Electronic Supplementary Information for:

Charge Neutral Rhenium(I) Tricarbonyl Complexes of Tridentate *N*-Heterocylic Carbene Ligands that Bind to Amyloid Plaques of Alzheimer's Disease

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Synthesis

6-nitro-2-(4-*N,N*-dimethylaminophenyl)benzothiazole: This compound was synthesised as reported by Racane[1] from 2-amino-5-nitrothiophenol (0.85 g, 5.00 mmol), 4-(dimethylamino)benzaldehyde (0.75 g, 5.00 mmol) in pyridine (10 mL). The product was obtained as an orange solid (Yield: 0.72g, 48%). ^{1}H NMR (400 MHz) ($CDCl_3$): δ (ppm) 3.11 (s, 6H, CH_3), 6.76 (d, 2H, $^3J_{H\text{-}H}$ = 9.04 Hz, H_{Ar}), 7.98-8.00 (m, 3H, H_{Ar}), 8.30-8.33 (dd, 1H, $^3J_{H\text{-}H}$ = 2.32, 8.96 Hz, H_{Ar}), 8.76 (d, 1H, $^3J_{H\text{-}H}$ = 2.28 Hz, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ (ppm) 40.1 CH_3, 111.6 C_{Ar}, 117.9 C_{Ar}, 120.3 C_q, 121.9 C_{Ar}, 121.9 C_{Ar}, 129.5 C_{Ar}, 134.8 C_q, 144.0 C_q, 153.0 C_q, 158.6 C_q, 174.5 C_q.

6-amino-2-(4-*N,N*-dimethylaminophenyl)benzothiazole: This compound was synthesised as reported by Racane[1] from anhydrous tin(II) chloride (2.17 g, 9.62 mmol), 6-nitro-2-(4-N,N-dimethylaminophenyl)benzothiazole (0.72 g, 2.41 mmol), conc. HCl (4.5 mL) and methanol (4.5 mL). The product was obtained as a brown solid. (Yield: 0.094 g, 15%). ^{1}H NMR (400 MHz) (DMSO-d_6): δ (ppm) 2.90 (s, 6H, $2CH_3$), 5.18 (s, 2H, NH_2), 6.53 (d, 2H, $^3J_{H\text{-}H}$ = 8.44 Hz, H_{Ar}), 6.69 (d, 2H, $^3J_{H\text{-}H}$ = 8.44 Hz, H_{Ar}), 6.78 (s, 2H, *H*C=C*H*), 7.29 (d, 2H, $^3J_{H\text{-}H}$ = 8.48 Hz, H_{Ar}), 7.32 (d, 2H, $^3J_{H\text{-}H}$ = 8.84 Hz, H_{Ar}). ^{13}C NMR (DMSO-d_6): δ (ppm) 39.5-40.5 CH_3, 104.5 C_{Ar}, 112.4 C_{Ar}, 115.1 C_{Ar}, 121.5 C_q,121.6 C_q, 122.7 C_{Ar}, 128.1 C_{Ar}, 135.7 C_q, 145.9 C_q, 147.1 C_q, 152.0 C_q, 162.0 C_q.

***p*-nitro-*p'*-*N,N*-dimethylaminostilbene**: This compound was synthesised as described by Gao[2] from *p*-nitro-phenylacetic acid (5.00 g, 30 mmol), *p*-dimethylaminobenzaldehyde (6.18 g, 41 mmol), and piperidine (10 mL). The product was obtained as a bright orange solid. (Yield: 2.96 g, 42%). ^{1}H NMR

(500 MHz) ($CDCl_3$): δ (ppm) 3.03 (s, 6H, CH_3), 6.72 (d, 2H, H_{Ar}), 6.94 (d, 1H, $^3J_{H\text{-}H}$ = 16.2 Hz, HC=CH), 7.22 (d, 1H, $^3J_{H\text{-}H}$ = 16.3 Hz, HC=CH), 7.45 (d, 2H, $^3J_{H\text{-}H}$ = 8.70 Hz, H_{Ar}), 7.57 (d, 2H, $^3J_{H\text{-}H}$ = 8.70 Hz, H_{Ar}), 8.19 (d, 2H, $^3J_{H\text{-}H}$ = 8.85 Hz, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ (ppm) 40.3 CH_3, 112.2 C_{Ar}, 121.6 C=C, 124.2 C_{Ar}, 126.1 C_{Ar}, 128.4 C_{Ar}, 133.4 C=C, 145.0 C_q, 150.9 C_q.

***p*-amino-*p'N,N*-dimethylaminostilbene**: This compound was prepared using the same procedure as described by Gao[2] from *p*-nitro-*p'-N,N*-dimethylaminostilbene (0.91 g, 3.54 mmol), anhydrous tin(II) chloride (3.20 g, 14.2 mmol), conc. HCl (10 mL) and methanol (10 mL). The product was obtained as a yellow solid. (Yield: 0.10 g, 12%). ^{1}H NMR (500 MHz) (DMSO-d_6): δ (ppm) 2.99 (s, 6H, $2CH_3$), 5.33 (s, 2H, NH_2), 6.72-6.74 (dd, 1H, H_{Ar}), 6.79 (d, 2H, $^3J_{H\text{-}H}$ = 8.85, H_{Ar}). ^{13}C NMR (DMSO-d_6): δ (ppm) 112.9 C_{Ar}, 114.4 C_{Ar}, 123.7 C_q, 125.1 H*C*=*C*H, 126.1 C_{Ar}, 126.6 C_{Ar}, 127.4 C_{Ar}, 148.4 C_q, 149.8 C_q.

1: This compound was synthesised as described by Hemelaere[3] from ethanolamine (5.00 g, 81.9 mmol), $MgSO_4$ (19.7 g, 164 mmol) and benzylaldehyde (8.69 g, 81.9 mmol) in methanol (150 mL). The product was obtained as a yellow oil. (Yield: 9.85 g, 79%). ^{1}H-NMR (400 MHz) ($CDCl_3$): δ (ppm) 2.76 (t, 2H, $^3J_{H\text{-}H}$ = 5.20 Hz, $H_2C\text{-}CH_2$), 2.94 (s, 2H, NH_2), 3.64 (t, 2H, $^3J_{H\text{-}H}$ = 5.12 Hz, CH_2CH_2), 3.78 (s, 2H, C*H*$_2$OH), 7.24-7.32 (m, 5H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ (ppm) 50.6 (CH_2CH_2), 53.5 (CH_2CH_2), 60.7 (*C*H_2N), 127.2 C_{Ar}, 128.3 C_{Ar}, 128.5 C_{Ar}.

2: To a stirred solution of **1** (0.5 g, 3.31 mmol) in acetonitrile (30 mL), $NaHCO_3$ (0.42 g, 4.95 mmol) was added. The mixture was cooled to 0 °C before a solution of *t*-butyl bromoacetate (0.65 g, 3.31 mmol) in acetonitrile (5 mL) was added dropwise, and the resultant mixture was stirred at room temperature for 2 h and the solvent was then removed on a rotatory evaporator. The crude product was redissolved in dichloromethane, washed with water (3 × 10 mL), dried with $MgSO_4$ and the solvent was evaporated to dryness on a rotatory evaporator. The crude product was purified on silica with methanol (3%) and dichloromethane (97%) as the eluent. The product was obtained as a yellow oil. (Yield: 0.37 g, 42%). ^{1}H-NMR (400 MHz) ($CDCl_3$): δ (ppm) 1.46 (s, 9H, $3CH_3$), 2.85 (t, 2H, $^3J_{H\text{-}H}$ = 5.20 Hz, C*H*$_2$CH$_2$), 3.23 (s, 2H, C*H*$_2$COO), 3.59 (t, 2H, $^3J_{H\text{-}H}$ = 5.08 Hz, CH_2CH_2), 3.82 (s, 2H, CH_2N), 7.28-7.34 (m, 5H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ (ppm) 27.8 *C*H3, 55.5 *C*H_2COO, 56.6 CH_2*C*H2, 58.6 *C*H_2CH$_2$, 59.0 *C*H_2N, 81.3 C_q, 127. 3 C_{Ar}, 128.4 C_{Ar}, 128.9 C_{Ar}, 138.5 C_q, 171.2 C_q.

3: To a solution of **2** in methanol (2.71 g, 10.2 mmol), was added 10% Pd/C (0.50 g) and the mixture was stirred overnight under a hydrogen atmosphere. The solution was filtered through a plug of Celite, evaporated to dryness on a rotatory evaporator and purified on silica with dichloromethane (2%) and

methanol (98%) as the eluent. The pure compound was obtained as a yellow oil (Yield: 1.53 g, 85%). ^{1}H-NMR (400 MHz) ($CDCl_3$): δ (ppm) 1.44 (s, 9H, $3CH_3$), 2.60 (s_{br}, 1H, NH), 2.74 (t, 2H, $^{3}J_{H\text{-}H}$ = 5.20 Hz, CH_2), 3.28 (s, 2H, OCCH_2), 3.59 (t, 2H, $^{3}J_{H\text{-}H}$ = 5.12 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ (ppm) 28.0 CH_3, 51.1 O*C*N, 51.2 CH_2, 60.9 CH_2, 81.4 C_q, 171.9 C_q.

4: To a solution of **3** (0.50 g, 2.85 mmol) in anhydrous DMF (5 mL) was added $NaHCO_3$ (0.29 g, 3.42 mmol). The mixture was cooled to 0 °C and a solution of benzyl bromoacetate (0.72 g, 3.14 mmol) in anhydrous DMF (2 mL) was added dropwise. The mixture was stirred at 0 °C for 1 h, allowed to warm to room temperature then stirred for another 12 h. The solution was filtered and the solvent was removed on a rotatory evaporator. The crude product was purified on silica with ethyl acetate (40%) and hexane (60%) as the eluent. The pure compound was obtained as a yellow oil. (Yield: 0.74g, 81%). ^{1}H-NMR (400 MHz) ($CDCl_3$): δ (ppm) 1.46 (s, 9H, CH_3), 2.90 (t, 2H, $^{3}J_{H\text{-}H}$ = 4.12 Hz, CH_2), 3.46 (s, 2H, NCH_2), 3.54 (t, 2H, $^{3}J_{H\text{-}H}$ = 2.12 Hz, CH_2), 3.61 (s, 2H, NCH_2), 5.16 (s, 2H, CH_2), 7.34-7.37 (m, 5H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ (ppm) 28.1 CH_3, 55.8 NCH_2, 56.5 NCH_2, 57.1 OCH_2, 59.3 NCH_2, 66.6 O-CH_2-Ar, 81.6 C_q, 128.3 C_{Ar}, 128.4 C_{Ar}, 128.6 C_{Ar}, 135.5 C_q, 171.3 C_q, 171.9 C_q.

5: A mixture of **4** (2.57 g, 7.95 mmol) and triphenylphosphine (2.09 g, 7.95 mmol) was dissolved in anhydrous DCM (20 mL) and cooled to 0 °C under a nitrogen atmosphere. *N*-bromosuccinimide (1.42 g, 7.95 mmol) was added portion-wise and the mixture was stirred for 2.5 h at 0 °C.[4] A pale orange crystalline solid was obtained after the solvent was removed on a rotatory evaporator. The crude product was washed with ether (2 $\times$ 20 mL) and then purified on silica with hexane (40%) and ethyl acetate (60%) as the eluent. The pure compound was obtained as a yellow oil. (Yield: 1.87 g, 43%). ^{1}H NMR (400 MHz) ($CDCl_3$): δ (ppm) 1.46 (s, 9H, CH_3), 3.17 (t, 2H, $^{3}J_{H\text{-}H}$ = 7.68 Hz, CH_2), 3.43 (s, 2H, CH_2), 3.66 (s, 2H, CH_2), 5.16 (s, 2H, CH_2), 7.35-7.39 (m, 5H, H_{Ar}). ^{13}C NMR ($CDCl_3$): δ (ppm) 28.1 CH_3, 30.2 CH_2Br, 55.6 NCH_2, 56.4 NCH_2, 56.7 NCH_2, 66.5 O-CH_2-Ar, 81.4 C_q, 128.3 C_{Ar}, 128.4 C_{Ar}, 128.6 C_{Ar}, 135.6 C_q, 170.4 C_q, 171.1 C_q.

NMR Spectra

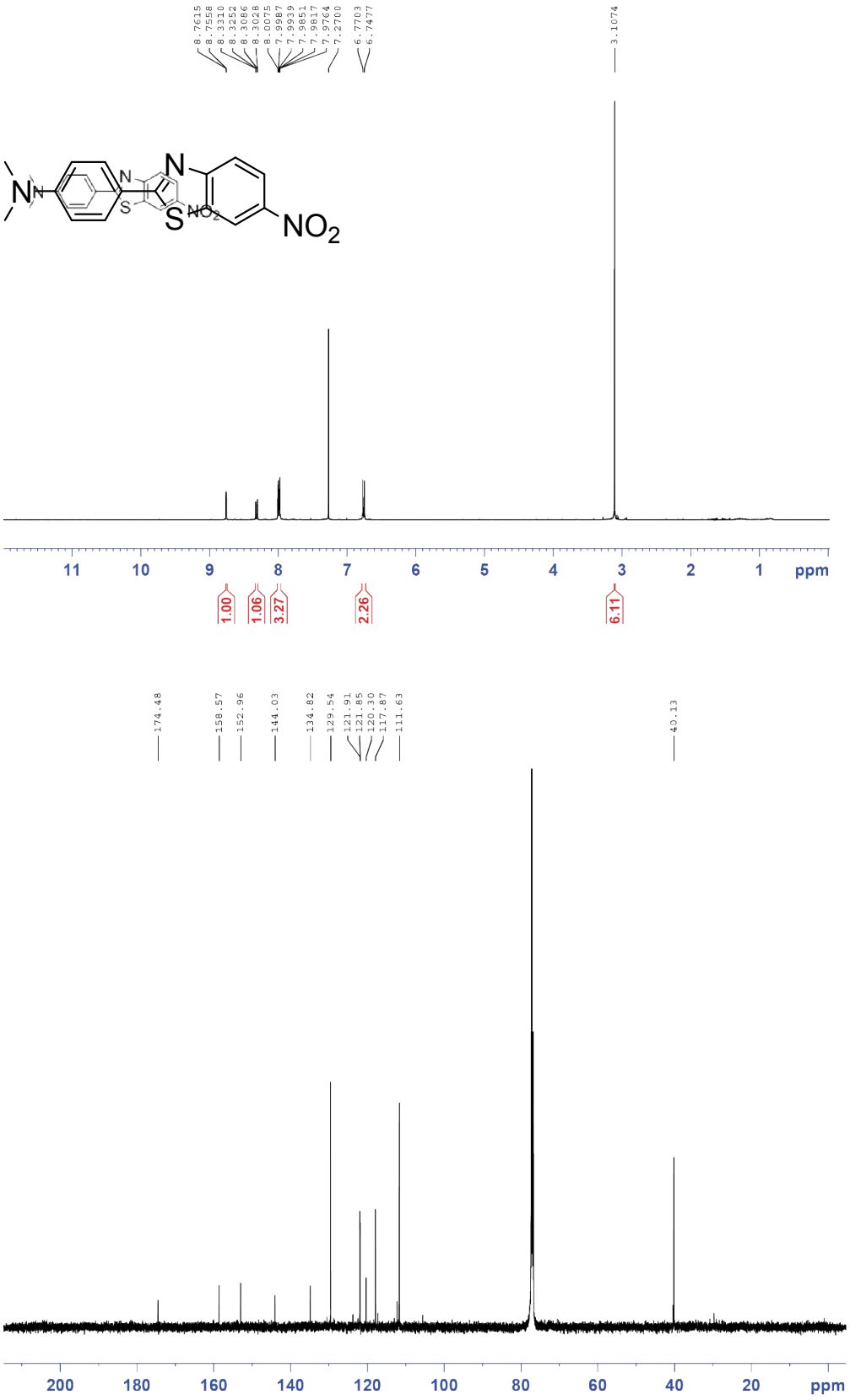

Figure S1. ^{1}H and ^{13}C NMR spectra for 6-nitro-2-(4-*N*,*N*-dimethylaminophenyl)benzothiazole.

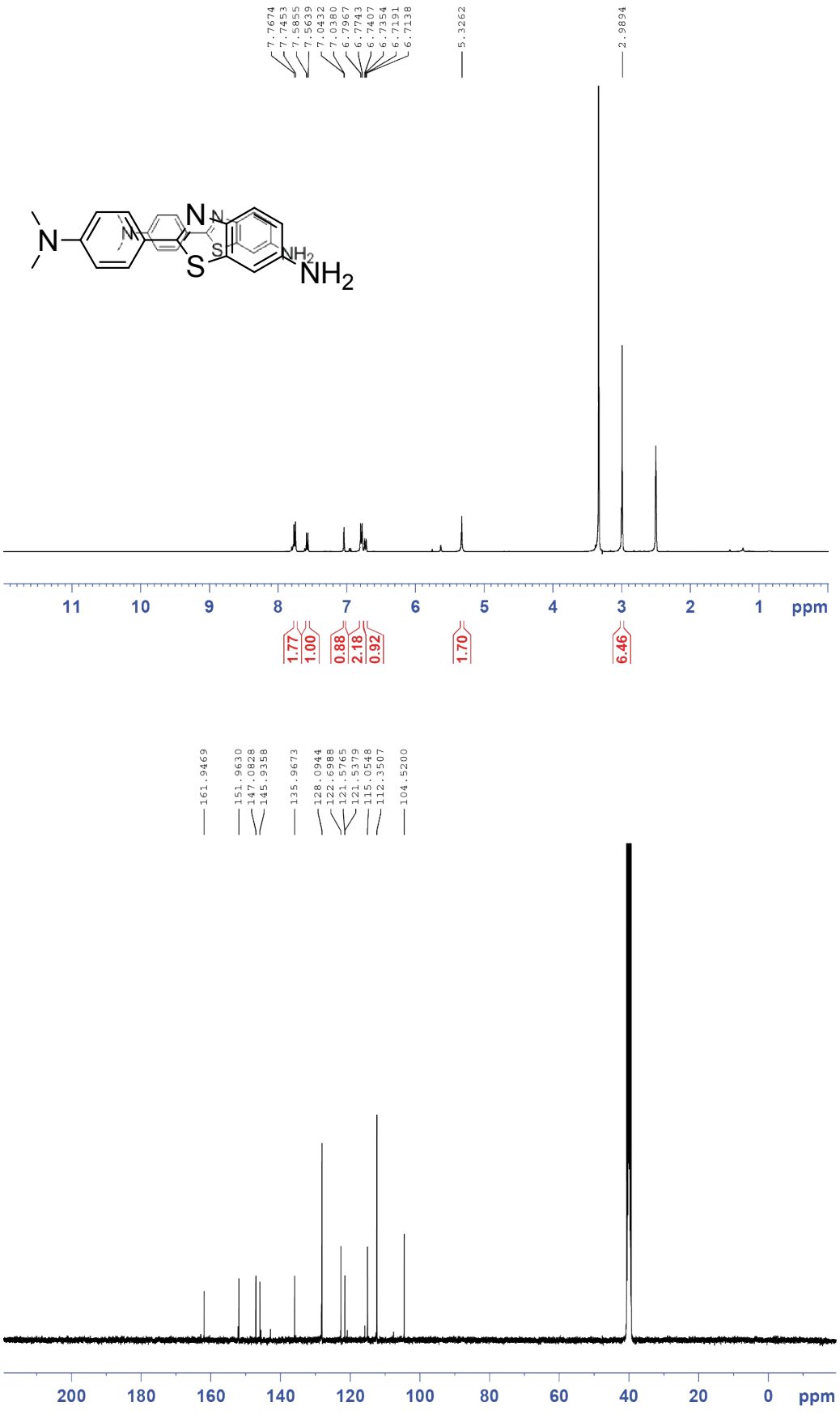

Figure S2. ^{1}H and ^{13}C NMR spectra for 6-amino-2-(4-*N,N*-dimethylaminophenyl)benzothiazole.

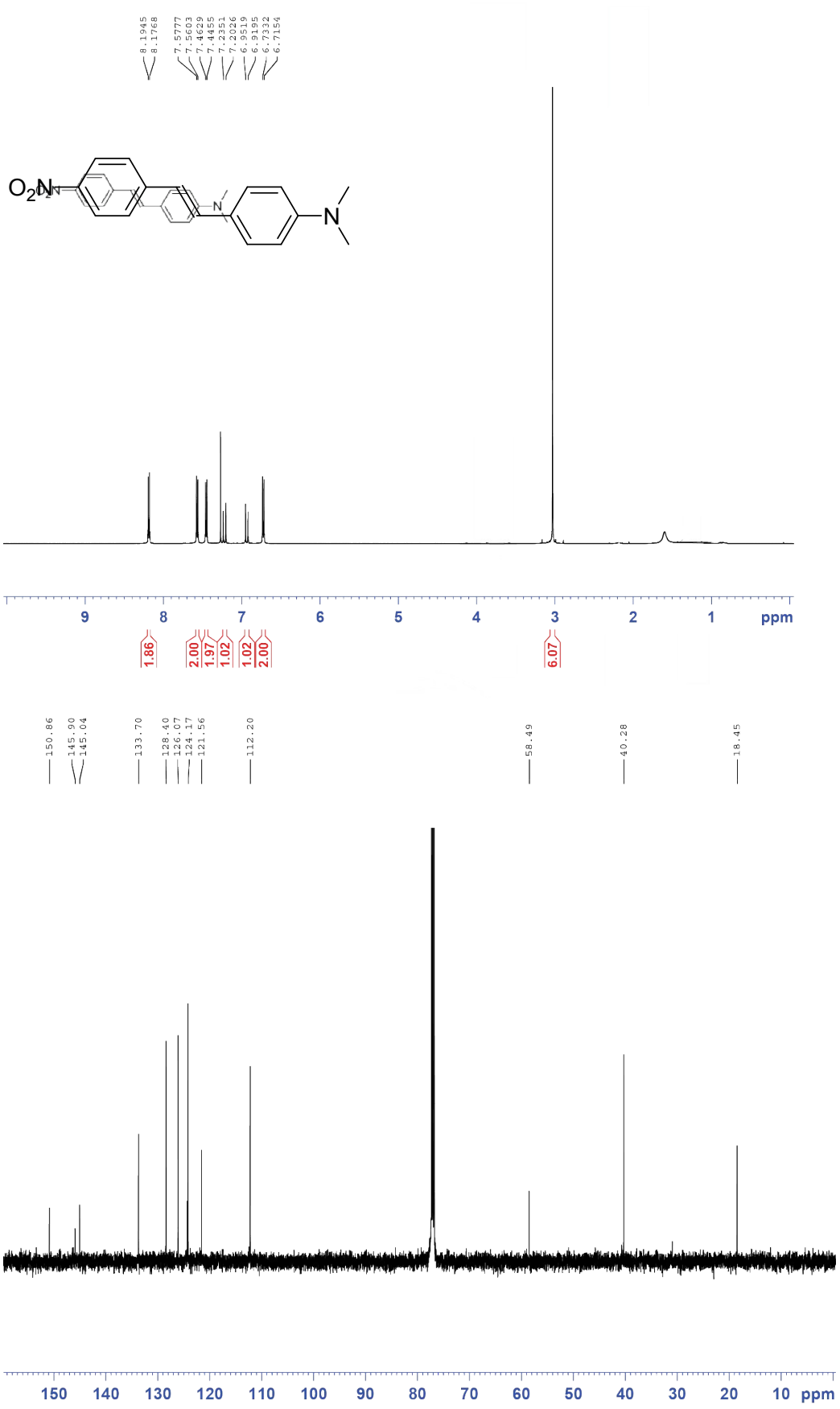

Figure S3. ^{1}H and ^{13}C NMR spectra for *p*-nitro-*p'*-*N,N*-dimethylaminostilbene.

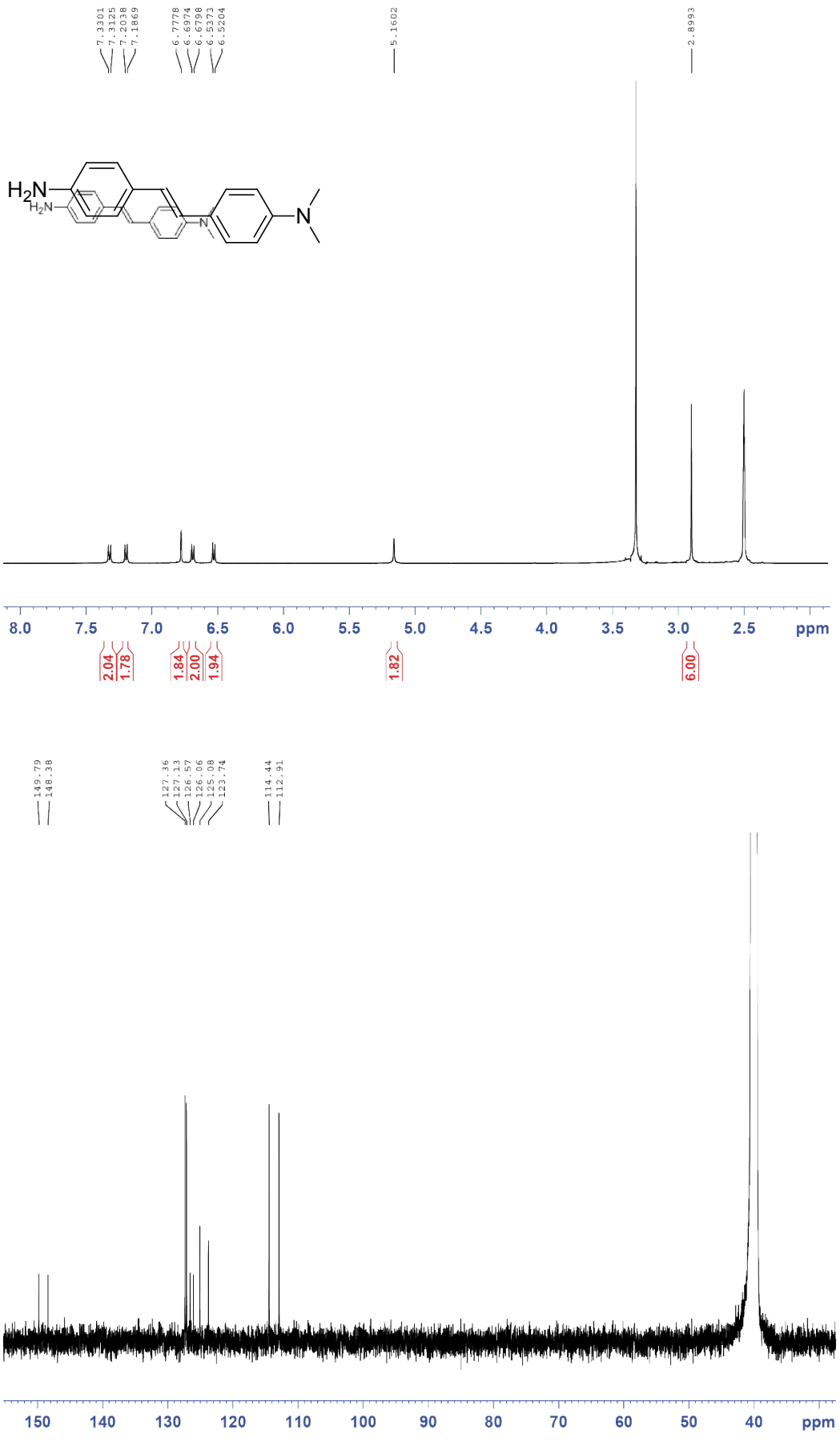

Figure S4. ^{1}H and ^{13}C NMR spectra for *p*-amino-*p'N,N*-dimethylaminostilbene.

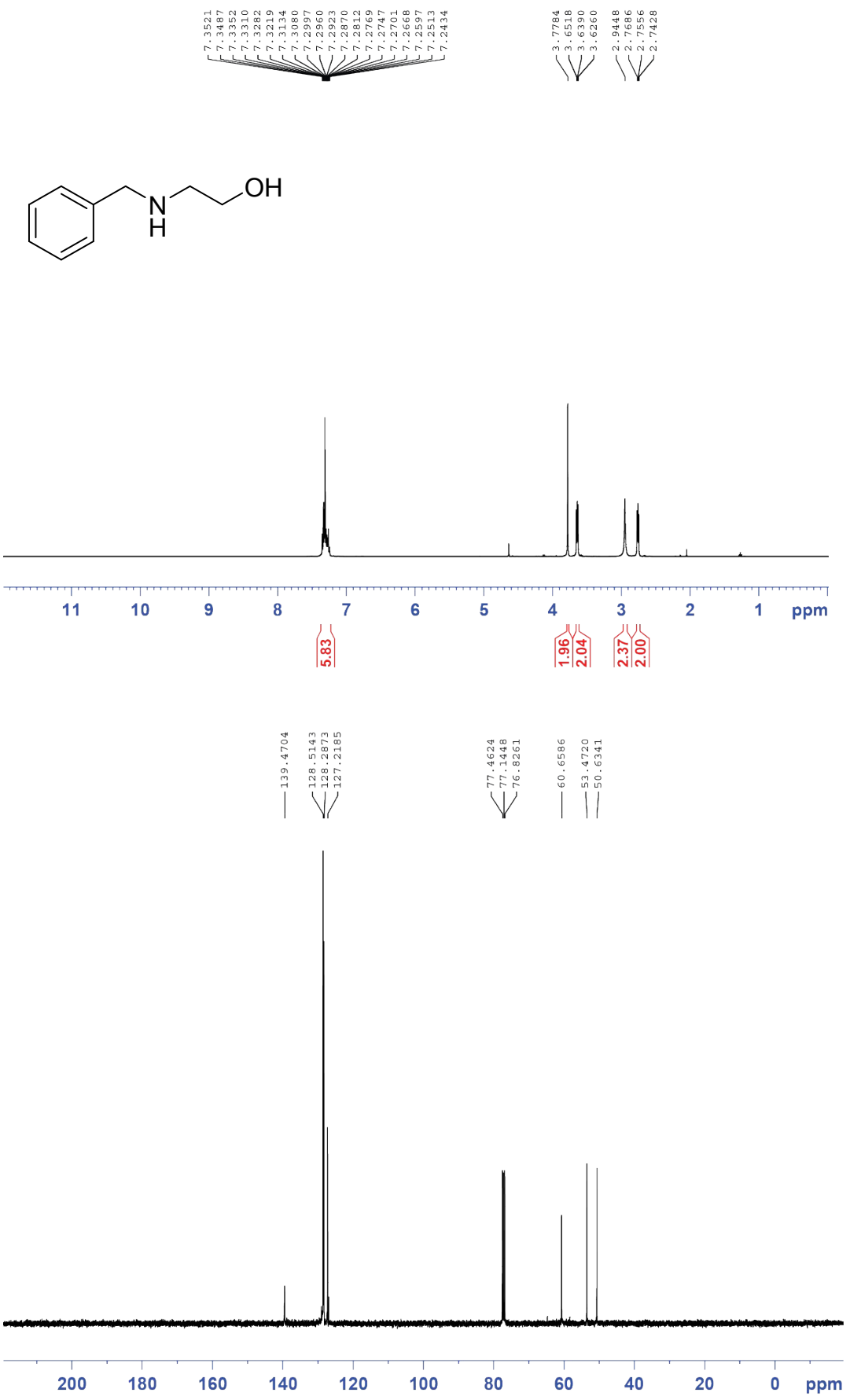

Figure S5. ^{1}H and ^{13}C NMR spectra for compound **1**.

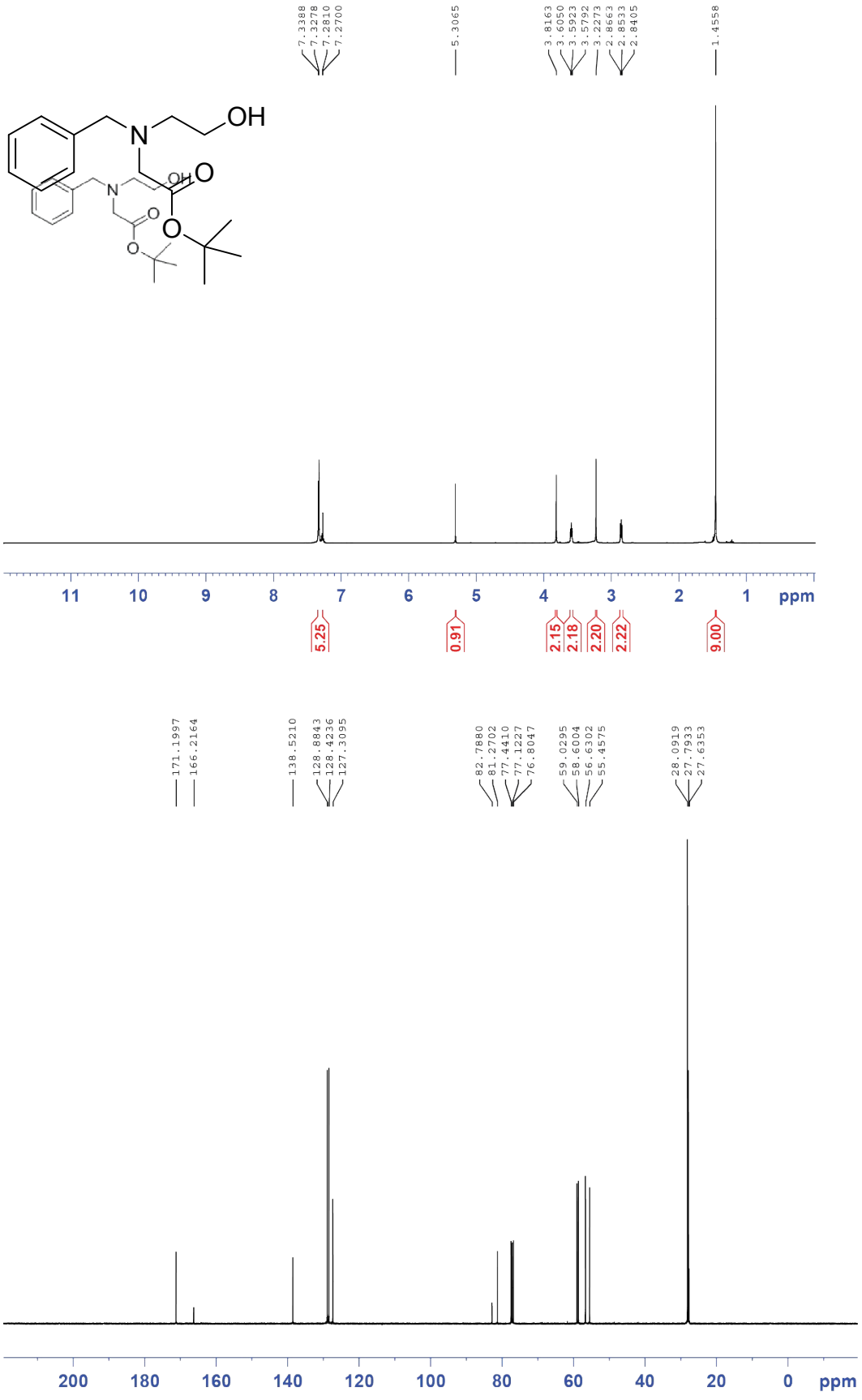

Figure S6. ^{1}H and ^{13}C NMR spectra for compound **2**.

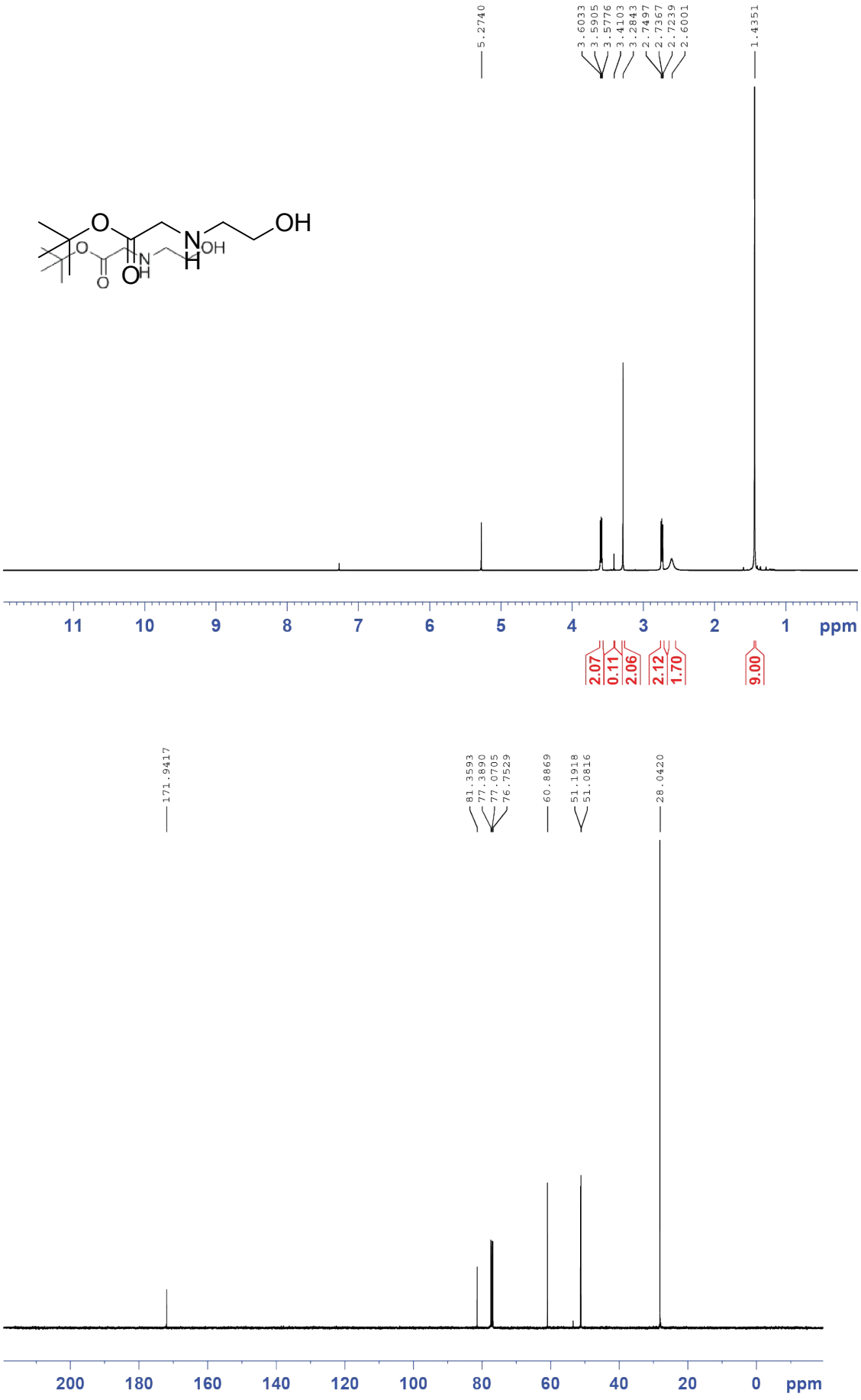

Figure S7. ^{1}H and ^{13}C NMR spectra for compound **3**.

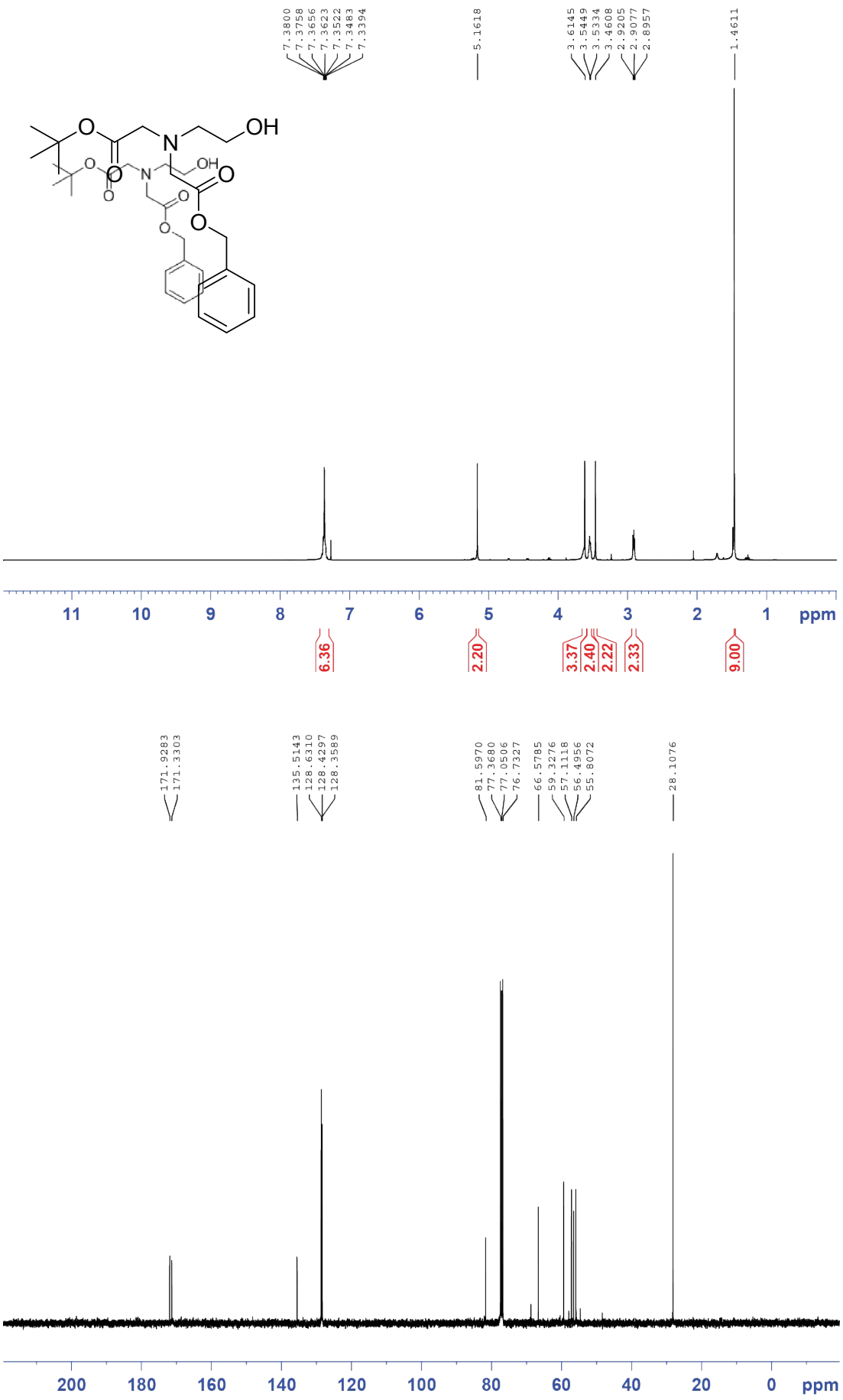

Figure S8. ^{1}H and ^{13}C NMR spectra for compound **4**.

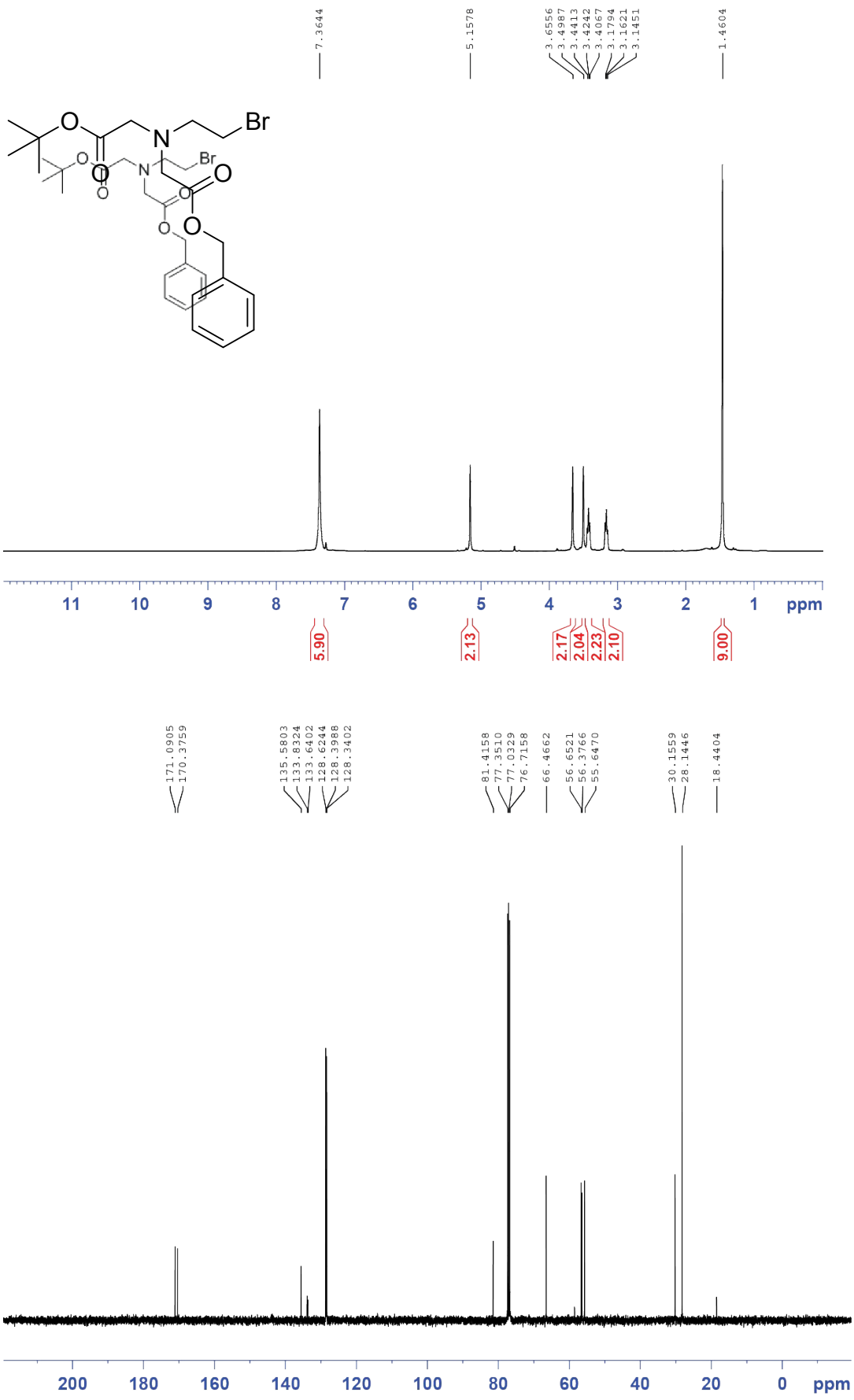

Figure S9. ^{1}H and ^{13}C NMR spectra for compound **5**.

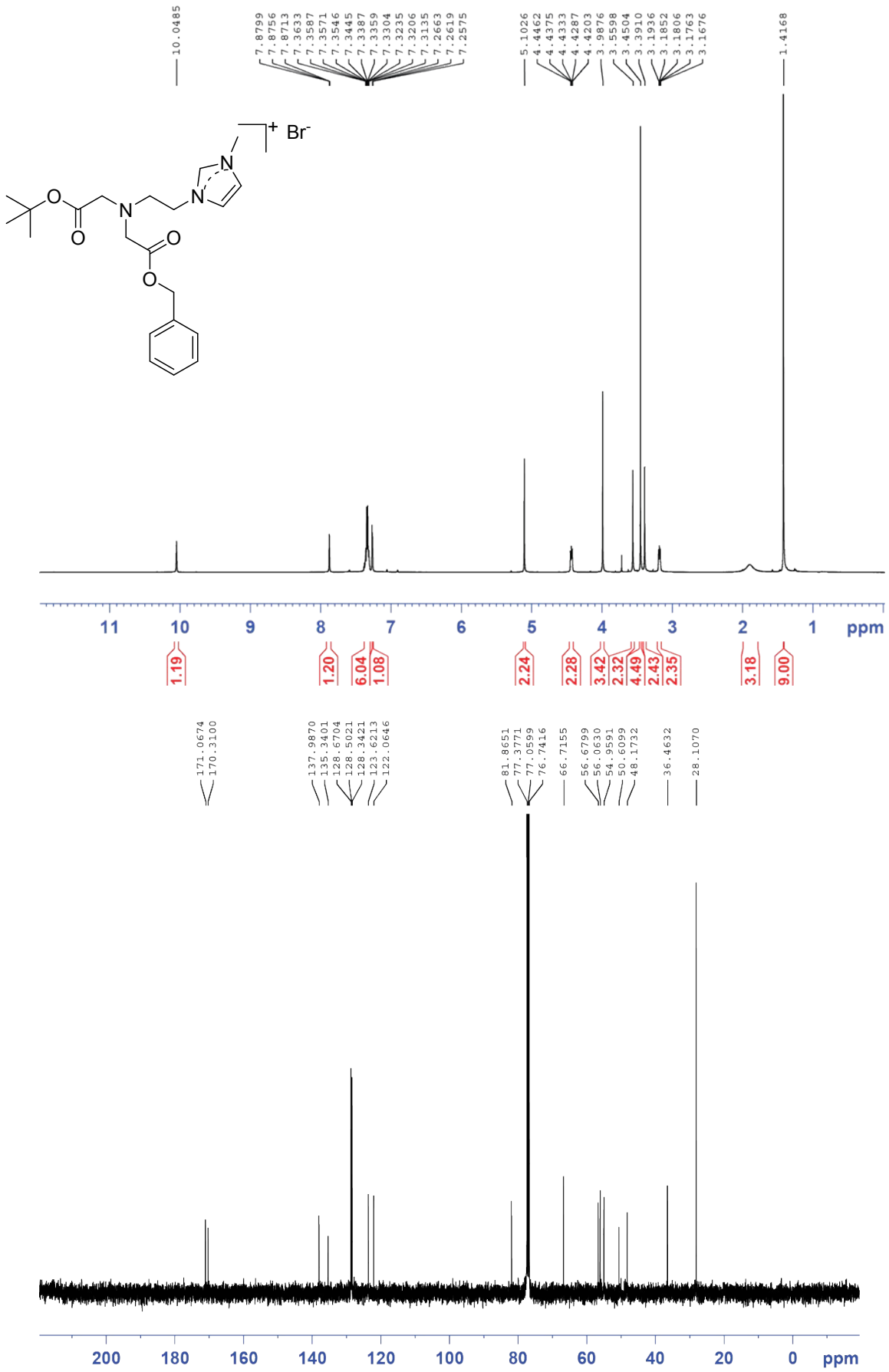

Figure S10. ^{1}H and ^{13}C NMR spectra for compound **6**.

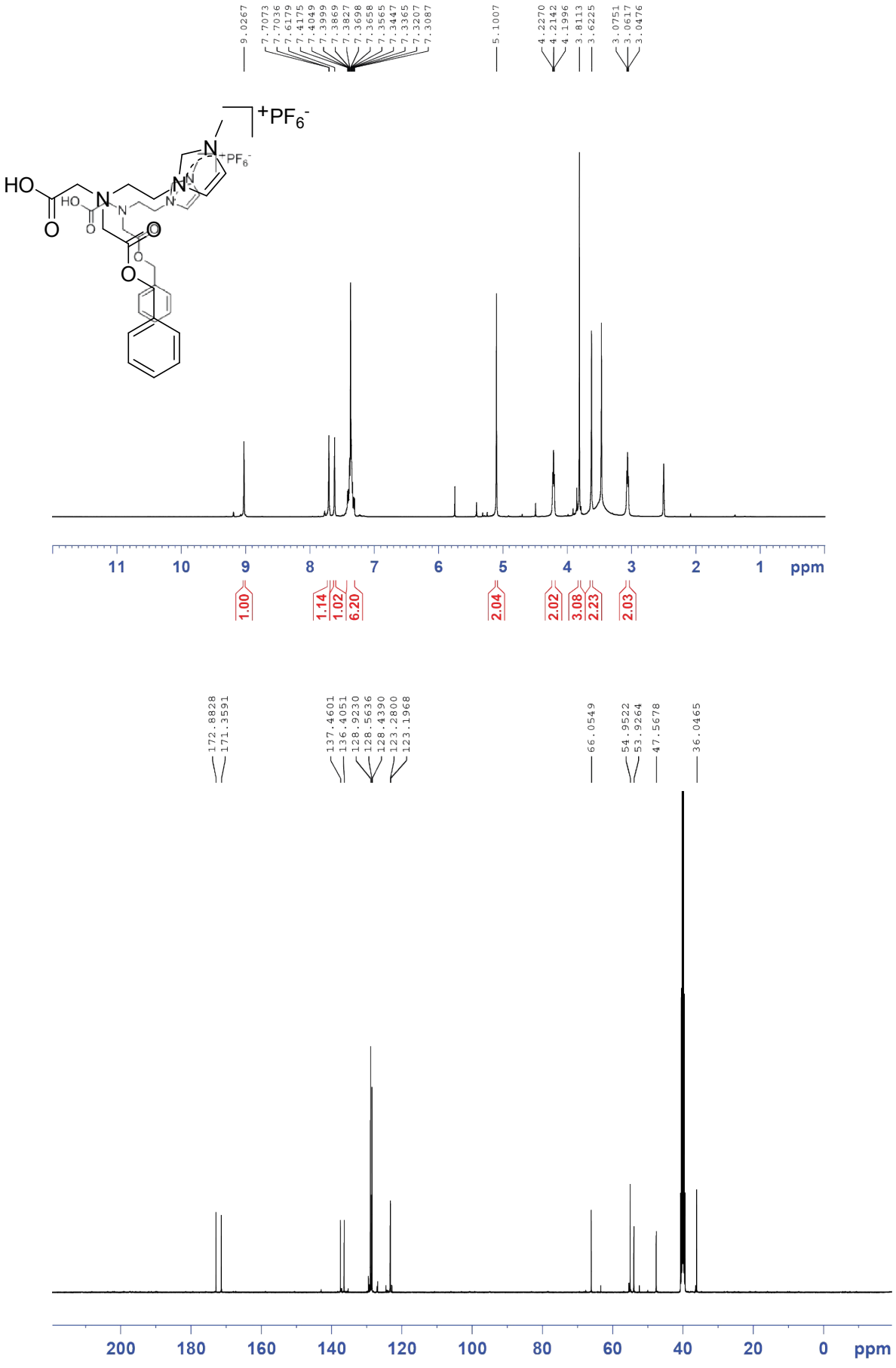

Figure S11. ^{1}H and ^{13}C NMR spectra for compound **7**.

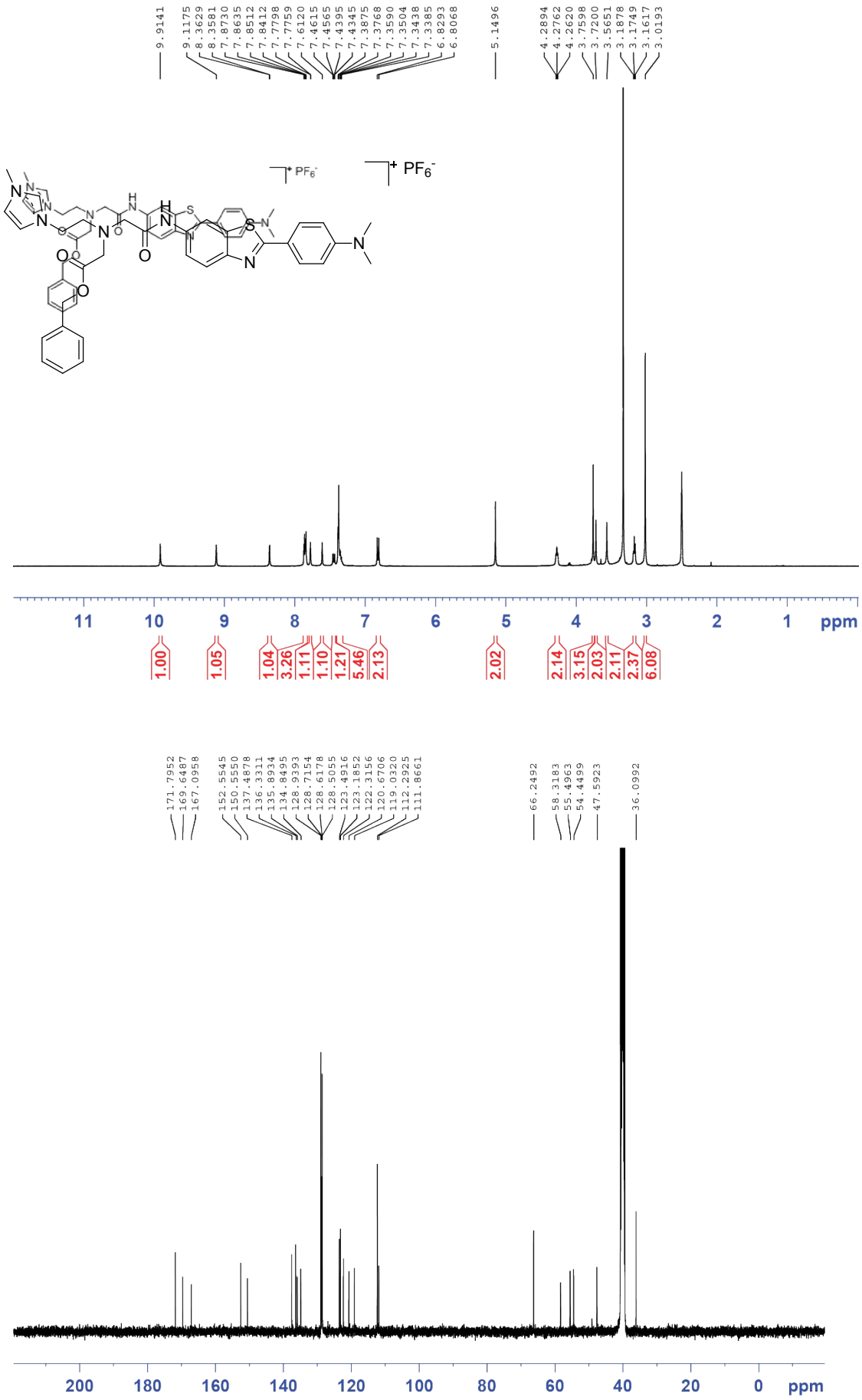

Figure S12. ^{1}H and ^{13}C NMR spectra for compound **8**.

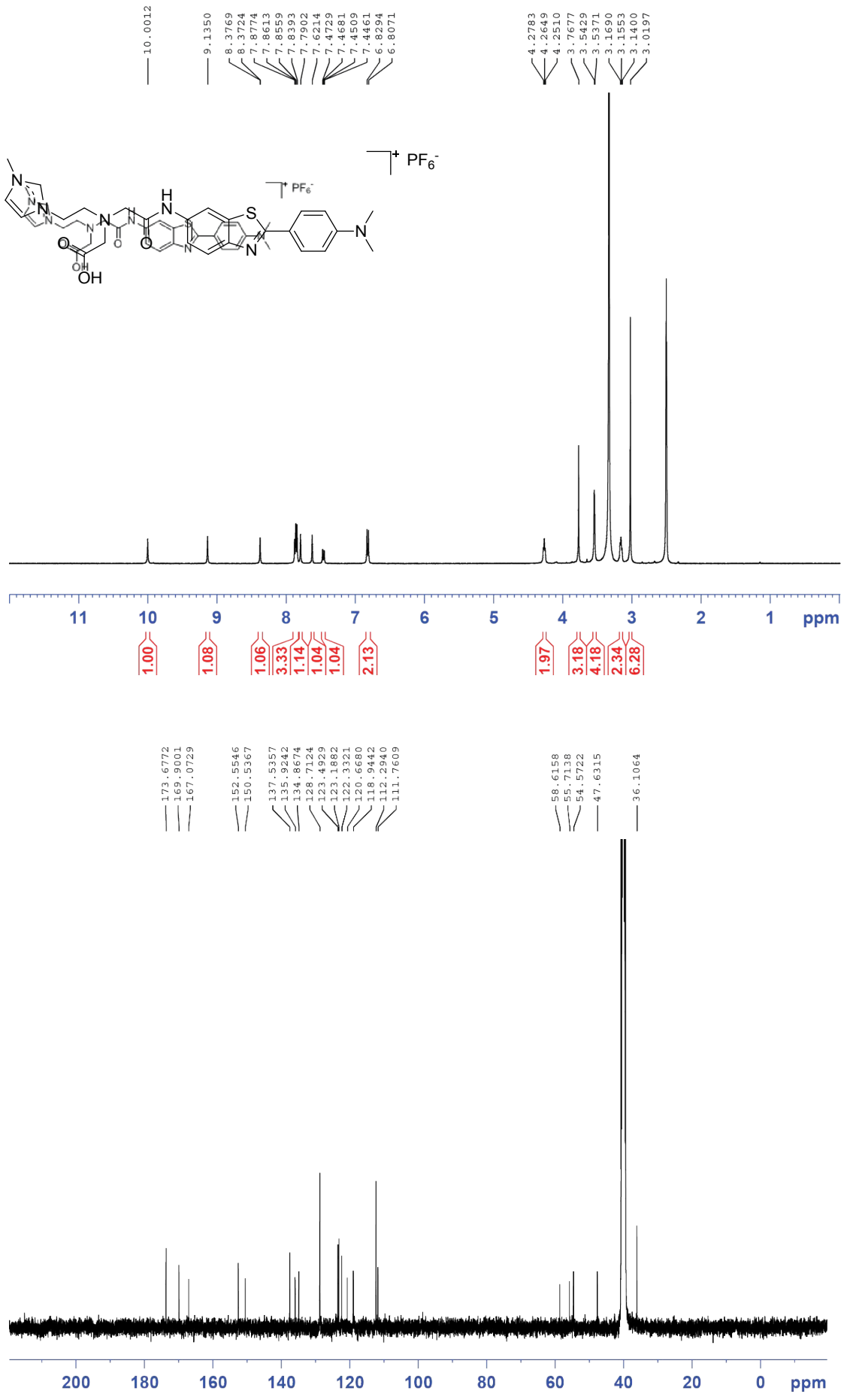

Figure S13. ^{1}H and ^{13}C NMR spectra for compound **9**.

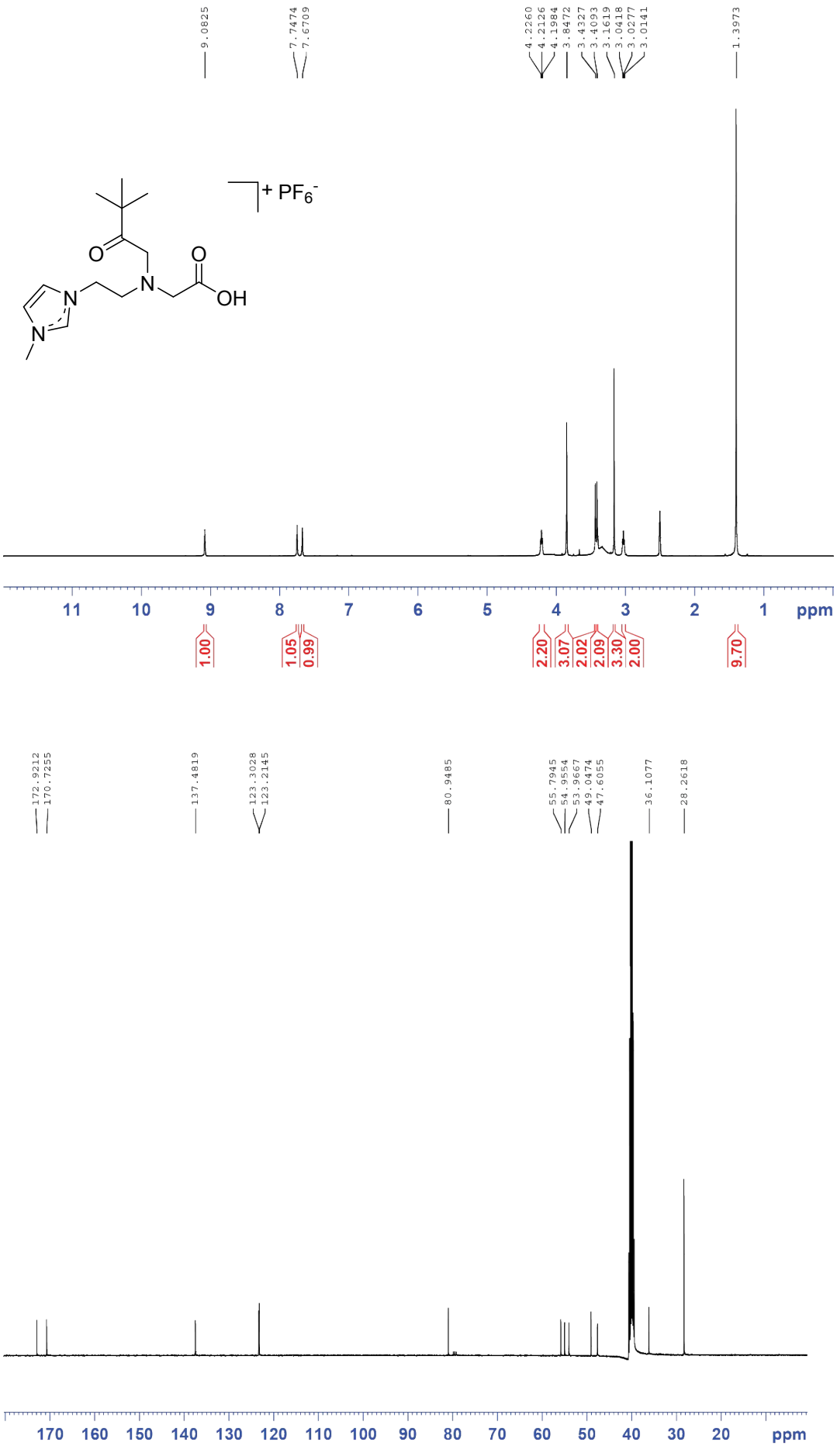

Figure S14. ^{1}H and ^{13}C NMR spectra for compound **10**.

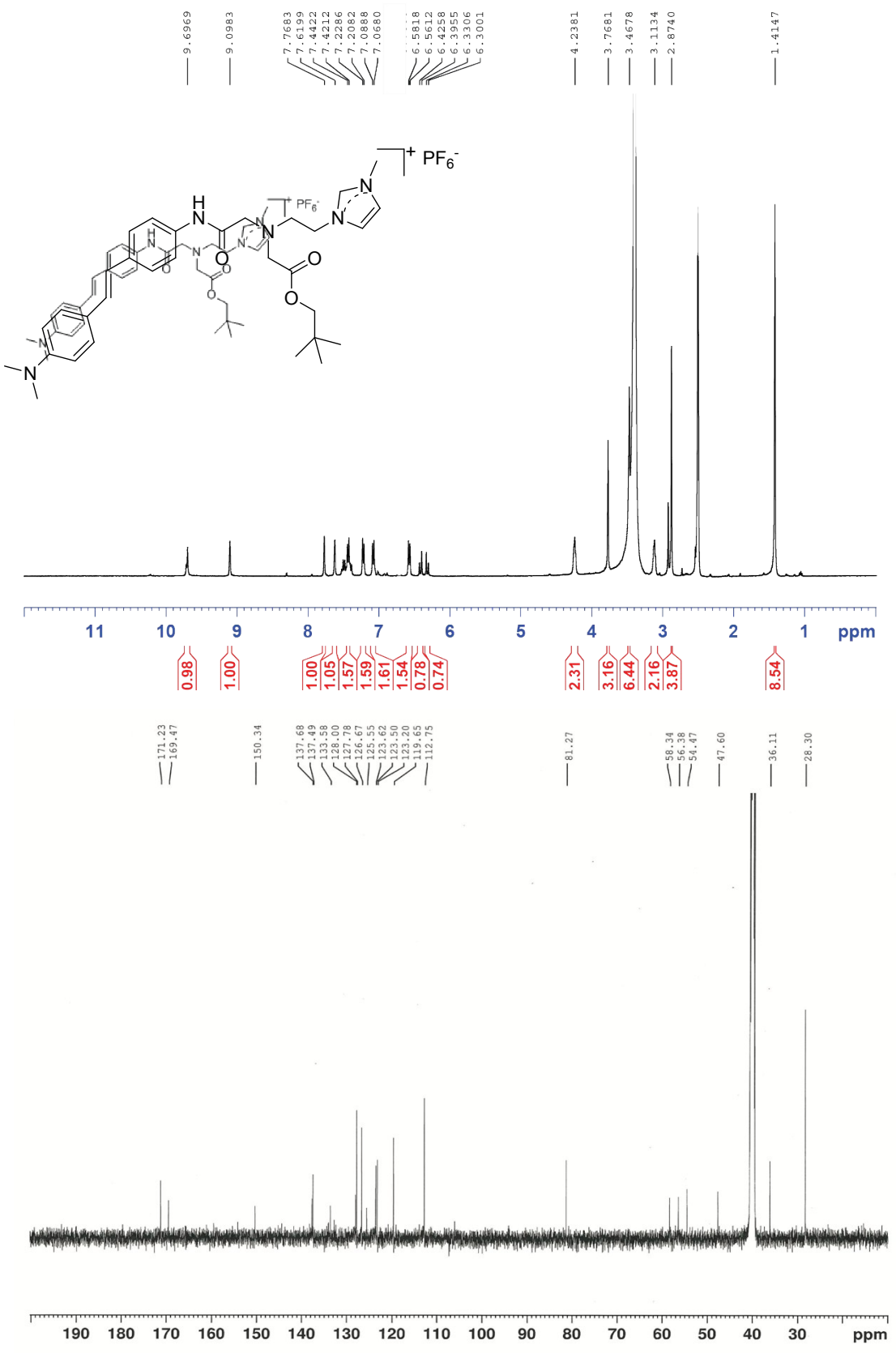

Figure S15. ^{1}H and ^{13}C NMR spectra for compound **11**.

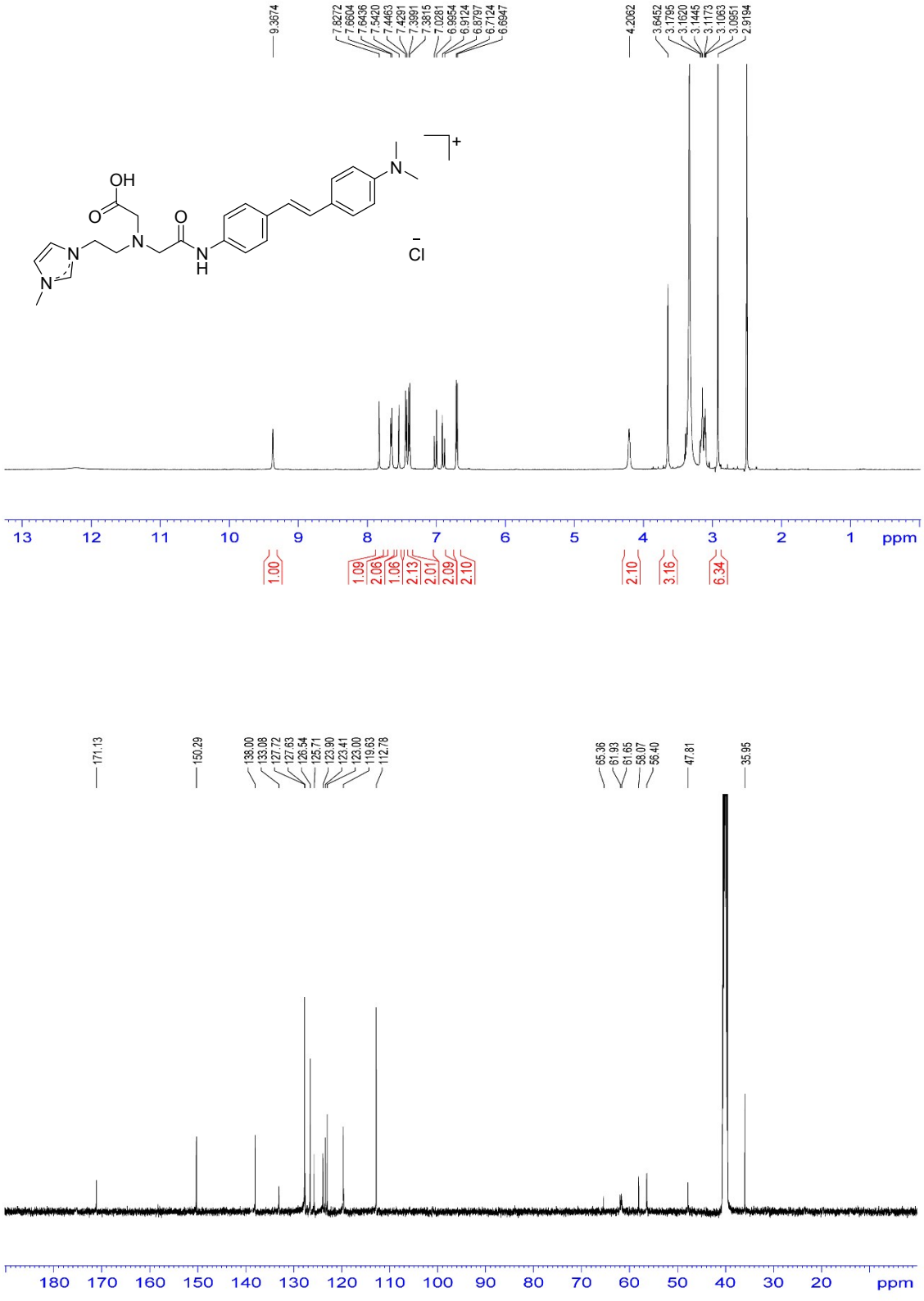

Figure S16. ^{1}H and ^{13}C NMR spectra for compound **12**.

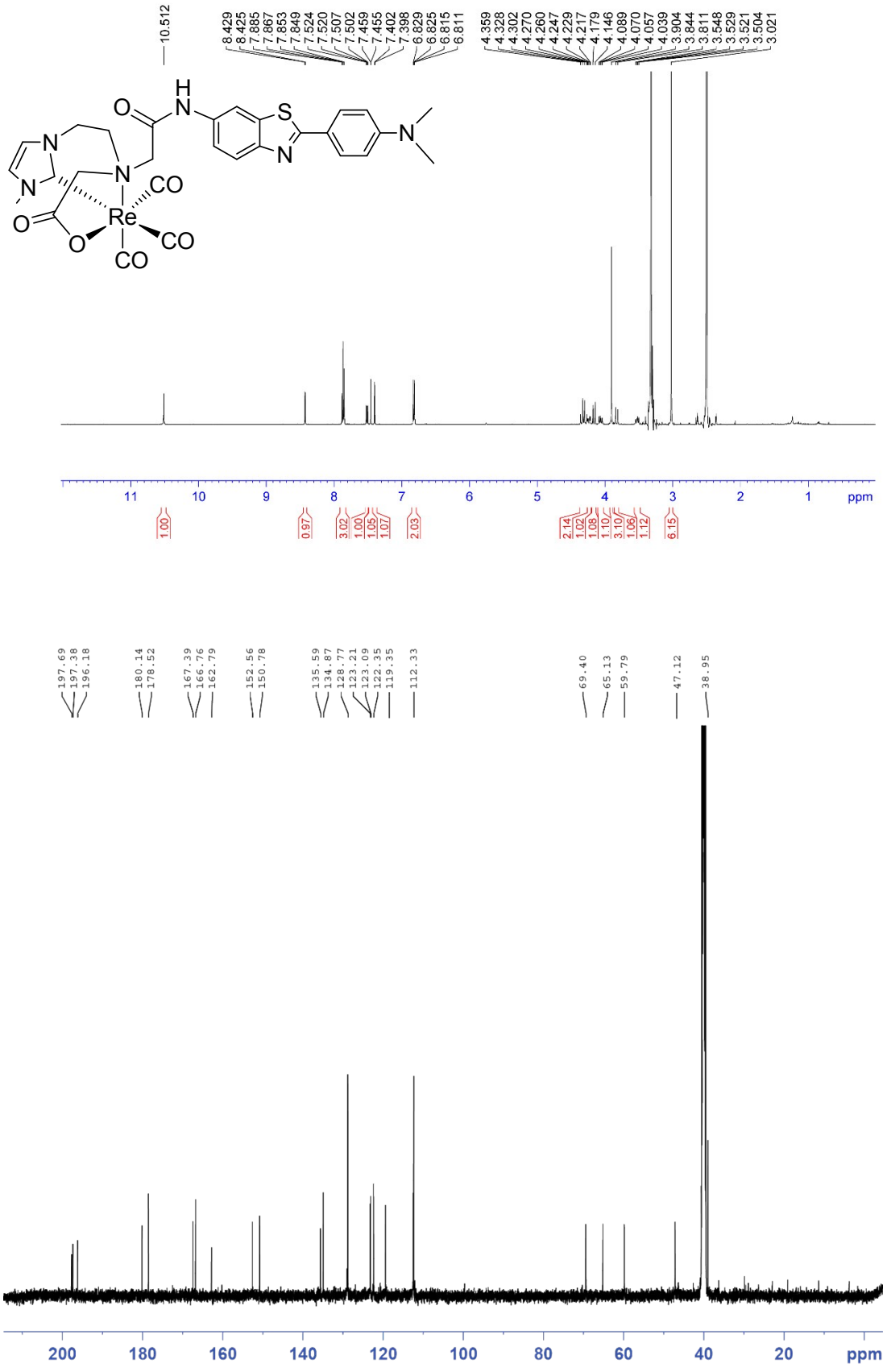

Figure S17. ^{1}H and ^{13}C NMR spectra for complex **13**.

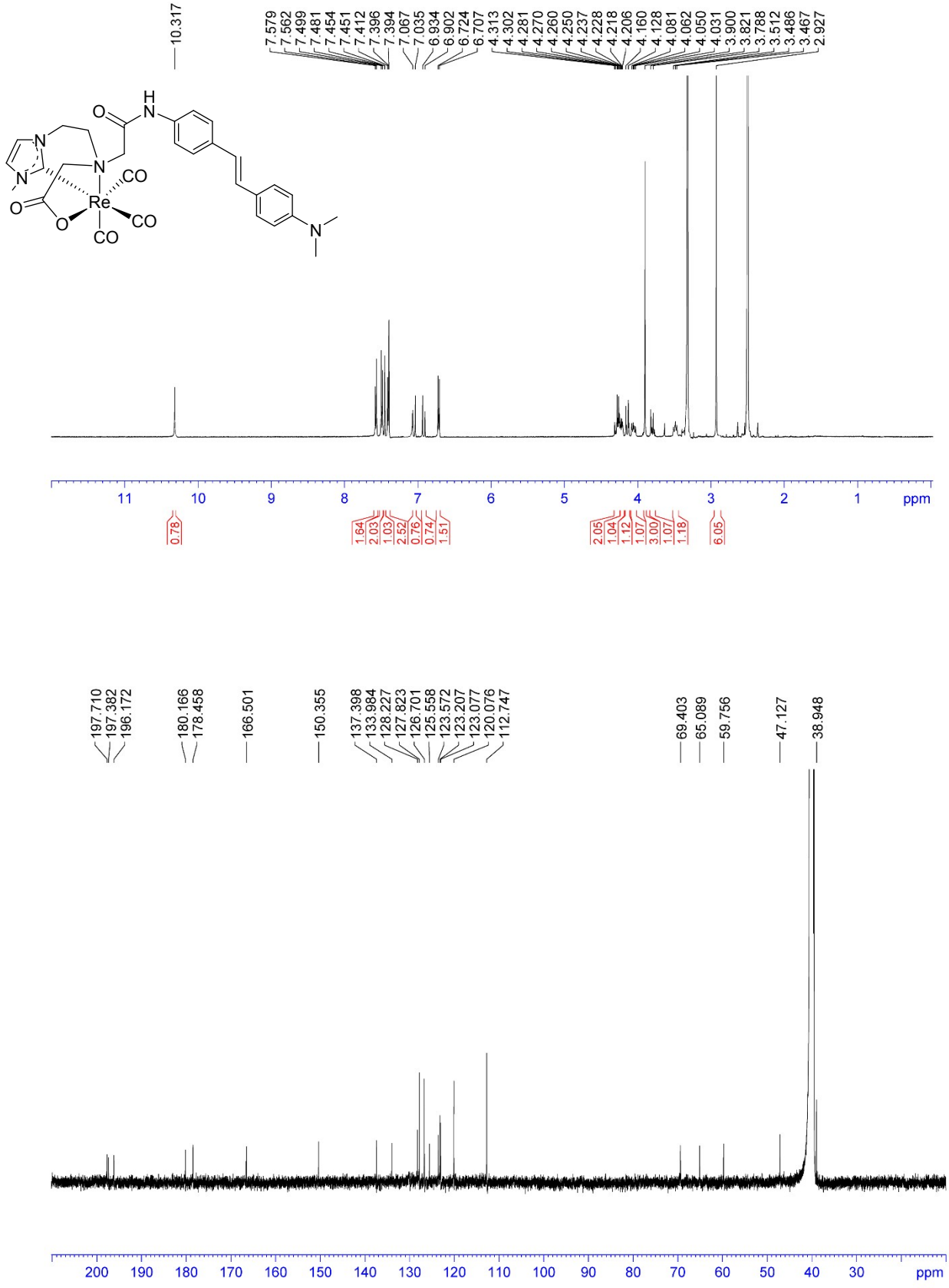

Figure S18. ^{1}H and ^{13}C NMR spectra for complex **14**.

FT-IR Spectra

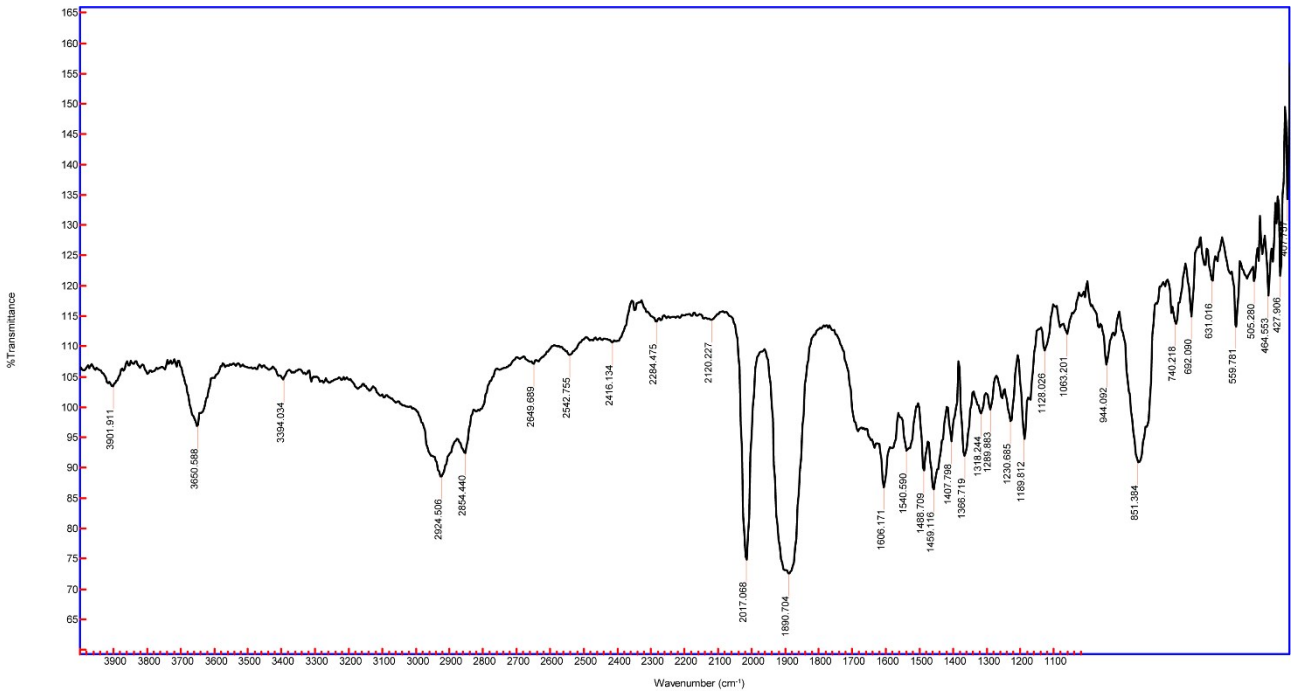

Figure S19. FT-IR spectrum for complex **13**.

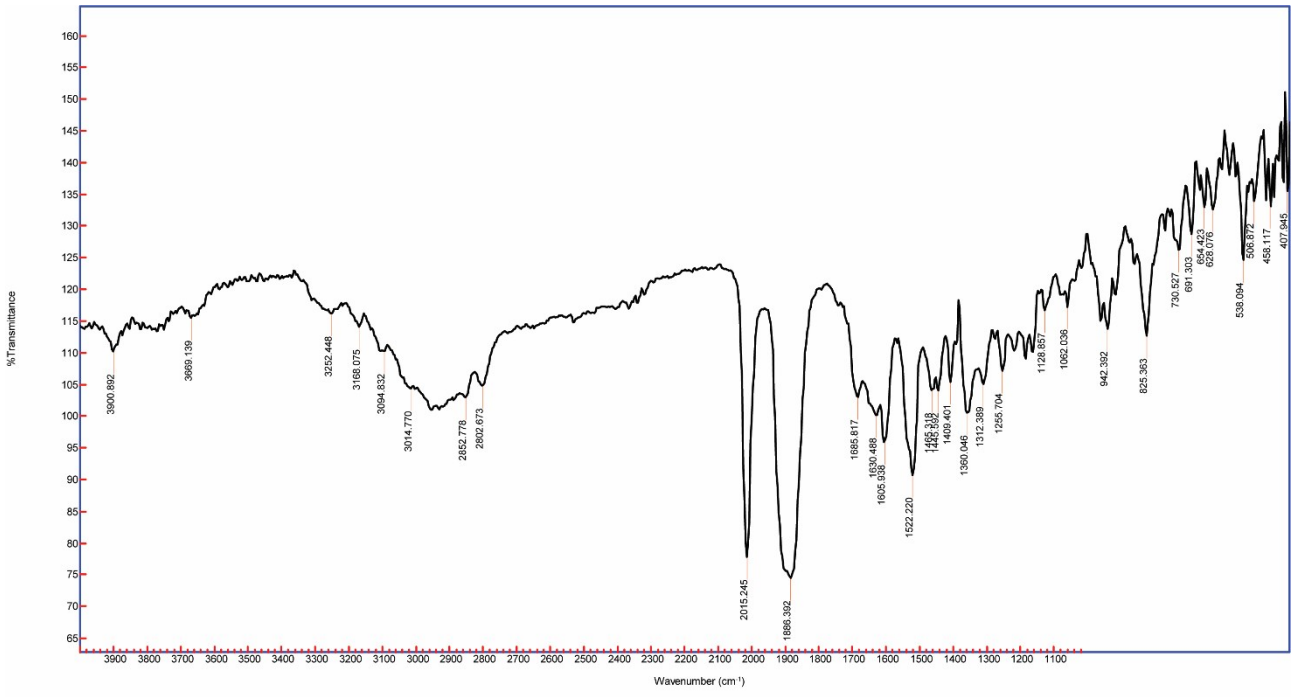

Figure S20. FT-IR spectrum for complex **14**.

X-ray Crystallography

Table S1. X-ray crystallographic data for compounds **13** and **14**

Identification code	**13**	**15**
Empirical formula	$C_{28}H_{27}N_6O_6ReS$	$C_{30}H_{32}Cl_2N_5O_6Re$
Formula weight	761.81	815.7
Temperature/K	150.00(10)	136(5)
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	7.20011(12)	15.6976(11)
b/Å	7.20961(14)	11.3209(5)
c/Å	27.7581(7)	19.2779(10)
α/°	91.5713(19)	90
β/°	93.4633(18)	109.671(7)
γ/°	108.3622(16)	90
Volume/Å^3	1363.42(5)	3226.0(3)
Z	2	4
ρ_{calc}g/cm^3	1.856	1.68
μ/mm^{-1}	9.911	9.31
F(000)	752	1616
Crystal size/mm^3	0.04 × 0.03 × 0.03	0.05 × 0.03 × 0.03
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.588 to 130.172	9.206 to 149.004
Index ranges	-8 ≤ h ≤ 8, -8 ≤ k ≤ 8, -32 ≤ l ≤ 32	-19 ≤ h ≤ 19, -14 ≤ k ≤ 13, -23 ≤ l ≤ 24
Reflections collected	8184	17006
Independent reflections	8184 [Rsigma = 0.0179]	6591 [R_{int} = 0.0409, R_{sigma} = 0.0472]
Data/restraints/parameters	8184/0/383	6591/0/400
Goodness-of-fit on F^2	1.04	1.049
Final R indexes [I>=2σ (I)]	R1 = 0.0452, wR2 = 0.1233	R_1 = 0.0506, wR_2 = 0.1275
Final R indexes [all data]	R1 = 0.0460, wR2 = 0.1246	R_1 = 0.0630, wR_2 = 0.1394
Largest diff. peak/hole / e Å^{-3}	3.11/-0.83	3.35/-1.42

13 Solved in the triclinic space group *P*-1. The structure is twinned, and Crysalis Twin Data Reduction was carried out. Hklf4 and hklf5 files were generated and final refinement on the hklf5 lowered R1 to 4.52%

14 Solved in the monoclinic space group $P2_1/c$. The cifcheck report lists 1 level B alert.

(1) PLAT971_ALERT_2_B Check Calcd Resid. Dens. 0.95A From Re01 3.18 eA-3

It is apparent that this residual electron density is associated with the heavy Re metal centre and no attempts were made to model this density.

Partition coefficient (Log*P*) studies

1-Octanol/water partition coefficients for complexes **13** and **14** were determined using the slow-stirring method as described by Pereiro and co-workers.[5] The 1-octanol and Mili-Q water were saturated prior their use and the starting concentration of complexes **13** and **14** in the 1-octanol phase was 80 μM. Approximately 5 mL of the pre-saturated water and 1-octanol were added to a glass vial containing a magnetic stir bar. The vials were slowly stirred and maintained at 25 ^{0}C for two days. The metal complex concentration in the 1-octanol phase was then analysed using an Agilent Technologies Cary 300 UV-visible spectrophotometer in a quartz cuvette (1 cm). A calibration curve for each complex was prepared at its λ_{max} value (365 nm for **13** and 360 nm for **14**).

Complex **13**

Table S2. Standard samples of **13** with its corresponding absorbance.

Concentration (μM)	Absorbance
1	0.046748
2	0.070164
5	0.227143
10	0.419519
20	1.040334
50	2.499851

Extinction coefficient = 0.0507 μmol^{-1} L cm^{-1}= 50700 mol^{-1} L cm^{-1}

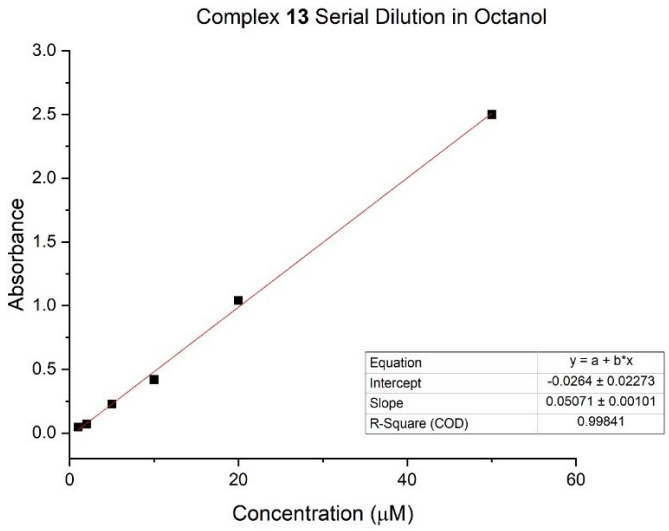

Figure S21. Calibration curve for complex **13** in 1-octanol.

Replicate 1: λ_{max} = 365 nm, A = 2.39

Concentration in octanol = A/εl = 2.39/(50700 × 1) = 4.71 × 10^{-5} M = 47.1 μM

Total concentration of **13** added for partition between water and octanol = 80 μM

Concentration in octanol = 47.1 μM and concentration in water = 32.9 μM

Log P = $\log\left(\frac{[13]octanol}{[13]water}\right) = \log\left(\frac{47.1}{32.9}\right) = 0.156$

Replicate 2: λ_{max} = 365 nm, A = 2.35

Concentration in octanol = A/εl = 2.35/(50700 × 1) = 4.64 × 10^{-5} M = 46.4 μM

Total concentration of **13** added for partition between water and octanol = 80 μM

Concentration in octanol = 46.4 μM and concentration in water = 33.6 μM

Log P = $\log\left(\frac{[13]octanol}{[13]water}\right) = \log\left(\frac{46.4}{33.6}\right) = 0.140$

Replicate 3: λ_{max} = 365 nm, A = 2.37

Concentration in octanol = A/εl = 2.37/(50700 × 1) = 4.67 × 10^{-5} M = 46.7 μM

Total concentration of **13** added for partition between water and octanol = 80 μM

Concentration in octanol = 46.7 μM and concentration in water = 33.3 μM

Log P = $\log\left(\frac{[13]octanol}{[13]water}\right) = \log\left(\frac{46.7}{33.3}\right) = 0.147$

Complex **13**, average log P = 0.15 ± 0.01

Complex **14**

Table S3. Standard samples of **14** with its corresponding absorbance.

Concentration (μM)	Absorbance
1	0.010805
2	0.02689
5	0.08842
10	0.199834
20	0.459253
50	1.223777

Max wavelength = 360 nm

Molar extinction coefficient = 0.0236 μmol^{-1} L cm^{-1}= 23600 mol^{-1} L cm^{-1}

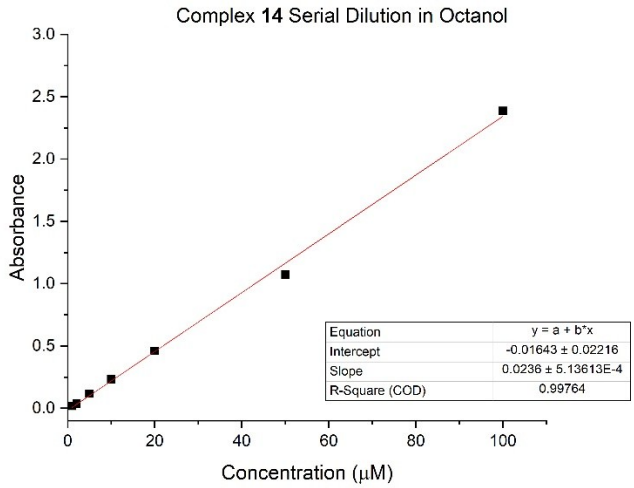

Figure S22. Calibration curve for complex **14** in 1-octanol.

$Replicate\ 1{:}\lambda_{max}$ = 360 nm, A = 1.34

Concentration in octanol = A/εl = 1.34/(23600 × 1) = 5.68 × 10^{-5} M = 56.8 μM

Total concentration of complex **14** added for partition between water and octanol = 80 μM

Concentration in octanol = 56.8 μM and concentration in water = 23.2 μM.

Log P = $\log\left(\frac{[15]octanol}{[15]water}\right) = \log\left(\frac{56.8}{23.2}\right) = 0.389$

$Replicate\ 2{:}\lambda_{max}$ = 360 nm, A = 1.33

Concentration in octanol = A/εl = 1.33/(23600 × 1) = 5.64 × 10^{-5} M = 56.4 μM

Total concentration of complex **14** added for partition between water and octanol = 80 μM

Concentration in octanol = 56.4 μM and concentration in water = 23.6 μM.

Log P = $\log\left(\frac{[15]octanol}{[15]water}\right) = \log\left(\frac{56.4}{23.6}\right) = 0.378$

$Replicate\ 3{:}\lambda_{max}$ = 360 nm, A = 1.34

Concentration in octanol = A/εl = 1.34/(23600 × 1) = 5.68 × 10^{-5} M = 56.8 μM

Total concentration of complex **14** added for partition between water and octanol = 80 μM

Concentration in octanol = 56.8 μM and concentration in water = 23.2 μM.

Log P = $\log\left(\frac{[15]octanol}{[15]water}\right) = \log\left(\frac{56.8}{23.2}\right) = 0.389$

Complex **14**, average log P log P = 0.39 ± 0.01

Photophysical studies

Table S4. UV-visible absorption and fluorescence spectroscopic data for compounds: benzothiazole ligand, Re(I)-benzothiazole, stilbene ligand and Re(I)-stilbene.

Compound (Solvent)	λ_{max}/nm (ε/$M^{-1}cm^{-1}$)	Photoluminescence λ_{max}/nm
9[a]	365 (41500)	424
12[a]	357 (34800)	454
13[b]	369 (27900)	417
14[b]	357 (20400)	457

[a]1 μM in acetonitrile, [b]10 μM in acetonitrile

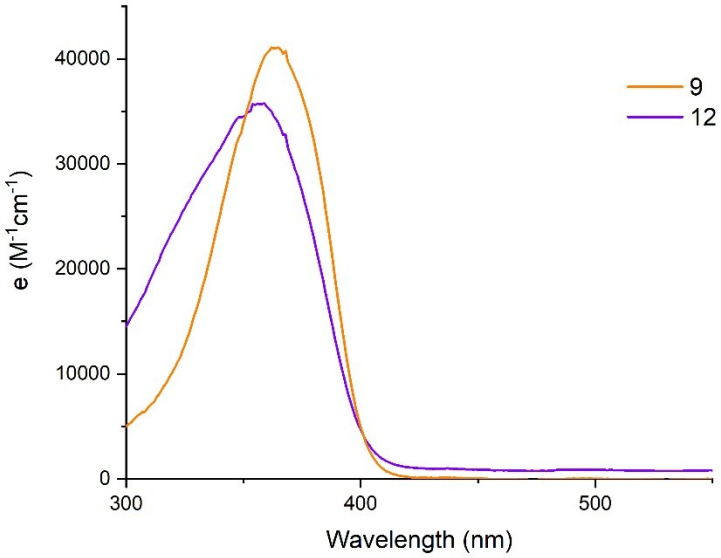

Figure S23. UV-vis spectra of **9** and **12** (1 μM in acetonitrile).

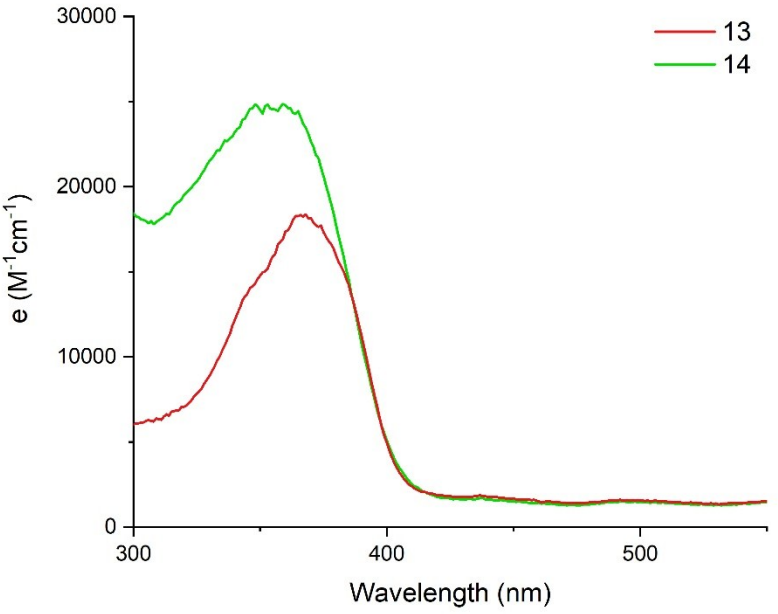

Figure S24. UV-vis spectra of **13** and **14** (10 µM in acetonitrile).

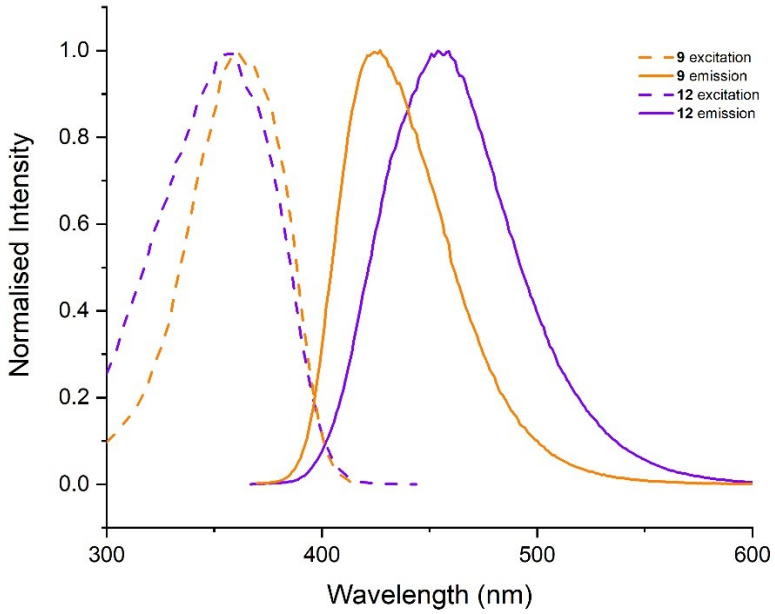

Figure S25. Excitation and emission spectra for compounds **9** and **12** (1 µM in acetonitrile).

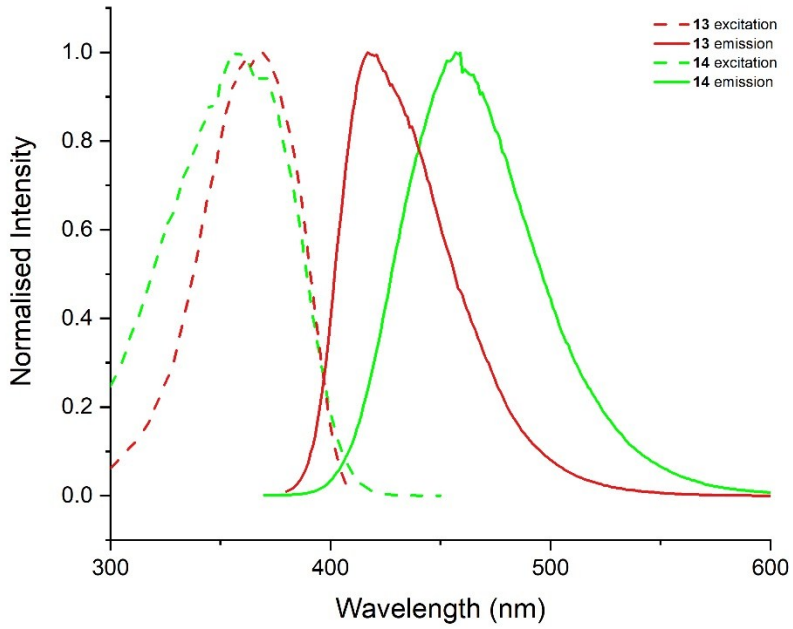

Figure S26. Excitation and emission spectra for compounds **13** and **14** (10 μM in acetonitrile).

Reference

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