Electronic Supplementary Information

A competitive and highly selective 7-, 6- and 5-annulation with 1,3-migration through C-H, N-H - alkyne coupling

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1. Materials and Methods

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred *via* syringe using standard Schlenk techniques. All the solvents and reagents were used as received unless otherwise noted. Petroleum ether used in our experiments was in the boiling range of 60-80 °C. Reaction temperatures above 25 °C refer to oil bath temperature. Thin layer chromatography was performed using silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, anisaldehyde stain and other stains. Silica gel of particle size 100-200 mesh was used for column chromatography. Melting points were recorded on a digital melting point apparatus from Jyoti Scientific (AN ISO 9001:2000) and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded 300 MHz and 400 MHz spectrometers with ^{13}C operating frequencies of 75 MHz and 100 MHz. Chemical shifts (δ) are reported in ppm relative to the residual solvent $CDCl_3$ signal (δ = 7.24 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR), DMSO-d_6 signal (δ = 2.47 for ^{1}H NMR and δ = 39.4-40.6 for ^{13}C NMR) and CD_3OD signal (δ = 49.0 for ^{13}C NMR). Data for ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, number of hydrogen and coupling constants). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a FT-IR system (Spectrum BX) and are reported in frequency of absorption (cm^{-1}). Only selected IR absorbance is reported. High-Resolution Mass Spectrometry (HRMS) data was recorded on Q-tof-micro quadruple mass spectrophotometer using acetonitrile as solvent.

2. Acetates and *ortho*-Alkynylanilines Used in the Condensation Reaction to Achieve 3 *insitu*

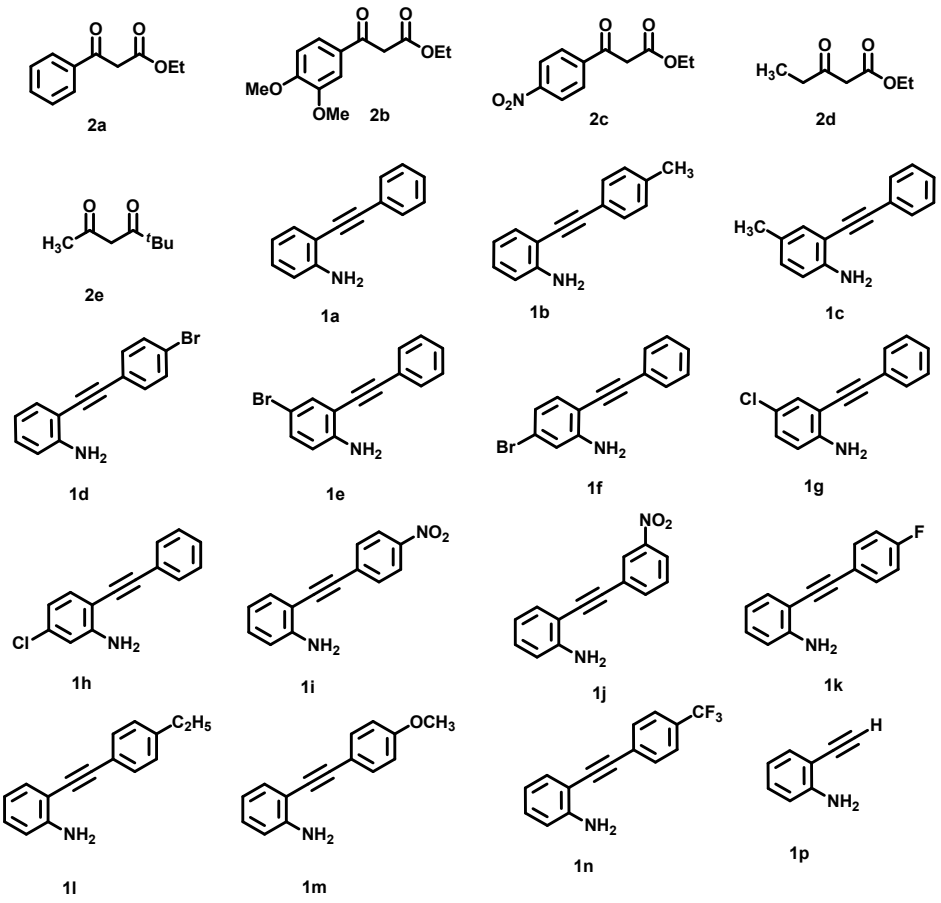


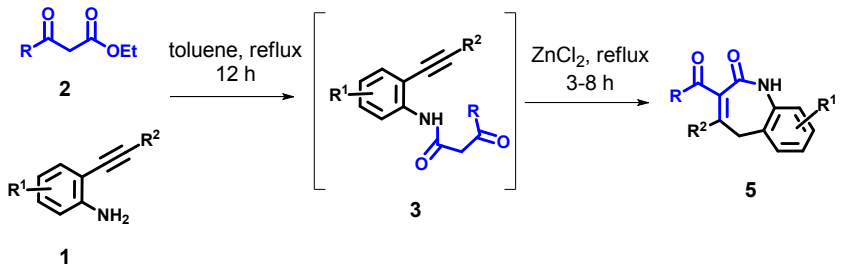
Figure S1. List of acetates and *ortho*-alkynylanilines used in the annulation reaction

3. General Procedure for the Synthesis of *O*-Alkynylanilines (1)[1]

Catalyst CuI (0.6 mmol), $Pd(PPh_3)_2Cl_2$ (0.6 mmol) and Et_3N (15 mmol) were added to a well stirred solution of 2-iodo aniline (3 mmol) in THF (10 mL). The reaction mixture was allowed to stir at room temperature for 30 minutes, phenyl acetylene derivative (3.3 mmol) was added drop wise and the reaction content was stirred at room temperature for 1 h. After complete consumption of the starting material, the solvent was removed under reduced pressure and the crude residue was purified over silica gel column chromatography to get pure *o*-alkynylanilines with excellent yields.

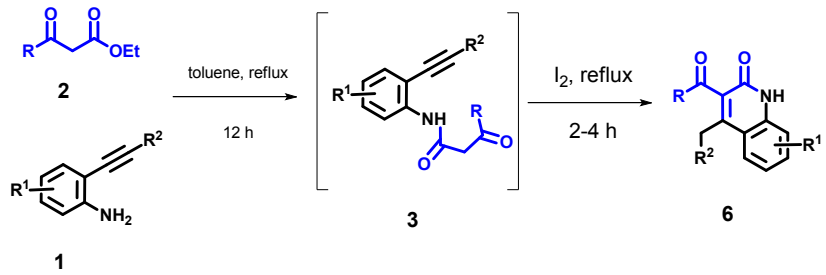
4. General Procedure for the Synthesis of Azepinones (5)

A mixture of ethyl benzoyl acetate/*tert*butyl acetoacetate (**2**, 1 mmol) and o-alkynyl anilines (**1**, 1 mmol) was taken in 10 mL of toluene and the reaction mixture was refluxed for 12 h. After complete consumption of both the starting materials (as indicated by TLC), 20 mmol of $ZnCl_2$ was added to the reaction mixture and it was further stirred under reflux for 3-8 h in open air. After completion of the reaction the solvent was removed under reduced pressure to get a crude residue which was purified over silica gel column chromatography using a mixture of ethyl acetate/ petroleum ether (15-30%) to get pure azepinone derivatives (**5**) with 80-95% yields. The formation of 3-oxo-3-phenyl-N-(2-(phenylethynyl)phenyl)propanamides was confirmed by the isolation and characterization of compounds (**3a**, **3c** and **3d**) with the help of ^{1}H, and ^{13}C NMR data.



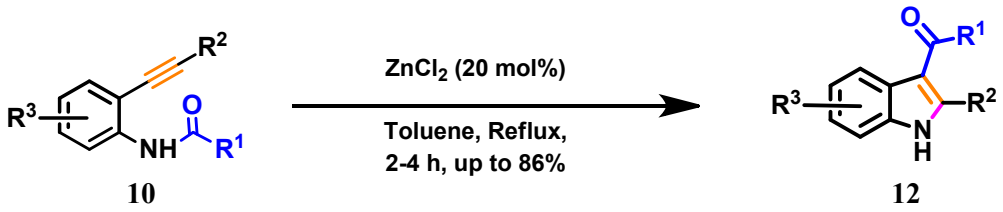
5. General Procedure for the Synthesis of Quinolinones (6)

A mixture of ethyl benzoyl acetate/tertbutyl acetoacetate (**2**, 1 mmol) and ortho-alkynyl anilines (**1**, 1 mmol) was taken in 10 mL of toluene and the reaction mixture was refluxed for 12 h. After complete consumption of both the starting materials (as indicated by TLC), 0.2 mmol of molecular iodine was added to the reaction mixture and it was further stirred under refluxing condition for additional 2-4 h in open air. After completion of the reaction the solvent was removed under reduced pressure to get a crude residue which was purified over silica gel column chromatography using a mixture of ethyl acetate/ petroleum ether (40-55%) to get pure quinolinone derivatives (**6**) with 84-95% yields.



6. General Procedure for the Synthesis of 3-Acyl Indole (12)

N-acyl 2-ethynylaniline (**10**, 1 mmol) was taken in 10 mL of toluene with 0.2 mmol of $ZnCl_2$ was added and the reaction mixture was refluxed for 3h. After completion of the reaction the solvent was removed under reduced pressure to get a crude residue which was purified over silica gel column chromatography using a mixture of ethyl acetate/ petroleum ether (10-20%) to get pure indole derivatives (**12**) with 75-86% yields.



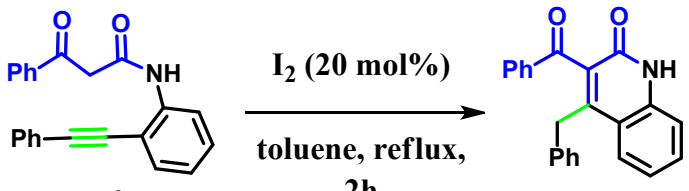
10 12

7. Procedure for the Gram-Scale Synthesis of Azepinone (5a) and Quinolinone (6a)

A mixture of ethyl benzoyl acetate (**2a**, 5 mmol, 960 mg) and 2-(phenylethynyl)aniline (**1a**, 5.5 mmol, 1 gm) was added to 30 mL of toluene and the reaction mixture was refluxed for 12 h. After complete consumption of both the starting materials (as indicated by TLC), 20 mol**%** of $ZnCl_2$ and/or molecular iodine was added to the reaction content and it was further stirred under refluxing condition for another 8 and 4 h in open air. After completion of the reaction the solvent was removed under reduced pressure to get a crude residue which was purified over silica gel column chromatography using a mixture of ethyl acetate/ petroleum ether to get pure azepinone (**5a**) and quinolinone (**6a**) with 85 and 92% yields respectively.

8. ESI-MS Data for Detecting the Intermediate (V) During the Formation of 6a from 3a

ESI-MS Kinetics Experiment. The 6-annulation reaction was performed using pure amide **3a** in the presence of catalyst $\mathbf{I_2}$ (20 mol%) under refluxed toluene. The ESI-MS kinetics experiments were



3a 6a

executed taking an aliquot after 1 h, and that was inject after passing through a filter and proper dilution in methanol. Three peaks appeared at 340.1278, 362.1050 and 488.0111 ppm in the ESIMS spectrum. The reaction was completed in 2h.

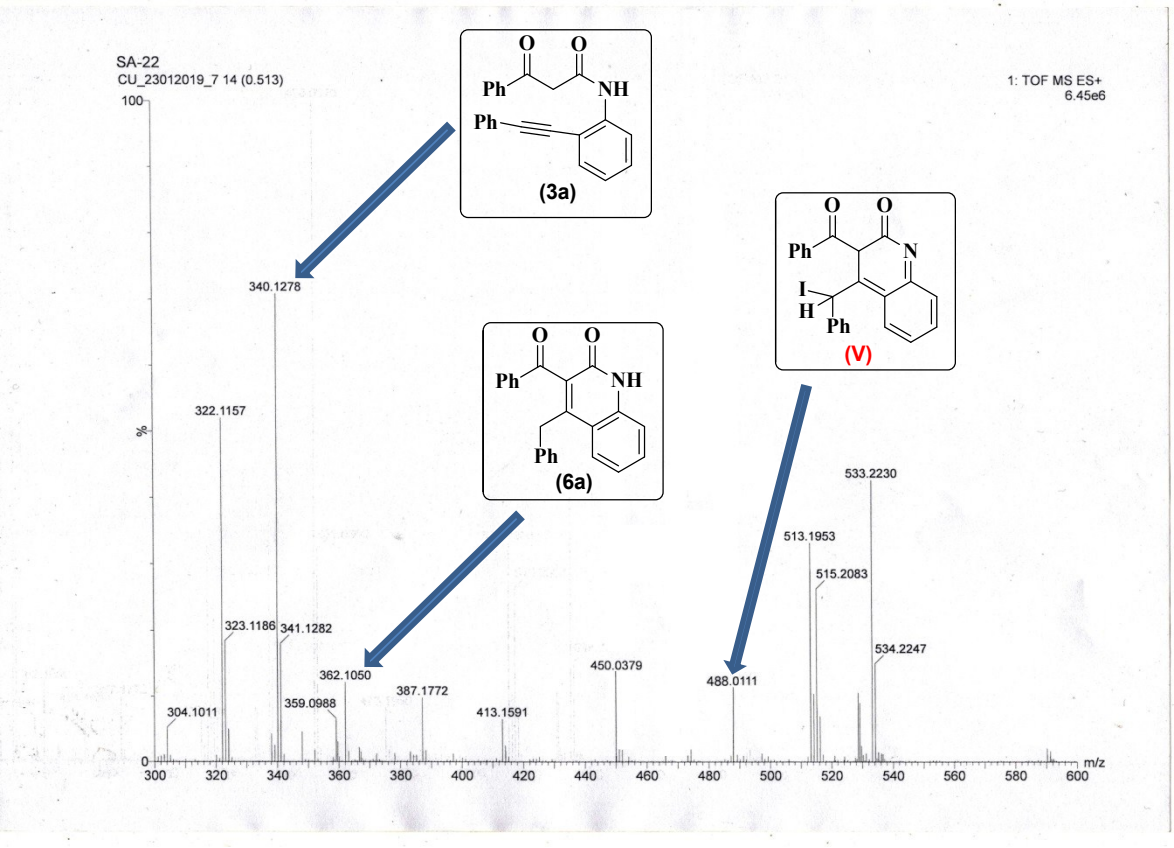


Figure S2. ESI-MS data for detecting the intermediate (**V)** during the formation of **6a** from **3a (Scheme 5).**

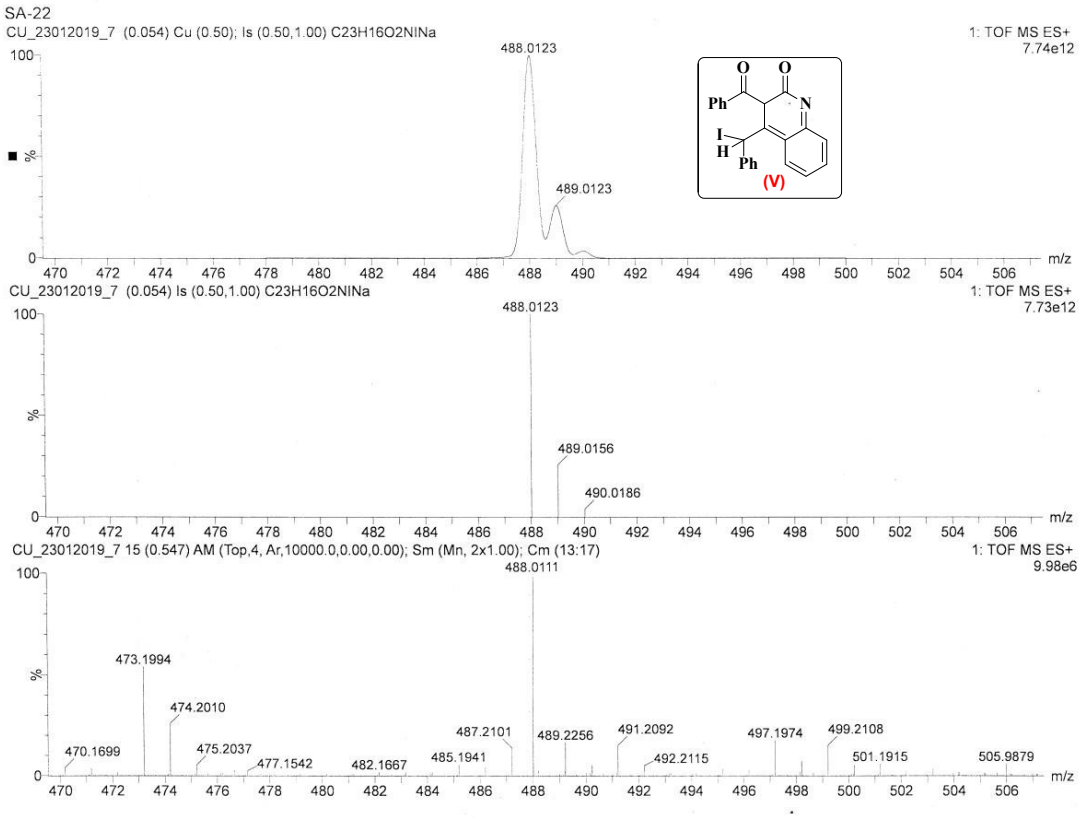


Figure S3. Experimental as well as simulated isotopic patterns of this peak (488.0111).

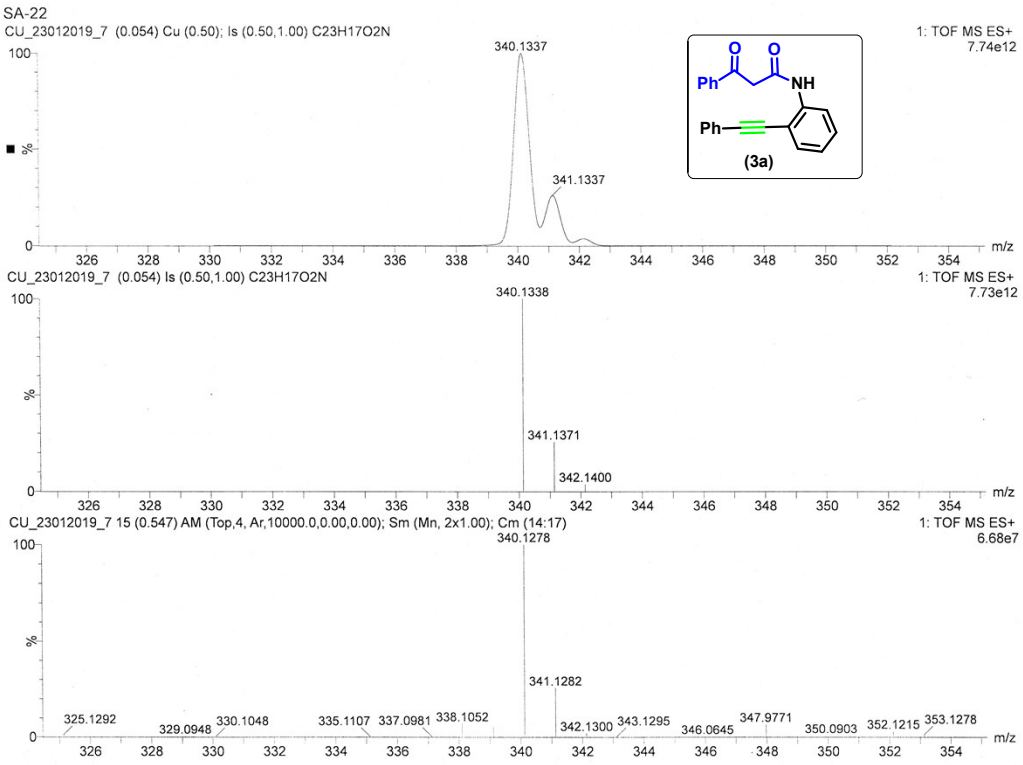


Figure S4. Experimental as well as simulated isotopic patterns of this peak (340.1338).

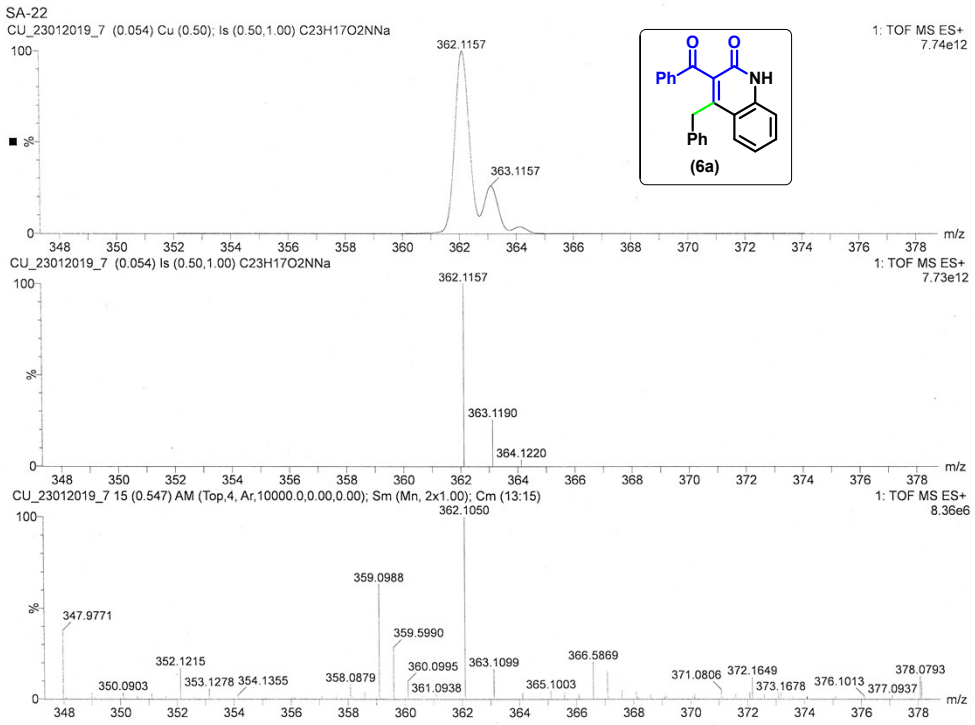
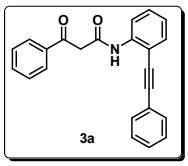


Figure S5. Experimental as well as simulated isotopic patterns of this peak (362.1157).

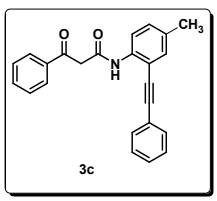
9. Reference: Wang,X.; Li, J.; Huang ,Y.; Zhu ,J.; Hu, R.; Wu,W.; Jiang,H. *J. Org. Chem.* **2018**, 83, 10453.

10. Spectral Data

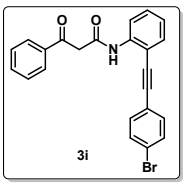
3-Oxo-3-phenyl-N-(2-(phenylethynyl)phenyl)propanamide (3a): Yield: 95% (0.95 mmol, 322 mg); Color: Colorless solid, R_f = 0.2 (10% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 4.20 (s, 2H), 7.11 (t, 1H, *J* = 7.5 Hz), 7.27-7.46 (m, 6H), 7.50-7.62 (m, 3H), 7.65 (t, 1H, *J* = 7.5 Hz), 7.81-7.84 (m, 2H), 8.05 (d, 2H, *J* = 7.5 Hz), 8.46 (d, 1H, *J* = 8.4 Hz), 10.10 (brs, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 46.0, 84.5, 96.7, 113.0, 119.9, 122.9, 123.8, 126.0, 128.4, 128.6, 129.0, 129.4, 131.7, 131.9, 132.0, 134.2, 136.1, 138.9, 163.8, 195.8. ESI-MS (*m*/*z*) for $C_{23}H_{18}NO_2$ $[M+H]^+$: Calculated 340.1338, found 340.1352.



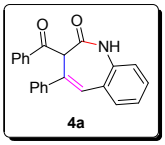
N-(4-Methyl-2-(phenylethynyl)phenyl)-3-oxo-3-phenylpropanamide (3c): Yield: 96% (0.96 mmol, 338 mg), Color: Colorless solid, R_f = 0.2 (10% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 2.34 (s, 3H), 4.18 (s, 2H), 7.16 (d, 1H, *J* = 8.4 Hz), 7.37-7.46 (m, 5H), 7.50-7.57 (m, 3H), 7.65 (t, 1H, *J* = 7.2 Hz), 7.81-7.84 (m, 2H), 8.05 (d, 2H, *J* = 8.1 Hz), 8.33 (d, 1H, *J* = 8.4 Hz), 10.03 (brs, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 20.5, 45.8, 84.5, 96.1, 112.7, 119.7, 122.8, 125.8, 128.2, 128.4, 128.4, 128.8, 130.0, 131.5, 131.7, 132.1, 133.2, 134.0, 136.0, 136.4, 163.5, 195.7. ESI-MS (*m*/*z*) for $C_{24}H_{20}NO_2$ $[M+H]^+$: Calculated 354.1494, found 354.1472.



N-(2-((4-Bromophenyl)ethynyl)phenyl)-3-oxo-3-phenylpropanamide (3d): Yield: 96% (0.96 mmol, 400 mg), Color: Colorless Solid, R_f = 0.2 (10% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 4.20 (s, 2H), 7.10 (t, 1H, *J* = 7.5 Hz), 7.36 (t, 2H, *J* = 7.5 Hz), 7.47-7.57 (m, 4H), 7.64-7.72 (m, 4H), 8.03 (d, 2H, *J* = 7.5 Hz), 8.46 (d, 1H, *J* = 8.4 Hz), 10.18 (brs, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 45.7, 85.6, 95.6, 112.6, 119.9, 121.9, 122.9, 123.7, 128.5, 129.0, 129.6, 131.6, 131.9, 133.3, 134.3, 136.0, 139.0, 163.7, 196.1. ESI-MS (*m*/*z*) for $C_{23}H_{17}BrNO_2$ $[M+H]^+$: Calculated 418.0443, found 418.0458.

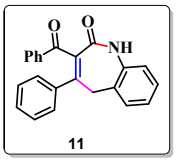


3-Benzoyl-4-phenyl-1*H*-benzo[*b*]azepin-2(3*H*)-one (4a). The isomer (**4a**) was isolated after purification by column chromatography as mentioned in Table 1. 15% (52 mg, 0.15 mmol, entry 8); 10% (33 mg, 0.10 mmol, entry 10); 3% (10 mg, 0.03 mmol, entry 11); 2% (7 mg, 0.02 mmol, entry 12); 20% (70 mg, 0.2 mmol, entry 14);

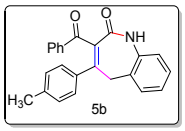


30% (102 mg, 0.3 mmol, entry 16); 35% (118 mg, 0.35 mmol, entry 17); 5% (17 mg, 0.05 mmol, entry 22); Colorless solid; R_f = 0.3 (15% EtOAc in hexane, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 2.19 (s, 3H), 5.51 (s, 1H), 6.78 (d, 1H, *J* = 8.1 Hz), 7.00 (s, 2H), 7.10 (s, 1H), 7.24-7.48 (m, 8H), 7.63 (d, 2H, *J* = 7.5 H), 10.44 (brs, 1H); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ 20.4, 61.9, 79.6, 121.0, 126.1, 127.6, 128.0, 128.1, 128.6, 129.0, 129.3, 130.3, 132.3, 132.8, 133.1, 134.7, 136.6, 140.7, 167.5, 193.4; **FT-IR** (film): υ_{max} 3190, 3048, 1889, 1668, 1561, 1456, 1437, 1384, 1324, 1209 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{18}NO_2$ $[M+H]^+$: Calculated 340.1338, found 340.1367.

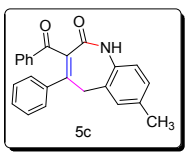
3-Benzoyl-4-phenyl-1*H*-benzo[*b*]azepin-2(5*H*)-one (5a): Yield: 90% (0.90 mmol, 305 mg), Color: Colorless Solid, R_f = 0.3 (20% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, $CDCl_3$+d_6-DMSO): δ 3.79 (s, 2H), 7.17 (m, 7H), 7.28 (m, 3H), 7.42 (d, 1H, *J*=7.2 Hz), 7.59 (d, 2H, *J*=7.5 Hz), 10.67 (brs, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$+d_6-DMSO): δ 37.4, 119.1, 123.2, 126.0, 126.2, 126.6, 126.7, 127.1, 128.9, 130.6, 131.3, 135.3, 135.4, 137.0, 149.0, 164.5, 192.4; **FT-IR** (film): υ_{max} 3192, 3068, 1930, 1668, 1560, 1466, 1439, 1432, 1374, 1324, 1218 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{18}NO_2$ $[M+H]^+$: Calculated 340.1338, found 340.1377.



3-Benzoyl-4-*p*-tolyl-1*H*-benzo[b]azepin-2(5*H*)-one (5b): Yield: 83% (0.83 mmol, 290 mg), Color: Brownish solid, R_f = 0.2 (20% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 3.78 (s, 2H), 6.99 – 7.10 (m, 6H), 7.23 – 7.38 (m, 4H), 7.47 (d, 1H *J* = 6.9 Hz), 7.59 (d, 2H, *J* = 7.2 Hz), 10.70 (brs, 1H); **^{13}C-NMR** (75 MHz, , d_6-DMSO): δ 20.9, 38.9, 120.7, 125.0, 127.9, 128.1, 128.5, 128.8, 128.9, 129.1, 130.9, 131.5, 135.5, 135.8, 136.9, 137.2, 138.7, 150.8, 166.2, 194.5; **FT-IR** (film): υ_{max} 3189, 3055, 2951, 1669, 1556, 1452, 1412, 1401, 1375, 1326, 1223 cm^{-1}; ESI-MS (*m*/*z*) for $C_{24}H_{20}NO_2$ $[M+H]^+$: Calculated 354.1494, found 354.1484.

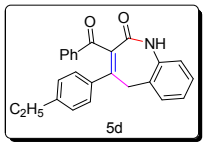


3-Benzoyl-7-methyl-4-phenyl-1*H*-benzo[*b*]azepin-2(5*H*)-one (5c): Yield: 82% (0.82 mmol, 289 mg), Color: Gray solid, R_f = 0.2 (15% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 3.80 (s, 2H), 6.93 (s, 1H), 7.11- 7.18 (m, 7 H), 7.32 – 7.37 (m, 2H), 7.45 – 7.50 (m, 1H), 7.58 (d, 2H, *J* = 7.8 Hz), 10.65 (brs, 1H); **^{13}C-NMR** (75 MHz, , d_6-DMSO): δ 20.4, 30.9, 120.7, 128.1, 128.4, 128.5, 128.8, 128.8, 129.0,

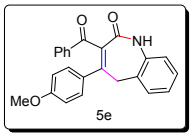


130.8, 132.1, 133.4, 134.2, 134.7, 136.9, 138.8, 150.8, 166.1, 194.4; **FT-IR** (film): υ_{max} 3188, 3045, 2960, 1656, 1524, 1442, 1410, 1392, 1365, 1306, 1233 cm^{-1}; ESI-MS (*m*/*z*) for $C_{24}H_{20}NO_2$ $[M+H]^+$: Calculated 354.1494, found 354.1492.

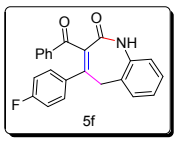
3-Benzoyl-4-(4-ethylphenyl)-1*H*-benzo[*b*]azepin-2(5*H*)-one (5d): Yield: 82% (0.82 mmol, 309 mg), Color: Colorless Solid, R_f = 0.2 (20% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 1.03 (t, 3H, *J* = 7.8 Hz), 2.36 (q, 2H, *J* = 7.5 Hz), 3.76 (s, 2H), 6.92 (t, 3H, *J* = 8.1 Hz), 7.00 – 7.07 (m, 3H), 7.17 – 7.21 (m, 4H), 7.32 (t, 1H, *J* = 7.2 Hz), 7.58 (d, 2H, *J* = 7.8 Hz), 8.61 (brs, 1H); **^{13}C-NMR** (75 MHz, , $CDCl_3$): δ 15.0, 28.4, 40.8, 120.4, 125.5, 127.8, 128.0, 128.2, 128.4, 128.7, 129.0, 129.2, 130.7, 131.5, 132.8, 136.0, 136.3, 137.2, 145.3, 166.8, 194.2; **FT-IR** (film): υ_{max} 3182, 3046, 2945, 1662, 1529, 1451, 1414, 1400, 1365, 1323, 1220 cm^{-1}; ESI-MS (*m*/*z*) for $C_{25}H_{22}NO_2$ $[M+H]^+$: Calculated 368.1650, found 368.1680.



3-Benzoyl-4-(4-methoxyphenyl)-1*H*-benzo[*b*]azepin-2(5*H*)-one (5e): Yield: 80% (0.80 mmol, 295 mg), Color: Colorless solid, R_f = 0.2 (30% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz,$CDCl_3$+ d_6-DMSO): δ 2.79 (s, 2H), 3.69 (s, 3H), 6.68 (d, 2H, *J* = 8.7 Hz), 7.07 – 7.13 (m, 4H), 7.27 – 7.32 (m, 4H), 7.40 – 7.45 (m, 1H), 7.63 (d, 2H, *J* = 7.5 Hz), 10.28 (brs, 1H); **^{13}C-NMR** (75 MHz, , $CDCl_3$+d_6-DMSO): δ, 37.3, 56.4, 112.9, 119.8, 124.2, 126.9, 127.3, 127.5, 128.0, 128.8, 129.7, 129.8, 130.2, 132.1, 136.0, 136.2, 159.1, 165.9, 193.9; **FT-IR** (film): υ_{max} 3120, 3012, 2910, 1663, 1502, 1425, 1402, 1385, 1365, 1336, 1243 cm^{-1}; ESI-MS (*m*/*z*) for $C_{24}H_{20}NO_3$ $[M+H]^+$: Calculated 370.1443, found 370.1445.

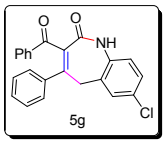


3-Benzoyl-4-(4-fluorophenyl)-1*H*-benzo[*b*]azepin-2(5*H*)-one (5f): Yield: 95% (0.95 mmol, 339 mg), Color: Brownish solid R_f = 0.2 (25% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 3.68 (s, 2H), 6.82–6.88 (m, 2H), 7.00 (s, 2H), 7.07 – 7.10(m, 2H), 7.18 – 7.25 (m, 4H), 7.36 (d, 1H, *J* = 7.2 Hz), 7.49 (d, 2H, *J* = 7.2 Hz), 10.56 (brs, 1H); **^{13}C-NMR** (75 MHz, , d_6-DMSO): δ 37.0, 113.5 (d, *J* = 21 Hz), 118.9, 124.6 (d, *J* = 214 Hz), 126.4, 126.7, 126.9, 128.4 (d, *J* = 9 Hz), 128.7, 130.3, 131.5, 133.0, 135.0 (d, *J* = 14 Hz), 148.0, 164.2, 168.4, 192.4; **FT-IR** (film): υ_{max} 3172, 3025, 2950, 1663, 1552, 1448,



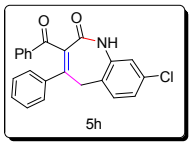
1413, 1405, 1368, 1327, 1243 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{17}FNO_2$ $[M+H]^+$: Calculated 358.1243, found 358.1279.

3-Benzoyl-7-chloro-4-phenyl-1*H*-benzo[*b*]azepin-2(5*H*)-one (5g): Yield: 90% (0.90 mmol, 335 mg), Color: Colorless Solid, R_f = 0.2 (25% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, $CDCl_3$+d_6-DMSO): δ 3.83 (s, 2H), 7.20 – 7.29 (m, 6H), 7.33 – 7.35 (m, 4H), 7.45 (d, 1H, *J* = 6.6 Hz), 7.62 (d, 1H, *J* = 7.5 Hz), 10.76 (br s, 1H); **^{13}C-NMR** (75 MHz, , $CDCl_3$+d_6-DMSO): δ, 37.1, 120.6, 126.0, 126.2, 126.3, 126.7, 126.8, 127.2, 127.3, 127.8, 130.7, 130.9, 131.5, 134.4, 136.8, 148.6, 164.4, 192.3; **FT-IR** (film): υ_{max} 3125, 2958, 1716, 1660, 1564, 1469, 1285, 766 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{17}ClNO_2$ $[M+H]^+$: Calculated 374.0948, found 374.0981.



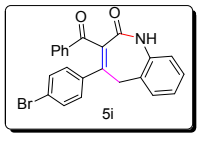
5g

3-Benzoyl-8-chloro-4-phenyl-1*H*-benzo[*b*]azepin-2(5*H*)-one (5h) Yield: 90% (0.90 mmol, 335 mg), Color: Gray solid R_f = 0.2 (25% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 3.83 (s, 2H), 7.16 – 7.30 (m, 6H), 7.36 (d, 3H, *J* = 7.2 Hz), 7.56 (s, 1H), 7.61 (d, 3H, *J* = 7.2 Hz), 10.84 (brs, 1H); **^{13}C-NMR** (75 MHz, , d_6-DMSO): δ, 38.3, 120.3, 124.7, 128.1, 128.5, 128.8, 128.9, 129.2, 129.5, 129.6, 130.2, 132.0, 133.5, 136.7, 138.5, 150.9, 166.0, 194.3; **FT-IR** (film): υ_{max} 3190, 3070, 2902, 1660, 1560, 1482, 1460, 1444, 1403, 1366, 1344, 1218 $cm^{-1}cm^{-1}$; ESI-MS (*m*/*z*) for $C_{23}H_{17}ClNO_2$ $[M+H]^+$: Calculated 374.0948, found 374.0975.



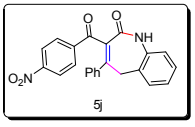
5h

3-Benzoyl-4-(4-bromophenyl)-1*H*-benzo[*b*]azepin-2(5*H*)-one (5i): Yield: 88% (0.88 mmol, 366 mg), Color: Brownish solid R_f = 0.2 (20% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 3.72 (s, 2H), 6.94 (d, 1H, *J* = 8.1 Hz), 7.03 – 7.08 (m, 1H), 7.22 – 7.32 (m, 6H), 7.49 (s, 1H), 7.67 (d, 4H, *J* = 9.0 Hz), 10.62 (brs, 1H); **^{13}C-NMR** (75 MHz, , d_6-DMSO): δ 38.2, 120.9, 121.2, 123.2, 127.3, 127.6, 128.0, 128.1, 128.4, 129.0, 120.3, 131.7, 132.6, 133.5, 135.4, 136.2, 139.5, 167.6, 193.4; **FT-IR** (film): υ_{max} 3193, 3066, 2907, 1662, 1566, 1492, 1450, 1434, 1403, 1376, 1334, 1228 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{17}BrNO_2$ $[M+H]^+$: Calculated 418.0443, found 418.0460.



5i

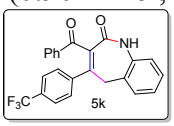
3-(4-Nitrobenzoyl)-4-phenyl-1*H*-benzo[*b*]azepin-2(5*H*)-one (5*J*): Yield: 90% (0.90 mmol, 345 mg), Color: Brownish solid R_f = 0.2 (20% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 3.89 (s, 2H), 7.12-7.35 (m, 9H), 7.81 (d, 2H, *J* = 8.7 Hz), 8.10 (d, 2H,



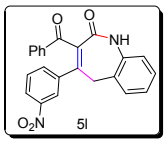
5j

J = 8.7 Hz), 9.13 (brs, 1H); **^{13}C-NMR** (75 MHz, , d_6-DMSO): δ 39.6, 120.7, 123.5, 125.9, 127.9, 128.3, 128.6, 128.6, 129.6, 129.9, 130.2, 131.0, 136.1, 138.1, 141.7, 149.9, 153.9, 166.7, 193.0; **FT-IR** (film): υ_{max} 3133, 3046, 2880, 1665, 1572, 1518, 1432, 1365, 1336, 1272, 1247, 1202, 1082, 983 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{17}N_2O_4$ $[M+H]^+$: Calculated 385.1188, found 385.1201.

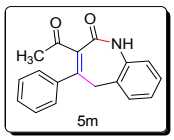
3-Benzoyl-4-(4-(trifluoromethyl)phenyl)-1*H*-benzo[*b*]azepin-2(5*H*)-one (5k): Yield: 90% (0.90 mmol, 366 mg), Color: Brownish solid R_f = 0.2 (30% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 3.64 (s, 2H), 7.16 (s, 1H), 7.29 – 7.35 (m, 5H), 7.46 – 7.51 (m, 4 H), 7.66 (s, 1H), 7.70 (d, 2H, *J* = 7.2 Hz), 10.96 (brs, 1H); **^{13}C-NMR** (75 MHz, , d_6-DMSO): 38.2, 88.3 (q, *J* = 28.5 Hz), 112.4, 120.9, 122.8, 122.9, 123.6, 123.8, 124.5, 126.7, 128.3, 130.5, 130.9, 131.1, 132.9, 140.2, 148.1, 148.1, 165.9, 192.9; **FT-IR** (film): υ_{max} 3188, 3056, 2910, 1678, 1570, 1552, 1505, 1465, 1386, 1212 cm^{-1}; ESI-MS (*m*/*z*) for $C_{24}H_{17}F_3NO_2$ $[M+H]^+$: Calculated 408.1211, found 408.1215.



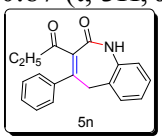
3-Benzoyl-4-(3-nitrophenyl)-1*H*-benzo[*b*]azepin-2(5*H*)-one (5l): Yield: 92% (0.92 mmol, 353 mg), Color: Brownish solid R_f = 0.2 (25% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 3.88 (s, 2H), 6.93 (d, 1H, *J* = 7.8 Hz), 7.04 – 7.09 (m, 1H), 7.22- 7.31 (m , 6H), 7.48 – 7.57 (m, 1H), 7.75 – 7.78 (m 1H), 8.10 (d, 1H, *J* = 7.8 Hz), 8.22 (d, 1H, *J* = 8.1 Hz), 8.44 (s, 1H), 10.66 (brs, 1H); **^{13}C-NMR** (75 MHz, , d_6-DMSO): δ 38.9, 119.7, 120.1, 121.7, 122.5, 126.6, 126.7, 127.1, 127.9, 129.5, 129.6, 130.0, 131.7, 131.8, 134.6, 135.5, 141.3, 147.5, 166.6, 192.4; **FT-IR** (film): υ_{max} 3143, 3066, 1908, 1661, 1583, 1528, 1443, 1376, 1346, 1280, 1237, 1219, 1086, 983; ESI-MS (*m*/*z*) for $C_{23}H_{17}N_2O_4$ $[M+H]^+$: Calculated 385.1188, found 385.1196.



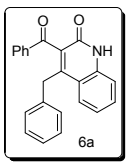
3-Acetyl-4-phenyl-1*H*-benzo[*b*]azepin-2(5*H*)-one (5m) Yield: 85% (0.85 mmol, 235 mg), Color: Gray solid R_f = 0.2 (15% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, $CDCl_3$+d_6-DMSO): δ 1.95 (s, 3H), 3.70 (s, 2H), 7.05 (d, 2H, *J* = 3.3 Hz), 7.07 – 7.25 (m, 3H), 7.30 – 7.40 (m, 3H), 7.80 (s, 1H), 10.47 (brs, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$+d_6-DMSO): δ 19.7, 38.1, 119.7, 123.7, 126.5, 126.5, 126.9, 127.4, 127.9, 129.2, 133.4, 135.7, 137.7, 148.6, 165.2, 200.6; **FT-IR** (film): υ_{max} 3180, 3060, 2975, 1723, 1680, 1510, 1475, 1386, 1339, 1260 cm^{-1}; ESI-MS (*m*/*z*) for $C_{18}H_{16}NO_2$ $[M+H]^+$: Calculated 278.1181, found 278.1208.



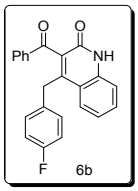
4-Phenyl-3-propionyl-1*H*-benzo[*b*]azepin-2(5*H*)-one (5n): Yield: 86% (0.86 mmol, 250 mg), Color: Colorless Solid, R_f = 0.2 (20% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 0.87 (t, 3H, *J* = 7.5 Hz), 2.34 (q, 2H, *J* = 7.2 Hz), 3.64 (s, 2H), 7.12 – 7.16 (m , 2H), 7.26 – 7.47 (m, 5H), 7.60 (d, 2H, J = 6.9 Hz), 9.68 (brs, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 7.7, 32.7, 35.3, 121.2, 124.3, 126.3, 126.3, 127.5, 128.2, 128.4, 128.9, 129.0, 129.1, 130.5, 134.8, 136.0, 141.2, 170.0, 202.5; **FT-IR** (film): υ_{max} 3190, 3058, 2965, 1713, 1667, 1574, 1486, 1376, 1343, 1250 cm^{-1}; ESI-MS (*m*/*z*) for $C_{19}H_{18}NO_2$ $[M+H]^+$: Calculated 292.1338, found 292.1389.



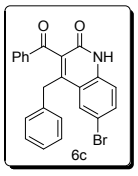
3-Benzoyl-4-benzylquinolin-2(1*H*)-one (6a): Yield: 95% (0.95 mmol, 322 mg), Color: Colorless Solid, R_f = 0.2 (40% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, , $CDCl_3$ + d_6-DMSO): δ 4.04 (s, 2H), 7.10 – 7.25 (m, 6H), 7.40 (d, 2H, *J* = 8.1 Hz), 7.48 – 7.53 (m, 2H), 7.65 (t, 2H, *J* = 7.5 Hz), 7.88 (d, 2H, *J* = 7.5 Hz), 12.19 (brs, 1H); **^{13}C-NMR** (75 MHz, , $CDCl_3$ + d_6-DMSO): δ 34.3, 115.5, 117.8, 121.7, 125.7, 125.9, 127.7, 128.0, 128.5, 130.4, 131.7, 133.5, 135.9, 137.4, 138.4, 145.5, 159.4, 195.1; **FT-IR** (film): υ_{max} 2980, 2870, 1690, 1647, 1555, 1542, 1448, 1398, 1342, 1280, 1230, 1050 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{18}NO_2$ $[M+H]^+$: Calculated 340.1338, found 340.1346.



3-Benzoyl-4-(4-fluorobenzyl)quinolin-2(1*H*)-one (6b): Yield: 92% (0.92 mmol, 329 mg), Color: Colorless solid, R_f = 0.2 (40% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 4.13 (s, 2H), 7.14 (t, 2H, *J* = 8.7 Hz), 7.24 (t, 1H, *J* = 7.5 Hz), 7.38 (t, 2H, *J* = 3.6 Hz), 7.50 (d, 1H, *J* = 8.1 Hz), 7.58 – 7.73 (m, 3H), 7.76 (t, 2H, *J* = 8.1 Hz), 7.97 (d, 2H, *J* = 7.2 Hz), 12.30 (brs, 1H); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ 34.1, 115.3 (d, *J* = 21 Hz), 116.1, 118.3, 122.4, 126.2, 129.1, 129.1, 130.2 (d, *J* = 7.5 Hz), 131.1, 132.3, 134.1 (d, *J* = 3.7 Hz), 136.5, 139.1, 146.0, 160.0, 195.7; **FT-IR** (film): υ_{max} 2912, 2851, 1649, 1592, 1540, 1507, 1478, 1450, 1427, 1370, 1303, 1212 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{17}FNO_2$ $[M+H]^+$: Calculated 358.1243, found 358.1241.

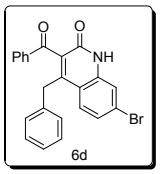


3-Benzoyl-4-benzyl-6-bromoquinolin-2(1*H*)-one (6c): Yield: 88% (0.88 mmol, 366 mg), Color: Brownish solid. R_f = 0.2 (40% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 4.01 (s, 2H), 7.14 (t, 1H, *J* = 4.2 Hz), 7.21 (d, 4H, *J* = 4.2 Hz), 7.31 (d, 1H, *J* = 8.7 Hz), 7.49 (t, 2H, *J* = 9.9 Hz), 7.64 (t, 2H, *J* = 7.5 Hz), 7.76 (s,



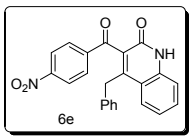
1H), 7.85 (d, 2H, *J* = 7.2 Hz), 12.27 (brs, 1H); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ, 34.7, 114.0, 118.3, 120.2, 126.7, 128.3, 128.4, 128.7, 129.1, 129.2, 133.4, 133.7, 134.3, 136.3, 137.7, 138.2, 145.1, 159.8, 195.3; **FT-IR** (film): υ_{max} 2981, 2923, 1662, 1593, 1487, 1445, 1403, 1371, 1243 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{17}BrNO_2$ $[M+H]^+$: Calculated 418.0443, found 418.0471.

3-Benzoyl-4-benzyl-6-bromoquinolin-2(1*H*)-one (6d): Yield: 86% (0.86 mmol, 358 mg), Color: Brownish solid. R_f = 0.2 (40% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 4.01 (s, 2H), 7.12-7.32 (m, 6H), 7.47 (t, 2H, *J*= 7.2 Hz), 7.56-7.67 (m, 2H), 7.76-7.86 (m, 3H), 12.28 (brs, 1H); **^{13}C-NMR** (75 MHz, , d_6-DMSO): δ 33.7, 113.1, 117.2, 119.2, 125.7, 127.3, 127.4, 127.7, 128.1, 132.3, 132.7, 133.3, 135.3, 136.7, 137.2, 144.1, 158.1, 194.3; **FT-IR** (film): υ_{max} 2980, 2922, 1660, 1592, 1480, 1440, 1400, 1371, 1240 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{17}BrNO_2$ $[M+H]^+$: Calculated 418.0443, found 418.0429.



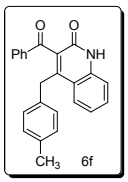
6d

4-Benzyl-3-(4-nitrobenzoyl)quinolin-2(1*H*)-one (6e): Yield: 90% (0.90 mmol, 345 mg), Color: Brownish solid. R_f = 0.2 (45% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 4.08 (s, 2H), 7.12 – 7.19 (m, 6H), 7.39 (d, 1H, *J* = 8.4 Hz), 7.53 (t, 1H, *J* = 7.5 Hz), 7.71 (d, 1H, *J* = 8.1 Hz), 8.06 (d, 2H, *J* = 8.4 Hz), 8.26 (d, 2H, *J* = 8.4 Hz), 12.23 (brs, 1H); **^{13}C-NMR** (75 MHz, , d_6-DMSO): δ, 34.7, 116.2, 118.5, 122.5, 124.1, 126.5, 126.6, 128.4, 128.6, 130.4, 131.2, 131.5, 137.9, 139.3, 141.0, 147.8, 150.4, 160.0, 194.9; **FT-IR** (film): υ_{max} 2929, 2859, 1660, 1543, 1496, 1448, 1390, 1340, 1248, 1208, 1150, 1090, 920 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{17}N_2O_4$ $[M+H]^+$: Calculated 385.1188, found 385.1172.



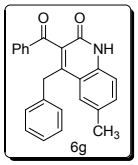
6e

3-Benzoyl-4-(4-methylbenzyl)quinolin-2(1*H*)-one (6f): Yield: 84% (0.84 mmol, 296 mg), Color: Brownish solid. R_f = 0.2 (40% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 2.28 (s, 3H), 4.13 (s, 1H), 7.11 (d, 2H, *J* = 7.5 Hz), 7.22 (d, 3H, *J* = 7.5 Hz), 7.49 (d, 1H, *J* = 8.4 Hz), 7.61 (t, 3H, *J* = 7.5 Hz), 7.74 (d, 2H, *J* = 7.5 Hz), 7.98 (d, 2H, *J* = 7.8 Hz), 12.29 (brs, 1H); **^{13}C-NMR** (75 MHz, , d_6-DMSO): δ, 20.0, 34.0, 115.5, 117.8, 121.7, 125.7, 127.6, 128.5, 128.6, 130.4, 131.6, 133.5, 134.3, 135.0, 135.9, 138.5, 145.7, 159.5, 195.1; **FT-IR** (film): υ_{max} 2928, 2852, 1652, 2598, 1526, 1452, 1350, 1248, 1160, 1112, 980, 890 cm^{-1}; ESI-MS (*m*/*z*) for $C_{24}H_{20}NO_2$ $[M+H]^+$: Calculated 354.1494, found 354.1478.



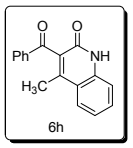
6f

3-Benzoyl-4-benzyl-6-methylquinolin-2(1*H*)-one (6g): Yield: 86% (0.86 mmol, 303 mg), Color: Colorless solid .R_f = 0.2 (40% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 2.34 (s, 3H), 4.12 (s, 2H), 7.25 – 7.48 (m, 7H), 7.61 (d, 3H, *J* = 8.1 Hz), 7.74 (d, 1H, *J* = 7.2 Hz), 7.95 (d, 2H, *J* = 7.8 Hz), 12.2 (brs, 1H); **^{13}C-NMR** (75 MHz, , d_6-DMSO): δ, 19.7, 33.7, 114.9, 117.3, 124.6, 125.5, 127.3, 127.5, 128.0, 130.2, 131.1, 131.2, 133.0, 135.5, 136.0, 137.0, 144.8, 158.8, 194.7; **FT-IR** (film): υ_{max} 2927, 2854, 1655, 1601, 1525, 1450. 1352, 1250, 1116, 983, 910, 856 cm^{-1}; ESI-MS (*m*/*z*) for $C_{24}H_{20}NO_2$ $[M+H]^+$: Calculated 354.1494, found 354.1500.



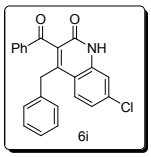
6g

3-Benzoyl-4-methylquinolin-2(1*H*)-one (6h): Yield: (90%) (0.90 mmol, 237 mg), Color: Colorless Solid, R_f = 0.3 (35% EtOAc in hexanes, TLC); **^{1}H-NMR** (400 MHz, d_6-DMSO): δ 2.27 (s, 3H), 7.28 (t, 1H, *J* = 7.2 Hz), 7.40 (d, 1H), 7.54 – 7.56 (m, 2H), 7.60 (s, 1H), 7.68 (s, 1H);7.86 (d, 3H, *J* =7.2 Hz), 12.06 (brs, 1H); **^{13}C-NMR** (75 MHz, , $CDCl_3$ + d_6-DMSO): δ 16.1, 116.2, 119.6, 122.7, 125.8, 129.4, 129.5, 131.2, 131.6, 134.4, 136.9, 138.7, 145.1, 160.2, 196.2; **FT-IR** (film): υ_{max} 2912, 2857, 1631, 1552, 1512, 1438, 1388, 1313, 1278, 1240, 1155 cm^{-1}; ESI-MS (*m*/*z*) for $C_{17}H_{14}NO_2$ $[M+H]^+$: Calculated 264.1024, found 264.1035.



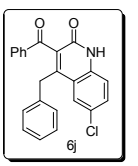
6h

3-Benzoyl-4-benzyl-7-chloroquinolin-2(1*H*)-one (6i): Yield: 90% (0.90 mmol, 335 mg), Color: Brownish solid. R_f = 0.2 (40% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 4.13 (s, 2H), 7.25 – 7.33 (m, 6H), 7.51 (d, 1H, *J* = 2.1 Hz), 7.61 (t, 2H, *J* = 7.8 Hz), 7.76 (d, 2H, *J* = 9 Hz), 7.97 (d, 2H, *J* = 8.4 Hz), 12.36 (brs, 1H); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ, 33.9, 114.2, 116.3, 121.4, 125.6, 127.2. 127.3, 127.6, 128.1, 128.1, 131.6, 133.2, 134.5, 135.4, 136.7, 139.0, 144.8, 159.0, 194.3; **FT-IR** (film): υ_{max} 2925, 2823, 1672, 1657, 1588, 1561, 1481, 1450, 1372, 1300, 1280, 1242 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{17}ClNO_2$ $[M+H]^+$: Calculated 374.0948, found 374.0969.



6i

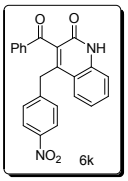
3-Benzoyl-4-benzyl-6-chloroquinolin-2(1*H*)-one (6*j*): Yield: 89% (0.89 mmol, 330 mg), Color: Brownish solid. R_f = 0.2 (40% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 4.01 (s, 2H), 7.11-7.15 (m, 1H), 7.21 (d, 4H, *J* = 4.2 Hz), 7.37 (d, 1H, *J* = 9.0 Hz), 7.46-7.57 (m, 3H), 7.62-7.76 (m, 2H), 7.85 (d, 2H, *J* = 7.5 Hz), 12.30 (brs, 1H); **^{13}C-NMR** (75 MHz d_6-DMSO): δ 33.7, 117.0, 118.7, 124.4, 124.8, 125.3, 125.7, 127.3,



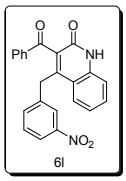
6j

127.7, 128.1, 128.1, 130.0, 132.4, 133.3, 135.3, 136.7, 136.9, 144.2, 158.8, 194.3; **FT-IR** (film): υ_{max} 2928, 2828, 1678, 1647, 1598, 1551, 1498, 1456, 1376, 1303, 1286, 1240 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{17}ClNO_2$ $[M+H]^+$: Calculated 374.0948, found 374.0982.

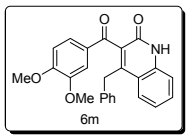
3-Benzoyl-4-(4-nitrobenzyl)quinolin-2(1*H*)-one (6k): Yield: 92% (0.92 mmol, 353 mg), Color: Yellowish solid. R_f = 0.2 (45% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 4.14 (s, 2H), 7.09 (t, 1H, *J* = 7.8 Hz), 7.32 – 7.62 (m, 8 H), 7.81 (d, 2H, *J* = 7.5 Hz), 8.03 (d, 2H, *J* = 8.7 Hz), 12.19 (brs, 1H); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ, 33.6, 115.2, 117.2, 121.5, 122.7, 125.0, 128.1, 128.2, 128.7, 130.3, 131.8, 133.2, 135.4, 138.2, 144.0, 145.1, 145.3, 159.0, 194.6; **FT-IR** (film): υ_{max} 2908, 2850, 1661, 1583, 1528, 1443, 1376, 1342, 1282, 1219, 1010, 982 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{17}N_2O_4$ $[M+H]^+$: Calculated 385.1188, found 385.1172.



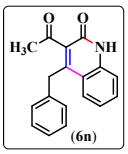
3-Benzoyl-4-(3-nitrobenzyl)quinolin-2(1*H*)-one (6l): Yield: 90% (0.90 mmol, 353 mg), Color: Yellowish solid. R_f = 0.2 (45% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 4.13 (s, 2H), 7.09 (t, 1H, *J* = 7.8 Hz), 7.34 (d, 1H, *J* = 8.1 Hz), 7.40 – 7.50 (m, 4H), 7.55 – 7.67 (m, 3H), 7.80 (d, 2H, *J* = 7.2 Hz), 7.93 (d, 1H, *J* = 8.1 Hz), 8.09 (s, 1H), 12.17 (brs, 1H); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ 33.2, 115.2, 117.1, 120.7, 121.5, 122.1, 125.1, 128.0, 128.1, 129.1, 130.3, 131.8, 133.2, 134.2, 135.4, 138.2, 139.3, 144.2, 146.9, 159.0, 194.7; **FT-IR** (film): υ_{max} 2927, 2854, 1650, 1534, 1486, 1437, 1383, 1341, 1286, 1244, 1115, 1080, 923 cm^{-1}; ESI-MS (*m*/*z*) for $C_{23}H_{17}N_2O_4$ $[M+H]^+$: Calculated 385.1188, found 385.1195.



4-Benzyl-3-(3,4-dimethoxybenzoyl)quinolin-2(1*H*)-one (6m): Yield: 90% (0.90 mmol, 359 mg), Color: Brownish solid R_f = 0.2 (55% EtOAc in hexanes, TLC); **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 3.9 (s, 6H, *J* = 11.7 Hz), 4.13 (s, 2H), 7.11 (d, 1H, *J* = 8.4 Hz), 7.21 – 7.34 (m, 2H), 7.38 (d, 3H, *J* = 5.7 Hz), 7.46 (s, 1H), 7.49 - 7.60 (m, 4H), 7.73 (d, 1H, *J* = 8.1 Hz), 12.22 (brs, 1H); **^{13}C-NMR** (75 MHz, , d_6-DMSO): δ, 30.0, 54.7, 55.0, 110.1, 115.0, 117.4, 121.2, 124.3, 125.2, 125.5, 127.3, 127.6, 127.7, 128.0, 129.9, 131.6, 137.1, 138.0, 144.5, 148.0, 153.0, 159.0, 192.9; **FT-IR** (film): υ_{max} 2926, 2812, 1632, 1558, 1516, 1422, 1320, 1238, 1110, 1102, 970, 890 cm^{-1}; ESI-MS (*m*/*z*) for $C_{25}H_{22}NO_4$ $[M+H]^+$: Calculated 400.1549, found 400.1568.

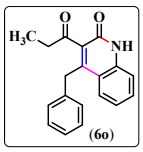


3-Acetyl-4-benzylquinolin-2(1*H*)-one (6n): Yield: 89% (0.89 mmol, 245 mg), Color: Colorless solid R_f = 0.2 (35% EtOAc in hexanes, TLC); **^{1}H-NMR** (400 MHz, d_6-DMSO): δ 2.43 (s, 3H),



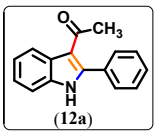
4.14 (s, 2H), 7.09 – 7.18 (m, 1H), 7.19 (s, 1H), 7.25 - 7.28 (m, 4H), 7.35 (d, 1H, J = 8. Hz), 7.47 – 7.51 (m, 1H), 7.69 (d, 1H, J = 8 Hz), 12.15 (brs, 1H); **^{13}C-NMR** (100 MHz, , d_6-DMSO): δ, 31.8, 34.6, 116.3, 118.7, 122.7, 126.8, 126.8, 128.7, 129.0, 131.4, 134.6, 138.7, 139.1, 145.3, 160.2, 206.8; **FT-IR** (film): υ_{max} 2928, 2862, 1732, 1658, 1516, 1422, 1320, 1248, 1210, 1102, cm^{-1}; ESI-MS (*m*/*z*) for $C_{18}H_{16}NO_2$ $[M+H]^+$: Calculated 277.1103, found 277.1112.

4-Benzyl-3-propionylquinolin-2(1*H*)-one (6o): Yield: 88% (0.88 mmol, 255 mg), Color: Colorless solid R_f = 0.2 (35% EtOAc in hexanes, TLC); **^{1}H-NMR** (400 MHz, d_6-DMSO): δ 1.00



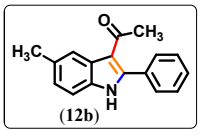
(t, 3H, J = 7.2 Hz), 2.75 (q, 2H, J = 7.2 Hz), 4.09 (s, 2H), 7.12 (s, 1H), 7.26 (d, 1H, J = 7.2. Hz), 7.33 – 7.49 (m, 5H), 7.49 (s, 1H), 7.68 (d, 1H, J = 8 Hz), 12.13 (brs, 1H); **^{13}C-NMR** (100 MHz, , d_6-DMSO): δ, 7.9, 34.7, 36.9, 116.3, 118.7, 122.7, 126.7, 126.9, 128.7, 129.0, 131.4, 134.5, 138.7, 139.1, 145.2, 160.2, 206.8 ; **FT-IR** (film): υ_{max} 2930, 2852, 1731, 1656, 1516, 1432, 1325, 1238, 1200, 1112, cm^{-1}; ESI-MS (*m*/*z*) for $C_{19}H_{18}NO_2$ $[M+H]^+$: Calculated 291.1259, found 291.1271

1-(2-Phenyl-1*H*-indol-3-yl)ethanone (12a): Yield: 84% (0.84 mmol, 197 mg), Color: Orange solid R_f = 0.2 (10% EtOAc in hexanes, TLC); **^{1}H-NMR** (400 MHz, $CDCl_3$+d_6-DMSO): δ 2.09



(s, 3H), 7.15 – 7.18 (m, 2H), 7.39 – 7.63 (m, 7H), 8.21(s, 1H), 11.6 (brs, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$+d_6-DMSO): δ, 29.29, 110.6, 113.9, 120.9, 121.0, 121.9, 126.3, 127.4, 128.3, 129.0, 132.3, 134.8, 144.1, 193.7; **FT-IR** (film): υ_{max} 3174, 1292, 1731, 1651, 1526, 1442, cm^{-1}; ESI-MS (*m*/*z*) for $C_{16}H_{14}NO$ $[M+H]^+$: Calculated 236.1075, found 236.1115

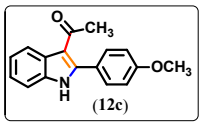
1-(5-Methyl-2-phenyl-1*H*-indol-3-yl)ethanone (12b): Yield: 88% (0.88 mmol, 219 mg), Color: Brown solid R_f = 0.2 (10% EtOAc in hexanes, TLC); **^{1}H-NMR** (400 MHz, $CDCl_3$+d_6-DMSO): δ



2.14 (s, 3H), 2.48(s, 3H),7.07(d, 1H, J = 8Hz), 7.31 (d, 1H, J = 8.8 Hz), 7.45 (s, 3H), 7.55(s, 2H), 8.15 (s, 1H), 10.57 (brs, 1H); **^{13}C-NMR** (100 MHz, , d_6-DMSO): δ, 21.6, 30.3, 111.0, 114.9, 121.9, 124.7, 127.6, 128.4, 129.3, 129.9,

131.7, 133.3, 133.9, 145.0, 195.4; **FT-IR** (film): υ_{max} 3120, 2830,1721, 1652, 1446, 1432, 1305, 1240 cm^{-1}; ESI-MS (*m*/*z*) for $C_{19}H_{16}NO$ $[M+H]^+$: Calculated 250.1232, found 250.1280

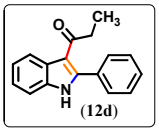
1-(2-(4-Methoxyphenyl)-1*H*-indol-3-yl)ethanone (12c): Yield: 86% (0.86 mmol, 228 mg), Color: Colorless solid R_f = 0.2 (20% EtOAc in hexanes, TLC); **^{1}H-NMR** (400 MHz, d_6-DMSO):



(12c)

δ 2.20 (s, 3H), 3.89 (s, 3H), 7.02 (d, 2H, *J* = 6.8 Hz), 7.03 – 7.26 (m, 2H), 7.32 – 7.43 (m, 1H), 7.52 (d, 2H, *J* = 6.8 Hz), 8.31 – 8.33 (m, 1H), 10.45 (brs, 1H); **^{13}C-NMR** (100 MHz, , d_6-DMSO): δ, 30.3, 55.38, 111.2, 113.9, 115.0, 122.0, 122.1, 123.0, 125.2, 127.5, 131.2, 135.3, 144.9, 160.5, 195.3; **FT-IR** (film): υ_{max} 3219, 3061,1710, 1556, 1416, 1412, 1315, 1218, 1140 cm^{-1}; ESI-MS (*m*/*z*) for $C_{17}H_{16}NO_2$ $[M+H]^+$: Calculated 266.1181, found 266.1192

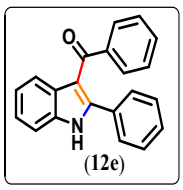
1-(2-Phenyl-1*H*-indol-3-yl)propan-1-one (12d): Yield: 75% (0.75 mmol, 187 mg), Color: Gray solid R_f = 0.2 (15% EtOAc in hexanes, TLC); **^{1}H-NMR** (400 MHz, d_6-DMSO): δ 1.05 (t, 3H, J =



(12d)

7.32 Hz), 2.52 (q, 2H, *J* = 7.2 Hz), 7.25 – 7.30 (m, 2H), 7.32 – 7.39 (m, 1H), 7.45 – 7.51 (m, 3H), 7.55 – 7.57 (m, 2H), 8.33 (brs, 1H), 8.35 (d, 1H, *J* = 2.8 Hz); **^{13}C-NMR** (100 MHz, d_6-DMSO+CD_3OD): δ, 8.7, 34.9, 111.1, 111.1, 114.5, 121.9, 122.2, 123.1, 125.4, 127.2, 128.4, 128.9, 129.2, 129.5, 133.0, 133.0, 135.3, 135.5, 144.2, 199.7 ; **FT-IR** (film): υ_{max} 3021, 2720,1725, 1546, 1526, 1452, 1335, 1328 cm^{-1}; ESI-MS (*m*/*z*) for $C_{17}H_{16}NO$ $[M+H]^+$: Calculated 250.1232 found 250.1280.

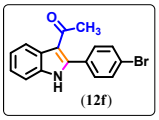
Phenyl(2-phenyl-1*H*-indol-3-yl)methanone (12e): Yield: 86% (0.86 mmol, 255 mg), Color: Yellow solid R_f = 0.2 (25% EtOAc in hexanes, TLC); **^{1}H-NMR** (400 MHz, d_6-DMSO): δ 7.15 –



(12e)

7.18 (m, 2H), 7.21 – 7.25 (m, 4H), 7.28 – 7.32 (m, 2H), 7.35 – 7.37 (m, 2H), 7.45 (d, 1H, *J* = 8.0 Hz), 7.64 (d, 2H, *J* =7.4 Hz), 7.94 (d, 1H, *J* = 7.8 Hz), 8.52 (brs, 1H); **^{13}C-NMR** (100 MHz, , d_6-DMSO+CD_3OD): δ, 111.2, 113.1, 121.3, 121.9, 123.2, 127.6, 128.0, 128.4, 128.5, 129.3, 129.5, 131.4, 131.7, 131.7, 135.7, 135.8, 139.7, 144.6, 194.0; **FT-IR** (film): υ_{max} 3040, 2930, 1731, 1656, 1516, 1432, cm^{-1}; ESI-MS (*m*/*z*) for $C_{21}H_{16}NO$ $[M+H]^+$: Calculated 298.1232, found 298.1271.

1-(2-(4-Bromophenyl)-1*H*-indol-3-yl)ethanone (12f): Yield: 80% (0.80 mmol, 250 mg), Color:

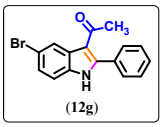


(12f)

Colorless solid R_f = 0.2 (15% EtOAc in hexanes, TLC); **^{1}H-NMR** (400 MHz, $CDCl_3$+ 2 drops CD_3OD): δ 2.19 (s, 3H), 7.21 – 7.23 (m, 2H), 7.33 – 7.35 (m,

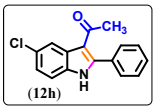
1H), 7.39 (d, 2H, *J* = 8.2 Hz), 7.57 (d, 2H, *J* = 8.2 Hz), 8.20 – 8.22 (m, 1H); **^{13}C-NMR** (100 MHz, d_6-DMSO): δ 30.3, 111.7, 114.4, 121.5, 121.8, 122.8, 122.9, 126.9, 131.3, 131.8, 132.0, 135.5, 143.2, 193.4; **FT-IR** (film): υ_{max} 3018, 2713,1730, 1515, 1526, 1458, 1337, 1338 cm^{-1}; ESI-MS (*m*/*z*) for $C_{16}H_{13}BrNO$ $[M+H]^+$: Calculated 314.0181 found 314.0178.

1-(5-Bromo-2-phenyl-1*H*-indol-3-yl)ethanone (12g): Yield: 82% (0.82 mmol, 256 mg), Color: Colorless solid R_f = 0.2 (10% EtOAc in hexanes, TLC); **^{1}H-NMR** (400 MHz, $CDCl_3$+ 2 drops CD_3OD): δ 2.04 (s, 3H), 7.18 (d, 1H, *J* = 8.5 Hz), 7.25 (d, 1H, *J* = 7.3 Hz), 7.43 – 7.45 (m, 5H), 8.41 (s, 1H); **^{13}C-NMR** (100 MHz, d_6-DMSO): δ, 29.8, 113.6, 113.7, 114.4, 123.7, 125.4, 128.4, 128.7,129.6,129.9,132.0,134.0,146.1,193.5 ; **FT-IR** (film): υ_{max} 3121, 2828,1730, 1643, 1420, 1408, 1315, 1250 cm^{-1}; ESI-MS (*m*/*z*) for $C_{16}H_{13}BrNO$ $[M+H]^+$: Calculated 314.0181 found 314.0185.



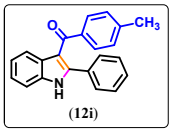
(12g)

1-(5-Chloro-2-phenyl-1*H*-indol-3-yl)ethanone (12h): Yield: 82% (0.82 mmol, 220 mg), Color: Brown solid R_f = 0.2 (15% EtOAc in hexanes, TLC); **^{1}H-NMR** (400 MHz, $CDCl_3$+ 2 drops CD_3OD): δ 2.11 (s, 3H), 7.20 (d, 1H, *J* = 8.1 Hz), 7.33 (s, 1H), 7.48 – 7.50 (m, 5H), 8.24 (d, 1H, *J* = 8.5 Hz); **^{13}C-NMR** (100 MHz, d_6-DMSO): δ, 30.0, 111.2, 114.2, 122.1, 123.0, 127.3, 128.5, 129.6, 130.0, 135.9, 145.7, 193.6; **FT-IR** (film): υ_{max} 3118, 2720,1722, 1642, 1440, 1431, 1308, 1246 cm^{-1}; ESI-MS (*m*/*z*) for $C_{16}H_{13}ClNO$ $[M+H]^+$: Calculated 270.0686 found 270.0680.



(12h)

(2-Phenyl-1*H*-indol-3-yl)(p-tolyl)methanone (12i): Yield: 72% (0.72 mmol, 223 mg), Color: Colorless solid R_f = 0.2 (10% EtOAc in hexanes, TLC); **^{1}H-NMR** (400 MHz, d_6-DMSO): δ 2.50(s, 3H), 7.24 – 7.34 (m, 6H), 7.39 (d, 2H, *J* = 7.9 Hz), 7.68 (t, 1H, *J* = 7.4 Hz), 7.82 – 7.85 (m, 2H), 8.27 (d, 1H, *J* = 7.9 Hz), 8.61 (d, 1H, 8.3 Hz), 12.20 (brs, 1H); **^{13}C-NMR** (100 MHz,$CDCl_3$+ d_6-DMSO): δ, 29.29, 110.6, 113.9, 120.9, 121.0, 121.9, 126.3, 127.4, 128.3, 129.0, 132.3, 134.8, 144.1, 193.7; **FT-IR** (film): υ_{max} 3125, 2822,1715, 1649, 1450, 1430, 1310, 1280 cm^{-1}; ESI-MS (*m*/*z*) for $C_{22}H_{18}NO$ $[M+H]^+$: Calculated 312.1388 found 312.1378.



(12i)

11. Spectral Graphics

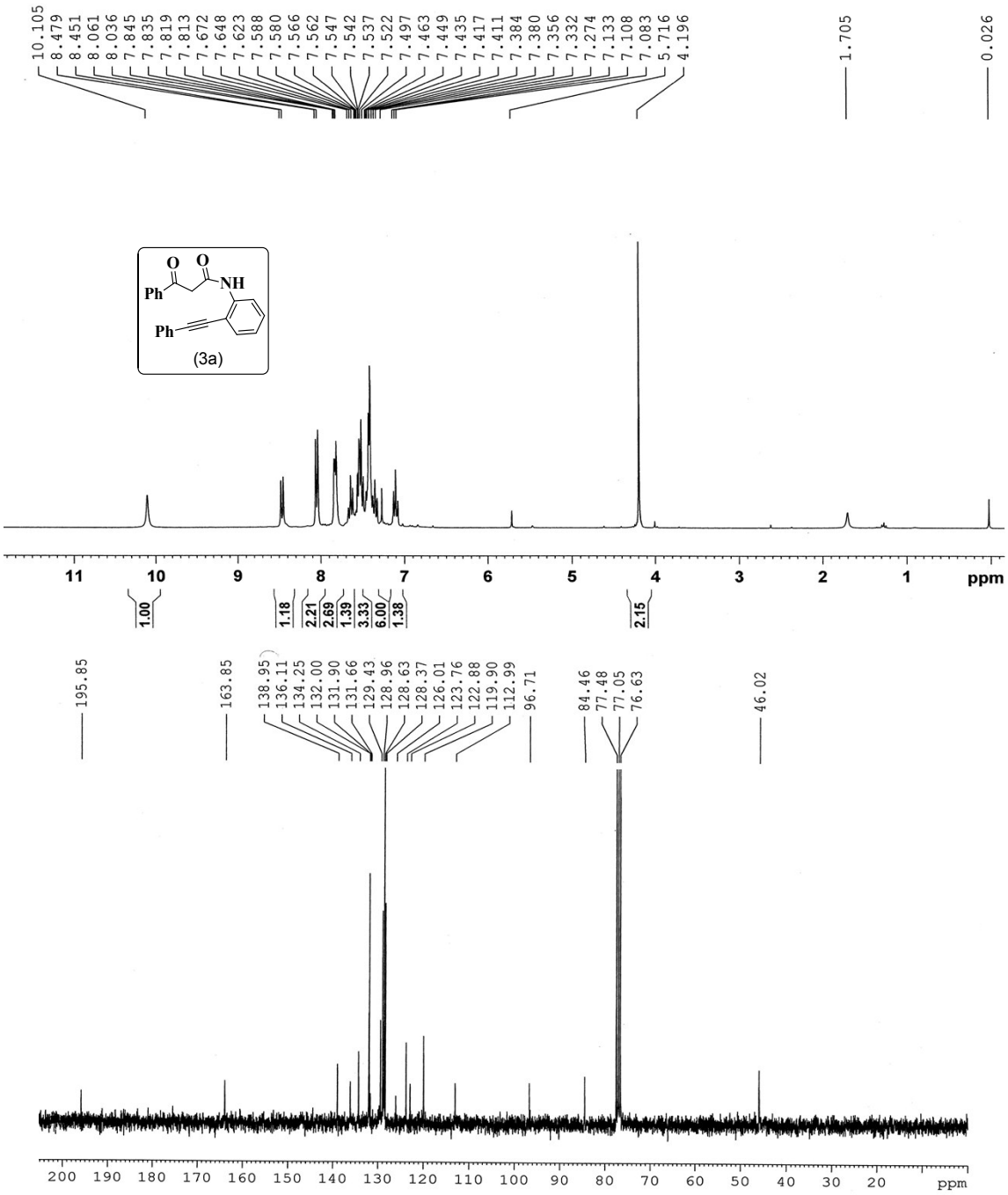


Figure S6. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, $CDCl_3$) of Compound (**3a**)

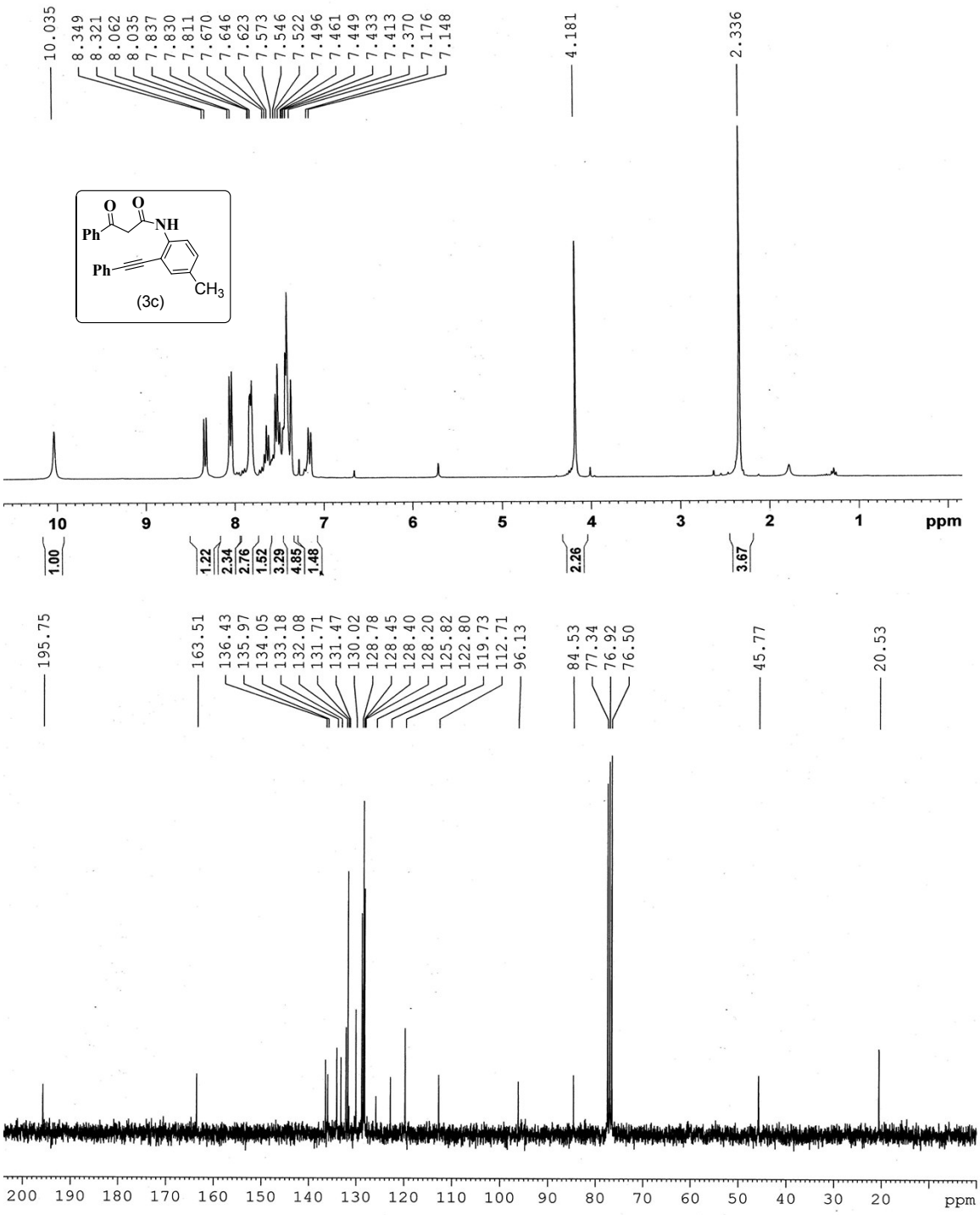


Figure S7. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, $CDCl_3$) of Compound (**3c**)

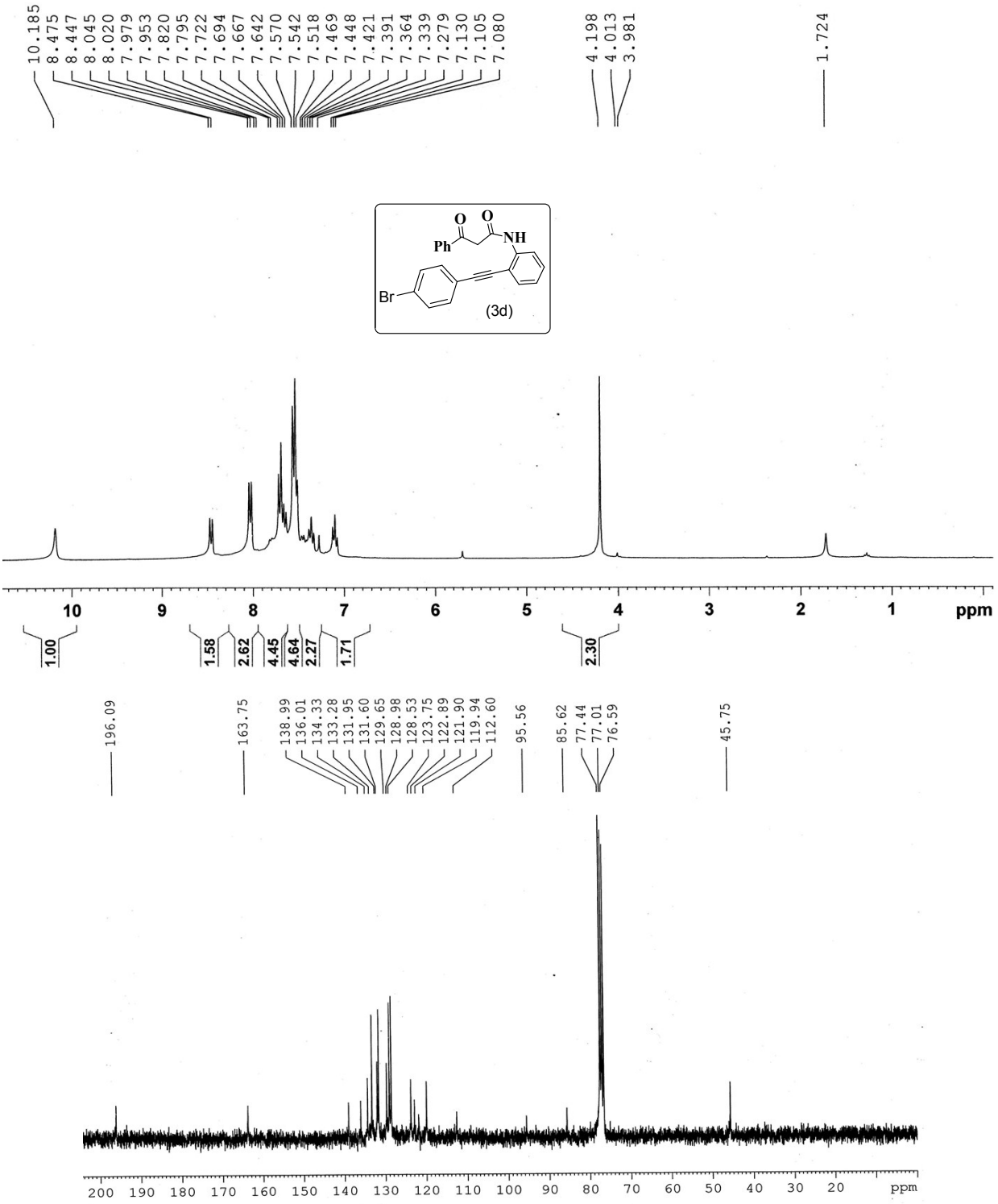


Figure S8. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, $CDCl_3$) of Compound (**3d**)

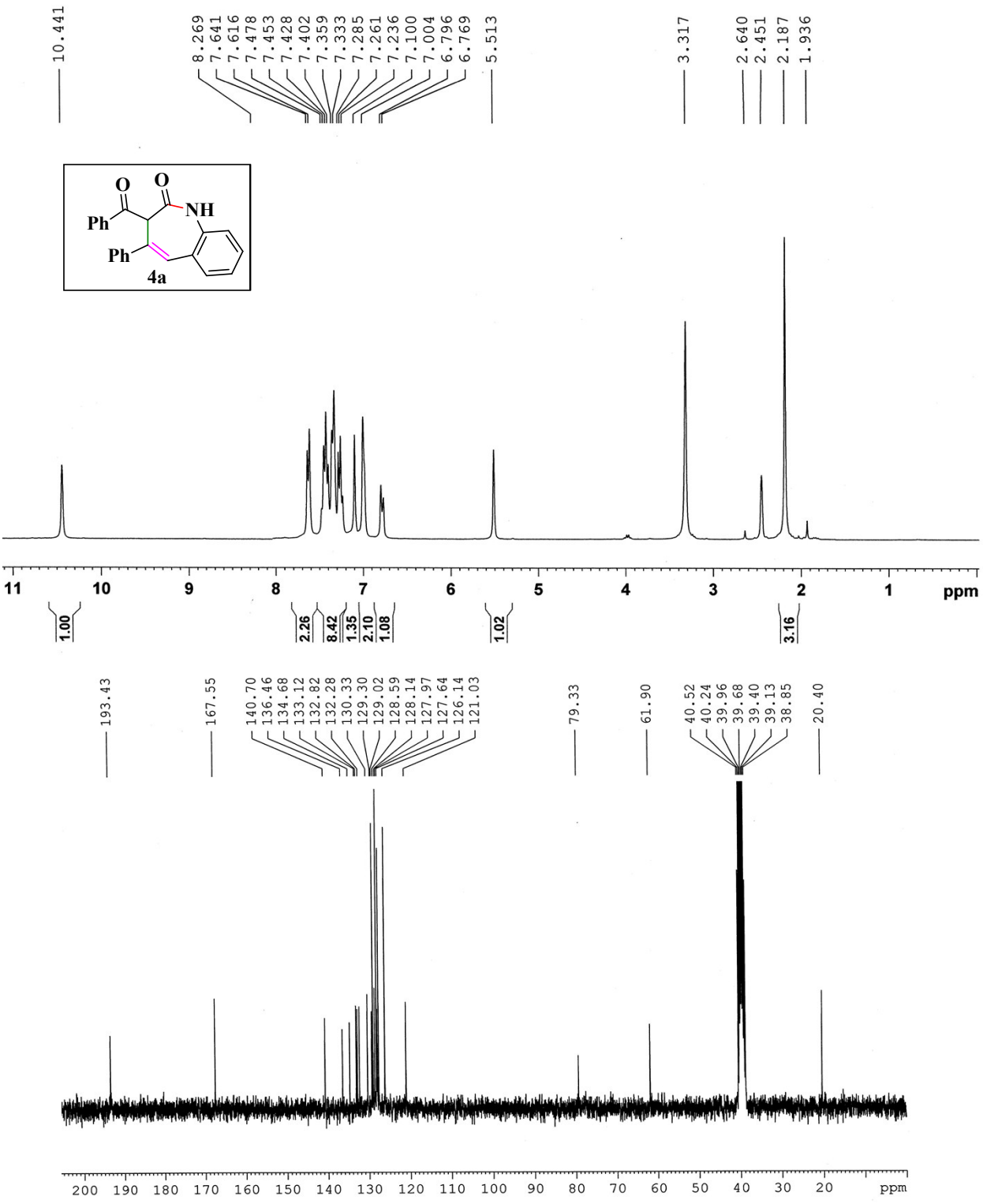


Figure S9. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6-DMSO) of Compound (**4a**)

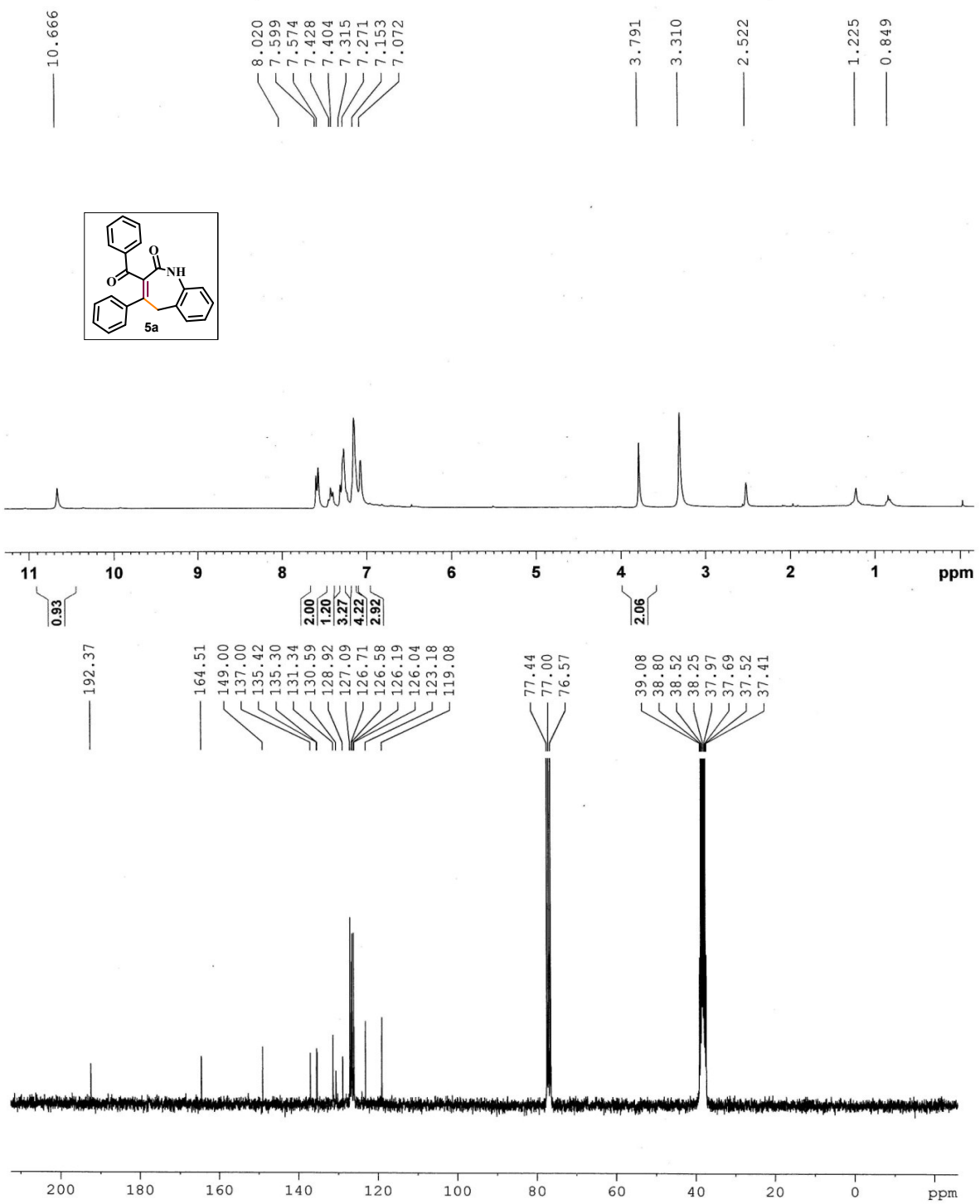


Figure S10. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, $CDCl_3$+ d_6- DMSO) of Compound (**5a**)

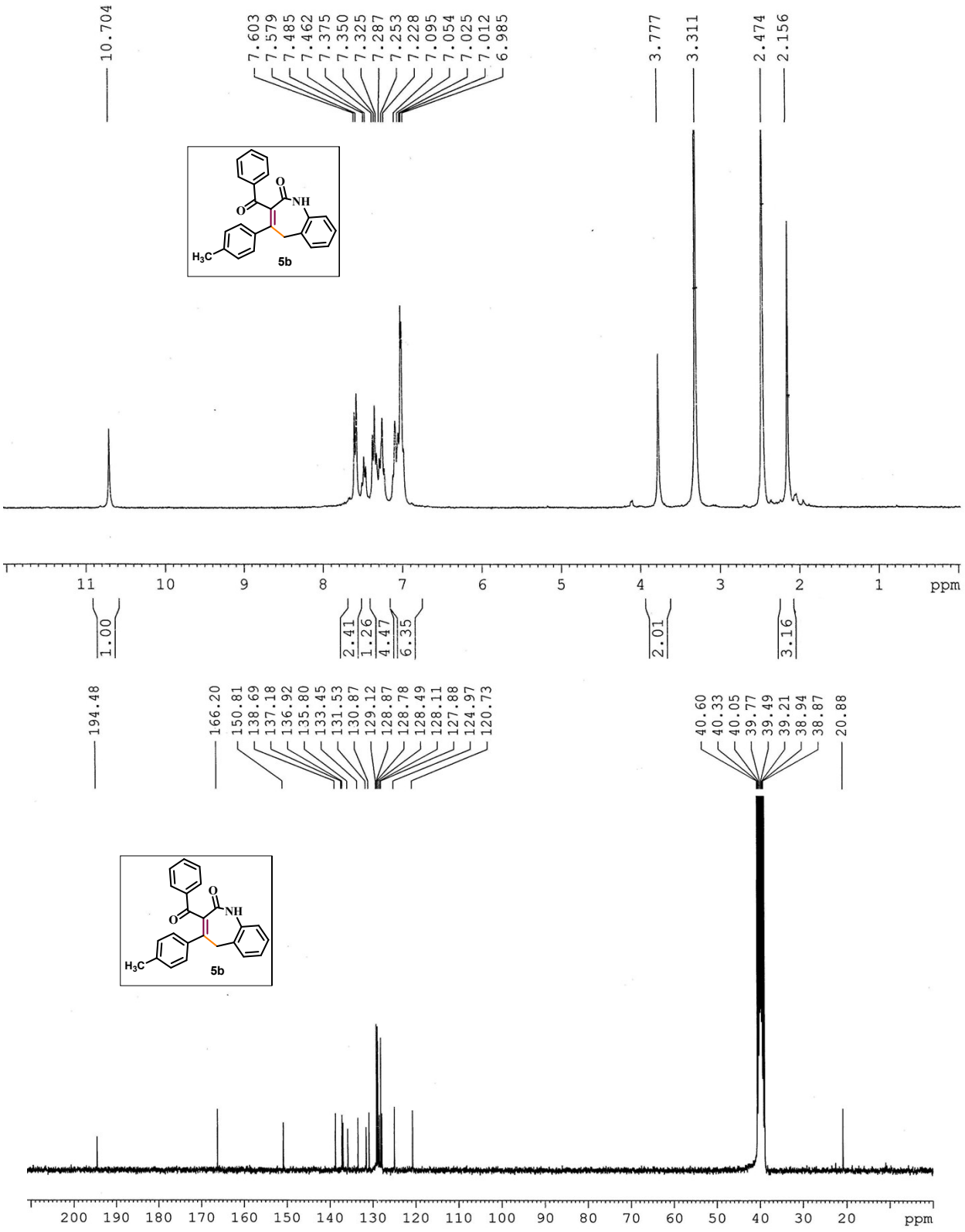


Figure S11. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**5b**)

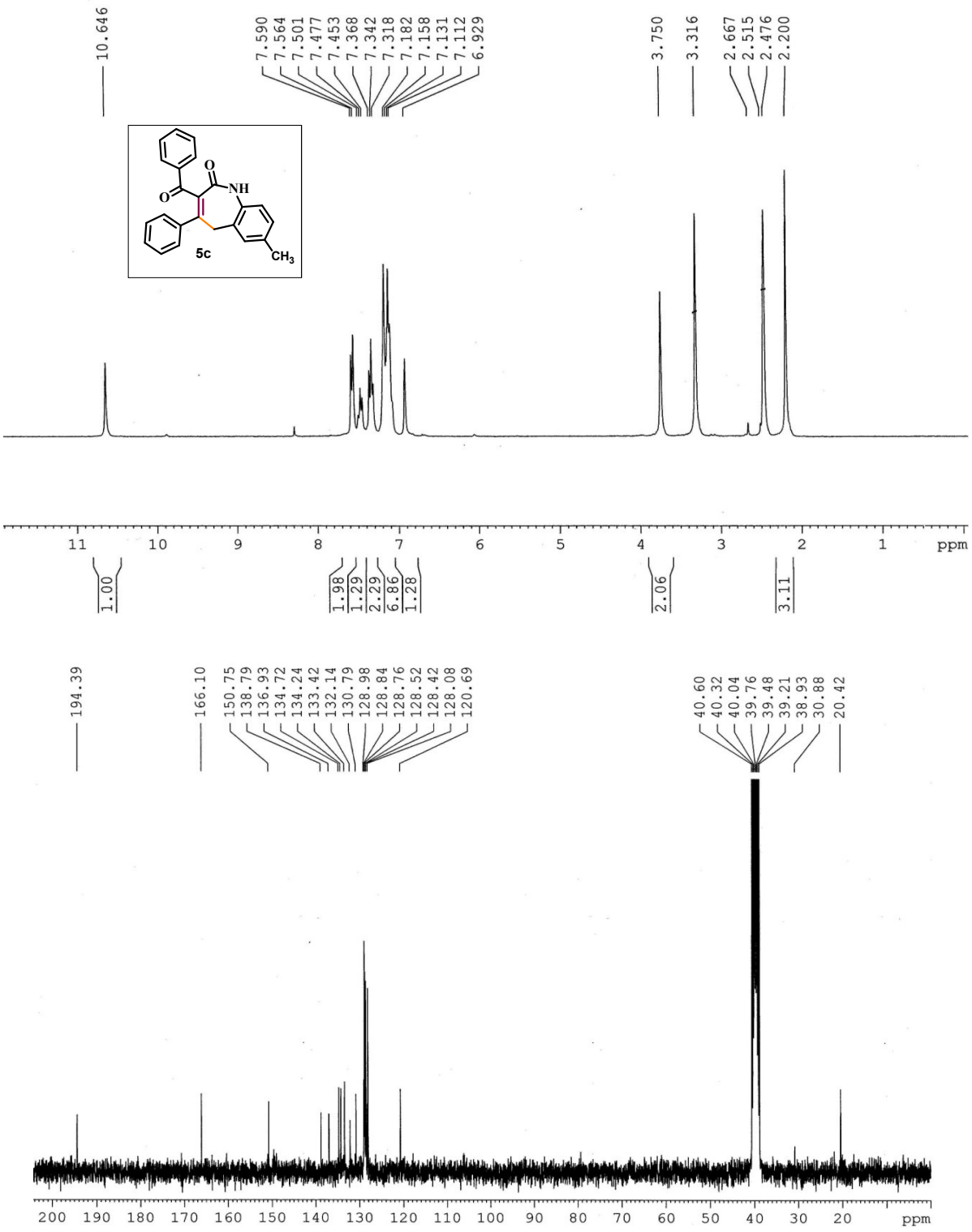


Figure S12. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**5c**)

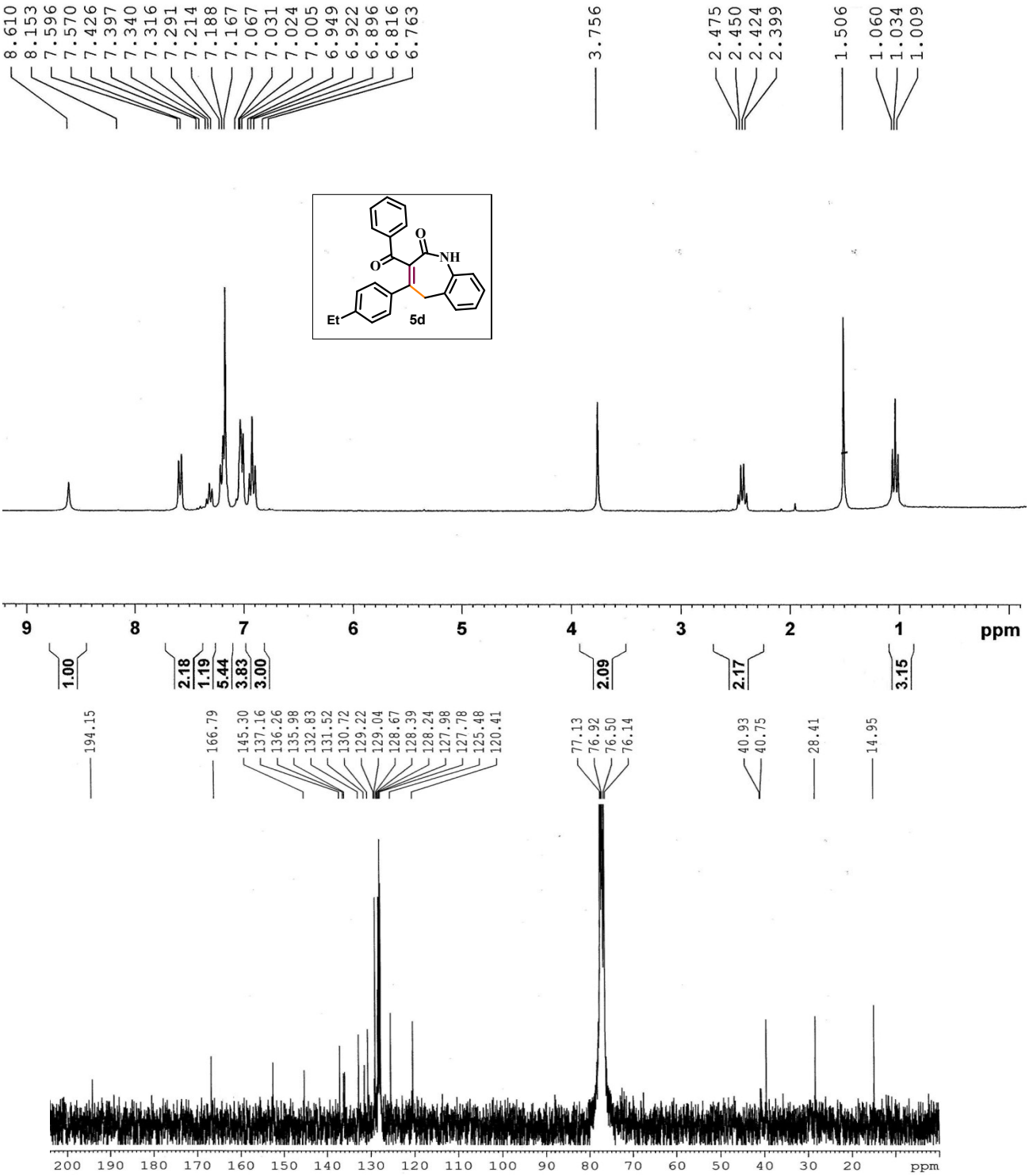


Figure S13. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz,) of Compound (**5d**)

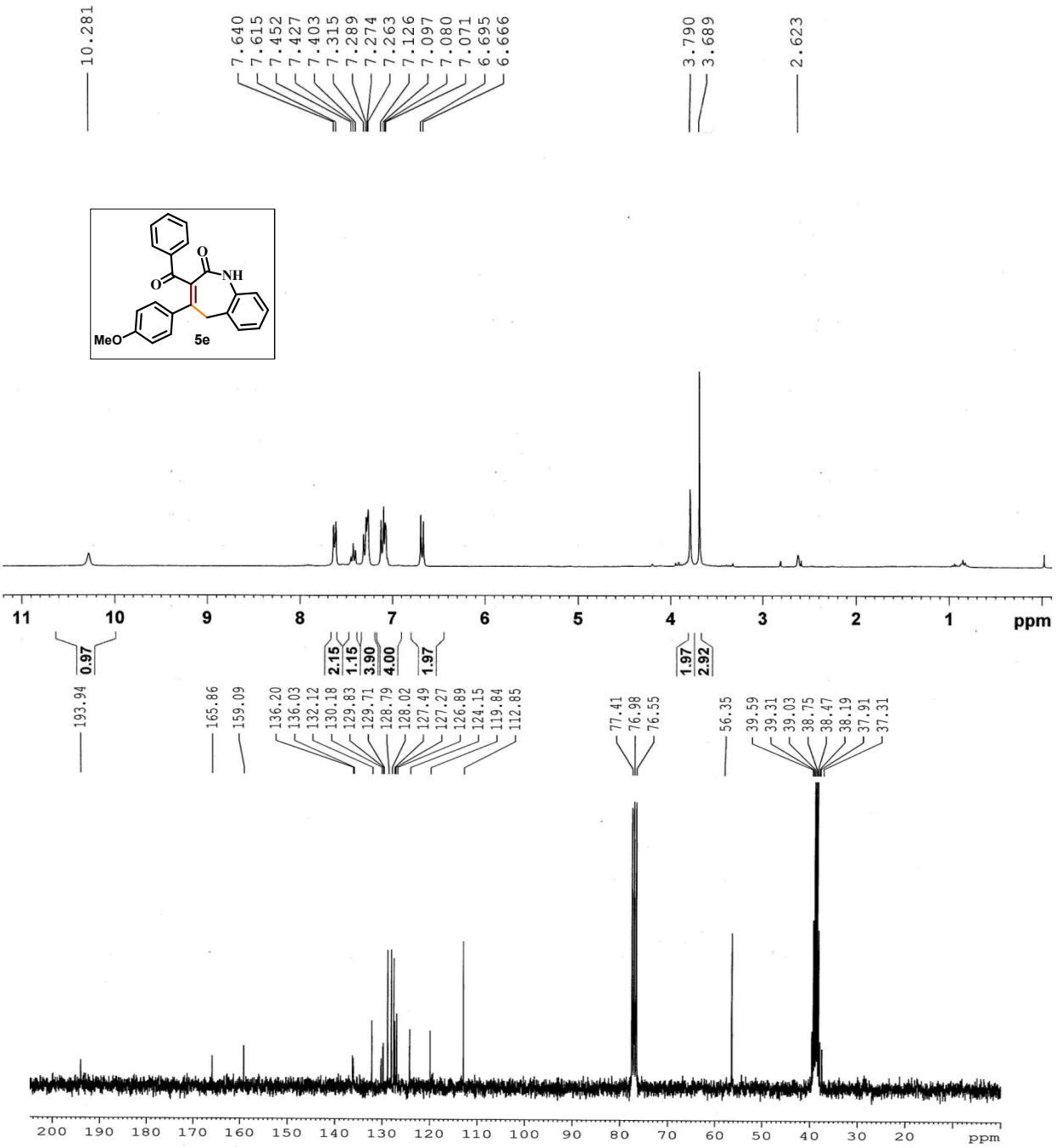


Figure S14. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, $CDCl_3$ + d_6- DMSO) of Compound (**5e**)

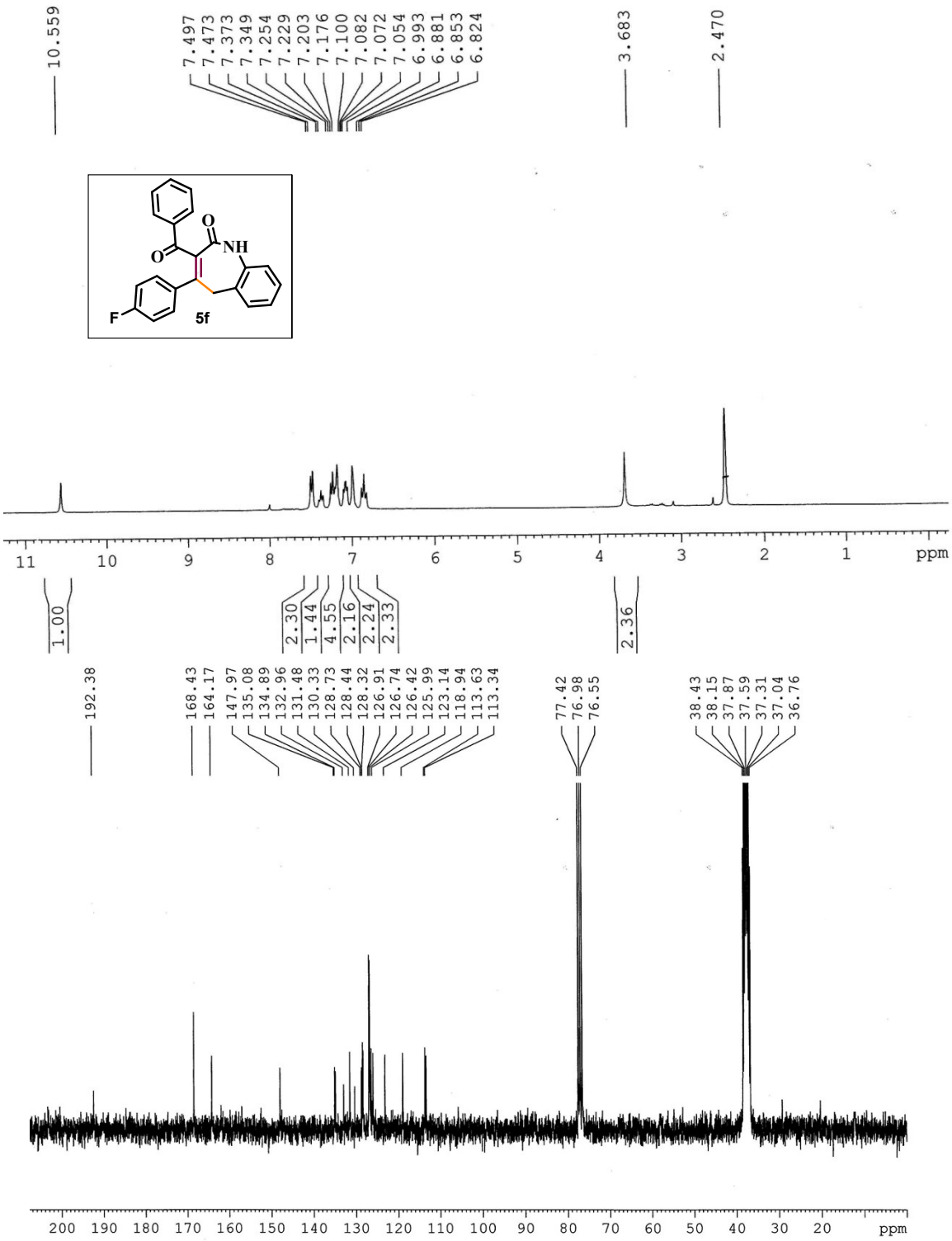


Figure S15. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, $CDCl_3$+d_6- DMSO) of Compound (**5f**)

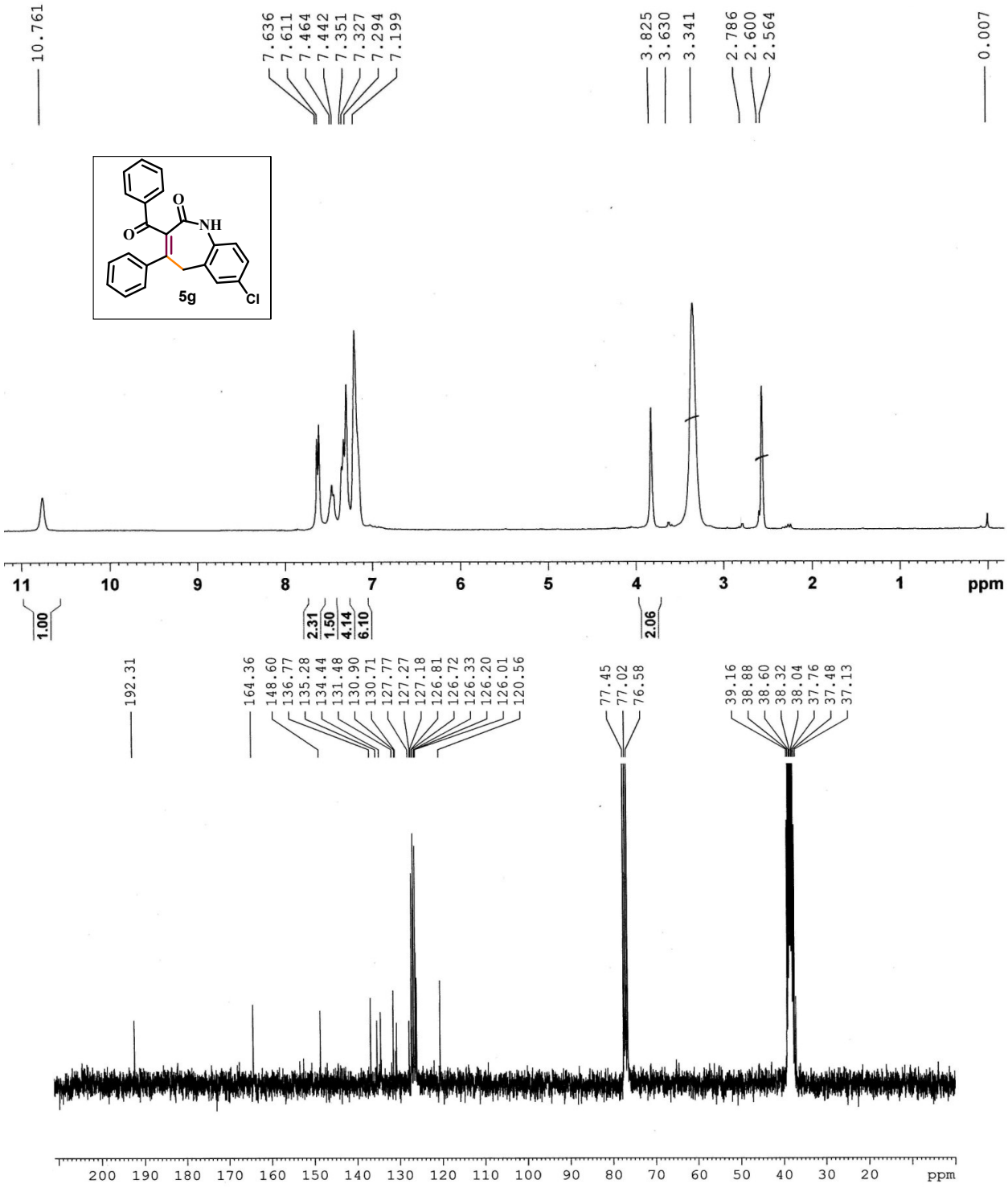


Figure S16. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, $CDCl_3$+d_6- DMSO) of Compound (**5g**)

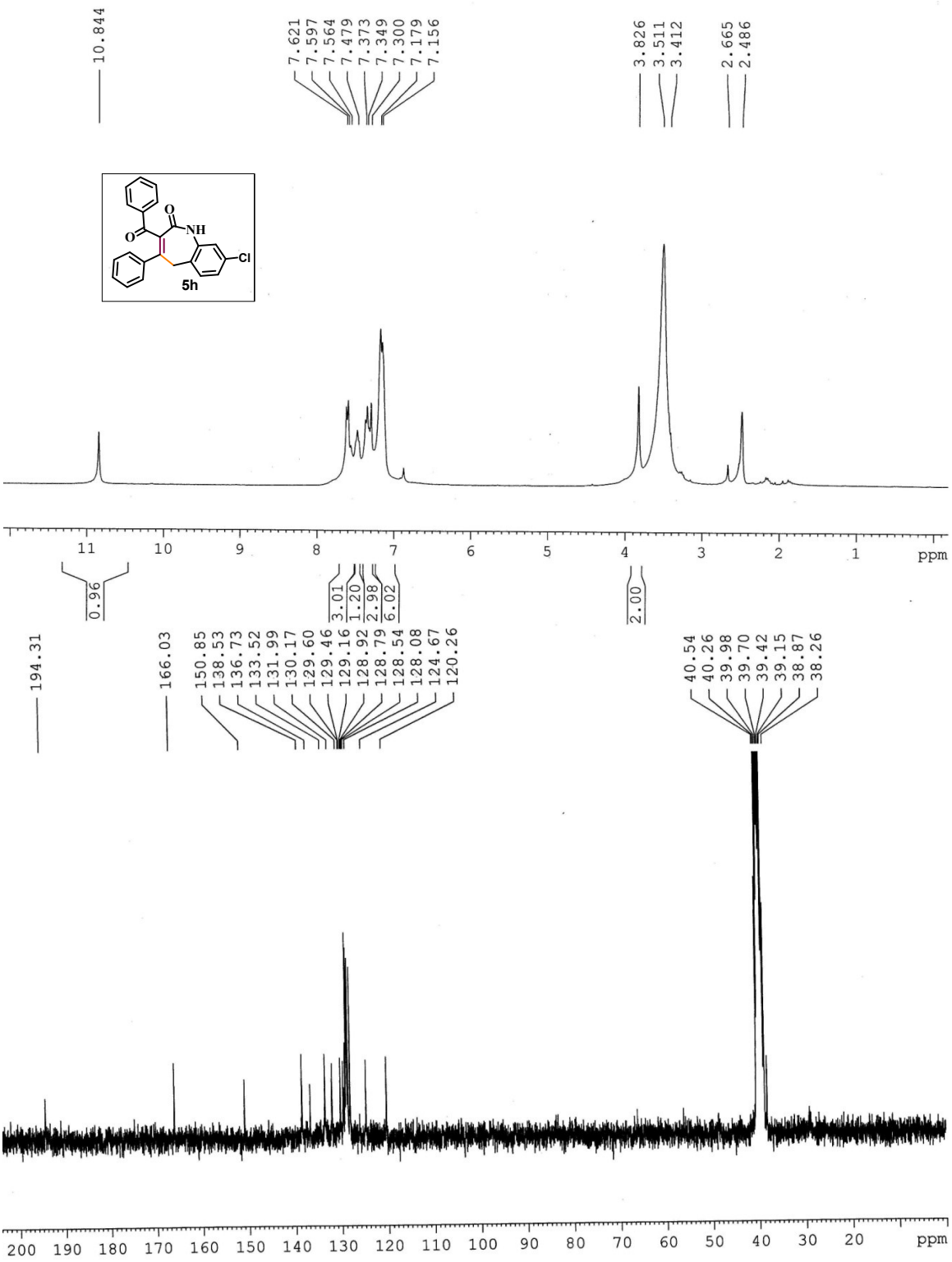


Figure S17. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**5h**)

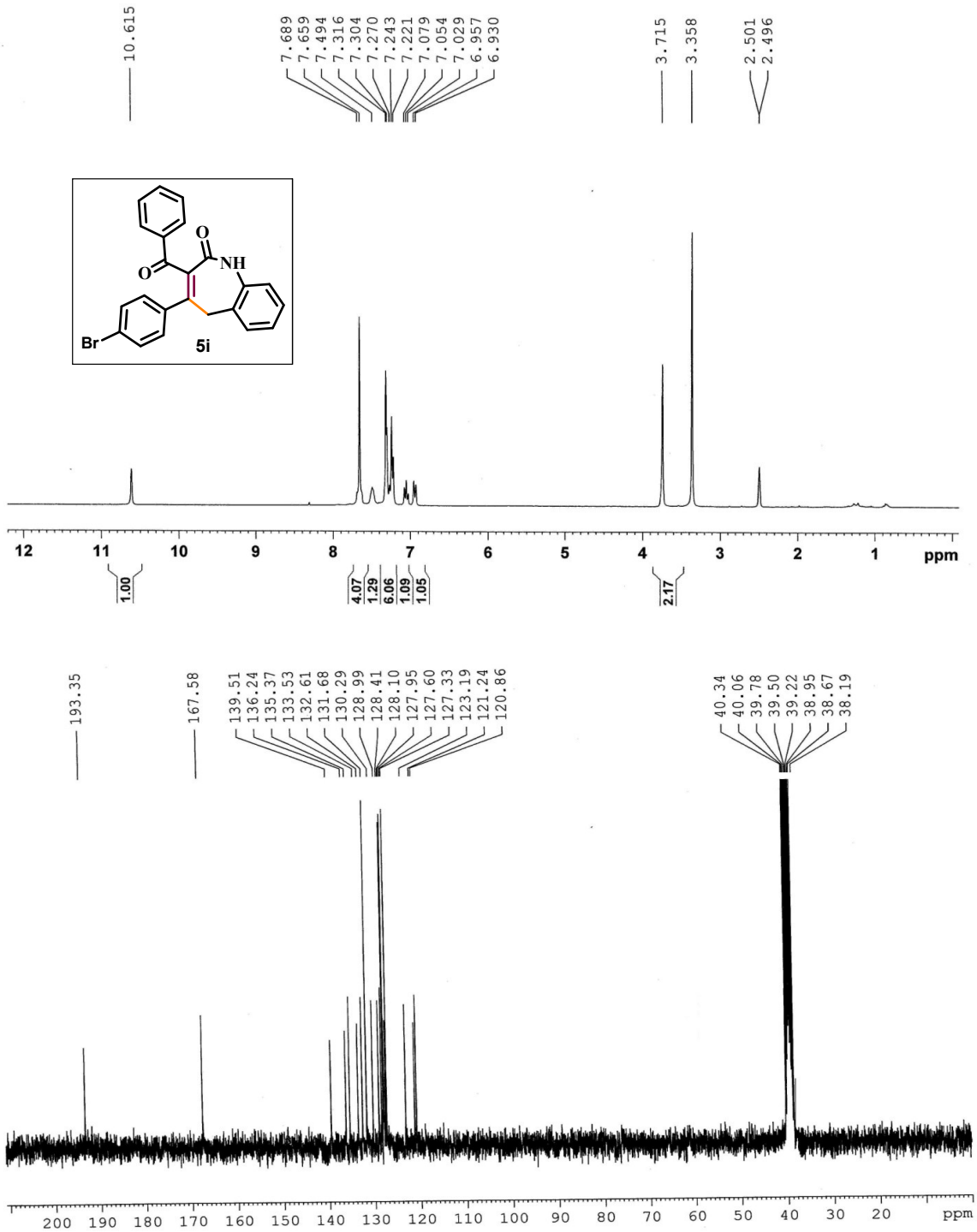


Figure S18. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**5i**)

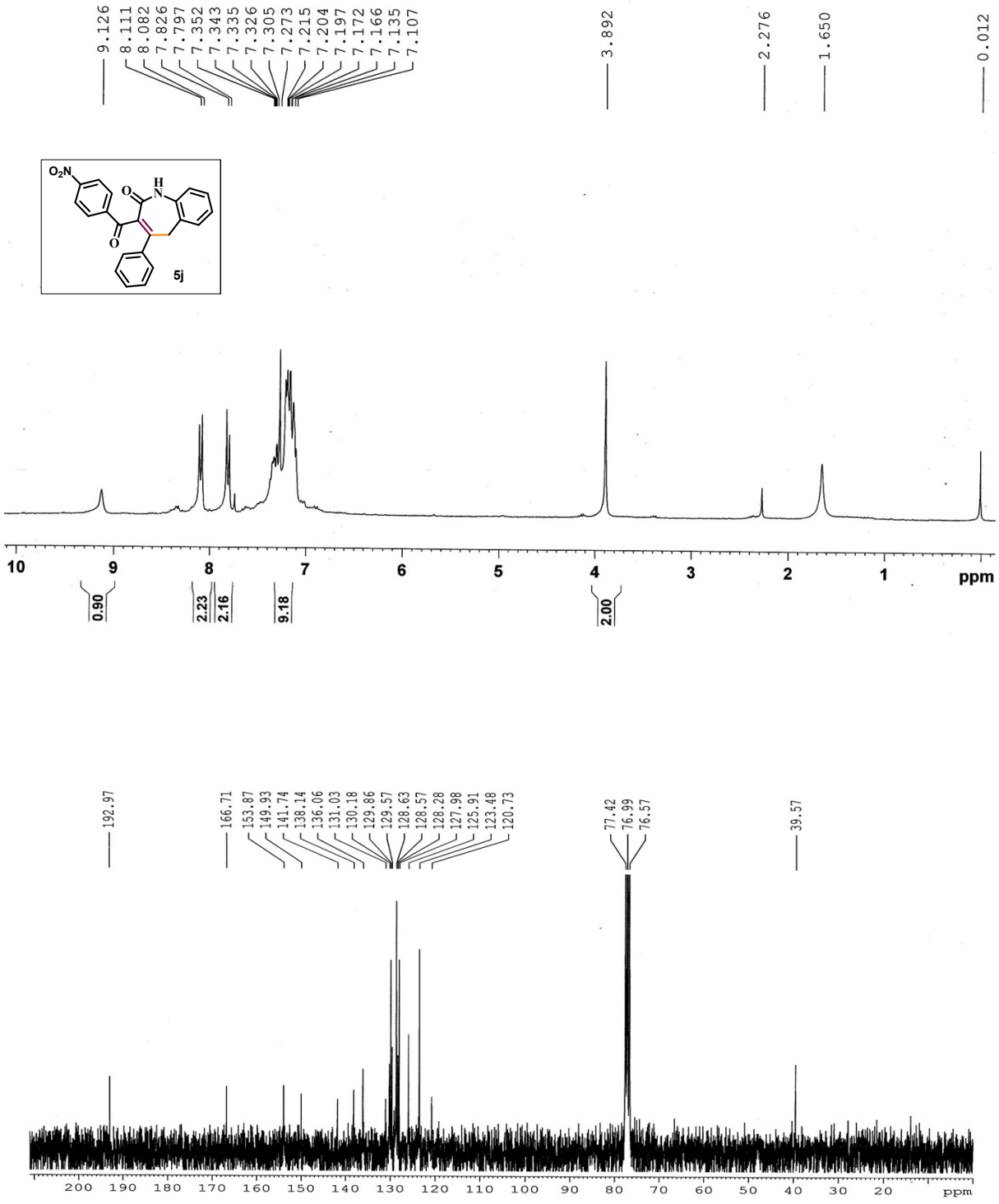


Figure S19. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, $CDCl_3$) of Compound (**5j**)

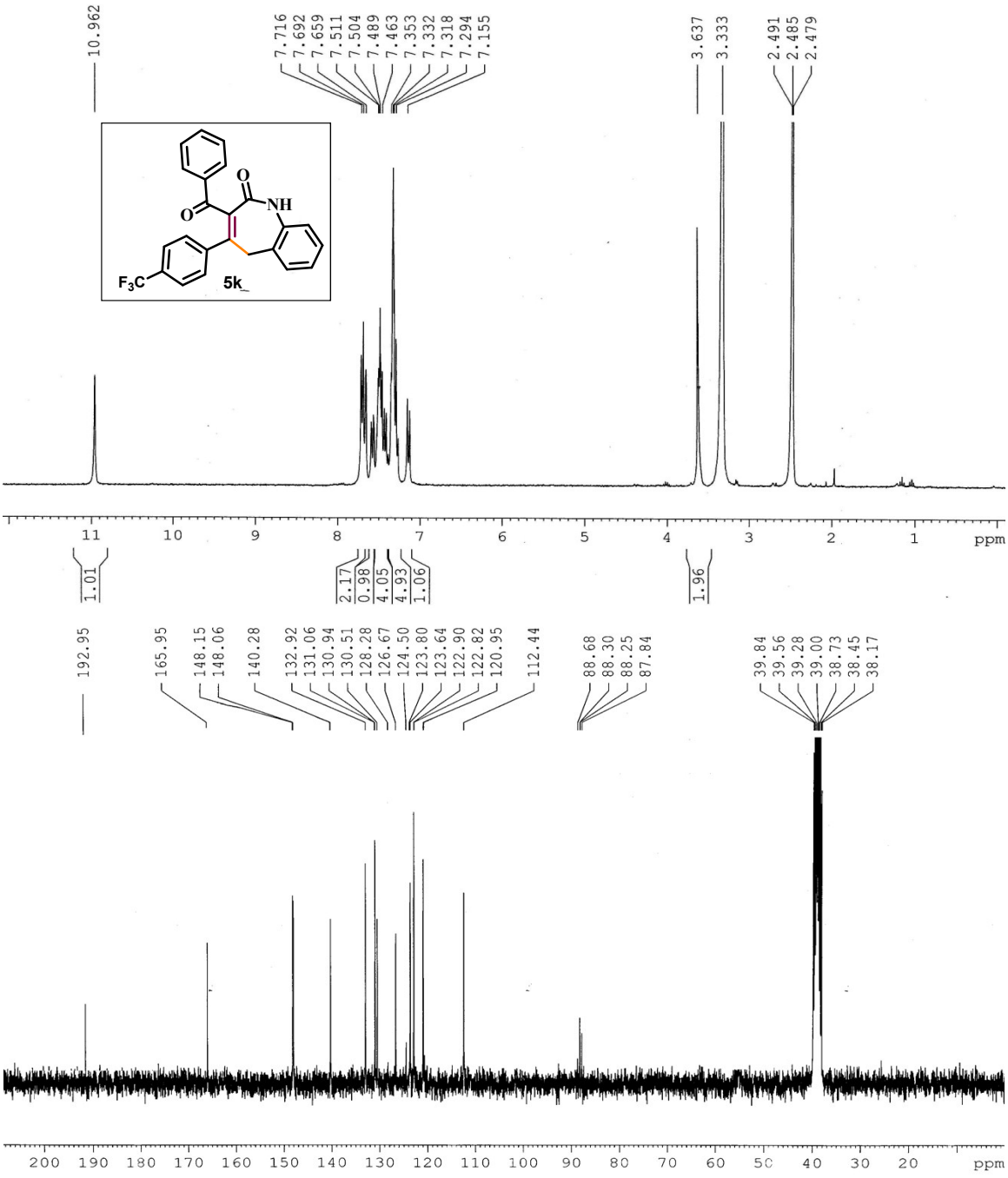


Figure S20. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**5k**)

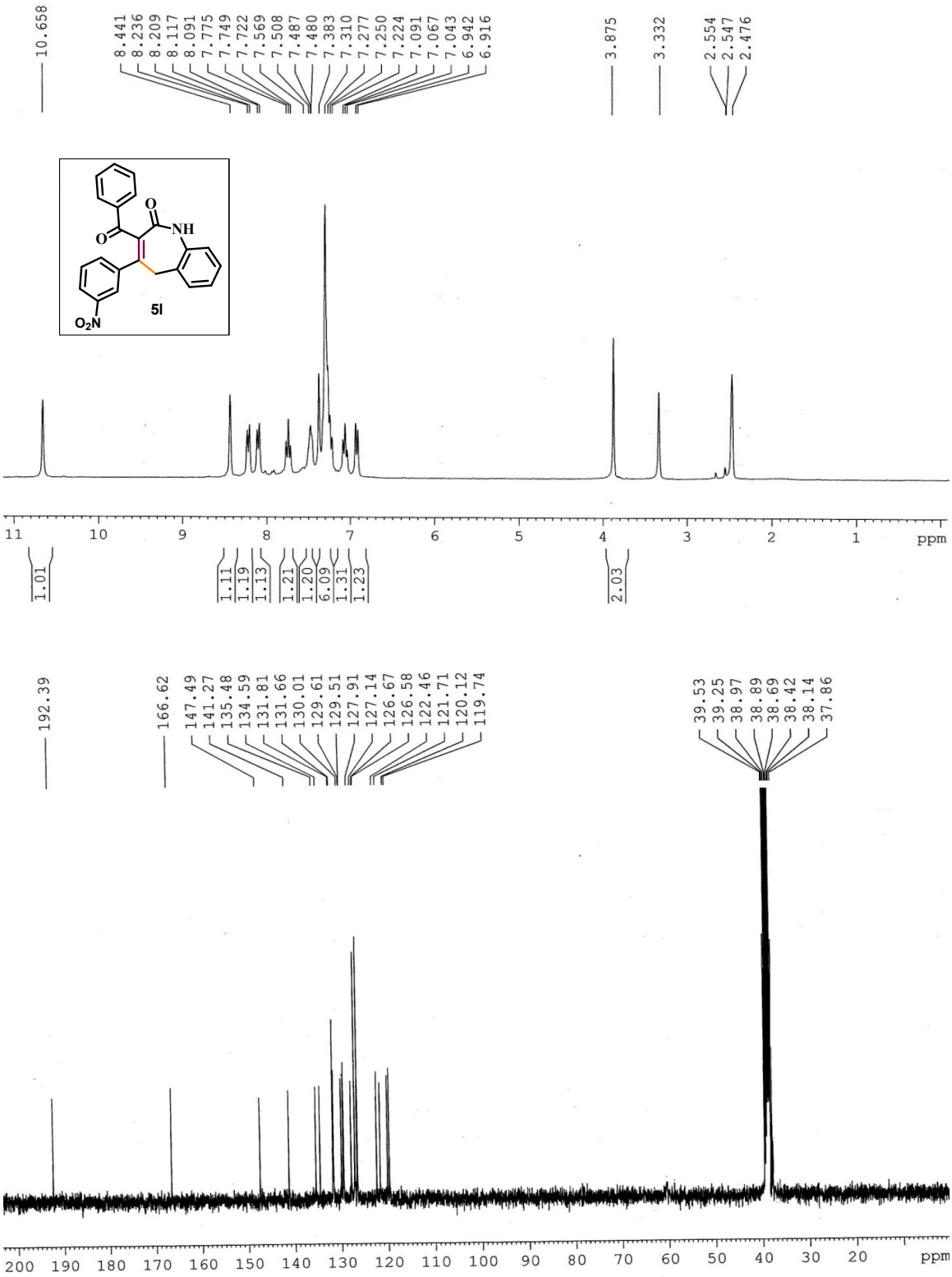


Figure S21. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**5l**)

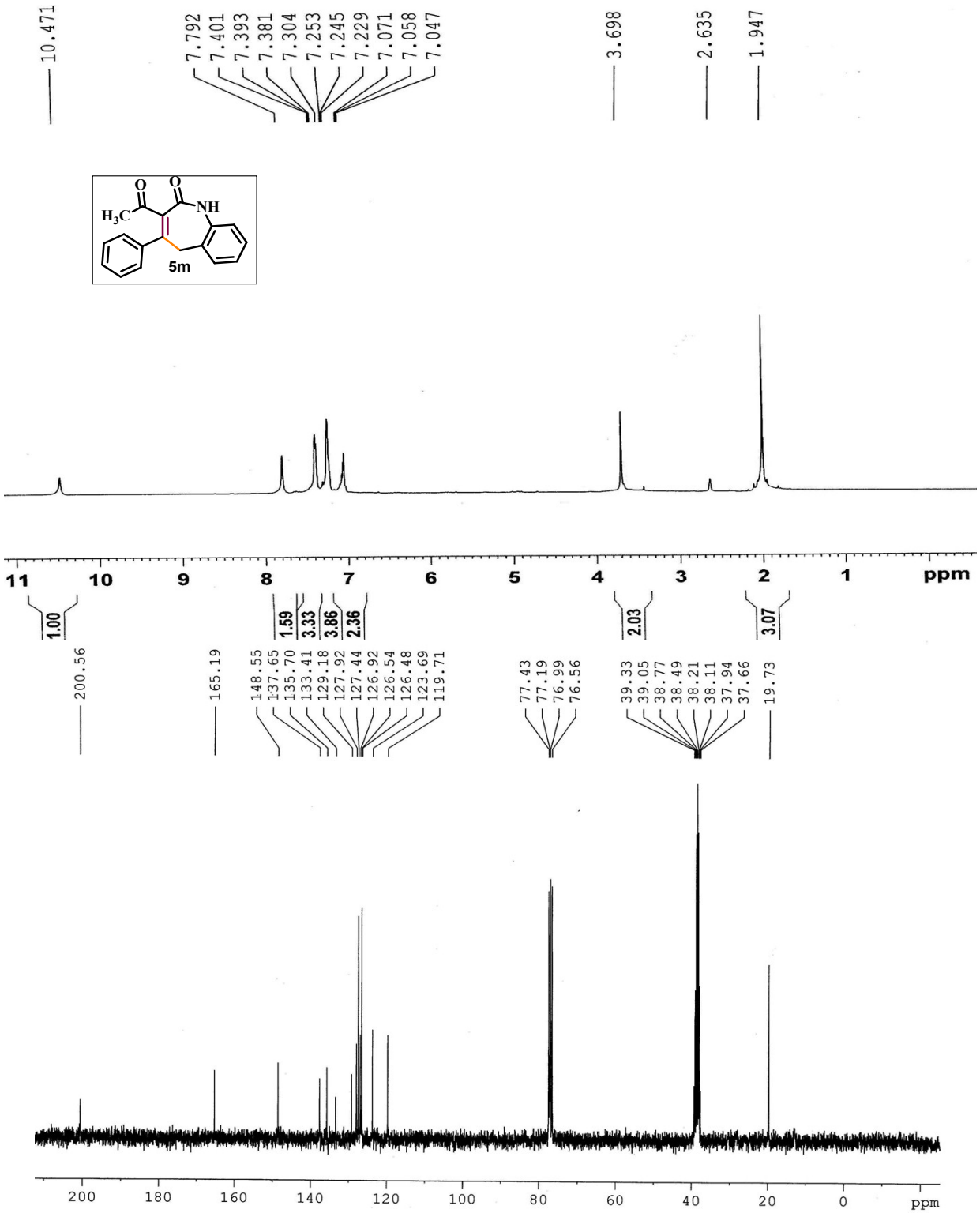


Figure S22. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, $CDCl_3$+d_6- DMSO) of Compound (**5m**)

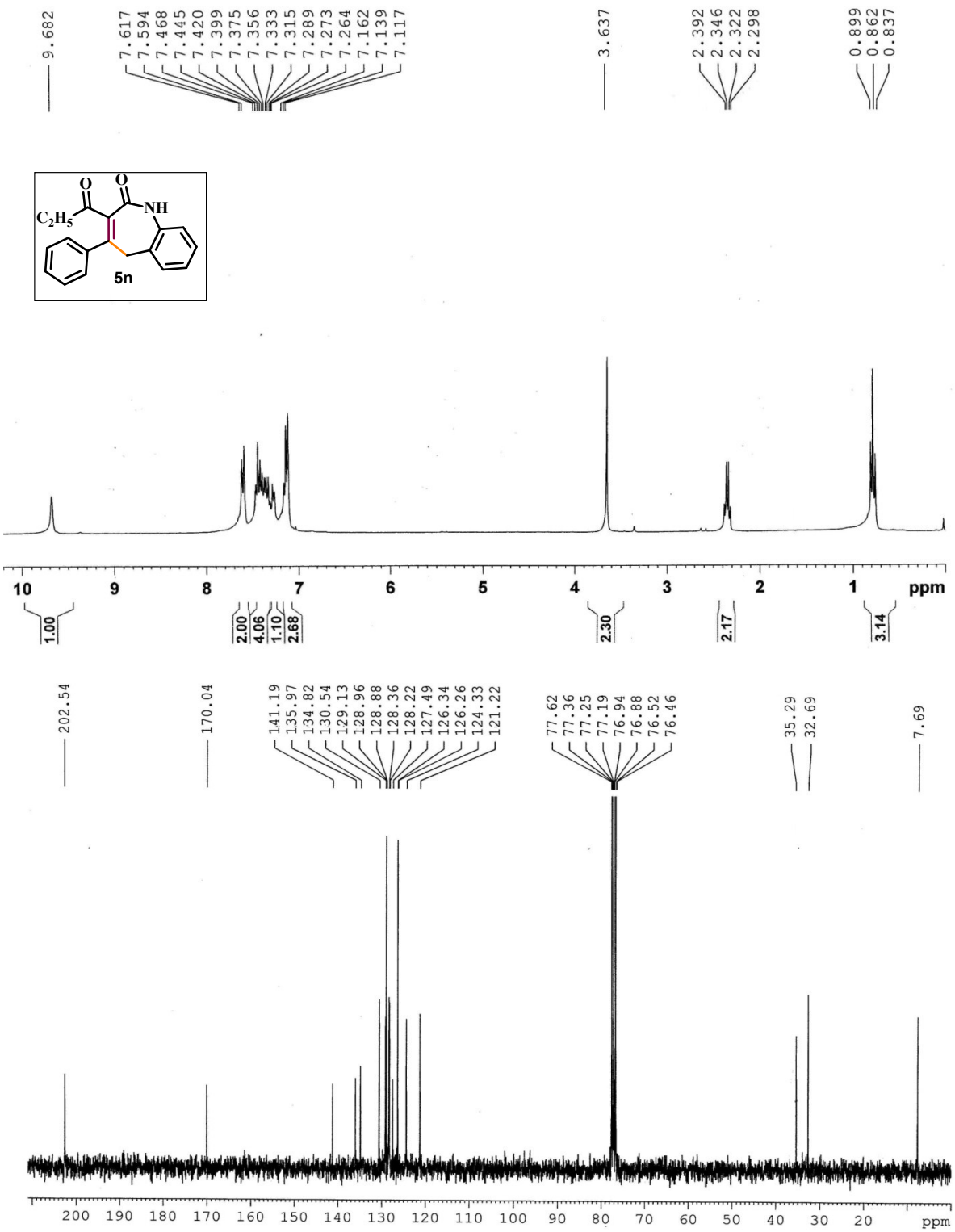


Figure S23. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, $CDCl_3$) of Compound (**5n**)

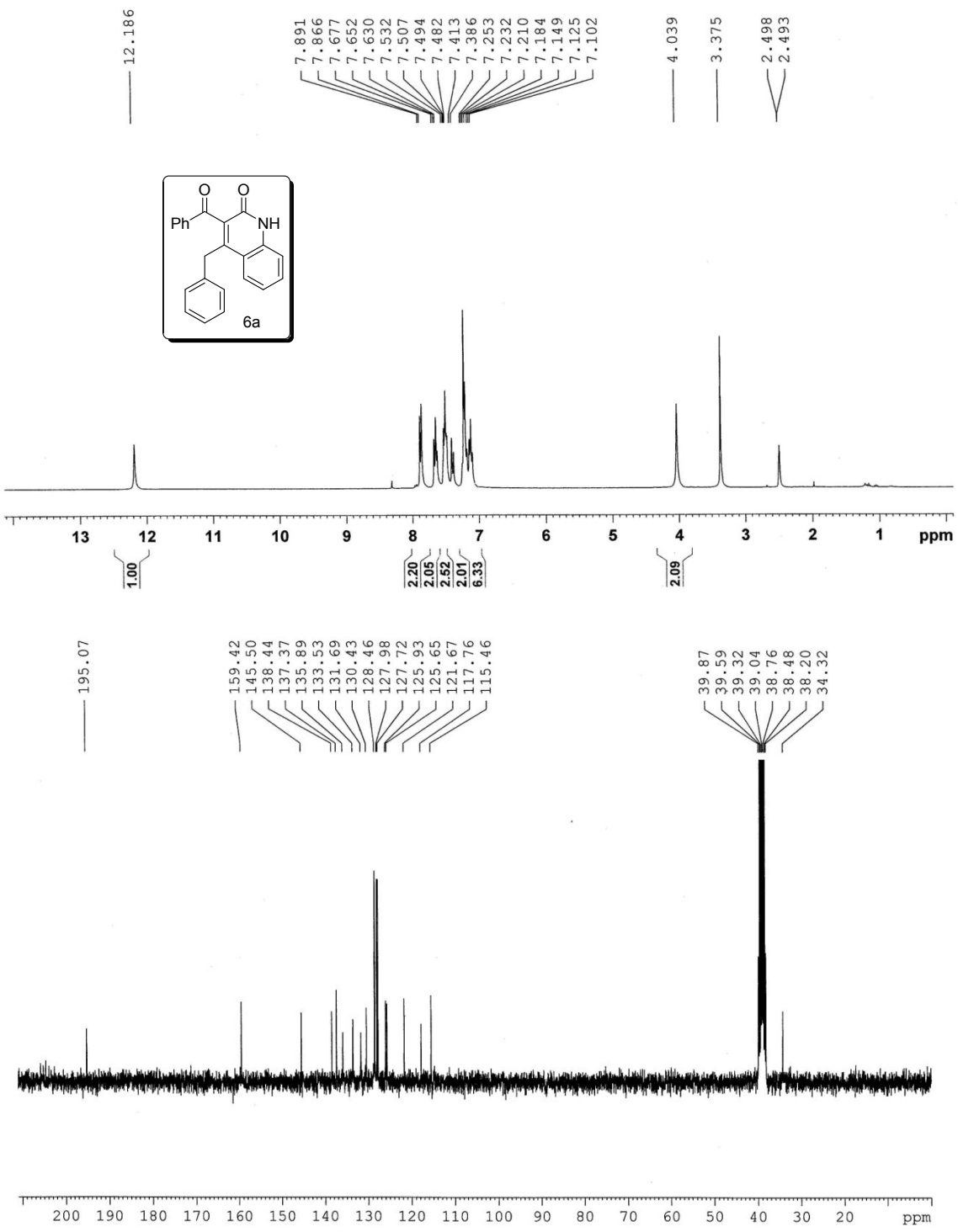


Figure S24. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**6a**)

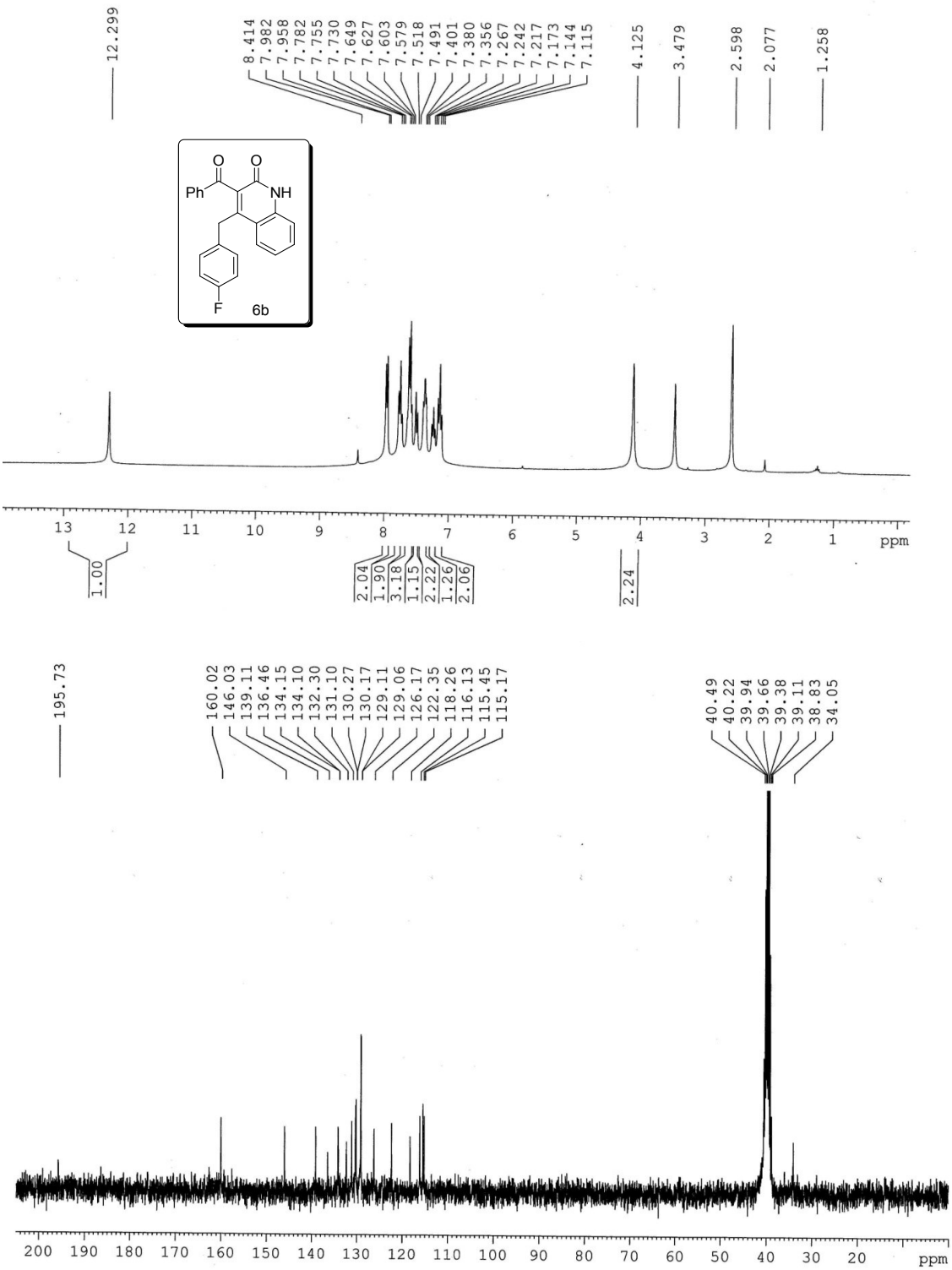


Figure S25. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**6b**)

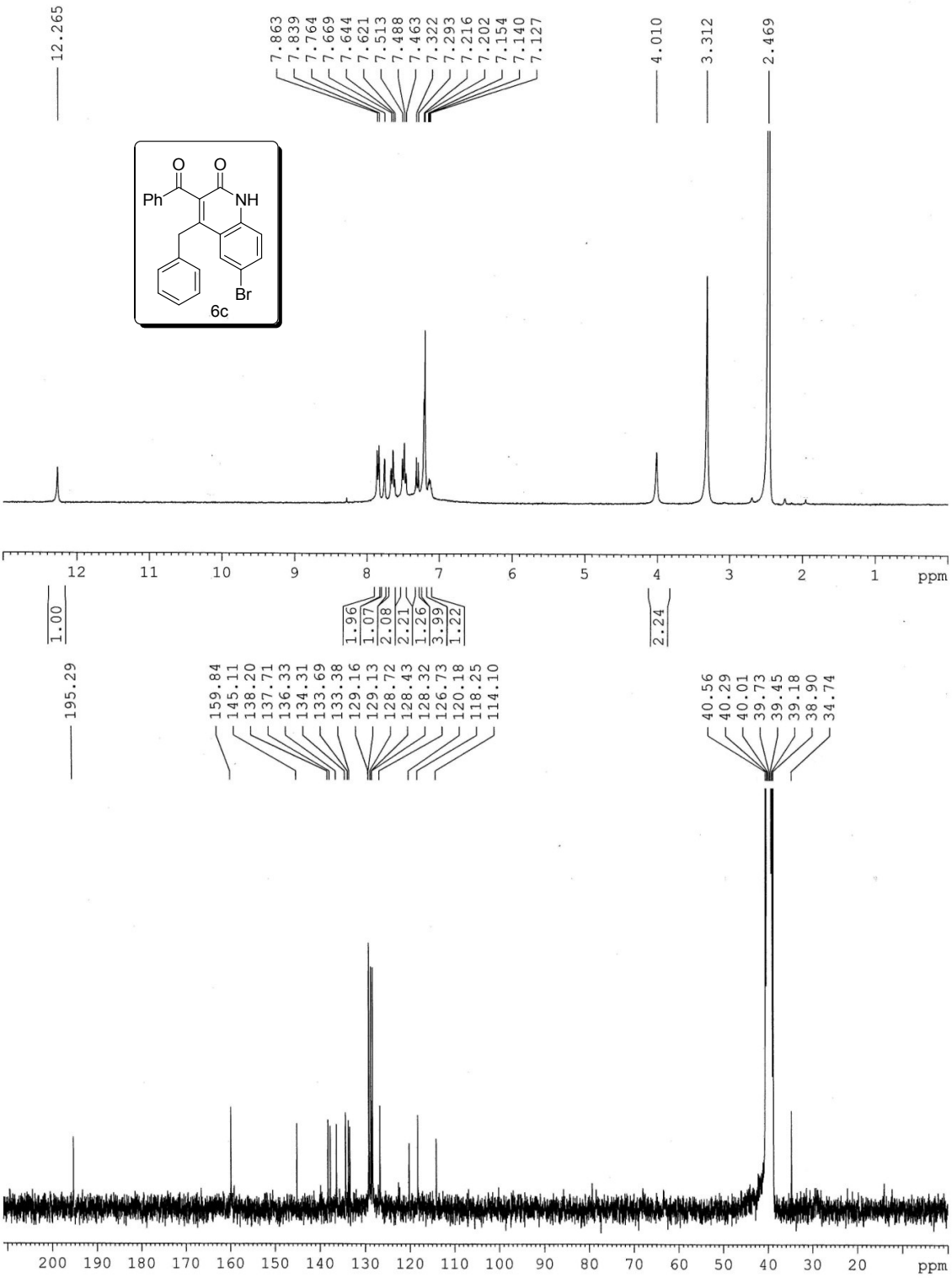


Figure S26. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**6c**)

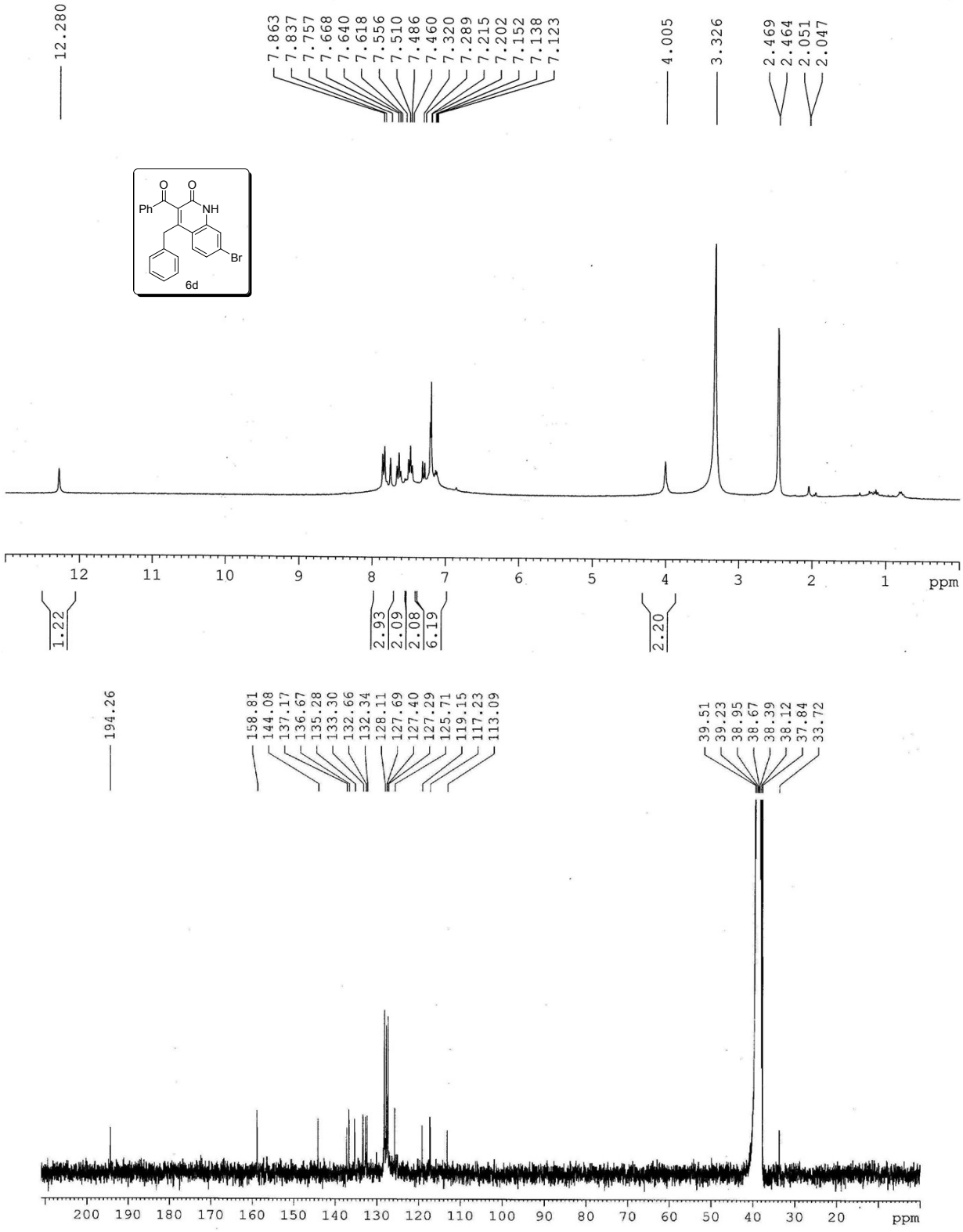


Figure S27. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**6d**)

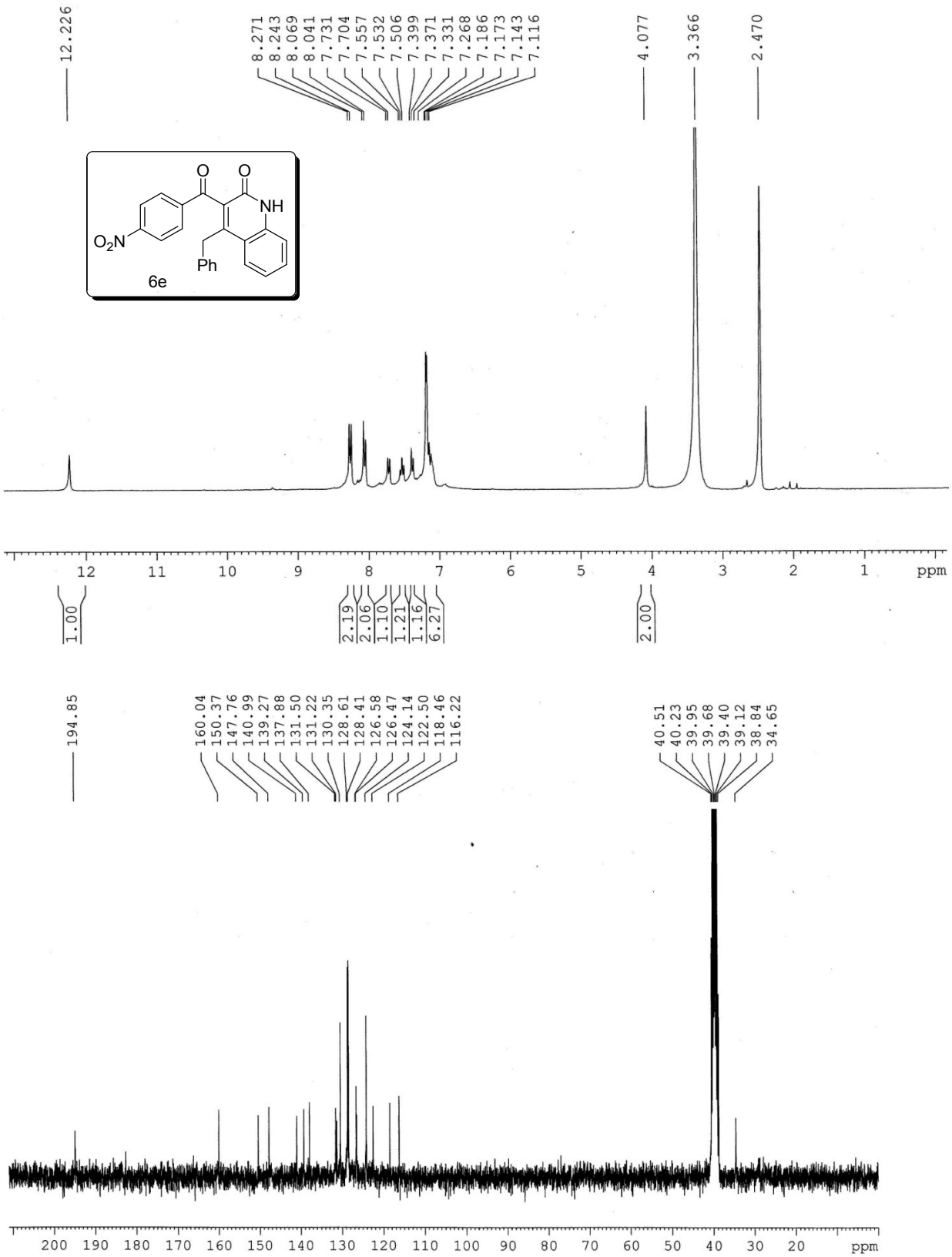


Figure S28. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**6e**)

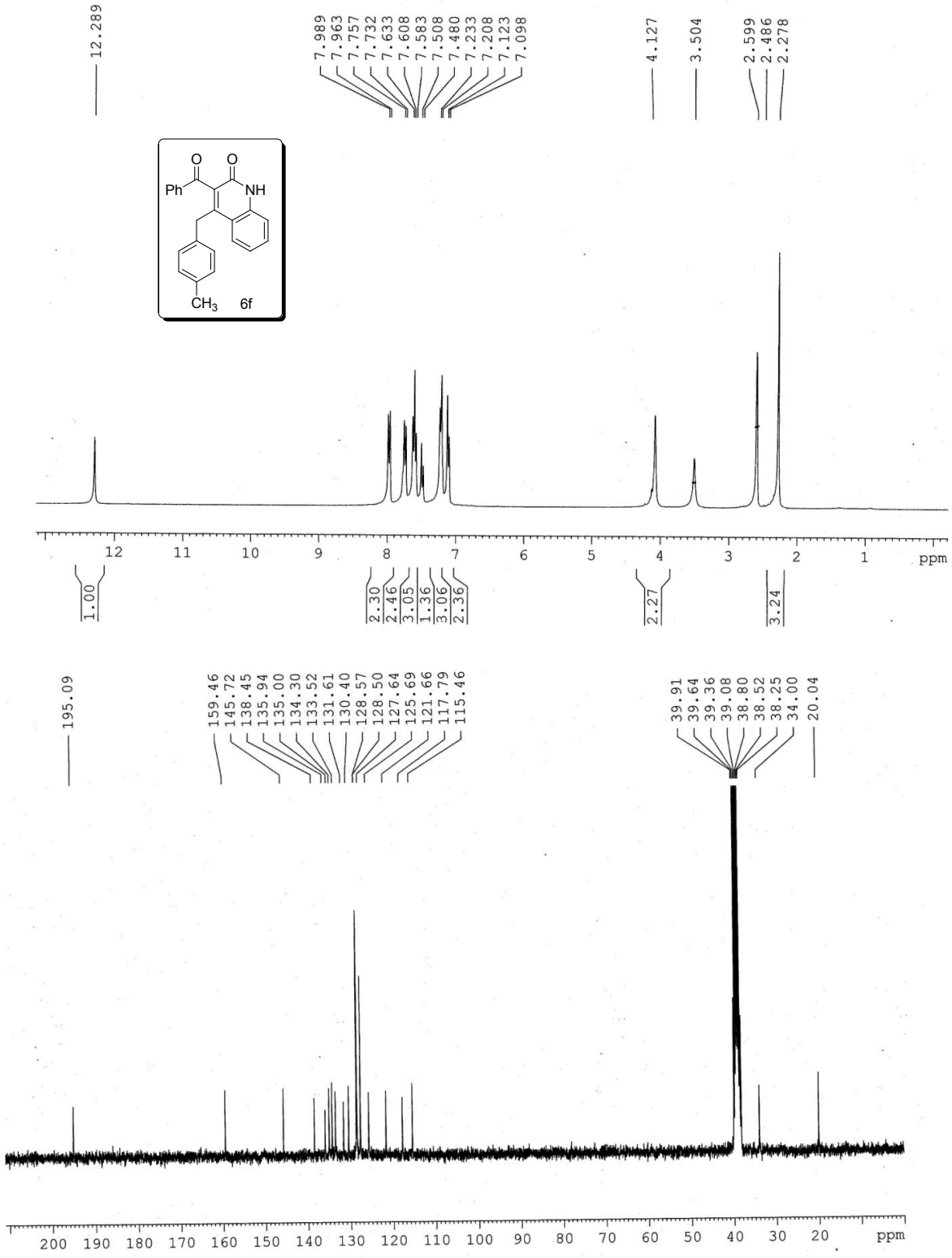


Figure S29. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**6f**)

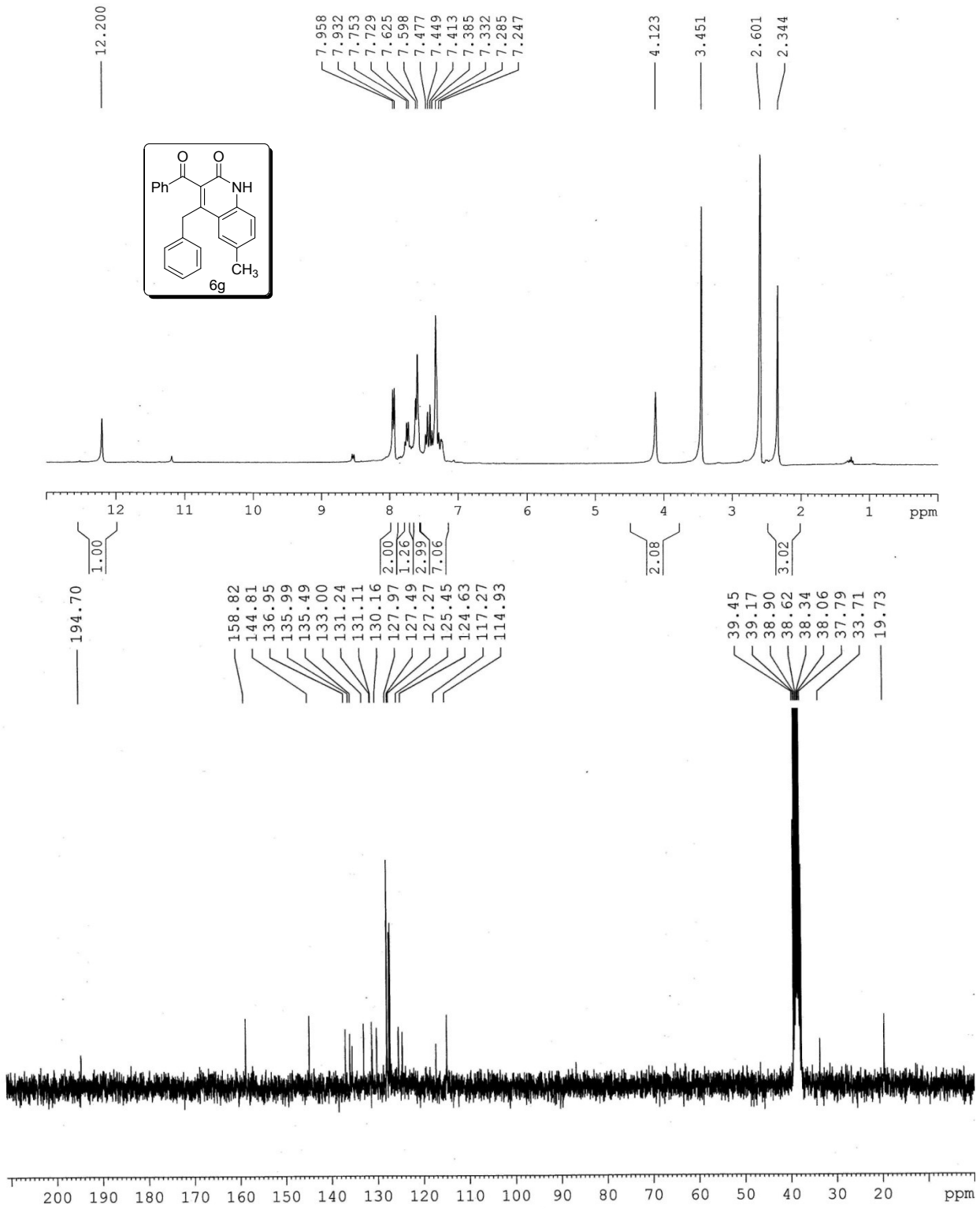


Figure S30. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**6g**)

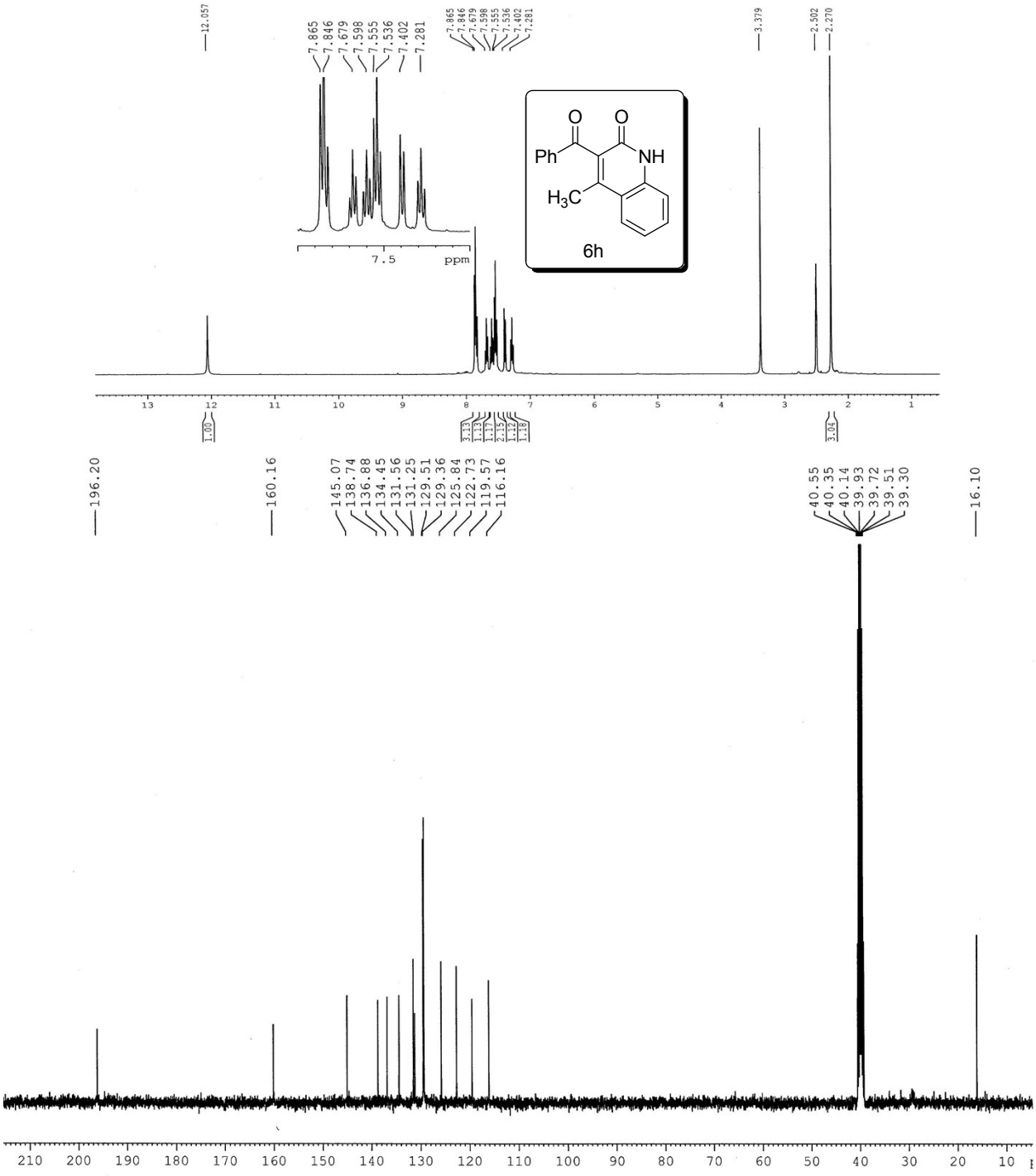


Figure S31. ^{1}H and ^{13}C NMR (400 MHz and 100 MHz, d_6- DMSO) of Compound (**6h**)

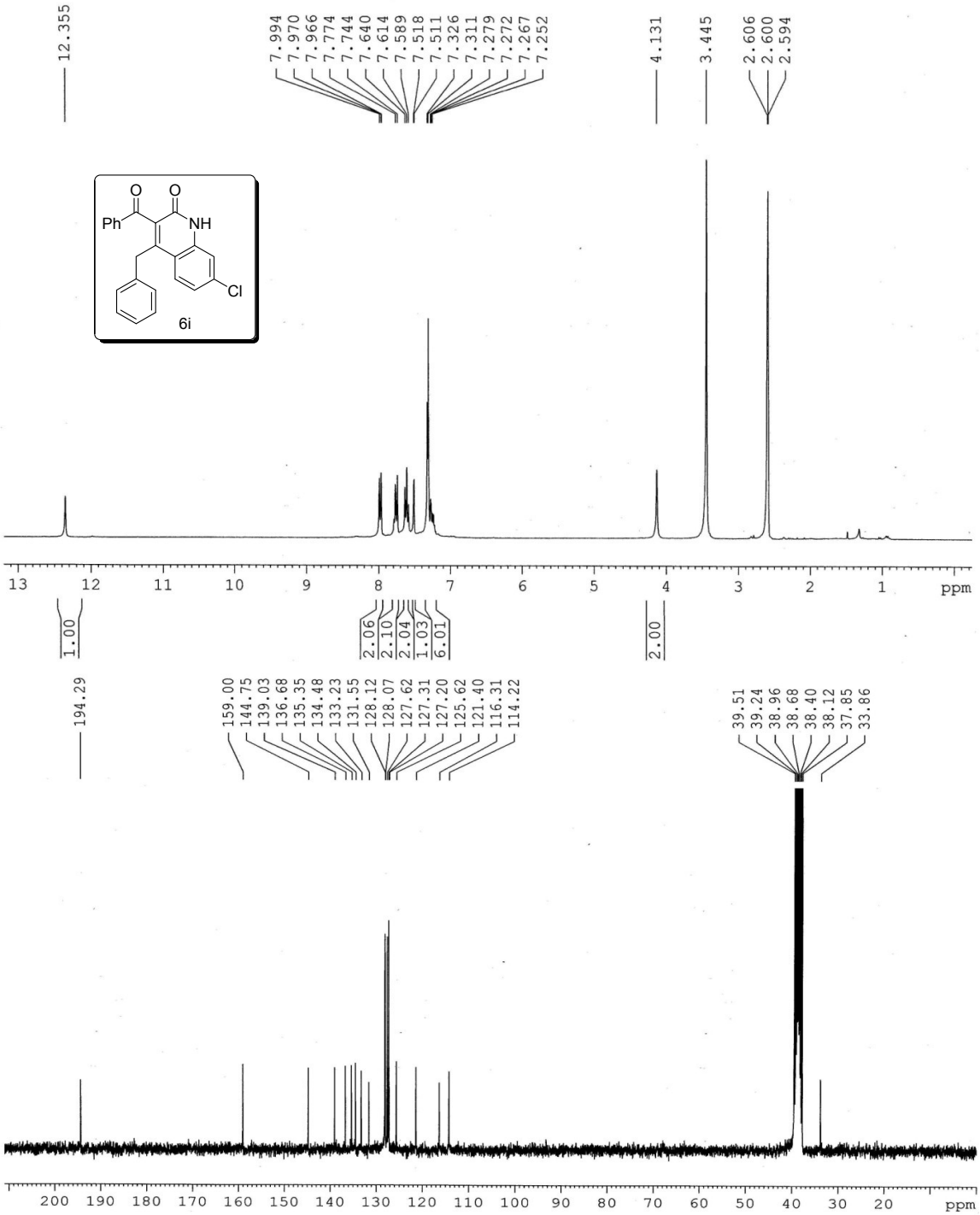


Figure S32. ^{1}H and ^{13}C NMR (400 MHz and 100 MHz, d_6- DMSO) of Compound (**6i**)

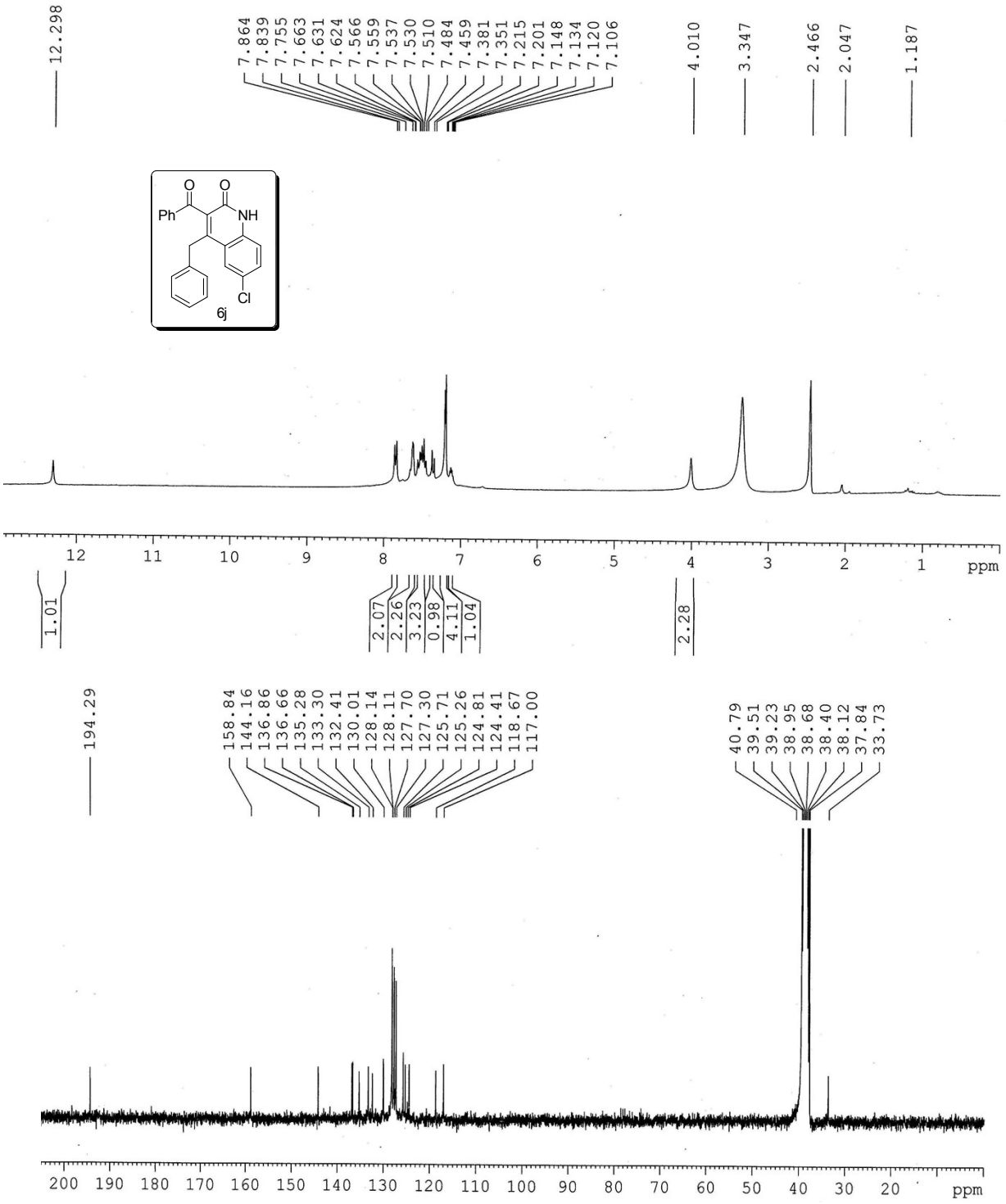


Figure S33. ^{1}H and ^{13}C NMR (400 MHz and 100 MHz, d_6- DMSO) of Compound (**6j**)

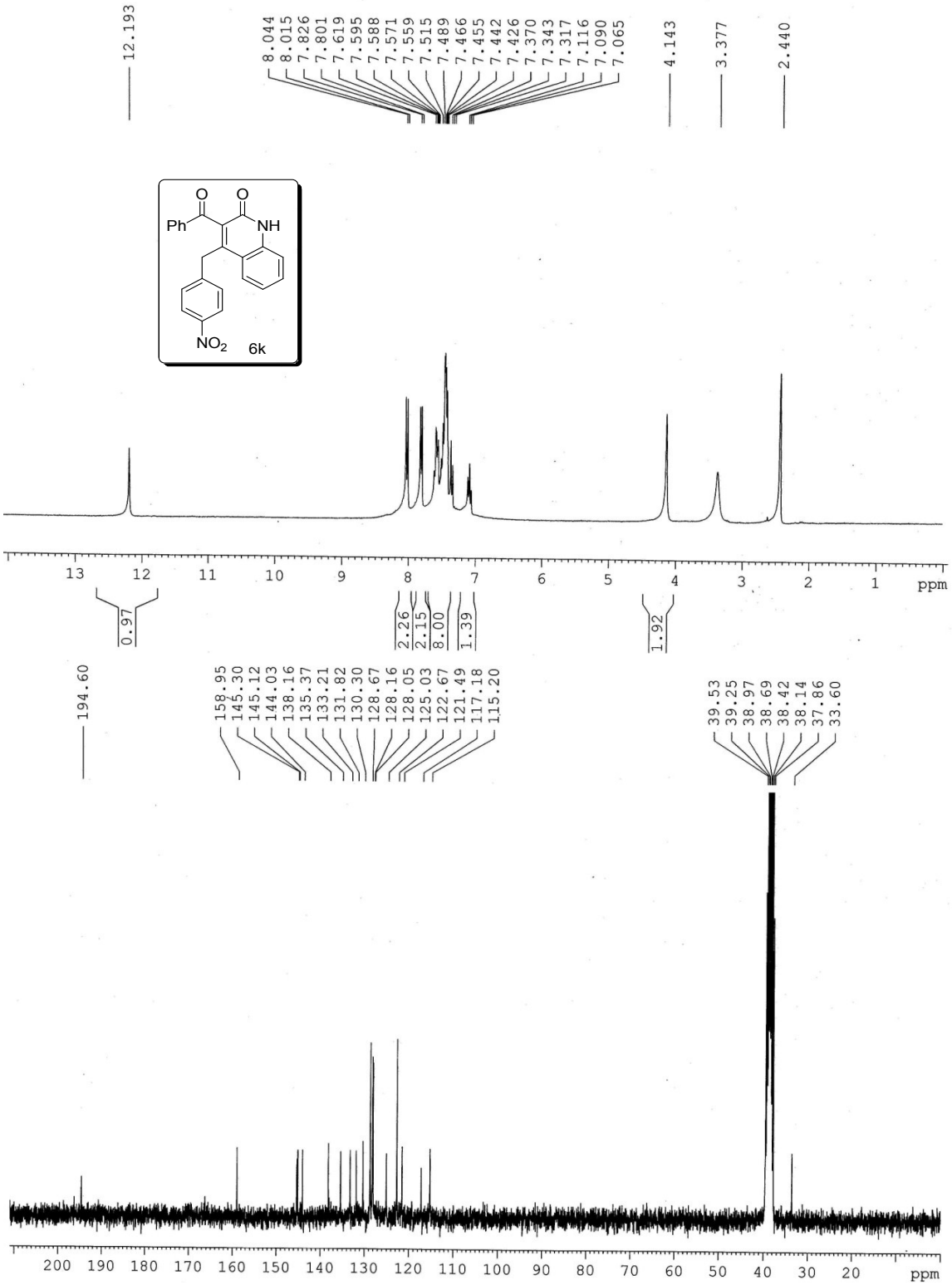


Figure S34. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**6k**)

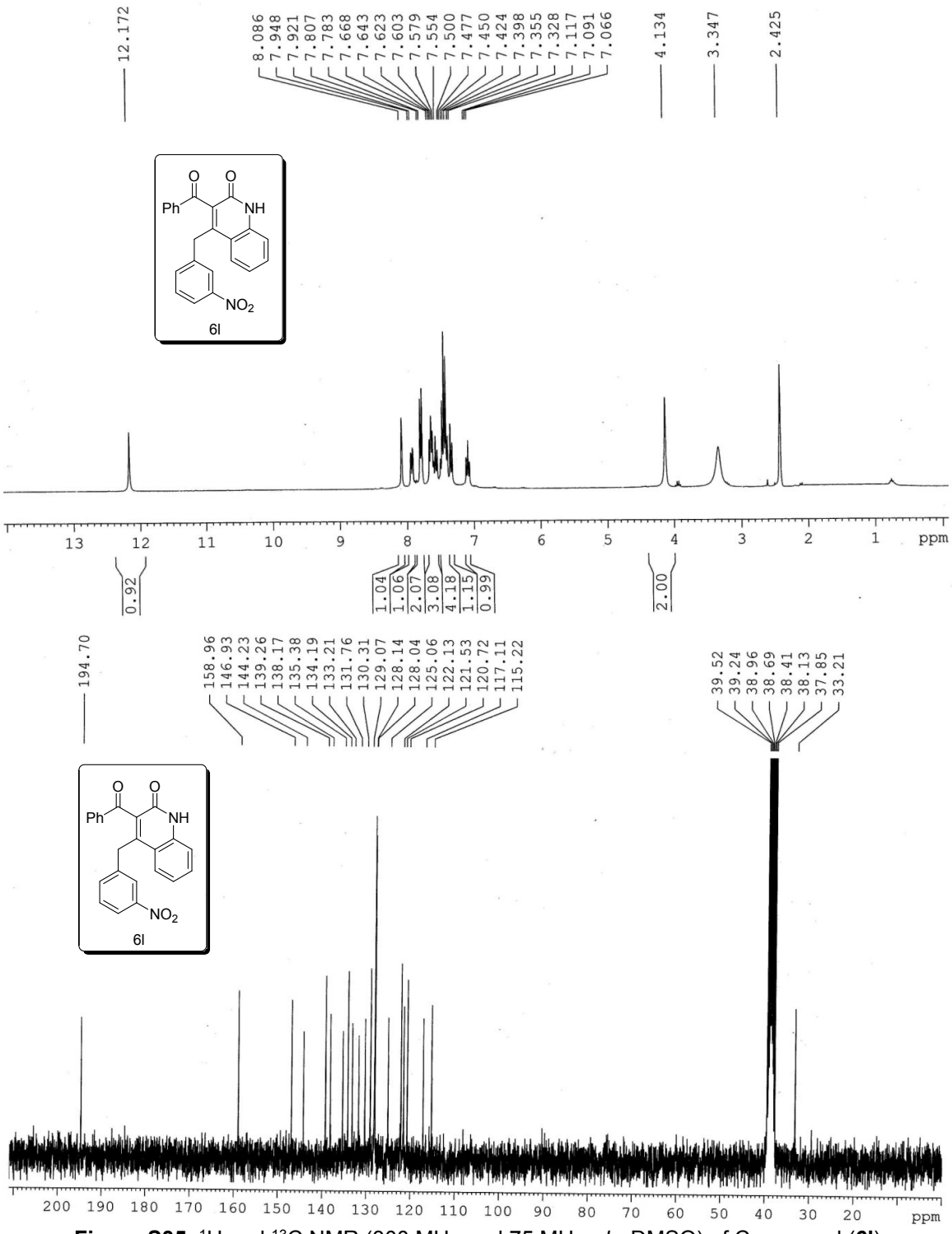


Figure S35. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**6l**)

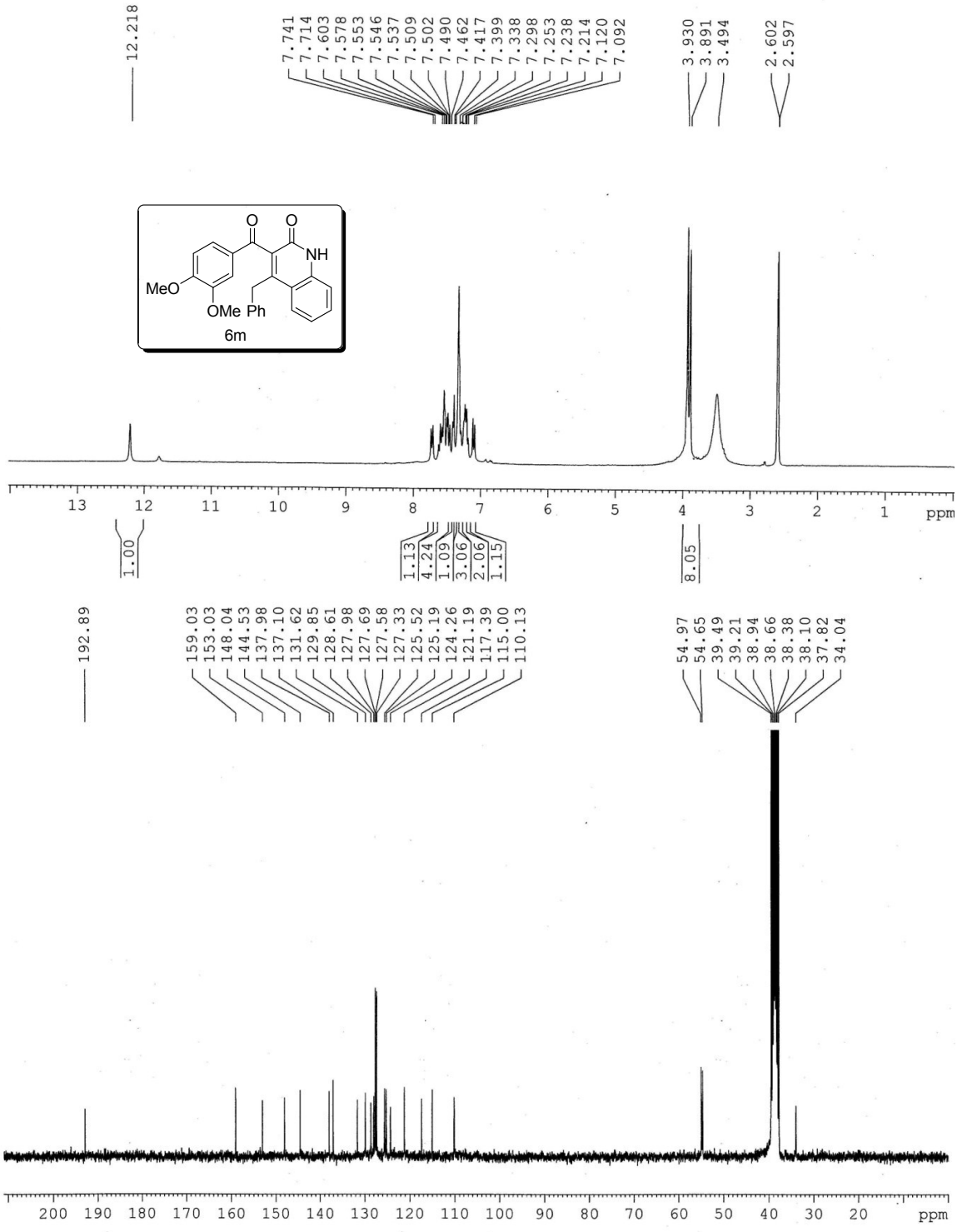


Figure S36. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**6m**)

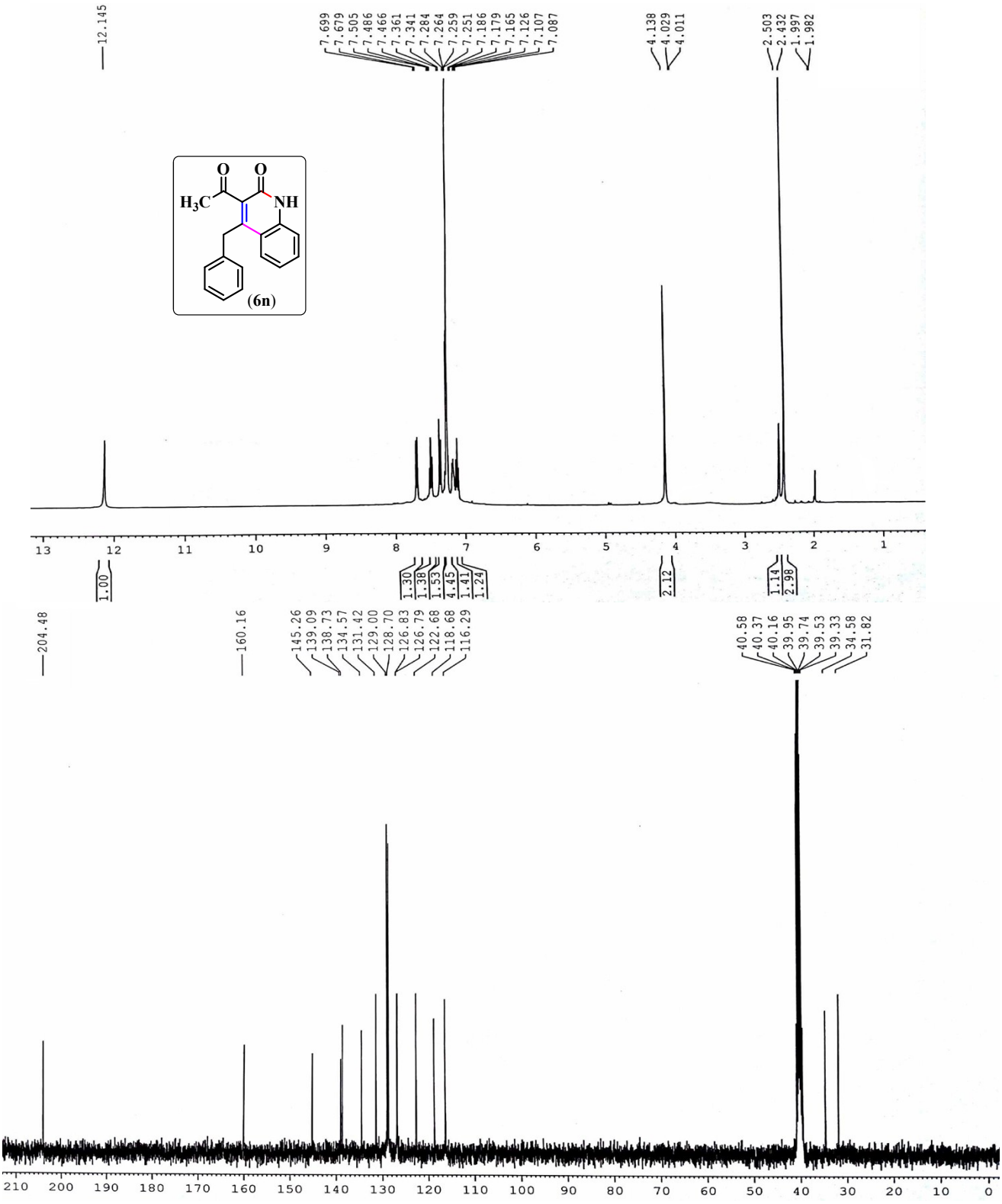


Figure S37. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, d_6- DMSO) of Compound (**6n**)

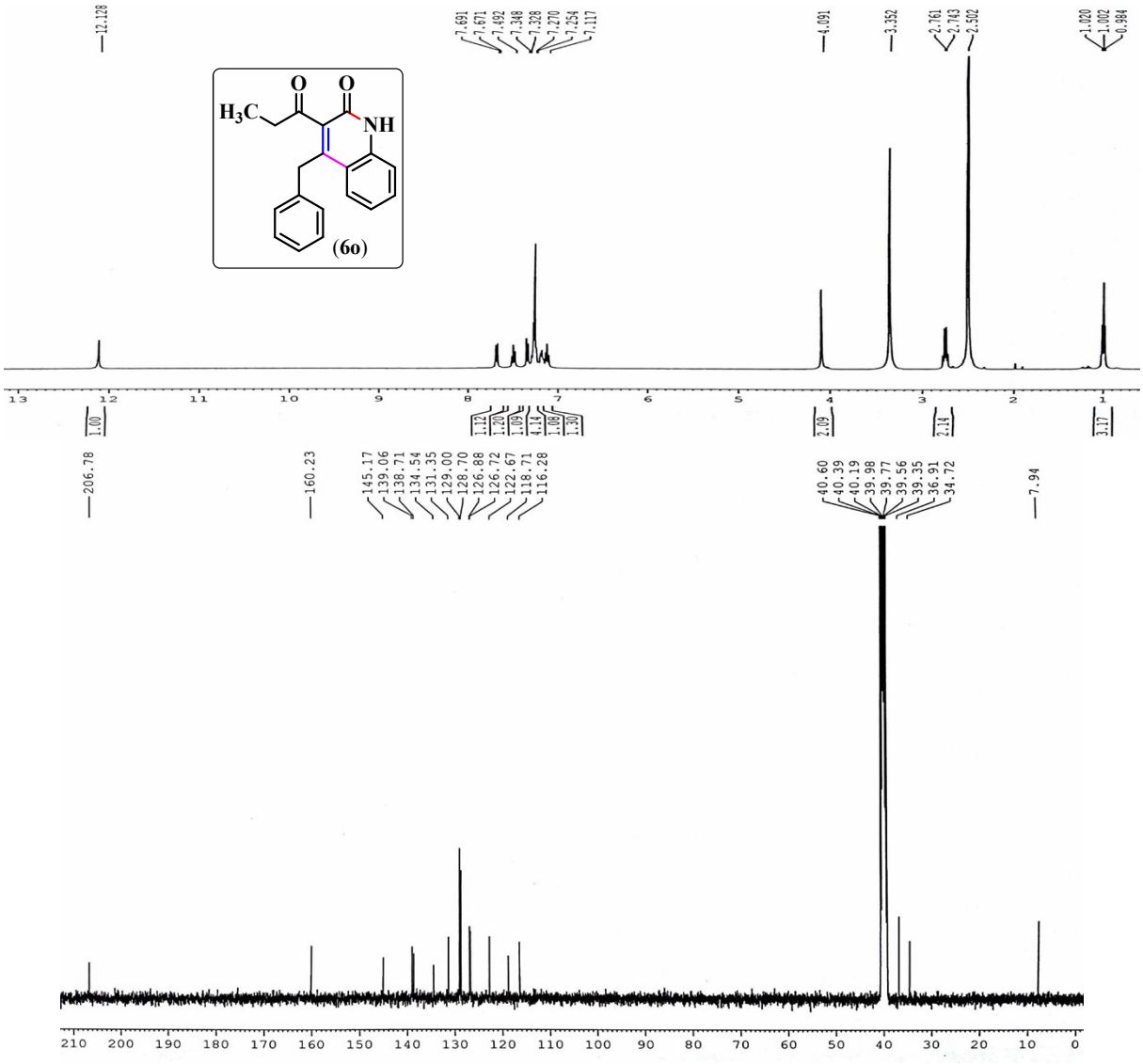


Figure S38. ^{1}H and ^{13}C NMR (400 MHz and 100 MHz, d_6- DMSO) of Compound (**6o**)

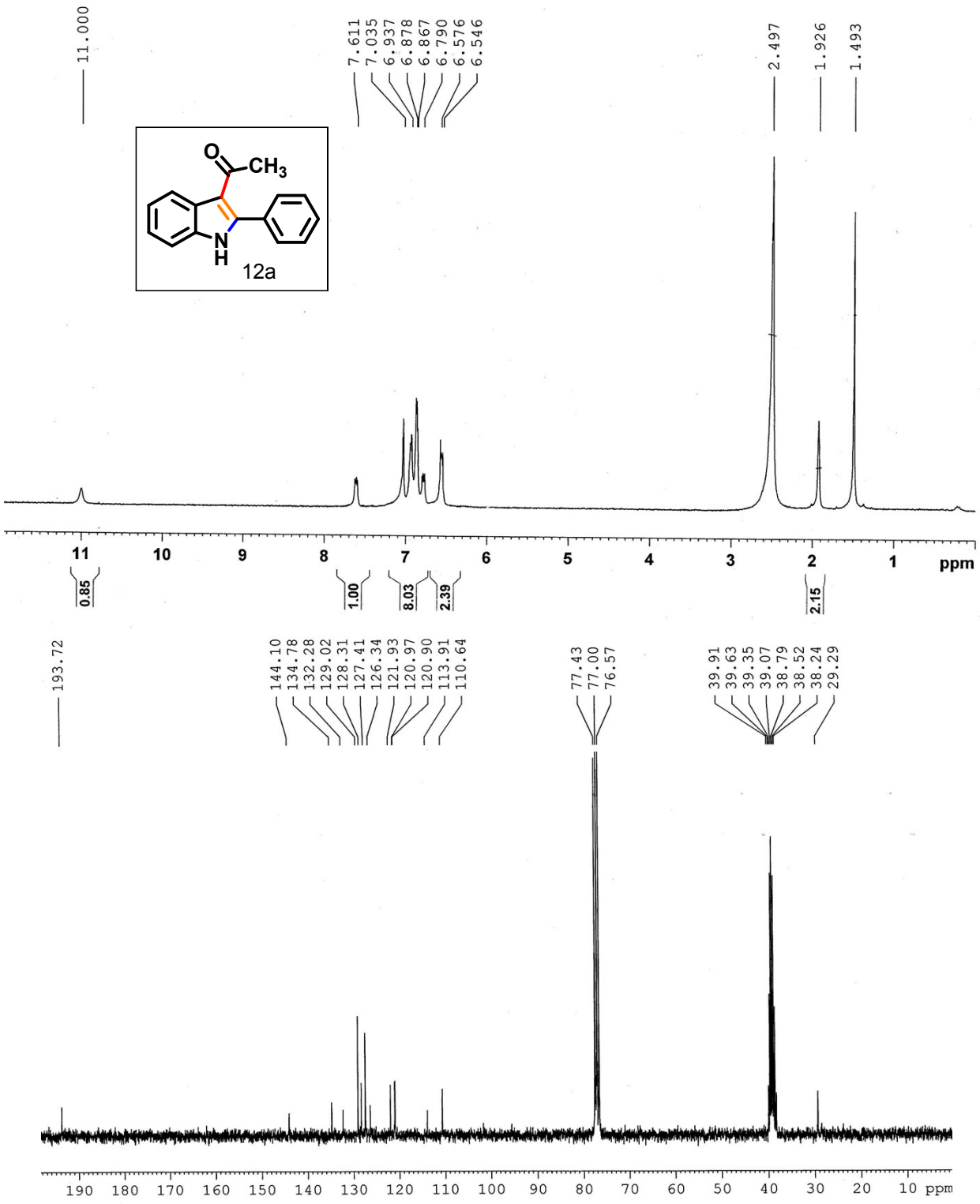


Figure S39. ^{1}H and ^{13}C NMR (400 MHz and 75 MHz,$CDCl_3$ +d_6- DMSO) of Compound (**12a**)

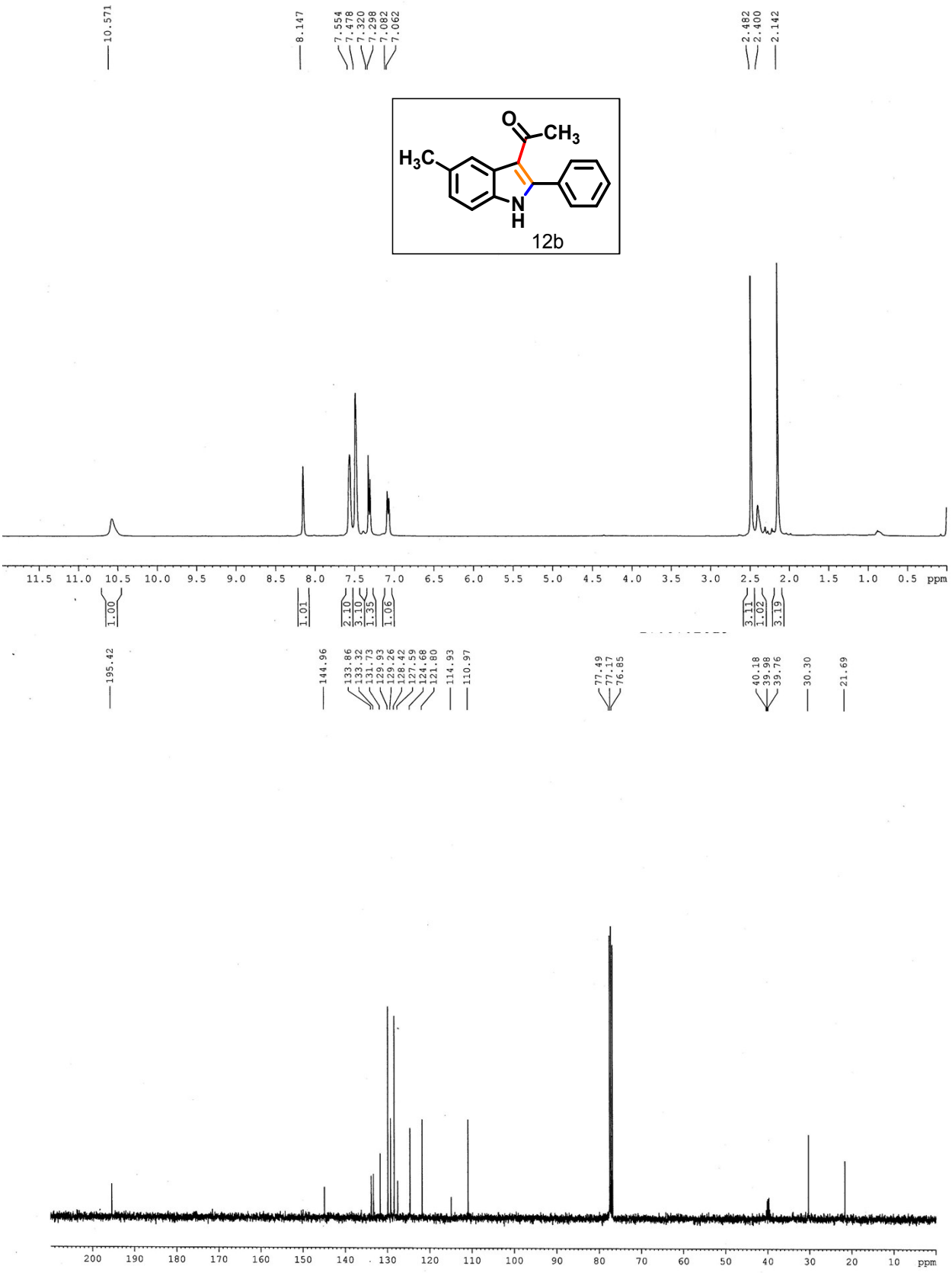


Figure S40. ^{1}H and ^{13}C NMR (400 MHz and 100 MHz,$CDCl_3$ +d_6- DMSO) of Compound (**12b**)

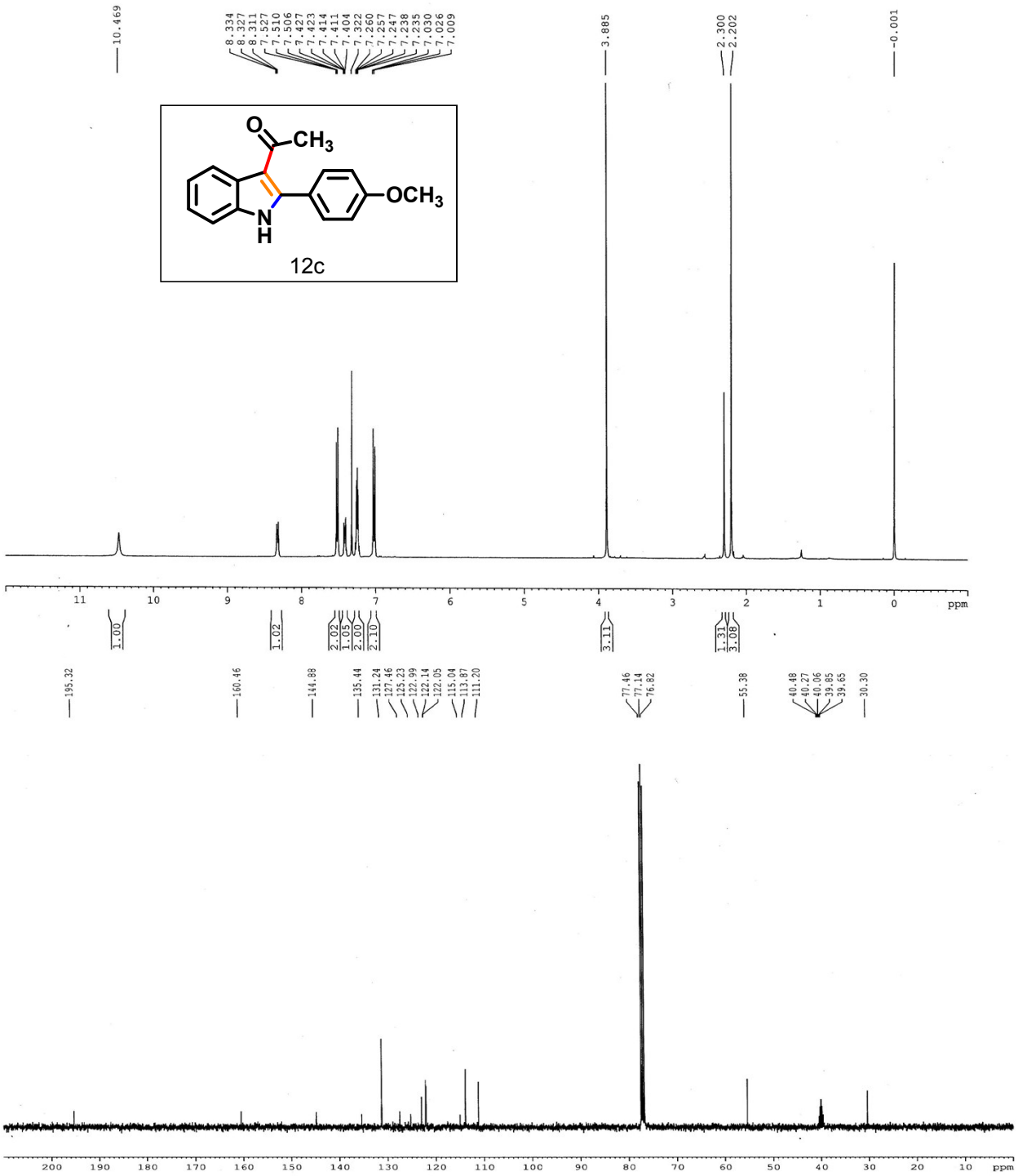


Figure S41. ^{1}H and ^{13}C NMR (400 MHz and 100 MHz,$CDCl_3$ +d_6- DMSO) of Compound (**12c**)

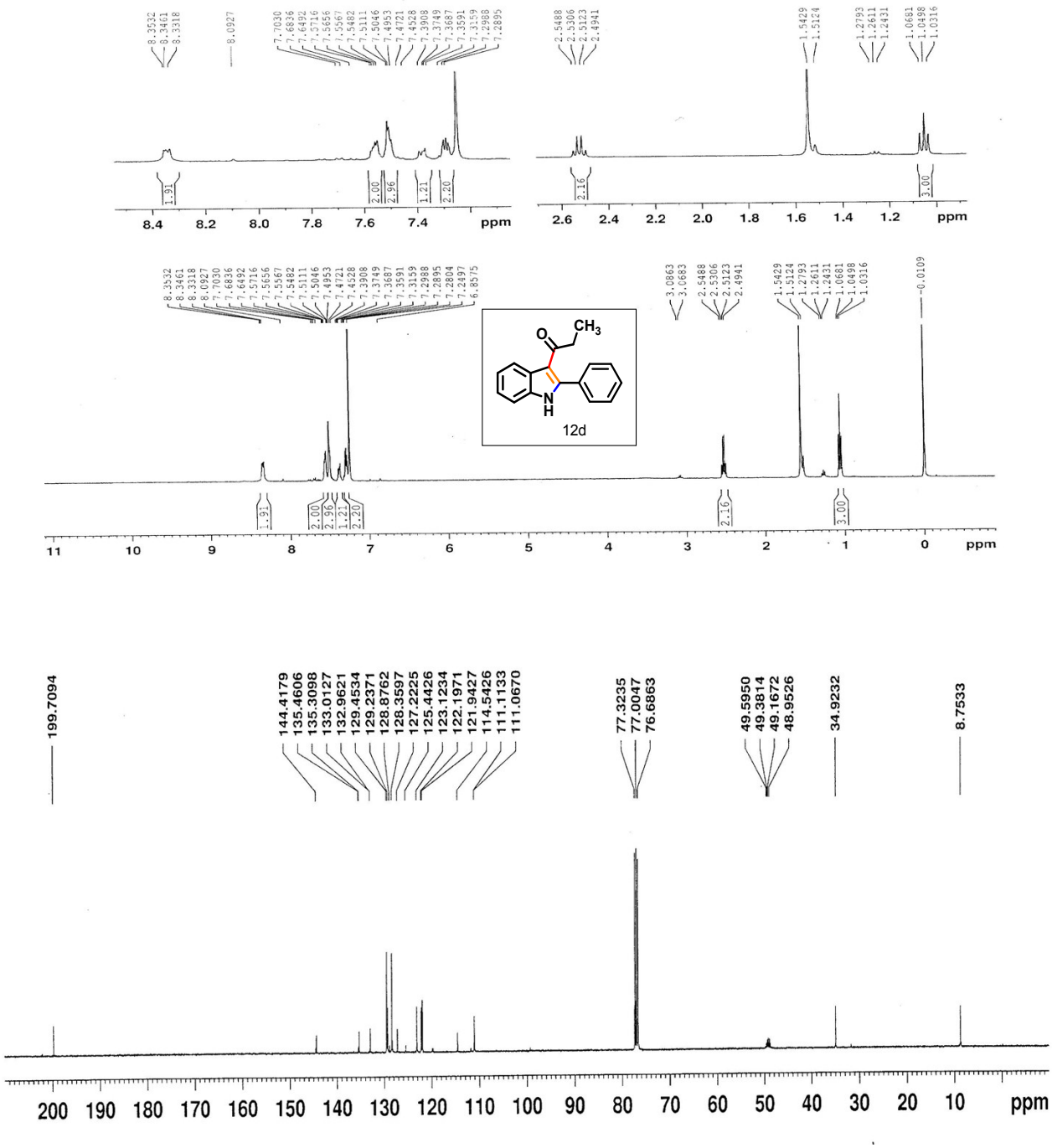


Figure S42. ^{1}H and ^{13}C NMR (400 MHz and 100 MHz,$CDCl_3$ +d_6- DMSO) of Compound (**12d**)

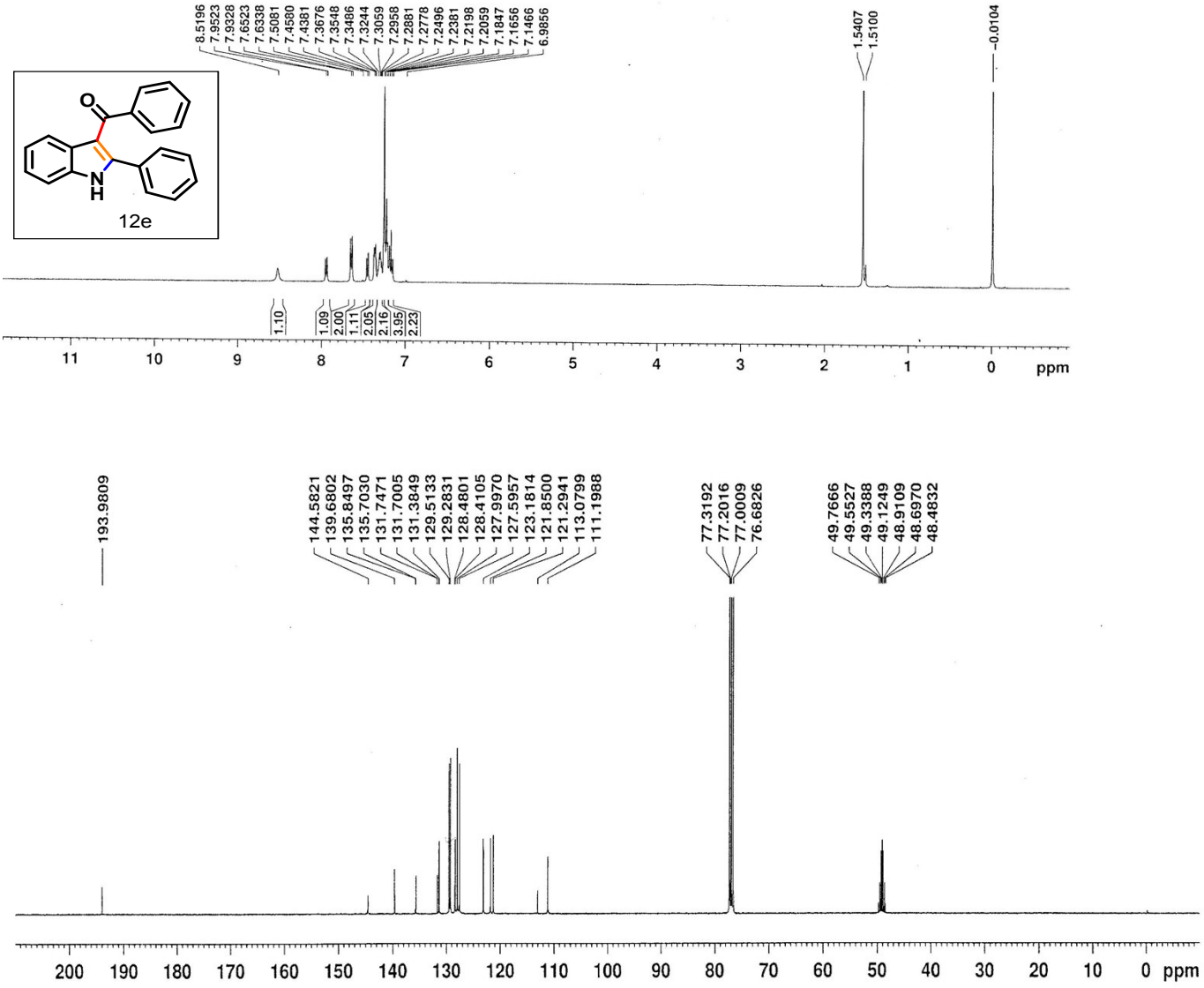


Figure S43. ^{1}H and ^{13}C NMR (400 MHz and 100 MHz,$CDCl_3$ +d_6- DMSO) of Compound (**12e**)

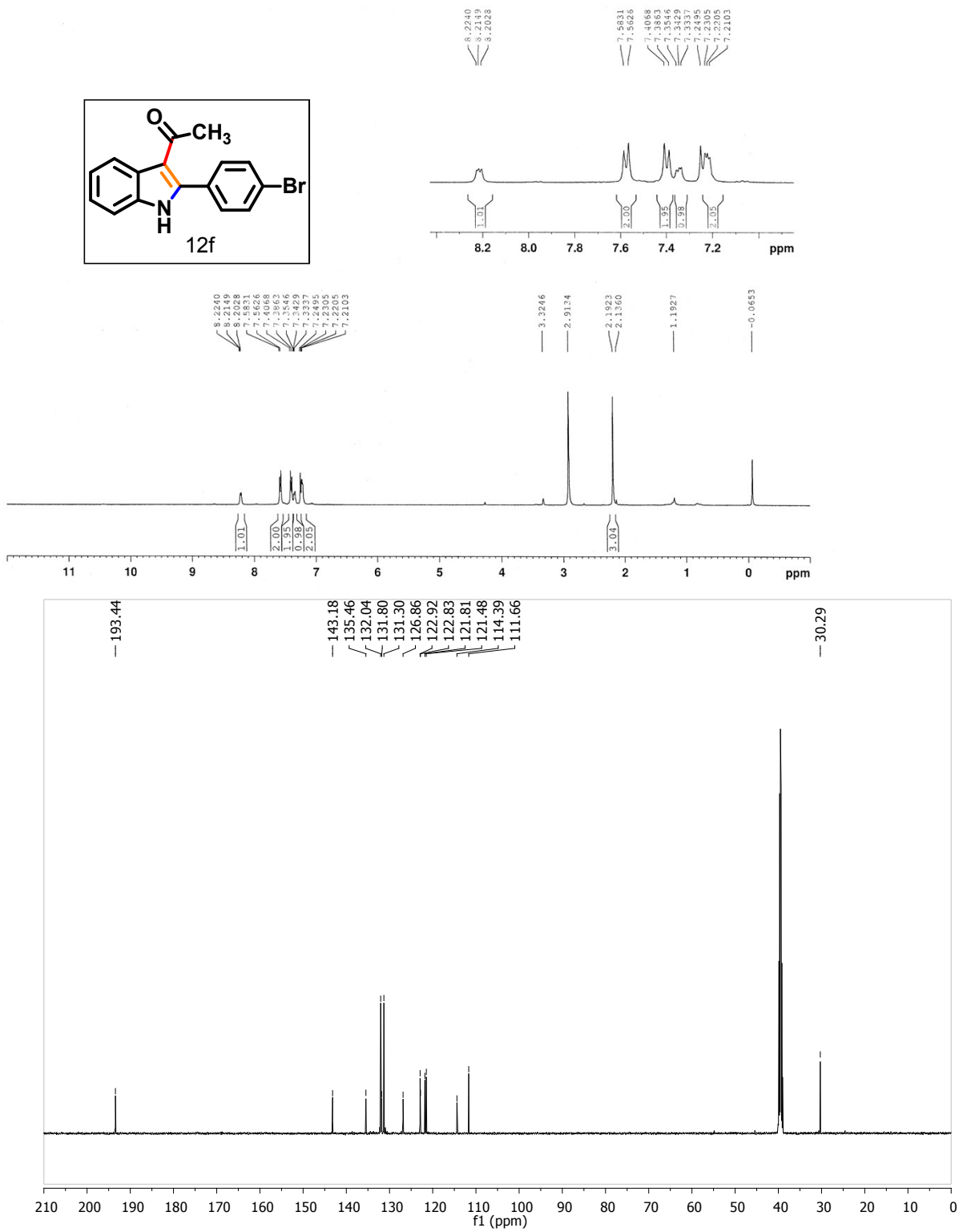


Figure S44. ^{1}H and ^{13}C NMR (400 MHz and 100 MHz, $CDCl_3$+ 2 drops CD_3OD, d_6-DMSO) of Compound (**12f**)

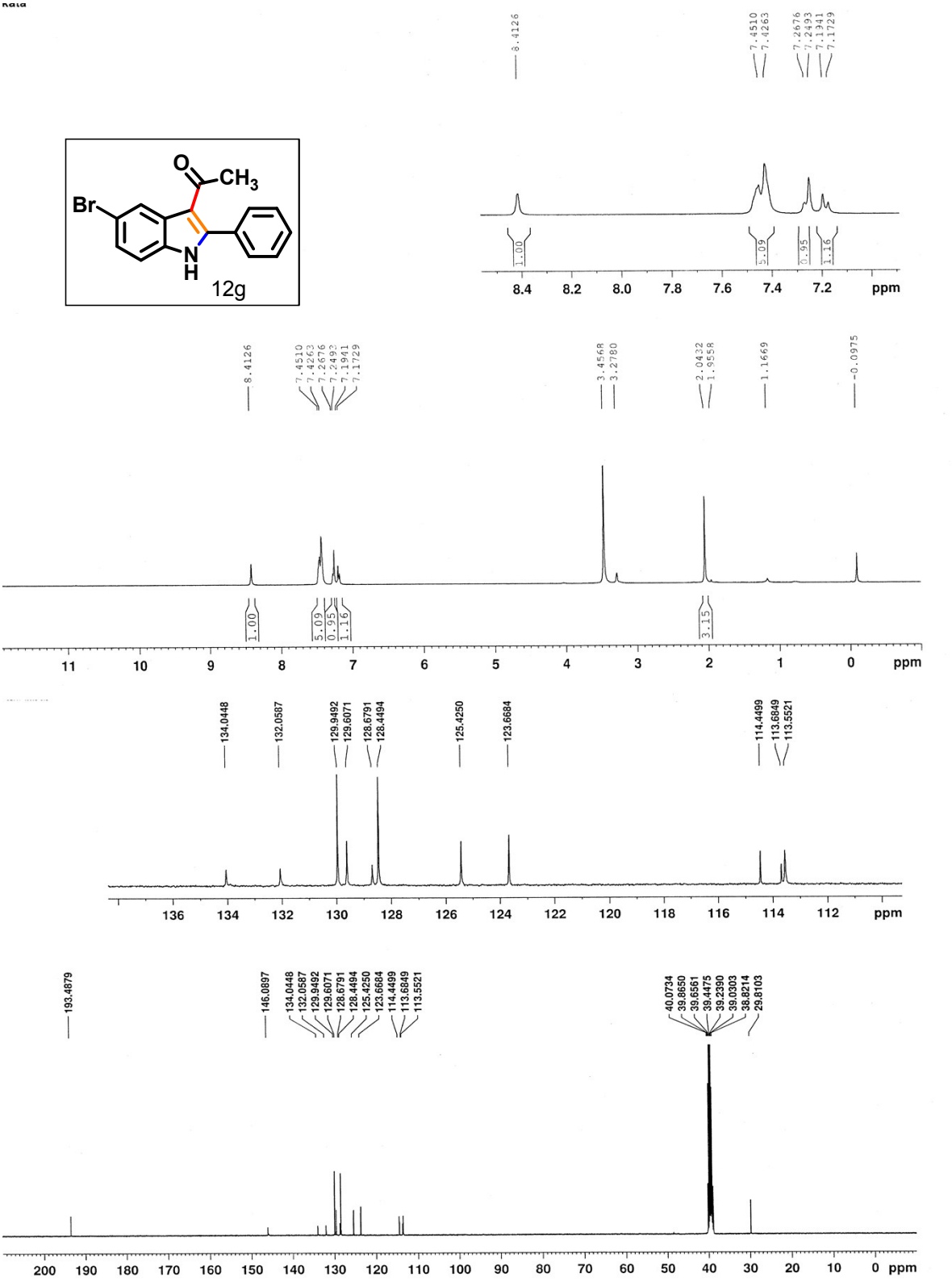


Figure S45. ^{1}H and ^{13}C NMR (400 MHz and 100 MHz, $CDCl_3$+ 2 drops CD_3OD) of Compound (**12g**)

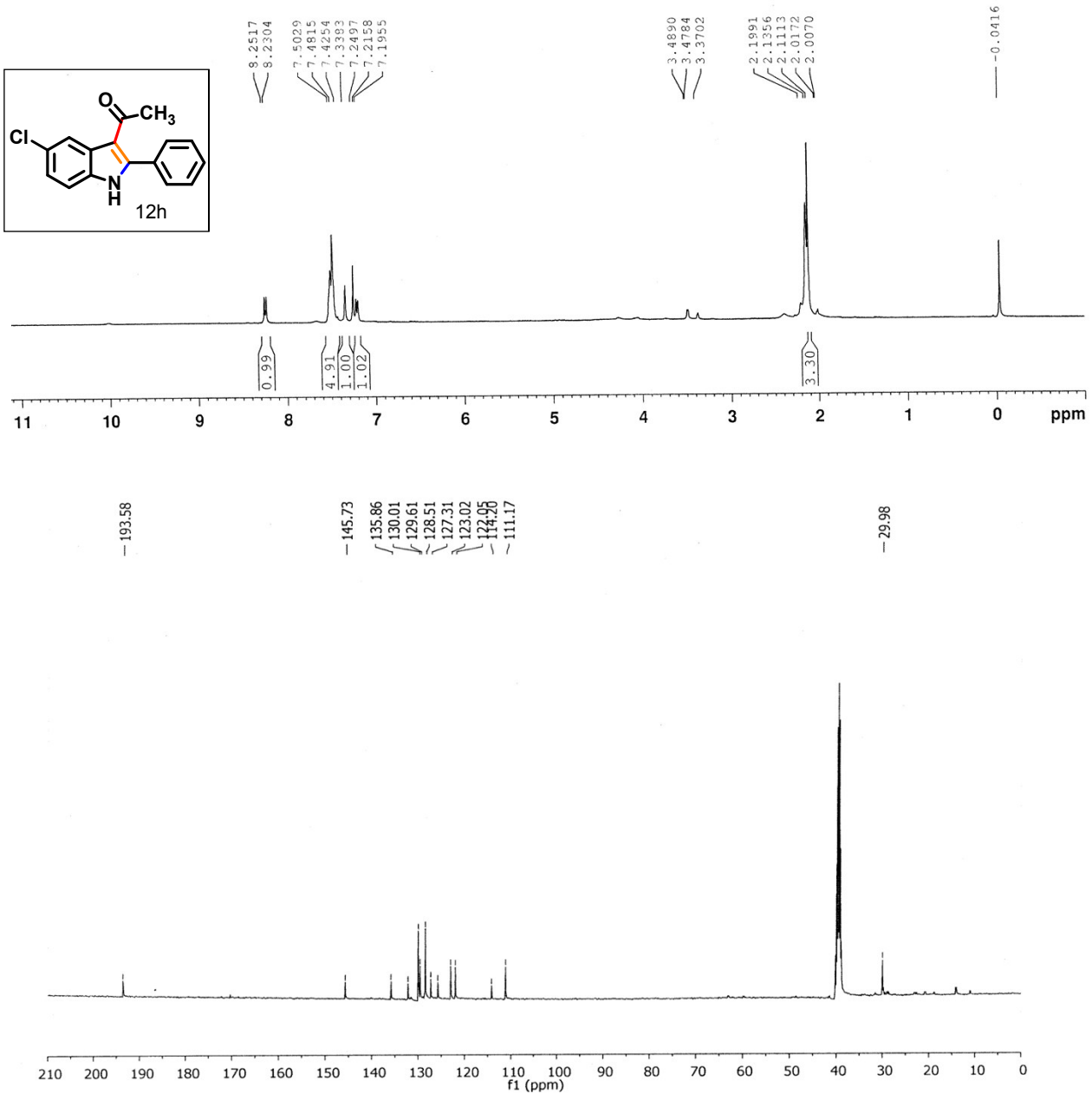


Figure S46. ^{1}H and ^{13}C NMR (400 MHz and 100 MHz, $CDCl_3$+ 2 drops CD_3OD, d_6-DMSO) of Compound (**12h**)

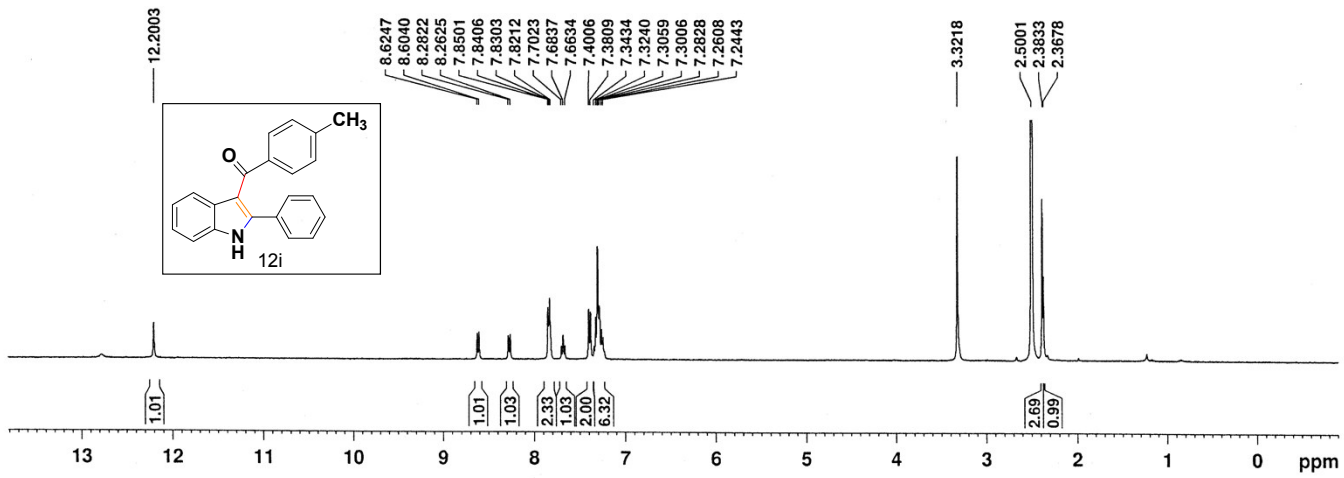
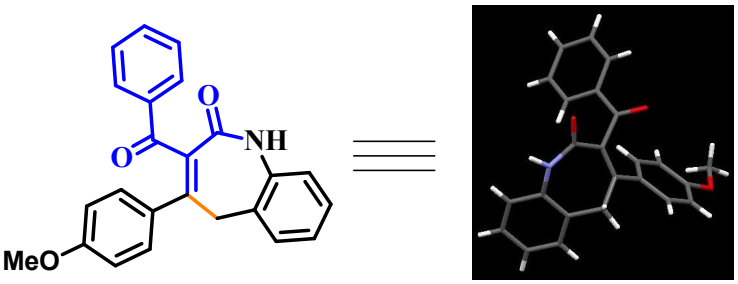


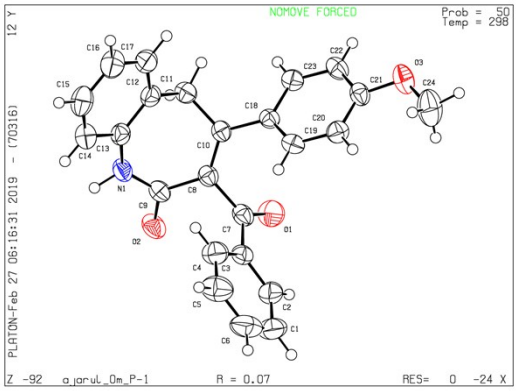
Figure S47. ^{1}H and ^{13}C NMR (400 MHz and 100 MHz, $CDCl_3$+d_6DMSO) of Compound (**12i**)

12. Crystal Structure of compound 5e (CCDC 1911211)



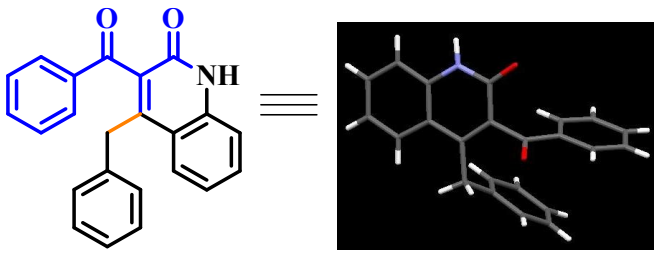
SI Figure48. Single crystal XRD structure of **5e**

13. Crystal summary data of compound 5e (CCDC1911211)



- Chemical formula and formula weight (M): $C_{24}H_{19}NO_3$ and 369.41
- Crystal system: Triclinic Unit-cell dimensions (angstrom or pm, degrees) and volume, with edges: a 8.893(9) b 10.210(11) c 11.258(10), 942.2(16), 80.88(4), 85.50(3), 69.03(3)
- Temperature: 298 K
- Space group symbol: P (-1)
- No. of formula units in unit cell (Z): 2
- Final R values (and whether quoted for all or observed data): 0.07

14. Crystal summary Data Compound 6a (CCDC 1911210)

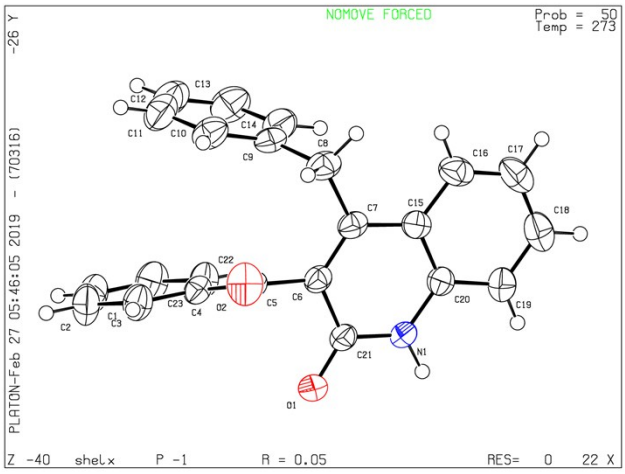


6a (3 h, 95%)

(6a)

SI Figure49. Single crystal XRD structure of **6a**

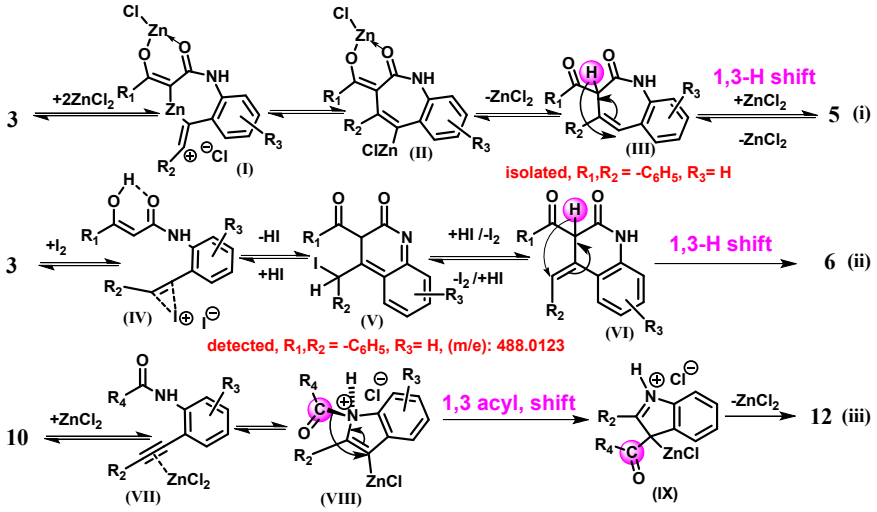
15. Crystal summary data of compound 5e (CCDC1911210)



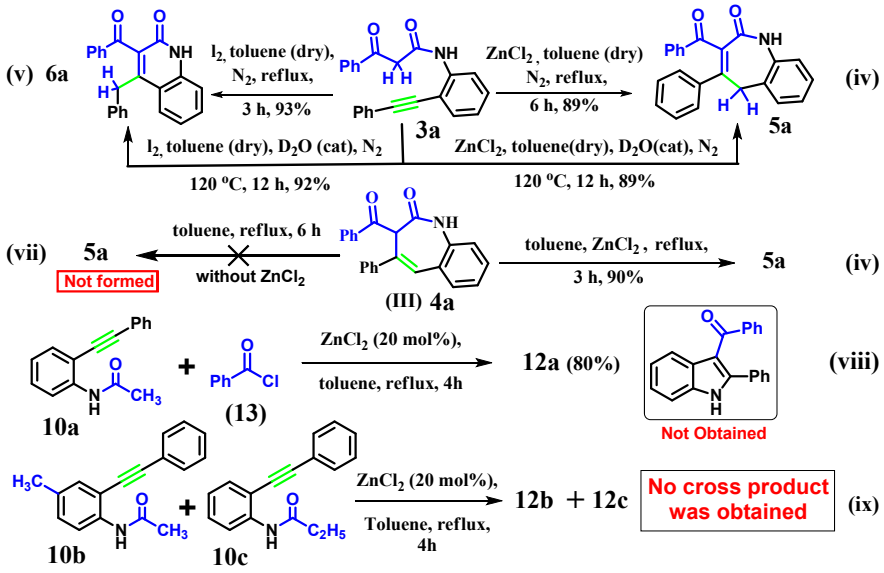
- Chemical formula and formula weight (M): $C_{23}H_{17}NO_2$ and 339.38
- Crystal system: Triclinic Unit-cell dimensions (angstrom or pm, degrees) and volume, with edges: a 9.2441(16) b 9.5954(16) c 10.6672(18), 852.3(3), 73.867(4), 70.650(4), 78.883(4)
- Temperature: 273 K
- Space group symbol: P (-1)
- No. of formula units in unit cell (Z): 2
- Final R values (and whether quoted for all or observed data): 0.05

13. Mechanistic Pathways

Scheme S5. Plausible mechanistic pathways



Scheme S6. Control experiments



The 7-annulation is expected to occur through the initiation of dual activation (**I**, eq. i, Scheme 5) of C-H and alkyne by Zn(II) to generate a transient intermediate **II**, which on the release of Zn(II) and protonation forms **III**. The intermediate **III** was isolated, characterized, and the role the catalyst and air in the 1,3 H-shift was confirmed for the concerted pathway as deuterium incorporation was not successful in the presence of D_2O and other control experiments (eq. iv, vi, vii, Scheme 6). In contrary to the Zn(II)-catalyzed dual activation (eq. i, Scheme 5), I_2 may activate only the triple bond (**IV**, eq. ii), which generates a putative intermediate **V** through the necessary assistance from the amide N. The transient **V** was detected only in the ESI-MS experiment. The ESI-MS kinetics experiment of the 6-annulation reaction was performed using pure amide **3a** (ESI), and injected aliquot of the ongoing reaction (after 1h) displayed three peaks

at 340.1278, 362.1050 and 488.0111. The peak appeared at 488.0111 ppm may be due the presence of intermediate **V** (3-benzoyl-4-(iodo(phenyl)methyl)quinolin-2(3*H*)-one, and 340.1278 and 362.1050 ppm are due to **3a** and product **6a**, respectively. The 1,3 H-shift of **VI** may lead the construction of 2-quinolinones (**6**) through the concerted mechanism (eq. v, Scheme 6). Unlike eq. i, the triple bond of **10** (VII, eq. iii, Scheme 5) may be activated by one molecule of Zn(II) and a N-C coupled 5-annulation occur (VIII) due to the absence of acidic C-H. The 5-annulation to **12** occurred through the 1,3-migration **11** of acyl group (**IX**), which was established through the cross over experiments using combination of **10a**, **13** (eq. viii, Scheme 6) and **10b**, **10c** (eq. ix). In turn, it supports the 1,3 H-sift in the 7- and 6- annulation reactions (eq. i, ii).