Electronic Supplementary Information

Nitro and amino BODIPYS: Crucial substituents to modulate their photonic behavior

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BODIPY dyes **1**[1] and **2**[2] were synthesized by the methods previously described.

General procedure for the nitration reactions

To a stirred solution of BODIPY (1 equiv) in Ac_2O was added HNO_3 (2-4 equiv) at 0 ºC under an argon atmosphere. The mixture was stirred for 10-30 min and after that time, the solvent was removed under reduced pressure. The products were purified by flash chromatography on silica gel (eluent hexane/EtOAc).

General procedure for the reduction reactions

A solution of the corresponding nitro-BODIPY in EtOAc was hydrogenated in an H-Cube continuous flow reactor with a flow rate of 1.0 mL/min, full pressure of hydrogen, at 40 ºC, and using a 10% Pd/C CatCart^{TM} cartridge. The solvent was removed under reduced pressure and the product was obtained in quantitative yield

Reactions of BODIPYs 1-2 with HNO_3/Ac_2O

Nitration of BODIPY 1. According to general procedure, BODIPY **1** (100 mg, 0.33 mmol), HNO_3 (0.03 mL, 0.66 mmol) in Ac_2O (15 mL) for 10 min were reacted. Flash chromatography using hexane/EtOAc (8:2) afforded, by order of elution, 2-ethyl-4,4-difluoro-1,3,8-trimethyl-6-nitro-4-bora-3a,4a-diaza-*s*-indacene (**3**) (11 mg, 11%) as a yellow solid and 2-ethyl-4,4-difluoro-1,3,8-trimethyl-5-nitro-4-bora-3a,4a-diaza-*s*-indacene (**4**) (37 mg, 37%) as a yellow solid.

*Compound **3**:* m.p. 238.0-239.0 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (1 H, s, H-5), 7.30 (1 H, s, H-7), 2.57 (3 H, s, CH_3-C3), 2.52 (3 H, s, CH_3-C8), 2.40 (2 H, q, J = 7.5 Hz, CH_2), 2.33 (3 H, s, CH_3-C1), 1.03 (3 H, t, J = 7.5 Hz, $C\underline{H}_3CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.2 (C), 143.5 (C), 140.2 (C), 139.1 (C), 138.6 (C), 137.4 (C), 132.2 (C), 130.9 (CH), 113.6 (CH), 17.1 (CH_2), 16.1 (CH_3), 14.4 (CH_3), 14.1 (CH_3), 13.8 (CH_3); IR (neat): 1596, 1505, 1367, 1298, 1086, 979, 757 cm^{-1}; HRMS-ESI$^+$: calcd for ($C_{14}H_{16}BF_2N_3O_2$+H$^+$) 308.1376 found 308.1385.

*Compound **4**:* m.p. 166.9-168.0 ºC; ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.10 (1 H, d, J = 4.2 Hz, H-6), 6.77 (1 H, d, J = 4.9 Hz, H-7), 2.62 (3 H, s, CH_3-C3), 2.53 (3 H, s, CH_3-C8), 2.40 (2 H, q, J = 7.7 Hz, CH_2), 2.32 (3 H, s, CH_3-C1), 1.03 (3 H, t, J = 7.7 Hz,

[1] J. Bañuelos Prieto, A. R. Agarrabeitia, I. Garcia-Moreno, I. López Arbeloa, A. Costela, L. Infantes, M. E. Pérez-Ojeda, M. Palacios Cuesta, M. J. Ortiz, *Chem. Eur. J.* **2010,** *16,* 14094-14105.
[2] A. Cui, X. Peng, J. Fan, X. Chen, Y. Wu, B. Guo *J. Photochem. Photobiol. A* **2007**, *186*, 85-92.

CH_3CH_2); ^{13}C NMR (176 MHz, $CDCl_3$): δ 170.1 (C), 147.2 (C), 143.2 (C), 139.8 (C), 138.2 (C), 137.8 (C), 135.2 (C), 117.7 (CH), 114.6 (CH), 17.2 (CH_2), 15.9 (CH_3), 14.4 (CH_3), 14.1 (CH_3), 14.0 (CH_3); IR (neat): 1604, 1296, 1160, 1119, 1018, 750 cm^{-1}; HRMS-ESI^+: calcd for ($C_{14}H_{16}BF_2N_3O_2$+H^+) 308.1376 found 308.1384.

Nitration of BODIPY 2. According to general procedure, BODIPY **2** (100 mg, 0.35 mmol), HNO_3 (0.06 mL, 1.4 mmol) in Ac_2O (15 mL) for 10 min were reacted. Flash chromatography using hexane/EtOAc (8:2) afforded, by order of elution, 4,4-difluoro-2-nitro-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (**5**) (7 mg, 6%) as a yellow solid and 4,4-difluoro-3-nitro-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (**6**) (41 mg, 36%) as a yellow solid.

*Compound **5**:* ^1H NMR (700 MHz, $CDCl_3$): δ 8.28 (1 H, s, H-3), 8.17 (1 H, s, H-5), 7.42 (2 H, d, *J* = 8.4 Hz, H-2´), 7.34 (2 H, d, *J* = 8.4 Hz, H-3´), 7.27 (1 H, s, H-1), 7.17 (1 H, d, *J* = 4.9 Hz, H-7), 6.71 (1 H, d, *J* = 4.9 Hz, H-6), 2.44 (3 H, s, CH_3); ^{13}C NMR (176 MHz, $CDCl_3$): δ 151.2 (CH), 150.0 (C), 143.1 (C), 141.7 (C), 137.6 (C), 136.1 (CH), 135.2 (CH), 131.9 (C), 130.7 (2 CH), 129.8 (2 CH), 129.7 (C), 122.3 (CH), 122.0 (CH), 21.6 (CH_3); IR (neat): 1590, 1298, 1108, 1051, 756 cm^{-1}; HRMS-ESI^-: calcd for ($C_{16}H_{12}BF_2N_3O_2$) 327.0996 found 327.1013.

*Compound **6**:* m.p. 192.5-193.0 ºC; ^1H NMR (300 MHz, $CDCl_3$): δ 8.23 (1 H, s, H-5), 7.38 (2 H, d, *J* = 8.1 Hz, H-2´), 7.31 (2 H, d, *J* = 8.1 Hz, H-3´), 7.14 (1 H, d, *J* = 4.5 Hz, H-2), 7.10 (1 H, d, *J* = 4.5 Hz, H-7), 6.73 (1 H, dd, *J* = 4.5 and 1.2 Hz, H-6), 6.71 (1 H, d, *J* = 4.5 Hz, H-1), 2.43 (3 H, s, CH_3); ^{13}C NMR (176 MHz, $CDCl_3$): δ 152.0 (CH), 149.5 (C), 148.4 (C), 141.6 (C), 136.7 (C), 135.1 (CH), 133.4 (C), 129.8 (2 CH), 128.8 (C), 128.6 (2 CH), 125.5 (CH), 122.5 (CH), 113.8 (CH), 20.5 (CH_3); IR (neat): 1600, 1498, 1278, 1100, 990, 759 cm^{-1}; HRMS-ESI^-: calcd for ($C_{16}H_{12}BF_2N_3O_2$) 327.0996 found 327.1022.

Independent synthesis of 2-ethyl-4,4-difluoro-1,3,8-trimethyl-6-nitro-4-bora-3a,4a-diaza-*s*-indacene (3).

To a solution of 2-acetyl-4-nitro-1*H*-pyrrole[3] (**10**) (500 mg, 3.25 mmol) in $CHCl_3$ (10 mL) was added $POCl_3$ (1.5 mL, 16.25 mmol), and the mixture was stirred for 30 min at rt. Then, 3-ethyl-2,4-dimethyl-1*H*-pyrrole (0.44 mL, 3.25 mmol) in $CHCl_3$ (5 mL) was

[3] H. Oda, T. Hanami, T. Iwashita, M. Kojima, M. Itoh, Y. Hayashizaki, *Tetrahedron*, **2007**, *63*, 12747-12753.

added and the resulting solution was stirred for 12 h at rt. Triethylamine (0.5 mL, 3.25 mmol) was added, followed by an addition of $BF_3{\cdot}Et_2O$ (0.4 mL, 3.25 mmol), and stirring was continued for 3 h before being quenched with 10% aqueous HCl and extracted with CH_2Cl_2. The organic extracts were washed with H_2O, dried over $MgSO_4$, filtered and evaporated to dryness. Flash chromatography using hexane/EtOAc (8:2) afforded **3** (200 mg, 24%).

Nitration of (1*H*-pyrrol-2-yl) (4-tolyl) methanone (11). According to general procedure, compound **11**[4] (200 mg, 1.17 mmol), HNO_3 (0.1 mL, 2.2 mmol) in Ac_2O (5 mL) for 30 min were reacted. Flash chromatography using hexane/EtOAc (95:5) afforded, by order of elution, (5-nitro-1*H*-pyrrol-2-yl) (4-tolyl) methanone (**12**) (82 mg, 32%) as a yellow solid and (4-nitro-1*H*-pyrrol-2-yl) (4-tolyl) methanone (**13**) (66 mg, 26%) as a yellow solid.

*Compound **12**:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.35 (NH), 7.76 (2 H, d, *J* = 8.1 Hz, 4-tolyl), 7.27 (2 H, d, *J* = 8.1 Hz, 4-tolyl), 7.07-7.05 (1 H, m, pyrrol), 6.80-6.79 (1 H, m, pyrrol), 2.40 (3 H, s, CH_3); ^{13}C NMR (75 MHz, C_3D_6O): δ 185.5 (CO), 152.4 (C), 144.7 (C), 138.1 (C), 135.6 (C), 130.2 (2 CH), 130.1 (2 CH), 118.1 (CH), 110.9 (CH), 21.6 (CH_3); IR (neat): 3130, 1618, 1490, 1317, 1101, 790 cm^{-1}; HRMS-EI: calcd for ($C_{12}H_{10}N_2O_3$) 230.0691 found 230.0687.

*Compound **13**:* ^{1}H NMR (300 MHz, C_3D_6O): δ 12.02 (NH), 8.14-8.12 (1 H, m, pyrrol), 7.89 (2 H, d, *J* = 8.1 Hz, 4-tolyl), 7.42 (2 H, d, *J* = 8.1 Hz, 4-tolyl), 7.35-7.34 (1 H, m, pyrrol), 2.46 (3 H, s, CH_3); ^{13}C NMR (75 MHz, C_3D_6O): δ 185.0 (CO), 144.8 (C), 139 .0 (C), 135.7 (C), 131.6 (C), 130.6 (2 CH), 130.3 (2 CH), 125.7 (CH), 112.8 (CH), 22.0 (CH_3); IR (neat): 3138, 1615, 1502, 1327, 1112, 782 cm^{-1}; HRMS-EI: calcd for ($C_{12}H_{10}N_2O_3$) 230.0691 found 230.0633.

Independent synthesis of 4,4-difluoro-2-nitro-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (5).

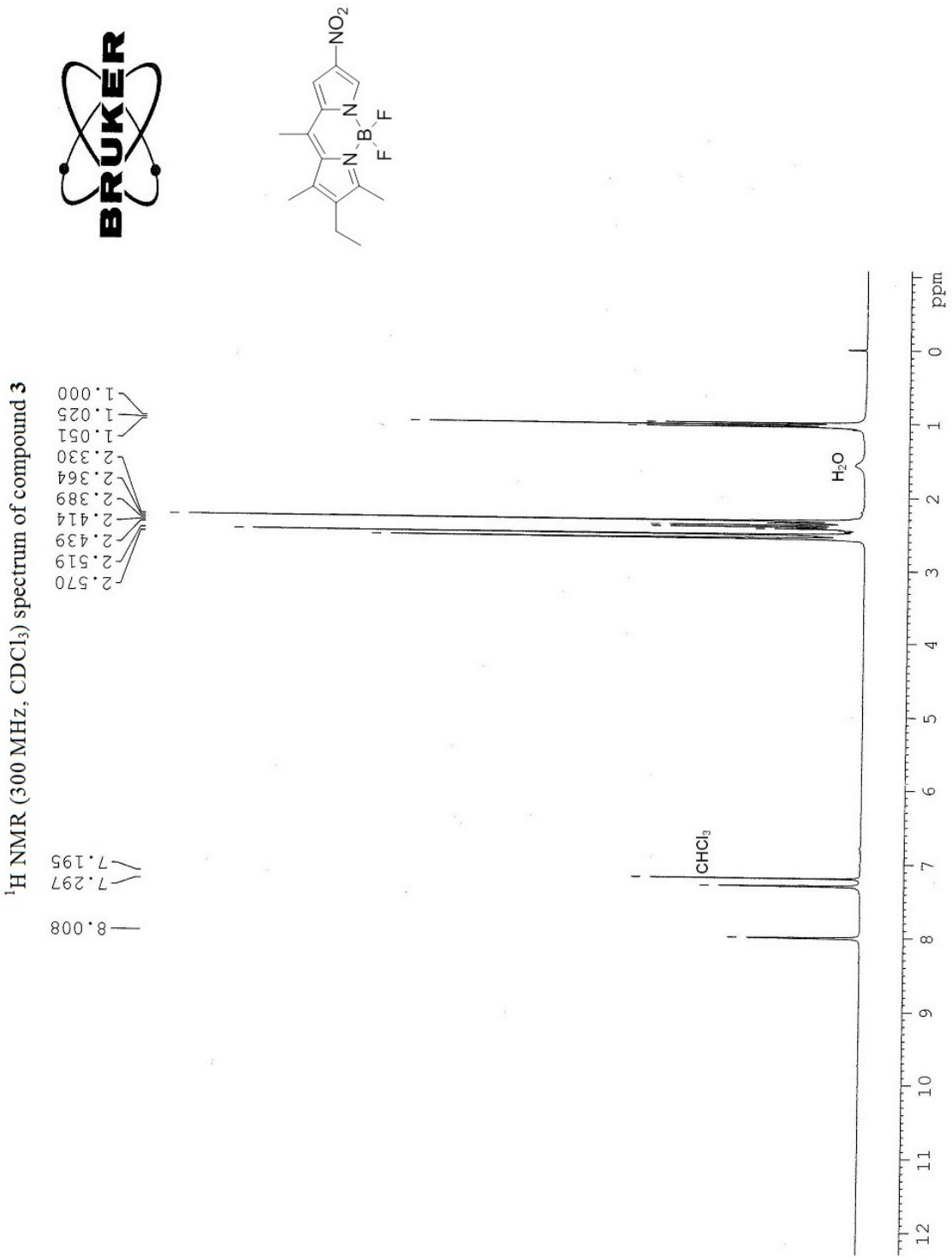
To a solution of **12** (90 mg, 0.42 mmol) in $CHCl_3$ (10 mL) was added $POCl_3$ (0.1 mL, 1.08 mmol), and the mixture was stirred for 30 min at rt. Then, pyrrole (0.04 mL, 0.3 mmol) in $CHCl_3$ (5 mL) was added and the resulting solution was stirred for 2 h at rt. Triethylamine (2 mL, 13 mmol) was added, followed by an addition of $BF_3{\cdot}Et_2O$ (2 mL, 13 mmol), and stirring was continued for 2 h before being quenched with 10% aqueous

[4] A. R. Katritzky, K. Suzuki, S. K. Singh, H.-Y. He, *J. Org. Chem*. **2003**, *68*, 5720-5723.

HCl and extracted with CH_2Cl_2. The organic extracts were washed with water, dried over $MgSO_4$, filtered and evaporated to dryness. Flash chromatography using hexane/EtOAc (9:1) afforded **5** (6 mg, 6%).

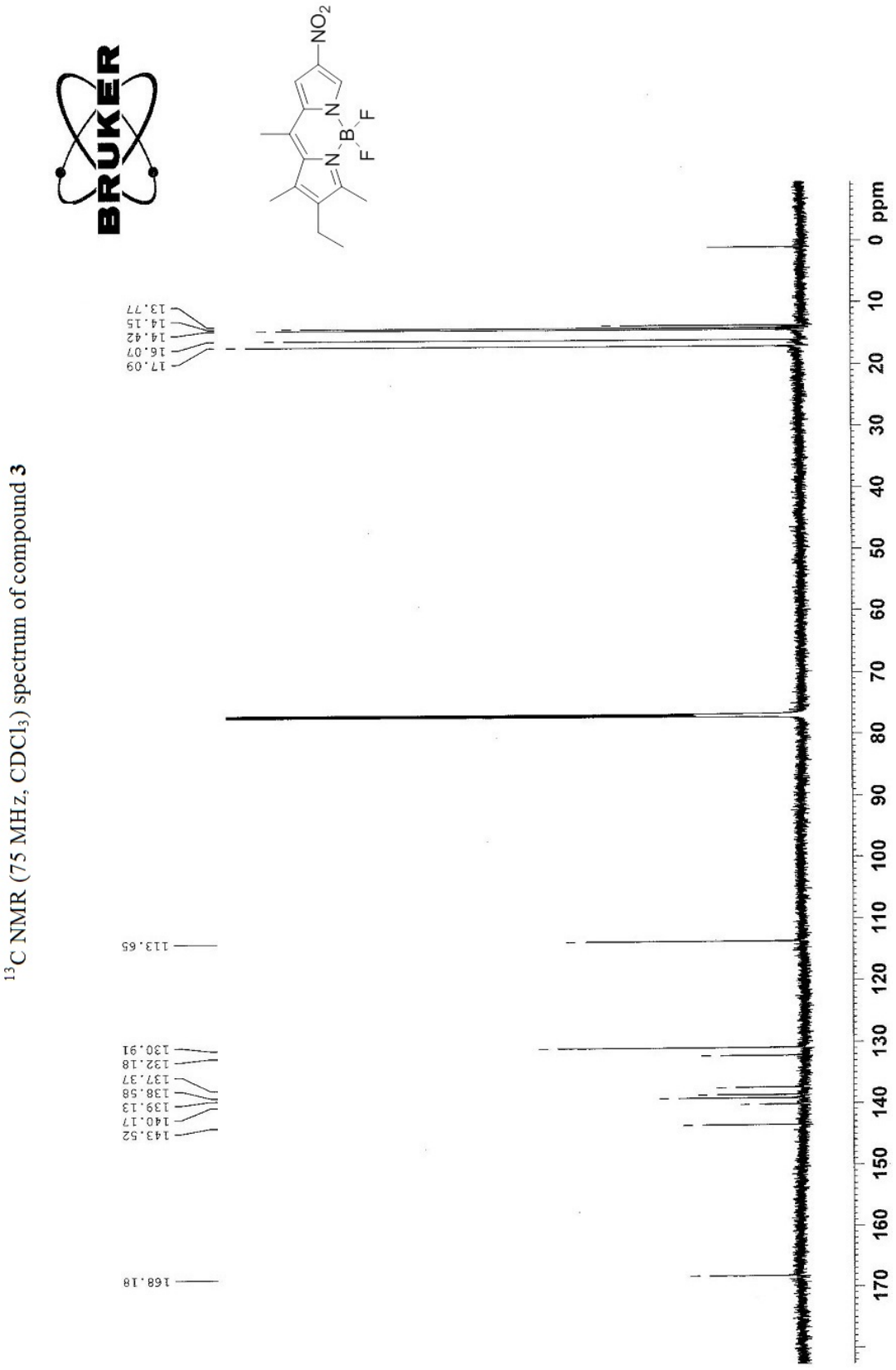
Synthesis of 5-amino-2-ethyl-4,4-difluoro-1,3,8-trimethyl-4-bora-3a,4a-diaza-*s*-indacene (7). According to general procedure, BODIPY **4** (37 mg, 0.12 mmol) in EtOAc (25 mL) was hydrogenated, yielding **7** (33 mg, 99%) as an orange solid. m.p. 230.8-231.8 ºC; ^{1}H NMR (700 MHz, C_6D_6): δ 6.61 (1 H, d, J = 2.1 Hz, H-7), 5.16 (1 H, d, J = 2.1 Hz, H-6), 4.51 (2 H, broad s, NH_2), 2.66 (3 H, s, CH_3), 2.23 (2 H, q, J = 7.7 Hz, CH_2), 1.96 (3 H, s, CH_3), 1.84 (3 H, s, CH_3), 0.95 (3 H, t, J = 7.7 Hz, $C\underline{H}_3CH_2$); ^{13}C NMR (176 MHz, C_6D_6): δ 158.1 (C-NH_2), 144.8 (C), 132.0 (C), 131.3 (C), 129.7 (C), 129.5 (CH), 129.4 (C), 106.8 (CH), 17.2 (CH_2), 15.7 (CH_3), 15.3 (CH_3), 12.7 (CH_3), 12.1 (CH_3); IR (neat): 3382, 1637, 1590, 1480, 1325, 1226, 1159, 772 cm^{-1}; HRMS-ESI$^-$: calcd for ($C_{14}H_{18}BF_2N_3$-H$^+$) 276.1489 found 276.1498.

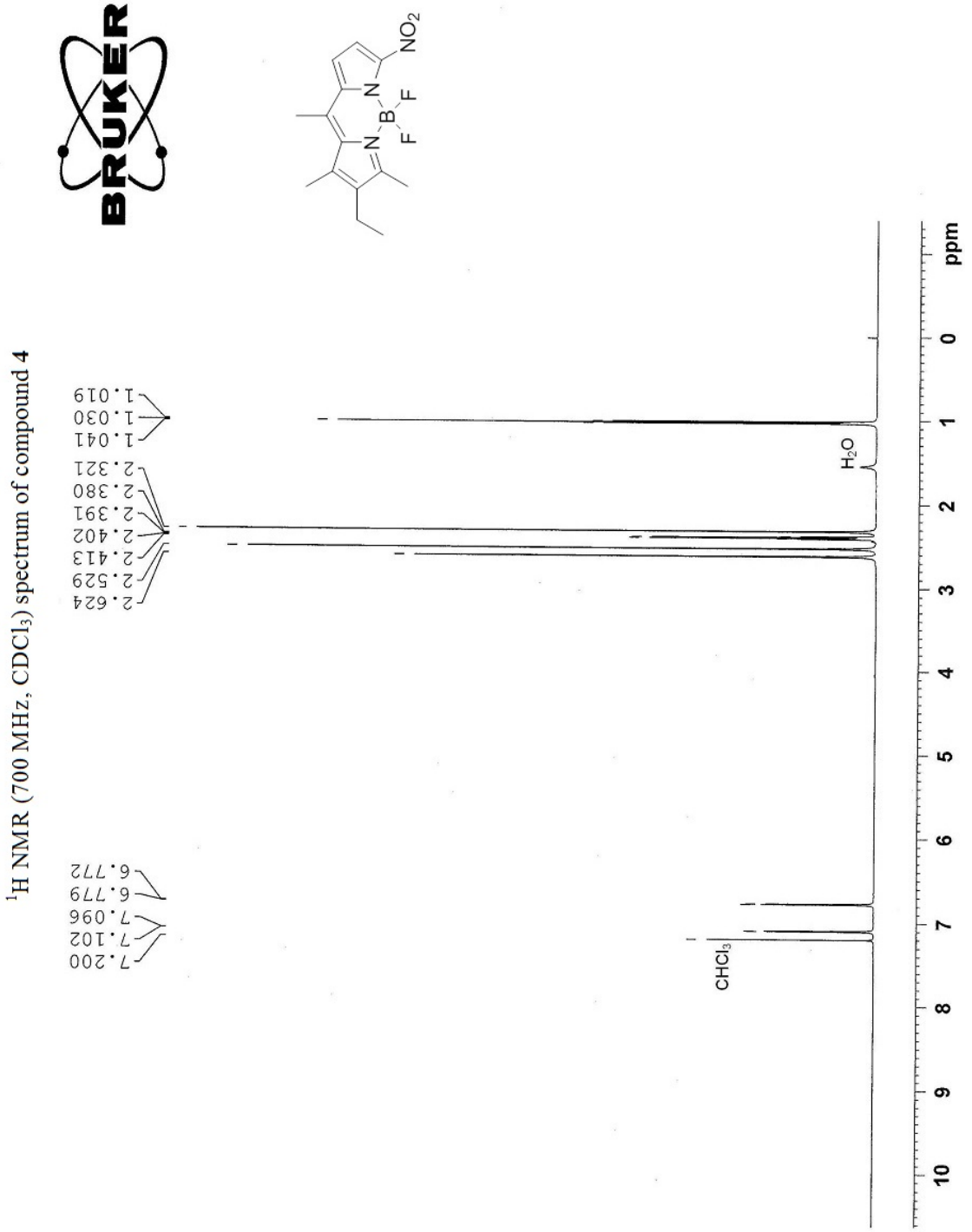
Synthesis of 3-amino-4,4-difluoro-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (8). According to general procedure, BODIPY **6** (23 mg, 0.07 mmol) in EtOAc (25 mL) was hydrogenated, yielding **8** (20 mg, 99%) as an orange solid. m.p. 192.0-193.0 ºC; ^{1}H NMR (300 MHz, C_6D_6): δ 7.75 (1 H, broad s, H-5), 7.07 (2 H, d, J = 8.1 Hz, H-2´), 6.85 (2 H, d, J = 8.1 Hz, H-3´), 6.53 (1 H, d, J = 3.3 Hz, H-7), 6.46 (1 H, d, J = 4.8 Hz, H-1), 6.28 (1 H, dd, J = 3.3 and 2.4 Hz, H-6), 5.08 (1 H, d, J = 4.8 Hz, H-2), 4.77 (2 H, broad s, NH_2), 2.06 (3 H, s, CH_3); ^{13}C NMR (176 MHz, C_6D_6): δ 159.2 (C-NH_2), 137.4 (C), 133.5 (CH), 133.3 (C), 131.7 (C), 131.5 (C), 131.0 (CH), 130.6 (C), 128.9 (2 CH), 127.3 (2 CH), 119.5 (CH), 112.4 (CH), 110.4 (CH), 19.5 (CH_3); IR (neat): 3375, 1643, 1582, 1400, 1167, 1056, 741 cm^{-1}; HRMS-ESI$^-$: calcd for ($C_{16}H_{14}BF_2N_3$-H$^+$) 296.1176 found 296.1187.



^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **3**

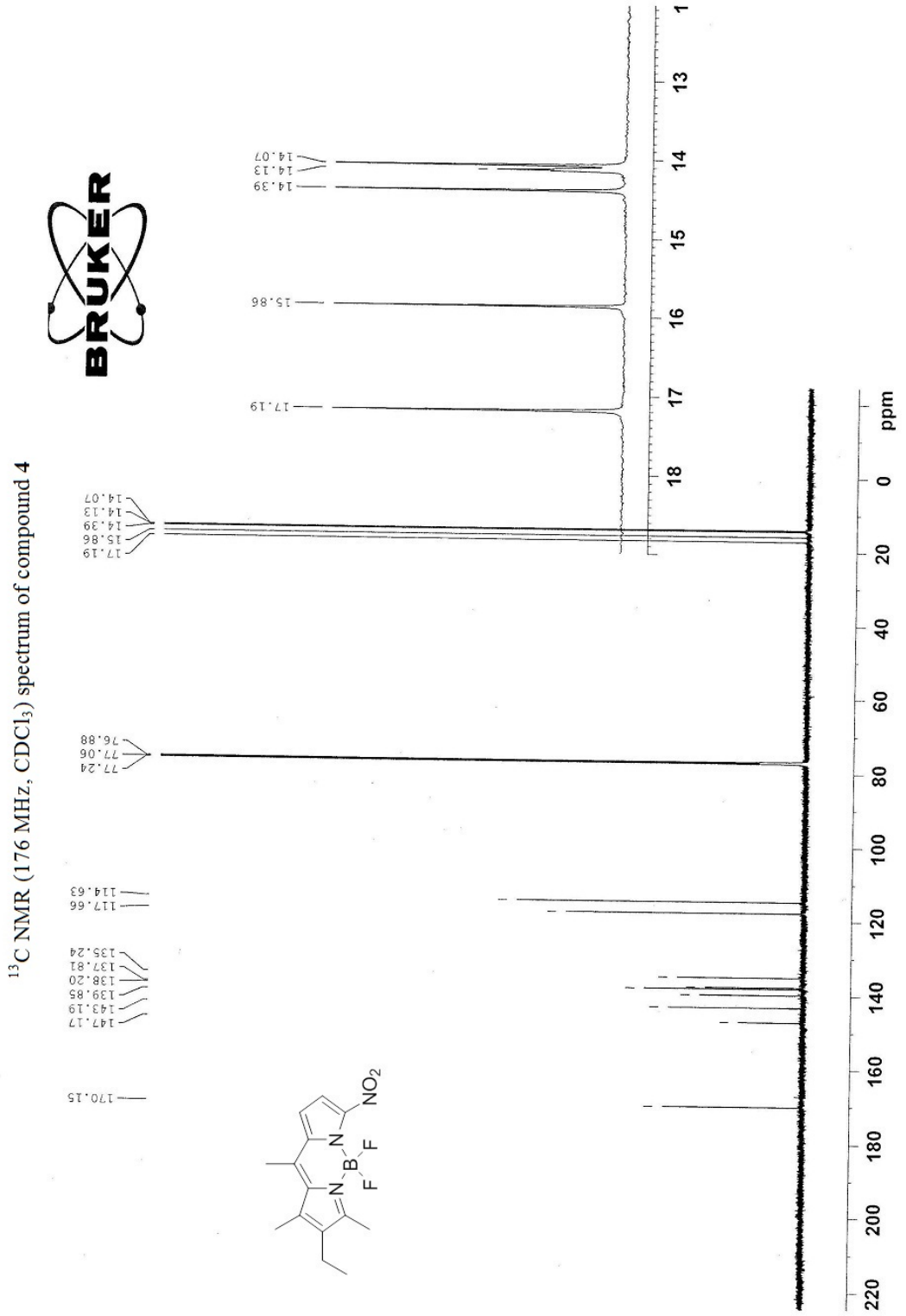
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **3**



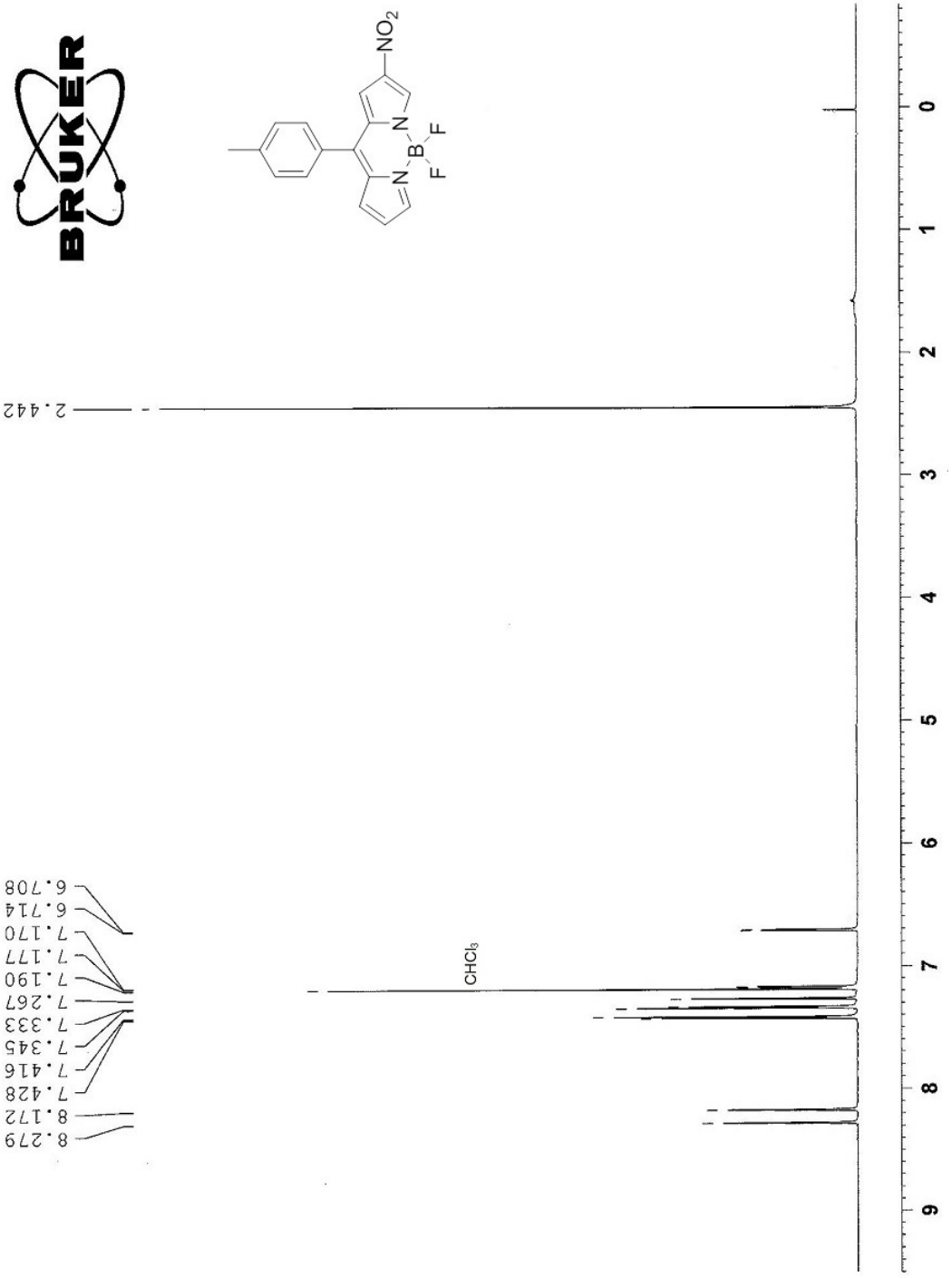


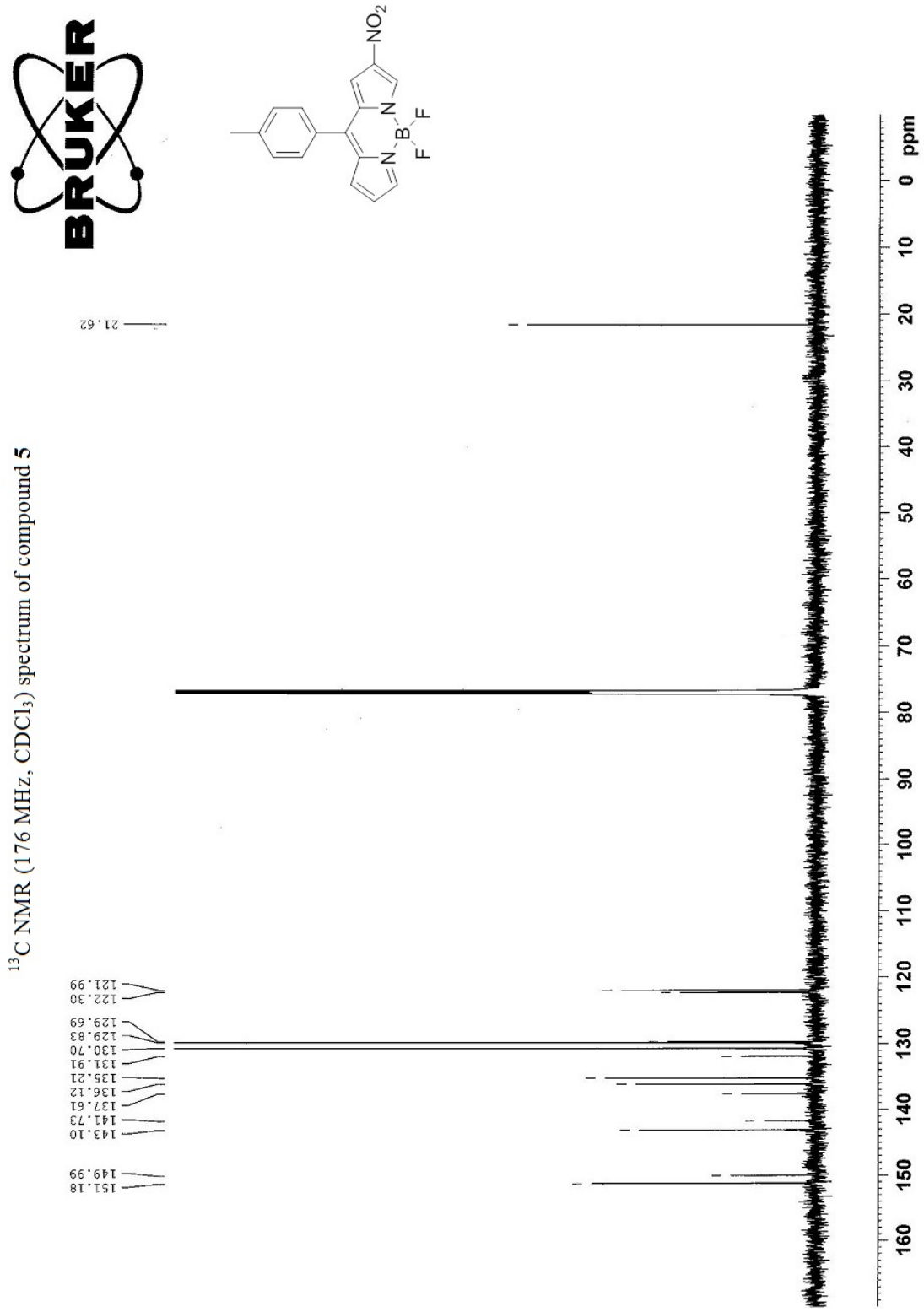
^{1}H NMR (700 MHz, $CDCl_3$) spectrum of compound **4**

^{13}C NMR (176 MHz, $CDCl_3$) spectrum of compound **4**

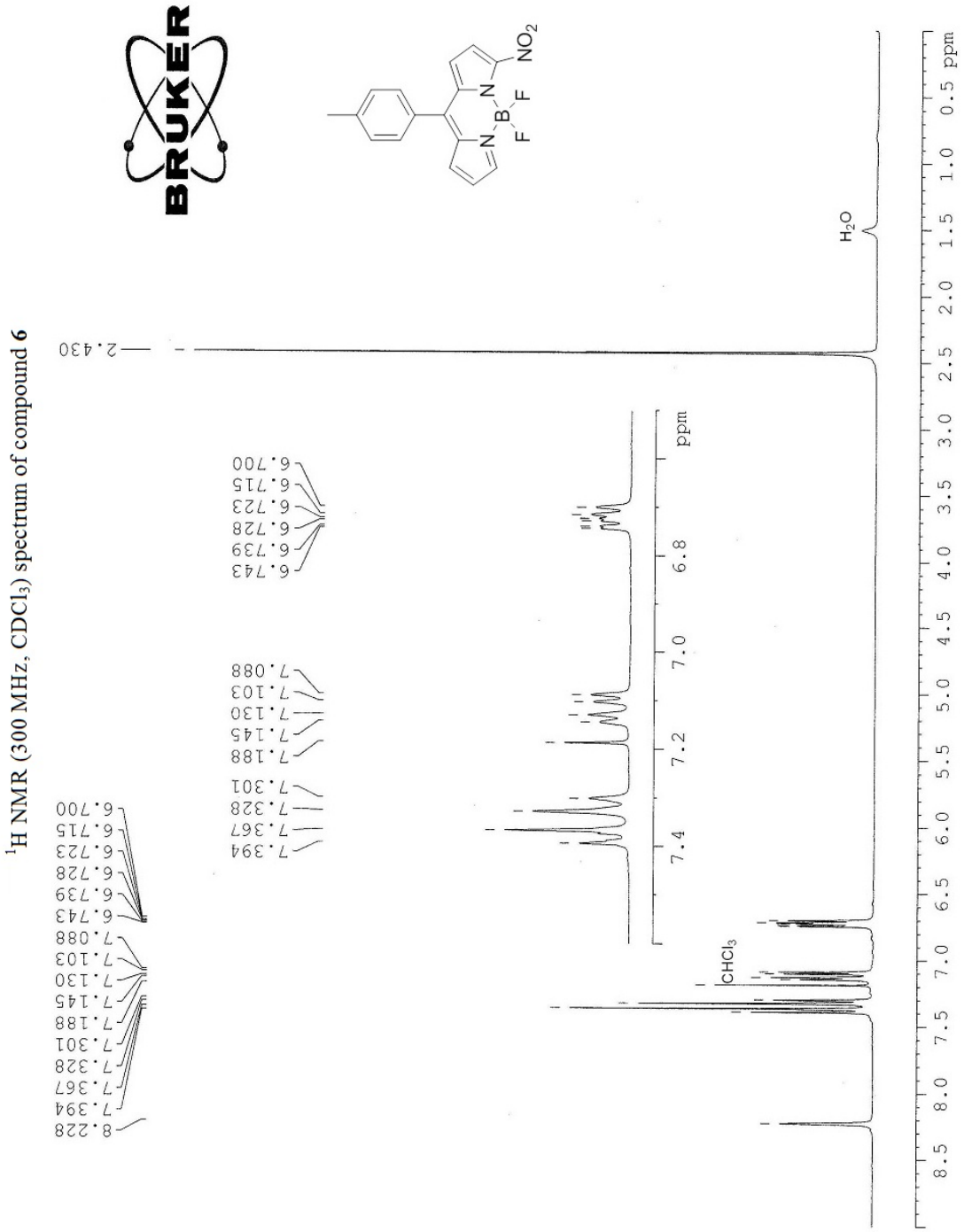


^{1}H NMR (700 MHz, $CDCl_3$) spectrum of compound **5**



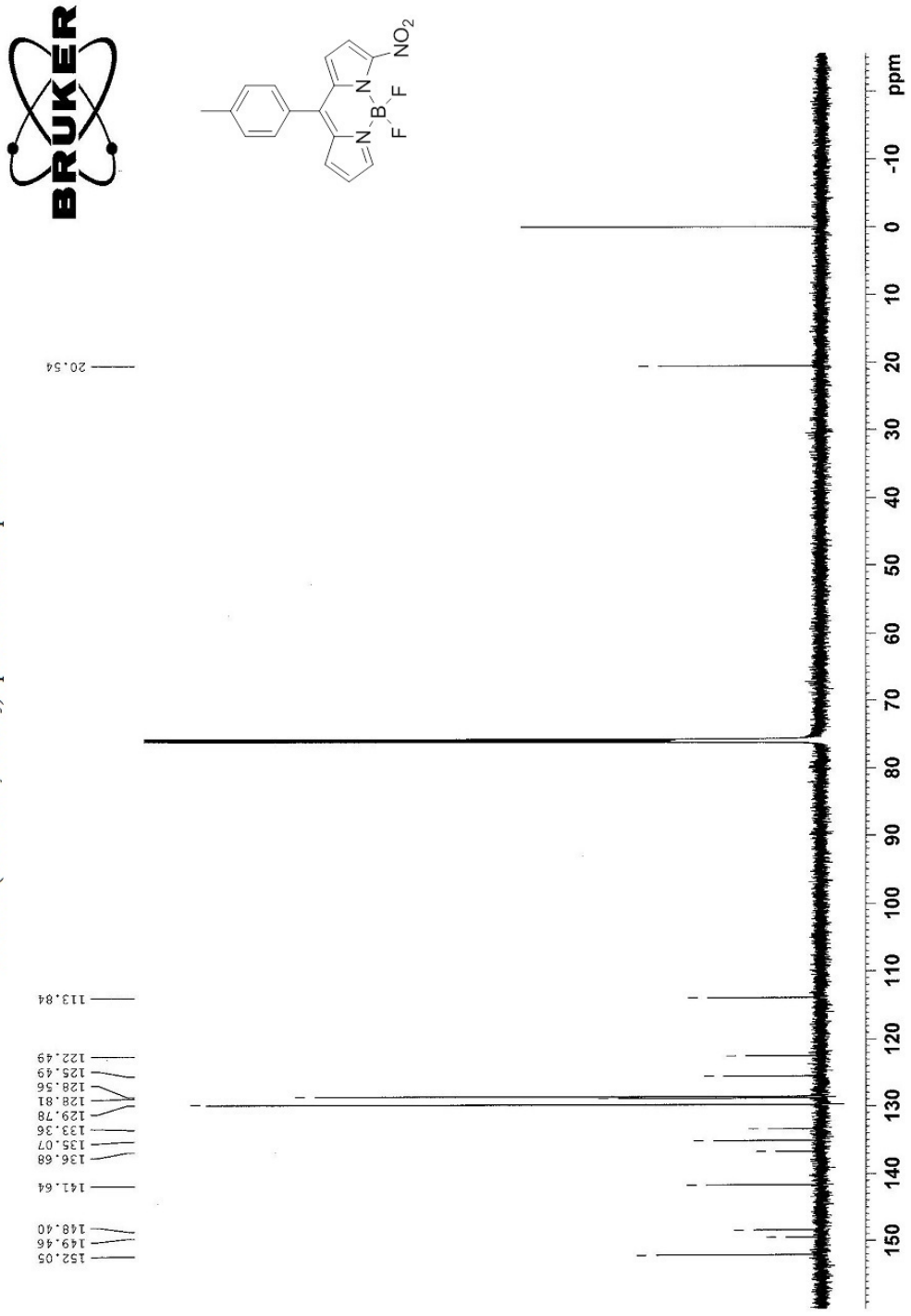


^{13}C NMR (176 MHz, $CDCl_3$) spectrum of compound **5**

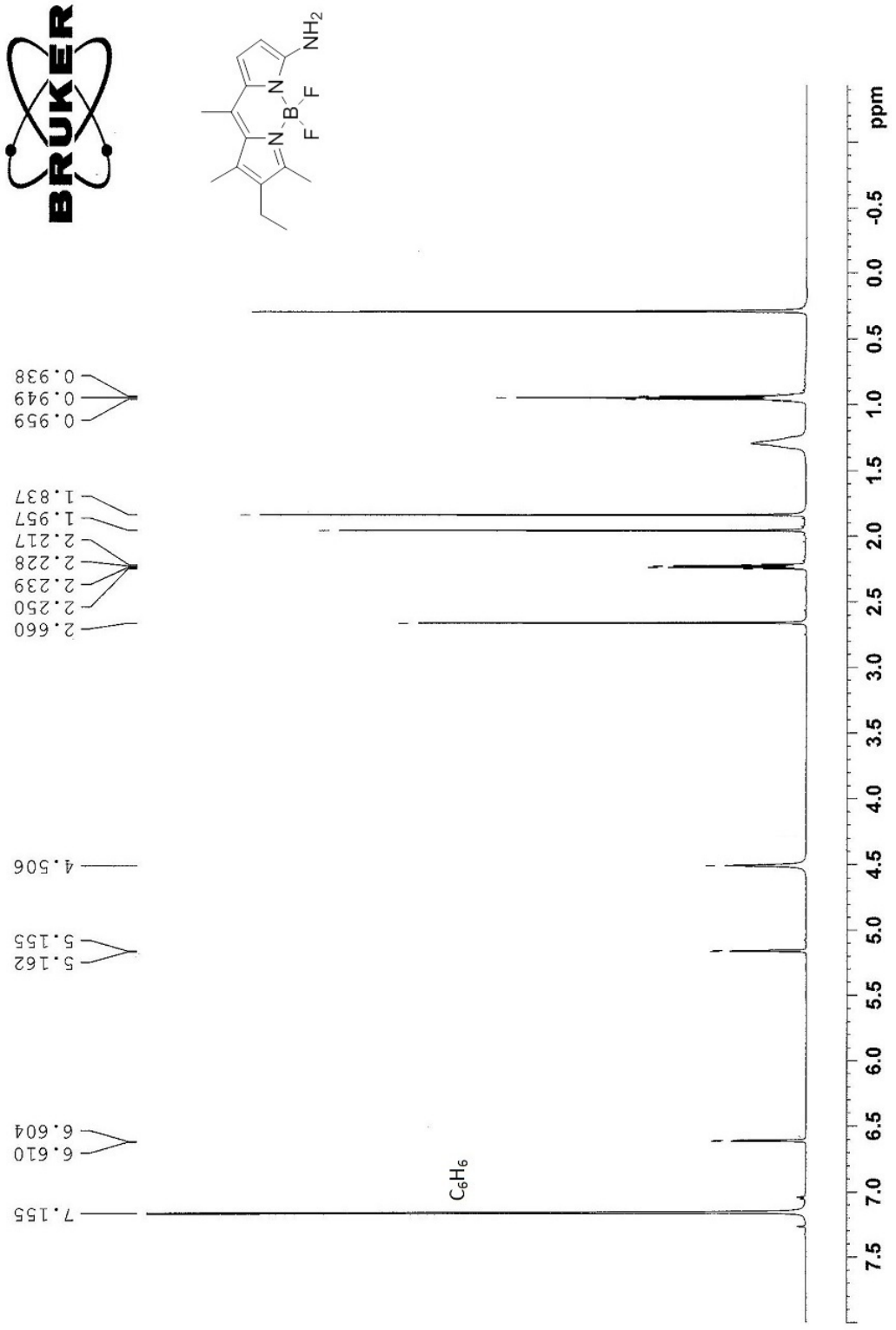


^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **6**

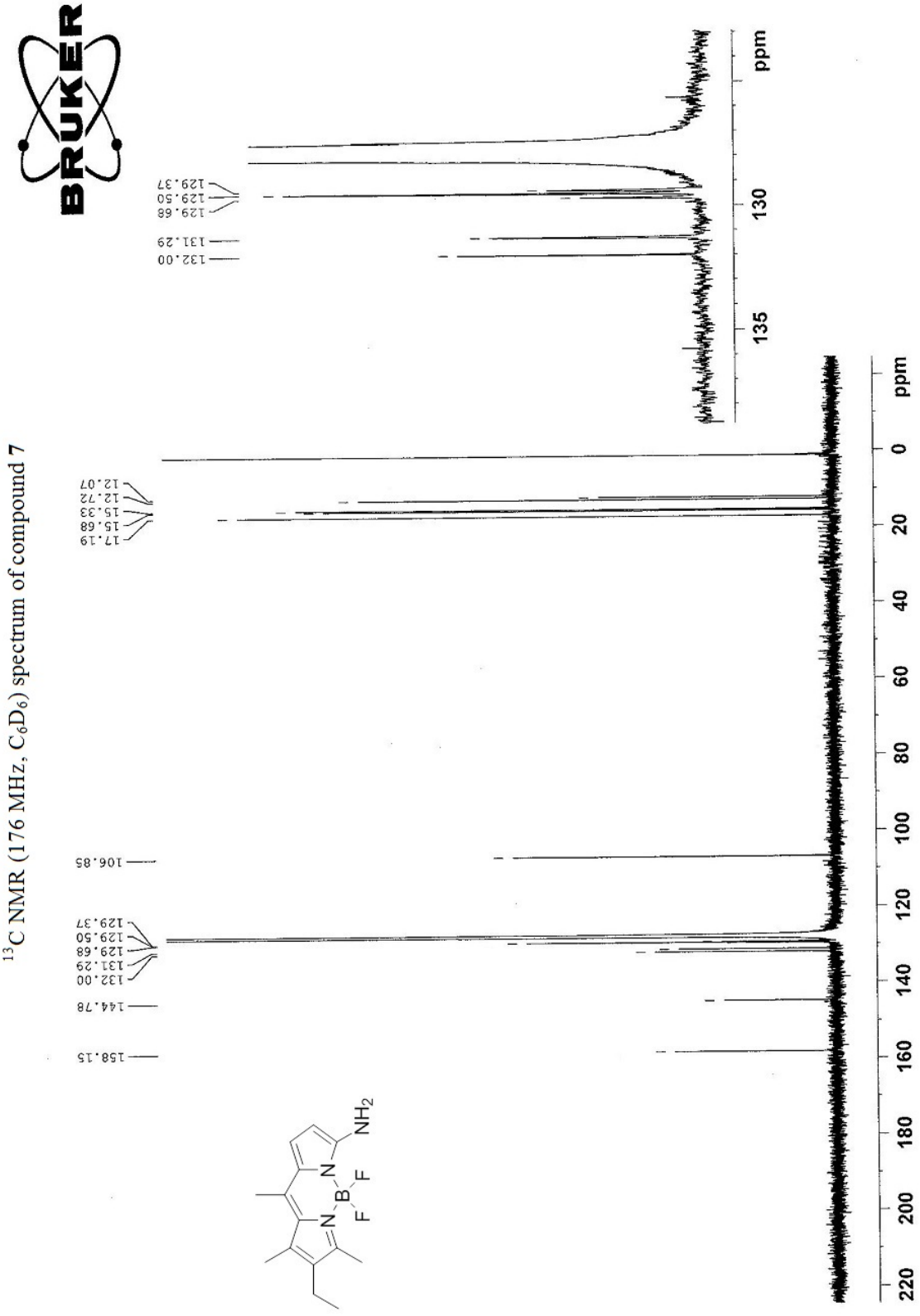
^{13}C NMR (176 MHz, $CDCl_3$) spectrum of compound **6**

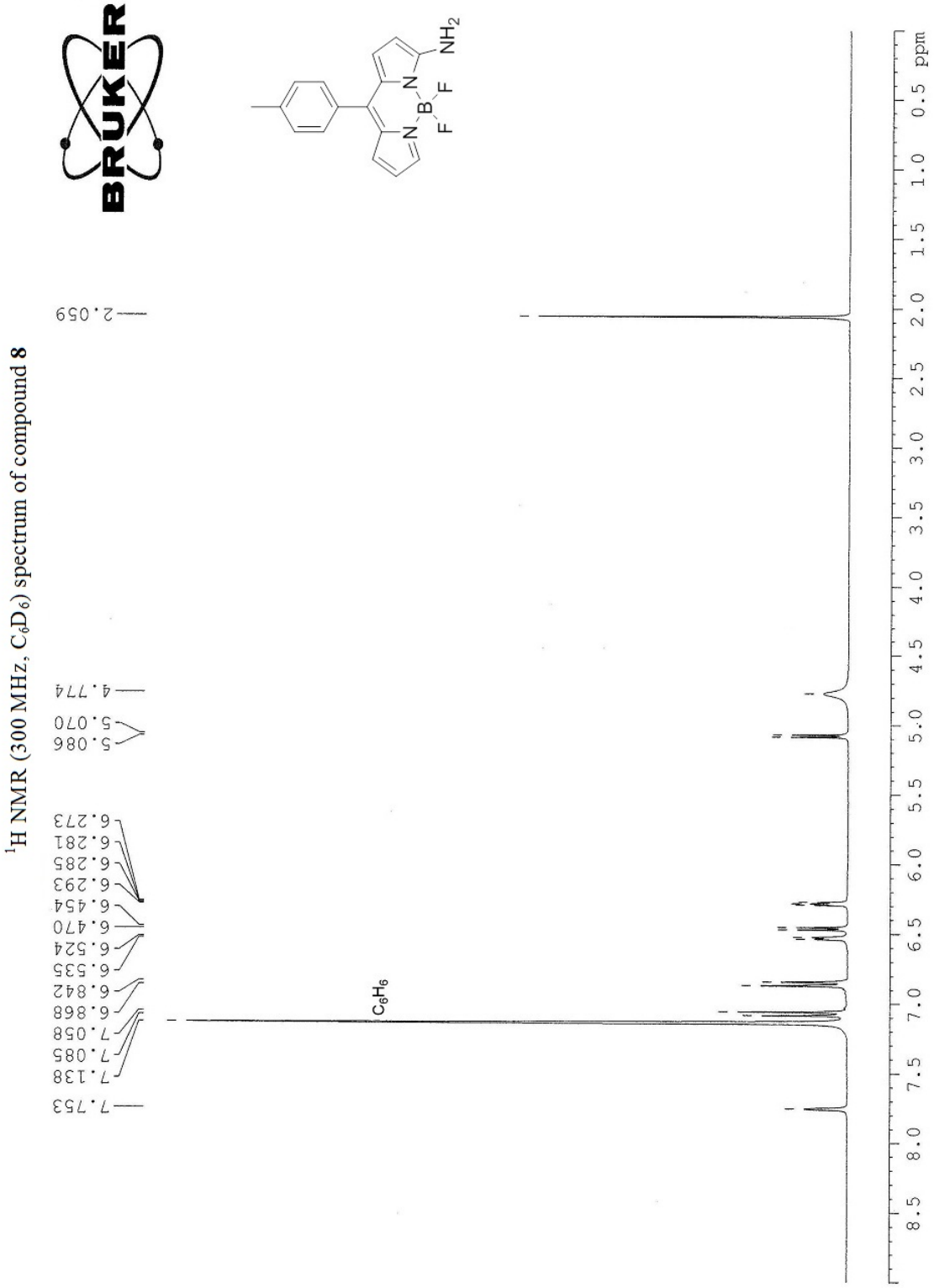


^{1}H NMR (700 MHz, C_6D_6) spectrum of compound **7**



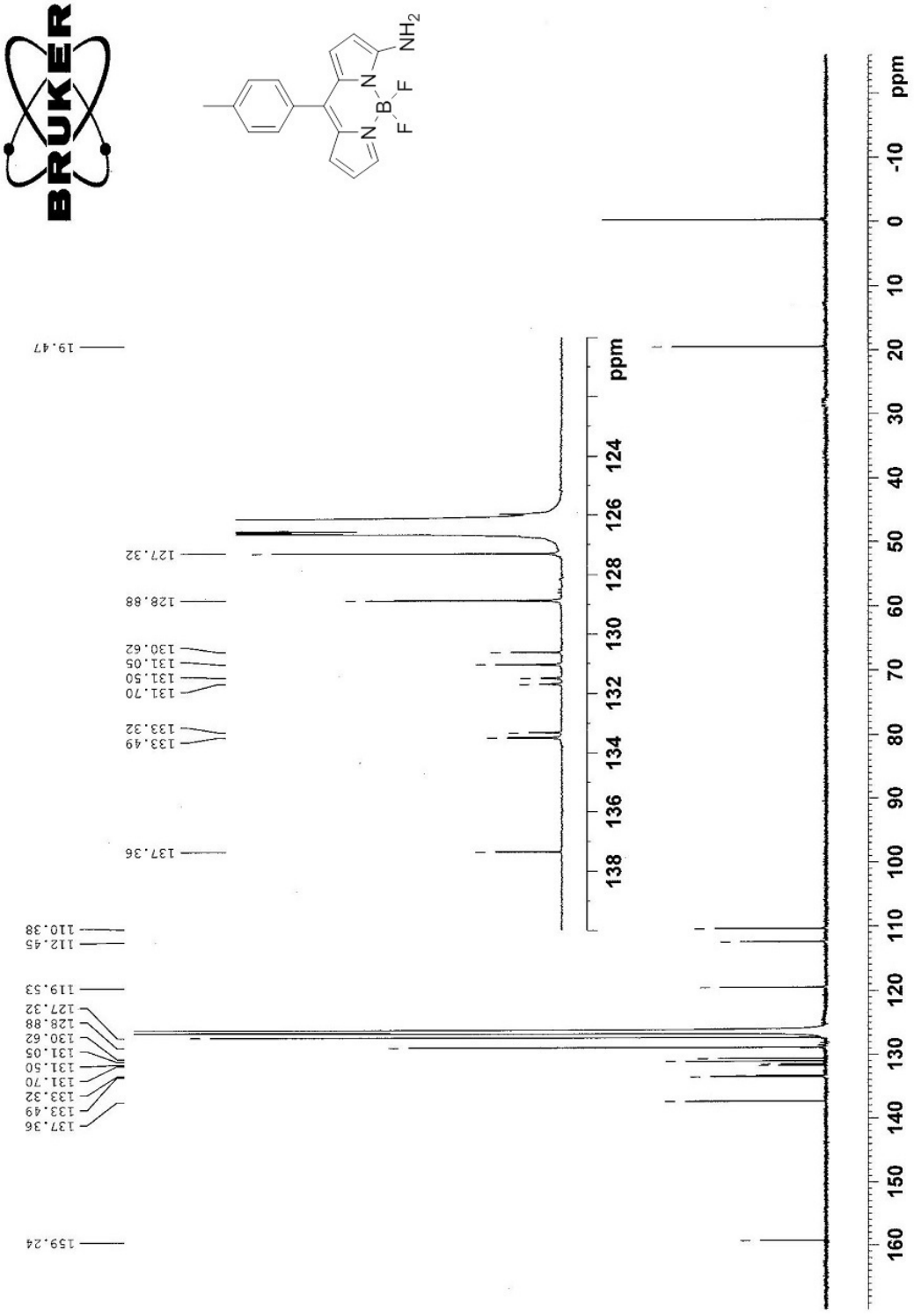
^{13}C NMR (176 MHz, C_6D_6) spectrum of compound **7**



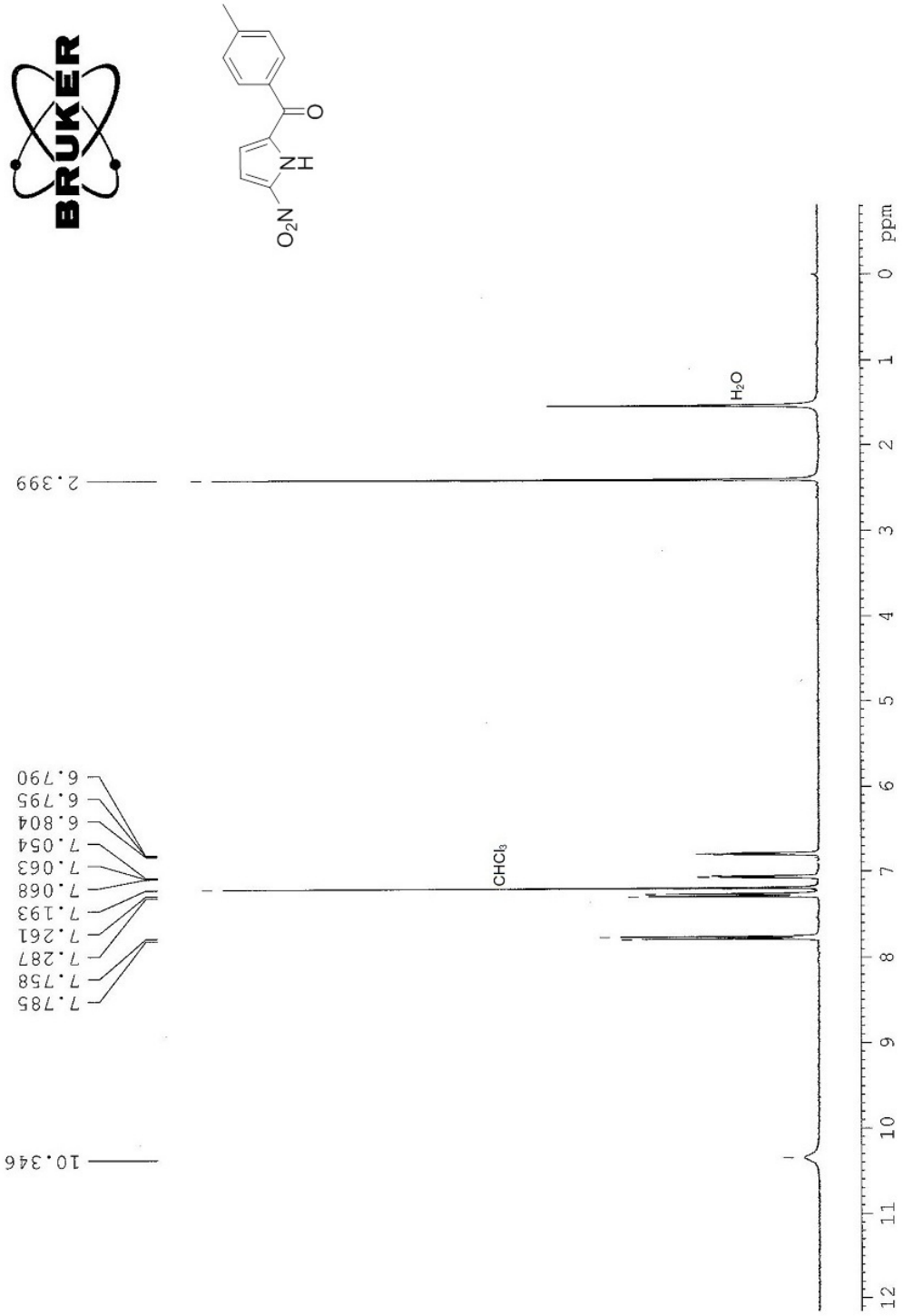


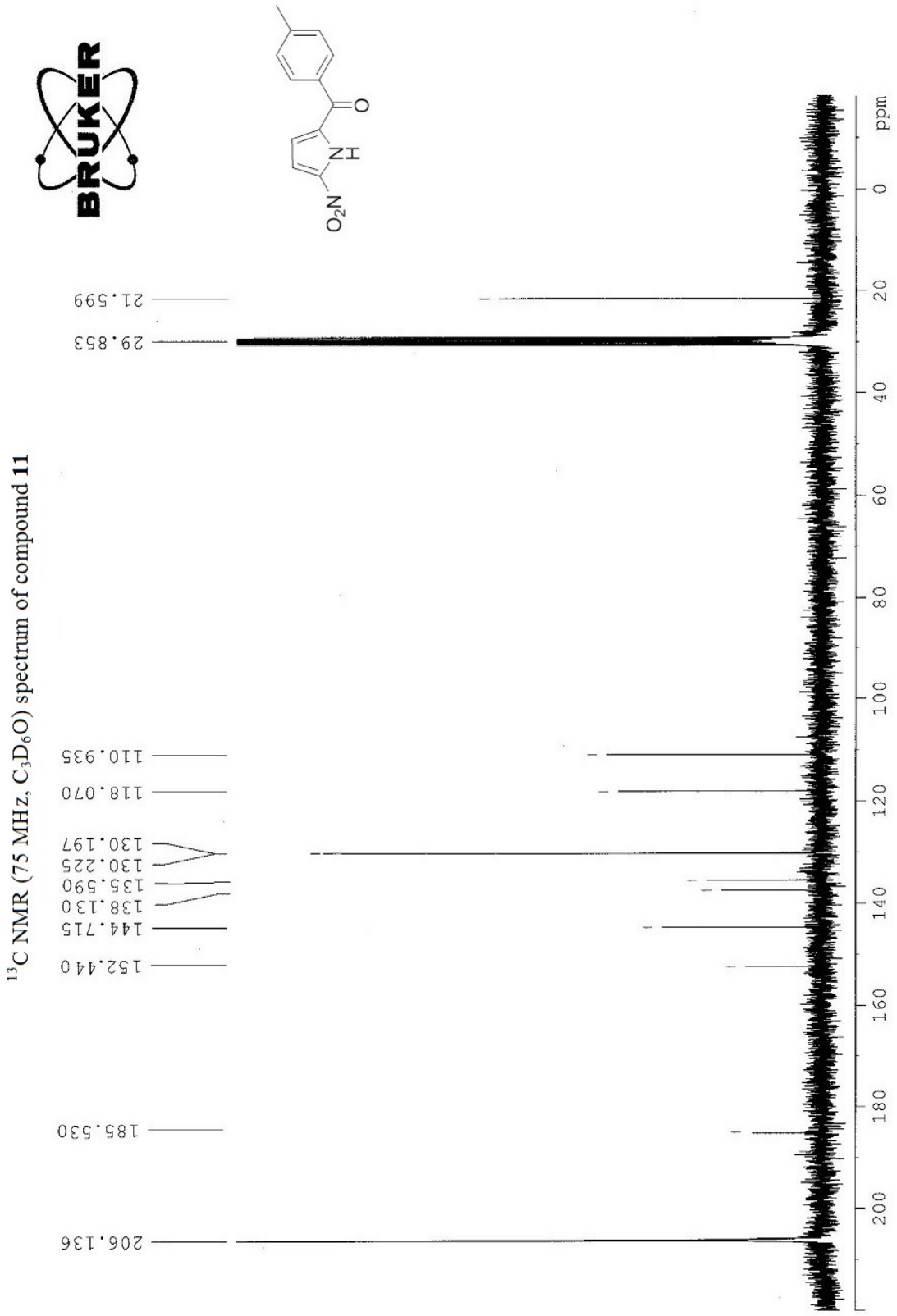
^{1}H NMR (300 MHz, C_6D_6) spectrum of compound **8**

^{13}C NMR (176 MHz, C_6D_6) spectrum of compound **8**

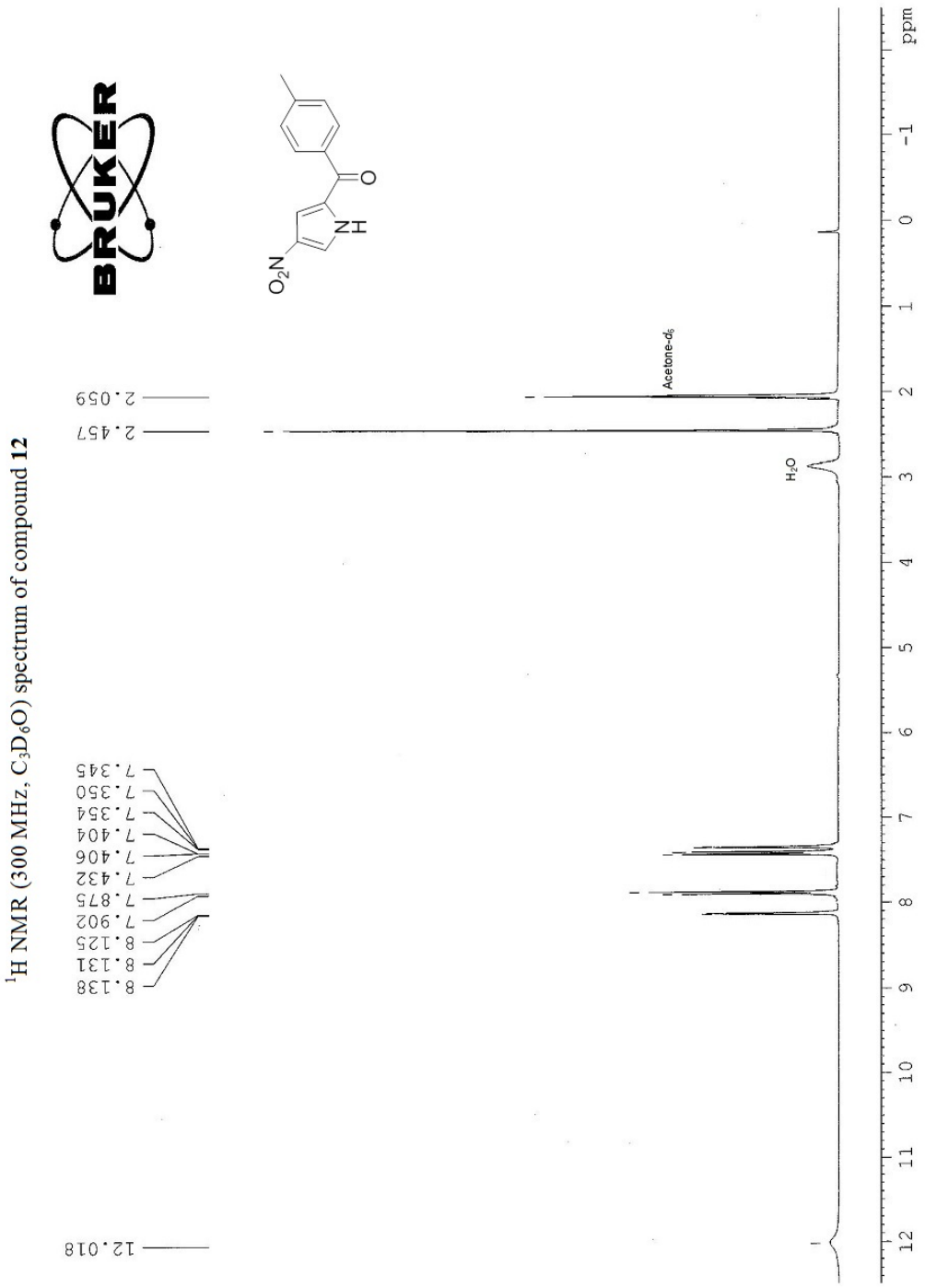


^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **11**

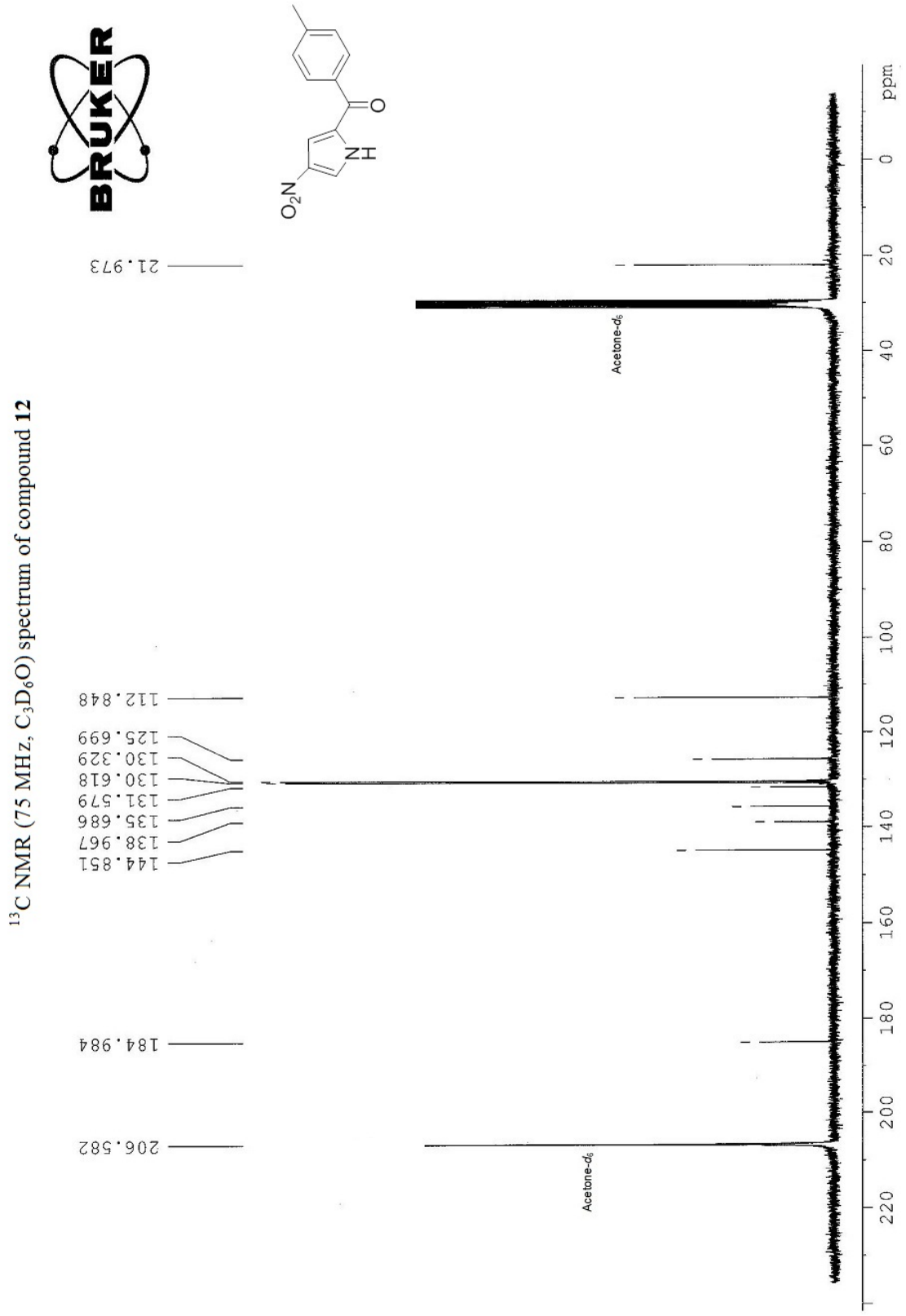




^{13}C NMR (75 MHz, C_3D_6O) spectrum of compound **11**



^{1}H NMR (300 MHz, C_3D_6O) spectrum of compound **12**



^{13}C NMR (75 MHz, C_3D_6O) spectrum of compound **12**

Table S1. Photophysical properties of compound **1** and its amino derivative **7** in different media ranking from apolar, to polar and polar/protic solvents; absorption (λ_{ab}) and emission (λ_{fl}) wavelength at the maximum, molar absorption (ε_{max}), fluorescence quantum yield (ϕ) and lifetime (τ), radiative (k_{fl}) and non-radiative rate constants (k_{nr}), and Stokes shift ($\Delta\nu_{St}$).

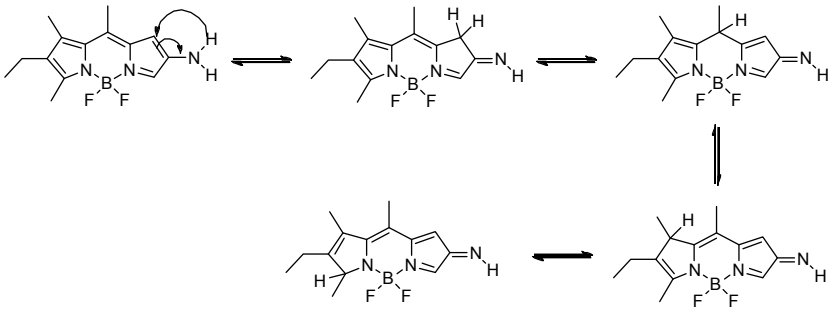
	λ_{ab} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	λ_{fl} (nm)	ϕ	τ (ns)	k_{fl} ($10^{-8}s^{-1}$)	k_{nr} ($10^{-8}s^{-1}$)	$\Delta\nu_{St}$ (cm^{-1})
1								
c-hexane	504.0	33000	515.0	0.96	5.46	1.75	0.07	760
ethyl acetate	496.0	25000	512.5	0.84	5.57	1.50	0.28	650
acetone	495.0	22000	512.5	0.79	5.66	1.39	0.37	690
ethanol	497.0	25000	513.5	0.84	5.73	1.46	0.28	630
methanol	495.5	25000	512.5	0.76	5.78	1.31	0.41	660
F_3-ethanol	492.0	19000	511.0	0.75	6.17	1.21	0.40	760
7								
c-hexane	522.0	19000	538.0	0.97	4.44	2.18	0.07	570
ethyl acetate	513.0	13000	535.0	0.79	4.21	1.87	0.50	800
acetone	510.5	12000	534.5	0.77	4.30	1.80	0.52	910
ethanol	512.0	10000	535.0	0.79	4.49	1.77	0.46	850
methanol	510.0	9000	534.0	0.74	4.54	1.62	0.58	880
F_3-ethanol	509.5	5000	533.5	0.69	5.63	1.23	0.55	885

Table S2. Photophysical properties of the nitro derivatives **3** and **4** in different media; absorption (λ_{ab}) and emission (λ_{fl}) wavelength at the maximum, molar absorption (ε_{max}), fluorescence quantum yield (ϕ) and lifetime (τ), radiative (k_{fl}) and non-radiative rate constants (k_{nr}).

	λ_{ab} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	λ_{fl} (nm)	ϕ	τ (ns)	k_{fl} ($10^{-8}s^{-1}$)	k_{nr} ($10^{-8}s^{-1}$)
3							
c-hexane	458.0 476.0	24000	509.0 530.0	0.53	3.13	1.70	1.49
Diethyl ether	452.0	21000	508.0 526.5	0.20	2.96	0.68	2.69
THF	451.5	21000	509.0 527.5	0.18	2.56	0.69	3.22
dioxane	456.5	22000	509.0 531.5	0.29	3.28	0.88	2.16
ethyl acetate	450.0	21000	507.5 526.0	0.33	2.56	1.27	2.63
acetone	446.5	15000	509.0 522.5	0.19	2.01	0.96	4.02
ethanol	449.0	21000	509.5 527.0	0.24	2.07	1.16	3.67
methanol	446.5	21000	509.5 526.5	0.17	1.54	1.10	5.39
F_3-ethanol	440.5	20000	510.0 527.5	0.02	0.19	0.89	51.74
4							
c-hexane	474.0	25000	530.5 556.0	0.174	1.53	1.11	5.42
Diethyl ether	466.0	27000	532.5 555.0	0.019	0.47 (95%) 3.55 (5%)	-	-
THF	468.0	24000	533.5 560.5	0.012	0.25 (91%) 3.03 (9%)	-	-
dioxane	470.0	26000	536.0 564.5	0.023	0.44 (92%) 3.40 (8%)	-	-
ethyl acetate	465.5	21000	533.0 558.0	0.023	0.27 (94%) 3.07 (6%)	-	-
acetone	461.5	17000	531.0	0.009	0.12 (92%) 2.05 (8%)	-	-
ethanol	465.0	19000	530.5	0.009	0.09 (93%) 2.00 (7%)	-	-
methanol	462.5	20000	530.5	0.005	0.05 (91%) 1.73 (9%)	-	-
F_3-ethanol	458.5	19000	506.5	0.004	-	-	-

Table S3. Photophysical properties of the reference compound **2** and its amino (**8**) and nitro (**6**) derivatives in different media; absorption (λ_{ab}) and emission (λ_{fl}) wavelength at the maximum, molar absorption (ε_{max}), fluorescence quantum yield (ϕ) and lifetime (τ), radiative (k_{fl}) and non-radiative rate constants (k_{nr}).

	λ_{ab} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	λ_{fl} (nm)	ϕ	τ (ps)	k_{fl} ($10^{-8}s^{-1}$)	k_{nr} ($10^{-8}s^{-1}$)
2							
c-hexane	500.5	69000	516.0	0.036	340	1.05	28.3
ethyl acetate	497.0	62000	514.5	0.024	237	1.01	41.2
acetone	496.5	61000	514.5	0.018	196	0.92	50.1
ethanol	497.5	62000	514.5	0.025	253	0.99	38.5
methanol	496.0	61000	513.5	0.018	197	0.91	49.8
F_3-ethanol	493.0	56000	509.5	0.031	323	0.96	30.0
8							
c-hexane	472.5 499.0	48000	515.5	0.017	88	1.93	110.5
Diethyl ether	462.0 481.0	32000	514.0	0.014	76	1.84	129.4
THF	463.0 477.5	30000	517.5	0.018	88	2.04	111.6
dioxane	466.0 484.0	31000	519.0	0.029	153	1.89	63.4
ethyl acetate	462.0 474.5	30000	517.5	0.017	78	2.18	126.0
acetone	460.0	29000	517.0	0.012	64	1.72	154.5
ethanol	458.0	30000	514.5	0.017	91	1.87	108.0
methanol	456.0	29000	515.0	0.013	66	1.82	149.7
F_3-ethanol	451.5	26000	512.5	0.023	140	1.64	69.8
6							
c-hexane	485.0 509.0	39000	519.0	0.131	1020	1.29	8.5
Diethyl ether	480.0 506.0	33000	521.0	0.100	930	1.08	9.7
THF	482.0 508.0	30000	528.0	0.144	1250	1.15	6.9
dioxane	475.0 509.0	19000	531.5	0.203	1935	1.05	4.1
ethyl acetate	483.0 505.0	23000	524.0	0.116	1197	0.97	7.4
acetone	481.0 505.5	21000	526.0	0.109	1060	1.02	8.4
ethanol	488.5 507.0	26000	524.0	0.089	1150	0.77	7.9
methanol	505.5	26000	525.5	0.038	530	0.72	18.1
F_3-ethanol	481.0 504.0	26000	525.0	0.035	480	0.74	20.2



Scheme S1. Enamine-imine tautomeric equilibrium upon substitution by amine at position 6 (compound **9**).

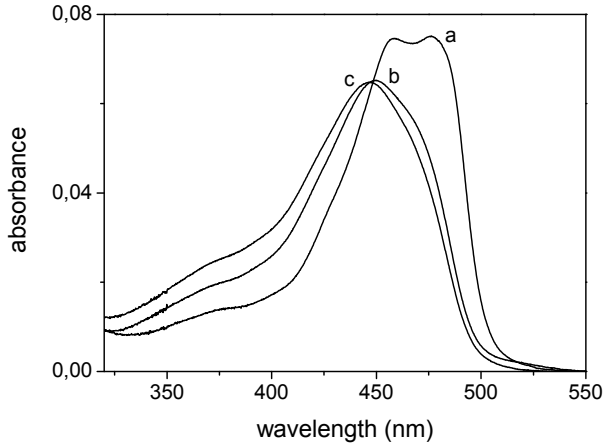


Figure S1. Absorption spectra of compound **3** in cyclohexane (a), acetone (b) and methanol (c).

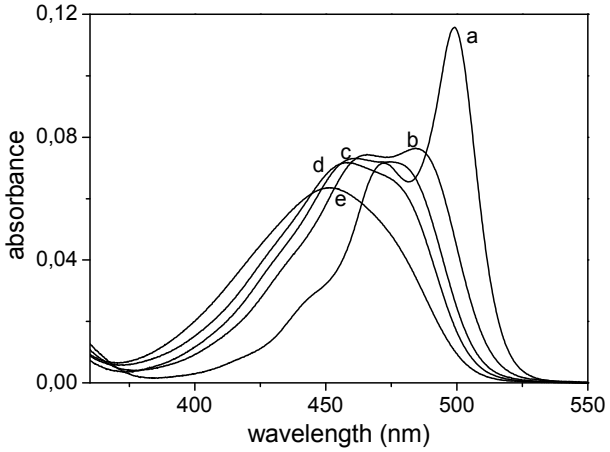


Figure S2. Absorption spectra of compound **6** in cyclohexane (a), dioxane (b), ethyl acetate (c), ethanol (d) and trifluoroethanol (e).