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Planarizable push-pull oligothiophenes: In search of the perfect twist

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Supplementary Information

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Materials and methods

As in ref. S1, Supporting Information. Briefly, reagents for synthesis were purchased from Fluka, Sigma-Aldrich, Acros Organics and Apollo scientific, buffers and salts of the best grade available from Fluka or Sigma-Aldrich and used as received. 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) and 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) were purchased from Avanti Polar Lipids.

Unless stated otherwise, column chromatography was carried out on silica gel 60 (Fluka, 70-230 mesh). Thin Layer Chromatography (TLC) was performed on silica gel 60 (Fluka, 0.2 mm). HPLC were recorded on a Jasco LC-2000 Plus system and LC-MS (ESI) were recorded using a Thermo Scientific Accela HPLC coupled with a LCQ Fleet three-dimensional ion trap mass spectrometer (Thermo Scientific). UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer equipped with a stirrer and a temperature controller and are reported as maximal absorption wavelength λ in nm (extinction coefficient ε in $M^{-1}cm^{-1}$). Fluorescence measurements were performed with a Fluoromax-3 or FluoroMax-4 spectrofluorometer (Horiba Scientific) equipped with a stirrer and a temperature controller. Unless stated, fluorescence spectra were corrected using instrument-supplied correction factors. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer (ATR, Golden Gate) and are reported as wavenumbers v in cm^{-1} with band intensities indicated as s (strong), m (medium), w (weak), br (broad). ^{1}H and ^{13}C NMR, proton decoupled, spectra were recorded (as indicated) on a Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and are reported as chemical shifts (δ) in ppm using (residual) solvent as calibration. In ^{1}H NMR, spin multiplicities are reported as a singlet (s), doublet (d), triplet (t), quartet (q) and quintet (quint) with coupling constants (J) given in Hz, or multiplet (m). ^{1}H and ^{13}C resonances were assigned with the aid of additional information from 1D & 2D NMR spectra (DEPT 135, HSQC) and reported, for ^{13}C NMR, as s (C), d (CH), t (CH_2) and q (CH_3). ESI-MS for the

characterization of new compounds was performed on an ESI API 150EX and are reported as mass-per-charge ratio m/z. ESI-HRMS for the characterization of new compounds was performed on a QSTAR Pulsar (AB/MDS Sciex) and DFS – Thermofisher and is reported as mass-per-charge ratio m/z calculated and observed. Vesicles were prepared with a Mini-Extruder from Avanti Polar Lipids (pore size 100 nm).

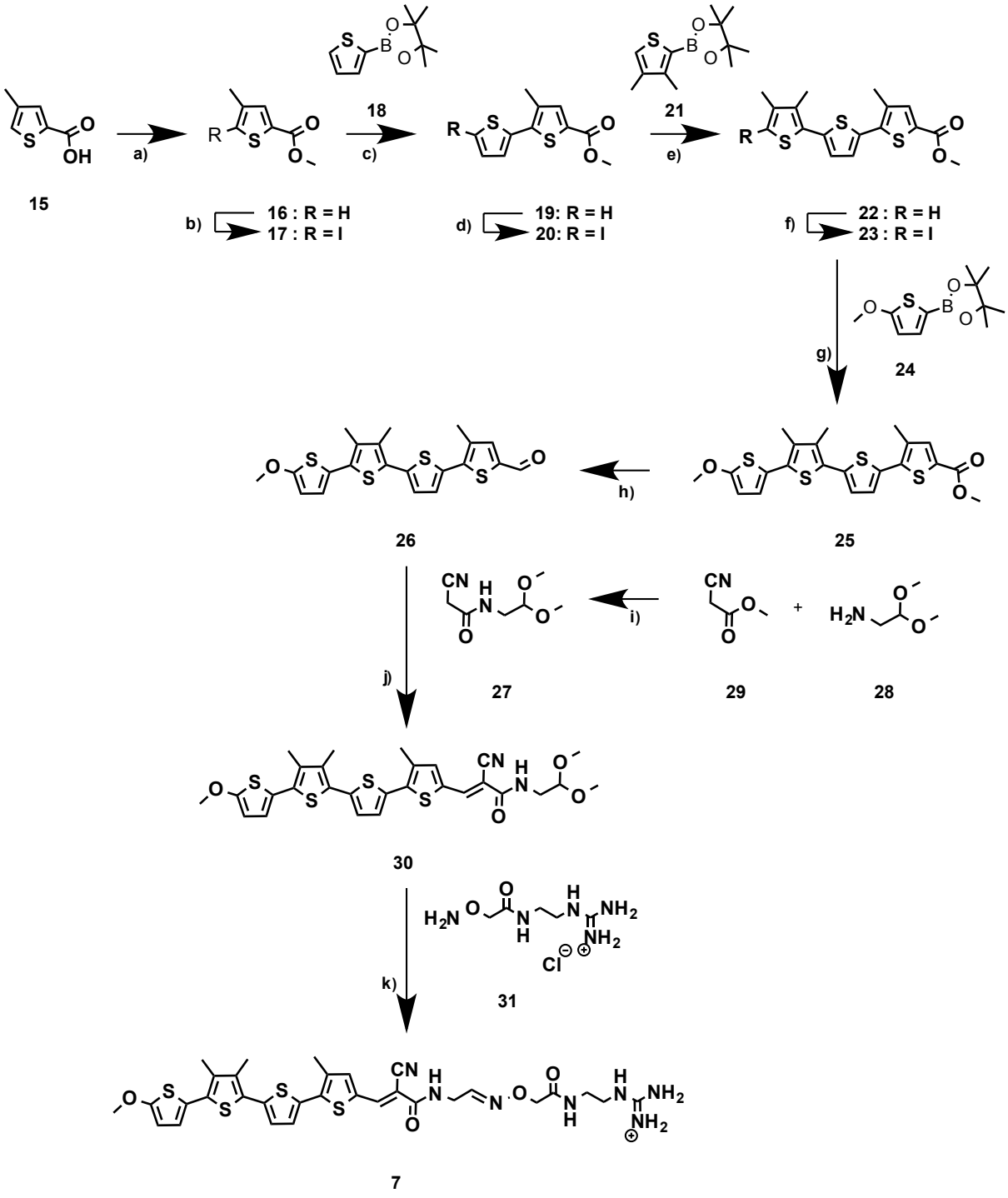
Abbreviations. ACN: Acetonitrile; AcOH: Acetic acid; Calcd: Calculated; DCM: Dichloromethane; DIBAL: Diisobutylaluminum hydride; DMF: *N*,*N*-Dimethylformamide; DMP: Dess-Martin periodinane; DMSO: Dimethylsulfoxide; DOPC: 1,2-dioleoyl-*sn*-glycero-3-phosphocholine; DPPC: 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine; LUVs: Large unilamellar vesicles; MeOH: Methanol; NIS: *N*-Iodosuccinimide; rt: room temperature; THF: Tetrahydrofuran; Tris: Tris(hydroxymethyl)aminomethane; $TsOH \cdot H_2O$: *p*-Toluenesulfonic acid monohydrate.

2. Synthesis

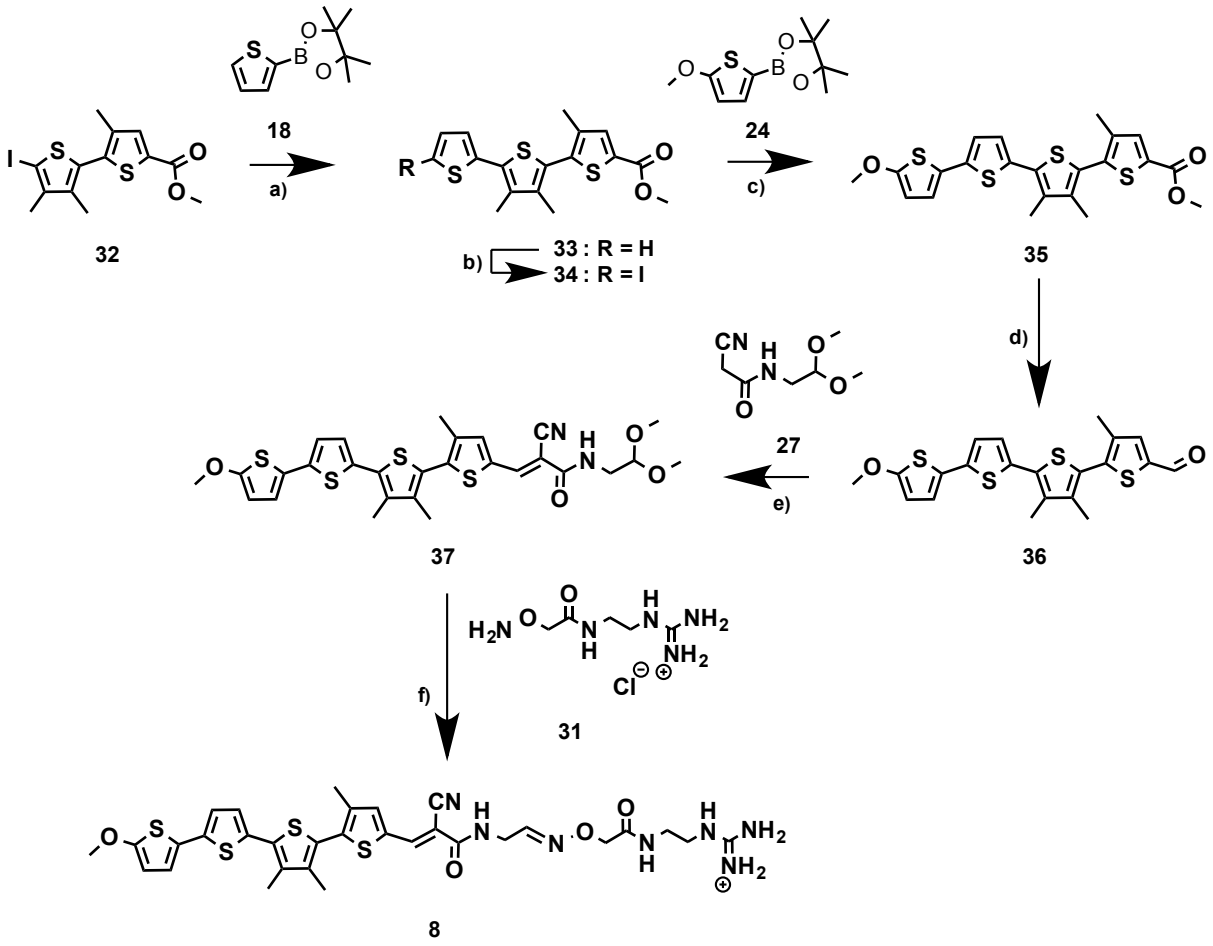
Compounds 1, 2, 3, 16, **17**, **32, 38**, **83** and **84** were synthesized according to procedures reported in refs. S1 and S2.

Compounds 21, **24**, **27** and **31** were synthesized according to procedures reported in refs. S3, S4, S5 and S7.

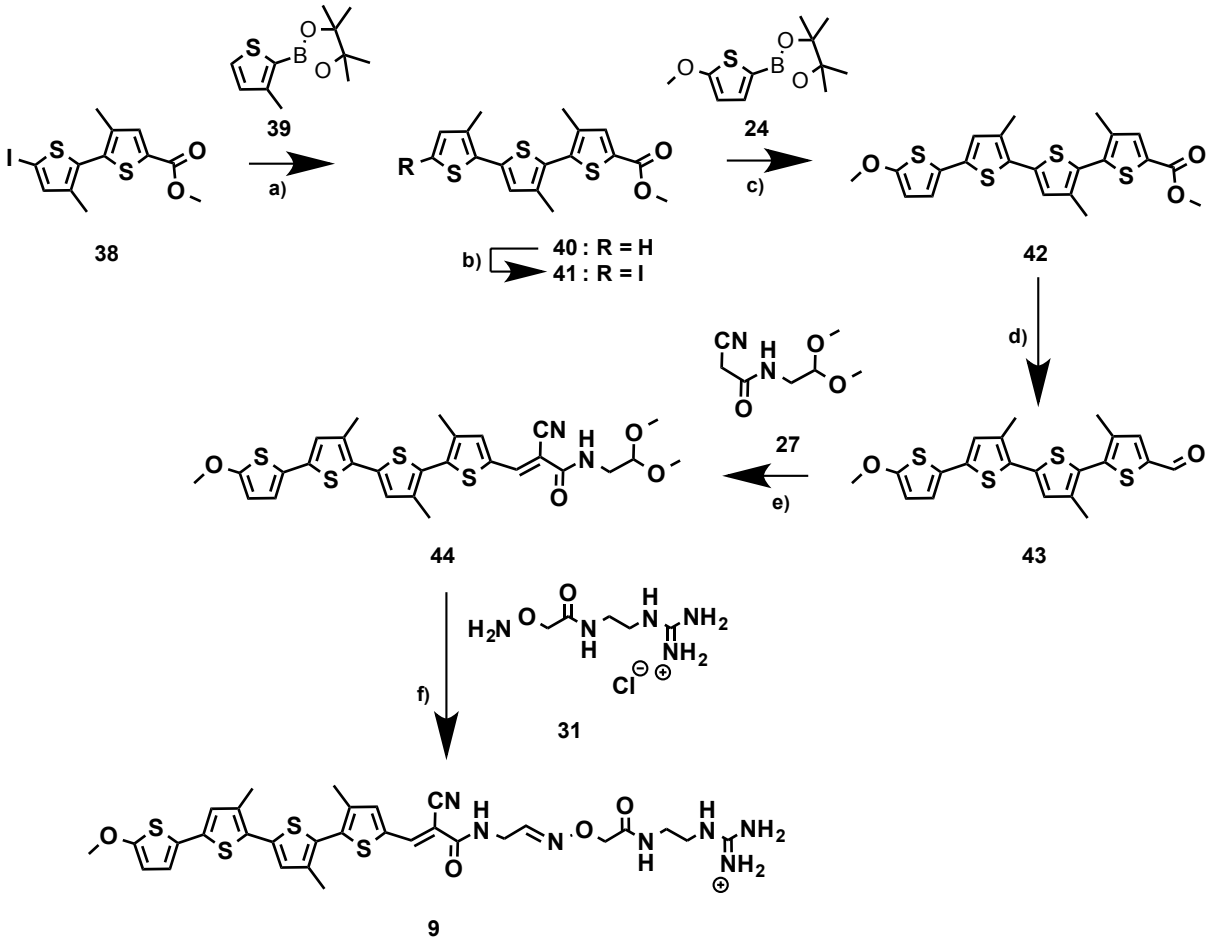
2.1. Synthetic schemes



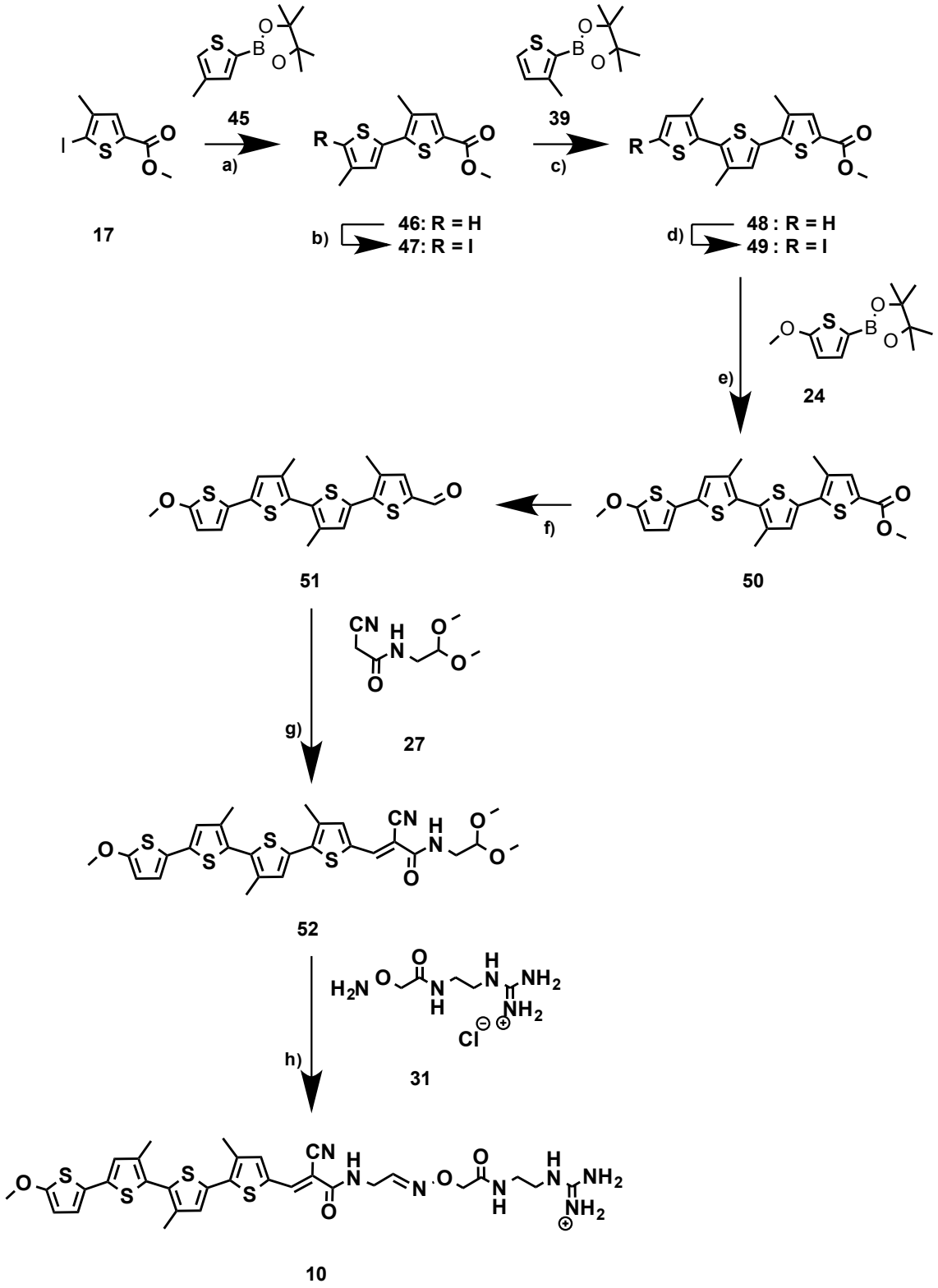
Scheme S1. Synthesis of probe **7**: (a) MeOH, H_2SO_4, μW, 100 °C, 15 min, 71%; (b) NIS, $CHCl_3$, AcOH, rt, 16 h, 73%; (c) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 87%; (d) NIS, $CHCl_3$, AcOH, rt, 16 h, 78%; (e) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 85%; (f) NIS, $CHCl_3$, AcOH, rt, 16 h, 78%; (g) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 81%; (h) 1. DIBAL, CH_2Cl_2, -78 °C, 2. DMP, CH_2Cl_2, rt, 20 min, 46%; (i) neat, rt, 48 h, 92%; (j) piperidine, ACN, 70 °C, 3 h, 83%; (k) 1. $TsOH{\cdot}H_2O$, CH_2Cl_2, rt, 10 min, 58%, 2. DMSO, 60 °C, 10 min, 42%.



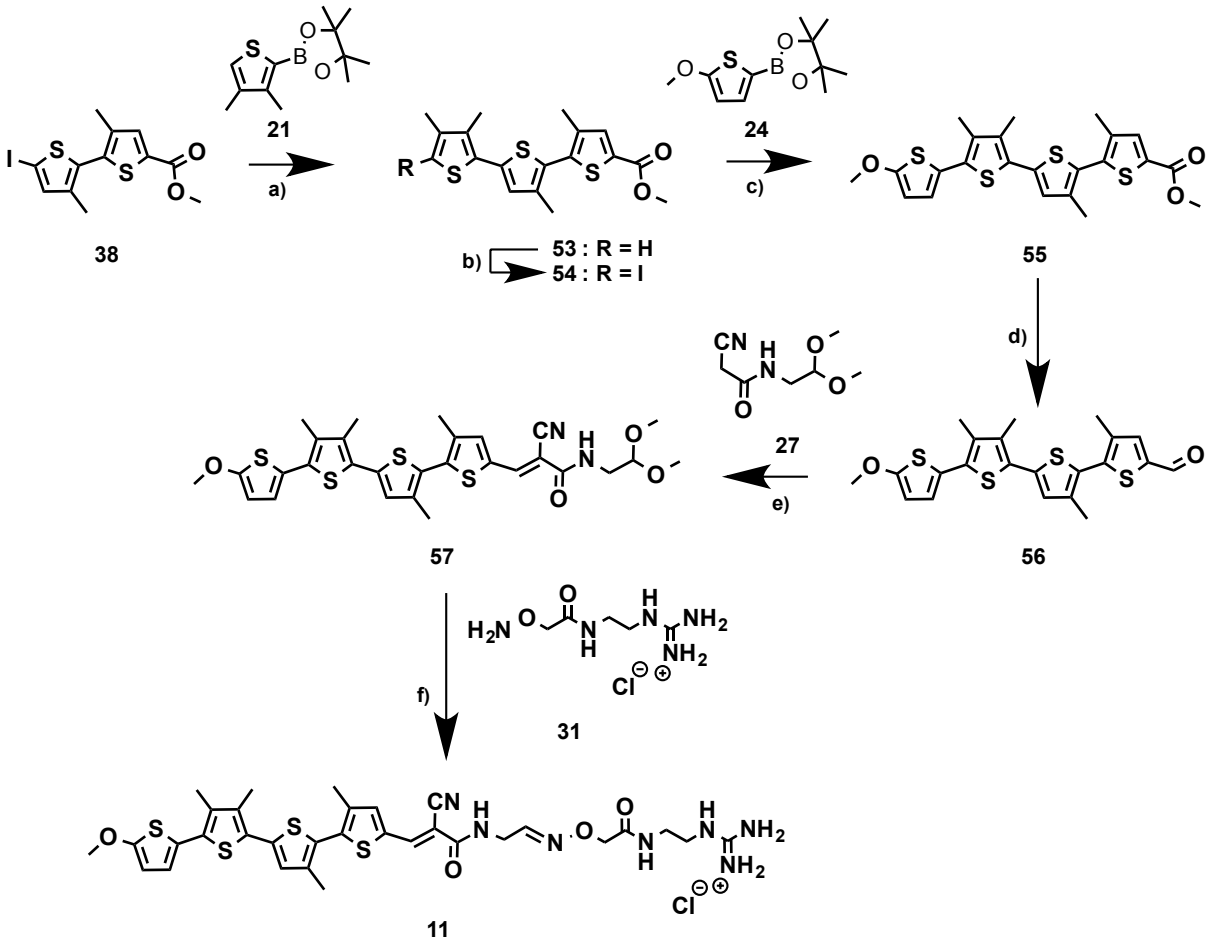
Scheme S2. Synthesis of probe **8**: (a) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 88%; (b) NIS, $CHCl_3$, AcOH, rt, 16 h, 87%; (c) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 71%; (d) 1. DIBAL, CH_2Cl_2, -78 °C, 2. DMP, CH_2Cl_2, rt, 20 min, 37%; (e) piperidine, ACN, 70 °C, 3 h, 69%; (f) 1. $TsOH{\cdot}H_2O$, CH_2Cl_2, rt, 10 min, 52%, 2. DMSO, 60 °C, 10 min, 54%.



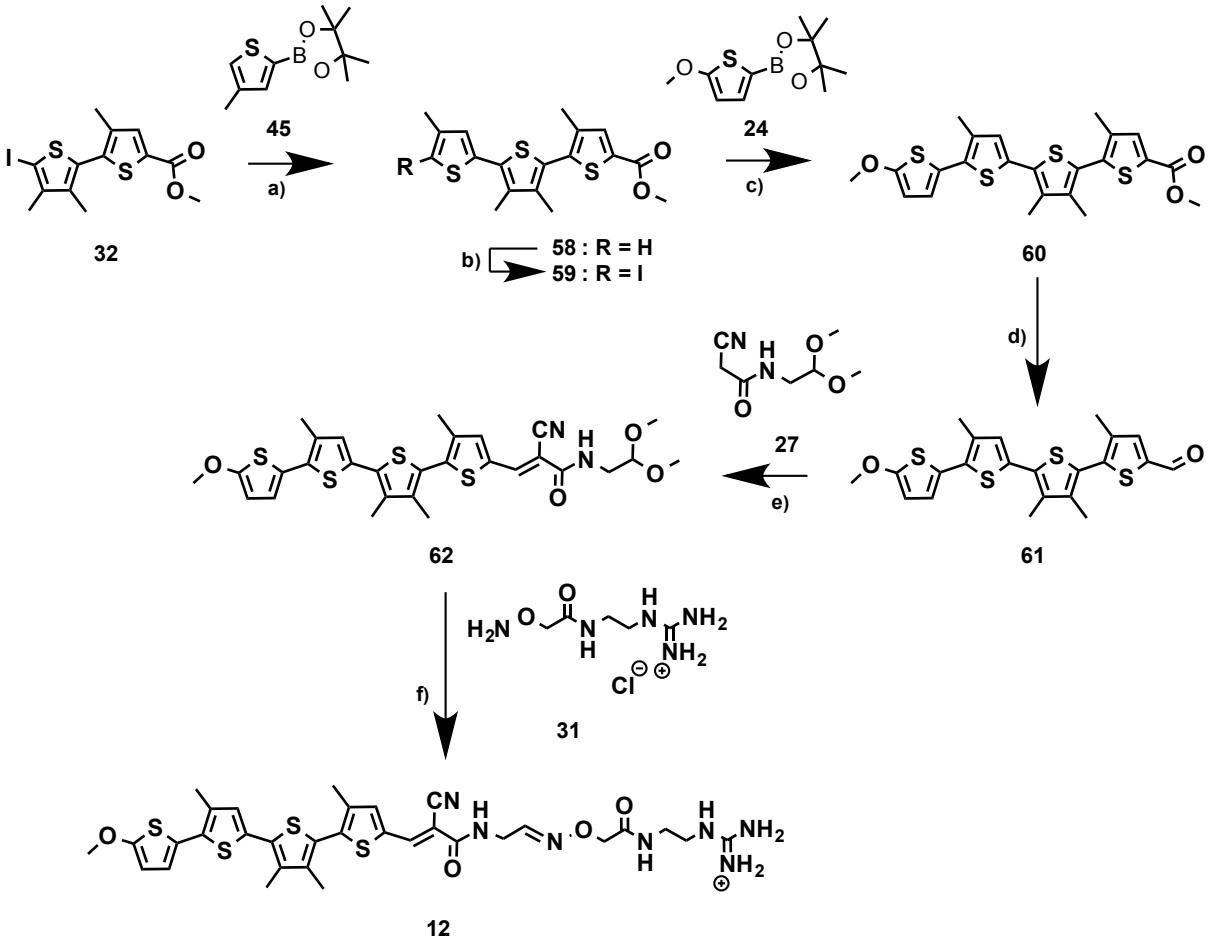
Scheme S3. Synthesis of probe **9**: (a) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 91%; (b) NIS, $CHCl_3$, AcOH, rt, 16 h, 88%; (c) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 84%; (d) 1. DIBAL, CH_2Cl_2, -78 °C, 2. DMP, CH_2Cl_2, rt, 20 min, 32%; (e) piperidine, ACN, 70 °C, 3 h, 82%; (f) 1. $TsOH{\cdot}H_2O$, CH_2Cl_2, rt, 10 min, 50%, 2. DMSO, 60 °C, 10 min, 57%.



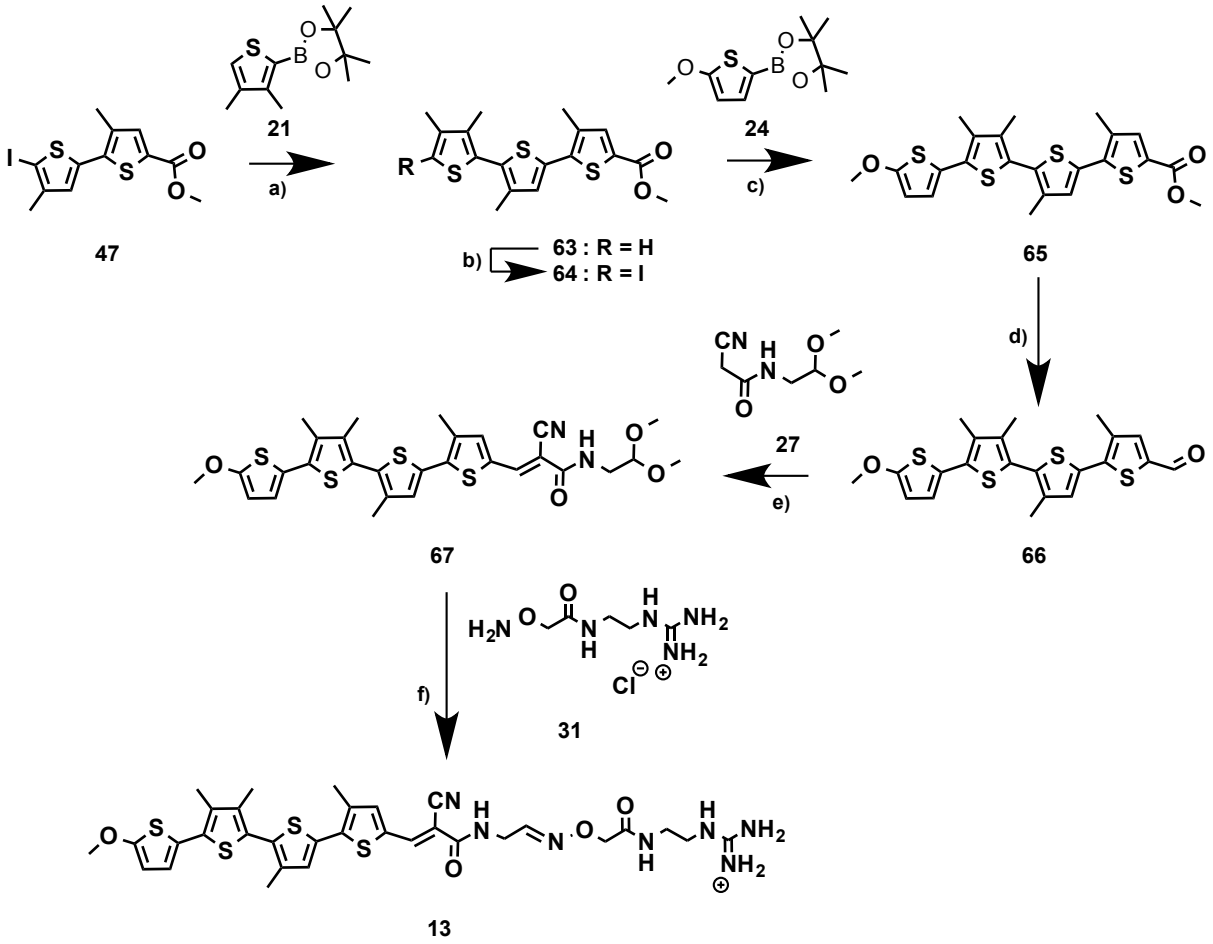
Scheme S4. Synthesis of probe **10**: (a) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 81%; (b) NIS, $CHCl_3$, AcOH, 0°C, 16 h, 90%; (c) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 80%; (d) NIS, $CHCl_3$, AcOH, rt, 16 h, 74%; (e) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 86%; (f) 1. DIBAL, CH_2Cl_2, -78 °C, 2. DMP, CH_2Cl_2, rt, 20 min, 52%; (g) piperidine, ACN, 70 °C, 3 h, 83%; (h) 1. $TsOH{\cdot}H_2O$, CH_2Cl_2, rt, 10 min, 56%, 2. DMSO, 60 °C, 10 min, 50%.



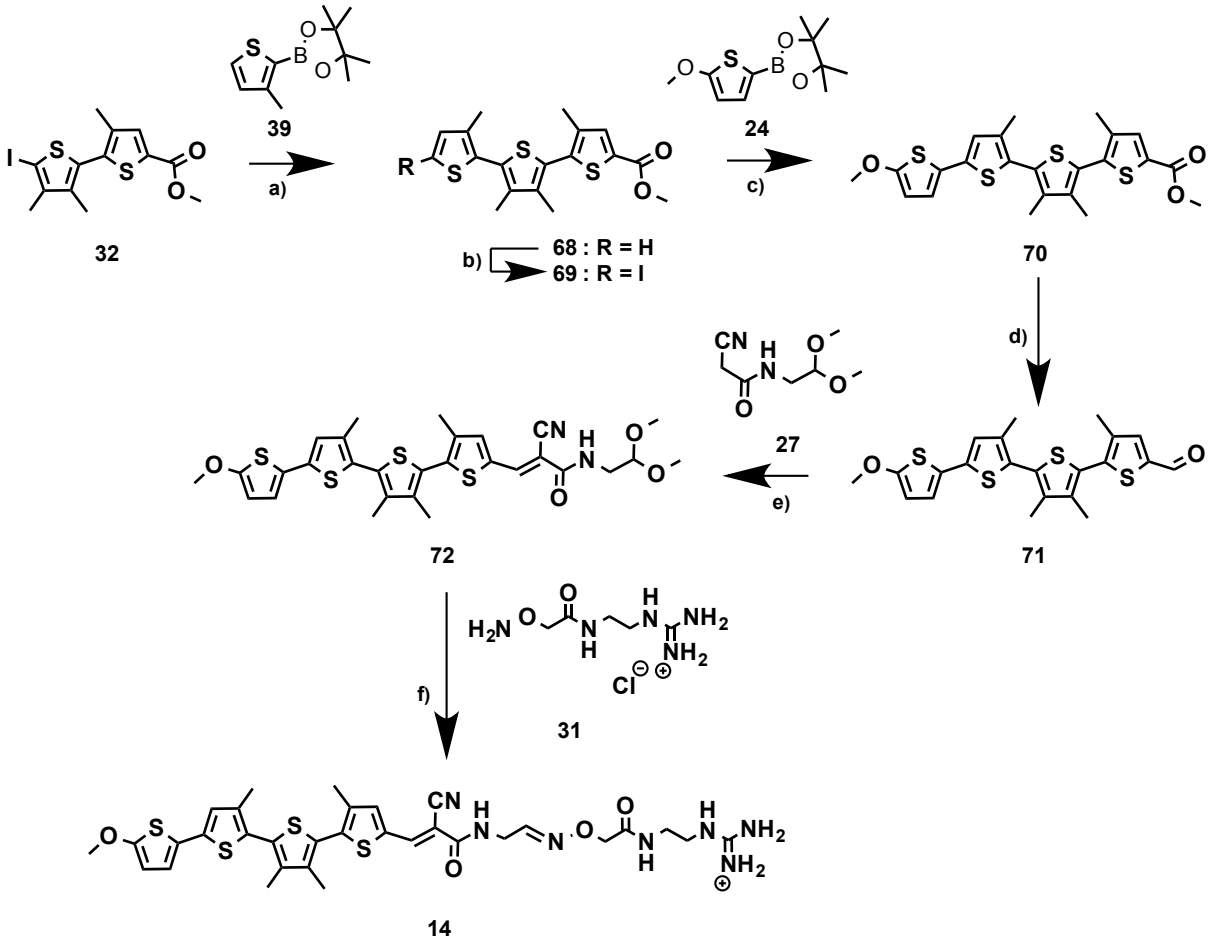
Scheme S5. Synthesis of probe **11**: (a) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 85%; (b) NIS, $CHCl_3$, AcOH, rt, 16 h, 85%; (c) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 92%; (d) 1. DIBAL, CH_2Cl_2, -78 °C, 2. DMP, CH_2Cl_2, rt, 20 min, 53%; (e) piperidine, ACN, 70 °C, 3 h, 85%; (f) 1. $TsOH \cdot H_2O$, CH_2Cl_2, rt, 10 min, 50%, 2. DMSO, 60 °C, 10 min, 47%.



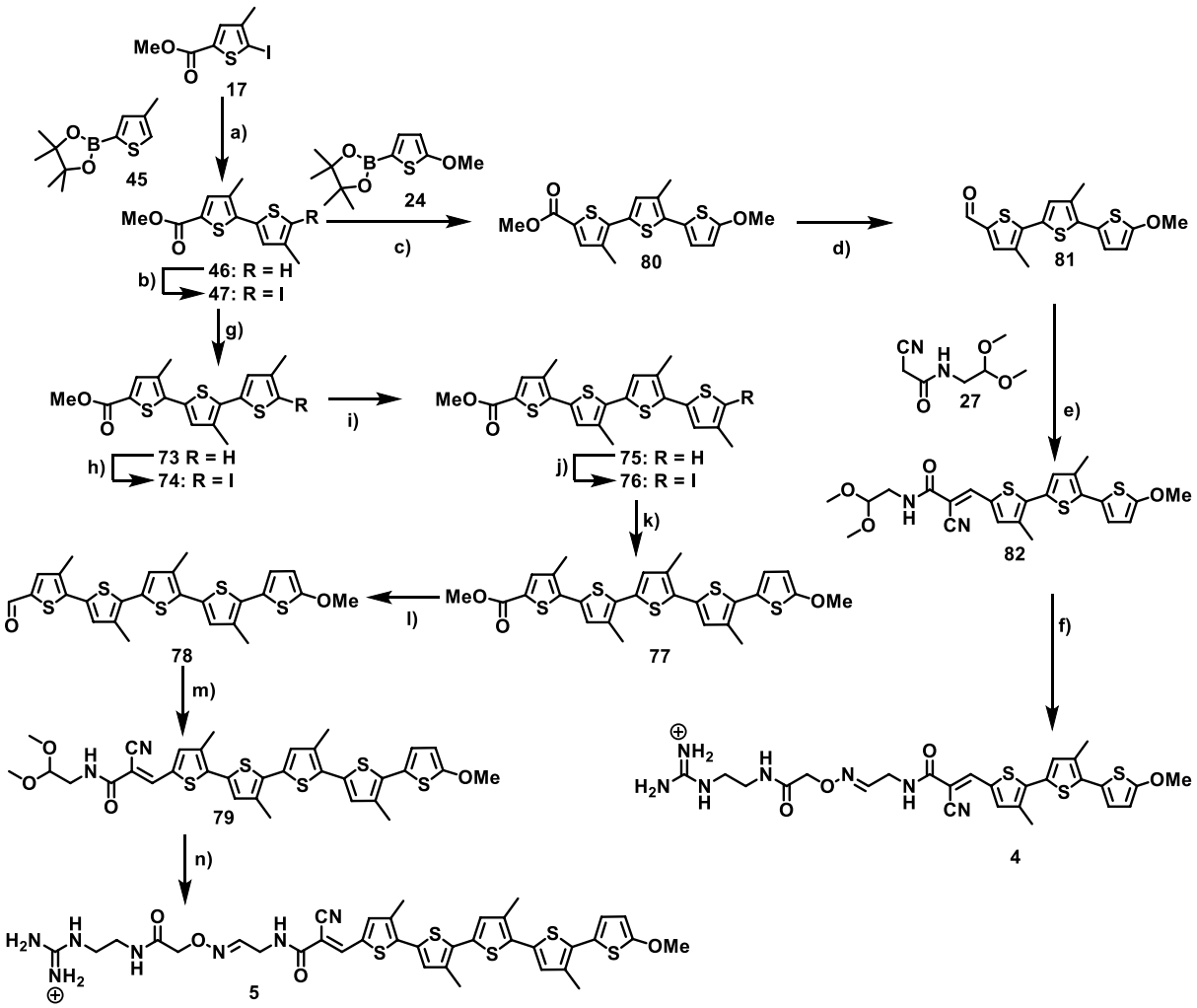
Scheme S6. Synthesis of probe **12**: (a) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 90%; (b) NIS, $CHCl_3$, AcOH, rt, 16 h, 91%; (c) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 81%; (d) 1. DIBAL, CH_2Cl_2, -78 °C, 2. DMP, CH_2Cl_2, rt, 20 min, 37%; (e) piperidine, ACN, 70 °C, 3 h, 74%; (f) 1. $TsOH{\cdot}H_2O$, CH_2Cl_2, rt, 10 min, 55%, 2. DMSO, 60 °C, 10 min, 50%.



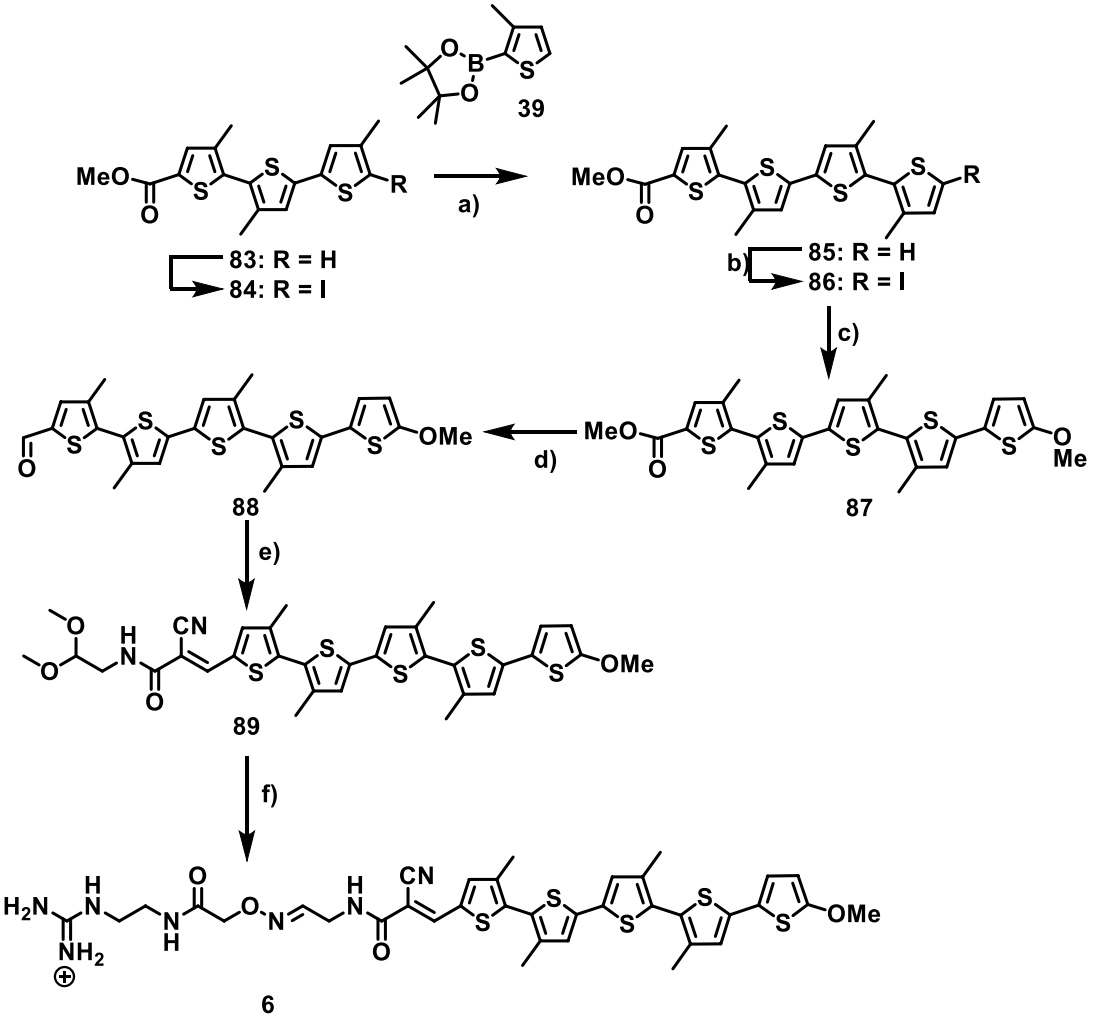
Scheme S7. Synthesis of probe **13**: (a) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 76%; (b) NIS, $CHCl_3$, AcOH, rt, 16 h, 76%; (c) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 74%; (d) 1. DIBAL, CH_2Cl_2, -78 °C, 2. DMP, CH_2Cl_2, rt, 20 min, 39%; (e) piperidine, ACN, 70 °C, 3 h, 87%; (f) 1. $TsOH \cdot H_2O$, CH_2Cl_2, rt, 10 min, 49%, 2. DMSO, 60 °C, 10 min, 59%.



Scheme S8. Synthesis of probe **14**: (a) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 83%; (b) NIS, $CHCl_3$, AcOH, rt, 16 h, 85%; (c) $Pd(PPh_3)_4$, CsF, DMF, 80 °C, 16 h, 64%; (d) 1. DIBAL, CH_2Cl_2, -78 °C, 2. DMP, CH_2Cl_2, rt, 20 min, 52%; (e) piperidine, ACN, 70 °C, 3 h, 64%; (f) 1. $TsOH \cdot H_2O$, CH_2Cl_2, rt, 10 min, 58%, 2. DMSO, 60 °C, 10 min, 48%.



Scheme S9. Synthesis of probes **4** and **5**: a) **45**, $Pd(PPh_3)_4$, CsF, DMF, 16 h, 80 °C, 81%. b) NIS, DCM, AcOH, 16 h, 0 °C to rt, 90%. c) **24**, $Pd(PPh_3)_4$, CsF, DMF, 16 h, 80 °C, 65%. d) 1. DIBAL, DCM, MeOH, 2 h, -78 ºC; 2. MnO_2, DCM, 15 min, rt, 73%. e) **27**, piperidine, ACN, 3 h, reflux, 63%. f) 1. $TsOH{\cdot}H_2O$, DCM, 15 h, rt, 2. **31**, DMSO, AcOH, 60 ºC, 14 h, quantitative. g) **45**, $Pd(PPh_3)_4$, CsF, DMF, 16 h, 80 °C, 75%. h) NIS, DCM, AcOH, 16 h, 0 °C to rt, quantitative. i) **45**, $Pd(PPh_3)_4$, CsF, DMF, 16 h, 80 °C, 74%. j) NIS, DCM, AcOH, 16 h, 0 °C to rt, quantitative. k) **24**, $Pd(PPh_3)_4$, CsF, DMF, 16 h, 80 °C, 52%. l) 1. DIBAL, DCM, MeOH, 1 h, -78 ºC; 2. MnO_2, DCM, 1 h, rt, 27%. m) **27**, piperidine, DMF, 16 h, 70 °C, 84%. n) 1.$TsOH{\cdot}H_2O$, DCM, 16 h, rt, 2. **31**, DMSO, AcOH, 70 ºC, 14 h.



Scheme S10. Synthesis probe **6**: a) **39**, $Pd(PPh_3)_4$, CsF, DMF, 16 h, 80 °C, 83%. b) NIS, DCM, AcOH, 16 h, 0 °C to rt, quantitative. c) **24**, $Pd(PPh_3)_4$, CsF, DMF, 16 h, 80 °C, 75%. d) 1. DIBAL, DCM, MeOH, 1 h, -78 ºC; 2. MnO_2, DCM, 1 hr, rt, 53%. e) **27**, piperidine, DMF, 2 h, 60 °C, 85%. f) 1. $TsOH \cdot H_2O$, DCM, 0.5 h, rt, 2. **31**, DMSO, AcOH, 60 ºC, 1 h.

2.2. Synthesis of bithiophenes

Compound 19. To a solution of **17** (482 mg, 1.72 mmol) and **18** (433 mg, 2.06 mmol) in freshly distilled DMF (40 mL) under argon atmosphere, CsF (782 mg, 5.15 mmol) and $Pd(PPh_3)_4$ (199 mg, 0.17 mmol) were added and the resulting mixture was stirred overnight at 80 °C. The solution was then cooled to rt, diluted with brine (30 mL) and extracted with ethyl acetate (3 x 25 mL). The collected organic fractions were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) to afford **19** (353 mg, 87%) as colorless oil. R_f (petroleum ether/ethyl acetate 99:1): 0.10; IR (neat): 2921 (w), 1698 (s), 1435 (m), 1248 (s), 1187 (m), 1070 (m), 967 (w), 868 (w), 749 (w), 721 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 7.50 (s, 1H), 7.29 (dd, ^3J (H,H) = 5.1 Hz, ^3J (H,H) = 1.0 Hz, 1H), 7.16 (dd, ^3J (H,H) = 3.6 Hz, ^3J (H,H) = 1.0 Hz, 1H), 7.01 (dd, ^3J (H,H) = 5.1 Hz, ^3J (H,H) = 3.6 Hz, 1H), 3.82 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.3 (s), 138.4 (s), 137.3 (d), 135.5 (s), 134.1 (s), 129.5 (s), 127.6 (d), 126.5 (d), 126.4 (d), 52.0 (q), 15.4 (q); MS (ESI+, DCM): 239 (100, $[M+H]^+$).

Compound 46. To a solution of **17** (650 mg, 2.3 mmol) and **45** (777 mg, 3.47 mmol) in freshly distilled DMF (30 mL) under Ar atmosphere, CsF (1.07 g, 7.04 mmol) and $Pd(PPh_3)_4$ (277 mg, 0.24 mmol) were added, then the mixture was stirred at 80 °C overnight. The mixture was cooled down to rt, water (50 mL) was added and the mixture was extracted with diethyl ether (4 x 30 mL). The organic layer was dried over Na_2SO_4 and the solvent evaporated *in vacuo*. Silica gel column chromatography (petroleum ether/ethyl acetate 95/5) of the residue gave **46** (472 mg, 81%) as a colorless solid. R_f (petroleum ether/ethyl acetate 9:5): 0.3; Mp: 83-84 °C; IR (neat): 2949 (w), 1715 (s), 1531 (w), 1455 (m), 1398 (w), 1366

(w), 1242 (s), 1191 (s), 1076 (s), 980 (m), 897 (w), 844 (m), 783 (w), 735 (s), 692 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.56 (s, 1H), 7.04 (s, 1H), 6.95 (s, 1H), 3.87 (s, 3H), 2.38 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.8 (s), 139.0 (s), 138.6 (s), 137.6 (d), 135.5 (s), 134.3 (s), 129.5 (s), 129.1 (d), 122.2 (d), 52.4 (q), 15.9 (q), 15.8 (q); MS (ESI+, $CHCl_3$/MeOH + HCOOH 0.1% 1:1): 253 (50, $[M+H]^+$), 221 (80, $[M-MeO]^+$, 194 (100, $[M-CH_3COO]^+$).

Compound 20. To a solution of **19** (353 mg, 1.48 mmol) in $CHCl_3$:AcOH (20 mL, 1:1) at 0 °C, NIS (350 mg, 1.56 mmol) was added in 3 portions over 10 minutes. The resulting mixture was slowly warmed to rt and then stirred overnight. The solution was quenched with 10% aqueous $Na_2S_2O_3$ (30 mL) and extracted with DCM (3 x 25 mL). The combined organic fractions were dried over anhydrous Na_2SO_3, filtered and concentrated under vacuum. The residue was purified with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) to afford **20** (420 mg, 78%) as a white solid. R_f (petroleum ether/ethyl acetate 99:1): 0.12; Mp: 88-89 °C; IR (neat): 2943 (w), 1694 (s), 1548 (w), 1508 (w), 1442 (s), 1411 (w), 1384 (w), 1303 (w), 1249 (s), 1193 (m), 1181 (m), 1081 (m), 1020 (w), 973 (m), 948 (w), 933 (w), 876 (w), 858 (w), 803 (w), 787 (s), 745 (s), 734 (w), 654 (w), 627 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 7.46 (s, 1H), 7.13 (d, ^{3}J (H,H) = 3.8 Hz, 1H), 6.80 (d, ^{3}J (H,H) = 3.8 Hz, 1H), 3.82 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.2 (s), 141.4 (s), 137.4 (d), 137.2 (d), 134.6 (2 x s), 129.9 (s), 127.8 (d), 74.7 (s), 52.2 (q), 15.6 (q); MS (ESI+, DCM): 365 (100, $[M+H]^+$), 237 (49, $[M-I+H]^+$).

Compound 47. To a solution of **46** (1.36 g, 5.38 mmol) in $CHCl_3$ and AcOH (15 mL, 2:1) at 0 °C, NIS (1.20 g, 5.33mmol) was added in three portions over a period of 5 min. Then the reaction was stirred at 0 °C for 1 h and at rt overnight. DCM (10 mL) was added, then the solution was washed with $Na_2S_2O_3$ 0.1 M (2 x 10 mL) and water (4 x 20 mL). The organic

layer was dried over $MgSO_4$ and the solvent evaporated *in vacuo* to give analytically pure **47** (1.84 g, 90%) as a yellow solid. R_f (petroleum ether/ethyl acetate 95:5): 0.3; Mp: 110-111 °C; IR (neat): 2948 (w), 1699 (s), 1529 (w), 1449 (s), 1378 (m), 1333 (w), 1249 (s), 1190 (m), 1078 (m), 980 (w), 897 (w), 866 (w), 812 (w), 784 (w), 746 (m), 692 (w), 629 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 7.55 (s, 1H), 6.88 (s, 1H), 3.87 (s, 3H), 2.35 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.6 (s), 143.4 (s), 140.0 (s), 137.8 (s), 137.4 (d), 134.7 (s), 129.9 (s), 128.1 (d), 76.3 (s), 52.3 (q), 18.3 (q), 15.6 (q); MS (ESI+, $CHCl_3$/MeOH + HCOOH 0.1% 1:1): 379 (100, $[M+H]^+$).

2.3. Synthesis of terthiophenes

Compound 22 (general procedure A). To a solution of **20** (500 mg, 1.37 mmol) and **21** (392 mg, 1.65 mmol) in freshly distilled DMF (40 mL) under argon atmosphere, CsF (626 mg, 4.12 mmol) and $Pd(PPh_3)_4$ (159 mg, 0.13 mmol) were added and the resulting mixture was stirred overnight at 80 °C. The solution was then cooled to rt, diluted with brine (30 mL) and extracted with ethyl acetate (3 x 25 mL). The collected organic fractions were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) to afford **22** (406 mg, 85%) as a light yellow solid (406 mg, 85%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 91-92 °C; IR (neat): 2949 (w), 2915 (w), 1711 (s), 1551 (w), 1434 (m), 1382 (w), 1321 (w), 1243 (m), 1193 (m), 1078 (m), 1024 (w), 982 (w), 926 (w), 881 (w), 858 (w), 782 (m), 744 (m), 716 (m), 662 (w), 626 (w), 581 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.54 (s, 1H), 7.14 (d, ^3J (H,H) = 3.7 Hz, 1H), 7.04 (d, ^3J (H,H) = 3.7 Hz, 1H), 6.84 (s, 1H), 3.87 (s, 3H), 2.38 (s, 3H), 2.28 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.4 (s), 139.0 (s), 138.4 (2 X s), ,

137.4 (d), 134.8 (s), 134.2 (s), 134.1 (s), 130.4 (s), 129.3 (s), 126.7 (d), 125.8 (d), 119.8 (d), 52.0 (q), 15.7 (q), 15.4 (q), 13.8 (q); MS (ESI+, DCM): 349 (100, $[M+H]^+$).

Compound 33. Starting from the corresponding iodinated bithiophene **32** (630 mg, 1.61 mmol) and the boronate ester **18** (405 mg, 1.93 mmol) and following the general procedure A, the desired compound **33** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) as a light yellow solid (492 mg, 88%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 69-70 °C; IR (neat): 2947 (w), 1706 (s), 1542 (w), 1441 (m), 1385 (w), 1298 (s), 1193 (m), 1088 (m), 1013 (w), 991 (w), 948 (w), 914 (w), 863 (w), 849 (w), 823 (m), 749 (m), 719 (w), 682 (m), 592 (w), 535 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.65 (s, 1H), 7.29 (dd, ^3J (H,H) = 5.1 Hz, ^4J (H,H) = 1.1 Hz, 1H), 7.14 (dd, ^3J (H,H) = 3.6 Hz, ^4J (H,H) = 1.1 Hz, 1H), 7.05 (dd, ^3J (H,H) = 5.1, 3.6 Hz, 1H), 3.88 (s, 3H), 2.31 (s, 3H), 2.21 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.4 (s), 138.2 (s), 137.2 (2 X s), , 136.2 (d), 136.0 (s), 134.5 (s), 131.9 (s), 131.9 (s), 127.5 (d), 126.5 (s), 126.0 (d), 125.5 (d), 52.1 (q), 14.9 (q), 14.4 (q), 14.3 (q); MS (ESI+, DCM): 349 (100, $[M+H]^+$).

Compound 40. Starting from the corresponding iodinated bithiophene **38** (802 mg, 2.12 mmol) and the boronate ester **39** (572 mg, 2.54 mmol) and following the general procedure A, the desired compound **40** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) as a light yellow solid (739 mg, 91%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 78-79 °C; IR (neat): 2920 (w), 1719 (s), 1435 (m), 1251 (s), 1188 (m), 1079 (m), 976 (m), 855 (m), 830 (m), 786 (m), 743 (m), 688 (m), 636 (m), 608 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 7.64 (s, 1H), 7.14 (d, ^3J (H,H) = 5.1 Hz, 1H), 6.98 (s, 1H), 6.88 (d, ^3J (H,H) = 5.1 Hz, 1H), 3.89 (s, 3H), 2.41 (s, 3H), 2.25 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.5 (s), 137.5 (s), 137.1 (s), 136.9 (2 X s), 136.2 (d), 134.2 (s),

131.7 (s), 131.5 (d), 130.5 (s), 128.4 (d), 127.8 (s), 123.4 (d), 52.1 (q), 15.4 (q), 15.0 (2 x q); MS (ESI+, DCM): 349 (100, $[M+H]^+$).

Compound 48. Starting from the corresponding iodinated bithiophene **47** (822 mg, 2.17 mmol) and the boronate ester **39** (585 mg, 2.61 mmol) and following the general procedure A, the desired compound **48** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) as a light yellow solid (608 mg, 80%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 80-81 °C; IR (neat): 2921 (w), 1699 (s), 1434 (m), 1248 (s), 1187 (m), 1070 (m), 967 (w), 830 (w), 749 (w), 721 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 7.56 (s, 1H), 7.28 (d, ^3J (H,H) = 5.1 Hz, 1H), 7.07 (s, 1H), 6.93 (d, ^3J (H,H) = 5.1 Hz, 1H), 3.88 (s, 3H), 2.40 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.5 (s), 138.4 (s), 137.4 (d), 137.0 (s), 136.8 (s), 134.7 (s), 134.1 (s), 130.9 (s), 130.2 (d), 129.4 (d), 129.3 (s), 128.6 (s), 125.4 (d), 52.1 (q), 15.6 (q), 14.8 (2 X q); MS (ESI+, DCM): 349 (100, $[M+H]^+$).

Compound 53. Starting from the corresponding iodinated bithiophene **38** (807 mg, 2.13 mmol) and the boronate ester **21** (609 mg, 2.56 mmol) and following the general procedure A, the desired compound **53** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) as a yellow solid (661 mg, 85%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 102-103 °C; IR (neat): 2921 (m), 1699 (s), 1542 (w), 1432 (s), 1240 (s), 1192 (s), 1080 (m), 979 (m), 866 (m), 819 (m), 772 (m), 747 (m), 597.73 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 7.65 (s, 1H), 6.97 (s, 1H), 6.84 (s, 1H), 3.89 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H), 2.24 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.5 (s), 138.9 (s), 137.4 (2 X s), 137.0 (2 X s), 136.2 (d), 134.0 (s), 131.7 (s), 130.5 (s), 128.5 (d), 127.7 (s), 119.6 (d), 52.0 (q), 15.4 (q), 15.0 (2 X q), 13.7 (q); MS (ESI+, DCM): 363 (100, $[M+H]^+$).

Compound 58. Starting from the corresponding iodinated bithiophene **32** (670 mg, 1.71 mmol) and the boronate ester **45** (459 mg, 2.05 mmol) and following the general procedure A, the desired compound **58** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) as a light yellow solid (559 mg, 90%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 68-69 °C; IR (neat): 2952 (w), 1715 (s), 1547 (w), 1486 (m), 1438 (m), 1391 (m), 1368 (w), 1243 (s), 1182 (m), 1076 (m), 1001 (w), 974 (w), 877 (w), 854 (w), 814 (w), 783 (w), 749 (s), 629 (w), 589 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.64 (s, 1H), 6.97 (s, 1H), 6.88 (s, 1H), 3.88 (s, 3H), 2.32 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.5 (s), 138.2 (s), 138.0 (s), 137.3 (s), 137.2 (s), 136.1 (d), 135.8 (s), 134.2 (s), 132.2 (s), 131.8 (s), 128.2 (d), 126.3 (s), 121.0 (d), 52.0 (q), 15.7 (q), 14.9 (q), 14.3 (q), 14.2 (q); MS (ESI+, DCM): 363 (100, $[M+H]^+$).

Compound 63. Starting from the corresponding iodinated bithiophene **47** (826 mg, 2.18 mmol) and the boronate ester **21** (676 mg, 2.84 mmol) and following the general procedure A, the desired compound **63** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) as a light yellow solid (600 mg, 76%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 96-97 °C; IR (neat): 2921 (w), 1715 (m), 1442 (m), 1253 (s), 1190 (m), 1080 (m), 979 (m), 866 (m), 814 (m), 744 (m), 709 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 7.57 (s, 1H), 7.07 (s, 1H), 6.98 (s, 1H), 3.88 (s, 3H), 2.41 (s, 3H), 2.21 (s, 3H), 2.18 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.5 (s), 138.5 (s), 138.0 (s), 137.4 (d), 136.9 (s), 136.6 (s), 134.7 (s), 134.1 (s), 131.8 (s), 129.3 (d), 129.3 (s), 128.5 (s), 121.1 (d), 52.1 (q), 15.6 (q), 15.3 (q), 14.7 (q), 13.5 (q); MS (ESI+, DCM): 363 (100, $[M+H]^+$).

Compound 68. Starting from the corresponding iodinated bithiophene **32** (650 mg, 1.66 mmol) and the boronate ester **39** (445 mg, 1.99 mmol) and following the general procedure A, the desired compound **68** was obtained after purification with flash chromatography (SiO_2,

petroleum ether/ethyl acetate 99:1) as a white solid (501 mg, 83%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 82-83 °C; IR (neat): 2915 (w), 1719 (s), 1537 (w), 1491 (w), 1445 (m), 1385 (w), 1364 (w), 1250 (s), 1198 (m), 1075 (m), 1021 (w), 988 (w), 964 (w), 917 (w), 883 (w), 833 (w), 791 (w), 746 (w), 709 (s), 635 (w), 613 (w), 557 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.48 (s, 1H), 7.08 (d, ^3J (H,H) = 5.1 Hz, 1H), 7.75 (d, ^3J (H,H) = 5.1 Hz, 1H), 3.71 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 1.97 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.5 (s), 137.4 (s), 137.3 (s), 137.0 (s), 136.9 (s), 136.6 (s), 136.2 (d), 131.8 (s), 130.4 (s), 130.1 (d), 129.1 (s), 128.1 (s), 125.3 (d), 52.0 (q), 14.9 (q), 14.8 (q), 14.3 (q), 14.1 (q); MS (ESI+, DCM): 363 (100, $[M+H]^+$).

Compound 73. Starting from the corresponding iodinated bithiophene **47** (83.0 mg, 0.22 mmol) and the boronate ester **45** (88.0 mg, 0.39 mmol) and following the general procedure A, the desired compound **73** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a pale yellow solid (57 mg, 75%). R_f (petroleum ether/ethyl acetate 95:5): 0.31; Mp: 74-75 °C; IR (neat): 2921 (w), 1709 (s), 1536 (w), 1437 (m), 1247 (s), 1190 (m), 1076 (m), 977 (w), 860 (w), 828 (m), 785 (w), 766 (w), 744 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 7.56 (s, 1H), 7.02 (s, 1H), 6.99 (s, 1H), 6.90 (s, 1H), 3.88 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.7 (s), 138.5 (s), 138.3 (s), 137.6 (s), 135.7 (s), 134.30 (d), 134.29 (s), 132.9 (s), 132.7 (s), 130.8 (d), 129.4 (s), 128.1 (d), 121.1 (d), 52.3 (q), 15.9 (2 X q), 15.6 (q); MS (ESI+, $CHCl_3$/MeOH 1:1): 349 (100, $[M+H]^+$).

Compound 80. Starting from the corresponding iodinated bithiophene **47** (690 mg, 1.82 mmol) and the boronate ester **24** (520 mg, 2.17 mmol) and following the general procedure A, the desired compound **80** was obtained after purification with flash chromatography (SiO_2,

DCM) as a pale yellow solid (430 mg, 65%). R_f (DCM): 0.4; Mp: 95-96 °C; IR (neat): 3058 (w), 2952 (w), 1701 (s), 1543 (m), 1444 (m), 1244 (s), 1199 (s), 1077 (m), 982 (m), 748 (m), 615 (w); ^{1}H NMR (400 MHz, $CDCl_3$): 7.55 (s, 1H), 6.99 (s, 1H), 6.79 (d, ^3J (H,H) = 4.0 Hz, 1H), 6.18 (d, ^3J (H,H) = 4.0 Hz, 1H), 3.92 (s, 3H), 3.87 (s, 3H), 2.40 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.7 (s), 162.6 (s), 138.6 (s), 137.5 (d), 134.0 (s), 133.5 (s), 133.0 (s), 132.0 (s), 130.6 (d), 129.1 (s), 123.7 (d), 122.0 (s), 104.0 (d), 100.0 (s), 60.3 (q), 52.1 (q), 15.7 (q), 15.3 (q); MS (ESI+, $CHCl_3$/MeOH 1/1): 365 (100, $[M+H]^+$); HRMS (ESI, +ve) calcd for $C_{17}H_{17}O_3S_3$: 365.3340 found: 365.0332.

Compound 23 (general procedure B). To a solution of **22** (383 mg, 1.10 mmol) in $CHCl_3$:AcOH (20 mL, 1:1) at 0 °C, NIS (250 mg, 1.11 mmol) was added in 3 portions over 10 minutes. The resulting mixture was slowly warmed to rt and then stirred overnight. The solution was quenched with 10% aqueous $Na_2S_2O_3$ (30 mL) and extracted with DCM (3 x 25 mL). The combined organic fractions were dried over anhydrous Na_2SO_3, filtered and concentrated under vacuum. The residue was purified with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) to afford **23** (405 mg, 78%) as a yellow solid. R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 176-177 °C; IR (neat): 2949 (w), 1698 (s), 1547 (w), 1453 (m), 1438 (m), 1375 (w), 1311 (w), 1251 (s), 1188 (m), 1079 (m), 1006 (w), 975 (m), 866 (m), 834 (w), 780 (m), 745 (m), 630 (m), 578 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.57 (s, 1H), 7.17 (d, ^3J (H,H) = 3.8 Hz, 1H), 7.03 (d, ^3J (H,H) = 3.8 Hz, 1H), 3.88 (s, 3H), 2.41 (s, 3H), 2.34 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.4 (s), 143.6 (s), 138.0 (s), 137.4 (d), 136.9 (s), 135.5 (s), 135.0 (s), 134.4 (s), 134.0 (s), 132.0 (s), 129.6 (s), 126.8 (d), 126.4 (d), 74.1 (s), 52.1 (q), 17.7 (q), 15.7 (q), 14.9 (q); MS (ESI+, DCM): 492 (20, $[M+NH_4]^+$), 475 (100, $[M+H]^+$), 348 (80, $[M-I+H]^+$).

Compound 34. Starting from the corresponding terthiophene **33** (474 mg, 1.36 mmol) and following the general procedure B, the desired compound **34** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) as a yellow solid (560 mg, 87%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 99-100 °C; IR (neat): 2943 (w), 1712 (s), 1538 (w), 1444 (m), 1402 (m), 1383 (m), 1238 (s), 1194 (m), 1078 (m), 1001 (w), 977 (w), 947 (w), 856 (w), 798 (w), 784 (m), 744 (w), 626 (w), 581 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.61 (s, 1H), 7.15 (d, ^3J (H,H) = 3.7 Hz, 1H), 6.77 (d, ^3J (H,H) = 3.7 Hz, 1H), 3.86 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.3 (s), 142.0 (s), 138.2 (s), 137.3 (d), 137.3 (s), 136.9 (s), 136.2 (d), 134.9 (s), 132.0 (s), 130.8 (s), 127.4 (d), 127.1 (s), 73.5 (s), 52.2 (q), 15.1 (q), 14.4 (2 X q); MS (ESI+, DCM): 492 (20, $[M+NH_4]^+$), 475 (100, $[M+H]^+$), 348 (20, $[M-I+H]^+$).

Compound 41. Starting from the corresponding terthiophene **40** (673 mg, 1.93 mmol) and following the general procedure B, the desired compound **41** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) as a light yellow solid (804 mg, 88%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 107-108 °C; IR (neat): 2959 (w), 1718 (s), 1437 (m), 1256 (s), 1189 (m), 1078 (m), 832 (w), 745 (m), 511 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.60 (s, 1H), 6.96 (s, 1H), 6.88 (s, 1H), 3.86 (s, 3H), 2.32 (s, 3H), 2.22 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.4 (s), 141.1 (d), 137.5 (s), 137.1 (s), 136.6 (2 X s), 136.2 (d), 135.8 (s), 135.4 (s), 131.8 (s), 128.7 (d), 128.4 (s), 71.6 (s), 52.2 (q), 15.2 (q), 15.1 (2 x q); MS (ESI+, DCM): 492 (20, $[M+NH_4]^+$), 475 (100, $[M+H]^+$).

Compound 49. Starting from the corresponding terthiophene **48** (575 mg, 1.65 mmol) and following the general procedure B, the desired compound **49** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) as a light yellow solid (577 mg, 74%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 109-110 °C; IR (neat):

2920 (w), 1710 (s), 1437 (m), 1384 (w), 1283 (w), 1246 (s), 1185 (m), 1076 (m), 973 (w), 861 (w), 832 (m), 784 (w), 745 (m), 627 (w), 515 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.56 (s, 1H), 7.07 (s, 1H), 7.06 (s, 1H), 3.88 (s, 3H), 2.39 (s, 3H), 2.19 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.3 (s), 140.0 (d), 138.6 (s), 138.1 (s), 137.4 (s), 137.4 (d), 135.3 (s), 134.7 (s), 134.3 (s), 129.5 (s), 129.4 (s), 129.3 (d), 73.6 (s), 52.1 (q), 15.7 (q), 14.8 (q), 14.5 (q); MS (ESI+, DCM): 492 (20, $[M+NH_4]^+$), 475 (100, $[M+H]^+$).

Compound 54. Starting from the corresponding terthiophene **53** (645 mg, 1.78 mmol) and following the general procedure B, the desired compound **54** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) as a light yellow solid (740 mg, 85%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 140-141 °C; IR (neat): 2920 (w), 1713 (s), 1445 (m), 1242 (s), 1191 (m), 1079 (m), 1003 (m), 855 (m), 814 (m), 743 (m), 575 (w), 538 (w), 515 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.63 (s, 1H), 6.90 (s, 1H), 3.89 (s, 3H), 2.33 (s, 3H), 2.25 (s, 3H), 2.22 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.4 (s), 143.5 (s), 137.4 (s), 137.1 (s), 136.7 (s), 136.2 (d), 136.1 (s), 135.2 (s), 133.6 (s), 131.8 (s), 129.0 (d), 128.4 (s), 74.0 (s), 52.1 (q), 17.8 (q), 15.1 (q), 14.9 (2 x q); MS (ESI+, DCM): 506 (40, $[M+NH_4]^+$), 489 (90, $[M+H]^+$), 362 (100, $[M-I+H]^+$).

Compound 59. Starting from the corresponding terthiophene **58** (525 mg, 1.45 mmol) and following the general procedure B, the desired compound **59** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) as a dark yellow solid (650 mg, 91%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 114-115 °C; IR (neat): 2915 (w), 1713 (s), 1543 (w), 1453 (m), 1434 (m), 1294 (s), 1185 (w), 1078 (w), 1005 (w), 929 (w), 848 (w), 829 (w), 812 (m), 747 (m), 629 (w), 580 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.60 (s, 1H), 6.77 (s, 1H), 3.85 (s, 3H), 2.25 (s, 3H), 2.18 (s, 6H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.3 (s), 143.0 (s), 140.4 (s), 138.2 (s), 137.2 (s), 137.0 (s), 136.1 (d), 134.7

(s), 131.9 (s), 131.3 (s), 127.4 (d), 126.8 (s), 74.9 (s), 52.1 (q), 18.3 (q), 15.1 (q), 14.4 (2 X q); MS (ESI+, DCM): 506 (20, $[M+NH_4]^+$), 489 (80, $[M+H]^+$), 362 (100, $[M-I+H]^+$).

Compound 64. Starting from the corresponding terthiophene **63** (554 mg, 1.53 mmol) and following the general procedure B, the desired compound **64** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) as a yellow solid (569 mg, 76%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 131-132 °C; IR (neat): 2920 (w), 1712 (s), 1441 (m), 1385 (w), 1247 (s), 1182 (m), 1077 (m), 828 (m), 745 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 7.55 (s, 1H), 7.05 (s, 1H), 3.87 (s, 3H), 2.39 (s, 3H), 2.17 (s, 6H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.4 (s), 142.8 (s), 138.2 (s), 137.4 (s), 137.4 (d), 136.4 (s), 135.2 (s), 134.2 (s), 133.3 (s), 130.4 (s), 129.5 (s), 129.3 (d), 75.5 (s), 52.1 (q), 17.7 (q), 15.7 (q), 14.8 (q), 14.6 (q); MS (ESI+, DCM): 506 (20, $[M+NH_4]^+$), 489 (100, $[M+H]^+$), 362 (30, $[M-I+H]^+$).

Compound 69. Starting from the corresponding terthiophene **68** (469 mg, 1.29 mmol) and following the general procedure B, the desired compound **69** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 99:1) as a light yellow solid (540 mg, 85%). R_f (petroleum ether/ethyl acetate 99:1): 0.10; Mp: 98-99 °C; IR (neat): 2913 (w), 1702 (s), 1525 (w), 1476 (m), 1442 (m), 1390 (m), 1371 (w), 1251 (s), 1190 (m), 1074 (m), 1021 (w), 999 (w), 976 (w), 867 (w), 819 (m), 785 (w), 746 (m), 694 (w), 627 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.61 (s, 1H), 7.04 (s, 1H), 3.85 (s, 3H), 2.19 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.3 (s), 139.9 (d), 138.5 (s), 137.4 (s), 137.1 (2 x s), 136.2 (d), 135.2 (s), 131.9 (s), 129.0 (s), 128.7 (s), 73.5 (s), 52.1 (q), 15.1 (q), 14.5 (q), 14.4 (q), 14.2 (q); MS (ESI+, DCM): 506 (30, $[M+NH_4]^+$), 489 (100, $[M+H]^+$), 362 (10, $[M-I+H]^+$).

Compound 74. Starting from the corresponding terthiophene **73** (57 mg, 0.16 mmol) and following the general procedure B, the desired compound **74** was obtained analytically pure as a bright yellow solid (73 mg, quantitative yield). R_f (petroleum ether/ethyl acetate 95:5): 0.31; Mp: 87-88 °C; IR (neat): 2920 (w), 1697 (s), 1538 (w), 1598 (w), 1439 (m), 1392 (m), 1281 (s), 1245 (m), 1188 (s), 1085 (s), 1011 (w), 961 (w), 922 (w), 861 (w), 813 (m), 747 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 7.56 (s, 1H), 7.01 (s, 1H), 6.83 (s, 1H), 3.88 (s, 3H), 2.40 (s, 3H), 2.37 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.6 (s), 143.3 (s), 140.4 (s), 138.2 (s), 137.6 (d), 134.9 (s), 134.5 (s), 133.3 (s), 131.9 (s), 130.7 (d), 129.6 (s), 127.2 (d), 74.9 (s), 52.3 (q), 18.3 (q), 15.8 (q), 15.5 (q); MS (ESI+, $CHCl_3$/MeOH 1/1): 475 (100, $[M+H]^+$), 348 (100, $[M-I+H]^+$).

2.4. Synthesis of quaterthiophenes

Compound 25 (general procedure C). To a solution of **23** (380 mg, 0.80 mmol) and **24** (259 mg, 1.08 mmol) in freshly distilled DMF (30 mL) under argon atmosphere, CsF (365 mg, 2.40 mmol) and $Pd(PPh_3)_4$ (93 mg, 0.80 mmol) were added and the resulting mixture was stirred overnight at 80 °C. The solution was then cooled to rt, diluted with brine (30 mL) and extracted with ethyl acetate (3 x 25 mL). The collected organic fractions were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) to obtain **25** as an orange solid (300 mg, 81%). R_f (petroleum ether/ethyl acetate 95:5): 0.20; Mp: 120-121 °C; IR (neat): 2950 (w), 1706 (s), 1540 (m), 1487 (m), 1435 (m), 1415 (m), 1325 (w), 1277 (w), 1242 (s), 1212 (m), 1193 (m), 1076 (m), 1052 (m), 988 (m), 908 (w), 859 (w), 831 (w), 784 (m), 763 (m), 747 (m), 714 (w), 678 (w), 629 (w), 593 (w), 567 (w), 525 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.56 (s, 1H), 7.16 (d, ^3J(H, H) = 3.7 Hz, 1H), 7.06 (d, ^3J(H, H) = 3.7 Hz, 1H), 6.75

(d, ^3J(H, H) = 3.8 Hz, 1H), 6.17 (d, ^3J(H, H) = 3.8 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.41 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.5 (s), 162.4 (s), 138.4 (s), 137.7 (s), 137.5 (s), 135.5 (s), 134.9 (d), 134.6 (s), 134.1 (s), 130.5 (s), 129.3 (s), 128.1 (d), 126.8 (s), 125.9 (s), 123.9 (d), 122.2 (d), 104.2 (d), 60.2 (q), 52.1 (q), 15.7 (q), 14.5 (q), 14.2 (q); MS (ESI+, DCM): 461 (100, $[M+H]^+$).

Compound 35. Starting from the corresponding iodinated terthiophene **34** (608 mg, 1.28 mmol) and the boronate ester **24** (415 mg, 1.73 mmol) and following the general procedure C, the desired compound **34** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a yellow solid (419 mg, 71%). R_f (petroleum ether/ethyl acetate 95:5): 0.20; Mp: 131-132 °C; IR (neat): 2921 (w), 1701 (s), 1526 (m), 1493 (m), 1452 (m), 1431 (m), 1385 (w), 1295 (s), 1265 (m), 1233 (w), 1183 (s), 1082 (m), 1051 (m), 988 (m), 945 (w), 919 (w), 861 (w), 783 (w), 759 (s), 718 (w), 665 (w), 615 (w), 575 (w), 534 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.63 (s, 1H), 6.98 (s, 1H), 6.93 (s, 1H), 6.80 (d, ^3J(H, H) = 2.9 Hz, 1H), 6.10 (d, ^3J(H, H) = 2.9 Hz, 1H), 3.88 (s, 6H), 2.32 (s, 3H), 2.21 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 165.7 (s), 162.5 (s), 138.3 (s), 138.1 (s), 137.2 (2 x s), 136.2 (d), 134.3 (s), 133.6 (s), 131.9 (s), 131.8 (s), 126.4 (d), 126.4 (s), 123.3 (s), 122.4 (d), 121.4 (d), 104.5 (d), 60.2 (q), 52.1 (q), 14.9 (q), 14.4 (q), 14.3 (q); MS (ESI+, DCM): 461 (100, $[M+H]^+$).

Compound 42. Starting from the corresponding iodinated terthiophene **41** (634 mg, 1.34 mmol) and the boronate ester **24** (433 mg, 1.80 mmol) and following the general procedure C, the desired compound **42** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as an orange solid (518 mg, 84%). R_f (petroleum ether/ethyl acetate 95:5): 0.20; Mp: 110-111 °C; IR (neat): 2959 (w), 1718 (s), 1567 (w), 1538 (m), 1496 (m), 1432 (m), 1393 (w), 1376 (w), 1323 (w), 1243 (s), 1212 (m), 1190 (m), 1077

(m), 1056 (m), 998 (w), 975 (w), 858 (w), 810 (m), 778 (w), 760 (m), 744 (m), 703 (w), 617 (w), 599 (w), 576 (w), 551 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.63 (s, 1H), 6.94 (s, 1H), 6.80-6.73 (m, 2H), 6.09 (d, ^{3}J(H, H) = 3.8 Hz, 1H), 3.88 (s, 6H), 2.35 (s, 3H), 2.24 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 165.7 (s), 162.5 (s), 137.5 (s), 137.0 (s), 136.9 (s), 136.7 (s), 136.2 (d), 135.6 (s), 134.7 (s), 131.6 (s), 128.2 (s), 128.0 (d), 127.5 (s), 126.5 (d), 123.3 (s), 121.4 (d), 104.4 (d), 60.2 (q), 52.1 (q), 15.7 (q), 15.1 (2 X q); MS (ESI+, DCM): 461 (100, $[M+H]^+$).

Compound 50. Starting from the corresponding iodinated terthiophene **49** (577 mg, 1.22 mmol) and the boronate ester **24** (394 mg, 1.64 mmol) and following the general procedure C, the desired compound **50** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a deep orange solid (479 mg, 86%). R_f (petroleum ether/ethyl acetate 95:5): 0.20; Mp: 85-86 °C; IR (neat): 2946 (w), 1705 (s), 1544 (m), 1498 (m), 1444 (m), 1384 (m), 1346 (m), 1260 (s), 1194 (m), 1082 (m), 1052 (m), 985 (m), 805 (m), 746 (m), 626 (w), 553 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.54 (s, 1H), 7.05 (s, 1H), 6.82 (s, 1H), 6.77 (d, ^{3}J(H, H) = 3.9 Hz, 1H), 6.08 (d, ^{3}J(H, H) = 3.9 Hz, 1H), 3.87 (s, 6H), 2.38 (s, 3H), 2.22 (s, 6H), 2.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 165.7 (s), 162.4 (s), 138.4 (s), 137.6 (s), 137.4 (d), 137.3 (s), 137.0 (s), 134.7 (s), 134.1 (s), 130.8 (s), 129.4 (d), 129.3 (s), 126.2 (s), 125.2 (d), 123.3 (s), 121.4 (d), 104.4 (d), 60.1 (q), 52.0 (q), 15.7 (q), 15.0 (q), 14.9 (q); MS (ESI+, DCM): 461 (100, $[M+H]^+$).

Compound 55. Starting from the corresponding iodinated terthiophene **54** (642 mg, 1.31 mmol) and the boronate ester **24** (426 mg, 1.77 mmol) and following the general procedure C, the desired compound **55** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a yellow solid (575 mg, 92%). R_f (petroleum ether/ethyl acetate 95:5): 0.20; Mp: 118-119 °C; IR (neat): 2969 (w), 1708 (s), 1535 (w), 1490 (m), 1450

(m), 1251 (s), 1199 (m), 1078 (m), 1049 (m), 989 (m), 896 (w), 830 (w), 772 (m), 754 (m), 711 (w), 594 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.63 (s, 1H), 6.97 (s, 1H), 6.75 (d, ^{3}J(H, H) = 3.9 Hz, 1H), 6.16 (d, ^{3}J(H, H) = 3.9 Hz, 1H), 3.88 (s, 6H), 2.30 (s, 3H), 2.26 (s, 6H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.4 (s), 162.4 (s), 137.5 (s), 137.0 (2 X s), 136.8 (s), 136.3 (d), 135.2 (s), 134.5 (s), 131.6 (s), 130.3 (s), 128.6 (d), 128.2 (s), 127.8 (s), 123.8 (d), 122.3 (s), 104.1 (d), 60.1 (q), 52.1 (q), 15.1 (q), 14.5 (q), 14.2 (2 x q); MS (ESI+, DCM): 475 (100, $[M+H]^+$).

Compound 60. Starting from the corresponding iodinated terthiophene **59** (655 mg, 1.34 mmol) and the boronate ester **24** (435 mg, 1.81 mmol) and following the general procedure C, the desired compound **60** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a yellow solid (514 mg, 81%). R_f (petroleum ether/ethyl acetate 95:5): 0.20; Mp: 98-99 °C; IR (neat): 2921 (w), 2852 (w), 1699 (s), 1532 (m), 1492 (m), 1446 (m), 1422 (m), 1367 (w), 1246 (s), 1199 (m), 1074 (m), 1054 (m), 992 (w), 967 (w), 892 (w), 818 (w), 786 (w), 767 (m), 754 (m), 713 (w), 629 (w), 583 (w), 540.55 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.63 (s, 1H), 6.90 (s, 1H), 6.76 (d, ^{3}J(H, H) = 3.7 Hz, 1H), 6.15 (d, ^{3}J(H, H) = 3.7 Hz, 1H), 3.88 (s, 6H), 2.34 (s, 3H), 2.32 (s, 3H), 2.21 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.4 (s), 162.4 (s), 138.3 (s), 137.3 (s), 137.1 (s), 136.2 (d), 134.2 (s), 133.2 (s), 132.5 (s), 131.9 (s), 131.8 (2 x s), 129.9 (d), 126.2 (s), 123.3 (d), 122.3 (s), 104.2 (d), 60.1 (q), 52.0 (q), 15.3 (q), 14.9 (q), 14.4 (q), 14.3 (q); MS (ESI+, DCM): 475 (100, $[M+H]^+$).

Compound 65. Starting from the corresponding iodinated terthiophene **64** (569 mg, 1.16 mmol) and the boronate ester **24** (378 mg, 1.57 mmol) and following the general procedure C, the desired compound **65** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a light orange solid (405 mg, 74%). R_f (petroleum

ether/ethyl acetate 95:5): 0.20; Mp: 140-141 °C; IR (neat): 2922 (w), 2853 (w), 1719 (m), 1544 (m), 1492 (m), 1442 (m), 1425 (m), 1386 (w), 1346 (w), 1254 (s), 1048 (m), 1081 (m), 1048 (m), 998 (w), 980 (w), 868 (w), 816 (w), 773 (w), 744 (m), 717 (w), 652 (w), 629 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.57 (s, 1H), 7.08 (s, 1H), 6.76 (d, ^{3}J(H, H) = 3.7 Hz, 1H), 6.18 (d, ^{3}J(H, H) = 3.7 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 2.41 (s, 3H), 2.28 (s, 3H), 2.21 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.5 (s), 162.5 (s), 138.4 (s), 137.8 (s), 137.4 (d), 137.0 (s), 134.8 (s), 134.1 (s), 133.8 (s), 131.9 (s), 131.1 (s), 129.4 (d), 129.3 (s), 126.2 (s), 123.8 (d), 122.3 (s), 104.2 (d), 60.2 (q), 52.1 (q), 15.7 (q), 14.8 (q), 14.3 (q), 14.1 (q); MS (ESI+, DCM): 475 (100, $[M+H]^+$).

Compound 70. Starting from the corresponding iodinated terthiophene **69** (622 mg, 1.27 mmol) and the boronate ester **24** (413 mg, 1.72 mmol) and following the general procedure C, the desired compound **70** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a yellow solid (389 mg, 64%). R_f (petroleum ether/ethyl acetate 95:5): 0.20; Mp: 101-102 °C; IR (neat): 2932 (w), 1726 (s), 1543 (m), 1501 (m), 1447 (m), 1429 (m), 1394 (w), 1319 (w), 1245 (s), 1197 (m), 1076 (m), 1048 (m), 996 (w), 976 (w), 856 (w), 809 (w), 777 (w), 746 (m), 710 (w), 628 (w), 579 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.64 (s, 1H), 6.85 (s, 1H), 6.78 (d, ^{3}J(H, H) = 3.9 Hz, 1H), 6.10 (d, ^{3}J(H, H) = 3.9 Hz, 1H), 3.88 (s, 6H), 2.23 (s, 3H), 2.17 (s, 3H), 2.14 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 165.6 (s), 162.5 (s), 137.6 (s), 137.4 (2 X s),137.1 (s), 137.1 (d), 137.0 (s), 136.2 (s), 131.8 (s), 130.2 (s), 128.1 (s), 126.7 (d), 125.2 (s), 123.4 (d), 121.3 (s), 104.4 (d), 60.1 (q), 52.1 (q), 15.0 (2 x q), 14.3 (q), 14.2 (q); MS (ESI+, DCM): 475 (100, $[M+H]^+$).

Compound 75. Starting from the corresponding iodinated terthiophene **74** (272 mg, 0.57 mmol) and the boronate ester **45** (196 mg, 0.87 mmol) and following the general procedure C, the desired compound was precipitated from DCM and washed with petroleum ether to obtain

analytically pure **75** as an orange solid (189 mg, 74%). R_f (petroleum ether/ethyl acetate 9:1) 0.25; Mp: 163-164 °C; IR (neat): 3095 (w), 2920 (w), 1702 (s), 1538 (w), 1437 (m), 1238 (s), 1188 (m), 1078 (m), 1029 (w), 981 (m), 850 (w), 816 (m), 747 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 7.56 (s, 1H), 7.02 (s, 1H), 6.98 (s, 1H), 6.96 (s, 1H), 6.89 (s, 1H), 3.88 (s, 3H), 2.43 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.8 (s), 138.4 (s), 138.3 (s), 137.7 (d), 136.0 (s), 134.5 (s), 134.4 (s), 134.2 (s), 133.1 (s), 132.8 (s), 132.5 (s), 131.8 (s), 130.9 (d), 129.9 (d), 129.4 (s), 127.9 (d), 120.8 (d), 52.3 (q), 15.90 (q), 15.89 (q), 15.79 (q), 15.6 (q); MS (ESI+, $CHCl_3$/MeOH 1/1): 445 (100, $[M+H]^+$).

Compound 85. Starting from the corresponding iodinated terthiophene **84** (493 mg, 1.04 mmol) and the boronate ester **39** (350 mg, 1.56 mmol) and following the general procedure C, the desired compound **85** was obtained after purification with gravity chromatography (SiO_2, petroleum ether/ethyl acetate 98:2) as a yellow solid (398 mg, 83%). R_f (petroleum ether/ethyl acetate 9:1): 0.53; IR (neat): 2948 (w), 2919 (w), 1709 (s), 1537 (w), 1431 (m), 1281 (m), 1187 (s), 1077 (s), 973 (m), 910 (m), 869 (m), 825 (m), 730 (s), 606 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 7.64 (s, 1H), 7.30 (d, ^3J(H,H) = 5.2 Hz, 1H), 7.02 (s, 1H), 7.01 (s, 1H), 6.95 (d, ^3J(H,H) = 5.2 Hz, 1H), 3.90 (s, 3H), 2.26 (s, 3H), 2.24 (s 3H), 2.21 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 162.6 (s), 137.9 (s), 137.3 (2 X s), 137.2 (s), 136.9 (s), 136.8 (s), 136.3 (d), 135.9 (s), 131.7 (s), 130.2 (d), 128.1 (s), 127.1 (s), 126.8 (d), 126.6 (d), 125.3 (d), 52.2 (q), 15.1 (q), 15.0 (q), 14.9 (q), 14.8 (q); MS (ESI+, $CHCl_3$): 445 (100, $[M+H]^+$), 430 (65, $[M-CH_3+H]^+$).

Compound 76 (general procedure D). To a solution of **75** (128 mg, 0.29 mmol) in $CHCl_3$:AcOH (10 mL, 2:1) at 0 °C, NIS (62 mg, 0.28 mmol) was added in 3 portions over 10 minutes. The resulting mixture was slowly warmed to rt and then stirred overnight. The

solution was quenched with 10% aqueous $Na_2S_2O_3$ (30 mL) and extracted with DCM (3 x 25 mL). The combined organic fractions were dried over anhydrous Na_2SO_3, filtered and concentrated to obtain analytically pure **76** as a yellow solid (154 mg, 93%). R_f (petroleum ether/ethyl acetate 9:1): 0.25; Mp: >170 °C (decomposed); IR (neat): 2950 (w), 1702 (s), 1534 (w), 1436 (m), 1374 (w), 1252 (s), 1187 (m), 1082 (m), 1032 (w), 982 (w), 867 (w), 849 (w), 810 (m), 786 (w), 747 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 7.56 (s, 1H), 7.02 (s, 1H), 6.95 (s, 1H), 6.82 (s, 1H), 3.88 (s, 3H), 2.42 (m, 6H), 2.37 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.7 (s), 143.3 (s), 140.7 (s), 138.3 (s), 137.6 (d), 134.8 (s), 134.7 (s), 134.5 (s), 133.7 (s), 132.2 (s), 131.0 (s), 130.9 (d), 129.8 (d), 129.6 (s), 127.0 (d), 74.6 (s), 52.3 (q), 18.4 (q), 15.9 (q), 15.8 (q), 15.6 (q); MS (ESI+, $CHCl_3$/MeOH + HCOOH 0.1%): 571 (100, $[M+H]^+$), 444 (100, $[M-I+H]^+$).

Compound 86. Starting from the corresponding quaterthiophene **85** (231 mg, 0.50 mmol) and following the general procedure D, the desired compound **86** was obtained analytically pure as a light yellow solid (297 mg, quantitative yield). IR (neat): 2924 (w), 2852 (w), 1703 (s), 1542 (w), 1428 (m), 1291 (m), 1247 (s), 1187 (s), 1081 (m), 912 (w), 820 (m), 736 (m), 604 (w); ^{1}H NMR (500 MHz, $CDCl_3$): 7.56 (s, 1H), 7.01 (s, 1H), 6.92 (s, 1H), 6.92 (s, 1H), 2.17 (s, 3H), 2.13 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): 162.6 (s), 139.9 (d), 138.7 (s), 138.0 (s), 137.8 (s), 137.3 (s), 136.9 (s), 136.8 (s), 136.4 (s), 136.3 (d), 135.1 (s), 131.8 (s), 127.5 (s), 127.4 (s), 126.9 (d), 126.8 (d), 73.2 (s), 52.2 (q), 15.1 (2 X q), 14.9 (q), 14.4 (q); MS (ESI+, $CHCl_3$): 571 (100, $[M+H]^+$), 556 (40, $[M-CH_3+H]^+$).

2.5. Synthesis of quinquethiophenes

Compound 77 (general procedure E). To a solution of **76** (88 mg, 0.15 mmol) and **24** (60 mg, 0.25 mmol) in freshly distilled DMF (10 mL) under argon atmosphere, CsF (104 mg, 0.68 mmol) and $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) were added and the resulting mixture was stirred overnight at 90 °C. The mixture was cooled down to rt, petroleum ether (10 mL) was added to induce precipitation of an orange solid, which was recovered by filtration. Recrystallization from DCM gave **77** (45.5 mg, 52%) as a bright orange solid, which was stored under Ar atmosphere in presence of neat thioanisole. R_f (Petroleum ether/Ethyl acetate 8:2): 0.38; Mp: 188-189 °C; IR (neat): 2957 (w), 1699 (s), 1532 (w), 1483 (m), 1432 (s), 1247 (s), 1077 (m), 996 (w), 816 (m), 779 (m), 750 (m), 727 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 7.56 (s, 1H), 7.02 (s, 1H), 6.96 (s, 1H), 6.93 (s, 1H), 6.78 (d, ^3J(H,H) = 3.9 Hz, 1H), 6.19 (d, ^3J(H,H) = 3.9 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H), 2.42 (m, 9H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.6 (s), 162.7 (s), 138.4 (s), 137.7 (d), 134.5 (s), 134.4 (s), 134.3 (s), 133.6 (s), 133.1 (s), 133.0 (s), 132.9 (s), 132.5 (s), 131.7 (s), 131.5 (s), 131.0 (d), 130.0 (d), 129.5 (d), 129.5 (s), 123.5 (d), 122.5 (s), 104.5 (d), 60.4 (q), 52.3 (q), 15.9 (q), 15.81 (q), 15.77 (q), 15.4 (q); MS (ESI+, $CHCl_3$/MeOH 1/1 + HCOOH 0.1%): 557 (100, $[M+H]^+$).

Compound 87. Iodinated quaterthiophene **86** (100 mg, 0.18 mmol) and the boronate ester **24** (240 mg, 0.26 mmol) were coupled following the general procedure E with modified work-up procedure. After cooling to rt, H_2O (10 mL) was added and the mixture was extracted with dichloromethane (3 x 25 mL). The organic phase was washed with saturated brine solution (2 x 20 mL) and the organic phase was dried over Na_2SO_4, filtered and concentrated under vacuum. The desired compound **87** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 9:1) as an orange solid (74 mg, 75%). R_f (petroleum

ether/ethyl acetate 9:1): 0.31; IR (neat): 2959 (w), 1699 (s), 1532 (w), 1483 (m), 1432 (s), 1247 (s), 1074 (m), 996 (w), 816 (m), 779 (m), 750 (m), 727 (w); ^{1}H NMR (500 MHz, $CDCl_3$): 7.56 (s, 1H), 6.93 (s, 2H), 6.77 (s, 1H), 6.72 (d, ^{3}J(H,H) = 3.9 Hz, 1H), 6.05 (d, ^{3}J(H,H) = 3.9 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.17 (s, 3H), 2.13 (s, 6H), 2.11 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): 165.7 (s), 162.6 (s), 138.0 (s), 137.5 (s), 137.4 (s), 137.3 (s), 137.2 (2 X s), 136.9 (s), 136.3 (d), 135.8 (s), 131.7 (s), 128.8 (s), 127.1 (d), 126.9 (d), 126.7 (d), 125.3 (d), 123.5 (s), 121.3 (d), 104.5 (d), 60.3 (q), 52.2 (q), 15.1 (2 X q), 15.0 (q); MS (ESI+, $CHCl_3$/MeOH 1/1 + HCOOH 0.1%) 557 (100 $[M+H]^+$).

2.6. Preparation of aldehydes

Compound 26 (general procedure F). A solution of **25** (282 mg, 0.61 mmol) in dry DCM (30 mL) was cooled to -78 °C under nitrogen atmosphere and DIBAL (1.84 mL, 1.0 M in hexane) was added dropwise to the mixture. After 1 hour the solution was quenched with MeOH (10 mL), brine (10 mL) and slowly allowed to warm to rt. The reaction was then diluted with brine (30 ml) and extracted with DCM (3 x 25 mL). The collected organic fractions were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified with flash chromatography (SiO_2, DCM, R_f (DCM): 0.20) to obtain a yellow solid (250 mg, 0.58 mmol, 94%), which was then dissolved in DCM (30 mL). Dess-Martin periodinane (245 mg, 0.57 mmol) was added portion wise as a solid and the resulting suspension was stirred at rt for 20 min. The solution was then poured into 10% aqueous $Na_2S_2O_3$ (30 mL) and extracted with DCM (3 x 25 mL). The collected organic fractions were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified with flash chromatography (SiO_2, petroleum ether/DCM 3:7) to obtain **26** as a red solid (114 mg, 46%). R_f (petroleum ether/DCM 3:7): 0.32; Mp: 118-119 °C; IR (neat): 2920 (w), 1650 (s),

1537 (w), 1483 (w), 1420 (m), 1378 (w), 1273 (w), 1235 (m), 1159 (m), 996 (w), 866 (w), 799 (s), 669 (w), 631 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 9.76 (s, 1H), 7.49 (s, 1H), 7.23 (d, ^{3}J(H, H) = 3.8 Hz, 1H), 7.07 (d, ^{3}J(H, H) = 3.8 Hz, 1H), 6.74 (d, ^{3}J(H, H) = 3.9 Hz, 1H), 6.17 (d, ^{3}J(H, H) = 3.9 Hz, 1H), 3.90 (s, 3H), 2.44 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 182.3 (d), 166.6 (s), 141.6 (s), 140.4 (d), 139.5 (s), 138.7 (s), 135.7 (s), 134.7 (s), 134.6 (s), 134.5 (s), 130.8 (s), 127.9 (s), 127.6 (d), 126.0 (d), 124.0 (d), 122.1 (s), 104.2 (d), 60.2 (q), 15.9 (q), 14.6 (q), 14.2 (q); MS (ESI+, DCM): 431 (100, $[M+H]^+$).

Compound 36. Starting from the corresponding quaterthiophene **35** (392 mg, 0.85 mmol) and following the general procedure F, the desired compound **36** was obtained in two steps after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a yellow solid (130 mg, 37%). R_f (petroleum ether/DCM 3:7): 0.30; Mp: 121-122 °C; IR (neat): 2920 (w), 1666 (s), 1523 (m), 1429 (m), 1238 (m), 1153 (s), 996 (m), 860 (m), 789 (m), 674 (m), 566 (w), 505 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 9.83 (s, 1H), 7.58 (s, 1H), 7.00 (d, ^{3}J(H, H) = 3.4 Hz, 1H), 6.95 (d, ^{3}J(H, H) = 3.4 Hz, 1H), 6.82 (d, ^{3}J(H, H) = 3.7 Hz, 1H), 6.12 (d, ^{3}J(H, H) = 3.7 Hz, 1H), 3.90 (s, 3H), 2.33 (s, 3H), 2.26 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 182.7 (d), 165.8 (s), 141.9 (s), 140.5 (s), 139.0 (d), 138.6 (s), 138.3 (s), 137.7 (s), 134.5 (s), 133.4 (s), 132.3 (s), 126.6 (d), 126.2 (s), 123.2 (s), 122.5 (d), 121.5 (d), 104.5 (d), 60.3 (q), 15.0 (q), 14.5 (q), 14.4 (q); MS (ESI+, DCM): 431 (100, $[M+H]^+$).

Compound 43. Starting from the corresponding quaterthiophene **42** (488 mg, 1.06 mmol) and following the general procedure F, the desired compound **43** was obtained in two steps after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a red solid (140 mg, 32%). R_f (petroleum ether/DCM 3:7): 0.30; Mp: 122-123 °C; IR (neat): 2924 (w), 1655 (s), 1536 (m), 1491 (s), 1423 (s), 1374 (m), 1230 (m), 1203 (m), 1150 (m), 1058 (m), 997 (m), 850 (m), 813 (m), 764 (m), 672 (m), 576 (m); ^{1}H NMR (300 MHz,

$CDCl_3$): 9.82 (s, 1H), 7.57 (s, 1H), 6.95 (s, 1H), 6.78-6.77 (m, 2H), 6.10 (d, ^3J(H, H) = 4.0 Hz, 1H), 3.89 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 182.6 (d), 165.7 (s), 141.6 (s), 140.3 (s), 139.2 (d), 137.9 (s), 137.4 (s), 137.2 (s), 135.8 (s), 134.9 (s), 128.2 (d), 128.0 (s), 127.3 (s), 126.5 (d), 123.2 (s), 121.5 (d), 104.5 (d), 60.2 (q), 15.7 (q), 15.3 (q), 15.2 (q); MS (ESI+, DCM): 431 (100, $[M+H]^+$).

Compound 51. Starting from the corresponding quaterthiophene **50** (480 mg, 1.04 mmol) and following the general procedure F, the desired compound **51** was obtained in two steps after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a light yellow solid (200 mg, 52%). R_f (petroleum ether/DCM 3:7): 0.30; Mp: 113-114 °C; IR (neat): 2924 (w), 1650 (s), 1496 (m), 1450 (m), 1193 (w), 1154 (m), 1056 (w), 989 (m), 846 (w), 786 (s), 666 (m), 634 (w), 566 (w), 526 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 9.79 (s, 1H), 7.51 (s, 1H), 7.14 (s, 1H), 6.84 (s, 1H), 6.79 (d, ^3J(H, H) = 4.0 Hz, 1H), 6.11 (d, ^3J(H, H) = 4.0 Hz, 1H), 3.90 (s, 3H), 2.44 (s, 3H), 2.23 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 182.4 (d), 165.7 (s), 141.6 (s), 140.4 (d), 139.5 (s), 137.8 (s), 137.5 (s), 137.2 (s), 134.6 (s), 134.4 (s), 131.8 (s), 130.1 (d), 126.0 (s), 125.3 (d), 123.2 (s), 121.5 (d), 104.5 (d), 60.2 (q), 15.8 (q), 15.0 (q), 14.9 (q); MS (ESI+, DCM): 431 (100, $[M+H]^+$).

Compound 56. Starting from the corresponding quaterthiophene **55** (575 mg, 1.21 mmol) and following the general procedure F, the desired compound **56** was obtained in two steps after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a yellow solid (238 mg, 53%). R_f (petroleum ether/DCM 3:7): 0.31; Mp: 166-167 °C; IR (neat): 2924 (w), 1663 (s), 1540 (w), 1492 (m), 1428 (m), 1200 (m), 1158 (m), 1053 (w), 982 (w), 873 (w), 819 (w), 766 (s), 671 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 9.84 (s, 1H), 7.59 (s, 1H), 6.97 (s, 1H), 6.75 (d, ^3J(H, H) = 3.9 Hz, 1H), 6.18 (d, ^3J(H, H) = 3.9 Hz, 1H), 3.91 (s, 3H), 2.31 (s, 6H), 2.27 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 182.6 (d), 166.5 (s),

141.7 (s), 140.3 (s), 139.1 (d), 137.8 (s), 137.4 (s), 137.3 (s), 135.4 (s), 134.7 (s), 130.4 (s), 128.8 (d), 128.0 (s), 127.6 (s), 123.9 (d), 122.2 (s), 104.2 (d), 60.2 (q), 15.3 (q), 15.2 (q), 14.5 (q), 14.2 (q); MS (ESI+, DCM): 445 (100, $[M+H]^+$).

Compound 61. Starting from the corresponding quaterthiophene **60** (514 mg, 1.08 mmol) and following the general procedure F, the desired compound **61** was obtained in two steps after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a light yellow solid (175 mg, 37%). R_f (petroleum ether/DCM 3:7): 0.33; Mp: 122-123 °C; IR (neat): 2924 (w), 1657 (s), 1488 (m), 1428 (m), 1241 (s), 1156 (s), 997 (m), 774. (s), 675 (m), 615 (w), 582 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 9.80 (s, 1H), 7.56 (s, 1H), 6.90 (s, 1H), 6.76 (d, ^3J(H, H) = 3.9 Hz, 1H), 6.16 (d, ^3J(H, H) = 3.9 Hz, 1H), 3.89 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H), 2.25 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 182.6 (d), 166.4 (s), 141.9 (s), 140.6 (s), 139.1 (d), 138.7 (s), 137.6 (s), 134.4 (s), 133.4 (s), 132.4 (2 X s), 132.0 (s), 130.0 (d), 126.1 (s), 123.4 (d), 122.2 (s), 104.2 (d), 60.2 (q), 15.3 (q), 15.1 (q), 14.5 (q), 14.4 (q); MS (ESI+, DCM): 445 (100, $[M+H]^+$).

Compound 66. Starting from the corresponding quaterthiophene **65** (580 mg, 1.22 mmol) and following the general procedure F, the desired compound **66** was obtained in two steps after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a yellow solid (150 mg, 39%). R_f (petroleum ether/DCM 3:7): 0.32; Mp: 125-126 °C; IR (neat): 2924 (w), 1650 (s), 1537 (w), 1493 (w), 1451 (m), 1203 (m), 1154 (m), 1055 (w), 989 (m), 867 (w), 789 (s), 711 (w), 665 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 9.81 (s, 1H), 7.54 (s, 1H), 7.17 (s, 1H), 6.78 (d, ^3J(H, H) = 3.9 Hz, 1H), 6.20 (d, ^3J(H, H) = 3.9 Hz, 1H), 3.93 (s, 3H), 2.47 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 182.4 (d), 166.5 (s), 141.7 (s), 140.4 (d), 139.5 (s), 137.9 (s), 137.2 (s), 134.5 (2 X s), 133.9 (s), 132.2

(s), 132.0 (s), 130.1 (d), 126.0 (s), 123.8 (d), 122.2 (s), 104.2 (d), 60.2 (q), 15.8 (q), 14.9 (q), 14.4 (q), 14.1 (q); MS (ESI+, DCM): 445 (100, $[M+H]^+$).

Compound 71. Starting from the corresponding quaterthiophene **70** (360 mg, 0.76 mmol) and following the general procedure F, the desired compound **71** was obtained in two steps after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 95:5) as a light yellow solid (160 mg, 52%). R_f (petroleum ether/DCM 3:7): 0.30; Mp: 112-113 °C; IR (neat): 2920 (w), 1661 (s), 1539 (w), 1498 (s), 1426 (m), 1379 (w), 1236 (m), 1199 (m), 1152 (m), 990 (m), 907 (w), 768 (m), 729 (m), 670 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 9.83 (s, 1H), 7.59 (s, 1H), 6.84 (s, 1H), 6.78 (d, ^3J(H, H) = 3.9 Hz, 1H), 6.11 (d, ^3J(H, H) = 3.9 Hz, 1H), 3.89 (s, 3H), 2.27 (s, 3H), 2.16 (s, 3H), 2.14 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 182.7 (d), 165.6 (s), 141.9 (s), 140.7 (s), 139.1 (d), 137.7 (s), 137.6 (2 X s), 137.3 (s), 137.2 (s), 130.7 (s), 127.9 (s), 126.5 (s), 125.2 (d), 123.4 (s), 121.4 (d), 104.4 (d), 60.2 (q), 15.1 (q), 15.0 (q), 14.4 (q), 14.2 (q); MS (ESI+, DCM): 445 (100, $[M+H]^+$).

Compound 78 (general procedure G). A solution of **77** (46 mg, 0.082 mmol) in dry DCM (20 mL) was cooled to -78 °C under nitrogen atmosphere and DIBAL (0.5 mL, 1.0 M in hexane) was added dropwise to the mixture. After 1 hour the solution was quenched with MeOH (5 mL), brine (5 mL) and slowly allowed to warm to rt. The reaction was then diluted with brine (30 mL) and extracted with DCM (3 x 25 mL). The collected organic fractions were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified with flash chromatography to obtain a yellow solid which was then directly dissolved in DCM (30 mL). MnO_2 (41 mg, 0.47 mmol) was added portion wise as a solid and the resulting suspension was stirred at rt for 1 hour. The solution was then filtered on celite and concentrated in vacuum to obtain a red residue. Silicagel column chromatography (DCM) of the residue gave **78** (12 mg, 27% over two steps) as a red solid, which was stored under Ar

atmosphere in presence of neat thioanisole. R_f (DCM) 0.31; IR (neat): 2921 (w), 1980 (w, br), 1648 (s), 1530 (m), 1482 (m), 1450 (m), 1337 (w), 1246 (m), 1224 (m), 1153 (m), 1026 (w), 999 (w), 851 (m), 815 (m), 778 (w), 738 (w), 672 (m), 613 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 9.81 (s, 1H), 7.53 (s, 1H), 7.11 (s, 1H), 6.98 (s, 1H), 6.94 (s, 1H), 6.78 (d, ^3J(H,H) = 3.9 Hz, 1H), 6.19 (d, ^3J(H,H) = 3.9 Hz, 1H), 3.93 (s, 3H), 2.47 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 182.5 (s), 166.6 (s), 141.7 (s), 140.6 (d), 139.7 (s), 134.8 (s), 134.7 (s), 134.4 (s), 133.7 (s), 133.5 (s), 132.9 (s), 132.8 (s), 132.6 (s), 131.8 (s), 131.7 (d), 130.2 (d), 129.6 (s), 129.6 (d), 123.5 (d), 122.5 (s), 104.5 (d), 60.5 (q), 16.1 (q), 15.83 (q), 15.78 (q), 15.4 (q); MS (ESI+, $CHCl_3$): 527 (100, $[M+H]^+$).

Compound 81. Starting from the corresponding terthiophene **80** (220 mg, 0.61 mmol) and following the general procedure G, the desired compound **81** was obtained in two steps after purification with flash chromatography (SiO_2, DCM) as a dark orange solid (147 mg, 73%). R_f (DCM): 0.5; Mp: 82-83 °C; IR (neat): 2925 (w), 2802 (w), 1644 (s), 1539 (m), 1483 (m), 1442 (m), 1356 (m), 1244 (m), 1157 (m), 988 (m), 851 (m), 763 (m), 673 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 9.79 (s, 1H), 7.52 (s, 1H), 7.08 (s, 1H), 6.81 (d, ^3J (H,H) = 4.0 Hz, 1H), 6.19 (d, ^3J (H,H) = 4.0 Hz, 1H), 3.93 (s, 3H), 2.45 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 182.5 (d), 167.1 (s), 141.9 (s), 140.6 (d), 139.4 (s), 134.5 (s), 134.2 (s), 133.8 (s), 131.9 (s), 131.4 (d), 124.1 (d), 121.9 (s), 104.5 (d), 60.4 (q), 16.0 (q), 15.4 (q); MS (ESI+, $CHCl_3$/MeOH 1/1): 335 (100, $[M+H]^+$), 320 (24, $[M-CH_3+H]^+$); HRMS (ESI, +ve) calcd for $C_{16}H_{15}O_2S_3$: 335.0228 found: 335.0233.

Compound 88. Starting from the corresponding quinquethiophene **87** (40 mg, 0.07 mmol) and following the general procedure G, the desired compound **88** was obtained in two steps after purification with flash chromatography (SiO_2, petroleum ether/DCM 3:7) as an orange

solid (15 mg, 53%) which was stored under Ar atmosphere in presence of neat thioanisole. R_f (petroleum ether/DCM 3:7): 0.6; IR (neat): 2922 (w), 2853 (w), 1938 (w, br), 1648 (s), 1580 (m), 1482 (m), 1450 (m), 1380 (w), 1246 (m), 1199 (m), 1156 (m), 1024 (w), 998 (w), 819 (m), 641 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 9.88 (s, 1H), 7.62 (s, 1H), 7.04 (s, 2H), 6.87 (s, 1H), 6.82 (d, ^3J(H,H) = 3.9 Hz, 1H), 6.15 (d, ^3J(H,H) = 3.9 Hz, 1H), 3.93 (s, 3H), 2.34 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): 182.7 (d), 165.7 (s), 141.8 (s), 140.3 (s), 139.1 (d), 138.4 (s), 137.8 (s), 137.5 (2 X s), 137.4 (s), 137.3 (s), 135.6 (s), 129.1 (s), 127.1 (d), 126.9 (d), 126.6 (s), 125.3 (s), 123.5 (s), 121.4 (d), 104.5 (d), 60.3 (q), 15.3 (q), 15.2 (q), 15.0 (q); MS (ESI+, $CHCl_3$): 527 (100, $[M+H]^+$), 512 (25, $[M-CH_3+H]^+$).

2.7. Knoevenagel condensations

Compound 30 (general procedure H). To a solution of **26** (59 mg, 0.13 mmol) and **27** (59 mg, 0.13 mmol) in dry ACN (10 mL), piperidine (2 μl, 20 μmol) was added under nitrogen atmosphere and the resulting solution was stirred for 3 h at 70 °C. The mixture was then cooled to rt, diluted with H_2O (30 mL), and extracted with ethyl acetate (3 x 25 mL). The collected organic fractions were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified with flash chromatography (SiO_2, petroleum ether/ethyl acetate 6:4) to obtain **30** as an orange solid (67 mg, 83%). R_f (petroleum ether/ethyl acetate 6:4): 0.25; Mp: 158-159 °C; IR (neat): 3338 (w), 2932 (w), 2827 (w), 2210 (w), 1659 (m), 1567 (m), 1533 (s), 1503 (w), 1485 (w), 1416 (s), 1372 (m), 1266 (m), 1211 (m), 1170 (m), 1124 (m), 1104 (m), 1054 (s), 1025 (w), 990 (w), 966 (w), 920 (w), 867 (w), 785 (w), 765 (s), 741 (w), 715 (w), 629 (m), 594 (w), 568 (w), 544 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 8.26 (s, 1H), 7.48 (s, 1H), 7.29 (d, ^3J(H,H) = 3.9 Hz, 1H), 7.11 (d, ^3J(H,H) = 3.0 Hz, 1H), 6.77 (d, ^3J(H,H) = 3.0

Hz, 1H), 6.43 (t, ^{3}J(H,H) = 5.5 Hz, 1H), 6.19 (d, ^{3}J(H,H) = 3.9 Hz, 1H), 4.46 (t, ^{3}J(H,H) = 5.5 Hz, 1H), 3.92 (s, 3H), 3.56 (t, ^{3}J(H,H) = 5.5 Hz, 2H), 3.44 (s, 6H), 2.46 (s, 3H), 2.26 (s, 3H), 2.33 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.6 (s), 160.9 (s), 144.1 (d), 141.3 (s), 141.0 (d), 138.9 (s), 135.8 (s), 134.8 (s), 134.4 (s), 132.7 (s), 130.9 (s), 127.7 (s), 126.1 (d), 126.1 (s), 124.0 (s), 124.0 (d), 122.1 (d), 117.1 (s), 104.3 (d), 102.3 (d), 98.6 (s), 60.2 (q), 54.5 (2 x q), 41.9 (t), 15.7 (q), 14.6 (q), 14.2 (q); MS (ESI+, DCM): 585 (20, $[M+H]^+$), 553 (100, $[M-CH_3O]^+$); HRMS (ESI, +ve) calcd for $C_{28}H_{28}N_2O_4S_4$: 584.0926, found: 584.0938.

Compound 37. Starting from the corresponding quaterthiophene aldehyde **36** (59 mg, 0.13 mmol) and following the general procedure H, the desired compound **27** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 6:4) as an orange solid (55 mg, 69%). R_f (petroleum ether/ethyl acetate 6:4): 0.25; Mp: 133-134 °C; IR (neat): 3344 (w), 2924 (w), 2205 (w), 1655 (m), 1562 (s), 1528 (s), 1485 (w), 1423 (s), 1370 (s), 1269 (m), 1181 (m), 1125 (m), 1060 (m), 962 (w), 873 (w), 794 (w), 617 (w), 571 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 8.29 (s, 1H), 7.57 (s, 1H), 7.01 (d, ^{3}J(H,H) = 3.8 Hz, 1H), 6.96 (d, ^{3}J(H,H) = 3.8 Hz, 1H), 6.83 (d, ^{3}J(H,H) = 3.9 Hz, 1H), 6.44 (t, ^{3}J(H,H) = 5.5 Hz, 1H), 6.13 (d, ^{3}J(H,H) = 3.9 Hz, 1H), 4.45 (t, ^{3}J(H,H) = 5.5 Hz, 1H), 3.91 (s, 3H), 3.56 (t, ^{3}J(H,H) = 5.5 Hz, 2H), 3.43 (s, 6H), 2.33 (s, 3H), 2.26 (s, 3H), 2.14 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 165.8 (s), 160.8 (s), 144.4 (d), 140.0 (s), 139.4 (d), 138.8 (s), 138.3 (s), 137.9 (s), 135.0 (s), 134.6 (s), 133.5 (s), 132.5 (s), 126.6 (d), 126.0 (s), 123.3 (s), 122.5 (d), 121.5 (d), 117.0 (s), 104.5 (d), 102.3 (d), 99.4 (s), 60.3 (q), 54.5 (2 x q), 41.9 (t), 14.8 (q), 14.6 (q), 14.3 (q); MS (ESI+, DCM): 585 (20, $[M+H]^+$), 553 (100, $[M-CH_3O]^+$); HRMS (ESI, +ve) calcd for $C_{28}H_{28}N_2O_4S_4$: 584.0926, found: 584.0938.

Compound 44. Starting from the corresponding quaterthiophene aldehyde **43** (57 mg, 0.13 mmol) and following the general procedure H, the desired compound **44** was obtained after

purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 6:4) as a deep orange solid (67 mg, 86%). R_f (petroleum ether/ethyl acetate 6:4): 0.25; Mp: 159-160 °C; IR (neat): 3398 (w), 2935 (w), 2828 (w), 2196 (w), 1663 (m), 1565 (s), 1515 (s), 1492 (m), 1441 (w), 1409 (s), 1372 (s), 1320 (w), 1247 (m), 1178 (m), 1118 (m), 1047 (m), 924 (w), 865 (w), 811 (w), 763 (m), 600 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 8.28 (s, 1H), 7.55 (s, 1H), 6.96 (s, 1H), 6.80-6.75 (m, 2H), 6.46 (t, ^3J(H,H) = 5.5 Hz, 1H), 6.11 (d, ^3J(H,H) = 3.9 Hz, 1H), 4.46 (t, ^3J(H,H) = 5.5 Hz, 1H), 3.89 (s, 3H), 3.56 (t, ^3J(H,H) = 5.5 Hz, 2H), 3.43 (s, 6H), 2.36 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 165.7 (s), 160.8 (s), 144.3 (d), 139.7 (s), 139.6 (d), 138.0 (s), 137.6 (s), 137.4 (s), 135.8 (s), 135.0 (s), 134.7 (s), 128.2 (d), 128.0 (s), 126.1 (s), 126.5 (d), 123.2 (s), 121.5 (d), 117.0 (s), 104.5 (d), 102.3 (d), 99.2 (s), 60.2 (q), 54.5 (2 x q), 41.9 (t), 15.7 (q), 15.3 (q), 15.0 (q); MS (ESI+, DCM): 585 (30, $[M+H]^+$), 553 (100, $[M-CH_3O]^+$); HRMS (ESI, +ve) calcd for $C_{28}H_{28}N_2O_4S_4$: 584.0926, found: 584.0937.

Compound 52. Starting from the corresponding quaterthiophene aldehyde **51** (59 mg, 0.13 mmol) and following the general procedure H, the desired compound **27** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 6:4) as a deep orange solid (67 mg, 83%). R_f (petroleum ether/ethyl acetate 6:4): 0.25; Mp: 146-147 °C; IR (neat): 3413 (w), 2922 (w), 2192 (w), 1666 (s), 1569 (s), 1512 (m), 1458 (m), 1423 (s), 1370 (m), 1347 (w), 1319 (w), 1255 (m), 1193 (m), 1168 (m), 1109 (s), 1048 (s), 922 (m), 861 (w), 827 (w), 756 (s), 630 (w), 596 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 8.26 (s, 1H), 7.47 (s, 1H), 7.18 (s, 1H), 6.84 (s, 1H), 6.79 (d, ^3J(H,H) = 3.9 Hz, 1H), 6.44 (t, ^3J(H,H) = 5.5 Hz, 1H), 6.12 (d, ^3J(H,H) = 3.9 Hz, 1H), 4.46 (t, ^3J(H,H) = 5.5 Hz, 1H), 3.90 (s, 3H), 3.56 (t, ^3J(H,H) = 5.5 Hz, 2H), 3.43 (s, 6H), 2.44 (s, 3H), 2.24 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 165.7 (s), 161.0 (s), 144.2 (d), 141.4 (d), 141.1 (s), 137.8 (s), 137.5 (s), 137.3 (s), 134.7 (s), 134.2 (s), 132.6 (s), 132.1 (s), 130.3 (d), 126.0 (s), 125.3 (d), 123.2 (s), 121.5 (d), 117.1 (s),

104.5 (d), 102.3 (d), 98.7 (s), 60.2 (q), 54.5 (2 x q), 41.9 (t), 15.6 (q), 15.1 (q), 14.9 (q); MS (ESI+, DCM): 585 (30, $[M+H]^+$), 553 (100, $[M-CH_3O]^+$); HRMS (ESI, +ve) calcd for $C_{28}H_{28}N_2O_4S_4$: 584.0926, found: 584.0935.

Compound 57. Starting from the corresponding quaterthiophene aldehyde **56** (58 mg, 0.13 mmol) and following the general procedure H, the desired compound **57** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 6:4) as an orange solid (66 mg, 85%). R_f (petroleum ether/ethyl acetate 6:4): 0.25; Mp: 171-172 °C; IR (neat): 2927 (w), 2500 (w), 2196 (w), 1657 (m), 1564 (s), 1487 (w), 1437 (w), 1403 (s), 1369 (s), 1308 (w), 1266 (m), 1189 (m), 1126 (s), 1060 (m), 995 (w), 942 (w), 878 (w), 842 (w), 805 (w), 758 (w), 660 (w), 601 (w), 566 (w), 3398 (w), 2935 (w), 2828 (w), 2196 (w), 1663 (m), 1565 (s), 1515 (s), 1492 (m), 1441 (w), 1409 (s), 1372 (s), 1320 (w), 1247 (m), 1178 (m), 1118 (m), 1047 (m), 924 (w), 865 (w), 811 (w), 763 (m), 600 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 8.29 (s, 1H), 7.56 (s, 1H), 6.97 (s, 1H), 6.75 (d, ^3J(H,H) = 3.9 Hz, 1H), 6.46 (t, ^3J(H,H) = 5.5 Hz, 1H), 6.17 (d, ^3J(H,H) = 3.9 Hz, 1H), 4.46 (t, ^3J(H,H) = 5.5 Hz, 1H), 3.91 (s, 3H), 3.56 (t, ^3J(H,H) = 5.5 Hz, 2H), 3.43 (s, 6H), 2.31 (s, 3H), 2.29 (s, 3H), 2.26 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.5 (s), 160.8 (s), 144.3 (d), 139.7 (s), 139.6 (d), 138.0 (s), 137.6 (s), 137.4 (s), 135.4 (s), 134.7 (s), 134.6 (s), 130.4 (s), 128.8 (d), 128.0 (s), 127.4 (s), 123.9 (d), 122.2 (s), 117.0 (s), 104.2 (d), 102.3 (d), 99.2 (s), 60.2 (q), 54.5 (2 x q), 41.9 (t), 15.4 (q), 15.0 (q), 14.5 (q), 14.2 (q); MS (ESI+, DCM): 599 (20, $[M+H]^+$), 567 (100, $[M-CH_3O]^+$); HRMS (ESI, +ve) calcd for $C_{29}H_{30}N_2O_4S_4$: 598.1082, found: 598.1090.

Compound 62. Starting from the corresponding quaterthiophene aldehyde **61** (57 mg, 0.12 mmol) and following the general procedure H, the desired compound **27** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 6:4) as an orange solid (57 mg, 74%). R_f (petroleum ether/ethyl acetate 6:4): 0.25; Mp: 145-146 °C; IR (neat):

3321 (w), 2922 (w), 2210 (w), 1654 (s), 1563 (m), 1531 (s), 1419 (m), 1371 (m), 1265 (m), 1186 (m), 1130 (m), 1061 (m), 761 (m), 639 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 8.29 (s, 1H), 7.57 (s, 1H), 6.91 (s, 1H), 6.77 (d, ^{3}J(H,H) = 3.9 Hz, 1H), 6.44 (t, ^{3}J(H,H) = 5.5 Hz, 1H), 6.18 (d, ^{3}J(H,H) = 3.9 Hz, 1H), 4.46 (t, ^{3}J(H,H) = 5.5 Hz, 1H), 3.92 (s, 3H), 3.56 (t, ^{3}J(H,H) = 5.5 Hz, 2H), 3.43 (s, 6H), 2.43 (s, 3H), 2.27 (s, 3H), 2.26 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.4 (s), 160.8 (s), 144.3 (d), 140.0 (s), 139.4 (d), 138.7 (s), 137.9 (s), 134.9 (s), 134.4 (s), 133.4 (s), 132.5 (s), 132.4 (s), 132.0 (s), 130.1 (d), 125.8 (s), 123.4 (d), 122.2 (s), 117.0 (s), 104.3 (d), 102.3 (d), 99.3 (s), 60.2 (q), 54.5 (2 x q), 41.9 (t), 15.3 (q), 14.8 (q), 14.6 (q), 14.3 (q); MS (ESI+, DCM): 599 (20, $[M+H]^+$), 567 (100, $[M-CH_3O]^+$); HRMS (ESI, +ve) calcd for $C_{29}H_{30}N_2O_4S_4$: 598.1082, found: 598.1091.

Compound 67. Starting from the corresponding quaterthiophene aldehyde **66** (57 mg, 0.12 mmol) and following the general procedure H, the desired compound **67** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 6:4) as an orange solid (67 mg, 87%). R_f (petroleum ether/ethyl acetate 6:4): 0.25; Mp: 151-152 °C; IR (neat): 3394 (w), 2927 (w), 2207 (w), 1681 (m), 1591 (m), 1541 (s), 1493 (m), 1425 (m), 1376 (w), 1272 (m), 1210 (m), 1171 (m), 1120 (m), 1066 (m), 1050 (m), 983 (m), 945 (w), 854 (w), 828 (w), 811 (w), 758 (m), 718 (w), 611 (m), 566 (w), 532 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 8.26 (s, 1H), 7.47 (s, 1H), 7.19 (s, 1H), 6.75 (d, ^{3}J(H,H) = 3.9 Hz, 1H), 6.45 (t, ^{3}J(H,H) = 5.5 Hz, 1H), 6.18 (d, ^{3}J(H,H) = 3.9 Hz, 1H), 4.46 (t, ^{3}J(H,H) = 5.5 Hz, 1H), 3.91 (s, 3H), 3.56 (t, ^{3}J(H,H) = 5.5 Hz, 2H), 3.43 (s, 6H), 2.43 (s, 3H), 2.27 (s, 3H), 2.21 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.5 (s), 161.0 (s), 144.2 (d), 141.3 (s), 141.1 (d), 137.9 (s), 137.3 (s), 134.7 (s), 134.2 (s), 133.9 (s), 132.6 (s), 132.5 (s), 132.1 (s), 130.3 (d), 126.0 (s), 123.8 (d), 122.2 (s), 117.1 (s), 104.2 (d), 102.3 (d), 98.6 (s), 60.2 (q), 54.5 (2 x q), 41.9 (t), 15.6 (q), 14.8 (q), 14.4 (q), 14.1 (q); MS (ESI+, DCM): 599 (30, $[M+H]^+$), 567 (100, $[M-CH_3O]^+$); HRMS (ESI, +ve) calcd for $C_{29}H_{30}N_2O_4S_4$: 598.1082, found: 598.1095.

Compound 72. Starting from the corresponding quaterthiophene aldehyde **71** (64 mg, 0.14 mmol) and following the general procedure H, the desired compound **27** was obtained after purification with flash chromatography (SiO_2, petroleum ether/ethyl acetate 6:4) as an orange solid (55 mg, 64%). R_f (petroleum ether/ethyl acetate 6:4): 0.25; Mp: 158-159 °C; IR (neat): 2928 (w), 2206 (w), 1667 (m), 1582 (m), 1528 (m), 1501 (s), 1447 (m), 1426 (m), 1383 (w), 1255 (m), 1200 (m), 1128 (m), 1052 (m), 991 (m), 849 (w), 817 (w), 767 (m), 705 (w), 596 (w), 556 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 8.29 (s, 1H), 7.57 (s, 1H), 6.84 (s, 1H), 6.79 (d, ^3J(H,H) = 3.9 Hz, 1H), 6.44 (t, ^3J(H,H) = 5.5 Hz, 1H), 6.11 (d, ^3J(H,H) = 3.9 Hz, 1H), 4.45 (t, ^3J(H,H) = 5.5 Hz, 1H), 3.90 (s, 3H), 3.56 (t, ^3J(H,H) = 5.5 Hz, 2H), 3.43 (s, 6H), 2.26 (s, 3H), 2.16 (s, 3H), 2.15 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 165.6 (s), 160.8 (s), 144.4 (d), 140.1 (s), 139.4 (d), 137.9 (s), 137.8 (s), 137.6 (s), 137.3 (s), 137.2 (s), 134.9 (s), 130.9 (s), 127.6 (s), 126.5 (s), 125.2 (d), 123.4 (s), 121.3 (d), 117.0 (s), 104.4 (d), 102.3 (d), 99.3 (s), 60.2 (q), 54.5 (2 x q), 41.9 (t), 14.9 (q), 14.8 (q), 14.5 (q), 14.2 (q); MS (ESI+, DCM): 599 (20, $[M+H]^+$), 567 (100, $[M-CH_3O]^+$); HRMS (ESI, +ve) calcd for $C_{29}H_{30}N_2O_4S_4$: 598.1082, found: 598.1089.

Compound 79. Starting from the corresponding quinquethiophene aldehyde **78** (18 mg, 0.033 mmol) and following the general procedure H, using DMF as solvent. After the reaction, the desired compound **79** was obtained after distillation of DMF and purification with flash chromatography (SiO_2, DCM/ethyl acetate 9:1) as black solid (11 mg, 50%), which was stored under Ar in presence of neat thioanisole. R_f (DCM/EtOAc 9:1): 0.41; IR (neat): 3341 (w), 2921 (m), 2852 (w), 2207 (w), 1726 (w), 1663 (m), 1576 (s), 1522 (s), 1483 (w), 1429 (s), 1377 (m), 1358 (m), 1258 (s), 1201 (m), 1060 (s, br), 827 (w), 812 (s), 614 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 8.26 (s, 1H), 7.47 (s, 1H), 7.15 (s, 1H), 6.99 (s, 1H), 6.94 (m, 1H),

6.79 (d, ^{3}J(H,H) = 4.0 Hz, 1H), 6.42 (t, ^{3}J(H,H) = 5.5 Hz, 1H), 6.19 (d, ^{3}J(H,H) = 4.0 Hz, 1H), 4.46 (t, ^{3}J(H,H) = 5.5 Hz, 1H), 3.93 (s, 3H), 3.56 (t, ^{3}J(H,H) = 5.5 Hz, 2H), 3.44 (s, 6H), 2.46 (m, 9H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): 166.6 (s), 161.2 (s), 144.3 (d), 141.6 (d), 141.2 (s), 134.9 (s), 134.8 (s), 134.4 (s), 133.8 (s), 133.7 (s), 132.93 (s) , 132.86 (s), 132.8 (s), 132.3 (s) , 131.9 (2 X d), 131.8 (s), 130.2 (s), 129.6 (2 X d), 123.5 (d), 122.5 (s), 117.4 (s), 104.5 (d), 102.5 (d), 98.8 (s), 60.5 (q), 54.7 (q), 42.1 (t), 15.9 (q), 15.81 (q), 15.79 (q), 15.4 (q); MS (ESI+, $CHCl_3$/MeOH 1/1 + HCOOH 0.1%): 681 (20, $[M+H]^+$), 649 (100, $[M-MeO]^+$).

Compound 82. Starting from the corresponding terthiophene aldehyde **81** (108 mg, 0.32 mmol) and following the general procedure H, the desired compound **82** was obtained after purification with flash chromatography (SiO_2, DCM) as dark red solid (98 mg, 63%). R_f (DCM): 0.4; Mp: 149-150 °C; IR (neat): 3359 (w), 2930 (w), 2203 (w), 1659 (m), 1570 (s), 1524 (s), 1424 (s), 1372 (m), 1255 (m), 1120 (m), 1054 (m), 994 (m), 817 (m), 763 (m), 617 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 8.24 (s, 1H), 7.45 (s, 1H), 7.11 (s, 1H), 6.82 (d, ^{3}J (H,H) = 4.0 Hz, 1H), 6.43 (m, 1H), 6.19 (d, ^{3}J (H,H) = 4.0 Hz, 1H), 4.46 (m, 1H), 3.93 (s, 3H), 3.56 (m, 2H), 3.43 (s, 6H), 2.43 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.1 (s), 161.2 (s), 144.3 (d), 141.7 (d), 141.4 (s), 134.6 (s), 134.5 (s), 133.9 (s), 132.5 (s), 131.6 (d), 131.5 (s), 124.1 (d), 121.9 (s), 117.4 (s), 104.6 (d), 102.5 (d), 94.5 (s), 60.4 (q), 54.7 (2 X q), 42.0 (t), 15.8 (q), 15.4 (q); MS (ESI+, $CHCl_3$/MeOH 1:1): 489 (60, $[M+H]^+$), 457 (100, $[M-OCH_3]^+$); HRMS (ESI, +ve) calcd for $C_{23}H_{25}N_2O_4S_3$: 489.0970 found: 489.0974.

Compound 89. Starting from the corresponding quinquethiophene aldehyde **88** (17 mg, 0.031 mmol) and following the general procedure H in presence of thioanisole, the desired compound **89** was obtained after purification with flash chromatography (SiO_2, petroleum

ether/ethyl acetate 75:25) as dark brown solid (18 mg, 85%), which was stored under Ar in presence of neat thioanisole. R_f (petroleum ether/ethyl acetate 6:4): 0.3; IR (neat): 2920 (w), 2851 (w) 2195 (w), 1727 (m), 1573 (s), 1514 (s), 1424 (s), 1376 (m), 1248 (m), 1170 (m), 1045 (m), 848 (m), 817 (m), 788 (m), 648 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 8.32 (s, 1H), 7.59 (s, 1H), 7.04 (s, 2H), 6.87 (s, 1H), 6.82 (d, ^3J(H,H) = 3.9 Hz, 1H), 6.46 (t, ^3J(H,H) = 5.5 Hz, 1H), 6.15 (d, ^3J(H,H) = 3.9 Hz, 1H), 5.32 (s, 6H), 4.48 (t, ^3J(H,H) = 5.5 Hz, 1H), 3.93 (s, 3H), 3.59 (t, ^3J(H,H) = 5.5 Hz, 2H), 3.46 (s, 6H), 2.32 (s, 3H), 2.28 (s, 3H), 2.23 (m, 3H), 2.21 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): 165.7 (s), 160.9 (s), 144.3 (d), 139.6 (s), 139.5 (d), 138.5 (s), 137.9 (s), 137.8 (s), 137.5 (s), 137.4 (s), 137.3 (s), 135.6 (s), 134.8 (s), 129.1 (s), 127.1 (d), 126.9 (s), 126.7 (s), 126.6 (s), 125.3 (d), 123.5 (s), 121.4 (d), 117.0 (s), 104.5 (d), 102.4 (d), 99.4 (s), 60.3 (q), 54.6 (q), 41.9 (t), 29.7 (q), 15.4 (q), 15.1 (q), 15.0 (2 X q); MS (ESI+, $CHCl_3$): 681 (100, $[M+H]^+$), 649 (25, $[M-CH_3+H]^+$).

2.8. Synthesis of the amphiphiles

Compound 4. To a solution of **82** (10 mg, 0.02 mmol) in DCM (4 mL), $TsOH\cdot H_2O$ (1 mg, 5.26 μmol) was added and the resulting mixture was stirred at rt overnight. Then the solvent was evaporated *in vacuo*, to obtain a residue which was purified with flash chromatography (SiO_2, acetone/DCM 1:9), R_f (acetone/DCM 1:9): 0.4 to obtain a dark red solid (8 mg, 30 μmol, 84%). The obtained compound (1 mg, 2.3 μmol) was then dissolved in dry DMSO (100 μL) and AcOH (1 μL) under nitrogen atmosphere and containing 3 Å molecular sieves. Compound **31** (1.8 mg, 8.6 μmol) was added as a solid and the resulting solution was stirred at 60 °C for 15 min. Then, the reaction mixture was diluted with DCM (2 mL), and purified with flash chromatography (SiO_2, AcOH/MeOH/DCM 1:10:89) to afford pure **4** (1.3 mg,

quantitative yield) as an orange solid. R_f (AcOH/MeOH/DCM 1:10:89): 0.2; MS (ESI+, chloroform/MeOH 1:1 + 1% AcOH): 600 (100, $[M+H]^+$).

Compound 5. To a solution of **79** (11 mg, 17 μmol) in DCM (2 mL), $TsOH \cdot H_2O$ (5.3 mg, 28 μmol) was added and the mixture was stirred at rt for 30 min, until formation of a black solid. DCM (2 mL) and petroleum ether (2 mL) were added and the precipitate was recovered after centrifugation. To a suspension of the obtained compound (5 mg, 7 μmol) and **31** as mono hydrochloric salt (1.8 mg, 8.6 μmol) in DMSO (100 μL), AcOH (1 μL) was added and the mixture was stirred at 60 °C overnight. The residue was purified with preparative HPLC (YMC-Pack OSD-A semiprep C18, 5μm, ACN + TFA 0.1% / H_2O + TFA 0.1%; gradient: ACN from 10% to 90% in 20 min, ACN 90% for 20 min; flow 2 mL/min, R_t: 35.4 min). The fractions containing the product were collected and subjected to freeze drying to obtain a black solid. MS (ESI+): 792 (100, $[M]^+$).

Compound 6. Starting from the corresponding quinquethiophene acetal **89** (8 mg, 12 μmol) and following the procedure reported for compound **5**, the desired compound **6** was obtained after purification by preparative HPLC (YMC-Pack OSD-A semiprep C18, 5μm, ACN + TFA 0.1% / H_2O + TFA 0.1%; gradient: ACN from 10% to 90% in 20 min, ACN 90% for 20 min; flow 2 mL/min, R_t: 32.0 min). The fractions containing the product were collected and subjected to freeze drying to obtain a black solid. MS (ESI+): 792 (100 $[M]^+$).

Compound 7 (general procedure I). To a solution of **30** (30 mg, 51 μmol) in DCM (16 mL), $TsOH \cdot H_2O$ (8 mg, 39 μmol) was added and the resulting mixture was stirred for 10 min at rt. The solution was then diluted with H_2O (30 mL), and extracted with ethyl acetate (3 x 25

mL). The collected organic fractions were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified with flash chromatography (SiO_2, petroleum ether/ethyl acetate 4:6, R_f (petroleum ether/ethyl acetate 4:6): 0.30) to obtain a black solid (16 mg, 58%), which was then dissolved in dry DMSO (300 μL) under nitrogen atmosphere and containing 3 Å molecular sieves. Compound **31** (15 mg, 59 μmol) was added as a solid and the resulting solution was stirred at 60 °C for 15 min. Then, the reaction mixture was diluted with MeOH (0.5 mL), filtered through a 0.45 μm Millipore filter and purified by reversed phase HPLC to afford pure **7** (10 mg, 42%) as a black solid. HPLC: t_R = 32.0 min, column VP (250 mm x 21 mm) Nucleodure 100-7 C18 ec, elution gradient from 50% of A (MeOH + 0.1% TFA) and 50% of B (H_2O + 0.1% TFA) to 80% of A and 20% of B in 12 min and from 80% of A and 20% of B to 90% of A and 10% of B in 10 min, flow rate: 10 mL/min; LC-MS (ESI+): t_R = 5.30 min, *m/z*: 696 (100, $[M]^+$), column (50 mm x 2.1 mm) Pinnacle DB C18, elution gradient: from 5% of A (ACN + 0.1% TFA) and 95% of B (H_2O + 0.1% TFA) to 90% of A and 10% of B in 8 min, flow rate: 0.5 mL/min; ^{1}H NMR (400 MHz, DMSO-*d*$_6$, N/N: oxime stereoisomers): 8.79/8.71 (t, ^3J (H,H) = 5.5 Hz, 1H), 8.33/8.31 (s, 1H), 7.93-7.88 (m, 1H), 7.79/7.78 (s, 1H), 7.54/6.90 (t, ^3J (H,H) = 5.5 Hz, 1H), 7.49 (d, ^3J (H,H) = 3.8 Hz, 1H), 7.48-7.44 (m, 1H), 7.32 (d, ^3J (H,H) = 4.0 Hz, 1H), 6.90 (d, ^3J (H,H) = 4.0 Hz, 1H), 6.39 (d, ^3J (H,H) = 4.0 Hz, 1H), 4.49/4.42 (s, 2H), 4.18/3.97 (t, ^3J (H,H) = 5.5 Hz, 2H), 3.91 (s, 3H), 3.29-3.19 (m, 4H), 2.45/2.45 (s, 6H), 2.33 (s, 3H), 2.26 (s, 3H); MS (ESI+, DCM): 696 (100, $[M]^+$).

Compound 8. Starting from the corresponding quaterthiophene acetal **37** (30 mg, 51 μmol) and following the general procedure I, the desired compound **8** was obtained after purification by reversed phase HPLC as a black solid (12 mg, 54%). HPLC: t_R = 28.0 min, column VP (250 mm x 21 mm) Nucleodure 100-7 C18 ec, elution gradient from 50% of A (MeOH + 0.1% TFA) and 50% of B (H_2O + 0.1% TFA) to 85% of A and 15% of B in 12 min and from

85% of A and 15% of B to 90% of A and 10% of B in 10 min, flow rate: 10 mL/min; LC-MS (ESI): t_R = 5.29 min, *m/z* found: 696 (100, $[M]^+$), column (50 mm x 2.1 mm) Pinnacle DB C18, elution gradient: from 5% of A (ACN + 0.1% TFA) and 95% of B (H_2O + 0.1% TFA) to 90% of A and 10% of B in 8 min, flow rate: 0.5 mL/min; ^{1}H NMR (400 MHz, DMSO-*d*$_6$, N/N: oxime stereoisomers): 8.81/8.73 (t, ^3J (H,H) = 5.5 Hz, 1H), 8.36/8.34 (s, 1H), 7.93-7.89 (m, 1H), 7.83/7.81 (s, 1H), 7.54/6.90 (t, ^3J (H,H) = 5.5 Hz, 1H), 7.47-7.44 (m, 1H), 7.20 (d, ^3J (H,H) = 3.8 Hz, 1H), 7.16 (d, ^3J (H,H) = 4.0 Hz, 1H), 7.04 (d, ^3J (H,H) = 4.0 Hz, 1H), 6.33 (d, ^3J (H,H) = 4.0 Hz, 1H), 4.49/4.42 (s, 2H), 4.18/3.97 (t, ^3J (H,H) = 5.5 Hz, 2H), 3.90 (s, 3H), 3.29-3.20 (m, 4H), 2.33 (s, 6H), 2.23/2.22 (s, 3H), 2.14/2.13 (s, 3H); MS (ESI+, DCM): 696 (100, $[M]^+$).

Compound 9. Starting from the corresponding quaterthiophene acetal **44** (23 mg, 39 μmol) and following the general procedure I, the desired compound **9** was obtained after purification by reversed phase HPLC as a black solid (8.5 mg, 57%). HPLC: t_R = 28.0 min, column VP (250 mm x 21 mm) Nucleodure 100-7 C18 ec, elution gradient from 50% of A (MeOH + 0.1% TFA) and 50% of B (H_2O + 0.1% TFA) to 85% of A and 15% of B in 12 min and from 85% of A and 15% of B to 90% of A and 10% of B in 10 min, flow rate: 10 mL/min; LC-MS (ESI): t_R = 5.73 min, *m/z* found: 696 (100, $[M]^+$), column (50 mm x 2.1 mm) Pinnacle DB C18, elution gradient: from 5% of A (ACN + 0.1% TFA) and 95% of B (H_2O + 0.1% TFA) to 90% of A and 10% of B in 8 min, flow rate: 0.5 mL/min; ^{1}H NMR (400 MHz, DMSO-*d*$_6$, N/N: oxime stereoisomers): 8.80/8.72 (t, ^3J (H,H) = 5.5 Hz, 1H), 8.36/8.34 (s, 1H), 7.92-7.88 (m, 1H), 7.83/7.82 (s, 1H), 7.55/6.91 (t, ^3J (H,H) = 5.5 Hz, 1H), 7.43-7.39 (m, 1H), 7.22/7.22 (s, 1H), 7.04 (s, 1H), 6.99 (d, ^3J (H,H) = 4.0 Hz, 1H), 6.33 (d, ^3J (H,H) = 4.0 Hz, 1H), 4.50/4.42 (s, 2H), 4.18/3.98 (t, ^3J (H,H) = 5.5 Hz, 2H), 3.90 (s, 3H), 3.27-3.19 (m, 4H), 2.36 (s, 3H), 2.28/2.28 (s, 3H), 2.26/2.26 (s, 3H); MS (ESI+, DCM): 696 (100, $[M]^+$).

Compound 10. Starting from the corresponding quaterthiophene acetal **52** (20 mg, 34 µmol) and following the general procedure I, the desired compound **10** was obtained after purification by reversed phase HPLC as a black solid (6.0 mg, 50%). HPLC: t_R = 28.5 min, column VP (250 mm x 21 mm) Nucleodure 100-7 C18 ec, elution gradient from 50% of A (MeOH + 0.1% TFA) and 50% of B (H_2O + 0.1% TFA) to 85% of A and 15% of B in 12 min and from 85% of A and 15% of B to 90% of A and 10% of B in 10 min, flow rate: 10 mL/min; LC-MS (ESI): t_R = 5.21 min, *m/z* found: 696 (100, $[M]^+$), column (50 mm x 2.1 mm) Pinnacle DB C18, elution gradient: from 5% of A (ACN + 0.1% TFA) and 95% of B (H_2O + 0.1% TFA) to 90% of A and 10% of B in 8 min, flow rate: 0.5 mL/min; ^{1}H NMR (400 MHz, DMSO-*d*$_6$, N/N: oxime stereoisomers): 8.78/8.71 (t, ^3J (H,H) = 5.5 Hz, 1H), 8.33/8.31 (s, 1H), 7.93-7.88 (m, 1H), 7.78/7.77 (s, 1H), 7.54/6.90 (t, ^3J (H,H) = 5.5 Hz, 1H), 7.45-7.42 (m, 1H), 7.41/7.41 (s, 1H), 7.07 (s, 1H), 6.99 (d, ^3J (H,H) = 4.0 Hz, 1H), 6.32 (d, ^3J (H,H) = 4.0 Hz, 1H), 4.49/4.42 (s, 2H), 4.18/3.97 (t, ^3J (H,H) = 5.5 Hz, 2H), 3.90 (s, 3H), 3.29-3.20 (m, 4H), 2.44/2.43 (s, 3H), 2.24 (s, 3H) 2.19 (s, 3H); MS (ESI+, DCM): 696 (100, $[M]^+$).

Compound 11. Starting from the corresponding quaterthiophene acetal **57** (22 mg, 37 µmol) and following the general procedure I, the desired compound **11** was obtained in two steps after purification by reversed phase HPLC as a black solid (7.0 mg, 47%). HPLC: t_R = 29.0 min, column VP (250 mm x 21 mm) Nucleodure 100-7 C18 ec, elution gradient from 50% of A (MeOH + 0.1% TFA) and 50% of B (H_2O + 0.1% TFA) to 85% of A and 15% of B in 12 min and from 85% of A and 15% of B to 90% of A and 10% of B in 10 min, flow rate: 10 mL/min; LC-MS (ESI): t_R = 5.84 min, *m/z* found: 710 (100, $[M]^+$), column (50 mm x 2.1 mm) Pinnacle DB C18, elution gradient: from 5% of A (ACN + 0.1% TFA) and 95% of B (H_2O + 0.1% TFA) to 90% of A and 10% of B in 8 min, flow rate: 0.5 mL/min; ^{1}H NMR (400 MHz, DMSO-*d*$_6$, N/N: oxime stereoisomers): 8.81/8.73 (t, ^3J (H,H) = 5.5 Hz, 1H), 8.36/8.34 (s, 1H), 7.94-7.89 (m, 1H), 7.83/7.81 (s, 1H), 7.54/6.90 (t, ^3J (H,H) = 5.5 Hz, 1H), 7.47-7.44 (m, 1H),

7.22 (s, 1H), 6.90 (d, ^3J (H,H) = 4.0 Hz, 1H), 6.38 (d, ^3J (H,H) = 4.0 Hz, 1H), 4.49/4.42 (s, 2H), 4.18/3.97 (t, ^3J (H,H) = 5.5 Hz, 2H), 3.91 (s, 3H), 3.29-3.20 (m, 4H), 2.30 (s, 3H), 2.28/2.27 (s, 3H), 2.26/2.26 (s, 3H), 2.25 (s, 3H); MS (ESI+, DCM): 710 (100, $[M]^+$).

Compound 12. Starting from the corresponding quaterthiophene acetal **62** (15 mg, 25 μmol) and following the general procedure I, the desired compound **31** was obtained after purification by reversed phase HPLC as a black solid (5.0 mg, 50%). HPLC: t_R = 30.0 min, column VP (250 mm x 21 mm) Nucleodure 100-7 C18 ec, elution gradient from 50% of A (MeOH + 0.1% TFA) and 50% of B (H_2O + 0.1% TFA) to 85% of A and 15% of B in 12 min and from 85% of A and 15% of B to 90% of A and 10% of B in 10 min, flow rate: 10 mL/min; LC-MS (ESI): t_R = 5.38 min, *m/z* found: 710 (100, $[M]^+$), column (50 mm x 2.1 mm) Pinnacle DB C18, elution gradient: from 5% of A (ACN + 0.1% TFA) and 95% of B (H_2O + 0.1% TFA) to 90% of A and 10% of B in 8 min, flow rate: 0.5 mL/min; ^{1}H NMR (400 MHz, DMSO-*d*$_6$, N/N: oxime stereoisomers): 8.80/8.72 (t, ^3J (H,H) = 5.5 Hz, 1H), 8.34/8.34 (s, 1H), 7.93-7.88 (m, 1H), 7.83/7.81 (s, 1H), 7.55/6.90 (t, ^3J (H,H) = 5.5 Hz, 1H), 7.43-7.39 (m, 1H), 7.15 (s, 1H), 6.93 (d, ^3J (H,H) = 4.0 Hz, 1H), 6.38 (d, ^3J (H,H) = 4.0 Hz, 1H), 4.49/4.42 (s, 2H), 4.18/3.97 (t, ^3J (H,H) = 5.5 Hz, 2H), 3.91 (s, 3H), 3.29-3.20 (m, 4H), 2.33 (s, 6H), 2.23/2.23 (s, 3H), 2.13/2.13 (s, 3H); MS (ESI+, DCM): 710 (100, $[M]^+$).

Compound 13. Starting from the corresponding quaterthiophene acetal **67** (16 mg, 27 μmol) and following the general procedure I, the desired compound **13** was obtained after purification by reversed phase HPLC as a black solid (7.0 mg, 59%). HPLC: t_R = 29.0 min, column VP (250 mm x 21 mm) Nucleodure 100-7 C18 ec, elution gradient from 50% of A (MeOH + 0.1% TFA) and 50% of B (H_2O + 0.1% TFA) to 85% of A and 15% of B in 12 min and from 85% of A and 15% of B to 90% of A and 10% of B in 10 min, flow rate: 10 mL/min; LC-MS (ESI): t_R = 5.27 min, *m/z* found: 710 (100, $[M]^+$), column (50 mm x 2.1 mm)

Pinnacle DB C18, elution gradient: from 5% of A (ACN + 0.1% TFA) and 95% of B (H_2O + 0.1% TFA) to 90% of A and 10% of B in 8 min, flow rate: 0.5 mL/min; ^{1}H NMR (400 MHz, DMSO-*d*$_6$, N/N: oxime stereoisomers): 8.78/8.71 (t, ^3J (H,H) = 5.5 Hz, 1H), 8.33/8.31 (s, 1H), 7.93-7.88 (m, 1H), 7.78/7.77 (s, 1H), 7.54/6.90 (t, ^3J (H,H) = 5.5 Hz, 1H), 7.46-7.44 (m, 1H), 7.41/7.40 (s, 1H), 6.90 (d, ^3J (H,H) = 4.0 Hz, 1H), 6.38 (d, ^3J (H,H) = 4.0 Hz, 1H), 4.49/4.42 (s, 2H), 4.18/3.97 (t, ^3J (H,H) = 5.5 Hz, 2H), 3.91 (s, 3H), 3.29-3.20 (m, 4H), 2.43/2.43 (s, 3H), 2.26 (s, 3H), 2.20 (s, 3H), 2.10 (s, 3H); MS (ESI+, DCM): 710 (100, $[M]^+$).

Compound 14. Starting from the corresponding quaterthiophene acetal **72** (16 mg, 27 μmol) and following the general procedure I, the desired compound **14** was obtained after purification by reversed phase HPLC as a black solid (5.0 mg, 48%). HPLC: t_R = 26.0 min, column VP (250 mm x 21 mm) Nucleodure 100-7 C18 ec, elution gradient from 50% of A (MeOH + 0.1% TFA) and 50% of B (H_2O + 0.1% TFA) to 80% of A and 20% of B in 12 min and from 80% of A and 20% of B to 90% of A and 10% of B in 10 min, flow rate: 10 mL/min; LC-MS (ESI): t_R = 5.29 min, *m/z* found: 710 (100, $[M]^+$), column (50 mm x 2.1 mm) Pinnacle DB C18, elution gradient: from 5% of A (ACN + 0.1% TFA) and 95% of B (H_2O + 0.1% TFA) to 90% of A and 10% of B in 8 min, flow rate: 0.5 mL/min; ^{1}H NMR (400 MHz, DMSO-*d*$_6$, N/N: oxime stereoisomers): 8.81/8.73 (t, ^3J (H,H) = 5.5 Hz, 1H), 8.36/8.35 (s, 1H), 7.93-7.89 (m, 1H), 7.83/7.82 (s, 1H), 7.55/6.90 (t, ^3J (H,H) = 5.5 Hz, 1H), 7.46-7.43 (m, 1H), 7.06 (s, 1H), 6.97 (d, ^3J (H,H) = 4.0 Hz, 1H), 6.32 (d, ^3J (H,H) = 4.0 Hz, 1H), 4.49/4.42 (s, 2H), 4.18/3.97 (t, ^3J (H,H) = 5.5 Hz, 2H), 3.90 (s, 3H), 3.29-3.19 (m, 4H), 2.23/2.23 (s, 6H), 2.15/2.14 (s, 6H), 2.13/2.13 (s, 3H); MS (ESI+, DCM): 710 (100, $[M]^+$).

3. Studies in lipid bilayer membranes

3.1. Vesicle preparation

The large unilamellar vesicles (LUVs) used in these studies were prepared according to the procedure reported in ref. S6.

3.2. Fluorescence measurements

Amphiphile 4. To a 1900 μL gently stirred, thermostated buffer (25 ± 0.1 °C, 10 mM Tris, 100 mM NaCl, pH 7.4) in a glass cuvette, DOPC LUVs (100 μL, ~1.6 mM lipid in a cuvette) and **4** (20 μL of 0.8 mM in DMSO) were added. The solution was stirred at 25 ± 0.1 °C for 30 minutes before the spectra acquisition (λ_{ex} = 430 nm, λ_{em} = 570 nm). The temperature was then raised to 55 ± 0.1 °C and the solution was kept at this temperature for 45 minutes before the spectra acquisition. Then the temperature was lowered down to 25 ± 0.1 °C and the spectra were acquired after 45 minutes. The temperature cycle was repeated a second time. The same procedure was applied for DPPC LUVs (100 μL).

Amphiphiles 5 and 6. To a 1900 μL gently stirred, thermostated buffer (55 ± 0.1 °C, 10 mM Tris, 100 mM NaCl, pH 7.4) in a glass cuvette, DOPC LUVs (20 μL, ~0.3 mM lipid in a cuvette) and **5** or **6** (40 μL, 0.8 mM in DMSO) were added. The solution was stirred at 55 ± 0.1 °C for 30 minutes before the spectra acquisition. The temperature was then lowered to 25 ± 0.1 °C and the solution was kept at this temperature for 45 minutes before the spectra acquisition. Then the temperature was raised again to 55 ± 0.1 °C and the spectra were acquired after 45 minutes. The temperature cycle was repeated a second time. The same procedure was applied for DPPC LUVs (20 μL). Higher temperature (55 °C) was used at the

beginning, in order to facilitate the partitioning process. The excitation spectra of amphiphile **5** at different concentration with respect to DOPC and DPPC LUVs (2.5%, 5%, 7.5% mol/mol) did not change significantly, confirming the absence of aggregation effects on the measurement.

Amphiphiles 7-14. To a dispersion of LUVs (DOPC or DPPC, 75 μM lipid) in a buffer (2 mL, 10 mM Tris, 100 mM NaCl, pH 7.4), compounds **7-14** (2.5 μL of 0.8 mM in DMSO) were added. The mixture was stirred at 50 °C for 1 h to allow maximal partitioning of the compounds in the lipid bilayer. The mixture was then cooled down to 25 °C and the solution was kept at the same temperature for 1.5 h before the spectra acquisition. The process of partitioning and the conformational change was monitored by the fluorescence intensity, and occasionally shape change. Spectral corrections were not applied.

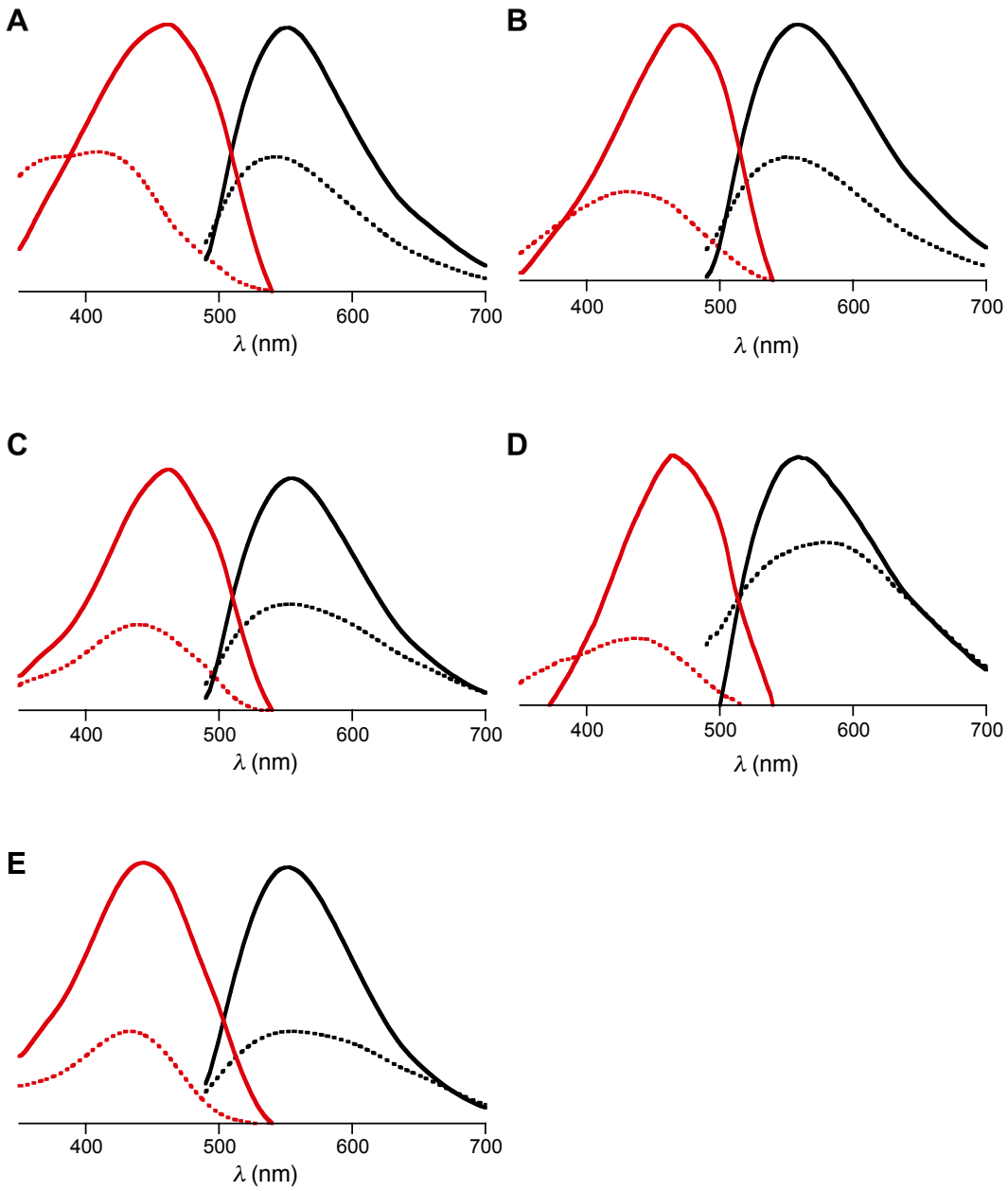


Figure S1. Excitation (red, λ_{em} = 560 nm) and emission spectra (black, λ_{ex} = 430 nm) of probes (A) **8**, (B) **9**, (C) **10**, (D) **11** and (E) **13** in DPPC (solid) and DOPC (dotted) LUVs at 25 °C.

4. Studies in organic solvents

4.1. Solvatochromism

As in ref S6. In a typical experiment, aliquots (20 μl) of a solution of compound **80** (0.8 mM, DCM) were diluted with air saturated solvents (2 mL, Table S1). The solutions were stirred at 25 ± 0.1 °C for 5 minutes before the spectra (absorption and emission) were acquired.

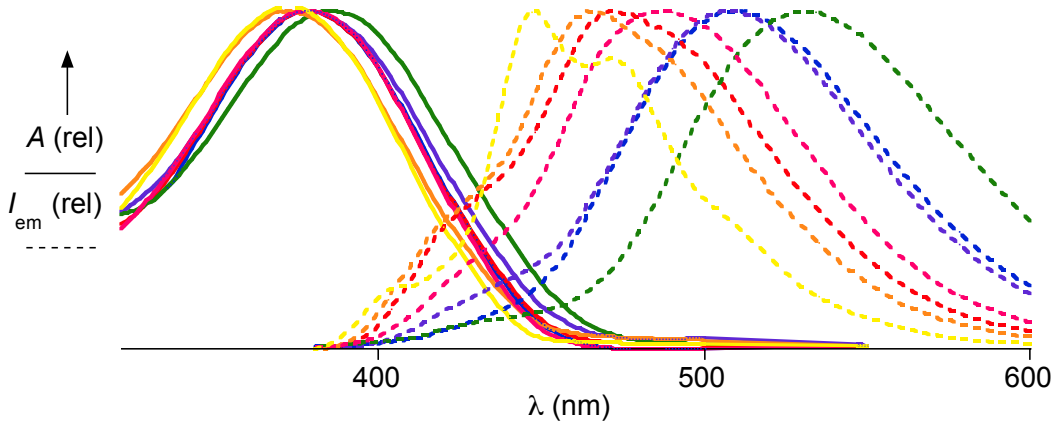


Figure S2. Normalized absorption (solid) and emission spectra (dotted) of **80** in, with increasingly red-shifted emission, hexane (yellow), diethyl ether (orange), dioxane (red), ethyl acetate (magenta), acetone (purple), DCM (blue) and DMSO (dark green).

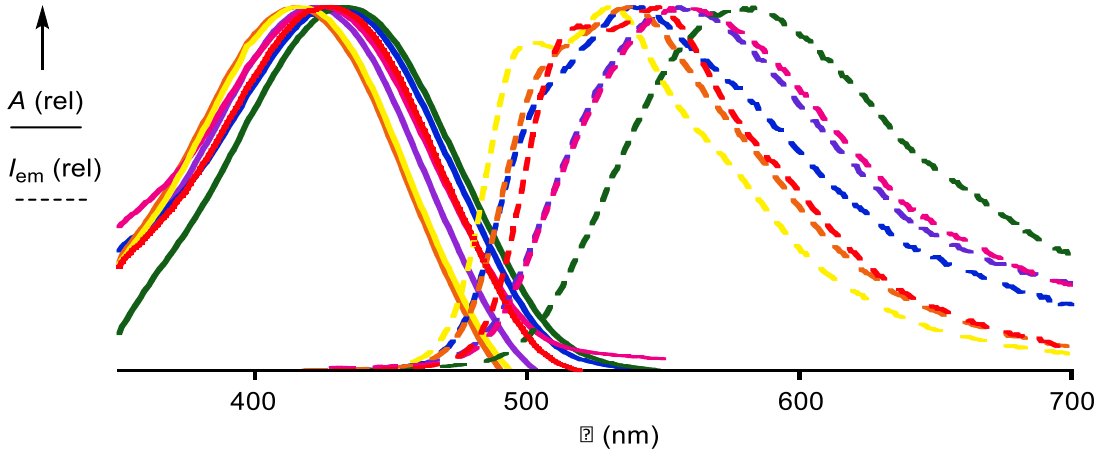


Figure S3. Normalized absorption (solid) and emission (dotted) spectra of **77** in, with increasingly red-shifted emission, hexane (yellow), diethyl ether (orange), toluene (red), THF (magenta), acetone (purple), DMF (blue), DMSO (dark green).

4.2. Transition dipole moments

Lippert parameters (f_L) were calculated for each solvent with the Equation S1 (Table S1). The experimental Stokes shifts were plotted as a function of f_L and then fit with a linear Equation S2 in which the slope parameter (m_L) is defined by the Equation S3 and q_L is the intercept with the y axis.

$$f_L = \frac{\varepsilon_r - 1}{2\varepsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad \text{(S1)}$$

$$\nu_a - \nu_f = m_L \cdot f_L + q_L \quad \text{(S2)}$$

$$m_L = \frac{2\Delta\mu^2}{hca^3} \quad \text{(S3)}$$

In Equation S2: ν_a is the maximum absorption wavenumber (cm^{-1}), ν_f is the maximum emission wavenumber (cm^{-1}), h (erg) is the Planck constant, c ($cm \cdot s^{-1}$) is the light speed, a (cm) is the push-pull group distance parameter, calculated by the optimized structures of the molecules (ChemBioDraw). The transition dipole moment ($\Delta\mu_L$) was calculated with the Equation S3, using the parameters derived from the linear fitting of Equation S2.

Table S1. Solvents physical parameters and calculated polarity functions

Solvent	n	ε_r	f_L
Acetone	1.357	20.490	0.285
DCM	1.421	8.819	0.217
1,4-Dioxane	1.420	2.210	0.021
DMSO	1.476	46.826	0.264
Diethyl ether	1.352	4.240	0.164
Ethyl acetate	1.370	5.987	0.200
Toluene	1.494	2.374	0.014
THF	1.404	7.426	0.209
DMF	1.427	37.219	0.276
Hexane	1.372	1.882	0.000

Table S2. Linear fit parameters for Lippert plot analysis and transition dipole moments.

Cpd	$y = m_L f_L + q_L$			
	a (Å)	m_L	q_L	$\Delta\mu$ **(D)**
80	12.6	8833	4446	10.6
77	22.0	2137	5188	12.0

5. Supplementary references

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6. NMR spectra

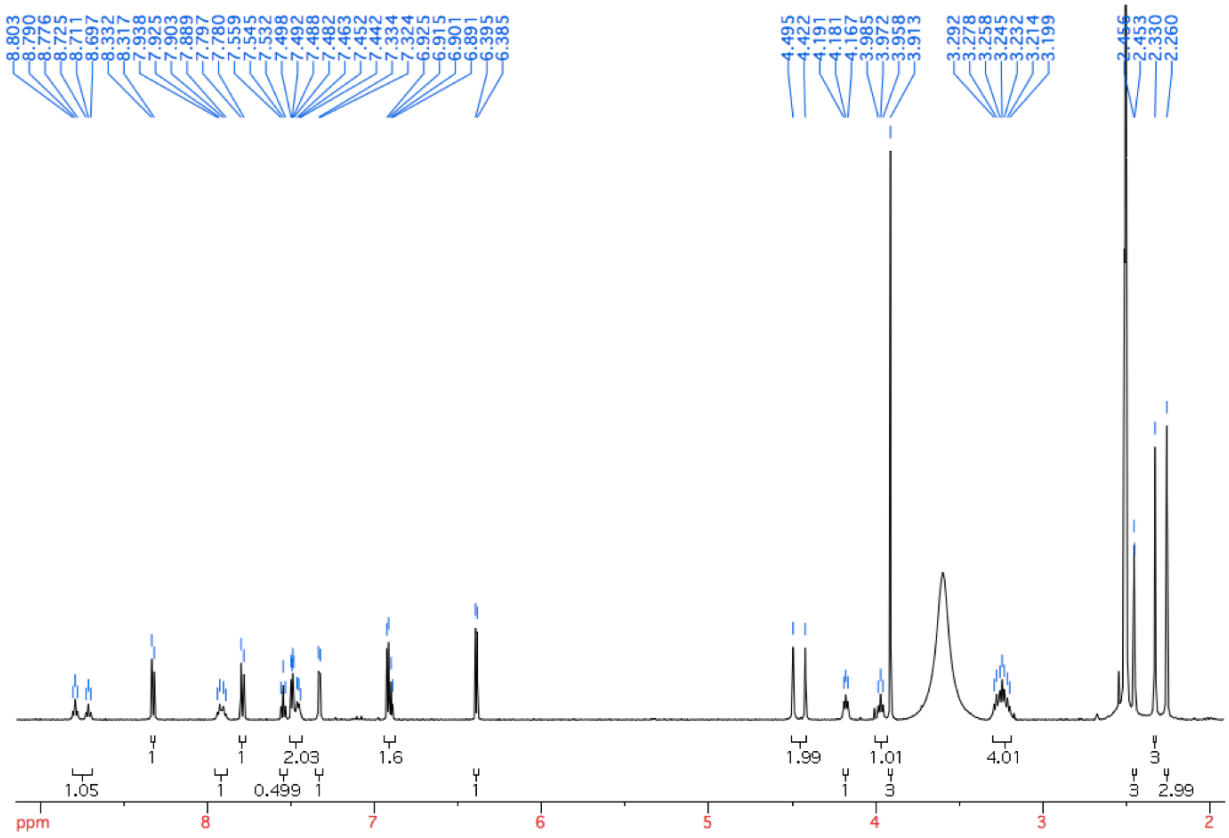

Figure S4. [1]H NMR spectrum of **7** in DMSO-*d6*.

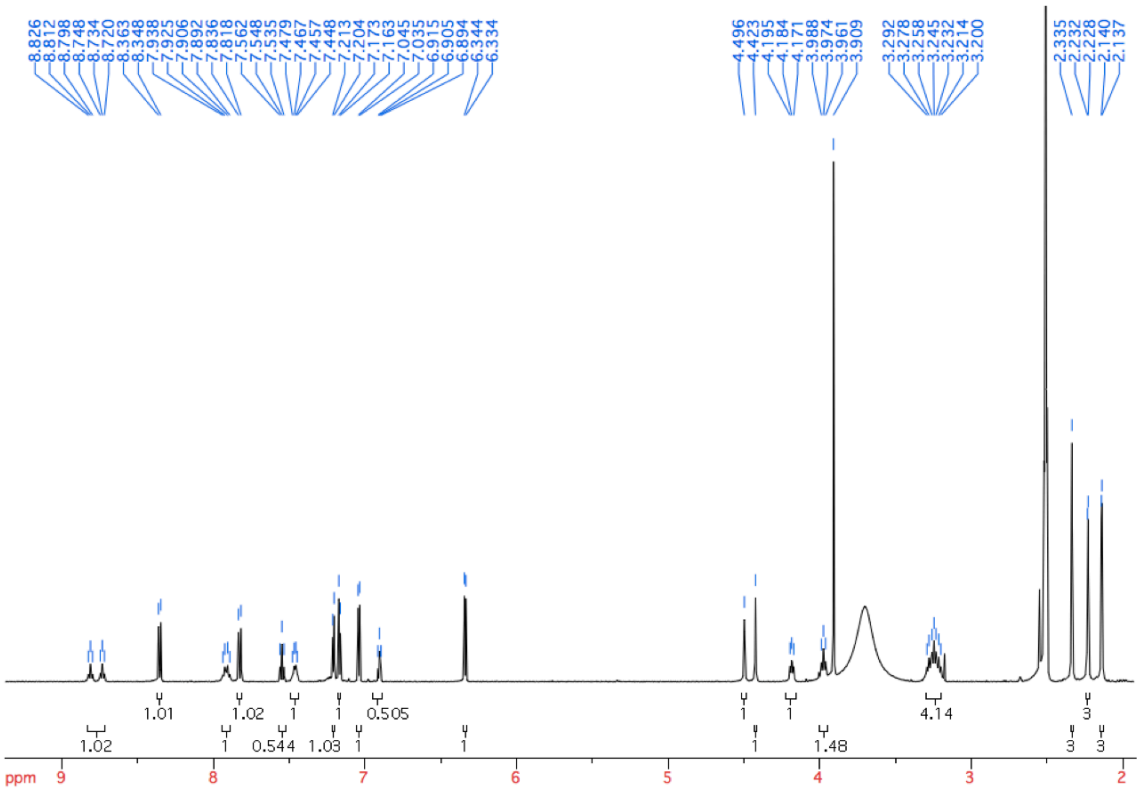

Figure S5. [1]H NMR spectrum of **8** in DMSO-*d6*.

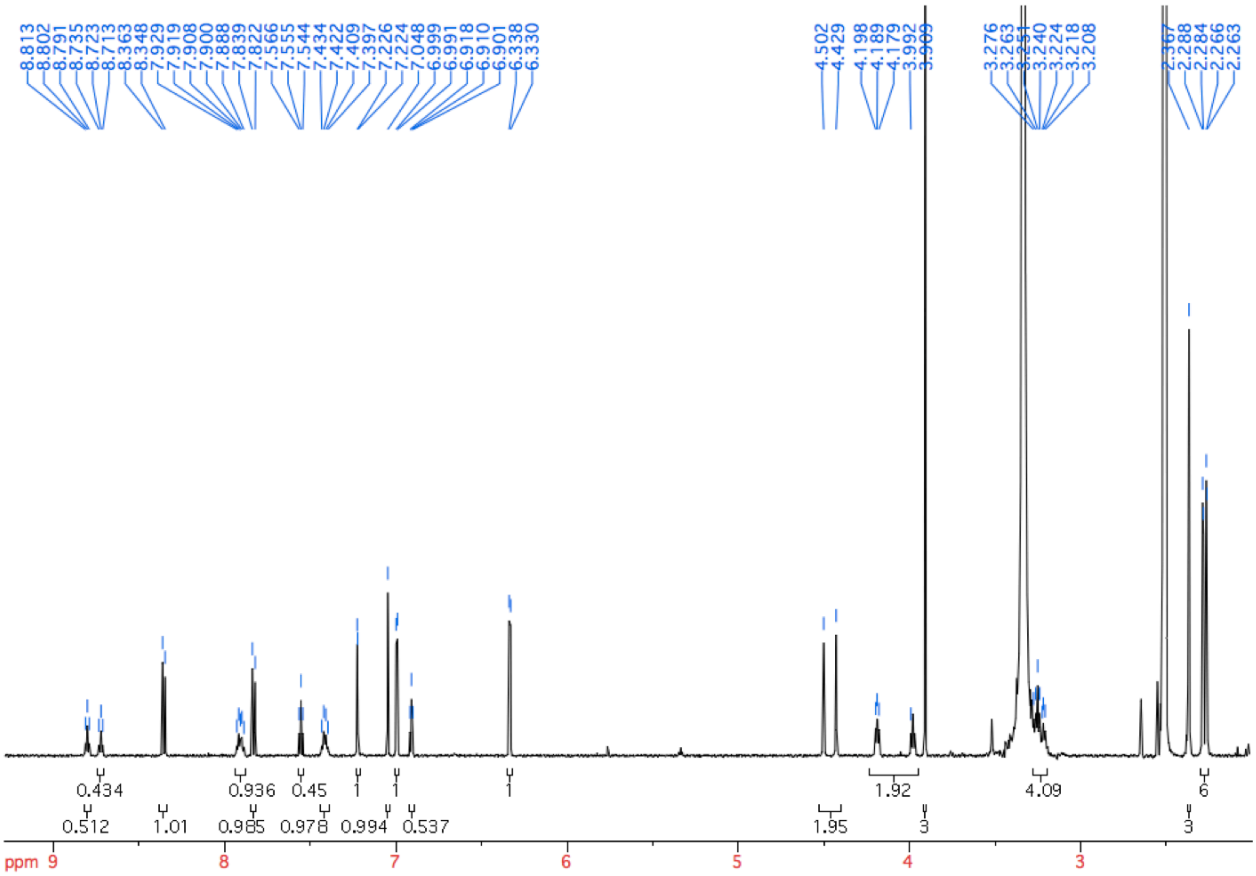

Figure S6. [1]H NMR spectrum of **9** in DMSO-*d6*.

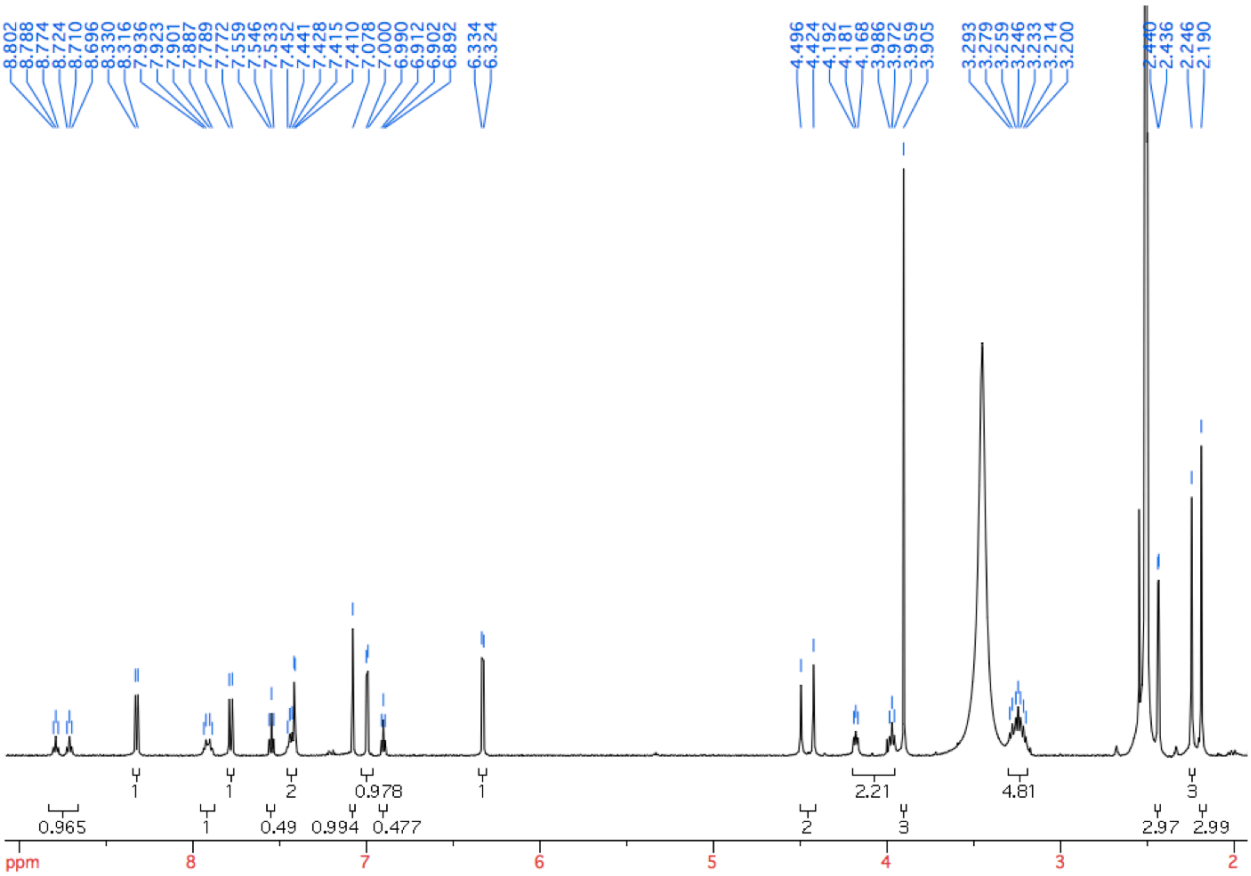

Figure S7. [1]H NMR spectrum of **10** in DMSO-*d6*.

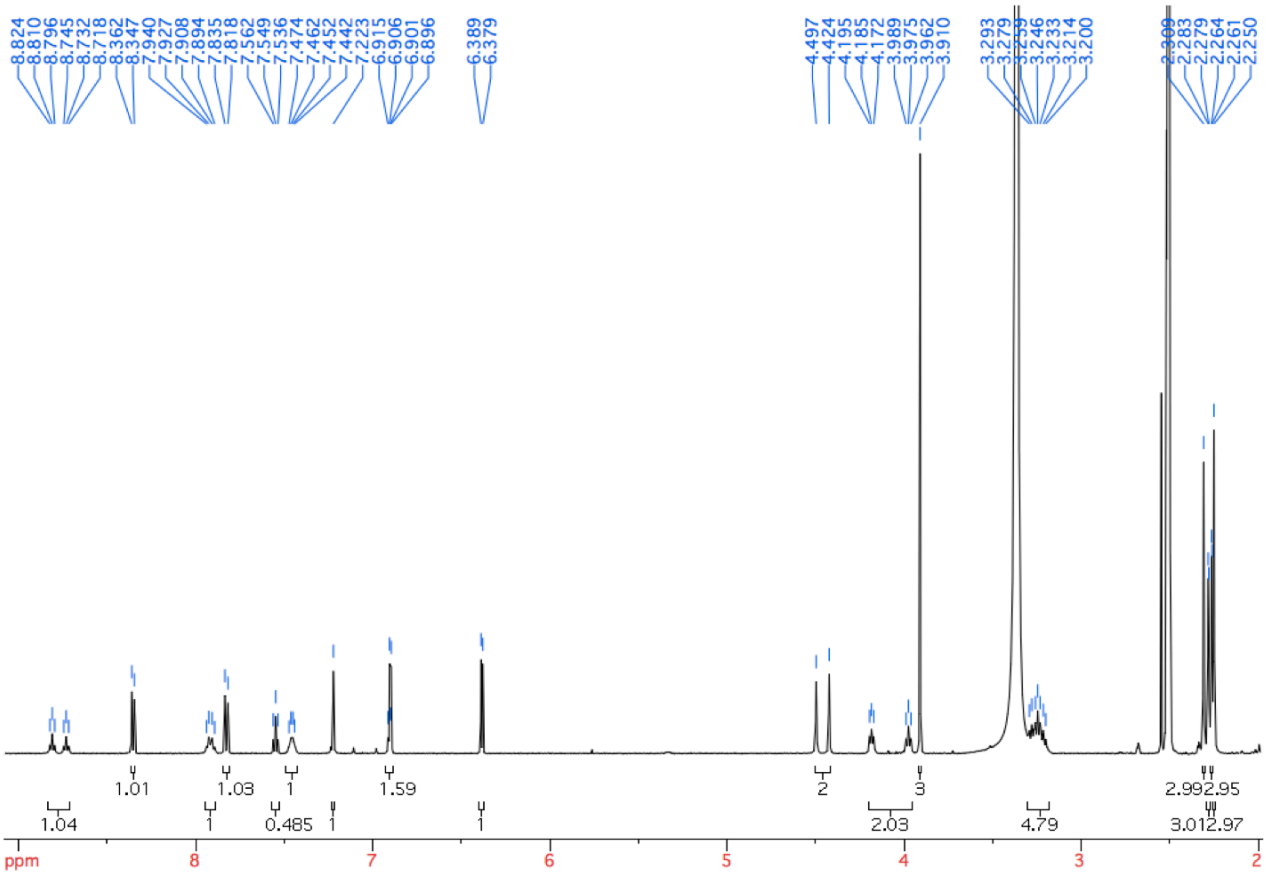

Figure S8. [1]H NMR spectrum of **11** in DMSO-*d6*.

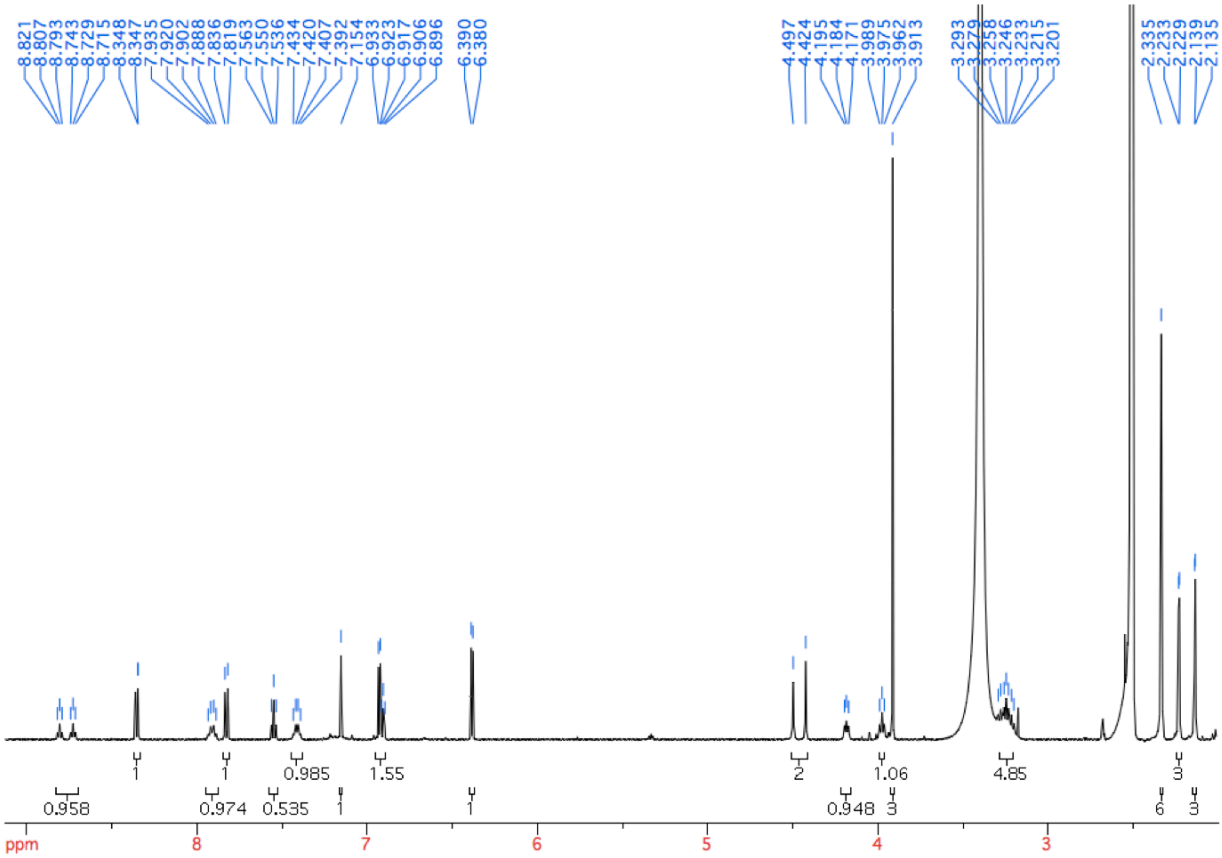

Figure S9. [1]H NMR spectrum of **12** in DMSO-*d6*.

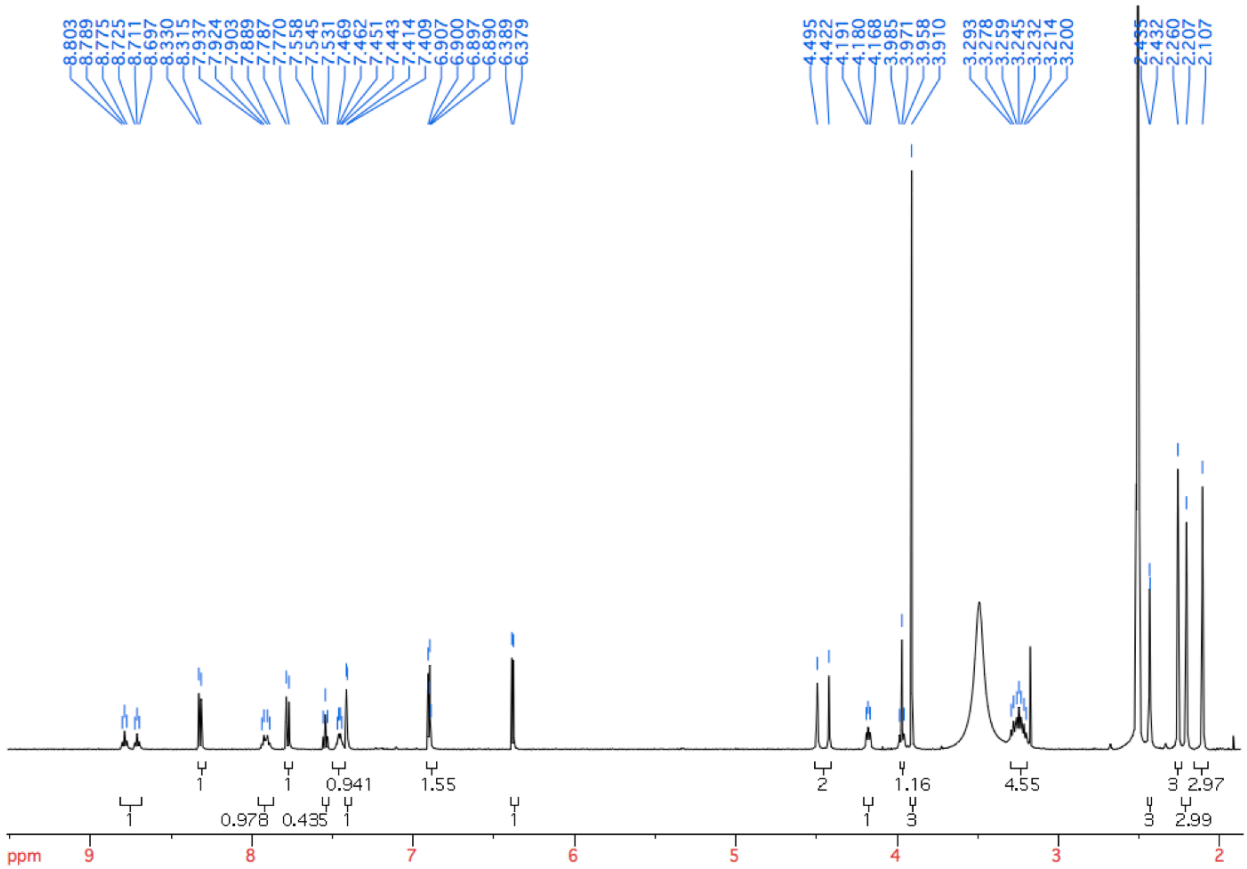

Figure S10. ^{1}H NMR spectrum of **13** in DMSO-*d6*.

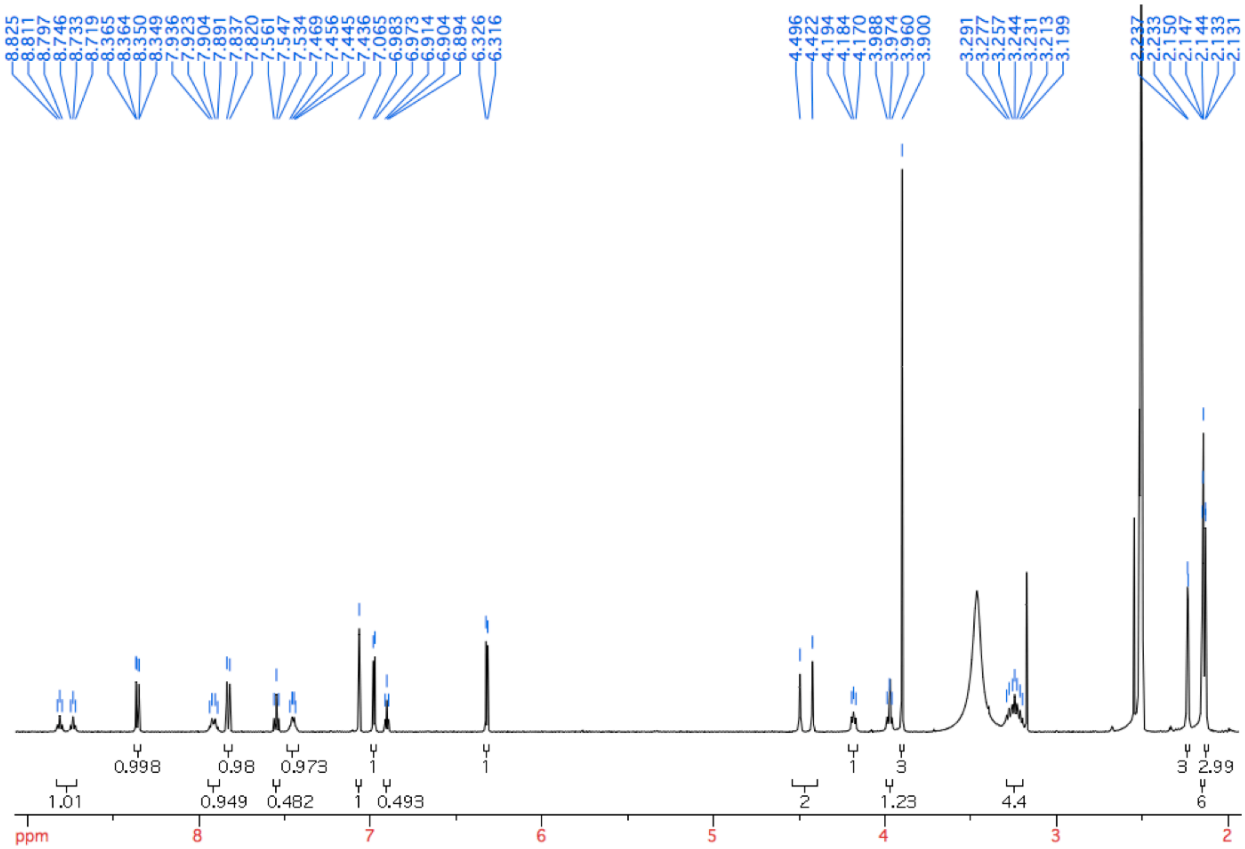

Figure S11. ^{1}H NMR spectrum of **14** in DMSO-*d6*.

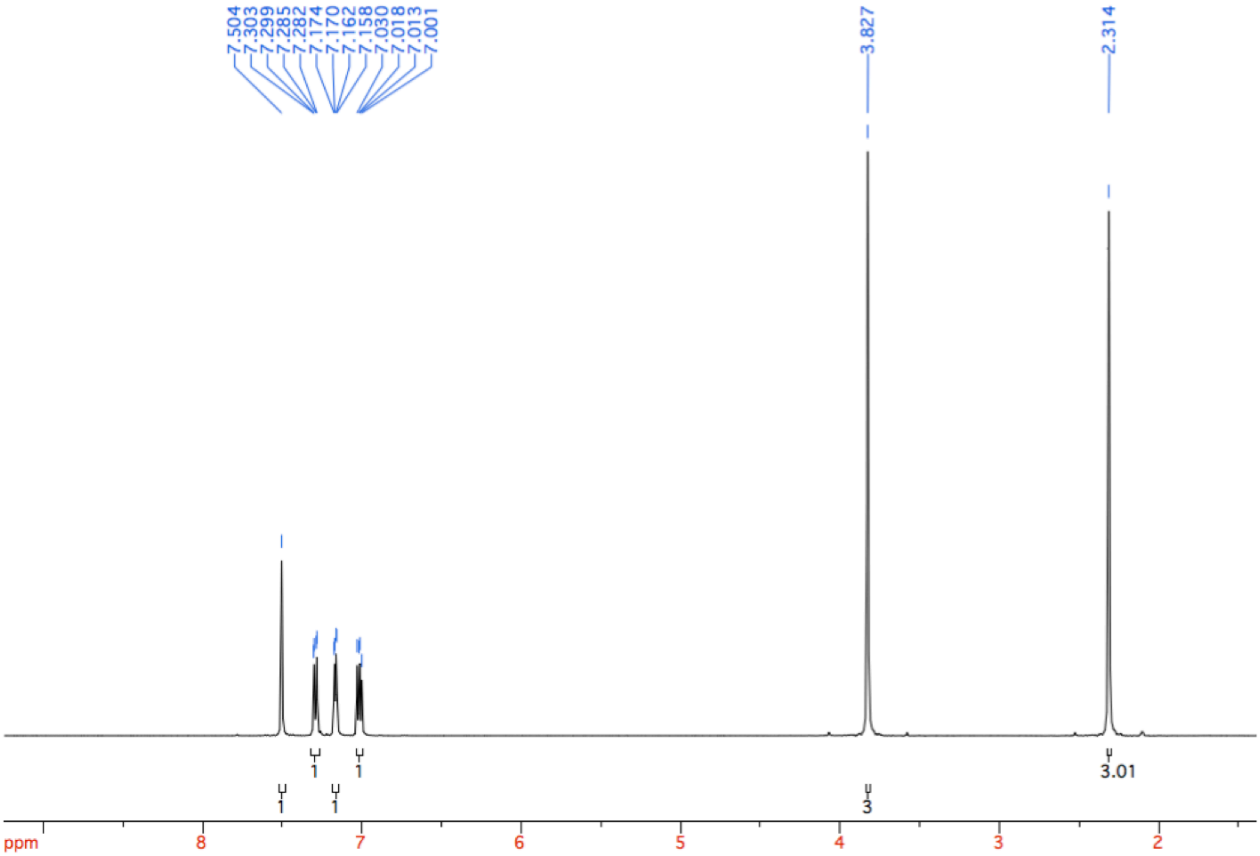

Figure S12. ^{1}H NMR spectrum of **19** in $CDCl_3$.

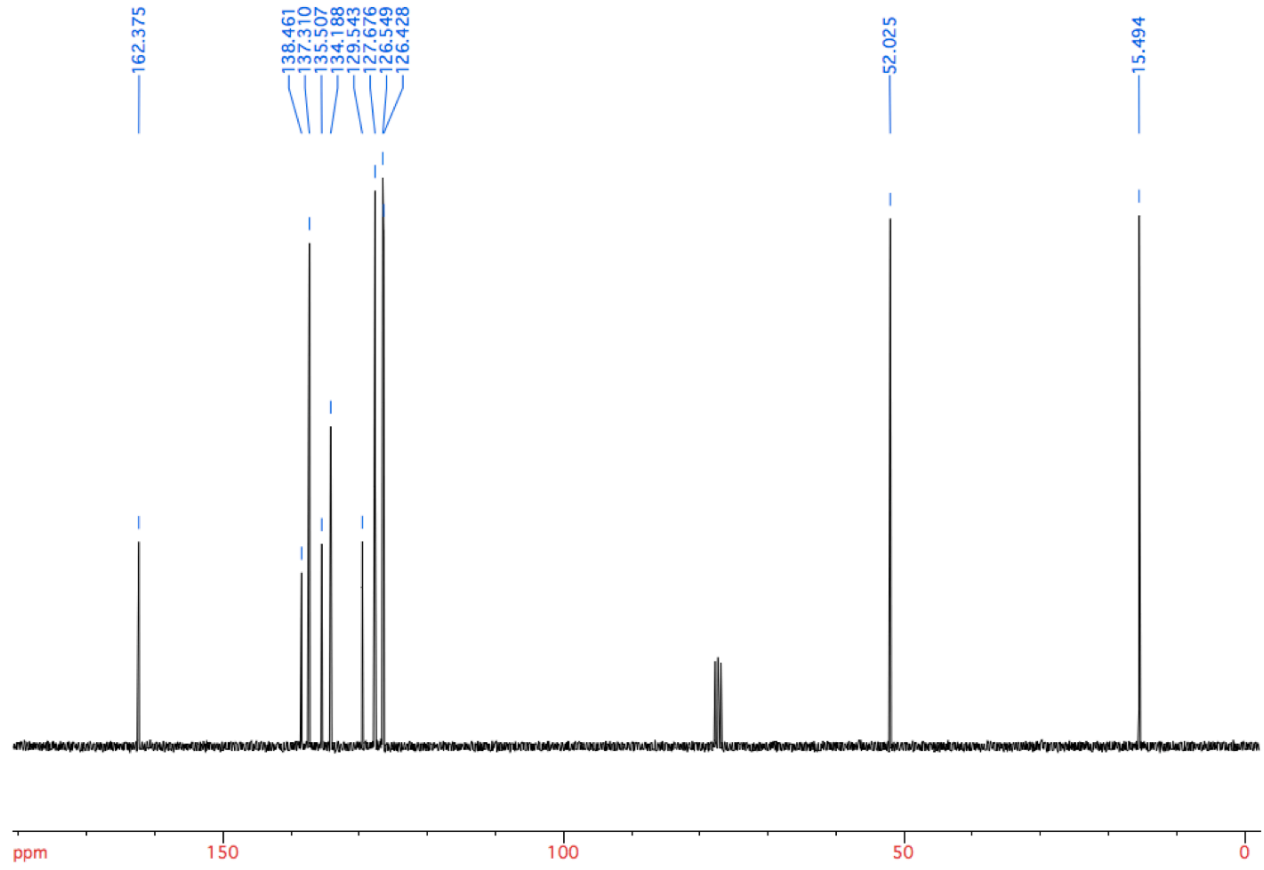

Figure S13. ^{13}C NMR spectrum of **19** in $CDCl_3$.

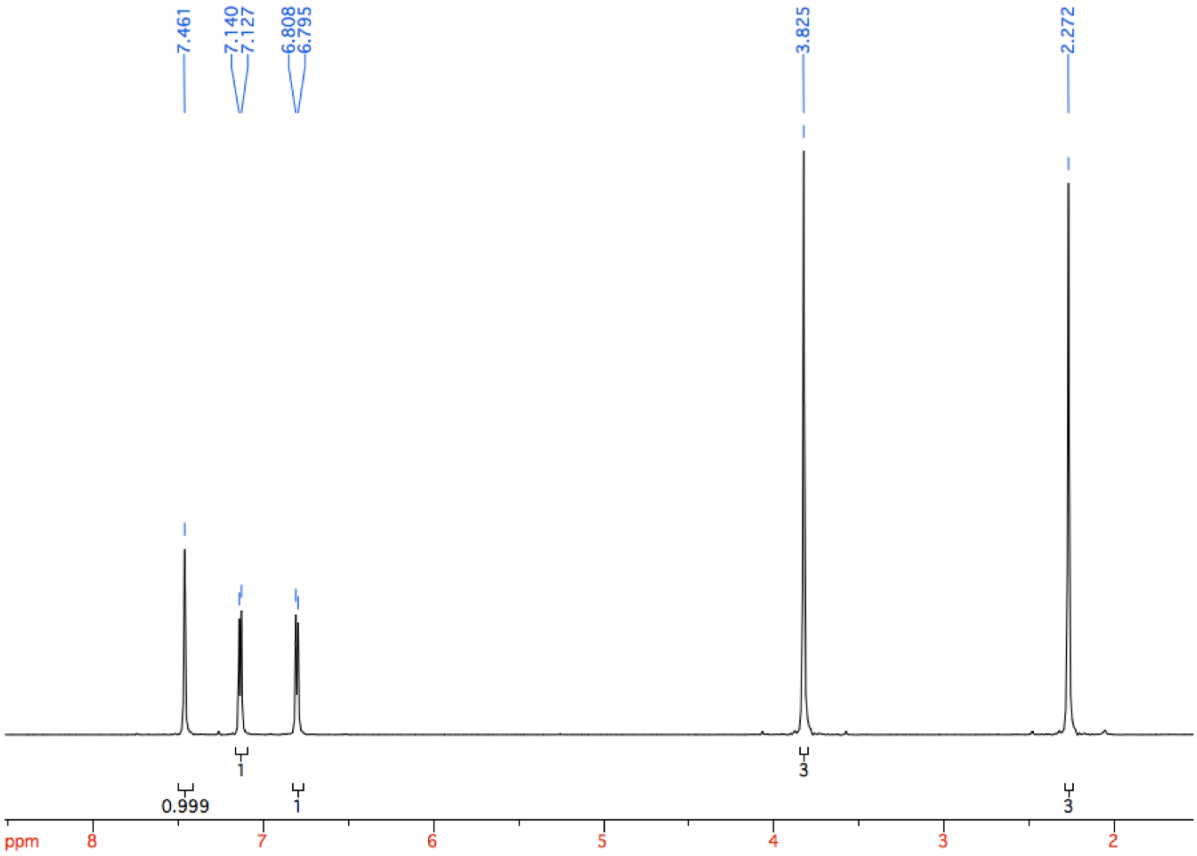

Figure S14. ^{1}H NMR spectrum of **20** in $CDCl_3$.

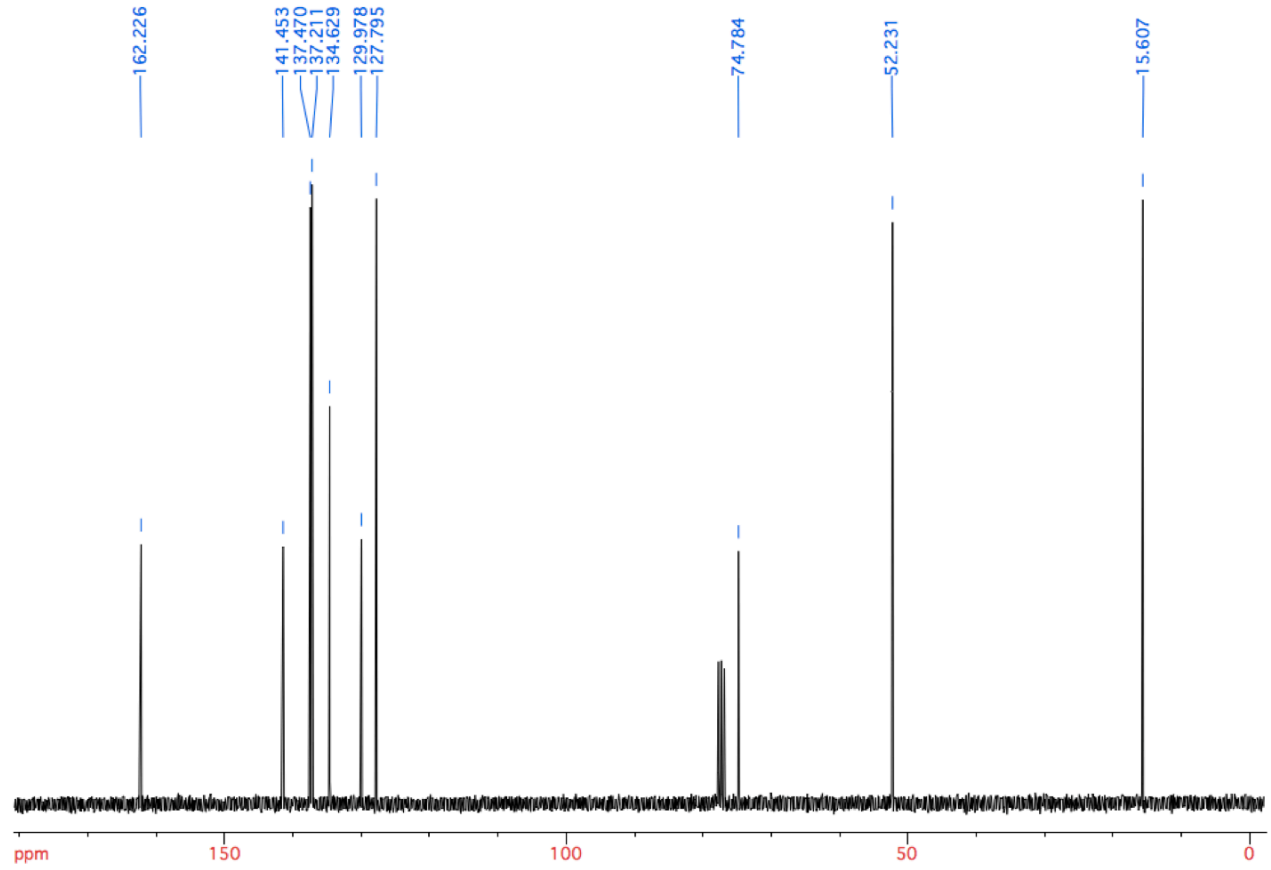

Figure S15. ^{13}C NMR spectrum of **20** in $CDCl_3$.

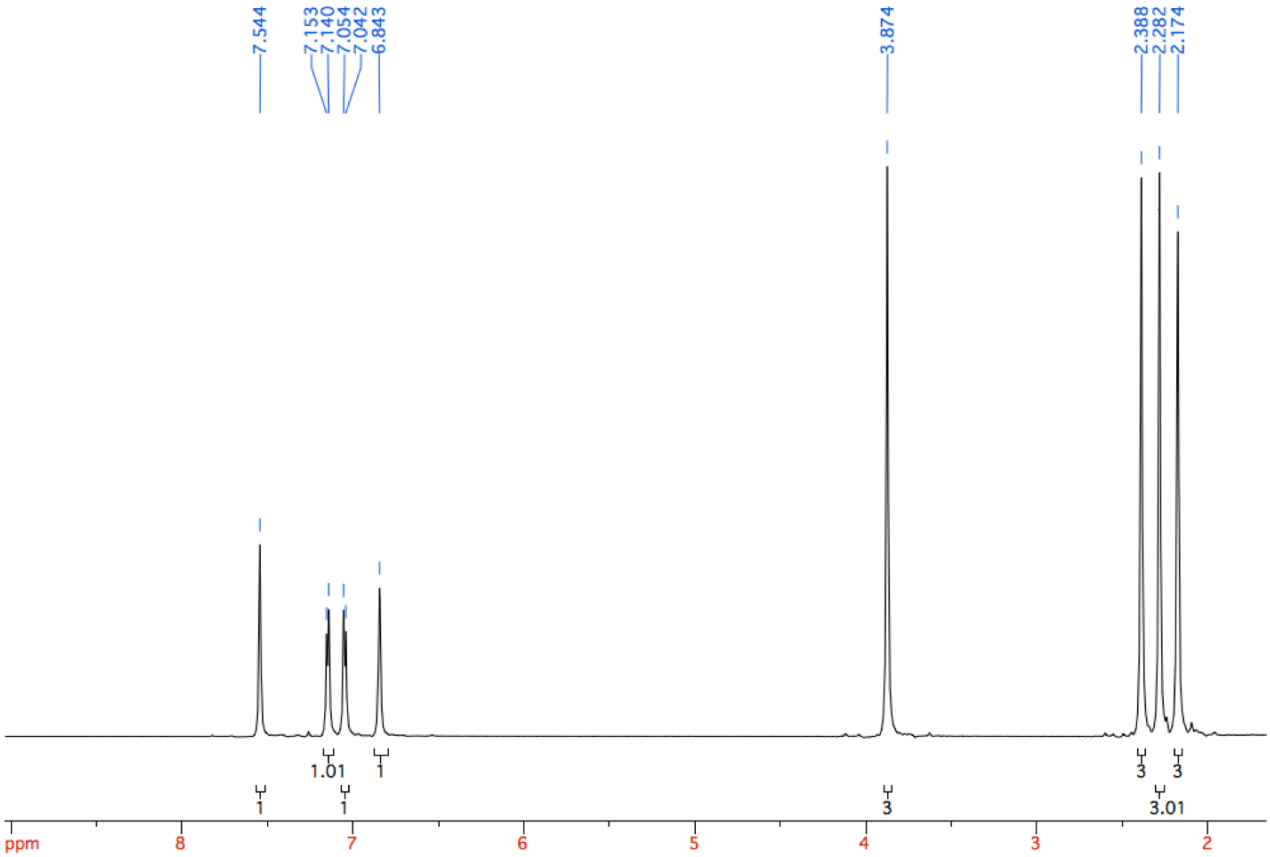

Figure S16. ^{1}H NMR spectrum of **22** in $CDCl_3$.

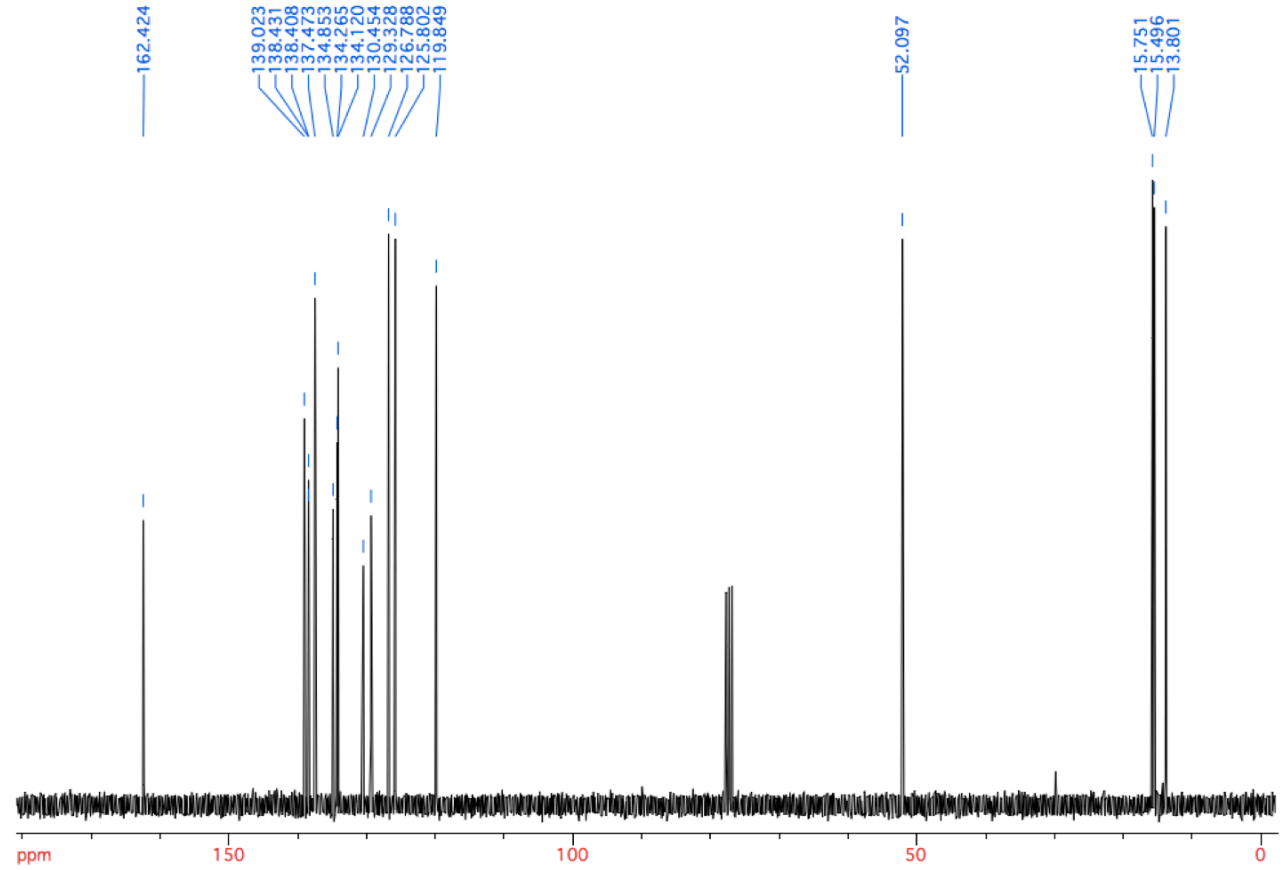

Figure S17. ^{13}C NMR spectrum of **22** in $CDCl_3$.

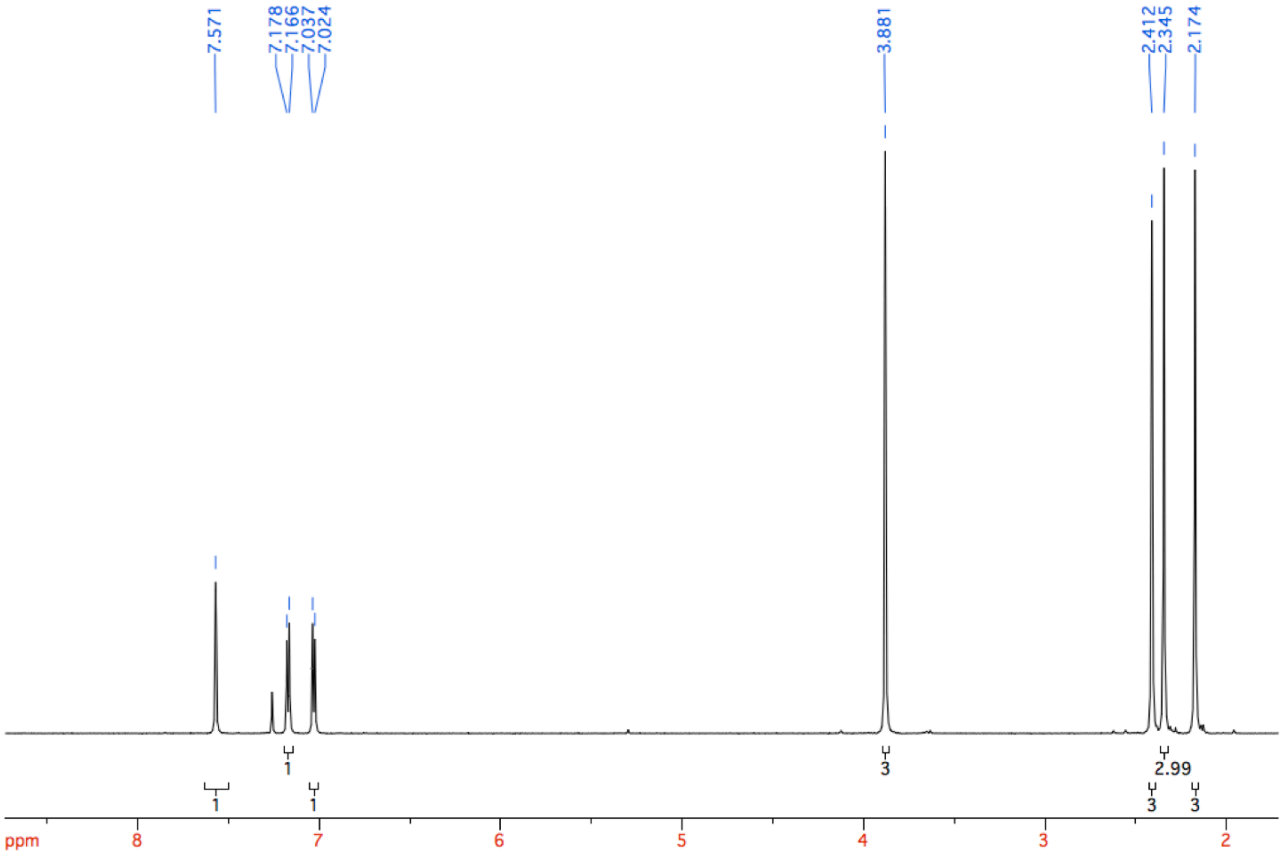

Figure S18. ^{1}H NMR spectrum of **23** in $CDCl_3$.

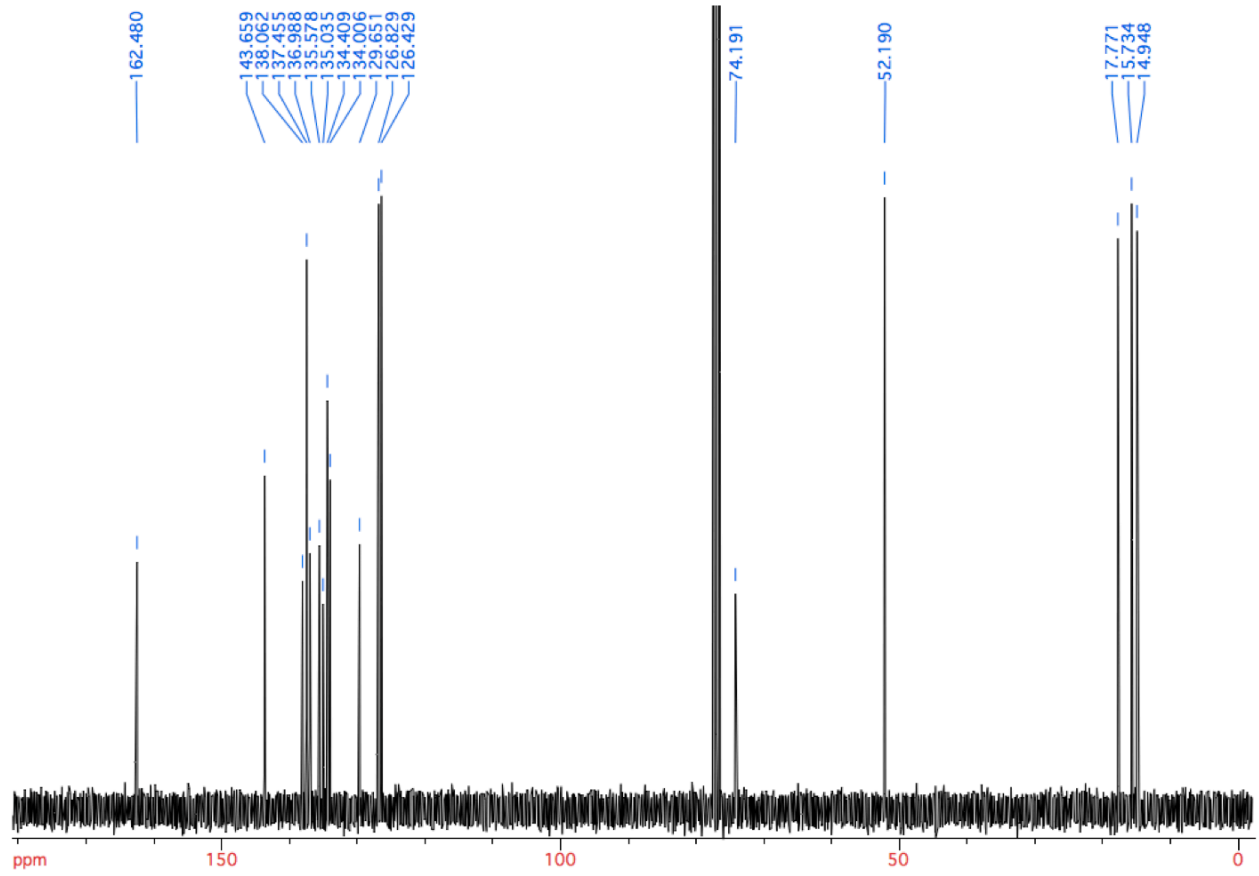

Figure S19. ^{13}C NMR spectrum of **23** in $CDCl_3$.

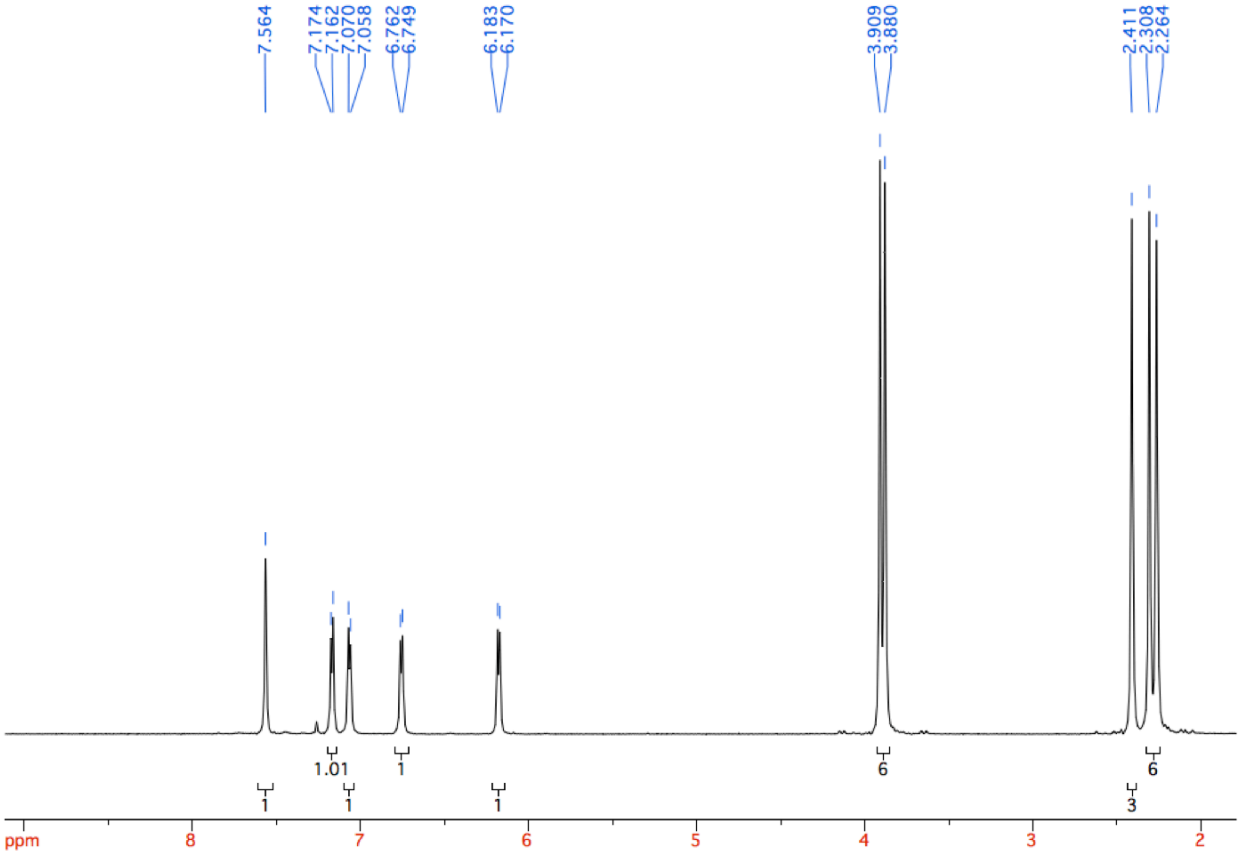

Figure S20. ^{1}H NMR spectrum of **25** in $CDCl_3$.

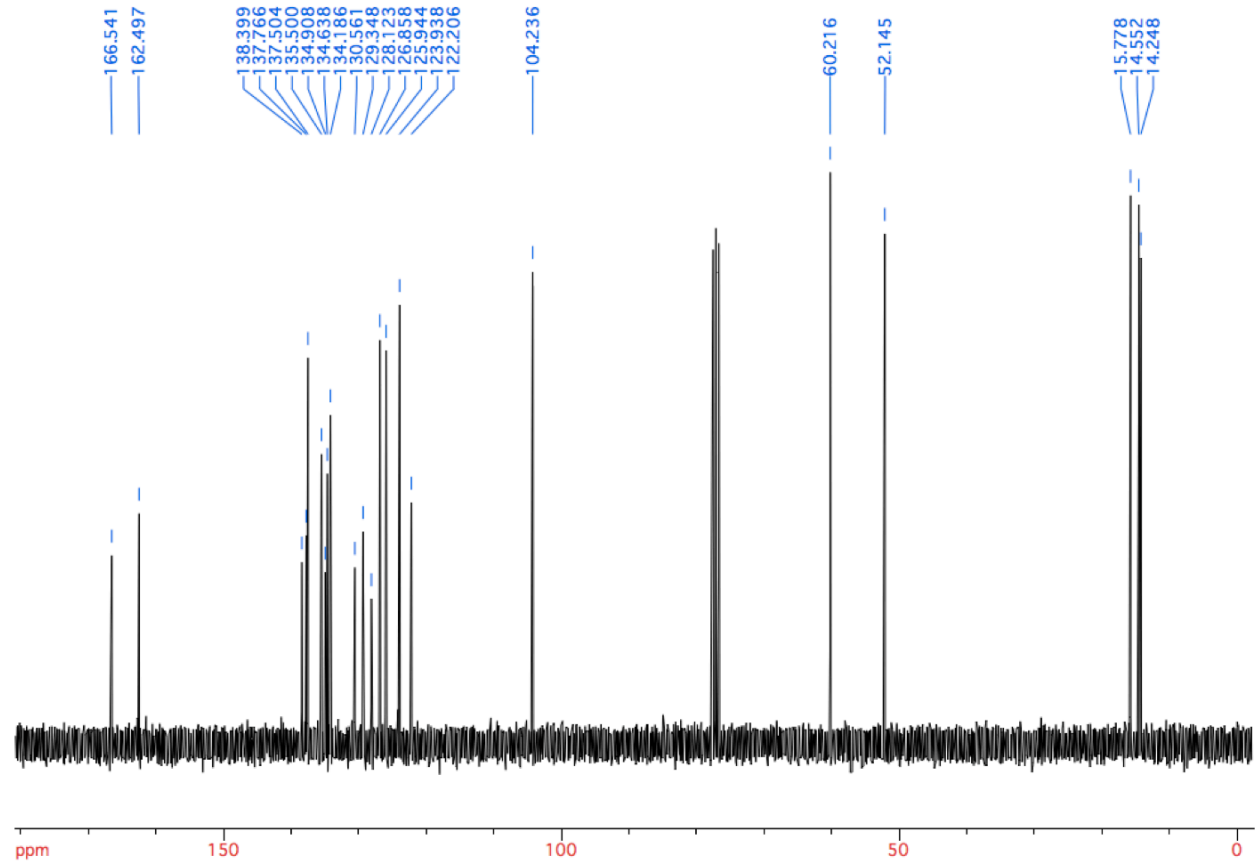

Figure S21. ^{13}C NMR spectrum of **25** in $CDCl_3$.

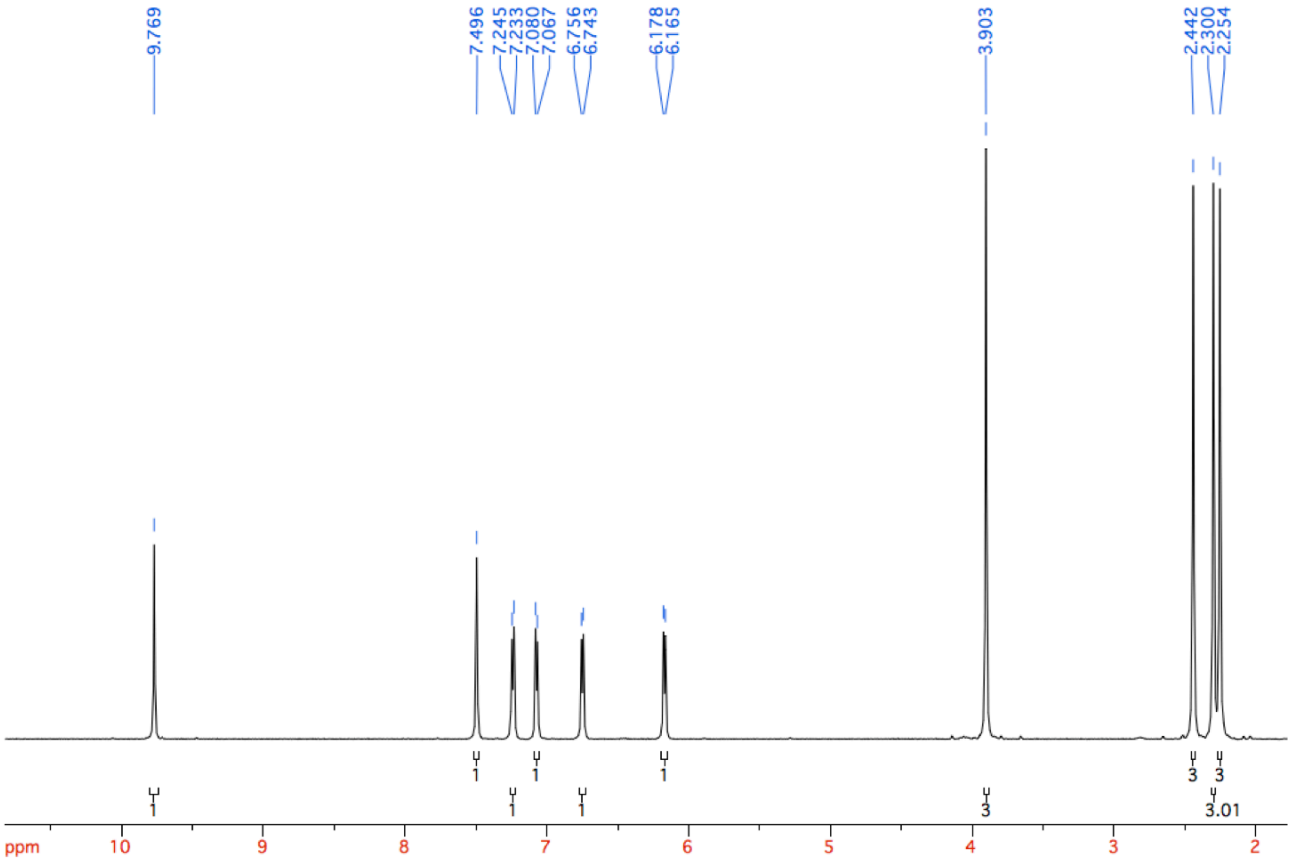

Figure S22. ^{1}H NMR spectrum of **26** in $CDCl_3$.

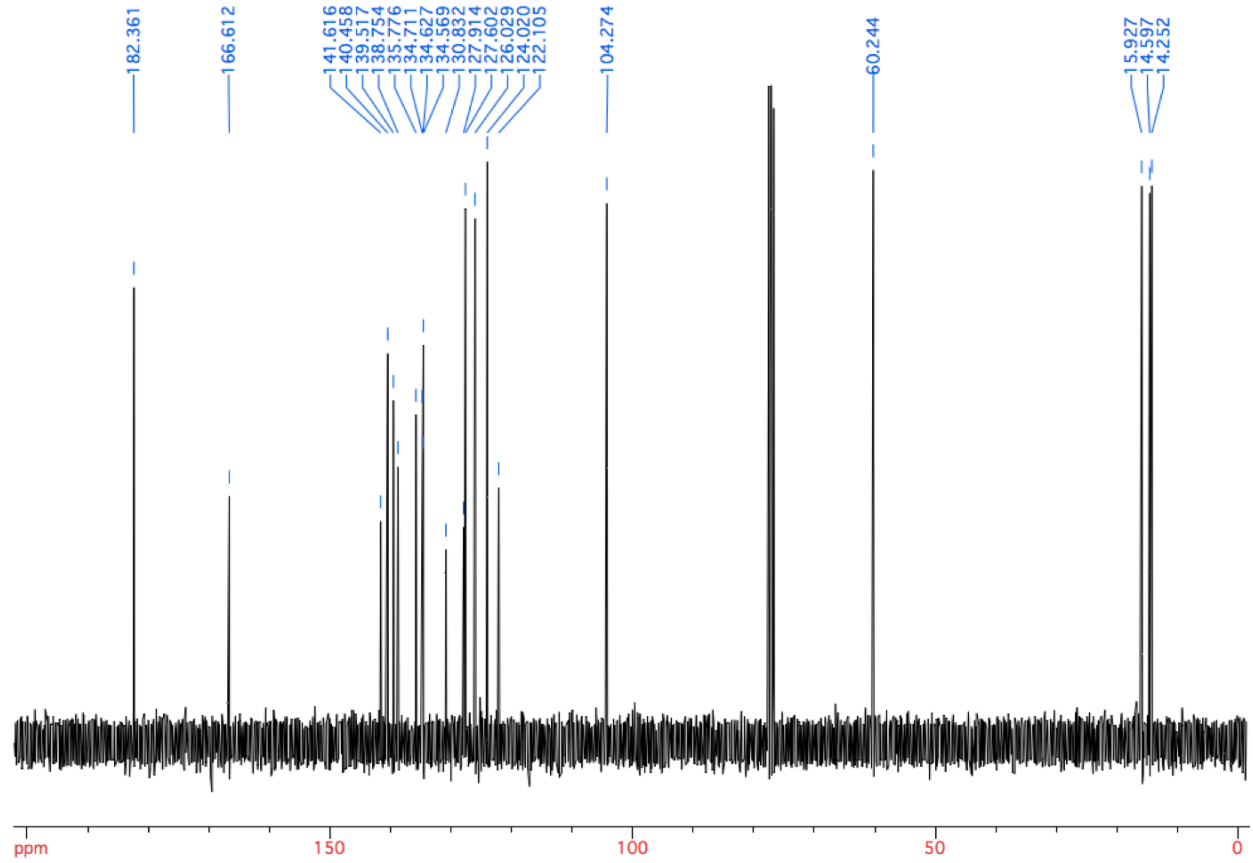

Figure S23. ^{13}C NMR spectrum of **26** in $CDCl_3$.

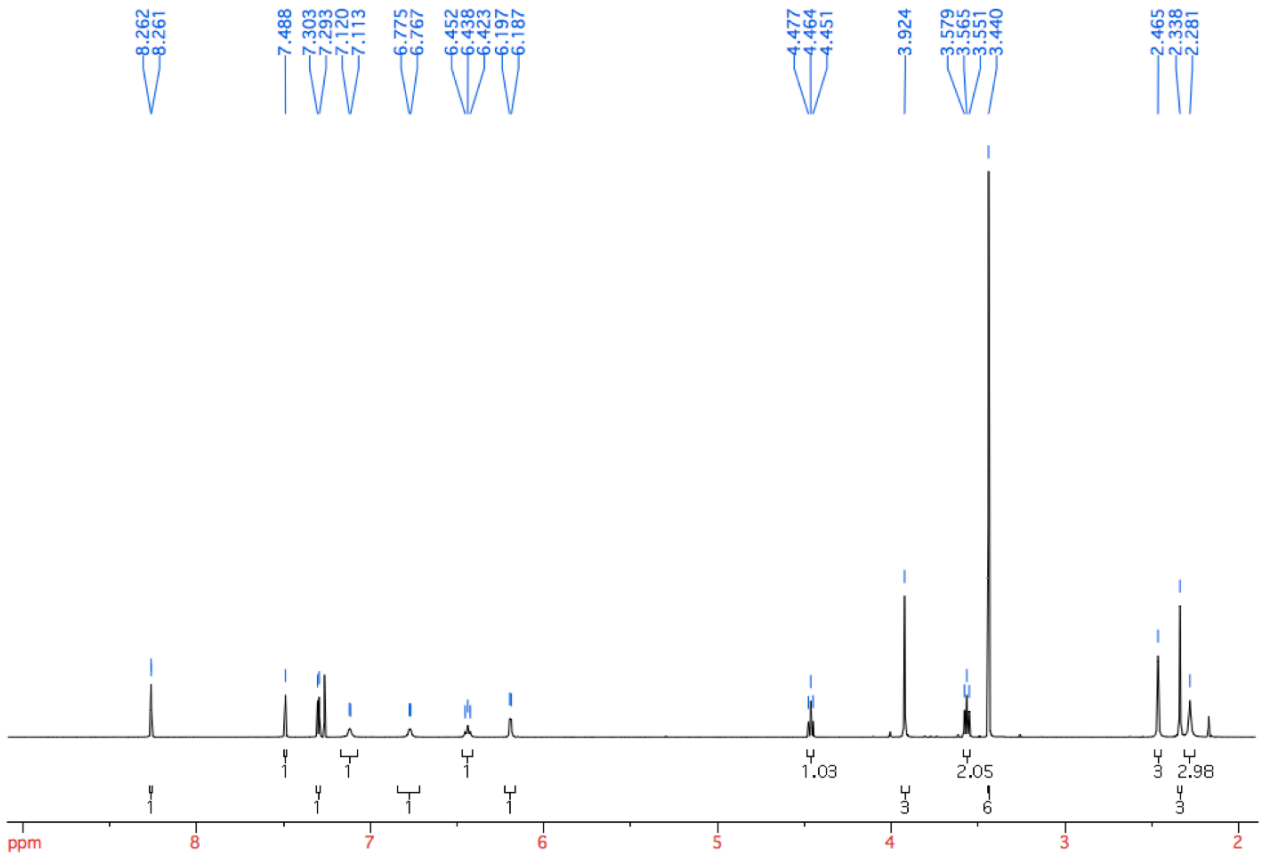

Figure S24. ^{1}H NMR spectrum of **30** in $CDCl_3$.

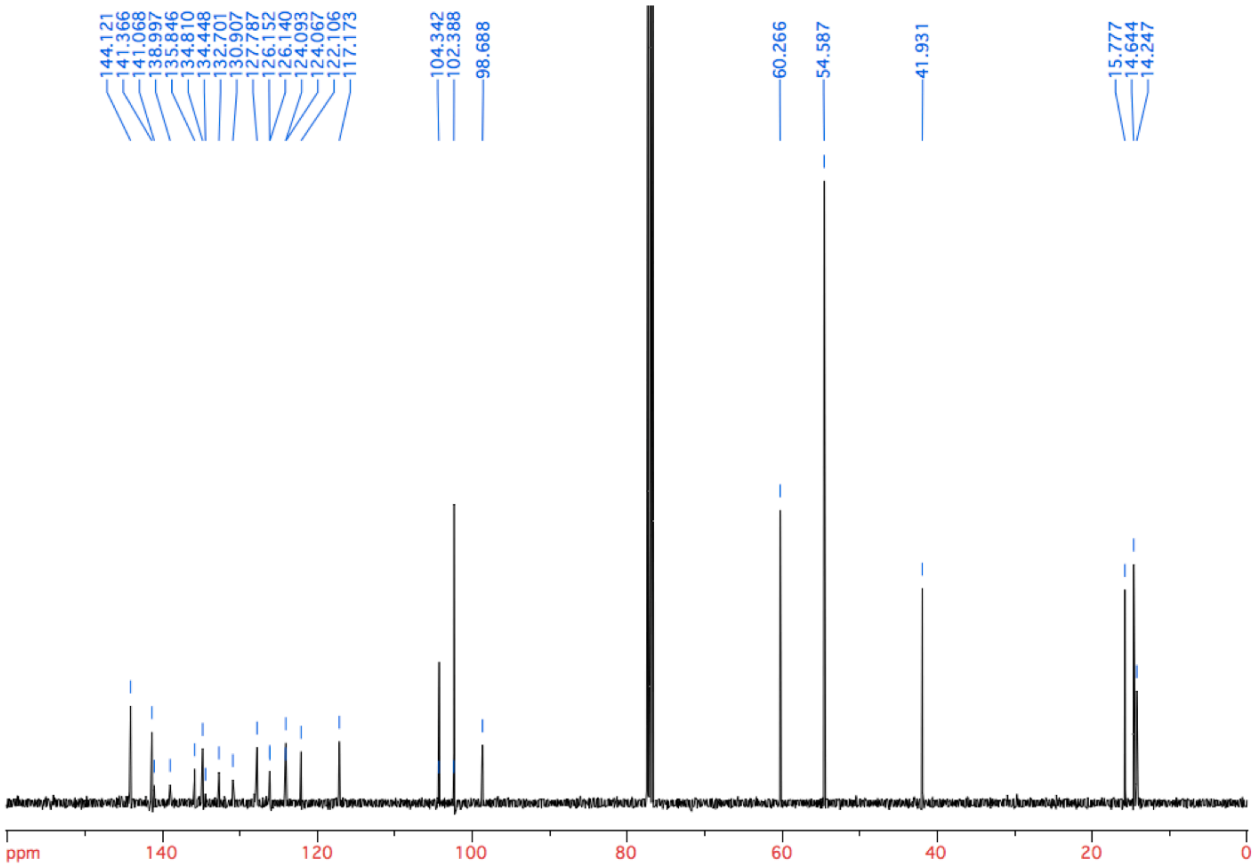

Figure S25. ^{13}C NMR spectrum of **30** in $CDCl_3$.

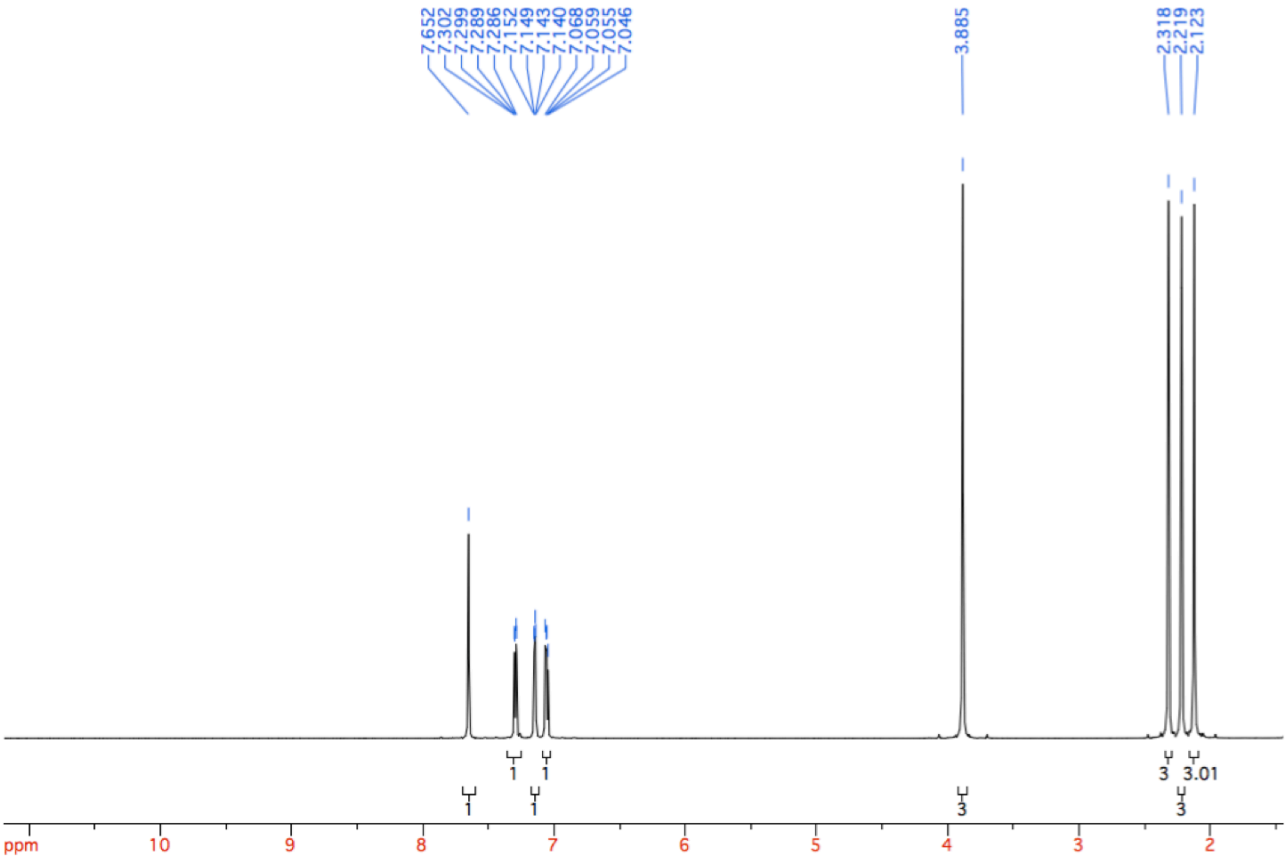

Figure S26. ^{1}H NMR spectrum of **33** in $CDCl_3$.

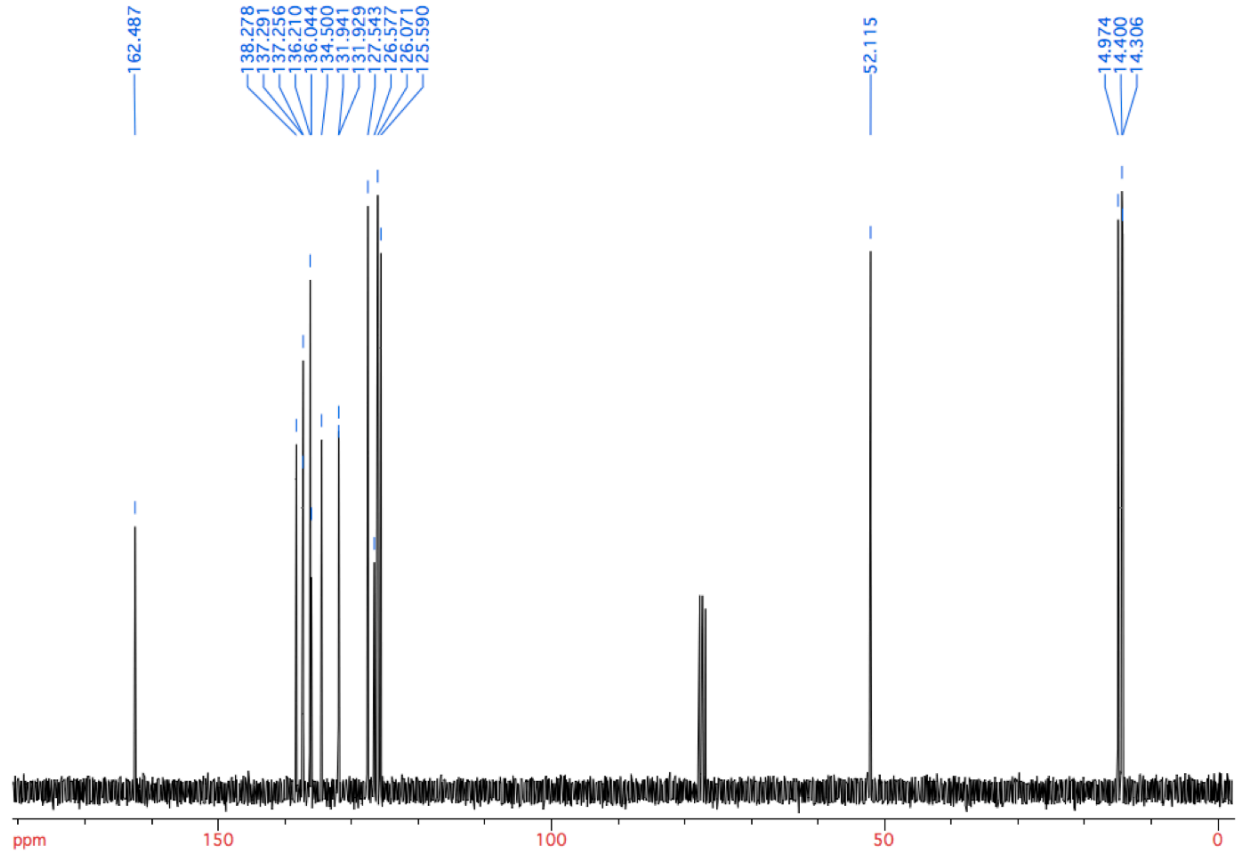

Figure S27. ^{13}C NMR spectrum of **33** in $CDCl_3$.

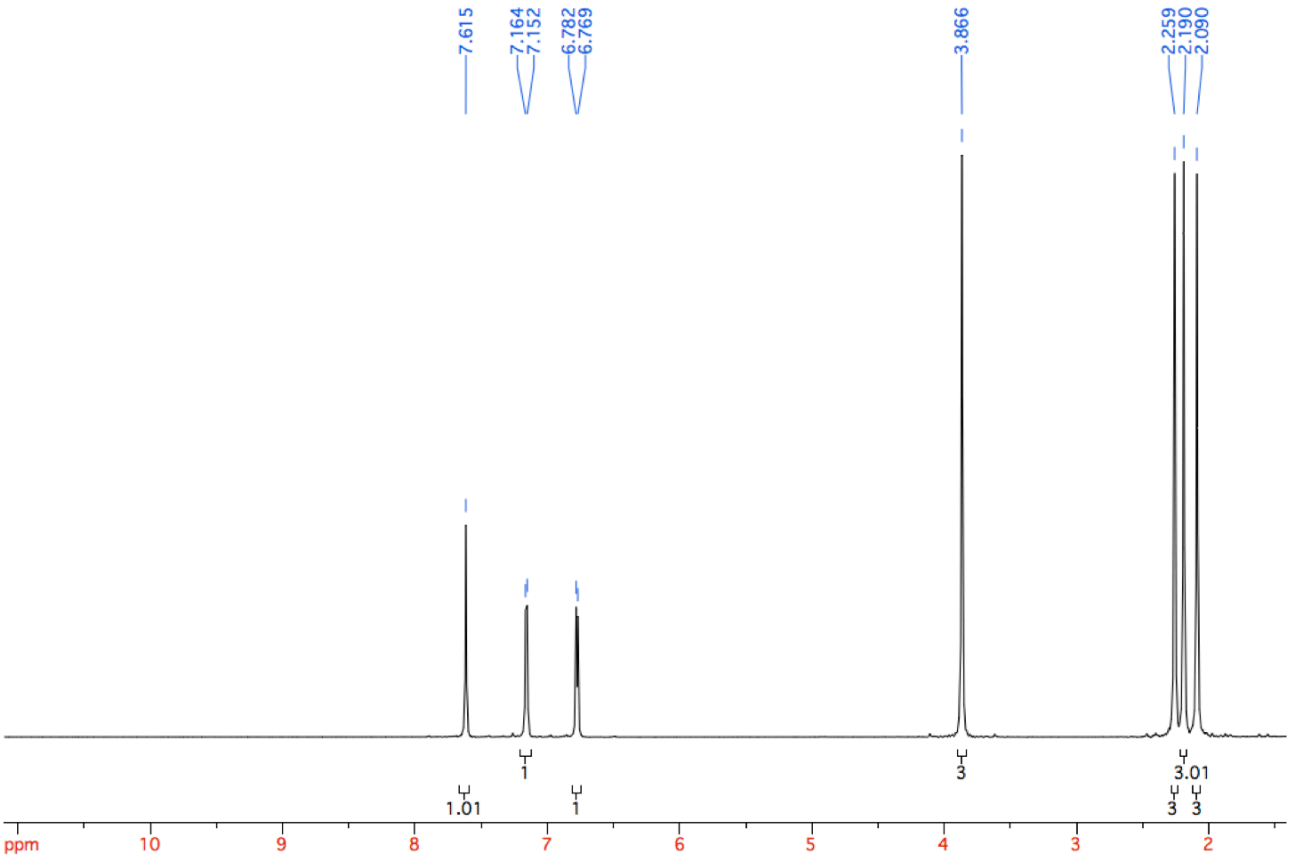

Figure S28. ^{1}H NMR spectrum of **34** in $CDCl_3$.

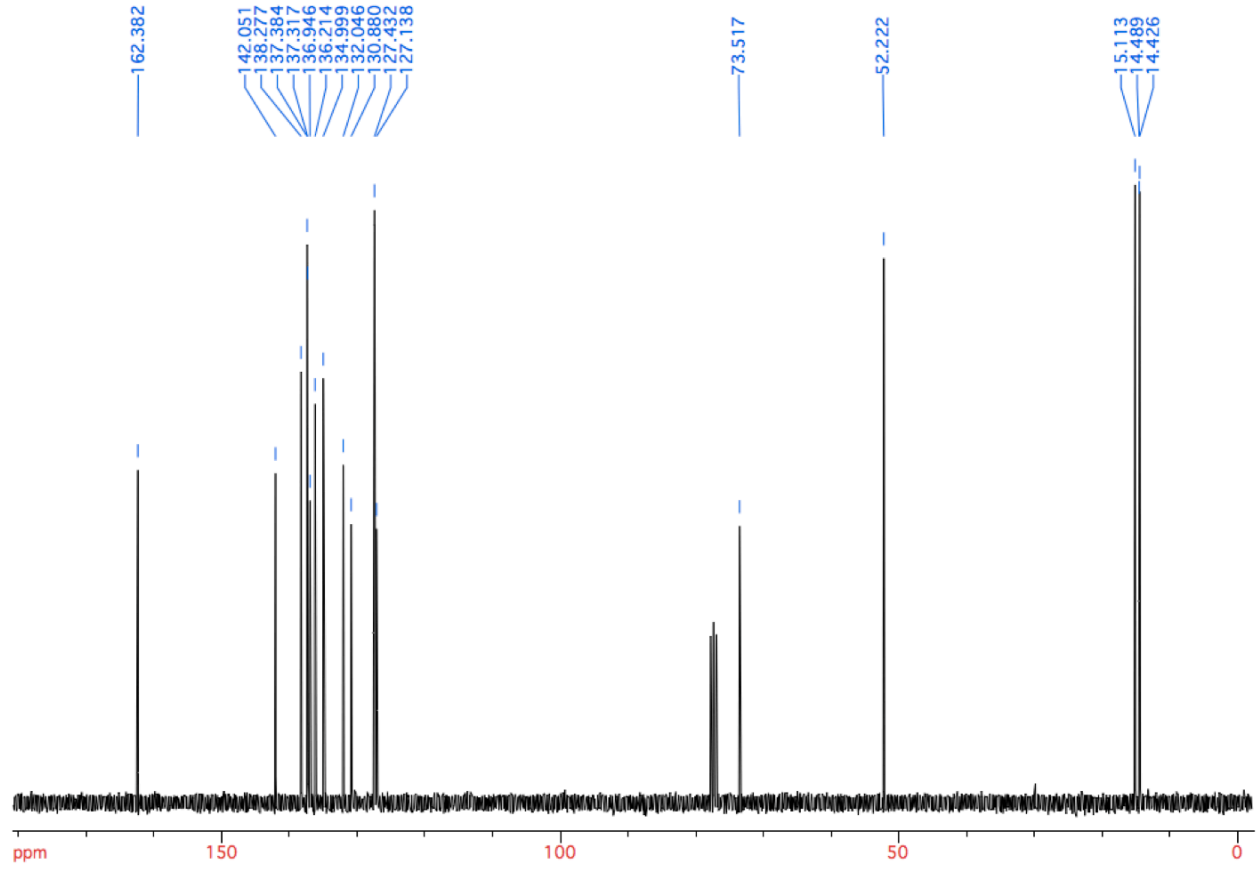

Figure S29. ^{13}C NMR spectrum of **34** in $CDCl_3$.

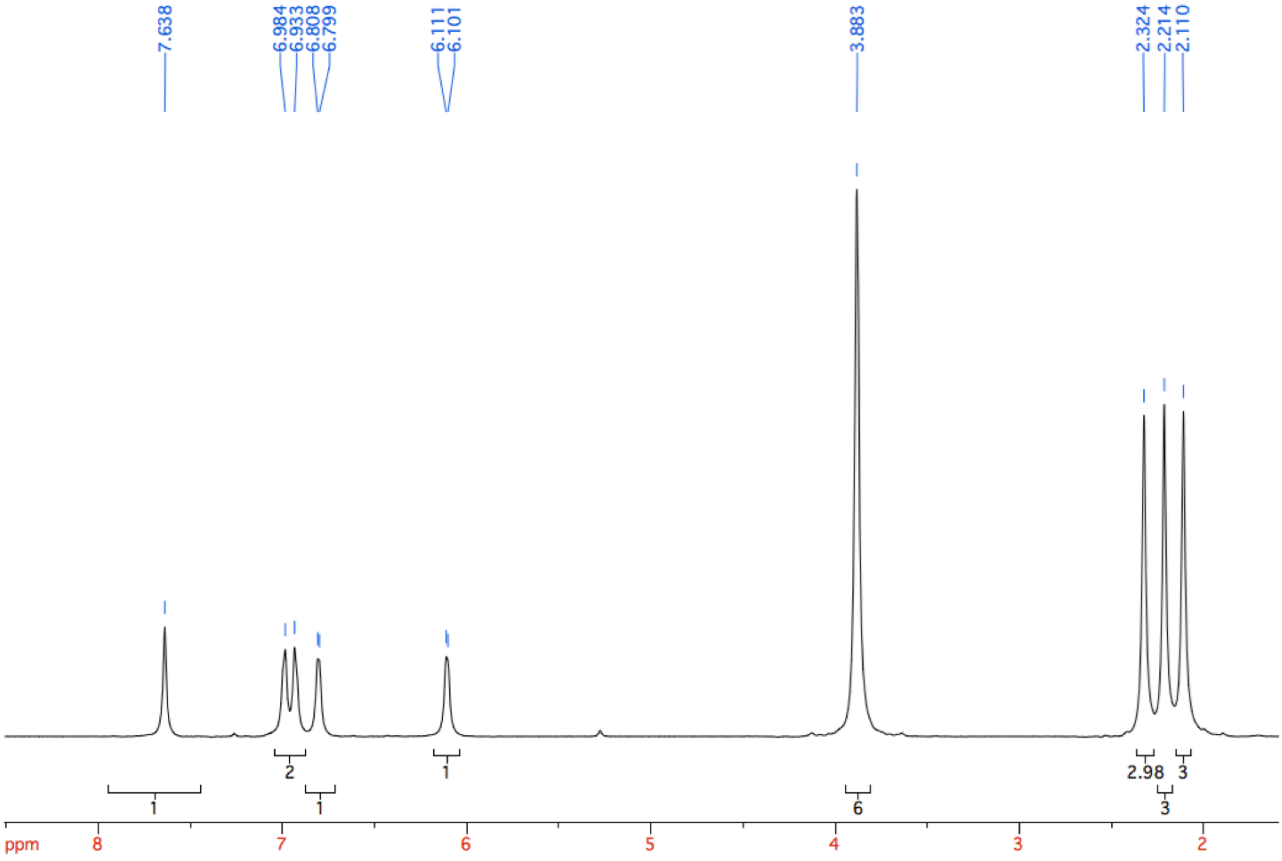

Figure S30. ^{1}H NMR spectrum of **35** in $CDCl_3$.

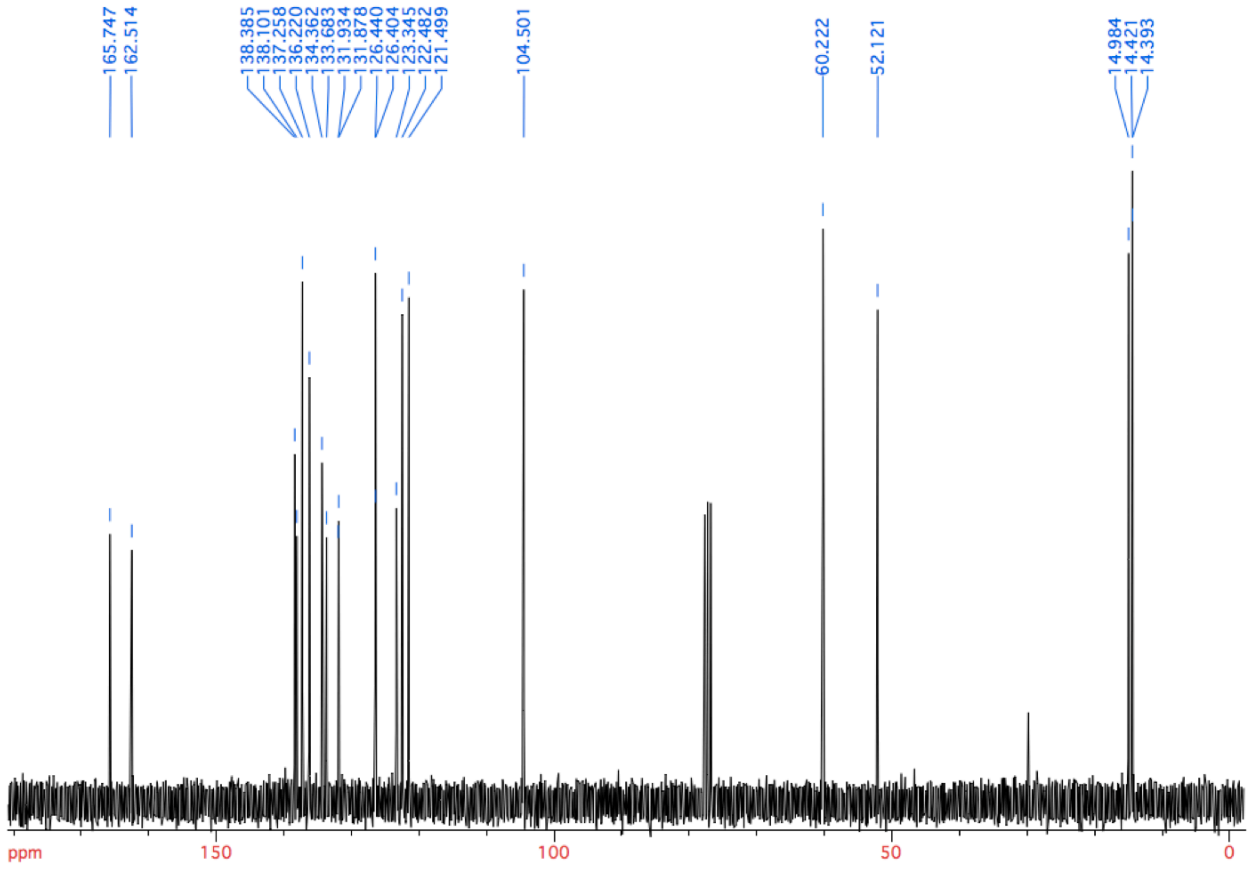

Figure S31. ^{13}C NMR spectrum of **35** in $CDCl_3$.

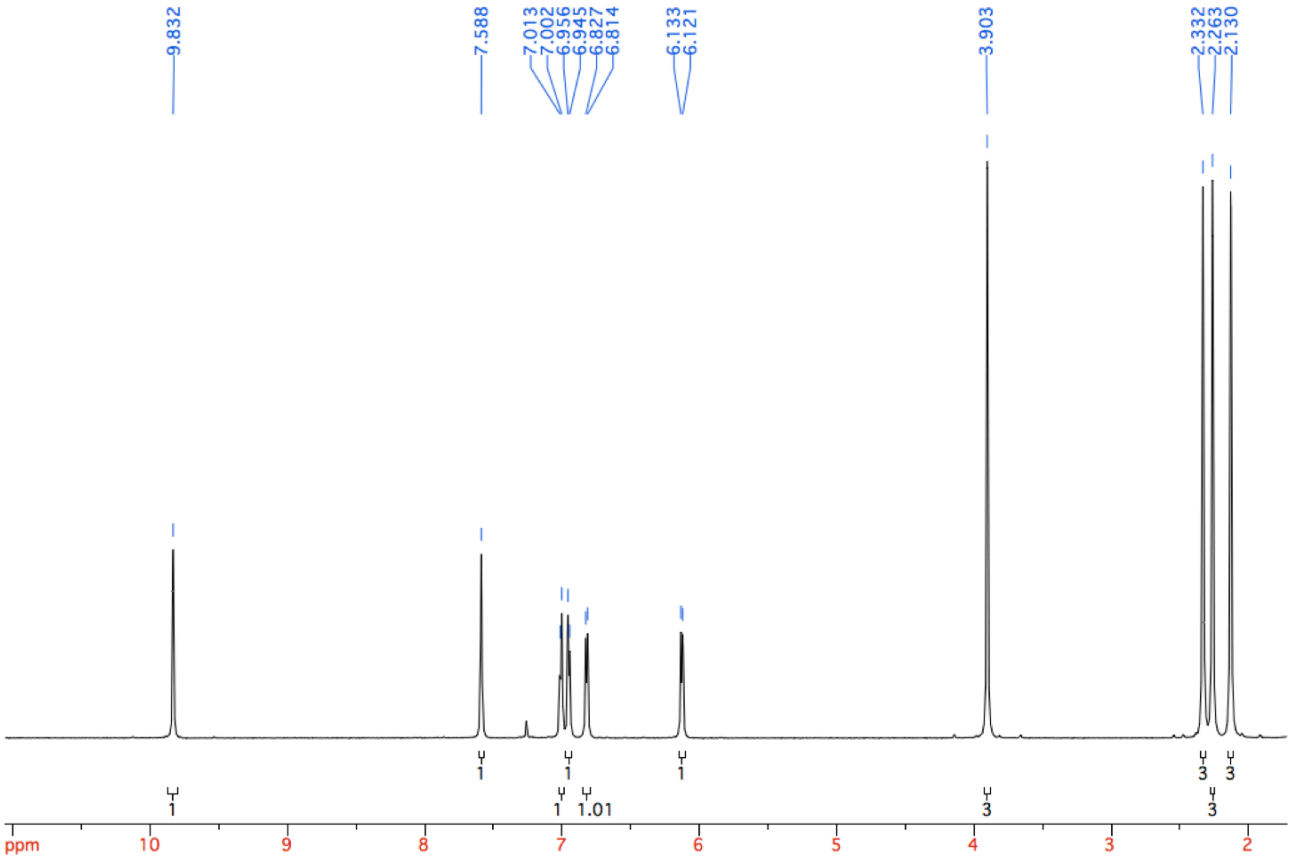

Figure S32. ^{1}H NMR spectrum of **36** in $CDCl_3$.

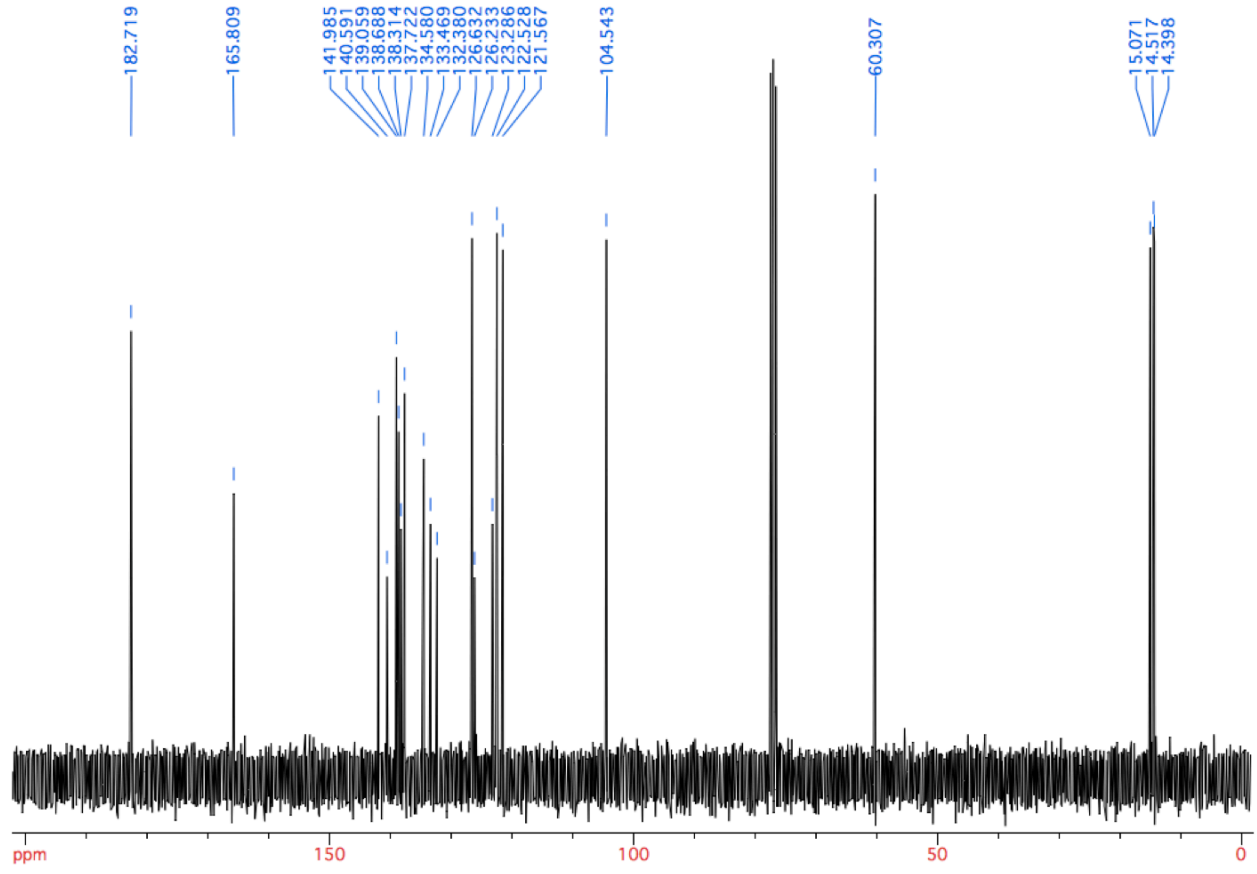

Figure S33. ^{13}C NMR spectrum of **36** in $CDCl_3$.

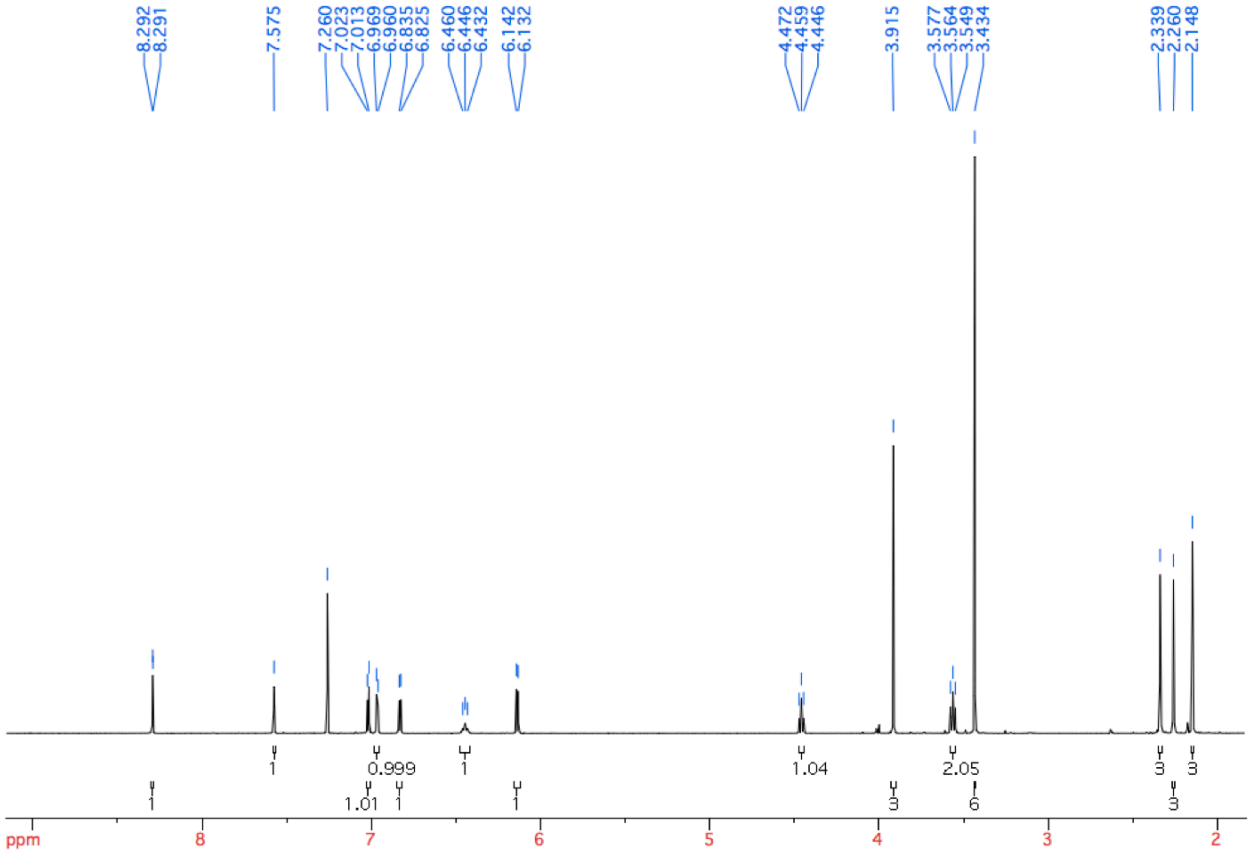

Figure S34. ^{1}H NMR spectrum of **37** in $CDCl_3$.

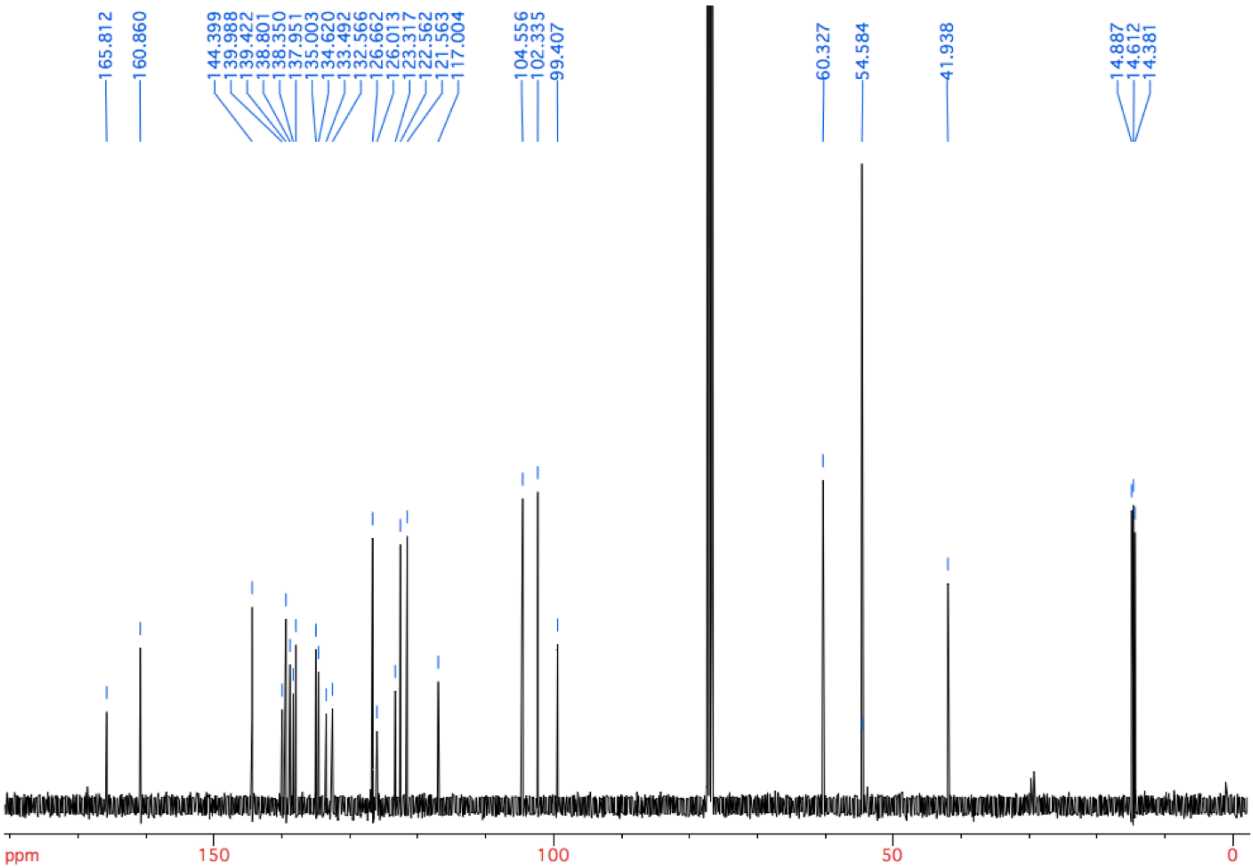

Figure S35. ^{13}C NMR spectrum of **37** in $CDCl_3$.

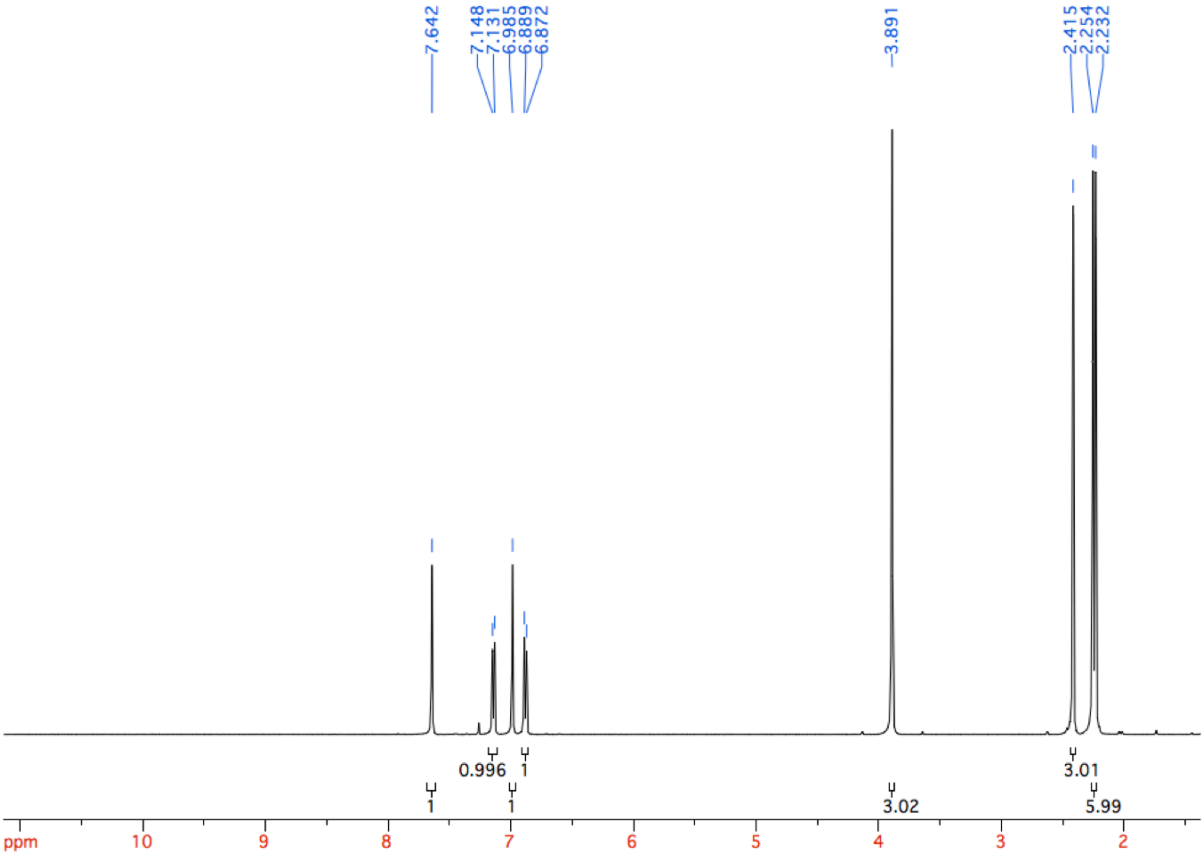

Figure S36. ^{1}H NMR spectrum of **40** in $CDCl_3$.

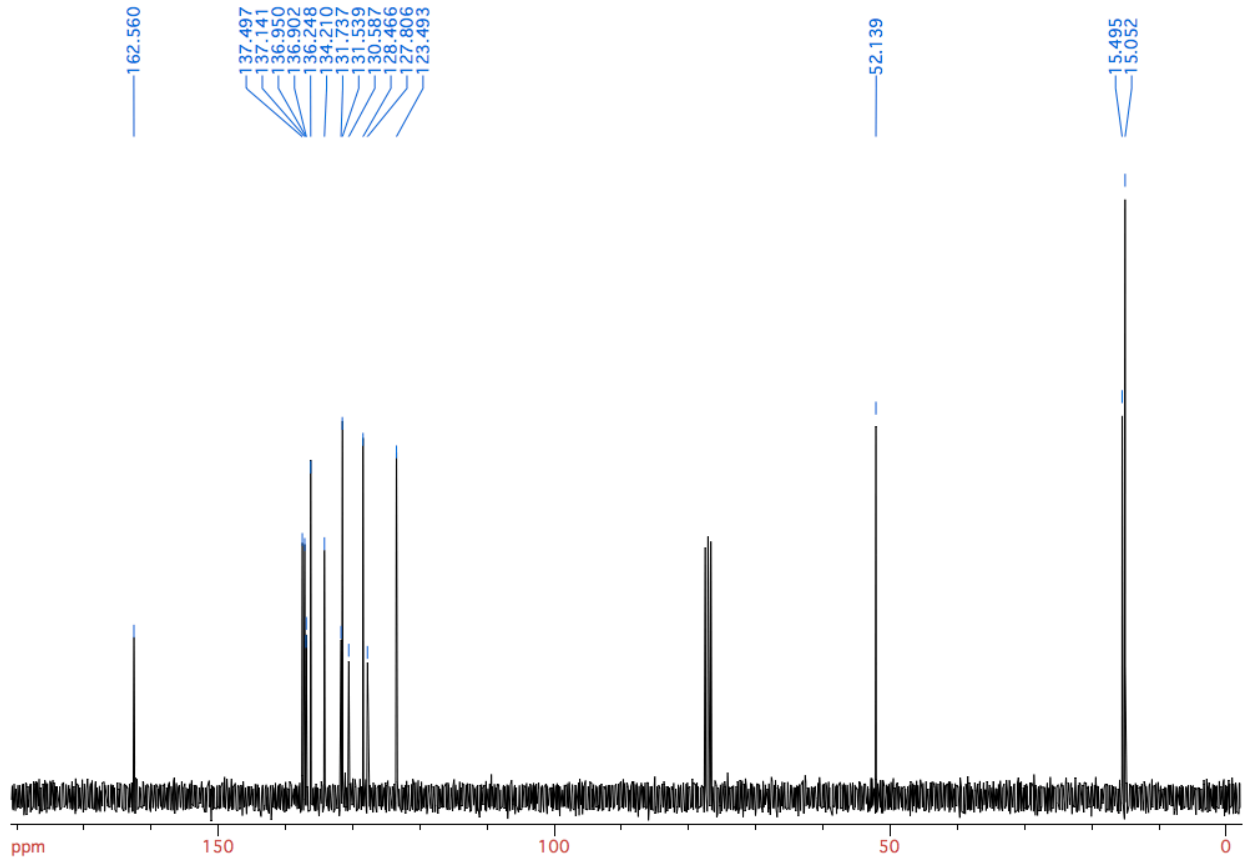

Figure S37. ^{13}C NMR spectrum of **40** in $CDCl_3$.

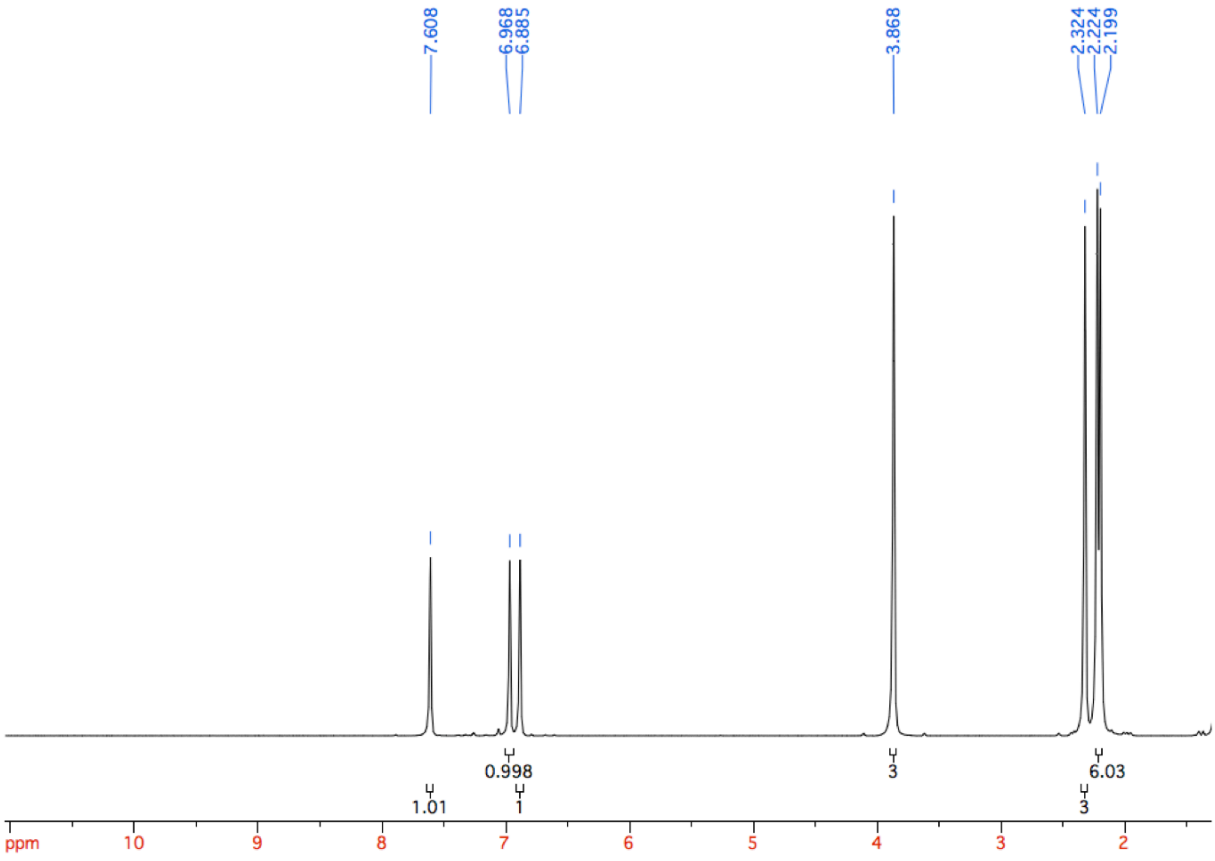

Figure S38. ^{1}H NMR spectrum of **41** in $CDCl_3$.

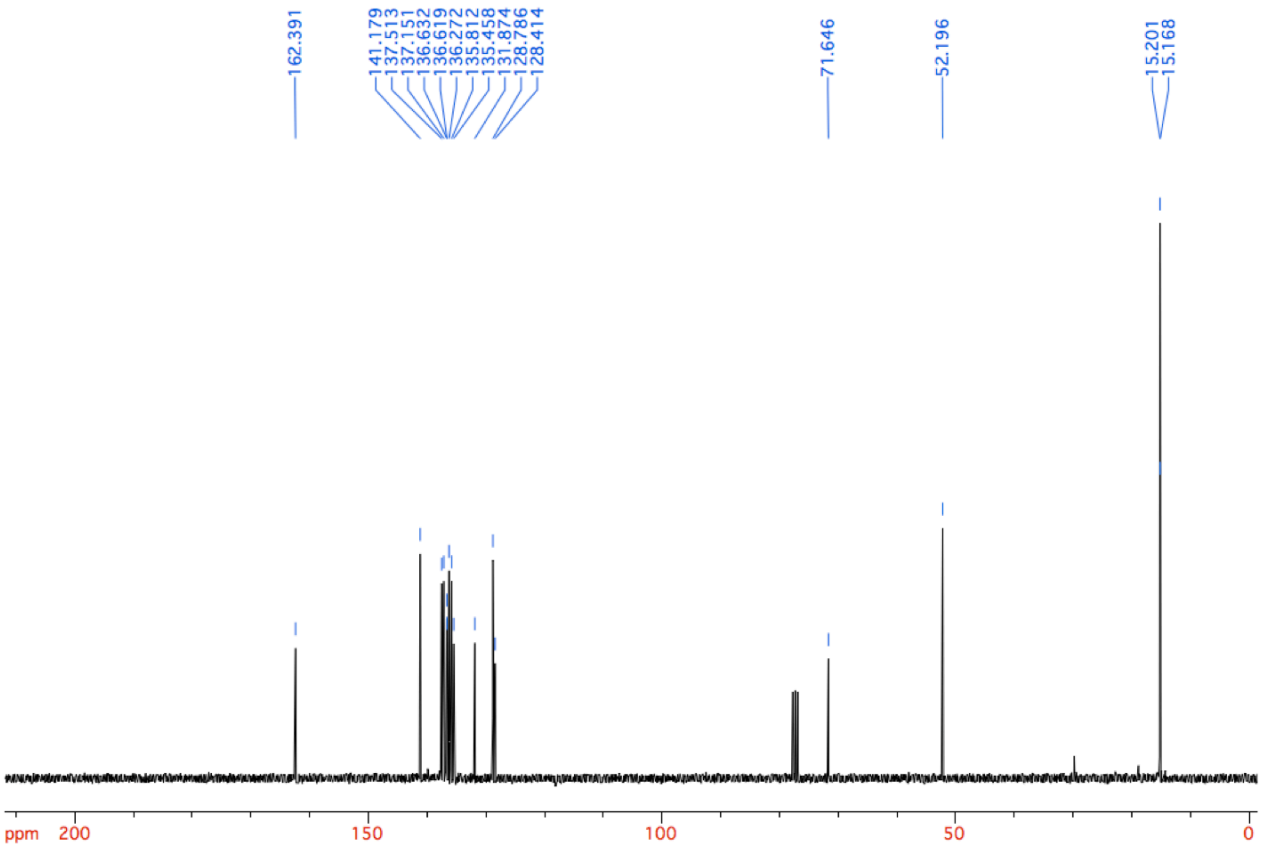

Figure S39. ^{13}C NMR spectrum of **41** in $CDCl_3$.

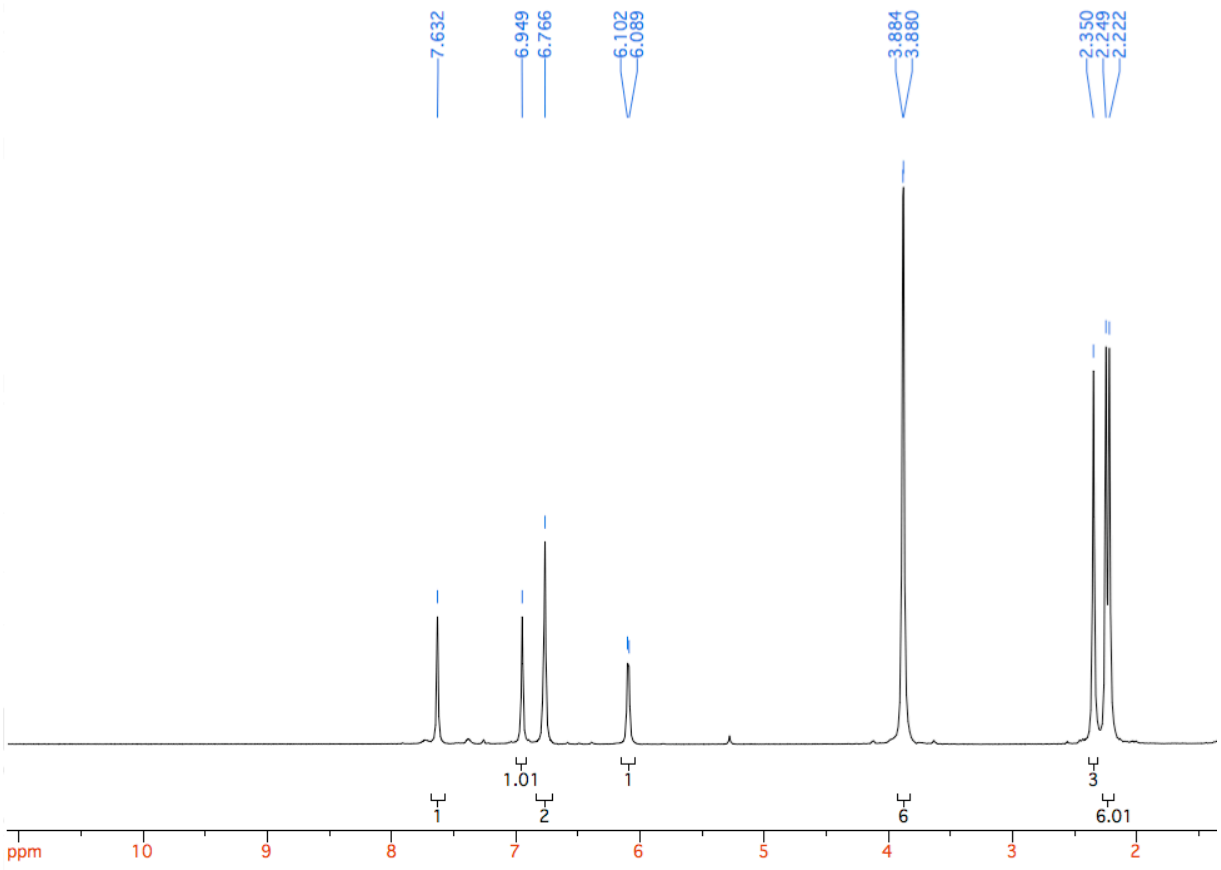

Figure S40. ^{1}H NMR spectrum of **42** in $CDCl_3$.

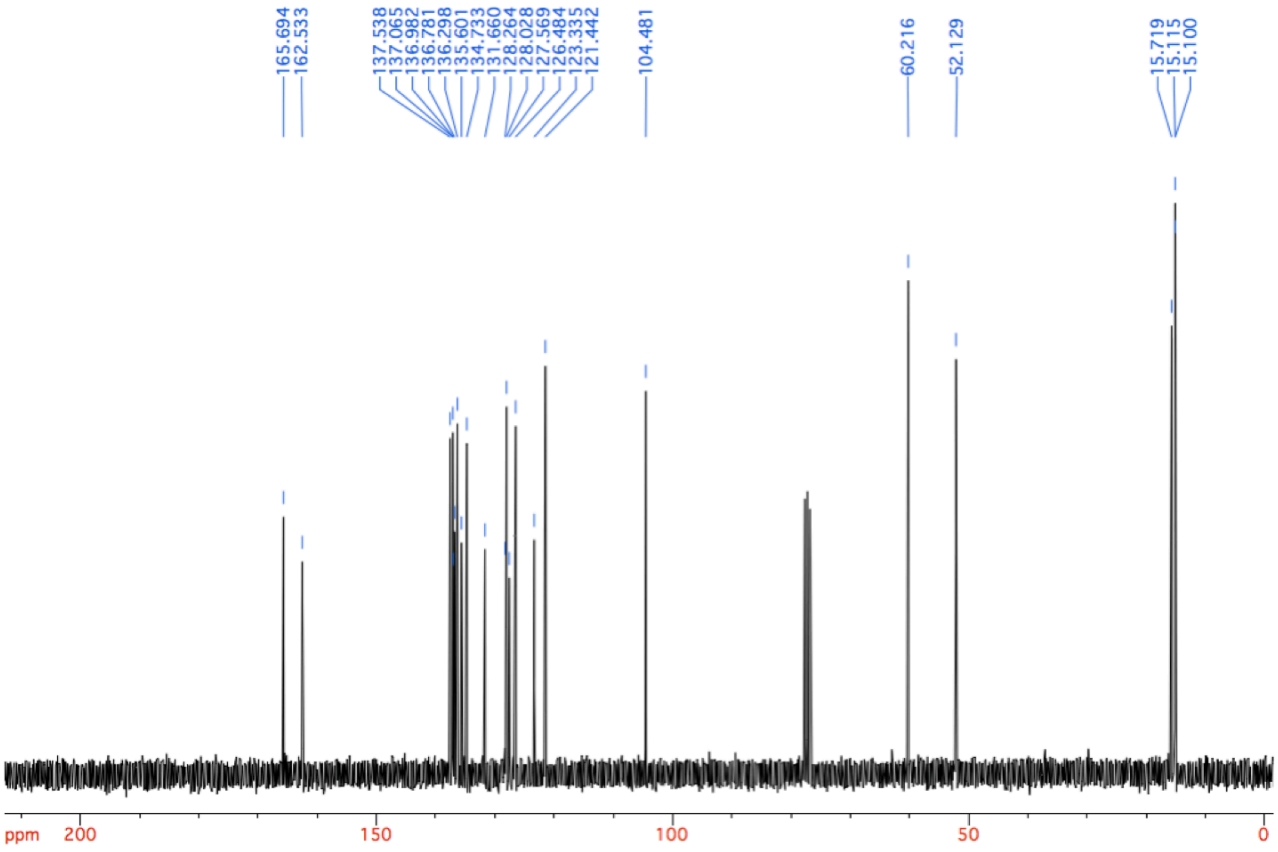

Figure S41. ^{13}C NMR spectrum of **42** in $CDCl_3$.

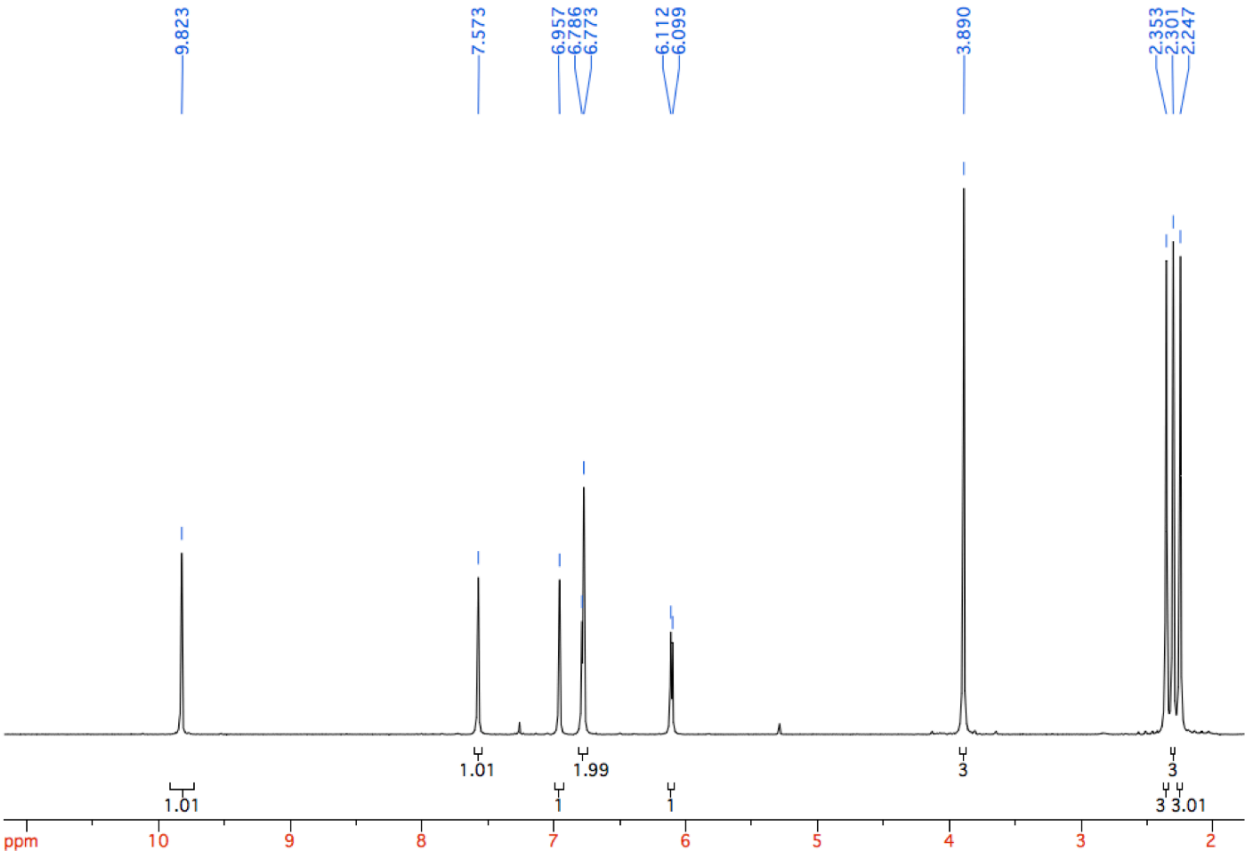

Figure S42. ^{1}H NMR spectrum of **43** in $CDCl_3$.

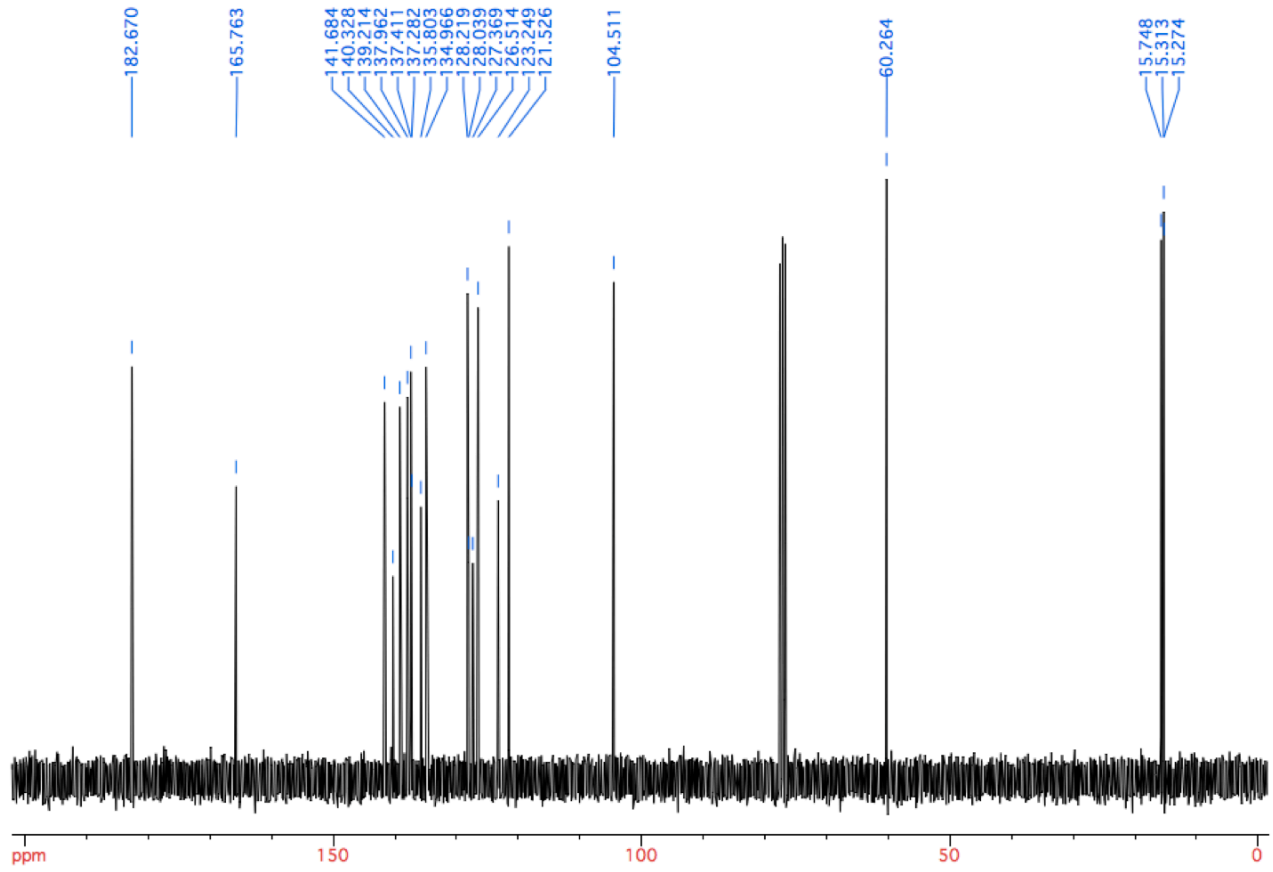

Figure S43. ^{13}C NMR spectrum of **43** in $CDCl_3$.

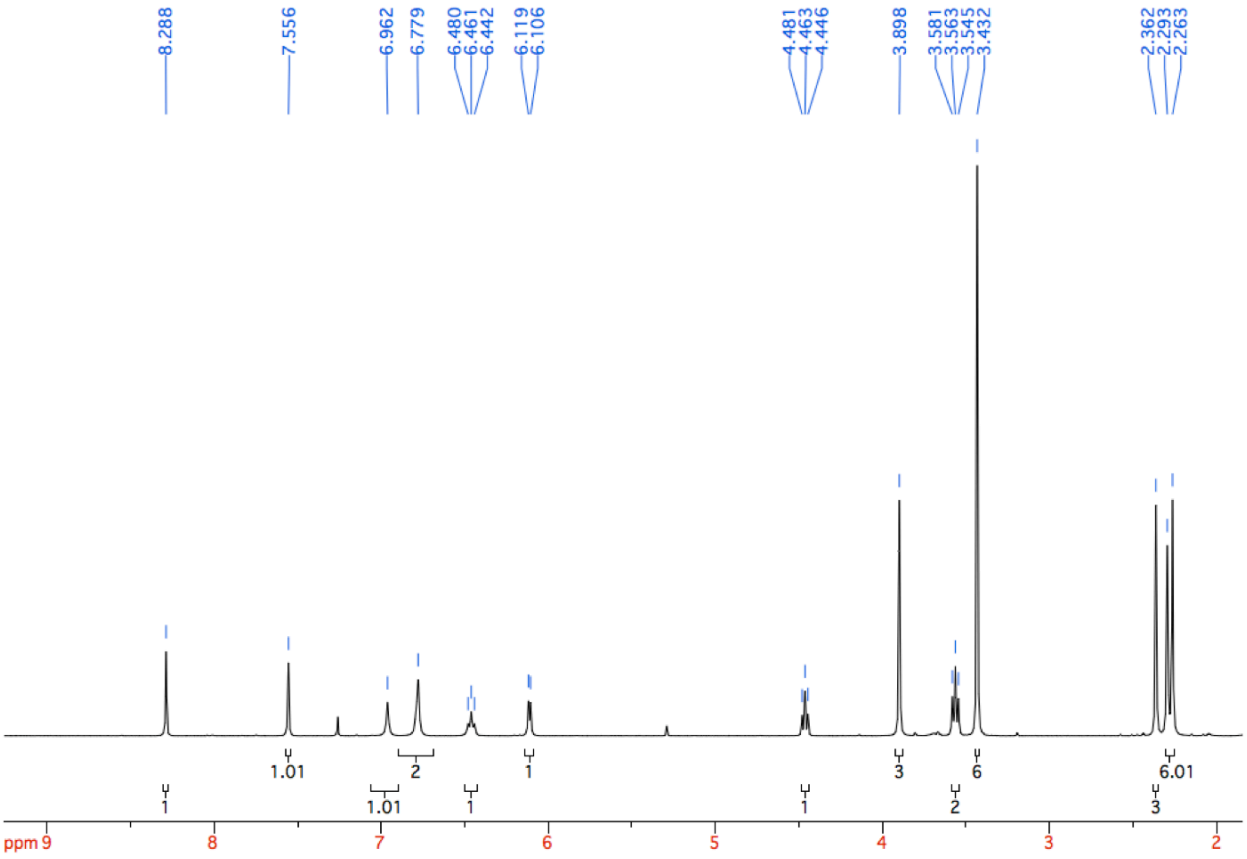

Figure S44. ^{1}H NMR spectrum of **44** in $CDCl_3$.

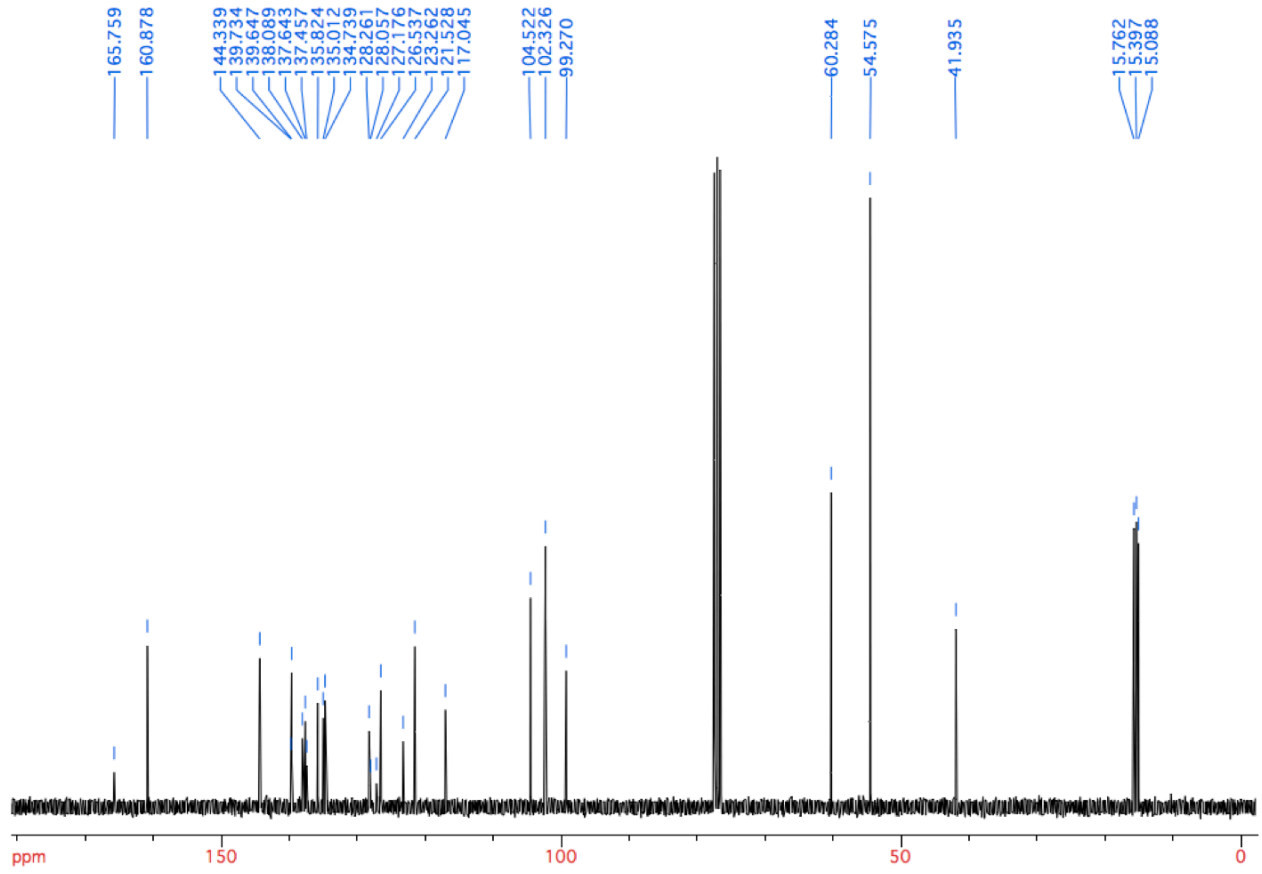

Figure S45. ^{13}C NMR spectrum of **44** in $CDCl_3$.

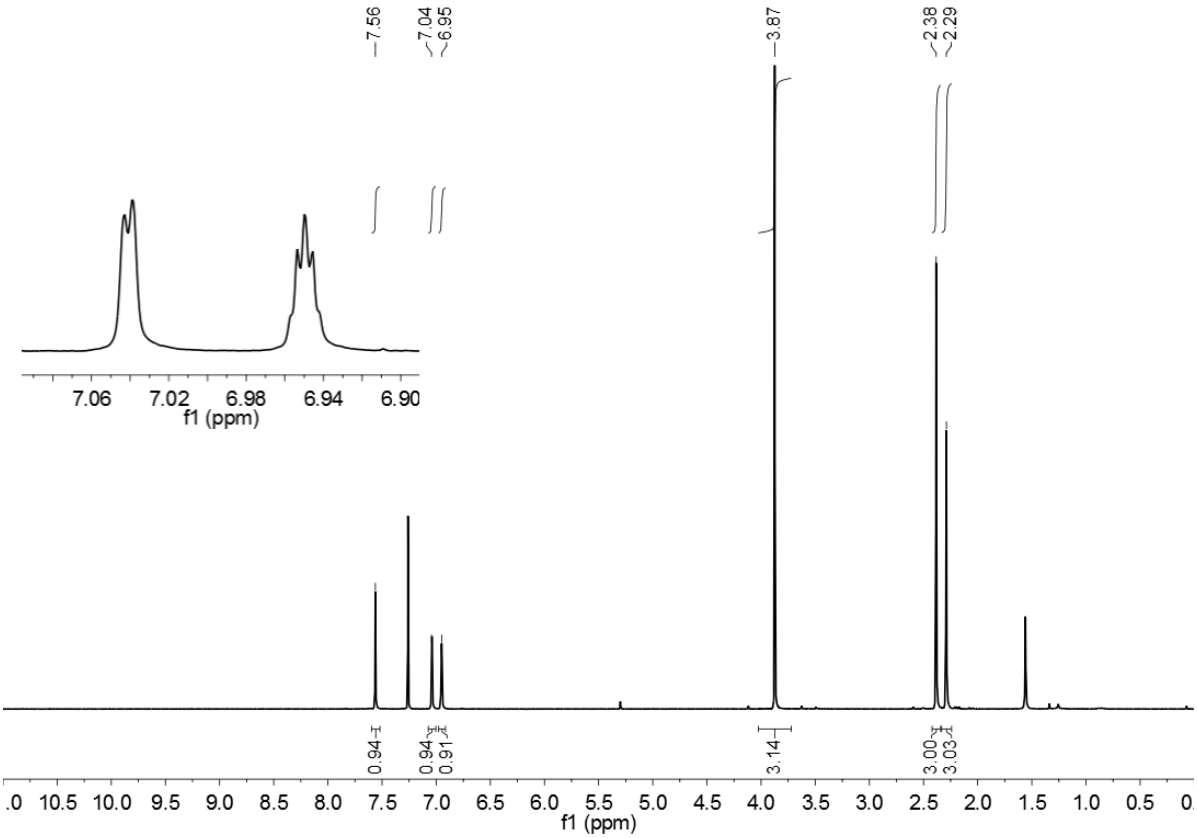

Figure S46. ^{1}H NMR spectrum of **46** in $CDCl_3$.

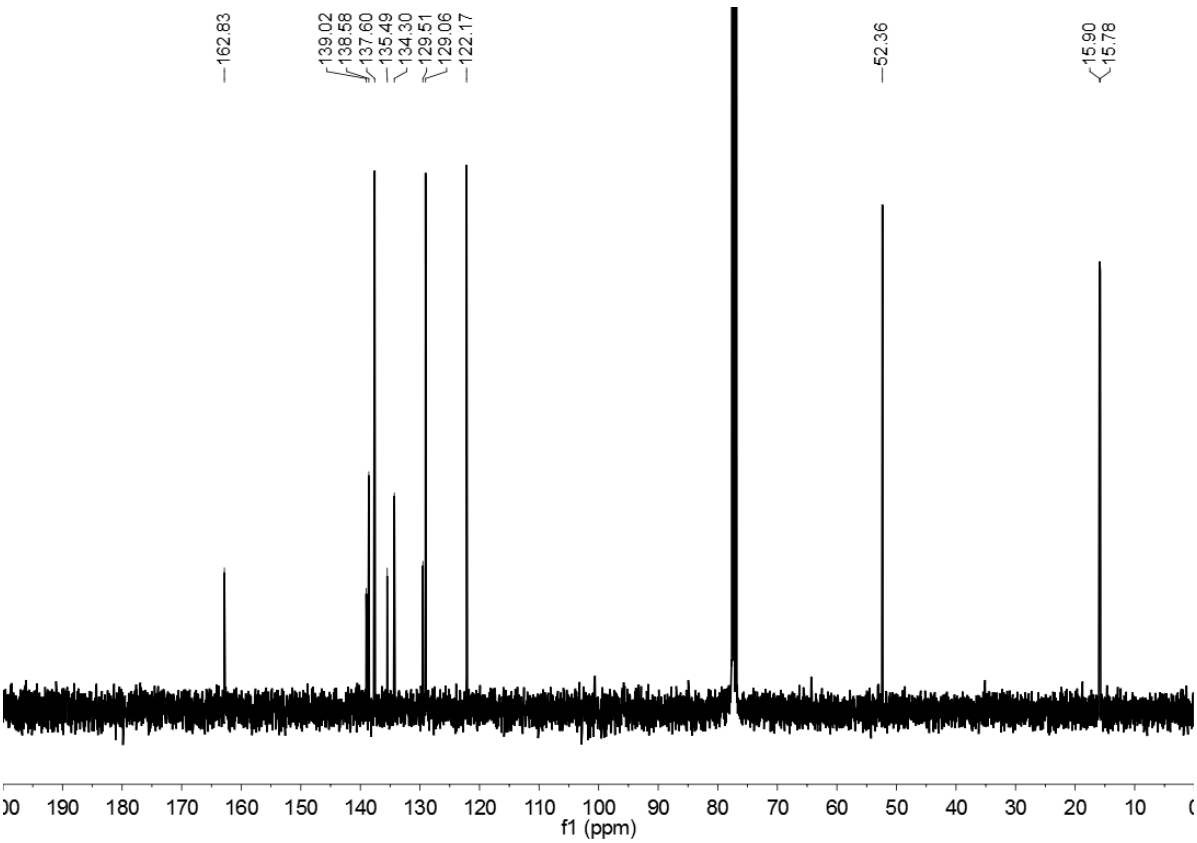

Figure S47. ^{13}C NMR spectrum of **46** in $CDCl_3$

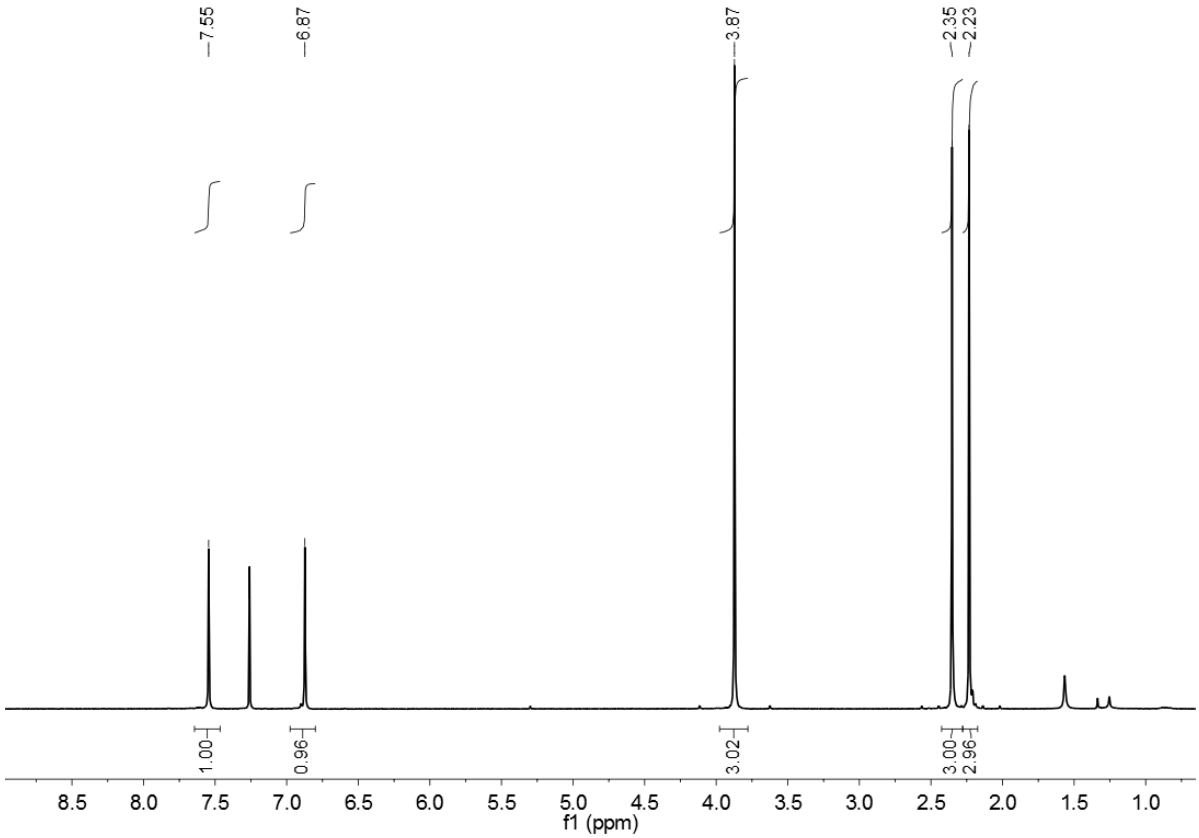

Figure S48. ^{1}H NMR spectrum of **47** in $CDCl_3$.

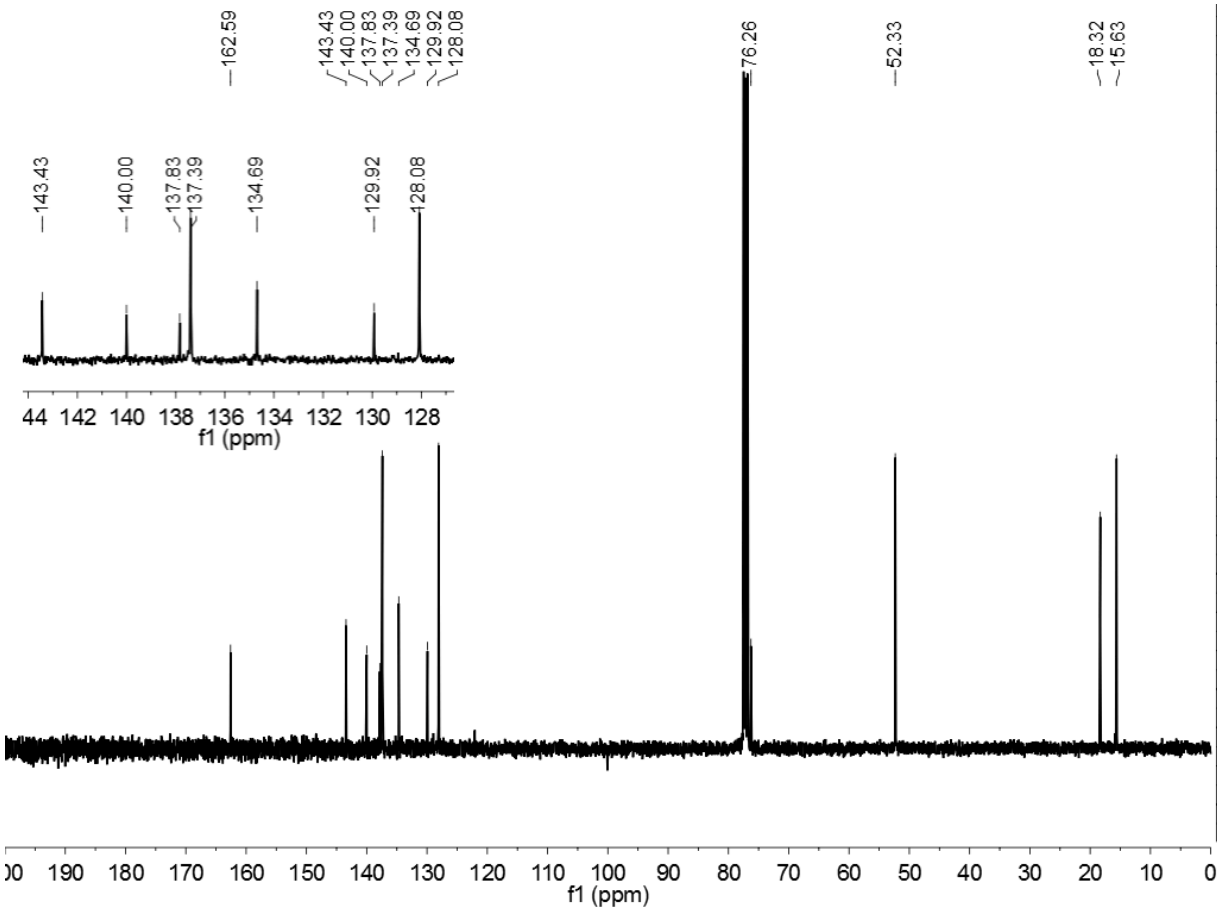

Figure S49. ^{13}C NMR spectrum of **47** in $CDCl_3$

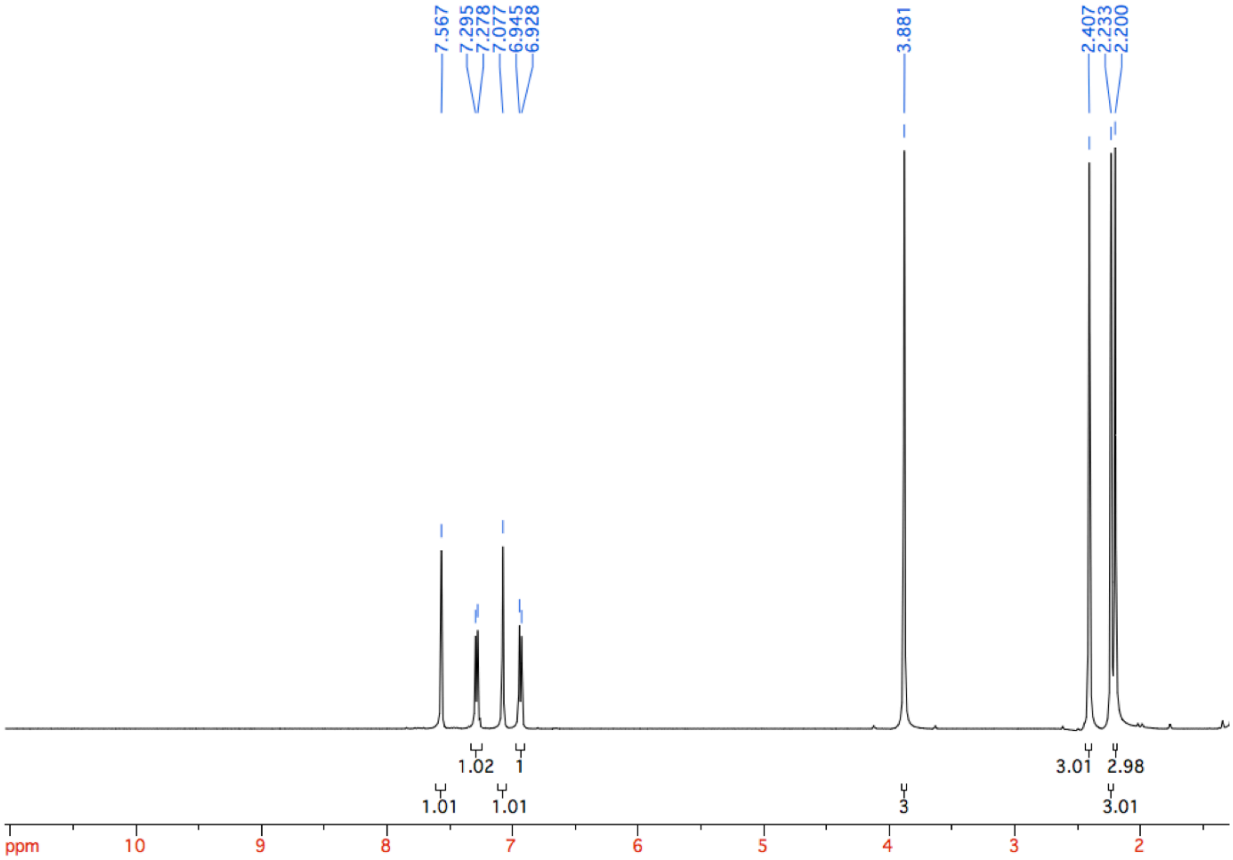

Figure S50. ^{1}H NMR spectrum of **48** in $CDCl_3$.

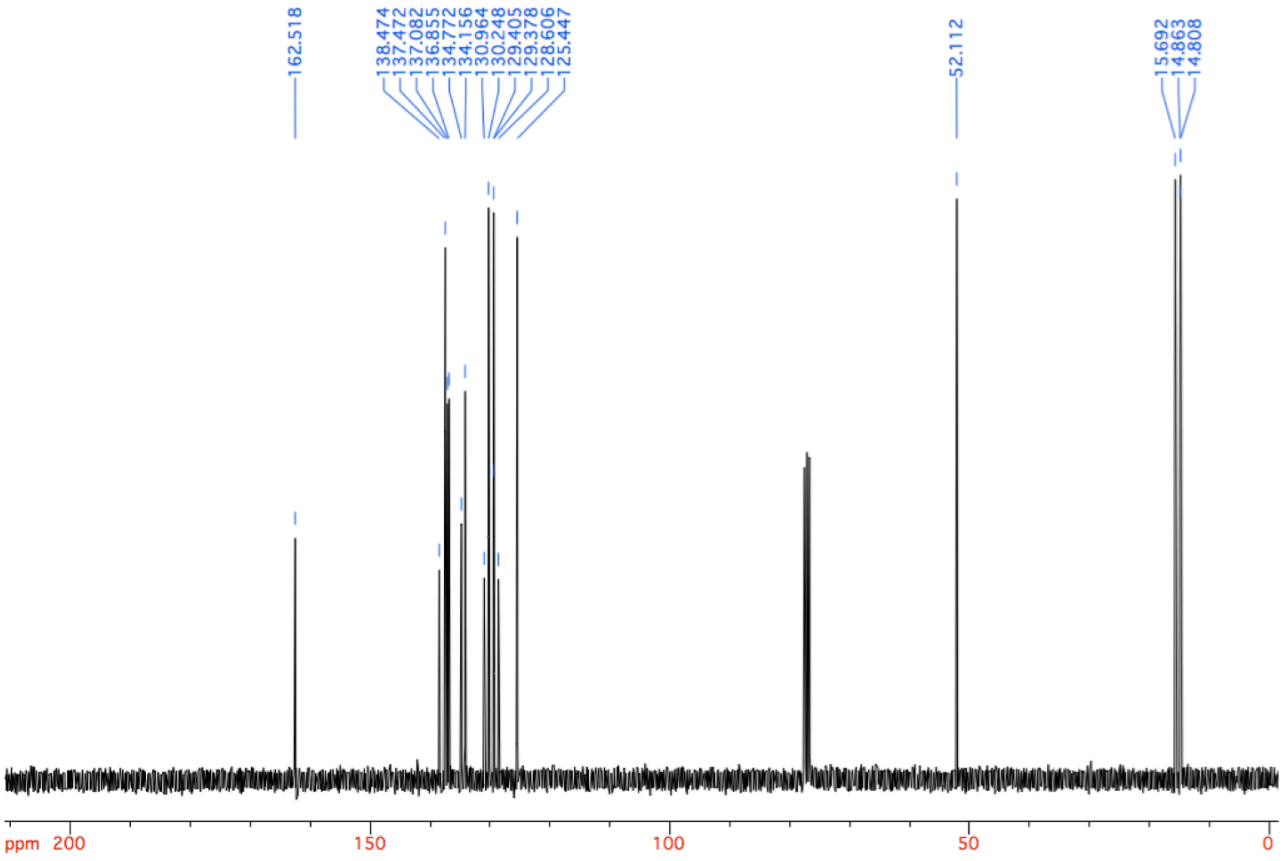

Figure S51. ^{13}C NMR spectrum of **48** in $CDCl_3$.

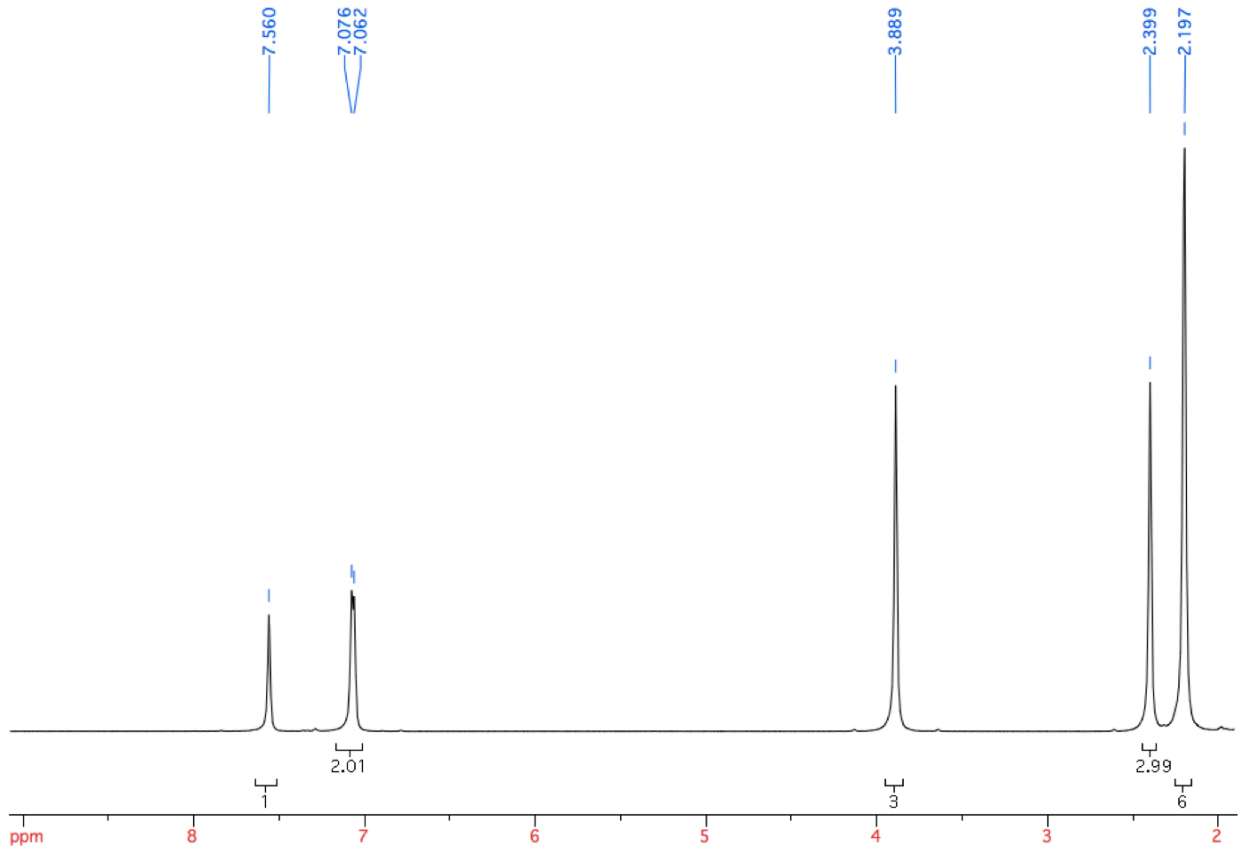

Figure S52. ^{1}H NMR spectrum of **49** in $CDCl_3$.

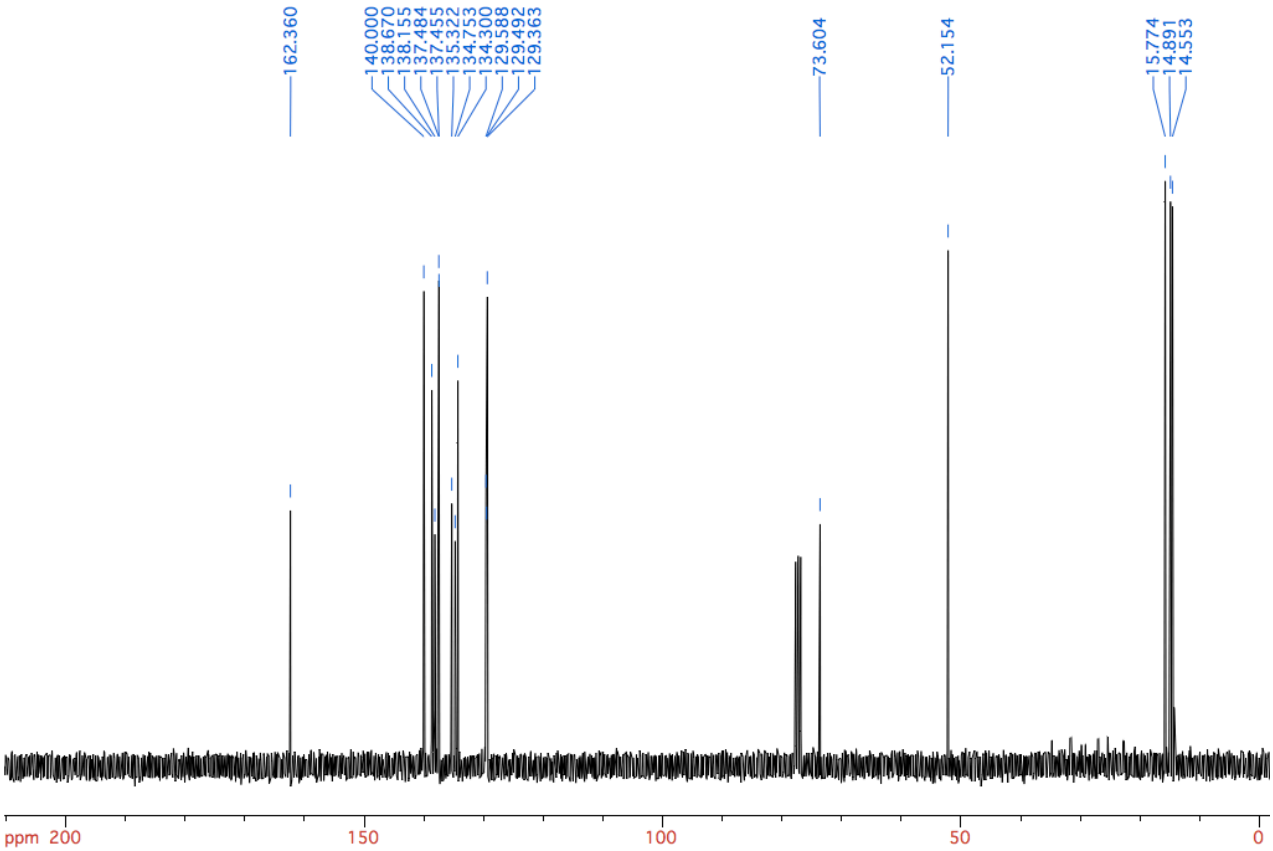

Figure S53. ^{13}C NMR spectrum of **49** in $CDCl_3$.

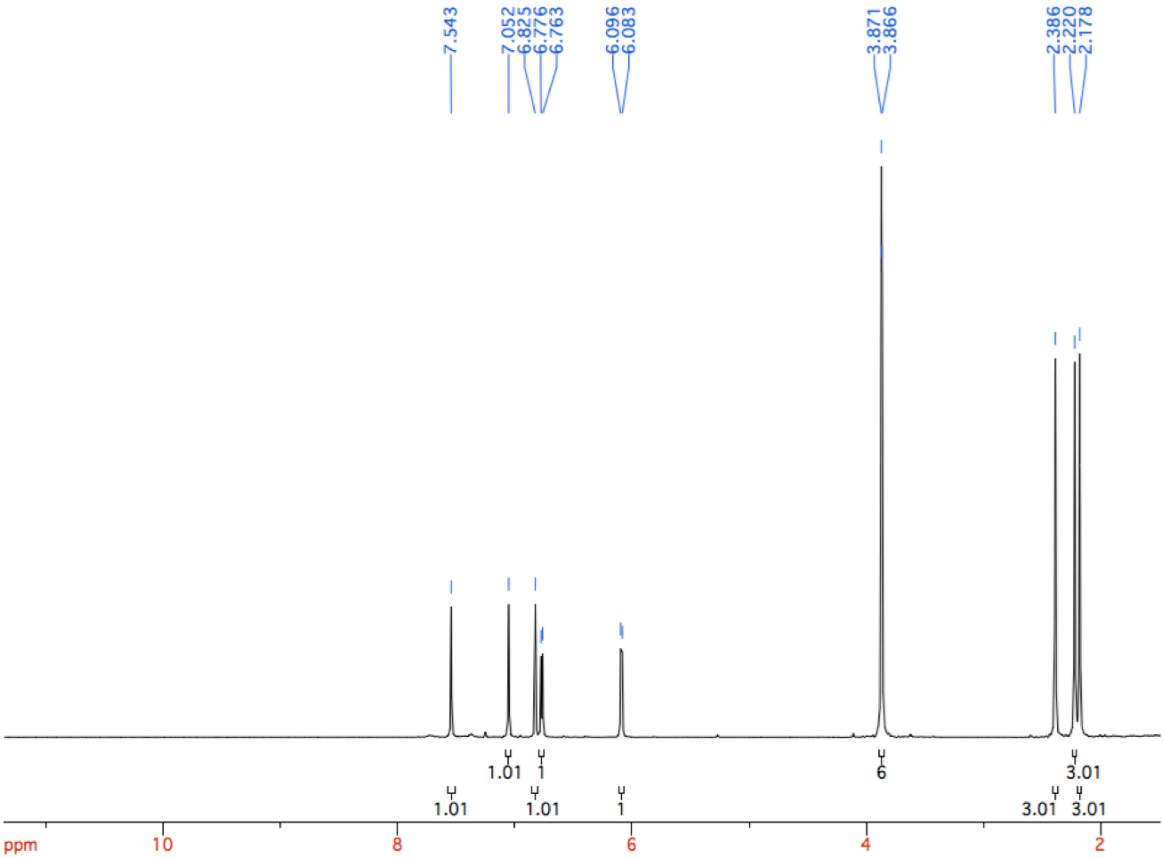

Figure S54. ^{1}H NMR spectrum of **50** in $CDCl_3$.

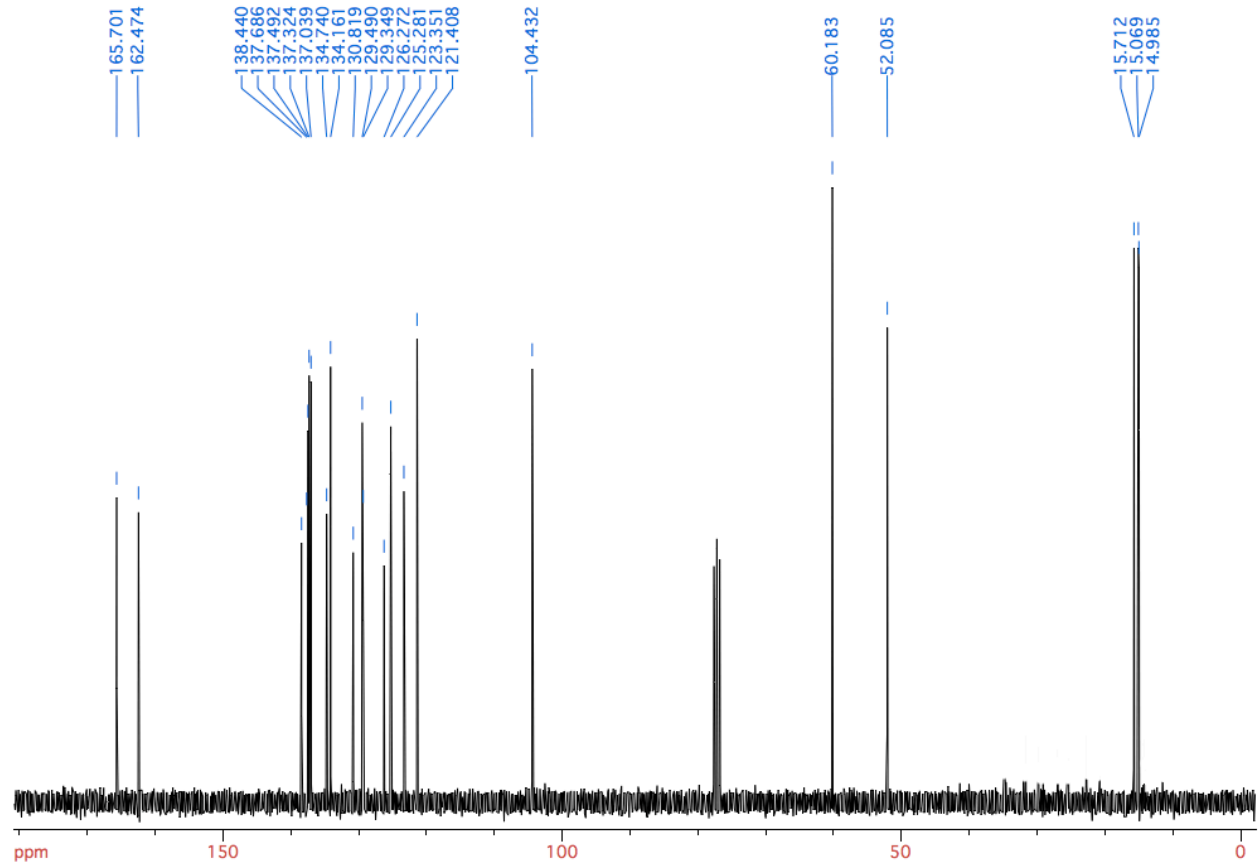

Figure S55. ^{13}C NMR spectrum of **50** in $CDCl_3$.

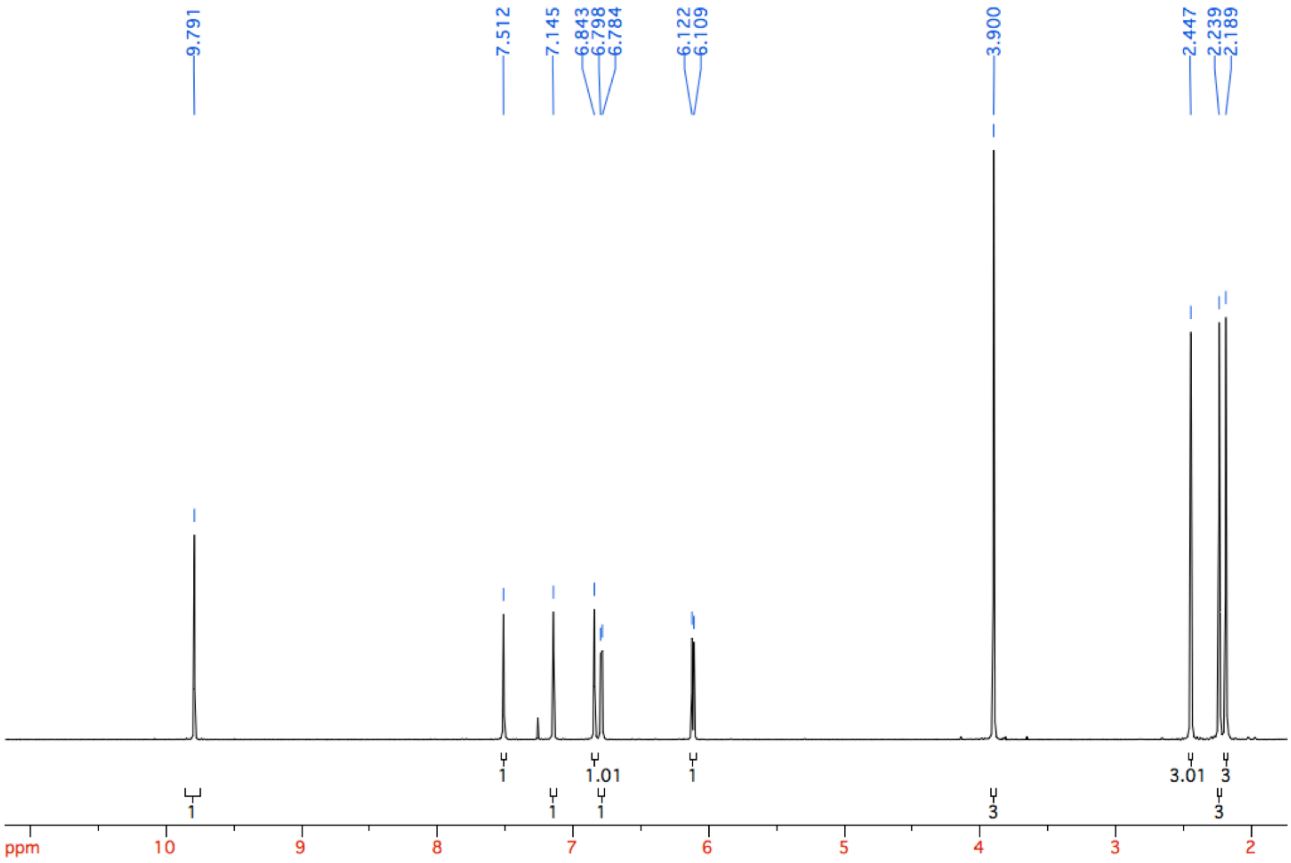

Figure S56. ^{1}H NMR spectrum of **51** in $CDCl_3$.

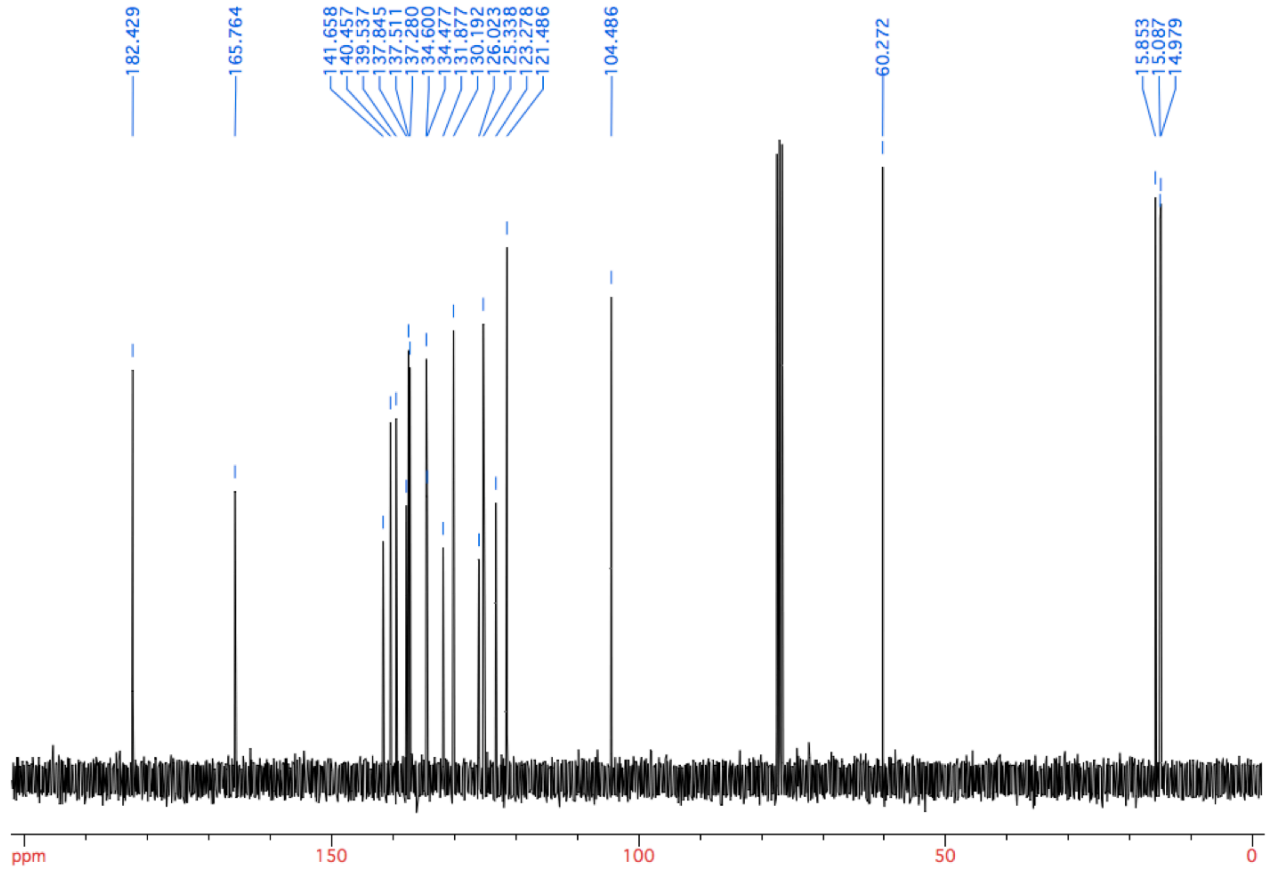

Figure S57. ^{13}C NMR spectrum of **51** in $CDCl_3$.

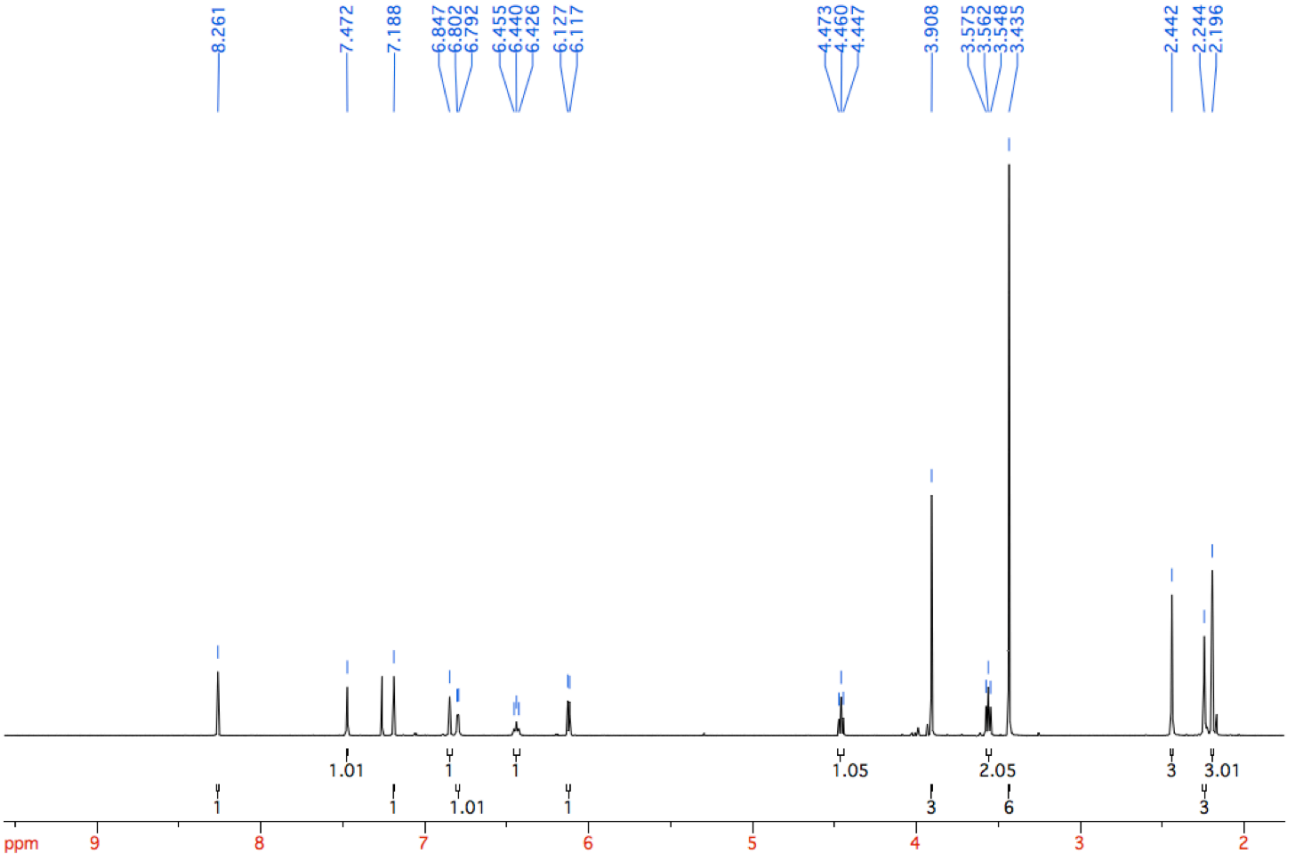

Figure S58. ^{1}H NMR spectrum of **52** in $CDCl_3$.

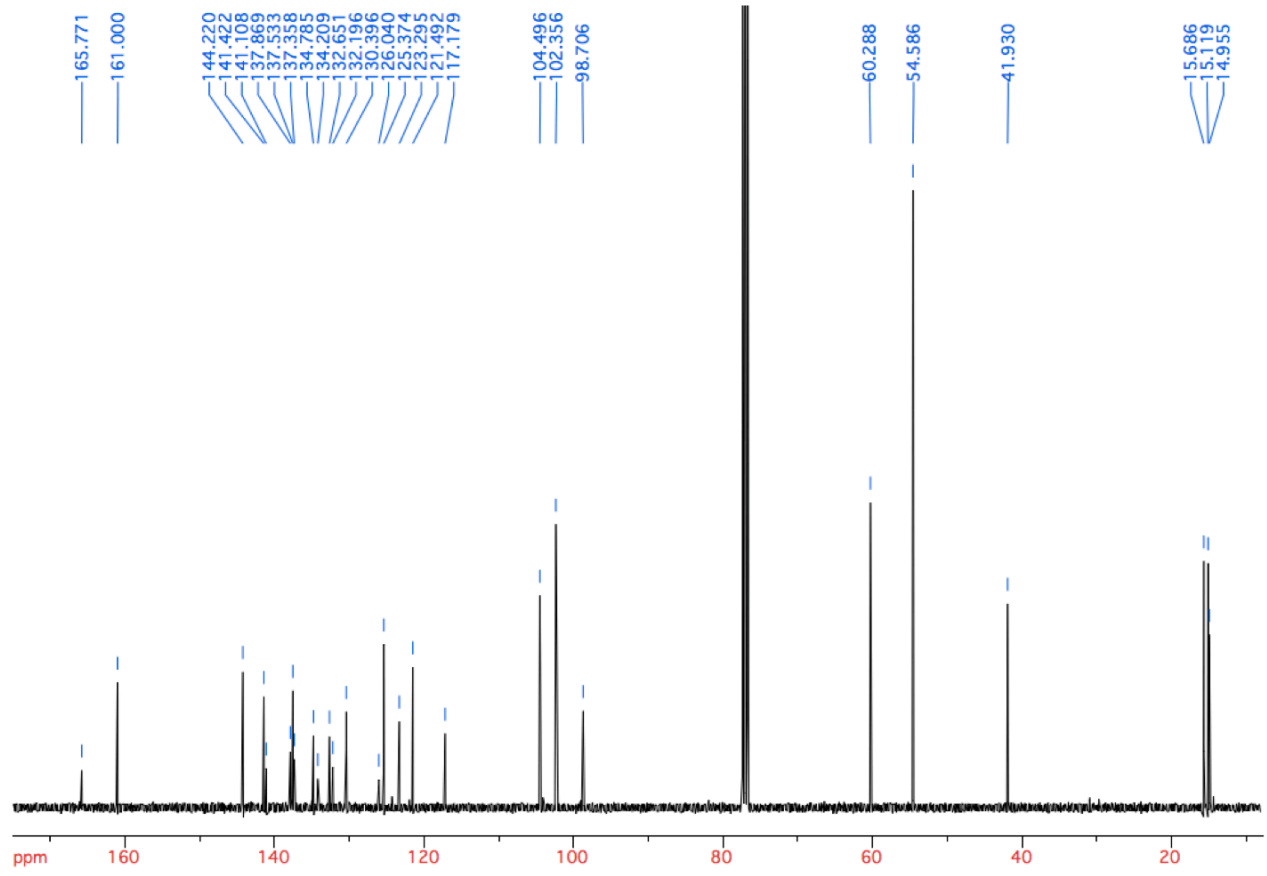

Figure S59. ^{13}C NMR spectrum of **52** in $CDCl_3$.

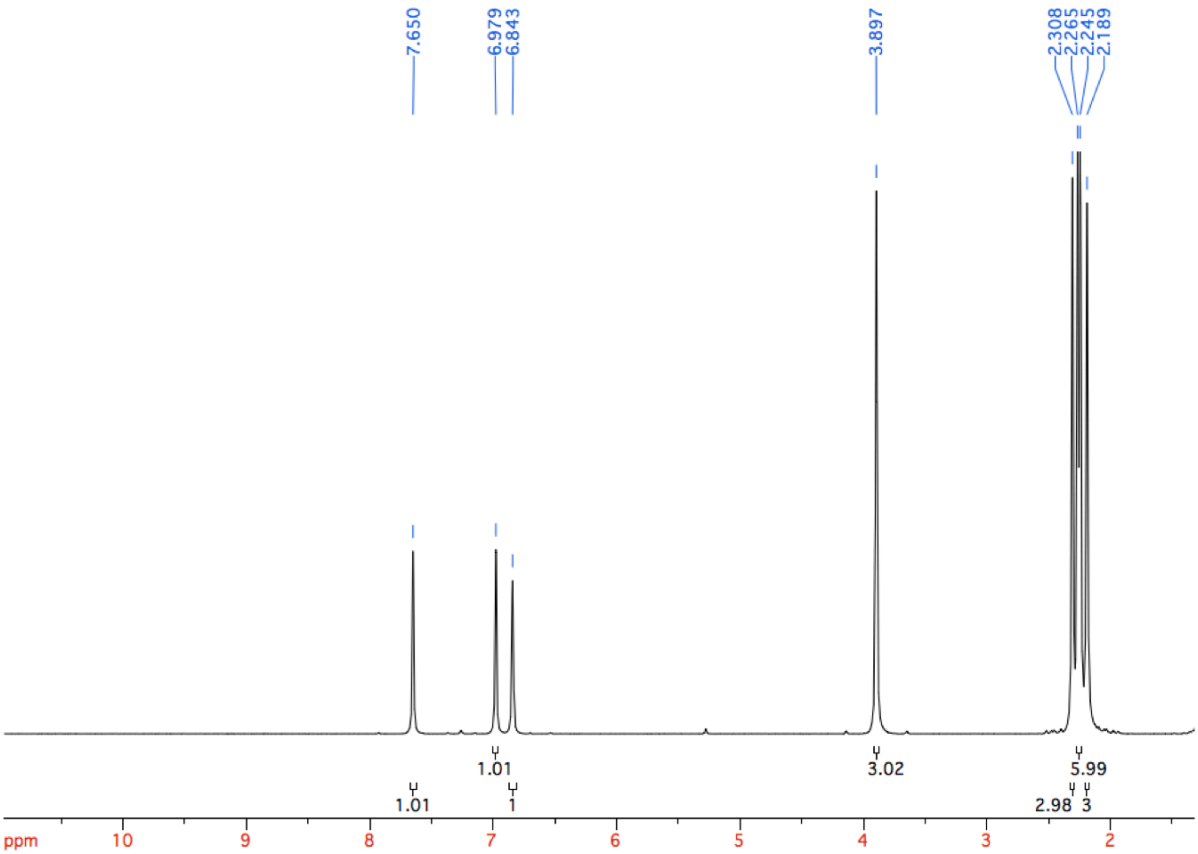

Figure S60. ^{1}H NMR spectrum of **53** in $CDCl_3$.

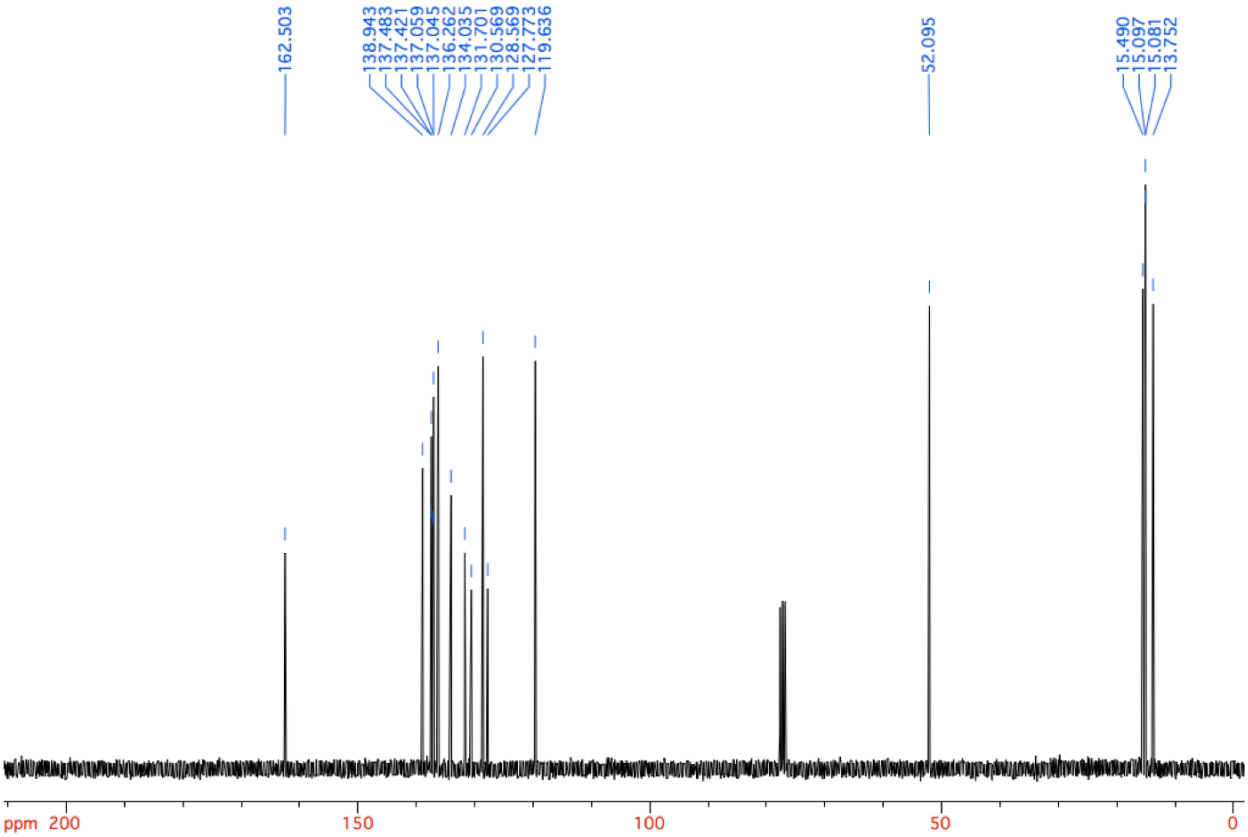

Figure S61. ^{13}C NMR spectrum of **53** in $CDCl_3$.

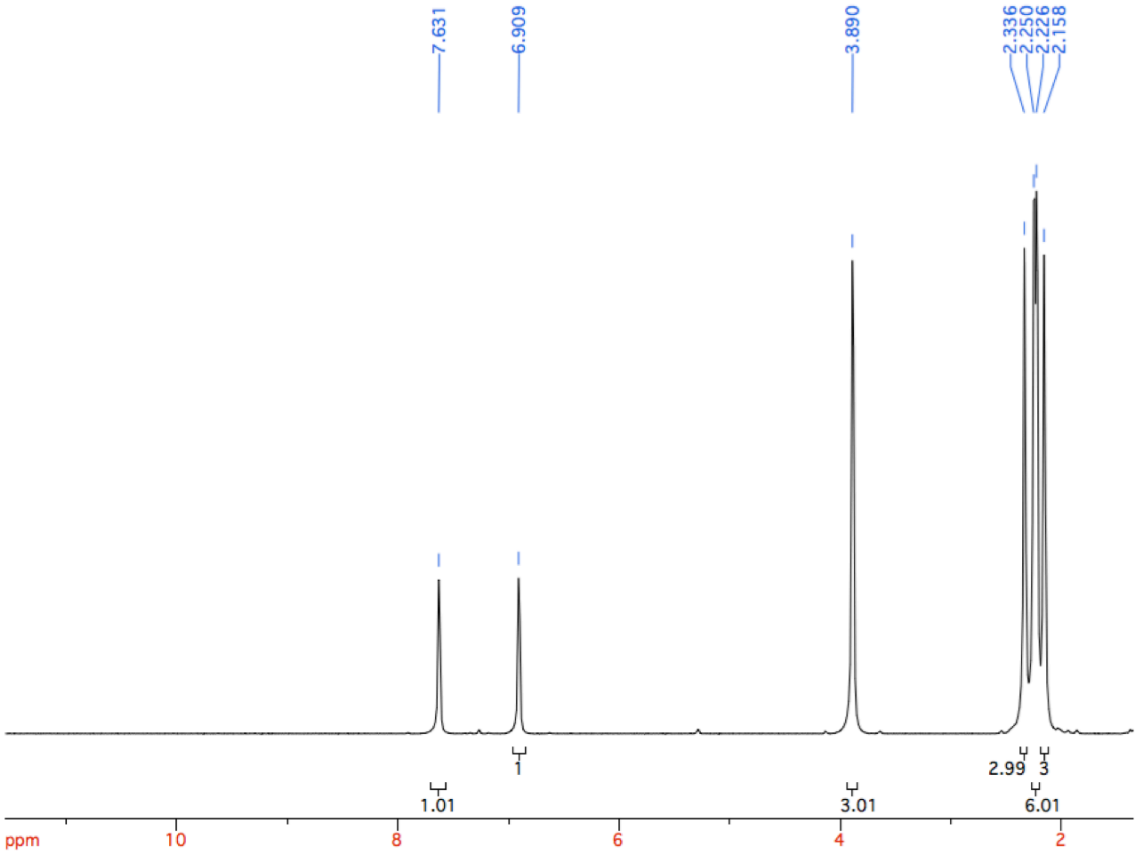

Figure S62. ^{1}H NMR spectrum of **54** in $CDCl_3$.

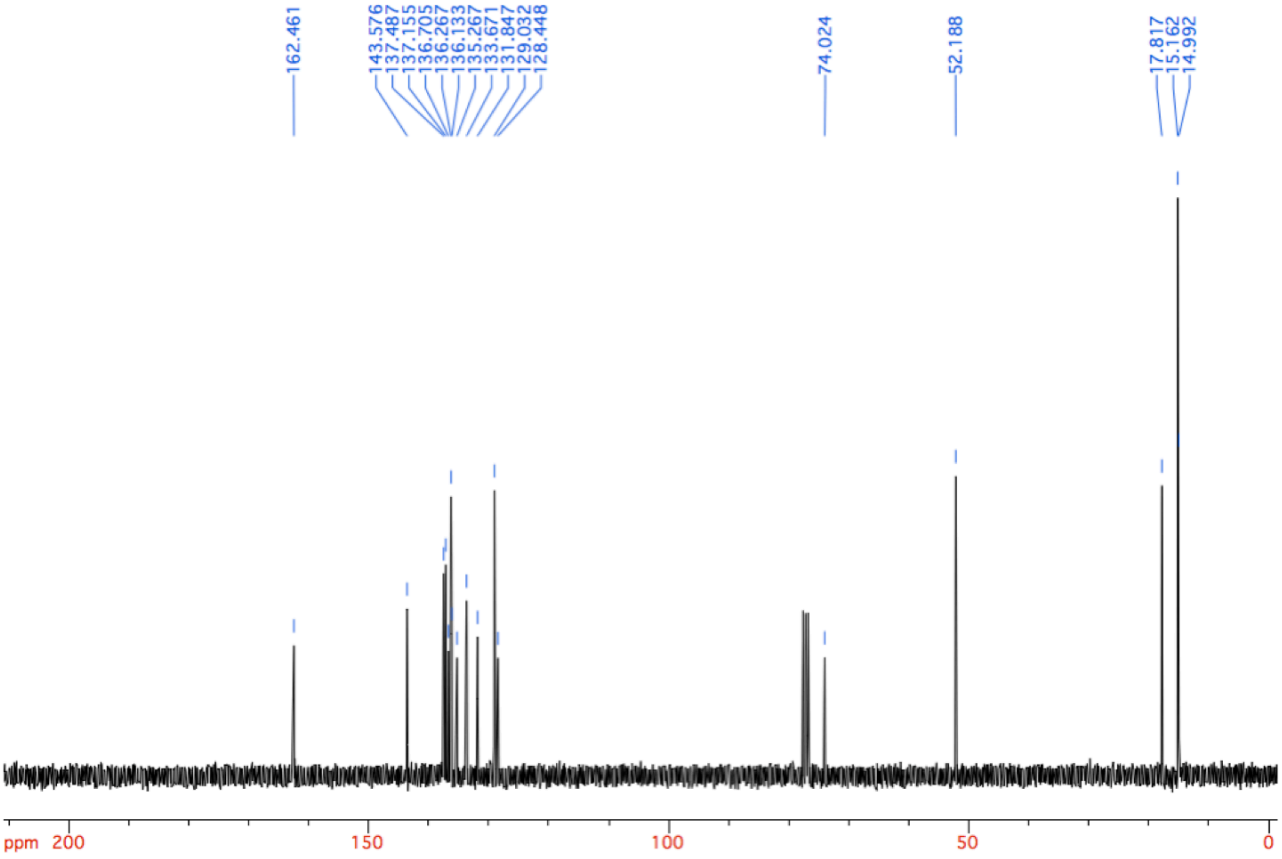

Figure S63. ^{13}C NMR spectrum of **54** in $CDCl_3$.

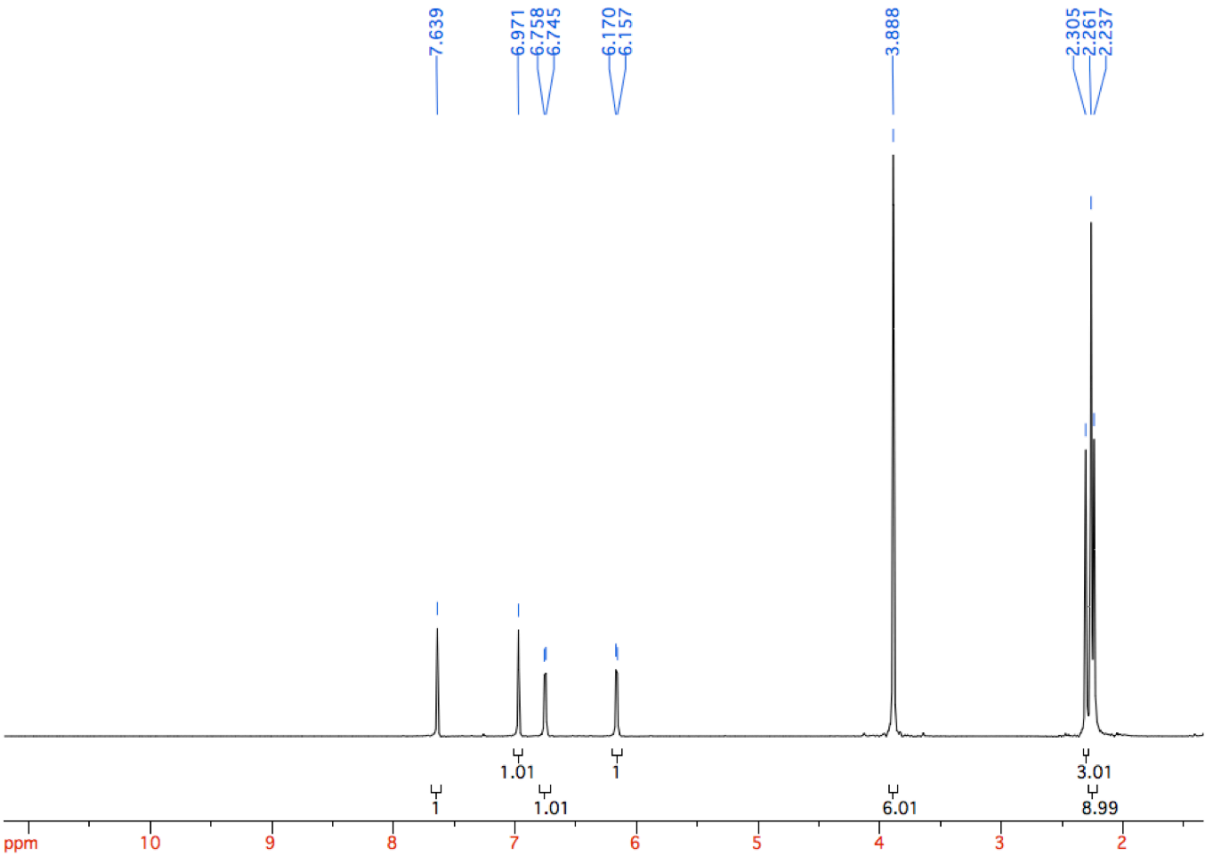

Figure S64. ^{1}H NMR spectrum of **55** in $CDCl_3$.

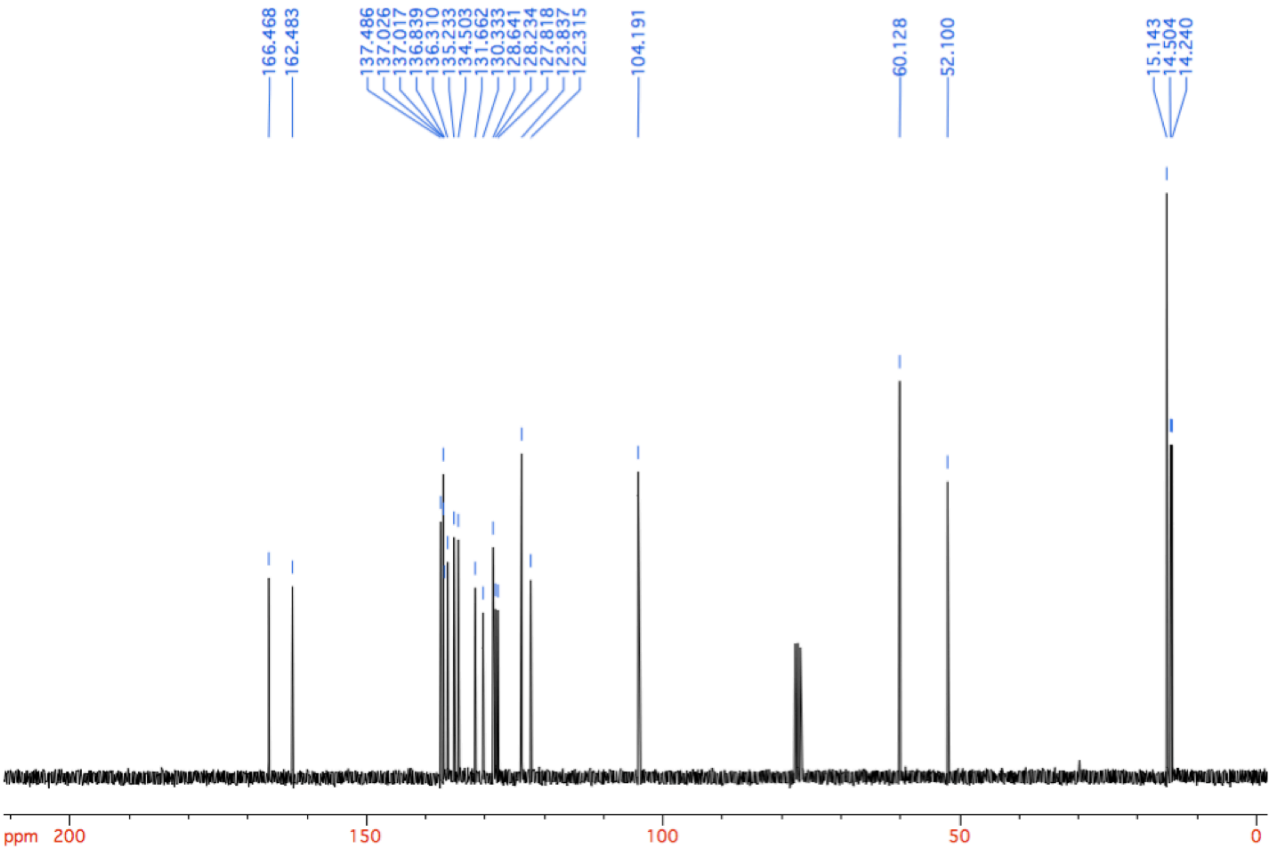

Figure S65. ^{13}C NMR spectrum of **55** in $CDCl_3$.

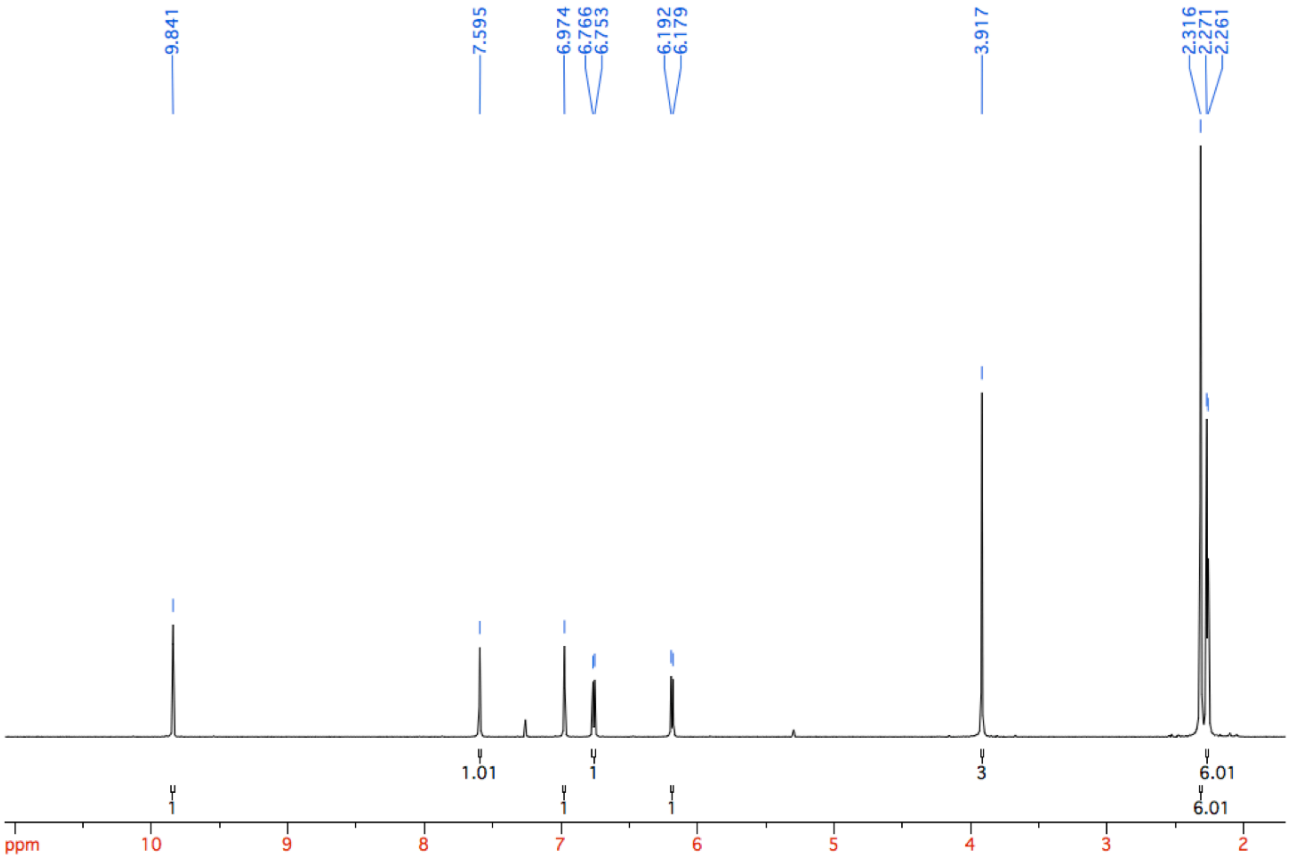

Figure S66. ^{1}H NMR spectrum of **56** in $CDCl_3$.

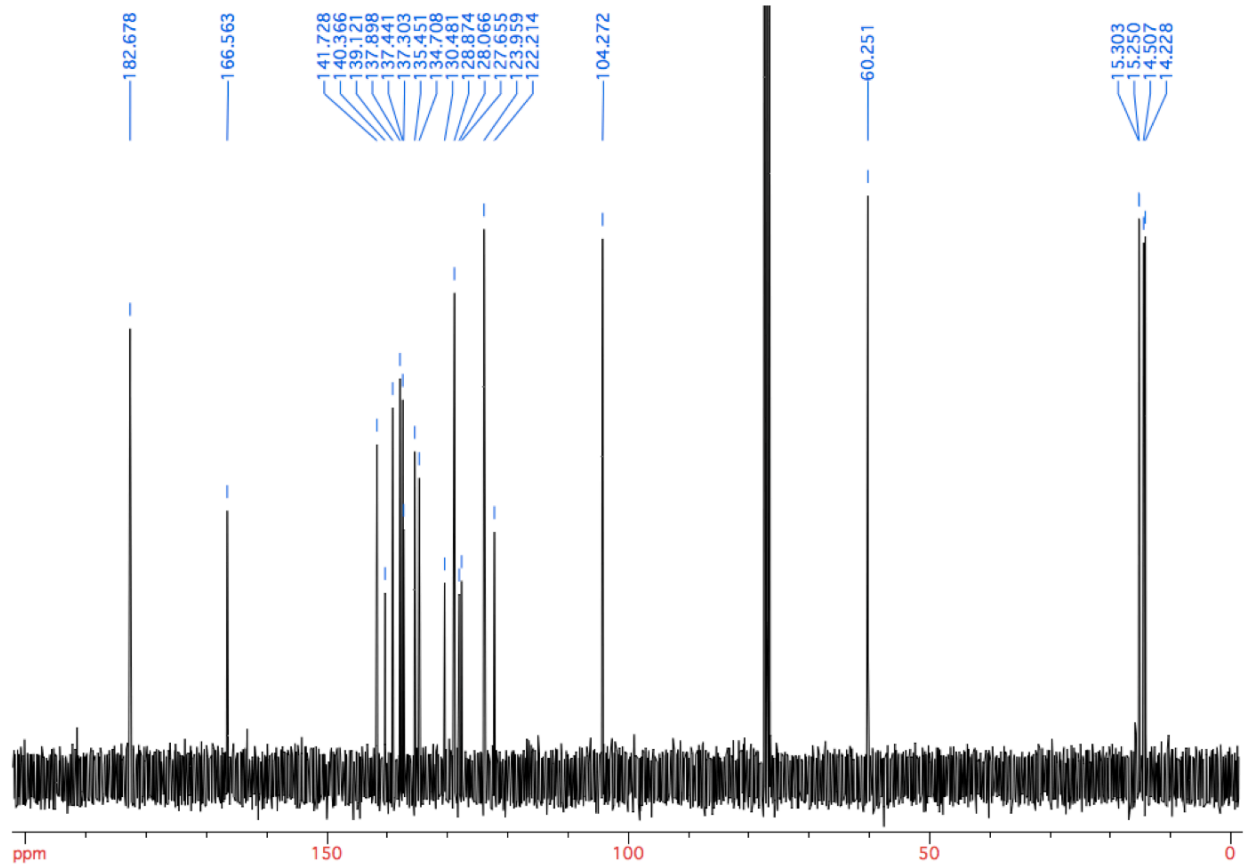

Figure S67. ^{13}C NMR spectrum of **56** in $CDCl_3$.

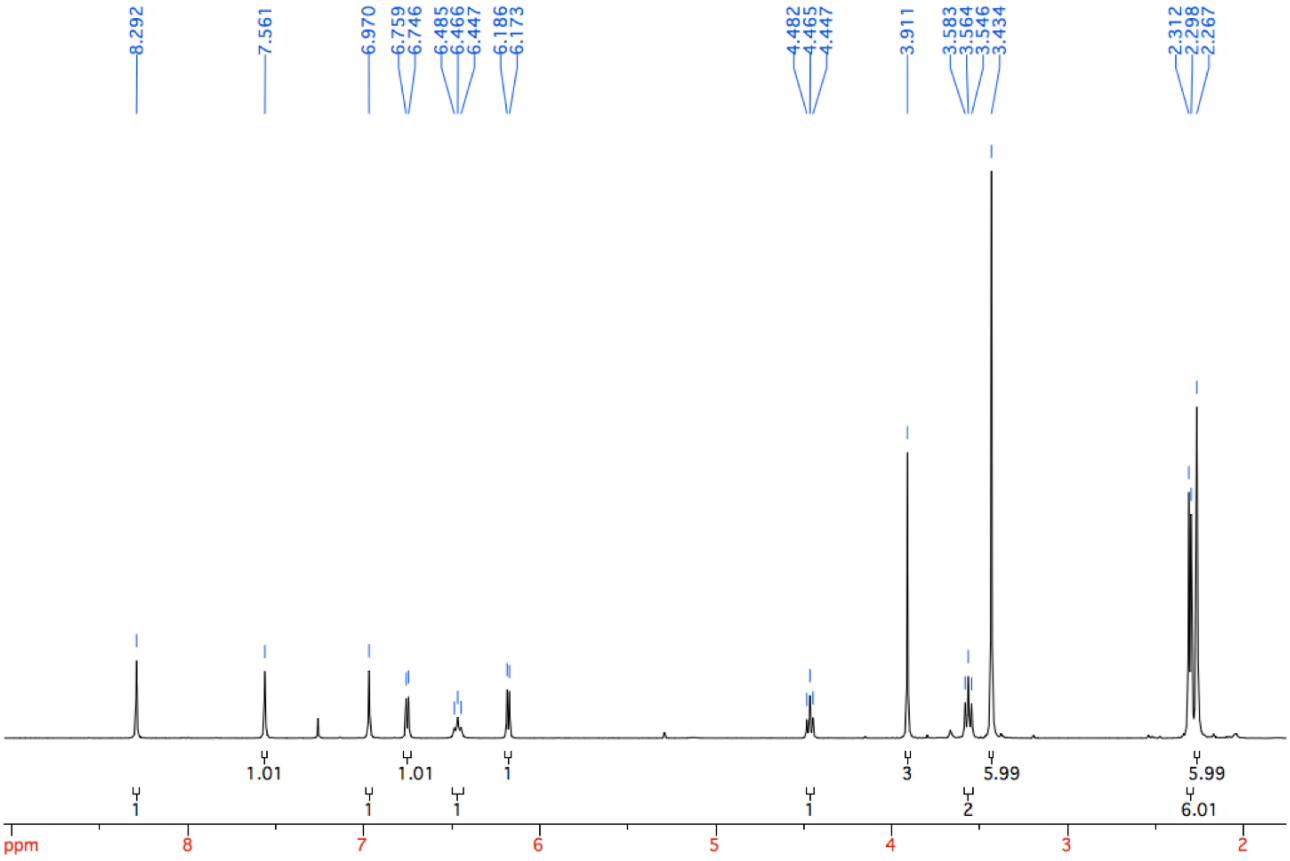

Figure S68. ^{1}H NMR spectrum of **57** in $CDCl_3$.

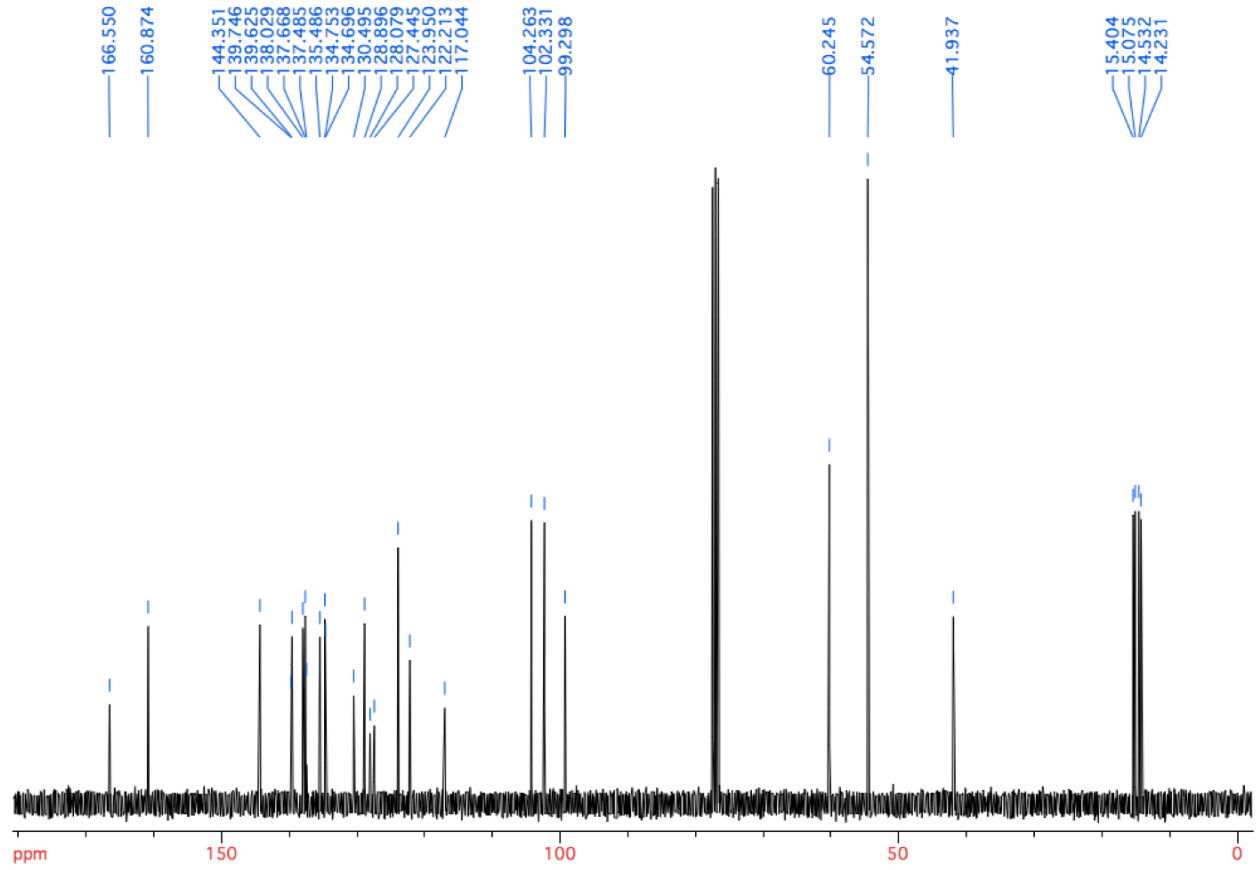

Figure S69. ^{13}C NMR spectrum of **57** in $CDCl_3$.

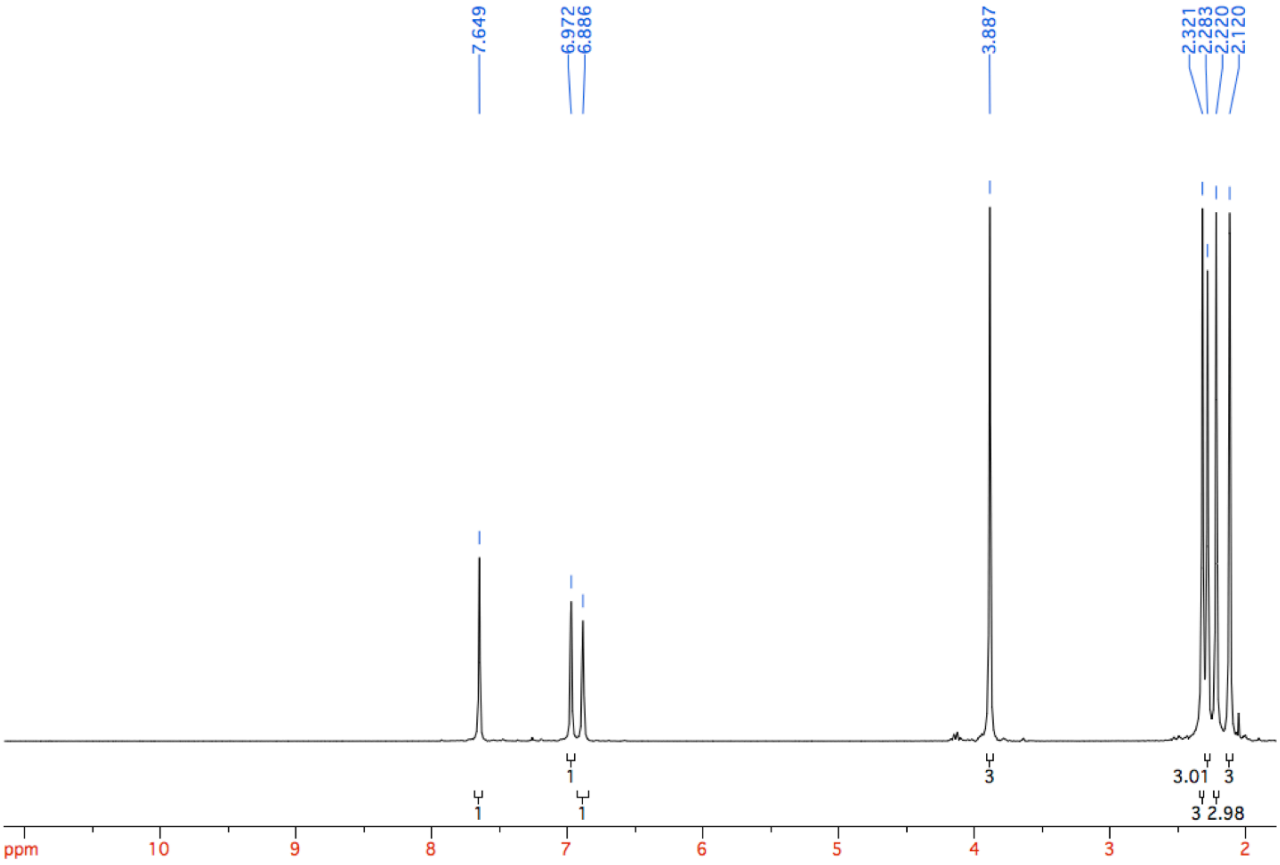

Figure S70. ^{1}H NMR spectrum of **58** in $CDCl_3$.

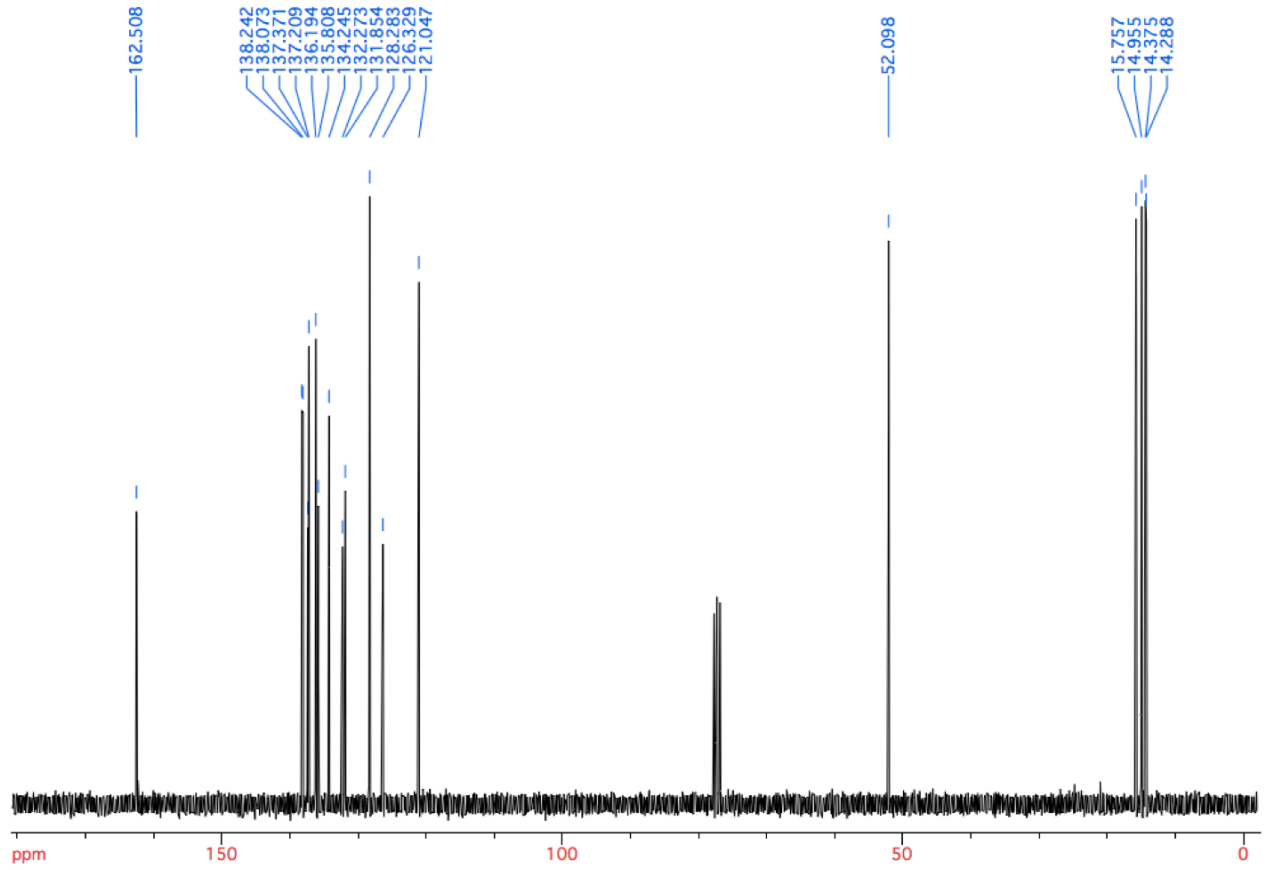

Figure S71. ^{13}C NMR spectrum of **58** in $CDCl_3$.

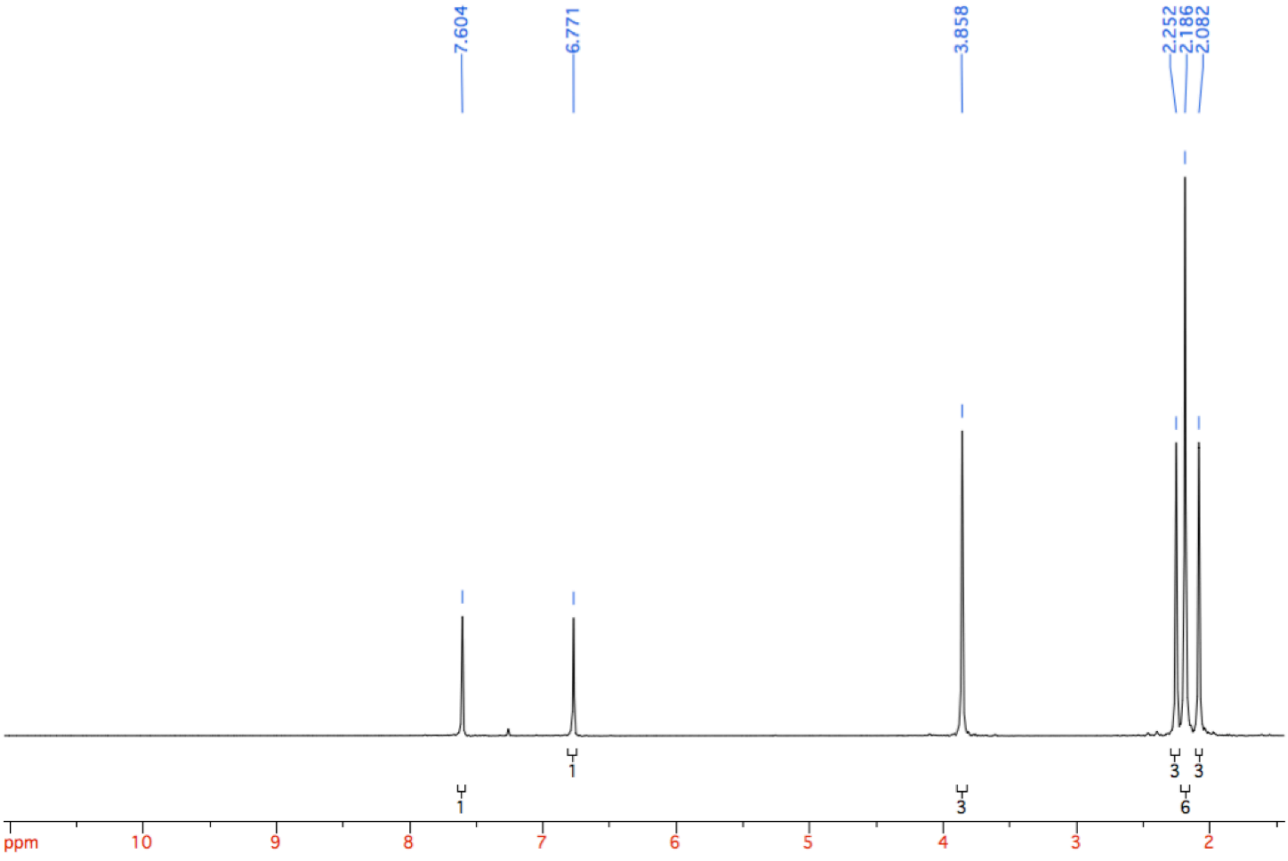

Figure S72. ^{1}H NMR spectrum of **59** in $CDCl_3$.

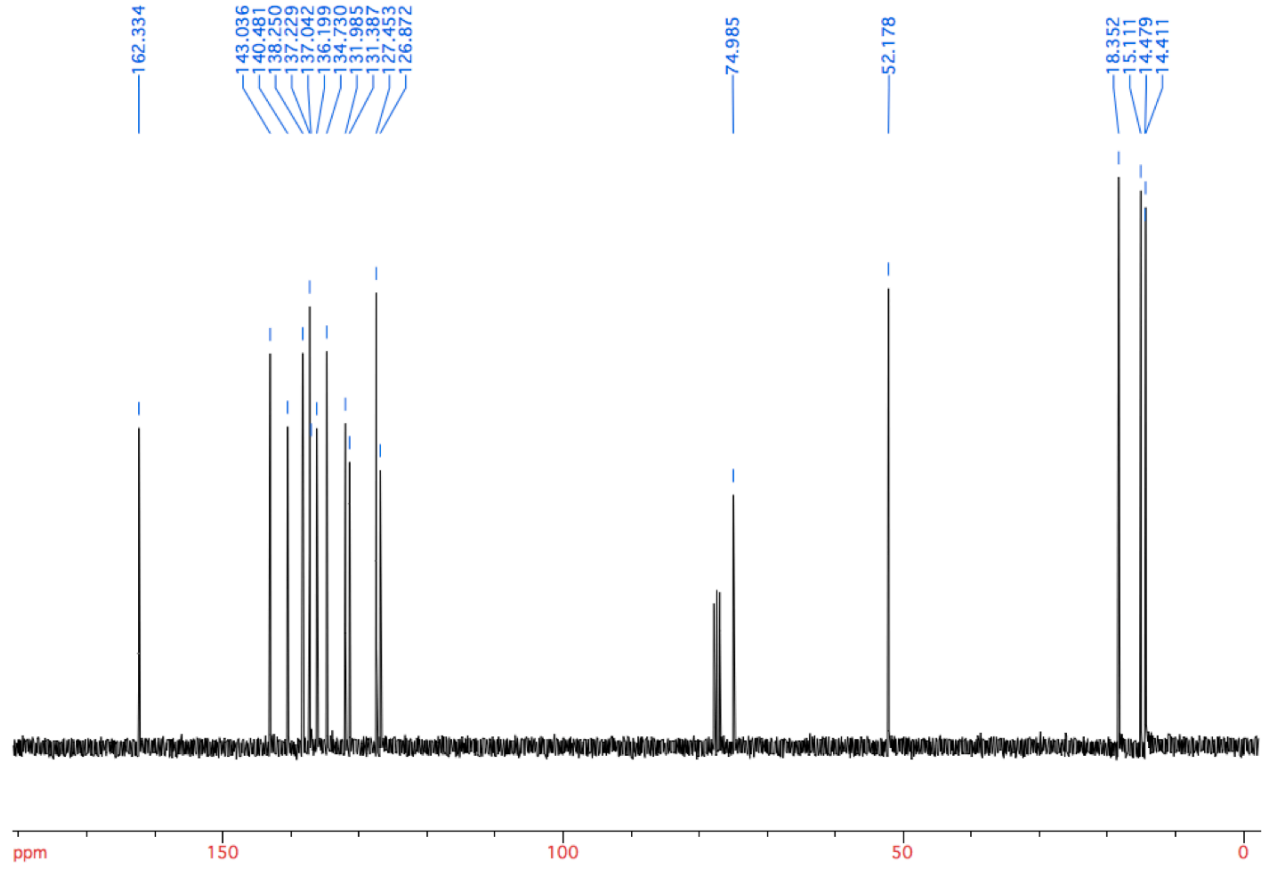

Figure S73. ^{13}C NMR spectrum of **59** in $CDCl_3$.

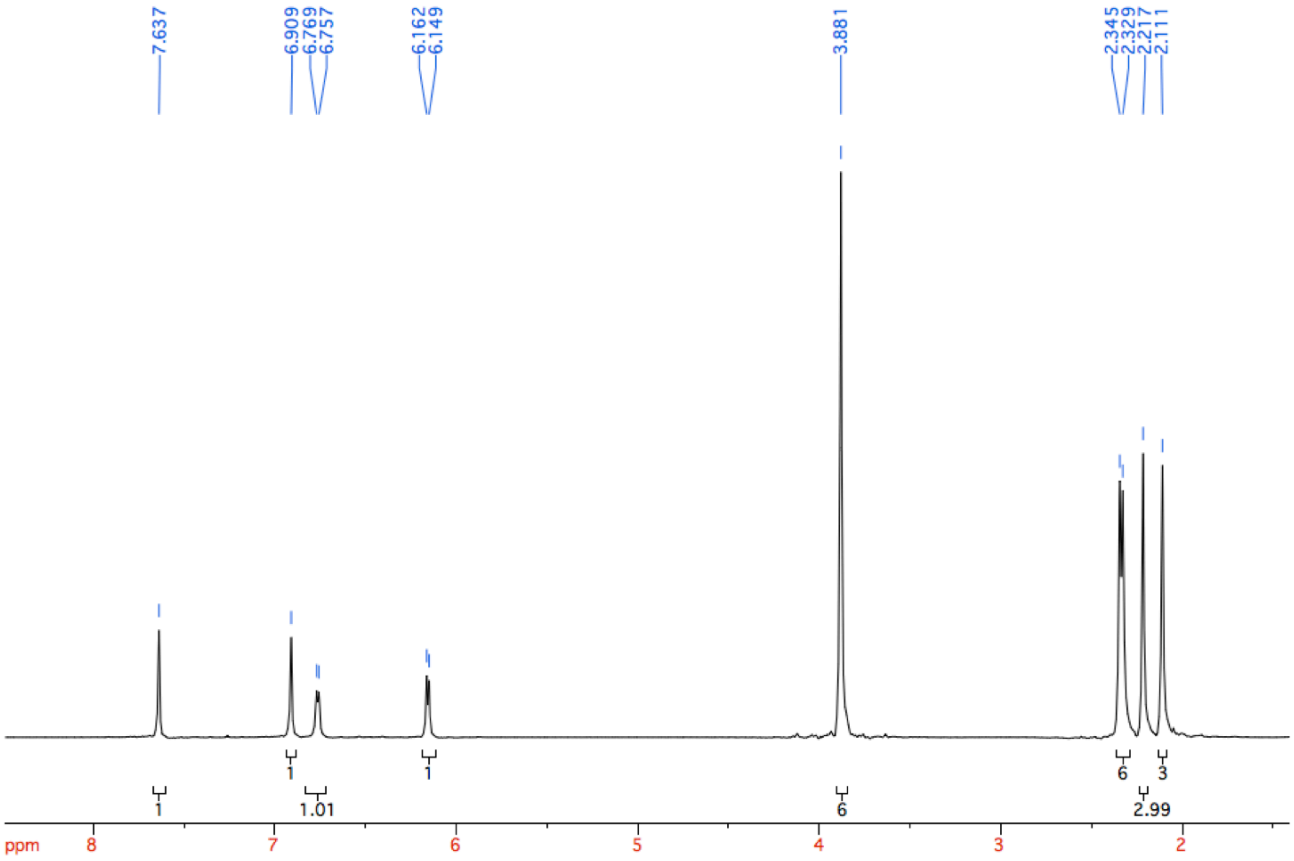

Figure S74. ^{1}H NMR spectrum of **60** in $CDCl_3$.

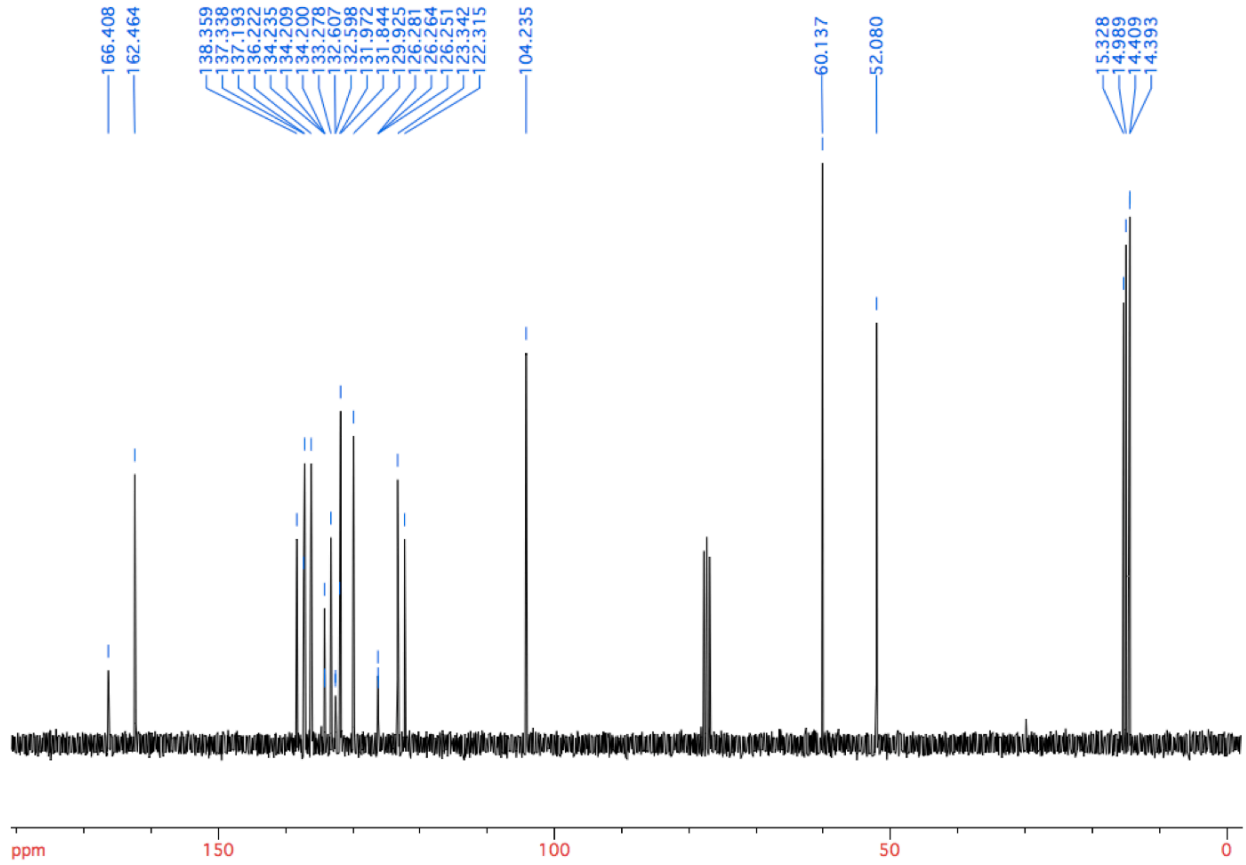

Figure S75. ^{13}C NMR spectrum of **60** in $CDCl_3$.

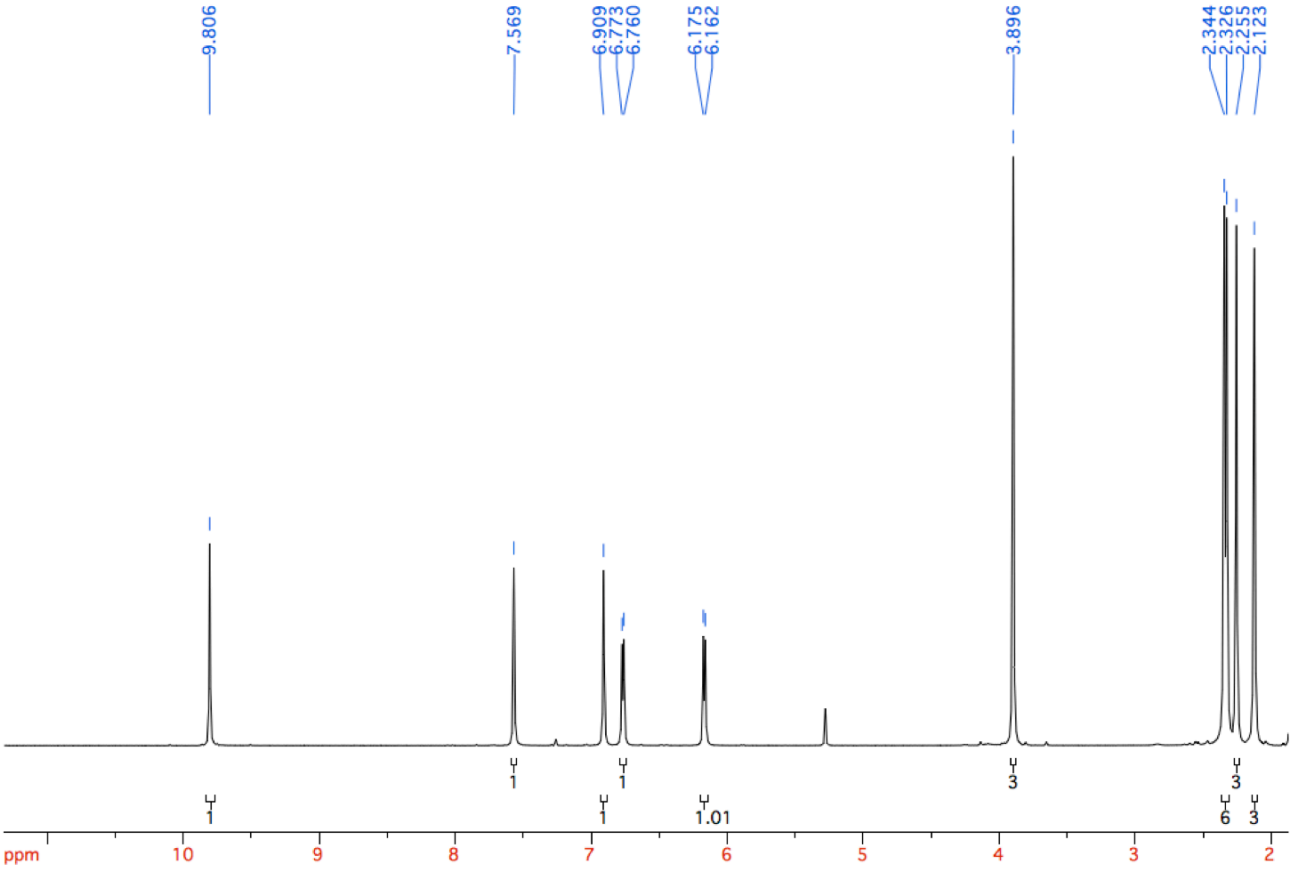

Figure S76. ^{1}H NMR spectrum of **61** in $CDCl_3$.

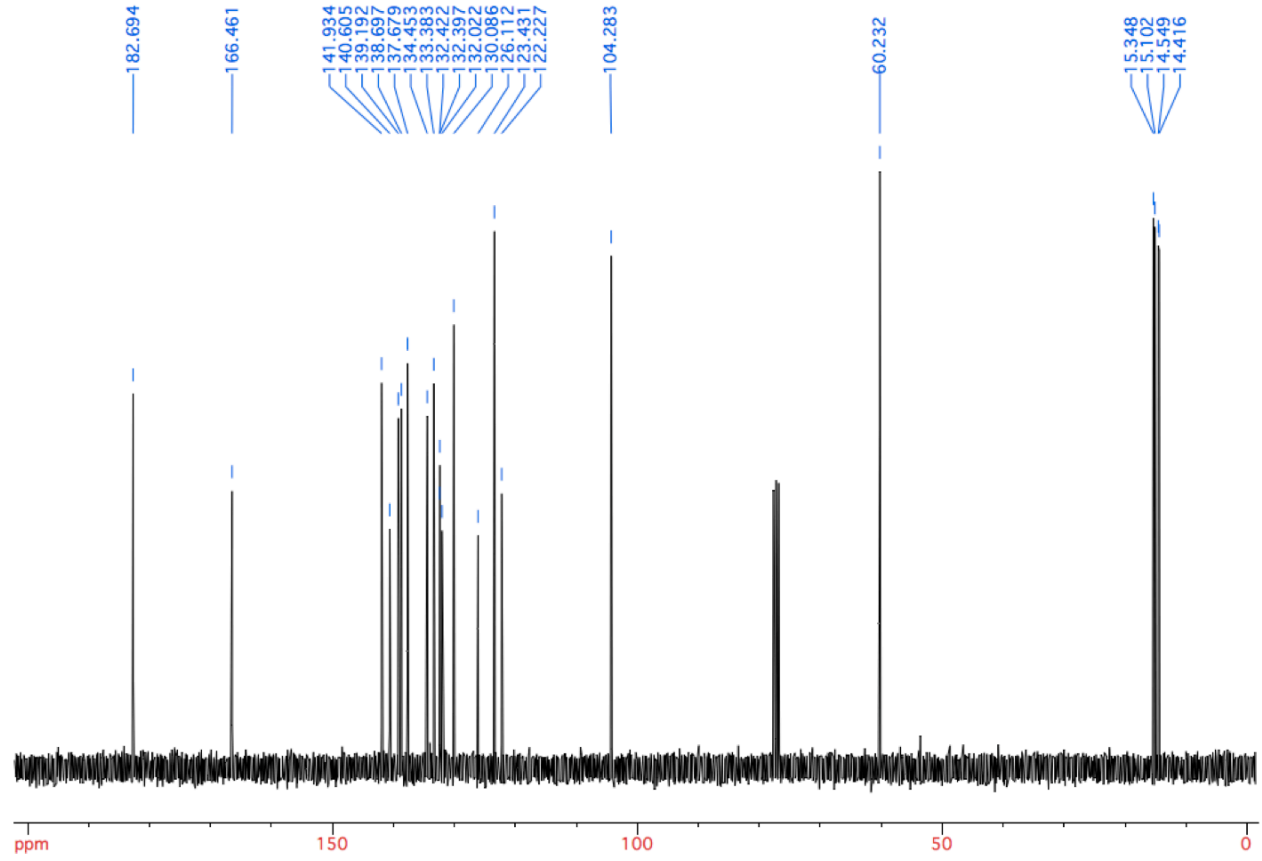

Figure S77. ^{13}C NMR spectrum of **61** in $CDCl_3$.

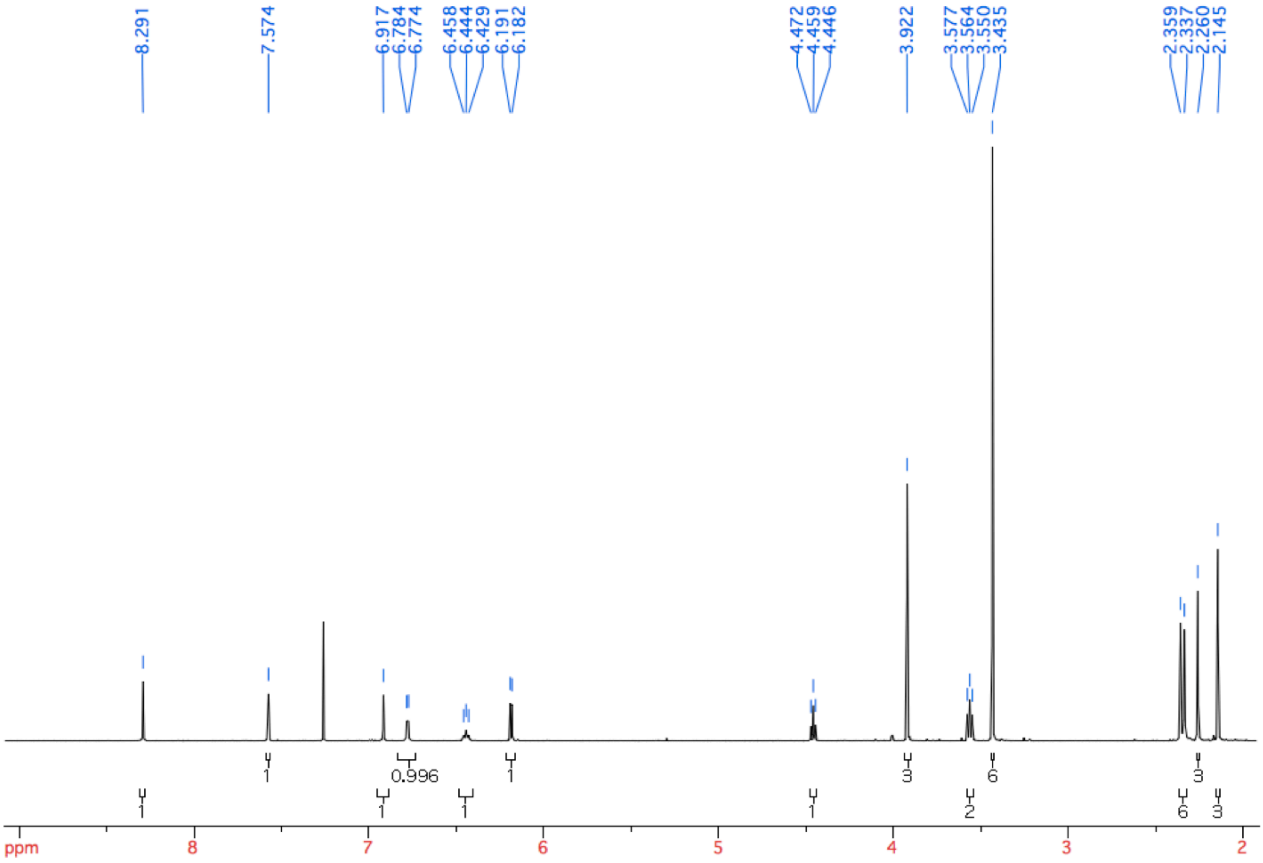

Figure S78. ^{1}H NMR spectrum of **62** in $CDCl_3$.

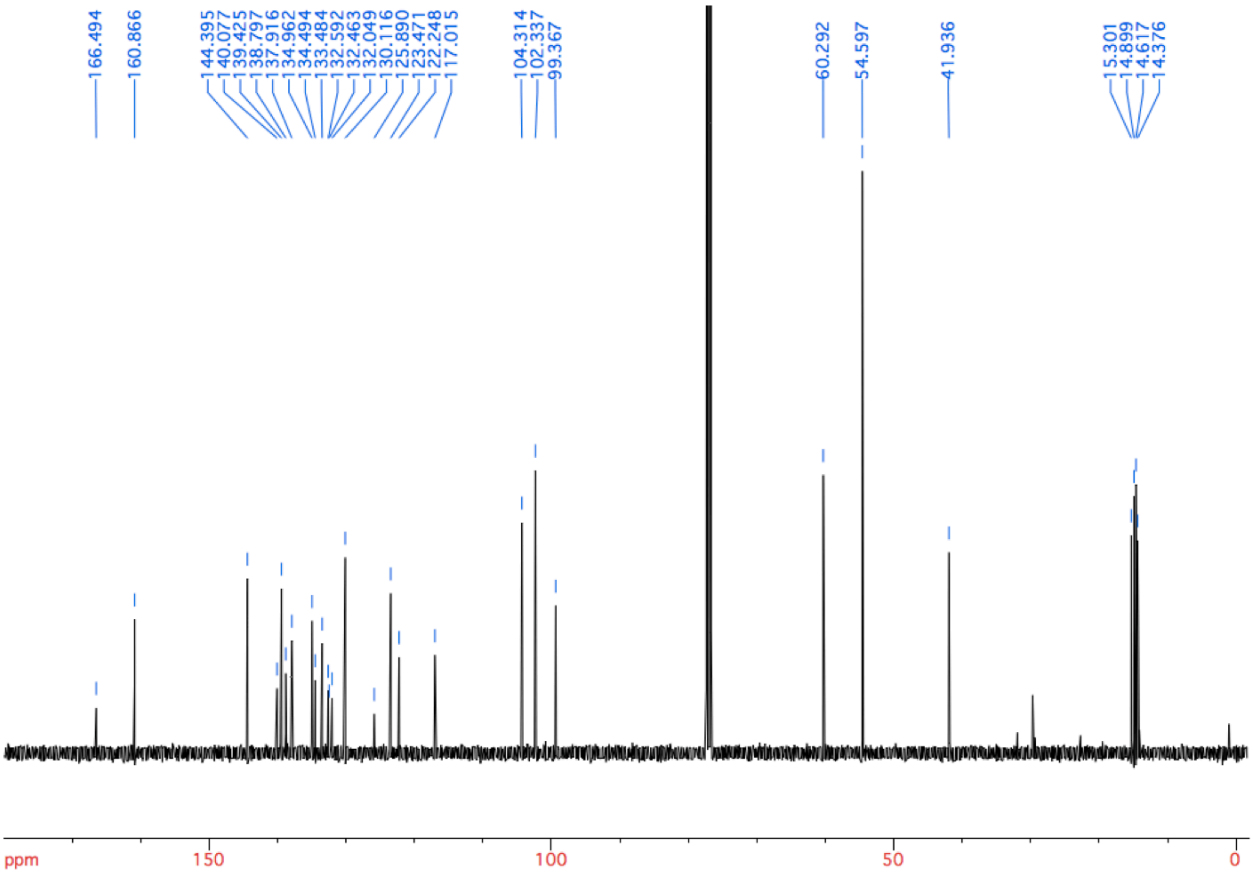

Figure S79. ^{13}C NMR spectrum of **62** in $CDCl_3$.

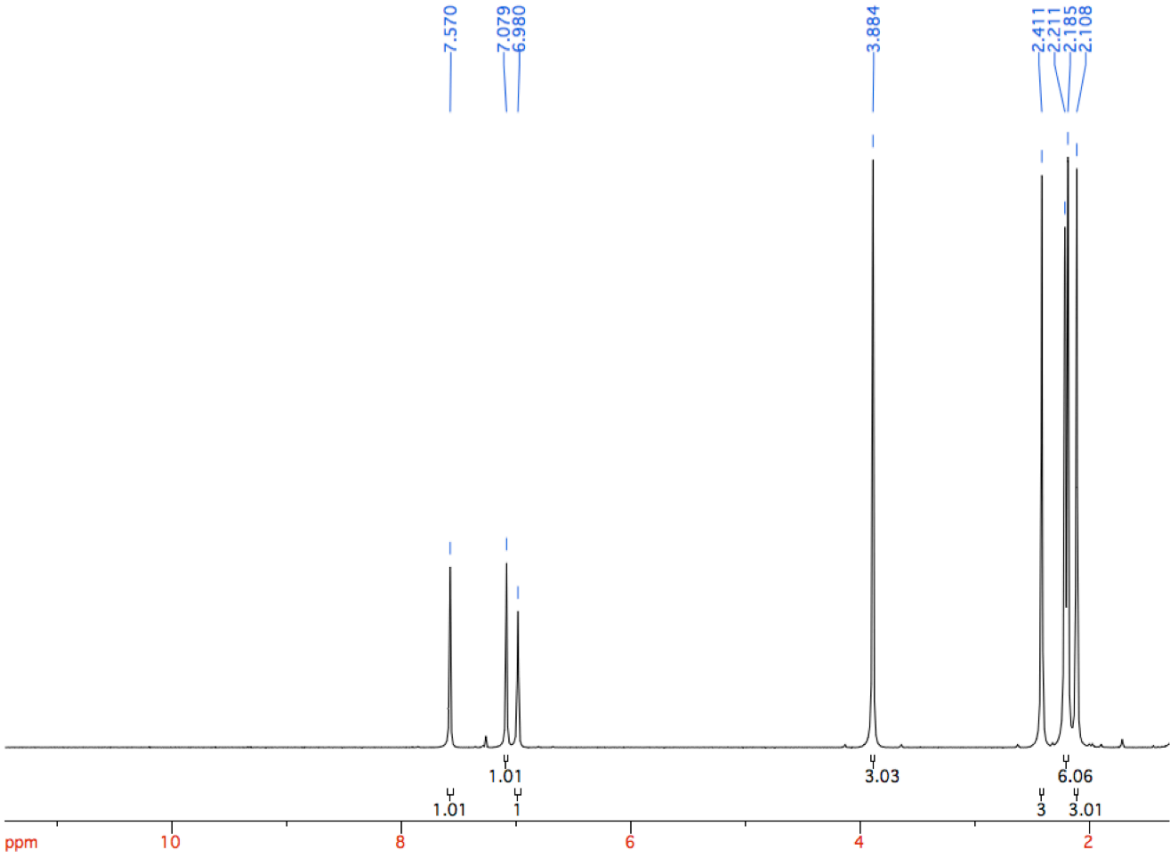

Figure S80. ^{1}H NMR spectrum of **63** in $CDCl_3$.

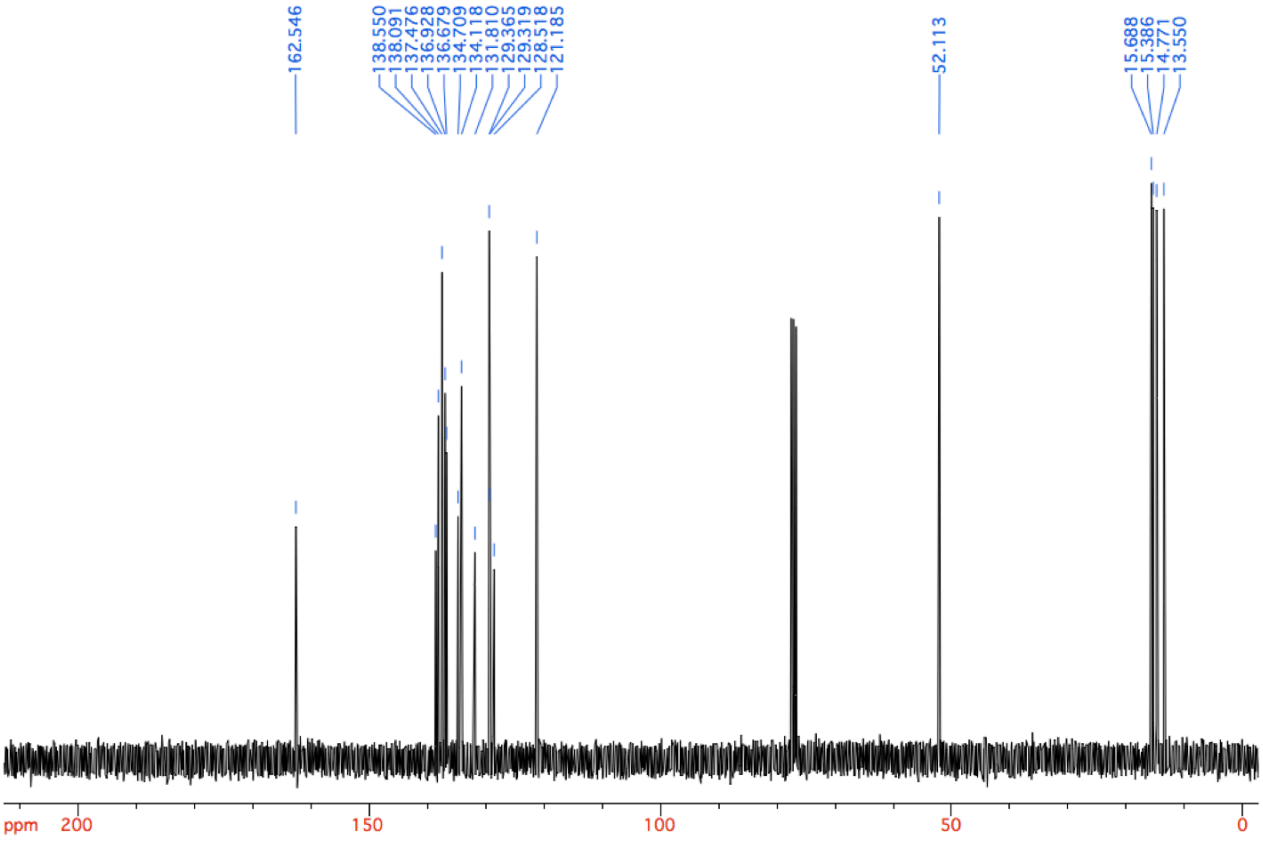

Figure S81. ^{13}C NMR spectrum of **63** in $CDCl_3$.

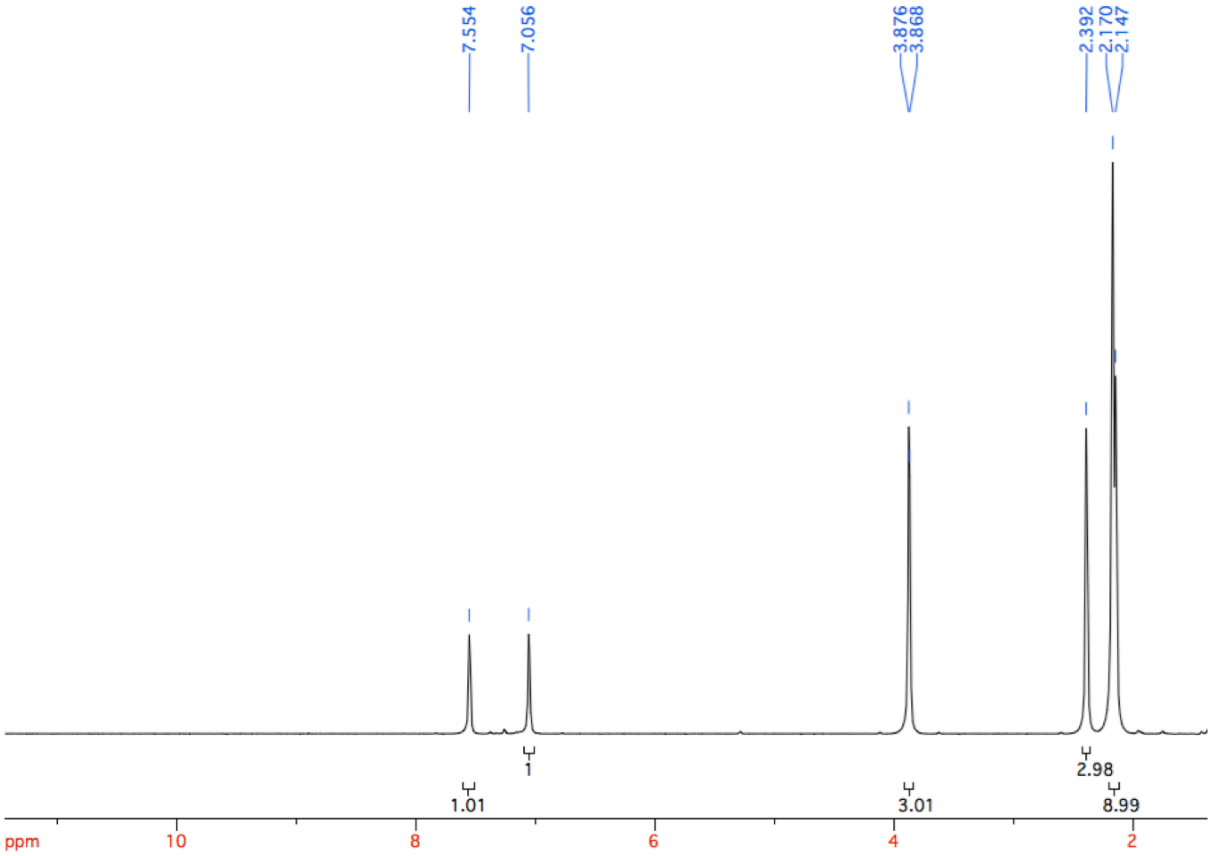

Figure S82. ^{1}H NMR spectrum of **64** in $CDCl_3$.

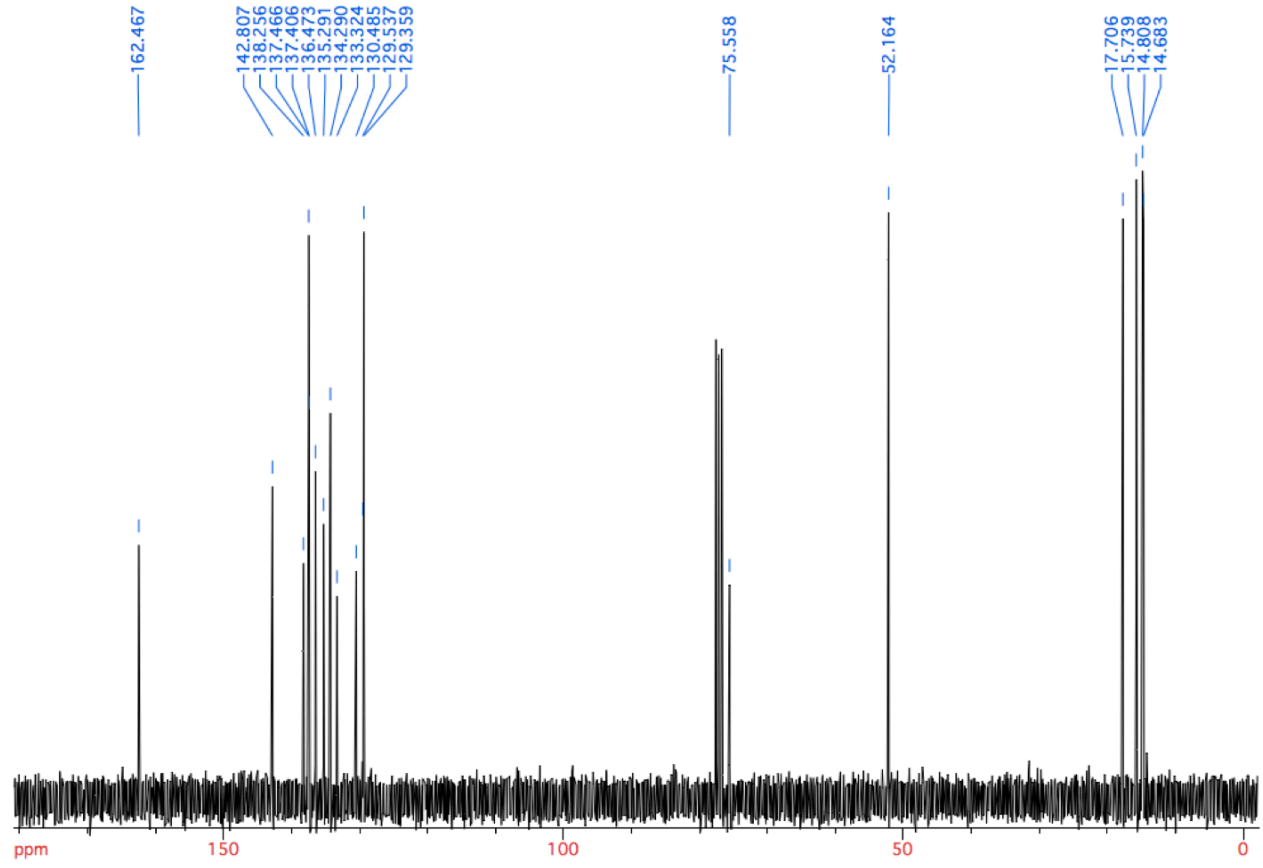

Figure S83. ^{13}C NMR spectrum of **64** in $CDCl_3$.

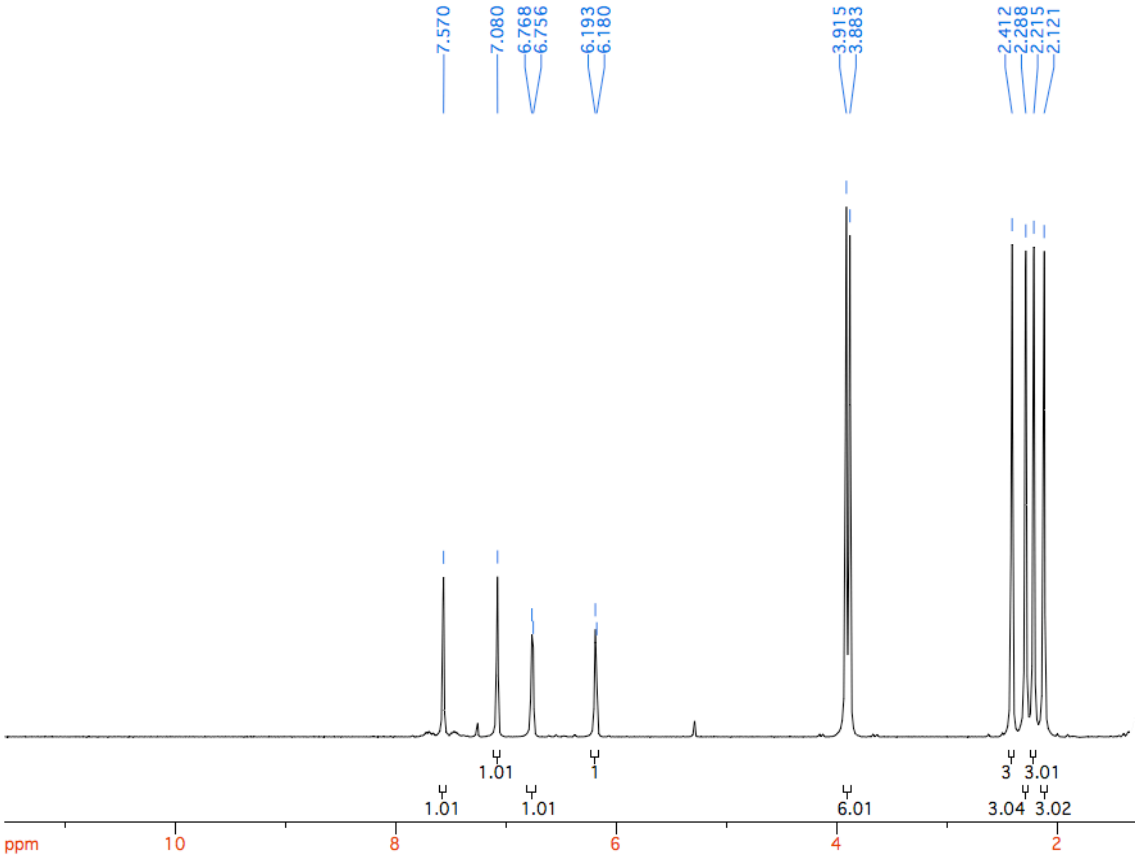

Figure S84. ^{1}H NMR spectrum of **65** in $CDCl_3$.

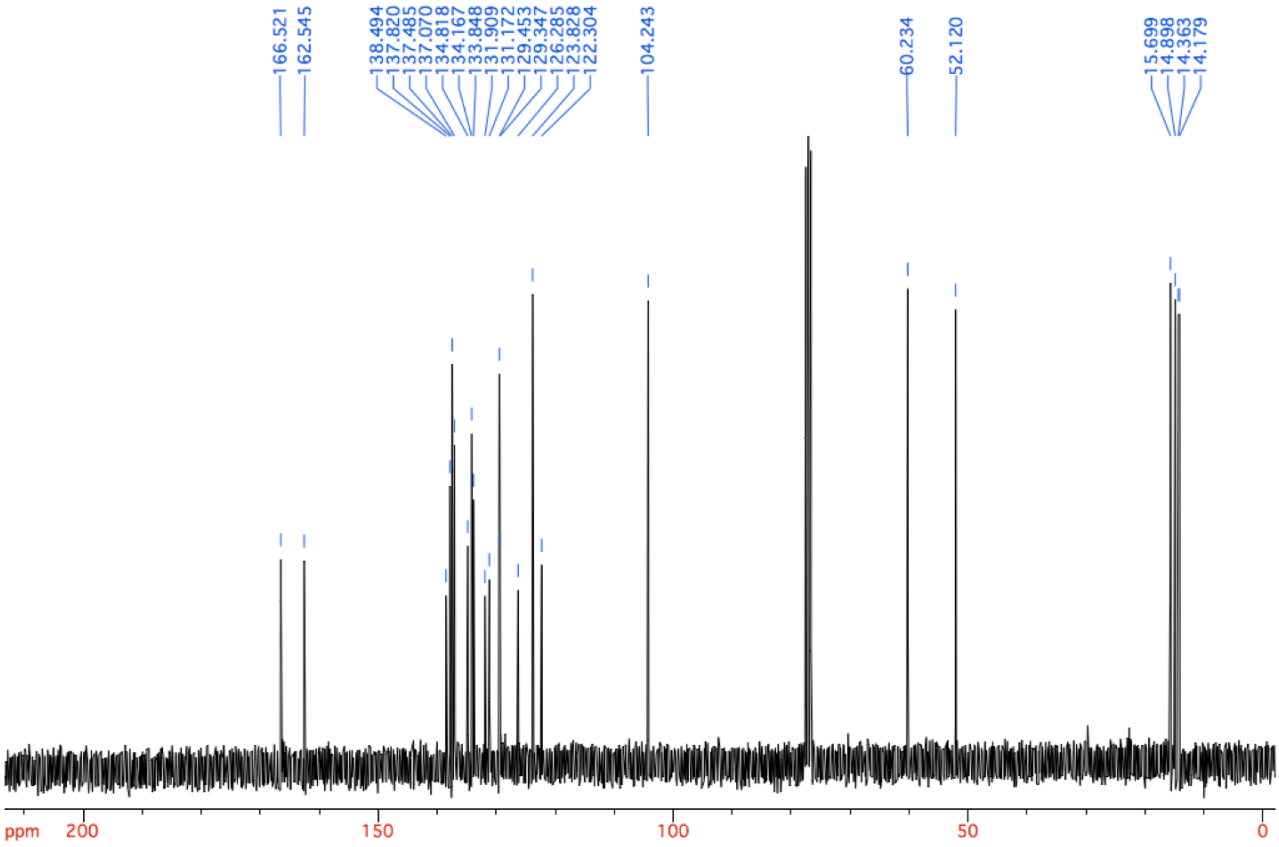

Figure S85. ^{13}C NMR spectrum of **65** in $CDCl_3$.

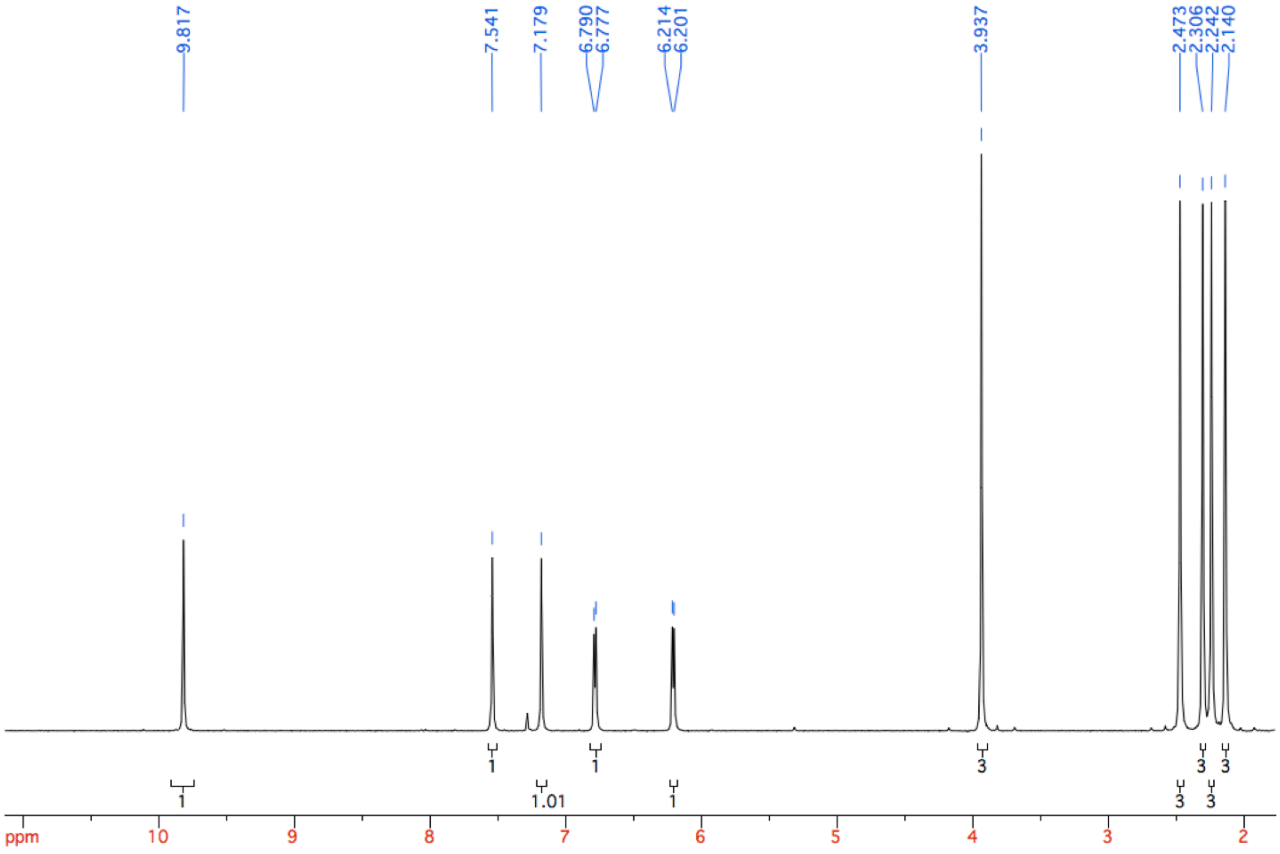

Figure S86. ^{1}H NMR spectrum of **66** in $CDCl_3$.

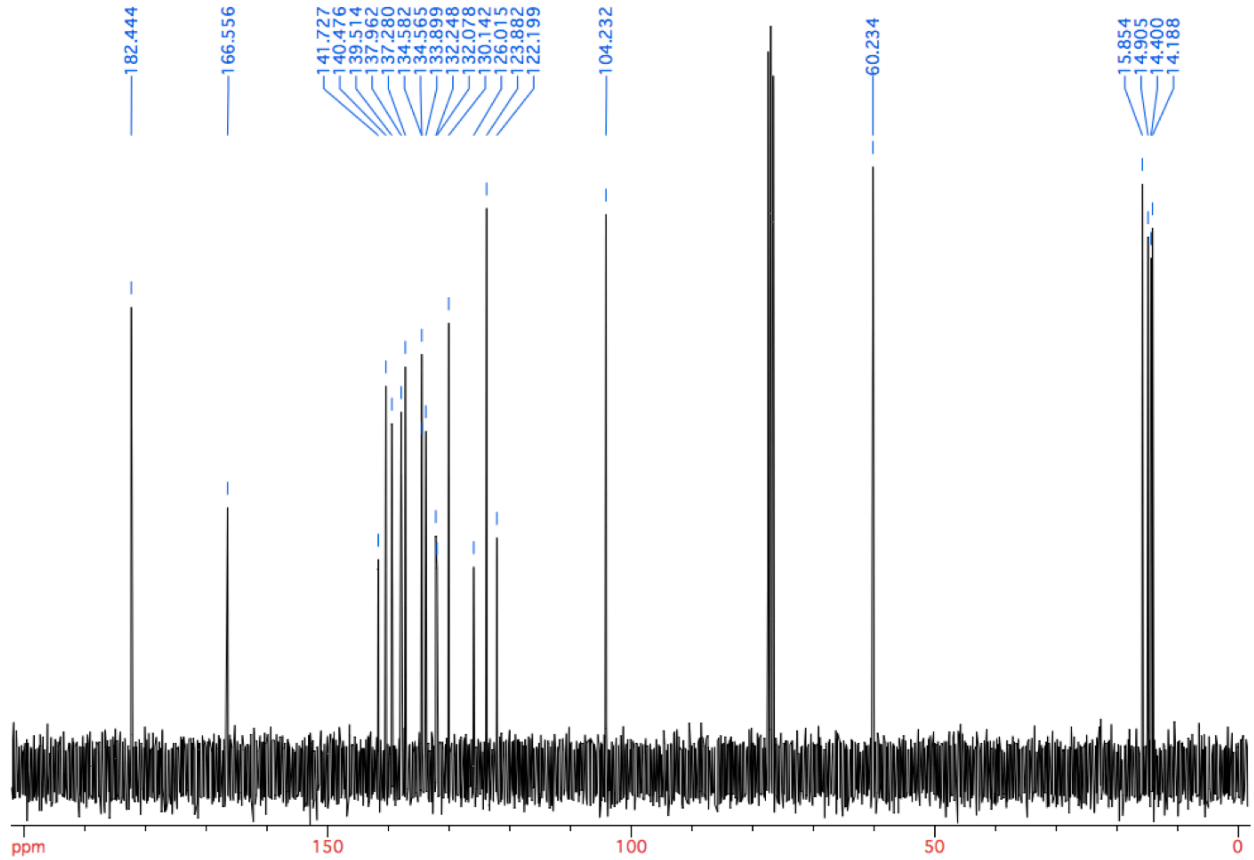

Figure S87. ^{13}C NMR spectrum of **66** in $CDCl_3$.

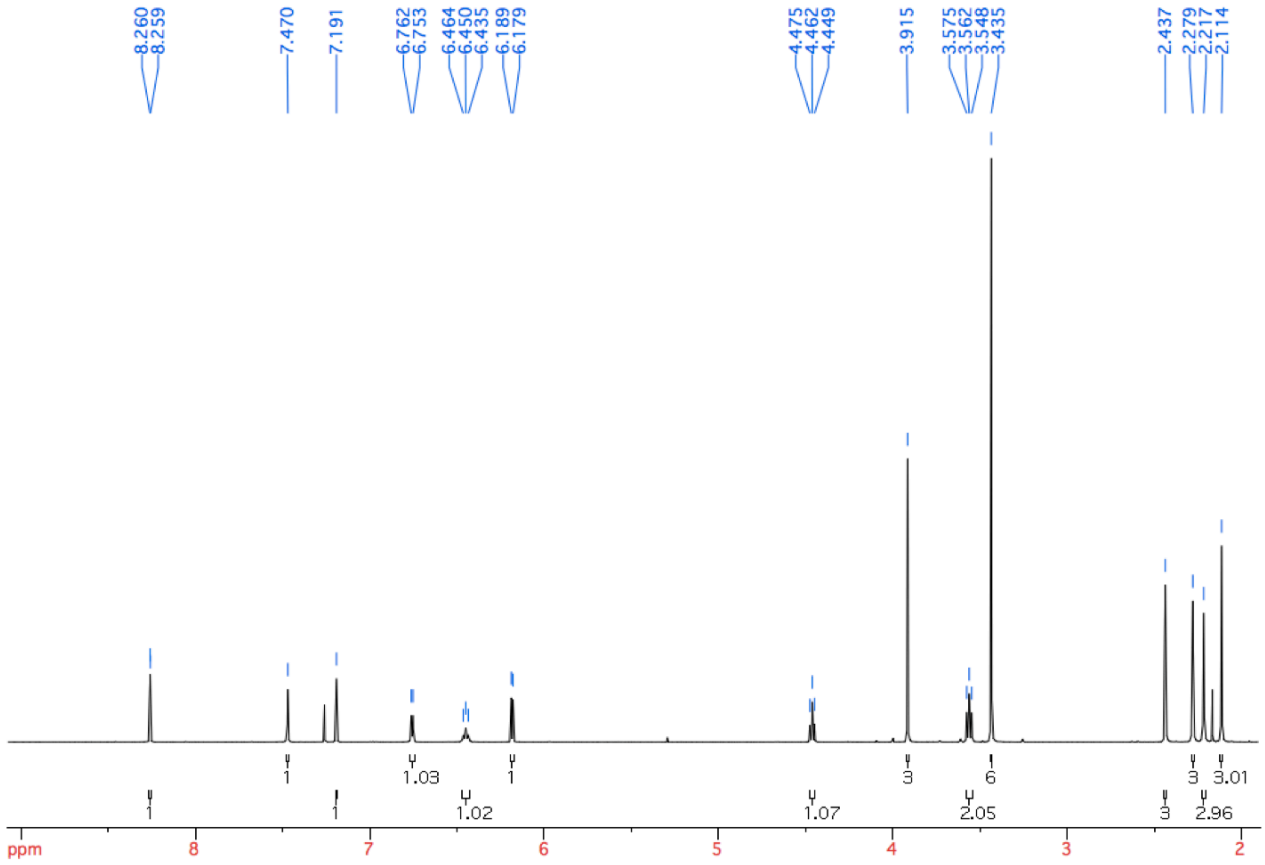

Figure S88. ^{1}H NMR spectrum of **67** in $CDCl_3$.

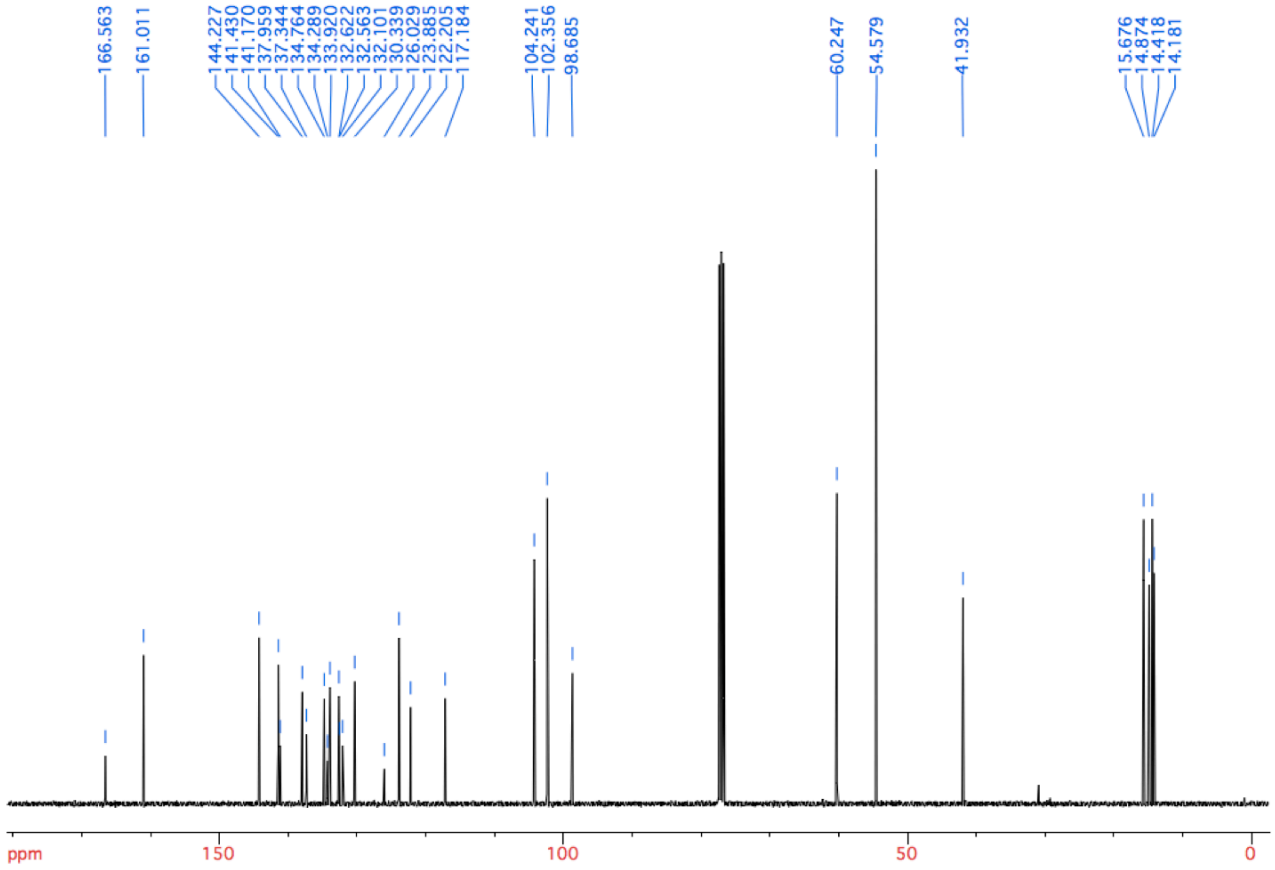

Figure S89. ^{13}C NMR spectrum of **67** in $CDCl_3$.

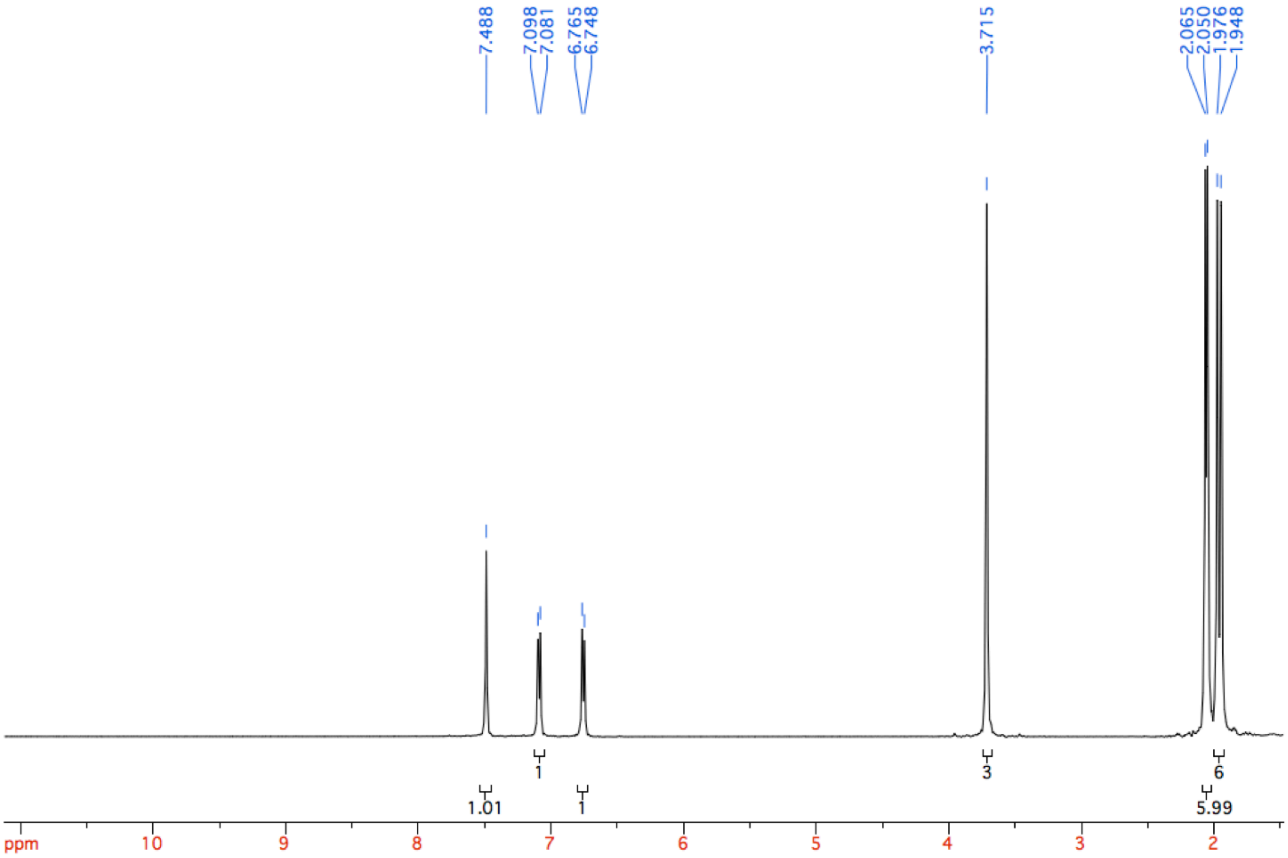

Figure S90. ^{1}H NMR spectrum of **68** in $CDCl_3$.

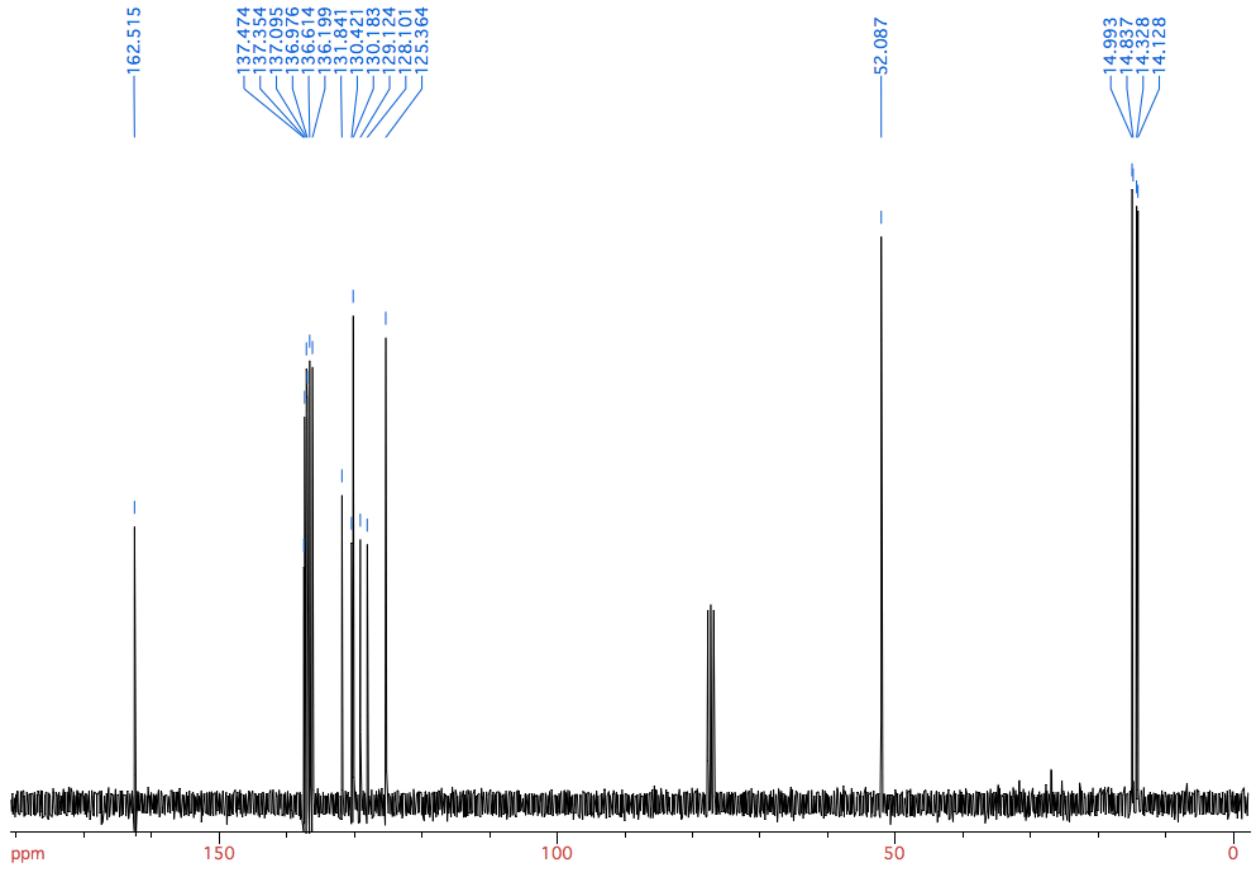

Figure S91. ^{13}C NMR spectrum of **68** in $CDCl_3$.

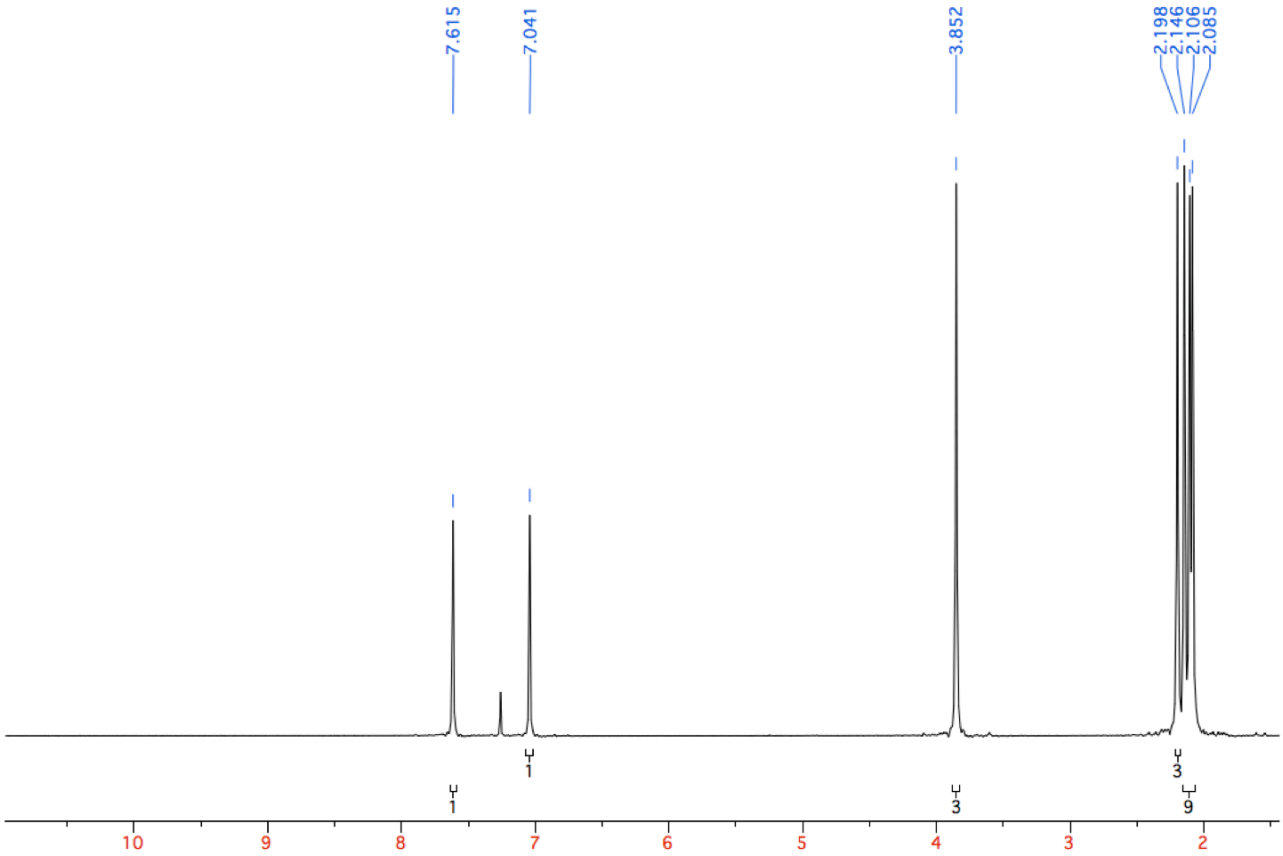

Figure S92. ^{1}H NMR spectrum of **69** in $CDCl_3$.

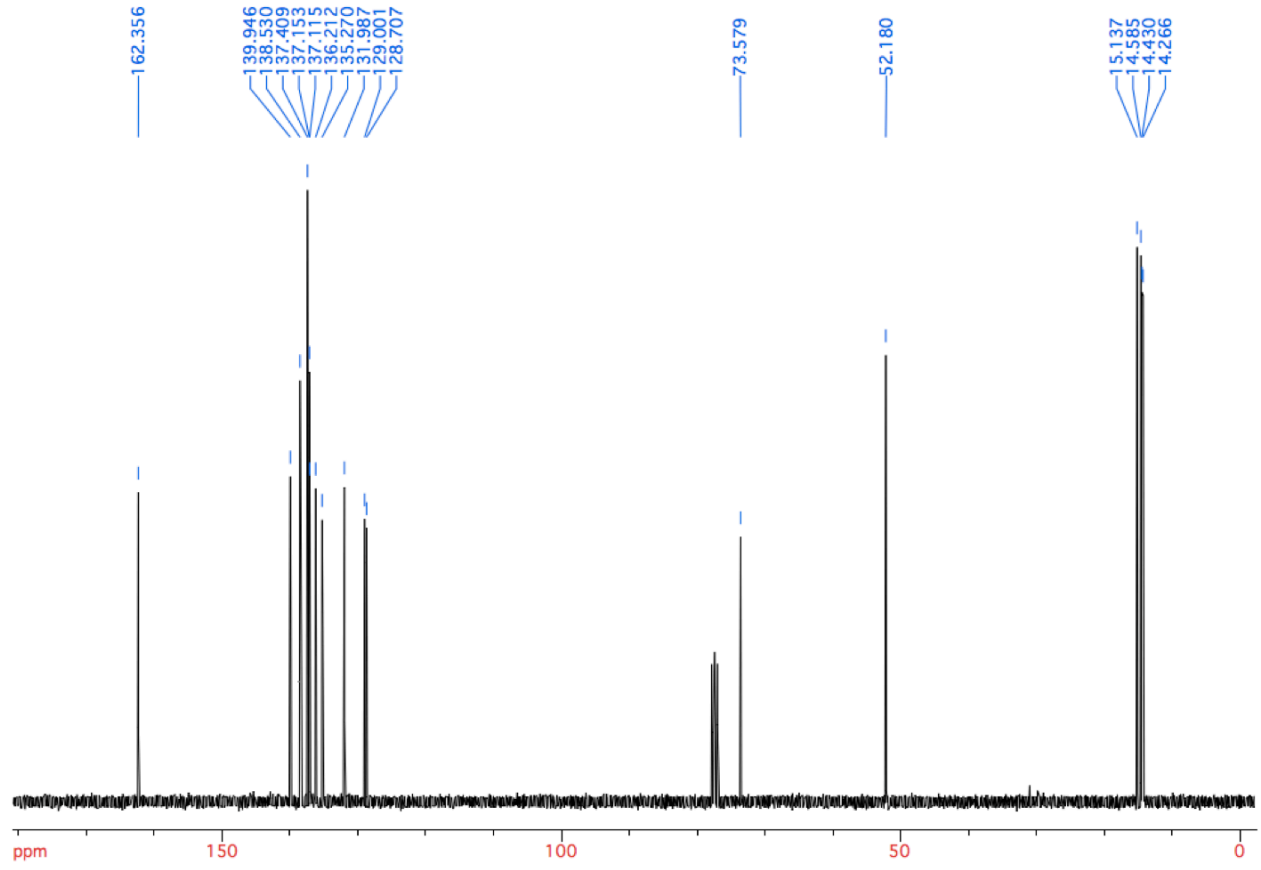

Figure S93. ^{13}C NMR spectrum of **69** in $CDCl_3$.

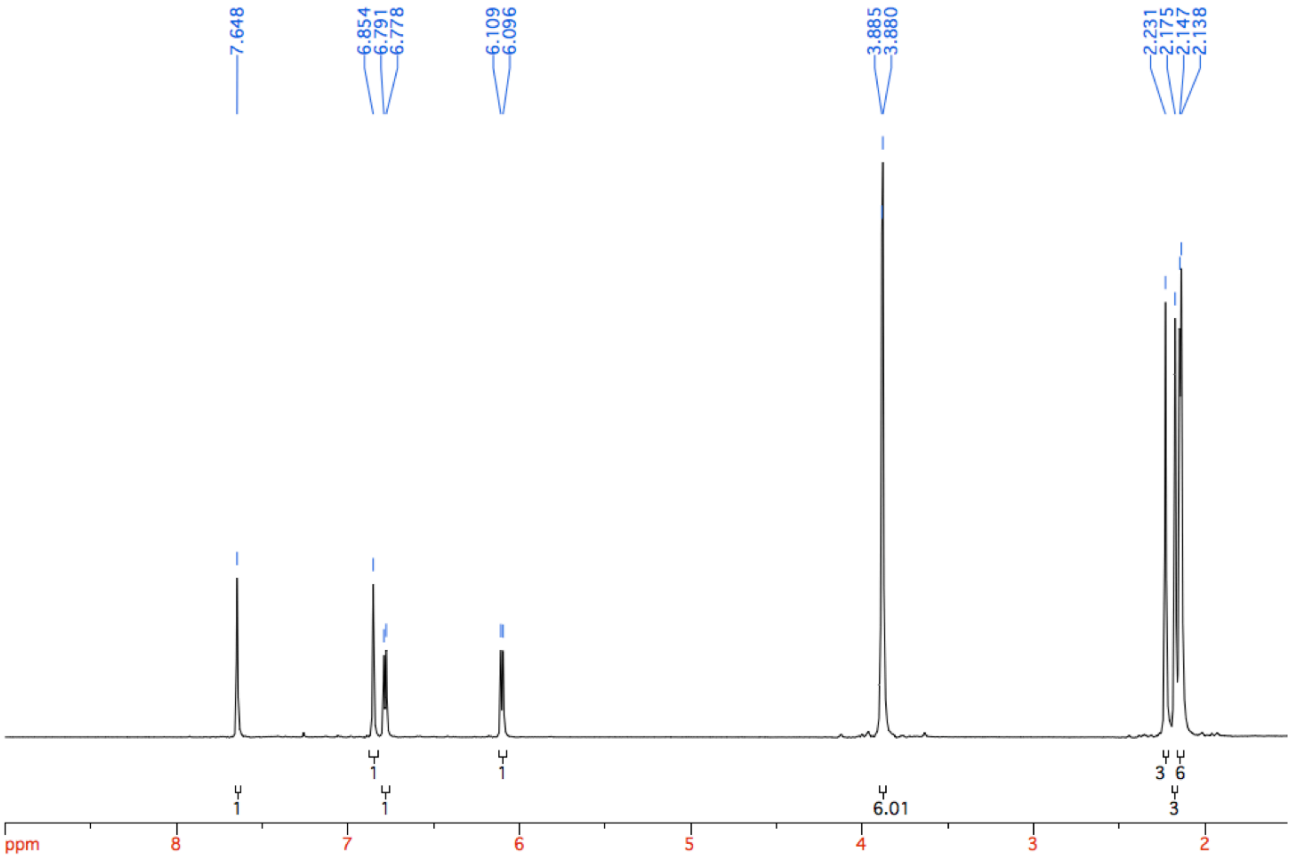

Figure S94. ^{1}H NMR spectrum of **70** in $CDCl_3$.

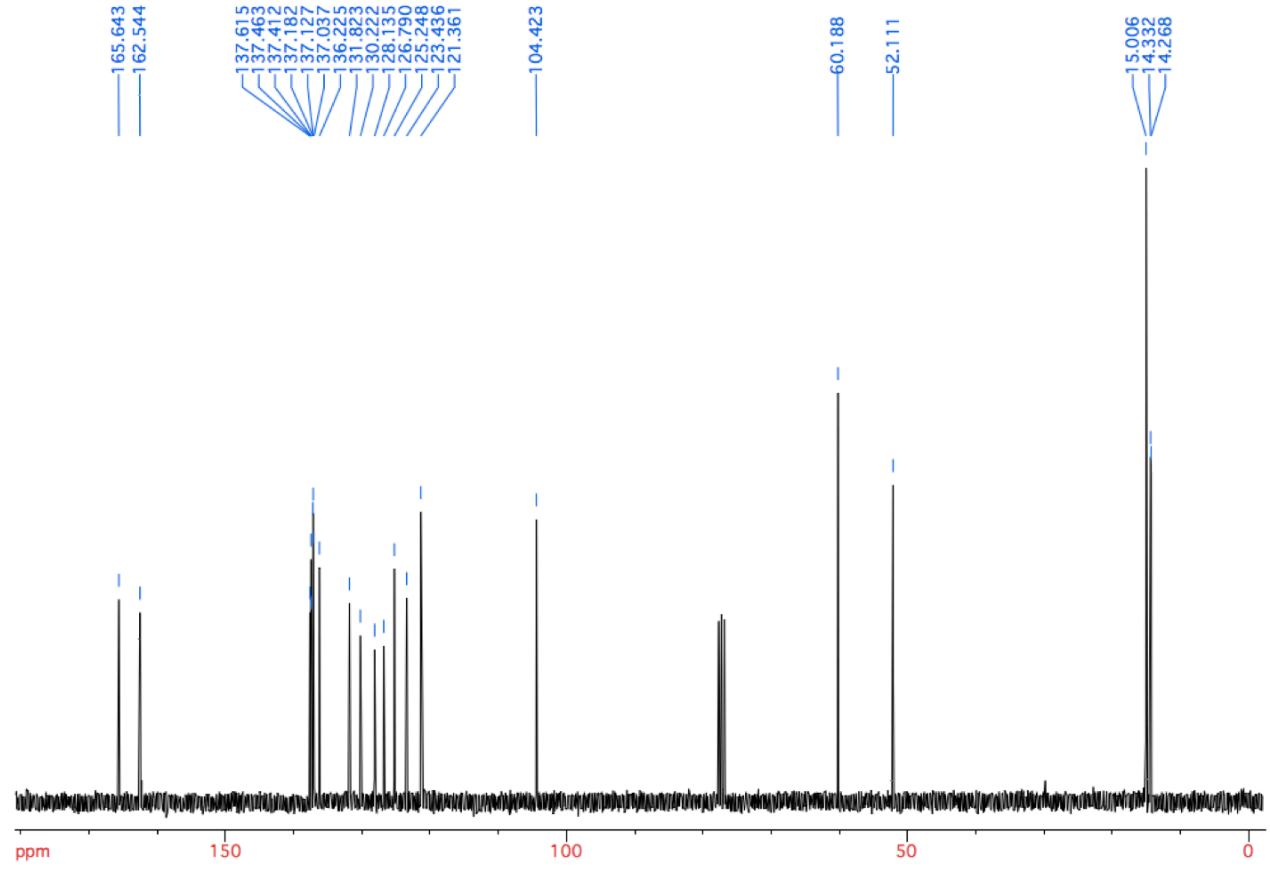

Figure S95. ^{13}C NMR spectrum of **70** in $CDCl_3$.

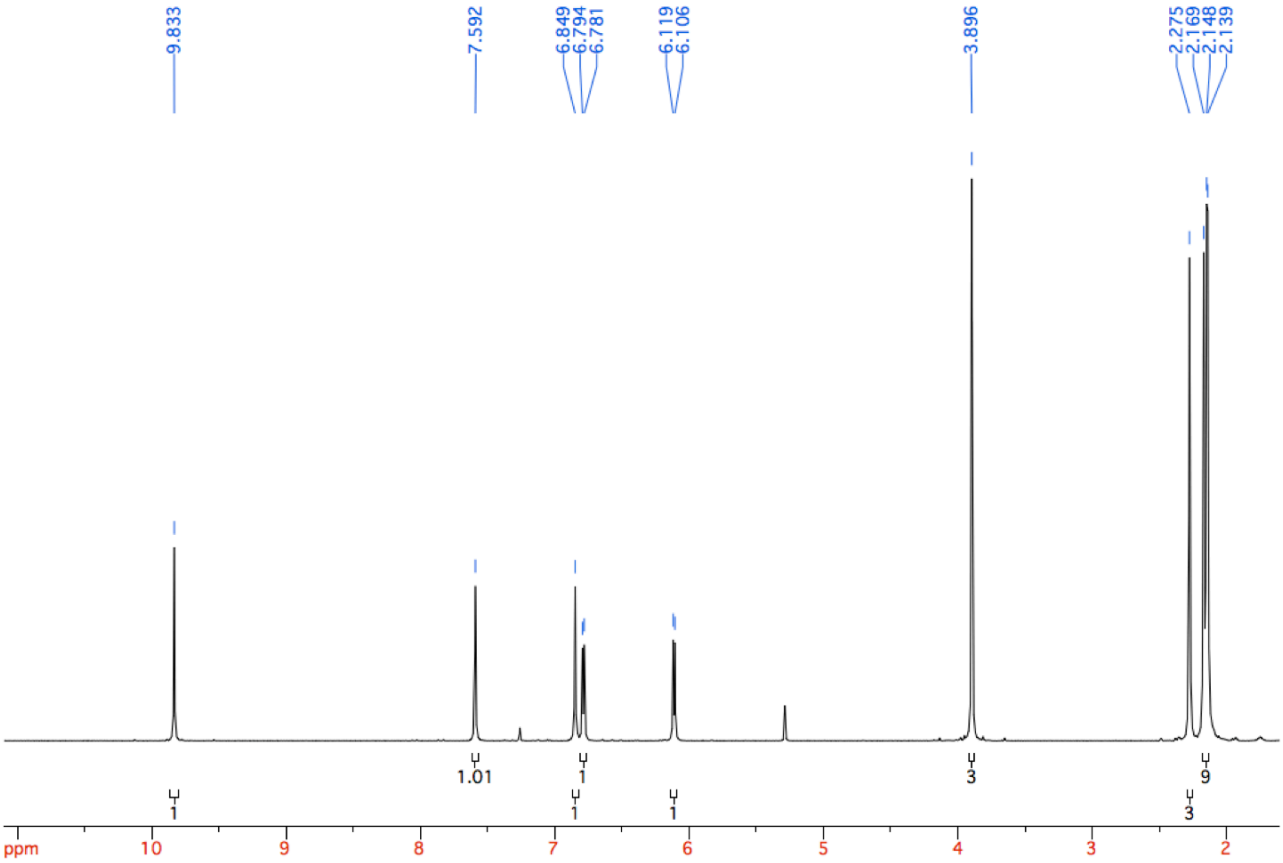

Figure S96. ^{1}H NMR spectrum of **71** in $CDCl_3$.

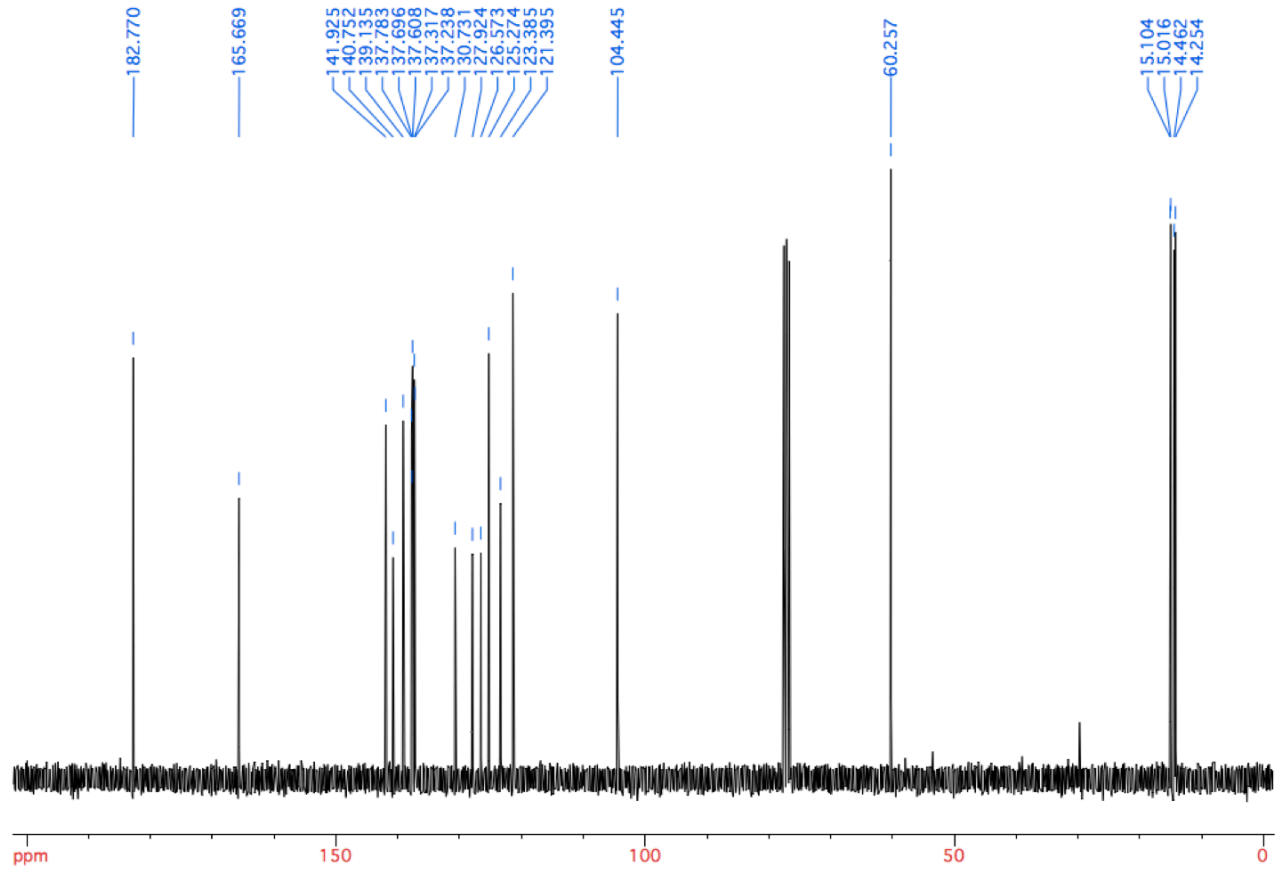

Figure S97. ^{13}C NMR spectrum of **71** in $CDCl_3$.

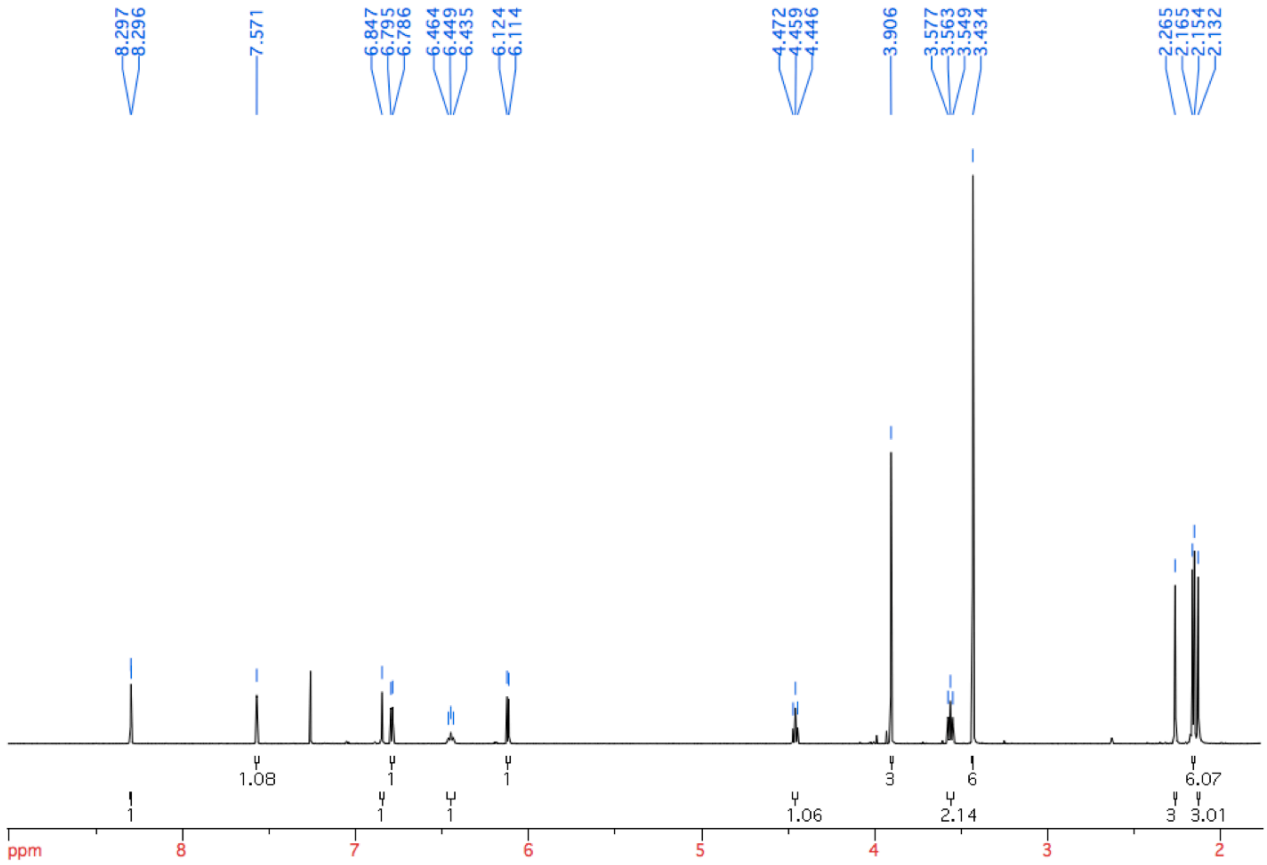

Figure S98. ^{1}H NMR spectrum of **72** in $CDCl_3$.

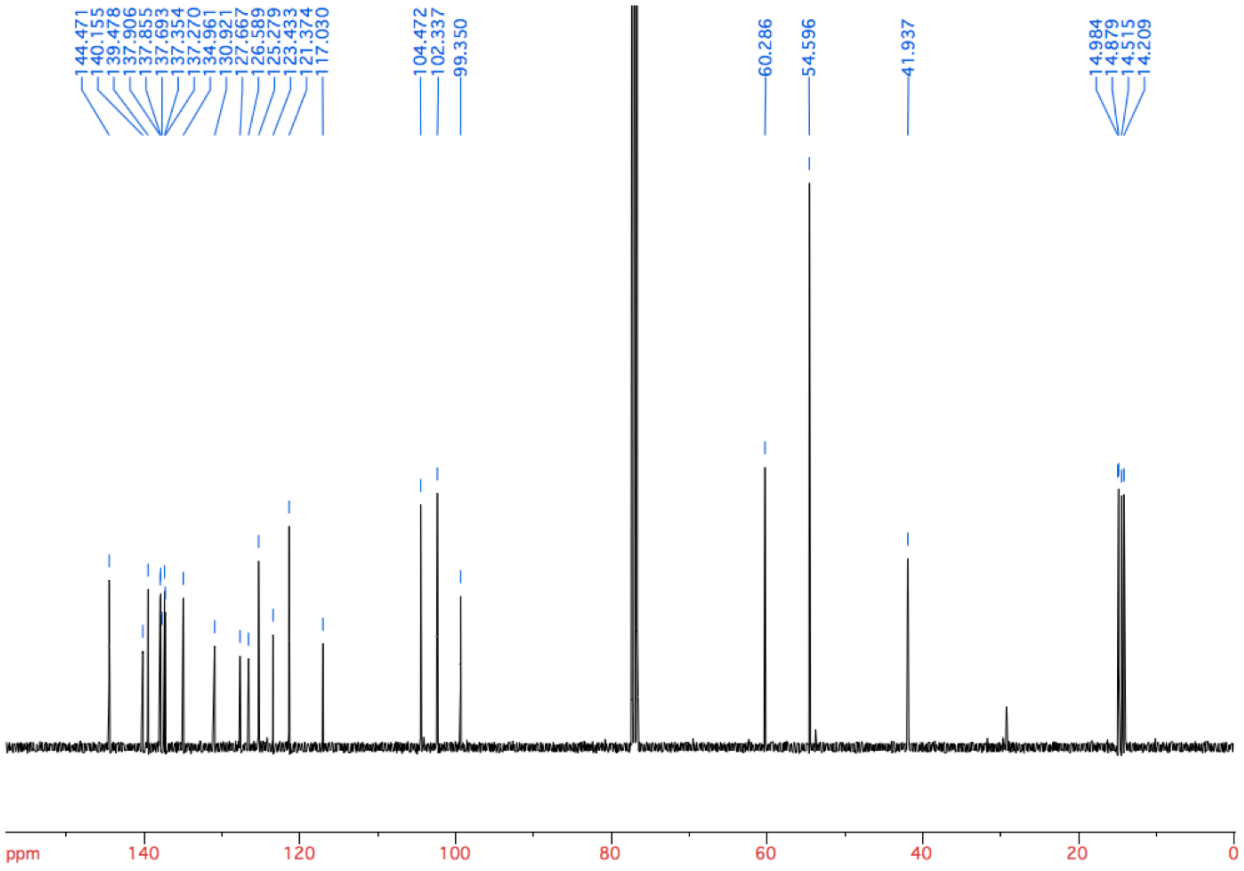

Figure S99. ^{13}C NMR spectrum of **72** in $CDCl_3$.

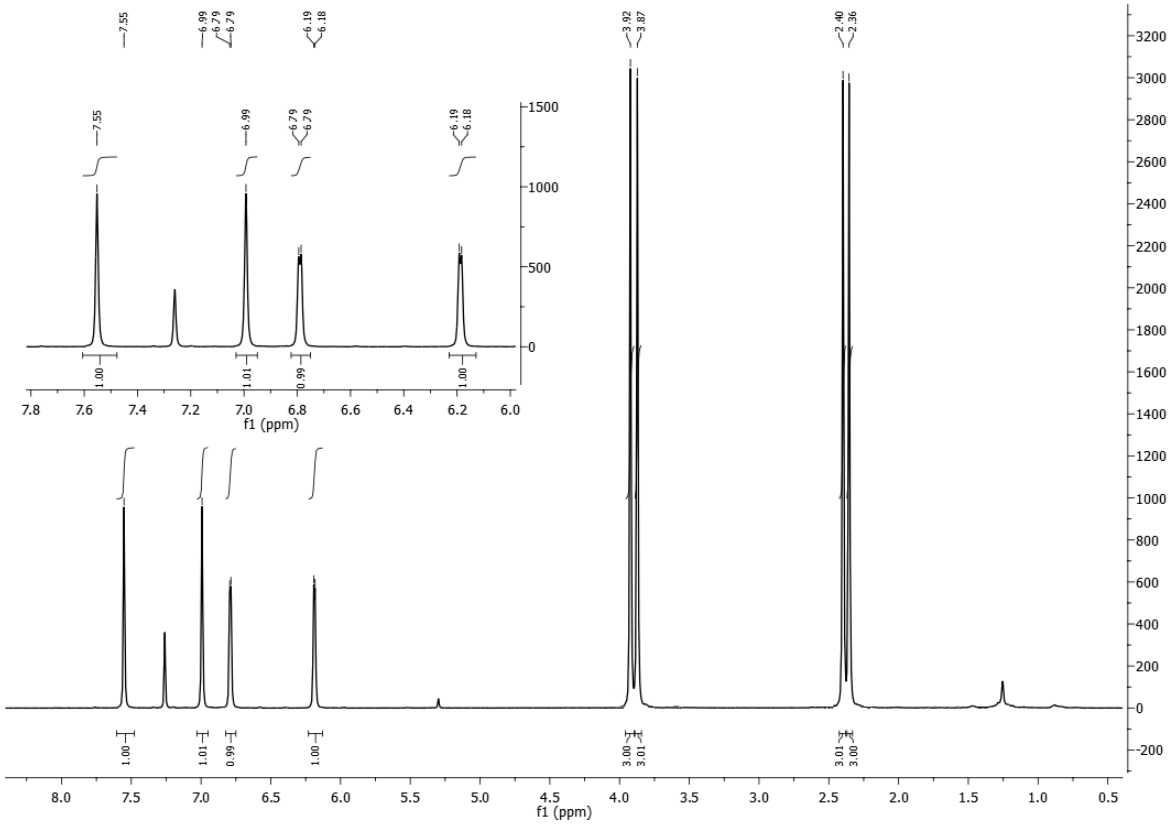

Figure S100. ^{1}H NMR spectrum of **80** in $CDCl_3$.

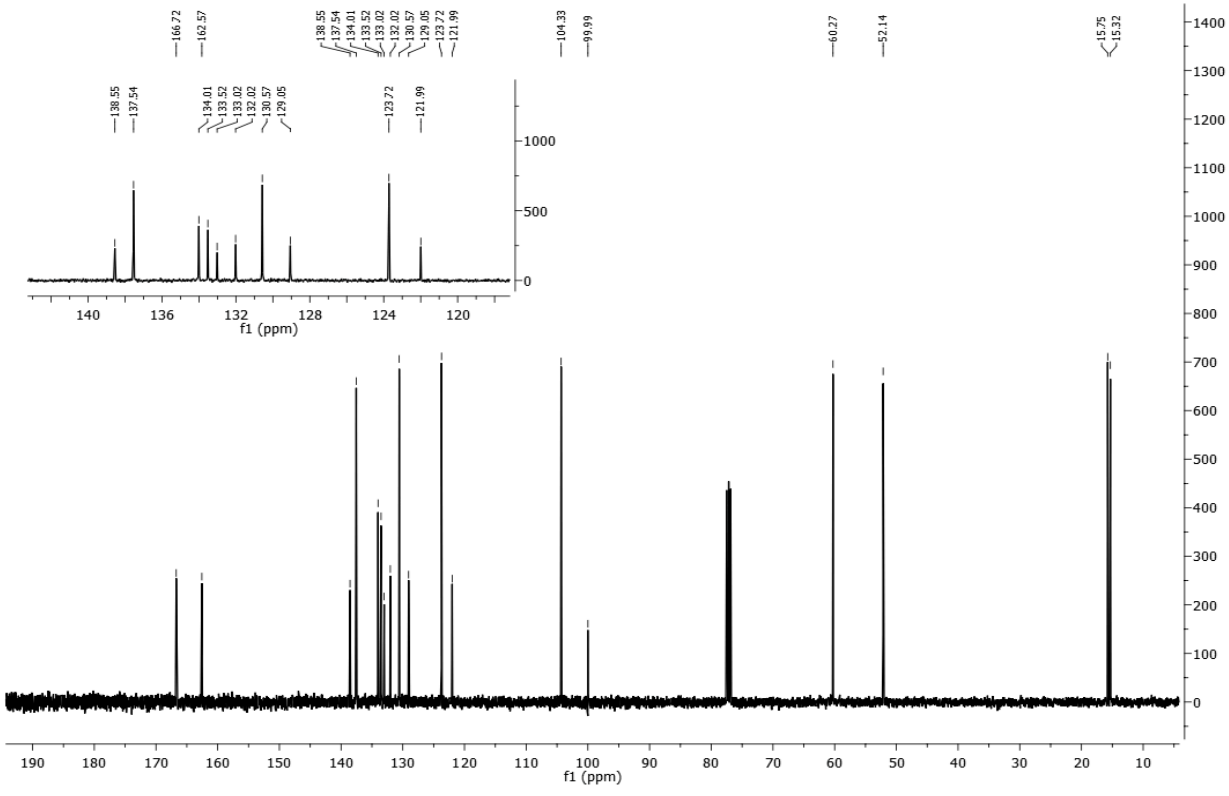

Figure S101. ^{13}C NMR spectrum of **80** in $CDCl_3$.

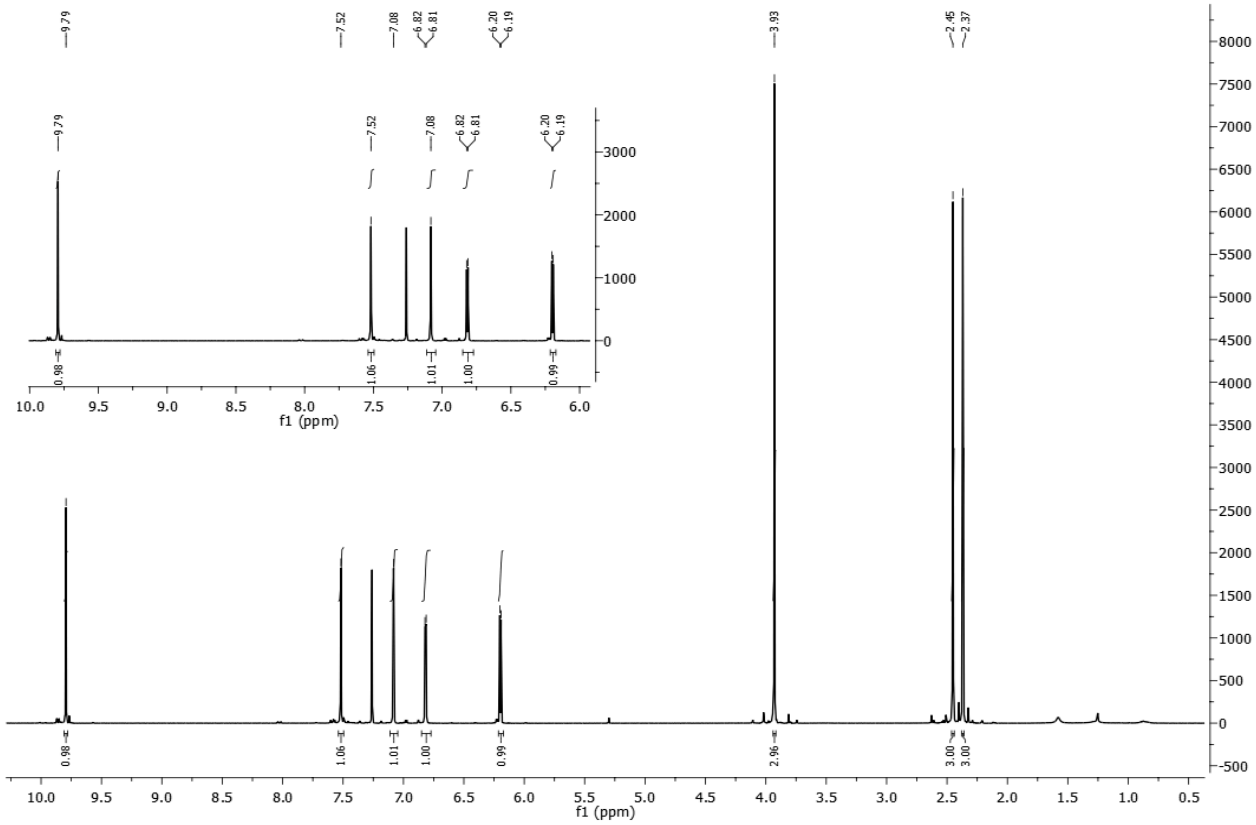

Figure S102. ^{1}H NMR spectrum of **81** in $CDCl_3$.

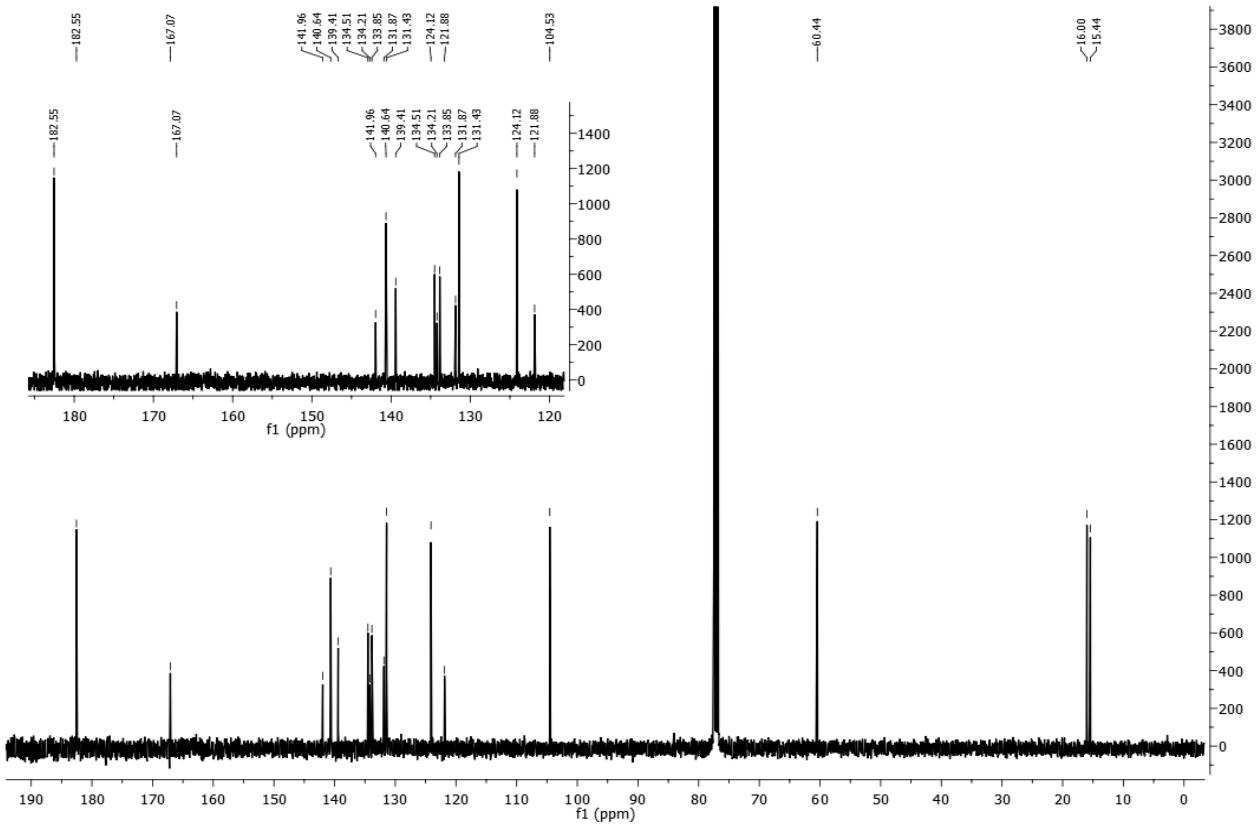

Figure S103. ^{13}C NMR spectrum of **81** in $CDCl_3$.

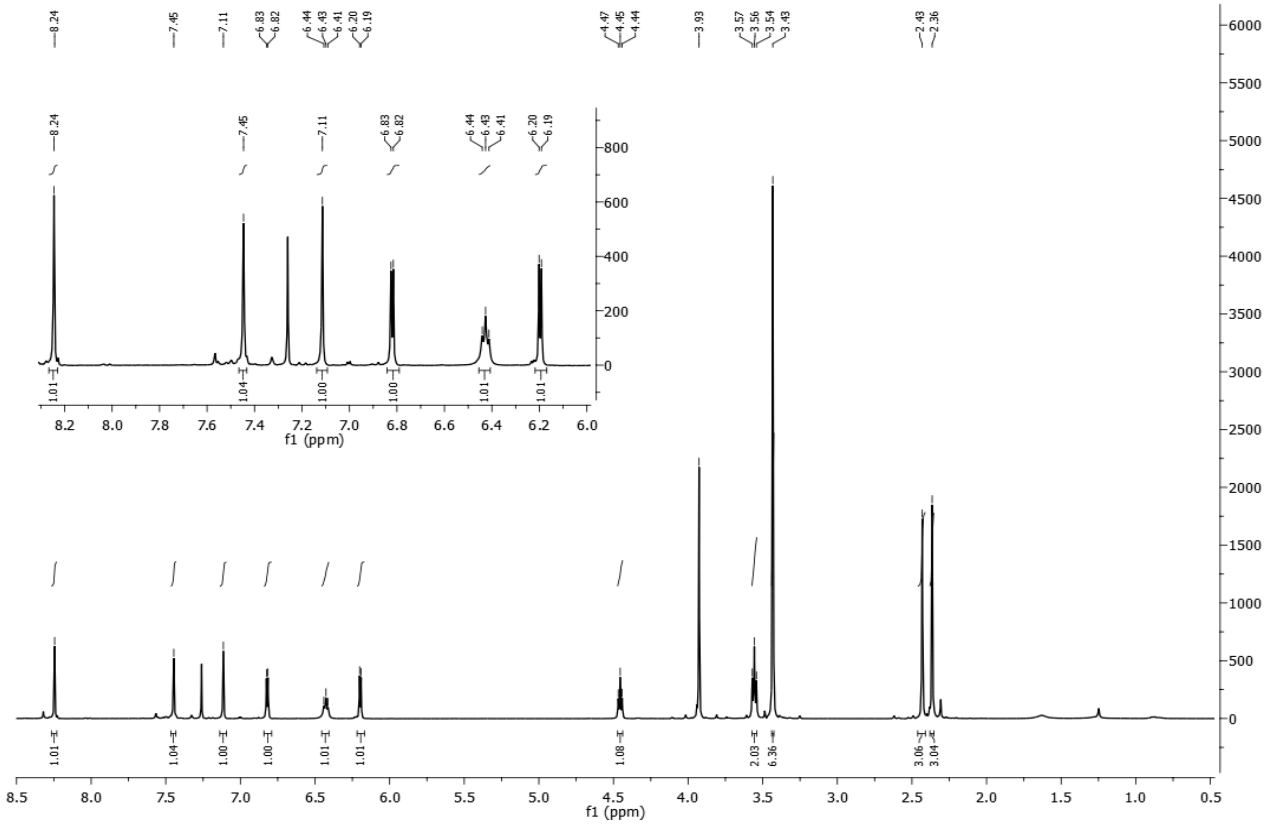

Figure S104. ^{1}H NMR spectrum of **82** in $CDCl_3$.

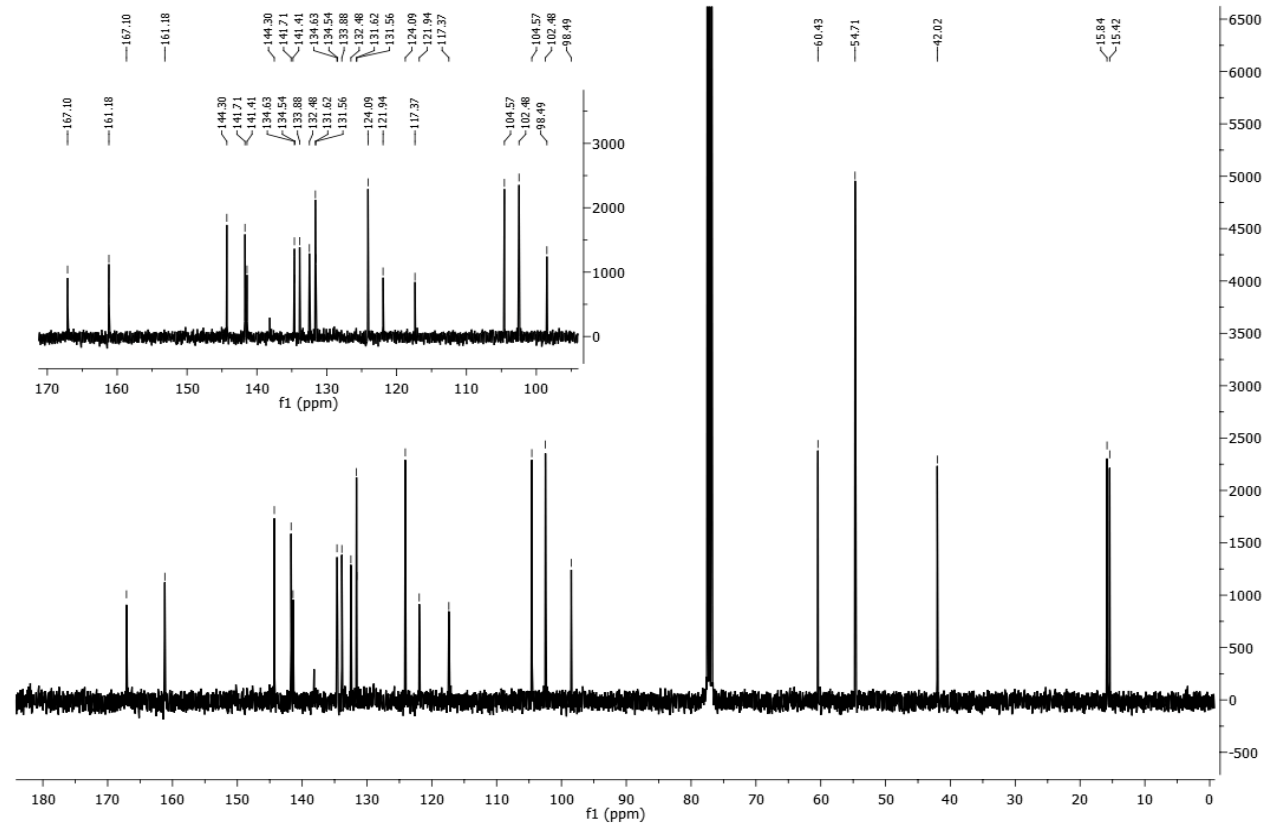

Figure S105. ^{13}C NMR spectrum of **82** in $CDCl_3$.

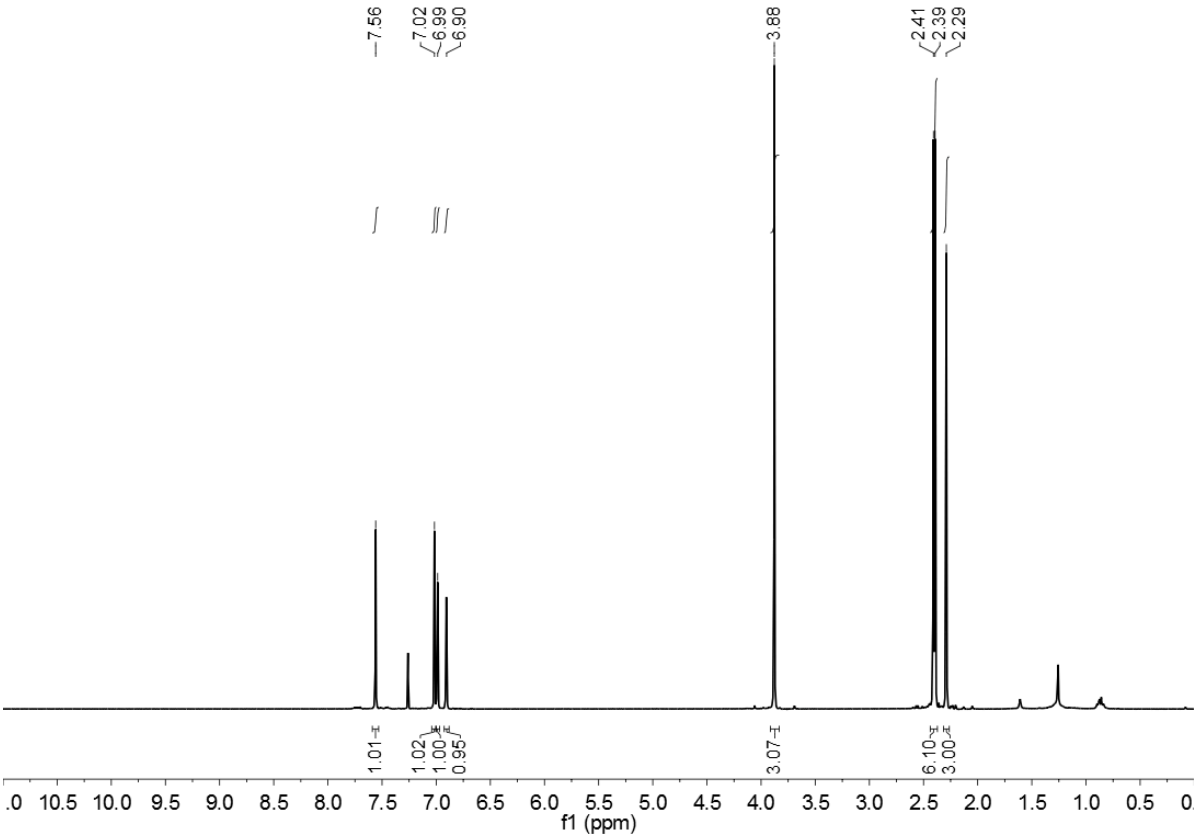

Figure S106. ^{1}H NMR spectrum of **73** in $CDCl_3$.

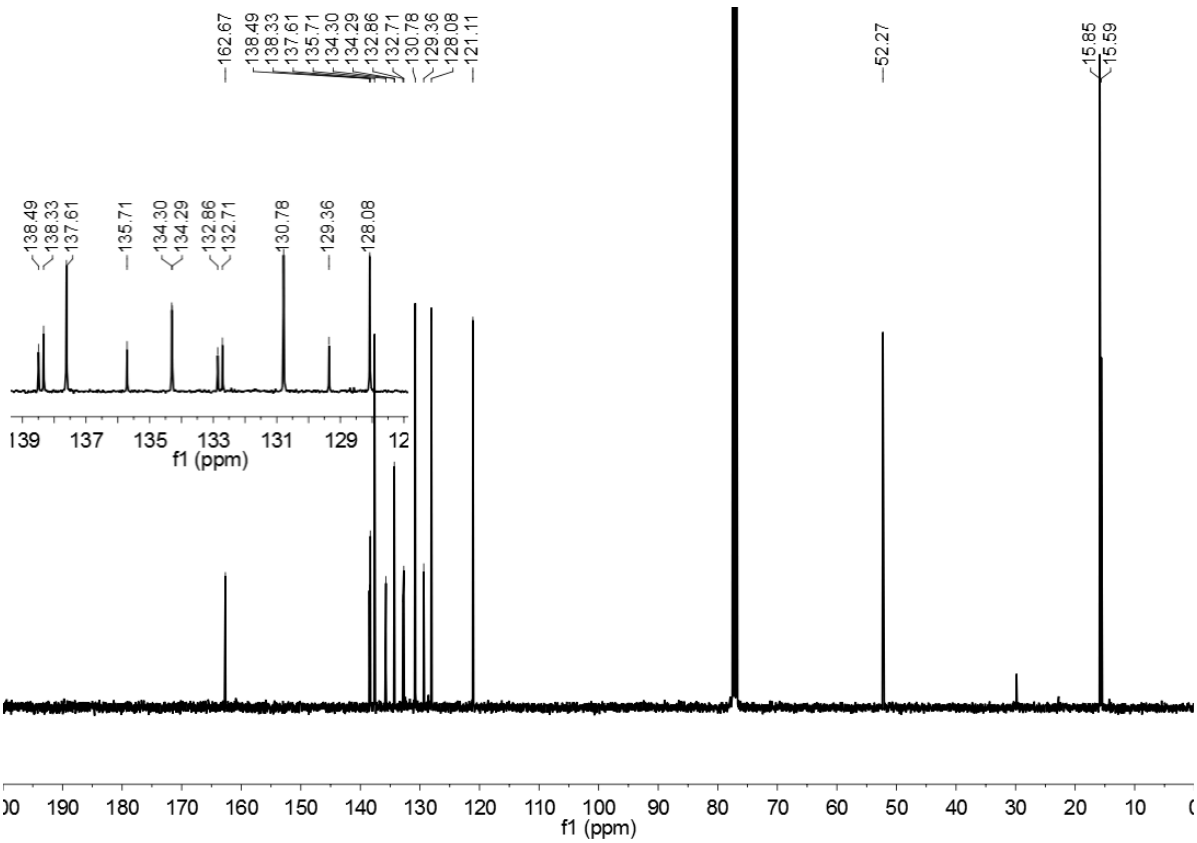

Figure S107. ^{13}C NMR spectrum of **73** in $CDCl_3$.

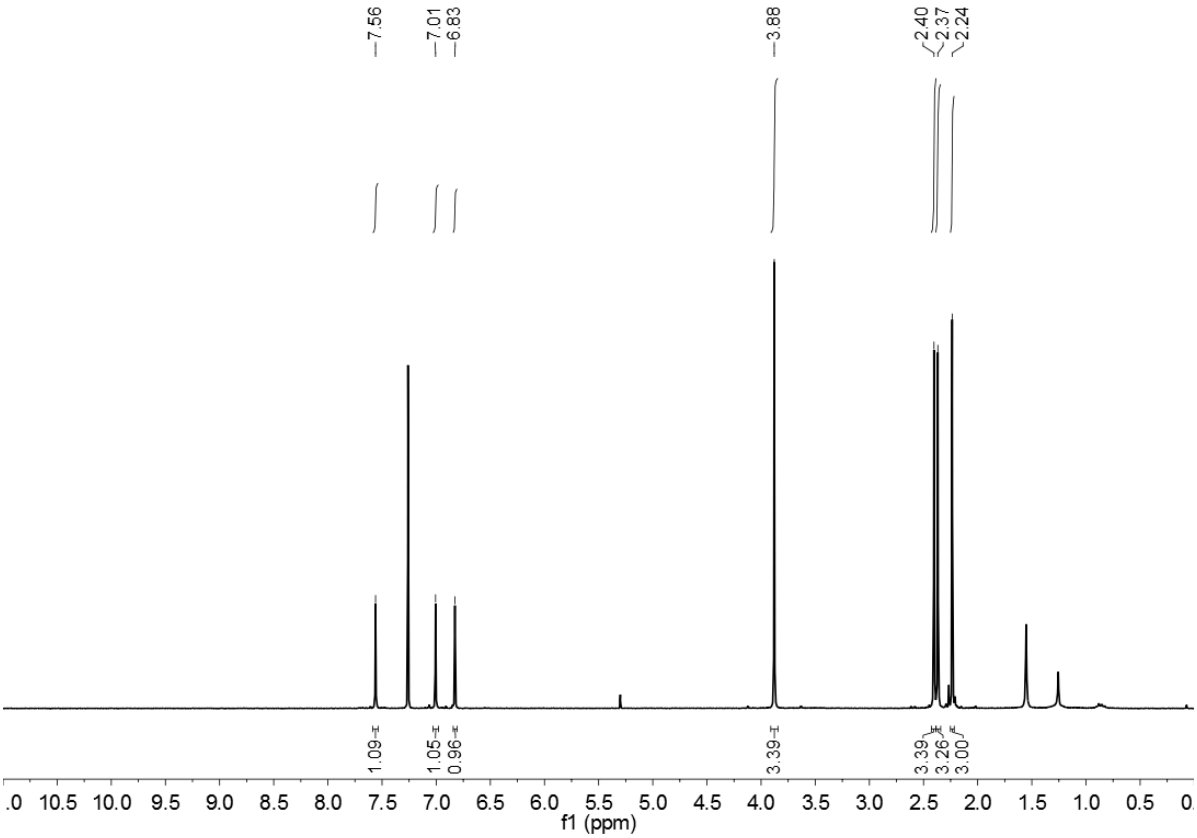

Figure S108. ^{1}H NMR spectrum of **74** in $CDCl_3$.

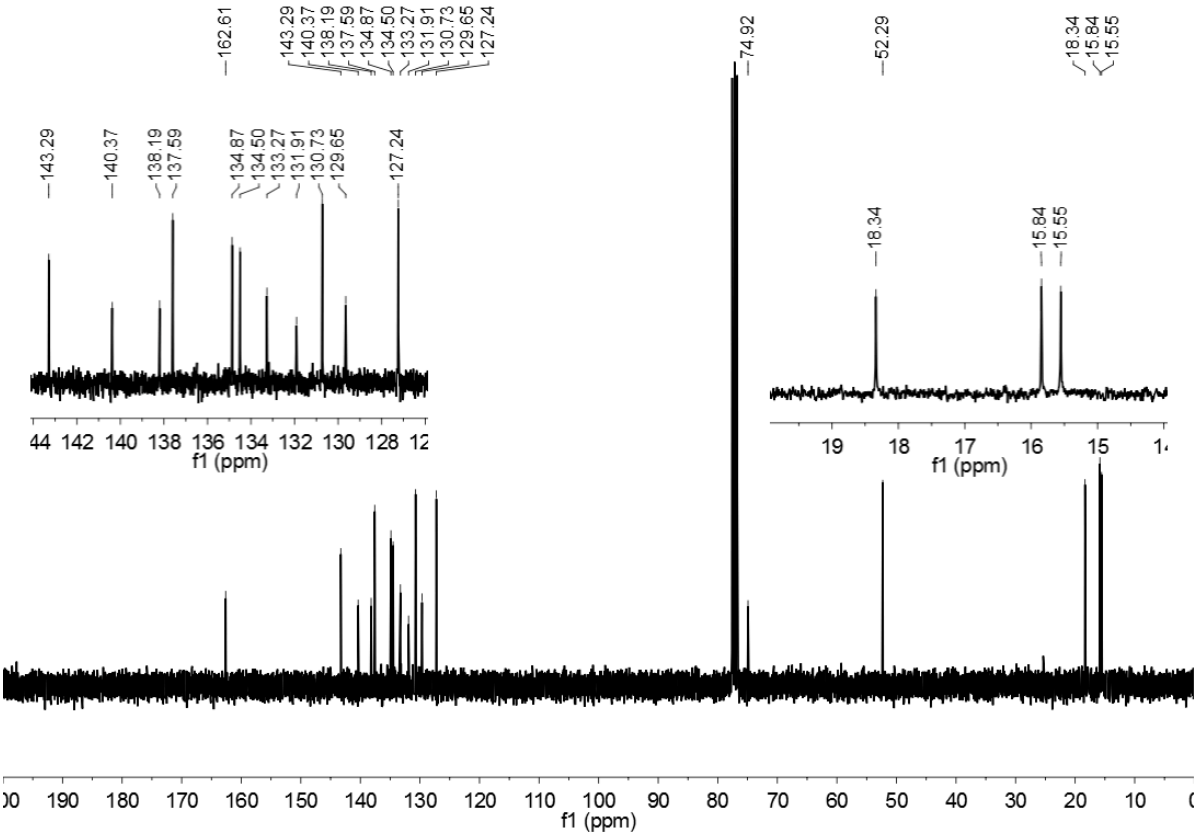

Figure S109. ^{13}C NMR spectrum of **74** in $CDCl_3$.

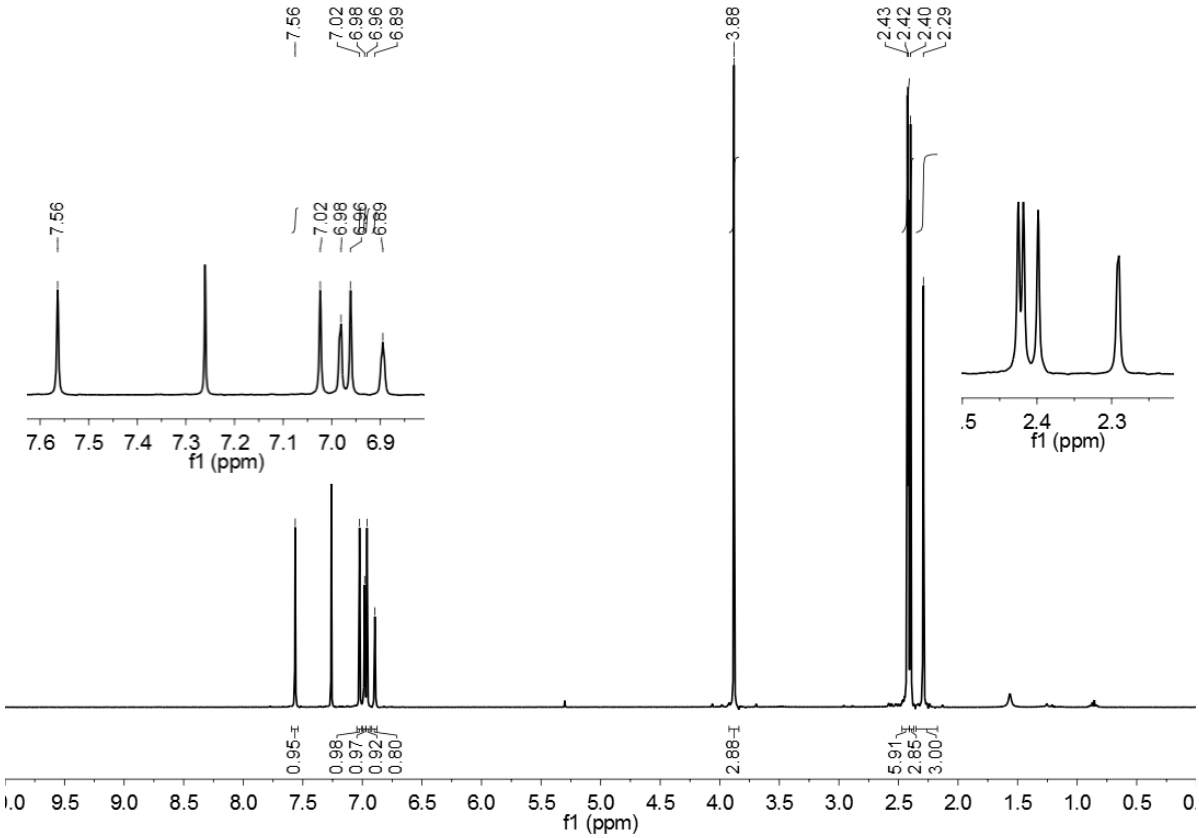

Figure S110. ^{1}H NMR spectrum of **75** in $CDCl_3$.

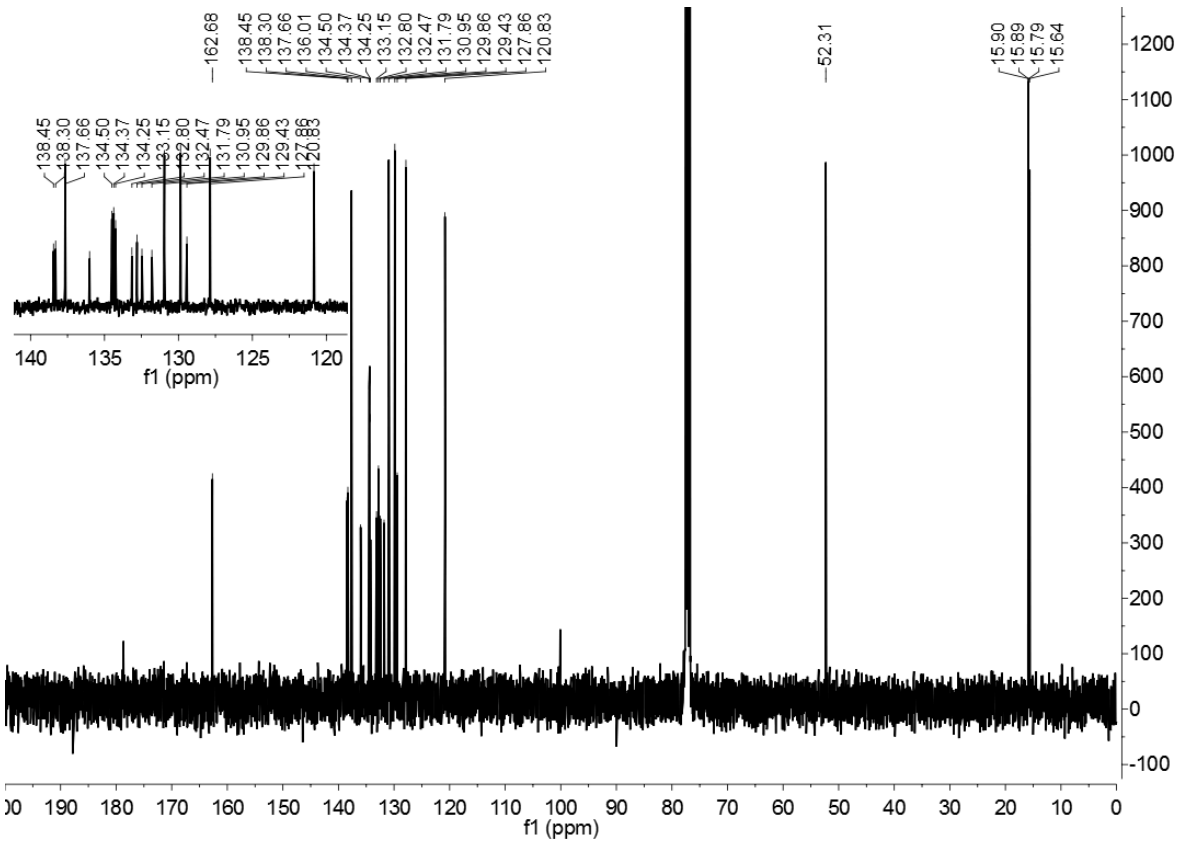

Figure S111. ^{13}C NMR spectrum of **75** in $CDCl_3$.

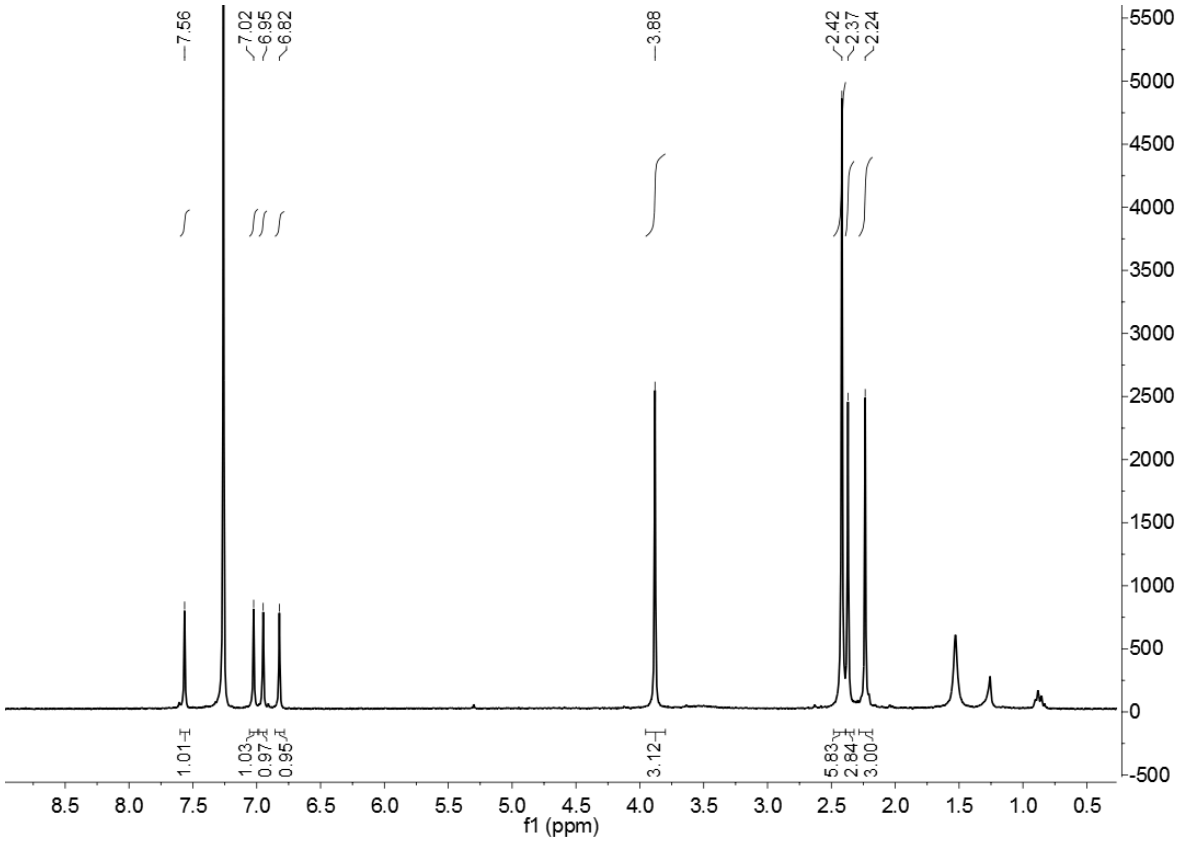

Figure S112. ^{1}H NMR spectrum of **76** in $CDCl_3$.

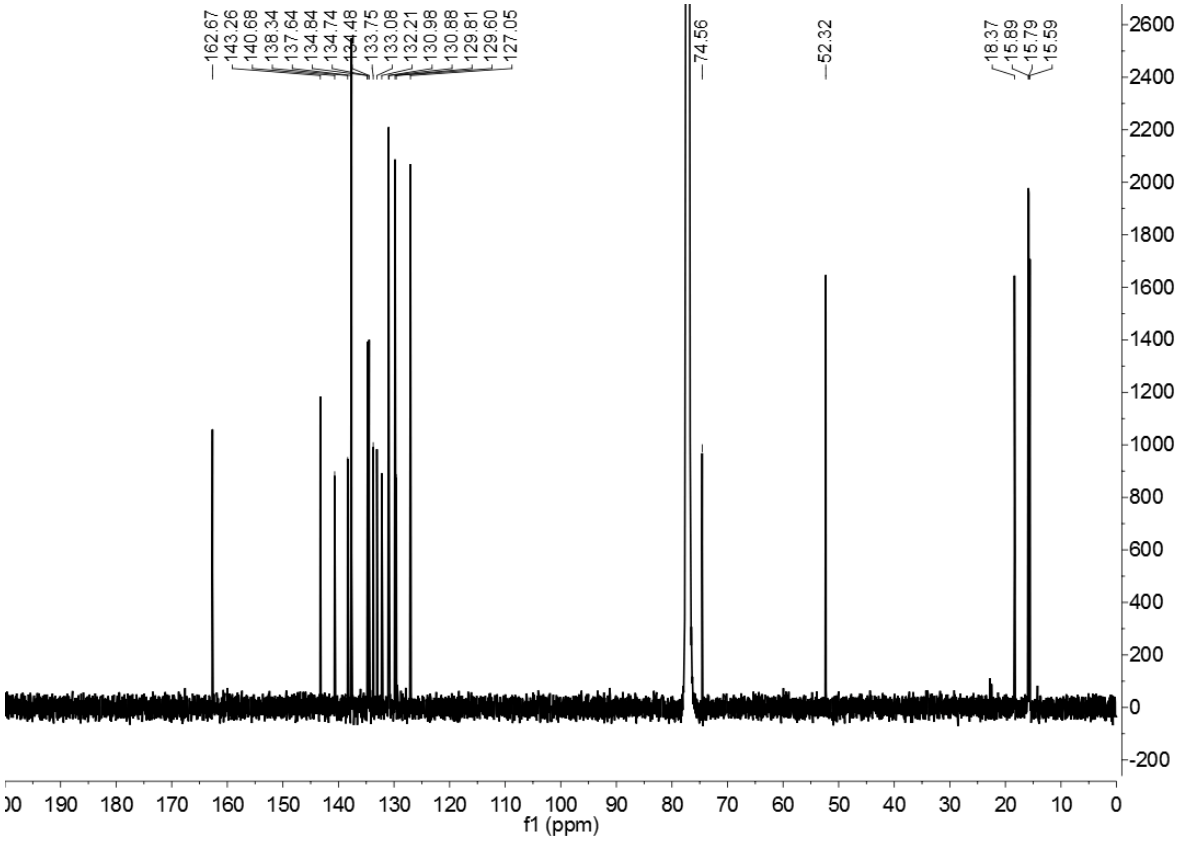

Figure S113. ^{13}C NMR spectrum of **76** in $CDCl_3$.

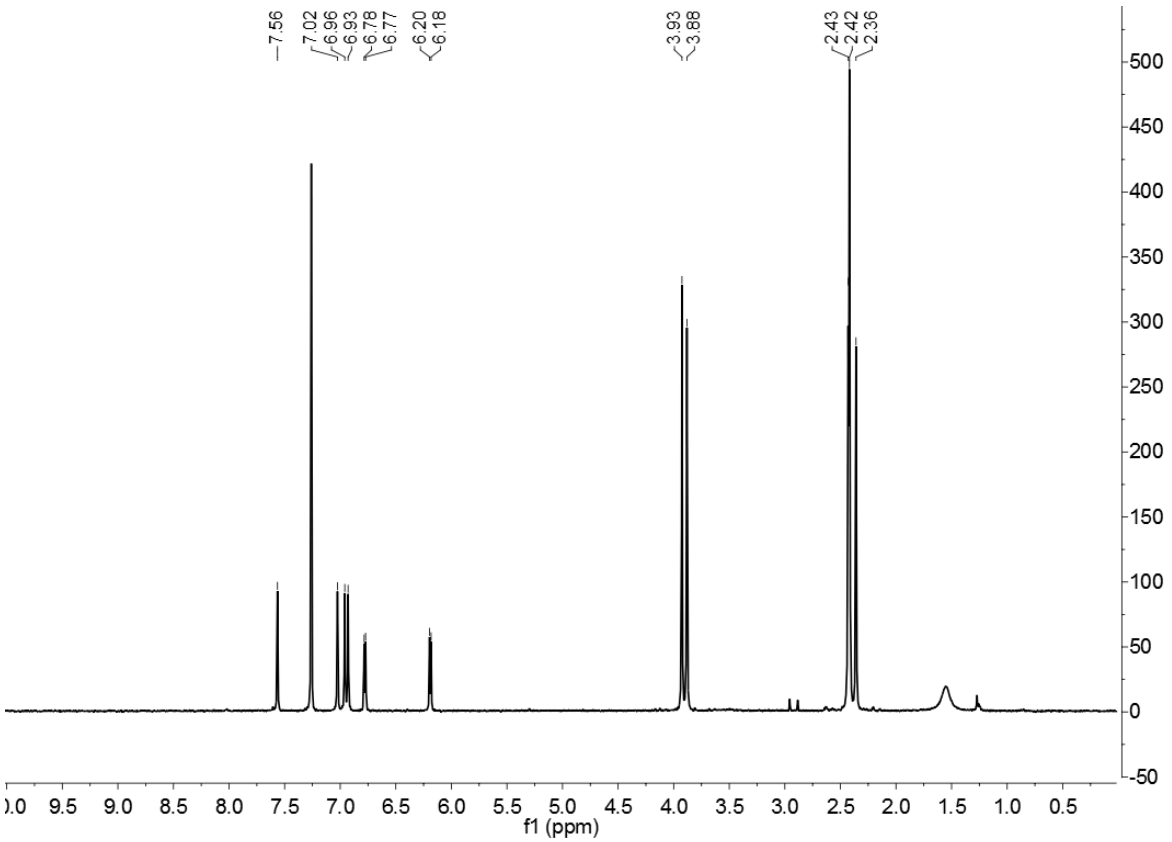

Figure S114. ^{1}H NMR spectrum of **77** in $CDCl_3$.

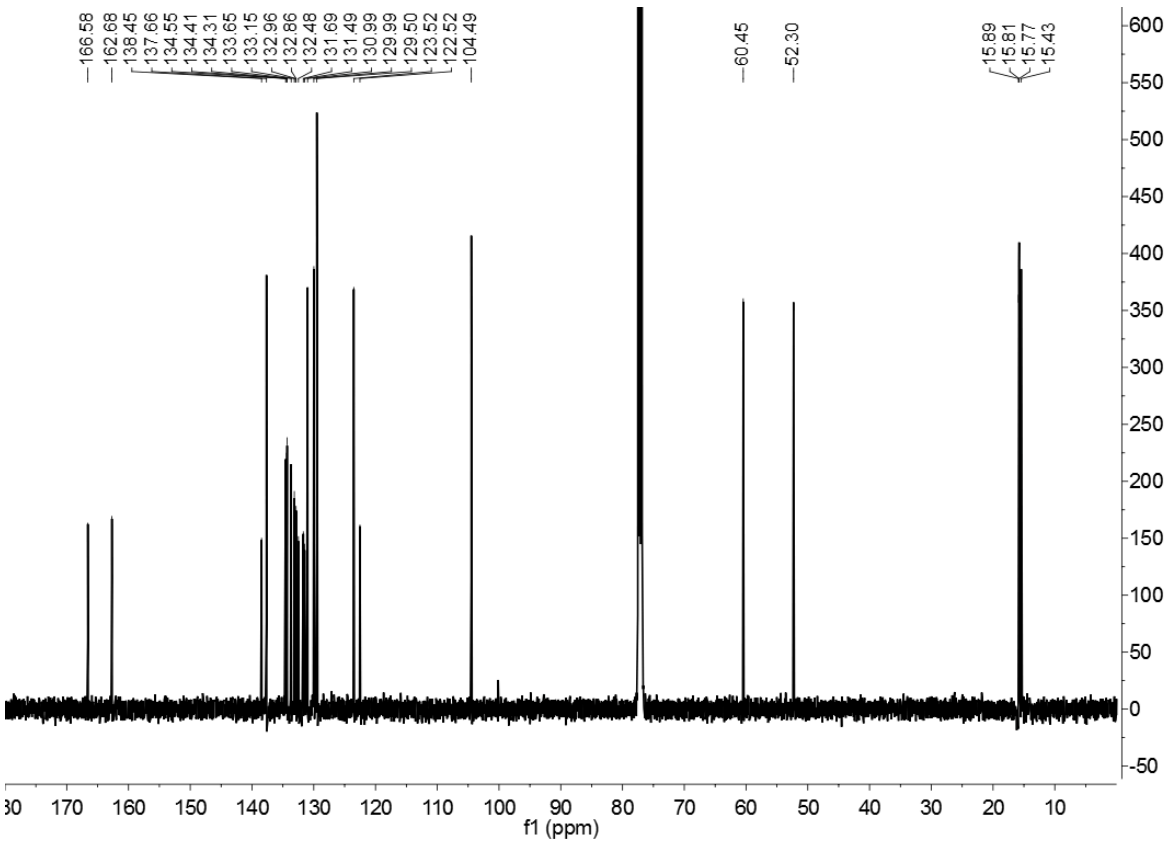

Figure S115. ^{13}C NMR spectrum of **77** in $CDCl_3$.

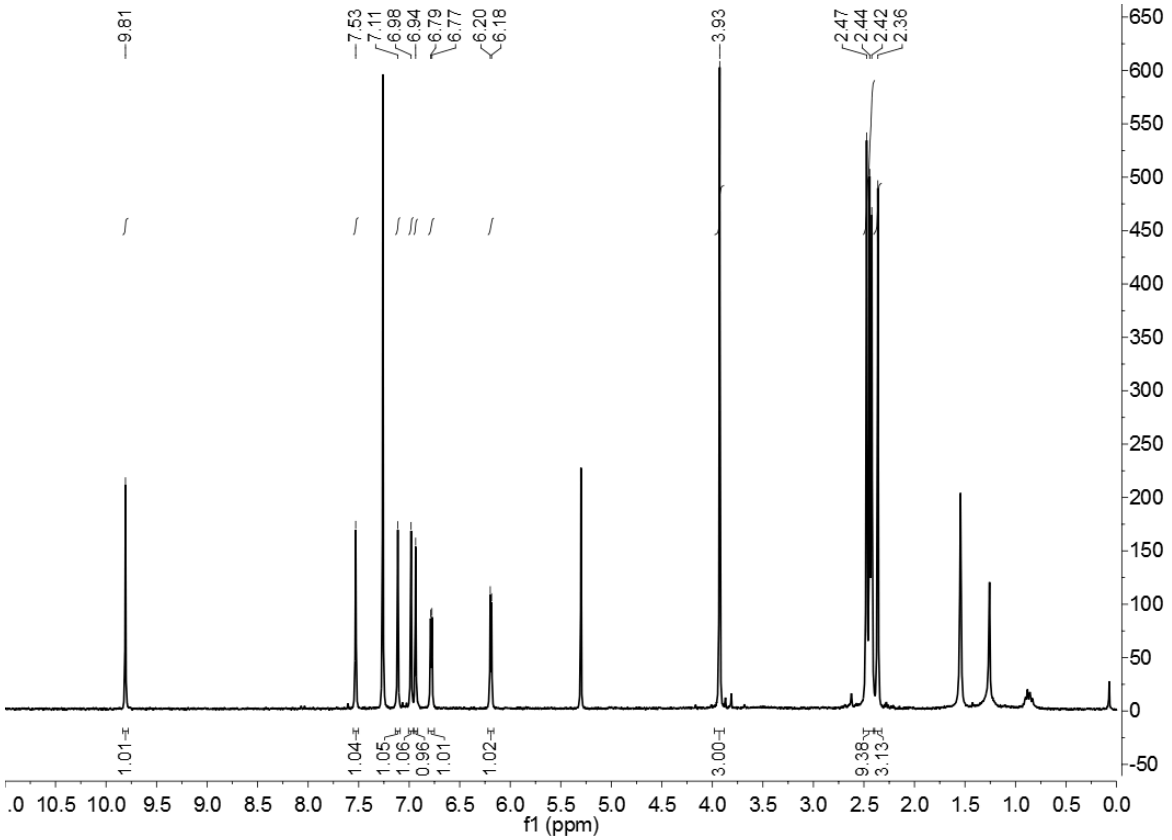

Figure S116. ^{1}H NMR spectrum of **78** in $CDCl_3$.

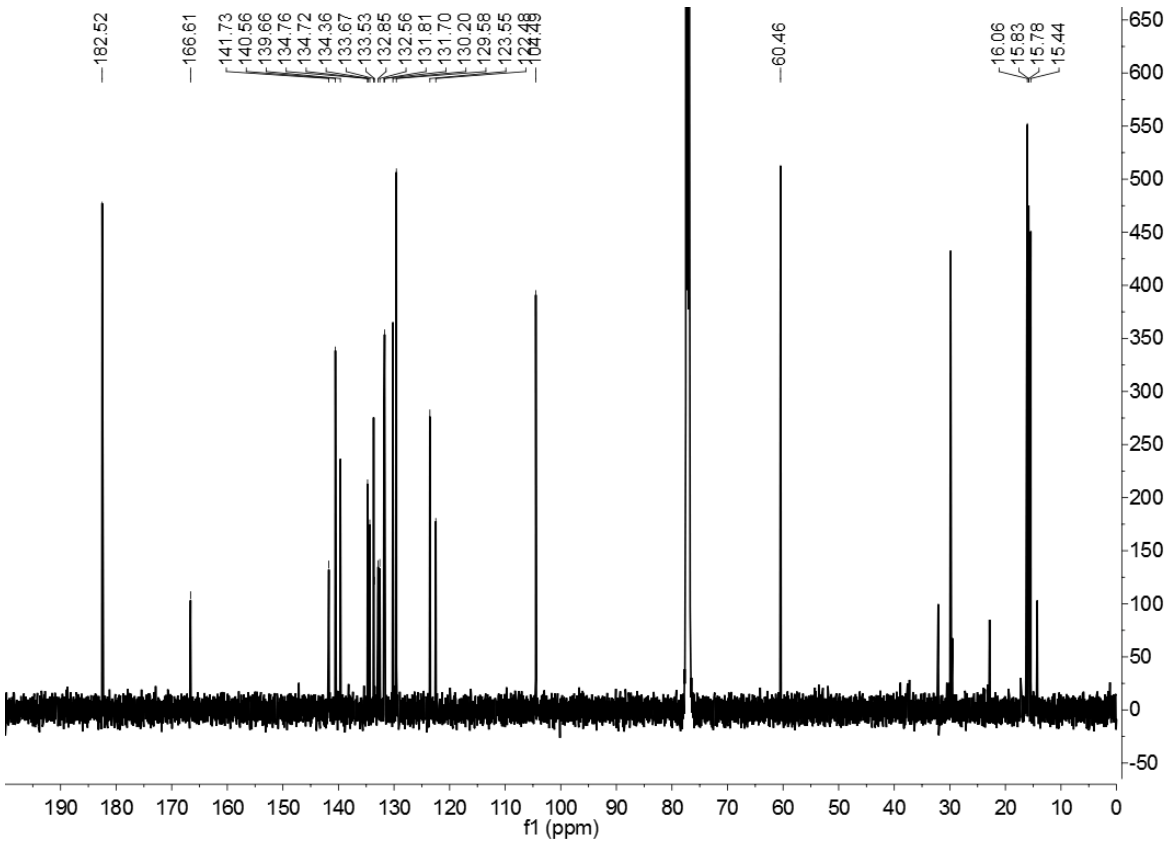

Figure S117. ^{13}C NMR spectrum of **78** in $CDCl_3$.

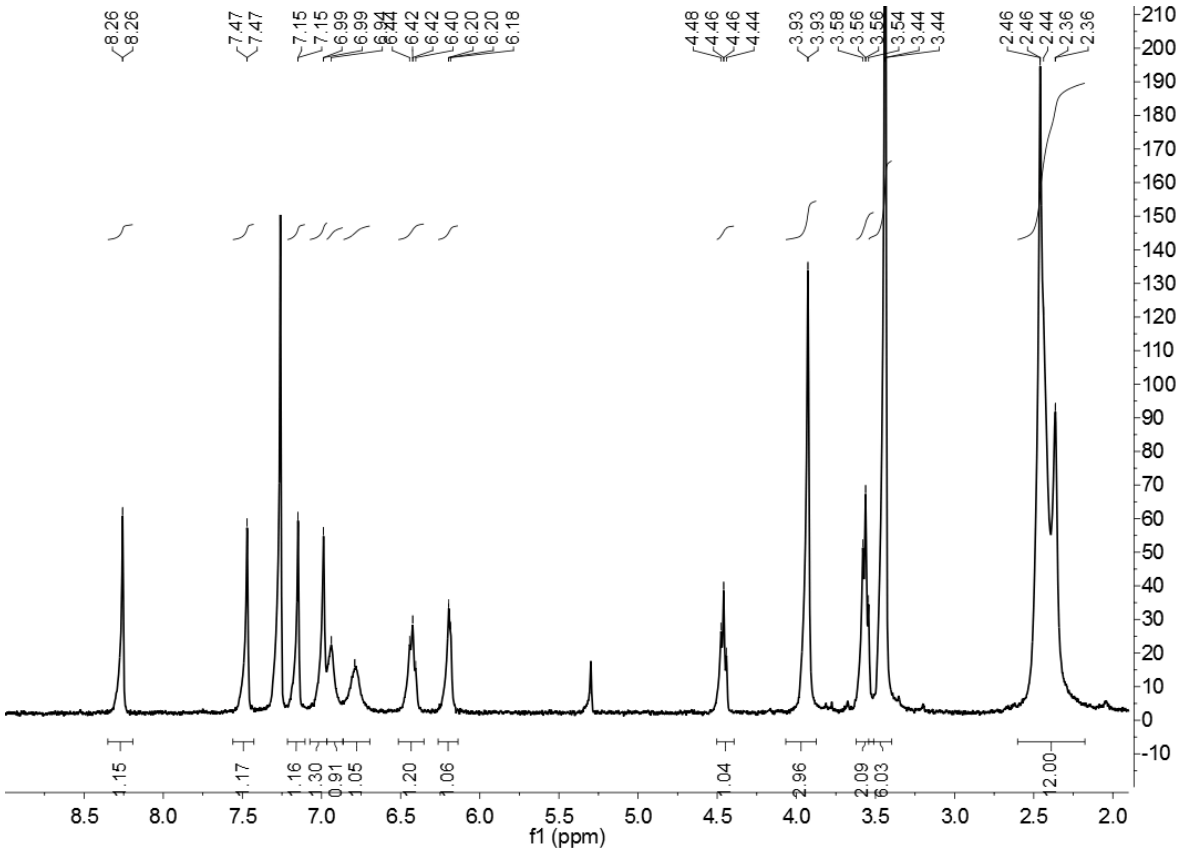

Figure S118. ^{1}H NMR spectrum of **79** in $CDCl_3$.

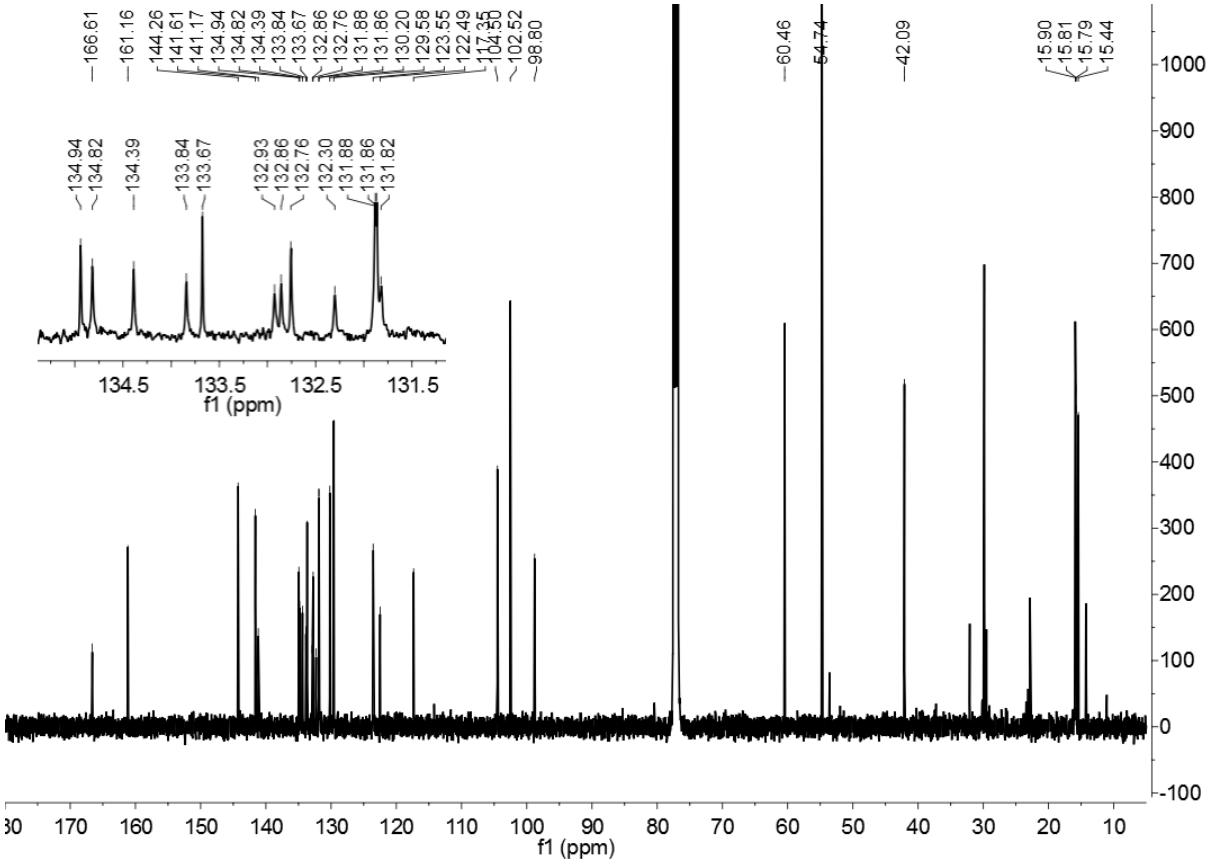

Figure S119. ^{13}C NMR spectrum of **79** in $CDCl_3$.

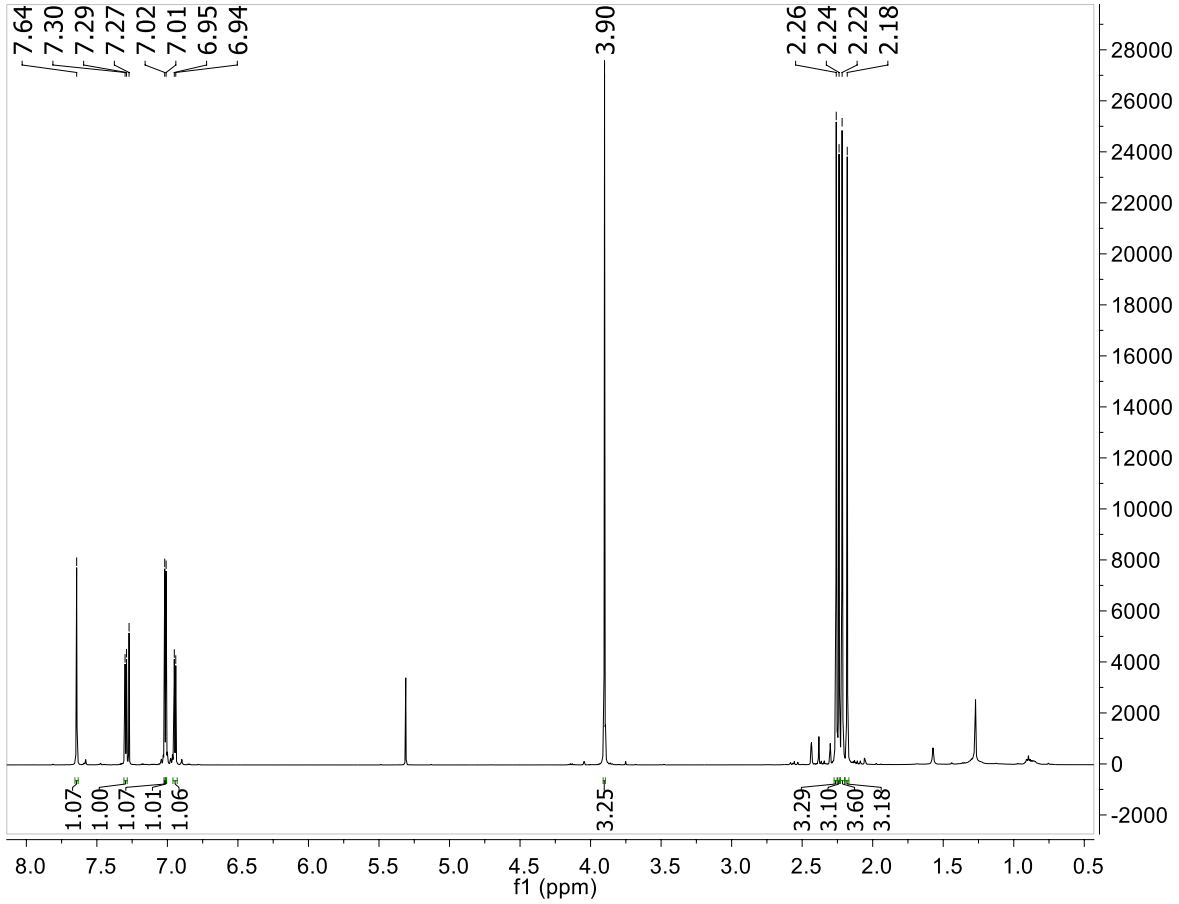

Figure S120. ^{1}H NMR spectrum of **85** in $CDCl_3$.

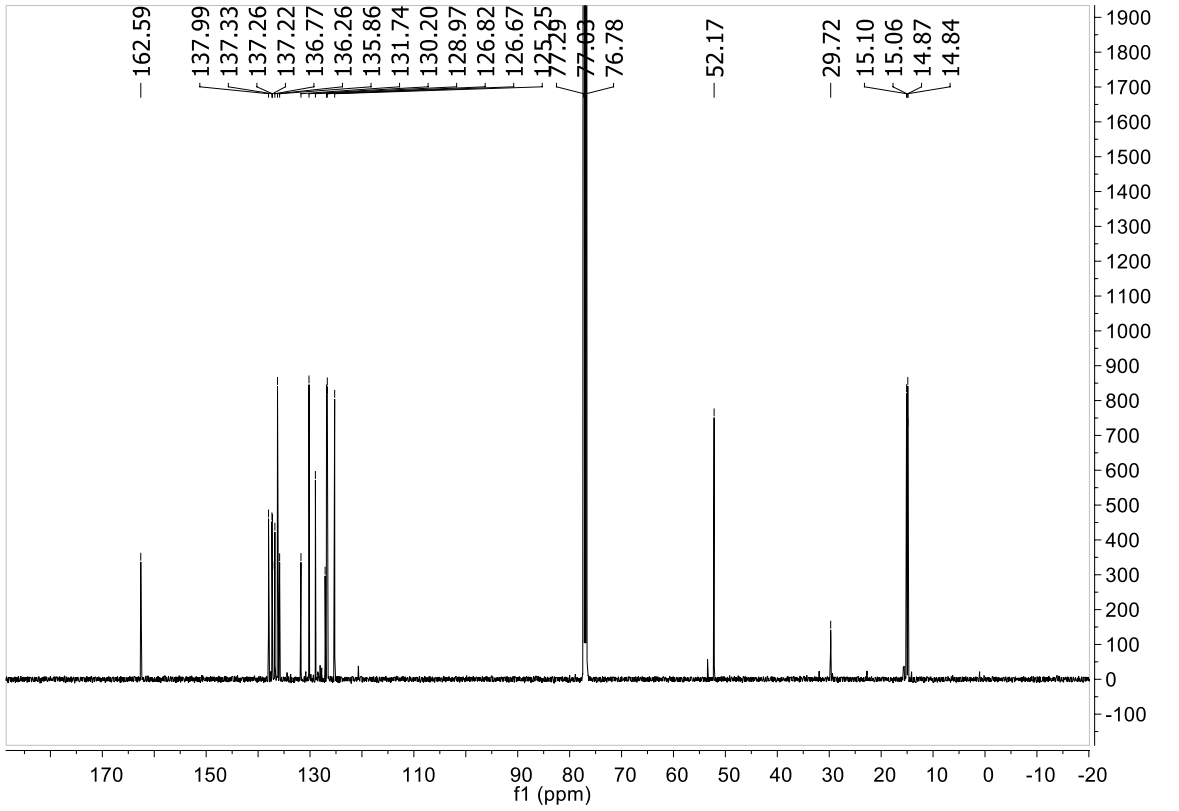

Figure S121. ^{13}C NMR spectrum of **85** in $CDCl_3$.

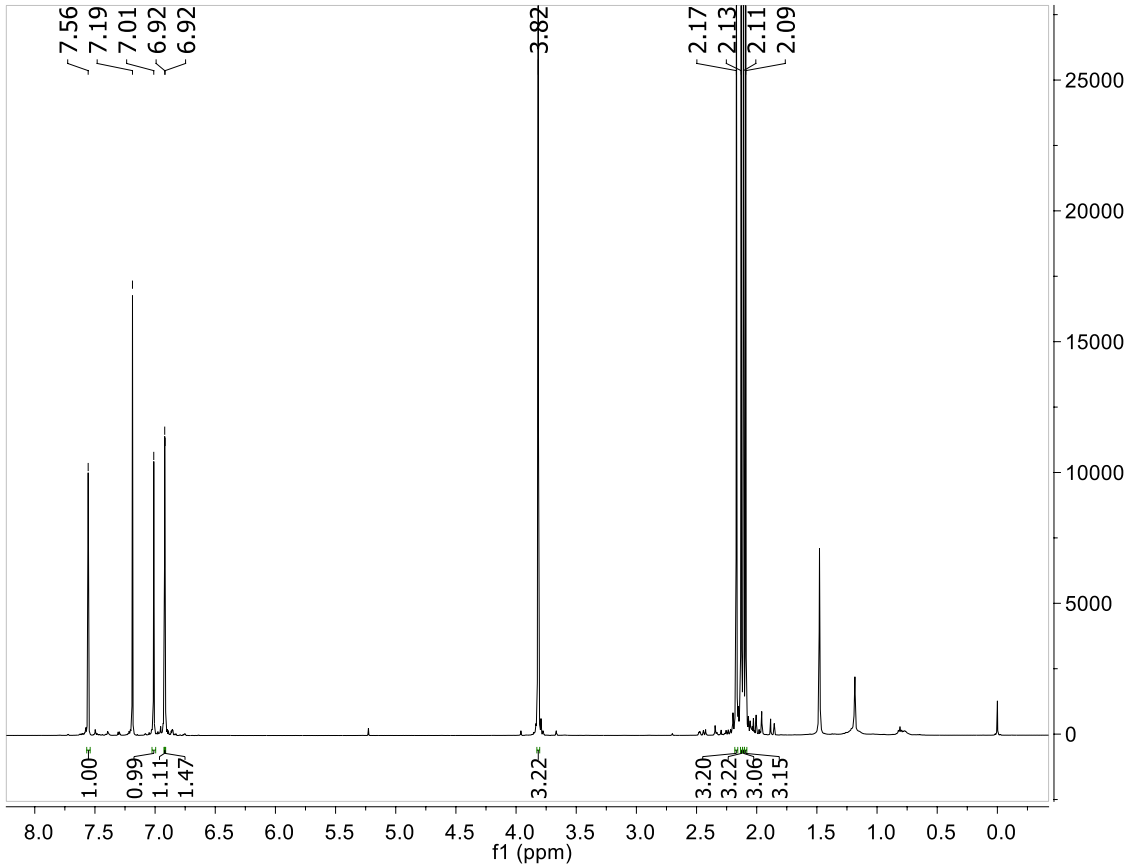

Figure S122. ^{1}H NMR spectrum of **86** in $CDCl_3$.

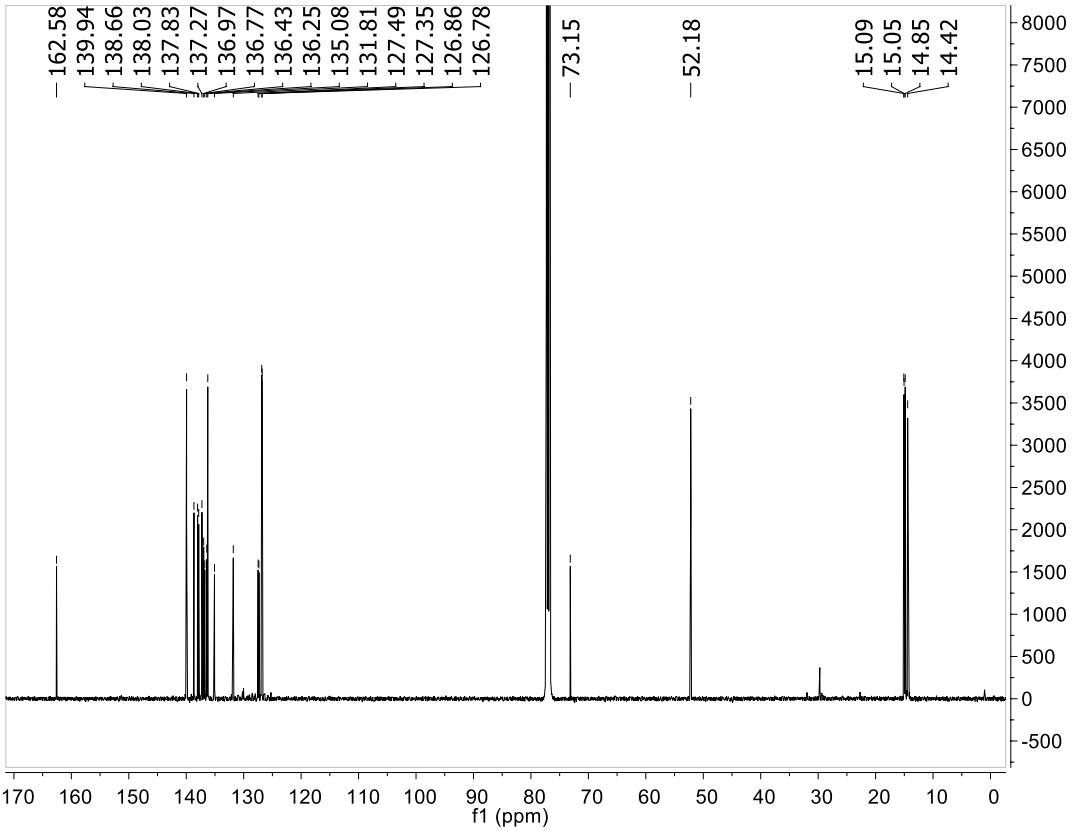

Figure S123. ^{13}C NMR spectrum of **86** in $CDCl_3$.

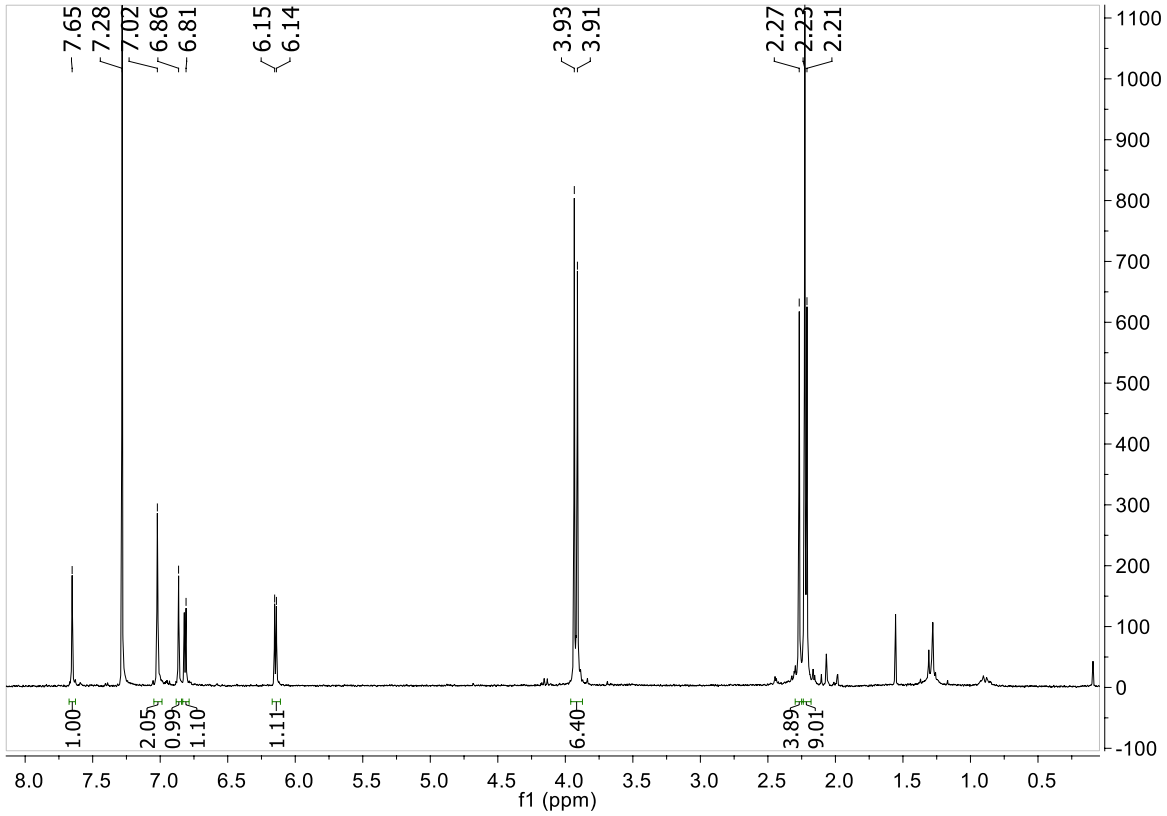

Figure S124. ^{1}H NMR spectrum of **87** in $CDCl_3$.

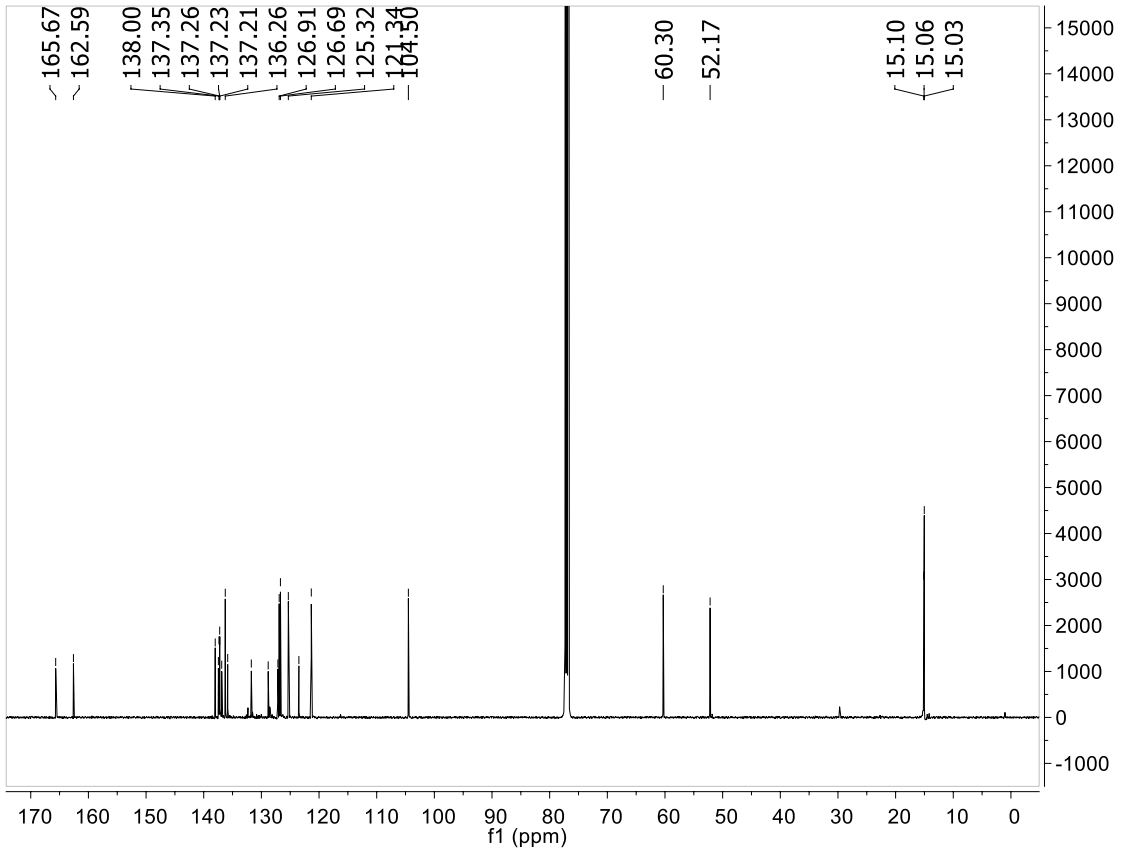

Figure S125. ^{13}C NMR spectrum of **87** in $CDCl_3$.

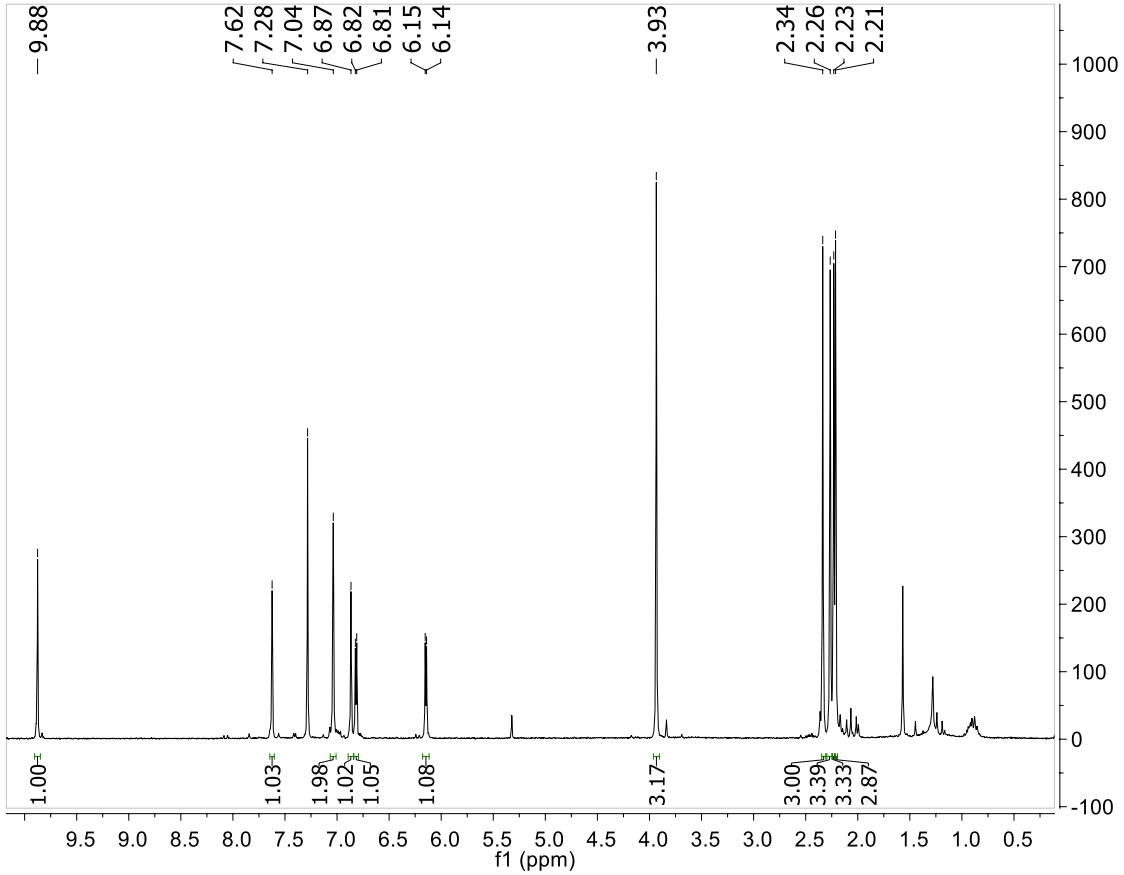

Figure S126. ^{1}H NMR spectrum of **88** in $CDCl_3$.

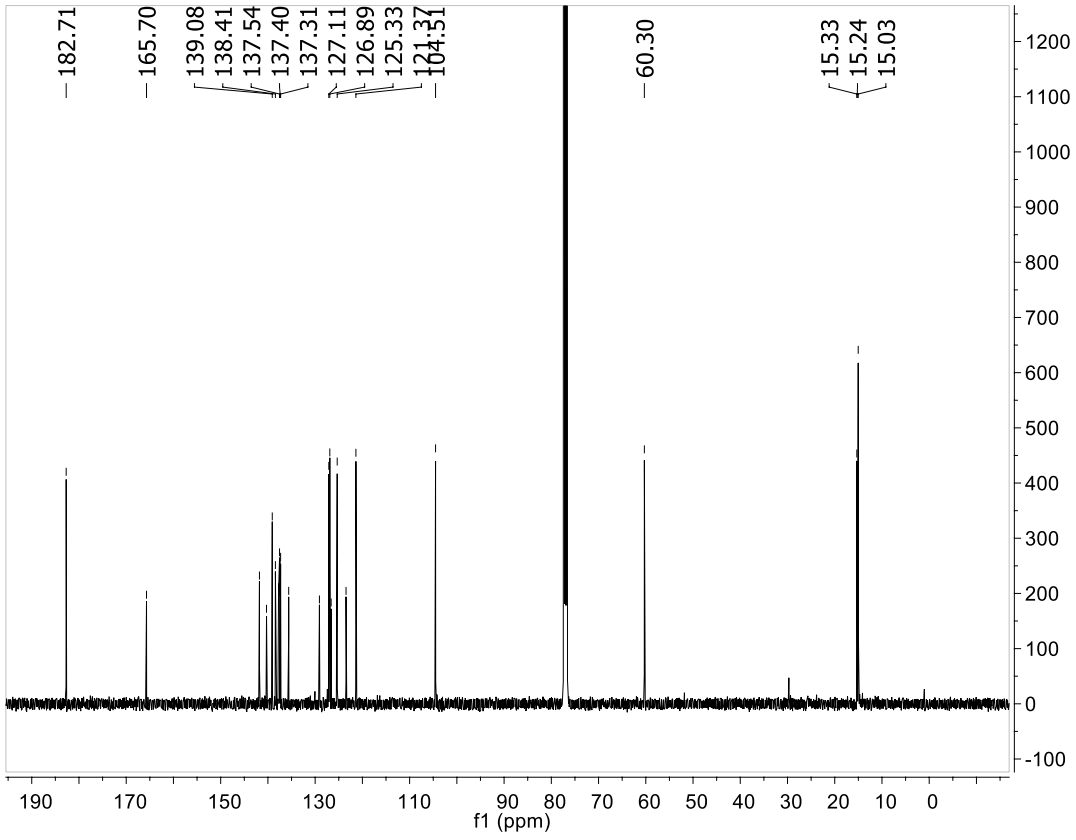

Figure S127. ^{13}C NMR spectrum of **88** in $CDCl_3$.

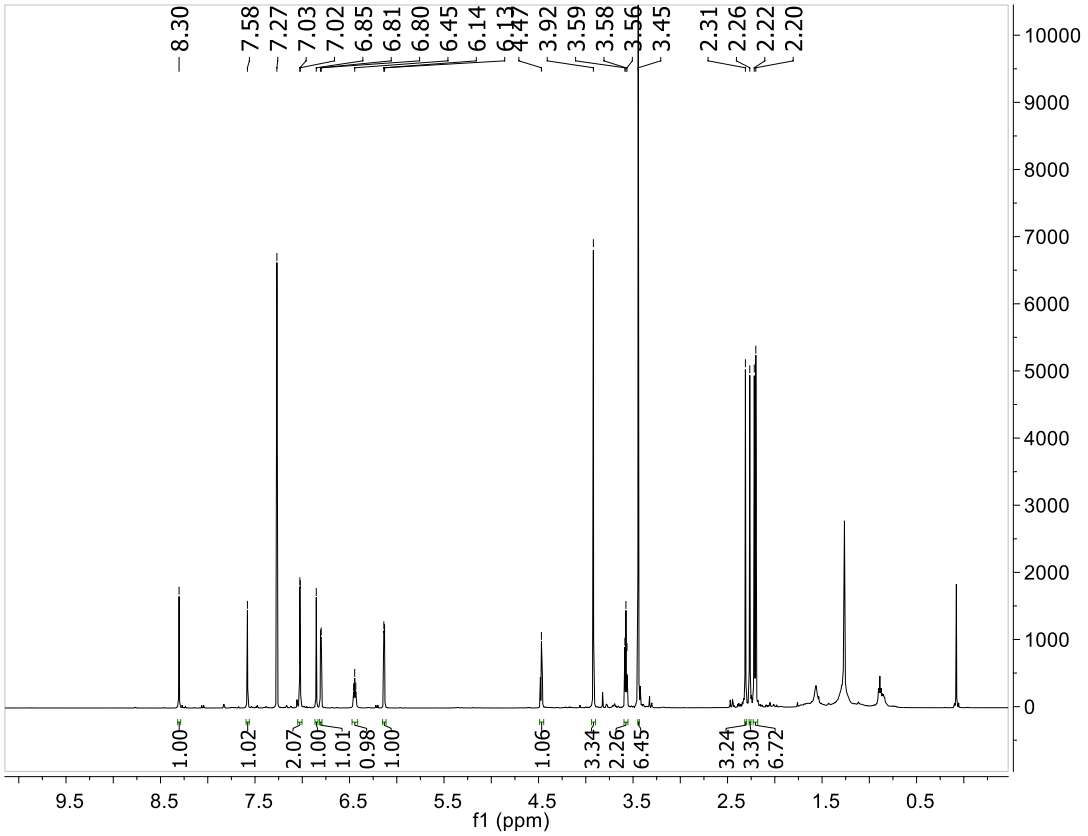

Figure S128. ^{1}H NMR spectrum of **89** in $CDCl_3$.

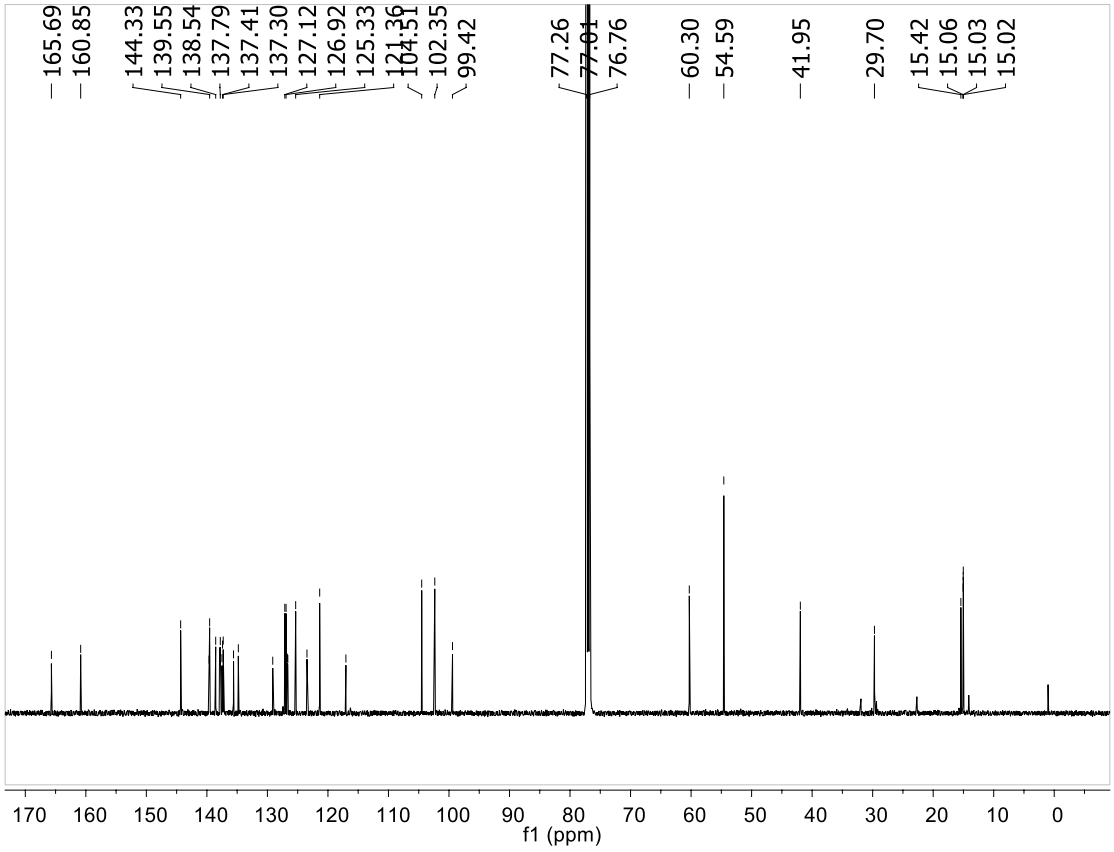

Figure S129. ^{13}C NMR spectrum of **89** in $CDCl_3$.