Electronic supplementary information (ESI).

Synthesis of a Family of 3-Alkyl- or 3-Aryl-Substituted 1,2-Dihydroquinazolinium Salts and their Isomerization to 4-Iminium-1,2,3,4-Tetrahydroquinolines

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Contents:

^{1}H + ^{13}C NMR spectra of

X-ray Crystallography.

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Experimental Section:

General. When not stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. All compounds were dried first by suction and then under vacuum (1 mBar). Melting points were measured on a Reichert apparatus and are uncorrected. IR spectra were recorded on Nujol mulls between polyethylene sheets. The NMR assignments were performed, in some cases, with the help of APT, HMQC and HMBC experiments. The solvents were distilled before use. Although the syntheses of **1a**,[1] **1b**,[1] **2b**,[2] and **2d**[3] have been reported, we include them here because their characterization was incomplete.

Synthesis of $O_2NC_6H_4CH$=NR-2 (R = Xy (1a),[1] Tol (1b)[1]). A flask was charged with $O_2NC_6H_4CHO$-2 (for **1a**, 6.14 g, 40.63 mmol; for **1b**, 3.68 g, 24.36 mmol), the appropriate amine (for **1a**, $XyNH_2$, 5 mL, 40.60 mmol; for **1b**, $TolNH_2$, 2.6 g, 24.36 mmol), toluene (40 mL), and activated 4 Å molecular sieves. The mixture was refluxed for 2 h, allowed to cool to room temperature and filtered. The yellow solution was concentrated in a rotary evaporator to dryness to give an oily material. After cooling at 0 ºC, a yellow suspension formed, which was filtered and dried to give **1a**. In the case of **1b**, the residue was stirred with cold *n*-pentane (30 mL, 0 ºC) for 15 min, the resulting suspension was filtered and the solid was washed with cold *n*-pentane (3 x 5 mL, 0 ºC) and dried to give **1b** as a yellow solid.

1a: Yield: 10.04 g, 39.48 mmol, 97%. Mp: 55 ºC (56–58 ºC).[1] ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ 2.20 (s, 6 H, Me), 6.98 (dd, 1 H, *p*-Xy, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.6 Hz), 7.07 (d, 2 H, *m*-Xy, $^3J_{HH}$ = 7.5 Hz), 7.62 (ddd, 1 H, H^4, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz), 7.75 (“dt”, 1 H, H^5, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 0.6 Hz), 8.07 (dd, 1 H, H^3, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 0.9 Hz), 8.31 (dd, 1 H, H^6, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz), 8.63 (s, 1 H, H^7). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 ºC, TMS): δ 18.2 (Me), 124.2 ($CH^{p\text{-}Xy}$), 124.4 (CH^3), 126.9 ($C^{o\text{-}Xy}$), 128.1 ($CH^{m\text{-}Xy}$), 129.5 (CH^6), 131.1 (C^1), 131.2 (CH^4), 133.7 (CH^5), 149.1 (C^2), 150.3 ($C^{i\text{-}Xy}$), 158.8 (CH^7). IR (Nujol, cm^{-1}): ν(C=N + C=C) 1626, 1608, 1591, 1571; $\nu_{asym}NO_2$ 1526. HRMS (ESI) *m/z* calcd for $C_{15}H_{15}N_2O_2$ $[M + H]^+$, 255.1128; found 255.1128. Anal. calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.61; H, 5.55; N, 11.09.

1b: Yield: 5.01 g, 20.81 mmol, 85%. Mp: 73 ºC (71-72 ºC).[1] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 2.37 (s, 3 H, Me), 7.20 (sr s, 4 H, Tol), 7.57 ("dt", 1 H, H^4, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.2 Hz), 7.70 (t, 1 H, H^5, $^3J_{HH}$ = 7.6 Hz), 8.03 (dd, 1 H, H^3, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.2 Hz), 8.28 (dd, 1 H, H^6, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz), 8.93 (s, 1 H, H^7). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 21.0 (Me), 121.1 ($CH^{o\text{-}Tol}$), 124.4 (CH^3), 129.6 (CH^6), 129.8 ($CH^{m\text{-}Tol}$), 130.9 (CH^4), 131.1 (C^1), 133.4 (CH^5), 136.9 ($C^{p\text{-}Tol}$), 148.4 ($C^{i\text{-}Tol}$), 149.2 (C^2), 154.7 (CH^7). IR (Nujol, cm^{-1}): ν(C=N + C=C) + $\nu_{asym}NO_2$ 1616, 1605, 1567, 1516. HRMS (ESI) *m/z* calcd for $C_{14}H_{13}N_2O_2$ $[M + H]^+$, 241.0972; found 241.0974. Anal. calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.66; H, 4.82; N, 11.56.

Synthesis of $H_2NC_6H_4CH$=NR-2 (R = Xy (2a), Tol (2b)[2]). To a boiling solution of the appropriate nitro-derivative (for **2a**: **1a**, 3 g, 11.75 mmol; for **2b**: **1b**, 3 g, 12.49 mmol) in ethanol (60 mL) was added $Na_2S·9H_2O$ (for **2a**, 6.23 g, 25.94 mmol; for **2b**, 6.6 g, 27.49 mmol). After a few minutes, a vigorous reaction occurred and the heating was maintained for 15 min. The mixture was immediately concentrated under vacuum to dryness to give a dark brown oily residue, which was extracted with Et_2O (3 x 30 mL); the combined extracts were filtered through a short pad of Celite and the solution was concentrated under vacuum to dryness. This procedure yielded **2a**·$0.3H_2O$ as an orange viscous oil. In the case of **2b** a solid formed, which was stirred with cold *n*-pentane (20 mL, 0 ºC) for 30 min. The resulting suspension was filtered, the solid collected was washed with cold *n*-pentane (3 x 5 mL, 0 ºC) and dried by suction to give **2b**·$0.1H_2O$ as a yellow solid

2a·$0.3H_2O$**:** Yield: 2.63 g, 11.45 mmol, 97%. ^1H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.80 (vb s, 0.6 H, H_2O), 2.16 (s, 6 H, Me), 6.49 (s br, 2 H, NH_2), 6.71 (m, 2 H, H^{3+5}), 6.95 (t, 1 H, *p*-Xy, $^3J_{HH}$ = 7.6 Hz), 7.07 (d, 2 H, *m*-Xy, $^3J_{HH}$ = 7.6 Hz), 7.22 (m, 2 H, H^{4+6}), 8.24 (s, 1 H, H^7). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 25 ºC, TMS): δ 18.4 (Me), 115.7 (CH^3), 115.9 (CH^5), 117.2 (C^1), 123.6 ($CH^{p\text{-}Xy}$), 127.4 ($C^{o\text{-}Xy}$), 128.0

($CH^{m\text{-Xy}}$), 131.7 (CH^4), 134.1 (CH^6), 148.8 (C^2), 151.0 ($C^{i\text{-Xy}}$), 165.7 (CH^7). IR (cm^{-1}): ν(NH) 3459, 3279; ν(C=N + C=C) 1625, 1585, 1556. HRMS (ESI) *m/z* calcd for $C_{15}H_{17}N_2$ $[M + H]^+$, 225.1386; found 225.1385. Anal. calcd for $C_{15}H_{16}N_2{\cdot}0.3H_2O$: C, 78.43; H, 7.28; N, 12.20. Found: C, 78.27; H, 6.95; N, 12.26.

2b·$0.1H_2O$: Yield: 1.89 g, 8.91 mmol, 72%. Mp: 90 ºC (dec) (69-70 ºC).[2] ^1H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.54 (s br, 0.2 H, H_2O), 2.37 (s, 3 H, Me), 6.53 (s br, 2 H, NH_2), 6.72 (m, 2 H, H^{3+5}), 7.11 (d, 2 H, *o*-Tol, $^3J_{HH}$ = 8.0 Hz), 7.20 (m, 3 H, *m*-Tol + H^4), 7.32 (dd, 1 H, H^6, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.6 Hz), 8.53 (s, 1 H, H^7). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 20.9 (Me), 115.7 (CH^3), 116.2 (CH^5), 117.8 (C^1) 120.8 ($CH^{o\text{-Tol}}$), 129.7 ($CH^{m\text{-Tol}}$), 131.6 (CH^4), 134.2 (CH^6), 135.3 ($C^{p\text{-Tol}}$), 148.7 (C^2), 149.3 ($C^{i\text{-Tol}}$), 162.4 (CH^7). IR (Nujol, cm^{-1}): ν(NH) 3446, 3256; ν(C=N + C=C) 1623, 1583, 1551, 1518, 1505. HRMS (ESI) *m/z* calcd for $C_{14}H_{15}N_2$ $[M + H]^+$, 211.1230; found 211.1230. Anal. calcd for $C_{14}H_{14}N_2{\cdot}0.1H_2O$: C, 79.29; H, 6.75; N, 13.21. Found: C, 78.99; H, 6.75; N, 13.21.

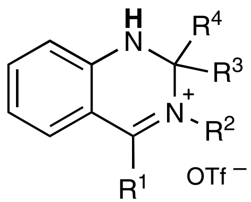
Synthesis of $H_2NC_6H_4CH$=NCy-2 (2c). $H_2NC_6H_4CHO$-2[4] (500 mg, 4.16 mmol), $CyNH_2$ (3.5 mL, 30.6 mmol), and *p*-toluensulfonic acid (TSA, 80 mg, 0.42 mmol) were refluxed in toluene (80 mL) in a Dean-Stark apparatus for 14 h. The resulting solution was concentrated in a rotary evaporator to give a brown oily residue, which was treated with Et_2O (100 mL). The white suspension obtained was filtered and the solution was concentrated under vacuum to give an oily residue, which was treated with Et_2O (20 mL) and concentrated under vacuum to dryness. After repeating this procedure three times in order to remove residual amounts of $CyNH_2$, a pale brown solid formed, which was dried under vacuum for 8 h. Yield: 693.7 mg, 3.43 mmol, 82%. Mp: 59 ºC. ^1H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.26-1.67 (various m, 6 H,

CH_2^{Cy}), 1.74-1.83 (m, 4 H, CH_2^{Cy}), 3.10 (m, 1 H, CH^{Cy}), 6.41 (s br, 2 H, NH_2), 6.66 (m, 2 H, H^{3+5}), 7.11 ("dt", 1 H, H^4, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.5 Hz), 7.18 (dd, 1 H, H^6, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz), 8.35 (s, 1 H, H^7). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 ºC, TMS): δ 24.6 (CH_2^{Cy}), 25.7 (CH_2^{Cy}), 34.8 (2 x CH_2^{Cy}), 69.8 (CH^{Cy}), 115.4 (CH^3), 115.9 (CH^5), 117.9 (C^1), 130.4 (CH^4), 133.1 (CH^6), 148.4 (C^2), 161.3 (CH^7). IR (Nujol, cm^{-1}): ν(NH) 3486, 3256, ν(C=N + C=C) 1632, 1609, 1589, 1557. HRMS (ESI) *m/z* calcd for $C_{13}H_{19}N_2$ $[M + H]^+$, 203.1543; found 203.1545. Anal. calcd for $C_{13}H_{18}N_2$: C, 77,18; H, 8.97; N, 13.85. Found: C, 77.44; H, 9.20; N, 13.77.

Synthesis of $H_2NC_6H_4$\{C(Me)=NCy\}-2 (2d).[3] $H_2NC_6H_4C(O)Me$-2 (2.50 g, 18.52 mmol), $CyNH_2$ (15.75 mL, 138 mmol), toluene (25 mL), and activated 4 Å molecular sieves were mixed in a Carius tube, which was sealed and heated at 100 ºC for 4 days. The reaction mixture was allowed to cool and filtered through a short pad of Celite. The solution was concentrated under vacuum to dryness, the residue was dissolved in hot *n*-pentane (30 mL, 36 ºC), filtered thought a short pad of Celite, concentrated under vacuum (15 mL) and cooled at 0 ºC. The resulting suspension was filtered and the solid collected was washed with cold *n*-pentane (3 x 5 mL, –33 ºC) and dried to give **2d**·0.1H_2O as a white crystalline solid. Yield: 3.78 g, 17.47 mmol, 94% (63%)[3]. Mp: 94 ºC. ^1H and $^{13}C\{^1H\}$ NMR.[3] IR (Nujol, cm^{-1}): ν(NH) 3341, 3182; ν(C=N + C=C) 1620, 1574. HRMS (ESI) *m/z* calcd for $C_{14}H_{21}N_2$ $[M + H]^+$, 217.1699; found 217.1702. Anal. calcd for $C_{14}H_{21}N_2O·0.1H_2O$: C, 77.09; H, 9.33; N, 12.84. Found: C, 77.09; H, 9.15; N, 12.97.

Synthesis of *R*-$H_2NC_6H_4$C(Me)=NCH(Me)Ph-2 (*R*-2e). A mixure of $H_2NC_6H_4C(O)Me$-2 (2.2 g, 16.28 mmol), (R)-(+)-PhCH(Me)NH_2 (10 mL, 78.64 mmol), activated 4 Å molecular sieves and toluene (10 mL) was heated in a Carius tube at 110 ºC for 2 days. The reaction mixture was allowed to cool, filtered through a short pad of Celite, and the orange solution was concentrated under vacuum to dryness. The oily residue was washed with cold *n*-pentane (4 x 30 mL, –78 ºC) giving a pale brown solid, which was dissolved in *n*-pentane and crystallized upon cooling to –34 ºC to give ***R*-2e** as white needles. Yield: 1.966 g, 8.25 mmol, 51%. Mp: 35 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.56 (d, 3 H, *Me*CHPh, $^{3}J_{HH}$ = 6.4 Hz), 2.26 (s, 3 H, Me^{7}), 4.88 (q, 1 H, C*H*(Me)Ph, $^{3}J_{HH}$ = 6.4 Hz), 6.60 (br s, 2 H, NH_2), 6.62-6.65 (m, 2 H, H^{3+5}), 7.09 (“dt”, 1 H, H^{4}, $^{3}J_{HH}$ = 7.2 Hz, $^{4}J_{HH}$ = 1.6 Hz), 7.21 (m, 1 H, *p*-Ph), 7.31 (m, 2 H, Ph^{m}), 7.38 (m, 2 H, Ph^{o}), 7.46 (dd, 1 H, H^{6}, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HH}$ = 1.6 Hz). $^{13}C\{^{1}H\}$ NMR (400 MHz, $CDCl_3$, 2 ºC, TMS): δ 16.2 (Me^{7}), 25.5 (*Me*CHPh), 59.8 (*C*H(Me)Ph), 115.8 ($CH^{3\text{ or }5}$), 116.9 ($CH^{3\text{ or }5}$), 121.2 (C^{1}), 126.5 ($CH^{o\text{-}+p\text{-Ph}}$), 128.4 ($CH^{m\text{-Ph}}$), 129.4 ($CH^{6}$), 130.0 ($CH^{4}$), 146.0 ($C^{i\text{-Ph}}$), 148.3 ($C^{2}$), 166.7 ($C^{7}$). IR (Nujol, cm^{-1}): ν(NH) 3475, 3208, ν(C=N + C=C) 1615, 1574, 1543. HRMS (ESI) *m/z* calcd for $C_{16}H_{19}N_2$ $[M + H]^{+}$, 239.1543; found 239.1545. Anal. calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.31; H, 7.60; N, 11.82.

Synthesis of 1,2-Dihydroquinazolinium Triflates:



^{1}H and $^{13}C\{^{1}H\}$ NMR assignment for 3a1 (R^{1} = H, R^{2} = Xy, R^{3} = R^{4} = Me): ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.67 (s, 6 H, *Me*$_2$C), 2.29 (s, 6 H, Me^{Xy}), 6.91 ("dt", 1 H, H^6, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 0.4 Hz), 7.21 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, *m*-Xy), 7.32 (m, 2 H, *p*-Xy + H^8) 7.59 (ddd, 1 H, H^7, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.6 Hz), 7.64 (d, 1 H, H^5, $^3J_{HH}$ = 8.0 Hz), 8.28 (s, 1 H, H^4), 8.45 (br s, 1 H, NH). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 18.6 (Me^{Xy}), 24.3 (*Me*$_2$C), 75.9 (C^2), 114.9 (C^{4a}), 117.0 (CH^8), 120.3 (q, $^1J_{CF}$ = 320 Hz, OTf), 121.8 (CH^6), 129.6 (CH$^{m\text{-}Xy}$), 130.3 (C$^{p\text{-}Xy}$) 132.7 (CH^5), 134.9 (C$^{o\text{-}Xy}$), 138.6 (C$^{i\text{-}Xy}$), 141.3 (CH^7), 147.9 (C^{8a}), 160.5 (CH^4).

3a2 (R^1 = H, R^2 = Xy, R^3 = Tol, R^4 = H): Reagents, **2a** (218 mg, 0.97 mmol), TolCHO (140 µL, 1.18 mmol) and HOTf (86 µL, 0.99 mmol, added with 20 min delay). The resulting solution was stirred for 8 h and concentrated under vacuum to dryness to give an oily residue, which was washed with a 1:20 mixture of CH_2Cl_2 and Et_2O (21 mL), dissolved in $CHCl_3$ (2 mL) and filtered through a short pad of anhydrous $MgSO_4$. The solution was slowly added dropwise to a cold mixture of *n*-pentane and Et_2O (1:2, 60 mL, 0 ºC) with stirring. The suspension was stirred for 15 min at 0 ºC, filtered, and the solid collected was dried first by suction and then under vacuum (6 h) to give **3a2**·0.6$CHCl_3$ as an orange solid. Yield: 228.3 mg, 0.48 mmol, 49%. Mp: 74 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, -35 ºC, TMS): δ 1.54 (s, 3 H, Me^{Xy}), 2.33 (s, 3 H, Me^{Tol}), 2.52 (s, 3 H, Me^{Xy}), 6.45 (d, 1 H, H^2, $^3J_{HH}$ = 4.0 Hz), 6.86 (t, 1 H, H^6, $^3J_{HH}$ = 7.6 Hz), 7.07 (m, 6 H, *o*- + *m*-Tol + *m*-Xy + H^8), 7.22 (d, 1 H, *m*-Xy , $^3J_{HH}$ = 7.2 Hz), 7.30 (t, 1 H, *p*-Xy , $^3J_{HH}$ = 7.6 Hz), 7.55 (d, 1 H, H^5, $^3J_{HH}$ = 8.0 Hz), 7.62 ("dt", 1 H, H^7, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz), 8.24 (s, 1 H, H^4), 8.31 (d br, 1 H, NH, $^3J_{HH}$ = 4.0 Hz). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 2.30 (s, 3 H, Me^{Tol}), 6.43 (d, 1 H, H^2, $^3J_{HH}$ = 3.6 Hz), 6.83 ("dt", 1 H, H^6, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.4 Hz), 7.01-7.11 (m, 7 H, H^8 + *o*- + *m*-Tol + *m*-Xy), 7.26 (t, 1 H, *p*-Xy, $^3J_{HH}$ = 7.6 Hz), 7.54 (d, 1 H, H^5, $^3J_{HH}$ = 9.2 Hz), 7.58 (ddd, 1 H, H^7, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.2 Hz), 8.27 (s, 1 H, H^4), 8.33 (d br, 1 H, NH, $^3J_{HH}$ = 3.6

Hz). ^{1}H NMR (400 MHz, $CDCl_3$, 55 ºC, TMS): δ 2.05 (s br, 6 H, Me^{Xy}), 2.30 (s, 3 H, Me^{Tol}), 6.45 (s, 1 H, H^2), 6.82 (t, 1 H, H^6, $^3J_{HH}$ = 7.6 Hz), 7.03-7.14 (m, 7 H, H^8 + *o*- + *m*-Tol + *m*-Xy), 7.25 (t, 1 H, *p*-Xy, $^3J_{HH}$ = 7.6 Hz), 7.51 (d, 1 H, H^5, $^3J_{HH}$ = 8.0 Hz), 7.57 (t, 1 H, H^7, $^3J_{HH}$ = 7.6 Hz), 8.23 (s, 1 H, H^4), 8.38 (s br, 1 H, NH). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, -35 ºC, TMS): δ 16.7 (Me^{Xy}), 17.7 (Me^{Xy}), 21.4 (Me^{Tol}), 74.4 (CH^2), 111.0 (C^{4a}), 116.2 (CH^8), 119.7 (CH^6), 119.8 (q, $^1J_{CF}$ = 319 Hz, CF_3SO_3), 126.0 ($CH^{o\text{-}Tol}$), 129.4 ($CH^{m\text{-}Xy}$), 129.5 ($CH^{m\text{-}Xy}$), 129.7 ($CH^{m\text{-}Tol}$), 130.2 ($CH^{p\text{-}Xy}$), 132.0 ($C^{o\text{-}Xy}$), 132.5 ($C^{p\text{-}Tol}$), 133.1 (CH^5), 134.8 ($C^{o\text{-}Xy}$), 138.5 ($C^{i\text{-}Xy}$), 141.4 ($C^{i\text{-}Tol}$), 142.4 (CH^7), 148.2 (C^{8a}), 160.1 (CH^4). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 17.5 (s v br, Me^{Xy}), 21.3 (Me^{Tol}), 75.2 (CH^2), 111.6 (C^{4a}), 116.2 (CH^8), 120.0 (CH^6), 120.3 (q, $^1J_{CF}$ = 320 Hz, CF_3SO_3), 126.5 ($CH^{o\text{-}Tol}$), 129.6 ($CH^{m\text{-}Xy}$), 129.8 ($CH^{m\text{-}Tol}$), 130.4 ($CH^{p\text{-}Xy}$), 132.6 ($C^{p\text{-}Tol}$), 133.1 (CH^5), 139.0 ($C^{i\text{-}Tol}$), 141.6 ($C^{i\text{-}Tol}$), 142.4 (CH^7), 148.7 (C^{8a}), 160.6 (CH^4). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, 55 ºC, TMS): δ 17.5 (Me^{Xy}), 21.2 (Me^{Tol}), 75.7 (CH^2), 111.9 (C^{4a}), 116.5 (CH^8), 120.2 (CH^6), 120.5 (q, $^1J_{CF}$ = 320 Hz, CF_3SO_3), 126.7 ($CH^{o\text{-}Tol}$), 129.6 ($CH^{m\text{-}Xy}$), 129.9 ($CH^{m\text{-}Tol}$), 130.5 ($CH^{p\text{-}Xy}$), 132.7 ($C^{p\text{-}Tol}$), 133.1 (CH^5), 134.0 ($C^{o\text{-}Xy}$), 139.2 ($C^{i\text{-}Xy}$), 141.7 ($C^{i\text{-}Tol}$), 142.5 (CH^7), 149.0 (C^{8a}), 160.8 (CH^4). IR (Nujol, cm^{-1}): ν(NH) 3224, 3186, ν(C=N + C=C) 1633, 1573, 1568, 1558. HRMS (ESI) *m/z* calcd for $C_{23}H_{23}N_2$ $[M]^+$, 327.2856; found 327.1862. Anal. calcd for $C_{24}H_{23}F_3N_2O_3S{\cdot}0.6CHCl_3$: C: 53.90; H, 4.33; N, 5.11; S, 5.85. Found: C, 53.63; H, 4.10; N, 5.20; S, 5.86. Crystals of **3a2**·$CHCl_3$ suitable for an X-ray diffraction study were obtained by slow evaporation of a solution of the product in $CHCl_3$.

3a3 (R^1 = H, R^2 = Xy, R^3 = CH(Me)Ph, R^4 = H): Reagents, **2a** (400 mg, 1.74 mmol), *rac*-PhCH(Me)CHO (260 µL, 1.92 mmol) and HOTf (160 µL, 1.83 mmol, added with 20 min delay). The resulting solution was stirrred overnight, filtered through anhydrous $MgSO_4$ and concentrated under vacuum to dryness giving an orange oily residue, which was washed first with a cold mixture of CH_2Cl_2 and Et_2O (1:20, 3 x 21 mL, 0 ºC) and then with a cold mixture of CH_2Cl_2 and *n*-pentane (1:20, 3 x 21 mL, 0 ºC) and dried under vacuum for 6 h to give **3a3**·H_2O as a dark orange solid consisting of a mixture of two isomers, D and d, in a 2.3:1 molar ratio. Yield: 587.3 mg, 1.15 mmol, 66%. Mp: 64 ºC. ^1H NMR (300 MHz, $CDCl_3$, –55 ºC, TMS): δ 1.25 (d, 3 H, CH*Me*Ph^{d}, $^3J_{HH}$ = 5.4 Hz), 1.31 (d, 3 H, CH*Me*Ph^{D}, $^3J_{HH}$ = 6.9 Hz), 1.88 (s, 3 H, Me$^{Xy, D}$), 2.38 (s, 6 H, Me$^{Xy, d}$), 2.41 (s, 3 H, Me$^{Xy, D}$), 2.54 (s, 2 H, H_2O), 3.45 (m, 1H, C*H*MePh^{d}), 3.52 (m, 1H, C*H*MePh^{D}), 5.66 (m, 1 H, H$^{2, d}$), 5.94 (dd, 1 H, H$^{2, D}$, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 4.5 Hz), 6.64 (several m, 20 H, Xy^{D+d} + Ph^{D+d} + H$^{6, D+d}$, H$^{8, D+d}$), 7.59 (t, 1 H, $^3J_{HH}$ = 7.8 Hz, H$^{7, D+d}$), 7.67 (d, 1 H, $^3J_{HH}$ = 8.1 Hz, H$^{5, D+d}$), 8.00 (br s, 1 H, NH^{d}), 8.28 (br d, 1 H, NH^{D}, $^3J_{HH}$ = 3.6 Hz), 8.32 (s, 2 H, H$^{4, D+d}$). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 ºC, TMS): δ 17.1 (CH*Me*Ph^{D+d}), 18.0 (Me$^{Xy, D}$), 18.4 (Me$^{Xy, D}$), 19.5 (Me$^{Xy, d}$), 42.0 (*CH*MePh^{D}), 44.1 (*CH*MePh^{d}), 75.6 (CH$^{2, D+d}$), 113.6 (C$^{4a, D}$), 113.9 (C$^{4a, d}$), 116.3 (CH$^{8, d}$), 116.7 (CH$^{8, D}$), 119.5 (q, CF_3SO_3, $^1J_{CF}$ = 320 Hz), 120.1 (CH$^{6, d}$), 120.6 (CH$^{6, D}$), 125.0 (CH^{d}), 127.4 (CH), 127.5 (CH), 128.6 (CH), 128.8 (CH), 129.2 (CH), 129.7 (CH), 130.2 (CH), 131.4 (Xy$^{o, D}$), 131.8 (Xy$^{o, d}$), 132.5 (CH$^{5, d}$), 133.0 (CH$^{5, D}$), 133.5 (Xy$^{o, D}$) 139.1 (Xy$^{i, D}$), 140. 4 (Ph$^{i, D}$), 141.7 (CH$^{7, d}$), 141.9 (CH$^{7, D}$), 147.5 (C$^{8a, D}$), 148.1 (C$^{8a, d}$), 160.7 (CH$^{4, D+d}$). IR (Nujol, cm^{-1}): ν(NH) 3234 br, ν(C=N + C=C) 1629, 1565, 1555. HRMS (ESI) *m/z* calcd for $C_{24}H_{23}N_2$ $[M]^+$, 341.2012; found 341.2011. $C_{25}H_{25}F_3N_2O_3S{\cdot}H_2O$: C, 59.04; H, 5.35; N, 5.51; S, 6.30. Found: C, 58.87; H, 5.10; N, 5.58; S, 6.67.

3b2 (R^1 = H, R^2 = Tol, R^3 = Tol, R^4 = H): Reagents, **2b** (100 mg, 0.48 mmol), TolCHO (60 µL, 0.51 mmol) and HOTf (45 µL, 0.52 mmol, added with 20 min delay). After 3.5 h of stirring, the reaction mixture was filtered through a short pad of Celite and concentrated under vacuum (2 mL). Cold Et_2O was added (20 mL, 0 ºC), the suspension was stirred for 15 min at 0 ºC and filtered. The solid was dissolved in $CHCl_3$ (2 mL) and added dropwise to rapidly stirred cold Et_2O (30 mL, 0 ºC); the suspension was stirred for 15 min at 0 ºC and filtered. The solid collected was washed with Et_2O and dried first by suction and then under vacuum for 8 h to give **3b2**·$0.5H_2O$ as an orange solid. Yield: 132.0 mg, 0.2721 mmol, 58%. Mp: 177 ºC. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.56 (s br, 1 H, H_2O), 2.28 (d, 3 H, Me), 2.37 (s, 3 H, Me), 6.76 (t, 1 H, H^6, $^3J_{HH}$ = 7.7 Hz), 6.99 (m, 2 H, H^8 + Tol), 7.00 (s, 1 H, H^2), 7.11 (d, 2 H, *o/m*-Tol, $^3J_{HH}$ = 8.1 Hz), 7.24-7.35 (m, 5 H, Tol), 7.43 (t, 1 H, H^7, $^3J_{HH}$ = 8.0 Hz), 7.56 (d, 1 H, H^5, $^3J_{HH}$ = 8.1 Hz), 8.59 (d br, 1 H, NH, $^3J_{HH}$ = 3.9 Hz), 8.84 (s, 1 H, H^4). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 ºC, TMS): δ 21.1 (Me), 21.2 (Me), 72.7 (CH^2), 113.9 (C^{4a}), 116.8 (CH^8), 120.8 (CH^6), 122.2 (*o/m*-Tol), 125.8 (*o/m*-Tol), 129.8 (*o/m*-Tol), 131.1 ($CH^{o/m\text{-Tol}}$), 132.3 ($C^{p\text{-Tol}}$), 132.7 (CH^5), 138.9 ($C^{p\text{-Tol}}$), 140.4 ($C^{i\text{-Tol}}$), 141.4 ($C^{i\text{-Tol}}$), 141.7 (CH^7), 146.7 (C^{8a}), 156.0 (CH^4). IR (Nujol, cm^{-1}): ν(NH) 3250, ν(C=N + C=C) 1628, 1600, 1564. HRMS (ESI) *m/z* calcd for $C_{22}H_{21}N_2$ $[M]^+$, 313.1699; found 313.1703. Anal. calcd for $C_{23}H_{21}F_3N_2O_{31}S\cdot0.5H_2O$: C, 58.59; H, 4.70; N, 5.94; S, 6.80. Found: C, 58.69; H, 4.70; N, 5.94; S, 6.80.

3b3 (R^1 = H, R^2 = Tol, R^3 = CH(Me)Ph, R^4 = H): Reagents, **2b** (220 mg, 1.05 mmol), *Rac*-PhCH(Me)CHO (150 µL, 1.11 mmol) and HOTf (100 µL, 1.15 mmol). After 18 h of stirring, the reaction mixture was concentrated to dryness. The oily residue was extracted with a 1:30 mixture of CH_2Cl_2 and Et_2O (3 x 31 mL) and the combined extracts were concentrated under vacuum to *ca* 10 mL. The resulting suspension was stirred at 0 ºC for 15 min, filtered, and the solid collected was washed with cold Et_2O (3 x 3 mL, 0 ºC) and dried, first by suction and then under vacuum (6 h) to give **3b3** as a red solid consisting of a mixture of two isomers, D and d, in a 2:1 molar ratio. Yield: 365.2 mg, 0.77 mmol, 73%.

Mp: 152 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.33 (d, 3 H, CH*Me*Ph^{D}, $^{3}J_{HH}$ = 7.2 Hz), 1.36 (d, 3 H, CH*Me*Ph^{d}, $^{3}J_{HH}$ = 7.2 Hz,), 2.21 (s, 3 H, Me$^{Tol, D}$), 2.40 (s, 3 H, Me$^{Tol, d}$), 3.13 (m, 1 H, C*H*MePh^{d}), 3.48 (m, 1 H, C*H*MePh^{D}), 6.21 (m, 1 H, H$^{2, D}$), 6.32 (m, 1 H, H$^{2, d}$), 6.50 (t, 1 H, H$^{6, d}$, $^{3}J_{HH}$ = 7.4 Hz,), 6.79 (d, 1 H, H$^{8, d}$, $^{3}J_{HH}$ = 8.4 Hz), 6.88-6.94 (m, 5 H, *o*- + *m*-Tol^{D} + H$^{6, D}$), 6.99-7.11 (various m, 6 H, *o*- + *m*- + *p*-Ph + H$^{8, D}$ + H$^{5, d}$), 7.32 ("dt", 1 H, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 1.2 Hz, H^{7}, m), 7.37 (d, 2 H, $^{3}J_{HH}$ = 8.4 Hz, *m*-Tol^{d}), 7.56 (t, 1 H, H$^{7, D}$, $^{3}J_{HH}$ = 7.8 Hz), 7.62 (d, 2 H, *o*-Tol^{d}, $^{3}J_{HH}$ = 8.4 Hz), 7.66 (d br, 1 H, NH^{d}, $^{3}J_{HH}$ = 5.2 Hz), 7.72 (d, 1 H, H$^{5, D}$, $^{3}J_{HH}$ = 8.0 Hz), 8.22 (d br, 1 H, NH^{D}, $^{3}J_{HH}$ = 4.8 Hz), 8.39 (s, 1 H, H$^{4, d}$), 8.54 (s, 1 H, H$^{4, D}$). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): 15.0 (CH*Me*Ph^{d}), 16.9 (CH*Me*Ph^{D}), 20.9 (Me$^{Tol, D}$), 21.1 (Me$^{Tol, d}$), 41.0 (*CH*MePh^{D}), 43.8 (*CH*MePh^{d}), 76.3 (CH$^{2, D+d}$), 113.9 (C$^{4a, d}$), 114.8 (C$^{4a, D}$), 115.6 (CH$^{8, d}$), 116.7 (CH$^{8, D}$), 119.6 (CH$^{6, d}$), 120.6 (q, $^{1}J_{CF}$ = 319.6 Hz, CF_3SO_3), 120.7 (CH$^{6, D}$), 122.2 (C$^{o\text{-Tol}, D}$), 122.4 (C$^{o\text{-Tol}, d}$), 127.7 (CH$^{p\text{-Ph}, D}$), 127.9 (CH$^{p\text{-Ph}, d}$), 128.0 (CH$^{o\text{-Ph}, D}$), 128.5 (CH$^{m\text{-Ph}, d}$), 128.7 (CH$^{o\text{-}Ph, d}$), 128.8 (CH$^{m\text{-}Ph, D}$), 130.4 (CH$^{\text{m-Tol}, D}$), 133.1 (CH$^{5, D}$), 131.5 (CH$^{m\text{-Tol}, d}$), 132.6 (CH$^{5, d}$), 138.0 (C$^{i\text{-Ph}, d}$), 138.80 (C$^{i\text{-C}, D}$), 138.85 (C$^{p\text{-Tol}, d}$), 139.5 (C$^{i\text{-Tol}, D+d}$), 141.1 (CH$^{7, D}$), 141.2 (CH$^{7, d}$), 146.3 (C$^{8a, D}$), 148.3 (C$^{8a, d}$), 157.0 (CH$^{4, D}$), 158.3 (CH$^{4, d}$). IR (Nujol, cm^{-1}): ν(NH) 3242, ν(C=N + C=C) 1627, 1599, 1557. HRMS (ESI) *m/z* calcd for $C_{23}H_{23}N_2$ $[M]^+$, 327.1856; found 327.1859. Anal. calcd for $C_{24}H_{23}F_3N_2O_3S$: C, 60.49; H, 4.87; N, 6.01; S, 6.66. Found: C, 60.45; H, 4.66; N, 5.92; S, 6.26. Crystals of **3b3** suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of the product in $CHCl_3$.

3c1 (R^1 = H, R^2 = Cy, R^3 = R^4 = Me): Reagents, **2c** (120 mg, 0.59 mmol), Me_2CO (10 mL) and HOTf (52 µL, 0.60 mmol). The solution was stirred for 1.5 h and concentrated under vacuum to dryness. The yellow oily residue was washed with a 1:20 mixture of CH_2Cl_2 and Et_2O (4 x 21 mL) and converted into a solid under vacuum. The solid was dissolved in CH_2Cl_2 (1 mL) and a 10:20 mL mixture of Et_2O/*n*-pentane (0 ºC) was added. The suspension was stirred at 0 ºC for 15 min, filtered and the solid collected was washed with *n*-pentane (3 x 5 mL, 0 ºC), dried first by suction under a N_2 atmosphere and then under vacuum (6 h) to give **3c1** as a yellow solid, which must be stored below 4 ºC. Yield: 164.5 mg, 0.42 mmol, 71 %. Dec.p: 86 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.31-1.48 (various m, 3 H, CH_2^{Cy}), 1.62-1.82 (various m, 3 H, CH_2^{Cy}), 1.78 (s, 6 H, *Me*$_2$C), 1.94-2.06 (various m, 4 H, CH_2^{Cy}), 3.68 (m, 1 H, CH^{Cy}), 6.74 (t, 1 H, $^3J_{HH}$ = 7.6 Hz, H^6), 7.00 (d, 1 H, $^3J_{HH}$ = 8.4 Hz, H^8), 7.43 ("dt", 1 H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, H^7), 7.49 (d, H^5, $^3J_{HH}$ = 8.4 Hz) 7.51 (s, NH), 8.50 (s, 1 H, H^4). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 24.1 (CH_2^{Cy}), 24.4 (CH_2^{Cy}), 25.6 (CH_2^{Cy}), 25.7 (*Me*$_2$C), 30.6 (CH_2^{Cy}), 34.7 (CH_2^{Cy}), 61.4 (CH^{Cy}), 76.5 (C^2), 112.0 (C^{4a}), 116.5 (C^8), 119.7 (C^6), 132.1 (C^5), 141.0 (C^7), 147.2 (C^{8a}), 157.8 (C^4). IR (Nujol, cm^{-1}): ν(NH) 3257, ν(C=N + C=C) 1643, 1633, 1581, 1574. HRMS (ESI) m/z calcd for $C_{16}H_{23}N_2$ $[M]^+$, 243.1856; found 243.1858. The scarce stability of **3c1** in solution and in the solid state prevented to get good elemental analysis.

3c2 (R^1 = H, R^2 = Cy, R^3 = Tol R^4 = H): Reagents, **2c** (135 mg, 0.67 mmol), TolCHO (80 µL, 0.68 mmol) and HOTf (60 µL, 0.69 mmol, added with 20 min delay). The solution was stirred for 21 h and concentrated to dryness; the oily residue was dissolved in $CHCl_3$ (3 mL), filtered through a short pad of anhydrous $MgSO_4$ and slowly added dropwise to a mixture of Et_2O and *n*-pentane (20:40 mL) with stirring. The suspension was filtered and the solid collected was washed with *n*-pentane (3 x 5 mL) and dried under vacuum (6 h) to give **3c2**·0.7H_2O as an orange solid. Yield: 214.8 mg, 0.47 mmol, 71%. Mp: 148 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.12-1.48 (various m, 4 H, CH_2^{Cy}), 1.61 (s br, 1.5 H, H_2O), 1.65 (m, 1 H, CH_2^{Cy}), 1.81-1.94 (various m, 4 H, CH_2^{Cy}), 2.18 (m, 1 H, CH_2^{Cy}), 2.27 (s, 3 H, Me), 6.57 (d, 1 H, H^2, $^3J_{HH}$ = 4.4 Hz), 6.70 (t, 1 H, H^6, $^3J_{HH}$ = 7.6 Hz), 6.77 (d, 1 H, H^8, $^3J_{HH}$ = 8.4 Hz), 7.10 (d, 2 H, *m*-Tol, $^3J_{HH}$ = 8.4 Hz), 7.31 (d, 2 H, *o*-Tol, $^3J_{HH}$ = 8.4 Hz), 7.35 (ddd, 1 H, H^7, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz), 7.59 (d, 1 H, H^5, $^3J_{HH}$ = 8.0 Hz), 8.76 (d br, 1 H, NH, $^3J_{HH}$ = 4.0 Hz), 8.97 (s, 1 H, H^4). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 21.1 (Me^{Tol}), 24.1 (CH_2^{Cy}), 25.1 (CH_2^{Cy}), 31.8 (CH_2^{Cy}), 32.6 (CH_2^{Cy}), 67.6 (CH^{Cy}), 69.9 (CH^2), 113.0 (C^{4a}), 116.0 (CH^8), 119.0 (CH^6), 120.5 (q, $^1J_{CF}$ = 320 Hz, CF_3SO_3), 125.7 ($CH^{o\text{-Tol}}$), 129.8 ($CH^{m\text{-Tol}}$), 132.7 (CH^5), 133.3 ($C^{p\text{-Tol}}$), 140.3 ($C^{i\text{-Tol}}$), 140.5 (CH^7), 145.8 (C^{8a}), 158.6 (CH^4). IR (Nujol, cm^{-1}): ν(NH) 3271, ν(C=N + C=C) 1633, 1614, 1574, 1577. HRMS (ESI) *m/z* calcd for $C_{21}H_{25}N_2$ $[M]^+$, 305.2012; found 305.2018. Anal. calcd for $C_{22}H_{25}F_3N_2O_3S{\cdot}0.7H_2O$: C, 56.57; H, 5.70; N, 6.00; S, 6.86. Found: C, 56.32; H, 5.45; N, 6.27; S, 6.81.

3c4 (R^1 = H, R^2 = Cy, R^3 = Me, R^4 = H): Reagents, **2c** (120 mg, 0.59 mmol), MeCHO (0.1 mL, 1.77 mmol) and HOTf (52 µL, 0.60 mmol). After 3.5 h of stirring, the solution was concentrated under vacuum to dryness. The oily residue was washed with a cold mixture of CH_2Cl_2 and Et_2O (1:30, 31 mL), dissolved in $CHCl_3$ (1 mL), filtered through a short pad of anhydrous $MgSO_4$ and added dropwise to a cold mixture of Et_2O and *n*-pentane (2:18 mL, 0 ºC) to give a suspension. The mother liquor was decanted and the residue dried under vacuum for 6 h to give **3c4** as an orange solid. Yield: 160.3 mg, 0.42 mmol, 71%. Mp: 81 ºC. ^1H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.23-1.38 (m, 2 H, CH_2^{Cy}), 1.43-1.58 (m, 2 H, CH_2^{Cy}), 1.46 (d, 3 H Me, $^3J_{HH}$ = 6.4 Hz,), 1.70-2.24 (various m, 7 H, CH_2^{Cy} + H_2O), 3.78 (m, 1 H, CH^{Cy}), 5.65 ("quint", 1 H, H^2), 6.81 (t, 1 H, H^6, $^3J_{HH}$ = 7.4 Hz), 6.92 (d, 1 H, H^8, $^3J_{HH}$ = 8.4 Hz), 7.30 (d br, 1 H, NH, $^3J_{HH}$ = 4.0 Hz), 7.47 ("dt", 1 H, H^7, $^3J_{HH}$

= 7.8 Hz, $^{4}J_{HH}$ = 1.2 Hz), 7.56 (d, 1 H, H^5, $^{3}J_{HH}$ = 8.0 Hz), 8.63 (s, 1 H, H^4). $^{13}C\{^{1}H\}$ NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 18.5 (Me), 24.4 (CH_2^{Cy}), 25.0 (CH_2^{Cy}), 31.9 (CH_2^{Cy}), 32.6 (CH_2^{Cy}), 65.2 (CH^2), 67.0 (CH^{Cy}), 112.8 (C^{4a}), 116.3 (CH^8), 119.8 (CH^6), 120.5 (q, $^{1}J_{CF}$ = 320 Hz, CF_3SO_3), 132.7 (CH^5), 140.3 (CH^7), 146.1 (C^{8a}), 157.2 (CH^4). IR (Nujol, cm^{-1}): ν(NH) 3229, ν(C=N + C=C) 1631, 1594, 1563. HRMS (ESI) *m/z* calcd for $C_{15}H_{21}N_2$ $[M]^+$, 230.1778; found 229.1703. Anal. calcd for $C_{16}H_{21}F_3N_2O_{3.5}S$: C, 49.60; H, 5.7; N, 7.23; S, 8.28. Found: C, 49.39; H, 5.58; N, 6.91; S, 7.96.

3d2 (R^1 = Me, R^2 = Cy, R^3 = Tol, R^4 = H): Reagents, **2d** (200 mg, 0.92 mmol), TolCHO (110 μL, 0.93 mmol) and HOTf (82 μL, 0.94 mmol). After 18 h of stirring, the yellow solution was concentrated under vacuum to dryness. The oily residue was washed with a CH_2Cl_2/Et_2O mixture (1:20, 3 x 21 mL) and dried under vacuum for 8 h to give **3d2**·H_2O as a deep yellow solid, which must be stored below 4 ºC. Yield: 376.8 mg, 0.80 mmol, 84%. Mp: 78 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.12-2.03 (several m, 12 H, CH_2^{Cy} + H_2O), 2.23 (s, 3 H, Me^{Tol}), 2.91 (s, 3 H, Me^4), 4.37 (m, 1 H, CH^{Cy}), 6.78 (t overlapped with s, 2 H, H^{2+6}, $^{3}J_{HH}$ = 7.6 Hz), 6.94 (d, 1 H, H^8, $^{3}J_{HH}$ = 8.4 Hz), 7.05 (d, 2 H, *m*-Tol, $^{3}J_{HH}$ = 8.0 Hz), 7.21 (d, 2 H, *o*-Tol, $^{3}J_{HH}$ = 8.0 Hz), 7.36 (t, 1 H, H^7, $^{3}J_{HH}$ = 7.8 Hz), 7.55 (d, 1 H, H^5, $^{3}J_{HH}$ = 8.4 Hz), 8.34 (s br, 1 H, NH). $^{13}C\{^{1}H\}$ NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 17.9 (Me), 21.0 (Me^{Tol}), 24.2 (CH_2^{Cy}), 25.0 (CH_2^{Cy}), 25.3 (CH_2^{Cy}), 29.8 (CH_2^{Cy}), 32.2 (CH_2^{Cy}), 64.2 (CH^{Cy}), 65.3 (CH^2), 116.1 (C^{4a}), 117.5 (CH^8), 120.0 (CH^6), 120.5 (q, $^{1}J_{CF}$ = 319.6 Hz, TfO), 126.1 ($CH^{o\text{-}Tol}$), 129.0 (CH^5), 129.4 ($CH^{m\text{-}Tol}$), 132.7 ($C^{p\text{-}Tol}$), 138.9 (CH^7), 139.3 ($C^{i\text{-}Tol}$), 145.3 (C^{8a}), 168.0 (C^4). IR (Nujol, cm–1): ν(NH) 3262, ν(C=N + C=C) 1621, 1590, and 1557. HRMS (ESI) *m/z* calcd for $C_{22}H_{27}N_2$ $[M]^+$, 319.2169; found 319.2173. Anal. calcd for $C_{23}H_{27}F_3N_2O_3S{\cdot}H_2O$: C, 56.78; H, 6.01; N, 5.76; S, 6.59. Found: C, 56.35; H, 6.00; N, 5.87; S, 6.92.

3d3 (R^1 = Me, R^2 = Cy, R^3 = CH(Me)Ph, R^4 = H): Reagents, **2d** (200 mg, 0.92 mmol), *rac*-PhCH(Me)CHO (150 µL, 1.11 mmol) and HOTf (100 µL, 1.15 mmol). After 4 h of stirring, the reaction mixture was concentrated to dryness. The oily residue was dissolved in CH_2Cl_2 and cold Et_2O (30 mL, 0 ºC) was added; the suspension was stirred at 0 ºC for 30 min and filtered. The solid collected was washed with cold Et_2O (3 x 5 mL, 0ºC), filtered and dried under vacuum for 6 h to give **3d3**·$0.5H_2O$ as orange solid mixture of isomers, D and d, in a 65:35 molar ratio. Yield: 323.7 mg, 0.67 mmol, 73%. Mp: 154 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 0.52 (m, 1 H, $CH_2^{Cy, d}$), 0.64 (m, 1 H, $CH_2^{Cy, d}$), 0.97-2.06 (various m, 10 H, $CH_2^{Cy, D+d}$ + H_2O), 1.34 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH(*Me*)Ph^d), 1.51 (d, 3 H, CH(*Me*)Ph^D, $^3J_{HH}$ = 7.2 Hz), 2.46 (m, 1 H, $CH_2^{Cy, D}$), 2.51 (s, 3 H, $Me^{4, D}$), 2.71 (s, 3 H, $Me^{4, d}$), 2.90 (m, 1 H, C*H*(Me)Ph^D), 3.13 (m, 1 H, C*H*(Me)Ph^d), 3.68 (m, 1 H, $CH^{Cy, d}$), 4.32 (m, 1 H, $CH^{Cy, D}$), 5.64 (m, 1 H, $H^{2, d}$), 5.80 (m, 1 H, $H^{2, D}$), 6.42 ("dt", 1 H, $H^{6, D}$, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz), 6.74 (dd, 1 H, $H^{5, D}$, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 0.8 Hz), 6.90 (m, 3 H, $H^{8, D}$ + *o*-Ph^D), 6.94-7.02 (various m, 4 H, *m*- + *p*-Ph^D + $H^{6, d}$), 7.15 (d, 2 H, *o*-Ph, $^3J_{HH}$ = 8.0 Hz), 7.20 (d, 1 H, $H^{8, d}$, $^3J_{HH}$ = 8.4 Hz), 7.24-7.30 (m, $H^{7, D}$ + *p*-Ph^d), 7.35 (m, 2 H, *m*-Ph^d) 7.58 (ddd, 1 H, $H^{7, d}$, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.0 Hz), 7.68 (d br, 1 H, $^3J_{HH}$ = 5.2 Hz, NH^D), 7.75 (d, 1 H, H^5, $^3J_{HH}$ = 8.8 Hz), 8.27 (d br, 1 H, NH^d, $^3J_{HH}$ = 4.4 Hz). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 14.5 (CH(*Me*)Ph, M), 16.9 (CH(*Me*)Ph, m), 17.4 ($Me^{4, D}$), 18.7 ($Me^{4, d}$), 24.3 ($CH_2^{Cy, D}$), 24.1 ($CH_2^{Cy, d}$), 25.1 ($CH_2^{Cy, d}$), 25.3 ($CH_2^{Cy, D}$), 25.4 ($CH_2^{Cy, D}$), 25.9 ($CH_2^{Cy, d}$), 29.0 ($CH_2^{Cy, d}$), 31.3 ($CH_2^{Cy, D}$), 32.4 ($CH_2^{Cy, D}$), 33.4 ($CH_2^{Cy, d}$), 37.3 (*C*H(Me)Ph^d), 45.4 (*C*H(Me)Ph^D), 64.4 ($CH^{Cy, D+d}$), 69.1 ($CH^{2, D}$), 70.3 ($CH^{2, d}$), 116.0 ($CH^{8, D}$), 116.7 ($C^{4a, D}$), 117.2 ($C^{4a, d}$), 117.3 ($CH^{8, d}$), 118.5 ($CH^{6, D}$), 120.1 ($CH^{6, d}$), 120.6 (q, $^1J_{CF}$ = 319.6

Hz, CF_3SO_3), 127.4 ($CH^{p\text{-Ph, D}}$), 127.9 ($CH^{p\text{-Ph, d}}$), 128.0 ($CH^{m\text{-Ph, D}}$), 128.3 ($CH^{5,\, D}$ + $CH^{o\text{-Ph, D}}$), 128.7 ($CH^{o\text{-Ph, d}}$), 129.0 ($CH^{m\text{-Ph, d}}$), 138.3 ($CH^{7,\, D}$), 139.0 ($C^{i\text{-Ph, D}}$), 139.0 ($CH^{7,\, d}$), 139.6 ($C^{i\text{-Ph, d}}$), 144.3 ($C^{8a,\, d}$), 146.6 ($C^{8a,\, D}$), 168.4 ($C^{4,\, D}$), 166.8 ($C^{4,\, d}$). IR (Nujol, cm^{-1}): ν(NH) 3291, ν(C=N + C=C) 1622, 1588, 1558. HRMS (ESI) *m/z* calcd for $C_{23}H_{29}N_2$ $[M]^+$, 333.2325; found 333.2330. Anal. calcd for $C_{24}H_{29}F_3N_2O_3S·0.5H_2O$: C, 58.64; H, 6.15; N, 5.70; S, 6.52. Found: C, 58.86; H, 6.01; N, 5.76; S, 5.97.

3d4 (R^1 = Me, R^2 = Cy, R^3 = Me, R^4 = H): Reagents, **2d** (90 mg, 0.42 mmol), MeCHO (200 μL, 3.54 mmol) and HOTf (38 μL, 0.44 mmol). After 6.5 h of stirring, the solution was concentrated under vacuum to dryness. The oily residue was washed successively with a mixture of CH_2Cl_2 and Et_2O (1:200, 20.1 mL) and with *n*-pentane (20 mL), dried under vacuum for 6 h, stirred with cold Et_2O (20 mL, 0 ºC), and filtered. The solid collected was dried first by suction and then under vacuum for 6h to give **3d4** as a pale yellow solid. Yield: 145.0 mg, 0.37 mmol, 89%. Mp: 114 ºC. ^1H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.19-1.48 (various m, 2 H, CH_2^{Cy}), 1.35 (d, 3 H, $^3J_{HH}$ = 6.4 Hz, C^2*Me*), 1.72-2.10 (various m, 8 H, CH_2^{Cy}), 2.71 (s, 3 H, C^4*Me*), 4.18 (m, 1 H, CH^{Cy}), 5.84 (q, 1 H, H^2, $^3J_{HH}$ = 6.0 Hz), 6.89 (“dt”, 1 H, $H^{6/7}$, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.4 Hz), 7.04 (d, 1 H, $H^{5/8}$, $^3J_{HH}$ = 8.4 Hz), 7.50 (“dt”, 1 H, $H^{6/7}$, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz), 7.58 (d, 1 H, $H^{5/8}$, $^3J_{HH}$ = 8.0 Hz), 7.67 (s br, 1 H, NH). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 17.8 (C^2*Me* + C^4*Me*), 24.3 (CH_2^{Cy}), 25.2 (CH_2^{Cy}), 25.3 (CH_2^{Cy}), 30.4 (CH_2^{Cy}), 31.8 (CH_2^{Cy}), 61.5 (CH^{Cy} or CH^2), 63.6 (CH^{Cy} or CH^2), 114.5 (C^{4a}), 117.6 (CH^8), 119.7 (CH^6), 120.5 (q, $^1J_{CF}$ = 320 Hz, TfO), 129.2 (CH^5), 138.9 (CH^7), 145.7 (C^{8a}), 166.1 (C^4). IR (Nujol, cm^{-1}): ν(NH) 3250, ν(C=N + C=C) 1622, 1573, 1587, 1562. HRMS (ESI) *m/z* calcd for $C_{16}H_{23}N_2$ $[M]^+$, 243.1856; found 243.1857. Anal. calcd for $C_{17}H_{23}F_3N_2O_3S$: C, 52.03; H, 5.91; N, 7.14; S, 8.17. Found: C, 51.59; H, 5.47; N, 7.18; S, 7.88.

Crystals of **3d4** suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a solution of the product in $CHCl_3$.

^{1}H and ^{13}C{^{1}H} NMR assignment for 3d5 (R^1 = Me, R^2 = Cy, R^3 = Fc, R^4 = H): ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.28-1.40 (m, 3 H, CH_2^{Cy}), 1.70-2.03 (various m, 7 H, CH_2^{Cy}), 2.63 (s, 3 H, Me), 3.53 (s br, 1 H, Fc), 3.98 (s br, 1 H, Fc), 4.09 (m, 1 H, CH^{Cy}), 4.16 (s br, 1 H, Fc), 4.26 (s, 5 H, Fc), 4.34 (s br, 1 H, Fc), 6.47 (s br, 1 H, H^2), 6.92 (t, 1 H, H^6, $^3J_{HH}$ = 7.6 Hz), 7.23 (d, 1 H, H^8, $^3J_{HH}$ = 8.4 Hz), 7.54-7.60 (m, 2 H, H^{5+7}), 8.29 (s br, 1 H, NH). ^{1}H NMR (400 MHz, $CDCl_3$, 0 ºC, TMS): δ 1.24-1.40 (m, 3 H, CH_2^{Cy}), 1.71-2.02 (various m, 7 H, CH_2^{Cy}), 2.63 (s, 3 H, Me), 3.50 (s br, 1 H, Fc), 3.98 (s br, 1 H, Fc), 4.09 (m, 1 H, CH^{Cy}), 4.16 (s br, 1 H, Fc), 4.28 (s, 5 H, Fc), 4.34 (s br, 1 H, Fc), 6.42 (d, 1 H, H^2, $^3J_{HH}$ = 4.4 Hz), 6.93 (t, 1 H, H^6, $^3J_{HH}$ = 7.4 Hz), 7.22 (d, 1 H, H^8, $^3J_{HH}$ = 8.0 Hz), 7.55-7.60 (m, 2 H, H^{5+7}), 8.25 (d br, 1 H, NH, $^3J_{HH}$ =3.6 Hz). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$, 0 ºC, TMS): δ 17.9 (Me), 24.3 (CH_2^{Cy}), 25.3 (CH_2^{Cy}), 25.4 (CH_2^{Cy}), 31.7 (CH_2^{Cy}), 32.0 (CH_2^{Cy}), 63.9 (CH^2), 64.1 (CH^{Cy}), 66.5 (CH^{Fc}), 68.1 (CH^{Fc}), 68.7 (CH^{Fc}), 68.9 (CH^{Fc}), 69.5 (CH^{Fc}), 85.9 (C^{Fc}), 115.7 (C^{4a}), 116.7 (CH^8), 118.9 (CH^6), 120.5 (q, $^1J_{CF}$ = 320 Hz, CF_3SO_3), 128.9 (CH^5), 138.8 (CH^7), 145.5 (C^{8a}), 165.3 (C^4). IR (Nujol, cm^{-1}): ν(NH) 3226, ν(C=N + C=C) 1621, 1583, 1557. HRMS (ESI) *m/z* calcd for $C_{25}H_{29}N_2Fe$ $[M]^+$, 413.1675; found 413.1677. Anal. calcd for $C_{26}H_{29}F_3FeN_2O_3S$: C, 55.52; H, 5.20; N, 4.98; S, 5.70. Found: C, 55.54; H, 4.94; N, 5.06; S, 5.43.

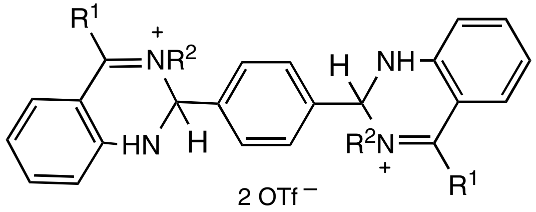
3e2 (R^1 = Me, R^2 = *R*-CH(Me)Ph, R^3 = Tol, R^4 = H): Reagents, *R*-**2e** (300 mg, 1.33 mmol), TolCHO (160 µL, 1.35 mmol) and HOTf (120 µL, 1.38 mmol). After 1 h of stirring, the solution was concentrated under vacuum to dryness. The residue was washed with a mixture of CH_2Cl_2/Et_2O (1:30, 5 x 31 mL) and dried under vacuum (6 h) to give **3e2**·$0.5H_2O$ as a yellow solid, which consists of a mixture of two isomers, D and d, in 65:35 molar ratio. This compound must be stored below -34 ºC. Yield: 308.3 mg, 0.66 mmol, 50%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.690 (d, 3 H, CH(*Me*)Ph^{D}, $^{3}J_{HH}$ = 6.8 Hz), 1.694 (d, 4 H, H_2O + CH(*Me*)Ph^{d}, $^{3}J_{HH}$ = 7.2 Hz), 2.07 (s, 3 H, Me$^{Tol, d}$), 2.20 (s, 3 H, Me$^{Tol, D}$), 2.82 (s, 3 H, Me$^{4, D}$), 3.03 (s, 3 H, Me$^{4, d}$), 5.82 (q, 1 H, C*H*(Me)Ph^{d}, $^{3}J_{HH}$ = 6.4 Hz), 5.92 (q, 1 H, C*H*(Me)Ph^{D}, $^{3}J_{HH}$ = 6.8 Hz), 6.69-6.88 (various m, 7 H, M + m), 6.97 (d, 2 H, *m*-Tol^{d}, $^{3}J_{HH}$ = 8.8 Hz), 7.07 (d, 2 H, *m*-Tol^{D}, $^{3}J_{HH}$ = 8.0 Hz), 7.13-7.51 (several m, 14 H^{D+d}), 7.57 (d, 1 H, H$^{5, d}$, $^{3}J_{HH}$ = 8.4 Hz), 8.27 (s br, 1 H, NH^{d}), 8.49 (d br, 1 H, NH^{D}, $^{3}J_{HH}$ = 4.0 Hz). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 18.5 (Me$^{4, D+d}$), 19.3 (CH(*Me*)Ph^{d}), 19.6 (CH(*Me*)Ph^{D}), 20.8 (Me$^{Tol, d}$), 20.9 (Me$^{Tol, D}$), 63.5 (*C*H(Me)Ph^{d}), 63.7 (*C*H(Me)Ph^{D}), 66.3 (CH$^{2, D}$), 66.4 (CH$^{2, d}$), 116.4 (C$^{4a, D}$), 116.5 (C$^{4a, d}$), 117.2 (CH$^{8, d}$), 117.3 (CH$^{8, D}$), 120.0 (CH$^{6, D+d}$), 120.6 (q, $^{1}J_{CF}$ = 320 Hz, TfO), 125.7 (CH$^{o\text{-Tol, d}}$), 126.1 [CH$^{o\text{-Tol, D}}$ + CH$^{Ph, D+d}$], 128.6 (CH$^{Ph, D}$), 128.8 (CH$^{Ph, D}$), 129.0 (CH$^{Ph, D}$), 129.05 (C$^{5, D}$), 129.11 (CH$^{Ph, d}$), 129.2 (CH$^{Ph, D}$), 129.3 (CH$^{Ph, d}$), 129.5 (CH$^{m\text{-Tol, d}}$ + CH$^{Ph, d}$), 129.7 (CH$^{m\text{-Tol, D}}$), 129.8 (CH$^{Ph, d}$), 131.9 (C$^{p\text{-Tol, d}}$), 132.7 (C$^{p\text{-Tol, D}}$), 133.2 (C$^{i\text{-Ph, d}}$), 138.2 (C$^{i\text{-Ph, D}}$), 138.7 (C$^{i\text{-Tol, d}}$), 139.0 (CH$^{7, d}$), 139.1 (CH$^{7, D}$), 139.4 (C$^{i\text{-Tol, D}}$), 145.5 (C$^{8a, d}$), 145.8 (C$^{8a, D}$), 168.2 (C$^{4, d}$), 170.7 (C$^{4, D}$). Trace amounts of **7e2**, are always present in the NMR spectra. IR (Nujol, cm–1): ν(NH) 3251, ν(C=N + C=C) 1620, 1588, and 1556. HRMS (ESI) *m/z* calcd for $C_{24}H_{25}N_2$ $[M]^+$, 341.2012; found 341.2013. Anal. calcd for $C_{24}H_{26}F_3N_2O_3S \cdot 0.5H_2O$: C, 60.11; H, 5.25; N, 5.61; S, 6.42. Found: C, 59.99; H, 5.29; N, 5.62; S, 6.47.

3e4 (R^1 = Me, R^2 = *R*-CH(Me)Ph, R^3 = Me, R^4 = H): Reagents, ***R*-2e** (92 mg, 0.41 mmol), MeCHO (0.1 mL, 1.77 mmol) and HOTf (50 μL, 0.57 mmol, added with 20 min delay). After 18 h of stirring, the reaction mixture was filtered through anhydrous $MgSO_4$ and concentrated under vacuum to dryness. The oily residue was washed successively with a cold mixture of CH_2Cl_2 and Et_2O (1:30, 3 x 31 mL, 0 ºC) and with a cold mixture of CH_2Cl_2 and *n*-pentane (1:40, 2 x 41 mL, 0 ºC) and dried under vacuum for 6 h to give **3e4**·H_2O as a hygroscopic orange solid, consisting of a mixture of the *RR* + *RS* isomers, D and d, in 3:2 molar ratio, which was stored under a nitrogen atmosphere. Yield: 119.4 mg, 0.28 mmol, 68%. Mp: 133 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 0.63 (d, 3 H, $Me^{2, D}$, $^3J_{HH}$ = 6.4 Hz), 1.46 (d, 3 H, $Me^{2, d}$, $^3J_{HH}$ = 6.4 Hz), 1.86-1.92 (v br, 2 H, H_2O), 1.87 (d, 3 H, CH(*Me*)Ph^D, $^3J_{HH}$ = 6.8 Hz), 1.91 (d, 3 H, CH(*Me*)Ph^d, $^3J_{HH}$ = 6.8 Hz), 2.73 (s, 3H, $Me^{4, d}$), 2.93 (s, 3H, $Me^{4, D}$), 5.69-5.76 (m, 4 H, $H^{2, D+d}$ + C*H*(Me)Ph^{D+d}), 6.86 (t, 1 H, $H^{6, d}$, $^3J_{HH}$ = 7.6 Hz), 6.89 (t, 1 H, $H^{6, D}$, $^3J_{HH}$ = 7.6 Hz), 6.97 (d, 1 H, $H^{8, D}$, $^3J_{HH}$ = 8.4 Hz), 7.03 (d, 1 H, $H^{8, d}$, $^3J_{HH}$ = 8.4 Hz), 7.27-7.65 (several m, 16 H, $H^{7, D+d}$ + $H^{5, D+d}$ + Ph^{D+d} + NH^{D+d}). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 16.8 ($Me^{2, D}$), 18.0 ($Me^{2, d}$), 18.3 ($Me^{4, D}$), 18.4 ($Me^{4, d}$ + CH(*Me*)Ph^D), 19.1 (CH(*Me*)Ph^d), 62.0 (*C*H(Me)Ph^D), 62.1 ($CH^{2, d}$), 62.6 (*C*H(Me)Ph^d), 62.7 ($CH^{2, D}$), 115.0 ($C^{4a, d}$), 115.2 ($C^{4a, D}$), 117.5 ($CH^{8, d}$), 117.6 ($CH^{8, D}$), 119.8 ($CH^{6, d}$), 119.9 ($CH^{6, D}$), 120.6 (q, $^1J_{CF}$ = 320 Hz, TfO), 126.1 ($CH^{o/m\text{-Ph}, d}$), 128.7 ($PhCH^{o/m\text{-Ph}, D}$), 129.1 ($CH^{p\text{-Ph}, d}$), 129.45 ($CH^{5, d}$), 129.47 ($CH^{5, D}$), 129.60 ($CH^{o/m\text{-Ph}, D}$), 129.62 ($CH^{o/m\text{-Ph}, d}$), 130.1 ($CH^{p\text{-Ph}, D}$), 134.0 ($C^{i\text{-Ph}, D}$), 137.2 ($C^{i\text{-Ph}, d}$), 138.9 ($CH^{7, D}$), 139.1 ($CH^{7, d}$), 145.9 ($C^{8a, D}$), 146.1 ($C^{8a, d}$), 165.8 ($C^{4, D}$), 168.6 ($C^{4, d}$). IR (Nujol, cm^{-1}): ν(NH) 3272, ν(C=N + C=C) 1621, 1615, and 1592. HRMS (ESI) *m/z* calcd for $C_{18}H_{21}N_2$ $[M]^+$, 265.1699; found 265.1703. Anal. calcd for $C_{19}H_{21}F_3N_2O_3S{\cdot}H_2O$: C, 52.77; H, 5.36; N, 6.48; S, 7.41. Found: C, 52.64; H, 5.32; N, 6.16; S, 7.41.

^{1}H and $^{13}C\{^1H\}$ NMR assignment for ($H_2NC_6H_4C(Me)=NHCy\text{-}2$) OTf (4). ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.13-1.42 (m, 3 H, CH_2^{Cy}), 1.53-1.67 (m, 3 H, CH_2^{Cy}), 1.77 (m, 2 H, CH_2^{Cy}), 2.03 (m 2 H, CH_2^{Cy}), 2.78 (s, 3 H, Me), 3.93 (m, 1 H, CH^{Cy}), 6.05 (s br, 3 H, NH_3), 6.83 (d, 1 H, H^3, $^3J_{HH}$ = 8.1 Hz), 6.90 (t, 1 H, H^5, $^3J_{HH}$ = 7.7 Hz), 7.33-7.38 (m, 2 H, H^{4+6}). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ

18.8 (Me), 24.2 (CH_2^{Cy}), 24.4 (CH_2^{Cy}), 30.5 (CH_2^{Cy}), 58.0 (CH^{Cy}), 119.1 (C^1), 119.7 ($CH^{3/5}$), 119.8 ($CH^{3/5}$), 130.4 (CH^6), 135.5 (CH^4), 147.1 (C^2), 182.9 (C^7).

Synthesis of bis-(1,2-Dihydroquinazolinium) Triflates:



5b (R^1 = H, R^2 = To). **2b** (300 mg, 1.43 mmol) was dissolved in MeCN (30 mL) in a Carius tube. To the solution were successively added terephthalaldehyde (47.8 mg, 0.36 mmol) and HOTf (70 μL, 0.80 mmol) and the reaction mixture was heated at 100 ºC overnight, allowed to cool to room temperature and filtered through a short pad of anhydrous $MgSO_4$. The solution was concentrated under vacuum (1 mL) and cold Et_2O (60 mL, 0 ºC) was added. The resulting suspension was stirred for 15 min at 0 ºC and filtered. The solid collected was recrystallized from MeCN/Et_2O (2 mL/50 mL) at 0 ºC and dried under vacuum (6 h) to give **5b** as an orange solid consisting of a mixture of isomers *RR*+*SS*+*RS* in 1:1:2 molar ratio. Yield: 173.0 mg, 0.21 mmol, 58%. Mp: 286 ºC. ^{1}H NMR (600 MHz, CD_3CN, -10 ºC): δ 2.38 (s, 12 H, $Me^{RR+SS+RS}$), 6.97 ("dt", 4 H, $H^{6,\ RR+SS+RS}$, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 3 Hz), 6.98 (d, 4 H, $H^{8,\ RR+SS+RS}$, $^3J_{HH}$ = 9.0 Hz), 7.05 (d, 4 H, $H^{2,\ RR+SS+RS}$, $^3J_{HH}$ = 4.8 Hz), 7.34-7.39 (m, 8 H, $H^{5+Tol/Ar}$), 7.47 (br s, 8 H, $H^{7+Tol/Ar}$), 7.59 (s br, 4 H, $NH^{RR+SS+RS}$), 7.63 (m, 8 H, $H^{5+Tol/Ar}$), 9.02 (s br, 2 H, $H^{4,\ (RR+SS)/RS}$), 9.03 (s br, 2 H, $H^{4,}$

$^{(RR+SS)/RS}$). ^{1}H NMR (400 MHz, CD_3CN, 25 ºC): δ 2.40 (s, 6 H, Me), 6.97 ("dt", 2 H, H^6, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 0.8 Hz), 7.00 (d, 2 H, H^8, $^3J_{HH}$ = 8.4 Hz), 7.04 (d, 2 H, H^2, $^3J_{HH}$ = 4.4 Hz), 7.37 (m, 4 H, $H^{5+Tol/Ar}$), 7.44 (d br, 2 H, NH, $^3J_{HH}$ = 4.0 Hz), 7.48 (s br, 4 H, $H^{7+Tol/Ar}$), 7.65 (m, 4 H, $H^{5+Tol/Ar}$), 8.97 (s, 2 H, H^4). ^{13}C{H} NMR (100.8 MHz, CD_3CN, 25 ºC): δ 21.2 (Me), 73.1 (CH^2), 114.9 (C^{4a}), 116.0 (CH^8), 121.9 (CH^6), 123.8 ($CH^{o/m\text{-}Tol}$), 128.2 ($CH^{C_6H_4}$), 131.7 ($CH^{o/m\text{-}Tol}$), 134.6 (CH^5), 138.7 ($C^{p\text{-}Tol}$), 139.3 ($C^{C_6H_4}$), 142.7 ($C^{i\text{-}Tol}$), 143.1 (CH^7), 147.1 (C^{8a}), 160.7 (CH^4). ^{13}C{^{1}H} NMR (150.9 MHz, CD_3CN, -10 ºC): δ 21.0 (Me), 72.3 (CH^2), 114.68 ($C^{4a,\ (RR+SS)/RS}$), 114.70 ($C^{4a,\ (RR+SS)/RS}$), 116.7 (CH^8), 121.6 (CH^6), 123.31 ($CH^{o/m\text{-}Tol,\ (RR+SS)/RS}$), 123.32 ($CH^{o/m\text{-}Tol,\ (RR+SS)/RS}$), 127.7 ($CH^{C_6H_4}$), 131.5 ($CH^{o/m\text{-}Tol,\ (RR+SS)/RS}$), 134.31 ($CH^{o/m\text{-}Tol,\ (RR+SS)/RS}$), 134.33 ($CH^5$), 138.4 ($C^{p\text{-}Tol}$), 139.0 ($C^{C_6H_4}$), 142.4 ($C^{i\text{-}Tol}$), 142.8 ($CH^7$), 146.6 ($C^{8a}$), 160.1 ($CH^4$). IR (Nujol, cm^{-1}): ν(NH) 3323, 3243, ν(C=N + C=C) 1626, 1600, 1563. HRMS (ESI) *m/z* calcd for $C_{36}H_{32}N_4$ $[M]^{2+}$, 260.1308; found 329.1307; *m/z* calcd for $C_{36}H_{31}N_4$ $[M – H]^+$, 519.2543; found 519.2542. Anal. calcd for $C_{38}H_{32}F_6N_4O_6S_2$: C, 55.74; H, 3.94; N, 6.84; S, 7.83. Found: C, 55.65; H, 3.86; N, 6.92; S, 7.73.

5d (R^1 = Me, R^2 = Cy). To a solution of **2d** (200 mg, 0.92 mmol) in CH_2Cl_2 (20 mL) were successively added terephthalaldehyde (62 mg, 0.46 mmol) and HOTf (82 μL, 0.94 mmol). A yellow suspension formed, which was stirred for 3.5 h at room temperature and filtered through a short pad of Celite. The solution was concentrated under vacuum (1 mL), Et_2O (20 mL) was added and the yellow suspension was filtered. The solid collected was washed with Et_2O (3 x 5 mL), dissolved in MeCN (1 mL) and cold Et_2O (30 mL, 0ºC) was added; the suspension was stirred at 0 ºC for 15 min and then filtered. The solid collected was washed with Et_2O (3 x 5 mL) and dried under vacuum (6 h) to give **5d**·0.5H_2O as a lemon yellow solid consisting of a mixture of isomers in *RR*+*SS*+*RS* in 1:1:2 molar ratio. Yield: 243.2 mg, 0.29 mmol, 63%. Mp: 193 ºC. ^{1}H

NMR (400 MHz, CD_3CN, 25 ºC): δ 1.11-1.21 (m, 4 H, $CH_2^{Cy,\ RR+SS+RS}$), 1.31-1.53 (m, 12 H, $CH_2^{Cy,\ RR+SS+RS}$), 1.64 (m, 4 H, $CH_2^{Cy,\ RR+SS+RS}$), 1.73-1.88 (m, 16 H, $CH_2^{Cy,\ RR+SS+RS}$), 1.95 (m, 4 H, $CH_2^{Cy,\ RR+SS+RS}$), 2.20 (s, 1 H, H_2O), 2.88 (s, 6 H, $Me^{(RR+SS)/RS}$), 2.89 (s, 6 H, $Me^{(RR+SS)/RS}$), 4.49 (m, 4 H, $CH^{Cy,\ RR+SS+RS}$), 6.64 (d, 2 H, $H^{2,\ (RR+SS)/RS}$, $^3J_{HH}$ = 4.8 Hz), 6.65 (d, 2 H, $H^{2,\ (RR+SS)/RS}$, $^3J_{HH}$ = 5.2 Hz), 6.86-6.92 (various m, 4 H, $H^{6+8,\ RR+SS+RS}$), 7.30 (s br, 8 H, $C_6H_4^{RR+SS+RS}$), 7.43-7.50 (m, 4 H, $H^{5+7,\ RR+SS+RS}$), 7.72 (s br, 2 H, $NH^{(RR+SS)/RS}$), 7.74 (s br, 2 H, $NH^{RR\ or\ SR}$). ^1H NMR (600 MHz, CD_3CN, 25 ºC): δ 1.13-1.21 (m, 4 H, $CH_2^{Cy,\ RR+SS+RS}$), 1.30-1.51 (m, 12 H, $CH_2^{Cy,\ RR+SS+RS}$), 1.64 (m, 4 H, $CH_2^{Cy,\ RR+SS+RS}$), 1.73-1.87 (m, 16 H, $CH_2^{Cy,\ RR+SS+RS}$), 1.95 (m, 4 H, $CH_2^{Cy,\ RR+SS+RS}$), 2.20 (s, 1 H, H_2O), 2.88 (s, 6 H, $Me^{(RR+SS)/RS}$), 2.89 (s, 6 H, $Me^{(RR+SS)/RS}$), 4.49 (m, 4 H, $CH^{Cy,\ RR+SS+RS}$), 6.64 (d, 2 H, $H^{2,\ (RR+SS)/RS}$, $^3J_{HH}$ = 5.4 Hz), 6.65 (d, 2 H, $H^{2,\ (RR+SS)/RS}$, $^3J_{HH}$ = 4.8 Hz), 6.86-6.92 (various m, 4 H, $H^{6+8,\ RR+SS+RS}$), 7.30 (s, br, 4 H, $Tol^{(RR+SS)/RS}$), 7.31 (s, br, 4 H, $Tol^{(RR+SS)/RS}$), 7.44-7.48 (m, 4 H, $H^{5+7,\ RR+SS+RS}$), 7.72 (d br, 2 H, $NH^{(RR+SS)/RS}$, $^3J_{HH}$ = 3.6 Hz), 7.74 (d br, 2 H, $NH^{(RR+SS)/RS}$, $^3J_{HH}$ = 4.2 Hz). $^{13}C\{^1H\}$ NMR (100.8 MHz, CD_3CN, 25 ºC): δ 19.0 (Me), 25.07 ($CH_2^{Cy,\ (RR+SS)/RS}$), 25.09 ($CH_2^{Cy,\ (RR+SS)/RS}$), 25.4 (CH_2^{Cy}), 25.8 (CH_2^{Cy}), 29.94 ($CH_2^{Cy,\ (RR+SS)/RS}$), 29.96 ($CH_2^{Cy,\ (RR+SS)/RS}$), 32.50 ($CH_2^{Cy,\ (RR+SS)/RS}$), 32.53 ($CH_2^{Cy,\ (RR+SS)/RS}$), 65.0 ($CH^{2,\ (RR+SS)/RS}$), 65.7 ($CH^{2,\ (RR+SS)/RS}$), 117.50 ($CH^{8,\ (RR+SS)/RS}$), 117.54 ($CH^{8,\ (RR+SS)/RS}$), 117.91 ($C^{4a,\ (RR+SS)/RS}$), 117.93 ($C^{4a,\ (RR+SS)/RS}$), 121.36 ($CH^{6,\ (RR+SS)/RS}$), 121.37 ($CH^{6,\ (RR+SS)/RS}$), 122.1 (q, $^1J_{CF}$ = 320 Hz, CF_3SO_3), 127.6 (CH), 131.35 ($CH^{5,\ (RR+SS)/RS}$), 131.37 ($CH^{5,\ (RR+SS)/RS}$), 138.46 ($C^{7,\ (RR+SS)/RS}$), 138.47 ($C^{7,\ (RR+SS)/RS}$), 140.0 (CH), 145.50 ($C^{8a,\ (RR+SS)/RS}$), 145.55 ($C^{8a,\ (RR+SS)/RS}$), 172.32 ($C^{4,\ (RR+SS)/RS}$), 172.33 ($C^{4,\ (RR+SS)/RS}$). $^{13}C\{^1H\}$ NMR (150.9 MHz, CD_3CN, 25 ºC): δ 19.0 (Me), 25.10 ($CH_2^{Cy,\ (RR+SS)/RS}$), 25.12 ($CH_2^{Cy,\ (RR+SS)/RS}$), 25.4 (CH_2^{Cy}), 25.8 (CH_2^{Cy}), 29.99 ($CH_2^{Cy,\ (RR+SS)/RS}$), 30.00 ($CH_2^{Cy,\ (RR+SS)/RS}$), 32.54 ($CH_2^{Cy,\ (RR+SS)/RS}$), 32.56 ($CH_2^{Cy,\ (RR+SS)/RS}$), 65.0 ($CH^{2,\ (RR+SS)/RS}$), 65.8 ($CH^{2,\ (RR+SS)/RS}$), 117.53

($CH^{8, (RR+SS)/RS}$), 117.57 ($CH^{8, (RR+SS)/RS}$), 117.95 ($C^{4a, (RR+SS)/RS}$), 117.97 ($C^{4a, (RR+SS)/RS}$), 121.4 ($CH^{6, RR+SS+RS}$), 122.1 (q, $^{1}J_{CF}$ = 320 Hz, CF_3SO_3), 127.6 (CH), 131.35 ($CH^{5, (RR+SS)/RS}$), 131.37 ($CH^{5, (RR+SS)/RS}$), 138.5 ($C^{7, RR+SS+RS}$), 140.0 (C), 145.53 ($C^{8a, RR+SS+RS}$), 172.34 ($C^{4, (RR+SS)/RS}$), 172.35 ($C^{4, (RR+SS)/RS}$). IR (Nujol, cm^{-1}): ν(NH) 3235, ν(C=N + C=C) 1621, 1587, 1557. HRMS (ESI) *m/z* calcd for $C_{36}H_{44}N_4$ $[M]^{2+}$, 266.1778; found 266.1778. Anal. calcd for $C_{38}H_{44}F_6N_4O_6S_2\cdot0.5H_2O$: C, 54.34; H, 5.40; N, 6.67; S, 7.64. Found: C, 54.27; H, 5.39; N, 6.69; S, 7.57.

^{1}H and ^{13}C{^{1}H} NMR assignment for 6d·H_2O: ^{1}H NMR (600 MHz, CD_2Cl_2, 25 ºC): δ 1.19 (m, 6 H, CH_2^{Cy}), 1.48 (m, 18 H, CH_2^{Cy}), 1.66-1.75 (various m, 12 H, CH_2^{Cy}), 1.92-2.05 (various m + br s, 28 H, CH_2^{Cy} + H_2O), 2.96 (s, 18 H, Me), 4.53 (m, 6 H, CH^{Cy}), 6.66 (m, 6 H), 6.83 (m, 12 H), 6.88 (d, 6 H, $^{3}J_{HH}$ = 6.6 Hz), 6.98–7.00 (m, 12 H), 7.18–7.25 (m, 6 H), 7.43 (d, 12 H, $^{3}J_{HH}$ = 7.8 Hz), 7.58–7.60 (m 6 H), 8.19 (d, 2 H, NH, $^{3}J_{HH}$ = 4.8 Hz), 8.22 (d, 3 H, NH, $^{3}J_{HH}$ = 4.8 Hz), 8.25 (br d, 1 H, NH). ^{1}H NMR (600 MHz, CD_2Cl_2, –10 ºC): δ 1.14 (m, 6 H, CH_2^{Cy}), 1.43 (m, 18 H, CH_2^{Cy}), 1.63–1.69 (various m, 12 H, CH_2^{Cy}), 1.90-2.00 (various m, 24 H, CH_2^{Cy}), 2.22-2.71 (br s, 4 H, H_2O), 2.93 (s br, 12 H, Me), 2.94 (s br, 6 H, Me), 4.49 (m, 6 H, CH^{Cy}), 6.59 (m, 6 H), 6.79–6.85 (various m, 18 H), 6.70 (m, 12 H), 7.16 (m, 6 H), 7.41 (m, 12 H), 7.55 (m, 12 H), 8.17 (s br, 1 H, NH), 8.24 (s br, 5 H, NH). ^{13}C{^{1}H} NMR (100.8 MHz, CD_2Cl_2, 25 ºC): δ 18.51 (Me), 18.52 (Me), 24.7 (CH_2^{Cy}), 25.13 (CH_2^{Cy}), 25.19 (CH_2^{Cy}), 25.6 (CH_2^{Cy}), 29.89 (CH_2^{Cy}), 29.94 (CH_2^{Cy}), 32.48 (CH_2^{Cy}), 64.50 (CH), 64.56 (CH), 65.46 (CH), 65.53 (CH), 117.09 (C), 117.11 (C), 117.16 (CH), 117.29 (CH), 120.5 (CH), 121.1 (q, $^{1}J_{CF}$ = 320 Hz, CF_3SO_3), 125.0 (CH), 127.12 (CH), 127.23 (CH), 127.68 (CH), 127.83 (CH), 130.0 (CH), 130.4 (CH), 135.6 (C), 139.12 (CH), 139.17 (CH), 140.95 (C), 140.96 (C), 140.98 (C), 141.53 (C), 141.56 (C), 145.28 (C), 145.31 (C), 145.40 (C), 170.08 (C), 170.09 (C). ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, -10 ºC): δ 18.29 ($Me^{(RRR+SSS)/(RRS+SSR)}$), 18.32

($Me^{RRR+SSS+RRS+SSR}$), 24.4 (CH_2^{Cy}), 24.6 (CH_2^{Cy}), 24.8 (CH_2^{Cy}), 25.3 (CH_2^{Cy}), 29.37 (CH_2^{Cy}), 29.4 (CH_2^{Cy}), 30.5 (CH_2^{Cy}), 32.02 (CH_2^{Cy}), 32.07 (CH_2^{Cy}), 64.00 ($CH^{2,\ RRR+SSS+RRS+SSR}$), 64.04 ($CH^{2,\ (RRR+SSS)/(RRS+SSR)}$), 64.9 ($CH^{Cy}$), 116.66 ($C^{4a}$), 116.74 ($CH^{8a}$), 120.1 ($CH^6$), 120.7 (q, ${}^1J_{CF}$ = 320 Hz, CF_3SO_3), 124.8 (CH), 126.9 (CH), 127.39 (CH), 127.51 (CH), 129.8 (CH^5), 135.3 (C), 138.8 (CH), 140.64 (C), 140.70 (C), 141.12 (C), 141.15 (C), 144.87 (C^{8a}), 144.94 (C^{8a}), 169.7 (C^4).

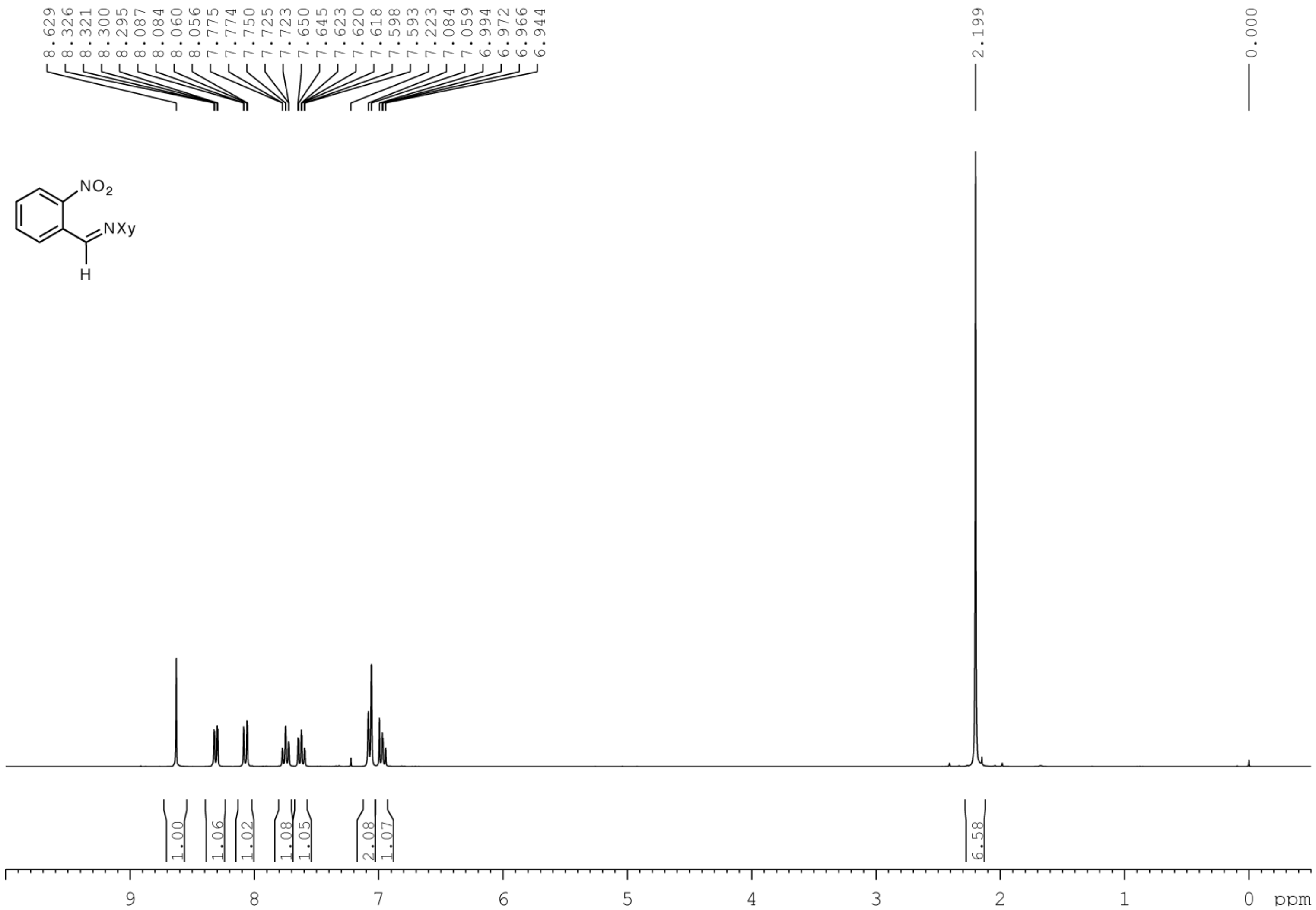
^{1}H and ^{13}C{^{1}H} NMR assignment for 7d2: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.25 (m, 2 H, CH_2^{Cy}), 1.63-2.01 (various m, 8.4 H, CH_2^{Cy} + H_2O), 2.38 (s, 3 H, Me), 3.02, 3.20 (AB part of an ABX system, 2 H, CH_2, ${}^2J_{AB}$ = 16.7 Hz, ${}^3J_{BX}$ = 13.8 Hz, ${}^3J_{BX}$ = 4.2 Hz), 3.72 (m, 1 H, CH^{Cy}), 4.69 (dd, X part of an ABX system, 1 H, H^2, ${}^3J_{HH}$ = 13.2 Hz, ${}^3J_{HH}$ = 4.0 Hz), 5.43 (v br s, N^1H), 6.78-6.83 (m, 2 H, H^{6+8}), 7.24 (d, 2 H, *m*-Tol, ${}^3J_{HH}$ = 7.6 Hz), 7.38 (m, 3 H, *o*-Tol + H^7), 8.19 (d, 1 H, H^5, ${}^3J_{HH}$ = 8.4 Hz), 10.70 (s br, 1 H, N^2H). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 21.2 (Me), 24.2 (CH_2^{Cy}), 24.6 (CH_2^{Cy}), 24.7 (CH_2^{Cy}), 30.8 (CH_2^{Cy}), 31.0 (CH_2^{Cy}), 35.4 (CH_2), 55.5 (CH^2), 57.8 (CH^{Cy}), 110.0 (C^{4a}), 117.3 (CH^8), 119.8 (CH^6), 126.6 (*o*-Tol), 127.5 (CH^5), 130.0 (*m*-Tol), 135.5 (*p*-Tol), 138.9 (CH^7), 139.3 (Tol^i), 152.4 (C^{8a}), 171.0 (C^4).

^{1}H and ^{13}C{^{1}H} NMR assignment for 7d5: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.30 (m, 3 H, CH_2^{Cy}), 1.63-1.99 (various m, 8.5 H, CH_2^{Cy} + H_2O), 3.26, 2.95 (AB part of an ABX system, 1 H, CH_2, ${}^2J_{AB}$ = 14.2 Hz, ${}^3J_{BX}$ = 13.8 Hz, ${}^3J_{BX}$ = 2.2 Hz), 3.77 (m, 1 H, CH^{Cy}), 4.22-4.30 (m, 9 H, Fc), 4.42 (d br, X part of an ABX system, 1 H, H^2, ${}^3J_{HH}$ = 7.6 Hz), 5.83 (s, 1 H, N^1H), 6.73 (t, 1 H, H^6, ${}^3J_{HH}$ = 7.6 Hz), 6.84 (d, 1 H, H^8, ${}^3J_{HH}$ = 8.4 Hz), 7.35 (t, 1 H, H^7, ${}^3J_{HH}$ = 7.6 Hz), 8.12 (d, 1 H, H^5, ${}^3J_{HH}$ = 8.4 Hz), 10.50 (s br, 1 H, N^2H). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 24.2 (CH_2^{Cy}), 24.7 (CH_2^{Cy}), 24.8 (CH_2^{Cy}), 30.9 (CH_2^{Cy}), 31.1 (CH_2^{Cy}), 34.8 (CH_2), 50.2 (CH^2), 57.5 (CH^{Cy}), 66.4 (CH^{Fc}), 67.0

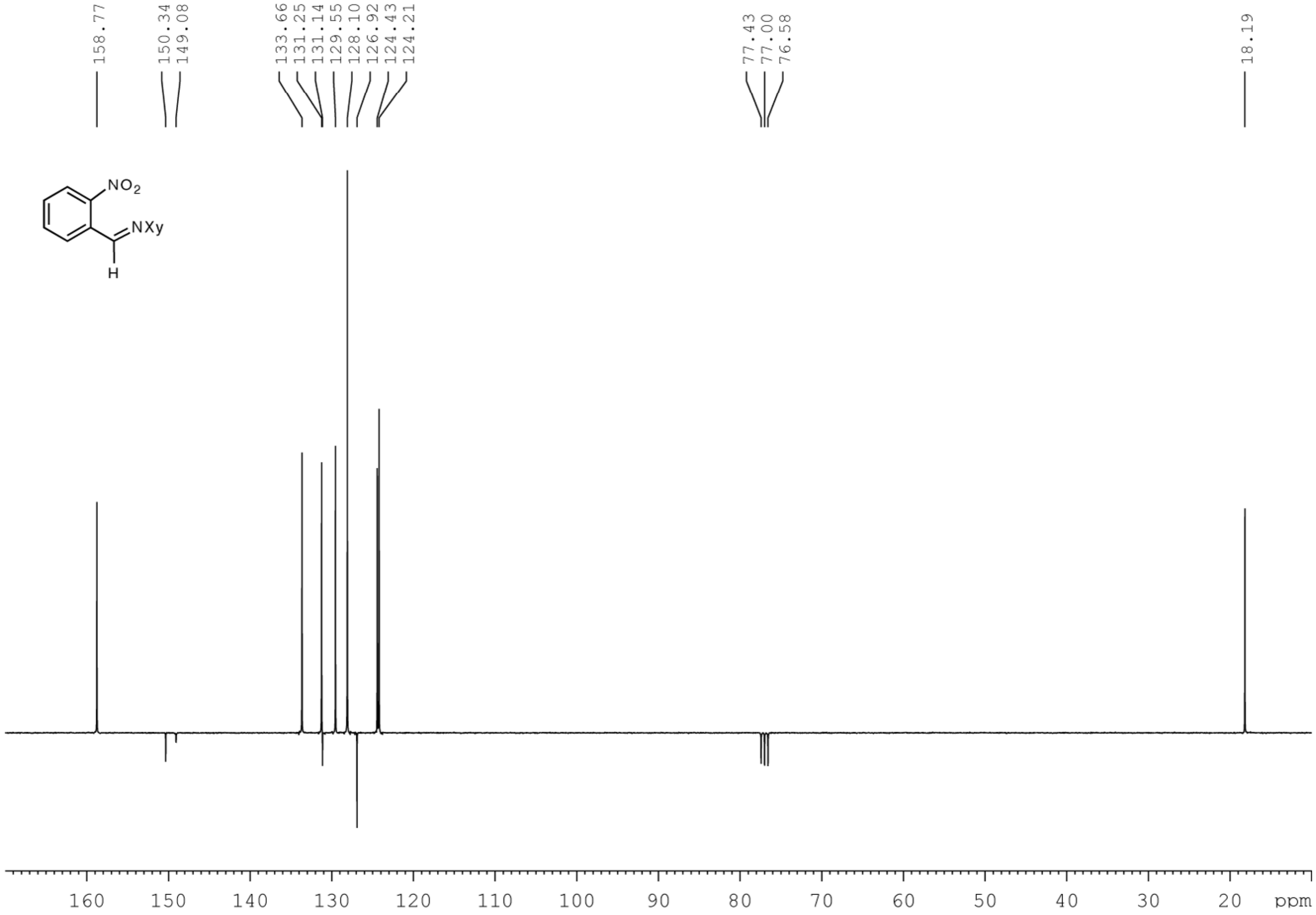
(CH^{Fc}), 68.9 (CH^{Fc}), 109.6 (C^{4a}), 117.2 (CH^{8}), 119.2 (CH^{6}), 127.1 (CH^{5}), 138.8 (CH^{7}), 151.9 (C^{8a}), 171.0 (C^{4}).

^{1}H and ^{13}C{^{1}H} NMR assignment for 7e2·0.5H_2O (*RR* and *RS* isomers, D and d, in a 5:1 molar ratio)**:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ 1.69-1.82 (very broad s, 1 H, H_2O), 1.76 (d, 3 H, CH(*Me*)Ph^{D}, $^{3}J_{HH}$ = 6.8 Hz), 1.80 (d, 3 H, CH(*Me*)Ph^{d}, $^{3}J_{HH}$ = 6.4 Hz), 2.25 (s, 3 H, $Me^{Tol, d}$), 2.28 (s, 3 H, $Me^{Tol, D}$), 2.68, 3,32 (AB part of an ABX system, 2 H, CH_2^{d}, $^{2}J_{AB}$ = 16.8 Hz, $^{3}J_{BX}$ = 12.2 Hz, $^{3}J_{AX}$ = 5.4 Hz), 2.94, 3.14 (AB part of an ABX system, 2 H, CH_2^{D}, $^{2}J_{AB}$ = 16.7 Hz, $^{3}J_{BX}$ = 12.6 Hz, $^{3}J_{AX}$ = 4.2 Hz), 4.34 (dd, X part of an ABX system, 1 H, $H^{2, D}$, $^{3}J_{HH}$ = 12.6 Hz, $^{3}J_{HH}$ = 4.6 Hz), 4.61 (dd, X part of an ABX system, 1 H, $H^{2, d}$, $^{3}J_{HH}$ = 12.0 Hz, $^{3}J_{HH}$ = 4.8 Hz), 4.98 ("quint", 1 H, C*H*(Me)Ph^{D}, $^{3}J_{HH}$ = 6.8 Hz), 5.14 (m, 1 H, C*H*(Me)Ph^{d}, $^{3}J_{HH}$ = 7.0 Hz), 5.94 (s v br, 2 H, $N^{1}H^{D+d}$), 6.67 (m, 2 H, $H^{6, D+d}$), 6.77 (d, 1H, $H^{8, d}$, $^{3}J_{HH}$ = 8.8 Hz), 6.81 (d, 1H, $H^{8, D}$, $^{3}J_{HH}$ = 8.4 Hz), 6.98 (d, 2 H, *m*-Tol^{d}), 7.04-7.42 (several m, 18 H, *o*-Tol^{D+d} + *m*-Tol^{D} + Ph^{D+d} + $H^{5, D+d}$), 8.17 (d overlapped d, 2 H, $H^{7, D+d}$, $^{3}J_{HH}$ = 8.0 Hz), 10.71 (v br d, 1 H, $N^{2}H^{d}$, $^{3}J_{HH}$ = 6.8 Hz), 10.86 (v br d, 1 H, $N^{2}H^{D}$, $^{3}J_{HH}$ = 6.4 Hz). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$, 25 ºC, TMS): δ 21.02 (Me^{d}), 21.04 (Me^{D}), 21.8 (Me^{D}), 21.9 (Me^{d}), 34.9 (CH_2^{d}), 35.5 (CH_2^{D}), 53.9 ($CH^{2, d}$), 54.6 ($CH^{2, D}$), 57.7 (*C*H(Me)Ph^{d}), 57.9 (*C*H(Me)Ph^{D}), 109.4 ($C^{4a, d}$), 109.5 ($C^{4a, D}$), 117.5 ($CH^{8, d}$), 117.6 ($CH^{8, D}$), 119.1 ($CH^{6, d}$), 119.3 ($CH^{6, D}$), 120.4 (q, $^{1}J_{CF}$ = 320 Hz, CF_3SO_3), 126.1 (*o*-Tol^{D+d} or Ph^{D+d}), 126.2 (*o*-Tol^{D+d} or Ph^{D+d}), 127.1 ($CH^{5, d}$), 127.3 ($CH^{5, D}$), 128.3 (*p*-Ph^{d}), 128.7 (*p*-Ph^{D}), 129.3 (*m*-Ph), 129.5 (Ph^{D}), 129.6 (*m*-Tol^{d}), 129.8 (*m*-Tol^{D}), 135.1 (*p*-Tol^{D+d}), 138.4 (*i*-Tol^{d}), 138.8 (*i*-Tol^{D}), 139.1 ($CH^{7, d}$), 139.3 ($CH^{7, D}$), 139.7 (*i*-Ph^{D}), 139.9 (*i*-Ph^{d}), 152.9 ($C^{8a, d}$), 153.0 ($C^{8a, D}$), 172.8 ($C^{4, d}$). 173.1 ($C^{4, D}$)

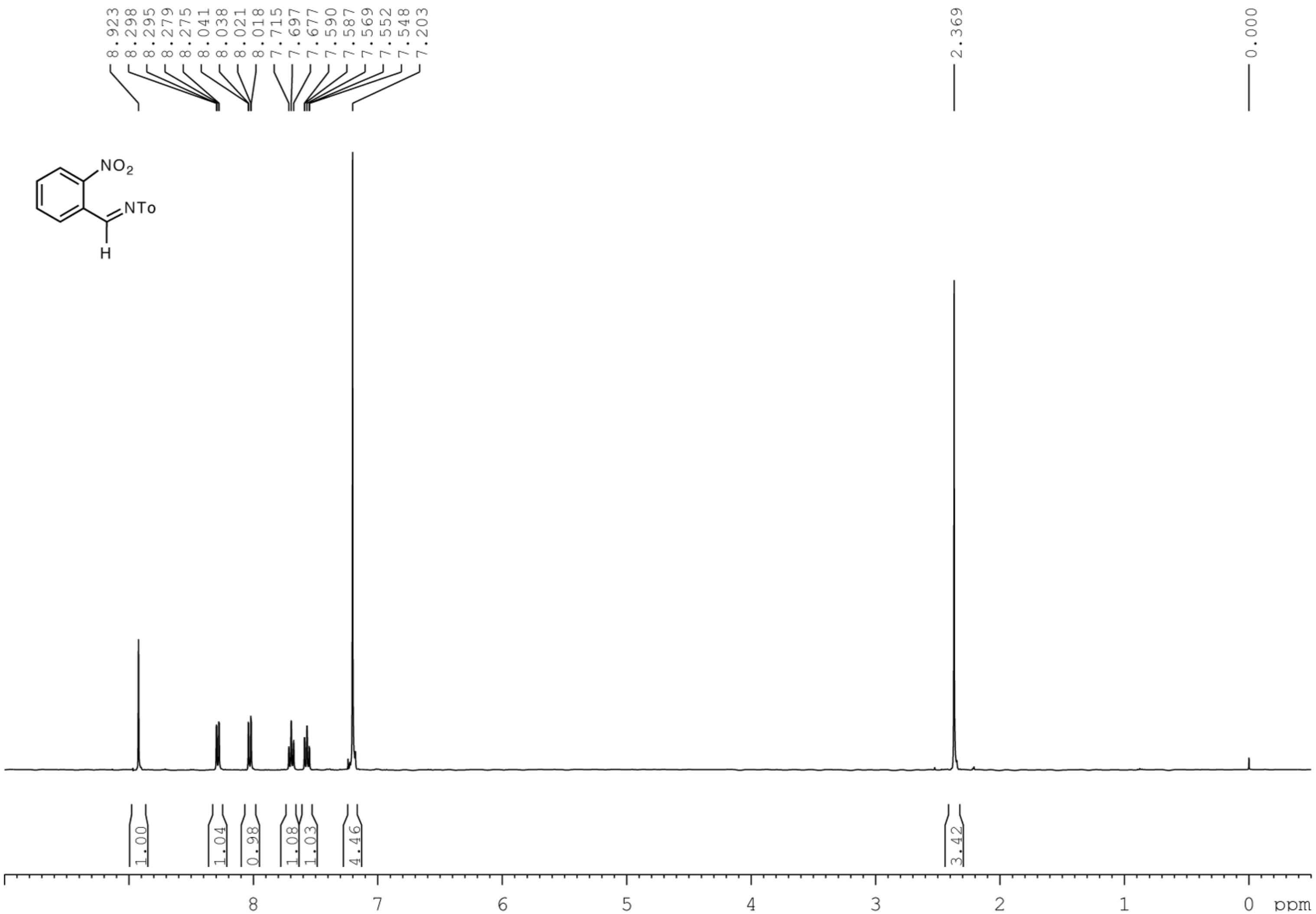
^{1}H NMR spectra of **1a** (300 MHz, $CDCl_3$, 25 ºC, TMS).



$^{13}C\{^{1}H\}$ NMR APT spectra of **1a** (75.5 MHz, $CDCl_3$, 25 ºC, TMS).



^{1}H NMR spectra of **1b** (400 MHz, $CDCl_3$, 25 ºC, TMS).



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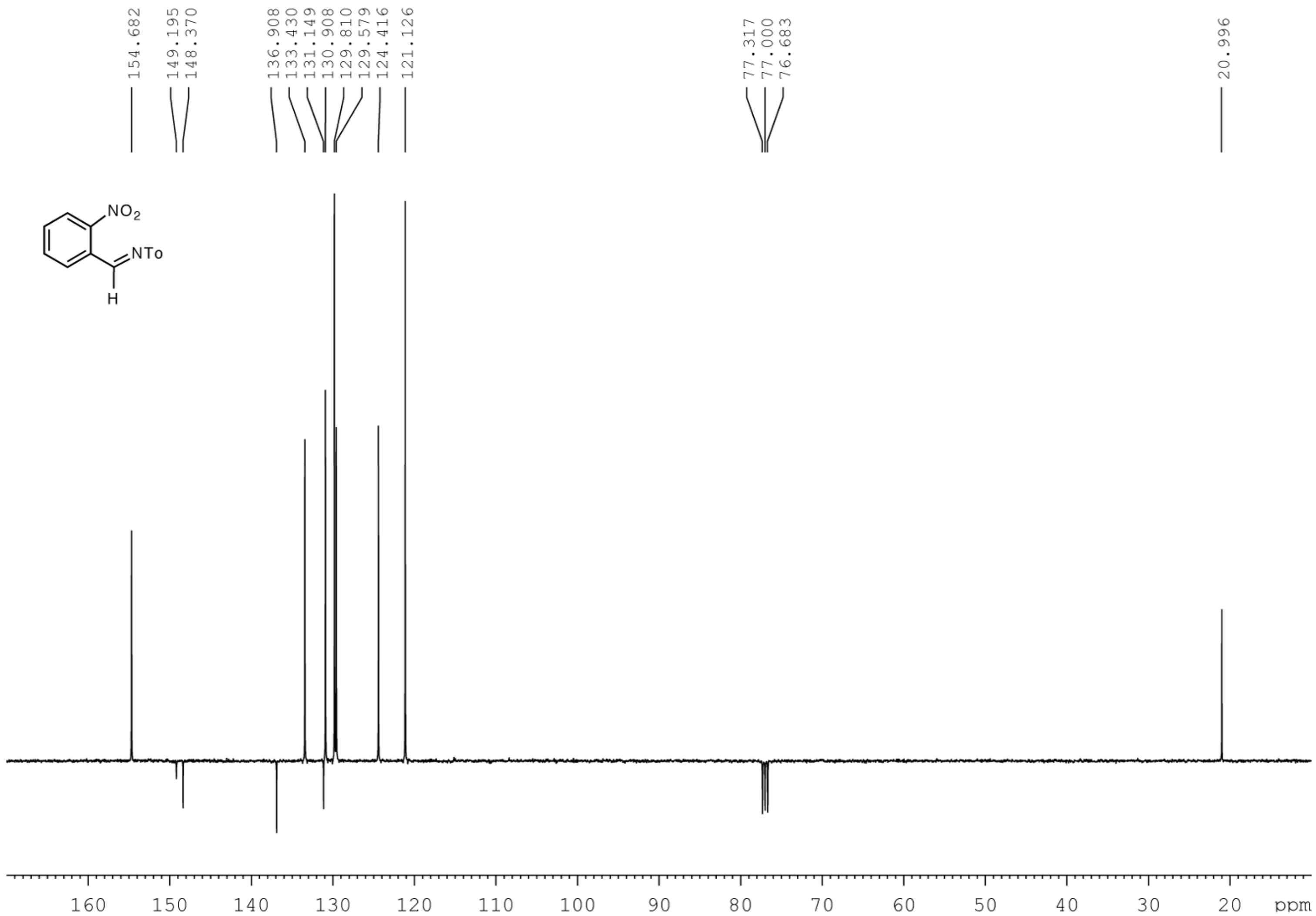
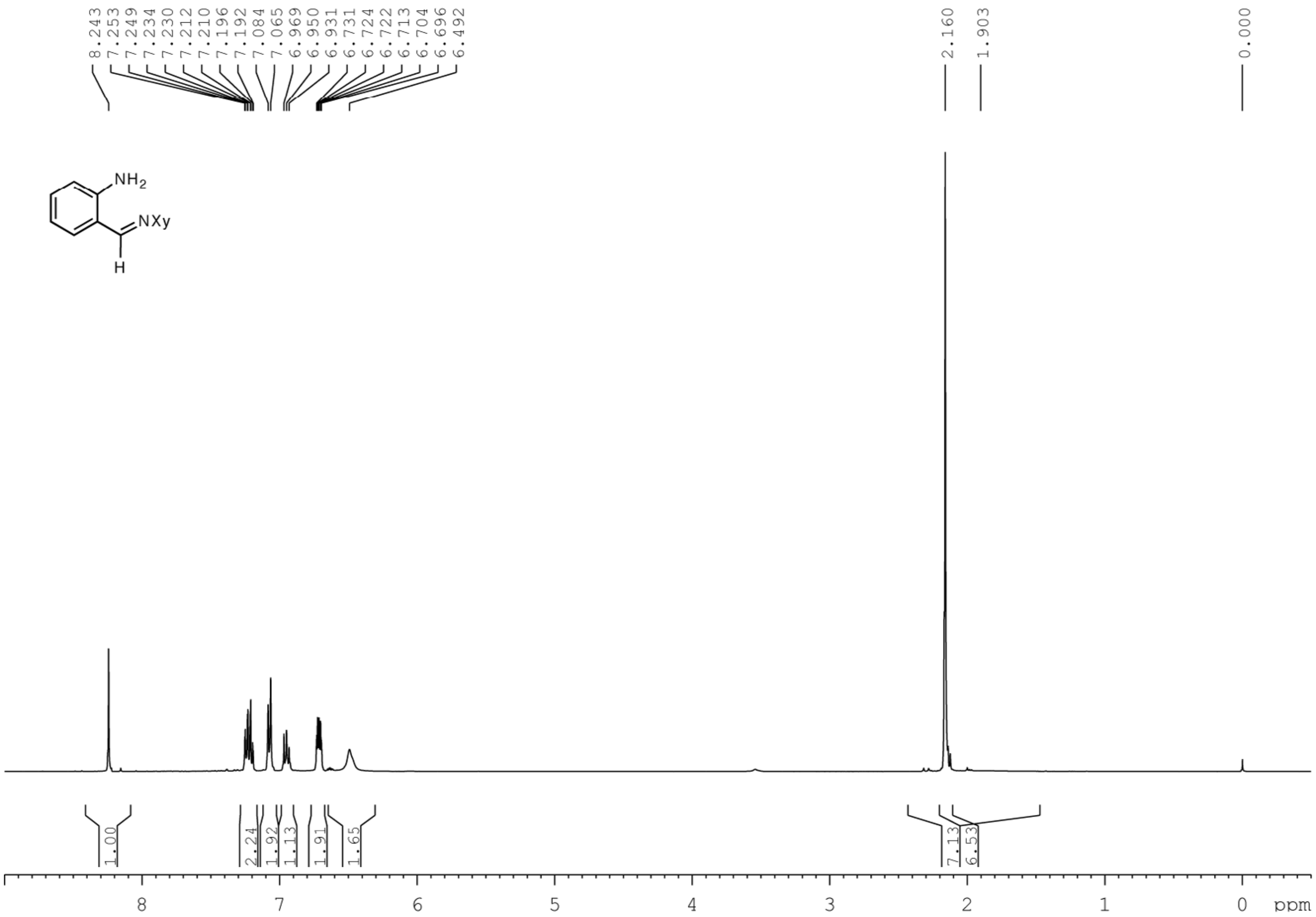
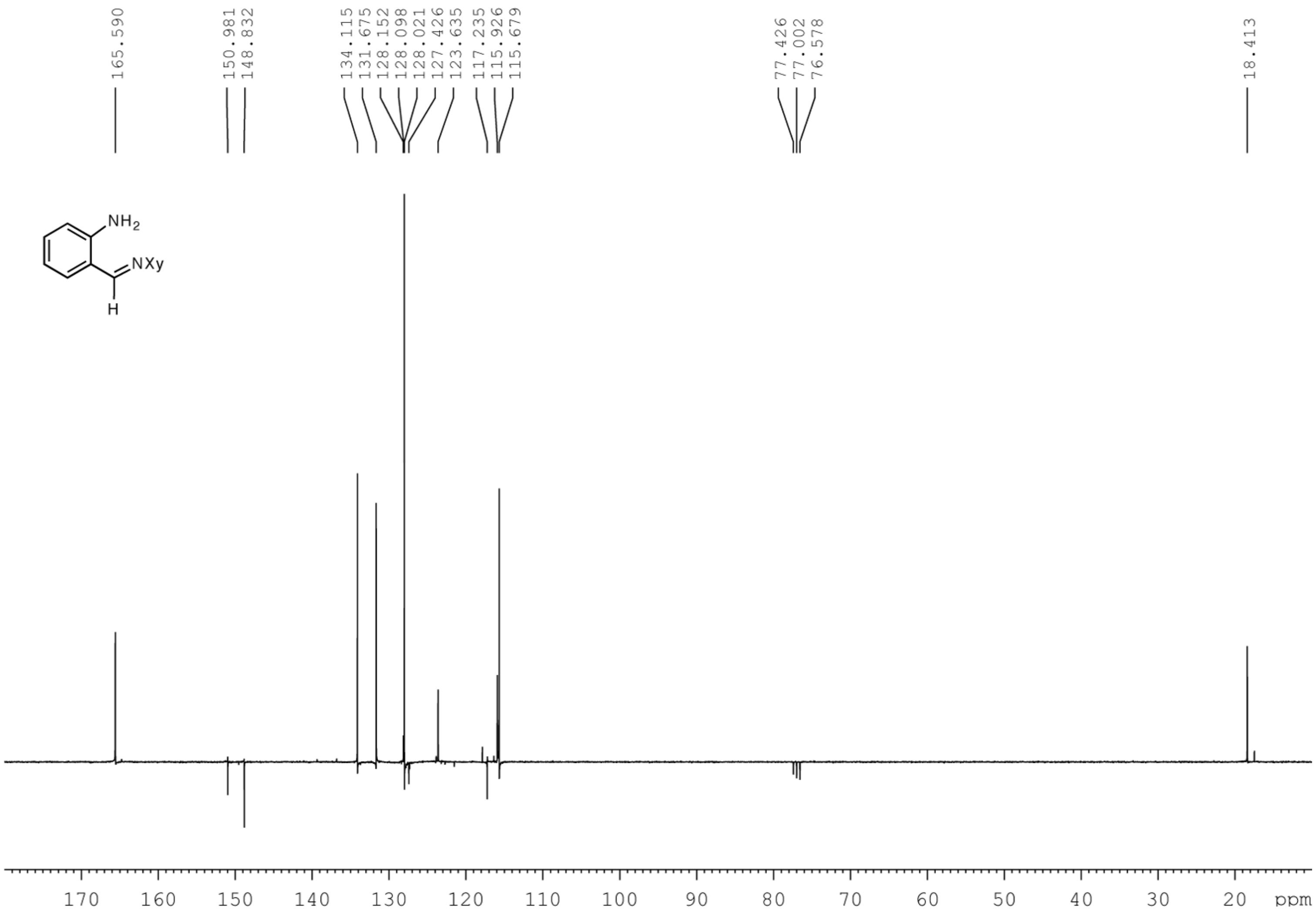
$^{13}C\{^{1}H\}$ NMR APT spectra of **1b** (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



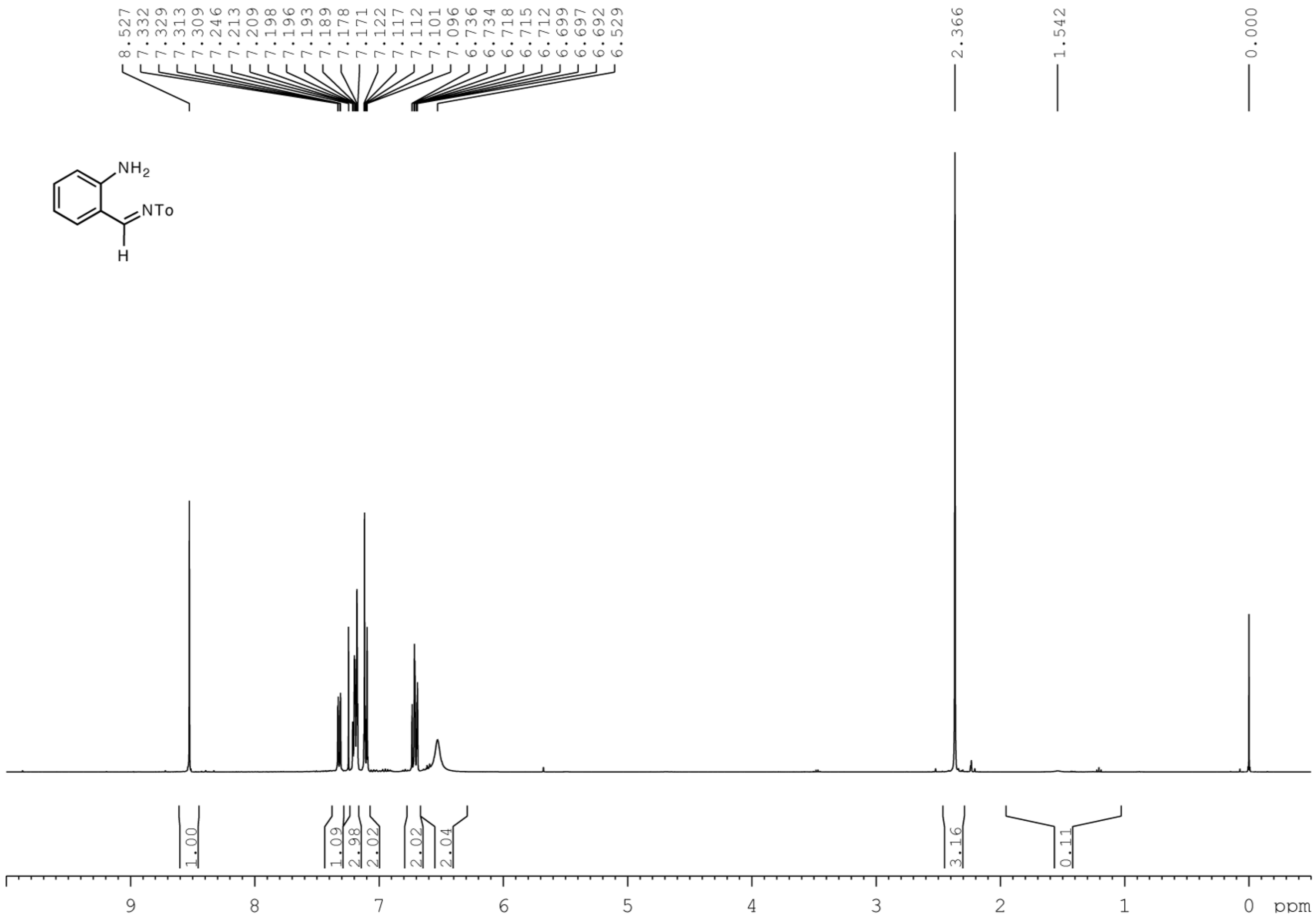
[1]H NMR spectra of **2a**·$0.3H_2O$ (400 MHz, $CDCl_3$, 25 ºC, TMS).



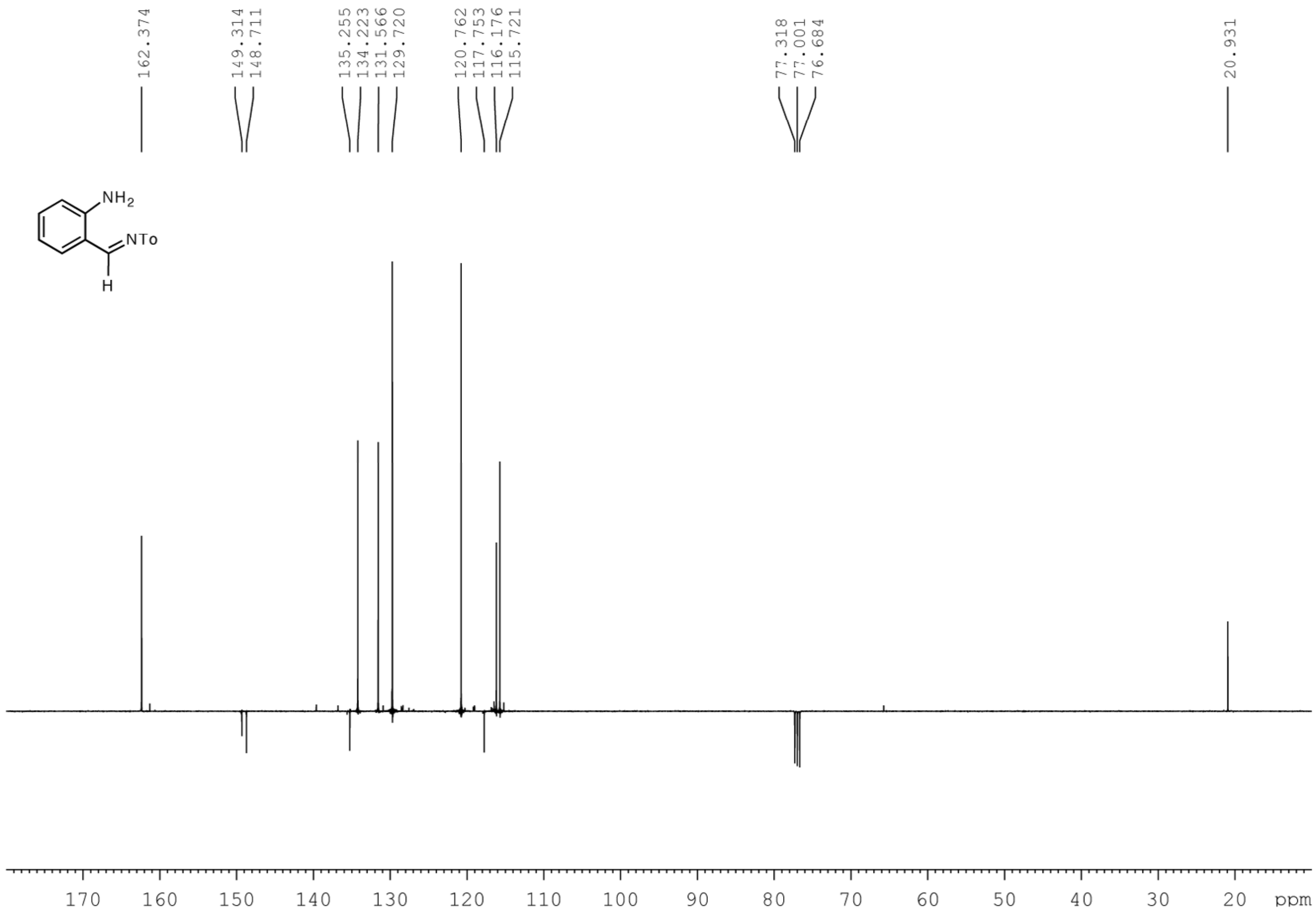
$^{13}C\{^{1}H\}$ NMR APT spectra of **2a** (75.4 MHz, $CDCl_3$, 25 ºC, TMS).



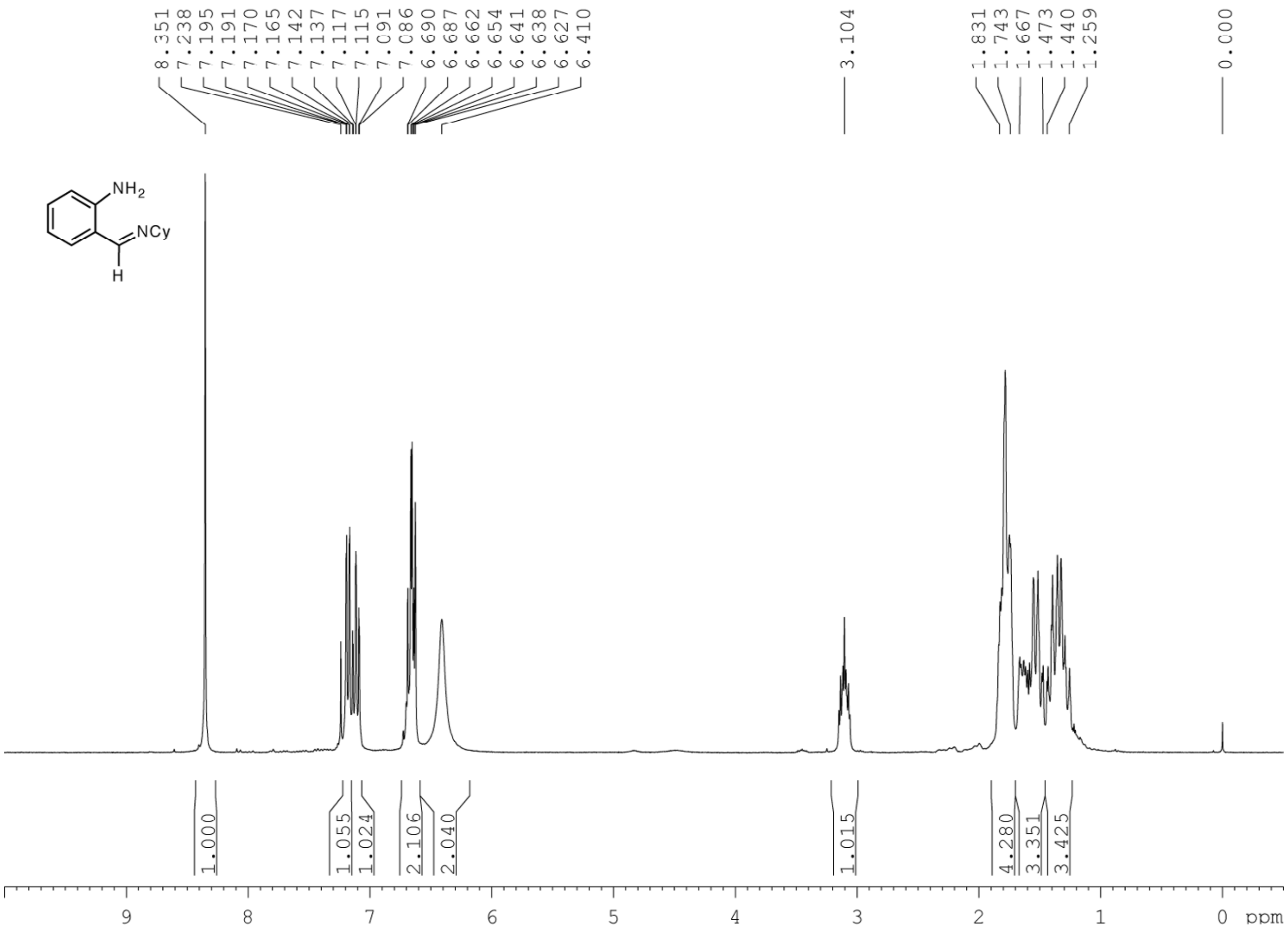
^{1}H NMR spectra of **2b**·0.1H_2O (400 MHz, $CDCl_3$, 25 ºC, TMS).



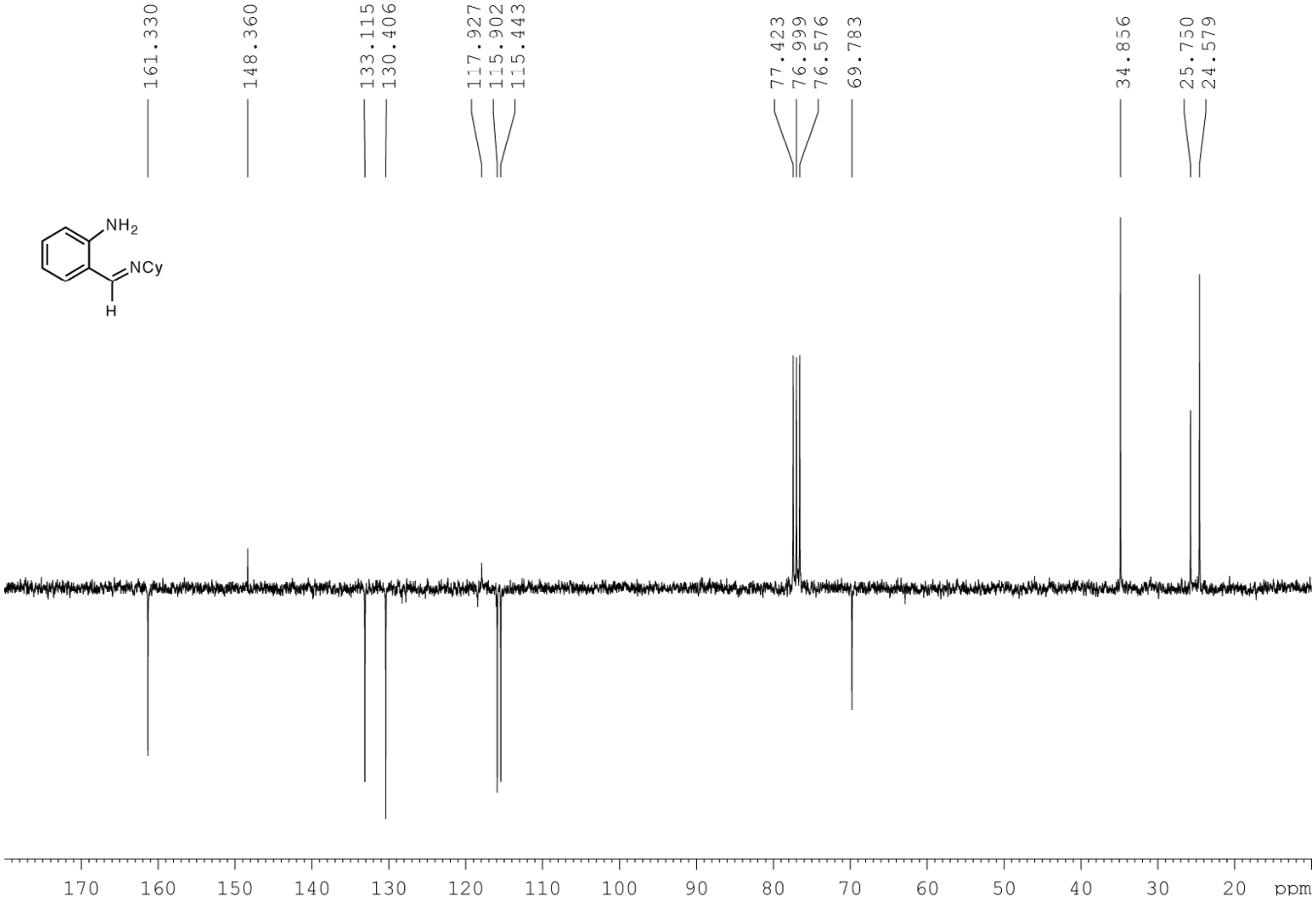
$^{13}C\{^{1}H\}$ NMR APT spectra of **2b** (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



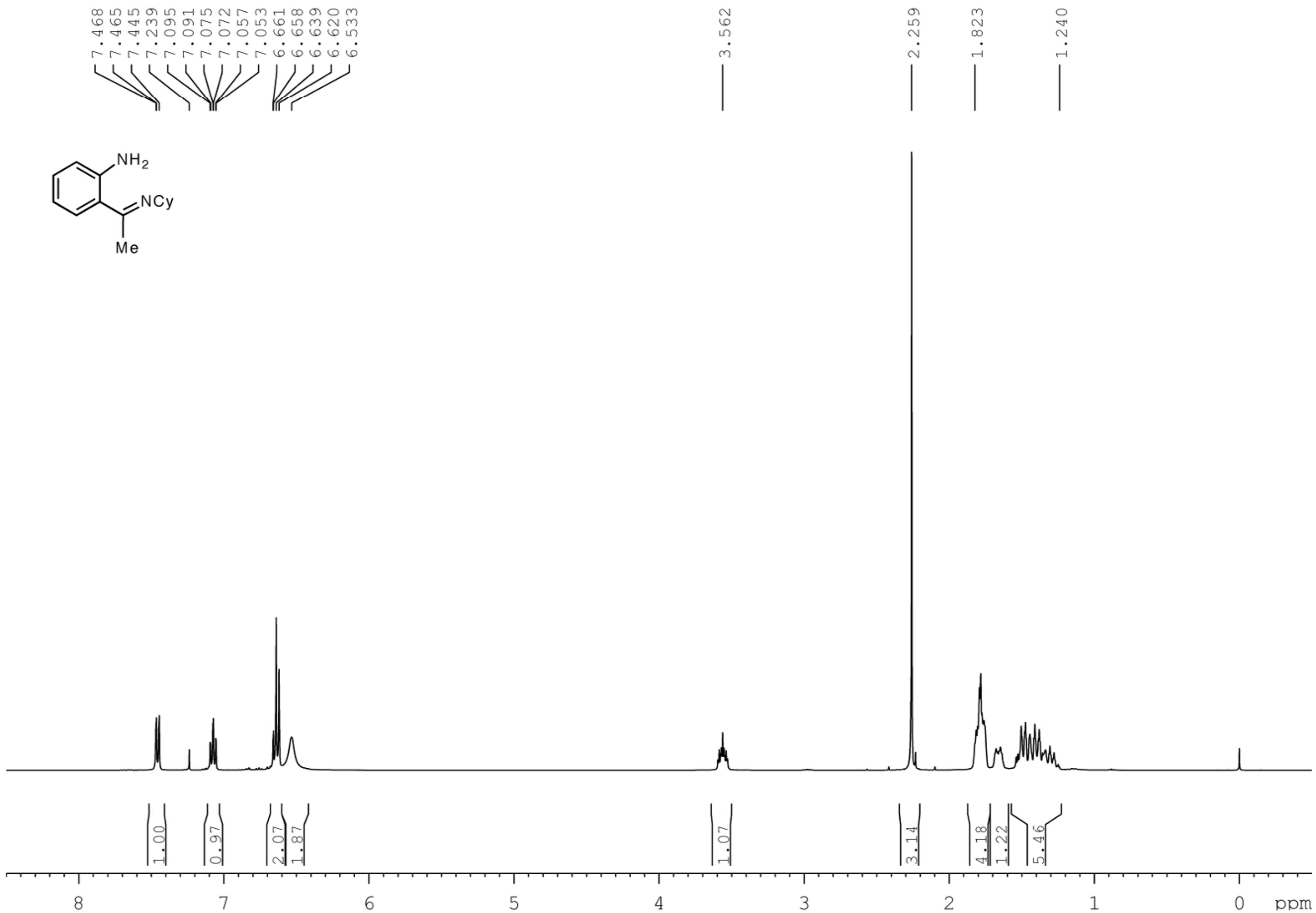
[1]H NMR spectra of **2c** (300 MHz, $CDCl_3$, 25 ºC, TMS).



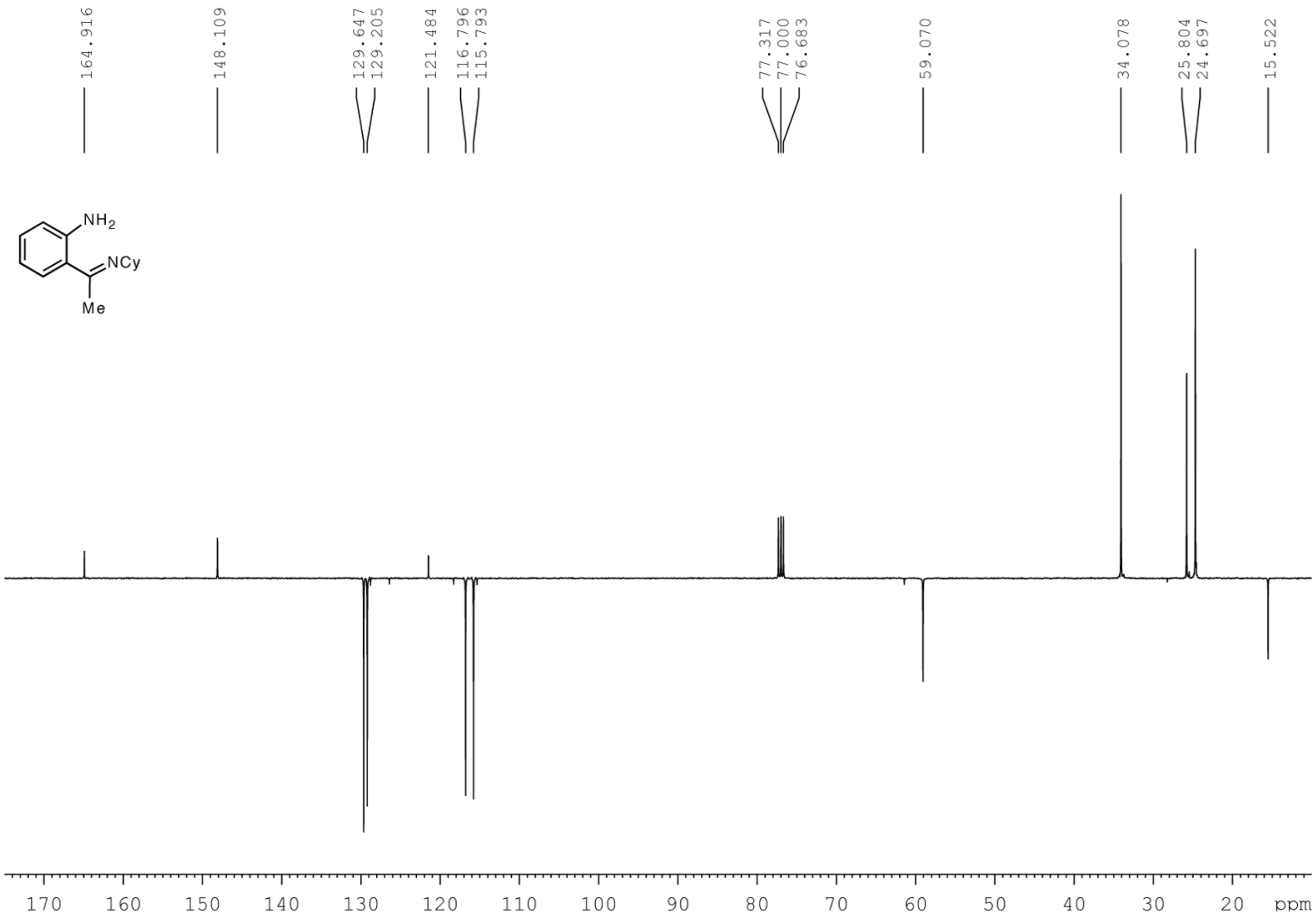
$^{13}C\{^{1}H\}$ NMR APT spectra of **2c** (75.5 MHz, $CDCl_3$, 25 ºC, TMS).



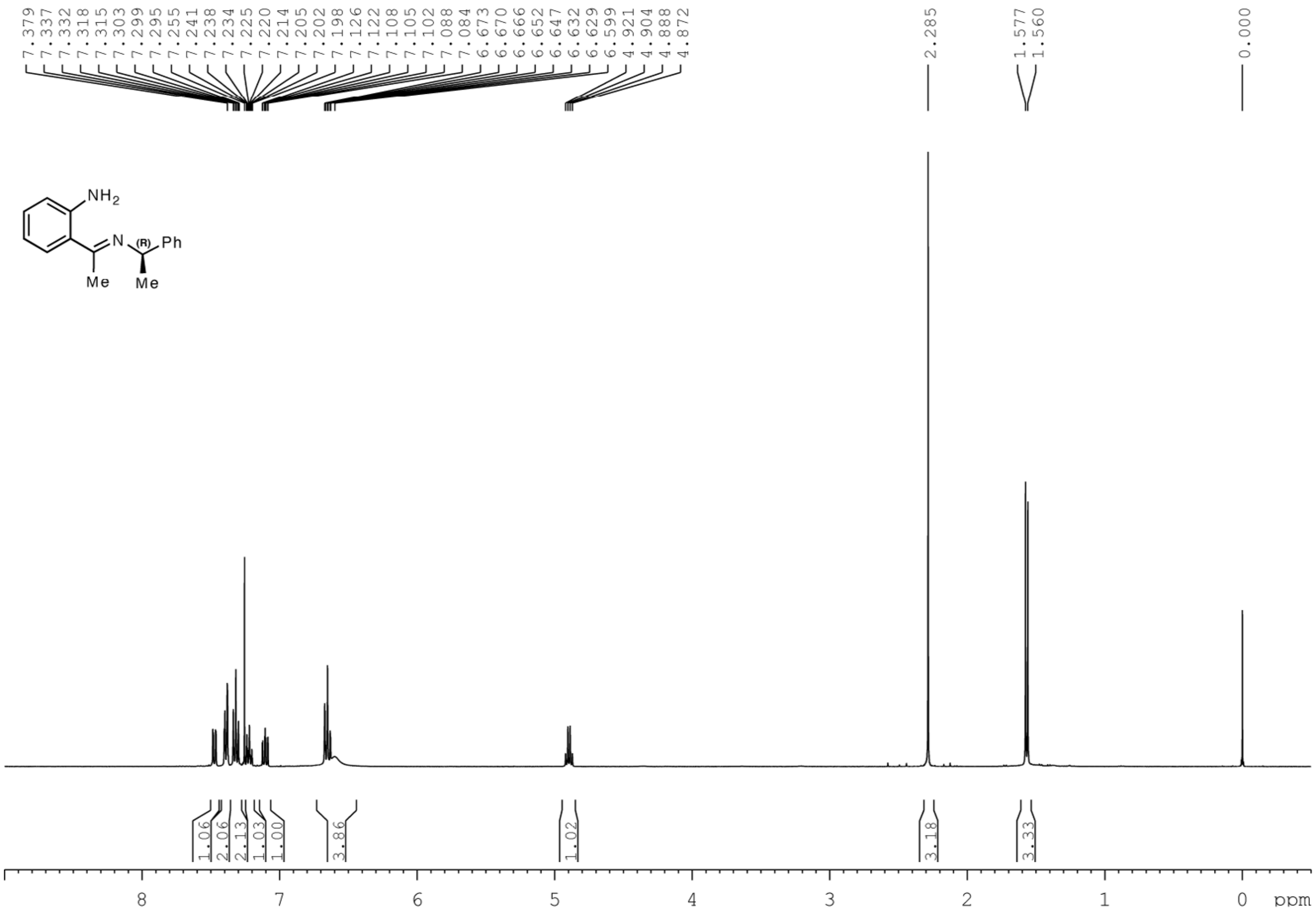
^{1}H NMR spectra of **2d**·0.1H_2O (400 MHz, $CDCl_3$, 25 ºC, TMS).



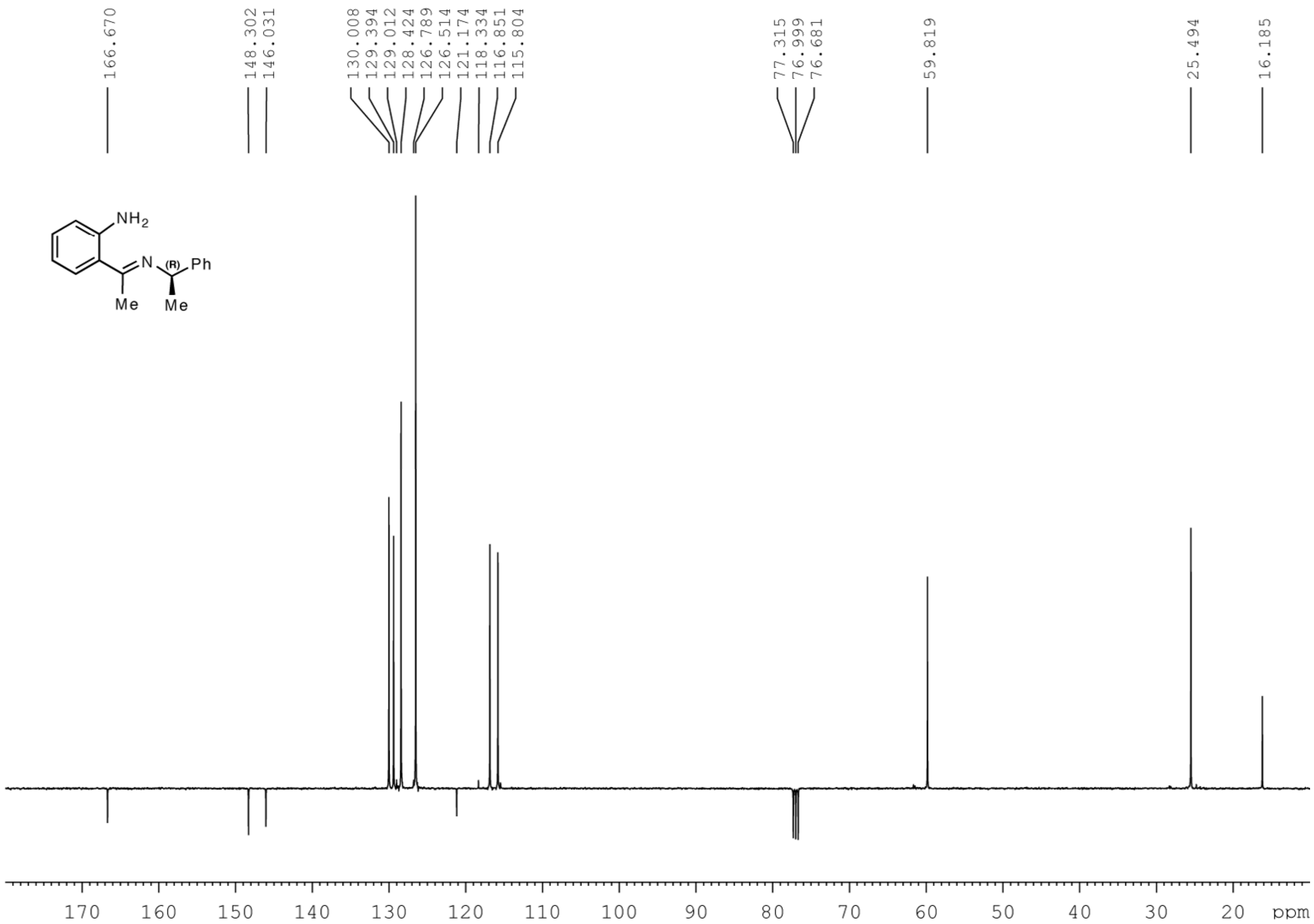
$^{13}C\{^{1}H\}$ NMR APT spectra of **2d**·0.1H_2O (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



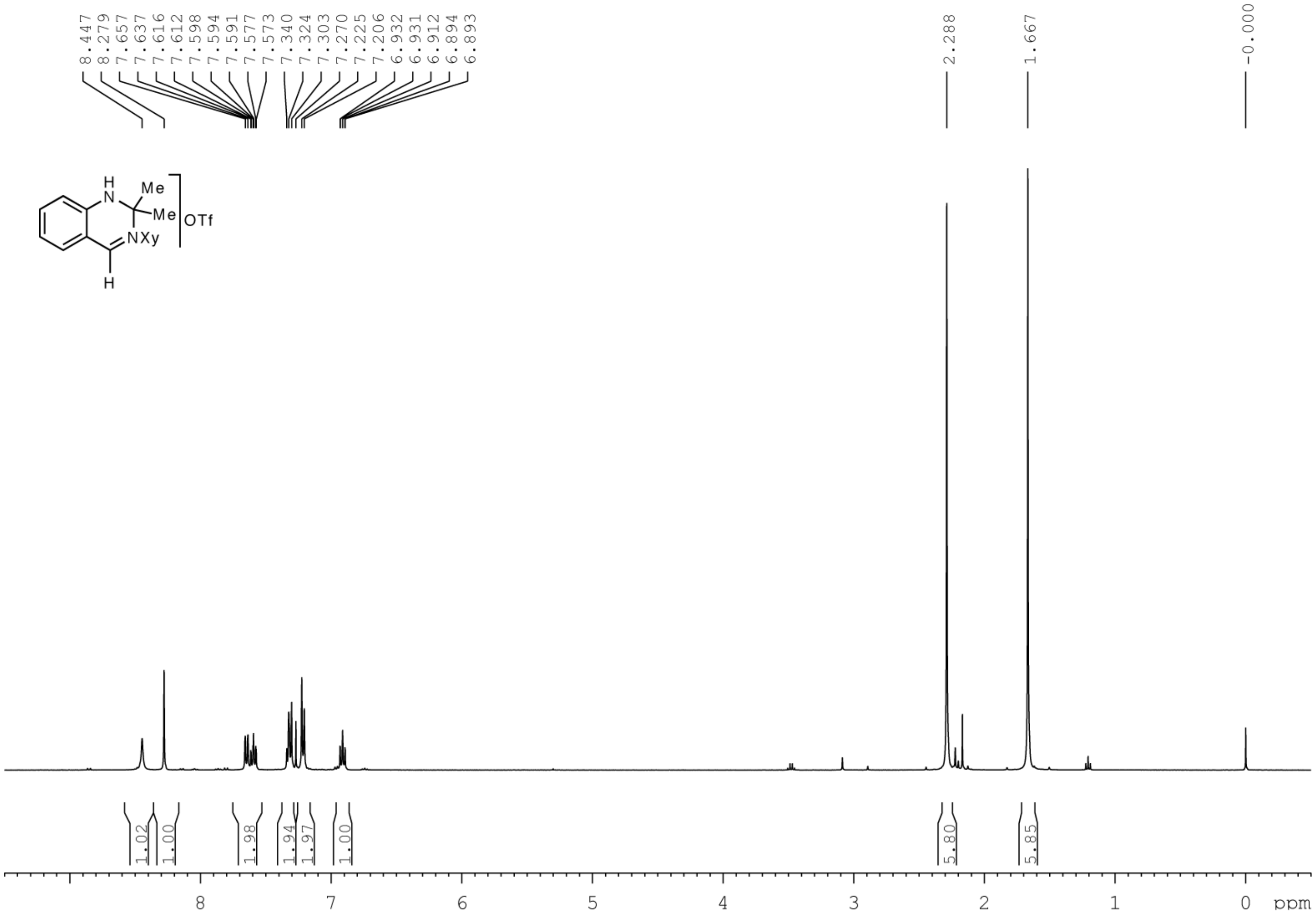
[1]H NMR spectra of ***R*-2e** (400 MHz, $CDCl_3$, 25 ºC, TMS).



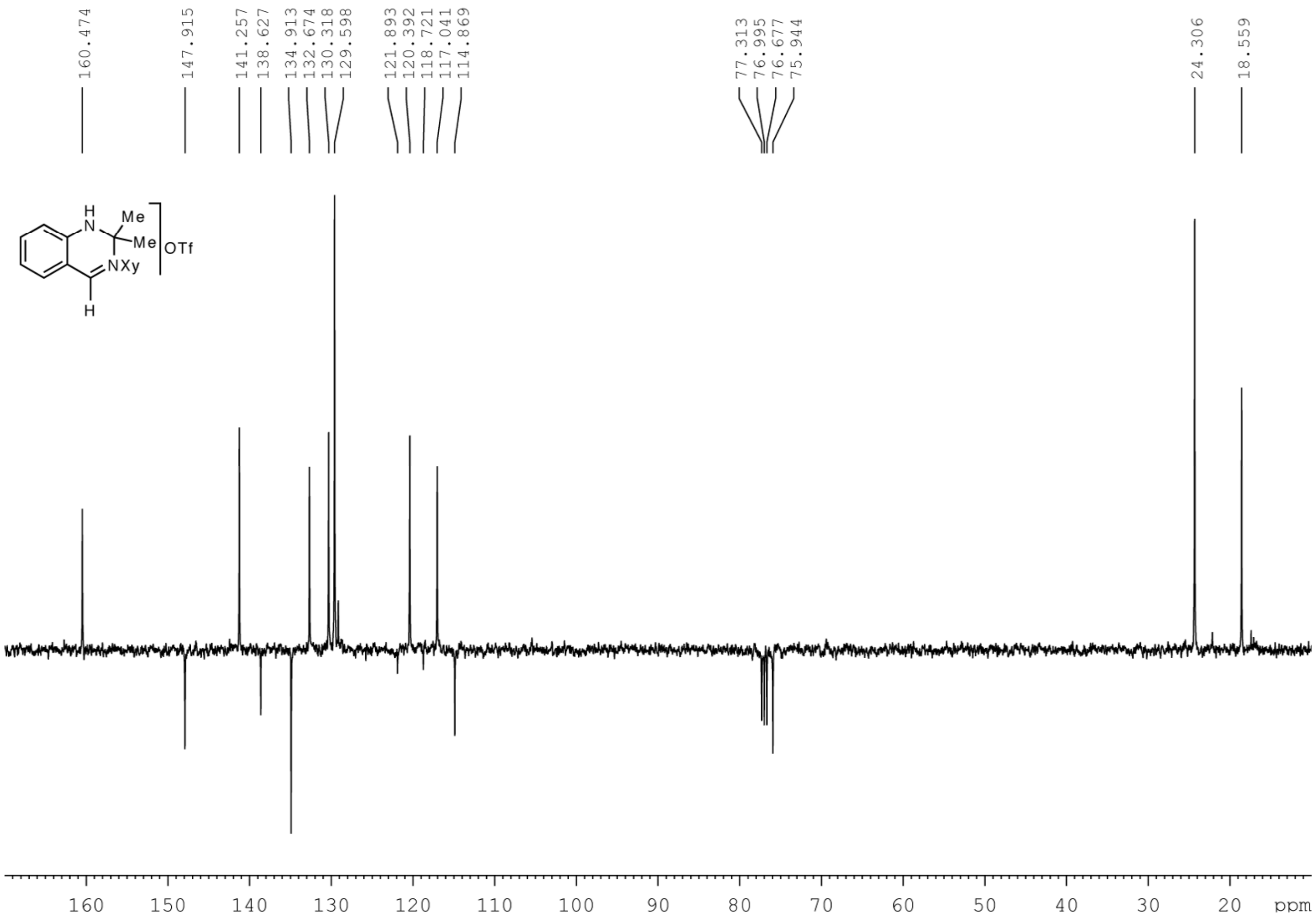
$^{13}C\{^1H\}$ NMR APT spectra of ***R*-2e** (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



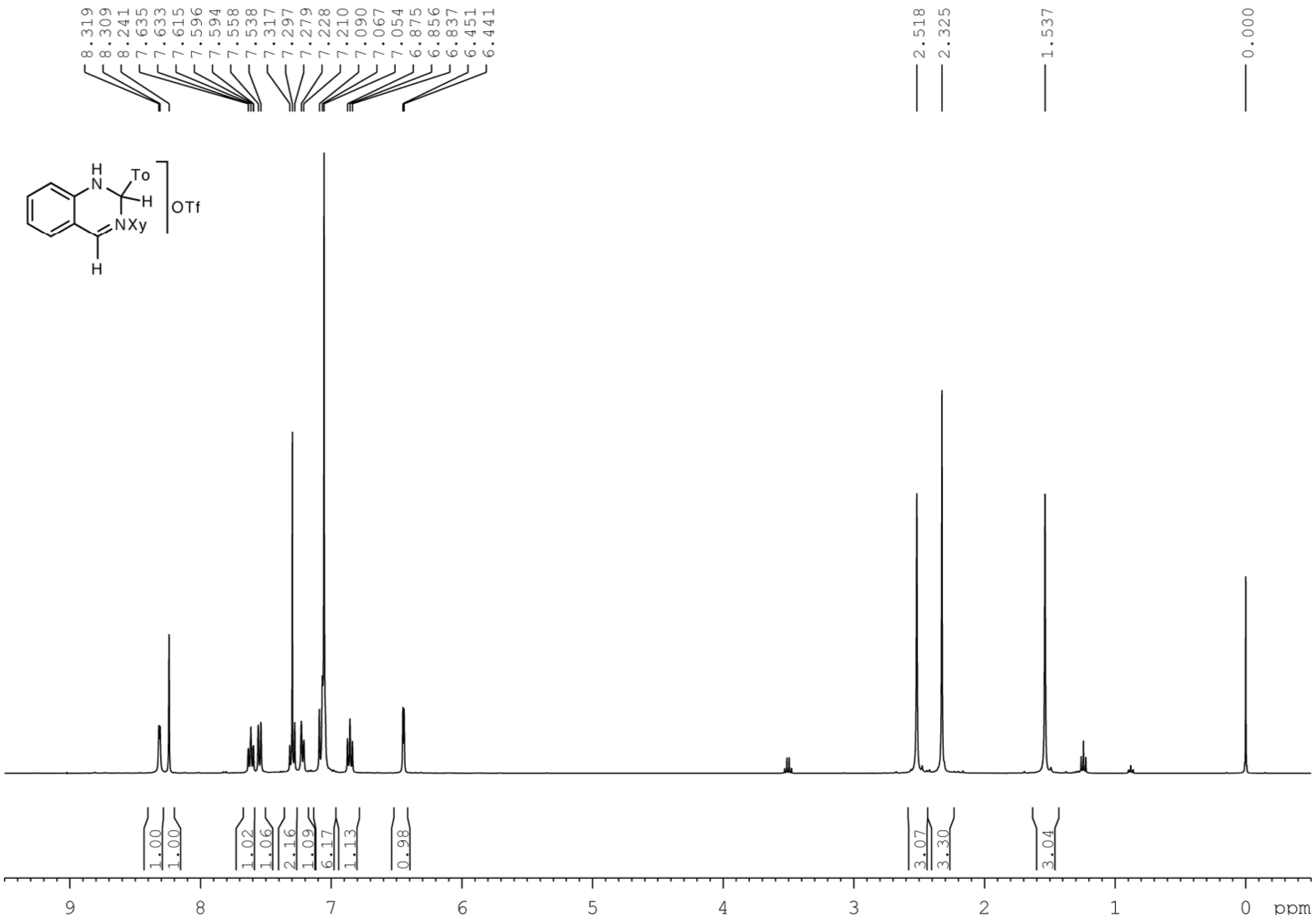
[1]H NMR spectra of **3a1** (400 MHz, $CDCl_3$, 25 ºC, TMS)



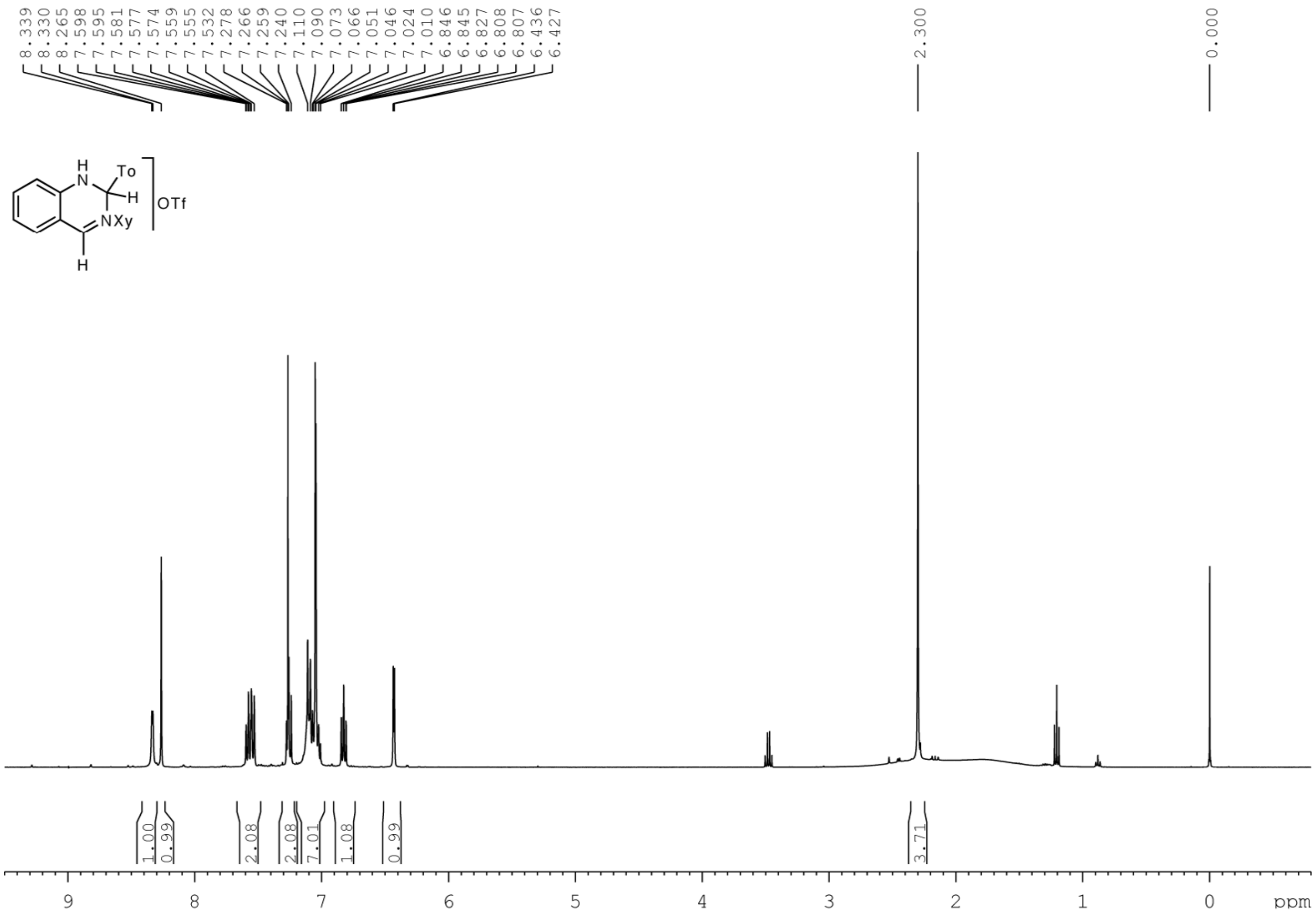
$^{13}C\{^{1}H\}$ NMR APT spectra of **3a1** (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



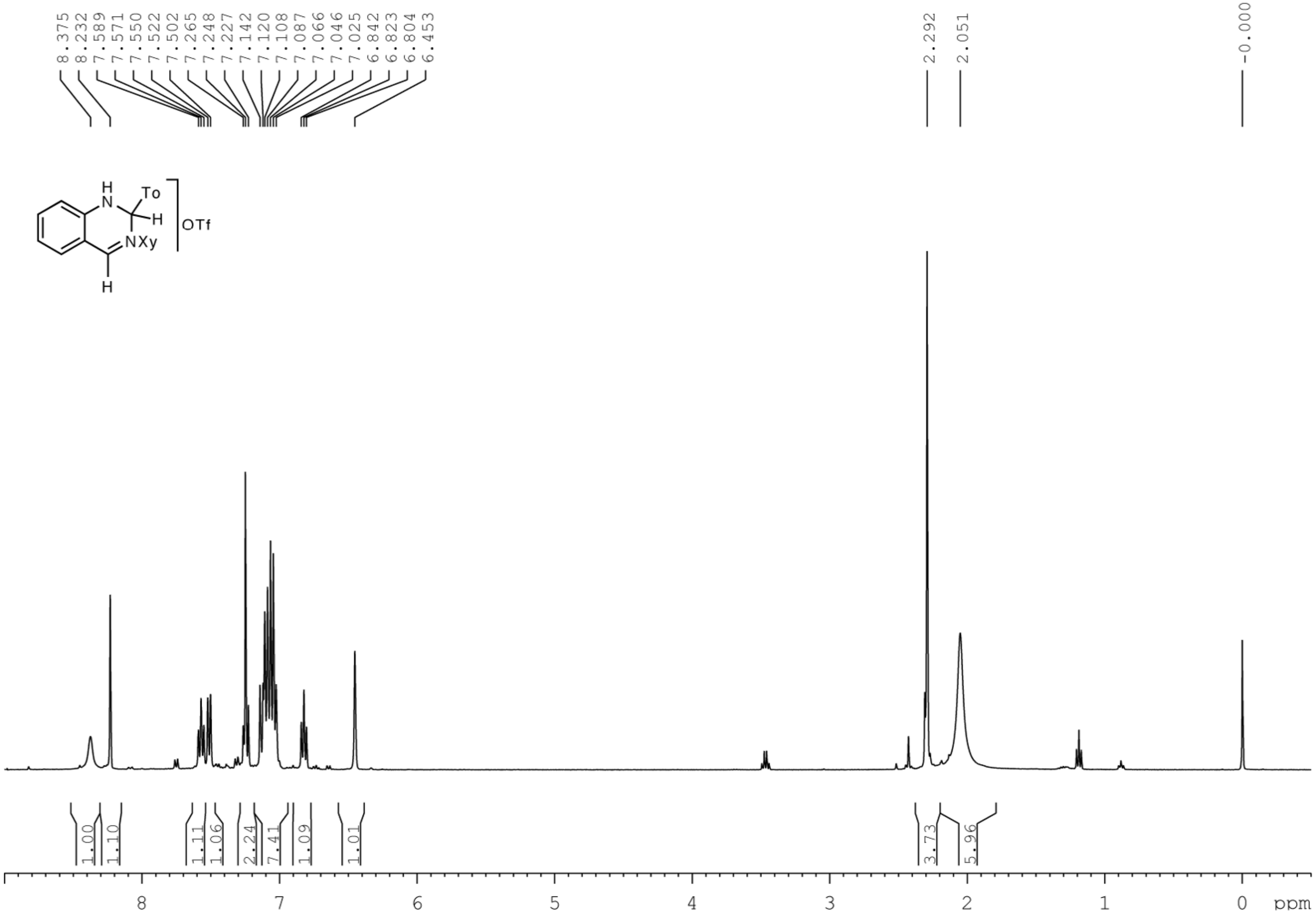
[1]H NMR spectra of **3a2**·0.6$CHCl_3$ (400 MHz, $CDCl_3$, -35 ºC, TMS).



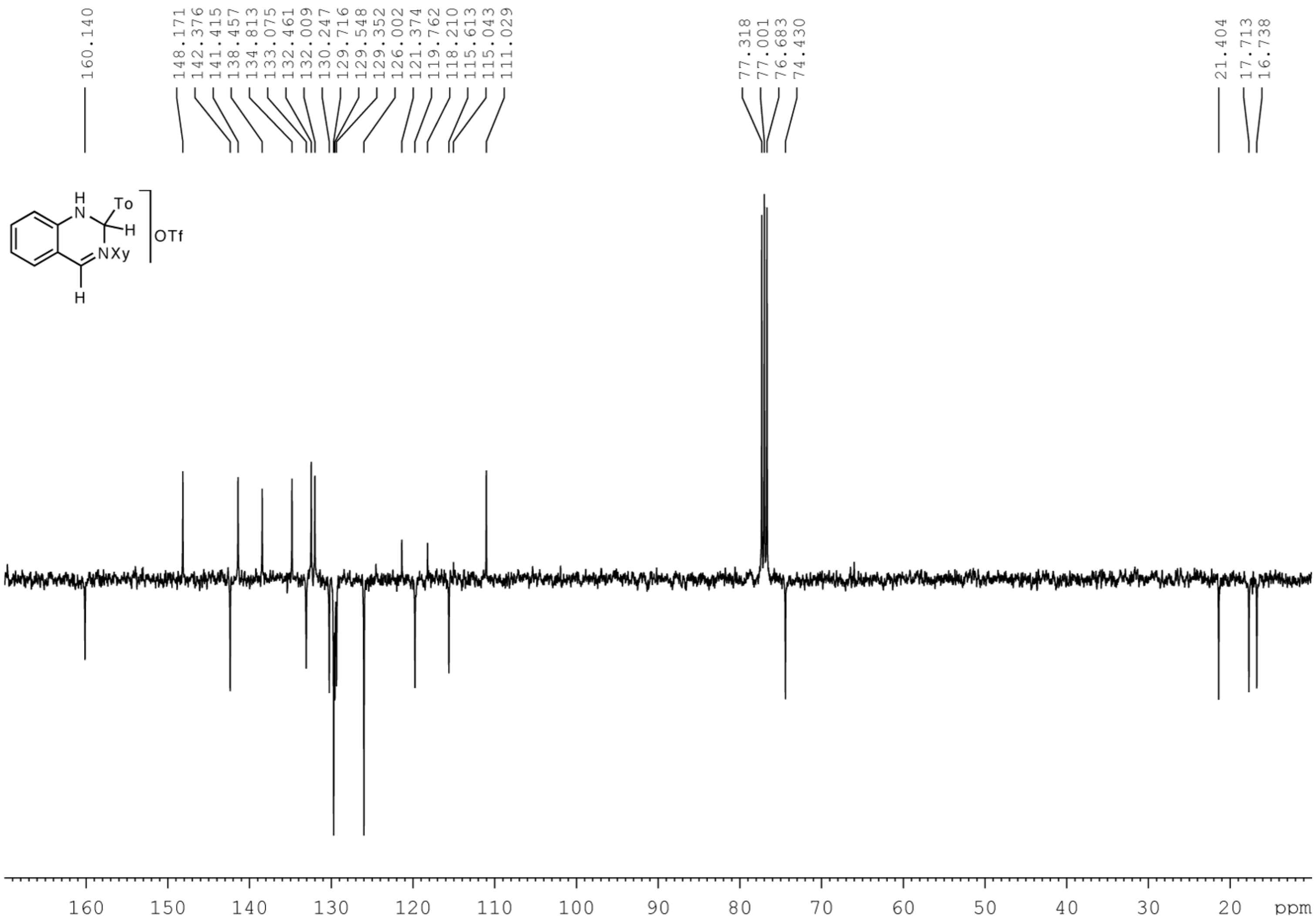
[1]H NMR spectra of **3a2**·0.6$CHCl_3$ (400 MHz, $CDCl_3$, 25 ºC, TMS).



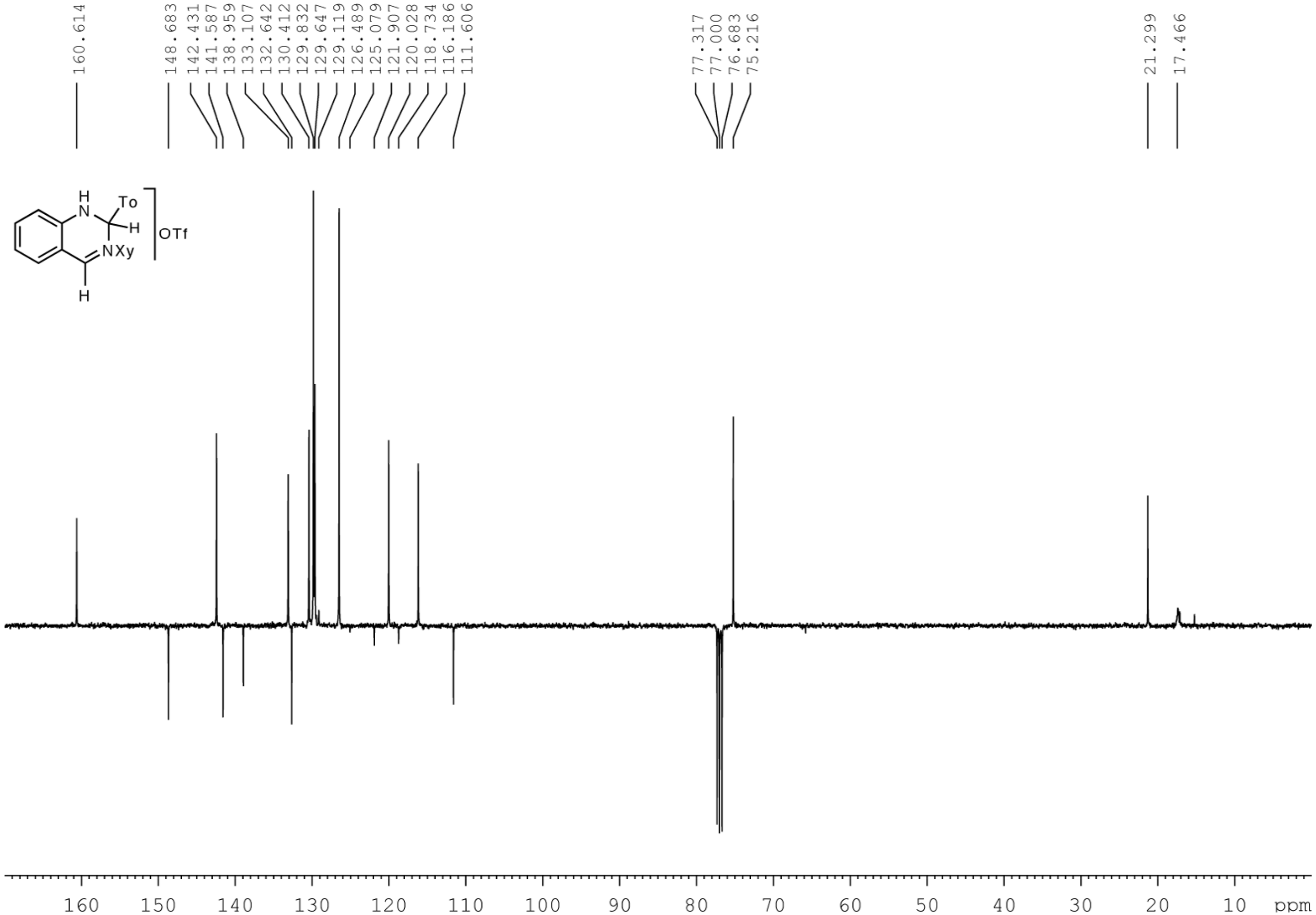
[1]H NMR spectra of **3a2**·0.6CHCl$_3$ (400 MHz, CDCl$_3$, 55 ºC, TMS).



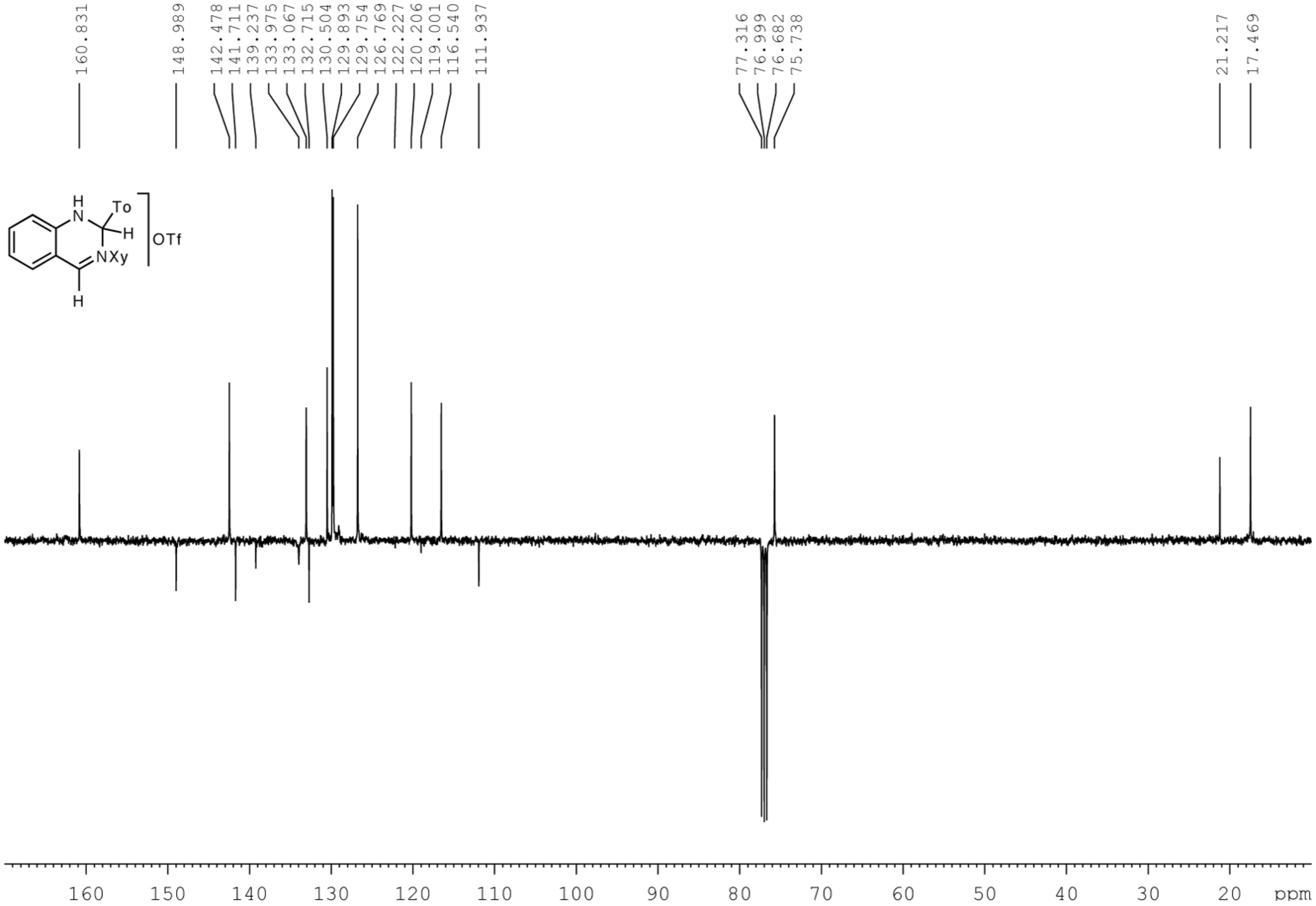
$^{13}C\{^1H\}$ NMR APT spectra of **3a2**·0.6CHCl$_3$ (100.8 MHz, CDCl$_3$, -35 ºC, TMS).



$^{13}C\{^{1}H\}$ NMR APT spectra of **3a2**·0.6$CHCl_3$ (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



$^{13}C\{^{1}H\}$ NMR APT spectra of **3a2**·0.6$CHCl_3$ (100.8 MHz, $CDCl_3$, 55 ºC, TMS).



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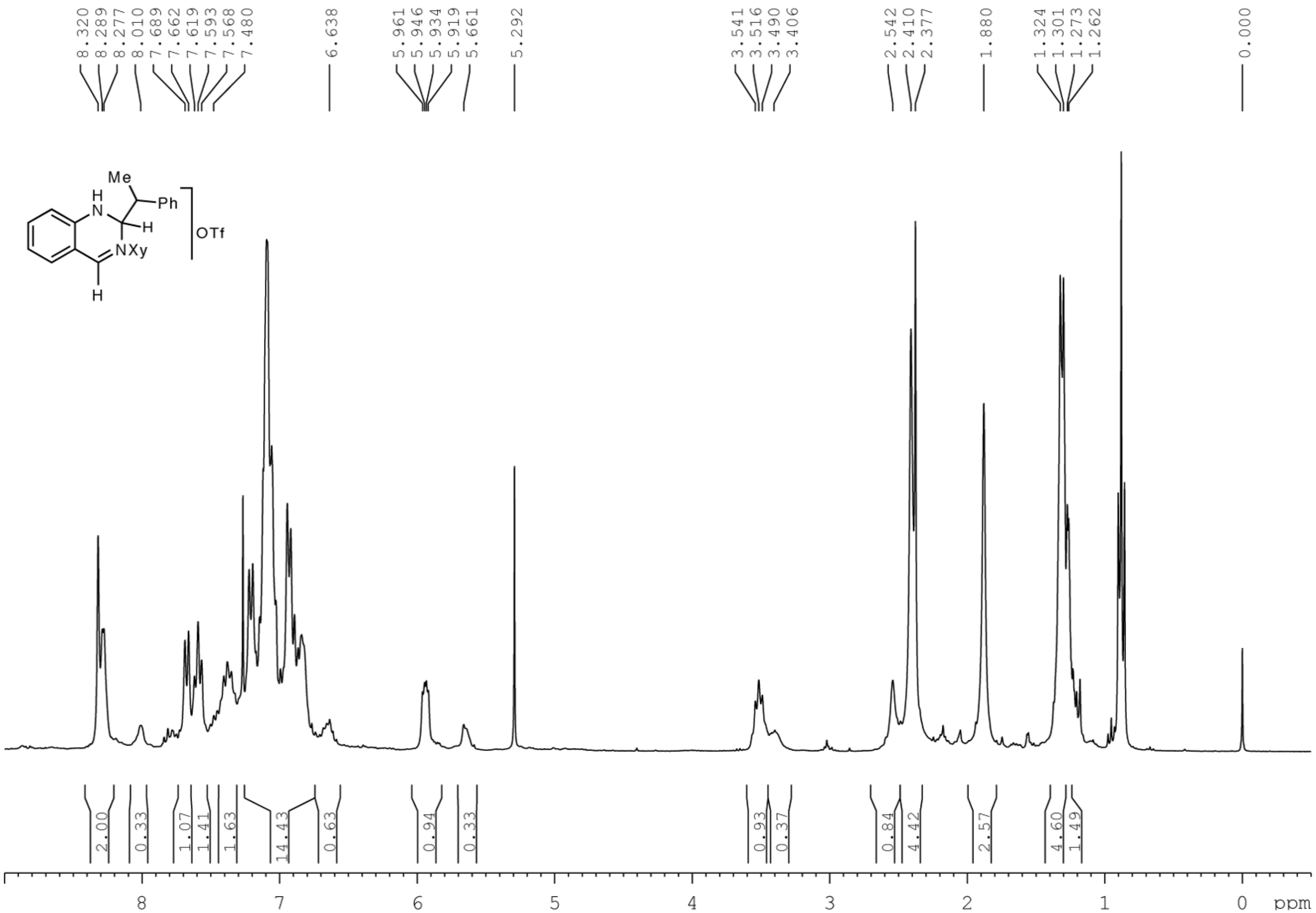
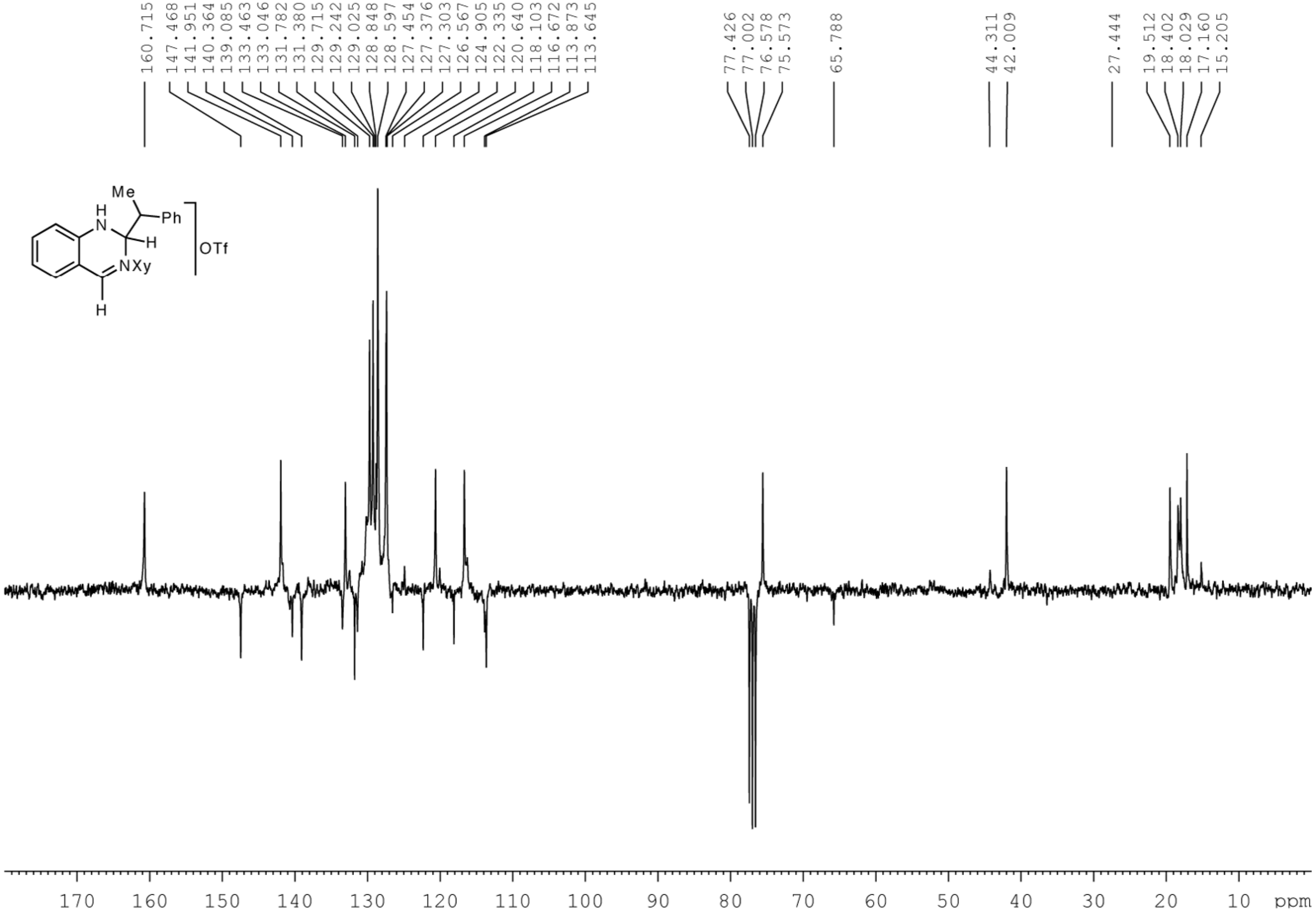
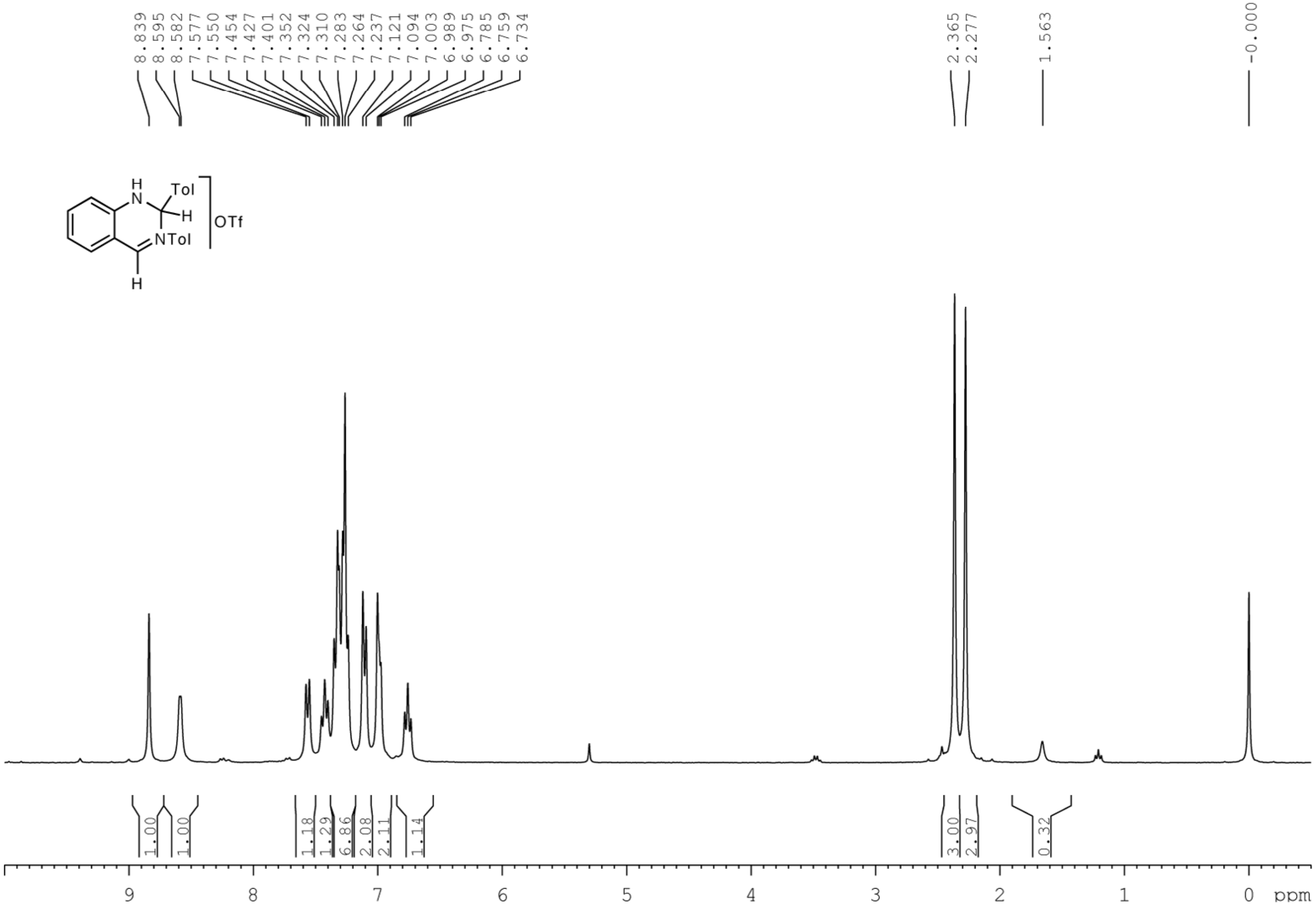
[1]H NMR spectra of **3a3**·H_2O (300 MHz, $CDCl_3$, 55 ºC, TMS).



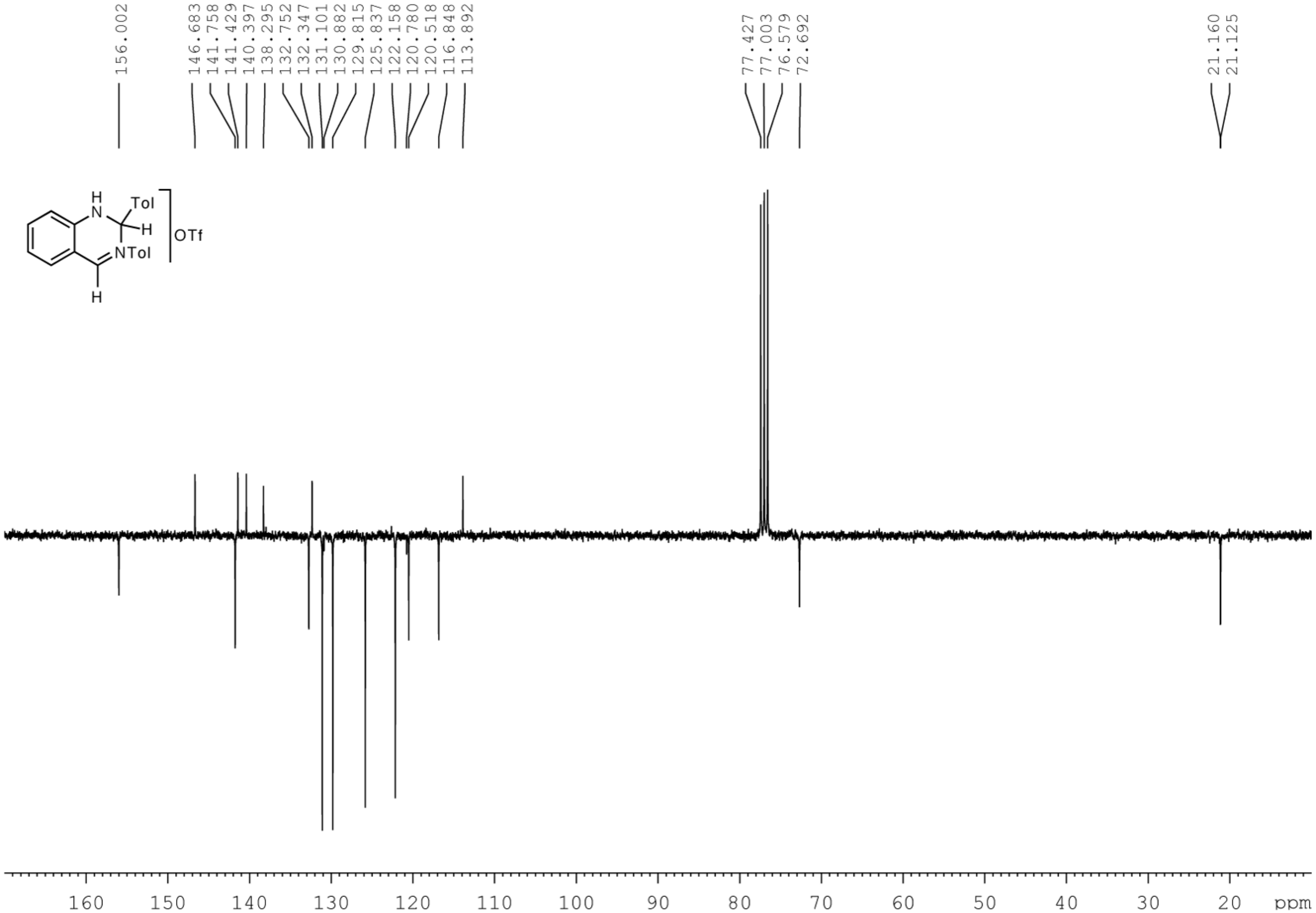
$^{13}C\{^{1}H\}$ NMR APT spectra of **3a3** (75.5 MHz, $CDCl_3$, 25 ºC, TMS).



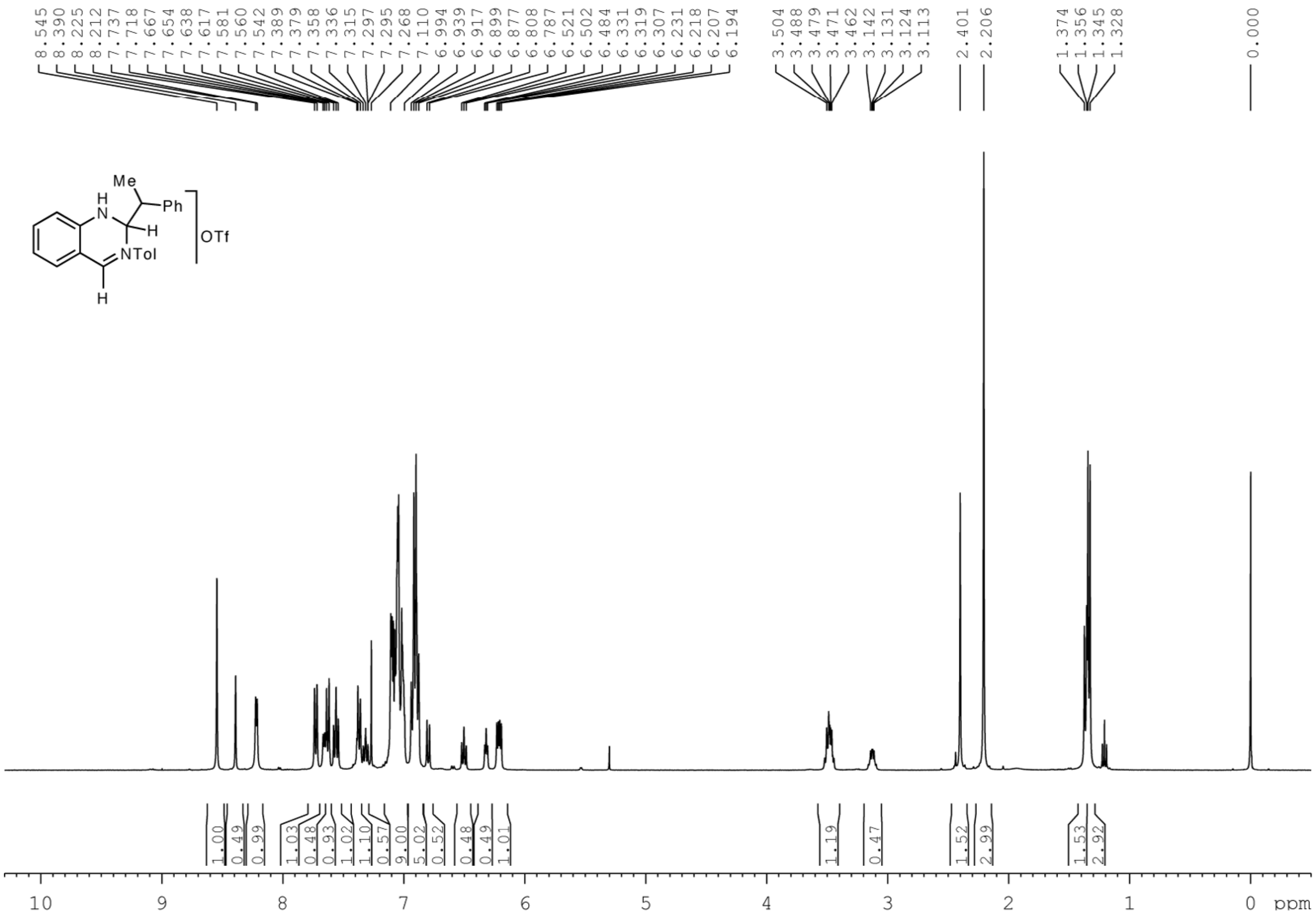
^{1}H NMR spectra of **3b2**·0.5H_2O (300 MHz, $CDCl_3$, 25 ºC, TMS).



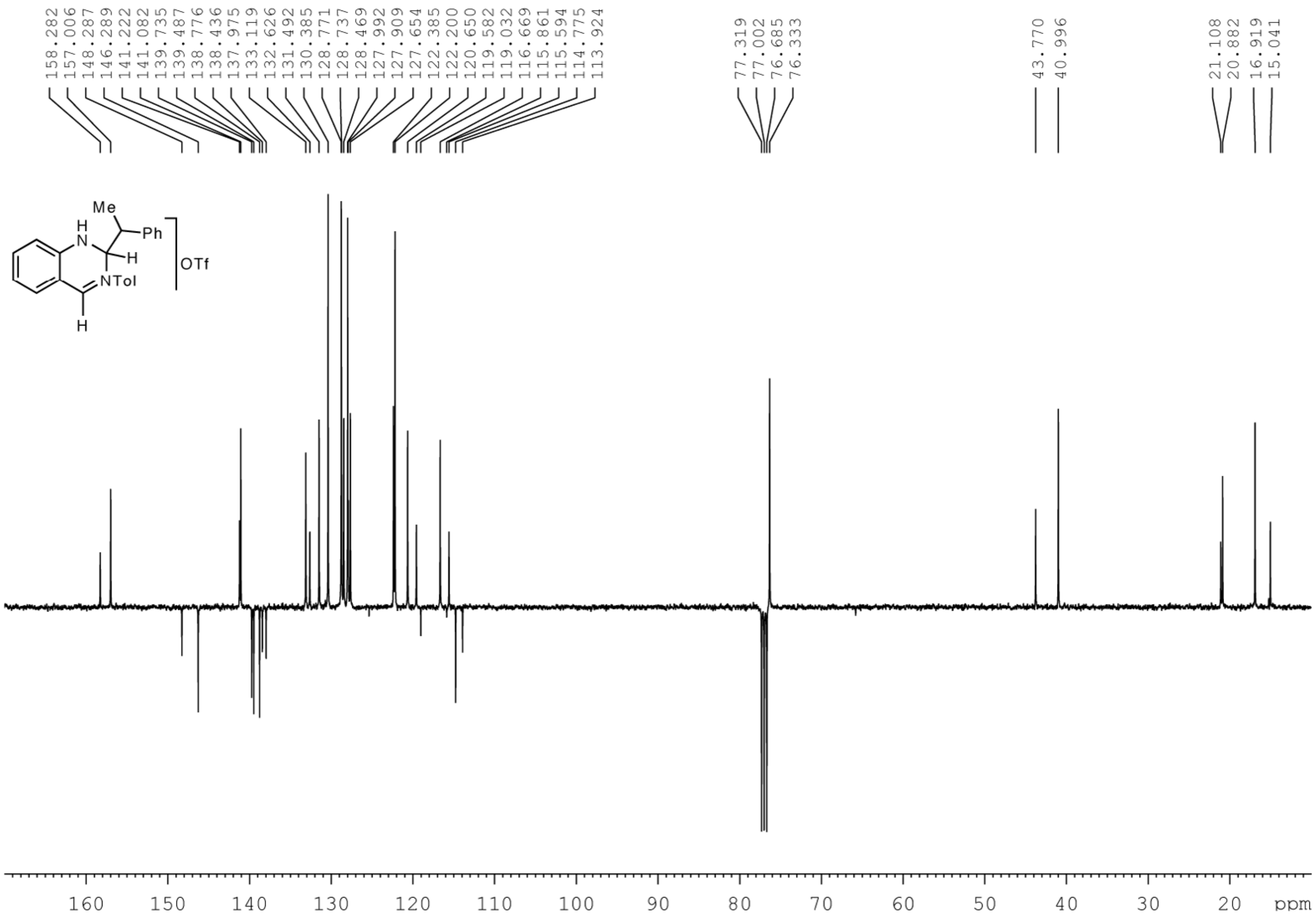
$^{13}C\{^{1}H\}$ NMR APT spectra of **3b2** (75.5 MHz, $CDCl_3$, 25 ºC, TMS).



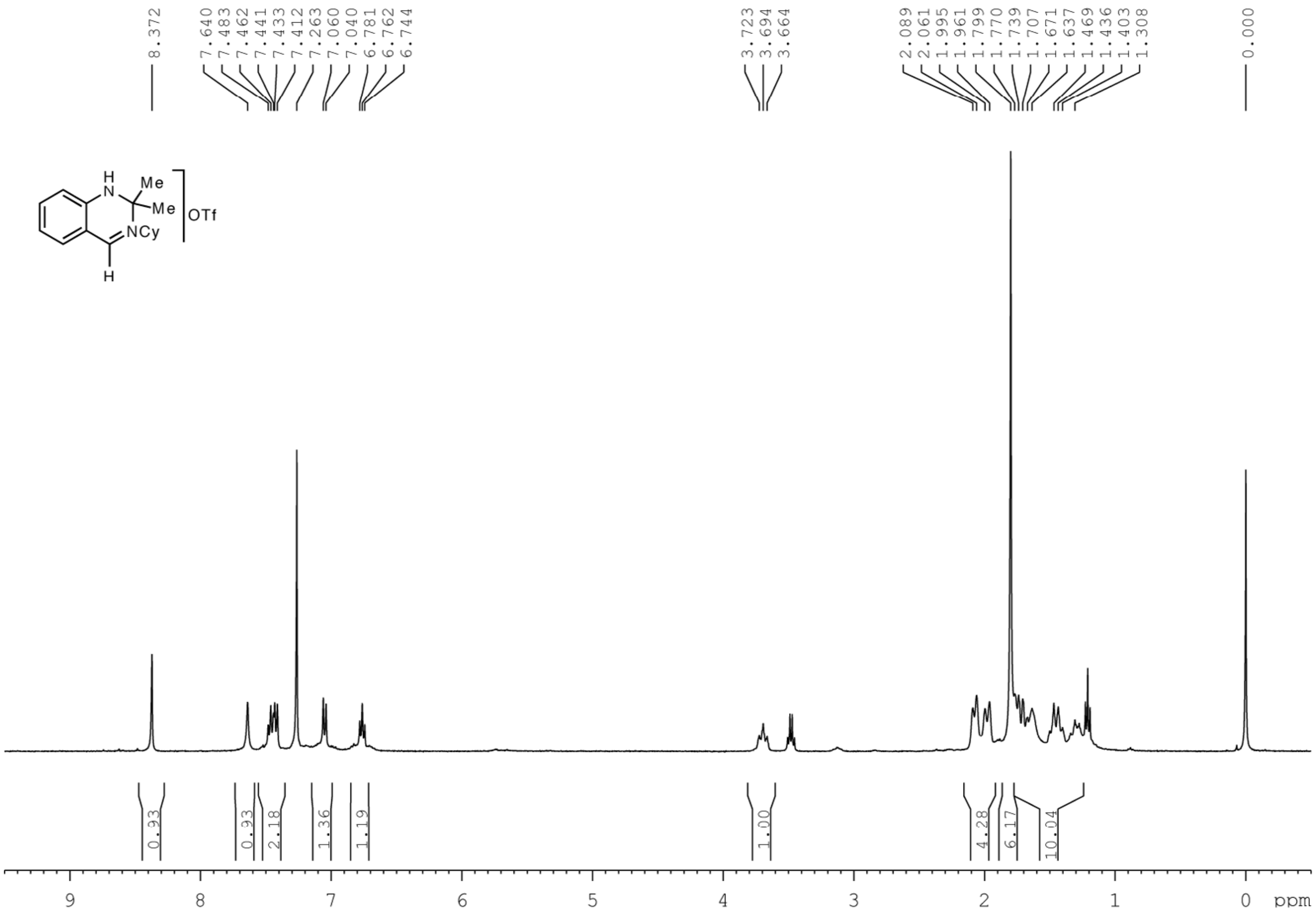
[1]H NMR spectra of **3b3** (400 MHz, $CDCl_3$, 25 ºC, TMS).



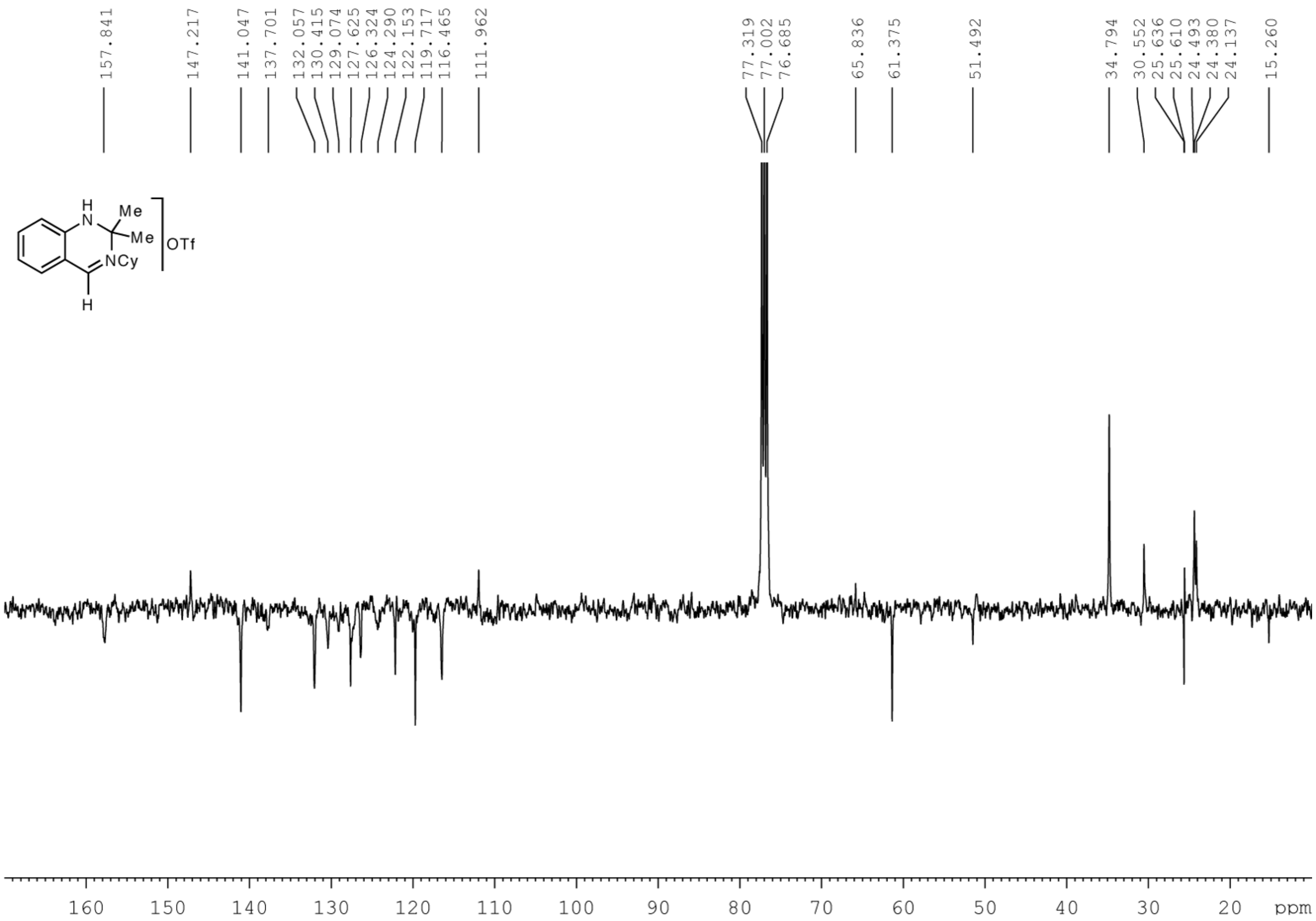
$^{13}C\{^{1}H\}$ NMR APT spectra of **3b3** (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



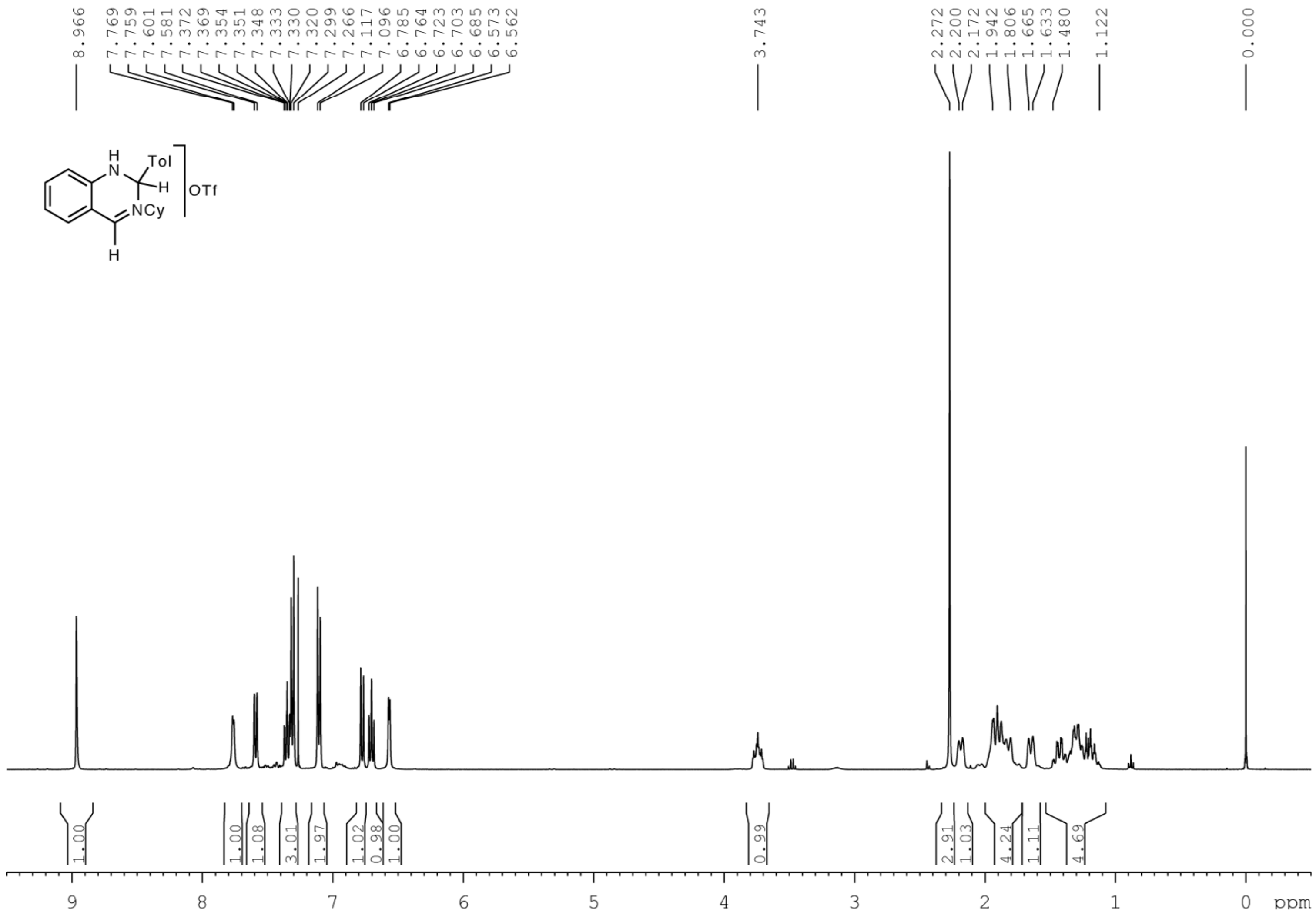
^{1}H NMR spectra of **3c1** (400 MHz, $CDCl_3$, 25 ºC, TMS).



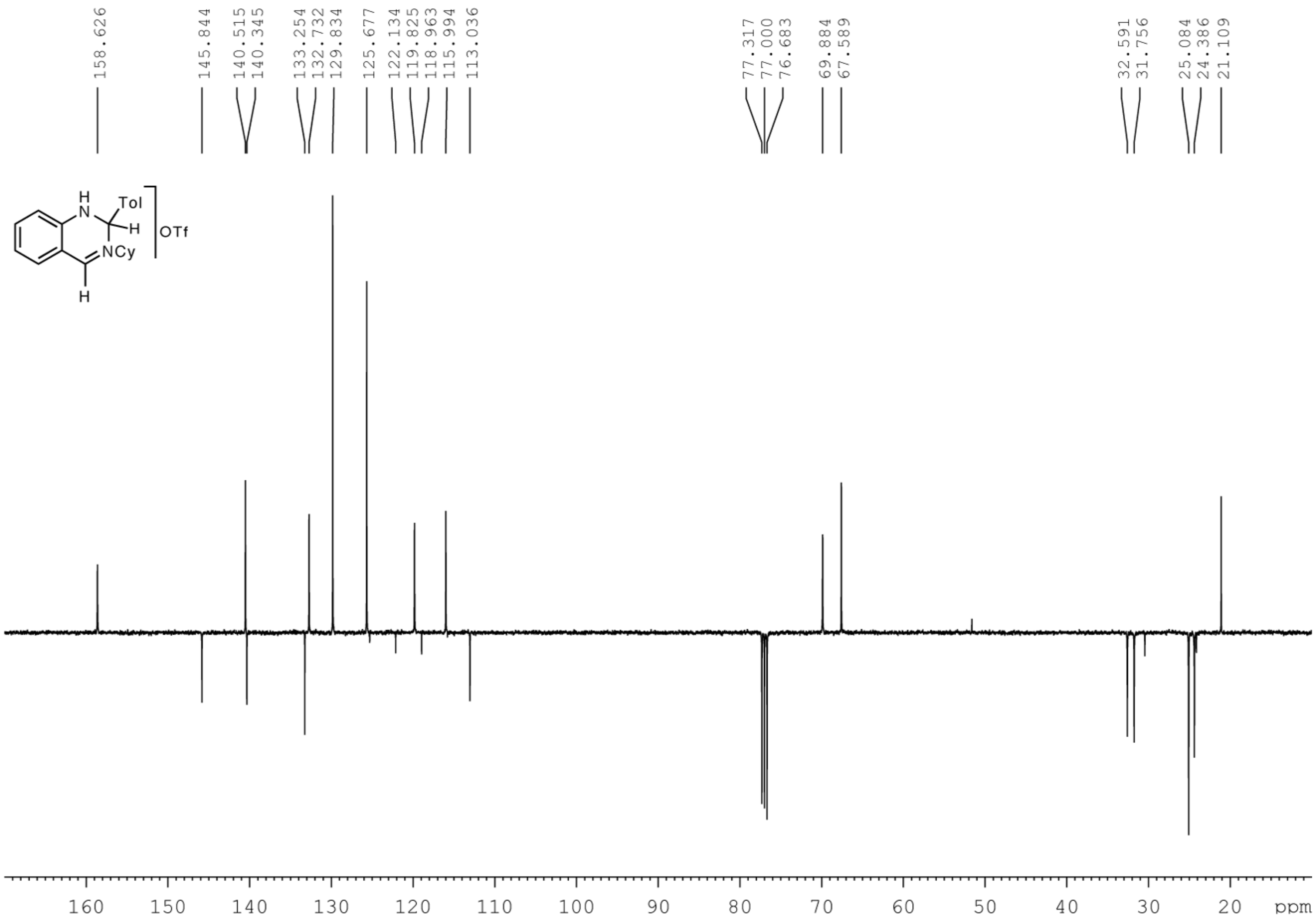
$^{13}C\{^{1}H\}$ NMR APT spectra of **3c1** (see Discussion; 100.8 MHz, $CDCl_3$, 25 ºC, TMS).



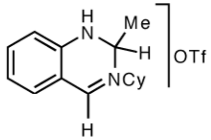
^{1}H NMR spectra of **3c2**·0.7H_2O (400 MHz, $CDCl_3$, 25 ºC, TMS).

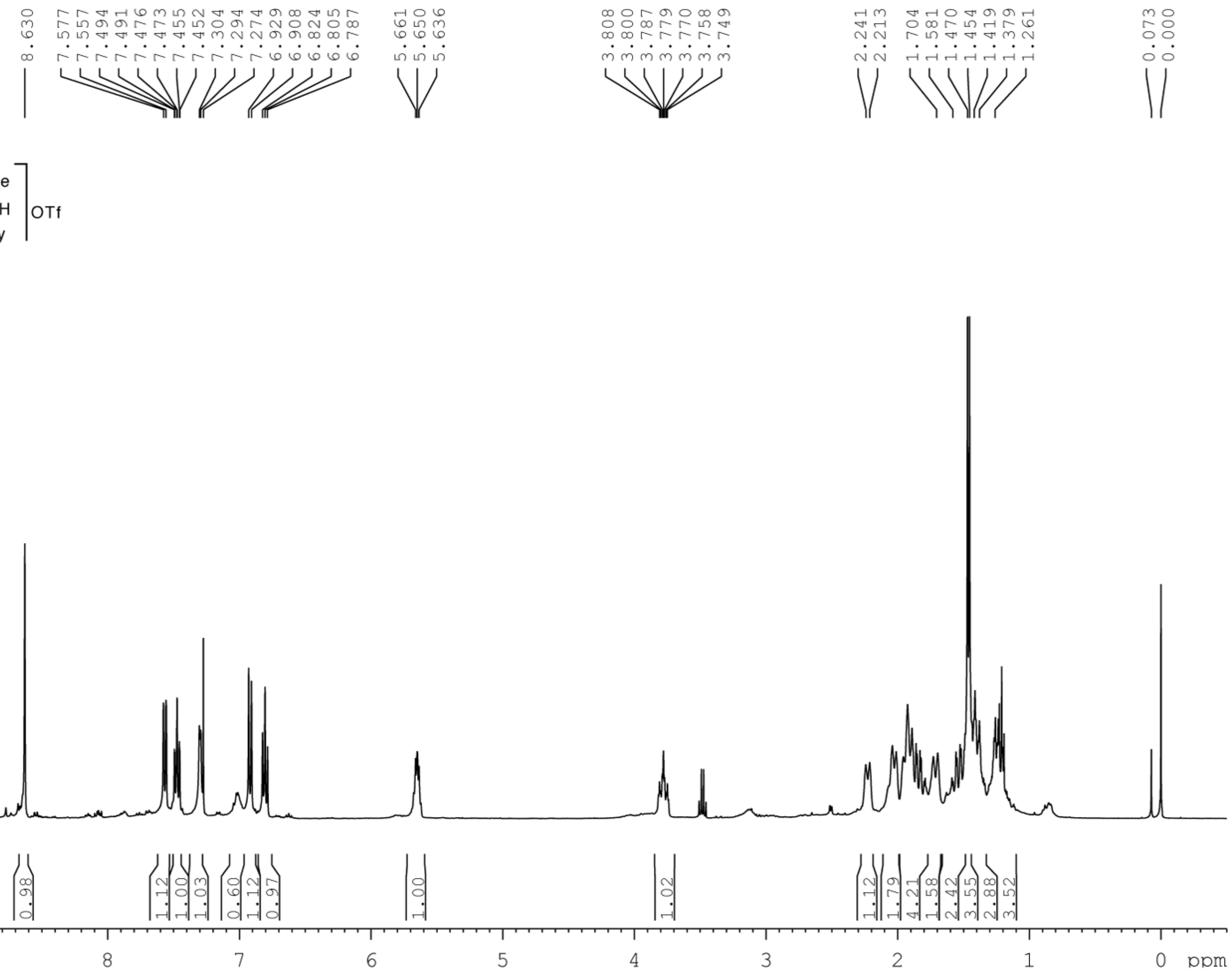


$^{13}C\{^{1}H\}$ NMR APT spectra of **3c2**·0.7H_2O (100.8 MHz, $CDCl_3$, 25 ºC, TMS).

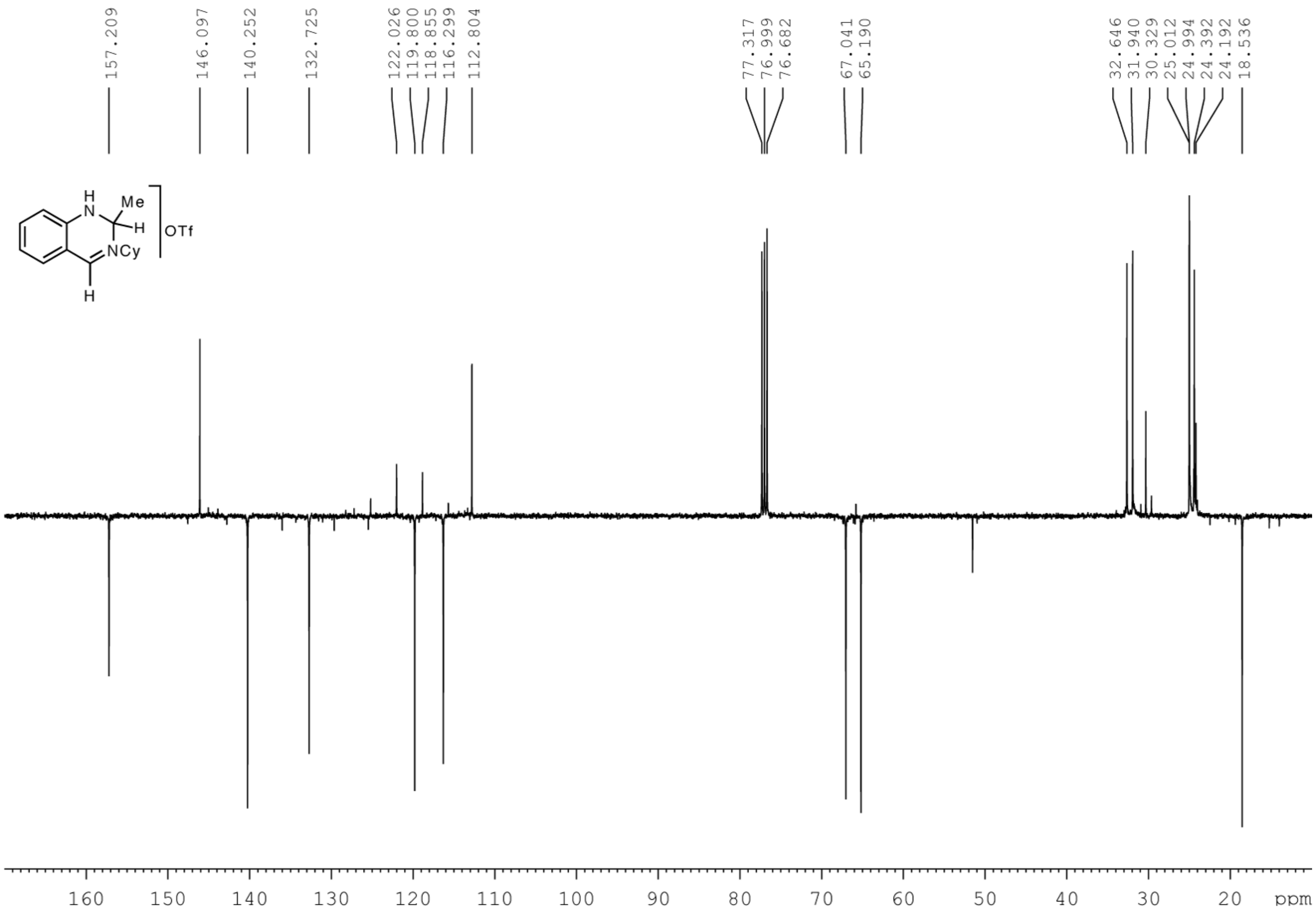


^{1}H NMR spectra of **3c4** (400 MHz, $CDCl_3$, 25 ºC, TMS).

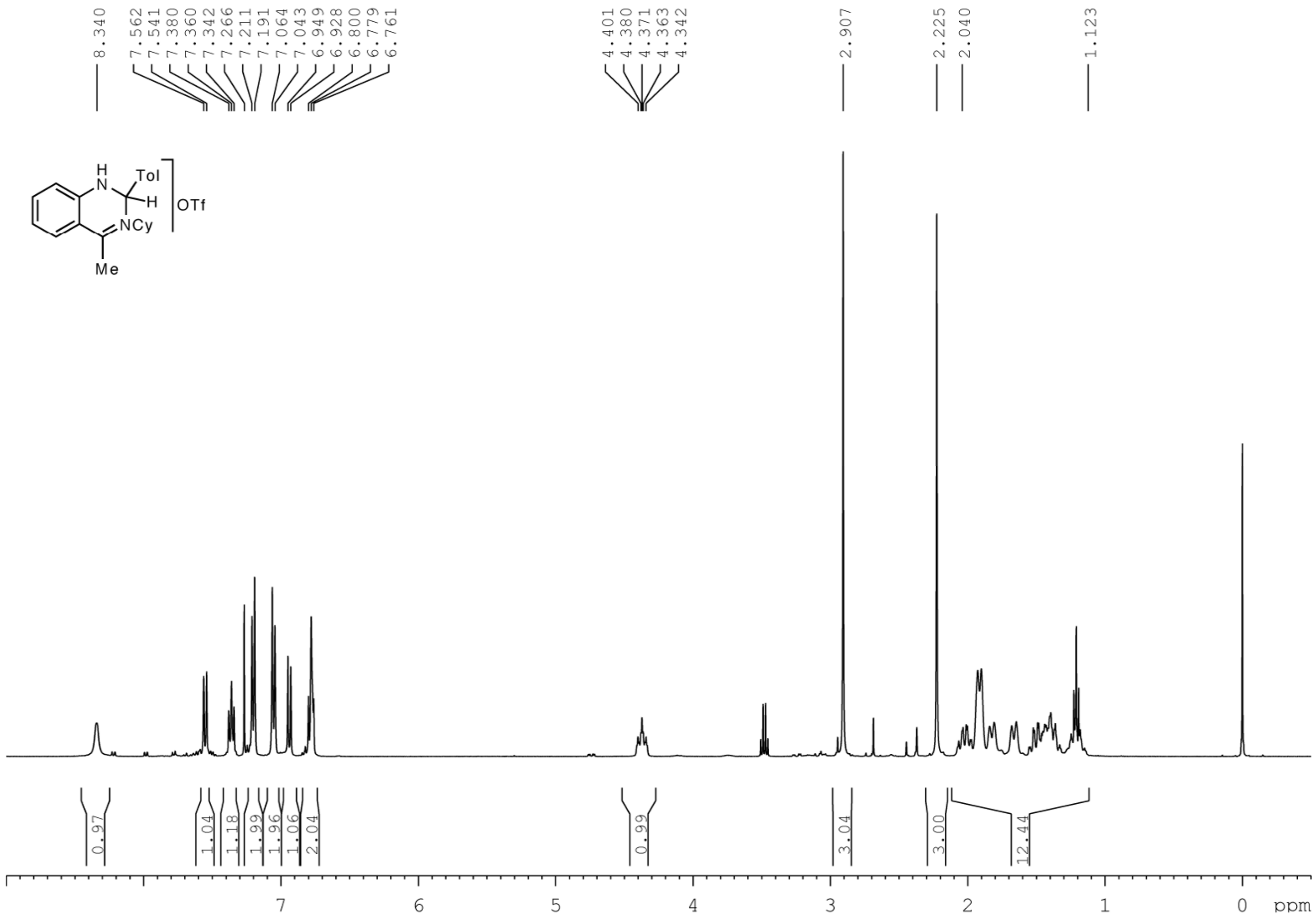




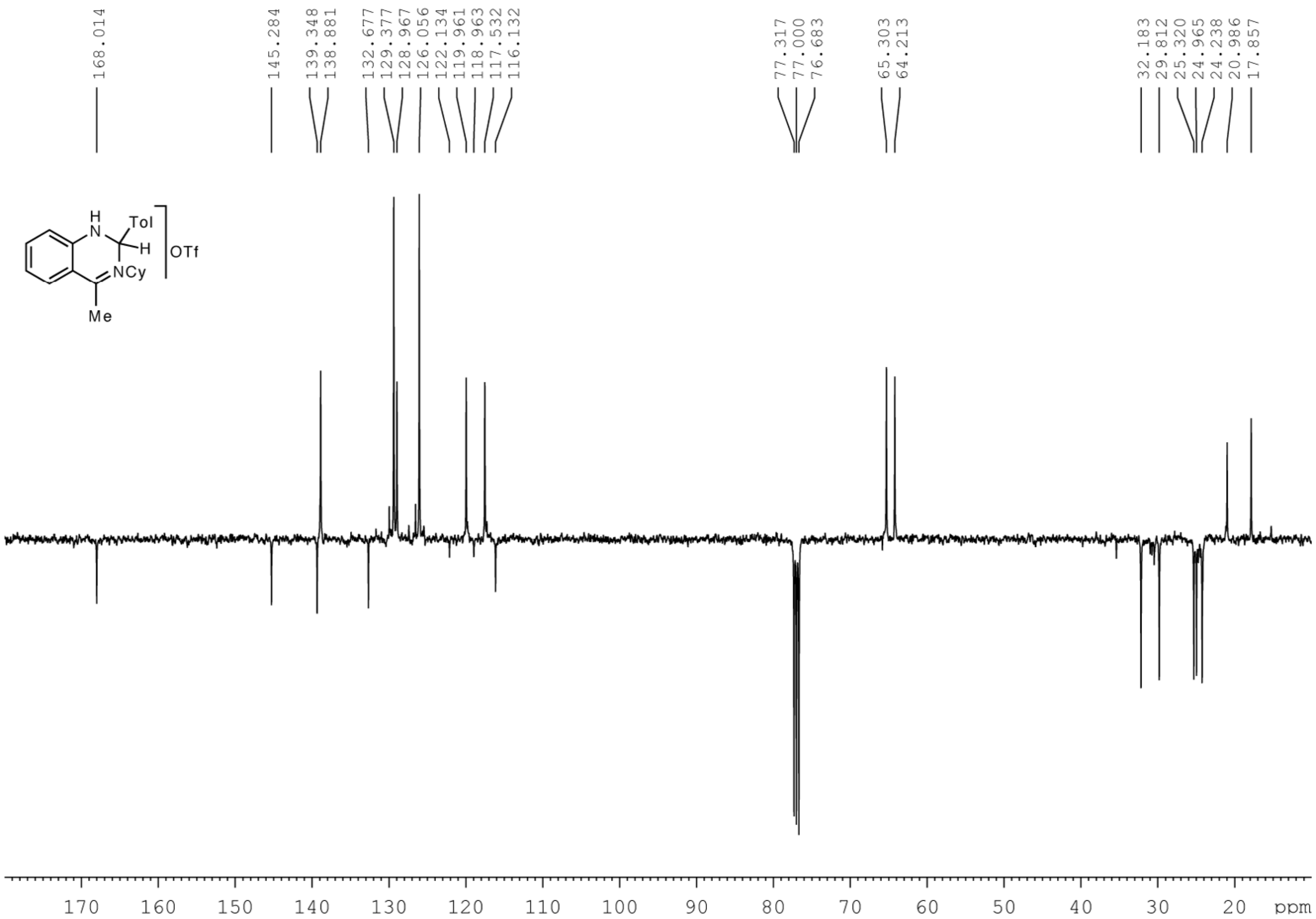
$^{13}C\{^{1}H\}$ NMR APT spectra of **3c4** (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



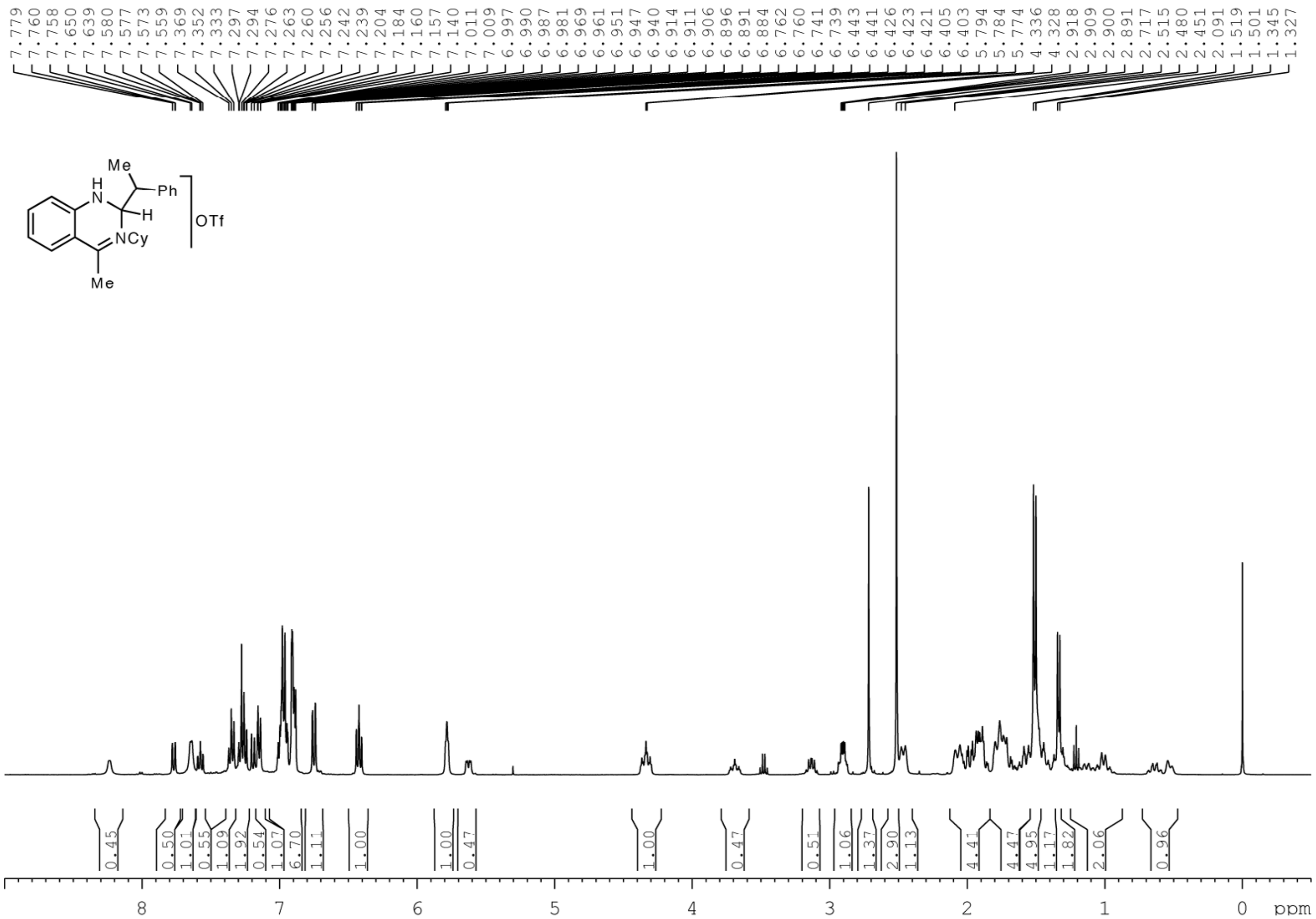
[1]H NMR spectra of **3d2**·H_2O (400 MHz, $CDCl_3$, 25 ºC, TMS).



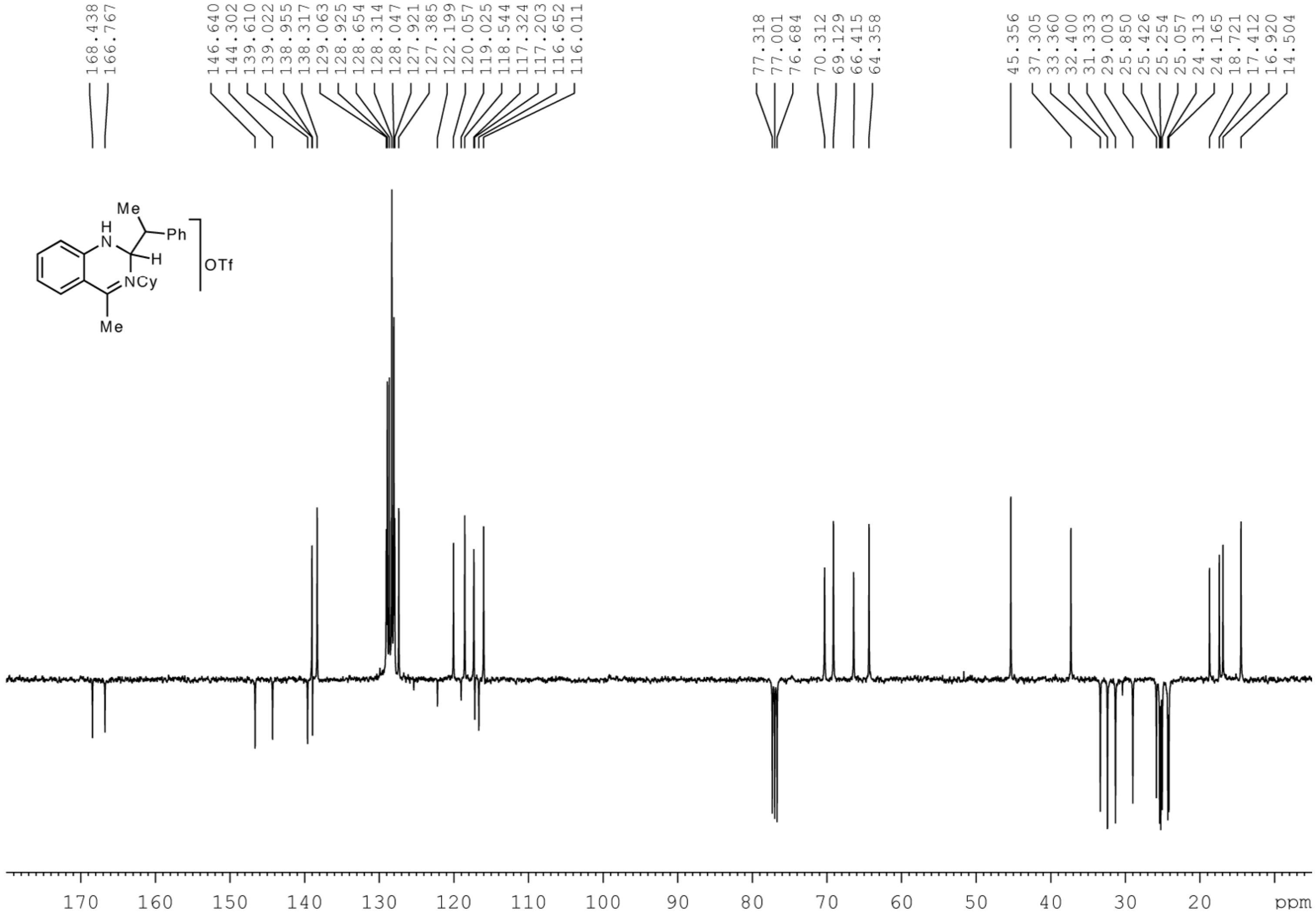
$^{13}C\{^{1}H\}$ NMR APT spectra of **3d2** (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



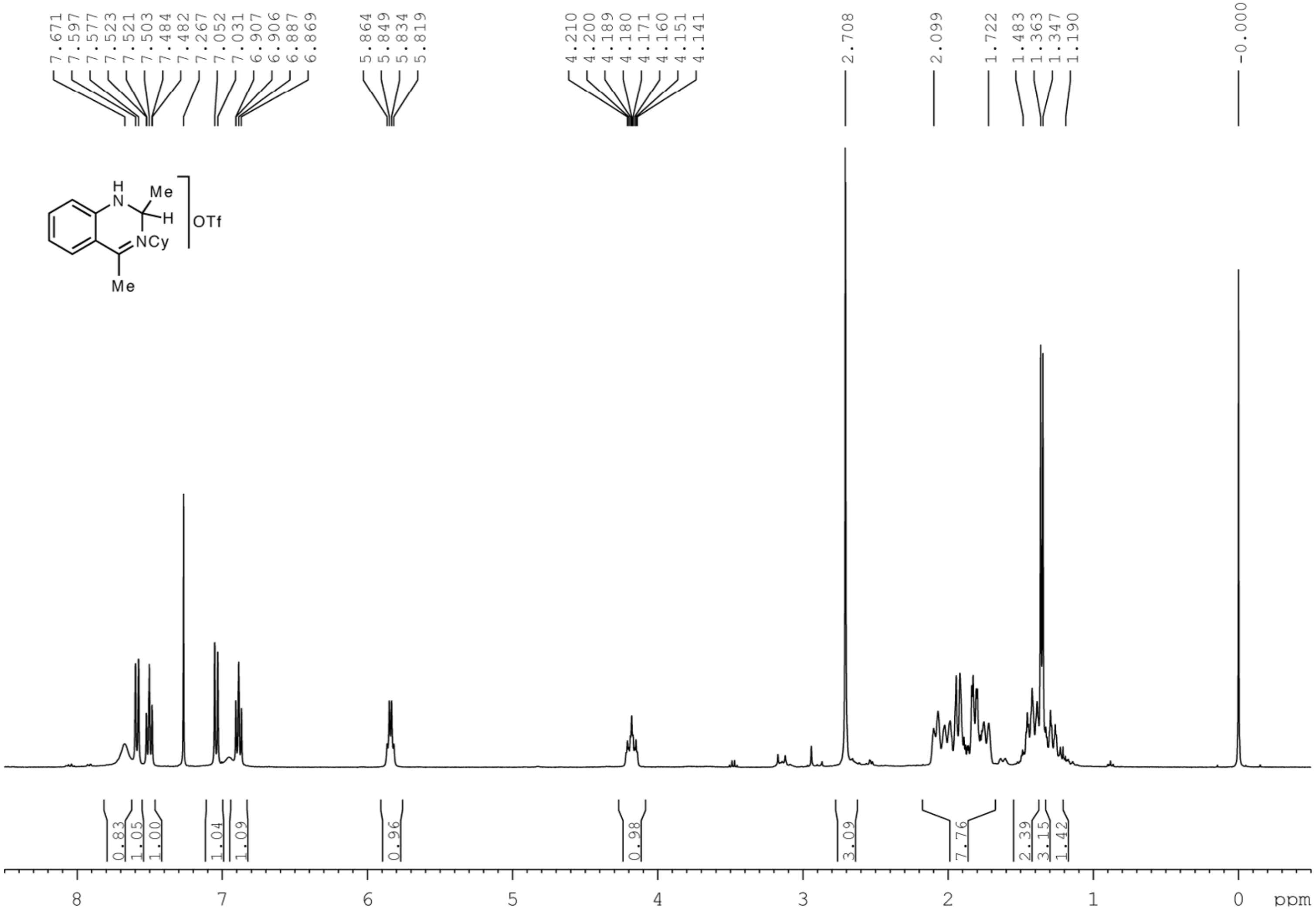
^{1}H NMR spectra of **3d3**·0.5H_2O (400 MHz, $CDCl_3$, 25 ºC, TMS).



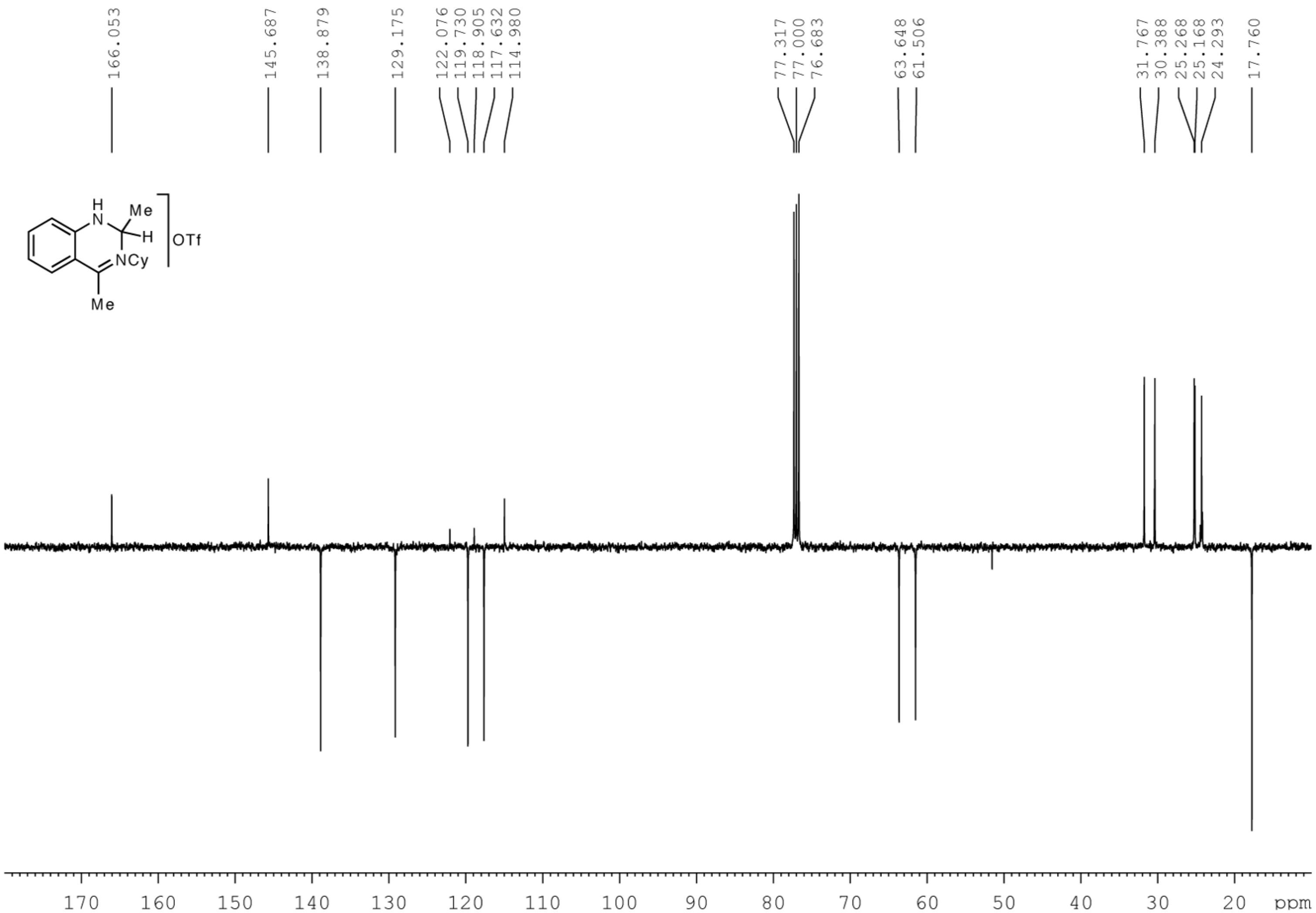
$^{13}C\{^{1}H\}$ NMR APT spectra of **3d3** (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



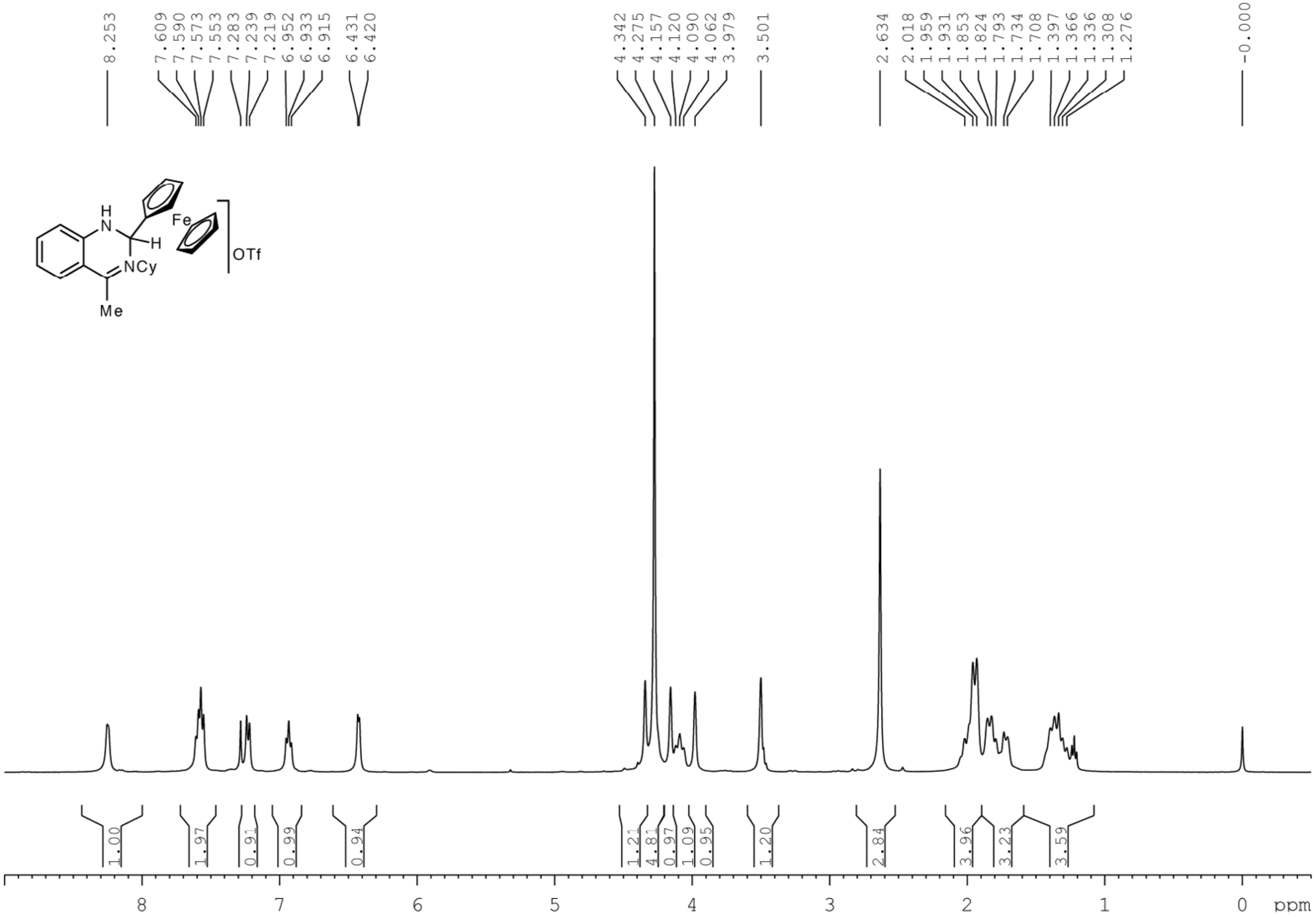
^{1}H NMR spectra of **3d4** (400 MHz, $CDCl_3$, 25 ºC, TMS).



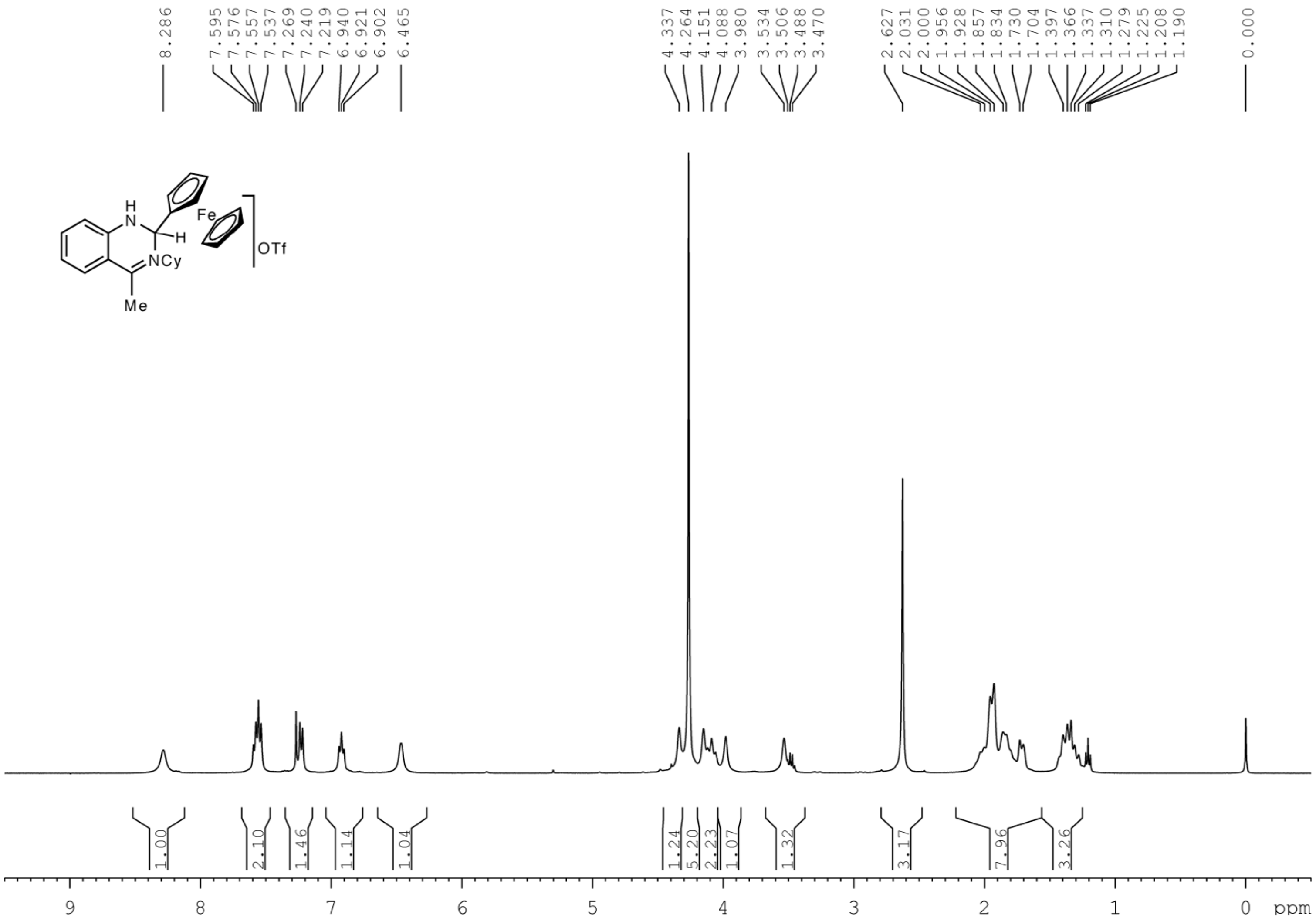
$^{13}C\{^{1}H\}$ NMR APT spectra of **3d4** (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



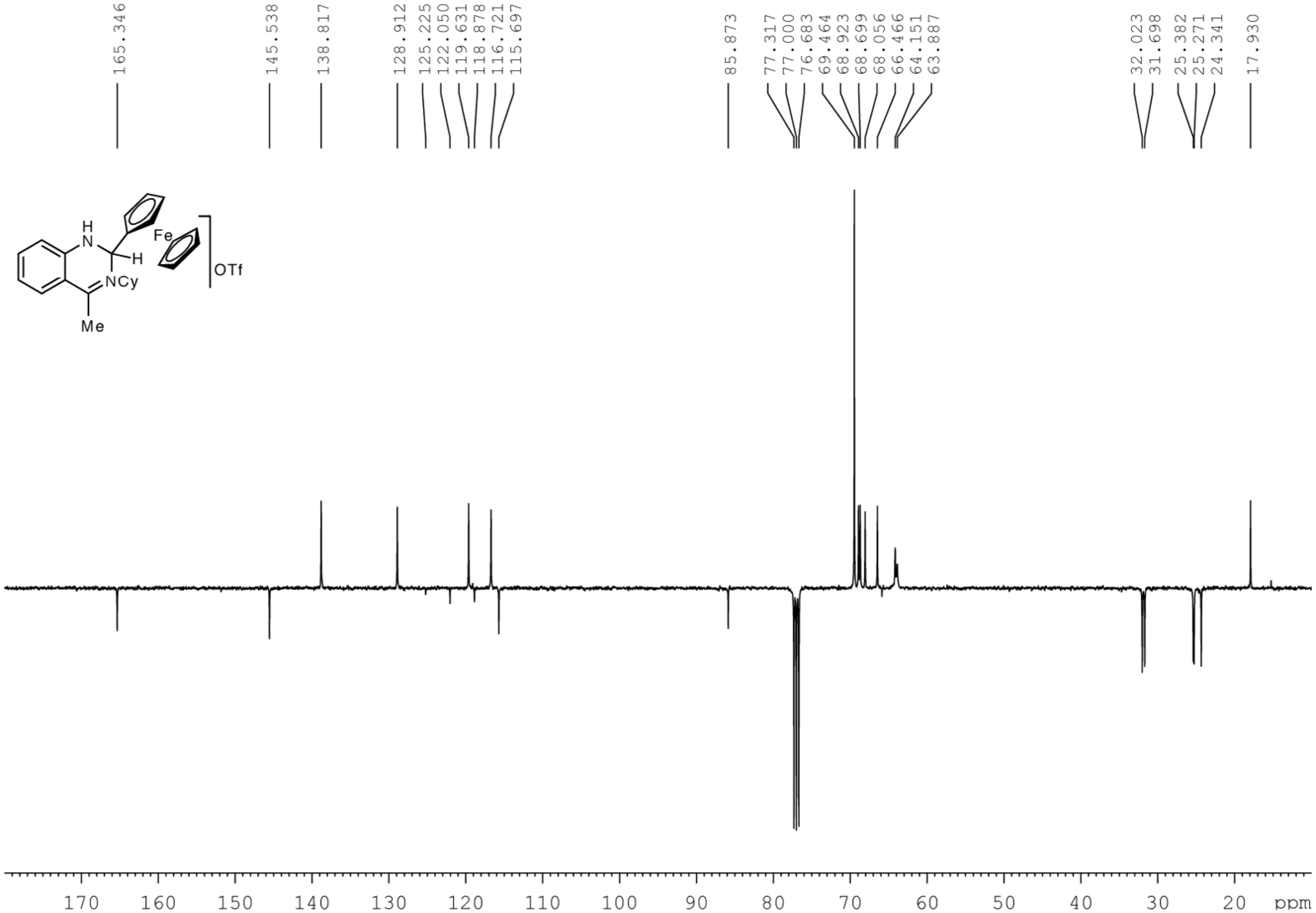
^{1}H NMR spectra of **3d5** (400 MHz, $CDCl_3$, 0 ºC, TMS).



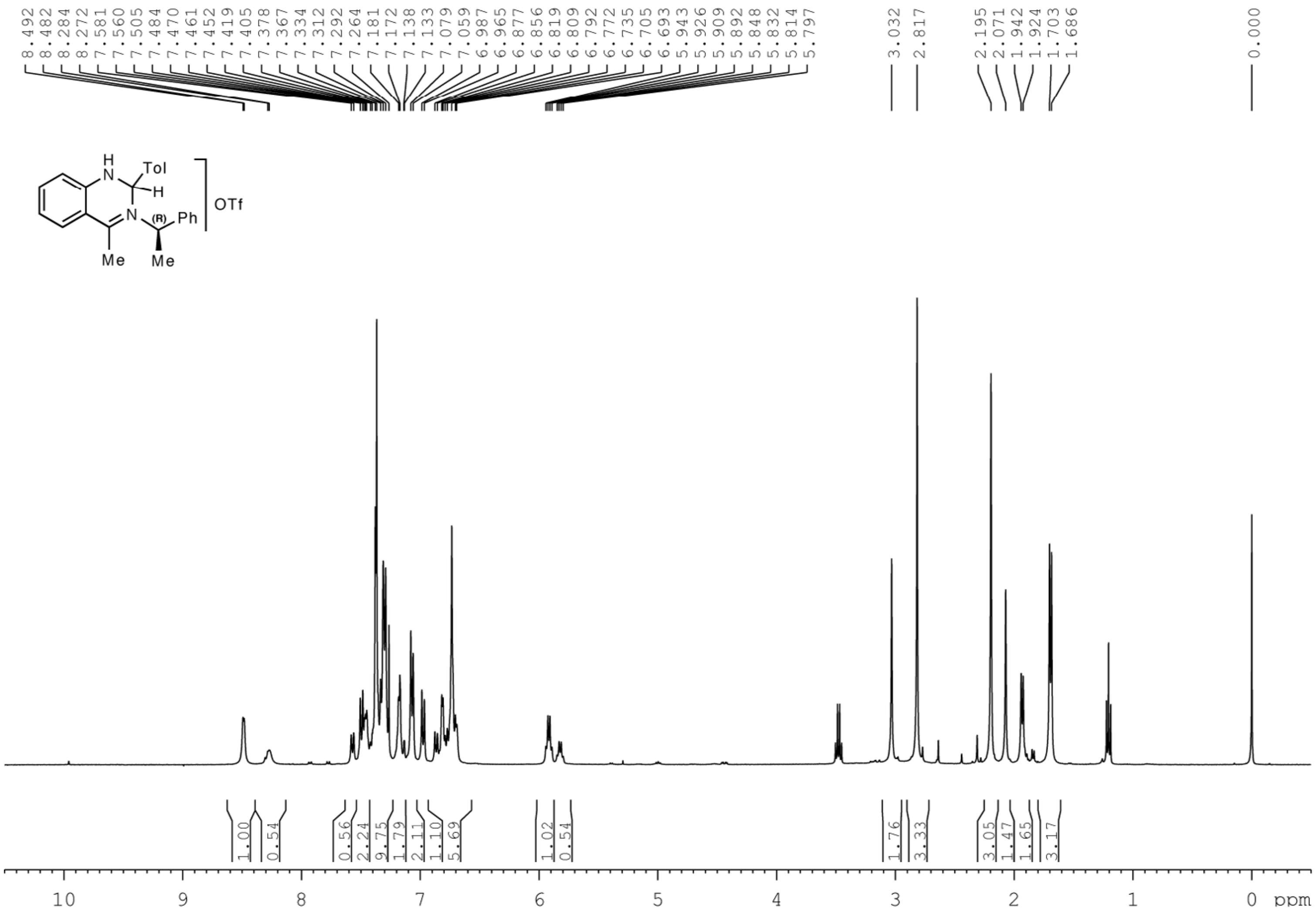
[1]H NMR spectra of **3d5** (400 MHz, $CDCl_3$, 25 ºC, TMS).



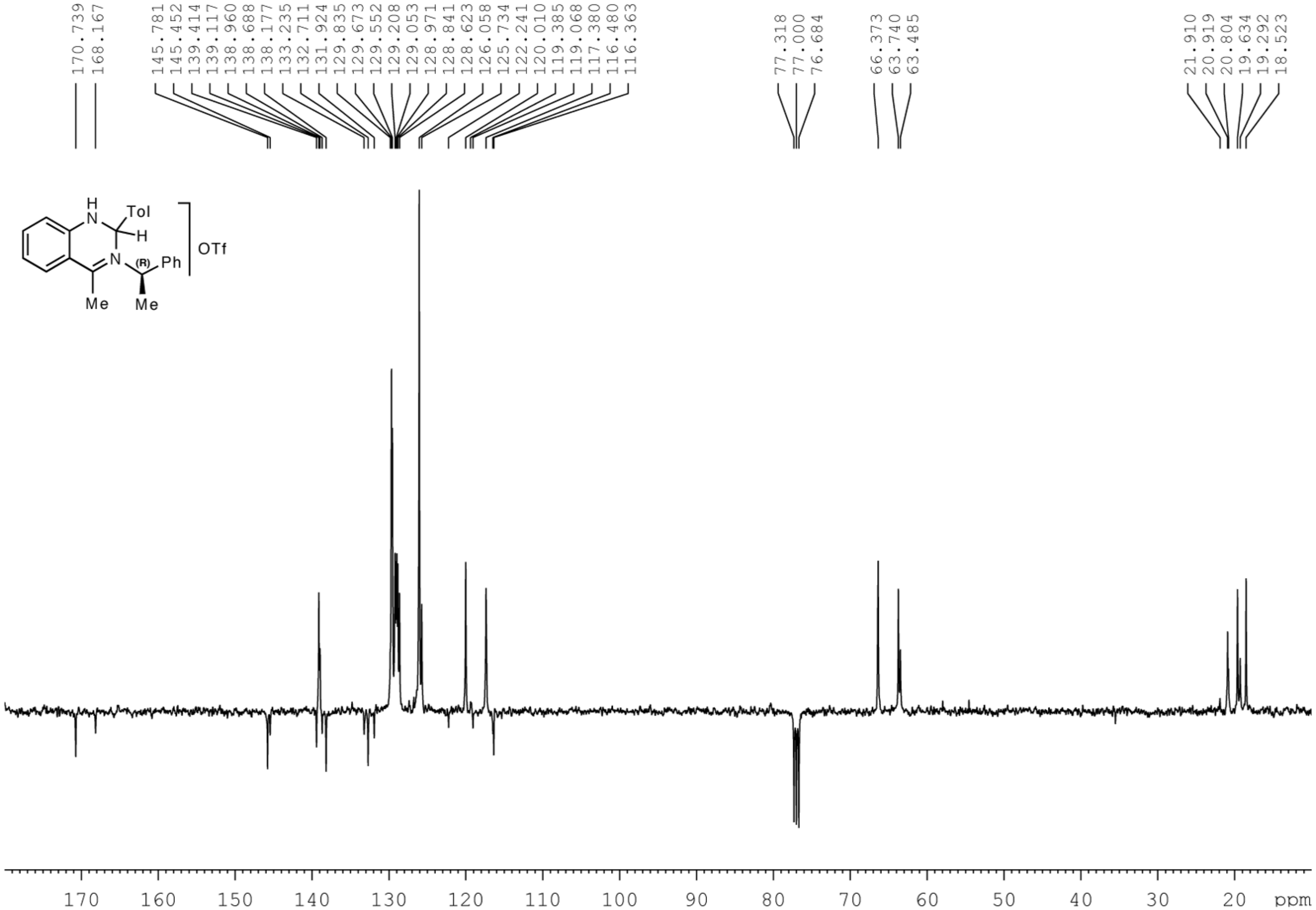
$^{13}C\{^{1}H\}$ NMR APT spectra of **3d5** (100.8 MHz, $CDCl_3$, 0 ºC, TMS).



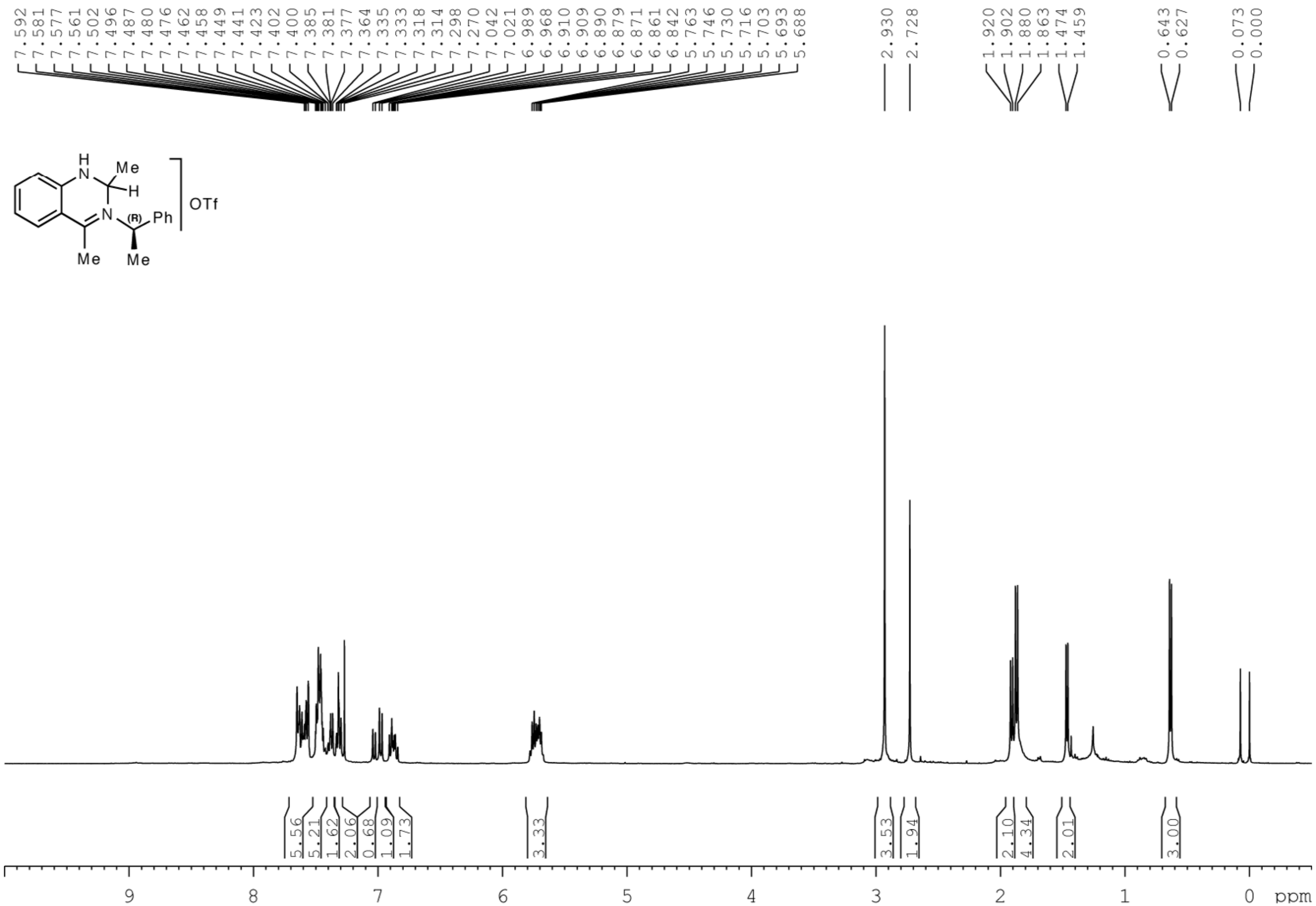
[1]H NMR spectra of **3e2**·0.5H_2O (400 MHz, $CDCl_3$, 25 ºC, TMS).



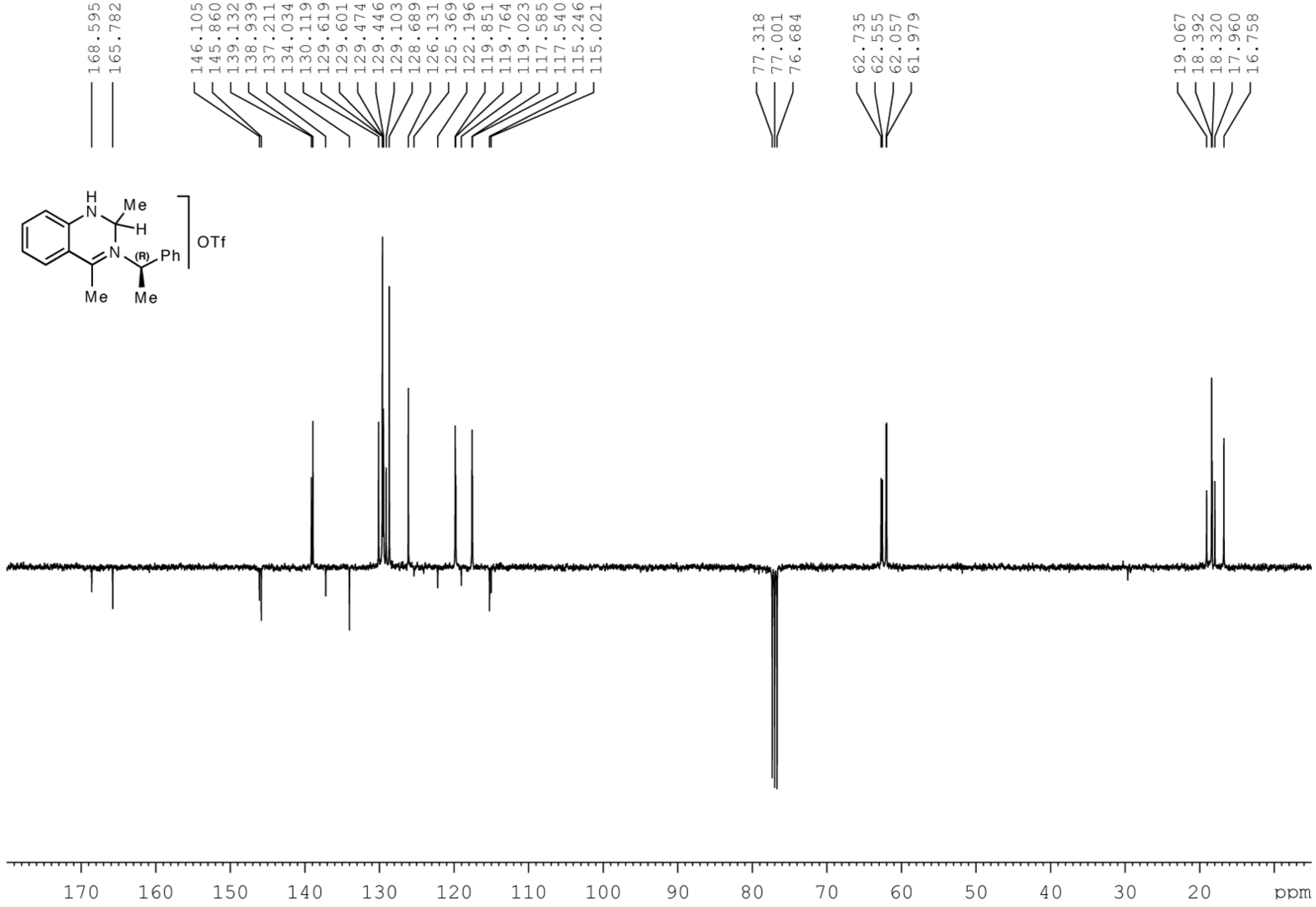
$^{13}C\{^{1}H\}$ NMR APT spectra of **3e2** (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



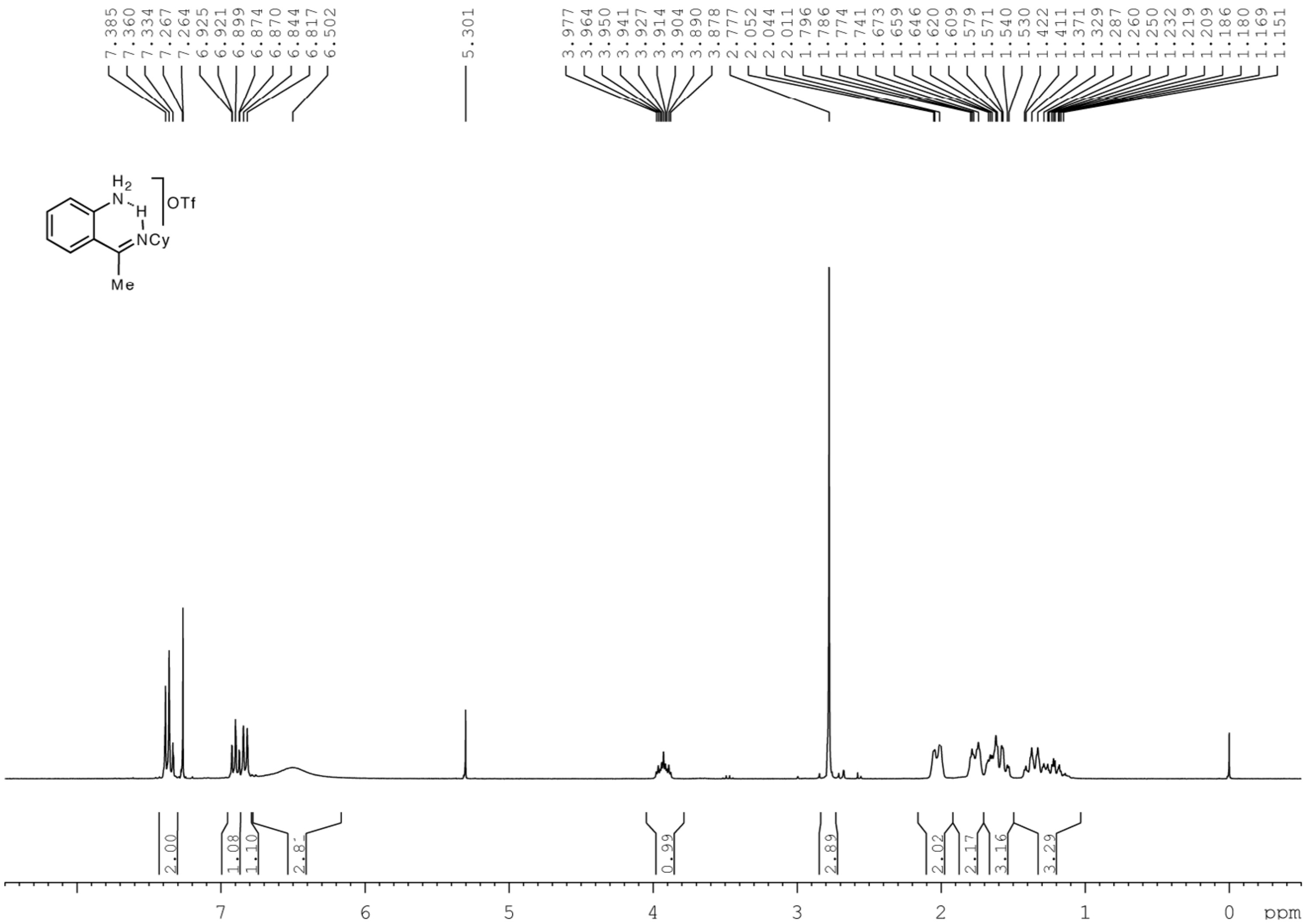
[1]H NMR spectra of **3e4** (400 MHz, $CDCl_3$, 25 ºC, TMS).



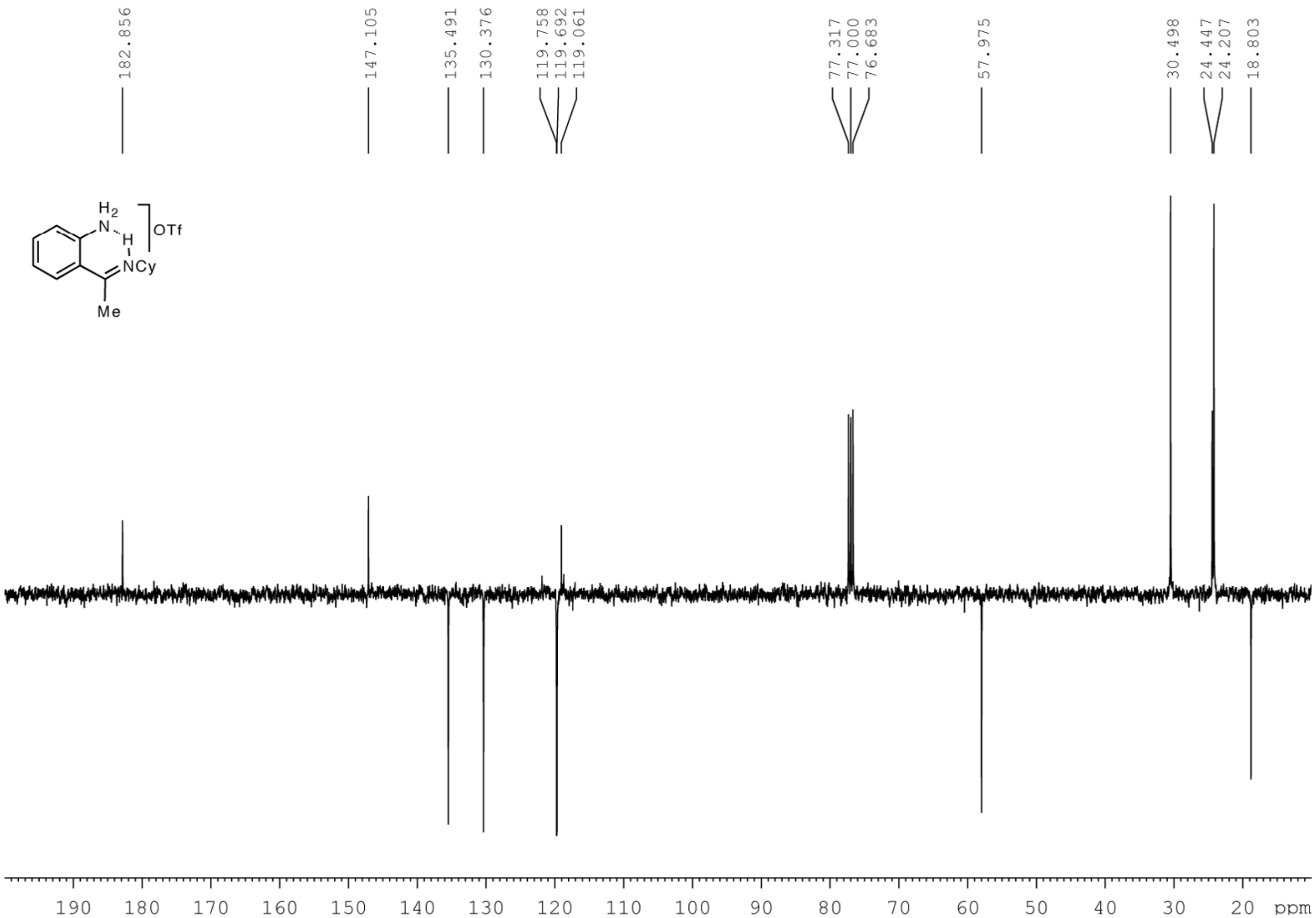
$^{13}C\{^{1}H\}$ NMR APT spectra of **3e4** (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



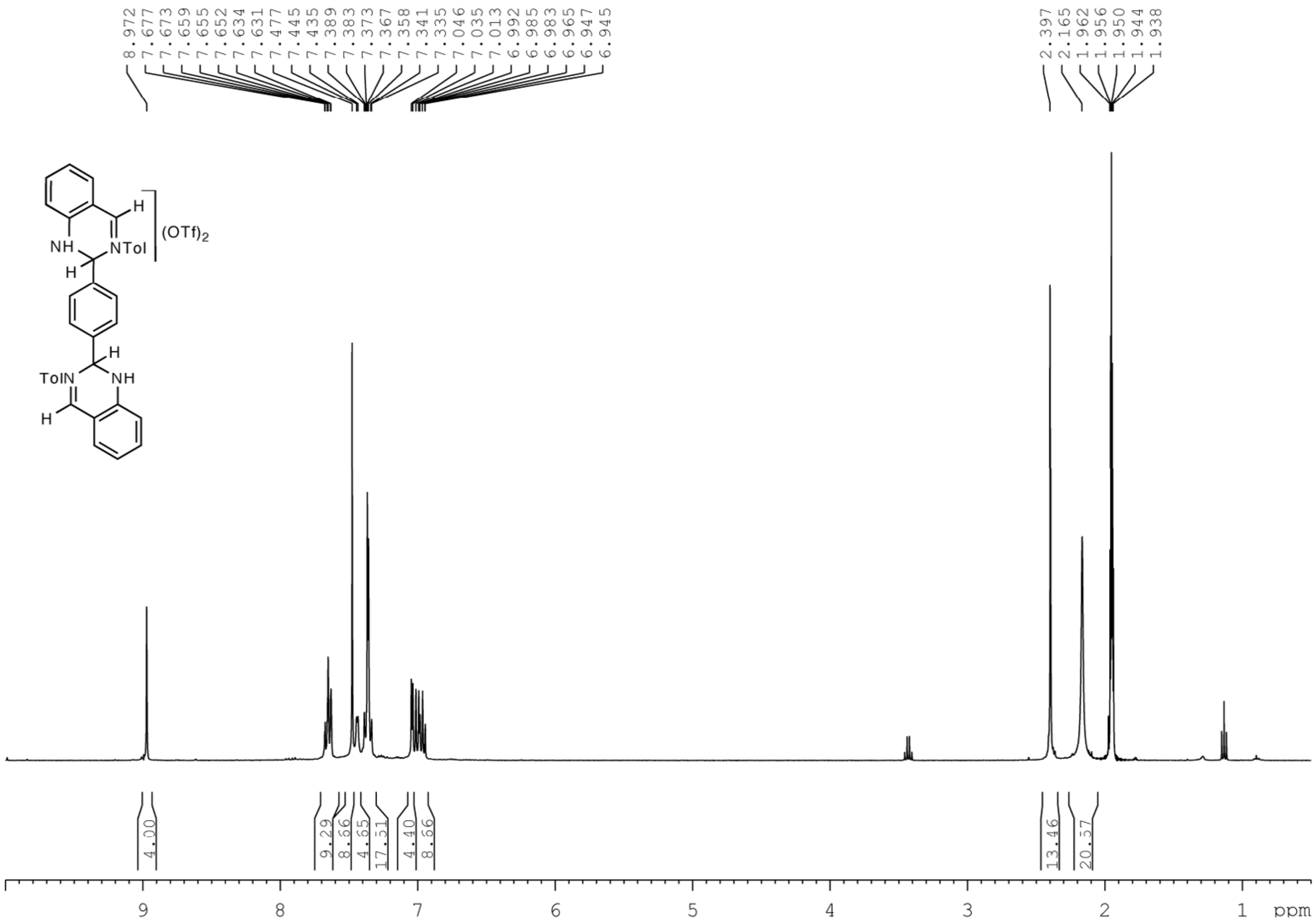
[1]H NMR spectra of **4** (300 MHz, $CDCl_3$, 25 ºC, TMS).



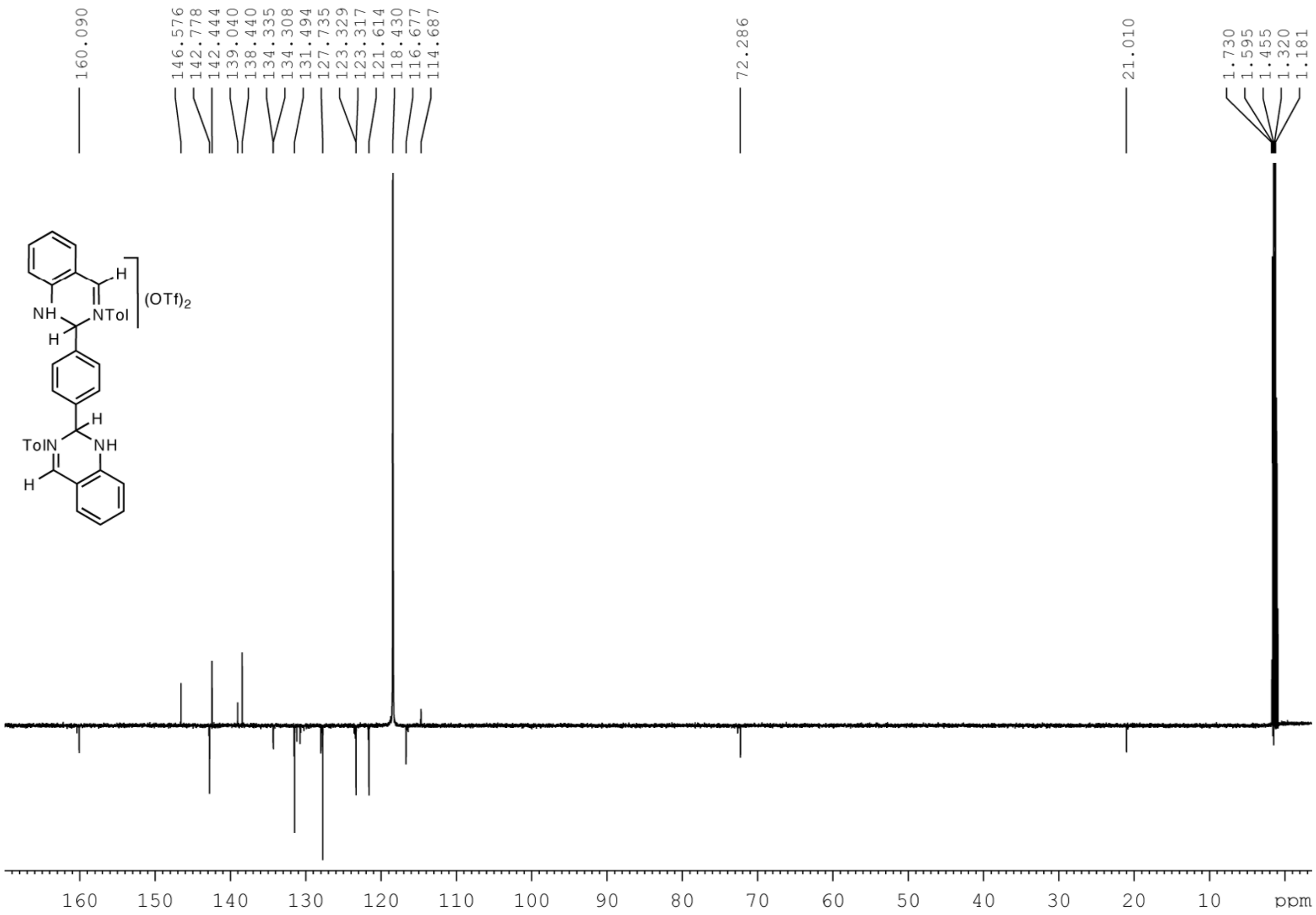
$^{13}C\{^{1}H\}$ NMR APT spectra of **4** (100.8 MHz, $CDCl_3$, 25 ºC, TMS).



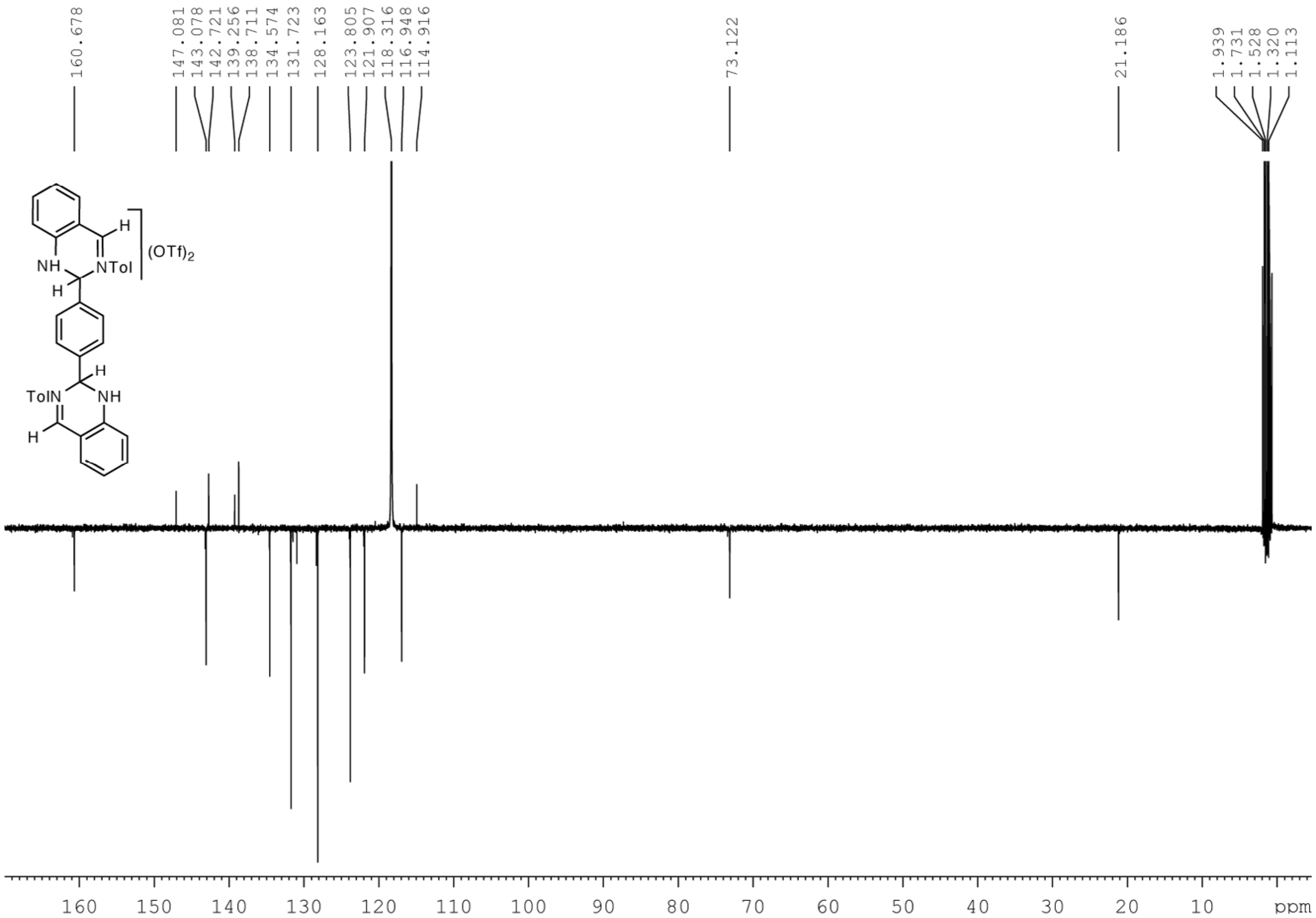
^{1}H NMR spectra of **5b** (400 MHz, CD_3CN, 25 ºC, TMS).



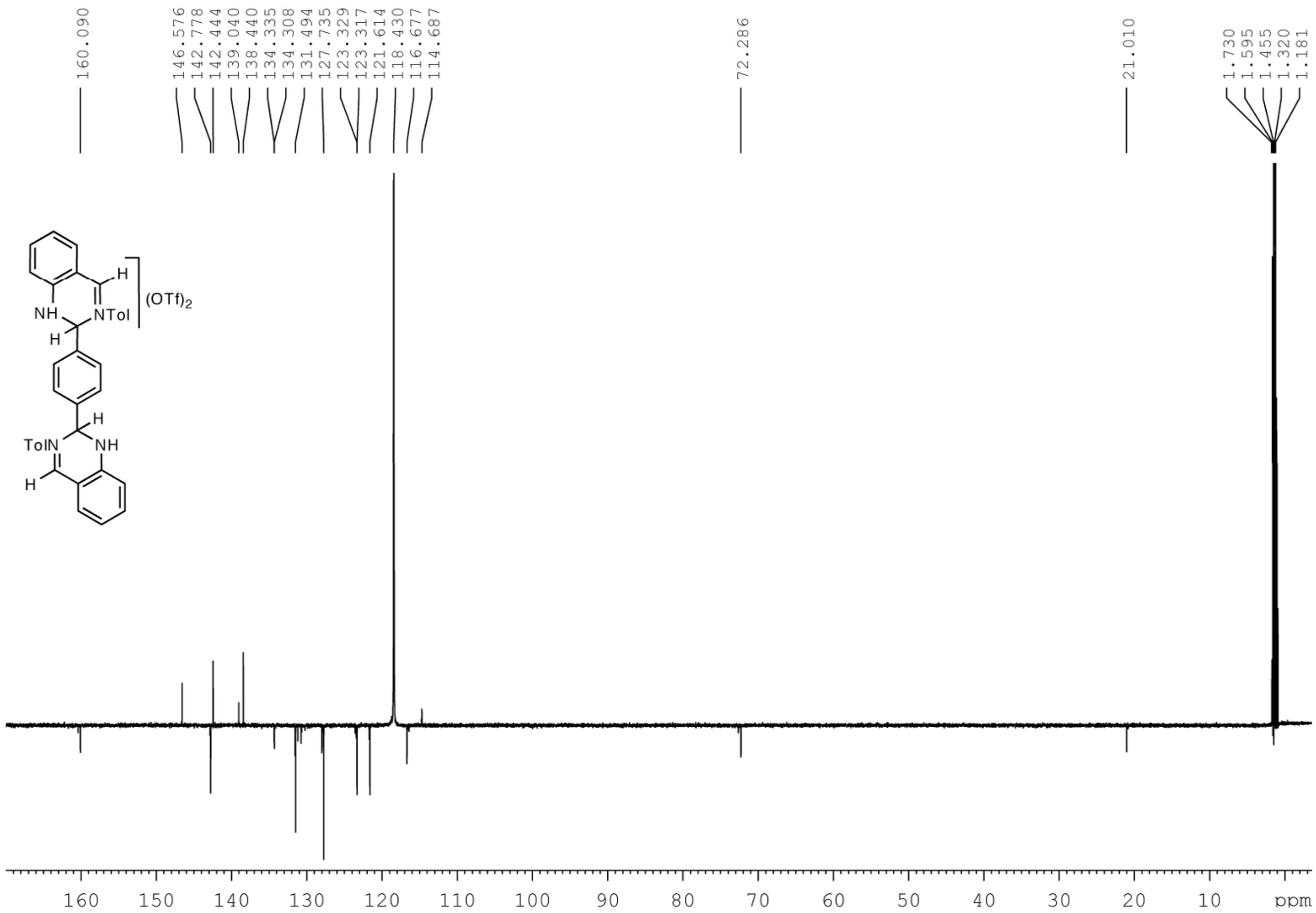
^{1}H NMR spectra of **5b** (600 MHz, CD_3CN, -10 ºC, TMS).



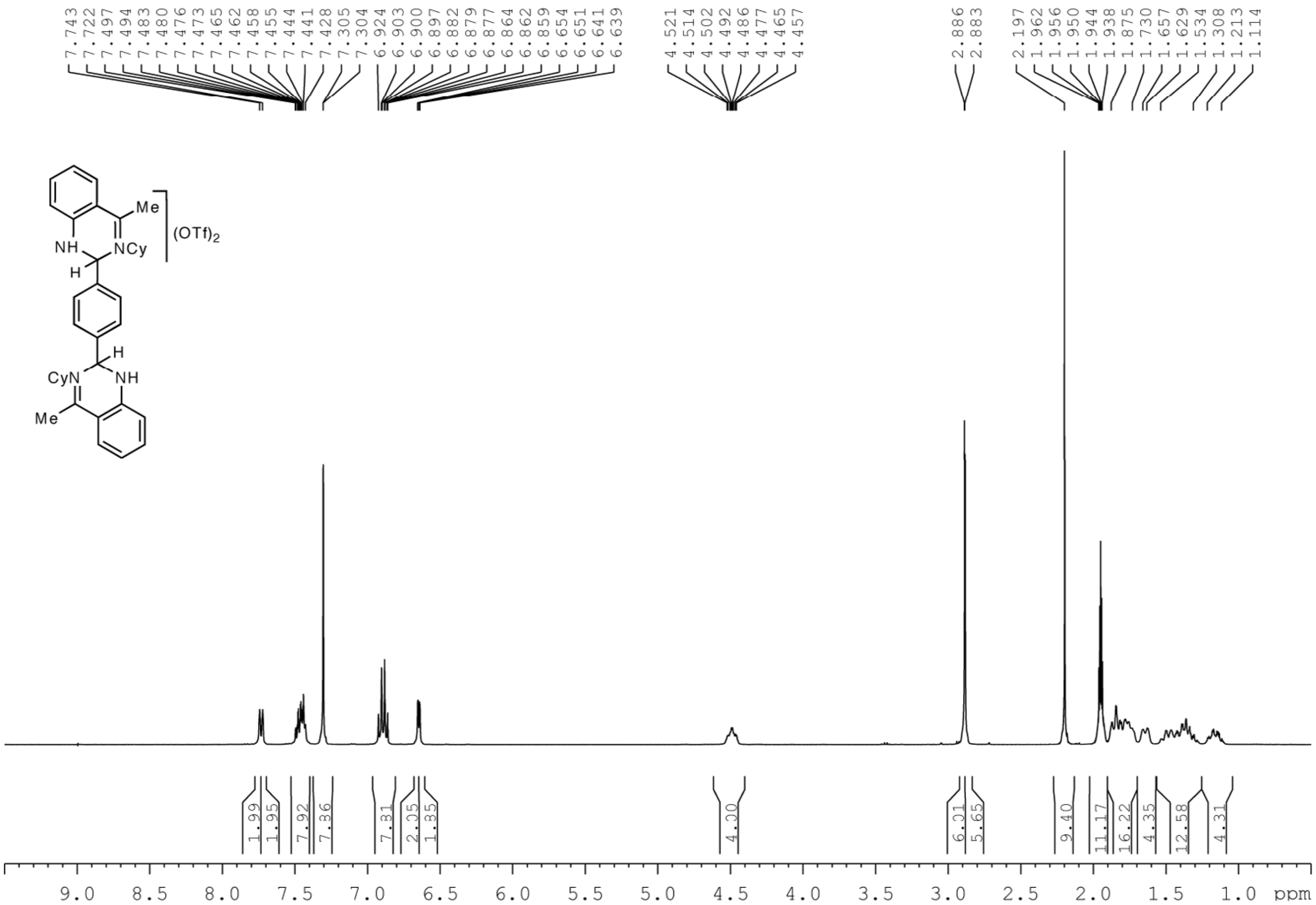
$^{13}C\{^{1}H\}$ NMR APT spectra of **5b** (100.8 MHz, CD_3CN, 25 ºC, TMS).



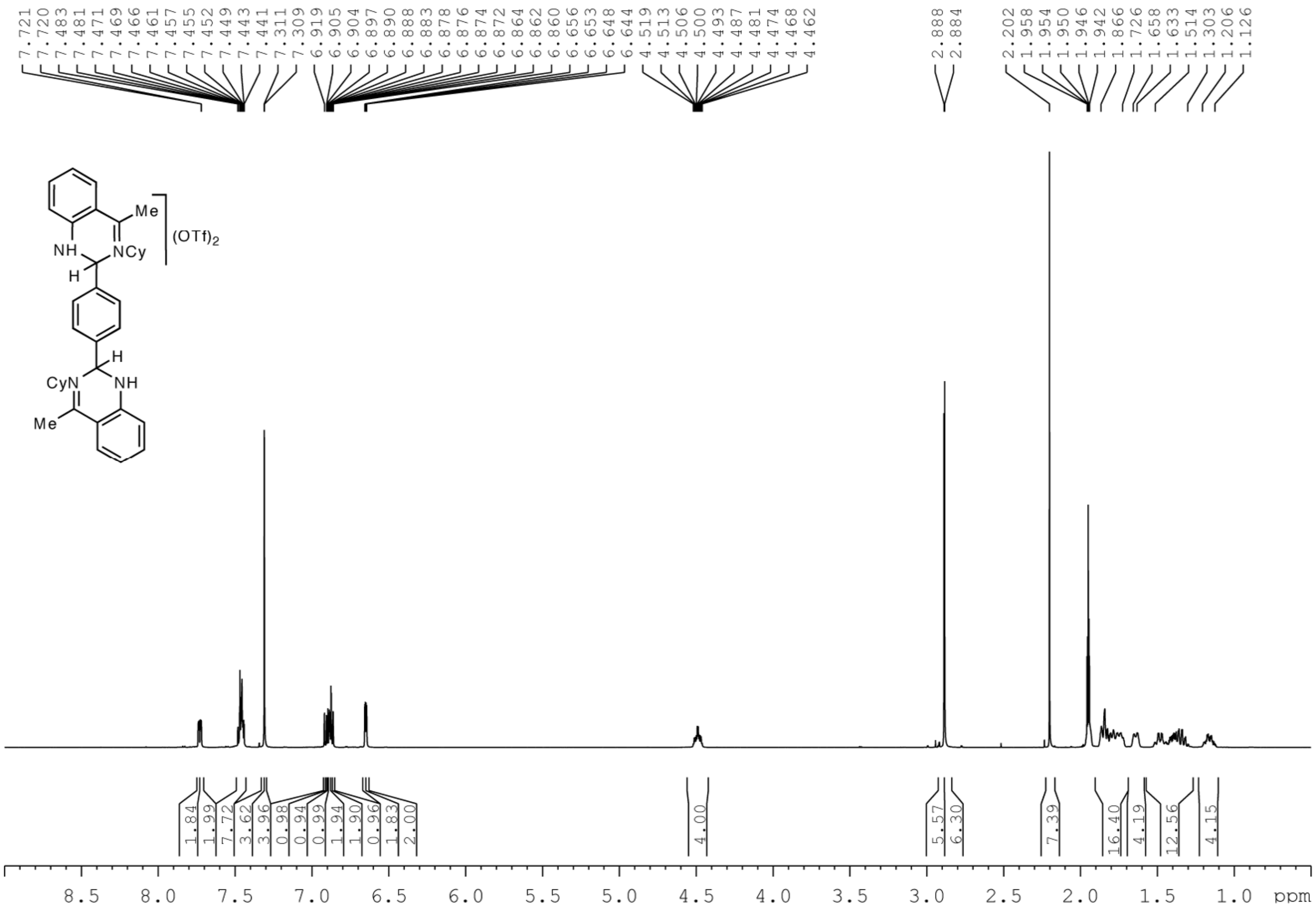
$^{13}C\{^{1}H\}$ NMR APT spectra of **5b** (150.9 MHz, CD_3CN, -10 ºC, TMS).



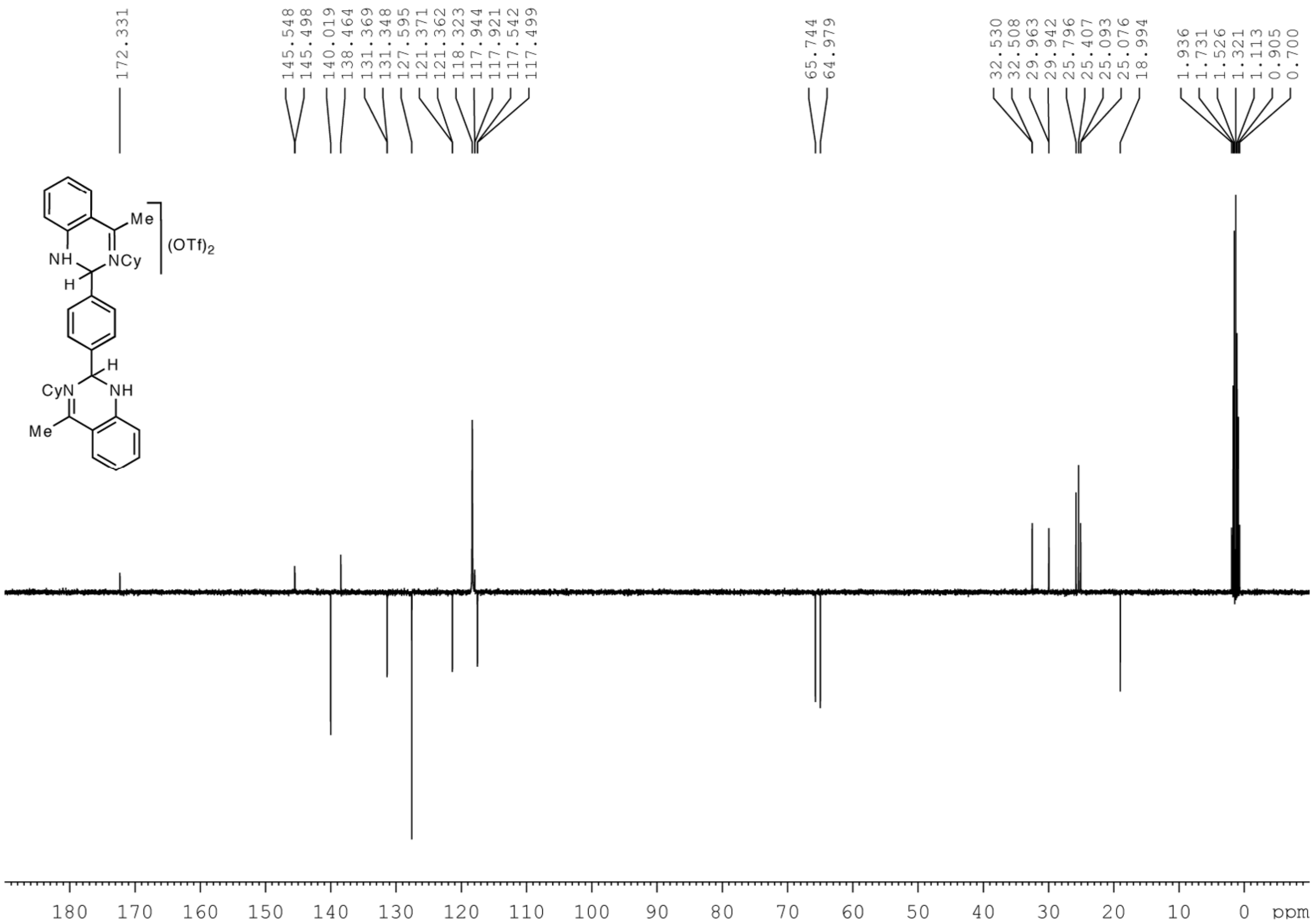
^{1}H NMR spectra of **5d**·0.5H_2O (400 MHz, CD_3CN, 25 ºC, TMS).



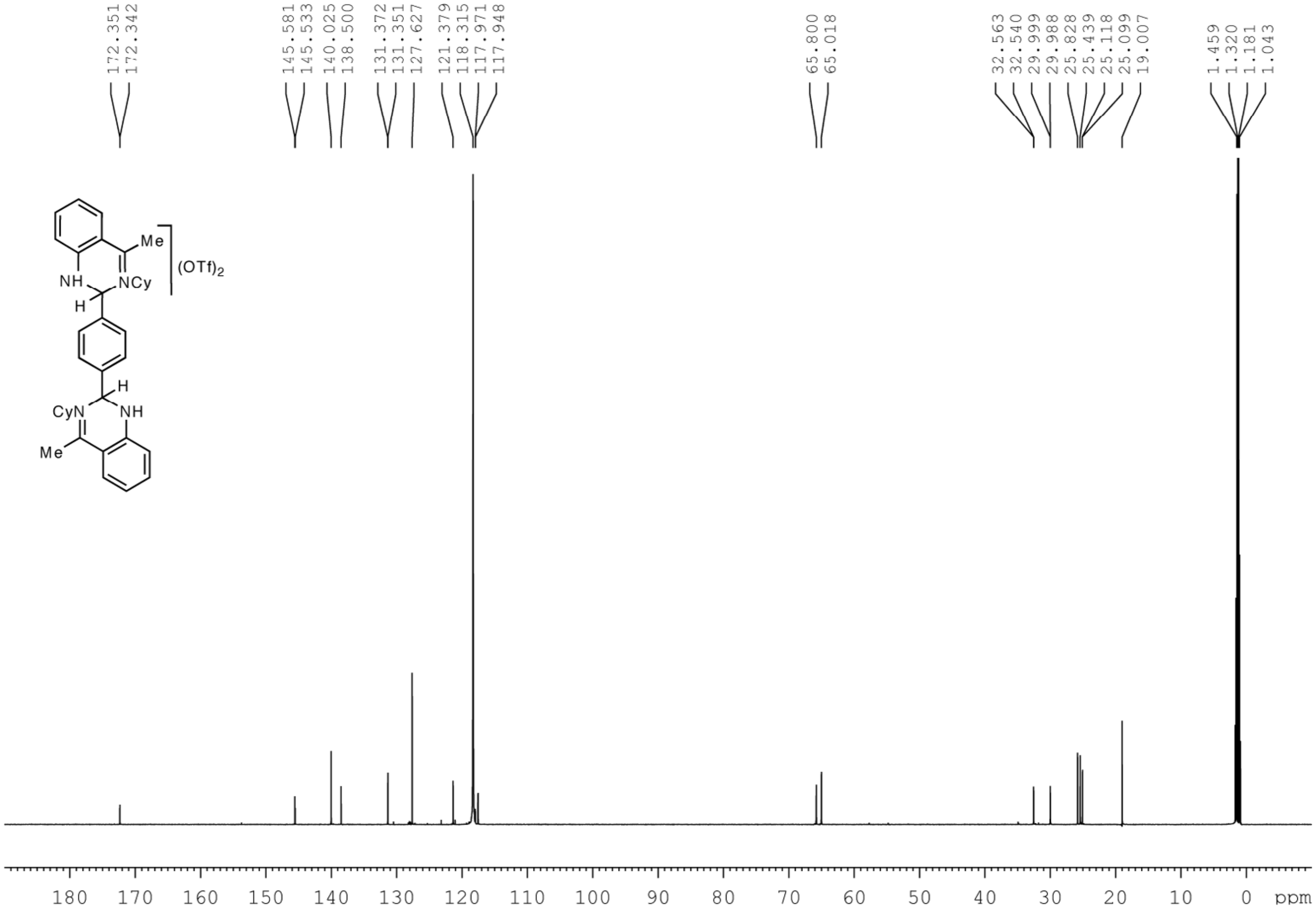
^{1}H NMR spectra of **5d**·0.5H_2O (600 MHz, CD_3CN, 25 ºC, TMS).



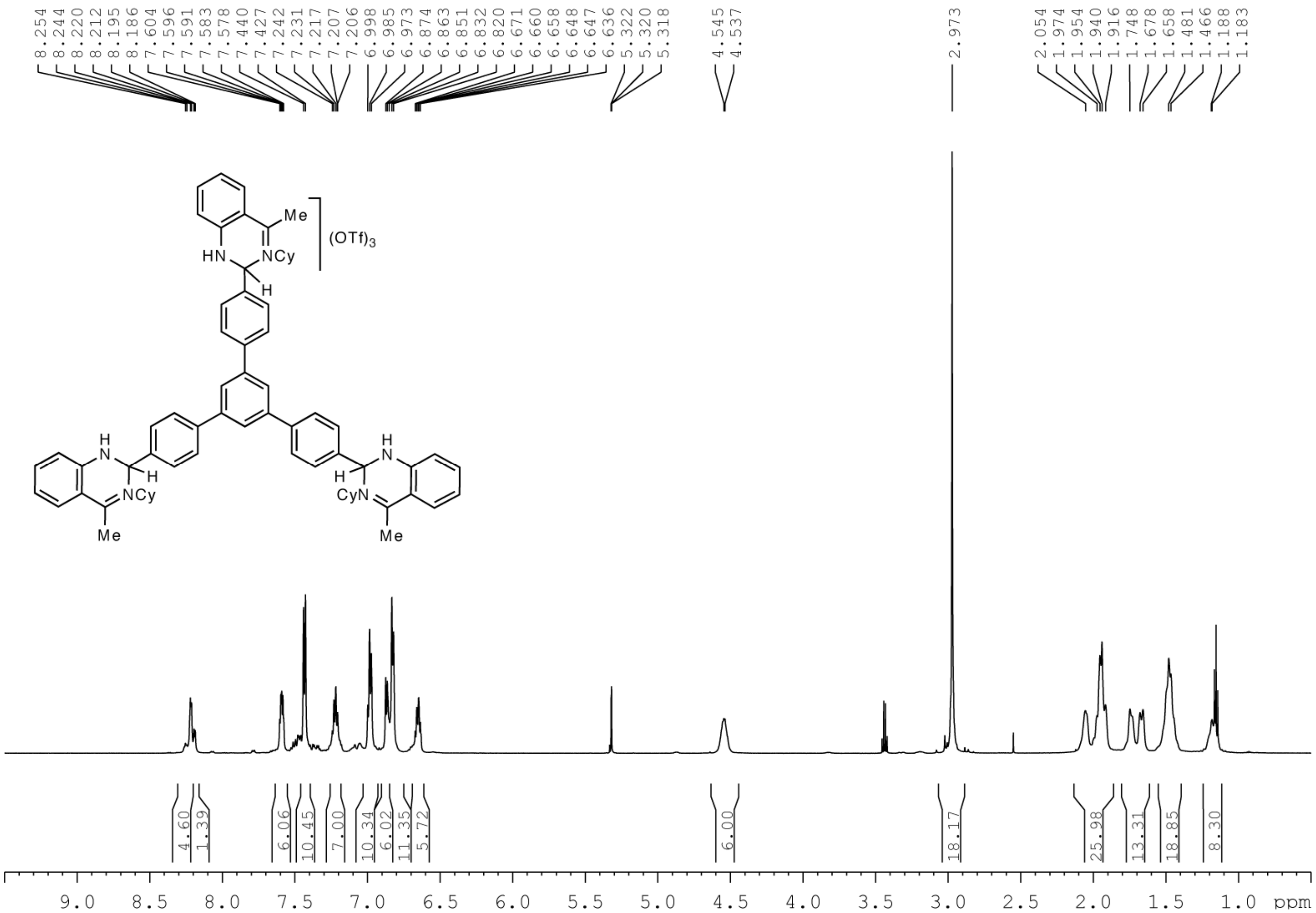
$^{13}C\{^{1}H\}$ NMR APT spectra of **5d** (100.8 MHz, CD_3CN, 25 ºC, TMS).



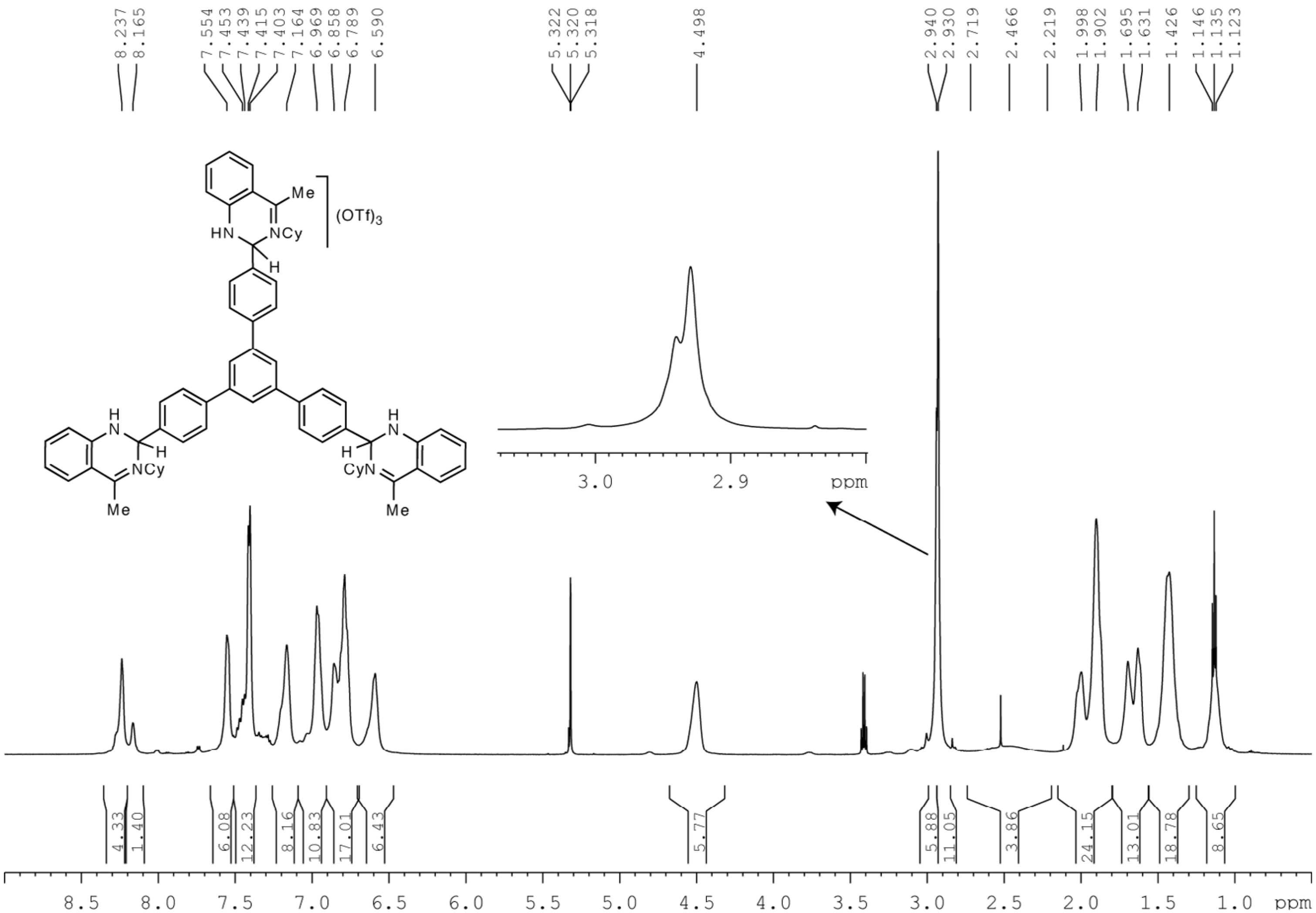
$^{13}C\{^{1}H\}$ NMR spectra of **5d** (150.9 MHz, CD_3CN, 25 ºC, TMS).



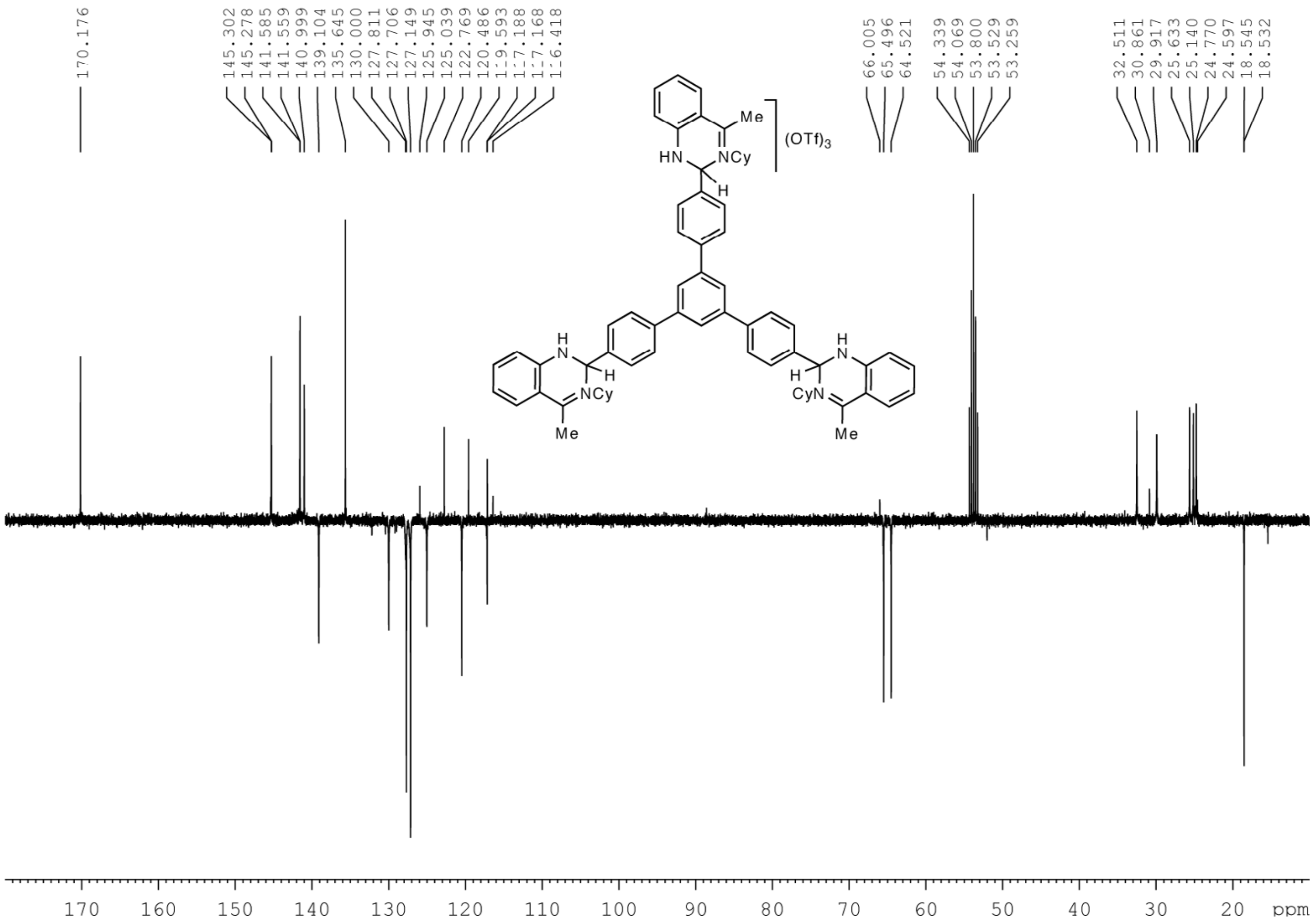
[1]H NMR spectra of **6d**·$2H_2O$ (600 MHz, CD_2Cl_2, 25 ºC, TMS).



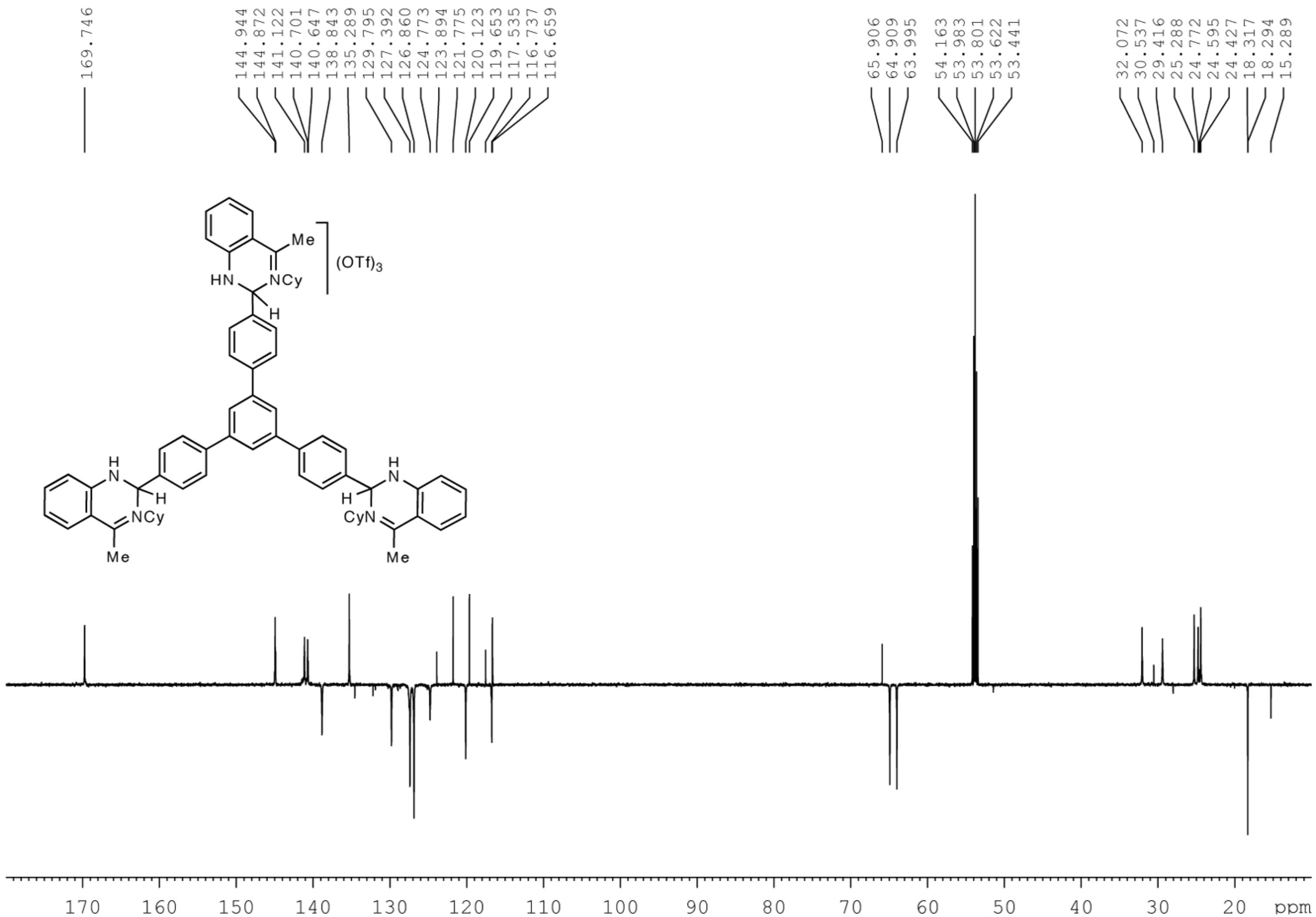
^{1}H NMR spectra of **6d**·$2H_2O$ (600 MHz, CD_2Cl_2, -10 ºC, TMS).



$^{13}C\{^{1}H\}$ NMR APT spectra of **6d** (100.8 MHz, CD_2Cl_2, 25 ºC, TMS).



$^{13}C\{^{1}H\}$ NMR APT spectra of **6d** (150.9 MHz, CD_2Cl_2, -10 ºC, TMS).



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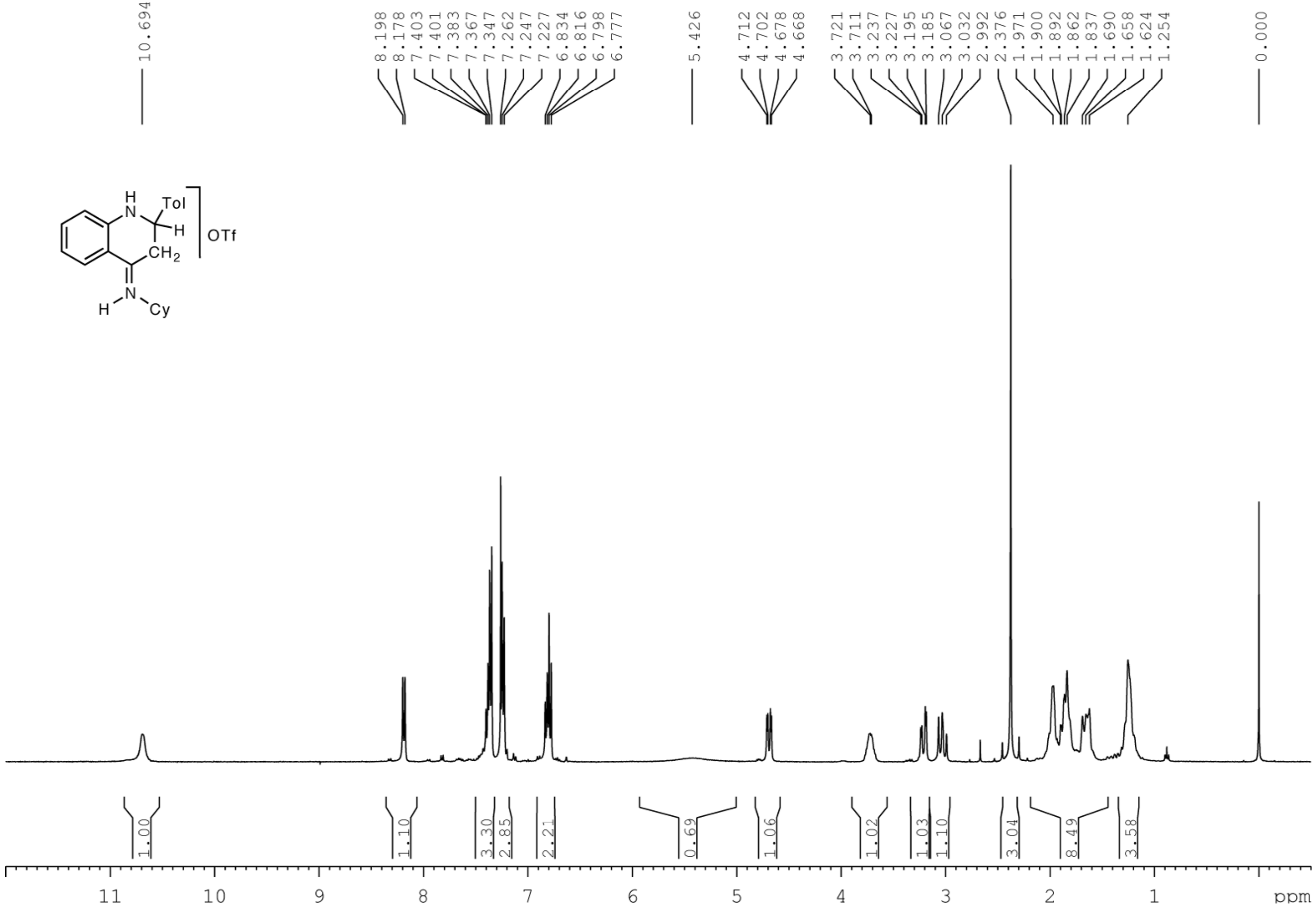
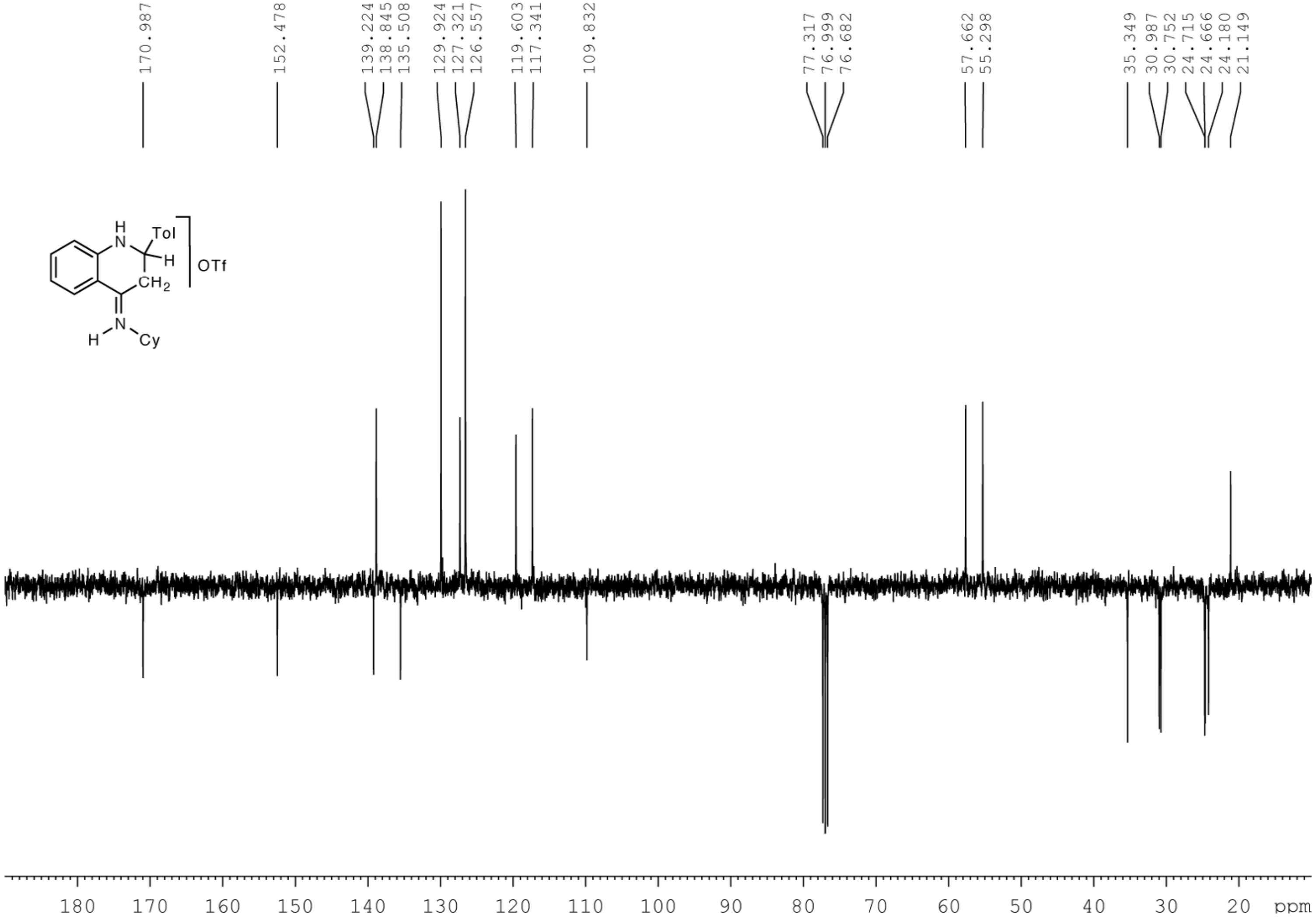
[1]H NMR spectra of ***E*-7d2**·0.2H_2O (400 MHz, $CDCl_3$, 25 ºC, TMS).



$^{13}C\{^{1}H\}$ NMR APT spectra of ***E*-7d2** (100.8 MHz, CD_2Cl_2, 25 ºC, TMS).



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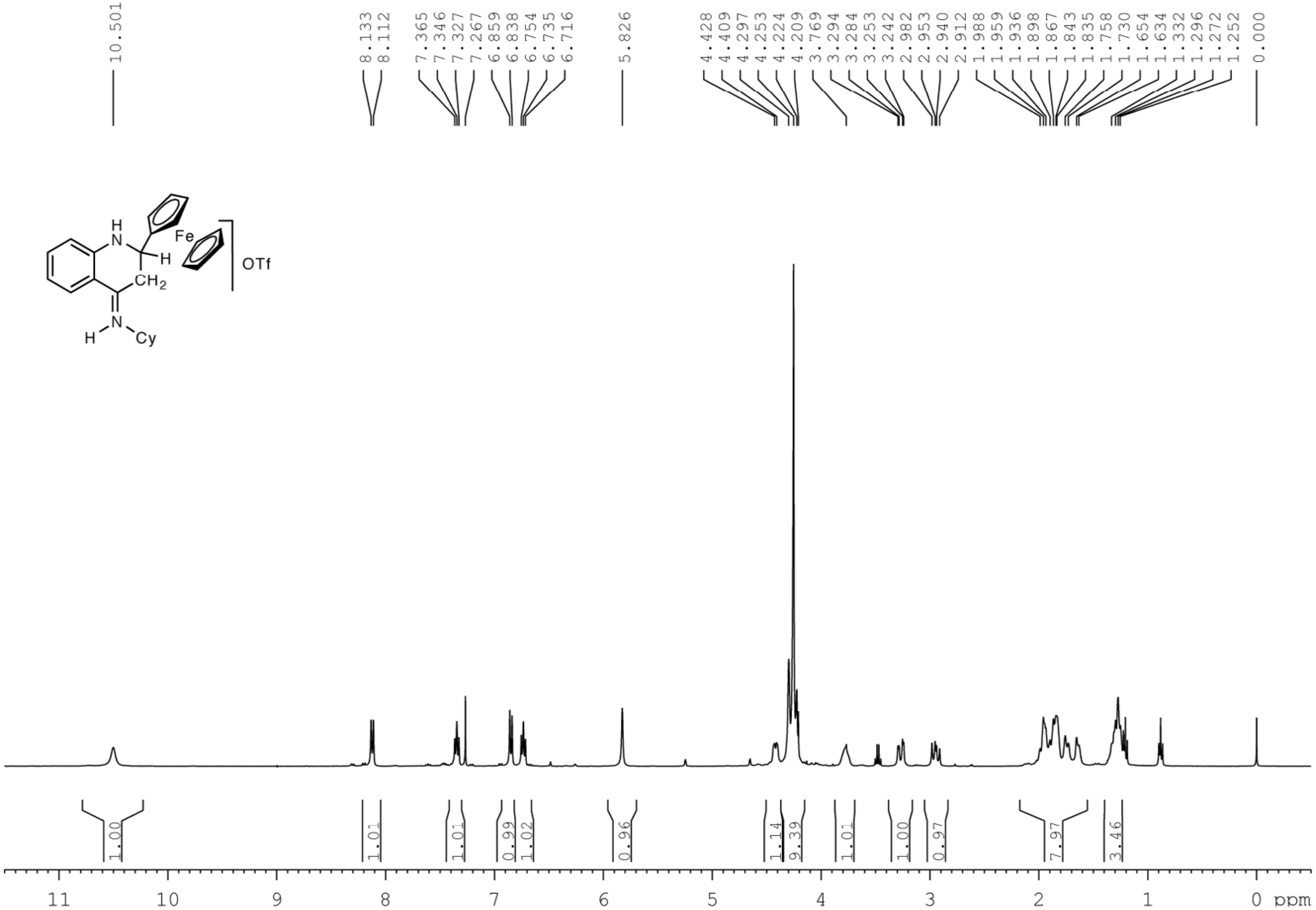
[1]H NMR spectra of ***E*-7d5**·0.5H_2O (400 MHz, $CDCl_3$, 25 ºC, TMS).



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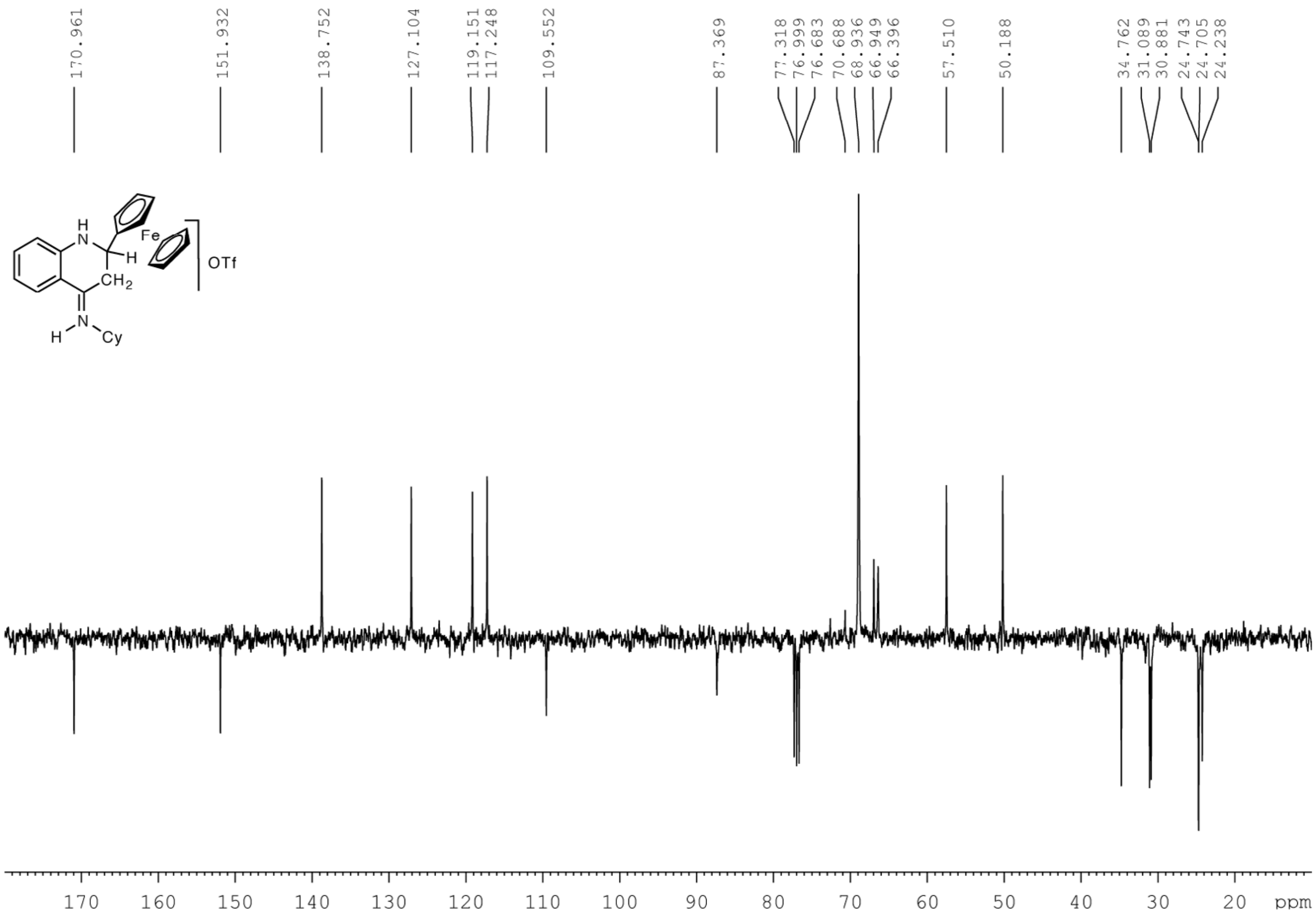
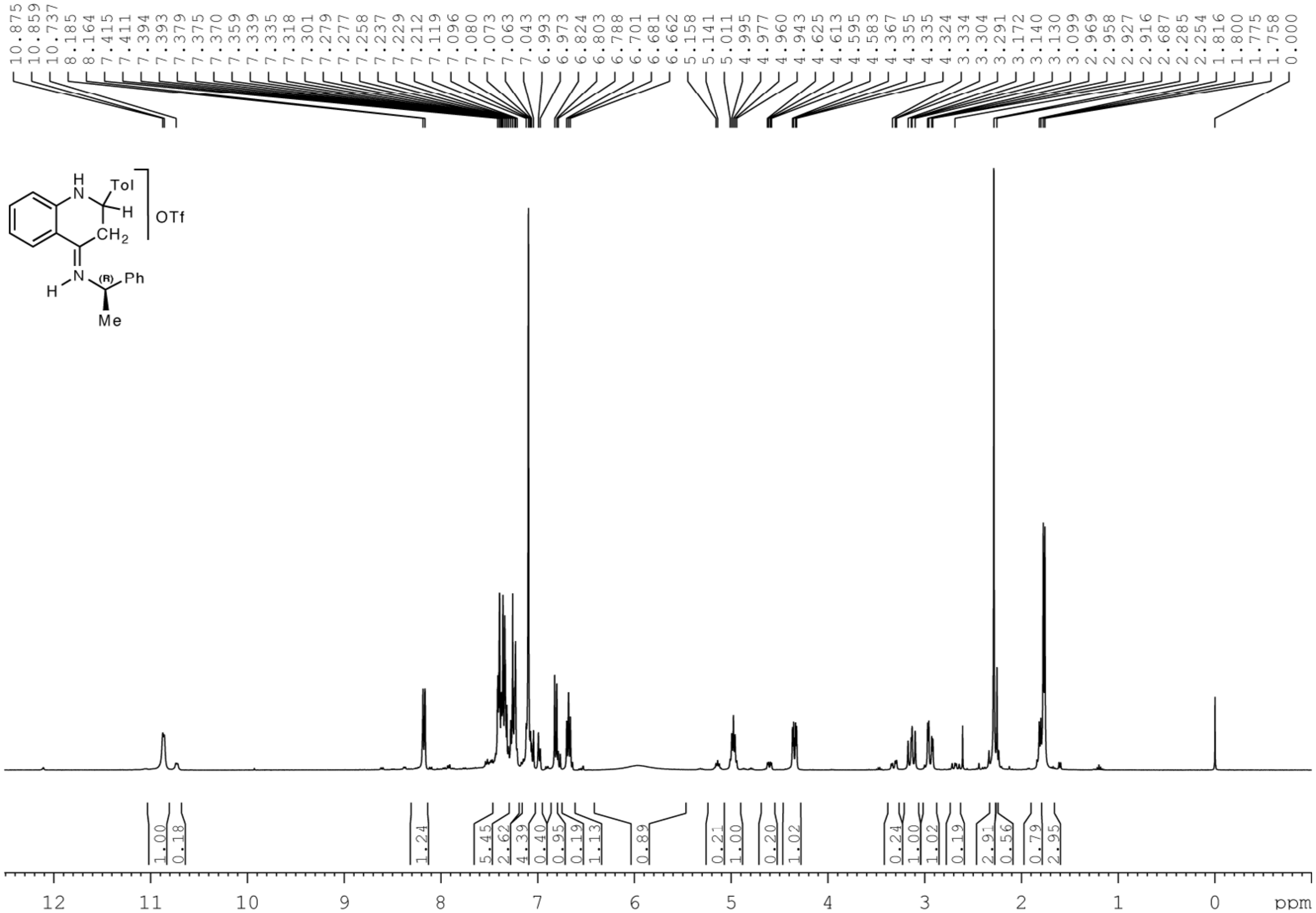
$^{13}C\{^1H\}$ NMR APT spectra of ***E*-7d5** (100.8 MHz, CD_2Cl_2, 25 ºC, TMS).

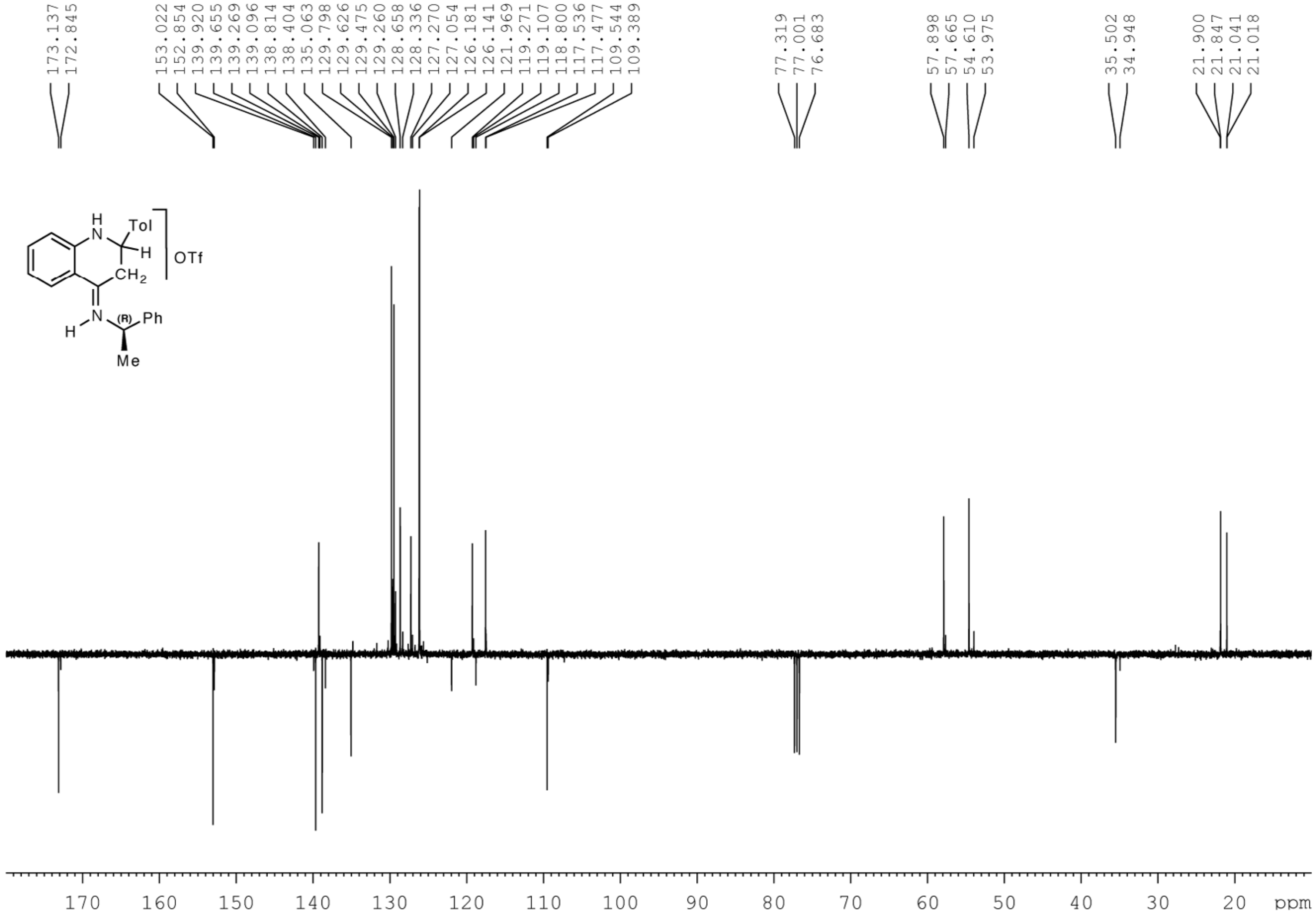


Supplementary Material (ESI) for Organic & Biomolecular Chemistry

[1]H NMR spectra of ***E*-7e2**·0.5H_2O (400 MHz, $CDCl_3$, 25 ºC, TMS).



$^{13}C\{^1H\}$ NMR APT spectra of ***E*-7e2** (100.8 MHz, CD_2Cl_2, 25 ºC, TMS).



Experimental details of the X-ray Crystallographic studies. Compounds **3a2**·$CHCl_3$, **3b3**, **3d4** and **7d2** were measured on a Bruker Smart APEX diffractometer. **6d**·$2CHCl_3$·CH_2Cl_2 was measured on a Oxford Diffraction Xcalibur Nova diffractometer. Data were collected using monochromated Mo-Kα radiation with the Bruker diffractometer and monochromated Cu-Kα with the Oxford diffractometer in ω scan mode. Absorption corrections were applied on the basis of multi-scans (Program SADABS for the compounds **3a2**·$CHCl_3$, **3b3**, **3d4** and **7d2** and CrysAlisPro for **6d**·$2CHCl_3$·CH_2Cl_2). All structures were refined anisotropically on F^2. The NH hydrogens were refined freely (with DFIX for compounds **3a2** and **7d2** and with SADI for compound **6d**), the methyl groups were refined using rigid groups (AFIX 137), and the other hydrogens were refined using a riding model. *Special features and exceptions*: Complex **3b3**: The triflate anion is disordered over two positions, 58:42%. Complexes **6d**·$2CHCl_3$·CH_2Cl_2: C(8), C(8') and C(8'') are chiral and, in the refined molecule, they all adopt the same S configuration. Refinement of the solvent sites proved difficult. One chloroform (at C82) is well-ordered. The molecules at C81 and C83 were interpreted as disordered dichloromethane and chloroform respectively. A system of restraints was used to improve stability of refinement, but the results are not entirely satisfactory (see e.g. U values). However, we prefer this model to the use of SQUEEZE. The triflates are all well-ordered. Complex **7d2**: The chloroform solvent is disordered over two positions, ca 65:35%.

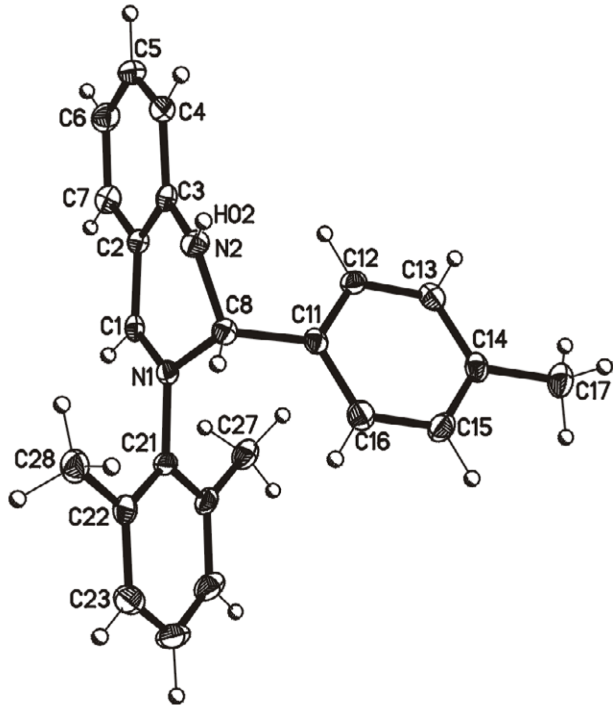


Table 1. Crystal data and structure refinement of **3a2**.

Identification code	ajf49rbs	
Empirical formula	C25 H24 Cl3 F3 N2 O3 S	
Formula weight	595.87	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2(1)/c	
Unit cell dimensions	a = 10.8646(11) Å	α= 90°
	b = 12.0601(11) Å	β= 94.238(2)°
	c = 20.4915(18) Å	γ = 90°
Volume	2677.6(4) $Å^3$	
Z	4	
Density (calculated)	1.478 Mg/m^3	
Absorption coefficient	0.472 mm^{-1}	
F(000)	1224	
Crystal size	0.15 x 0.12 x 0.06 mm^3	
Theta range for data collection	1.88 to 28.73°	
Index ranges	-14<=h<=14, -15<=k<=15, -27<=l<=27	
Reflections collected	32587	
Independent reflections	6510 [R(int) = 0.0460]	
Completeness to theta = 26.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9722 and 0.8680	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6510 / 0 / 341	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.1024	
R indices (all data)	R1 = 0.0666, wR2 = 0.1093	
Largest diff. peak and hole	0.513 and -0.298 e.$Å^{-3}$	

3a2. Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	-477.4(18)	3817.5(16)	2185.0(9)	15.4(4)
N(1)	599.2(15)	4242.3(13)	2087.6(8)	14.8(3)
C(2)	-1286.7(18)	4297.2(16)	2616.2(9)	16.1(4)
C(3)	-805.9(18)	5154.3(17)	3028.7(9)	16.3(4)
C(4)	-1528(2)	5566.5(18)	3512.8(10)	20.7(4)
C(5)	-2684(2)	5141.1(19)	3566.4(11)	25.0(5)
C(6)	-3172(2)	4293.5(19)	3160.5(11)	24.9(5)
C(7)	-2476.1(19)	3864.6(18)	2689.0(10)	20.3(4)
C(8)	962.1(18)	5365.7(16)	2362.5(9)	15.5(4)
N(2)	363.0(17)	5512.3(15)	2960.8(8)	17.8(4)
C(11)	688.7(18)	6239.8(16)	1842.1(9)	15.6(4)
C(12)	-433.2(19)	6795.8(17)	1766.1(10)	17.4(4)
C(13)	-644(2)	7564.2(17)	1262.4(10)	19.4(4)
C(14)	253(2)	7798.0(17)	833.4(10)	18.8(4)
C(15)	1372(2)	7239.2(18)	915.8(10)	21.6(4)
C(16)	1590.7(19)	6471.2(17)	1412.5(10)	20.5(4)
C(17)	32(2)	8650.1(18)	299.4(11)	25.3(5)
C(21)	1420.1(19)	3765.5(16)	1635.4(10)	16.7(4)
C(22)	2586(2)	3409.8(17)	1876.4(11)	20.5(4)
C(23)	3385(2)	3028.4(18)	1425.8(12)	25.8(5)
C(24)	3034(2)	3023.8(19)	765.7(12)	29.7(5)
C(25)	1863(2)	3370.1(18)	538.6(11)	25.9(5)
C(26)	1018(2)	3747.5(17)	967.2(10)	19.6(4)
C(27)	-242(2)	4137.7(18)	709.2(10)	23.0(5)
C(28)	3007(2)	3426.2(19)	2595.1(11)	23.9(5)
C(98)	5353(2)	5401(2)	1099.7(11)	24.2(5)
Cl(1)	6916.8(5)	5738.6(6)	1056.6(3)	39.3(2)
Cl(2)	4886.1(5)	5724.2(5)	1885.4(3)	28.3(1)
Cl(3)	4436.9(6)	6115.5(6)	492.0(3)	34.9(2)
C(99)	6413(2)	762(2)	618.4(12)	32.6(6)
F(1)	5203.2(15)	609.8(17)	601.4(8)	60.7(6)
F(2)	6956.3(19)	-195.4(13)	781.0(10)	61.8(5)
F(3)	6703.0(15)	1013.6(15)	18.0(7)	48.9(5)
S(1)	6892.4(5)	1840.7(4)	1199.9(2)	19.0(1)
O(1)	6528.4(16)	1417.3(15)	1812.1(8)	31.4(4)
O(2)	8219.1(13)	1887.0(13)	1157.2(8)	24.5(3)
O(3)	6250.1(15)	2804.4(14)	951.7(8)	33.2(4)

3a2. Table 3. Bond lengths [Å] and angles [°].

(1)-N(1)	1.306(3)	C(11)-C(12)	1.390(3)
C(1)-C(2)	1.416(3)	C(11)-C(16)	1.393(3)
N(1)-C(21)	1.451(2)	C(12)-C(13)	1.393(3)
N(1)-C(8)	1.509(2)	C(13)-C(14)	1.388(3)
C(2)-C(3)	1.411(3)	C(14)-C(15)	1.390(3)
C(2)-C(7)	1.412(3)	C(14)-C(17)	1.507(3)
C(3)-N(2)	1.358(3)	C(15)-C(16)	1.384(3)
C(3)-C(4)	1.400(3)	C(21)-C(22)	1.393(3)
C(4)-C(5)	1.369(3)	C(21)-C(26)	1.406(3)
C(5)-C(6)	1.398(3)	C(22)-C(23)	1.391(3)
C(6)-C(7)	1.371(3)	C(22)-C(28)	1.510(3)
C(8)-N(2)	1.441(3)	C(23)-C(24)	1.378(3)
C(8)-C(11)	1.513(3)	C(24)-C(25)	1.386(3)

C(25)-C(26)	1.393(3)	C(14)-C(13)-C(12)	121.30(19)
C(26)-C(27)	1.506(3)	C(13)-C(14)-C(15)	118.24(19)
C(98)-Cl(1)	1.756(2)	C(13)-C(14)-C(17)	121.13(19)
C(98)-Cl(3)	1.761(2)	C(15)-C(14)-C(17)	120.62(19)
C(98)-Cl(2)	1.767(2)	C(16)-C(15)-C(14)	121.01(19)
C(99)-F(1)	1.325(3)	C(15)-C(16)-C(11)	120.55(19)
C(99)-F(3)	1.327(3)	C(22)-C(21)-C(26)	123.32(19)
C(99)-F(2)	1.328(3)	C(22)-C(21)-N(1)	118.78(18)
C(99)-S(1)	1.814(2)	C(26)-C(21)-N(1)	117.79(18)
S(1)-O(3)	1.4297(17)	C(23)-C(22)-C(21)	117.5(2)
S(1)-O(1)	1.4368(16)	C(23)-C(22)-C(28)	119.5(2)
S(1)-O(2)	1.4516(15)	C(21)-C(22)-C(28)	122.93(19)
N(1)-C(1)-C(2)	122.67(18)	C(24)-C(23)-C(22)	120.8(2)
C(1)-N(1)-C(21)	122.80(17)	C(23)-C(24)-C(25)	120.6(2)
C(1)-N(1)-C(8)	120.51(16)	C(24)-C(25)-C(26)	121.2(2)
C(21)-N(1)-C(8)	115.99(15)	C(25)-C(26)-C(21)	116.5(2)
C(3)-C(2)-C(7)	120.58(18)	C(25)-C(26)-C(27)	120.3(2)
C(3)-C(2)-C(1)	116.99(18)	C(21)-C(26)-C(27)	123.09(18)
C(7)-C(2)-C(1)	122.05(19)	Cl(1)-C(98)-Cl(3)	110.45(12)
N(2)-C(3)-C(4)	122.44(19)	Cl(1)-C(98)-Cl(2)	109.79(12)
N(2)-C(3)-C(2)	118.63(18)	Cl(3)-C(98)-Cl(2)	110.52(12)
C(4)-C(3)-C(2)	118.85(19)	F(1)-C(99)-F(3)	108.1(2)
C(5)-C(4)-C(3)	119.3(2)	F(1)-C(99)-F(2)	107.9(2)
C(4)-C(5)-C(6)	122.4(2)	F(3)-C(99)-F(2)	107.4(2)
C(7)-C(6)-C(5)	119.4(2)	F(1)-C(99)-S(1)	110.66(16)
C(6)-C(7)-C(2)	119.4(2)	F(3)-C(99)-S(1)	111.64(17)
N(2)-C(8)-N(1)	107.81(15)	F(2)-C(99)-S(1)	110.98(19)
N(2)-C(8)-C(11)	115.89(17)	O(3)-S(1)-O(1)	116.16(10)
N(1)-C(8)-C(11)	109.28(15)	O(3)-S(1)-O(2)	114.08(10)
C(3)-N(2)-C(8)	122.20(17)	O(1)-S(1)-O(2)	113.89(10)
C(12)-C(11)-C(16)	118.99(18)	O(3)-S(1)-C(99)	103.91(12)
C(12)-C(11)-C(8)	122.68(18)	O(1)-S(1)-C(99)	103.56(11)
C(16)-C(11)-C(8)	118.31(18)	O(2)-S(1)-C(99)	103.07(10)
C(11)-C(12)-C(13)	119.91(19)		

3a2. Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	19.1(10)	12.3(9)	14.3(9)	3.4(7)	-1.2(7)	0.2(8)
N(1)	17.7(8)	12.0(8)	14.8(8)	0.5(6)	1.8(6)	-0.1(7)
C(2)	19.0(10)	15.8(10)	13.7(9)	2.9(7)	2.0(7)	2.9(8)
C(3)	19.7(10)	16.4(10)	12.7(9)	4.8(7)	0.0(8)	2.2(8)
C(4)	28.6(12)	17.4(10)	16.6(10)	0.9(8)	4.1(8)	3.6(9)
C(5)	29.6(12)	24.8(11)	21.8(11)	3.6(9)	11.0(9)	8.8(9)
C(6)	19.0(10)	28.3(12)	28.1(11)	6.5(9)	6.5(9)	2.3(9)
C(7)	20.4(10)	20.9(10)	19.4(10)	1.5(8)	0.7(8)	-1.9(9)
C(8)	16.3(9)	14.3(9)	15.9(9)	-1.2(7)	0.2(7)	-2.2(8)
N(2)	22.3(9)	18.1(9)	12.9(8)	-3.0(7)	0.5(7)	-2.9(7)
C(11)	20.5(10)	11.2(9)	14.9(9)	-2.6(7)	0.4(8)	-1.7(8)
C(12)	19.8(10)	17.3(10)	15.5(9)	-2.1(8)	4.2(8)	-1.1(8)
C(13)	21.7(10)	16.9(10)	19.3(10)	-0.9(8)	-0.9(8)	3.0(8)
C(14)	27.1(11)	12.7(9)	16.2(9)	-1.1(8)	-1.4(8)	-2.7(8)
C(15)	22.4(11)	21.6(11)	21.5(10)	2.4(8)	5.7(8)	-4.0(9)
C(16)	17.1(10)	18.4(10)	26.1(11)	1.6(8)	1.9(8)	-0.7(8)
C(17)	33.3(12)	21.6(11)	20.7(11)	4.5(9)	-1.2(9)	-2.6(9)
C(21)	19.8(10)	11.9(9)	19.6(10)	-0.8(8)	8.3(8)	-2.1(8)
C(22)	22.5(11)	12.9(10)	26.9(11)	3.1(8)	6.7(9)	-3.2(8)
C(23)	20.4(11)	18.5(11)	39.6(13)	0.3(9)	10.0(10)	-1.1(9)

C(24)	34.3(13)	22.3(12)	35.1(13)	-6.0(10)	21.3(11)	-4.9(10)
C(25)	36.1(13)	22.1(11)	20.8(11)	-4.7(9)	11.6(9)	-8.4(10)
C(26)	27.2(11)	14.5(10)	17.8(10)	0.8(8)	6.7(8)	-5.4(8)
C(27)	29.3(12)	23.5(11)	16.1(10)	0.7(8)	1.5(8)	-5.8(9)
C(28)	19.8(10)	24.5(11)	27.5(12)	7.3(9)	1.7(9)	2.9(9)
C(98)	19.0(11)	28.5(12)	25.1(11)	2.7(9)	2.1(9)	-1.1(9)
Cl(1)	19.6(3)	56.3(4)	42.5(4)	5.5(3)	5.7(2)	-5.2(3)
Cl(2)	25.6(3)	36.3(3)	23.0(3)	3.0(2)	2.0(2)	-4.3(2)
Cl(3)	32.0(3)	47.7(4)	24.8(3)	5.3(3)	0.8(2)	13.6(3)
C(99)	29.6(13)	38.5(15)	31.2(13)	-15.5(11)	12.2(10)	-14.2(11)
F(1)	33.2(9)	101.0(15)	50.0(10)	-40.5(10)	16.9(7)	-36.5(9)
F(2)	84.2(14)	25.4(9)	78.5(14)	-17.8(9)	25.1(11)	-6.5(9)
F(3)	45.4(9)	78.6(12)	24.2(8)	-21.5(8)	12.4(7)	-22.7(9)
S(1)	19.2(3)	20.0(3)	17.5(2)	-1.6(2)	-0.2(2)	0.2(2)
O(1)	36.5(10)	39.6(10)	18.4(8)	0.7(7)	4.2(7)	-4.6(8)
O(2)	19.0(8)	24.3(8)	29.4(8)	5.8(6)	-3.4(6)	-1.6(6)
O(3)	30.1(9)	30.8(9)	38.5(10)	4.3(8)	0.6(7)	11.5(7)

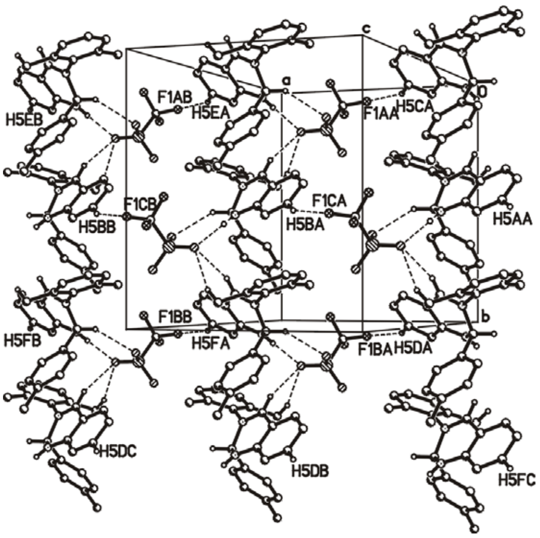
3a2. Table 5.
Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}).

	x	y	z	U(eq)
H(1)	-728	3160	1957	18
H(4)	-1218	6135	3801	25
H(5)	-3173	5433	3892	30
H(6)	-3978	4017	3211	30
H(7)	-2792	3281	2414	24
H(8)	1874	5360	2475	19
H(02)	730(20)	5900(20)	3234(12)	17(6)
H(12)	-1056	6652	2057	21
H(13)	-1416	7935	1212	23
H(15)	1997	7387	627	26
H(16)	2362	6099	1461	25
H(17A)	430	9349	438	38
H(17B)	-857	8770	213	38
H(17C)	381	8385	-100	38
H(23)	4182	2768	1575	31
H(24)	3599	2781	464	36
H(25)	1633	3350	82	31
H(27A)	-290	4142	230	34
H(27B)	-385	4889	870	34
H(27C)	-871	3636	860	34
H(28A)	3550	4065	2687	36
H(28B)	3457	2741	2710	36
H(28C)	2287	3484	2854	36
H(98)	5248	4586	1025	29

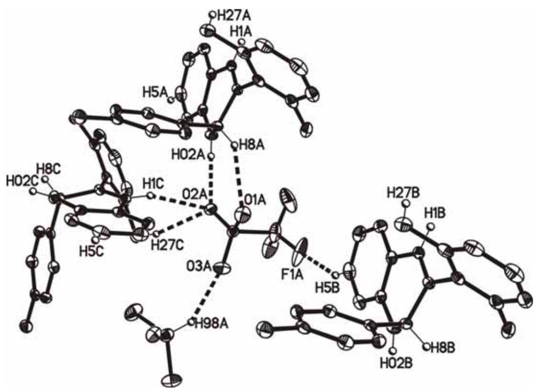
3a2. Table 6. Hydrogen bonds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(98)-H(98)...O(3)	1.00	2.42	3.300(3)	146.7
N(2)-H(02)...O(2)#1	0.81(2)	2.01(3)	2.824(2)	174(2)
C(8)-H(8)...O(1)#1	1.00	2.53	3.350(3)	139.0
C(1)-H(1)...O(2)#2	0.95	2.46	3.379(3)	161.6
C(27)-H(27C)...O(2)#2	0.98	2.43	3.351(3)	157.3
C(5)-H(5)...F(1)#3	0.95	2.52	3.378(3)	150.9

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+1/2 #2 x-1,y,z #3 -x,y+1/2,-z+1/2



View of the hydrogen bond interactions in **3a2**.



The hydrogen bond environment of the anions in **3a2**.

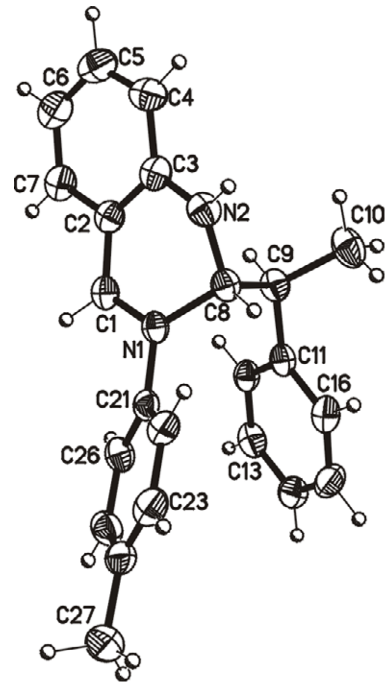


Table 1. Crystal data and structure refinement of **3b3**.

Identification code	ajf53bsi	
Empirical formula	C24 H23 F3 N2 O3 S	
Formula weight	476.50	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P bca	
Unit cell dimensions	a = 17.6246(14) Å	α= 90°
	b = 12.9407(11) Å	β= 90°
	c = 20.1134(17) Å	γ = 90°
Volume	4587.4(7) $Å^3$	
Z	8	
Density (calculated)	1.380 Mg/m^3	
Absorption coefficient	0.194 mm^{-1}	
F(000)	1984	
Crystal size	0.12 x 0.12 x 0.12 mm^3	
Theta range for data collection	2.03 to 28.81°	
Index ranges	-23<=h<=22, -17<=k<=17, -25<=l<=27	
Reflections collected	54529	
Independent reflections	5745 [R(int) = 0.0599]	
Completeness to theta = 26.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9771 and 0.8769	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5745 / 46 / 297	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0837, wR2 = 0.2030	
R indices (all data)	R1 = 0.1136, wR2 = 0.2232	
Largest diff. peak and hole	1.303 and -0.985 e.$Å^{-3}$	

3b3. Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	4622.6(19)	4457(2)	3054.3(16)	29.1(7)
N(1)	4434.5(14)	4278.7(19)	2435.1(13)	26.8(5)
C(2)	4147.0(19)	4152(2)	3587.0(16)	30.9(7)
C(3)	3382(2)	3930(2)	3429.1(17)	32.6(7)
C(4)	2847(2)	3871(3)	3949.3(19)	40.5(8)
C(5)	3085(2)	4011(3)	4593(2)	46.0(9)
C(6)	3845(3)	4202(3)	4755.1(18)	44.6(9)
C(7)	4368(2)	4282(3)	4257.7(17)	37.6(8)
C(8)	3783.1(18)	3565(2)	2313.4(16)	30.0(7)
N(2)	3197.0(16)	3843(2)	2778.4(15)	33.8(6)
C(9)	4045.1(18)	2427(2)	2396.9(17)	31.9(7)
C(10)	3379(2)	1720(3)	2218(2)	45.4(9)
C(11)	4763.2(18)	2213(2)	2009.6(16)	30.1(7)
C(12)	5447.4(19)	2096(2)	2342.8(17)	30.2(7)
C(13)	6117(2)	1912(3)	2000.2(19)	38.7(8)
C(14)	6109(2)	1847(3)	1313(2)	42.3(9)
C(15)	5431(2)	1978(3)	973.3(18)	42.6(9)
C(16)	4765(2)	2148(3)	1316.2(17)	36.6(8)
C(21)	4844.2(18)	4725(2)	1879.7(15)	27.6(6)
C(22)	4442(2)	5165(3)	1359.8(16)	33.3(7)
C(23)	4848(2)	5630(3)	847.5(17)	39.6(8)
C(24)	5635(2)	5674(3)	847.7(18)	39.4(8)
C(25)	6013(2)	5214(3)	1375.4(19)	39.7(8)
C(26)	5628.9(19)	4728(2)	1889.5(18)	33.4(7)
C(27)	6063(3)	6210(3)	295(2)	56.7(11)
C(99)	2004(4)	3085(5)	750(3)	38.1(15)
F(1)	1952(3)	3471(4)	133(2)	52.1(14)
F(2)	1505(4)	2345(5)	868(3)	84(2)
F(3)	2676(2)	2668(3)	812(2)	50.1(13)
S(1)	1869.5(12)	4087(2)	1341.5(10)	24.4(6)
O(1)	1903(4)	3598(5)	1983(3)	35.4(18)
O(2)	2580(4)	4583(6)	1174(4)	56(2)
O(3)	1135(3)	4497(5)	1184(3)	46.0(14)
C(99')	1708(6)	3146(7)	833(4)	48(3)
F(1')	1739(4)	3263(6)	181(3)	54(2)
F(2')	1011(4)	2734(5)	894(3)	70(2)
F(3')	2180(5)	2337(6)	925(4)	81(3)
S(1')	1879.5(16)	4276(3)	1352.1(14)	24.1(9)
O(1')	1860(5)	3816(7)	2015(4)	33(2)
O(2')	2504(4)	4853(6)	1189(3)	30.1(17)
O(3')	1236(3)	4879(5)	1205(3)	26.7(14)

3b3. Table 3. Bond lengths [Å] and angles [°].

C(1)-N(1)	1.309(4)	C(6)-C(7)	1.364(5)
C(1)-C(2)	1.416(5)	C(8)-N(2)	1.439(4)
N(1)-C(21)	1.450(4)	C(8)-C(9)	1.552(4)
N(1)-C(8)	1.494(4)	C(9)-C(11)	1.512(5)
C(2)-C(3)	1.414(5)	C(9)-C(10)	1.532(5)
C(2)-C(7)	1.414(5)	C(11)-C(12)	1.388(4)
C(3)-N(2)	1.353(4)	C(11)-C(16)	1.397(5)
C(3)-C(4)	1.411(5)	C(12)-C(13)	1.387(5)
C(4)-C(5)	1.374(6)	C(13)-C(14)	1.386(5)
C(5)-C(6)	1.400(6)	C(14)-C(15)	1.385(6)

C(15)-C(16)	1.380(5)	C(10)-C(9)-C(8)	108.3(3)
C(21)-C(26)	1.383(5)	C(12)-C(11)-C(16)	118.3(3)
C(21)-C(22)	1.385(5)	C(12)-C(11)-C(9)	119.9(3)
C(22)-C(23)	1.391(5)	C(16)-C(11)-C(9)	121.8(3)
C(23)-C(24)	1.389(5)	C(13)-C(12)-C(11)	121.2(3)
C(24)-C(25)	1.387(5)	C(14)-C(13)-C(12)	119.9(3)
C(24)-C(27)	1.512(5)	C(15)-C(14)-C(13)	119.5(3)
C(25)-C(26)	1.387(5)	C(16)-C(15)-C(14)	120.5(3)
C(99)-F(3)	1.308(7)	C(15)-C(16)-C(11)	120.7(3)
C(99)-F(2)	1.321(7)	C(26)-C(21)-C(22)	121.4(3)
C(99)-F(1)	1.341(7)	C(26)-C(21)-N(1)	119.2(3)
C(99)-S(1)	1.777(7)	C(22)-C(21)-N(1)	119.4(3)
S(1)-O(3)	1.434(5)	C(21)-C(22)-C(23)	118.3(3)
S(1)-O(1)	1.438(6)	C(24)-C(23)-C(22)	122.0(3)
S(1)-O(2)	1.446(6)	C(25)-C(24)-C(23)	117.6(3)
C(99')-F(1')	1.320(9)	C(25)-C(24)-C(27)	121.3(4)
C(99')-F(2')	1.344(10)	C(23)-C(24)-C(27)	121.2(4)
C(99')-F(3')	1.350(10)	C(26)-C(25)-C(24)	122.0(3)
C(99')-S(1')	1.822(9)	C(21)-C(26)-C(25)	118.7(3)
S(1')-O(2')	1.370(7)	F(3)-C(99)-F(2)	106.6(5)
S(1')-O(3')	1.408(6)	F(3)-C(99)-F(1)	107.7(5)
S(1')-O(1')	1.460(7)	F(2)-C(99)-F(1)	113.0(5)
		F(3)-C(99)-S(1)	111.0(4)
N(1)-C(1)-C(2)	121.4(3)	F(2)-C(99)-S(1)	108.7(5)
C(1)-N(1)-C(21)	122.5(3)	F(1)-C(99)-S(1)	109.8(4)
C(1)-N(1)-C(8)	117.3(3)	O(3)-S(1)-O(1)	113.4(4)
C(21)-N(1)-C(8)	120.2(2)	O(3)-S(1)-O(2)	124.5(4)
C(3)-C(2)-C(7)	120.1(3)	O(1)-S(1)-O(2)	111.6(4)
C(3)-C(2)-C(1)	116.8(3)	O(3)-S(1)-C(99)	104.0(3)
C(7)-C(2)-C(1)	121.7(3)	O(1)-S(1)-C(99)	105.9(3)
N(2)-C(3)-C(4)	123.4(3)	O(2)-S(1)-C(99)	93.0(4)
N(2)-C(3)-C(2)	117.6(3)	F(1')-C(99')-F(2')	100.1(7)
C(4)-C(3)-C(2)	118.8(3)	F(1')-C(99')-F(3')	101.5(8)
C(5)-C(4)-C(3)	119.2(4)	F(2')-C(99')-F(3')	104.1(7)
C(4)-C(5)-C(6)	122.3(4)	F(1')-C(99')-S(1')	118.0(7)
C(7)-C(6)-C(5)	119.3(4)	F(2')-C(99')-S(1')	114.7(7)
C(6)-C(7)-C(2)	120.3(4)	F(3')-C(99')-S(1')	116.2(7)
N(2)-C(8)-N(1)	106.9(3)	O(2')-S(1')-O(3')	107.1(5)
N(2)-C(8)-C(9)	112.3(3)	O(2')-S(1')-O(1')	117.4(5)
N(1)-C(8)-C(9)	109.9(2)	O(3')-S(1')-O(1')	113.5(4)
C(3)-N(2)-C(8)	118.4(3)	O(2')-S(1')-C(99')	115.7(5)
C(11)-C(9)-C(10)	114.2(3)	O(3')-S(1')-C(99')	101.0(4)
C(11)-C(9)-C(8)	111.6(3)	O(1')-S(1')-C(99')	101.1(5)

3b3. Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	32.5(16)	22.9(14)	31.9(16)	0.7(12)	-6.8(13)	2.5(12)
N(1)	28.8(13)	21.2(12)	30.4(13)	0.4(10)	-4.2(10)	1.0(10)
C(2)	34.5(17)	25.1(15)	33.0(16)	1.5(12)	-1.7(13)	4.7(13)
C(3)	35.3(17)	25.0(15)	37.5(18)	0.9(13)	-2.6(14)	8.5(13)
C(4)	38.0(18)	31.8(17)	52(2)	6.9(16)	8.4(16)	7.3(15)
C(5)	62(3)	33.7(19)	42(2)	7.9(16)	15.1(18)	9.5(17)
C(6)	70(3)	32.1(18)	31.6(18)	6.9(14)	1.9(17)	4.6(18)
C(7)	47(2)	31.6(17)	34.1(18)	3.3(14)	-5.4(15)	2.4(15)
C(8)	29.7(16)	29.1(16)	31.3(16)	1.4(12)	-5.1(13)	-0.7(12)
N(2)	26.2(14)	34.7(15)	40.5(16)	1.6(12)	-3.4(12)	3.8(11)
C(9)	30.4(16)	27.7(15)	37.6(17)	0.0(13)	-3.3(13)	1.1(13)
C(10)	36.0(19)	30.5(17)	70(3)	-2.2(17)	-4.4(18)	-0.4(15)
C(11)	33.6(17)	22.2(14)	34.5(17)	-0.9(12)	-4.7(13)	-1.8(12)
C(12)	36.0(17)	22.9(14)	31.5(16)	-0.2(12)	-4.2(13)	-0.6(12)
C(13)	33.2(18)	32.4(17)	50(2)	-3.1(15)	-6.1(15)	-2.0(14)
C(14)	45(2)	34.3(18)	48(2)	-9.1(16)	9.8(17)	-4.5(16)
C(15)	61(2)	36.9(19)	29.7(17)	-5.5(14)	3.8(16)	-2.8(17)
C(16)	42.7(19)	30.5(17)	36.6(18)	-3.0(14)	-9.9(15)	0.0(14)
C(21)	33.9(16)	19.5(13)	29.4(15)	-2.6(12)	0.1(12)	-0.2(12)
C(22)	39.6(18)	31.2(16)	29.0(16)	-1.8(13)	-2.0(14)	3.3(14)
C(23)	58(2)	30.0(17)	30.7(17)	0.7(14)	-1.9(16)	5.6(16)
C(24)	54(2)	25.8(17)	38.5(19)	-4.9(14)	11.2(16)	-3.1(15)
C(25)	38.0(19)	28.5(17)	53(2)	-3.6(15)	7.4(16)	-2.7(14)
C(26)	34.3(17)	25.2(15)	40.7(18)	0.7(13)	-4.5(14)	0.7(13)
C(27)	80(3)	40(2)	50(2)	1.0(18)	16(2)	-14(2)

3b3. Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2 x 10^3$).

	x	y	z	U(eq)
H(1)	5088	4797	3148	35
H(4)	2328	3735	3855	49
H(5)	2721	3977	4941	55
H(6)	3995	4276	5206	53
H(7)	4883	4426	4362	45
H(8)	3591	3669	1850	36
H(02)	2730(20)	3860(30)	2640(20)	46(11)
H(9)	4162	2317	2878	38
H(10A)	3241	1825	1750	68
H(10B)	2944	1884	2501	68
H(10C)	3527	998	2286	68
H(12)	5457	2143	2814	36
H(13)	6580	1832	2236	46
H(14)	6564	1713	1076	51
H(15)	5426	1950	501	51
H(16)	4302	2223	1078	44
H(22)	3904	5149	1353	40
H(23)	4577	5927	486	48
H(25)	6552	5233	1385	48
H(26)	5899	4405	2241	40
H(27A)	5728	6302	-89	85
H(27B)	6501	5789	166	85
H(27C)	6238	6887	451	85

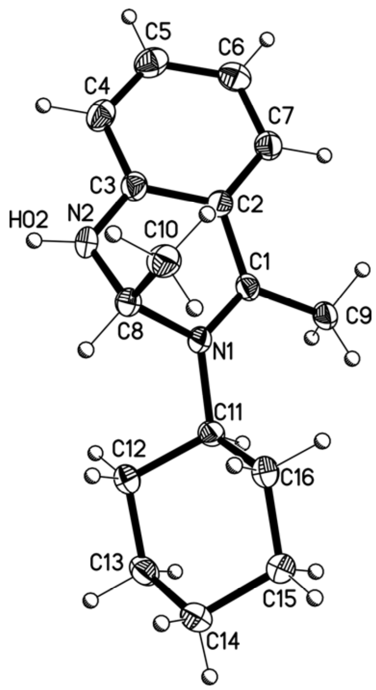


Table 1. Crystal data and structure refinement **3d4**.

Identification code	j30s	
Empirical formula	C17 H23 F3 N2 O3 S	
Formula weight	392.43	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2(1)/n	
Unit cell dimensions	a = 10.9025(11) Å	α= 90°
	b = 13.0141(13) Å	β= 96.094(2)°
	c = 13.1294(14) Å	γ = 90°
Volume	1852.4(3) $Å^3$	
Z	4	
Density (calculated)	1.407 Mg/m^3	
Absorption coefficient	0.223 mm^{-1}	
F(000)	824	
Crystal size	0.26 x 0.08 x 0.07 mm^3	
Theta range for data collection	2.21 to 28.70°	
Index ranges	-14<=h<=14, -17<=k<=17, -17<=l<=17	
Reflections collected	21913	
Independent reflections	4547 [R(int) = 0.0335]	
Completeness to theta = 26.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9846 and 0.8676	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4547 / 0 / 241	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0464, wR2 = 0.1106	
R indices (all data)	R1 = 0.0592, wR2 = 0.1176	
Largest diff. peak and hole	0.518 and -0.443 e.$Å^{-3}$	

3d4. Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	2246.2(15)	4931.4(12)	948.1(12)	18.8(3)
N(1)	2446.8(13)	3981.4(11)	1273.1(10)	19.0(3)
C(2)	1239.8(15)	5502.2(13)	1301.6(13)	20.0(3)
C(3)	324.5(16)	4938.5(13)	1753.9(13)	22.0(3)
N(2)	591.4(14)	3960.8(12)	2045.1(12)	24.9(3)
C(4)	-824.2(16)	5398.4(15)	1860.9(14)	25.9(4)
C(5)	-1016.8(17)	6408.5(15)	1598.1(14)	28.1(4)
C(6)	-90.0(17)	6994.7(14)	1207.8(14)	26.5(4)
C(7)	1010.1(16)	6543.9(13)	1049.5(13)	22.9(4)
C(8)	1858.7(16)	3660.2(13)	2200.2(13)	22.3(4)
C(9)	2996.0(16)	5388.6(13)	178.1(13)	21.7(3)
C(10)	2551.1(17)	4125.4(14)	3158.4(13)	26.0(4)
C(11)	3226.5(15)	3238.3(12)	760.0(13)	19.5(3)
C(12)	2664.2(16)	2162.7(13)	701.9(14)	22.6(4)
C(13)	3409.9(17)	1482.3(13)	45.9(14)	25.1(4)
C(14)	4750.9(17)	1423.6(13)	505.7(15)	27.2(4)
C(15)	5314.1(17)	2494.5(14)	646.5(16)	29.1(4)
C(16)	4547.8(16)	3201.4(13)	1263.1(15)	25.1(4)
C(99)	6016.2(17)	5797.6(14)	3662.6(14)	27.5(4)
F(1)	7241.4(10)	5768.9(9)	3829.3(10)	39.0(3)
F(2)	5609.4(14)	6333.5(13)	4422.2(9)	55.0(4)
F(3)	5609.2(12)	4843.9(10)	3716.3(11)	51.3(4)
S(1)	5517.0(4)	6382.9(3)	2425.4(3)	19.1(1)
O(1)	6007.9(12)	5703.7(10)	1707.2(10)	31.0(3)
O(2)	6101.5(12)	7379.1(9)	2509.4(11)	28.9(3)
O(3)	4193.6(11)	6399.6(10)	2391.5(10)	26.5(3)

3d4. Table 3. Bond lengths [Å] and angles [°].

C(1)-N(1)	1.319(2)	S(1)-O(3)	1.4390(13)
C(1)-C(2)	1.442(2)	S(1)-O(2)	1.4437(13)
C(1)-C(9)	1.490(2)		
N(1)-C(11)	1.494(2)	N(1)-C(1)-C(2)	118.99(14)
N(1)-C(8)	1.494(2)	N(1)-C(1)-C(9)	120.66(15)
C(2)-C(7)	1.412(2)	C(2)-C(1)-C(9)	120.25(14)
C(2)-C(3)	1.419(2)	C(1)-N(1)-C(11)	122.93(13)
C(3)-N(2)	1.351(2)	C(1)-N(1)-C(8)	117.07(13)
C(3)-C(4)	1.408(2)	C(11)-N(1)-C(8)	119.99(13)
N(2)-C(8)	1.430(2)	C(7)-C(2)-C(3)	118.66(15)
C(4)-C(5)	1.370(3)	C(7)-C(2)-C(1)	122.78(15)
C(5)-C(6)	1.405(3)	C(3)-C(2)-C(1)	117.48(15)
C(6)-C(7)	1.371(2)	N(2)-C(3)-C(4)	122.61(16)
C(8)-C(10)	1.522(3)	N(2)-C(3)-C(2)	117.74(16)
C(11)-C(16)	1.520(2)	C(4)-C(3)-C(2)	119.64(16)
C(11)-C(12)	1.527(2)	C(3)-N(2)-C(8)	118.28(14)
C(12)-C(13)	1.528(2)	C(5)-C(4)-C(3)	119.80(17)
C(13)-C(14)	1.523(3)	C(4)-C(5)-C(6)	121.05(17)
C(14)-C(15)	1.526(2)	C(7)-C(6)-C(5)	119.84(17)
C(15)-C(16)	1.531(2)	C(6)-C(7)-C(2)	120.78(16)
C(99)-F(3)	1.323(2)	N(2)-C(8)-N(1)	107.40(14)
C(99)-F(2)	1.331(2)	N(2)-C(8)-C(10)	113.32(14)
C(99)-F(1)	1.331(2)	N(1)-C(8)-C(10)	110.11(14)
C(99)-S(1)	1.8240(19)	N(1)-C(11)-C(16)	112.50(13)
S(1)-O(1)	1.4367(13)	N(1)-C(11)-C(12)	111.79(13)

C(16)-C(11)-C(12)	110.46(14)	F(3)-C(99)-S(1)	111.67(13)
C(11)-C(12)-C(13)	108.94(14)	F(2)-C(99)-S(1)	110.91(13)
C(14)-C(13)-C(12)	110.57(14)	F(1)-C(99)-S(1)	110.94(12)
C(13)-C(14)-C(15)	111.04(14)	O(1)-S(1)-O(3)	115.54(8)
C(14)-C(15)-C(16)	112.19(15)	O(1)-S(1)-O(2)	114.23(8)
C(11)-C(16)-C(15)	109.53(14)	O(3)-S(1)-O(2)	114.95(8)
F(3)-C(99)-F(2)	108.15(16)	O(1)-S(1)-C(99)	103.36(9)
F(3)-C(99)-F(1)	107.54(15)	O(3)-S(1)-C(99)	103.72(8)
F(2)-C(99)-F(1)	107.45(16)	O(2)-S(1)-C(99)	102.68(8)

3d4. Table 4. Anisotropic displacement parameters ($Å^2$x 10^3). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	21.0(8)	17.1(8)	18.4(8)	-2.3(6)	3.3(6)	-4.7(6)
N(1)	21.1(7)	17.6(6)	19.3(7)	-0.2(5)	7.8(5)	-2.7(5)
C(2)	19.4(8)	20.5(8)	20.4(8)	-2.0(6)	3.9(6)	-2.1(6)
C(3)	22.7(8)	23.2(8)	20.6(8)	-3.0(6)	4.3(6)	-5.0(7)
N(2)	22.4(7)	22.2(7)	32.0(8)	0.9(6)	11.1(6)	-5.9(6)
C(4)	19.4(8)	33.1(10)	25.5(9)	-2.8(7)	3.6(7)	-3.8(7)
C(5)	21.1(8)	35.7(10)	26.9(9)	-4.3(8)	0.5(7)	3.1(7)
C(6)	28.7(9)	23.3(9)	26.7(9)	-1.3(7)	-0.6(7)	3.4(7)
C(7)	24.9(8)	22.3(8)	21.8(8)	-0.5(6)	3.6(7)	-2.4(7)
C(8)	27.4(9)	18.3(8)	23.1(8)	2.2(6)	11.3(7)	-1.5(7)
C(9)	26.2(9)	17.8(8)	22.0(8)	-0.3(6)	7.4(7)	-4.1(6)
C(10)	30.9(9)	26.1(9)	21.9(9)	1.2(7)	6.8(7)	1.1(7)
C(11)	23.9(8)	16.7(7)	18.7(8)	-0.6(6)	6.6(6)	-0.4(6)
C(12)	22.5(8)	19.0(8)	26.6(9)	-2.8(7)	3.0(7)	-4.4(6)
C(13)	33.0(10)	17.9(8)	25.0(9)	-2.6(6)	5.8(7)	-2.5(7)
C(14)	30.3(10)	18.8(8)	33.4(10)	0.3(7)	8.0(8)	1.9(7)
C(15)	21.6(9)	22.7(9)	44.0(11)	-3.5(8)	8.8(8)	-1.7(7)
C(16)	21.0(8)	21.6(8)	32.9(10)	-4.4(7)	4.1(7)	-5.1(7)
C(99)	25.1(9)	31.1(10)	26.5(9)	5.8(7)	3.2(7)	-2.7(7)
F(1)	24.3(6)	43.0(7)	47.3(7)	15.4(6)	-7.5(5)	-1.0(5)
F(2)	57.4(9)	87.8(11)	20.9(6)	-3.3(6)	9.0(6)	9.6(8)
F(3)	43.3(7)	41.8(7)	66.6(9)	30.0(7)	-4.4(6)	-14.3(6)
S(1)	18.9(2)	19.5(2)	19.6(2)	-0.9(2)	5.8(2)	3.0(2)
O(1)	29.3(7)	35.1(7)	30.2(7)	-11.5(6)	10.6(5)	3.5(6)
O(2)	26.3(7)	19.6(6)	42.4(8)	2.8(5)	10.6(6)	2.0(5)
O(3)	20.4(6)	30.5(7)	28.8(7)	-2.6(5)	3.7(5)	3.6(5)

3d4. Table 5. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(02)	50(20)	3561(17)	2203(18)	35(6)
H(4)	-1463	5009	2115	31
H(5)	-1789	6718	1681	34
H(6)	-226	7702	1054	32
H(7)	1625	6937	767	28
H(8)	1901	2894	2257	27
H(9A)	3842	5126	291	33
H(9B)	3005	6138	249	33
H(9C)	2634	5202	-513	33
H(10A)	2530	4877	3107	39
H(10B)	3410	3890	3224	39
H(10C)	2160	3909	3762	39

H(11)	3255	3482	41	23
H(12A)	1796	2197	395	27
H(12B)	2679	1869	1399	27
H(13A)	3050	783	2	30
H(13B)	3369	1766	-656	30
H(14A)	5230	1015	50	33
H(14B)	4798	1072	1177	33
H(15A)	5379	2804	-35	35
H(15B)	6158	2436	1003	35
H(16A)	4561	2942	1973	30
H(16B)	4905	3901	1291	30

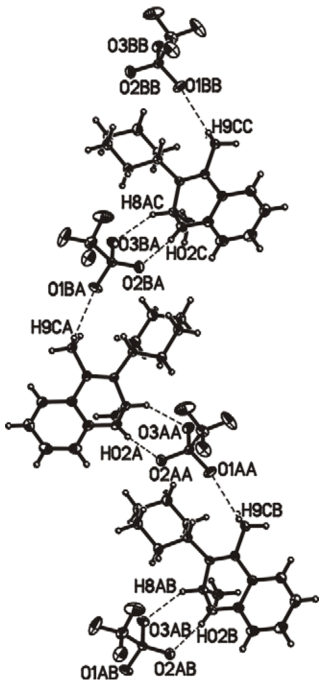
3d4. Table 6. Torsion angles [°].

C(2)-C(1)-N(1)-C(11)	163.44(15)	C(11)-N(1)-C(8)-N(2)	-131.79(15)
C(9)-C(1)-N(1)-C(11)	-12.8(2)	C(1)-N(1)-C(8)-C(10)	-75.36(18)
C(2)-C(1)-N(1)-C(8)	-16.8(2)	C(11)-N(1)-C(8)-C(10)	104.39(17)
C(9)-C(1)-N(1)-C(8)	166.92(14)	C(1)-N(1)-C(11)-C(16)	95.85(18)
N(1)-C(1)-C(2)-C(7)	175.55(15)	C(8)-N(1)-C(11)-C(16)	-83.87(18)
C(9)-C(1)-C(2)-C(7)	-8.2(2)	C(1)-N(1)-C(11)-C(12)	-139.18(16)
N(1)-C(1)-C(2)-C(3)	-16.5(2)	C(8)-N(1)-C(11)-C(12)	41.1(2)
C(9)-C(1)-C(2)-C(3)	159.77(15)	N(1)-C(11)-C(12)-C(13)	172.43(14)
C(7)-C(2)-C(3)-N(2)	-176.15(15)	C(16)-C(11)-C(12)-C(13)	-61.48(18)
C(1)-C(2)-C(3)-N(2)	15.4(2)	C(11)-C(12)-C(13)-C(14)	59.37(19)
C(7)-C(2)-C(3)-C(4)	5.4(2)	C(12)-C(13)-C(14)-C(15)	-55.7(2)
C(1)-C(2)-C(3)-C(4)	-163.12(15)	C(13)-C(14)-C(15)-C(16)	53.8(2)
C(4)-C(3)-N(2)-C(8)	-161.36(16)	N(1)-C(11)-C(16)-C(15)	-175.37(14)
C(2)-C(3)-N(2)-C(8)	20.2(2)	C(12)-C(11)-C(16)-C(15)	58.94(19)
N(2)-C(3)-C(4)-C(5)	176.77(17)	C(14)-C(15)-C(16)-C(11)	-55.0(2)
C(2)-C(3)-C(4)-C(5)	-4.8(3)	F(3)-C(99)-S(1)-O(1)	-58.14(15)
C(3)-C(4)-C(5)-C(6)	0.9(3)	F(2)-C(99)-S(1)-O(1)	-178.84(13)
C(4)-C(5)-C(6)-C(7)	2.5(3)	F(1)-C(99)-S(1)-O(1)	61.81(15)
C(5)-C(6)-C(7)-C(2)	-1.8(3)	F(3)-C(99)-S(1)-O(3)	62.80(15)
C(3)-C(2)-C(7)-C(6)	-2.0(2)	F(2)-C(99)-S(1)-O(3)	-57.91(15)
C(1)-C(2)-C(7)-C(6)	165.78(16)	F(1)-C(99)-S(1)-O(3)	-177.25(13)
C(3)-N(2)-C(8)-N(1)	-50.2(2)	F(3)-C(99)-S(1)-O(2)	-177.21(13)
C(3)-N(2)-C(8)-C(10)	71.6(2)	F(2)-C(99)-S(1)-O(2)	62.09(15)
C(1)-N(1)-C(8)-N(2)	48.46(19)	F(1)-C(99)-S(1)-O(2)	-57.25(15)

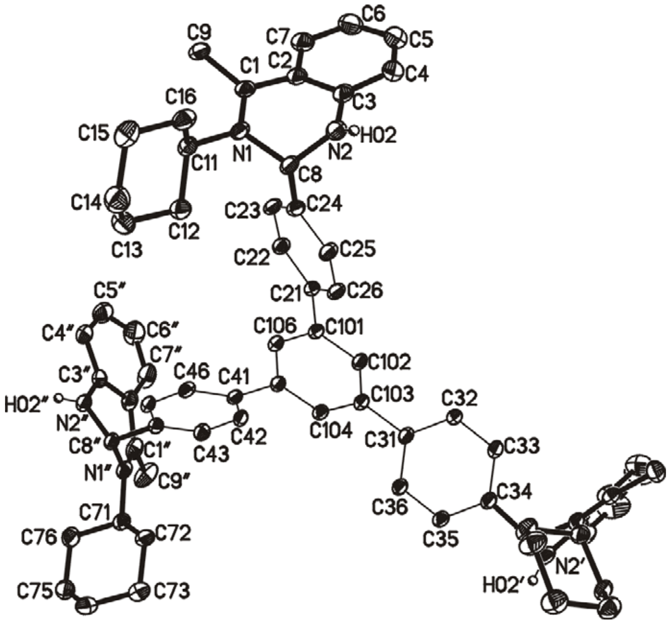
3d4. Table 7. Hydrogen bonds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(02)...O(2)#1	0.83(2)	2.05(2)	2.8663(19)	170(2)
C(8)-H(8)...O(3)#1	1.00	2.35	3.223(2)	144.9
C(9)-H(9C)...O(1)#2	0.98	2.56	3.146(2)	118.7

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y-1/2,-z+1/2 #2 -x+1,-y+1,-z



View of a chain formed by hydrogen bonds in **3d4**



Thermal ellipsoid representation plot (30% probability) of the cation of complex
6d·2CHCl$_3$·CH$_2$Cl$_2$

Table 1. Crystal data and structure refinement of **6d**.

Identification code	aiff	
Empirical formula	C75 H79 Cl8 F9 N6 O9 S3	
Formula weight	1759.22	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.531(2) Å	α= 108.267(13)°
	b = 17.185(2) Å	β= 106.724(13)°
	c = 19.511(2) Å	γ = 101.091(14)°
Volume	3921.8(8) Å^3	
Z	2	
Density (calculated)	1.490 Mg/m^3	
Absorption coefficient	4.074 mm^{-1}	
F(000)	1816	
Crystal size	0.08 x 0.02 x 0.02 mm^3	
Theta range for data collection	3.55 to 75.82°	
Index ranges	-17<=h<=15, -20<=k<=21, -24<=l<=24	
Reflections collected	83238	
Independent reflections	16034 [R(int) = 0.0761]	
Completeness to theta = 72.50°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.56041	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16034 / 931 / 1031	
Goodness-of-fit on F^2	0.987	
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1666	
R indices (all data)	R1 = 0.0942, wR2 = 0.1843	
Largest diff. peak and hole	1.115 and -1.195 e.Å^{-3}	

6d. Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(2)	1373(2)	1944.5(17)	566.2(14)	26.8(6)
N(1)	2786(2)	2871.8(15)	424.2(13)	22.8(5)
C(1)	2058(2)	3115.9(19)	4.7(16)	23.8(6)
C(2)	988(3)	2965(2)	36.1(16)	25.7(6)
C(3)	618(3)	2286(2)	254.4(16)	27.3(7)
C(4)	-490(3)	1968(2)	104.8(19)	34.5(8)
C(5)	-1185(3)	2381(3)	-175(2)	39.9(8)
C(6)	-814(3)	3098(2)	-341(2)	37.5(8)
C(7)	255(3)	3369(2)	-252.4(18)	32.0(7)
C(8)	2483(3)	2474.9(19)	944.1(16)	23.7(6)
C(9)	2274(3)	3472(2)	-563.5(17)	28.3(7)
C(11)	3889(3)	2929(2)	395.5(17)	24.6(6)
C(12)	4753(3)	3159(2)	1197.5(18)	29.2(7)
C(13)	5857(3)	3248(2)	1122(2)	35.7(8)
C(14)	5854(3)	2418(3)	547(2)	39.4(8)
C(15)	4966(3)	2152(2)	-252(2)	36.9(8)
C(16)	3857(3)	2089(2)	-198.3(18)	28.5(7)
N(1')	1814(2)	2910.7(16)	7212.1(13)	22.5(5)
N(2')	2413(2)	4320.0(17)	8217.2(14)	26.8(6)
C(1')	795(3)	2858(2)	7107.0(17)	25.5(6)
C(2')	532(3)	3621(2)	7475.8(18)	30.4(7)
C(3')	1385(3)	4328(2)	8093.7(18)	31.0(7)
C(4')	1136(4)	4995(3)	8590(2)	43.3(9)
C(5')	72(4)	4972(3)	8430(3)	56.9(11)
C(6')	-764(4)	4308(3)	7799(3)	60.4(12)
C(7')	-547(3)	3626(3)	7331(2)	43.7(9)
C(8')	2661(3)	3770.7(19)	7607.1(16)	23.6(6)
C(9')	-90(3)	2010(2)	6641(2)	33.7(7)
N(1")	8086(2)	10209.0(16)	7043.0(14)	24.1(5)
N(2")	7891(2)	9979.8(16)	5741.4(15)	24.4(5)
C(1")	7513(3)	10741(2)	7041(2)	31.3(7)
C(2")	6869(3)	10746(2)	6309(2)	30.6(7)
C(3")	7175(2)	10422(2)	5669.3(18)	26.0(6)
C(4")	6773(3)	10609(2)	5007(2)	32.5(7)
C(5")	6013(3)	11026(3)	4959(2)	42.6(9)
C(6")	5644(3)	11296(3)	5557(3)	48.0(10)
C(7")	6081(3)	11181(3)	6235(3)	43.0(9)
C(8")	7979(2)	9573.5(18)	6286.7(16)	21.7(6)
C(9")	7604(4)	11405(2)	7789(2)	43.8(9)
C(101)	3487(2)	4898.9(18)	4091.3(15)	18.9(6)
C(102)	3164(2)	4633.3(18)	4626.7(16)	20.4(6)
C(103)	3547(2)	5177.4(18)	5406.1(15)	18.3(5)
C(104)	4256(2)	6006.1(18)	5656.9(15)	19.1(6)
C(105)	4587(2)	6287.7(17)	5138.1(15)	18.3(5)
C(106)	4194(2)	5726.2(18)	4355.8(16)	20.1(6)
C(21)	3149(2)	4289.9(18)	3268.6(15)	19.2(6)
C(22)	3048(2)	4579.9(18)	2666.5(16)	21.2(6)
C(23)	2840(2)	4021.9(19)	1914.9(16)	22.8(6)
C(24)	2711(2)	3156.8(19)	1746.3(16)	21.6(6)
C(25)	2793(2)	2856.6(19)	2338.1(16)	23.0(6)
C(26)	3006(2)	3412.4(18)	3088.5(16)	22.3(6)
C(31)	3255(2)	4854.9(17)	5973.5(16)	19.3(6)
C(32)	2235(2)	4288.0(19)	5774.1(16)	22.8(6)
C(33)	2011(2)	3943(2)	6291.6(17)	24.5(6)
C(34)	2804(2)	4154.2(18)	7016.1(16)	21.6(6)

C(35)	3812(2)	4727.9(19)	7222.6(16)	22.3(6)
C(36)	4039(2)	5082.0(18)	6711.4(16)	21.1(6)
C(41)	5405(2)	7148.3(17)	5418.9(15)	18.6(5)
C(42)	5459(2)	7847.1(19)	6045.3(16)	21.4(6)
C(43)	6264(2)	8640.1(19)	6337.5(17)	22.7(6)
C(44)	7030(2)	8741.9(18)	5999.2(16)	20.4(6)
C(45)	6971(2)	8049.4(19)	5367.7(16)	21.1(6)
C(46)	6174(2)	7266.3(18)	5079.5(16)	20.6(6)
C(61')	2200(3)	2147(2)	6977.6(17)	25.2(6)
C(62')	3070(3)	2300(2)	6638(2)	32.5(7)
C(63')	3404(3)	1491(3)	6404(2)	38.9(8)
C(64')	3852(3)	1264(2)	7104(2)	37.5(8)
C(65')	3003(3)	1119(2)	7460.5(19)	32.6(7)
C(66')	2602(3)	1911(2)	7675.8(17)	26.6(6)
C(71)	8904(3)	10212(2)	7758.7(17)	27.5(7)
C(72)	8793(3)	9297(2)	7722.7(19)	31.5(7)
C(73)	9672(3)	9301(3)	8420(2)	40.3(8)
C(74)	10795(3)	9727(3)	8461(2)	44.4(9)
C(75)	10912(3)	10641(3)	8528(2)	41.2(9)
C(76)	10041(3)	10686(2)	7853.6(19)	34.8(8)
S(1)	4268.7(6)	5641.8(5)	10736.9(4)	28.4(2)
O(1)	4233(2)	4899.6(15)	10931.9(13)	37.5(6)
O(2)	5329.2(19)	6258.1(16)	11037.4(14)	36.7(6)
O(3)	3610(2)	5474.7(16)	9950.1(13)	38.5(6)
C(97)	3564(3)	6194(2)	11300(2)	38.2(8)
F(1)	4062(2)	6402.4(17)	12063.2(14)	58.1(6)
F(2)	2546.1(19)	5691.2(17)	11084.1(16)	56.0(6)
F(3)	3501(2)	6926.5(15)	11208.2(16)	53.1(6)
S(2)	9788.0(7)	10803.3(6)	4508.8(5)	35.8(2)
O(4)	10878(2)	11165(2)	5083.2(15)	48.9(7)
O(5)	9663(2)	10090.6(19)	3829.1(16)	47.5(7)
O(6)	8938(2)	10697.8(19)	4801.4(16)	47.3(7)
C(98)	9648(3)	11653(3)	4161(2)	47.9(10)
F(4)	10369(3)	11805(2)	3830.0(17)	68.1(8)
F(5)	9831(3)	12383.7(18)	4739.5(19)	74.3(8)
F(6)	8669(3)	11457(2)	3634.0(19)	81.9(9)
S(3)	2943.1(8)	363.9(6)	994.1(6)	37.6(2)
O(7)	3749(2)	1201.0(16)	1420.6(16)	43.4(6)
O(8)	1933(2)	361.2(17)	479.9(18)	47.7(7)
O(9)	2832(3)	-154(2)	1427(2)	60.2(9)
C(99)	3517(3)	-214(2)	330(3)	41.8(9)
F(7)	4457(2)	-269.4(17)	720.1(18)	63.6(7)
F(8)	2856(2)	-1005.7(14)	-128.8(17)	58.9(7)
F(9)	3690(3)	186.6(16)	-124.6(17)	63.1(7)
C(81)	1553(5)	-3921(3)	4466(3)	44.3(13)
Cl(1)	2223.3(12)	-2825.5(9)	4738.6(9)	48.8(5)
Cl(2)	1057.6(14)	-4123.2(10)	5153.6(10)	59.8(6)
C(81')	1760(20)	-3557(17)	5226(14)	116(9)
Cl(1')	2360(20)	-2769(17)	4959(19)	296(12)
Cl(2')	660(8)	-4314(6)	4398(6)	124(3)
C(82)	6157(4)	-8535(3)	2377(3)	50.2(10)
Cl(3)	6657.6(11)	-7438.1(8)	2960.1(9)	70.3(4)
Cl(4)	5940.3(13)	-9161.4(9)	2901.8(9)	71.0(4)
Cl(5)	7018.1(11)	-8843.9(10)	1903.6(7)	71.8(4)
C(83)	9191(5)	3377(4)	2775(4)	49.9(15)
Cl(6)	8735.8(14)	4274.3(11)	2964.4(10)	45.4(5)
Cl(7)	10557.2(16)	3681.8(18)	3333.0(19)	101.8(11)
Cl(8)	9036(4)	2929.6(16)	1788.8(12)	118.9(15)
C(83')	9180(20)	3204(19)	2554(13)	160(13)
Cl(6')	8863(16)	4160(13)	2888(12)	223(8)

Cl(7')	10181(7)	3173(6)	3346(5)	115(3)
Cl(8')	10020(30)	3193(19)	2027(16)	360(14)

6d. Table 3. Bond lengths [Å] and angles [°].

N(2)-C(3)	1.362(5)	C(104)-C(105)	1.394(4)
N(2)-C(8)	1.430(4)	C(105)-C(106)	1.398(4)
N(1)-C(1)	1.314(4)	C(105)-C(41)	1.492(4)
N(1)-C(8)	1.492(4)	C(21)-C(22)	1.396(4)
N(1)-C(11)	1.495(4)	C(21)-C(26)	1.397(4)
C(1)-C(2)	1.443(5)	C(22)-C(23)	1.388(4)
C(1)-C(9)	1.494(4)	C(23)-C(24)	1.382(4)
C(2)-C(7)	1.404(5)	C(24)-C(25)	1.391(4)
C(2)-C(3)	1.416(4)	C(25)-C(26)	1.383(4)
C(3)-C(4)	1.402(5)	C(31)-C(32)	1.394(4)
C(4)-C(5)	1.374(6)	C(31)-C(36)	1.400(4)
C(5)-C(6)	1.408(5)	C(32)-C(33)	1.395(4)
C(6)-C(7)	1.373(5)	C(33)-C(34)	1.391(4)
C(8)-C(24)	1.534(4)	C(34)-C(35)	1.383(4)
C(11)-C(16)	1.525(4)	C(35)-C(36)	1.395(4)
C(11)-C(12)	1.534(4)	C(41)-C(42)	1.392(4)
C(12)-C(13)	1.526(5)	C(41)-C(46)	1.401(4)
C(13)-C(14)	1.512(5)	C(42)-C(43)	1.398(4)
C(14)-C(15)	1.533(5)	C(43)-C(44)	1.392(4)
C(15)-C(16)	1.520(5)	C(44)-C(45)	1.389(4)
N(1')-C(1')	1.315(4)	C(45)-C(46)	1.382(4)
N(1')-C(8')	1.489(4)	C(61')-C(66')	1.523(4)
N(1')-C(61')	1.494(4)	C(61')-C(62')	1.528(5)
N(2')-C(3')	1.345(5)	C(62')-C(63')	1.520(5)
N(2')-C(8')	1.438(4)	C(63')-C(64')	1.527(5)
C(1')-C(2')	1.448(5)	C(64')-C(65')	1.524(5)
C(1')-C(9')	1.502(4)	C(65')-C(66')	1.542(5)
C(2')-C(7')	1.408(5)	C(71)-C(76)	1.525(5)
C(2')-C(3')	1.415(5)	C(71)-C(72)	1.529(5)
C(3')-C(4')	1.415(5)	C(72)-C(73)	1.525(5)
C(4')-C(5')	1.373(7)	C(73)-C(74)	1.522(5)
C(5')-C(6')	1.385(7)	C(74)-C(75)	1.509(6)
C(6')-C(7')	1.382(6)	C(75)-C(76)	1.527(5)
C(8')-C(34)	1.535(4)	S(1)-O(1)	1.437(2)
N(1")-C(1")	1.307(5)	S(1)-O(2)	1.438(2)
N(1")-C(8")	1.482(4)	S(1)-O(3)	1.439(2)
N(1")-C(71)	1.509(4)	S(1)-C(97)	1.821(4)
N(2")-C(3")	1.343(4)	C(97)-F(3)	1.340(4)
N(2")-C(8")	1.435(4)	C(97)-F(1)	1.341(5)
C(1")-C(2")	1.448(5)	C(97)-F(2)	1.342(4)
C(1")-C(9")	1.498(5)	S(2)-O(6)	1.430(3)
C(2")-C(3")	1.412(5)	S(2)-O(5)	1.436(3)
C(2")-C(7")	1.415(5)	S(2)-O(4)	1.441(3)
C(3")-C(4")	1.412(4)	S(2)-C(98)	1.811(5)
C(4")-C(5")	1.361(6)	C(98)-F(5)	1.321(5)
C(5")-C(6")	1.382(6)	C(98)-F(6)	1.324(5)
C(6")-C(7")	1.378(6)	C(98)-F(4)	1.344(5)
C(8")-C(44)	1.543(4)	S(3)-O(9)	1.421(3)
C(101)-C(106)	1.391(4)	S(3)-O(7)	1.440(3)
C(101)-C(102)	1.405(4)	S(3)-O(8)	1.442(3)
C(101)-C(21)	1.490(4)	S(3)-C(99)	1.827(4)
C(102)-C(103)	1.387(4)	C(99)-F(7)	1.320(5)
C(103)-C(104)	1.398(4)	C(99)-F(9)	1.325(5)
C(103)-C(31)	1.497(4)	C(99)-F(8)	1.326(5)

C(81)-Cl(1)	1.757(5)
C(81)-Cl(2)	1.759(5)
C(81')-Cl(1')	1.740(16)
C(81')-Cl(2')	1.751(16)
C(82)-Cl(3)	1.740(5)
C(82)-Cl(4)	1.743(5)
C(82)-Cl(5)	1.744(5)
C(83)-Cl(7)	1.729(6)
C(83)-Cl(6)	1.741(6)
C(83)-Cl(8)	1.766(7)
C(83')-Cl(8')	1.738(15)
C(83')-Cl(6')	1.751(15)
C(83')-Cl(7')	1.761(15)

C(3)-N(2)-C(8)	118.2(3)
C(1)-N(1)-C(8)	118.2(3)
C(1)-N(1)-C(11)	124.6(2)
C(8)-N(1)-C(11)	117.1(2)
N(1)-C(1)-C(2)	119.6(3)
N(1)-C(1)-C(9)	121.5(3)
C(2)-C(1)-C(9)	118.6(3)
C(7)-C(2)-C(3)	119.1(3)
C(7)-C(2)-C(1)	122.6(3)
C(3)-C(2)-C(1)	117.6(3)
N(2)-C(3)-C(4)	123.4(3)
N(2)-C(3)-C(2)	116.8(3)
C(4)-C(3)-C(2)	119.7(3)
C(5)-C(4)-C(3)	119.4(3)
C(4)-C(5)-C(6)	121.4(3)
C(7)-C(6)-C(5)	119.3(4)
C(6)-C(7)-C(2)	120.8(3)
N(2)-C(8)-N(1)	109.3(2)
N(2)-C(8)-C(24)	112.3(3)
N(1)-C(8)-C(24)	111.8(2)
N(1)-C(11)-C(16)	110.0(2)
N(1)-C(11)-C(12)	112.2(2)
C(16)-C(11)-C(12)	111.2(3)
C(13)-C(12)-C(11)	108.7(3)
C(14)-C(13)-C(12)	110.8(3)
C(13)-C(14)-C(15)	111.0(3)
C(16)-C(15)-C(14)	111.6(3)
C(15)-C(16)-C(11)	110.4(3)
C(1')-N(1')-C(8')	119.7(3)
C(1')-N(1')-C(61')	123.9(2)
C(8')-N(1')-C(61')	116.4(2)
C(3')-N(2')-C(8')	120.0(3)
N(1')-C(1')-C(2')	119.4(3)
N(1')-C(1')-C(9')	120.8(3)
C(2')-C(1')-C(9')	119.7(3)
C(7')-C(2')-C(3')	119.1(3)
C(7')-C(2')-C(1')	122.1(3)
C(3')-C(2')-C(1')	117.9(3)
N(2')-C(3')-C(2')	118.4(3)
N(2')-C(3')-C(4')	121.9(3)
C(2')-C(3')-C(4')	119.6(4)
C(5')-C(4')-C(3')	119.2(4)
C(4')-C(5')-C(6')	121.6(4)
C(7')-C(6')-C(5')	120.3(4)
C(6')-C(7')-C(2')	120.0(4)
N(2')-C(8')-N(1')	109.6(2)
N(2')-C(8')-C(34)	113.8(3)
N(1')-C(8')-C(34)	111.0(2)
C(1")-N(1")-C(8")	118.5(3)
C(1")-N(1")-C(71)	125.2(3)
C(8")-N(1")-C(71)	116.2(3)
C(3")-N(2")-C(8")	118.7(3)
N(1")-C(1")-C(2")	119.6(3)
N(1")-C(1")-C(9")	120.7(3)
C(2")-C(1")-C(9")	119.4(3)
C(3")-C(2")-C(7")	118.4(3)
C(3")-C(2")-C(1")	117.2(3)
C(7")-C(2")-C(1")	123.5(3)
N(2")-C(3")-C(4")	122.9(3)
N(2")-C(3")-C(2")	117.4(3)
C(4")-C(3")-C(2")	119.6(3)
C(5")-C(4")-C(3")	119.7(3)
C(4")-C(5")-C(6")	121.5(3)
C(7")-C(6")-C(5")	120.1(4)
C(6")-C(7")-C(2")	120.3(4)
N(2")-C(8")-N(1")	108.7(2)
N(2")-C(8")-C(44)	113.3(2)
N(1")-C(8")-C(44)	111.7(2)
C(106)-C(101)-C(102)	118.7(2)
C(106)-C(101)-C(21)	120.2(2)
C(102)-C(101)-C(21)	121.0(2)
C(103)-C(102)-C(101)	121.1(2)
C(102)-C(103)-C(104)	119.1(2)
C(102)-C(103)-C(31)	119.9(2)
C(104)-C(103)-C(31)	120.9(2)
C(105)-C(104)-C(103)	121.1(2)
C(104)-C(105)-C(106)	118.8(2)
C(104)-C(105)-C(41)	120.8(2)
C(106)-C(105)-C(41)	120.3(2)
C(101)-C(106)-C(105)	121.3(2)
C(22)-C(21)-C(26)	117.9(3)
C(22)-C(21)-C(101)	121.6(3)
C(26)-C(21)-C(101)	120.3(2)
C(23)-C(22)-C(21)	121.4(3)
C(24)-C(23)-C(22)	120.1(3)
C(23)-C(24)-C(25)	119.1(3)
C(23)-C(24)-C(8)	125.3(3)
C(25)-C(24)-C(8)	115.5(3)
C(26)-C(25)-C(24)	120.9(3)
C(25)-C(26)-C(21)	120.6(3)
C(32)-C(31)-C(36)	118.3(2)
C(32)-C(31)-C(103)	121.8(2)
C(36)-C(31)-C(103)	119.8(2)
C(31)-C(32)-C(33)	120.7(3)
C(34)-C(33)-C(32)	120.7(3)
C(35)-C(34)-C(33)	118.9(3)
C(35)-C(34)-C(8')	116.4(2)
C(33)-C(34)-C(8')	124.7(3)
C(34)-C(35)-C(36)	120.8(3)
C(35)-C(36)-C(31)	120.6(3)
C(42)-C(41)-C(46)	118.0(2)
C(42)-C(41)-C(105)	121.2(3)
C(46)-C(41)-C(105)	120.8(3)
C(41)-C(42)-C(43)	121.3(3)
C(44)-C(43)-C(42)	119.9(3)
C(45)-C(44)-C(43)	119.0(3)

C(45)-C(44)-C(8")	116.3(3)	O(5)-S(2)-O(4)	113.44(19)
C(43)-C(44)-C(8")	124.7(3)	O(6)-S(2)-C(98)	103.7(2)
C(46)-C(45)-C(44)	121.0(3)	O(5)-S(2)-C(98)	103.59(19)
C(45)-C(46)-C(41)	120.8(3)	O(4)-S(2)-C(98)	102.29(19)
N(1')-C(61')-C(66')	109.0(2)	F(5)-C(98)-F(6)	108.2(4)
N(1')-C(61')-C(62')	112.2(2)	F(5)-C(98)-F(4)	106.9(4)
C(66')-C(61')-C(62')	111.7(3)	F(6)-C(98)-F(4)	107.3(4)
C(63')-C(62')-C(61')	108.8(3)	F(5)-C(98)-S(2)	111.0(3)
C(62')-C(63')-C(64')	111.0(3)	F(6)-C(98)-S(2)	112.1(3)
C(65')-C(64')-C(63')	110.5(3)	F(4)-C(98)-S(2)	111.1(3)
C(64')-C(65')-C(66')	110.8(3)	O(9)-S(3)-O(7)	115.8(2)
C(61')-C(66')-C(65')	110.9(3)	O(9)-S(3)-O(8)	114.8(2)
N(1")-C(71)-C(76)	109.2(2)	O(7)-S(3)-O(8)	114.37(16)
N(1")-C(71)-C(72)	111.2(2)	O(9)-S(3)-C(99)	102.59(18)
C(76)-C(71)-C(72)	112.3(3)	O(7)-S(3)-C(99)	103.24(17)
C(73)-C(72)-C(71)	110.8(3)	O(8)-S(3)-C(99)	103.53(19)
C(74)-C(73)-C(72)	110.6(3)	F(7)-C(99)-F(9)	107.4(3)
C(75)-C(74)-C(73)	110.1(3)	F(7)-C(99)-F(8)	108.4(3)
C(74)-C(75)-C(76)	112.1(3)	F(9)-C(99)-F(8)	107.4(4)
C(71)-C(76)-C(75)	111.6(3)	F(7)-C(99)-S(3)	110.8(3)
O(1)-S(1)-O(2)	115.11(16)	F(9)-C(99)-S(3)	111.3(3)
O(1)-S(1)-O(3)	115.77(15)	F(8)-C(99)-S(3)	111.4(3)
O(2)-S(1)-O(3)	115.05(15)	Cl(1)-C(81)-Cl(2)	113.4(3)
O(1)-S(1)-C(97)	101.61(17)	Cl(1')-C(81')-Cl(2')	107.3(16)
O(2)-S(1)-C(97)	103.66(16)	Cl(3)-C(82)-Cl(4)	112.1(2)
O(3)-S(1)-C(97)	102.84(18)	Cl(3)-C(82)-Cl(5)	110.9(3)
F(3)-C(97)-F(1)	107.1(3)	Cl(4)-C(82)-Cl(5)	110.6(3)
F(3)-C(97)-F(2)	107.5(3)	Cl(7)-C(83)-Cl(6)	109.5(4)
F(1)-C(97)-F(2)	107.3(3)	Cl(7)-C(83)-Cl(8)	107.6(4)
F(3)-C(97)-S(1)	112.3(3)	Cl(6)-C(83)-Cl(8)	110.9(3)
F(1)-C(97)-S(1)	111.7(3)	Cl(8')-C(83')-Cl(6')	116.4(19)
F(2)-C(97)-S(1)	110.7(3)	Cl(8')-C(83')-Cl(7')	92.6(14)
O(6)-S(2)-O(5)	115.55(17)	Cl(6')-C(83')-Cl(7')	107.8(15)
O(6)-S(2)-O(4)	115.87(17)		

6d. Table 4. Anisotropic displacement parameters ($Å^2$x 10^3). The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(2)	32.4(14)	20.7(13)	20.1(12)	6.3(10)	7.3(10)	0.0(11)
N(1)	29.3(13)	21.2(12)	15.4(11)	7.1(9)	8.5(10)	2.6(10)
C(1)	28.6(15)	20.9(14)	14.0(12)	3.4(11)	5.0(11)	1.4(12)
C(2)	29.4(15)	24.9(14)	15.1(13)	4.1(11)	6.0(11)	2.0(12)
C(3)	32.4(16)	27.2(15)	15.5(13)	3.9(11)	9.2(12)	2.1(13)
C(4)	31.0(17)	37.9(18)	24.7(15)	8.2(14)	8.0(13)	0.2(14)
C(5)	29.7(17)	51(2)	31.3(17)	13.3(16)	8.2(14)	5.2(15)
C(6)	32.3(17)	44(2)	30.4(17)	11.7(15)	6.9(14)	10.5(15)
C(7)	34.9(17)	30.8(16)	21.8(15)	6.3(13)	6.8(13)	4.8(13)
C(8)	29.9(15)	23.1(14)	16.8(13)	9.4(11)	8.9(11)	2.7(12)
C(9)	32.4(16)	30.9(16)	18.1(14)	11.4(12)	6.3(12)	3.8(13)
C(11)	27.9(15)	25.5(15)	20.6(14)	10.8(12)	9.9(12)	4.9(12)
C(12)	30.1(16)	29.7(16)	21.6(14)	9.2(12)	7.0(12)	1.8(13)
C(13)	28.5(16)	37.4(18)	35.3(18)	16.6(15)	5.8(14)	2.9(14)
C(14)	36.4(19)	45(2)	44(2)	21.8(17)	17.6(16)	16.6(16)
C(15)	44(2)	39.8(19)	36.0(18)	17.4(15)	22.1(15)	16.9(16)
C(16)	38.2(17)	23.6(15)	19.7(14)	6.8(12)	9.9(13)	5.2(13)
N(1')	26.1(13)	23.6(12)	16.6(11)	9.9(9)	7.9(9)	1.7(10)
N(2')	35.7(15)	25.5(13)	15.6(12)	8.4(10)	9.1(11)	2.1(11)

C(1')	28.3(15)	31.9(16)	17.8(13)	13.2(12)	9.4(12)	5.7(12)
C(2')	36.9(17)	36.7(17)	21.7(14)	14.7(13)	12.1(13)	12.7(14)
C(3')	46.1(19)	32.2(16)	20.4(14)	14.2(13)	15.1(13)	13.9(14)
C(4')	63(2)	41(2)	30.3(18)	12.7(15)	20.2(17)	23.3(18)
C(5')	76(3)	59(3)	40(2)	11.8(19)	23(2)	41(2)
C(6')	55(3)	79(3)	54(3)	21(2)	22(2)	42(2)
C(7')	42(2)	58(2)	33.6(18)	16.0(17)	13.1(16)	25.0(18)
C(8')	29.0(15)	22.3(14)	15.3(13)	8.4(11)	6.9(11)	-0.7(12)
C(9')	27.2(16)	35.9(18)	30.1(16)	10.5(14)	9.0(13)	-0.3(14)
N(1'')	29.1(13)	20.5(12)	21.4(12)	8.4(10)	10.8(10)	2.3(10)
N(2'')	25.3(13)	25.6(13)	22.0(12)	10.8(10)	9.8(10)	2.9(10)
C(1'')	40.9(18)	22.8(15)	34.7(17)	13.2(13)	20.4(14)	6.5(13)
C(2'')	32.0(17)	29.9(16)	38.6(17)	20.4(14)	18.1(14)	9.1(13)
C(3'')	22.7(14)	25.2(15)	28.3(15)	13.2(12)	8.6(12)	0.5(12)
C(4'')	30.5(17)	37.9(18)	35.1(17)	22.9(15)	13.3(14)	7.4(14)
C(5'')	42(2)	53(2)	48(2)	35.3(19)	18.2(17)	18.3(17)
C(6'')	44(2)	58(2)	69(3)	44(2)	28(2)	30.5(19)
C(7'')	47(2)	47(2)	59(2)	34.4(19)	34.3(19)	24.1(18)
C(8'')	24.2(14)	20.9(13)	20.0(13)	9.2(11)	9.5(11)	3.1(11)
C(9'')	75(3)	31.9(18)	38.7(19)	16.0(15)	34(2)	23.6(19)
C(101)	20.5(13)	20.8(13)	14.2(12)	8.2(10)	5.5(10)	2.9(11)
C(102)	23.9(14)	19.4(13)	16.7(13)	9.0(11)	7.4(11)	1.1(11)
C(103)	20.5(13)	20.6(13)	16.5(12)	9.3(11)	8.8(11)	5.8(11)
C(104)	21.6(14)	20.1(13)	13.5(12)	6.0(10)	6.5(10)	3.3(11)
C(105)	20.3(13)	18.4(13)	16.4(12)	8.0(10)	7.2(10)	3.8(11)
C(106)	21.6(14)	22.4(13)	17.1(13)	10.5(11)	7.3(11)	3.7(11)
C(21)	18.9(13)	22.8(13)	12.8(12)	6.7(10)	5.1(10)	1.6(11)
C(22)	25.8(14)	17.8(13)	16.5(13)	7.1(10)	6.0(11)	1.8(11)
C(23)	28.5(15)	23.4(14)	15.2(13)	10.4(11)	6.7(11)	2.6(12)
C(24)	24.2(14)	22.2(14)	15.2(12)	8.2(11)	4.8(11)	2.7(11)
C(25)	30.9(16)	19.4(13)	15.9(13)	7.8(11)	7.8(11)	1.3(12)
C(26)	27.5(15)	21.5(14)	15.1(13)	8.9(11)	6.2(11)	1.2(12)
C(31)	23.7(14)	17.8(13)	16.8(12)	8.1(10)	8.7(11)	3.6(11)
C(32)	21.2(14)	27.8(15)	16.4(13)	10.5(11)	5.4(11)	0.8(12)
C(33)	24.9(15)	27.2(15)	19.6(13)	11.3(12)	8.6(11)	0.2(12)
C(34)	24.9(14)	22.0(14)	16.5(13)	8.7(11)	7.7(11)	2.3(11)
C(35)	25.8(14)	23.1(14)	13.6(12)	6.6(11)	6.2(11)	0.9(11)
C(36)	24.1(14)	20.6(13)	15.0(12)	6.7(11)	7.0(11)	0.2(11)
C(41)	21.5(14)	18.7(13)	15.4(12)	8.9(10)	5.8(10)	3.5(11)
C(42)	22.5(14)	22.9(14)	18.3(13)	8.9(11)	9.1(11)	2.0(11)
C(43)	26.6(15)	19.9(13)	20.7(13)	7.8(11)	9.7(11)	4.6(11)
C(44)	20.8(13)	20.0(13)	19.2(13)	9.1(11)	6.7(11)	3.0(11)
C(45)	22.5(14)	23.8(14)	18.7(13)	10.9(11)	9.6(11)	3.4(11)
C(46)	26.6(15)	20.0(13)	14.7(12)	6.9(10)	8.8(11)	4.8(11)
C(61')	27.9(15)	24.3(14)	18.5(13)	6.8(11)	6.9(12)	3.0(12)
C(62')	38.4(18)	38.9(18)	30.5(16)	21.1(14)	17.9(14)	14.2(15)
C(63')	48(2)	51(2)	32.1(18)	20.8(16)	22.2(16)	26.1(18)
C(64')	41(2)	40.8(19)	37.2(18)	17.8(15)	16.6(15)	20.1(16)
C(65')	40.7(19)	26.3(16)	28.7(16)	11.9(13)	10.4(14)	8.2(14)
C(66')	30.9(16)	25.9(15)	23.0(14)	12.5(12)	10.1(12)	3.5(12)
C(71)	29.1(16)	30.3(16)	19.0(14)	8.7(12)	8.1(12)	3.2(13)
C(72)	32.6(17)	33.8(17)	26.1(16)	17.1(13)	6.1(13)	4.4(14)
C(73)	39.6(19)	49(2)	35.7(18)	25.7(17)	10.9(15)	10.6(16)
C(74)	34.9(19)	71(3)	31.1(18)	27.5(18)	10.2(15)	16.6(18)
C(75)	31.9(18)	53(2)	23.0(16)	11.4(15)	4.9(13)	-5.4(16)
C(76)	33.8(17)	33.7(17)	25.7(16)	8.4(13)	8.6(13)	-4.1(14)
S(1)	30.7(4)	26.0(4)	23.3(4)	11.3(3)	4.6(3)	3.3(3)
O(1)	51.0(15)	28.4(12)	29.1(12)	15.5(10)	7.6(11)	7.8(11)
O(2)	26.8(12)	36.2(13)	37.8(13)	14.3(10)	4.2(10)	2.4(10)
O(3)	42.6(14)	36.5(13)	24.9(11)	15.7(10)	0.0(10)	0.9(11)

C(97)	34.8(19)	38.4(19)	43(2)	17.8(16)	15.1(16)	9.2(15)
F(1)	72.5(17)	64.0(16)	39.0(12)	16.1(11)	25.1(12)	24.3(13)
F(2)	39.1(13)	61.1(15)	81.4(18)	39.9(14)	30.0(12)	13.1(11)
F(3)	56.1(15)	42.6(12)	73.1(16)	27.1(12)	31.9(13)	22.8(11)
S(2)	27.5(4)	46.9(5)	27.1(4)	10.3(4)	10.3(3)	6.2(4)
O(4)	28.8(13)	72.6(19)	36.1(14)	24.3(13)	6.5(11)	-0.2(13)
O(5)	50.0(16)	51.3(16)	38.4(14)	9.2(12)	22.4(12)	15.2(13)
O(6)	34.0(14)	53.6(16)	44.0(15)	7.9(12)	20.7(12)	1.3(12)
C(98)	42(2)	55(2)	42(2)	15.4(19)	13.9(17)	15.3(19)
F(4)	84(2)	81.7(19)	71.9(18)	51.9(16)	43.7(16)	37.9(16)
F(5)	85(2)	51.1(16)	79(2)	11.7(14)	33.5(17)	24.3(15)
F(6)	60.5(18)	95(2)	79(2)	40.4(18)	-1.2(15)	31.7(16)
S(3)	41.7(5)	30.0(4)	50.8(5)	19.7(4)	25.5(4)	13.0(4)
O(7)	44.6(15)	32.7(13)	50.7(15)	16.2(12)	13.9(12)	13.5(11)
O(8)	36.5(14)	33.6(13)	67.1(18)	12.5(13)	18.4(13)	11.9(11)
O(9)	84(2)	54.4(18)	81(2)	45.4(17)	56(2)	34.6(17)
C(99)	41(2)	33.1(19)	60(2)	21.0(17)	26.1(18)	13.5(16)
F(7)	52.7(15)	55.5(15)	89(2)	23.3(14)	33.3(14)	29.3(12)
F(8)	62.0(16)	31.0(11)	79.7(18)	9.6(11)	37.9(14)	8.5(11)
F(9)	92(2)	47.7(14)	78.0(18)	31.3(13)	60.7(17)	26.9(14)
C(81)	44(3)	40(3)	54(3)	23(2)	22(2)	12(2)
Cl(1)	50.3(8)	40.8(7)	51.6(8)	24.2(6)	14.5(6)	3.1(5)
Cl(2)	71.0(11)	53.7(9)	73.3(11)	35.1(8)	43.5(8)	17.0(7)
C(82)	51(2)	60(3)	47(2)	25(2)	21.0(19)	25(2)
Cl(3)	78.4(8)	49.5(6)	93.1(9)	20.1(6)	59.2(7)	13.2(6)
Cl(4)	95.3(10)	69.1(8)	90.7(9)	50.6(7)	59.3(8)	45.3(7)
Cl(5)	71.6(8)	106.8(10)	45.5(6)	24.7(6)	29.9(6)	42.3(7)
Cl(6)	43.1(8)	43.9(8)	49.8(9)	23.6(6)	13.2(6)	12.4(6)
Cl(7)	40.5(10)	78.3(16)	156(2)	36.5(15)	4.9(12)	17.9(10)
Cl(8)	224(4)	76.5(15)	43.0(11)	10.0(9)	27.9(15)	74(2)

6d. Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(02)	1260(30)	1419(19)	480(20)	39(11)
H(4)	-758	1472	196	41
H(5)	-1932	2177	-258	48
H(6)	-1298	3392	-512	45
H(7)	501	3834	-388	38
H(8)	2941	2093	1022	28
H(9A)	2284	4075	-395	42
H(9B)	1701	3136	-1079	42
H(9C)	2978	3439	-589	42
H(11)	4094	3399	216	29
H(12A)	4766	3707	1573	35
H(12B)	4581	2701	1390	35
H(13A)	6035	3720	947	43
H(13B)	6423	3398	1637	43
H(14A)	5730	1955	742	47
H(14B)	6571	2495	497	47
H(15A)	5141	2581	-475	44
H(15B)	4946	1587	-606	44
H(16A)	3635	1608	-43	34
H(16B)	3314	1967	-714	34
H(02')	2940(30)	4650(20)	8629(19)	40(11)
H(4')	1699	5453	9028	52
H(5')	-95	5423	8759	68

H(6')	-1491	4321	7688	73
H(7')	-1126	3161	6911	52
H(8')	3364	3683	7857	28
H(9'1)	-323	1906	6087	51
H(9'2)	-708	2025	6806	51
H(9'3)	183	1547	6727	51
H(02")	8300(30)	9930(20)	5498(18)	17(8)
H(4")	7033	10444	4597	39
H(5")	5730	11134	4505	51
H(6")	5088	11562	5500	58
H(7")	5852	11396	6655	52
H(8")	8663	9413	6366	26
H(9"1)	7278	11120	8070	66
H(9"2)	7223	11808	7677	66
H(9"3)	8371	11721	8109	66
H(102)	2676	4072	4452	24
H(104)	4516	6383	6189	23
H(106)	4413	5913	3998	24
H(22)	3124	5172	2773	25
H(23)	2786	4235	1516	27
H(25)	2702	2262	2226	28
H(26)	3055	3195	3485	27
H(32)	1686	4135	5281	27
H(33)	1311	3559	6148	29
H(35)	4356	4883	7719	27
H(36)	4733	5481	6865	25
H(42)	4938	7784	6279	26
H(43)	6288	9109	6767	27
H(45)	7487	8115	5130	25
H(46)	6147	6802	4646	25
H(61')	1565	1651	6567	30
H(62A)	2781	2437	6178	39
H(62B)	3707	2793	7029	39
H(63A)	3964	1582	6180	47
H(63B)	2768	1005	6000	47
H(14')	4063	735	6938	45
H(64B)	4508	1738	7499	45
H(64A)	3322	1011	7933	39
H(65B)	2381	605	7085	39
H(65A)	2006	1783	7861	32
H(66B)	3203	2406	8104	32
H(71)	8755	10540	8221	33
H(72A)	8069	9037	7716	38
H(72B)	8853	8940	7237	38
H(73A)	9576	9618	8904	48
H(73B)	9602	8701	8376	48
H(74A)	11356	9726	8917	53
H(74B)	10904	9396	7987	53
H(75A)	11638	10904	8537	49
H(75B)	10864	10981	9024	49
H(76A)	10103	11297	7948	42
H(76B)	10161	10427	7366	42
H(81A)	2062	-4254	4388	53
H(81B)	939	-4129	3962	53
H(81C)	1500	-3296	5644	140
H(81D)	2286	-3837	5419	140
H(82)	5441	-8644	1969	60
H(83)	8773	2934	2905	60
H(83')	8525	2679	2298	192

6d. Table 6. Torsion angles [°].

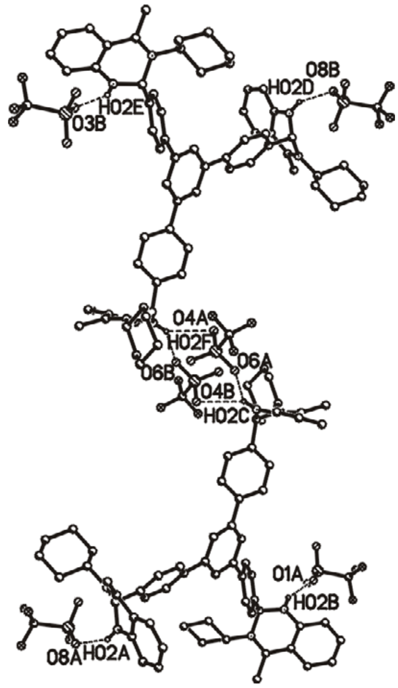
C(8)-N(1)-C(1)-C(2)	-2.3(4)	C(5')-C(6')-C(7')-C(2')	-2.4(7)
C(11)-N(1)-C(1)-C(2)	175.0(3)	C(3')-C(2')-C(7')-C(6')	-1.4(6)
C(8)-N(1)-C(1)-C(9)	-176.5(3)	C(1')-C(2')-C(7')-C(6')	167.7(4)
C(11)-N(1)-C(1)-C(9)	0.9(4)	C(3')-N(2')-C(8')-N(1')	-42.5(4)
N(1)-C(1)-C(2)-C(7)	165.6(3)	C(3')-N(2')-C(8')-C(34)	82.4(3)
C(9)-C(1)-C(2)-C(7)	-20.1(4)	C(1')-N(1')-C(8')-N(2')	36.9(3)
N(1)-C(1)-C(2)-C(3)	-24.5(4)	C(61')-N(1')-C(8')-N(2')	-141.4(3)
C(9)-C(1)-C(2)-C(3)	149.8(3)	C(1')-N(1')-C(8')-C(34)	-89.6(3)
C(8)-N(2)-C(3)-C(4)	-158.2(3)	C(61')-N(1')-C(8')-C(34)	92.1(3)
C(8)-N(2)-C(3)-C(2)	25.5(4)	C(8")-N(1")-C(1")-C(2")	-5.4(4)
C(7)-C(2)-C(3)-N(2)	-176.9(3)	C(71)-N(1")-C(1")-C(2")	171.5(3)
C(1)-C(2)-C(3)-N(2)	12.8(4)	C(8")-N(1")-C(1")-C(9")	-179.0(3)
C(7)-C(2)-C(3)-C(4)	6.6(4)	C(71)-N(1")-C(1")-C(9")	-2.2(5)
C(1)-C(2)-C(3)-C(4)	-163.7(3)	N(1")-C(1")-C(2")-C(3")	-22.3(4)
N(2)-C(3)-C(4)-C(5)	176.8(3)	C(9")-C(1")-C(2")-C(3")	151.4(3)
C(2)-C(3)-C(4)-C(5)	-6.9(5)	N(1")-C(1")-C(2")-C(7")	168.5(3)
C(3)-C(4)-C(5)-C(6)	2.3(5)	C(9")-C(1")-C(2")-C(7")	-17.8(5)
C(4)-C(5)-C(6)-C(7)	2.8(5)	C(8")-N(2")-C(3")-C(4")	-159.4(3)
C(5)-C(6)-C(7)-C(2)	-3.1(5)	C(8")-N(2")-C(3")-C(2")	24.2(4)
C(3)-C(2)-C(7)-C(6)	-1.5(5)	C(7")-C(2")-C(3")-N(2")	-177.3(3)
C(1)-C(2)-C(7)-C(6)	168.2(3)	C(1")-C(2")-C(3")-N(2")	12.9(4)
C(3)-N(2)-C(8)-N(1)	-49.7(4)	C(7")-C(2")-C(3")-C(4")	6.1(5)
C(3)-N(2)-C(8)-C(24)	75.0(3)	C(1")-C(2")-C(3")-C(4")	-163.7(3)
C(1)-N(1)-C(8)-N(2)	37.4(4)	N(2")-C(3")-C(4")-C(5")	177.1(3)
C(11)-N(1)-C(8)-N(2)	-140.2(3)	C(2")-C(3")-C(4")-C(5")	-6.5(5)
C(1)-N(1)-C(8)-C(24)	-87.6(3)	C(3")-C(4")-C(5")-C(6")	1.9(6)
C(11)-N(1)-C(8)-C(24)	94.9(3)	C(4")-C(5")-C(6")-C(7")	3.0(6)
C(1)-N(1)-C(11)-C(16)	-91.9(3)	C(5")-C(6")-C(7")-C(2")	-3.3(6)
C(8)-N(1)-C(11)-C(16)	85.5(3)	C(3")-C(2")-C(7")-C(6")	-1.2(5)
C(1)-N(1)-C(11)-C(12)	143.8(3)	C(1")-C(2")-C(7")-C(6")	167.9(4)
C(8)-N(1)-C(11)-C(12)	-38.8(3)	C(3")-N(2")-C(8")-N(1")	-49.1(3)
N(1)-C(11)-C(12)-C(13)	-177.2(3)	C(3")-N(2")-C(8")-C(44)	75.7(3)
C(16)-C(11)-C(12)-C(13)	59.2(3)	C(1")-N(1")-C(8")-N(2")	38.9(4)
C(11)-C(12)-C(13)-C(14)	-59.3(4)	C(71)-N(1")-C(8")-N(2")	-138.2(3)
C(12)-C(13)-C(14)-C(15)	57.6(4)	C(1")-N(1")-C(8")-C(44)	-86.8(3)
C(13)-C(14)-C(15)-C(16)	-54.9(4)	C(71)-N(1")-C(8")-C(44)	96.1(3)
C(14)-C(15)-C(16)-C(11)	54.3(4)	C(106)-C(101)-C(102)-C(103)	-0.6(5)
N(1)-C(11)-C(16)-C(15)	178.0(2)	C(21)-C(101)-C(102)-C(103)	174.9(3)
C(12)-C(11)-C(16)-C(15)	-57.1(3)	C(101)-C(102)-C(103)-C(104)	0.7(4)
C(8')-N(1')-C(1')-C(2')	-9.1(4)	C(101)-C(102)-C(103)-C(31)	-175.5(3)
C(61')-N(1')-C(1')-C(2')	169.1(3)	C(102)-C(103)-C(104)-C(105)	-0.5(4)
C(8')-N(1')-C(1')-C(9')	173.9(3)	C(31)-C(103)-C(104)-C(105)	175.6(3)
C(61')-N(1')-C(1')-C(9')	-8.0(4)	C(103)-C(104)-C(105)-C(106)	0.3(4)
N(1')-C(1')-C(2')-C(7')	174.2(3)	C(103)-C(104)-C(105)-C(41)	-175.5(3)
C(9')-C(1')-C(2')-C(7')	-8.7(5)	C(102)-C(101)-C(106)-C(105)	0.4(4)
N(1')-C(1')-C(2')-C(3')	-16.6(4)	C(21)-C(101)-C(106)-C(105)	-175.2(3)
C(9')-C(1')-C(2')-C(3')	160.5(3)	C(104)-C(105)-C(106)-C(101)	-0.2(4)
C(8')-N(2')-C(3')-C(2')	19.8(4)	C(41)-C(105)-C(106)-C(101)	175.6(3)
C(8')-N(2')-C(3')-C(4')	-164.0(3)	C(106)-C(101)-C(21)-C(22)	-31.7(4)
C(7')-C(2')-C(3')-N(2')	-179.0(3)	C(102)-C(101)-C(21)-C(22)	152.8(3)
C(1')-C(2')-C(3')-N(2')	11.5(4)	C(106)-C(101)-C(21)-C(26)	143.2(3)
C(7')-C(2')-C(3')-C(4')	4.7(5)	C(102)-C(101)-C(21)-C(26)	-32.2(4)
C(1')-C(2')-C(3')-C(4')	-164.8(3)	C(26)-C(21)-C(22)-C(23)	-1.6(4)
N(2')-C(3')-C(4')-C(5')	179.5(4)	C(101)-C(21)-C(22)-C(23)	173.4(3)
C(2')-C(3')-C(4')-C(5')	-4.4(5)	C(21)-C(22)-C(23)-C(24)	1.0(5)
C(3')-C(4')-C(5')-C(6')	0.6(7)	C(22)-C(23)-C(24)-C(25)	-0.1(5)
C(4')-C(5')-C(6')-C(7')	2.8(8)	C(22)-C(23)-C(24)-C(8)	-179.7(3)

N(2)-C(8)-C(24)-C(23)	-103.6(3)	C(8')-N(1')-C(61')-C(62')	-41.3(3)
N(1)-C(8)-C(24)-C(23)	19.7(4)	N(1')-C(61')-C(62')-C(63')	-179.2(3)
N(2)-C(8)-C(24)-C(25)	76.8(3)	C(66')-C(61')-C(62')-C(63')	58.1(4)
N(1)-C(8)-C(24)-C(25)	-160.0(3)	C(61')-C(62')-C(63')-C(64')	-59.5(4)
C(23)-C(24)-C(25)-C(26)	-0.3(5)	C(62')-C(63')-C(64')-C(65')	59.1(4)
C(8)-C(24)-C(25)-C(26)	179.4(3)	C(63')-C(64')-C(65')-C(66')	-55.5(4)
C(24)-C(25)-C(26)-C(21)	-0.4(5)	N(1')-C(61')-C(66')-C(65')	179.6(2)
C(22)-C(21)-C(26)-C(25)	1.3(4)	C(62')-C(61')-C(66')-C(65')	-55.8(3)
C(101)-C(21)-C(26)-C(25)	-173.8(3)	C(64')-C(65')-C(66')-C(61')	54.0(4)
C(102)-C(103)-C(31)-C(32)	-36.9(4)	C(1")-N(1")-C(71)-C(76)	-98.6(4)
C(104)-C(103)-C(31)-C(32)	147.0(3)	C(8")-N(1")-C(71)-C(76)	78.3(3)
C(102)-C(103)-C(31)-C(36)	139.2(3)	C(1")-N(1")-C(71)-C(72)	136.8(3)
C(104)-C(103)-C(31)-C(36)	-36.9(4)	C(8")-N(1")-C(71)-C(72)	-46.2(3)
C(36)-C(31)-C(32)-C(33)	-1.4(5)	N(1")-C(71)-C(72)-C(73)	176.1(3)
C(103)-C(31)-C(32)-C(33)	174.8(3)	C(76)-C(71)-C(72)-C(73)	53.3(4)
C(31)-C(32)-C(33)-C(34)	-0.3(5)	C(71)-C(72)-C(73)-C(74)	-57.2(4)
C(32)-C(33)-C(34)-C(35)	1.4(5)	C(72)-C(73)-C(74)-C(75)	59.1(4)
C(32)-C(33)-C(34)-C(8')	-176.3(3)	C(73)-C(74)-C(75)-C(76)	-57.2(4)
N(2')-C(8')-C(34)-C(35)	82.6(4)	N(1")-C(71)-C(76)-C(75)	-174.9(3)
N(1')-C(8')-C(34)-C(35)	-153.2(3)	C(72)-C(71)-C(76)-C(75)	-51.1(4)
N(2')-C(8')-C(34)-C(33)	-99.6(4)	C(74)-C(75)-C(76)-C(71)	53.3(4)
N(1')-C(8')-C(34)-C(33)	24.5(4)	O(1)-S(1)-C(97)-F(3)	179.8(3)
C(33)-C(34)-C(35)-C(36)	-0.8(5)	O(2)-S(1)-C(97)-F(3)	60.1(3)
C(8')-C(34)-C(35)-C(36)	177.1(3)	O(3)-S(1)-C(97)-F(3)	-60.1(3)
C(34)-C(35)-C(36)-C(31)	-0.8(5)	O(1)-S(1)-C(97)-F(1)	59.5(3)
C(32)-C(31)-C(36)-C(35)	1.9(5)	O(2)-S(1)-C(97)-F(1)	-60.3(3)
C(103)-C(31)-C(36)-C(35)	-174.3(3)	O(3)-S(1)-C(97)-F(1)	179.6(2)
C(104)-C(105)-C(41)-C(42)	-33.5(4)	O(1)-S(1)-C(97)-F(2)	-60.1(3)
C(106)-C(105)-C(41)-C(42)	150.8(3)	O(2)-S(1)-C(97)-F(2)	-179.8(2)
C(104)-C(105)-C(41)-C(46)	143.7(3)	O(3)-S(1)-C(97)-F(2)	60.1(3)
C(106)-C(105)-C(41)-C(46)	-32.0(4)	O(6)-S(2)-C(98)-F(5)	64.0(3)
C(46)-C(41)-C(42)-C(43)	-1.0(4)	O(5)-S(2)-C(98)-F(5)	-175.0(3)
C(105)-C(41)-C(42)-C(43)	176.3(3)	O(4)-S(2)-C(98)-F(5)	-56.8(3)
C(41)-C(42)-C(43)-C(44)	0.2(5)	O(6)-S(2)-C(98)-F(6)	-57.1(4)
C(42)-C(43)-C(44)-C(45)	0.7(4)	O(5)-S(2)-C(98)-F(6)	63.9(4)
C(42)-C(43)-C(44)-C(8")	-177.8(3)	O(4)-S(2)-C(98)-F(6)	-177.9(3)
N(2")-C(8")-C(44)-C(45)	67.5(4)	O(6)-S(2)-C(98)-F(4)	-177.2(3)
N(1")-C(8")-C(44)-C(45)	-169.4(3)	O(5)-S(2)-C(98)-F(4)	-56.1(3)
N(2")-C(8")-C(44)-C(43)	-114.0(3)	O(4)-S(2)-C(98)-F(4)	62.0(3)
N(1")-C(8")-C(44)-C(43)	9.1(4)	O(9)-S(3)-C(99)-F(7)	-59.9(3)
C(43)-C(44)-C(45)-C(46)	-0.6(4)	O(7)-S(3)-C(99)-F(7)	60.8(3)
C(8")-C(44)-C(45)-C(46)	177.9(3)	O(8)-S(3)-C(99)-F(7)	-179.7(3)
C(44)-C(45)-C(46)-C(41)	-0.2(4)	O(9)-S(3)-C(99)-F(9)	-179.4(3)
C(42)-C(41)-C(46)-C(45)	1.1(4)	O(7)-S(3)-C(99)-F(9)	-58.7(3)
C(105)-C(41)-C(46)-C(45)	-176.3(3)	O(8)-S(3)-C(99)-F(9)	60.8(3)
C(1')-N(1')-C(61')-C(66')	-95.2(3)	O(9)-S(3)-C(99)-F(8)	60.8(3)
C(8')-N(1')-C(61')-C(66')	83.0(3)	O(7)-S(3)-C(99)-F(8)	-178.5(3)
C(1')-N(1')-C(61')-C(62')	140.5(3)	O(8)-S(3)-C(99)-F(8)	-59.0(3)

6d. Table 7. Hydrogen bonds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(02)...O(8)	0.84(3)	2.18(3)	2.930(4)	148(4)
N(2')-H(02')...O(3)	0.84(3)	2.31(3)	3.066(3)	150(4)
N(2")-H(02")...O(6)	0.83(3)	2.38(3)	3.023(4)	135(3)
N(2")-H(02")...O(4)#1	0.83(3)	2.50(3)	3.171(4)	139(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+2,-z+1



View of the dimers formed in **6d** through N-H···O hydrogen bonding

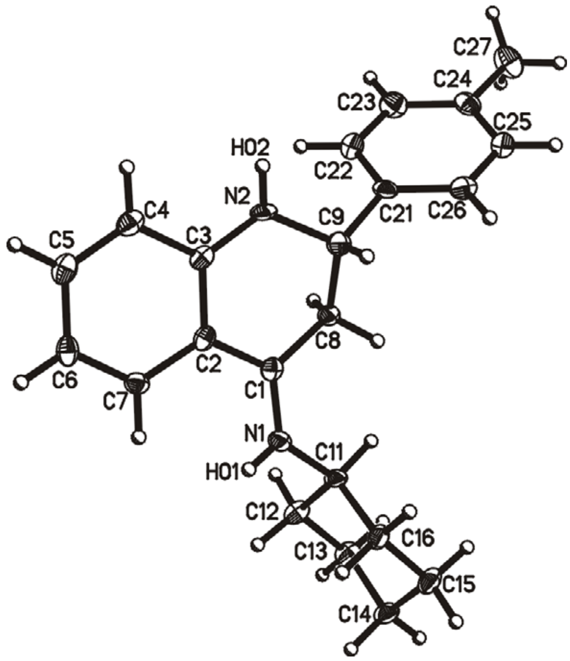


Table 1. Crystal data and structure refinement of **7d2**.

Identification code	ajf44bs	
Empirical formula	C24 H28 Cl3 F3 N2 O3 S	
Formula weight	587.89	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2(1)/n	
Unit cell dimensions	a = 11.8166(17) Å	α= 90°
	b = 16.328(2) Å	β= 102.356(3)°
	c = 13.928(2) Å	γ = 90°
Volume	2625.0(7) Å^3	
Z	4	
Density (calculated)	1.488 Mg/m^3	
Absorption coefficient	0.480 mm^{-1}	
F(000)	1216	
Crystal size	0.22 x 0.11 x 0.01 mm^3	
Theta range for data collection	1.95 to 28.75°	
Index ranges	-15<=h<=15, -21<=k<=21, -18<=l<=17	
Reflections collected	31789	
Independent reflections	6412 [R(int) = 0.0734]	
Completeness to theta = 27.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9952 and 0.8720	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6412 / 25 / 350	
Goodness-of-fit on F^2	1.242	
Final R indices [I>2sigma(I)]	R1 = 0.0959, wR2 = 0.1528	
R indices (all data)	R1 = 0.1243, wR2 = 0.1627	
Largest diff. peak and hole	0.720 and -0.455 e.Å^{-3}	

7d2. Table 2. Atomic coordinates (x 10^4) and equivalentisotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	4304(3)	4906(2)	2609(2)	18.2(7)
C(1)	5040(3)	4426(2)	3168(3)	15.1(7)
C(2)	5798(3)	4720(2)	4052(3)	15.7(7)
C(3)	6517(3)	4146(2)	4662(3)	15.2(7)
N(2)	6448(3)	3332(2)	4479(2)	19.9(7)
C(4)	7352(3)	4441(2)	5471(3)	20.4(8)
C(5)	7450(3)	5263(2)	5659(3)	20.9(8)
C(6)	6735(3)	5835(2)	5069(3)	19.0(8)
C(7)	5929(3)	5563(2)	4282(3)	16.9(7)
C(8)	5175(3)	3556(2)	2878(3)	16.5(7)
C(9)	5497(3)	2979(2)	3761(3)	18.4(8)
C(11)	3584(3)	4747(2)	1624(3)	17.3(8)
C(12)	3961(3)	5330(3)	894(3)	21.1(8)
C(13)	3173(3)	5245(3)	-119(3)	22.2(8)
C(14)	1911(3)	5400(2)	-75(3)	20.2(8)
C(15)	1541(3)	4798(3)	635(3)	21.9(8)
C(16)	2314(3)	4868(2)	1660(3)	18.4(8)
C(21)	5825(3)	2154(2)	3406(3)	17.0(8)
C(22)	6943(3)	2009(2)	3267(3)	24.0(9)
C(23)	7212(3)	1279(2)	2864(3)	24.7(9)
C(24)	6386(3)	676(2)	2570(3)	20.7(8)
C(25)	5274(3)	827(2)	2716(3)	22.0(8)
C(26)	4993(3)	1549(2)	3127(3)	20.9(8)
C(27)	6684(4)	-107(3)	2106(3)	30.9(10)
C(98)	5611(5)	2368(4)	-60(5)	26.2(18)
Cl(1)	6875(2)	2596.4(16)	723(3)	36.2(7)
Cl(2)	5130(3)	1351.0(18)	-55(3)	30.9(9)
Cl(3)	4510(2)	3077(2)	40(3)	33.8(7)
C(98')	5397(7)	2190(6)	649(8)	20(3)
Cl(1')	6747(5)	2475(4)	943(4)	27.4(13)
Cl(2')	5109(10)	1316(6)	-57(11)	88(4)
Cl(3')	4371(6)	2923(4)	225(5)	37.2(18)
C(99)	200(3)	2854(2)	1874(3)	23.8(9)
F(1)	-330(2)	2663.0(17)	959(2)	40.7(7)
F(2)	-446(2)	2560.6(17)	2465(2)	45.8(7)
F(3)	209(2)	3665.8(14)	1956(2)	36.8(7)
S(1)	1663.9(8)	2428.0(6)	2170.6(7)	17.9(2)
O(1)	2138(3)	2753(2)	3129(2)	44.6(9)
O(2)	1436(3)	1558.1(16)	2138(2)	30.2(7)
O(3)	2182(2)	2718.1(17)	1396(2)	27.9(7)

7d2. Table 3. Bond lengths [Å] and angles [°].

N(1)-C(1)	1.299(5)	C(6)-C(7)	1.363(5)
N(1)-C(11)	1.475(5)	C(8)-C(9)	1.530(5)
C(1)-C(2)	1.441(5)	C(9)-C(21)	1.515(5)
C(1)-C(8)	1.494(5)	C(11)-C(16)	1.525(5)
C(2)-C(7)	1.415(5)	C(11)-C(12)	1.526(5)
C(2)-C(3)	1.418(5)	C(12)-C(13)	1.522(5)
C(3)-N(2)	1.352(5)	C(13)-C(14)	1.526(5)
C(3)-C(4)	1.415(5)	C(14)-C(15)	1.523(5)
N(2)-C(9)	1.453(5)	C(15)-C(16)	1.526(5)
C(4)-C(5)	1.367(6)	C(21)-C(26)	1.388(5)
C(5)-C(6)	1.401(5)	C(21)-C(22)	1.396(5)

C(22)-C(23)	1.384(6)	C(21)-C(9)-C(8)	108.8(3)
C(23)-C(24)	1.384(5)	N(1)-C(11)-C(16)	108.8(3)
C(24)-C(25)	1.394(5)	N(1)-C(11)-C(12)	108.5(3)
C(24)-C(27)	1.508(5)	C(16)-C(11)-C(12)	111.8(3)
C(25)-C(26)	1.381(5)	C(13)-C(12)-C(11)	110.7(3)
C(98)-Cl(1)	1.692(6)	C(12)-C(13)-C(14)	110.9(3)
C(98)-Cl(2)	1.756(6)	C(15)-C(14)-C(13)	109.8(3)
C(98)-Cl(3)	1.770(6)	C(14)-C(15)-C(16)	111.2(3)
C(98')-Cl(1')	1.627(9)	C(11)-C(16)-C(15)	110.8(3)
C(98')-Cl(3')	1.717(9)	C(26)-C(21)-C(22)	118.4(3)
C(98')-Cl(2')	1.725(11)	C(26)-C(21)-C(9)	120.6(3)
C(99)-F(2)	1.327(5)	C(22)-C(21)-C(9)	120.7(3)
C(99)-F(3)	1.330(4)	C(23)-C(22)-C(21)	120.5(4)
C(99)-F(1)	1.332(5)	C(22)-C(23)-C(24)	121.6(4)
C(99)-S(1)	1.828(4)	C(23)-C(24)-C(25)	117.2(4)
S(1)-O(3)	1.430(3)	C(23)-C(24)-C(27)	121.0(4)
S(1)-O(1)	1.434(3)	C(25)-C(24)-C(27)	121.7(4)
S(1)-O(2)	1.445(3)	C(26)-C(25)-C(24)	121.9(4)
		C(25)-C(26)-C(21)	120.3(4)
C(1)-N(1)-C(11)	129.0(3)	Cl(1)-C(98)-Cl(2)	116.6(4)
N(1)-C(1)-C(2)	121.6(3)	Cl(1)-C(98)-Cl(3)	111.5(3)
N(1)-C(1)-C(8)	120.6(3)	Cl(2)-C(98)-Cl(3)	111.9(3)
C(2)-C(1)-C(8)	117.7(3)	Cl(1')-C(98')-Cl(3')	118.0(6)
C(7)-C(2)-C(3)	119.0(3)	Cl(1')-C(98')-Cl(2')	116.3(7)
C(7)-C(2)-C(1)	122.4(3)	Cl(3')-C(98')-Cl(2')	110.0(6)
C(3)-C(2)-C(1)	118.3(3)	F(2)-C(99)-F(3)	107.5(3)
N(2)-C(3)-C(4)	119.2(3)	F(2)-C(99)-F(1)	107.1(3)
N(2)-C(3)-C(2)	122.1(3)	F(3)-C(99)-F(1)	108.0(3)
C(4)-C(3)-C(2)	118.6(3)	F(2)-C(99)-S(1)	111.4(3)
C(3)-N(2)-C(9)	121.7(3)	F(3)-C(99)-S(1)	111.8(3)
C(5)-C(4)-C(3)	120.2(4)	F(1)-C(99)-S(1)	110.9(3)
C(4)-C(5)-C(6)	121.8(4)	O(3)-S(1)-O(1)	115.8(2)
C(7)-C(6)-C(5)	118.9(4)	O(3)-S(1)-O(2)	114.17(18)
C(6)-C(7)-C(2)	121.5(3)	O(1)-S(1)-O(2)	115.2(2)
C(1)-C(8)-C(9)	113.0(3)	O(3)-S(1)-C(99)	103.94(18)
N(2)-C(9)-C(21)	111.3(3)	O(1)-S(1)-C(99)	103.4(2)
N(2)-C(9)-C(8)	109.4(3)	O(2)-S(1)-C(99)	101.89(18)

7d2. Table 4. Anisotropic displacement parameters ($Å^2$x 10^3). The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	19.6(15)	13.6(16)	19.4(17)	-3.0(13)	-0.1(13)	3.8(13)
C(1)	11.6(16)	17.7(18)	17.7(18)	1.8(14)	6.9(14)	-1.7(14)
C(2)	13.1(16)	20.4(19)	13.9(17)	-1.5(14)	3.4(14)	-2.0(14)
C(3)	13.6(16)	21.3(19)	11.1(17)	1.4(14)	3.3(13)	-0.7(14)
N(2)	22.4(17)	17.5(16)	15.4(16)	4.8(13)	-5.8(13)	5.2(13)
C(4)	16.5(18)	27(2)	17.4(19)	4.4(16)	2.2(15)	-1.0(16)
C(5)	20.4(18)	28(2)	14.7(18)	-1.7(16)	4.2(15)	-4.4(16)
C(6)	19.1(18)	20.5(19)	19.1(19)	-4.4(16)	8.0(15)	-6.1(15)
C(7)	15.7(17)	15.7(18)	19.6(19)	1.3(15)	4.4(14)	2.3(14)
C(8)	18.4(18)	15.1(18)	14.1(18)	-0.2(14)	-0.8(14)	1.3(14)
C(9)	19.1(18)	17.7(19)	17.8(19)	-0.9(15)	2.3(15)	1.0(15)
C(11)	18.5(18)	15.1(18)	14.7(18)	-2.3(14)	-4.5(14)	4.9(14)
C(12)	15.0(17)	28(2)	20(2)	0.9(16)	3.0(15)	1.5(16)
C(13)	23.2(19)	25(2)	17.7(19)	4.8(16)	3.6(15)	0.7(17)
C(14)	17.6(18)	23(2)	16.9(19)	1.8(15)	-2.5(15)	3.6(16)
C(15)	16.5(18)	28(2)	19(2)	3.3(16)	-2.8(15)	-3.7(16)

C(16)	16.0(17)	20(2)	17.5(19)	1.0(15)	-0.6(14)	-3.5(15)
C(21)	22.0(18)	13.8(18)	13.3(18)	3.5(14)	-0.1(14)	4.0(15)
C(22)	18.5(19)	24(2)	28(2)	0.5(17)	0.7(16)	-3.2(16)
C(23)	20.8(19)	25(2)	30(2)	1.2(18)	9.8(17)	3.3(17)
C(24)	27(2)	18.5(19)	16.7(19)	3.9(15)	6.2(16)	1.0(16)
C(25)	20.0(19)	21(2)	24(2)	0.8(16)	2.1(16)	-2.4(16)
C(26)	18.4(18)	23(2)	21(2)	3.7(16)	4.0(15)	3.3(15)
C(27)	39(2)	24(2)	34(2)	-6.5(19)	17(2)	-0.1(19)
C(98)	22(3)	27(4)	29(4)	-3(3)	4(3)	0(3)
Cl(1)	21.4(10)	28.3(11)	61.0(17)	13.0(11)	13.5(10)	-1.0(7)
Cl(2)	27.4(11)	17.3(10)	50.1(16)	-8.4(7)	13.2(8)	-6.9(6)
Cl(3)	17.9(10)	31.3(13)	48.3(16)	0.7(13)	-1.7(10)	9.5(9)
C(99)	20.7(19)	15.6(19)	36(2)	-0.1(17)	8.9(17)	-0.3(15)
F(1)	26.2(13)	42.4(16)	44.2(16)	-2.2(13)	-13.3(12)	4.3(12)
F(2)	38.9(15)	39.0(16)	69(2)	6.0(15)	32.4(14)	-4.1(13)
F(3)	28.2(13)	17.8(13)	65.7(19)	-0.9(12)	13.2(13)	5.3(10)
S(1)	18.4(4)	13.6(4)	19.5(5)	-1.4(4)	-1.1(3)	0.5(4)
O(1)	51(2)	42(2)	30.3(18)	-11.9(15)	-14.4(15)	4.5(16)
O(2)	33.2(16)	14.3(14)	42.1(18)	2.3(13)	6.0(14)	-1.0(12)
O(3)	25.0(15)	20.7(15)	40.7(18)	0.9(13)	13.1(13)	-1.7(12)

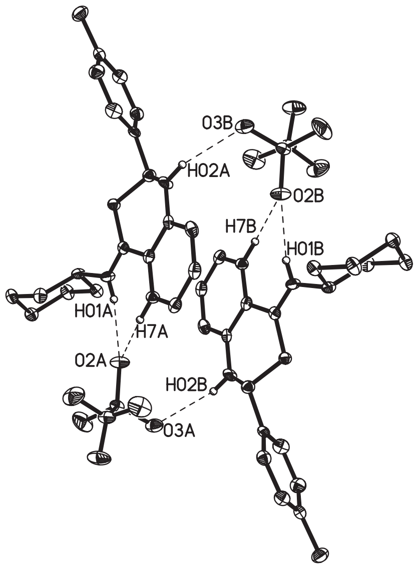
7d2. Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(01)	4240(40)	5360(30)	2790(30)	22
H(02)	6780(30)	3020(20)	4930(20)	24(12)
H(4)	7847	4068	5885	24
H(5)	8017	5451	6204	25
H(6)	6811	6403	5215	23
H(7)	5445	5949	3879	20
H(8A)	5784	3526	2489	20
H(8B)	4440	3368	2453	20
H(9)	4812	2911	4069	22
H(11)	3705	4169	1430	21
H(12A)	3935	5901	1128	25
H(12B)	4769	5205	853	25
H(13A)	3250	4687	-376	27
H(13B)	3412	5642	-575	27
H(14A)	1822	5968	146	24
H(14B)	1411	5333	-738	24
H(15A)	1582	4233	387	26
H(15B)	727	4909	671	26
H(16A)	2212	5415	1938	22
H(16B)	2084	4450	2096	22
H(22)	7524	2416	3452	29
H(23)	7981	1189	2787	30
H(25)	4692	422	2528	26
H(26)	4228	1632	3220	25
H(27A)	6865	15	1467	46
H(27B)	6023	-483	2016	46
H(27C)	7358	-362	2535	46
H(98)	5763	2455	-732	31
H(98')	5222	2023	1293	24

7d2. Table 6. Hydrogen bonds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(01)...O(2)#1	0.79(4)	2.12(4)	2.880(4)	160(4)
C(7)-H(7)...O(2)#1	0.95	2.57	3.463(5)	157.6
N(2)-H(02)...O(3)#2	0.840(19)	2.33(2)	3.136(4)	161(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+1/2 #2 x+1/2,-y+1/2,z+1/2



View of the dimers formed in **7d2** through N-H···O and CH···O hydrogen bonding

Cyclic voltammetry. *Experimental details*: Square Wave Voltammetry was performed at 297 K using a home-made computer-driven potentiostat-galvanostat. A three-electrode cell was employed in the experiments with a gold ball of radius 0.0113 cm as working electrode. The counter electrode was a Pt foil, and the reference electrode was a saturated calomel electrode (SCE). Nitrogen gas was passed through the solutions for de-aeration for 20 min prior to measurements, with nitrogen atmosphere maintained over the solution during all the experiments. Pulse time 50 ms. Step amplitude 5 mV. Square wave amplitude 50 mV. The results are the mean of the five experimental values. The errors correspond to the standard deviation. Acetonitrile solutions of **3d5** (0.17 mM) and **7d5** (0.182 mmol) with 0.1 M $LiClO_4$ as supporting electrolyte were used and the cyclic voltammograms were obtained at 100 mVs^{-1}. The value of the reduction potential is referenced to the redox couple $[Fe(C_5H_5)_2]^{+/0}$ (E_0^{red} = 320 mV *vs* SCE).

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