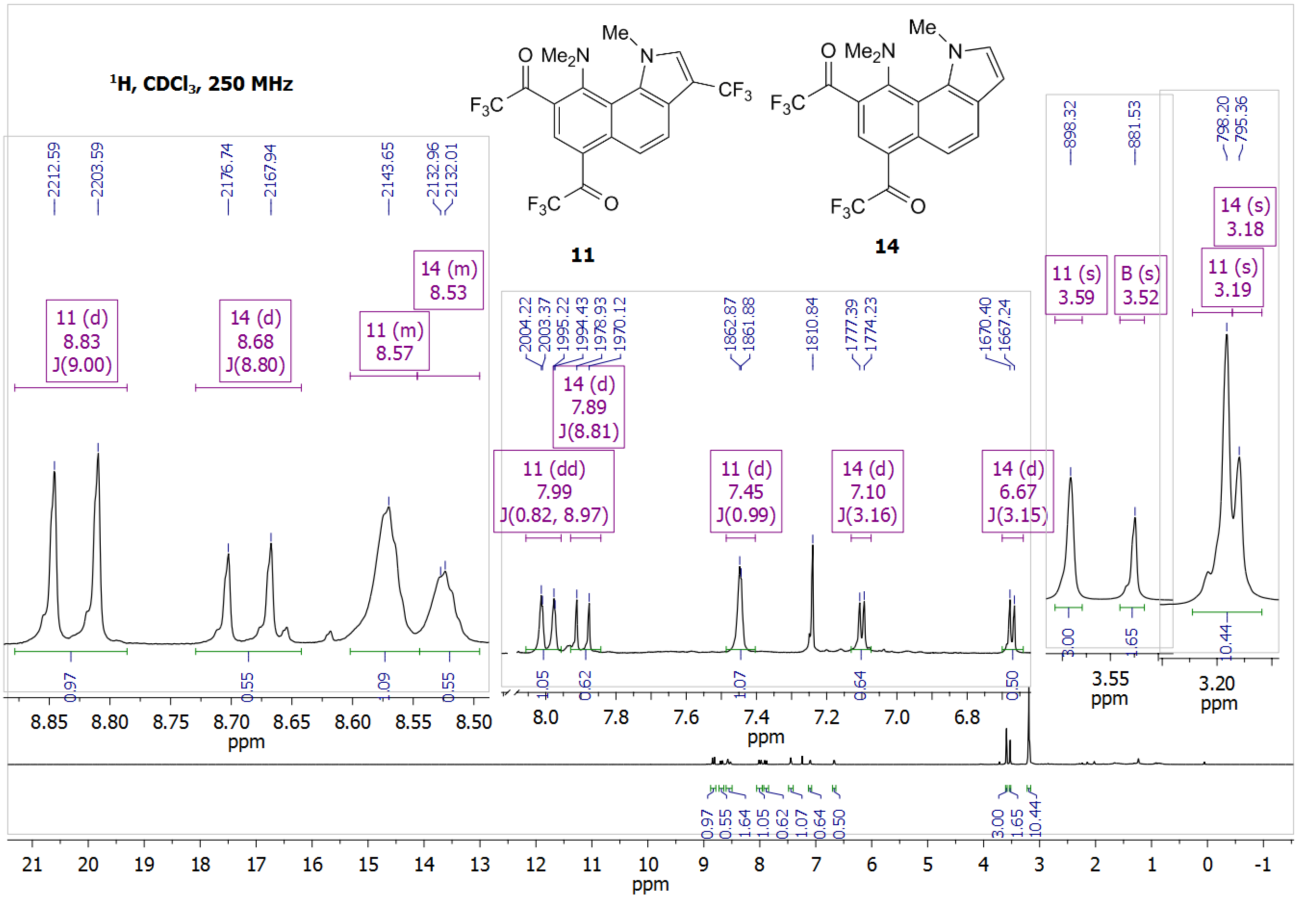


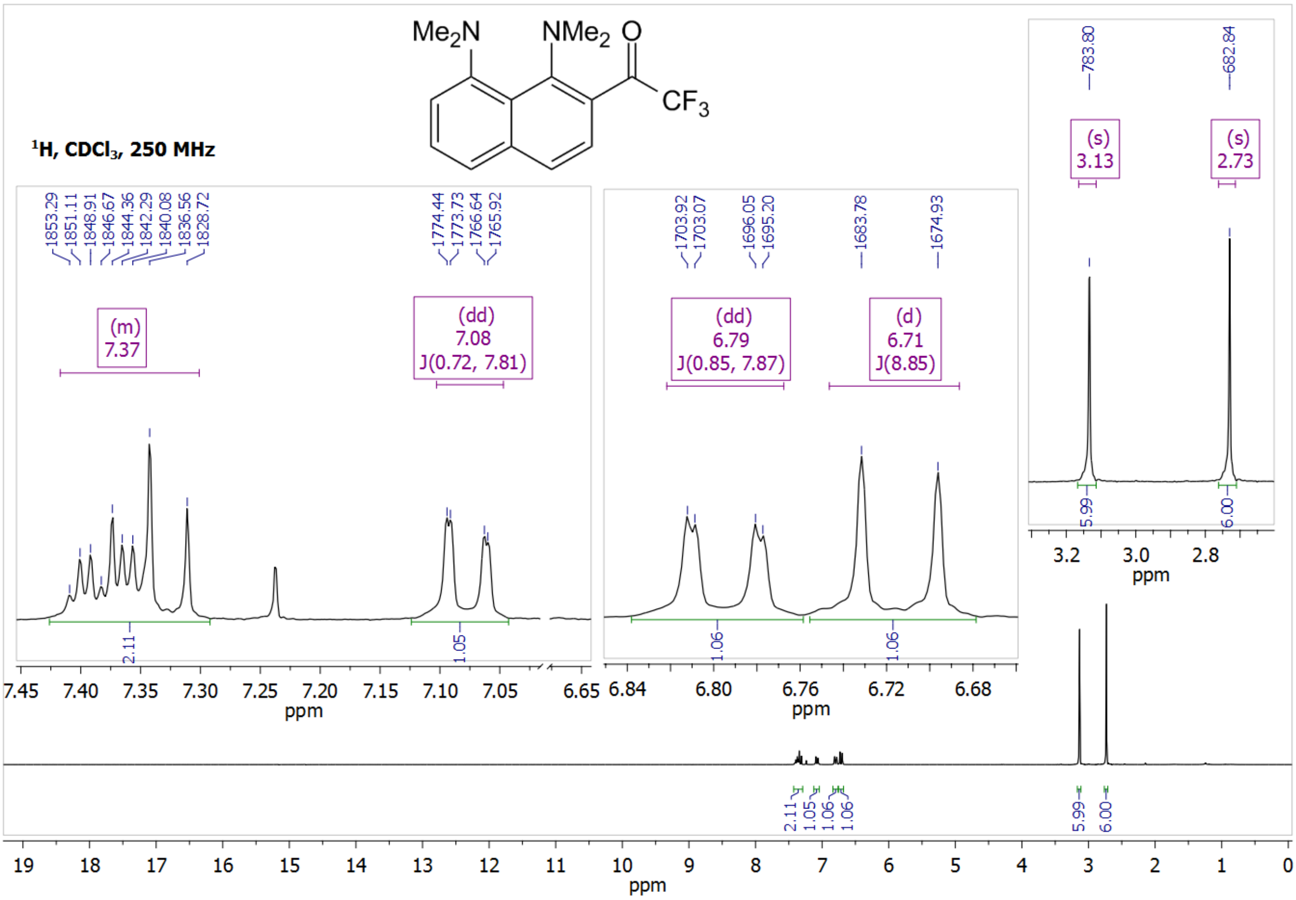


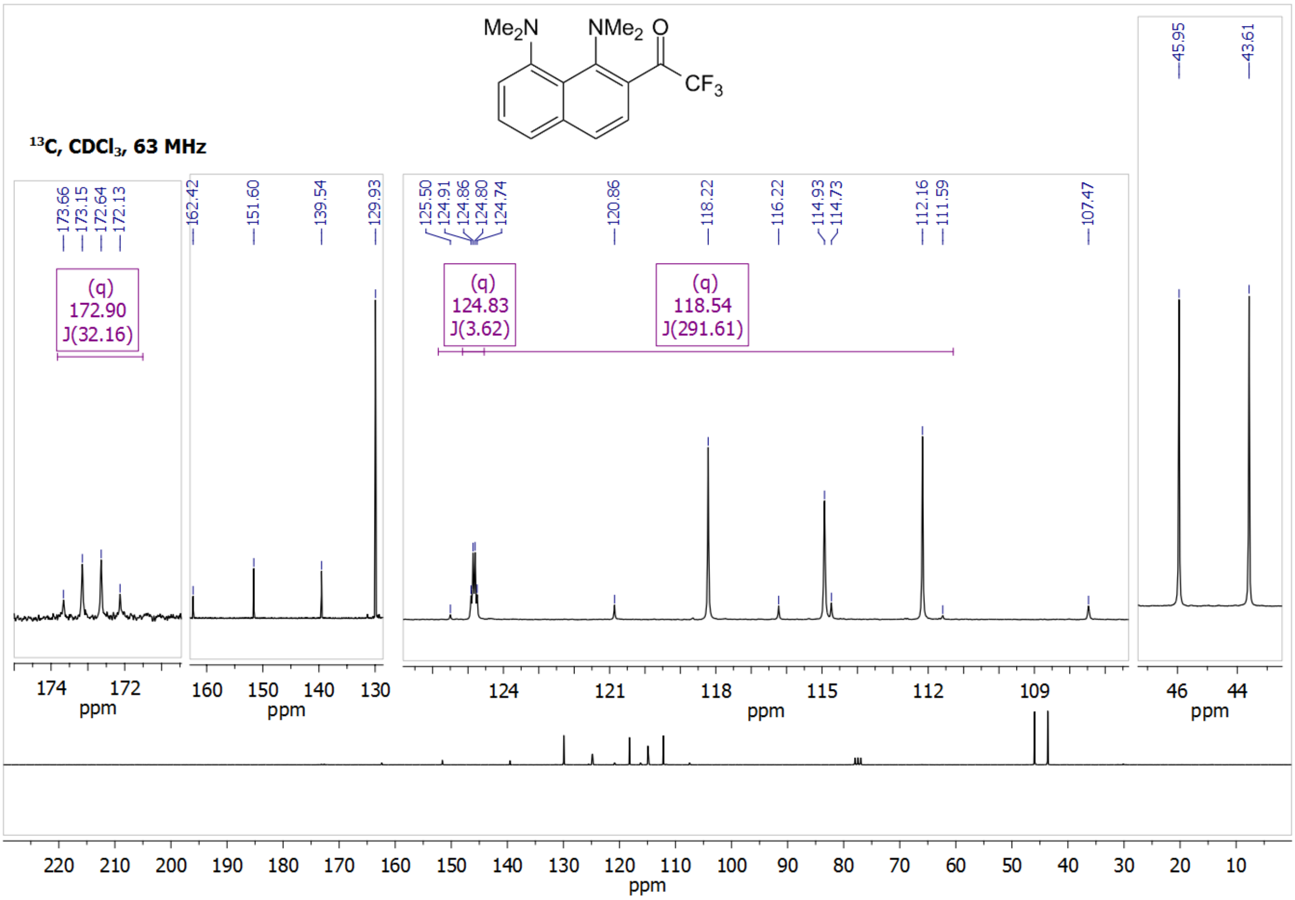

13C, CDCl3, 151 MHz
Me2N
Me
N
O
CF3
F3C
O
180.25
180.04
179.82
179.60
175.56
175.33
175.10
174.87
154.96
(q) 179.93 J(32.72)
(q) 175.22 J(35.21)
139.25
139.22
139.19
139.16
134.16
133.81
133.11
133.09
133.06
133.03
C (dd) 139.21 J(4.79, 9.64)
B (dd) 133.07 J(4.07, 8.30)
125.43
124.42
121.82
120.19
119.80
118.25
118.14
117.87
116.31
115.94
115.01
114.36
114.01
110.66
110.59
(q) 117.28 J(293.31)
(q) 116.90 J(291.23)
42.37
39.62
178
ppm
ppm
139
137
135
133
ppm
124
121
118
115
112
ppm
42
40
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

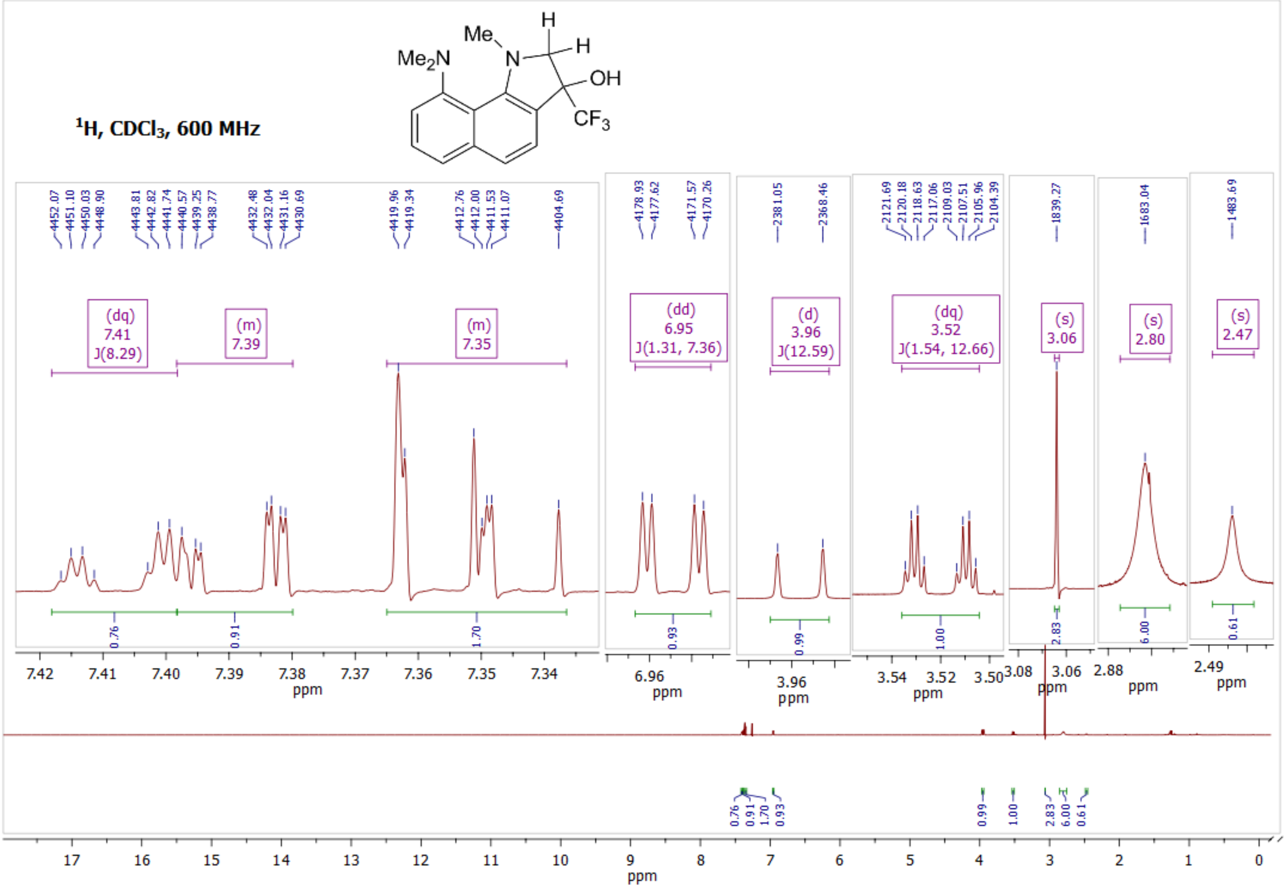

1H, CDCl3, 600 MHz
Me2N
Me
N
F3C
O
5318.91
5309.98
(d) 8.85 J(8.93)
4853.19
4851.01
4848.87
4846.72
4844.49
4842.42
4840.28
4838.08
(dq) 8.07 J(2.19, 8.64)
4723.20
4714.27
(d) 7.86 J(8.93)
4361.81
(s) 7.27
4279.06
4276.00
(d) 7.13 J(3.06)
4203.29
4194.68
(d) 7.00 J(8.61)
4006.94
4003.89
(d) 6.67 J(3.05)
2285.26
(s) 3.81
1720.07
(s) 2.87
0.80
0.91
0.89
0.40
0.86
0.97
0.80
2.85
6.00
8.85
ppm
8.10
8.00
7.90
ppm
7.25
7.20
7.15
7.10
7.05
7.00
ppm
6.70
6.65
6.60
ppm
4.0
3.5
3.0
ppm
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

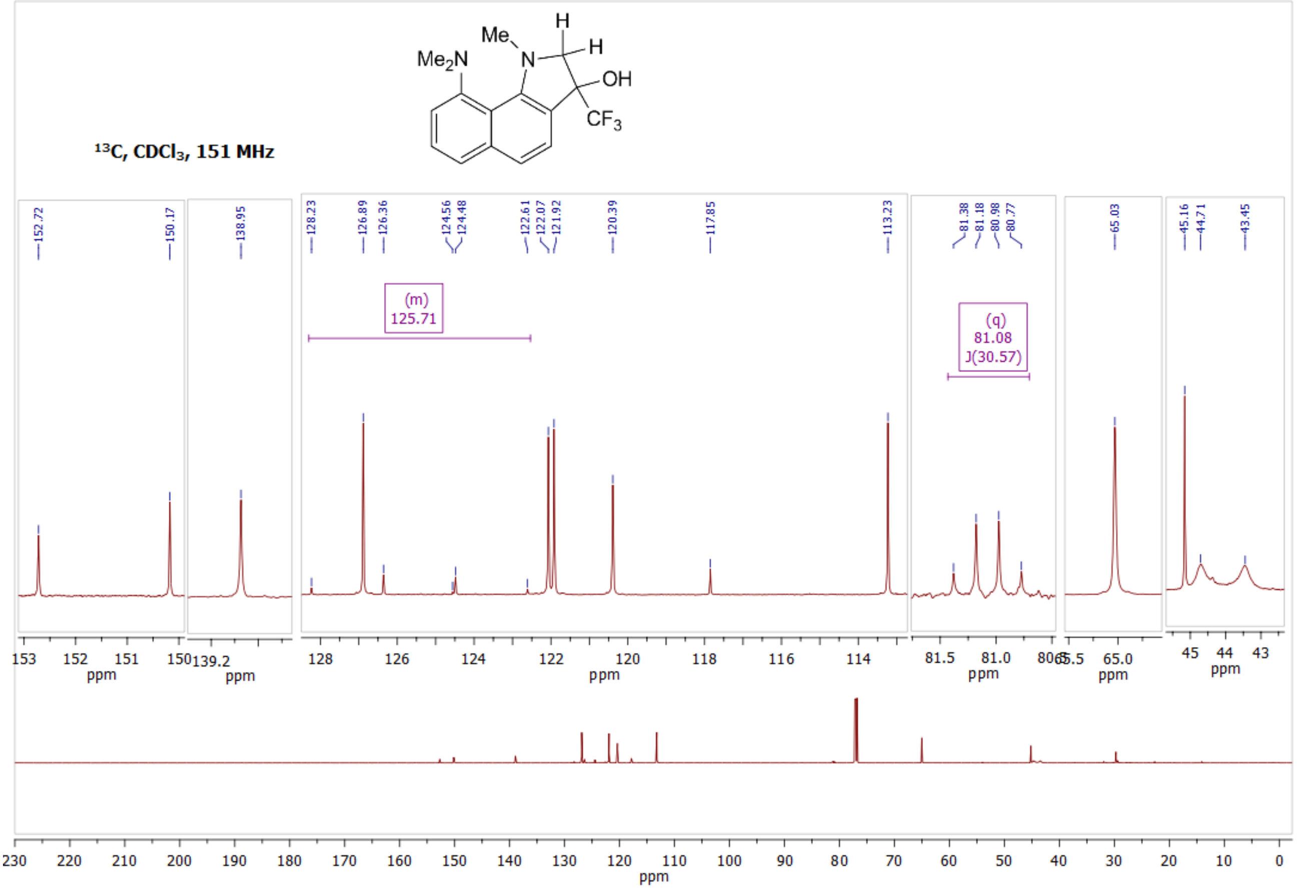

13C, CDCl3, 151 MHz
Me
Me2N
N
F3C
O
180.07
179.86
179.65
179.43
(q)
179.75
J(32.03)
155.24
133.13
133.12
133.12
133.11
132.95
132.30
132.27
132.24
132.21
131.19
(dd)
133.12
J(0.71, 1.34)
(q)
132.26
J(4.36)
126.98
124.69
120.48
118.53
117.56
116.59
115.44
114.64
109.33
103.36
42.13
37.97
(q)
117.56
J(293.61)
180
179
ppm
156
ppm
133.5
132.5
131.5
ppm
126
ppm
120
118
116
ppm
108
ppm
42
40
38
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

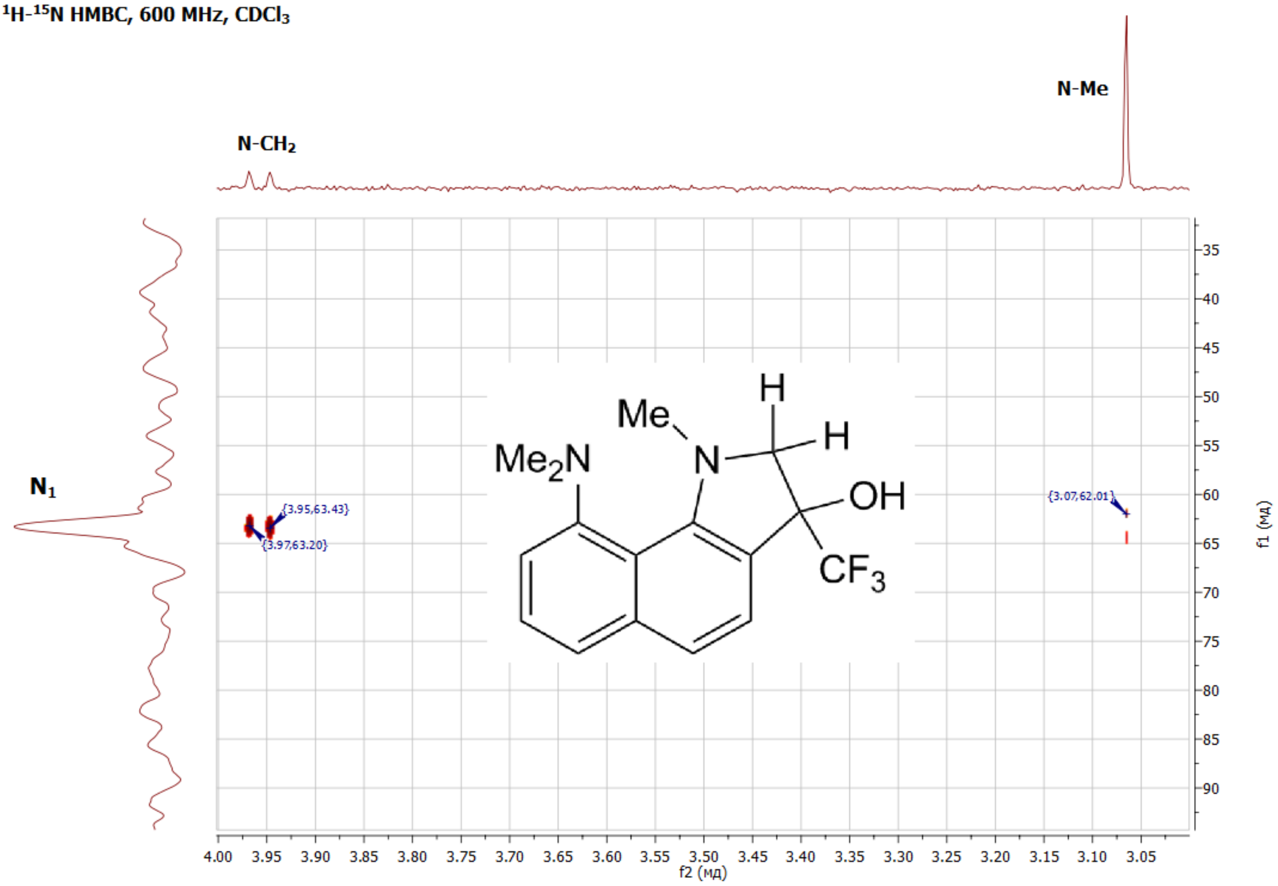

1H, CDCl3, 250 MHz
Me
Me2N
N
O
F3C
CF3
F3C
O
11
Me
O Me2N
N
F3C
F3C
O
14
2212.59
2203.59
2176.74
2167.94
2143.65
2132.96
2132.01
11 (d)
8.83
J(9.00)
14 (d)
8.68
J(8.80)
11 (m)
8.57
14 (m)
8.53
0.97
0.55
1.09
0.55
8.85
8.80
8.75
8.70
8.65
8.60
8.55
8.50
ppm
2004.22
2003.37
1995.22
1994.43
1978.93
1970.12
1862.87
1861.88
1810.84
1777.39
1774.23
1670.40
1667.24
14 (d)
7.89
J(8.81)
11 (dd)
7.99
J(0.82, 8.97)
11 (d)
7.45
J(0.99)
14 (d)
7.10
J(3.16)
14 (d)
6.67
J(3.15)
1.05
0.62
1.07
0.64
0.50
8.0
7.8
7.6
7.4
7.2
7.0
6.8
ppm
898.32
881.53
11 (s)
3.59
B (s)
3.52
3.00
1.65
3.55
ppm
798.20
795.36
14 (s)
3.18
11 (s)
3.19
10.44
3.20
ppm
0.97
0.55
1.64
1.05
0.62
1.07
0.64
0.50
3.00
1.65
10.44
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

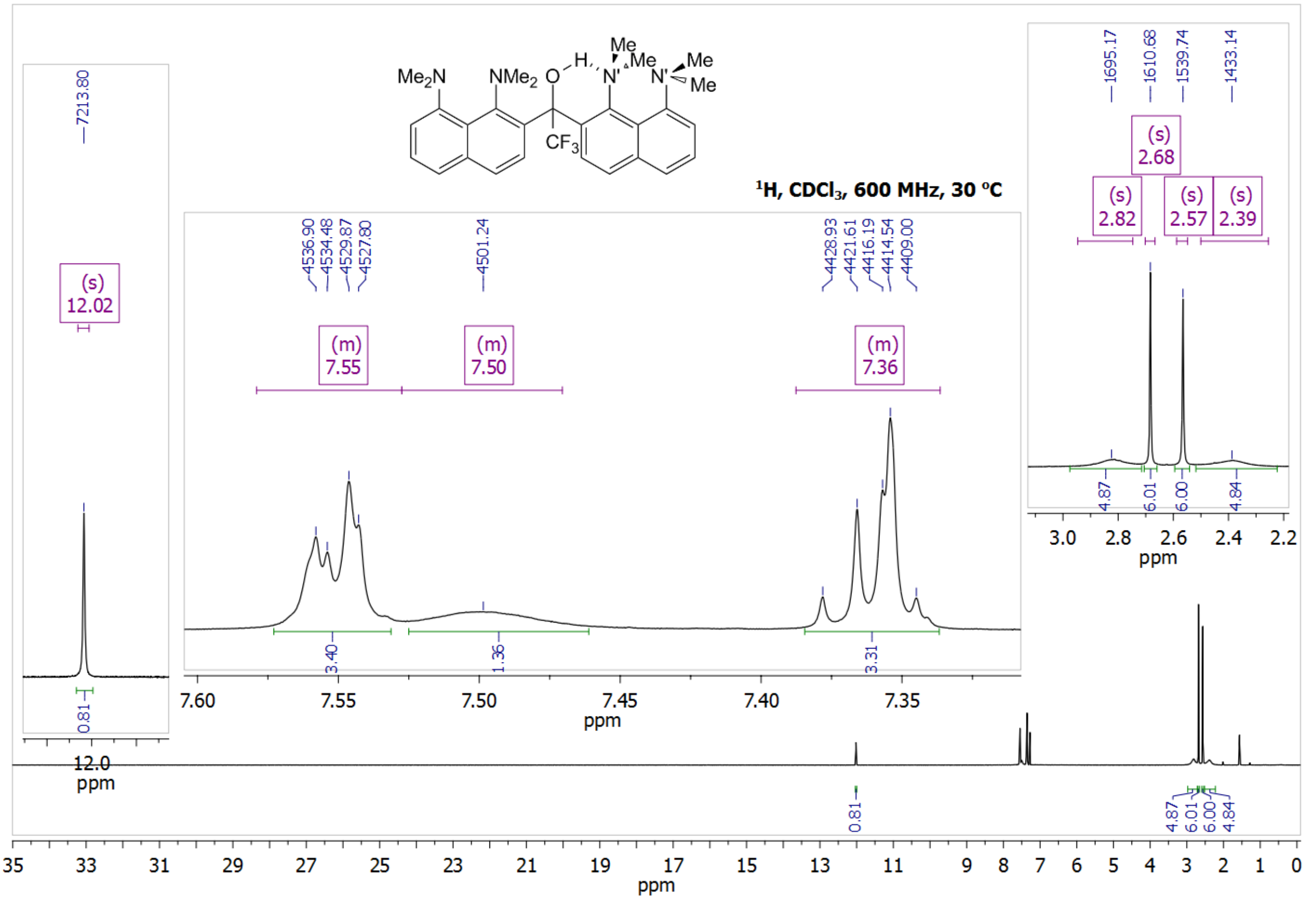

Me2N
NMe2
O
CF3
1H, CDCl3, 250 MHz
1853.29
1851.11
1848.91
1846.67
1844.36
1842.29
1840.08
1836.56
1828.72
(m)
7.37
1774.44
1773.73
1766.64
1765.92
(dd)
7.08
J(0.72, 7.81)
2.11
1.05
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
6.65
ppm
1703.92
1703.07
1696.05
1695.20
1683.78
1674.93
(dd)
6.79
J(0.85, 7.87)
(d)
6.71
J(8.85)
1.06
1.06
6.84
6.80
6.76
6.72
6.68
ppm
783.80
682.84
(s)
3.13
(s)
2.73
5.99
6.00
3.2
3.0
2.8
ppm
2.11
1.05
1.06
1.06
5.99
6.00
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

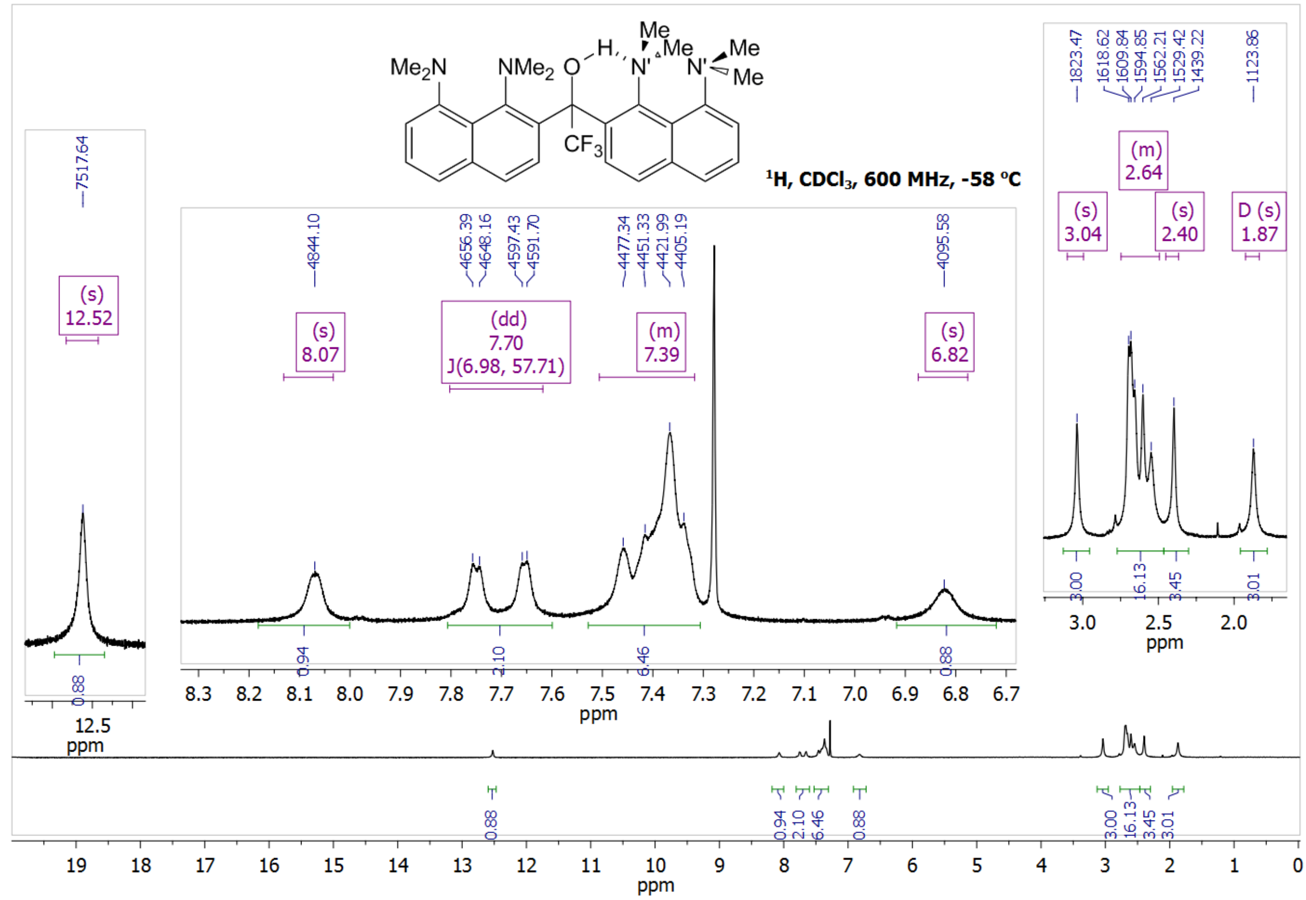

Me2N
NMe2 O
CF3
13C, CDCl3, 63 MHz
173.66
173.15
172.64
172.13
(q)
172.90
J(32.16)
162.42
151.60
139.54
129.93
125.50
124.91
124.86
124.80
124.74
(q)
124.83
J(3.62)
120.86
118.22
(q)
118.54
J(291.61)
116.22
114.93
114.73
112.16
111.59
107.47
45.95
43.61
174
172
ppm
160
150
140
130
ppm
124
121
118
115
112
109
ppm
46
44
ppm
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

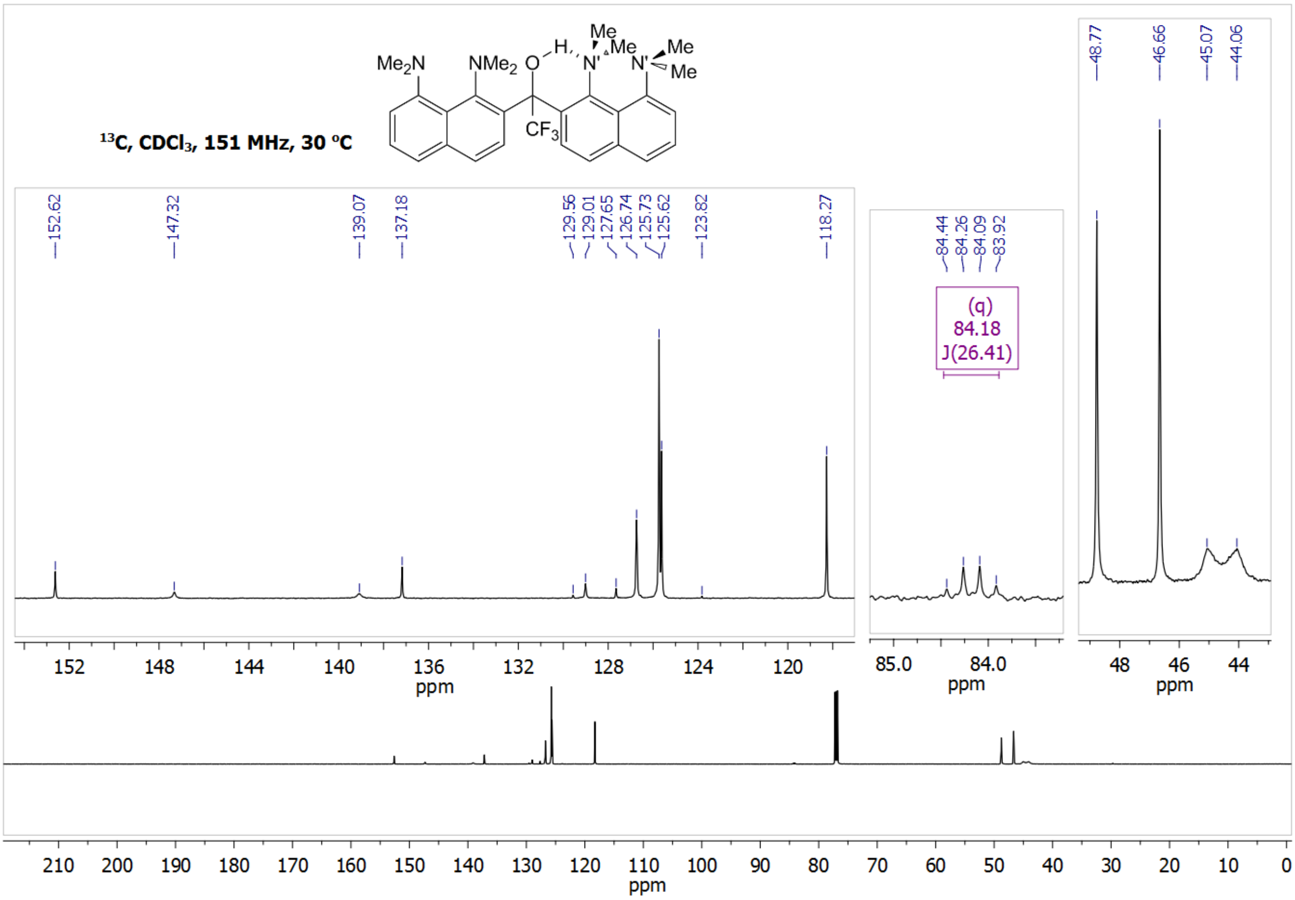

H
Me
N
H
Me2N
OH
CF3
1H, CDCl3, 600 MHz
4452.07
4451.10
4450.03
4448.90
4443.81
4442.82
4441.74
4440.57
4439.25
4438.77
4432.48
4432.04
4431.16
4430.69
4419.96
4419.34
4412.76
4412.00
4411.53
4411.07
4404.69
(dq)
7.41
J(8.29)
(m)
7.39
(m)
7.35
4178.93
4177.62
4171.57
4170.26
(dd)
6.95
J(1.31, 7.36)
2381.05
2368.46
(d)
3.96
J(12.59)
2121.69
2120.18
2118.63
2117.06
2109.03
2107.51
2105.96
2104.39
(dq)
3.52
J(1.54, 12.66)
1839.27
(s)
3.06
1683.04
(s)
2.80
1483.69
(s)
2.47
0.76
0.91
1.70
0.93
0.99
1.00
2.83
6.00
0.61
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.34
ppm
6.96
ppm
3.96
ppm
3.54
3.52
3.50
ppm
3.08
3.06
ppm
2.88
ppm
2.49
ppm
0.76
0.91
1.70
0.93
0.99
1.00
2.83
6.00
0.61
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

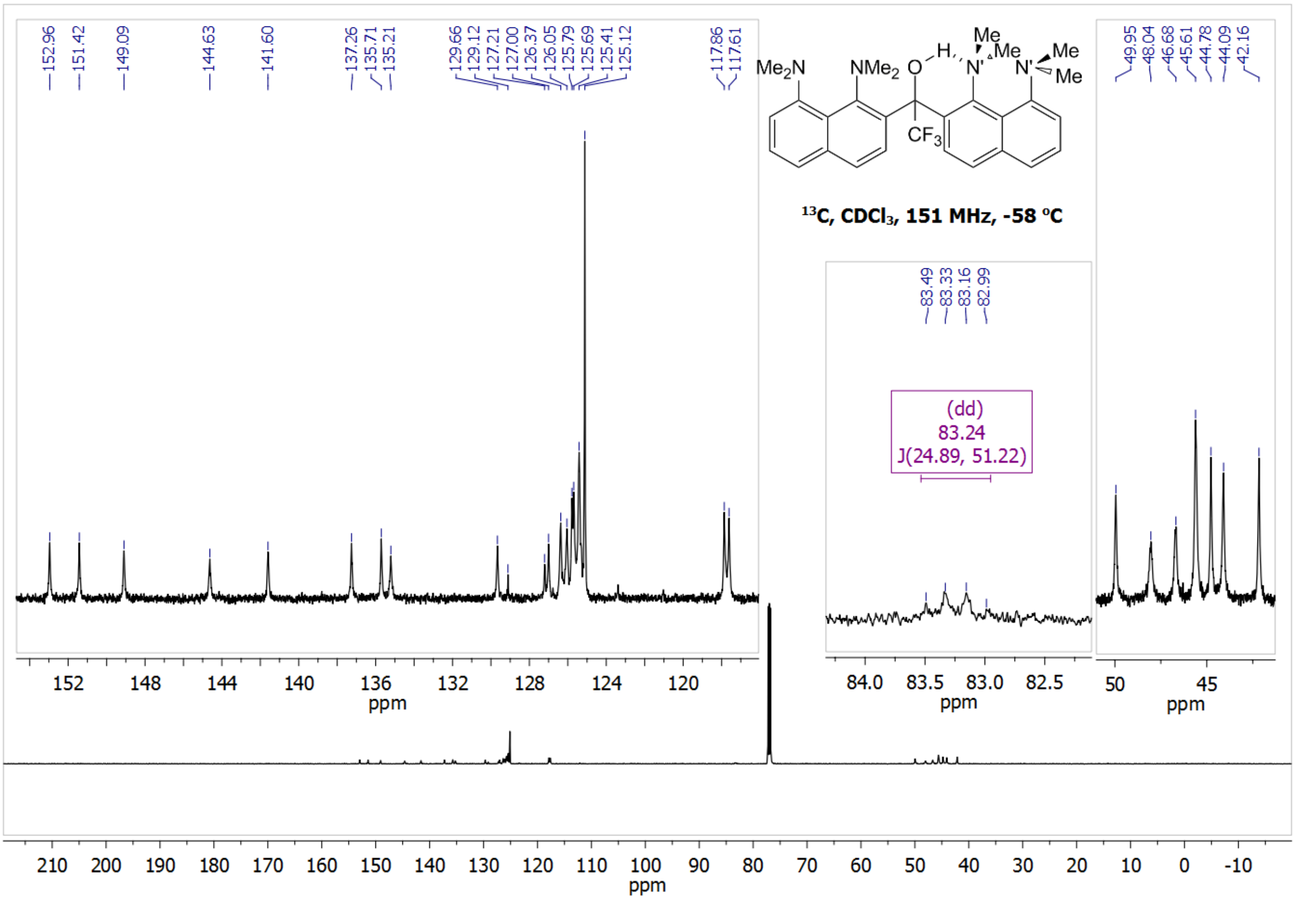

¹³C, CDCl₃, 151 MHz
Me₂N
Me
N
H
H
OH
CF₃
152.72
150.17
138.95
128.23
126.89
126.36
124.56
124.48
122.61
122.07
121.92
120.39
117.85
113.23
81.38
81.18
80.98
80.77
65.03
45.16
44.71
43.45
(m)
125.71
(q)
81.08
J(30.57)
ppm

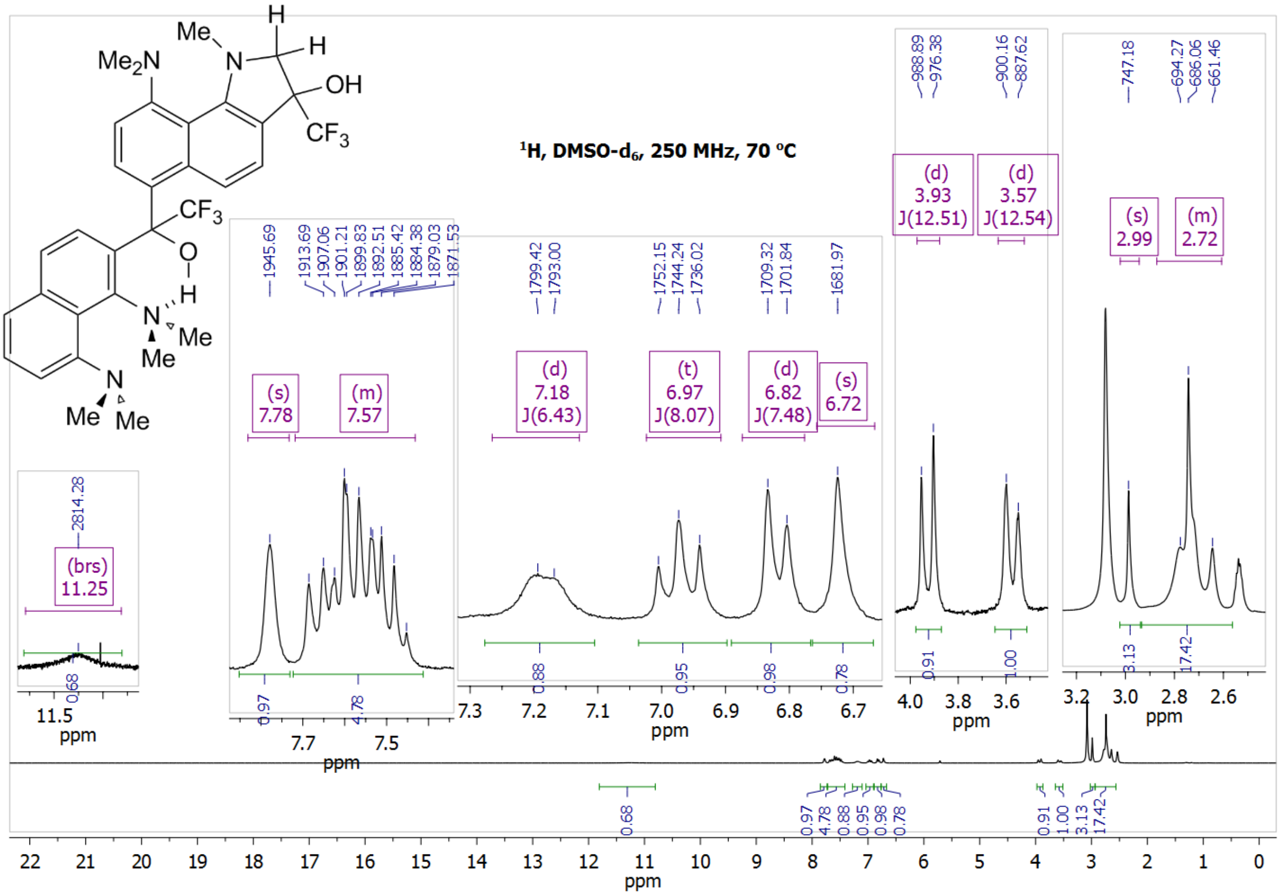

¹H-¹⁵N HMBC, 600 MHz, CDCl₃
N-CH₂
N-Me
N₁
{3.95,63.43}
{3.97,63.20}
{3.07,62.01}
Me₂N
Me
N
H
H
OH
CF₃
f2 (мд)
f1 (мд)


Me₂N
NMe₂
O
H
N'
Me
Me
N'
Me
Me
CF₃
¹H, CDCl₃, 600 MHz, 30 °C
7213.80
(s) 12.02
0.81
12.0
ppm
4536.90
4534.48
4529.87
4527.80
4501.24
4428.93
4421.61
4416.19
4414.54
4409.00
(m) 7.55
(m) 7.50
(m) 7.36
3.40
1.36
3.31
7.60
7.55
7.50
7.45
7.40
7.35
ppm
1695.17
1610.68
1539.74
1433.14
(s) 2.68
(s) 2.82
(s) 2.57
(s) 2.39
4.87
6.01
6.00
4.84
3.0
2.8
2.6
2.4
2.2
ppm
0.81
4.87
6.01
6.00
4.84
35
33
31
29
27
25
23
21
19
17
15
13
11
9
8
7
6
5
4
3
2
1
0
ppm

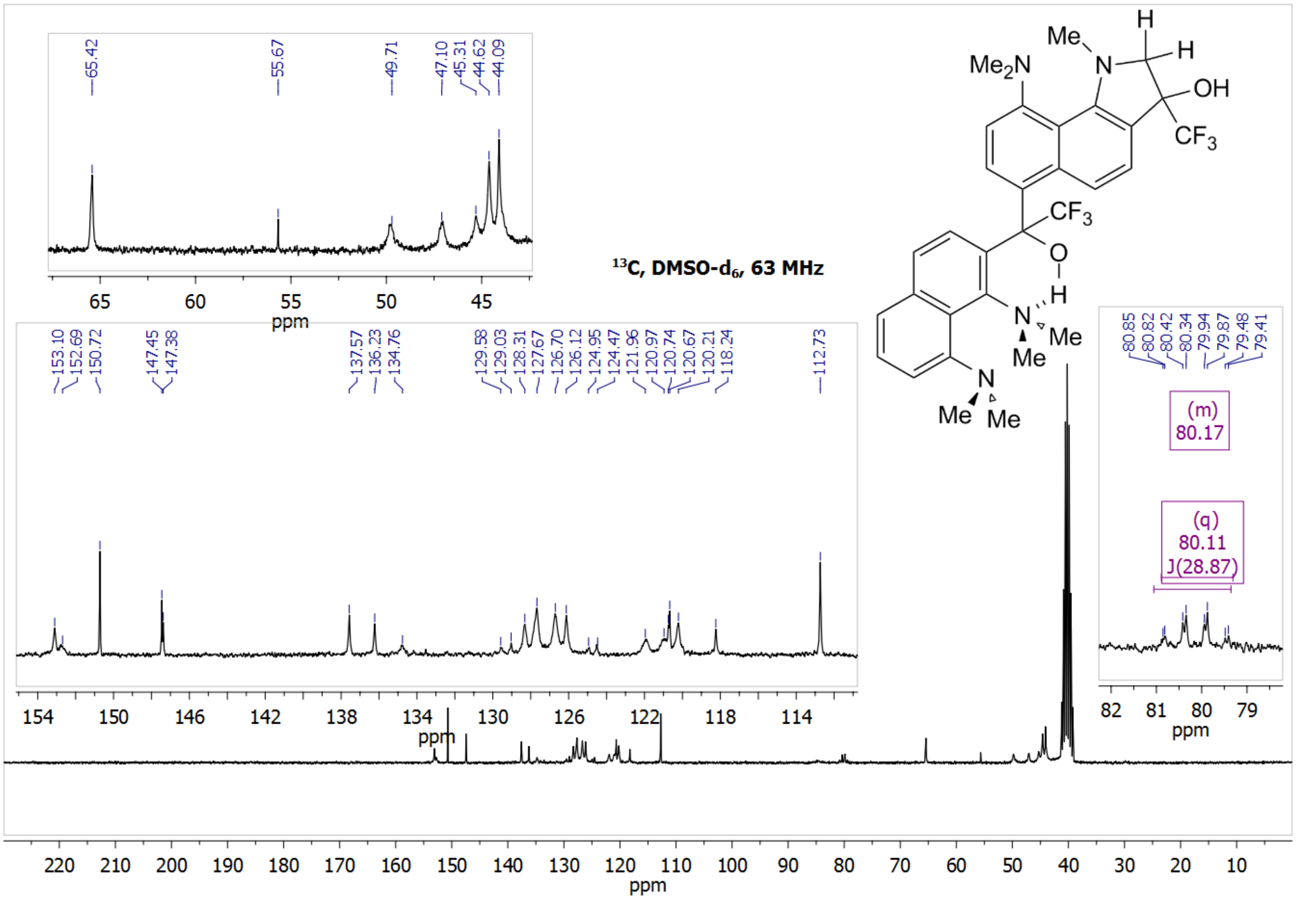

Me₂N
NMe₂
O
H
N'
Me
Me
N'
Me
Me
CF₃
¹H, CDCl₃, 600 MHz, -58 °C
7517.64
(s) 12.52
0.88
12.5
ppm
4844.10
4656.39
4648.16
4597.43
4591.70
4477.34
4451.33
4421.99
4405.19
4095.58
(s) 8.07
(dd) 7.70 J(6.98, 57.71)
(m) 7.39
(s) 6.82
0.94
2.10
6.46
0.88
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
ppm
1823.47
1618.62
1609.84
1594.85
1562.21
1529.42
1439.22
1123.86
(m) 2.64
(s) 3.04
(s) 2.40
D (s) 1.87
3.00
16.13
3.45
3.01
3.0
2.5
2.0
ppm
0.88
0.94
2.10
6.46
0.88
3.00
16.13
3.45
3.01
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm


^{13}C, CDCl$_3$, 151 MHz, 30 °C
Me$_2$N
NMe$_2$
O
H
N'
Me
Me
N'
Me
Me
CF$_3$
152.62
147.32
139.07
137.18
129.56
129.01
127.65
126.74
125.73
125.62
123.82
118.27
84.44
84.26
84.09
83.92
(q)
84.18
J(26.41)
48.77
46.66
45.07
44.06
152
148
144
140
136
132
128
124
120
ppm
85.0
84.0
ppm
48
46
44
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

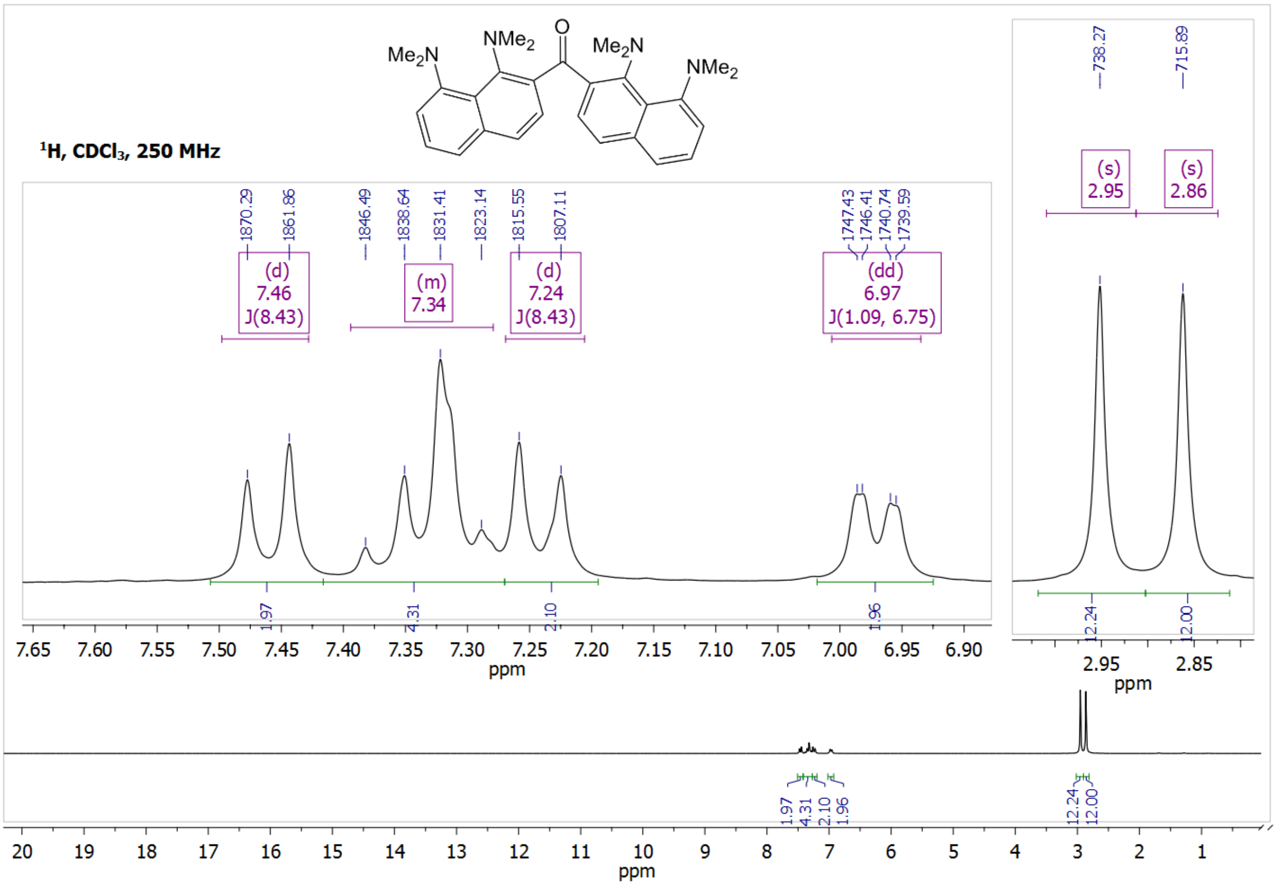

152.96
151.42
149.09
144.63
141.60
137.26
135.71
135.21
129.66
129.12
127.21
127.00
126.37
126.05
125.79
125.69
125.41
125.12
117.86
117.61
Me$_2$N
NMe$_2$
O
H
N'
Me
Me
N'
Me
Me
CF$_3$
^{13}C, CDCl$_3$, 151 MHz, -58 °C
49.95
48.04
46.68
45.61
44.78
44.09
42.16
83.49
83.33
83.16
82.99
(dd)
83.24
J(24.89, 51.22)
152
148
144
140
136
132
128
124
120
ppm
84.0
83.5
83.0
82.5
ppm
50
45
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm



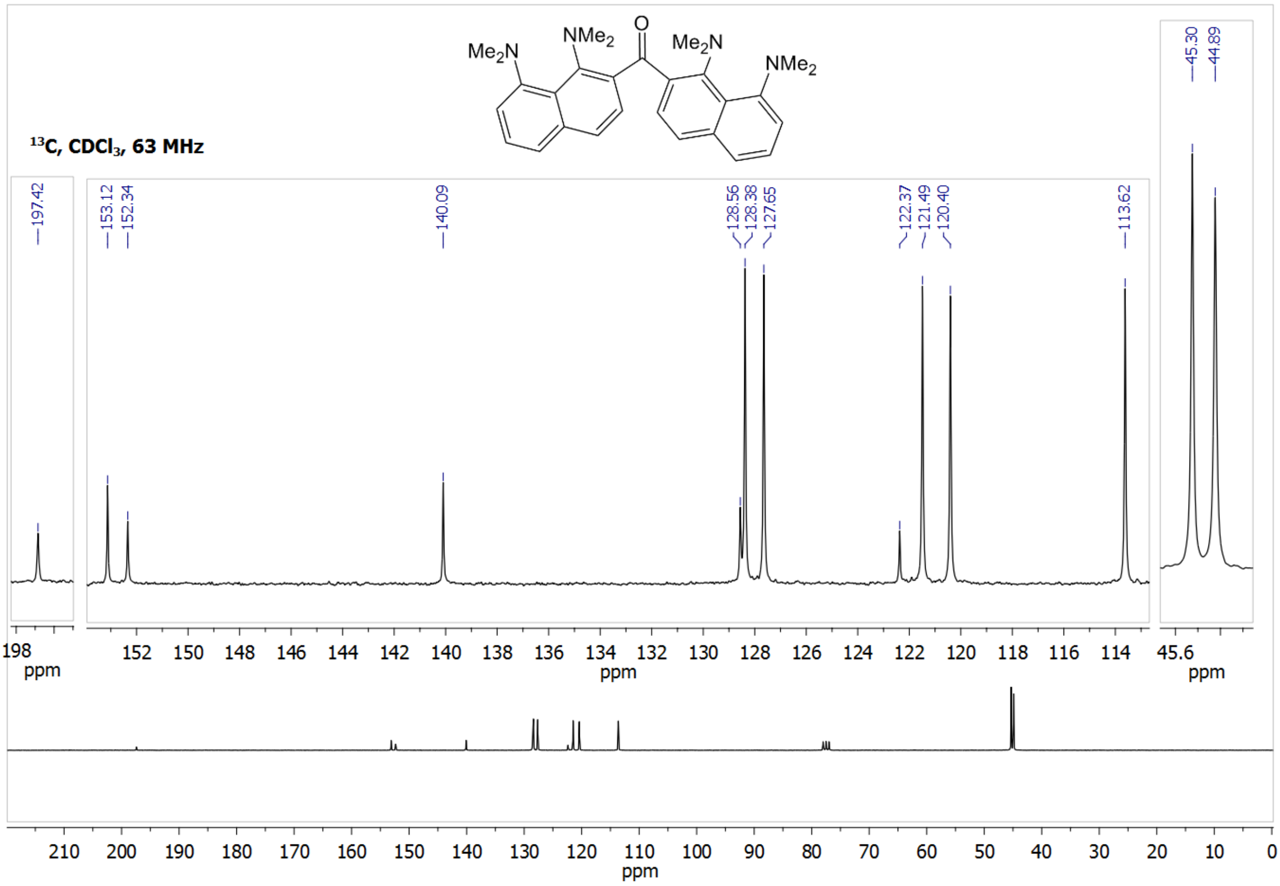
Me2N
Me
N
H
H
OH
CF3
CF3
O
H
N
Me
Me
N
Me
Me
1H, DMSO-d6, 250 MHz, 70 °C
(brs) 11.25
(s) 7.78
(m) 7.57
(d) 7.18 J(6.43)
(t) 6.97 J(8.07)
(d) 6.82 J(7.48)
(s) 6.72
(d) 3.93 J(12.51)
(d) 3.57 J(12.54)
(s) 2.99
(m) 2.72
2814.28
1945.69
1913.69
1907.06
1901.21
1899.83
1892.51
1885.42
1884.38
1879.03
1871.53
1799.42
1793.00
1752.15
1744.24
1736.02
1709.32
1701.84
1681.97
988.89
976.38
900.16
887.62
747.18
694.27
686.06
661.46
0.68
0.97
4.78
0.88
0.95
0.98
0.78
0.91
1.00
3.13
17.42
ppm



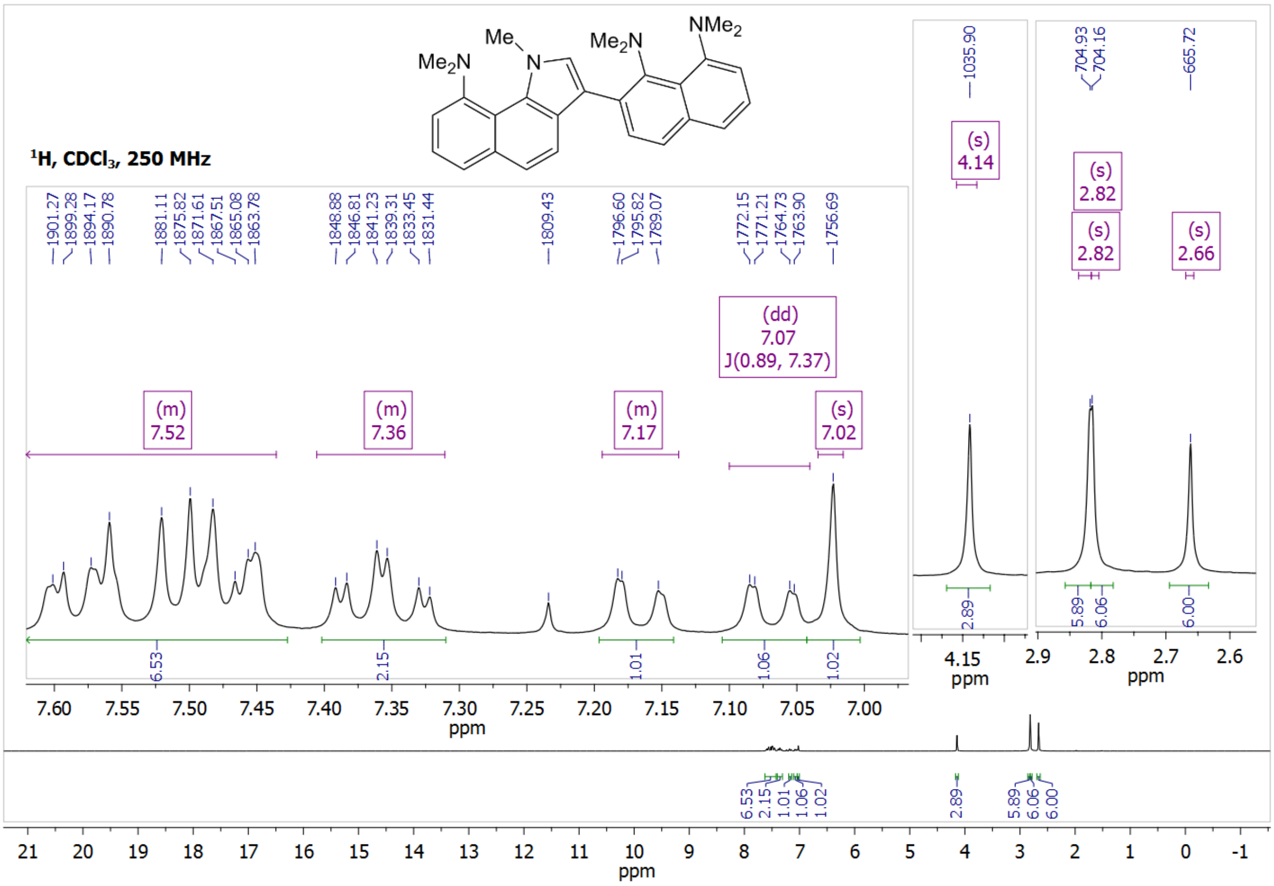
13C, DMSO-d6, 63 MHz
Me2N
Me
N
H
H
OH
CF3
CF3
O
H
N
Me
Me
N
Me
Me
65.42
55.67
49.71
47.10
45.31
44.62
44.09
153.10
152.69
150.72
147.45
147.38
137.57
136.23
134.76
129.58
129.03
128.31
127.67
126.70
126.12
124.95
124.47
121.96
120.97
120.74
120.67
120.21
118.24
112.73
80.85
80.82
80.42
80.34
79.94
79.87
79.48
79.41
(m) 80.17
(q) 80.11 J(28.87)
ppm

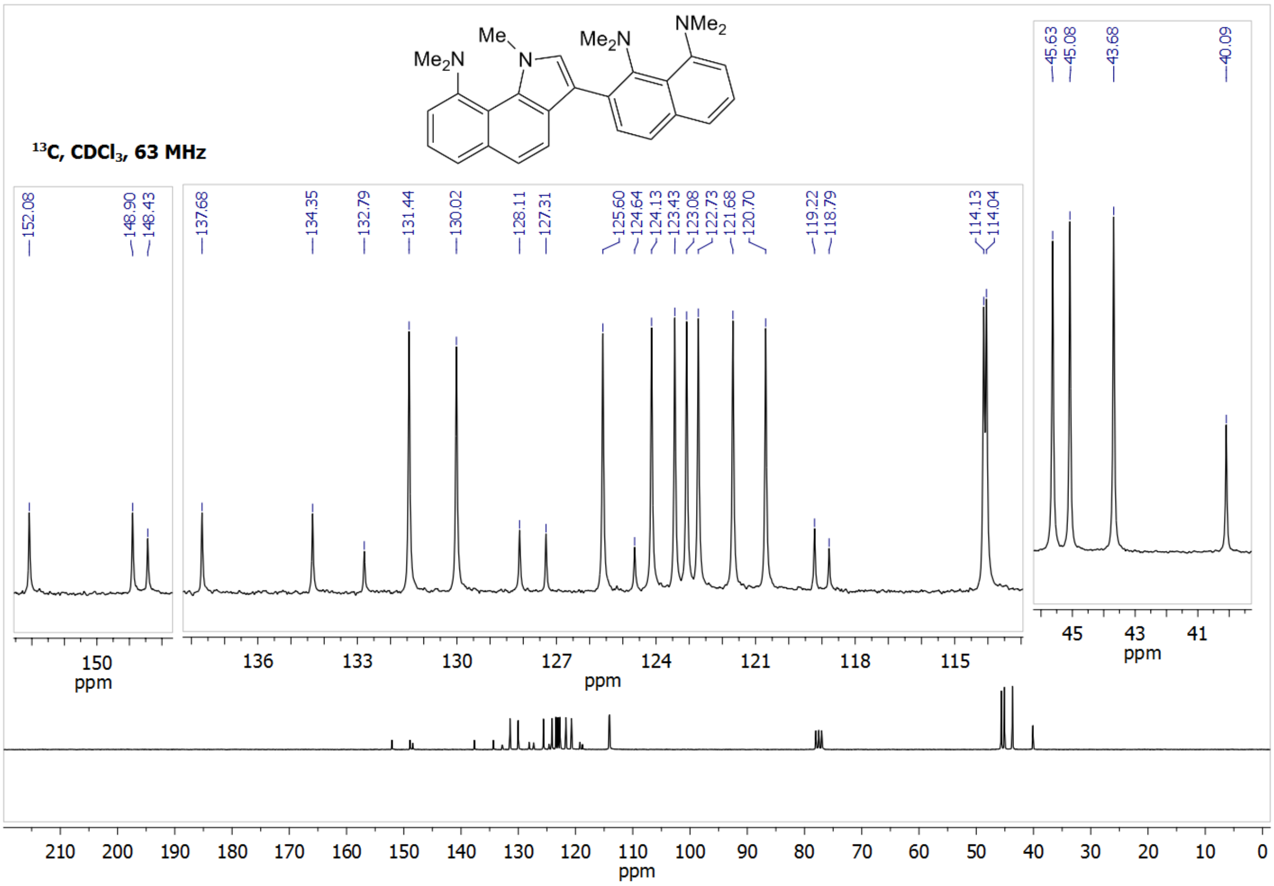


¹H, CDCl₃, 250 MHz
Me₂N
NMe₂
O
Me₂N
NMe₂
1870.29
1861.86
1846.49
1838.64
1831.41
1823.14
1815.55
1807.11
1747.43
1746.41
1740.74
1739.59
(d) 7.46 J(8.43)
(m) 7.34
(d) 7.24 J(8.43)
(dd) 6.97 J(1.09, 6.75)
1.97
4.31
2.10
1.96
7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90
ppm
738.27
715.89
(s) 2.95
(s) 2.86
12.24
12.00
2.95 2.85
ppm
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1
ppm



¹³C, CDCl₃, 63 MHz
Me₂N
NMe₂
O
Me₂N
NMe₂
197.42
153.12
152.34
140.09
128.56
128.38
127.65
122.37
121.49
120.40
113.62
45.30
44.89
198
ppm
152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114
ppm
45.6
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


1H, CDCl3, 250 MHz
Me2N
Me
N
Me2N
NMe2
1901.27
1899.28
1894.17
1890.78
1881.11
1875.82
1871.61
1867.51
1865.08
1863.78
1848.88
1846.81
1841.23
1839.31
1833.45
1831.44
1809.43
1796.60
1795.82
1789.07
1772.15
1771.21
1764.73
1763.90
1756.69
1035.90
704.93
704.16
665.72
(m) 7.52
(m) 7.36
(m) 7.17
(dd) 7.07 J(0.89, 7.37)
(s) 7.02
(s) 4.14
(s) 2.82
(s) 2.82
(s) 2.66
6.53
2.15
1.01
1.06
1.02
2.89
5.89
6.06
6.00
ppm


13C, CDCl3, 63 MHz
Me2N
Me
N
Me2N
NMe2
152.08
148.90
148.43
137.68
134.35
132.79
131.44
130.02
128.11
127.31
125.60
124.64
124.13
123.43
123.08
122.73
121.68
120.70
119.22
118.79
114.13
114.04
45.63
45.08
43.68
40.09
ppm

Crystal data and structure refinement for compounds

Crystals suitable for X-ray studies were grown up by slow evaporation from solutions of compounds in appropriate solvents or solvent mixtures: acetone for **5**, Et_2O–hexane 1:1 for **20**, MeCN for **22**. X-Ray measurements were conducted with Bruker APEX II diffractometers (Mo-K_α line, graphite monochromator, ω-scanning). The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic (for non-hydrogen atoms) approximation. All hydrogen atoms were placed in geometrically calculated positions and were refined in isotropic approximation in riding model with the $U_{iso}(H)$ parameters equal to $n \cdot U_{eq}(C_i)$ (n = 1.2 for CH and CH_2 groups and n = 1.5 for CH_3 groups), where $U(C_i)$ are respectively the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded. The H(O) hydrogen atom for **20** was found in difference Fourier synthesis.

Parameter	**5**	**20**	**22**
CCDC registration number	1035188	1035189	1035190
Empirical formula	$C_{16}H_{17}F_3N_2O$	$C_{32}H_{32}F_6N_4O$	$C_{29}H_{34}N_4O$
Formula weight	310.32	602.62	454.60
T (K)	100(2)	120(2)	100(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pbca*	$P2_1/c$	$P\bar{1}$
a (Å)	17.3704(11)	12.819(9)	12.282(8)
b (Å)	7.9575(5)	13.786(10)	13.024(8)
c (Å)	21.6807(14)	16.801(12)	16.571(10)
α (°)	90	90	108.054(11)
β (°)	90	96.45(2)	95.805(11)
γ (°)	90	90	90.129(11)
V (Å^3)	2996.8(3)	2950(4)	2506(3)
Z, D_c (Mg m^{-3})	8, 1.376	4, 1.357	2, 1.205
μ (mm^{-1})	0.112	0.110	0.074
Reflections collected/unique	34843/4337	23955/7849	21497/9732
R(int)	0.0370	0.0287	0.1131
R_1, wR_2 (all data)	0.0556, 0.1004	0.0649, 0.1318	0.1798, 0.1488
R factor (%)	4.28	4.82	7.27

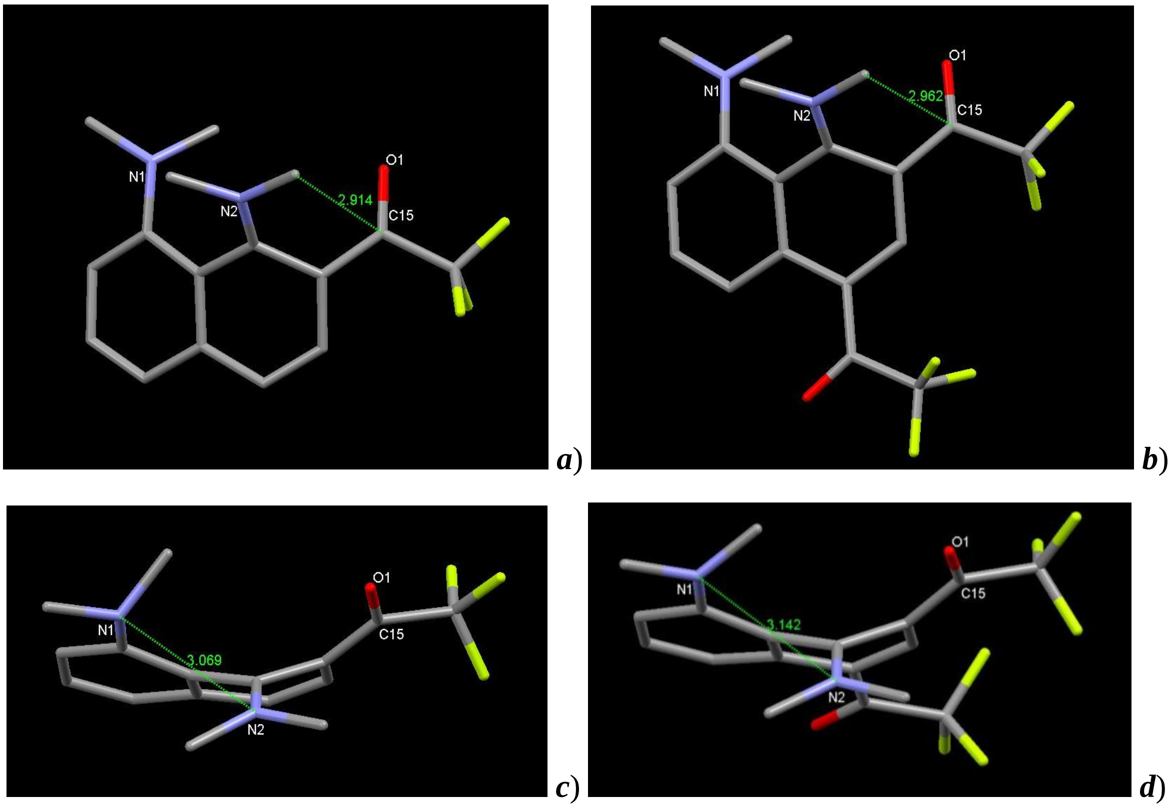


Figure S2 Molecular structures of trifluoroacetyl derivatives **5** (***a***,***c***) and **7** (***b***,***d***)[a] at 100 K showing the Me(N)…C(O) (***a***,***b***) and N1…N2 distances (***c***,***d***) (Å) (H atoms are omitted for clarity).

(a) L. Z. Boiko, V. I. Sorokin, E. A. Filatova, Z. A.Starikova, V. A. Ozeryanskii and A. F. Pozharskii, *J. Mol. Struct.*, 2011, **1005**, 12.

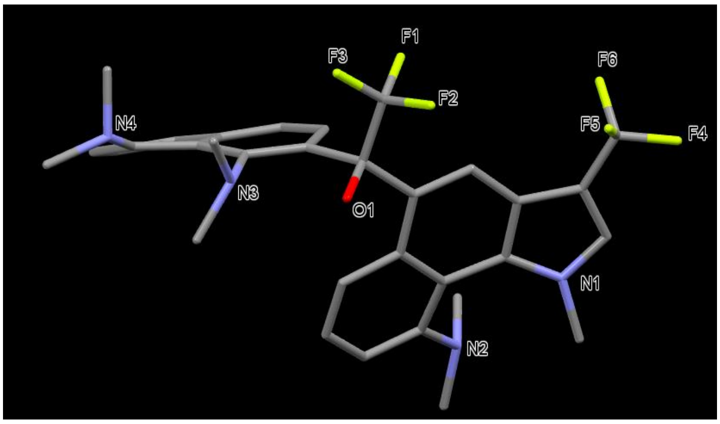


Figure S3 Molecular structure of indole **20** at 120 K (H atoms are omitted for clarity).

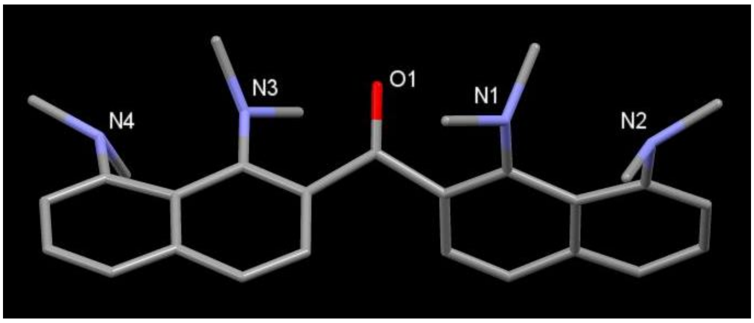
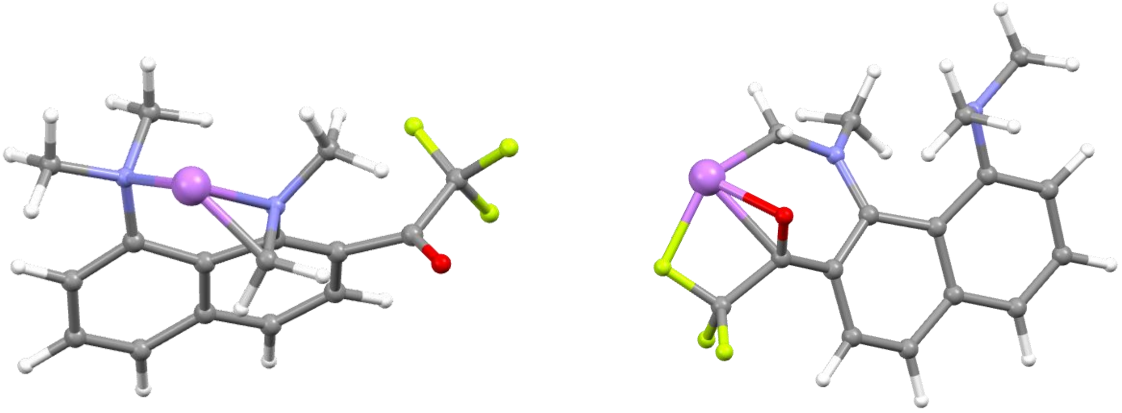


Figure S4 Molecular structure of binaphthylketone **22** at 100 K (H atoms are omitted for clarity).

DFT calculations

The quantum mechanical simulations were carried out using the Gaussian 09 suite of programs.[b] The energy minimization was performed using the Møller-Plesset second order perturbation theory (MP2)[2] and DFT with the B3LYP functional.[c,d] The 6-311+G(d,p) basis set was applied during the simulations.[e–h] Harmonic frequencies calculations were performed to confirm that the obtained structures corresponded to the minimum on the potential energy surface.



6a $E^{6b} - E^{6a}$ = 14.30 (14.89)* kcal/mol **6b**

Figure S5 The calculated gas-phase structure of **6** with the chelation of lithium to *peri*-NMe_2 groups (**6a**) and carbonyl group (**6b**) [B3LYP/6-311+G(d,p), *MP2/6-311+G(d,p)].

(b) M. J. Frisch, *et al.*, *Gaussian 09, Revision B01*, Gaussian, Inc., Wallingford CT, 2009; (c) C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618; (d) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (e) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **15**, 785; (f) K. Raghavachari, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650; (g) T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. v. R. Schleyer, *J. Comp. Chem.*, 1983, **4**, 294; (h) M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265.