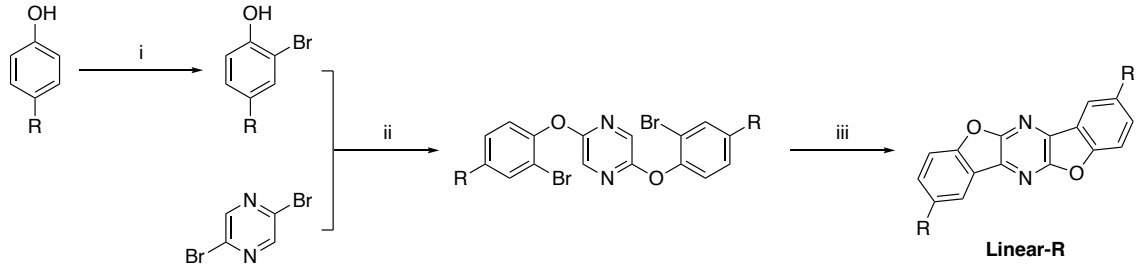
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

General experimental methods. Nuclear magnetic resonance spectra were measured operating at 400 MHz (^{1}H NMR) and at 100 MHz (^{13}C{^{1}H}NMR). ^{1}H NMR chemical shifts were reported in ppm relative to the resonance in TMS at δ 0.00. ^{13}C{^{1}H} NMR chemical shifts were reported in ppm relative to the residual solvent signals of $CDCl_3$ at δ 77.16. High resolution mass spectra (HRMS) were recorded with APCI-TOF. Melting points were measured with Mettler Toledo MP90. UV-vis spectra were acquired with JASCO V-750 spectrometer. PL spectra measurement was conducted with JASCO FP-8500 Spectro Fluoro Photometer. PLQY measurement was conducted with HAMAMATSU C11347 absolute PL quantum yield spectrometer with an integrating sphere. Fluorescence lifetime measurement was conducted on a HAMAMATSU C11366 fluorescence lifetime spectrometer. Ground samples for the fluorescence measurement were prepared by placing a spatulaful of bisbenzofuropyrazines on a 2 cm square quartz plate and manually grinding with a mortar for about 1 minute.

These compounds were previously reported in the literature: 2-bromo-4-(*sec*-butyl)phenol,[S1)] 2,5-bis(2-bromo-4-methylphenoxy)pyrazine,[S2)] 2,8-dimethylbis(benzofuro)[2,3-*b*:2',3'-*e*]pyrazine.[S2)]



Scheme S1. Synthetic routes toward **Linear-R**. i) *N*-bromosuccinimide, *p*-TsOH·H_2O, 2 h; ii) K_2CO_3, DMSO, 160 °C; iii) $PdCl_2(PPh_3)_2$, PivOK, DMAc, 160 °C, 15 h.

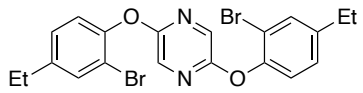
General synthetic method of bromophenol

To a stirred solution of 4-alkylphenol (1.0 eq.) and *p*-TsOH·H_2O (10 mol %) in MeOH (0.5 M) was added NBS (1.0 eq.) in one portion. The reaction mixture was stirred at RT for 2 h and then concentrated in vacuo. To the resulting mixture, hexane was added, and filtered. The filtrate was dried over Na_2SO_4/silica gel, and then concentrated in vacuo. The obtained product was directly used in the next step without further purification.

General synthetic method of 2,6-bis(2-bromo-4-alkylphenoxy)pyrazine

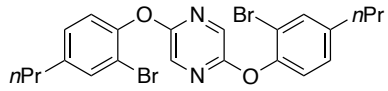
A mixture of 2-bromo-4-alkylphenol (2.0 eq.), 2,5-dibromopyrazine (1.0 eq.), and K_2CO_3 (2.4 eq.) in DMSO (1.0 M) was heated at 160 °C for 24 h. After the reaction was quenched with water, the mixture extracted with EtOAc. The organic layer was washed with water, dried over Na_2SO_4, and evaporated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 40/1) to give the product.

2,5-bis(2-bromo-4-ethylphenoxy)pyrazine



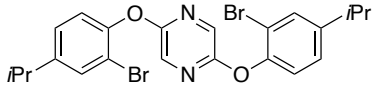
822 mg (86%, 2.0 mmol scale); white solid; m.p. 129.5-131.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 7.48 (d, *J* = 2.09 Hz, 2H), 7.18 (dd, *J* = 2.07, 8.26 Hz, 2H), 7.10 (d, *J* = 8.45 Hz, 2H), 2.66 (q, *J* = 7.61 Hz, 4H), 1.26 (t, *J* = 7.78 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 148.6, 143.1, 132.9, 130.4, 128.2, 123.0, 115.9, 28.0, 15.2; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{20}H_{19}Br_2N_2O_2$: 476.9808, found: 476.9817.

2,5-bis(2-bromo-4-propylphenoxy)pyrazine



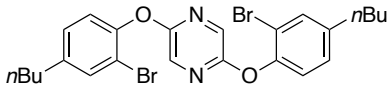
951 mg (94%, 2.0 mmol scale); white solid; m.p. 81.3-82.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.46 (d, *J* = 1.97 Hz, 2H), 7.15 (dd, *J* = 2.03, 8.20 Hz, 2H), 7.09 (d, *J* = 8.20 Hz, 2H), 2.58 (t, *J* = 7.88 Hz, 4H), 1.69-1.60 (m, 4H), 0.96 (t, *J* = 7.45 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.91, 148.69, 141.70, 133.50, 130.41, 128.78, 122.93, 115.81, 37.14, 24.34, 13.80; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{22}H_{23}Br_2N_2O_2$: 505.0121, found: 505.0133.

2,5-bis(2-bromo-4-isopropylphenoxy)pyrazine



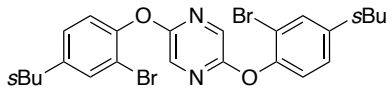
2577 mg (92%, 5.5 mmol scale); brown solid; m.p. 86.1-87.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.48 (d, *J* = 2.11 Hz, 2H), 7.19 (ddd, *J* = 0.37, 8.30 Hz, 2H), 7.09 (d, *J* = 8.30 Hz, 2H), 2.95-2.85 (m, 2H), 1.26 (s, 6H), 1.24 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 148.7, 147.7, 131.6, 130.4, 126.8, 123.0, 115.8, 33.5, 23.9; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{22}H_{23}Br_2N_2O_2$: 505.0121, found: 505.0132.

2,5-bis(2-bromo-4-butylphenoxy)pyrazine



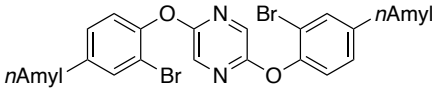
849 mg (79%, 2.0 mmol scale); white solid; m.p. 71.9-73.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.46 (d, *J* = 2.00 Hz, 2H), 7.16 (dd, *J* = 2.00, 8.24 Hz, 2H), 7.08 (d, *J* = 8.24, 2H), 2.60 (t, *J* = 7.80 Hz, 4H), 1.64-1.55 (m, 4H), 1.41-1.32 (m, 4H), 0.94 (t, *J* = 7.38 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 148.6, 141.9, 133.4, 130.4, 128.7, 122.9, 115.8, 34.4, 33.3, 22.3, 13.9; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{24}H_{27}Br_2N_2O_2$: 533.0434, found: 533.0444.

2,5-bis(2-bromo-4-(*sec*-butyl)phenoxy)pyrazine



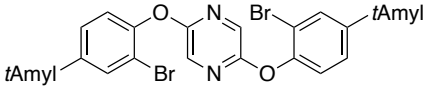
2754 mg (94%, 5.5 mmol scale); orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.36 (d, *J* = 2.11 Hz, 2H), 7.07 (dd, *J* = 2.11, 8.24 Hz, 2H), 7.01 (d, *J* = 2.11, 8.24 Hz, 2H), 2.56-2.47 (m, 2H), 1.50 (d, *J* = 7.28 Hz, 4H), 1.15 (d, *J* = 6.98 Hz, 6H), 0.76 (t, *J* = 7.28 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 148.7, 146.6, 132.1, 130.4, 127.4, 122.8, 115.7, 40.9, 31.1, 21.6, 12.1; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{24}H_{27}Br_2N_2O_2$: 533.0434, found: 533.0450.

2,5-bis(2-bromo-4-pentylphenoxy)pyrazine



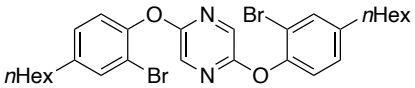
589 mg (70%, 1.5 mmol scale); white solid; m.p. 50.2-52.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.37 (d, *J* = 1.85 Hz, 2H), 7.08 (dd, *J* = 1.85, 8.44 Hz, 2H), 7.00 (d, *J* = 8.24 Hz, 2H), 2.52 (t, *J* = 7.90 Hz, 4H), 1.58-1.49 (m, 4H), 1.27-1.25 (m, 8H), 0.83 (t, *J* = 6.86 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 148.6, 141.9, 133.4, 130.4, 128.7. 122.9, 115.8, 35.0, 31.4, 30.9, 22.5, 14.0; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{26}H_{31}Br_2N_2O_2$: 561.0747, found: 561.0765.

2,5-bis(2-bromo-4-(*tert*-amyl) phenoxy)pyrazine



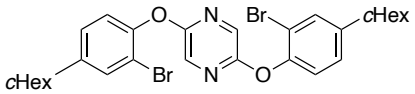
1641 mg (58%, 5.0 mmol scale); brown solid; m.p. 146.3-147.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 2H), 7.56 (d, *J* = 2.31 Hz, 2H), 7.29 (dd, *J* = 2.31, 8.55 Hz, 2H), 7.10 (d, *J* = 8.55 Hz, 2H), 1.63 (q, *J* = 7.56 Hz, 4H), 1.28 (s, 12H), 0.71 (t, *J* = 7.56 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.8, 148.6, 148.4, 131.3, 130.3, 126.4, 122.4, 115.5, 37.8, 36.8, 28.3, 9.1; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{26}H_{31}Br_2N_2O_2$: 561.0747, found: 561.0765.

2,5-bis(2-bromo-4-hexylphenoxy)pyrazine



1130 mg (96%, 2.0 mmol scale); white solid; m.p. 62.2-63.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 7.46 (d, *J* = 1.91 Hz, 2H), 7.16 (dd, *J* = 2.05, 8.47 Hz, 2H), 7.08 (d, *J* = 8.22 Hz, 2H), 2.56 (t, *J* = 8.01 Hz, 4H), 1.65-1.57 (m, 4H), 1.38-1.26 (m, 12H), 0.89 (t, *J* = 6.94 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 148.6, 141.9, 133.4, 130.4, 128.7, 122.9, 115.8, 35.1, 31.6, 31.2, 28.9, 22.6, 14.1; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{28}H_{35}Br_2N_2O_2$: 589.1060, found: 589.1062.

2,5-bis(2-bromo-4-cyclohexylphenoxy)pyrazine



2355 mg (80%, 5.0 mmol scale); brown solid; m.p. 117.9-118.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 7.47 (d, *J* = 2.03 Hz, 2H), 7.18 (dd, *J* = 2.03, 8.29 Hz, 2H), 7.09 (d, *J* = 8.29 Hz, 2H), 2.52-2.47 (m, 2H), 1.90-1.84 (m, 8H), 1.77-1.73 (m, 2H), 1.44-1.32 (m, 8H), 1.28-1.21 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.8, 148.6, 146.9, 131.9, 130.4, 127.1, 122.8, 115.7, 43.7, 34.3, 26.7, 26.0; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{28}H_{31}Br_2N_2O_2$: 585.0747, found: 585.0757.

General synthetic method of Linear-R

A mixture of 2,5-bis(2-bromo-4-alkylphenoxy)pyrazine (1.0 eq.), $PdCl_2(PPh_3)_2$ (20 mol%), PivOK (4.0 eq.), DMAc (0.16 M) was heated at 160 °C for 15 h. After the reaction was completed, the reaction was quenched with water, and then extracted with EtOAc. The organic layer was washed with water, dried over Na_2SO_4, and evaporated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 20/1) and GPC ($CHCl_3$) to give the product.

2,8-diethylbis(benzofuro)[2,3-*b*:2',3'-*e*]pyrazine (**Linear-Et**)

59 mg (47%, 0.4 mmol scale); white solid; m.p. 200.1-201.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 0.67, 1.86 Hz, 2H), 7.62 (d, *J* = 8.52 Hz, 2H), 7.48 (dd, *J* = 1.90, 8.54 Hz, 2H), 2.86 (q, *J* = 7.62 Hz, 4H), 1.36 (t, *J* = 7.56 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.6, 155.4, 140.4, 132.8, 130.4, 121.8, 120.2, 112.3, 28.8, 15.9; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{20}H_{17}N_2O_2$: 317.1285, found: 317.1287.

2,8-dipropylbis(benzofuro)[2,3-*b*:2',3'-*e*]pyrazine (**Linear-*n*Pr**)

61 mg (45%, 0.4 mmol scale); white solid; m.p. 177.8-179.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.29 Hz, 2H), 7.60 (d, *J* = 8.53 Hz, 2H), 7.48 (dd, *J* = 1.84, 8.55 Hz, 2H), 2.78 (t, *J* = 7.58 Hz, 4H), 1.80-1.70 (m, 4H), 1.00 (t, *J* = 7.36 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.5, 155.4, 138.8, 132.7, 130.9, 121.7, 120.9, 112.2, 37.8, 24.8, 13.7; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{22}H_{21}N_2O_2$: 345.1598, found: 345.1599.

2,8-diisopropylbis(benzofuro)[2,3-*b*:2',3'-*e*]pyrazine (**Linear-*i*Pr**)

157 mg (46%, 1.0 mmol scale); white solid; m.p. 218.4-219.2°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 1.91 Hz, 2H), 7.64 (d, *J* = 8.37 Hz, 2H), 7.52 (dd, *J* = 1.91, 8.37 Hz, 2H), 3.16-3.08 (m, 2H), 1.38 (s, 6H), 1.37 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.6, 155.4, 145.2, 132.8, 129.3, 121.7, 118.8, 112.3, 34.1, 24.3; HRMS (APCI) m/z ($M+H^+$) calcd for $C_{22}H_{21}N_2O_2$: 345.1598, found: 345.1602.

2,8-dibutylbis(benzofuro)[2,3-*b*:2',3'-*e*]pyrazine (**Linear-*n*Bu**)

70 mg (47%, 0.4 mmol scale); white solid; m.p. 158.6-160.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 1.29 Hz, 2H), 7.62 (d, *J* = 8.48 Hz, 2H), 7.46 (dd, *J* = 1.85, 8.71 Hz, 2H), 2.82 (t, *J* = 7.86 Hz, 4H), 1.75-1.67 (m, 4H), 1.46-1.35 (m, 4H), 0.97 (t, *J* = 7.42 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.6, 155.4, 139.1, 132.7, 130.9, 121.7, 120.8, 112.2, 35.4, 33.9, 22.2, 13.9; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{24}H_{25}N_2O_2$: 373.1911, found: 373.1913.

2,8-di(*sec*-butyl) bis(benzofuro)[2,3-*b*:2',3'-*e*]pyrazine (**Linear-*s*Bu**)

13 mg (4%, 0.9 mmol scale); white solid; m.p. 168.2-169.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 1.77 Hz, 2H), 7.63 (d, *J* = 8.57 Hz, 2H), 7.47 (dd, *J* = 1.77, 8.57 Hz, 2H), 2.86-2.78 (m, 2H), 1.75-1.67 (m, 4H), 1.36 (d, *J* = 6.93 Hz, 6H), 0.87 (t, *J* = 7.28 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.6, 155.4, 143.9, 132.8, 129.7, 121.7, 119.5, 112.3, 41.7, 31.4, 22.2, 12.2; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{24}H_{25}N_2O_2$: 373.1911, found: 373.1909.

2,8-dipentylbis(benzofuro)[2,3-*b*:2',3'-*e*]pyrazine (**Linear-*n*Amyl**)

57 mg (36%, 0.4 mmol scale); white solid; m.p. 152.1-153.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.32 Hz, 2H), 7.60 (d, *J* = 8.50 Hz, 2H), 7.44 (dd, *J* = 1.82, 8.43 Hz, 2H), 2.80 (t, *J* = 8.25 Hz, 4H), 1.76-1.69 (m, 4H), 1.40-1.30 (m, 8H), 0.92-0.89 (m. 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.5, 155.3, 139.1, 132.7, 130.9, 121.7, 120.8, 112.2, 35.7, 31.4, 31.3, 22.5, 14.0; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{26}H_{29}N_2O_2$: 401.2224, found: 401.2237.

2,8-di(*tert*-pentyl)bis(benzofuro)[2,3-*b*:2',3'-*e*]pyrazine (**Linear-*t*Amyl**)

111 mg (28%, 1.0 mmol scale); white solid; m.p. 213.9-214.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (t, *J* = 1.32 Hz, 2H), 7.65 (d, *J* = 1.32 Hz, 4H), 1.77 (q, *J* = 7.50 Hz, 4H), 1.42 (s, 12H), 0.73 (t, *J* = 7.50 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.6, 155.1, 145.8, 132.9, 128.6, 121.4, 118.8, 112.0, 38.3, 37.1, 28.9, 9.1 HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{26}H_{29}N_2O_2$: 401.2224, found: 401.2243.

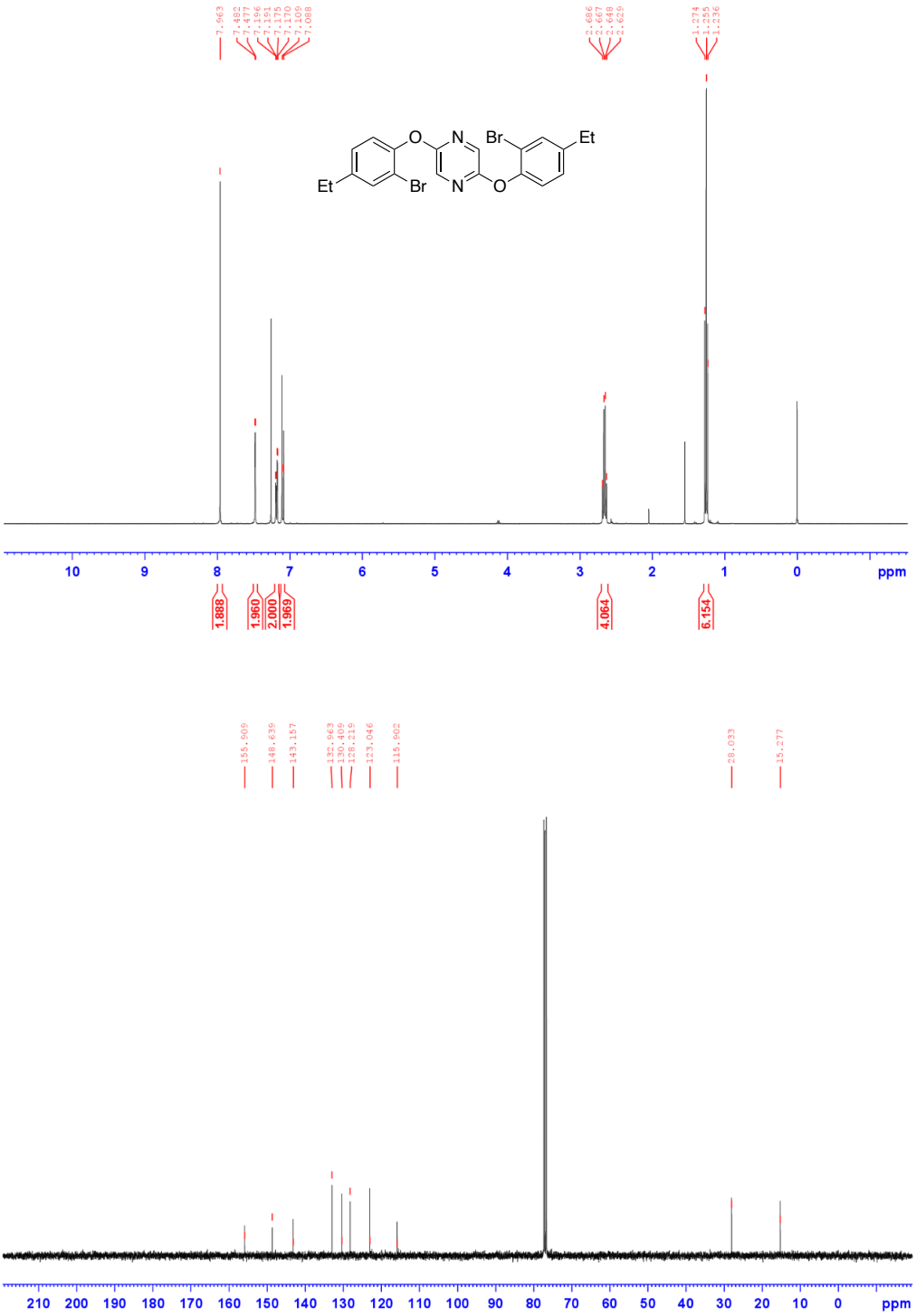
2,8-dihexylbis(benzofuro)[2,3-*b*:2',3'-*e*]pyrazine (**Linear-*n*Hex**)

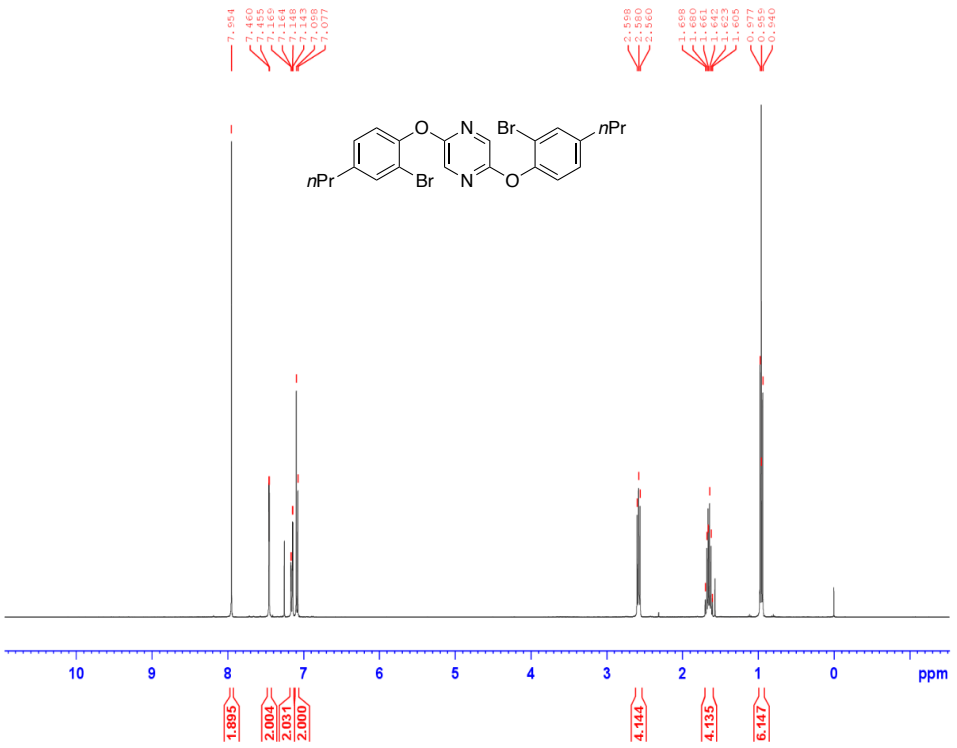
82 mg (48%, 0.4 mmol scale); white solid; m.p. 144.6-146.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 1.29 Hz, 2H), 7.61 (d, *J* = 8.51 Hz, 2H), 7.46 (dd, *J* = 1.86, 8.54 Hz, 2H), 2.81 (t, *J* = 7.55 Hz, 4H), 1.75-1.68 (m, 4H), 1.40-1.30 (m, 12H), 0.89 (t, *J* = 6.87 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.6, 155.4, 139.1, 132.7, 130.9, 121.7, 120.8, 112.2, 35.8, 31.78, 31.72, 28.8, 22.6, 14.1; HRMS (APCI) *m/z* ($M+H^+$) calcd for $C_{28}H_{33}N_2O_2$: 429.2537, found: 429.2541.

2,8-dicyclohexylbis(benzofuro)[2,3-*b*:2',3'-*e*]pyrazine (**Linear-*c*Hex**)

17 mg (30%, 0.15 mmol scale); white solid; m.p. 271.1-272.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 1.89 Hz, 2H), 7.62 (d, *J* = 8.72 Hz, 2H), 7.49 (dd, *J* = 1.89, 8.72 Hz, 2H), 2.74-2.67 (m, 2H), 2.00-1.91 (m, 4H), 1.89-1.81 (m, 4H), 1.79-1.78 (m, 2H), 1.56-1.40 (m, 8H), 1.36-1.25 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, CDCl3) δ 155.6, 155.4, 144.4, 132.8, 129.7, 121.7, 119.1, 112.2, 44.5, 34.9, 26.9, 26.1; HRMS (APCI) *m/z* $(M+H)^+$ calcd for $C_{28}H_{29}N_2O_2$: 425.2224, found: 425.2213.

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of intermediate




7.954
7.460
7.455
7.165
7.164
7.148
7.143
7.088
7.077
2.588
2.580
2.560
1.688
1.680
1.661
1.642
1.623
1.605
0.957
0.559
0.540
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nPr
nPr
Br
N
O
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9
8
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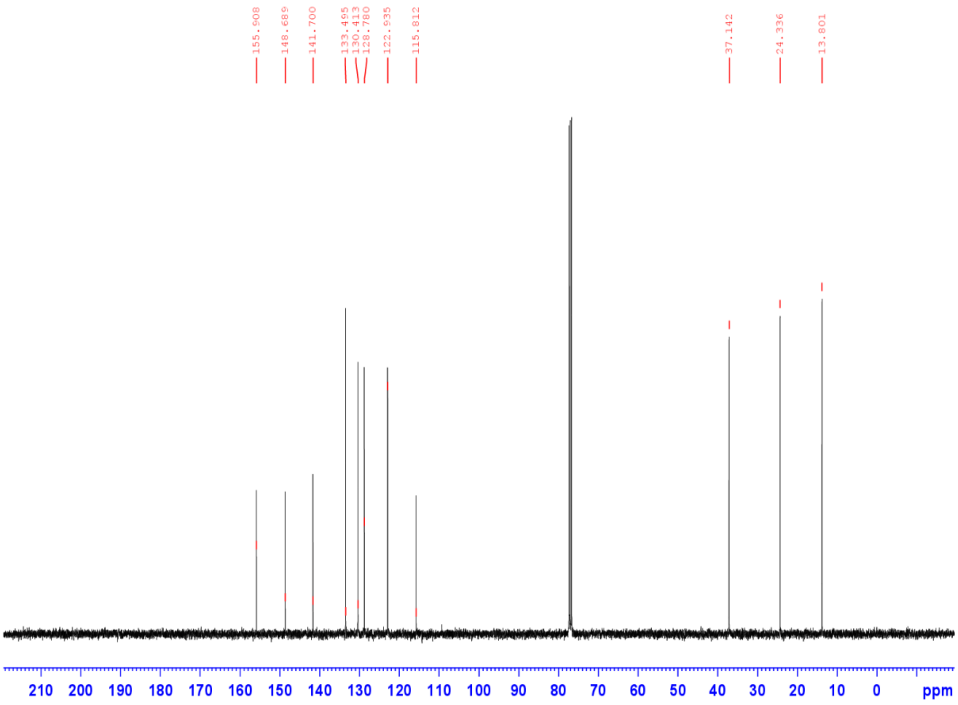
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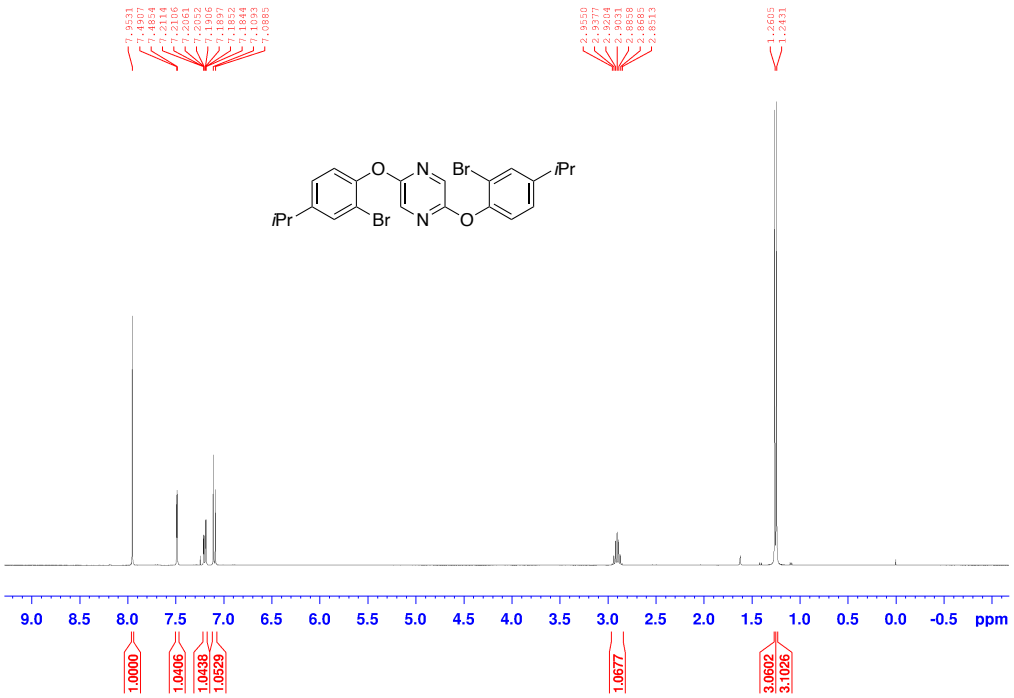
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2.8513
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Br
iPr
iPr
Br
N
O
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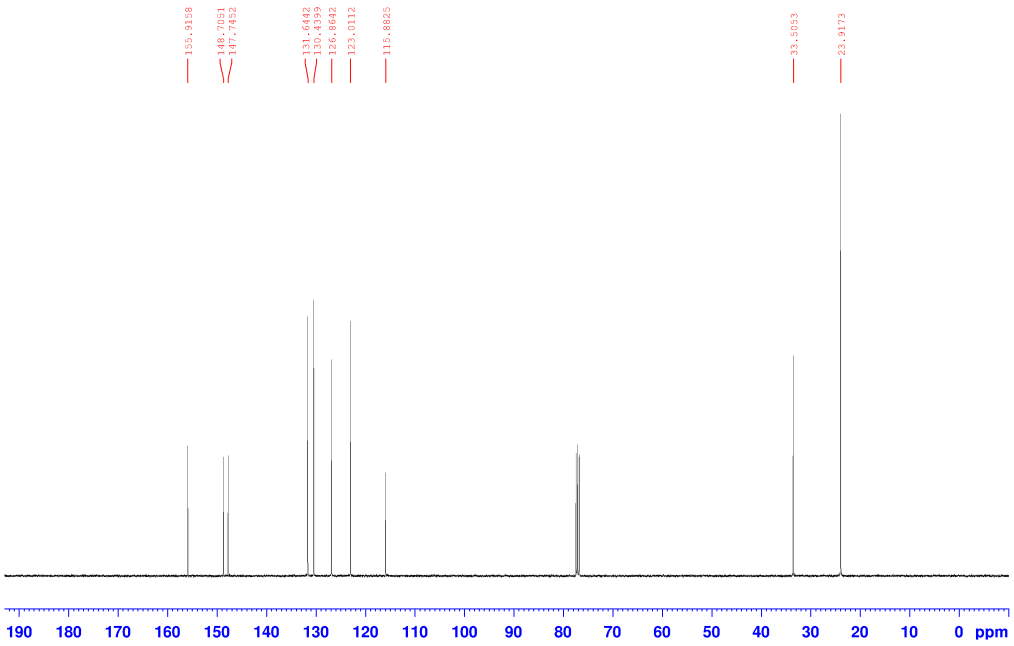
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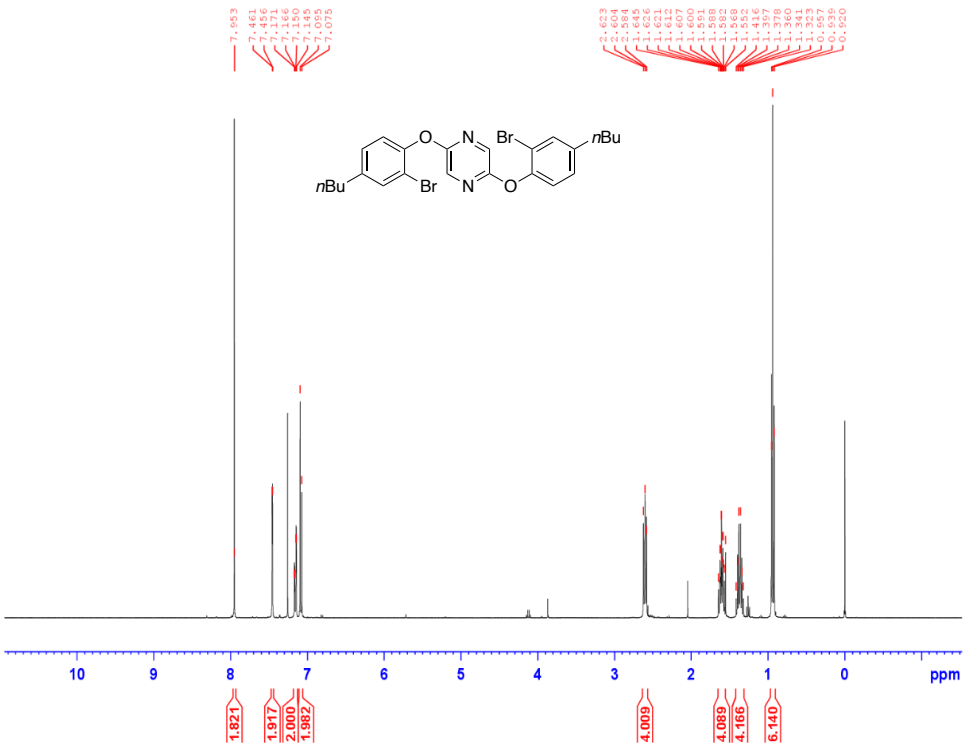
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1.621
1.612
1.607
1.600
1.591
1.588
1.582
1.568
1.552
1.416
1.397
1.378
1.360
1.341
1.323
0.957
0.939
0.920
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Br
nBu
nBu
Br
N
O
10
9
8
7
6
5
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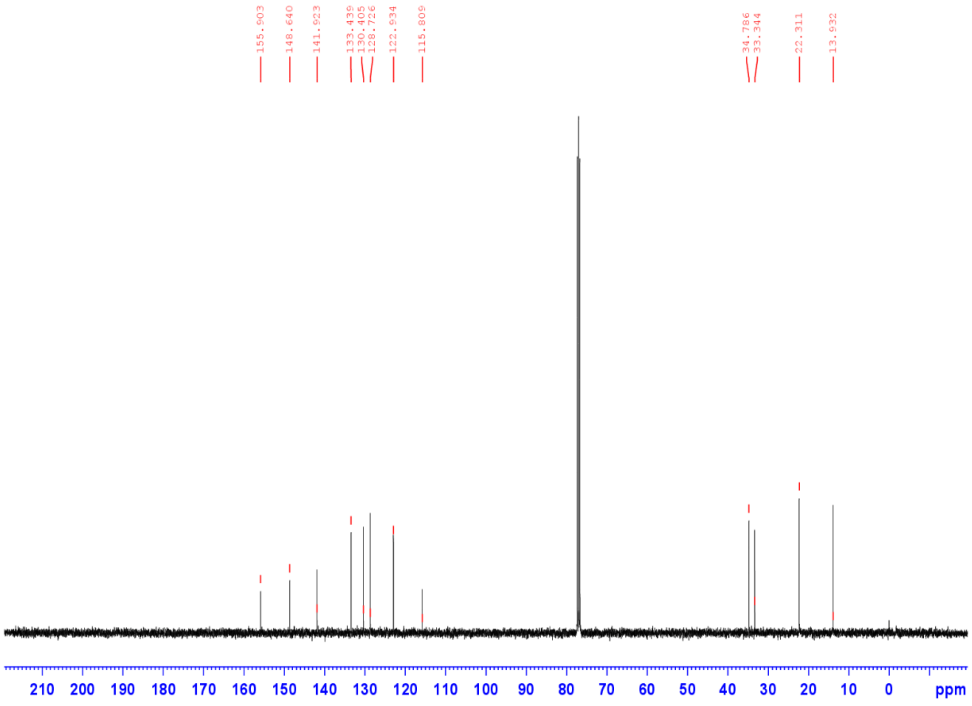
6.140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200
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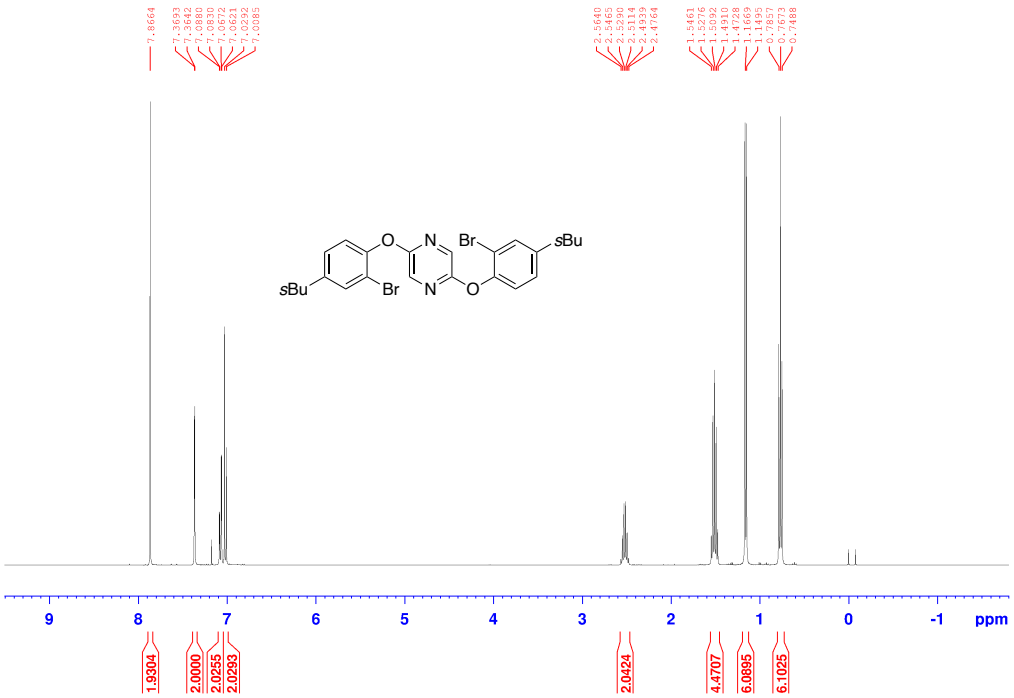
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2.5290
2.5114
2.4939
2.4764
1.5461
1.5276
1.5092
1.4910
1.4728
1.1669
1.1495
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0.7673
0.7488
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Br
sBu
sBu
Br
N
O
9
8
7
6
5
4
3
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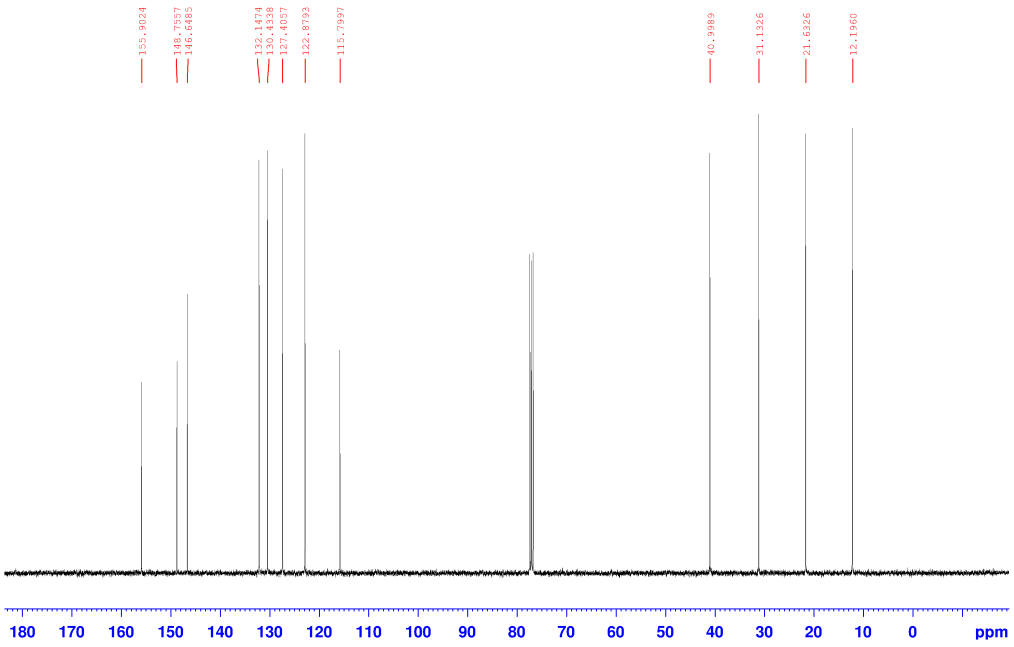
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12.1960
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140
130
120
110
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80
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60
50
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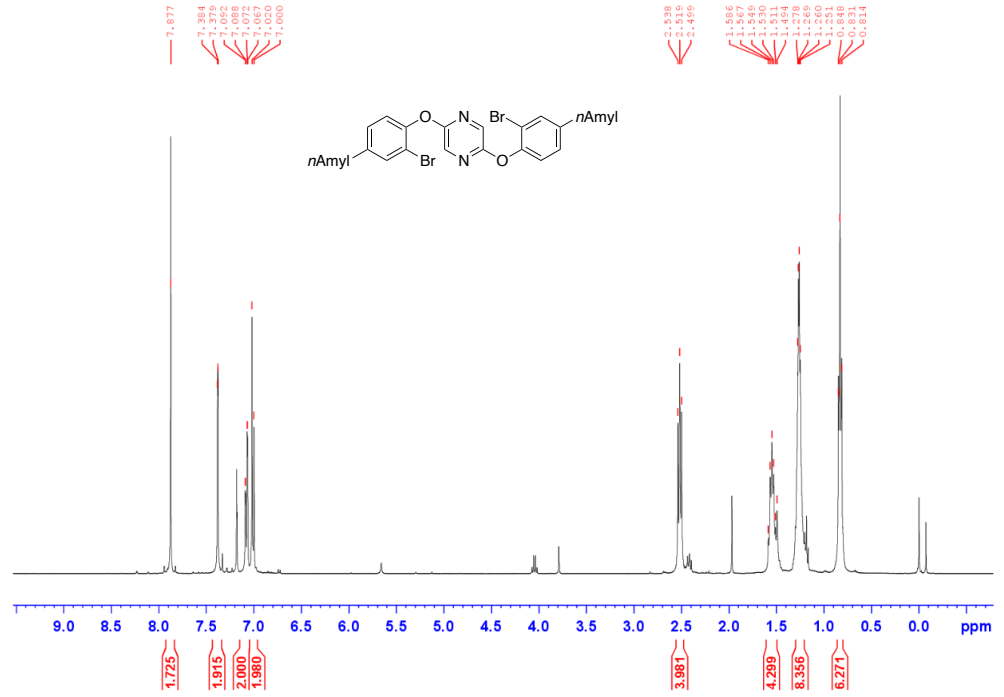
20
10
0
ppm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7.072
7.067
7.020
7.000
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2.515
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1.586
1.567
1.549
1.530
1.511
1.494
1.278
1.266
1.260
1.251
0.848
0.831
0.814
O
N
Br
nAmyl
nAmyl
Br
N
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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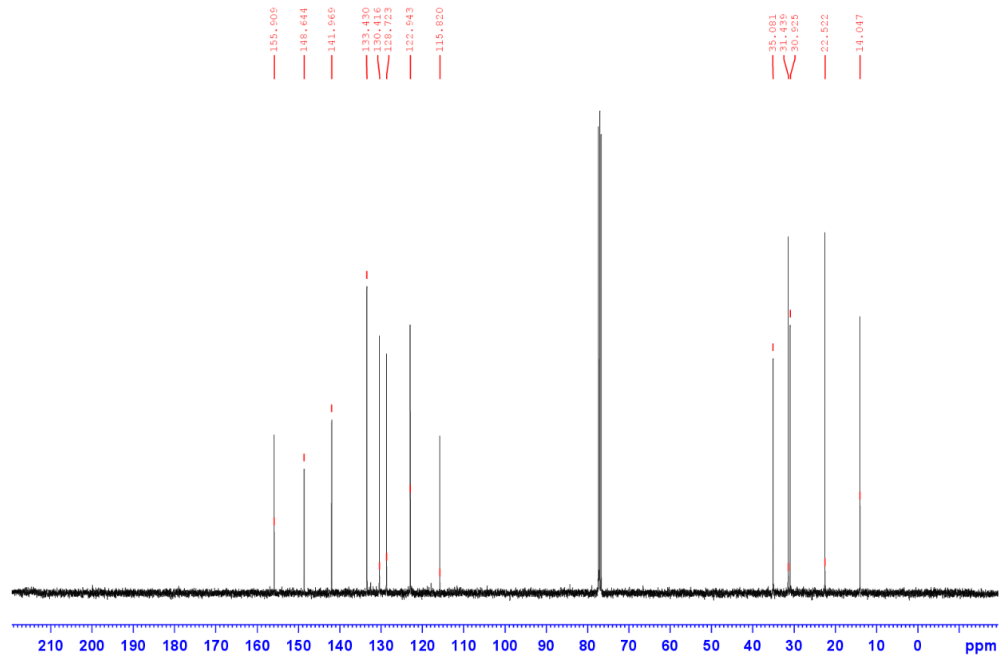
6.271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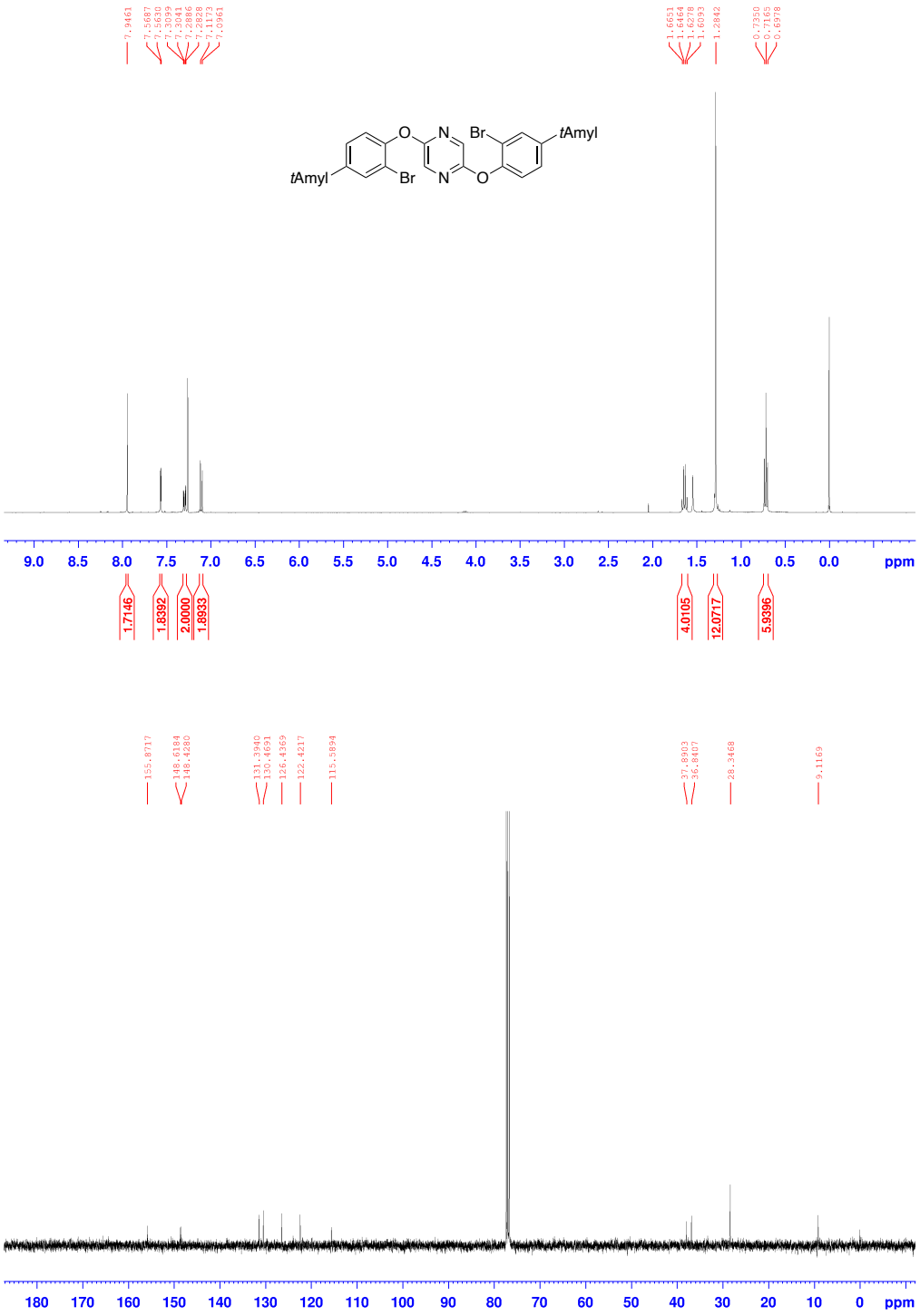
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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1.6278
1.6093
1.2842
0.7350
0.7165
0.6978
O
N
Br
tAmyl
tAmyl
Br
N
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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1.8392
2.0000
1.8933
4.0105
12.0717
5.9996
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148.4280
131.3940
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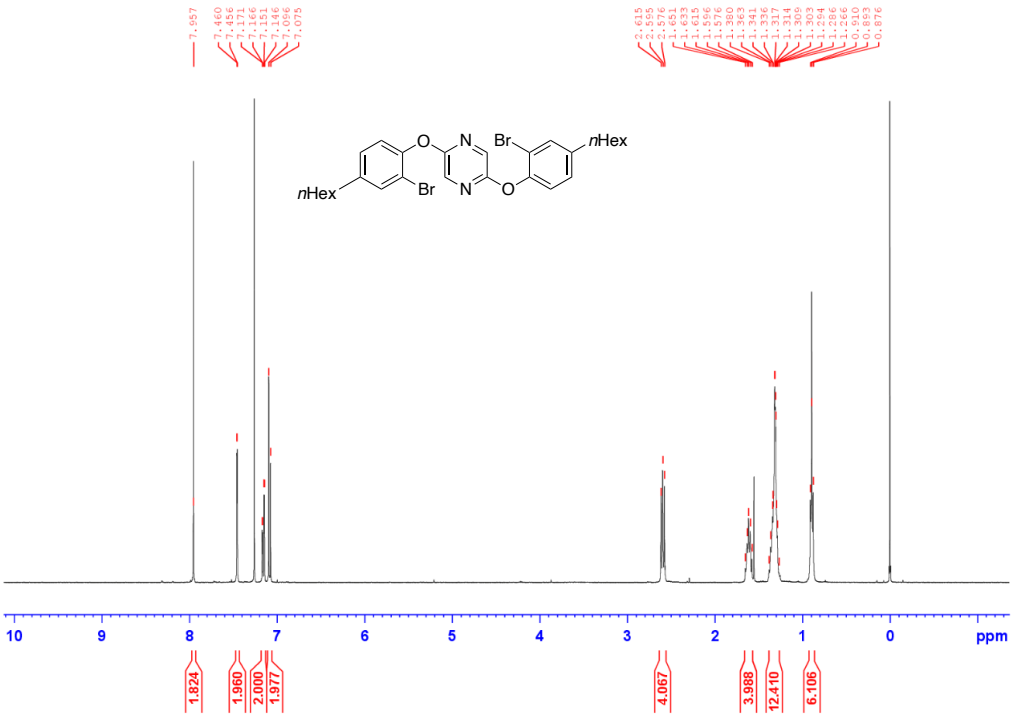
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1.633
1.615
1.596
1.576
1.360
1.363
1.341
1.336
1.317
1.314
1.309
1.303
1.294
1.286
1.266
0.910
0.893
0.876
O
N
Br
nHex
nHex
Br
N
O
10
9
8
7
6
5
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ppm
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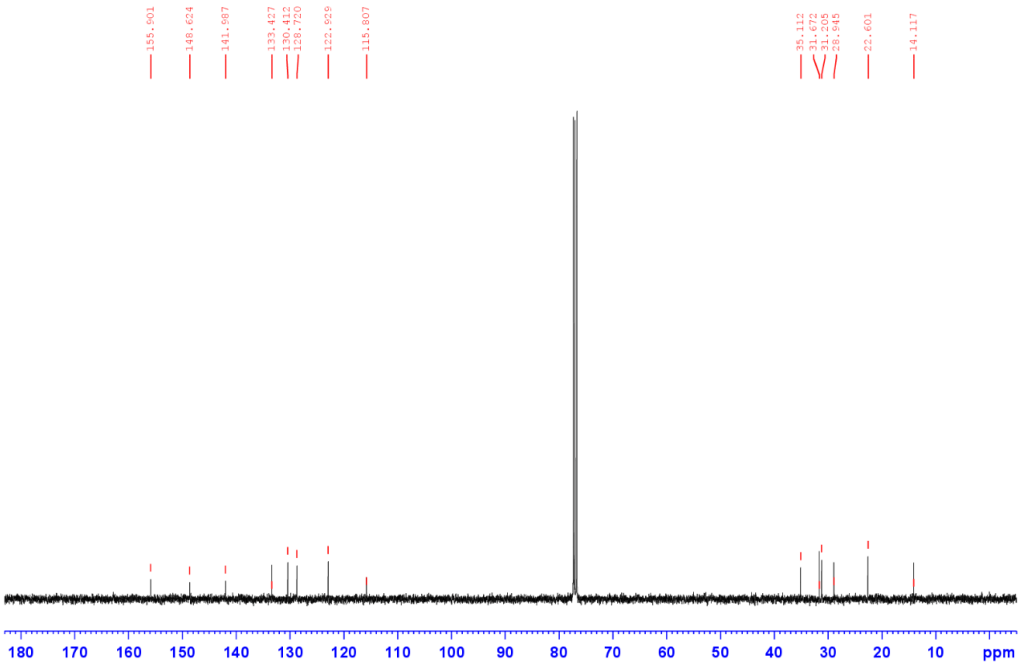
6.106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150
140
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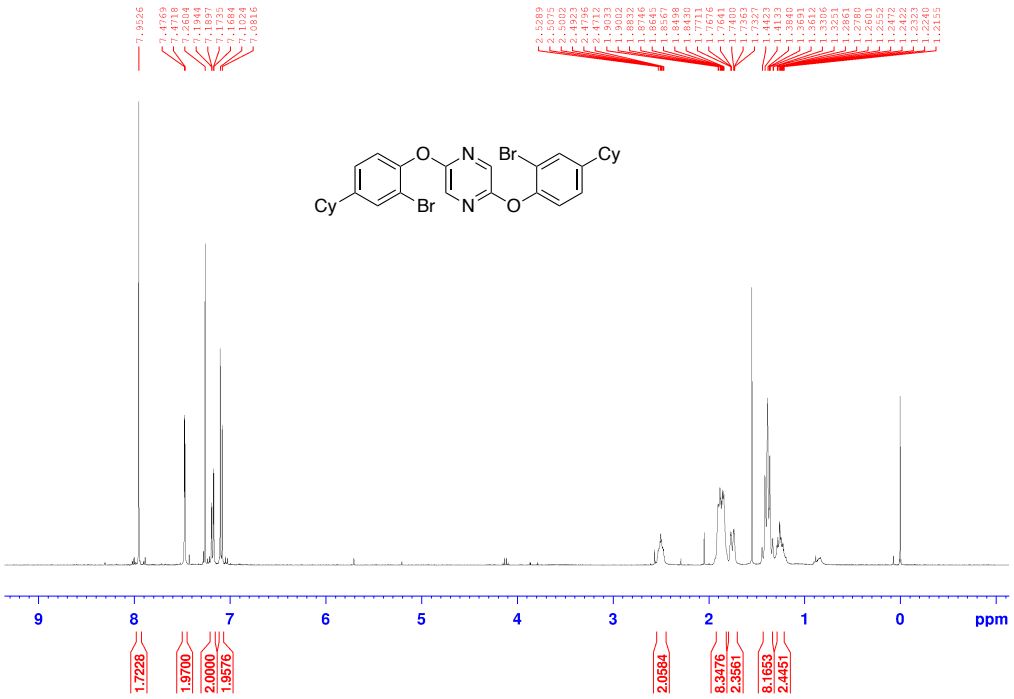
30
20
10
ppm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2.5075
2.4930
2.4923
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1.8643
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1.2552
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Br
Cy
Cy
Br
N
O
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7
6
5
4
3
2
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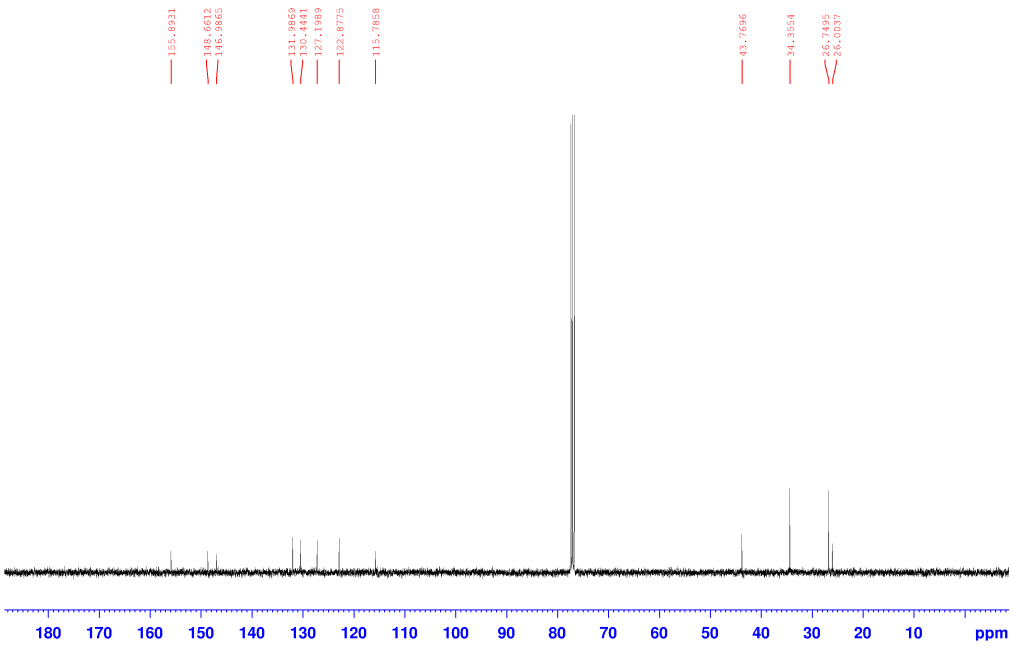
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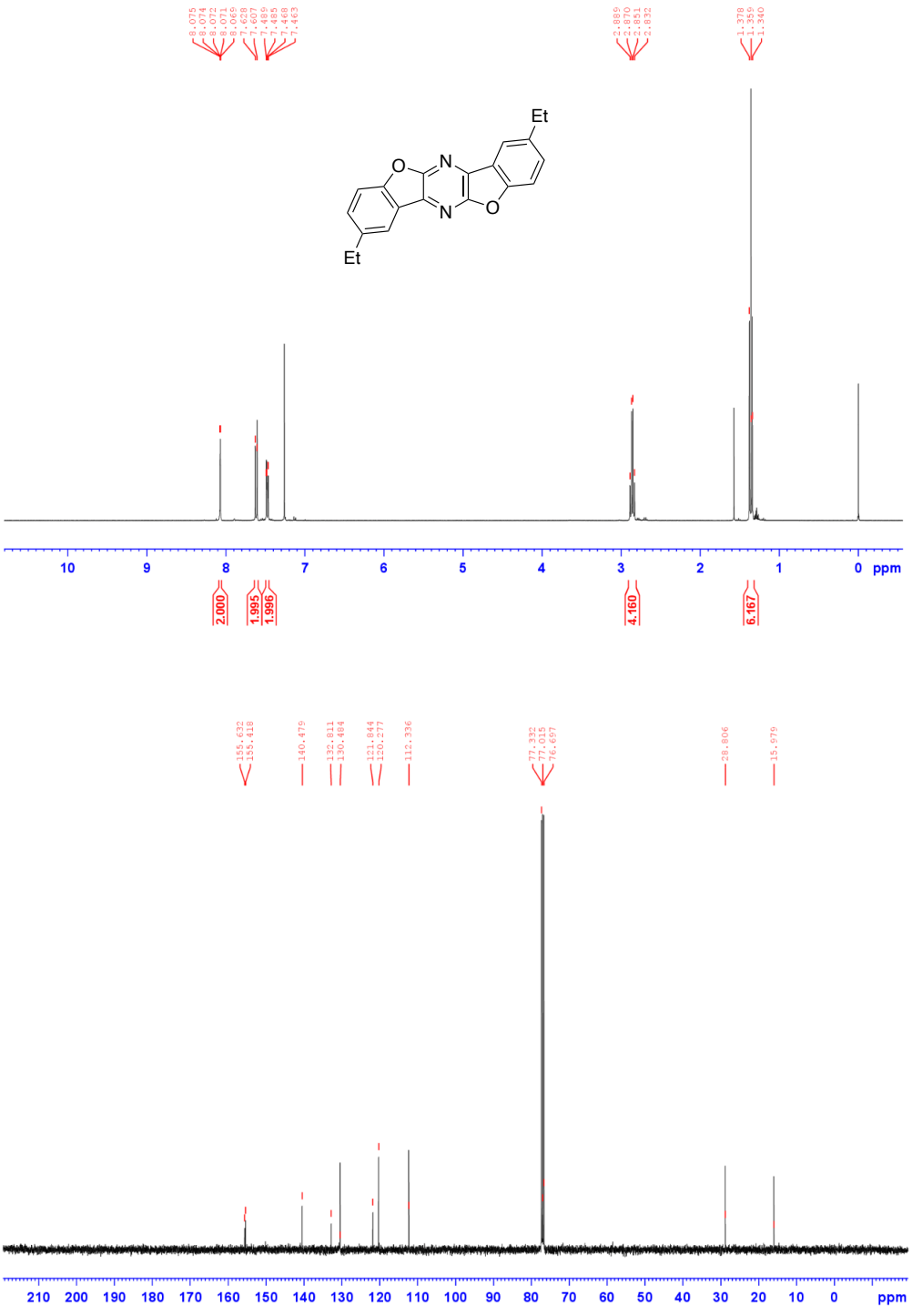
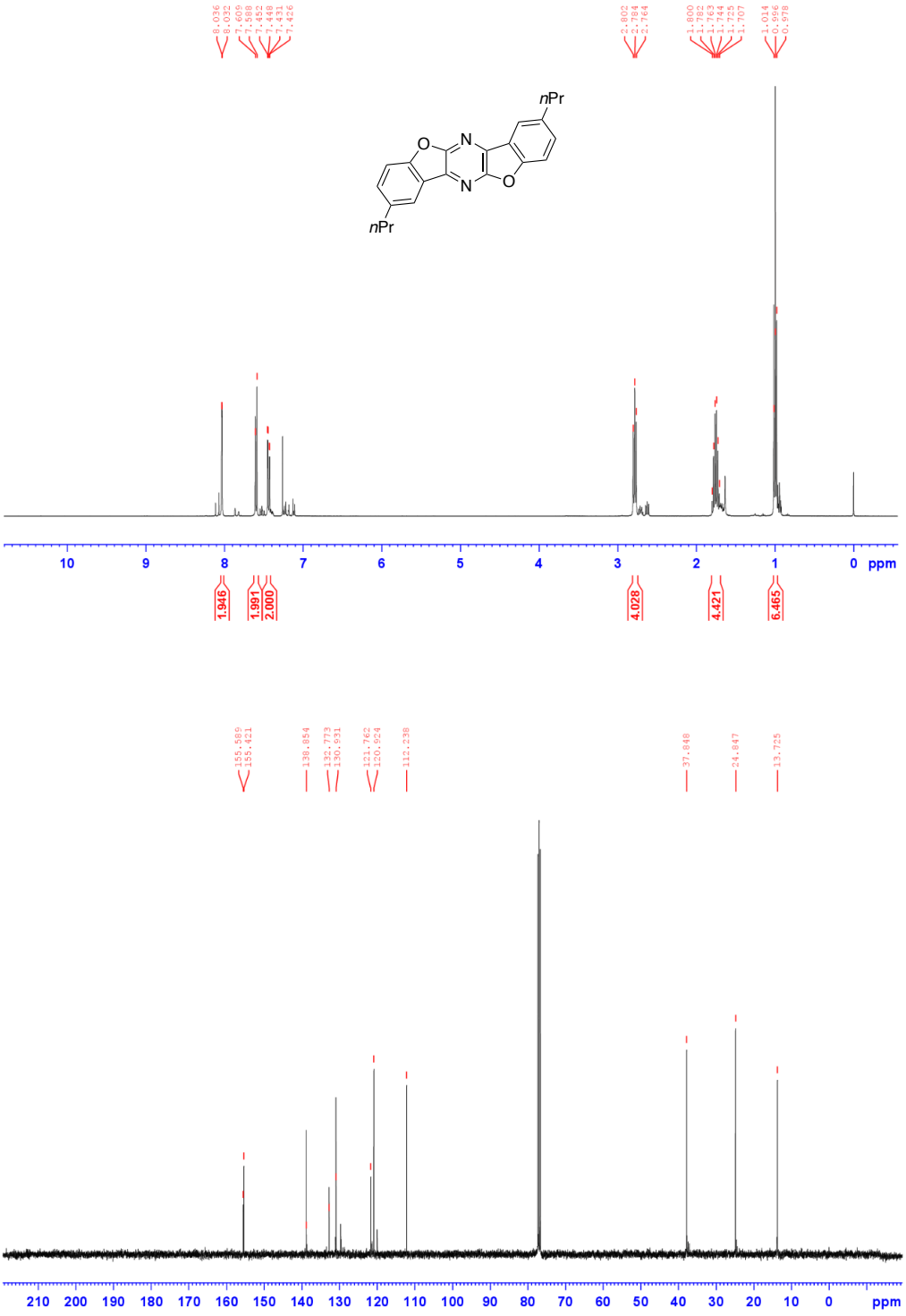
26.0037
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **Linear-Et**



^{1}H and ^{13}C{^{1}H} NMR spectra of **Linear-*n*Pr**



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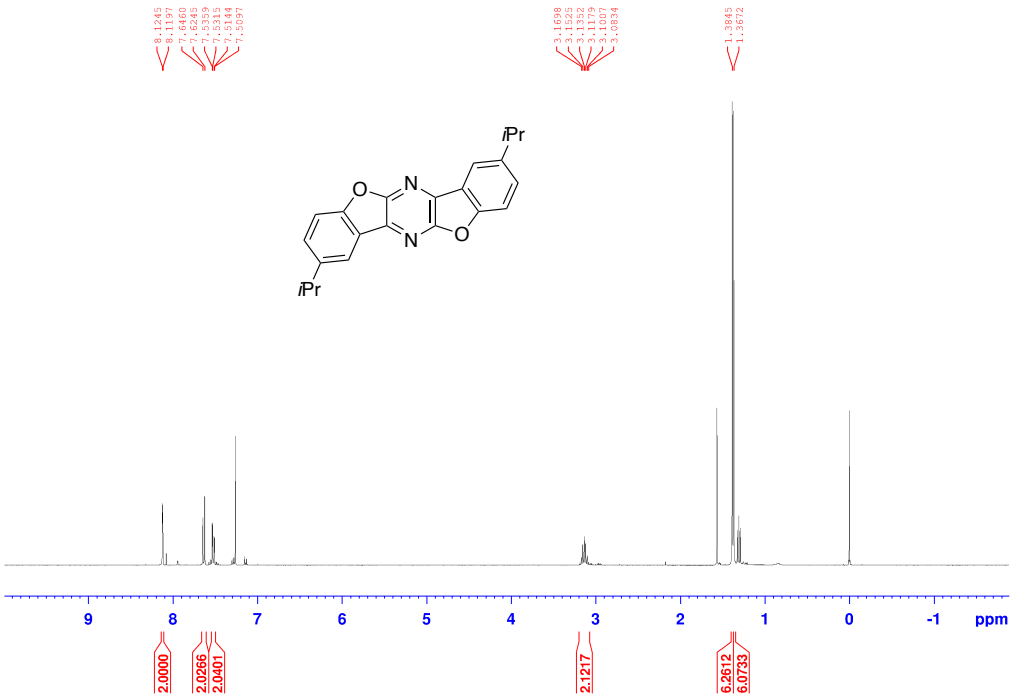
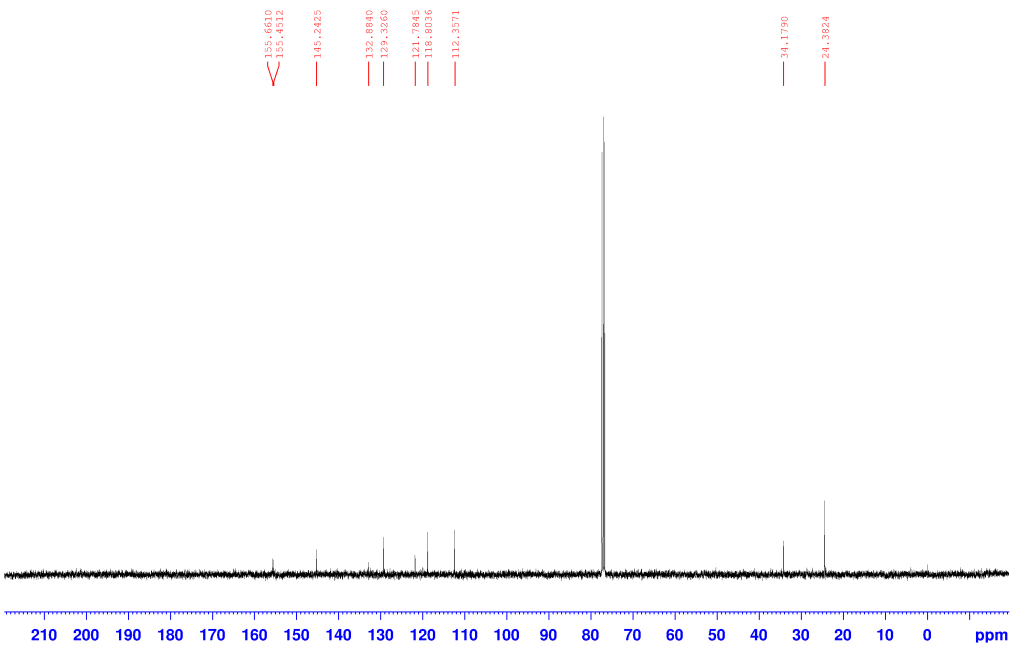
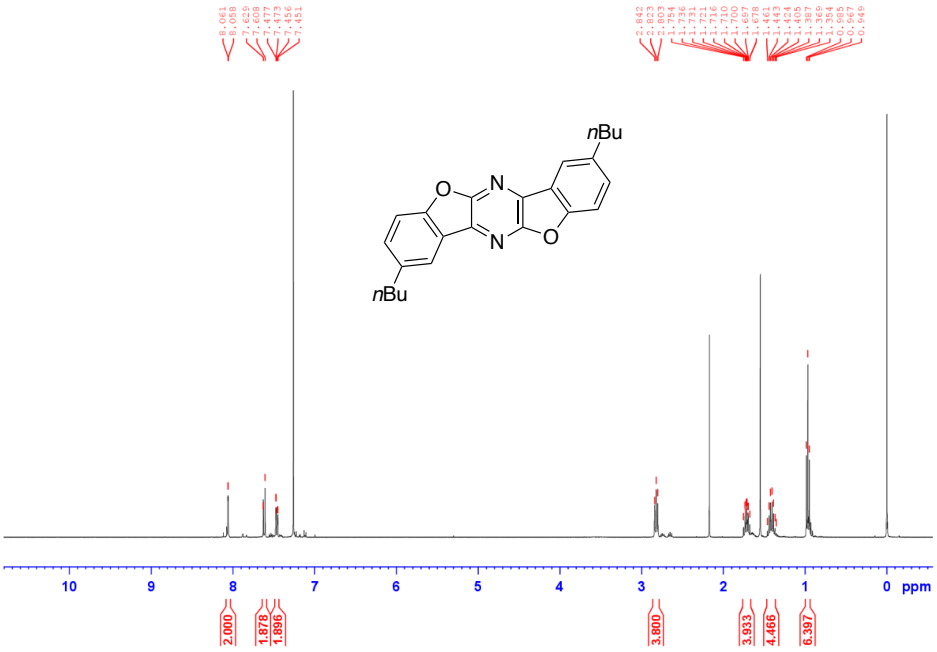
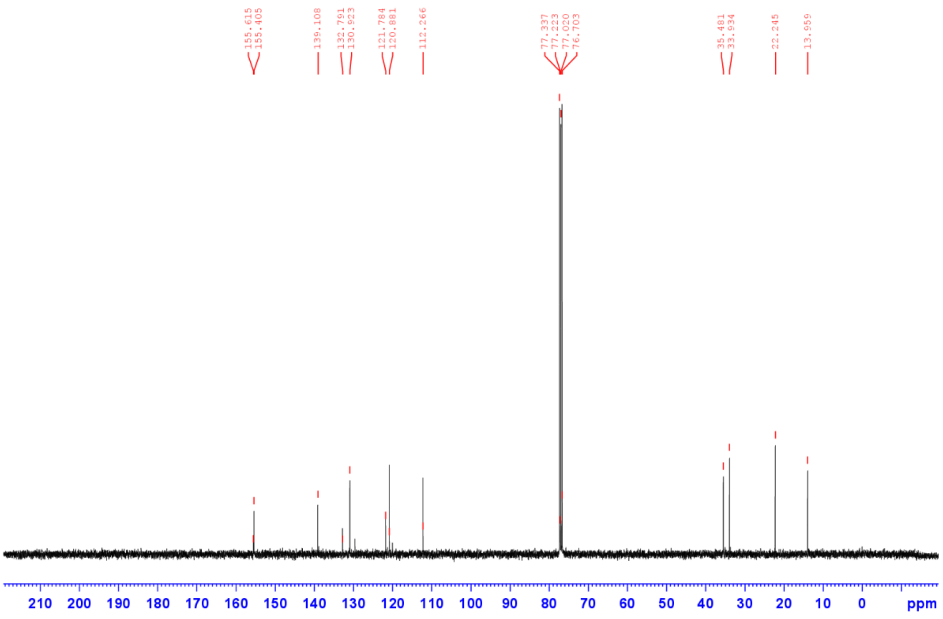


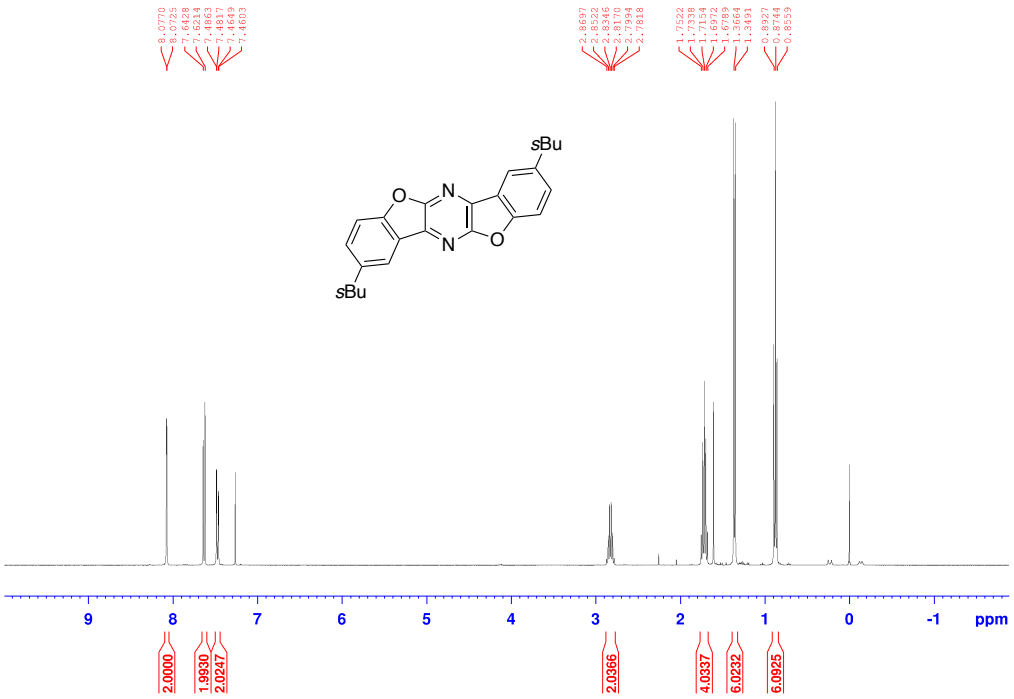


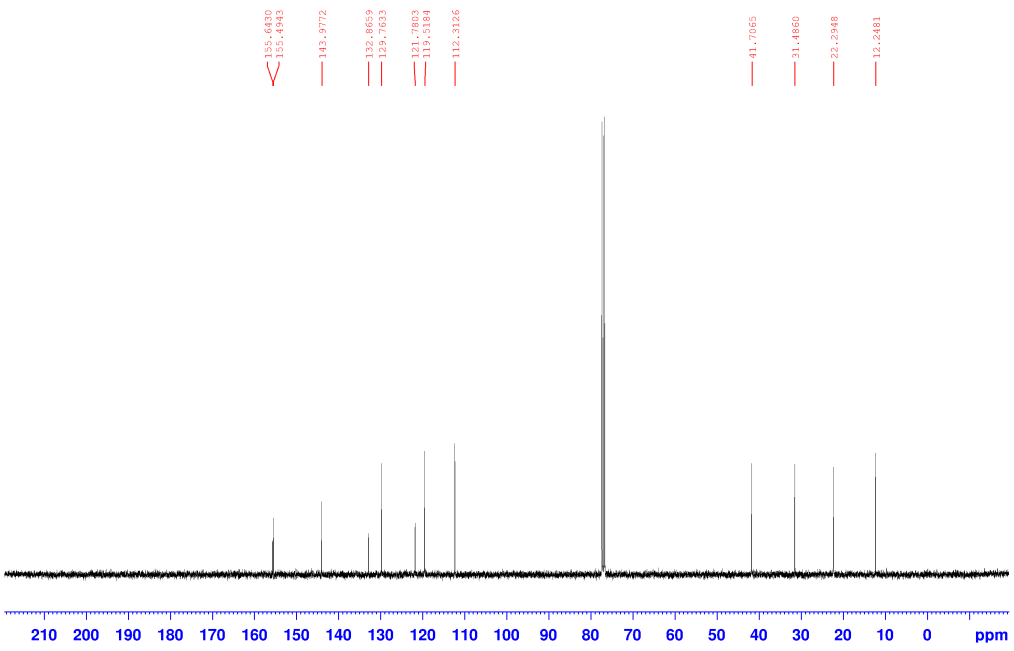
^{1}H and ^{13}C{^{1}H} NMR spectra of **Linear-*n*Bu**



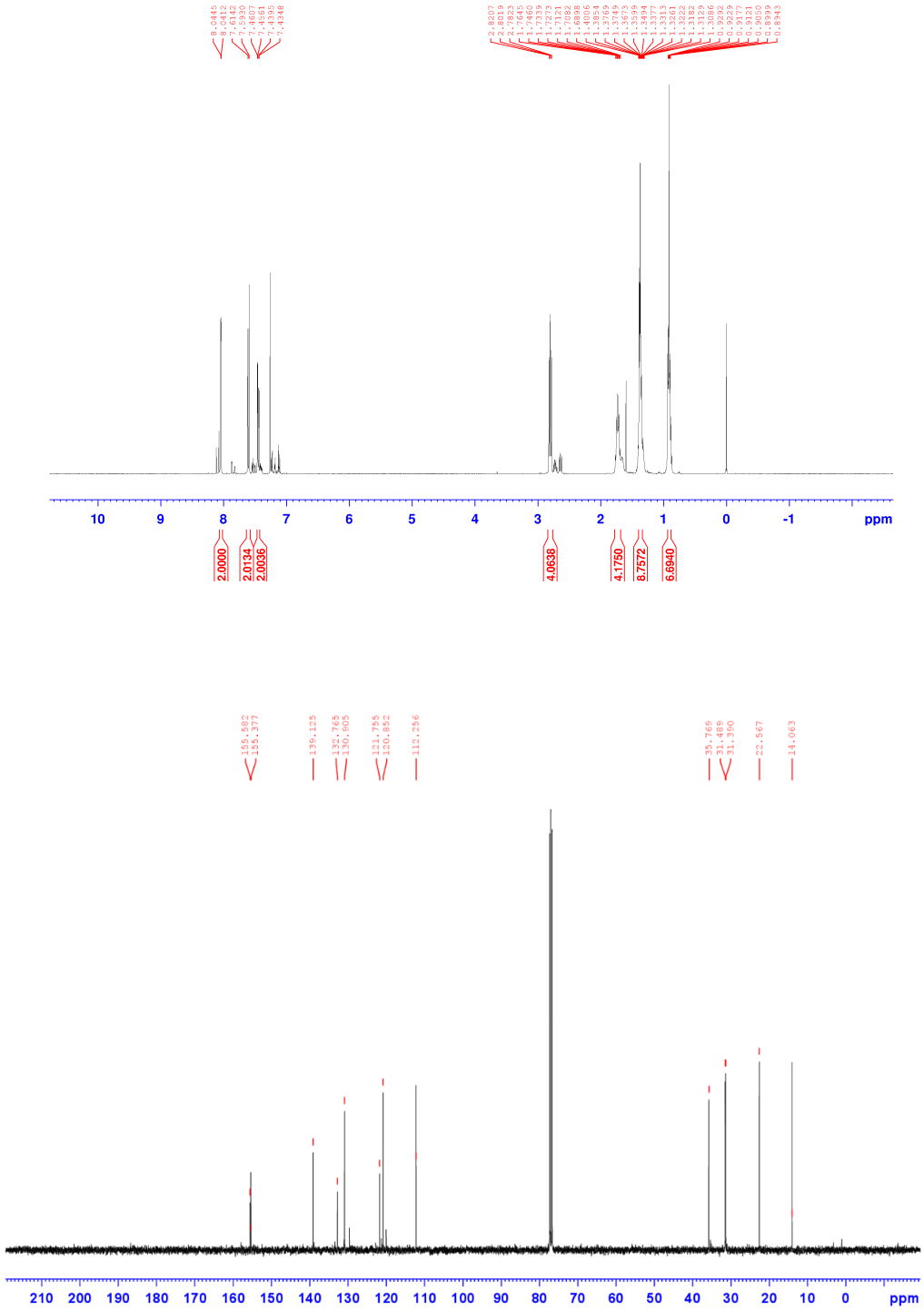


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **Linear-*s*Bu**

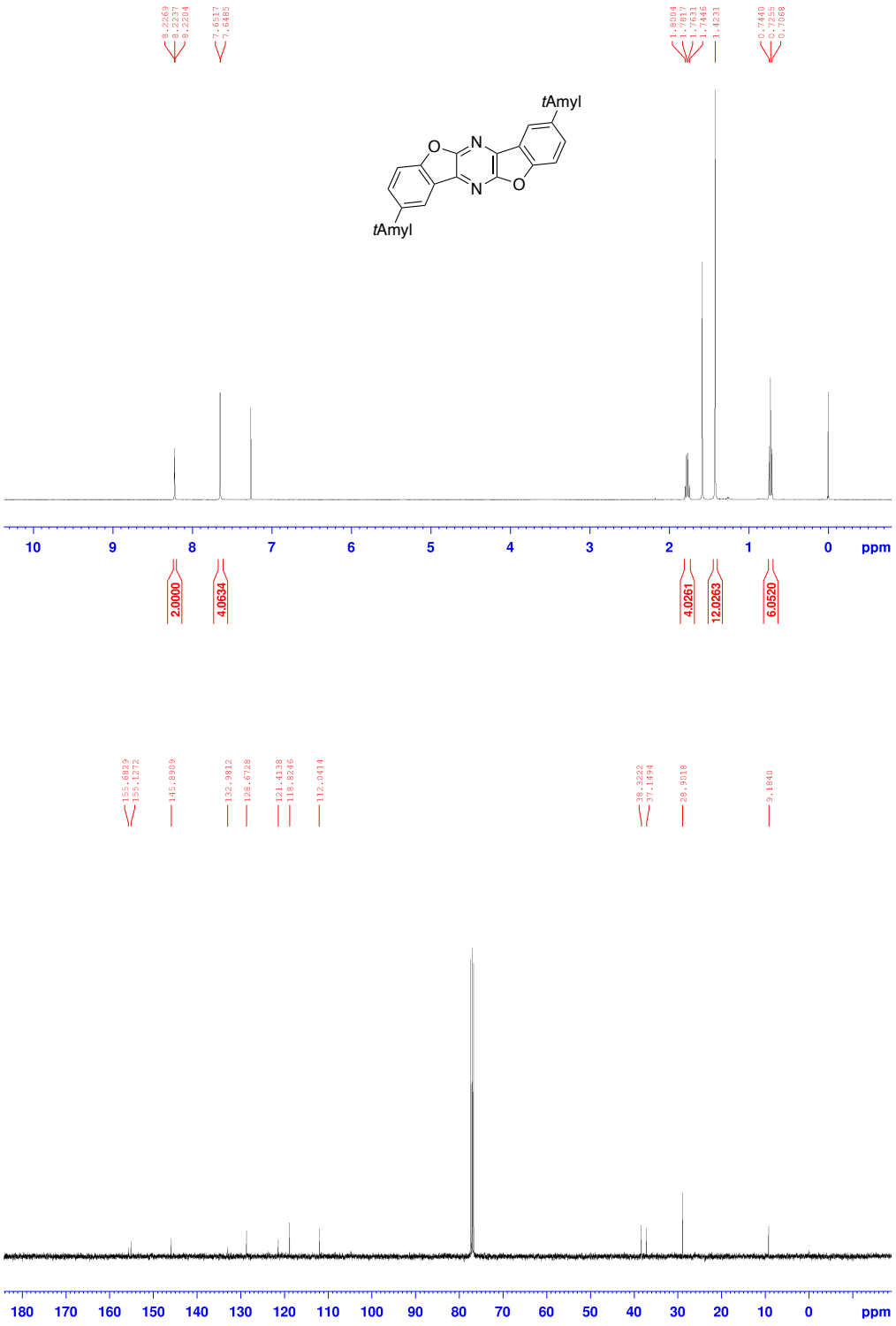




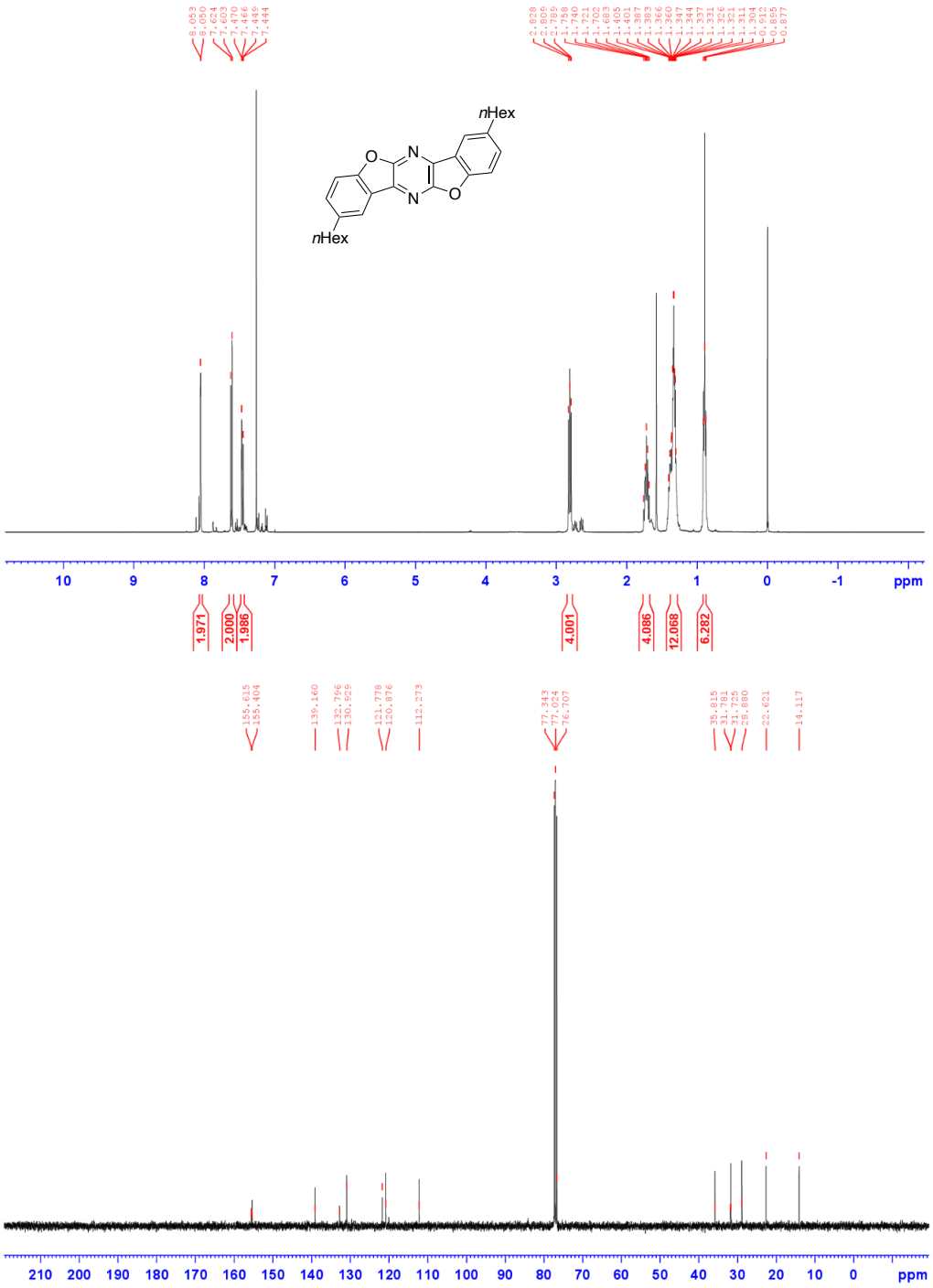
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **Linear-*n*Amyl**



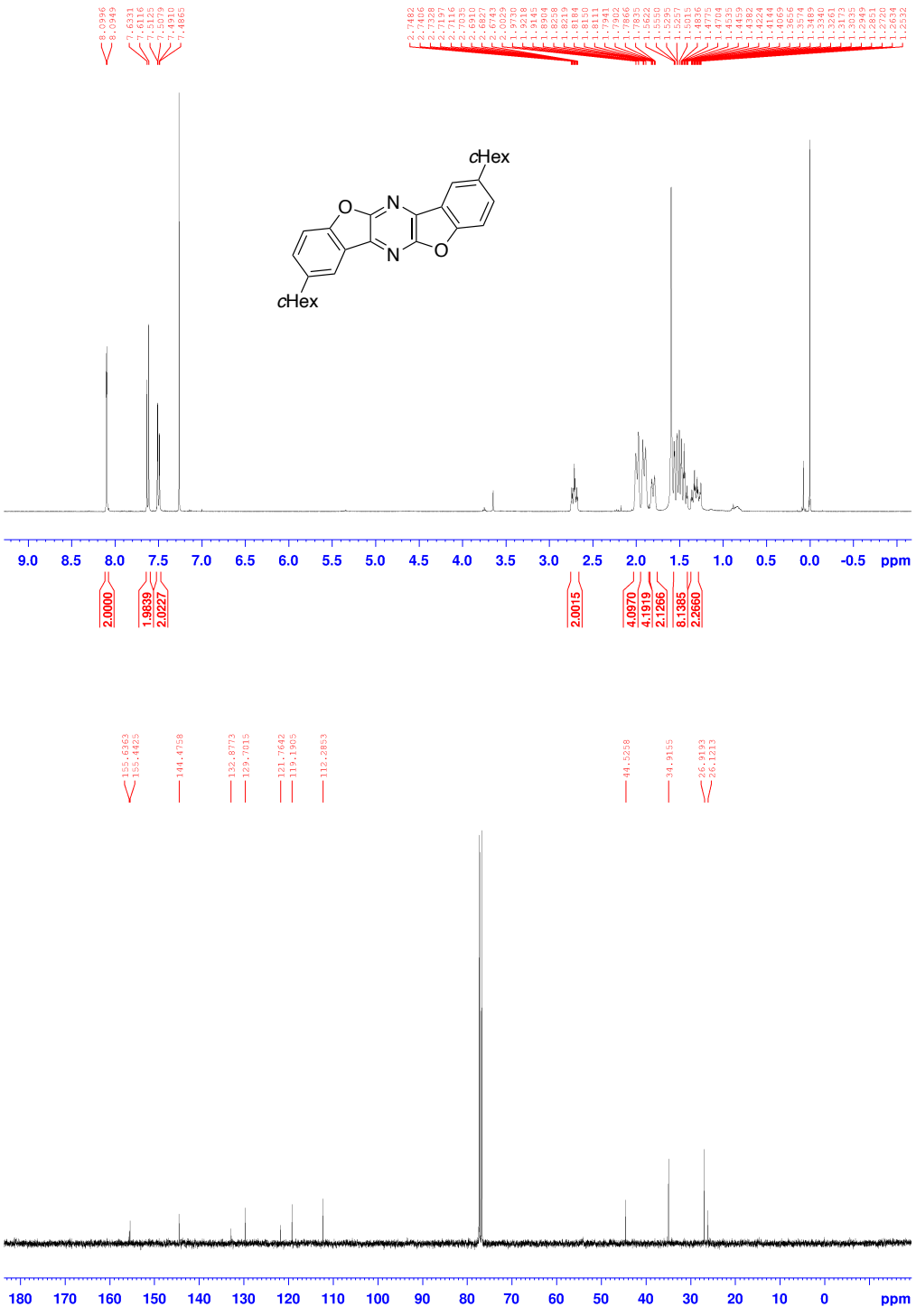
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **Linear-*t*Amyl**



^{1}H and ^{13}C{^{1}H} NMR spectra of **Linear-*n*Hex**



^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **Linear-*c*Hex**



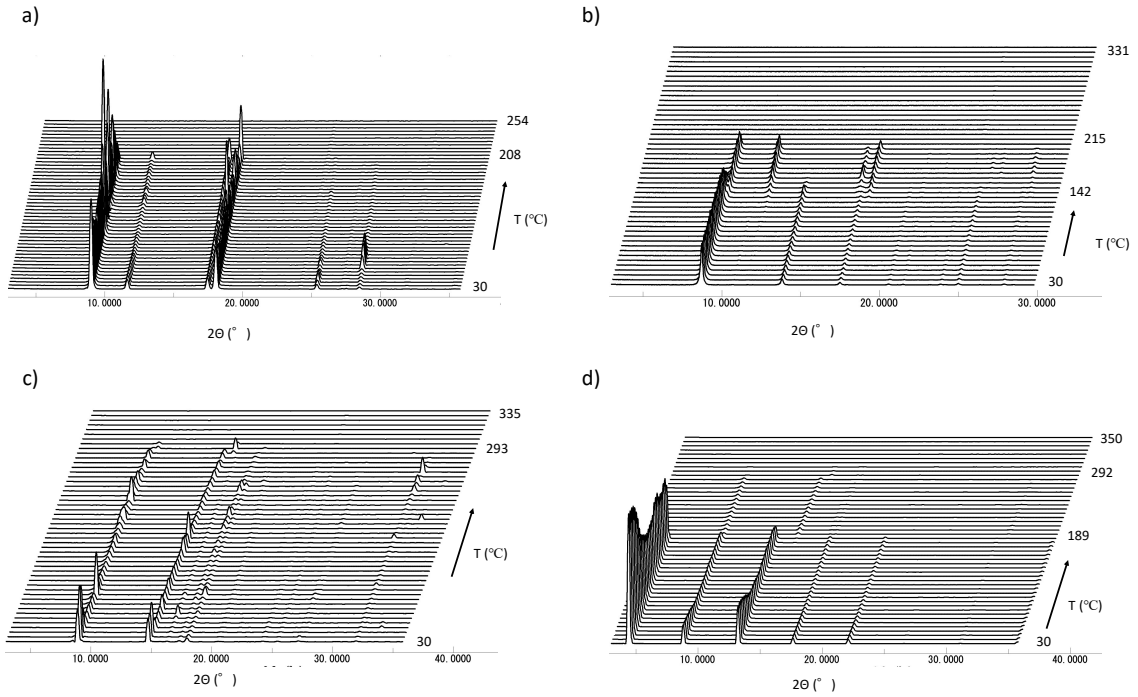


Figure S1. Changes of PXRD patterns of a) Form 1 crystal of **Linear-Et**, b) Form 2 crystal of **Linear-Et**, c) Form 1 crystal of **Linear-*c*Hex**, and d) Form 2 crystal of **Linear-*c*Hex** upon heating.

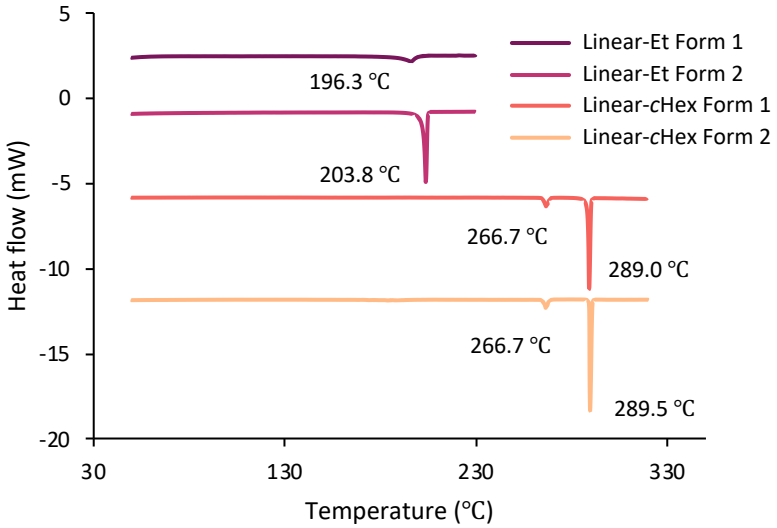


Figure S2. Differential scanning calorimetry measurements of **Linear-Et** Form 1, Form 2 and **Linear-*c*Hex** Form 1, and Form 2.

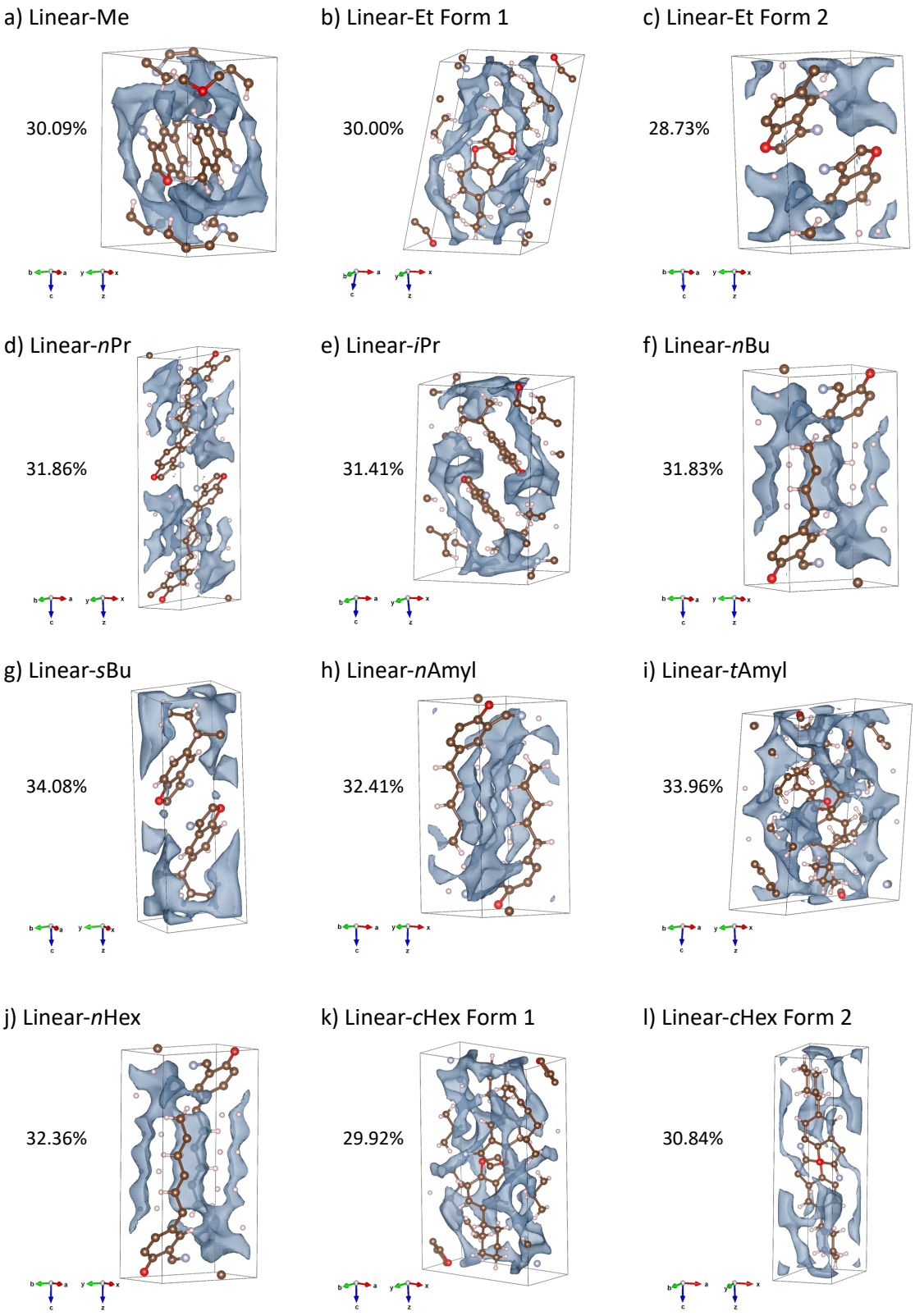


Figure S3. Free volume fractions of **Linear-R** obtained by Multiwfn 3.8 (dev) package.[S3)]

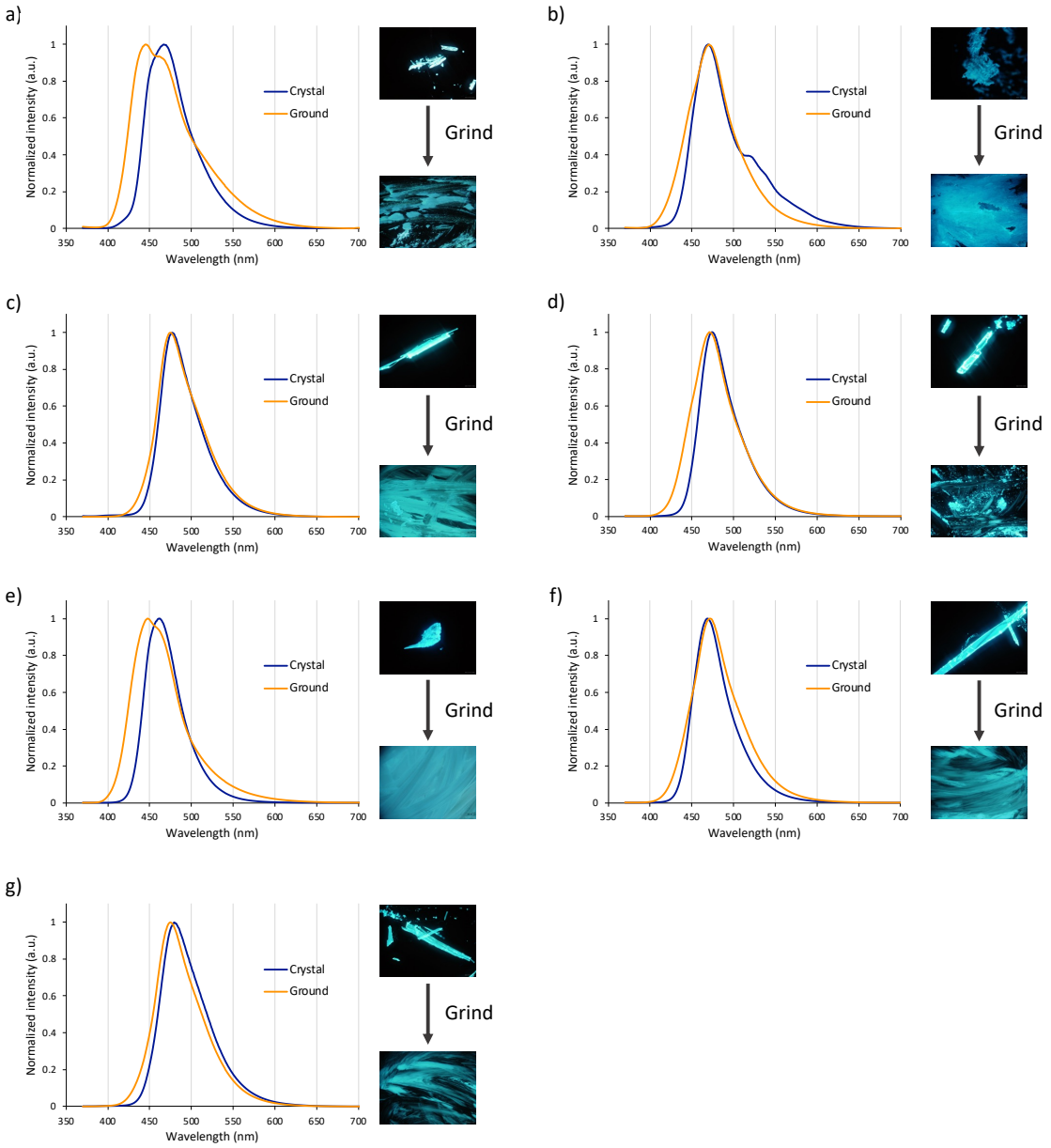


Figure S4. Fluorescence spectra and photographs of crystal and ground powder of a) **Linear-Et** Form 1, b) **Linear-Et** Form 2, c) **Linear-*n*Pr**, d) **Linear-*n*Bu**, e) **Linear-*s*Bu**, f) **Linear-*n*Amyl**, and g) **Linear-*n*Hex** under UV light irradiation.

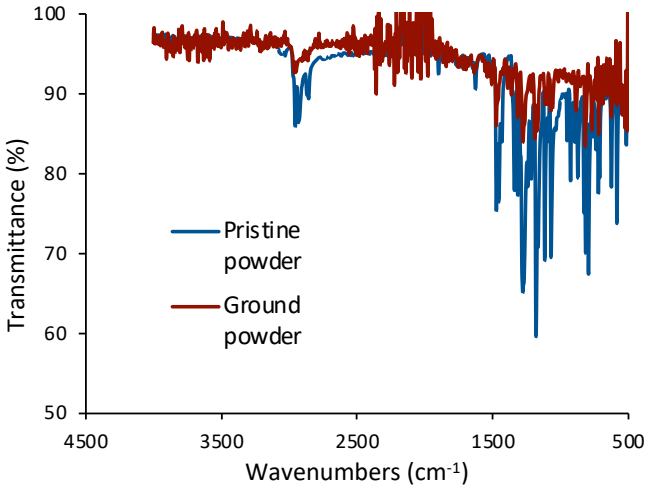


Figure S5. Changes of the IR spectra of **Linear-*i*Pr** before and after grinding.

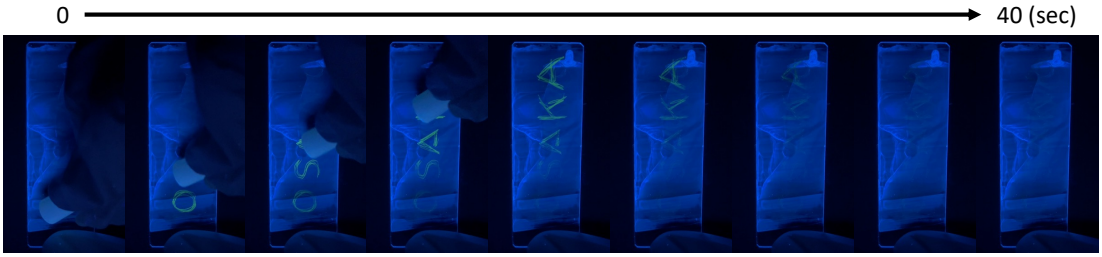


Figure S6. Picture of the fast self-recovery behavior of **Linear-Et** Form 1 upon grinding.

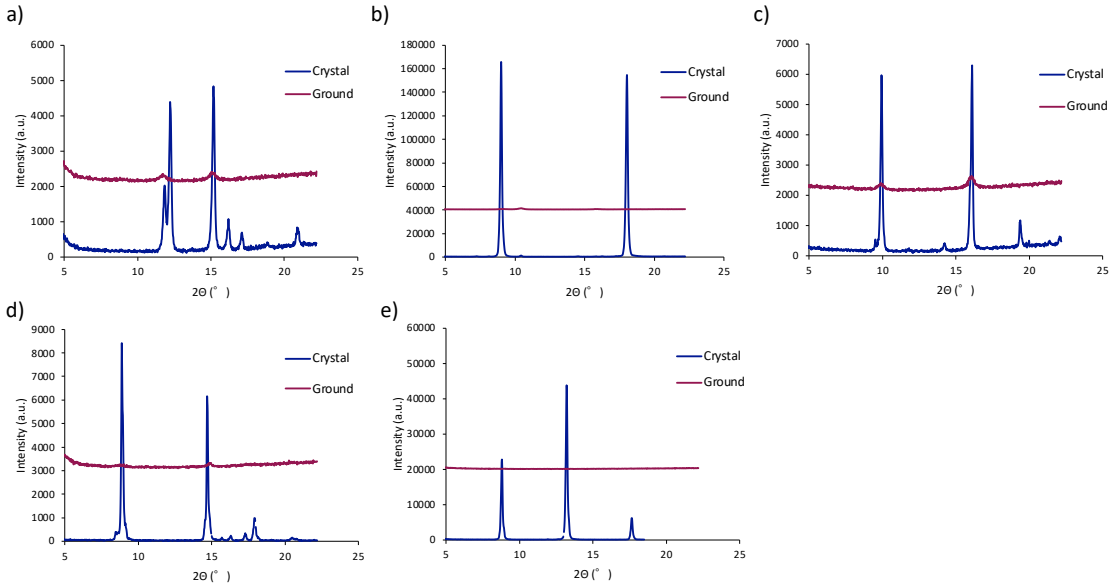


Figure S7. PXRD pattern changes before and after grinding of a) **Linear-Me**, b) **Linear-*i*Pr**, c) **Linear-*t*Amyl**, d) Form 1 of **Linear-*c*Hex**, and e) Form 2 of **Linear-*c*Hex**.

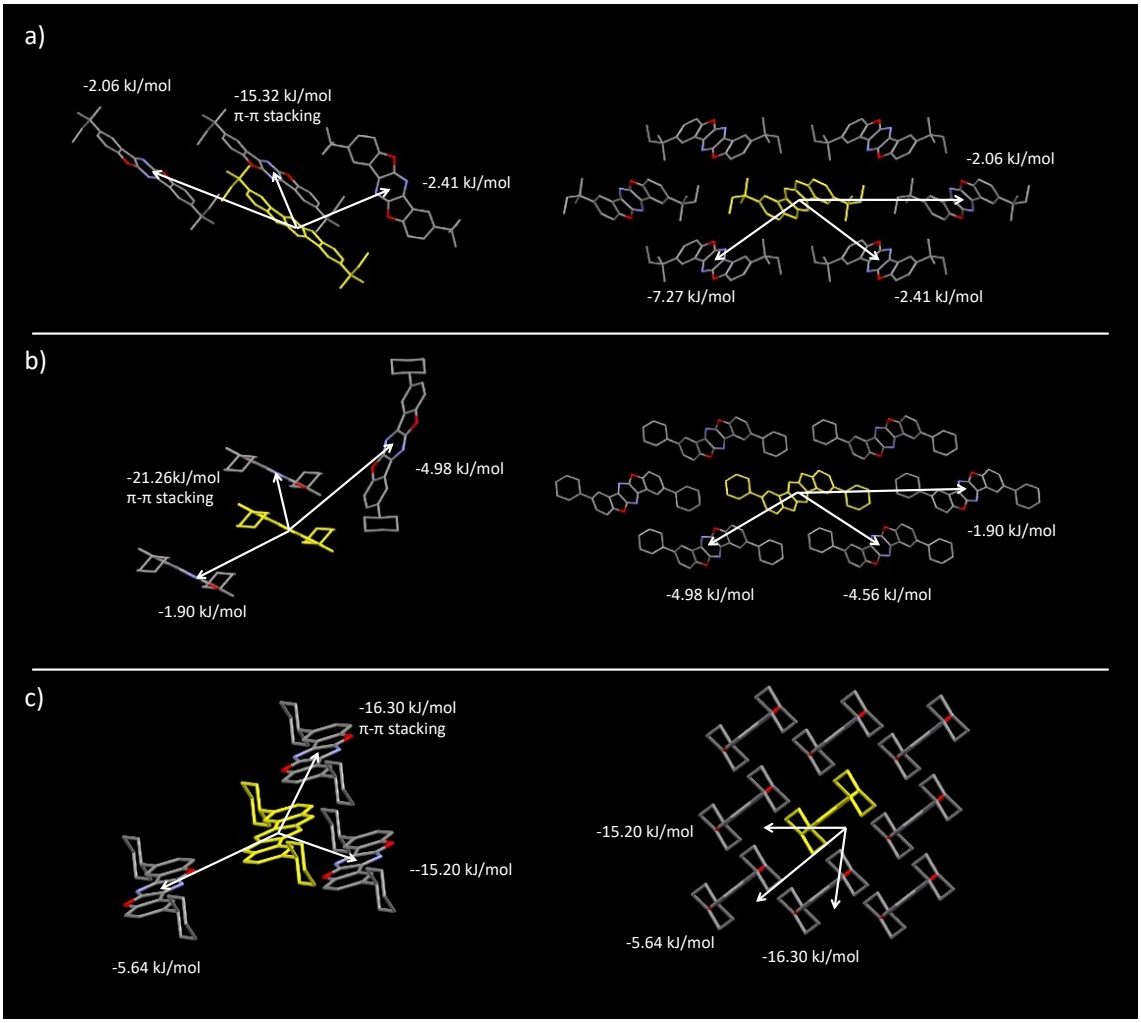


Figure S8. Intermolecular potentials among adjacent molecules in the crystalline state calculated at B3LYP-D3/6-311G** level. a) crystal of **Linear-*t*Amyl**, b) Form 1 crystal of **Linear-*c*Hex**, c) Form 2 crystal of **Linear-*c*Hex**. [S4,S5)]

The crystal of **Linear-*c*Hex** Form 1 and 2, which showed smaller change in their spectral shapes upon grinding, had larger potential energy along the π stacking direction (-21.26, and -16.30 kcal/mol, respectively). In contrast, **Linear-*t*Amyl**, which exhibited distinct mechanochromic luminescence, had the smallest potential energy (-15.32 kcal/mol).

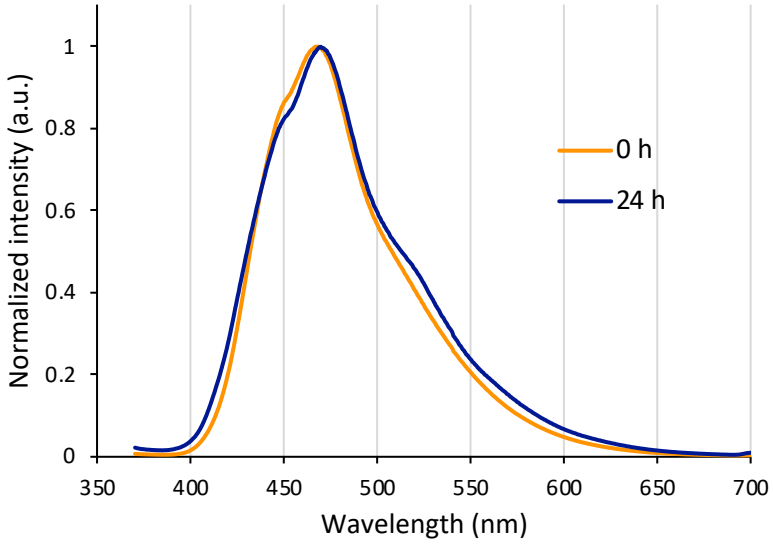


Figure S9. Fluorescence spectra of ground powder of **Linear-Me** after 0 h and 24 h.

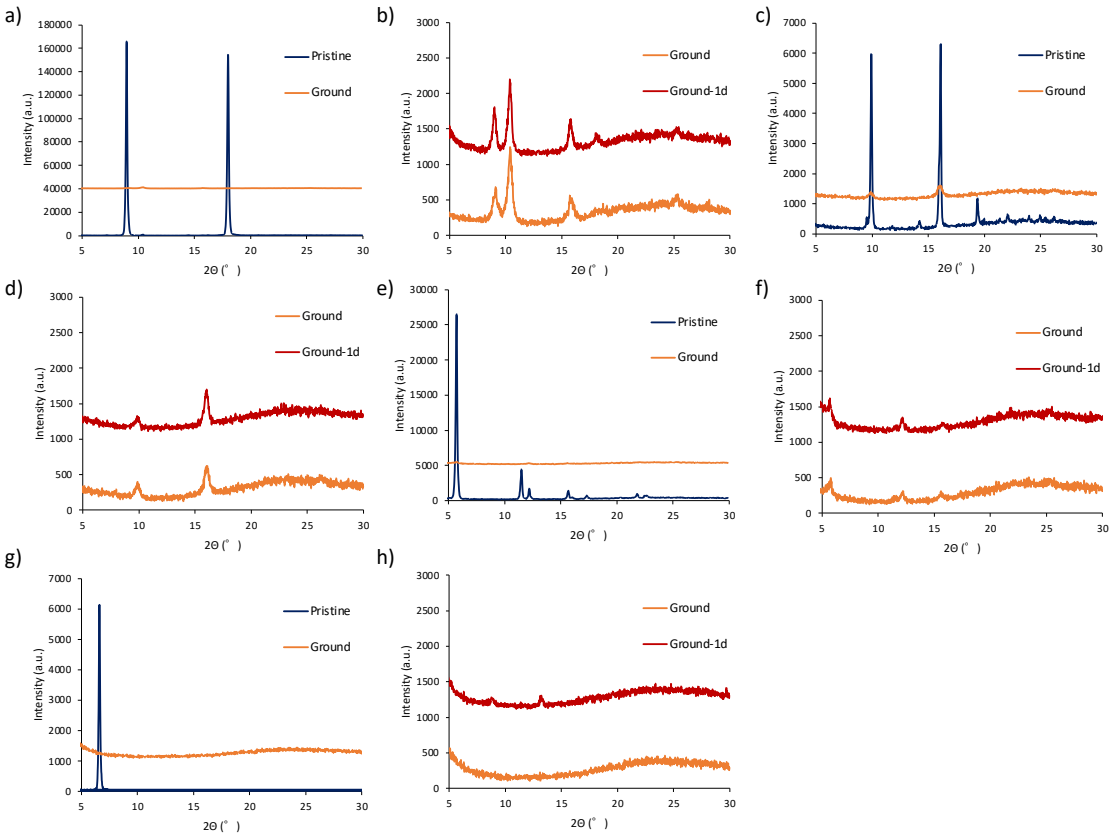


Figure S10. PXRD patterns of pristine, ground powder, and ground powder after 1 d of a,b) **Linear-*i*Pr**, c,d) **Linear-*t*Amyl**, e,f) Form 1 of **Linear-*c*Hex**, and g,h) Form 2 of **Linear-*c*Hex**.

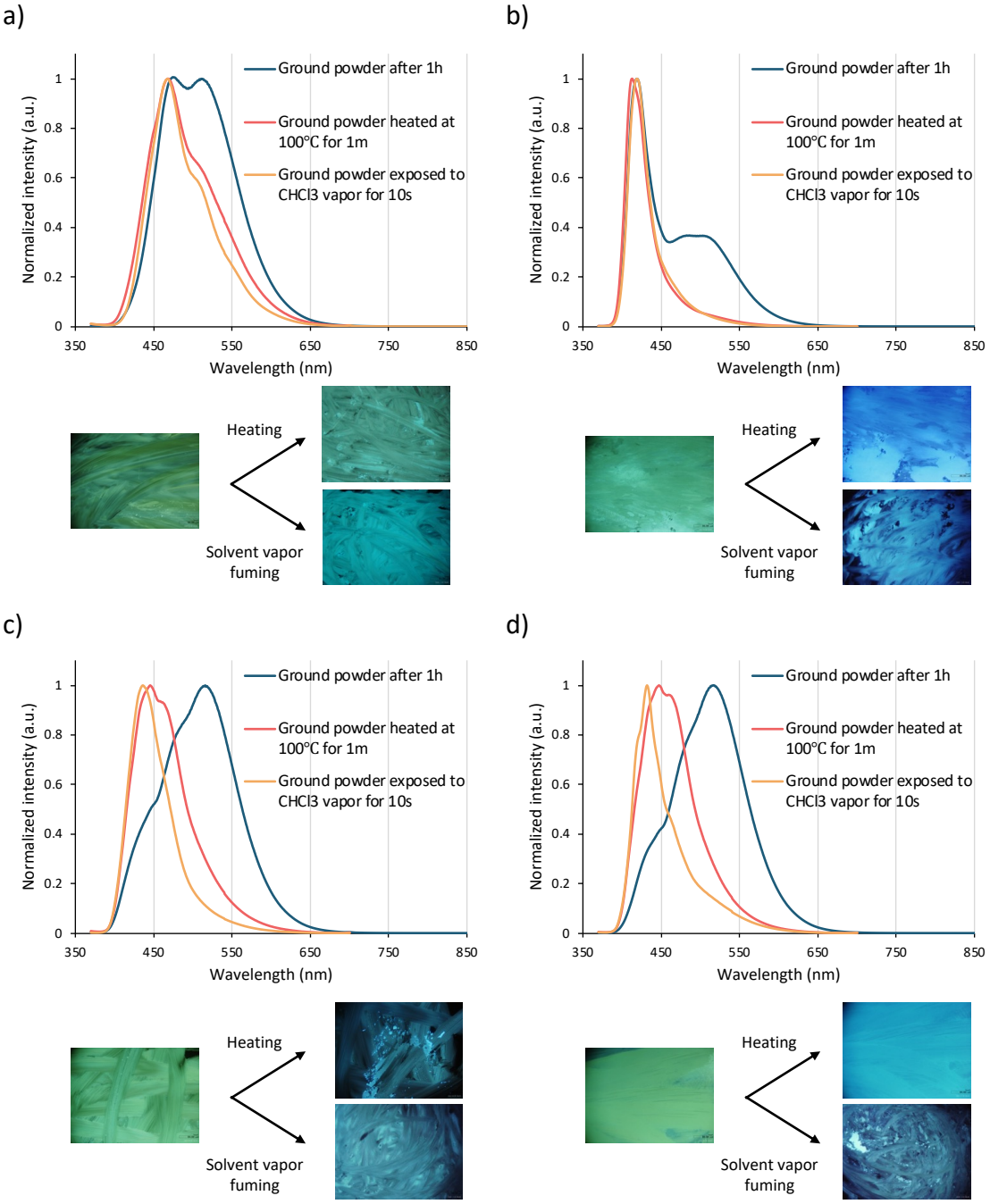


Figure S11. Heating and $CHCl_3$ fuming effects on self-recovery process of a) **Linear-*i*Pr**, b) **Linear-*t*Amyl**, c) Form 1 of **Linear-*c*Hex**, and d) Form 2 of **Linear-*c*Hex**.

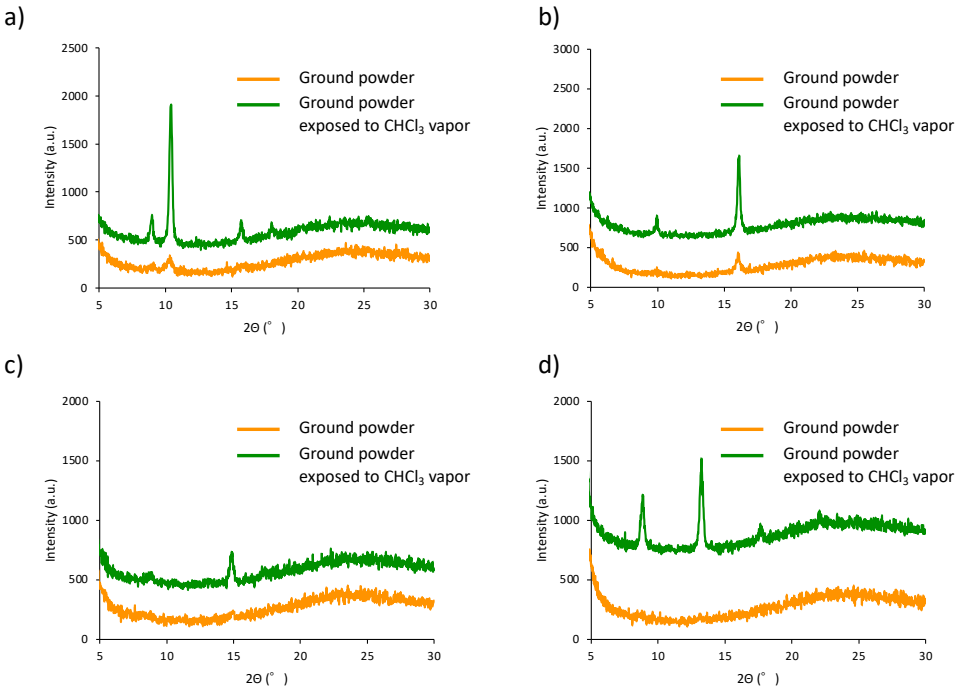


Figure S12. PXRD pattern changes of the ground powder exposed to $CHCl_3$ vapor. a) **Linear-*i*Pr**, b) **Linear-*t*Amyl**, c) **Linear-*c*Hex** Form 1, and d) **Linear-*c*Hex** Form2.

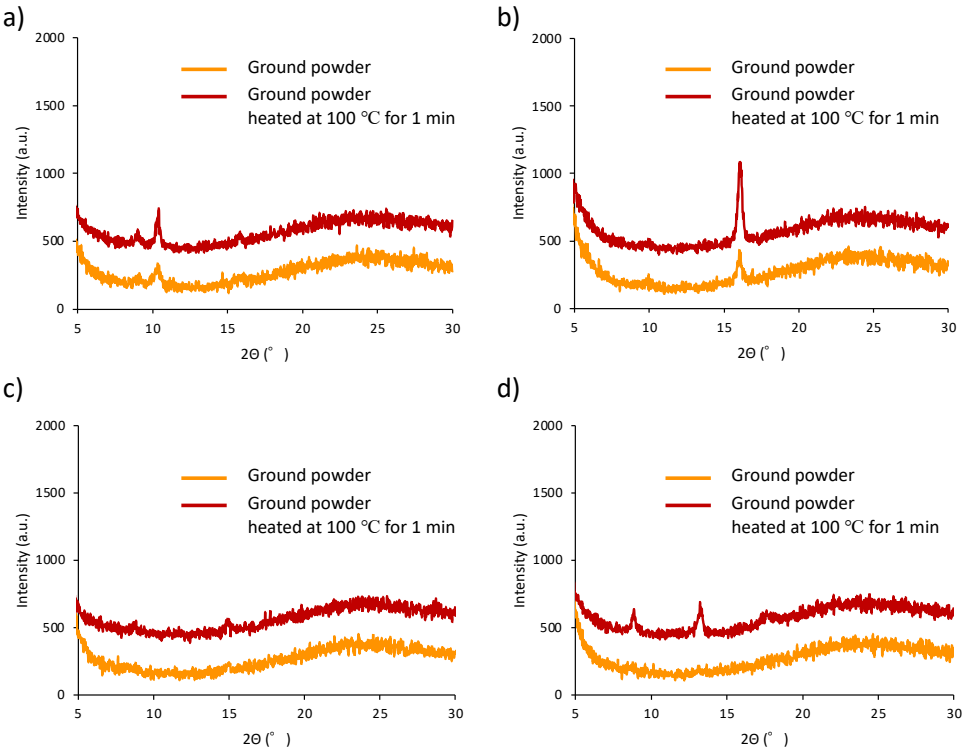


Figure S13. PXRD pattern changes of the ground powder heated at 100 °C. a) **Linear-*i*Pr**, b) **Linear-*t*Amyl**, c) **Linear-*c*Hex** Form 1, and d) **Linear-*c*Hex** Form2.

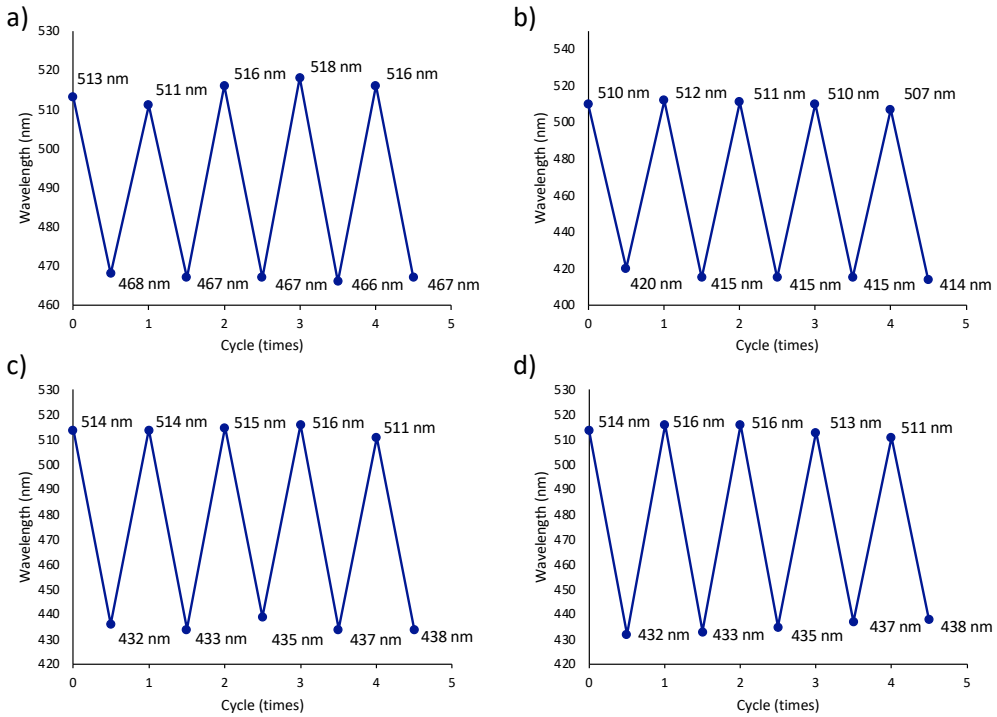


Figure S14. The corresponding peak wavelength treated by $CHCl_3$ fuming and grinding versus repeating cycle. a) **Linear-*i*Pr**, b) **Linear-*t*Amyl**, c) Form 1 of **Linear-*c*Hex**, and d) Form 2 of **Linear-*c*Hex**.

Table S1. Luminescence quantum yields (QY) and free volume fraction (FVF).

Type-B		
compd. (**Linear-**)	QY (-)	FVF (%)
***i*Pr**	0.21	31.37
Me	0.28	30.14
Et Form 1	0.41	30.13
***c*Hex Form 1**	0.52	29.9

Type-D		
compd. (**Linear-**)	QY (-)	FVF (%)
***n*Hex**	0.29	32.85
***n*Pr**	0.35	31.88
***n*Amyl**	0.44	32.48
***n*Bu**	0.49	31.88
Et Form 2	0.67	28.63

Table S2. Interaction energy between stacked two BBFPz molecules [S4,S5].

Linear-	**Et**	***n*Pr**	***n*Bu**	***n*Amyl**	***n*Hex**
E_{int} [kcal/mol][a]	-16.72	-17.08	-19.12	-20.13	-21.53

a) Interaction energy was calculated at the B3LYP-D3/6-311G** level.

Table S3. Crystal Data of **Linear-Me**: CCDC-2305891

Empirical Fomura	$C_{18}H_{12}N_2O_2$	
Formula weight	288.31	
Crystal System	monoclinic	
Space Group	$P2_1/c$ (#14)	
Unit cell dimensions	a = 9.4411	α = 90
	b = 6.1954	β = 91.836
	c = 11.6634	γ = 90
V	681.86 Å^3	
Z	4	
Density (calculated)	1404 g/cm^3	
R1 [I>2σ(I)]	0.0406	
wR2 (all data)	0.1116	
Crystal size Goodness-of-fit on F2	0.265 × 0.159 × 0.051mm	
Reflections collectred/unique	6327/1361[R(int) = 0.0435]	

Table S4. Crystal Data of **Linear-Et** Form 1: CCDC-2305892

Empirical Fomura	$C_{20}H_{16}N_2O_2$	
Formula weight	316.36	
Crystal System	monoclinic	
Space Group	$P2_1/c$ (#14)	
Unit cell dimensions	a = 10.5642	α = 90
	b = 4.6703	β = 105.796
	c = 16.2364	γ = 90
V	770.82 Å^3	
Z	4	
Density (calculated)	1.363 g/cm^3	
R1 [I>2σ(I)]	0.053	
wR2 (all data)	0.1406	
Crystal size Goodness-of-fit on F2	0.756 × 0.182 × 0.119mm	
Reflections collectred/unique	4662/1546[R(int) = 0.0354]	

Table S5. Crystal Data of **Linear-Et** Form 2: CCDC-2305893

Empirical Fomura	$C_{20}H_{16}N_2O_2$	
Formula weight	316.36	
Crystal System	triclinic	
Space Group	*P*-1 (#2)	
Unit cell dimensions	a = 4.6059	α = 89.474
	b = 8.2192	β = 85.283
	c = 10.0903	γ = 84.126
V	378.69 Å^3	
Z	2	
Density (calculated)	1.387 g/cm^3	
R1 [I>2σ(I)]	0.0629	
wR2 (all data)	0.1805	
Crystal size Goodness-of-fit on F2	0.304 × 0.083 × 0.038mm	
Reflections collectred/unique	3407/1468[R(int) = 0.0422]	

Table S6. Crystal Data of **Linear-*n* Pr**: CCDC-2305894

Empirical Fomura	$C_{22}H_{20}N_2O_2$	
Formula weight	344.41	
Crystal System	monoclinic	
Space Group	$P2_1/c$ (#14)	
Unit cell dimensions	a = 4.7476	α = 90
	b = 8.2212	β = 92.392
	c = 22.6292	γ = 90
V	882.47 Å^3	
Z	4	
Density (calculated)	1.296 g/cm^3	
R1 [I>2σ(I)]	0.0428	
wR2 (all data)	0.1214	
Crystal size Goodness-of-fit on F2	0.462 × 0.185 × 0.06mm	
Reflections collectred/unique	6364/1752[R(int) = 0.0326]	

Table S7. Crystal Data of **Linear-*i* Pr**: CCDC-2305895

Empirical Fomura	$C_{22}H_{20}N_2O_2$	
Formula weight	344.41	
Crystal System	monoclinic	
Space Group	$P2_1/c$ (#14)	
Unit cell dimensions	a = 11.3694	α = 90
	b = 4.9871	β = 98.944
	c = 15.6263	γ = 90
V	875.24 Å^3	
Z	4	
Density (calculated)	1.307 g/cm^3	
R1 [I>2σ(I)]	0.0425	
wR2 (all data)	0.1129	
Crystal size Goodness-of-fit on F2	0.716 × 0.158 × 0.102mm	
Reflections collectred/unique	11654/1765[R(int) = 0.0392]	

Table S8. Crystal Data of **Linear-*n* Bu**: CCDC-2305896

Empirical Fomura	$C_{24}H_{24}N_2O_2$	
Formula weight	372.47	
Crystal System	triclinic	
Space Group	P-1 (#2)	
Unit cell dimensions	a = 4.6829	α = 89.289
	b = 8.209	β = 86.831
	c = 12.7307	γ = 85.18
V	486.90 Å^3	
Z	2	
Density (calculated)	1.270 g/cm^3	
R1 [I>2σ(I)]	0.0647	
wR2 (all data)	0.2177	
Crystal size Goodness-of-fit on F2	0.354 × 0.134 × 0.055mm	
Reflections collectred/unique	5841/1953[R(int) = 0.0499]	

Table S9. Crystal Data of **Linear-*s* Bu**: CCDC-2305897

Empirical Fomura	$C_{24}H_{24}N_2O_2$	
Formula weight	372.47	
Crystal System	triclinic	
Space Group	*P*-1 (#2)	
Unit cell dimensions	a = 5.0896	α = 88.944
	b = 6.4884	β = 86.138
	c = 15.6421	γ = 76.245
V	500.60 Å^3	
Z	2	
Density (calculated)	1.235 g/cm^3	
R1 [I>2σ(I)]	0.0806	
wR2 (all data)	0.2482	
Crystal size Goodness-of-fit on F2	0.285 × 0.033 × 0.017mm	
Reflections collectred/unique	4594/1934[R(int) = 0.0459]	

Table S10. Crystal Data of **Linear-*n* Amyl**: CCDC-2305898

Empirical Fomura	$C_{26}H_{28}N_2O_2$	
Formula weight	400.52	
Crystal System	triclinic	
Space Group	*P*-1 (#2)	
Unit cell dimensions	a = 4.7285	α = 95.036
	b = 8.2545	β = 91.036
	c = 13.9117	γ = 96.682
V	537.00 Å^3	
Z	2	
Density (calculated)	1.238 g/cm^3	
R1 [I>2σ(I)]	0.069	
wR2 (all data)	0.2051	
Crystal size Goodness-of-fit on F2	0.239 × 0.091 × 0.026mm	
Reflections collectred/unique	5319/2100[R(int) = 0.0396]	

Table S11. Crystal Data of **Linear-*t* Amyl**: CCDC-2305899

Empirical Fomura	$C_{26}H_{30}N_2O_2$	
Formula weight	400.52	
Crystal System	monoclinic	
Space Group	$P2_1/c$ (#14)	
Unit cell dimensions	a = 6.5784	α = 90
	b = 11.0323	β = 99.443
	c = 15.2453	γ = 90
V	1091.43 Å^3	
Z	4	
Density (calculated)	1.219 g/cm^3	
R1 [I>2σ(I)]	0.046	
wR2 (all data)	0.1283	
Crystal size Goodness-of-fit on F2	0.715 × 0.179 × 0.076mm	
Reflections collectred/unique	8424/2196[R(int) = 0.0329]	

Table S12. Crystal Data of **Linear-*n* Hex**: CCDC-2305900

Empirical Fomura	$C_{28}H_{32}N_2O_2$	
Formula weight	428.58	
Crystal System	triclinic	
Space Group	P-1 (#2)	
Unit cell dimensions	a = 4.6872	α = 88.441
	b = 8.137	β = 87.919
	c = 15.3378	γ = 85.811
V	582.86 Å^3	
Z	2	
Density (calculated)	1.221 g/cm^3	
R1 [I>2σ(I)]	0.0703	
wR2 (all data)	0.2382	
Crystal size Goodness-of-fit on F2	0.629 × 0.114 × 0.06mm	
Reflections collectred/unique	6945/2310[R(int) = 0.0843]	

Table S13. Crystal Data of **Linear-*c*Hex** Form 1: CCDC-2305901

Empirical Fomura	$C_{28}H_{28}N_2O_2$	
Formula weight	428.58	
Crystal System	monoclinic	
Space Group	$P2_1/c$ (#14)	
Unit cell dimensions	a = 11.9199	α = 90
	b = 4.7806	β = 92.523
	c = 18.7426	γ = 90
V	1067.00 Å^3	
Z	4	
Density (calculated)	1.321 g/cm^3	
R1 [I>2σ(I)]	0.0461	
wR2 (all data)	0.1297	
Crystal size Goodness-of-fit on F2	0.679 × 0.254 × 0.127mm	
Reflections collectred/unique	6689/2120[R(int) = 0.0316]	

Table S14. Crystal Data of **Linear-*c*Hex** Form 2: CCDC-2305902

Empirical Fomura	$C_{28}H_{28}N_2O_2$	
Formula weight	428.58	
Crystal System	triclinic	
Space Group	P-1 (#2)	
Unit cell dimensions	a = 5.2466	α = 90.874
	b = 5.2604	β = 92.964
	c = 20.0763	γ = 102.471
V	540.09 Å^3	
Z	2	
Density (calculated)	1.305 g/cm^3	
R1 [I>2σ(I)]	0.0496	
wR2 (all data)	0.1594	
Crystal size Goodness-of-fit on F2	1.16 × 0.301 × 0.272mm	
Reflections collectred/unique	8213/2557[R(int) = 0.0368]	

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Reference

S1) S. Nakamura, K. Okubo, Y. Nishii, K. Hirano, N. Tohnai, M. Miura, *Chem. Eur. J*. **2023**, e202302605.

S2) S. Nakamura, M. Tsuboi, T. Taniguchi, Y. Nishii, N. Tohnai, M. Miura, *Chem. Lett*. **2020**, *49*, 921-924.

S3) T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-592.

S4) A. Gavezzotti, *Acc. Chem. Res.* **1994**, *27*, 309-314.

S5) A. Gavezzotti, G. Filippini, *J. Phys. Chem.* **1994**, *98*, 4831-4837.