

Electronic supplementary information (ESI)

Novel 3-substituted fluorine imidazolium/triazolium salt derivatives: Synthesis and antitumor activity

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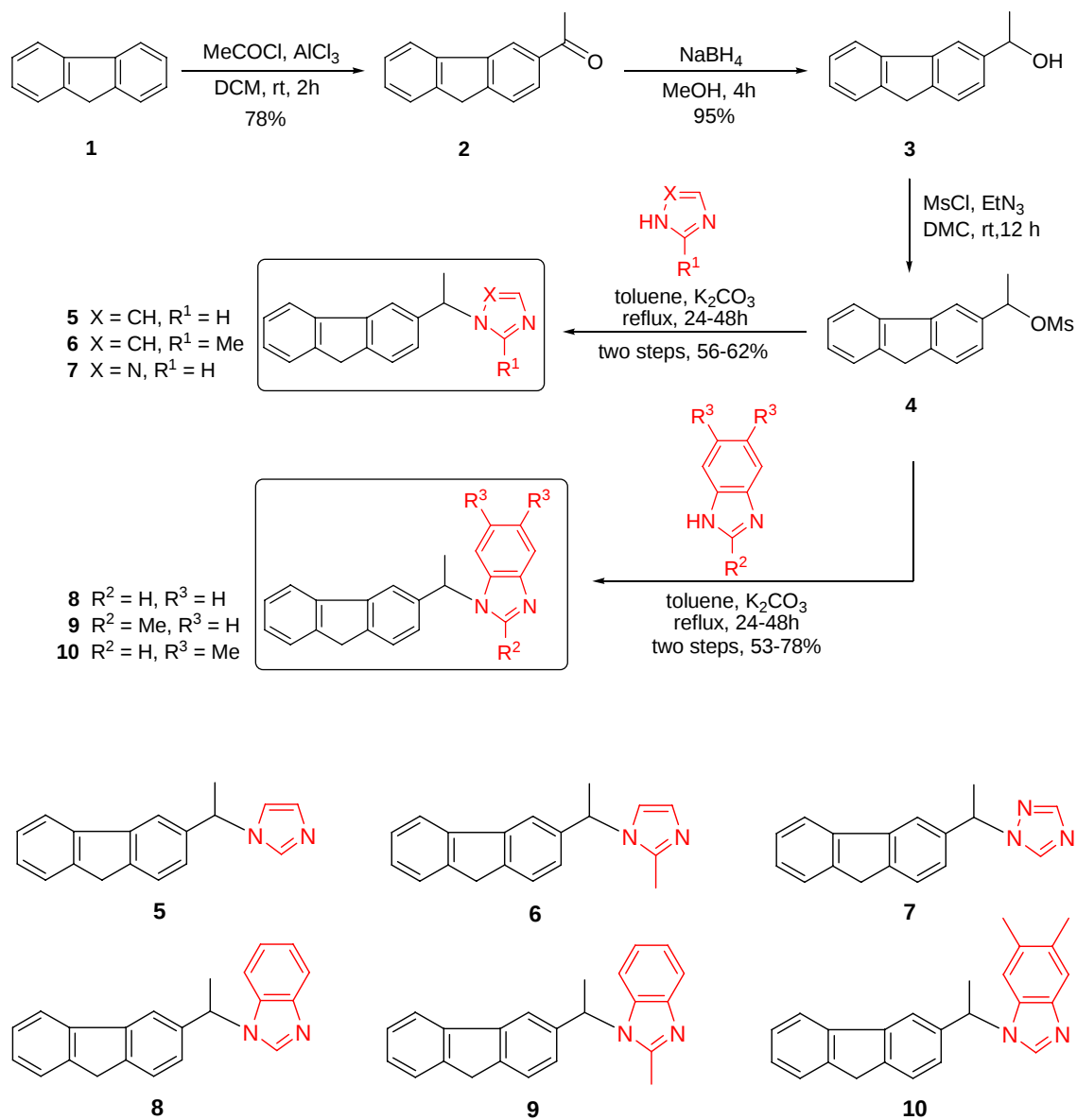
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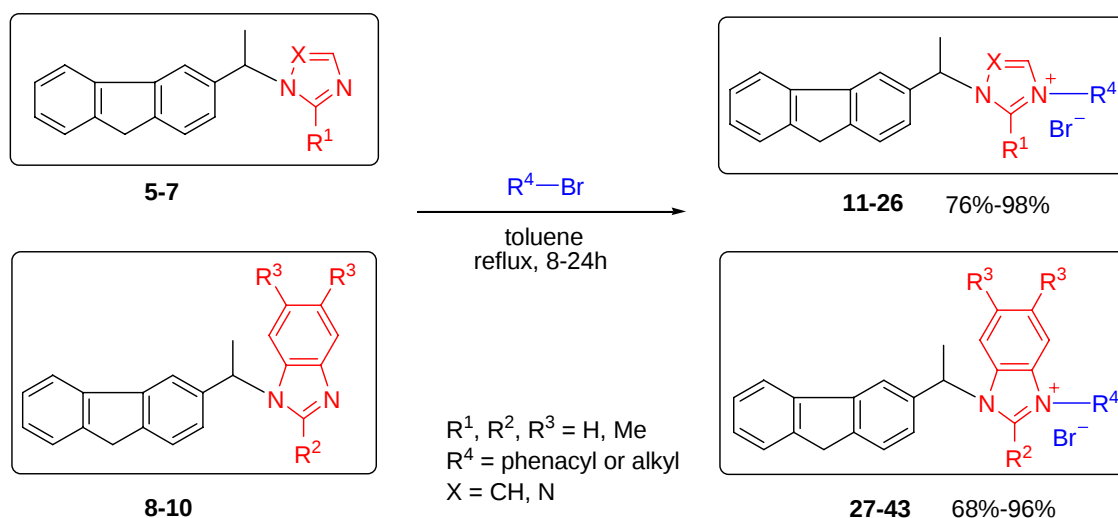
1. General Experimental

Melting points were obtained on a XT-4 melting-point apparatus and were uncorrected. Proton nuclear magnetic resonance (^1H -NMR) spectra were recorded on a BrukerAvance 300 spectrometer at 300 MHz. Carbon-13 nuclear magnetic resonance (^{13}C -NMR) was recorded on BrukerAvance 300 spectrometer at 75 MHz. Chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS) for all recorded NMR spectra. Low-resolution Mass spectra were recorded on a VG Auto Spec-3000 magnetic sector MS spectrometer. High Resolution Mass spectra were taken on AB QSTAR Pulsar mass spectrometer.

Silica gel (200–300 mesh) for column chromatography and silica GF₂₅₄ for TLC were produced by Qingdao Marine Chemical Company (China). All air- or moisture-sensitive reactions were conducted under an argon atmosphere. Starting materials and reagents used in reactions were obtained commercially from Acros, Aldrich, Fluka and were used without purification, unless otherwise indicated.

2. Experimental Procedures and Analytical Data

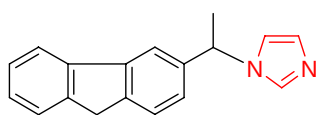




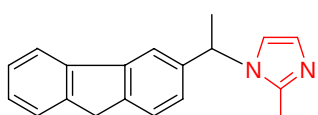
Synthesis of 3-substituted fluorene-imidazolium/triazolium salt derivatives **11-43**.

Entry	Compound no.	Imidazole/triazole ring	R^4	Molecular formula	Mp (°C)	Yields (%)
1	5	imidazole	—	$C_{18}H_{16}N_2$	188-190	62
2	6	2-methyl-imidazole	—	$C_{19}H_{18}N_2$	134-136	56
3	7	triazole	—	$C_{17}H_{15}N_3$	108-110	58
4	8	benzimidazole	—	$C_{22}H_{18}N_2$	179-181	78
5	9	2-methyl-benzimidazole	—	$C_{23}H_{20}N_2$	166-168	53
6	10	5,6-dimethyl-benzimidazole	—	$C_{24}H_{22}N_2$	182-184	60
7	11	imidazole	4-bromobenzyl	$C_{25}H_{22}Br_2N_2$	173-175	98
8	12	imidazole	phenacyl	$C_{26}H_{23}BrN_2O$	220-222	97
9	13	imidazole	4-bromophenacyl	$C_{26}H_{22}Br_2N_2O$	229-231	96
10	14	imidazole	4-fluorophenacyl	$C_{26}H_{22}BrFN_2O$	228-230	86
11	15	imidazole	4-methoxyphenacyl	$C_{27}H_{25}BrN_2O_2$	234-236	95
12	16	imidazole	naphthylacyl	$C_{30}H_{25}BrN_2O$	219-221	94
13	17	2-methyl-imidazole	4-bromobenzyl	$C_{26}H_{24}Br_2N_2$	215-217	85
14	18	2-methyl-imidazole	phenacyl	$C_{27}H_{25}BrN_2O$	158-160	80
15	19	2-methyl-imidazole	4-bromophenacyl	$C_{27}H_{24}Br_2N_2O$	193-195	89
16	20	2-methyl-imidazole	4-methoxyphenacyl	$C_{28}H_{27}BrN_2O_2$	195-197	88
17	21	2-methyl-imidazole	naphthylacyl	$C_{31}H_{27}BrN_2O$	170-172	90
18	22	triazole	4-bromobenzyl	$C_{24}H_{21}Br_2N_3$	112-114	80

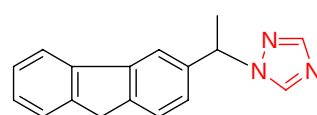
19	23	triazole	phenacyl	C ₂₅ H ₂₂ BrN ₃ O	150-152	78
20	24	triazole	4-bromophenacyl	C ₂₅ H ₂₁ Br ₂ N ₃ O	190-192	76
21	25	triazole	4-methoxyphenacyl	C ₂₆ H ₂₄ BrN ₃ O ₂	172-174	85
22	26	triazole	naphthylacyl	C ₂₉ H ₂₄ BrN ₃ O	153-155	80
23	27	benzimidazole	4-bromobenzyl	C ₂₉ H ₂₄ Br ₂ N ₂	182-184	90
24	28	benzimidazole	phenacyl	C ₃₀ H ₂₅ BrN ₂ O	149-151	83
25	29	benzimidazole	4-bromophenacyl	C ₃₀ H ₂₄ Br ₂ N ₂ O	174-176	86
26	30	benzimidazole	4-methoxyphenacyl	C ₃₁ H ₂₇ BrN ₂ O ₂	163-165	92
27	31	benzimidazole	naphthylacyl	C ₃₄ H ₂₇ BrN ₂ O	164-166	88
28	32	2-methyl-benzimidazole	4-bromobenzyl	C ₃₀ H ₂₆ Br ₂ N ₂	191-193	80
29	33	2-methyl-benzimidazole	phenacyl	C ₃₁ H ₂₇ BrN ₂ O	203-205	76
30	34	2-methyl-benzimidazole	4-bromophenacyl	C ₃₁ H ₂₆ Br ₂ N ₂ O	165-167	76
31	35	2-methyl-benzimidazole	4-fluorophenacyl	C ₃₁ H ₂₆ BrFN ₂ O	165-167	70
32	36	2-methyl-benzimidazole	4-methoxyphenacyl	C ₃₂ H ₂₉ BrN ₂ O ₂	157-159	89
33	37	2-methyl-benzimidazole	naphthylacyl	C ₃₅ H ₂₉ BrN ₂ O	165-167	80
34	38	5,6-dimethyl-benzimidazole	4-bromobenzyl	C ₃₁ H ₂₈ Br ₂ N ₂	172-174	95
35	39	5,6-dimethyl-benzimidazole	phenacyl	C ₃₂ H ₂₉ BrN ₂ O	173-175	82
36	40	5,6-dimethyl-benzimidazole	4-bromophenacyl	C ₃₂ H ₂₈ Br ₂ N ₂ O	176 -178	70
37	41	5,6-dimethyl-benzimidazole	4-fluorophenacyl	C ₃₂ H ₂₉ BrFN ₂ O	172-174	82
38	42	5,6-dimethyl-benzimidazole	4-methoxyphenacyl	C ₃₃ H ₃₁ BrN ₂ O ₂	239-241	96
39	43	5,6-dimethyl-benzimidazole	naphthylacyl	C ₃₆ H ₃₁ BrN ₂ O	244-246	92



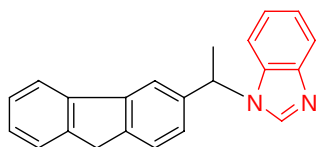
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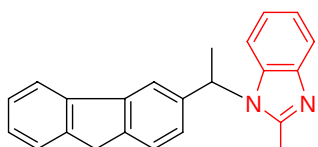
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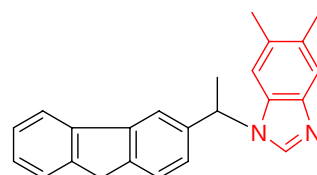
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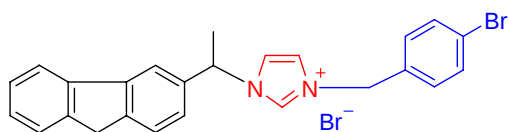
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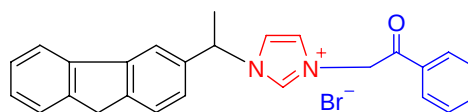
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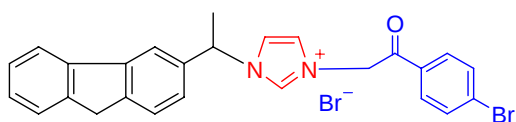
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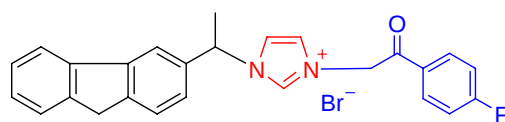
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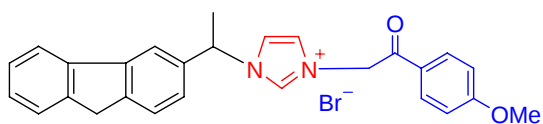
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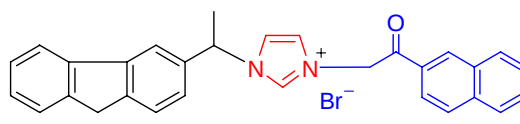
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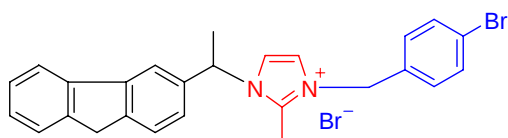
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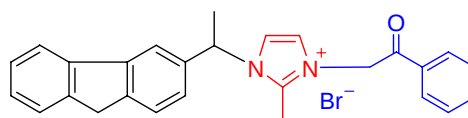
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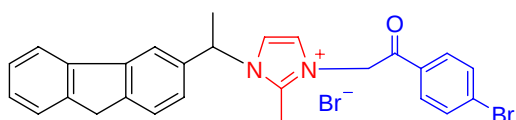
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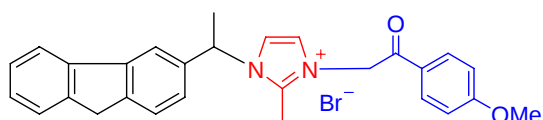
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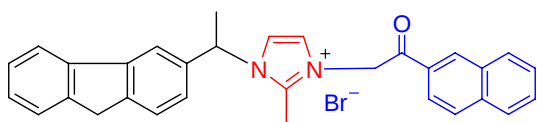
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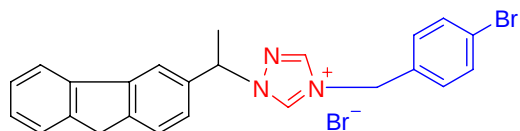
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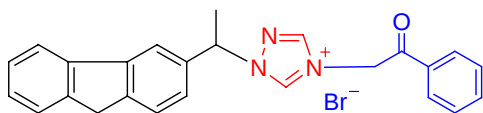
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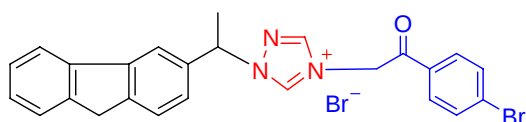
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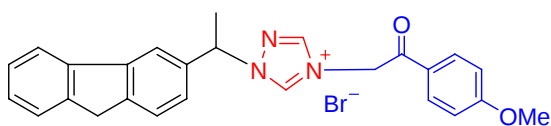
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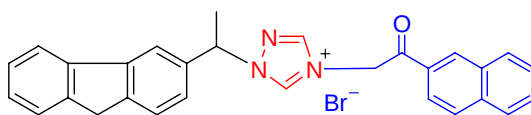
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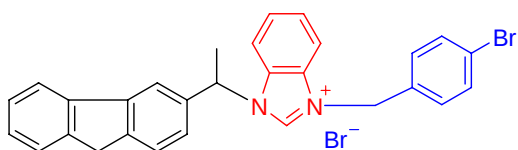
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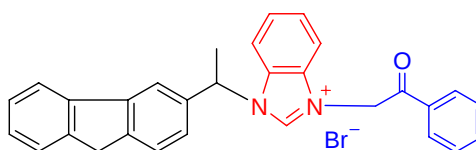
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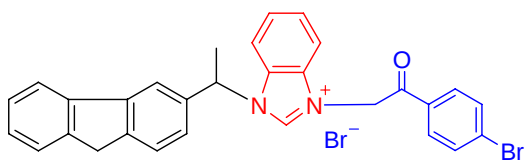
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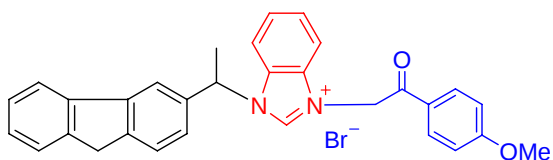
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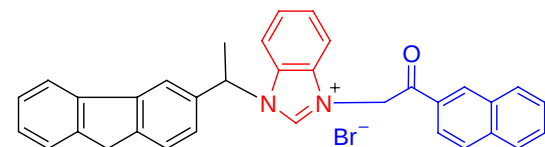
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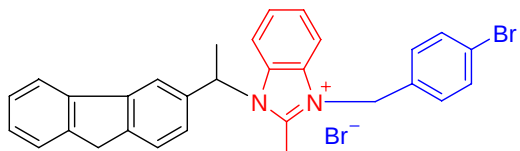
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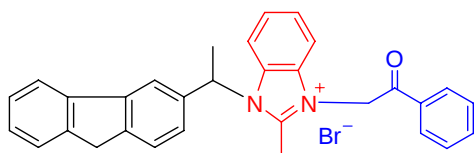
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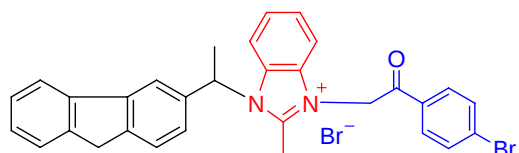
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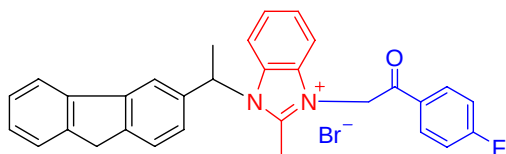
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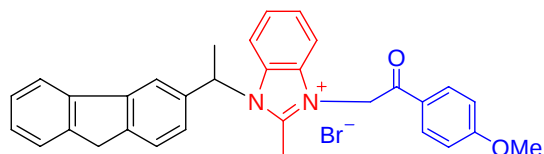
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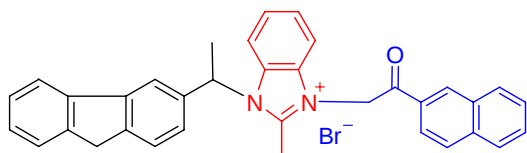
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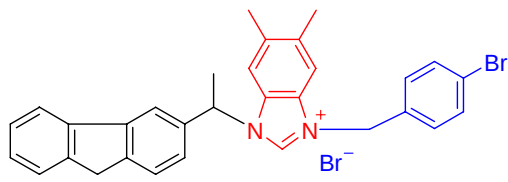
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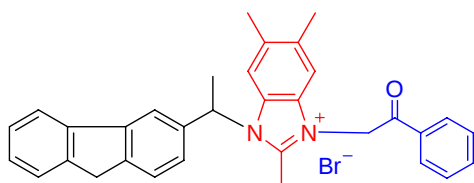
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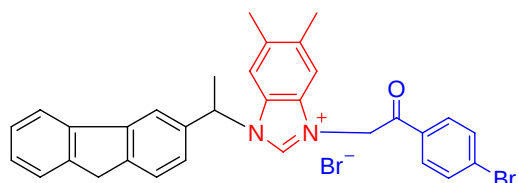
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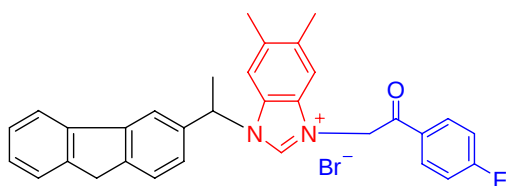
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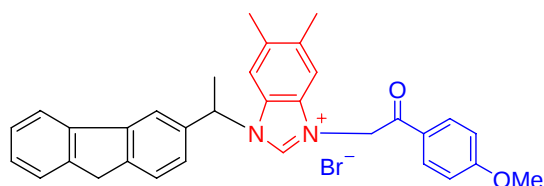
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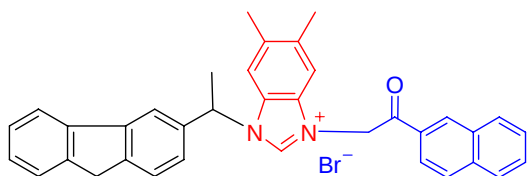
40 (70%)



41 (82%)

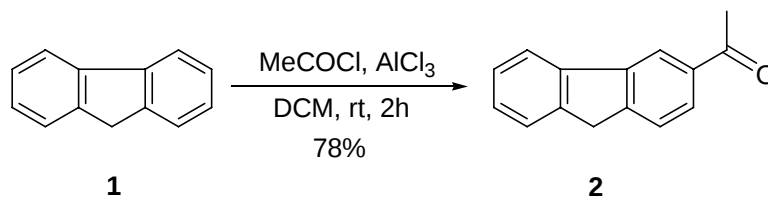


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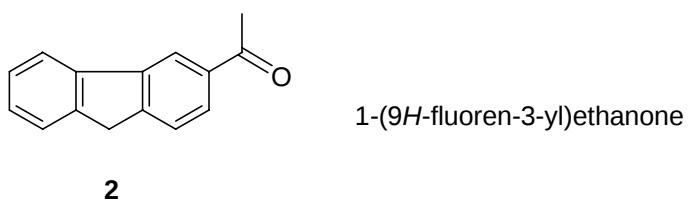


43 (92%)

2.1 Synthesis of compound 2

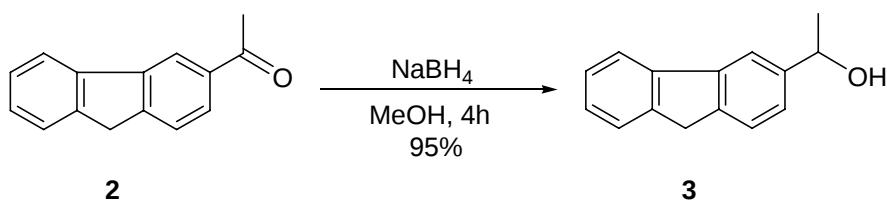


Anhydrous AlCl₃ (4.83 g, 36.20 mmol) in dichloromethane (50 mL) was added to acetyl chloride (1.71 g, 21.70 mmol) at 0 °C and then fluorene **1** (3.00 g, 18.10 mmol) in dichloromethane (100 mL) slowly, and then at ambient temperature for 2 h. After the reaction (TLC) was completed, the reaction mixture was quenched with 1 N HCl and extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with H₂O, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuum. The residue was chromatographed on silica gel (petroleum ether 60-90 °C : EtOAc = 15:1) to afford the product **2** (2.94 g, 78%) as white powder.

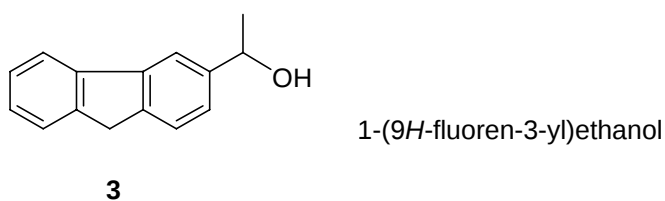


Yield 78%. White solid. ¹H NMR (300 MHz, CDCl₃) δ: 8.11 (1H, s), 7.98 (1H, d, J = 7.8 Hz), 7.78-7.83 (2H, dd, J = 12.6, 5.1 Hz), 7.56 (1H, d, J = 6.9 Hz), 7.36-7.40 (2H, m), 3.91 (2H, s), 2.63 (3H, s). ¹³C NMR (75 MHz, CDCl₃) δ: 197.91 (C), 146.41 (C), 144.51 (C), 143.30 (C), 140.49 (C), 135.66 (C), 128.01 (CH), 127.73 (CH), 127.06 (CH), 125.24 (CH), 124.93 (CH), 120.87 (CH), 119.63 (CH), 36.88 (CH₂), 26.72 (CH₃).

2.2 Synthesis of compound 3

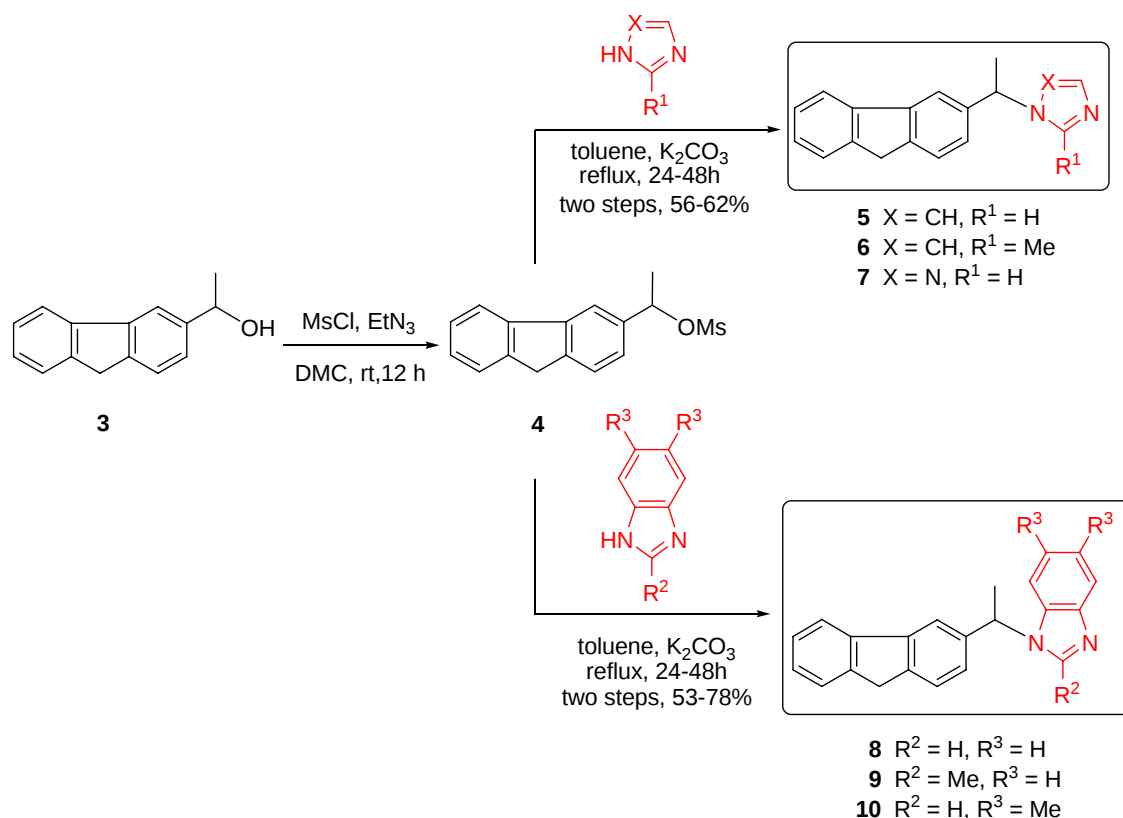


To a stirred solution of 1-(9*H*-fluoren-3-yl)ethanone **2** (2.30 g, 11.10 mmol) in methanol (25 mL) at 0 °C was added NaBH₄ (0.63 g, 16.65 mmol) in small portions over a period of 20 minutes, and then at ambient temperature for 4 h. Reaction progress was monitored by TLC. A small amount of water was added and the mixture was stirred for 15 min before rotary evaporation. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel (petroleum ether 60-90 °C : EtOAc = 10:1) to afford the products **3** (2.21 g, 95%) as white powder.

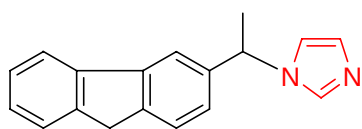


Yield 95%. White solid. ¹H NMR (300 MHz, CDCl₃) δ: 7.74 (2H, dd, J = 16.2, 8.1 Hz), 7.54 (1H, s), 7.51 (1 H, s), 7.37 (2H, d, J = 6.3 Hz), 7.24-7.33 (1H, m), 4.92-4.98 (1H, m), 3.86 (2H, s), 1.95 (1H, s), 1.53 (3H, d, J = 6.3 Hz). ¹³C NMR (75 MHz, CDCl₃) δ: 144.56 (C), 143.62 (C), 143.38 (C), 141.45 (C), 141.17 (C), 126.75 (CH), 1126.65 (CH), 125.03 (CH), 124.20 (CH), 122.07 (CH), 119.84 (CH), 70.65 (CH), 36.90 (CH₂), 25.31 (CH₃).

2.3 Synthesis of hybrid compounds 5-10



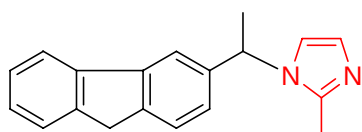
To a solution of 1-(9H-fluoren-3-yl)ethanol **3** (210 mg, 1.00 mmol) in dichloromethane (50 mL) was added methanesulfonyl chloride (1.2 mmol) and triethylamine (2 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 12 h. After quenching the reaction with water (50 mL), the layers were separated. The organic phase was dried over anhydrous Na_2SO_4 and concentrated, and used for the next synthetic step. A mixture of the previous methanesulfonate **4** and various substituted imidazole, benzimidazole or triazole (6 mmol) and K_2CO_3 (3 mmol) was stirred in toluene (20 mL) at reflux for 24–48 h (monitored by TLC). After cooling to room temperature, the solvent was concentrated, and the residue was diluted with EtOAc (20 mL). The organic layer was washed with water (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, petroleum ether 60–90 °C : EtOAc = 1:1) to afford **5-10** in 53-78% yield as white powder.



(±)-1-(1-(9H-fluoren-3-yl)ethyl)-1H-imidazole

5

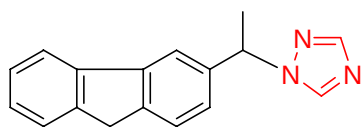
Yield 62%. White solid, Mp 188-190 °C. IR $\nu_{\max}$ (cm⁻¹): 2971, 1605, 1498, 1397, 1225, 1085, 740. ¹H NMR (300 MHz, CDCl₃) δ : 7.70-7.75 (2H, m), 7.62 (1H, s), 7.51 (1H, d, J = 7.2 Hz), 7.31-7.38 (3H, m), 7.16 (1H, d, J = 7.8 Hz), 7.09 (1H, s), 6.95 (1H, s), 5.34-5.41 (1H, m), 3.83 (2H, s), 1.87 (3H, d, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 143.97 (C), 143.34 (C), 141.75 (C), 140.94 (C), 140.03 (C), 136.08 (CH), 129.32 (CH), 127.02 (CH), 126.86 (CH), 125.08 (CH), 124.85 (CH), 122.68 (CH), 120.11 (CH), 120.00 (CH), 118.03 (CH), 56.78 (CH), 36.87 (CH₂), 22.21 (CH₃). Anal. Calcd for C₁₈H₁₆N₂: C, 83.04; H, 6.19; N, 10.76. Found: C, Found: C, 82.74; H, 5.81; N 10.65. HRMS (ESI-TOF) m/z Calcd for C₁₈H₁₇N₂ [M+1]⁺ 261.1392, found 261.1395.



(±)-1-(1-(9H-fluoren-3-yl)ethyl)-2-methyl-1H-imidazole

6

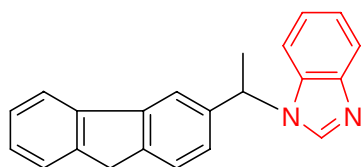
Yield 56%. White solid, Mp 134-136 °C. IR $\nu_{\max}$ (cm⁻¹): 3161, 2974, 1660, 1490, 1268, 1105, 990, 737. ¹H NMR (300 MHz, CDCl₃) δ : 7.70-7.76 (2H, m), 7.53 (1H, d, J = 7.2 Hz), 7.26-7.39 (2H, m), 7.18 (1H, s), 7.01-7.10 (3H, m), 5.33-5.40 (1H, m), 3.84 (2H, s), 2.31 (3H, s), 1.85 (3H, d, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 143.99 (C), 143.31 (C), 141.42 (C), 140.99 (C), 140.31 (C), 126.95 (CH), 126.84 (CH), 125.07 (CH), 124.55 (CH), 122.32 (C), 120.09 (CH), 119.95 (CH), 116.78 (CH), 55.27 (CH), 36.89 (CH₂), 22.55 (CH₃), 13.52 (CH₃). Anal. Calcd for C₁₉H₁₈N₂: C, 83.18; H, 6.61; N, 10.21. Found: C, 83.13; H, 6.65; N 9.69. HRMS (ESI-TOF) m/z Calcd for C₁₉H₁₉N₂ [M+1]⁺ 275.1548, found 275.1553.



(±)-1-(1-(9H-fluoren-3-yl)ethyl)-1H-1,2,4-triazole

7

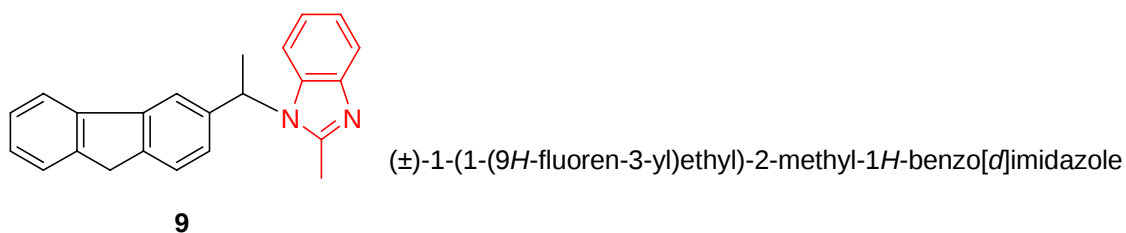
Yield 58%. White solid, Mp 108-110 °C. IR $\nu_{\max}$ (cm⁻¹): 3118, 3085, 2968, 2933, 1678, 1614, 1499, 1269, 1140, 1005, 946, 841, 734. ¹H NMR (300 MHz, CDCl₃) δ : 8.07 (1H, s), 7.99 (1H, s), 7.70-7.74 (2H, m), 7.50 (1H, d, J = 7.2 Hz), 7.40 (1H, s), 7.37 (1H, s), 7.24-7.35 (2H, m), 5.55-5.61 (1H, m), 3.83 (2H, s), 1.95 (3H, d, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 151.93 (CH), 144.01 (CH), 143.39 (C), 142.11 (C), 140.91 (C), 138.38 (C), 127.10 (CH), 126.87 (CH), 125.37 (CH), 125.08 (CH), 123.23 (CH), 120.21 (CH), 120.07 (CH), 59.87 (CH), 36.88 (CH₂), 21.47 (CH₃). Anal. Calcd for C₁₇H₁₅N₃: C, 78.13; H, 5.79; N, 16.08. Found: C, 78.03; H, 5.72; N 15.80. HRMS (ESI-TOF) m/z Calcd for C₁₇H₁₆N₃ [M+H]⁺ 262.1344, found 262.1349.



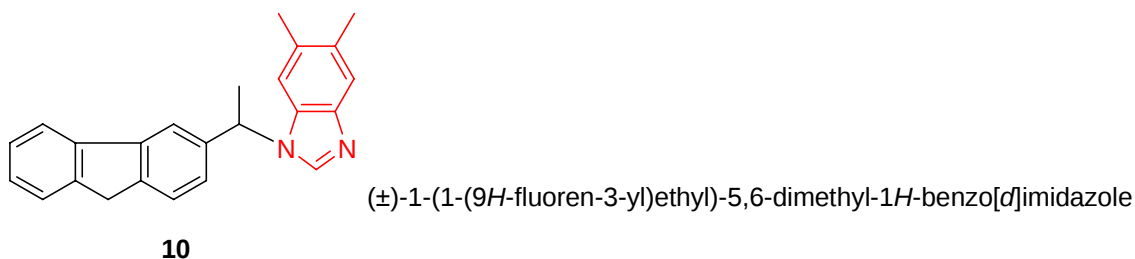
(±)-1-(1-(9H-fluoren-3-yl)ethyl)-1H-benzo[d]imidazole

8

Yield 68%. White solid, Mp 179-181 °C. IR $\nu_{\max}$ (cm⁻¹): 3051, 2970, 1607, 1484, 1223, 744. ¹H NMR (300 MHz, CDCl₃) δ : 8.15 (1H, s), 7.83 (1H, d, J = 7.8 Hz), 7.71 (2H, dd, J = 15.0, 7.2 Hz), 7.48 (1H, d, J = 6.9 Hz), 7.27-7.36 (3H, m), 7.14-7.23 (4H, m), 5.61-5.68 (1H, m), 3.78 (2H, s), 2.00 (3H, d, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 144.11 (C), 143.71 (C), 143.35 (C), 141.85 (C), 141.03 (CH), 140.93 (CH), 139.11 (C), 133.64 (C), 127.05 (CH), 126.87 (CH), 125.08 (CH), 124.84 (CH), 122.99 (CH), 122.63 (CH), 122.44 (CH), 120.22 (CH), 120.00 (CH), 110.82 (CH), 55.57 (CH), 36.87 (CH₂), 21.80 (CH₃). Anal. Calcd for C₂₂H₁₈N₂: C, 85.13; H, 5.85; N, 9.03. Found: C, 85.03; H, 5.89; N 8.86. HRMS (ESI-TOF) m/z Calcd for C₂₂H₁₉N₂ [M+1]⁺ 311.1548, found 311.1551.



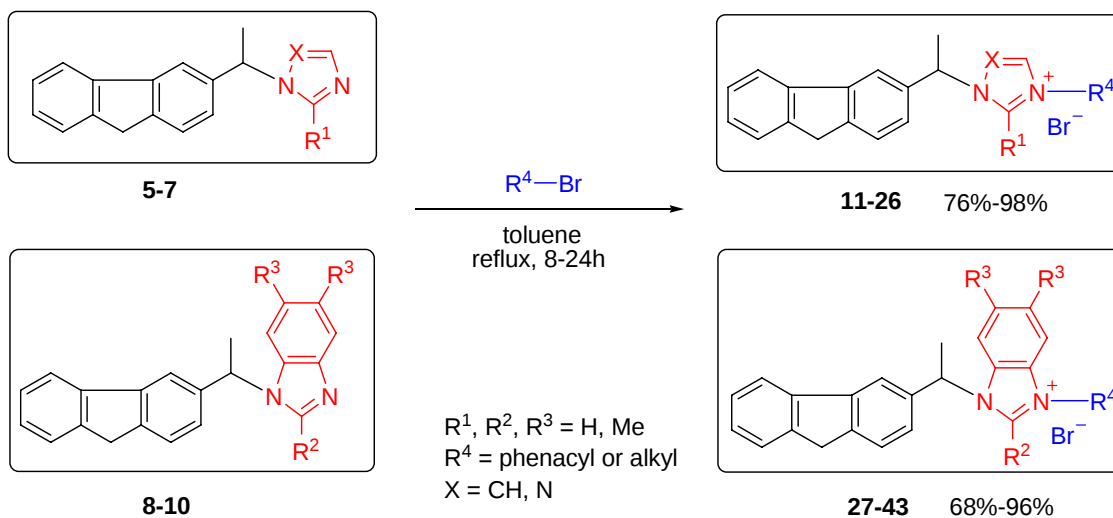
Yield 53%. White solid, Mp 166-168 °C. IR $\nu_{\max}$ (cm⁻¹): 3048, 2991, 2880, 1609, 1520, 1391, 1283, 1145, 1007, 737. ¹H NMR (300 MHz, CDCl₃) δ : 7.71-7.76 (3H, m), 7.52 (1H, d, J = 7.2 Hz), 7.25-7.39 (3H, m), 7.16-7.22 (2H, m), 7.07 (2H, d, J = 3.6 Hz), 5.80-5.87 (1H, m), 3.83 (2H, s), 2.64 (3H, s), 2.01 (3H, d, J = 7.2 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 151.50 (C), 143.97 (C), 143.39 (C), 141.71 (C), 141.57 (C), 140.92 (C), 137.67 (C), 133.67 (C), 127.07 (CH), 126.89 (CH), 125.11 (CH), 124.95 (CH), 123.07 (CH), 122.24 (CH), 122.14 (CH), 120.07 (CH), 118.79 (CH), 111.25 (CH), 53.74 (CH), 36.92 (CH₂), 18.84 (CH₃), 14.45 (CH₃). Anal. Calcd for C₂₃H₂₀N₂: C, 85.15; H, 6.21; N, 8.63. Found: C, 84.97; H, 6.17; N 8.36. HRMS (ESI-TOF) m/z Calcd for C₂₃H₂₁N₂ [M+1]⁺ 325.1705, found 325.1705.



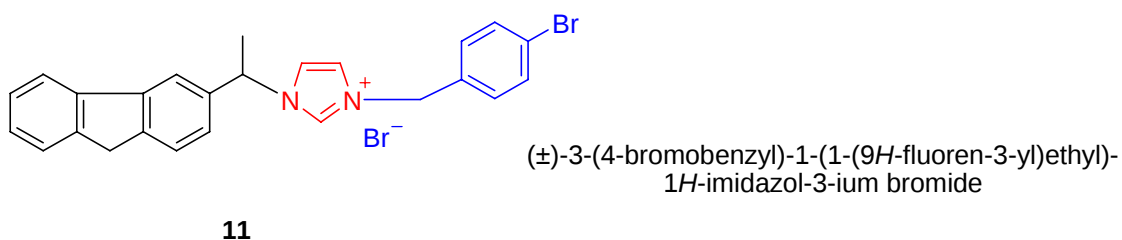
Yield 60%. White solid, Mp 182-184 °C. IR $\nu_{\max}$ (cm⁻¹): 3007, 2969, 2933, 2876, 1617, 1480, 1392, 1224, 1030, 839, 743. ¹H NMR (300 MHz, CDCl₃) δ : 8.00 (1H, s), 7.73 (2H, t, J = 7.2 Hz), 7.58 (1H, s), 7.50 (1H, d, J = 7.2 Hz), 7.24-7.37 (2H, m), 7.21 (2H, d, J = 7.8 Hz), 6.98 (1H, s), 5.58-5.65 (1H, m), 3.80 (2H, s), 2.33 (3H, s), 2.27 (3H, s), 2.00 (3H, d, J = 7.2 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 144.04 (C), 143.35 (C), 142.80 (C), 141.66 (C), 141.01 (C), 140.30 (CH), 139.57 (C), 132.31 (C), 131.96 (C), 131.13 (C), 126.97 (CH), 126.84 (CH), 125.06 (CH), 124.77 (CH), 122.55 (CH), 120.33 (CH), 120.16 (CH), 119.96 (CH), 110.77 (CH), 55.25 (CH), 36.87 (CH₂), 21.88 (CH₃), 20.59 (CH₃), 20.22 (CH₃). Anal. Calcd for C₂₄H₂₃N₂: C, 85.17; H, 6.55; N, 8.28. Found: C,

84.79; H, 6.39; N 7.98. HRMS (ESI-TOF) m/z Calcd for $C_{24}H_{23}N_2$ $[M+1]^+$ 339.1861, found 339.1863.

2.4 Synthesis of compounds 11-43

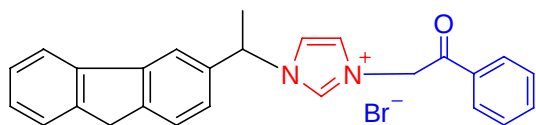


A mixture of ($\pm$)-3-substituted fluorene-imidazole hybrids **5-10** (0.2 mmol) and phenacyl bromides or alkyl bromides (0.24 mmol) was stirred in toluene (5 ml) at reflux for 8-12 h. An insoluble substance was formed. After completion of the reaction as indicated by TLC, the precipitate was filtered through a small pad of Celite, and washed with toluene (3×10 ml), then dried to afford imidazolium salts **11-43** in 68–98% yields.



Yield 98%. White solid, Mp 173-175 °C. IR $\nu_{\max}$ (cm^{-1}): 3012, 1646, 1553, 1150, 1011, 918, 759. ^1H NMR (300 MHz, CDCl_3) δ : 10.82 (1H, s), 7.70 (2H, d, $J = 6.9$ Hz), 7.59 (2H, s), 7.48-7.50 (3H, m), 7.40-7.42 (3H, m), 7.29-7.37 (3H, m), 5.88 (1H, m), 5.66 (2H, m), 3.82 (2H, s), 2.03 (3H, s). ^{13}C NMR (75 MHz, CDCl_3) δ : 144.39 (C), 143.44

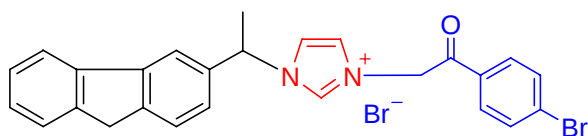
(C), 142.96 (C), 140.43 (C), 135.97 (C), 132.41 (CH), 131.03 (CH), 127.40 (CH), 126.91 (CH), 125.75 (CH), 125.12 (CH), 123.64 (CH), 122.32 (CH), 121.09 (CH), 120.57 (CH), 120.22 (CH), 60.41 (CH), 52.30 (CH₂), 36.89 (CH₂), 21.58 (CH₃). HRMS (ESI-TOF) m/z Calcd for C₂₅H₂₂BrN₂ [M-Br]⁺ 429.0961, found 429.0973.



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(±)-3-(2-oxo-2-phenylethyl)-1-(1-(9H-fluoren-3-yl)ethyl)-1H-imidazol-3-ium bromide

Yield 97%. White solid, Mp 220-222 °C. IR $\nu_{\max}$ (cm⁻¹): 3048, 2929, 1699, 1605, 1564, 1441, 1234, 1002, 826, 753. ¹H NMR (300 MHz, CDCl₃) δ : 9.27 (1H, s), 8.08 (2H, d, J = 7.5 Hz), 7.86 (2H, dd, J = 14.4, 8.1 Hz), 7.80 (1H, d, J = 5.1 Hz), 7.67-7.71 (3H, m), 7.56-7.61 (3H, m), 7.48 (1H, d, J = 7.8 Hz), 7.32-7.38 (2H, m), 6.03 (2H, s), 5.88-5.95 (1H, m), 3.90 (2H, s), 2.05 (3H, d, J = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 192.06 (C), 145.80 (C), 144.95 (C), 144.07 (C), 141.95 (C), 138.40 (C), 138.16 (CH), 135.74 (CH), 135.14 (C), 130.22 (CH), 129.40 (CH), 128.48 (CH), 128.05 (CH), 126.82 (CH), 126.22 (CH), 125.76 (CH), 124.66 (CH), 122.28 (CH), 121.62 (CH), 121.28 (CH), 61.66 (CH), 56.75 (CH₂), 37.73 (CH₂), 21.59 (CH₃). HRMS (ESI-TOF) m/z Calcd for C₂₆H₂₃N₂O [M-Br]⁺ 379.1805, found 379.1809.

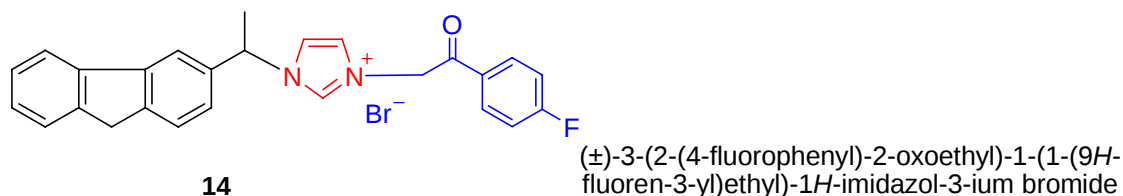


13

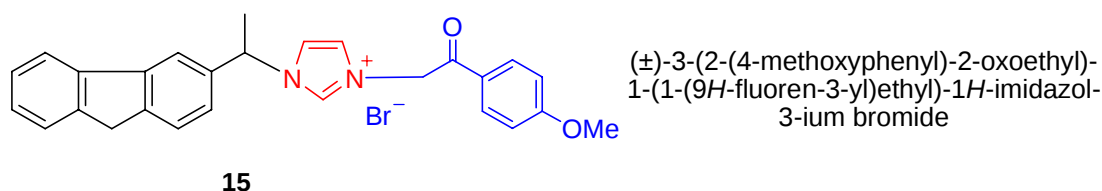
(±)-3-(2-(4-bromophenyl)-2-oxoethyl)-1-(1-(9H-fluoren-3-yl)ethyl)-1H-imidazol-3-ium bromide

Yield 96%. White solid, Mp 229-231 °C. IR $\nu_{\max}$ (cm⁻¹): 3078, 1694, 1577, 1458, 1393, 1153, 1070, 997, 825, 746. ¹H NMR (300 MHz, CDCl₃) δ : 9.35 (1H, s), 7.88 (2H, d, J = 6.6 Hz), 7.74 (2H, dd, J = 11.4, 8.1 Hz), 7.62 (2H, d, J = 8.1 Hz), 7.48-7.53 (3H, m), 7.39 (1H, s), 7.24-7.35 (3H, m), 6.00 (2H, s), 5.74-5.76 (1H, m), 3.86 (2H, s), 1.99 (3H, d, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 189.47 (C), 144.20 (C), 143.13 (C),

142.77 (C), 136.27 (C), 135.67 (C), 132.07 (CH), 129.72 (CH), 129.49 (CH), 127.08 (C), 126.57 (CH), 125.21 (CH), 124.74 (CH), 124.11 (CH), 123.08 (CH), 120.25 (CH), 119.82 (CH), 60.20 (CH), 55.21 (CH₂), 36.44 (CH₂), 20.63 (CH₃). HRMS (ESI-TOF) m/z Calcd for C₂₆H₂₂BrN₂O [M-Br]⁺ 457.0910, found 457.0911.

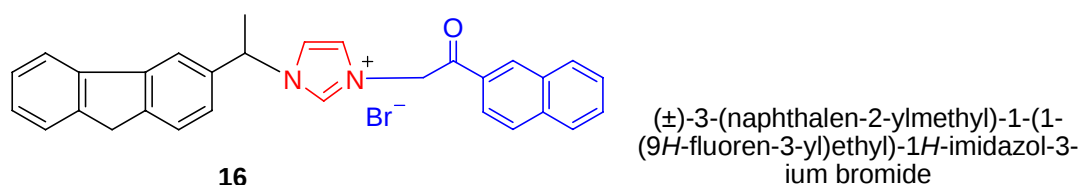


Yield 86%. White solid, Mp 228-230 °C. IR $\nu_{\max}$ (cm⁻¹): 3052, 1698, 1600, 1558, 1455, 1232, 1160, 1003, 836, 746. ¹H NMR (300 MHz, CDCl₃) δ : 9.48-9.53 (1H, m), 8.09 (2H, dd, J = 2.1, 2.4 Hz), 7.76 (2H, dd, J = 9.3, 16.5 Hz), 7.51 (2H, d, J = 9 Hz), 7.46 (1H, s), 7.27-7.34 (4H, m), 7.17 (2H, dd, J = 8.4, 15.6 Hz), 6.07-6.10 (2H, m), 5.74-5.76 (1H, m), 3.88 (2H, s), 2.02 (3H, d, J = 5.1 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 189.16 (C), 144.52 (C), 143.11 (C), 140.35 (C), 136.72 (C), 135.78 (C), 131.39 (CH), 131.27 (CH), 129.86 (C), 127.41 (CH), 126.89 (CH), 125.55 (CH), 125.07 (CH), 123.34 (CH), 123.45 (CH), 120.58 (CH), 120.16 (CH), 116.46 (CH), 116.16 (CH), 60.52 (CH), 55.63 (CH₂), 36.79 (CH₂), 21.08 (CH₃). Anal. Calcd for C₂₆H₂₂BrFN₂O: C, 65.42; H, 4.65; N, 5.87. Found: C, 65.44; H, 5.05; N 5.85. HRMS (ESI-TOF) m/z Calcd for C₂₆H₂₂FN₂O [M-Br]⁺ 397.1711, found 397.1715.

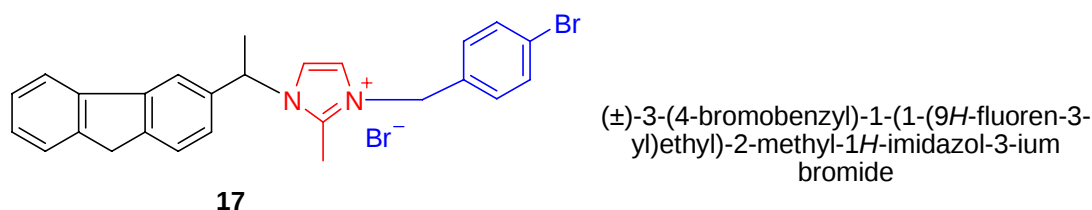


Yield 95%. White solid, Mp 234-236 °C. IR $\nu_{\max}$ (cm⁻¹): 2976, 1686, 1602, 1563, 1251, 1168, 1023, 836, 741. ¹H NMR (300 MHz, CDCl₃) δ : 9.53 (1H, s), 8.07 (2H, d, J = 1.5 Hz), 8.05 (1H, s), 7.92-8.02 (2H, m), 7.84 (1H, s), 7.44 (1H, s), 7.59 (1H, d, J = 7.2 Hz), 7.53 (1H, d, J = 7.8 Hz), 7.33-7.41 (2H, m), 7.13 (2H, d, J = 8.7 Hz), 6.05-6.09 (3H, m),

3.94 (2H, s), 3.87 (3H, s), 1.97 (3H, d, $J = 6.9$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 189.49 (C), 164.08 (C), 143.75 (C), 143.26 (C), 141.69 (C), 140.27 (C), 137.69 (C), 136.65 (CH), 130.58 (CH), 127.17 (CH), 126.84 (CH), 126.44 (CH), 125.56 (CH), 125.18 (CH), 124.44 (CH), 123.52 (CH), 120.76 (CH), 120.48 (CH), 120.31 (CH), 114.32 (CH), 58.89 (CH), 55.75 (CH_3), 55.16 (CH_2), 36.43 (CH_2), 20.69 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_{27}\text{H}_{25}\text{N}_2\text{O}_2$ $[\text{M}-\text{Br}]^+$ 409.1911, found 409.1898.

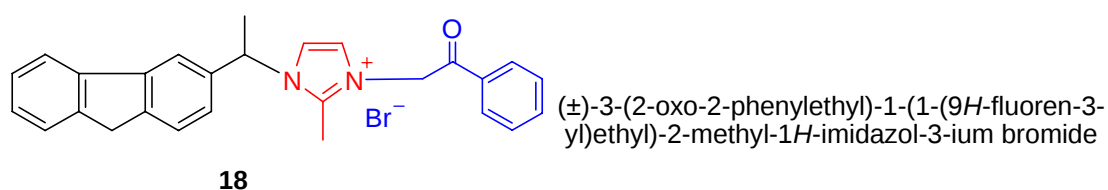


Yield 94%. White solid, Mp 219-221 °C. IR ν_{max} (cm^{-1}): 3030, 2295, 1693, 1617, 1562, 1458, 1170, 919, 816, 734. ^1H NMR (300 MHz, CDCl_3) δ : 9.55 (1H, s), 8.60 (1H, s), 7.89 (3H, dd, $J = 17.4, 8.4$ Hz), 7.65-7.76 (5H, m), 7.44-7.46 (4H, m), 7.20-7.28 (3H, m), 6.15 (2H, s), 5.65-5.71 (1H, m), 3.43 (2H, s), 1.90 (3H, d, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 190.42 (C), 144.35 (C), 143.38 (C), 142.88 (C), 140.33 (C), 136.63 (CH), 136.02 (C), 135.79 (C), 132.25 (C), 130.97 (CH), 130.49 (C), 129.81 (CH), 129.23 (CH), 128.23 (CH), 127.57 (CH), 127.27 (CH), 127.03 (CH), 126.76 (CH), 125.47 (CH), 124.96 (CH), 124.28 (CH), 123.38 (CH), 122.94 (CH), 120.44 (CH), 120.16 (CH), 120.05 (CH), 60.30 (CH), 55.63 (CH_2), 36.69 (CH_2), 21.03 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_{30}\text{H}_{25}\text{N}_2\text{O}$ $[\text{M}-\text{Br}]^+$ 429.1961, found 429.1960.

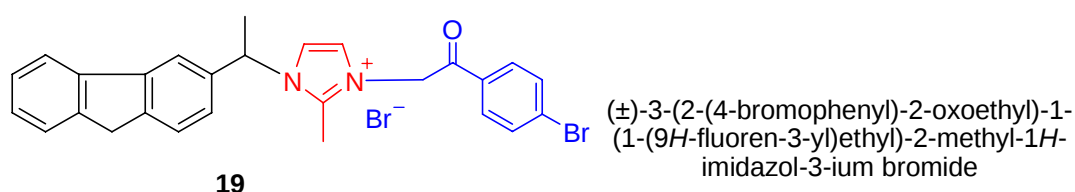


Yield 85%. White solid, Mp 215-217 °C. IR ν_{max} (cm^{-1}): 3056, 1582, 1512, 1456, 1189, 1004, 834, 766. ^1H NMR (300 MHz, CDCl_3) δ : 8.01 (1H, s), 7.89-7.94 (3H, m),

7.57-7.64 (4H, m), 7.30-7.45 (5H, m), 5.92-5.95 (1H, m), 5.45 (2H, s), 3.92 (2H, s), 2.70 (3H, s), 1.90 (3H, d, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 144.07 (C), 143.75 (C), 143.21 (C), 141.40 (C), 140.25 (C), 137.52 (C), 133.72 (C), 131.88 (CH), 130.23 (CH), 127.13 (CH), 126.82 (CH), 125.42 (CH), 125.17 (CH), 123.36 (CH), 122.12 (CH), 121.85 (CH), 120.41 (CH), 120.27 (CH), 119.20 (CH), 57.11 (CH), 49.97 (CH_2), 36.40 (CH_2), 20.79 (CH_3), 10.11 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_{26}\text{H}_{24}\text{BrN}_2$ $[\text{M}-\text{Br}]^+$ 443.1117, found 443.1129.

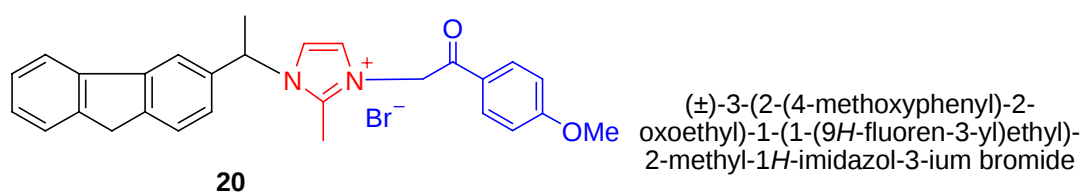


Yield 80%. White solid, Mp 158-160 °C. IR ν_{max} (cm^{-1}): 3054, 2907, 1695, 1587, 1453, 1228, 992, 832, 744. ^1H NMR (300 MHz, CDCl_3) δ : 8.08 (3H, dd, $J = 17.7, 1.5$ Hz), 7.95 (2H, dd, $J = 11.4, 8.1$ Hz), 7.76 (2H, dd, $J = 13.5, 6.0$ Hz), 7.68 (1H, s), 7.59-7.65 (3H, m), 7.33-7.46 (3H, m), 6.15 (2H, s), 6.01-6.08 (1H, m), 3.95 (2H, s), 2.62 (3H, s), 1.96 (3H, d, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 191.09 (C), 145.41 (C), 143.81 (C), 143.23 (C), 141.44 (C), 140.27 (C), 137.60 (C), 134.49 (CH), 133.64 (C), 128.95 (CH), 128.35 (CH), 127.15 (CH), 126.84 (CH), 125.28 (CH), 125.18 (CH), 123.29 (CH), 123.13 (CH), 120.48 (CH), 120.28 (CH), 118.73 (CH), 57.18 (CH), 54.56 (CH_2), 36.43 (CH_2), 20.83 (CH_3), 9.86 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_{27}\text{H}_{25}\text{N}_2\text{O}$ $[\text{M}-\text{Br}]^+$ 471.1067, found 471.1082.

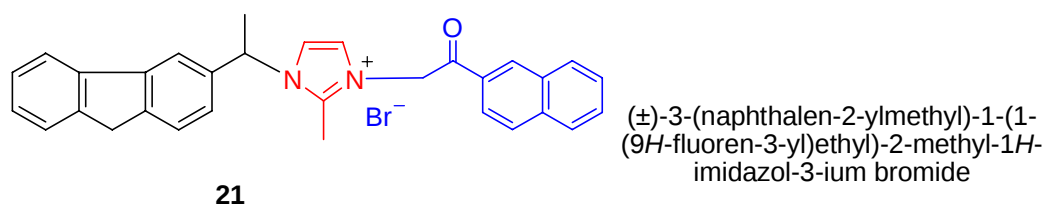


Yield 89%. White solid, Mp 193-195 °C. IR ν_{max} (cm^{-1}): 3050, 2894, 1696, 1579, 1455, 1392, 1227, 1061, 993, 872, 742. ^1H NMR (300 MHz, CDCl_3) δ : 8.11 (1H, s), 7.91-8.10

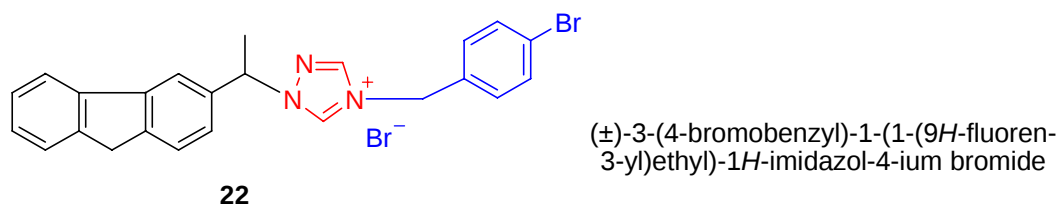
(4H, m), 7.85 (2H, d, $J = 8.4$ Hz), 7.78 (1H, d, $J = 1.5$ Hz), 7.68 (1H, s), 7.60 (1H, d, $J = 7.2$ Hz), 7.33-7.46 (3H, m), 6.15 (2H, s), 6.03-6.08 (1H, m), 3.95 (2H, s), 2.62 (3H, s), 1.95 (3H, d, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 190.51 (C), 145.43 (C), 143.80 (C), 141.44 (C), 140.27 (C), 137.58 (C), 132.72 (C), 132.02 (CH), 130.33 (CH), 128.59 (CH), 127.15 (CH), 126.83 (CH), 125.29 (CH), 125.18 (CH), 123.30 (CH), 123.11 (CH), 120.47 (CH), 120.28 (CH), 118.75 (CH), 57.19 (CH), 54.55 (CH_2), 36.43 (CH_2), 20.83 (CH_3), 9.90 (CH_3). Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{Br}_2\text{N}_2\text{O}$: C, 58.72; H, 4.38; N, 5.07. Found: C, 59.15; H, 4.34; N 5.01. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{27}\text{H}_{24}\text{BrN}_2\text{O}$ $[\text{M}-\text{Br}]^+$ 393.1961, found 393.1968.



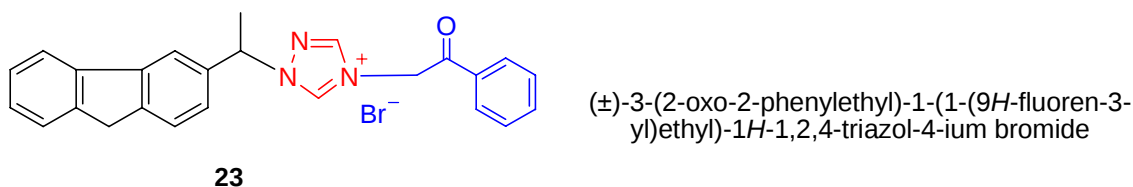
Yield 88%. White solid, Mp 195-197 °C, IR ν_{max} (cm^{-1}): 3059, 1681, 1600, 1585, 1451, 1265, 1179, 1021, 997, 835, 736. ^1H NMR (300 MHz, CDCl_3) δ : 8.08 (1H, s), 8.02 (2H, d, $J = 7.5$ Hz), 7.95 (2H, dd, $J = 10.5, 8.1$ Hz), 7.75 (1H, s), 7.67 (1H, s), 7.60 (1H, d, $J = 7.2$ Hz), 7.33-7.45 (3H, m), 7.14 (2H, d, $J = 8.4$ Hz), 6.01-6.06 (3H, m), 3.95 (2H, s), 3.87 (3H, s), 2.58 (3H, s), 1.95 (3H, d, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 189.26 (C), 164.13 (C), 145.36 (C), 143.81 (C), 143.22 (C), 141.43 (C), 140.26 (C), 137.60 (C), 130.79 (CH), 127.15 (CH), 126.84 (CH), 126.46 (CH), 125.25 (CH), 123.27 (CH), 123.14 (CH), 120.47 (CH), 120.28 (CH), 118.66 (CH), 114.23 (CH), 57.15 (CH_3), 55.76 (CH), 54.15 (CH_2), 36.42 (CH_2), 20.80 (CH_3), 9.83 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_{28}\text{H}_{27}\text{N}_2\text{O}_2$ $[\text{M}-\text{Br}]^+$ 423.2067, found 423.2062.



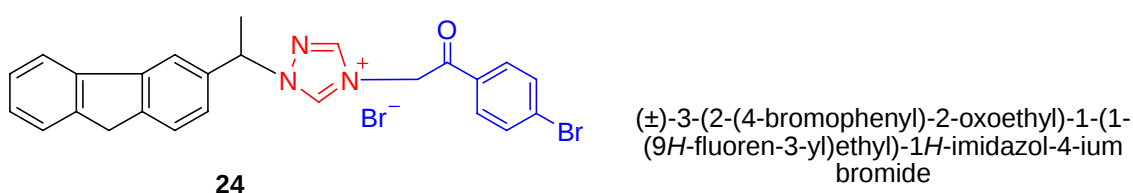
Yield 90%. White solid, Mp 170-172 °C. IR $\nu_{\max}$ (cm⁻¹): 3049, 1688, 1624, 1584, 1469, 1270, 1038, 996, 826, 735. ¹H NMR (300 MHz, CDCl₃) δ : 8.78 (1H, s), 8.12 (1H, d, J = 7.8 Hz), 7.94-8.06 (3H, m), 7.81-7.88 (3H, m), 7.55-7.66 (4H, m), 7.32-7.39 (4H, m), 7.13-7.21 (1H, m), 6.18 (2H, s), 5.96-5.98 (1H, m), 3.91 (2H, s), 2.59 (3H, s), 2.03 (3H, d, J = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 191.79 (C), 147.35 (C), 145.82 (C), 144.87 (C), 143.73 (C), 141.97 (C), 138.55 (C), 137.66 (C), 133.90 (C), 132.34 (C), 132.14 (CH), 130.94 (CH), 130.53 (CH), 130.02 (CH), 129.24 (CH), 128.99 (CH), 128.41 (CH), 128.05 (CH), 126.33 (CH), 126.21 (CH), 124.34 (CH), 124.20 (CH), 121.59 (CH), 121.23 (CH), 120.10 (CH), 59.73 (CH), 55.90 (CH₂), 37.74 (CH₂), 21.67 (CH₃), 10.62 (CH₃). HRMS (ESI-TOF) m/z Calcd for C₃₁H₂₇N₂O [M-Br]⁺ 443.2112, found 443.2132.



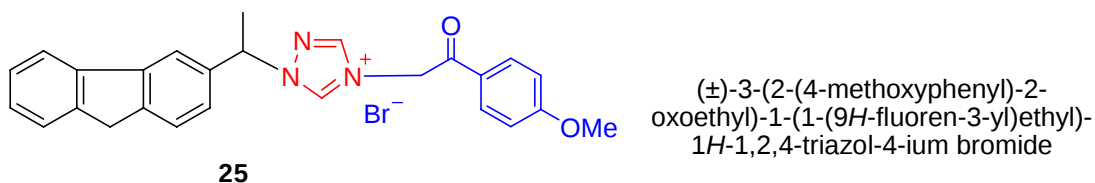
Yield 80%. White solid, Mp 112-114 °C. IR $\nu_{\max}$ (cm⁻¹): 2985, 1573, 1498, 1143, 1006, 836, 755, 622. ¹H NMR (300 MHz, CDCl₃) δ : 10.50 (1H, s), 9.36 (1H, s), 7.93 (2H, dd, J = 7.5, 14.4 Hz), 7.67 (2H, dd, J = 3.9, 12.3 Hz), 7.60 (1H, d, J = 7.2 Hz), 7.50-7.53 (3H, m), 7.31-7.42 (3H, m), 5.92-6.07 (1H, m), 5.52 (2H, s), 3.93 (2H, s), 1.94 (3H, d, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 144.73 (CH), 143.56 (C), 143.27 (C), 142.08 (CH), 141.73 (C), 140.25 (C), 136.49 (C), 132.75 (C), 131.93 (CH), 131.25 (CH), 127.18 (CH), 126.83 (CH), 126.03 (CH), 125.18 (CH), 123.91 (CH), 122.51 (CH), 120.29 (CH), 61.85 (CH), 49.89 (CH₂), 36.38 (CH₂), 20.14 (CH₃). HRMS (ESI-TOF) m/z Calcd for C₂₄H₂₁BrN₃ [M-Br]⁺ 430.0913, found 430.0917.



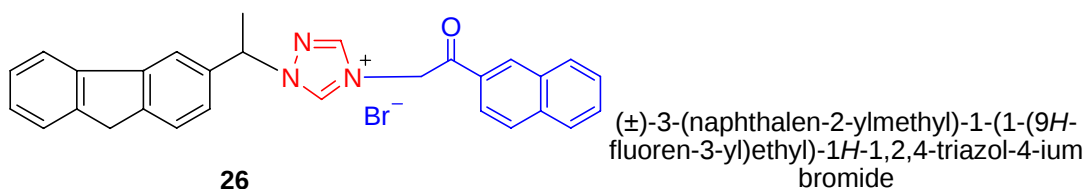
Yield 78%. White solid, 150-152 °C. IR $\nu_{\max}$ (cm⁻¹): 3043, 1694, 1568, 1443, 1235, 1153, 994, 830, 752. ¹H NMR (300 MHz, CDCl₃) δ : 10.41 (1H, s), 9.29 (1H, s), 8.07 (2H, d, J = 4.5 Hz), 7.96 (2H, dd, J = 14.7, 7.8 Hz), 7.76-7.81 (2H, m), 7.54- 7.67 (4H, m), 7.32-7.42 (2H, m), 6.22-6.29 (3H, m), 3.96 (2H, s), 2.01 (3H, d, J = 6.9Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 190.35 (C), 145.92 (CH), 143.66 (C), 143.30 (C), 142.94 (CH), 141.86 (C), 140.25 (C), 136.35 (C), 134.71 (CH), 133.34 (C), 129.15 (CH), 128.22 (CH), 127.22 (CH), 126.85 (CH), 126.00 (CH), 125.20 (CH), 123.92 (CH), 120.41 (CH), 120.35 (CH), 61.71 (CH), 53.98 (CH₂), 36.43 (CH₂), 20.08 (CH₃). HRMS (ESI-TOF) m/z Calcd for C₂₅H₂₂N₃O [M-Br]⁺ 380.1757, found 380.1763.



Yield 76%. White solid. Mp 190-192 °C. IR $\nu_{\max}$ (cm⁻¹): 3039, 2964, 1697, 1575, 1460, 1393, 1231, 1153, 1067, 992, 823, 749. ¹H NMR (300 MHz, CDCl₃) δ : 10.54 (1H, s), 9.37 (1H, s), 7.92-8.04 (6H, m), 7.81 (1H, s), 7.63 (2H, dd, J = 12.0, 6.0 Hz), 7.41 (2H, dd, J = 16.5, 8.1 Hz), 6.30 (3H, m), 3.98 (2H, s), 2.09 (3H, d, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 189.84 (C), 145.94 (CH), 143.71 (C), 143.36 (C), 142.98 (CH), 141.90 (CH), 140.31 (C), 136.41 (C), 132.30 (CH), 130.25 (CH), 128.91 (C), 127.27 (CH), 126.90 (CH), 126.06 (CH), 125.25 (CH), 123.98 (CH), 120.42 (CH), 61.75 (CH), 54.07 (CH₂), 36.49 (CH₂), 20.16 (CH₃). HRMS (ESI-TOF) m/z Calcd for C₂₅H₂₁BrN₃O [M-Br]⁺ 458.0863, found 458.0871.

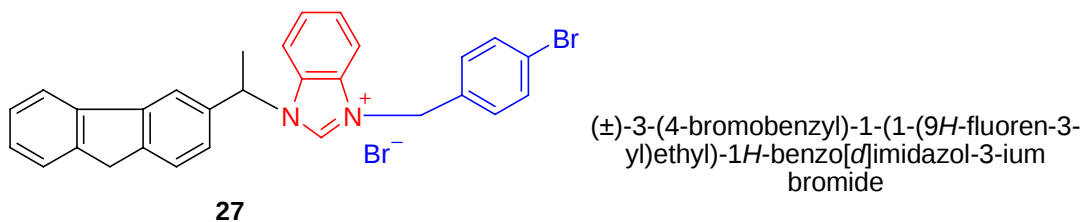


Yield 85%. White solid, Mp 172-174 °C, IR $\nu_{\max}$ (cm⁻¹): 3043, 2944, 1685, 1601, 1512, 1457, 1252, 1170, 981, 838, 740. ¹H NMR (300 MHz, CDCl₃) δ : 10.36 (1H, s), 9.25 (1H, s), 8.05 (2H, d, *J* = 8.7 Hz), 7.96 (2H, dd, *J* = 14.4, 7.8 Hz), 7.75 (1H, s), 7.61 (1H, d, *J* = 6.9 Hz), 7.54 (1H, d, *J* = 7.8 Hz), 7.34-7.40 (2H, m), 7.16 (2H, d, *J* = 8.7 Hz), 6.21-6.28 (1H, m), 6.12 (2H, s), 3.96 (2H, s), 3.88 (3H, s), 2.00 (3H, d, *J* = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 188.52 (C), 164.26 (C), 145.94 (CH), 143.67 (C), 143.30 (C), 142.95 (CH), 141.86 (C), 140.25 (C), 136.36 (C), 130.69 (CH), 128.85 (CH), 128.16 (CH), 127.22 (CH), 126.85 (CH), 126.12 (CH), 125.98 (CH), 125.20 (CH), 123.90 (CH), 120.40 (CH), 114.42 (CH), 61.72 (CH), 55.77 (CH₃), 53.54 (CH₂), 36.41 (CH₂), 20.06 (CH₃). HRMS (ESI-TOF) *m/z* Calcd for C₂₆H₂₄N₃O₂ [M-Br]⁺ 410.1863, found 410.1869.

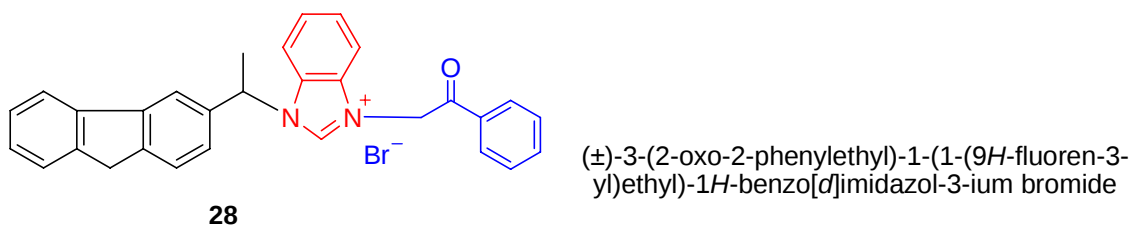


Yield 80%. White solid, Mp 153-155 °C. IR $\nu_{\max}$ (cm⁻¹): 2953, 1692, 1576, 1459, 1167, 978, 817, 740, 637. ¹H NMR (300 MHz, CDCl₃) δ : 10.45 (1H, s), 9.32 (1H, s), 8.86 (1H, s), 8.22 (1H, d, *J* = 7.2 Hz), 8.13 (1H, d, *J* = 8.4 Hz), 7.93-8.05 (4H, m), 7.69-7.77 (3H, m), 7.58 (2H, dd, *J* = 14.1, 6.9 Hz), 7.37 (2H, dd, *J* = 17.1, 9.0 Hz), 6.28-6.34 (3H, m), 3.96 (2H, s), 2.02 (3H, d, *J* = 5.7 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 190.28 (C), 145.98 (CH), 143.67 (C), 143.30 (C), 143.02 (C), 141.86 (CH), 140.25 (C), 136.37 (C), 135.57 (C), 131.98 (C), 130.70 (CH), 129.71 (CH), 129.44 (CH), 128.84 (CH), 127.85 (CH), 127.40 (CH), 127.22 (CH), 126.85 (CH), 126.01 (CH), 125.20 (CH), 123.93 (CH), 123.10 (CH), 120.41 (CH), 120.35 (CH), 61.73 (CH), 54.00 (CH₂), 36.42 (CH₂), 20.08

(CH₃). HRMS (ESI-TOF) m/z Calcd for C₂₉H₂₄N₃O [M-Br]⁺ 430.1914, found 430.1934.

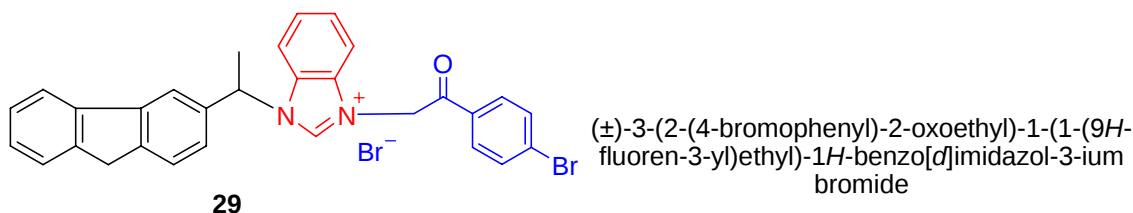


Yield 90%. White solid, Mp 182-184 °C. IR $\nu_{\max}$ (cm⁻¹): 2975, 1608, 1553, 1480, 1207, 1067, 1011, 837, 746. ¹H NMR (300 MHz, CDCl₃) δ : 11.89 (1H, s), 7.75 (2H, dd, J = 14.4, 7.5 Hz), 7.65 (1H, s), 7.46-7.57 (10H, m), 7.28-7.38 (2H, m), 6.01-6.16 (3H, m), 3.88 (2H, s), 2.35 (3H, s). ¹³C NMR (75 MHz, CDCl₃) δ : 144.64 (C), 143.50 (C), 142.89 (C), 142.08 (CH), 140.50 (C), 136.01 (C), 132.45 (CH), 132.14 (C), 131.61 (C), 131.05 (C), 130.35 (CH), 127.39 (CH), 127.19 (CH), 127.03 (CH), 126.90 (CH), 125.33 (CH), 125.14 (CH), 123.36 (C), 123.16 (CH), 120.65 (CH), 120.16 (CH), 114.38 (CH), 113.79 (CH), 59.77 (CH), 50.79 (CH₂), 36.96 (CH₂), 22.26 (CH₃). HRMS (ESI-TOF) m/z Calcd for C₂₉H₂₄BrN₂ [M-Br]⁺ 479.1117, found 479.1119.

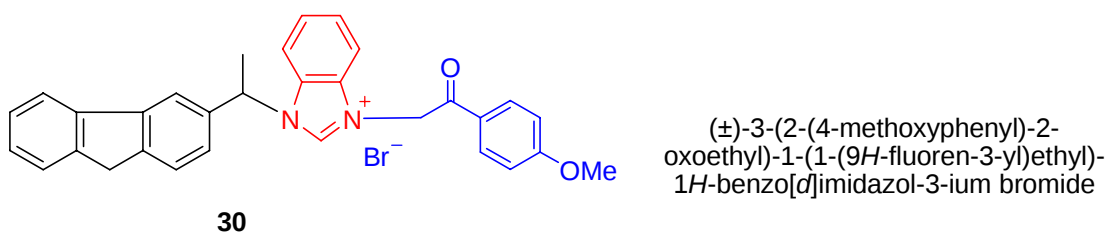


Yield 83%. White solid, Mp 149-151 °C. IR $\nu_{\max}$ (cm⁻¹): 3056, 2884, 1696, 1605, 1561, 1477, 1230, 1072 987, 763. ¹H NMR (300 MHz, CDCl₃) δ : 11.26 (1H, s), 8.18 (2H, d, J = 7.5 Hz), 7.75 (2H, dd, J = 16.8, 8.1 Hz), 7.58-7.64 (3H, m), 7.43-7.51 (7H, m), 7.28-7.35 (2H, m), 6.75 (2H, s), 5.97-5.99 (1H, m), 3.88 (2H, s), 2.26 (3H, d, J = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 190.47 (C), 144.70 (C), 143.54 (C), 142.91 (C), 142.53 (C), 140.54 (C), 135.93 (C), 134.83 (CH), 133.58 (C), 132.72 (C), 130.65 (C), 129.20 (CH), 128.76 (CH), 127.36 (CH), 126.89 (CH), 125.27 (CH), 125.13 (CH),

123.04 (CH), 120.68 (CH), 120.16 (CH), 114.12 (CH), 113.49 (CH), 59.60 (CH), 53.83 (CH₂), 36.94 (CH₂), 22.18 (CH₃). HRMS (ESI-TOF) *m/z* Calcd for C₃₀H₂₅N₂O [M–Br]⁺ 429.1961, found 429.1968.

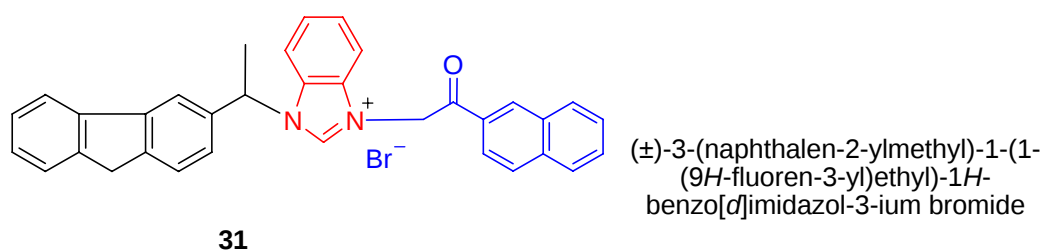


Yield 86%. White solid. Mp 174-176 °C. IR $\nu_{\max}$ (cm⁻¹): 3015, 2917, 1695, 1617, 1572, 1474, 1220, 1072, 990, 824, 744. ¹H NMR (300 MHz, CDCl₃) δ : 9.92 (1H, s), 8.11 (2H, d, *J* = 8.1 Hz), 7.92 (1H, d, *J* = 7.5 Hz), 7.79-7.863 (5H, m), 7.69 (1H, s), 7.62 (2H, d, *J* = 5.4 Hz), 7.48-7.56 (2H, m), 7.29-7.35 (2H, m), 6.37-6.39 (2H, m), 6.26-6.28 (1H, m), 3.87 (2H, s), 2.18 (3H, d, *J* = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 191.31 (C), 145.92 (C), 144.89 (C), 144.02 (C), 143.35 (CH), 141.91 (C), 138.05 (C), 134.10 (C), 133.58 (CH), 132.28 (C), 131.33 (CH), 130.88 (C), 128.58 (CH), 128.45 (CH), 128.21 (CH), 128.02 (CH), 126.49 (CH), 126.17 (CH), 124.30 (CH), 121.67 (CH), 121.222 (CH), 115.45 (CH), 114.73 (CH), 60.11 (CH), 54.3 (CH₂), 37.70 (CH₂), 21.91 (CH₃). HRMS (ESI-TOF) *m/z* Calcd for C₃₀H₂₄BrN₂O [M–Br]⁺ 507.1067, found 507.1090.

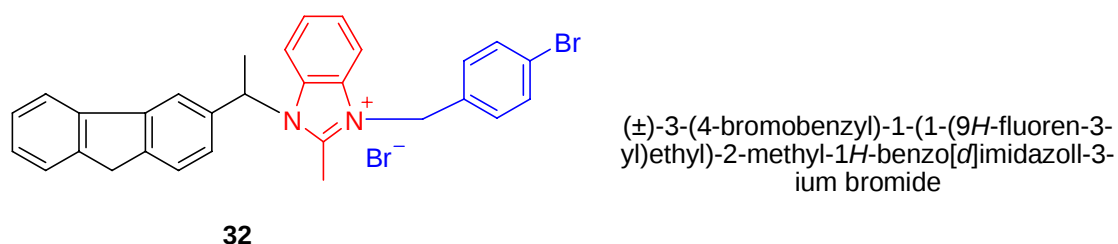


Yield 92%. White solid. Mp 163-165 °C. IR $\nu_{\max}$ (cm⁻¹): 3015, 2974, 2932, 1683, 1601, 1458, 1564, 1260, 1176, 1021, 984, 836, 748. ¹H NMR (300 MHz, CDCl₃) δ : 11.22 (1H, s), 8.17 (2H, d, *J* = 8.4 Hz), 7.75 (2H, dd, *J* = 16.5, 8.1 Hz), 7.64 (1H, s), 7.60 (1H, s), 7.51 (2H, d, *J* = 7.2 Hz), 7.42-7.46 (5H, m), 7.28-7.39 (2H, m), 6.97 (2H, d, *J* = 8.4 Hz), 6.68 (2H, s), 5.95-5.97 (1H, m), 3.88 (2H, s), 3.86 (3H, s), 2.27 (3H, d, *J* = 6.3 Hz).

^{13}C NMR (75 MHz, CDCl_3) δ : 188.65 (C), 164.88 (C), 144.70 (C), 143.54 (C), 142.89 (C), 142.55 (CH), 140.54 (C), 135.97 (C), 132.81 (C), 131.25 (CH), 130.63 (C), 127.35 (CH), 127.18 (CH), 126.87 (CH), 126.53 (CH), 125.26 (CH), 125.13 (CH), 123.04 (CH), 120.66 (CH), 120.16 (CH), 114.46 (CH), 114.02 (CH), 113.63 (CH), 59.58 (CH), 55.65 (CH_3), 53.44 (CH_2), 36.94 (CH_2), 22.19 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_{31}\text{H}_{27}\text{N}_2\text{O}_2 [\text{M}-\text{Br}]^+$ 459.2067, found 459.2057.

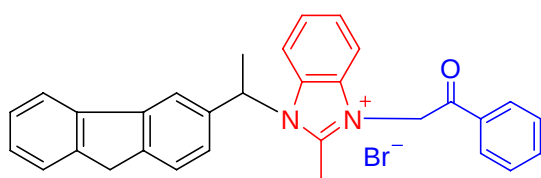


Yield 88%. White solid, Mp 164-166 °C. IR ν_{max} (cm^{-1}): 3012, 2925, 1694, 1558, 1486, 1217, 987, 826, 749. ^1H NMR (300 MHz, CDCl_3) δ : 11.21 (1H, s), 8.99 (1H, s), 8.05 (2H, dd, J = 16.2, 6.9 Hz), 7.71-7.80 (5H, m), 7.67 (1H, m), 7.54-7.61 (2H, m), 7.41-7.50 (5H, m), 7.32 (2H, dd, J = 10.8, 8.7 Hz), 6.89 (2H, s), 5.92-5.94 (1H, m), 3.84 (2H, s), 2.23 (3H, d, J = 6 Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 190.54 (C), 144.66 (C), 143.52 (C), 142.83 (C), 142.54 (CH), 140.55 (C), 136.14 (C), 136.02 (C), 132.72 (C), 132.44 (C), 131.65 (CH), 130.76 (CH), 130.60 (CH), 130.17 (CH), 129.31 (CH), 128.94 (CH), 127.65 (CH), 127.24 (CH), 127.08 (CH), 126.86 (CH), 125.23 (CH), 123.31 (CH), 123.00 (CH), 120.65 (CH), 120.15 (CH), 114.03 (CH), 113.71 (CH), 59.54 (CH), 53.98 (CH_2), 36.92 (CH_2), 22.17 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_{34}\text{H}_{27}\text{N}_2\text{O} [\text{M}-\text{Br}]^+$ 479.2118, found 479.2117.



Yield 80%. White solid, Mp 191-193 °C. IR ν_{max} (cm^{-1}): 3026, 2896, 1606, 1515, 1472,

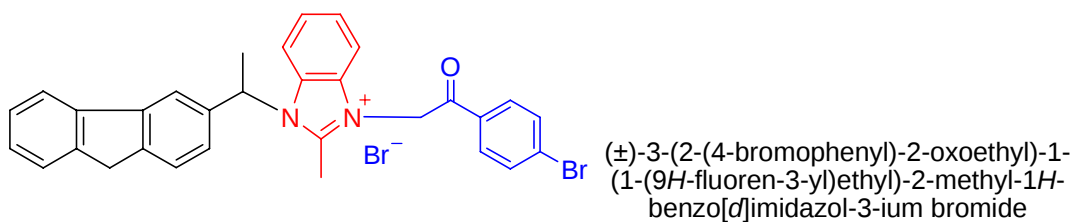
1138, 1066, 841, 752. ^1H NMR (300 MHz, CDCl_3) δ : 7.80 (3H, dd, $J = 16.2, 8.7$ Hz), 7.54-7.59 (5H, m), 7.31-7.48 (5H, m), 7.21 (2H, d, $J = 7.8$ Hz), 6.34-6.36 (1H, m), 5.82 (2H, s), 3.93 (2H, s), 3.10 (3H, s), 2.21 (3H, d, $J = 6.9$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 150.78 (C), 144.30 (C), 143.27 (C), 142.54 (C), 140.22 (C), 134.08 (C), 132.43 (CH), 131.91 (C), 131.65 (C), 129.82 (C), 128.48 (CH), 127.27 (CH), 126.82 (CH), 126.75 (CH), 126.63 (CH), 125.11 (CH), 124.91 (CH), 123.15 (CH), 122.85 (C), 120.31 (CH), 119.99 (CH), 114.25 (CH), 112.92 (CH), 57.10 (CH), 48.54 (CH_2), 36.64 (CH_2), 17.98 (CH_3), 11.84 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_{30}\text{H}_{26}\text{BrN}_2$ $[\text{M}-\text{Br}]^+$ 493.1274, found 493.1280.



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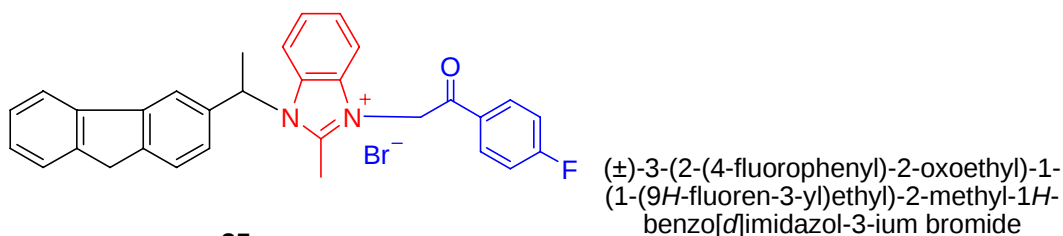
(±)-3-(2-oxo-2-phenylethyl)-1-(1-(9H-fluoren-3-yl)ethyl)-2-methyl-1H-benzo[d]imidazol-3-ium bromide

Yield 76%. White solid, Mp 203-205 °C, IR ν_{max} (cm^{-1}): 3002, 1682, 1603, 1520, 1473, 1228, 1073, 991, 828, 748, 683. ^1H NMR (300 MHz, CDCl_3) δ : 8.32 (2H, d, $J = 7.5$ Hz), 7.80 (2H, dd, $J = 17.7, 8.1$ Hz), 7.65-7.69 (2H, m), 7.53-7.59 (4H, m), 7.31-7.46 (5H, m), 7.28 (1H, s), 6.82 (2H, s), 6.25-6.32 (1H, m), 3.91 (2H, s), 3.20 (3H, s), 2.21 (3H, d, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 190.68 (C), 152.67 (C), 144.57 (C), 143.55 (C), 142.70 (C), 140.48 (C), 135.05 (CH), 134.11 (C), 133.37 (C), 132.28 (C), 129.83 (C), 129.27 (CH), 129.10 (CH), 127.48 (CH), 126.97 (CH), 126.61 (CH), 126.36 (CH), 125.15 (CH), 123.39 (CH), 120.59 (CH), 120.26 (CH), 114.08 (CH), 112.87 (CH), 57.03 (CH), 54.14 (CH_2), 36.99 (CH_2), 18.61 (CH_3), 13.53 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_{31}\text{H}_{27}\text{N}_2\text{O}$ $[\text{M}-\text{Br}]^+$ 443.2118, found 443.2130.



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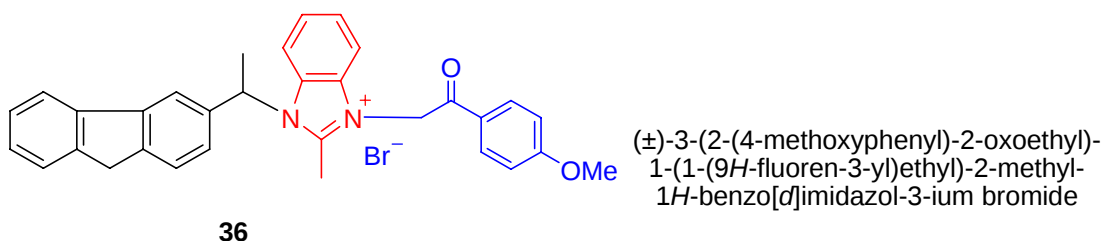
Yield 76%. White solid, Mp 165-167 °C. IR $\nu_{\max}$ (cm⁻¹): 3019, 2917, 1692, 1579, 1470, 1228, 1071, 1071, 990, 825, 746. ¹H NMR (300 MHz, CDCl₃) δ : 8.13 (2H, d, J = 8.1 Hz), 7.71-7.82 (6H, m), 7.51-7.54 (2H, m), 7.33-7.37 (5H, m), 6.47 (2H, s), 6.24-6.27 (1H, m), 3.89 (2H, s), 2.96 (3H, s), 2.18 (3H, d, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 189.61 (C), 152.02 (C), 144.32 (C), 143.26 (C), 142.50 (C), 140.22 (C), 133.95 (C), 132.34 (CH), 131.94 (C), 130.39 (CH), 130.19 (CH), 129.59 (C), 127.25 (CH), 126.75 (CH), 126.54 (CH), 126.34 (CH), 124.93 (CH), 123.03 (CH), 120.34 (CH), 120.00 (CH), 113.86 (CH), 112.60 (CH), 56.83 (CH), 52.62 (CH₂), 36.67 (CH₂), 17.92 (CH₃), 11.93 (CH₃). HRMS (ESI-TOF) m/z Calcd for C₃₁H₂₆BrN₂O [M-Br]⁺ 521.1223, found 521.1218.



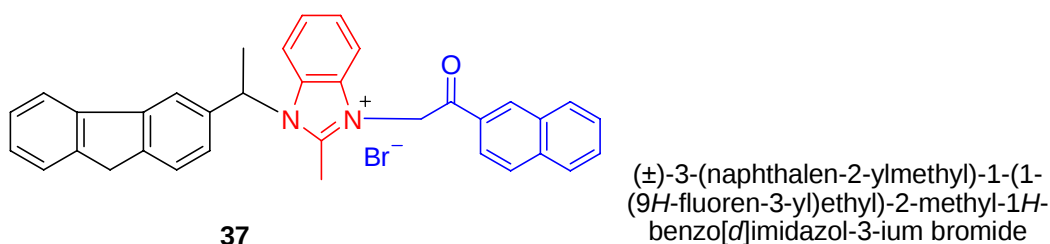
35

Yield 70%. White solid, Mp 165-167 °C. IR $\nu_{\max}$ (cm⁻¹): 3037, 1689, 1598, 1469, 1228, 991, 836, 749. ¹H NMR (300 MHz, CDCl₃) δ : 8.37-8.38 (2H, m), 7.82-7.89 (3H, m), 7.58-7.61 (3H, m), 7.34-7.44 (7H, m), 6.48 (2H, s), 6.36-6.41 (1H, m), 3.97 (2H, s), 3.00 (3H, s), 2.25-2.27 (3H, d, J = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 188.73 (C), 151.98 (C), 144.30 (C), 143.24 (C), 142.49 (C), 140.22 (C), 134.01 (C), 131.94 (C), 131.69 (CH), 131.57 (CH), 129.62 (C), 127.22 (CH), 126.71 (CH), 126.57 (CH), 126.39 (CH), 124.87 (CH), 123.01 (CH), 120.29 (CH), 119.95 (CH), 116.34 (CH), 116.05 (CH),

113.91 (CH), 112.53 (CH), 56.84 (CH), 52.14 (CH₂), 36.61 (CH₂), 17.77 (CH₃), 11.49 (CH₃). HRMS (ESI-TOF) *m/z* Calcd for C₃₁H₂₆FN₂O [M-Br]⁺ 461.2024, found 461.2006.

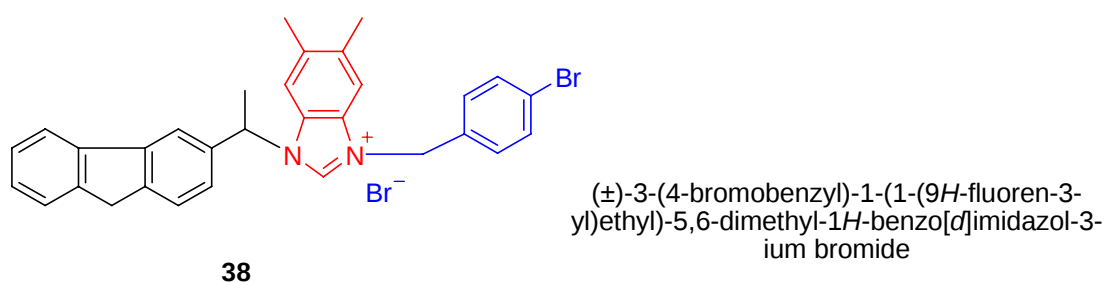


Yield 89%. White solid. 157-159 °C. IR $\nu_{\max}$ (cm⁻¹): 2925, 1679, 1601, 1517, 1469, 1023, 990, 835, 746. ¹H NMR (300 MHz, CDCl₃) δ : 8.32 (2H, d, *J* = 8.4 Hz), 7.79 (2H, dd, *J* = 15.9, 8.1 Hz), 7.72 (1H, d, *J* = 8.1 Hz), 7.54 (2H, d, *J* = 7.5 Hz), 7.32-7.38 (3H, m), 7.27-7.30 (3H, m), 7.02 (2H, d, *J* = 8.1 Hz), 6.73 (2H, s), 6.27-6.29 (1H, m), 3.89 (2H, s), 3.87 (3H, s), 3.15 (3H, s), 2.19 (3H, d, *J* = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 188.79 (C), 165.04 (C), 152.53 (C), 144.50 (C), 143.53 (C), 142.61 (C), 140.48 (C), 134.20 (C), 132.32 (C), 131.65 (CH), 129.76 (C), 127.44 (CH), 126.95 (CH), 126.54 (CH), 126.29 (CH), 125.17 (CH), 123.38 (CH), 120.56 (CH), 120.24 (CH), 114.49 (CH), 114.02 (CH), 113.02 (CH), 56.94 (CH₃), 55.69 (CH), 53.59 (CH₂), 36.97 (CH₂), 18.59 (CH₃), 13.35 (CH₃). HRMS (ESI-TOF) *m/z* Calcd for C₃₂H₂₉N₂O₂ [M-Br]⁺ 473.2224, found 473.2231.

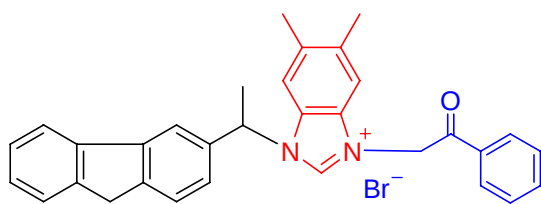


Yield 80%. White solid, Mp 165-167 °C. IR $\nu_{\max}$ (cm⁻¹): 3021, 1685, 1623, 1520, 1470, 1075, 926, 823, 739. ¹H NMR (300 MHz, CDCl₃) δ : 9.24 (1H, s), 8.21 (1H, d, *J* = 8.1 Hz), 8.12 (1H, d, *J* = 7.2 Hz), 7.92 (1H, d, *J* = 8.4 Hz), 7.74-7.86 (4H, m), 7.53-7.65 (4H, m), 7.27-7.46 (5H, m), 7.25 (1H, s), 6.95 (2H, s), 6.25-6.31 (1H, m), 3.91 (2H, s), 3.21

(3H, s), 2.21 (3H, d, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 190.66 (C), 152.64 (C), 144.58 (C), 143.55 (C), 142.72 (C), 140.49 (C), 136.37 (C), 134.14 (C), 132.60 (C), 132.48 (CH), 130.59 (CH), 130.49 (CH), 129.84 (C), 129.54 (CH), 129.04 (CH), 127.66 (CH), 127.48 (CH), 127.19 (CH), 126.97 (CH), 126.64 (CH), 126.35 (CH), 125.19 (CH), 123.40 (CH), 123.25 (CH), 120.60 (CH), 120.26 (CH), 114.03 (CH), 113.06 (CH), 57.03 (CH), 54.07 (CH_2), 36.99 (CH_2), 18.60 (CH_3), 13.52 (CH_3). Anal. Calcd for $\text{C}_{35}\text{H}_{29}\text{BrN}_2\text{O}$: C, 73.30; H, 5.10; N, 4.88. Found: C, 72.97; H, 5.29; N 4.47. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{35}\text{H}_{29}\text{N}_2\text{O} [\text{M}-\text{Br}]^+$ 493.2274, found 493.2277.



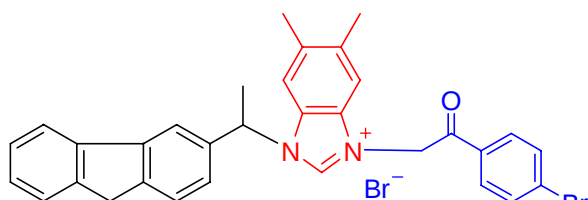
Yield 95%. White solid, Mp 172-174 °C. IR ν_{max} (cm^{-1}): 2975, 1607, 1554, 1483, 1211, 1009, 843, 738. ^1H NMR (300 MHz, CDCl_3) δ : 11.69 (1H, s), 7.75 (2H, dd, $J = 14.4$, 7.5 Hz), 7.62 (1H, s), 7.48-7.53 (5H, m), 7.23-7.43 (4H, m), 7.20 (1H, s), 5.98-6.06 (2H, m), 5.91-5.93 (1H, m), 3.88 (2H, s), 2.31 (3H, s), 2.29 (3H, s), 2.26 (3H, s). ^{13}C NMR (75 MHz, CDCl_3) δ : 144.61 (C), 143.51 (C), 142.78 (C), 140.71 (CH), 140.56 (C), 137.52 (C), 137.29 (C), 136.21 (C), 132.40 (CH), 130.14 (CH), 129.55 (C), 127.34 (CH), 126.88 (CH), 125.14 (CH), 123.21 (CH), 123.00 (CH), 120.57 (CH), 120.13 (CH), 113.86 (CH), 113.21 (CH), 59.38 (CH), 50.41 (CH_2), 36.95 (CH_2), 22.25 (CH_3), 20.68 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_{31}\text{H}_{28}\text{BrN}_2$ $[\text{M}-\text{Br}]^+$ 507.1430, found 507.1427.



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(±)-3-(2-oxo-2-phenylethyl)-1-(1-(9H-fluoren-3-yl)ethyl)-5,6-dimethyl-1H-benzo[d]imidazol-3-ium bromide

Yield 82%. White solid, Mp 173-175 °C. IR $\nu_{\max}$ (cm⁻¹): 2964, 1695, 1558, 1482, 1222, 994, 735, 687. ¹H NMR (300 MHz, CDCl₃) δ : 11.16 (1H, s), 8.19 (2H, d, J = 7.5 Hz), 7.77 (2H, dd, J = 17.4, 8.1 Hz), 7.62-7.66 (2H, m), 7.51- 7.56 (3H, m), 7.43 (1H, d, J = 7.8 Hz), 7.16-7.39 (4H, m), 6.60-6.75 (2H, m), 5.88-5.90 (1H, m), 3.90 (2H, s), 2.33 (3H, s), 2.29 (3H, s), 2.25 (3H, d, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 190.55 (C), 144.69 (C), 143.56 (C), 142.81 (C), 141.28 (CH), 140.60 (C), 137.55 (C), 137.12 (C), 136.17 (C), 134.77 (CH), 133.67 (C), 131.23 (C), 129.20 (CH), 129.01 (CH), 128.73 (CH), 128.20 (CH), 127.31 (CH), 126.86 (CH), 125.18 (CH), 122.91 (CH), 120.62 (CH), 120.14 (CH), 113.65 (CH), 112.96 (CH), 59.27 (CH), 53.61 (CH₂), 36.95 (CH₂), 22.25 (CH₃), 20.65 (CH₃), 20.52 (CH₃). HRMS (ESI-TOF) m/z Calcd for C₃₂H₂₉BrN₂O [M-Br]⁺ 457.2274, found 457.2282.

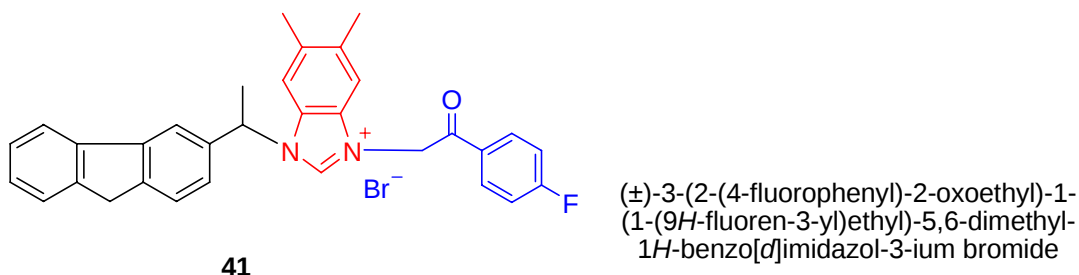


40

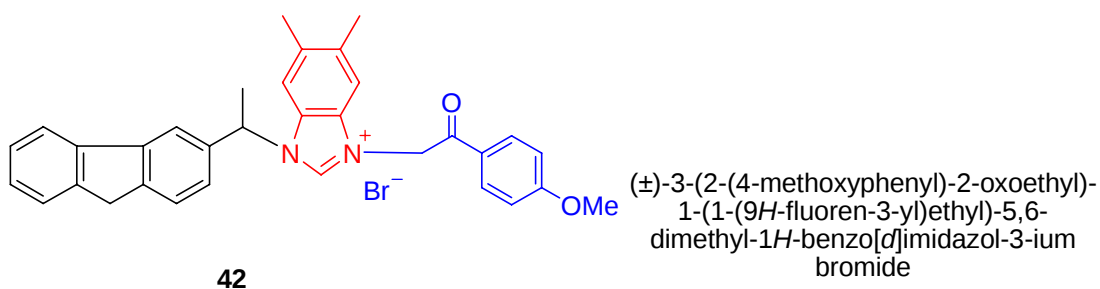
(±)-3-(2-(4-bromophenyl)-2-oxoethyl)-1-(1-(9H-fluoren-3-yl)ethyl)-5,6-dimethyl-1H-benzo[d]imidazol-3-ium bromide

Yield 70%. White solid, Mp 176 -178 °C. IR $\nu_{\max}$ (cm⁻¹): 2973, 2929, 1691, 1557, 1442, 1224, 1138, 996, 841, 746, 688. ¹H NMR (300 MHz, CDCl₃) δ : 11.10 (1H, s), 8.18 (2H, d, J = 7.8 Hz), 7.76 (2H, dd, J = 17.7, 8.4 Hz), 7.61-7.68 (2H, m), 7.51-7.56 (3H, m), 7.42 (1H, d, J = 7.8 Hz), 7.22-7.38 (3H, m), 6.65-6.68 (2H, m), 5.86-5.92 (1H, s), 3.89 (2H, s), 2.32 (3H, s), 2.28 (3H, s), 2.24 (3H, d, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 190.57 (C), 144.68 (C), 143.56 (C), 142.80 (C), 141.25 (CH), 140.60 (C), 137.55 (C),

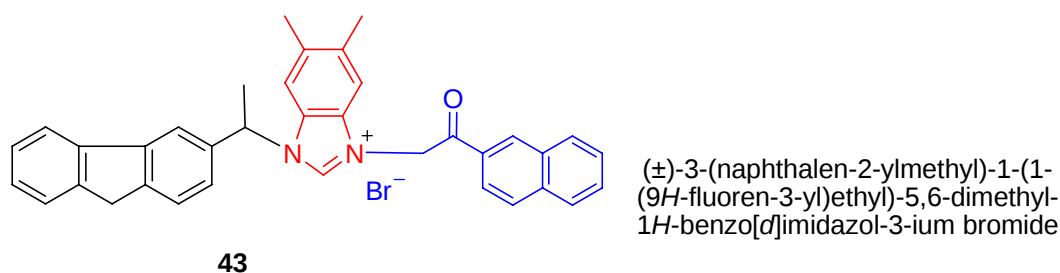
137.11 (C), 136.16 (C), 134.78 (CH), 133.66 (C), 131.22 (C), 129.19 (CH), 128.73 (CH), 127.31 (CH), 126.86 (CH), 125.18 (CH), 122.91 (CH), 120.61 (CH), 120.13 (CH), 113.66 (CH), 112.95 (CH), 59.27 (CH), 53.62 (CH₂), 36.94 (CH₂), 22.21 (CH₃), 20.66 (CH₃), 20.52 (CH₃). HRMS (ESI-TOF) *m/z* Calcd for C₃₂H₂₈BrN₂O [M-Br]⁺ 535.1380, found 535.1372.



Yield 82%. White solid, Mp 172-174 °C. IR ν_{max} (cm⁻¹): 2971, 1696, 1598, 1557, 1496, 1230, 997, 839, 733. ¹H NMR (300 MHz, CDCl₃) δ : 11.09 (1H, s), 8.26 (2H, dd, *J* = 12.3, 6.6 Hz), 7.74 (2H, dd, *J* = 15.9, 8.1 Hz), 7.58 (1H, s), 7.49 (1H, d, *J* = 6.6 Hz), 7.26-7.42 (4H, m), 7.22 (1H, s), 7.13 (2H, dd, *J* = 7.8, 15.6 Hz), 6.66-6.81 (2H, m), 5.85-5.92 (1H, m), 3.86 (2H, s), 2.31 (3H, s), 2.27 (3H, s), 2.21 (3H, d, *J* = 6 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 189.31 (C), 164.87 (C), 144.65 (C), 143.52 (C), 142.77 (C), 141.07 (CH), 140.57 (C), 137.63 (C), 137.18 (C), 136.16 (C), 131.80 (CH), 131.67 (CH), 130.22 (C), 130.18 (C), 129.13 (C), 127.30 (CH), 126.85 (CH), 125.13 (CH), 122.85 (CH), 120.61 (CH), 120.12 (CH), 116.49 (C), 116.20 (C), 113.56 (C), 113.20 (C), 59.217 (CH), 53.68 (CH₂), 36.91 (CH₂), 22.25 (CH₃), 20.63 (CH₃), 20.49 (CH₃). HRMS (ESI-TOF) *m/z* Calcd for C₃₂H₂₈FN₂O [M-Br]⁺ 475.2180, found 475.2191.



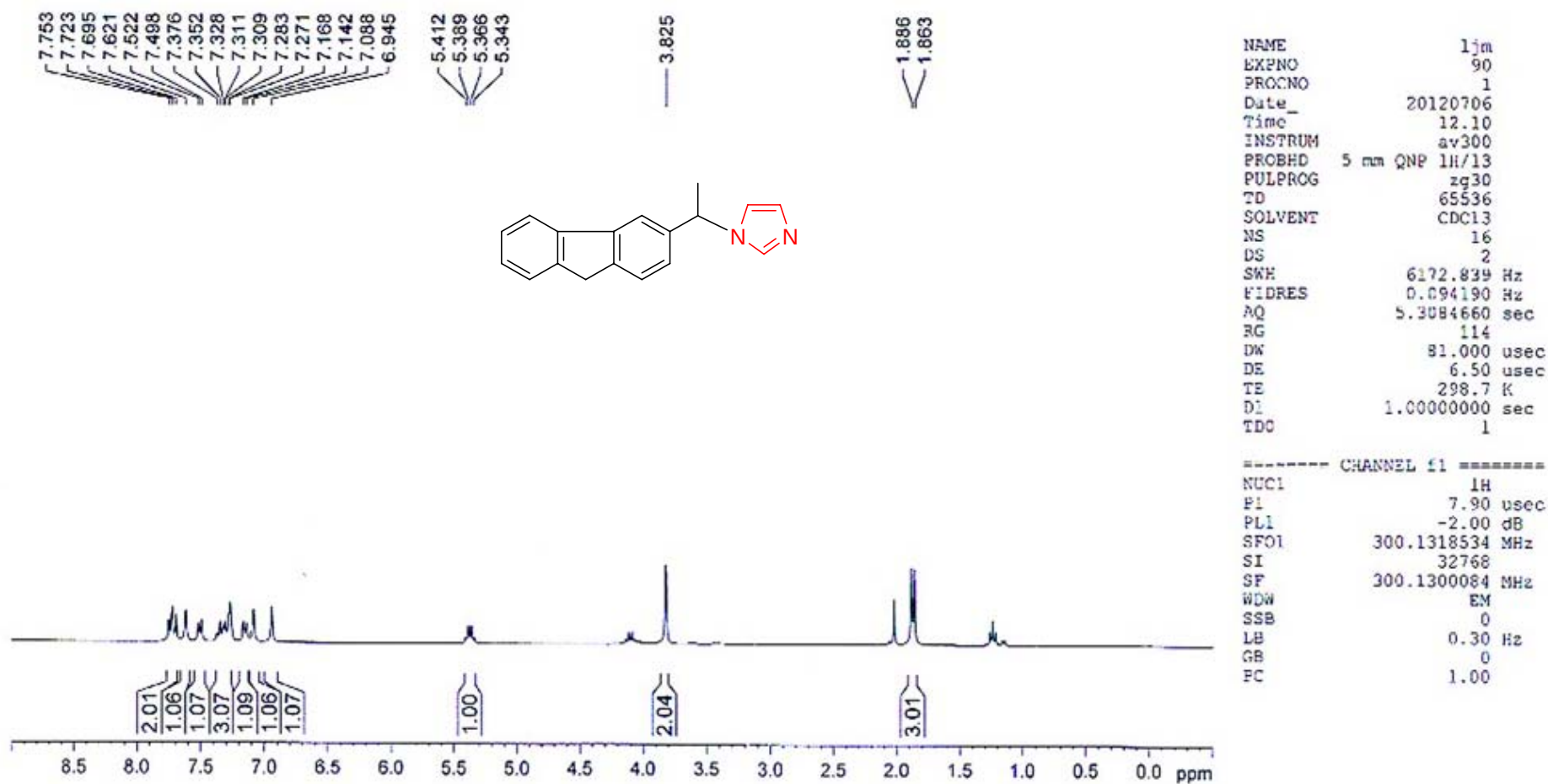
Yield 96%. White solid, Mp 239-241 °C. IR ν_{max} (cm⁻¹): 3191, 2986, 1682, 1597, 1450, 1018, 838, 740. ¹H NMR (300 MHz, CDCl₃) δ : 11.13 (1H, s), 8.17 (2H, d, J = 8.1 Hz), 7.77 (2H, dd, J = 16.5, 8.4 Hz), 7.61 (1H, s), 7.52 (1H, d, J = 7.2 Hz), 7.30-7.43 (3H, m), 7.28 (1H, s), 7.20 (1H, s), 6.99 (2H, d, J = 8.1 Hz), 6.60 (2H, s), 5.85-5.87 (1H, m), 3.89 (2H, s), 3.88 (3H, s), 2.32 (3H, s), 2.28 (3H, s), 2.25 (3H, d, J = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 188.76 (C), 164.85 (C), 144.69 (C), 143.57 (C), 142.79 (C), 141.24 (CH), 140.60 (C), 137.48 (C), 137.04 (C), 136.20 (C), 131.22 (CH), 129.17 (C), 127.31 (C), 126.86 (CH), 126.62 (CH), 125.14 (CH), 122.91 (CH), 120.61 (CH), 120.14 (CH), 114.44 (CH), 113.56 (CH), 113.11 (CH), 59.25 (CH), 55.66 (CH₃), 53.21 (CH₂), 36.95 (CH₂), 22.30 (CH₃), 20.68 (CH₃), 20.55 (CH₃). Anal. Calcd for C₃₃H₃₁BrN₂O₂: C, 69.84; H, 5.51; N, 4.94. Found: C, 69.77; H, 5.52; N 4.46. HRMS (ESI-TOF) m/z Calcd for C₃₃H₃₁BrN₂O₂ [M-Br]⁺ 487.2380, found 487.2389.

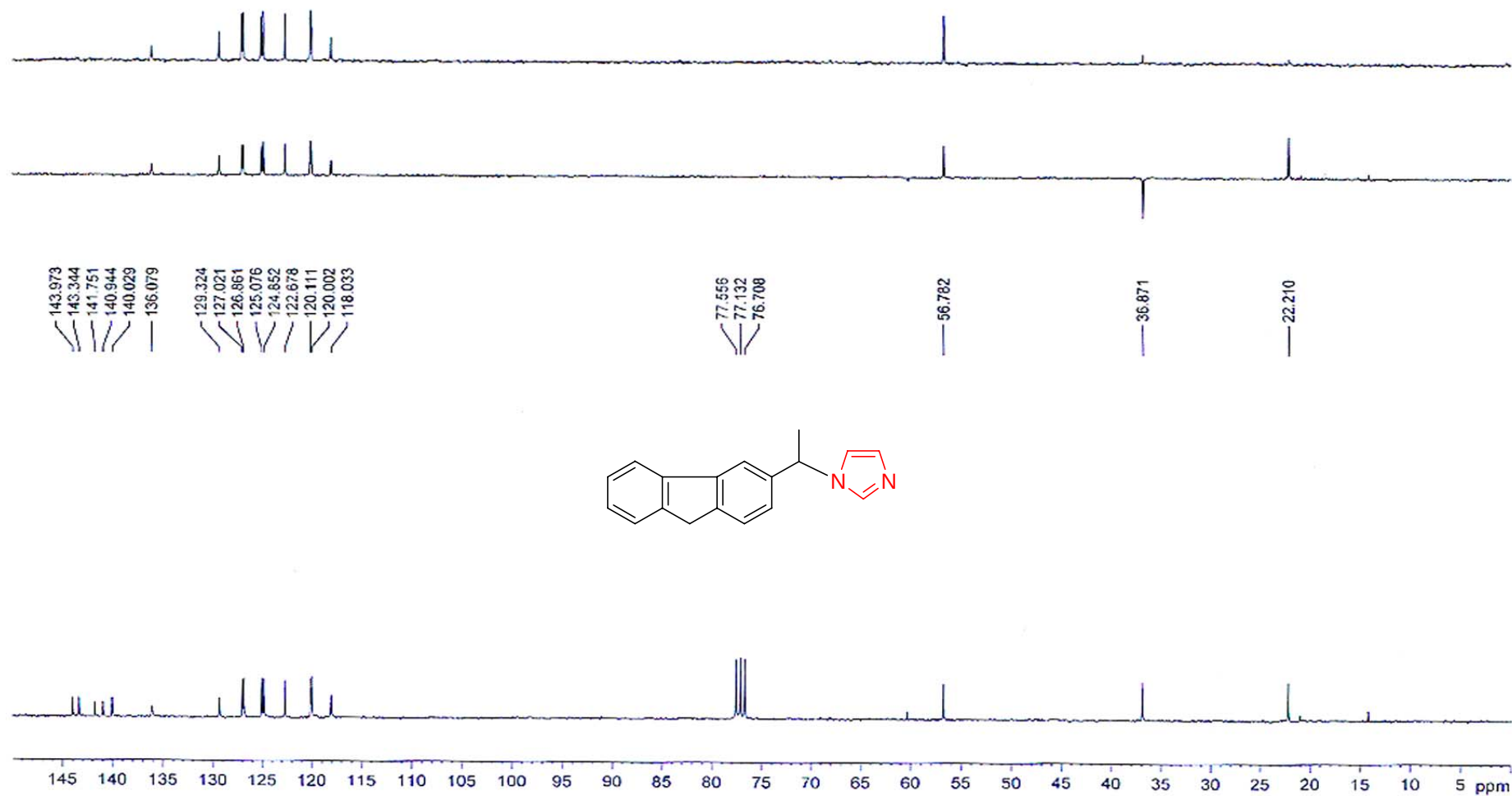


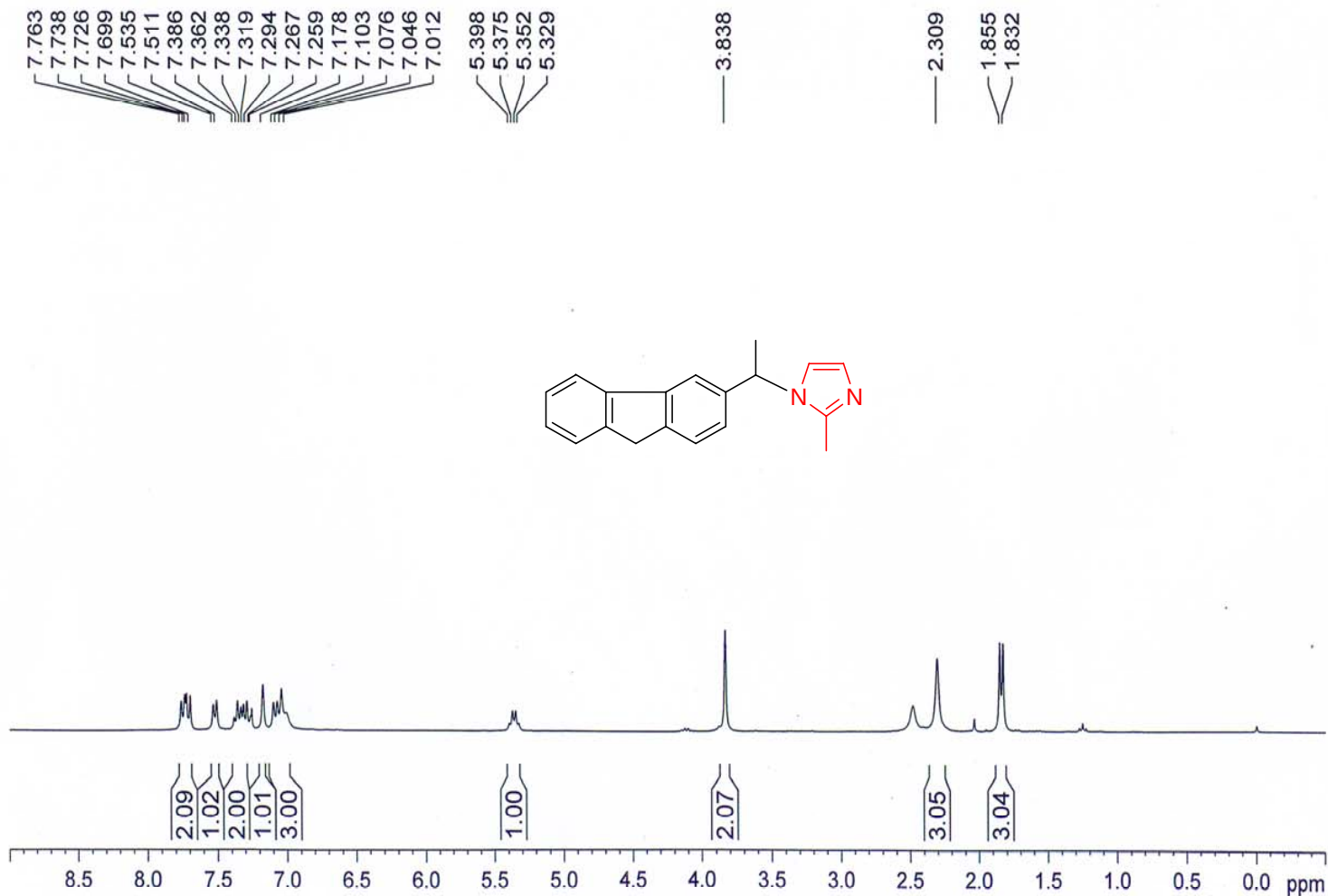
Yield 92%. White solid, Mp 244-246 °C. IR ν_{max} (cm⁻¹): 3192, 3007, 1681, 1555, 1459, 1186, 1011, 837, 743. ¹H NMR (300 MHz, CDCl₃) δ : 10.44 (1H, s), 8.92 (1H, s), 8.13 (2H, dd, J = 11.4, 8.1 Hz), 7.93 (2H, dd, J = 18.6, 8.4 Hz), 7.79 (2H, dd, J = 11.1, 8.1 Hz), 7.63-7.67 (3H, m), 7.60 (1H, s), 7.54 (1H, d, J = 7.2 Hz), 7.43 (1H, d, J = 7.8 Hz), 7.31-7.37 (3H, m), 7.17 (1H, d, J = 7.5 Hz), 6.61 (2H, s), 5.89-5.96 (1H, m), 3.91 (2H, s), 2.33 (3H, s), 2.30 (3H, s), 2.23 (3H, d, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 190.54 (C), 144.63 (C), 143.49 (C), 142.77 (C), 140.93 (CH), 140.56 (C), 137.62 (CH), 137.14 (C), 136.27 (C), 136.16 (C), 132.51 (C), 131.43 (C), 131.21 (C), 130.77 (C), 130.09 (CH), 129.43 (CH), 129.23 (CH), 129.03 (CH), 128.15 (CH), 127.74 (CH), 127.30 (CH), 127.23 (CH), 126.85 (CH), 125.08 (CH), 123.24 (CH), 122.83 (CH), 120.59 (CH), 120.10 (CH), 113.61 (CH), 112.95 (CH), 59.15 (CH), 53.56 (CH₂), 36.86

(CH₂), 21.77 (CH₃), 20.55 (CH₃), 20.39 (CH₃). HRMS (ESI-TOF) m/z Calcd for C₃₆H₃₁BrN₂O [M-Br]⁺ 507.2431, found 507.2440.

3. ^1H -NMR and ^{13}C -NMR Spectral of New Compounds







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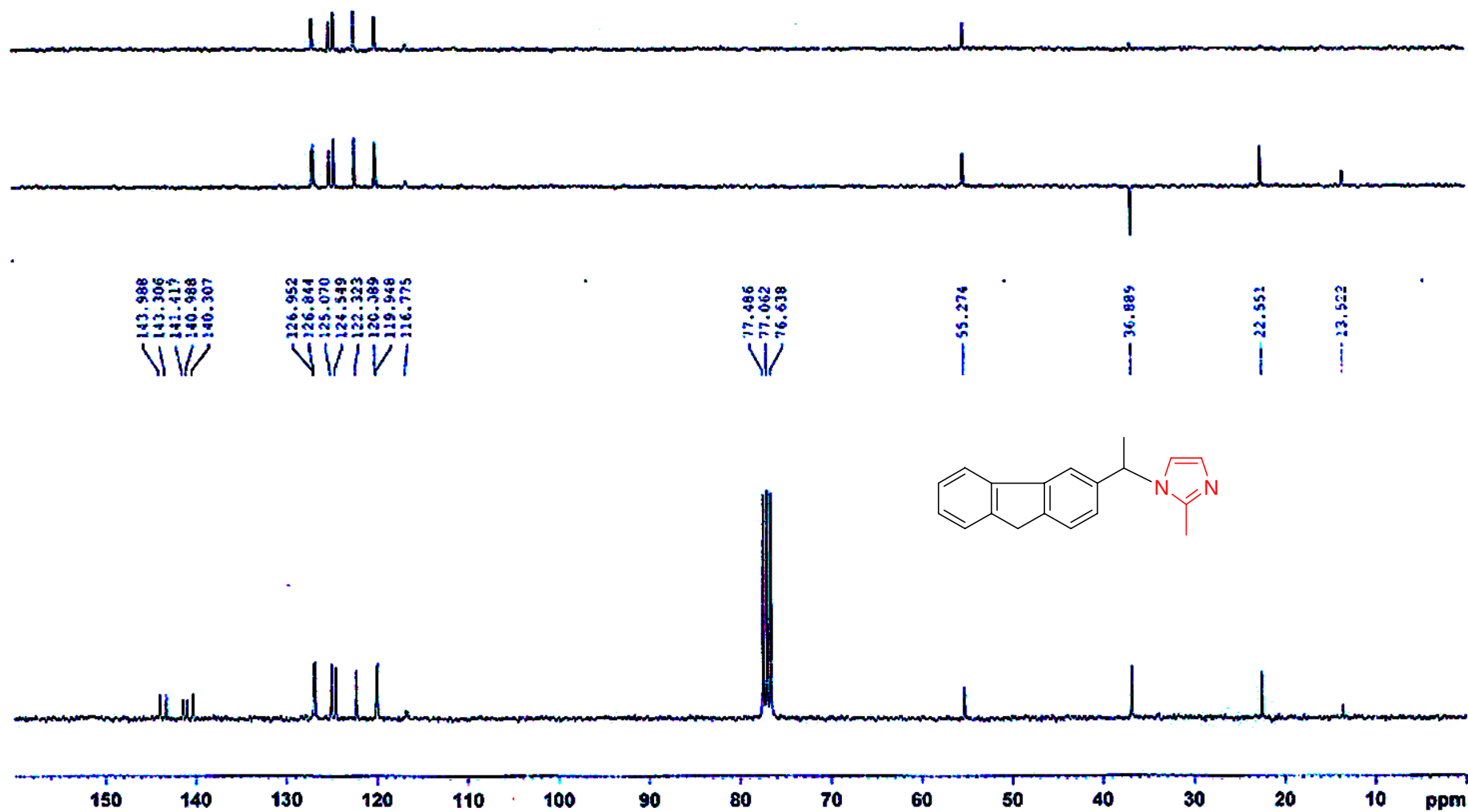
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FIDRES         0.094190 Hz
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DE             6.50 usec
TE            296.5 K
D1            1.00000000 sec
TD0            1

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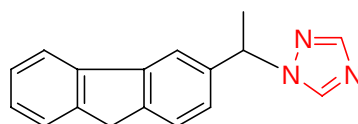


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7.236

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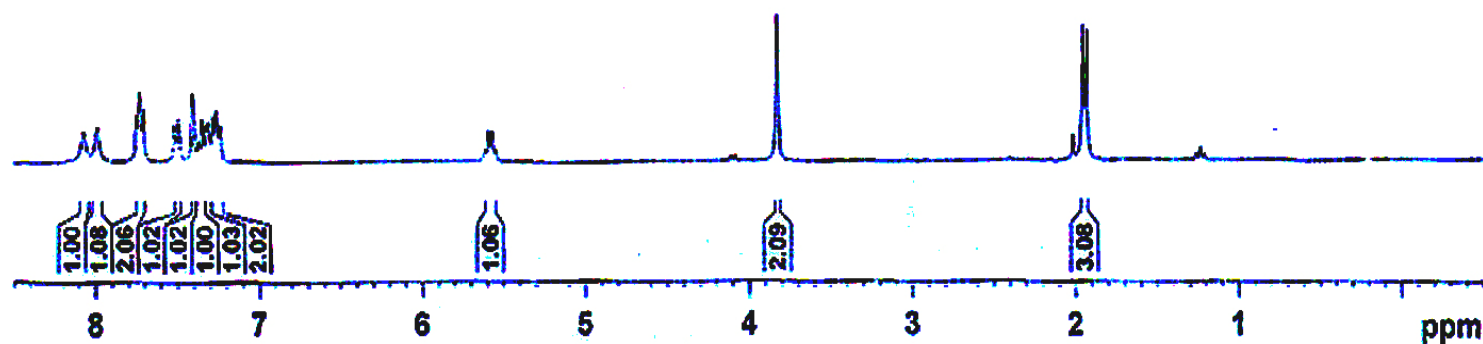
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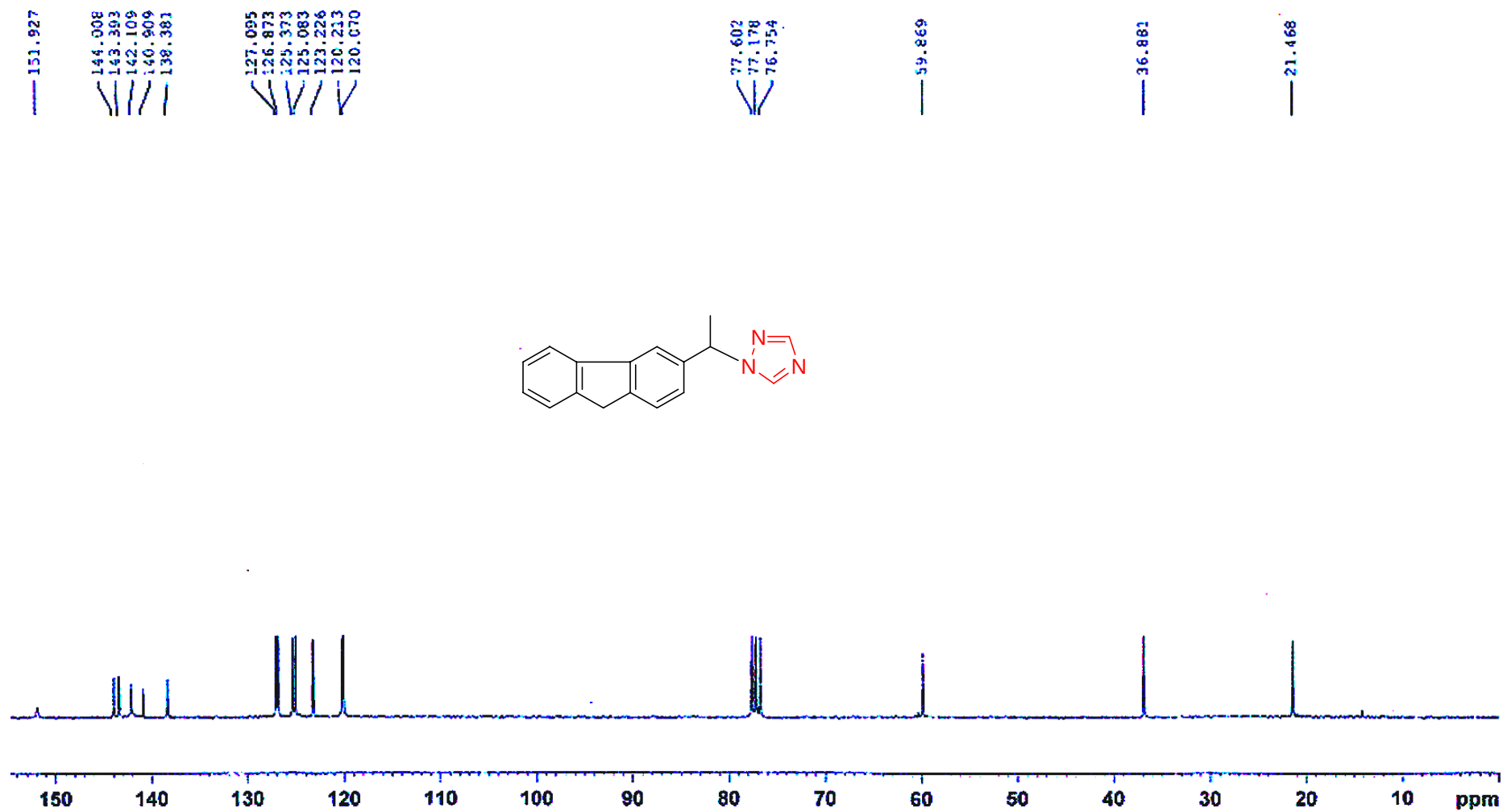
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1.933

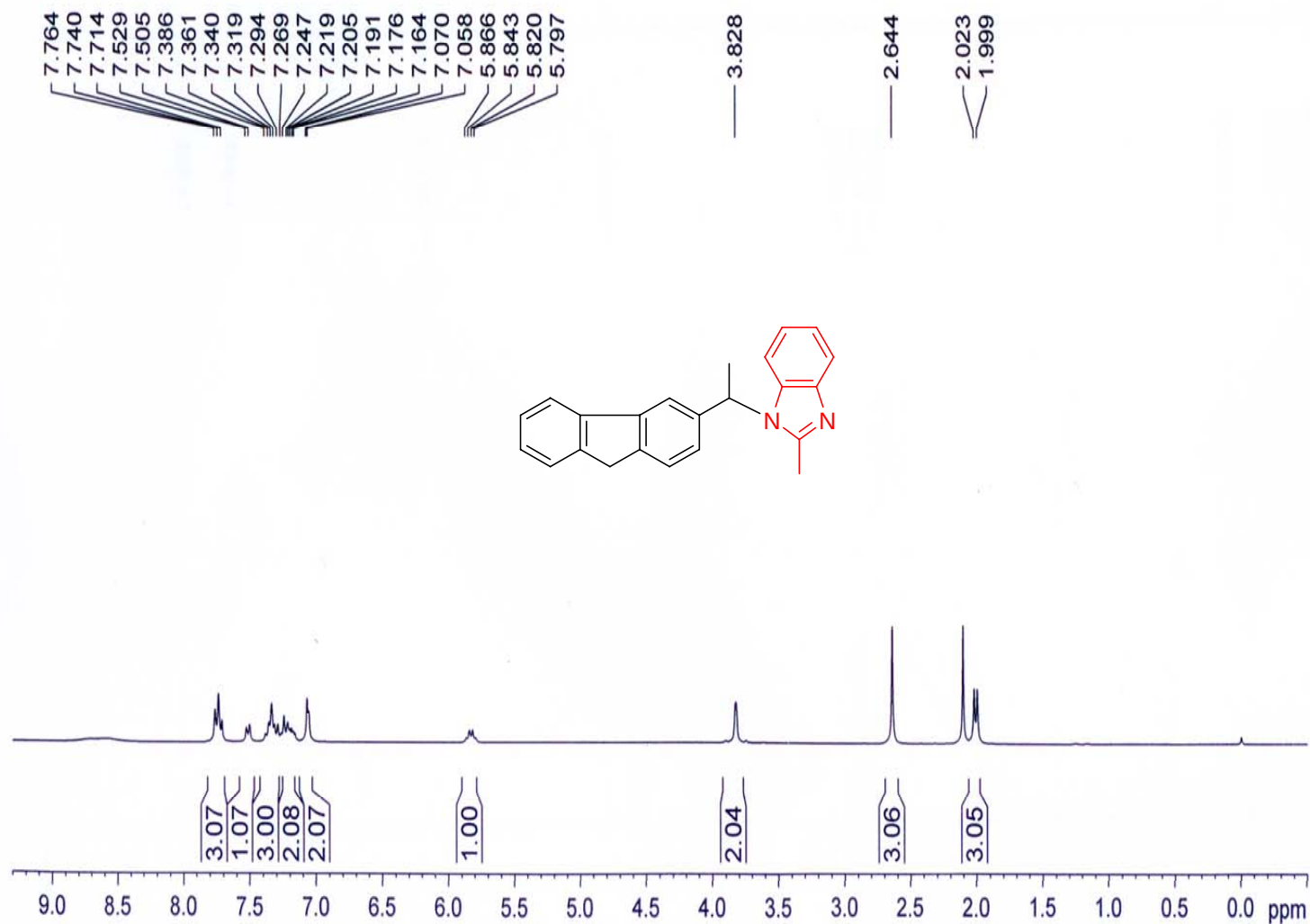


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DE 6.50 usec
TE 297.0 K
D1 1.90000000 sec
TDG 1

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GB 0
PC 1.00







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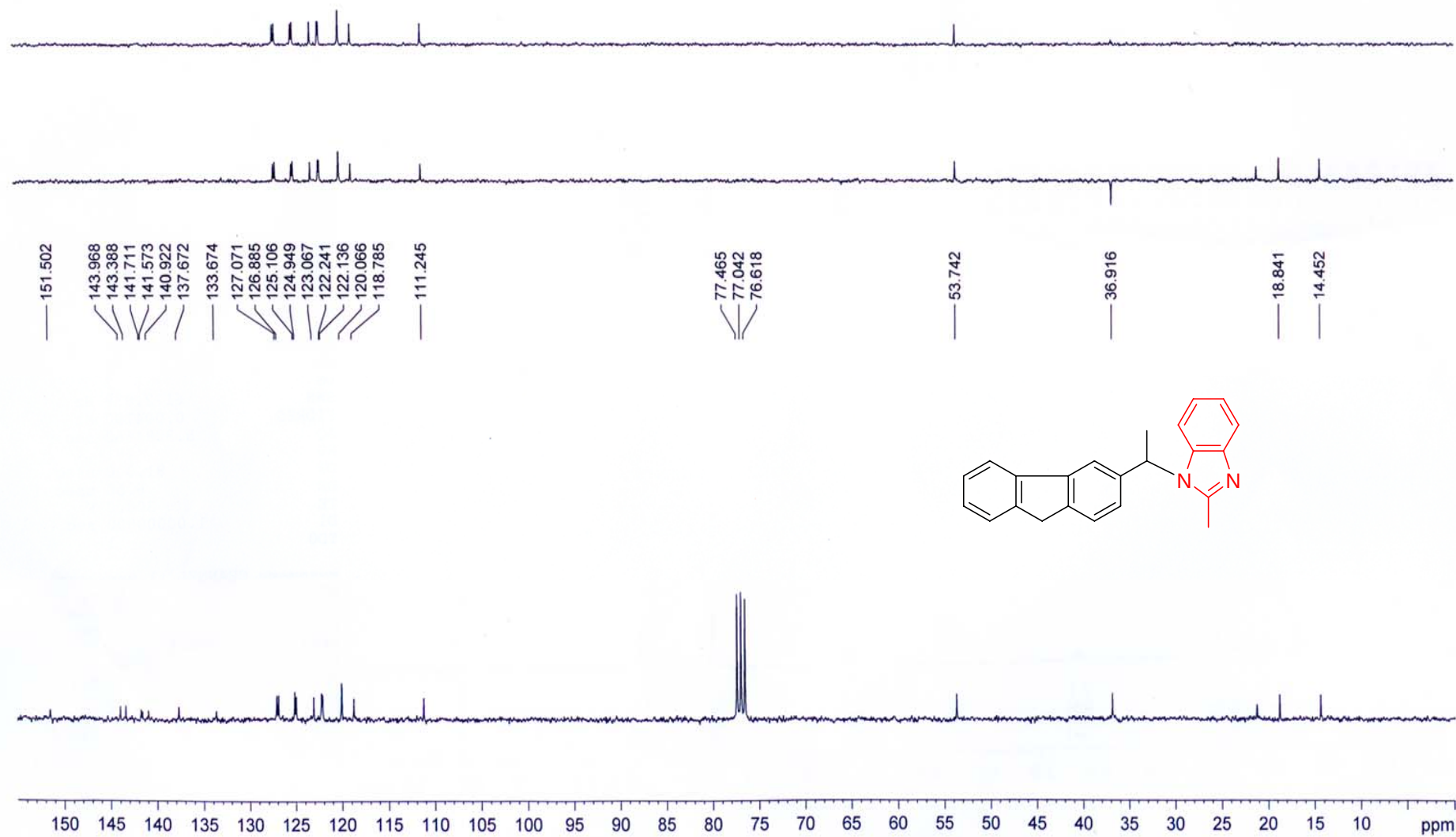
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FIDRES        0.094190 Hz
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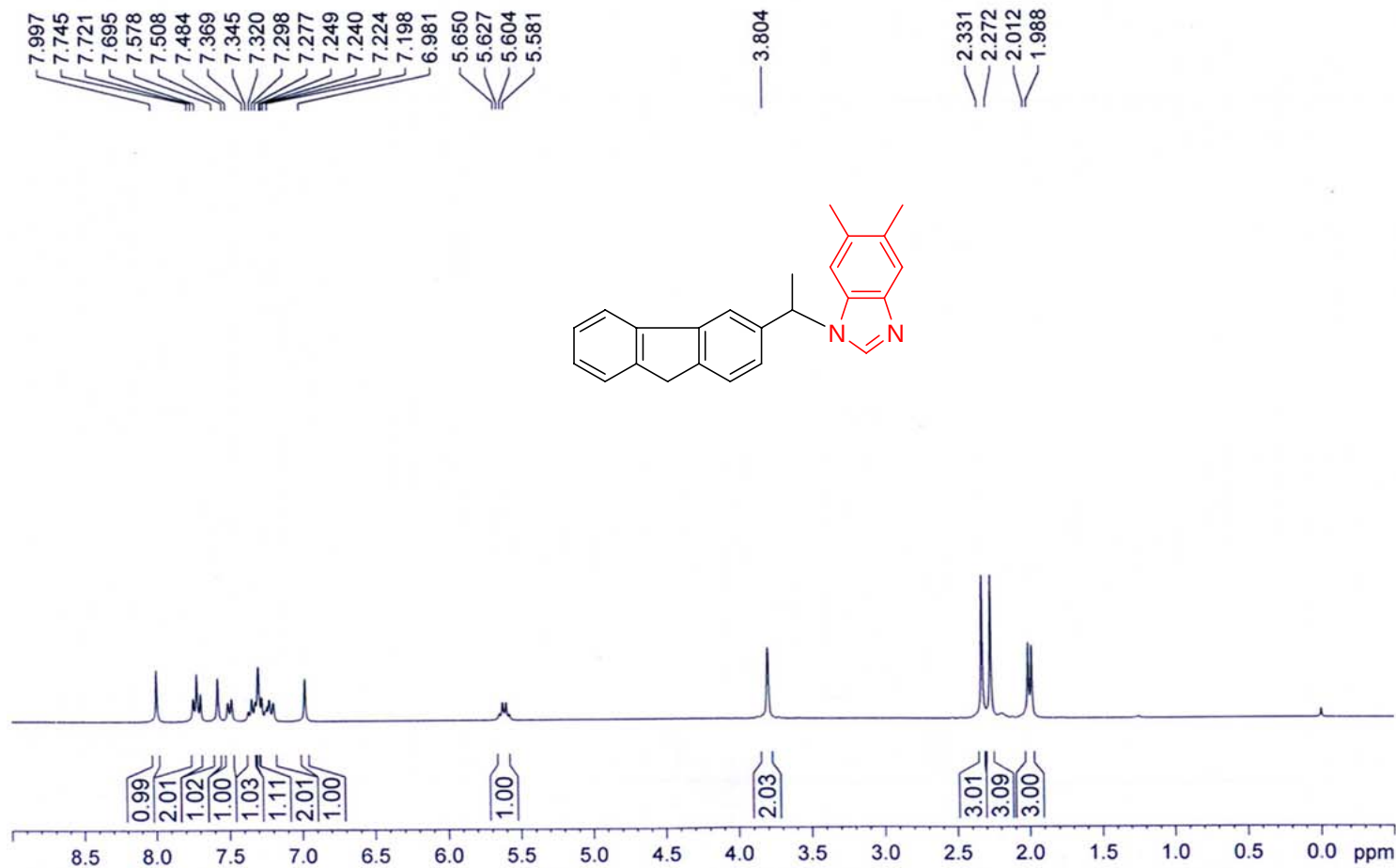
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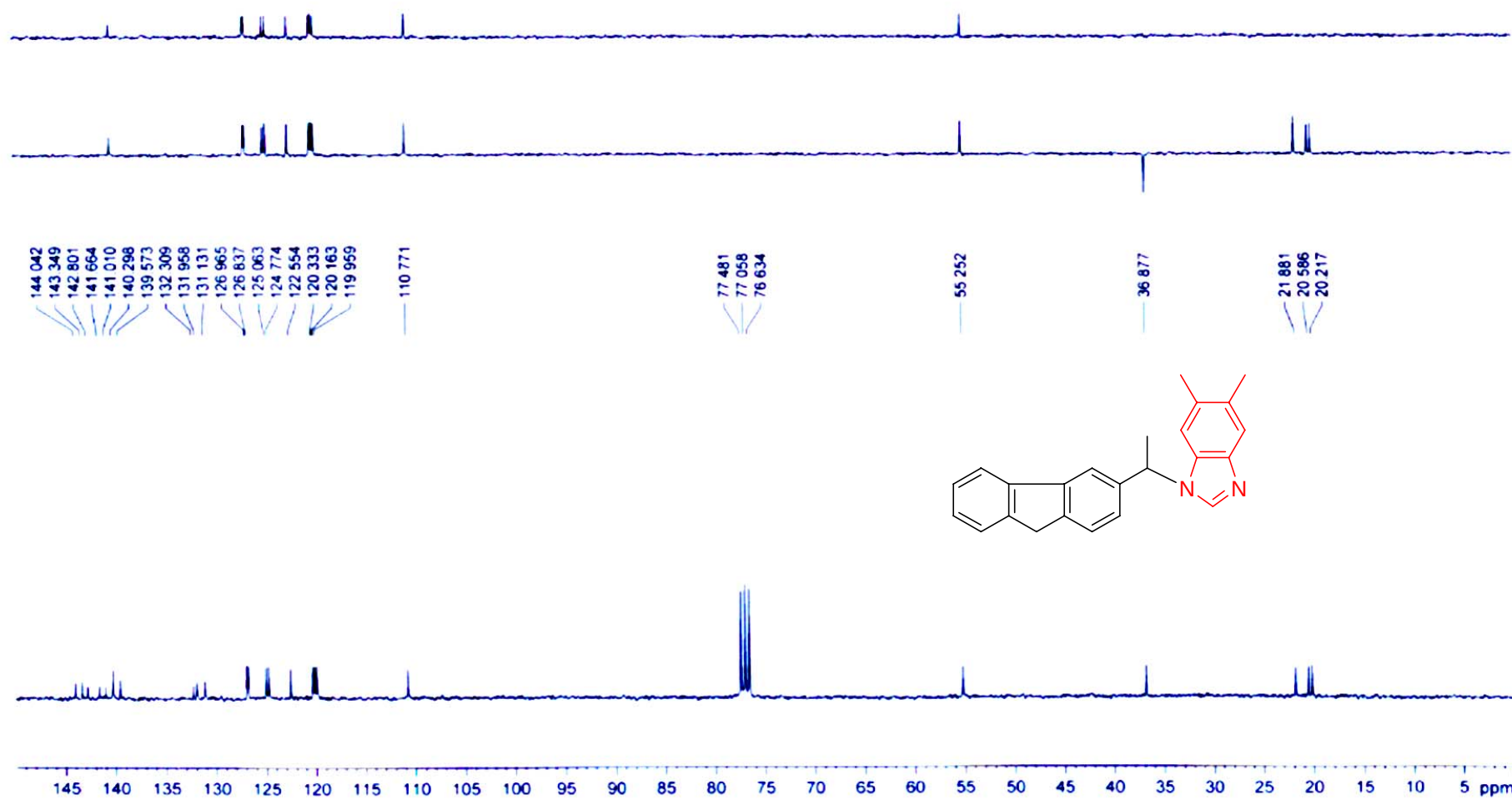
NAME          ljm
EXPNO         106
PROCNO        1
Date_         20120716
Time_         12.12
INSTRUM       av300
PROBHD        5 mm QNP 1H/13
PULPROG       zg30
TD            65536
SOLVENT       CDC13
NS            16
DS            2
SWH           6172.839 Hz
FIDRES        0.094190 Hz
AQ            5.3084660 sec
RG            181
DW            81.000 usec
DE            6.50 usec
TE            299.0 K
D1            1.00000000 sec
TD0           1

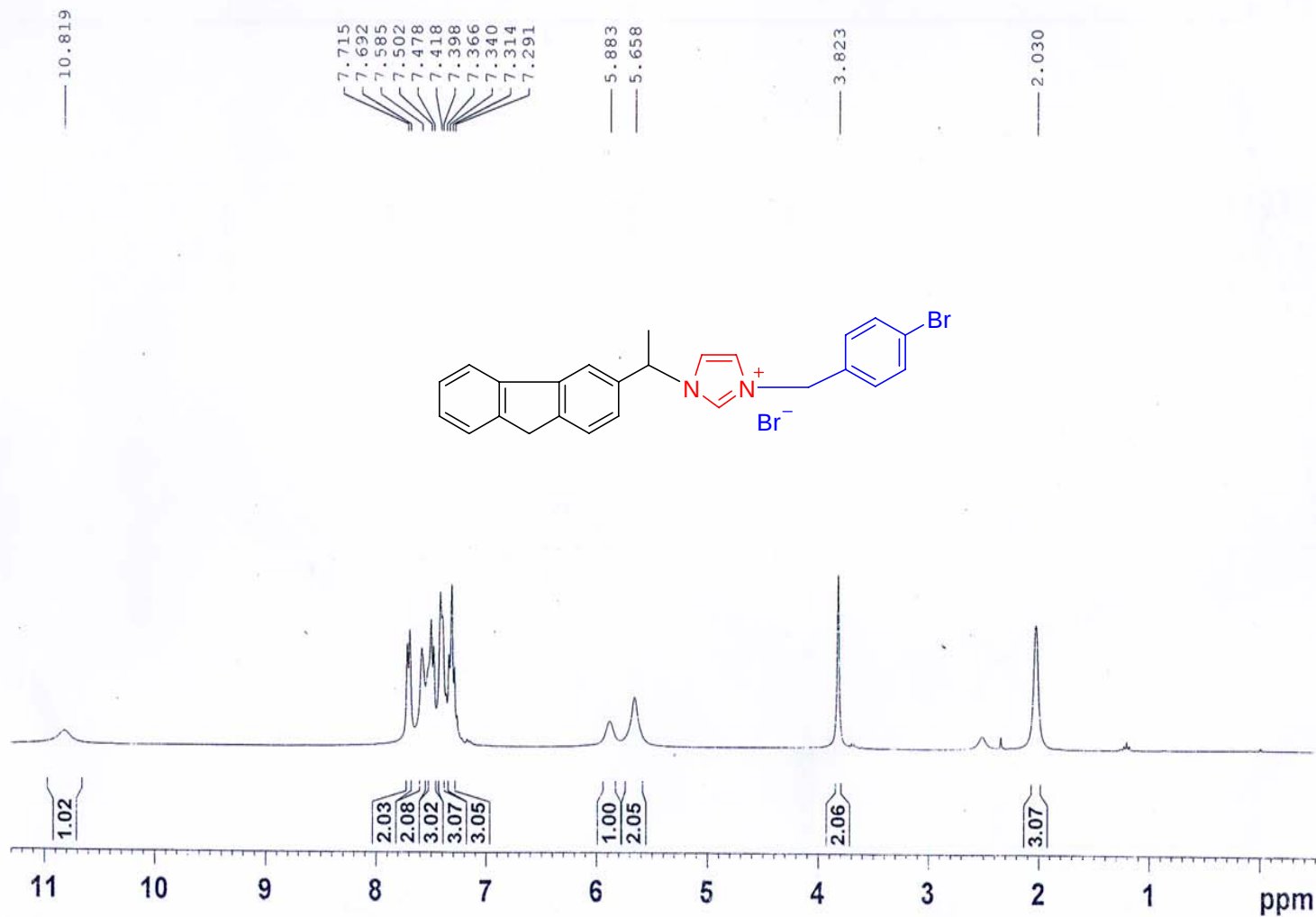
```

```

===== CHANNEL f1 =====
NUC1          1H
P1            7.90 usec
PL1           -2.00 dB
SFO1          300.1318534 MHz
SI            32768
SF            300.1300120 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00

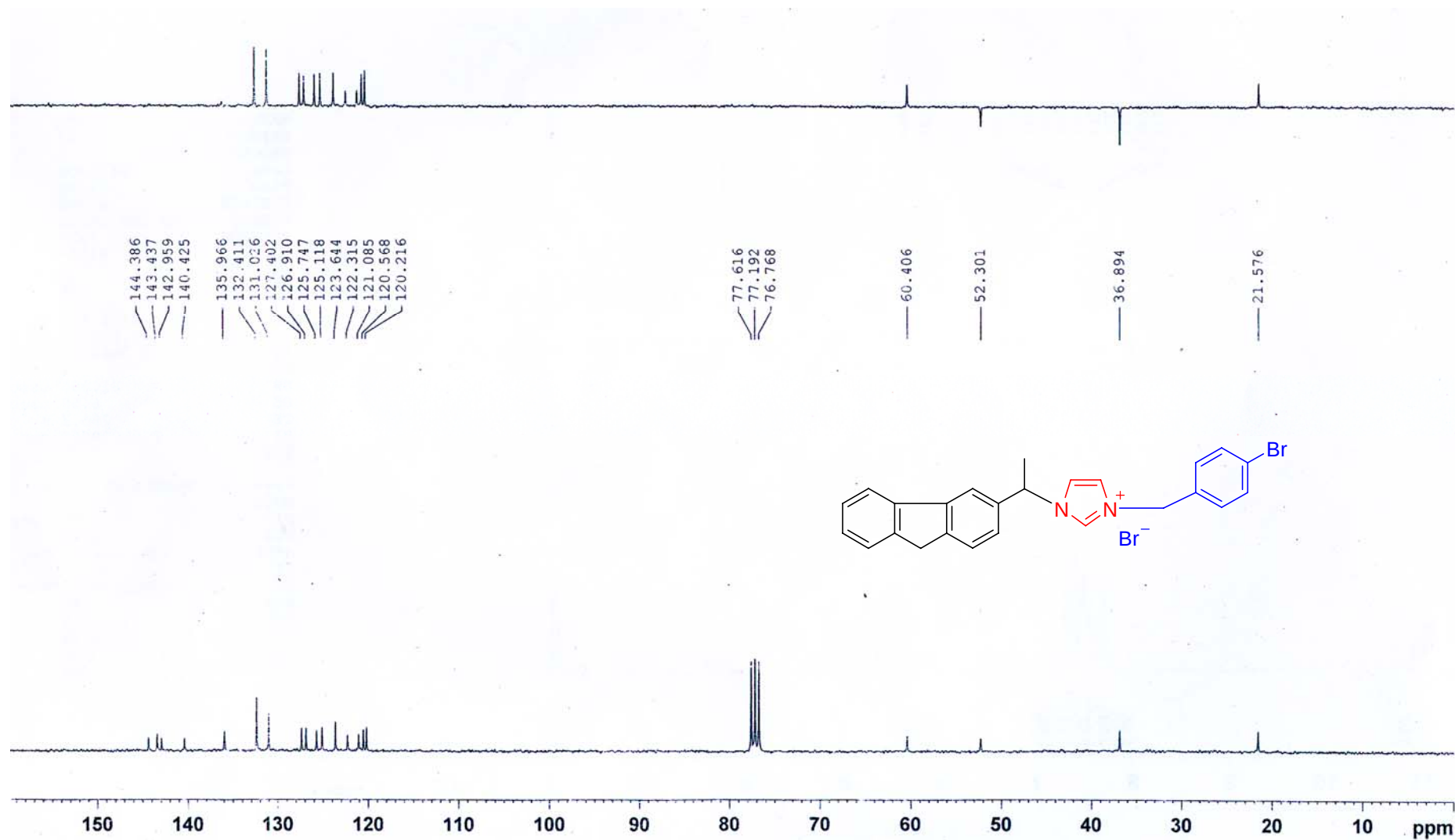
```

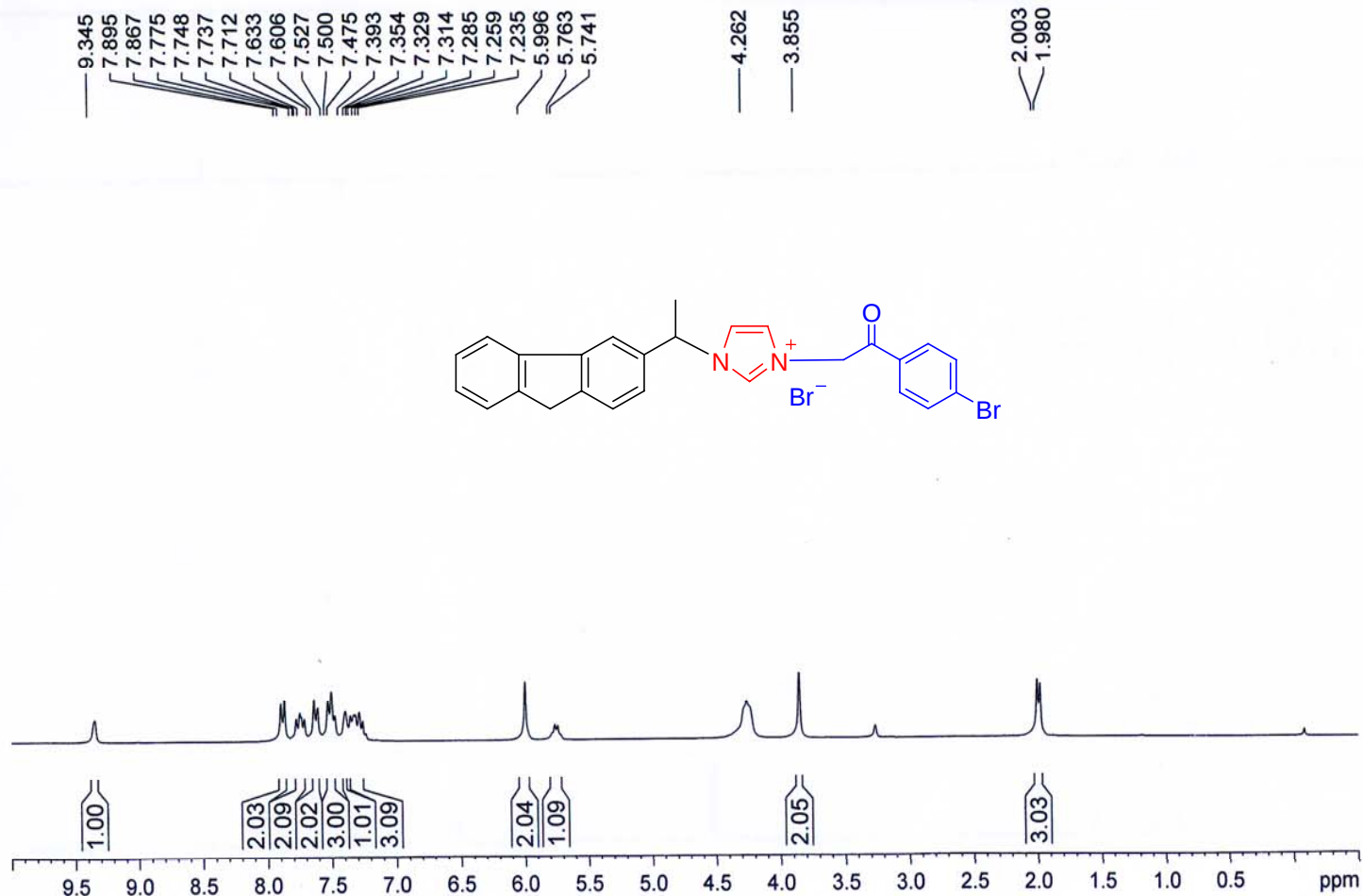




NAME ljm
 EXPNO 69
 PROCNO 1
 Date 20121208
 Time 11.38
 INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 NS 76
 DS 0
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 114
 DW 81.000 usec
 DE 6.50 usec
 TE 295.2 K
 D1 2.00000000 sec
 TDO 1

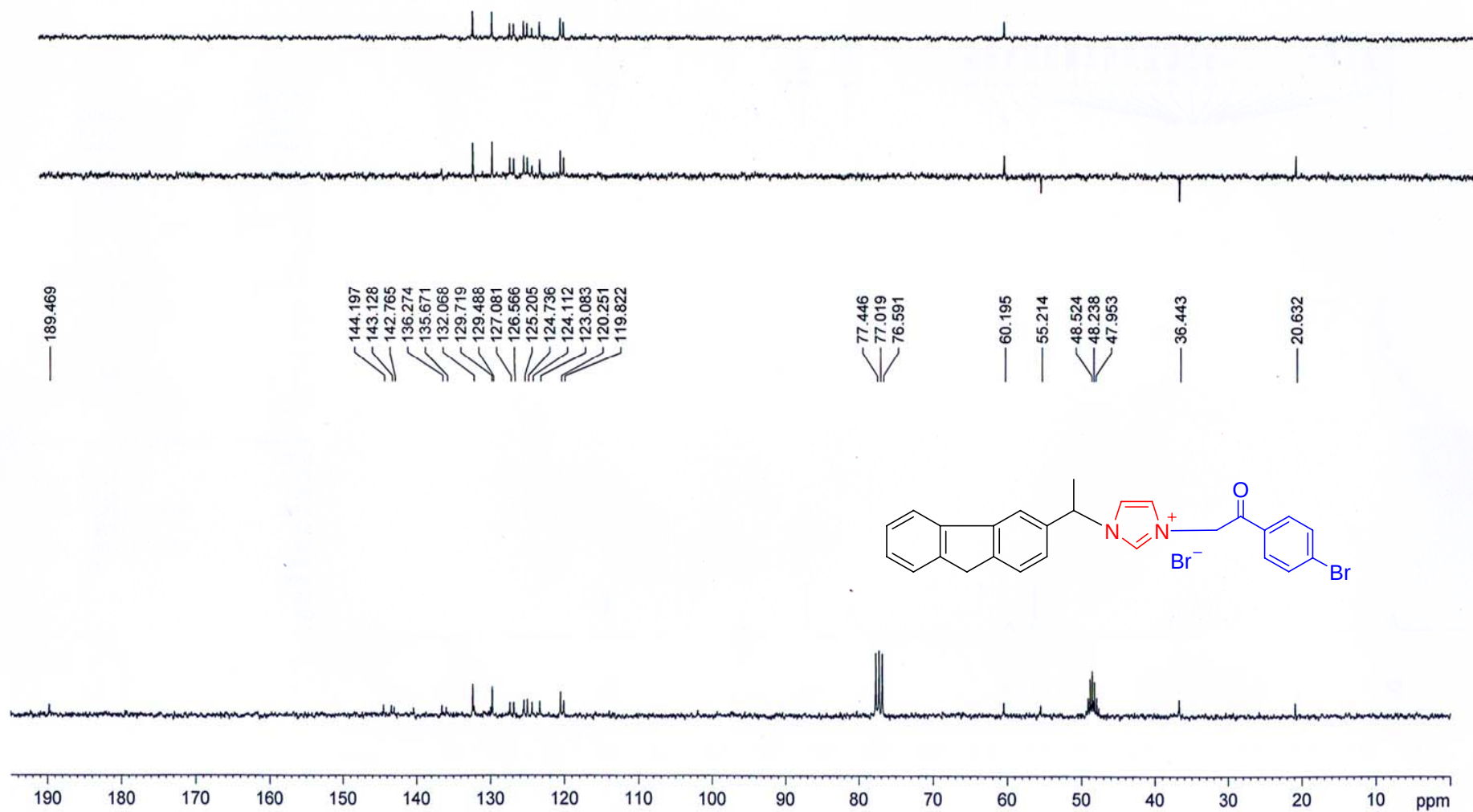
===== CHANNEL f1 =====
 NUC1 1H
 P1 7.90 usec
 PL1 -2.00 dB
 SFO1 300.1318534 MHz
 SI 32768
 SF 300.1299917 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





NAME 1jm
 EXPNO 141
 PROCNO 1
 Date_ 20120805
 Time_ 15.14
 INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 256
 DW 81.000 usec
 DE 6.50 usec
 TE 300.1 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.90 usec
 PL1 -2.00 dB
 SFO1 300.1318534 MHz
 SI 32768
 SF 300.1312005 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



8.075
8.037
8.008
7.976
7.949
7.941
7.915
7.748
7.670
7.613
7.589
7.445
7.419
7.395
7.369
7.359
7.334
7.156
7.128

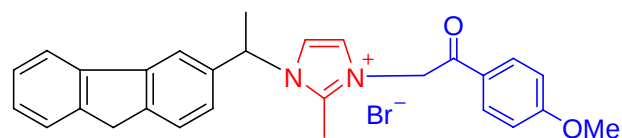
6.059
6.033
6.010

3.950
3.870

3.451

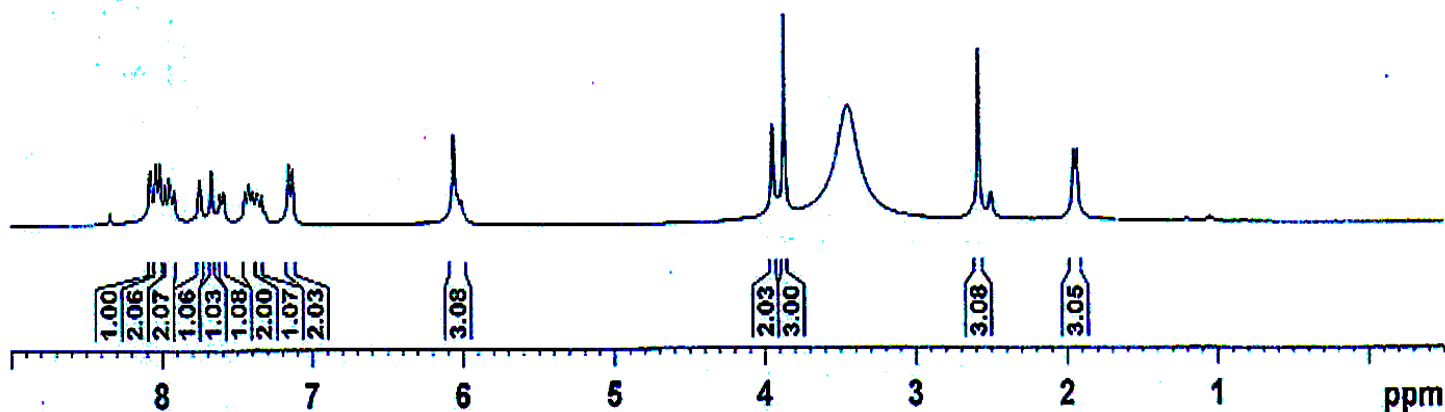
2.584
2.531
2.504

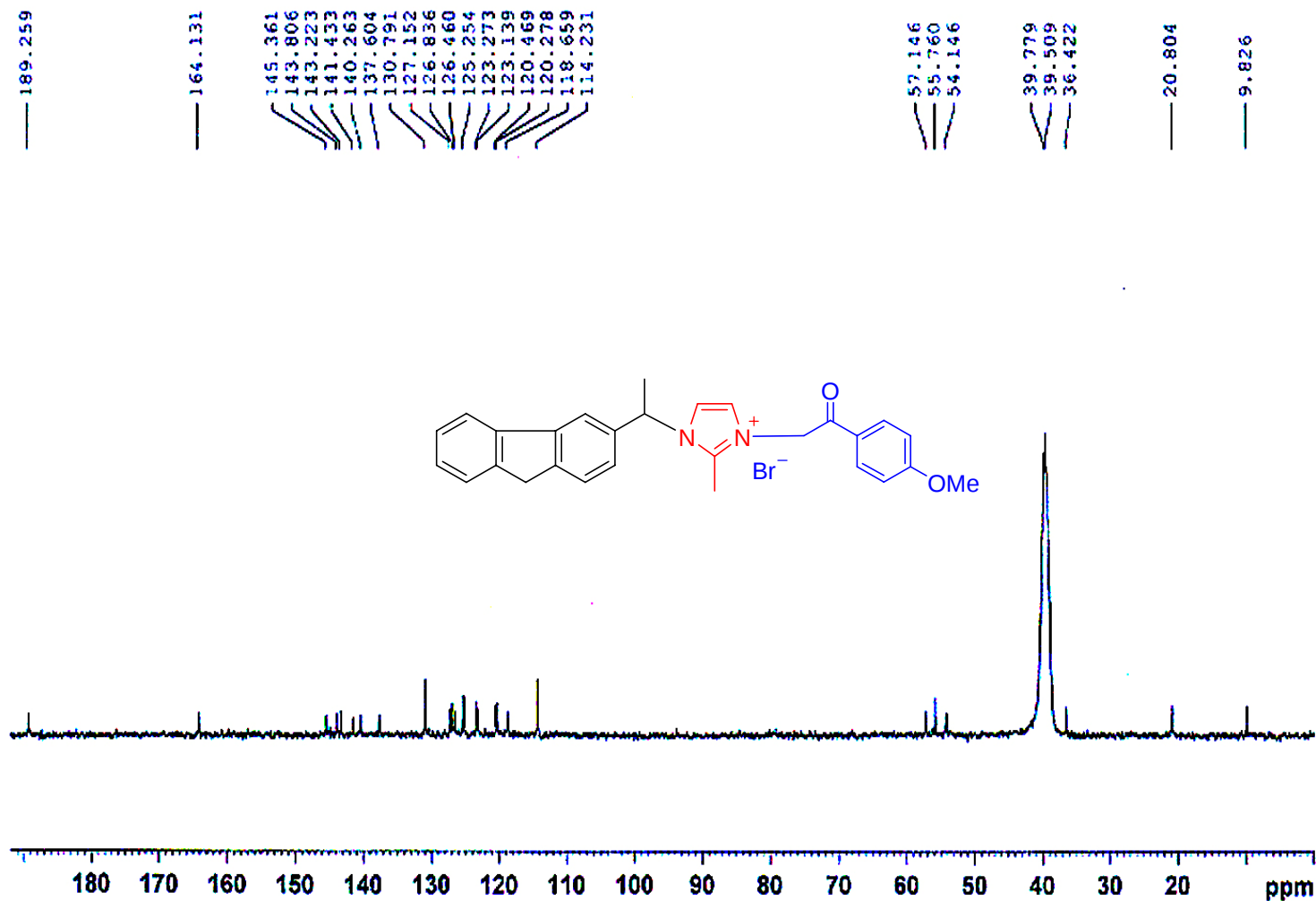
1.958
1.936



NAME ljm
EXPNO 45
PROCNO 1
Date 20121122
Time 15.40
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 103
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 114
DW 81.000 usec
DE 6.50 usec
TE 297.8 K
D1 2.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

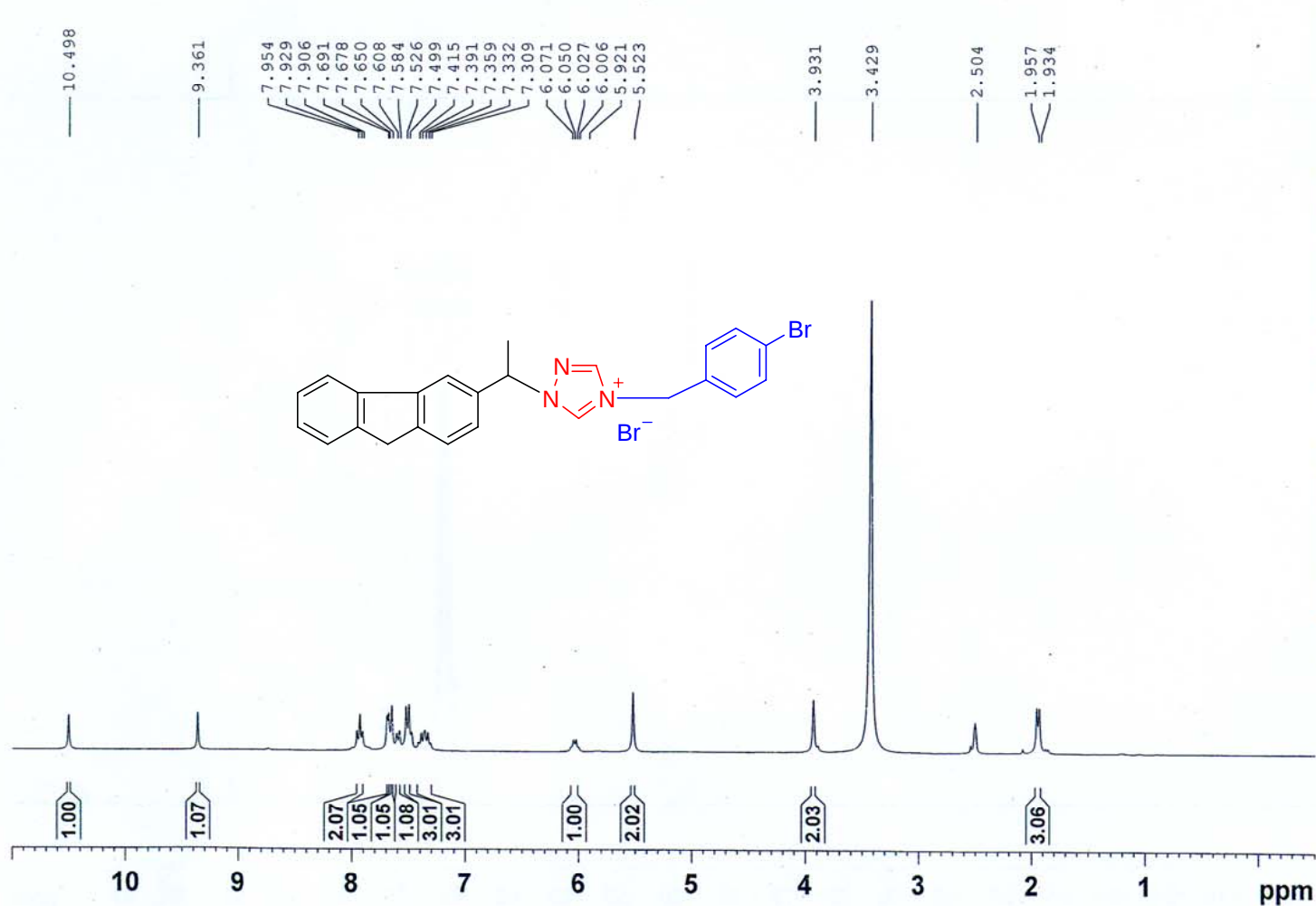




NAME ljm
 EXPNO 46
 PROCNO 1
 Date_ 20121122
 Time_ 15.58
 INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zgpg30
 TD 65536
 SOLVENT DMSO
 NS 217
 DS 0
 SWH 20325.203 Hz
 FIDRES 0.310138 Hz
 AQ 1.6122355 sec
 RG 16384
 DW 24.600 usec
 DE 6.50 usec
 TE 298.8 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

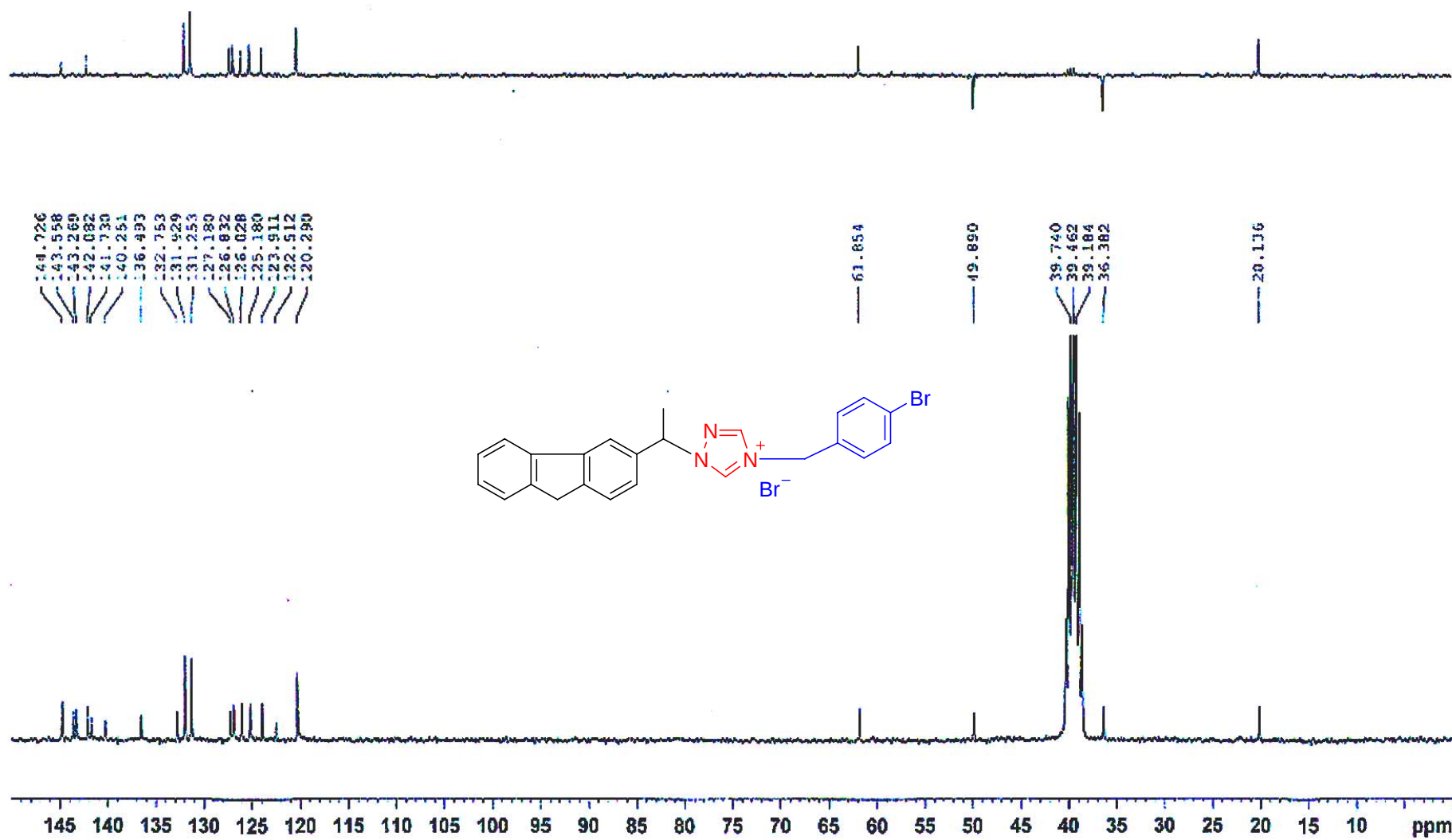
===== CHANNEL f1 =====
 NUC1 13C
 P1 8.20 usec
 PL1 -3.00 dB
 SFO1 75.4752953 MHz

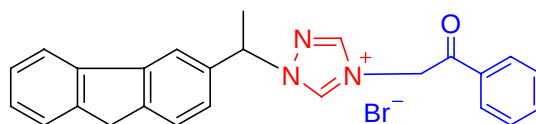
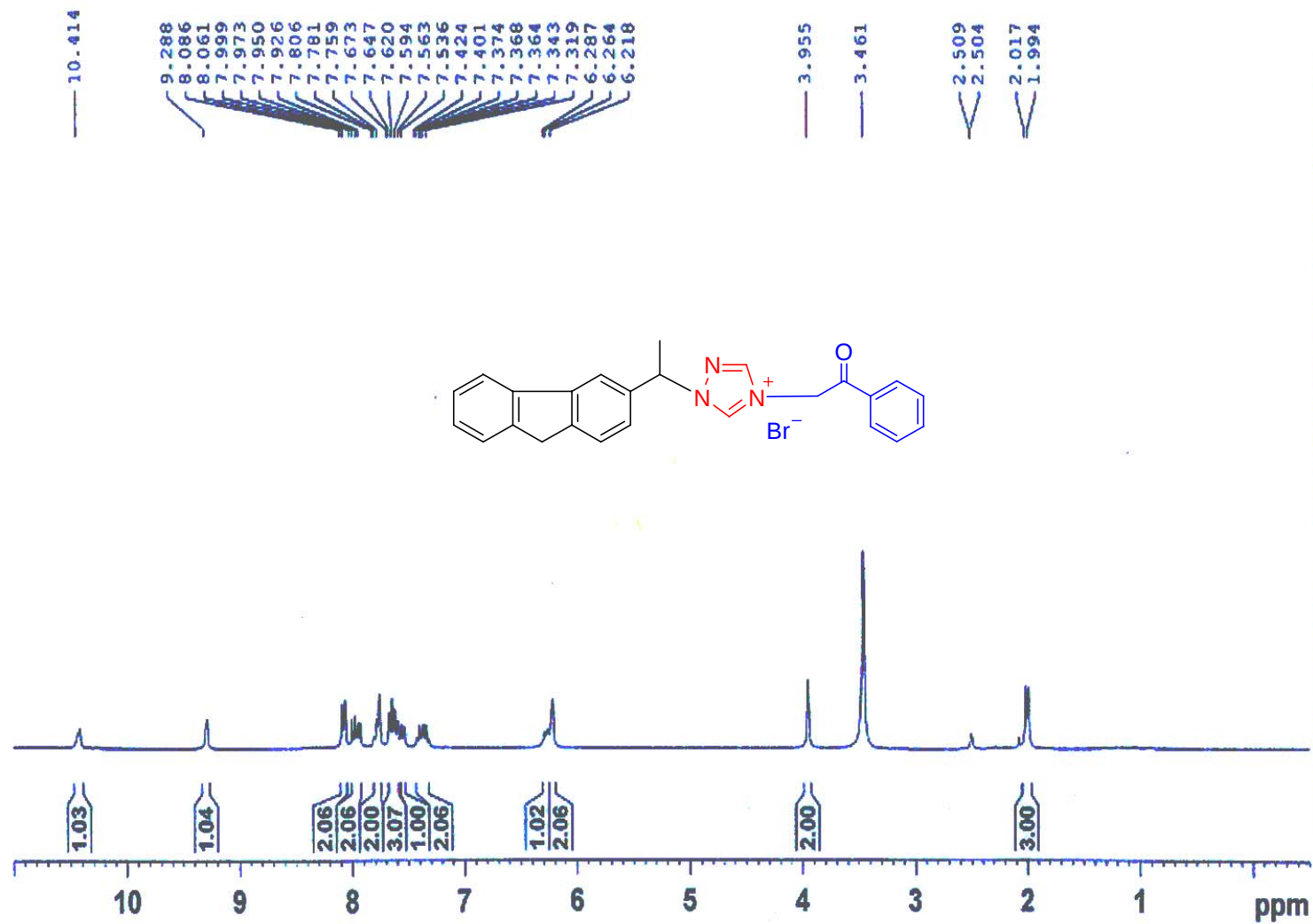
===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 -2.00 dB
 PL12 20.05 dB
 PL13 18.00 dB
 SFO2 300.1312005 MHz
 SI 32768
 SF 75.4677867 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz



NAME ljm
 EXPNO 107
 PROCNO 1
 Date_ 20121222
 Time_ 15.24
 INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT DMSO
 NS 86
 DS 0
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 128
 DW 81.000 usec
 DE 6.50 usec
 TE 295.0 K
 D1 2.00000000 sec
 TD0 1

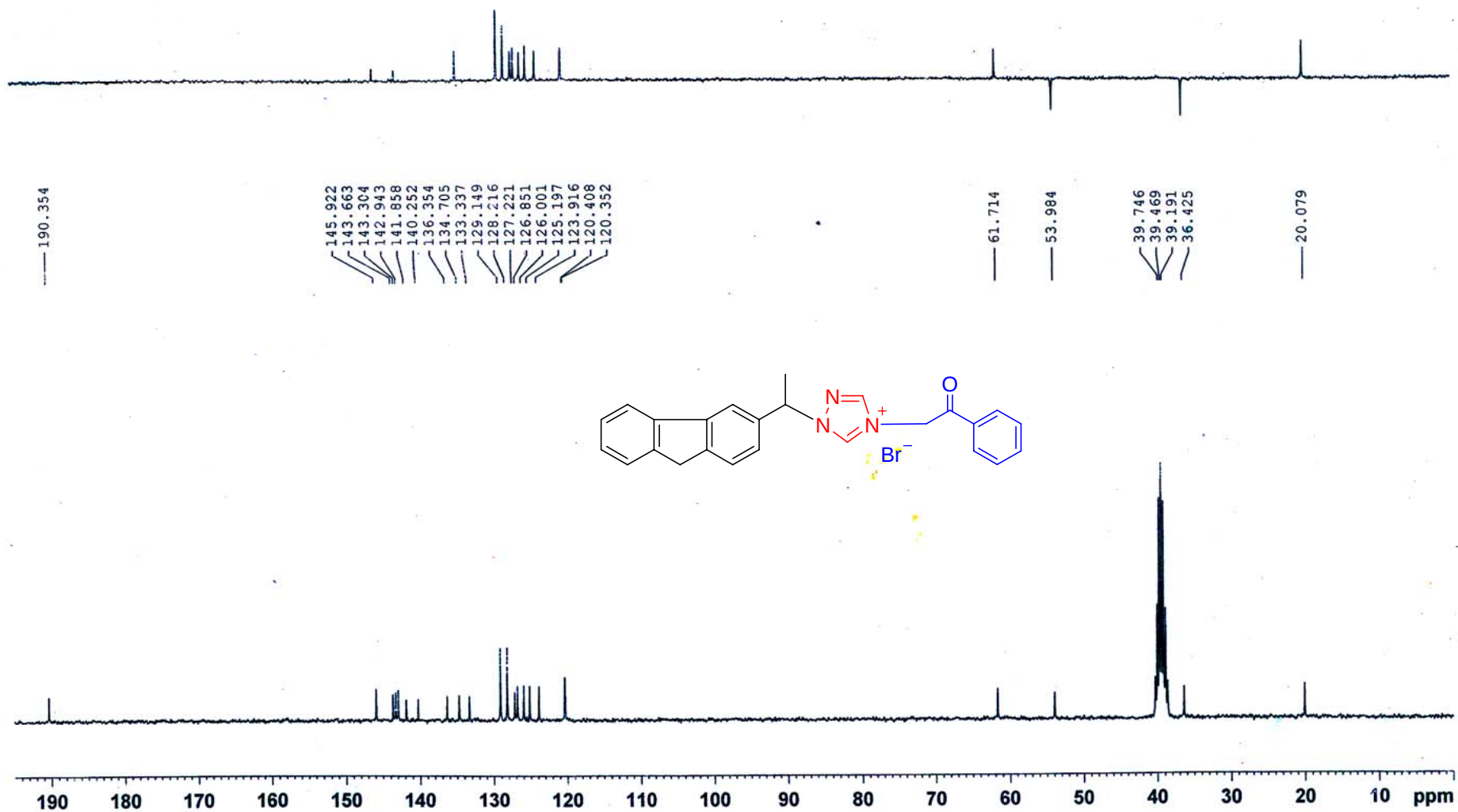
===== CHANNEL f1 =====
 NUC1 1H
 P1 7.90 usec
 PL1 -2.00 dB
 SFO1 300.1318534 MHz
 SI 32768
 SF 300.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

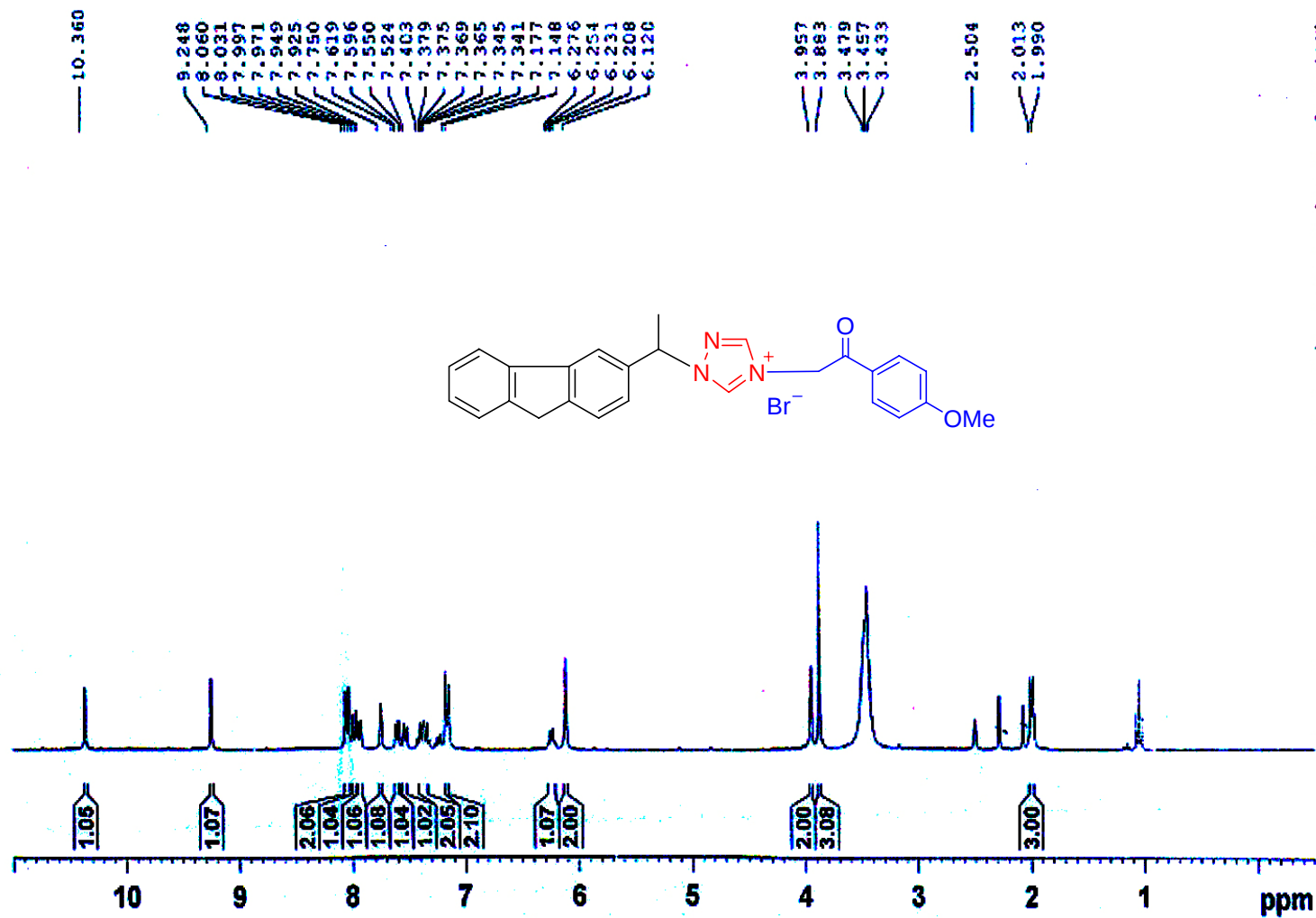




NAME ljm
EXPNO 104
PROCNO 1
Date_ 20121215
Time_ 14.28
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 128
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 90.5
DW 81.000 usec
DE 6.50 usec
TE 295.2 K
D1 2.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





```

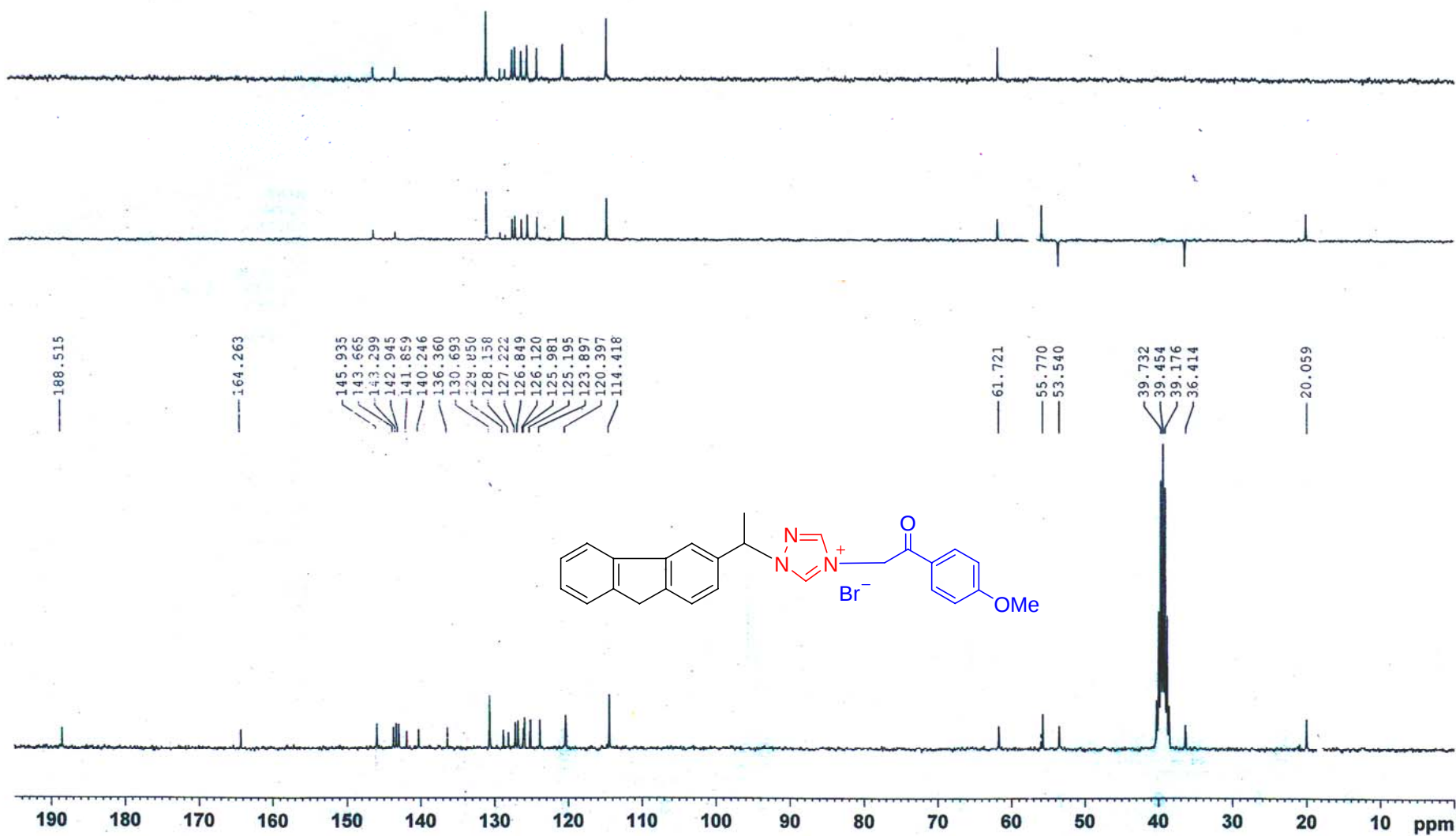
NAME      1jm
EXPNO     100
PROCNO    1
Date_     20121215
Time      13.37
INSTRUM   av300
PROBHD    5 mm QNP 1H/13
PULPROG   zg30
TD         65536
SOLVENT   DMSO
NS         78
DS         0
SWH        6172.839 Hz
FIDRES     0.094190 Hz
AQ         5.3084660 sec
RG         90.5
DW         81.000 usec
DE         6.50 usec
TE         295.3 K
D1         2.00000000 sec
TD0        !

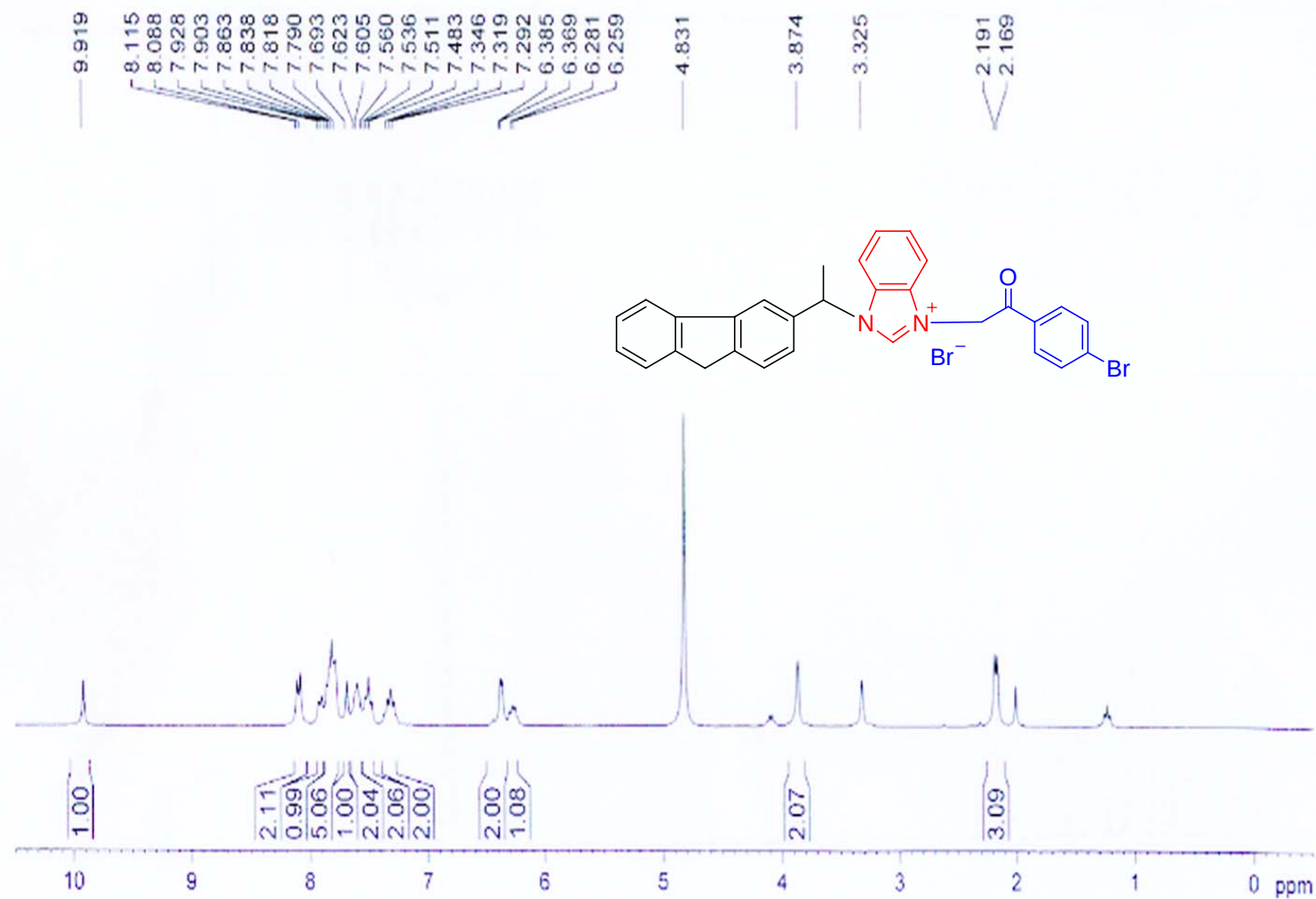
```

```

===== CHANNEL f1 =====
NUC1      1H
P1         7.90 usec
PL1        -2.00 dB
SFO1      300.1318534 MHz
SI         32768
SF         300.1300000 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```



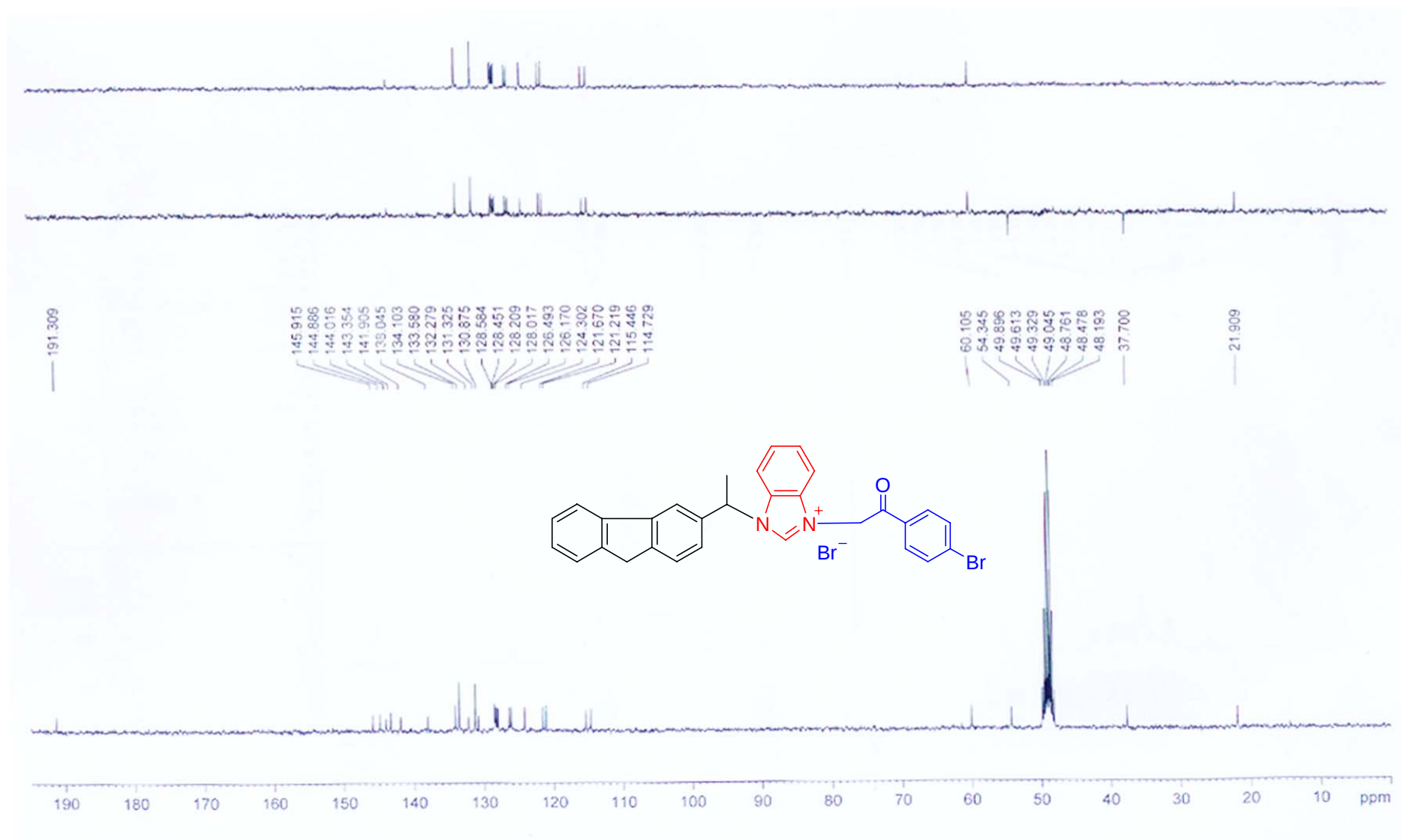


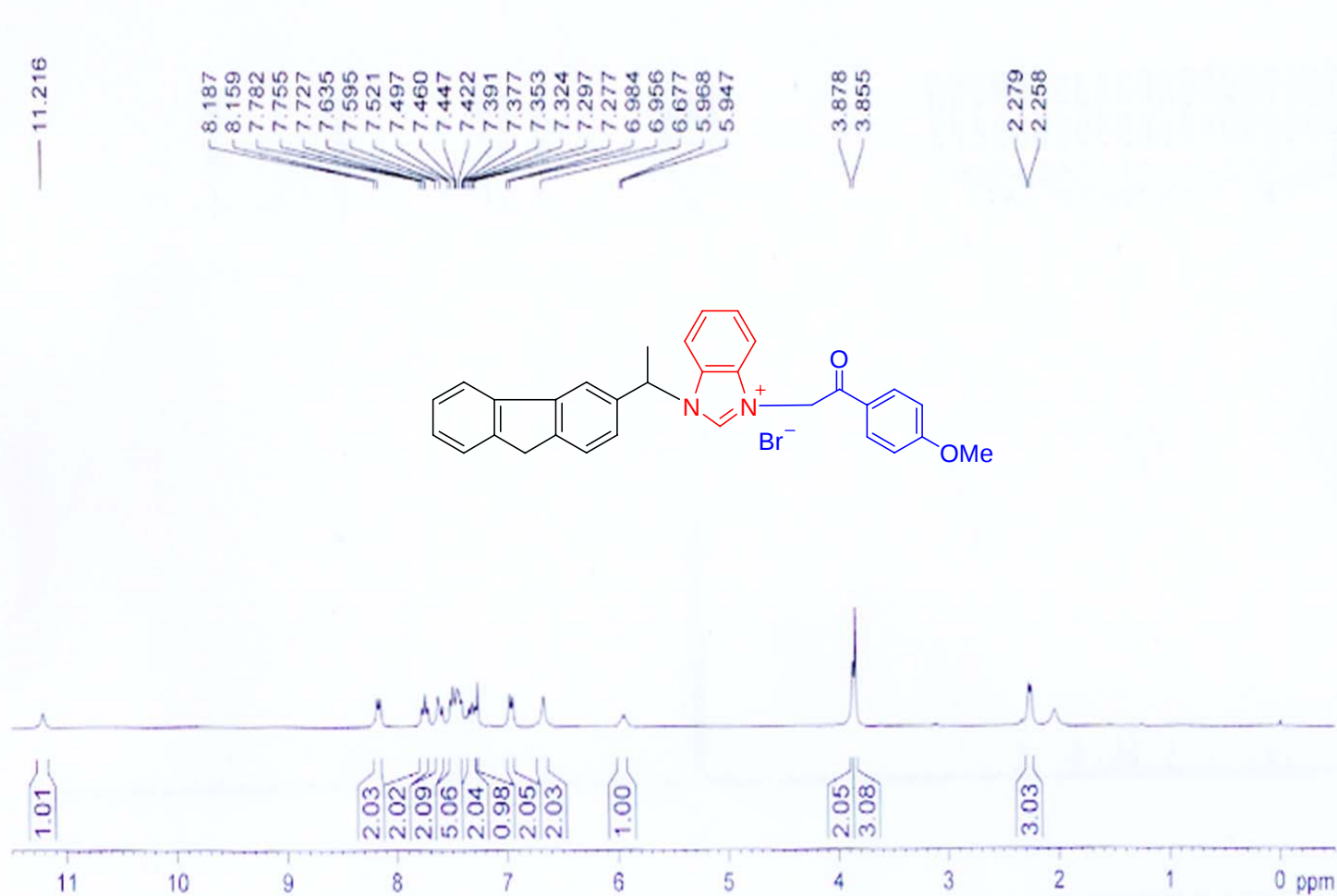
```

NAME          ljm
EXPNO          86
PROCNO         1
Date_          20120701
Time_          20.36
INSTRUM        av300
PROBHD         5 mm QNP 1H/13
PULPROG        zg30
TD             65536
SOLVENT        MeOD
NS             16
DS             2
SWH            6172.839 Hz
FIDRES         0.094190 Hz
AQ            5.3084660 sec
RG            181
DW            81.000 usec
DE            6.50 usec
TE            300.7 K
D1            1.00000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1           1H
P1            7.90 usec
PL1           -2.00 dB
SFO1          300.1310534 MHz
SI            32768
SF            300.1300006 MHz
WDW            EM
SSB            0
LB            0.30 Hz
GB            0
PC            1.00

```





```

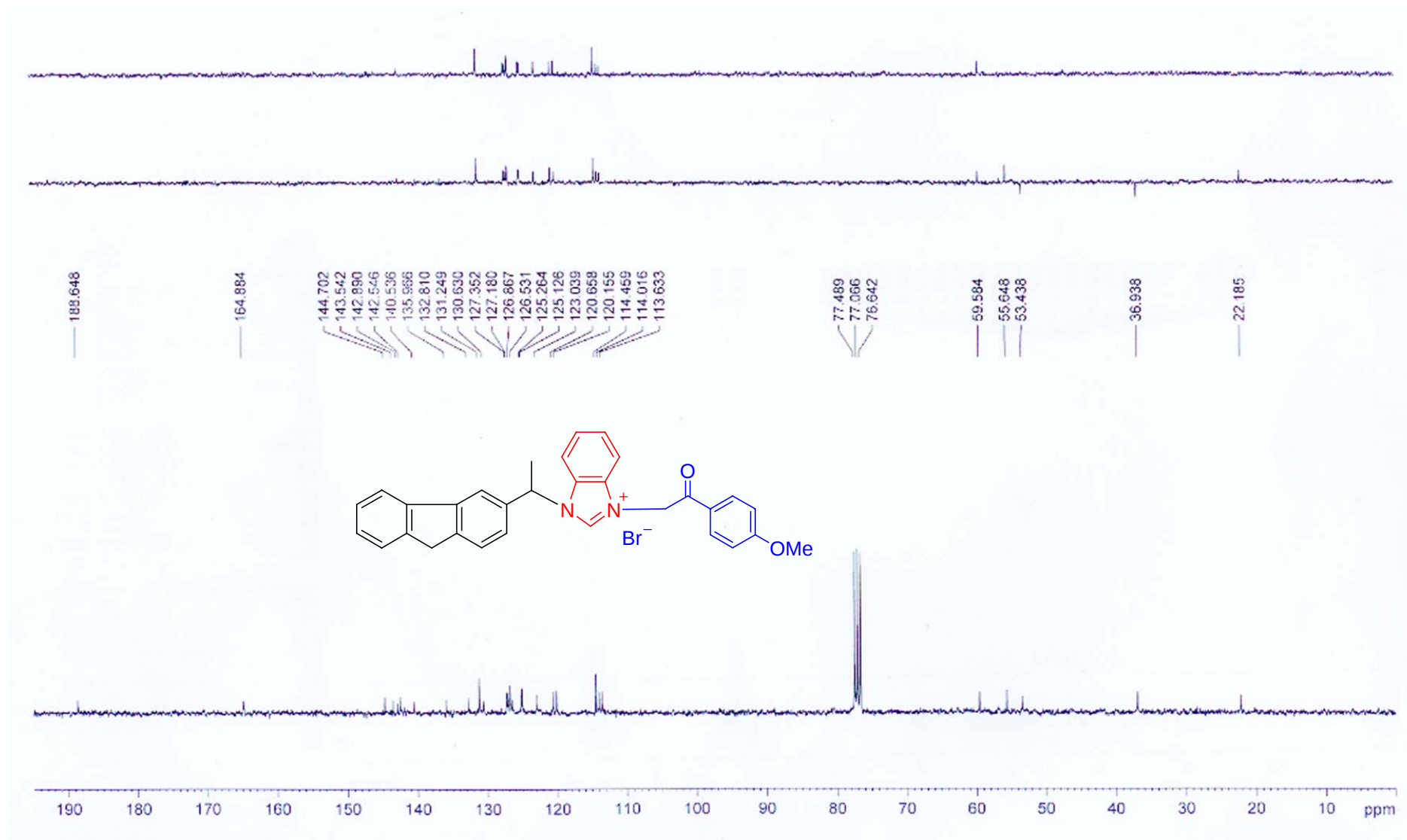
NAME          1jm
EXPNO         118
PROCNO        1
Date_         20120720
Time_         11.41
INSTRUM       av300
PROBHD        5 mm QNP 1H/13
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           6172.839 Hz
FIDRES        0.094190 Hz
AQ            5.3084660 sec
RG            181
DW            81.000 usec
DE            6.50 usec
TE            300.5 K
D1            1.00000000 sec
TD0           1

```

```

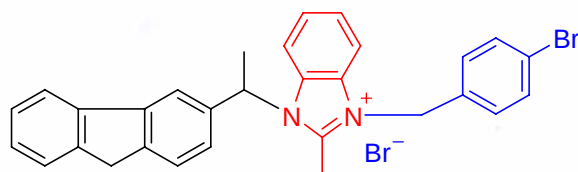
===== CHANNEL f1 =====
NUC1          1H
P1            7.90 usec
PL1           -2.00 dB
SFO1          300.1318534 MHz
SI            32768
SF            300.1300014 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00

```



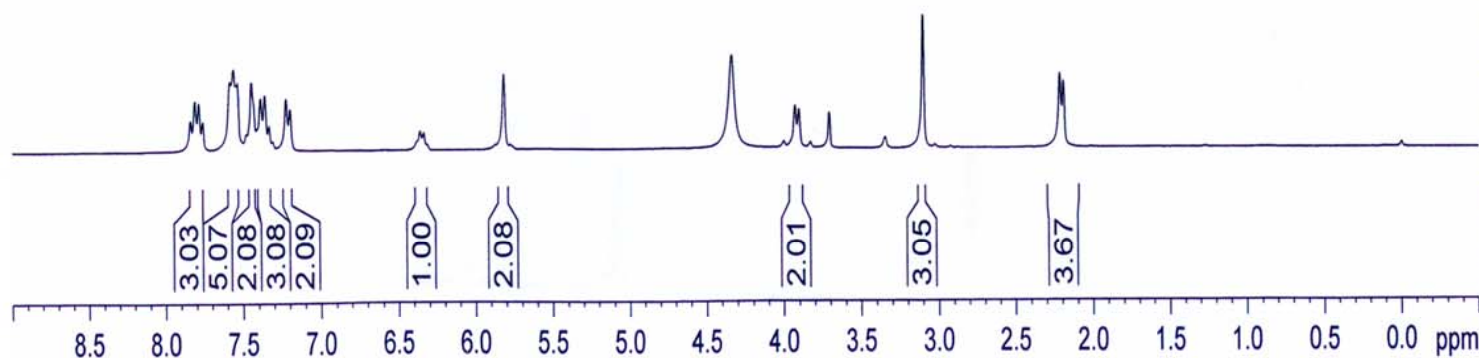
7.844
7.815
7.790
7.764
7.587
7.564
7.547
7.539
7.481
7.449
7.391
7.364
7.337
7.313
7.225
7.199
6.363
6.340
5.818

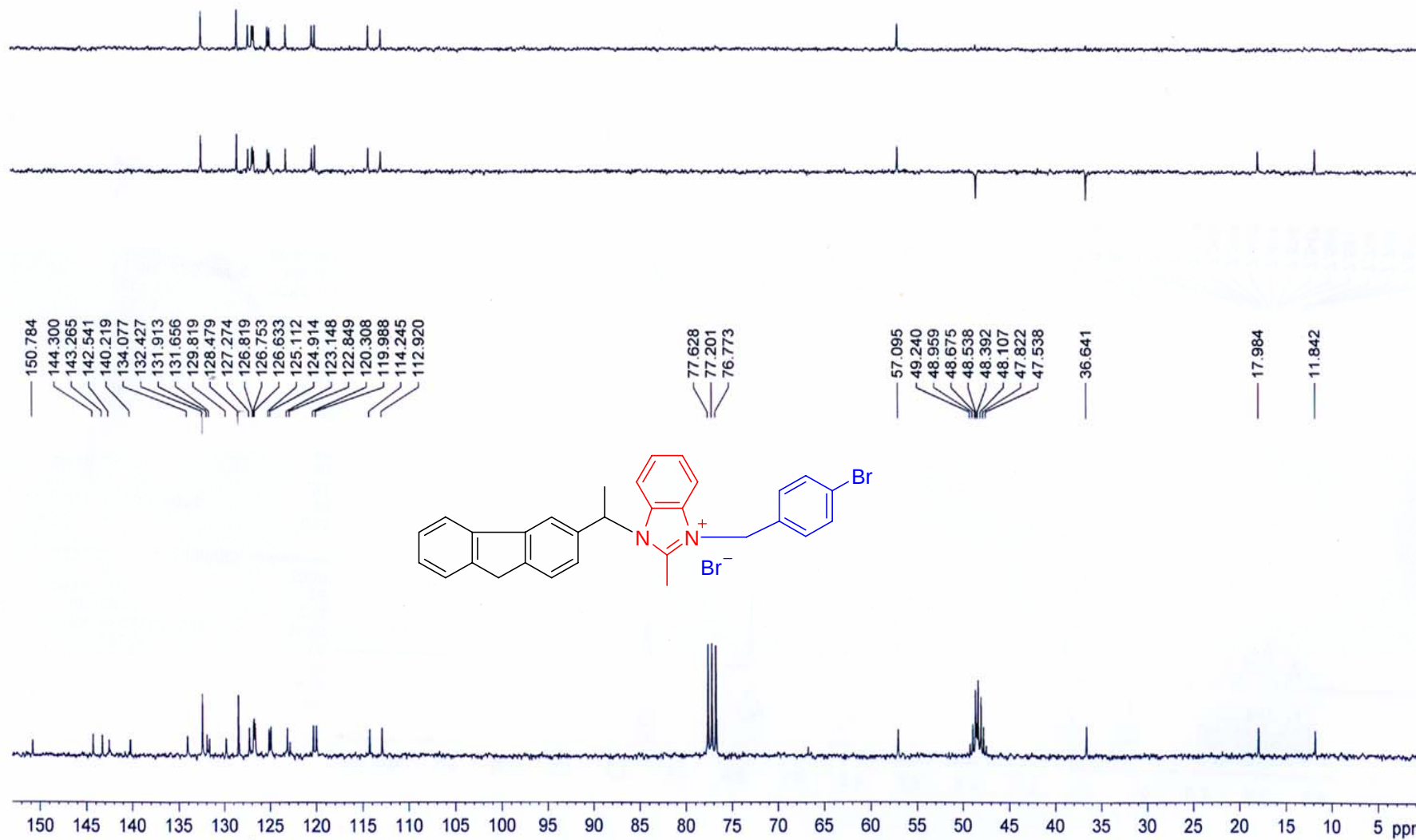
4.339
3.928
3.904
3.709
3.350
3.102
2.217
2.194

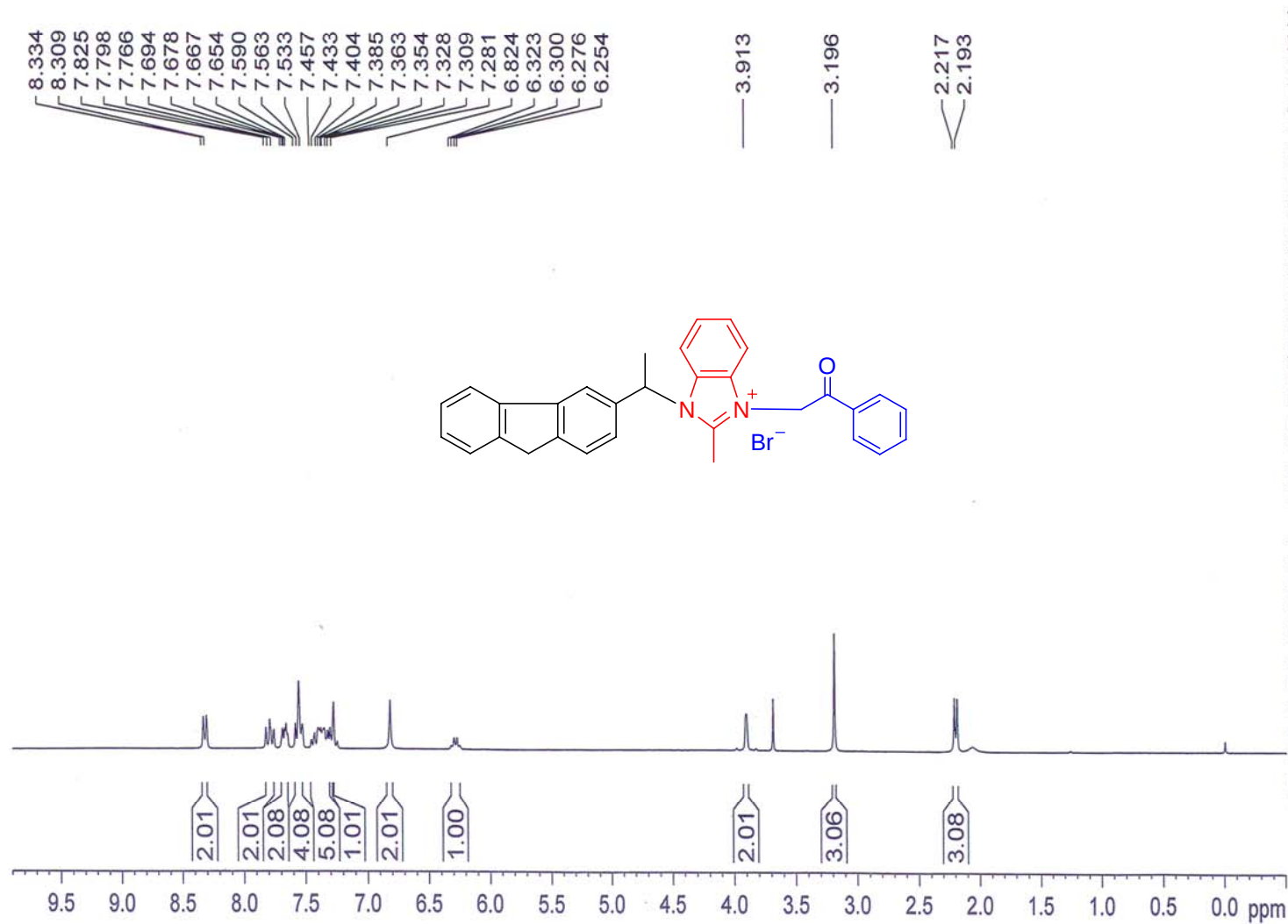


NAME ljm
EXPNO 192
PROCNO 1
Date_ 20120822
Time_ 21.31
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 181
DW 81.000 usec
DE 6.50 usec
TE 300.5 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SF01 300.1318534 MHz
SI 32768
SF 300.1299383 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

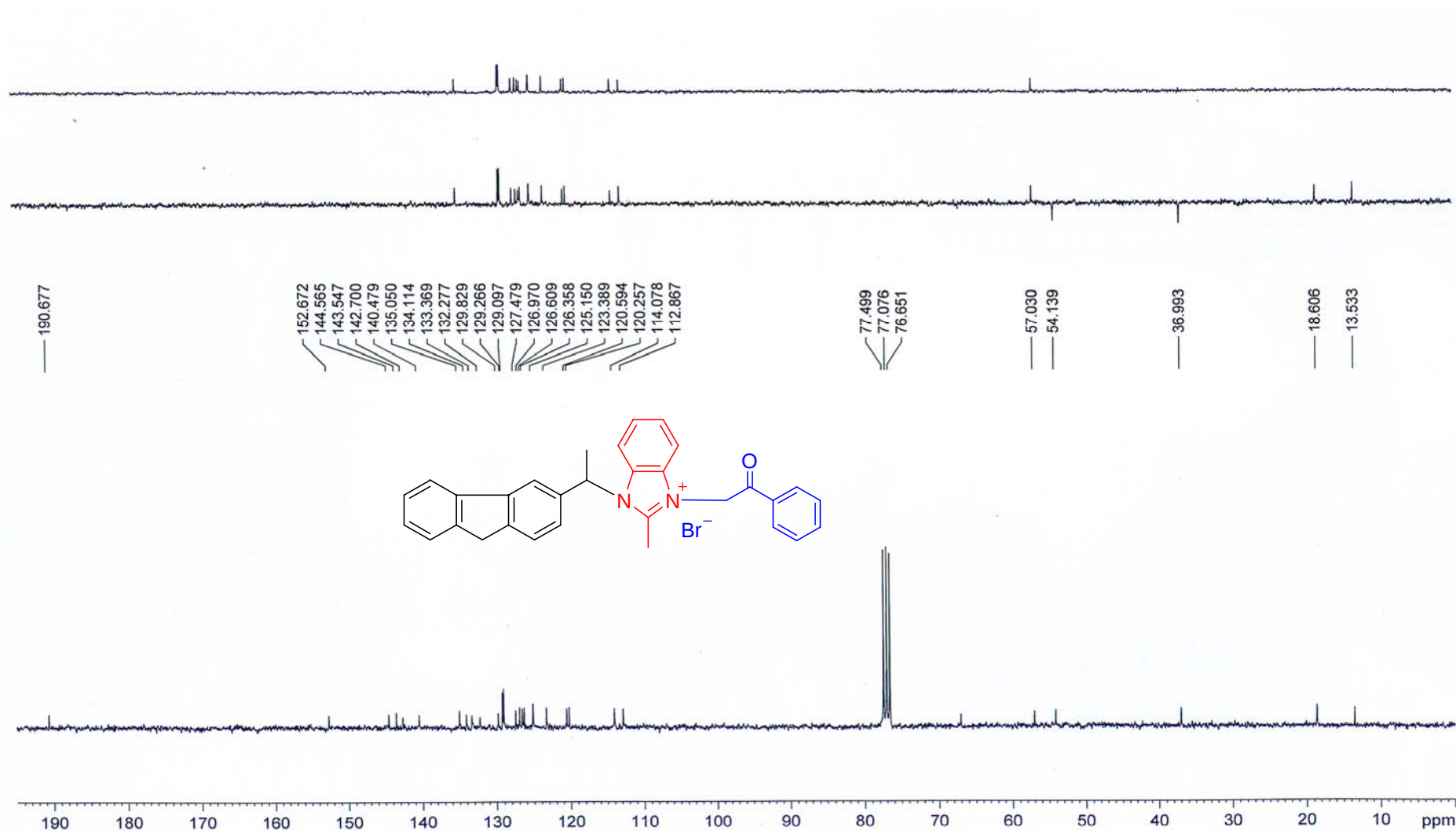


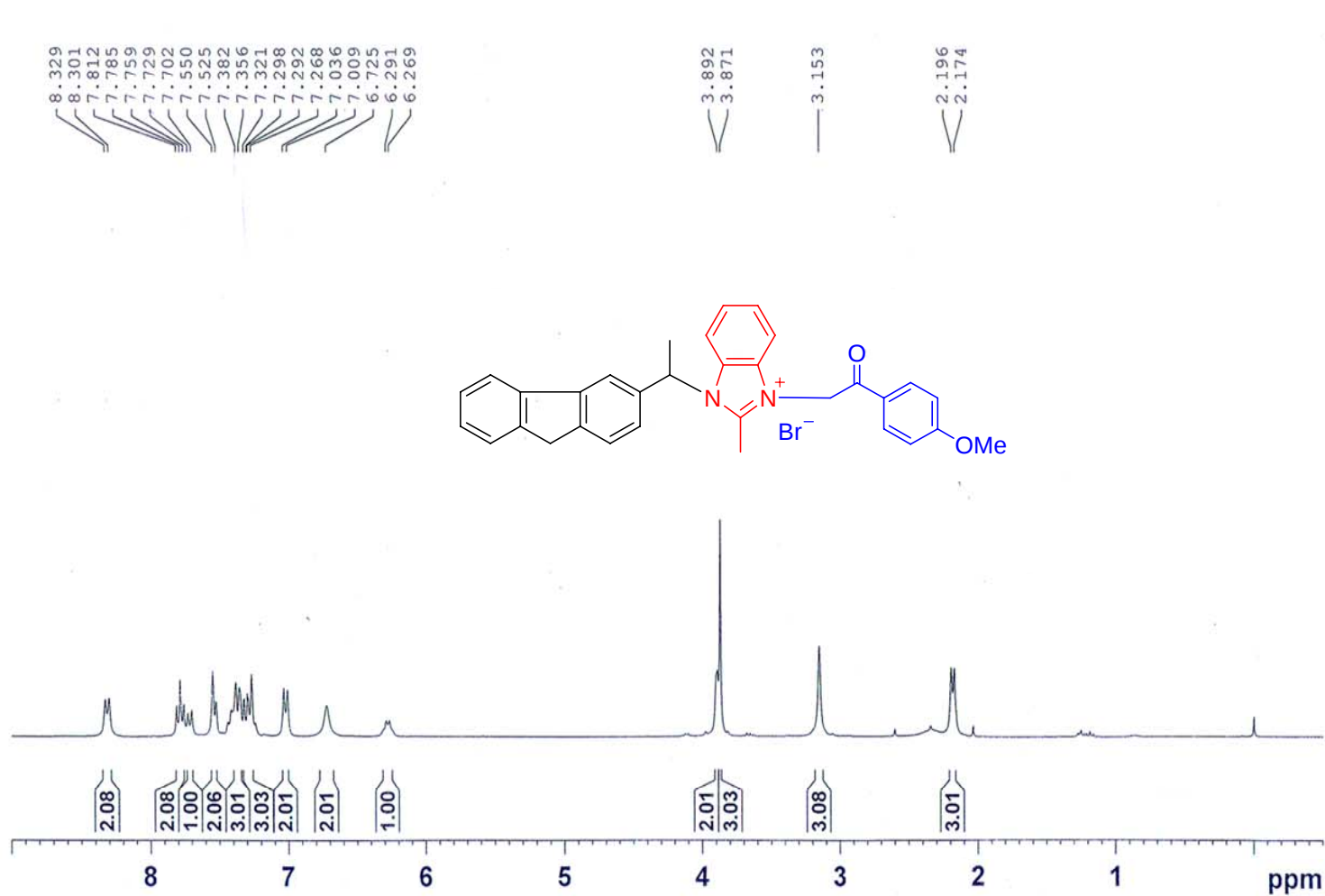




NAME 1jm
 EXPNO 196
 PROCNO 1
 Date_ 20120822
 Time_ 22.08
 INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 NS 16
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 256
 DW 81.000 usec
 DE 6.50 usec
 TE 300.6 K
 D1 1.00000000 sec
 TD0 1

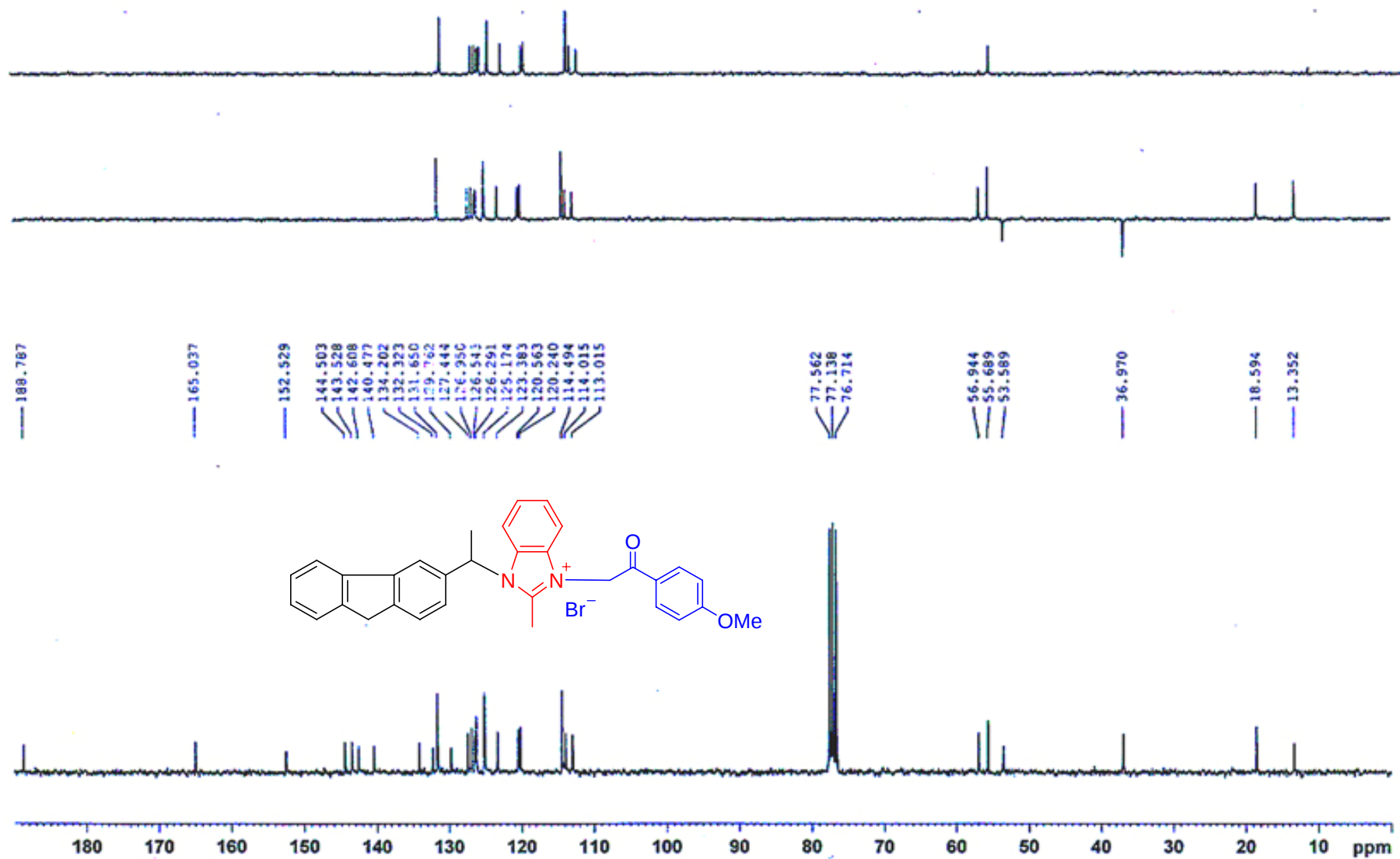
===== CHANNEL f1 =====
 NUC1 1H
 P1 7.90 usec
 PL1 -2.00 dB
 SFO1 300.1318534 MHz
 SI 32768
 SF 300.1300004 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





NAME ljm
 EXPNO 110
 PROCNO 1
 Date_ 20121222
 Time_ 16.39
 INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 104
 DS 0
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 128
 DW 81.000 usec
 DE 6.50 usec
 TE 295.4 K
 D1 2.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.90 usec
 PL1 -2.00 dB
 SFO1 300.1318534 MHz
 SI 32768
 SF 300.1299952 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

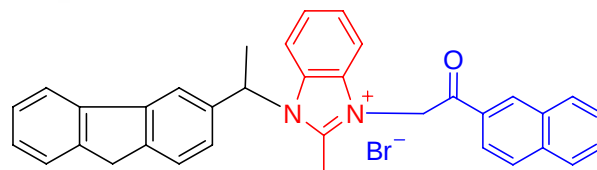


9.239
8.220
8.193
8.136
8.108
7.930
7.902
7.836
7.826
7.798
7.768
7.742
7.649
7.625
7.601
7.568
7.531
7.435
7.408
7.384
7.356
7.331
7.307
7.274
6.947
6.316
6.295
6.272
6.250

3.911
3.905

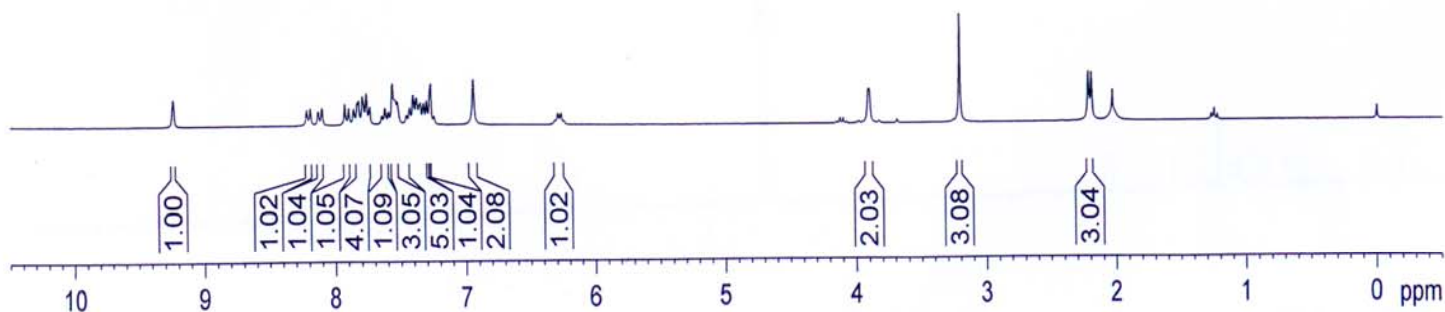
3.212

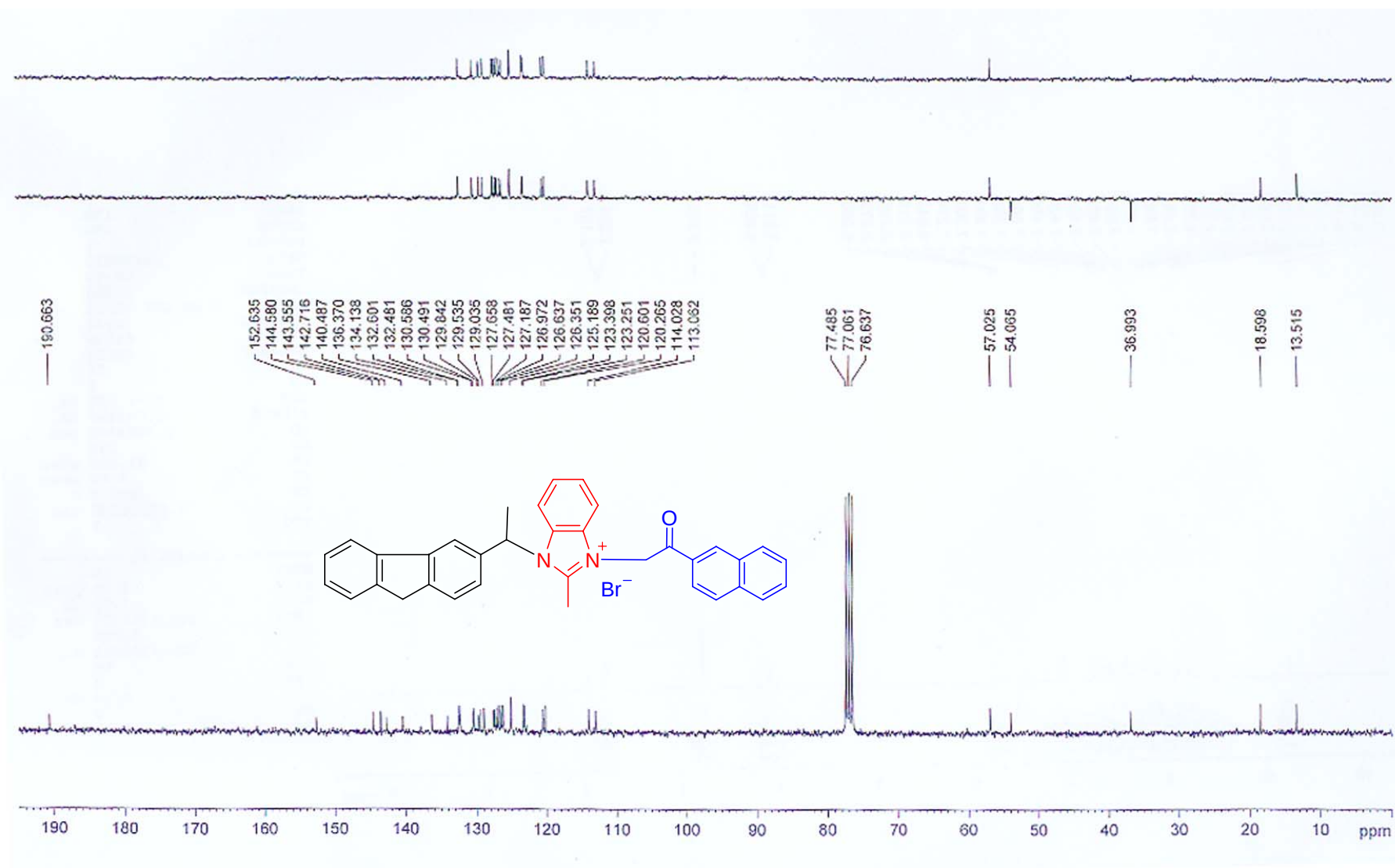
2.221
2.197

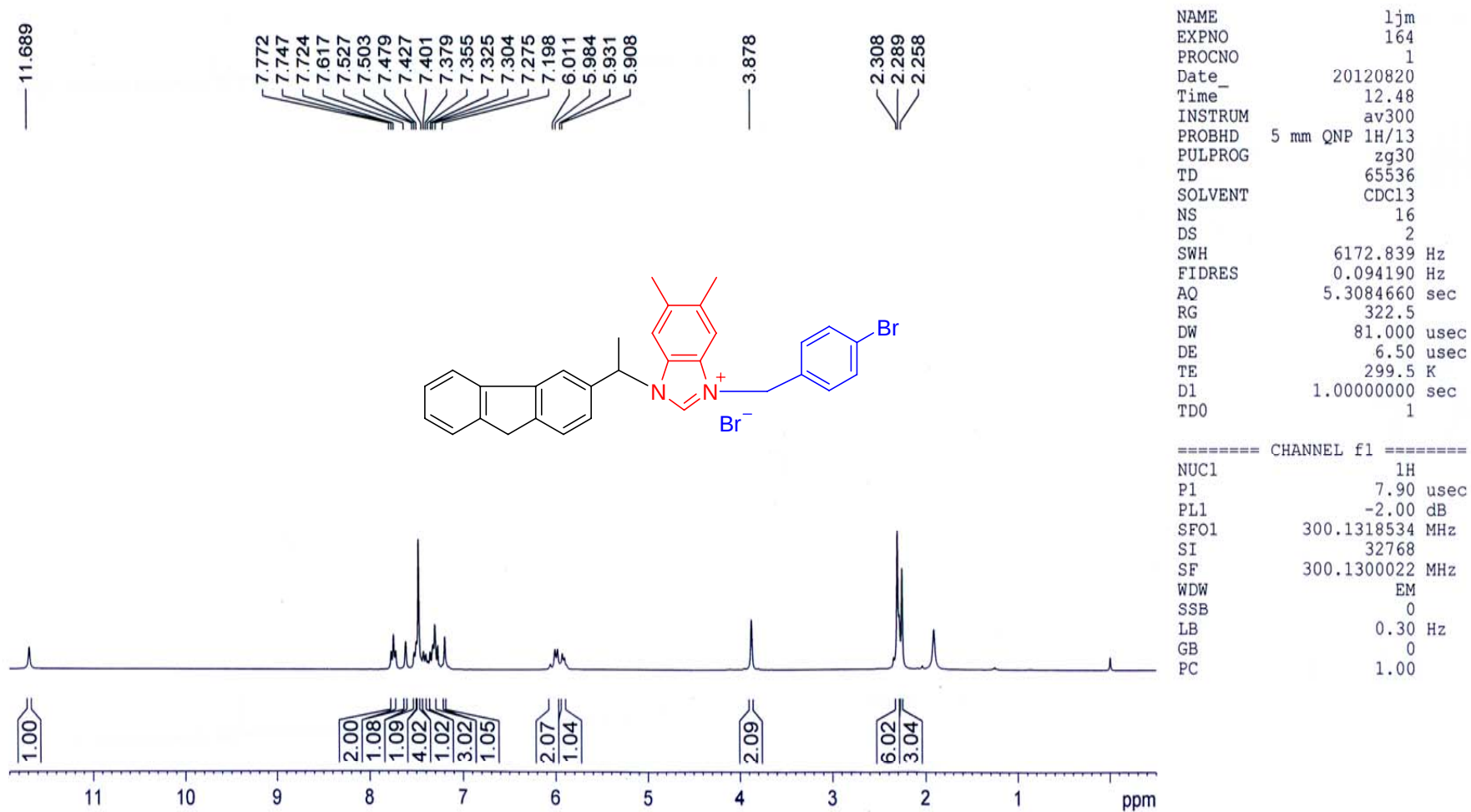


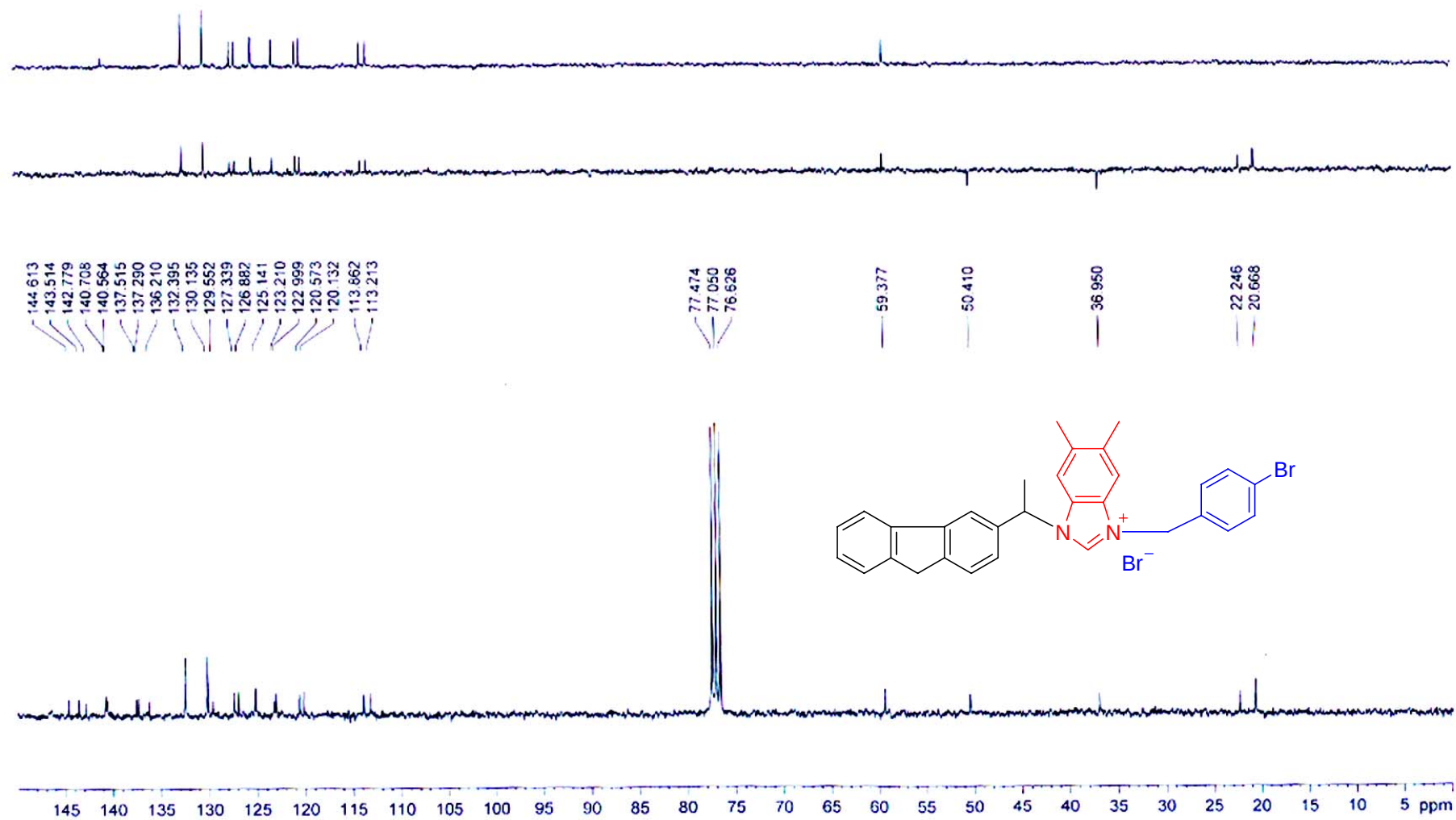
NAME ljm
EXPNO 188
PROCNO 1
Date_ 20120822
Time_ 20.49
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 256
DW 81.000 usec
DE 6.50 usec
TE 300.5 K
D1 1.00000000 sec
TD0 1

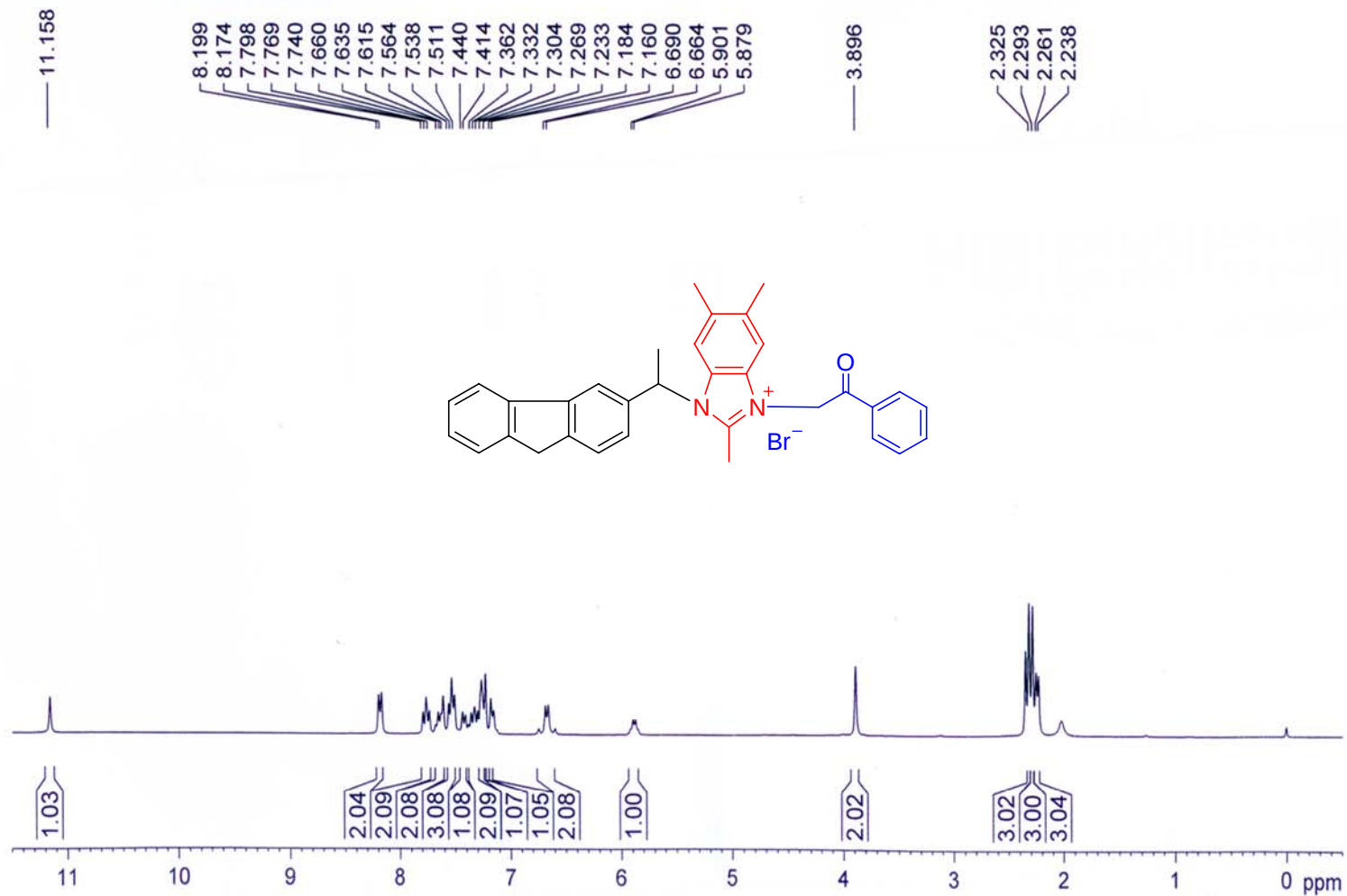
===== CHANNEL f1 =====
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300021 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00











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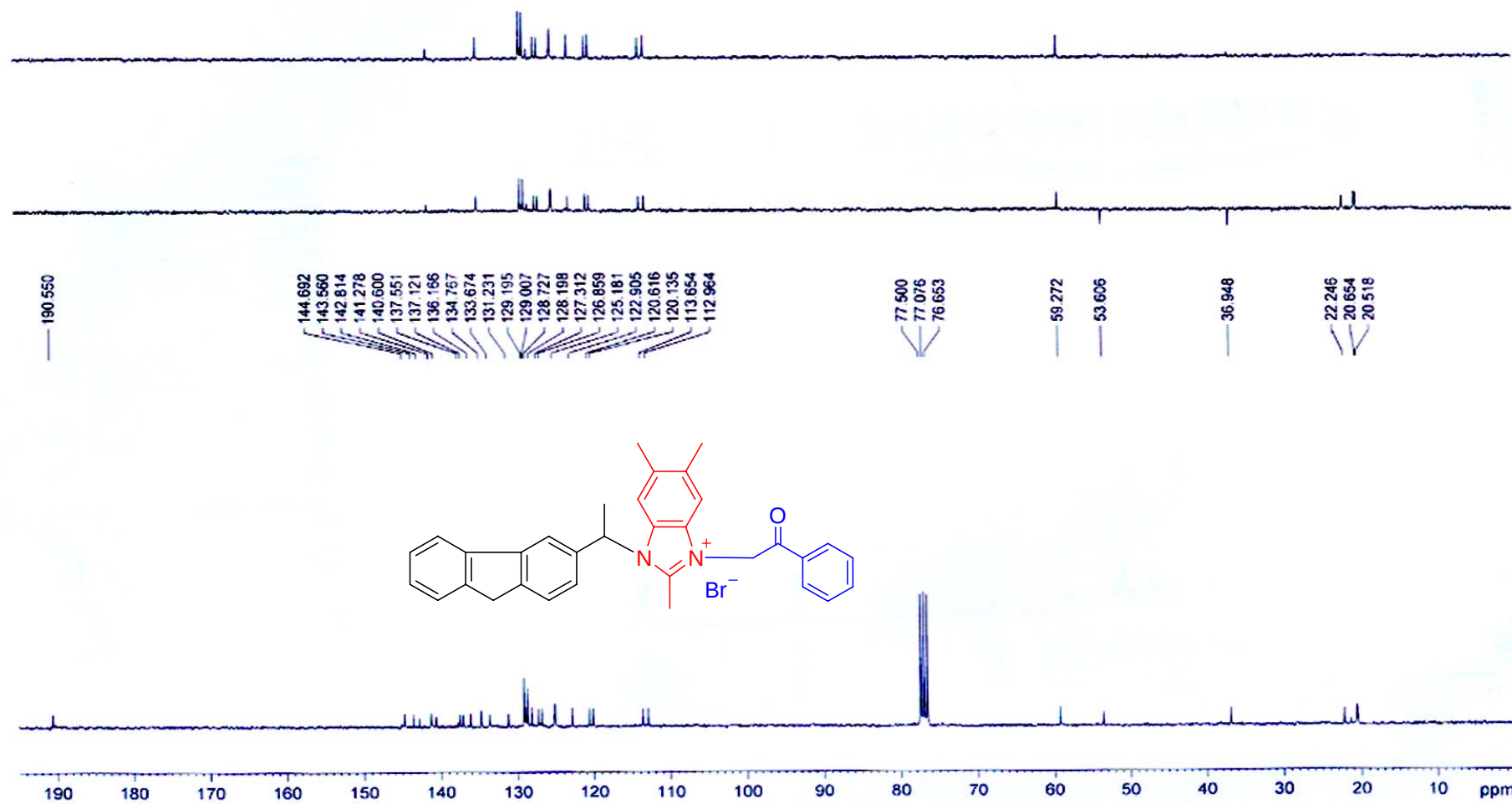
NAME          ljm
EXPNO         176
PROCNO        1
Date_         20120822
Time_         18.50
INSTRUM       av300
PROBHD        5 mm QNP 1H/13
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           6172.839 Hz
FIDRES        0.094190 Hz
AQ            5.3084660 sec
RG            181
DW            81.000 use
DE            6.50 use
TE            300.5 K
D1            1.00000000 sec
TD0           1

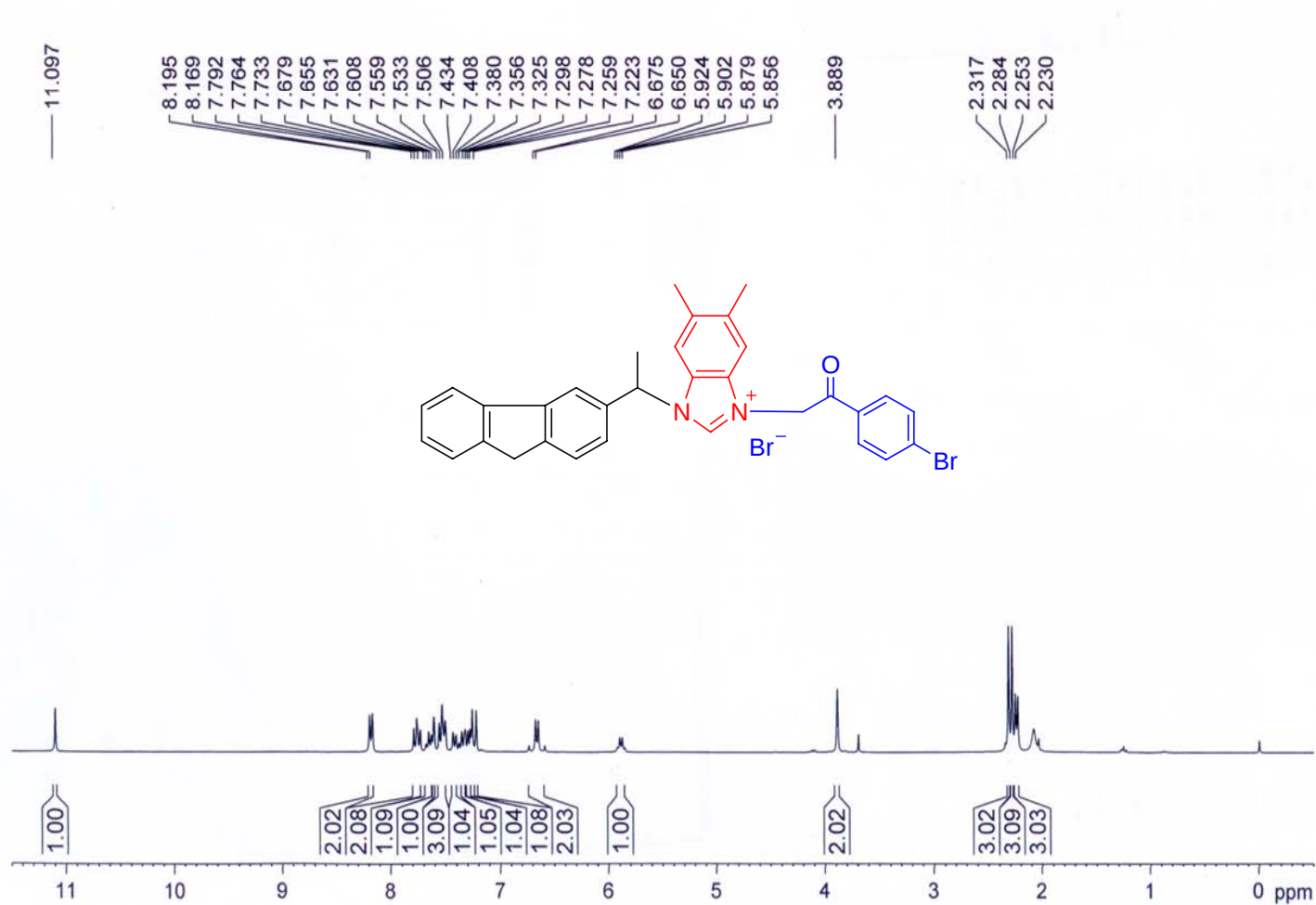
```

```

===== CHANNEL f1 =====
NUC1          1H
P1            7.90 use
PL1           -2.00 dB
SFO1          300.1318534 MHz
SI            32768
SF            300.1300000 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00

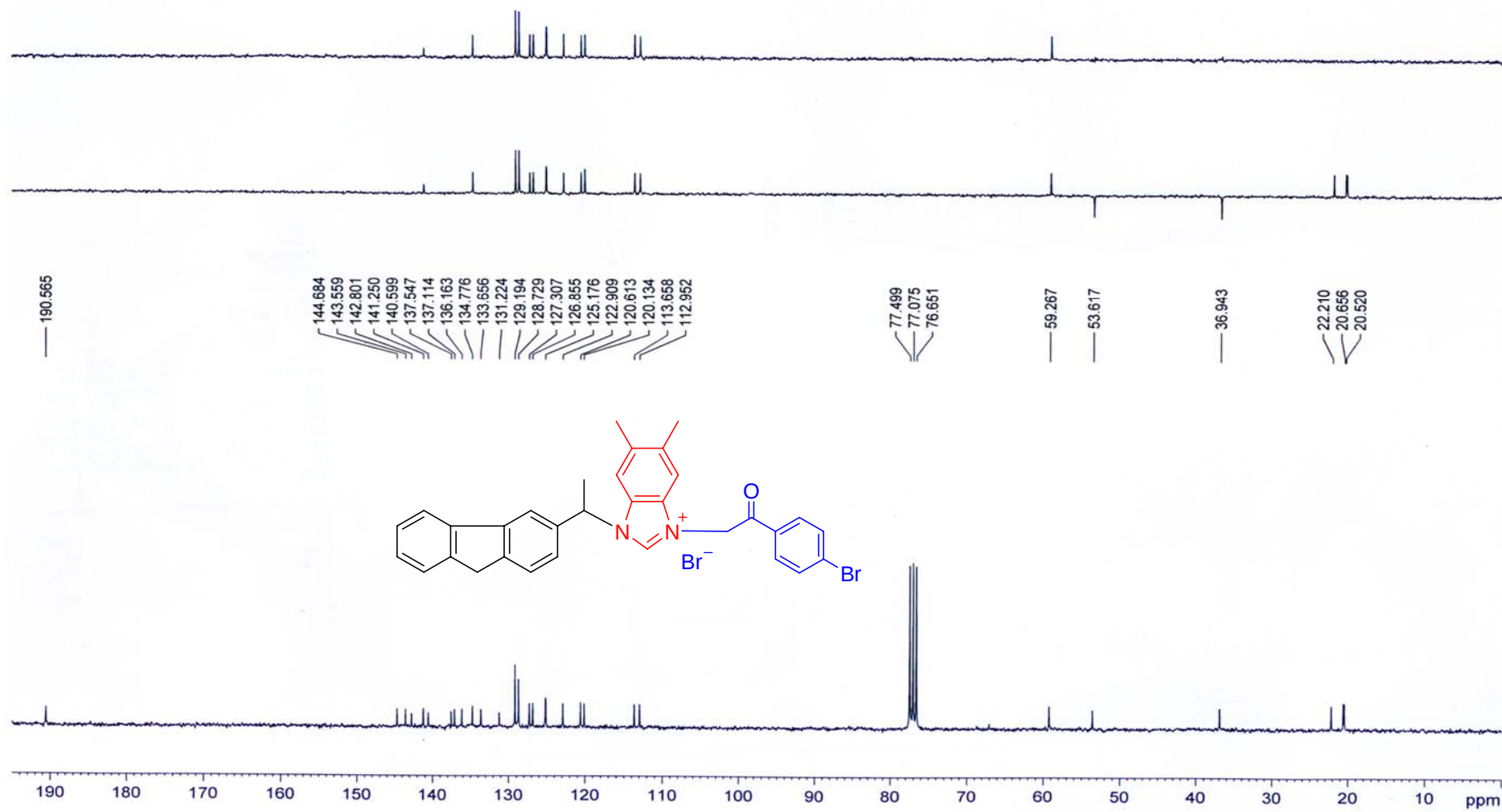
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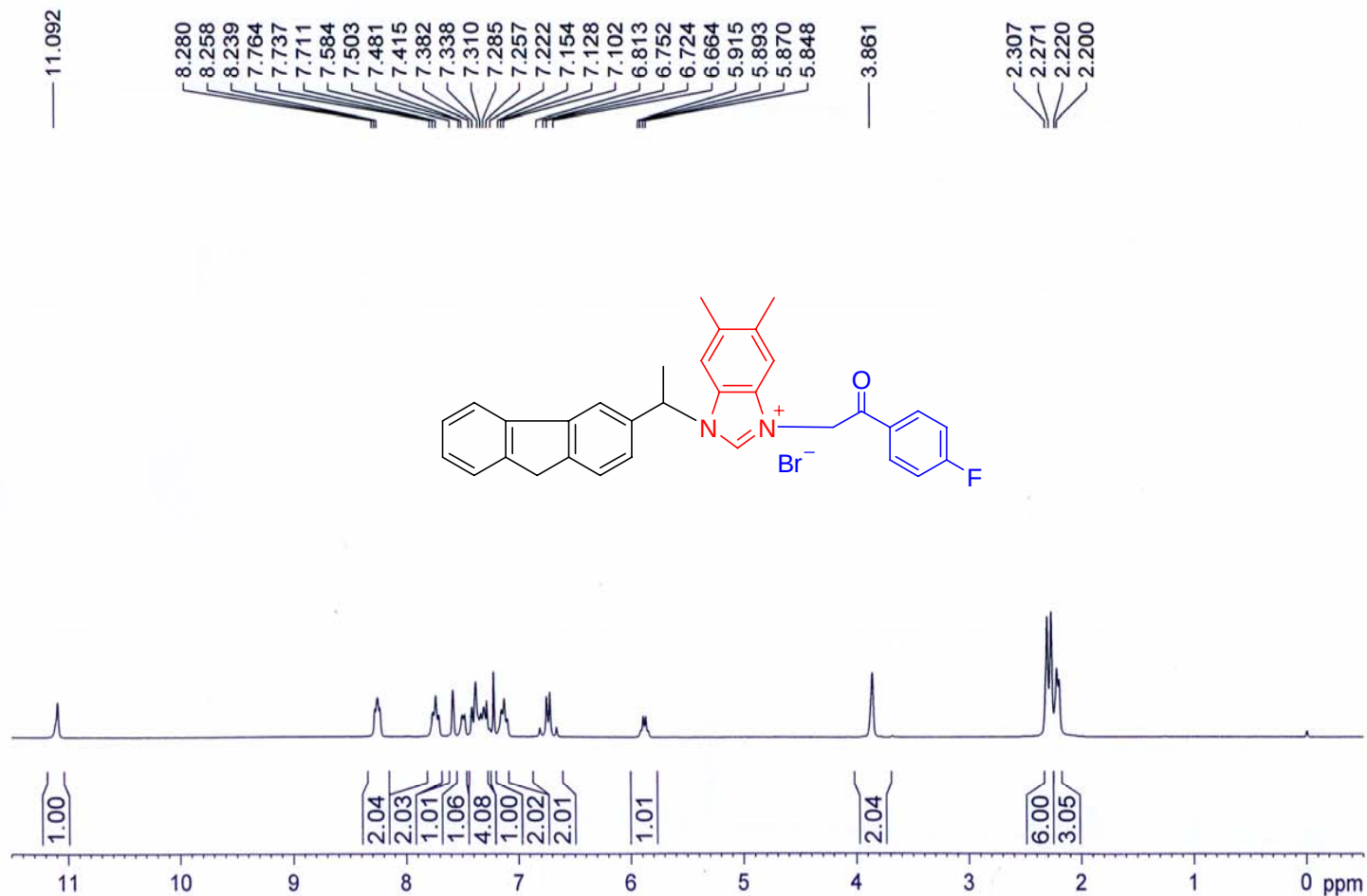




NAME ljm
EXPNO 160
PROCNO 1
Date_ 20120820
Time_ 12.08
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 181
DW 81.000 usec
DE 6.50 usec
TE 299.4 K
D1 1.00000000 sec
TD0 1

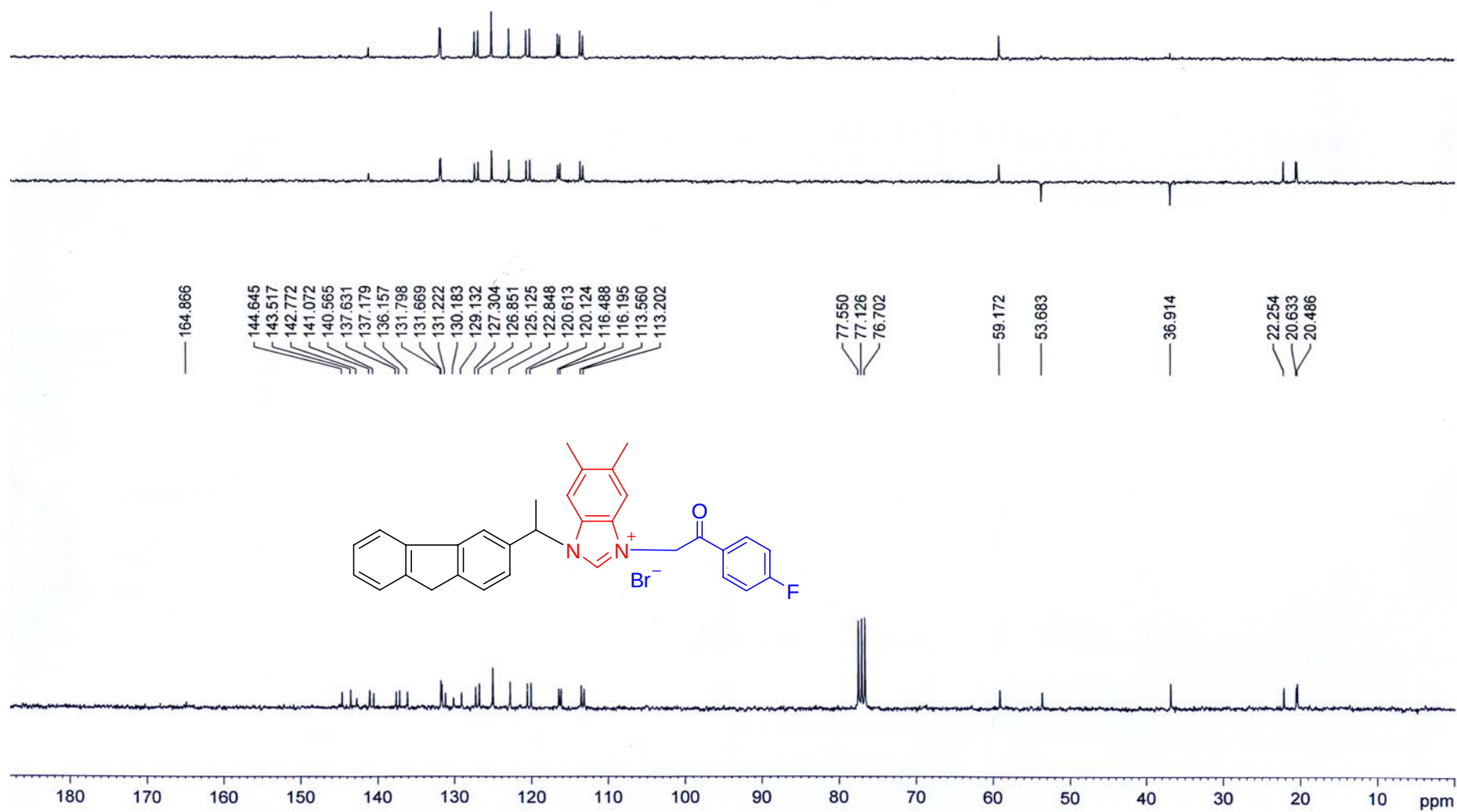
===== CHANNEL f1 =====
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300008 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

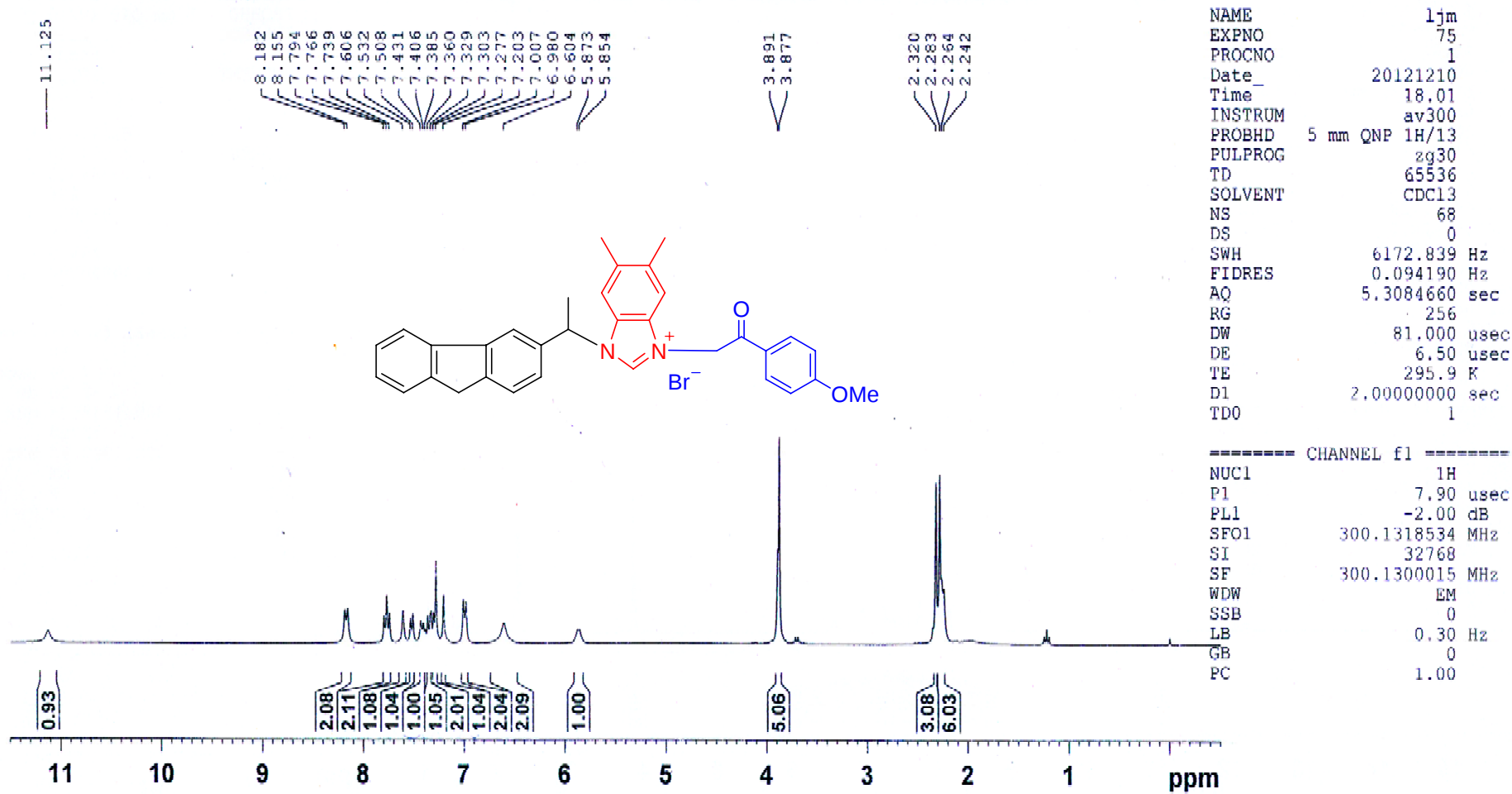


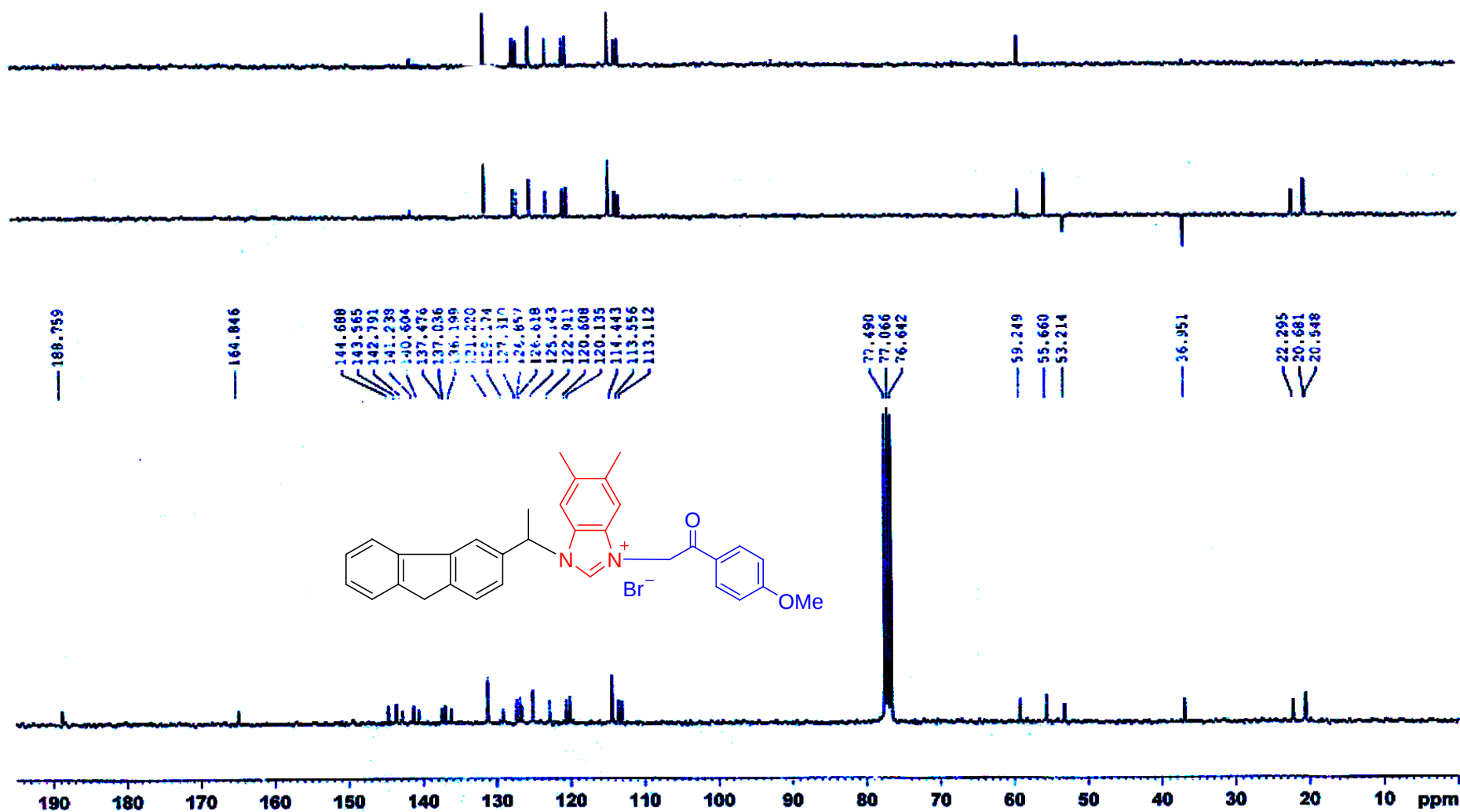


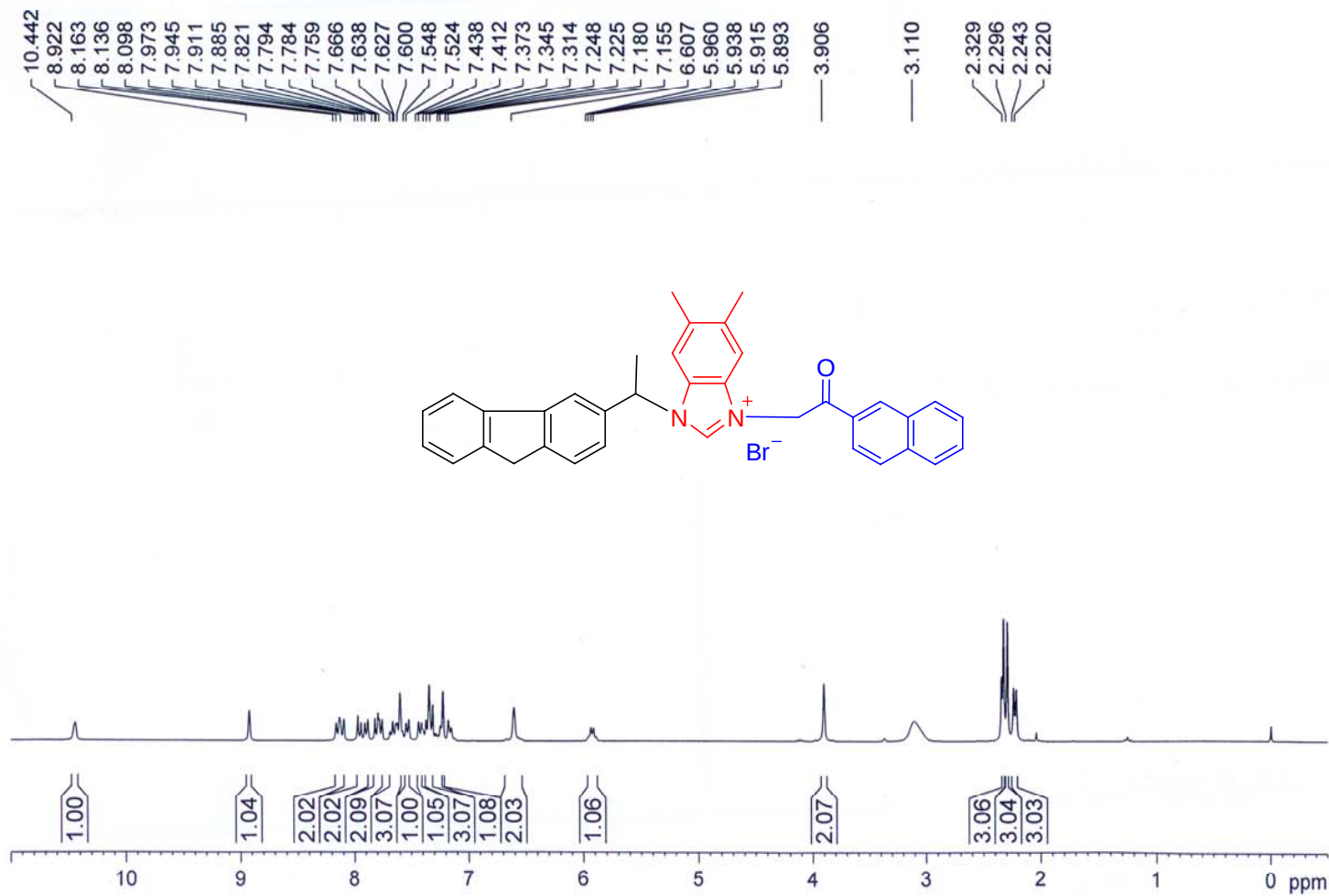
NAME ljm
EXPNO 172
PROCNO 1
Date_ 20120822
Time_ 18.13
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 15
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 161.3
DW 81.000 usec
DE 6.50 usec
TE 300.4 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1299991 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00









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NAME          1jm
EXPNO         168
PROCNO        1
Date_         20120822
Time_         17.36
INSTRUM       av300
PROBHD        5 mm QNP 1H/13
PULPROG       zg30
TD            65536
SOLVENT       CDC13
NS            16
DS            2
SWH           6172.839 Hz
FIDRES        0.094190 Hz
AQ            5.3084660 sec
RG            228.1
DW            81.000 usec
DE            6.50 usec
TE            300.2 K
D1            1.00000000 sec
TD0           1

```

```

===== CHANNEL f1 =====
NUC1          1H
P1            7.90 usec
PL1           -2.00 dB
SFO1          300.1318534 MHz
SI            32768
SF            300.1299896 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00

```

