Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Regioselective Functionalization at the 7-Position of 1,2,3-Triphenylbenzo[*b*]phosphole Oxide via P=O-Directed Lithiation

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General

All melting points were recorded on a Yazawa micro melting point apparatus and are uncorrected. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on 700 MHz (Agilent) and/or 400 MHz (Agilent or AVANCEIII HD Nanobay) spectrometers. Chemical shifts are reported in ppm as relative values vs. tetramethylsilane (for ^{1}H and ^{13}C) or phosphoric acid (for ^{31}P). High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer (electron spray–quadrupole). UV-vis absorption and fluorescence spectra were measured on JASCO V-530 and EP-8300 spectrometers, respectively. All the excitation spectra were essentially identical to the corresponding absorption spectra. Absolute fluorescence quantum yields were measured on a Hamamatsu Photonics Quantaurus-QY spectrometer. Redox potentials were measured on a CH Instruments model 650E electrochemical workstation using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag^+ [0.01 M $AgNO_3$, 0.1 M Bu_4NPF_6 (MeCN)] reference electrode. The potentials were calibrated with a ferrocene/ferrocenium couple. Compounds **1**[1] and **12**[2] were prepared according to the reported procedures. Other chemicals and solvents were of reagent grade quality and used without further purification. Thin-layer chromatography was performed with Alt. 5554 DC-Alufolien Kieselgel 60 F254 (Merck), and preparative column chromatography was performed using silica gel (spherical, neutrality). All reactions were performed under an argon or nitrogen atmosphere unless otherwise noted.

Synthesis and Characterization of New Compounds

2. To a solution of **1** (1.133 g, 2.99 mmol) in THF (20 mL) was added fleshly prepared LiTMP (1.0 M, 10.8 mL, 10.8 mmol) and stirred for 2 h at –78 °C, followed by the addition of a solution of 1,2-diiodoethane (3.233 g, 11.47 mmol) in THF (5 mL). The mixture was stirred for 1 h at –78 °C

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[1] Y. Unoh, K. Hirano, T. Satoh and M. Miura, *Angew. Chem. Int. Ed.*, 2013, **52**, 12975.

[2] T. Sakida, S. Yamaguchi and H. Shinokubo, *Angew. Chem. Int. Ed.*, 2011, **50**, 2280.

and then warmed up to room temperature. The mixture was diluted with an aqueous $NaHSO_3$ solution, and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (hexane/AcOEt = 1/1) to give **2** (0.7165 g, 1.421 mmol, 47%). When LDA or lithium bis(trimethyldisilazide) was used as the base, **2** was not obtained. R_f = 0.3 (hexane/AcOEt = 1/1); mp 186–190 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08–7.13 (m, 4H), 7.16–7.19 (m, 1H), 7.21–7.23 (m, 2H), 7.29–7.31 (m, 2H), 7.39–7.44 (m, 5H), 7.49–7.55 (m, 1H), 7.68–7.71 (m, 1H), 7.83–7.89 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 95.9 (d, $J_{C\text{–}P}$ = 7.6 Hz), 123.4 (d, $J_{C\text{–}P}$ = 9.9 Hz), 127.3 (d, $J_{C\text{–}P}$ = 101.0 Hz), 127.9 (s), 128.09 (s), 128.13 (s), 128.7 (d, $J_{C\text{–}P}$ = 12.1 Hz), 128.7 (s), 128.9 (s), 129.0 (d, $J_{C\text{–}P}$ = 6.0 Hz), 131.6 (d, $J_{C\text{–}P}$ = 10.6 Hz), 132.3 (s), 132.3 (d, $J_{C\text{–}P}$ = 9.9 Hz), 133.6 (d, $J_{C\text{–}P}$ = 15.2 Hz), 133.8 (d, $J_{C\text{–}P}$ = 1.5 Hz), 134.9 (d, $J_{C\text{–}P}$ = 96.3 Hz), 136.4 (d, $J_{C\text{–}P}$ = 108.5 Hz), 138.7 (d, $J_{C\text{–}P}$ = 7.6 Hz), 146.6 (d, $J_{C\text{–}P}$ = 27.3 Hz), 148.5 (d, $J_{C\text{–}P}$ =19.7 Hz) ppm; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$); δ = 40.5 ppm; HRMS (ESI): m/z = 505.0212 ([M + H]$^+$, Calcd 505.0213).

3. To a degassed solution of **2** (0.200 g, 0.395 mmol), *p*-(*N*,*N*-diphenylamino)phenylboronic acid (0.232 g, 0.565 mmol), SPhos (72.4 mg, 0.176 mmol), $Pd(OAc)_2$ (19.1 mg, 0.085 mmol) in 1,4-dioxane (10 mL) was added an aqueous K_3PO_4 solution (3 M, 2 mL), and the resulting mixture was refluxed for 5 h. After cooling to room temperature, the mixture was diluted with an aqueous NaOH solution (1.0 M) and AcOEt, and the aqueous phase was extracted with AcOEt. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to to column chromatography on silica gel (hexane/AcOEt = 5/1). The yellow fluorescent fraction was collected and evaporated to give **3a** (0.307 g, 100%) as a yellow solid. R_f = 0.8 (hexane/AcOEt = 1/1). Compound **3b** and **3c** were synthesized in 100% and 69% yields, respectively, from **2** and the corresponding arylboronic acids according to a similar procedure described for the synthesis of **3a**.

3a: Mp 236–239 °C; ^{1}H NMR (700 MHz, CD_2Cl_2): δ = 6.48–6.78 (broad–s, 1H), 6.99–7.00 (m, 2H), 7.04–7.06 (m, 5H), 7.08–7.11 (m, 3H), 7.16–7.18 (m, 1H), 7.19–7.20 (m, 2H), 7.26–7.30 (m, 6H), 7.37-7.42 (m, 4H), 7.44–7.53 (m, 8H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 122.6 (d, $J_{C–P}$ = 10.6 Hz), 122.9 (s), 123.5 (s), 124.2 (s), 127.7 (s), 128.1 (s), 128.2 (d, $J_{C–P}$ = 12.9 Hz), 128.6 (s), 129.0 (s), 129.1 (s), 129.17 (s), 129.22 (s), 129.3 (d, $J_{C–P}$ = 100.2 Hz), 130.0 (d, $J_{C–P}$ = 102.4 Hz), 130.0 (d, $J_{C–P}$ = 9.1 Hz), 130.3 (s), 130.8 (d, $J_{C–P}$ = 10.6 Hz), 131.7 (d, $J_{C–P}$ = 3.0 Hz), 132.8 (d, $J_{C–P}$ = 9.9 Hz), 132.9 (d, $J_{C–P}$ = 1.5 Hz), 133.3 (d, $J_{C–P}$ = 3.0 Hz), 133.6 (d, $J_{C–P}$ = 97.9 Hz), 134.6 (d, $J_{C–P}$ = 14.4 Hz), 144.5 (d, $J_{C–P}$ = 27.4 Hz), 145.4 (d, $J_{C–P}$ = 8.3 Hz), 147.6 (s), 147.7 (s), 150.1 (d, $J_{C–P}$ = 20.5 Hz) ppm; $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2); δ = 40.0 ppm; HRMS (ESI): *m*/*z* = 622.2295 ([*M* + H]$^+$, calcd 622.2294).

3b: Mp 208–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05–7.09 (m, 3H), 7.11–7.16 (m, 2H), 7.17–7.20 (m, 1H), 7.24–7.39 (m, 12H), 7.43–7.49 (m, 3H), 7.51–7.55 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 122.9 (d, $J_{C–P}$ = 10.6 Hz), 127.7 (d, $J_{C–P}$ = 1.5 Hz), 127.95 (s), 127.99 (s), 128.1 (s), 128.2 (d, $J_{C–P}$ = 12.1 Hz), 128.6 (s), 129.0 (s), 129.12 (d, $J_{C–P}$ = 3.0 Hz), 129.14 (d, $J_{C–P}$ = 3.8 Hz), 129.2 (d, $J_{C–P}$ = 100.1 Hz), 129.3 (s), 130.2 (d, $J_{C–P}$ = 8.3 Hz), 130.3 (d, $J_{C–P}$ = 102.5 Hz), 130.5 (d, $J_{C–P}$ = 11.3 Hz), 131.7 (d, $J_{C–P}$ = 3.0 Hz), 132.8 (d, $J_{C–P}$ = 9.9 Hz), 132.9 (d, $J_{C–P}$ = 1.5 Hz), 133.6 (d, $J_{C–P}$ = 97.1 Hz), 134.6 (d, $J_{C–P}$ = 15.2 Hz), 139.0 (d, $J_{C–P}$ = 3.0 Hz), 144.3 (d, $J_{C–P}$ = 27.3 Hz), 145.7 (d, $J_{C–P}$ = 8.4 Hz), 150.0 (d, $J_{C–P}$ = 21.3 Hz) ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 39.8 ppm; HRMS (ESI): *m*/*z* = 455.1559 ([*M* + H]$^+$, calcd 455.1559).

3c: Mp 275–279 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05–7.10 (m, 3H), 7.17–7.23 (m, 4H), 7.28–7.32 (m, 2H), 7.34–7.40 (m, 5H), 7.44–7.49 (m, 3H), 7.52–7.56 (m, 1H), 7.61–7.69 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 111.7 (s), 118.8 (s), 123.9 (d, $J_{C–P}$ = 10.5 Hz), 128.0 (s), 128.2 (s), 128.5 (d, $J_{C–P}$ = 12.5 Hz), 128.7 (d, $J_{C–P}$ = 99.8 Hz), 128.8 (s), 129. 0 (s), 129.1 (s, two carbons), 129.8 (d, $J_{C–P}$ = 8.2 Hz), 130.1 (s), 130.5 (d, $J_{C–P}$ = 10.8 Hz), 130.6 (d, $J_{C–P}$ = 101.2 Hz), 131.8 (s), 132.1 (d, $J_{\mathrm{C–P}}$ = 2.8 Hz), 132.4 (d, $J_{\mathrm{C–P}}$ = 10.4 Hz), 133.3 (d, $J_{\mathrm{C–P}}$ = 1.8 Hz), 134.0 (d, $J_{\mathrm{C–P}}$ = 97.6 Hz), 134.2 (d, $J_{\mathrm{C–P}}$ = 15.2 Hz), 143.4 (d, $J_{\mathrm{C–P}}$ = 8.3 Hz), 143.5 (d, $J_{\mathrm{C–P}}$ = 3.6 Hz), 144.7 (d, $J_{\mathrm{C–P}}$ = 26.6 Hz), 149.9 (d, $J_{\mathrm{C–P}}$ = 20.8 Hz) ppm; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$); δ = 1 ppm; HRMS (ESI): m/z = 480.1514 ([M + H]$^{+}$, Calcd 480.1512).

4a. To a degassed solution of **2** (0.556 g, 1.10 mmol), *N*-Boc-pyrrole-2-boronic acid MIDA (*N*-methyliminodiacetic acid) ester (0.419 g, 1.30 mmol), SPhos (181 mg, 0.441 mmol), $Pd(OAc)_2$ (49.3 mg, 0.220 mmol) in 1,4-dioxane (20 mL) was added an aqueous K_3PO_4 solution (3 M, 4.6 mL), and the resulting mixture was refluxed for 22 h. After cooling to room temperature, the mixture was diluted with an aqueous NaOH solution (1.0 M) and AcOEt, and the aqueous phase was extracted with AcOEt. The combined organic extracts were washed with brine, dried over Na_2SO_4, and evaporated. The residue was subjected to silica gel column chromatography (hexane/AcOEt = 4/1). The yellow fluorescent fraction was collected and evaporated to give **4a**, which was used for the next reaction without purification. The formation of **4a** was confirmed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Crude **4a** (0.518 g, ca. 0.95 mmol) was heated at 180 °C in a sealed tube for 3 h. Recrystallization of the resulting solid from hexane to give **4b** (0.364 g, 0.820 mmol, 86%) as a yellow solid.

4a: R_{f} = 0.8 (hexane/AcOEt = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (s, 9H), 6.25 (s, 1H), 6.55 (broad-s, 2H), 7.04–7.10 (m, 3H), 7.15–7.16 (m, 1H), 7.19–7.23 (m, 3H), 7.28–7.32 (m, 3H), 7.34–7.38 (m, 3H), 7.39–7.48 (m, 5H) ppm; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 38.5 ppm.

4b: R_{f} = 0.4 (hexane/AcOEt = 1/1); mp 180–184 °C; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 6.20–6.21 (m, 1H), 6.55–6.56 (m, 1H), 6.97–6.98 (m, 1H), 6.99–7.01 (m, 1H), 7.10–7.14 (m, 3H), 7.22–7.28 (m, 4H), 7.34–7.38 (m, 3H), 7.41–7.46 (m, 4H), 7.59–7.64 (m, 3H), 11.63 (s, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 108.7 (s), 109.4 (s), 120.9 (s), 121.4 (d, $J_{\mathrm{C–P}}$ = 10.6 Hz), 123.5 (d, $J_{\mathrm{C–P}}$ = 102.0 Hz), 127.5 (d, $J_{\mathrm{C–P}}$ = 9.0 Hz), 127.7 (s), 128.0 (s), 128.4 (d, $J_{\mathrm{C–P}}$ = 98.7 Hz), 128.5 (d, $J_{\mathrm{C–P}}$ =

12.6 Hz), 128.5 (s), 128.7 (s, two carbons), 128.8 (d, $J_{\mathrm{C-P}}$ = 6.2 Hz), 130.4 (s), 130.4 (d, $J_{\mathrm{C-P}}$ = 10.4 Hz), 131.9 (d, $J_{\mathrm{C-P}}$ = 2.6 Hz), 132.0 (d, $J_{\mathrm{C-P}}$ = 10.0 Hz), 132.0 (d, $J_{\mathrm{C-P}}$ = 99.0 Hz), 133.0 (s), 133.9 (d, $J_{\mathrm{C-P}}$ = 15.9 Hz), 136.0 (d, $J_{\mathrm{C-P}}$ = 7.8 Hz), 143.6 (d, $J_{\mathrm{C-P}}$ = 26.5 Hz), 150.5 (d, $J_{\mathrm{C-P}}$ = 21.9 Hz) ppm; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$); δ = 44.0 ppm; HRMS (ESI): *m*/*z* = 444.1514 ([*M* + H]$^+$, calcd 444.1512).

5a. To a solution of **2** (0.189 g, 0.375 mmol), ethynylbenzene (0.11 mL, 1.0 mmol), $PdCl_2(PPh_3)_2$ (139 mg, 0.199 mmol), CuI (18.7 mg, 0.098 mmol) in benzene (4 mL) was added $^{i}Pr_2NH$ (1.1 mL, 6.3 mmol), and the resulting mixture was stirred for 7 h at room temperature. The mixture was then diluted with water and AcOEt. The aqueous phase was extracted with AcOEt, and the combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (hexane/CH_2Cl_2/acetone = 20/20/1). The blue fluorescent fraction was collected to give **5a** as a sticky oil (0.205 g, 85%): R_f = 0.7 (hexane/AcOEt = 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07–7.12 (m, 3H), 7.13–7.18 (m, 1H), 7.27–7.31 (m, 2H), 7.31–7.37 (m, 7H), 7.40–7.51 (m, 8H), 7.84–7.90 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 86.1 (d, $J_{\mathrm{C-P}}$ = 5.3 Hz), 95.2 (s), 122.5 (s), 123.4 (d, $J_{\mathrm{C-P}}$ = 10.7 Hz), 124.9 (d, $J_{\mathrm{C-P}}$ = 6.8 Hz), 127.9 (s), 128.25 (s), 128.27 (s), 128.6 (d, $J_{\mathrm{C-P}}$ = 12.9 Hz), 128.76 (s), 128.79 (s), 128.8 (d, $J_{\mathrm{C-P}}$ = 100.9 Hz), 129.0 (s), 129.1 (s), 129.2 (s), 131.2 (d, $J_{\mathrm{C-P}}$ = 10.7 Hz), 131.7 (d, $J_{\mathrm{C-P}}$ = 7.6 Hz), 131.9 (s), 132.2 (d, $J_{\mathrm{C-P}}$ = 3.1 Hz), 132.7 (d, $J_{\mathrm{C-P}}$ = 10.6 Hz), 132.8 (s), 133.5 (d, $J_{\mathrm{C-P}}$ = 104.7 Hz), 134.1 (d, $J_{\mathrm{C-P}}$ = 15.2 Hz), 134.5 (d, $J_{\mathrm{C-P}}$ = 95.6 Hz), 144.2 (d, $J_{\mathrm{C-P}}$ = 25.8 Hz), 149.3 (d, $J_{\mathrm{C-P}}$ = 20.5 Hz) ppm; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$); δ = 38.0 ppm; HRMS (ESI): *m*/*z* = 479.1550 ([*M* + H]$^+$, calcd 479.1559).

5b. To a solution of **2** (0.369 g, 0.732 mmol), triisopropylsilylacetylene (0.8 mL, 4 mmol), $PdCl_2(PPh_3)_2$ (157 mg, 0.223 mmol), CuI (22.7 mg, 0.119 mmol) in toluene (7 mL) was added $^{i}Pr_2NH$ (2.0 mL, 11 mmol), and the resulting mixture was stirred for 16 h at room temperature. The mixture was diluted with water and toluene, and the aqueous phase was extracted with toluene. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (hexane/CH_2Cl_2/Acetone = 25/15/1). The blue fluorescent fraction was collected and evaporated to give **5b.** The formation of **5b** was confirmed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. To a solution of crude **5b** (0.501 g, 0.897 mmol) in THF (50 mL) was added tetrabutylammonium fluoride (1M, 4.4 mL, 4.4 mmol), and the resulting mixture was stirred for 0.5 h at room temperature. The mixture was concentrated under reduced pressure, and then CH_2Cl_2 and water were added to the mixture. The aqueous phase was extracted with CH_2Cl_2, and the combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (hexane/AcOEt = 1/1). The blue fluorescent fraction was collected, evaporated, and reprecipitated from hexane to give **5c** (0.280 g, 0.700 mmol, 78%).

5b: R_f = 0.8 (hexane/AcOEt = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02–1.07 (m, 21H), 7.05–7.10 (m, 3H), 7.12–7.15 (m, 1H), 7.22–7.25 (m, 2H), 7.27–7.30 (m, 2H), 7.32–7.47 (m, 8H), 7.76–7.82 (m, 2H) ppm; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 37.9 ppm; HRMS (ESI): *m*/*z* = 559.2567 ($[M + H]^+$, calcd 559.2581).

5c. R_f = 0.4 (hexane/AcOEt = 1/1); mp 188–190 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.27 (s, 1H), 7.06–7.12 (m, 3H), 7.16–7.19 (m, 1H), 7.23–7.28 (m, 2H), 7.31–7.33 (m, 2H), 7.38–7.52 (m, 8H), 7.81–7.86 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 79.7 (s), 83.1 (s), 123.6 (d, $J_{C\text{–}P}$ = 6.9 Hz), 124.0 (d, $J_{C\text{–}P}$ = 9.9 Hz), 127.9 (s), 128.2 (s), 128.5 (d, $J_{C\text{–}P}$ = 101.2 Hz), 128.6 (d, $J_{C\text{–}P}$ = 12.9 Hz), 128.8 (s), 129.0 (s, two carbons), 129.1 (d, $J_{C\text{–}P}$ = 6.0 Hz), 131.3 (d, $J_{C\text{–}P}$ = 10.6 Hz), 132.2 (d, $J_{C\text{–}P}$ = 2.3 Hz), 132.5 (s), 132.5 (d, $J_{C\text{–}P}$ = 2.3 Hz), 132.7 (d, $J_{C\text{–}P}$ = 1.5 Hz), 134.0 (d, $J_{C\text{–}P}$ = 15.2 Hz), 134.1 (d, $J_{C\text{–}P}$ = 103.9 Hz), 134.6 (d, $J_{C\text{–}P}$ = 97.9 Hz), 144.2 (d, $J_{C\text{–}P}$ = 25.8 Hz), 149.0 (d, $J_{C\text{–}P}$ =

20.4 Hz) ppm; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 37.9$ ppm; HRMS (ESI): $m/z = 403.1235$ ($[M + H]^+$, calcd 403.1246).

6. A mixture of $Pd(dba)_3$ (37.5 mg, 0.0410 mmol), tri(2-furyl)phosphine (37.3 mg, 0.161 mmol), and *N*-methyl-2-pyrrolidone (NMP) (2 mL) was stirred for 1 h at room temperature, followed by the addition of CuI (0.154 g, 0.809 mmol) and an NMP solution (8 mL) containing **2** (0.403 g, 0.798 mmol) and (*E*)-styryltributylstannane (0.54 g, 1.0 mmol). The resulting mixture was stirred for 15 h at 120 °C, and then diluted with an aqueous KF solution and AcOEt. The aqueous phase was extracted with AcOEt, and the combined organic extracts were washed with NH_4Cl and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (CH_2Cl_2/acetone = 60/1). The blue fluorescent fraction was collected, evaporated, and reprecipitated from hexane to give **6** (0.101 g, 0.209 mmol, 26%) as a colorless solid: $R_f = 0.6$ (CH_2Cl_2/acetone = 60/1); mp 185–186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.07–7.12 (m, 4H), 7.20–7.29 (m, 5H), 7.32–7.51 (m, 13H), 7.62–7.65 (m, 1H), 7.79–7.85 (m, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): $\delta =$ 122.9 (d, $J_{C-P} = 10.6$ Hz), 124.6 (d, $J_{C-P} = 6.1$ Hz), 125.4 (d, $J_{C-P} = 8.4$ Hz), 127.0 (s), 127.8 (d, $J_{C-P} = 1.5$ Hz), 128.2 (s), 128.3 (s), 128.6 (s), 128.7 (s), 128.9 (d, $J_{C-P} = 12.2$ Hz), 128.9 (s), 129.1 (s), 129.1 (d, $J_{C-P} = 6.2$ Hz), 129.2 (d, $J_{C-P} = 103.1$ Hz), 129.9 (d, $J_{C-P} = 98.6$ Hz), 130.9 (d, $J_{C-P} = 9.9$ Hz), 132.1 (d, $J_{C-P} = 3.0$ Hz), 132.6 (d, $J_{C-P} = 10.7$ Hz), 132.6 (s), 133.0 (d, $J_{C-P} = 2.3$ Hz), 134.0 (d, $J_{C-P} = 96.3$ Hz), 134.4 (d, $J_{C-P} = 14.5$ Hz), 136.6 (s), 139.9 (d, $J_{C-P} = 7.6$ Hz), 144.2 (d, $J_{C-P} = 26.6$ Hz), 149.9 (d, $J_{C-P} = 21.3$ Hz) ppm; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$); $\delta = 39.5$ ppm; HRMS (ESI): $m/z = 481.1703$ ($[M + H]^+$, calcd 481.1716).

7. To a solution containing **4b** (0.108 g, 0.243 mmol) and 2,4,6-trimethylbenzaldehyde (17 μL, 0.12 mmol) in $CHCl_3$ (5 mL) was added trifluoroacetic acid (22 μL, 2.9 mmol), and the resulting mixture was stirred for 26.5 h at 60 °C. After cooling to room temperature, the mixture was diluted with an aqueous $NaHCO_3$ solution and CH_2Cl_2, and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was dissolved in THF (5 mL), and DDQ (27.4 mg, 0.121 mmol) was added to the resulting solution at –78 °C. The mixture was stirred for 0.5 h at room temperature, and evaporated. The residue was quickly subjected to column chromatography on silica gel (hexane/AcOEt=3/1), and the pink fluorescent fraction (R_f = 0.3, hexane/AcOEt = 3/1) was evaporated to give crude **7** (0.076 g). The formation of **7** was confirmed by HRMS spectrometry and used for the following reaction, as **7** slowly decomposed when stood in air. HRMS (ESI): m/z = 1015.3565 ($[M + H]^+$, calcd 1015.3577).

8. To a solution of **7** (76.0 mg, 0.075 mmol) in CH_2Cl_2 (5 mL) was added boron trifluoride diethyl ether (488 μL, 3.88 mmol) and *N*,*N*-diisopropylethylamine (654 μL, 3.85 mmol), and the resulting mixture was stirred for 14.5 h at room temperature. The mixture was then diluted with water and CH_2Cl_2 (10 mL), and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (hexane/AcOEt = 5/2). The pink fluorescent fraction (R_f = 0.6, hexane/AcOEt = 1/1) was collected and evaporated to give **8** (27.0 mg, 0.020 mmol, 27%): mp 222–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.87 (s, 3H), 2.34 (s, 3H), 2.38 (s, 3H), 6.16–6.32 (m, 4H), 6.39 (d, 2H, J = 4.4 Hz), 6.92 (s, 1H), 7.01 (s, 1H), 7.05–7.08 (m, 5H), 7.19–7.28 (m, 10H), 7.32–7.35 (m, 5H), 7.41–7.44 (m, 6H), 7.49–7.59 (m, 4H + 2H), 7.89–7.93 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 19.7 (s), 20.07 (s), 21.15 (s), 122.3 (s), 124.5 (d, $J_{C\text{–}P}$ = 10.7 Hz), 127.7 (s), 127.8 (s), 128.0 (s), 128.1 (s), 128.4 (d, $J_{C\text{–}P}$ = 12.9 Hz), 128.6 (s), 128.6 (d, $J_{C\text{–}P}$ = 118.0 Hz), 128.9 (s), 129.0 (d, $J_{C\text{–}P}$ = 5.3 Hz), 129.1 (s), 128.8–129.3 (three carbons), 130.3 (d, $J_{C\text{–}P}$ = 102.1 Hz), 130.5 (s), 131.1 (d, $J_{C\text{–}P}$ = 10.6 Hz), 131.7 (s), 131.92 (s), 131.94 (s), 132.6 (d, $J_{C\text{–}P}$ = 10.2 Hz), 133.7 (d, $J_{C\text{–}P}$ = 97.1 Hz), 134.2 (d, $J_{C\text{–}P}$ = 14.7 Hz), 136.0 (s), 136.3 (d, $J_{C\text{–}P}$ = 8.3 Hz), 136.4 (s), 136.6 (s), 138.3 (s), 145.6 (s), 150.0 (d, $J_{C\text{–}P}$ = 21.3 Hz) ppm; $^{31}P\{^1H\}$

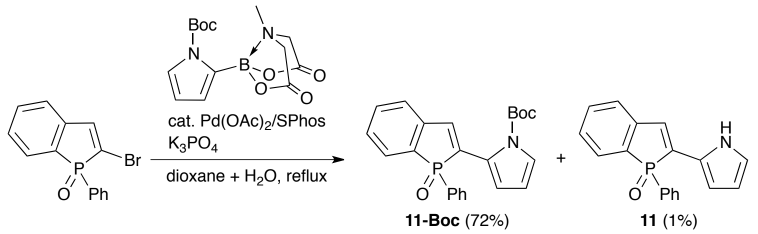
NMR (162 MHz, $CDCl_3$): δ = 40.1 ppm; HRMS (ESI): m/z = 1061.3606 ($[M + H]^+$, calcd 1061.3603).

9. A mixture of **5c** (0.102 g, 0.255 mmol), CuI (0.294 g, 1.545 mmol), and DMF (3 mL) was stirred for 24 h at room temperature under air. The mixture was passed through a Celite pad, and water was added to the filtrate. The aqueous phase was extracted with toluene, and the combined organic phases washed with aq. NH_4Cl and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was evaporated to give **9** (0. 242 g, 100%) after precipitation from hexane. R_f = 0.2 (hexane/AcOEt = 1/1); mp 195–197 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.07–7.14 (m, 6H), 7.15–7.20 (m, 2H), 7.27–7.30 (m, 4H), 7.33–7.35 (m, 4H), 7.39–7.54 (m, 16H), 7.83–7.89 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 79.0 (s), 79.5 (d, J_{C-P} = 5.3 Hz), 122.9 (d, J_{C-P} = 6.1 Hz), 124.4 (d, J_{C-P} = 9.9 Hz), 128.0 (s), 128.2 (d, J_{C-P} = 101.6 Hz), 128.3 (s), 128.8 (s), 128.8 (d, J_{C-P} = 6.0 Hz), 129.0 (d, J_{C-P} = 31.8 Hz), 129.1 (s), 129.1 (d, J_{C-P} = 14.1 Hz), 131.2 (d, J_{C-P} = 10.6 Hz), 132.5 (d, J_{C-P} = 9.8 Hz), 132.5 (d, J_{C-P} = 3.0 Hz), 132.7 (d, J_{C-P} = 1.5 Hz), 133.0 (d, J_{C-P} = 7.6 Hz), 134.1 (d, J_{C-P} = 14.4 Hz), 134.2 (d, J_{C-P} = 96.3 Hz), 135.2 (d, J_{C-P} = 103.2 Hz), 144.1 (d, J_{C-P} = 25.8 Hz), 149.3 (d, J_{C-P} = 20.5 Hz) ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$); δ = 38.0 ppm; HRMS (ESI): m/z = 803.2246 ($[M + H]^+$, calcd 803.2263).

11. A degassed mixture of 2-bromo-1-phenylbenzo[*b*]phosphole *P*-oxide (0.916 g, 3.00 mmol), *N*-Boc-pyrrole-2-boronic acid MIDA ester (1.432 g, 4.45 mmol), JohnPhos (210 mg, 0.598 mmol), $Pd(OAc)_2$ (67.7 mg, 0.302 mmol), K_3CO_4 (2.07 g, 15.0 mmol), MeCN (15 mL), and water (15 mL) was stirred for 1.5 h at 70 °C. After cooling to room temperature, the mixture was diluted with an aqueous NaOH solution (1.0 M) and CH_2Cl_2, and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4, and evaporated. The residue was then subjected to silica gel column chromatography (hexane/AcOEt = 2/1). The orange (R_f = 0.3, hexane/AcOEt = 1/1) and yellow (R_f = 0.2, hexane/AcOEt = 1/1) fractions were collected and evaporated to give **11-Boc** (0.840 g, 2.15 mmol, 72%) and **11** (7.1 mg, 0.024 mmol, 0.8%), respectively. Compound **11** could also be prepared by thermal deprotection of **11-Boc**.

11-Boc. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.58 (s, 9H), 6.12–6.14 (m, 1H), 6.78–6.80 (m, 1H), 7.26–7.30 (m, 1H), 7.31–7.32 (m, 1H), 7.35–7.41 (m, 3H), 7.45–7.49 (m, 2H), 7.57 (d, J = 36.4 Hz, 1H), 7.56–7.61 (m, 1H), 7.74–7.79 (m, 2H) ppm; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 40.6 ppm.

11. mp 235–238 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 6.20–6.23 (m, 1H), 6.53–6.54 (m, 1H), 6.82–6.83 (m, 1H), 7.16 (d, 1H, J = 35.6 Hz), 7.24–7.32 (m, 5H), 7.37–7.41 (m, 2H), 7.45–7.51 (m, 2H), 7.57–7.61 (m, 1H), 7.70–7.76 (m, 2H), 9.14 (s, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 110.4 (s), 112.6 (s), 122.7 (s), 125.0 (d, $J_{C–P}$ = 14.3 Hz), 125.5 (s), 128.8 (d, $J_{C–P}$ = 11.4 Hz), 129.3 (d, $J_{C–P}$ = 18.2 Hz), 129.5 (d, $J_{C–P}$ = 10.6 Hz), 129.9 (d, $J_{C–P}$ = 12.1 Hz), 130.3 (d, $J_{C–P}$ = 100.9 Hz), 130.9 (d, $J_{C–P}$ = 57.9 Hz), 131.4 (d, $J_{C–P}$ = 10.6 Hz), 131.7 (d, $J_{C–P}$ = 41.8 Hz), 133.6 (d, $J_{C–P}$ = 3.1 Hz), 134.8 (d, $J_{C–P}$ = 2.3 Hz), 144.5 (s) ppm; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 40.0 ppm; HRMS (ESI): m/z = 292.0876 ($[M + H]^+$, calcd 292.0886).



Scheme S1. Synthesis of **11**.

Selected X-ray Crystallographic Data

Single crystals of **3a** and **8** were grown from CH_2Cl_2–hexane and CH_2Cl_2–Et_2O, respectively. The measurement conditions and detailed crystallographic data were deposited in the Cambridge Crystallographic Data Centre (CCDC). Selected parameters are as follows.

3a (ccdc-1819535): $C_{44}H_{32}NOP$, 0.10 × 0.10 × 0.05 mm, triclinic, P–1, a = 9.9250(4) Å, b = 10.1565(3) Å, c = 17.6017(7) Å, α = 100.887(1)°, β = 93.347(1)°, γ = 112.723(2)°, V = 1590.2(1)

Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.298$ g cm^{-3}, $\mu = 1.24$ cm^{-1}, collected 14419, independent 7030, parameters 424, $R_w = 0.2269$, $R_1 = 0.0518$ ($I > 2.0\sigma(I)$), GOF = 1.089. **8** (ccdc-1819536): $C_{72}H_{58}BFN_2O_{4.5}P_2$, 0.02 × 0.01 × 0.01 mm, monoclinic, $C2/c$, $a = 35.941(1)$ Å, $b = 10.2627(4)$ Å, $c = 32.0520(7)$ Å, $\beta = 94.421(2)°$, $V = 11787.2(6)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.258$ g cm^{-3}, $\mu = 1.64$ cm^{-1}, collected 39607, independent 7698, parameters 762, $R_w = 0.1716$, $R_1 = 0.0573$ ($I > 2.0\sigma(I)$), GOF = 1.175.

DFT Calculations

The geometry optimization was performed by B3LYP method[3] with basis sets of 6-31G(d) for all atoms.[4] The geometries of **3a**, **4b**, and **11** in solution were optimized with the DFT method, in which the solvent effect of CH_2Cl_2 was included by the polarizable continuum model (PCM) method.[5] The Cartesian coordinates are summarized in Table S1. All calculations were carried out with the Gaussian 09 package.[6]

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[3] (*a*) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648; (*b*) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

[4] (*a*) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; (*b*) J. D. Dill and J. A. Pople, *J. Chem. Phys.*, 1975, **62**, 2921; (*c*) P. C. Hariharan and J. A. Pople, *Theoret. Chimica Acta*, 1973, **28**, 213.

[5] E. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 3032.

[6] *Gaussian 09, Revision E.01*; M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

Lippert-Mataga Analysis

The absorption and fluorescence maxima of **3a** were measured in six different solvents (toluene, $CHCl_3$, THF, CH_2Cl_2, DMF, acetonitrile) and analyzed using the Lippert-Mataga equation.[7] The results including the data for **10** are summarized in Table S2 and Fig. S3.[8]

Fluorescence Lifetime Measurement

The fluorescence lifetimes of **3a** and **8** were measured in CH_2Cl_2 using a streak camera as a fluorescence detector. The excitation pulse (330 nm for **3a** or 520 nm for **8**) was generated by taking the second harmonic pulse of the output of an optical parametric amplifier (660 nm for **3a** or 1040 nm for **8**) operated by an amplified Ti:Sapphire laser system. Compound **8** showed a single-exponential decay profile with the lifetime of 5.1 ns, whereas **3a** displayed a rather complicated decay profile (Figure S4). A rapidly decaying component within the time response of the streak camera (ca. 30 ps) appeared around 500 nm after the photo-excitation of **3a**. The fluorescence component around 600 nm rose almost simultaneously, which showed the shift to the longer wavelength, and then decayed with the average lifetime of 9.7 ns (in the range of 0–50 ns). These results suggest that the initially excited state of **3a** is a different electronic state from the final CT state and support the reorganization in the excited state.

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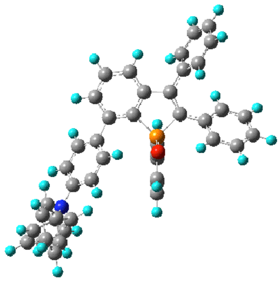
[7] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*; 3rd ed.; Springer, Berlin 2006.

[8] Y. Matano, Y. Motegi, S. Kawatsu and Y. Kimura, *J. Org. Chem.*, 2015, **80**, 5944.

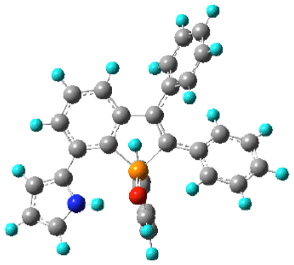
Table S1 Cartesian coordinates (Å) and energies of the optimized structures of **3a**, **4b**, and **11** calculated at the level of B3LYP/6-31G(d) with solvent effects (PCM, CH_2Cl_2).



Compound **3a** (*E* = -2167.33093230 a.u.)

	x	*y*	*z*
C	-1.929314	-3.708699	-1.667841
C	-0.641875	-3.249633	-1.412899
C	-0.414135	-2.051820	-0.698759
C	-1.542201	-1.338352	-0.264919
C	-2.852688	-1.786647	-0.549963
C	-3.046143	-2.983562	-1.239625
H	-2.069419	-4.643384	-2.203589
H	0.211763	-3.832828	-1.744714
H	-4.046376	-3.346427	-1.448825
C	-3.501194	0.246420	0.554354
C	-3.937506	-0.881823	-0.069762
C	-1.044707	1.575788	-0.415661
C	-0.072367	2.441263	0.101334
C	-1.511926	1.757106	-1.726457
C	0.430614	3.478946	-0.686773
H	0.282933	2.294891	1.116513
C	-1.008236	2.794167	-2.510137
H	-2.268360	1.092116	-2.135014
C	-0.036375	3.655425	-1.990665
H	1.184094	4.148498	-0.281397
H	-1.373024	2.931854	-3.524129
H	0.354188	4.463600	-2.602990
C	-4.289003	1.376877	1.085271
C	-3.913125	1.994905	2.293853
C	-5.398524	1.892207	0.387925
C	-4.638132	3.075061	2.796983
H	-3.052156	1.616903	2.835952
C	-6.116704	2.974854	0.891866
H	-5.689449	1.447309	-0.557791
C	-5.743374	3.568680	2.100800
H	-4.336392	3.532054	3.735674
H	-6.967218	3.359552	0.335353
H	-6.305500	4.412120	2.492301
P	-1.669742	0.235717	0.653550
O	-1.093371	0.297366	2.051132
C	-5.365445	-1.263413	-0.246615

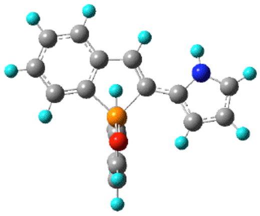
C	-5.918743	-1.429871	-1.527243
C	-6.183281	-1.472199	0.875516
C	-7.260030	-1.785043	-1.680201
H	-5.300408	-1.265726	-2.405515
C	-7.520922	-1.836040	0.720618
H	-5.763712	-1.351579	1.869873
C	-8.064131	-1.991172	-0.557043
H	-7.675234	-1.900478	-2.677630
H	-8.138953	-1.998481	1.599389
H	-9.106867	-2.271902	-0.676551
C	0.986014	-1.606545	-0.471189
C	1.443889	-1.170176	0.783563
C	1.913393	-1.641187	-1.528262
C	2.763269	-0.766551	0.968446
H	0.759044	-1.129214	1.623137
C	3.234286	-1.247102	-1.348931
H	1.592934	-1.972142	-2.512290
C	3.680484	-0.794651	-0.094921
H	3.086388	-0.424788	1.946322
H	3.925630	-1.282753	-2.184451
N	5.021728	-0.375785	0.088253
C	5.708511	-0.681517	1.297454
C	5.619457	-1.964133	1.862294
C	6.488182	0.293926	1.939540
C	6.288686	-2.257155	3.049849
H	5.025814	-2.726288	1.367288
C	7.169051	-0.013292	3.116996
H	6.555983	1.289638	1.512714
C	7.070740	-1.287229	3.682327
H	6.208648	-3.254705	3.473585
H	7.767840	0.753673	3.601036
H	7.596639	-1.521195	4.603465
C	5.682642	0.370345	-0.927813
C	5.015564	1.406747	-1.601829
C	7.014645	0.082697	-1.267295
C	5.667765	2.128615	-2.600638
H	3.988830	1.642402	-1.339640
C	7.664566	0.822378	-2.254464
H	7.534524	-0.721024	-0.755510
C	6.995665	1.845676	-2.930949
H	5.136998	2.927076	-3.112430
H	8.695476	0.586021	-2.504407
H	7.502302	2.415382	-3.704633



Compound **4b** (*E* = -1627.81239148 a.u.)

	x	*y*	*z*
C	-0.991810	-3.921168	0.491076
C	-2.206699	-3.321321	0.192793
C	-2.287423	-1.958029	-0.186329
C	-1.077658	-1.240305	-0.224472
C	0.163732	-1.857246	0.056968
C	0.209495	-3.203435	0.412586
H	-0.969865	-4.971894	0.766423
H	-3.115586	-3.913481	0.217087
H	1.154458	-3.692430	0.620467
C	1.053702	0.314605	-0.473063
C	1.347293	-0.960724	-0.094084
C	-1.313764	1.548674	0.759268
C	-2.060980	2.697378	0.468889
C	-1.000904	1.239192	2.092006
C	-2.492915	3.530302	1.503296
H	-2.300525	2.929563	-0.564071
C	-1.434504	2.072734	3.121514
H	-0.421927	0.350035	2.326898
C	-2.180503	3.218712	2.827615
H	-3.072882	4.419711	1.273641
H	-1.192202	1.829281	4.152083
H	-2.517545	3.866570	3.632066
C	-3.597014	-1.401985	-0.521229
C	-4.866680	-1.833631	-0.136131
C	-5.818820	-0.975551	-0.736645
H	-5.075082	-2.657334	0.533464
H	-6.894689	-1.027266	-0.635751
N	-3.781088	-0.303934	-1.342371
H	-3.024897	0.209339	-1.803298
C	-5.114260	-0.043839	-1.480921
H	-5.456822	0.774159	-2.098661
C	1.957387	1.467686	-0.656103
C	1.727015	2.381241	-1.702830
C	3.032788	1.710581	0.219633
C	2.559119	3.486663	-1.879760
H	0.894541	2.214600	-2.379349
C	3.858855	2.818421	0.041704
H	3.211476	1.034133	1.048663
C	3.629125	3.709135	-1.010733
H	2.368979	4.175166	-2.698688

H	4.680841	2.990313	0.731443
H	4.275120	4.572033	-1.147339
P	-0.759229	0.500139	-0.627743
O	-1.307636	0.997755	-1.956862
C	2.720868	-1.496516	0.106015
C	3.119890	-2.018148	1.348141
C	3.639724	-1.499616	-0.955777
C	4.410588	-2.519008	1.525469
H	2.421699	-2.018243	2.180680
C	4.925648	-2.009978	-0.779100
H	3.338937	-1.105247	-1.921847
C	5.316093	-2.518539	0.462161
H	4.706801	-2.910194	2.494876
H	5.622929	-2.010104	-1.612356
H	6.319035	-2.912979	0.599466



Compound **11** (E = -1165.69655737 a.u.)

	x	*y*	*z*
C	-4.693896	-0.864760	-0.567154
C	-6.047171	-0.665318	-0.805185
C	-5.133261	-3.058956	0.374039
C	-4.223744	-2.060512	0.018749
H	-6.403309	0.254928	-1.260458
H	-4.785840	-3.982257	0.830175
C	-2.071218	-1.021552	-0.257141
C	-2.763425	-2.106860	0.174907
H	-2.290520	-2.990303	0.597626
P	-3.268539	0.214227	-0.922611
O	-3.083214	0.679963	-2.347883
C	-3.309460	1.607042	0.257806
C	-3.246845	2.909849	-0.253090
C	-3.408820	1.407793	1.643631
C	-3.285056	4.004544	0.613686
H	-3.167028	3.057624	-1.325681
C	-3.446974	2.502677	2.505622
H	-3.453906	0.401018	2.050342
C	-3.385399	3.801830	1.991118
H	-3.236022	5.012904	0.212273
H	-3.523068	2.343903	3.577639
H	-3.414665	4.653538	2.665147
C	-0.624865	-0.804328	-0.199457
C	0.008817	0.123522	-1.050024

C	0.191001	-1.513160	0.706323
C	1.383826	0.320405	-1.013104
H	-0.582733	0.671125	-1.777678
C	1.562595	-1.313655	0.757112
H	-0.262007	-2.208546	1.407180
C	2.188795	-0.393546	-0.107229
H	1.842641	1.026676	-1.696794
H	2.158689	-1.858937	1.481150
C	-6.498028	-2.856792	0.134939
C	-6.955744	-1.674216	-0.450683
C	4.460653	-1.279120	0.228038
C	4.286872	-2.519132	-0.406913
C	5.514380	-1.120055	1.141763
C	5.145124	-3.580362	-0.121399
H	3.480615	-2.644713	-1.122798
C	6.378700	-2.181346	1.408075
H	5.650977	-0.164951	1.639203
C	6.197534	-3.417913	0.783277
H	4.997777	-4.533810	-0.621546
H	7.189834	-2.042493	2.117820
H	6.868942	-4.244348	0.997752
N	3.585154	-0.190781	-0.056721
C	4.138222	1.101764	-0.291335
C	3.572823	2.239712	0.305889
C	5.265402	1.250300	-1.114578
C	4.120131	3.500526	0.071746
H	2.707000	2.131150	0.951497
C	5.817043	2.512908	-1.328893
H	5.704181	0.374919	-1.582949
C	5.246535	3.645372	-0.742370
H	3.670633	4.371406	0.541275
H	6.689647	2.610961	-1.969118
H	5.674546	4.628298	-0.916836
H	-8.017148	-1.533818	-0.632693
H	-7.208798	-3.631886	0.407760

Table S2. Absorption and emission maxima of **3a** and **10** in solution.

	toluene	$CHCl_3$	THF	CH_2Cl_2	DMF	MeCN
3a						
λ_{abs}/nm	335	333	332	334	331	328
λ_{em}/nm	496	542	569	592	605	610
Stokes shift/cm^{-1}	9700	11600	12700	13000	13700	14100
10 [a]						
λ_{abs}/nm	412	417	407	414	407	404
λ_{em}/nm	478	516	511	533	551	561
Stokes shift/cm^{-1}	3350	4600	5000	5390	6420	6930

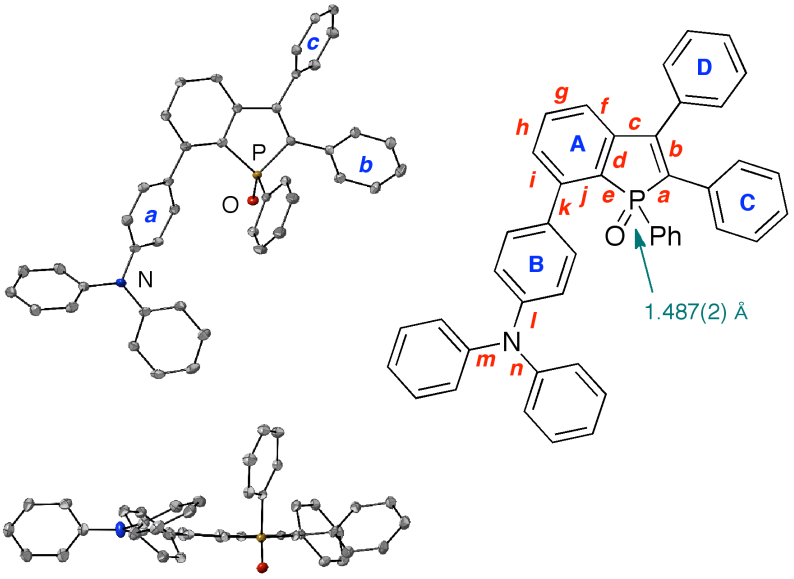
[a] Data from ref. 8.

Table S3. Excitation energies and oscillator strengths of **3a**, **4b**, and **11** calculated by the TD-DFT method [B3LYP/6-31G(d)//B3LYP/6-31G(d)] with solvent effects (PCM, CH_2Cl_2).[a]

State	Excitation energy (eV)	Excitation energy (nm)	Oscillator strength	Excitation	Weight (%)
Compound **3a**					
1	2.76	449	0.036	HOMO → LUMO	99.0
2	3.40	365	0.340	HOMO−1 → LUMO	74.5
				HOMO → LUMO+1	23.2
3	3.50	354	0.394	HOMO → LUMO+1	73.6
				HOMO−1 → LUMO	23.1
7	4.06	305	0.268	HOMO → LUMO+5	51.4
				HOMO → LUMO+4	46.2
Compound **4b**					
1	2.90	427	0.085	HOMO → LUMO	98.4
2	3.42	362	0.211	HOMO−1 → LUMO	97.5
3	3.87	320	0.185	HOMO → LUMO+1	88.6
Compound **11**					
1	3.13	396	0.435	HOMO → LUMO	96.6
2	3.90	318	0.074	HOMO → LUMO+1	95.4

[a] The states whose excitation energies are more than 4.1 eV are not included.

(a)



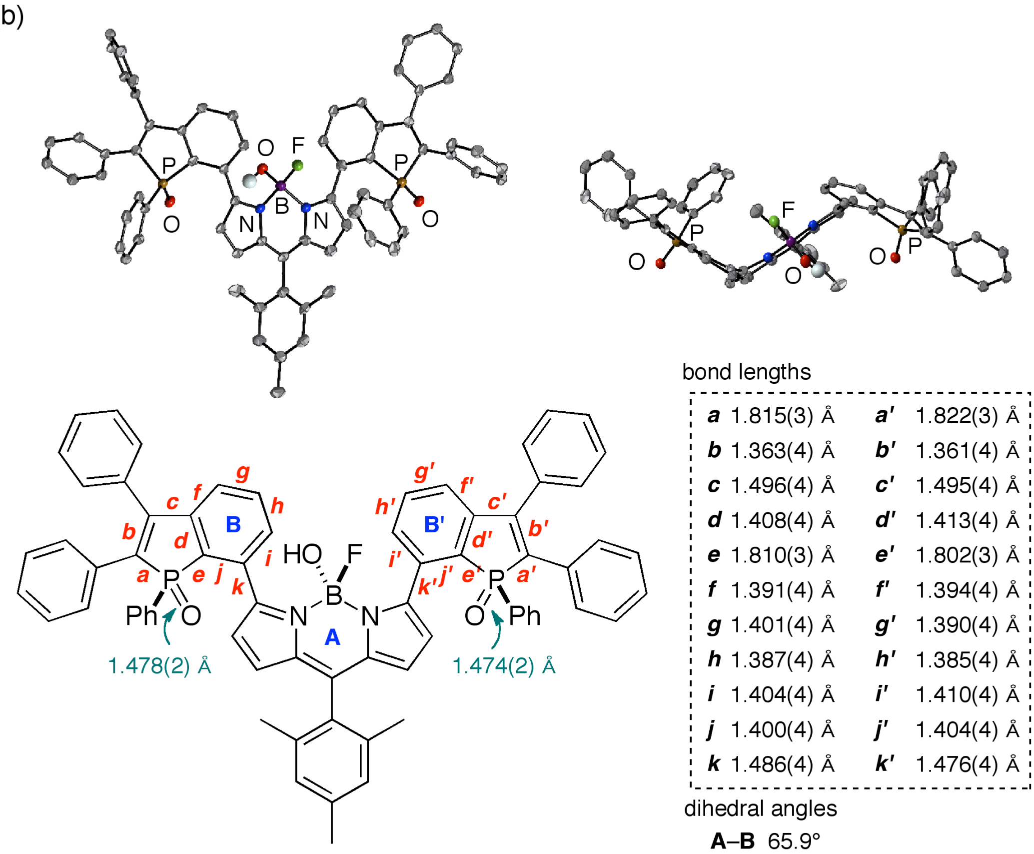
bond lengths

a	1.804(2) Å
b	1.347(2) Å
c	1.489(3) Å
d	1.417(2) Å
e	1.823(2) Å
f	1.386(3) Å
g	1.392(3) Å
h	1.390(2) Å
i	1.390(2) Å
j	1.391(3) Å
k	1.486(2) Å
l	1.421(2) Å
m	1.416(3) Å
n	1.415(3) Å

dihedral angles

A–B	43.8°
A–C	45.0°
A–D	58.8°

(b)



bond lengths

a	1.815(3) Å	***a'***	1.822(3) Å
b	1.363(4) Å	***b'***	1.361(4) Å
c	1.496(4) Å	***c'***	1.495(4) Å
d	1.408(4) Å	***d'***	1.413(4) Å
e	1.810(3) Å	***e'***	1.802(3) Å
f	1.391(4) Å	***f'***	1.394(4) Å
g	1.401(4) Å	***g'***	1.390(4) Å
h	1.387(4) Å	***h'***	1.385(4) Å
i	1.404(4) Å	***i'***	1.410(4) Å
j	1.400(4) Å	***j'***	1.404(4) Å
k	1.486(4) Å	***k'***	1.476(4) Å

dihedral angles

A–B	65.9°
A–B'	57.6°

Fig. S1 X-ray crystal structures and bond parameters of (a) **3a** (50% probability ellipsoids) and (b) **8** (30% probability ellipsoids). Hydrogen atoms and a water molecule (for **8**) are omitted for clarity.

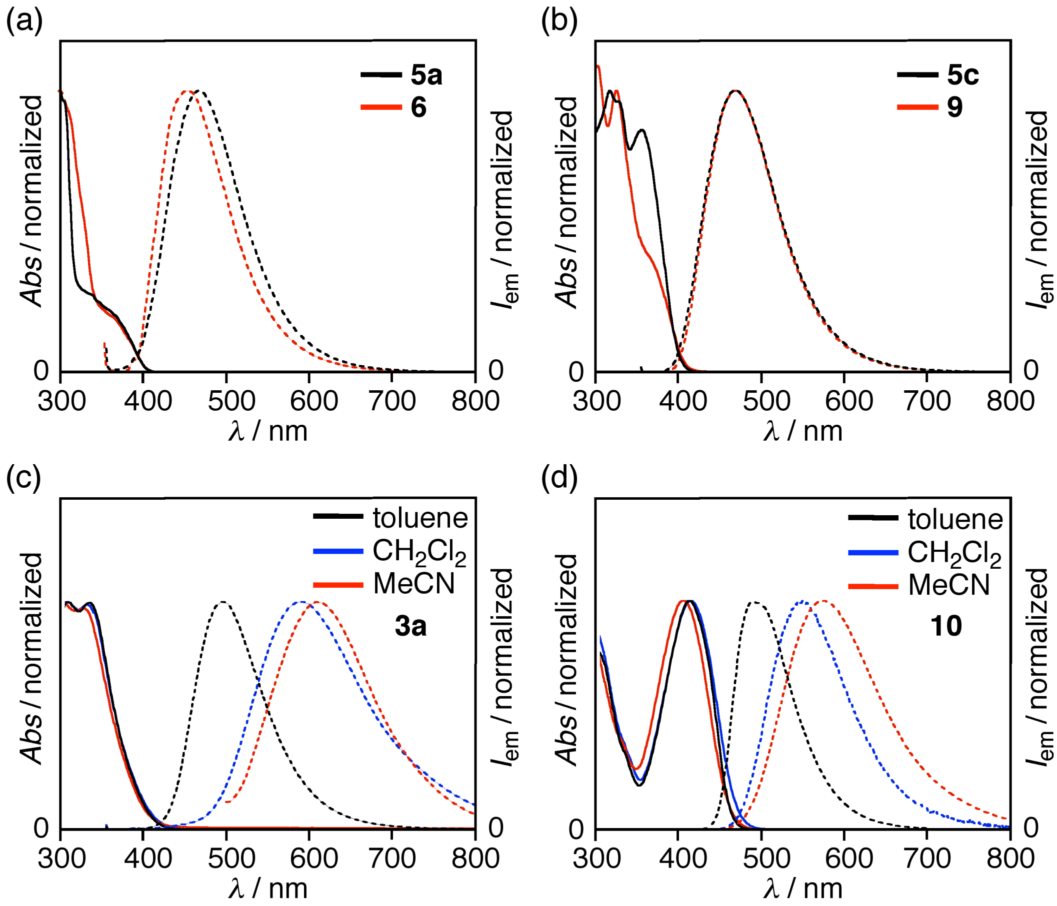


Fig. S2 UV-vis absorption (solid lines) and fluorescence spectra (dotted lines) of (a) **5a** and **6** and (b) **5c** and **9** in CH$_2$Cl$_2$. Solvatochromism of (c) **3a** and (d) **10**. λ_{ex} = absorption maxima.

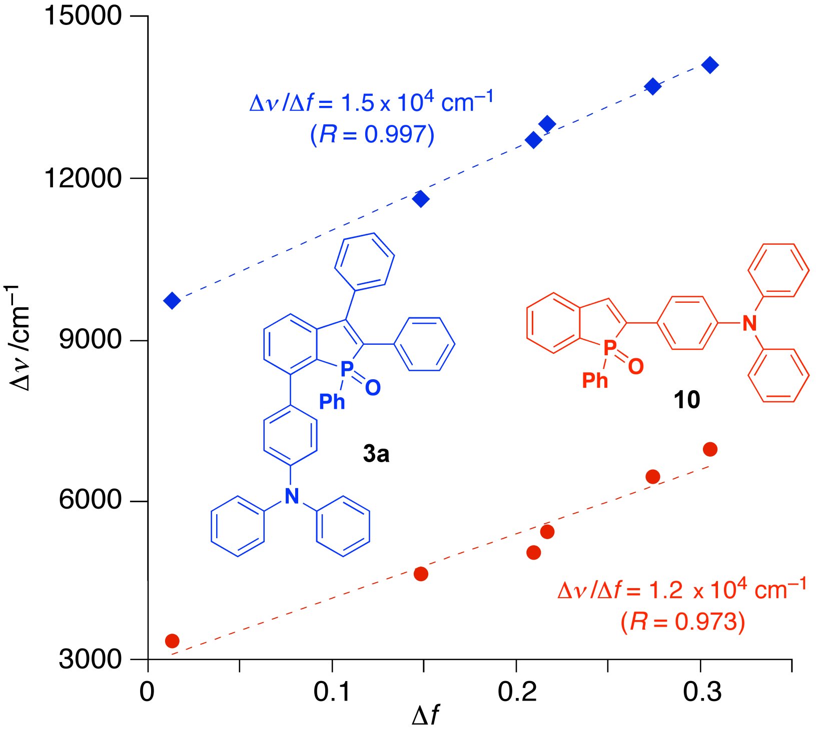


Figure S3. Lippert–Mataga plots for the solvatochromism of **3a** (blue) and **10** (red). Calculated from the data listed in Table S3. $\Delta\nu = \nu_{abs} - \nu_{em}$; $\Delta f = (\varepsilon-1)/(2\varepsilon+1) - (n^2-1)/(2n^2+1)$. ε = dielectric constant; n = refractive index.

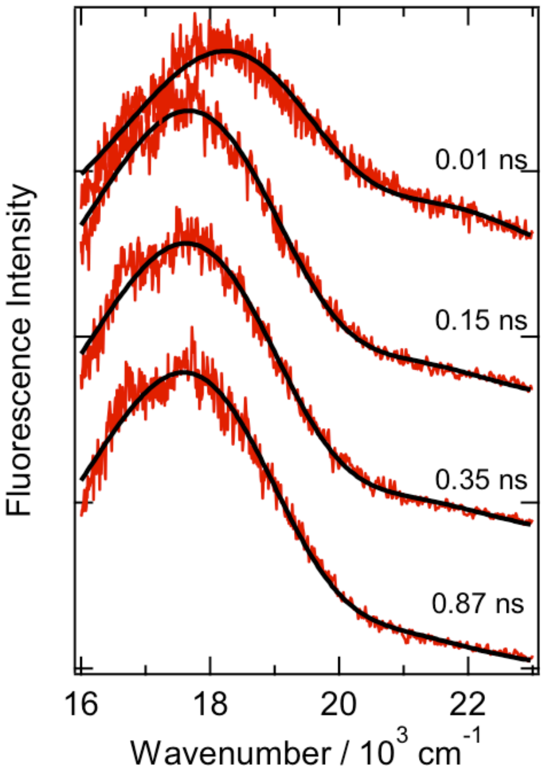


Figure S4. Fluorescence spectra of **3a** in CH_2Cl_2 at different delay times after the photo-excitation at 330 nm. Each spectrum is shown with a different offset for clarity.

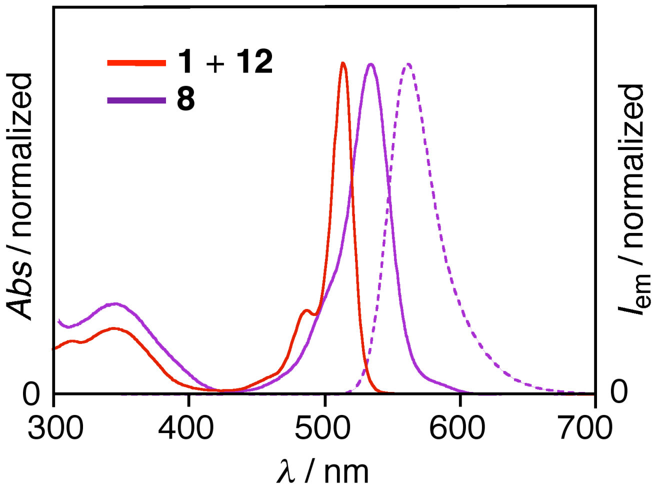


Fig. S5 UV-vis absorption (solid line) and fluorescence spectra (dotted line, excited at λ_{ex} = 350 nm) of **8** (purple) and a superimposed spectrum (solid line, red) of UV-vis absorption spectra of **1** and **12** in CH_2Cl_2. The extinction coefficients of **1** were doubled when they were added to those of **12**.

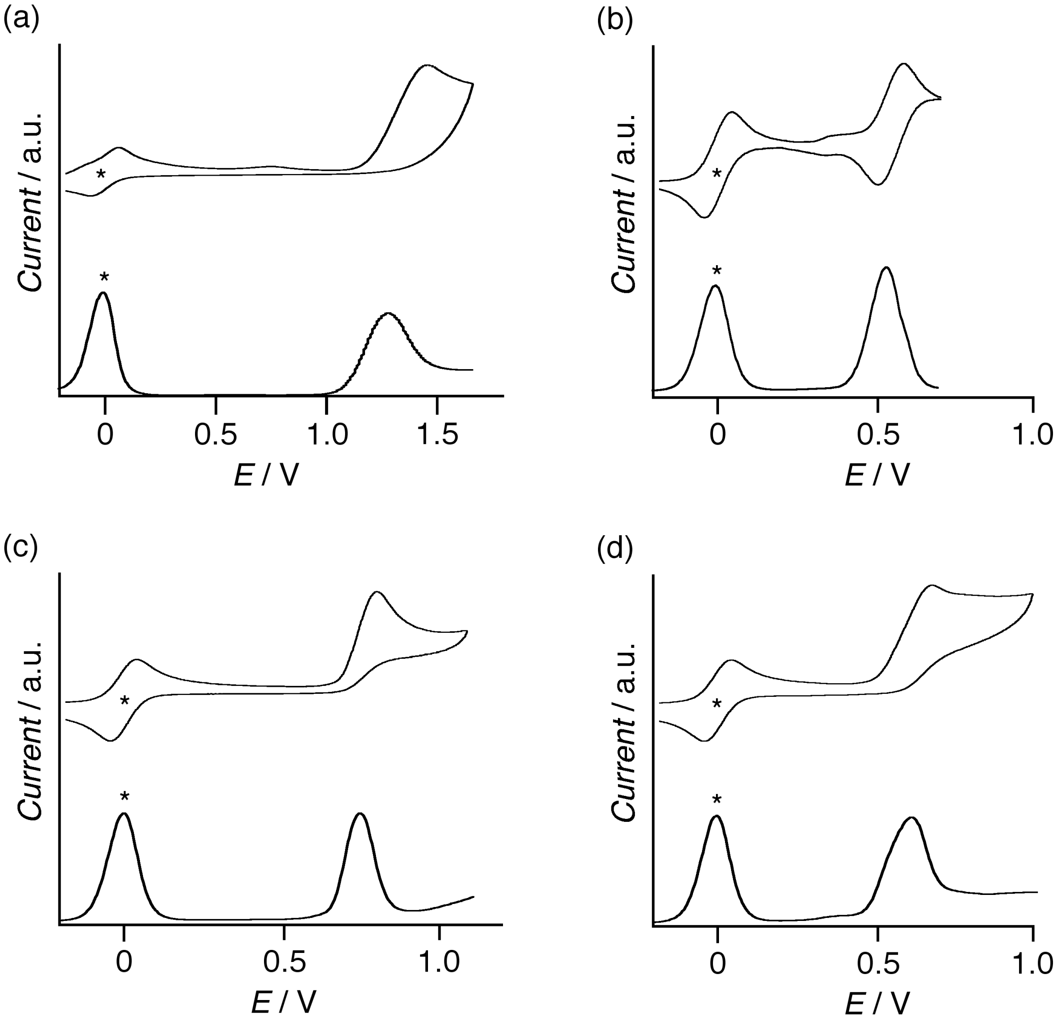
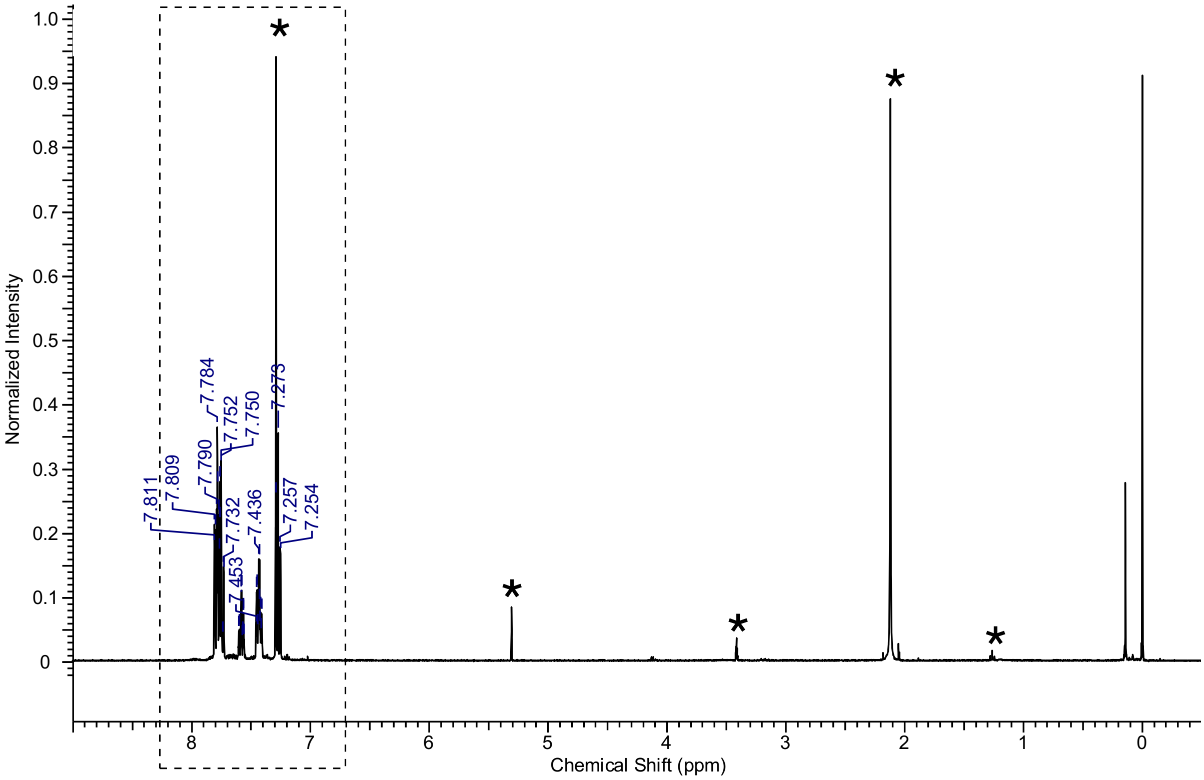
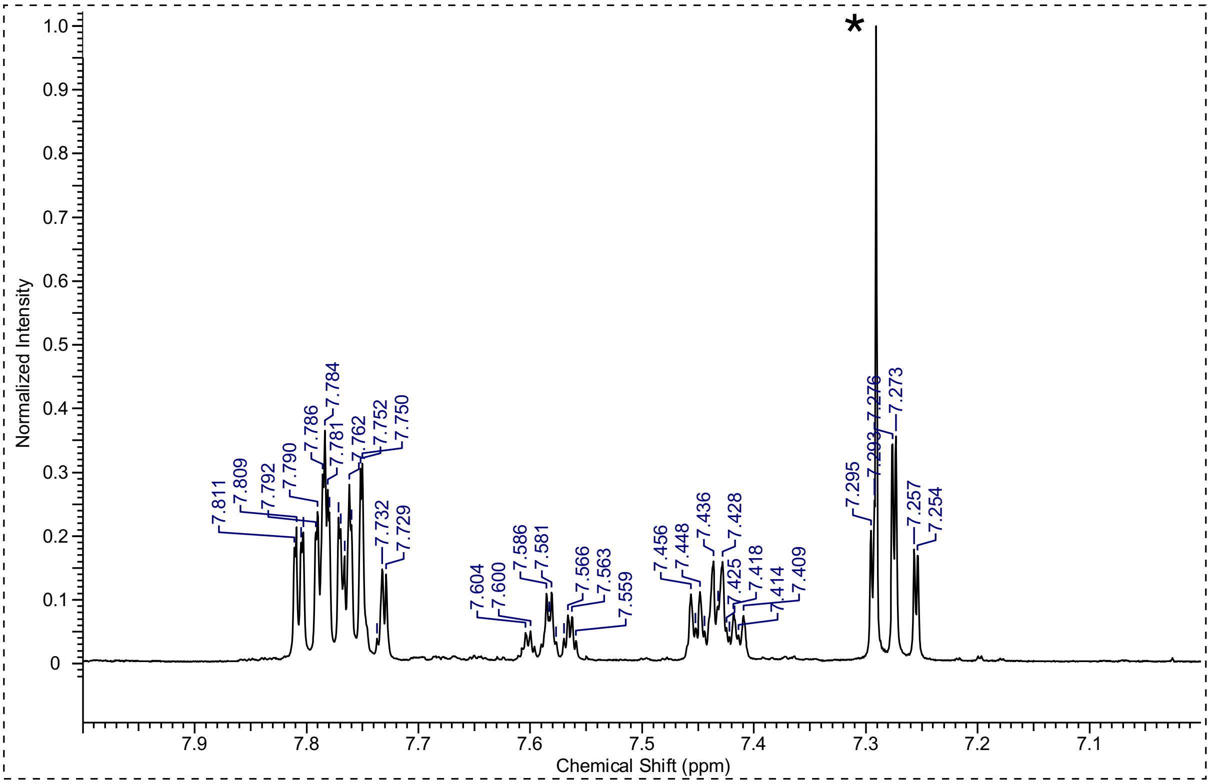


Fig. S6 Cyclic voltammograms (upper) and differential pulse voltammograms (lower) of (a) **1**, (b) **3a**, (c) **4b**, and (c) **11**. Scan rate 60 mV s^{-1}. Asterisk (*) indicates Fc/Fc^+.

^{1}H and ^{13}C{^{1}H} NMR Charts (**Figures S7–S19**) Asterisks (*) indicate the residual solvents.

(a)





(b)

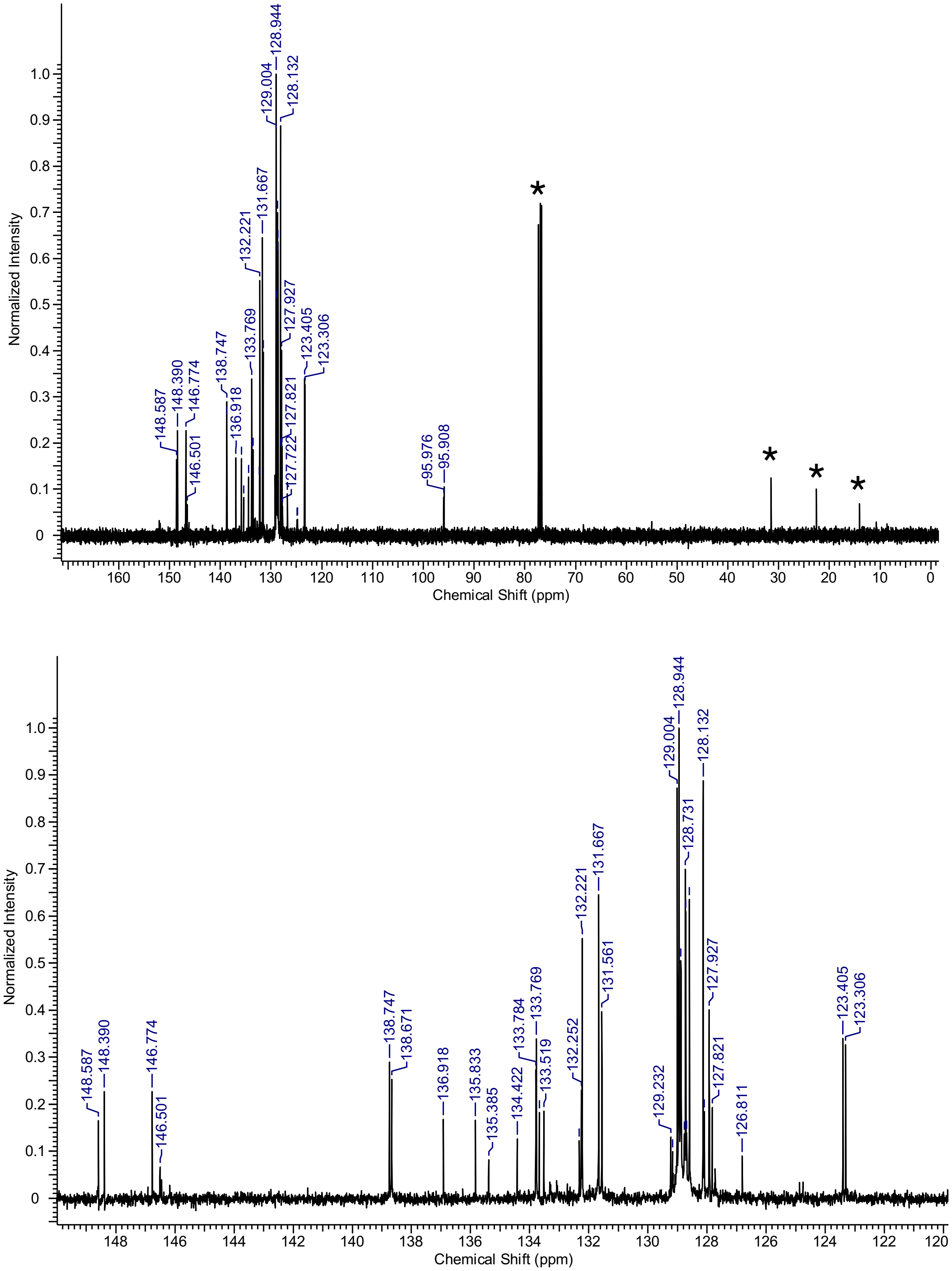
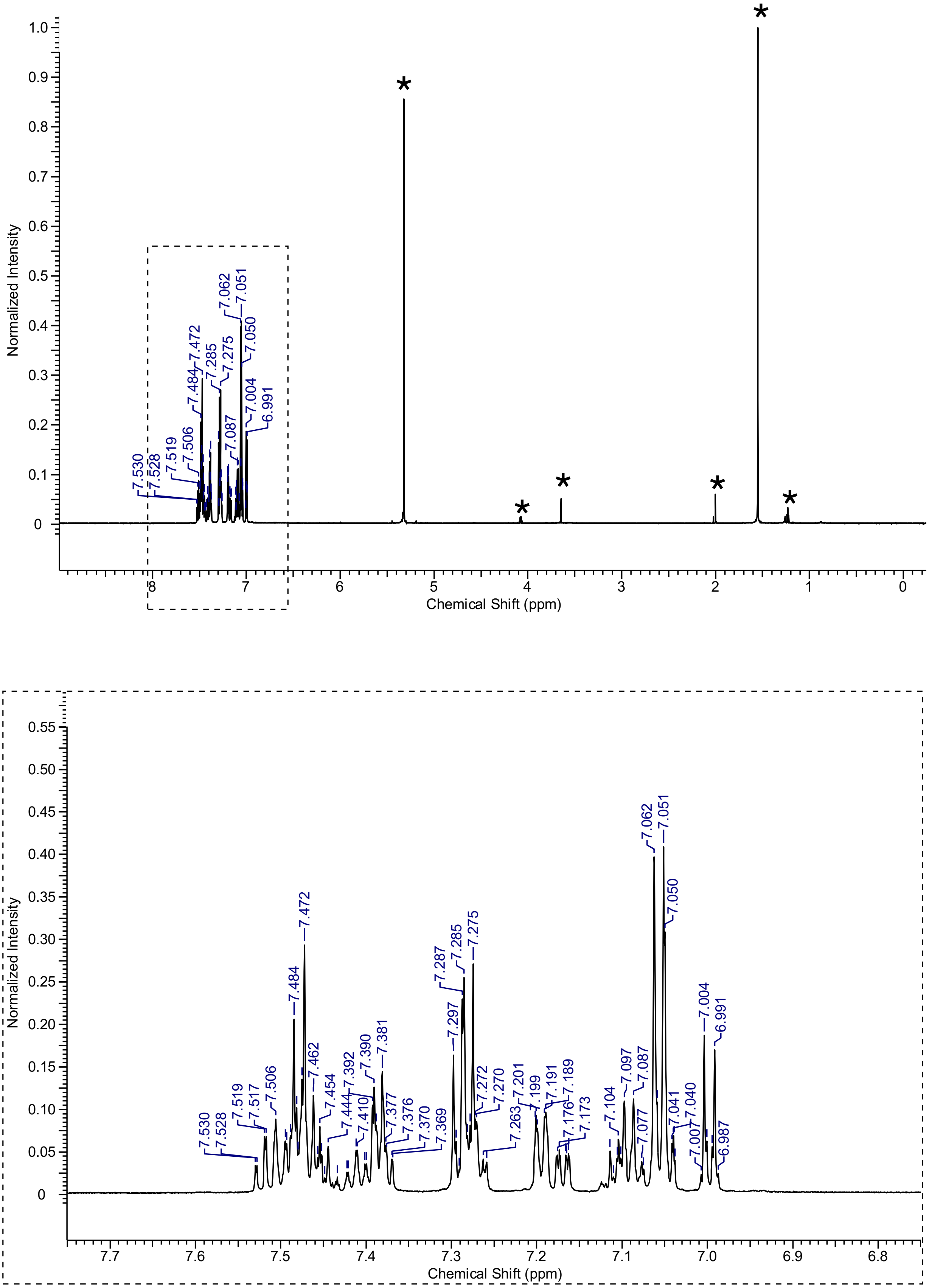


Figure S7 (a) ^{1}H NMR and (b) $^{13}C\{^{1}H\}$ NMR spectra of **2** in $CDCl_3$.

(a)


Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
*
7.530
7.528
7.519
7.506
7.484
7.472
7.285
7.275
7.087
7.062
7.051
7.050
7.004
6.991
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
7.530
7.528
7.519
7.517
7.506
7.484
7.472
7.462
7.454
7.444
7.410
7.392
7.390
7.381
7.377
7.376
7.370
7.369
7.297
7.287
7.285
7.275
7.272
7.270
7.263
7.201
7.199
7.191
7.189
7.176
7.173
7.104
7.097
7.087
7.077
7.062
7.051
7.050
7.041
7.040
7.007
7.004
6.991
6.987
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8

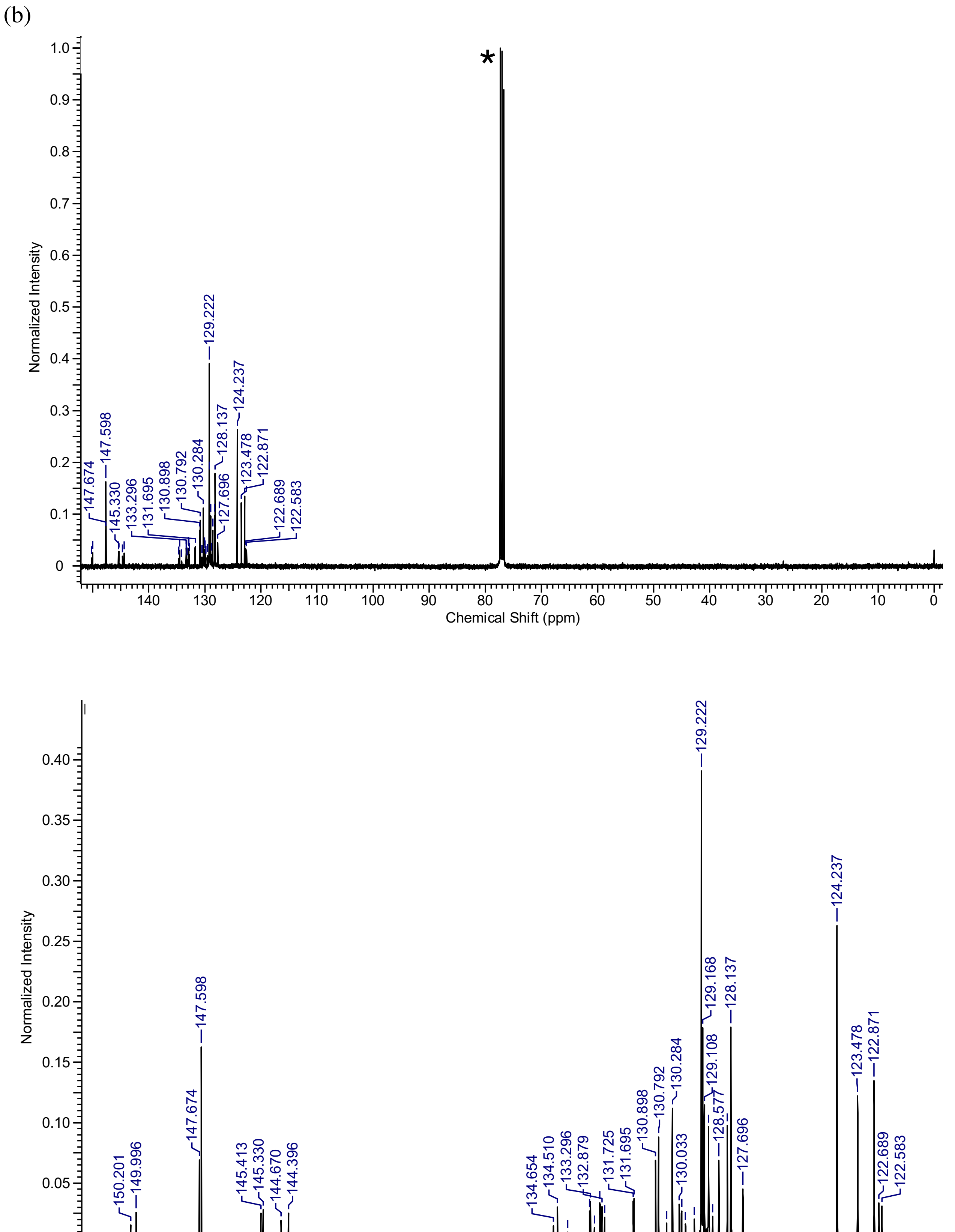
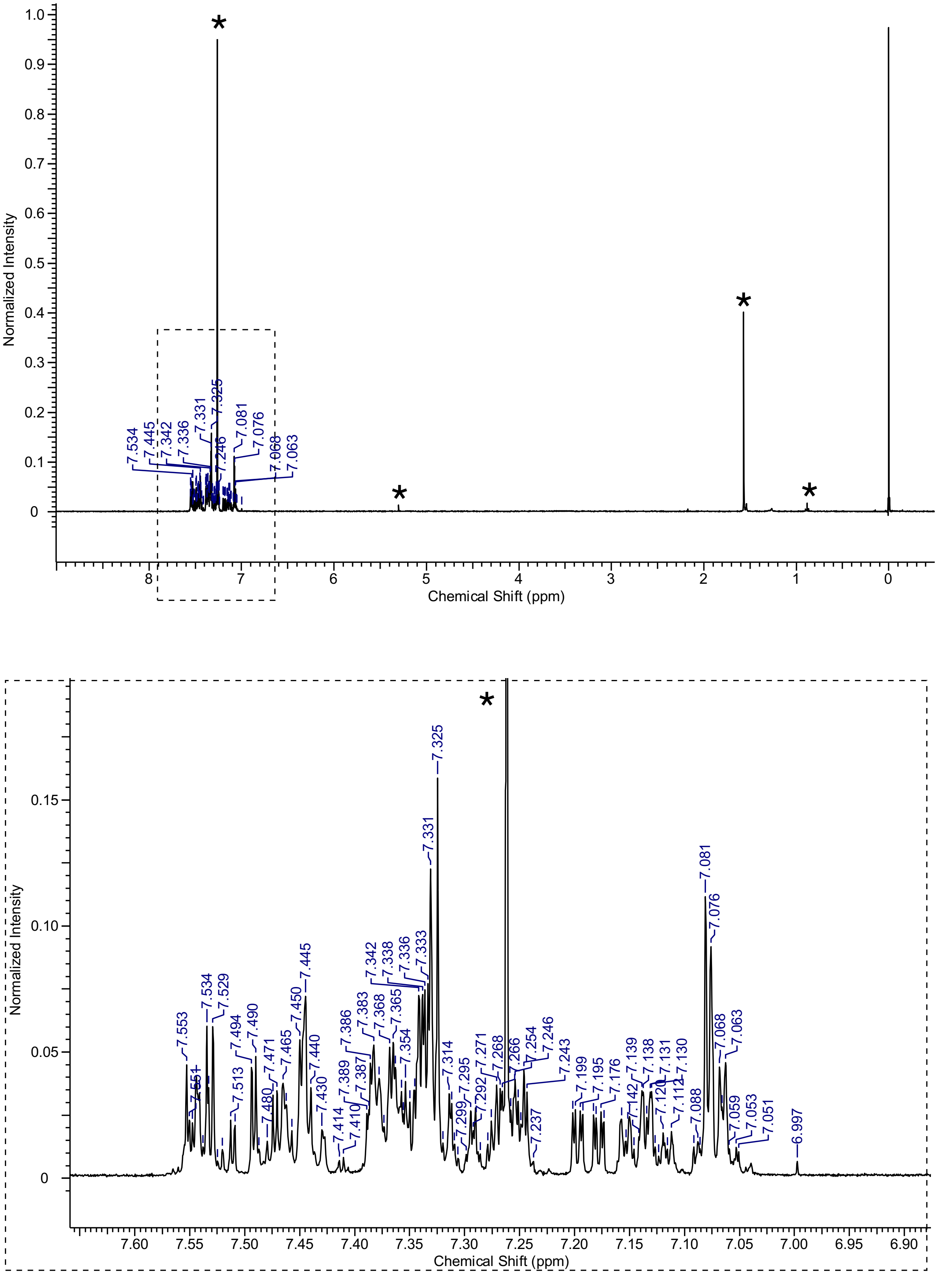


Figure S8 (a) ^{1}H NMR in CD_2Cl_2 and (b) $^{13}C\{^1H\}$ NMR spectra of **3a** in $CDCl_3$.

(a)


Normalized Intensity
Chemical Shift (ppm)
*
7.534
7.445
7.342
7.336
7.331
7.325
7.246
7.081
7.076
7.068
7.063
7.553
7.551
7.529
7.513
7.494
7.490
7.480
7.471
7.465
7.450
7.440
7.430
7.414
7.410
7.389
7.387
7.386
7.383
7.368
7.365
7.354
7.338
7.333
7.314
7.299
7.295
7.292
7.271
7.268
7.266
7.254
7.243
7.237
7.199
7.195
7.176
7.142
7.139
7.138
7.131
7.130
7.120
7.112
7.088
7.059
7.053
7.051
6.997

(b)

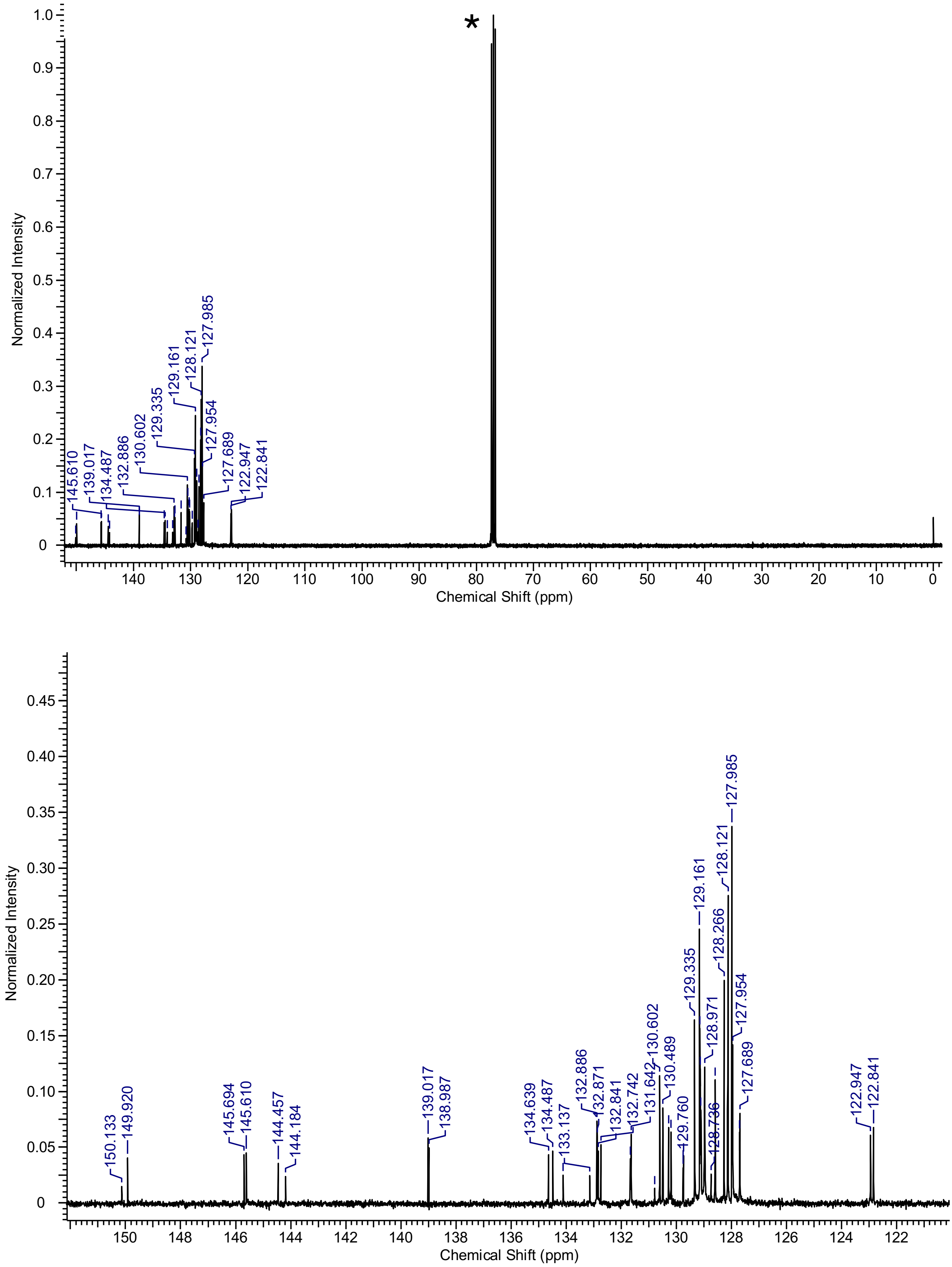
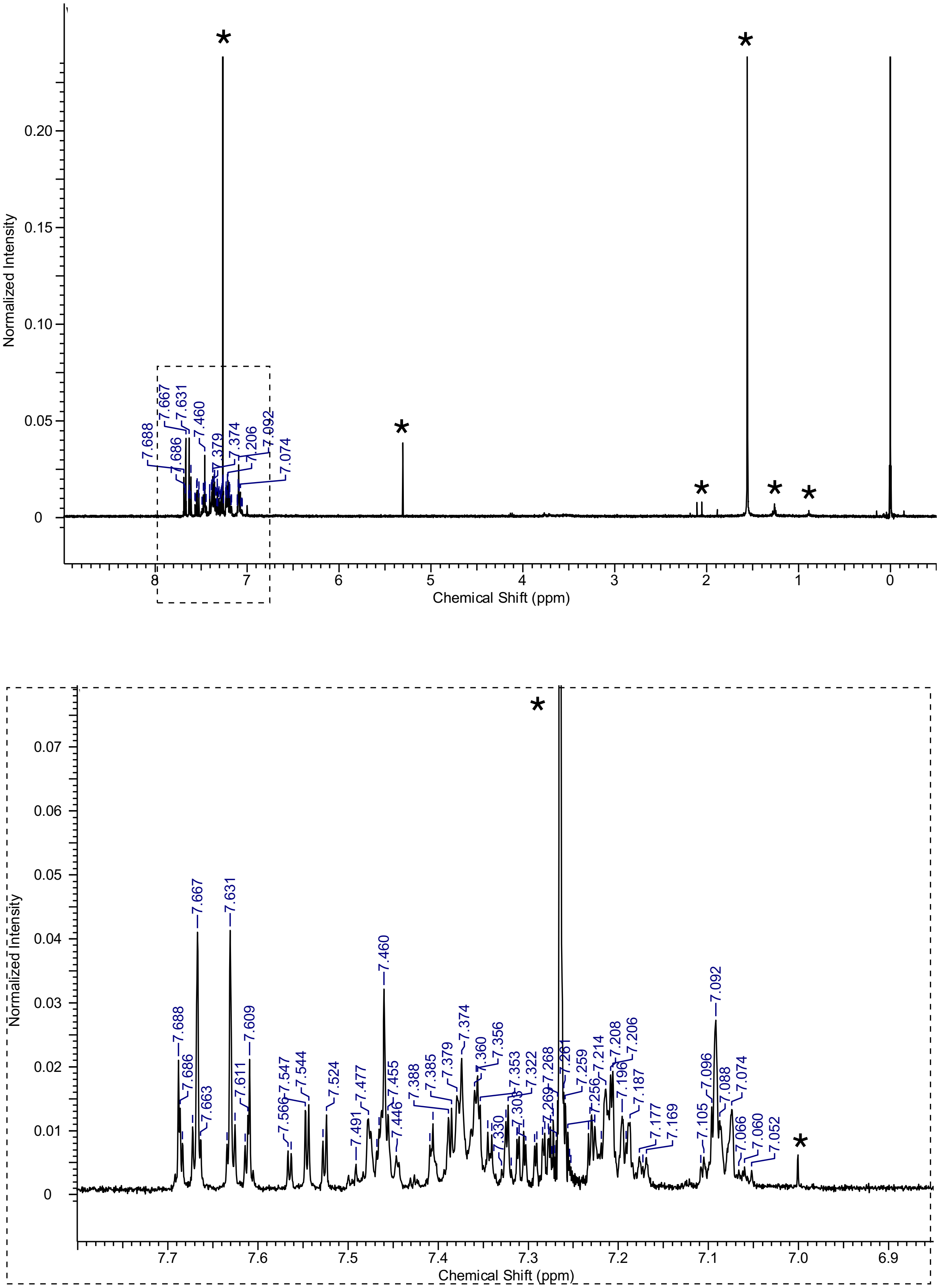


Figure S9 (a) ^{1}H NMR and (b) ^{13}C{^{1}H} NMR spectra of **3b** in CDCl$_3$.

(a)



Normalized Intensity
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0.10
0.05
0
*
*
*
*
*
*
7.688
7.686
7.667
7.631
7.460
7.379
7.374
7.206
7.092
7.074
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
Normalized Intensity
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
*
*
7.688
7.686
7.667
7.663
7.631
7.611
7.609
7.566
7.547
7.544
7.524
7.491
7.477
7.460
7.455
7.446
7.388
7.385
7.379
7.374
7.360
7.356
7.353
7.330
7.322
7.303
7.269
7.268
7.261
7.259
7.256
7.214
7.208
7.206
7.196
7.187
7.177
7.169
7.105
7.096
7.092
7.088
7.074
7.066
7.060
7.052
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
Chemical Shift (ppm)

(b)

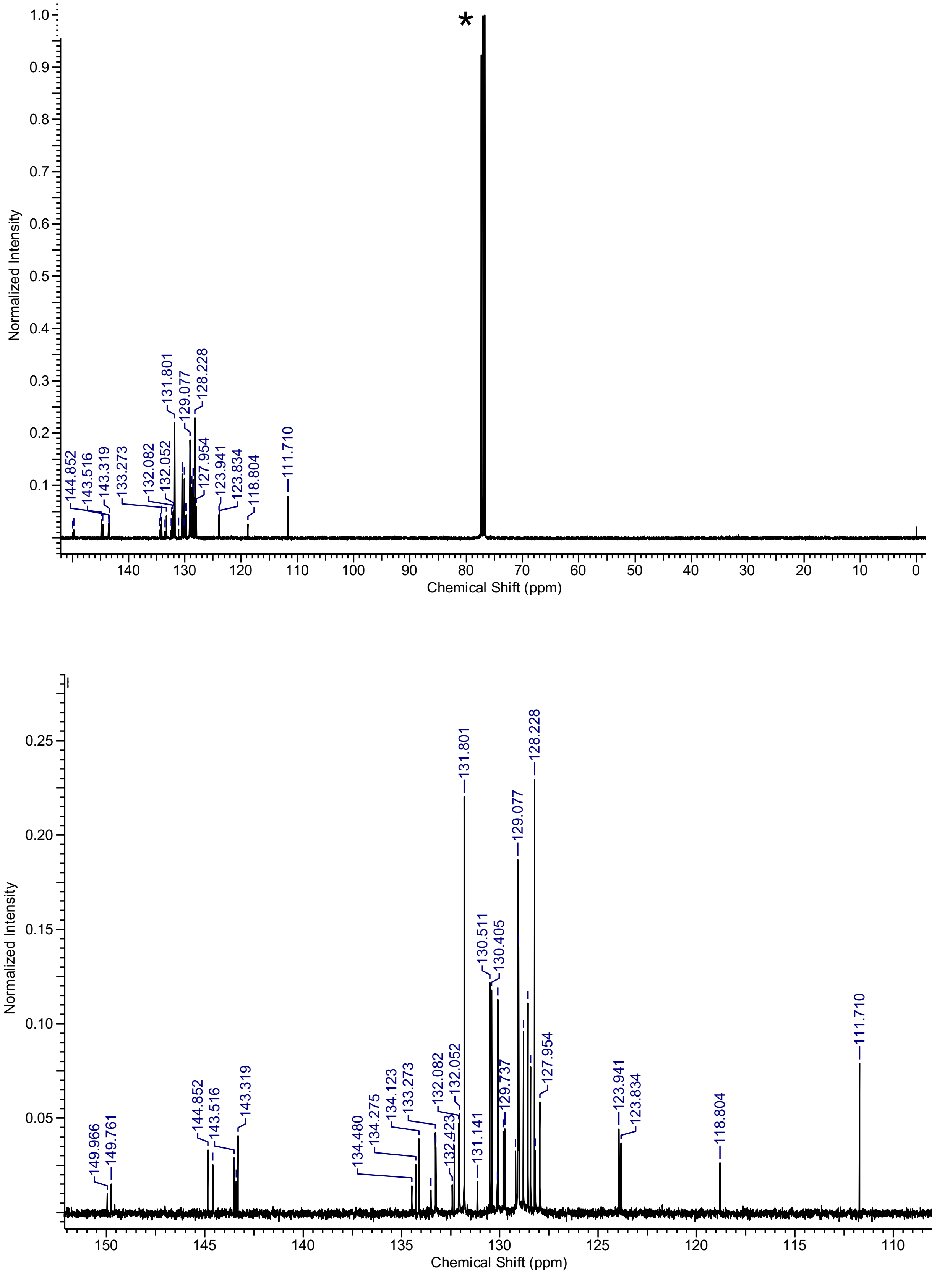


Figure S10 (a) ^{1}H NMR and (b) ^{13}C{^{1}H} NMR spectra of **3c** in CDCl$_3$.

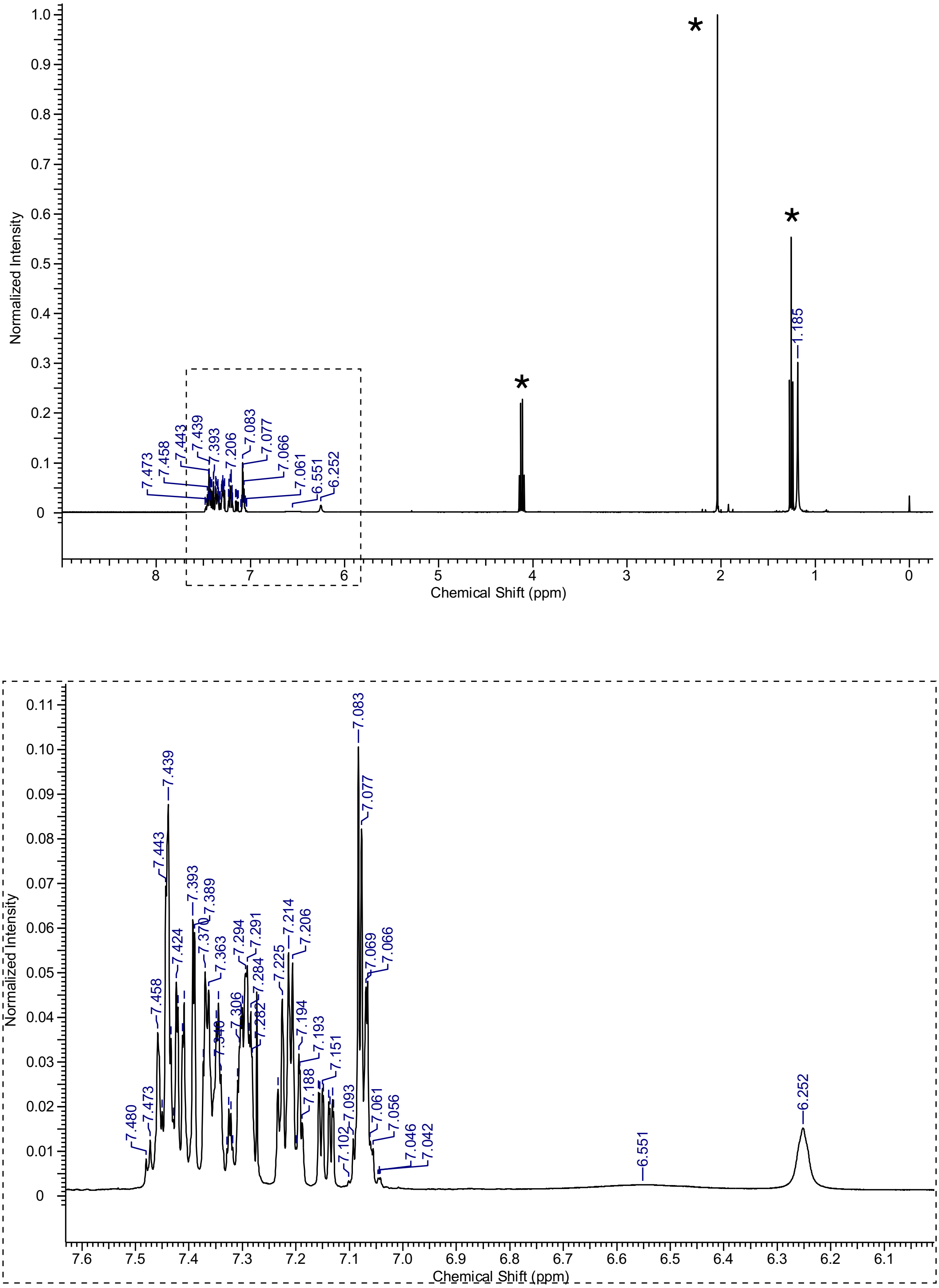
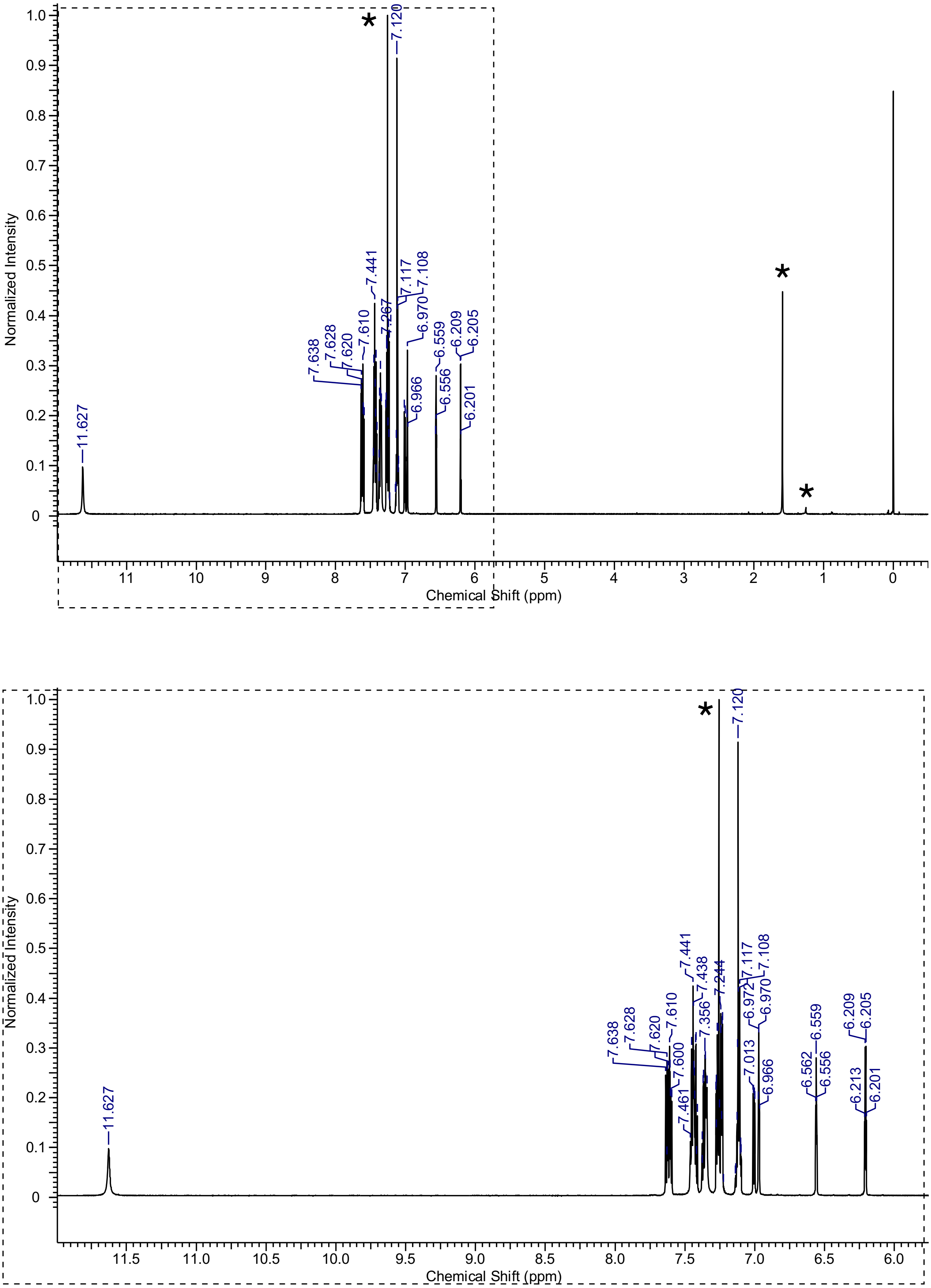


Figure S11 ^{1}H NMR spectra of **4a** in $CDCl_3$.

(a)


Normalized Intensity
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0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Chemical Shift (ppm)
11
10
9
8
7
6
5
4
3
2
1
0
*
*
*
11.627
7.638
7.628
7.620
7.610
7.441
7.267
7.120
7.117
7.108
6.970
6.966
6.559
6.556
6.209
6.205
6.201
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Chemical Shift (ppm)
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
*
11.627
7.638
7.628
7.620
7.610
7.600
7.461
7.441
7.438
7.356
7.244
7.120
7.117
7.108
7.013
6.972
6.970
6.966
6.562
6.559
6.556
6.213
6.209
6.205
6.201

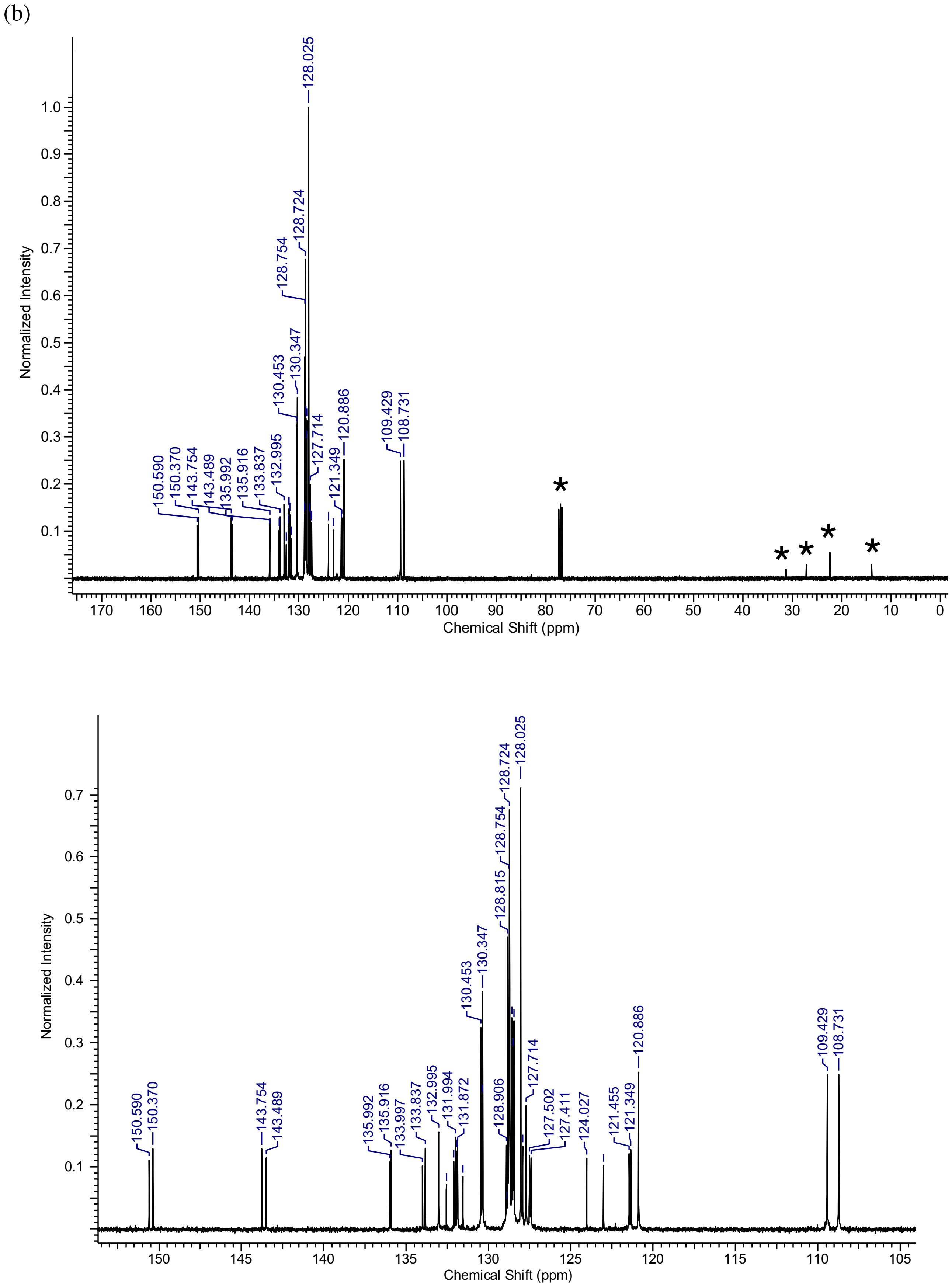
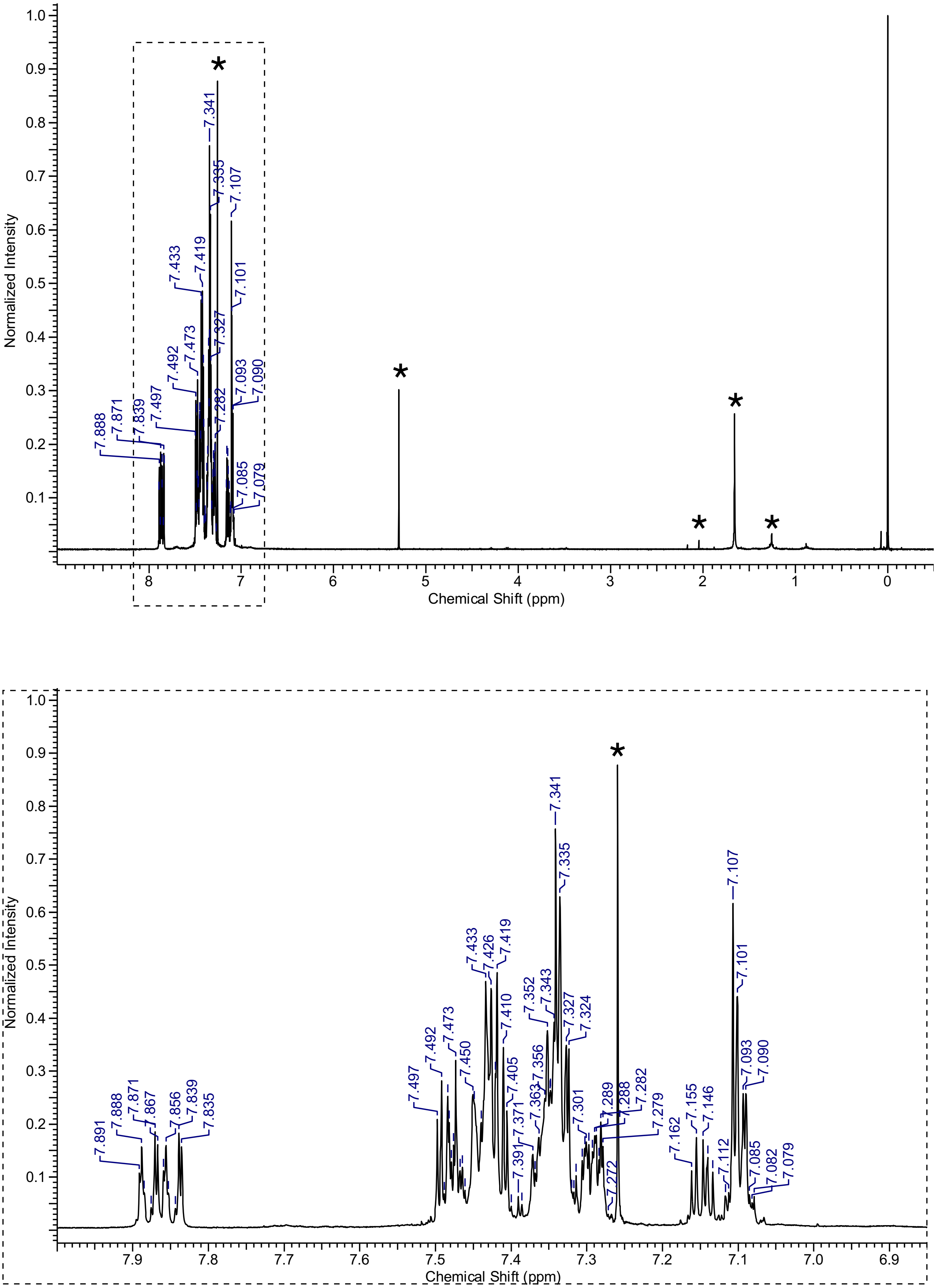


Figure S12 (a) ^{1}H NMR and (b) $^{13}C\{^1H\}$ NMR spectra of **4b** in CDCl$_3$.

(a)


Normalized Intensity
Chemical Shift (ppm)
*
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7.839
7.497
7.492
7.473
7.433
7.419
7.341
7.335
7.327
7.282
7.107
7.101
7.093
7.090
7.085
7.079
7.891
7.867
7.856
7.835
7.450
7.426
7.410
7.405
7.391
7.371
7.363
7.356
7.352
7.343
7.324
7.301
7.289
7.288
7.279
7.272
7.162
7.155
7.146
7.112
7.082

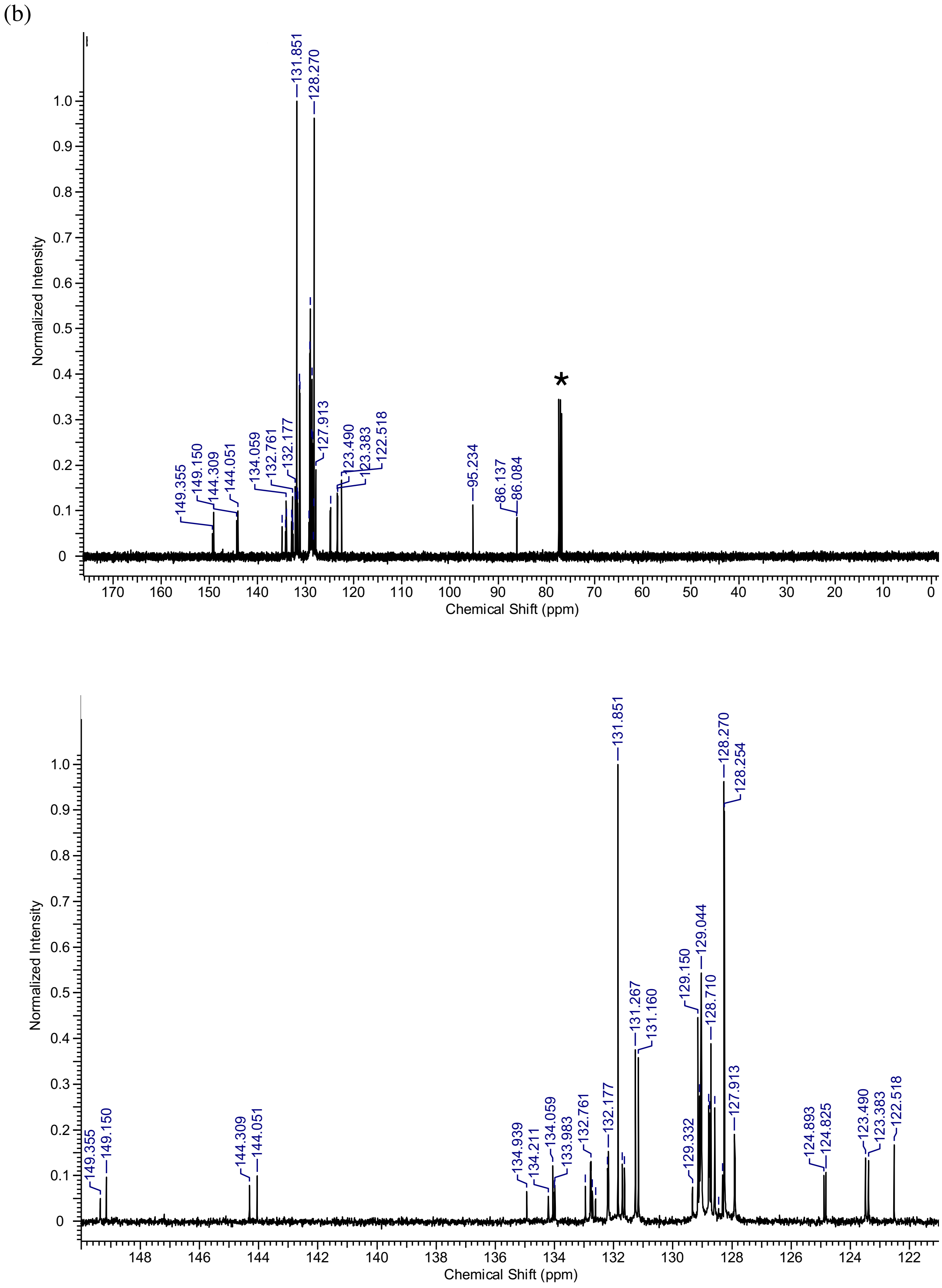


Figure S13 (a) ^{1}H NMR and (b) ^{13}C{^{1}H} NMR spectra of **5a** in CDCl$_3$.

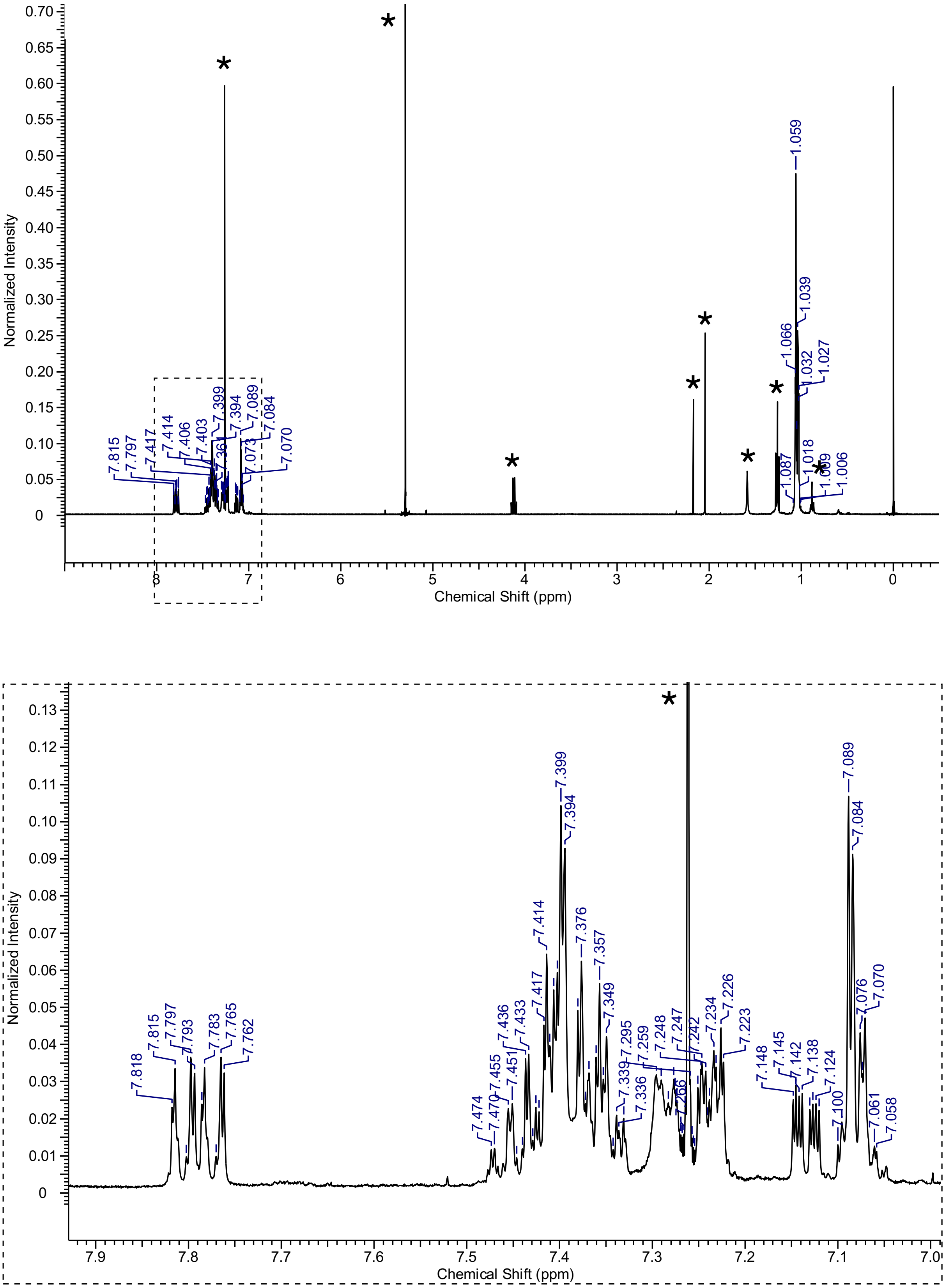
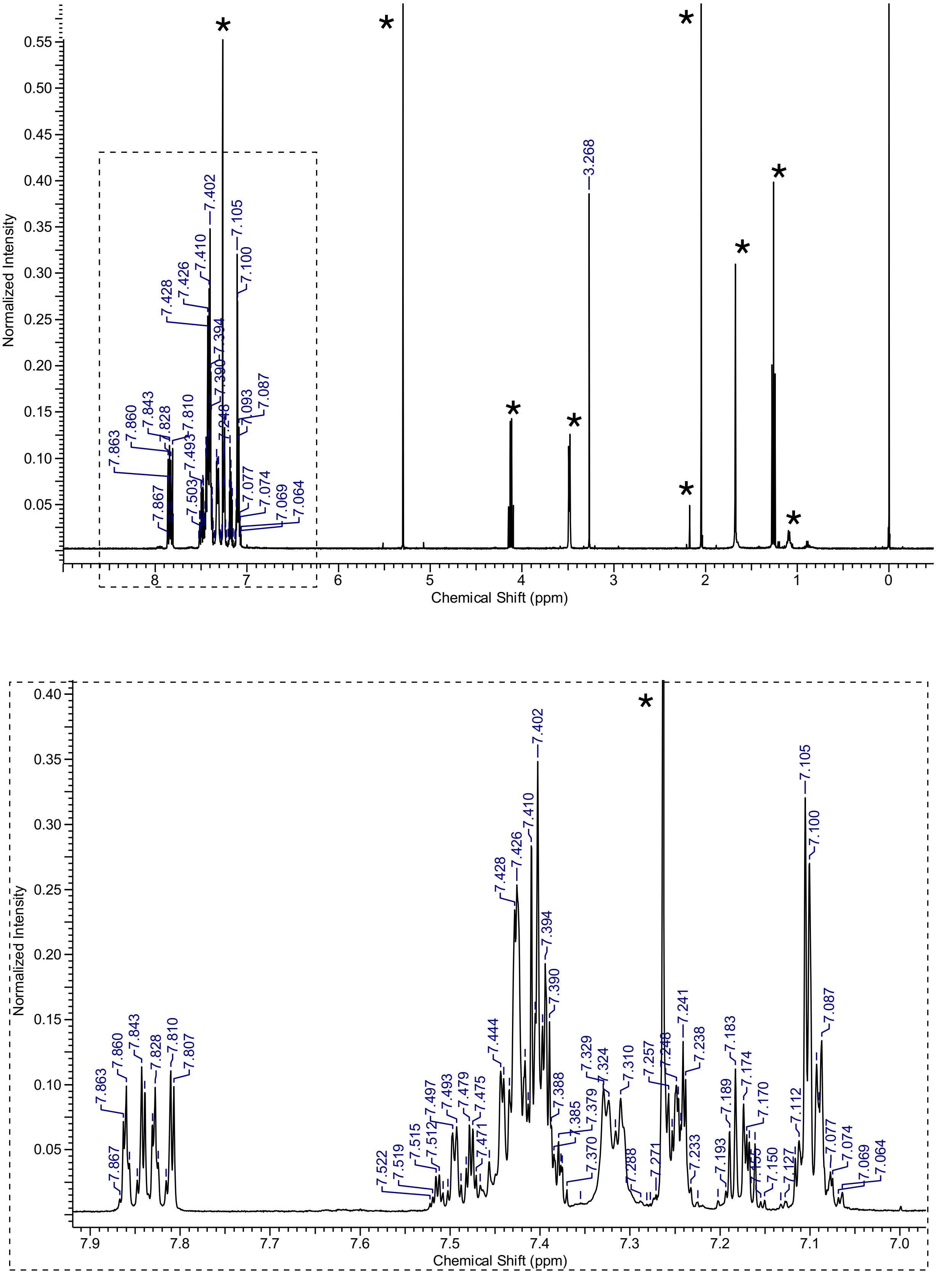


Figure S14 ^{1}H NMR spectra of **5b** in $CDCl_3$.

(a)


Normalized Intensity
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
Chemical Shift (ppm)
8
7
6
5
4
3
2
1
0
*
7.863
7.867
7.860
7.843
7.828
7.810
7.503
7.493
7.428
7.426
7.410
7.402
7.394
7.390
7.248
7.105
7.100
7.093
7.087
7.077
7.074
7.069
7.064
3.268
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
7.807
7.522
7.519
7.515
7.512
7.497
7.479
7.475
7.471
7.444
7.388
7.385
7.379
7.370
7.329
7.324
7.310
7.288
7.271
7.257
7.241
7.238
7.233
7.193
7.189
7.183
7.174
7.170
7.155
7.150
7.127
7.112

(b)

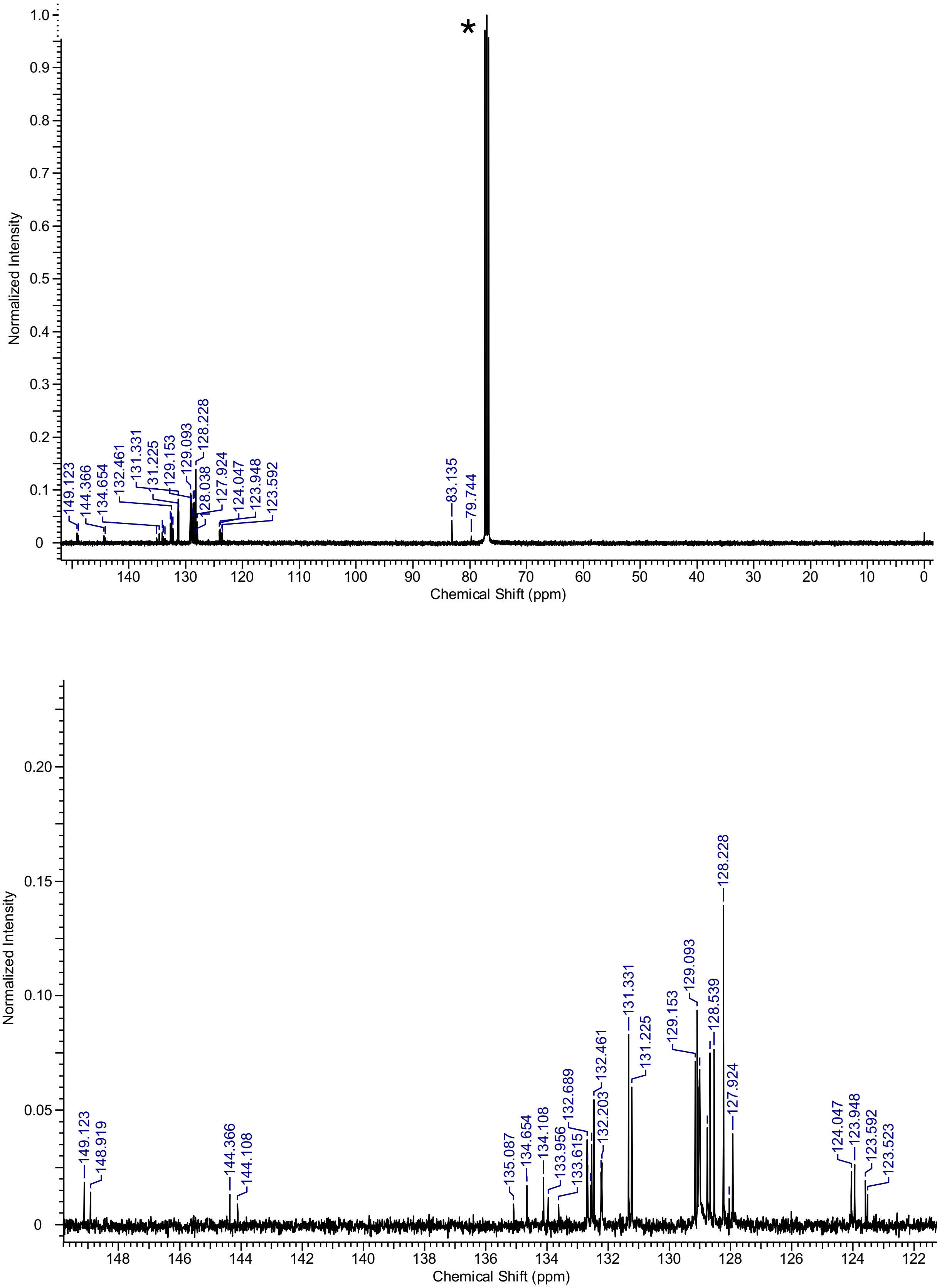
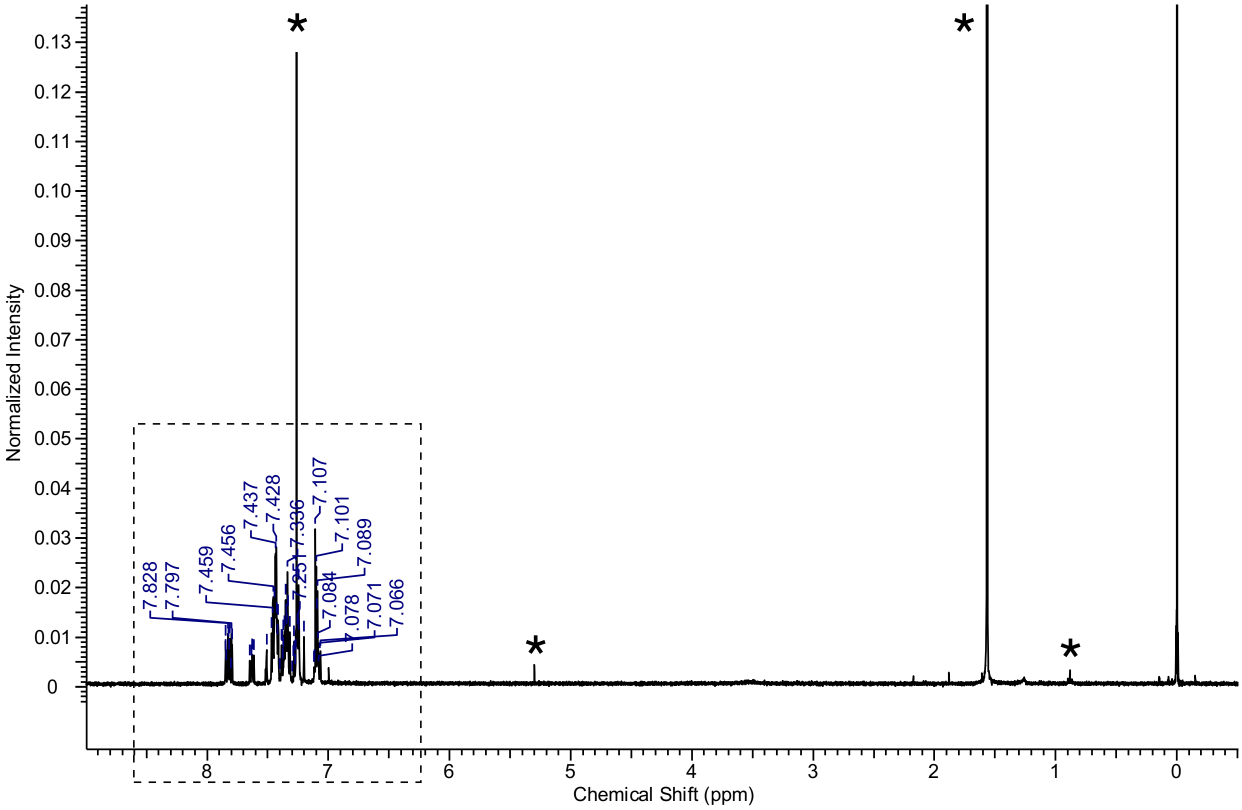
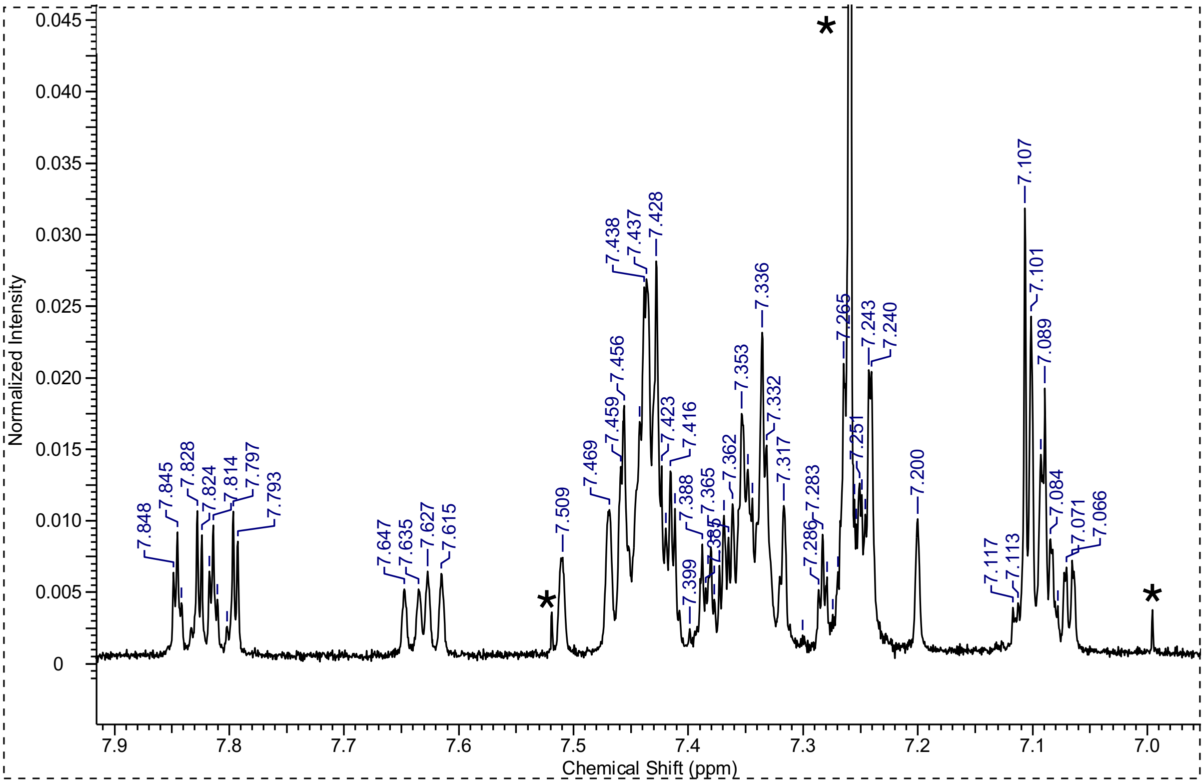


Figure S15 (a) ^{1}H NMR and (b) $^{13}C\{^{1}H\}$ NMR spectra of **5c** in $CDCl_3$.

(a)


Normalized Intensity
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
*
*
*
*
7.828
7.797
7.459
7.456
7.437
7.428
7.336
7.251
7.107
7.101
7.089
7.084
7.078
7.071
7.066
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


Normalized Intensity
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0
*
*
*
7.848
7.845
7.828
7.824
7.814
7.797
7.793
7.647
7.635
7.627
7.615
7.509
7.469
7.459
7.456
7.438
7.437
7.428
7.423
7.416
7.399
7.388
7.385
7.365
7.362
7.353
7.336
7.332
7.317
7.286
7.283
7.265
7.251
7.243
7.240
7.200
7.117
7.113
7.107
7.101
7.089
7.084
7.071
7.066
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
Chemical Shift (ppm)

(b)

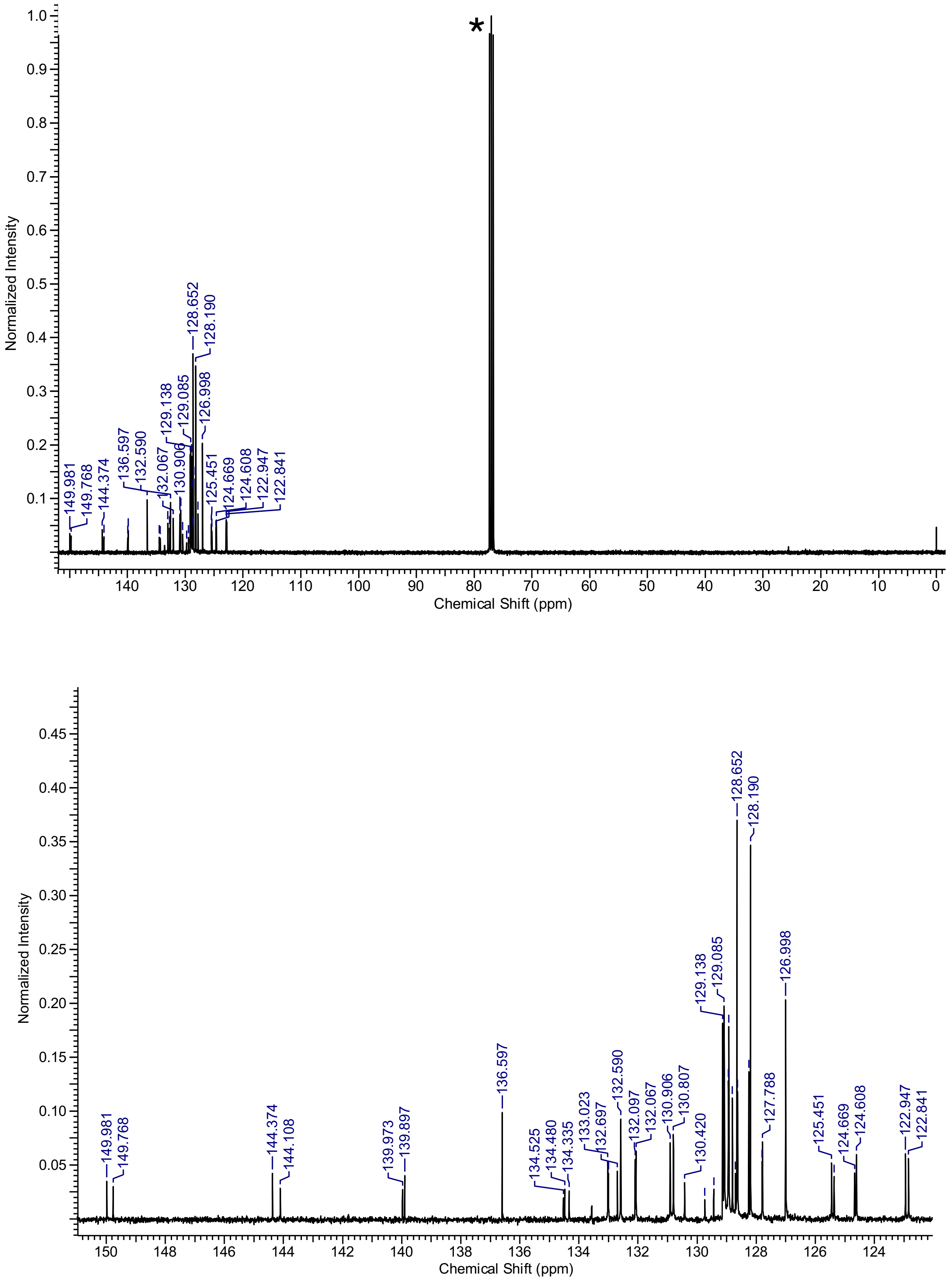
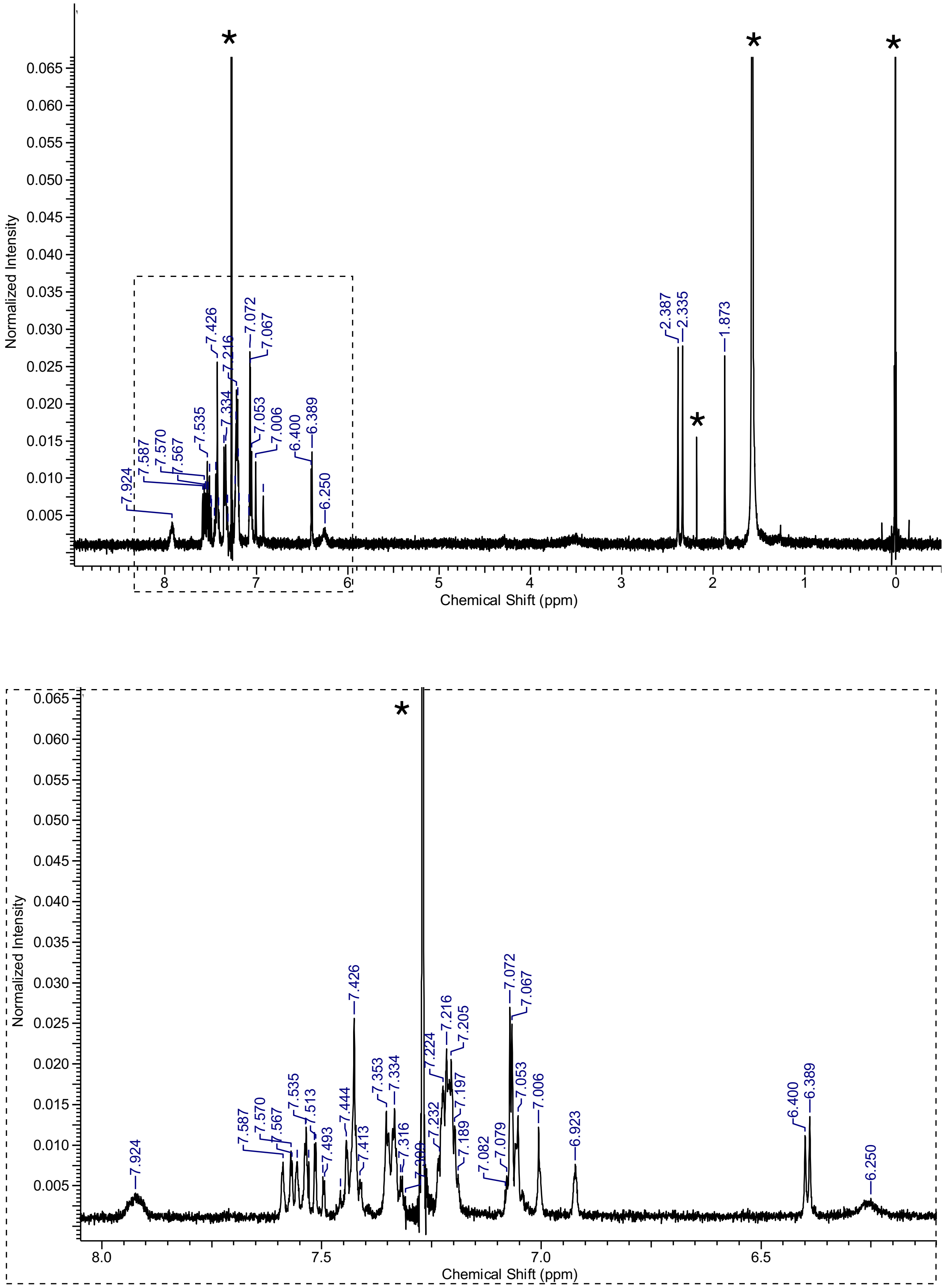


Figure S16 (a) ^{1}H NMR and (b) ^{13}C{^{1}H} NMR spectra of **6** in CDCl$_3$.

(a)


*
*
*
*
Normalized Intensity
0.065
0.060
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
7.924
7.587
7.570
7.567
7.535
7.426
7.334
7.216
7.072
7.067
7.053
7.006
6.400
6.389
6.250
2.387
2.335
1.873
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
*
Normalized Intensity
0.065
0.060
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
7.924
7.587
7.570
7.567
7.535
7.513
7.493
7.444
7.426
7.413
7.353
7.334
7.316
7.299
7.232
7.224
7.216
7.205
7.197
7.189
7.082
7.079
7.072
7.067
7.053
7.006
6.923
6.400
6.389
6.250
8.0
7.5
7.0
6.5
Chemical Shift (ppm)

(b)

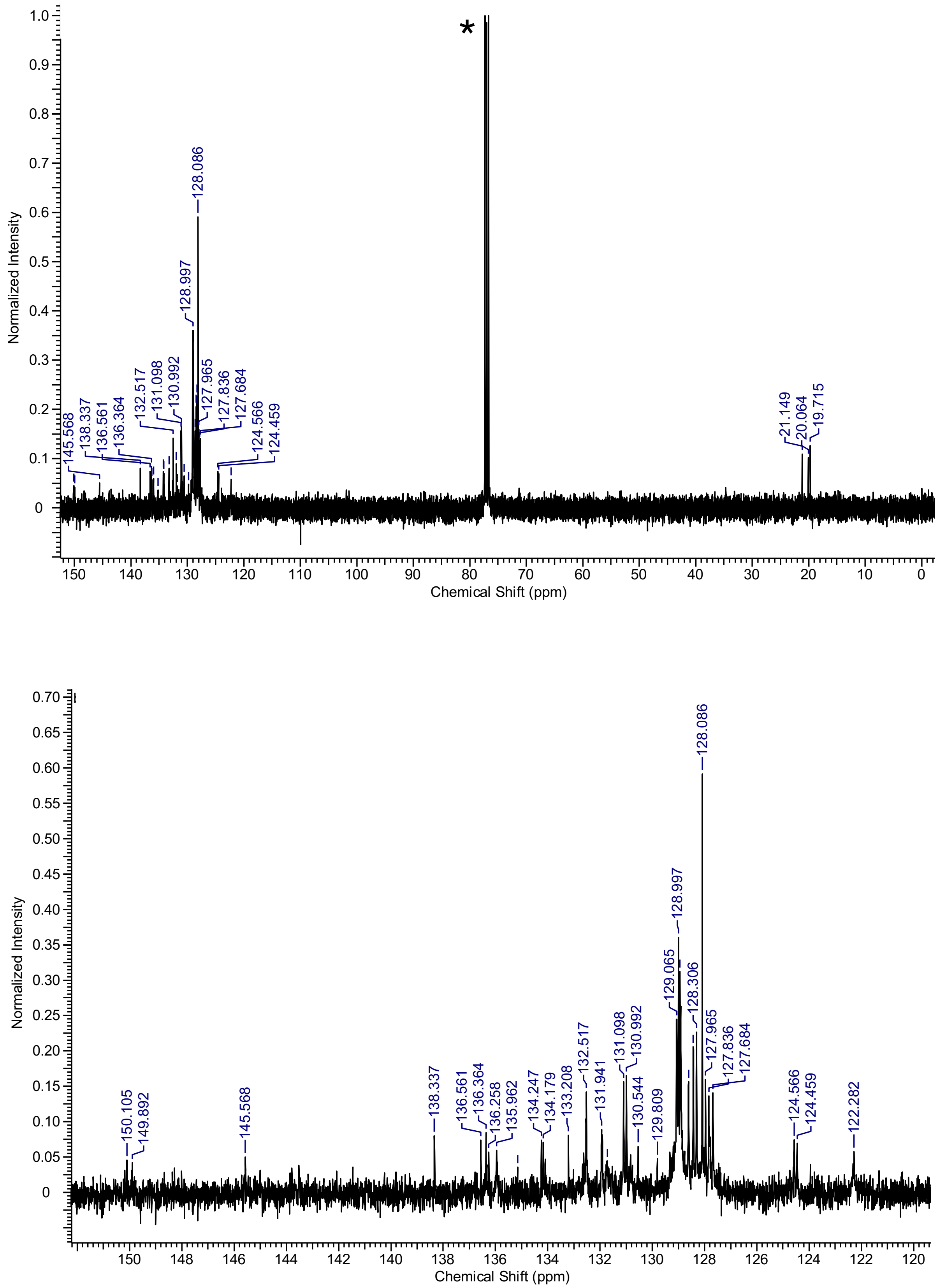
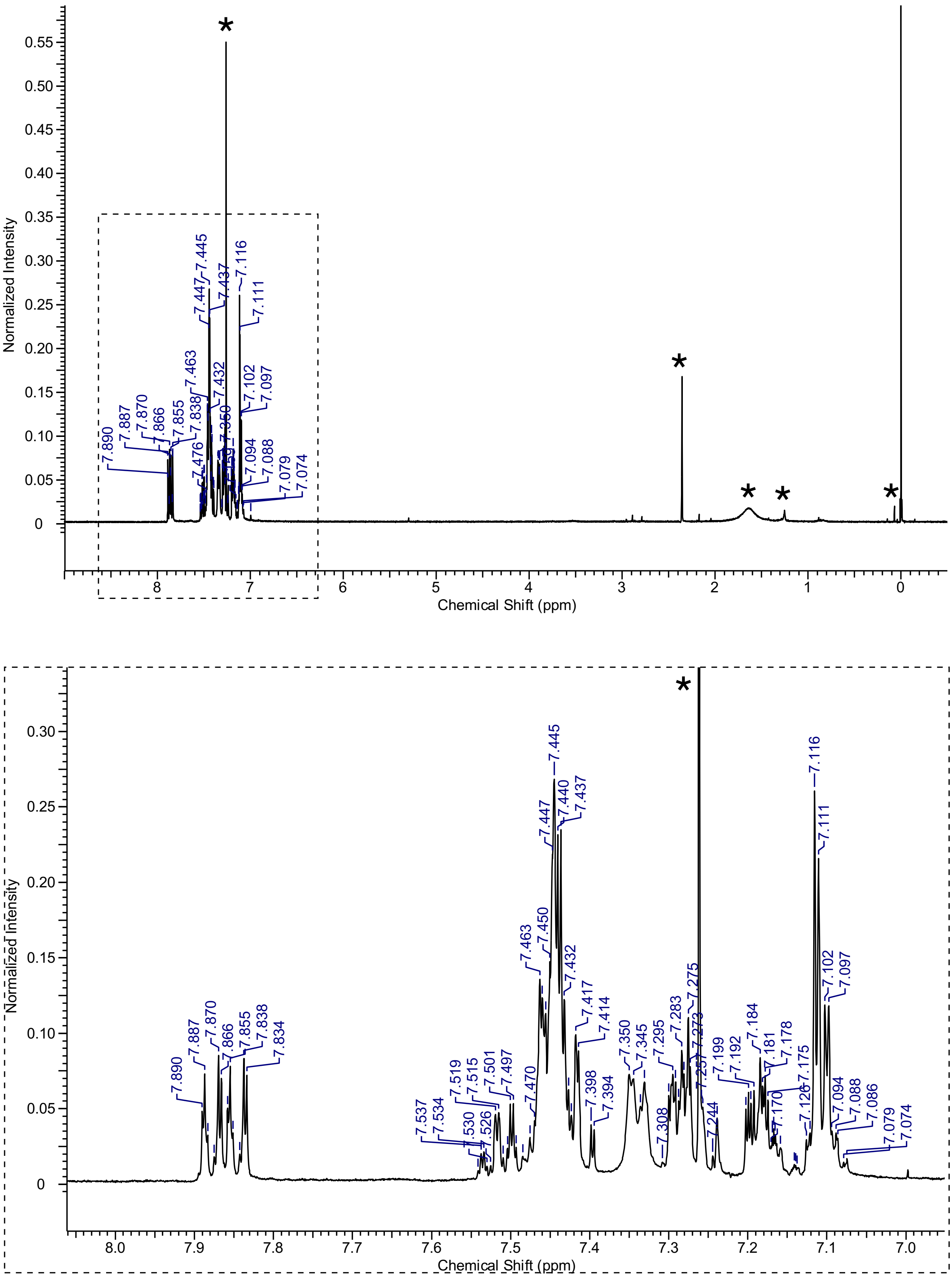


Figure S17 (a) ^{1}H NMR and (b) ^{13}C{^{1}H} NMR spectra of **8** in CDCl$_3$.

(a)



*
Normalized Intensity
Chemical Shift (ppm)
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
8
7
6
5
4
3
2
1
0
7.890
7.887
7.870
7.866
7.855
7.838
7.476
7.463
7.447
7.445
7.437
7.432
7.350
7.116
7.111
7.102
7.097
7.094
7.088
7.079
7.074
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
7.834
7.537
7.534
7.530
7.526
7.519
7.515
7.501
7.497
7.470
7.450
7.440
7.417
7.414
7.398
7.394
7.345
7.308
7.295
7.283
7.275
7.273
7.257
7.244
7.199
7.192
7.184
7.181
7.178
7.175
7.170
7.126
7.086

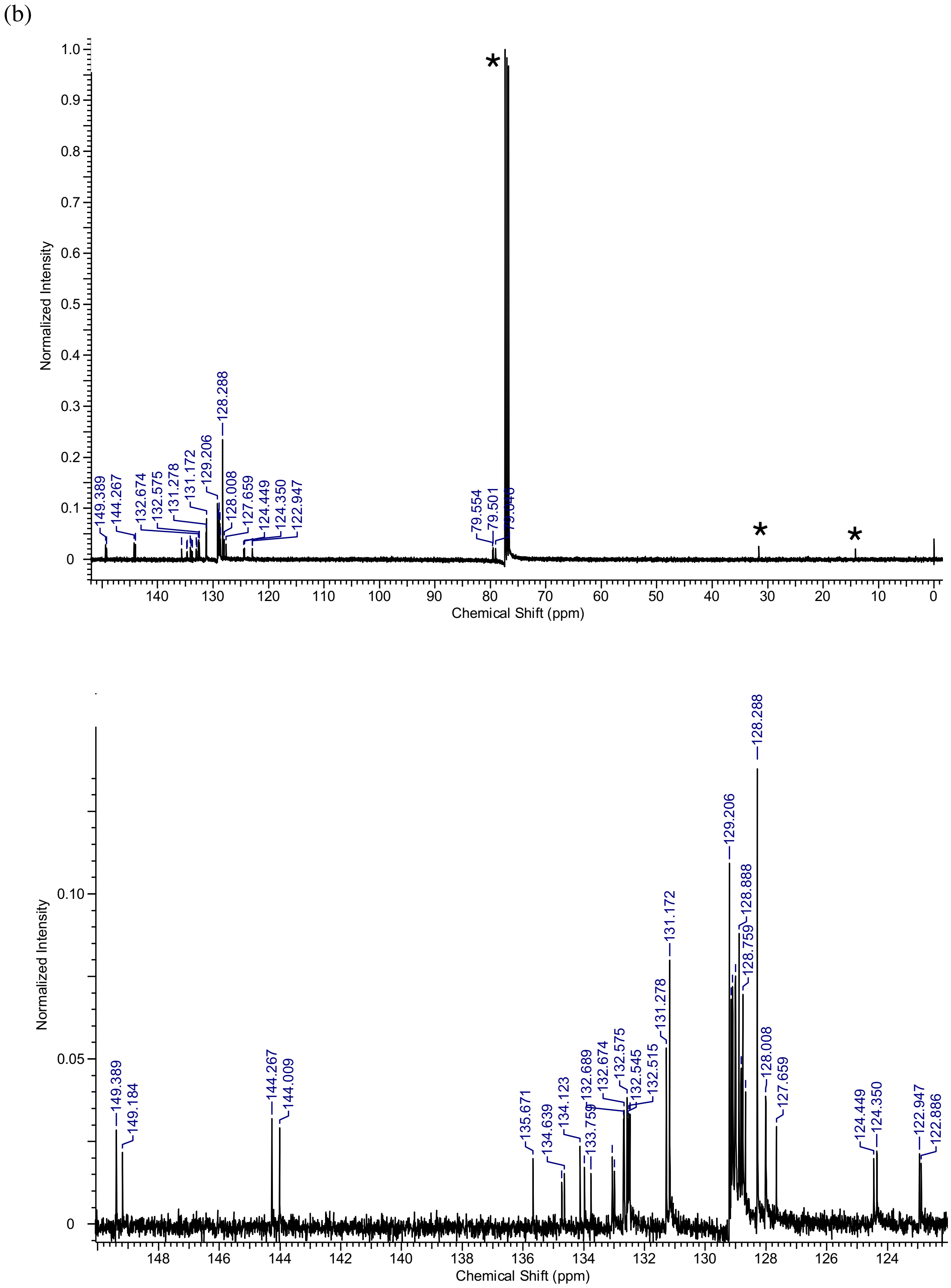
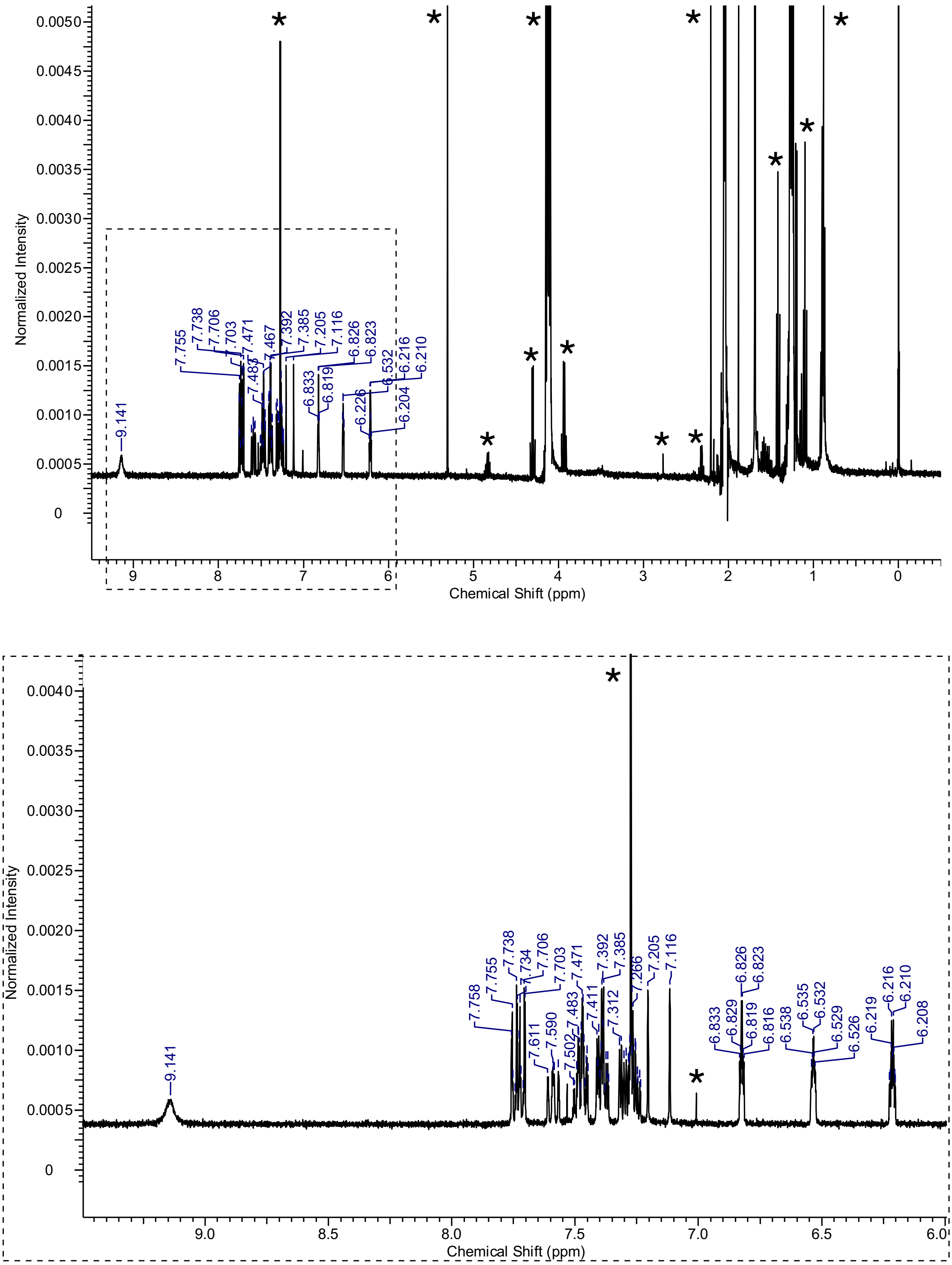


Figure S18 (a) ^{1}H NMR and (b) ^{13}C{^{1}H} NMR spectra of **9** in CDCl$_3$.

(a)


Normalized Intensity
0.0050
0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0
Chemical Shift (ppm)
9
8
7
6
5
4
3
2
1
0
9.141
7.755
7.738
7.706
7.703
7.471
7.483
7.467
7.392
7.385
7.205
7.116
6.833
6.819
6.826
6.823
6.532
6.226
6.216
6.210
6.204
*
9.0
8.5
8.0
7.5
7.0
6.5
6.0
7.758
7.755
7.738
7.734
7.706
7.703
7.611
7.590
7.502
7.483
7.471
7.411
7.392
7.385
7.312
7.266
7.205
7.116
6.833
6.829
6.826
6.819
6.823
6.816
6.538
6.535
6.532
6.529
6.526
6.219
6.216
6.210
6.208

(b)

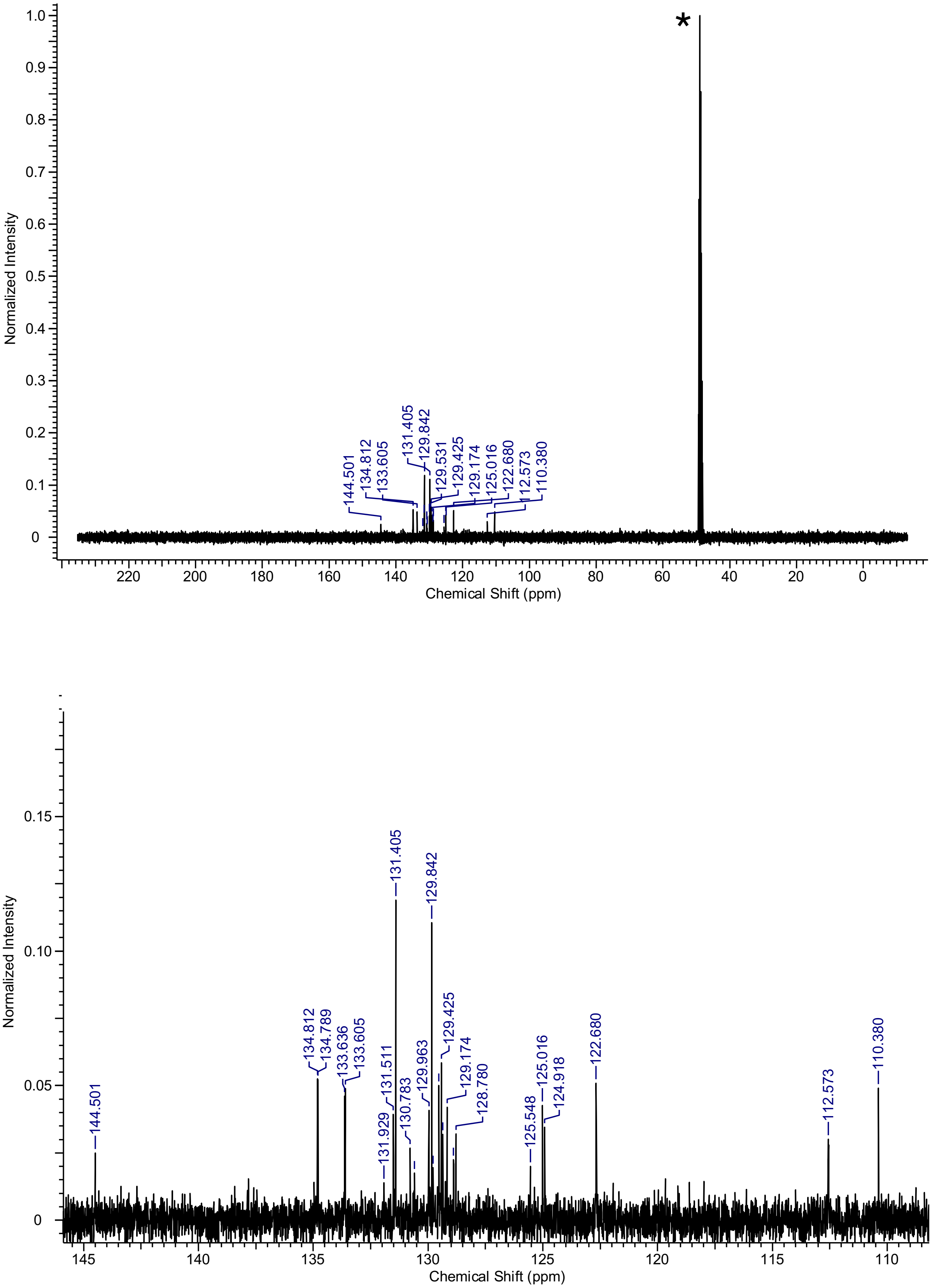


Figure S19 (a) ^{1}H NMR and (b) ^{13}C{^{1}H} NMR spectra of **11** in CD_3OD.