Supporting Information

Ruthenium(II) CNN Pincer Complexes as Efficient Catalysts in Oxidative Annulation of Aromatic Acids with Alkynes to isocoumarins

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*†Electronic supplementary information (ESI) available: ^{1}H, ^{13}C, ^{31}P NMR and ESI-MS spectra of ligands and complexes (**1–4**), general experimental procedures and characterization data for the isocoumarin products.* CCDC 2215424, 2215425, and 2215427. *For ESI and crystallographic data in CIF or other electronic format see DOI:10.1039/*

Table of Contents **Page No**

1.	MS (ESI) spectra of the ligands and complexes (1-4) in $CDCl_3$	3 – 8
2.	NMR spectra of the ligands and complexes (1-4) in $CDCl_3$	9 – 22
3.	Catalysis – General Information	23
4.	General experimental procedure of synthesized isocoumarins	23
5.	Characterization data of the synthesized isocoumarins	23 – 27
6.	NMR spectra of the synthesized isocoumarins	28 – 66
7.	References	67

1. **MS (ESI) spectra of the ligands and complexes (1-4) in $CDCl_3$**

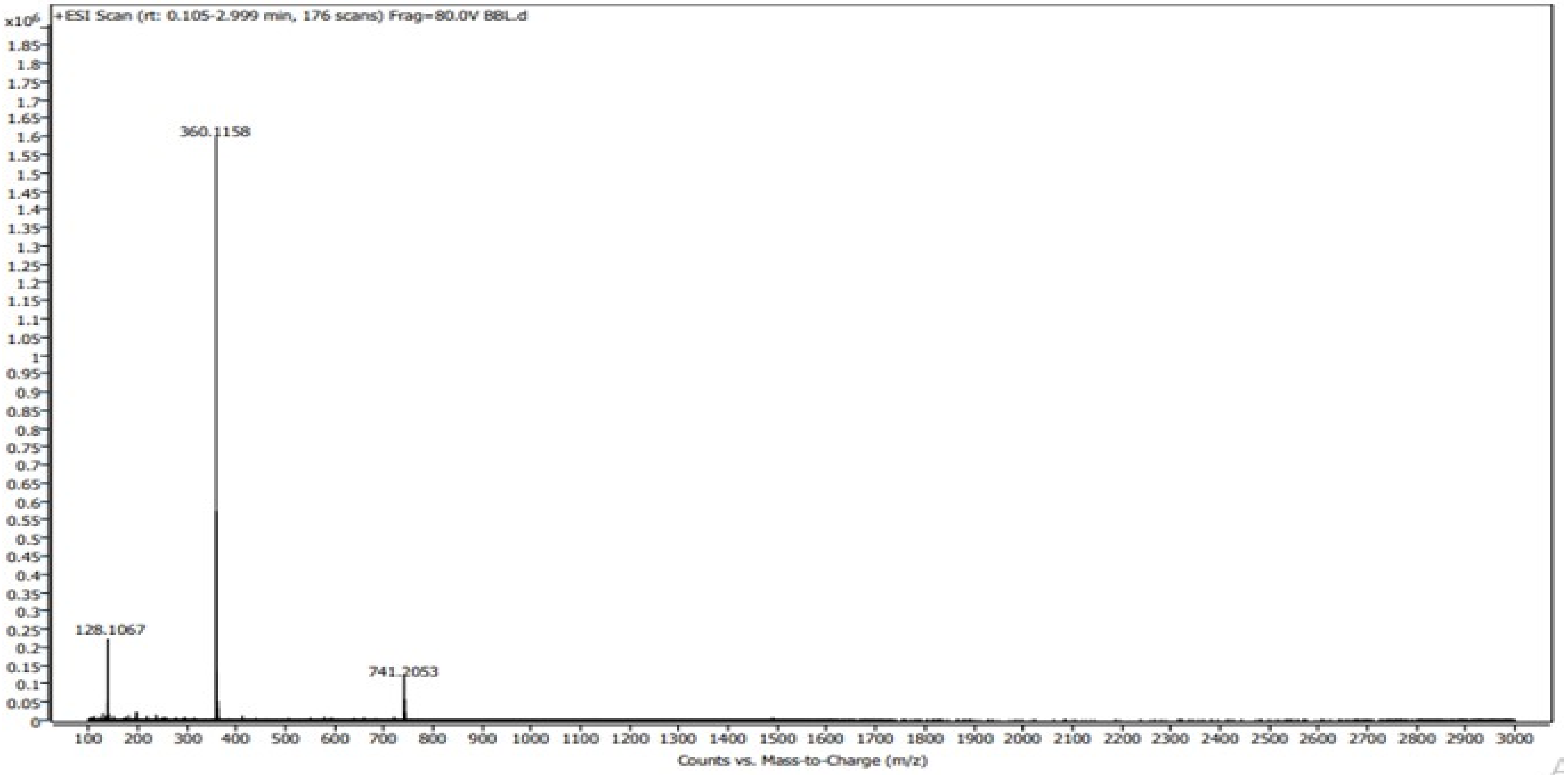


Figure S1: ESI-Ms spectrum for ligand **BZBT**

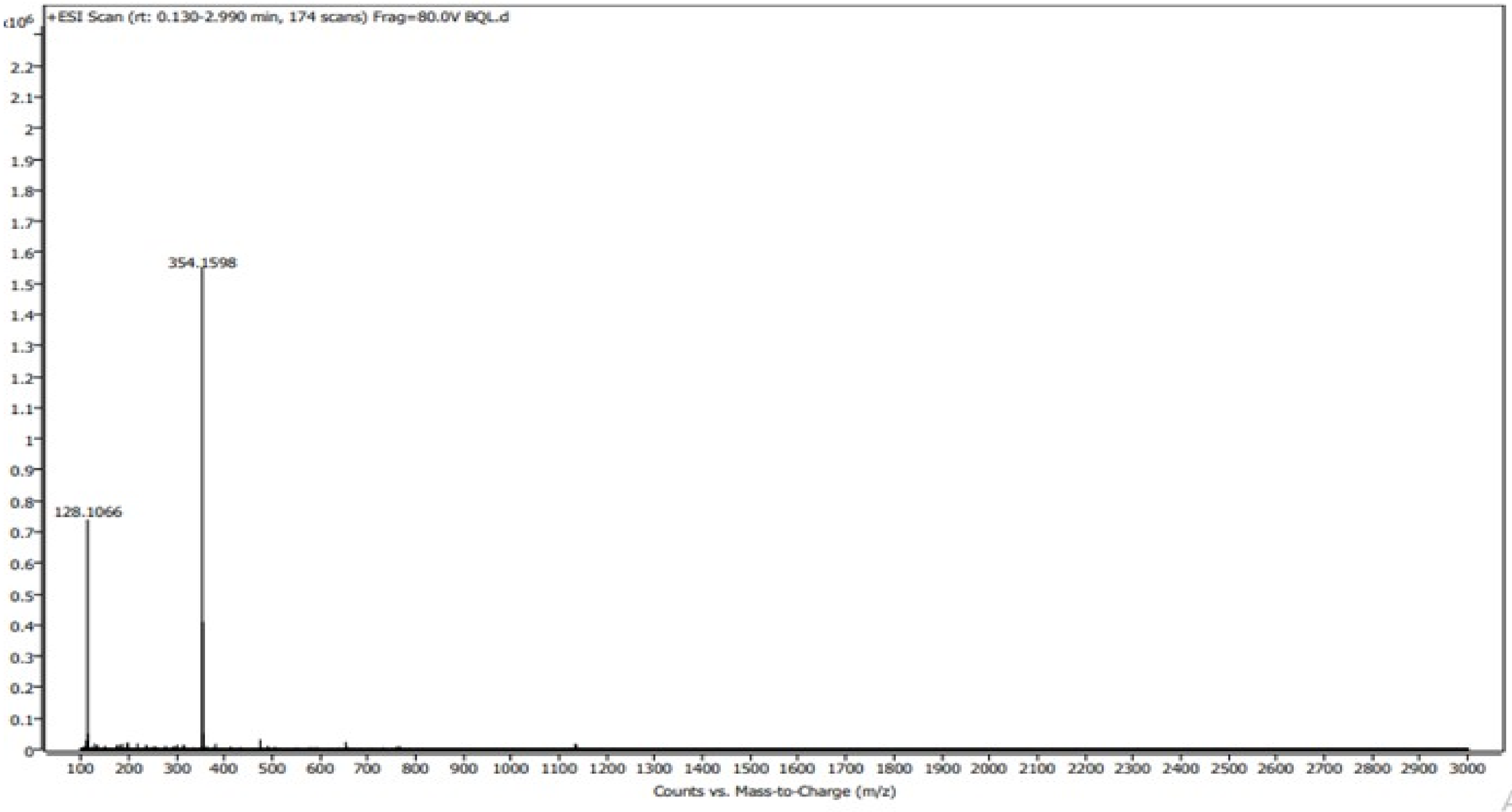


Figure S2: ESI-Ms spectrum for ligand **BZQH**

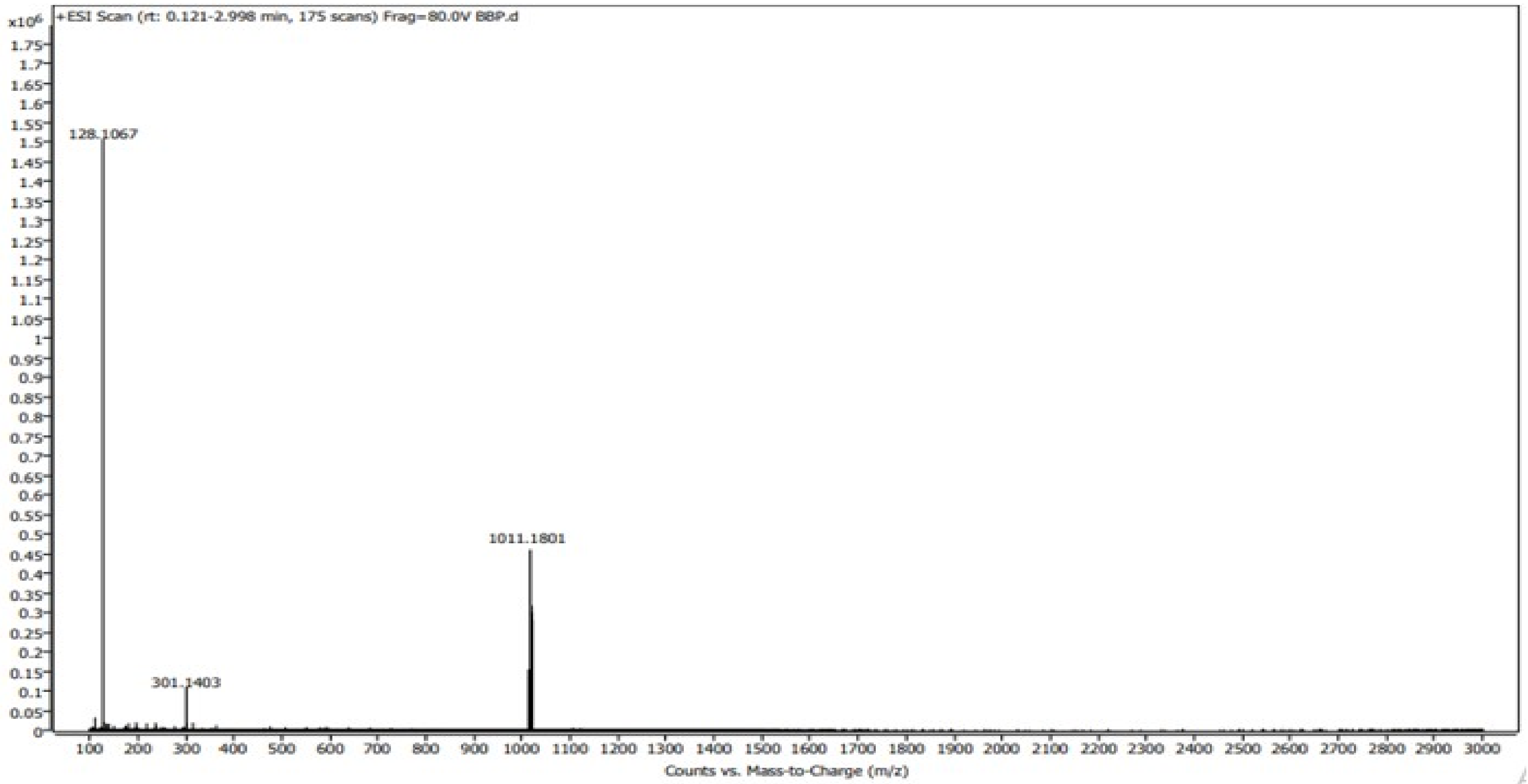


Figure S3: ESI-Ms spectrum for complex **[Ru(CO)(PPh$_3$)$_2$(BZBT)]**

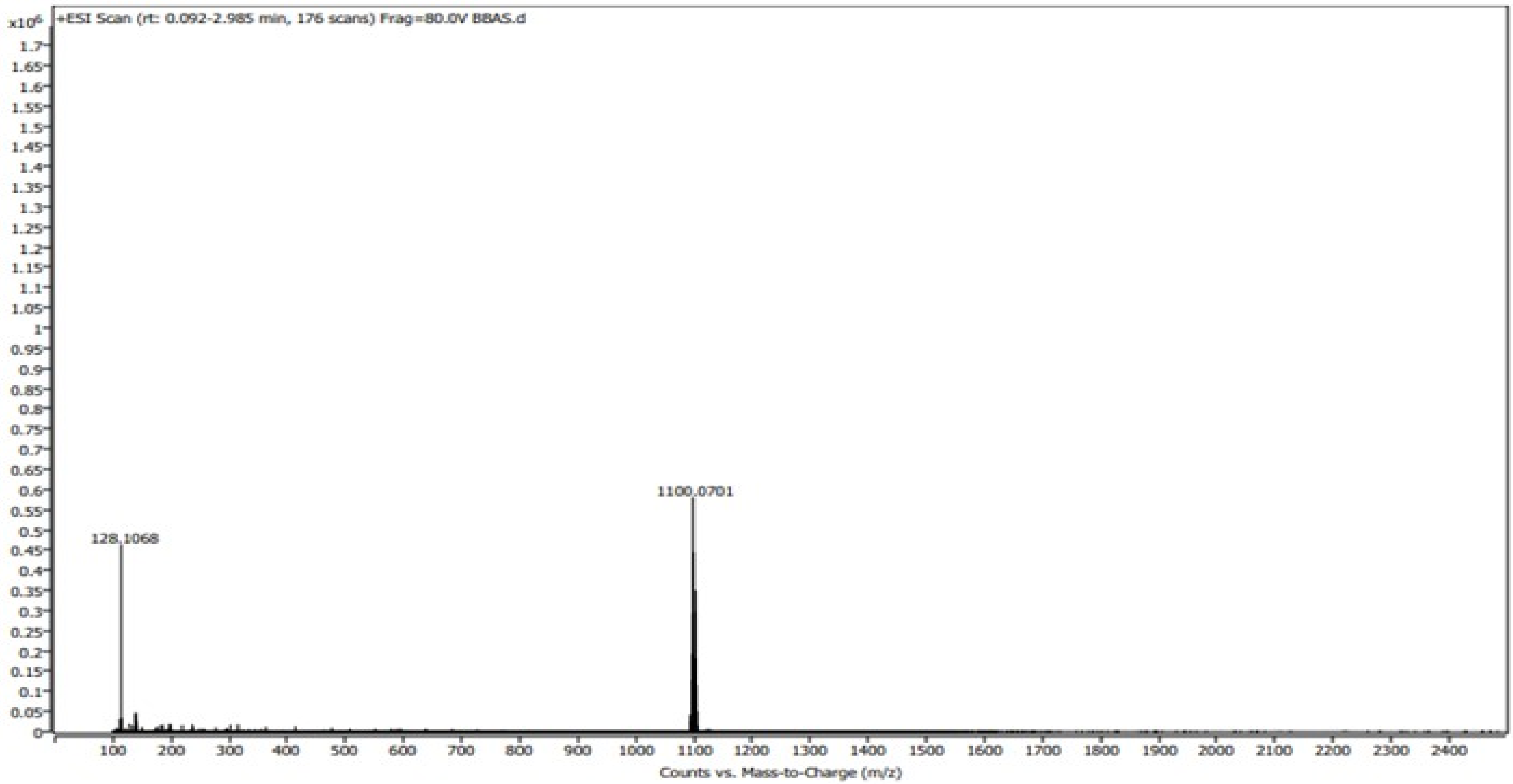


Figure S4: ESI-Ms spectrum for complex [**Ru(CO)(AsPh$_3$)$_2$(BZBT)**]

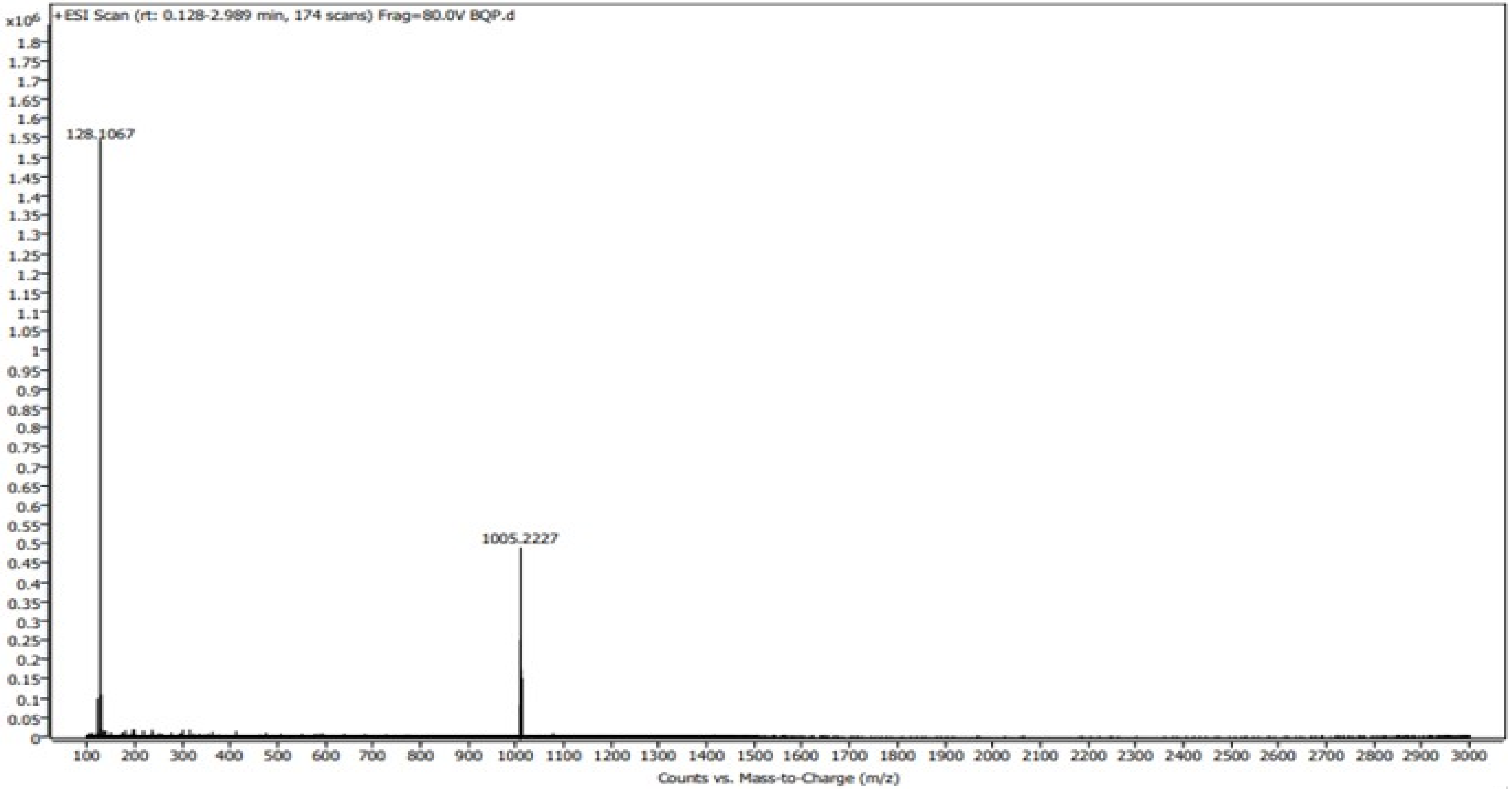


Figure S5: ESI-Ms spectrum for complex **[Ru(CO)(PPh_3)$_2$(BZQH)]**

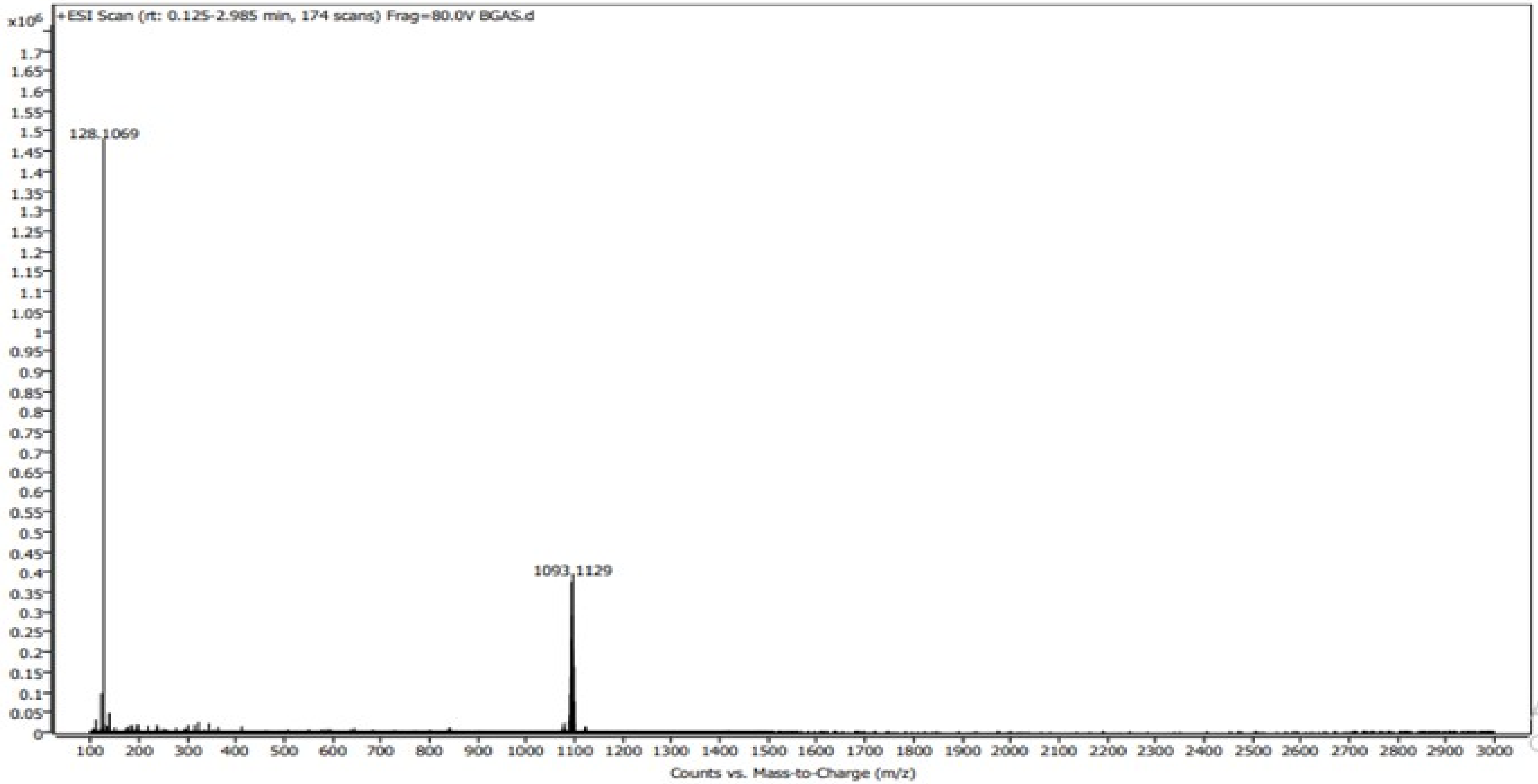


Figure S6: ESI-Ms spectrum for complex **[Ru(CO)($AsPh_3$)$_2$(BZQH)]**

2. NMR spectra of the ligands and complexes (1-4) in $CDCl_3$

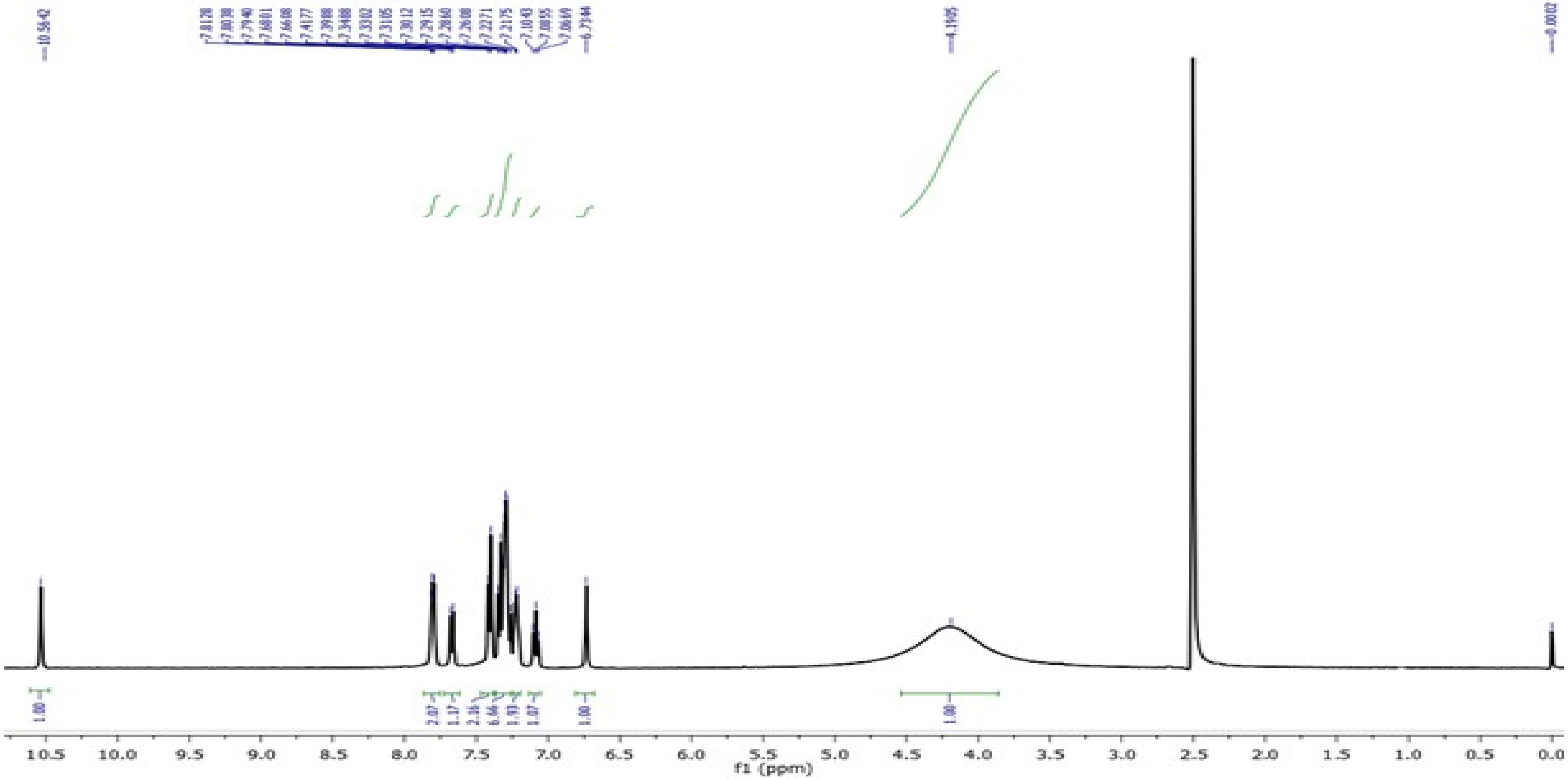


Figure S7: ^{1}H-NMR (400 MHz, DMSO-d_6) spectrum of **BZBT**

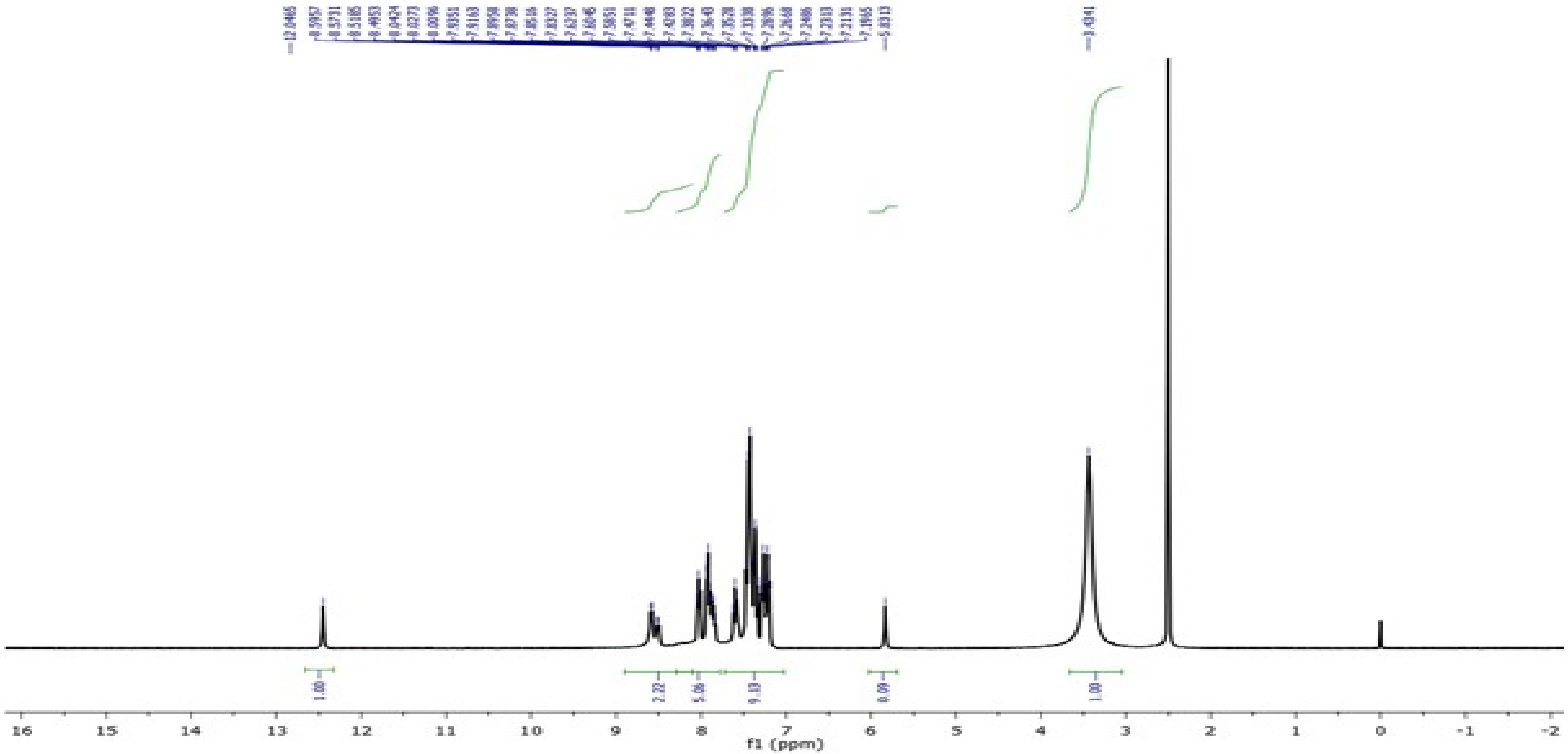


Figure S8: ^{1}H-NMR (400 MHz, DMSO-d_6) spectrum of BZQH

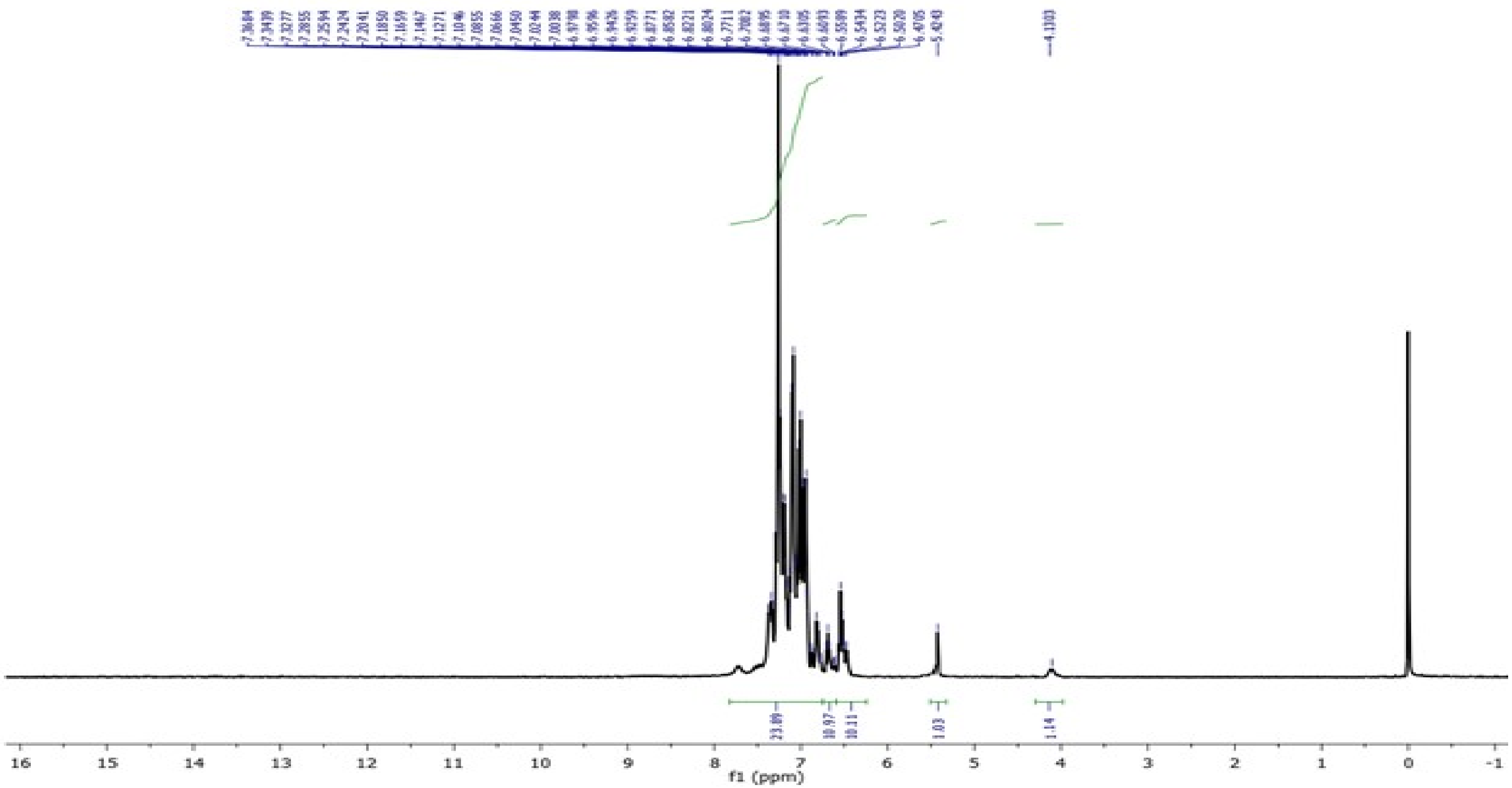


Figure S9: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **$[Ru(CO)(PPh_3)_2(BZBT)]$**

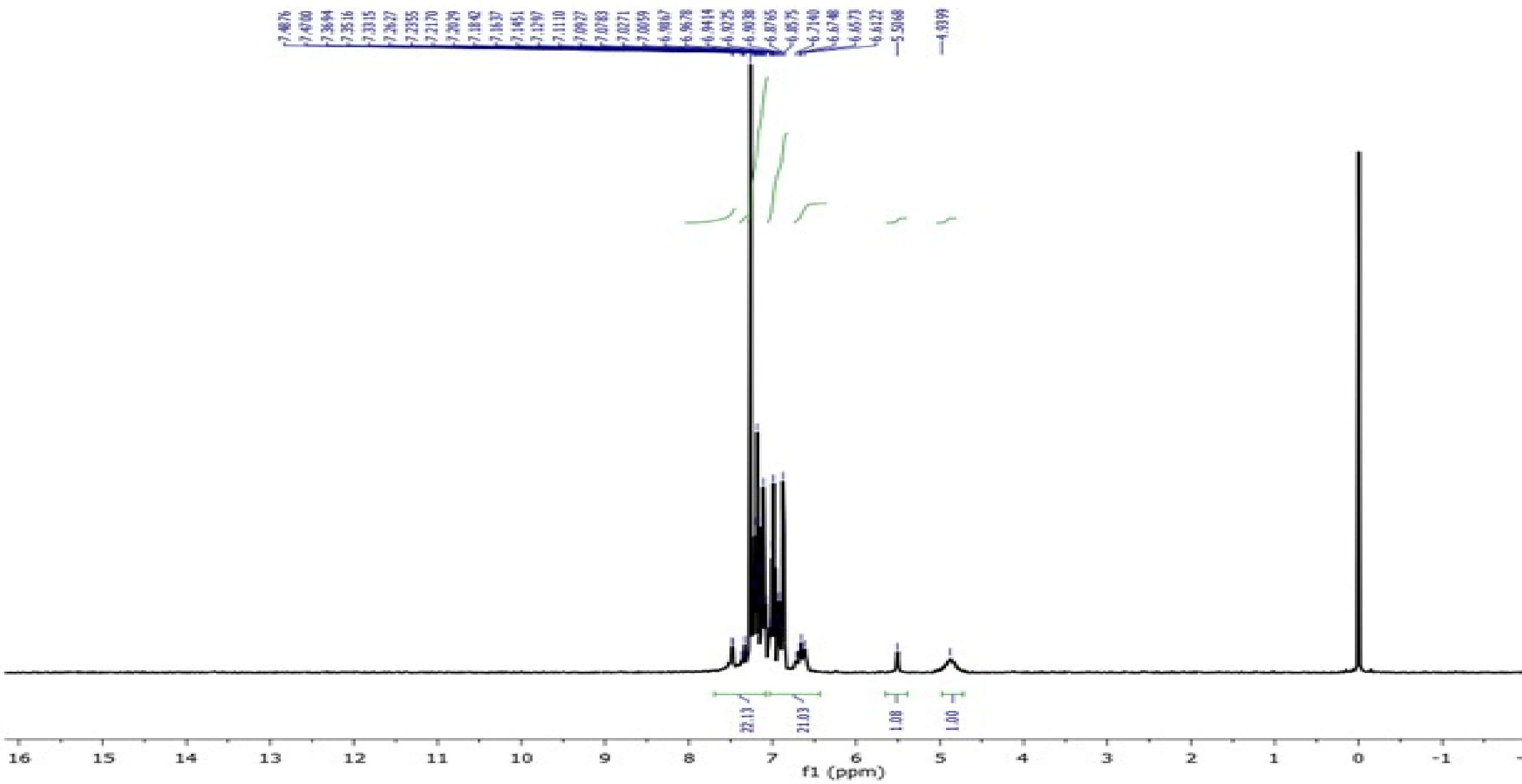


Figure S10: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **[Ru(CO)(AsPh$_3$)$_2$(BZBT)]**

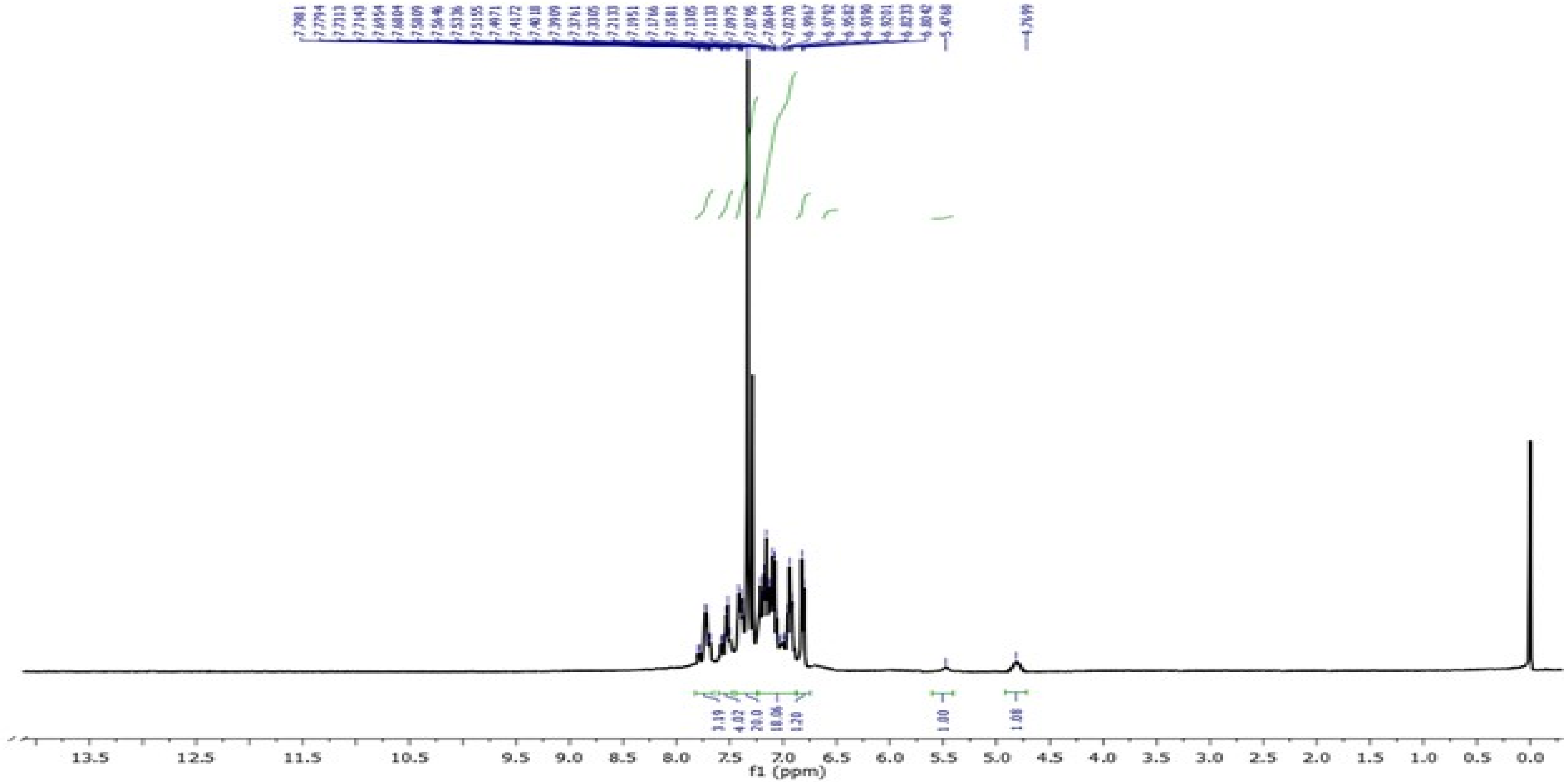


Figure S11: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **[Ru(CO)(PPh$_3$)$_2$(BZQH)]**

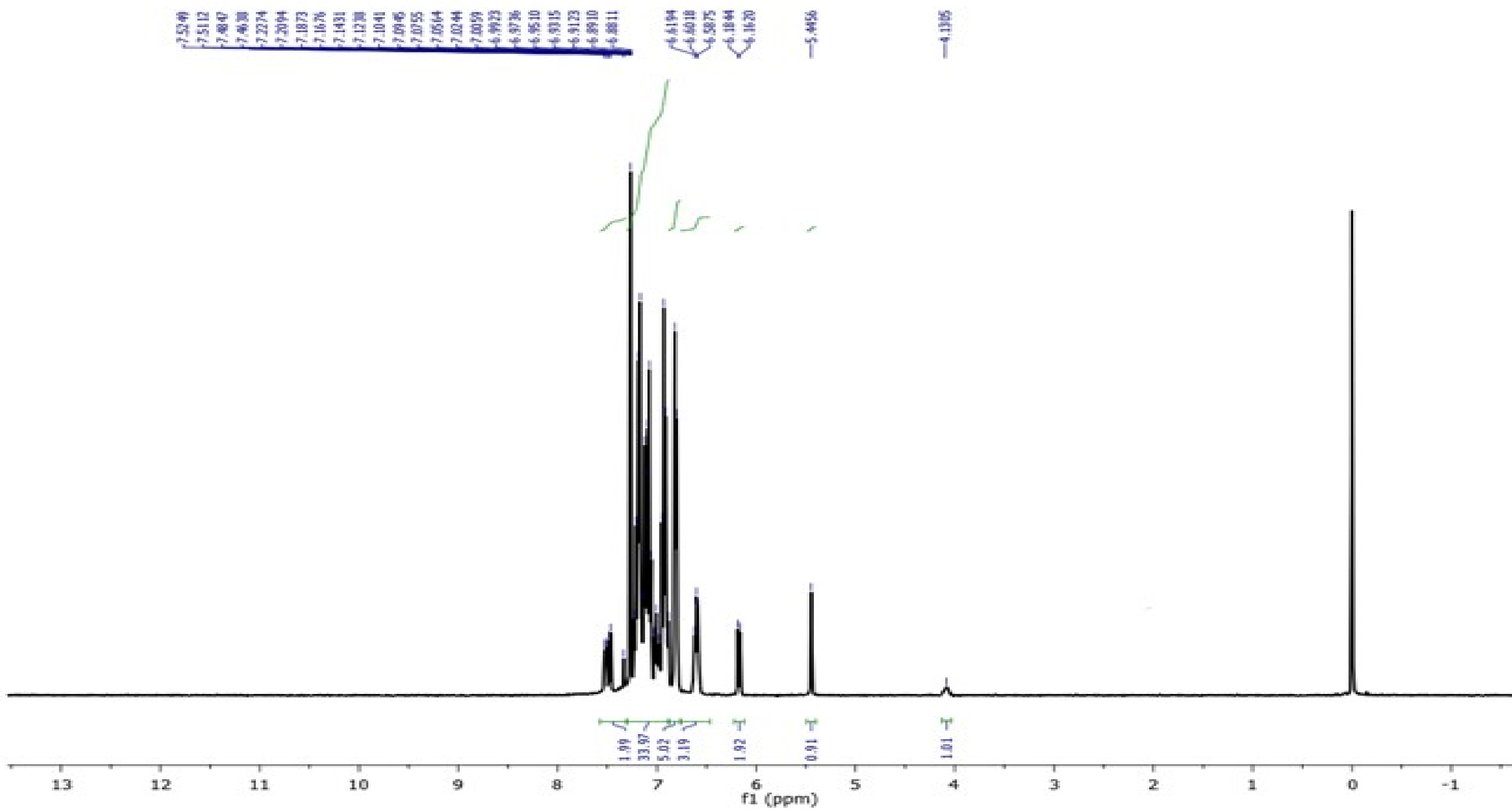


Figure S12: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **[Ru(CO)(AsPh$_3$)$_2$(BZQH)]**

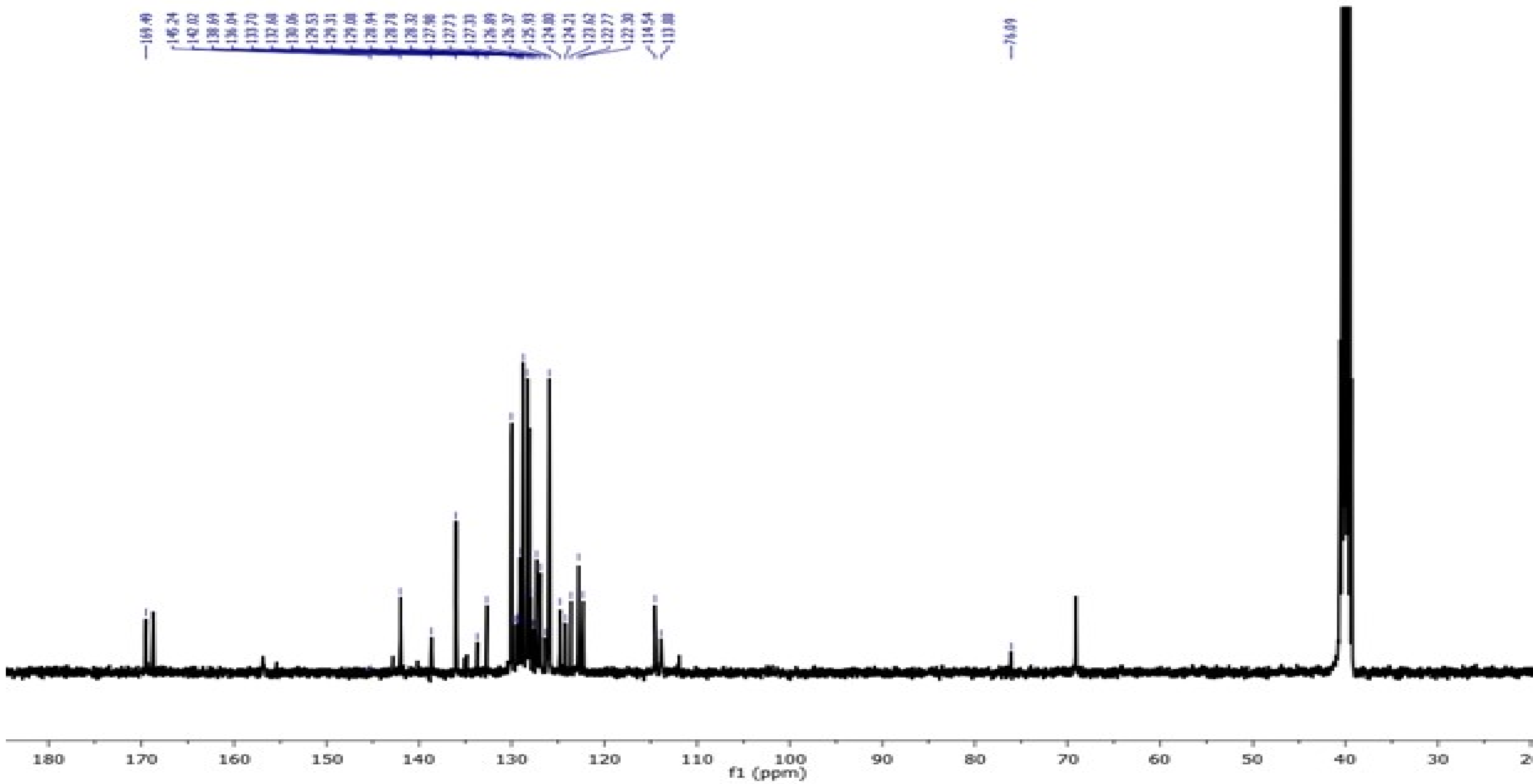


Figure S13: ^{13}C-NMR (100 MHz, DMSO-d_6) spectrum of **BZBT**

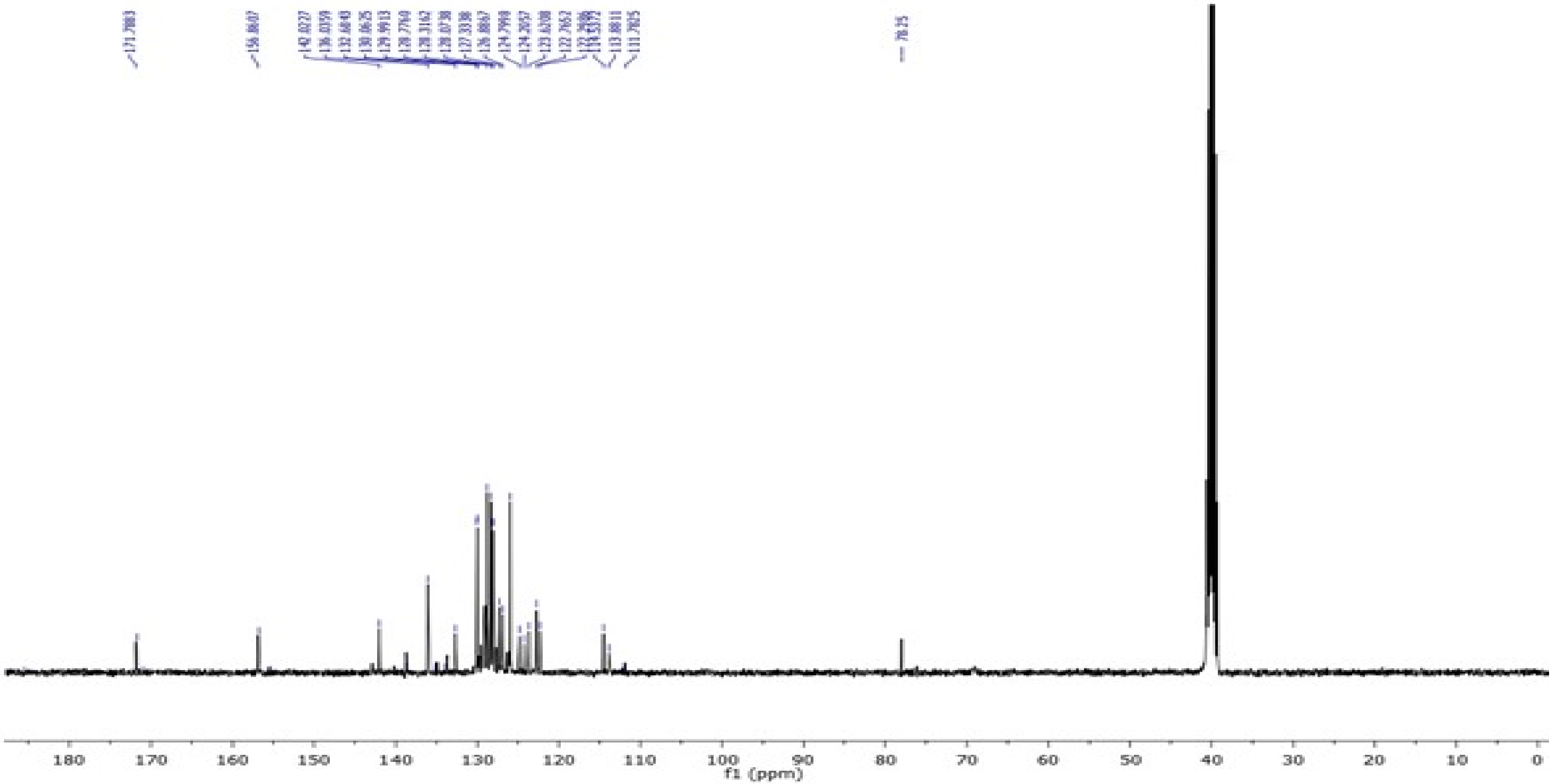


Figure S14: ^{13}C-NMR (100 MHz, DMSO-d$_6$) spectrum of **BZQH**

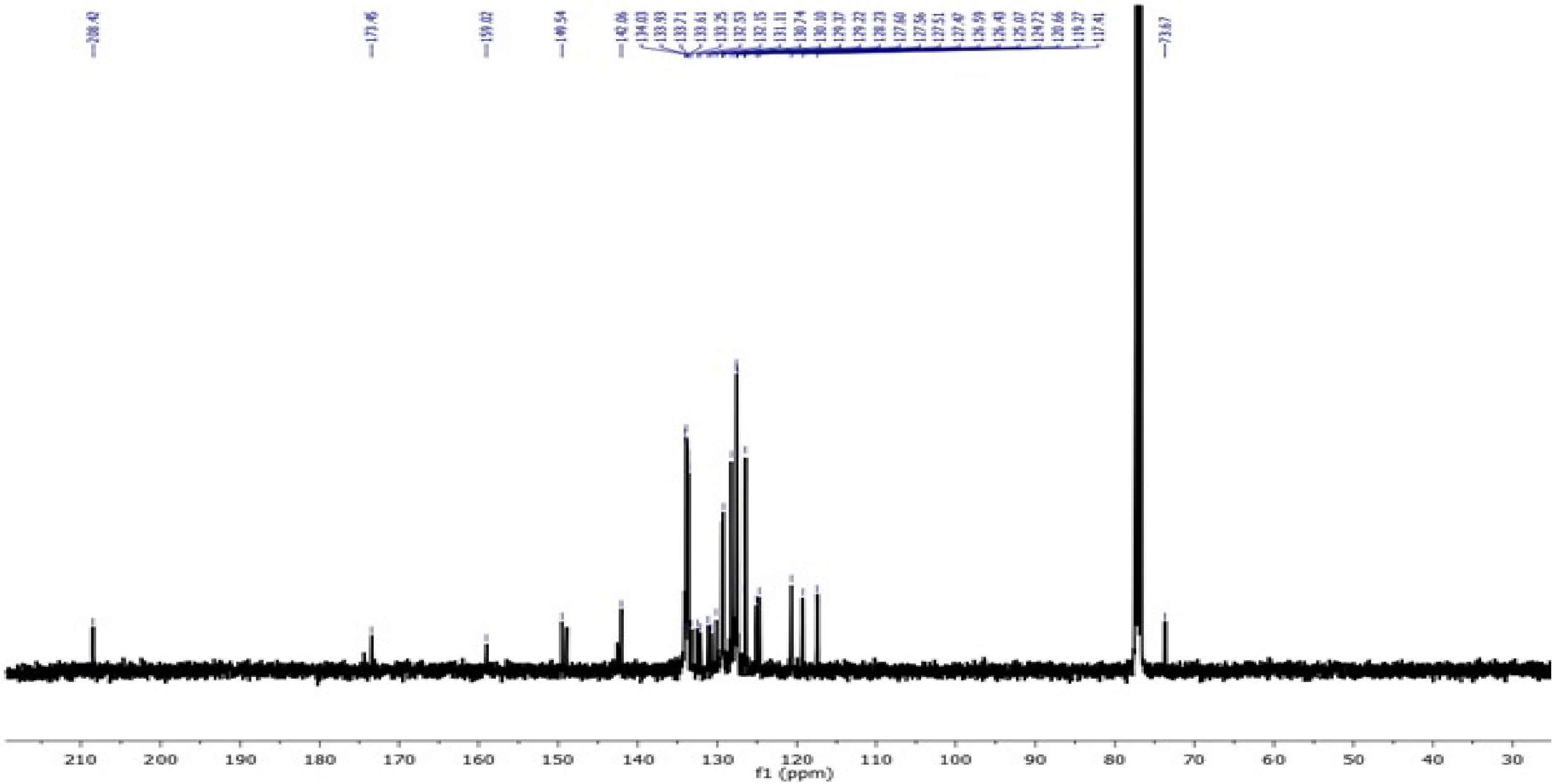


Figure S15: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of [**Ru(CO)(PPh$_3$)$_2$(BZBT)**]

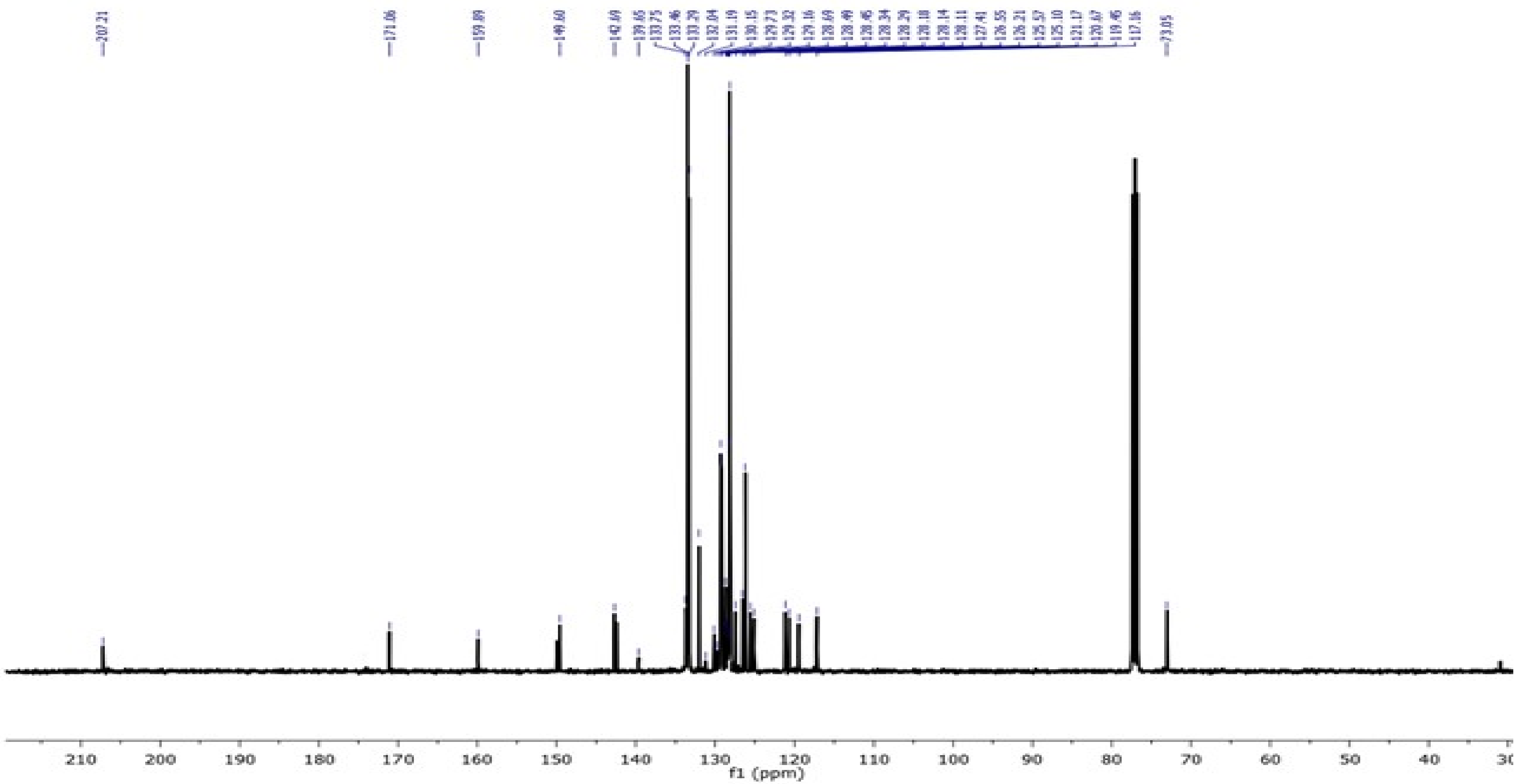


Figure S16: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **[Ru(CO)($AsPh_3$)$_2$(BZBT)]**

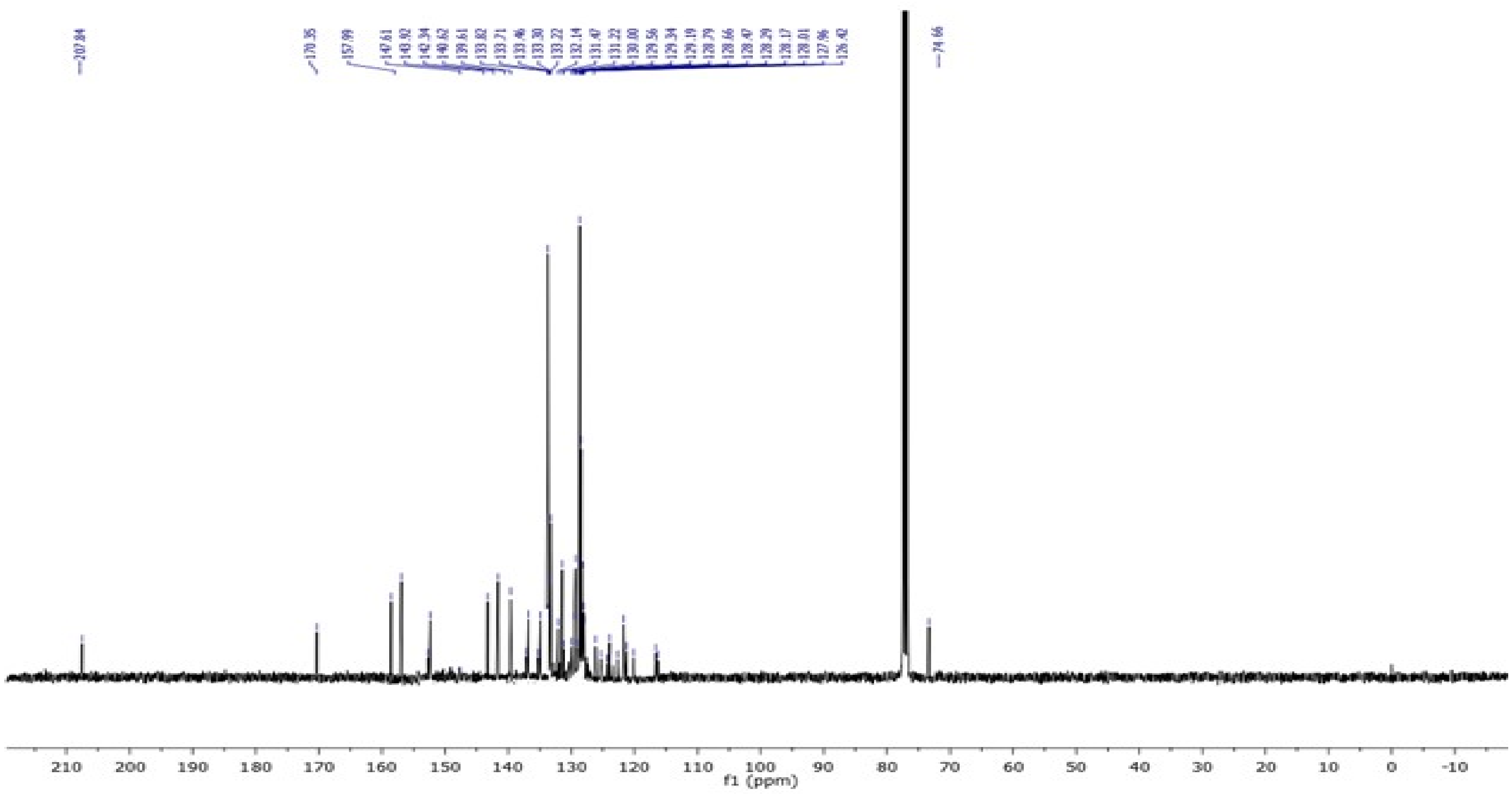


Figure S17: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of [**Ru(CO)(PPh_3)$_2$(BZQH)**]

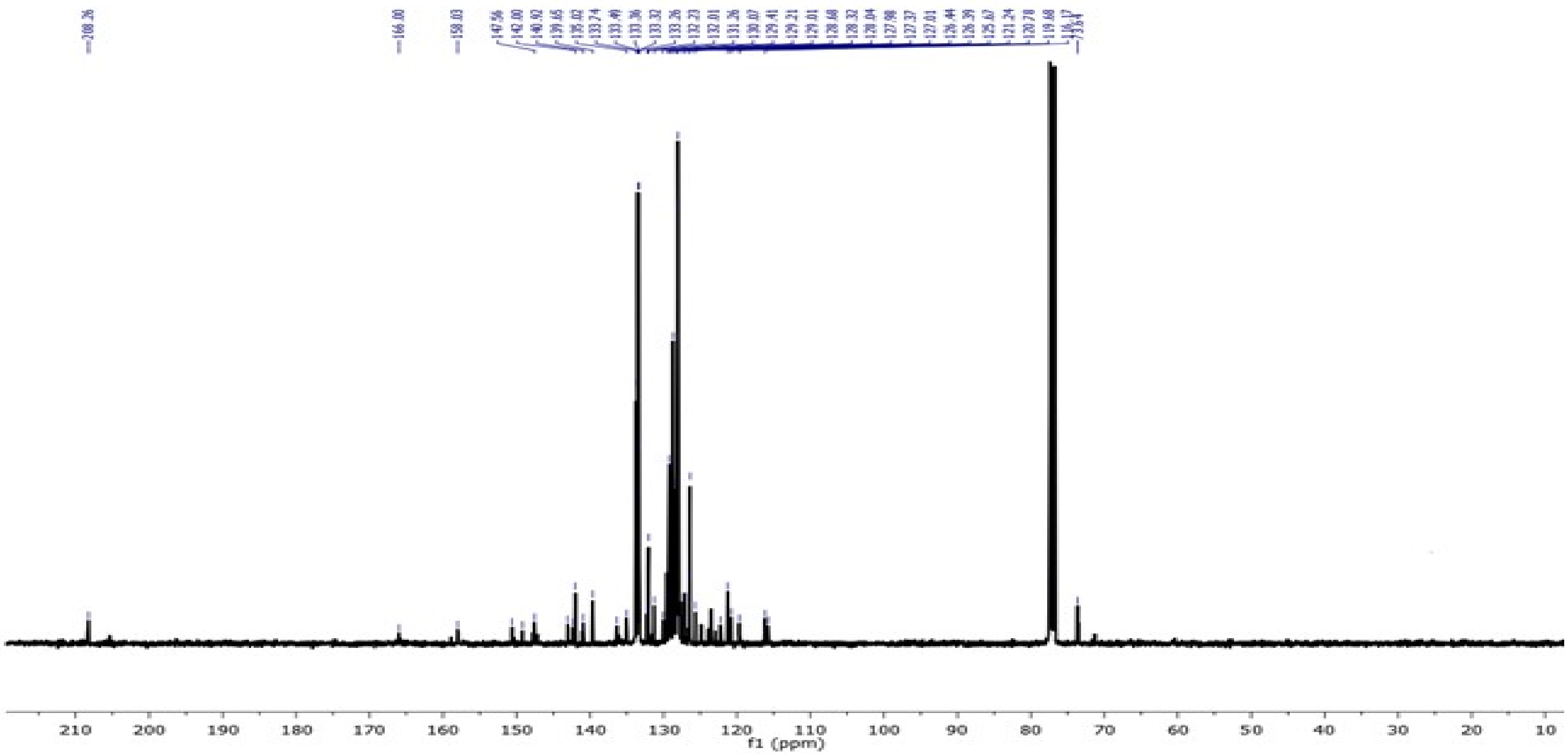


Figure S18: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **[Ru(CO)($AsPh_3$)$_2$(BZQH)]**

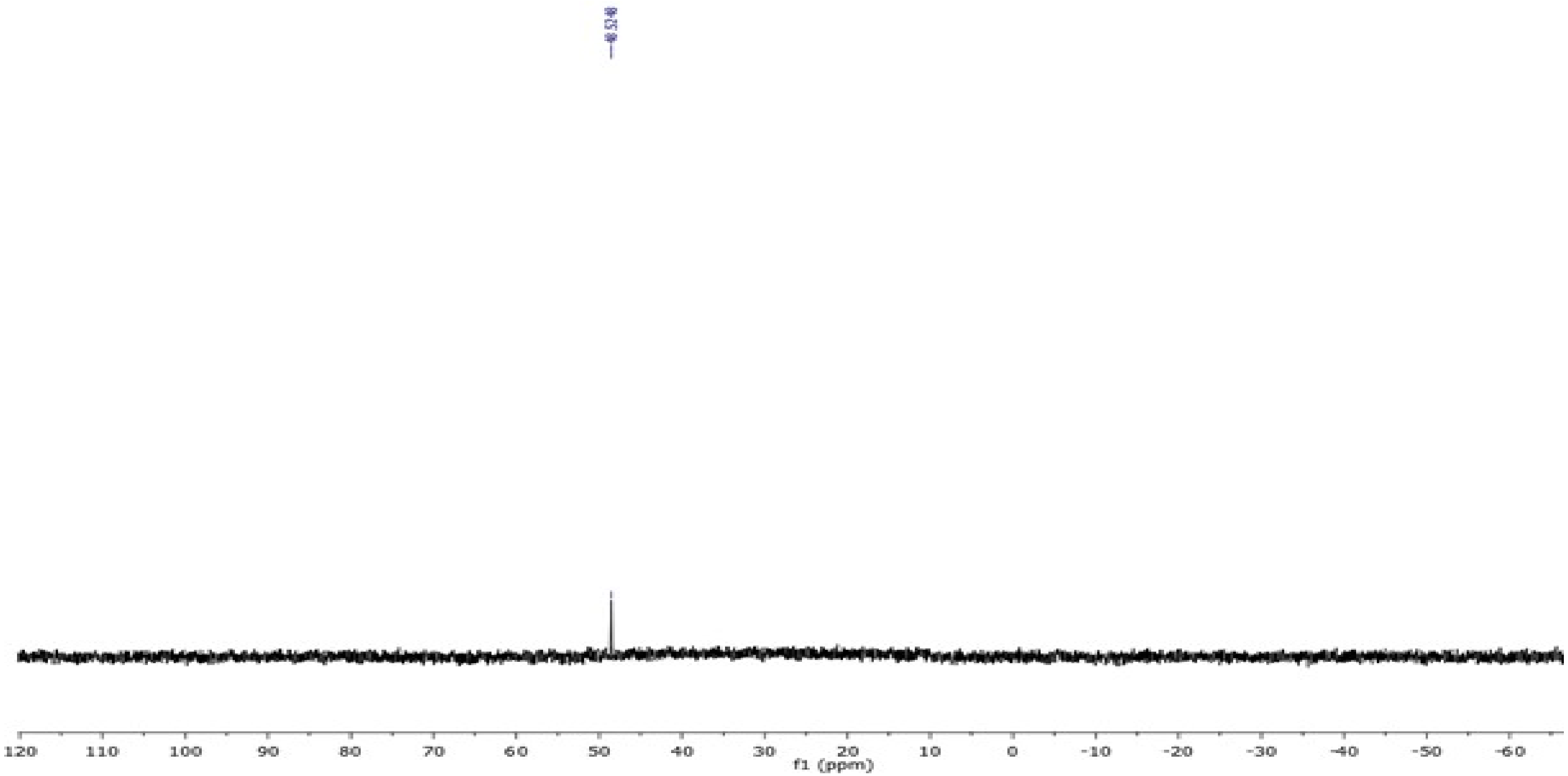


Figure S19: ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum for complex **$[Ru(CO)(PPh_3)_2(BZBT)]$**

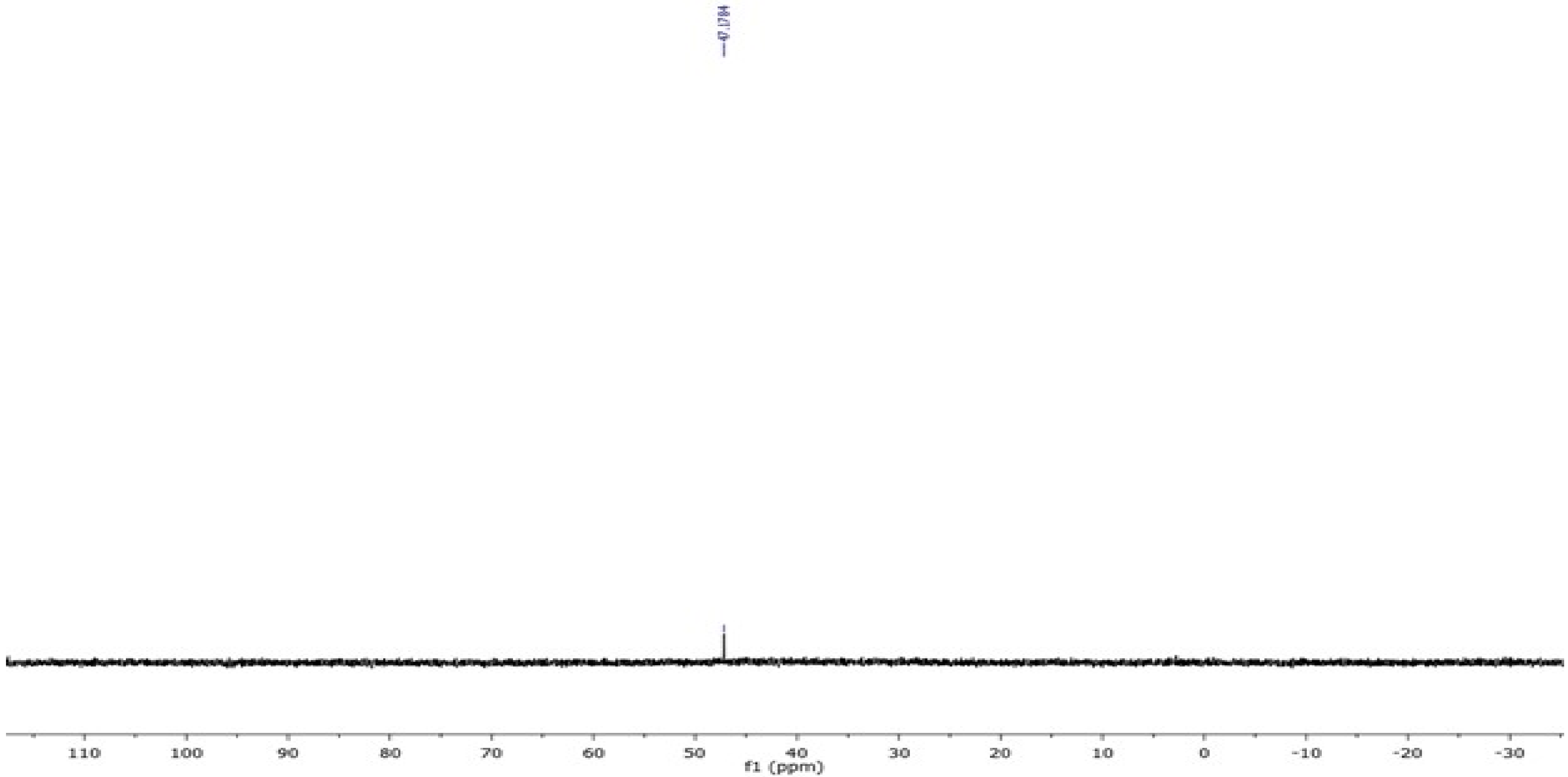


Figure S20: ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum for complex **[Ru(CO)(PPh$_3$)$_2$(BZQH)]**

3. Catalysis

General Information

Thin-layer chromatography (TLC) was carried out on Merck 1.05554 aluminum sheets precoated with silica gel 60 F254, and the spots were monitored by UV light at 254 nm. Column chromatography purifications were executed using Merck silica mesh (100-200). Infrared spectra of the ligands and the metal complexes were recorded in the range of 4000-400 cm^{-1} using a Bruker model FT-IR spectrophotometer. The ^1H (400 MHz) & ^{13}C (100 MHz) NMR spectra were measured on a Bruker AV400 instrument by using $CDCl_3$ as a solvent. Tetramethylsilane was used as an internal standard for the measuring of chemical shifts (ppm).

4. General experimental procedure

[Ru catalyst] (0.001 mmol, 1 mol %) and $Cu(OAc)_2.H_2O$ (0.002 mmol, 2 mol %) were placed in a container under O_2 atmosphere. Then aromatic acid (1.00 mol), alkyne (1.20 mol) and *t*-BuOH (3 mL) were added and the reaction mixture was allowed to stir at room temperature for 5 min followed by reflux at 90 °C for 12 h under stirring. At the end of the reaction, the reaction mixture was cooled to room temperature. The catalyst was separated by the addition of a dichloromethane and hexane filtered through silica gel. After the filtrate was concentrated, petroleum ether and ethyl acetate were used as eluents to purify the residue through a silica gel column to get pure results. All of the products were characterised using ^1H and ^{13}C NMR spectroscopy.

5. Characterization data of the synthesized isocoumarins[1-3]

3, 4-diphenyl-1*H*-isochromen-1-one (**aa**; Table 5, entry 1): Yield: 92%. ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.13 (d, 2H, J = 7.24 Hz, CH_{Ar}), 7.63 - 7.60 (t, 2H, J = 3.15 Hz, CH_{Ar}), 7.54 (d, 2H, J = 8.06 Hz, CH_{Ar}, 7.50 - 7.46 (t, 3H, J = 1.35 Hz, CH_{Ar}), 7.36 (d, 2H, J = 4.58 Hz, CH_{Ar}), 7.34 - 7.32 (t, 3H, J = 3.15 Hz, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 171.22 (C=O), 133.77 (C-O), 133.22 (C_{Ar}), 131.62 (C_{Ar}), 130.99 (C_{Ar}), 130.62 (C_{Ar}), 130.22 (C_{Ar}), 129.21 (C_{Ar}), 128.51 (C_{Ar}), 128.34 (C_{Ar}), 128.26 (C_{Ar}), 123.29 (C_{Ar}).

6-methyl-3, 4-diphenyl-1H-isochromen-1-one (**ab**; Table 5, entry 2): Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.21 (d, 1H, J = 7.08 Hz, CH_{Ar}), 8.01 (d, 2H, J = 8.16 Hz, CH_{Ar}), 7.81 (d, 2H, J = 6.40 Hz, CH_{Ar}), 7.48 (d, 2H, J = 7.52 Hz, CH_{Ar}), 7.28 - 7.25 (t, 3H, J = 2.75 Hz, CH_{Ar}), 7.11 - 7.06 (t, 3H, J = 1.75 Hz, CH_{Ar}), 2.43 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 172.04 (C=O), 144.64 (C-C), 133.29 (C-O), 130.27 (C_{Ar}), 130.20 (C_{Ar}), 129.31 (C_{Ar}), 129.22 (C_{Ar}), 129.15 (C_{Ar}), 128.31 (C_{Ar}), 126.69 (C_{Ar}), 126.57 (C_{Ar}), 21.76 (-CH_3).

6-methoxy-3, 4-diphenyl-1H-isochromen-1-one (**ac**; Table 5, entry 3): Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.00 (d, 1H, J = 8.58 Hz, CH_{Ar}), 7.80 - 7.77 (t, 3H, J = 3.75 Hz, CH_{Ar}), 7.60 - 7.55 (t, 3H, J = 2.15 Hz, CH_{Ar}), 7.13 (d, 2H, J = 8.44 Hz, CH_{Ar}), 6.98 (d, 2H, J = 8.48 Hz, CH_{Ar}), 6.73 (d, 1H, J = 8.40 Hz, CH_{Ar}), 3.96 (s, 3H, -OCH_3), 3.95 (s, 3H, -OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 171.76 (C=O), 153.76 (C-O), 148.71 (C-O), 131.95 (C-O), 125.70 (C_{Ar}), 124.61 (C_{Ar}), 123.00 (C_{Ar}), 121.69 (C_{Ar}), 121.61 (C_{Ar}), 112.35 (C_{Ar}), 110.35 (C_{Ar}), 56.08 (-OCH_3), 56.02 (-OCH_3).

6-fluoro-3, 4-diphenyl-1H-isochromen-1-one (**ad**; Table 5, entry 4): Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.06 (d, 2H, J = 5.52 Hz, CH_{Ar}), 7.91 (d, 1H, J = 7.16 Hz, CH_{Ar}), 7.66 (d, 4H, J = 7.00 Hz, CH_{Ar}), 7.49-7.46 (t, 4H, J = 3.60 Hz, CH_{Ar}), 7.32 – 7.29 (t, 2H, J = 4.52 Hz, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, 25ºC): δ = 169.66 (C-F), 150.50 (C=O), 141.19 (C_{Ar}), 133.92 (C_{Ar}), 131.65 (C_{Ar}), 129.01 (C_{Ar}), 128.78 (C_{Ar}), 128.57 (C_{Ar}), 128.51 (C_{Ar}), 128.15 (C_{Ar}), 127.61 (C_{Ar}), 127.20 (C_{Ar}), 114.38 (C_{Ar}), 111.69 (C_{Ar}).

6-chloro-3, 4-diphenyl-1H-isochromen-1-one (**ae**; Table 5, entry 5): Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.23 (d, 2H, J = 8.84 Hz, CH_{Ar}), 8.05 (d, 1H, J = 8.56 Hz, CH_{Ar}), 7.85 - 7.75 (m, 3H, CH_{Ar}), 7.50 - 7.44 (m, 3H, CH_{Ar}), 7.26 (d, 4H, J = 7.24 Hz, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 147.83 (C=O), 141.56 (C-Cl), 139.38 (C_{Ar}), 133.64 (C_{Ar}), 133.59 (C_{Ar}), 132.98 (C_{Ar}), 132.94 (C_{Ar}), 132.16 (C_{Ar}), 132.06 (C_{Ar}), 132.00 (C_{Ar}), 131.98 (C_{Ar}), 129.23 (C_{Ar}), 128.60 (C_{Ar}), 128.48 (C_{Ar}), 127.99 (C_{Ar}), 127.82 (C_{Ar}), 127.77 (C_{Ar}), 105.49 (C_{Ar}).

6-bromo-3, 4-diphenyl-1H-isochromen-1-one (**af**; Table 5, entry 6): Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.02 (d, 3H, J = 9.84 Hz, CH_{Ar}), 7.73 (d, 4H, J = 7.24 Hz, CH_{Ar}), 7.53 - 7.49 (m, 4H, CH_{Ar}), 7.40 - 7.33 (m, 2H, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, 25ºC): δ =

152.28 (C=O), 144.61 (C-Br), 143.38 (C_{Ar}), 137.69 (C_{Ar}), 132.38 (C_{Ar}), 130.76 (C_{Ar}), 129.54 (C_{Ar}), 129.50 (C_{Ar}), 128.94 (C_{Ar}), 128.26 (C_{Ar}), 127.58 (C_{Ar}), 127.28 (C_{Ar}), 107.22 (C_{Ar}).

6-iodo-3, 4-diphenyl-1H-isochromen-1-one (**ag**; Table 5, entry 7): Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.02 (d, 3H, J = 9.44 Hz, CH_{Ar}), 7.73 (d, 4H, J = 7.13 Hz, CH_{Ar}), 7.53 - 7.49 (m, 4H, CH_{Ar}), 7.40 - 7.33 (m, 2H, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, 25ºC): δ = 151.47 (C=O), 141.36 (C_{Ar}), 133.83 (C_{Ar}), 133.63 (C_{Ar}), 133.23 (C_{Ar}), 132.14 (C_{Ar}), 132.04 (C_{Ar}), 132.00 (C_{Ar}), 129.92 (C_{Ar}), 128.72 (C_{Ar}), 128.59 (C_{Ar}), 128.53 (C_{Ar}), 128.47 (C_{Ar}), 128.14 (C_{Ar}), 111.44 (C_{Ar}), 102.49 (C-I).

6-acetyl-3, 4-diphenyl-1H-isochromen-1-one (**ah**; Table 5, entry 8): Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.20 (d, 2H, J = 8.44 Hz, CH_{Ar}), 8.05 (d, 2H, J = 8.48 Hz, CH_{Ar}), 7.52 (d, 4H, J = 3.15 Hz, CH_{Ar}), 7.14 - 7.08 (t, 4H, J = 3.15 Hz, CH_{Ar}), 7.02 - 6.98 (t, 2H, J = 4.75 Hz, CH_{Ar}), 2.66 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 198.47 (C=O), 152.16 (C=O), 141.58 (C-C), 138.60 (C=C), 134.56 (C_{Ar}), 130.46 (C_{Ar}), 129.64 (C_{Ar}), 128.31 (C_{Ar}), 125.68 (C_{Ar}), 123.68 (C_{Ar}), 120.69 (C_{Ar}), 109.42 (C_{Ar}), 26.91 ($-CH_3$).

5, 6-dimethyl-3, 4-diphenyl-1*H*-isochromen-1-one (**ai**; Table 5, entry 9): Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.98 (d, 2H, J = 11.80 Hz, CH_{Ar}), 7.78 (d, 2H, J = 3.12 Hz, CH_{Ar}), 7.76 (d, 2H, J = 3.60 Hz, CH_{Ar}), 7.08 - 7.05 (t, 4H, J = 3.15 Hz, CH_{Ar}), 7.00 - 6.99 (t, 2H, J = 2.15 Hz, CH_{Ar}), 2.62 (s, 3H, CH_3), 2.37 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 172.72 (C=O), 149.60 (C-C), 143.64 (C-C), 141.49 (C-O), 135.82 (C_{Ar}), 132.73 (C_{Ar}), 131.81 (C_{Ar}), 129.81 (C_{Ar}), 126.62 (C_{Ar}), 125.40 (C_{Ar}), 22.10 ($-CH_3$), 21.47 ($-CH_3$).

5, 6-dimethoxy-3, 4-diphenyl-1H-isochromen-1-one (**aj**; Table 5, entry 10): Yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.00 (d, 1H, J = 8.58 Hz, CH_{Ar}), 7.80 - 7.77 (t, 3H, J = 3.75 Hz, CH_{Ar}), 7.60 - 7.55 (t, 3H, J = 2.15 Hz, CH_{Ar}), 7.13 (d, 2H, J = 8.44 Hz, CH_{Ar}), 6.98 (d, 2H, J = 8.48 Hz, CH_{Ar}), 6.73 (d, 1H, J = 8.40 Hz, CH_{Ar}), 3.96 (s, 3H, $-OCH_3$), 3.95 (s, 3H, $-OCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 171.76 (C=O), 153.76 (C-O), 148.71 (C-O), 131.95 (C-O), 125.70 (C_{Ar}), 124.61 (C_{Ar}), 123.00 (C_{Ar}), 121.69 (C_{Ar}), 121.61 (C_{Ar}), 112.35 (C_{Ar}), 110.35 (C_{Ar}), 56.08 ($-OCH_3$), 56.02 ($-OCH_3$).

3, 4-diphenyl-1H-benzo[h]isochromen-1-one (**ak**; Table 5, entry 11): Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 9.07 (d, 1H, J = 4.64 Hz, CH_{Ar}), 8.39 - 8.37 (t, 2H, J = 3.15 Hz, CH_{Ar}), 8.10 (d, 2H, J = 8.06 Hz, CH_{Ar}), 7.93 (d, 4H, J = 7.96 Hz, CH_{Ar}), 7.68 - 7.64 (t, 3H, J = 2.15 Hz, CH_{Ar}), 7.58 - 7.53 (m, 3H, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 171.03 (C=O), 134.53 (C-O), 134.13 (C_{Ar}), 131.69 (C_{Ar}), 128.70 (C_{Ar}), 128.64 (C_{Ar}), 128.12 (C_{Ar}), 128.03 (C_{Ar}), 126.35 (C_{Ar}), 126.26 (C_{Ar}), 125.90 (C_{Ar}), 125.19 (C_{Ar}), 124.53 (C_{Ar}).

5, 6-diphenyl-2H-pyran-2-one (**al**; Table 5, entry 12): Yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.66 (d, 1H, J = 6.72 Hz, CH_{Ar}), 7.59 (d, 4H, J = 7.92 Hz, CH_{Ar}), 7.31 - 7.22 (m, 4H, CH_{Ar}), 7.18 - 7.10 (m 2H, CH_{Ar}), 6.39 (d, 1H, J = 6.16 Hz, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, 25ºC): δ = 163.69 (C=O), 151.20 (C_{Ar}), 133.53 (C_{Ar}), 133.47 (C_{Ar}), 133.03 (C_{Ar}), 132.16 (C_{Ar}), 132.06 (C_{Ar}), 131.98 (C_{Ar}), 131.95 (C_{Ar}), 129.30 (C_{Ar}), 128.58 (C_{Ar}), 128.46 (C_{Ar}), 127.74 (C_{Ar}), 127.69 (C_{Ar}).

3, 4-diphenylpyrano [4, 3-b] indol-1(5H)-one (**am**; Table 5, entry 13): Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.90 (s, 1H, NH), 7.73 (d, 2H, J = 8.12 Hz, CH_{Ar}), 7.51 (d, 2H, J = 6.92 Hz, CH_{Ar}), 7.46 (d, 2H, J = 7.92 Hz, CH_{Ar}), 7.38 - 7.34 (t, 2H, J = 3.15 Hz, CH_{Ar}), 7.20 - 7.16 (t, 6H, J = 6.15 Hz, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 165.93 (C=O), 137.31 (C-O), 127.90 (C_{Ar}), 126.12 (C_{Ar}), 122.91 (C_{Ar}), 122.60 (C_{Ar}), 121.11 (C_{Ar}), 119.83 (C_{Ar}), 111.98 (C_{Ar}), 110.83 (C_{Ar}).

6, 7-diphenyl-4H-furo [3, 2-c] pyran-4-one (**an**; Table 5, entry 14): Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.72 (d, 1H, J = 9.92 Hz, CH_{Ar}), 7.67 (d, 1H, J = 9.20 Hz, CH_{Ar}), 7.58 – 7.55 (t, 4H, J = 8.02 Hz, CH_{Ar}), 7.50 – 7.46 (t, 2H, J = 6.08 Hz, CH_{Ar}), 7.30 (d, 2H, J = 7.52 Hz, CH_{Ar}), 7.05 (d, 2H, J = 9.82 Hz, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, 25ºC): δ = 162.97 (C-O), 149.25 (C-O), 144.61 (C=O), 141.28 (C_{Ar}), 139.94 (C_{Ar}), 129.91 (C_{Ar}), 129.24 (C_{Ar}), 128.94 (C_{Ar}), 127.60 (C_{Ar}), 126.91 (C_{Ar}), 125.94 (C_{Ar}), 116.89 (C_{Ar}), 112.55 (C_{Ar}).

6, 7-diphenyl-4H-thino [3, 2-c] pyran-4-one (**ao**; Table 5, entry 15): Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.11 (d, 1H, J = 3.84 Hz, CH_{Ar}), 7.90 (d, 1H, J = 4.88 Hz, CH_{Ar}), 7.66 (d, 2H, J = 6.08 Hz, CH_{Ar}), 7.48 (d, 2H, J = 7.80 Hz, CH_{Ar}), 7.36 - 7.34 (t, 2H, J = 2.75 Hz, CH_{Ar}), 7.15 - 7.13 (t, 2H, J = 1.25 Hz, CH_{Ar}), 6.94 - 6.92 (t, 2H, J = 4.55 Hz, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 167.41 (C=O), 138.60 (C-O), 136.58 (C_{Ar}), 135.92 (C_{Ar}), 135.02 (C_{Ar}), 134.01 (C_{Ar}), 132.84 (C_{Ar}), 132.28 (C_{Ar}), 130.32 (C_{Ar}), 128.53 (C_{Ar}), 128.08 (C_{Ar}).

3,4,6,7-tetraphenyl-1H,9H-dipyrano[3,4,4',3']pyridine-1,9-dione (**ap**; Table 5, entry 16): Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.69 (s, 1H, CH_{Ar}), 8.36 – 8.18 (m, 8H, CH_{Ar}), 7.62 - 7.45 (m, 8H, CH_{Ar}), 7.41 – 7.28 (m, 4H, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, 25ºC): δ = 161.01 (C=O), 149.95 (C=N), 138.58 (C_{Ar}), 137.35 (C_{Ar}), 135.26 (C_{Ar}), 133.81 (C_{Ar}), 132.10 (C_{Ar}), 129.77 (C_{Ar}), 129.01 (C_{Ar}), 128.60 (C_{Ar}), 128.04 (C_{Ar}), 127.56 (C_{Ar}), 126.70 (C_{Ar}), 113.22 (C_{Ar}).

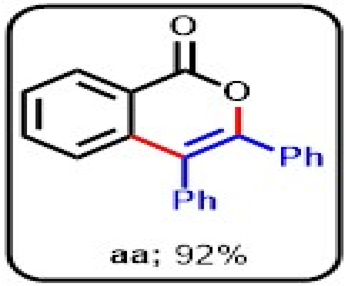
3-methyl-5, 6-diphenyl-2H-pyran-2-one (**aq**; Table 5, entry 17): Yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.87 - 7.85 (d, 4H, J = 8.02 Hz, CH_{Ar}), 7.65 – 7.61 (t, 4H, J = 5.08 Hz, CH_{Ar}), 7.29 - 7.25 (t, 2H, J = 4.59 Hz, CH_{Ar}), 7.19 (s, 1H, CH_{Ar}).

4-methyl-3-phenyl-1H-isochromen-1-one (**ar**; Table 5, entry 18): Yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.34 (d, 1H, J = 7.56 Hz, CH_{Ar}), 8.14 (d, 1H, J = 9.36 Hz, CH_{Ar}), 7.93 (d, 2H, J = 8.76 Hz, CH_{Ar}), 7.68 (d, 2H, J = 7.16 Hz, CH_{Ar}), 7.64 - 7.60 (t, 2H, J = 1.85 Hz, CH_{Ar}), 7.50 - 7.46 (t, 3H, J = 5.05 Hz, CH_{Ar}), 1.28 (s, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 171.71 (C=O), 133.79 (C-O), 132.13 (C_{Ar}), 131.19 (C_{Ar}), 130.22 (C_{Ar}), 129.76 (C_{Ar}), 129.54 (C_{Ar}), 129.28 (C_{Ar}), 128.86 (C_{Ar}), 128.50 (C_{Ar}), 11.46 ($-CH_3$).

3, 4-diethyl-1H-isochromen-1-one (**at**; Table 5, entry 20): Yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.34 (d, 1H, J = 7.64 Hz, CH_{Ar}), 8.13 (d, 1H, J = 7.44 Hz, CH_{Ar}), 7.64 - 7.60 (t, 1H, J = 2.15 Hz, CH_{Ar}), 7.50 - 7.46 (t, 1H, J = 3.65 Hz, CH_{Ar}), 2.20 - 2.17 (q, 4H, $-CH_2$), 1.28 (s, 3H, $-CH_3$), 1.25 (s, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 171.75 (C=O), 150.54 (C-O), 134.44 (C_{Ar}), 133.80 (C_{Ar}), 131.96 (C_{Ar}), 130.99 (C_{Ar}), 130.23 (C_{Ar}), 129.64 (C_{Ar}), 129.27 (C_{Ar}), 128.50 (C_{Ar}), 128.02 (C_{Ar}), 24.05 ($-CH_2$), 11.07 ($-CH_3$).

3-phenyl-1H-isochromen-1-one (**au**; Table 5, entry 21): Yield: 30%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.34 (d, 2H, J = 7.84 Hz, CH_{Ar}), 8.13 - 8.11 (t, 2H, J = 3.15 Hz, CH_{Ar}), 7.93 (d, 2H, J = 8.32 Hz, CH_{Ar}), 7.64 - 7.60 (t, 2H, J = 1.75 Hz, CH_{Ar}), 7.50 - 7.46 (t, 1H, J = 5.65 Hz, CH_{Ar}), 7.25 (s, 1H, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 171.93 (C=O), 153.30 (C-O), 133.80 (C_{Ar}), 130.23 (C_{Ar}), 129.95 (C_{Ar}), 129.60 (C_{Ar}), 129.30 (C_{Ar}), 128.81 (C_{Ar}), 128.50 (C_{Ar}).

6. NMR spectra of the synthesized isocoumarins (aa - aq)



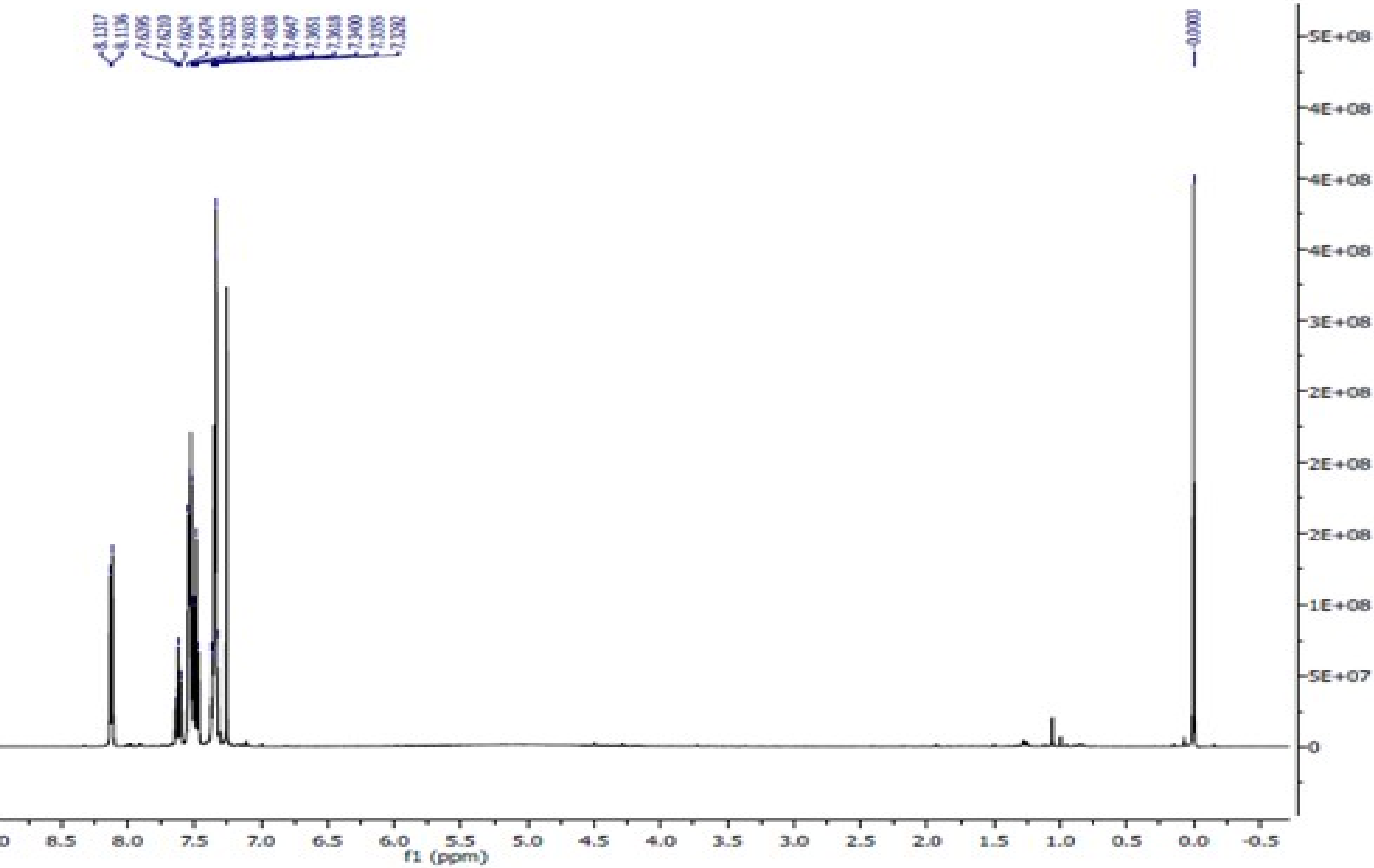


Figure S21: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **aa**

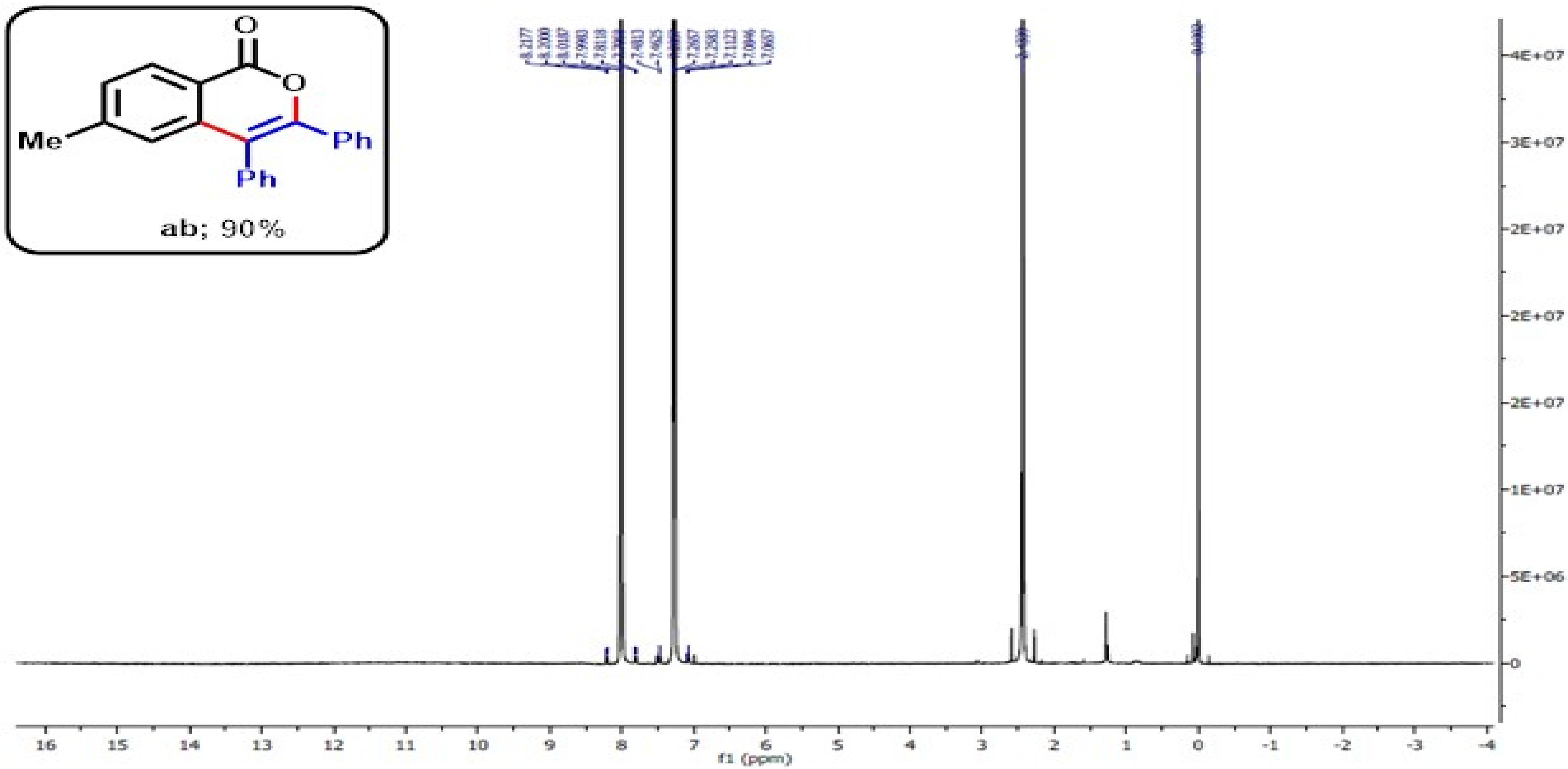


Figure S22: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **ab**

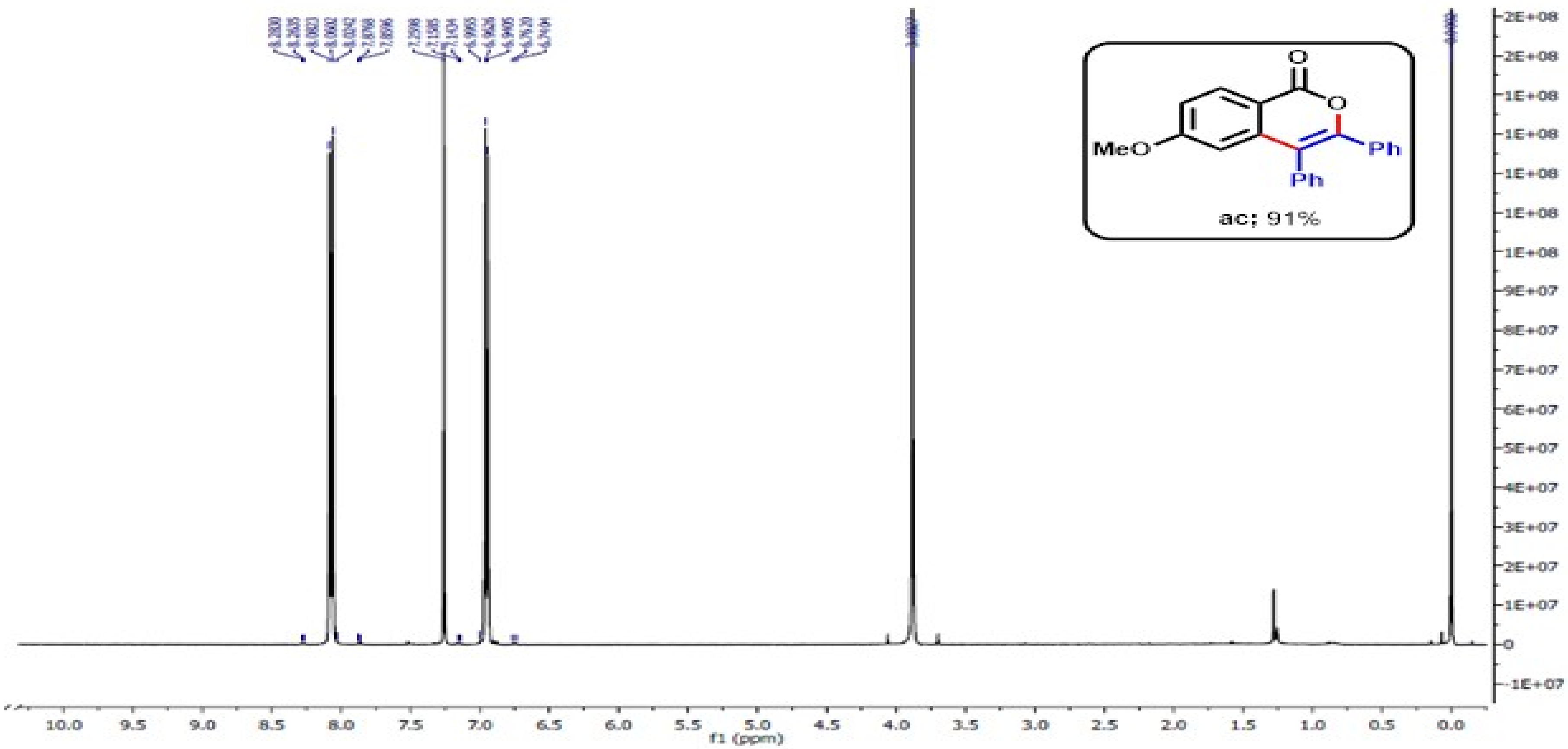


Figure S23: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **ac**

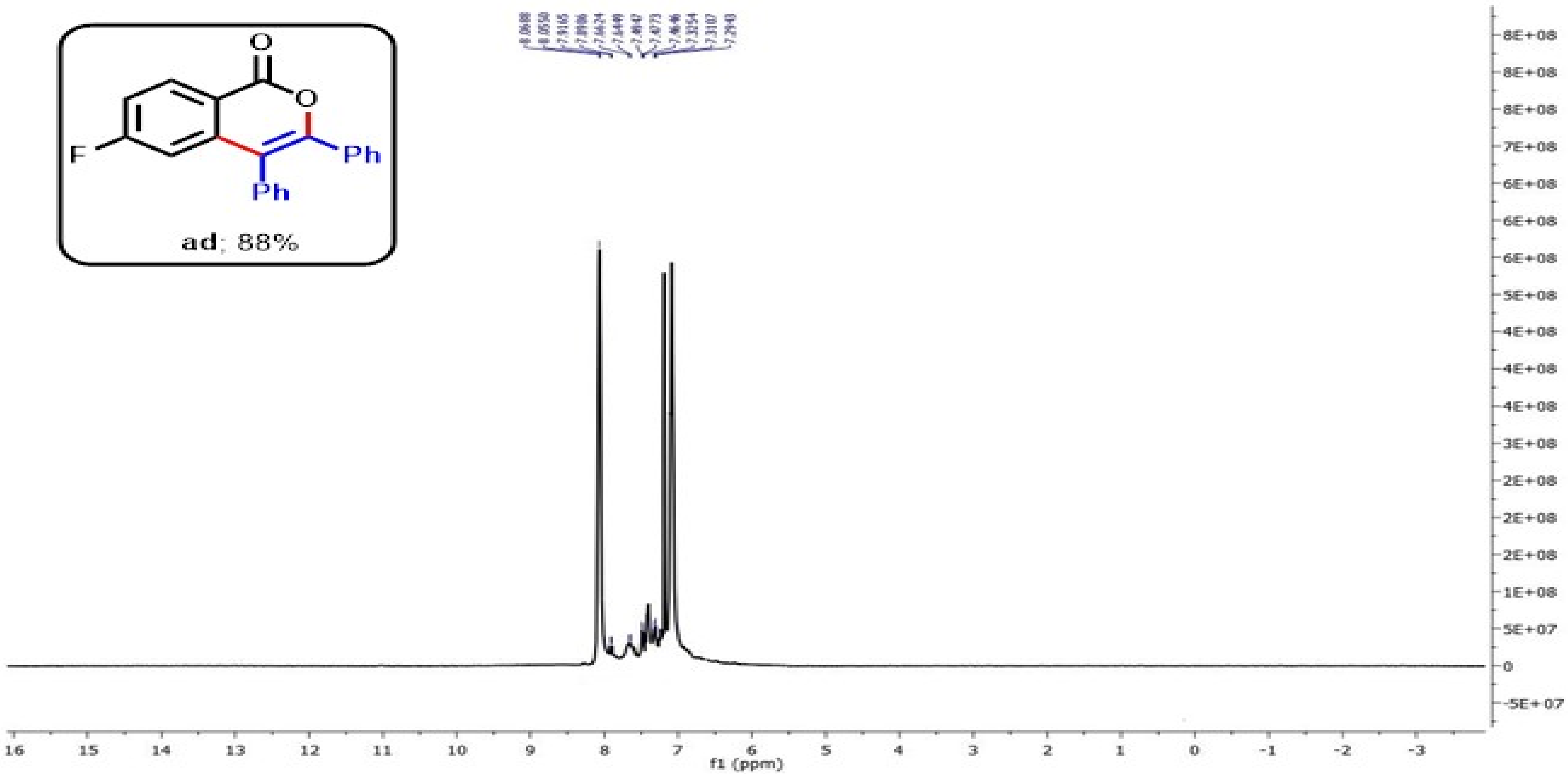


Figure S24: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **ad**

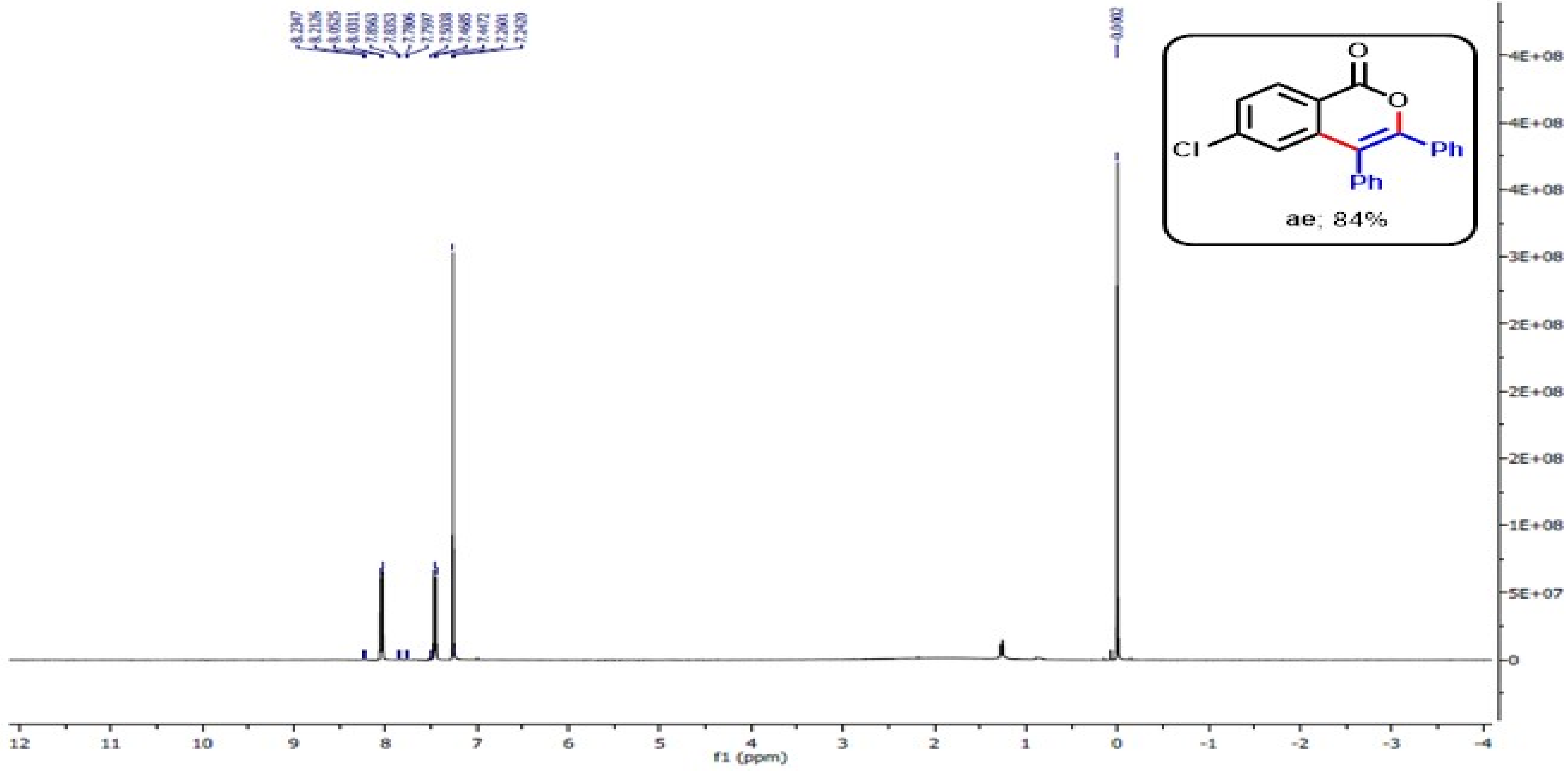


Figure S25: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **ae**

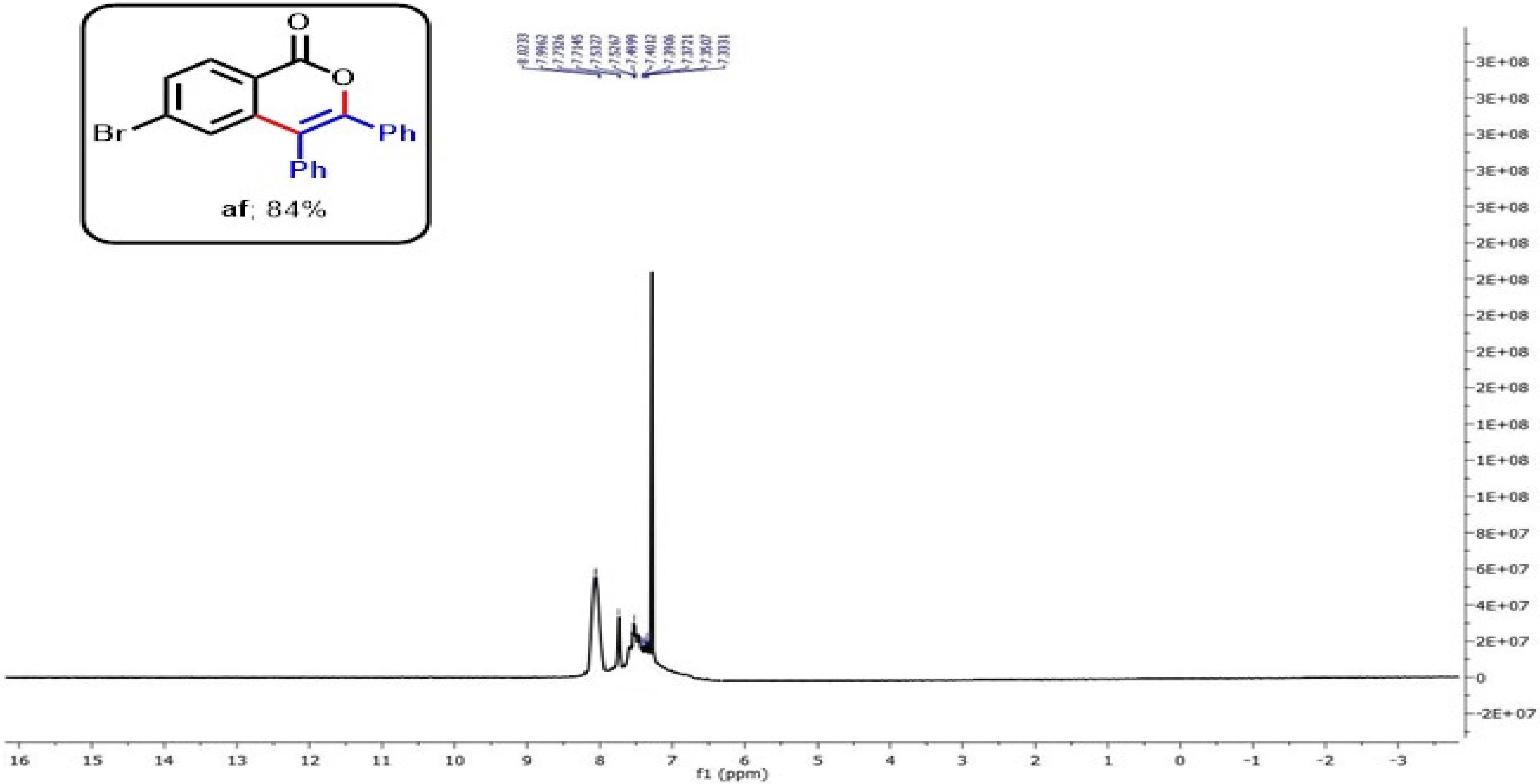


Figure S26: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **af**

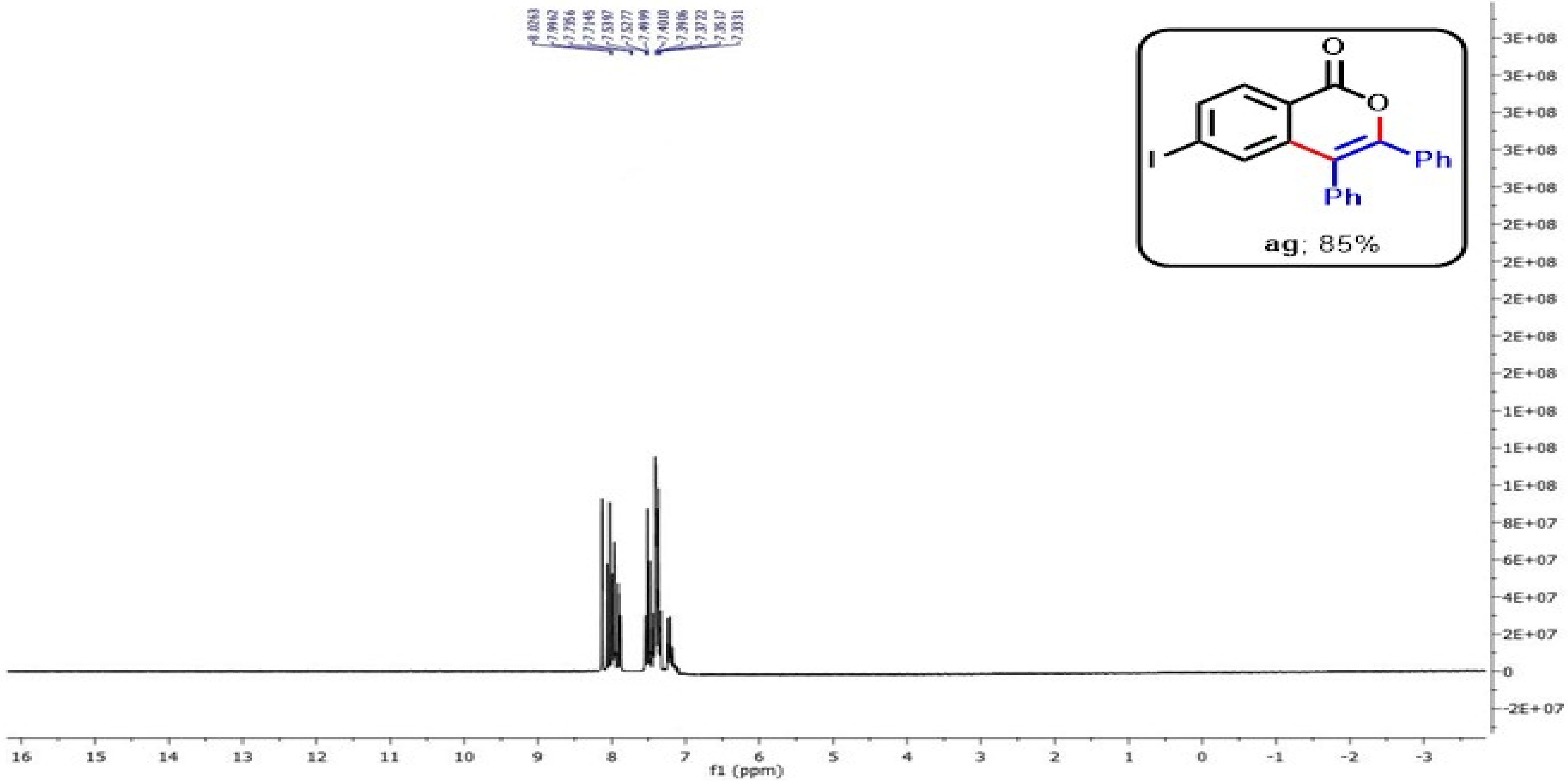


Figure S27: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **ag**

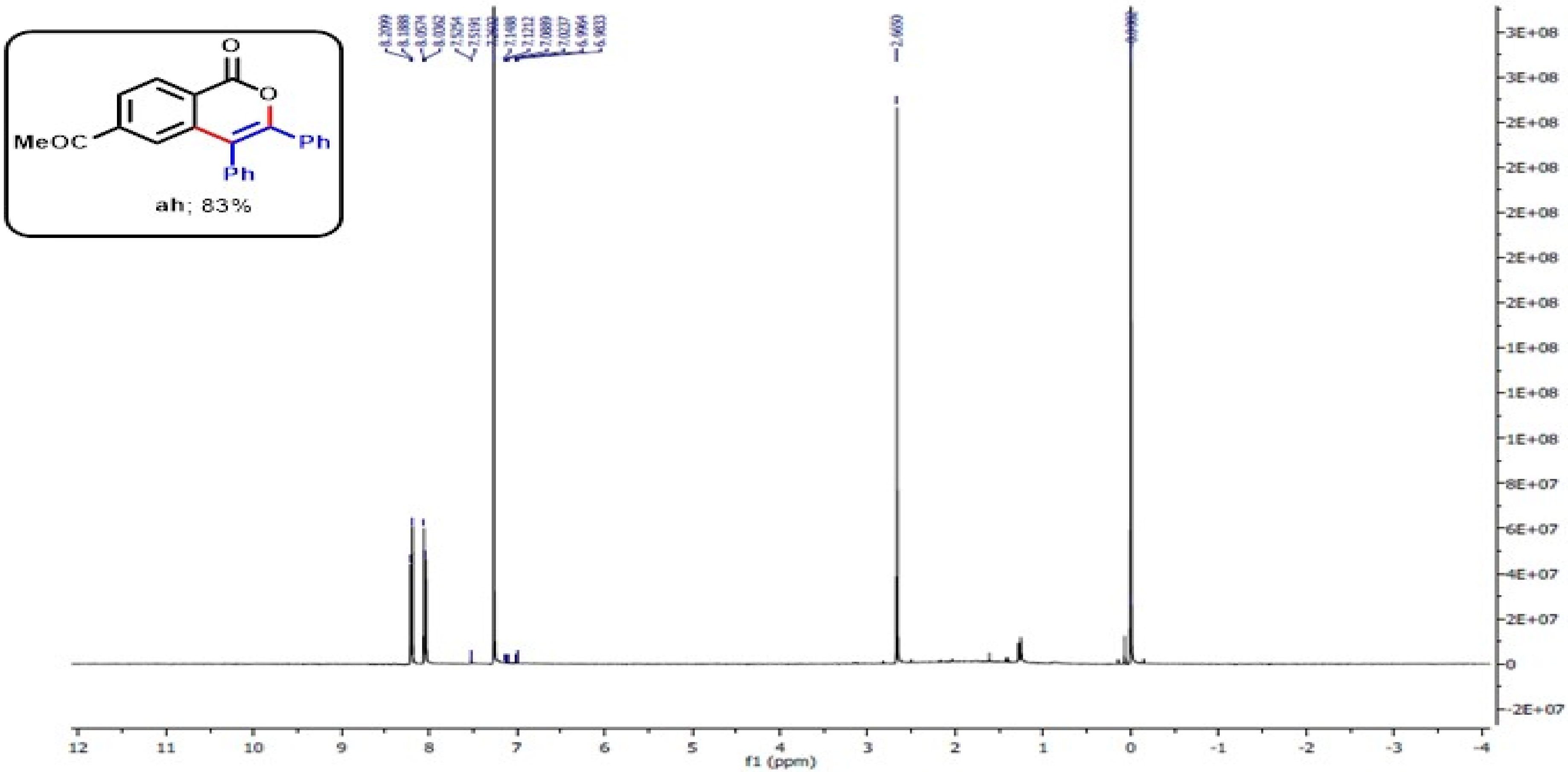


Figure S28: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **ah**

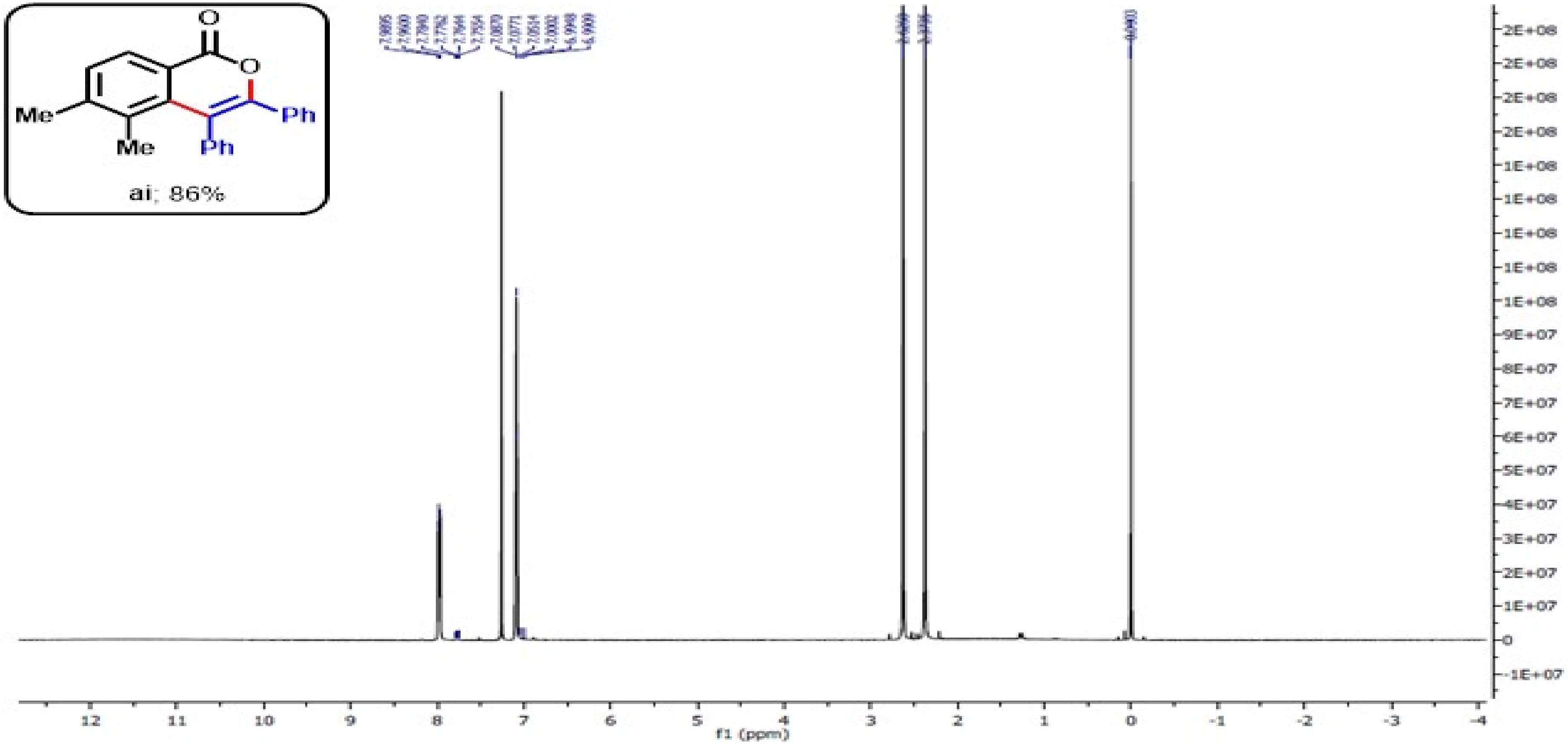


Figure S29: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **ai**

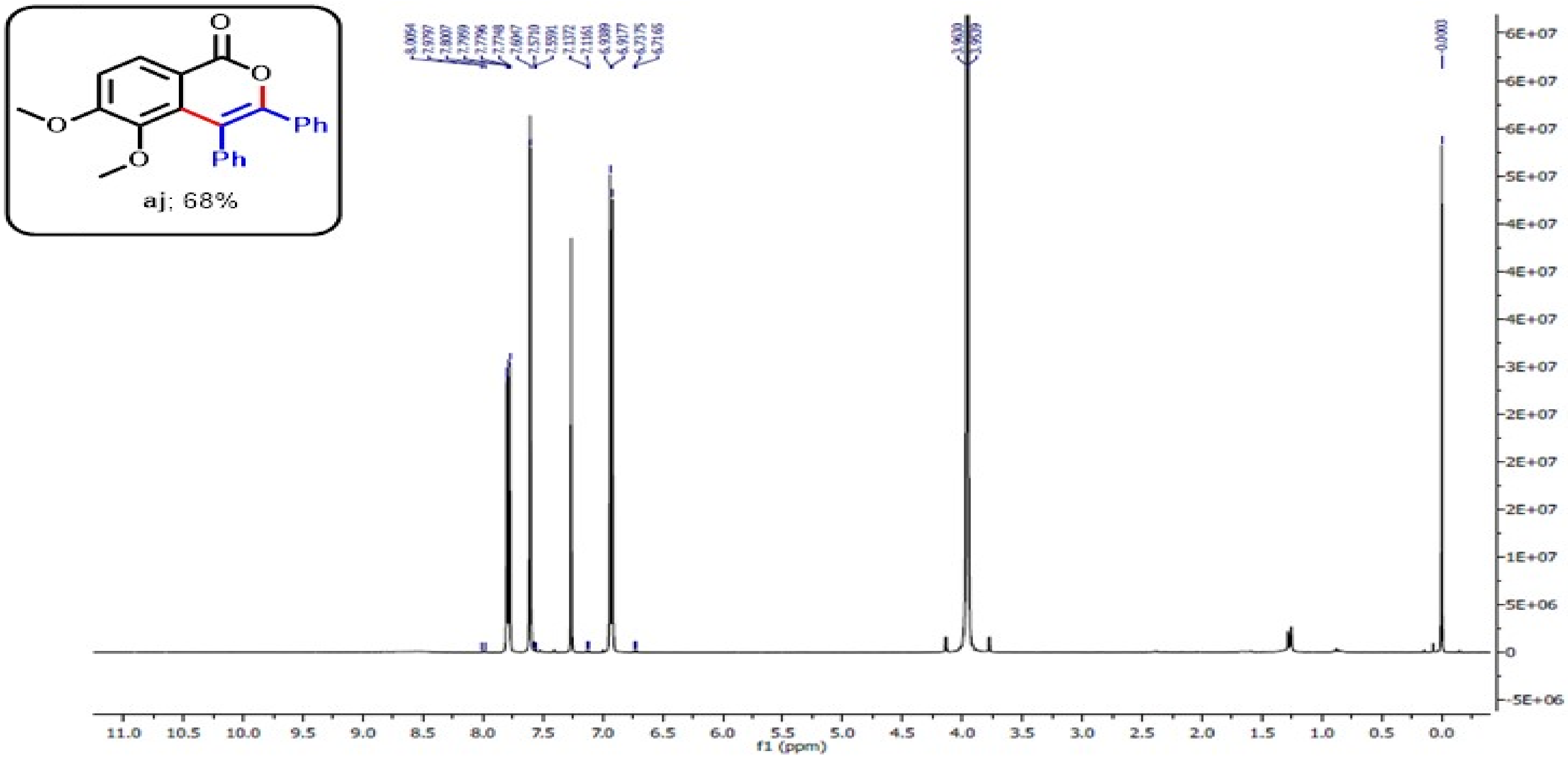


Figure S30: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **aj**

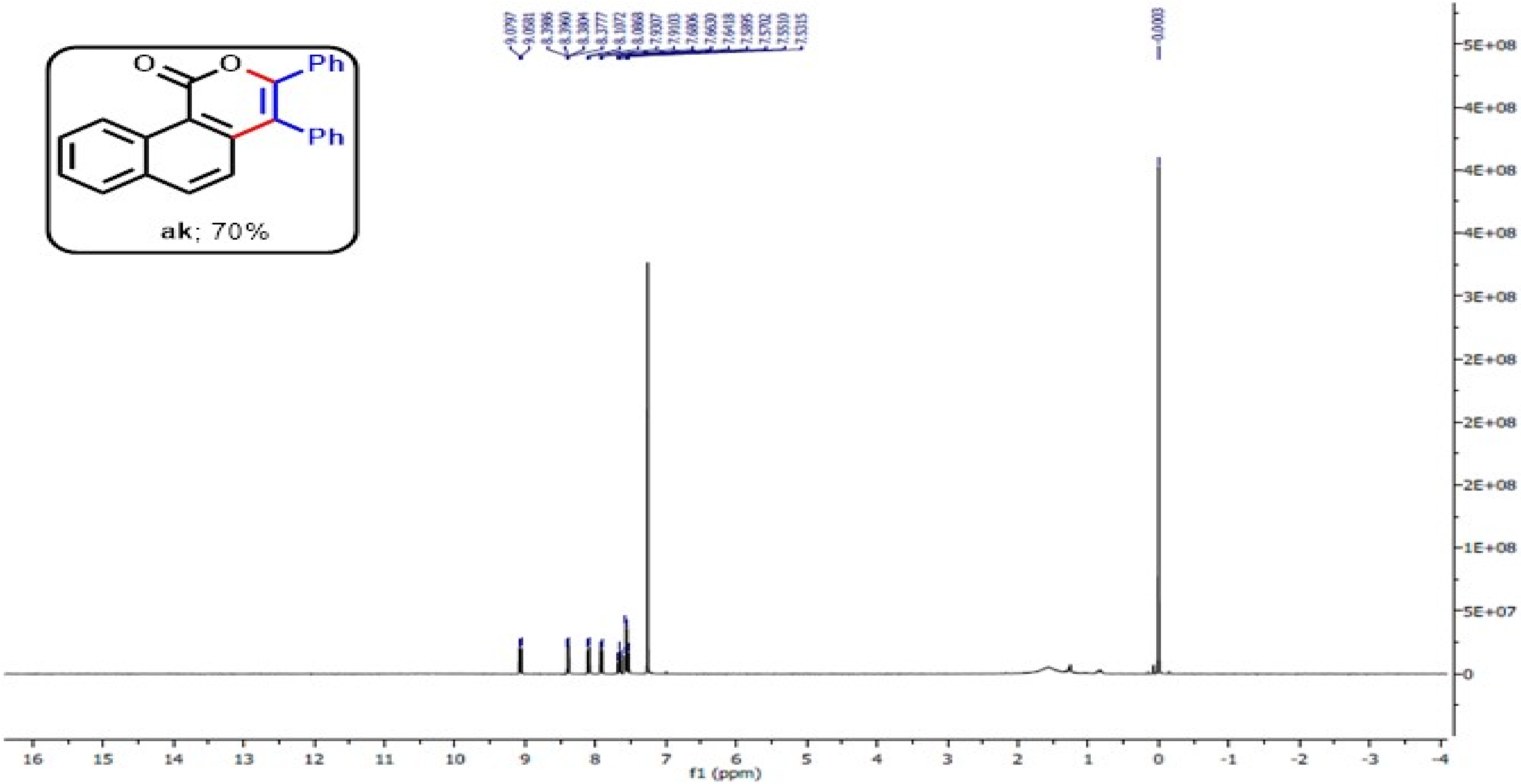
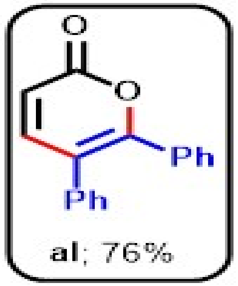


Figure S31: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **ak**



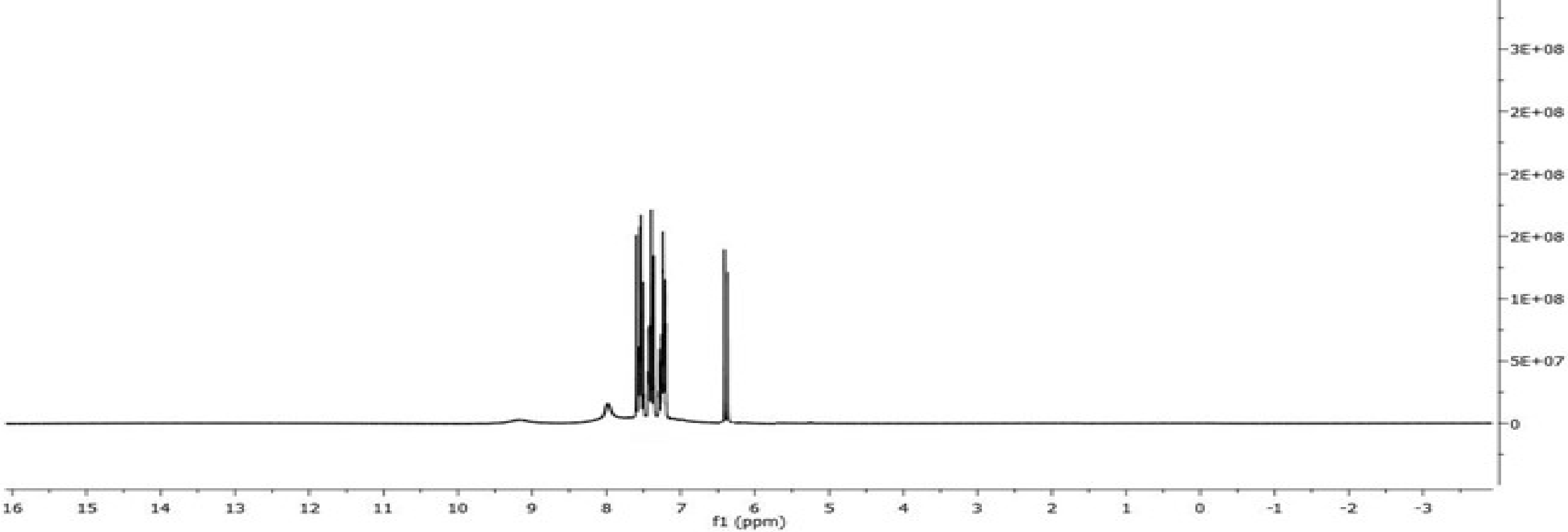


Figure S32: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **al**

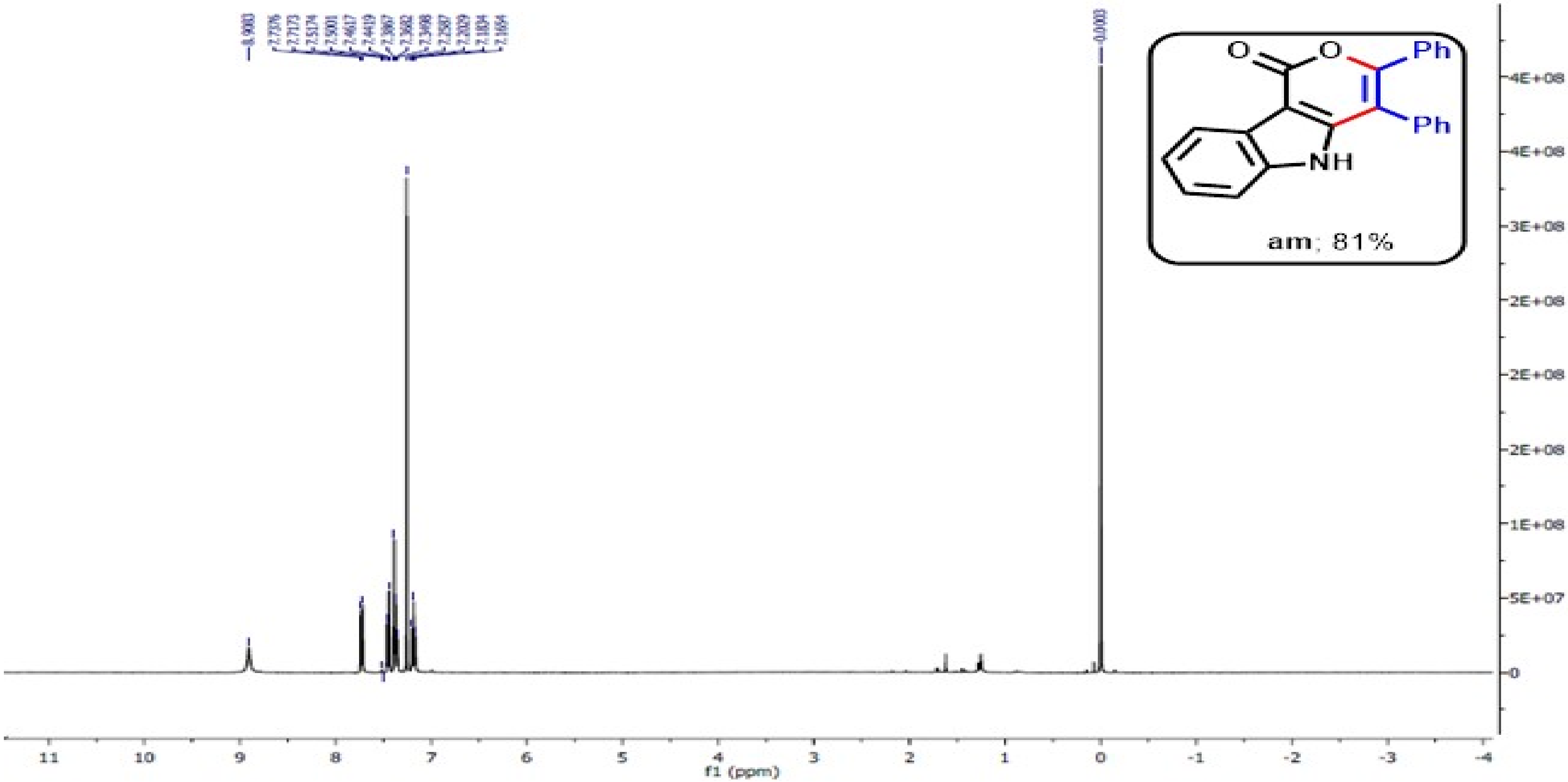


Figure S33: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **am**

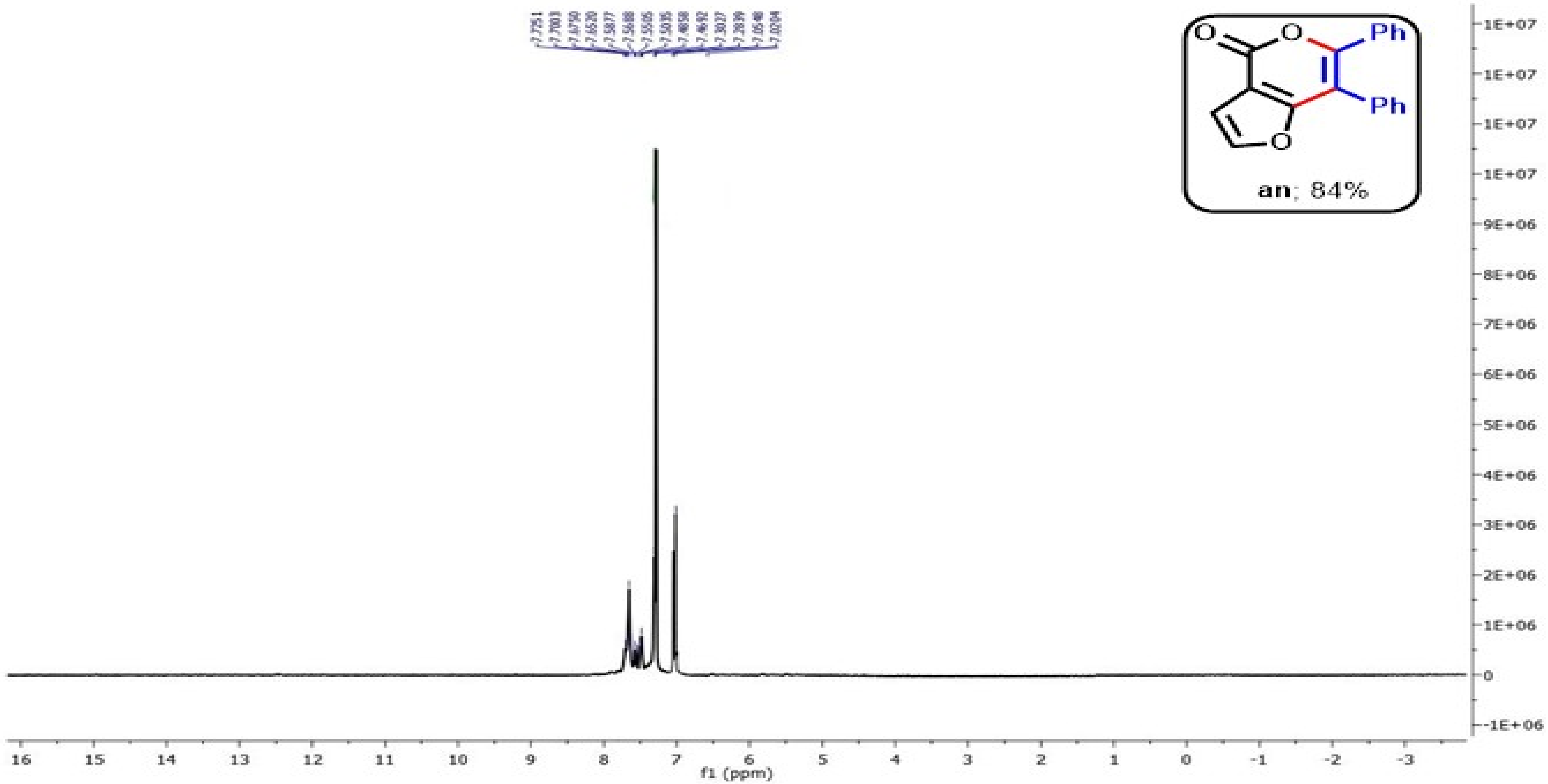


Figure S34: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **an**

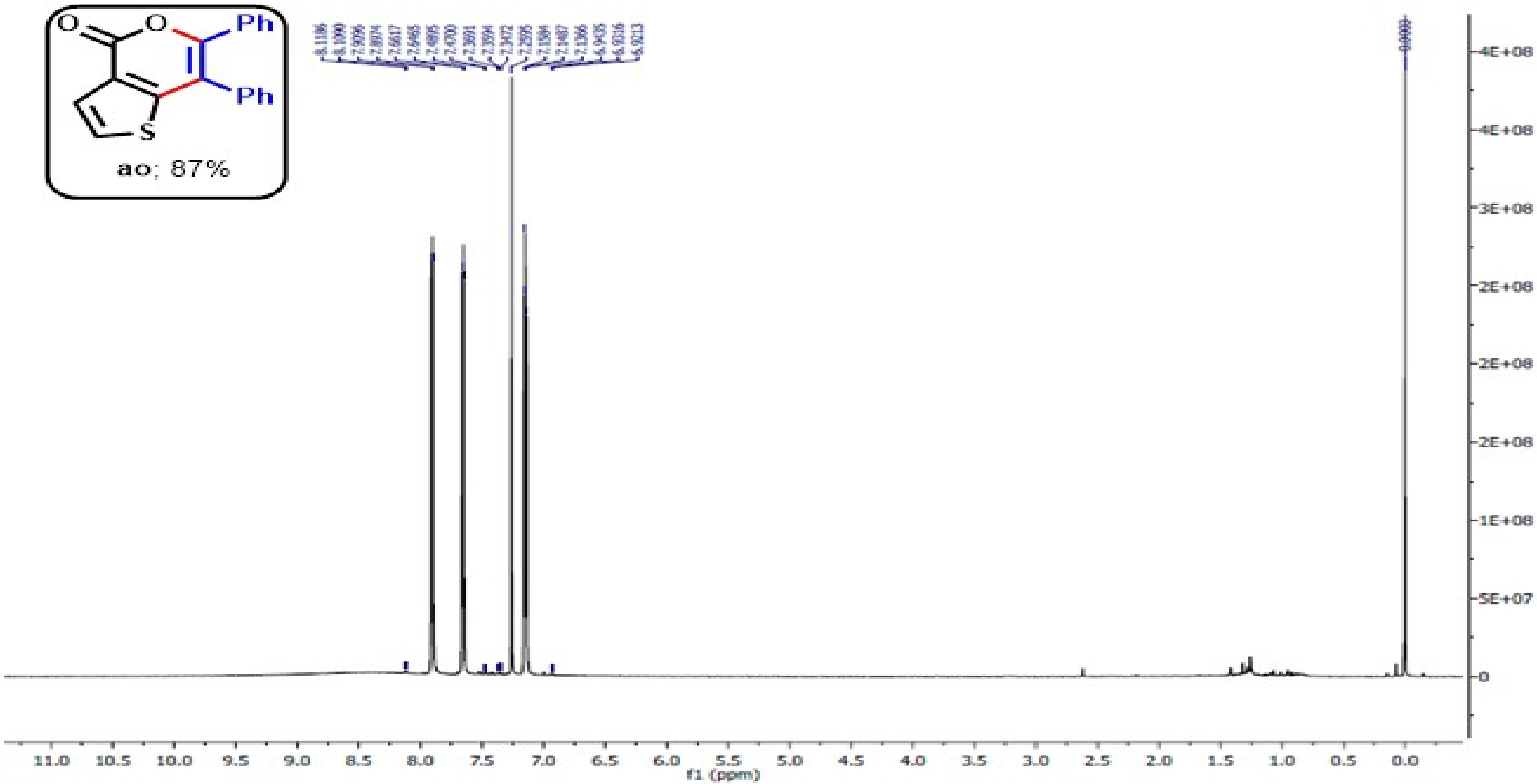


Figure S35: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **ao**

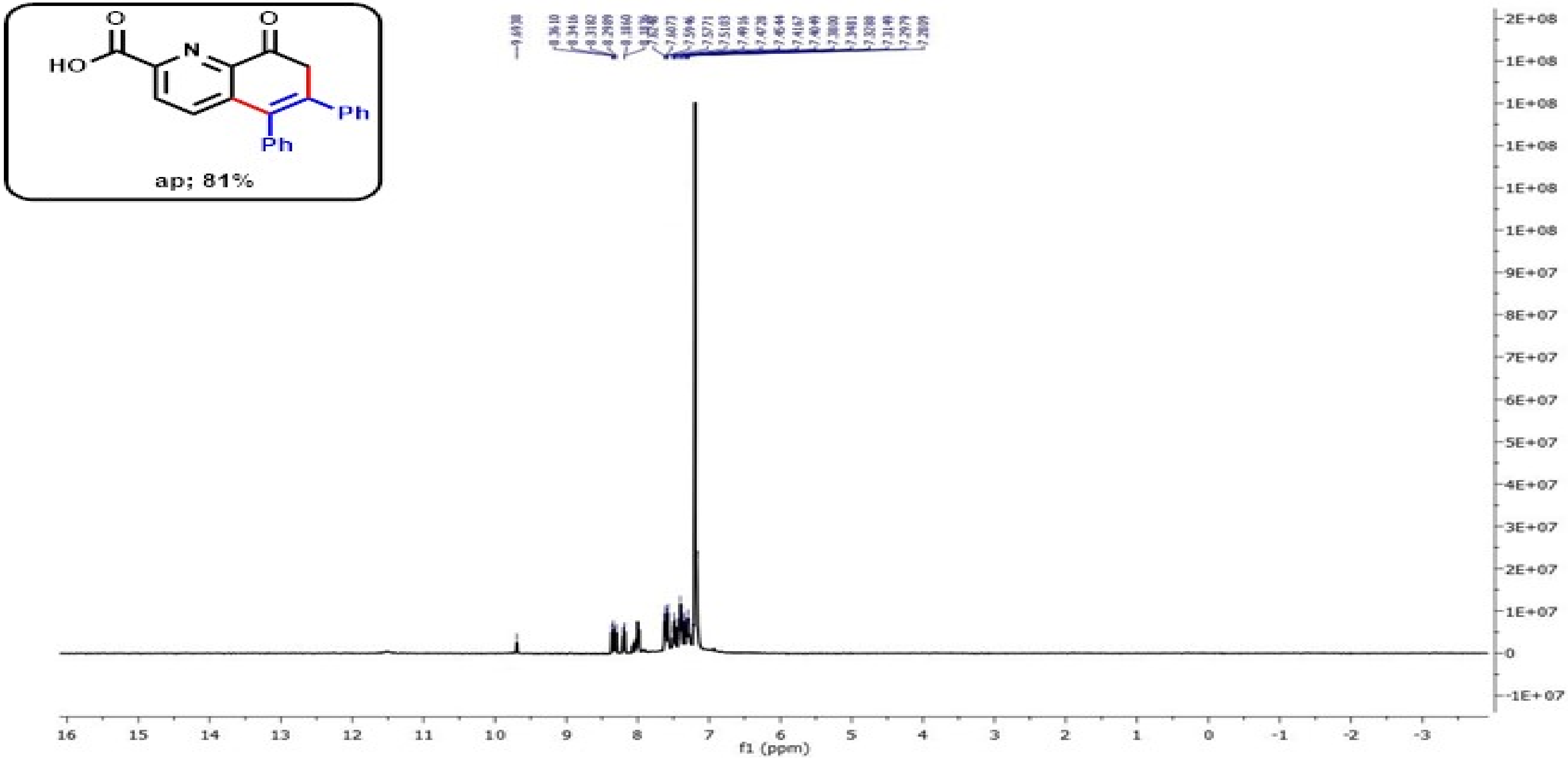


Figure S36: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **ap**

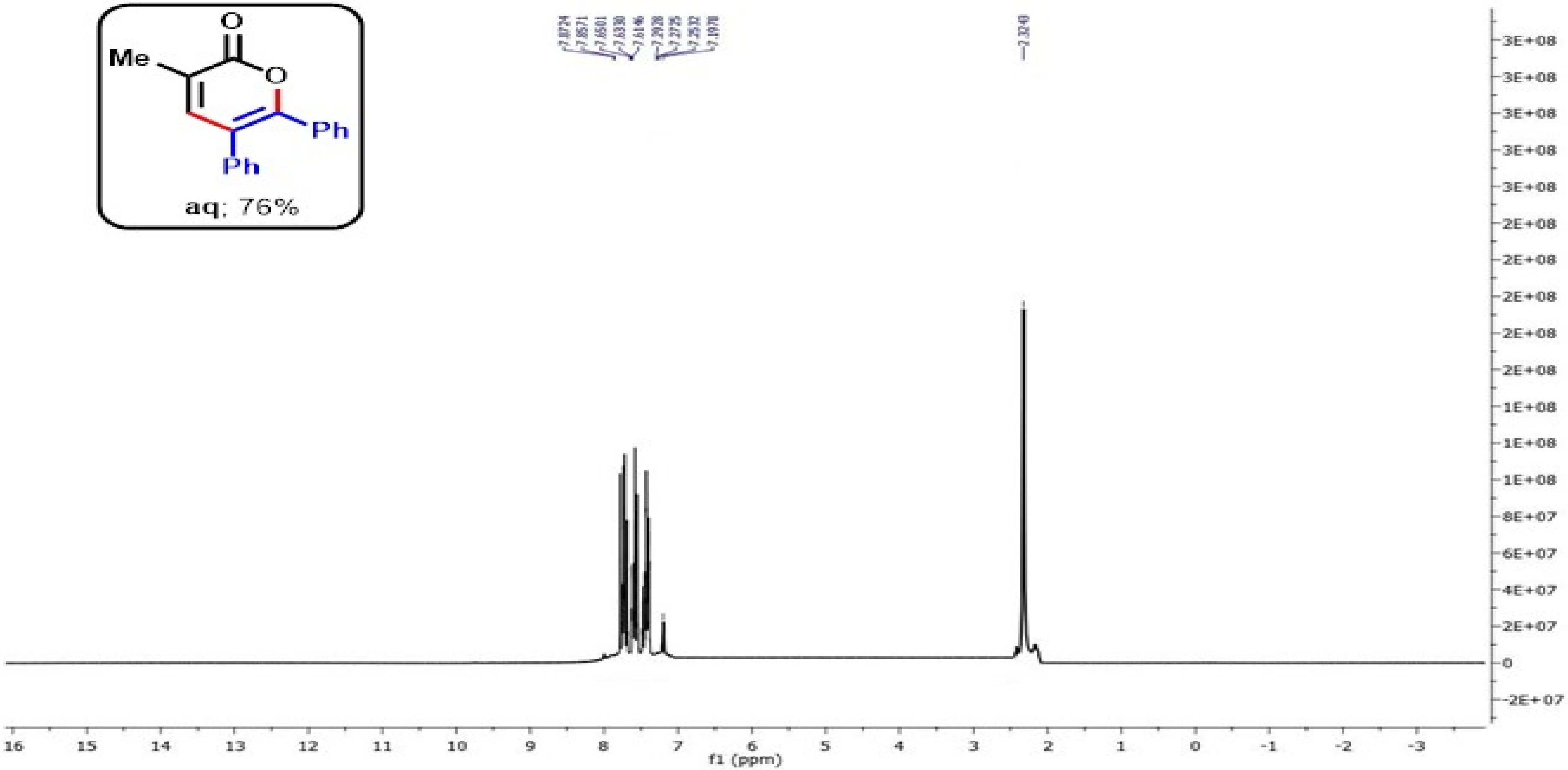


Figure S37: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **aq**

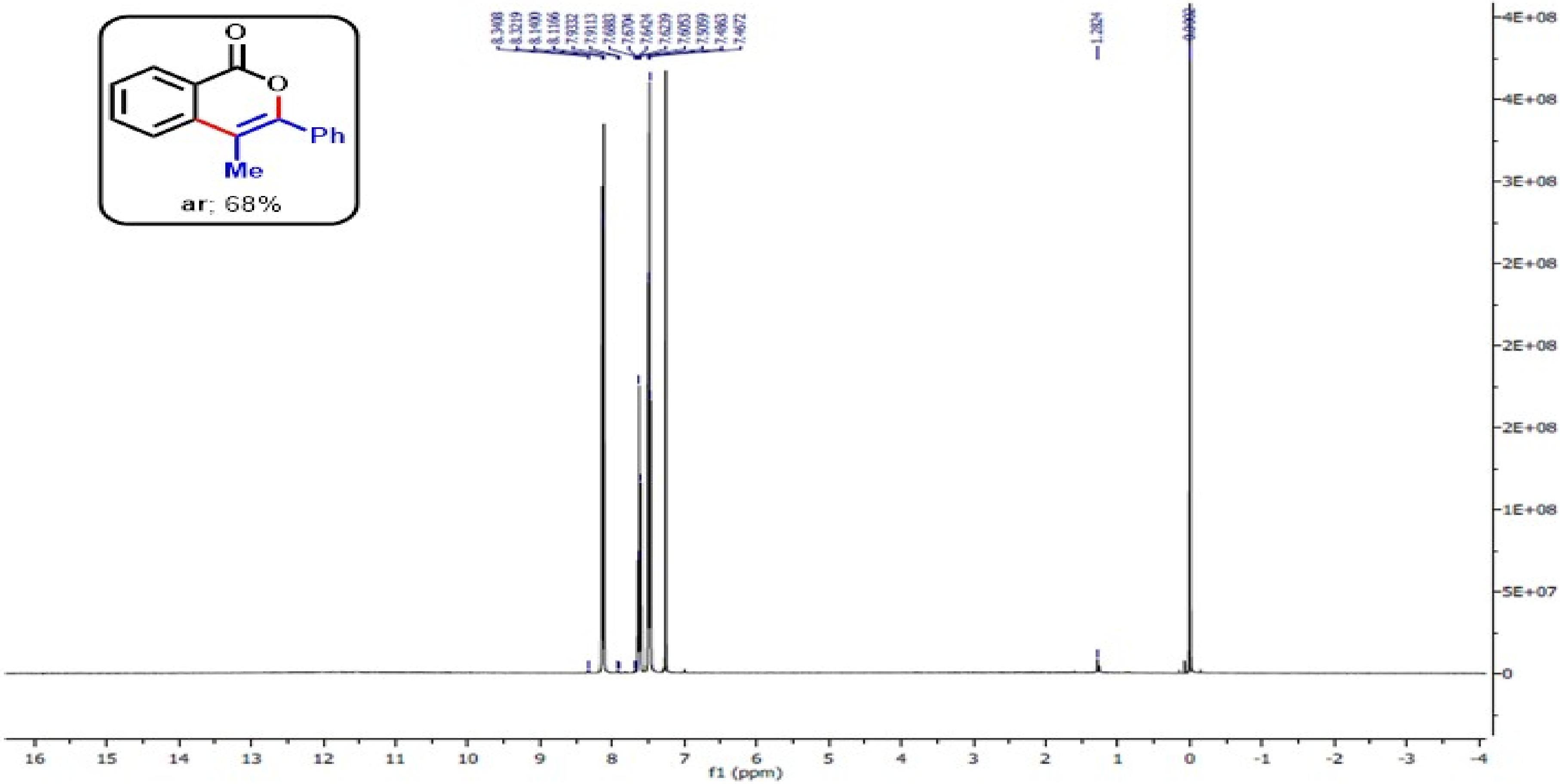


Figure S38: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **ar**

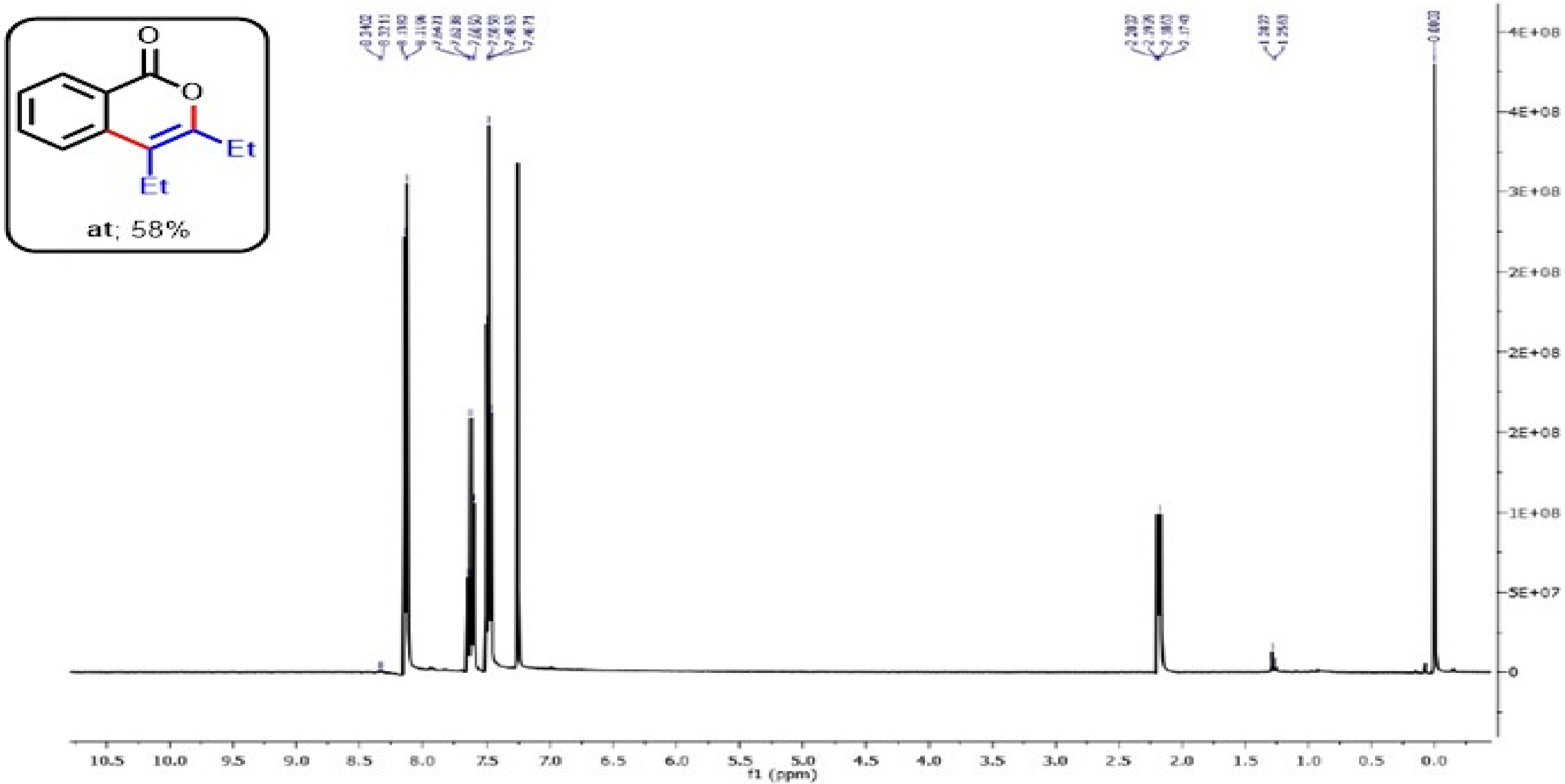


Figure S39: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **at**

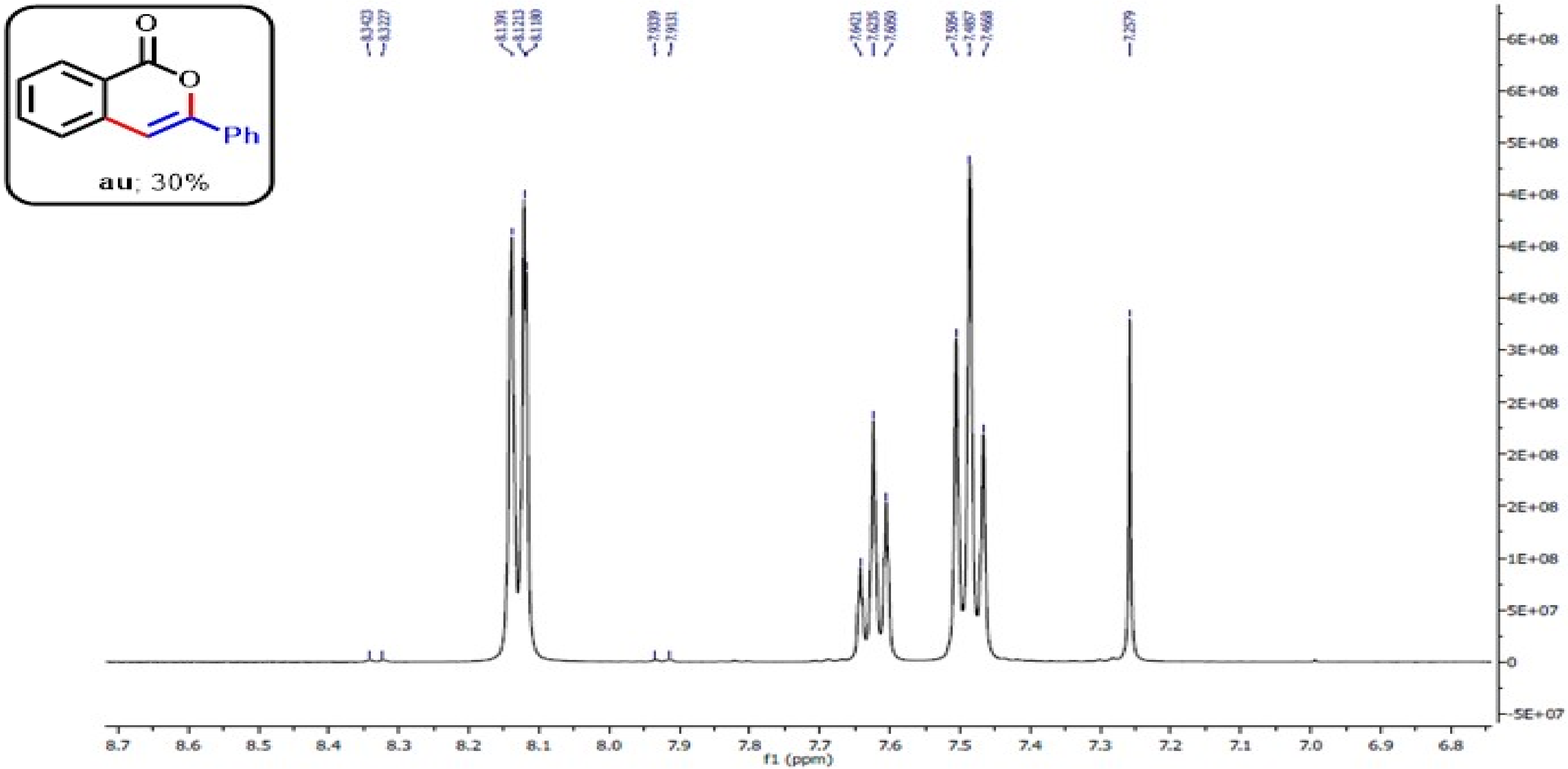


Figure S40: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **au**

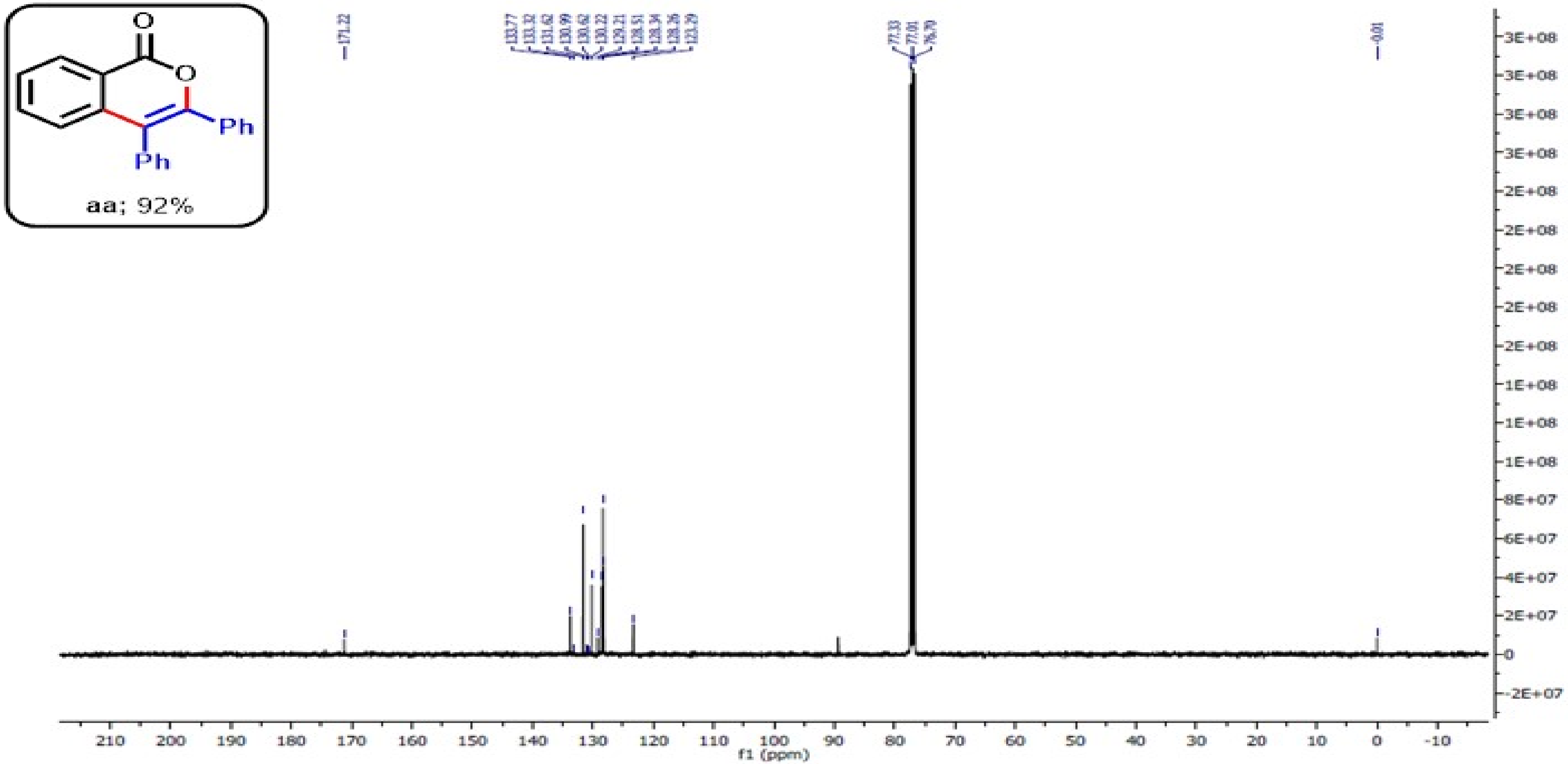
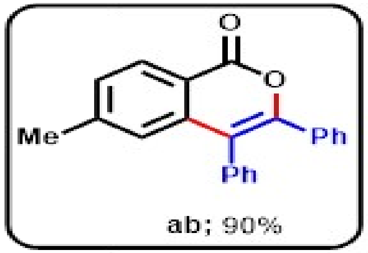


Figure S41: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **aa**



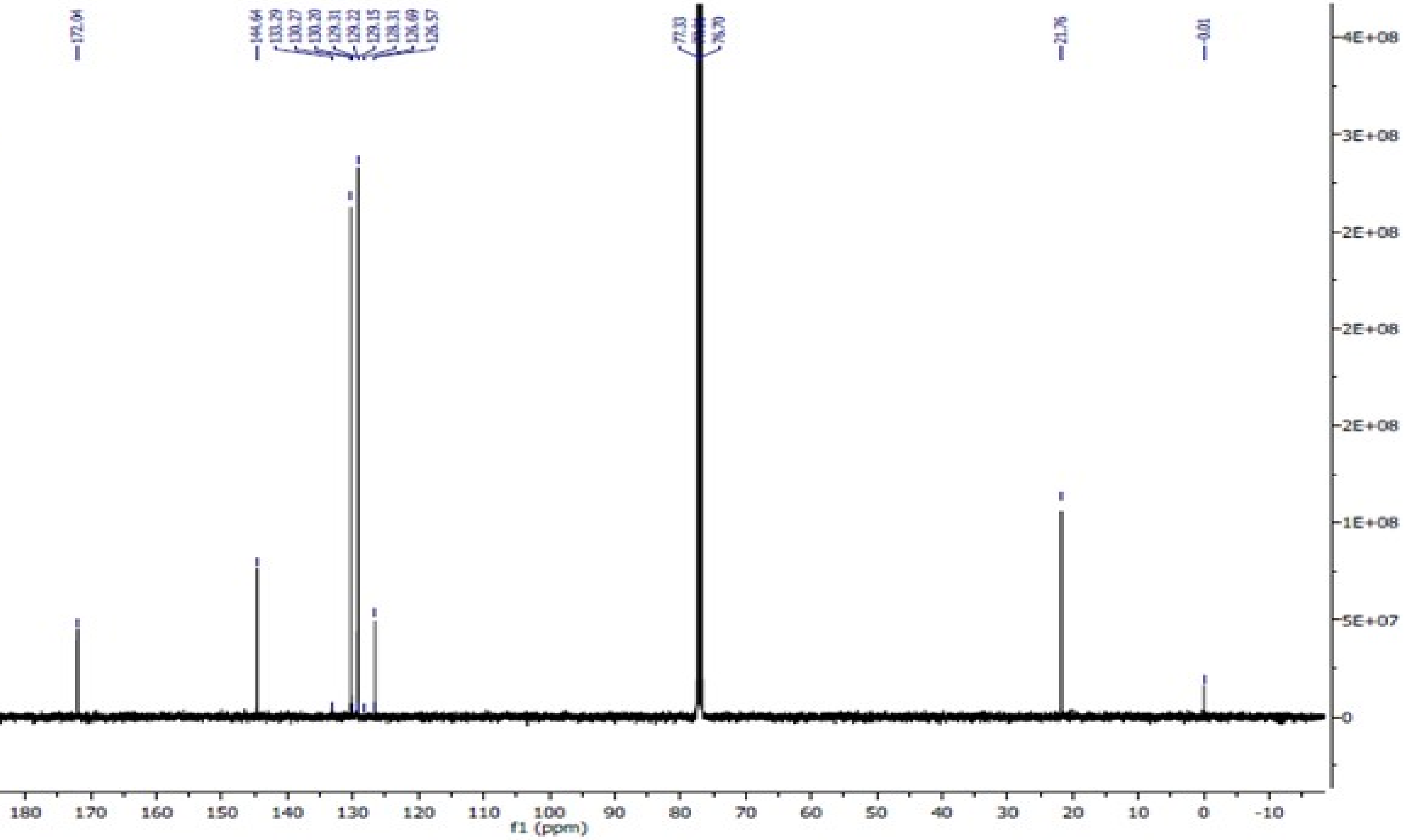
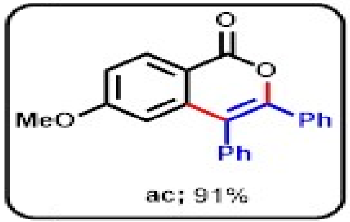


Figure S42: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **ab**



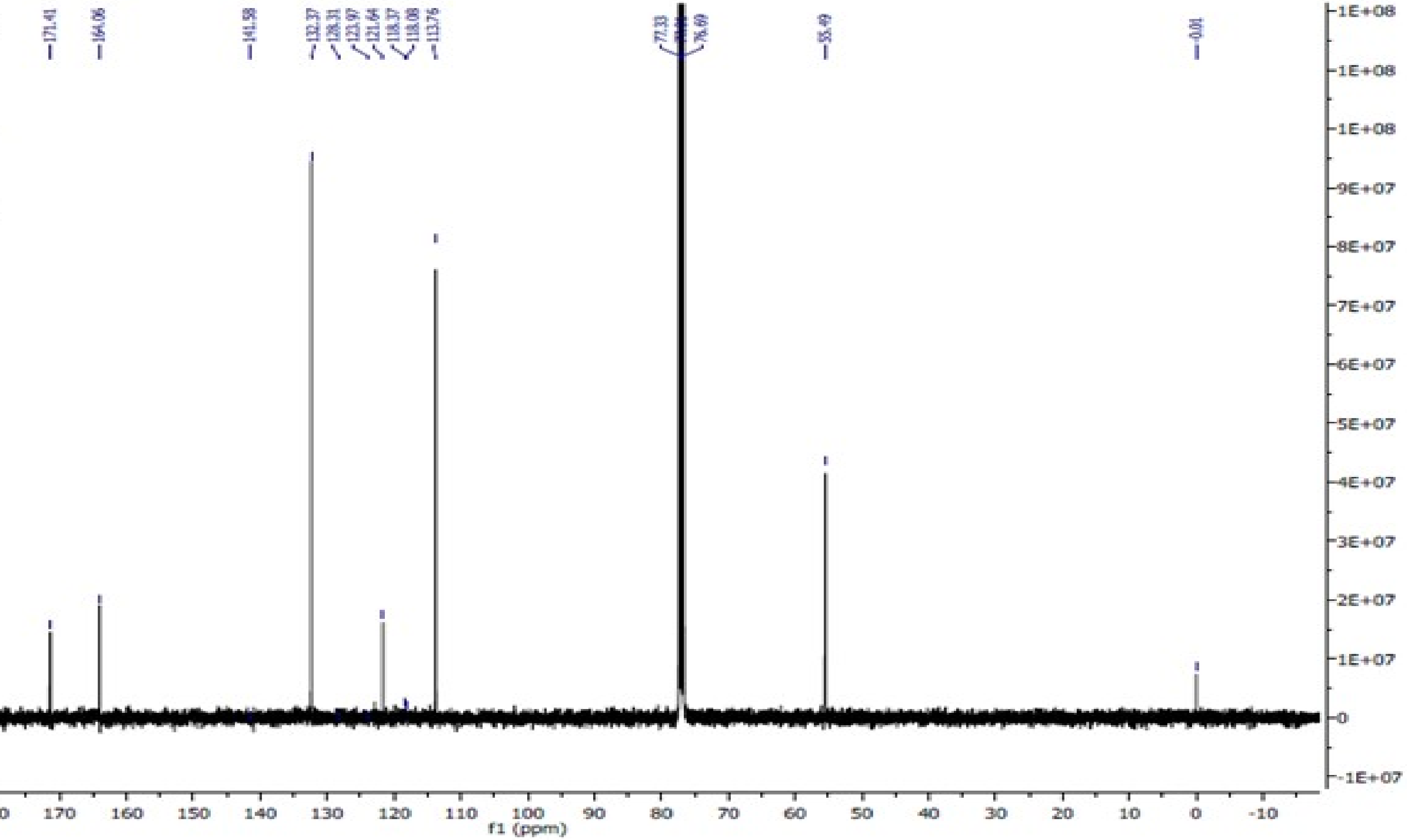


Figure S43: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **ac**

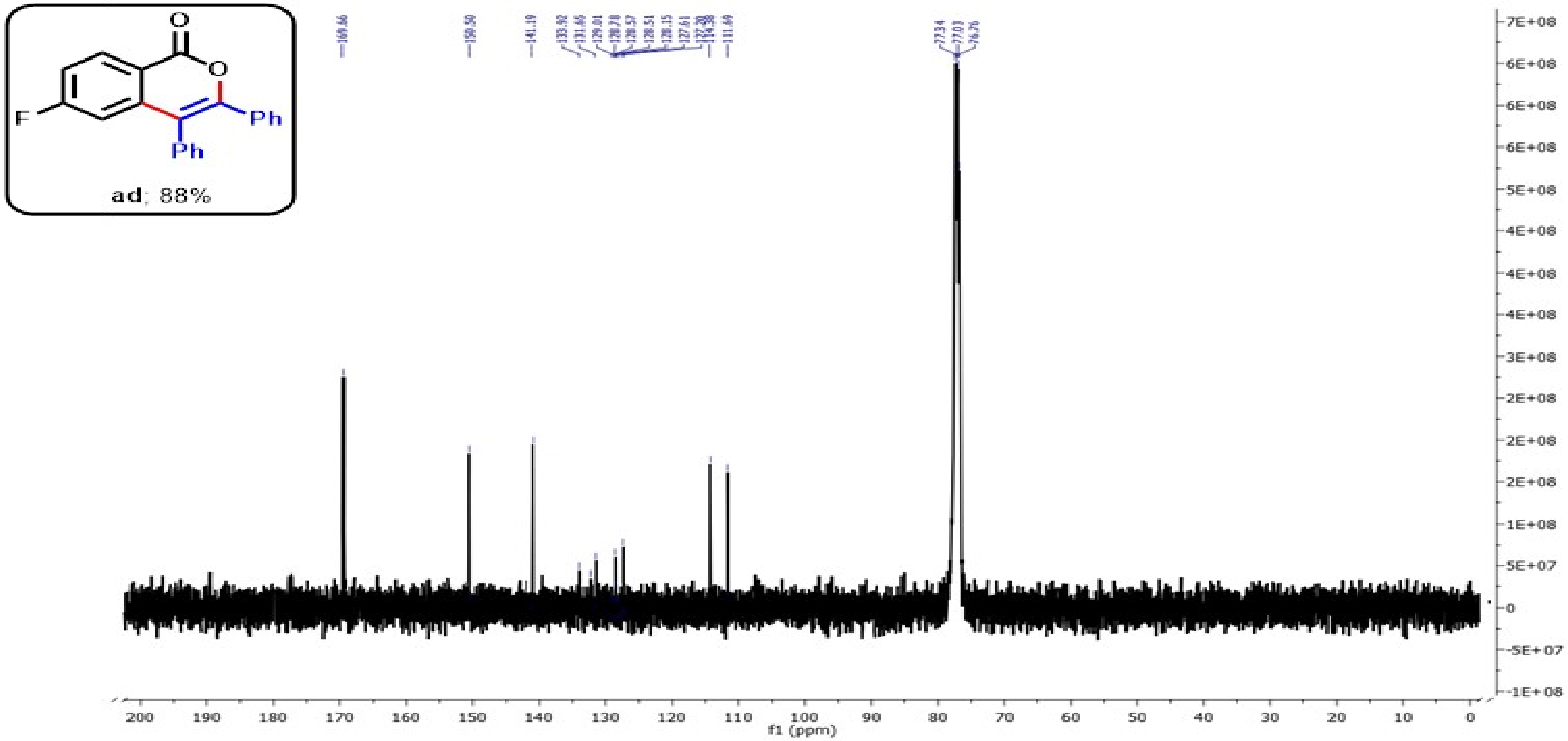


Figure S44: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **ad**

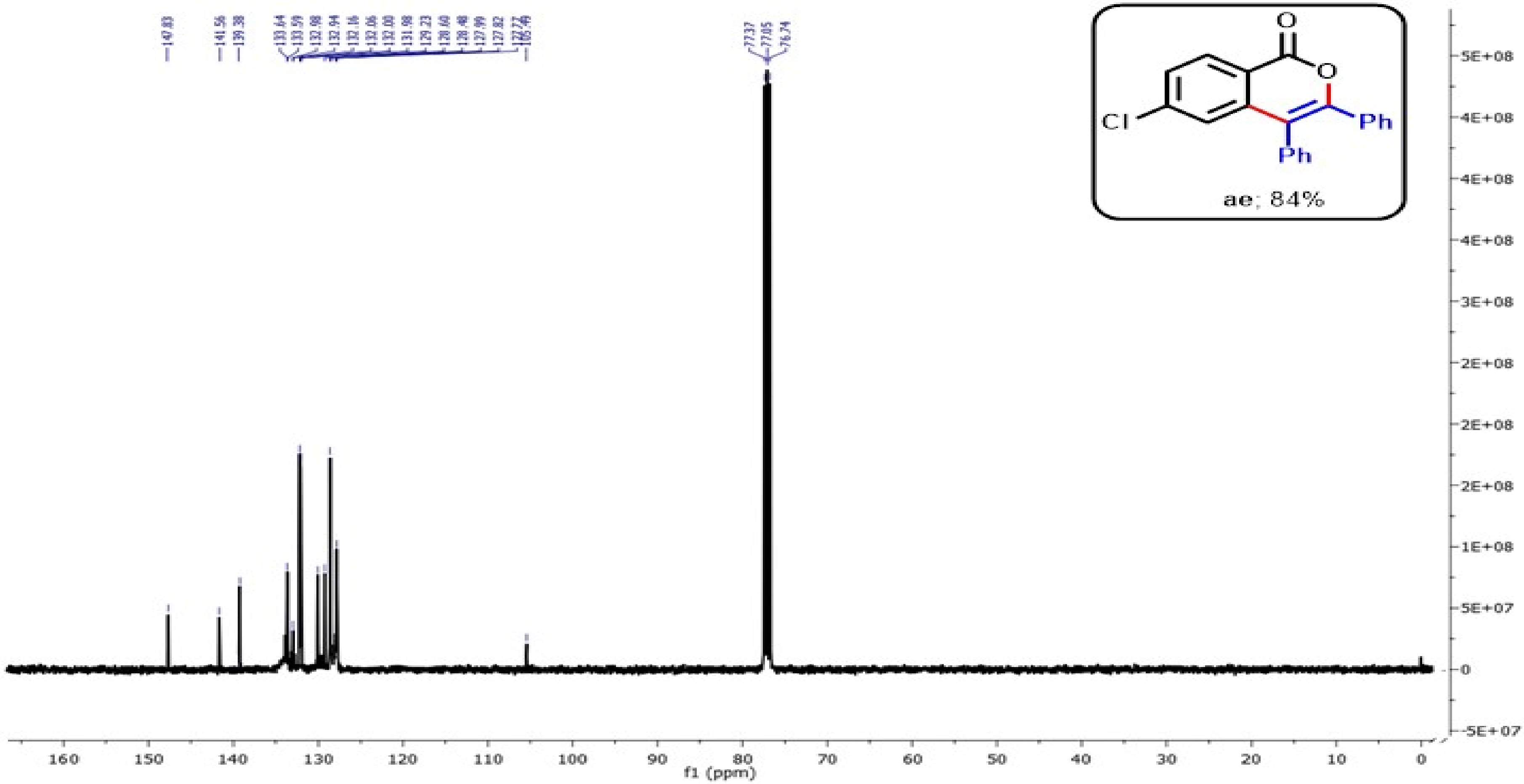


Figure S45: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **ae**

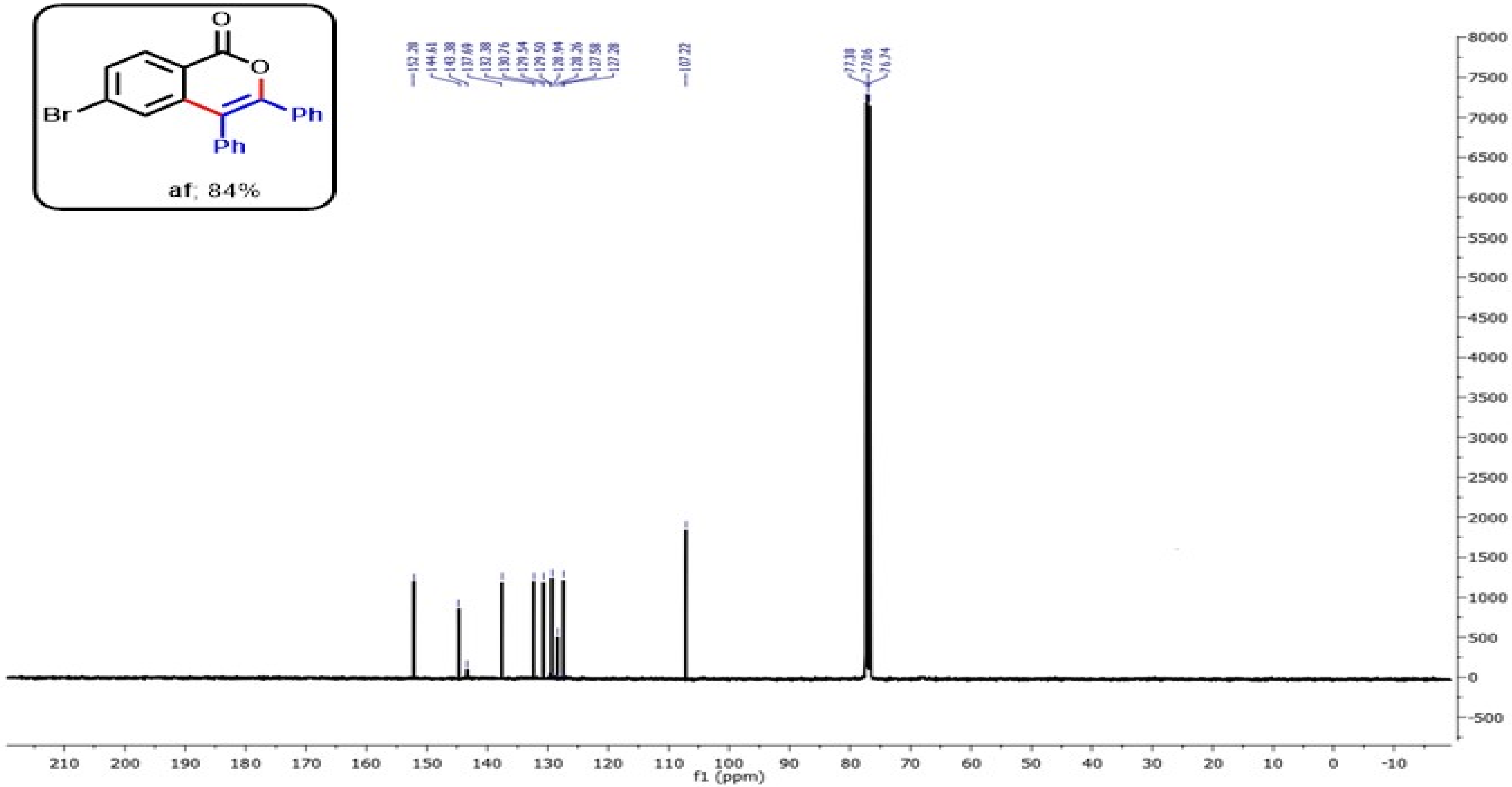


Figure S46: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **af**

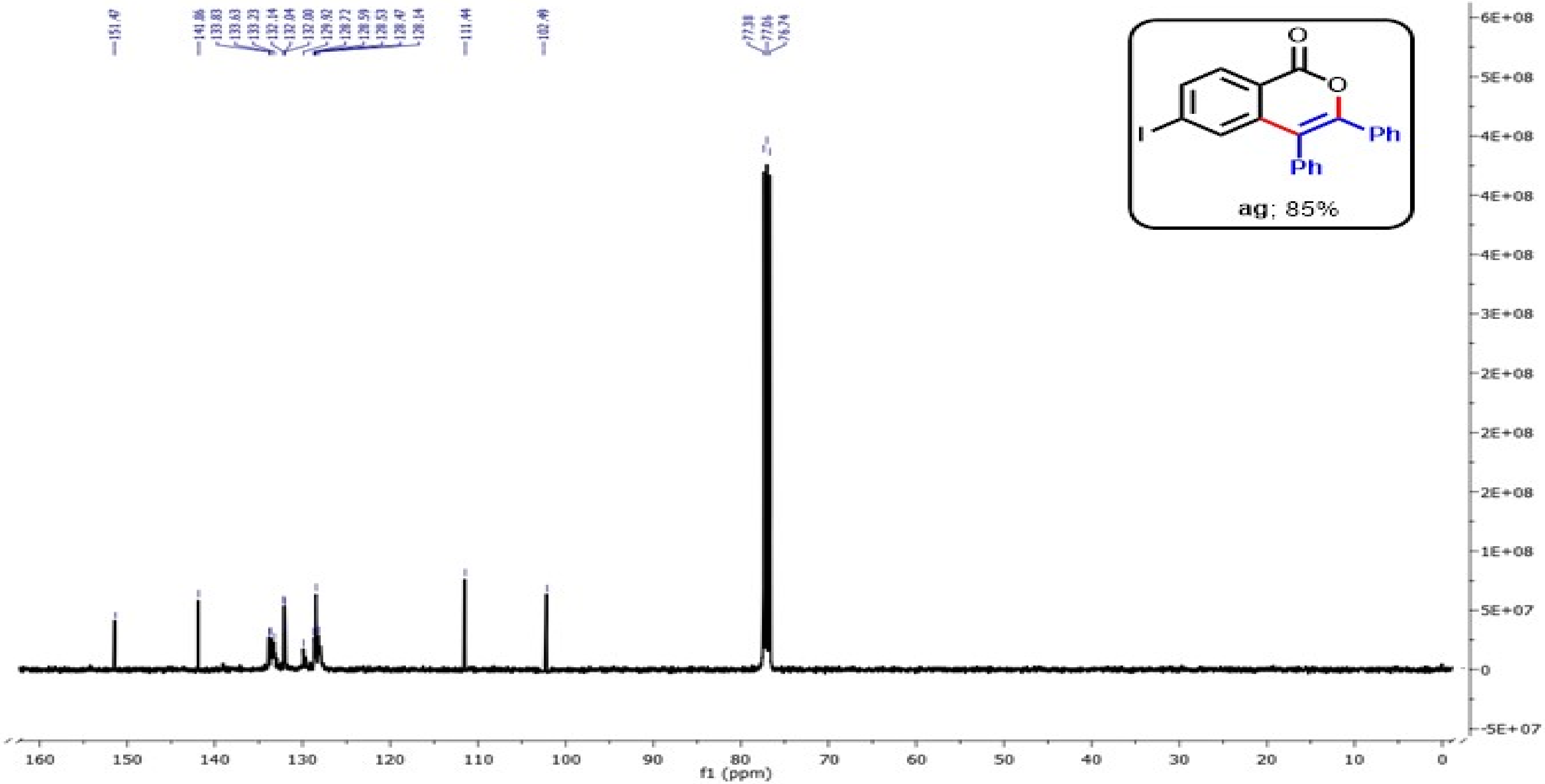


Figure S47: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **ag**

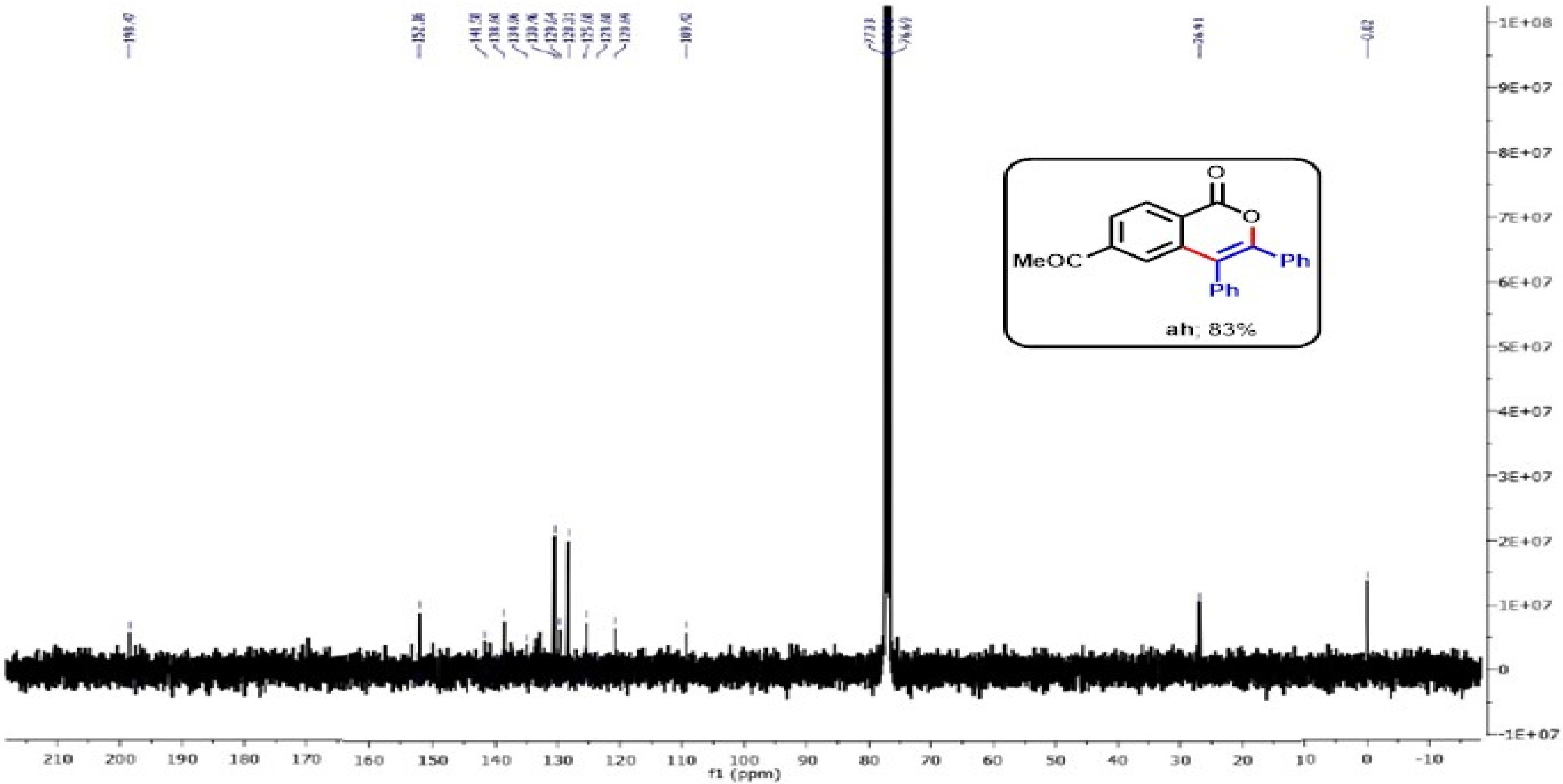


Figure S48: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **ah**

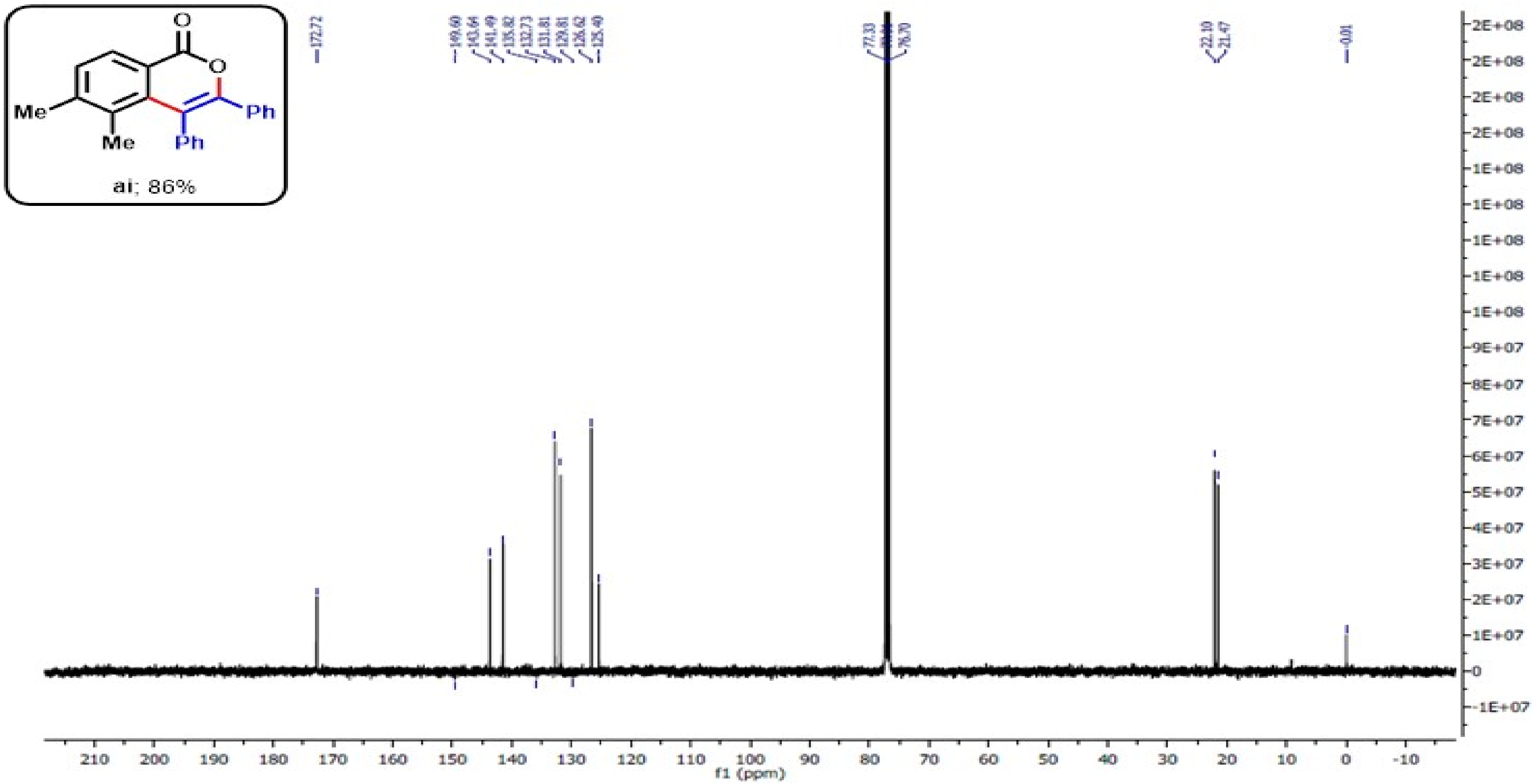


Figure S49: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **ai**

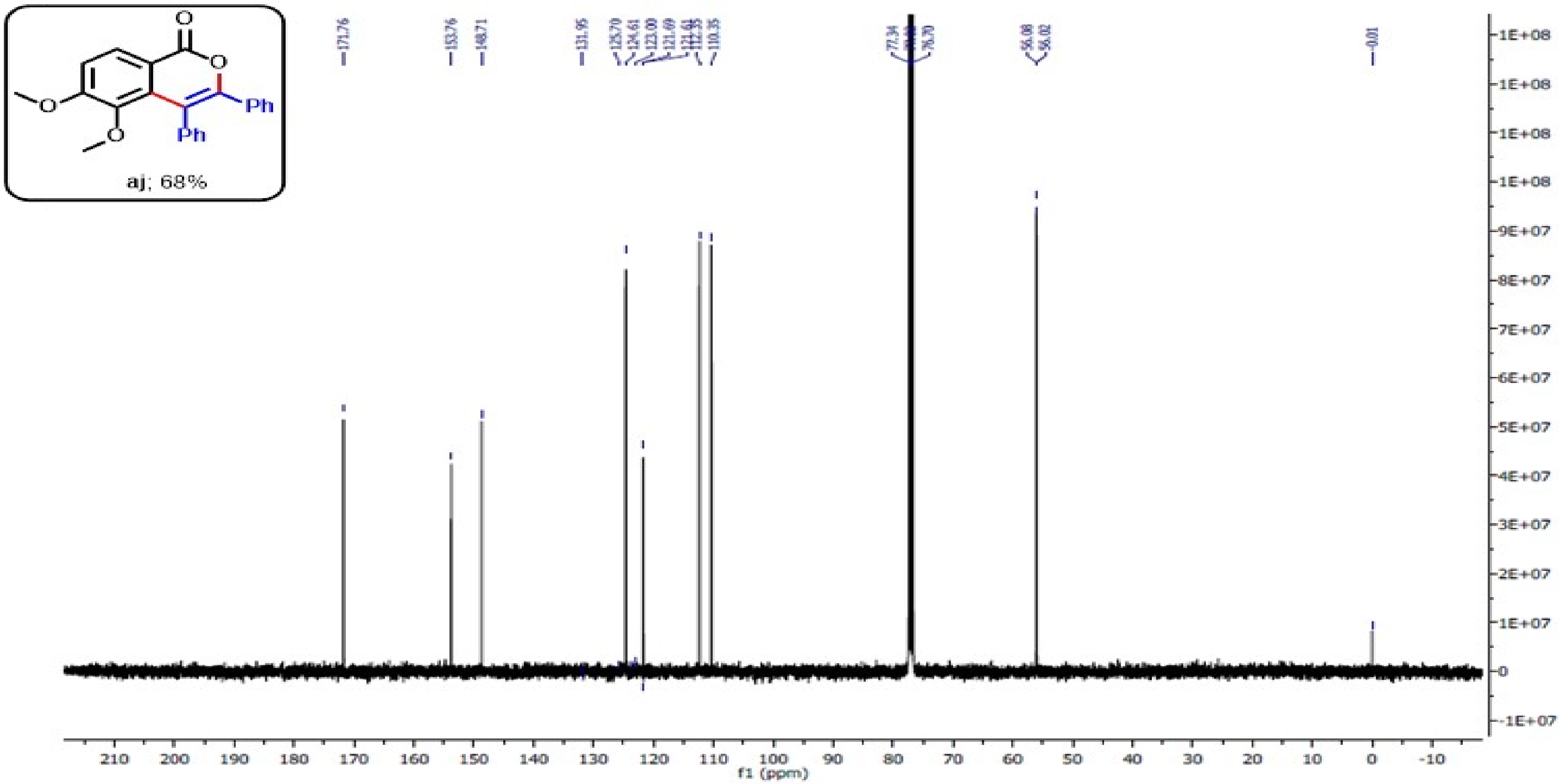


Figure S50: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **aj**

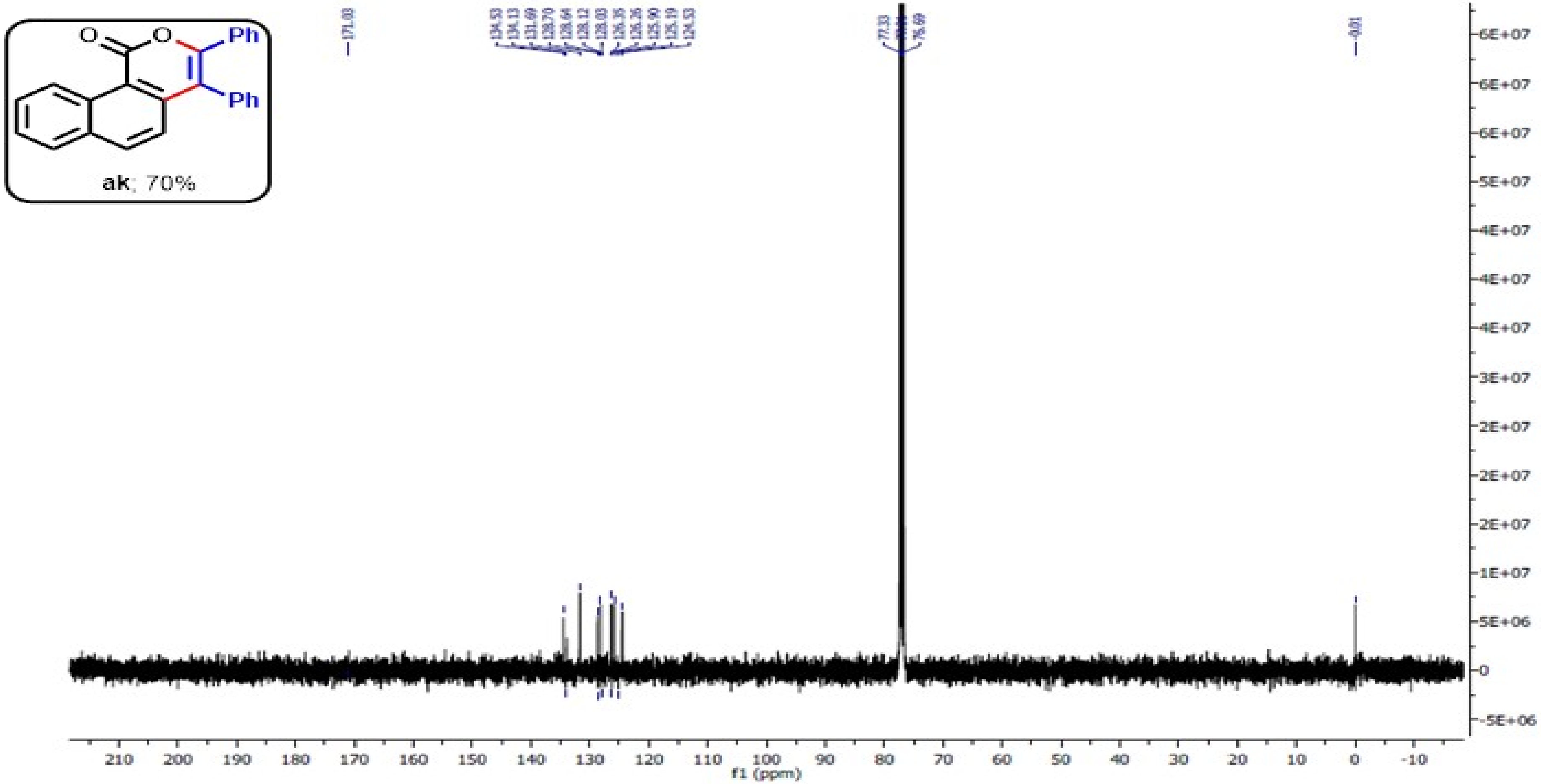


Figure S51: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **ak**

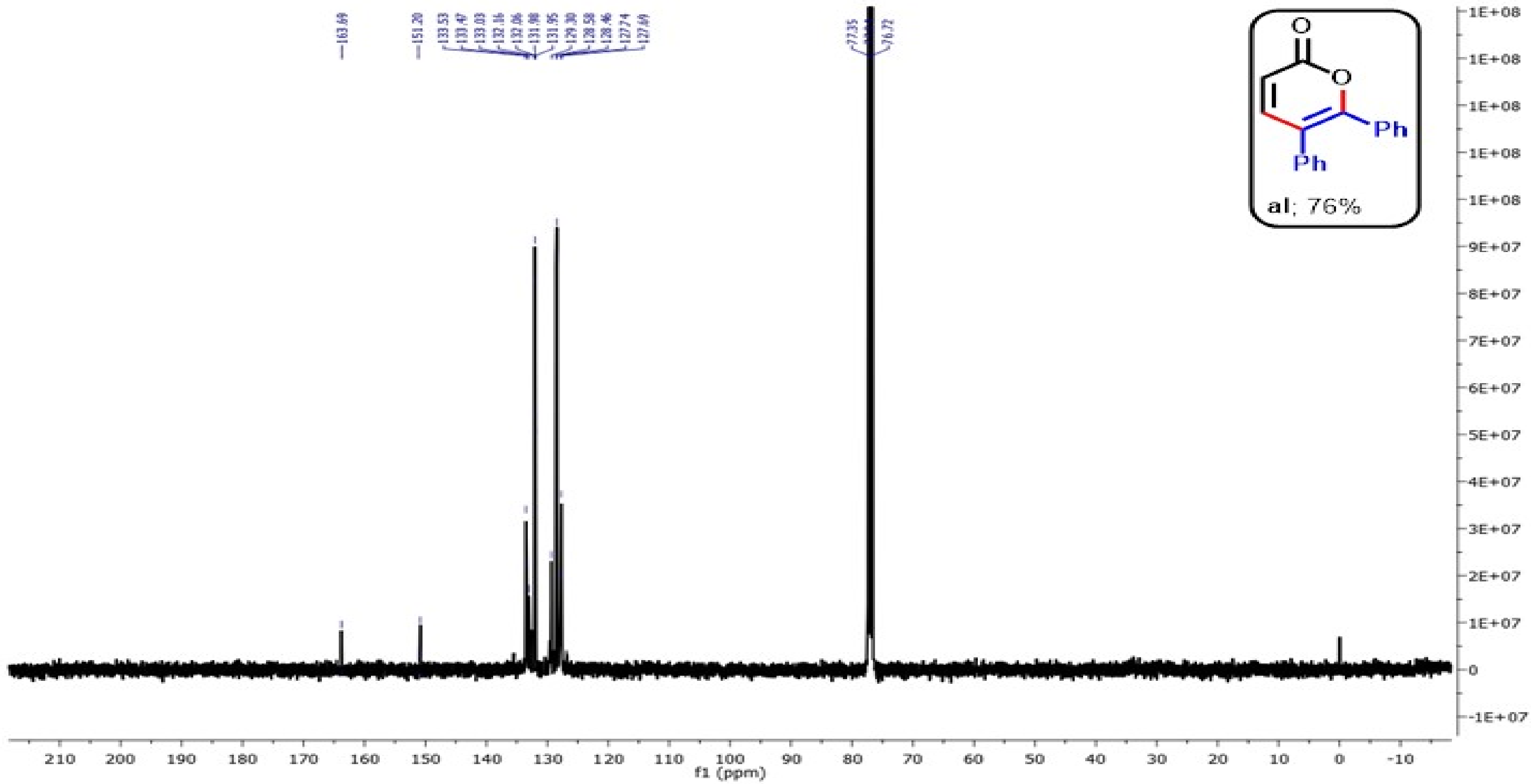


Figure S52: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **al**

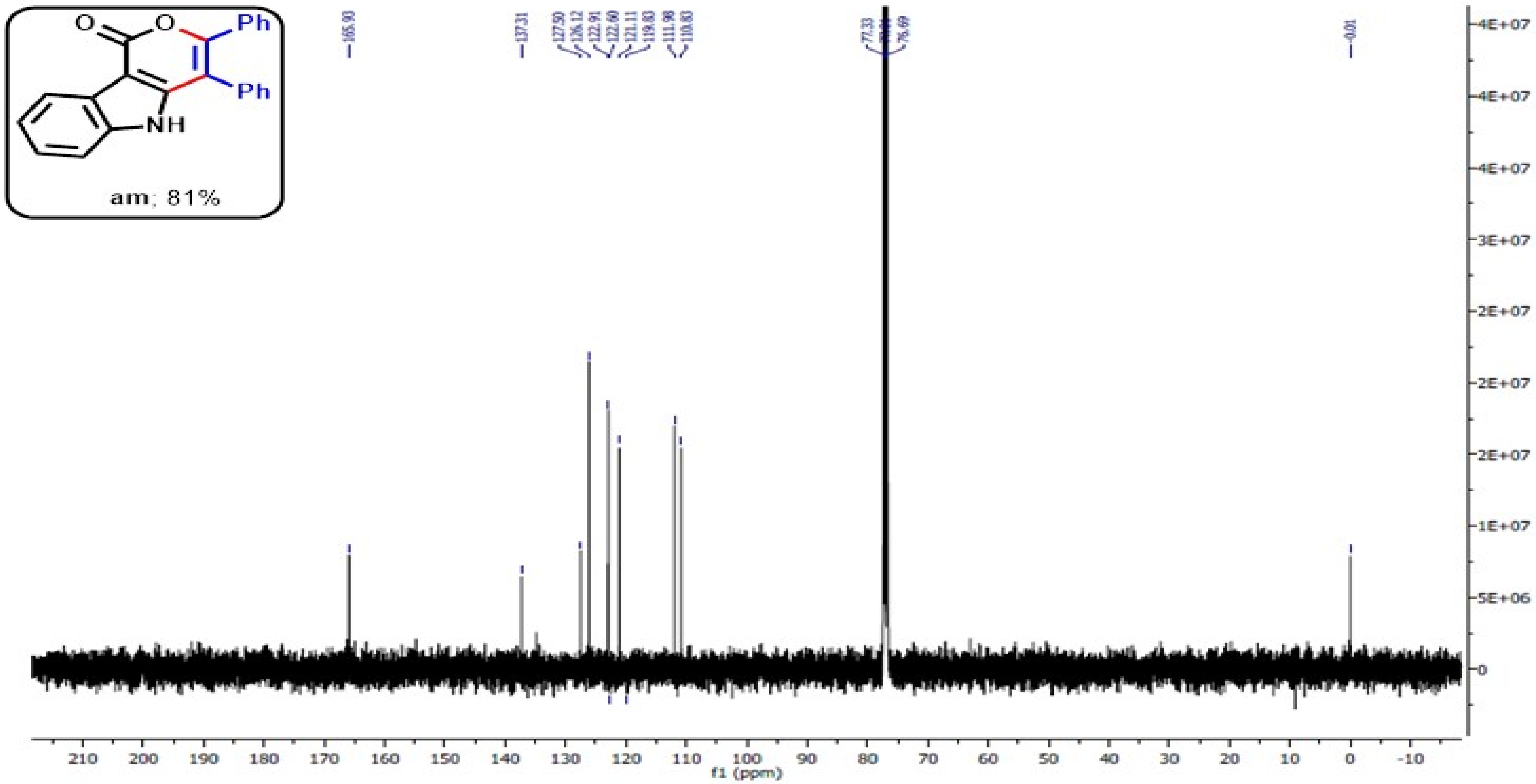


Figure S53: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **am**

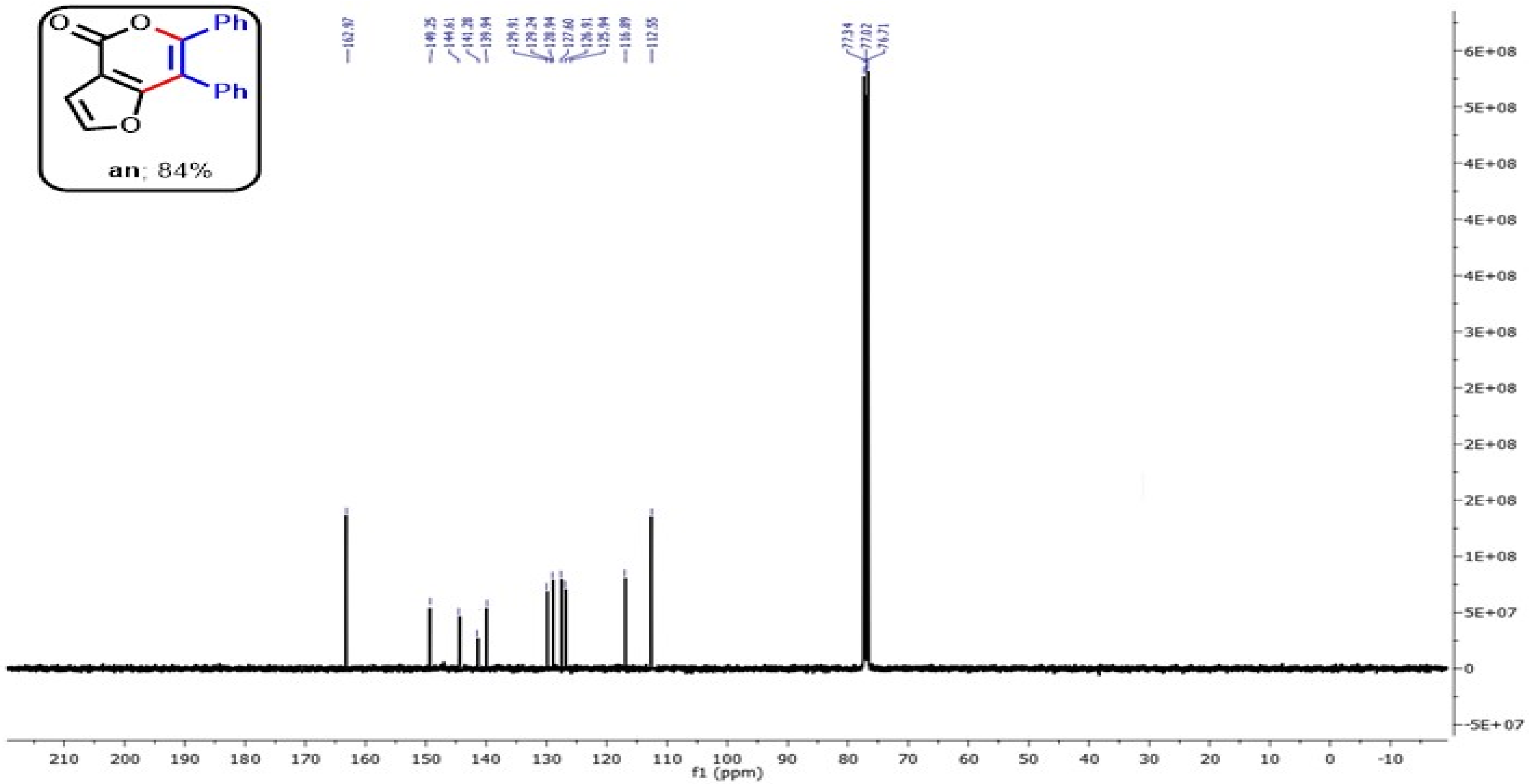


Figure S54: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **an**

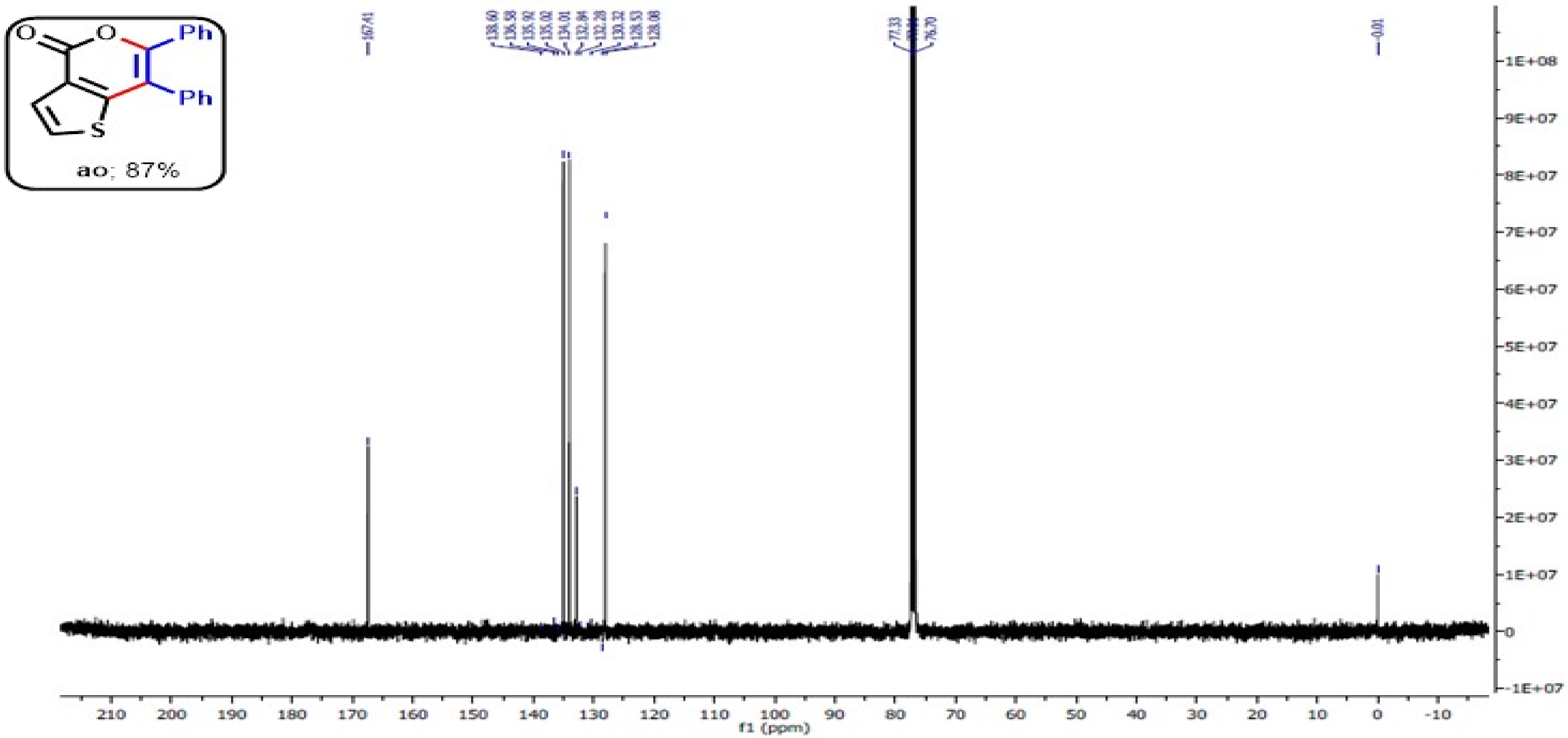


Figure S55: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **ao**

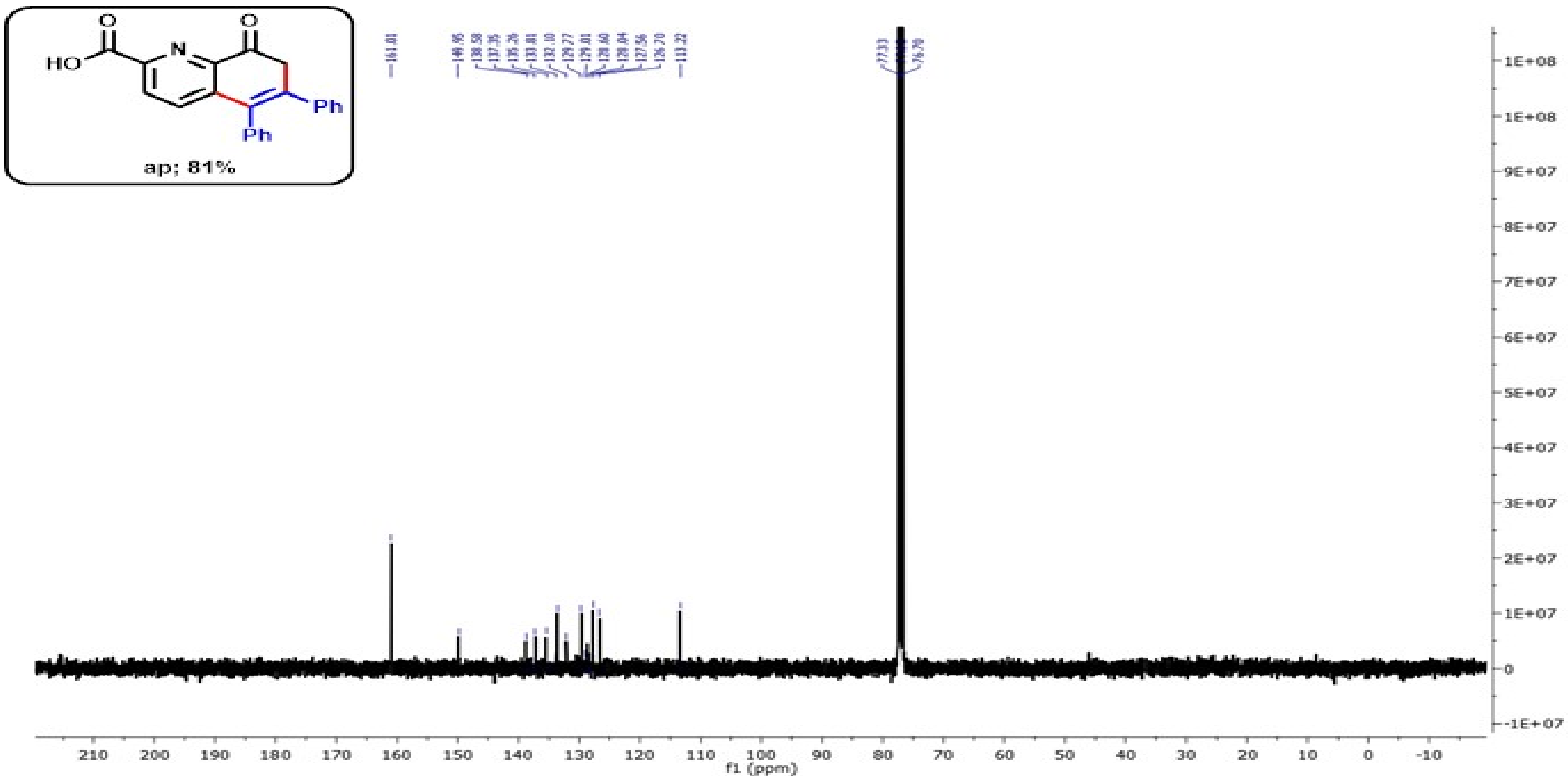


Figure S56: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **ap**

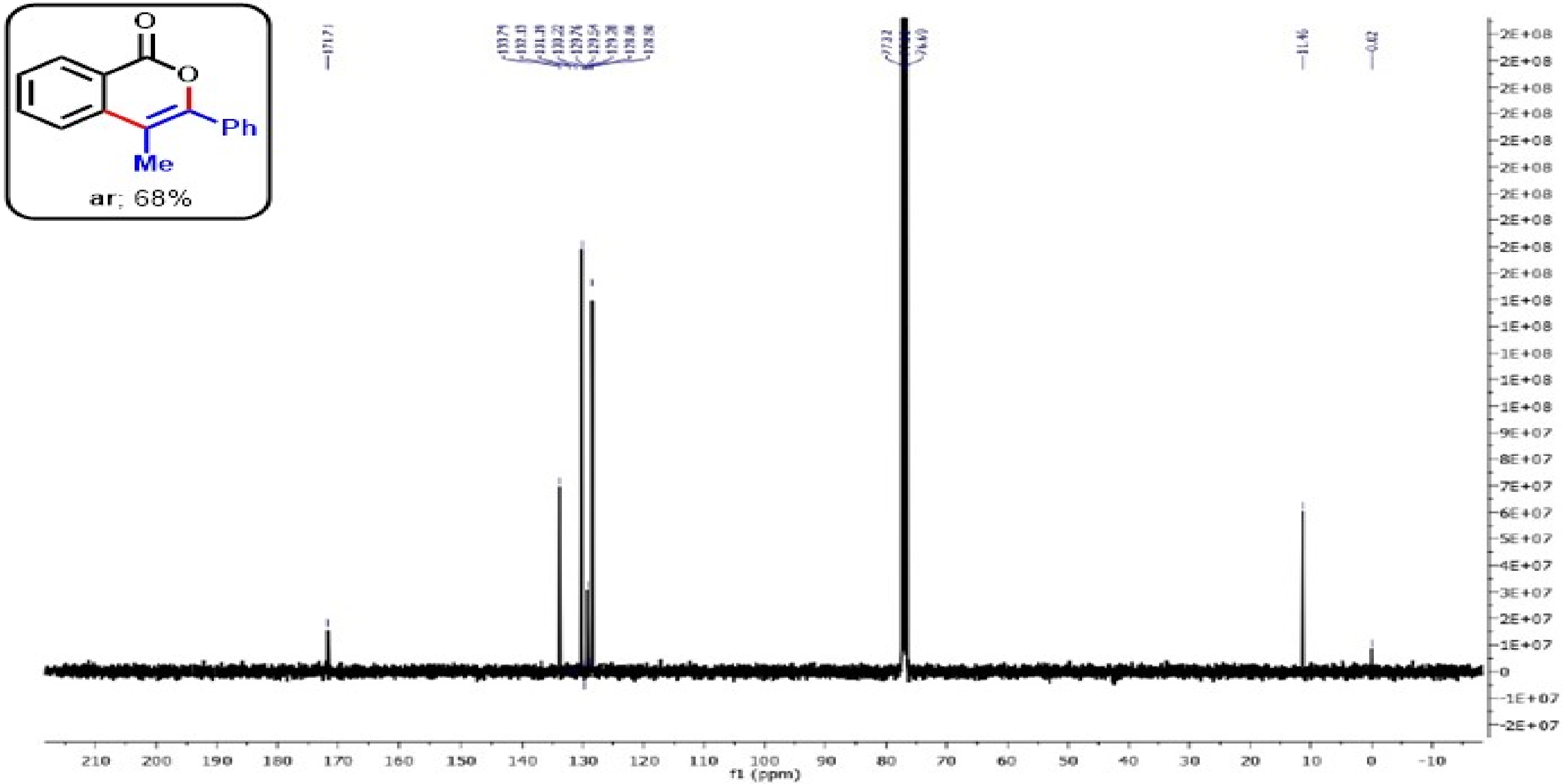
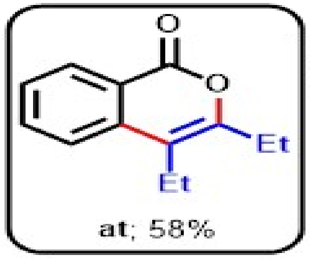


Figure S57: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **ar**



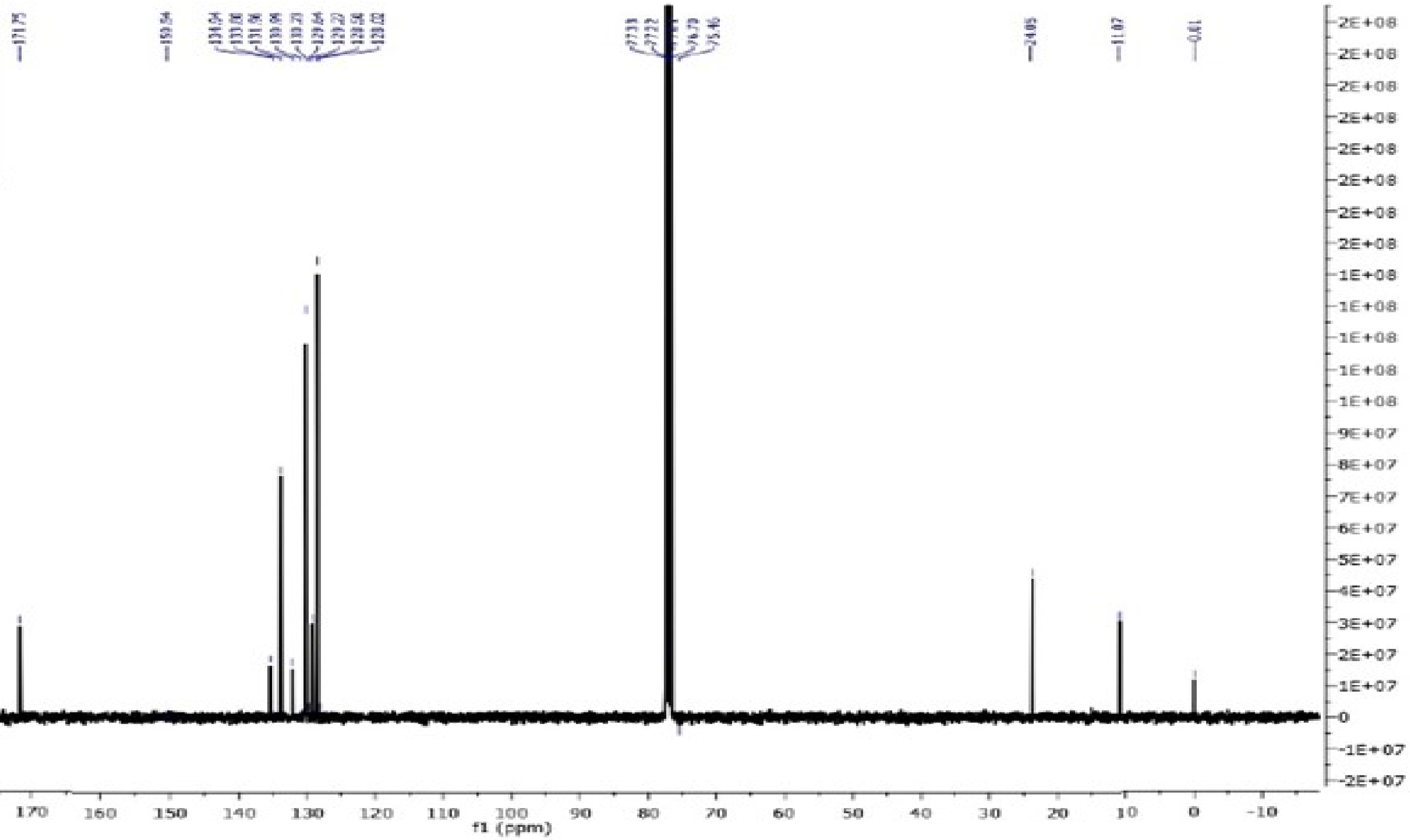


Figure S58: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **at**

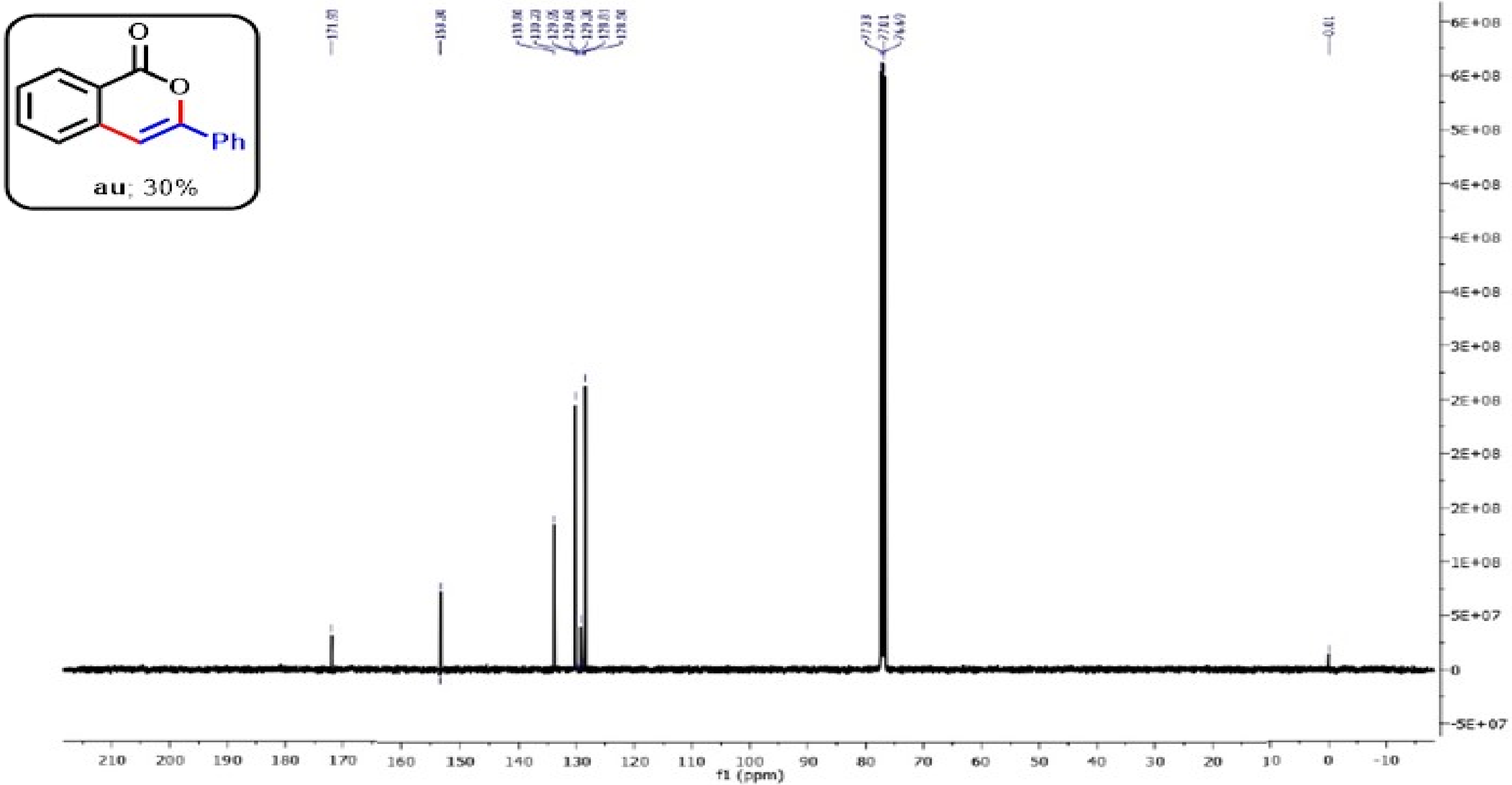


Figure S59: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of **au**

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[1] R. Kirana Chinnagolla, *Chem.Commun,* **2012**, *48*, 2030-2032.

[2] R. Prakash, K. Shekarrao, S. Gogoi, R. C. Boruah, *Chem. Commun.* **2015**, *51*, 9972-9974.

[3] S. Wen, Y. Chen, Z. Zhao, D. Ba, W. Lv, G. Cheng, *J.Org.Chem.* **2019**, *85*, 1216-1223.