Supporting Information for

Synthesis of imidazole-fused pentacyclic pyrrolo[3,4-*c*]coumarins *via* base-promoted rearrangement of coumarin-substituted N-heterocyclic carbene precursors

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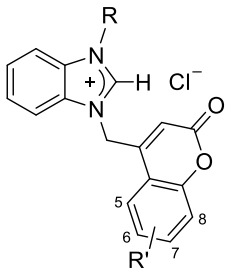
1. General Information

The reagents and solvents were purchased from commercial suppliers and used as received. For preparation of micro-column, Sigma-Aldrich silica gel sorbent (70-230 mesh particle size, pore size 60) was used as a stationary phase. Melting points were determined in open capillary tube and were uncorrected, using a Gallenkamp MPD350.BM3.5 apparatus. C, H and N analyses were carried out using a LECO CHNS-932 elemental analyzer. Attenuated total reflection infrared spectra (ATR-IR) were recorded using a Perkin Elmer Two Spectrum spectrophotometer. High resolution mass spectra (HRMS) were recorded on an Agilent Technologies 6200 Accurate-Mass Q-TOF-LC/MS. NMR spectra were recorded using Bruker Ascend^{TM} 400 Avance III HD operating at 400 MHz (^{1}H) and 100 MHz (^{13}C) and Bruker AC300P FT spectrometer operating at 300 MHz (^{1}H) and 75 MHz (^{13}C). Chemical shifts (expressed in part per million) are referenced to residual solvent peaks. Coupling constants, *J*, are given in Hz.

2. Synthesis of benzimidazolium chlorides

Some of the benzimidazolium salts and an imidazolium salt used in this study had been reported in our previous studies; **1a**, **1e**, **1l** and **1m** in [1], **1g,h** in [2], **1k** in [3]. Also, **1n** has been prepared according to literature [4]. The benzimidazolium chlorides, **1b**, **1c**, **1d**, **1f**, and **1j** have been prepared for the first time in this study, according to procedure described in our previous study [1].



1-(*n*-Butyl)-3-((5,7-dimethyl-*2H*-chromene-4-yl)methyl)benzimidazolium chloride, 1b. White solid, 1.82 g (92%). Melting point: 236-237 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.15 (s, 1H, –NC<u>H</u>N–), 8.21 (m, 1H, ArH), 8.10 (m, 1H, ArH), 7.72 (m, 2H, ArH), 7.18 (s, 1H, ArH), 7.14 (m, 1H, ArH), 6.47 (s, 2H, –NCH_2coumarin), 5.53 (s, 1H, –CH=C–), 4.58 (t, 2H, –NC<u>H_2</u>CH_2–, *J* = 7.2), 2.83 (s, 3H, ArCH_3), 2.40 (s, 3H, ArCH_3), 1.96 (quin, 2H, –NCH_2C<u>H_2</u>–, *J* = 7.3), 1.40 (sex, 2H, –C<u>H_2</u>CH_3, *J* = 7.4), 0.95 (t, 3H, –CH_2C<u>H_3</u>, *J* = 7.3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 159.0, 154.6, 151.3, 143.4, 142.6, 136.6, 131.4, 131.1, 129.9, 126.9, 126.8, 115.5, 114.5, 114.1, 114.0, 110.7, 49.7, 46.7, 30.3, 23.8, 20.6, 19.1, 13.4.

1-(4-Methylbenzyl)-3-((5,7-dimethyl-*2H*-chromene-4-yl)methyl)benzimidazolium chloride, 1c. White solid, 1.84 g (83%). Melting point: 180-183 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.99 (s, 1H, –NCHN–), 8.07 (m, 2H, ArH), 7.69 (m, 2H, ArH), 7.48 (m, 2H, ArH), 7.25 (m, 2H, ArH), 7.18 (s, 1H, ArH), 7.14 (s, 1H, ArH), 6.40 (s, 2H, –NCH_2coumarin), 5.79 (s, 2H, –NC<u>H_2</u>Ph-4-CH_3), 5.55 (s, 1H, –CH=C–), 2.80 (s, 3H, ArCH_3), 2.40 (s, 3H, ArCH_3), 2.31 (s, 3H, ArCH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 159.0, 154.6, 151.2, 143.5, 142.7, 138.3, 136.6, 131.3, 131.1, 130.6, 129.9, 129.5, 128.6, 127.0, 126.9, 115.6, 114.5, 114.2, 114.1, 110.7, 50.1, 49.8, 23.7, 20.7, 20.6.

1-(4-Methylbenzyl)-3-((6,7-dimethyl-*2H*-chromene-4-yl)methyl)benzimidazolium chloride, 1d. White solid, 1.93 g (87%). Melting point: 244-246 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.18 (s, 1H, –NCHN–), 8.04 (m, 2H, ArH), 7.72-7.65 (m, 3H, ArH), 7.48 (m, 2H, ArH), 7.32 (s, 1H, ArH), 7.24 (m, 2H, ArH), 6.21 (s, 2H, –NCH_2coumarin), 5.96 (s, 1H, –CH=C–), 5.78 (s, 2H, –NC<u>H_2</u>Ph-4-CH_3), 2.36 (s,

3H, $ArCH_3$), 2.33 (s, 3H, $ArCH_3$), 2.30 (s, 3H, $ArCH_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 159.6, 151.4, 148.5, 143.5, 142.7, 138.3, 133.2, 131.4, 131.1, 130.6, 129.5, 128.6, 127.1, 126.0, 124.5, 117.2, 114.5, 114.2, 113.9,111.9, 50.1, 46.5, 20.7, 19.7, 18.9.

1-(Benzyl)-3-((5,7-dimethyl-*2H*-chromene-4-yl)methyl)benzimidazolium chloride, 1f. White solid, 1.85 g (86%). Melting point: 234-236 °C. ^1H NMR (300 MHz, DMSO-d_6): δ 10.12 (s, 1H, –NCHN–), 8.09 (m, 2H, ArH), 7.69 (m, 2H, ArH), 7.61-7.58 (m, 2H, ArH), 7.48-7.40 (m, 3H, ArH), 7.18 (m, 1H, ArH), 7.14 (m, 1H, ArH), 6.44 (s, 2H, $–NCH_2$coumarin), 5.87 (s, 2H, $–NCH_2Ph$), 5.57 (s, 1H, –CH=C–), 2.82 (s, 3H, $ArCH_3$), 2.40 (s, 3H, $ArCH_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 159.0, 154.6, 151.2, 143.7, 142.7, 136.6, 133.7, 131.4, 131.2, 129.9, 129.0, 128.8, 128.5, 127.0, 126.9, 115.6, 114.5, 114.2, 114.1, 110.8, 50.2, 49.8, 23.7, 20.6.

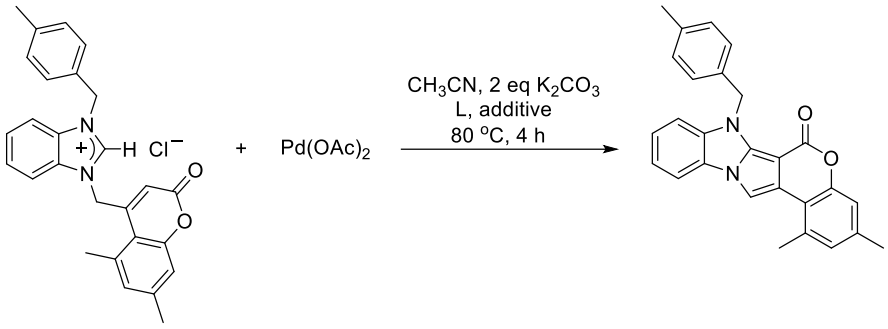
1-((2-methoxy)ethyl)-3-((5,7-dimethyl-*2H*-chromene-4-yl)methyl)benzimidazolium chloride, 1j. White solid, 1.31 g (66%). Melting point: 150-154 °C. ^1H NMR (300 MHz, DMSO-d_6): δ 9.96 (s, 1H, –NC<u>H</u>N–), 8.21 (m, 1H, ArH), 8.10 (m, 1H, ArH), 7.73 (m, 2H, ArH), 7.18 (s, 1H, ArH), 7.15 (s, 1H, ArH), 6.47 (s, 2H, $–NCH_2$coumarin), 5.43 (s, 1H, –CH=C–), 4.80 (t, 2H, $–NCH_2C\underline{H}_2O–$, J = 4.8), 3.85 (t, 2H, $–NC\underline{H}_2CH_2O–$, J = 4.8), 3.30 (s, 3H, $–OCH_3$), 2.83 (s, 3H, $ArCH_3$), 2.40 (s, 3H, $ArCH_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 159.0, 154.6, 151.4, 143.7, 142.7, 136.6, 131.4, 130.9, 129.9, 126.9, 126.8, 115.6, 114.5, 114.2, 114.1, 110.5, 68.8, 58.2, 49.6, 46.9, 23.8, 20.6.

3. Optimization experiments

An acetonitrile mixture of 0.1 mmol of corresponding benzimidazolium salt, and palladium source, base, ligand and oxidant specified in Tables 1-5 was heated at the temperatures given in Tables 1-5 for the specified reaction time. After, the solvent and volatile components were removed under vacuum, the crude product was dissolved in 5 mL of methylene chloride and filtered through Celite. From this point on, we used two different procedures to determine isolated and NMR yield. For isolated yield, the clean methylene chloride solution concentrated ca. 1 mL, and the solution was passed through a micro silica gel column, the methylene chloride was removed under vacuum and the crude product was washed with *n*-hexane (3x3 mL) and dried under vacuum. For NMR yield, methylene chloride was removed under vacuum and the crude product was dissolved in 0.5 mL of $CDCl_3$, and the yield was determined by ^1H NMR spectrum.

3.1. Determination of ligand and additive

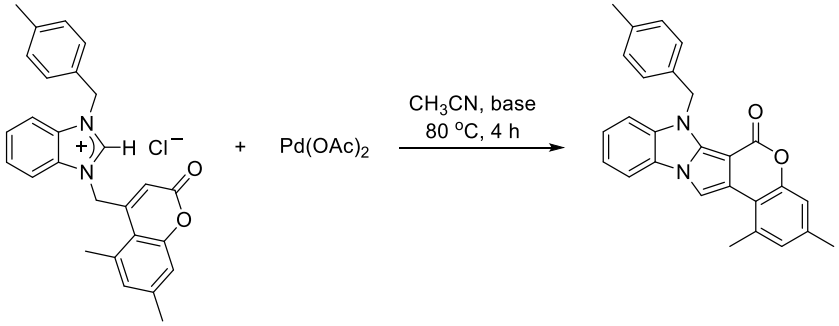
Table S1. Determination of ligand and additive.



No	Ligand	Additive	Isolated yield (%)
1	Pyridine (2 eq)	KCl (2 eq)	61
2	Pyridine (2 eq)	-	63
3	-	KCl (2 eq)	80
4	-	-	**83**
5	PPh_3 (2 eq)	-	60
6	*N*-Methylimidazole (2 eq)	-	59
7	NEt_3 (2 eq)	-	

3.2. Determination of base

Table S2. Determination of base.

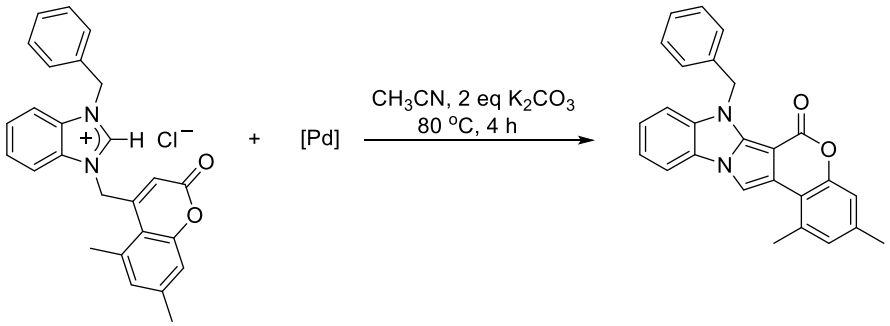


No	Base	Equivalent	Isolated yield (%)
1	**K_2CO_3**	**2**	**83**
2	Na_2CO_3	2	77
3	KOH	2	74
4	KOAc	2	72
5	K_2CO_3	1	52
6	K_2CO_3	3	80
7	-	-	<10[a]

[a]Determined by ^{1}H NMR.

3.3. Determination of palladium source

Table S3. Determination of palladium source.

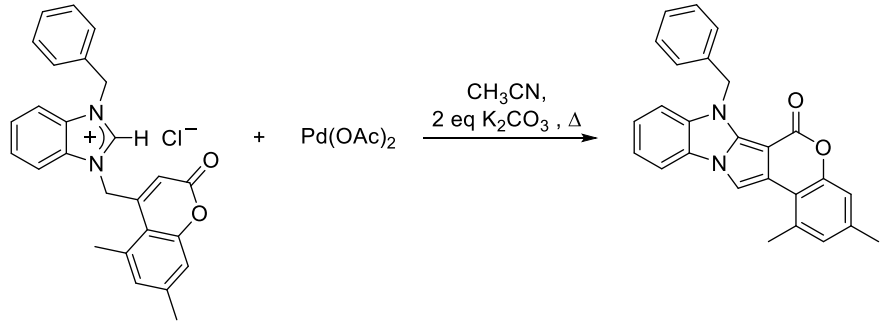


No	[Pd]	Isolated yield (%)
1	**$Pd(OAc)_2$**	**85**
2	$PdCl_2$	<20[a]
3	$PdCl_2(CH_3CN)_2$	<20[a]

[a]Determined by ^1H NMR.

3.4. Determination of optimum temperature and reaction time

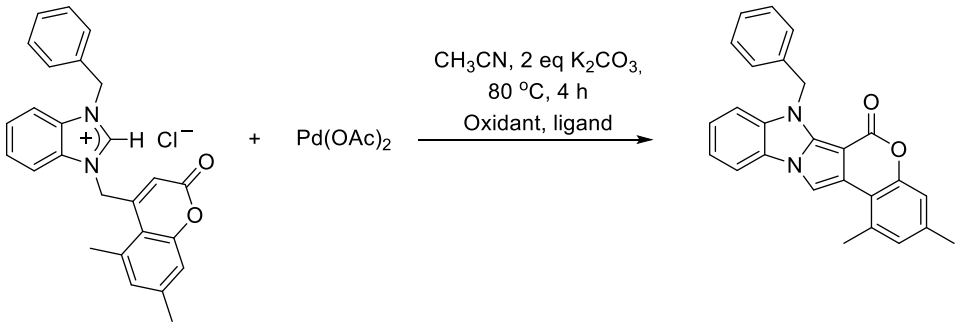
Table S4. Determination of optimum temperature and reaction time.



No	Temperature (°C)	Time (hour)	Isolated yield (%)
1	50	2	68
2	50	4	71
3	80	1	7
4	80	2	77
5	**80**	**4**	**85**
6	80	24	83

3.5. Catalytic reactions

Table S5. Catalytic reactions.



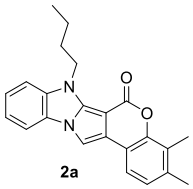
No	% $Pd(OAc)_2$	Oxidant	Ligand	Isolated yield (%)
1	10	-	3 eq Pyridine	<20[b]
2	10	-	-	<30[b]
3	20	-	-	43
4	50	-	-	66
5	10	1 eq MnO_2	-	<30[b]
6	10	1 eq MnO_2	3 eq Pyridine	<20[b]
7	10	-	-	<30[b,c]
8	10	1 eq BQ[a]	-	<10[b]
9	10	1 eq 2,3-$(Cl)_2$-4,5-$(CH_3CN)_2$-BQ[a]	-	<10[b]
10	10	1 eq Benzoyl peroxide	-	<10[b]
11	50	1 eq MnO_2	-	70
12	10	-	-	<30[b,d]

[a]BQ = Benzoquinone
[b]Determined by ^1H NMR
[c]Reaction time = 24 hours
[d]KOA_C was used instead of K_2CO_3

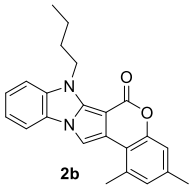
4. Synthesis and characterization data of fused chromeno-pyrrolo-(benz)imidazole (CP(B)I) derivatives (2)

An acetonitrile mixture (4 mL) of 0.2 mmol of corresponding (benz)imidazolium chloride, 0.2 mmol of palladium acetate (45 mg) and 0.4 mmol (55 mg) of potassium carbonate was stirred at 80 °C for 4 hours. After this period of time, the mixture was allowed to cool to ambient temperature, the solvent was removed under vacuum. The crude product was dissolved with methylene chloride and filtered through Celite. The clean solution was concentrated to ca. 1 mL and passed through a micro silica gel column. The methylene chloride was removed under vacuum, the product was washed with *n*-hexane (3x5 mL) and dried under vacuum.

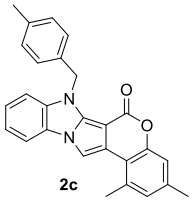
7,8-Me$_2$CPBI^{Bu} (2a). White solid, 74% (53 mg). Mp: 185-188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, 1H, ArH, *J* = 7.8), 7.43 (d, 1H, ArH, *J* = 7.8), 7.35 (m, 2H, ArH), 7.32 (s, 1H, –N–CH=C–), 7.25 (t, 1H, ArH, *J* = 7.3), 6.97 (d, 1H, ArH, *J* = 7.8), 4.77 (t, 2H, –NC$\underline{H}_2$CH$_2$–, *J* = 7.3), 2.35 (s, 3H, ArCH$_3$), 2.32 (s, 3H, ArCH$_3$), 1.90 (quin, 2H, –NCH$_2$C$\underline{H}_2$–, *J* = 7.4), 1.46 (sex, 2H, –C$\underline{H}_2$CH$_3$, *J* = 7.6), 0.96 (t, 3H, –CH$_2$C$\underline{H}_3$, *J* = 7.3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 149.8, 140.5, 136.7, 135.8, 125.51, 125.50, 124.9, 124.8, 123.8, 120.7, 119.5, 114.4, 111.1, 110.1, 95.4, 83.0, 45.1, 31.9, 20.2, 19.9, 13.9, 12.1. HRMS (ESI): Exact mass calculated for $C_{23}H_{23}N_2O_2$ $[(M+H)]^+$, *m/z* 359.1760; found *m/z* 359.1753.



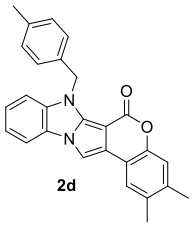
5,7-Me$_2$CPBI^{Bu} (2b). White solid, 64% (46 mg). Mp: 176-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, 1H, ArH, *J* = 7.8), 7.27-7.13 (m, 4H, 3 ArH and –N–CH=C–), 6.79 (s, 1H, ArH), 6.71 (s, 1H, ArH), 4.65 (t, 2H, –NC$\underline{H}_2$CH$_2$–, *J* = 7.1), 2.45 (s, 3H, ArCH$_3$), 2.20 (s, 3H, ArCH$_3$), 1.76 (quin, 2H, –NCH$_2$C$\underline{H}_2$–, *J* = 7.3), 1.31 (sex, 2H, –C$\underline{H}_2$CH$_3$, *J* = 7.3), 0.83 (t, 3H, –CH$_2$C$\underline{H}_3$, *J* = 7.3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 152.2, 140.1, 137.1, 135.9, 134.7, 126.7, 125.4, 124.4, 123.9, 120.8, 115.4, 113.7, 111.1, 110.1, 98.5, 83.4, 45.0, 31.8, 22.6, 21.1, 19.9, 13.9. HRMS (ESI): Exact mass calculated for $C_{23}H_{23}N_2O_2$ $[(M+H)]^+$, *m/z* 359.1760; found *m/z* 359.1759.



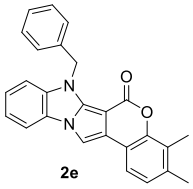
5,7-Me$_2$CPBI$^{Bz\text{-}4\text{-}Me}$ (2c). Gray solid, 83% (67 mg). Mp: 252-255 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, 1H, ArH, *J* = 7.8), 7.38-7.23 (m, 6H, 5 ArH and 1 –N–CH=C–), 7.07-7.05 (m, 2H, ArH), 7.00 (s, 1H, ArH), 6.89 (s, 1H, ArH), 6.06 (s, 2H, –NCH$_2$Ph), 2.62 (s, 3H, ArCH$_3$), 2.37 (s, 3H, ArCH$_3$), 2.26 (s, 3H, ArCH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 152.3, 140.2, 137.5, 137.4, 136.0, 134.8, 133.8, 129.4, 127.8, 126.9, 125.8, 124.6, 124.1, 121.2, 115.6, 113.8, 111.2, 98.8, 83.9, 48.5, 22.7, 21.2, 21.1. HRMS (ESI): Exact mass calculated for $C_{27}H_{23}N_2O_2$ $[(M+H)]^+$, *m/z* 407.1760; found *m/z* 407.1756.



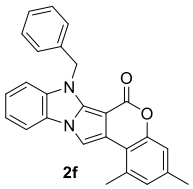
6,7-Me$_2$CPBI$^{Bz\text{-}4\text{-}Me}$ (2d). Gray solid, 73% (59 mg). Mp: 229-232 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 1H, ArH, *J* = 7.8), 7.49 (s, 1H, ArH), 7.40-7.24 (m, 6H, 5 ArH and 1 –N–CH=C–), 7.10-7.08 (m, 3H, ArH), 6.05 (s, 2H, –NCH$_2$Ph), 2.33 (s, 6H, ArCH$_3$), 2.28 (s, 3H, ArCH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 149.9, 140.6, 137.5, 137.0, 135.8, 133.7, 132.1, 129.4, 127.8, 125.9, 125.1, 124.0, 123.3, 121.1, 118.1, 114.4, 111.15, 111.13, 95.4, 83.7, 48.6, 21.1, 20.0, 19.3. HRMS (ESI): Exact mass calculated for $C_{27}H_{23}N_2O_2$ $[(M+H)]^+$, *m/z* 407.1760; found *m/z* 407.1757.



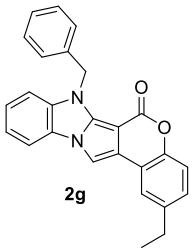
7,8-Me$_2$CPBI^{Bz} (2e). White solid, 61% (48 mg). Mp: 239-240 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, 1H, ArH, *J* = 7.7), 7.49 (d, 1H, ArH, *J* = 7.5), 7.45-7.23 (m, 9H, 8 ArH and 1 –N–CH=C–), 7.03 (d, 1H, ArH, *J* = 7.5), 6.09 (s, 2H, –NCH$_2$Ph), 2.41 (s, 3H, ArCH$_3$), 2.37 (s, 3H, ArCH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 149.8, 140.52, 140.50, 136.9, 136.8, 135.9, 128.7, 127.8, 125.9, 125.6, 125.1, 125.0, 124.0, 121.2, 119.5, 114.4, 111.2, 111.0, 95.6, 83.5, 48.8, 20.2, 12.2. HRMS (ESI): Exact mass calculated for $C_{26}H_{21}N_2O_2$ $[(M+H)]^+$, *m/z* 393.1603; found *m/z* 393.1595.



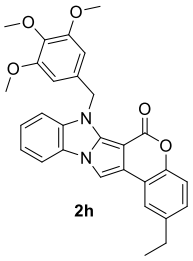
5,7-Me$_2$CPBI^{Bz} (2f). White solid, 85% (67 mg). Mp: 250-253 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, 1H, ArH, *J* = 7.8), 7.40-7.22 (m, 9H, 8 ArH and 1 –N–CH=C–), 7.00 (s, 1H, ArH), 6.90 (s, 1H, ArH), 6.11 (s, 2H, –NCH_2Ph), 2.62 (s, 3H, $ArCH_3$), 2.37 (s, 3H, $ArCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 152.3, 140.3, 137.4, 136.8, 135.9, 134.8, 128.7, 127.8, 127.7, 126.9, 125.8, 124.6, 124.1, 121.2, 115.6, 113.8, 111.2, 111.1, 98.8, 83.9, 48.8, 22.7, 21.2. HRMS (ESI): Exact mass calculated for $C_{26}H_{21}N_2O_2$ $[(M+H)]^+$, *m/z* 393.1603; found *m/z* 393.1591.



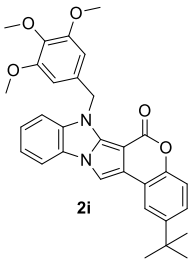
6-EtCPBI^{Bz} (2g). Beige solid, 51% (40 mg). Mp: 232-235 °C. Elemental analysis: Calculated for $C_{26}H_{20}N_2O_2$, C, 79.57; H, 5.14; N, 7.14, Found, C, 79.61; H, 5.45; N, 6.93. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, 1H, ArH, *J* = 7.7), 7.40 (s, 1H, ArH), 7.30-7.27 (m, 3H, 2 ArH and 1 –N–CH=C–), 7.22-7.08 (m, 7H, ArH), 7.03-7.00 (m, 1H, ArH), 5.92 (s, 2H, –NCH_2Ph), 2.60 (q, 2H, –C<u>H</u>$_2$CH$_3$, *J* = 7.6), 1.21 (t, 3H, –CH$_2$C<u>H</u>$_3$, *J* = 7.6). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 149.8, 140.6, 139.6, 136.7, 135.8, 128.7, 127.83, 127.80, 127.6, 125.8, 125.0, 124.1, 121.7, 121.2, 117.3, 116.8, 111.2, 111.1, 95.9, 83.7, 48.8, 28.4, 15.8.



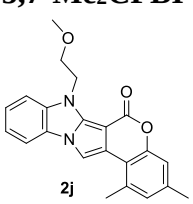
6-EtCPBI$^{Bz\text{-}3,4,5\text{-}(OMe)3}$ (2h). Beige solid, 70% (67 mg). Mp: 224-225 °C. Elemental analysis: Calculated for $C_{29}H_{26}N_2O_5$, C, 72.19; H, 5.43; N, 5.81, Found, C, 72.02; H, 4.97; N, 6.58. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, 1H, ArH, *J* = 7.9), 7.56 (s, 1H, ArH), 7.47-7.43 (m, 2H, ArH and –N–CH=C–), 7.37 (t, 1H, ArH, *J* = 7.6), 7.29 (t, 1H, ArH, *J* = 7.5), 7.25-7.23 (m, 1H, ArH), 7.17-7.14 (m, 1H, ArH), 6.71 (s, 2H, ArH), 5.97 (s, 2H, –NCH_2Ph), 3.78 (s, 3H, $ArOCH_3$), 3.76 (s, 6H, $ArOCH_3$), 2.72 (q, 2H, –C<u>H</u>$_2$CH$_3$, *J* = 7.6), 1.32 (t, 3H, –CH$_2$C<u>H</u>$_3$, *J* = 7.6). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 153.4, 149.8, 140.5, 139.7, 137.6, 135.9, 132.3, 127.7, 125.8, 125.0, 124.2, 121.7, 121.4, 117.3, 116.7, 111.3, 111.1, 105.2, 96.1, 83.6, 60.8, 56.2, 49.0, 28.4, 15.8.



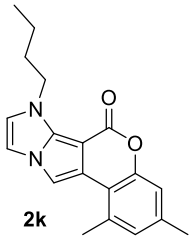
6-(*t*-Bu)CPBI$^{Bz\text{-}3,4,5\text{-}(OMe)3}$ (2i). White solid, 65% (66 mg). Mp: 240-241 °C. Elemental analysis: Calculated for $C_{31}H_{30}N_2O_5$, C, 72.92; H, 5.92; N, 5.49, Found, C, 72.56; H, 5.58; N, 5.56. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, 1H, ArH, *J* = 2.2), 7.68 (d, 1H, ArH, *J* = 7.8), 7.51 (s, 1H, ArH), 7.44-7.25 (m, 5H, 4 ArH and 1 –N–CH=C–), 6.71 (s, 2H, ArH), 5.96 (s, 2H, –NCH_2Ph), 3.79 (s, 3H, $ArOCH_3$), 3.76 (s, 6H, $ArOCH_3$), 1.42 (s, 9H, -C$(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 153.4, 149.5, 146.7, 140.5, 137.6, 135.9, 132.3, 125.8, 125.5, 125.5, 124.2, 121.4, 119.2, 117.1, 116.3, 111.3, 111.1, 105.2, 96.1, 83.7, 60.8, 56.1, 49.0, 34.5, 31.5.



5,7-Me$_2$CPBI$^{Et\text{-}2\text{-}OMe}$ (2j). Yellow solid, 54% (39 mg). Mp: 186-188 °C. Elemental analysis: Calculated for $C_{22}H_{20}N_2O_3$, C, 73.32; H, 5.59; N, 7.77, Found, C, 73.01; H, 5.03; N, 7.79. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, 1H, ArH, *J* = 7.9), 7.53 (d, 1H, ArH, *J* = 8.2), 7.40 (dt, 1H, ArH, J_1 = 7.8, J_2 = 1.0), 7.36 (s, 1H, –N–CH=C–), 7.29 (dt, 1H, ArH, J_1 = 7.5, J_2 = 1.0), 7.00 (s, 1H, ArH), 6.90 (s, 1H, ArH), 4.97 (t, 2H, –NCH_2C<u>H</u>$_2$O–, *J* = 5.1), 3.92 (t, 2H, –NC<u>H</u>$_2$CH$_2$O–, *J* = 5.1), 3.31 (s, 3H, –OCH_3), 2.63 (s, 3H, $ArCH_3$), 2.37 (s, 3H, $ArCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 152.2, 140.0, 137.3, 136.9, 134.7, 126.9, 125.4, 124.6, 124.1, 121.0, 115.6, 113.8, 111.2, 110.9, 98.7, 83.7, 72.3, 59.0, 45.5, 22.7, 21.1.



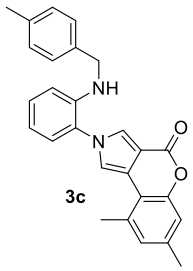
5,7-Me$_2$CPI^{Bu} (2k). White solid, 49% (30 mg). Mp: 162-164 °C. Elemental analysis: Calculated for $C_{19}H_{20}N_2O_2$, C, 74.00; H, 6.54; N, 9.08, Found, C, 74.38; H, 5.88; N, 8.62. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (s, 1H, –N–CH=C–), 7.06 (s, 1H, ArH), 7.01 (s, 1H, ArH), 6.87 (s, 2H, –N–CH=CH–N– imidazole), 4.65 (t, 2H, –NC$\underline{H}_2$CH$_2$–, *J* = 6.7), 2.54 (s, 3H, ArCH$_3$), 2.37 (s, 3H, ArCH$_3$), 1.86 (quin, 2H, –NCH$_2$C$\underline{H}_2$–, *J* = 7.1), 1.39 (sex, 2H, –C$\underline{H}_2$CH$_3$, *J* = 7.2), 0.95 (t, 3H, –CH$_2$C$\underline{H}_3$, *J* = 7.2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 152.4, 137.7, 136.9, 134.6, 126.6, 125.0, 121.3, 115.5, 114.1, 107.3, 98.9, 82.3, 48.1, 33.2, 22.5, 21.1, 19.6, 13.7.



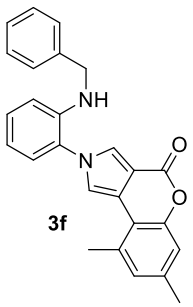
5. Synthesis and characterization data of fused chromeno-pyrrol (CP) derivatives (3)

An acetonitrile mixture (4 mL) of 0.20 mmol of corresponding (benz)imidazolium chloride and 0.22 mmol (30 mg) of potassium carbonate was stirred at 80 °C for 4 hours under argon atmosphere. After this period of time, the mixture was allowed to cool to ambient temperature, the solvent was removed under vacuum. The crude product was dissolved with acetone and filtered through Celite. The clean solution was concentrated to ca. 1 mL and passed through a micro silica gel column. The acetone was removed under vacuum, the product was washed with *n*-hexane (3x5 mL) and dried under vacuum.

5,7-Me$_2$CP$^{Bz\text{-}4\text{-}Me}$ (3c). Beige solid, 32% (26 mg). Mp: 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, 1H, ArH, *J* = 1.9), 7.30 (t, 1H, ArH, *J* = 7.8), 7.26 (d, 1H, ArH, *J* = 1.9), 7.22-7.11 (m, 5H), 7.00 (s, 1H, ArH), 6.90 (s, 1H, ArH), 6.81-6.78 (m, 2H, ArH), 4.31 (d, 2H, –N(H)C$\underline{H}_2$Ph, *J* = 5.5), 4.18 (t, –N($\underline{H}$)CH$_2$Ph, *J* = 5.5), 2.50 (s, 3H, ArCH$_3$), 2.37 (s, 3H, ArCH$_3$), 2.31 (s, 3H, ArCH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 151.9, 143.1, 137.4, 137.2, 135.3, 134.4, 130.4, 129.5, 127.10, 127.07, 125.6, 125.3, 122.2, 118.0, 117.1, 115.7, 113.2, 112.3, 110.8, 47.4, 22.3, 21.2, 21.1. HRMS (ESI): Exact mass calculated for $C_{27}H_{25}N_2O_2$ $[(M+H)]^+$, *m/z* 409.1916; found *m/z* 409.1904.



5,7-Me$_2$CP^{Bz} (3f). Beige solid, 27% (22 mg). Mp: 167-169 °C. Elemental analysis: Calculated for $C_{26}H_{22}N_2O_2$, C, 79.17; H, 5.62; N, 7.10, Found, C, 78.80; H, 5.42; N, 6.86. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (m, 1H, ArH), 7.22-7.09 (m, 8H, ArH), 6.80-6.67 (m, 4H, ArH), 4.33 (m, 1H, -N($\underline{H}$)CH$_2$Ph), 4.29 (m, 2H, -N(H)C$\underline{H}_2$Ph), 2.36 (s, 3H, ArCH$_3$), 2.24 (s, 3H, ArCH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 151.9, 143.1, 138.6, 137.2, 134.3, 130.4, 128.8, 127.4, 127.2, 127.1, 127.0, 125.7, 125.3, 122.1, 118.0, 117.1, 115.5, 113.2, 112.3, 110.7, 47.6, 22.3, 21.2.



6. Single Crystal X-Ray Diffraction Studies

X-ray diffraction data for **2a**, **2j** and **3f** were collected on a STOE IPDS II diffractometer, while crystallographic measurements for **2f** were carried out on a Bruker D8 QUEST diffractometer. Graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was used. The structures were solved by a dual-space algorithm using SHELXT-2018 [5] and refined with full-matrix least-squares calculations on F^2 using SHELXL-2019 [6]. All H atoms were located from difference maps and were included in the refinements as riding atoms, except for nitrogen-bound hydrogen in **3f** which was placed in a difference Fourier map and refined isotropically. The studied crystal of **3f** was a two component non-merohedral twin. The twinning was considered in the data reduction and structure refinement. The final refinement

cycles were performed with HKLF5/BASF method and TwinRotMat routine of PLATON [7] was used to generate the HKLF5 reflection file. Refinement of the ratio of the twin components yielded 0.779:0.221. For **2a**, **2j** and **3f**; Data collection: XAREA [8], cell refinement: X-AREA, data reduction: X-RED32 [8]. For **2f**; Data collection: APEX2 [9], cell refinement: SAINT [9], data reduction: SAINT. Molecular graphics were created by using OLEX2 [10]. CCDC 2314963 (**2a**), 2314964 (**2f**), 2314965 (**2j**) and 2314966 (**3f**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk/structures.

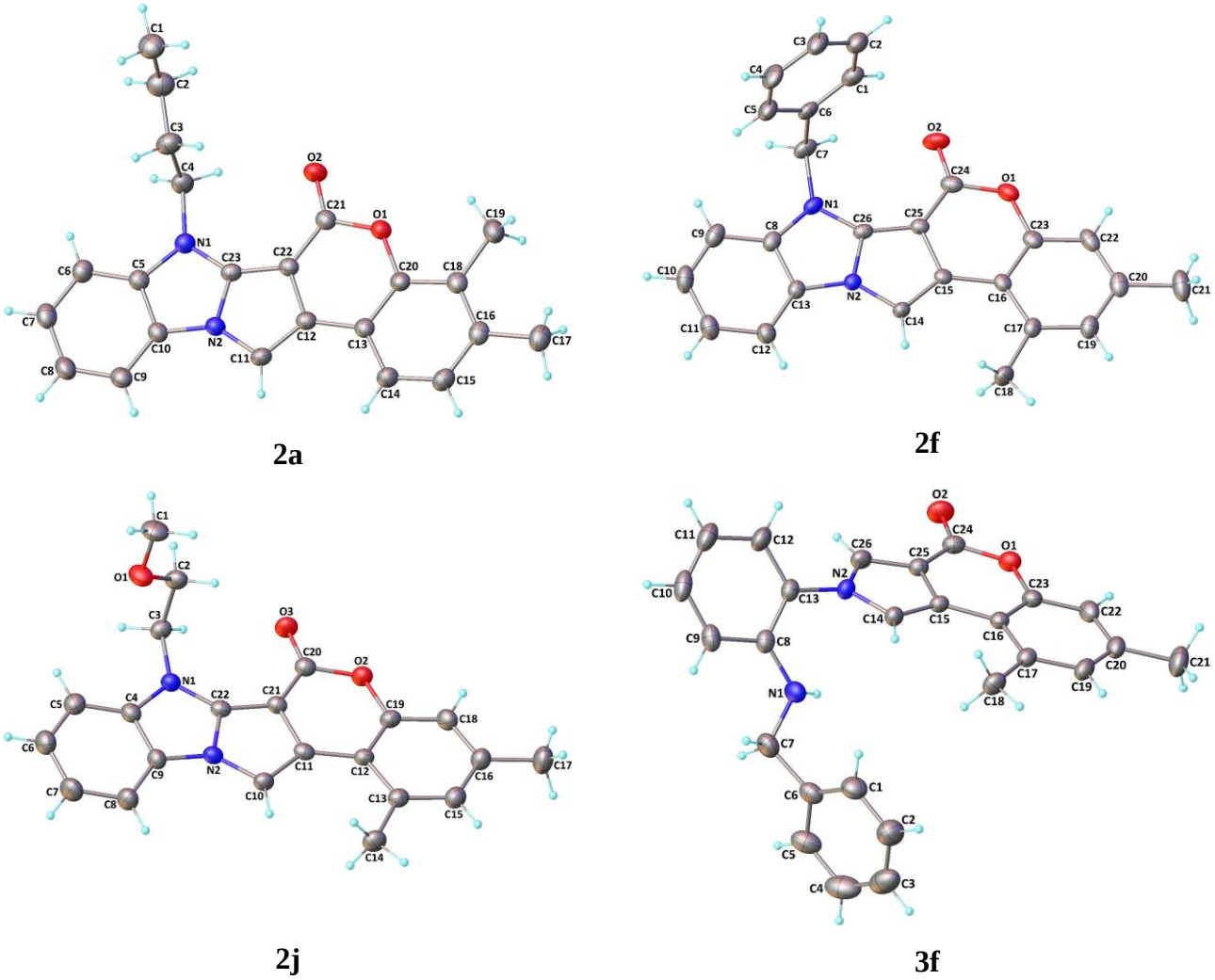


Figure S1. Molecular structure of **2a** (CCDC 2314963), **2f** (CCDC 2314964), **2j** (CCDC 2314965), **3f** (CCDC 2314966). Thermal ellipsoids are drawn at the 20% probability level.

Table S6. Crystal data and structure refinement parameters for **2a**.

CCDC depository	2314963
Color/shape	Colorless/prism
Chemical formula	$C_{23}H_{22}N_2O_2$
Formula weight	358.42
Temperature (K)	296(2)
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Orthorhombic
Space group	*Pbca* (No. 61)
Unit cell parameters	
a, *b*, *c* (Å)	8.9870(9), 17.1569(16), 24.1034(18)
α, β, γ (°)	90, 90, 90
Volume (Å^3)	3716.5(6)
Z	8
$D_{calc.}$ (g/cm^3)	1.281
μ (mm^{-1})	0.082
Absorption correction	Integration
$T_{min.}$, $T_{max.}$	0.9610, 0.9909
F_{000}	1520
Crystal size (mm^3)	0.62 × 0.43 × 0.12
Diffractometer	STOE IPDS II
Measurement method	ω scan
Index ranges	$-10 \le h \le 10$, $-20 \le k \le 18$, $-26 \le l \le 28$
θ range for data collection (°)	$1.690 \le \theta \le 25.050$
Reflections collected	15712
Independent/observed reflections	3294/1591
$R_{int.}$	0.0830
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3294/0/247
Goodness-of-fit on F^2	0.900
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0514$, $wR_2 = 0.0986$
R indices (all data)	$R_1 = 0.1333$, $wR_2 = 0.1210$
$\Delta\rho_{max.}$, $\Delta\rho_{min.}$ (e/Å^3)	0.20, −0.16

Table S7. Crystal data and structure refinement parameters for **2f**.

CCDC depository	2314964
Color/shape	Yellow/block
Chemical formula	$C_{26}H_{20}N_2O_2$
Formula weight	392.44
Temperature (K)	296(2)
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell parameters	
a, b, c (Å)	7.3332(6), 14.6008(14), 18.4846(17)
α, β, γ (°)	90, 93.359(3), 90
Volume (Å^3)	1975.8(3)
Z	4
$D_{calc.}$ (g/cm^3)	1.319
μ (mm^{-1})	0.084
Absorption correction	N/A
F_{000}	824
Crystal size (mm^3)	0.09 × 0.06 × 0.05
Diffractometer	Bruker D8 QUEST
Measurement method	φ and ω scan
Index ranges	$-8 \le h \le 8$, $-17 \le k \le 17$, $-21 \le l \le 21$
θ range for data collection (°)	$2.611 \le \theta \le 25.050$
Reflections collected	44473
Independent/observed reflections	3496/2284
$R_{int.}$	0.0680
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3496/0/274
Goodness-of-fit on F^2	1.056
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0534$, $wR_2 = 0.1139$
R indices (all data)	$R_1 = 0.0938$, $wR_2 = 0.1313$
$\Delta\rho_{max.}$, $\Delta\rho_{min.}$ (e/Å^3)	0.19, −0.15

Table S8. Crystal data and structure refinement parameters for **2j**.

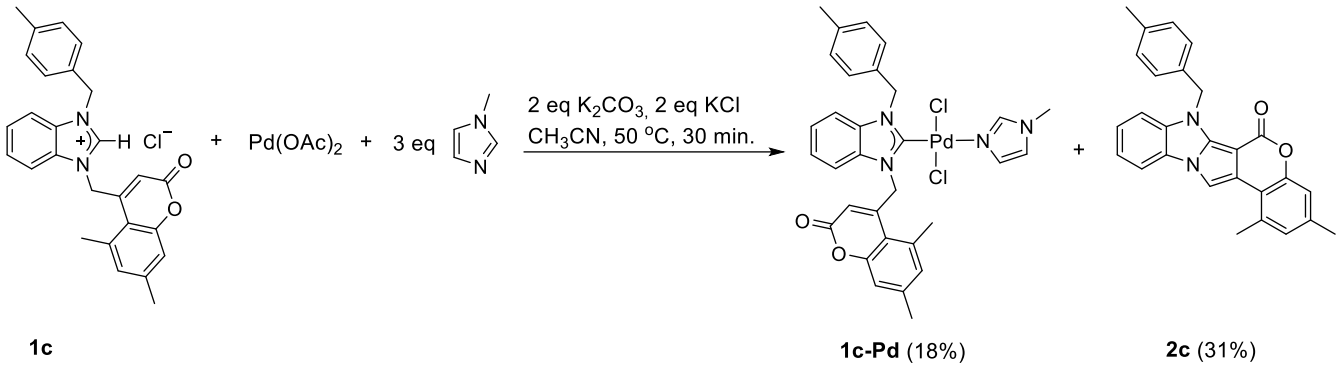
CCDC depository	2314965
Color/shape	Yellow/prism
Chemical formula	$C_{22}H_{20}N_2O_3$
Formula weight	360.40
Temperature (K)	296(2)
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell parameters	
a, b, c (Å)	8.0850(16), 9.5451(18), 12.413(3)
α, β, γ (°)	103.148(16), 100.212(16), 100.313(16)
Volume (Å^3)	893.7(3)
Z	2
$D_{calc.}$ (g/cm^3)	1.339
μ (mm^{-1})	0.090
Absorption correction	Integration
$T_{min.}$, $T_{max.}$	0.9751, 0.9932
F_{000}	380
Crystal size (mm^3)	0.61 × 0.16 × 0.08
Diffractometer	STOE IPDS II
Measurement method	ω scan
Index ranges	$-9 \le h \le 9$, $-11 \le k \le 11$, $-14 \le l \le 14$
θ range for data collection (°)	$1.730 \le \theta \le 25.049$
Reflections collected	9482
Independent/observed reflections	3167/1346
$R_{int.}$	0.0958
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3167/0/248
Goodness-of-fit on F^2	0.882
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0516$, $wR_2 = 0.0653$
R indices (all data)	$R_1 = 0.1585$, $wR_2 = 0.0864$
$\Delta\rho_{max.}$, $\Delta\rho_{min.}$ (e/Å^3)	0.15, −0.14

Table S9. Crystal data and structure refinement parameters for **3f**.

CCDC depository	2314966
Color/shape	Colorless/prism
Chemical formula	$C_{26}H_{22}N_2O_2$
Formula weight	394.45
Temperature (K)	296(2)
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell parameters	
a, b, c (Å)	19.6400(16), 14.6692(16), 7.1693(6)
α, β, γ (°)	90, 96.833(7), 90
Volume (Å^3)	2050.8(3)
Z	4
$D_{calc.}$ (g/cm^3)	1.278
μ (mm^{-1})	0.081
Absorption correction	Integration
$T_{min.}$, $T_{max.}$	0.9354, 0.9841
F_{000}	832
Crystal size (mm^3)	0.79 × 0.32 × 0.19
Diffractometer	STOE IPDS II
Measurement method	ω scan
Index ranges	$-24 \le h \le 24$, $-18 \le k \le 18$, $-6 \le l \le 9$
θ range for data collection (°)	$1.737 \le \theta \le 26.719$
Reflections collected	4280
Independent/observed reflections	4280/1909
$R_{int.}$	N/A
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4280/0/278
Goodness-of-fit on F^2	0.863
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0563$, $wR_2 = 0.1012$
R indices (all data)	$R_1 = 0.1397$, $wR_2 = 0.1224$
$\Delta\rho_{max.}$, $\Delta\rho_{min.}$ (e/Å^3)	0.16, −0.19

7. Miscellaneous Control and Mechanism Experiments

7.1. Synthesis and separation of 2c and Pd-NHC complex of 1c (1c-Pd)

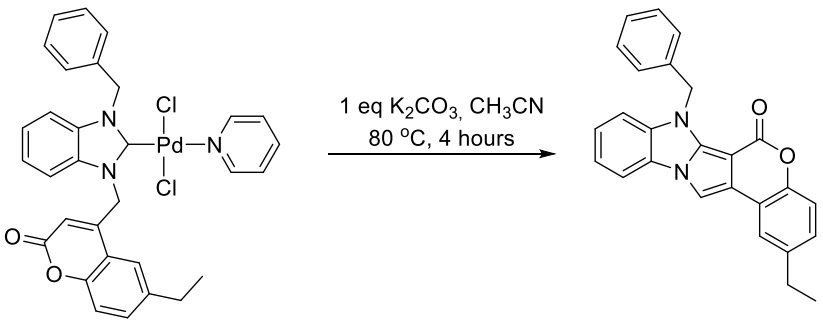


1c **1c-Pd** (18%) **2c** (31%)

An acetonitrile mixture (10 mL) of 0.5 mmol (220 mg) of **1c**, 0.5 mmol (112 mg) of palladium acetate, 1 mmol (138 mg) of potassium carbonate, 1 mmol (75 mg) of potassium chloride and 1.5 mmol (120 μL) of *N*-methylimidazole was stirred at 50 °C for 30 minutes. After this period of time, the mixture was allowed to cool to ambient temperature, the solvent was removed under vacuum. The crude product was dissolved in methylene chloride and filtered through Celite. The clean solution was concentrated to ca. 1 mL, and **2c** (R_f=0.80) and Pd-NHC complex of **1c (1c-Pd)** (R_f=0.35) were separated by a silica gel column.

1c-Pd. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H, –NCHN–), 7.52-7.49 (m, 3H, ArH), 7.23-7.14 (m, 6H, ArH), 7.09 and 7.02 (two s, 2H, –NCHCHN–), 6.79 (s, 2H, –NCH_2coumarin), 6.25 (s, 2H, –NCH_2Ph), 5.81 (s, 1H, –CH=C–), 3.65 (s, 3H, –NCH_3), 2.93 (s, 3H, $ArCH_3$), 2.44 (s, 3H, $ArCH_3$), 2.34 (s, 3H, $ArCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 160.0, 155.3, 149.9, 142.4, 138.6, 137.9, 135.4, 134.2, 134.1, 131.8, 130.1, 129.6, 128.4, 127.9, 123.9, 123.8, 119.7, 116.5, 115.2, 113.3, 112.1, 110.4, 53.2, 51.4, 34.3, 25.2, 21.24, 21.20.

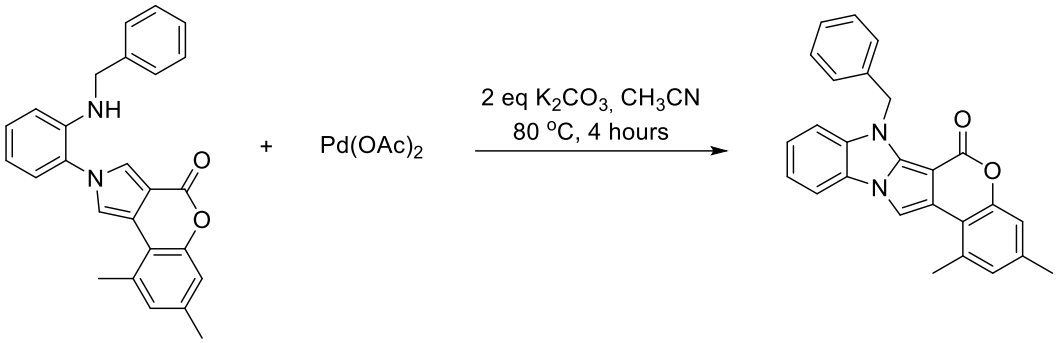
7.2. Transformation of a Pd-NHC (1g-Pd) to 2g



1g-Pd **2g** (68% by ^{1}H NMR)

An acetonitrile mixture (2 mL) of 0.05 mmol (33 mg) of a Pd-NHC complex of **1g** (the complex was ready from our previous study and can be encoded as **1g-Pd**) and 0.05 mmol (7 mg) of potassium carbonate was stirred at 80 °C for 4 hours. After this period of time, the mixture was allowed to cool to ambient temperature, the solvent was removed under vacuum. The crude product was dissolved in methylene chloride and filtered through Celite. The methylene chloride was removed under vacuum, the crude product was washed with *n*-hexane (3 x 3 mL), dried under vacuum and analyzed with ^{1}H NMR.

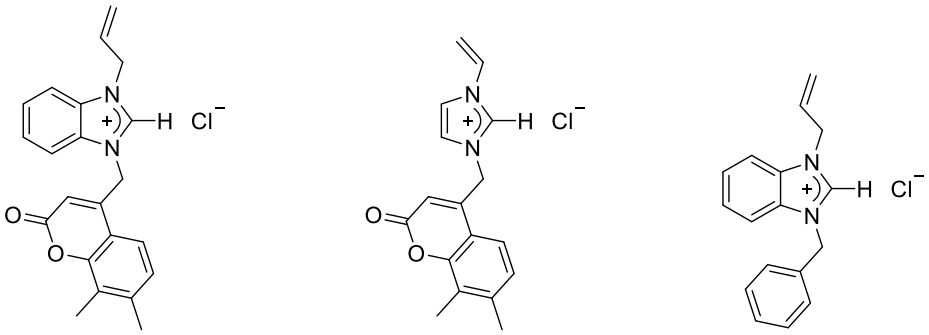
7.3. Synthesis of 2c using 3c and palladium acetate



3c **2c** (57% by ^{1}H NMR)

An acetonitrile mixture (2 mL) of 0.1 mmol (40 mg) of **3c**, 0.1 mmol (22 mg) of palladium acetate and 0.2 mmol (28 mg) of potassium carbonate was stirred at 80 °C for 4 hours. After this period of time, the mixture was allowed to cool to ambient temperature, the solvent was removed under vacuum. The crude product was dissolved in methylene chloride and filtered through Celite. The methylene chloride was removed under vacuum, the crude product was washed with *n*-hexane (3 x 3 mL), dried under vacuum and analyzed with ^{1}H NMR.

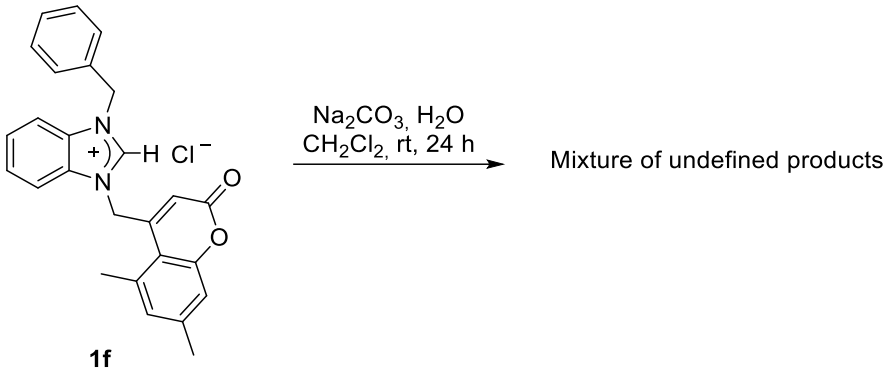
7.4. Experiments with the (benz)imidazolium salts containing double bond other than that of coumarin



1l **1m** **1n**

The experiments for the synthesis of CP(B)I derivatives with the salts given above, which containing double bond other than those of coumarin, were failed. The mixtures of undefined products were obtained as results of the experiments carried out with the procedure given under Section 4 for the synthesis of CP(B)I derivatives.

7.5. Hydrolysis reaction of 1f under basic aqueous conditions



The hydrolysis reaction of **1f** under basic conditions were also tested according to procedure described in literature [11]. 0.2 mmol (85 mg) of **1f** and 0.5 mmol (53 mg) of sodium carbonate weighed in a Schlenk tube, methylene chloride (2 mL) and deionized water (2 mL) were added and biphasic was vigorously stirred at room temperature for 24 hours. After this period of time, the organic phase was separated, washed with deionized water (2 x 3 mL) and dried over $MgSO_4$. The solvent was removed under vacuum, the crude product was dried under vacuum and analyzed by ^1H NMR.

8. References

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9. Spectra

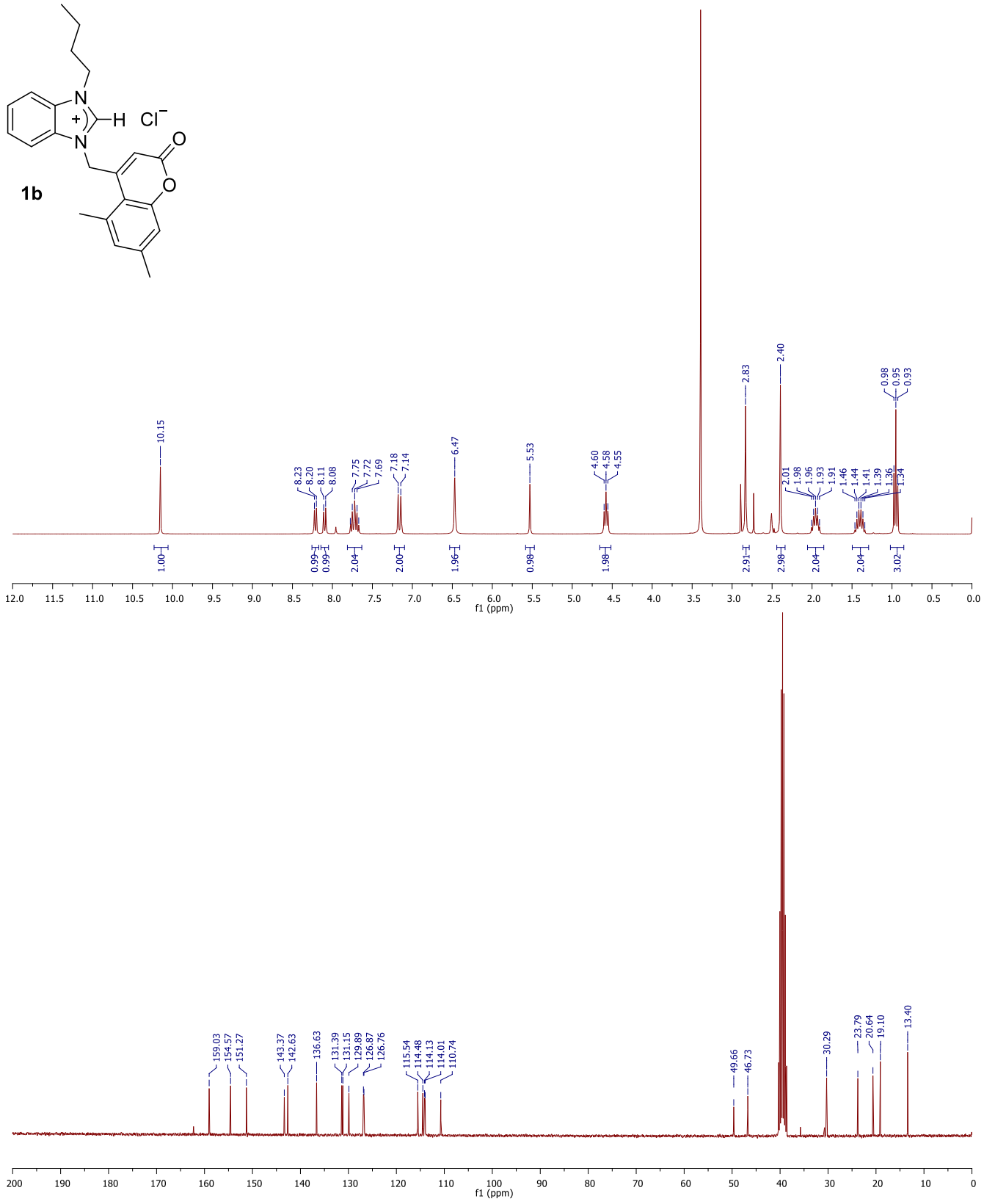

Figure S2. ^{1}H and ^{13}C NMR spectra of **1b**.

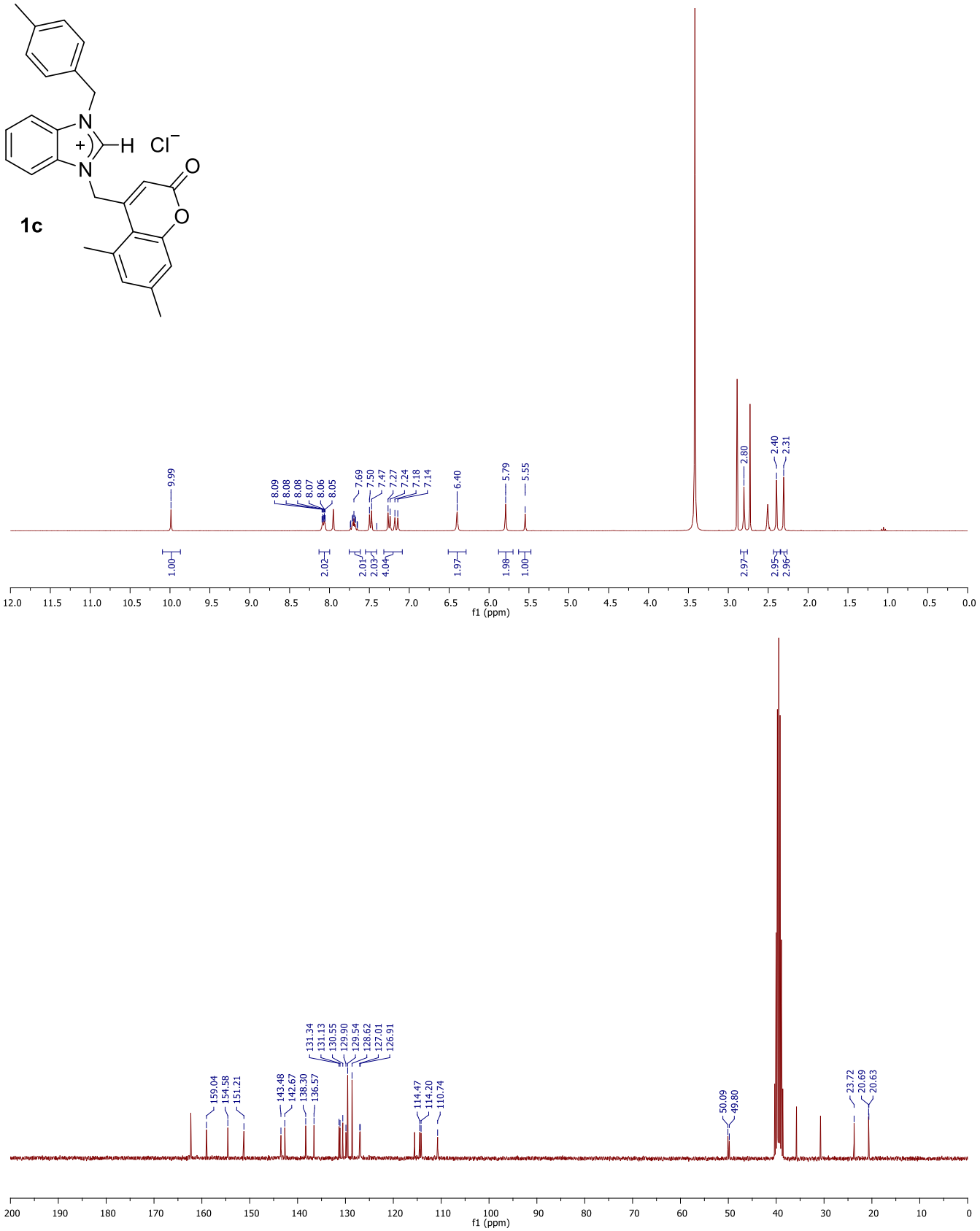

Figure S3. ^{1}H and ^{13}C NMR spectra of **1c**.

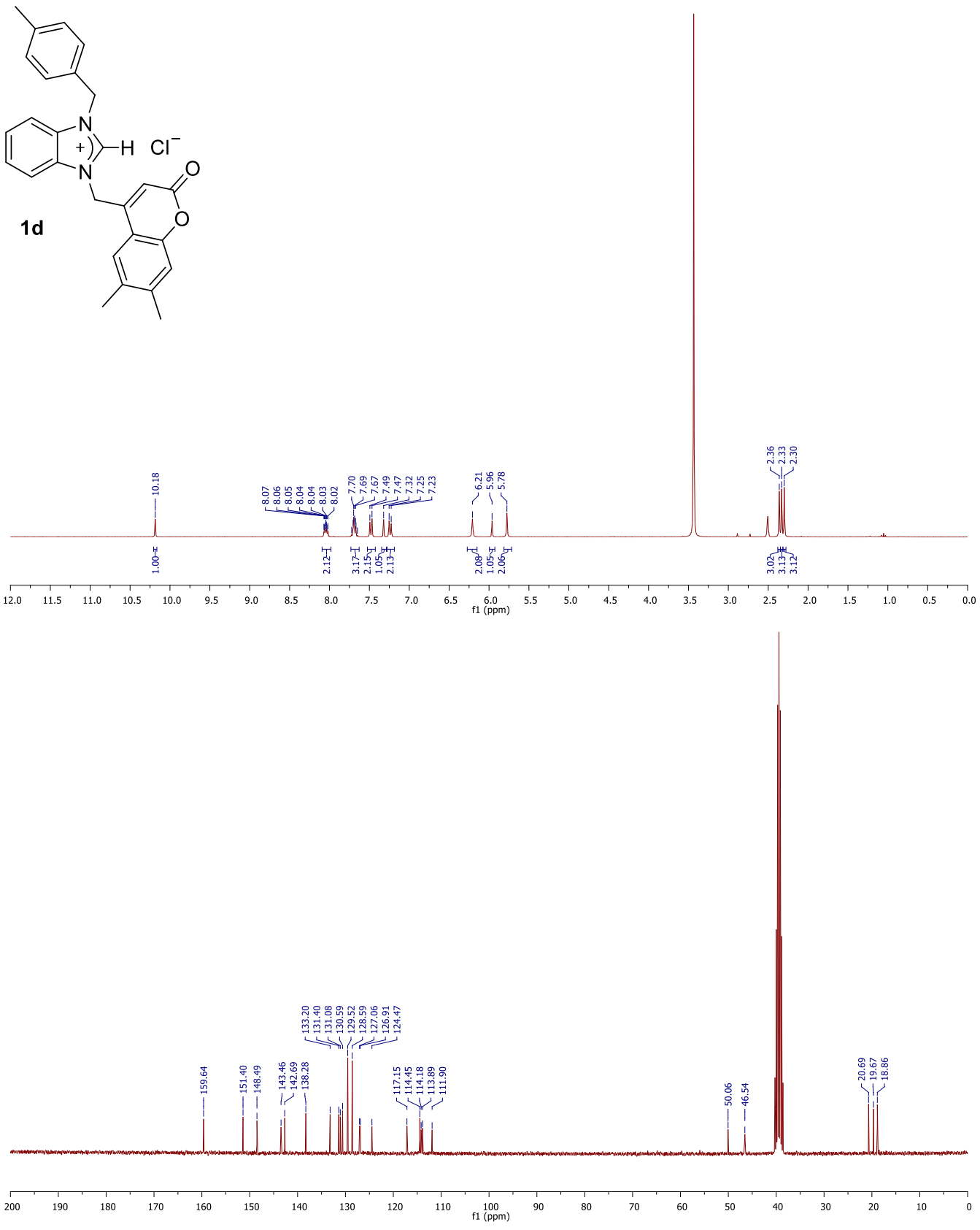

Figure S4. ^{1}H and ^{13}C NMR spectra of **1d**.

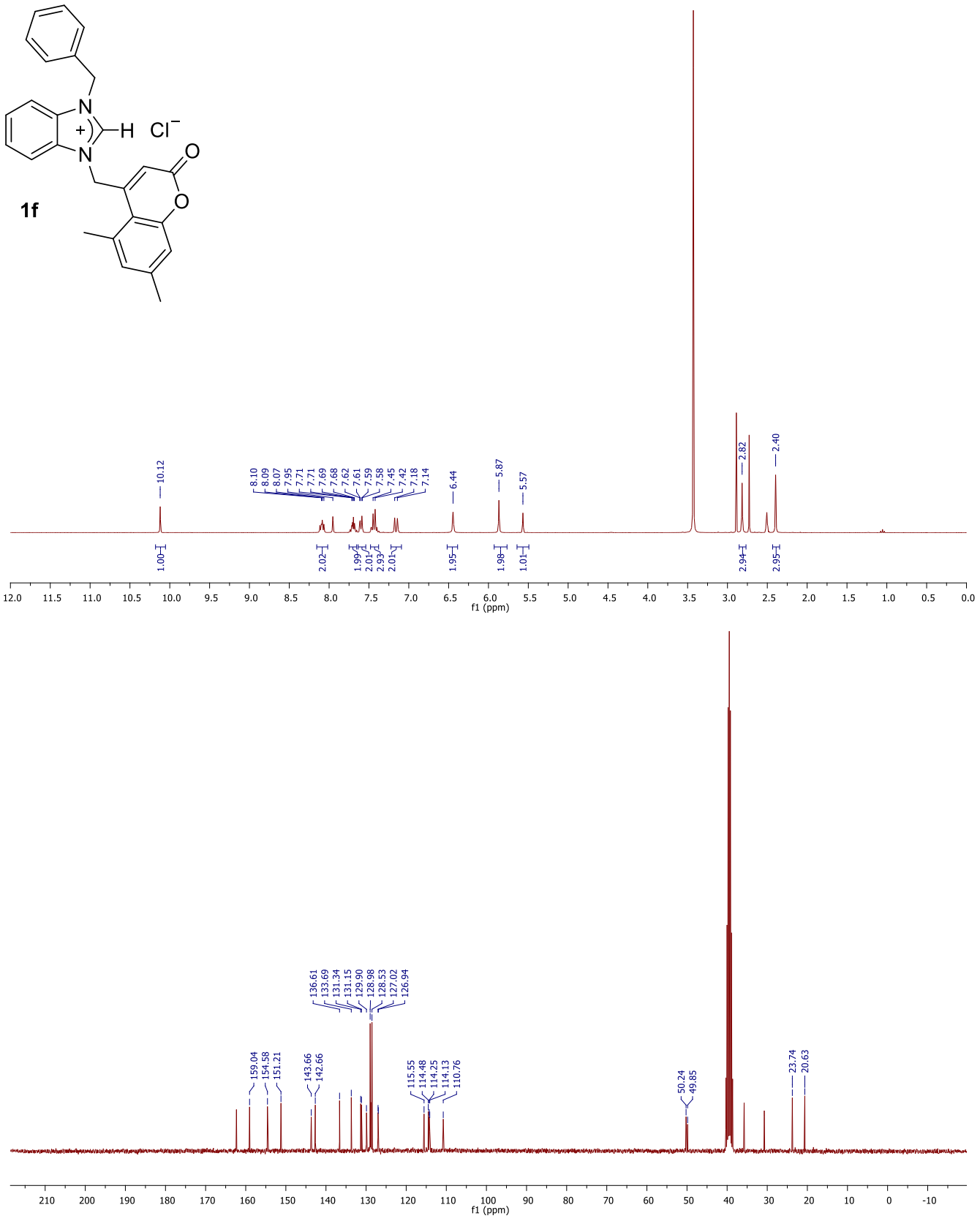

Figure S5. ^{1}H and ^{13}C NMR spectra of **1f**.

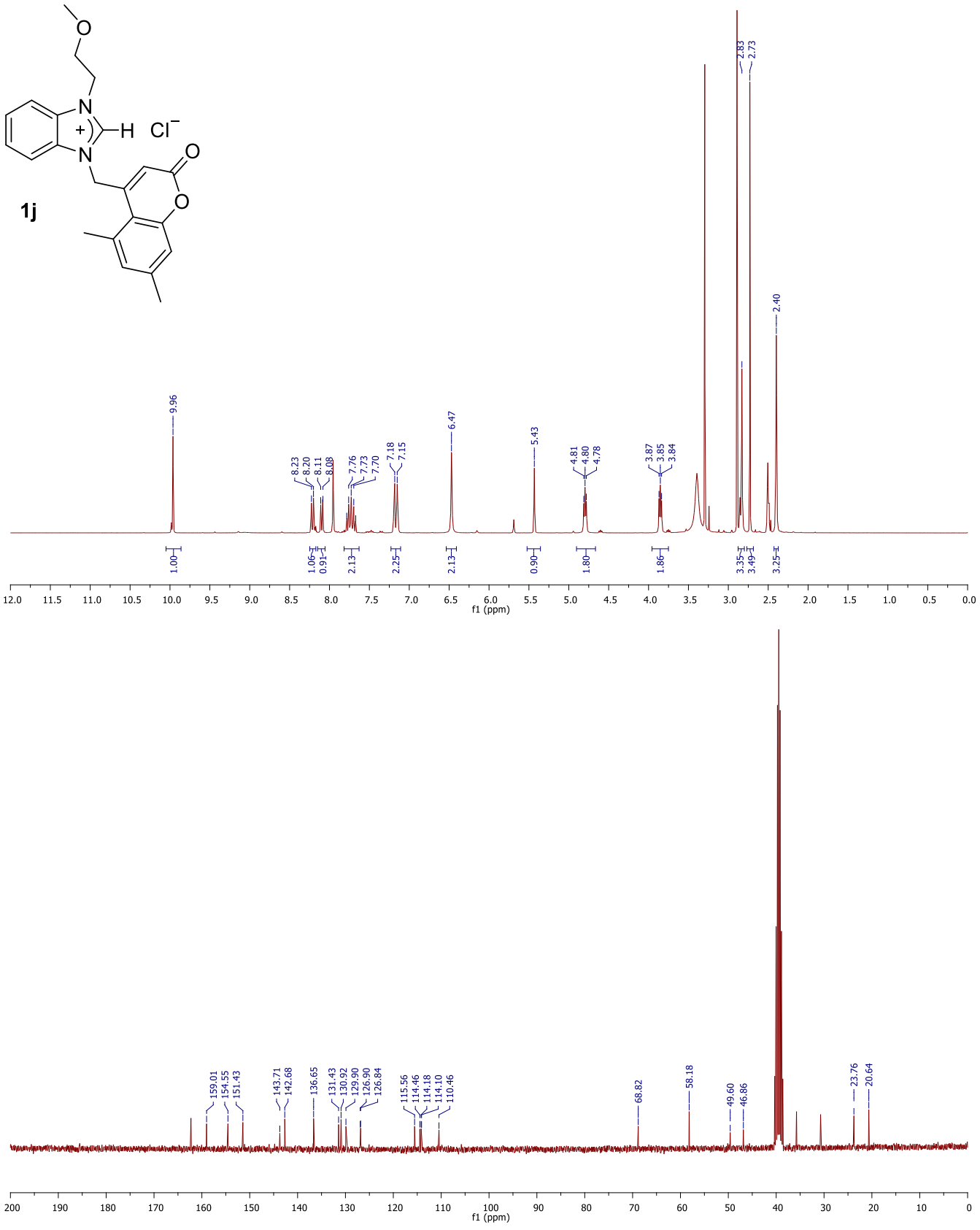

Figure S6. ^{1}H and ^{13}C NMR spectra of **1j**.

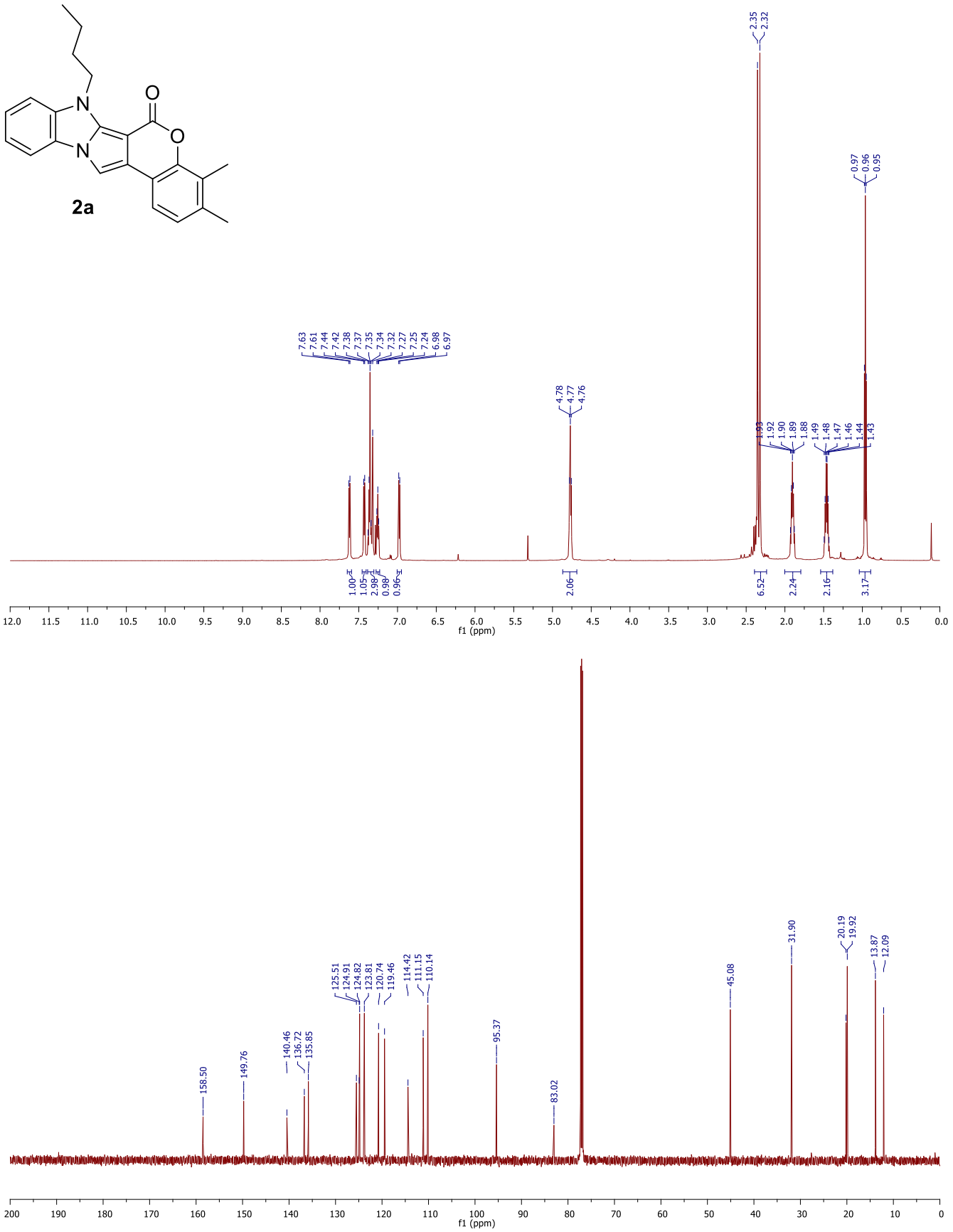

Figure S7. ^{1}H and ^{13}C NMR spectra of **2a**.

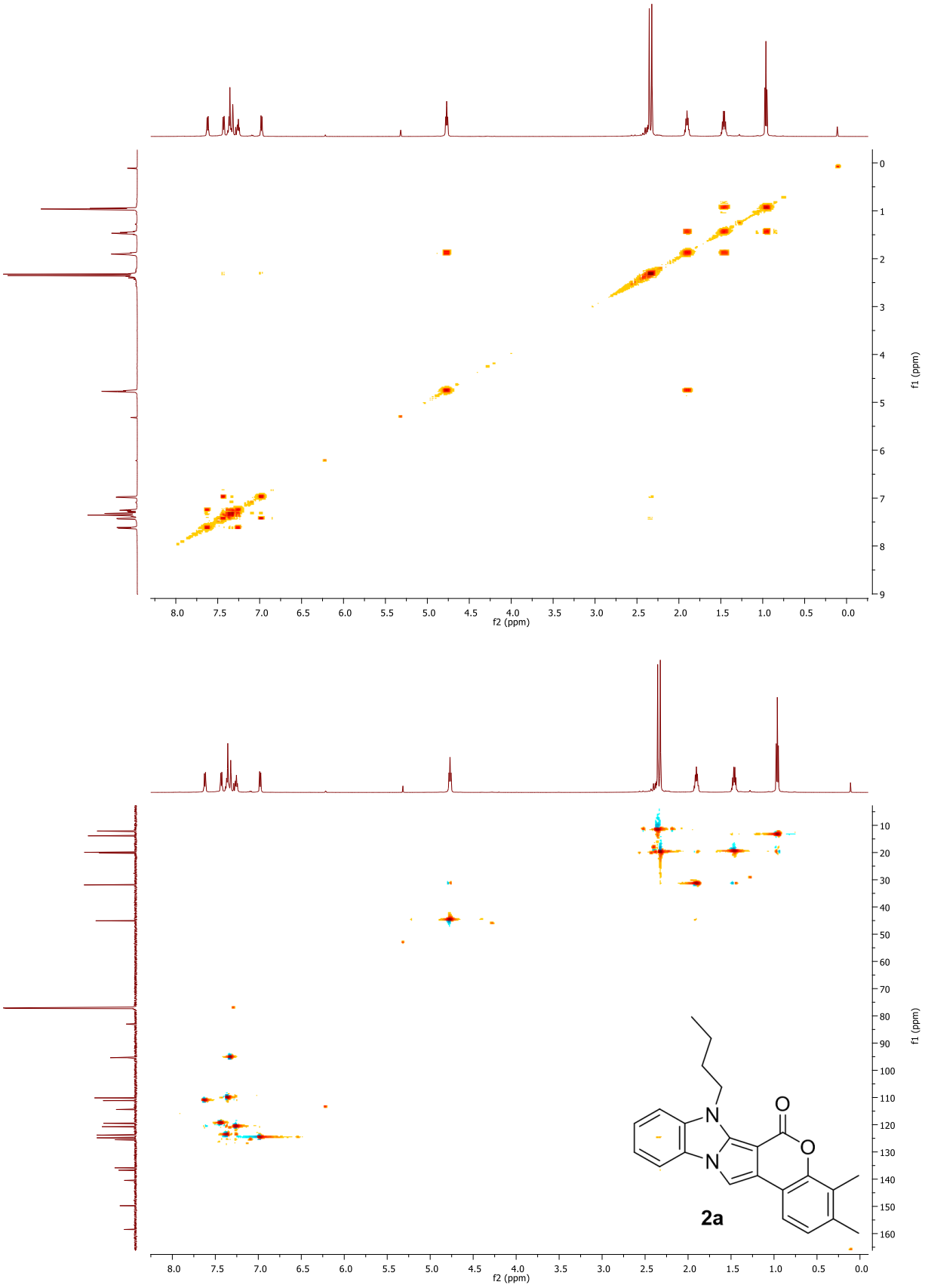

Figure S8. ^{1}H-^{1}H COSY (top) and ^{13}C-^{1}H HSQC (bottom) spectra of **2a**.

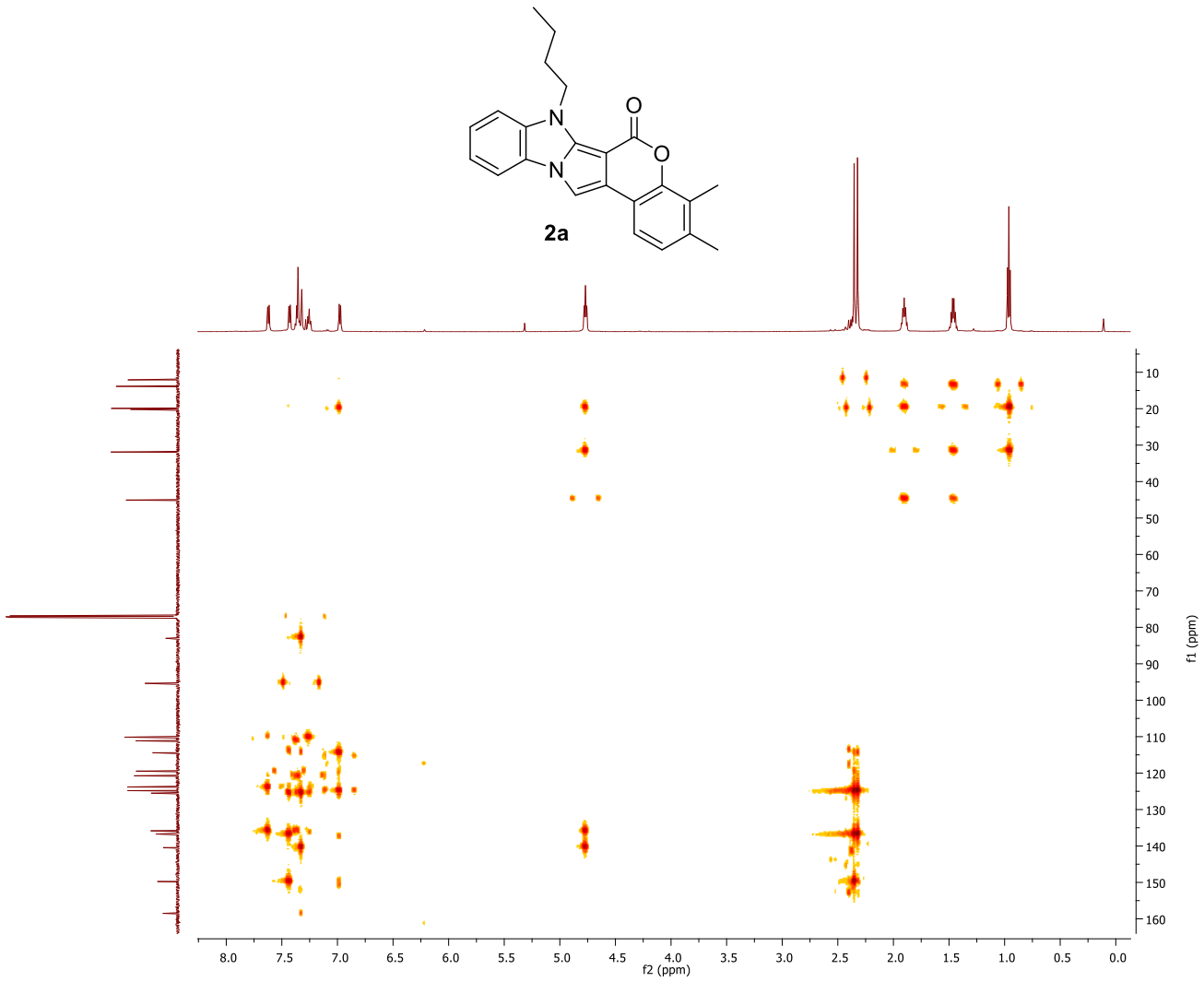

Figure S9. ^{13}C-^{1}H HMBC spectrum of **2a**.

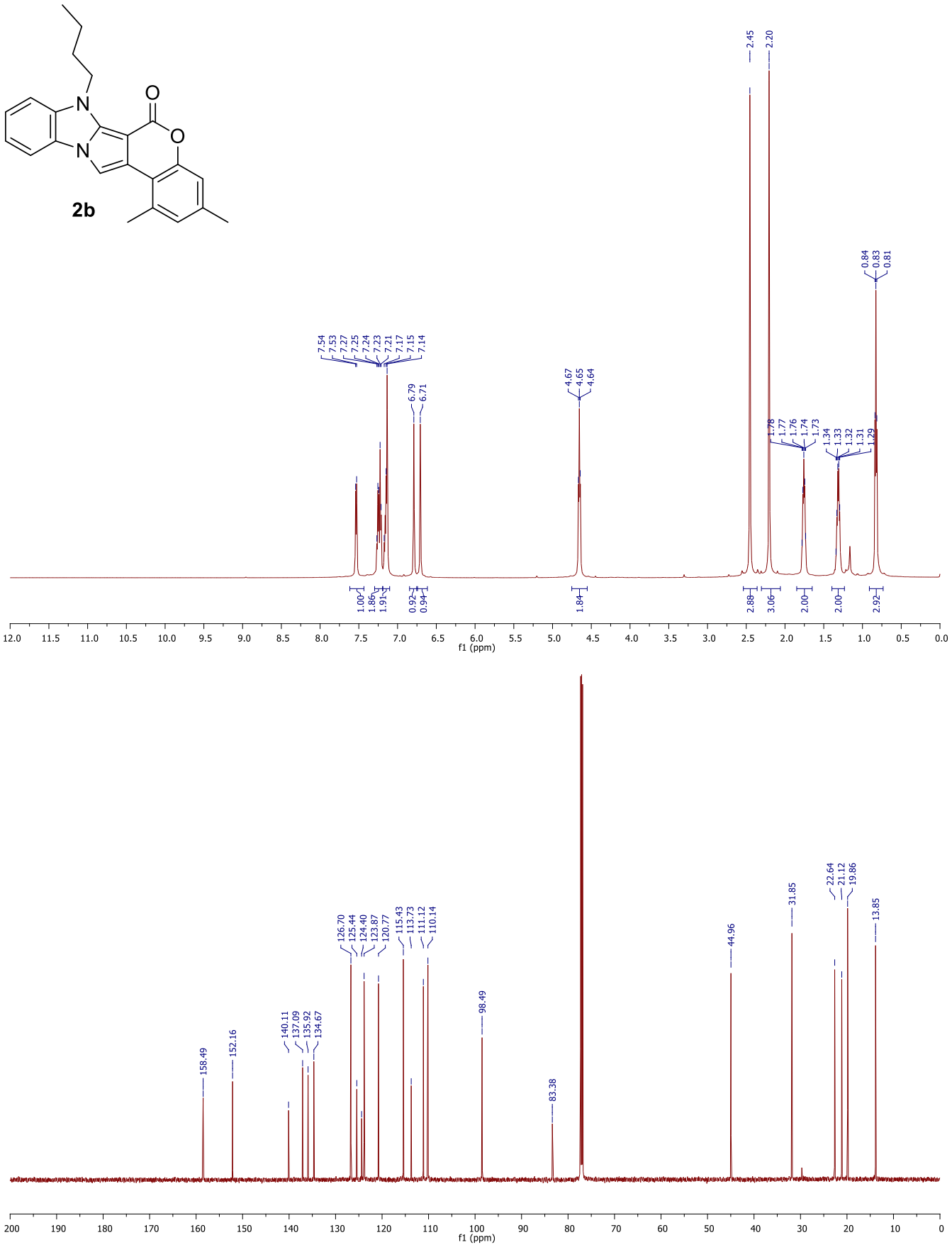

Figure S10. ^{1}H and ^{13}C NMR spectra of **2b**.

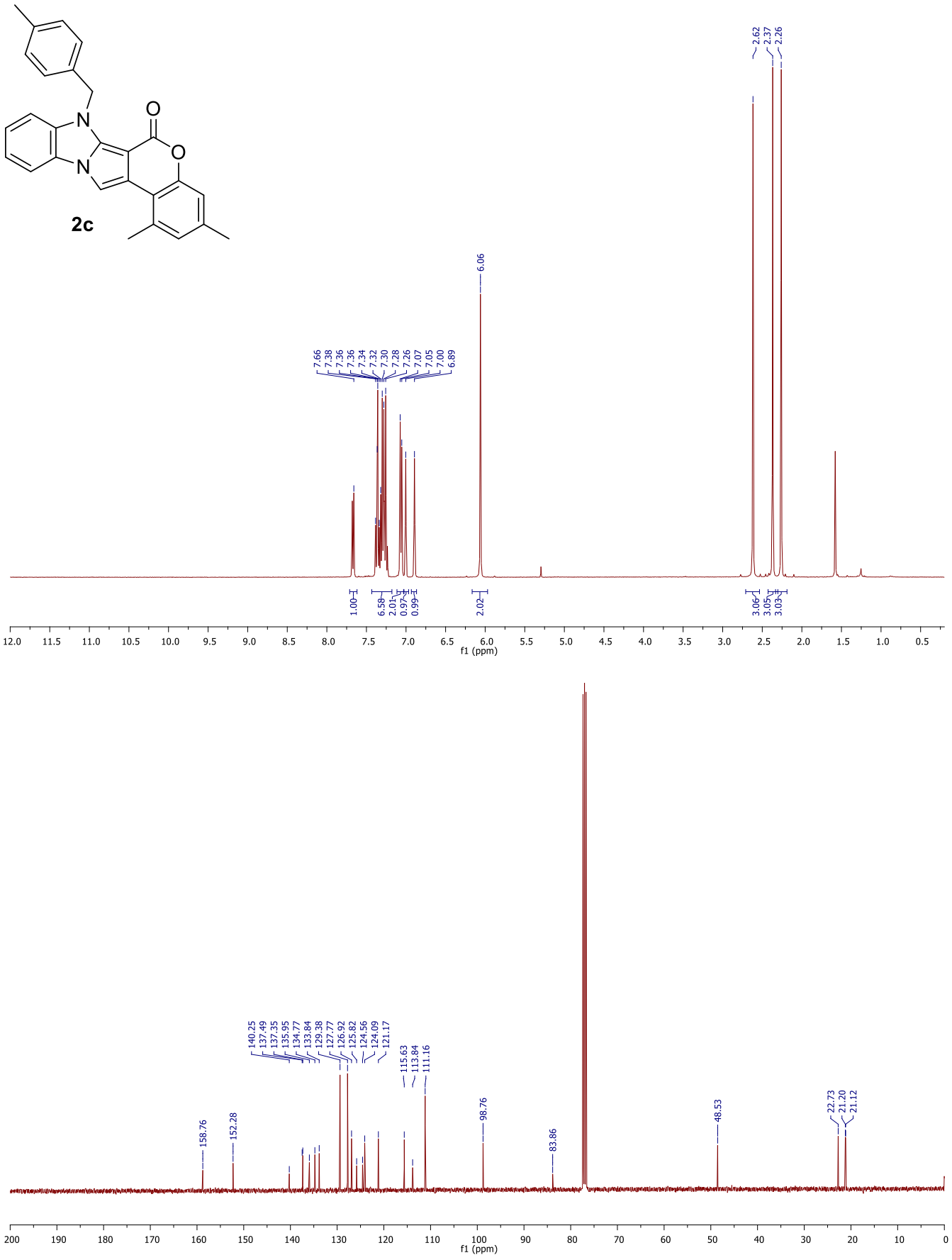

Figure S11. ^{1}H and ^{13}C NMR spectra of **2c**.

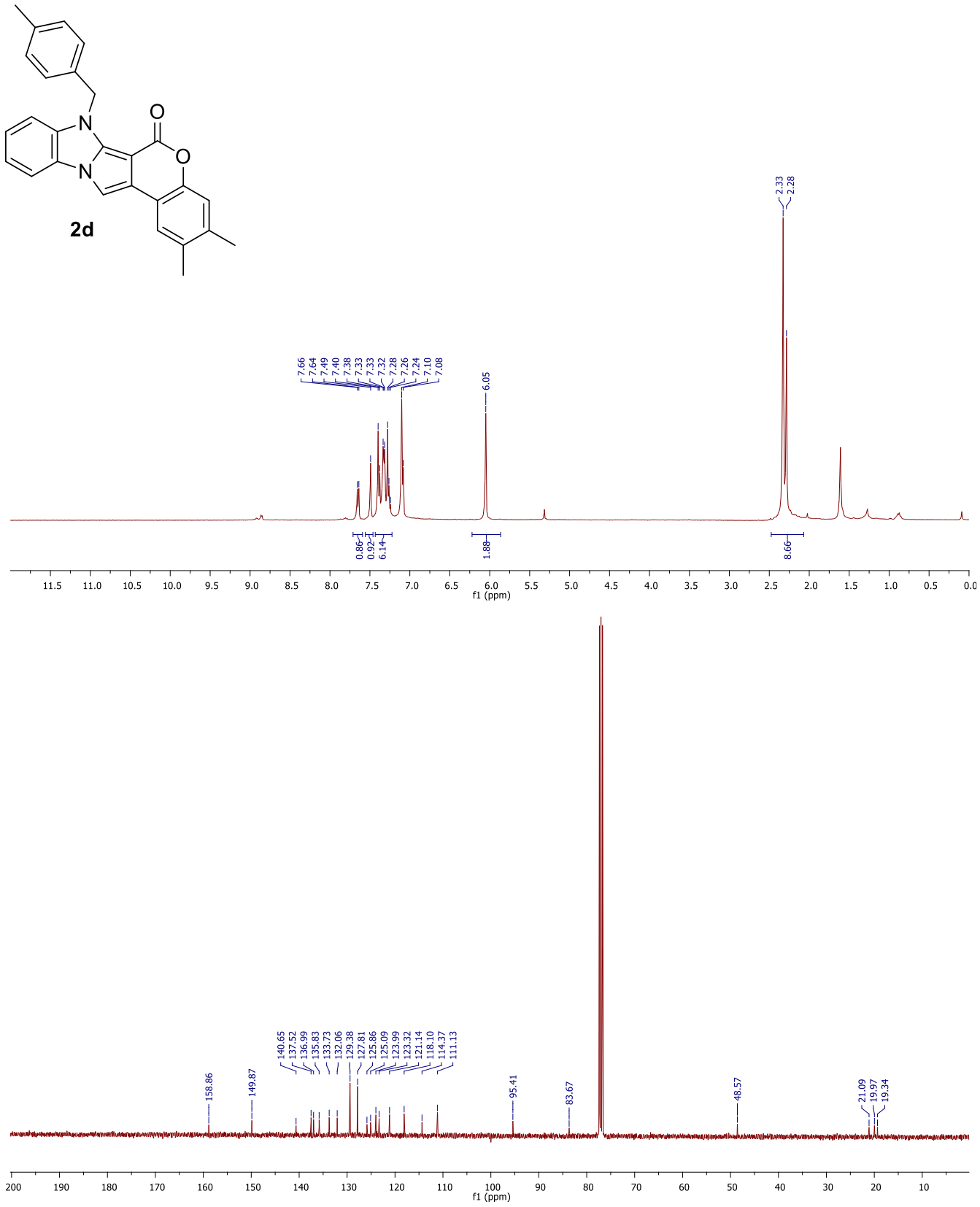

Figure S12. ^{1}H and ^{13}C NMR spectra of **2d**.

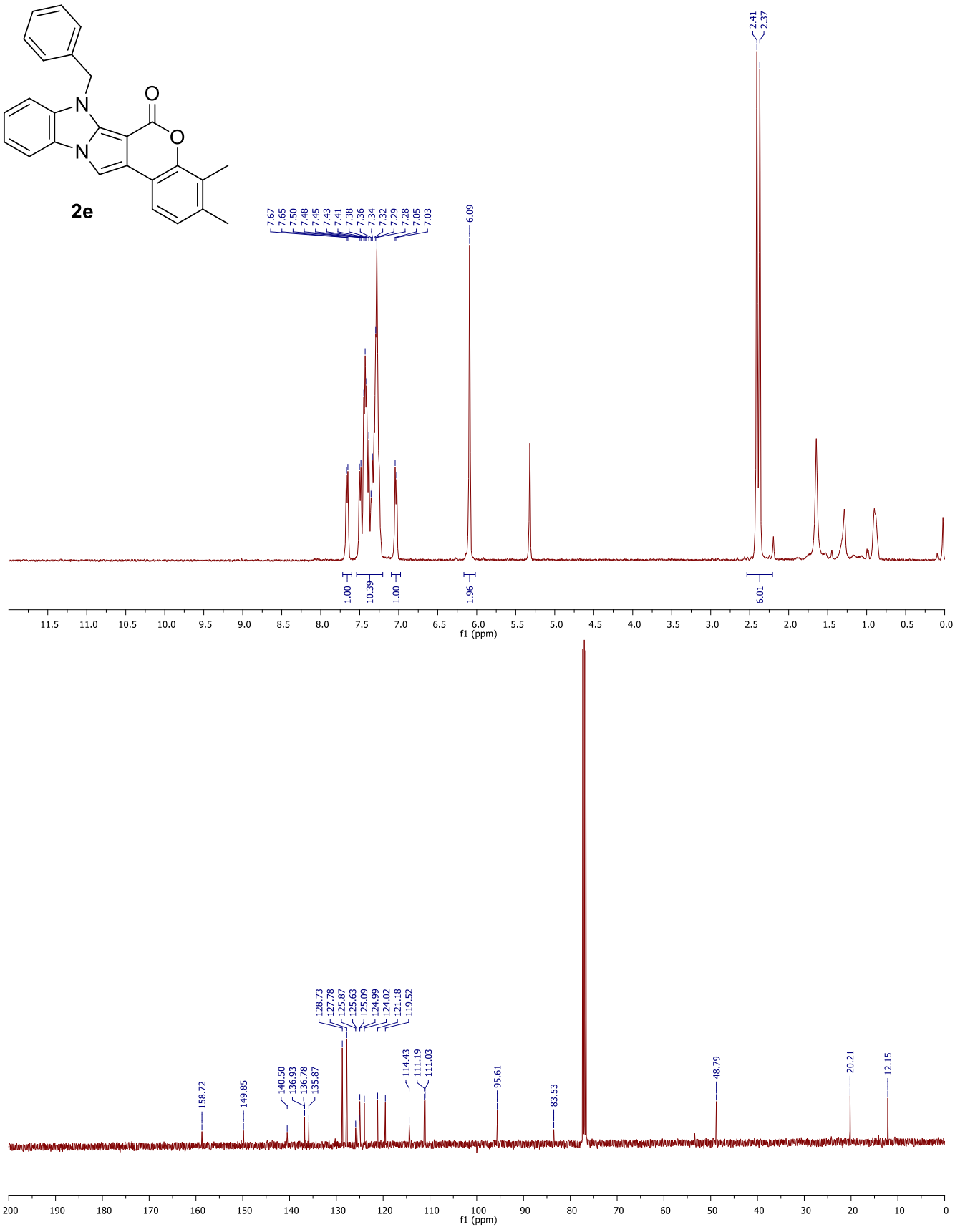

Figure S13. ^{1}H and ^{13}C NMR spectra of **2e**.

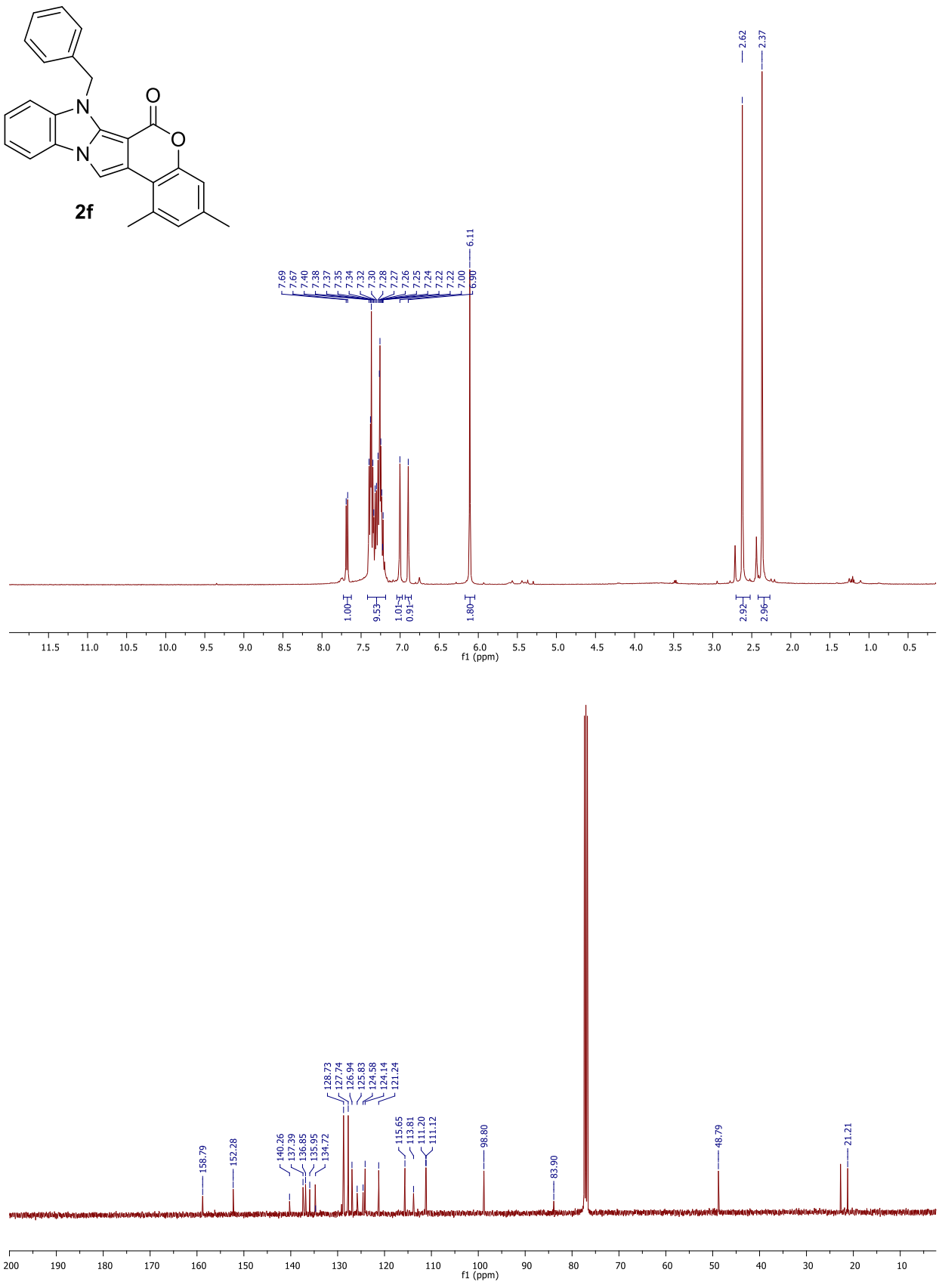

Figure S14. ^{1}H and ^{13}C NMR spectra of **2f**.

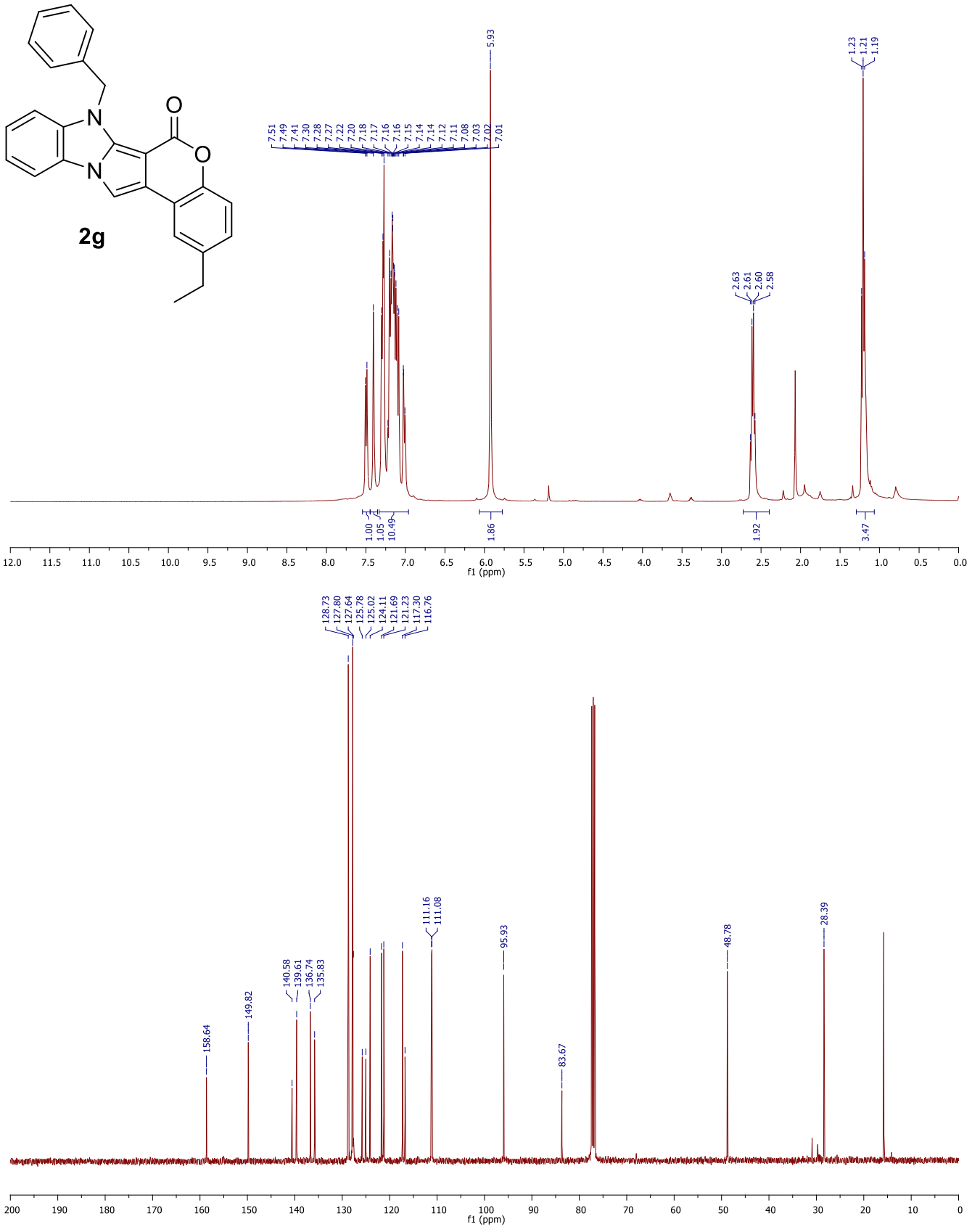

Figure S15. ^{1}H and ^{13}C NMR spectra of **2g**.

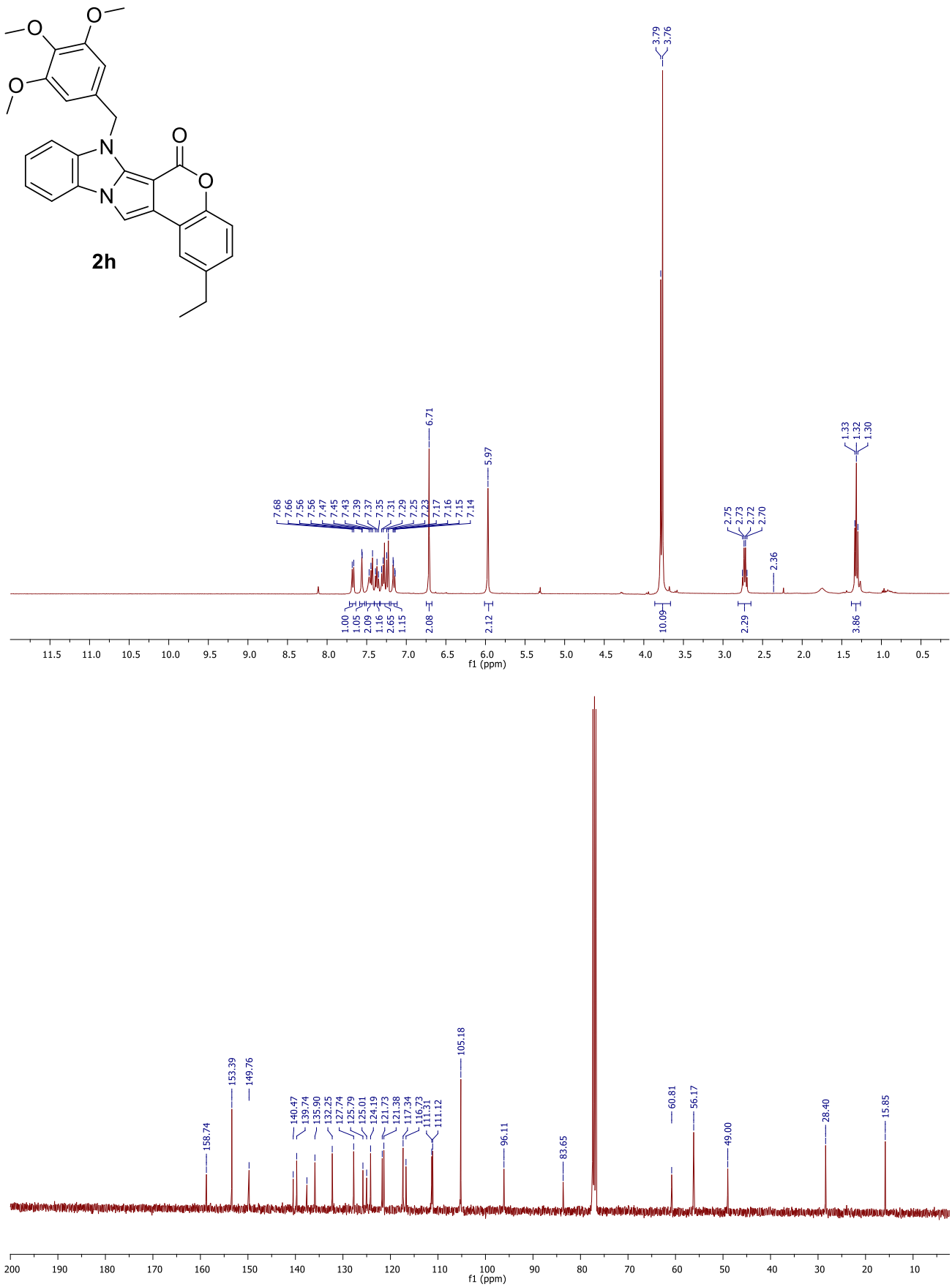

Figure S16. ^{1}H and ^{13}C NMR spectra of **2h**.

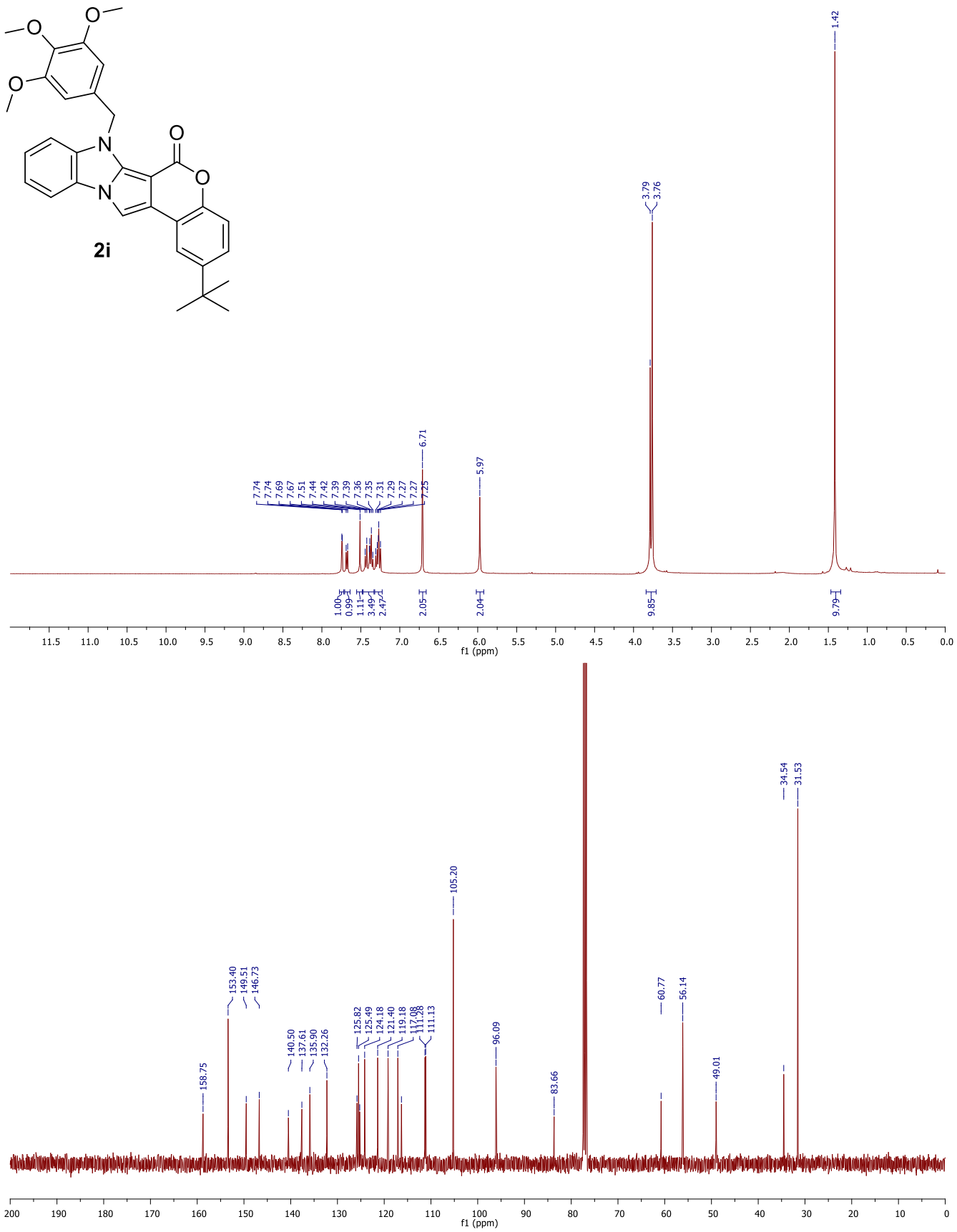

Figure S17. ^{1}H and ^{13}C NMR spectra of **2i**.

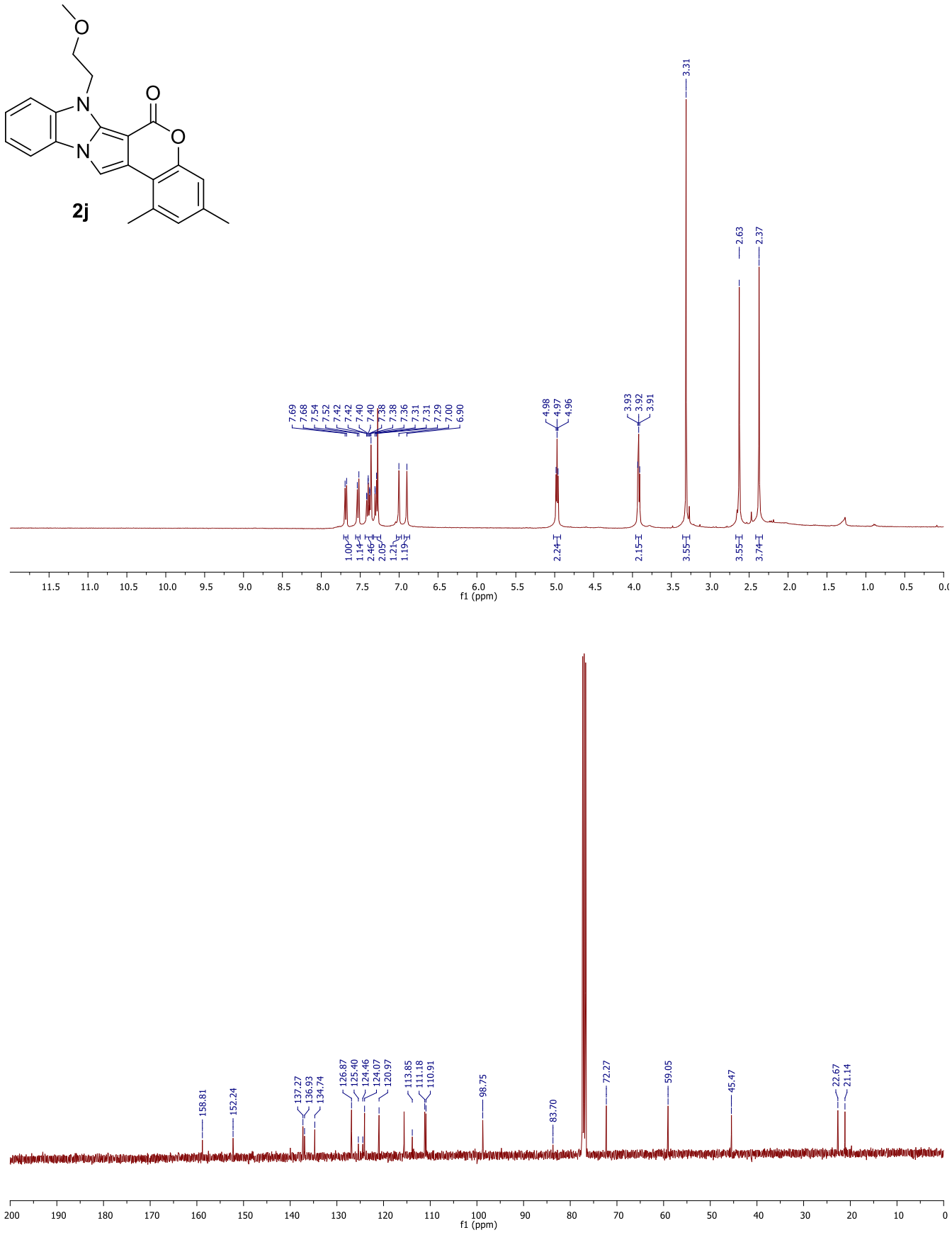

Figure S18. ^{1}H and ^{13}C NMR spectra of **2j**.

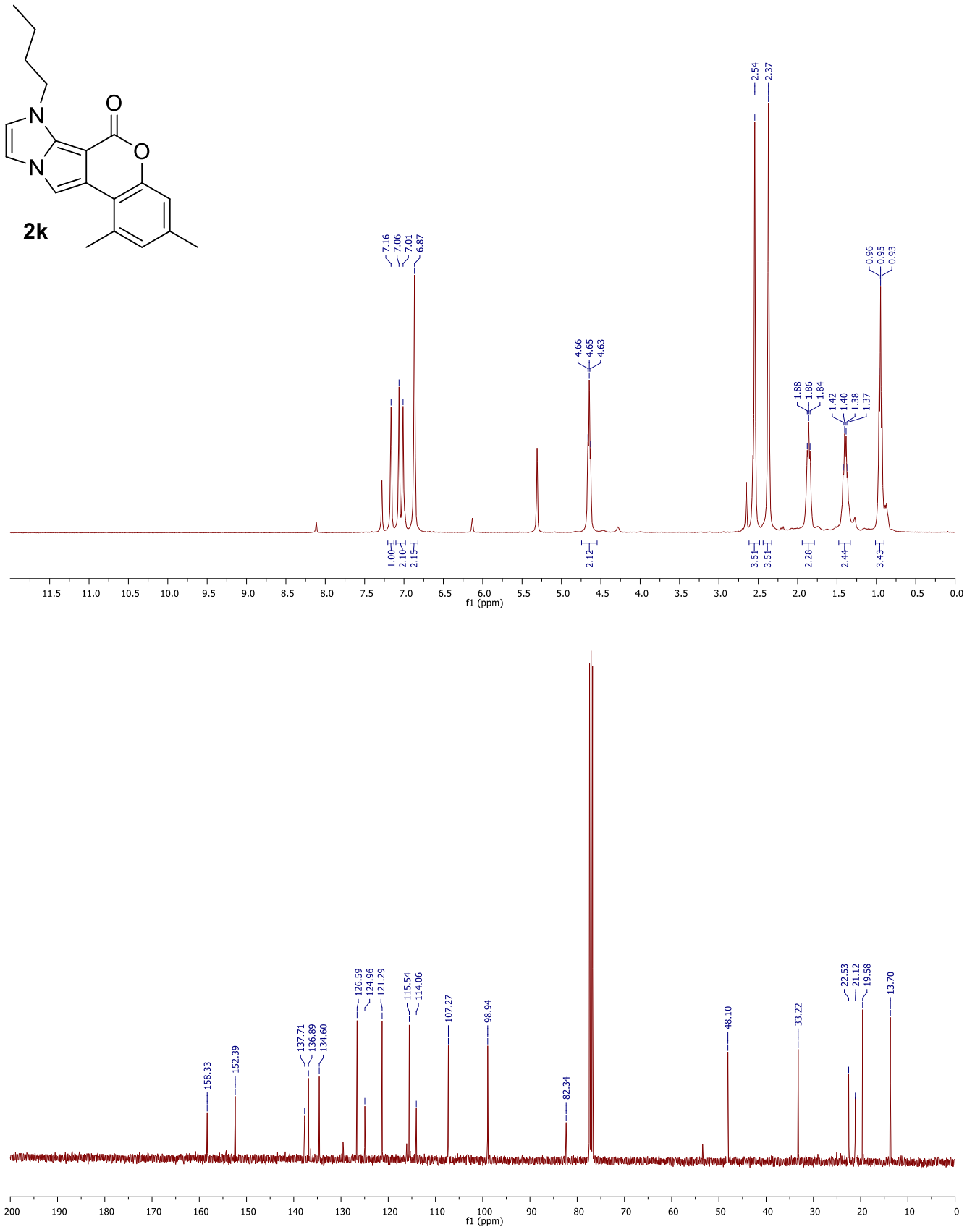

Figure S19. ^{1}H and ^{13}C NMR spectra of **2k**.

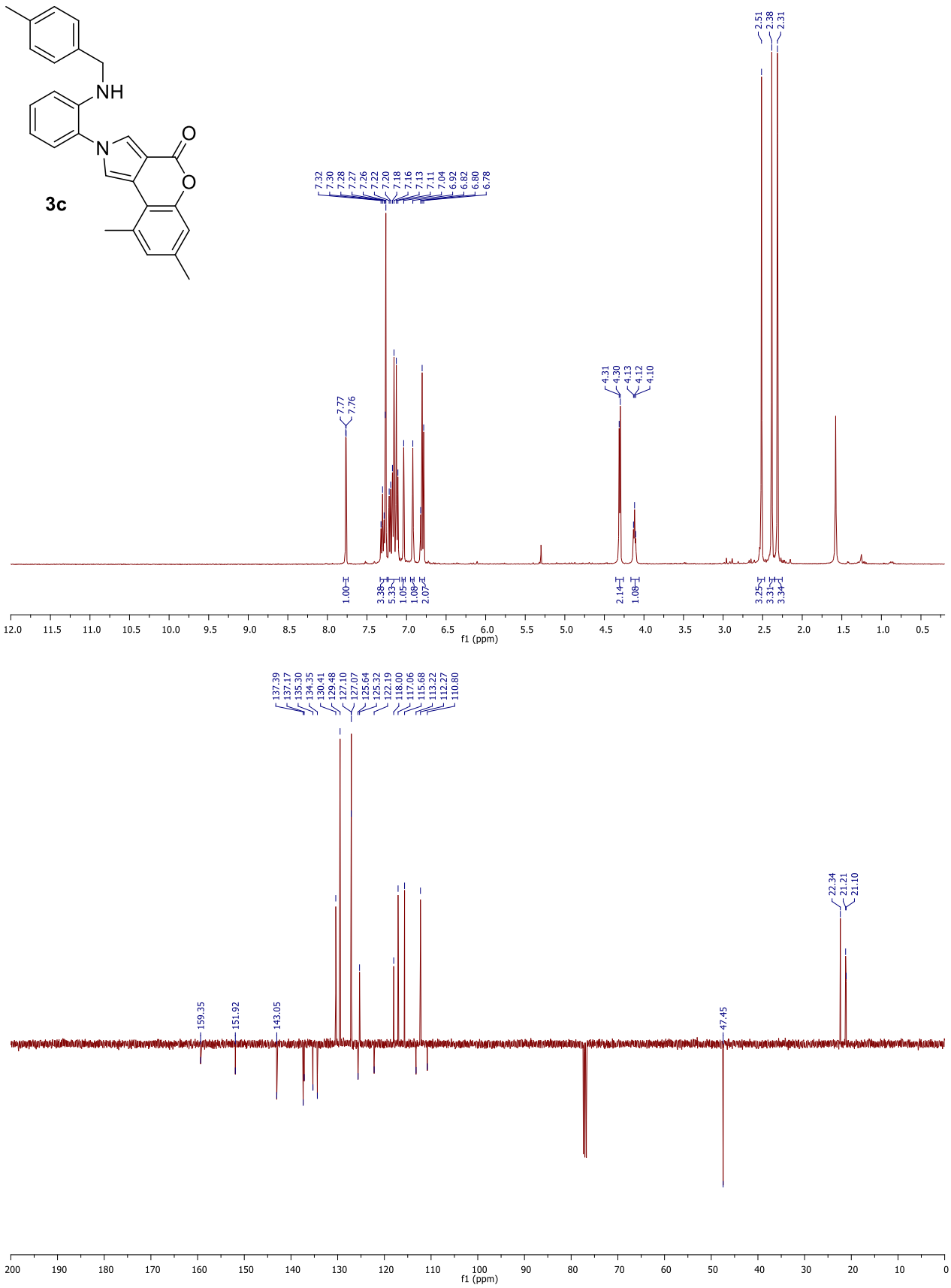

Figure S20. ^{1}H and ^{13}C-APT NMR spectra of **3c**.

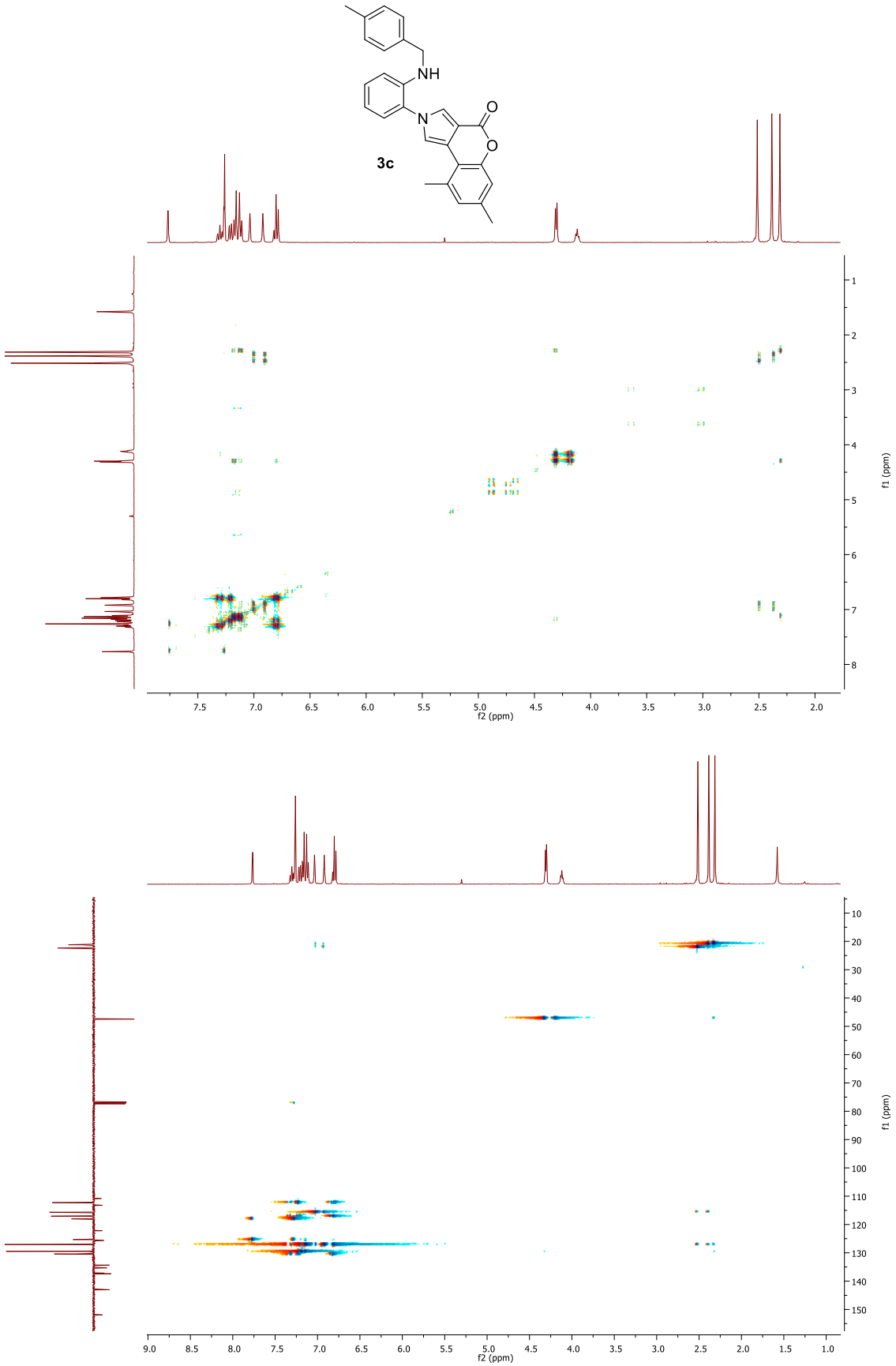

Figure S21. ^{1}H-^{1}H COSY (top) and ^{13}C-^{1}H HSQC (bottom) spectra of **3c**.

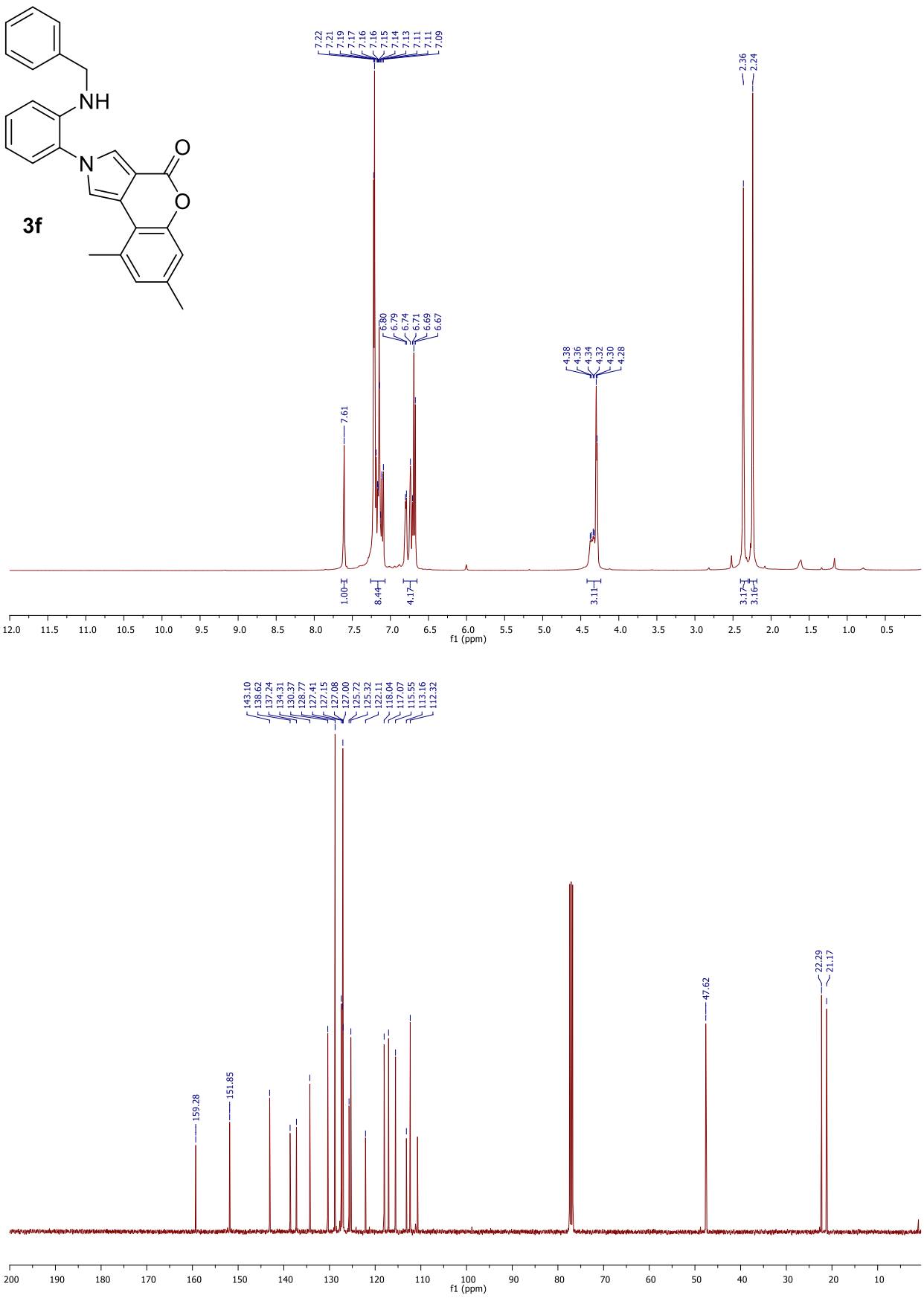

Figure S22. ^{1}H and ^{13}C NMR spectra of **3f**.

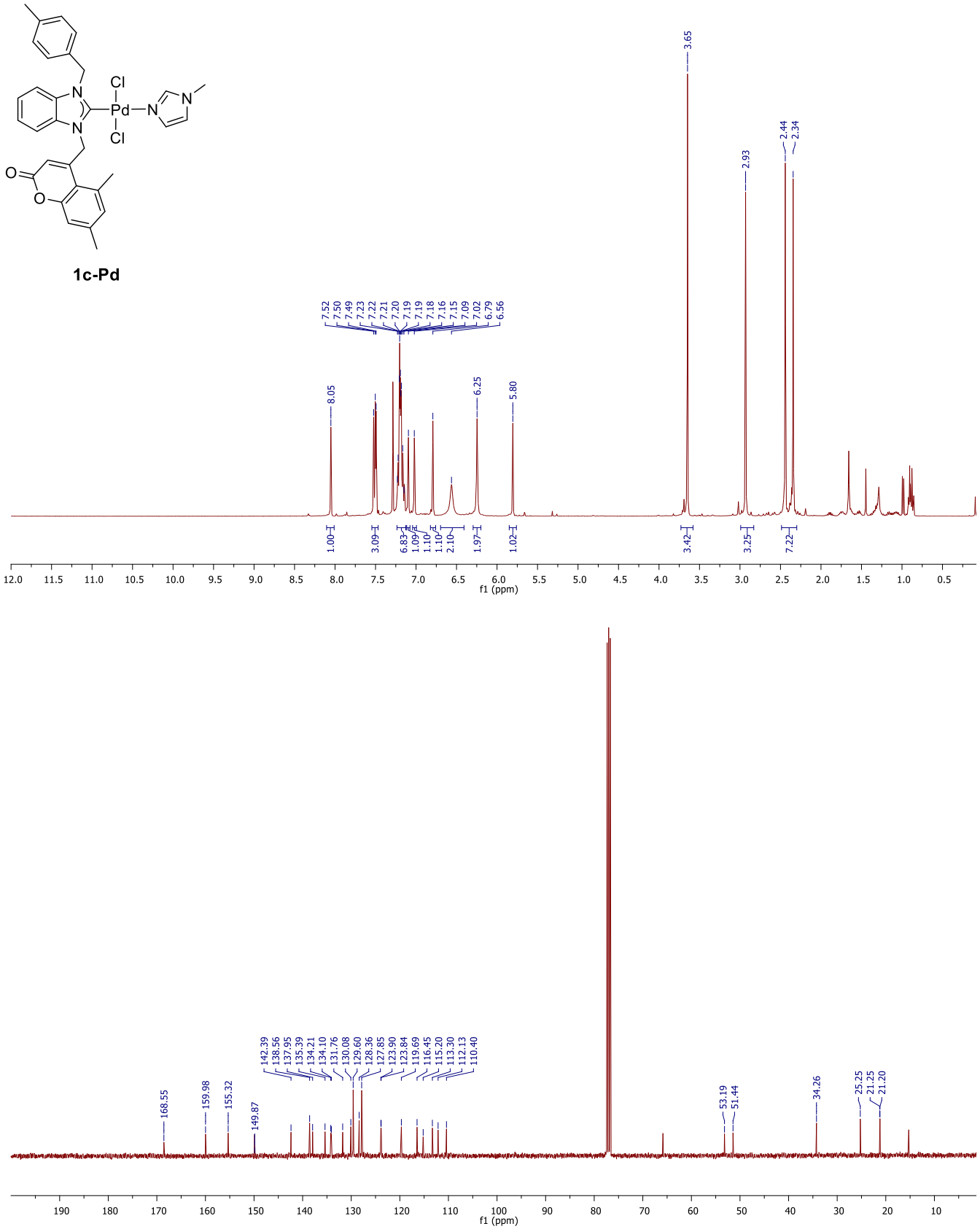

Figure S23. ^{1}H and ^{13}C NMR spectra of **1c-Pd**.

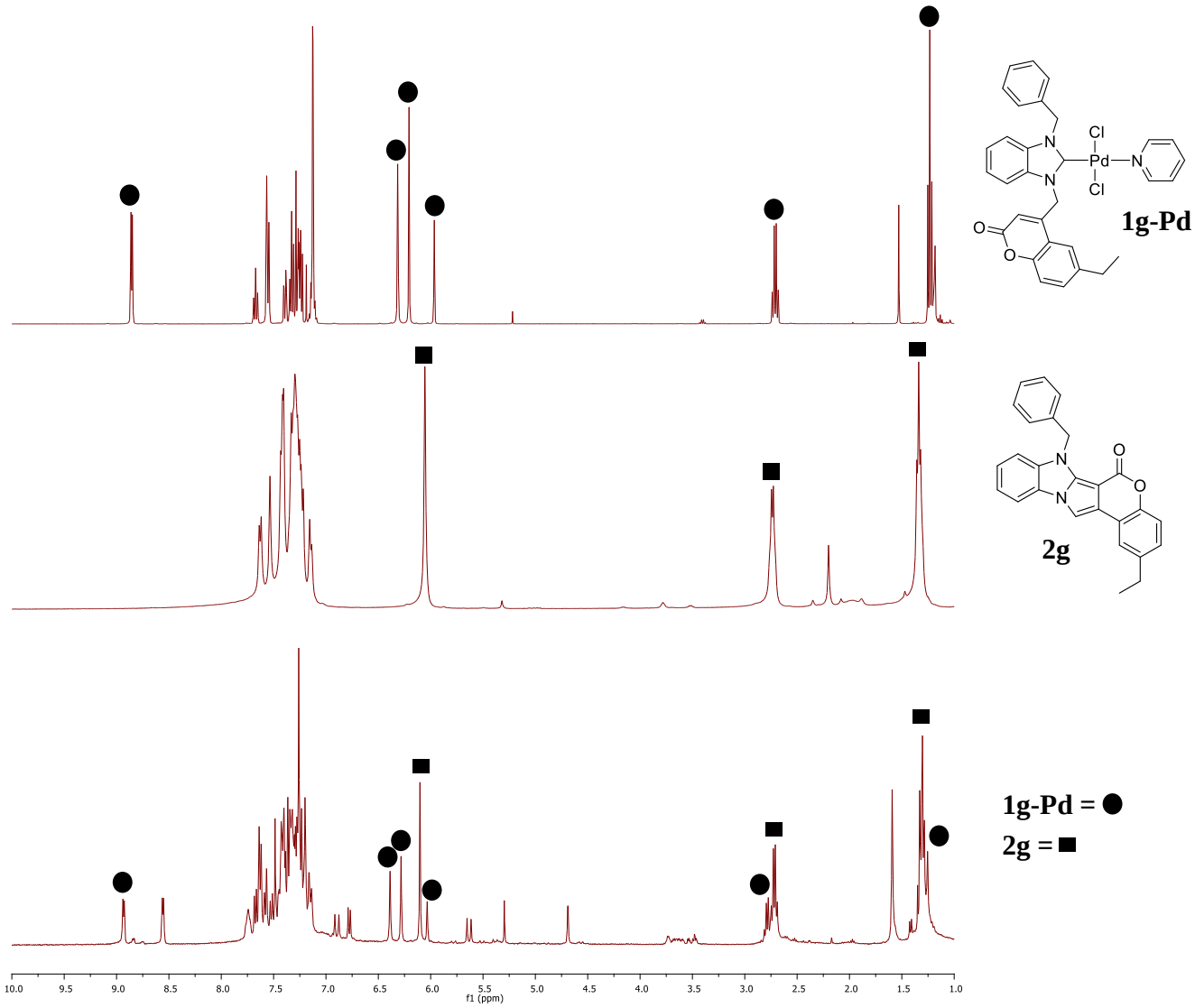

Figure S24. ^{1}H NMR spectra of the transformation of **1g-Pd** to **2g**.

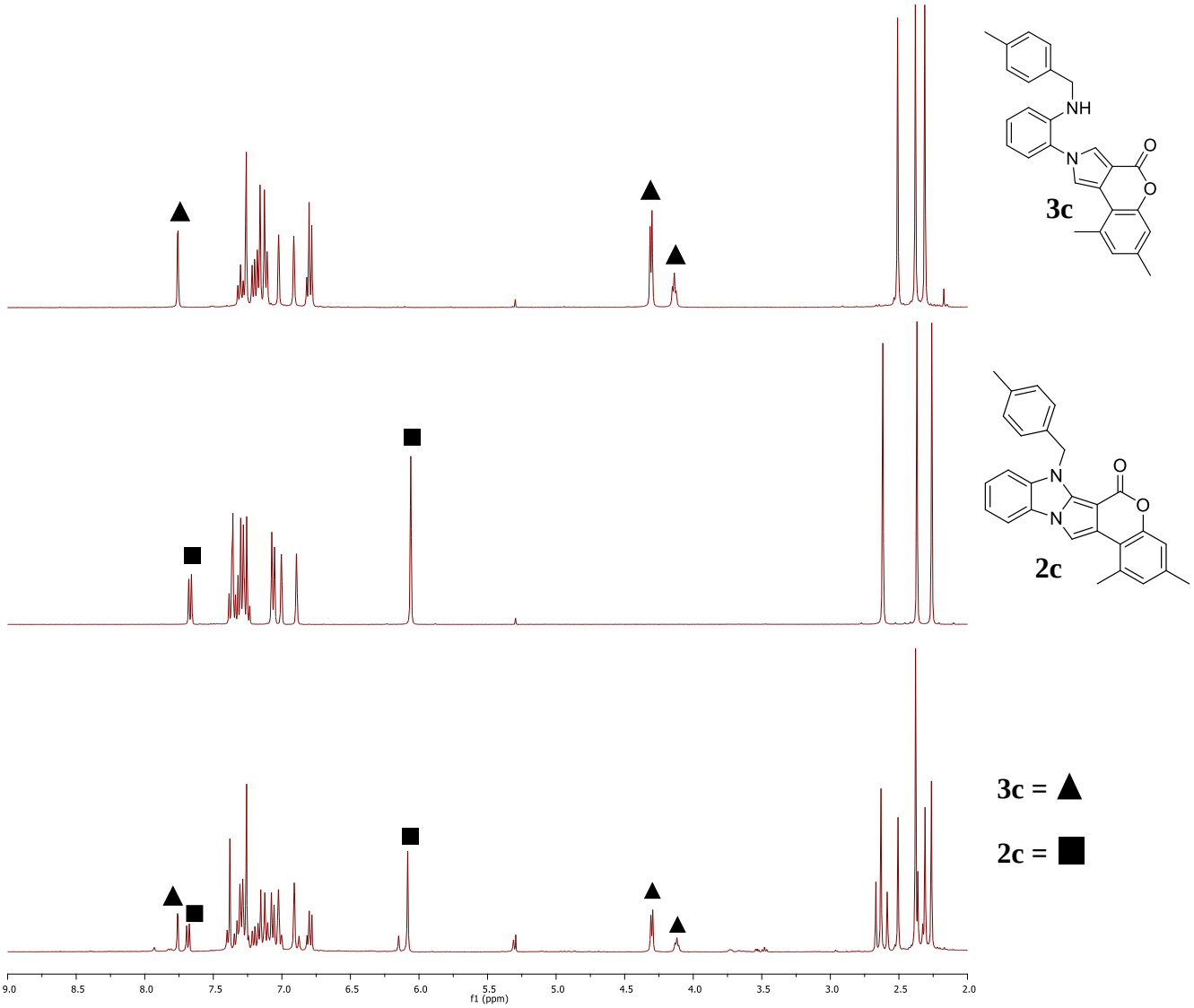

Figure S25. ^{1}H NMR spectra of the transformation of **3c** to **2c**.

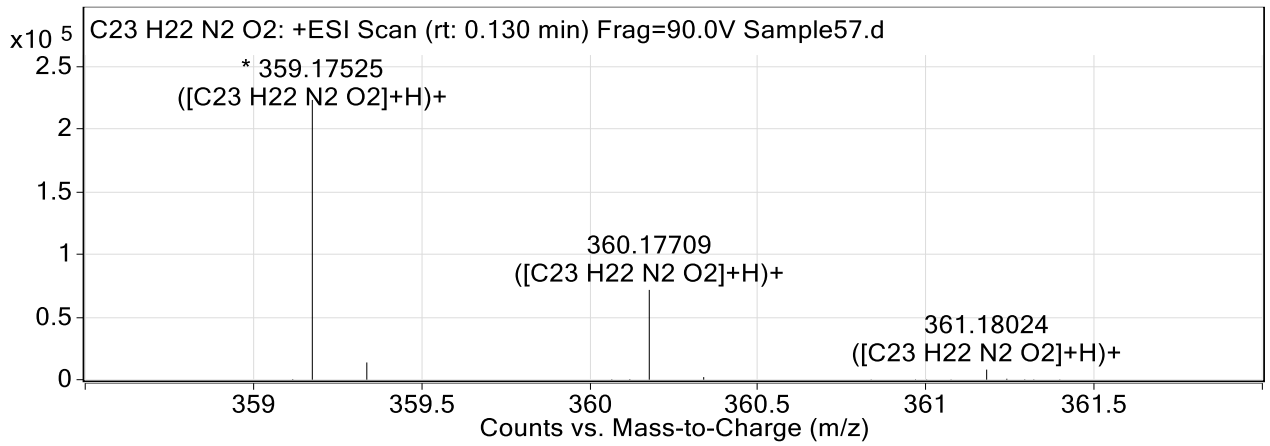

Figure S26. HRMS spectrum of **2a**.

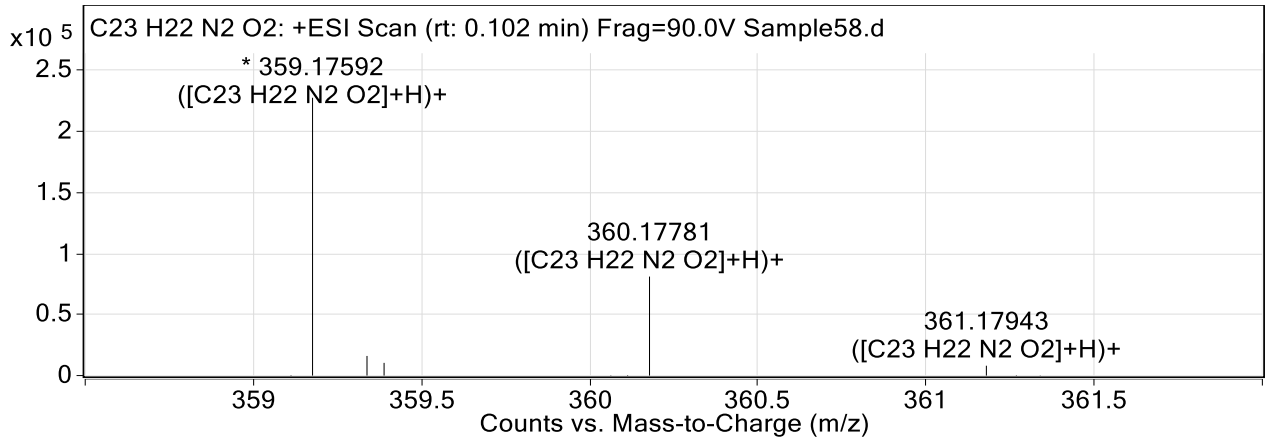

Figure S27. HRMS spectrum of **2b**.

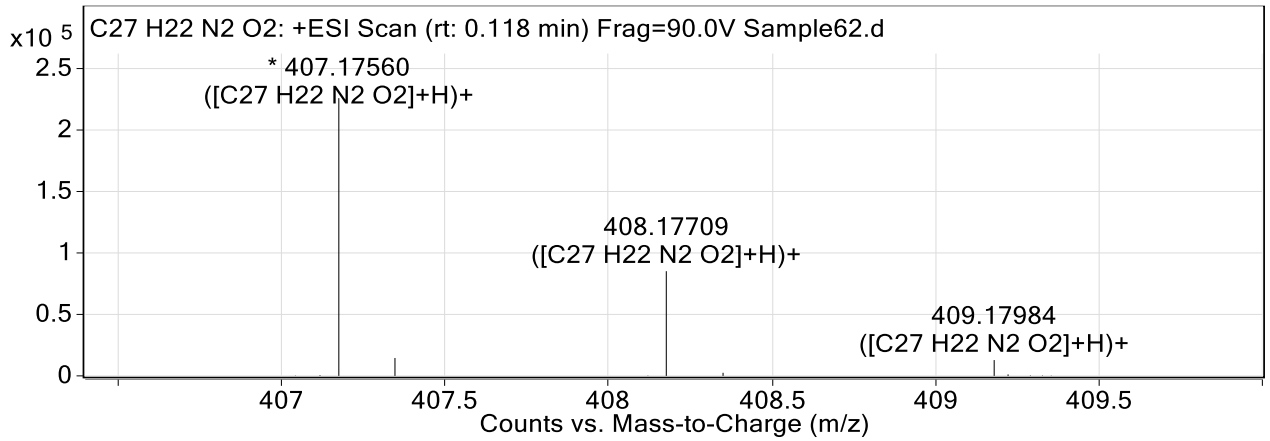

Figure S28. HRMS spectrum of **2c**.

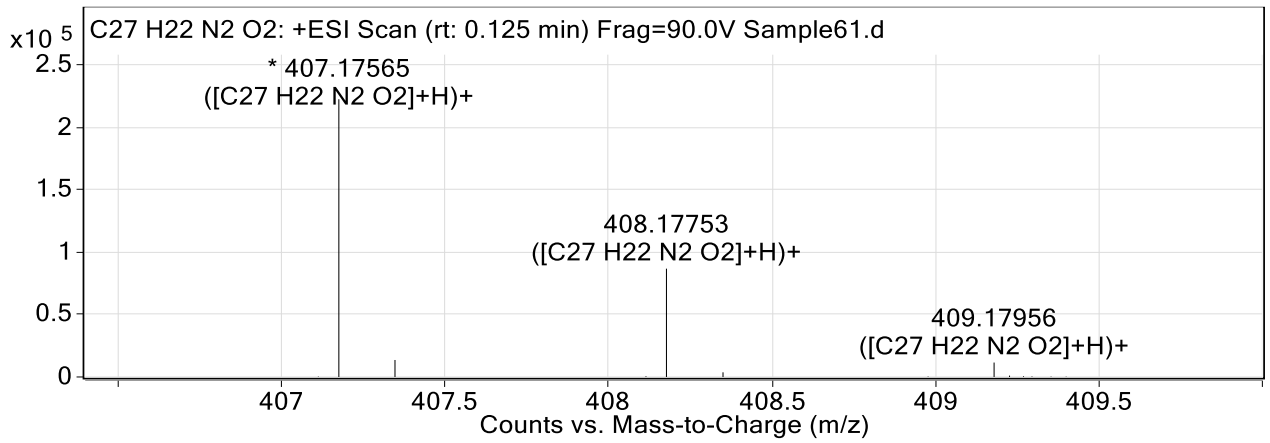

Figure S29. HRMS spectrum of **2d**.

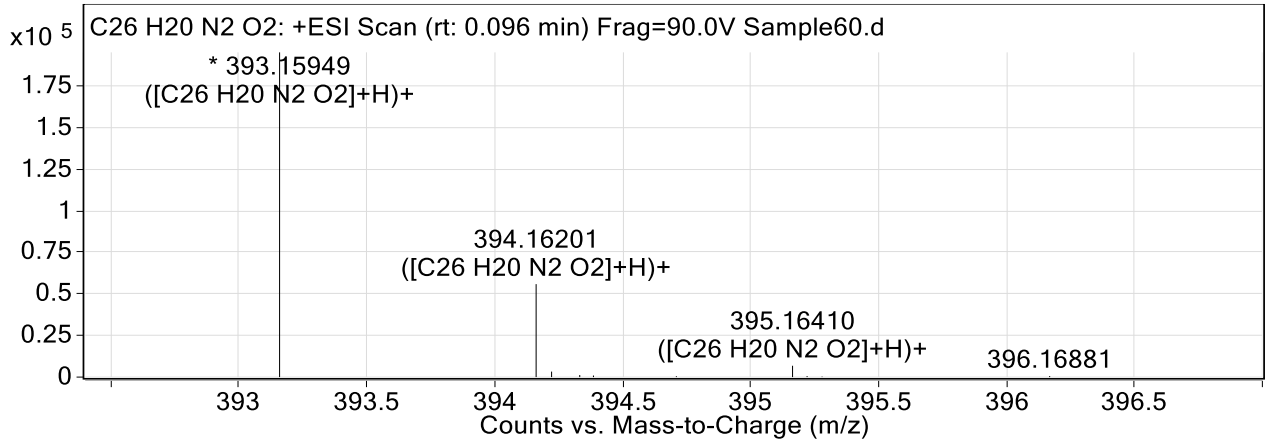

Figure S30. HRMS spectrum of **2e**.

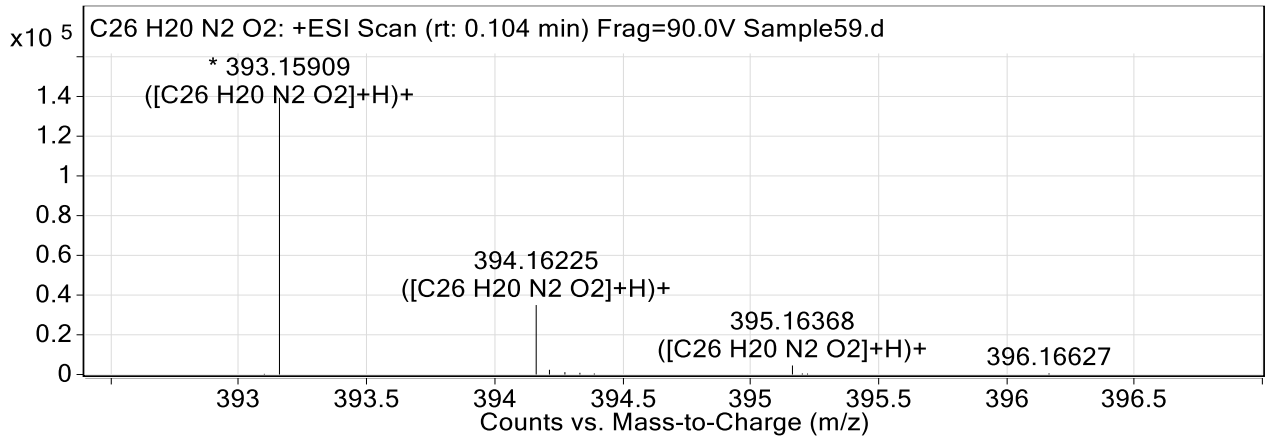

Figure S31. HRMS spectrum of **2f**.

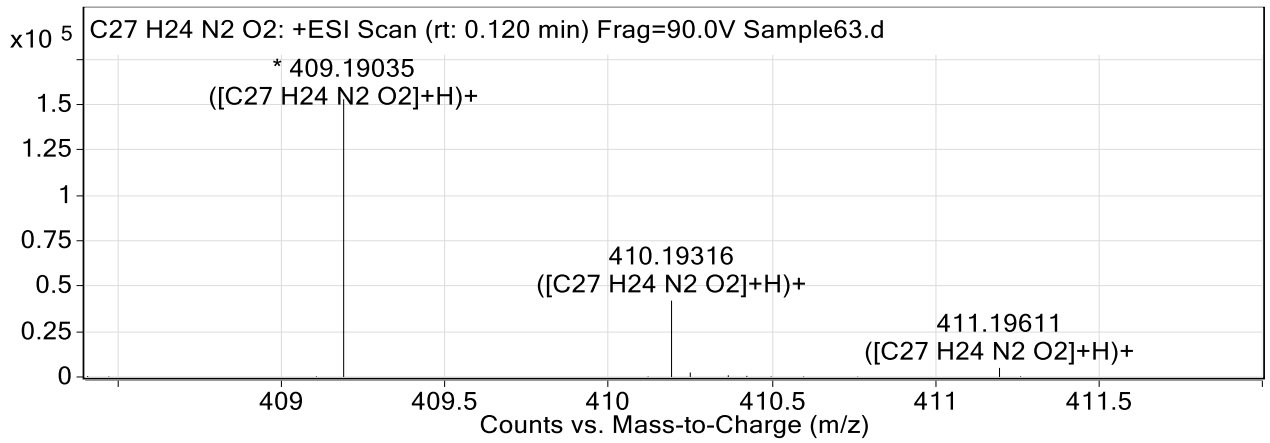

Figure S32. HRMS spectrum of **3c**.

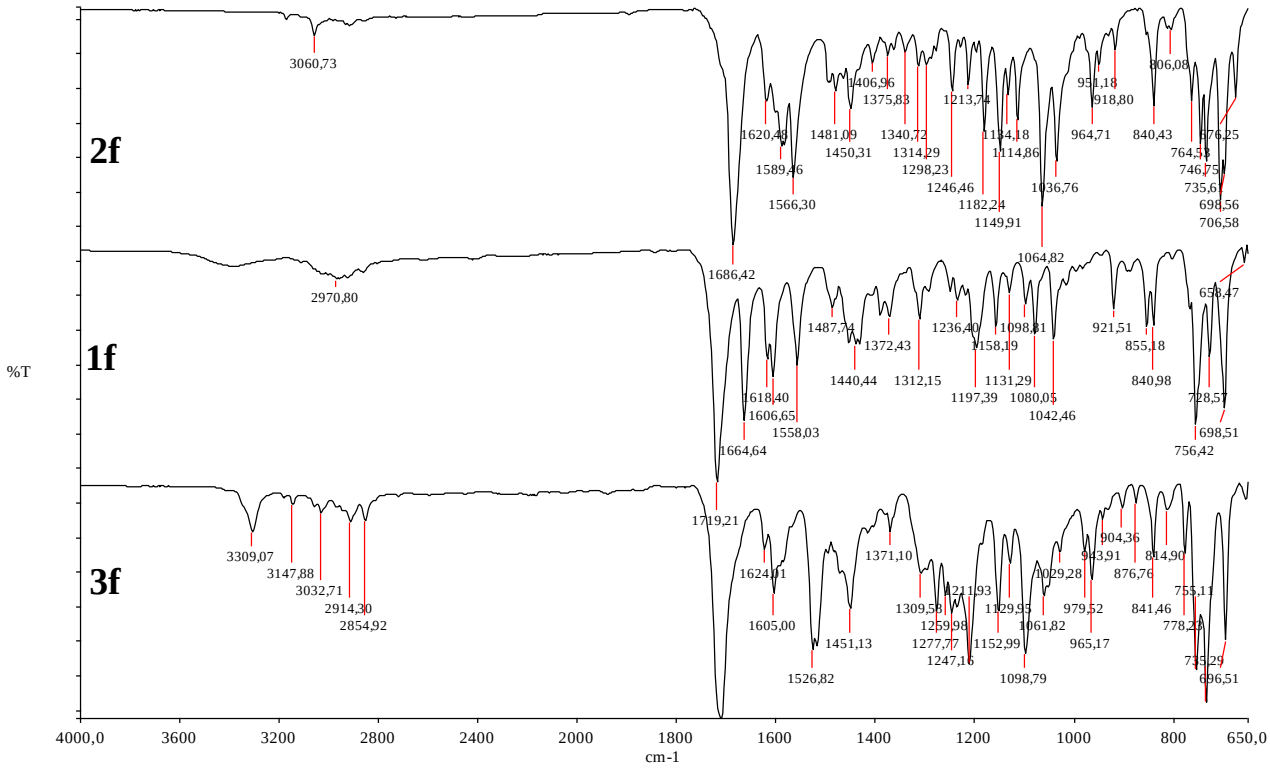

Figure S33. FT-IR spectra of **1f**, **2f** and **3f**.