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Supporting Information

Mechanical and Thermal Stimuli-induced Release of Toluene Included in Luminescent Crystals as One-dimensional Solvent Channels

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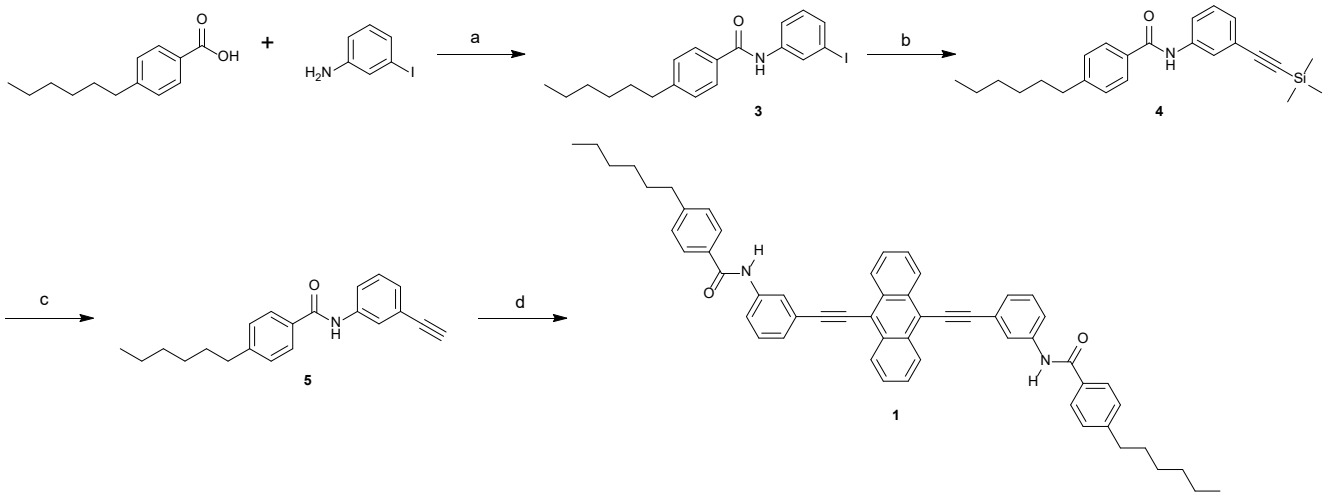
Synthesis

The synthetic route used to prepare compound **1** is shown in Scheme S1.

Scheme S1



Conditions: (a) 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, 4-dimethylaminopyridine, CH_2Cl_2, r.t., 5 h; (b) trimetylsilylacetylene, $Pd(PPh_3)_4$, CuI, Et_2NH, THF, 60 °C, 12 h; (c) tetrabutylammonium fluoride, THF, r.t., 2 h; (d) 9,10-dibromoanthracene, $Pd(PPh_3)_4$, CuI, Et_2NH, THF, 80 °C, 12 h.

***N*-(3-Iodophenyl)-4-hexylbenzamide (3).** A mixture of 3-iodoaniline (2.90 g, 13.2 mmol), 4-hexylbenzoic acid (3.00 g, 14.5 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (3.80 g, 19.8 mmol), and 4-dimethylaminopyridine (243 mg, 1.98 mmol) in CH_2Cl_2 (50 mL) was stirred for 5 h at r.t.. The reaction mixture was poured into a mixture of H_2O (50 mL) and dichloromethane (100 mL). The organic layer was separated off, washed with H_2O (100 mL) and saturated aq. NaCl (100 mL), and dried over Na_2SO_4 and filtered. The solvent was evaporated and the crude product was purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate = 5:1 v/v) to afford compound **3** (4.52 g, 11.1 mmol, 84%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.2 Hz, 3H), 1.28–1.36 (m, 6H), 1.63 (quin, J = 7.2 Hz, 2H), 2.67 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.47 (dt, J = 8.0, 1.2 Hz, 1H), 7.62 (ddd, J = 8.0, 2.0, 0.8 Hz, 1H), 7.75–7.78 (m, 3H), 7.42 (t, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.22, 22.70, 29.03, 31.25, 31.77, 35.97, 94.25, 119.59, 127.23, 128.91, 129.04, 130.56, 131.86, 133.46, 139.34, 147.72, 165.98. MS (MALDI-TOF): m/z: 408.16 (calcd. $[M+H]^+$ = 408.08).

***N*-(3-(Trimethylsilylethynyl)phenyl)-4-hexylbenzamide (4).** A mixture of compound **3** (2.00 g, 4.91 mmol), trimetylsilylacetylene (4.81 g, 49.1 mmol), $Pd(PPh_3)_4$ (284 mg, 0.246 mmol), CuI (46.9 mg, 0.246 mmol), and Et_2NH (20 mL) in THF (10 mL) was stirred for 12 h at 60 °C. After cooling to room temperature, the reaction mixture was

poured into ethyl acetate (100 mL) and the organic layer was washed with 5% aq. HCl (100 mL), saturated aq. $NaHCO_3$ (100 mL) and saturated aq. NaCl (100 mL). The organic layer was dried over Na_2SO_4 and filtered, and the solvent was evaporated. The crude product was then purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 5:1 v/v to hexane/ethyl acetate = 4:1 v/v) to afford compound **4** (1.79 g, 4.74 mmol, 97%) as a pale brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.25 (s, 9H), 0.89 (t, J = 7.2 Hz, 3H), 1.28–1.36 (m, 6H), 1.64 (quin, J = 7.6 Hz, 2H), 2.68 (t, J = 7.6 Hz, 2H), 7.24 (dt, J = 7.6, 1.2 Hz, 1H), 7.28–7.32 (m, 3H), 7.63–7.66 (m, 1H), 7.74 (br, 1H), 7.75–7.79 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.07, 14.22, 22.72, 29.04, 31.29, 31.79, 35.99, 94.71, 104.65, 120.43, 123.49, 124.05, 127.15, 128.02, 128.98, 129.11, 132.14, 138.11, 147.68, 165.80. MS (MALDI-TOF): m/z: 378.32 (calcd. $[M+H]^+$ = 378.23).

***N*-(3-Ethynylphenyl)-4-hexylbenzamide (5).** A THF solution of tetrabutylammonium fluoride (ca. 1 mol/L, 7.78 mL, 7.78 mmol) was added to a solution of compound **4** (1.47 g, 3.89 mmol) in THF (50 mL) at r.t.. After stirring the reaction mixture at r.t. for 2 h, ethyl acetate (150 mL) and brine (100 mL) were added to the reaction mixture. The organic layer was separated, washed with saturated aq. NaCl (100 mL), dried over $MgSO_4$ and filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate = 4:1 v/v) to afford compound **5** (1.08 g, 3.54 mmol, 91%) as a pale brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.2 Hz, 3H), 1.28–1.36 (m, 6H), 1.64 (quin, J = 7.6 Hz, 2H), 2.68 (t, J = 7.6 Hz, 2H), 3.08 (s, 1H), 7.26–7.35 (m, 4H), 7.68–7.71 (m, 1H), 7.75–7.79 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.20, 22.69, 29.02, 31.24, 31.76, 35.94, 77.59, 83.30, 121.00, 122.89, 123.82, 127.23, 128.16, 128.85, 129.11, 132.02, 138.23, 147.57, 166.09. MS (MALDI-TOF): m/z: 328.24 (calcd. $[M+Na]^+$ = 328.17).

Compound 1. A mixture of compound **5** (800 mg, 2.62 mmol), 9,10-dibromoanthracene (383 mg, 1.14 mmol), $Pd(PPh_3)_4$ (132 mg, 0.114 mmol), CuI (21.7 mg, 0.114 mmol), and Et_2NH (20 mL) in THF (20 mL) was stirred for 12 h at 80 °C. After cooling to room temperature, the reaction mixture was poured into MeOH (50 mL). The solid product was filtered off and washed with MeOH (100 mL). The solid was purified by flash column chromatography on silica gel (eluent: dichloromethane/MeOH = 30:1 v/v) to afford compound **1** (630 mg, 0.802 mmol, 70%) as a yellow crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.2 Hz, 6H), 1.29–1.37 (m, 12H), 1.65 (quin, J = 7.6 Hz, 4H), 2.69 (t, J = 7.6 Hz, 4H), 7.32 (d, J = 8.0 Hz, 4H), 7.46 (t, J = 8.0 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H), 7.62–7.66 (m, 4H), 7.73–7.76 (m, 2H), 7.84 (d, J = 8.0 Hz, 4H), 7.91 (s, 2H), 8.05 (s, 2H), 8.65–8.69 (m, 4H). ^{13}C NMR (100 MHz, THF-d_8): δ = 14.24, 23.32, 29.70, 32.03, 32.48, 36.41, 86.50, 103.55, 119.10, 121.18, 123.34, 124.19, 127.18, 127.66, 127.80, 128.20, 128.93, 129.62, 132.81, 133.71, 141.01, 147.37, 165.95. MS (MALDI-TOF): m/z: 784.55 (calcd. $[M]^+$ = 784.40). Elemental analysis (%) calcd. for $C_{56}H_{52}N_2O_2$: C 85.68, H 6.68, N 3.57; found: C 85.58, H 6.65, N 3.58.

Atom numbering for the crystallographically independent molecules in the crystal

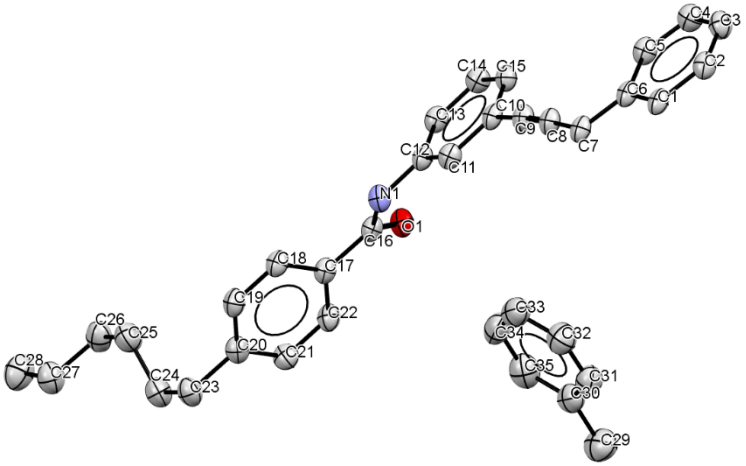


Figure S1. Crystallographically independent molecular structures with atom numbering.

Crystallographic data

Table S1. Crystal Data, Data Collection, and Reduction Parameter for **1Cr•Tol**.

	1Cr•Tol
Temperature / K	173
Crystal Dimensions / mm^3	0.50 × 0.12 × 0.02
Chemical formula	C_{35} H_{34} N O
Formula weight	484.63
Crystal System	Triclinic
Space group (number)	$P\bar{1}$ (#2)
a, Å	5.2904 (2)
b, Å	15.4505 (6)
c, Å	17.3028 (8)
α, deg	108.591 (4)
β, deg	92.630 (3)
γ, deg	91.885 (3)
V, $Å^3$	1337.42 (10)
Z	2
D_{calc}, $g \cdot cm^{-3}$	1.203
μ,(Cu Kα) cm^{-1}	0.545
$2\theta_{max}$, deg	147.884
Reflections measured	11022
Independent reflections	4619
Reflections used	4619
R_1 [a]	0.0562
$R_w(F^2)$ [a]	0.1665
GOF	1.069

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = (\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$.

Intermolecular interaction of compound 1 in 1Cr•Tol

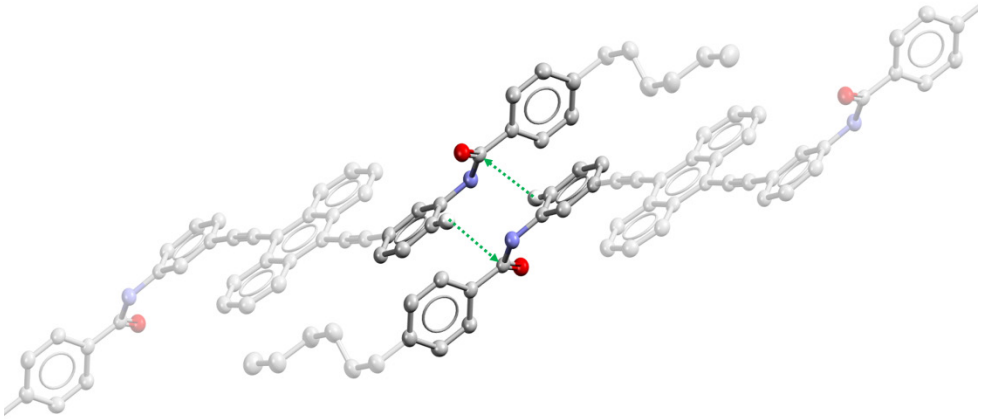


Figure S2. Intermolecular interaction between the 1D columns within the van der Waals radius.

Polarized optical microscopic images for the isotropic state

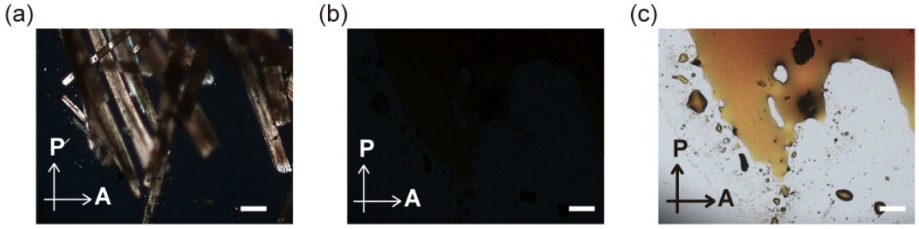


Figure S3. Polarized optical microscopic images of compound **1** at (a) 241°C and (b, c) 248 °C on heating. Scale bar: 100 μm.

DSC measurement for 1Am

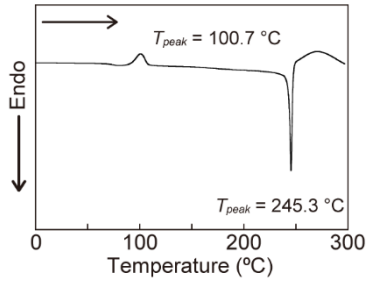


Figure S4. A heating DSC trace recorded for **1Am**. Scanning rate was 10 °C min^{-1}.

Gradual release of toluene from 1Cr•Tol under vacuum

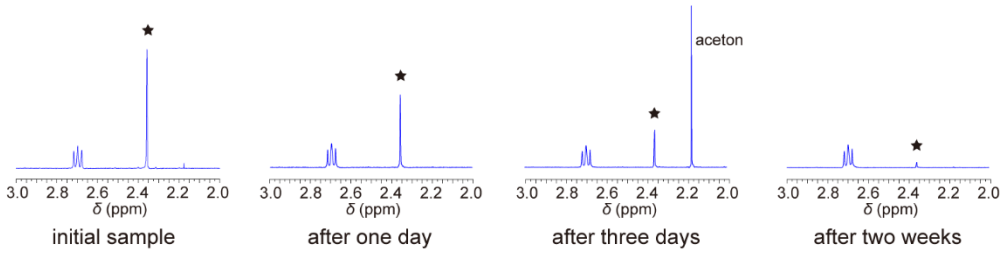


Figure S5. Partial 1H NMR spectra recorded for **1Cr•Tol** kept in a vacuum line with a pressure of 0.008 MPa.

Amorphous nature of the ground 1Cr

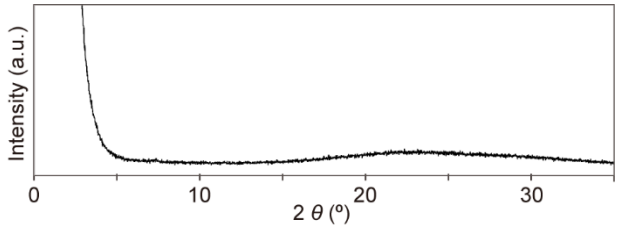


Figure S6. PXRD pattern obtained from ground **1Cr** at r.t.

Photophysical properties of ground 1Cr

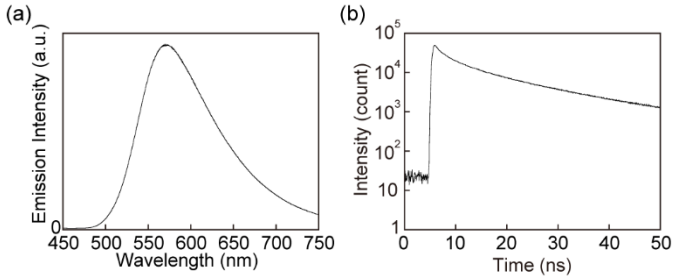
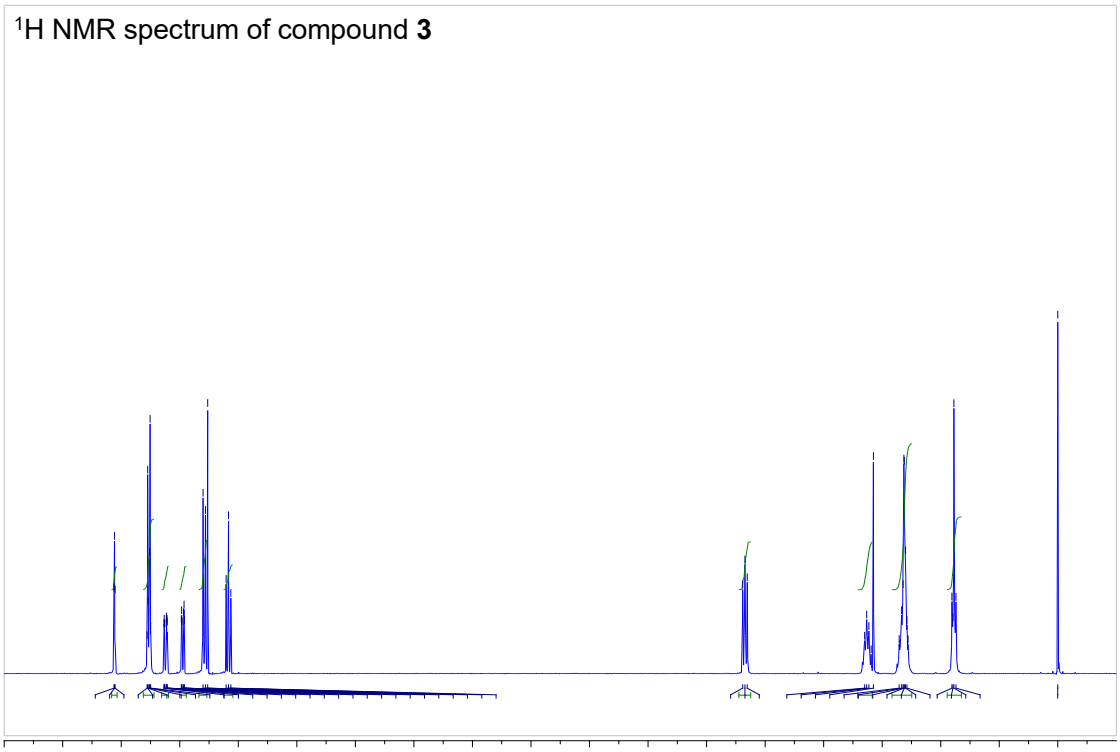


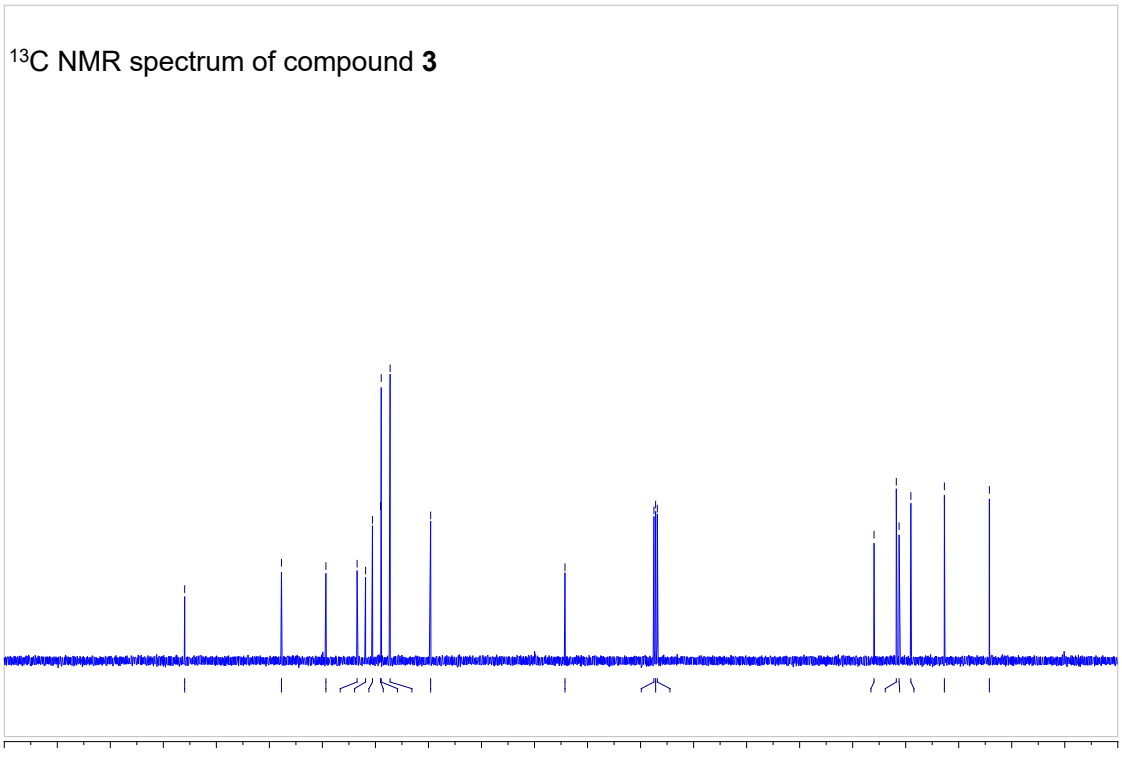
Figure S7. (a) A photoluminescence spectrum and (b) an emission decay profile of ground **1Cr**. The emission spectrum was recorded with excitation light of 400 nm. The emission decay profile was monitored with excitation light of 405 nm.

NMR data

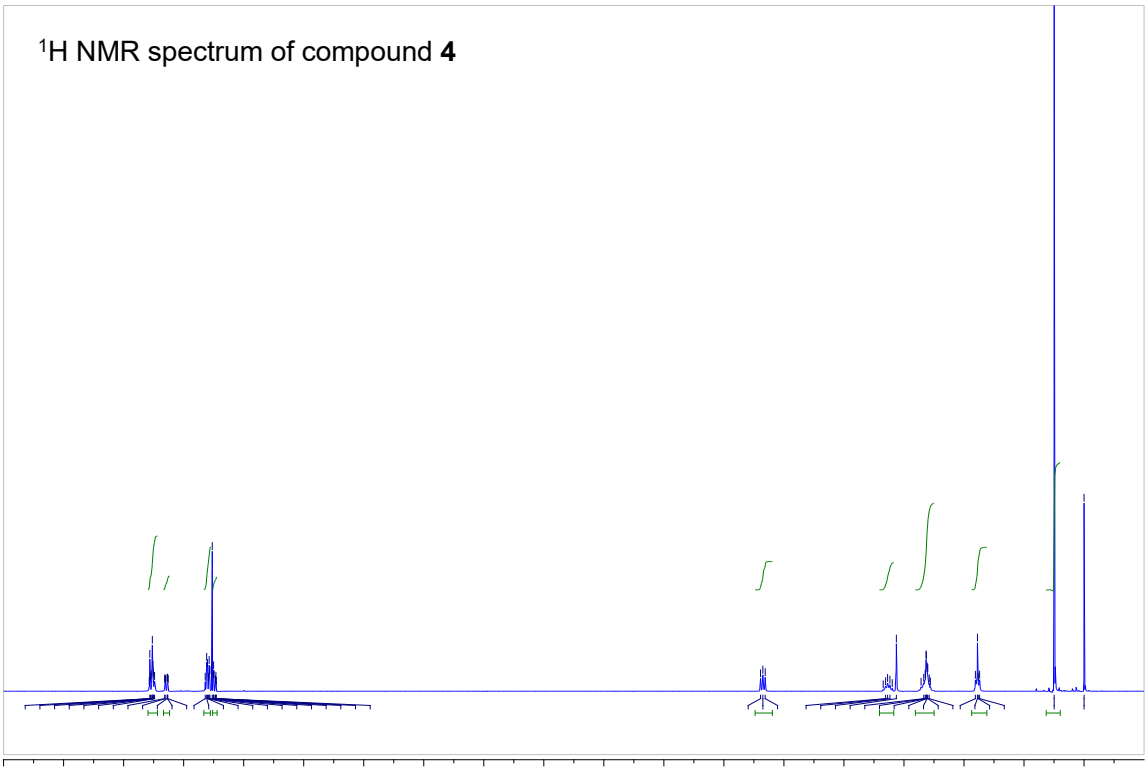
^{1}H NMR spectrum of compound **3**



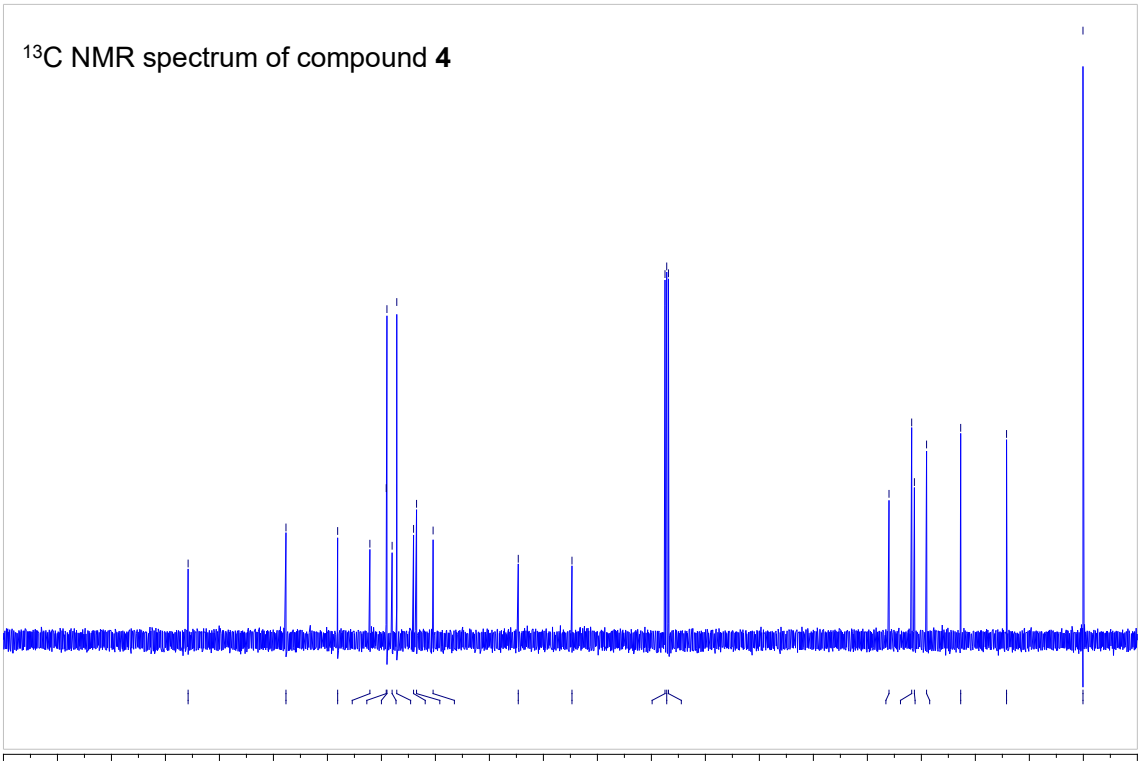
^{13}C NMR spectrum of compound **3**



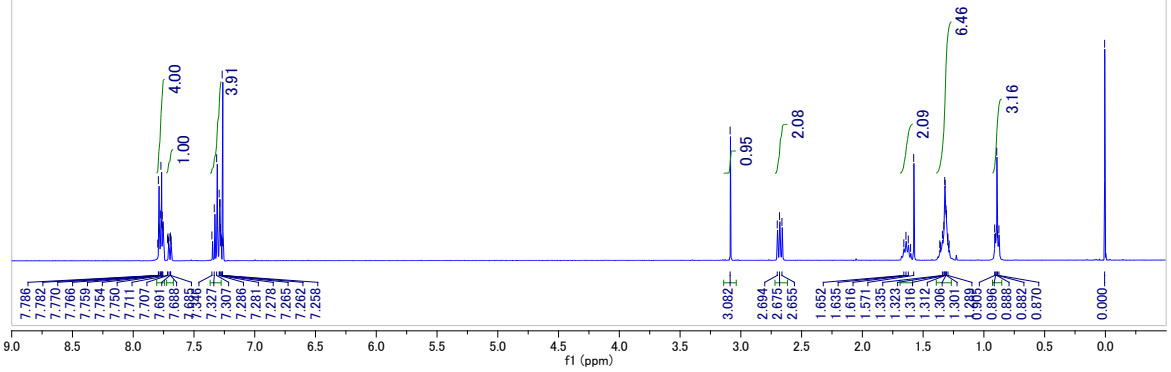
^{1}H NMR spectrum of compound **4**



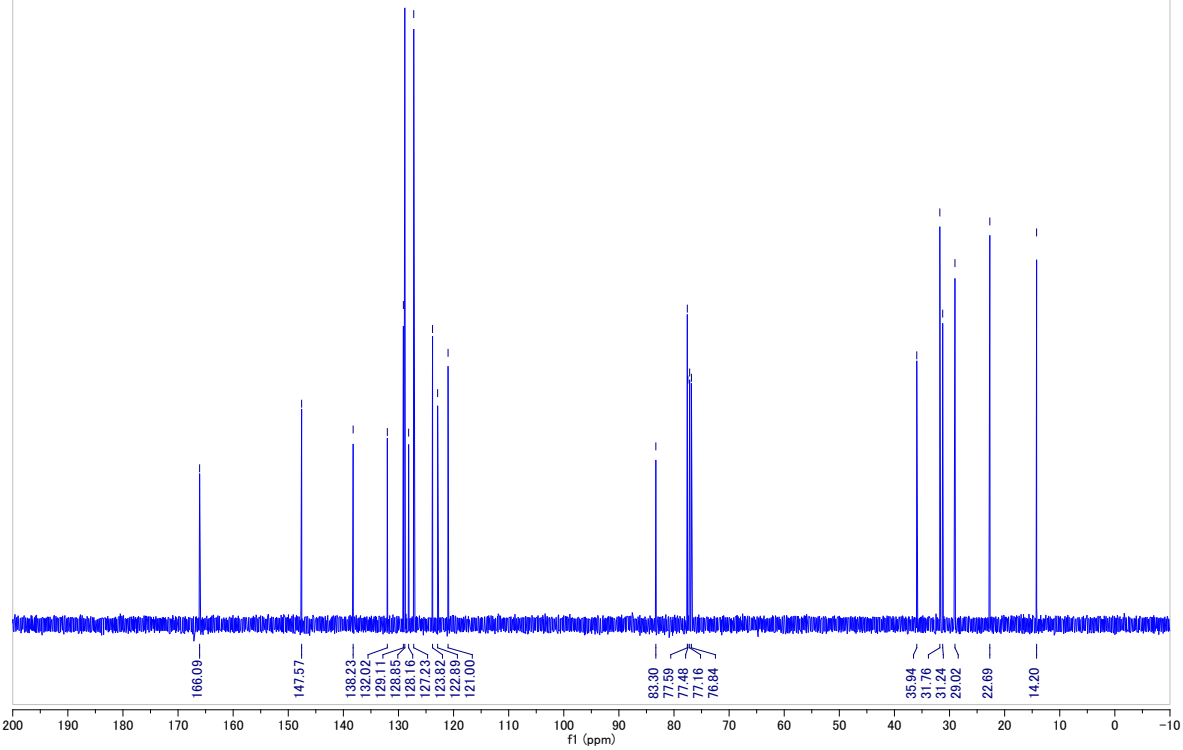
^{13}C NMR spectrum of compound **4**



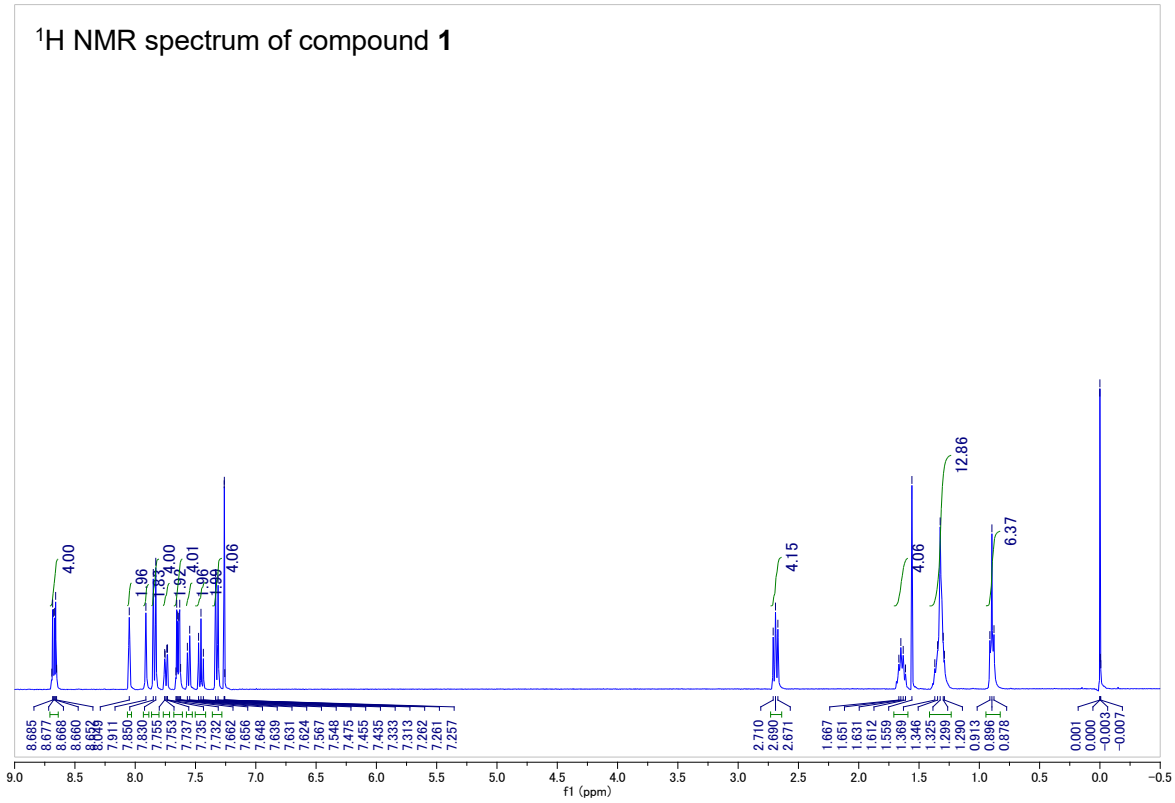
^{1}H NMR spectrum of compound **5**



^{13}C NMR spectrum of compound **5**



^{1}H NMR spectrum of compound **1**



^{13}C NMR spectrum of compound **1**