Synthesis of fused-pyran derivatives via a base-mediated annulation of bis-allenoates followed by auto-oxidation in air

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1. General Information

All solvents and reagents were obtained from commercial sources and used without further purification. All reactions were monitored by TLC or NMR analysis. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm silica gel. Purification of reaction products was achieved using flash chromatography on silica gel (300–400 mesh). NMR spectra were recorded using JNM-ECZ600R/S1 or JEOL ECZ400S spectrometers (1H NMR at 600/400 MHz, ^{13}C NMR at 151/101 MHz). Chemical shifts are reported in ppm. The 1H NMR spectra were referenced to $CDCl_3$ (δ = 7.26, containing 0.03% TMS), or CD_2Cl_2 (δ = 5.32, containing 0.05% TMS) as the internal standard. The ^{13}C NMR spectra were referenced to $CDCl_3$ (δ = 77.16) or CD_2Cl_2 (δ = 53.84). NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). High-resolution mass spectra were acquired under electron spray ionization (ESI) conditions using a ThermoFisher mass spectrometer (Q Exactive Focus) interfaced with an ultra-performance liquid chromatography system (Vanquish Flex). IR spectra were measured with a Bruker VERTEX 70 spectrometer. Single-crystal X-ray diffraction data were collected on a Bruker D8 VENTURE diffractometer equipped with a molybdenum microfocus source. Melting points were determined using an X-4A microscopic melting point apparatus; the reported temperatures are uncorrected.

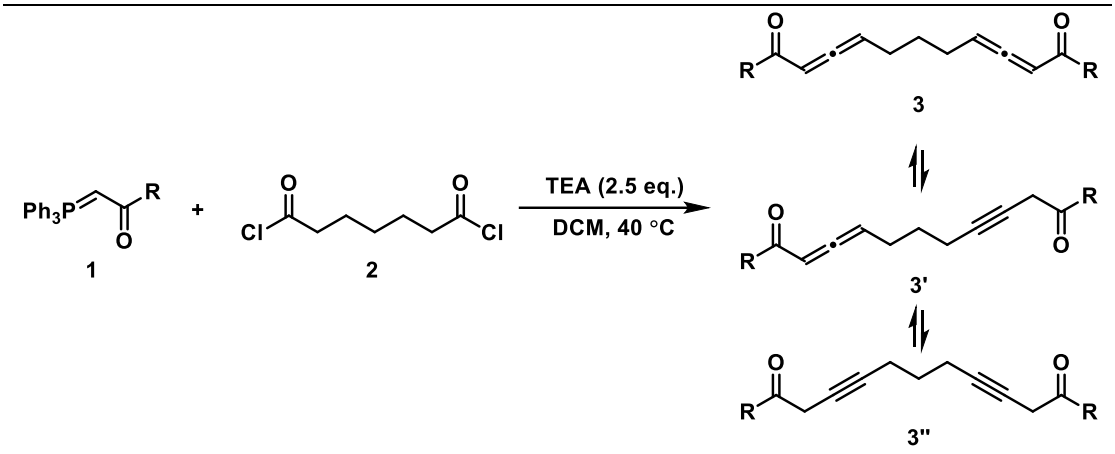
2. Experimental Procedures

2.1 Preparation and Characterization of Substrates 3

General Procedures: Substrates **3** were synthesized following a modified experimental procedure described in the literature.[1, 2]

A 25 mL round-bottomed flask was charged with a solution of the phosphoranylid **1** (760 mg, 2.0 mmol) in dichloromethane (DCM, 10 mL). To this solution, triethylamine (TEA, 253 mg, 2.5 mmol) was added, and the resulting mixture was stirred at 40 ℃ in an oil bath for 10 minutes. Subsequently, pimeloyl chloride **2** (197-236 mg, 1.0-1.2 mmol) was introduced dropwise to the reaction mixture over a period of 5 minutes. The progress of the reaction was monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was concentrated under reduced pressure to remove the solvent. The residue was then isolated via flash column chromatography on silica gel, employing a mixture of ethyl acetate and n-hexane as the eluent. The evaporation of the solvent under reduced pressure yielded a mixture of compounds **3**, **3'**, and **3''** as a gummy liquid. This product mixture was found to be unstable and was therefore directly transferred to the subsequent reaction without delay.

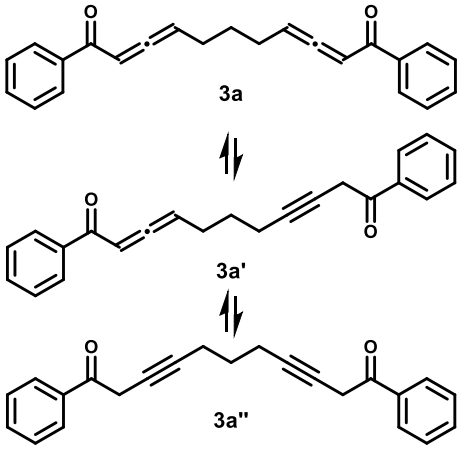
Table S1 Synthesis of the Substrates 3



R	Compound	Yield[a] (%)	[M + Na]+ Calcd for	found
C_6H_5	**3a/3a'/3a''**	95	351.1355	351.1355
2-$OMeC_6H_4$	**3b/3b'/3b''**	72[b]	411.1567	411.1559
3-$OMeC_6H_4$	**3c/3c'/3c''**	96	411.1567	411.1561
4-OMe C_6H_4	**3d/3d'/3d''**	93	411.1567	411.1563
3,4-$(OMe)_2C_6H_3$	**3e/3e'/3e''**	94[b]	471.1778	471.1776
5-F-2-$OMeC_6H_3$	**3f/3f'/3f''**	87	447.1378	447.1375
4-PhC_6H_4	**3g/3g'/3g''**	85	503.1982	503.1980
2-MeC_6H_4	**3h/3h'/3h''**	79	379.1669	379.1666
4-MeC_6H_4	**3i/3i'/3i''**	83	379.1669	379.1666
4-$OCF_3C_6H_4$	**3j/3j'/3j''**	86	519.1001	519.1001
3-FC_6H_4	**3k/3k'/3k''**	92	387.1167	387.1167
4-FC_6H_4	**3l/3l'/3l''**	91	387.1167	387.1166
2-ClC_6H_4	**3m/3m'/3m''**	78[b]	419.0576	419.0576
3-ClC_6H_4	**3n/3n'/3n''**	94	419.0576	419.0575
4-ClC_6H_4	**3o/3o'/3o''**	95	419.0576	419.0577
2,4- $Cl_2C_6H_4$	**3p/3p'/3p''**	73[b]	486.9797	486.9789
3-BrC_6H_4	**3q/3q'/3q''**	93	506.9566	506.9564
4-BrC_6H_4	**3r/3r'/3r''**	95	506.9566	506.9565
4-IC_6H_4	**3s/3s'/3s''**	69[b]	602.9288	602.9286
4-$COOMeC_6H_4$	**3t/3t'/3t''**	72[b]	467.1465	467.1456
4-$CF_3C_6H_4$	**3u/3u'/3u''**	88	487.1103	487.1099
2-naphthyl	**3v/3v'/3v''**	91	451.1669	451.1664
2-thienyl	**3w/3w'/3w''**	96	363.0484	363.0480
cyclopropyl	**3x/3x'/3x''**	82[c]	279.1356	279.1353

[a] Isolated yields. [b] PhMe, 80 ℃. [c] $CHCl_3$, 60 ℃.

1,11-diphenylundeca-2,3,8,9-tetraene-1,11-dione / 1,11-diphenylundeca-2,3-dien-8-yne-1,11-dione / 1,11-diphenylundeca-3,8-diyne-1,11-dione (**3a**/**3a'**/**3a''**)



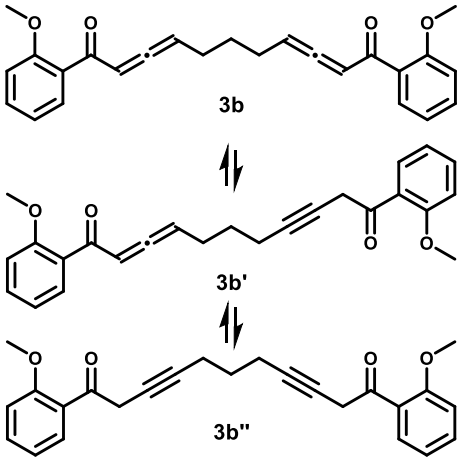
312 mg (95% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.98 (m, 2H), 7.92 – 7.68 (m, 4H), 7.65 – 7.27 (m, 11H), 6.40 – 6.31 (m, 2H), 5.57 (m, 2H), 3.81 (t, *J* = 2.4 Hz, 2H), 2.37 – 2.01 (m, 7H), 1.75 – 1.43 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 214.03, 214.01, 194.02, 193.96, 191.99, 191.78, 191.75, 137.82, 137.80, 135.64, 133.61, 133.59, 132.76, 132.72, 128.76, 128.73, 128.71, 128.59, 128.44, 128.42, 94.52, 94.51, 94.38, 94.28, 94.18, 94.17, 84.92, 73.24, 31.05, 31.01, 27.88, 27.86, 27.79, 26.95, 26.80, 18.30, 18.11.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{20}O_2Na^+$, 351.1355; found 351.1355.

1,11-bis(2-methoxyphenyl)undeca-2,3,8,9-tetraene-1,11-dione / 1,11-bis(2-methoxyphenyl)undeca-2,3-dien-8-yne-1,11-dione / 1,11-bis(2-methoxyphenyl)undeca-3,8-diyne-1,11-dione (**3b**/**3b'**/**3b''**)



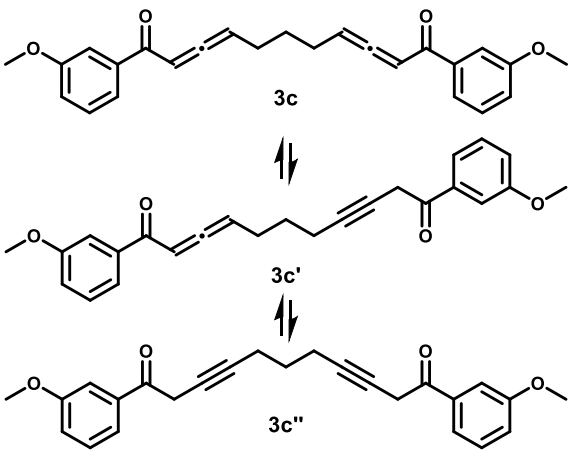
279 mg (72% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:3). R_f = 0.2.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.74 (dt, *J* = 7.7, 1.9 Hz, 1H), 7.48 – 7.36 (m, 3H), 7.02 – 6.89 (m, 4H), 6.35 – 6.28 (m, 1H), 5.49 – 5.40 (m, 1H), 3.91 – 3.79 (m, 7H), 2.13 (m, 2H), 1.99 (m, 3H), 1.53 (m, 1H), 1.46 – 1.38 (m, 1H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 214.14, 213.97, 196.18, 196.08, 194.14, 193.86, 193.81, 158.79, 157.59, 157.57, 157.51, 134.09, 134.06, 132.49, 132.40, 132.37, 132.32, 130.92, 129.80, 129.78, 129.71, 129.05, 128.66, 126.87, 120.86, 120.84, 120.37, 120.33, 111.64, 111.48, 111.44, 97.80, 97.70, 97.68, 94.45, 94.42, 83.65, 73.90, 73.81, 55.74, 55.70, 35.53, 35.49, 29.79, 28.19, 27.95, 27.92, 27.89, 26.76, 26.74, 26.61, 18.23, 18.06.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{24}O_4Na^+$, 411.1567； found 411.1559.

1,11-bis(3-methoxyphenyl)undeca-2,3,8,9-tetraene-1,11-dione / 1,11-bis(3-methoxyphenyl)undeca-2,3-dien-8-yne-1,11-dione / 1,11-bis(3-methoxyphenyl)undeca-3,8-diyne-1,11-dione (**3c/3c'/3c''**)



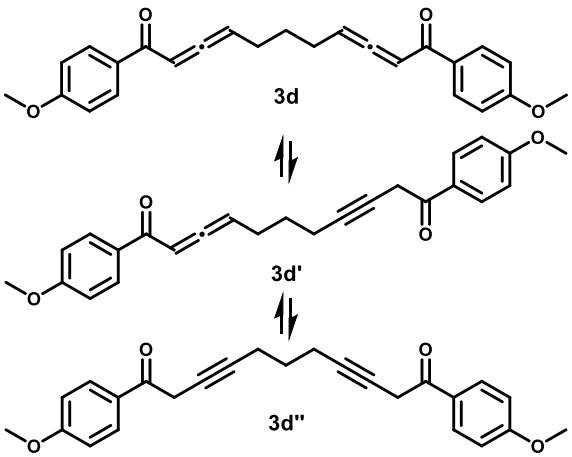
373 mg (96% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:3). R_f = 0.2.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.55 (m, 1H), 7.50 (m, 1H), 7.44 (m, 2H), 7.40 – 7.29 (m, 4H), 7.13 – 7.04 (m, 2H), 6.45 – 6.26 (m, 1H), 5.69 – 5.47 (m, 1H), 3.86 – 3.81 (m, 7H), 3.80 (m, 2H), 2.37 – 2.13 (m, 5H), 1.74 – 1.55 (m, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 213.93, 193.78, 191.58, 191.40, 191.36, 159.95, 159.73, 139.12, 139.10, 136.98, 129.73, 129.39, 129.37, 121.37, 121.35, 121.31, 120.11, 120.07, 119.19, 119.17, 113.19, 113.17, 112.91, 112.87, 94.53, 94.50, 94.39, 94.24, 94.13, 94.11, 84.88, 73.21, 55.57, 55.53, 31.13, 31.10, 27.90, 27.79, 26.96, 26.81, 18.31, 18.12.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{24}O_4Na^+$, 411.1567； found 411.1561.

1,11-bis(4-methoxyphenyl)undeca-2,3,8,9-tetraene-1,11-dione / 1,11-bis(4-methoxyphenyl)undeca-2,3-dien-8-yne-1,11-dione / 1,11-bis(4-methoxyphenyl)undeca-3,8-diyne-1,11-dione (**3d/3d'/3d''**)



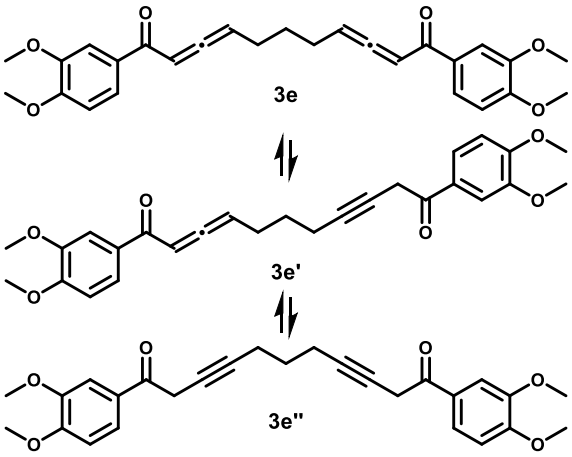
361 mg (93% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.95 (m, 2H), 7.90 – 7.85 (m, 4H), 6.90 (m, 6H), 6.39 – 6.33 (m, 2H), 5.57 (m, 2H), 3.85 (m, 10H), 3.74 (t, *J* = 2.5 Hz, 2H), 2.30 – 2.16 (m, 6H), 1.64 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 213.31, 213.27, 192.51, 189.95, 189.75, 189.69, 163.86, 163.40, 163.39, 131.05, 131.02, 131.01, 130.62, 128.66, 128.63, 113.88, 113.72, 113.65, 113.64, 94.34, 94.32, 94.16, 93.81, 93.69, 93.65, 84.62, 84.58, 73.58, 55.58, 55.54, 30.75, 30.72, 27.93, 27.91, 27.83, 27.00, 26.98, 26.83, 18.33, 18.11.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{24}O_4Na^+$, 411.1567； found 411.1563.

1,11-bis(3,4-dimethoxyphenyl)undeca-2,3,8,9-tetraene-1,11-dione / **1,11-bis(3,4-dimethoxyphenyl)undeca-2,3-dien-8-yne-1,11-dione** / **1,11-bis(3,4-dimethoxyphenyl)undeca-3,8-diyne-1,11-dione** (**3e**/**3e'**/**3e''**)



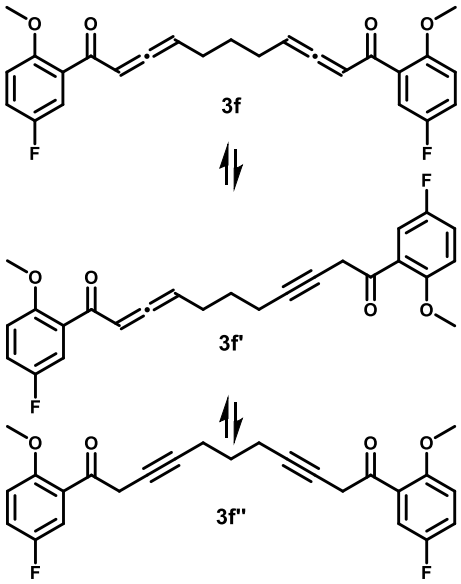
421 mg (94% yield) yellow gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.65 (m, 6H), 7.53 (m, 5H), 7.48 – 7.42 (m, 7H), 6.89 – 6.81 (m, 2H), 6.40 (m, 1H), 5.59 (m, 1H), 3.94 – 3.88 (m, 10H), 3.75 (t, *J* = 2.1 Hz, 1H), 2.24 (m, 3H), 1.65 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 213.24, 213.20, 213.16, 192.56, 189.63, 189.43, 189.36, 153.66, 153.21, 149.11, 149.02, 132.94, 132.25, 132.20, 132.13, 132.04, 132.02, 130.71, 128.75, 128.63, 128.55, 123.59, 123.56, 123.38, 123.31, 110.98, 110.95, 110.92, 110.62, 110.09, 109.89, 84.57, 73.58, 56.17, 56.13, 56.06, 56.03, 30.61, 30.57, 27.90, 27.80, 26.93, 26.80, 18.30, 18.10.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{28}O_6Na^+$, 471.1778； found 471.1776.

1,11-bis(5-fluoro-2-methoxyphenyl)undeca-2,3,8,9-tetraene-1,11-dione / **1,11-bis(5-fluoro-2-methoxyphenyl)undeca-2,3-dien-8-yne-1,11-dione** / **1,11-bis(5-fluoro-2-methoxyphenyl)undeca-3,8-diyne-1,11-dione** (**3f**/**3f'**/**3f''**)



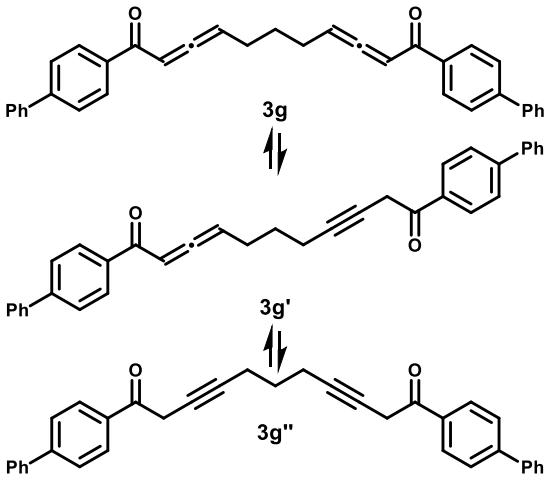
369 mg (87% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:3). R_f = 0.2.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.47 (m, 2H), 7.19 – 7.05 (m, 6H), 6.94 – 6.84 (m, 4H), 6.33 (m, 2H), 5.56 – 5.45 (m, 2H), 3.92 – 3.78 (m, 16H), 2.70 – 2.45 (m, 2H), 2.31 – 1.97 (m, 8H), 1.69 – 1.37 (m, 6H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 214.46, 214.31, 195.15, 191.39, 156.90 (d, J_{FC} = 240.1 Hz), 156.54 (d, J_{FC} = 240.1 Hz), 155.10, 153.80, 127.40, 120.62, 120.47, 118.68, 118.56, 118.42, 117.20, 117.04, 116.41 (d, J_{FC} = 9.7 Hz), 116.25 (d, J_{FC} = 9.5 Hz), 113.03 (d, J_{FC} = 7.4 Hz), 112.81 (d, J_{FC} = 7.8 Hz), 97.55, 97.44, 97.41, 94.73, 83.88, 73.57, 56.42, 56.32, 35.50, 27.91, 26.78, 26.76, 26.59, 18.24, 18.06.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{25}H_{22}F_2O_4Na^+$, 447.1378; found 447.1375.

1,11-di([1,1'-biphenyl]-4-yl)undeca-2,3,8,9-tetraene-1,11-dione / 1,11-di([1,1'-biphenyl]-4-yl)undeca-2,3-dien-8-yne-1,11-dione / 1,11-di([1,1'-biphenyl]-4-yl)undeca-3,8-diyne-1,11-dione (**3g/3g'/3g''**)



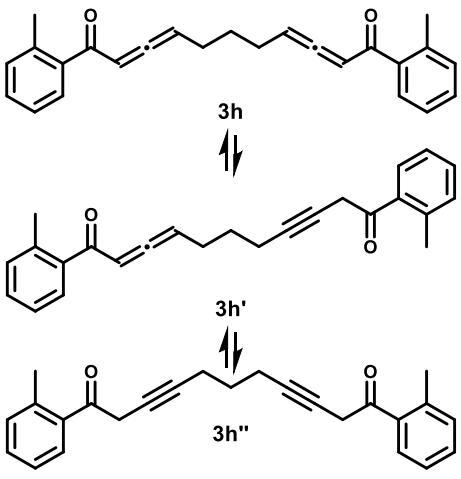
408 mg (85% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.00 (dt, *J* = 61.9, 7.7 Hz, 3H), 7.64 (m, 9H), 7.49 – 7.34 (m, 7H), 6.43 (m, 1H), 5.62 (m, 1H), 3.84 (m, 1H), 2.74 – 2.51 (m, 1H), 2.39 – 2.11 (m, 4H), 1.78 – 1.57 (m, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 213.88, 213.84, 193.58, 193.50, 191.30, 191.03, 190.93, 146.21, 145.45, 145.41, 140.04, 139.98, 139.80, 136.48, 136.45, 134.30, 129.38, 129.34, 129.32, 129.30, 129.24, 129.09, 129.05, 128.96, 128.44, 128.28, 128.25, 127.37, 127.35, 127.11, 127.07, 124.90, 94.58, 94.55, 94.41, 94.22, 94.07, 93.96, 84.93, 73.31, 31.08, 31.03, 27.86, 27.78, 26.95, 26.82, 18.32.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{35}H_{28}O_2Na^+$, 503.1982; found 503.1980.

1,11-di-o-tolylundeca-2,3,8,9-tetraene-1,11-dione / **1,11-di-o-tolylundeca-2,3-dien-8-yne-1,11-dione** / **1,11-di-o-tolylundeca-3,8-diyne-1,11-dione** (**3h/3h'/3h''**)



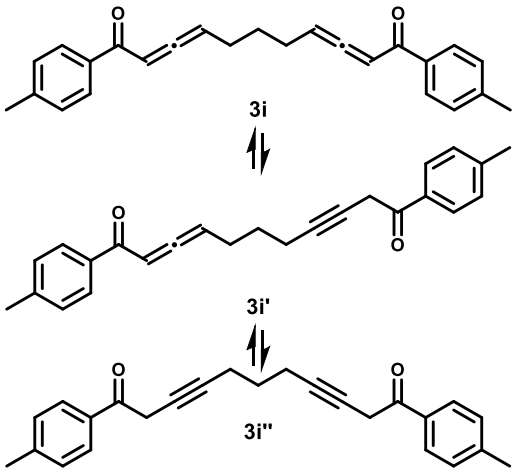
281 mg (79% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.40 – 7.26 (m, 3H), 7.23 – 7.11 (m, 3H), 6.12 (ddt, *J* = 8.9, 6.0, 2.9 Hz, 1H), 5.38 – 5.31 (m, 1H), 2.38 (d, *J* = 6.3 Hz, 5H), 1.92 (m, 2H), 1.36 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 214.94, 214.77, 214.74, 196.81, 196.72, 138.78, 138.75, 136.61, 136.55, 132.24, 131.96, 131.17, 131.15, 131.13, 130.43, 130.38, 129.19, 128.09, 128.07, 125.90, 125.76, 125.02, 97.71, 97.66, 94.41, 94.38, 94.30, 84.66, 73.40, 33.40, 29.82, 27.80, 27.78, 27.75, 26.70, 26.69, 26.65, 21.60, 20.05, 20.01, 18.11.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{25}H_{24}O_2Na^+$, 379.1669; found 379.1666.

1,11-di-p-tolylundeca-2,3,8,9-tetraene-1,11-dione / **1,11-di-p-tolylundeca-2,3-dien-8-yne-1,11-dione** / **1,11-di-p-tolylundeca-3,8-diyne-1,11-dione** (**3i/3i'/3i''**)



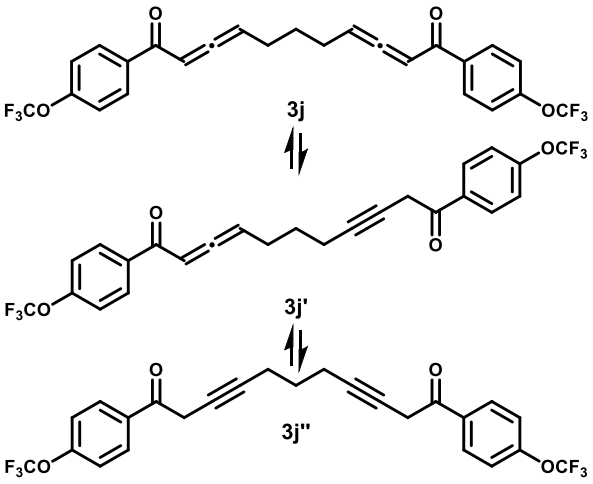
295 mg (83% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.87 (m, 2H), 7.77 (dd, *J* = 8.3, 3.0 Hz, 4H), 7.26 – 7.17 (m, 6H), 6.41 – 6.32 (m, 2H), 5.57 (m, 2H), 3.77 (t, *J* = 2.4 Hz, 2H), 2.42 – 2.34 (m, 10H), 2.29 – 2.14 (m, 6H), 1.69 – 1.58 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 213.6, 213.5, 193.6, 193.5, 191.3, 191.1, 191.0, 144.4, 143.5, 135.2, 133.1, 129.4, 129.2, 129.1, 128.9, 128.8, 128.6, 124.4, 94.4, 94.3, 94.2, 94.0, 93.9, 84.7, 73.4, 30.9, 30.8, 27.9, 27.8, 26.9, 26.8, 21.7, 18.3, 18.1.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{25}H_{24}O_2Na^+$, 379.1669; found 379.1666.

1,11-bis(4-(trifluoromethoxy)phenyl)undeca-2,3,8,9-tetraene-1,11-dione / 1,11-bis(4-(trifluoromethoxy)phenyl)undeca-2,3-dien-8-yne-1,11-dione / 1,11-bis(4-(trifluoromethoxy)phenyl)undeca-3,8-diyne-1,11-dione (3j/3j'/3j'')



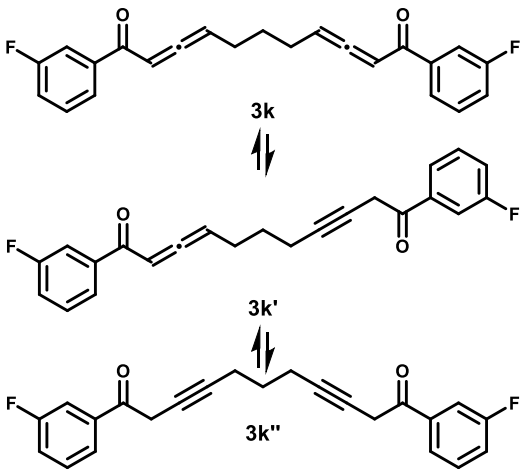
427 mg (86% yield) yellow gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.06 – 7.99 (m, 1H), 7.94 – 7.87 (m, 2H), 7.46 – 7.38 (m, 1H), 7.30 – 7.09 (m, 5H), 6.35 (m, 1H), 5.68 – 5.55 (m, 1H), 3.83 – 3.74 (m, 1H), 2.68 – 2.15 (m, 6H), 1.89 – 1.53 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 214.12, 214.10, 214.04, 213.97, 192.44, 192.35, 190.30, 189.99, 189.94, 170.56, 170.31, 153.77, 152.97, 152.38, 149.92, 136.02, 135.97, 133.79, 132.53, 132.38 (d, J_{FC} = 10.8 Hz), 130.82, 130.78, 130.71, 130.67, 130.43, 128.62 (d, J_{FC} = 12.6 Hz), 128.49, 126.09 (d, J_{FC} = 7.6 Hz), 122.99, 121.34, 121.28, 121.14, 120.53 (q, J_{FC} = 256.70 Hz), 119.63, 117.85, 99.23, 99.18, 94.76, 94.62, 94.15, 93.98, 93.94, 85.15, 75.69, 72.90, 33.74, 31.09, 31.03, 27.79, 27.72, 27.68, 26.86, 26.75, 24.57, 19.59, 18.21.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{25}H_{18}F_6O_4Na^+$, 519.1001; found 519.1001.

1,11-bis(3-fluorophenyl)undeca-2,3,8,9-tetraene-1,11-dione / 1,11-bis(3-fluorophenyl)undeca-2,3-dien-8-yne-1,11-dione / 1,11-bis(3-fluorophenyl)undeca-3,8-diyne-1,11-dione (3k/3k'/3k'')



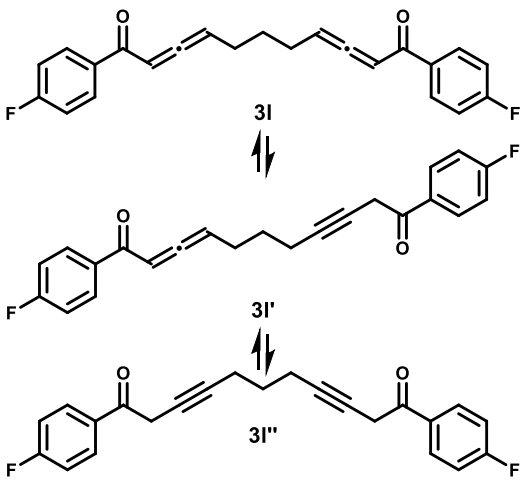
335 mg (92% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.84 – 6.94 (m, 11H), 6.34 (m, 1H), 5.70 – 5.48 (m, 1H), 3.86 – 3.68 (m, 1H), 2.78 – 2.10 (m, 6H), 2.07 – 1.47 (m, 5H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 214.18, 214.16, 214.10, 192.66, 190.48, 190.30, 190.24, 163.00 (d, J_{FC} = 246.13 Hz), 162.88 (d, J_{FC} = 247.64 Hz), 161.78, 153.70, 139.76, 137.65, 136.10, 132.35 (d, J = 10.8 Hz), 131.65, 130.41 (d, J = 7.6 Hz), 130.09 (d, J_{FC} = 7.6 Hz), 130.02, 128.60 (d, J = 12.6 Hz), 124.48, 124.45, 124.43, 124.41, 120.60 (d, J_{FC} = 21.7 Hz), 120.19, 119.63 (dd, J_{FC} = 21.3, 6.5 Hz), 116.27 (d, J_{FC} = 21.0 Hz), 115.62, 115.47, 111.50 (d, J_{FC} = 22.8 Hz), 99.70, 99.51, 94.75, 94.73, 94.63, 94.16, 94.06, 94.03, 85.17, 85.15, 75.68, 72.85, 72.69, 33.72, 33.60, 31.17, 27.79, 27.71, 27.66, 26.88, 26.71, 24.55, 24.27, 19.58, 19.20, 18.22, 18.03.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{18}F_2O_2Na^+$, 387.1167; found 387.1167.

1,11-bis(4-(trifluoromethoxy)phenyl)undeca-2,3,8,9-tetraene-1,11-dione / 1,11-bis(4-(trifluoromethoxy)phenyl)undeca-2,3-dien-8-yne-1,11-dione / 1,11-bis(4-(trifluoromethoxy)phenyl)undeca-3,8-diyne-1,11-dione (3l/3l'/3l'')



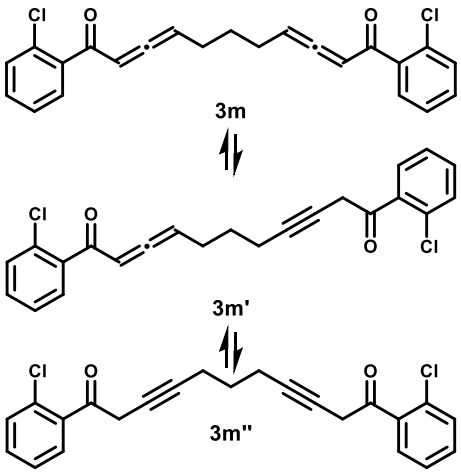
331 mg (91% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.05 – 7.80 (m, 4H), 7.52 – 7.33 (m, 1H), 7.10 (m, 5H), 6.34 (m, 1H), 5.59 (m, 1H), 3.77 (d, *J* = 1.9 Hz, 1H), 2.33 – 2.08 (m, 4H), 1.73 – 1.46 (m, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 213.86, 192.41, 192.33, 190.19, 189.92, 189.87, 166.02 (d, J_{FC} = 256.7 Hz), 165.57 (d, J_{FC} = 255.2 Hz), 134.03, 132.36 (d, J_{FC} = 10.5 Hz), 132.00, 131.65 (d, J_{FC} = 3.3 Hz), 131.47, 131.45, 131.41, 131.39, 131.36, 131.32, 131.29, 131.26, 131.07, 131.01, 128.61 (d, J_{FC} = 12.3 Hz), 126.54, 126.48, 115.87 (d, J_{FC} = 22.0 Hz), 115.52 (dd, J_{FC} = 21.9, 4.5 Hz), 98.10, 94.61, 94.59, 94.46, 94.06, 94.03, 93.88, 85.00, 73.10, 72.97, 33.76, 31.00, 30.96, 28.10, 27.82, 27.72, 26.89, 26.75, 18.25.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{18}F_2O_2Na^+$, 387.1167; found 387.1166.

1,11-bis(2-chlorophenyl)undeca-2,3,8,9-tetraene-1,11-dione / **1,11-bis(2-chlorophenyl)undeca-2,3-dien-8-yne-1,11-dione** / **1,11-bis(2-chlorophenyl)undeca-3,8-diyne-1,11-dione** (**3m**/**3m'**/**3m''**)



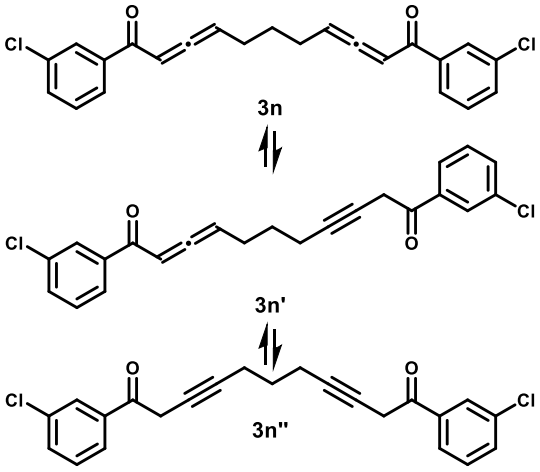
309 mg (78% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.42 – 7.20 (m, 8H), 6.11 (m, 2H), 5.41 – 5.34 (m, 2H), 2.03 (m, 2H), 1.93 – 1.77 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 215.46, 215.41, 194.37, 194.31, 139.00, 132.20, 131.04, 131.01, 130.99, 130.93, 130.78, 130.76, 130.56, 130.47, 130.40, 129.93, 129.88, 129.86, 129.53, 128.68, 128.65, 128.61, 128.58, 127.04, 126.97, 126.42, 126.38, 103.48, 97.77, 95.24, 95.04, 94.98, 84.57, 72.52, 34.52, 27.66, 27.64, 26.43, 17.95.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{18}Cl_2O_2Na^+$, 419.0576; found 419.0576.

1,11-bis(3-chlorophenyl)undeca-2,3,8,9-tetraene-1,11-dione / **1,11-bis(3-chlorophenyl)undeca-2,3-dien-8-yne-1,11-dione** / **1,11-bis(3-chlorophenyl)undeca-3,8-diyne-1,11-dione** (**3n**/**3n'**/**3n''**)



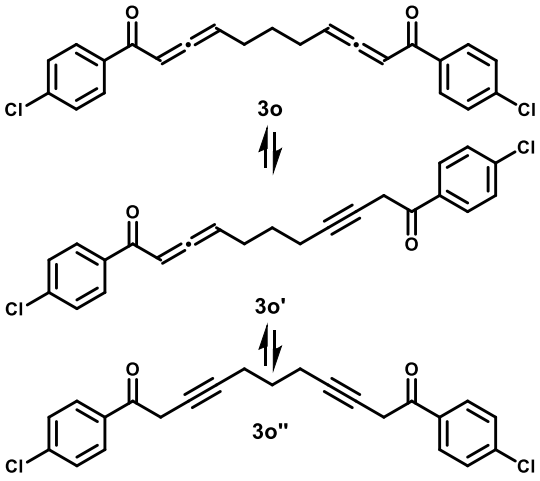
373 mg (94% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.98 – 7.64 (m, 4H), 7.56 – 7.16 (m, 8H), 6.32 (m, 1H), 5.93 (m, 1H), 5.67 – 5.56 (m, 1H), 3.78 (m, 1H), 2.69 – 2.09 (m, 7H), 1.96 – 1.48 (m, 6H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 214.31, 214.29, 214.22, 192.68, 190.49, 190.42, 139.28, 139.26, 137.10, 135.69, 135.08, 134.57, 133.53, 132.61, 132.57, 130.10, 129.81, 129.77, 129.42, 129.36, 128.88, 128.60, 126.86, 126.83, 124.65, 122.69, 99.81, 99.63, 97.93, 94.81, 94.70, 94.28, 94.19, 85.26, 75.69, 75.52, 72.85, 33.76, 33.64, 31.15, 28.23, 27.87, 27.68, 27.54, 26.98, 26.77, 24.58, 24.10, 19.62, 18.28.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{18}Cl_2O_2Na^+$, 419.0576; found 419.0575.

1,11-bis(4-chlorophenyl)undeca-2,3,8,9-tetraene-1,11-dione / 1,11-bis(4-chlorophenyl)undeca-2,3-dien-8-yne-1,11-dione / 1,11-bis(4-chlorophenyl)undeca-3,8-diyne-1,11-dione (**3o/3o'/3o''**)



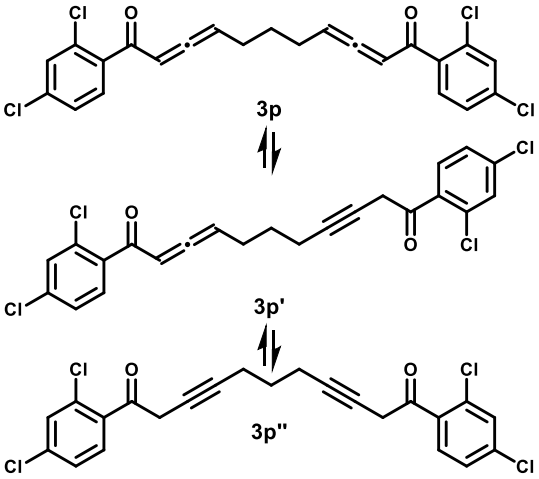
377 mg (95% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.93 – 7.69 (m, 5H), 7.46 – 7.26 (m, 10H), 6.34 (m, 1H), 5.95 – 5.84 (m, 1H), 5.67 – 5.54 (m, 1H), 3.77 (m, 1H), 2.67 – 2.10 (m, 11H), 1.95 – 1.46 (m, 10H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 214.02, 192.72, 190.34, 140.09, 139.15, 136.02, 135.40, 133.88, 132.41, 132.34, 130.19, 130.15, 130.13, 129.92, 129.03, 129.00, 128.75, 128.72, 128.67, 128.58, 128.49, 125.81, 125.77, 98.82, 97.57, 94.71, 94.69, 94.57, 94.14, 93.98, 93.93, 85.11, 75.75, 72.99, 33.75, 31.07, 28.10, 28.06, 27.79, 27.69, 26.89, 26.75, 24.57, 19.60, 18.26.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{18}Cl_2O_2Na^+$, 419.0576; found 419.0577.

1,11-bis(2,4-dichlorophenyl)undeca-2,3,8,9-tetraene-1,11-dione / **1,11-bis(2,4-dichlorophenyl)undeca-2,3-dien-8-yne-1,11-dione** / **1,11-bis(2,4-dichlorophenyl)undeca-3,8-diyne-1,11-dione** (**3p**/**3p'**/**3p''**)



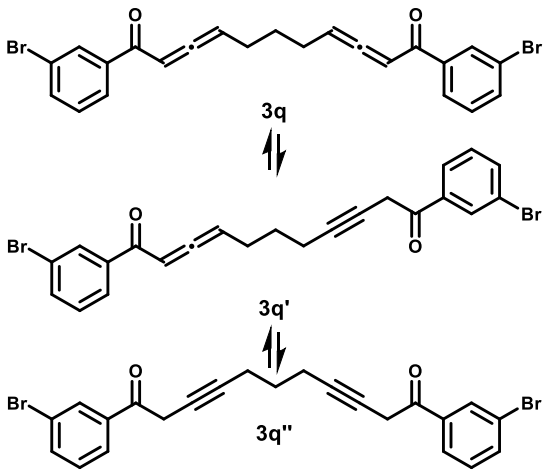
340 mg (73% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.47 – 7.37 (m, 4H), 7.36 – 7.22 (m, 8H), 6.16 – 6.08 (m, 3H), 5.44 (m, 5H), 2.66 – 1.74 (m, 8H), 1.71 – 1.28 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 215.49, 215.47, 193.19, 137.42, 137.40, 136.55, 131.98, 130.38, 129.94, 129.84, 129.79, 129.74, 127.33, 126.94, 126.92, 126.89, 104.05, 97.77, 97.74, 95.55, 95.30, 95.27, 95.10, 34.58, 33.78, 33.60, 28.11, 27.75, 27.72, 27.39, 27.13, 26.55, 26.54, 26.37, 26.29, 24.53, 23.80, 19.51, 18.75, 18.04.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{16}Cl_4O_2Na^+$, 486.9797; found 486.9789.

1,11-bis(3-bromophenyl)undeca-2,3,8,9-tetraene-1,11-dione / **1,11-bis(3-bromophenyl)undeca-2,3-dien-8-yne-1,11-dione** / **1,11-bis(3-bromophenyl)undeca-3,8-diyne-1,11-dione** (**3q**/**3q'**/**3q''**)



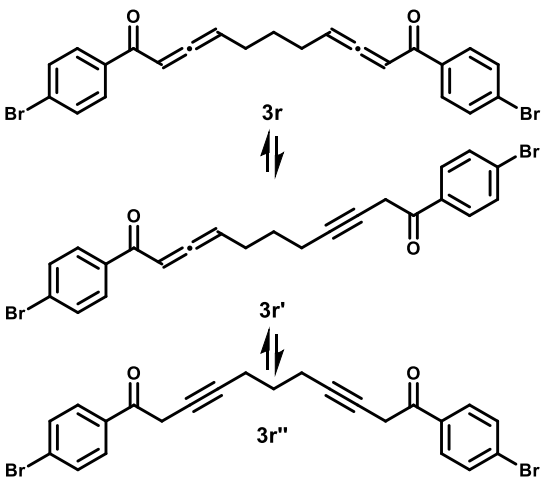
452 mg (93% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.96 (m, 1H), 7.89 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.78 – 7.60 (m, 3H), 7.53 (q, *J* = 2.0 Hz, 1H), 7.44 (m, 1H), 7.37 – 7.27 (m, 3H), 7.20 (m, 1H), 6.29 (m, 1H), 5.97 – 5.88 (m, 1H), 5.66 – 5.54 (m, 1H), 3.81 – 3.73 (m, 1H), 2.71 – 2.38 (m, 4H), 2.36 – 2.13 (m, 4H), 1.92 – 1.53 (m, 6H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 214.31, 214.30, 192.57, 190.40, 190.34, 139.48, 139.46, 139.45, 137.27, 136.43, 135.92, 135.51, 135.47, 132.41, 132.33, 132.27, 131.80, 131.77, 130.34, 130.30, 130.27, 130.07, 127.52, 127.50, 127.30, 127.24, 123.14, 123.05, 123.02, 122.56, 99.84, 99.66, 97.95, 94.81, 94.70, 94.27, 94.16, 85.27, 75.67, 72.84, 33.76, 31.12, 28.02, 27.87, 27.67, 26.98, 26.76, 24.57, 19.61, 18.28.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{18}Br_2O_2Na^+$, 506.9566; found 506.9564.

1,11-bis(4-bromophenyl)undeca-2,3,8,9-tetraene-1,11-dione / **1,11-bis(4-bromophenyl)undeca-2,3-dien-8-yne-1,11-dione** / **1,11-bis(4-bromophenyl)undeca-3,8-diyne-1,11-dione** (**3r**/**3r'**/**3r''**)



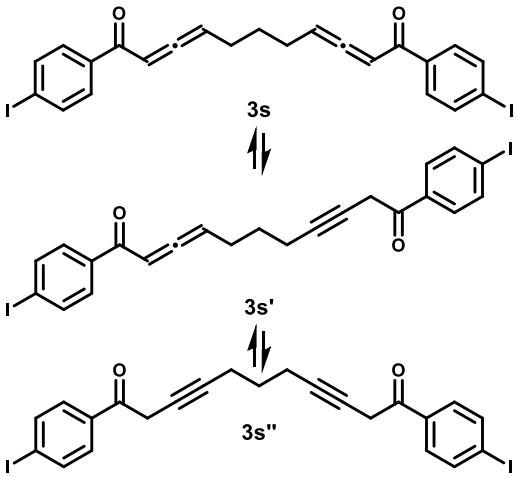
462 mg (95% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.87 – 7.79 (m, 1H), 7.76 – 7.67 (m, 3H), 7.63 – 7.51 (m, 4H), 7.49 – 7.41 (m, 2H), 7.30 – 7.26 (m, 1H), 6.33 (m, 1H), 5.67 – 5.53 (m, 1H), 3.77 (t, *J* = 2.5 Hz, 1H), 2.67 – 2.35 (m, 3H), 2.33 – 2.11 (m, 4H), 1.95 – 1.46 (m, 6H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 214.06, 192.92, 190.81, 190.54, 190.47, 136.46, 134.30, 132.81, 132.43, 132.10, 131.96, 131.75, 131.72, 131.66, 130.32, 130.28, 130.02, 128.86, 128.68, 128.60, 127.83, 127.75, 126.05, 126.02, 98.92, 94.92, 94.75, 94.72, 94.60, 94.16, 94.12, 94.01, 93.94, 85.15, 72.98, 33.76, 31.07, 31.01, 27.79, 27.69, 26.90, 26.75, 24.58, 19.63, 19.26, 18.27.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{18}Br_2O_2Na^+$, 506.9566; found 506.9565.

1,11-bis(4-iodophenyl)undeca-2,3,8,9-tetraene-1,11-dione / **1,11-bis(4-iodophenyl)undeca-2,3-dien-8-yne-1,11-dione** / **1,11-bis(4-iodophenyl)undeca-3,8-diyne-1,11-dione** (**3s**/**3s'**/**3s''**)



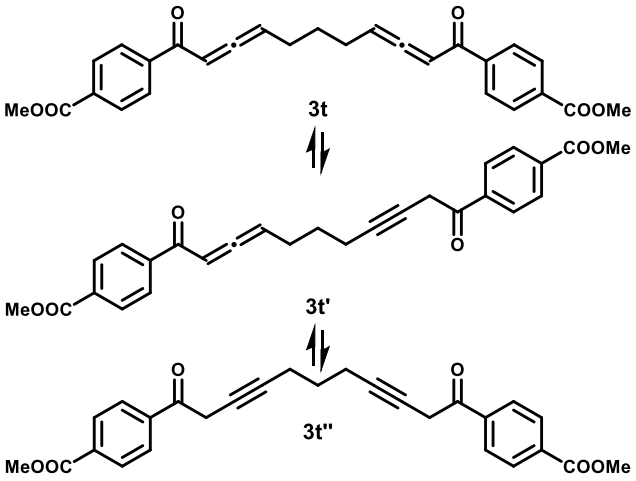
400 mg (69% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.86 – 7.48 (m, 16H), 7.44 (m, 1H), 7.20 – 7.08 (m, 2H), 6.32 (m, 1H), 5.97 – 5.86 (m, 1H), 5.60 (m, 1H), 3.76 (m, 1H), 3.08 – 2.83 (m, 1H), 2.72 – 2.06 (m, 10H), 1.92 – 1.47 (m, 8H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 214.06, 190.74, 170.54, 138.11, 138.03, 137.95, 137.91, 137.75, 137.71, 137.01, 134.84, 133.39, 132.43, 132.36, 131.66, 130.23, 130.18, 130.16, 130.10, 129.85, 128.68, 128.59, 126.21, 126.13, 101.72, 100.52, 98.97, 95.41, 94.75, 94.72, 94.60, 94.13, 93.98, 93.90, 33.75, 30.96, 29.81, 28.11, 27.79, 27.69, 27.60, 26.89, 26.75, 24.58, 24.09, 21.67, 19.63.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{18}I_2O_2Na^+$, 602.9288; found 602.9286.

dimethyl 4,4'-(undeca-2,3,8,9-tetraenedioyl)dibenzoate / **dimethyl 4,4'-(undeca-2,3-dien-8-ynedioyl)dibenzoate** / **dimethyl 4,4'-(undeca-3,8-diynedioyl)dibenzoate** (**3t/3t'/3t''**)



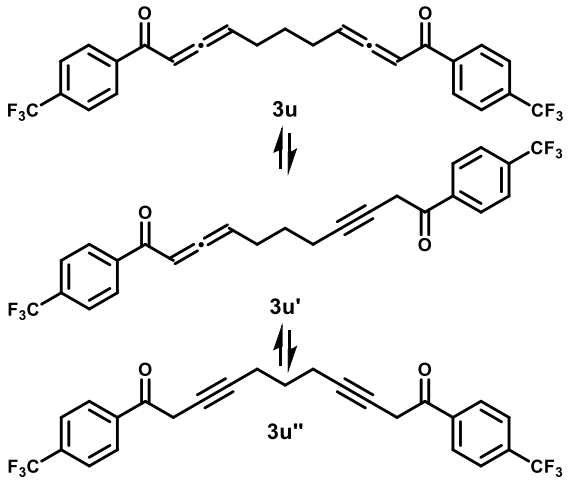
320 mg (72% yield) yellow gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:3). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.12 – 7.94 (m, 7H), 7.88 – 7.81 (m, 3H), 6.36 – 6.28 (m, 1H), 5.65 – 5.54 (m, 1H), 3.97 (d, *J* = 3.4 Hz, 1H), 3.94 – 3.87 (m, 8H), 3.82 (t, *J* = 2.4 Hz, 1H), 2.29 – 2.11 (m, 5H), 1.64 – 1.50 (m, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 214.44, 214.40, 193.42, 191.64, 191.37, 191.28, 166.37, 166.32, 166.17, 141.26, 141.21, 141.18, 139.52, 138.75, 134.28, 133.45, 133.39, 130.16, 130.03, 129.97, 129.89, 129.61, 129.58, 129.55, 128.63, 128.61, 128.58, 128.55, 128.53, 128.47, 128.35, 124.32, 124.30, 95.06, 94.77, 94.74, 94.65, 94.54, 94.41, 94.34, 85.19, 72.82, 52.57, 52.48, 48.94, 31.26, 28.12, 27.72, 27.60, 27.52, 27.11, 26.81, 26.66, 18.19.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{27}H_{24}O_6Na^+$, 467.1465; found 467.1456.

1,11-bis(4-(trifluoromethyl)phenyl)undeca-2,3,8,9-tetraene-1,11-dione / **1,11-bis(4-(trifluoromethyl)phenyl)undeca-2,3-dien-8-yne-1,11-dione** / **1,11-bis(4-(trifluoromethyl)phenyl)undeca-3,8-diyne-1,11-dione** (**3u**/**3u'**/**3u''**)



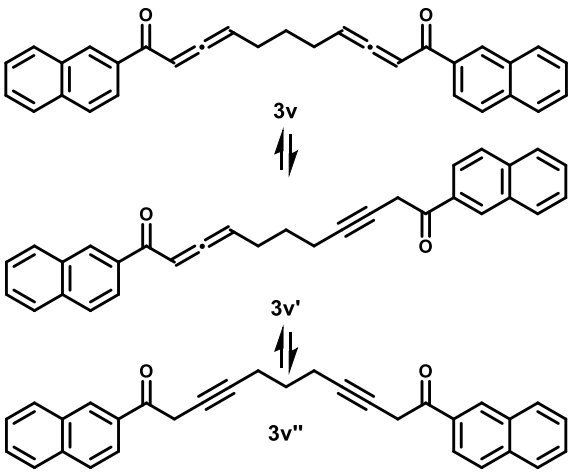
408 mg (88% yield) yellow gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:6). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.07 (m, 1H), 7.93 (dd, *J* = 8.4, 3.6 Hz, 3H), 7.76 – 7.46 (m, 11H), 6.35 (m, 2H), 6.06 – 5.96 (m, 2H), 5.70 – 5.57 (m, 1H), 3.84 (m, 2H), 2.71 – 2.12 (m, 7H), 1.99 – 1.48 (m, 5H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 214.56, 214.53, 214.51, 214.40, 192.94, 191.18, 190.85, 190.78, 140.63, 138.26, 137.25, 134.01 (d, J_{FC} = 32.9 Hz), 131.15 (q, J_{FC} = 32.7 Hz), 129.07, 129.04, 128.99, 128.76 (d, J_{FC} = 21.3 Hz), 127.12, 126.58 (d, J_{FC} = 32.2 Hz), 125.88, 125.85, 125.83, 125.80, 125.52, 125.49, 125.46, 125.43, 124.88, 124.80, 124.77, 124.75, 122.97 (d, J_{FC} = 32.5 Hz), 100.62, 98.47, 94.91, 94.52, 94.27, 85.36, 75.67, 75.50, 72.68, 33.75, 33.63, 31.25, 28.20, 28.13, 27.99, 27.76, 27.65, 26.86, 26.84, 26.71, 24.58, 24.26, 19.62.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{25}H_{18}F_6O_2Na^+$, 487.1103; found 487.1099.

1,11-di(naphthalen-2-yl)undeca-2,3,8,9-tetraene-1,11-dione / **1,11-di(naphthalen-2-yl)undeca-2,3-dien-8-yne-1,11-dione** / **1,11-di(naphthalen-2-yl)undeca-3,8-diyne-1,11-dione** (**3v**/**3v'**/**3v''**)



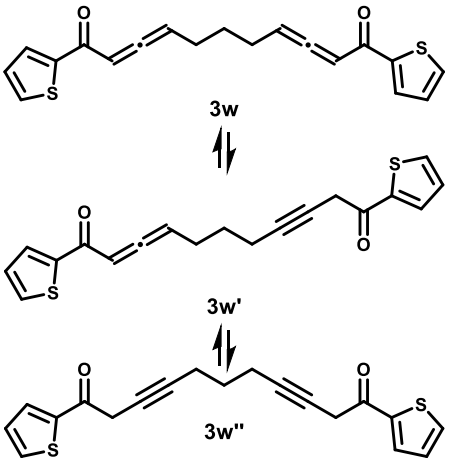
390 mg (91% yield) yellow gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.39 – 8.29 (m, 1H), 8.08 – 7.76 (m, 9H), 7.62 – 7.41 (m, 5H), 6.52 – 6.43 (m, 1H), 5.61 – 5.55 (m, 1H), 3.97 – 3.89 (m, 1H), 2.65 – 2.41 (m, 1H), 2.36 – 2.14 (m, 4H), 1.78 – 1.55 (m, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 213.96, 213.93, 213.90, 193.88, 191.62, 191.47, 191.34, 135.81, 135.46, 135.06, 135.03, 132.92, 132.51, 132.43, 132.42, 130.60, 130.58, 130.22, 130.20, 130.18, 129.76, 129.73, 129.71, 129.57, 129.54, 129.50, 128.79, 128.77, 128.66, 128.60, 128.58, 128.37, 128.34, 128.32, 128.29, 127.89, 127.88, 127.86, 127.76, 126.97, 126.95, 126.82, 126.80, 126.76, 124.76, 124.70, 124.67, 124.23, 124.21, 94.52, 94.48, 94.36, 94.25, 94.17, 94.08, 84.97, 73.48, 31.11, 31.09, 27.93, 27.91, 27.84, 27.78, 26.98, 26.94, 26.80, 18.35, 18.11.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{24}O_2Na^+$, 451.1669; found 451.1664.

1,11-di(thiophen-2-yl)undeca-2,3,8,9-tetraene-1,11-dione / 1,11-di(thiophen-2-yl)undeca-2,3-dien-8-yne-1,11-dione / 1,11-di(thiophen-2-yl)undeca-3,8-diyne-1,11-dione (**3w/3w'/3w''**)



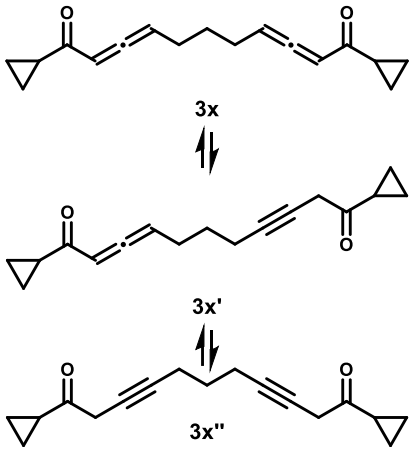
327 mg (96% yield) yellowish gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:5). R_f = 0.3.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.85 – 7.40 (m, 5H), 7.10 (m, 2H), 6.31 (m, 1H), 5.70 (m, 1H), 3.74 (d, *J* = 2.7 Hz, 1H), 2.68 – 2.46 (m, 1H), 2.29 (m, 4H), 1.70 (m, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 212.78, 212.74, 212.71, 186.81, 182.66, 182.55, 182.53, 143.69, 143.67, 143.65, 142.48, 134.36, 133.66, 133.62, 133.07, 133.04, 132.49, 132.46, 132.44, 132.36, 132.29, 131.64, 131.62, 128.63, 128.55, 128.32, 128.25, 127.99, 127.92, 95.43, 95.33, 94.47, 94.41, 94.38, 94.34, 84.61, 73.08, 31.52, 31.49, 27.60, 27.57, 27.05, 27.03, 26.83, 18.33, 18.07.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{16}O_2S_2Na^+$, 363.0484; found 363.0480.

1,11-dicyclopropylundeca-2,3,8,9-tetraene-1,11-dione / 1,11-dicyclopropylundeca-2,3-dien-8-yne-1,11-dione / 1,11-dicyclopropylundeca-3,8-diyne-1,11-dione (3x/3x'/3x'')



210 mg (82% yield) colorless gummy liquid, isolated by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:1). R_f = 0.3.

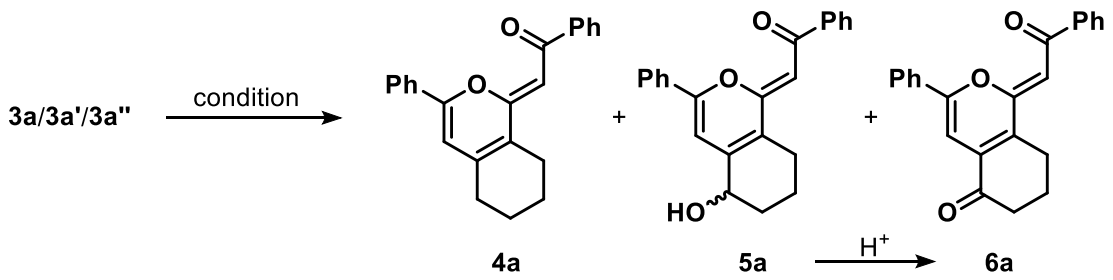
^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.78 (m, 2H), 5.65 (m, 2H), 2.36 – 2.15 (m, 6H), 1.73 – 1.59 (m, 2H), 1.02 – 0.91 (m, 4H), 0.85 – 0.74 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 213.10, 200.10, 98.30, 98.26, 94.93, 94.91, 83.78, 73.26, 34.83, 34.73, 27.89, 27.84, 27.80, 27.75, 27.37, 27.06, 27.04, 26.77, 23.53, 19.21, 18.24, 17.54, 17.47, 17.43, 17.38, 11.62, 10.97, 10.91.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{20}O_2Na^+$, 279.1356; found 279.1353.

2.2 Optimization of the reaction conditions

Table S2 Optimization of the reaction conditions

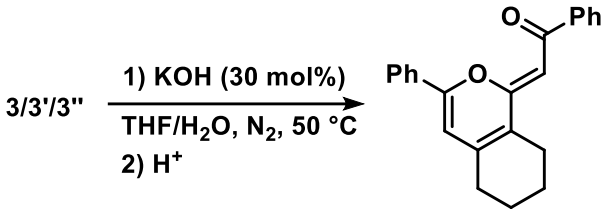


Entry	Additive	Atmosphere	Solvent	Temperature	Time	Yield[b]		
						4a	6a	total
1	Na_2S (30 mol%)/ H_2O	air	THF	rt	3 h	53	25	78
2	K_2CO_3 (30 mol%)/ H_2O	air	THF	rt	3 h	0	0	0
3	KOH (30 mol%)/ H_2O	air	THF	rt	2 h	62	17	79
4	t-BuOK (30 mol%)	air	THF	rt	0.2 h	59	2	61
5	4 + one drop of water	air	THF	rt	0.2 h	59	11	70
6	Et_3N (30 mol%)	air	THF	rt	3 h	0	0	0
7	PPh_3 (30 mol%)	air	THF	rt	3 h	0	0	0
8	Na_2S (20 mol%)/ H_2O	air	THF	rt	3.5 h	51	23	74
9	Na_2S (40 mol%)/ H_2O	air	THF	rt	2.5 h	55	20	75
10	Na_2S (30 mol%)	air	THF	rt	3 h	0	0	0

11	H_2O (30 mol%)	air	THF	rt	3 h	0	0	0
12	KOH (30 mol%)/ H_2O	N_2	THF	rt	2 h	83	2	85
13	KOH (30 mol%)/ H_2O	N_2	DCM	rt	5 h	81	3	84
14	KOH (30 mol%)/ H_2O	N_2	PhMe	rt	5 h	82	3	85
15	KOH (30 mol%)/ H_2O	N_2	CH_3CN	rt	2 h	75	4	79
16	KOH (30 mol%)/ H_2O	N_2	EA	rt	3 h	82	4	86
17	KOH (30 mol%)/ H_2O	N_2	THF	50 ℃	1 h	84	2	86
18	KOH (30 mol%)/ H_2O	N_2	THF	reflux	1 h	83	2	85
19	Na_2S (30 mol%)/ H_2O	air	THF	rt	5 h	35	41	76
20	Na_2S (30 mol%)/ H_2O	air	THF	rt	8 h	13	64	77
21	Na_2S (30 mol%)/ H_2O	air	THF	rt	10 h	12	64	76
22	Na_2S (30 mol%)/ H_2O	air	EA	rt	10 h	11	72	83
23	Na_2S (30 mol%)/ H_2O	air	CH_3CN	rt	8 h	13	63	76
24	Na_2S (30 mol%)/ H_2O	air	DCM	rt	12 h	12	56	68
25	Na_2S (30 mol%)/ H_2O	air	PhMe	rt	12 h	14	59	73
26	Na_2S (30 mol%)/ H_2O	air	EA	50 ℃	8 h	6	78	84
27	Na_2S (30 mol%)/ H_2O	air	EA	reflux	8 h	5	76	81
28	Na_2S (30 mol%)/ H_2O	O_2	EA	50 ℃	8 h	4	75	79
29	Na_2S (30 mol%)/ H_2O	N_2	THF	50 ℃	2 h	79	5	84
30	KOH (30 mol%)/ H_2O	air	EA	50 ℃	5 h[c]	12	67	79
31	NaOH (30 mol%)/ H_2O	air	EA	50 ℃	5 h[c]	9	71	80
32	$(NH_4)_2S$ (30 mol%)/ H_2O	air	EA	50 ℃	8 h	0	0	0
33	NaHS (30 mol%)/ H_2O	air	EA	50 ℃	8 h	0	0	0

[a] Reaction conditions: **3a/3a'/3a''** (0.50 mmol), solvent (5.0 mL). [b] Isolated yield. [c] After 5 hours, the yield of the products no longer changed.

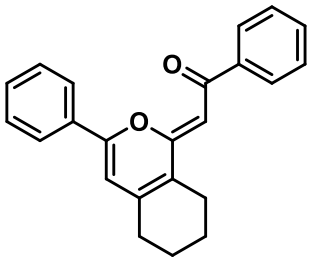
2.3 Synthesis and characterization of product 4



4

General Procedures: A 25 mL round-bottomed flask was charged with 0.5 mmol of the freshly prepared raw material **3**, followed by the addition of 5 mL of anhydrous tetrahydrofuran (THF). The resulting solution was stirred under a nitrogen (N_2) atmosphere at 50 ℃. Subsequently, 1 mL of an aqueous potassium hydroxide (KOH) solution (8.4 mg KOH in 1 mL water, 0.15 mmol) was added to the reaction mixture. The progress of the reaction was monitored using thin-layer chromatography (TLC). Upon completion, the reaction mixture was cooled to room temperature and neutralized by the cautious addition of 2 mL of hydrochloric acid (10 mol/L). The product was then extracted into dichloromethane (DCM) using three portions (3 × 3 mL). The combined organic phases were washed with saturated sodium chloride solution, dried over magnesium sulfate ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography, employing a gradient elution with a mixture of ethyl acetate and n-hexane (starting from 1:20 to 1:6) to afford the desired product **4**.

(Z)-1-phenyl-2-(3-phenyl-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4a)



138 mg (84% yield) yellow solid, purified by flash column chromatography (SiO_2, ethyl acetate: n-hexane, 1:10). R_f = 0.3.

m.p. = 165.8-166.2 ℃

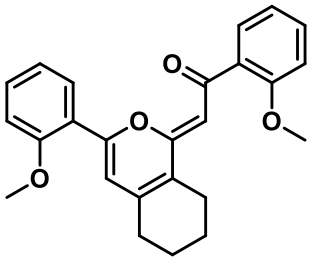
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.16 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.97 – 7.94 (m, 2H), 7.51 – 7.39 (m, 6H), 6.45 (s, 1H), 6.04 (s, 1H), 2.52 (t, *J* = 6.1 Hz, 2H), 2.38 (t, *J* = 6.3 Hz, 2H), 1.87 – 1.76 (m, 4H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 186.8, 160.0, 150.3, 143.4, 141.7, 132.1, 130.8, 130.2, 129.0, 128.3, 127.5, 124.8, 123.2, 107.9, 92.0, 30.3, 24.6, 22.7, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}O_2^+$, 329.1536； found 329.1520.

IR (neat) ν (cm^{-1}): 3053, 2927, 2860, 1643, 1616, 1563, 1478, 1258, 1211, 984.

(Z)-1-(2-methoxyphenyl)-2-(3-(2-methoxyphenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4b)



137mg (71% yield) yellow solid, purified by flash column chromatography (SiO_2, ethyl acetate:

n-hexane, 1: 6). R_f = 0.25.

m.p. = 86.7-88.0 ℃

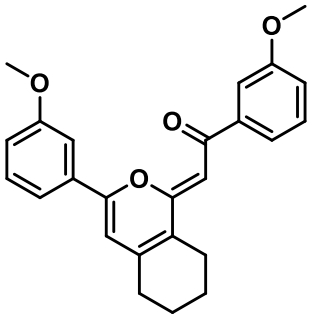
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.69 (d, *J* = 7.9 Hz, 1H), 7.63 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.34 (ddd, *J* = 8.7, 7.4, 1.8 Hz, 2H), 7.19 – 7.12 (m, 1H), 7.03 – 6.96 (m, 2H), 6.93 (ddd, *J* = 8.3, 6.3, 1.0 Hz, 2H), 5.92 (s, 1H), 3.93 (s, 3H), 3.86 (s, 3H), 2.49 (t, *J* = 6.1 Hz, 2H), 2.30 (t, *J* = 6.3 Hz, 2H), 1.83 – 1.72 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 187.9, 162.7, 157.2, 157.0, 151.4, 143.8, 133.5, 130.8, 129.8, 129.4, 122.8, 121.8, 120.7, 120.3, 111.6, 110.9, 110.1, 95.8, 55.9, 55.5, 30.2, 24.0, 22.3, 21.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{24}O_4Na^+$, 411.1566； found 411.1562.

IR (neat) ν (cm^{-1}): 3067, 2920, 1640, 1614, 1593, 1569, 1484, 1242, 1159, 1019.

(Z)-1-(3-methoxyphenyl)-2-(3-(3-methoxyphenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4c)



165 mg (85% yield) yellow solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:4). R_f = 0.25.

m.p. = 158.9-159.2 ℃

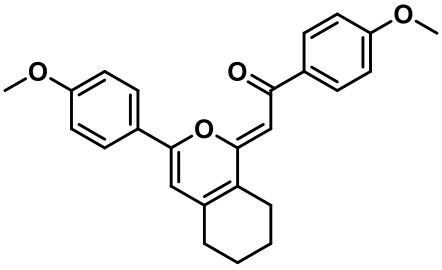
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.86 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.71 (ddd, *J* = 7.8, 1.6, 0.9 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.00 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 6.97 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 6.40 (s, 1H), 6.01 (s, 1H), 3.97 (s, 3H), 3.87 (s, 3H), 2.49 (t, *J* = 5.9 Hz, 2H), 2.35 (t, *J* = 6.1 Hz, 2H), 1.85 – 1.81 (m, 2H), 1.78 – 1.74 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 186.7, 163.3, 160.1, 159.7, 154.1, 143.7, 143.4, 133.0, 129.9, 129.2, 123.3, 119.9, 117.6, 117.0, 116.6, 112.4, 112.4, 110.2, 104.6, 91.3, 55.7, 55.5, 29.9, 24.1, 22.1, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{24}O_4Na^+$, 411.1566； found 411.1558.

IR (neat) ν (cm^{-1}): 3060, 2987, 2927, 1643, 1620, 1565, 1501, 1246, 1042.

(Z)-1-(4-methoxyphenyl)-2-(3-(4-methoxyphenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4d)



167 mg (86% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.20.

m.p. = 158.5-159.4 ℃

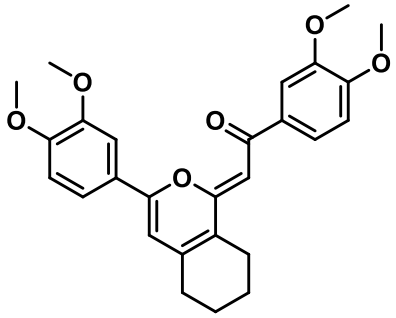
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.13 – 8.09 (m, 2H), 7.96 – 7.93 (m, 2H), 7.01 – 6.98 (m, 2H), 6.94 – 6.91 (m, 2H), 6.28 (s, 1H), 5.98 (s, 1H), 2.47 (t, *J* = 6.3 Hz, 2H), 2.34 (t, *J* = 6.3 Hz, 2H), 1.85 – 1.80 (m, 2H), 1.77 – 1.72 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 186.0, 163.3, 161.9, 161.2, 154.4, 143.3, 134.9, 129.5, 127.0, 124.4, 122.0, 114.3, 113.4, 102.9, 90.6, 55.5, 55.4, 29.9, 24.1, 22.2, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{25}O_4^+$, 389.1747； found 389.1733.

IR (neat) ν (cm^{-1}):2987, 2900, 1642, 1596, 1575, 1502, 1409, 1256.

(Z)-1-(3,4-dimethoxyphenyl)-2-(3-(3,4-dimethoxyphenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4e)



197 mg (88% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:4). R_f = 0.20.

m.p. = 165.1-166.0 ℃

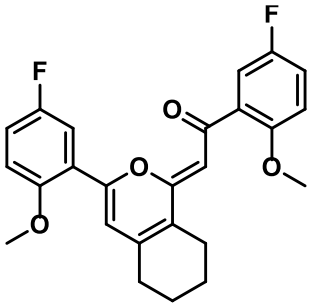
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.88 (d, *J* = 2.1 Hz, 1H), 7.74 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.53 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.29 (s, 1H), 6.00 (s, 1H), 2.48 (t, *J* = 6.2 Hz, 2H), 2.35 (t, *J* = 6.3 Hz, 2H), 1.86 – 1.74 (m, 4H).;

^{13}C NMR ($CDCl_3$, 151 MHz): δ 185.8, 163.1, 154.2, 151.4, 150.8, 149.3, 148.9, 143.3, 135.3, 124.7, 122.1, 120.9, 118.5, 111.2, 110.6, 110.0, 108.5, 103.0, 90.6, 56.3, 56.1, 56.0, 29.9, 24.1, 22.2, 21.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{28}O_6Na^+$, 471.1778； found 471.1771.

IR (neat) ν (cm^{-1}):2987, 2894, 1644, 1592, 1575, 1275, 1259, 1063.

(Z)-1-(5-fluoro-2-methoxyphenyl)-2-(3-(5-fluoro-2-methoxyphenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4f)



161 mg (76% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.25.

m.p. = 151.2-152.7 ℃

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.42 (d, *J* = 10.0 Hz, 1H), 7.36 (dd, *J* = 8.8, 3.3 Hz, 1H), 7.05 – 6.99 (m, 3H), 6.87 (ddd, *J* = 11.2, 9.0, 4.2 Hz, 2H), 5.94 (s, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 2.50 (t, *J* = 6.1 Hz, 2H), 2.31 (t, *J* = 6.2 Hz, 2H), 1.82 – 1.74 (m, 4H).

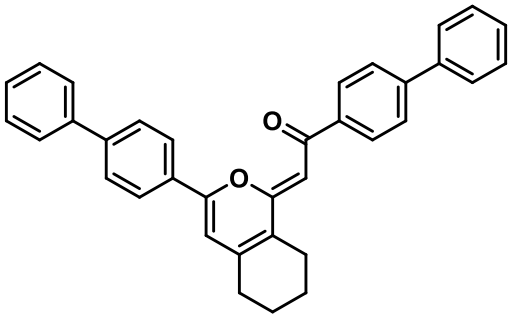
^{13}C NMR ($CDCl_3$, 151 MHz): δ 186.1, 162.7, 157.5 (d, J_{FC} = 238.6 Hz), 157.2 (d, J_{FC} = 240.1 Hz), 153.5, 153.2, 150.4, 144.0, 134.4, 123.6, 121.4 (d, J_{FC} = 8.2 Hz), 117.1 (d, J_{FC} = 21.1 Hz), 116.9 (d, J_{FC} = 21.1 Hz), 116.4 (d, J_{FC} = 23.9 Hz), 115.8 (d, J_{FC} = 26.4 Hz), 113.1 (d, J_{FC} = 7.6 Hz), 112.1 (d, J_{FC} = 8.1 Hz), 110.8, 95.6, 56.7, 56.1, 30.2, 24.1, 22.2, 21.7.

^{19}F NMR ($CDCl_3$, 565 MHz): δ -120.77, -123.65.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{22}F_2O_4Na^+$, 447.1378； found 447.1373.

IR (neat) ν (cm^{-1}): 3067, 2933, 1638, 1612, 1573, 1479, 1252, 1156, 1022.

(Z)-1-([1,1'-biphenyl]-4-yl)-2-(3-([1,1'-biphenyl]-4-yl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4g)



173 mg (72% yield) yellow solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.35.

m.p. = 169.4-170.3 ℃

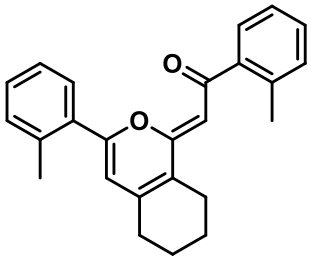
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.24 – 8.16 (m, 2H), 8.08 – 8.02 (m, 2H), 7.73 – 7.62 (m, 8H), 7.46 (t, *J* = 7.7 Hz, 4H), 7.38 (td, *J* = 7.2, 1.4 Hz, 2H), 6.49 (s, 1H), 6.10 (s, 1H), 2.53 (t, *J* = 6.4 Hz, 2H), 2.42 (t, *J* = 6.3 Hz, 2H), 1.87 (m, 2H), 1.82 – 1.76 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 186.8, 163.4, 154.1, 143.5, 143.4, 142.7, 140.9, 140.6, 140.4, 130.5, 129.0, 128.9, 128.1, 127.8, 127.6, 127.3, 127.1, 127.0, 125.7, 123.2, 104.5, 91.4, 29.9, 24.2, 22.2, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{35}H_{29}O_2^+$, 481.2162； found 481.2160.

IR (neat) ν (cm^{-1}): 3060, 2926, 2851, 1645, 1617, 1601, 1567, 1482, 1212.

(Z)-1-(o-tolyl)-2-(3-(o-tolyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4h)



119 mg (67% yield) yellow solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.35.

m.p. = 163.0-163.6 ℃

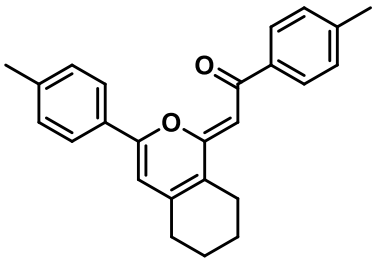
^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.51 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 6.8 Hz, 1H), 7.28 – 7.12 (m, 5H), 6.07 (s, 1H), 5.62 (s, 1H), 2.50 – 2.47 (m, 5H), 2.39 (s, 3H), 2.28 (t, *J* = 6.2 Hz, 2H), 1.78 (m, 4H).

^{13}C NMR (CD_2Cl_2, 151 MHz): δ 191.44, 163.09, 156.08, 144.29, 143.53, 137.48, 135.62, 132.70, 131.45, 131.03, 130.02, 129.23, 129.02, 127.18, 126.27, 125.67, 123.02, 109.59, 95.60, 30.13, 24.46, 22.50, 21.87, 21.21, 20.11.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{24}O_2Na^+$, 379.1668； found 379.1662.

IR (neat) ν (cm^{-1}): 3046, 2927, 1637, 1614, 1562, 1475, 1459, 1235, 1213, 1039, 986.

(Z)-1-(p-tolyl)-2-(3-(p-tolyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4i)



123 mg (69% yield) yellow solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.3.

m.p. = 188.6-190.4 ℃

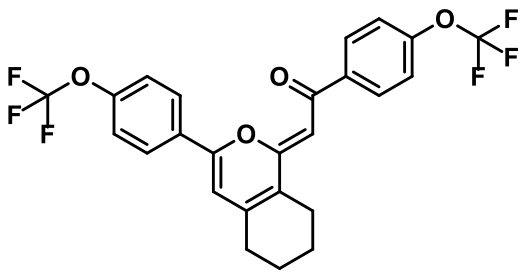
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.36 (s, 1H), 6.00 (s, 1H), 2.48 (t, *J* = 6.2 Hz, 2H), 2.39 (d, *J* = 4.6 Hz, 6H), 2.35 (t, *J* = 6.4 Hz, 2H), 1.83 (m, 2H), 1.76 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 187.0, 163.4, 154.6, 143.3, 141.1, 140.4, 139.5, 129.7, 129.0, 128.9, 127.7, 125.3, 122.7, 103.7, 91.2, 29.9, 24.1, 22.2, 21.6, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{25}O_2^+$, 357.1849； found 357.1842.

IR (neat) ν (cm^{-1}): 3053, 2933, 2867, 1645, 1621, 1605, 1569, 1495, 1169.

(Z)-1-(4-(trifluoromethoxy)phenyl)-2-(3-(4-(trifluoromethoxy)phenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4j)



206 mg (83% yield) yellow solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.30.

m.p. = 129.1-129.8 ℃

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.22 – 8.17 (m, 2H), 8.00 – 7.96 (m, 2H), 7.29 (dd, *J* = 39.5, 8.4 Hz, 4H), 6.42 (s, 1H), 5.99 (s, 1H), 2.51 (t, *J* = 6.3 Hz, 2H), 2.36 (t, *J* = 6.3 Hz, 2H), 1.87 – 1.76 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 185.5, 163.7, 153.1, 151.2, 150.6, 143.8, 140.3, 130.2, 129.4, 127.0, 123.7, 121.3, 120.6 (q, J_{FC} = 258.2 Hz), 120.4, 105.1, 91.1, 30.0, 24.1, 22.1, 21.5.

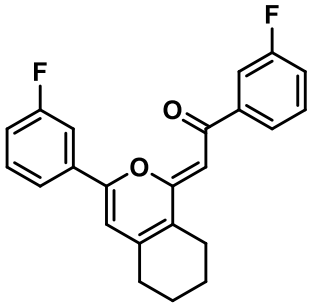
(the two -OCF_3 are very similar. $\Delta\delta < \pm 0.02$ppm)

^{19}F NMR ($CDCl_3$, 565 MHz): δ -57.54, -57.62.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{18}F_6O_4Na^+$, 519.1001； found 519.0997.

IR (neat) ν (cm^{-1}): 3046, 2940, 1651, 1623, 1514, 1490, 1252, 1202, 1153, 986.

(Z)-1-(3-fluorophenyl)-2-(3-(3-fluorophenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one 4k)



147 mg (81% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.30.

m.p. = 185.6-186.5 ℃

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.02 – 7.96 (m, 1H), 7.80 (dt, *J* = 10.0, 2.1 Hz, 1H), 7.71 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.64 (dt, *J* = 9.9, 2.0 Hz, 1H), 7.46 (td, *J* = 8.0, 5.8 Hz, 1H), 7.39 (td, *J* = 7.9, 5.5 Hz, 1H), 7.13 (m, 2H), 6.42 (s, 1H), 5.98 (s, 1H), 2.51 (t, *J* = 6.0 Hz, 2H), 2.36 (t, *J* = 6.3 Hz, 2H), 1.88 – 1.75 (m, 4H).

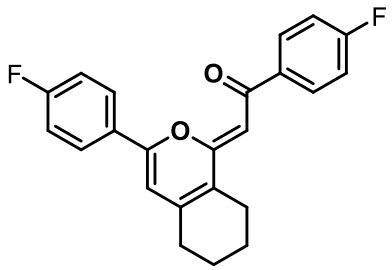
^{13}C NMR ($CDCl_3$, 151 MHz): δ 185.5, 163.6, 163.2 (d, J_{FC} = 246.1 Hz), 163.0 (d, J_{FC} = 246.1 Hz), 153.1, 144.2 (d, J_{FC} = 6.0 Hz), 143.7, 133.7 (d, J_{FC} = 7.9 Hz), 130.7 (d, J_{FC} = 8.2 Hz), 129.9 (d, J_{FC} = 7.7 Hz), 124.0, 123.2 (d, J_{FC} = 2.8 Hz), 121.1 (d, J_{FC} = 2.8 Hz), 117.8 (d, J_{FC} = 21.3 Hz), 117.2 (d, J_{FC} = 21.4 Hz), 114.5 (d, J_{FC} = 22.0 Hz), 112.1 (d, J_{FC} = 24.0 Hz), 105.4, 91.2, 29.9, 24.1, 22.1, 21.5.

^{19}F NMR ($CDCl_3$, 565 MHz): δ -111.69, -113.03.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{18}F_2O_2Na^+$, 387.1167； found 387.1158.

IR (neat) ν (cm^{-1}): 3060, 2933, 1645, 1624, 1566, 1505, 1470, 1263, 1004.

(Z)-1-(4-fluorophenyl)-2-(3-(4-fluorophenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4l)



151 mg (83% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.35.

m.p. = 196.3-197.9 ℃

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.19 – 8.13 (m, 2H), 7.98 – 7.93 (m, 2H), 7.17 (t, *J* = 8.6 Hz, 2H), 7.10 (t, *J* = 8.6 Hz, 2H), 6.37 (s, 1H), 5.98 (s, 1H), 2.50 (t, *J* = 6.2 Hz, 2H), 2.36 (t, *J* = 6.3 Hz, 2H), 1.87 – 1.75 (m, 4H).

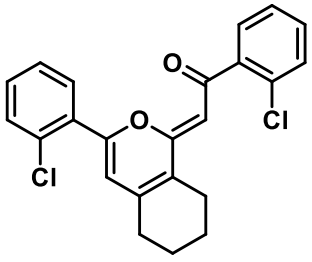
^{13}C NMR ($CDCl_3$, 151 MHz): δ 185.7, 164.6 (d, J_{FC} = 250.7 Hz), 164.1 (d, J_{FC} = 252.2 Hz), 163.6, 153.6, 143.8, 138.2, 129.9 (d, J_{FC} = 9.0 Hz), 127.8 (d, J_{FC} = 3.1 Hz), 127.5 (d, J_{FC} = 8.4 Hz), 123.1, 116.2 (d, J_{FC} = 22.0 Hz), 115.3 (d, J_{FC} = 21.5 Hz), 104.3, 90.9, 30.0, 24.1, 22.1, 21.6.

^{19}F NMR ($CDCl_3$, 565 MHz): δ -109.51, -109.79.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{18}F_2O_2Na^+$, 387.1167； found 387.1158.

IR (neat) ν (cm^{-1}): 3033, 2927, 1647, 1620, 1587, 1568, 1485, 1210, 1145.

(Z)-1-(2-chlorophenyl)-2-(3-(2-chlorophenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4m)



145 mg (73% yield) yellow solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.30.

m.p. = 149.2-150.5 ℃

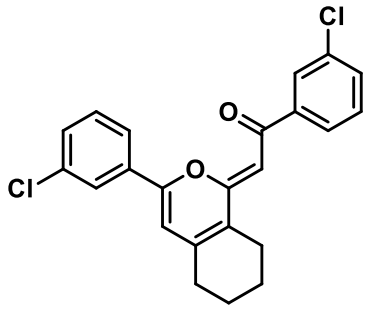
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.45 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.40 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.32 – 7.26 (m, 2H), 7.24 – 7.16 (m, 2H), 6.70 (s, 1H), 5.70 (s, 1H), 2.50 (t, *J* = 6.0 Hz, 2H), 2.31 (t, *J* = 6.3 Hz, 2H), 1.85 – 1.74 (m, 4H).;

^{13}C NMR ($CDCl_3$, 151 MHz): δ 188.7, 163.3, 151.5, 143.4, 143.2, 131.5, 130.7, 130.6, 130.5, 130.4, 129.9, 129.8, 128.8, 127.6, 126.7, 123.8, 110.8, 96.2, 30.1, 24.1, 22.1, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{18}Cl_2O_2Na^+$, 419.0576； found 419.0570.

IR (neat) ν (cm^{-1}): 3060, 2933, 1639, 1616, 1564, 1486, 1460, 1210, 985.

(Z)-1-(3-chlorophenyl)-2-(3-(3-chlorophenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4n)



151 mg (76% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.30.

m.p. = 185.1-186.0 ℃

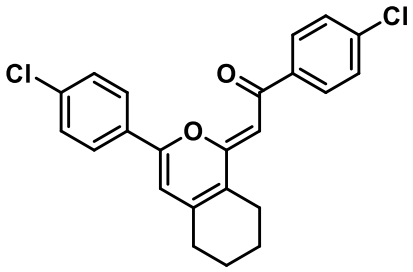
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.20 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.96 (t, *J* = 1.9 Hz, 1H), 7.91 (t, *J* = 1.9 Hz, 1H), 7.81 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.40 – 7.34 (m, 2H), 6.43 (s, 1H), 5.97 (s, 1H), 2.51 (t, *J* = 5.9 Hz, 2H), 2.37 (t, *J* = 6.1 Hz, 2H), 1.85 (m, 2H), 1.80 – 1.75 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 185.5, 163.5, 152.8, 143.6, 143.6, 134.8, 134.5, 133.3, 130.8, 130.6, 130.2, 129.6, 127.7, 125.7, 124.9, 124.1, 123.7, 105.4, 91.2, 29.9, 24.1, 22.0, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{18}Cl_2O_2Na^+$, 419.0576； found 419.0569.

IR (neat) ν (cm^{-1}): 3053, 2933, 1643, 1619, 1566, 1502, 1468, 1252, 998.

(Z)-1-(4-chlorophenyl)-2-(3-(4-chlorophenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4o)



157 mg (79% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.30.

m.p. = 194.6-196.1 ℃

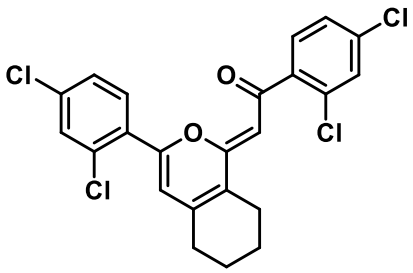
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.10 – 8.07 (m, 2H), 7.89 – 7.86 (m, 2H), 7.46 – 7.43 (m, 2H), 7.41 – 7.38 (m, 2H), 6.41 (s, 1H), 5.98 (s, 1H), 2.51 (t, *J* = 6.1 Hz, 2H), 2.36 (t, *J* = 6.2 Hz, 2H), 1.88 – 1.82 (m, 2H), 1.80 – 1.75 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 185.8, 163.6, 153.3, 143.7, 140.3, 137.1, 136.3, 130.0, 129.3, 129.0, 128.6, 126.6, 123.6, 104.8, 91.1, 29.9, 24.1, 22.1, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}Cl_2O_2^+$, 397.0756； found 397.0753.

IR (neat) ν (cm^{-1}): 3062, 2934, 2852, 1646, 1619, 1585, 1565, 1505, 1478, 1077.

(Z)-1-(2,4-dichlorophenyl)-2-(3-(2,4-dichlorophenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4p)



174 mg (75% yield) yellow sticky liquid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.30.

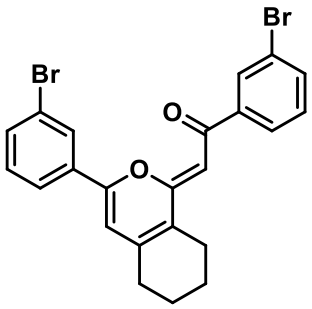
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.92 (d, J = 8.5 Hz, 1H), 7.43 (d, J = 2.1 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.26 (d, J = 2.0 Hz, 1H), 7.20 (dd, J = 8.2, 2.0 Hz, 1H), 6.65 (s, 1H), 5.66 (s, 1H), 2.49 (t, J = 6.2 Hz, 2H), 2.30 (t, J = 6.3 Hz, 2H), 1.84 – 1.74 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 187.6, 163.3, 150.7, 143.5, 141.6, 136.2, 135.1, 132.2, 131.4, 131.2, 130.6, 129.8, 129.6, 128.8, 127.9, 127.1, 124.1, 111.0, 96.3, 30.1, 24.0, 22.0, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{16}Cl_4O_2^+$, 464.9973； found 464.9977.

IR (neat) ν (cm^{-1}): 3053, 2927, 1644, 1621, 1581, 1494, 1265, 1099, 1036.

(Z)-1-(3-bromophenyl)-2-(3-(3-bromophenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4q)



175 mg (72% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.30.

m.p. = 168.5-169.1 ℃

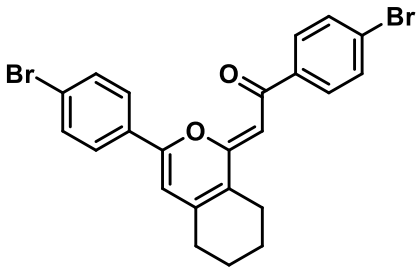
^{1}H NMR ($CDCl_3$, 600 MHz): 8.28 (dt, *J* = 7.9, 1.3 Hz, 1H), 8.08 (dt, *J* = 15.5, 1.8 Hz, 2H), 7.86 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.56 (m, 2H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 6.43 (s, 1H), 5.96 (s, 1H), 2.51 (t, *J* = 6.0 Hz, 2H), 2.37 (t, *J* = 6.2 Hz, 2H), 1.88 – 1.75 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 185.4, 163.5, 152.7, 143.8, 143.6, 133.8, 133.5, 133.2, 130.9, 130.6, 130.0, 127.7, 126.2, 124.3, 124.1, 122.9, 122.7, 105.4, 91.2, 29.9, 24.2, 22.1, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{18}Br_2O_2Na^+$, 506.9565； found 506.9565.

IR (neat) ν (cm^{-1}): 3060, 2940, 1640, 1613, 1557, 1488, 1467, 1455, 992.

(Z)-1-(4-bromophenyl)-2-(3-(4-bromophenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4r)



179 mg (74% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.35.

m.p. = 167.1-168.8 ℃

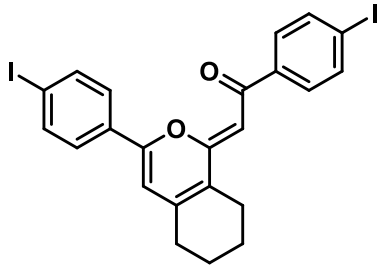
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.03 – 7.99 (m, 2H), 7.82 – 7.78 (m, 2H), 7.62 – 7.58 (m, 2H), 7.57 – 7.54 (m, 2H), 6.43 (s, 1H), 5.97 (s, 1H), 2.50 (t, *J* = 6.0 Hz, 2H), 2.35 (t, *J* = 6.0 Hz, 2H), 1.87 – 1.74 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 185.9, 163.6, 153.4, 143.7, 140.7, 132.2, 131.5, 130.4, 129.2, 126.8, 125.6, 124.7, 123.7, 104.9, 91.0, 29.9, 24.1, 22.1, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{19}O_2Br_2^+$, 484.9746； found 484.9744.

IR (neat) ν (cm^{-1}): 3060, 2927, 2860, 1643, 1618, 1565, 1505, 1476, 1209.

(Z)-1-(4-iodophenyl)-2-(3-(4-iodophenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4s)



201 mg (69 % yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.30.

m.p. = 194.2-195.5 ℃

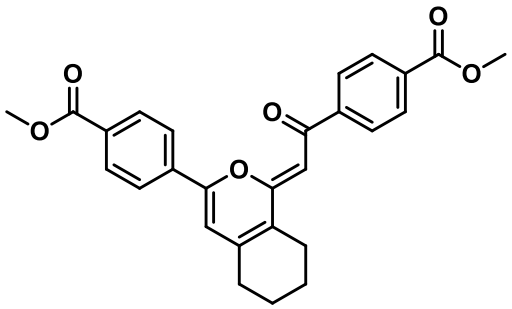
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.87 – 7.75 (m, 6H), 7.66 (d, *J* = 8.1 Hz, 2H), 6.43 (s, 1H), 5.96 (s, 1H), 2.50 (t, *J* = 6.1 Hz, 2H), 2.35 (t, *J* = 6.2 Hz, 2H), 1.81 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 186.2, 163.5, 153.5, 143.6, 141.3, 138.2, 137.5, 131.0, 129.2, 126.8, 123.8, 104.9, 98.0, 96.7, 91.1, 29.9, 24.2, 22.1, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{19}O_2I_2^+$, 580.9468； found 580.9458.

IR (neat) ν (cm^{-1}): 3053, 2933, 1642, 1609, 1568, 1502, 1474, 1210, 992.

methyl (Z)-4-(1-(2-(4-(methoxycarbonyl)phenyl)-2-oxoethylidene)-5,6,7,8-tetrahydro-1H-isochromen-3-yl)benzoate (4t)



144 mg (65% yield) red sticky liquid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:4). R_f = 0.25.

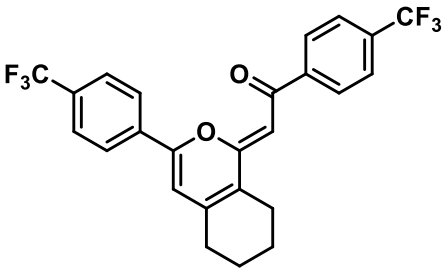
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.25 – 8.20 (m, 2H), 8.16 – 8.12 (m, 2H), 8.12 – 8.08 (m, 2H), 8.02 – 7.96 (m, 2H), 6.56 (s, 1H), 6.06 (s, 1H), 3.94 (d, *J* = 1.9 Hz, 6H), 2.54 (t, *J* = 6.1 Hz, 2H), 2.40 (t, *J* = 6.2 Hz, 2H), 1.90 – 1.83 (m, 2H), 1.83 – 1.76 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 186.3, 166.8, 166.7, 163.6, 153.2, 145.7, 143.7, 135.4, 132.0, 131.4, 130.3, 129.7, 127.5, 125.1, 124.6, 106.4, 91.7, 52.5, 52.41, 29.9, 24.2, 22.1, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{24}O_6Na^+$, 467.1465； found 467.1460.

IR (neat) ν (cm^{-1}): 3060, 2947, 1715, 1644, 1608, 1563, 1488, 1433, 1271,1102.

(Z)-1-(4-(trifluoromethyl)phenyl)-2-(3-(4-(trifluoromethyl)phenyl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4u)



183 mg (79% yield) yellow solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:15). R_f = 0.35.

m.p. = 169.4-170.7 ℃

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.26 (d, *J* = 8.2 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.71 (dd, *J* = 26.7, 8.1 Hz, 4H), 6.53 (s, 1H), 6.04 (s, 1H), 2.54 (t, *J* = 6.0 Hz, 2H), 2.39 (t, *J* = 6.3 Hz, 2H), 1.91 – 1.76 (m, 4H).

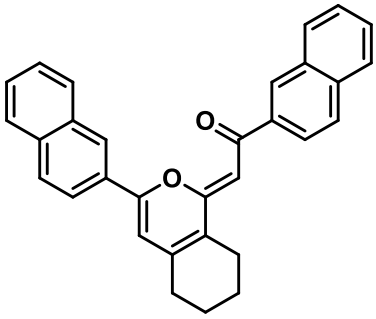
^{13}C NMR ($CDCl_3$, 151 MHz): δ 185.9, 163.7, 152.8, 144.9, 143.8, 134.8, 132.5 (q, J_{FC} = 31.7 Hz), 131.8 (q, J_{FC} = 31.7 Hz), 127.9, 126.0 (q, J_{FC} = 3.9 Hz), 125.5, 125.5 (q, J_{FC} = 3.7 Hz), 124.6, 124.1 (q, J_{FC} = 273.3 Hz), 124.0 (q, J_{FC} = 271.8 Hz), 106.2, 91.6, 30.0, 24.2, 22.0, 21.5.

^{19}F NMR ($CDCl_3$, 565 MHz): δ -62.60, -62.73.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{18}F_6O_2Na^+$, 487.1103； found 487.1094.

IR (neat) ν (cm^{-1}): 3013, 2940, 1644, 1621, 1566, 1486, 1317, 1114, 1066.

(Z)-1-(naphthalen-2-yl)-2-(3-(naphthalen-2-yl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4v)



175 mg (82% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.35.

m.p. = 182.6-183.7 ℃

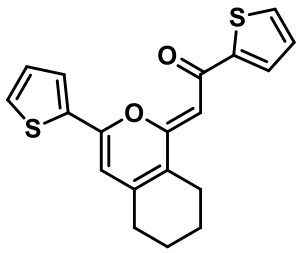
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.73 (s, 1H), 8.48 (s, 1H), 8.11 (ddd, *J* = 12.2, 8.6, 1.8 Hz, 2H), 7.99 (td, *J* = 7.4, 3.5 Hz, 2H), 7.92 – 7.82 (m, 4H), 7.57 – 7.48 (m, 4H), 6.52 (s, 1H), 6.18 (s, 1H), 2.50 (t, *J* = 6.2 Hz, 2H), 2.40 (t, *J* = 6.4 Hz, 2H), 1.87 – 1.75 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 187.2, 163.4, 154.3, 143.4, 139.5, 134.8, 134.2, 133.4, 133.0, 129.5, 129.4, 128.8, 128.6, 128.1, 127.8, 127.8, 127.7, 127.3, 127.2, 126.6, 126.4, 125.6, 124.9, 123.4, 122.2, 105.1, 91.8, 29.9, 24.2, 22.2, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{21}O_3Na^+$, 451.1668； found 451.1664.

IR (neat) ν (cm^{-1}): 3053, 2933, 1648, 1614, 1572, 1512, 1273, 1123, 991.

(Z)-1-(thiophen-2-yl)-2-(3-(thiophen-2-yl)-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4w)



155 mg (91% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:10). R_f = 0.30.

m.p. = 194.4-195.6 ℃

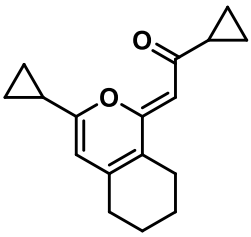
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.02 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.64 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.48 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.36 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.10 (ddd, *J* = 19.3, 5.0, 3.7 Hz, 2H), 6.17 (s, 1H), 5.95 (s, 1H), 2.46 (t, *J* = 6.3 Hz, 2H), 2.34 (t, *J* = 6.3 Hz, 2H), 1.86 – 1.72 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 179.0, 162.8, 150.4, 149.2, 143.4, 135.2, 130.5, 128.5, 128.2, 128.1, 127.7, 127.6, 122.5, 103.8, 90.7, 29.7, 24.1, 22.2, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{16}O_2S_2Na^+$, 363.0484； found 363.0482.

IR (neat) ν (cm^{-1}):3100, 2933, 1642, 1600, 1565, 1486, 1258, 1208.

(Z)-1-cyclopropyl-2-(3-cyclopropyl-5,6,7,8-tetrahydro-1H-isochromen-1-ylidene)ethan-1-one (4x)



68 mg (53% yield) yellow sticky liquid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:20). R_f = 0.35.

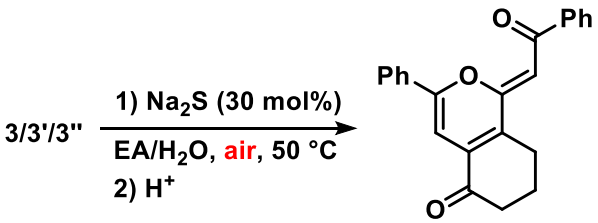
^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.63 (s, 1H), 5.32 (s, 1H), 2.31 (t, *J* = 6.3 Hz, 2H), 2.15 (t, *J* = 6.4 Hz, 2H), 1.99 (dt, *J* = 8.0, 3.5 Hz, 1H), 1.77 – 1.73 (m, 2H), 1.67 (m, 3H), 1.22 (dt, *J* = 6.6, 3.4 Hz, 2H), 1.04 – 1.01 (m, 2H), 0.87 (td, *J* = 7.1, 4.3 Hz, 2H), 0.74 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.6, 161.7, 159.6, 142.5, 119.9, 104.3, 94.9, 29.5, 23.9, 22.3, 21.6, 21.4, 13.8, 9.7, 7.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{20}O_2Na^+$, 279.1355； found 279.1351.

IR (neat) ν (cm^{-1}): 3006, 2920, 1690, 1654, 1506, 1385, 1277, 1063.

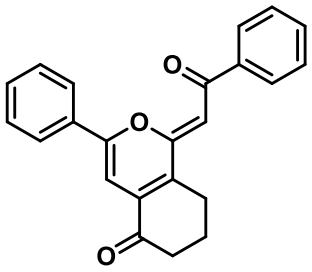
2.4 Synthesis and characterization of product 6



6

A 25 mL round-bottomed flask was charged with 0.5 mmol of the freshly prepared raw material **3**, followed by the addition of 5 mL of ethyl acetate (EA) to dissolve the material. To this solution, an aqueous sodium sulfide solution (11.7 mg Na_2S in water, corresponding to 0.15 mmol) was added. The reaction mixture was stirred under an atmospheric air environment at 50 ℃, and its progress was monitored by thin-layer chromatography (TLC). Upon completion of the reaction, the mixture was cooled to room temperature and neutralized by the addition of 2 mL of a 1 mol/L hydrochloric acid. The product was then extracted into dichloromethane (DCM) in three portions (3 × 3 mL). The combined organic phases were dried over magnesium sulfate ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using a gradient elution with a solvent system of n-hexane and ethyl acetate , starting from a ratio of 10:1 to 6:1, to afford the desired products **6**.

(Z)-1-(2-oxo-2-phenylethylidene)-3-phenyl-7,8-dihydro-1H-isochromen-5(6H)-one (6a)



133 mg (78% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

m.p. = 206.9-208.3 ℃

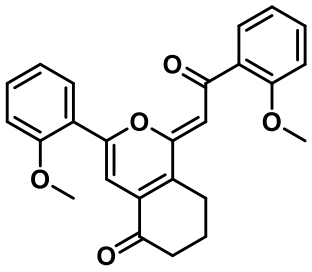
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.14 – 8.08 (m, 2H), 7.99 – 7.94 (m, 2H), 7.55 – 7.40 (m, 6H), 7.07 (s, 1H), 6.36 (s, 1H), 2.70 – 2.62 (m, 4H), 2.22 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.4, 187.7, 160.9, 155.6, 140.9, 136.0, 133.9, 131.7, 131.5, 130.5, 129.0, 128.6, 127.7, 125.4, 97.4, 95.7, 37.4, 24.2, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{19}O_3^+$, 343.1328； found 343.1320.

IR (neat) ν (cm^{-1}): 3053, 2933, 1682, 1620, 1482, 1448, 1200, 1161, 1020.

(Z)-3-(2-methoxyphenyl)-1-(2-(2-methoxyphenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6b)



108 mg (54% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:3). R_f = 0.25.

m.p. = 129.0-129.3 ℃

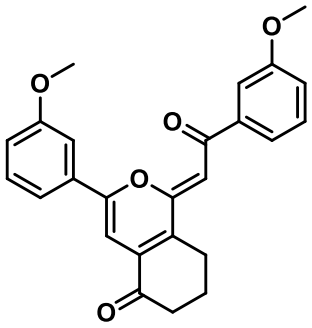
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.50 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.66 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.55 (s, 1H), 7.42 – 7.34 (m, 2H), 7.15 – 7.10 (m, 1H), 7.03 (td, *J* = 7.4, 1.0 Hz, 1H), 6.95 (m, 2H), 6.31 (s, 1H), 3.96 (s, 3H), 3.88 (s, 3H), 2.61 (dt, *J* = 12.5, 6.4 Hz, 4H), 2.20 – 2.14 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.6, 188.4, 159.8, 157.6, 157.3, 152.5, 135.8, 134.3, 132.3, 131.8, 131.1, 130.1, 129.1, 121.4, 120.9, 120.3, 111.7, 111.0, 101.8, 101.2, 55.9, 55.6, 37.6, 24.2, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{22}O_5Na^+$, 425.1359； found 425.1350.

IR (neat) ν (cm^{-1}):3153, 3053, 2933, 1680, 1621, 1593, 1564, 1508, 1252, 1021.

(Z)-3-(3-methoxyphenyl)-1-(2-(3-methoxyphenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6c)



149 mg (74% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:3). R_f = 0.20.

m.p. = 149.3-149.6 ℃

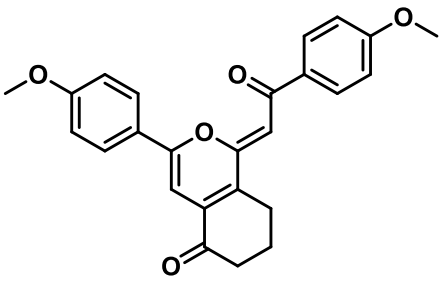
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.81 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.70 (ddd, *J* = 7.8, 1.6, 0.9 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.37 (dt, *J* = 13.8, 8.0 Hz, 2H), 7.08 – 7.03 (m, 1H), 7.05 (s, 2H), 6.98 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 6.34 (s, 1H), 3.96 (s, 3H), 3.88 (s, 3H), 2.68 – 2.62 (m, 4H), 2.21 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.4, 187.0, 160.8, 160.1, 159.9, 155.3, 142.4, 136.1, 133.9, 132.9, 130.0, 129.5, 120.1, 117.9, 117.8, 117.2, 112.6, 110.2, 97.3, 95.9, 55.7, 55.6, 37.4, 24.2, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{22}O_5Na^+$, 425.1359； found 425.1352.

IR (neat) ν (cm^{-1}): 3046, 2933, 1690, 1624, 1576, 1513, 1257, 1169, 1033.

(Z)-3-(4-methoxyphenyl)-1-(2-(4-methoxyphenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6d)



158 mg (79% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:4). R_f = 0.20.

m.p. = 202.7-203.2 ℃

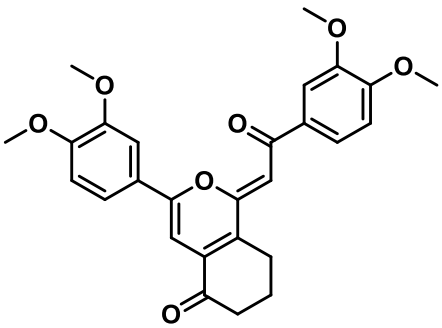
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.10 – 8.05 (m, 2H), 7.98 – 7.92 (m, 2H), 7.02 – 6.96 (m, 2H), 6.97 – 6.92 (m, 2H), 6.91 (s, 1H), 6.30 (s, 1H), 3.86 (d, *J* = 9.3 Hz, 6H), 2.67 – 2.60 (m, 4H), 2.23 – 2.16 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.7, 186.4, 162.6, 161.5, 160.7, 155.6, 134.8, 134.0, 133.8, 129.8, 127.2, 124.3, 114.4, 113.7, 96.8, 94.0, 55.6, 55.5, 37.5, 24.2, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{23}O_5^+$, 403.1540； found 403.1527.

IR (neat) ν (cm^{-1}): 3060, 2933, 2833, 1690, 1626, 1599, 1570, 1501, 1255, 1017.

(Z)-3-(3,4-dimethoxyphenyl)-1-(2-(3,4-dimethoxyphenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6e)



185 mg (80% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:3). R_f = 0.20.

m.p. = 173.5-174.0 ℃

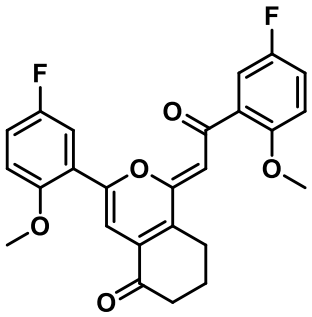
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.79 – 7.76 (m, 2H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.55 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.92 (s, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.33 (s, 1H), 4.07 (s, 3H), 3.97 (s, 3H), 3.94 (d, *J* = 7.2 Hz, 6H), 2.65 (dt, *J* = 10.8, 6.7 Hz, 4H), 2.20 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.7, 185.9, 160.5, 155.5, 152.3, 151.1, 149.3, 149.2, 135.0, 134.1, 133.9, 124.6, 121.4, 118.9, 111.2, 110.6, 110.1, 108.4, 96.6, 94.2, 56.4, 56.2, 56.1, 37.5, 24.1, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{26}O_7Na^+$, 485.1570； found 485.1565.

IR (neat) ν (cm^{-1}): 3080, 2940, 1684, 1625, 1593, 1580, 1563, 1504, 1256, 1162, 1019.

(Z)-3-(5-fluoro-2-methoxyphenyl)-1-(2-(5-fluoro-2-methoxyphenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6f)



151 mg (69% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.20.

m.p. = 193.8-194.4 ℃

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.28 (dd, *J* = 10.0, 3.2 Hz, 1H), 7.58 (s, 1H), 7.40 (dd, *J* = 8.7, 3.2 Hz, 1H), 7.06 (m, 2H), 6.88 (td, *J* = 8.9, 4.2 Hz, 2H), 6.33 (s, 1H), 3.93 (s, 3H), 3.86 (s, 3H), 2.64 – 2.58 (m, 4H), 2.20 – 2.15 (m, 2H).

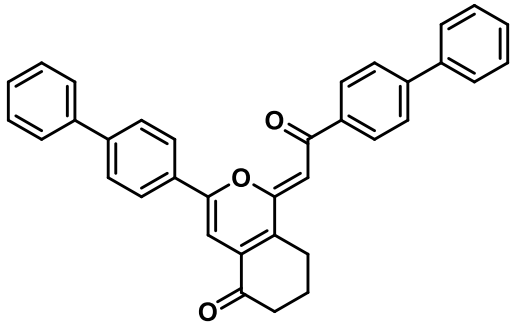
^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.4, 186.6, 159.9, 157.2 (d, J_{FC} = 238.6 Hz), 157.2 (d, J_{FC} = 240.1 Hz), 153.9, 153.5, 151.3, 136.5, 134.1, 133.0 (d, J_{FC} = 5.9 Hz), 121.3 (d, J_{FC} = 8.2 Hz), 118.0 (d, J_{FC} = 23.2 Hz), 117.3 (d, J_{FC} = 23.3 Hz), 116.7 (d, J_{FC} = 24.1 Hz), 115.4 (d, J_{FC} = 25.1 Hz), 113.1 (d, J_{FC} = 7.6 Hz), 112.1 (d, J_{FC} = 8.0 Hz), 102.0 (d, J_{FC} = 5.1 Hz), 101.5, 56.6, 56.2, 37.5, 24.1, 21.5.

^{19}F NMR ($CDCl_3$, 565 MHz): δ -121.32, -123.12.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{20}F_2O_5Na^+$, 461.1171； found 461.1165.

IR (neat) ν (cm^{-1}):3140, 3046, 2947, 1686, 1624, 1563, 1486, 1411, 1261, 1162.

(Z)-3-([1,1'-biphenyl]-4-yl)-1-(2-([1,1'-biphenyl]-4-yl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6g)



146 mg (59% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.3.

m.p. = 131.8-132.3 ℃

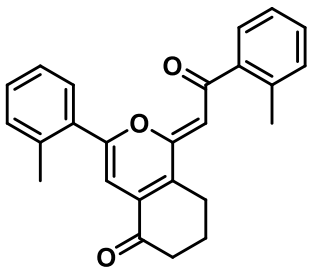
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.19 – 8.14 (m, 2H), 8.08 – 8.03 (m, 2H), 7.74 – 7.68 (m, 4H), 7.67 – 7.59 (m, 4H), 7.49 – 7.45 (m, 4H), 7.43 – 7.34 (m, 2H), 7.12 (s, 1H), 6.41 (s, 1H), 2.70 (dt, *J* = 27.2, 6.8 Hz, 4H), 2.24 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 195.4, 187.2, 160.9, 155.3, 144.4, 143.1, 140.3, 139.6, 135.9, 133.9, 130.4, 129.1, 129.0, 128.3, 128.1, 127.9, 127.6, 127.3, 127.2, 127.2, 125.9, 97.4, 95.8, 37.4, 29.8, 24.2, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{35}H_{27}O_3^+$, 495.1954； found 495.1952.

IR (neat) ν (cm^{-1}): 3045, 2935, 1680, 1628, 1604, 1559, 1509, 1485, 1186.

(Z)-1-(2-oxo-2-(o-tolyl)ethylidene)-3-(o-tolyl)-7,8-dihydro-1H-isochromen-5(6H)-one (6h)



89 mg (48% yield) orange sticky liquid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

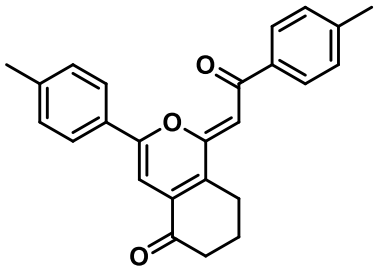
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.49 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.43 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.29 (td, *J* = 7.5, 1.4 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.18 – 7.14 (m, 2H), 6.68 (s, 1H), 5.96 (s, 1H), 2.65 – 2.57 (m, 4H), 2.47 (s, 3H), 2.44 (s, 3H), 2.19 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.3, 192.5, 160.2, 157.0, 142.6, 137.0, 135.8, 133.6, 132.0, 131.3, 131.1, 129.9, 129.6, 129.0, 127.2, 126.1, 125.6, 101.7, 100.3, 37.4, 29.8, 24.2, 21.5, 21.4, 20.2.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{22}O_3Na^+$, 393.1461； found 393.1454.

IR (neat) ν (cm^{-1}): 3000, 2927, 1682, 1636, 1567, 1524, 1278, 1256.

(Z)-1-(2-oxo-2-(p-tolyl)ethylidene)-3-(p-tolyl)-7,8-dihydro-1H-isochromen-5(6H)-one (6i)



94 mg (51% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

m.p. = 211.5-212.2 ℃

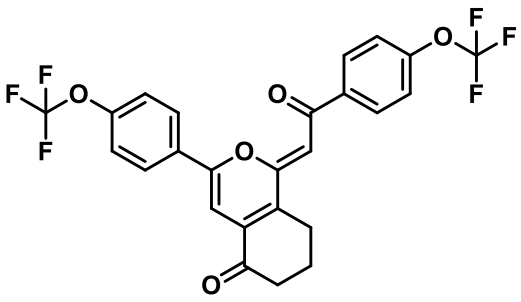
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.24 (m, 4H), 7.01 (s, 1H), 6.33 (s, 1H), 2.66 (dt, *J* = 14.0, 6.4 Hz, 4H), 2.41 (d, *J* = 13.3 Hz, 6H), 2.21 (dt, *J* = 6.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.6, 187.5, 160.8, 155.8, 142.3, 140.8, 138.4, 135.5, 133.9, 129.7, 129.3, 128.8, 127.8, 125.4, 97.2, 94.9, 37.4, 24.2, 21.7, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{23}O_3^+$, 371.1641； found 371.1633.

IR (neat) ν (cm^{-1}): 3004, 2925, 1689, 1629, 1608, 1523, 1508, 1275,1258.

(Z)-1-(2-oxo-2-(4-(trifluoromethoxy)phenyl)ethylidene)-3-(4-(trifluoromethoxy)phenyl)-7,8-dihydro-1H-isochromen-5(6H)-one (6j)



194 mg (76% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

m.p. = 138.1-138.9 ℃

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.17 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.99 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.31 (dd, *J* = 20.3, 8.3 Hz, 4H), 7.07 (s, 1H), 6.33 (s, 1H), 2.70 – 2.63 (m, 4H), 2.26 – 2.19 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.1, 185.9, 161.2, 154.3, 151.8, 150.8, 139.1, 136.2, 134.0, 130.0, 129.6, 127.2, 121.3, 120.6, 120.5 (q, J_{FC} = 258.2 Hz), 97.0, 96.4, 77.4, 77.2, 76.9, 37.4, 24.2, 21.5.

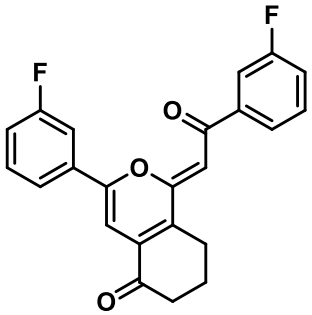
(the two -OCF_3 are very similar. $\Delta\delta < \pm 0.05$ ppm)

^{19}F NMR ($CDCl_3$, 565 MHz): δ -57.52, -57.60.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{16}F_6O_5Na^+$, 533.0794； found 533.0793.

IR (neat) ν (cm^{-1}): 3073, 2954, 1683, 1630, 1516, 1496, 1260, 1203, 1151, 1044.

(Z)-3-(3-fluorophenyl)-1-(2-(3-fluorophenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6k)



128 mg (68% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

m.p. = 212.0-212.7 ℃

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.93 (ddd, *J* = 7.9, 1.7, 0.9 Hz, 1H), 7.82 (ddd, *J* = 10.0, 2.6, 1.7 Hz, 1H), 7.73 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.65 (ddd, *J* = 9.6, 2.6, 1.6 Hz, 1H), 7.45 (dtd, *J* = 13.3, 8.0, 5.6 Hz, 2H), 7.22 (tdd, *J* = 8.3, 2.7, 0.9 Hz, 1H), 7.13 (tdd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 7.08 (s, 1H), 6.32 (s, 1H), 2.68 (dt, *J* = 13.8, 6.4 Hz, 4H), 2.23 (dt, *J* = 12.2, 6.3 Hz, 2H).

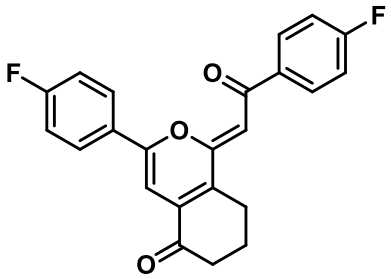
^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.1, 186.0, 163.2 (d, J_{FC} = 246.1 Hz), 163.1 (d, J_{FC} = 247.6 Hz), 161.1, 154.3, 143.0 (d, J_{FC} = 6.0 Hz), 136.5, 133.9, 133.6 (d, J_{FC} = 8.1 Hz), 130.7 (d, J_{FC} = 8.1 Hz), 130.2 (d, J_{FC} = 7.7 Hz), 123.4 (d, J_{FC} = 2.9 Hz), 121.2 (d, J_{FC} = 3.1 Hz), 118.8 (d, J_{FC} = 21.3 Hz), 117.6 (d, J_{FC} = 21.5 Hz), 114.7 (d, J_{FC} = 22.2 Hz), 112.5 (d, J_{FC} = 24.1 Hz), 97.1, 96.7, 37.4, 24.2, 21.5.

^{19}F NMR ($CDCl_3$, 565 MHz): δ -111.36, -112.23.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{16}F_2O_3Na^+$, 401.0959； found 401.0954.

IR (neat) ν (cm^{-1}): 3073, 2954, 1679, 1628, 1563, 1510, 1318, 1111.

(Z)-3-(4-fluorophenyl)-1-(2-(4-fluorophenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6l)



136 mg (72% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

m.p. = 234.7-235.2 ℃

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.16 – 8.10 (m, 2H), 8.00 – 7.93 (m, 2H), 7.20 – 7.10 (m, 4H), 7.00 (s, 1H), 6.31 (s, 1H), 2.65 (dt, *J* = 9.6, 6.8 Hz, 4H), 2.25 – 2.18 (m, 2H).

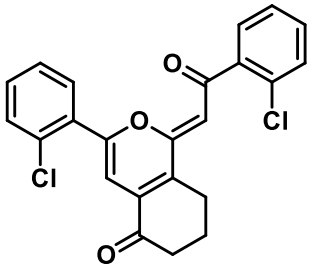
^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.3, 186.0, 165.1 (d, J_{FC} = 253.7 Hz), 164.2 (d, J_{FC} = 250.7 Hz), 161.0, 154.7, 137.1, 135.7, 134.0, 130.1 (d, J_{FC} = 9.0 Hz), 127.7, 127.6 (d, J_{FC} = 8.7 Hz), 116.2 (d, J_{FC} = 22.0 Hz), 115.6 (d, J_{FC} = 21.7 Hz), 96.8, 95.5, 37.4, 24.2, 21.5.

^{19}F NMR ($CDCl_3$, 565 MHz): δ -107.67, -109.16.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{16}F_2O_3Na^+$, 401.0959； found 401.0952.

IR (neat) ν (cm^{-1}): 3080, 2927, 1682, 1627, 1593, 1565, 1502, 1203, 1157, 837.

(Z)-3-(2-chlorophenyl)-1-(2-(2-chlorophenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6m)



144 mg (70% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

m.p. = 149.5-150.6 ℃

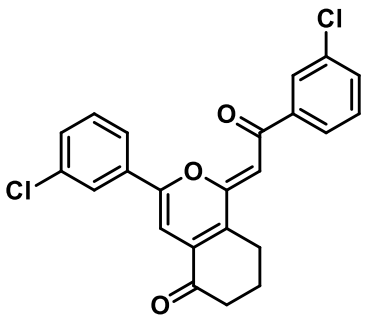
^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.75 (dt, *J* = 7.4, 2.3 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.38 – 7.31 (m, 2H), 7.26 (t, *J* = 7.9 Hz, 2H), 7.22 (dd, *J* = 8.7, 6.4 Hz, 1H), 7.15 (s, 1H), 6.01 (s, 1H), 2.61 (t, *J* = 6.5 Hz, 4H), 2.18 (dt, *J* = 5.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): *δ* 195.1, 189.2, 160.9, 152.9, 142.5, 137.2, 133.6, 132.2, 131.1, 131.0, 130.9, 130.7, 130.5, 130.2, 128.9, 127.5, 127.2, 102.3, 102.2, 37.5, 24.4, 21.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{16}Cl_2O_3Na^+$, 433.0368； found 433.0363.

IR (neat) ν (cm^{-1}): 3073, 2933, 1686, 1625, 1510, 1431, 1290, 1038.

(Z)-3-(3-chlorophenyl)-1-(2-(3-chlorophenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6n)



129 mg (63% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

m.p. = 217.0-217.3 ℃

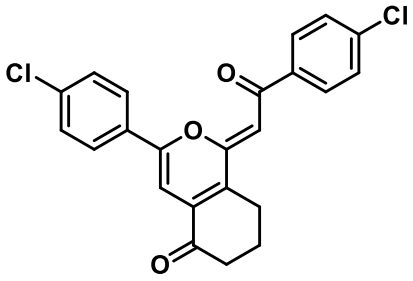
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.09 (dt, *J* = 7.8, 1.4 Hz, 1H), 8.01 (t, *J* = 1.9 Hz, 1H), 7.92 (t, *J* = 1.8 Hz, 1H), 7.83 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.49 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.40 (ddt, *J* = 7.9, 5.4, 3.1 Hz, 2H), 7.26 (s, 1H), 7.08 (s, 1H), 6.30 (s, 1H), 2.68 (dt, *J* = 13.9, 6.7 Hz, 4H), 2.27 – 2.20 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.1, 185.9, 161.0, 154.1, 142.4, 136.5, 135.1, 134.8, 133.9, 133.2, 131.8, 130.6, 130.5, 129.9, 127.9, 125.9, 125.3, 123.7, 97.1, 96.7, 37.3, 24.2, 21.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{16}Cl_2O_3Na^+$, 433.0368； found 433.0361.

IR (neat) ν (cm^{-1}): 3060, 2927, 1685, 1626, 1563, 1513, 1255, 1204, 1046.

(Z)-3-(4-chlorophenyl)-1-(2-(4-chlorophenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6o)



127 mg (62% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

m.p. = 210.9-211.2 ℃

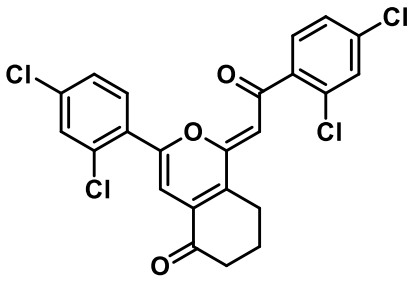
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.09 – 8.04 (m, 2H), 7.92 – 7.87 (m, 2H), 7.49 – 7.41 (m, 4H), 7.07 (s, 1H), 6.32 (s, 1H), 2.70 – 2.63 (m, 4H), 2.23 (dt, *J* = 12.3, 6.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.2, 186.2, 161.1, 154.6, 139.1, 138.1, 136.7, 136.1, 134.0, 129.9, 129.3, 129.2, 128.9, 126.7, 96.9, 96.1, 37.4, 24.2, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{17}Cl_2O_3^+$, 411.0549； found 411.0541.

IR (neat) ν (cm^{-1}): 3094, 2940, 1681, 1627, 1587, 1566, 1518, 1485, 1089, 1003.

(Z)-3-(2,4-dichlorophenyl)-1-(2-(2,4-dichlorophenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6p)



165 mg (69% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

m.p. = 192.8-193.3 ℃

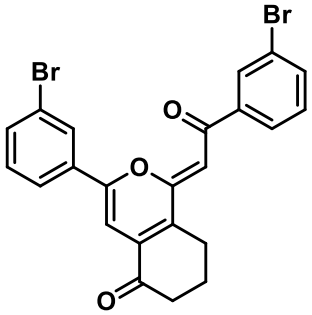
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.74 (d, *J* = 8.5 Hz, 1H), 7.46 (d, *J* = 2.1 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.26 (d, *J* = 2.0 Hz, 1H), 7.24 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.21 (s, 1H), 6.01 (s, 1H),2.67 – 2.59 (m, 4H), 2.21 (dt, *J* = 12.2, 6.3 Hz, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 194.7, 188.3, 160.7, 152.1, 140.5, 136. 8, 136.6, 136.0, 133.6, 132.9, 131.4, 130.9, 130.7, 129.9, 129.7, 128.9, 127.8, 127.4, 102.3, 102.1, 37.3, 24.1, 21.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{14}Cl_4O_3Na^+$, 500.9589； found 500.9582.

IR (neat) ν (cm^{-1}): 3060, 2920, 1681, 1621, 1581,1562, 1515, 1202, 1026.

(Z)-3-(3-bromophenyl)-1-(2-(3-bromophenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6q)



157 mg (63% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

m.p. = 103.7-105.0 ℃

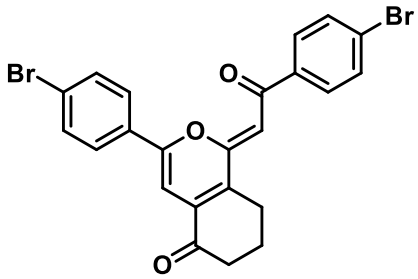
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.15 (dq, *J* = 4.2, 1.5 Hz, 2H), 8.08 (t, *J* = 1.8 Hz, 1H), 7.87 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.64 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 7.56 (ddd, *J* = 8.0, 1.9, 1.1 Hz, 1H), 7.36 (dt, *J* = 22.9, 8.0 Hz, 2H), 7.08 (s, 1H), 6.29 (s, 1H), 2.72 – 2.64 (m, 4H), 2.24 (dt, *J* = 6.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.1, 185.7, 161.0, 153.9, 142.6, 136.6, 134.7, 133.8, 133.5, 133.4, 130.8, 130.7, 130.2, 128.1, 126.3, 124.1, 123.1, 122.9, 97.0, 96.8, 37.3, 24.2, 21.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{16}O_3Br_2Na^+$, 520.9358； found 520.9354.

IR (neat) ν (cm^{-1}): 3060, 2933, 1681, 1627, 1560, 1516, 1253, 1202.

(Z)-3-(4-bromophenyl)-1-(2-(4-bromophenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6r)



170 mg (68% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.3.

m.p. = 214.9-215.7 ℃

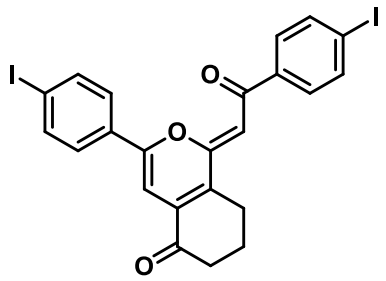
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.00 – 7.95 (m, 2H), 7.83 – 7.78 (m, 2H), 7.63 – 7.56 (m, 4H), 7.06 (s, 1H), 6.29 (s, 1H), 2.67 – 2.62 (m, 3H), 2.21 (dt, *J* = 12.2, 6.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.1, 186.2, 161.1, 154.6, 139.5, 136.2, 133.9, 132.3, 131.8, 130.3, 129.3, 126.9, 126.7, 125.1, 96.9, 96.2, 37.3, 24.2, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{17}Br_2O_3^+$, 498.9539； found 498.9542.

IR (neat) ν (cm^{-1}): 3084, 2939, 2864, 1681, 1627, 1581, 1565, 1488, 1005.

(Z)-3-(4-iodophenyl)-1-(2-(4-iodophenyl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6s)



160 mg (54% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

m.p. = 229.6-230.0 ℃

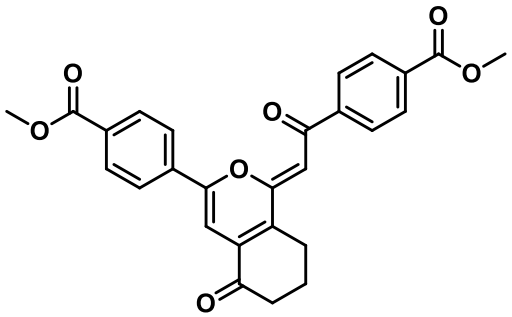
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.85 – 7.79 (m, 6H), 7.69 – 7.64 (m, 2H), 7.08 (s, 1H), 6.29 (s, 1H), 2.66 (td, *J* = 7.5, 6.7, 4.1 Hz, 4H), 2.22 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 195.2, 186.6, 161.1, 154.7, 140.1, 138.2, 137.8, 136.3, 133.9, 130.9, 129.3, 126.9, 99.2, 97.2, 96.9, 96.2, 37.3, 24.2, 21.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{16}O_3I_2^+$, 616.9081； found 616.9073.

IR (neat) ν (cm^{-1}): 3067, 2920, 1681, 1622, 1582, 1556, 1514, 1483, 1163, 999.

methyl (Z)-4-(1-(2-(4-(methoxycarbonyl)phenyl)-2-oxoethylidene)-5-oxo-5,6,7,8-tetrahydro-1H-isochromen-3-yl)benzoate (6t)



146 mg (64% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:1). R_f = 0.25.

m.p. = 228.8-229.2 ℃

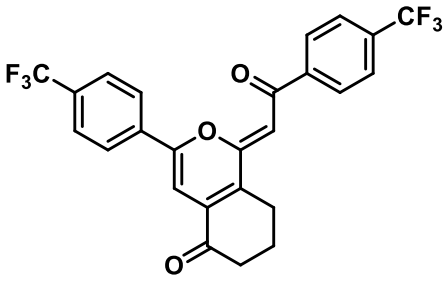
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.21 – 8.17 (m, 2H), 8.15 – 8.12 (m, 4H), 8.00 – 7.98 (m, 2H), 7.19 (s, 1H), 6.38 (s, 1H), 3.95 (d, *J* = 8.2 Hz, 6H), 2.69 (dt, *J* = 21.5, 6.8 Hz, 4H), 2.24 (dt, *J* = 6.3 Hz, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.0, 186.7, 166.6, 161.2, 154.4, 144.3, 136.9, 135.3, 133.9, 132.8, 131.7, 130.2, 129.9, 127.6, 125.3, 97.7, 97.4, 52.5, 52.4, 37.3, 24.2, 21.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{22}O_7Na^+$, 481.1257； found 481.1249.

IR (neat) ν (cm^{-1}): 3087, 2947, 1715, 1682, 1627, 1567, 1527, 1270, 1103.

(Z)-1-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)-3-(4-(trifluoromethyl)phenyl)-7,8-dihydro-1H-isochromen-5(6H)-one (6u)



155 mg (65% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:8). R_f = 0.30.

m.p. = 196.3-197.7 ℃

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.24 (d, *J* = 8.2 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.74 (dd, *J* = 8.1, 6.0 Hz, 4H), 7.20 (s, 1H), 6.38 (s, 1H), 2.70 (dt, *J* = 18.2, 6.6 Hz, 4H), 2.25 (m, 2H).

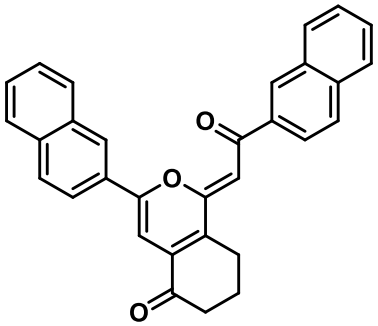
^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.0, 186.2, 161.3, 154.1, 143.6, 136.9, 134.6, 134.0, 133.3 (q, J_{FC} = 33.2 Hz), 132.2 (q, J_{FC} = 33.2 Hz), 128.1, 126.1 (q, J_{FC} = 3.0 Hz), 125.7 (q, J_{FC} = 4.5 Hz), 125.7, 124.0 (q, J_{FC} = 273.3 Hz), 123.9 (q, J_{FC} = 273.3 Hz), 97.6, 97.3, 37.3, 24.2, 21.4.

^{19}F NMR ($CDCl_3$, 565 MHz): δ -62.74, -62.79.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{16}F_6O_3Na^+$, 501.0895； found 501.0886.

IR (neat) ν (cm^{-1}): 3080, 2947, 1682, 1630, 1564, 1508, 1323, 1161, 1112.

(Z)-3-(naphthalen-2-yl)-1-(2-(naphthalen-2-yl)-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6v)



148 mg (67% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

m.p. = 192.6-193.0 ℃

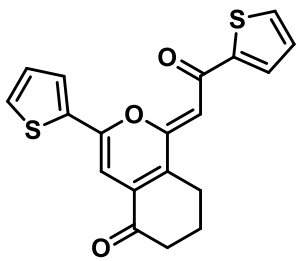
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.55 (d, *J* = 78.0 Hz, 1H), 8.08 (ddd, *J* = 22.2, 8.6, 1.8 Hz, 2H), 7.99 (d, *J* = 7.1 Hz, 1H), 7.95 – 7.85 (m, 4H), 7.82 (d, *J* = 7.1 Hz, 1H), 7.60 – 7.46 (m, 5H), 7.18 (s, 1H), 6.49 (s, 1H), 2.73 (t, *J* = 6.1 Hz, 2H), 2.67 (t, 2H), 2.24 (dt, *J* = 6.3 Hz, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.5, 187.8, 160.7, 155.6, 138.3, 136.1, 135.1, 134.3, 133.9, 133.3, 132.9, 129.5, 129.5, 128.7, 128.6, 128.5, 127.9, 127.9, 127.7, 127.4, 126.7, 126.6, 125.8, 124.6, 122.2, 97.8, 96.2, 37.4, 24.3, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{31}H_{22}O_3Na^+$, 465.1461； found 465.1454.

IR (neat) ν (cm^{-1}): 3060, 2940, 1682, 1622, 1562, 1511, 1274, 1179, 1122.

(Z)-1-(2-oxo-2-(thiophen-2-yl)ethylidene)-3-(thiophen-2-yl)-7,8-dihydro-1H-isochromen-5(6H)-one (6w)



145 mg (82% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.25.

m.p. = 230.2-231.0 ℃

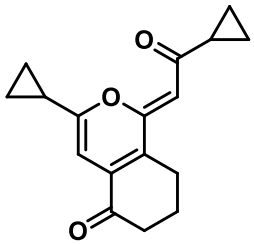
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.96 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.68 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.56 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.41 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.12 (ddd, *J* = 5.0, 3.7, 2.9 Hz, 2H), 6.81 (s, 1H), 6.26 (s, 1H), 2.67 – 2.61 (m, 4H), 2.20 (dt, *J* = 12.3, 6.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.2, 179.1, 160.3, 151.6, 148.1, 135.3, 135.1, 133.9, 132.0, 129.3, 128.5, 128.4, 128.2, 128.0, 96.7, 95.1, 37.4, 24.1, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{16}O_3S_2Na^+$, 377.0276； found 377.0276.

IR (neat) ν (cm^{-1}):3106, 2927, 1684, 1608, 1563, 1507, 1162, 1041.

(Z)-3-cyclopropyl-1-(2-cyclopropyl-2-oxoethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6x)



103 mg (76% yield) orange solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:15). R_f = 0.25.

m.p. = 95.7-96.3 ℃

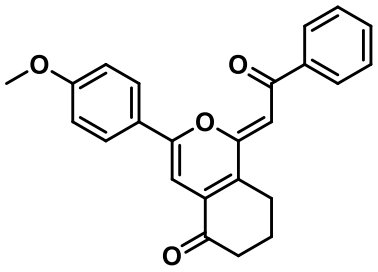
^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.26 (s, 1H), 5.62 (s, 1H), 2.54 (t, *J* = 6.3 Hz, 2H), 2.45 (t, *J* = 6.1 Hz, 2H), 2.10 (tt, *J* = 7.0, 5.2 Hz, 3H), 1.72 (tt, *J* = 8.3, 5.0 Hz, 1H), 1.19 – 1.15 (m, 2H), 1.09 – 1.05 (m, 2H), 0.92 – 0.88 (m, 2H), 0.83 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 196.5, 195.5, 160.8, 158.9, 134.1, 133.3, 101.6, 95.2, 37.4, 24.0, 21.8, 21.6, 14.1, 10.7, 7.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{18}O_3Na^+$, 293.1148； found 293.1143.

IR (neat) ν (cm^{-1}): 3087, 3006, 2927, 1678, 1637, 1570, 1526, 1376, 1098.

(Z)-3-(4-methoxyphenyl)-1-(2-oxo-2-phenylethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6ad)



33 mg (15% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:3). R_f = 0.30.

m.p. = 196.8-197.4 ℃

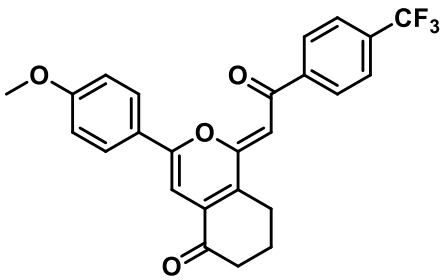
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.09 (d, *J* = 8.1 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.54 – 7.45 (m, 3H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.96 (s, 1H), 6.34 (s, 1H), 3.86 (s, 3H), 2.65 (dt, *J* = 13.2, 6.6 Hz, 4H), 2.21 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.6, 187.6, 161.6, 161.2, 155.8, 141.1, 134.6, 134.3, 131.6, 128.6, 127.7, 127.2, 124.2, 114.4, 96.9, 94.3, 55.5, 37.5, 24.1, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{20}O_4Na^+$, 395.1253； found 395.1248.

IR (neat) ν (cm^{-1}): 3053, 2947, 1683, 1627, 1605, 1566, 1507, 1255, 1180.

(Z)-3-(4-methoxyphenyl)-1-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)-7,8-dihydro-1H-isochromen-5(6H)-one (6du)



33 mg (15% yield) red solid, purified by flash column chromatography (SiO_2, Ethyl acetate: n-hexane, 1:6). R_f = 0.35.

m.p. = 181.0-181.3 ℃

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.05 (dd, *J* = 15.5, 8.5 Hz, 4H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 9.2 Hz, 3H), 6.30 (s, 1H), 3.86 (s, 3H), 2.70 – 2.63 (m, 4H), 2.26 – 2.20 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.4, 186.1, 162.1, 161.8, 156.1, 144.1, 134.8, 134.1, 133.0 (q, J_{FC} = 32.2 Hz), 127.9, 127.2, 125.6 (q, J_{FC} = 3.6 Hz), 124.0, 123.9 (q, J_{FC} = 271.8 Hz), 114.5, 96.3, 94.8, 55.5, 37.5, 24.1, 21.5.

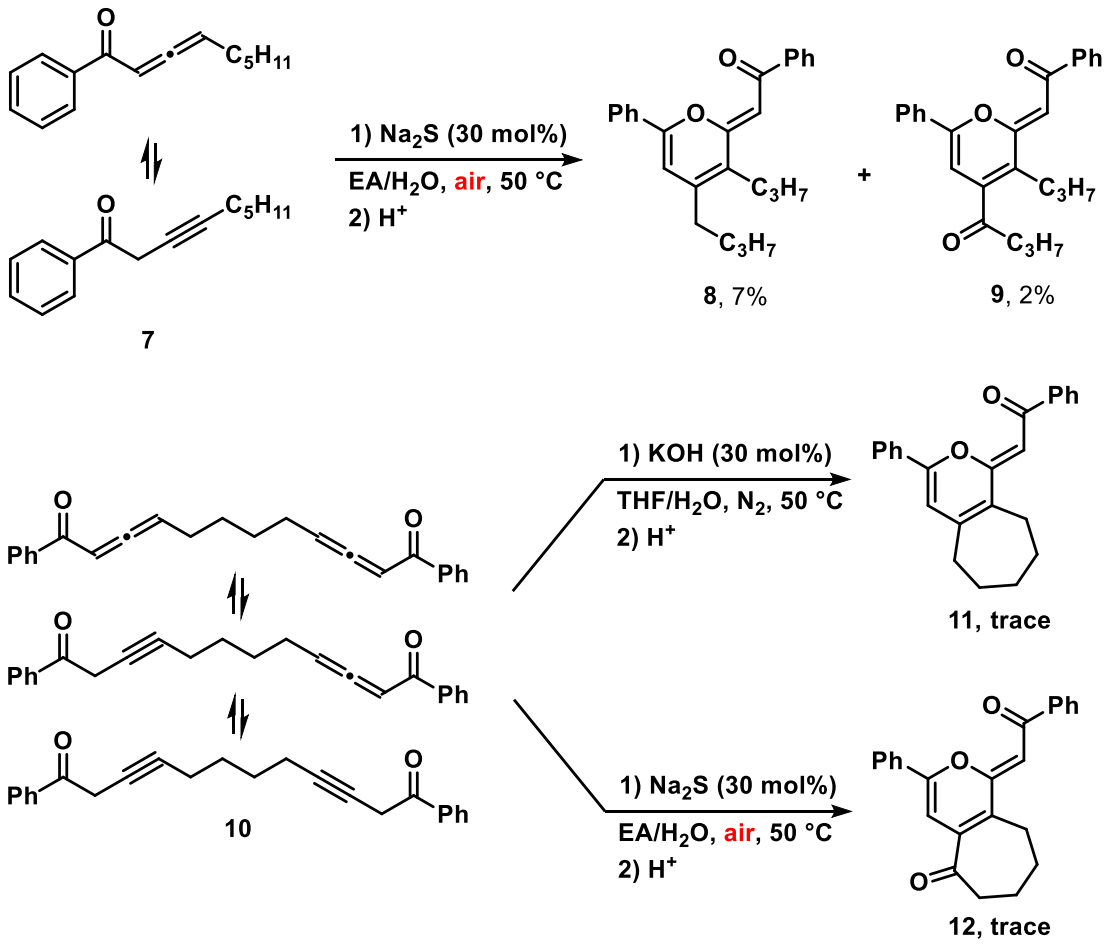
^{19}F NMR ($CDCl_3$, 565 MHz): δ -62.67.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{19}F_3O_4Na^+$, 463.1127； found 463.1119.

IR (neat) ν (cm^{-1}): 3067, 2933, 1686, 1631, 1598, 1569, 1500, 1318, 1252, 1164, 1112, 1063.

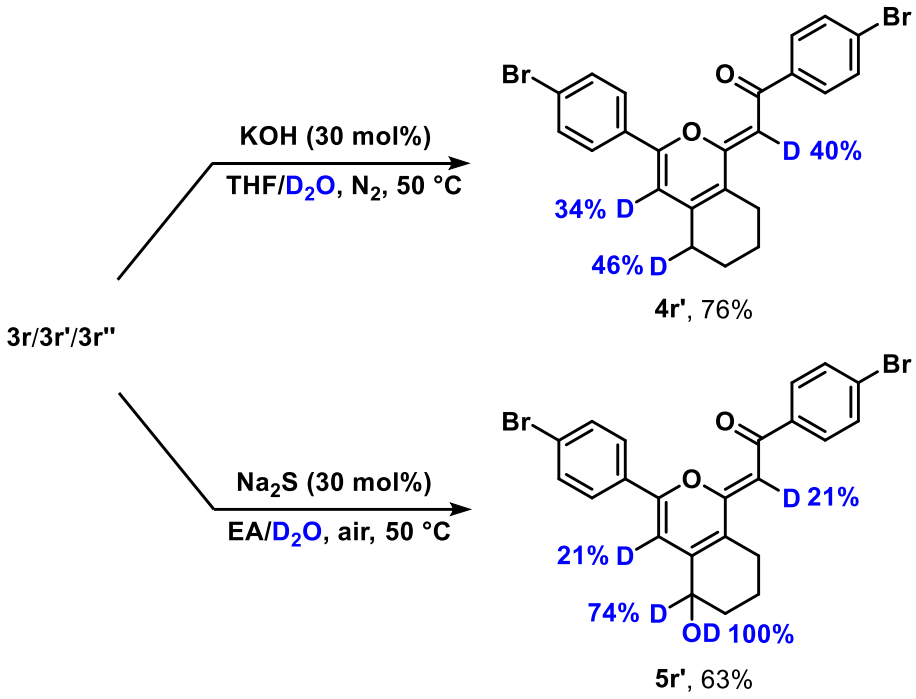
3. Mechanistic Studies

3.1 Control experiments



Scheme S1 Reactions of other Allenones / Alkynones.

3.2 Deuterium labelling experiments



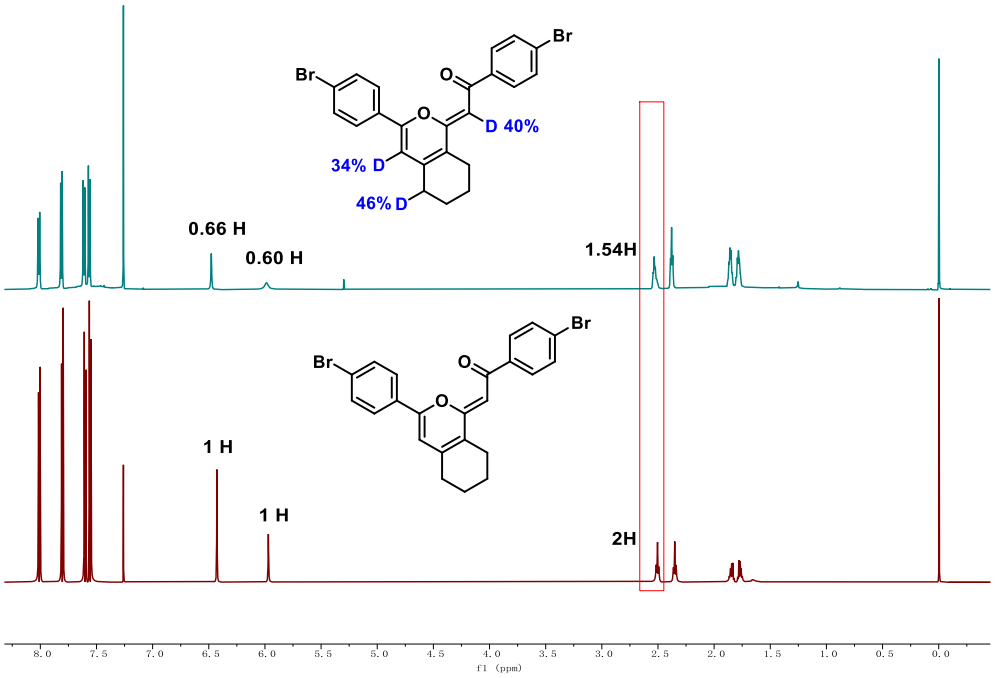


Figure S1 ^{1}H NMR comparison of **4r'** and **4r**

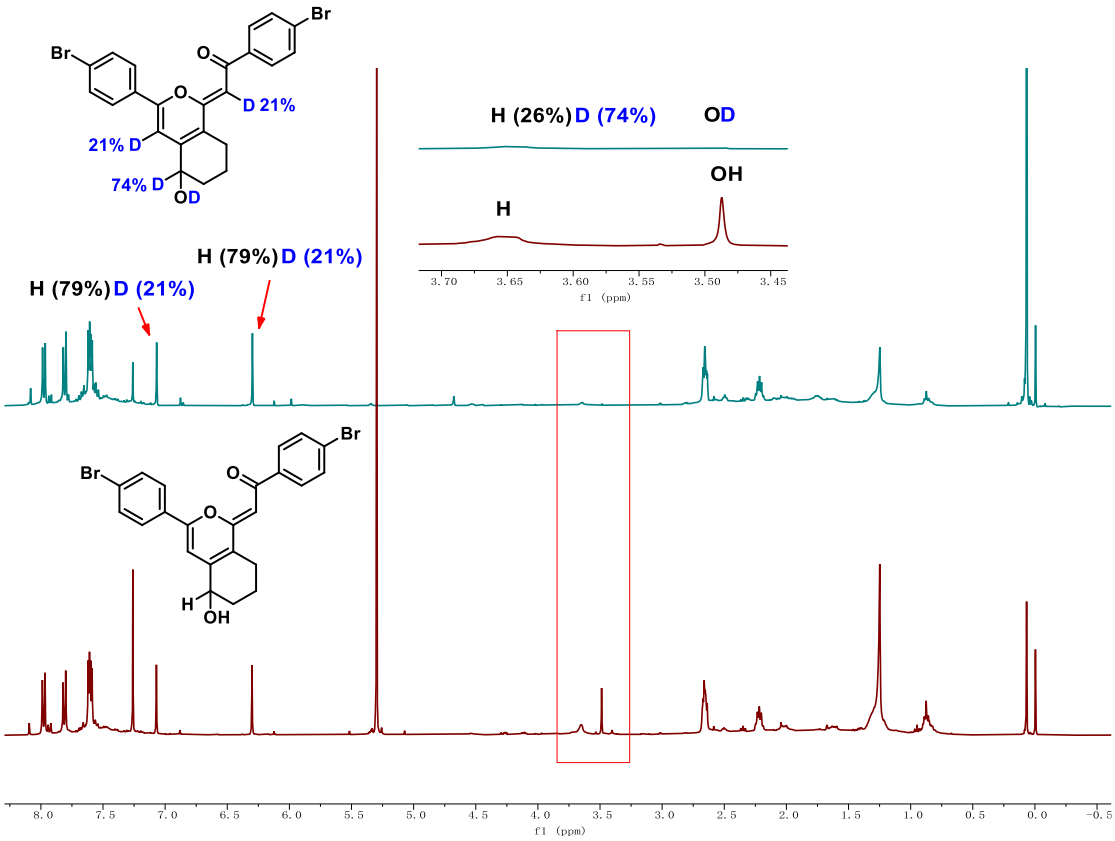
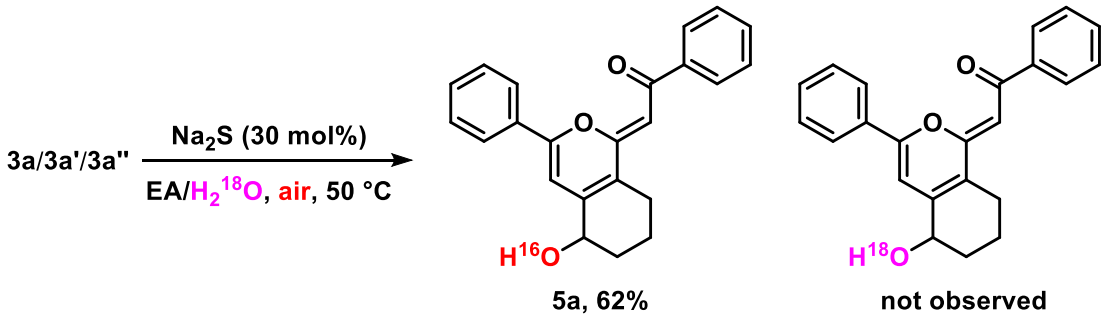


Figure S2 ^{1}H NMR comparison of **5r'** and **5r**

3.3 Oxygen-18 labelling experiments

Oxygen isotope labelling experiments were demonstrated to identify the source of oxygen in oxidation products. Dissolved the freshly prepared **3a**/**3a'**/**3a"** (328 mg, 1 mmol) in dry EA (5 mL), a solution of Na_2S (23 mg, 0.3 mmol) in $H_2{}^{18}O$ (1 mL) was added. Upon completion of the reaction, a small amount of the reaction liquid was taken for testing by HRMS, but no ^{18}O labelled products were detected.



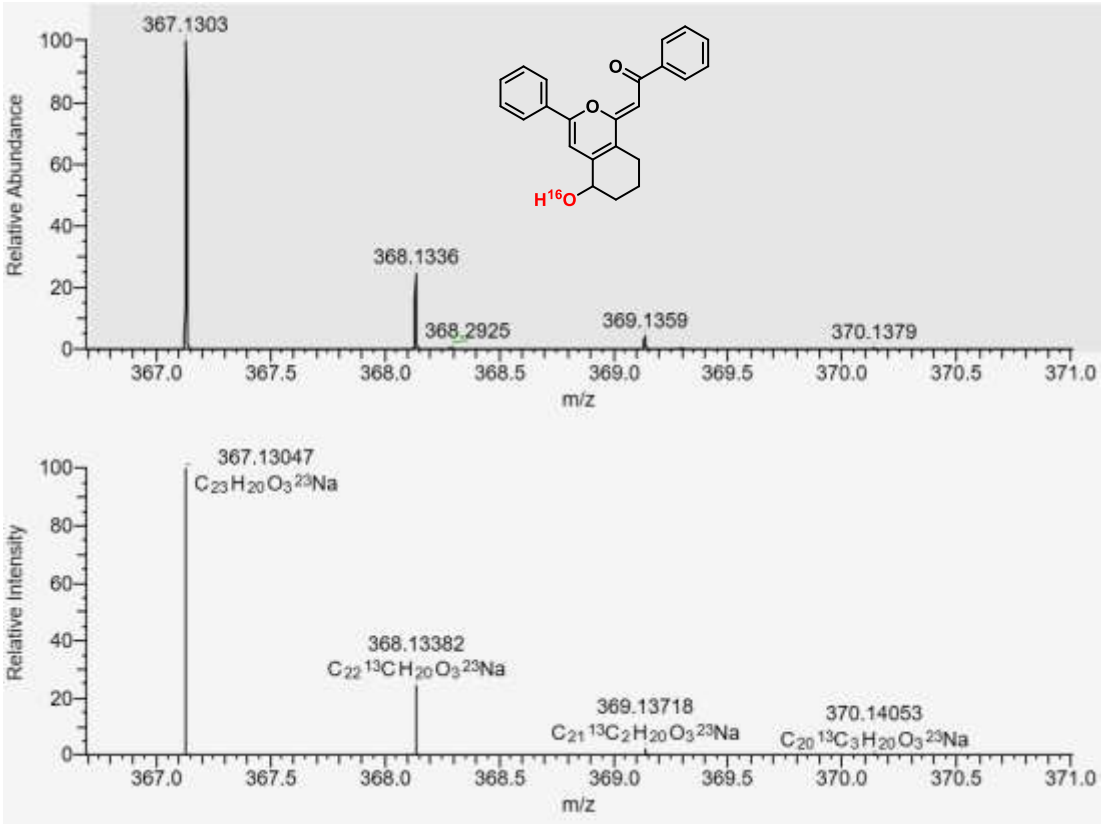
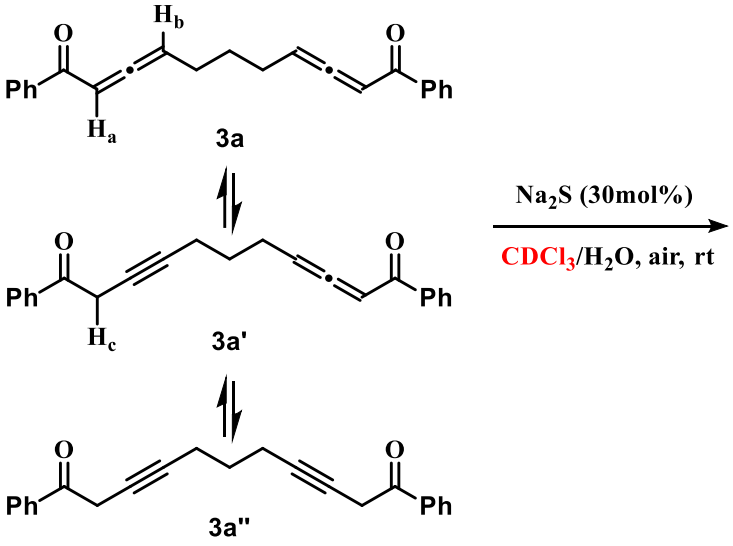


Figure S3 Mass spectra of **5a**

3.4 NMR monitoring experiments

To elucidate the course of reactant transformation during the reaction, we conducted NMR tracking experiments. It was observed that as the reaction progressed, the ratio of allenones to alkynones in the starting material continuously increased, indicating that alkynes are converted into allene intermediates during the reaction process.



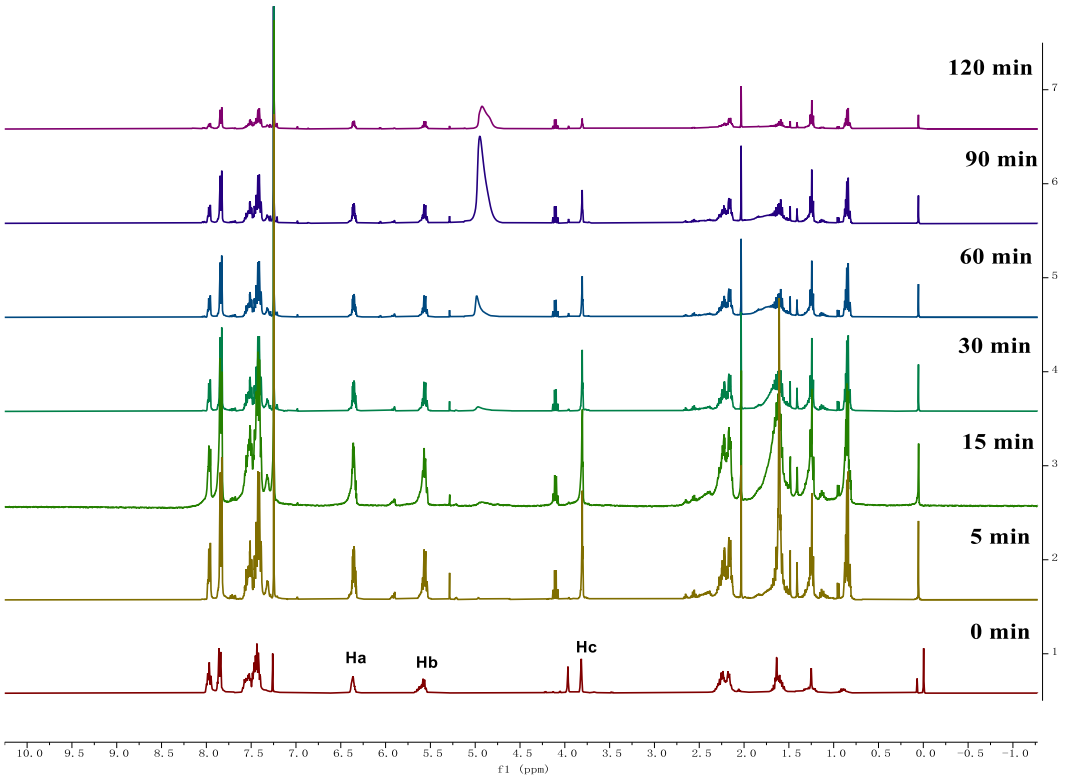


Figure S4 ^{1}H NMR monitoring in $CDCl_3$

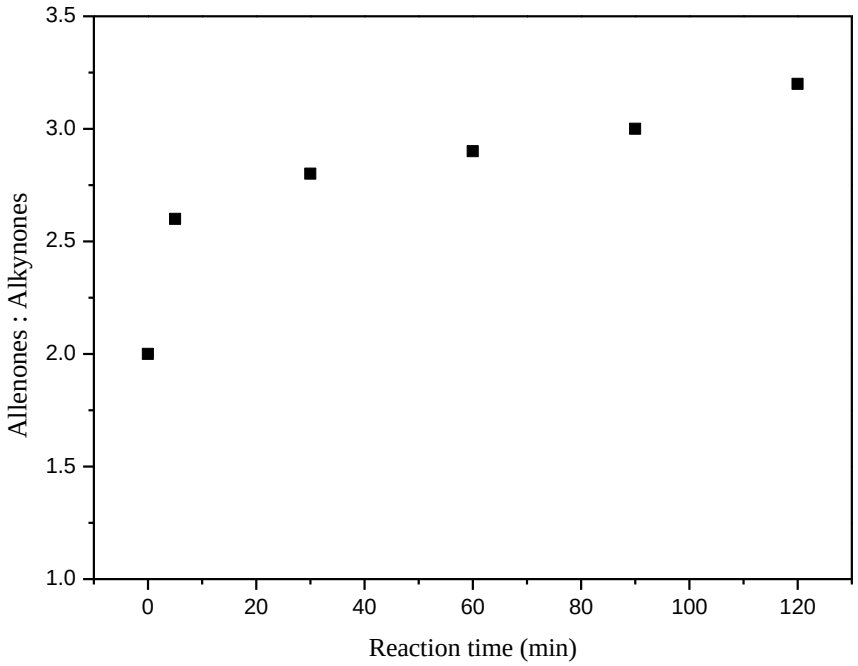


Figure S5 The ratio of allenones to alkynones during the reaction process

3.5 Mass spectra of T1 and T2

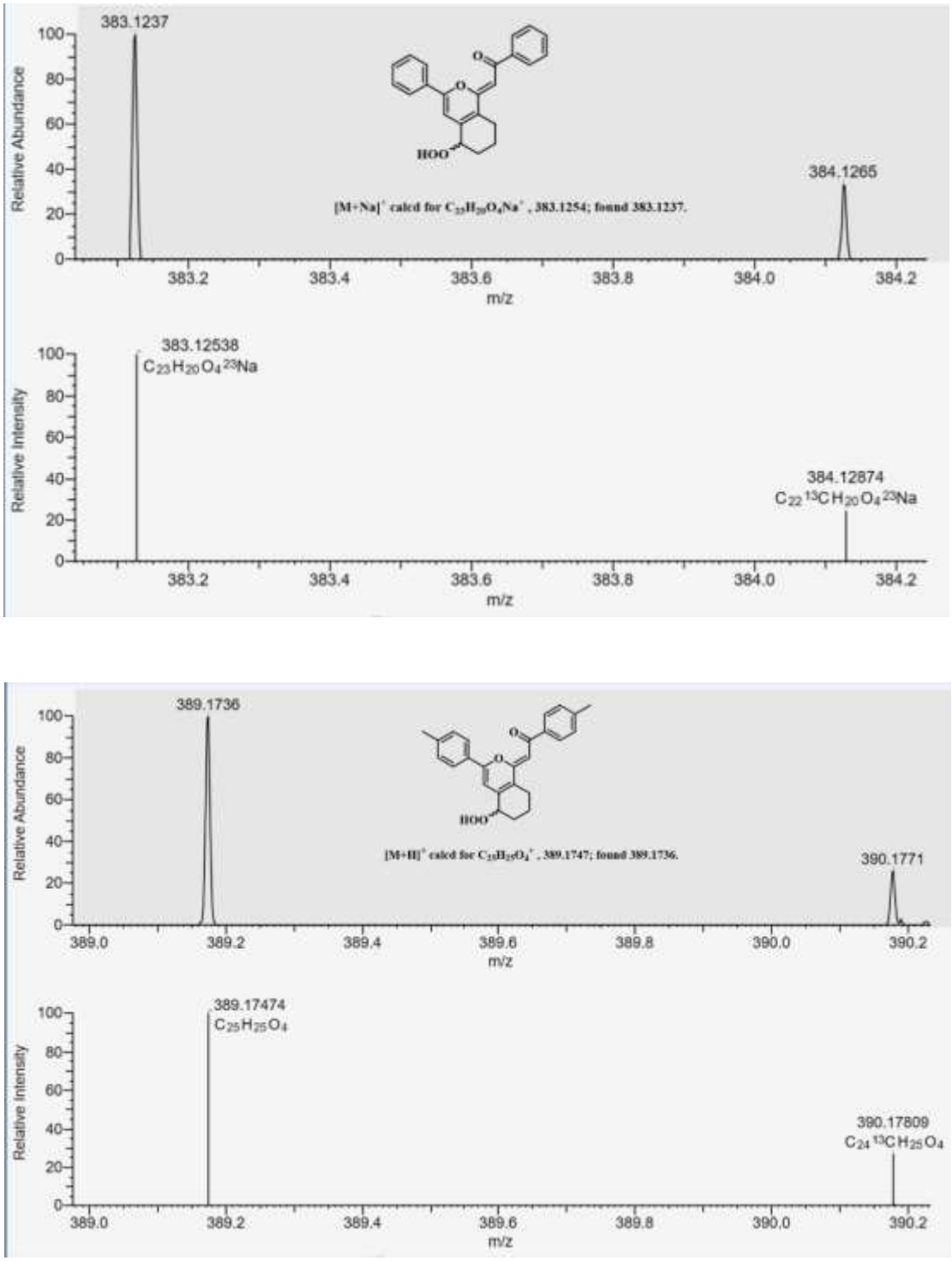


Figure S6 Mass spectra of **T1**

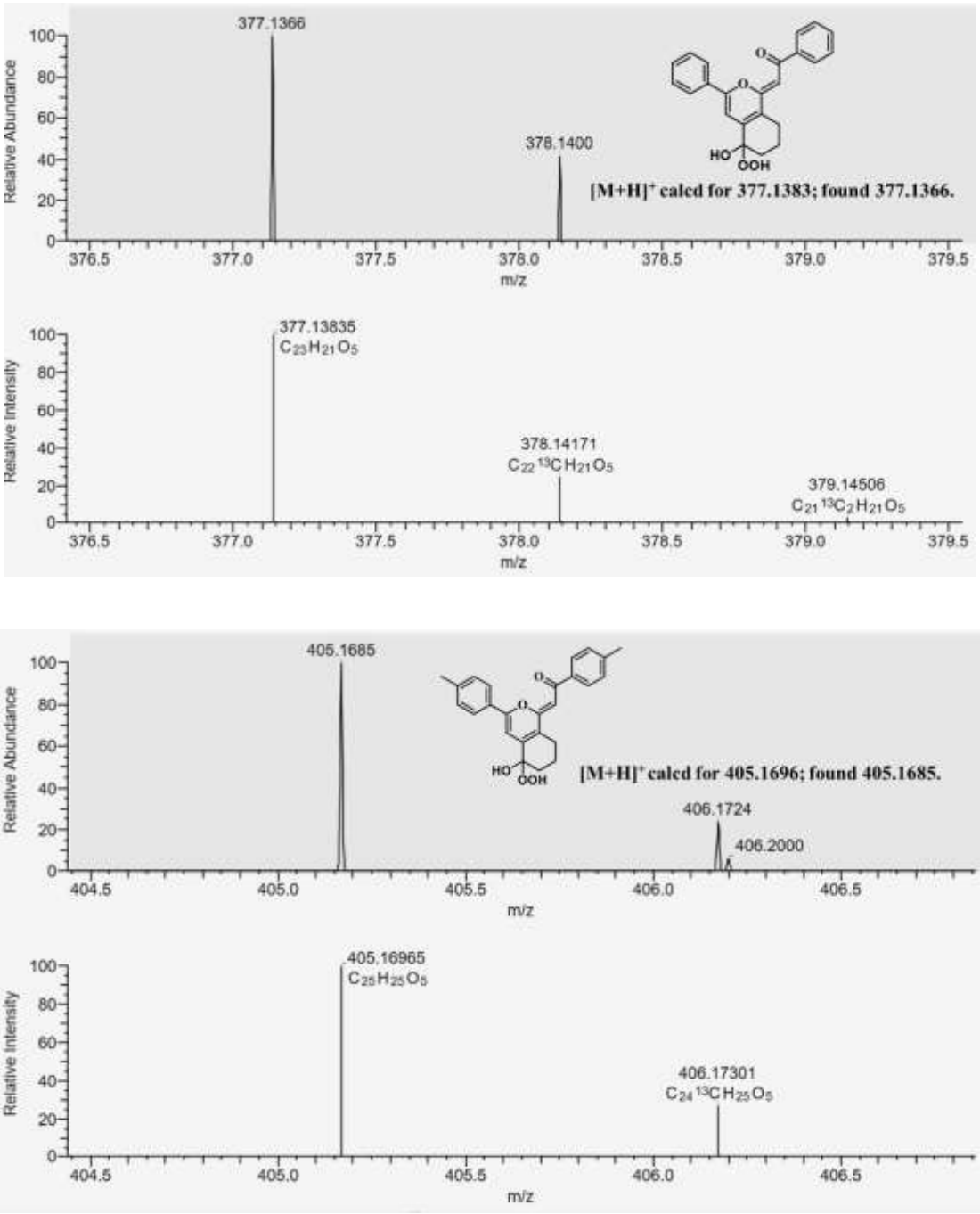
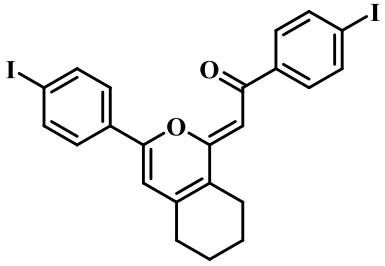


Figure S7 Mass spectra of **T2**

4. Single Crystal X-Ray Crystallography

Figure S8 Plot (50% probability thermal ellipsoids) of the molecular structure of **4s**.



Sample Preparation for Crystal: The compound **4s** (15mg) was dissolved in 10 mL mixed solution (PE : EA : DCM= 5:3:2) in a 15 mL sample vial and kept still at room temperature. The orange crystals were observed after one week. The single crystals were then submitted to X-ray diffraction analysis.

Table S3 Crystal data and structure refinement for mo_zjb_285_a_0m.

Identification code	mo_zjb_285_a_0m
Empirical formula	$C_{23}H_{18}I_2O_2$
Formula weight	580.17
Temperature/K	150(2)
Crystal system	monoclinic
Space group	P2/n
a/Å	16.5721(19)
b/Å	8.3586(8)
c/Å	17.0294(19)
α/°	90
β/°	92.605(4)
γ/°	90
Volume/Å^3	2356.5(4)
Z	4
ρ_{calc}g/cm^3	1.635
μ/mm^{-1}	2.682
F(000)	1112.0
Crystal size/mm^3	0.300 × 0.300 × 0.200
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.354 to 56.596
Index ranges	-22 ≤ h ≤ 22, -11 ≤ k ≤ 11, -22 ≤ l ≤ 22
Reflections collected	53896
Independent reflections	5851 [R_{int} = 0.0578, R_{sigma} = 0.0332]
Data/restraints/parameters	5851/0/244
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0524, wR_2 = 0.1512
Final R indexes [all data]	R_1 = 0.0712, wR_2 = 0.1651
Largest diff. peak/hole / e Å^{-3}	1.78/-0.84

Table S4 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for mo_zjb_285_a_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	5131.0(3)	2562.4(6)	9623.5(3)	82.78(19)
I2	1443.2(3)	12098.9(5)	3535.0(2)	66.33(16)
O1	5515.7(18)	6107(4)	5951.7(19)	45.0(7)
O2	4139(2)	7792(6)	6025(2)	66.3(11)
C1	5463(3)	3477(7)	8538(3)	57.6(13)
C2	6146(4)	2852(7)	8196(4)	66.8(16)
C3	6344(3)	3386(7)	7461(4)	59.6(13)
C4	5894(3)	4603(6)	7078(3)	47.4(11)
C5	6113(3)	5159(6)	6298(3)	47.5(11)
C6	5562(3)	6657(6)	5207(3)	44.7(10)
C7	4934(3)	7589(6)	4915(3)	43.4(10)
C8	4239(3)	8094(6)	5323(3)	46.5(10)
C9	3605(3)	9037(6)	4871(3)	42.3(9)
C10	3703(3)	9691(7)	4130(3)	52.2(12)
C11	3081(3)	10550(7)	3748(3)	56.4(12)
C12	2370(3)	10764(6)	4104(3)	49.0(11)
C13	5017(3)	4661(7)	8167(3)	58.4(13)
C14	5228(3)	5224(6)	7439(3)	47.5(11)
C15	6780(3)	4868(7)	5906(3)	55.1(13)
C16	6862(3)	5417(6)	5126(3)	52.0(12)
C17	6254(3)	6259(6)	4773(3)	45.8(10)
C18	6271(3)	6805(8)	3933(3)	63.0(15)
C19	6931(5)	5992(15)	3491(5)	114(3)
C20	7684(5)	5863(15)	3955(6)	120(3)
C21	7628(3)	5000(8)	4725(4)	68.9(17)
C22	2252(3)	10159(7)	4840(3)	53.8(12)
C23	2876(3)	9316(7)	5219(3)	50.0(11)

Table S5 Anisotropic Displacement Parameters ($Å^2×10^3$) for mo_zjb_285_a_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	86.8(4)	89.9(4)	71.6(3)	19.6(2)	2.9(2)	-11.6(2)
I2	69.0(3)	64.4(3)	64.4(3)	-5.95(17)	-9.87(18)	16.90(18)
O1	35.9(15)	53.8(19)	45.5(17)	-6.5(14)	4.1(13)	1.3(13)
O2	55(2)	100(3)	45(2)	5.5(19)	7.8(17)	24(2)
C1	60(3)	55(3)	56(3)	8(2)	-10(2)	-10(2)
C2	62(3)	56(3)	82(4)	11(3)	-1(3)	2(3)
C3	46(3)	62(3)	71(4)	-7(3)	4(2)	0(2)
C4	34(2)	50(3)	58(3)	-9(2)	-6(2)	-4.2(18)
C5	31(2)	51(3)	60(3)	-13(2)	-1(2)	0.3(18)
C6	39(2)	47(2)	48(3)	-10(2)	3.5(19)	-7.1(18)
C7	36(2)	51(3)	44(2)	-7.2(19)	7.8(19)	-4.1(18)
C8	43(2)	53(3)	44(2)	-6(2)	3.5(19)	1(2)
C9	44(2)	44(2)	39(2)	-6.3(18)	5.8(18)	-2.6(18)
C10	47(3)	61(3)	48(3)	1(2)	7(2)	1(2)
C11	64(3)	57(3)	48(3)	2(2)	3(2)	6(2)
C12	57(3)	40(2)	49(3)	-6(2)	-8(2)	2(2)
C13	44(3)	72(4)	59(3)	-3(3)	6(2)	-6(2)
C14	36(2)	57(3)	49(3)	-2(2)	-1.4(19)	1.1(19)

C15	34(2)	62(3)	70(3)	-12(3)	-1(2)	0(2)
C16	35(2)	58(3)	64(3)	-20(2)	9(2)	-5(2)
C17	36(2)	53(3)	49(3)	-14(2)	10.4(19)	-9.6(19)
C18	46(3)	84(4)	61(3)	-12(3)	19(2)	-9(3)
C19	70(5)	196(11)	79(5)	-25(6)	33(4)	10(6)
C20	81(5)	168(10)	116(7)	2(7)	54(5)	31(6)
C21	44(3)	77(4)	87(4)	-25(3)	20(3)	3(3)
C22	46(3)	61(3)	55(3)	-2(2)	7(2)	6(2)
C23	41(2)	62(3)	47(3)	1(2)	8(2)	5(2)

Table S6 Bond Lengths for mo_zjb_285_a_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C1	2.096(6)	C8	C9	1.497(7)
I2	C12	2.099(5)	C9	C23	1.390(6)
O1	C6	1.354(6)	C9	C10	1.392(7)
O1	C5	1.379(6)	C10	C11	1.394(7)
O2	C8	1.241(6)	C11	C12	1.361(8)
C1	C13	1.372(8)	C12	C22	1.373(7)
C1	C2	1.399(9)	C13	C14	1.385(7)
C2	C3	1.383(9)	C15	C16	1.418(8)
C3	C4	1.405(8)	C16	C17	1.349(7)
C4	C14	1.389(7)	C16	C21	1.508(7)
C4	C5	1.468(7)	C17	C18	1.503(8)
C5	C15	1.339(7)	C18	C19	1.515(9)
C6	C7	1.376(7)	C19	C20	1.449(12)
C6	C17	1.431(6)	C20	C21	1.504(11)
C7	C8	1.435(7)	C22	C23	1.385(7)

Table S7 Bond Angles for mo_zjb_285_a_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	O1	C5	121.6(4)	C10	C9	C8	124.3(4)
C13	C1	C2	120.4(5)	C9	C10	C11	120.7(5)
C13	C1	I1	120.9(5)	C12	C11	C10	119.8(5)
C2	C1	I1	118.8(4)	C11	C12	C22	121.3(5)
C3	C2	C1	119.2(6)	C11	C12	I2	119.6(4)
C2	C3	C4	120.7(5)	C22	C12	I2	119.1(4)
C14	C4	C3	118.8(5)	C1	C13	C14	120.4(5)
C14	C4	C5	121.1(5)	C13	C14	C4	120.5(5)
C3	C4	C5	120.1(5)	C5	C15	C16	121.6(5)
C15	C5	O1	119.0(5)	C17	C16	C15	119.0(4)
C15	C5	C4	129.6(5)	C17	C16	C21	123.1(5)
O1	C5	C4	111.5(4)	C15	C16	C21	117.9(5)
O1	C6	C7	117.2(4)	C16	C17	C6	119.4(5)
O1	C6	C17	119.1(4)	C16	C17	C18	122.4(4)
C7	C6	C17	123.7(5)	C6	C17	C18	118.2(5)
C6	C7	C8	127.1(5)	C17	C18	C19	112.5(6)
O2	C8	C7	123.5(5)	C20	C19	C18	112.7(7)
O2	C8	C9	118.7(4)	C19	C20	C21	115.2(8)
C7	C8	C9	117.8(4)	C20	C21	C16	111.7(6)
C23	C9	C10	117.5(5)	C12	C22	C23	118.7(5)

C23	C9	C8	118.2(4)		C22	C23	C9	122.0(5)	

Table S8 Torsion Angles for mo_zjb_285_a_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C13	C1	C2	C3	-3.1(9)	C1	C13	C14	C4	-0.3(8)
I1	C1	C2	C3	176.5(4)	C3	C4	C14	C13	0.6(7)
C1	C2	C3	C4	3.4(9)	C5	C4	C14	C13	178.5(5)
C2	C3	C4	C14	-2.1(8)	O1	C5	C15	C16	-4.4(8)
C2	C3	C4	C5	179.9(5)	C4	C5	C15	C16	175.2(5)
C6	O1	C5	C15	4.6(7)	C5	C15	C16	C17	0.3(8)
C6	O1	C5	C4	-175.1(4)	C5	C15	C16	C21	-178.7(5)
C14	C4	C5	C15	170.2(5)	C15	C16	C17	C6	3.6(7)
C3	C4	C5	C15	-11.9(8)	C21	C16	C17	C6	-177.5(5)
C14	C4	C5	O1	-10.2(6)	C15	C16	C17	C18	-176.5(5)
C3	C4	C5	O1	167.8(4)	C21	C16	C17	C18	2.5(8)
C5	O1	C6	C7	179.8(4)	O1	C6	C17	C16	-3.4(7)
C5	O1	C6	C17	-0.7(6)	C7	C6	C17	C16	176.1(5)
O1	C6	C7	C8	2.3(7)	O1	C6	C17	C18	176.6(4)
C17	C6	C7	C8	-177.2(5)	C7	C6	C17	C18	-3.9(7)
C6	C7	C8	O2	3.3(8)	C16	C17	C18	C19	13.3(8)
C6	C7	C8	C9	-176.7(4)	C6	C17	C18	C19	-166.7(6)
O2	C8	C9	C23	-9.9(7)	C17	C18	C19	C20	-41.9(11)
C7	C8	C9	C23	170.1(5)	C18	C19	C20	C21	56.9(13)
O2	C8	C9	C10	168.3(5)	C19	C20	C21	C16	-39.5(11)
C7	C8	C9	C10	-11.6(7)	C17	C16	C21	C20	9.7(9)
C23	C9	C10	C11	-1.9(8)	C15	C16	C21	C20	-171.4(7)
C8	C9	C10	C11	179.8(5)	C11	C12	C22	C23	0.0(8)
C9	C10	C11	C12	0.5(8)	I2	C12	C22	C23	-178.3(4)
C10	C11	C12	C22	0.5(8)	C12	C22	C23	C9	-1.5(8)
C10	C11	C12	I2	178.8(4)	C10	C9	C23	C22	2.4(8)
C2	C1	C13	C14	1.6(8)	C8	C9	C23	C22	-179.2(5)
I1	C1	C13	C14	-178.1(4)					

Table S9 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mo_zjb_285_a_0m.

Atom	*x*	*y*	*z*	U(eq)
H2	6469.86	2069.77	8464.51	80
H3	6790.62	2925.9	7212.16	72
H7	4962.98	7935.51	4385.94	52
H10	4200.36	9549.83	3881.75	63
H11	3151.98	10985.23	3240.77	68
H13	4562.28	5097.77	8410.12	70
H14	4913.72	6039.86	7185.15	57
H15	7208.86	4278.63	6157.47	66
H18A	6356.55	7976.69	3921.91	76
H18B	5742.07	6575.82	3663.55	76
H19A	6747.49	4907.88	3332.27	137
H19B	7026.08	6607.08	3007.18	137
H20A	7892.89	6954.62	4061.57	144
H20B	8081.82	5301.07	3637.82	144

H21A	8099.7	5285.45	5074.4	83
H21B	7643.93	3831.39	4631.83	83
H22	1754.1	10314.87	5083.71	65
H23	2802.11	8917.52	5733.65	60

Experimental

Single crystals of $C_{23}H_{18}I_2O_2$ **[mo_zjb_285_a_0m]** were **[]**. A suitable crystal was selected and **[]** on a diffractometer. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the Unknown [2] structure solution program using Unknown and refined with the Unknown [3] refinement package using Unknown minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2.
3.

Crystal structure determination of [mo_zjb_285_a_0m]

Crystal Data for $C_{23}H_{18}I_2O_2$ (M =580.17 g/mol): monoclinic, space group P2/n (no. 13), a = 16.5721(19) Å, b = 8.3586(8) Å, c = 17.0294(19) Å, β = 92.605(4)°, V = 2356.5(4) Å^3, Z = 4, T = 150(2) K, μ(MoKα) = 2.682 mm^{-1}, *Dcalc* = 1.635 g/cm^3, 53896 reflections measured (3.354° ⩽ 2Θ ⩽ 56.596°), 5851 unique (R_{int} = 0.0578, R_{sigma} = 0.0332) which were used in all calculations. The final R_1 was 0.0524 (I > 2σ(I)) and wR_2 was 0.1651 (all data). **The CCDC deposition number 2328809** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

Refinement model description

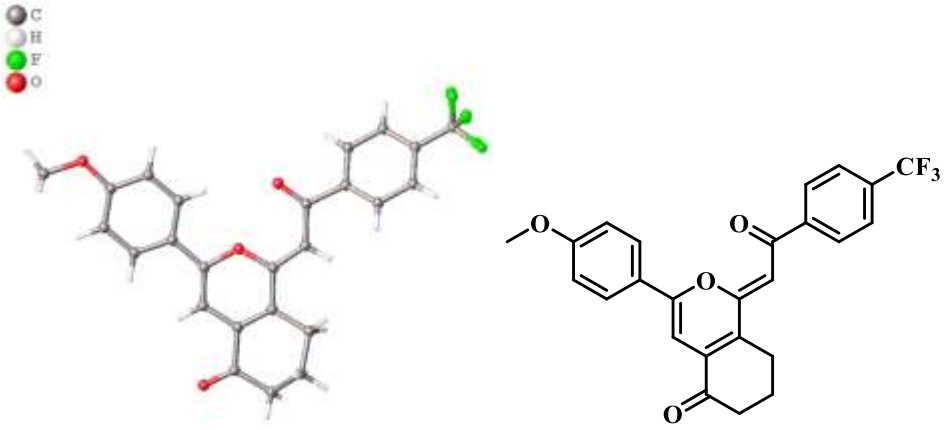
Number of restraints - 0, number of constraints - unknown.

Details:

N/A

This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Figure S9 Plot (50% probability thermal ellipsoids) of the molecular structure of **6du**.



Sample Preparation for Crystal: The compound **6du** (10 mg) was dissolved in 10 mL mixed solution (PE:EA:DCM= 5:3:2) in a 15 mL sample vial and kept still at room temperature. The red crystals was observed after three days. The single crystals were then submitted to X-ray diffraction analysis.

Table S10 Crystal data and structure refinement for 1.

Identification code	1
Empirical formula	$C_{25}H_{19}F_3O_4$
Formula weight	440.40
Temperature/K	300
Crystal system	triclinic
Space group	P-1
a/Å	9.6264(17)
b/Å	10.7417(18)
c/Å	11.025(2)
α/°	97.196(6)
β/°	113.780(6)
γ/°	92.477(6)
Volume/Å^3	1029.5(3)
Z	2
ρ_{calc}g/cm^3	1.421
μ/mm^{-1}	0.113
F(000)	456.0
Crystal size/mm^3	0.4 × 0.3 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.088 to 56.546
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	38754
Independent reflections	5079 [R_{int} = 0.0598, R_{sigma} = 0.0375]
Data/restraints/parameters	5079/114/318
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0815, wR_2 = 0.2446
Final R indexes [all data]	R_1 = 0.1031, wR_2 = 0.2684
Largest diff. peak/hole / e Å^{-3}	0.62/-0.38

Table S11 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	5448.1(18)	5009.6(13)	2140.9(17)	51.8(4)
C1	10544(4)	1717(3)	-227(4)	89.0(11)
O2	6616(3)	9180.9(19)	1193(3)	101.5(9)
O3	4326(3)	3125.3(19)	2936(3)	98.0(9)
C2	-462(5)	2146(4)	5462(5)	100.4(9)
C3	598(3)	2614(3)	4912(3)	71.5(8)
C4	1200(3)	3861(3)	5281(3)	65.6(7)
C5	2184(3)	4304(2)	4764(3)	58.3(6)
C6	2560(3)	3505(2)	3877(3)	54.5(6)
C7	3646(3)	3922(2)	3296(3)	60.8(6)
C8	3785(3)	5246(2)	3182(3)	54.7(6)
C9	4658(3)	5791(2)	2639(2)	49.4(5)
C10	6351(3)	5422.8(19)	1552(2)	47.2(5)
C11	7145(3)	4406.4(19)	1199(2)	48.1(5)
C12	6952(3)	3194(2)	1466(3)	52.2(5)
C13	7730(3)	2246(2)	1151(3)	57.1(6)

C14	8723(3)	2493(2)	565(3)	56.2(6)
O15	9431(2)	1489.6(17)	289(2)	75.2(6)
C16	6445(3)	6636(2)	1402(3)	53.8(6)
C17	5663(3)	7505(2)	1916(3)	51.7(5)
C18	4819(3)	7120(2)	2559(2)	50.6(5)
C19	4042(4)	8023(2)	3175(3)	65.9(7)
C20	4658(7)	9382(3)	3283(5)	127.2(19)
C21	4945(5)	9734(3)	2219(5)	96.0(12)
C22	5831(3)	8859(2)	1738(3)	69.1(7)
C23	973(4)	1807(3)	4040(4)	80.6(9)
C24	1971(4)	2251(3)	3540(3)	70.1(7)
C28	8113(3)	4622(2)	575(3)	70.1(8)
C29	8896(4)	3682(2)	265(4)	72.2(8)
F1	165(7)	1301(4)	6290(5)	123.6(15)
F2	-596(5)	3043(4)	6443(5)	113.5(13)
F3	-1744(7)	1771(9)	4668(7)	180(3)
F1A	-95(15)	1973(14)	6497(12)	161(3)
F2A	-1886(9)	2609(7)	4834(10)	107(2)
F3A	-1259(9)	900(7)	4708(11)	116(2)

Table S12 Anisotropic Displacement Parameters ($Å^2×10^3$) for 1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	64.5(10)	40.9(7)	72.1(10)	13.3(7)	49.0(9)	10.1(7)
C1	111(2)	74.7(18)	135(3)	36.0(19)	97(2)	41.0(17)
O2	129(2)	49.8(11)	182(3)	36.5(13)	114(2)	16.1(11)
O3	132(2)	54.8(11)	175(2)	31.3(13)	126(2)	27.5(12)
C2	97.4(18)	104(2)	141(2)	51.0(17)	82.1(18)	8.1(16)
C3	63.0(15)	85.7(19)	91(2)	46.4(16)	47.5(15)	18.5(13)
C4	68.0(15)	78.2(17)	74.7(16)	32.1(13)	46.7(14)	23.4(13)
C5	61.1(14)	61.3(14)	68.2(15)	22.1(11)	38.8(12)	12.4(11)
C6	56.5(13)	56.5(13)	67.3(14)	25.5(11)	37.5(12)	15.0(10)
C7	69.8(15)	55.0(13)	83.2(17)	19.3(12)	54.2(14)	13.4(11)
C8	62.2(13)	51.1(12)	71.1(15)	16.4(10)	45.2(12)	15.0(10)
C9	55.1(12)	46.3(11)	60.7(13)	11.5(9)	36.5(11)	12.0(9)
C10	53.0(11)	42.4(10)	59.5(12)	10.0(9)	36.3(10)	5.1(8)
C11	55.3(12)	39.1(10)	63.1(13)	9.1(9)	37.6(11)	5.7(8)
C12	61.8(13)	44.2(11)	69.4(14)	16.6(10)	43.9(12)	8.8(9)
C13	72.1(15)	40.7(11)	78.6(16)	19.5(10)	47.9(13)	13.1(10)
C14	63.7(14)	44.0(11)	77.2(16)	11.0(10)	44.5(13)	12.7(10)
O15	94.2(14)	49.3(9)	118.2(16)	20.6(10)	76.8(13)	23.4(9)
C16	63.4(13)	41.3(10)	75.1(15)	12.2(10)	46.4(12)	6.1(9)
C17	58.4(13)	38.7(10)	67.6(14)	9.7(9)	35.3(11)	7.5(9)
C18	57.6(12)	43.1(11)	60.3(13)	7.4(9)	33.3(11)	10.2(9)
C19	83.9(18)	54.3(13)	80.6(17)	9.1(12)	54.5(15)	19.5(12)
C20	230(5)	54.2(17)	176(4)	24(2)	159(4)	46(2)
C21	123(3)	41.8(13)	161(4)	14.1(17)	97(3)	15.5(15)
C22	81.3(18)	39.8(11)	104(2)	14.0(12)	55.8(17)	7.6(11)
C23	89(2)	64.1(16)	112(2)	32.0(16)	60(2)	5.4(15)
C24	83.3(18)	57.4(14)	92(2)	22.0(13)	55.8(17)	12.5(13)

C28	89.2(18)	38.3(11)	120(2)	18.7(12)	79.8(19)	8.8(11)
C29	86.3(18)	48.8(13)	121(2)	18.1(13)	81.1(19)	11.1(12)
F1	191(4)	85(2)	172(3)	67(2)	140(3)	30(2)
F2	132(3)	112(2)	172(3)	60(2)	127(3)	32(2)
F3	120(3)	245(7)	178(3)	44(4)	71(2)	-55(4)
F1A	172(6)	197(8)	151(3)	80(4)	92(4)	4(6)
F2A	99(3)	92(4)	194(5)	59(4)	113(3)	25(3)
F3A	100(4)	86(3)	212(5)	49(3)	110(4)	4(2)

Table S13 Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C9	1.364(2)	C8	C9	1.363(3)
O1	C10	1.367(2)	C9	C18	1.447(3)
C1	O15	1.426(3)	C10	C11	1.461(3)
O2	C22	1.202(3)	C10	C16	1.338(3)
O3	C7	1.222(3)	C11	C12	1.391(3)
C2	C3	1.481(4)	C11	C28	1.389(3)
C2	F1	1.354(6)	C12	C13	1.380(3)
C2	F2	1.407(6)	C13	C14	1.386(3)
C2	F3	1.203(7)	C14	O15	1.367(3)
C2	F1A	1.094(11)	C14	C29	1.379(3)
C2	F2A	1.409(9)	C16	C17	1.424(3)
C2	F3A	1.479(9)	C17	C18	1.357(3)
C3	C4	1.379(4)	C17	C22	1.503(3)
C3	C23	1.380(5)	C18	C19	1.506(3)
C4	C5	1.384(3)	C19	C20	1.523(5)
C5	C6	1.387(3)	C20	C21	1.400(5)
C6	C7	1.509(3)	C21	C22	1.484(4)
C6	C24	1.383(4)	C23	C24	1.381(4)
C7	C8	1.449(3)	C28	C29	1.375(3)

Table S14 Bond Angles for 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O1	C10	123.03(17)	C16	C10	O1	119.84(19)
F1	C2	C3	111.1(4)	C16	C10	C11	128.7(2)
F1	C2	F2	95.9(4)	C12	C11	C10	121.30(19)
F2	C2	C3	113.0(3)	C28	C11	C10	120.79(19)
F3	C2	C3	116.8(5)	C28	C11	C12	117.9(2)
F3	C2	F1	111.7(5)	C13	C12	C11	120.8(2)
F3	C2	F2	106.3(5)	C12	C13	C14	120.2(2)
F1A	C2	C3	123.5(8)	O15	C14	C13	115.6(2)
F1A	C2	F2A	118.8(9)	O15	C14	C29	124.8(2)
F1A	C2	F3A	101.2(9)	C29	C14	C13	119.5(2)
F2A	C2	C3	109.3(4)	C14	O15	C1	117.6(2)
F2A	C2	F3A	85.6(5)	C10	C16	C17	119.9(2)
F3A	C2	C3	110.6(4)	C16	C17	C22	117.5(2)
C4	C3	C2	119.2(3)	C18	C17	C16	120.9(2)
C4	C3	C23	120.7(2)	C18	C17	C22	121.6(2)
C23	C3	C2	120.1(3)	C9	C18	C19	119.4(2)
C3	C4	C5	119.4(3)	C17	C18	C9	118.27(19)

C4	C5	C6	120.5(3)	C17	C18	C19	122.3(2)
C5	C6	C7	123.1(2)	C18	C19	C20	110.7(2)
C24	C6	C5	119.3(2)	C21	C20	C19	118.7(3)
C24	C6	C7	117.5(2)	C20	C21	C22	114.2(3)
O3	C7	C6	118.2(2)	O2	C22	C17	120.2(2)
O3	C7	C8	124.6(2)	O2	C22	C21	123.2(2)
C8	C7	C6	117.2(2)	C21	C22	C17	116.5(2)
C9	C8	C7	125.8(2)	C3	C23	C24	119.6(3)
O1	C9	C18	117.86(18)	C23	C24	C6	120.4(3)
C8	C9	O1	116.71(19)	C29	C28	C11	121.5(2)
C8	C9	C18	125.4(2)	C28	C29	C14	120.0(2)
O1	C10	C11	111.41(17)				

Table S15 Torsion Angles for 1.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C9	C18	C17	4.3(3)	C12	C13	C14	C29	-1.8(4)
O1	C9	C18	C19	-176.2(2)	C13	C14	O15	C1	-175.7(3)
O1	C10	C11	C12	-0.3(3)	C13	C14	C29	C28	1.5(5)
O1	C10	C11	C28	179.3(2)	O15	C14	C29	C28	179.3(3)
O1	C10	C16	C17	3.1(4)	C16	C10	C11	C12	177.9(3)
O3	C7	C8	C9	1.4(5)	C16	C10	C11	C28	-2.5(4)
C2	C3	C4	C5	-179.6(3)	C16	C17	C18	C9	-3.7(4)
C2	C3	C23	C24	-179.6(3)	C16	C17	C18	C19	176.9(2)
C3	C4	C5	C6	0.2(4)	C16	C17	C22	O2	-0.9(5)
C3	C23	C24	C6	-1.9(5)	C16	C17	C22	C21	177.0(3)
C4	C3	C23	C24	0.5(5)	C17	C18	C19	C20	-14.3(4)
C4	C5	C6	C7	-178.9(2)	C18	C17	C22	O2	178.2(3)
C4	C5	C6	C24	-1.6(4)	C18	C17	C22	C21	-3.9(5)
C5	C6	C7	O3	154.4(3)	C18	C19	C20	C21	40.6(6)
C5	C6	C7	C8	-26.7(4)	C19	C20	C21	C22	-48.1(7)
C5	C6	C24	C23	2.4(4)	C20	C21	C22	O2	-153.9(4)
C6	C7	C8	C9	-177.4(2)	C20	C21	C22	C17	28.3(5)
C7	C6	C24	C23	179.9(3)	C22	C17	C18	C9	177.3(2)
C7	C8	C9	O1	1.1(4)	C22	C17	C18	C19	-2.1(4)
C7	C8	C9	C18	-178.4(3)	C23	C3	C4	C5	0.3(5)
C8	C9	C18	C17	-176.2(2)	C24	C6	C7	O3	-23.0(4)
C8	C9	C18	C19	3.3(4)	C24	C6	C7	C8	155.9(3)
C9	O1	C10	C11	175.9(2)	C28	C11	C12	C13	1.6(4)
C9	O1	C10	C16	-2.4(4)	C29	C14	O15	C1	6.4(5)
C9	C18	C19	C20	166.2(3)	F1	C2	C3	C4	-113.1(4)
C10	O1	C9	C8	179.1(2)	F1	C2	C3	C23	66.9(6)
C10	O1	C9	C18	-1.3(3)	F2	C2	C3	C4	-6.6(5)
C10	C11	C12	C13	-178.8(2)	F2	C2	C3	C23	173.5(4)
C10	C11	C28	C29	178.4(3)	F3	C2	C3	C4	117.1(7)
C10	C16	C17	C18	0.0(4)	F3	C2	C3	C23	-62.8(7)
C10	C16	C17	C22	179.0(2)	F1A	C2	C3	C4	-73.9(12)
C11	C10	C16	C17	-174.9(2)	F1A	C2	C3	C23	106.2(12)
C11	C12	C13	C14	0.2(4)	F2A	C2	C3	C4	73.7(6)
C11	C28	C29	C14	0.4(5)	F2A	C2	C3	C23	-106.2(6)
C12	C11	C28	C29	-1.9(5)	F3A	C2	C3	C4	166.3(5)

C12 C13 C14 O15 -179.8(2) F3A C2 C3 C23 -13.7(6)

Table S16 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2 ×10^3) for 1.

Atom	*x*	*y*	*z*	U(eq)
H1A	10078.79	2047.75	-1052.33	133
H1B	10944.33	940.17	-388.36	133
H1C	11358.31	2314.71	412.8	133
H4	946.3	4399.09	5872.87	79
H5	2595.83	5143.49	5011.98	70
H8	3229.25	5771.87	3508.68	66
H12	6290.95	3020.56	1861.73	63
H13	7586.82	1439.94	1332.55	68
H16	7018.64	6912.17	963.26	65
H19A	4211.67	7842.32	4061.14	79
H19B	2951.76	7911.57	2627.77	79
H20A	3937.13	9924.43	3420.43	153
H20B	5602.25	9564.12	4085.96	153
H21A	5499.95	10569.06	2502.89	115
H21B	3978.34	9785.83	1477.08	115
H23	555.81	969.31	3790.16	97
H24	2249.21	1703.24	2973.2	84
H28	8233.06	5418.74	363.18	84
H29	9542.75	3849.1	-146.78	87

Table S17 Atomic Occupancy for 1.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
F1	0.651(5)	F2	0.651(5)	F3	0.651(5)
F1A	0.349(5)	F2A	0.349(5)	F3A	0.349(5)

Experimental

Single crystals of $C_{25}H_{19}F_3O_4$ **[1]** were **[]**. A suitable crystal was selected and **[]** on a diffractometer. The crystal was kept at 300 K during data collection. Using Olex2 [1], the structure was solved with the Unknown [2] structure solution program using Unknown and refined with the Unknown [3] refinement package using Unknown minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2.
3.

Crystal structure determination of [6du]

Crystal Data for $C_{25}H_{19}F_3O_4$ (M =440.40 g/mol): triclinic, space group P-1 (no. 2), a = 9.6264(17) Å, b = 10.7417(18) Å, c = 11.025(2) Å, α = 97.196(6)°, β = 113.780(6)°, γ = 92.477(6)°, V = 1029.5(3) Å^3, Z = 2, T = 300 K, μ(MoKα) = 0.113 mm^{-1}, *Dcalc* = 1.421 g/cm^3, 38754 reflections measured (4.088° ≤ 2Θ ≤ 56.546°), 5079 unique (R_{int} = 0.0598, R_{sigma} = 0.0375) which were used in all calculations. The final R_1 was 0.0815 (I > 2σ(I)) and wR_2 was 0.2684 (all data). **The CCDC deposition number 2328810** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

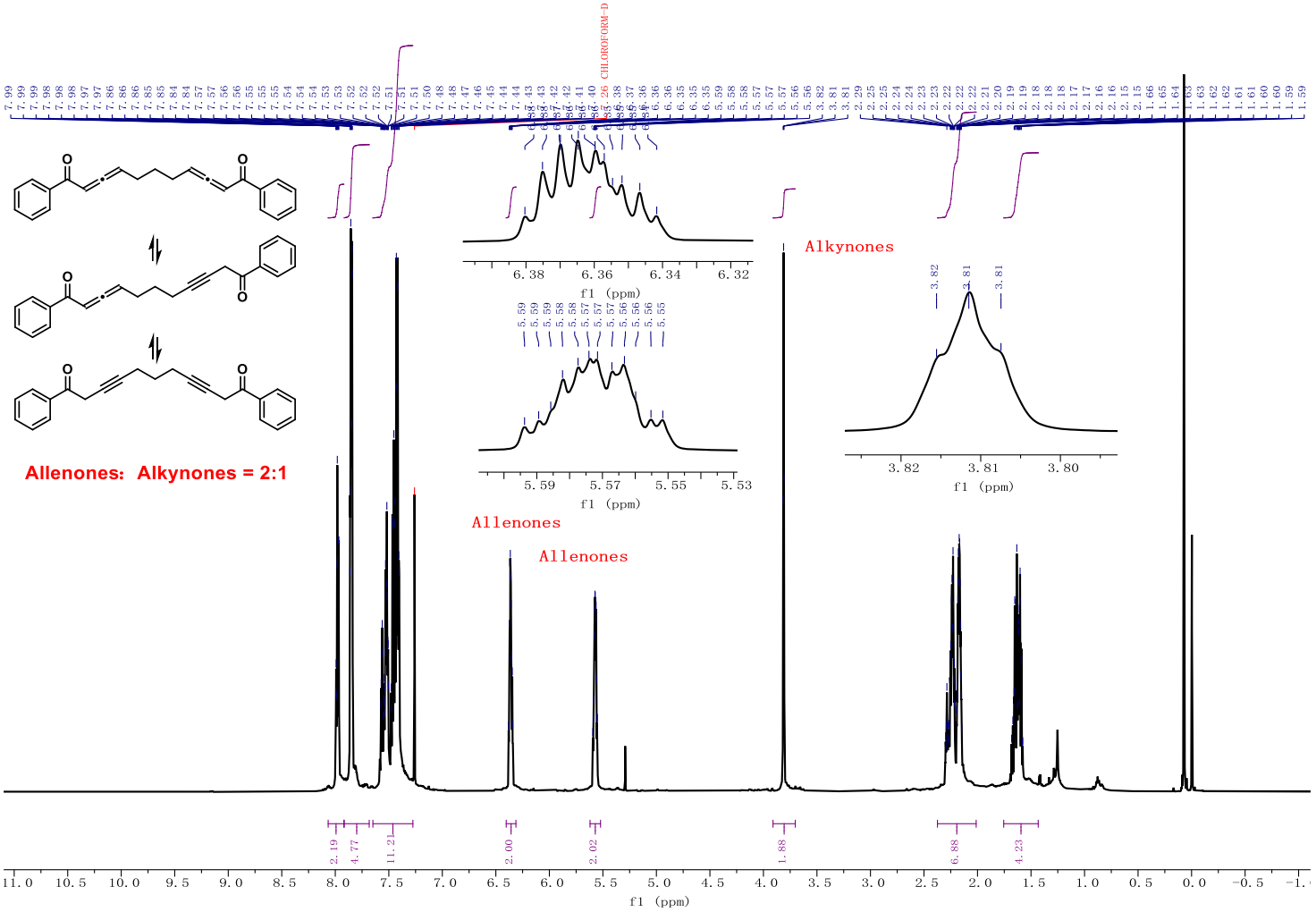
Refinement model description

Number of restraints - 114, number of constraints - unknown.

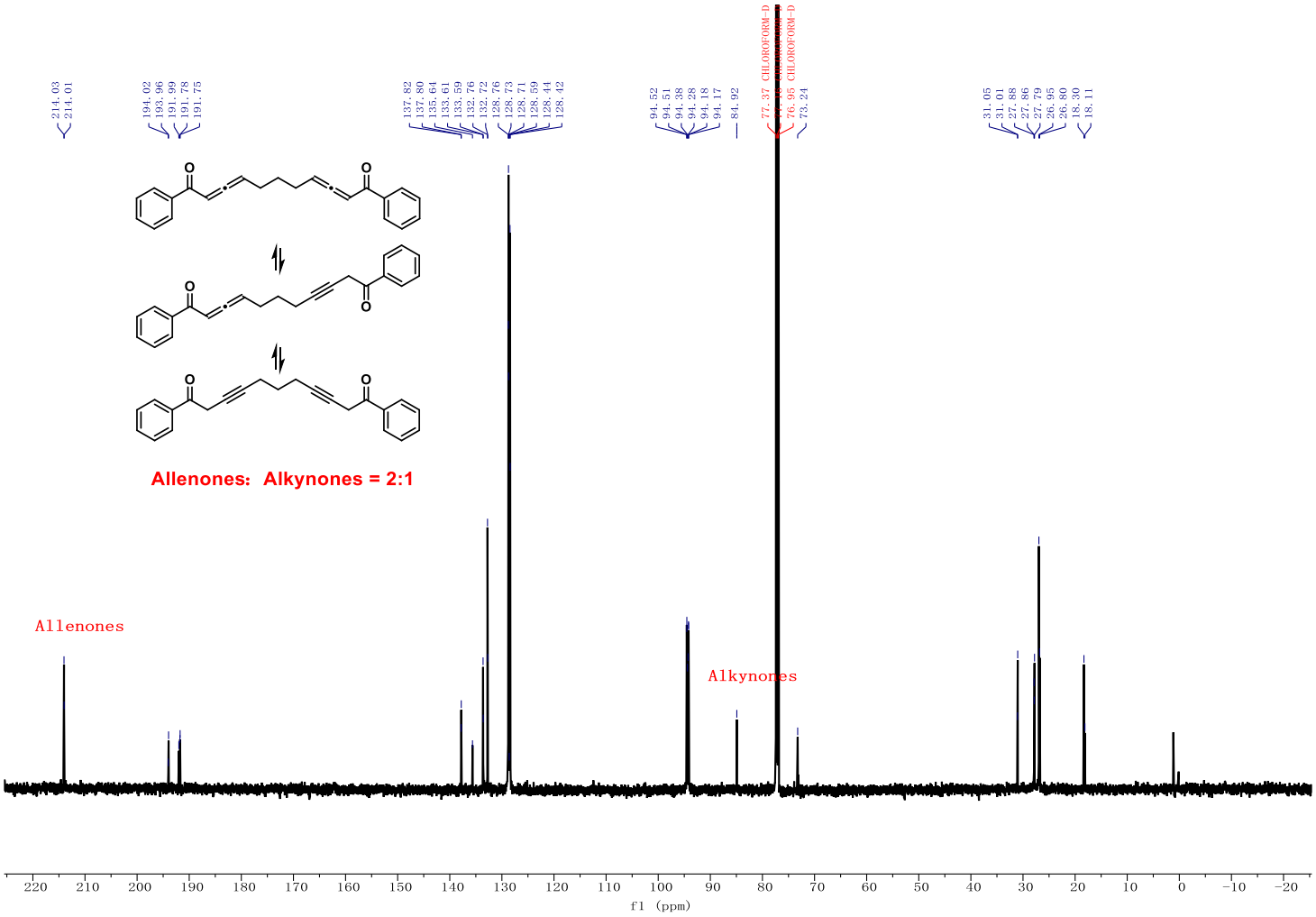
Details:
1. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups
At 1.5 times of:
All C(H,H,H) groups
2. Rigid bond restraints
C2, F1, F2, F3, F1A, F2A, F3A
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
3. Uiso/Uaniso restraints and constraints
C2 ≈ F1 ≈ F2 ≈ F3 ≈ F1A ≈ F2A ≈ F3A: within 1.7A with
sigma of 0.01 and sigma for terminal atoms of 0.02 within 1.7A
4. Rigid body (RIGU) restrains
C2, F1, F2, F3, F1A, F2A, F3A
with sigma for 1-2 distances of 0.001 and sigma for 1-3 distances of 0.001
5. Others
Sof(F1A)=Sof(F2A)=Sof(F3A)=1-FVAR(1)
Sof(F1)=Sof(F2)=Sof(F3)=FVAR(1)
6.a Secondary CH2 refined with riding coordinates:
C19(H19A,H19B), C20(H20A,H20B), C21(H21A,H21B)
6.b Aromatic/amide H refined with riding coordinates:
C4(H4), C5(H5), C8(H8), C12(H12), C13(H13), C16(H16), C23(H23), C24(H24),
C28(H28), C29(H29)
6.c Idealised Me refined as rotating group:
C1(H1A,H1B,H1C)
This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

5. NMR Spectra

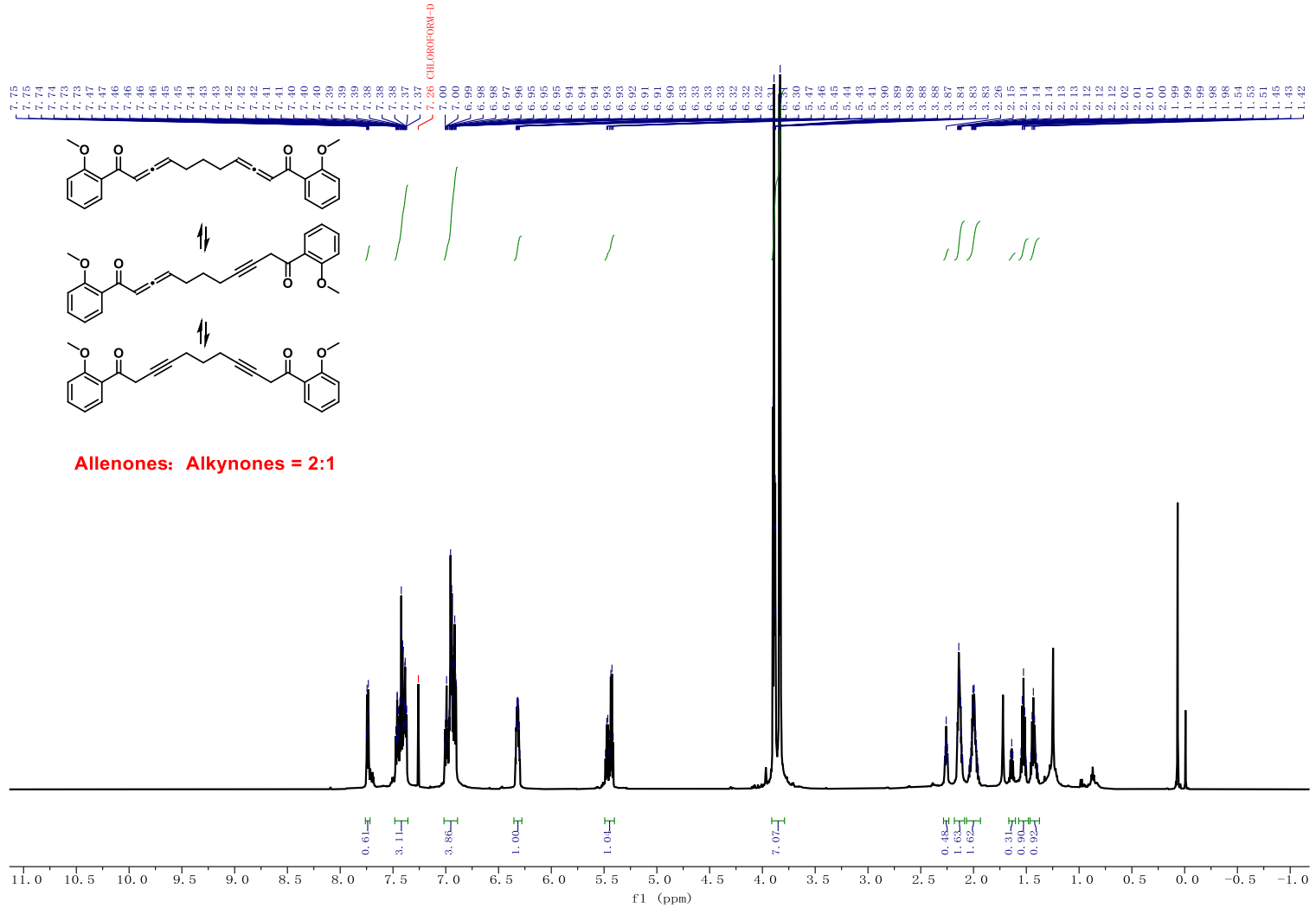
^{1}H NMR (600 MHz, $CDCl_3$) of **3a**



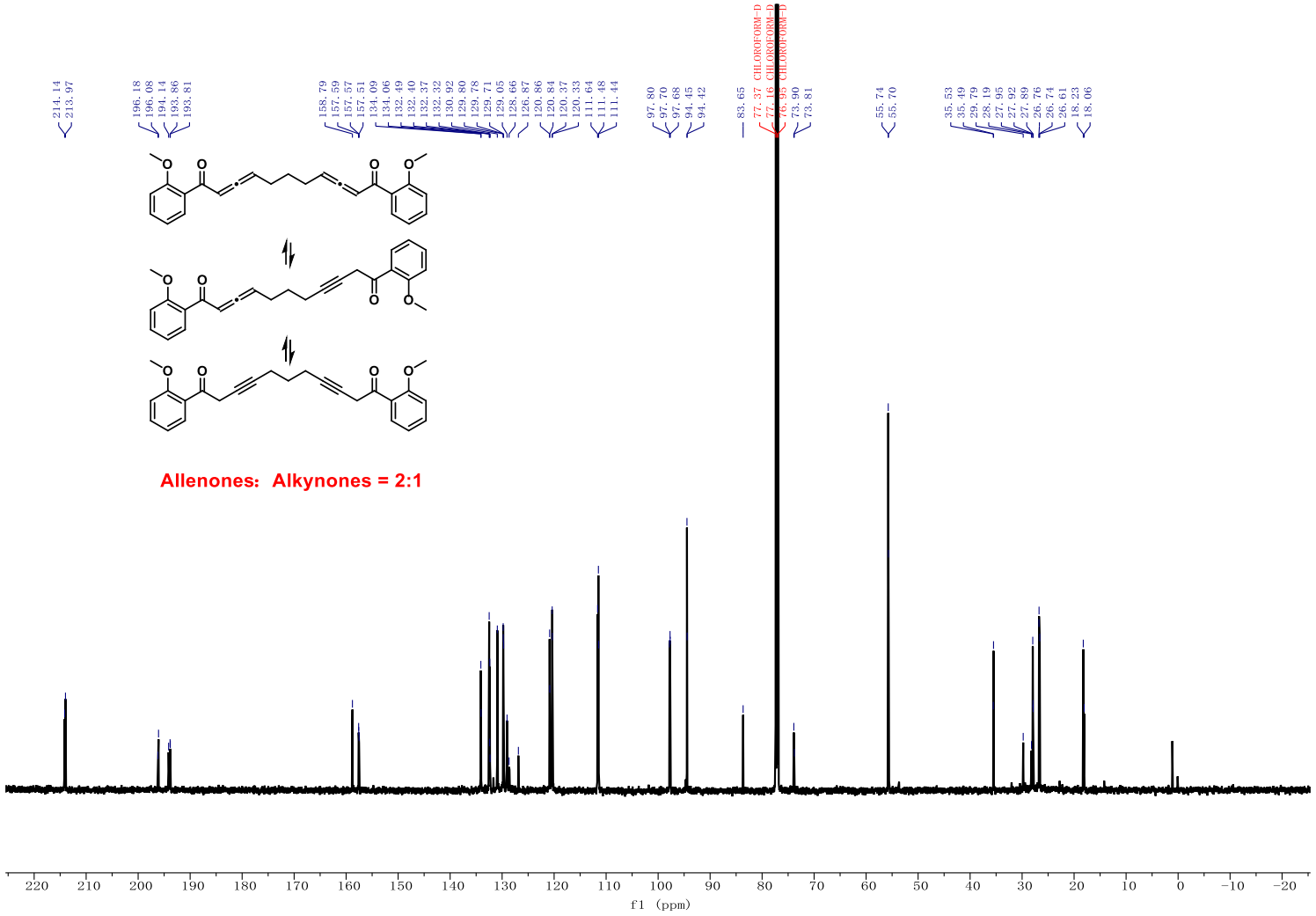
^{13}C NMR (151 MHz, $CDCl_3$) of **3a**



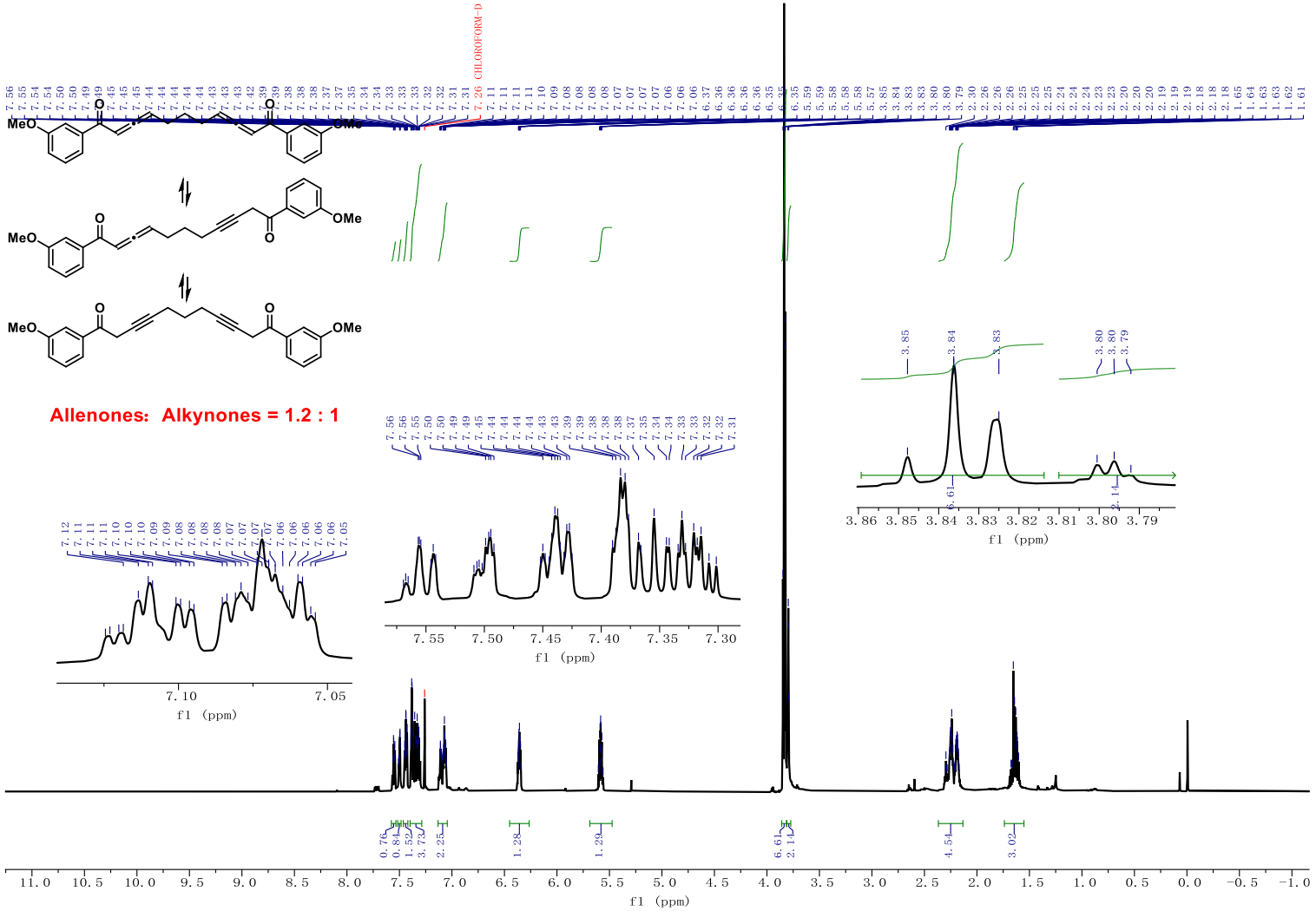
^{1}H NMR (600 MHz, $CDCl_3$) of **3b**



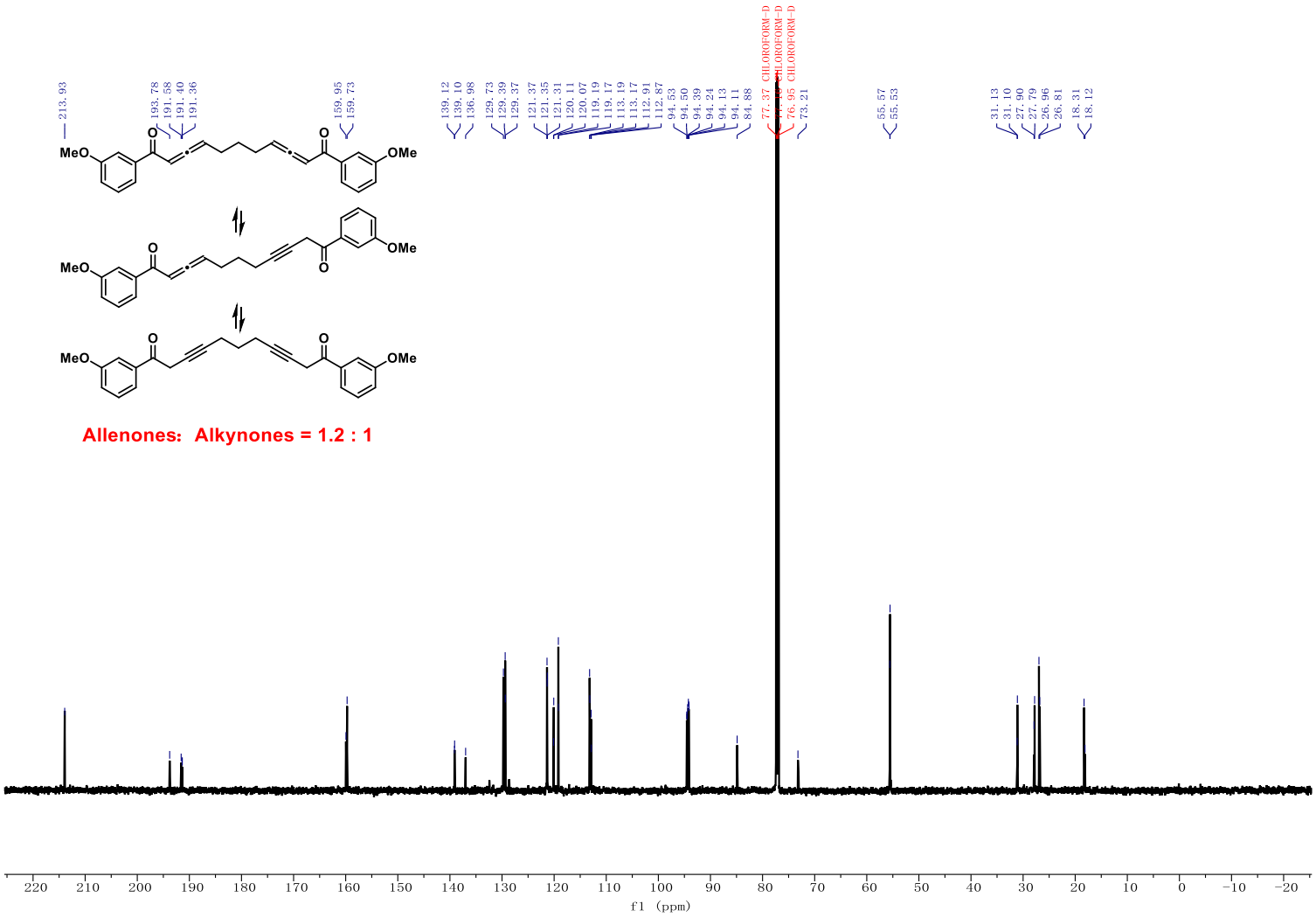
^{13}C NMR (151 MHz, $CDCl_3$) of **3b**



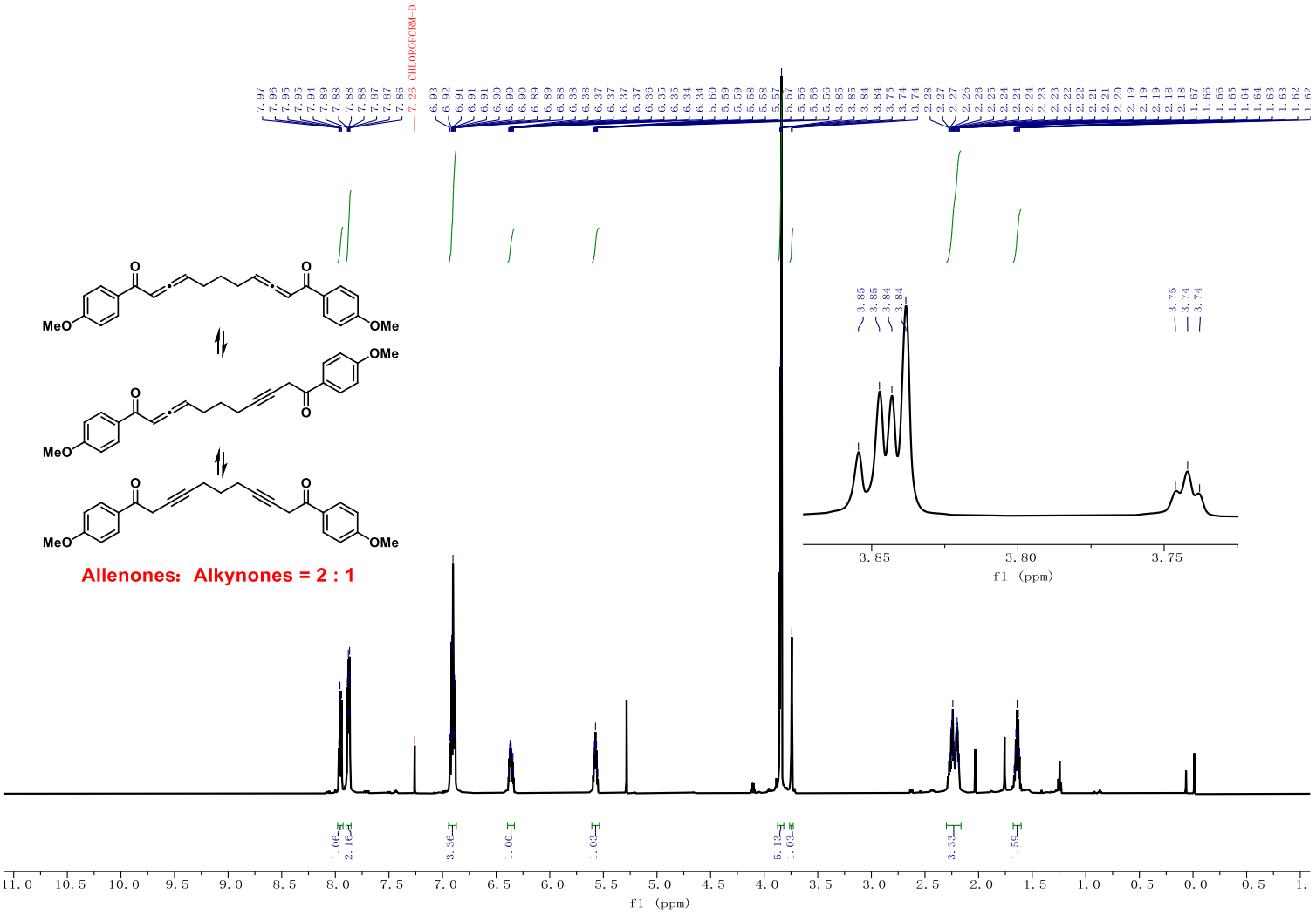
^{1}H NMR (600 MHz, $CDCl_3$) of **3c**



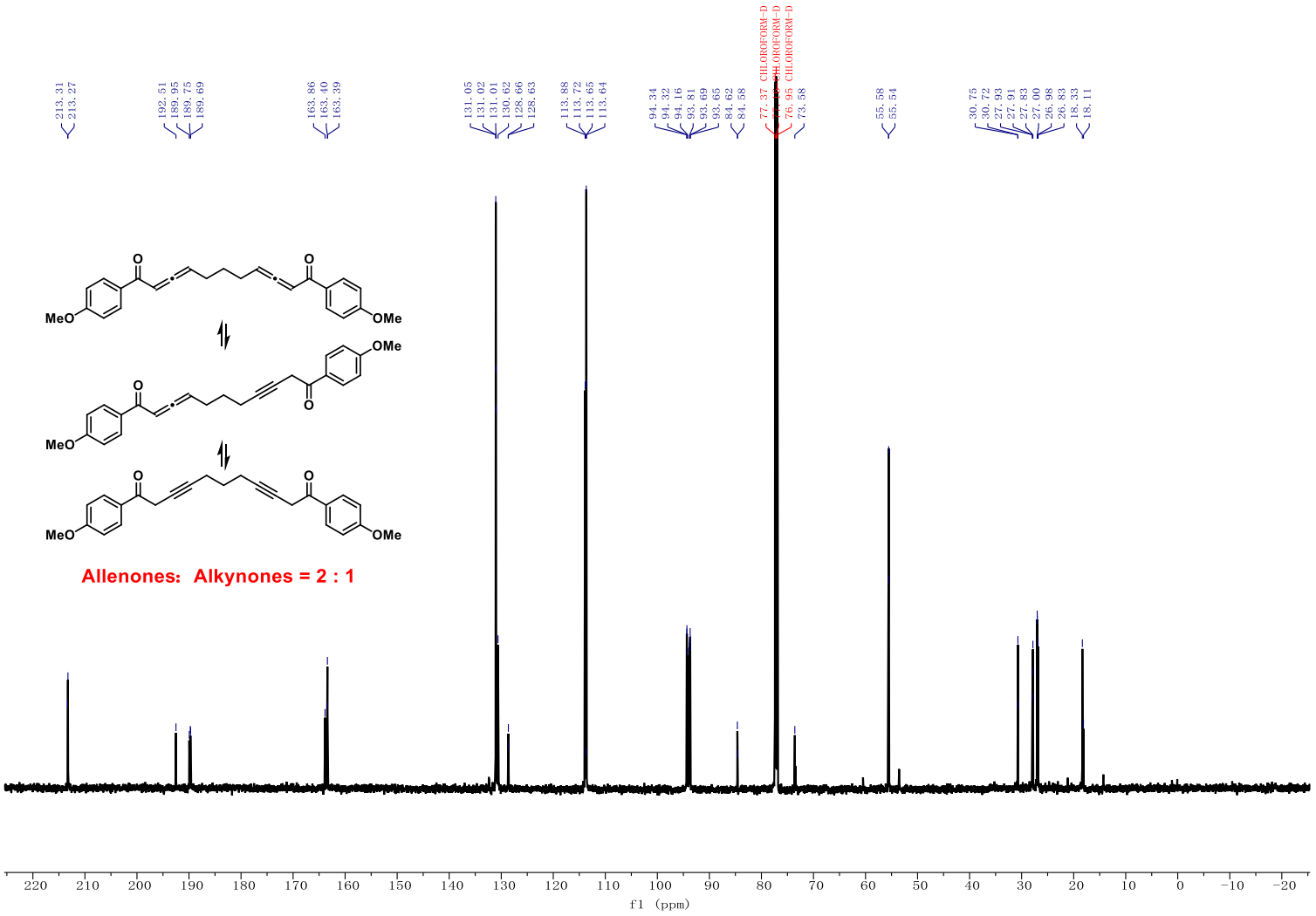
^{13}C NMR (151 MHz, $CDCl_3$) of **3c**



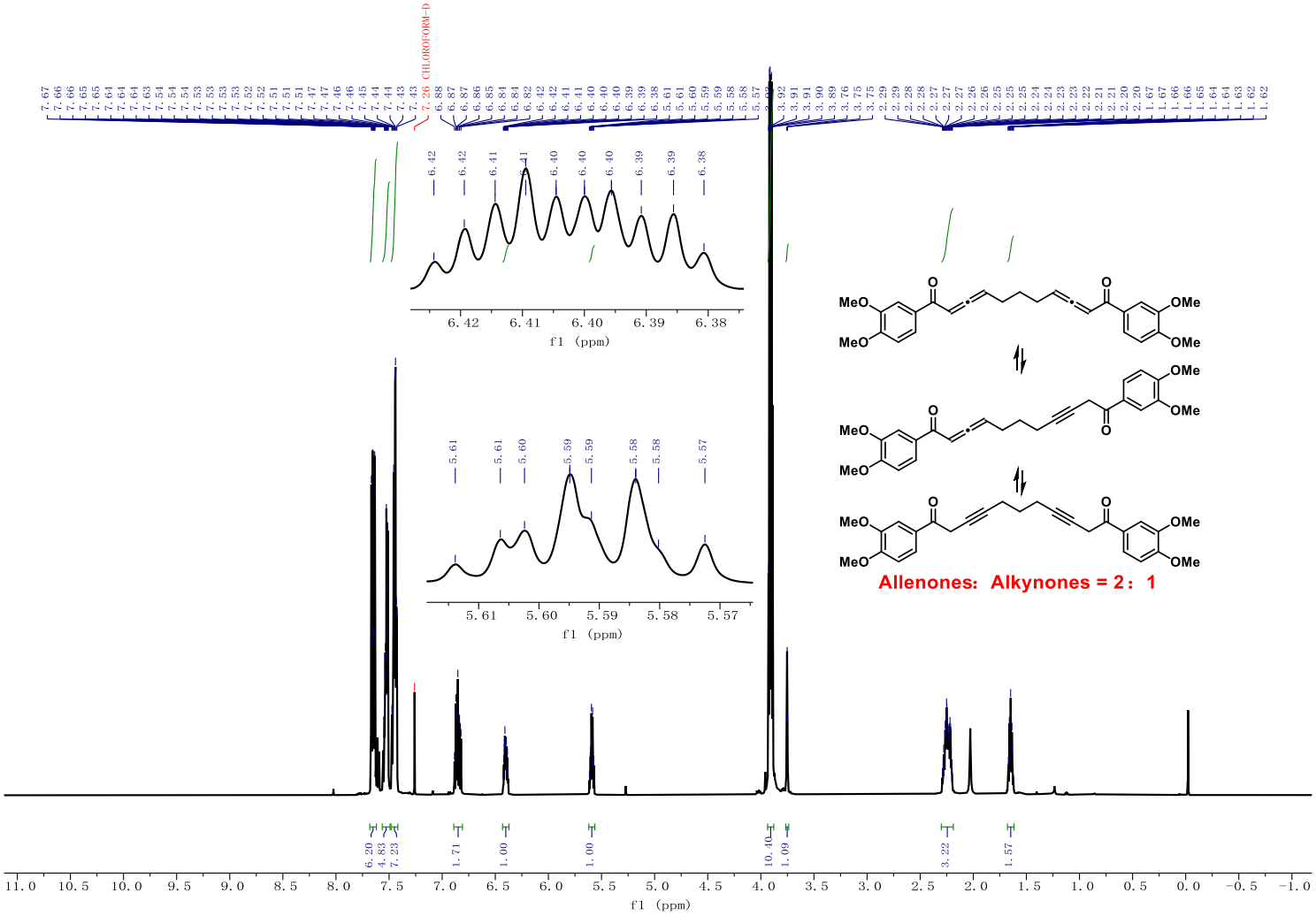
^{1}H NMR (600 MHz, $CDCl_3$) of **3d**



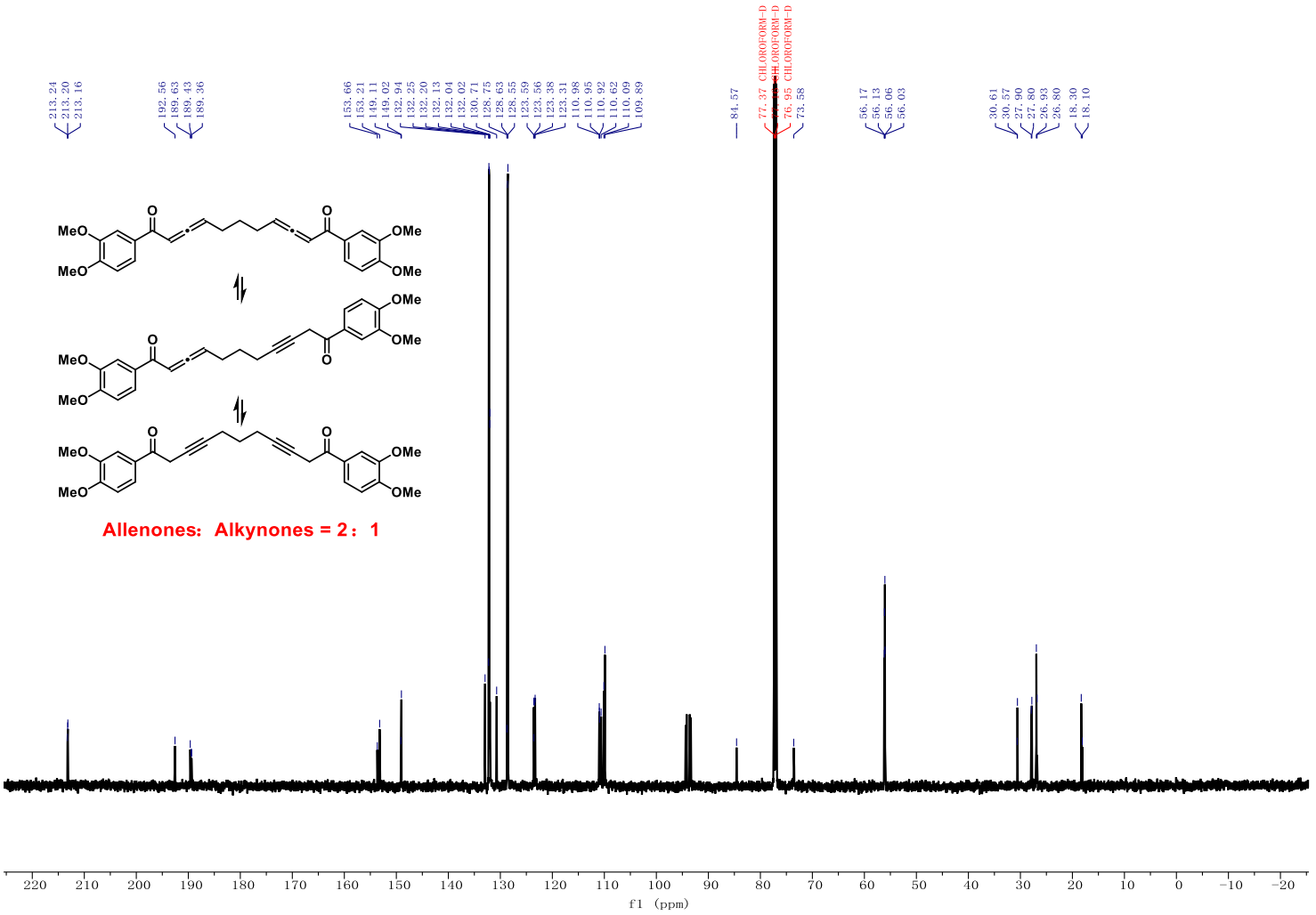
^{13}C NMR (151 MHz, $CDCl_3$) of **3d**



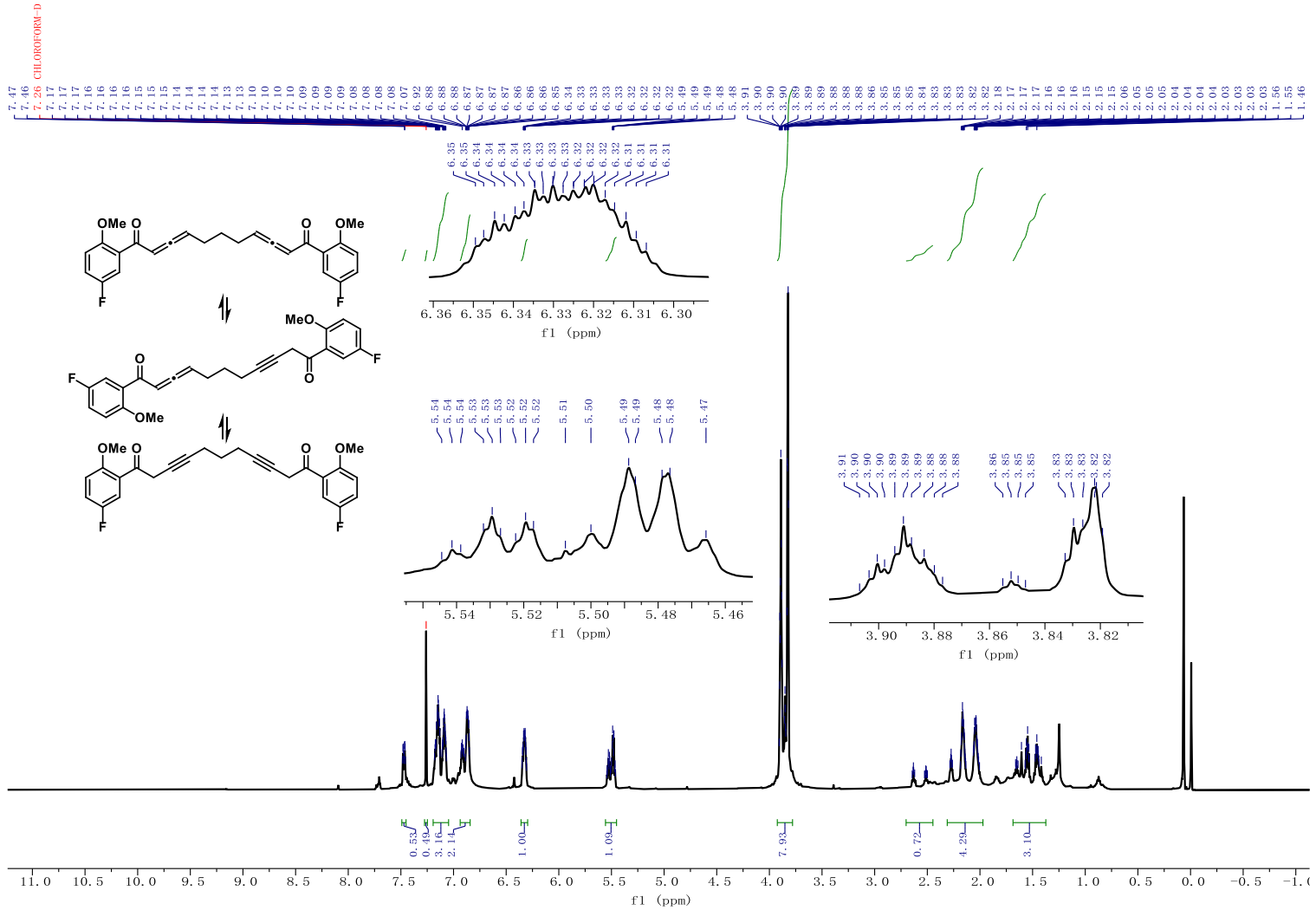
^{1}H NMR (600 MHz, $CDCl_3$) of **3e**



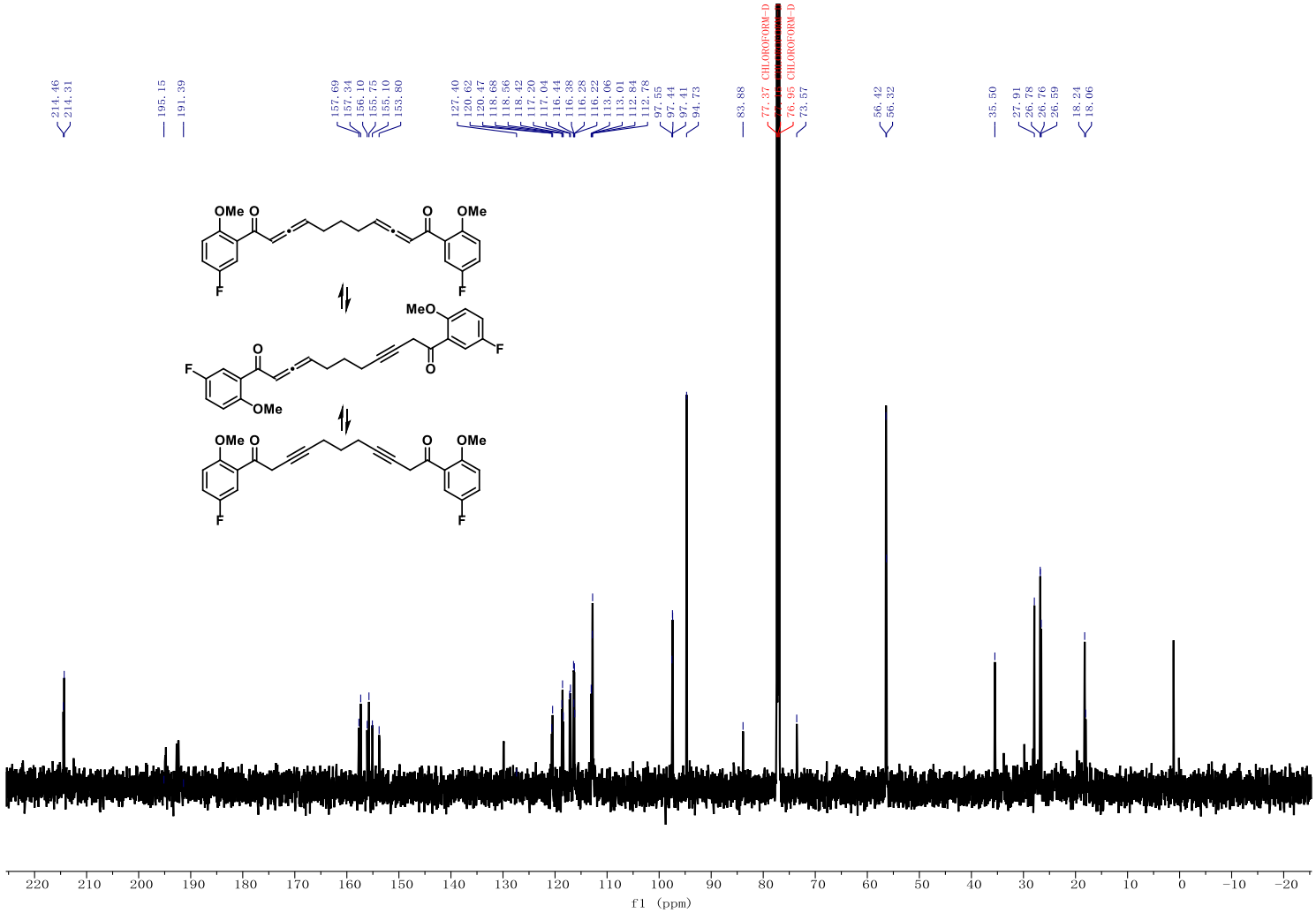
^{13}C NMR (151 MHz, $CDCl_3$) of **3e**



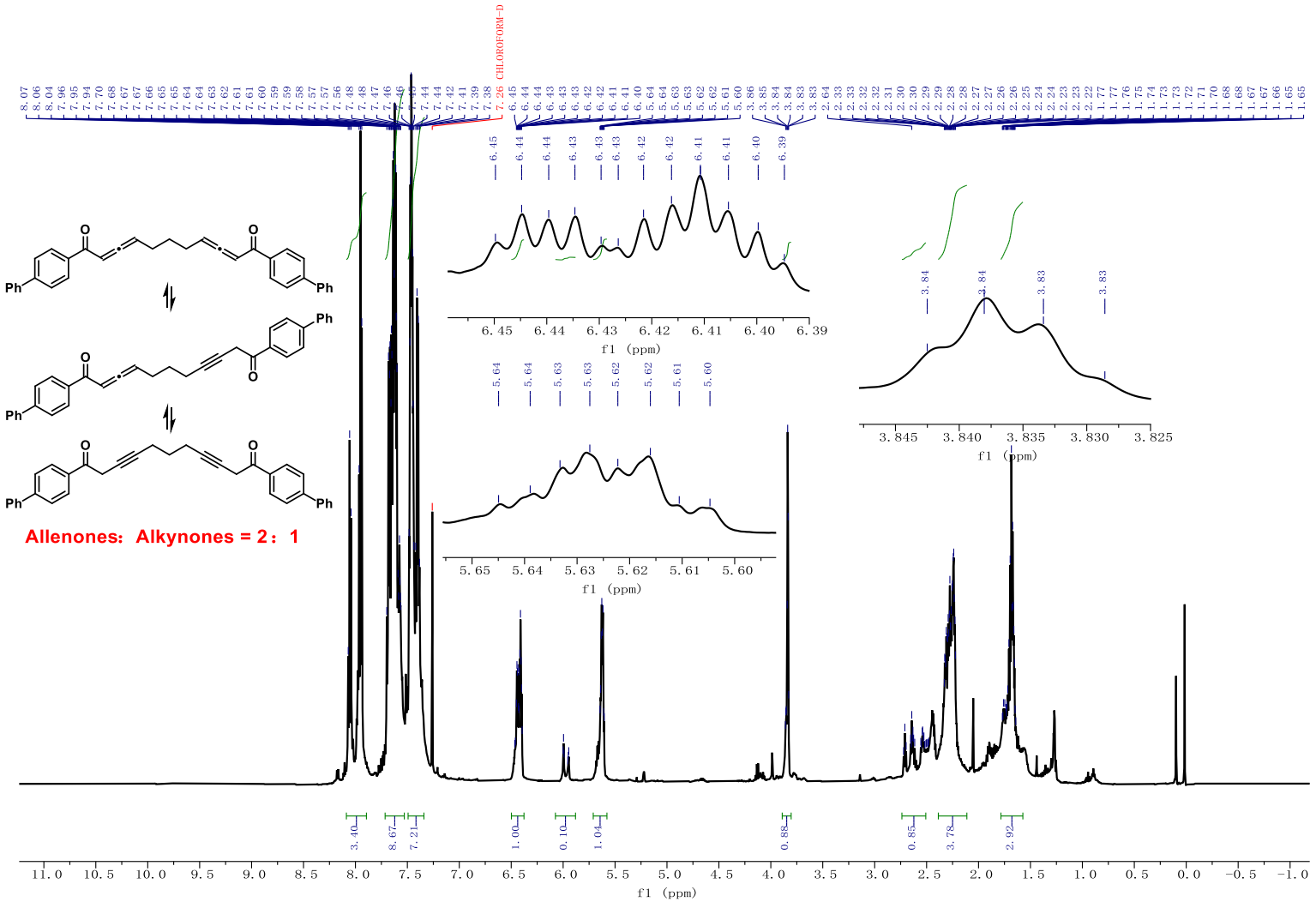
^{1}H NMR (600 MHz, $CDCl_3$) of **3f**



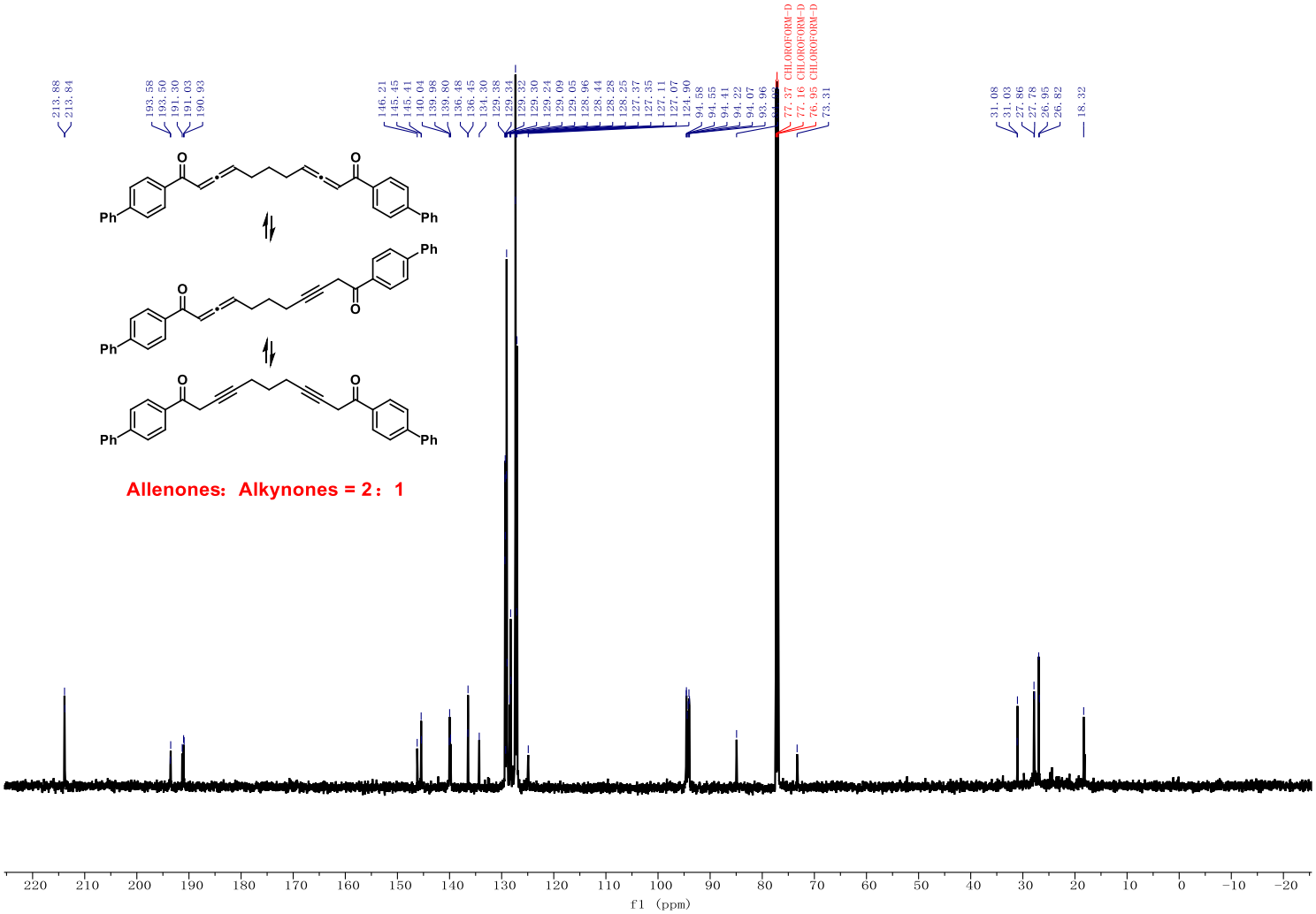
^{13}C NMR (151 MHz, $CDCl_3$) of **3f**



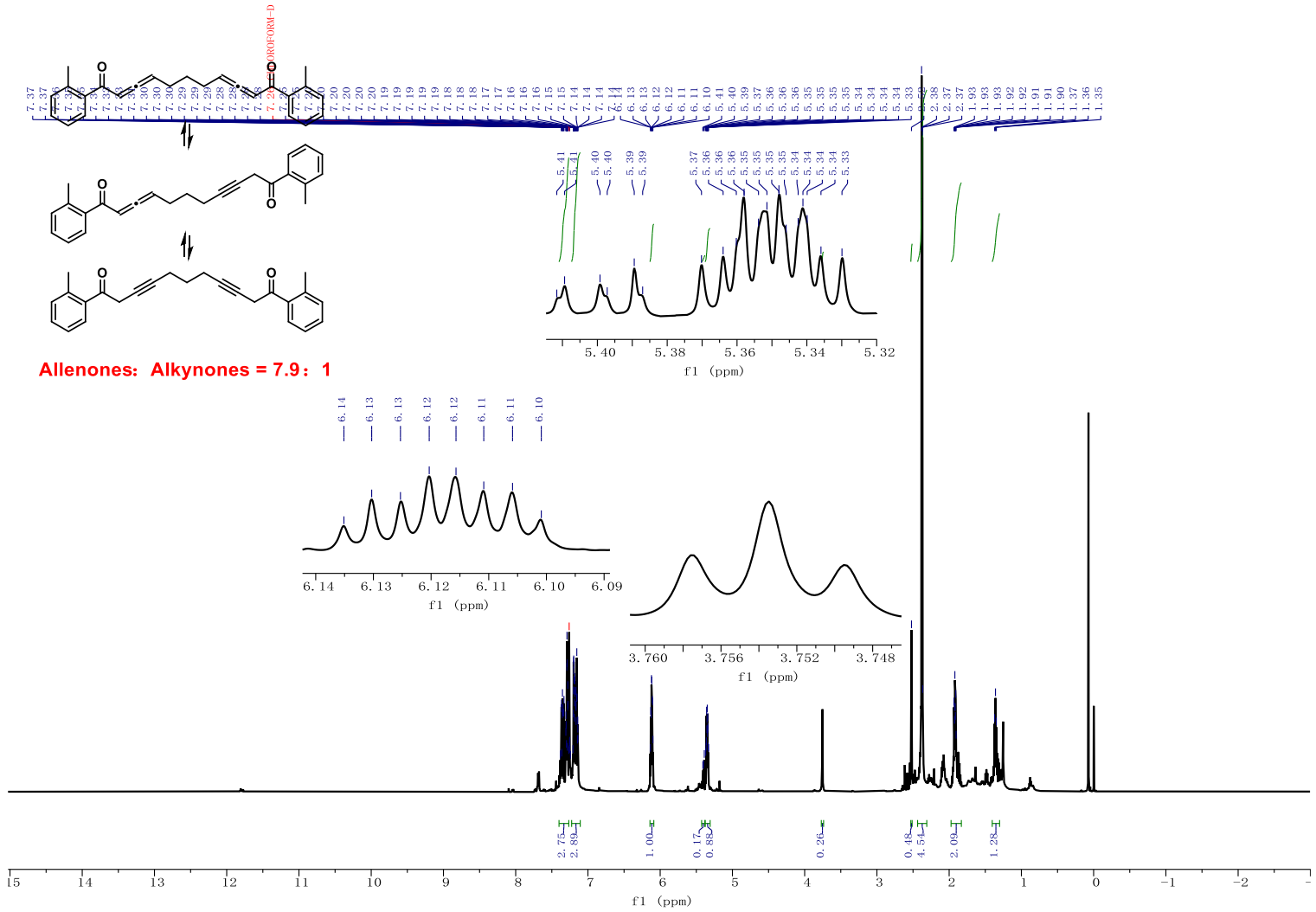
^{1}H NMR (600 MHz, $CDCl_3$) of **3g**



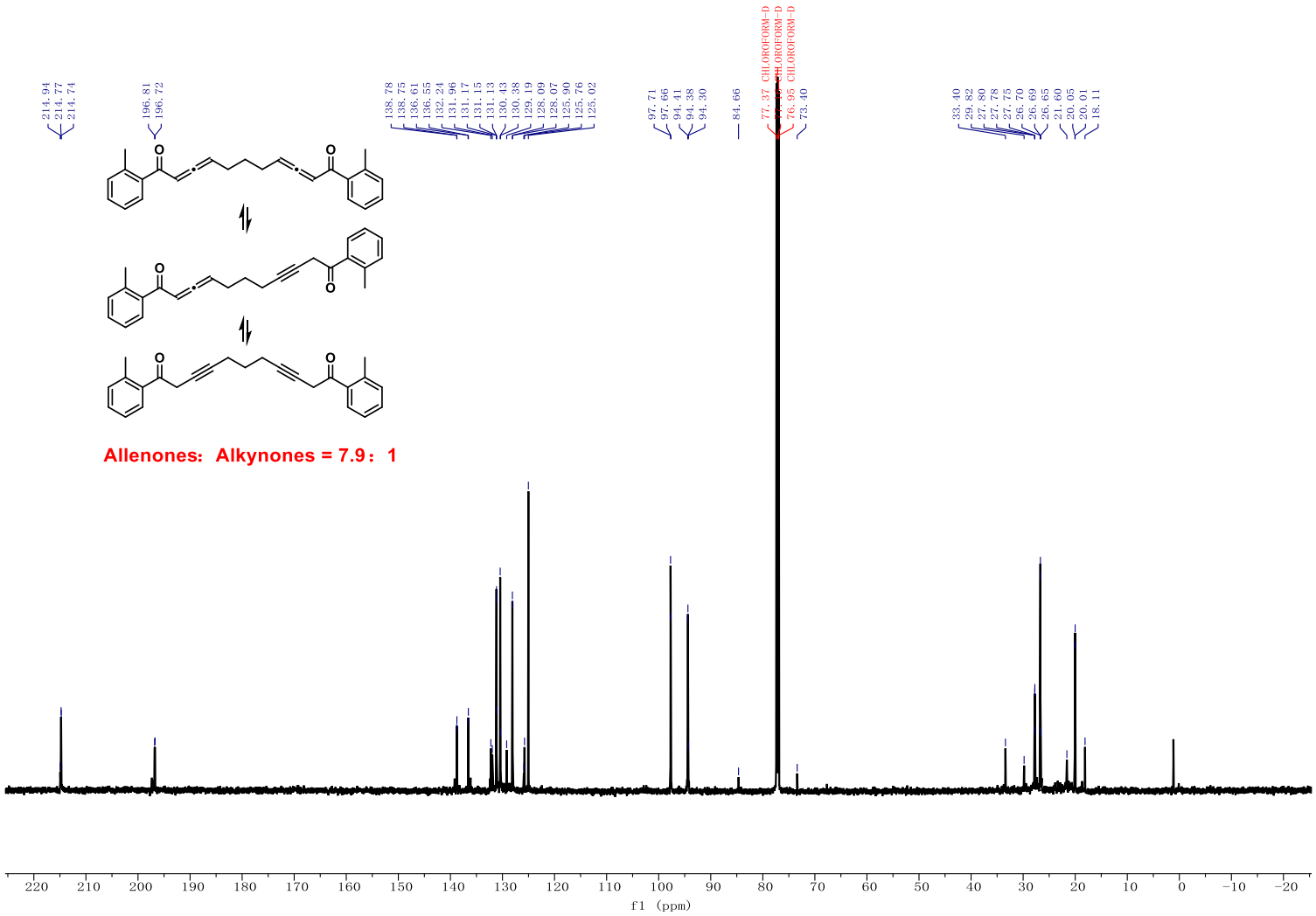
^{13}C NMR (151 MHz, $CDCl_3$) of **3g**



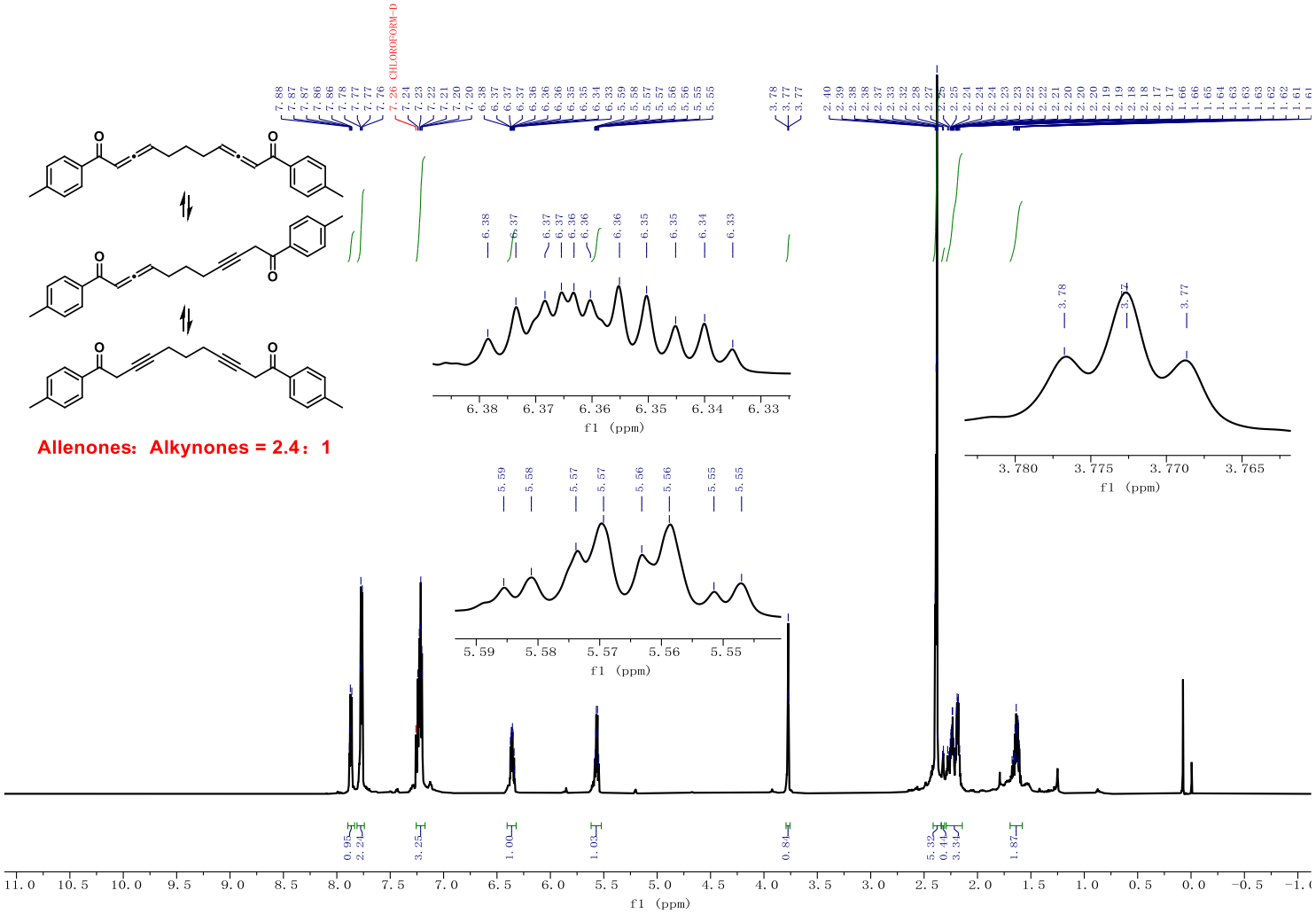
^{1}H NMR (600 MHz, $CDCl_3$) of **3h**



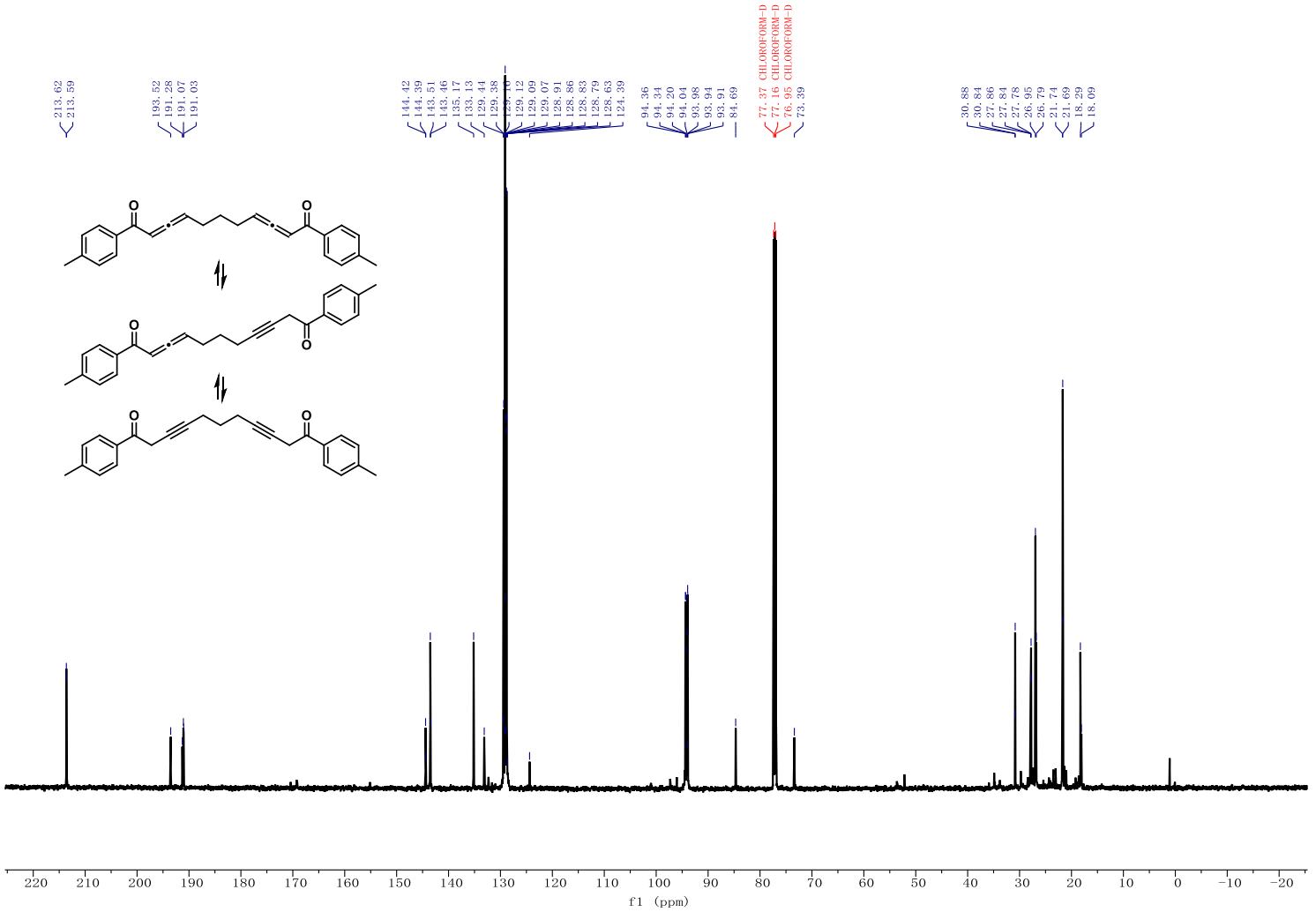
^{13}C NMR (151 MHz, $CDCl_3$) of **3h**



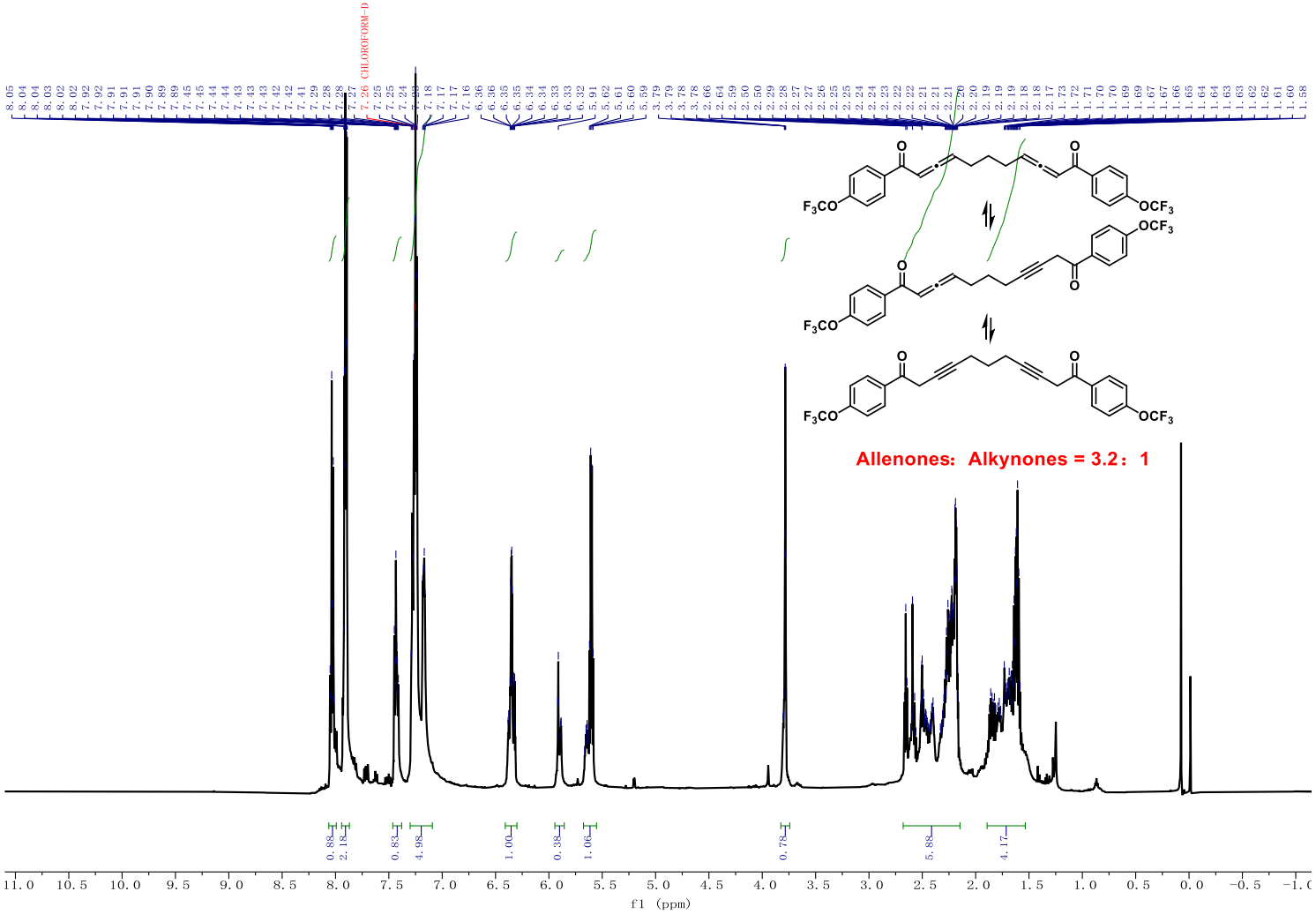
^{1}H NMR (600 MHz, $CDCl_3$) of **3i**



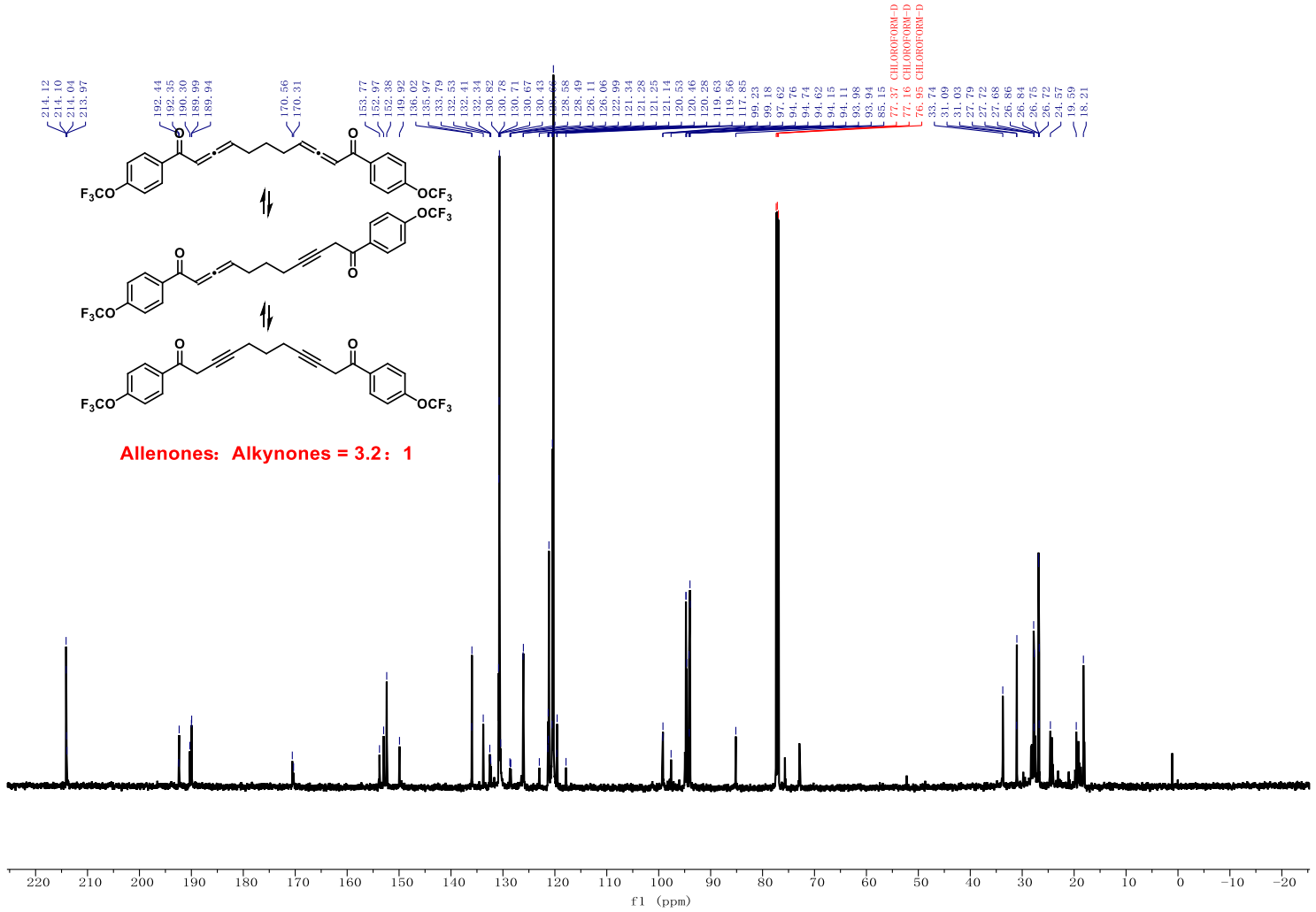
^{13}C NMR (151 MHz, $CDCl_3$) of **3i**



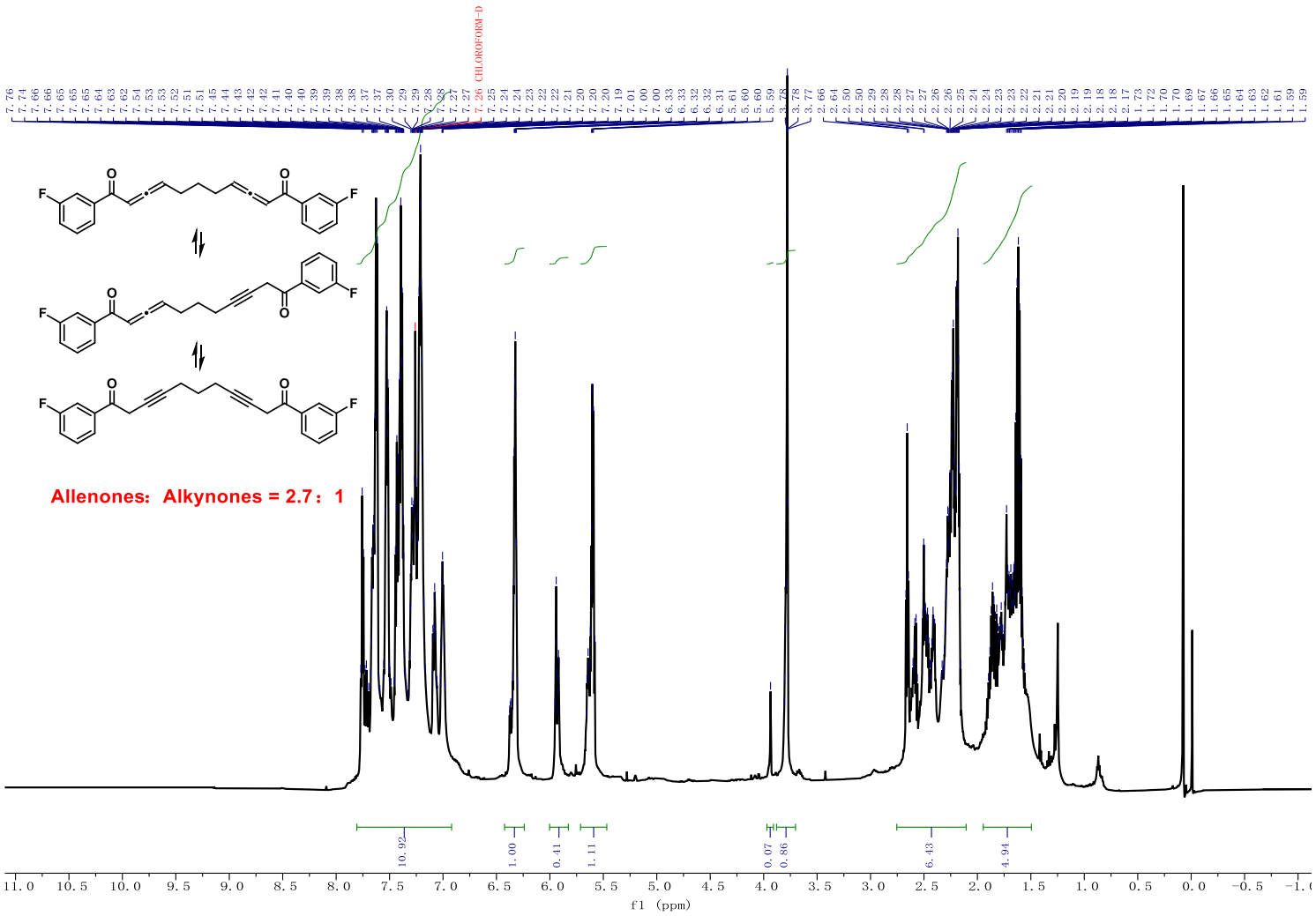
^{1}H NMR (600 MHz, $CDCl_3$) of **3j**



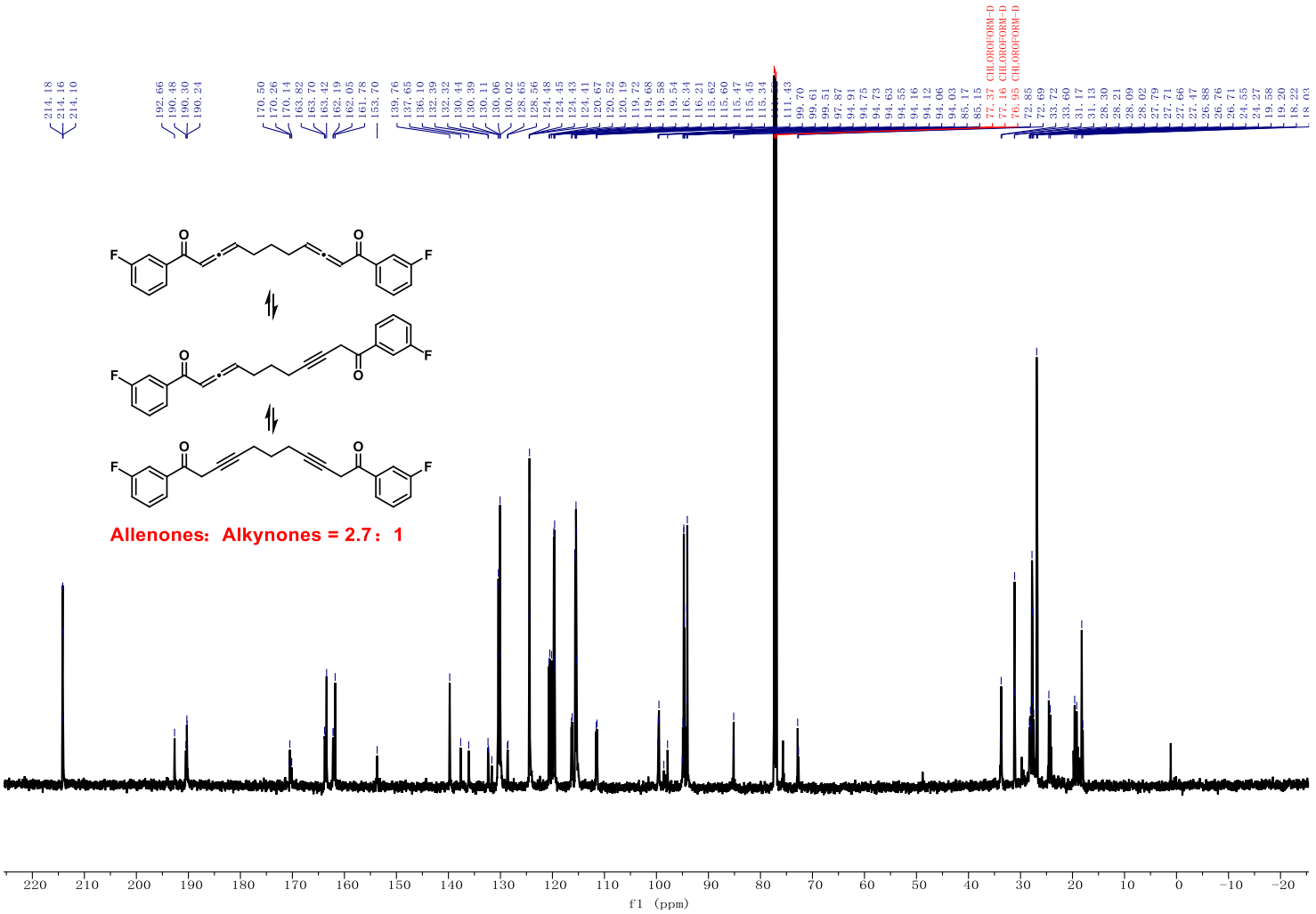
^{13}C NMR (151 MHz, $CDCl_3$) of **3j**



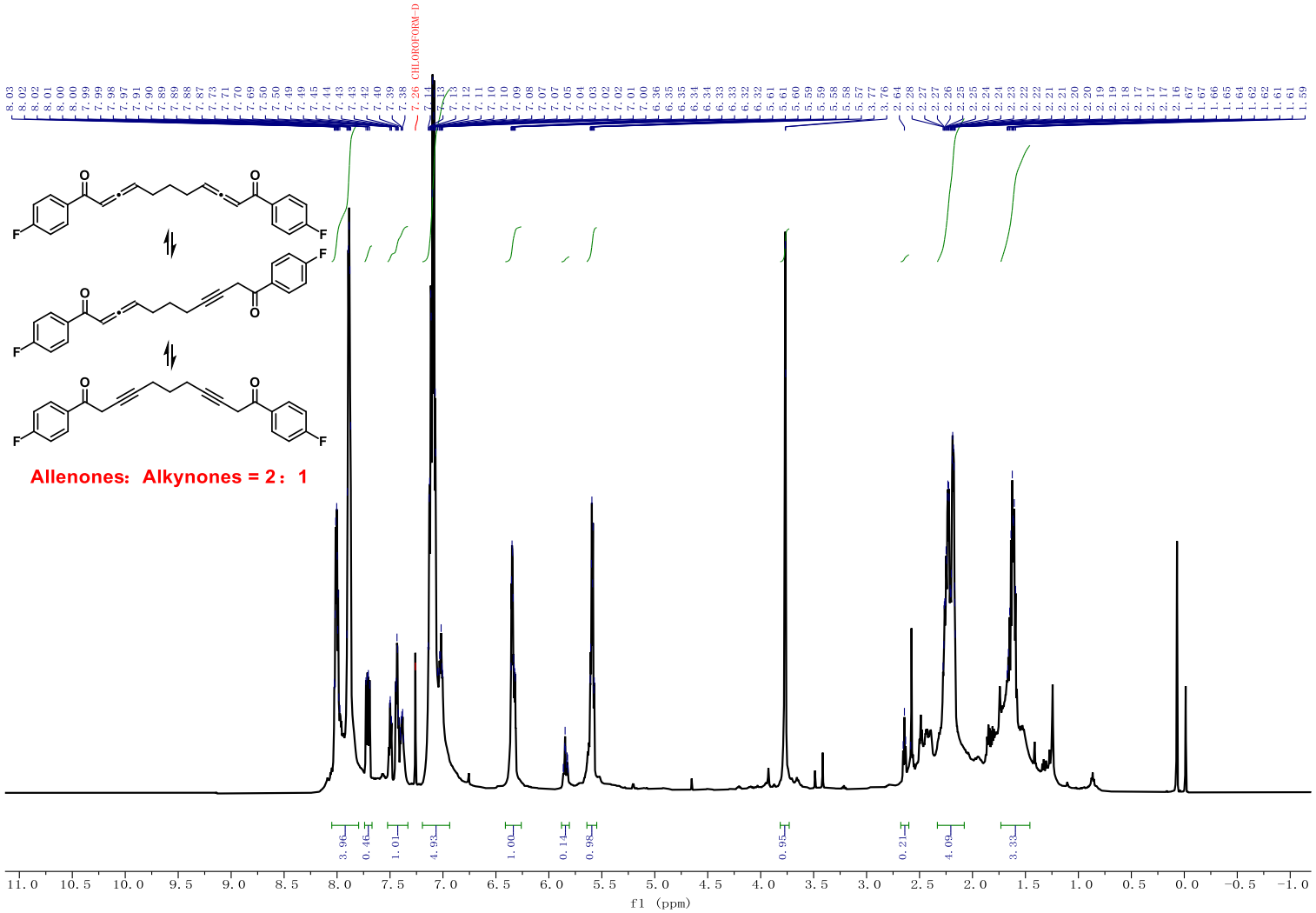
^{1}H NMR (600 MHz, $CDCl_3$) of **3k**



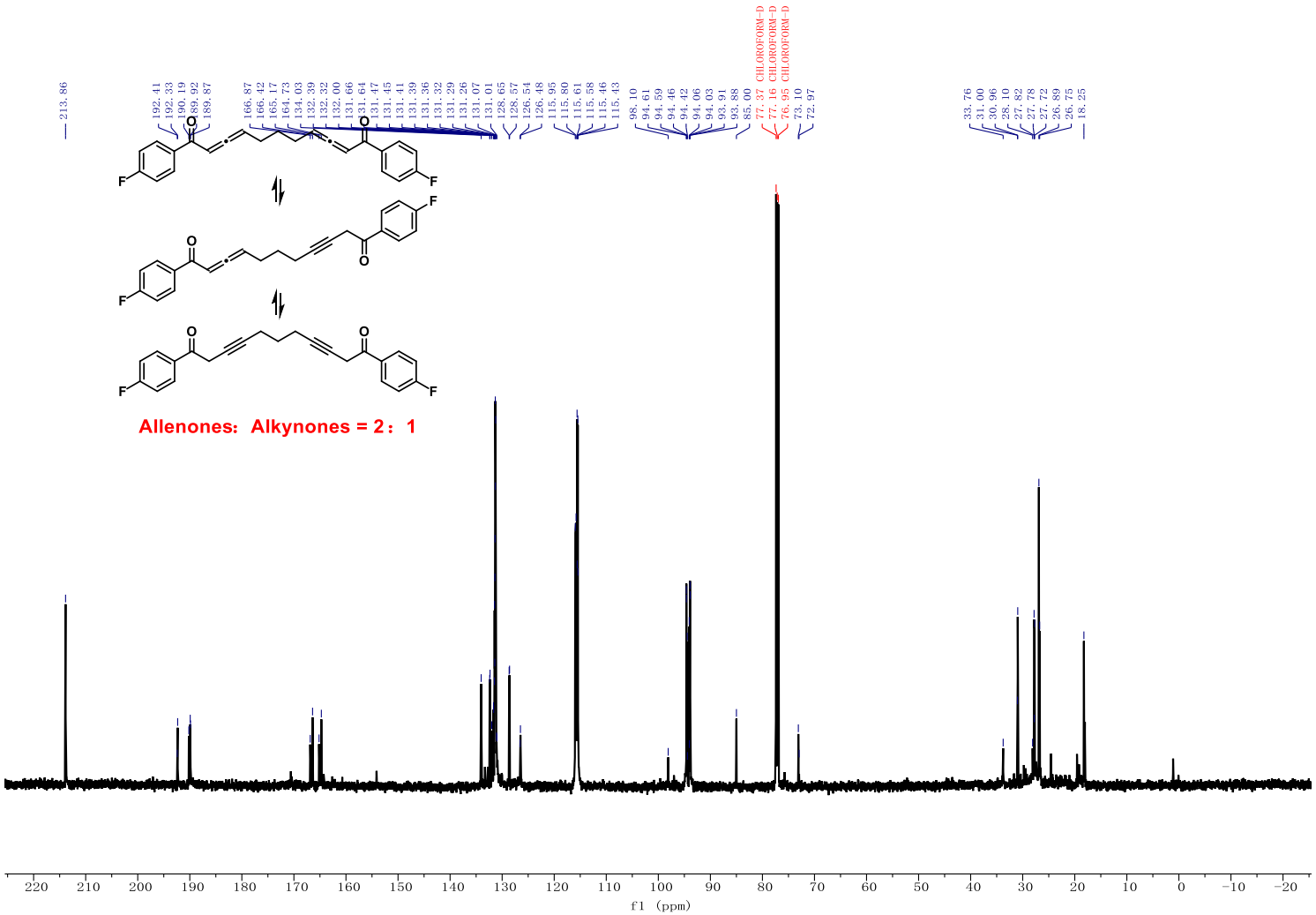
^{13}C NMR (151 MHz, $CDCl_3$) of **3k**



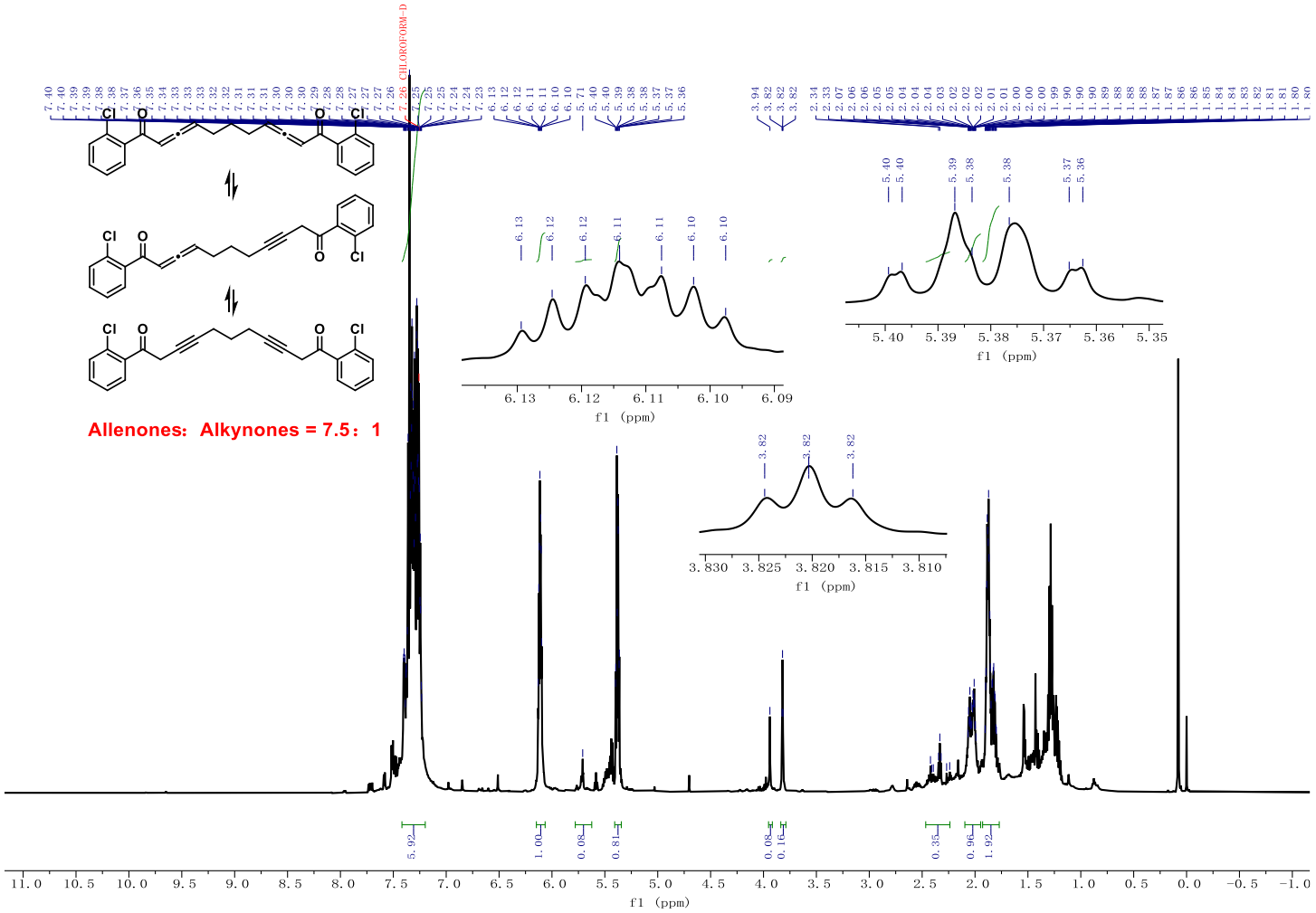
^{1}H NMR (600 MHz, $CDCl_3$) of **3l**



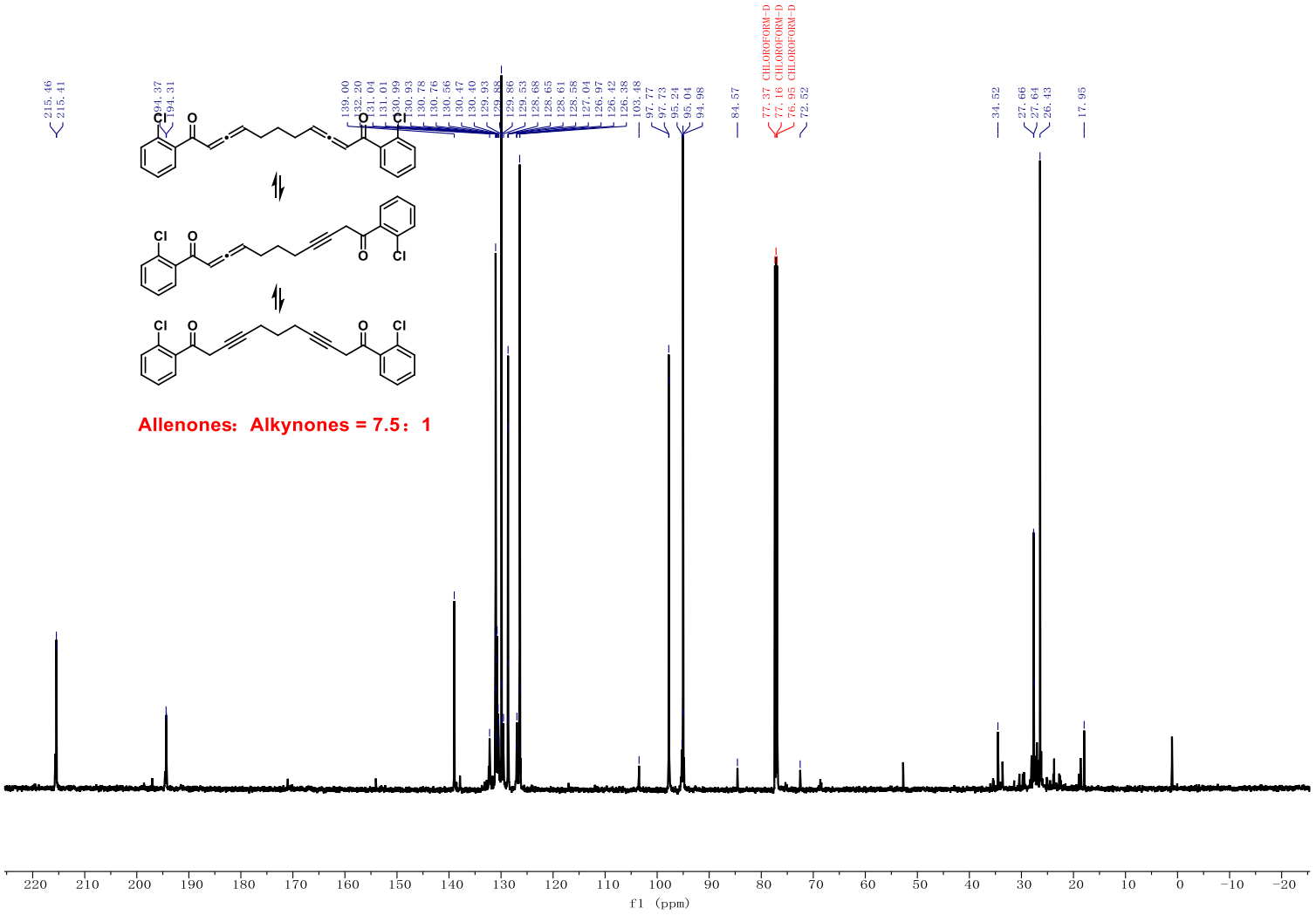
^{13}C NMR (151 MHz, $CDCl_3$) of **3l**



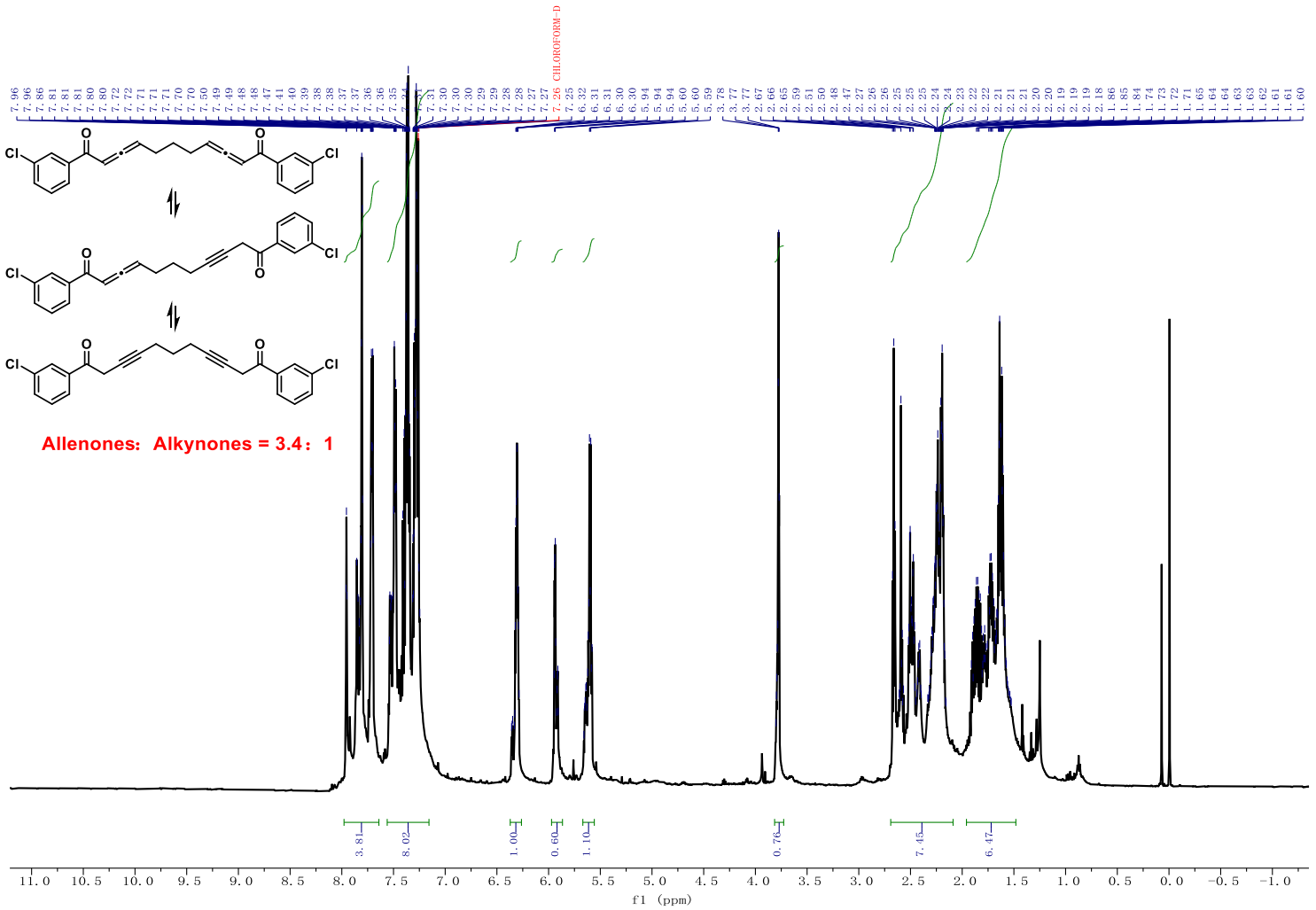
^{1}H NMR (600 MHz, $CDCl_3$) of **3m**



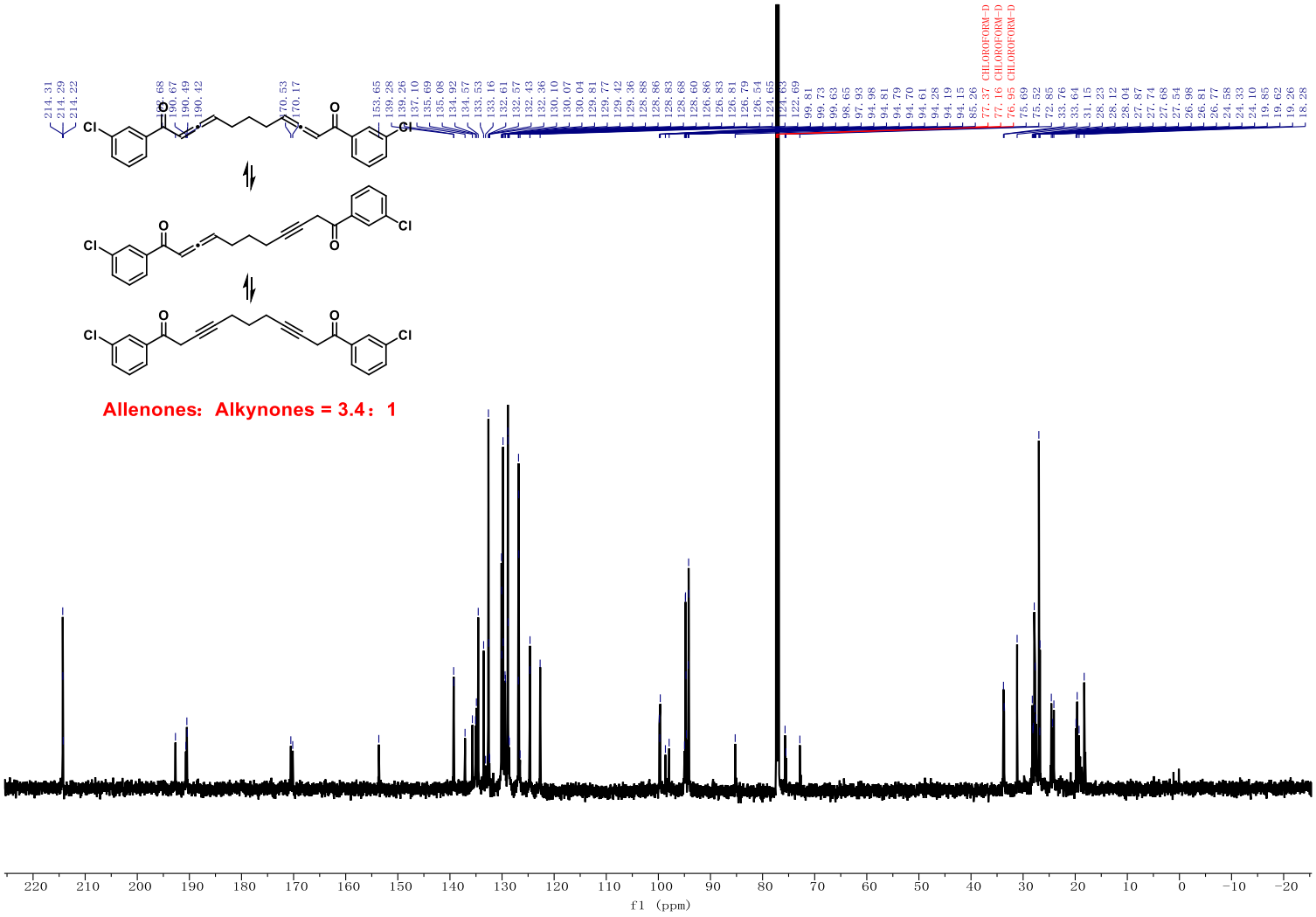
^{13}C NMR (151 MHz, $CDCl_3$) of **3m**



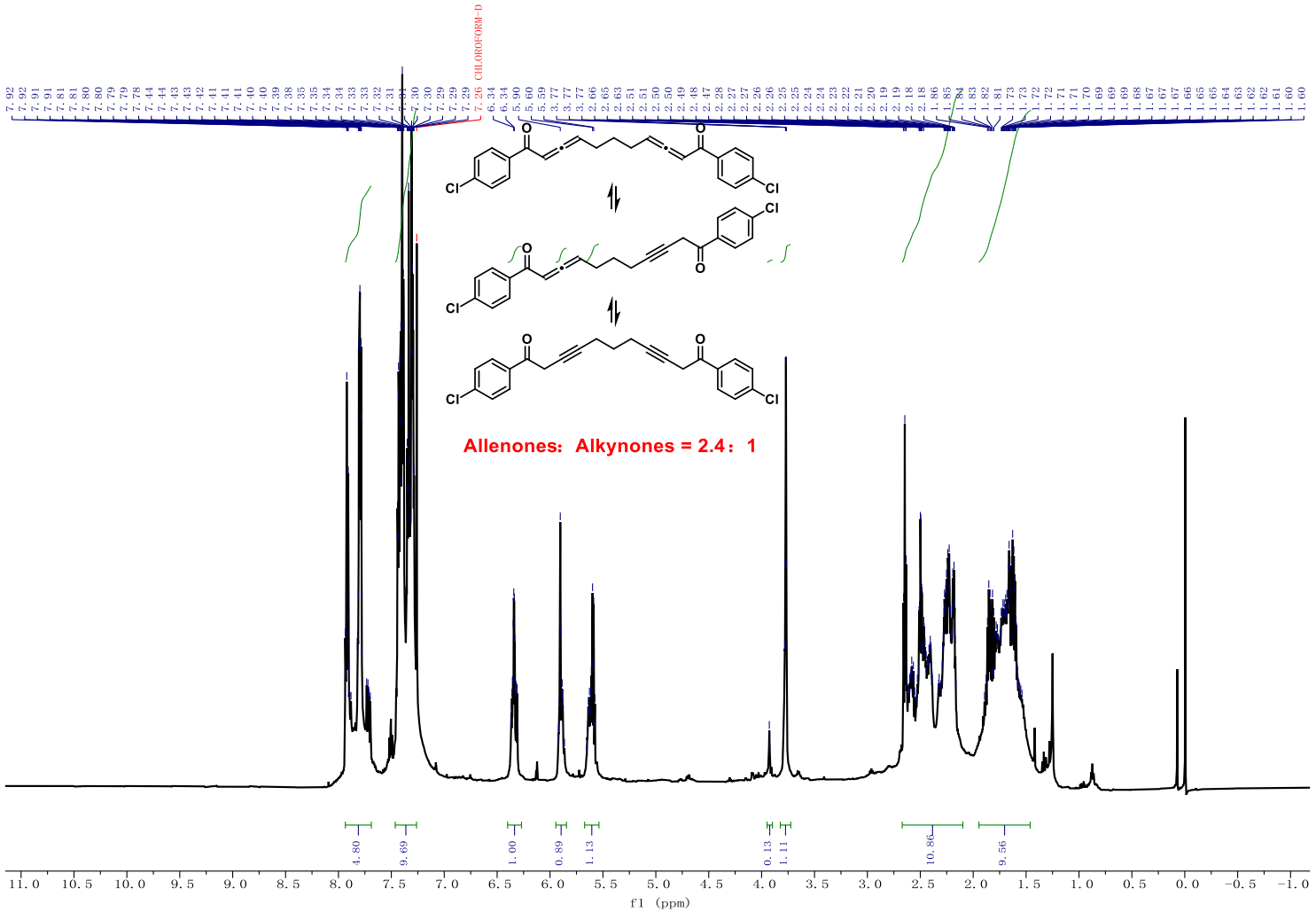
^{1}H NMR (600 MHz, $CDCl_3$) of **3n**



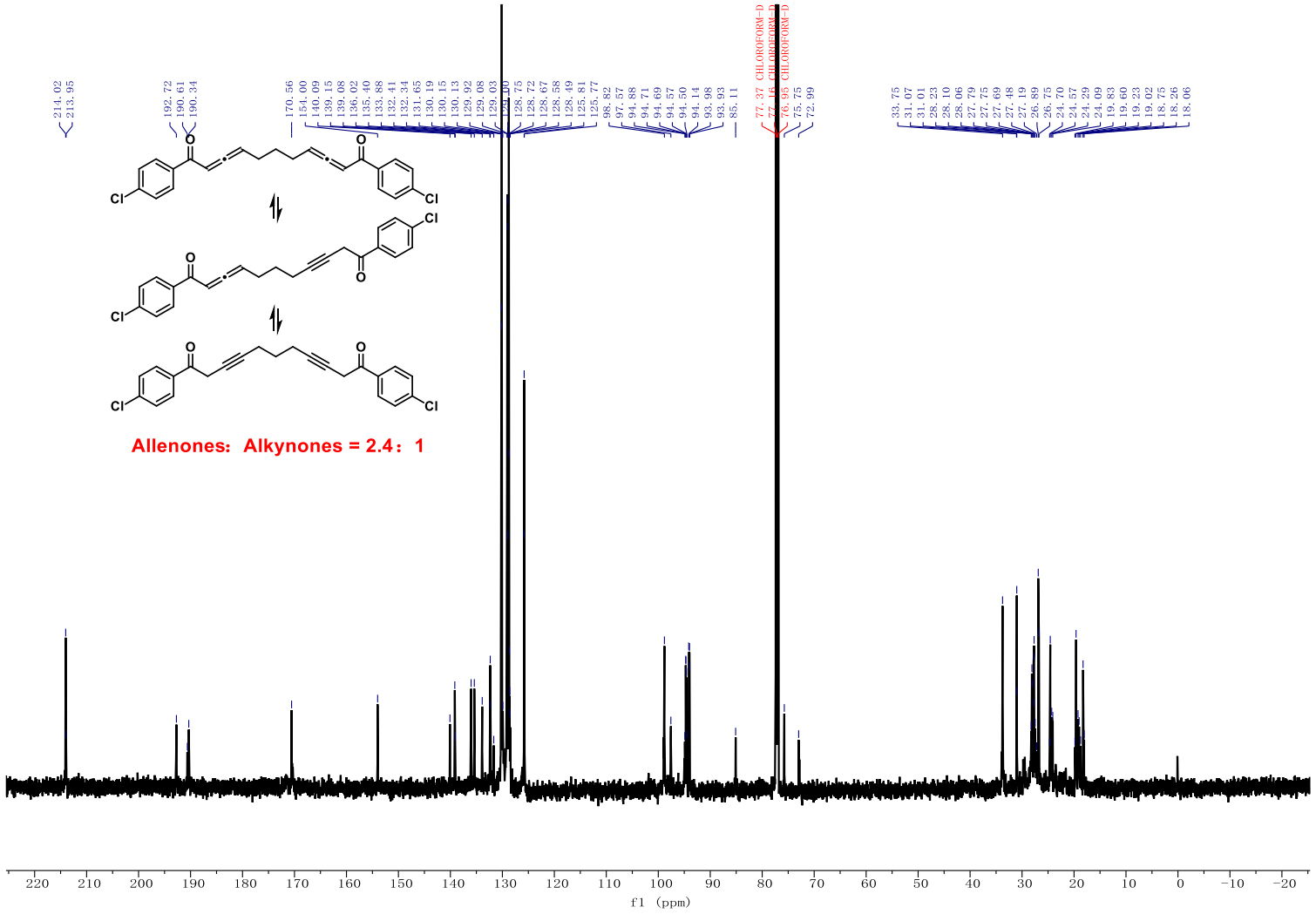
^{13}C NMR (151 MHz, $CDCl_3$) of **3n**



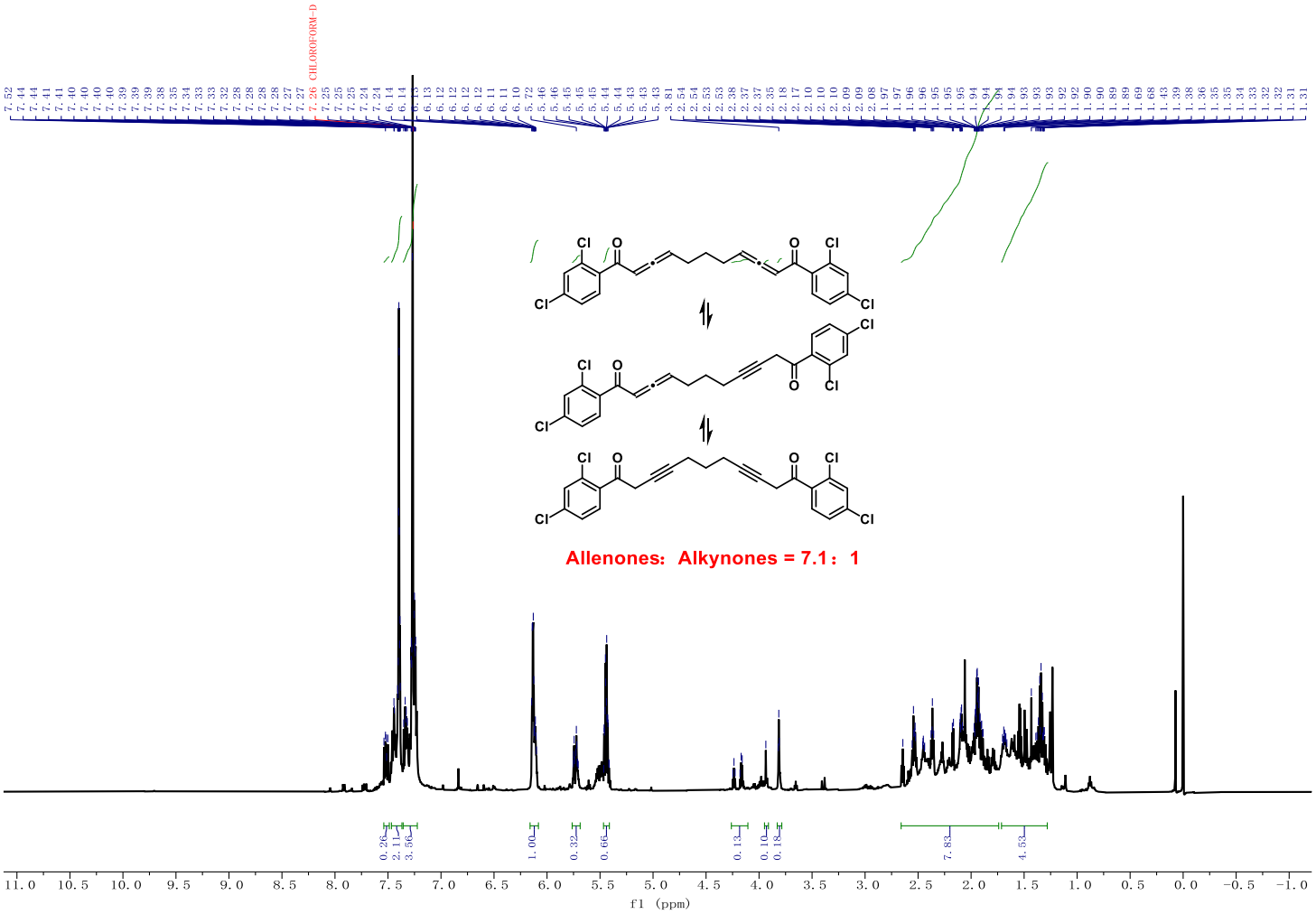
^{1}H NMR (600 MHz, $CDCl_3$) of **3o**



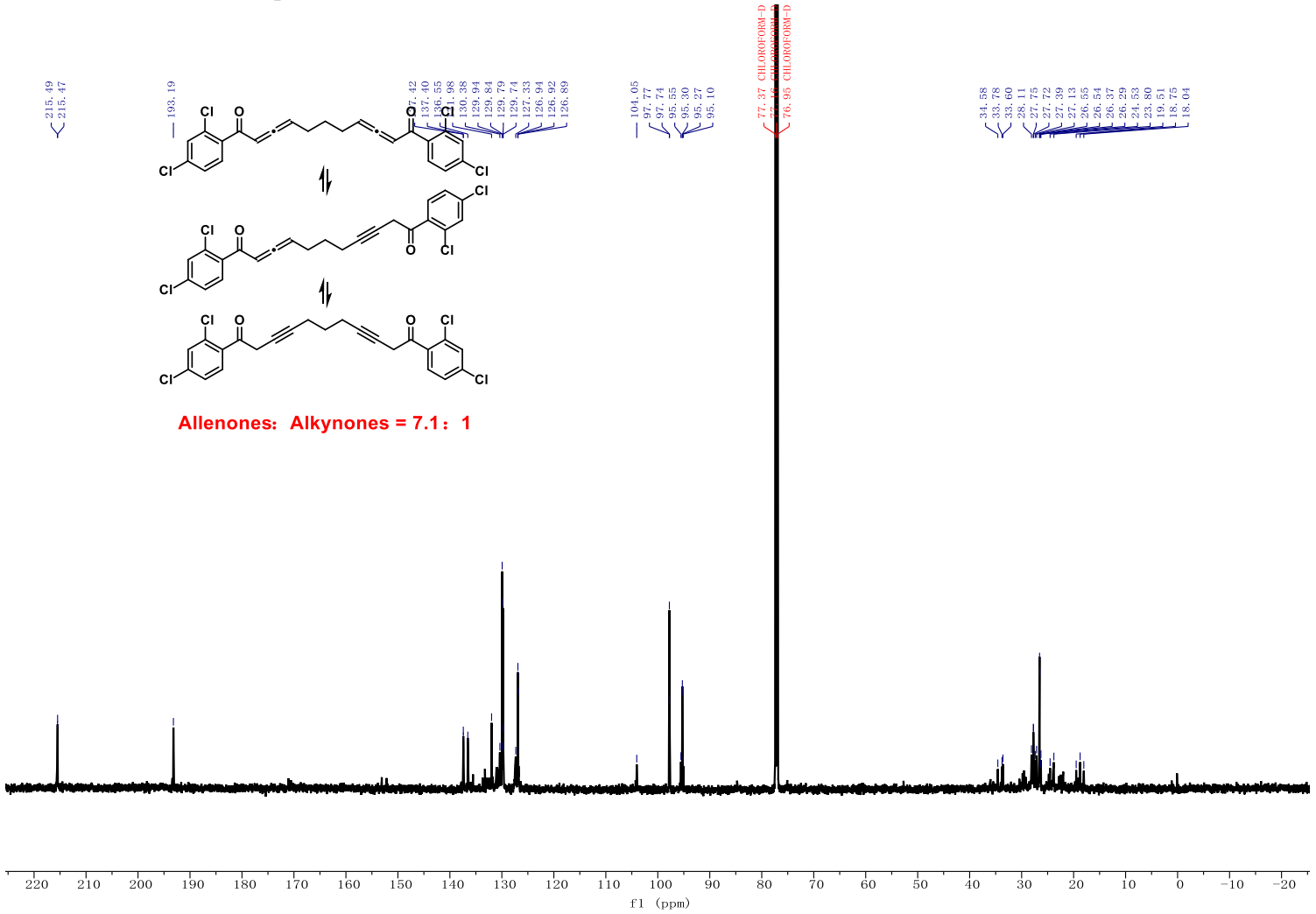
^{13}C NMR (151 MHz, $CDCl_3$) of **3o**



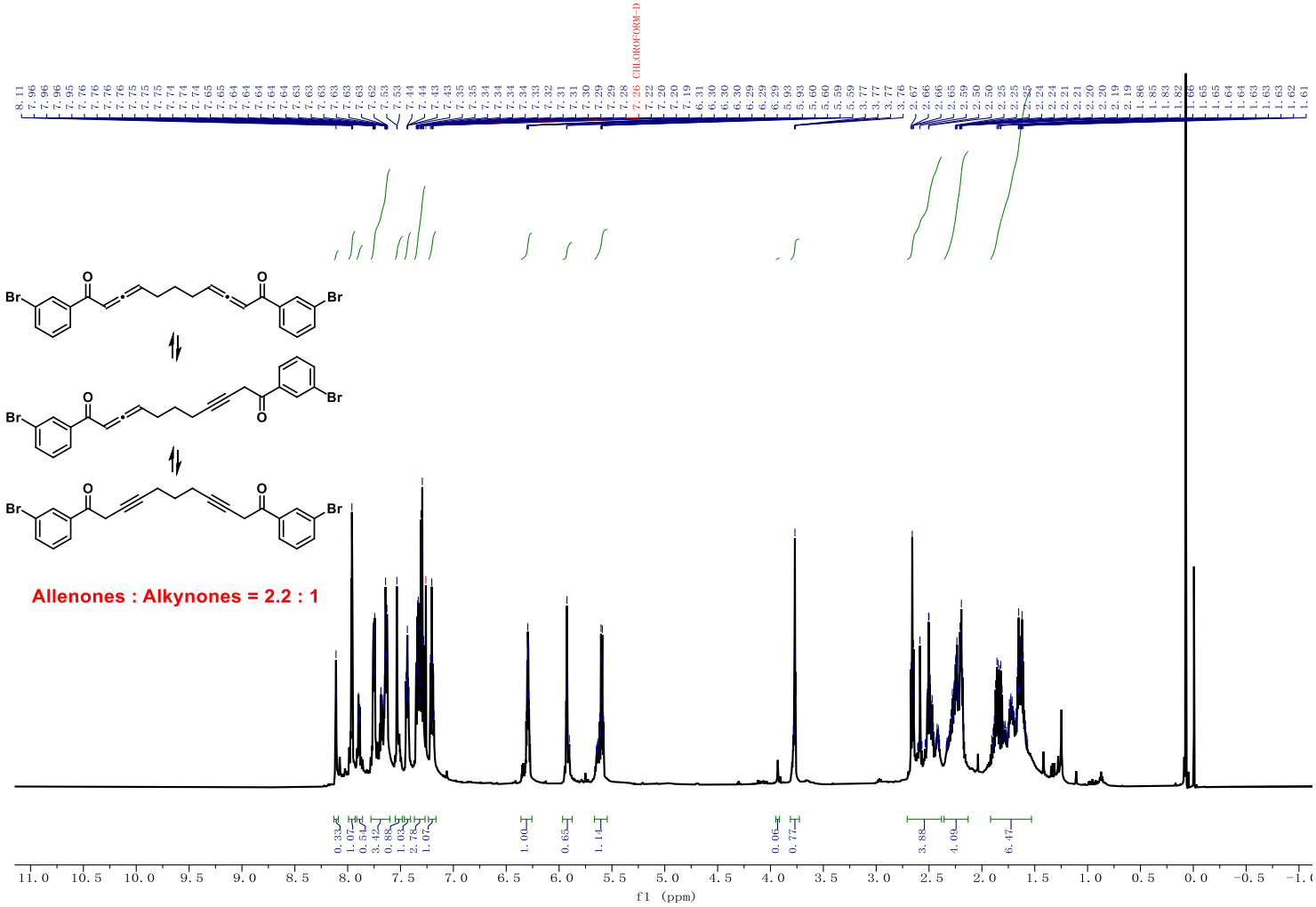
^{1}H NMR (600 MHz, $CDCl_3$) of **3p**



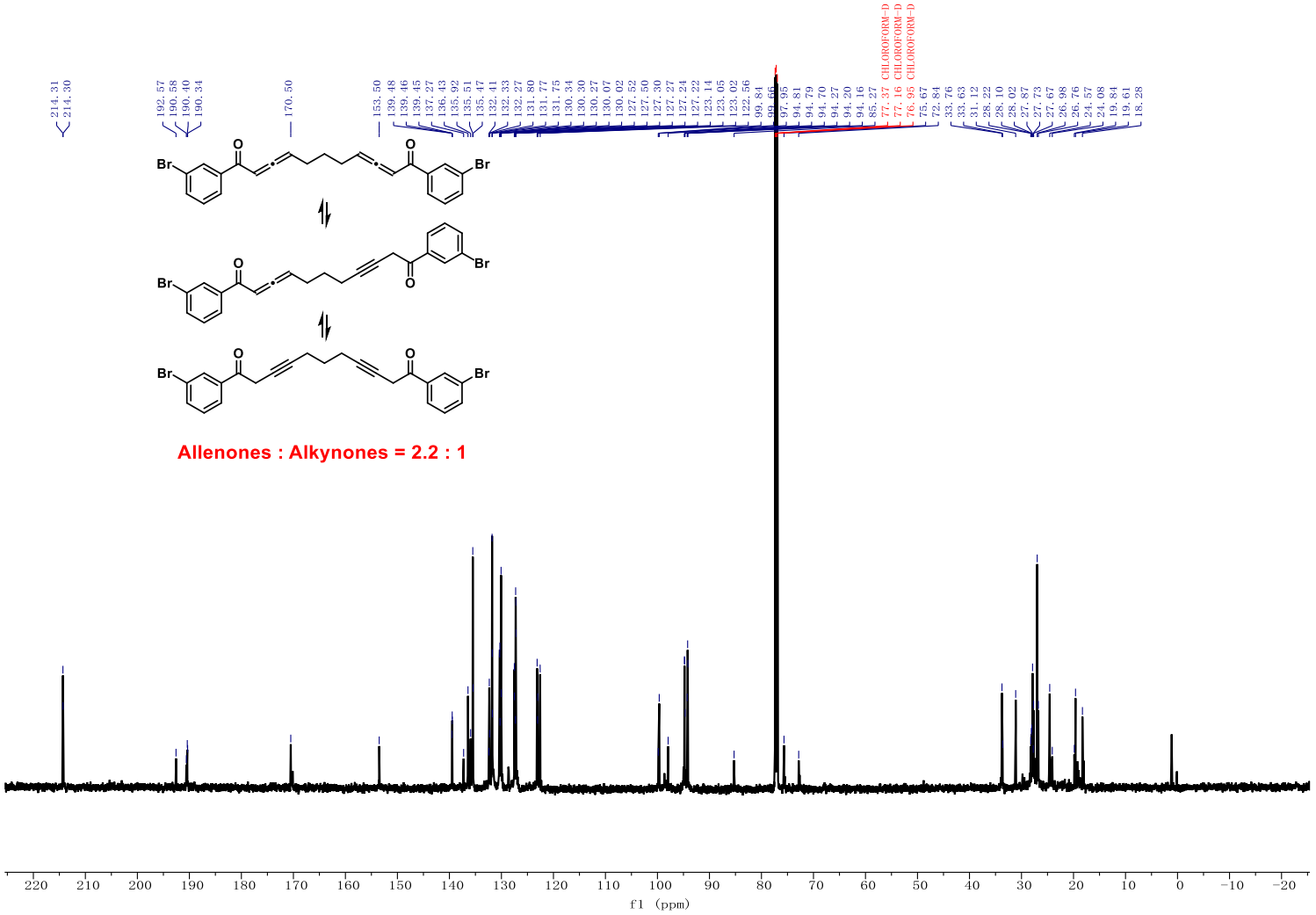
^{13}C NMR (151 MHz, $CDCl_3$) of **3p**



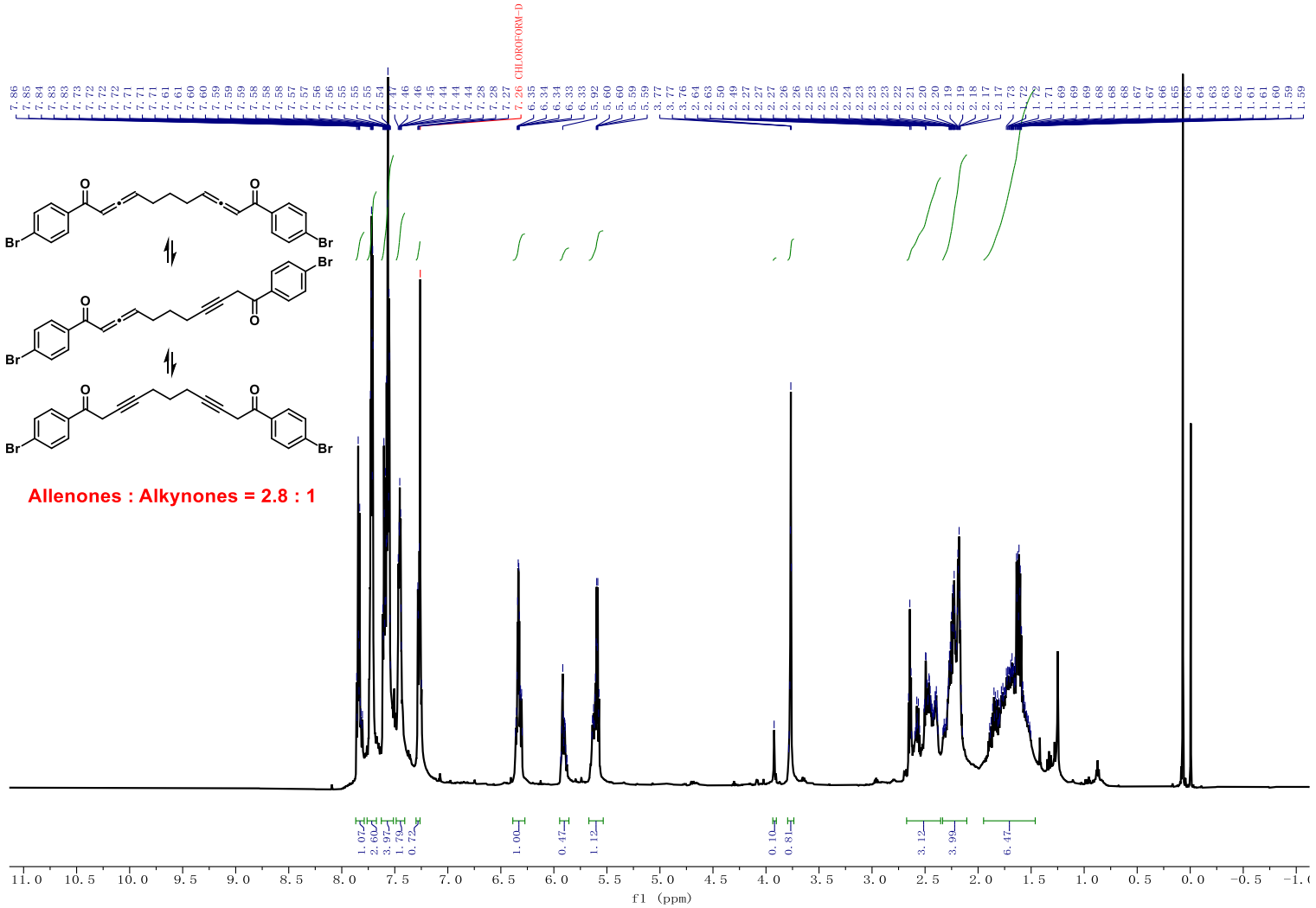
^{1}H NMR (600 MHz, $CDCl_3$) of **3q**



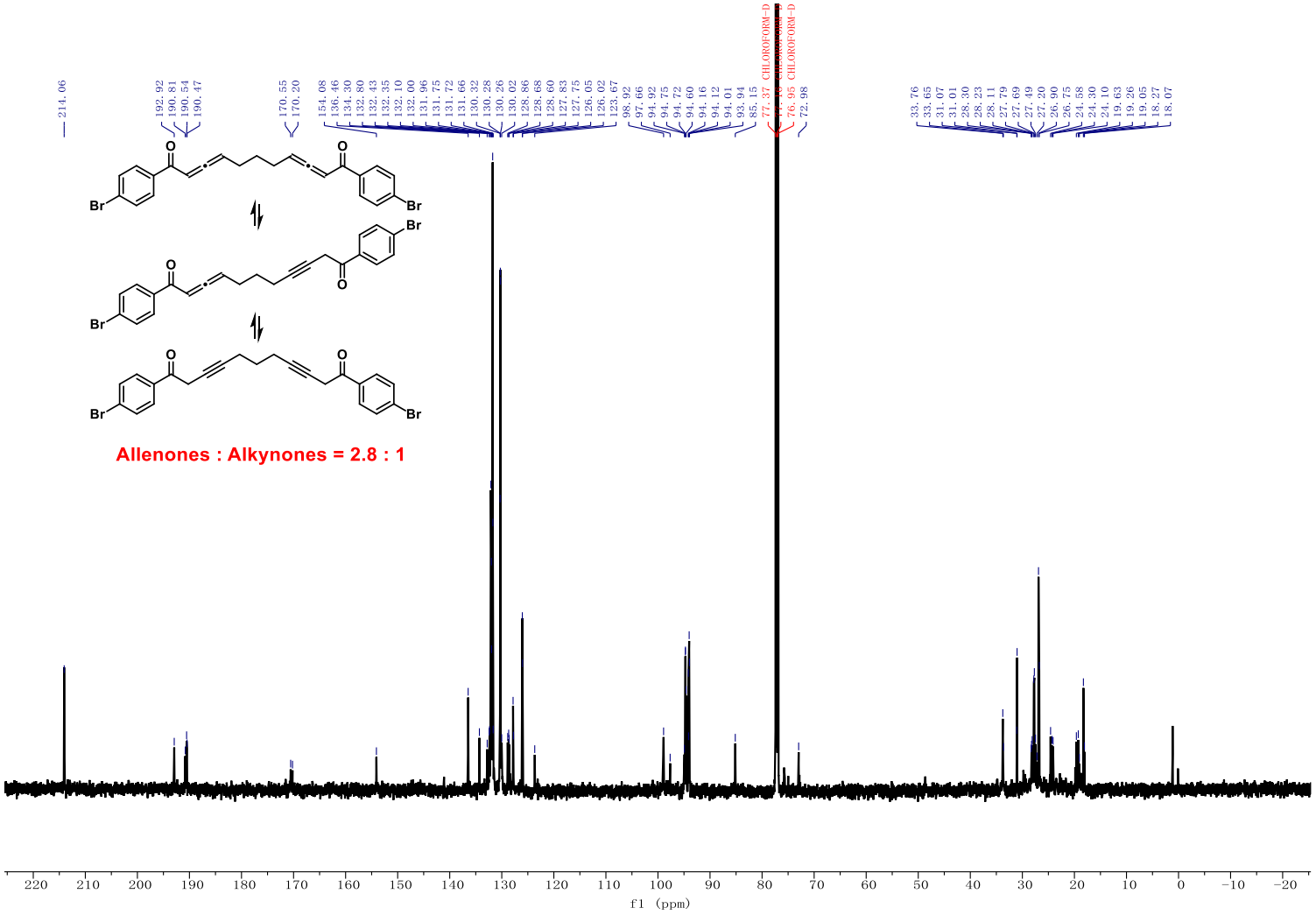
^{13}C NMR (151 MHz, $CDCl_3$) of **3q**



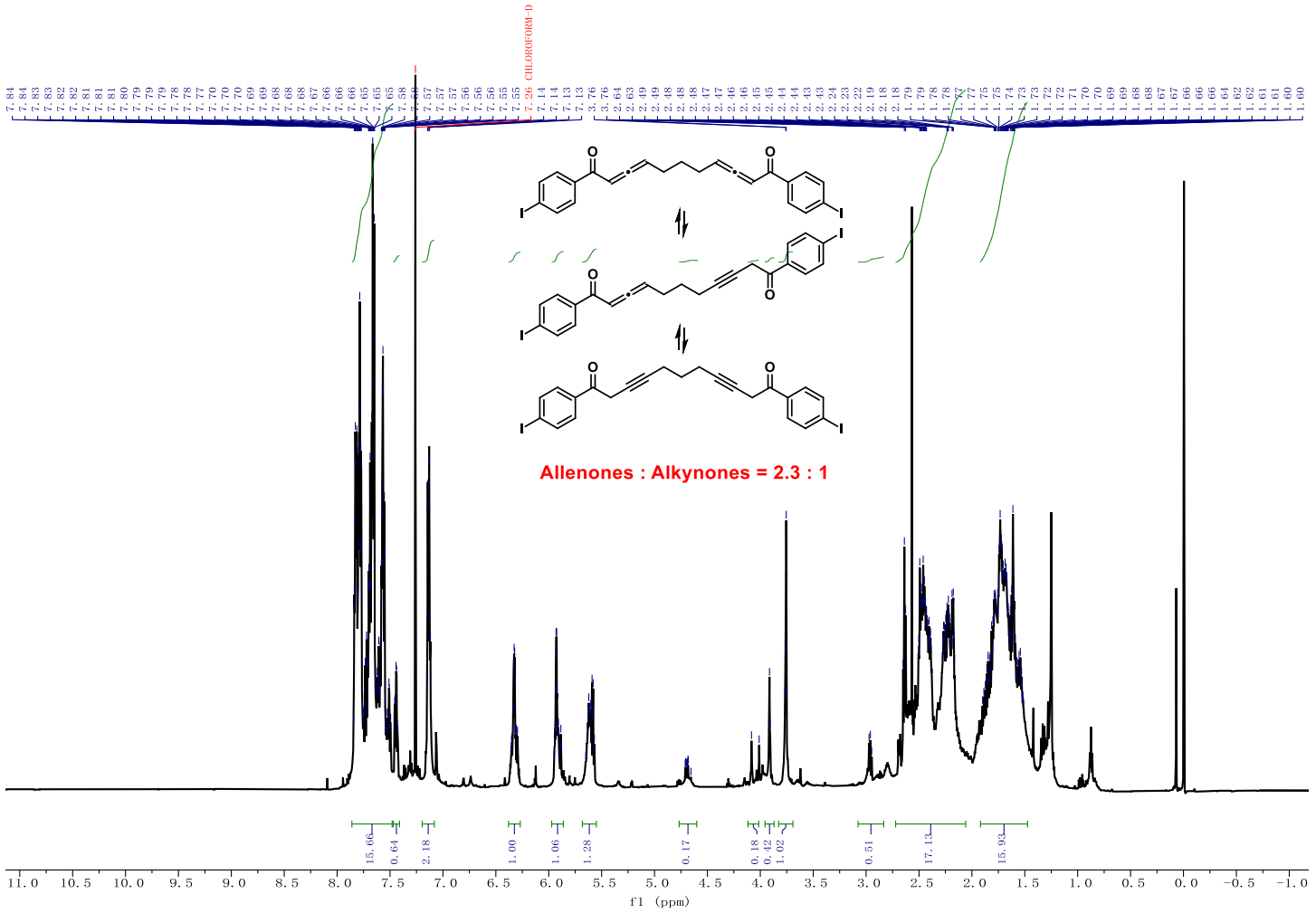
^{1}H NMR (600 MHz, $CDCl_3$) of **3r**



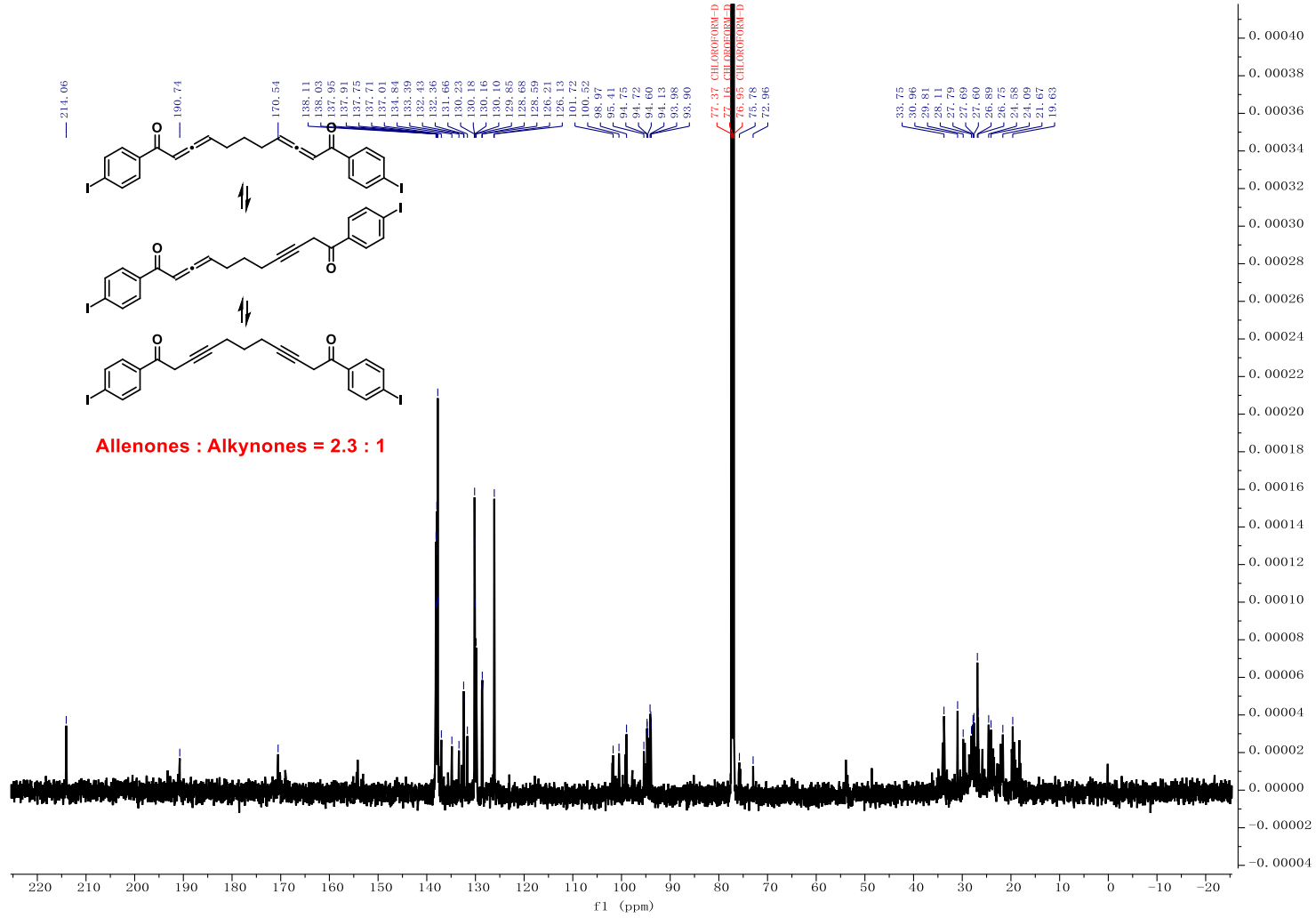
^{13}C NMR (151 MHz, $CDCl_3$) of **3r**



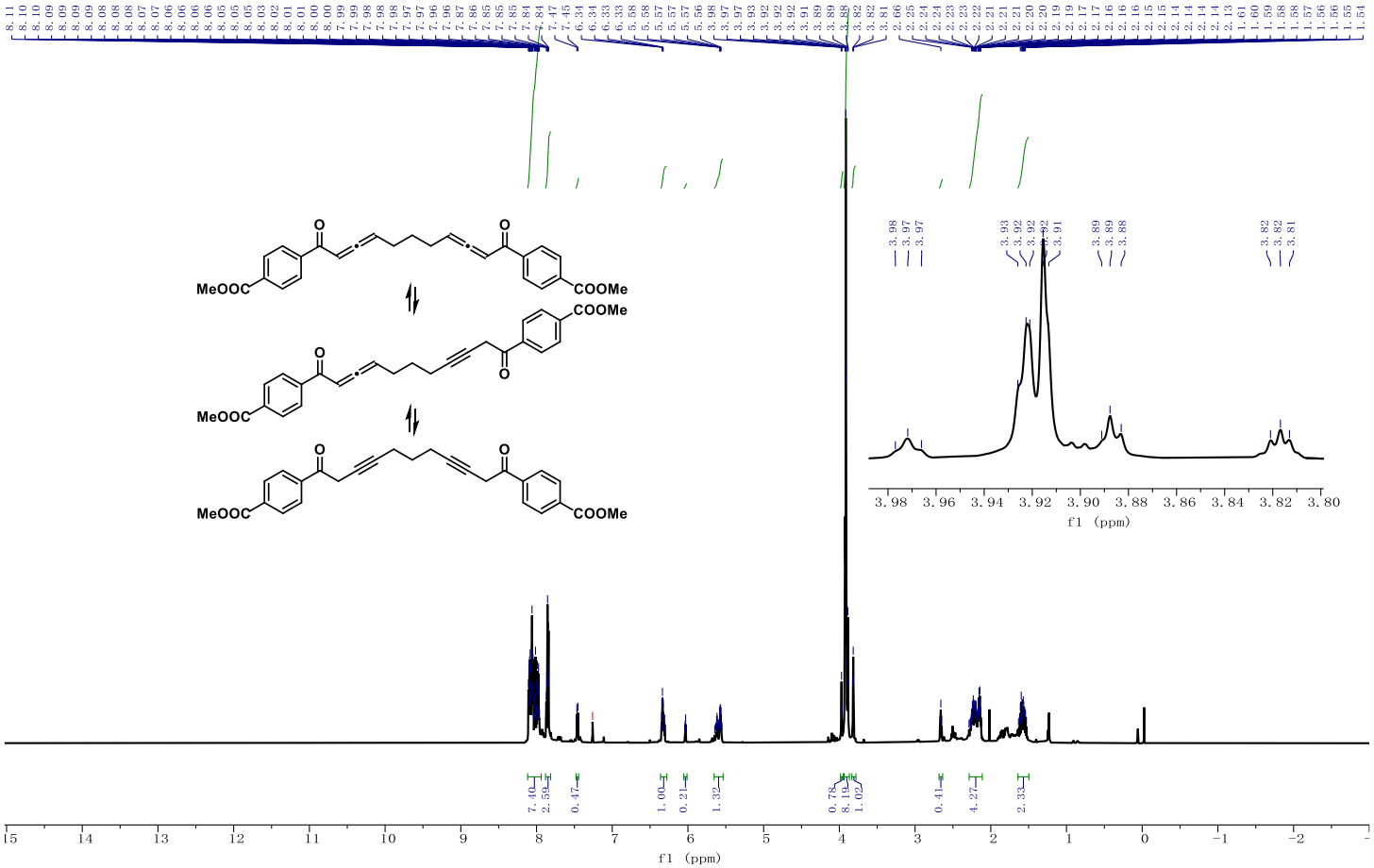
^{1}H NMR (600 MHz, $CDCl_3$) of **3s**



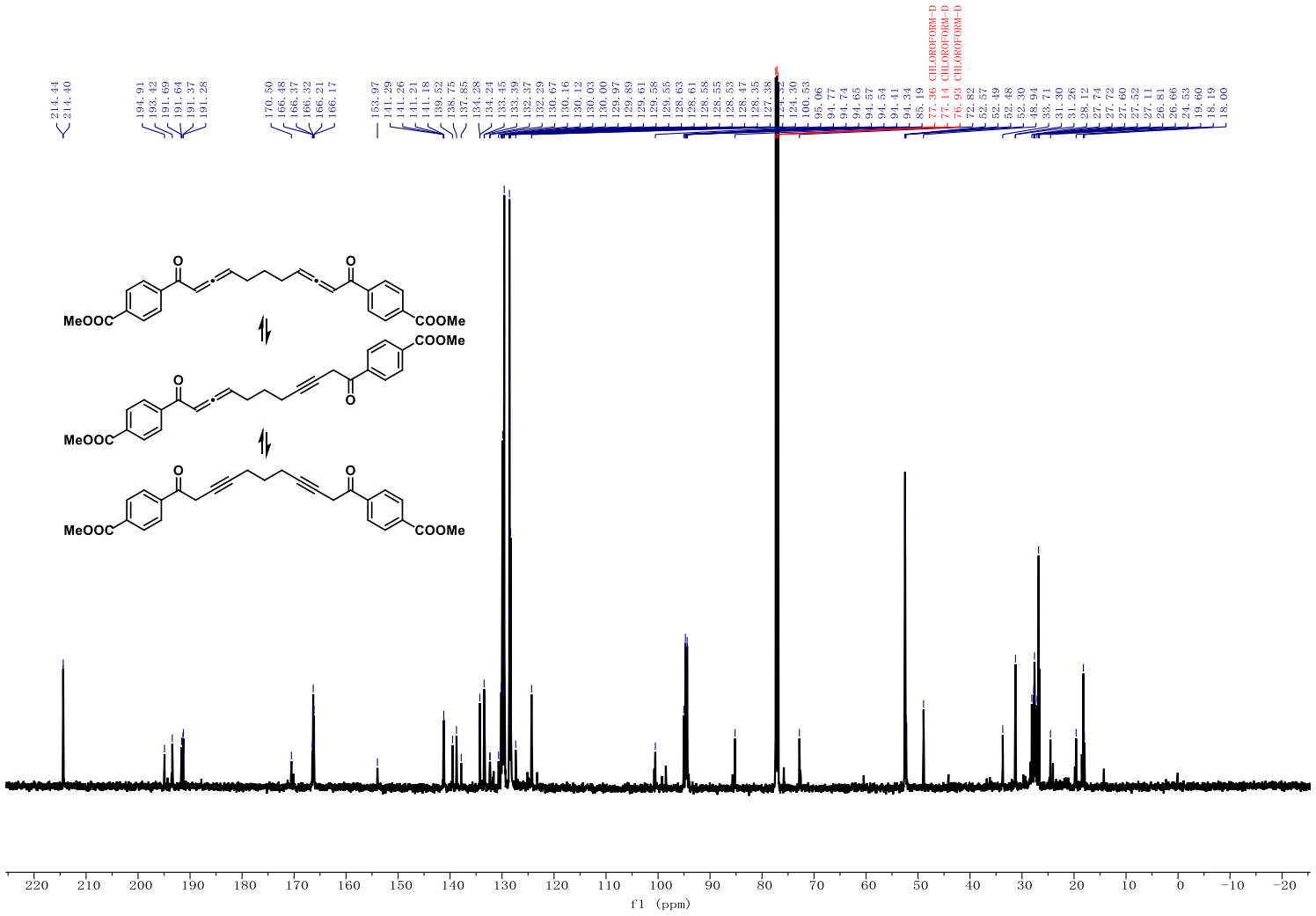
^{13}C NMR (151 MHz, $CDCl_3$) of **3s**



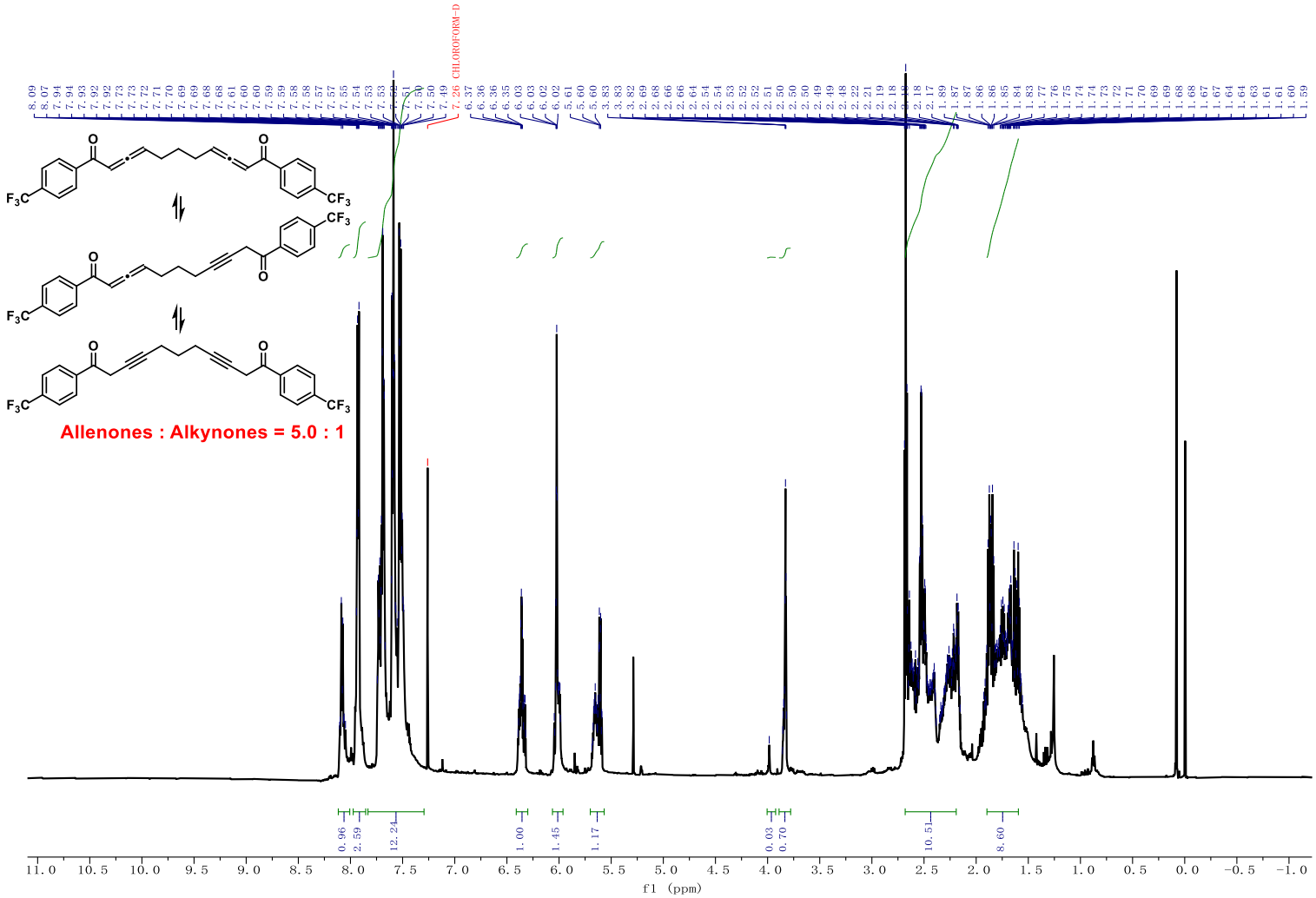
^{1}H NMR (600 MHz, $CDCl_3$) of **3t**



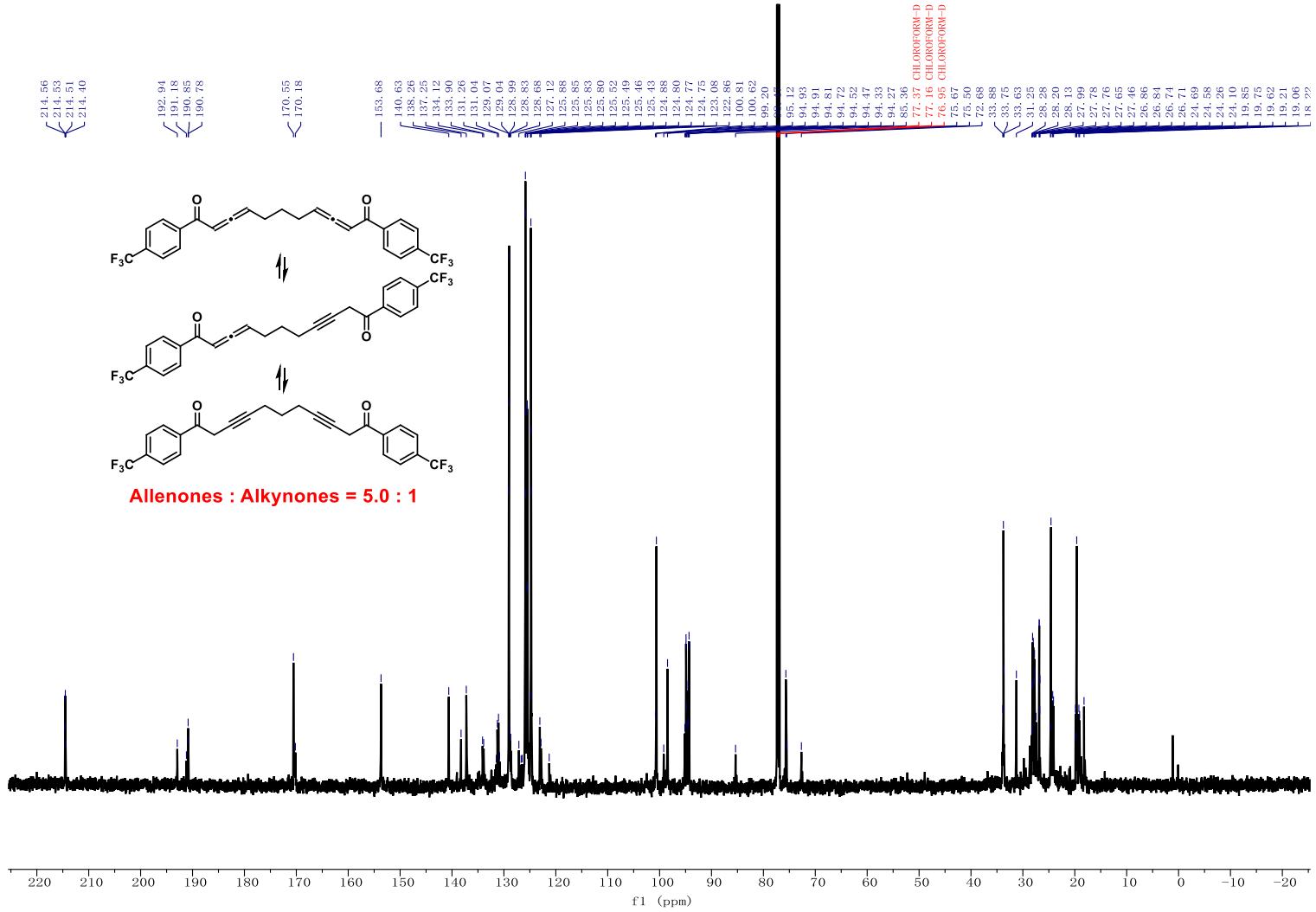
^{13}C NMR (151 MHz, $CDCl_3$) of **3t**



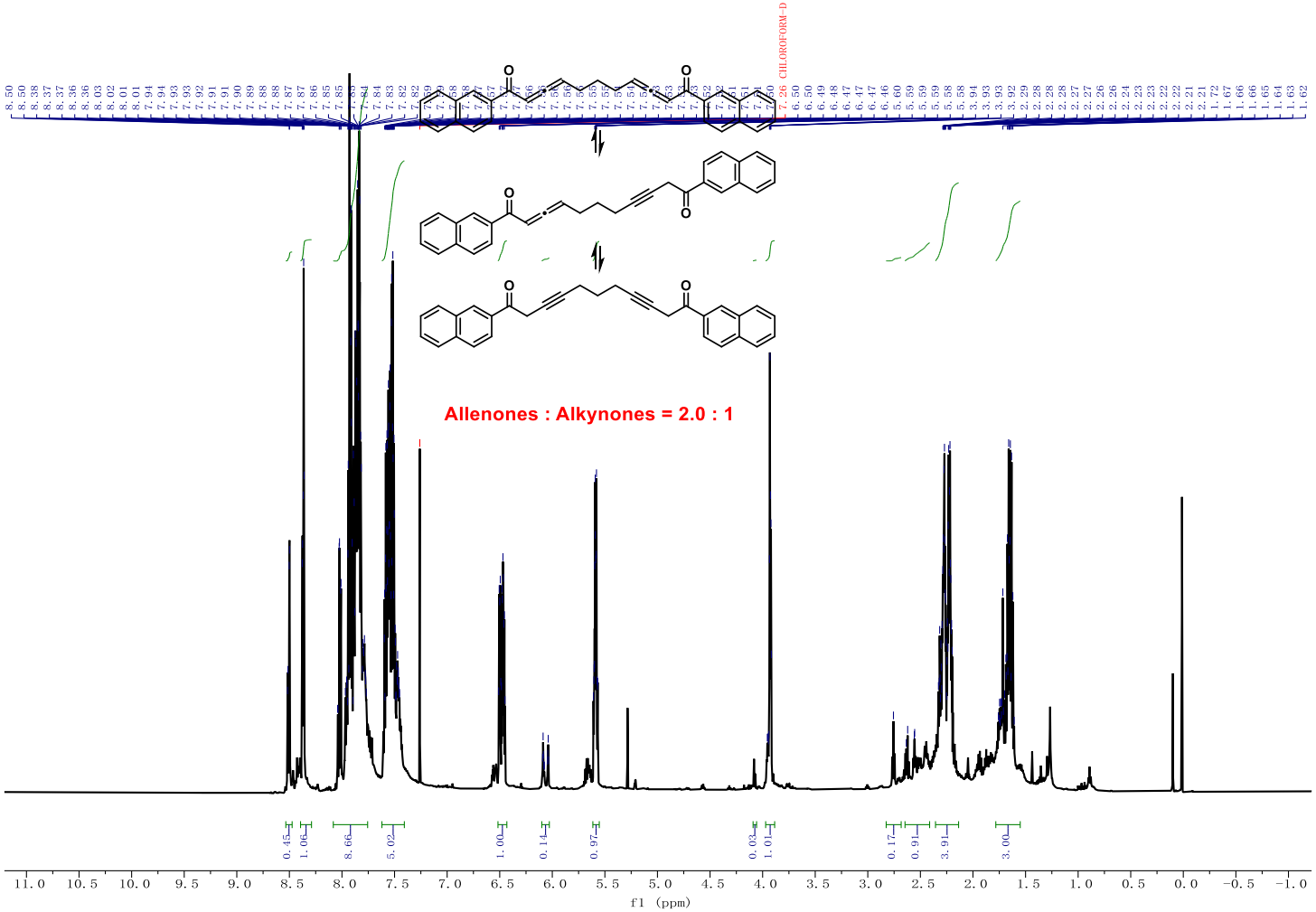
^{1}H NMR (600 MHz, $CDCl_3$) of **3u**



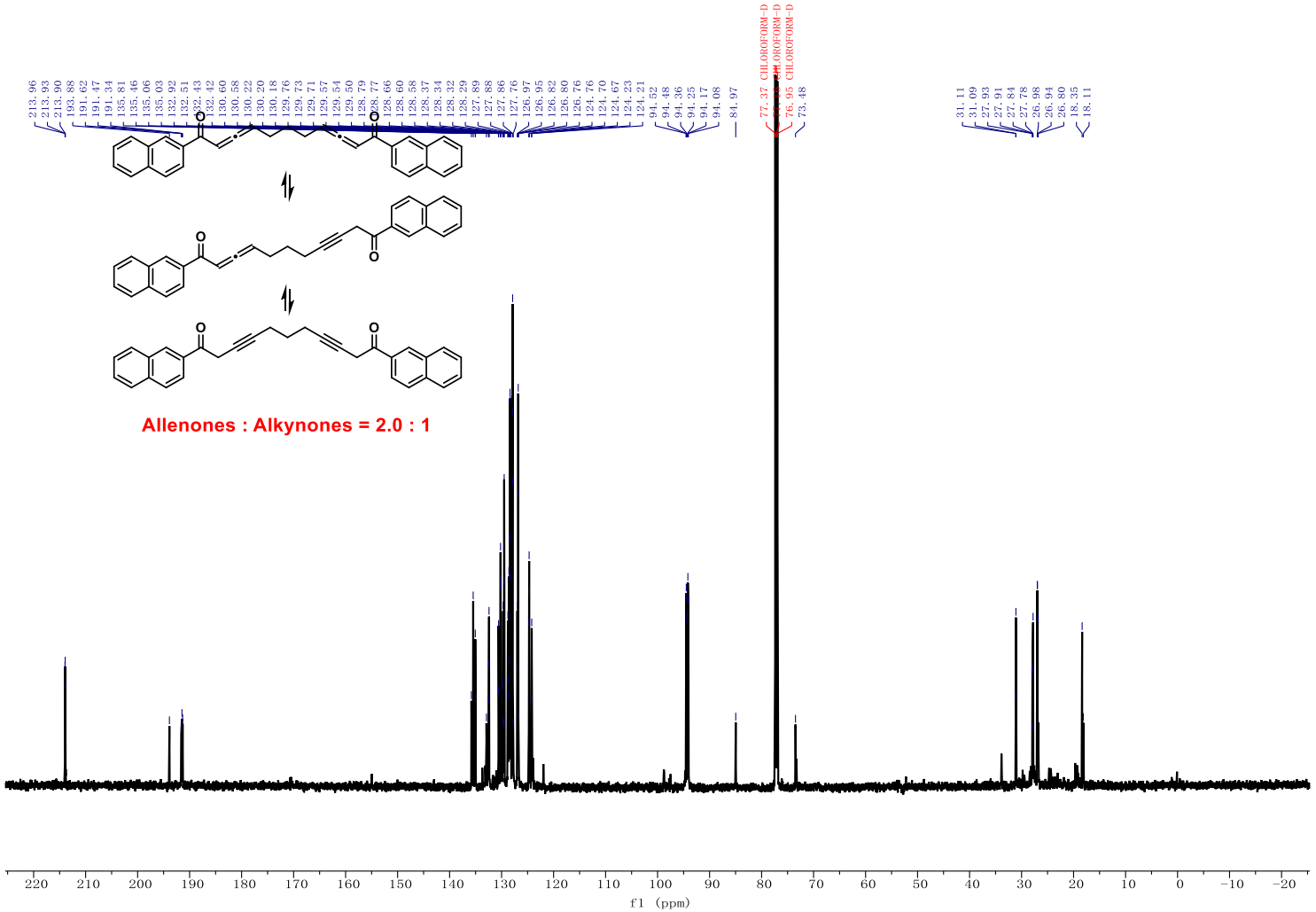
^{13}C NMR (151 MHz, $CDCl_3$) of **3u**



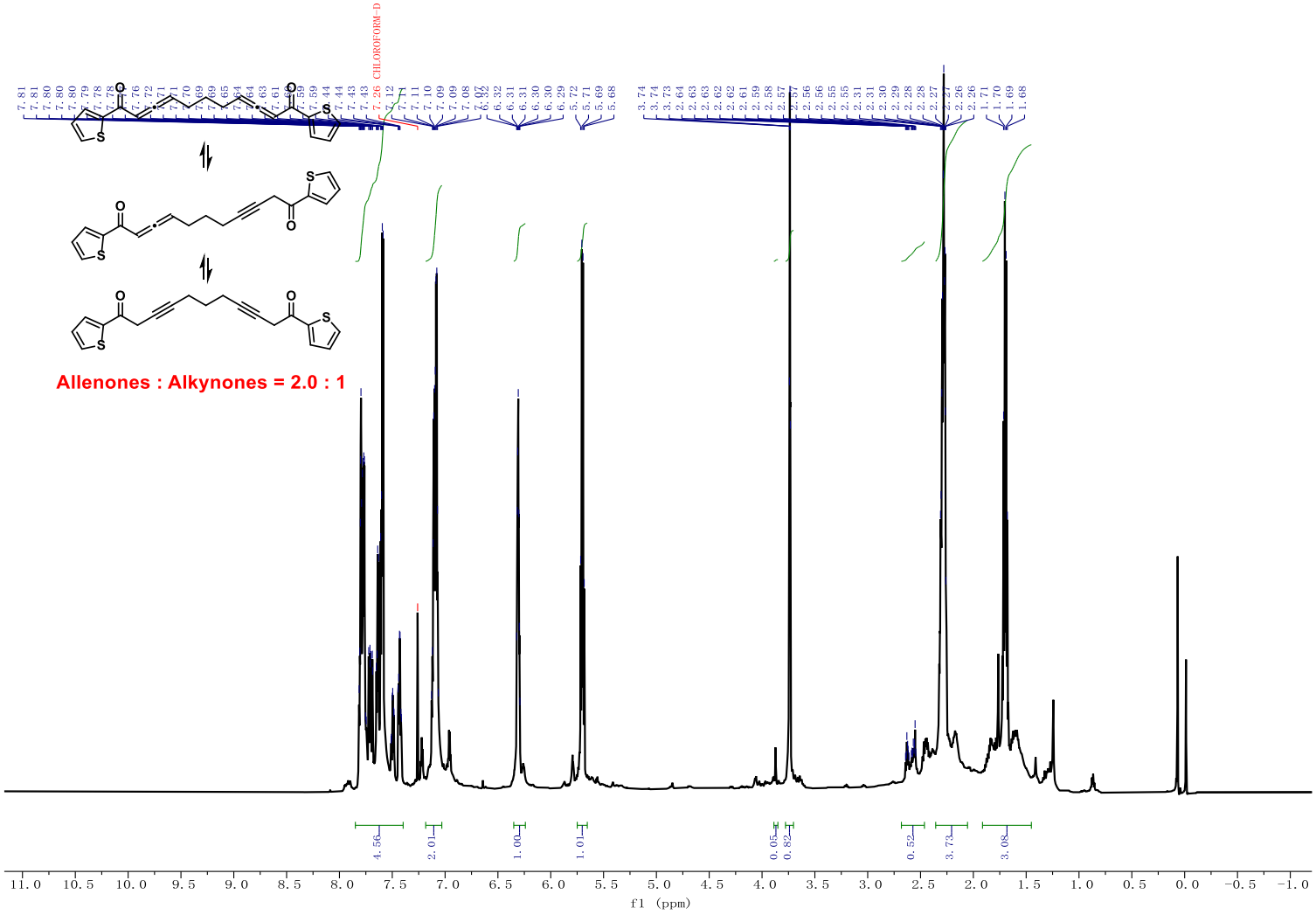
^{1}H NMR (600 MHz, $CDCl_3$) of **3v**



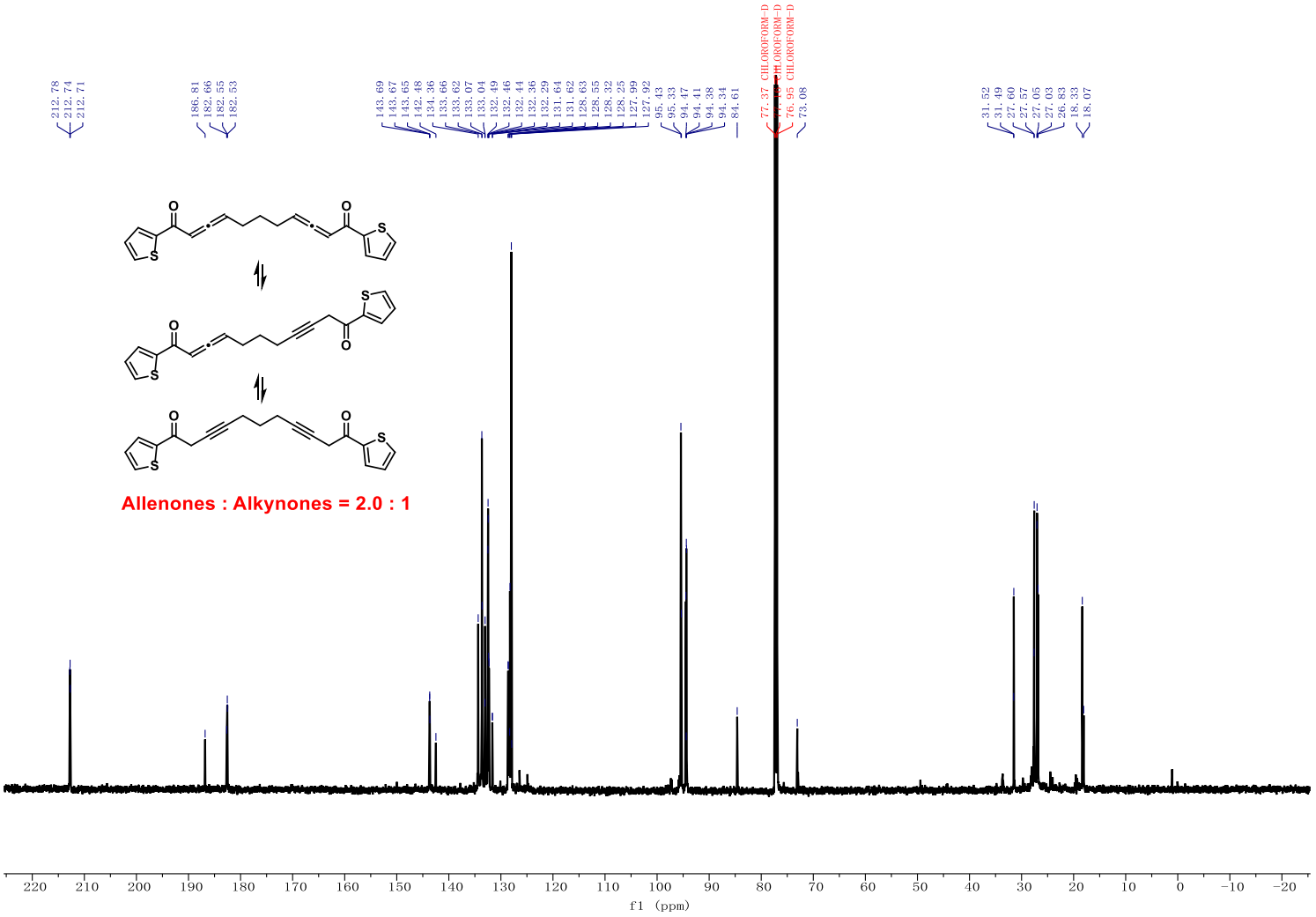
^{13}C NMR (151 MHz, $CDCl_3$) of **3v**



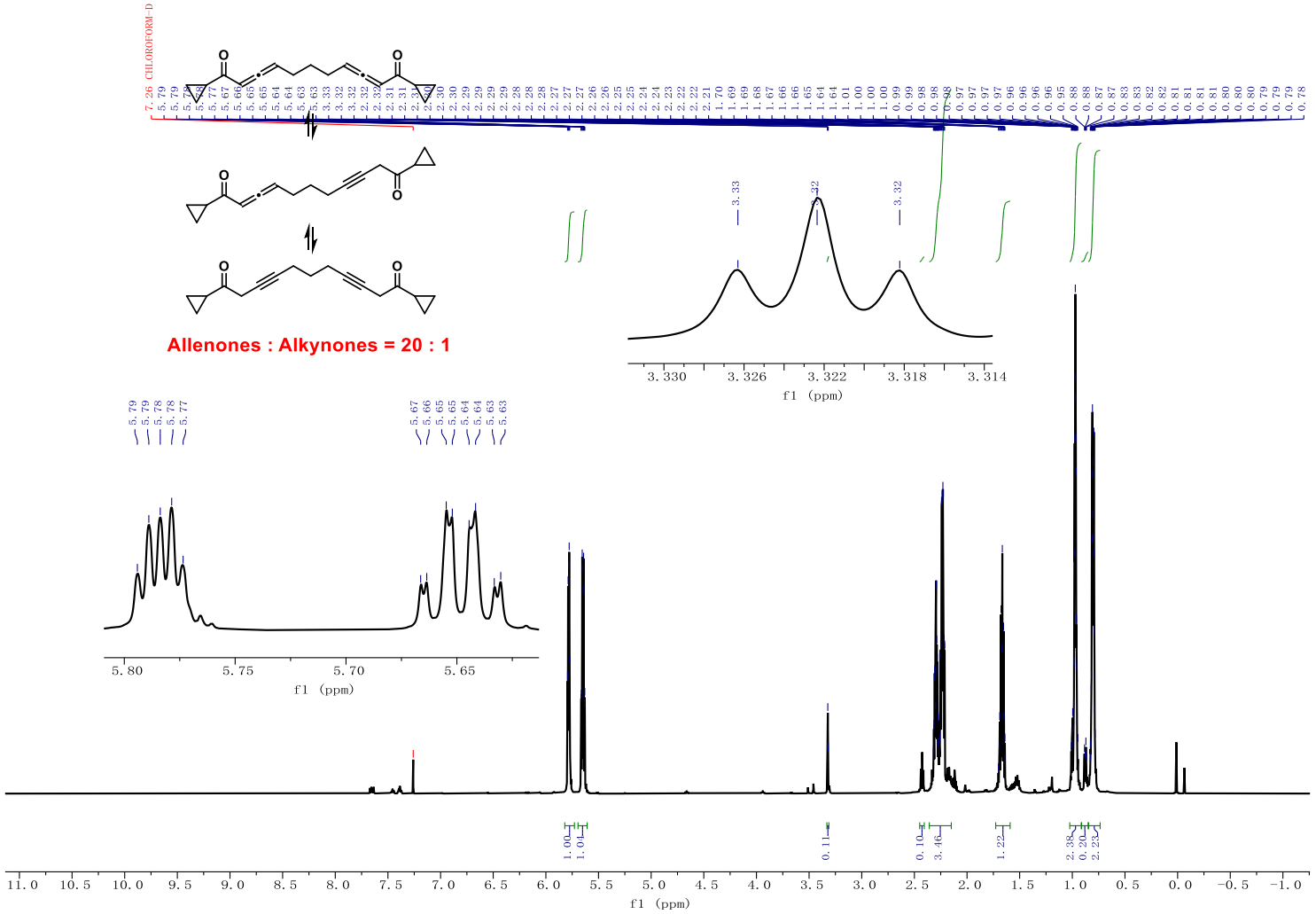
^{1}H NMR (600 MHz, $CDCl_3$) of **3w**



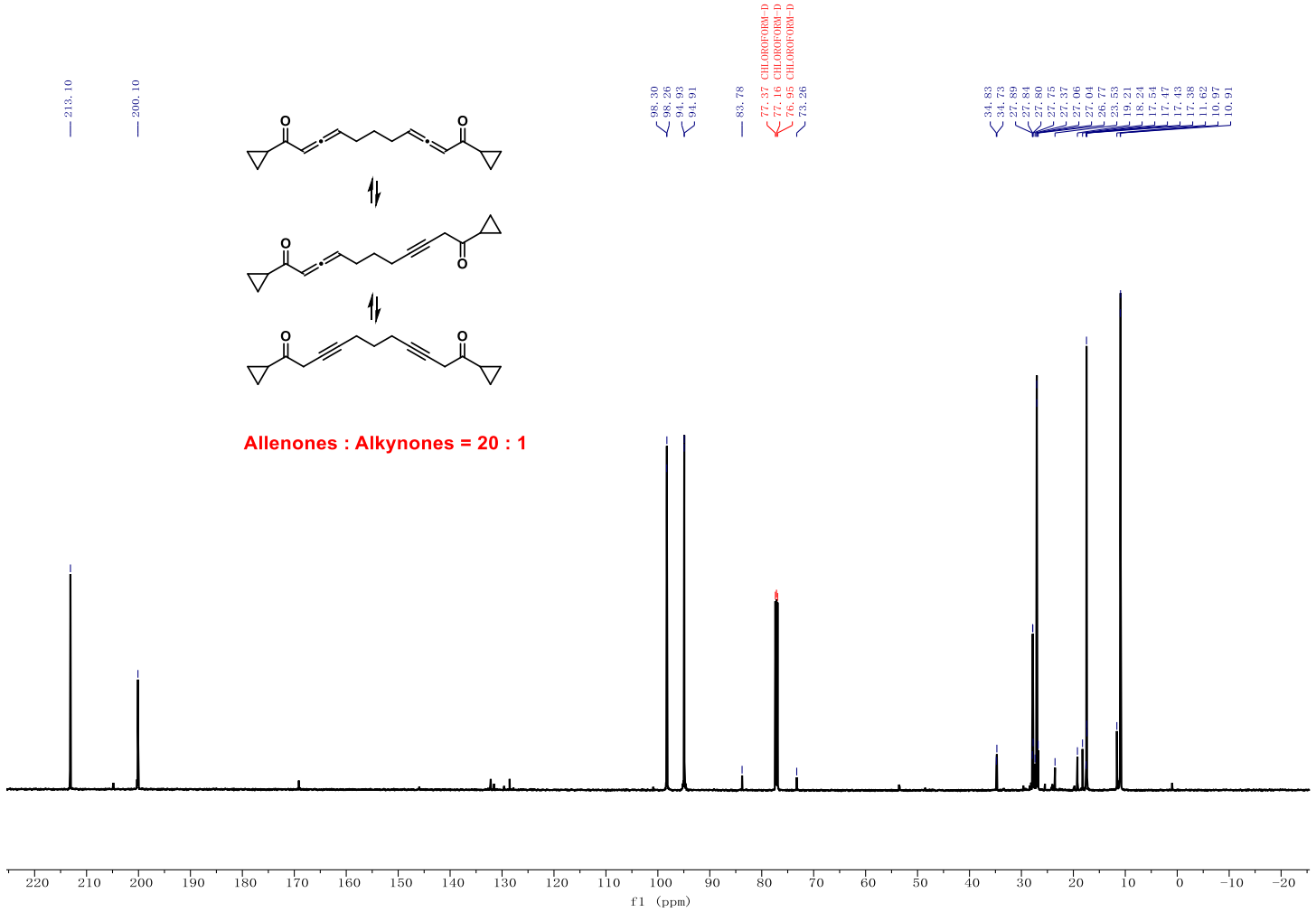
^{13}C NMR (151 MHz, $CDCl_3$) of **3w**



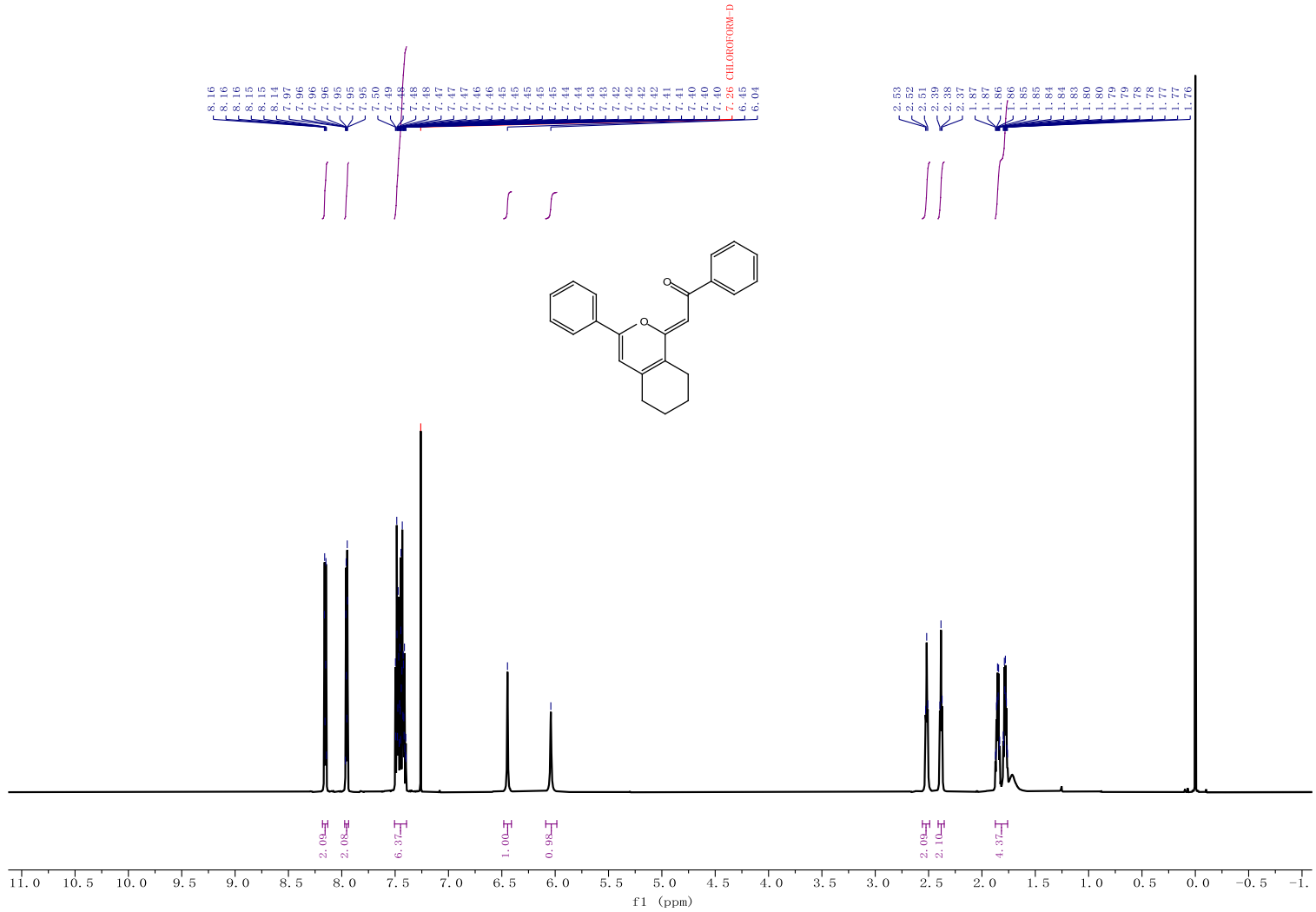
^{1}H NMR (600 MHz, $CDCl_3$) of **3x**



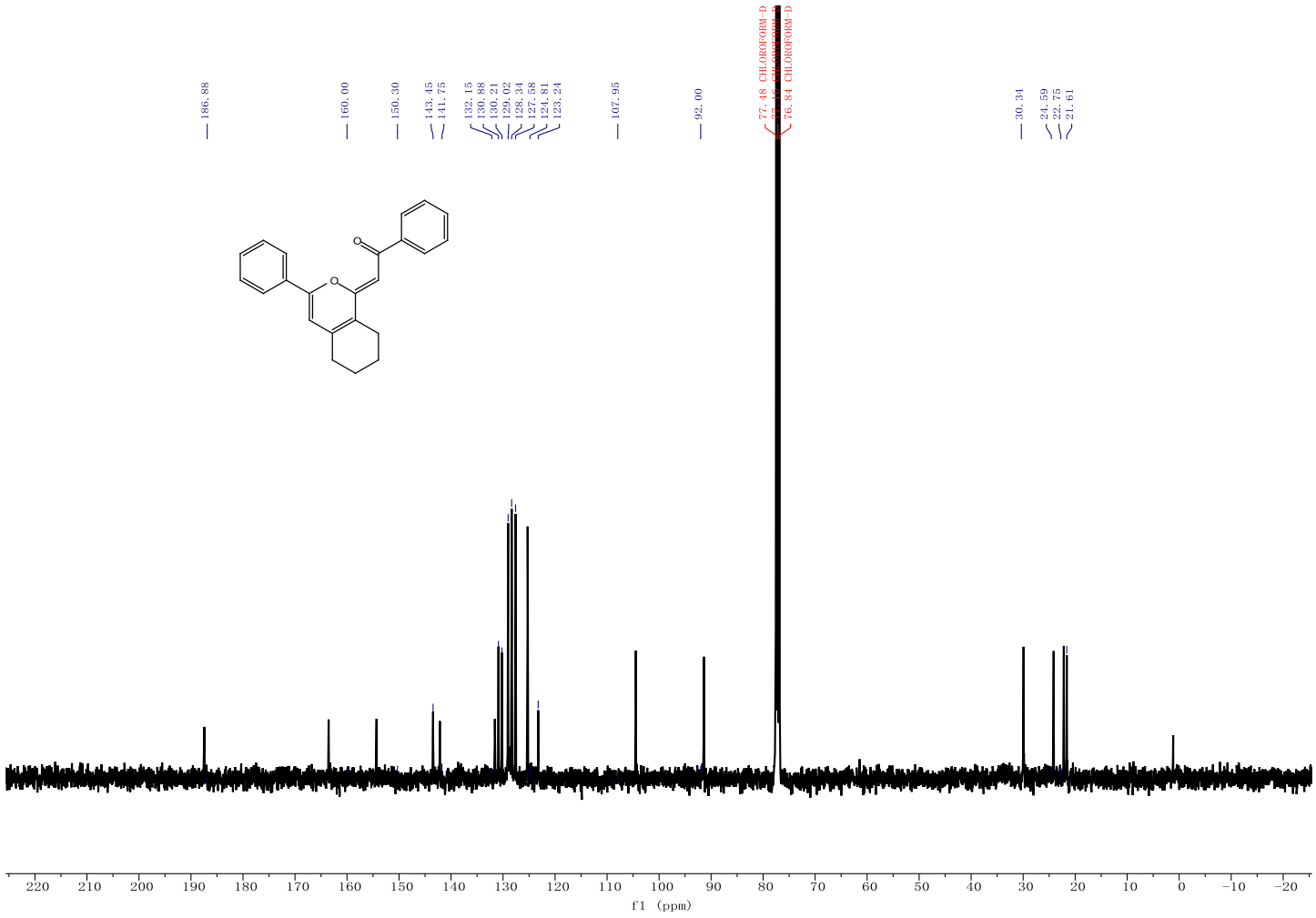
^{13}C NMR (151 MHz, $CDCl_3$) of **3x**



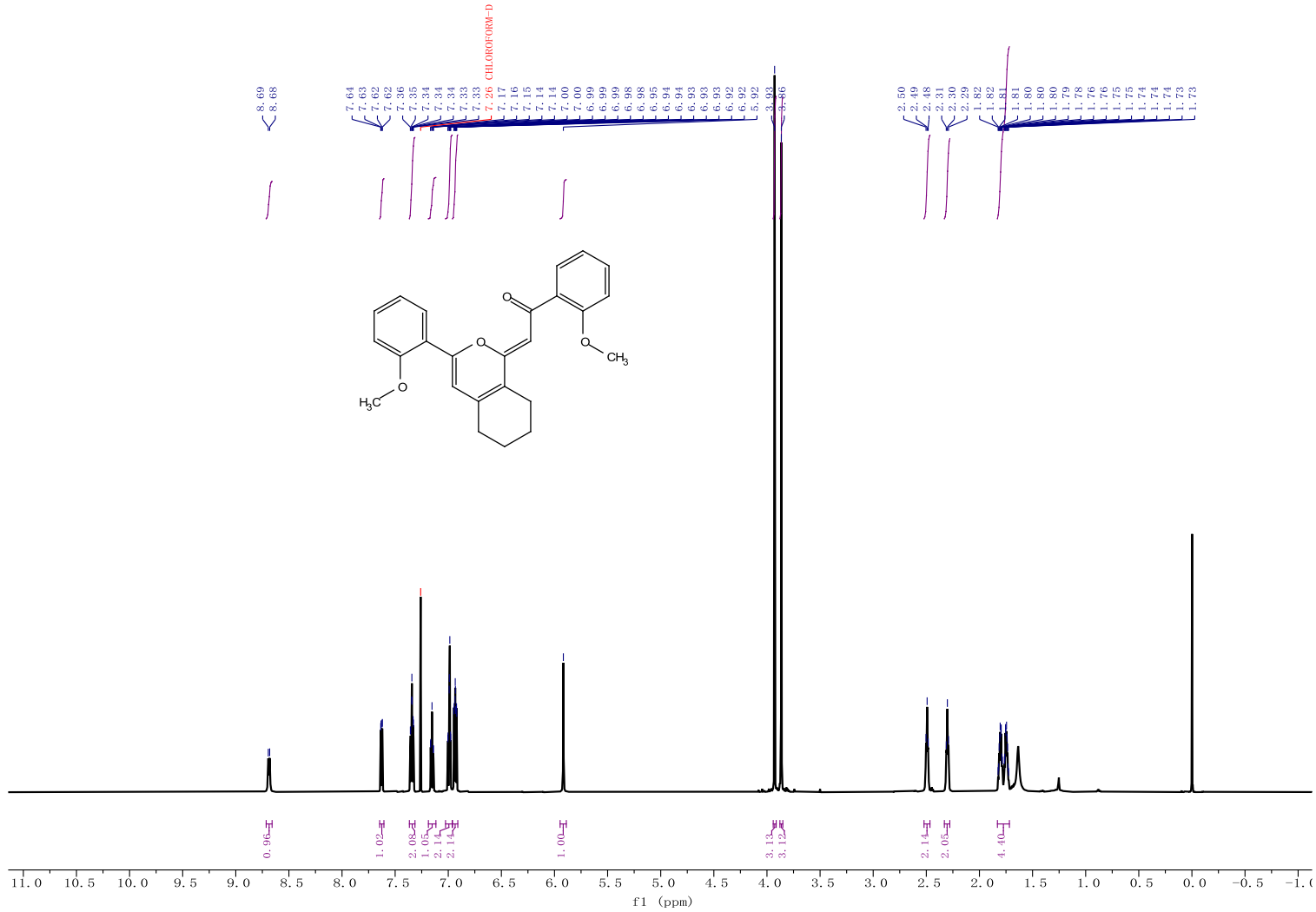
^{1}H NMR (600 MHz, $CDCl_3$) of **4a**



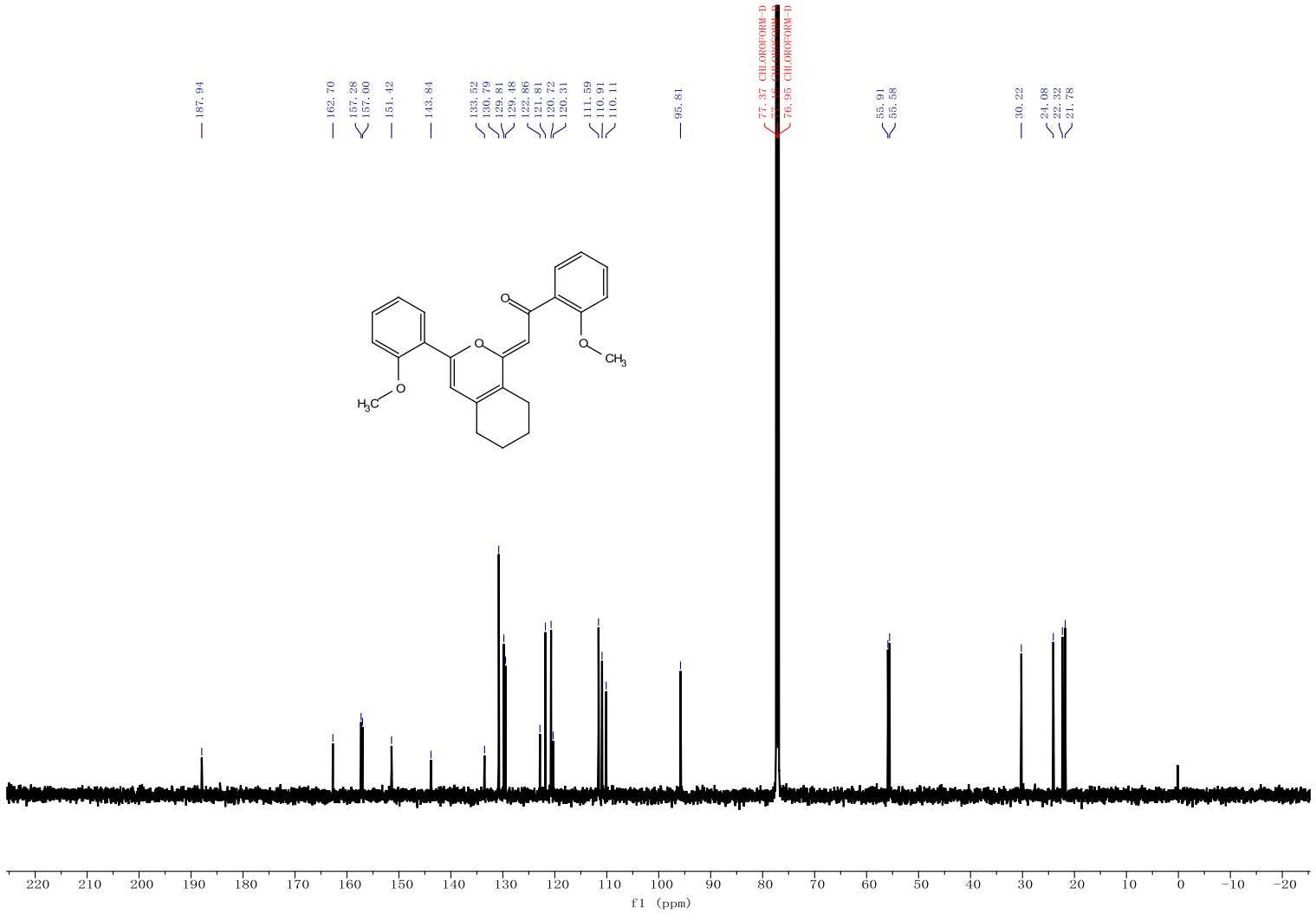
^{13}C NMR (101 MHz, $CDCl_3$) of **4a**



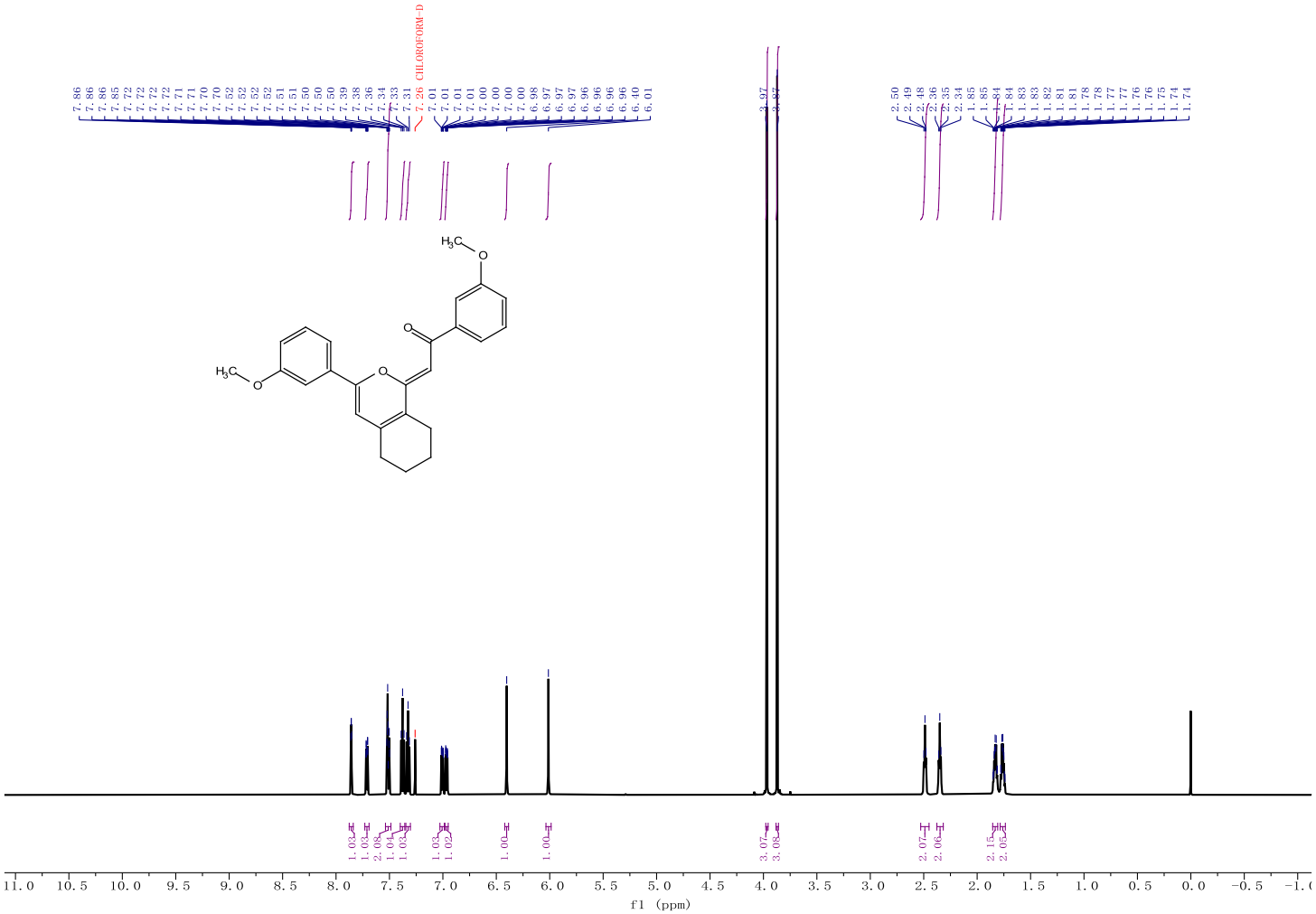
^{1}H NMR (600 MHz, $CDCl_3$) of **4b**



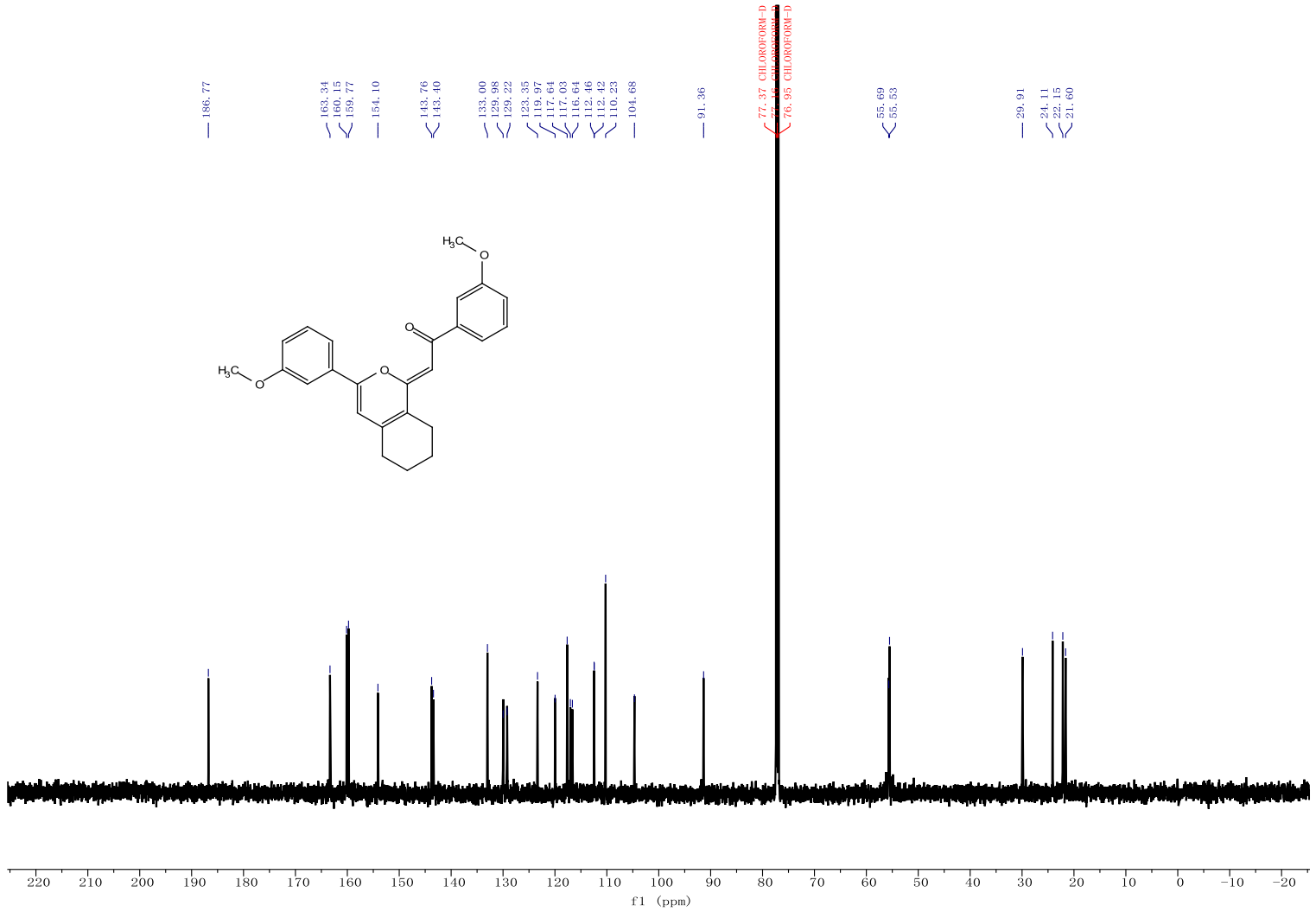
^{13}C NMR (151 MHz, $CDCl_3$) of **4b**



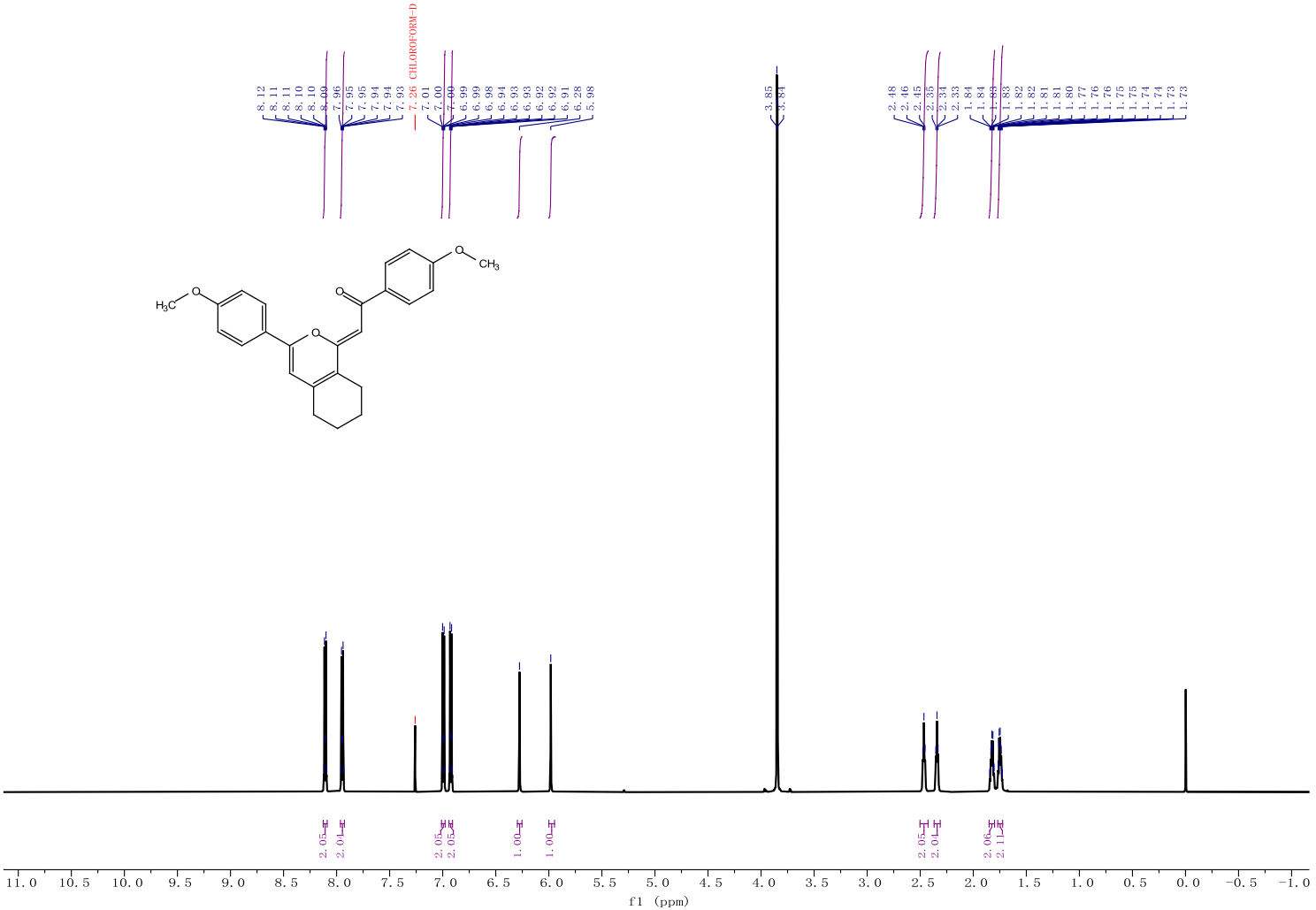
^{1}H NMR (600 MHz, $CDCl_3$) of **4c**



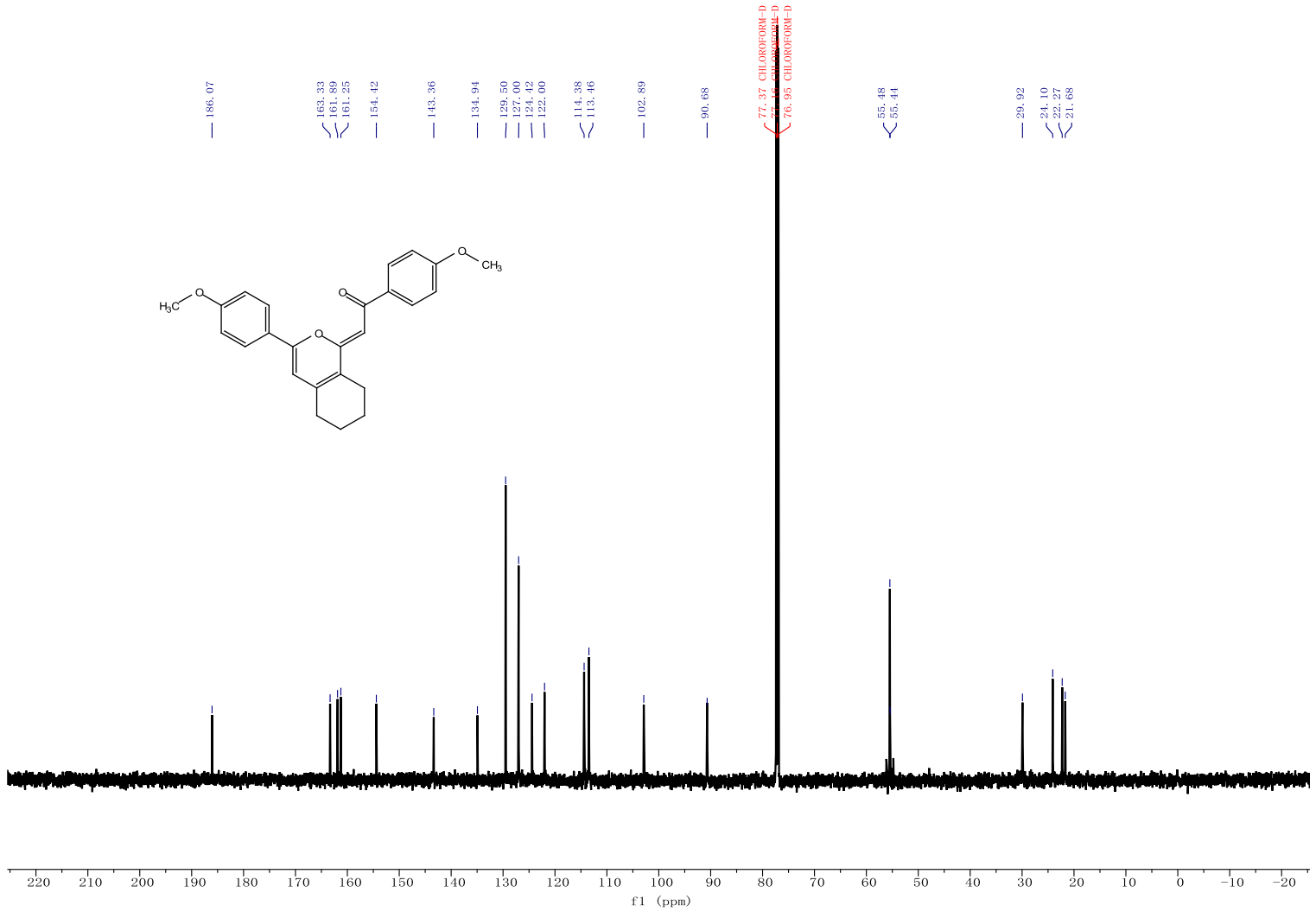
^{13}C NMR (151 MHz, $CDCl_3$) of **4c**



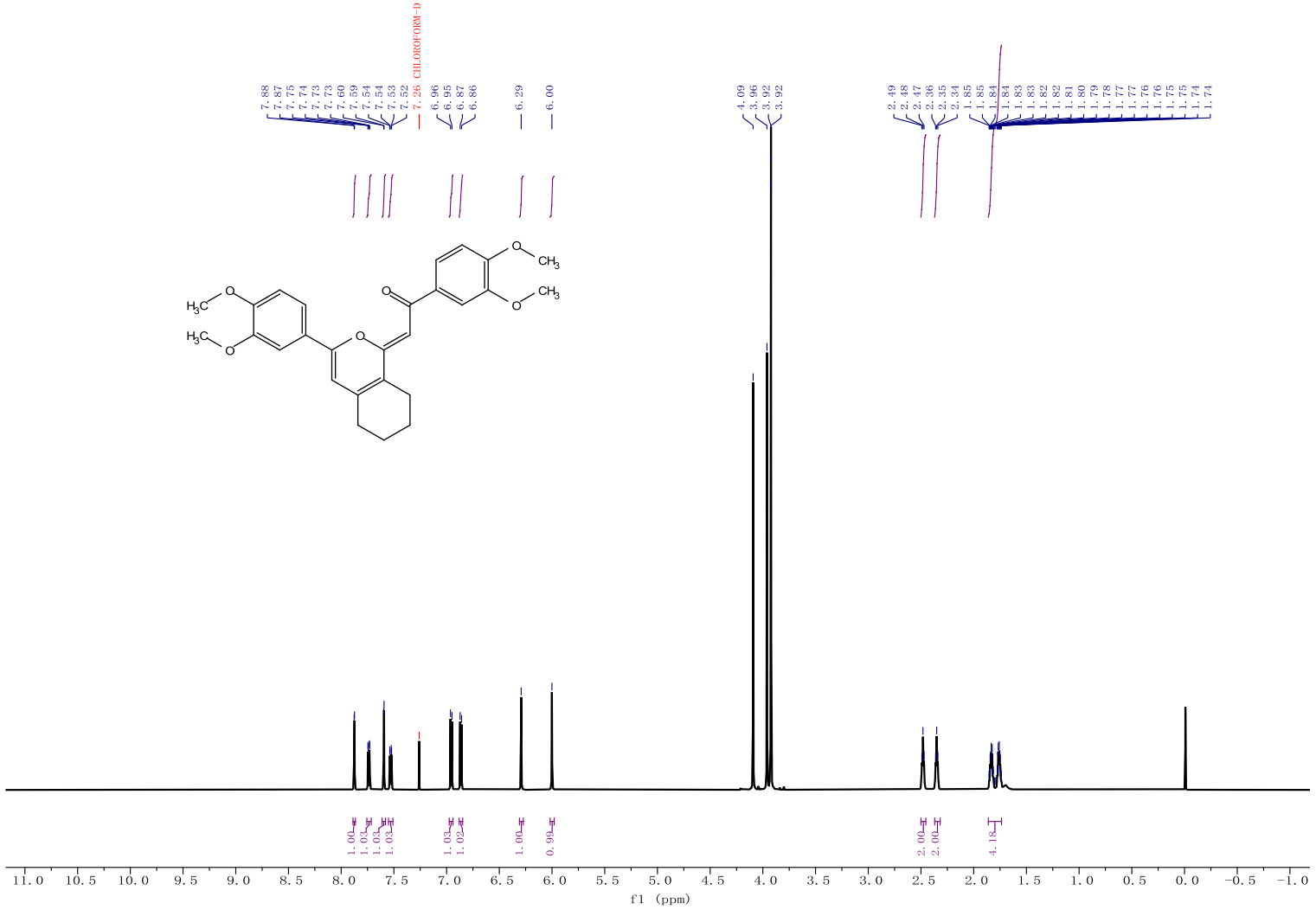
^{1}H NMR (600 MHz, $CDCl_3$) of **4d**



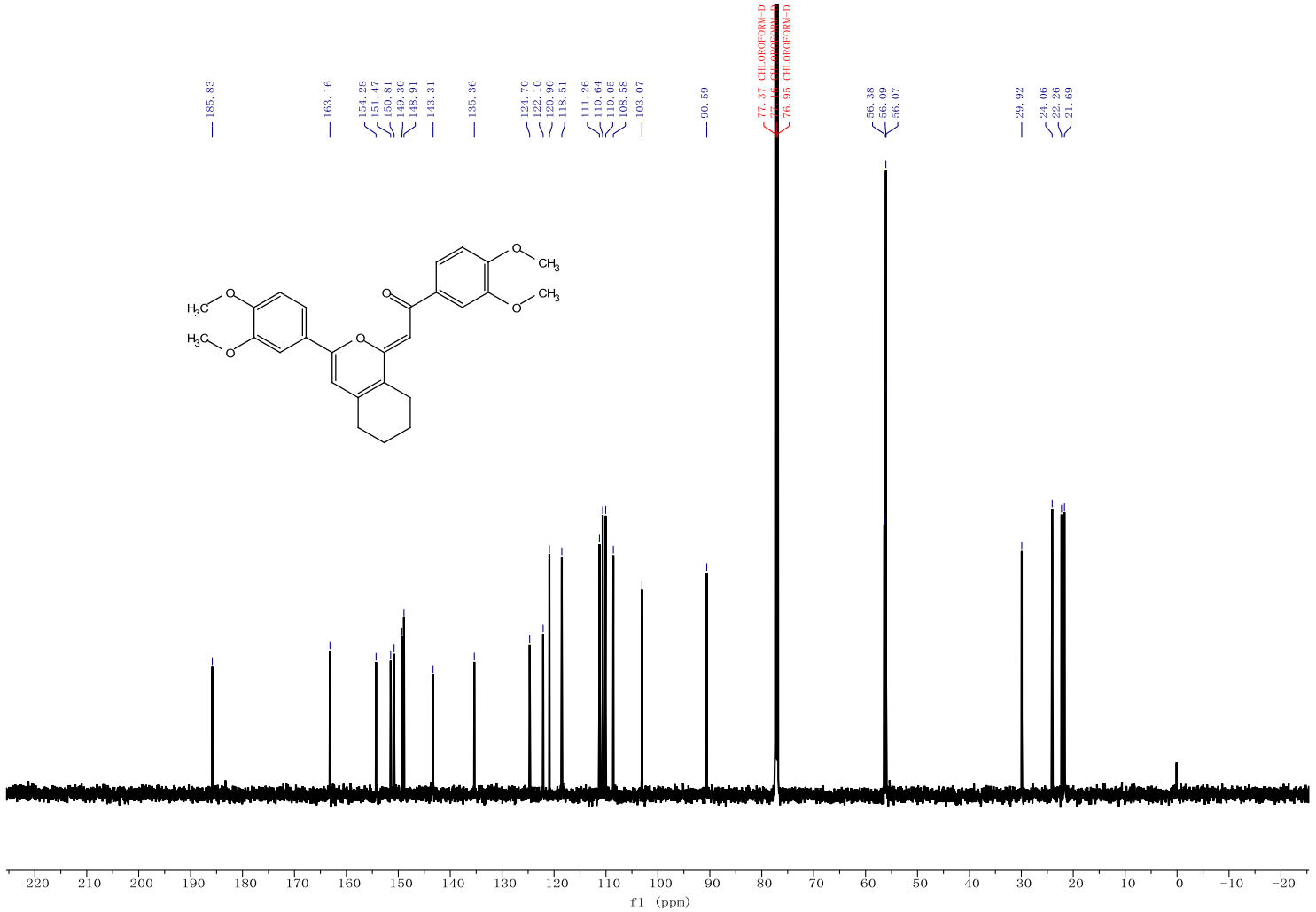
^{13}C NMR (151 MHz, $CDCl_3$) of **4d**



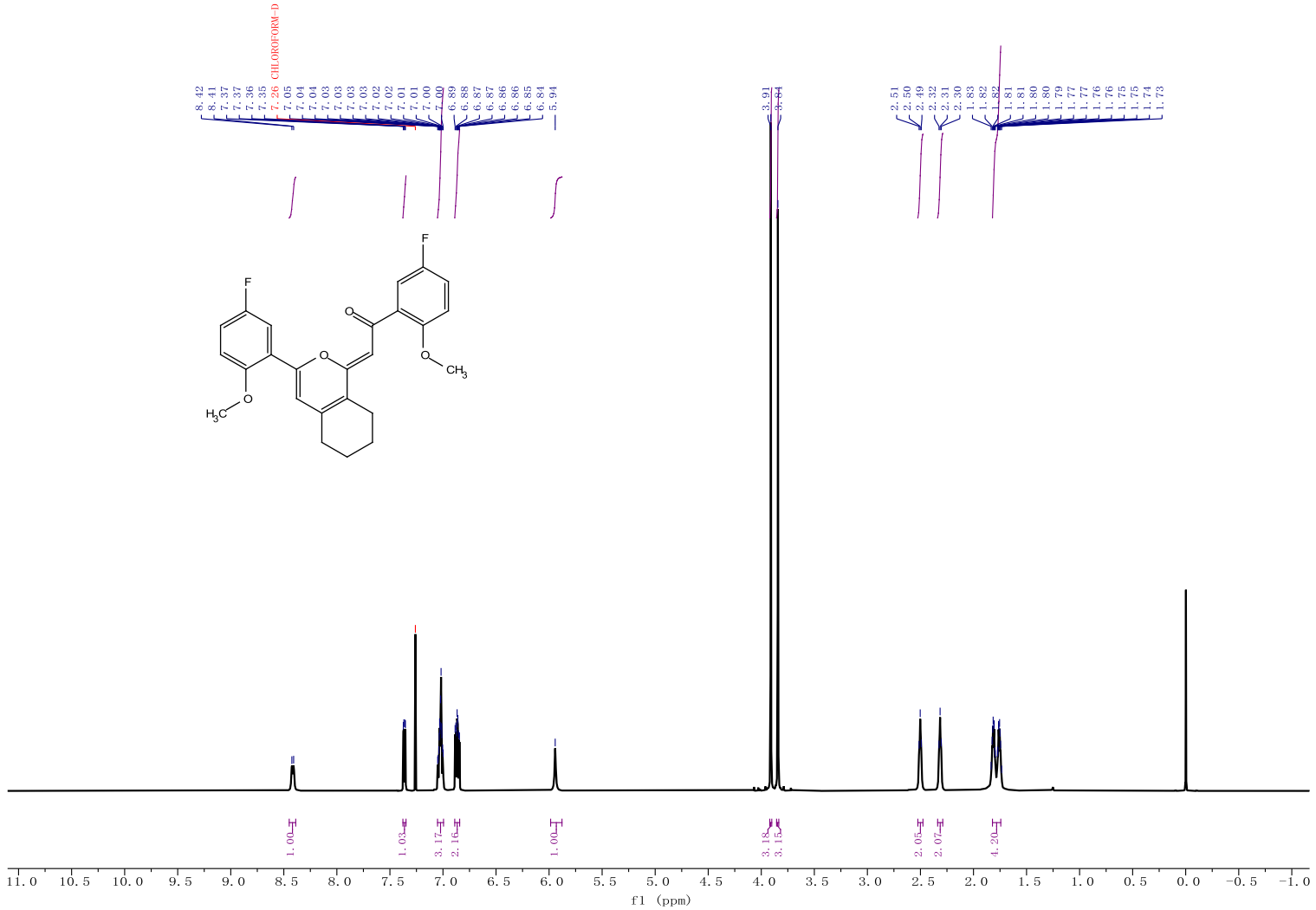
^{1}H NMR (600 MHz, $CDCl_3$) of **4e**



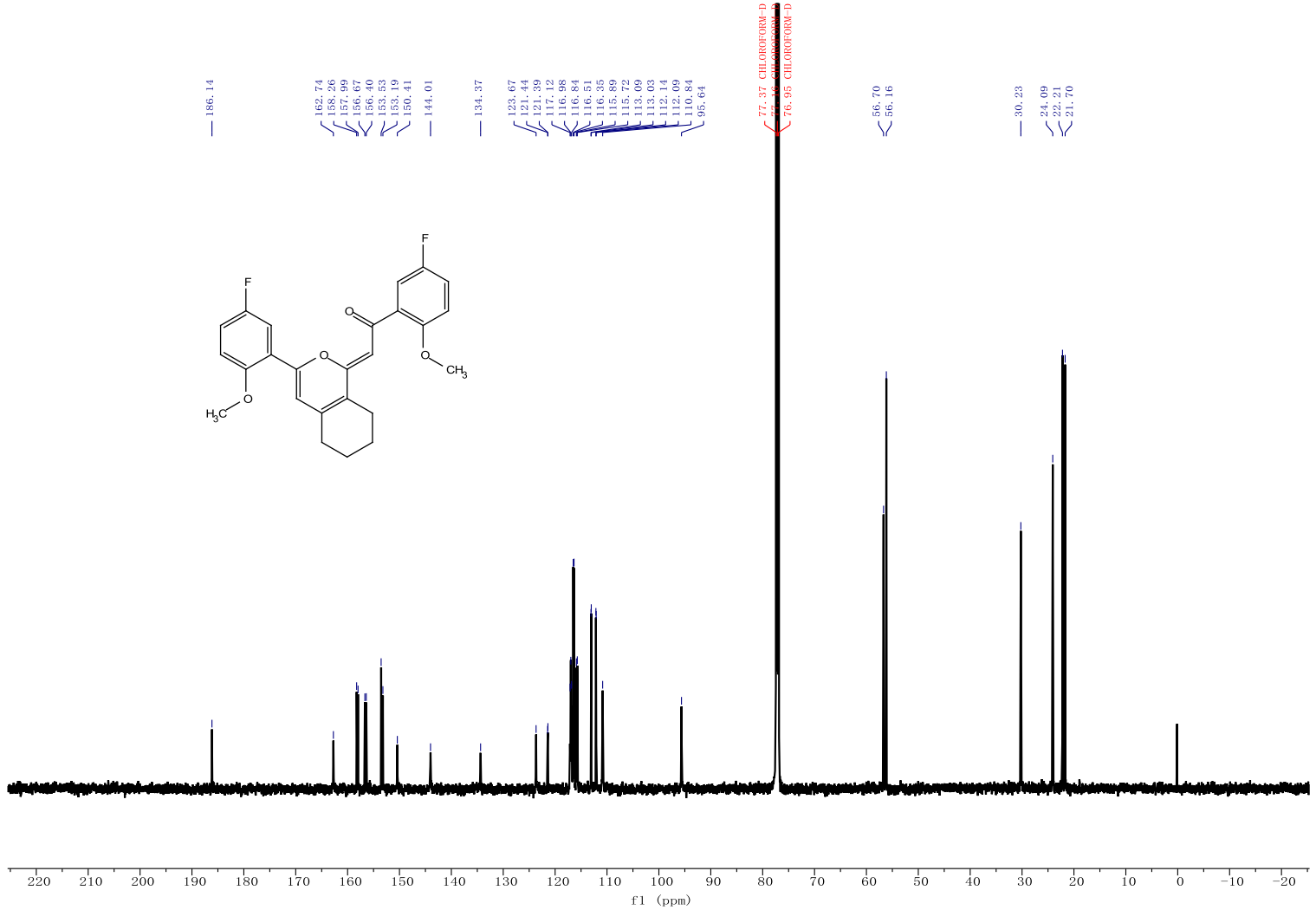
^{13}C NMR (151 MHz, $CDCl_3$) of **4e**



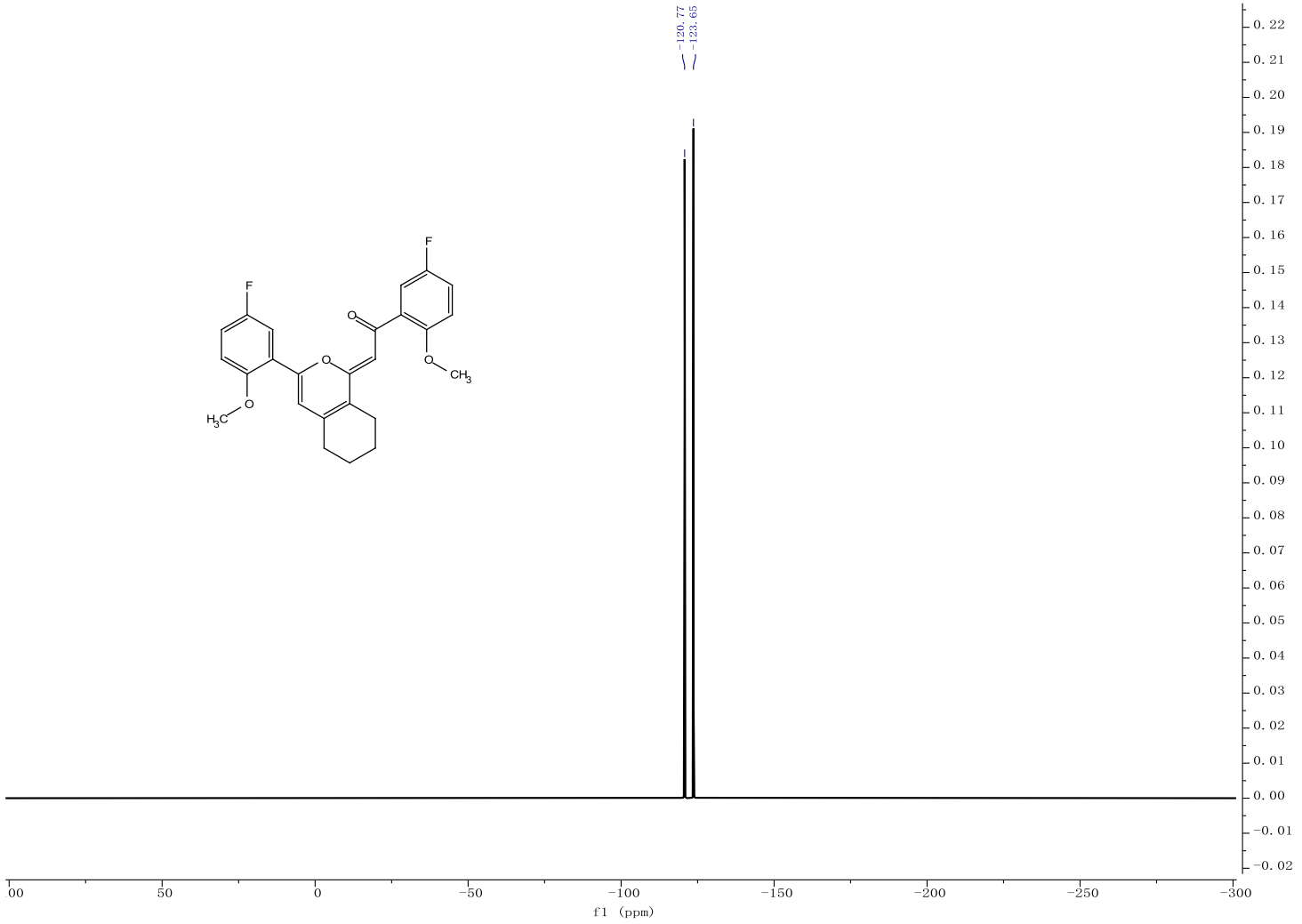
^{1}H NMR (600 MHz, $CDCl_3$) of **4f**



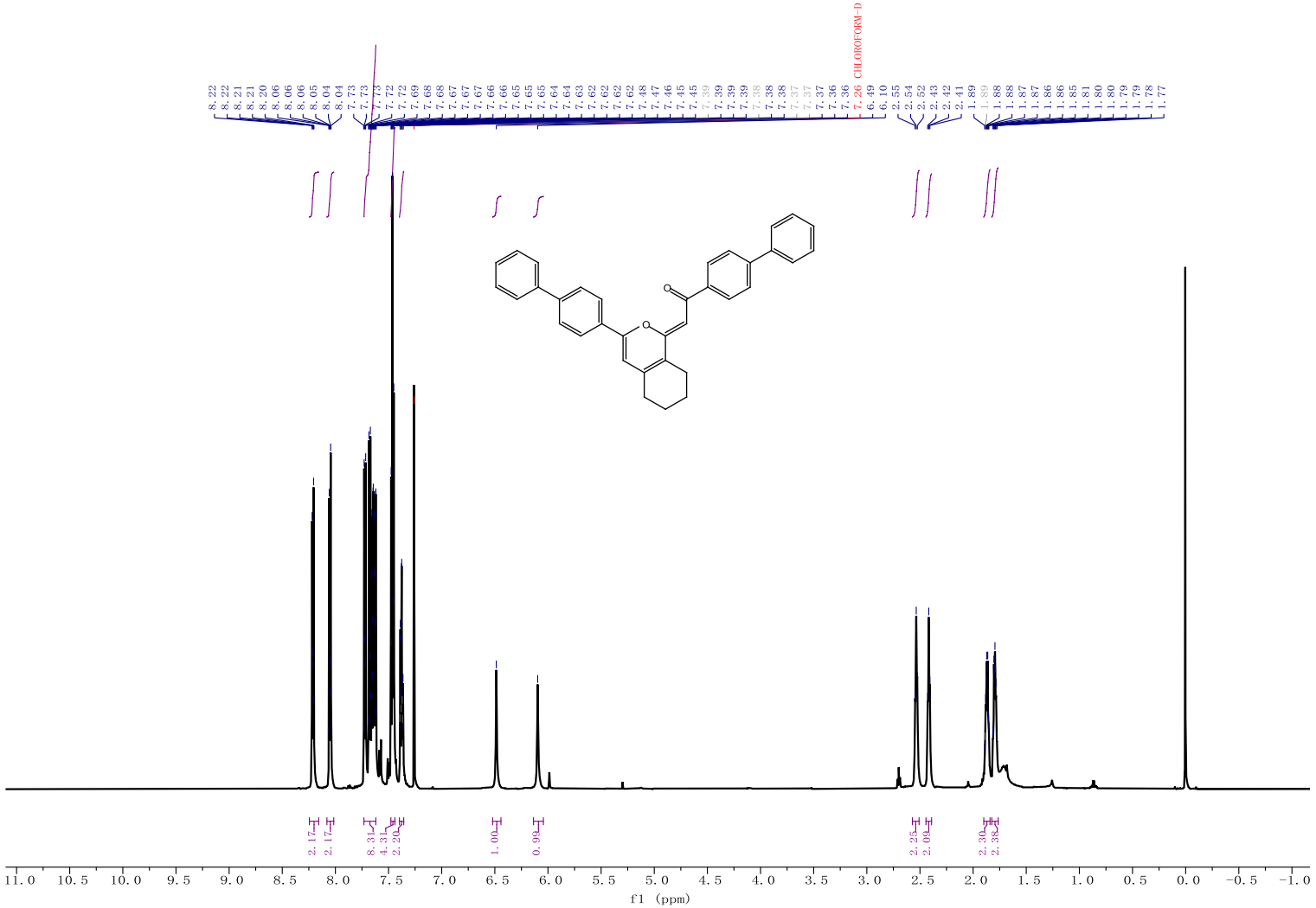
^{13}C NMR (151 MHz, $CDCl_3$) of **4f**



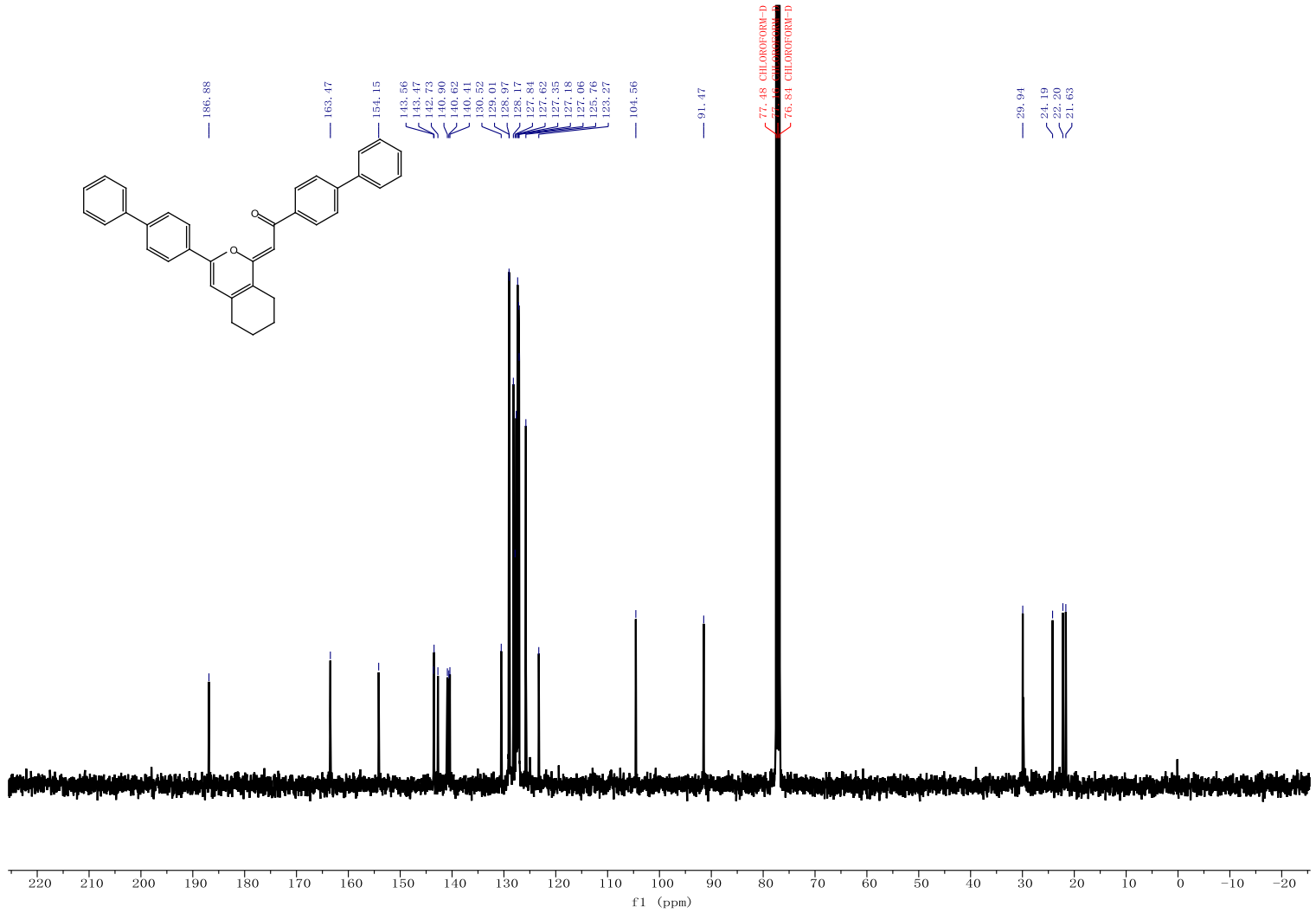
^{19}F NMR (565 MHz, $CDCl_3$) of **4f**



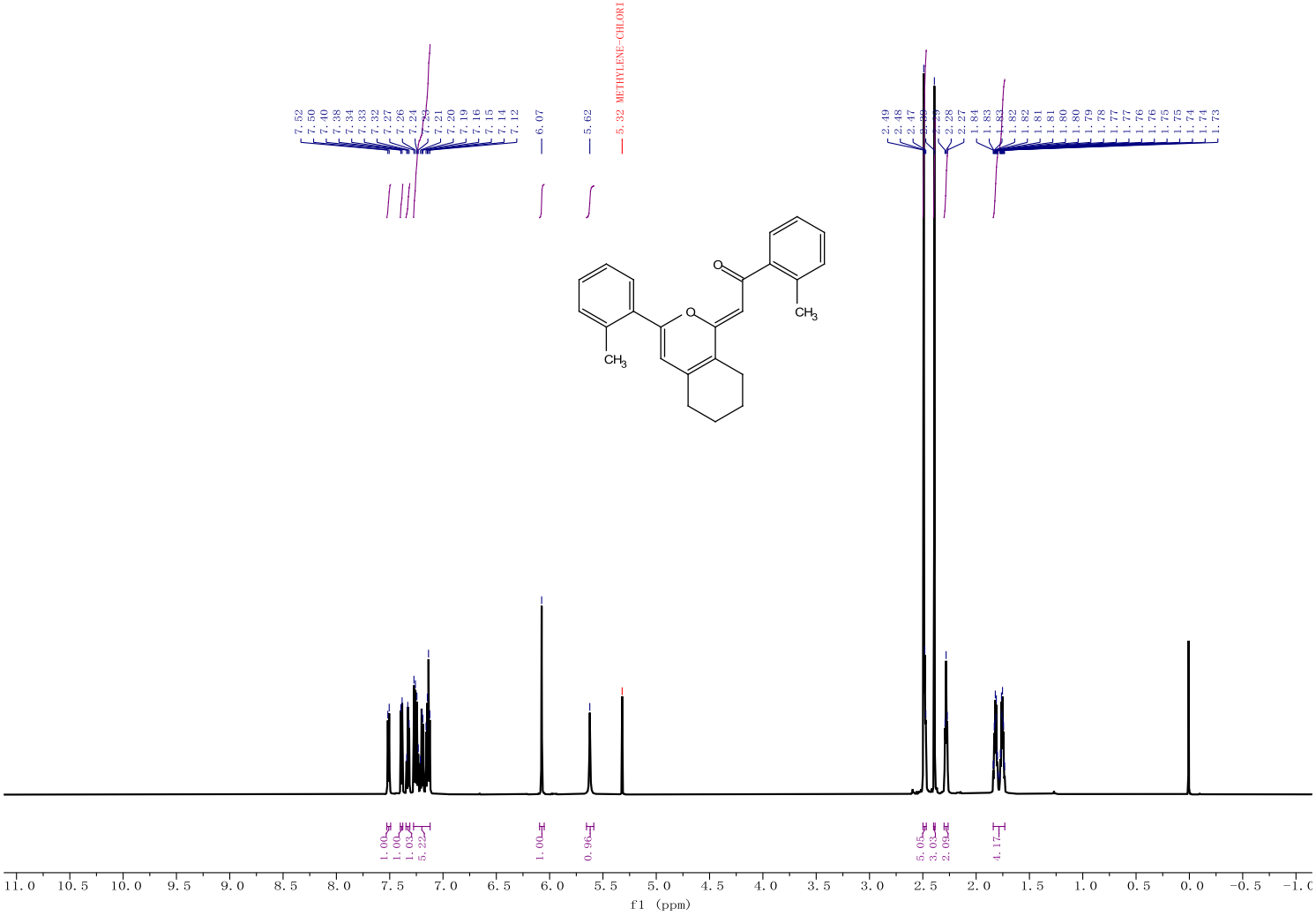
^{1}H NMR (600 MHz, $CDCl_3$) of **4g**



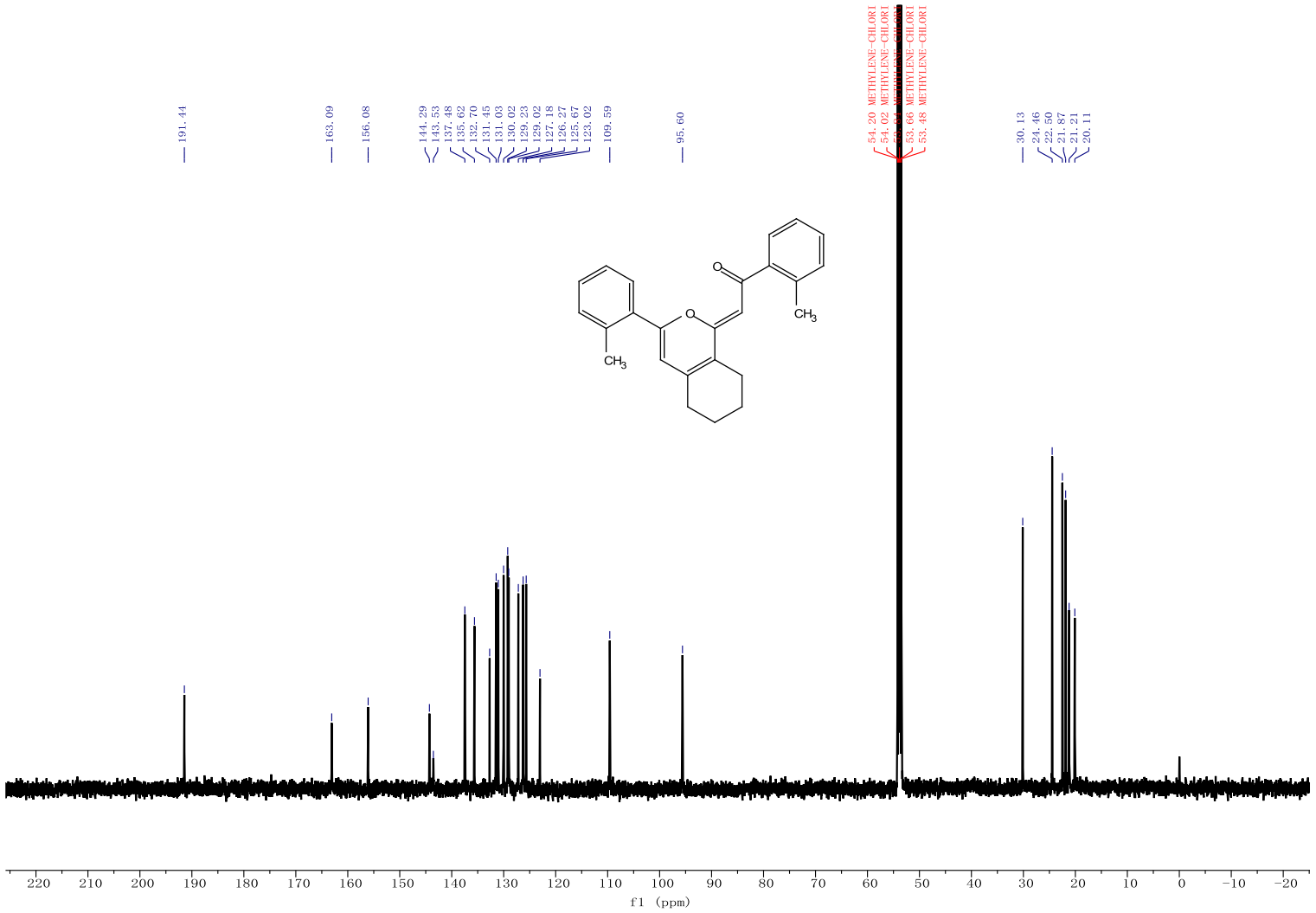
^{13}C NMR (101 MHz, $CDCl_3$) of **4g**



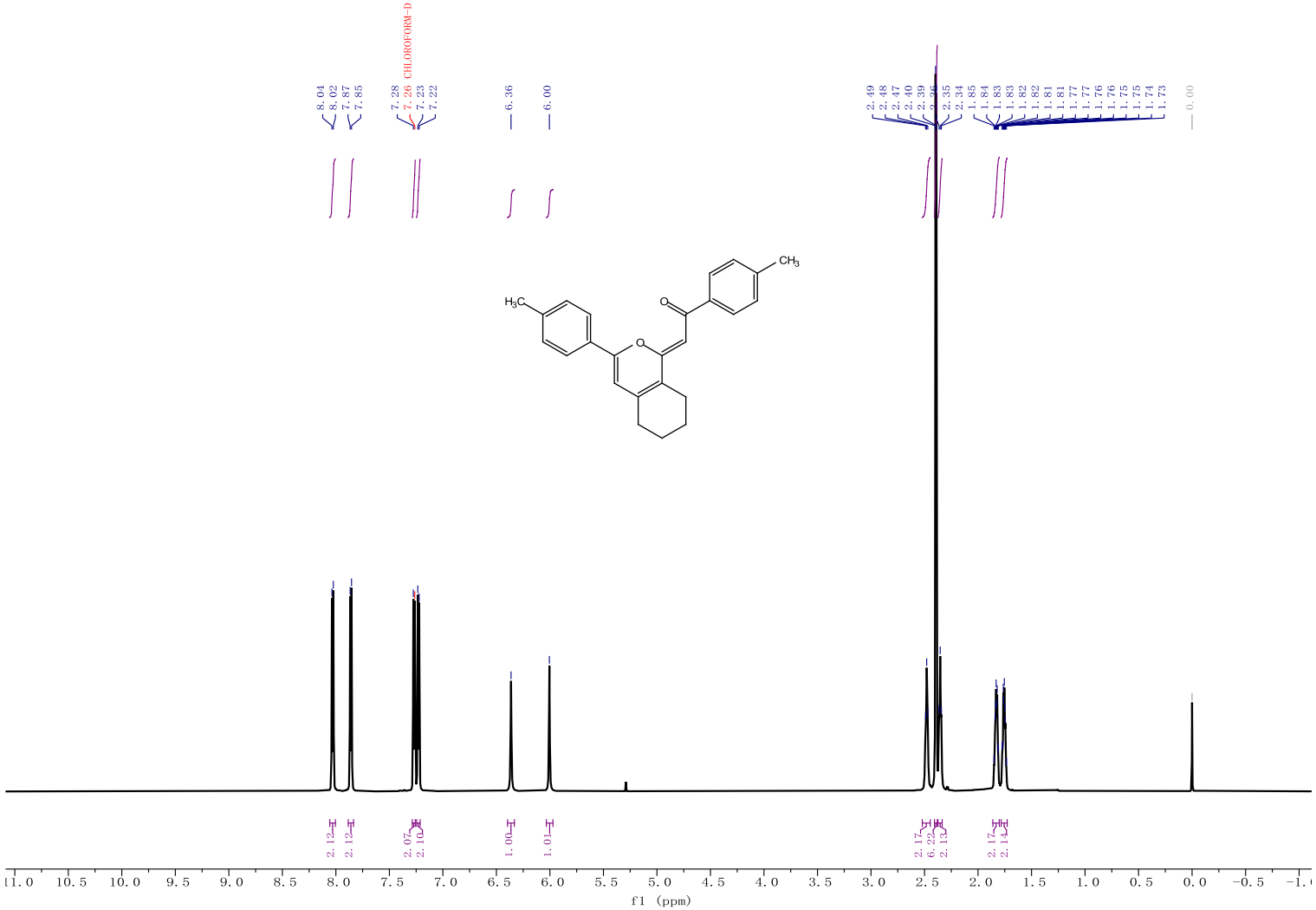
^{1}H NMR (600 MHz, CD_2Cl_2) of **4h**



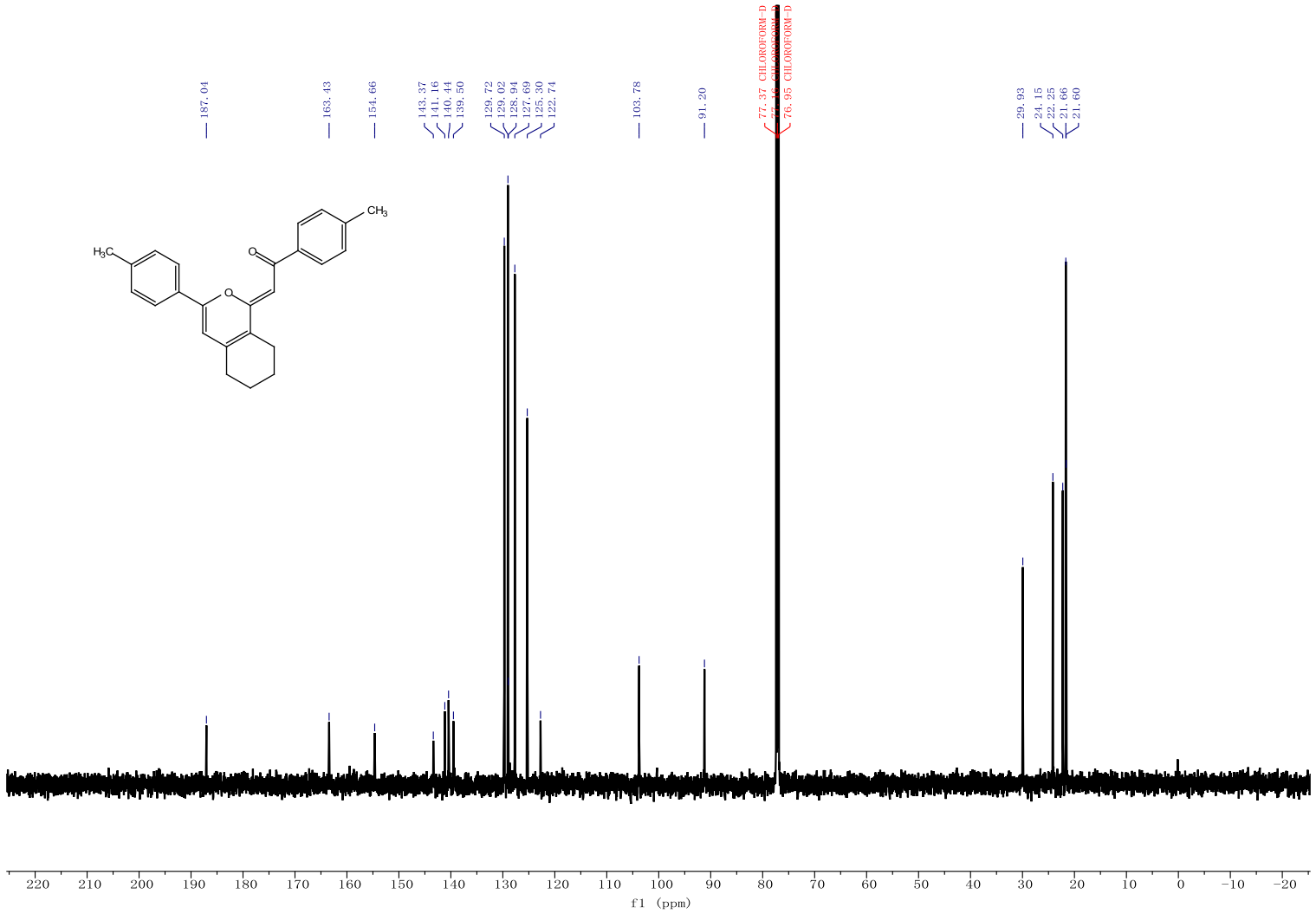
^{13}C NMR (151 MHz, CD_2Cl_2) of **4h**



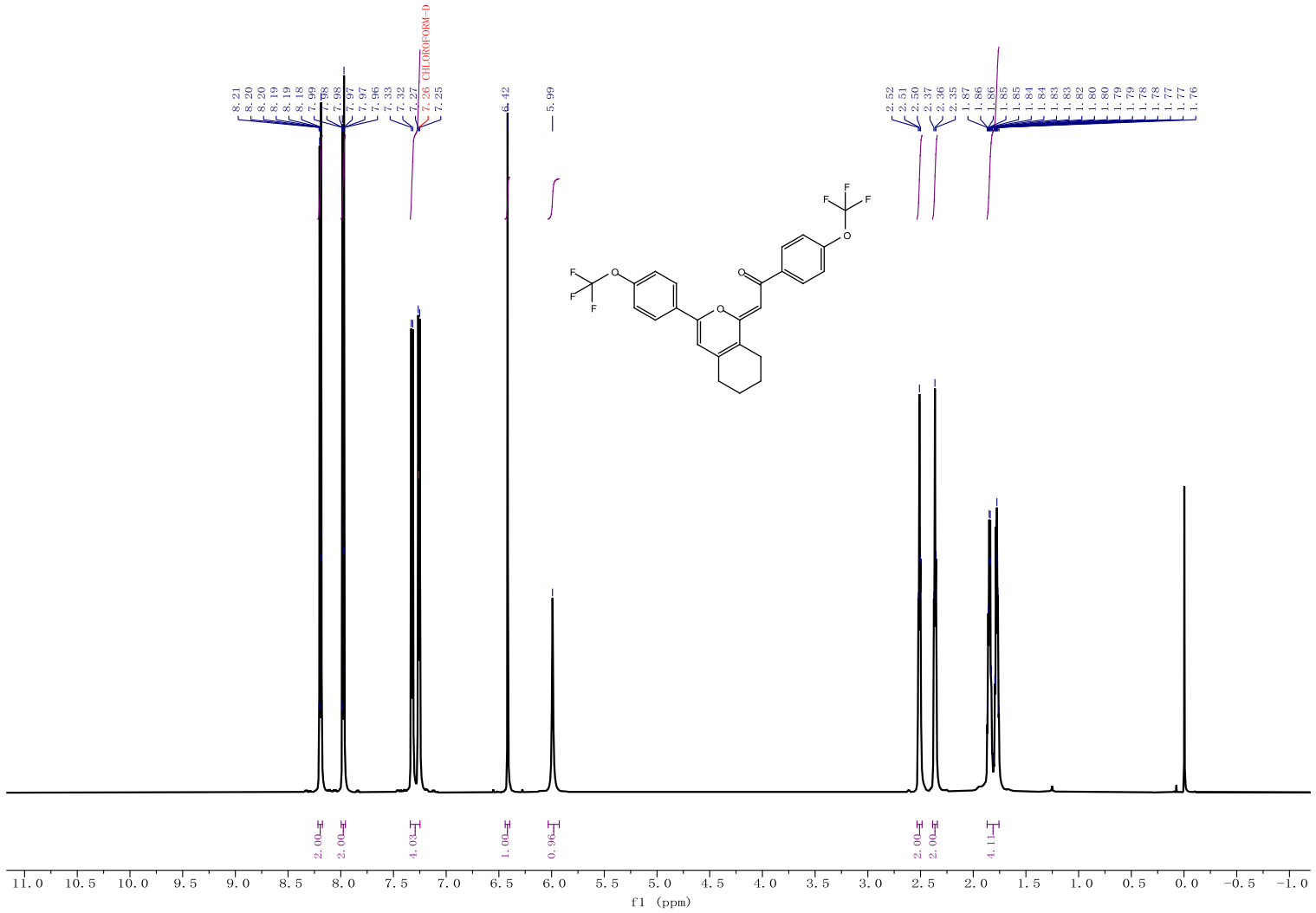
^{1}H NMR (600 MHz, $CDCl_3$) of **4i**



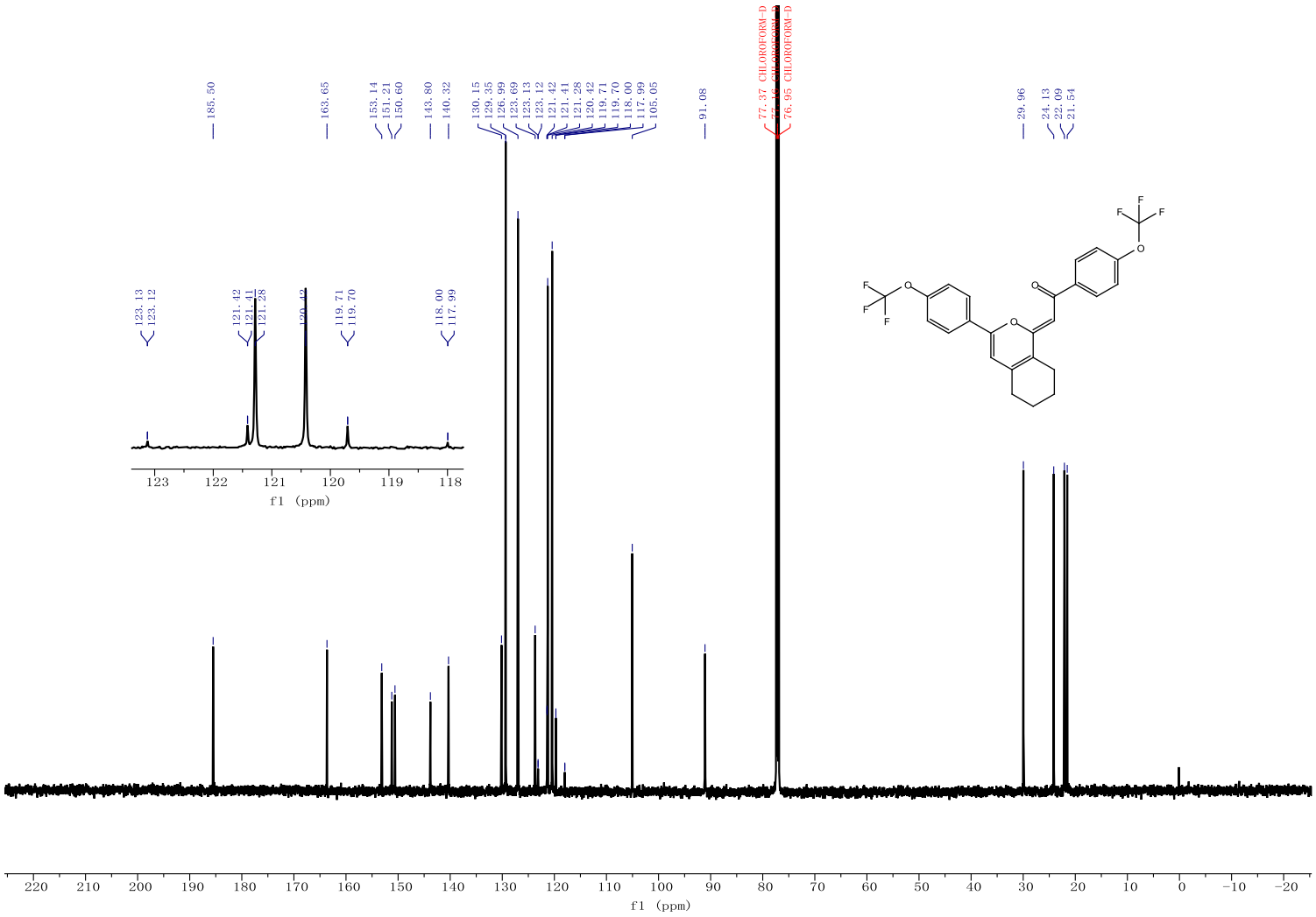
^{13}C NMR (151 MHz, $CDCl_3$) of **4i**



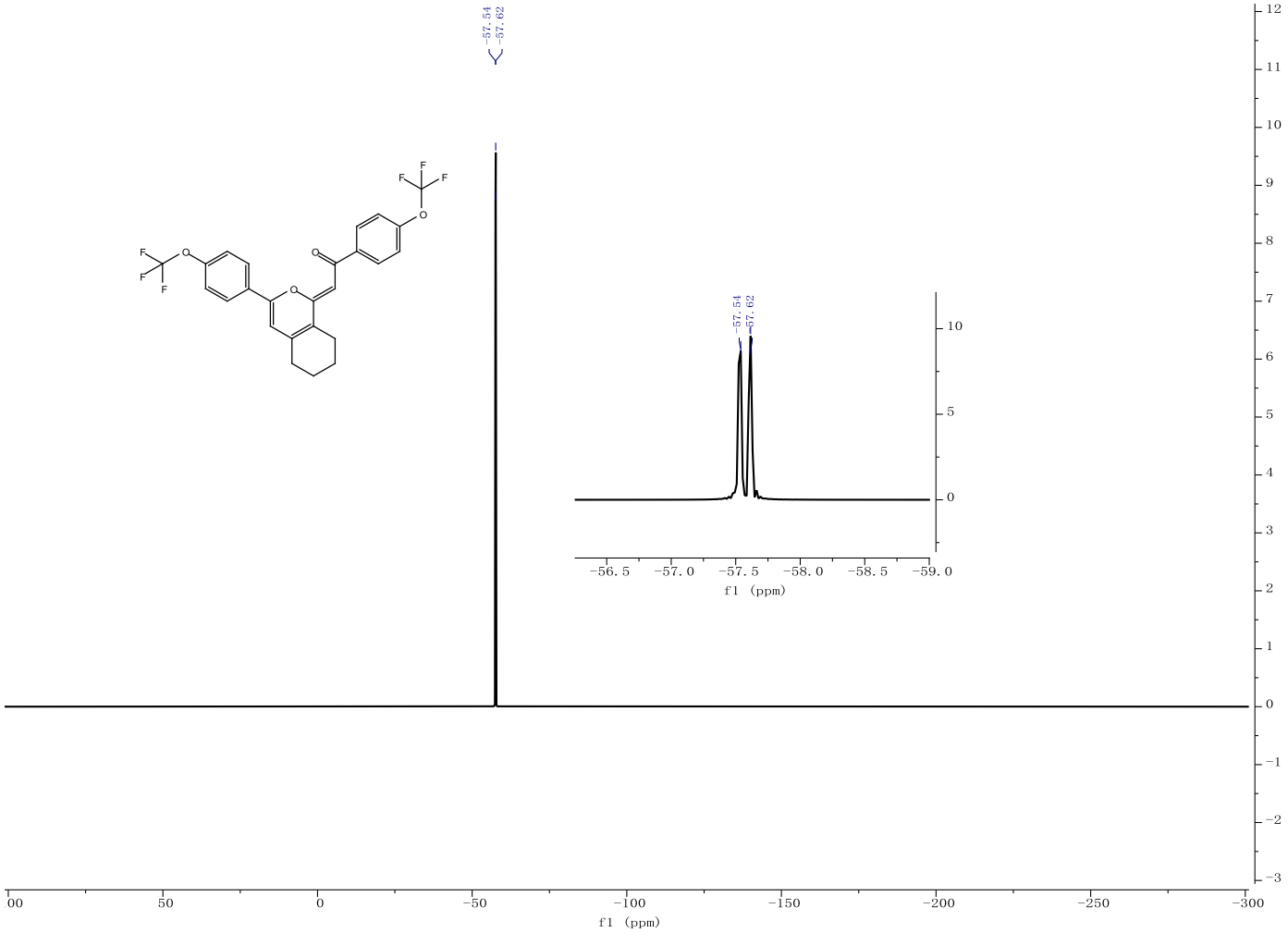
^{1}H NMR (600 MHz, $CDCl_3$) of **4j**



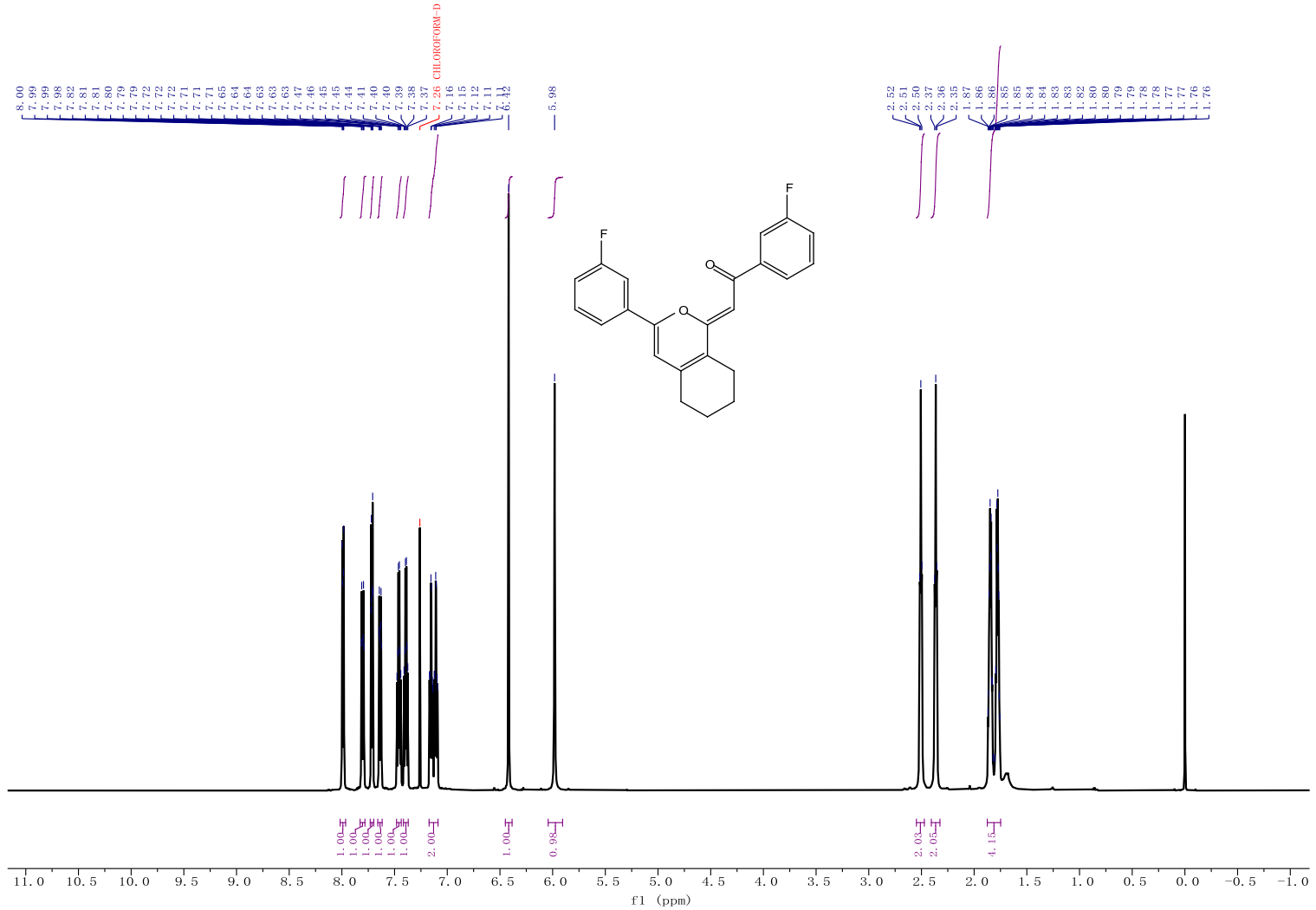
^{13}C NMR (151 MHz, $CDCl_3$) of **4j**



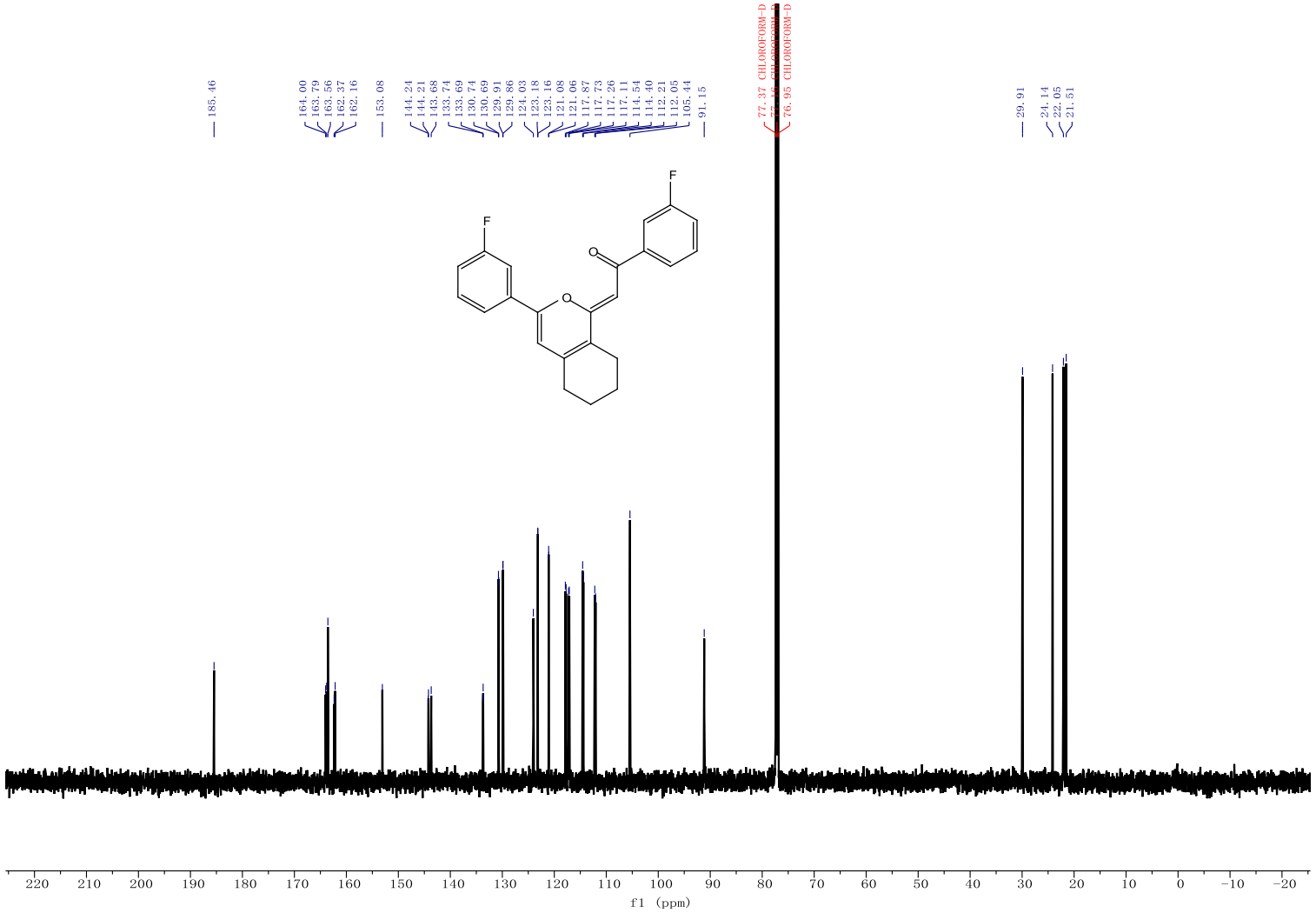
^{19}F NMR (565 MHz, $CDCl_3$) of **4j**



^{1}H NMR (600 MHz, $CDCl_3$) of **4k**

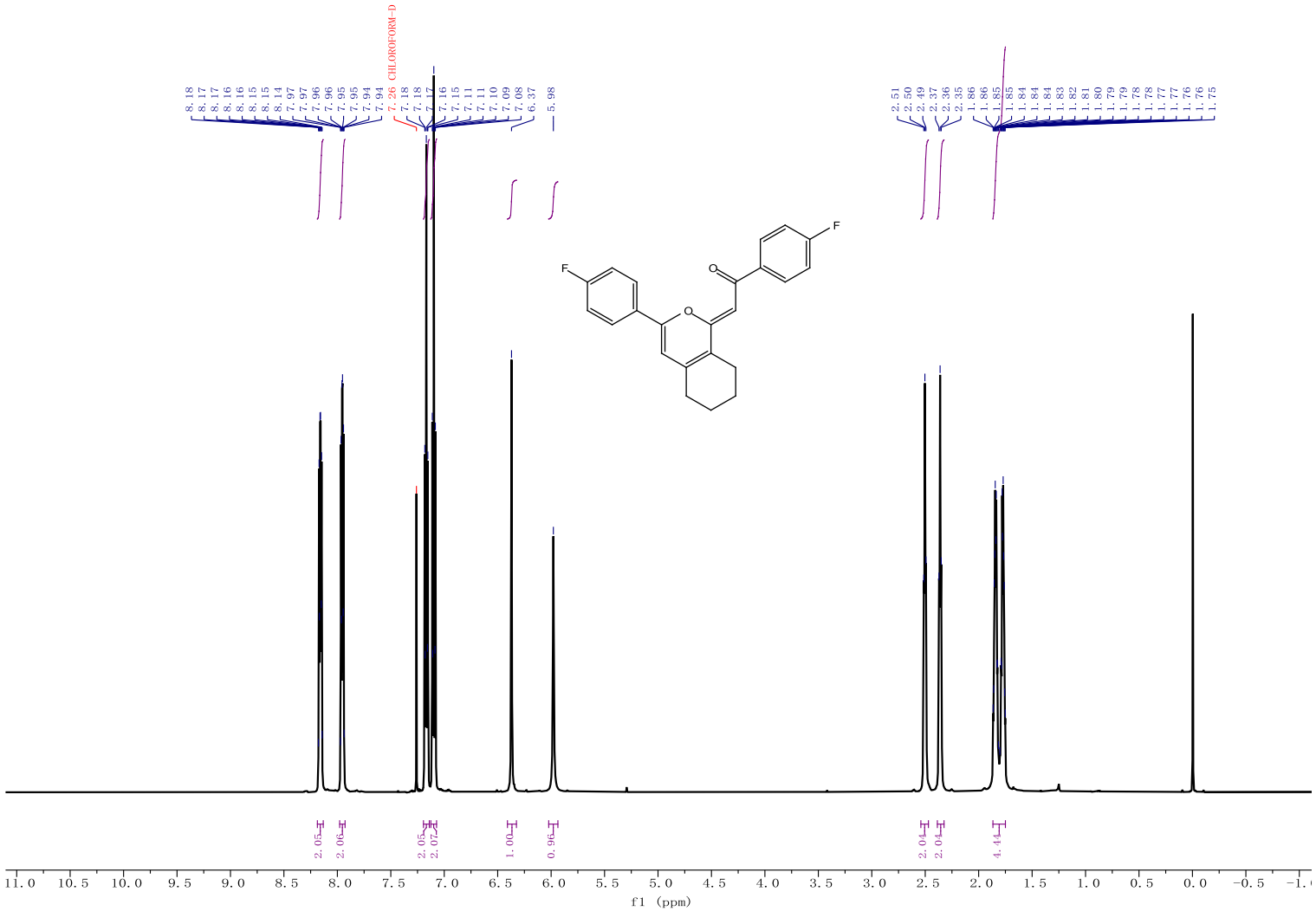


^{13}C NMR (151 MHz, $CDCl_3$) of **4k**

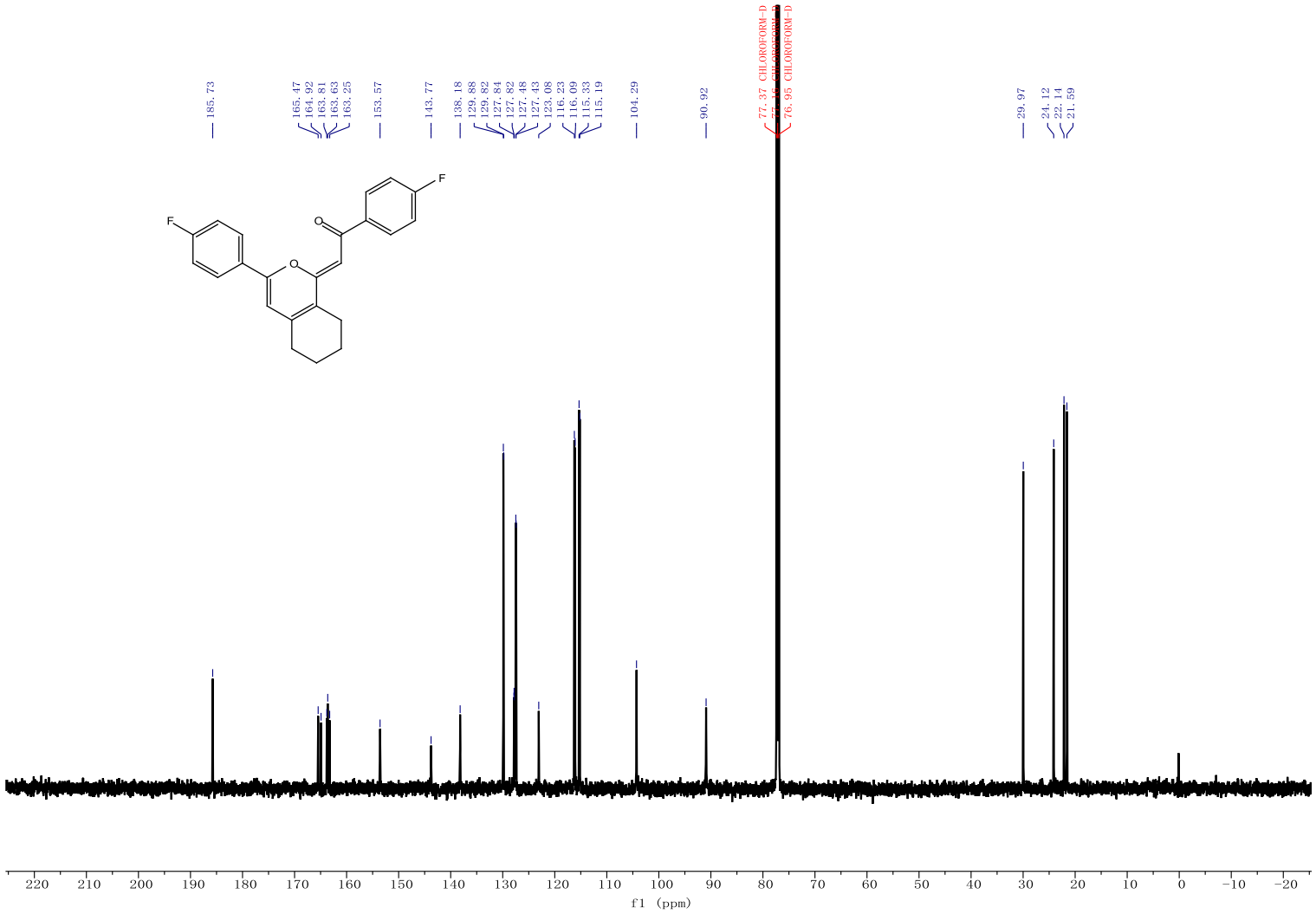


^{19}F NMR (565 MHz, $CDCl_3$) of **4k**

^{1}H NMR (600 MHz, $CDCl_3$) of **4l**

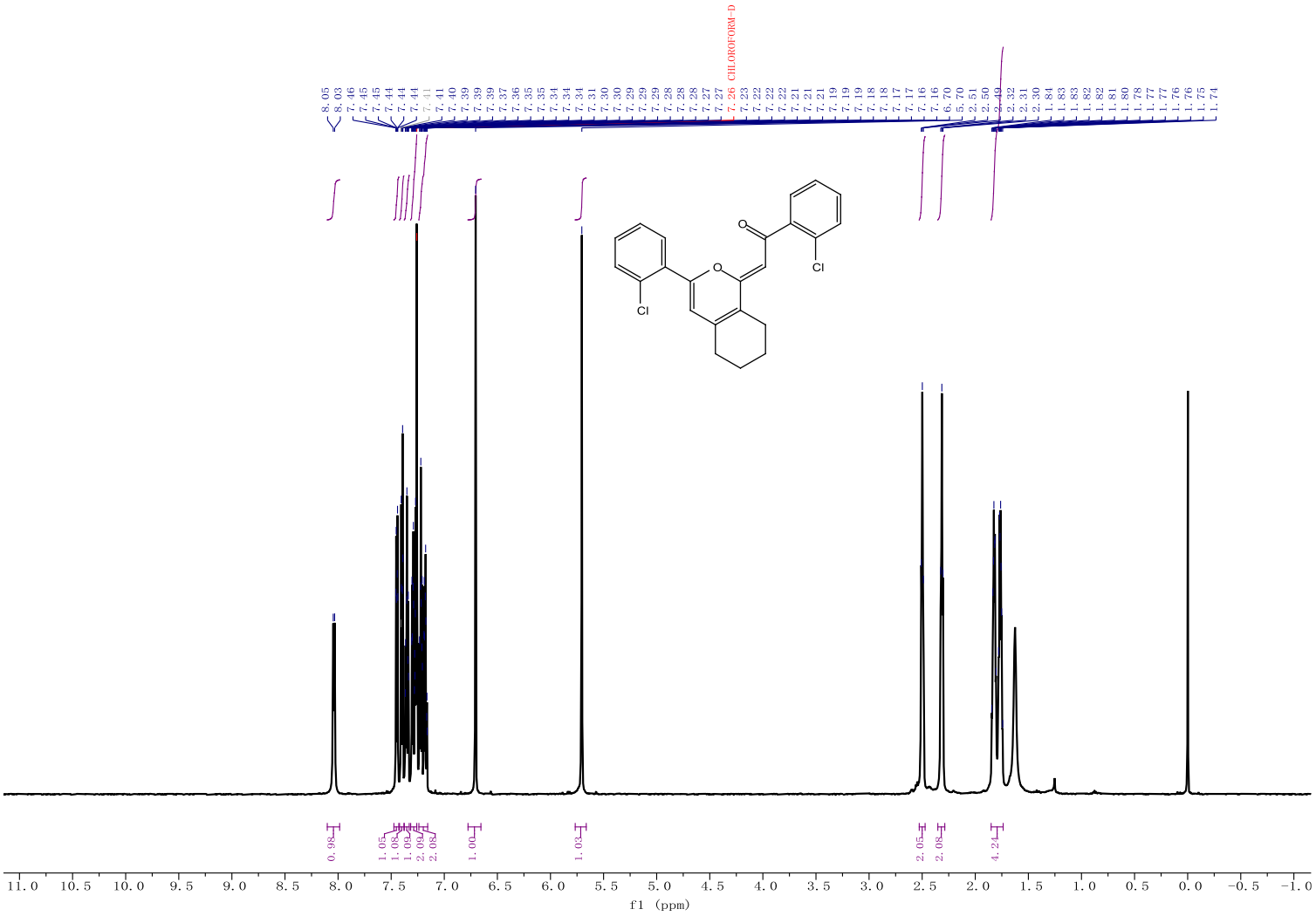


^{13}C NMR (151 MHz, $CDCl_3$) of **4l**

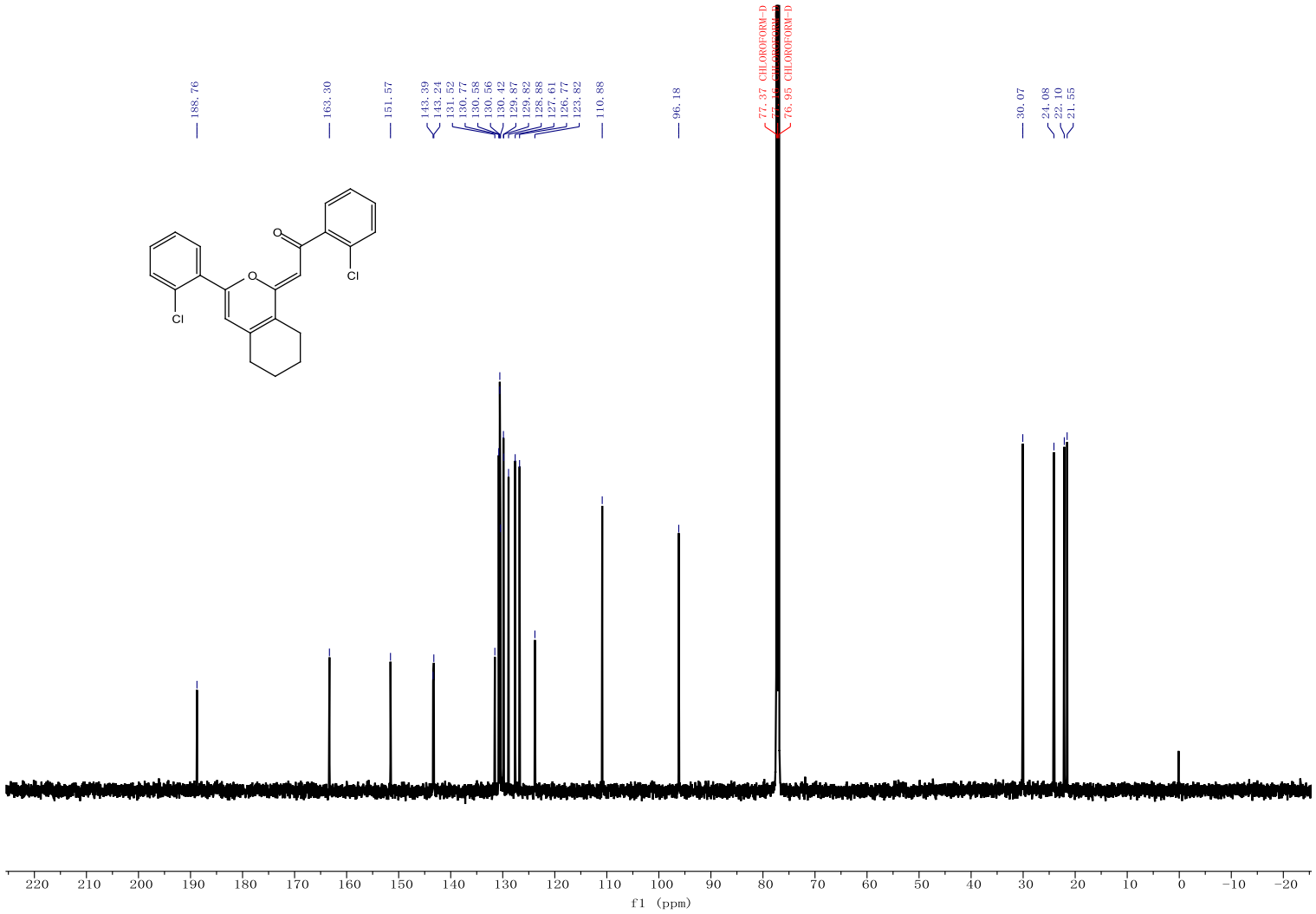


^{19}F NMR (565 MHz, $CDCl_3$) of **4l**

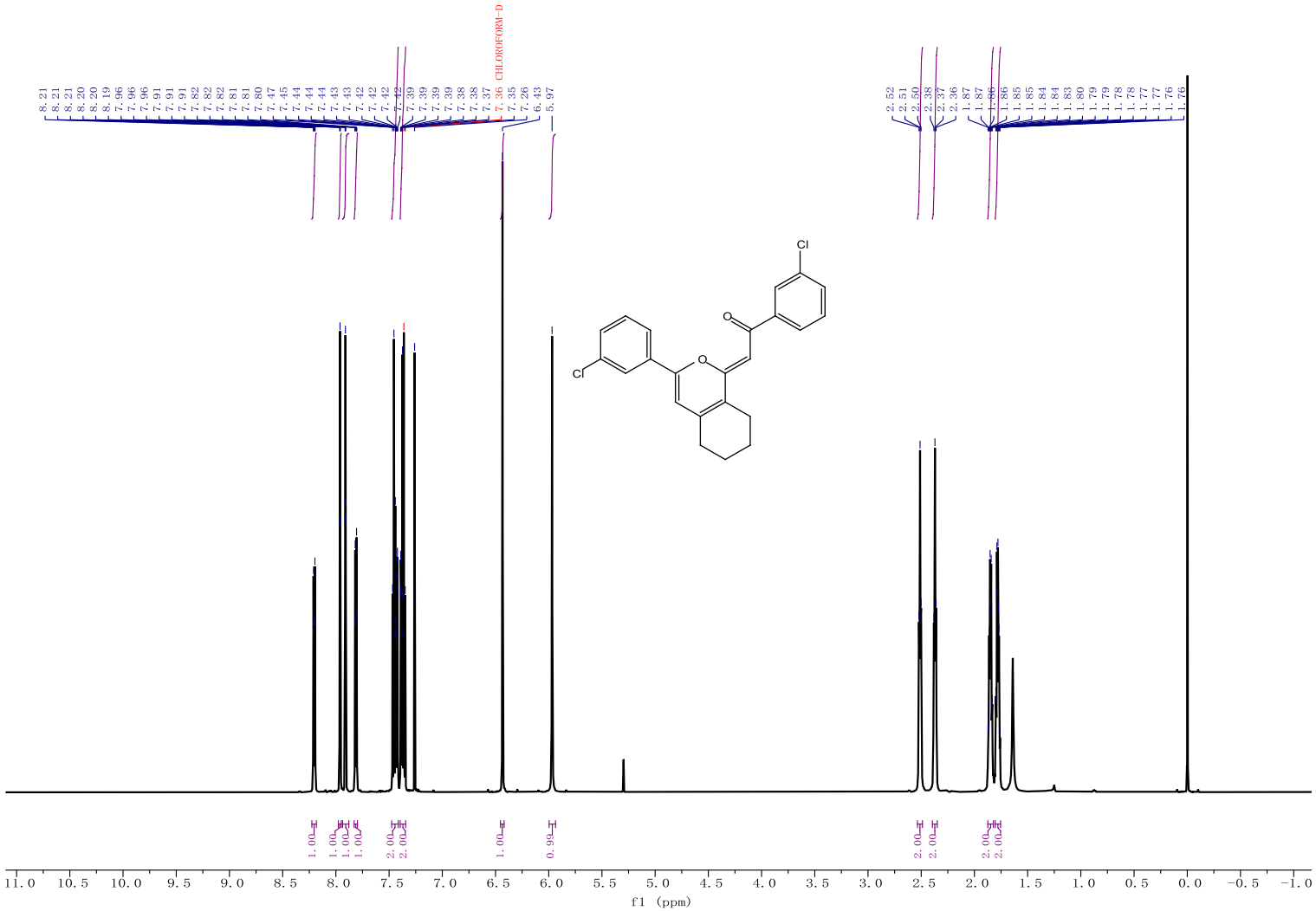
^{1}H NMR (600 MHz, $CDCl_3$) of **4m**



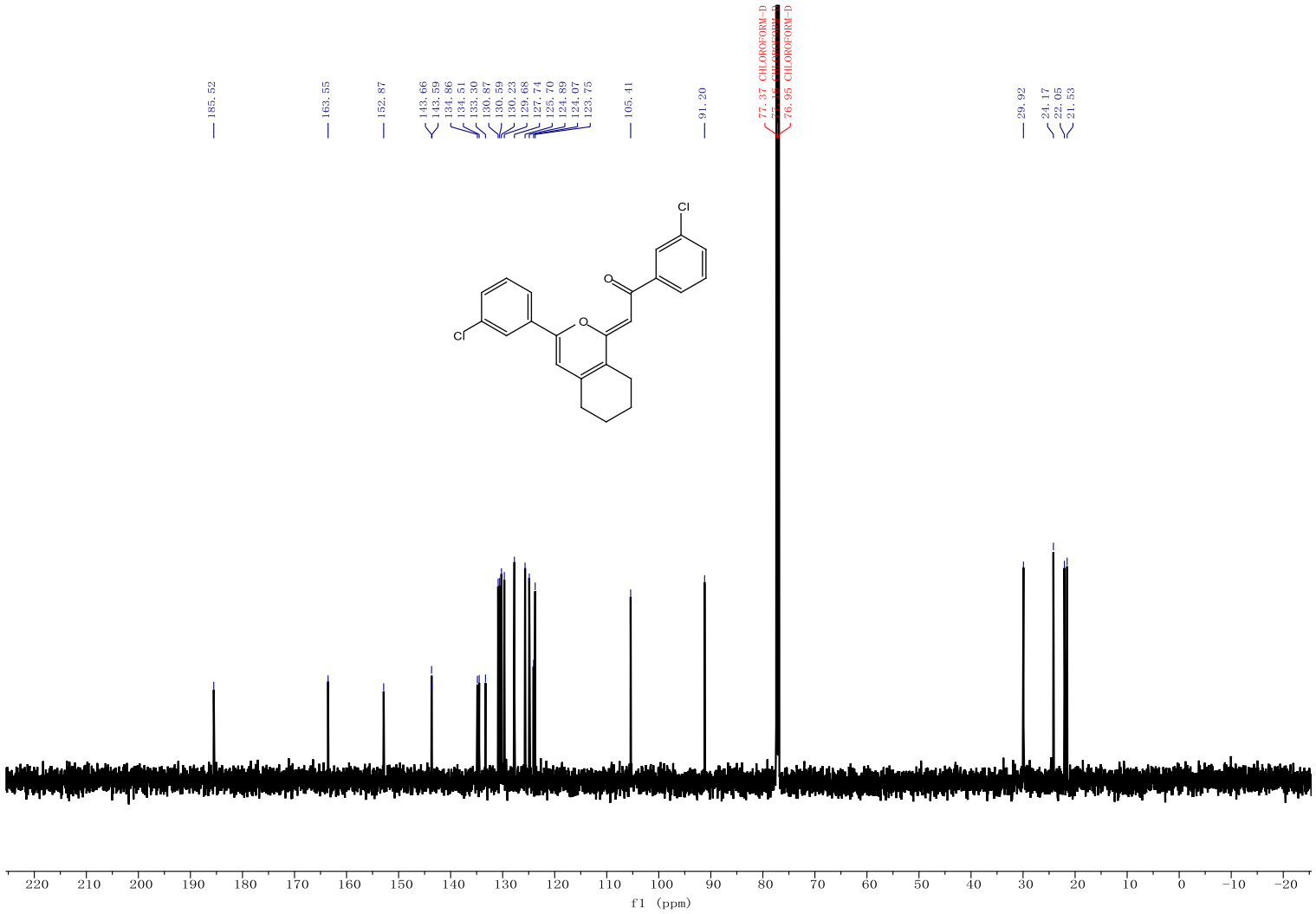
^{13}C NMR (151 MHz, $CDCl_3$) of **4m**



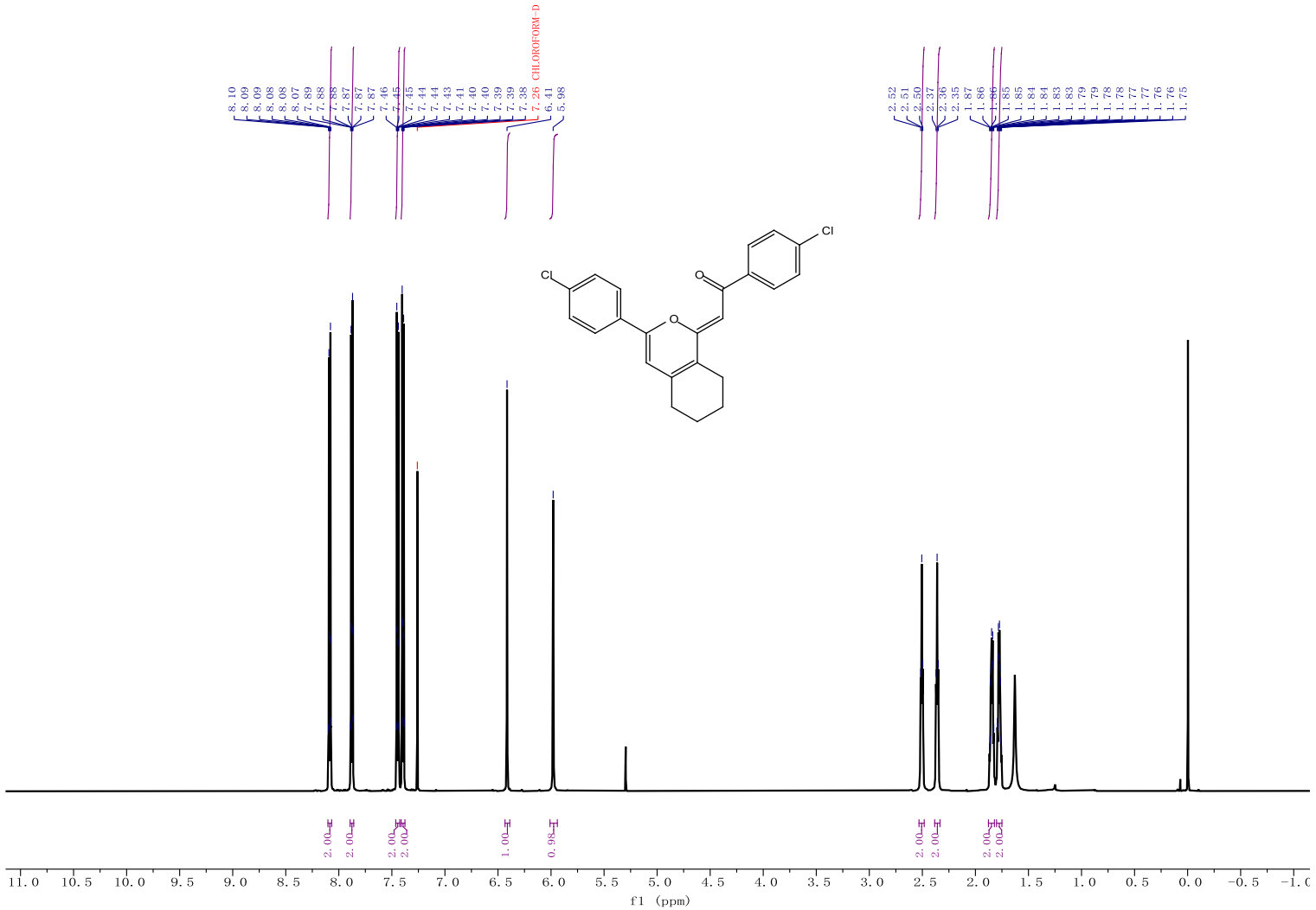
^{1}H NMR (600 MHz, $CDCl_3$) of **4n**



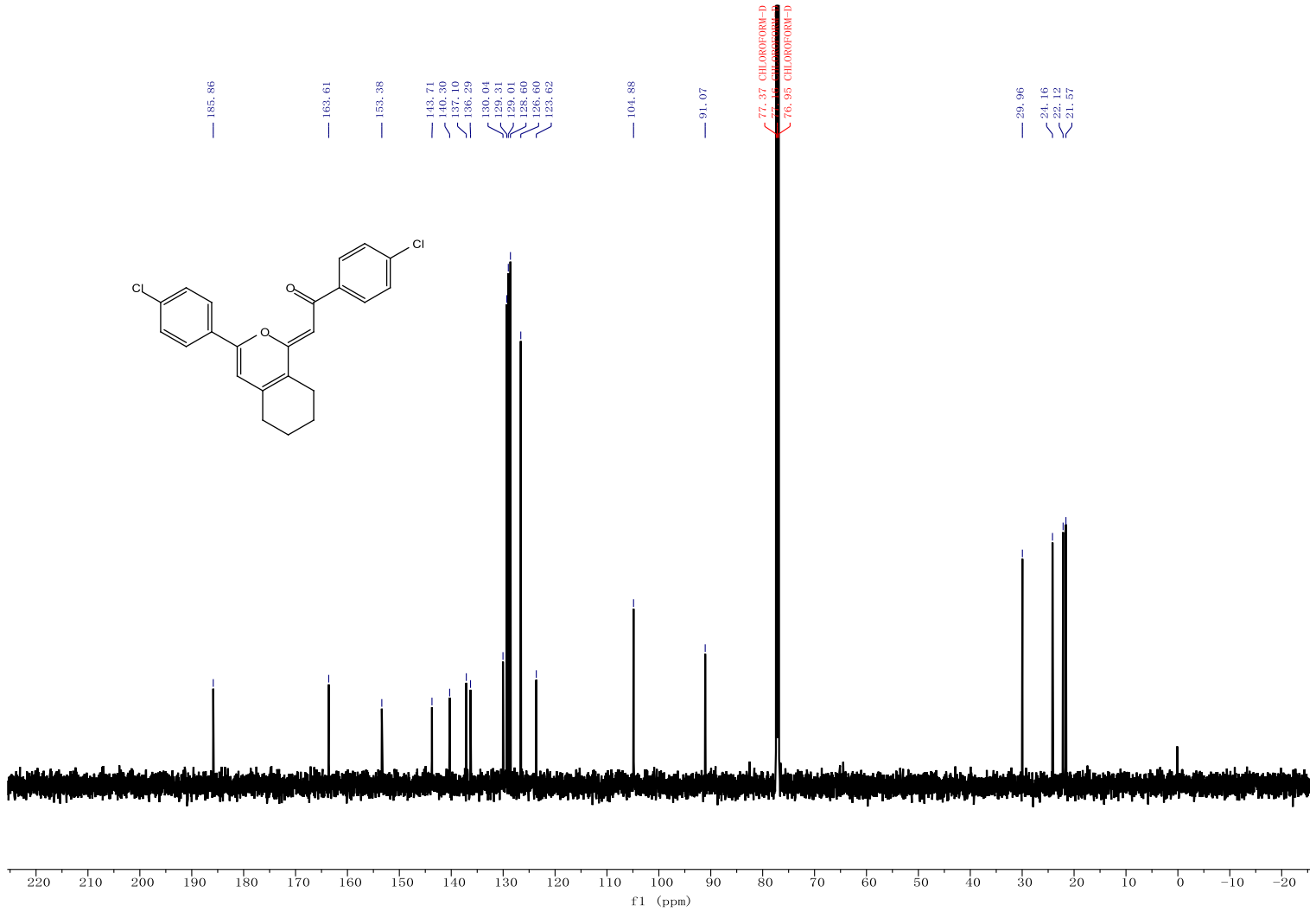
^{13}C NMR (151 MHz, $CDCl_3$) of **4n**



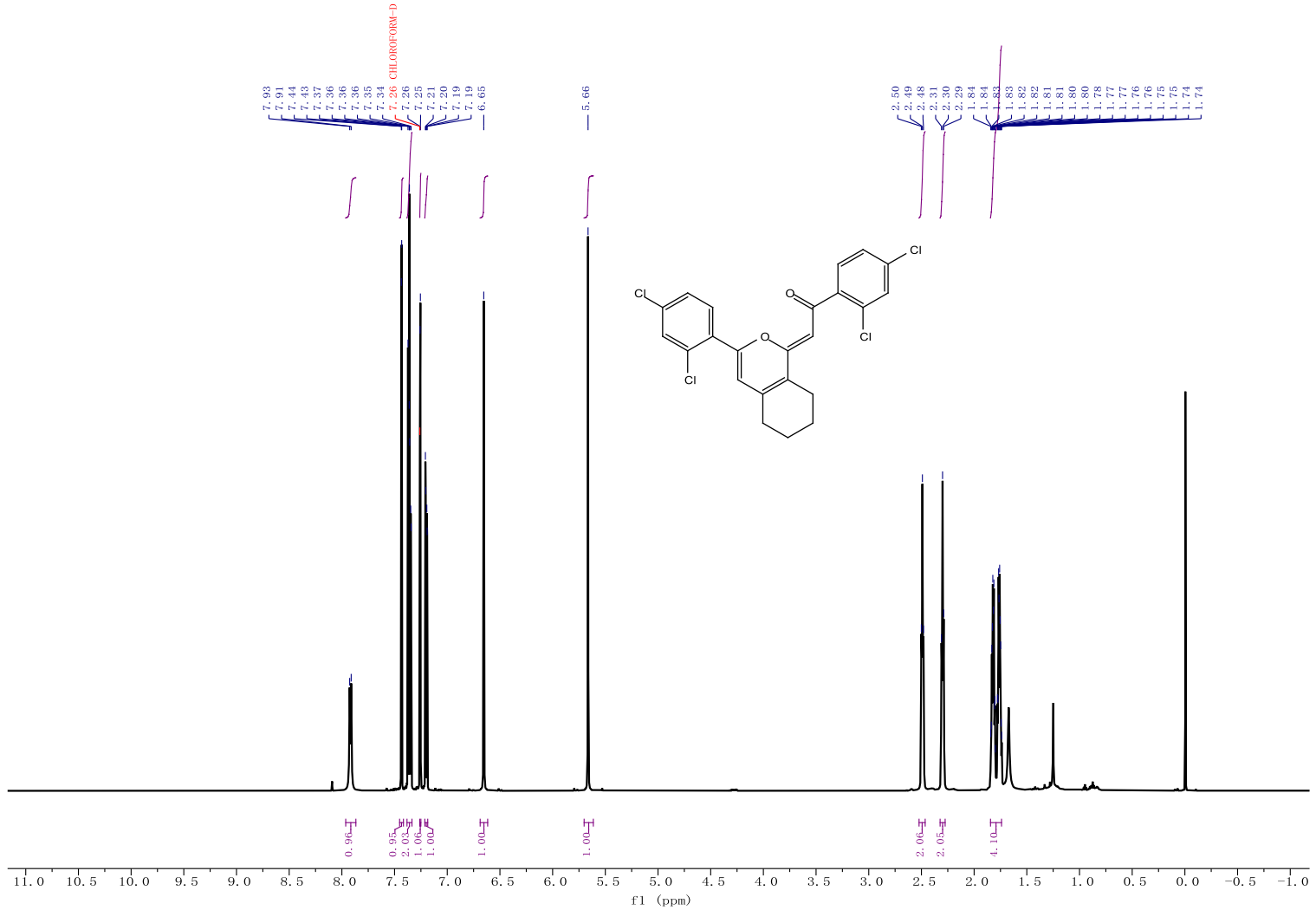
^{1}H NMR (600 MHz, $CDCl_3$) of **4o**



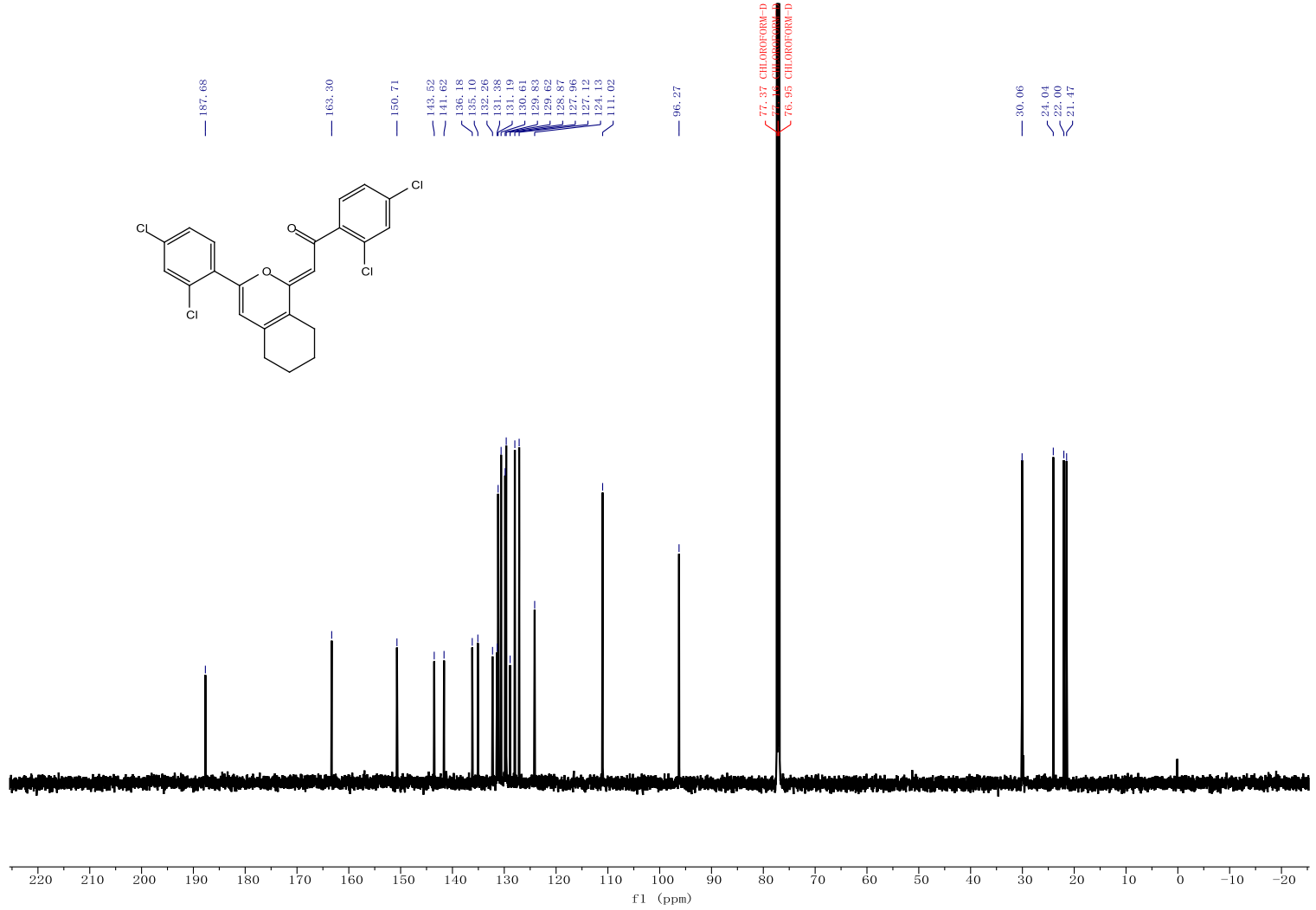
^{13}C NMR (151 MHz, $CDCl_3$) of **4o**



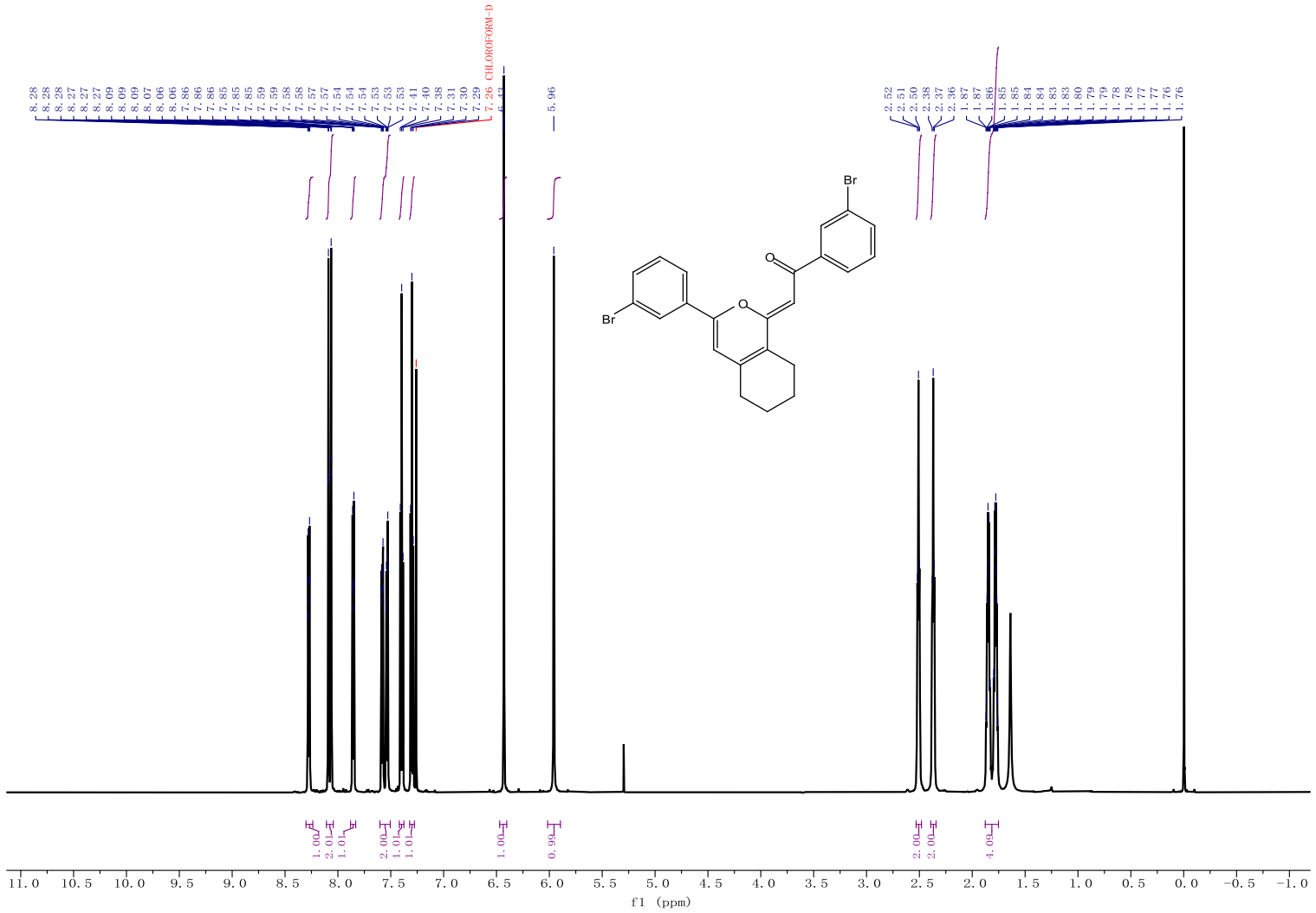
^{1}H NMR (600 MHz, $CDCl_3$) of **4p**



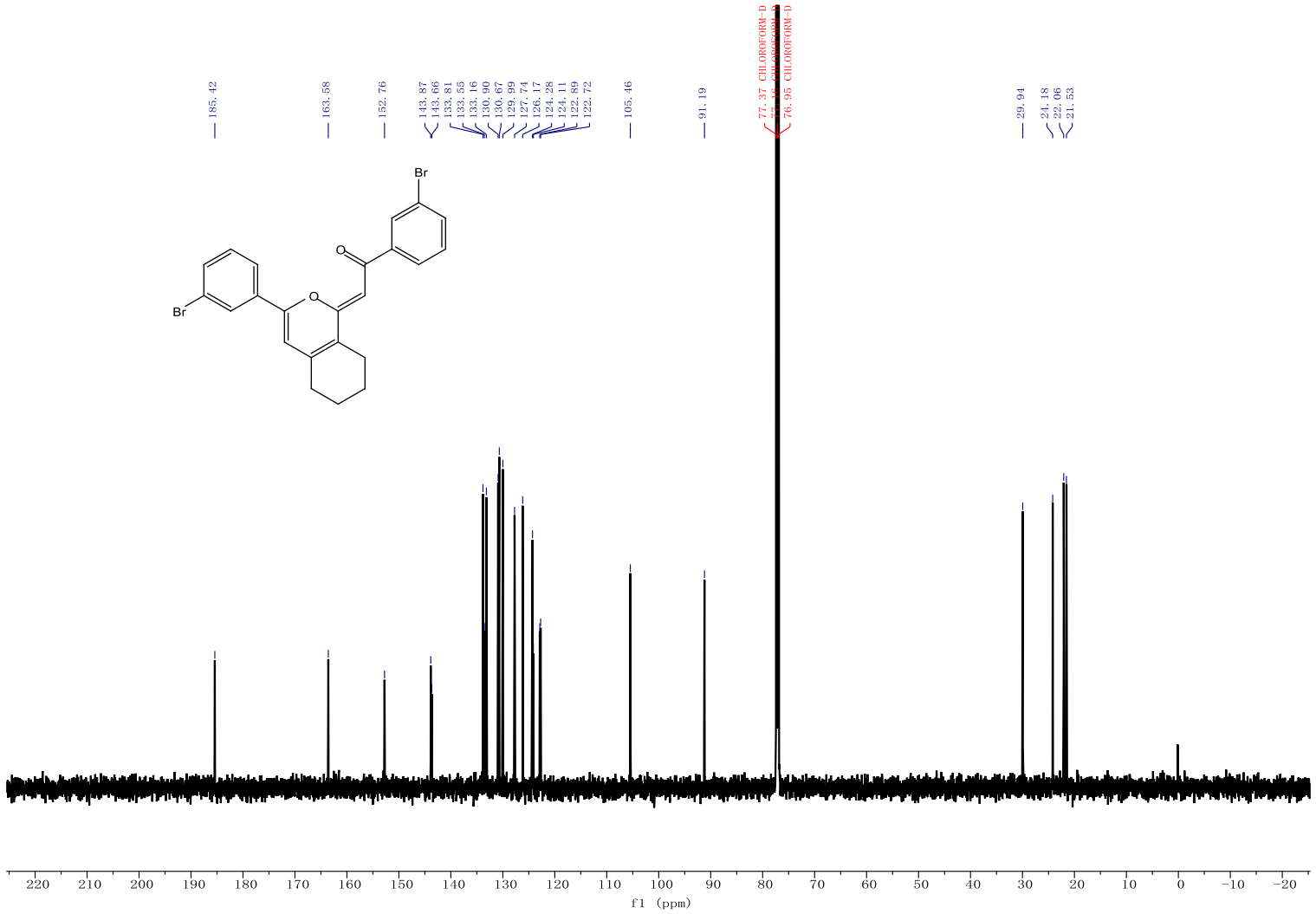
^{13}C NMR (151 MHz, $CDCl_3$) of **4p**



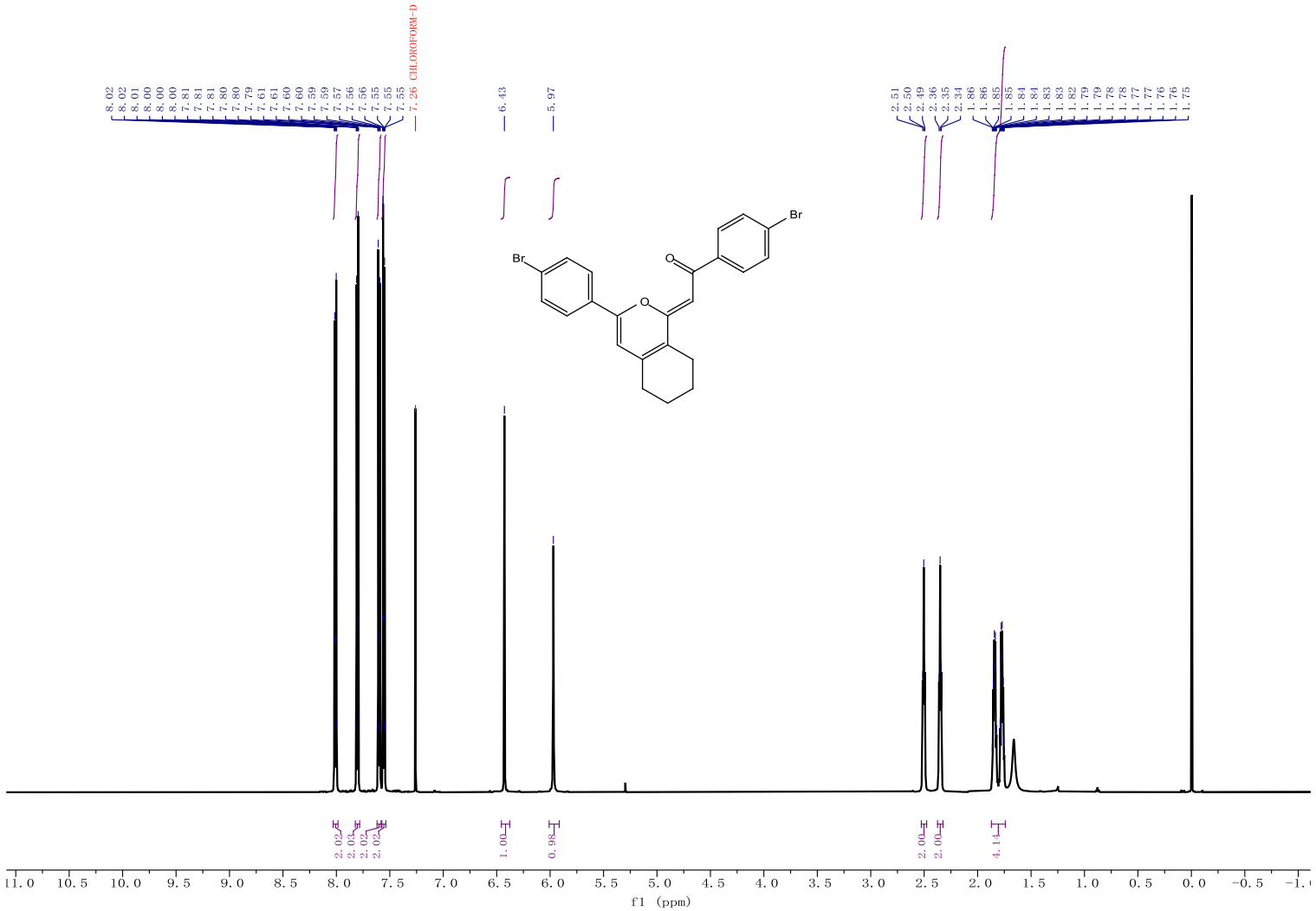
^{1}H NMR (600 MHz, $CDCl_3$) of **4q**



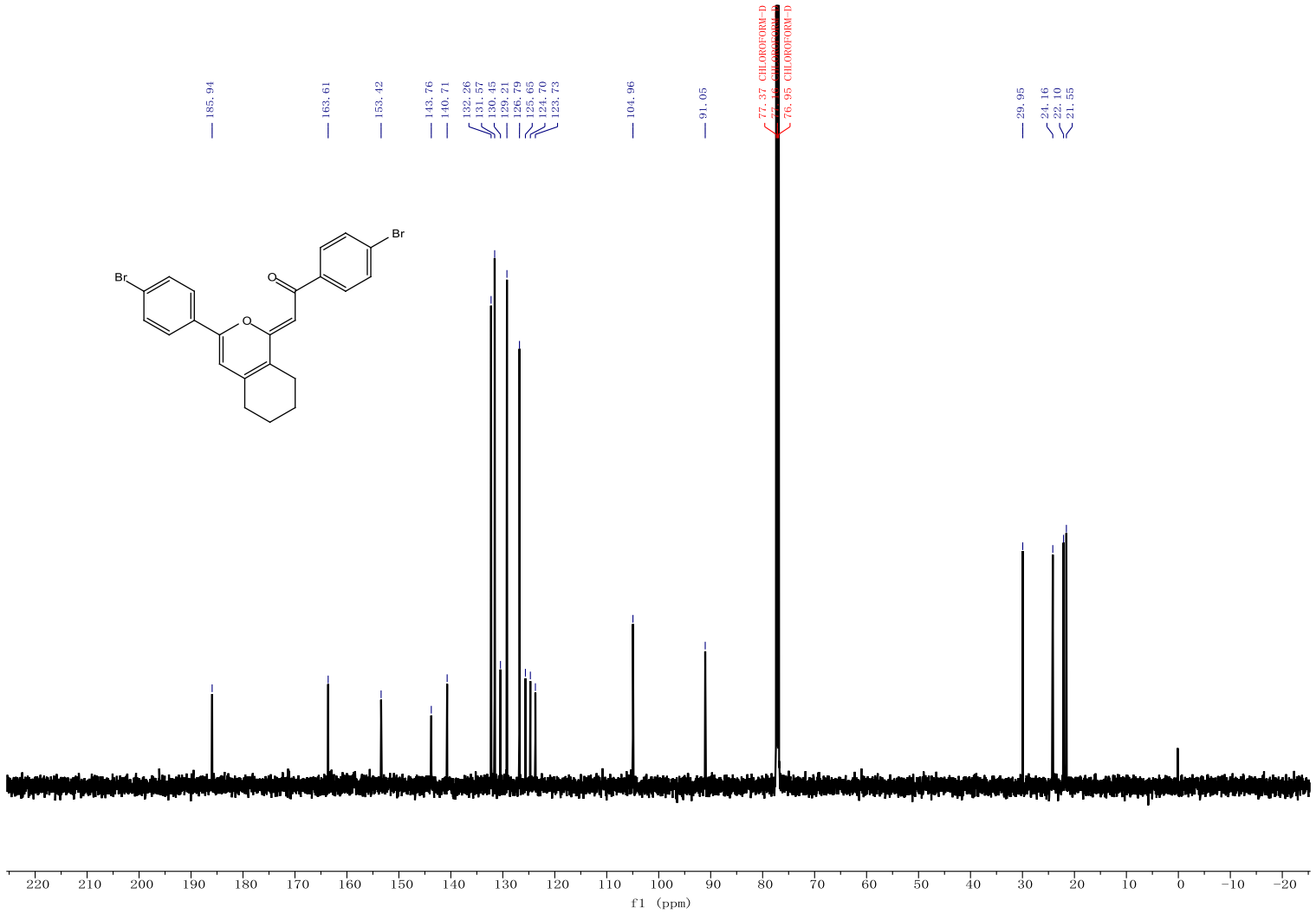
^{13}C NMR (151 MHz, $CDCl_3$) of **4q**



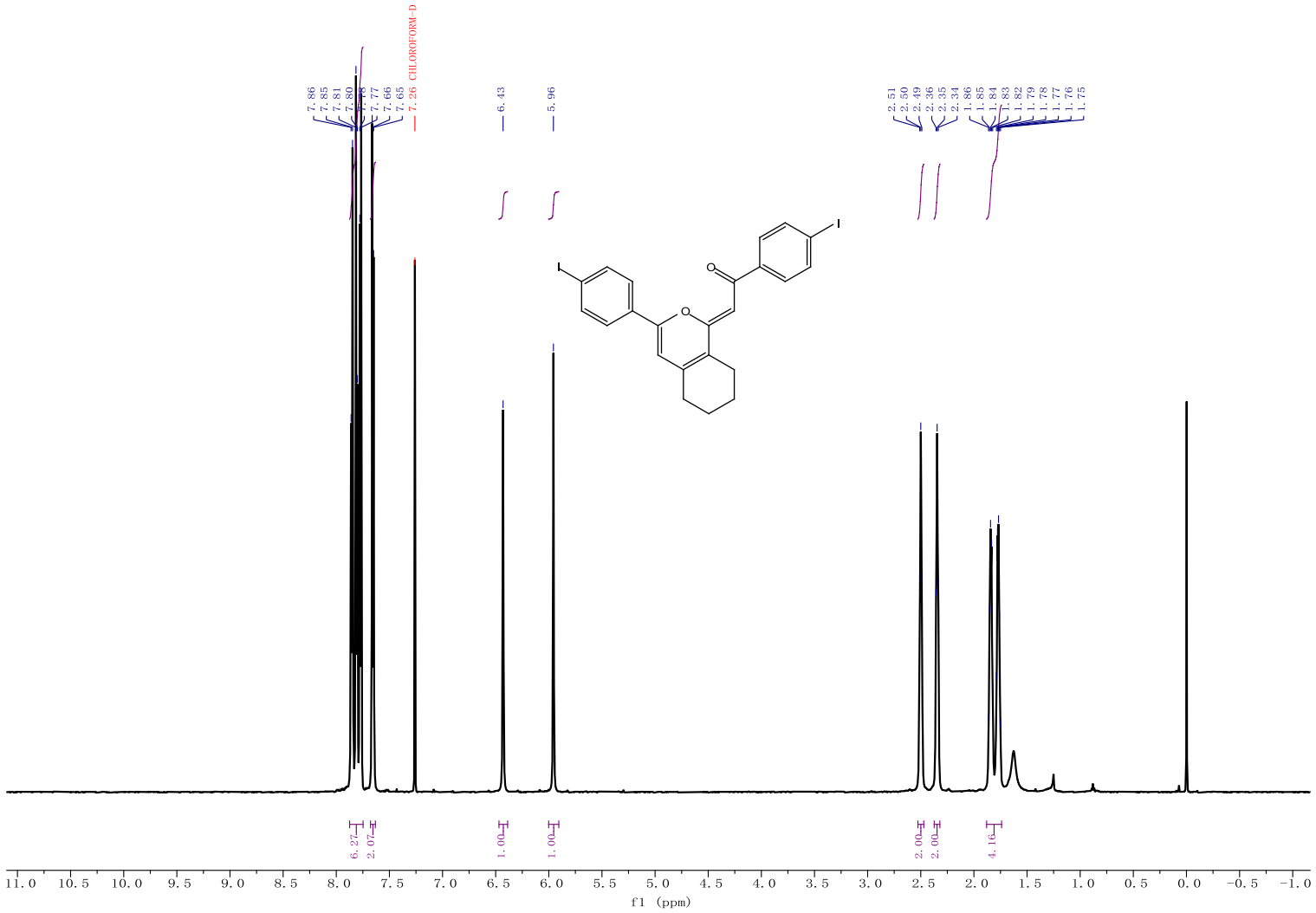
^{1}H NMR (600 MHz, $CDCl_3$) of **4r**



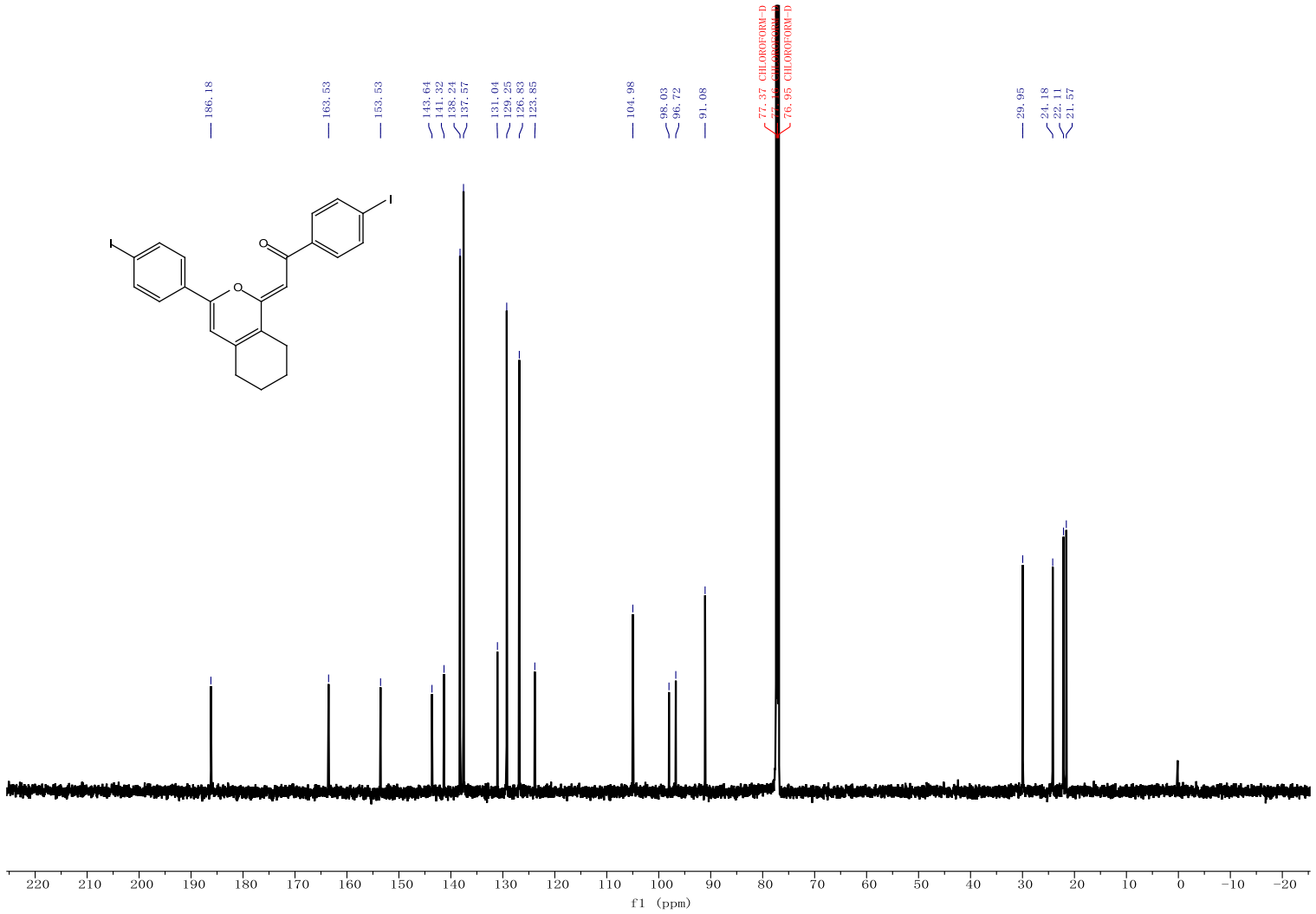
^{13}C NMR (151 MHz, $CDCl_3$) of **4r**



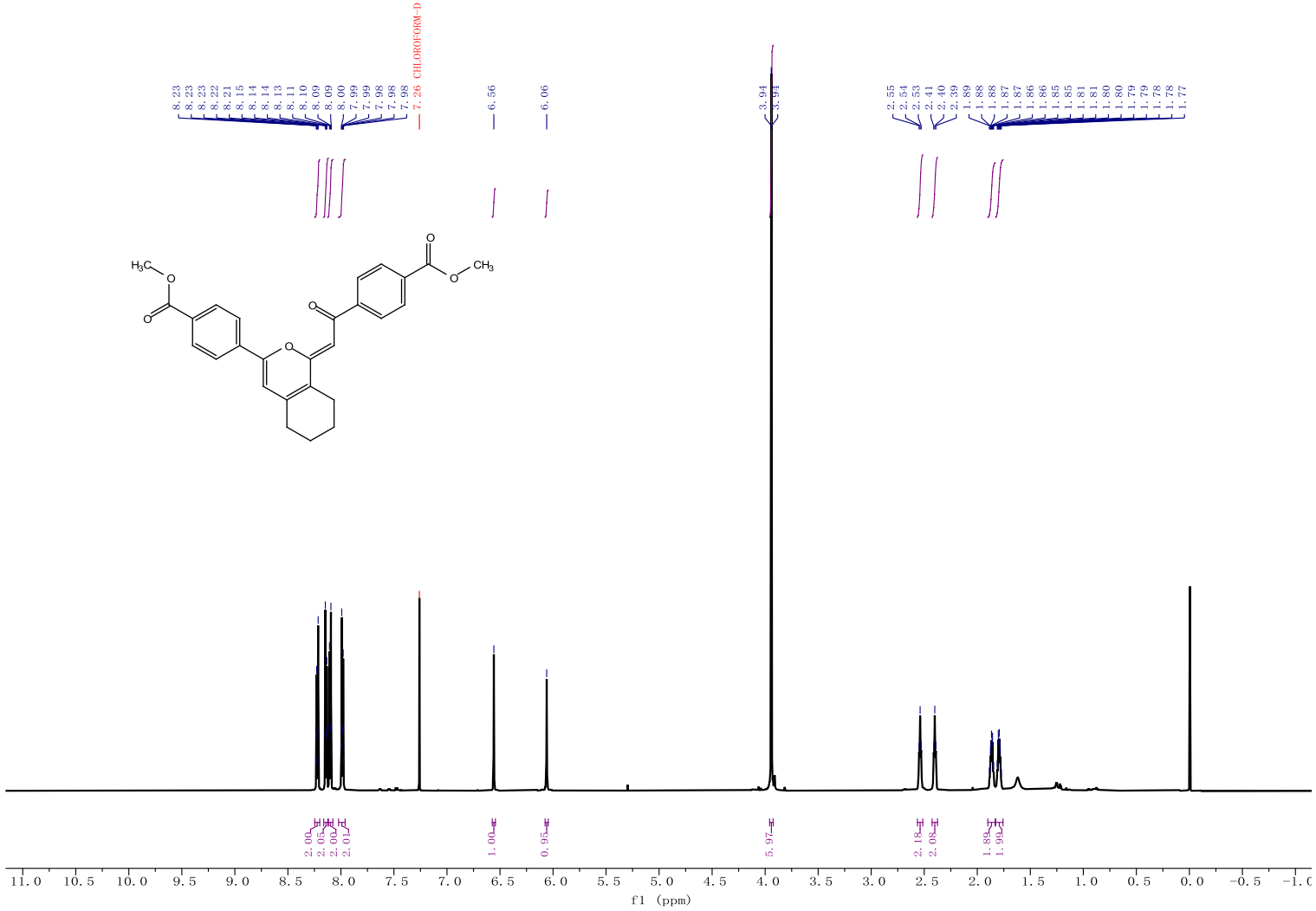
^{1}H NMR (600 MHz, $CDCl_3$) of **4s**



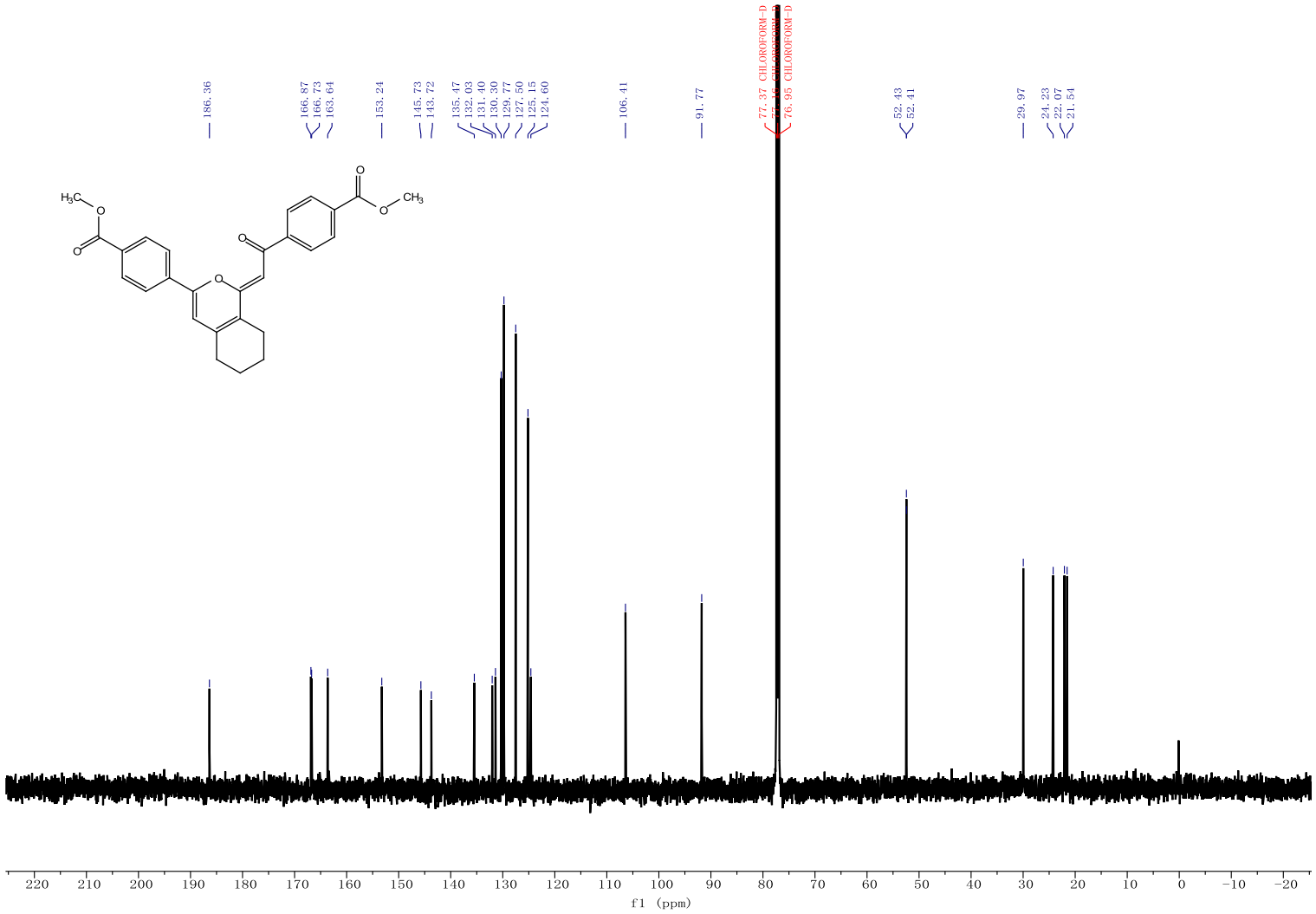
^{13}C NMR (151 MHz, $CDCl_3$) of **4s**



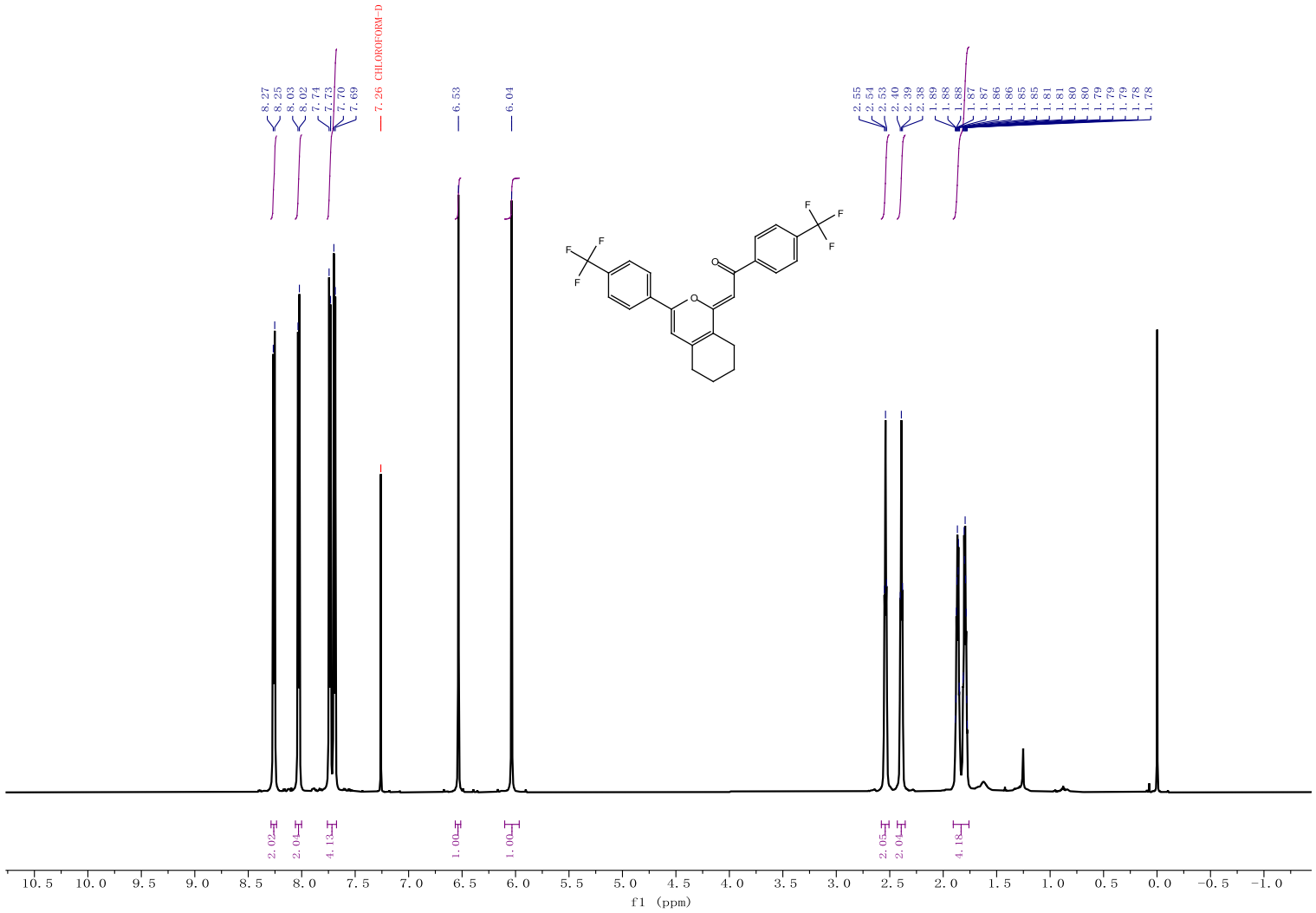
^{1}H NMR (600 MHz, $CDCl_3$) of **4t**



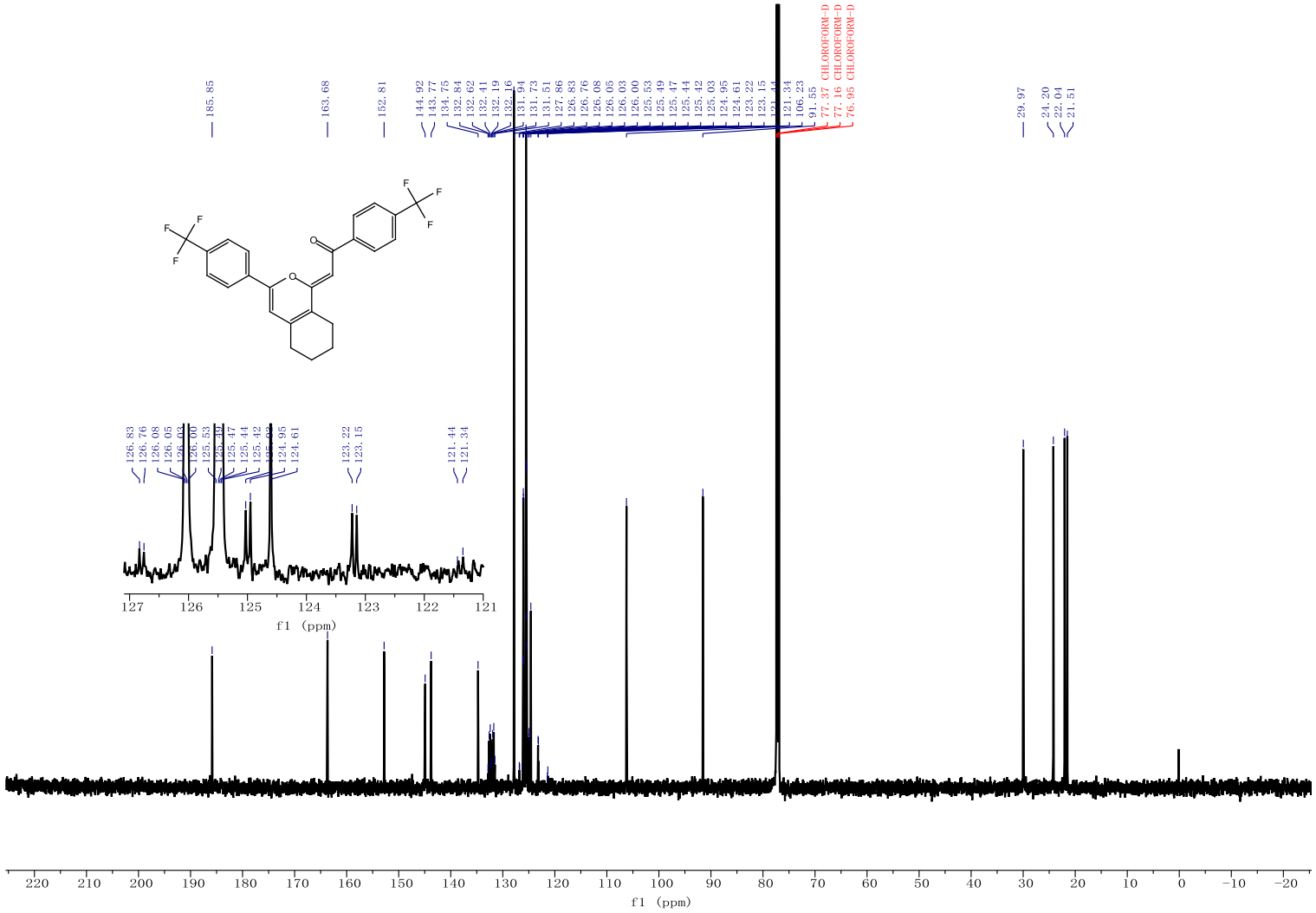
^{13}C NMR (151 MHz, $CDCl_3$) of **4t**



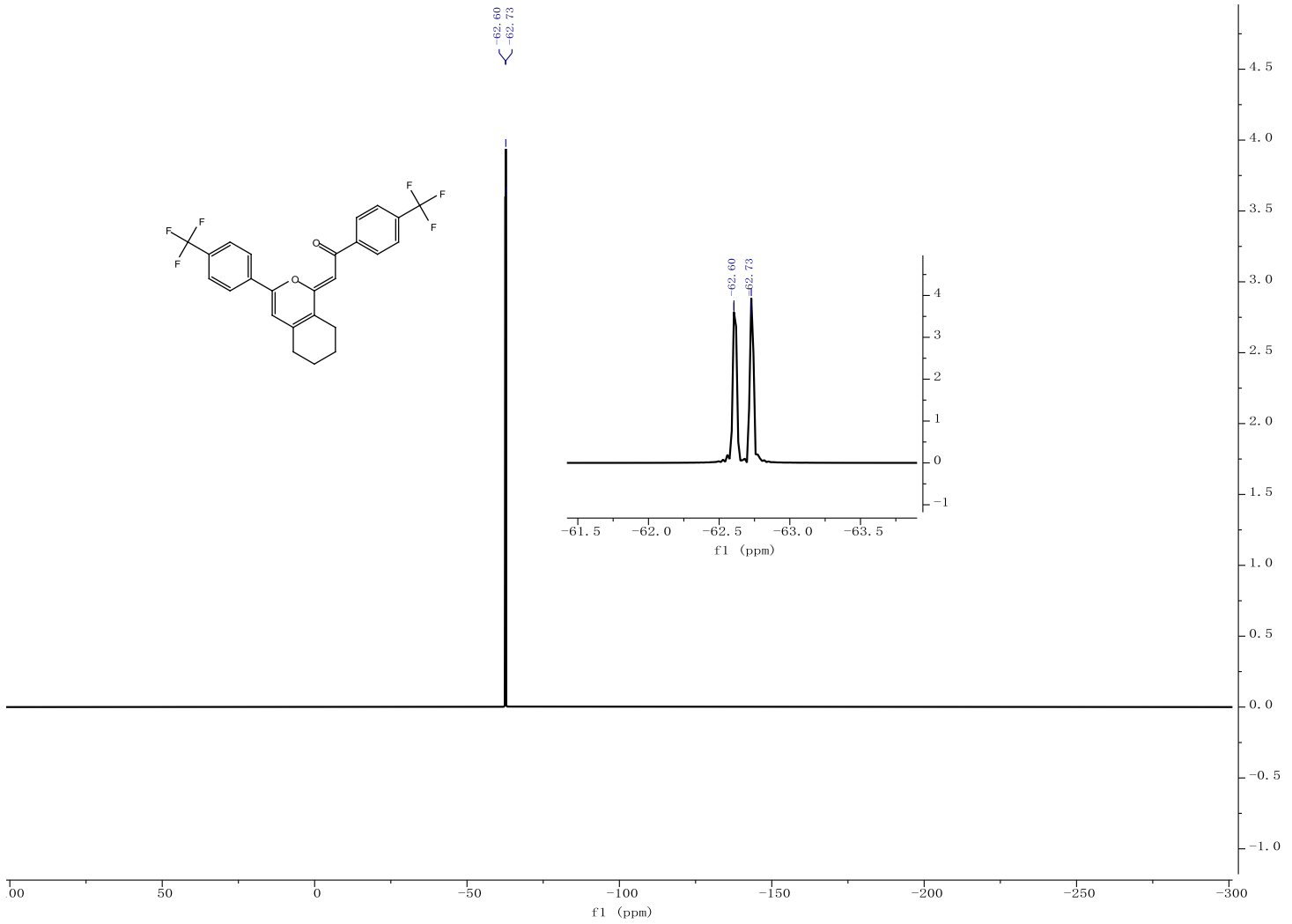
^{1}H NMR (600 MHz, $CDCl_3$) of **4u**



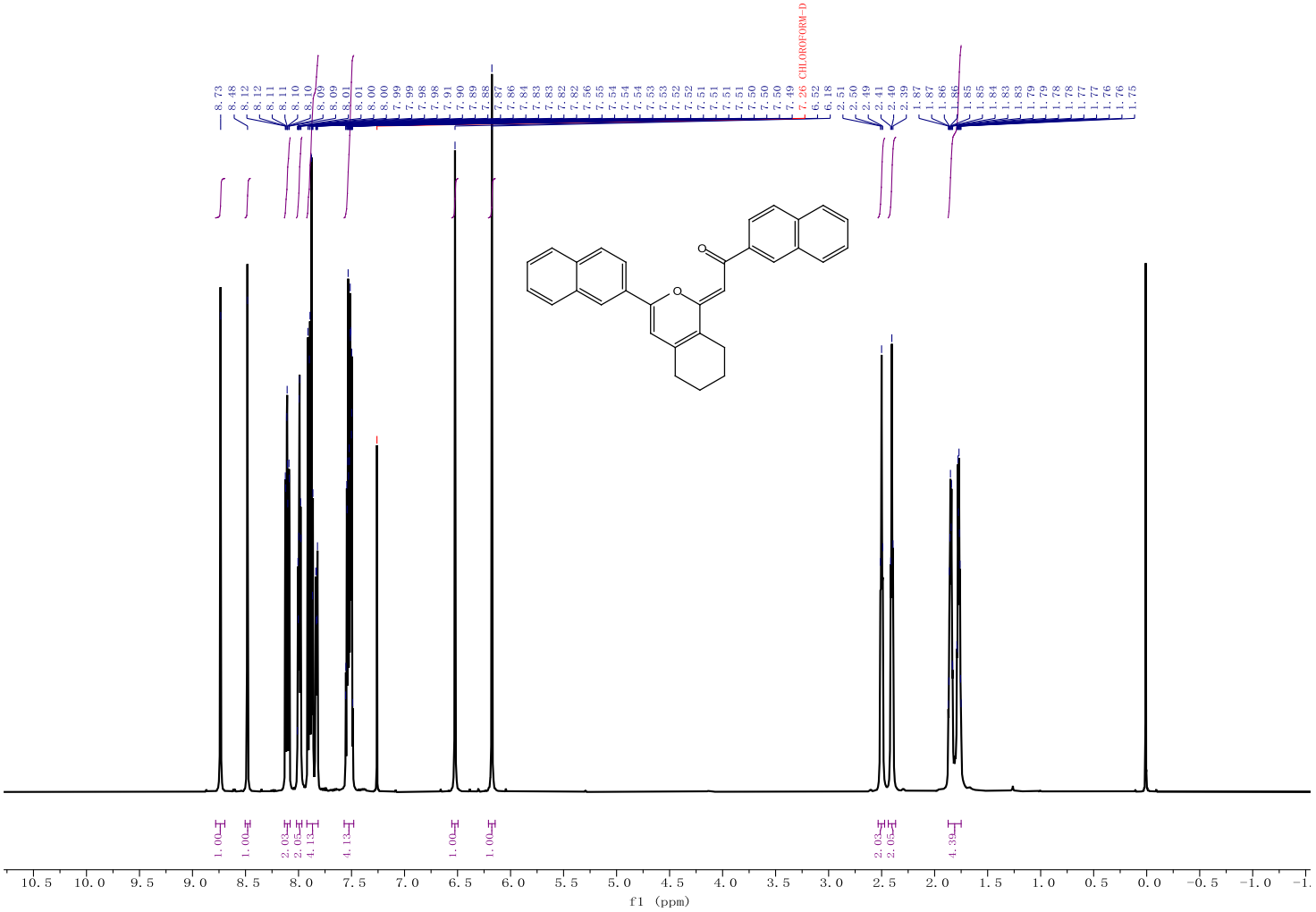
^{13}C NMR (151 MHz, $CDCl_3$) of **4u**



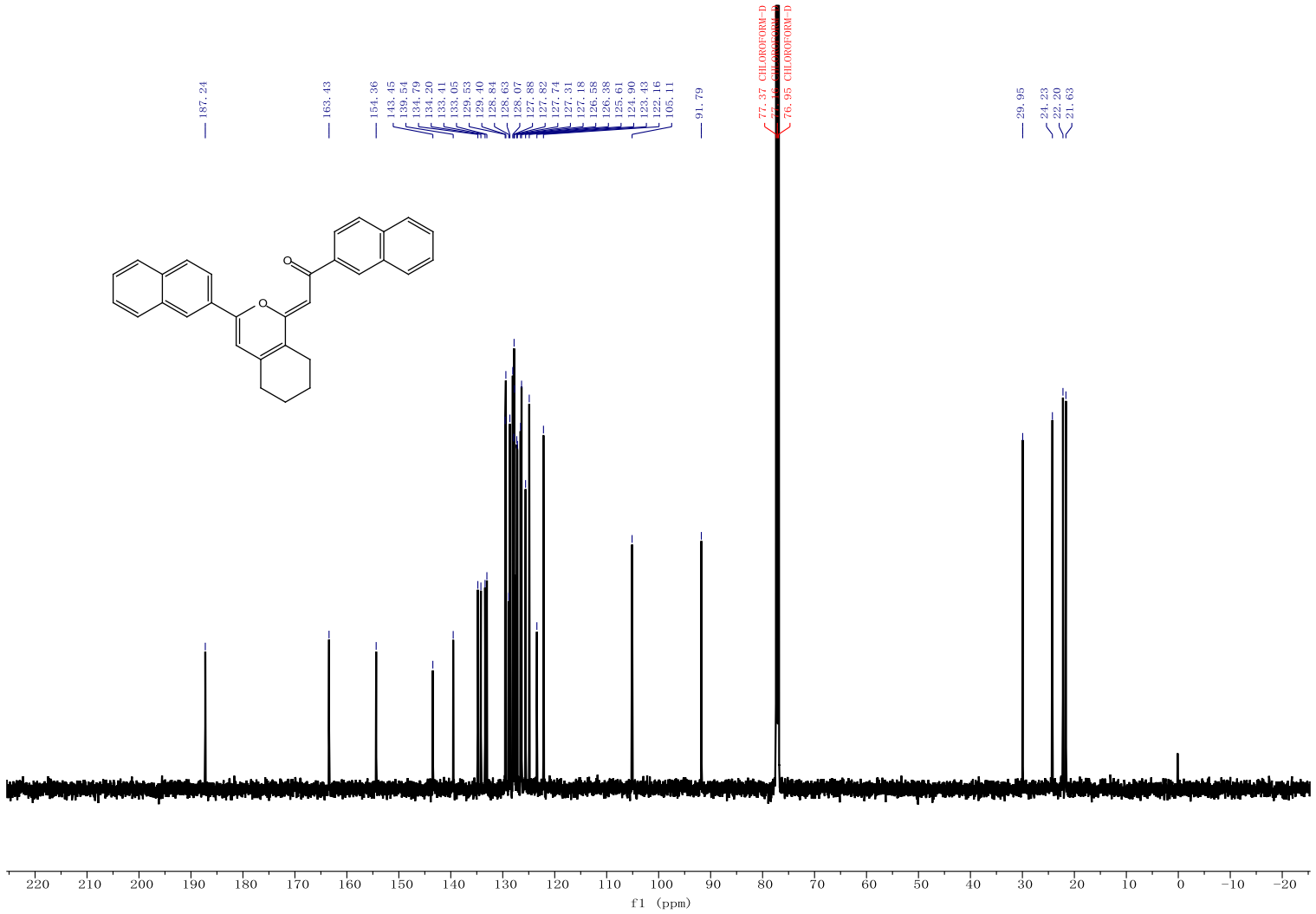
^{19}F NMR (565 MHz, $CDCl_3$) of **4u**



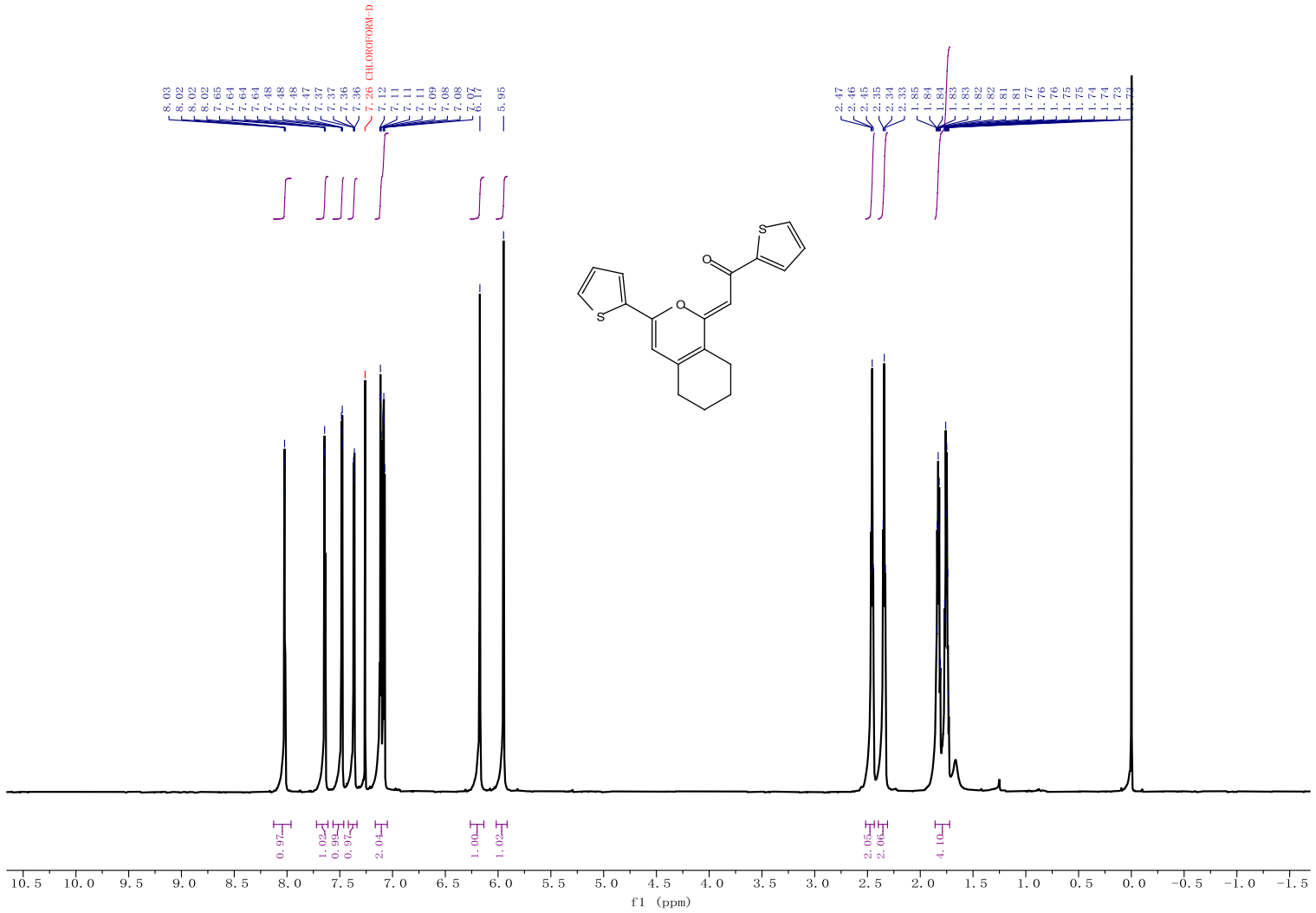
^{1}H NMR (600 MHz, $CDCl_3$) of **4v**



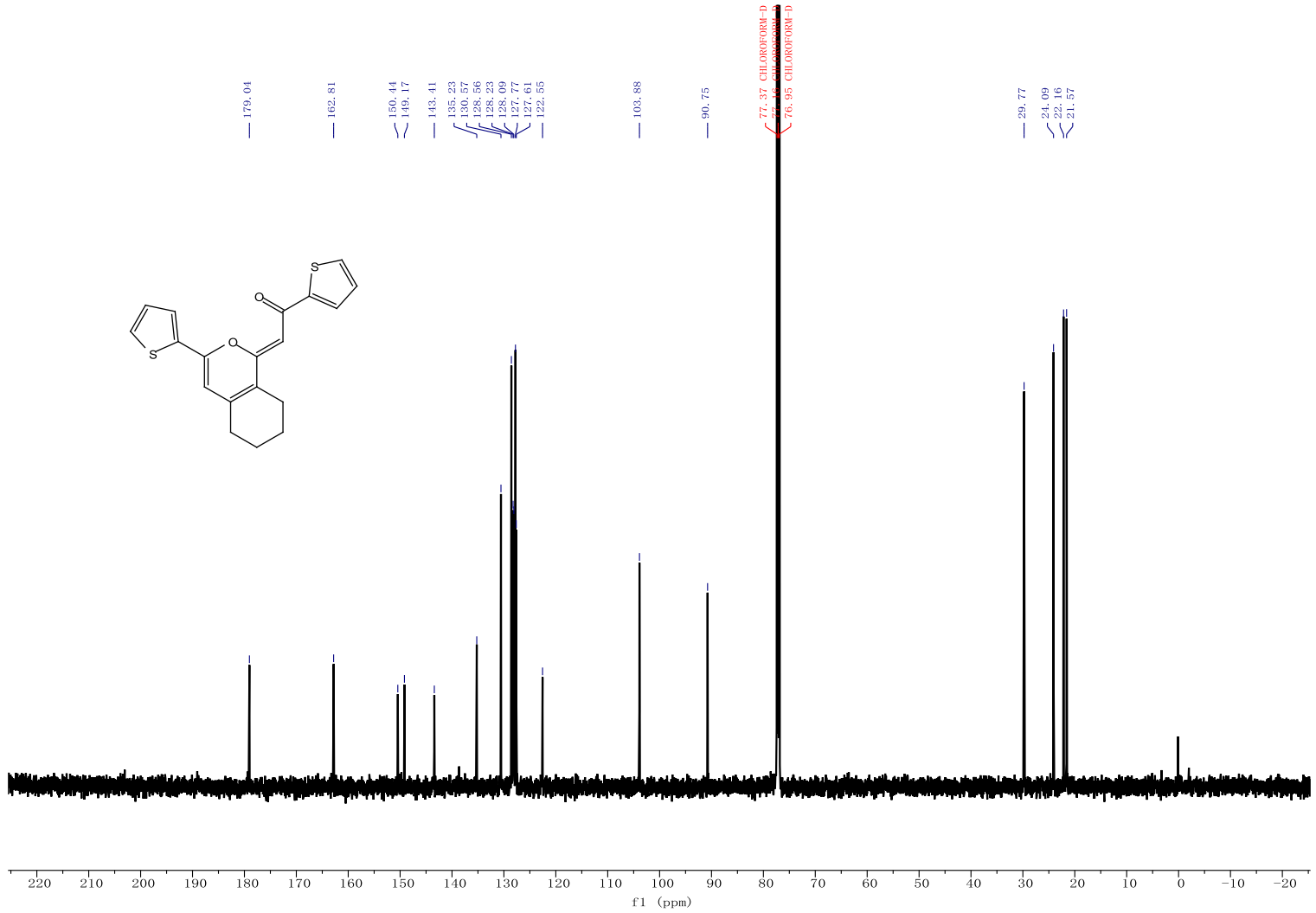
^{13}C NMR (151 MHz, $CDCl_3$) of **4v**



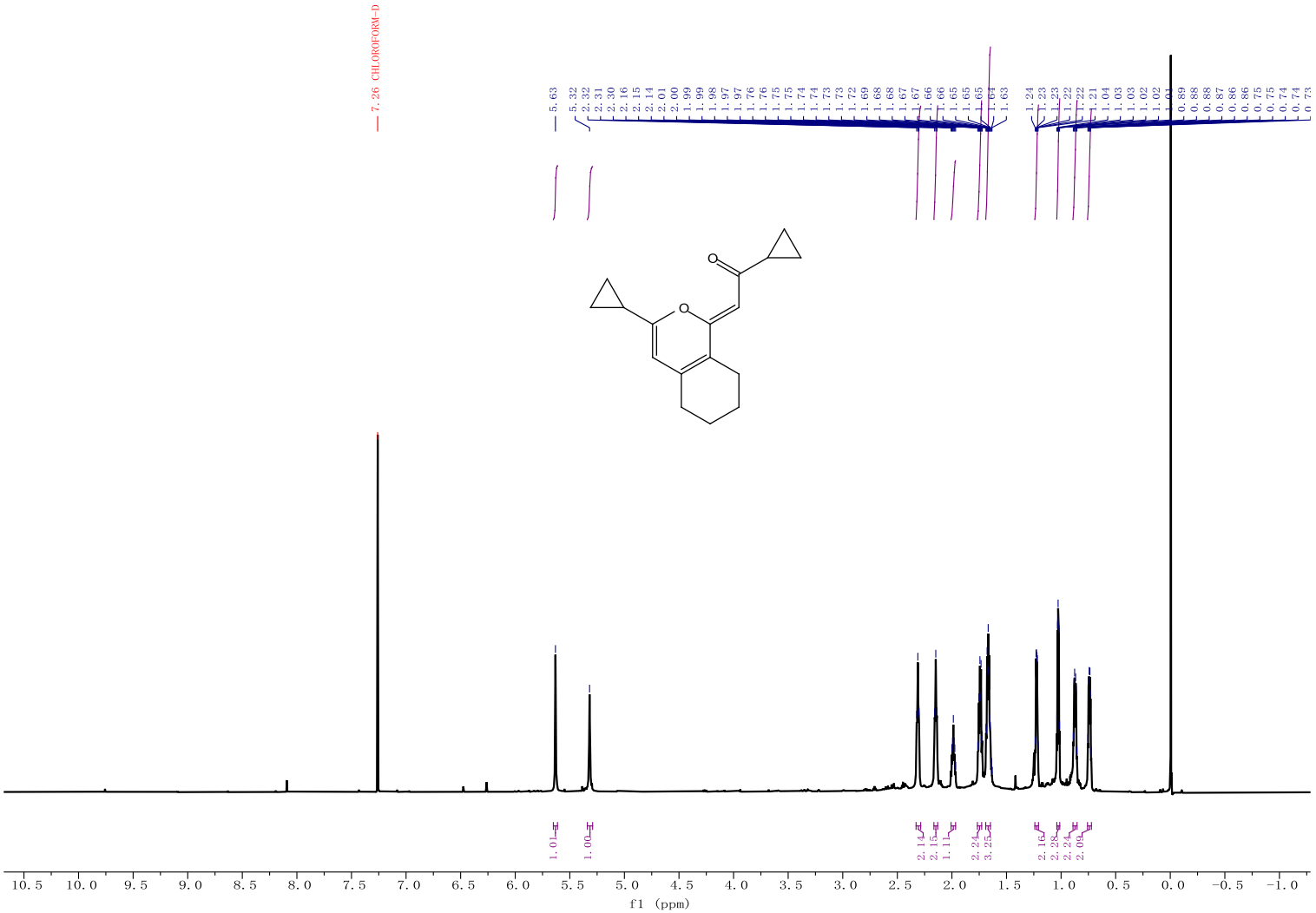
^{1}H NMR (600 MHz, $CDCl_3$) of **4w**



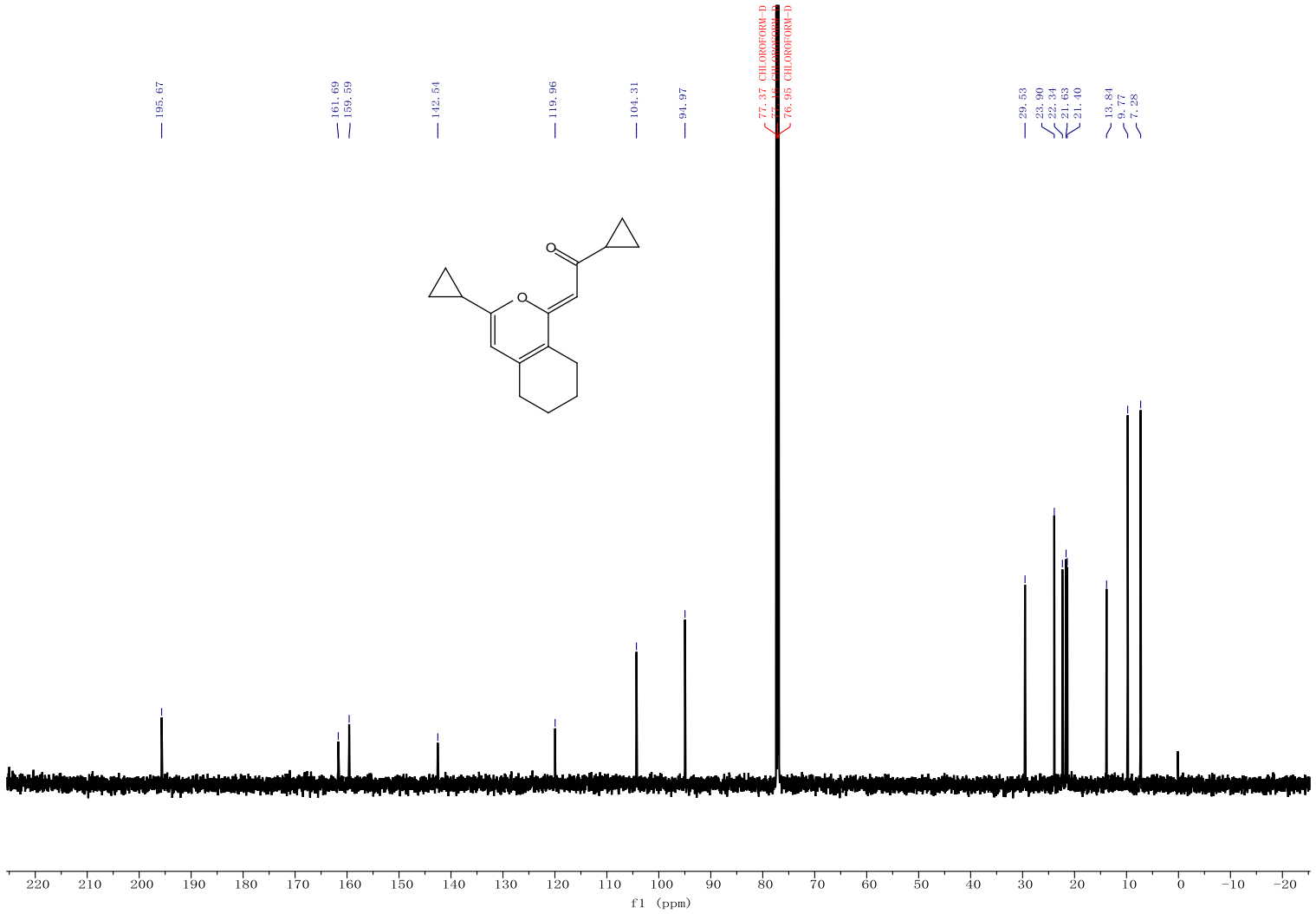
^{13}C NMR (151 MHz, $CDCl_3$) of **4w**



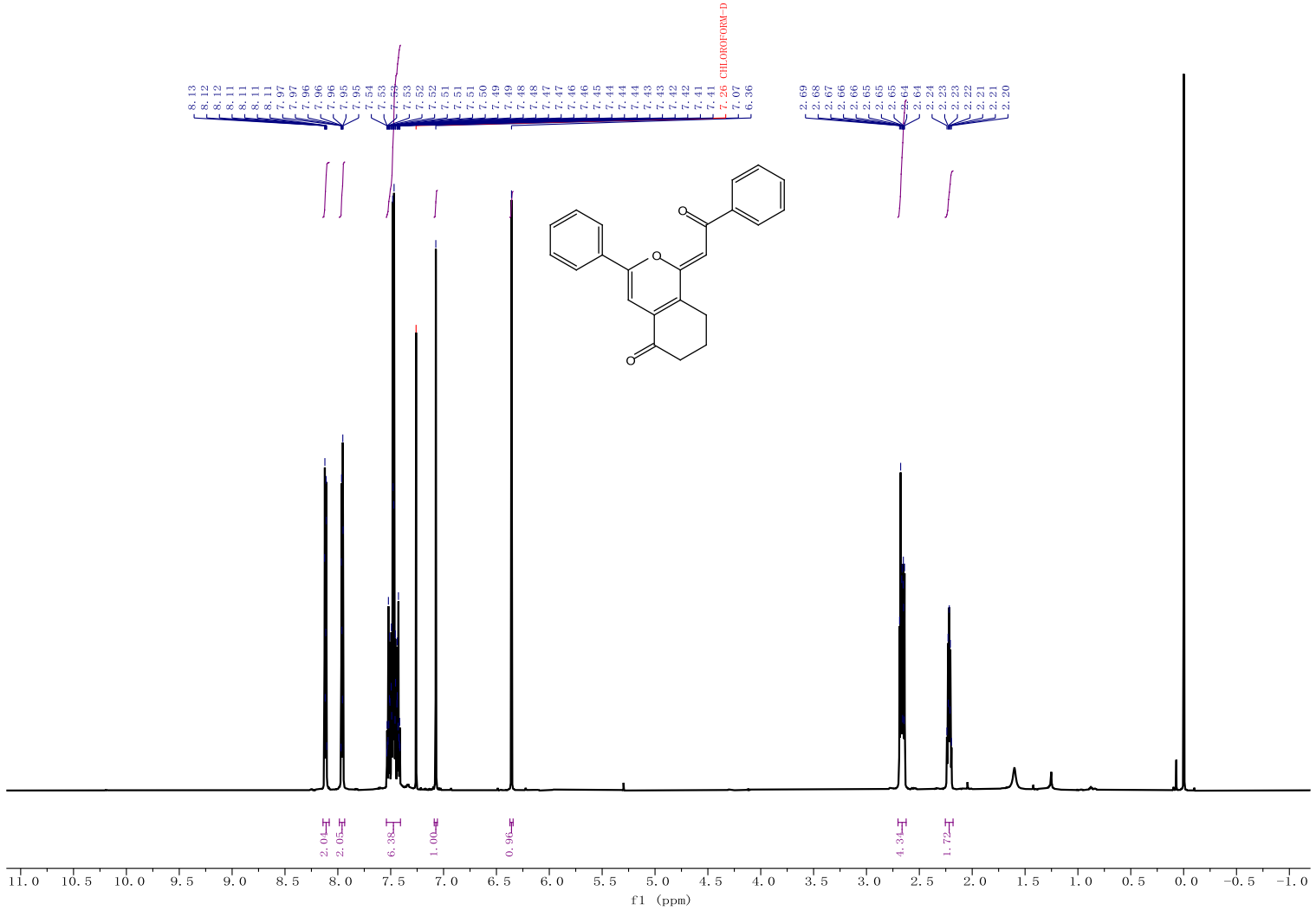
^{1}H NMR (600 MHz, $CDCl_3$) of **4x**



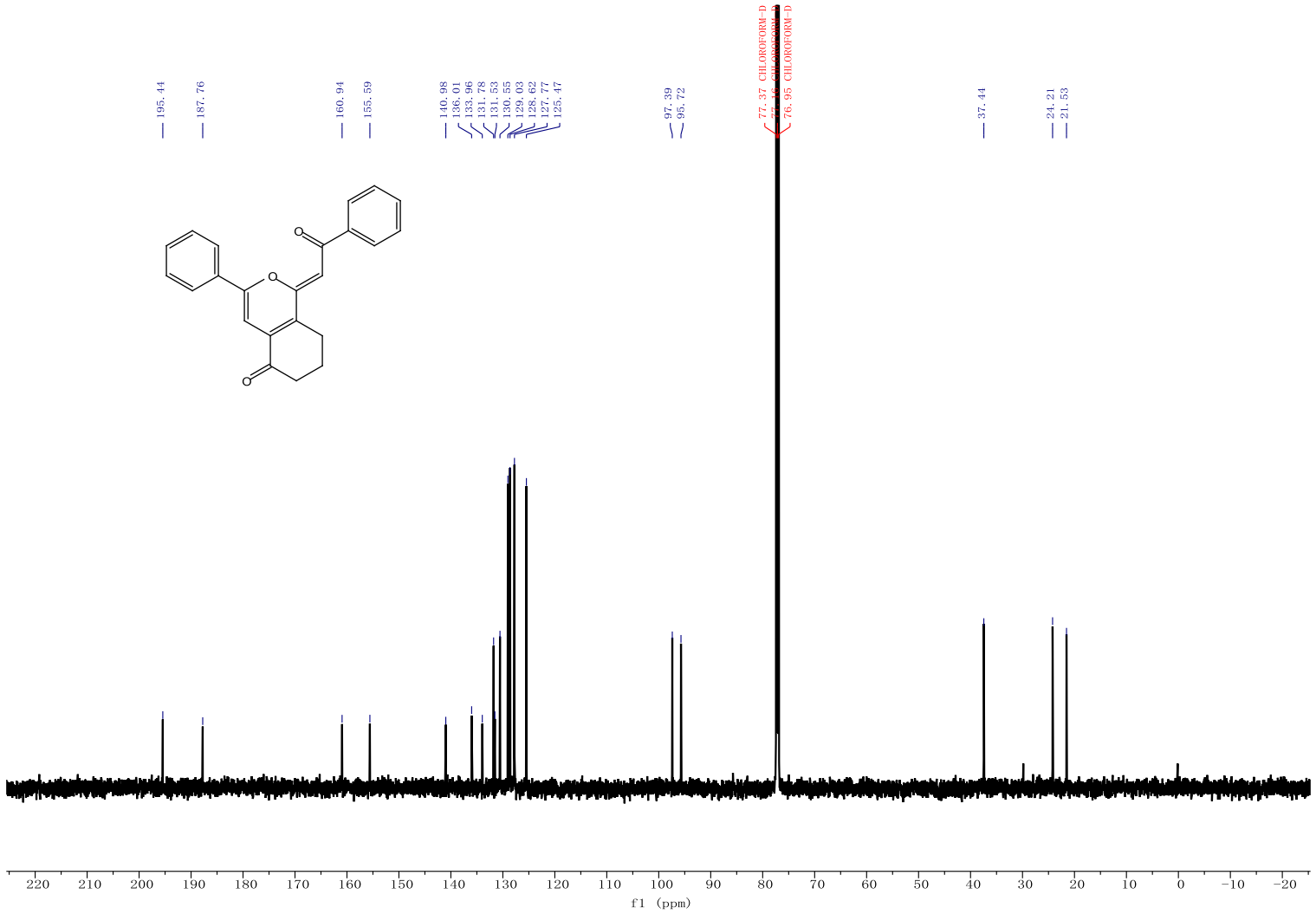
^{13}C NMR (151 MHz, $CDCl_3$) of **4x**



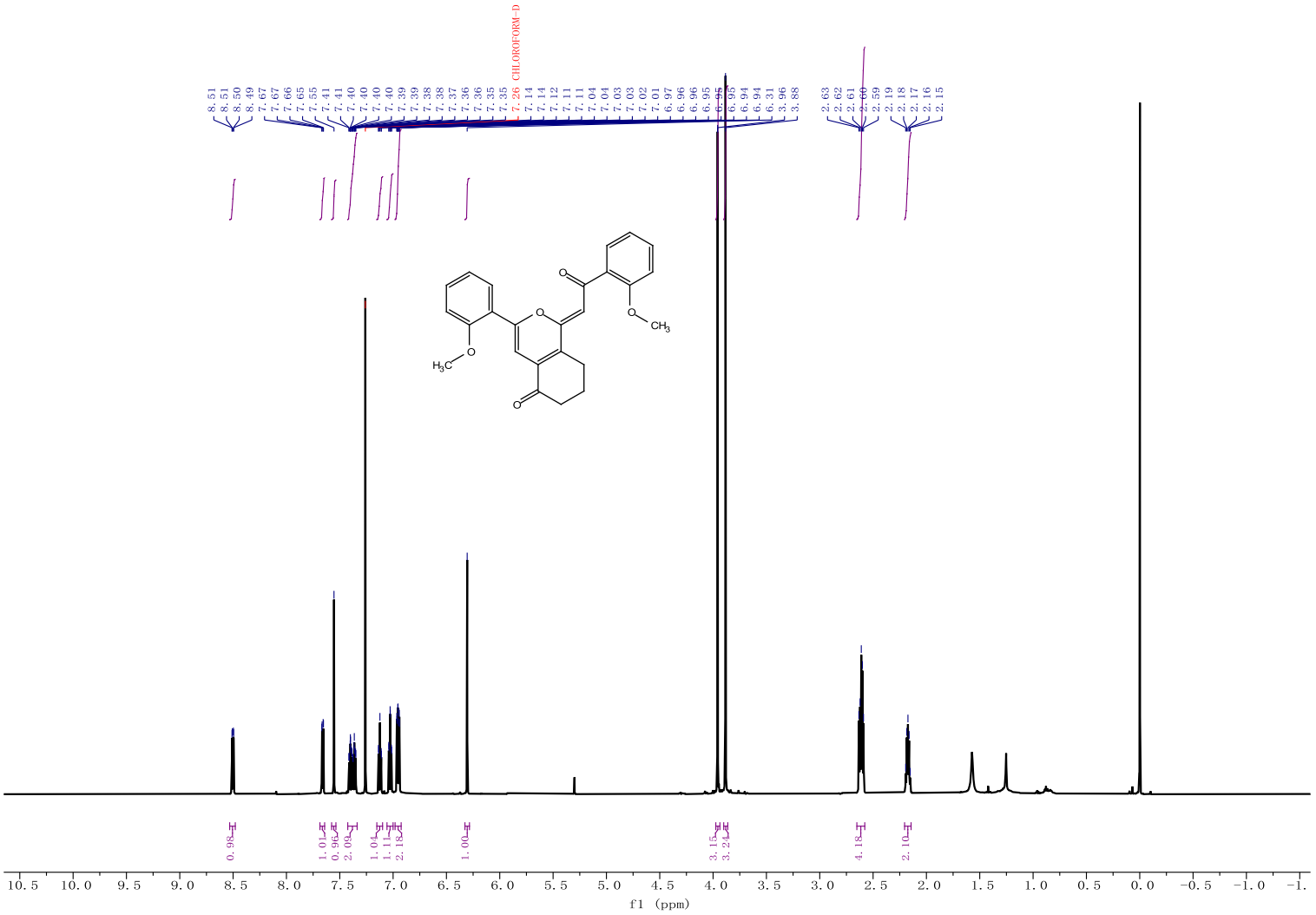
^{1}H NMR (600 MHz, $CDCl_3$) of **6a**



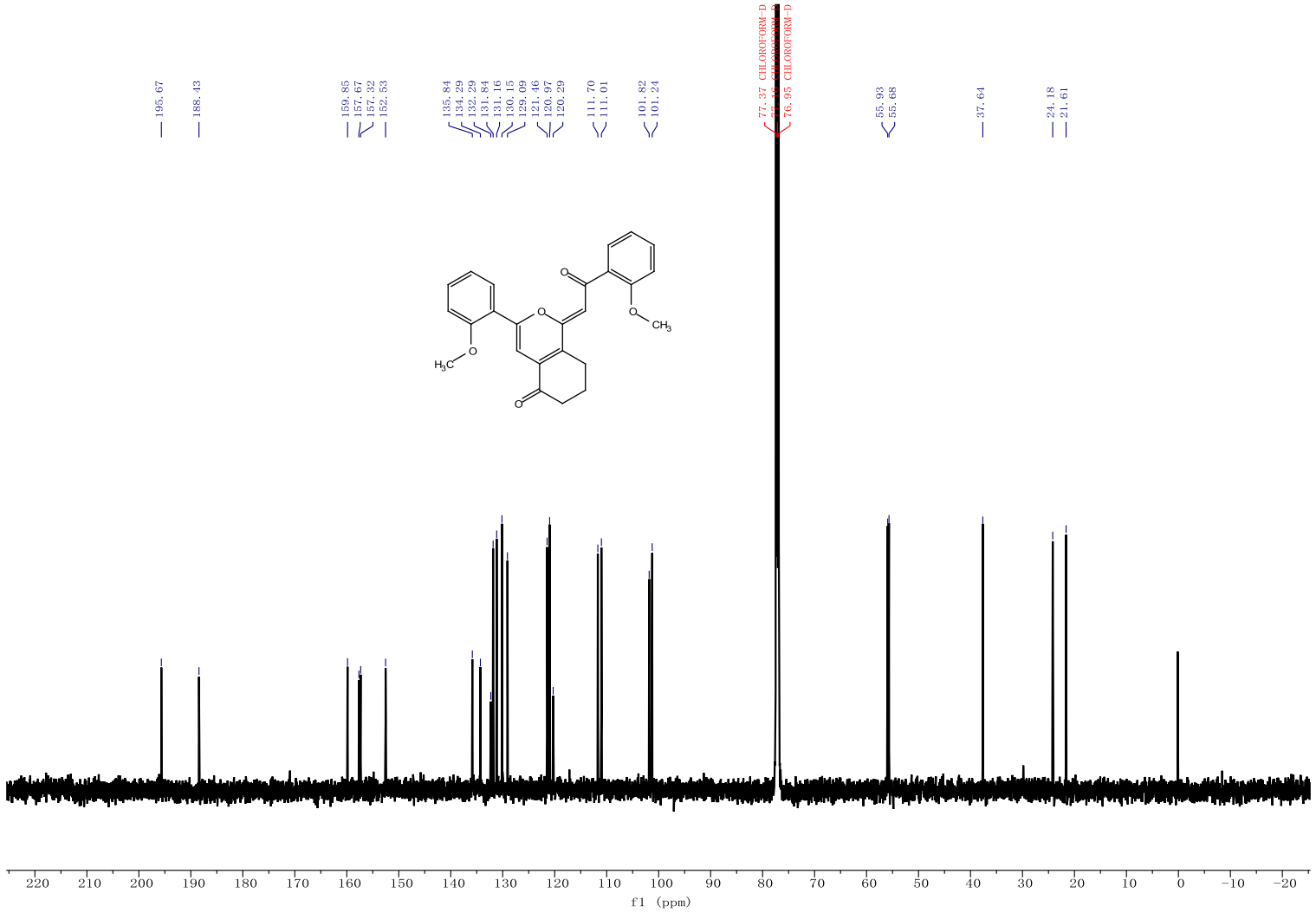
^{13}C NMR (151 MHz, $CDCl_3$) of **6a**



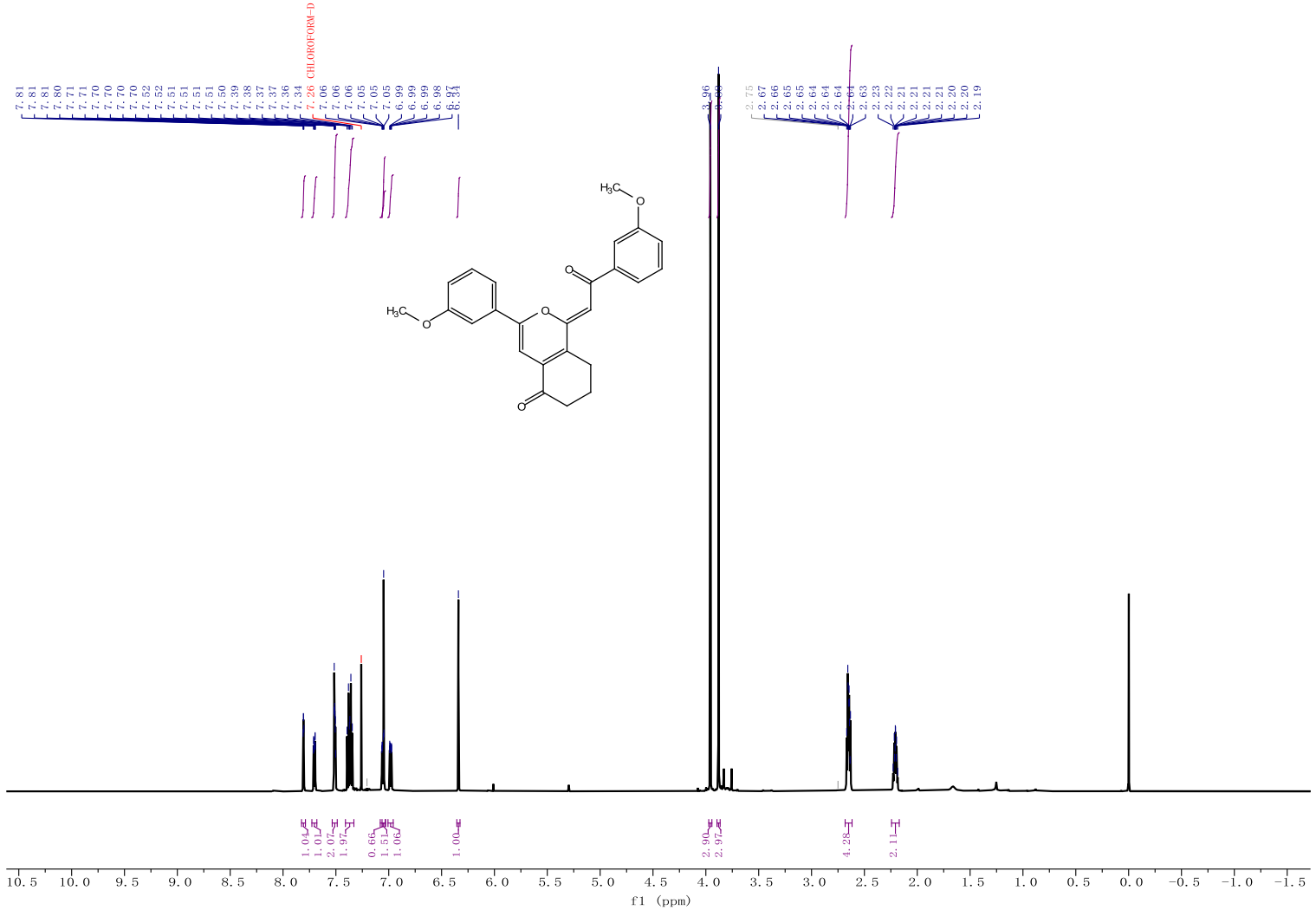
^{1}H NMR (600 MHz, $CDCl_3$) of **6b**



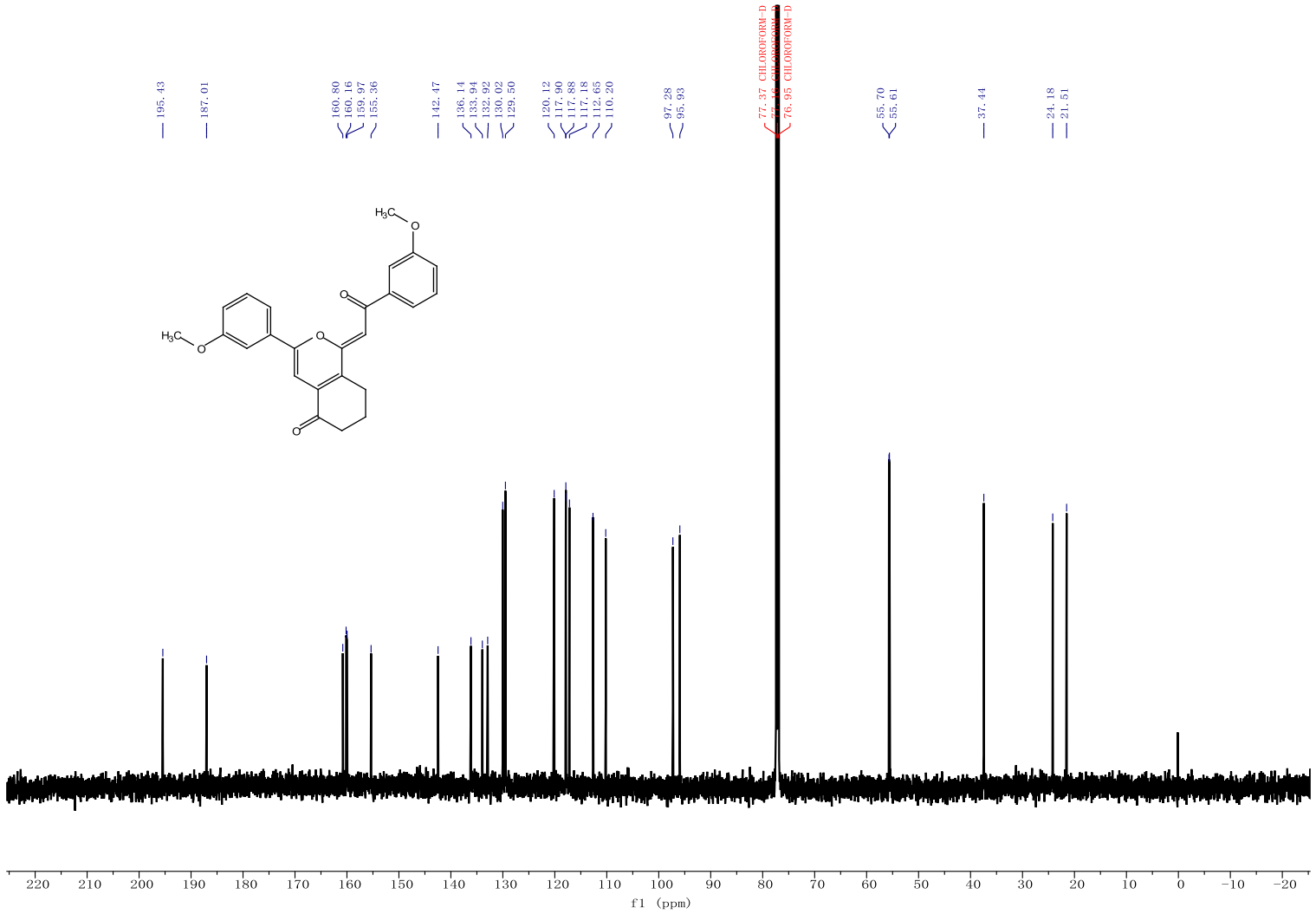
^{13}C NMR (151 MHz, $CDCl_3$) of **6b**



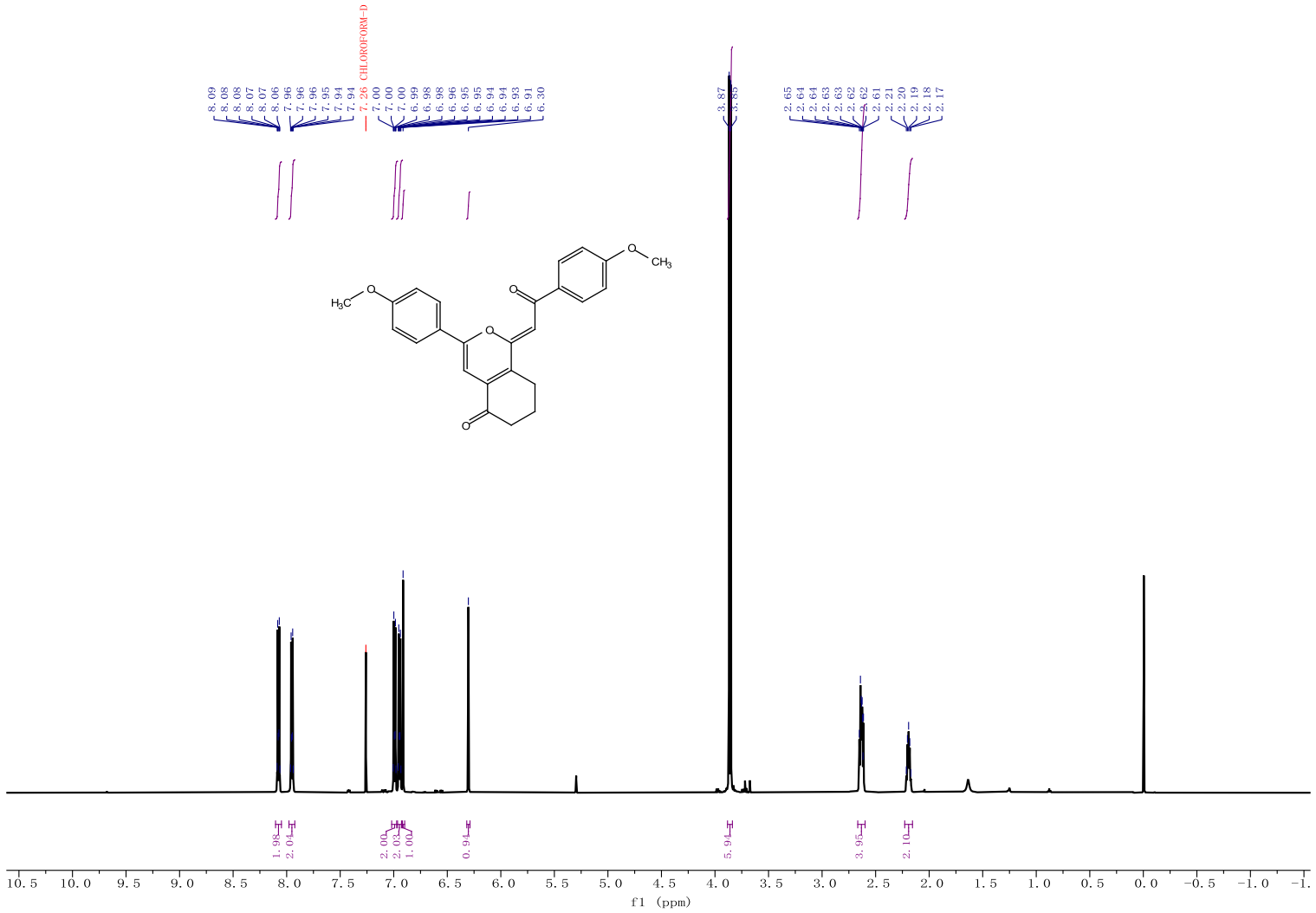
^{1}H NMR (600 MHz, $CDCl_3$) of **6c**



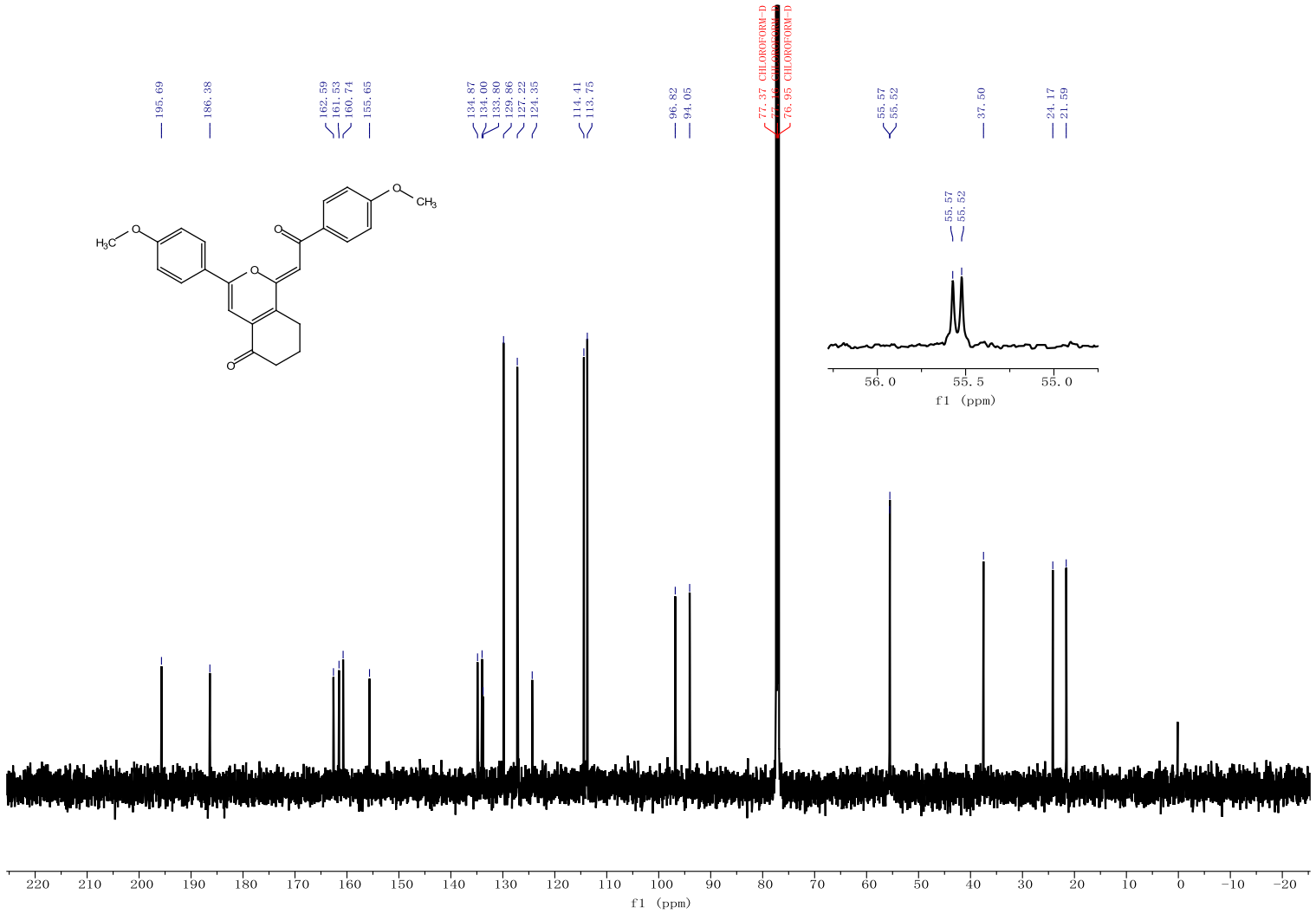
^{13}C NMR (151 MHz, $CDCl_3$) of **6c**



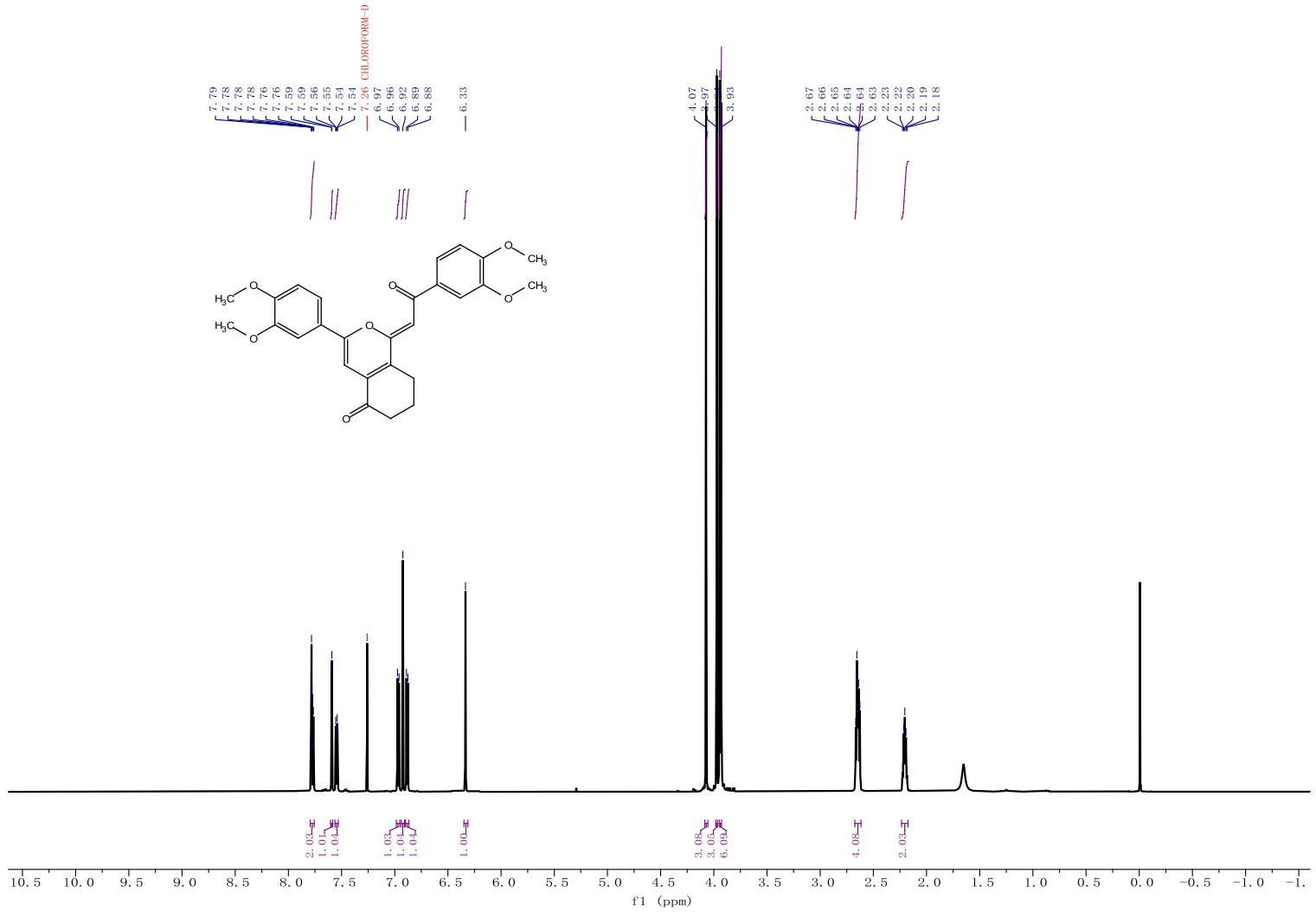
^{1}H NMR (600 MHz, $CDCl_3$) of **6d**



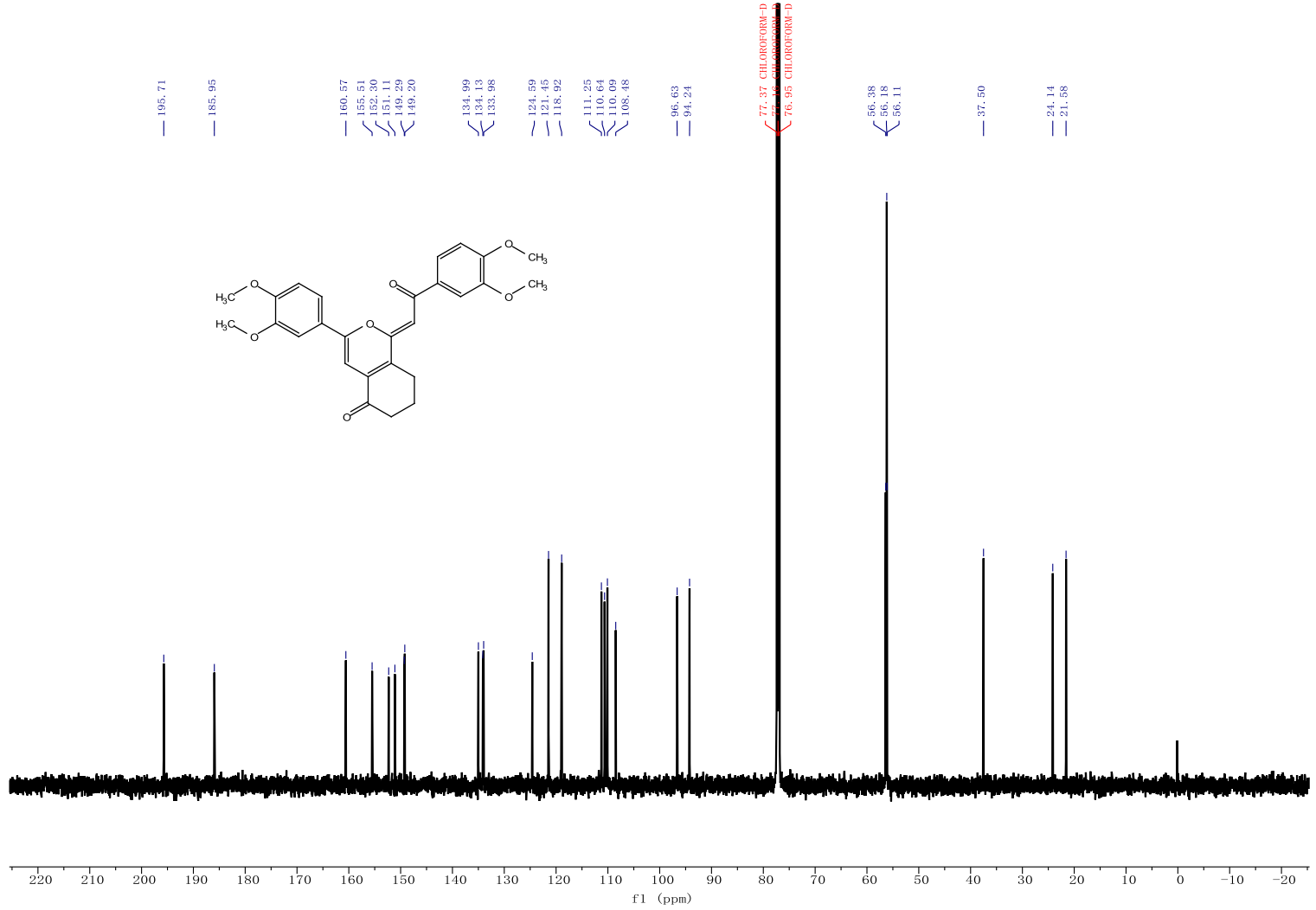
^{13}C NMR (151 MHz, $CDCl_3$) of **6d**



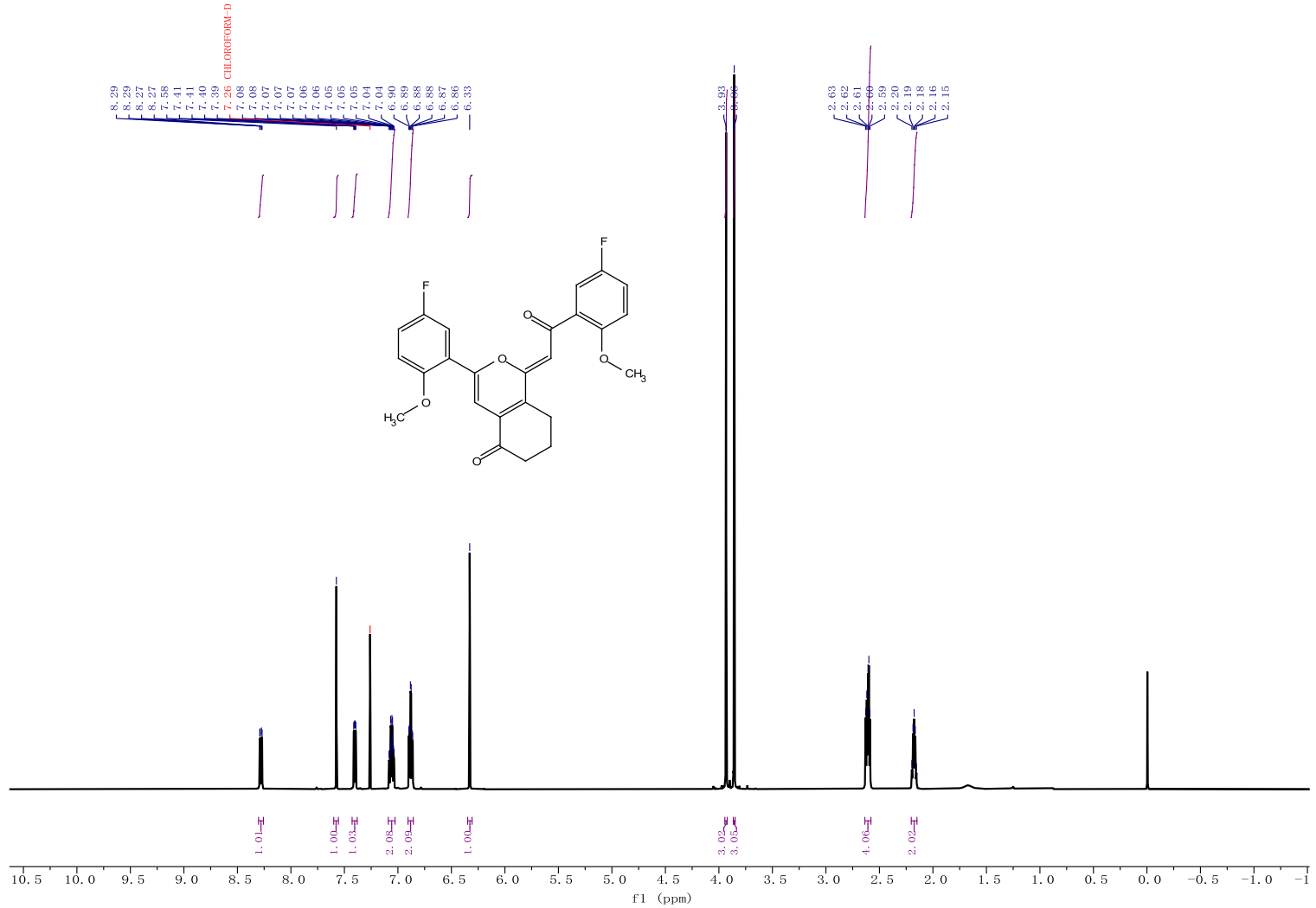
^{1}H NMR (600 MHz, $CDCl_3$) of **6e**



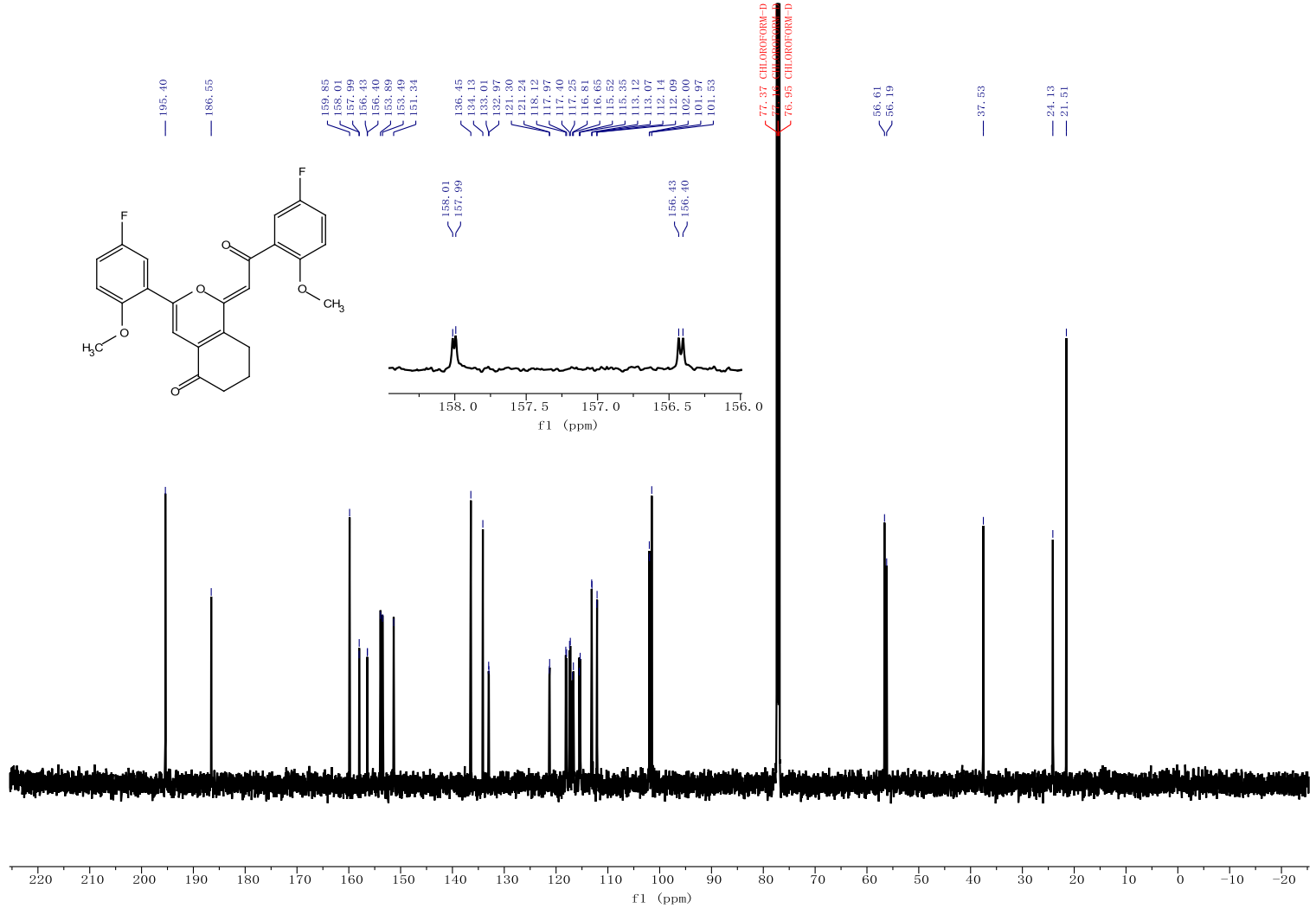
^{13}C NMR (151 MHz, $CDCl_3$) of **6e**



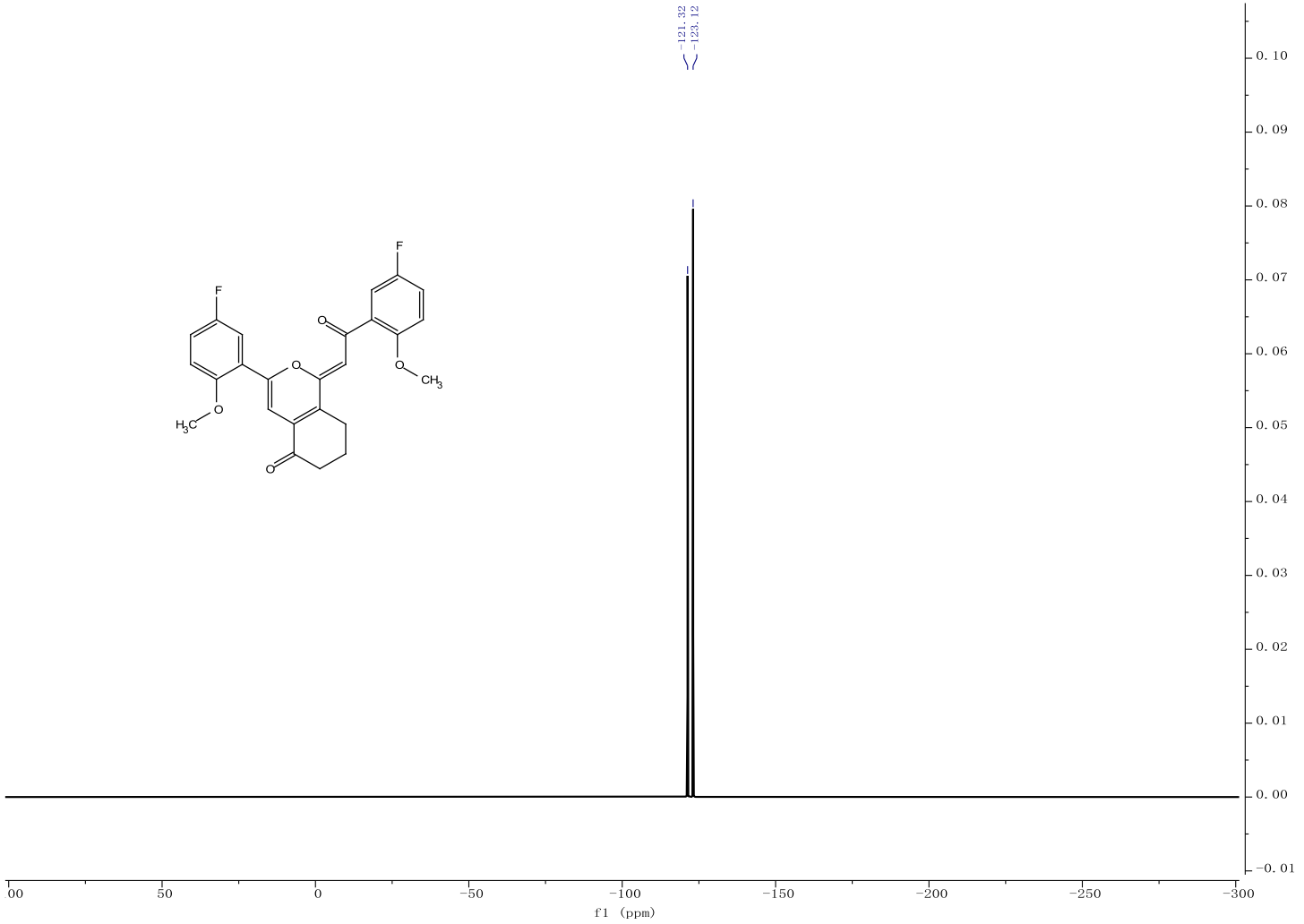
^{1}H NMR (600 MHz, $CDCl_3$) of **6f**



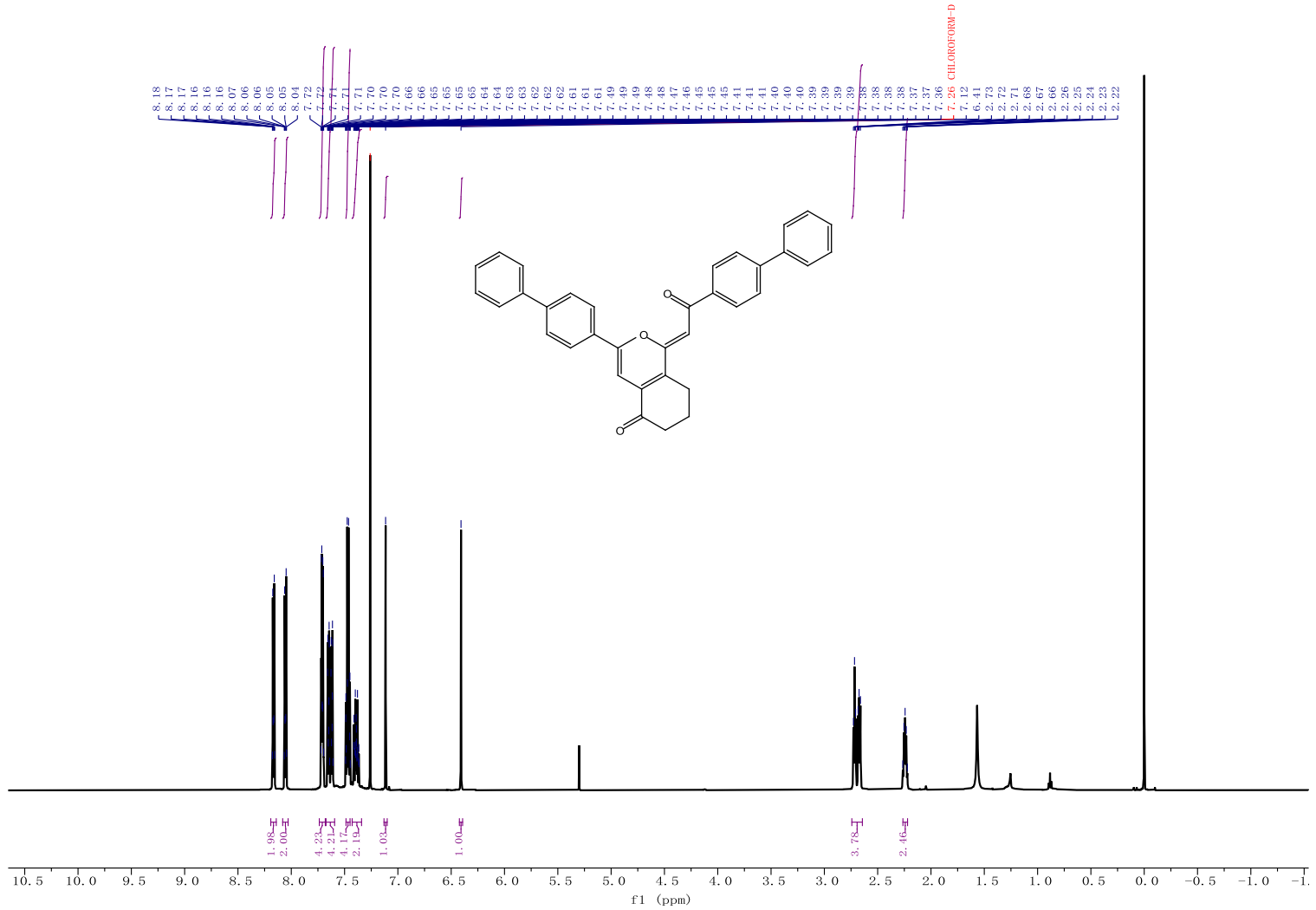
^{13}C NMR (151 MHz, $CDCl_3$) of **6f**



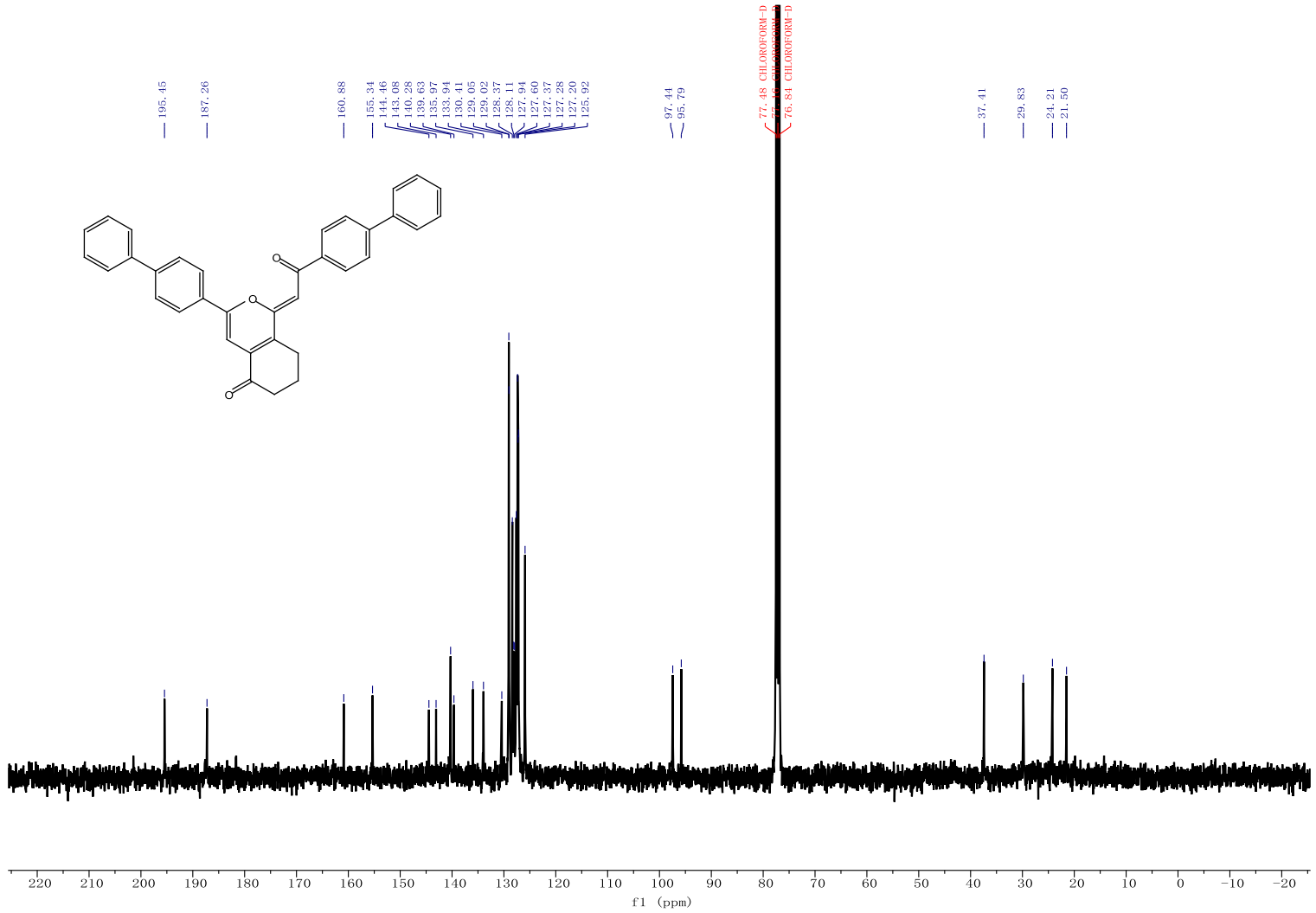
^{19}F NMR (565 MHz, $CDCl_3$) of **6f**



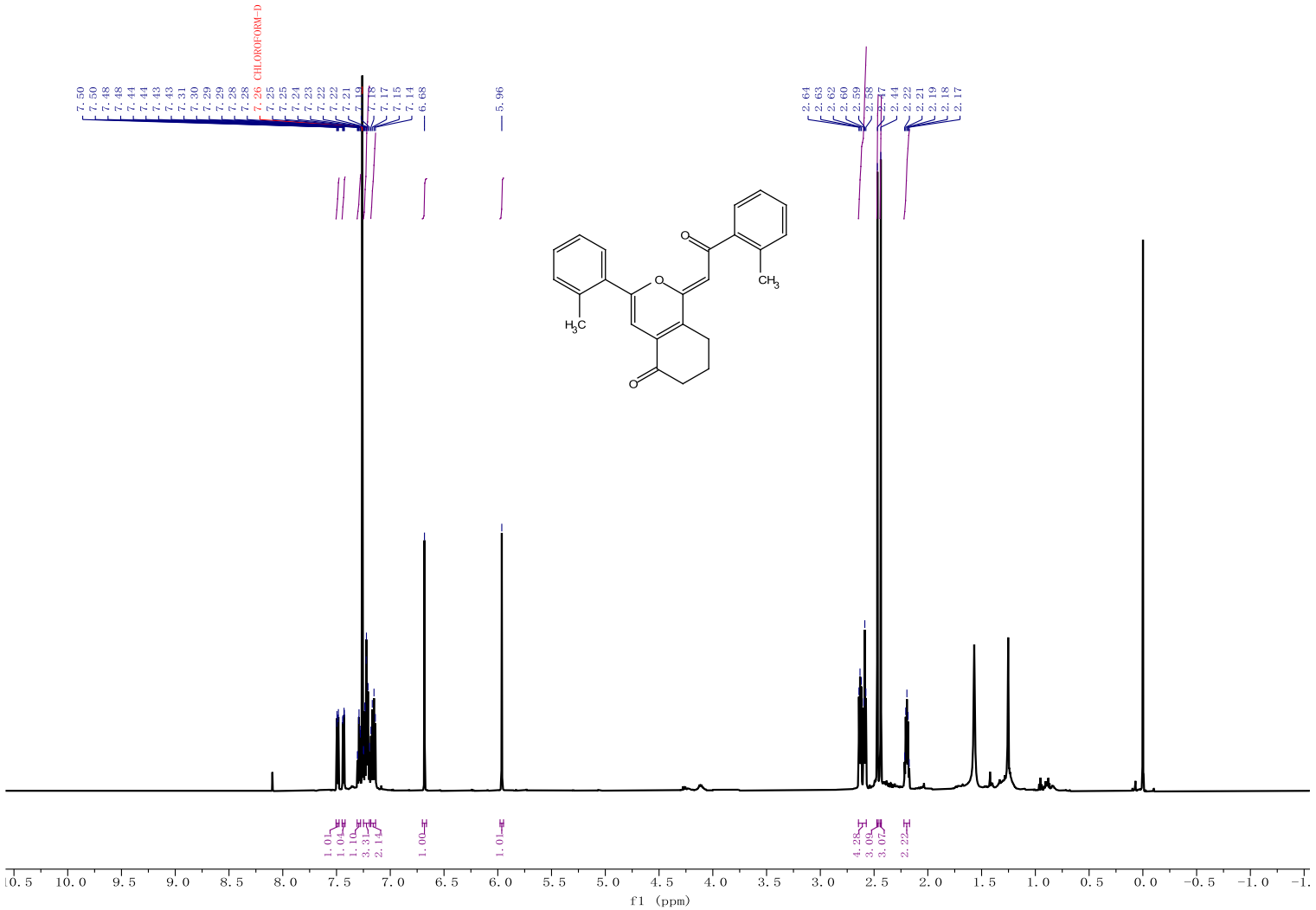
^{1}H NMR (600 MHz, $CDCl_3$) of **6g**



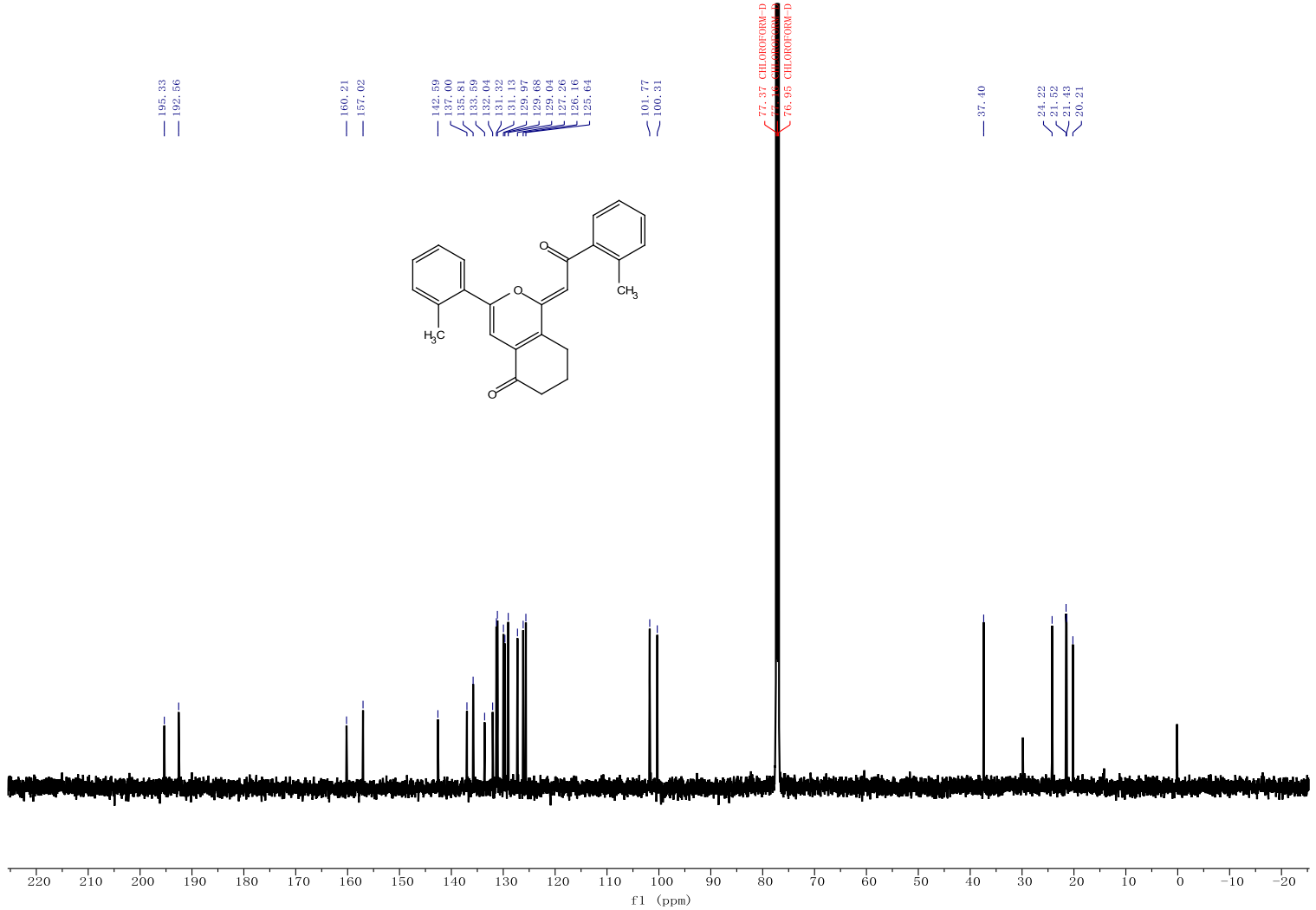
^{13}C NMR (101 MHz, $CDCl_3$) of **6g**



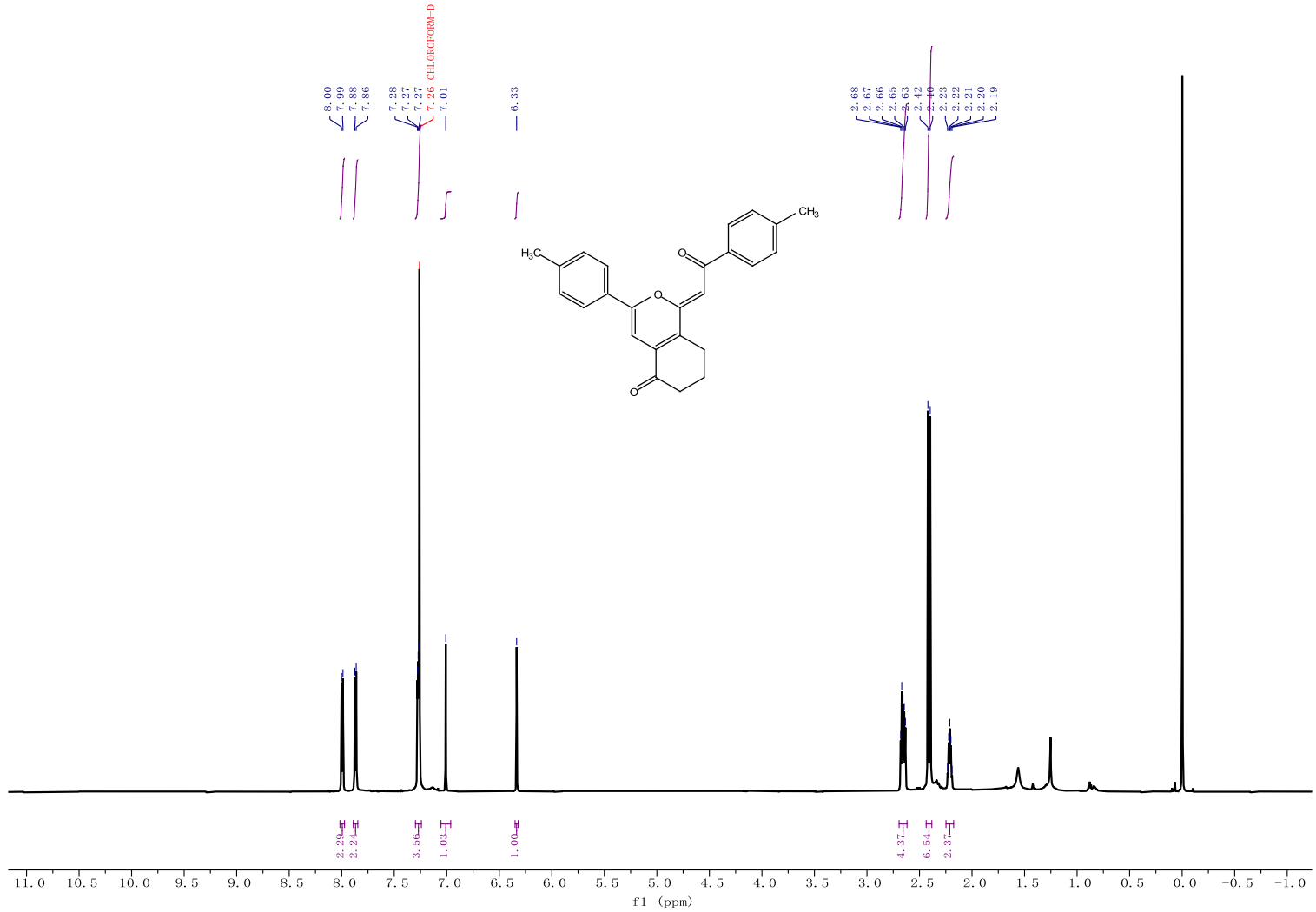
^{1}H NMR (600 MHz, $CDCl_3$) of **6h**



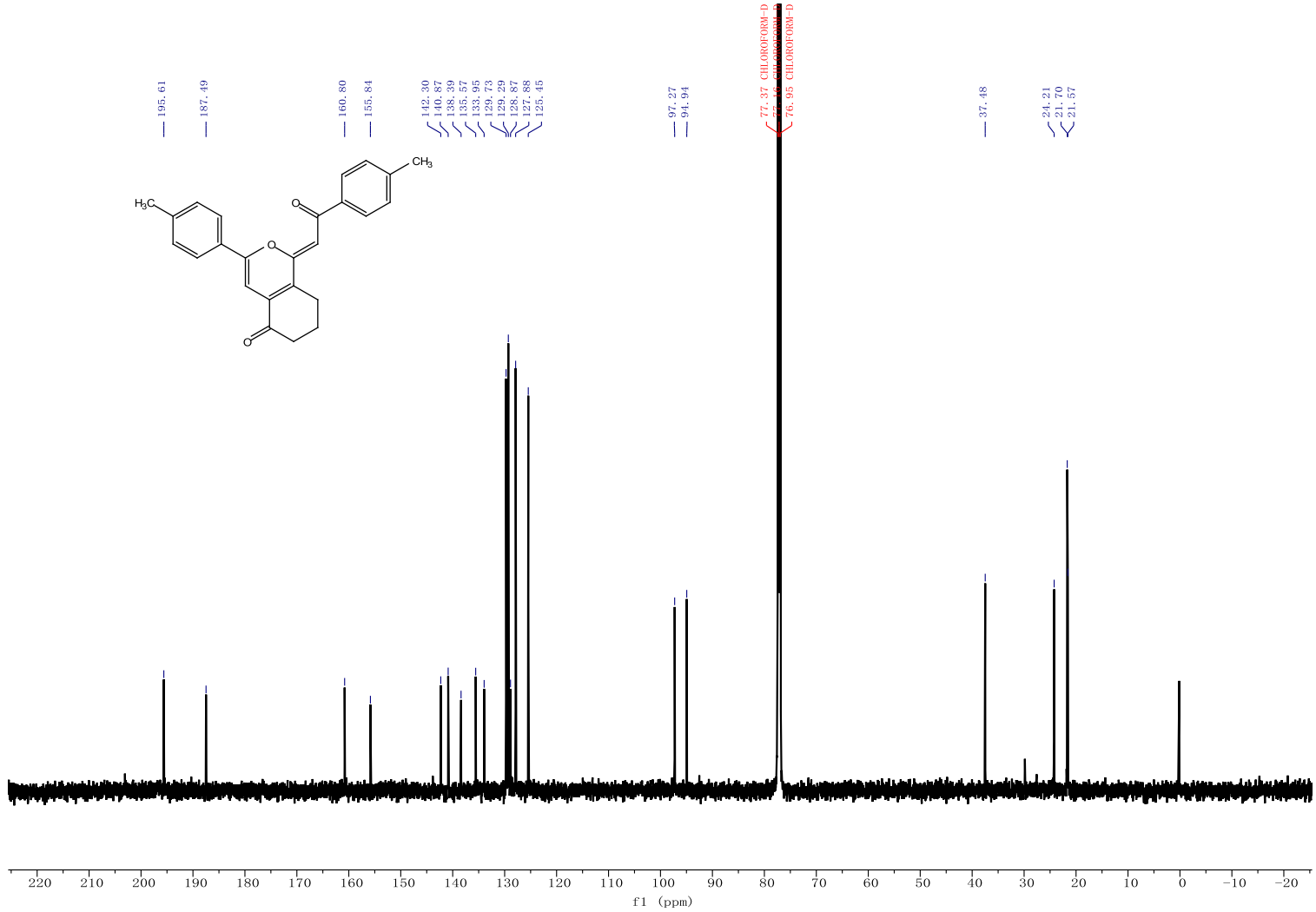
^{13}C NMR (151 MHz, $CDCl_3$) of **6h**



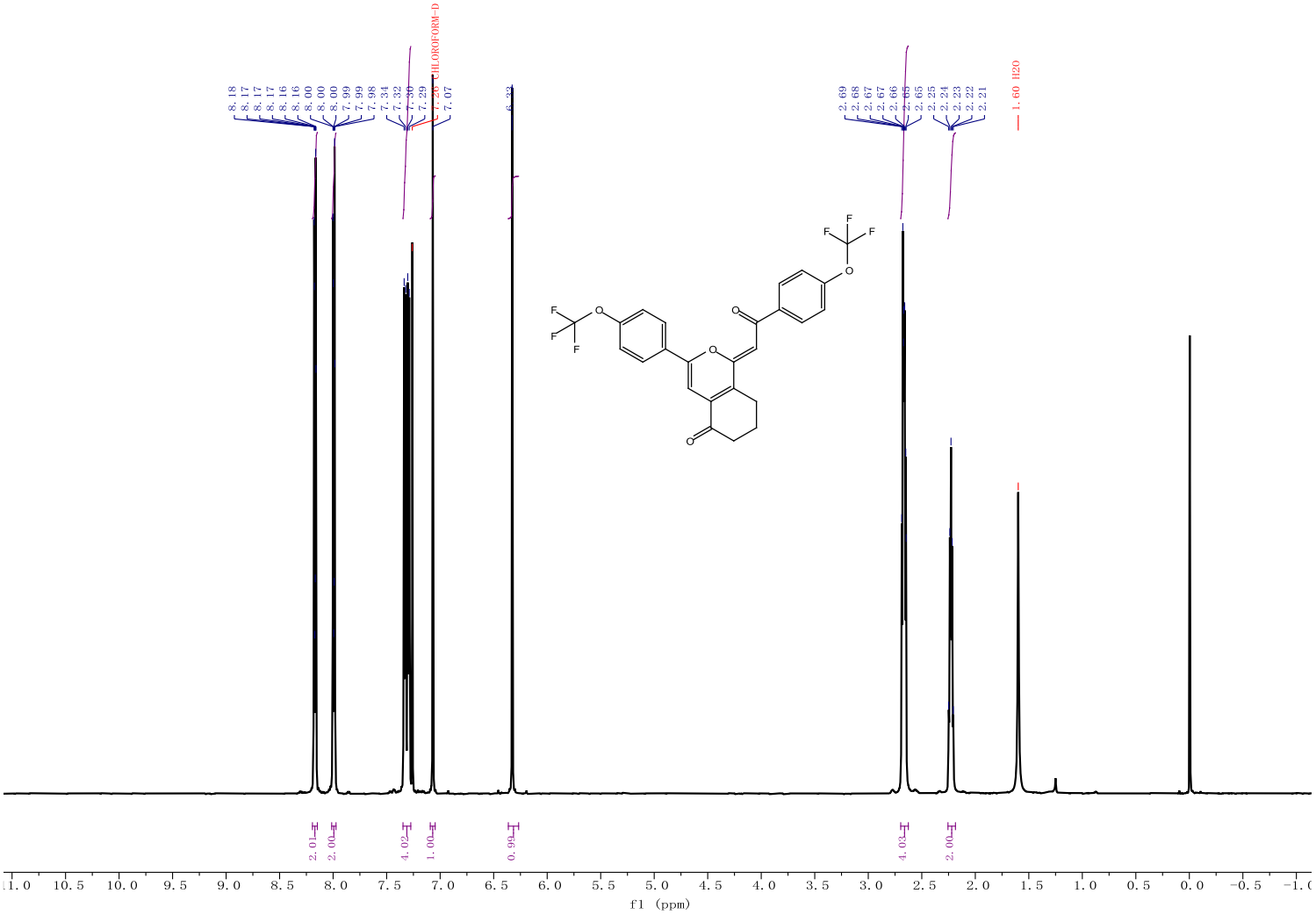
^{1}H NMR (600 MHz, $CDCl_3$) of **6i**



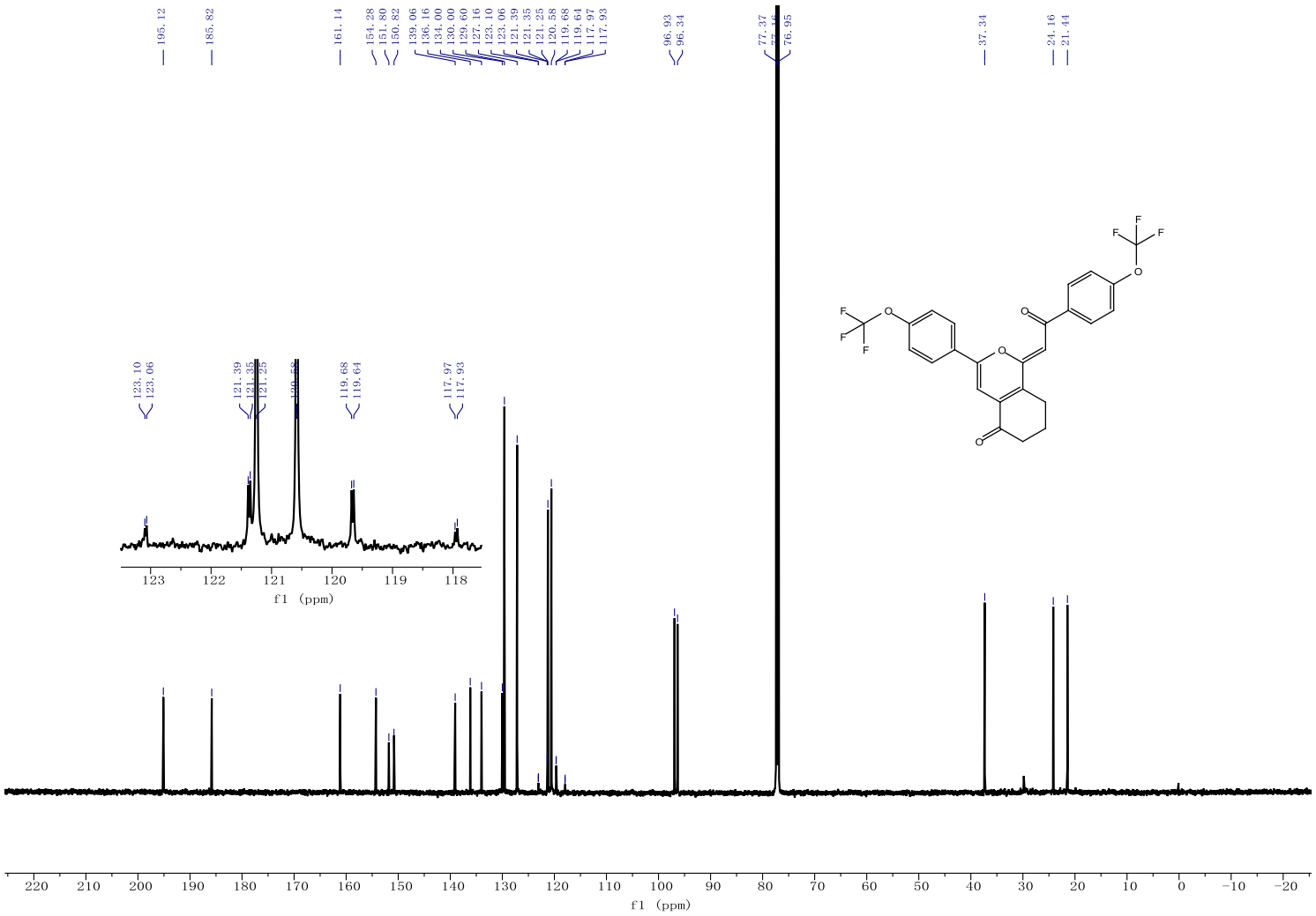
^{13}C NMR (151 MHz, $CDCl_3$) of **6i**



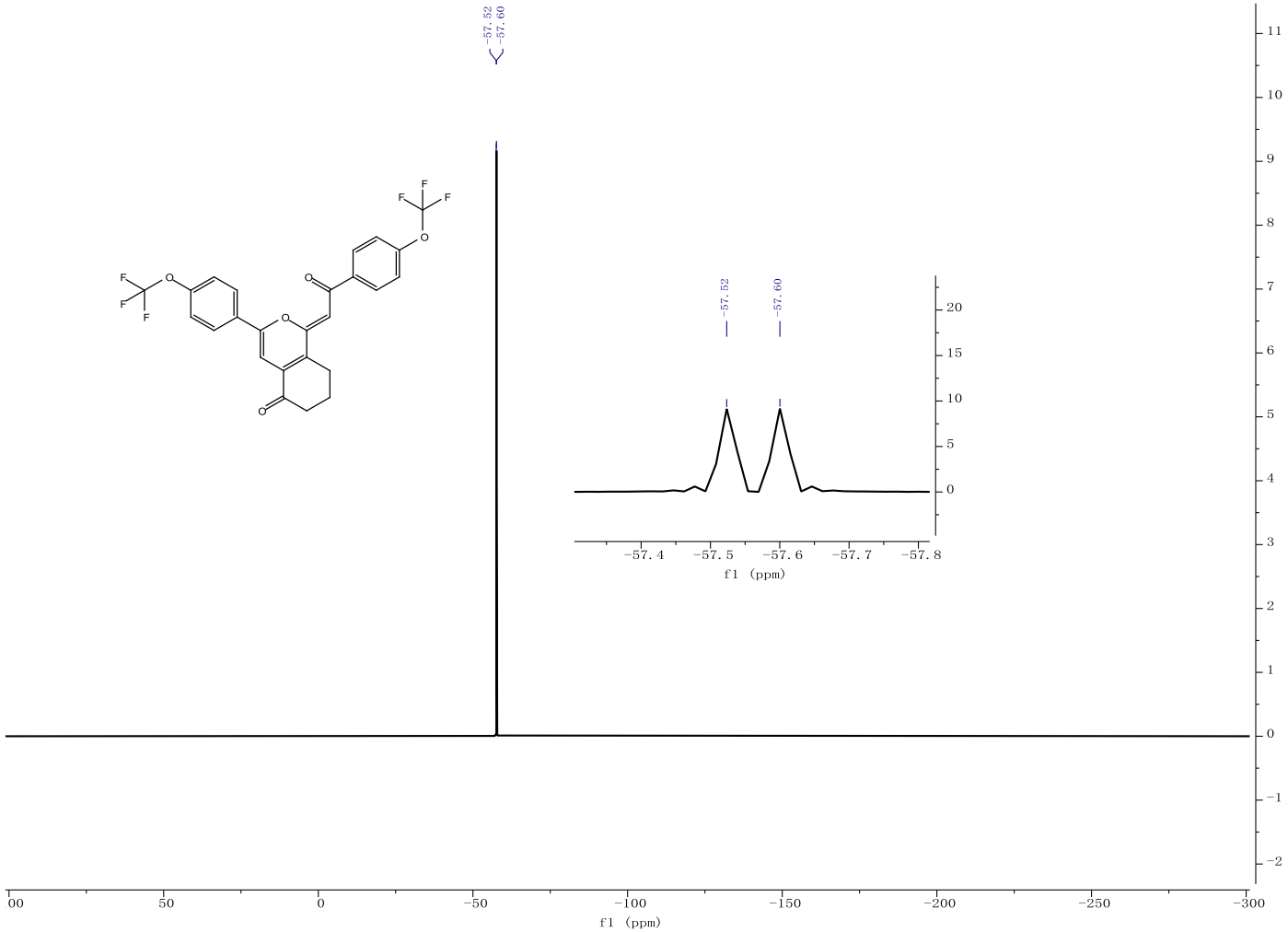
^{1}H NMR (600 MHz, $CDCl_3$) of **6j**



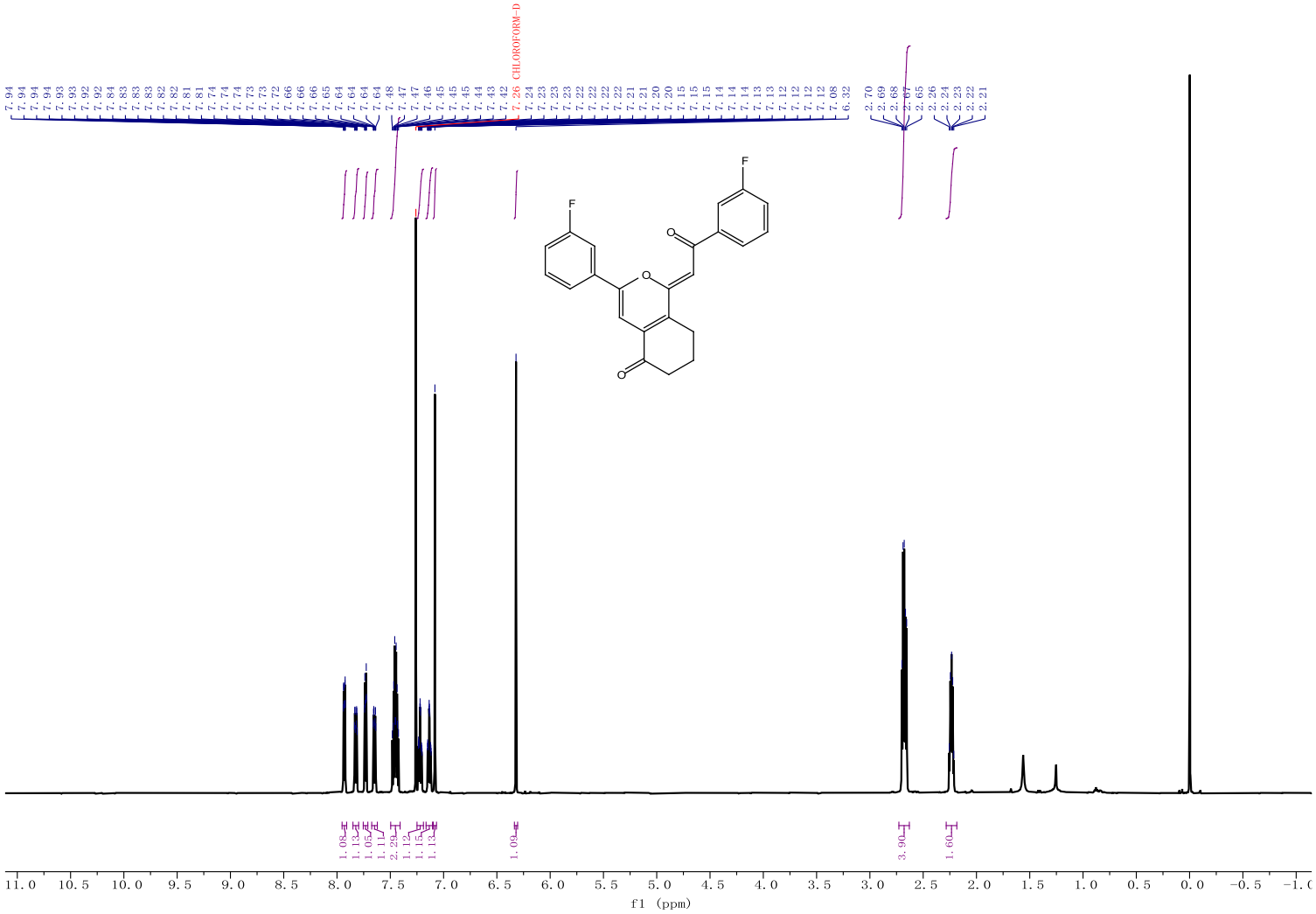
^{13}C NMR (151 MHz, $CDCl_3$) of **6j**



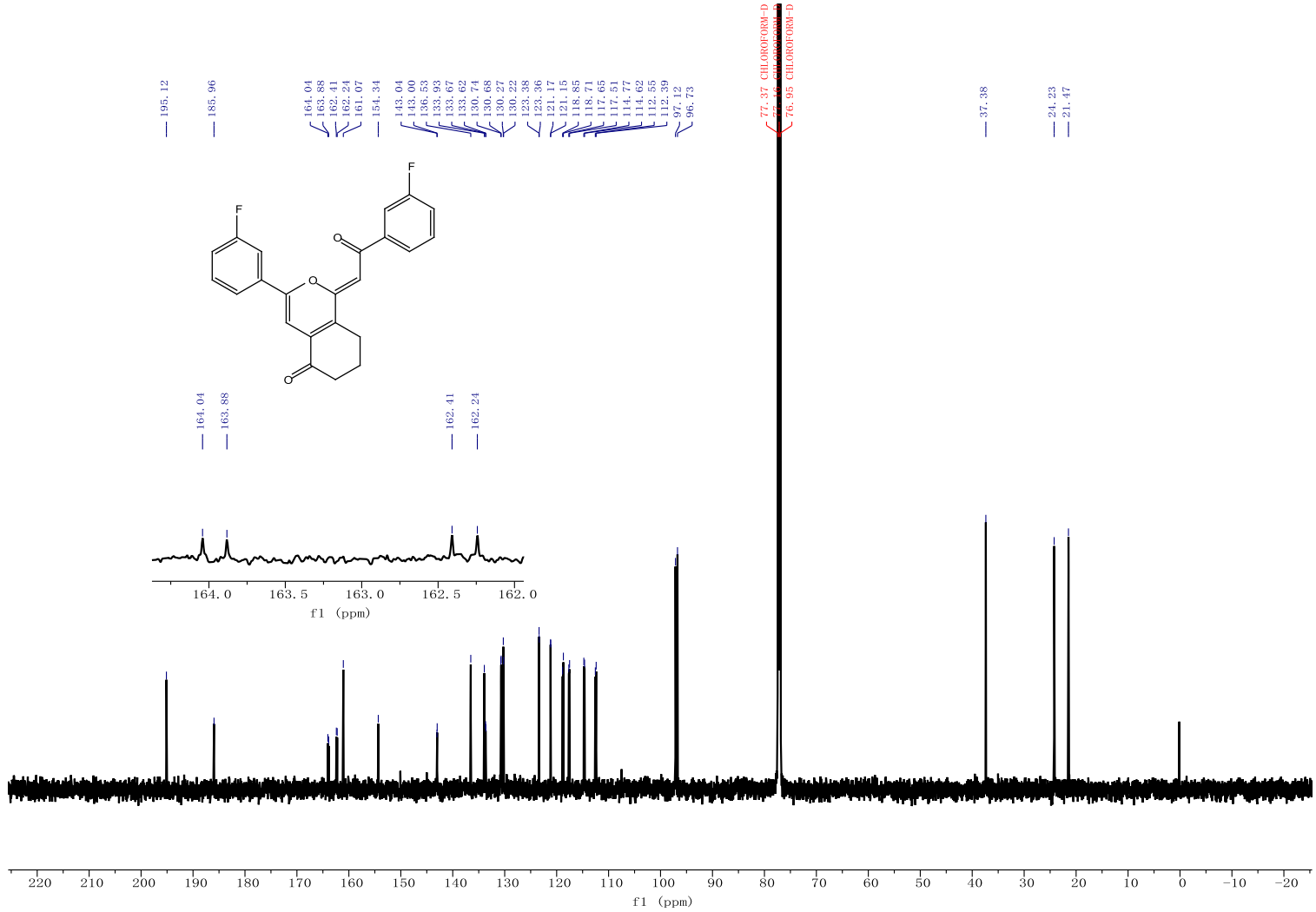
^{19}F NMR (565 MHz, $CDCl_3$) of **6j**



^{1}H NMR (600 MHz, $CDCl_3$) of **6k**

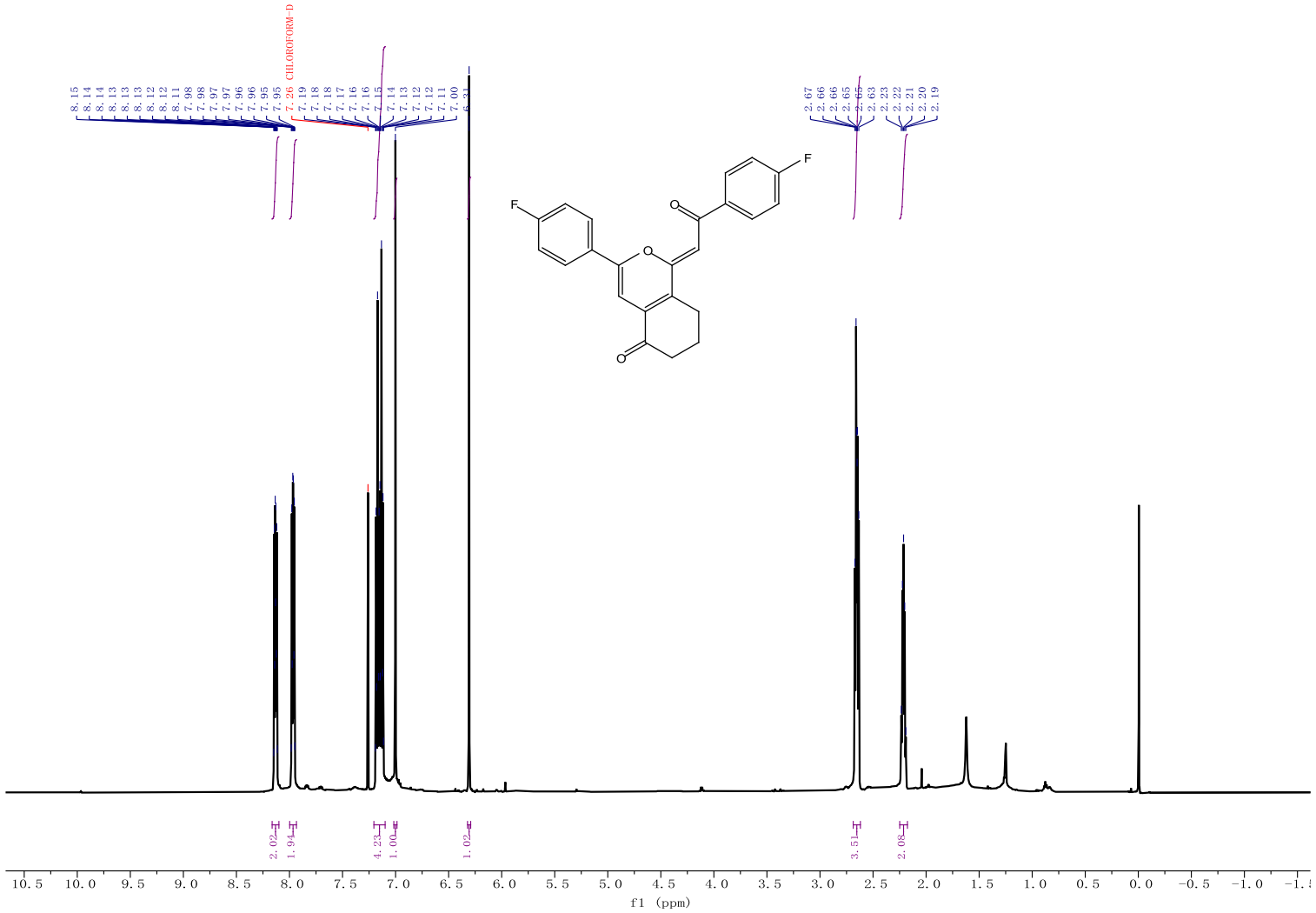


^{13}C NMR (151 MHz, $CDCl_3$) of **6k**

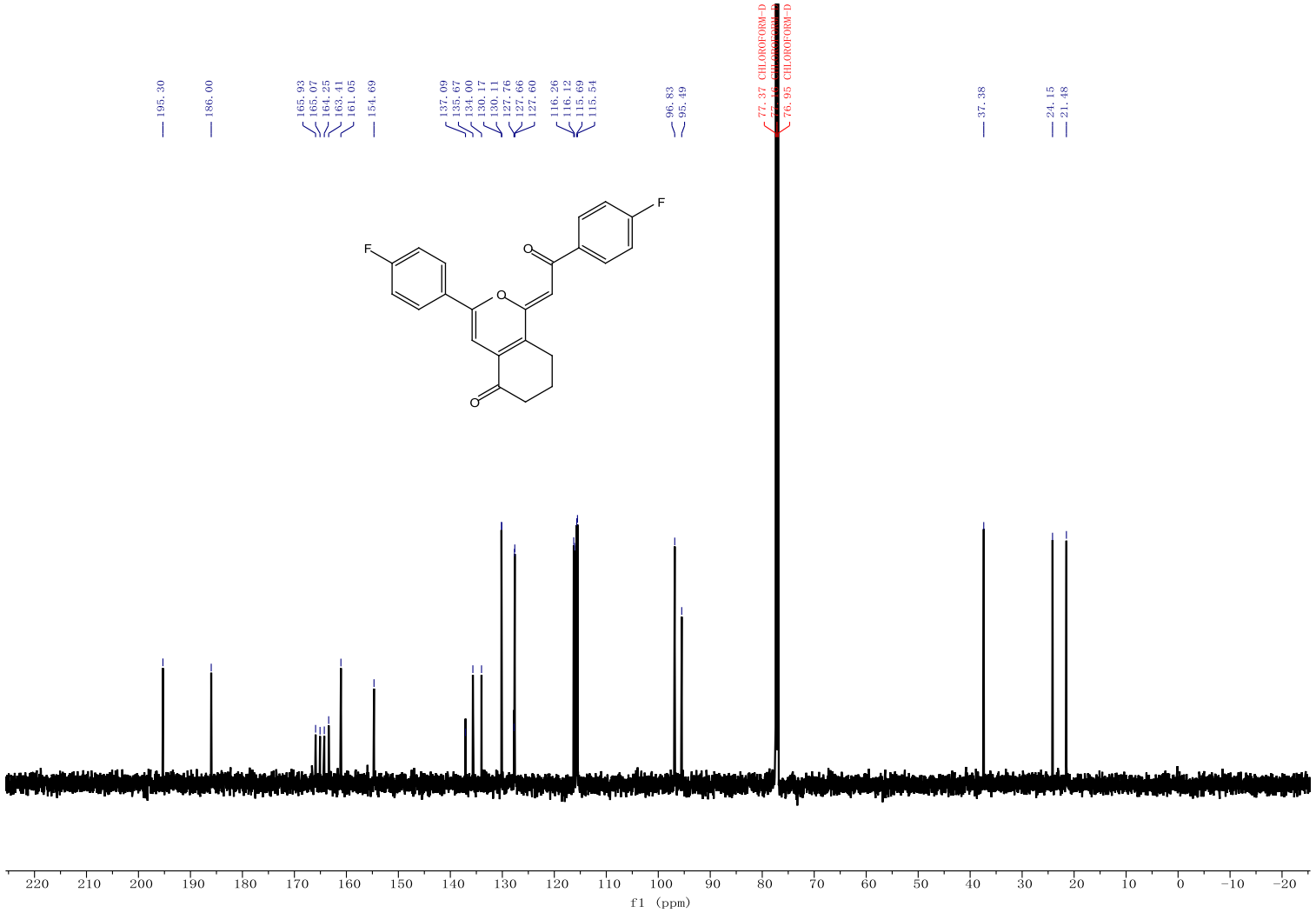


^{19}F NMR (565 MHz, $CDCl_3$) of **6k**

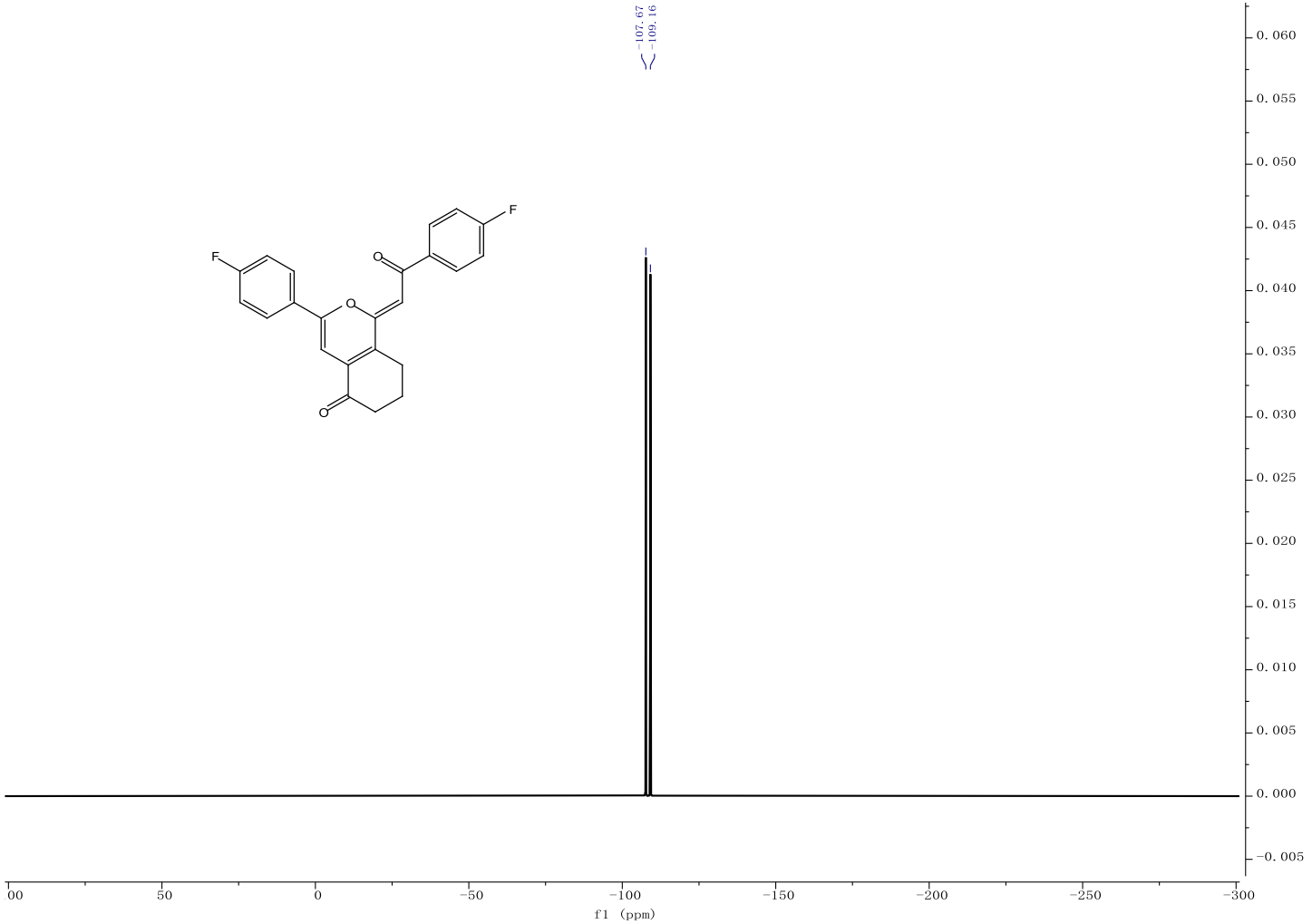
^{1}H NMR (600 MHz, $CDCl_3$) of **6l**



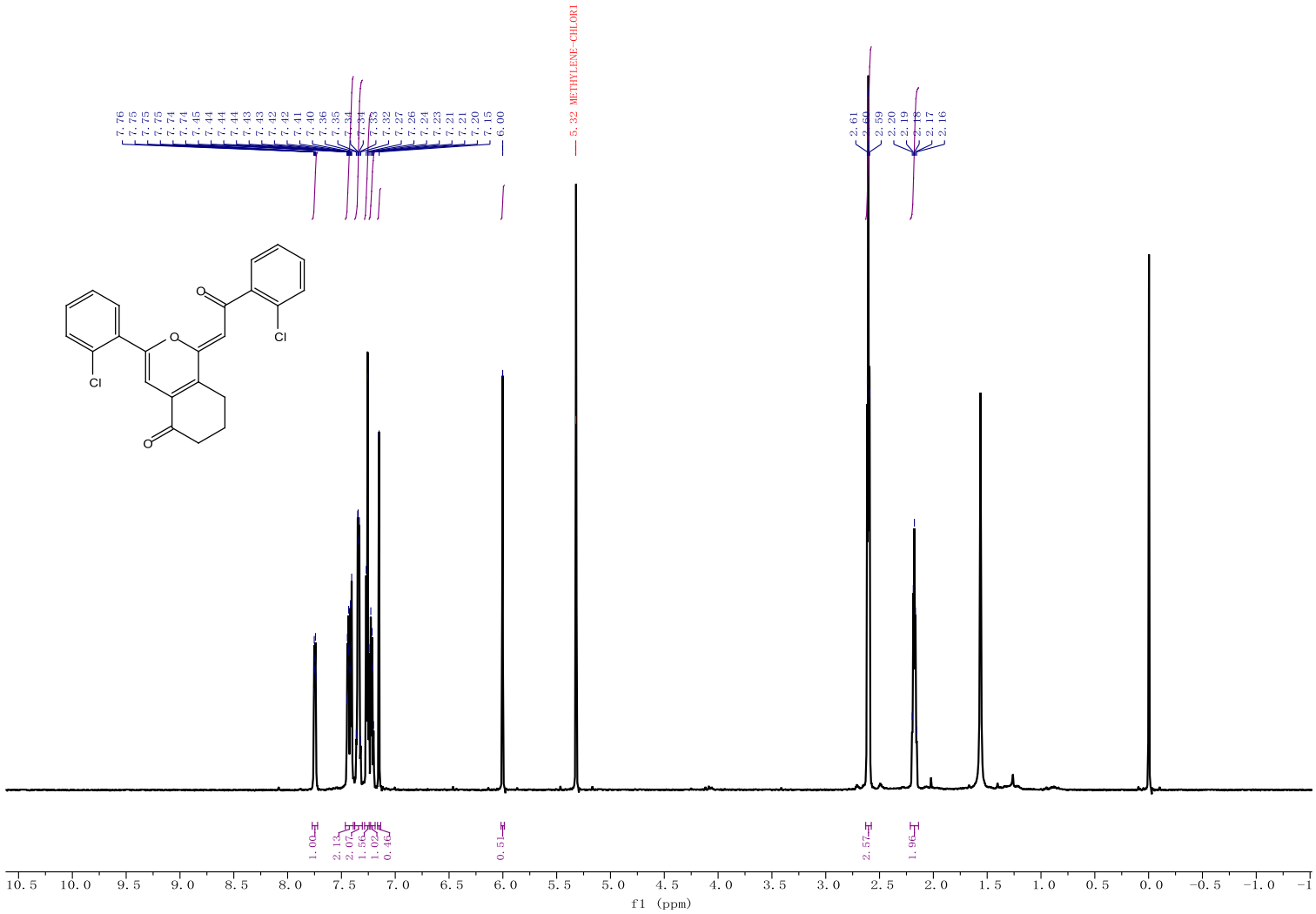
^{13}C NMR (151 MHz, $CDCl_3$) of **6l**



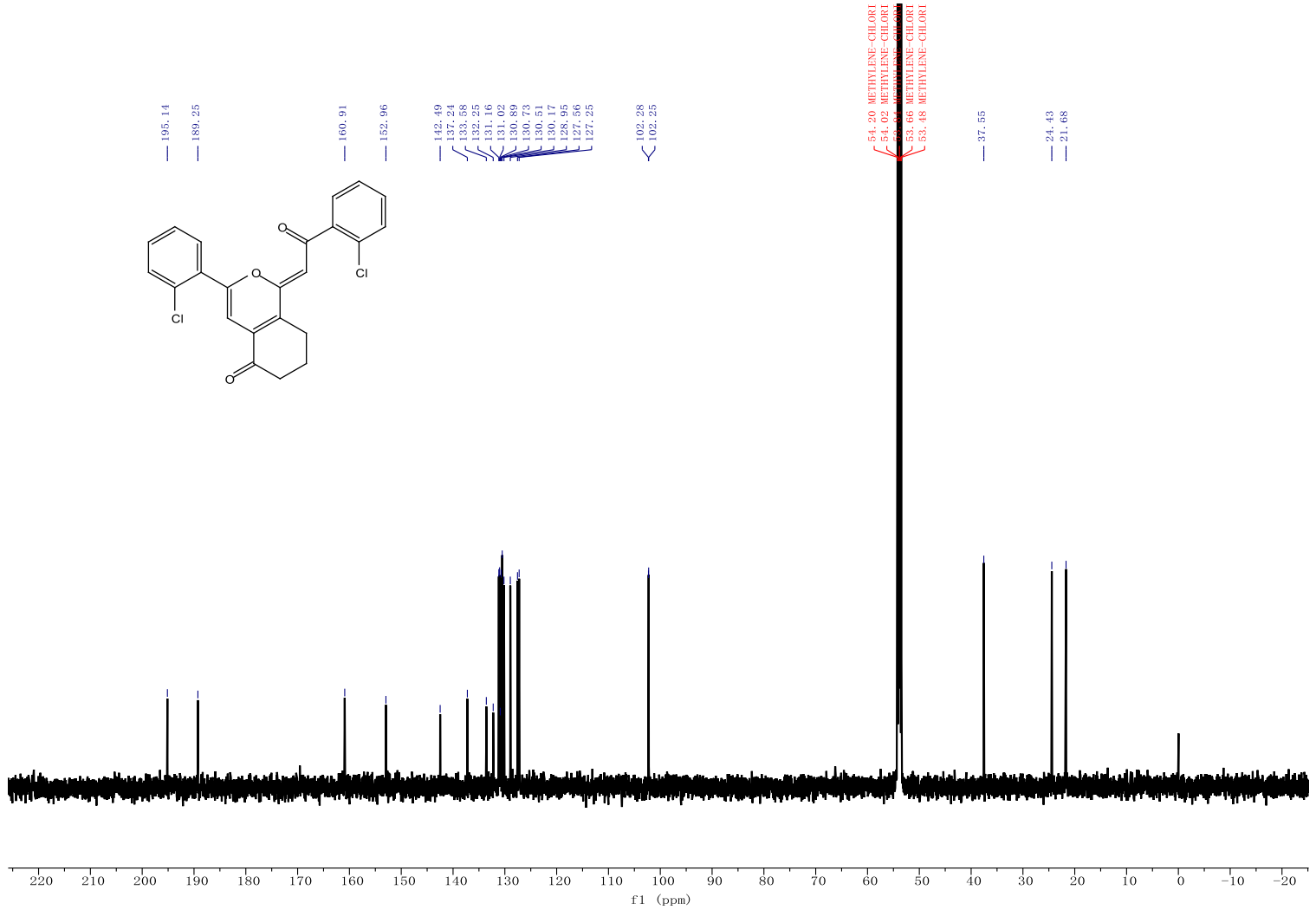
^{19}F NMR (565 MHz, $CDCl_3$) of **6l**



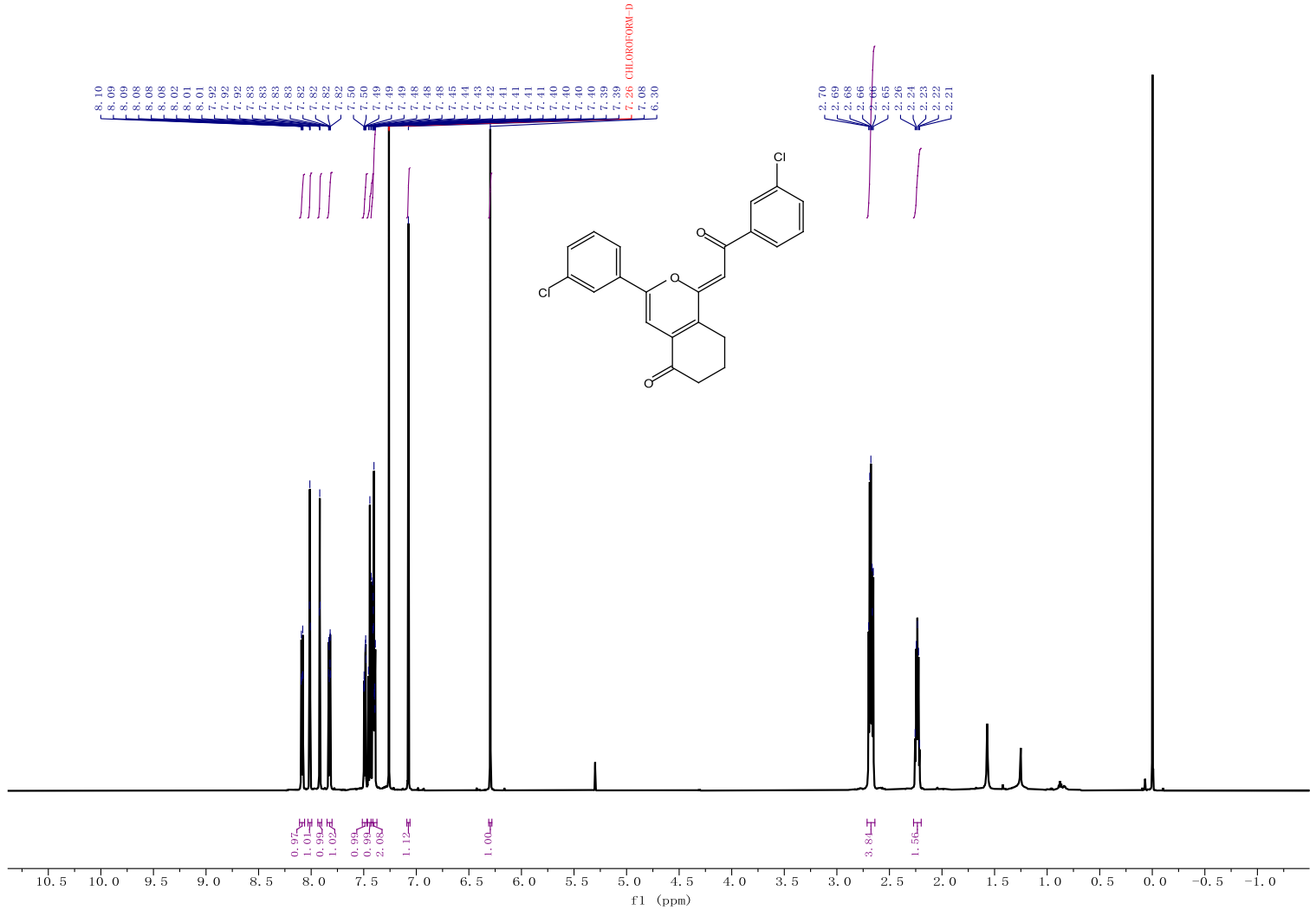
^{1}H NMR (600 MHz, CD_2Cl_2) of **6m**



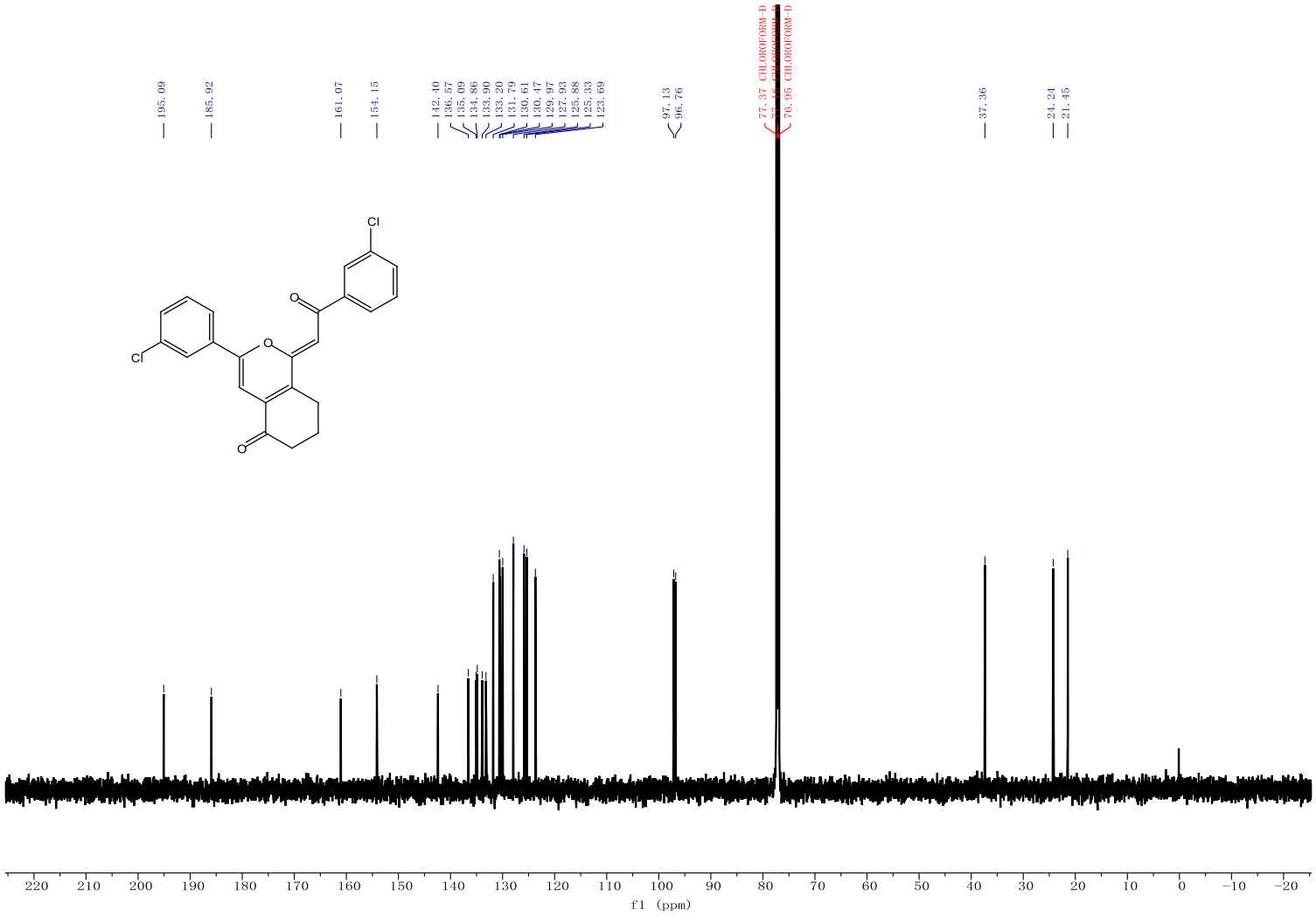
^{13}C NMR (151 MHz, CD_2Cl_2) of **6m**



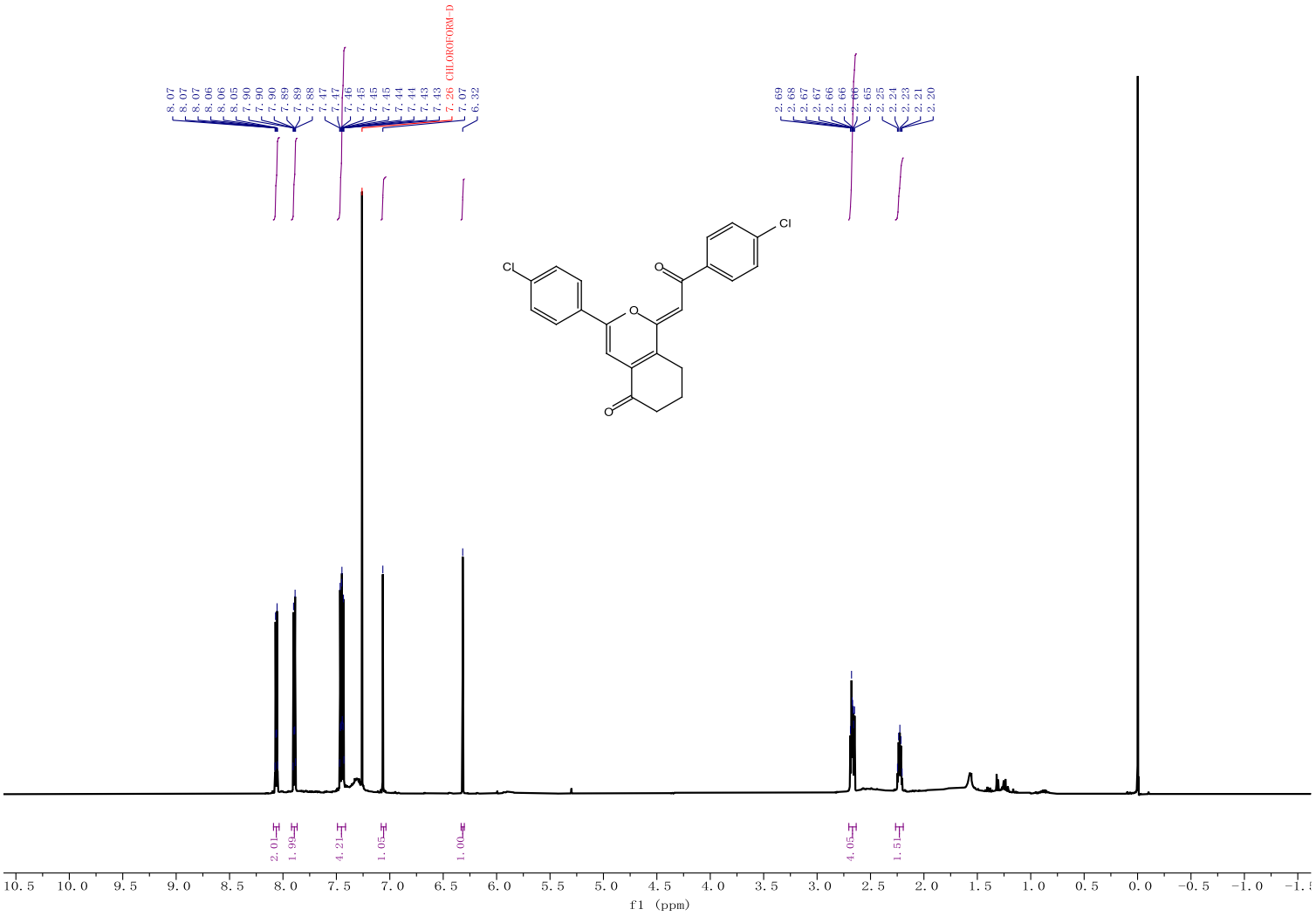
^{1}H NMR (600 MHz, $CDCl_3$) of **6n**



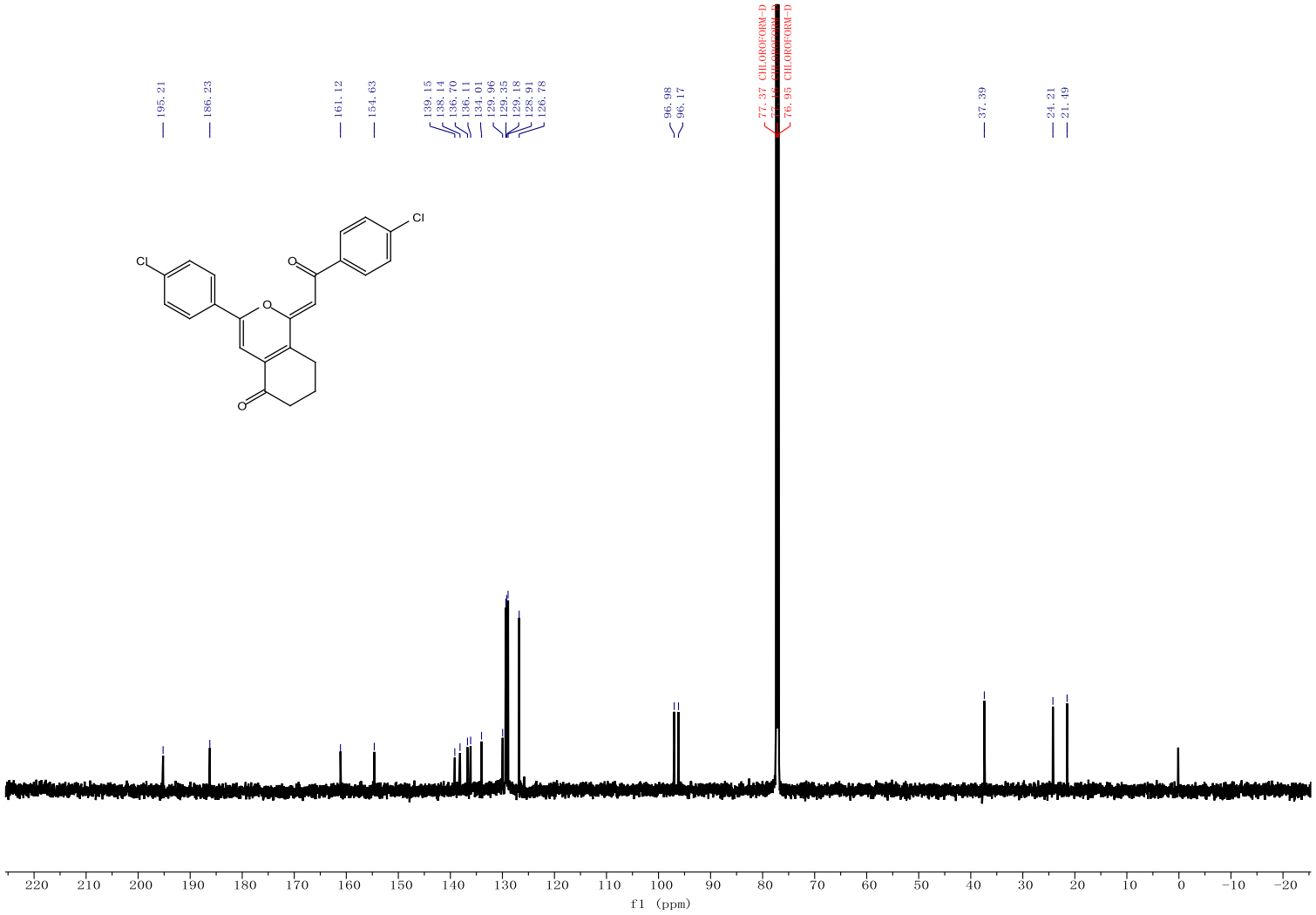
^{13}C NMR (151 MHz, $CDCl_3$) of **6n**



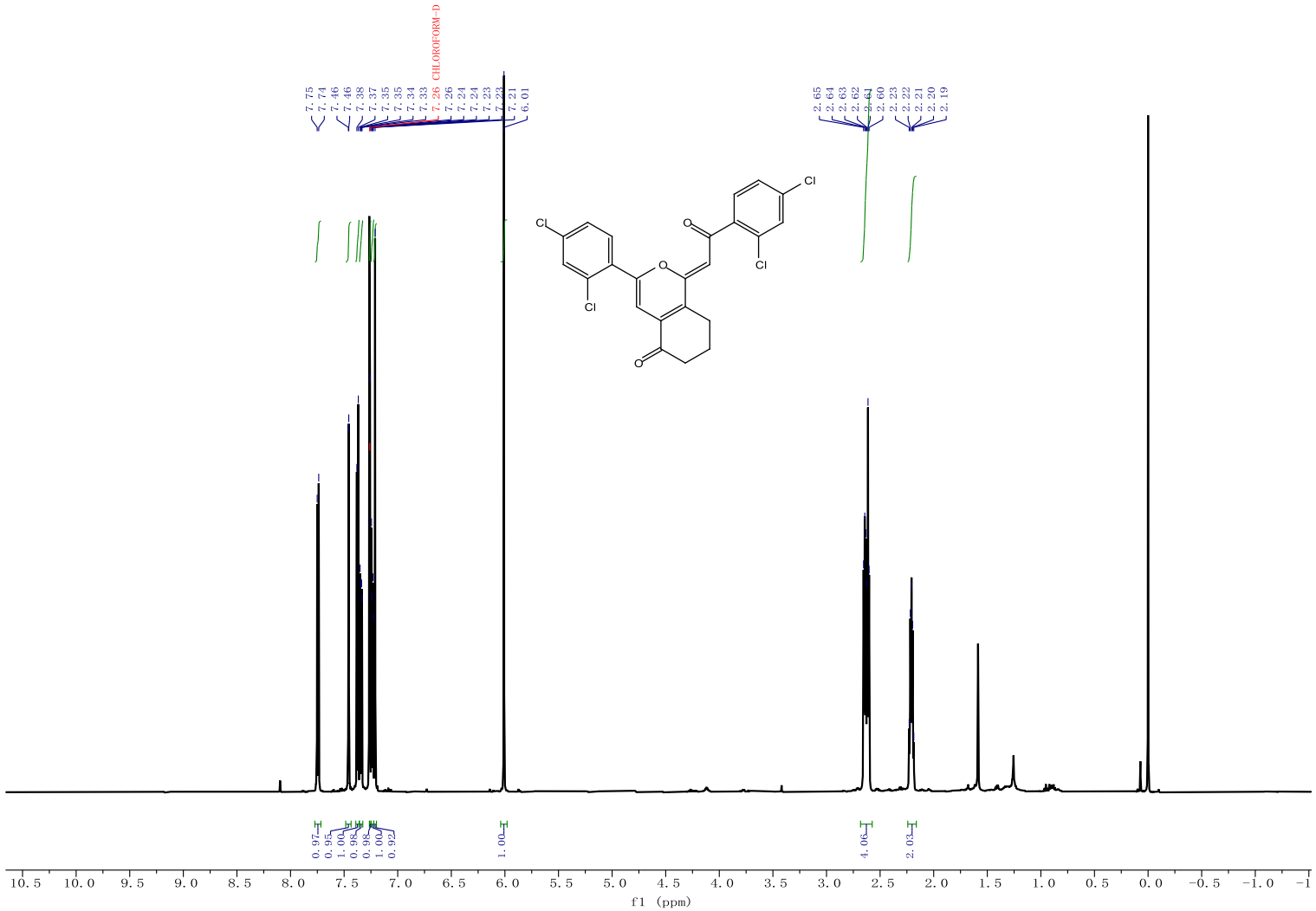
^{1}H NMR (600 MHz, $CDCl_3$) of **6o**



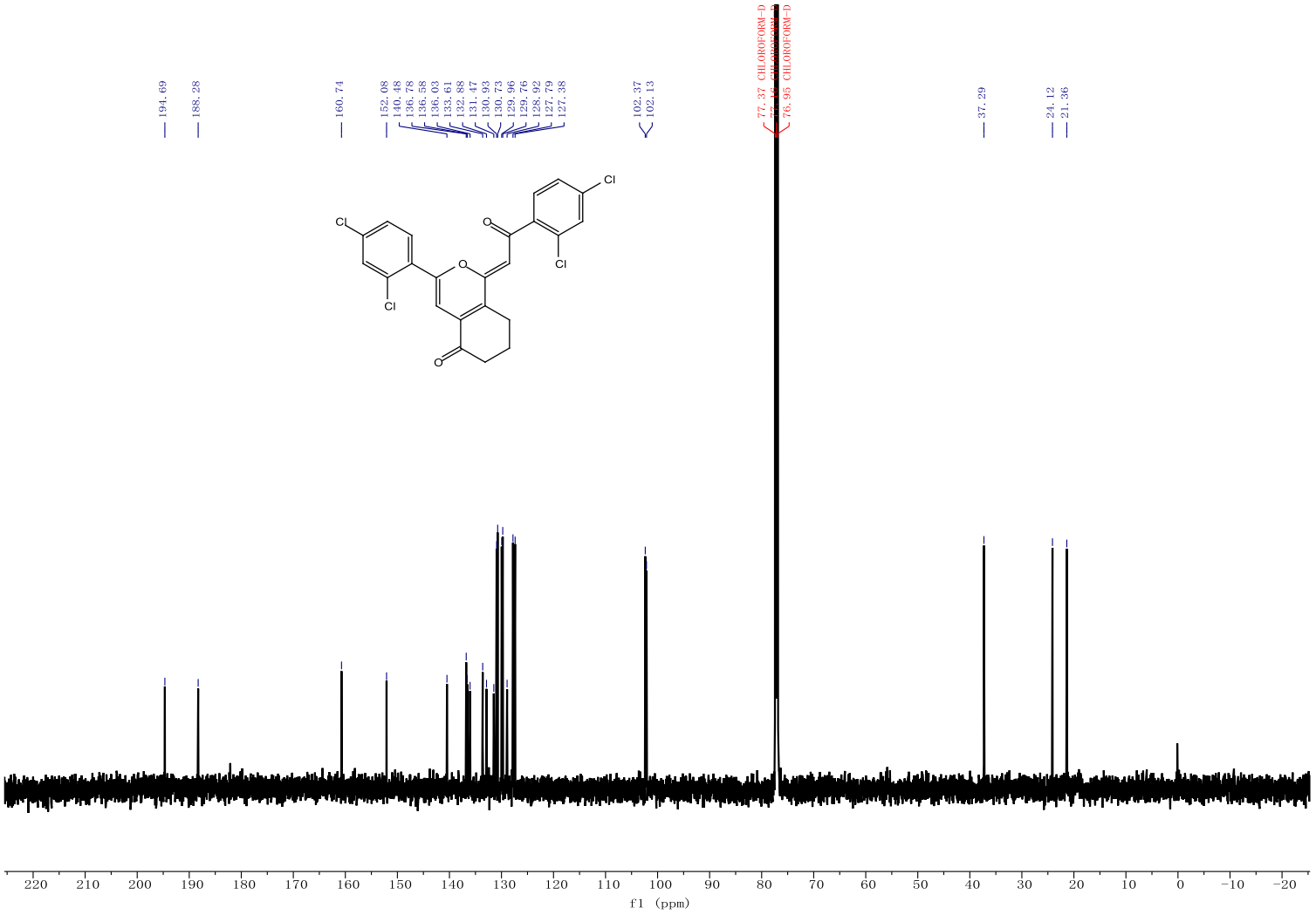
^{13}C NMR (151 MHz, $CDCl_3$) of **6o**



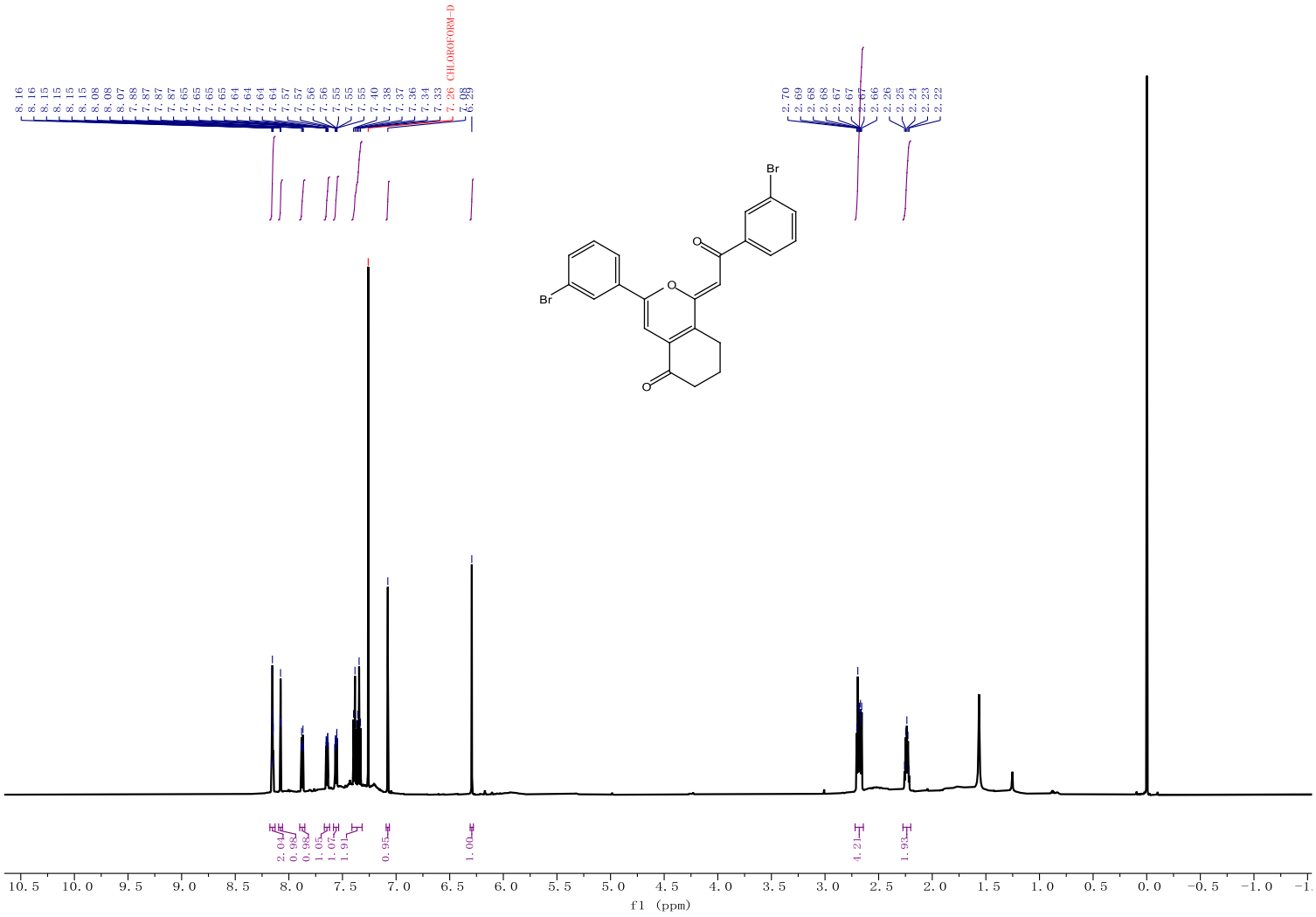
^{1}H NMR (600 MHz, $CDCl_3$) of **6p**



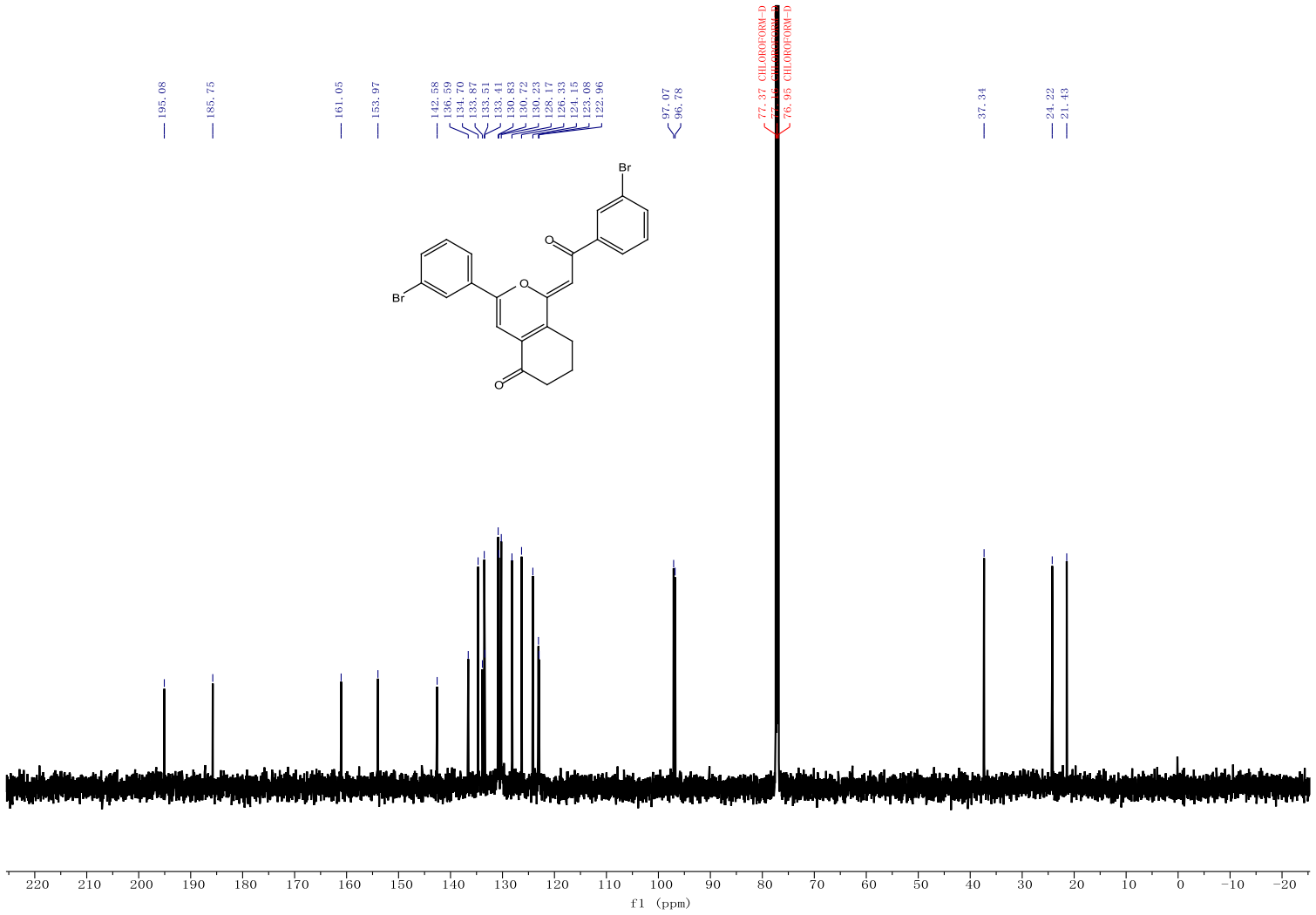
^{13}C NMR (151 MHz, $CDCl_3$) of **6p**



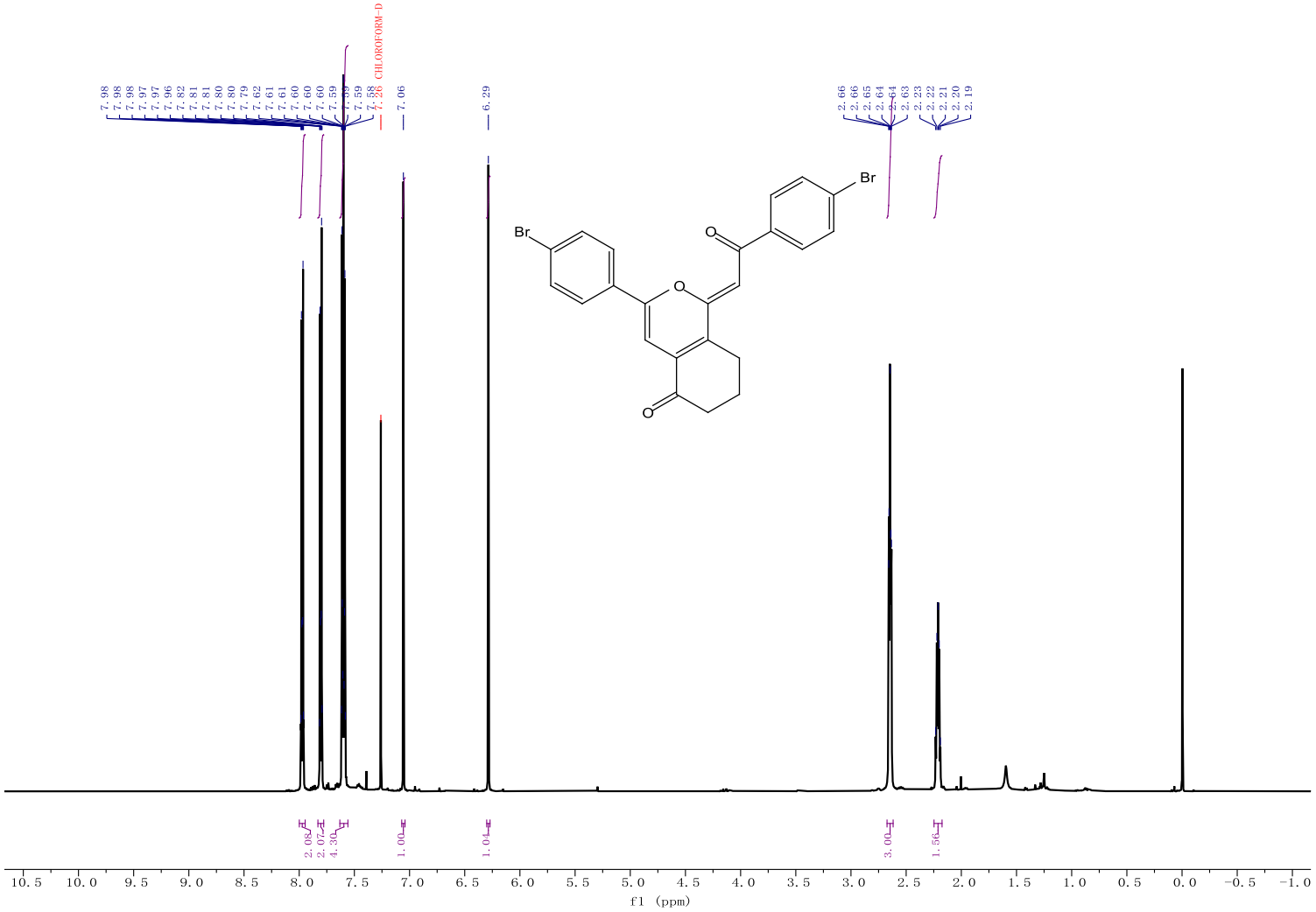
^{1}H NMR (600 MHz, $CDCl_3$) of **6q**



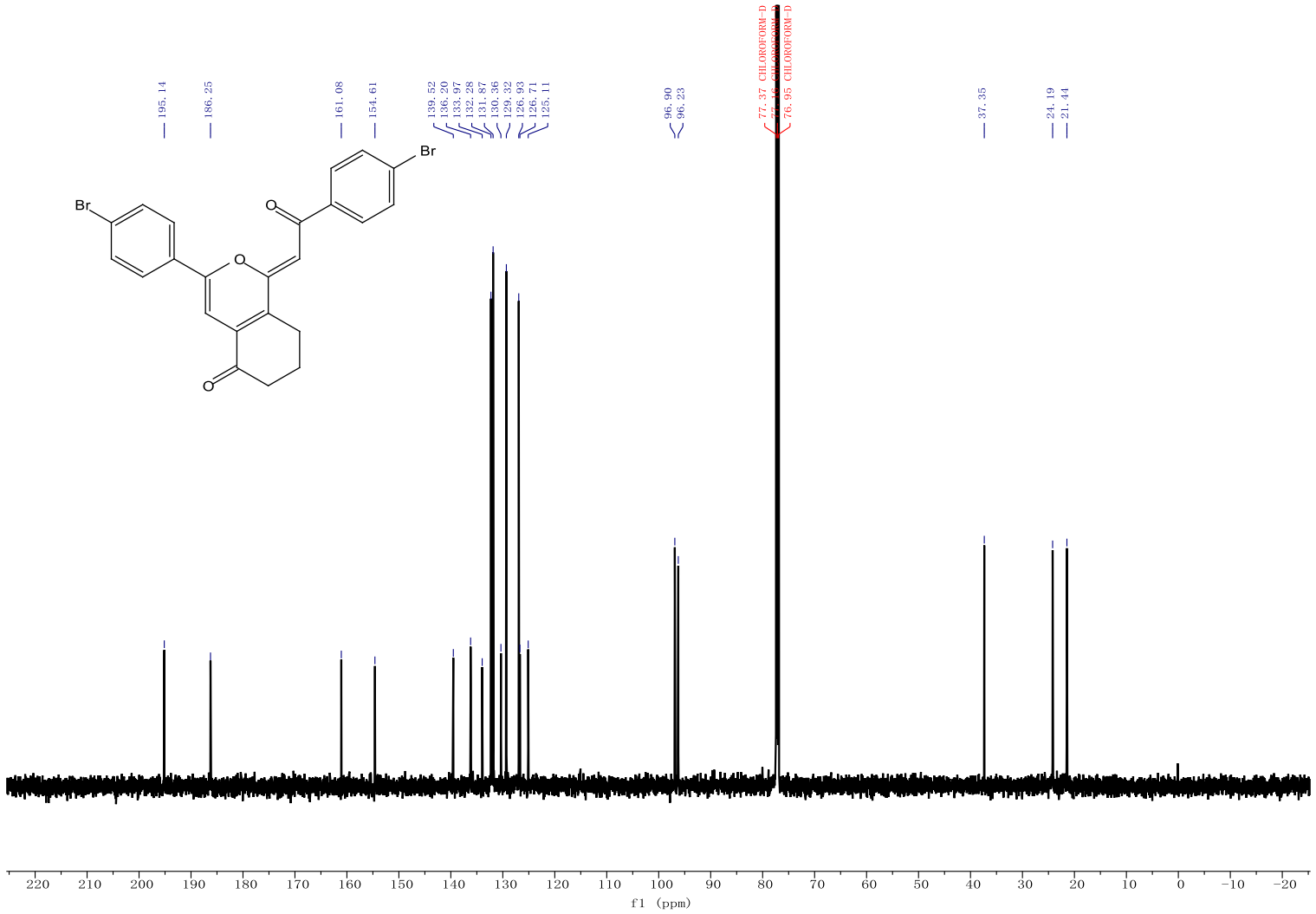
^{13}C NMR (151 MHz, $CDCl_3$) of **6q**



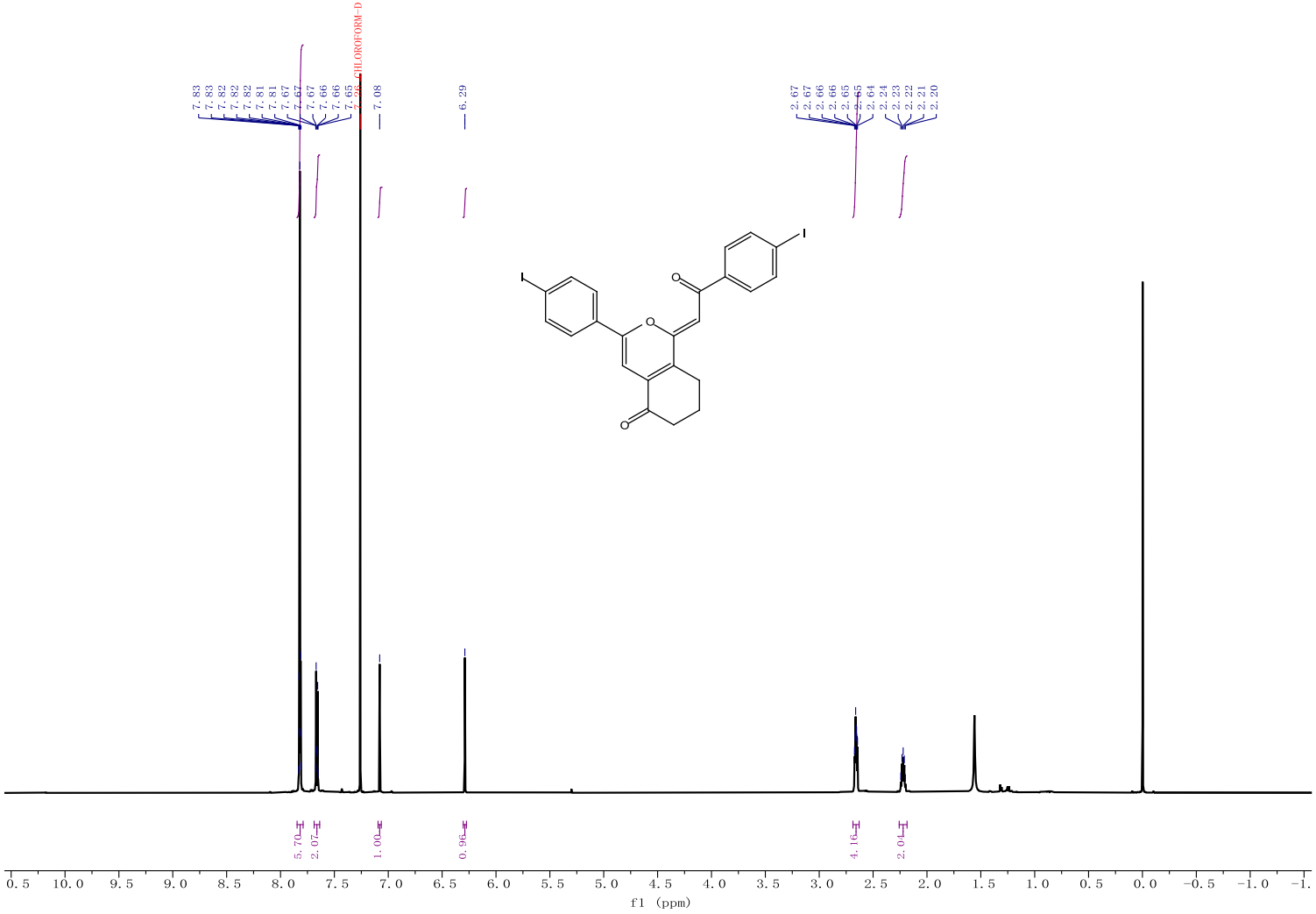
^{1}H NMR (600 MHz, $CDCl_3$) of **6r**



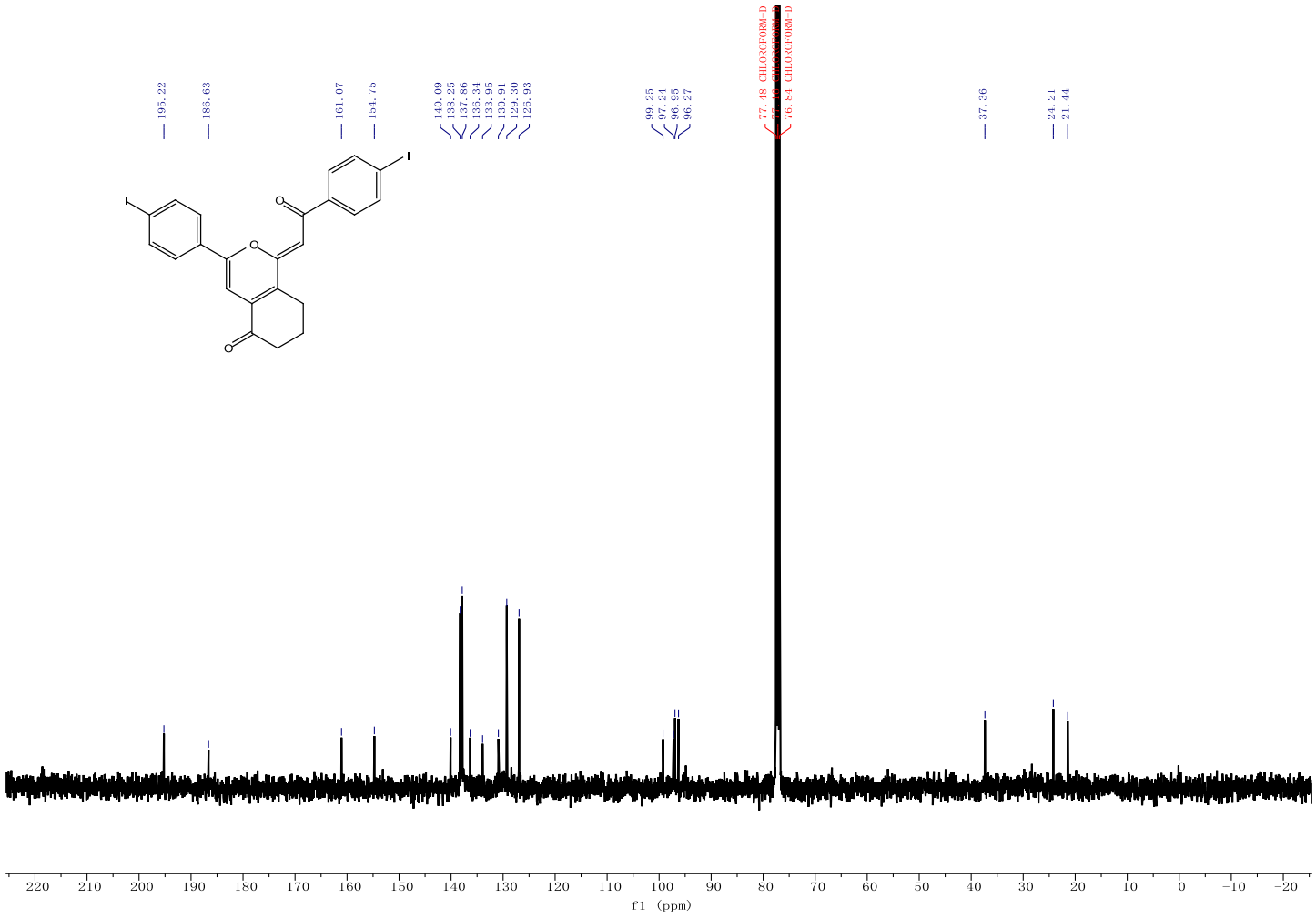
^{13}C NMR (151 MHz, $CDCl_3$) of **6r**



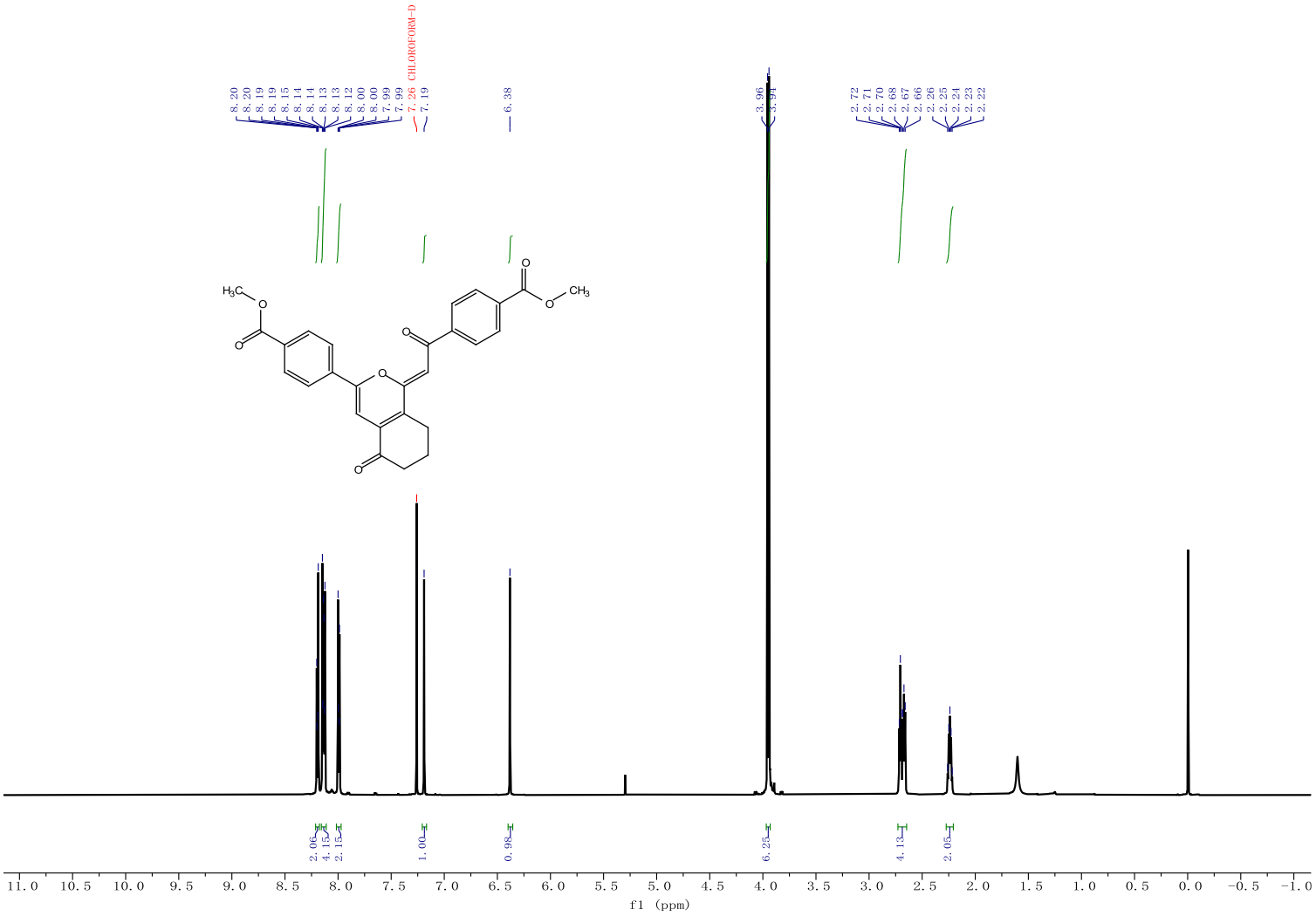
^{1}H NMR (600 MHz, $CDCl_3$) of **6s**



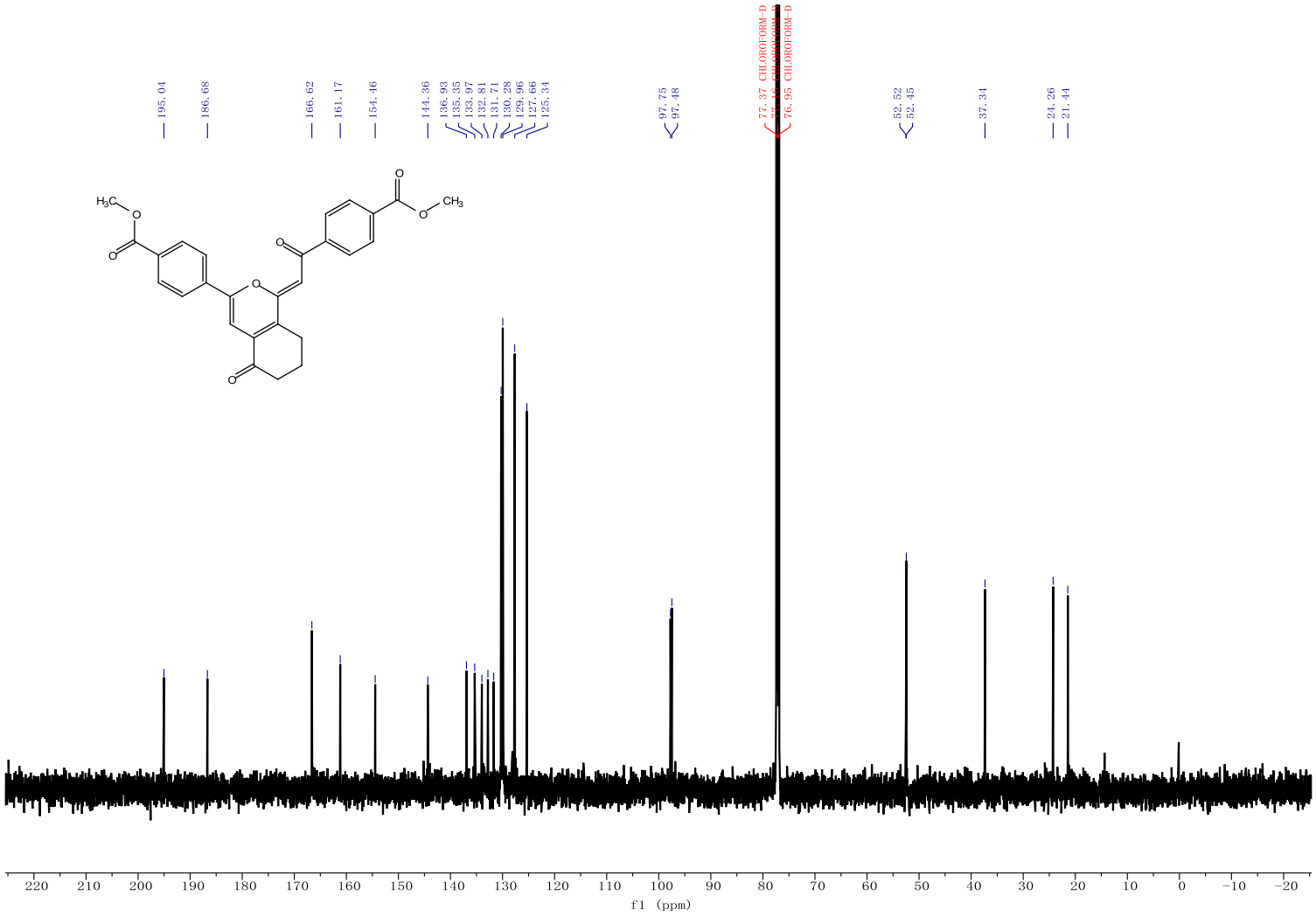
^{13}C NMR (101 MHz, $CDCl_3$) of **6s**



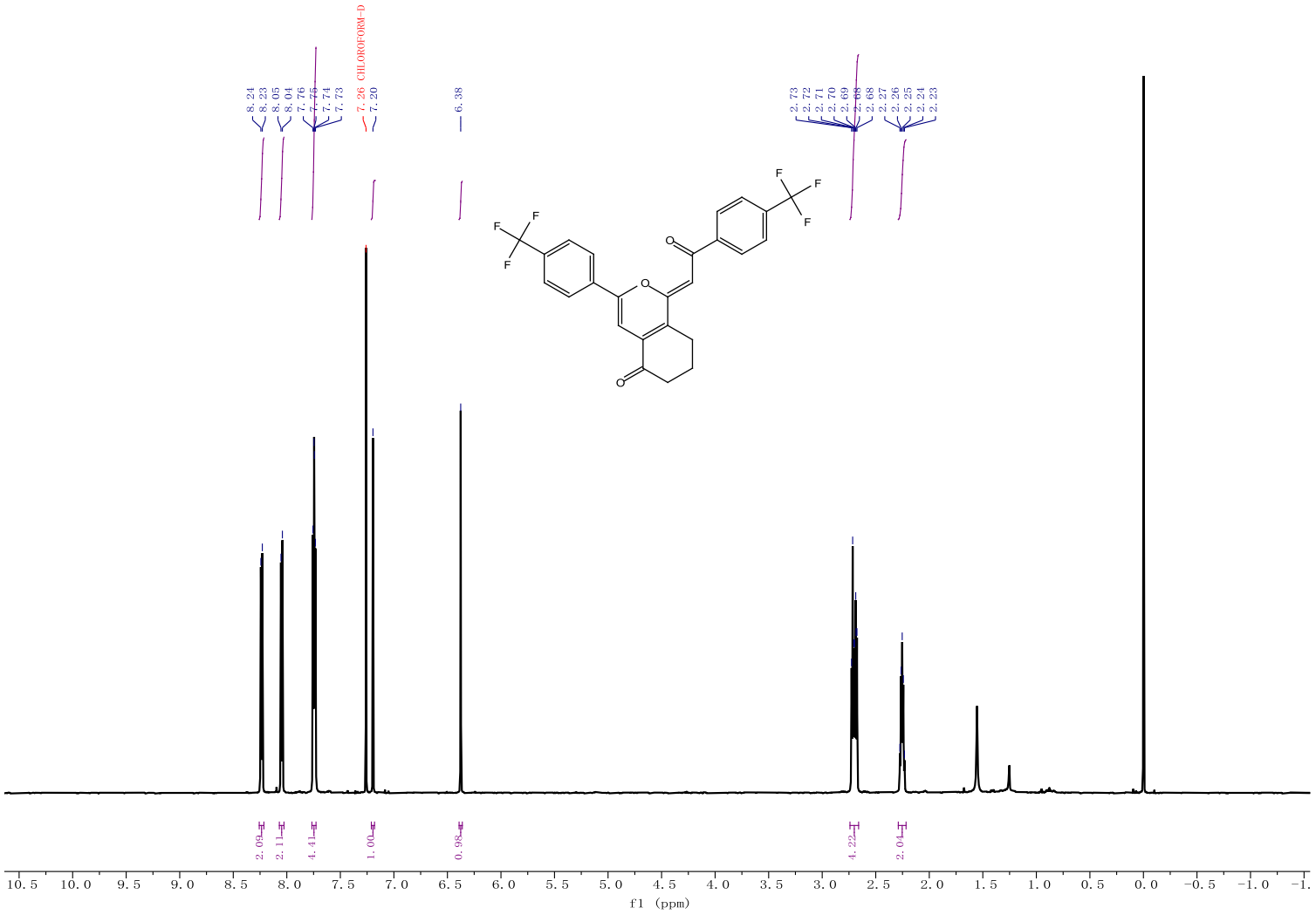
^{1}H NMR (600 MHz, $CDCl_3$) of **6t**



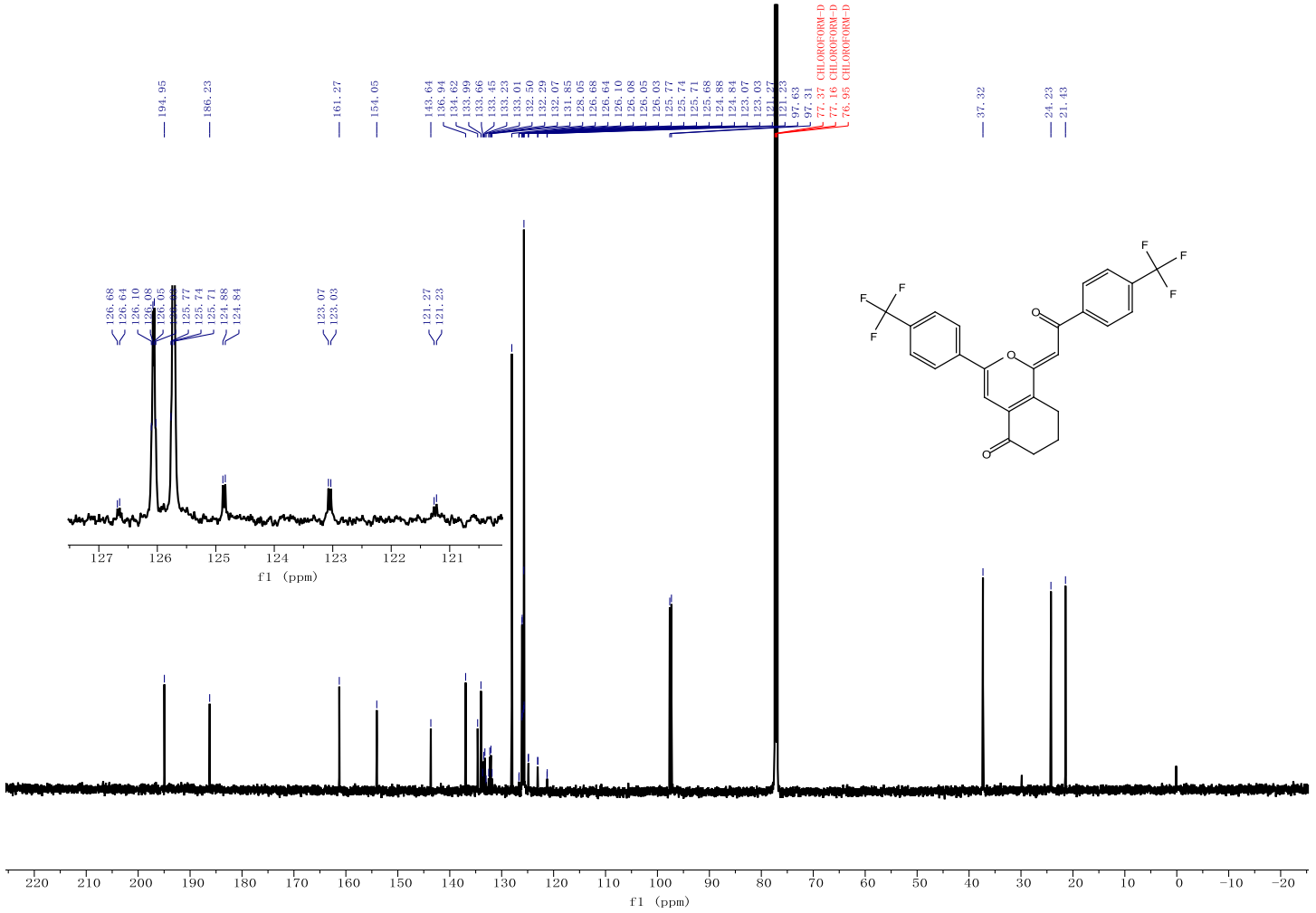
^{13}C NMR (151 MHz, $CDCl_3$) of **6t**



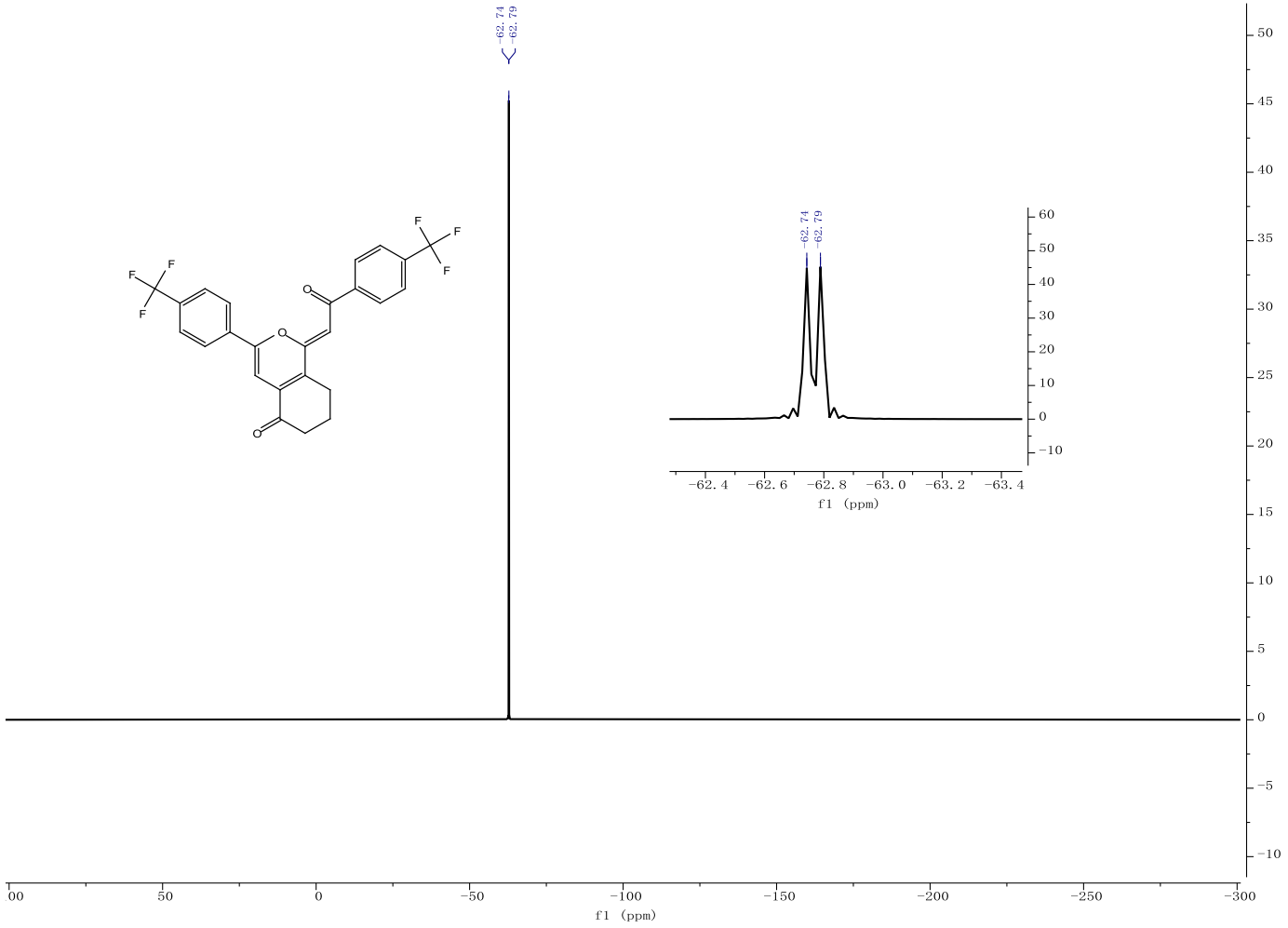
^{1}H NMR (600 MHz, $CDCl_3$) of **6u**



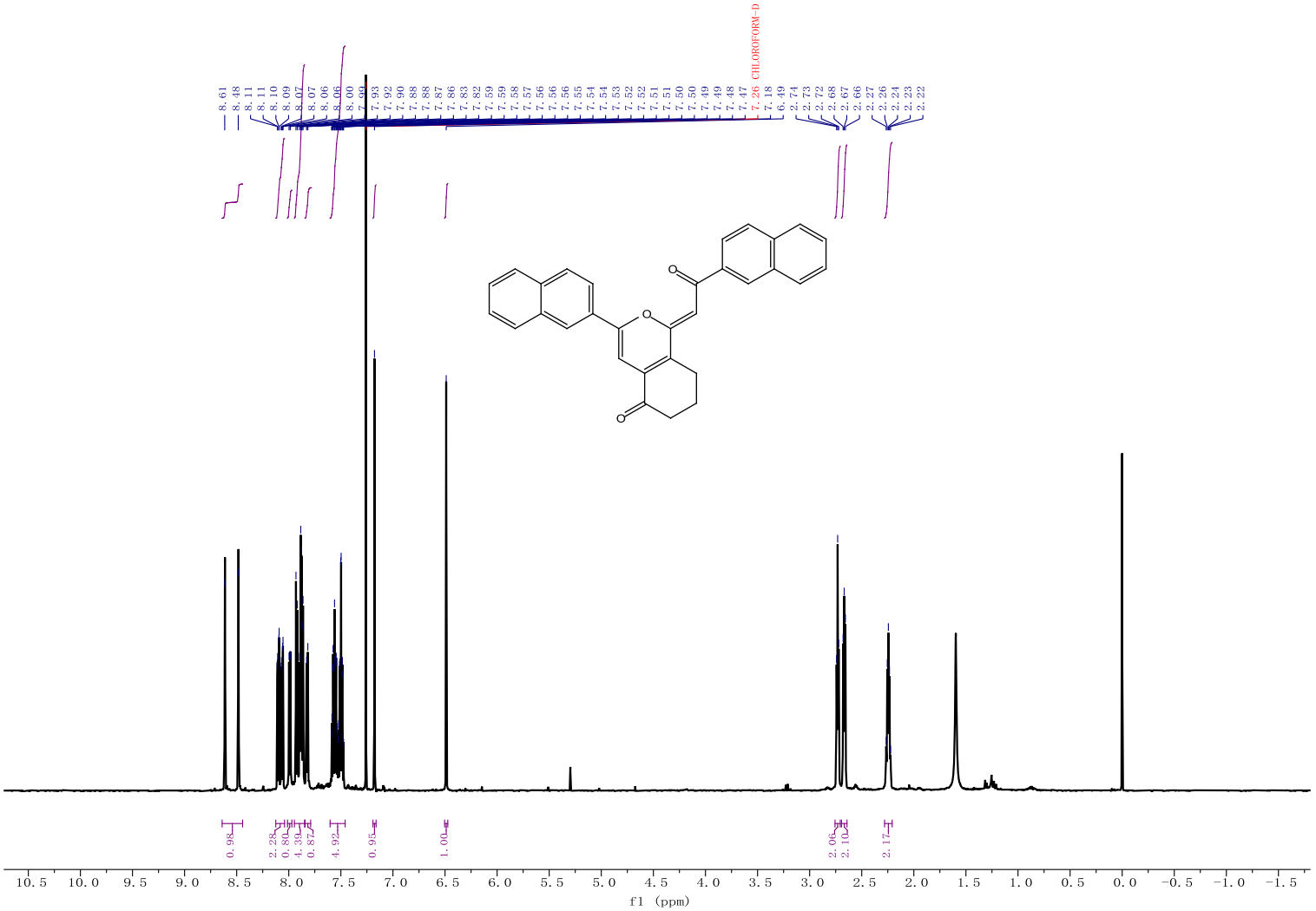
^{13}C NMR (151 MHz, $CDCl_3$) of **6u**



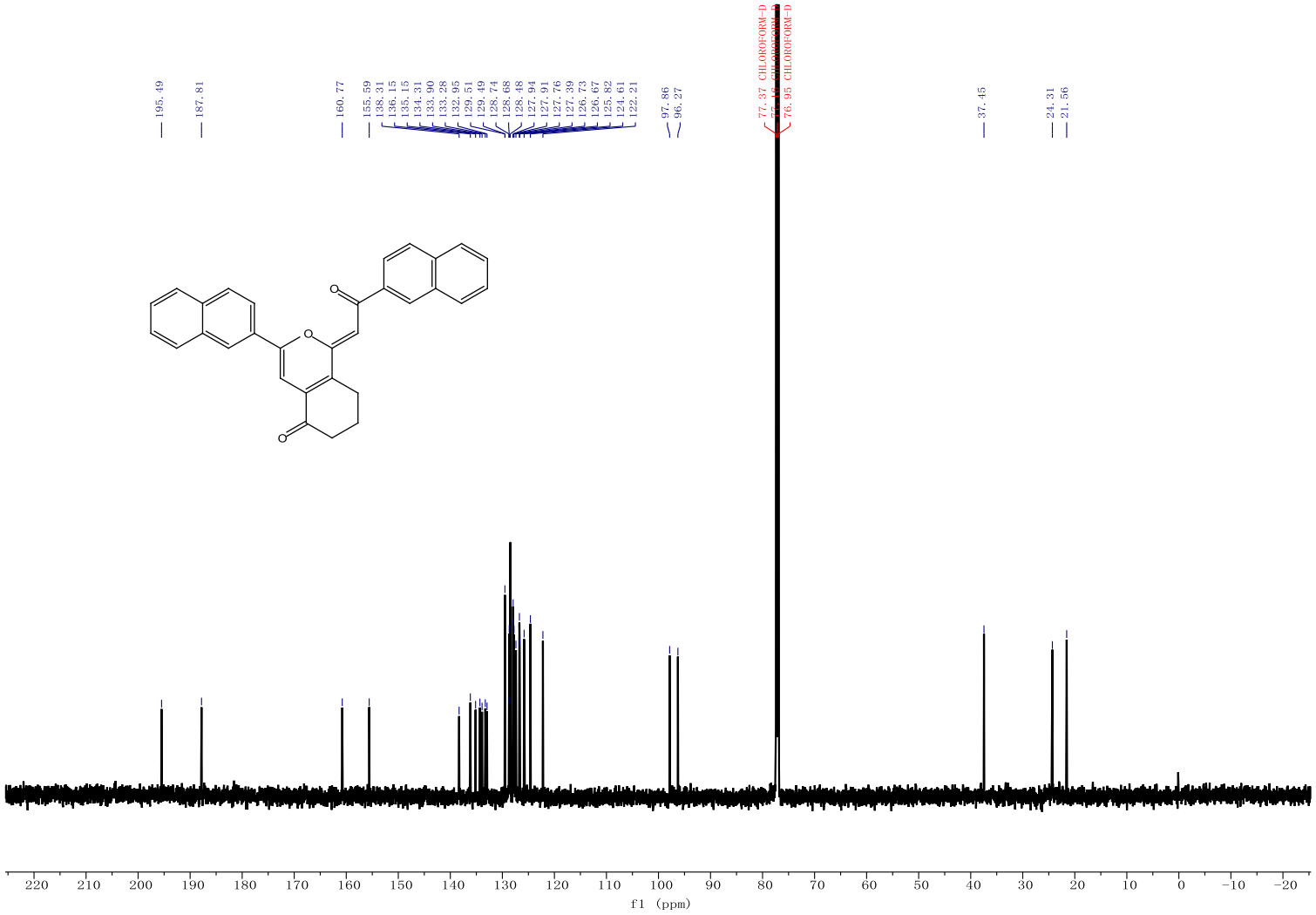
^{19}F NMR (565 MHz, $CDCl_3$) of **6u**



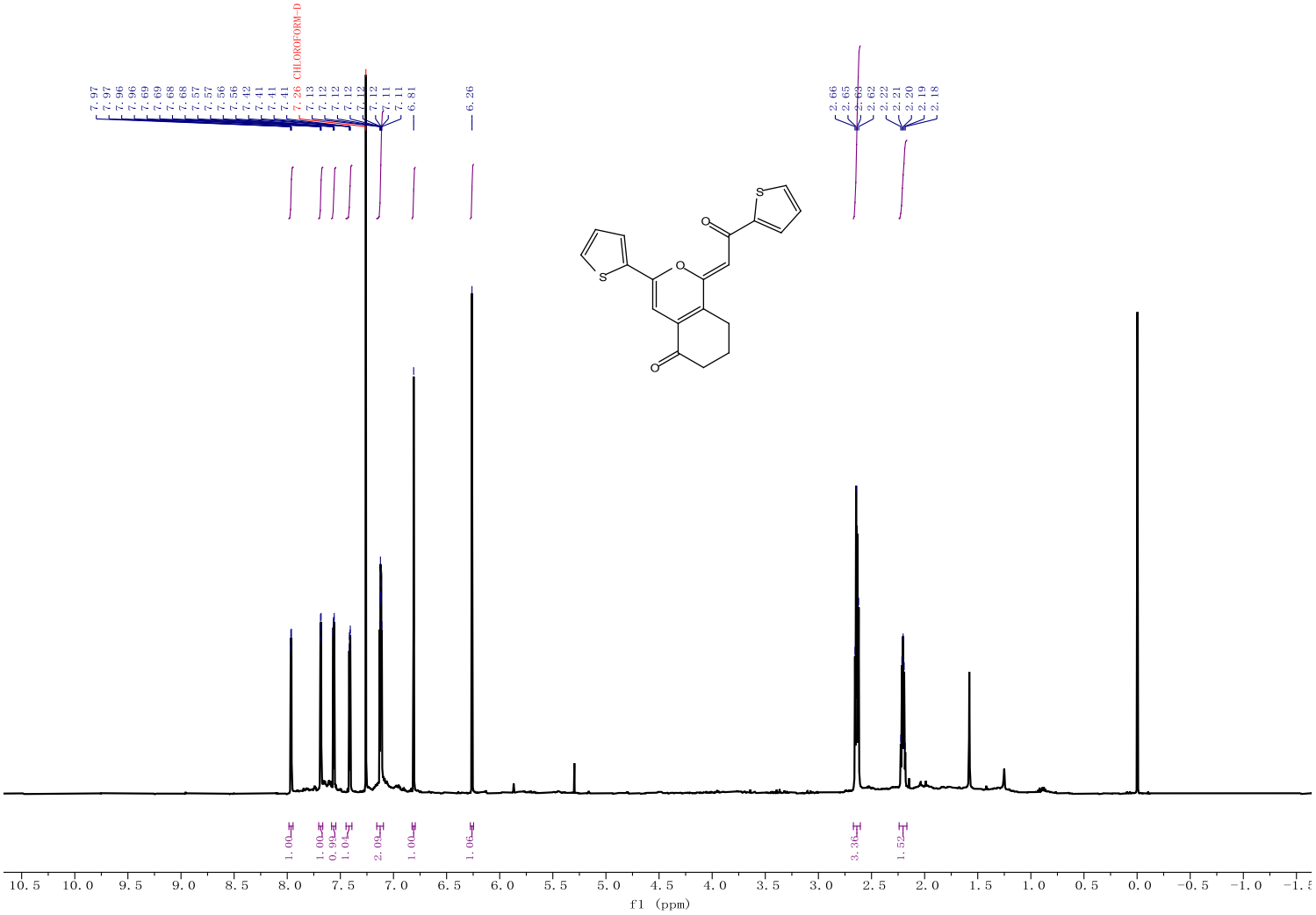
^{1}H NMR (600 MHz, $CDCl_3$) of **6v**



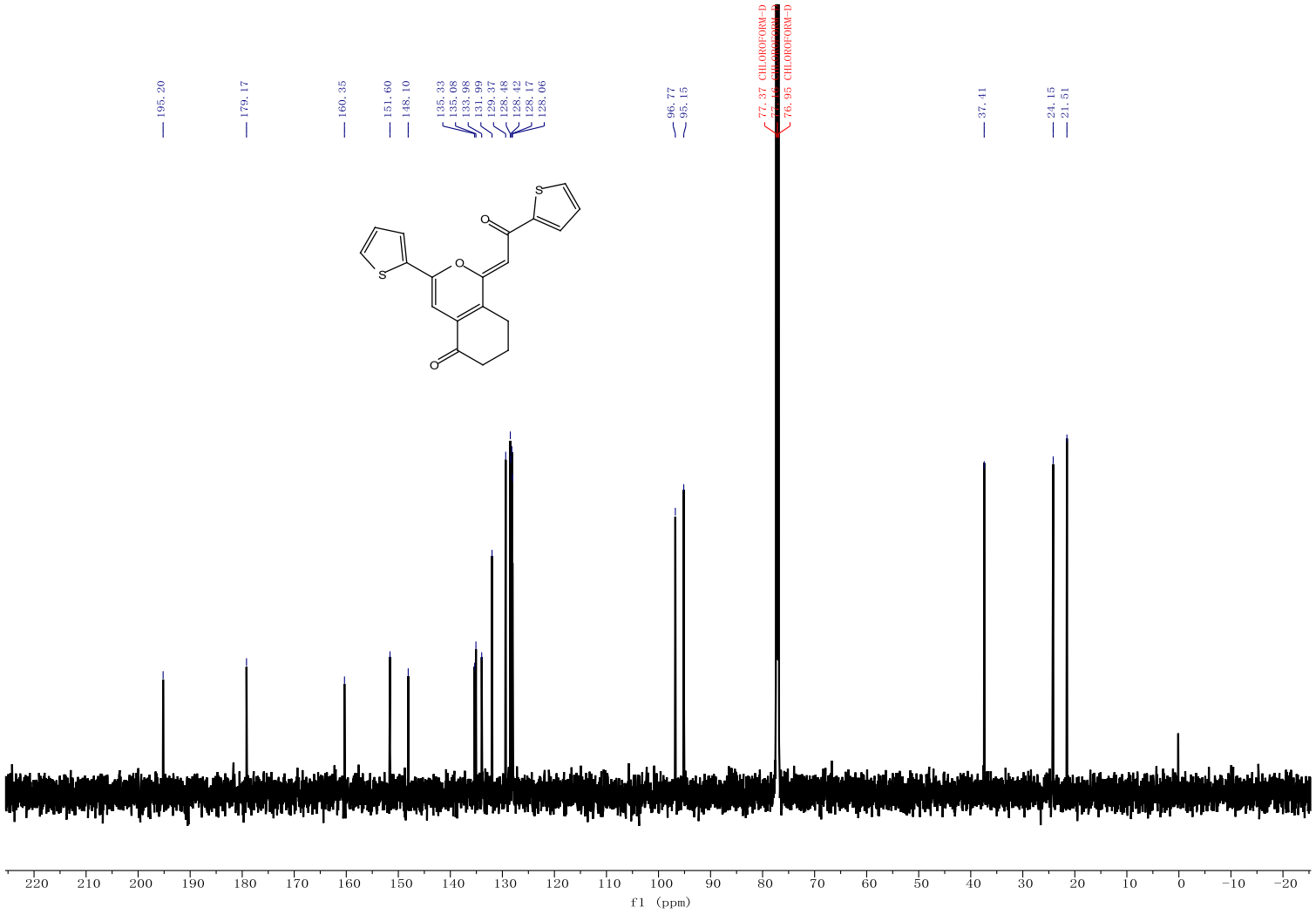
^{13}C NMR (151 MHz, $CDCl_3$) of **6v**



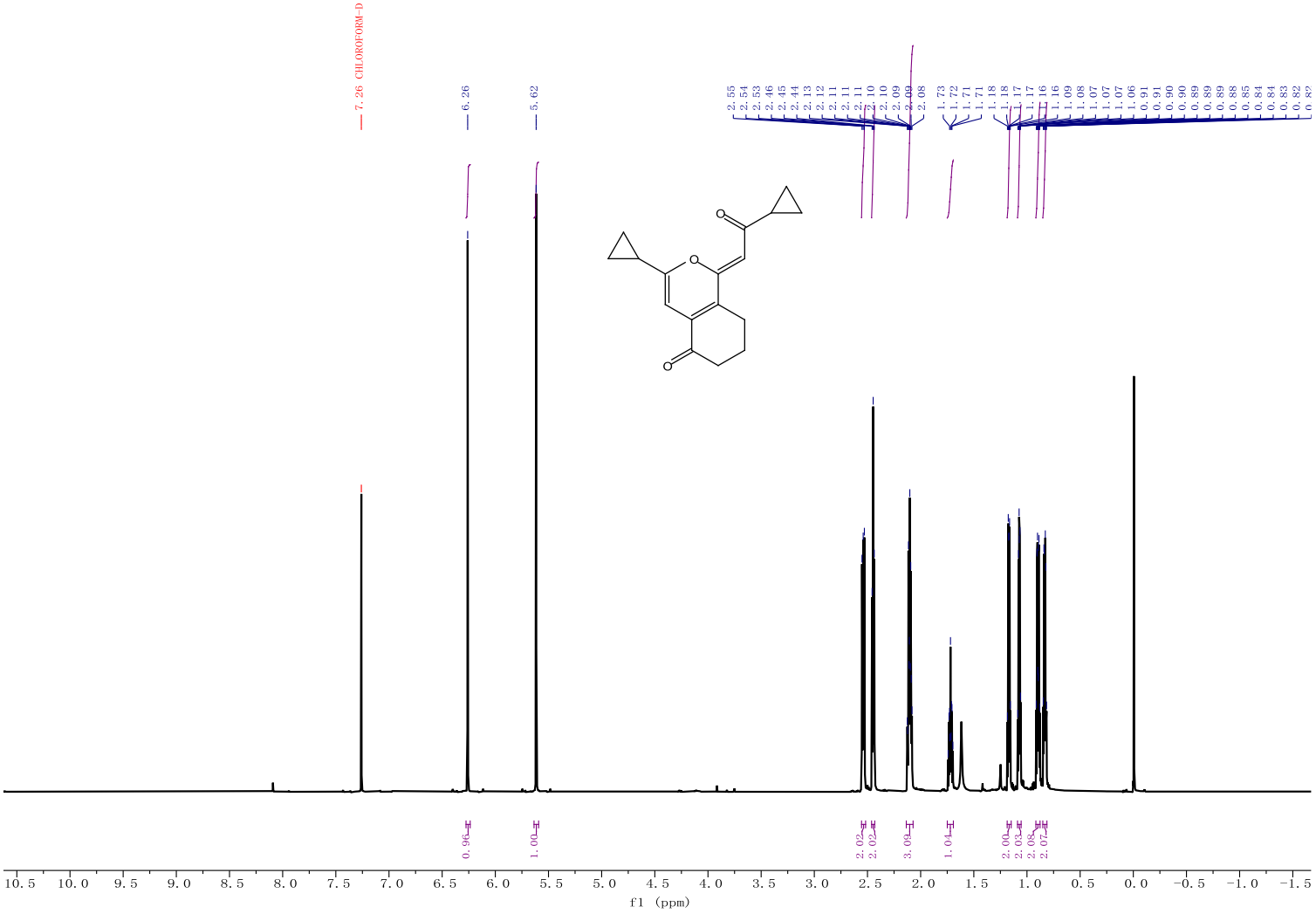
^{1}H NMR (600 MHz, $CDCl_3$) of **6w**



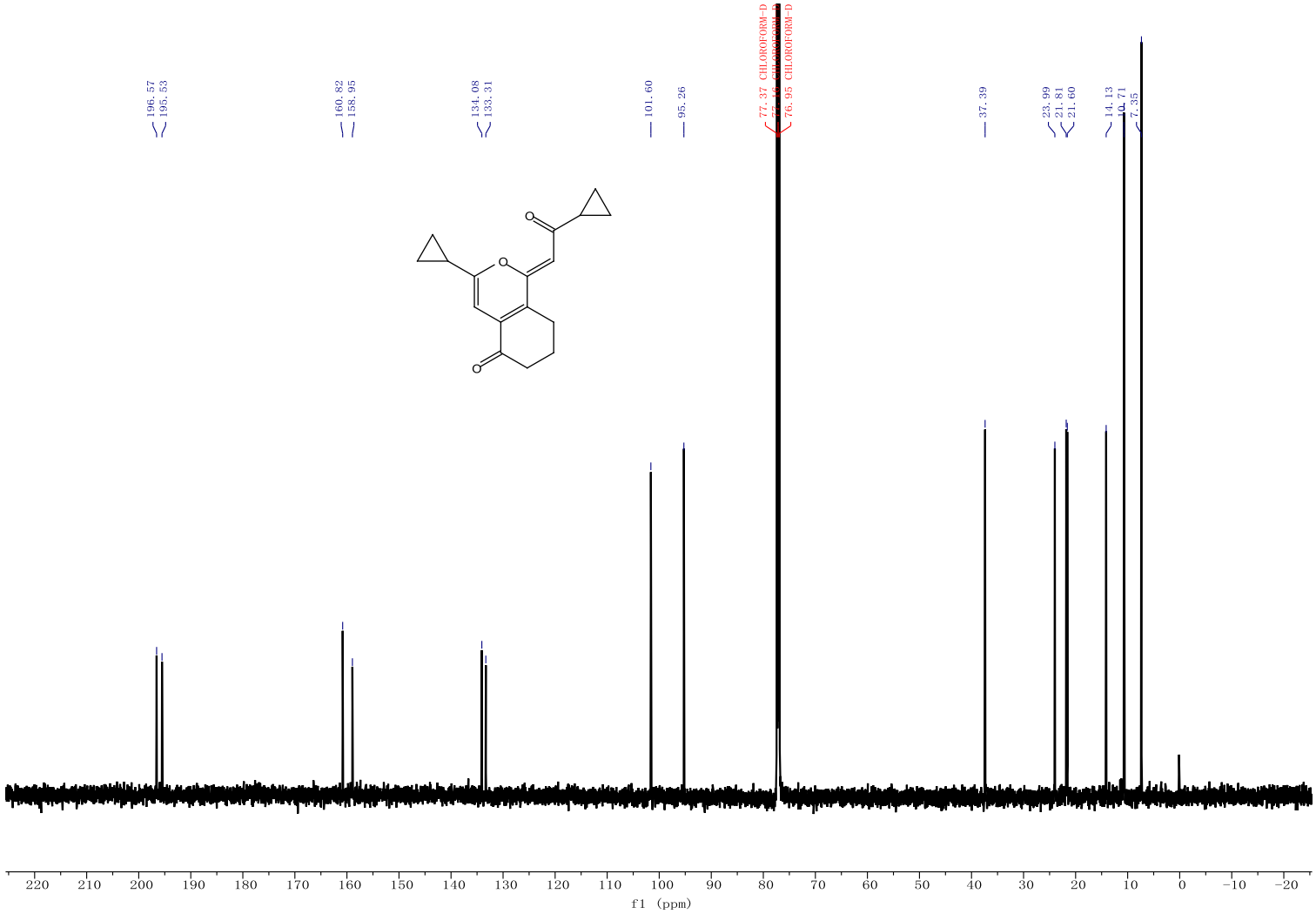
^{13}C NMR (151 MHz, $CDCl_3$) of **6w**



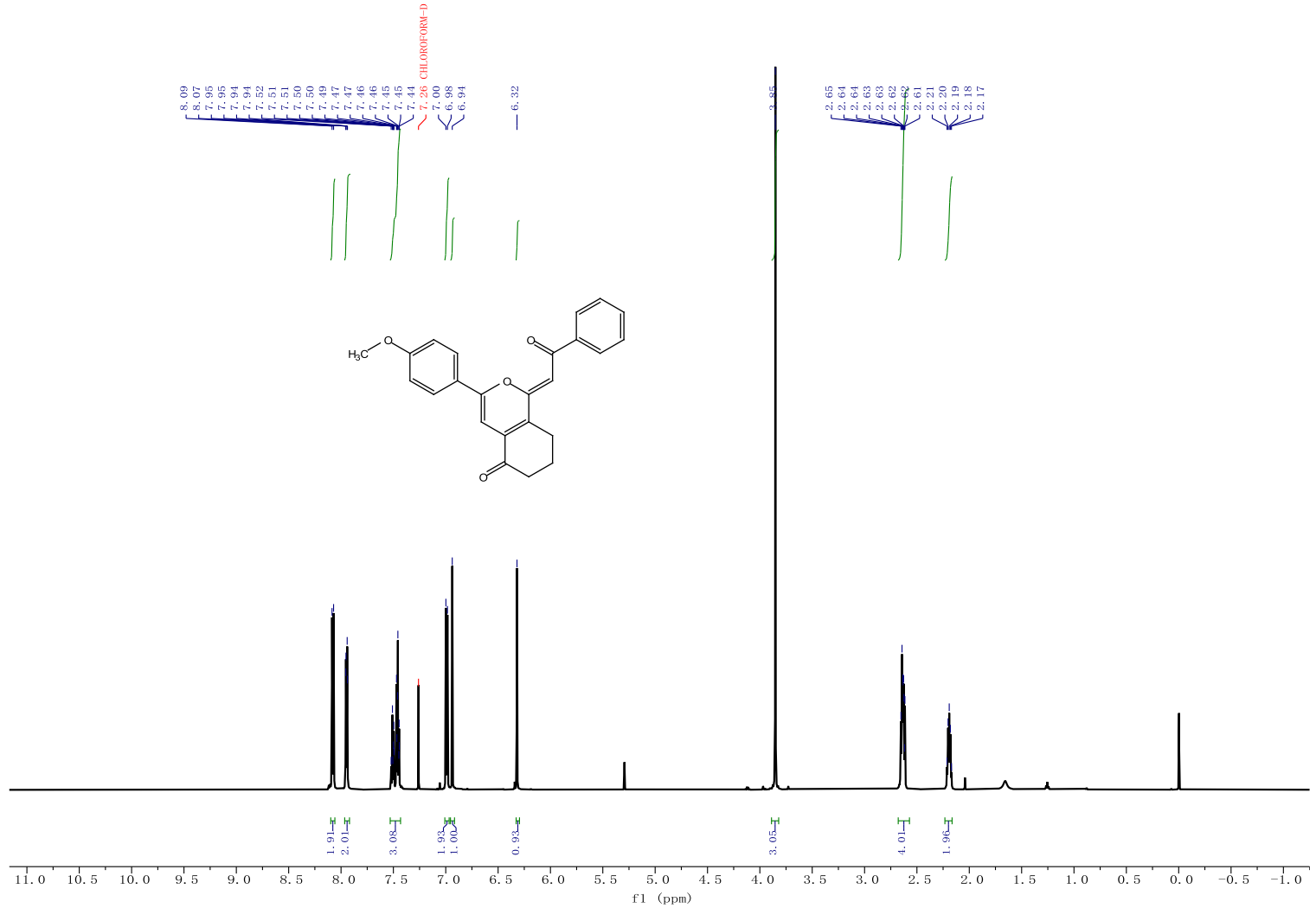
^{1}H NMR (600 MHz, $CDCl_3$) of **6x**



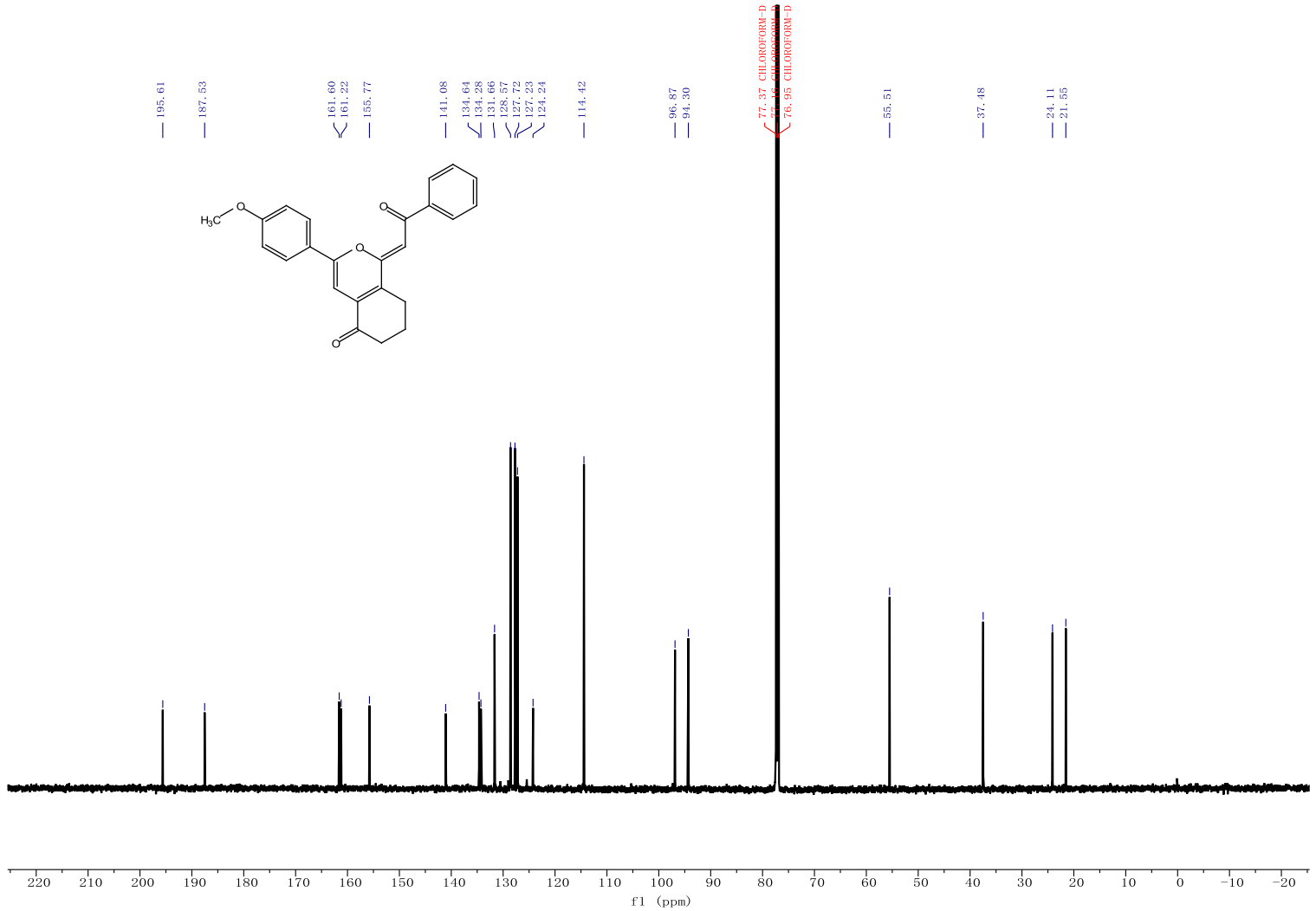
^{13}C NMR (151 MHz, $CDCl_3$) of **6x**



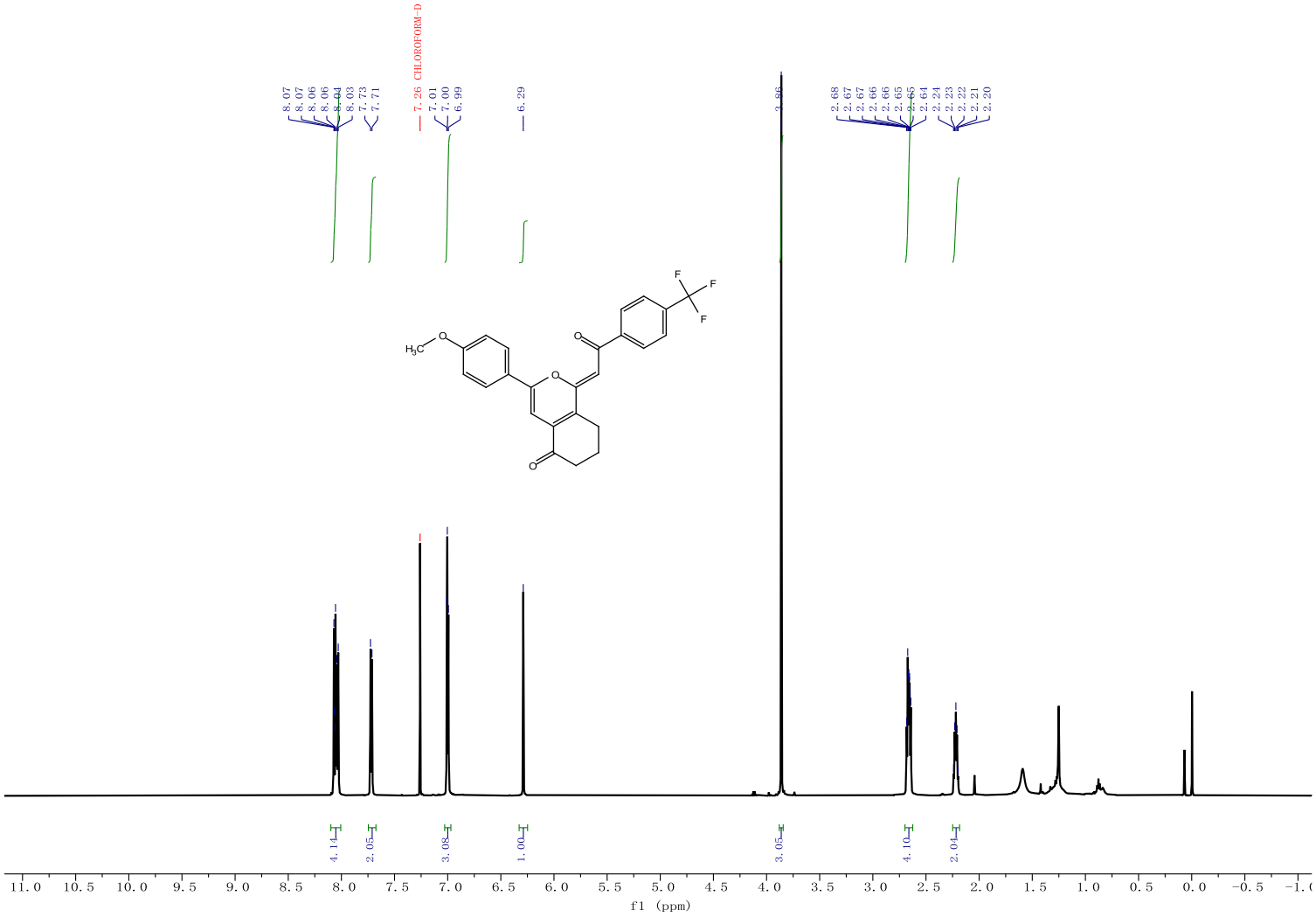
^{1}H NMR (600 MHz, $CDCl_3$) of **6ad**



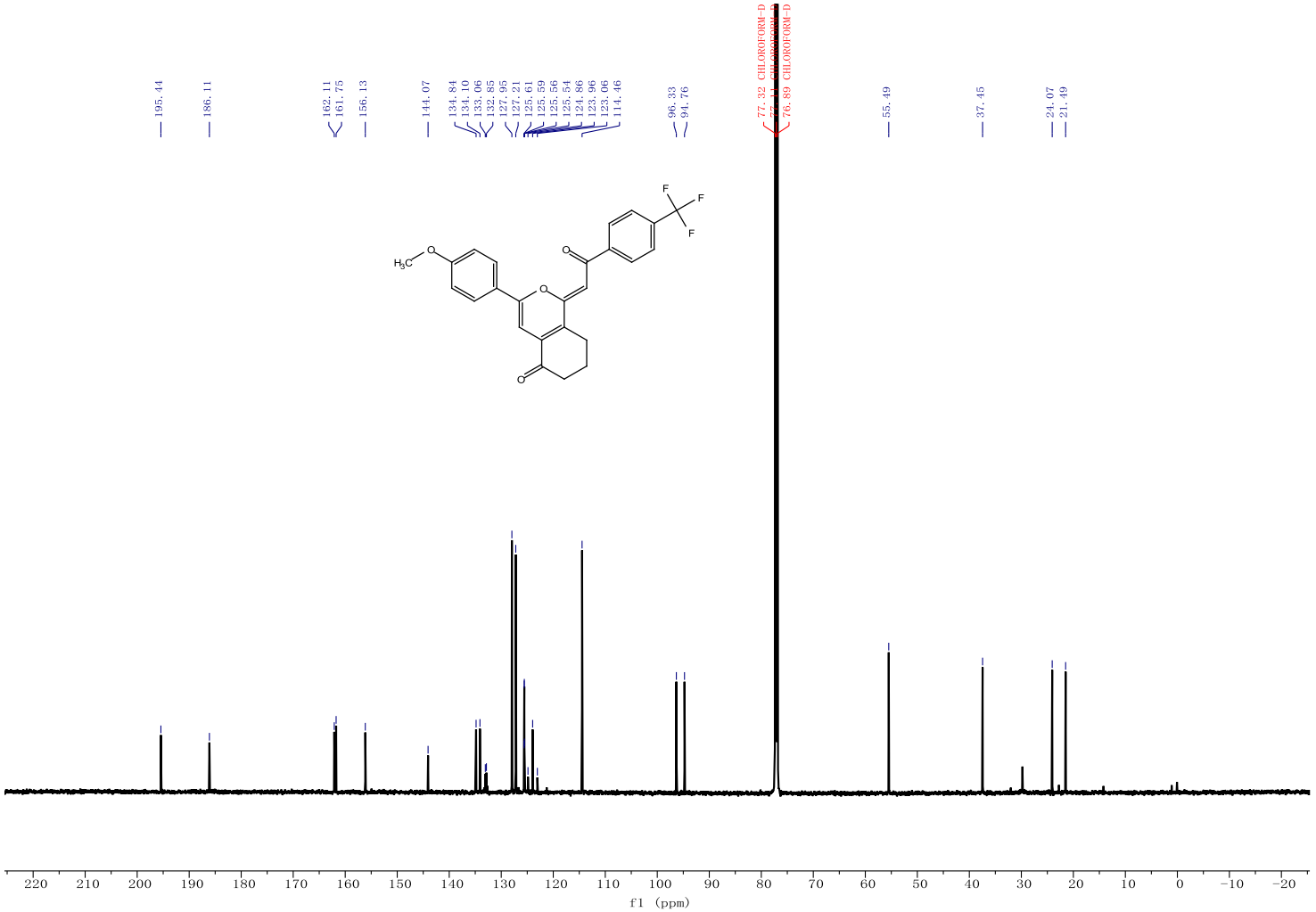
^{13}C NMR (151 MHz, $CDCl_3$) of **6ad**



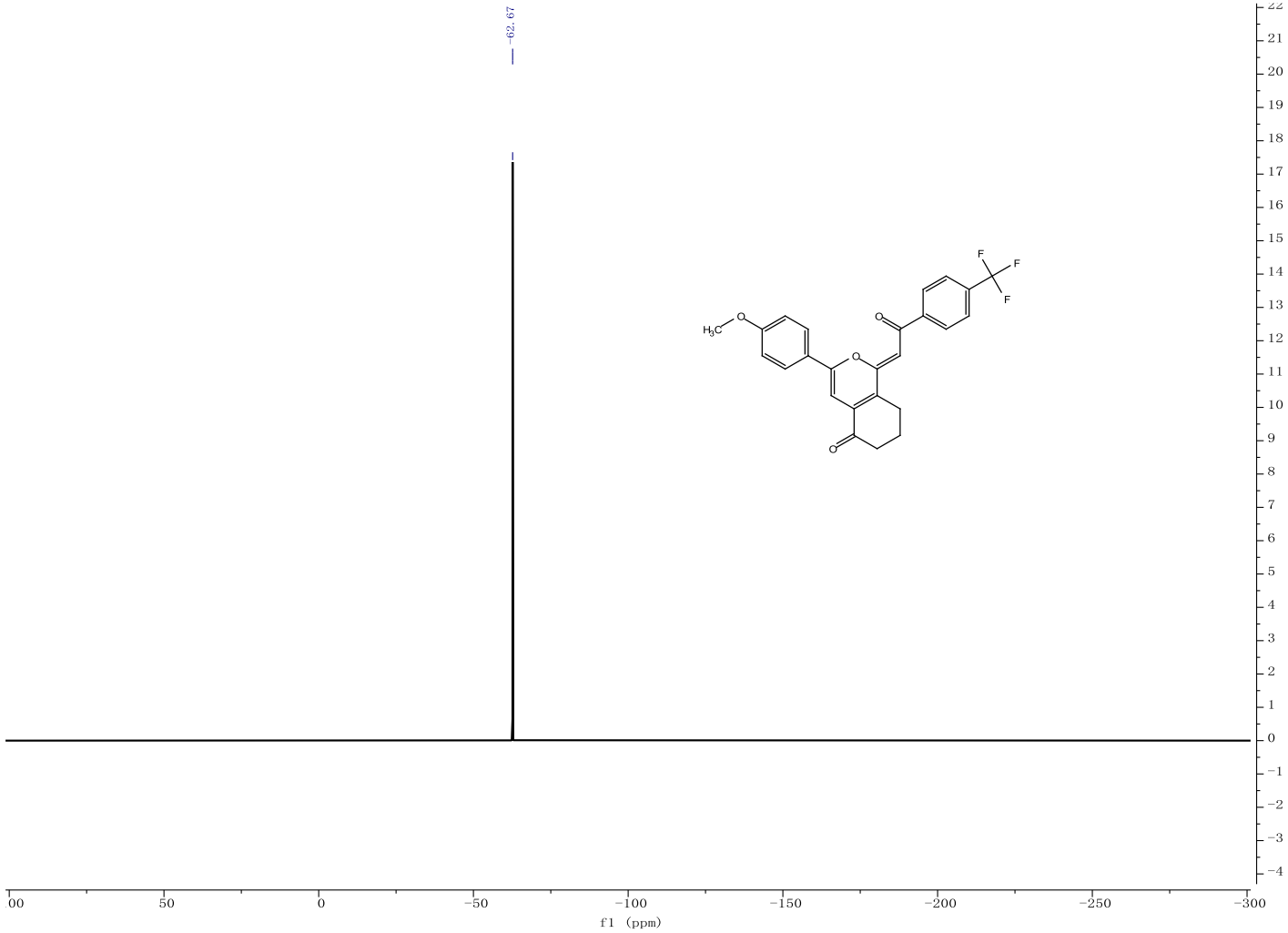
^{1}H NMR (600 MHz, $CDCl_3$) of **6du**



^{13}C NMR (151 MHz, $CDCl_3$) of **6du**



^{19}F NMR (565 MHz, $CDCl_3$) of **6du**



6. References

1. N. A. Petasis and K. A. Teets, *J. Am. Chem. Soc.*, 1992, **114**, 10328-10334.
2. J. Teske and B. Plietker, *Org. Lett.*, 2018, **20**, 2257-2260.