Electronic Supplementary Material (ESI) for Polymer Chemistry.

Dicyclopenta[cd,jk]pyrene Based Acceptors in Conjugated Polymers

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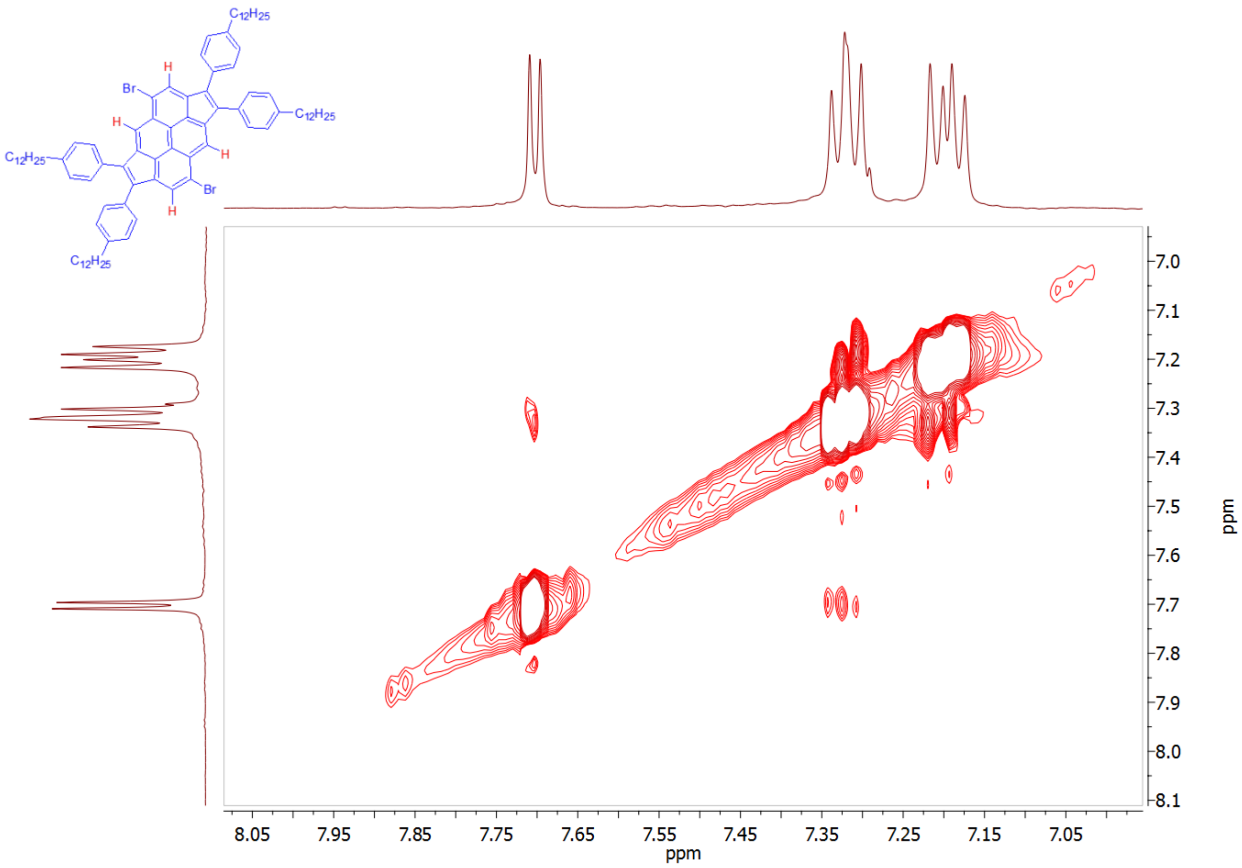
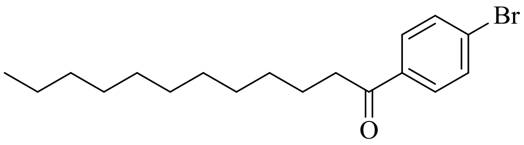
1) NOESY spectra of 5 in $CDCl_3$



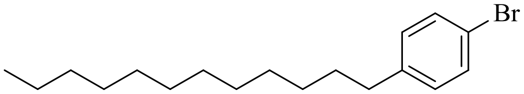
To lend support for the proposed regiochemistry for bromination, an NOESY spectra in $CDCl_3$ was taken. Although not unambiguous proof, NOE signals between two pyrene protons and two aryl protons (see bottom right quadrant) are evident. Furthermore, the high degree of polymerization suggests a less hindered halide position.

2) Experimental Procedures

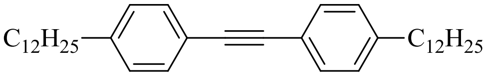
Unless otherwise noted, all reagents were used as received and all reactions were carried out under an argon atmosphere. Column chromatography was performed on a CombiFlash® Rf system with Redisep normal phase silica columns (Teledyne ISCO Inc., Lincoln, NE). ^{1}H NMR and ^{13}C NMR were recorded on a Varian 400 MHz NMR station at room temperature, unless otherwise noted. Millipore filtrations were accomplished with a 47 mm Millipore vacuum filter (PTFE or Nylon). Polymer molecular weights were determined versus polystyrene standards using an Waters 2690 seperations module, Waters 2410 refractive index detector, Waters 996 photodiode array detector and varian GPC/SEC columns. Cyclic voltammetry was performed on a CH-Instruments 700D potentiostat with a 0.1 M tetrabutylammonium hexafluorophosphate solution (THF) using a glassy carbon electrode, platinum counter electrode, and a Ag/AgCl reference electrode. High resolution mass spectra were obtained from the University of Illinois Mass Spectrometry Services.



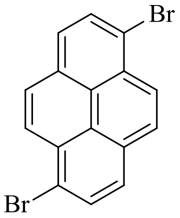
1-(4-bromo-phenyl)-dodecan-1-one (i): To a solution of bromobenzene (31.4 g, 0.217 mol) and $AlCl_3$ (16.0 g, 0.119 mol) was added lauroyl chloride (21.9 g, 0.100 mol) drop wise while stirring. The reaction mixture was stirred for one hour at 50 ^{0}C and then poured into ice water and extracted with dichloromethane. The organic solution was washed with 2N HCl followed by brine and then dried over $MgSO_4$. After removing the dichloromethane in vacuo, the crude product was recrystallized from ethanol to give 23.9 g (35.2 %) of **i** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H), 2.93 (t, J = 7.4 Hz, 2H), 1.72 (p, J = 7.2 Hz, 2H), 1.26 (m, 16H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 135.9, 131.9, 129.7, 128.1, 38.7, 32.0, 29.7, 29.6, 29.6, 29.5, 24.4, 22.8, 14.3. LRMS (EI+): m/z for $C_{18}H_{27}BrO$ calc: 338.1, found 338.1.



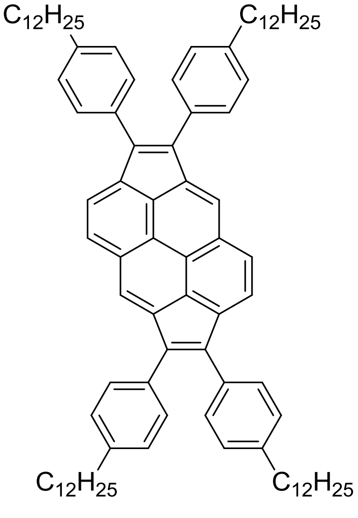
1-bromo-4-dodecyl-benzene (ii): A mixture of **i** (19.0 g, 0.0559 mol), hydrazine hydrate (19.4 g, 0.387 mol) and KOH (14.5 g, 0.259 mol) in diethylene glycol was heated for 4 h at 200 ^{0}C. The reaction mixture was cooled, poured into ice water, acidified with 1N HCl, and then extracted with dichloromethane. The organic layer was washed with brine and dried over $MgSO_4$. Solvent was removed in vacuo and the crude product was purified by column chromatography with hexane to give 5.74 g (31.5%) of **ii** as a clear oil. . ^{1}H NMR (400 MHz, $CDCl_3$) δ7.39 (d, J=8.4Hz, 2H), 7.05 (d, J=8.4Hz, 2H), 2.56 (t, J = 7.6 Hz, 2H), 1.59 (m, 2H), 1.27 (m, 18H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 131.2, 130.2, 119.2, 35.4, 31.9, 31.6, 31.4, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 22.7, 14.1.



4,4’-didodecyl,1,1’-diphenyl acetylene (iii): In a glove box, **ii** (5.30 g, 16.3 mmol), $PdCl_2(PPh_3)_2$ (345 mg, 0.491 mmol), and CuI (305mg, 1.60 mmol) were dissolved in toluene (22 ml) in a sealed tube. Argon purged H_2O (0.12 ml, 6.5 mmol), DBU (14.8 g, 97.5 mmol) and then trimethylsilylacetylene (0.801 g, 8.15 mmol) were added to the sealed tube outside the glove box and stirred at 70 ^{0}C overnight. The reaction mixture was cooled, acidified with 2N HCl, then extracted with diethyl ether. The organic layer was washed with 2×100 ml 1N HCl, 100 ml brine and dried over $MgSO_4$. The crude product was purified by column chromatography to give 2.70 g (64.5%) of **iii** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 4H), 7.15 (d, *J* = 8.0 Hz, 4H), 2.61 (t, J= 7.6 Hz, 4H), 1.60 (m, 4H), 1.29 (m, 36H), 0.89 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 131.6, 128.6, 120.7, 89.1, 36.1, 32.1, 31.4, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 22.9, 14.3. LRMS (EI+) 514.9 HRMS: m/z for $C_{38}H_{58}$ calc: 514.4539, found 514.4539.

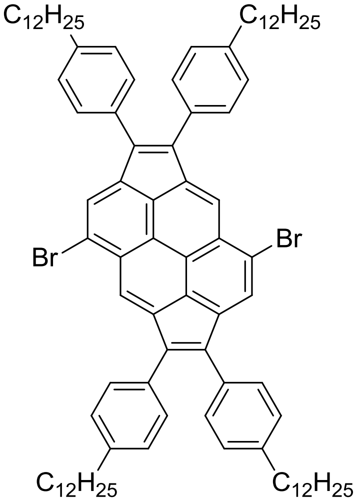


1,6-dibromopyrene (iv): To a solution of pyrene (19.0 g, 0.0941 mol) in dichloromethane (400 ml), a solution of Br_2 (30.11 g, 0.1882 mol) in dichloromethane (100 ml) was added drop wise via addition funnel. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed in vacuo and the crude product was recrystallized from toluene four times (800 ml, 500 ml, 500 ml, 500 ml of toluene respectively) to give 5.07 g (15%) of **iv** as an off white solid. ^{1}H NMR (400 MHz, DMSO) δ 7.58 (d, *J* = 9.2 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 9.3 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H). LRMS (EI+): m/z for $C_{16}H_8Br_2$ calc: 360.0, found 359.9.

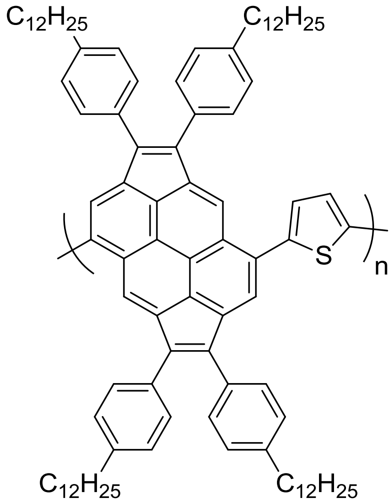


1,2,6,7-Tetra(4-dodecylphenyl)dicyclopenta[cd,jk]pyrene (4). In a glove box, 1,2-bis(4-dodecylphenyl)ethyne (282.5 mg, 0.5486 mmol), 1,6-dibromopyrene (99.3 mg, 0.276 mmol), Pd2(dba)3 (25.3 mg, 0.0276 mmol), P(o-Tol)3 (12.6 mg, 0.0414 mmol), KOAc (134.6 mg, 1.372 mmol), LiCl (23.3

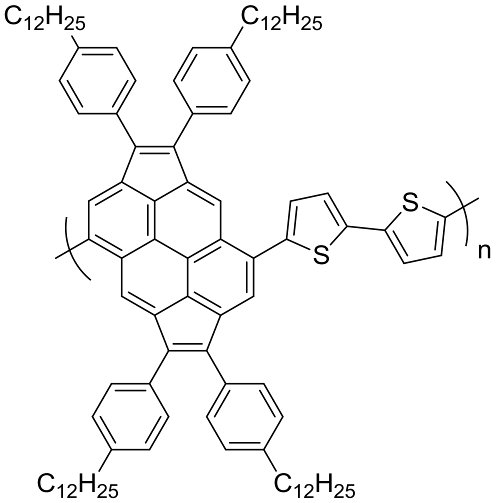
mg, 0.549 mmol) and DMF (15 ml) were combined in a sealed tube and stirred overnight at 130 °C. The reaction mixture was cooled to room temperature and poured into 100 ml methanol and filtered. The solid was washed with methanol and acetone to give 271 mg (80%) of **4** as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.9 Hz, 2H), 7.57 (m, 4H), 7.35 (dd, J = 8.1, 6.2 Hz, 8H), 7.17 (dd, J = 10.8, 8.3 Hz, 8H), 2.64 (m, 8H), 1.71 – 1.65 (m, 8H), 1.30 (m, 72H), 0.88 (t, J = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, CDCl3) δ 142.2, 142.0, 141.4, 141.3, 140.8, 139.4, 133.0, 132.34, 132.31, 132.28, 131.9, 130.4, 129.4, 129.3, 129.0, 128.4, 128.34, 128.27, 125.2, 121.8, 121.4, 35.9, 31.9, 31.39, 31.35, 29.71, 29.69, 29.67, 29.65, 29.6, 29.5, 29.5, 29.4, 22.7, 14.1. LRMS (EI+) 1228.0 HRMS: m/z for $C_{90}H_{122}$ calc: 1226.9541, found 1226.9480.



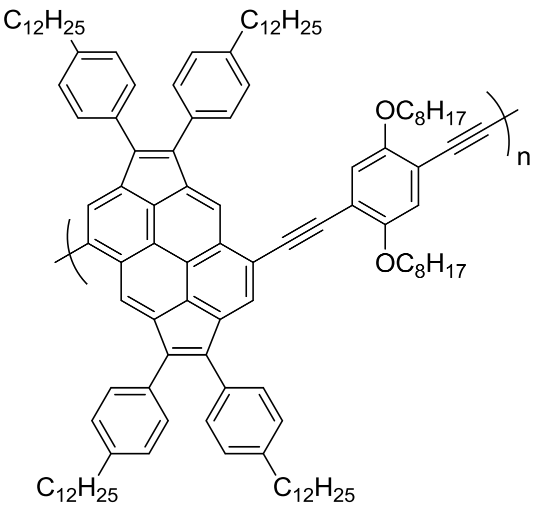
4,9-Dibromo-1,2,6,7-tetra(4-dodecylphenyl)dicyclopenta[cd,jk]pyrene (5). To the ice-bath cooled solution of **4** (120 mg, 0.0897 mmol) in dichloromethane (10 ml) was added Br_2 (28.7 mg, 0.18 mmol) in dichloromethane (10 ml) drop wise at 0 ^{0}C. The reaction mixture was stirred for 1 h at 0 ^{0}C. The solvent was removed in vacuo and the crude product was triturated with hot methanol to get 115 mg (85%) of a red solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.70 (s, 2H), 7.66 (s, 2H), 7.30 (t, *J* = 7.6 Hz, 8H), 7.20 (dd, *J* = 12.1, 8.2 Hz, 8H), 2.66 (dd, *J* = 15.4, 7.7 Hz, 8H), 1.72 – 1.61 (m, 8H), 1.29 (m, 72H), 0.89 (t, *J* = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.71, 142.50, 142.37, 142.06, 140.98, 140.40, 131.69, 130.97, 129.87, 129.61, 129.04, 128.56, 128.53, 126.42, 125.49, 125.38, 124.62, 122.08, 77.48, 77.16, 76.84, 36.06, 32.10, 31.48, 29.89, 29.88, 29.88, 29.84, 29.74, 29.73, 29.70, 29.66, 29.55, 22.87, 14.29. HRMS: m/z for $C_{92}H_{120}Br_2$ calc: 1384.7736, found: 1384.7801.



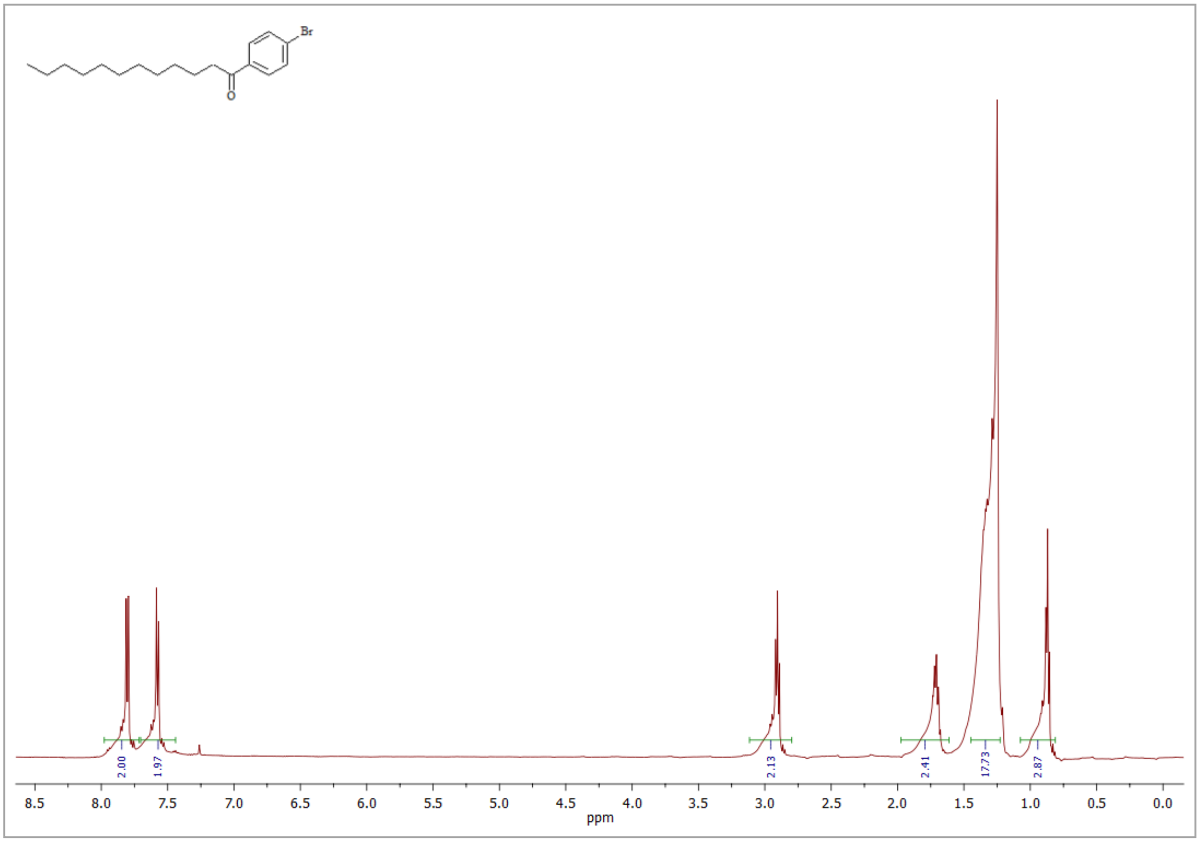
Poly(Thiophene-*co*-1,2,6,7-tetra(4-dodecylphenyl)dicyclopenta[*cd,jk*]pyrene (1). In a glovebox, **5** (80 mg, 0.058 mmol), 2,5-bis-tributylstannanyl-thiophene (38.2 mg, 0.058 mmol), $Pd_2(dba)_3$ (1.6 mg, 0.0017 mmol), P(*o*-Tol)$_3$ (4.2 mg, 0.014 mmol) and THF (5 ml) were combined in a sealed tube and stirred for two days at 80 ^{0}C. The reaction mixture was cooled to room temperature and poured in to 70 ml methanol and filtered. The solid was washed with methanol and acetone to give 62 mg (82%) of a dark green solid. M_n = 20,833 PDI = 2.6.



Poly(bithiophene-*co*-1,2,6,7-tetra(4-dodecylphenyl)dicyclopenta[*cd,jk*]pyrene (2). In a glovebox, **5** (50 mg, 0.0361 mmol), 5,5'-bis-tributylstannanyl-bithiophene (26.9 mg, 0.0361 mmol), $Pd_2(dba)_3$ (1.0 mg, 0.0011 mmol), P(*o*-Tol)$_3$ (3.1 mg, 0.010 mmol) and THF (5 ml) were combined in a sealed tube and stirred for two days at 80 ^{0}C. The reaction mixture was cooled to room temperature and poured in to 70 ml methanol and filtered. The solid was washed with methanol and acetone to give 42 mg (84%) of a dark green solid. M_n = 69,981 PDI = 2.5.



Poly(2,5-dioctyloxyphenylene-1,4-ethynylene-*co*-1,2,6,7-tetra(4-dodecylphenyl)dicyclopenta[*cd,jk*]pyrene (3). In a glovebox, **5** (24 mg, 0.017 mmol), 1,4-diethynyl-2,5-bis-octyloxy-benzene (6.6 mg, 0.017 mmol), Pd(PhCN)$_2$Cl$_2$ (0.2 mg, 0.0005 mmol), P(t-Bu)$_3$ (0.21 mg, 0.001 mmol), CuI (0.1 mg, 0.0005 mmol) and toluene (4 mL) and diisopropylamine (2 mL) were combined in a sealed tube and stirred for 2 days at room temperature. The reaction mixture was concentrated and precipitated from THF in to methanol and washed with methanol and acetone to give 20 mg (72%) of a dark green solid. M_n = 20,715 PDI = 2.6.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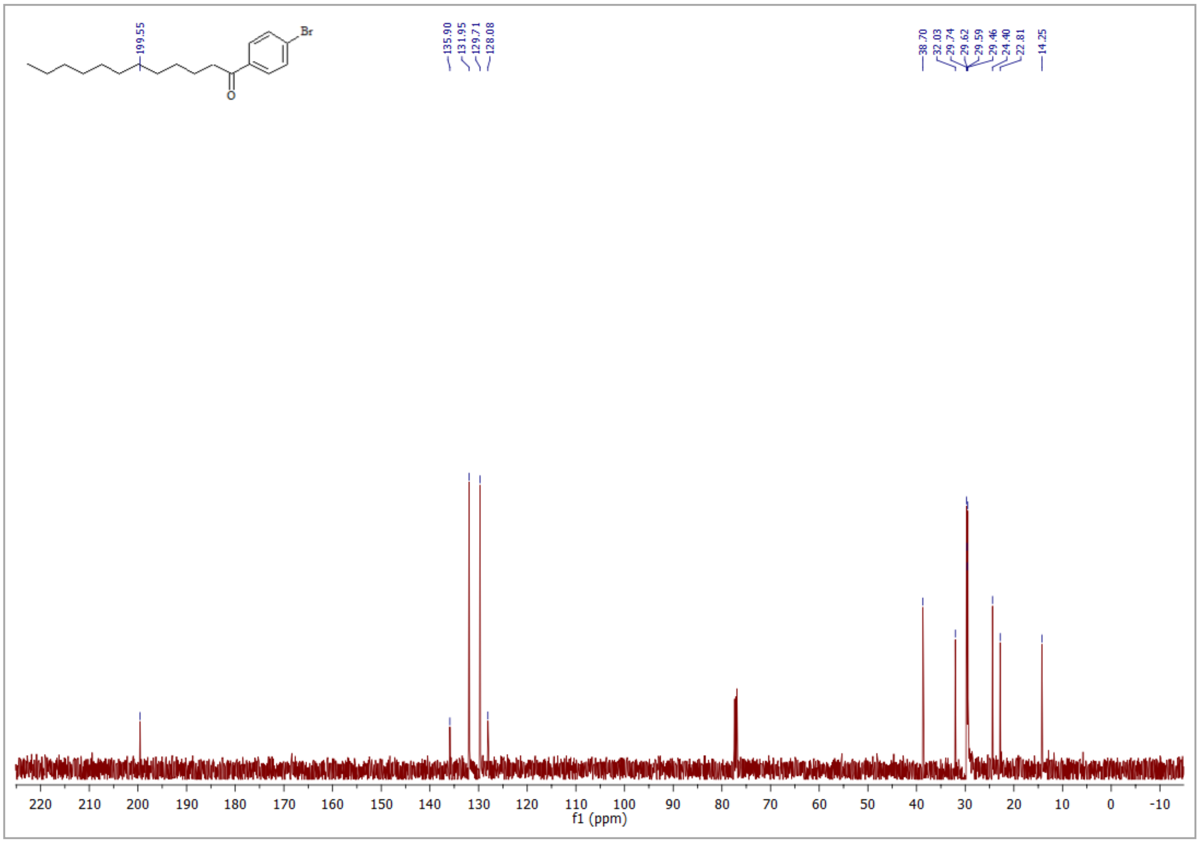
ppm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180
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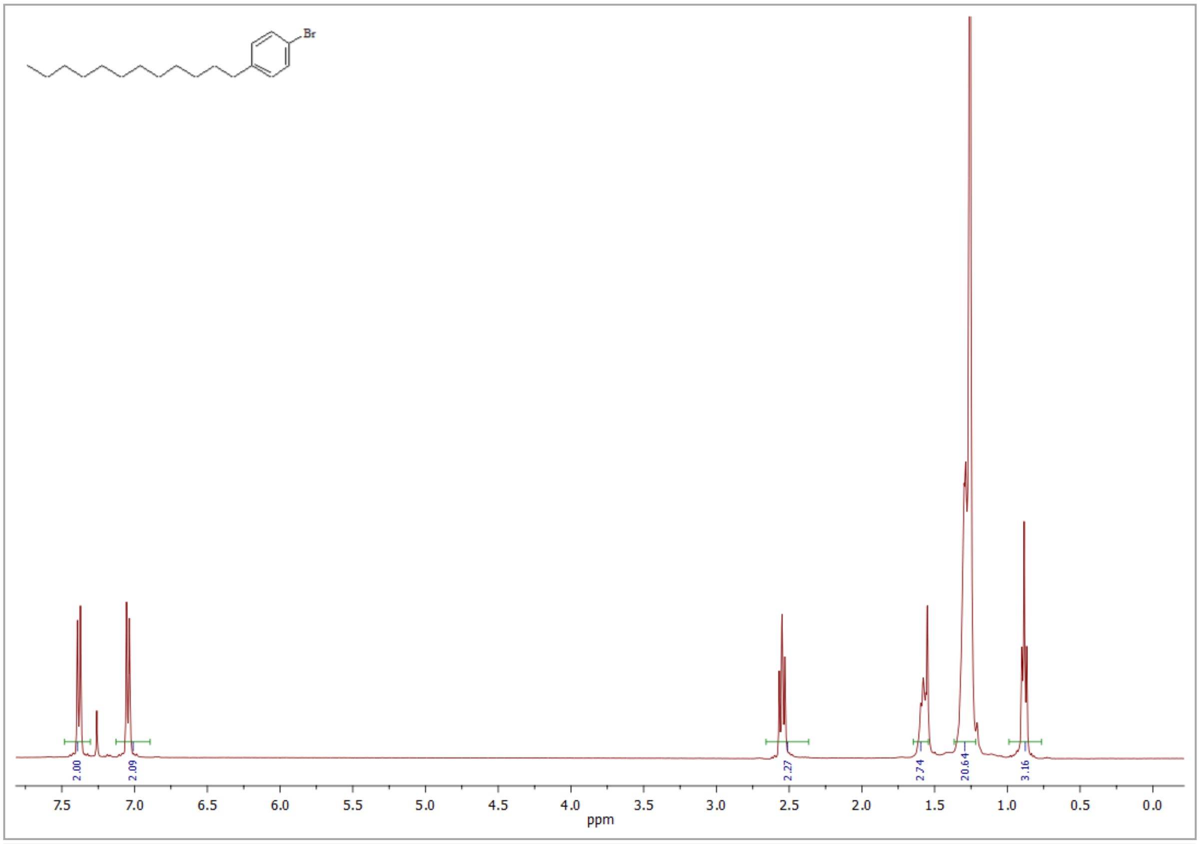
f1 (ppm)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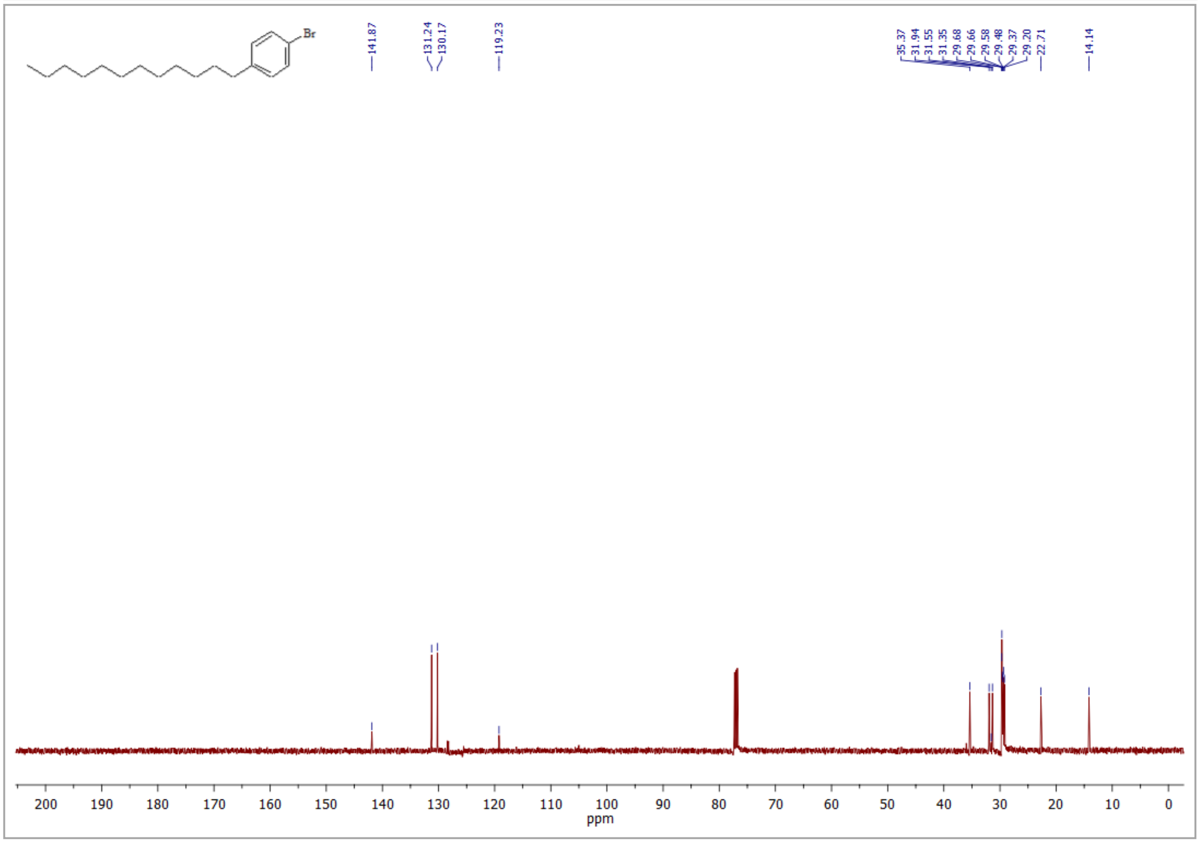
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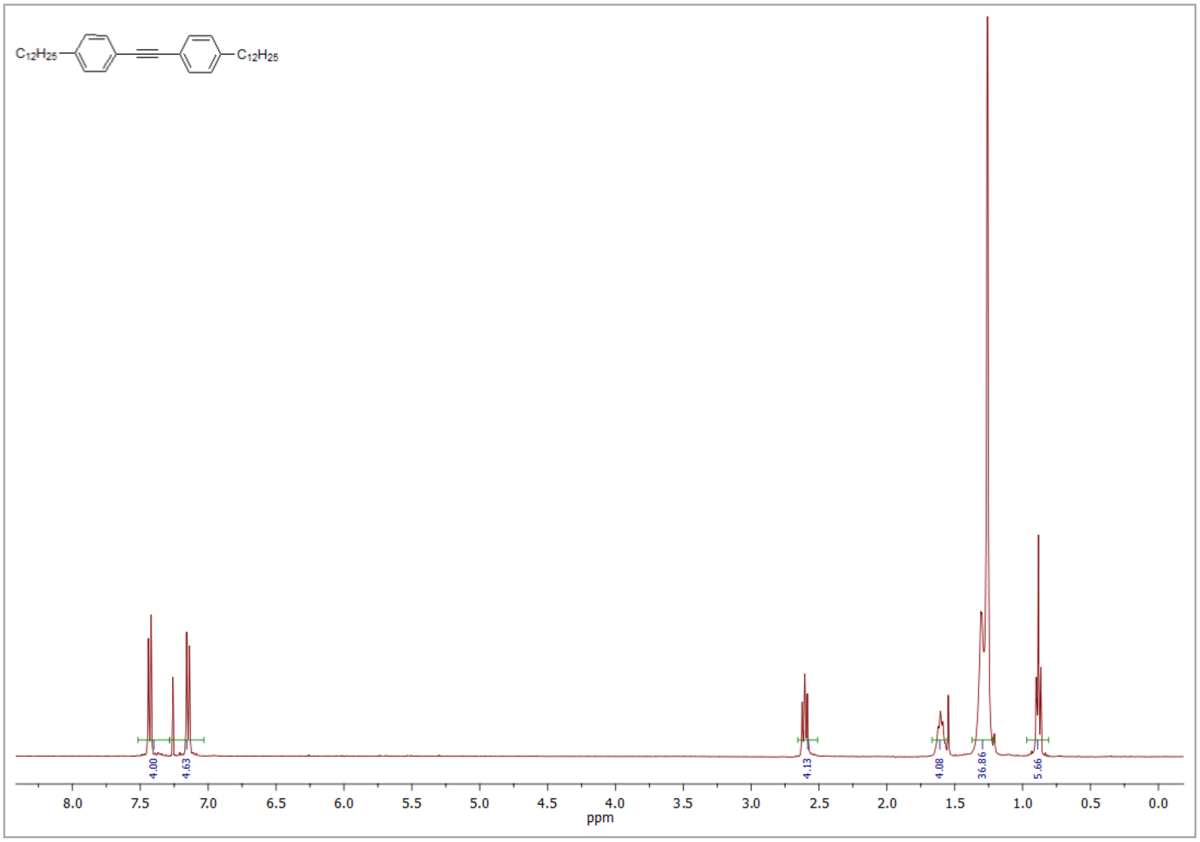

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$C_{12}H_{25}$
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6.0
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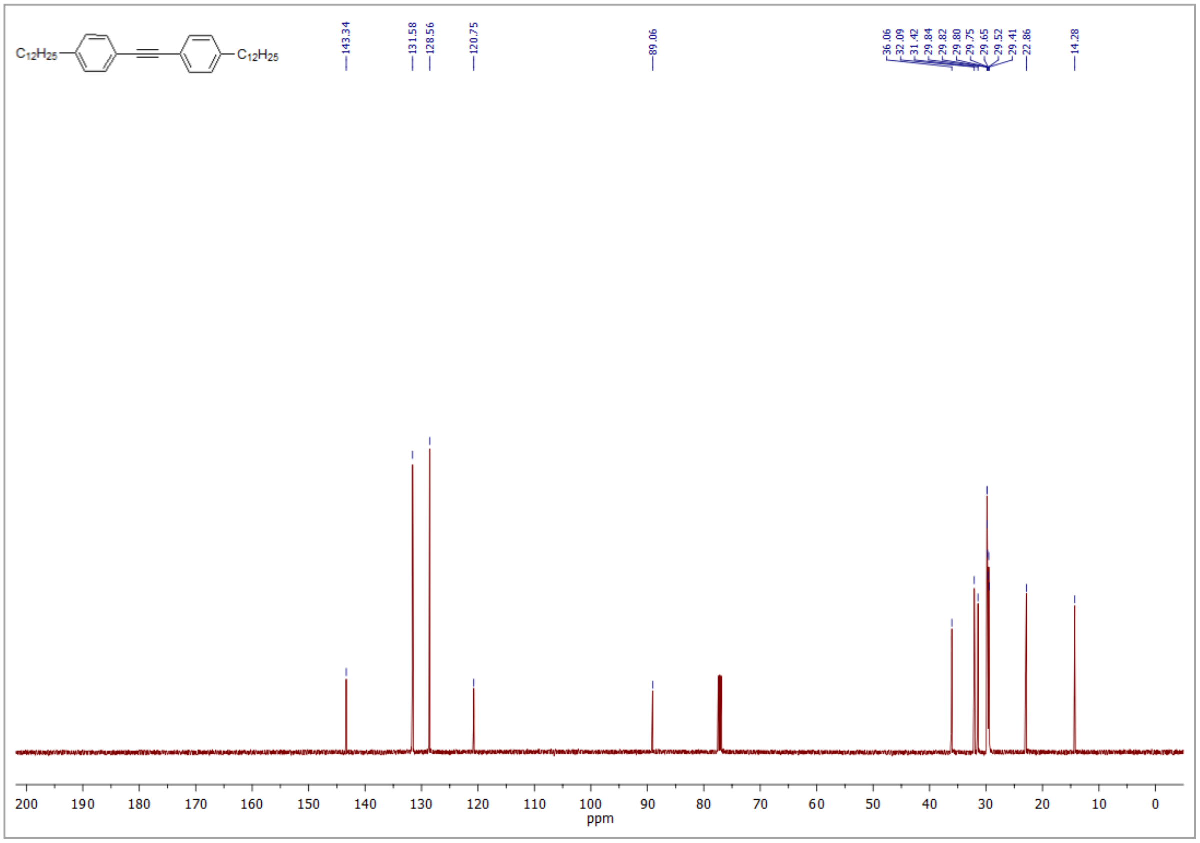

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$C_{12}H_{25}$
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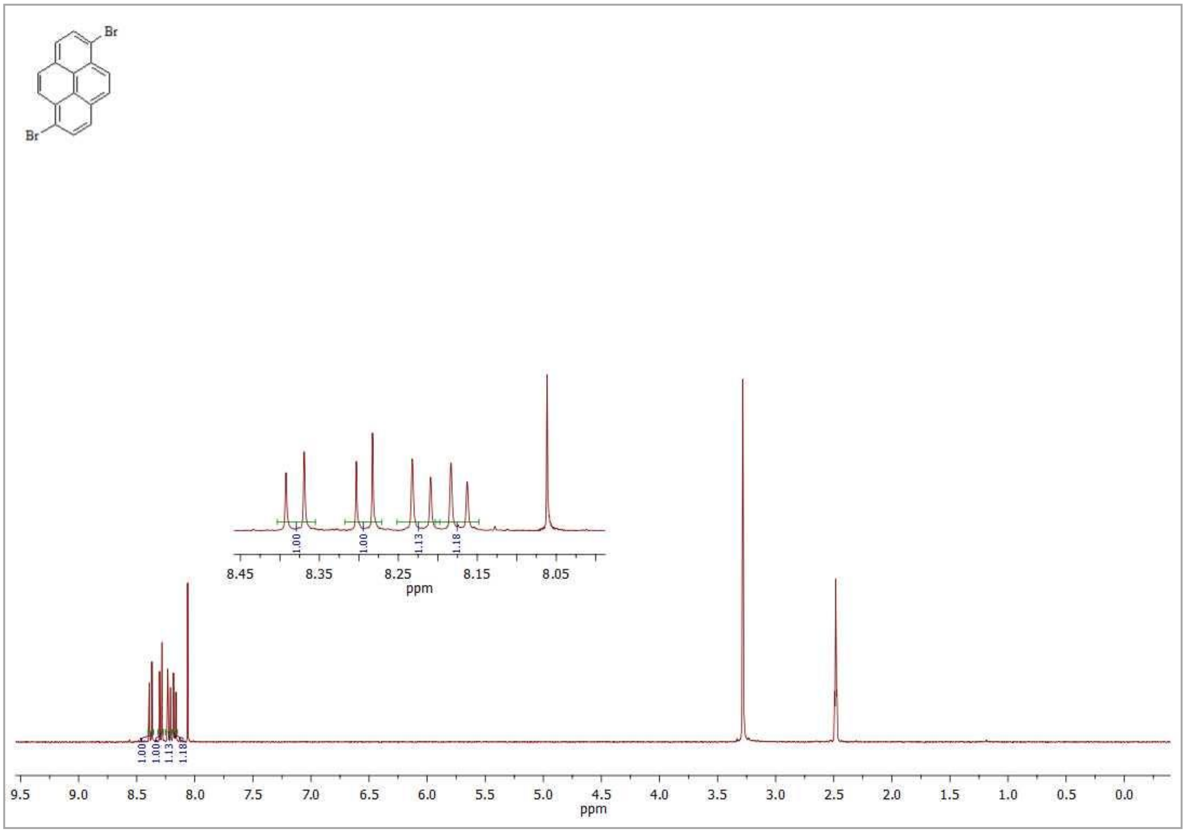
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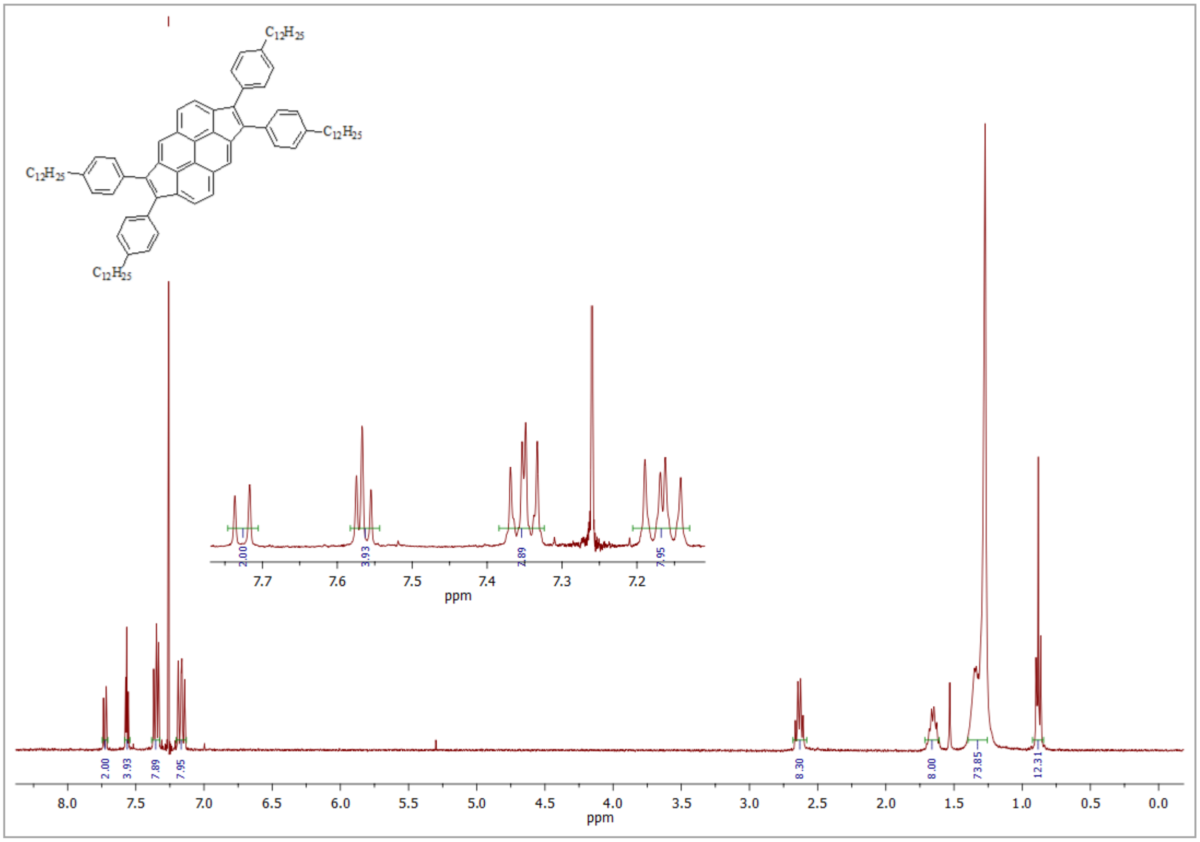
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C12H25
C12H25
C12H25
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ppm
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7.95
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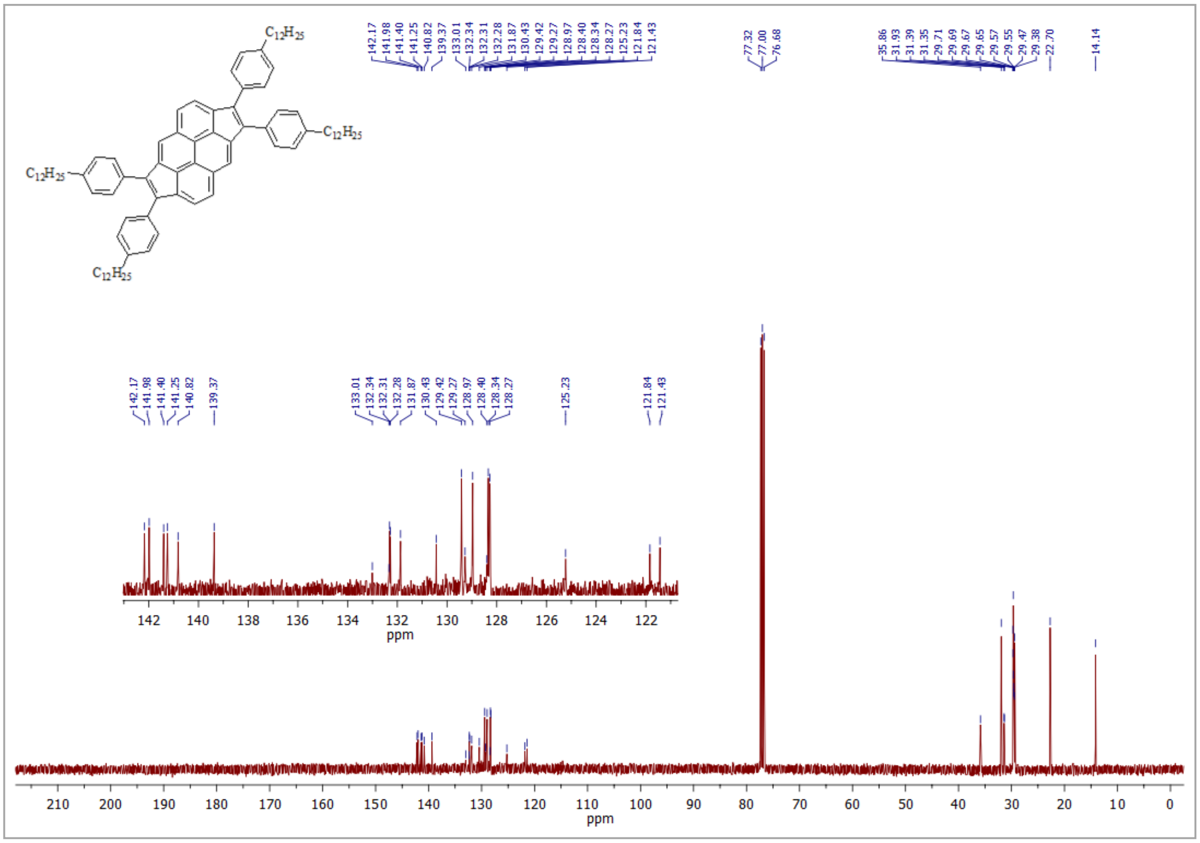
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128.34
128.27
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121.43
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31.35
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29.69
29.67
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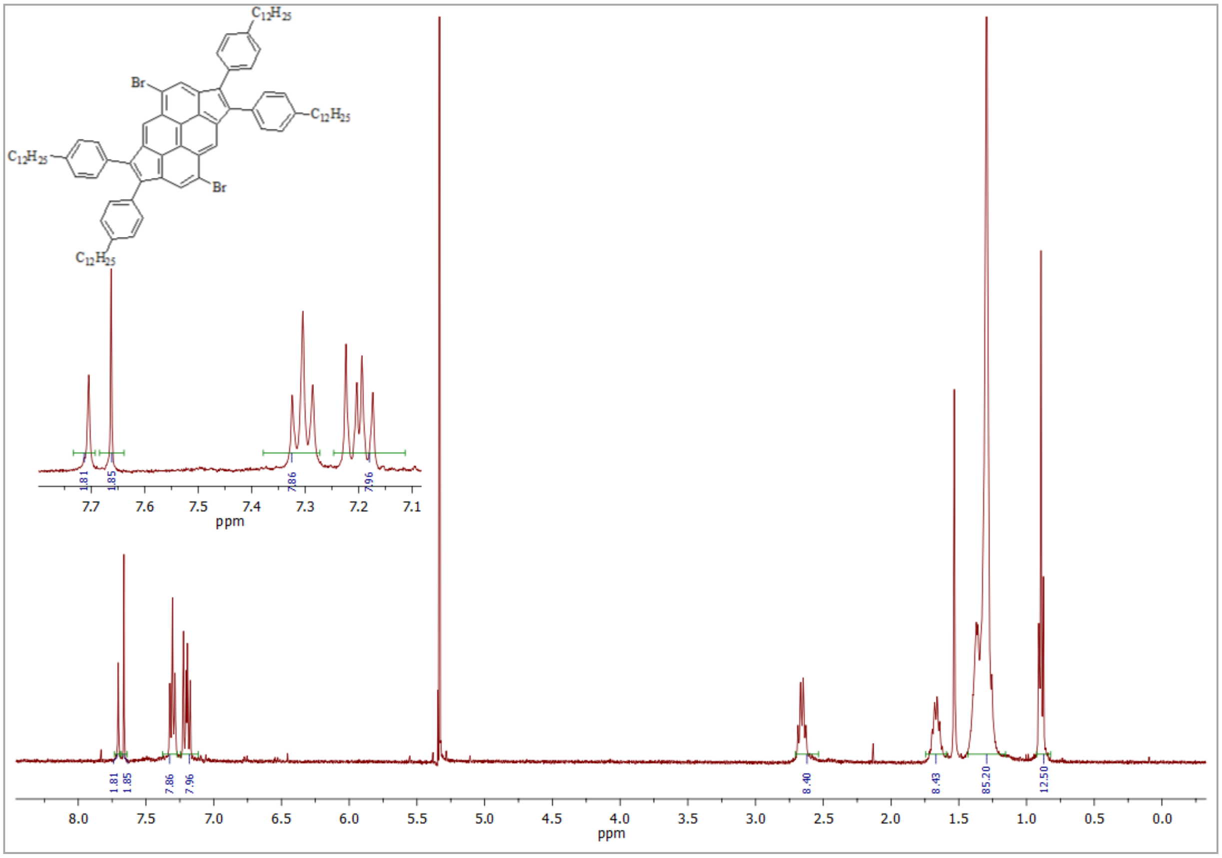
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C12H25
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C12H25
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7.0
6.5
6.0
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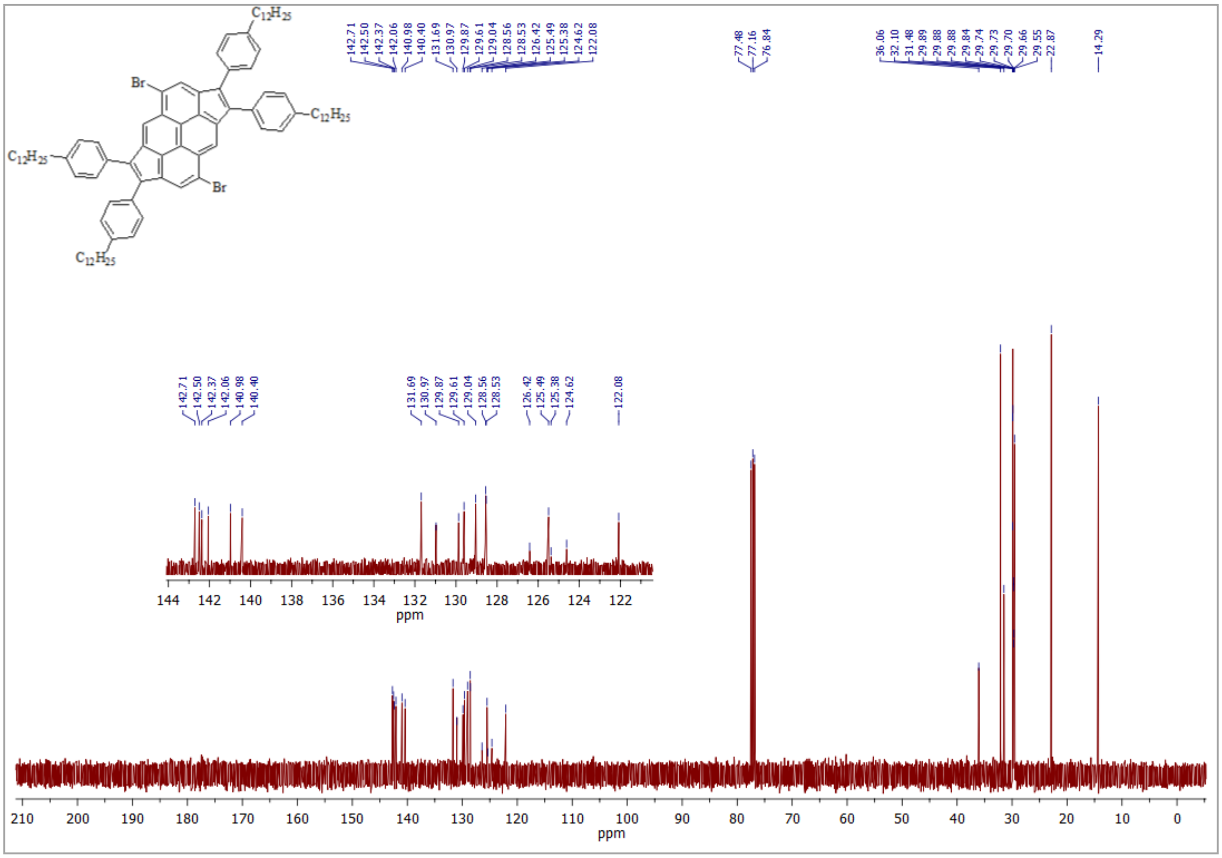
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C12H25
C12H25
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