Supporting Information

$FeCl_3$-Catalyzed Alkyne-Aldehyde Metathesis: A General and Efficient Synthesis of Functionalized Dibenzo[*b,f*]oxepines and Benzo[*b*]oxepines

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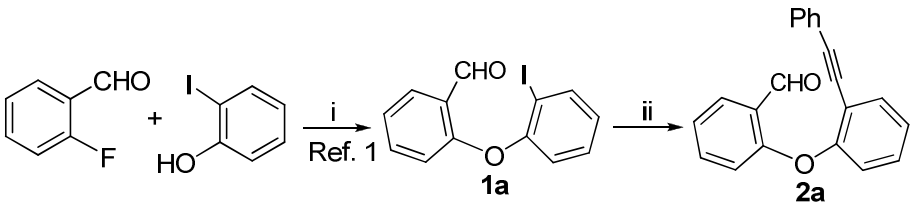
General: ^{1}H NMR spectra were recorded with a Bruker 300 (300 MHz)and 500 (500 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CHCl_3$ (δ = 7.26 ppm) as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals include: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets and brs = broad singlet. ^{13}C NMR spectra were recorded with a Bruker 300 (75 MHz) and 500 (125 MHz) spectrometer as solutions in $CDCl_3$ with complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CDCl_3$ (δ = 77.0 ppm) as an internal standard. High-Resolution Mass Spectra (HRMS) were performed with a Qtof Micro YA263 spectrometer in dichloromethane solvent. The molecular fragments are quoted as the relation between mass and charge (*m*/*z*). IR (infrared spectroscopy) was recorded with an FT-IR spectrometer, the IR spectra were recorded as thin films with KBr. The routine monitoring of reactions was performed with silica gel coated glass slides (Merck, silica gel G for TLC), and pre-coated Al plate, which were analyzed with iodine and uv light respectively. Solvents, reagents and chemicals were purchased from Aldrich, Fluka, Merck, SRL, Spectrochem and Process Chemicals. All reactions involving moisture-sensitive reactants were executed with oven-dried glassware.

Representative experimental procedure for preparation of compound 1a and 2a:



Step 1: The preparation of **1a-1j** was followed according to the reported method.[1]

Step 2. Preparation of 2-(2-(phenylethynyl)phenoxy)benzaldehyde (2a): To a solution of compound **1a** (500 mg, 1.5 mmol) in Et_3N, $Pd(PPh_3)_4$ (87 mg, .075 mmol, 0.05 eqv.), CuI (3 mg, 0.015 mmol, 0.01 eqv.), and phenyl acetylene (230 mg, 2.25 mmol, 1.5 eqv.) were added successively under argon atmosphere. The mixture was stirred at reflux for 4 h. After completion of reaction (monitored by TLC), the mixture was cooled to room temperature and water was added (20 mL). Then extracted with ethyl acetate and dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude compound was purified on silica gel (60-120 mesh) column chromatography (petroleum ether/EtOAc) to afford compound **2a (**376 mg, 1.26 mmol) as orange yellow liquid in 84% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.82 (d, J = 8.4 Hz, 1H), 7.12 – 7.23 (m, 2H), 7.26 – 7.28 (m, 6H), 7.38 (td, J = 7.8 Hz, 1.6 Hz, 1H), 7.45 – 7.51 (m, 1H), 7.63 (dd, J = 7.7 Hz, 1.6 Hz, 1H), 7.97 (dd, J = 7.7 Hz, 1.6 Hz, 1H), 10.71 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 84.4, 95.3, 116.8, 117.1, 119.1, 120.9, 122.7, 122.9, 125.0, 126.1, 128.3, 128.3, 128.4, 128.6, 128.7, 130.0, 131.5, 131.6,133.5, 134.0, 135.7,155.8, 160.4, 189.5 ppm. HRMS: calcd. for $C_{21}H_{15}O_2$ [M+H] 299.1072; found 299.1068.

The compounds **2b-2j** were synthesized by following similar procedure.

4-(phenylethynyl)-2-(2-(phenylethy)phenoxy)nylbenzaldehyde (2b): Brown Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92 (s, 1H), 7.18 (d, J = 8.1 Hz, 1H), 7.27 – 7.35 (m, 10 H), 7.42 (d, J = 7.8 Hz, 1H), 7.46 – 7.50 (m, 2H), 7.65 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 10.68 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 84.3, 88.4, 93.8, 95.5, 117.0, 119.5, 121.2, 122.3, 122.6, 125.4, 126.2, 128.3, 128.4, 128.5, 128.7, 129.1, 130.1, 130.8, 131.5, 131.8, 134.1, 155.4, 160.2, 188.8 ppm. HRMS: calcd. for $C_{29}H_{19}O_2$ [M+H] 399.1385; found 399.1380.

5-nitro-2-(2-(phenylethynyl)phenoxy)benzaldehyde (2c): Orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85 (d, J = 9.2 Hz, 1H), 7.12–7.15 (m, 2H), 7.23–7.32 (m, 4H0, 7.37 (t, J = 7.5 Hz, 1H0, 7.47–7.52 (m, 1H), 7.68 (d, J = 7.5 Hz, 1H), 8.31 (dd, J = 9.2 Hz, 2.8 Hz, 1H), 8.81 (s, 1H), 10.74 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 83.6, 96.3, 116.5, 117.4, 122.0, 122.1, 124.6, 125.2, 126.7, 128.5, 129.1, 130.3, 130.5, 131.3, 134.3, 142.8, 153.9, 164.5, 187.4 ppm. : HRMS: calcd. for $C_{21}H_{14}NO_4$ [M+H] 344.0923; found 344.0925.

2-methoxy-6-(2-(phenylethynyl)phenoxy)benzaldehyde (2d): Brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93 (s, 3H), 6.37 (d, J = 8.4 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.28 (brs, 5H), 7.33–7.40 (m, 2H), 7.59 (dd, J = 7.5 Hz, 1.2 Hz, 1H), 10.68 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.4, 84.6, 95.0, 106.0, 109.4, 116.0, 116.9, 121.1, 123.0, 124.9, 128.4, 128.5, 129.9, 131.6, 133.9, 135.6, 156.1, 161.1, 161.7, 189.0 ppm. HRMS: calcd. for $C_{22}H_{17}O_3$ [M+H] 329.1178; found 329.1174.

2-(4-methoxy-2-(phenylethynyl)phenoxy)benzaldehyde (2e): Orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.86 (s, 3H), 6.75 (d, J = 8.4 Hz, 1H), 6.95 (dd, J = 8.9 Hz, 3.0 Hz, 1H), 7.09 (s, 1H), 7.12–7.14 (m, 2H), 7.17–7.20 (m, 2H), 7.22–7.31 (m, 3H), 7.46 (t, J = 8.6 Hz, 1H), 7.94 (dd, J = 7.7 Hz, 1.6 Hz, 1H), 10.74 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.7, 84.4, 95.14, 116.0, 116.2, 117.7, 122.3, 122.4, 122.7, 125.5, 128.1, 128.3, 128.6, 131.4, 135.7, 148.9, 156.6, 161.1, 189.5 ppm. HRMS: calcd. for $C_{22}H_{17}O_3$ [M+H] 329.1178; found 329.1182.

2-(4-methyl-2-(phenylethynyl)phenoxy)benzaldehyde (2f): Yellow liquid**.** ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 6.79 (d, J = 8.4 Hz, 1H), 7.04 (d, J = 8.3 Hz, 1H), 7.11–7.26 (m, 8H), 7.43–7.49 (m, 2H), 7.95 (d, J = 7.0 Hz, 1H), 10.71 (s, 1H) ppm ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.8, 84.7, 95.3, 116.7, 116.8, 121.1, 122.7, 122.9, 123.1, 126.0, 128.3, 128.4, 128.6,

130.8, 131.6, 134.3, 134.9, 135.8, 139.4, 153.6, 160.9, 189.8 ppm. HRMS: calcd. for $C_{22}H_{17}O_2$ [M+H] 313.1229; found 313.1232.

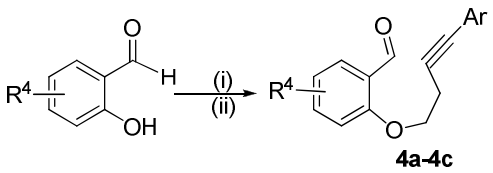
2-(2-((4-chlorophenyl)ethynyl)phenoxy)benzaldehyde (2g): Brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.82 (d, J = 8.4 Hz, 1H), 7.14–7.16 (m, 3H), 7.20–7.24 (m, 2H), 7.25–7.26 (m, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.47–7.52 (m, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.96 (d, J = 7.7 Hz, 1H), 10.67 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 85.4, 94.1, 116.4, 117.2, 120.8, 121.1, 123.0, 125.0, 126.1, 128.3, 128.7, 130.2, 132.6, 133.9, 134.6, 135.8, 155.9, 160.3, 189.4 ppm. HRMS: calcd. for $C_{21}H_{14}ClO_2$ [M+H] 333.0682; found 333.0687.

2-(2-((4-methoxyphenyl)ethynyl)phenoxy)benzaldehyde (2h): Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.79 (s, 3H), 6.77–6.82 (m, 3H), 7.12–7.20 (m, 4H), 7.22–7.26 (m, 1H), 7.37 (td, J = 7.7 Hz, 1.5 Hz, 1H), 7.48 (dt, J = 8.5 Hz, 1.6 Hz, 1H), 7.60 (dd, J = 7.6 Hz, 1.5 Hz, 1H), 7.96 (dd, J = 7.7 Hz, 1.5 Hz, 1H), 10.70 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.4, 83.2, 95.5, 114.1, 114.8, 117.1, 117.3, 121.1, 122.9, 125.1, 126.1, 128.3, 129.6, 133.0, 133.8, 135.8, 155.7, 159.9, 160.6, 189.7 ppm. HRMS: calcd. for $C_{22}H_{16}NaO_3$ [M+Na] 351.0997; found 351.0993.

2-(2-(p-tolylethynyl)phenoxy)benzaldehyde (2i): Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 3H), 6.81 (d, J = 8.3 Hz, 1H), 7.05–7.18(m, 5H), 7.20–7.26 (m, 2H), 7.34–7.41 (m, 1H), 7.45–7.51(m, 1H), 7.61 (dd, J = 7.6 Hz, 1.5 Hz, 1H), 7.95 (dd, J = 7.7 Hz, 1.6 Hz, 1H), 10.70 (s, 1H)ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 83.8, 95.6, 117.0, 119.6, 121.0, 122.9, 125.0, 126.0, 128.2, 129.1, 129.8, 131.4, 133.9, 135.7, 138.8, 155.7, 160.5, 189.5 ppm. HRMS: calcd. for $C_{22}H_{17}O_2$ [M+H] 313.1229; found 313.1234.

2-(2-((6-methoxynaphthalen-2-yl)ethynyl)phenoxy)benzaldehyde (2j): Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.91 (s, 1H), 6.85 (d, J = 8.3 Hz, 1H), 7.07 (s, 1H), 7.12–7.17 (m, 3H), 7.20–7.27 (m, 3H), 7.36–7.42 (m, 1H), 7.47–7.53 (m, 1H), 7.62–7.66 (m, 3H), 7.99 (dd, J = 7.8 Hz, 1.7 Hz, 1H), 10.74 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3, 84.3, 96.1, 105.9, 117.0, 117.2, 117.5, 119.5, 121.0, 123.0, 125.1, 126.2, 126.9, 128.3, 128.4, 128.6, 129.4, 129.8, 131.4, 133.9, 134.3, 135.8, 155.8, 158.5, 160.5, 189.5 ppm. HRMS: calcd. for $C_{26}H_{19}O_3$ [M+H] 379.1334; found 379.1339.

Substrates preparation for the synthesis of benzo[*b*]oxepines:



4a-4c

(i) Preparation of 2-(but-3-ynyloxy)benzaldehyde from 3,5-dichloro salicylaldehyde : To a solution of 3, 5-dichlorosalicylaldehyde (1.0 g, 5.26 mmol) in dry CH_3CN (10 mL), but-3-ynyl 4-methylbenzenesulfonate compound (1.42 g, 6.32 mmol) was added. To this solution K_2CO_3 (2.18 g, 15.8 mmol) was added and flashed with argon atomsphere. Then the mixture was stirred vigorously at reflux for 10 hrs. After completion of the reaction (monitered by TLC), the mixtire was filtered and solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel,60-120 mesh size) using petroleum ether/EtOAc and afforded a light yellow liquid (895 mg, 3.68 mmol) was obtained in 70% yield.

(ii) Preparation of 3,5-dichloro-2-(4-phenylbut-3-ynyloxy)benzaldehyde from 3,5-dichloro-2-(but-3-ynyloxy)benzaldehyde (4a): To a solution of compound 3,5-dichloro-2-(but-3-ynyloxy)benzaldehyde (500 mg, 2.0 mmol) in Et_3N (10 mL), (500 mg, 2.0 mmol) in Et_3N (10 mL), $Pd(PPh_3)_4$ (116 mg, 0.1 mmol, 0.05 eqv.), CuI (4 mg, 0.02 mmol, 0.01 eqv.), and iodobenzene (490 mg, 2.4 mmol, 1.2 eqv.)were added successively under argon atmosphere. The mixture was stirred at RT for overnight. After completion of reaction (monitored by TLC), water was added (20 mL), then extracted with ethyl acetate and dried over anhydrous Na_2SO_4. The crude compound was purified using silica gel (60-120 mesh) column

chromatography (petroleum ether/EtOAc) to afford the yellow white product **4a** (479 mg, 1.5 mmol) in 75 % yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.97 (t, J = 6.42 Hz, 2H), 4.33 (t, J = 6.42 Hz, 2H), 7.28–7.30 (m, 2H), 7.37–7.40 (m, 2H), 7.63 (d, J = 2.6 Hz, 1H), 7.72 (d, J = 2.6 Hz, 1H), 10.50 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 73.8, 82.9, 85.4, 123.1, 126.9, 128.3, 128.4, 129.8, 130.8, 131.6, 131.7, 135.9, 156.4, 188.0 ppm. HRMS: calcd. for $C_{17}H_{13}Cl_2O_2$ [M+H] 319.0293; found 319.0290.

The compounds **4b-4c** were synthesized by similar procedure.

3-methoxy-2-(4-*p*-tolylbut-3-ynyloxy)benzaldehyde (4b): Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 3H), 2.89 (t, J = 6.5 Hz, 2H), 3.91 (s, 3H), 4.36 (t, J = 6.7 Hz, 2H), 7.08–7.15(m, 4H), 7.28 (d, J = 8.9 Hz, 2H), 7.41–7.45 (m, 1H), 10.62 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.2, 56.1, 72.3, 82.3, 85.4, 118.1, 119.1, 120.3, 124.2, 129.0, 130.0, 131.5, 137.9, 151.1, 152.9, 190.4 ppm. HRMS: calcd. for $C_{19}H_{19}O_3$ [M+H] 295.1334; found 295.1330.

5-bromo-2-(4-(4-methoxyphenyl)but-3-ynyloxy)benzaldehyde (4c): Orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.94 (t, J = 6.8 Hz, 2H), 3.79 (s, 3H), 4.25 (t, J = 6.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.9 Hz, 1H0, 7.29–7.33 (m, 2H), 7.61 (dd, J = 8.8 Hz, 2.60 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.92 (s, 1H), 10.46 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.0, 55.3, 67.3, 82.4, 83.3, 114.0, 115.0, 115.2, 126.5, 127.0, 129.6, 130.9, 133.0, 137.5, 138.2, 159.5, 159.9, 188.3 ppm. HRMS: calcd. for $C_{18}H_{15}BrNaO_3$ [M+Na] 381.0102; found 381.0107.

General Experimental Procedure for the Synthesis of Dibenzo[*b,f*]oxepines.

Representative Experimental Procedure for the synthesis of dibenzo[*b,f*]oxepin-10-yl(phenyl)methanone (3a):

Compound **2a** (149 mg, 0.5 mmol) was taken in a 10 mL round bottom flask containing 3 mL of dry 1, 2-dichloroethane. Anhydrous $FeCl_3$ (12.0 mg, 0.075 mmol) was added to it and the reaction mixture was heated to reflux for 12 h under an Ar-atmosphere. After completion of the reaction (TLC), dichloroethane was distilled out under reduced pressure and the residue was purified by silica gel (mesh 100-200) column chromatography (petroleum ether/EtOAc) to afford **3a** (113 mg, 0.38 mmol, 76 %) as a yellow solid. m.p. 120 °C. IR (KBr) 3056, 1656, 1205, 754 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.03 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.17 (t, J = 7.0 Hz, 1H), 7.28–7.34(m, 5H), 7.37–7.45 (m, 3H), 7.53–7.56 (m, 1H), 7.94 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 121.4, 121.9, 125.2, 125.3, 128.4, 128.6, 129.2, 129.4, 130.3, 130.7, 130.8, 131.5, 133.1, 134.9, 137.4, 140.1, 158.3, 158.6, 197.0 ppm. HRMS: calcd. for $C_{21}H_{15}O_2$ [M+H] 299.1072; found 299.1069.

Phenyl(3-(phenylethynyl)dibenzo[*b,f*]oxepin-10-yl)methanone (3b):

Compound **2b** (200 mg, 0.5 mmol) and anhydrous $FeCl_3$ (12.0 mg, 0.075 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **3a** for 6 h to afford **3b** (160 mg, 0.40 mmol, 80%) as a yellow solid, m.p. 120 °C. IR (KBr) 3062, 1654, 1604, 1205 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.02–7.10 (m, 2H), 7.23–7.38 (m, 4H), 7.44 (t, J = 7.5 Hz, 3H), 7.48–7.58

(m, 3H), 7.94 (d, *J* = 8.7 HZ, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 88.5, 92.3, 122.0, 123.0, 124.4, 125.4, 126.5, 128.5, 128.6, 128.7, 128.8, 129.2, 129.4, 129.5, 130.3, 130.7, 130.9, 131.8, 133.2, 134.1, 137.3, 140.6, 158.0, 158.2, 196.9 ppm. HRMS: calcd. for $C_{29}H_{19}O_2$ [M+H] 399.1385; found 399.1388.

2-Nitrodibenzo[*b,f*]oxepin-10-yl)(phenyl)methanone (3c):

Compound **2c** (172 mg, 0.5 mmol) and anhydrous $FeCl_3$ (12.0 mg, 0.075 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **3a** for 5 h to afford **3c** (148 mg, 0.43 mmol, 86%) as a faint yellow solid, m.p. 118 °C. IR (KBr) 3067, 1656, 1344, 734 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09–7.11 (m, 2H), 7.16 (s, 1H), 7.26–7.30 (m, 1H), 7.34–7.39 (m, 2H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.94 (d, *J* = 7.2 Hz, 2H), 8.19 (s, 1H), 8.24 (dd, *J* = 8.8 Hz, 2.7 Hz, 1H), ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 121.9, 122.4, 125.9, 126.2, 128.5, 128.7, 129.5, 130.1, 131.4, 131.8, 133.5, 136.6, 142.2, 145.0, 157.3, 162.8, 196.1 ppm. HRMS: calcd. for $C_{21}H_{14}NO_4$ [M+H] 344.0923; found 344.0920.

1-Methoxydibenzo[*b,f*]oxepin-10-yl)(phenyl)methanone (3d): Compound **2d** (165 mg, 0.5 mmol) and anhydrous $FeCl_3$ (12.0 mg, 0.075 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **3a** for 9 h to afford **3d** (87 mg, 0.27 mmol, 53%) as a faint yellow solid, m.p. 118 °C. IR (KBr) 3055, 1652, 1274, 1085 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.69 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 7.03–7.08 (m, 1H), 7.18–7.24 (m, 1H), 7.26 (s, 1H), 7.29–7.36 (m, 2H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 2H), 7.60 (s, 1H), 7.95 (d, *J* = 7.3 Hz, 2H), ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.0, 107.0, 121.6, 125.0, 127.3, 128.3, 129.2, 129.3, 129.4, 129.6, 130.2, 130.3, 130.7, 130.8, 131.7, 131.8,

132.7, 137.7, 138.4, 158.3, 160.2, 197.0 ppm. HRMS: calcd. for $C_{22}H_{17}O_3$ [M+H] 329.1178; found 329.1182.

(8-Methoxydibenzo[*b,f*]oxepin-10-yl)(phenyl)methanone (3e): Compound **2e** (164 mg, 0.5 mmol) and anhydrous $FeCl_3$ (12.0 mg, 0.075 mmol) with anhydrous AgOTf (39.0 mg, 0.15 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **3a** for 16 h to afford **3e** (135 mg, 0.41 mmol, 82%) as a orange liquid. IR (KBr) 2832, 1655, 1203, 739 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.61 (s, 3H), 6.63 (s, 1H), 6.86 (dd, J = 8.8 Hz, 2.9 Hz, 1H), 7.14–7.19 (m, 2H), 7.23 (d, J = 6.3Hz, 1H), 7.27–7.30 (m, 2H), 7.37 (d, J = 7.8 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.95 (d, J = 7.4 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7, 113.6, 116.4, 121.2, 122.4, 125.2, 128.6, 128.7, 129.0, 129.1, 129.6, 130.2, 130.8, 131.5, 133.1, 135.3, 137.4, 139.9, 152.1, 156.6, 158.9, 196.9 ppm. HRMS: calcd. for $C_{22}H_{17}O_3$ [M+H] 329.1178; found 329.1174.

(8-Methyldibenzo[*b,f*]oxepin-10-yl)(phenyl)methanone (3f): Compound **2f** (156 mg, 0.5 mmol) and anhydrous $FeCl_3$ (12.0 mg, 0.075 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **3a** for 14 h to afford **3f** (141 mg, 0.45 mmol, 90%) as a orange solid, m.p. 112 °C. IR (KBr) 3051,1650, 1201 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.17 (s, 3H), 6.91 (s, 1H), 7.11–7.20 (m, 4H), 7.24–7.29 (m, 3H), 7.35–7.40 (m, 1H), 7.42–7.47 (m, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.97 (d, J = 7.4 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7, 121.2, 121.4, 125.0, 128.5, 128.6, 129.1, 129.4, 130.2, 130.6, 131.2, 133.0, 134.4, 134.6, 137.3, 140.1, 156.2, 158.6, 197.1 ppm. HRMS: calcd. for $C_{22}H_{17}O_2$ [M+H] 313.1229; found 313.1224.

(4-chlorophenyl)(dibenzo[*b,f*]oxepin-10-yl)methanone (3g): Compound **2g** (166 mg, 0.5 mmol) and anhydrous $FeCl_3$ (12.0 mg, 0.075 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **3a** for 6 h to afford **3g** (133 mg, 0.40 mmol, 80%) as a reddish orange solid, m.p. 90 °C. IR (KBr) 2922, 1660, 1254, 763 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.05 (s, 2H), 7.14–7.22 (m, 2H), 7.26–7.32 (m, 4H), 7.39 (d, J = 8.5 Hz, 3H), 7.87 (d, J = 8.5 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 117.2, 121.3, 121.9, 123.0, 124.9, 125.1, 125.2, 128.3, 128.7, 128.8, 128.9, 129.2, 130.2, 130.7, 131.5, 132.6, 134.9, 135.5, 139.5, 139.6, 158.1, 158.4, 195.5 ppm. HRMS: calcd. for $C_{21}H_{14}ClO_2$ [M+H] 333.0682; found 333.0678.

Dibenzo[*b,f*]oxepin-10-yl(4-methoxyphenyl)methanone (3h): Compound **2h** (164 mg, 0.5 mmol) and anhydrous $FeCl_3$ (12.0 mg, 0.075 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **3a** for 9 h to afford **3h** (156 mg, 0.40 mmol, 95%) as a brown black sticky solid. ^1H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 3H), 6.90 (d, J = 8.8 Hz, 2H), 7.00–7.10 (m, 2H), 7.14–7.19 (m, 2H), 7.23–7.32 (m, 4H), 7.35–7.40 (m, 1H), 7.95 (d, J = 8.8 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5, 113.8, 121.2, 121.8, 125.1, 125.1, 129.1, 129.2, 129.4, 129.9, 130.5, 131.1, 132.6, 133.2, 140.4, 158.0, 158.3, 163.3, 195.5 ppm. HRMS: calcd. for $C_{22}H_{16}NaO_3$ [M+Na] 351.0997; found 351.0994.

Dibenzo[*b,f*]oxepin-10-yl(p-tolyl)methanone (3i): Compound **2i** (156 mg, 0.5 mmol) and anhydrous $FeCl_3$ (12.0 mg, 0.075 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **3a** for 9 h to afford **3i** (97 mg, 0.31 mmol, 62%) as a orange liquid. ^1H NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 3H), 7.02–7.06 (m, 1H), 7.09 (dd, J = 7.5 Hz, 1.4 Hz, 1H), 7.17 (dt, J = 7.4 Hz, 1.2 Hz, 1H), 7.21–7.27 (m, 4H), 7.28–7.32 (m, 3H), 7.35–7.41 (m, 1H), 7.85 (d,

J = 8.2 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 121.2, 121.8, 125.1, 129.2, 129.3, 130.3, 130.6, 131.2, 134.0, 134.6, 140.2, 144.0, 158.1, 158.4, 197.6 ppm. HRMS: calcd. for $C_{22}H_{17}O_2$ [M+H] 313.1229; found 313.1225.

Dibenzo[*b,f*]oxepin-10-yl(6-methoxynaphthalen-2-yl)methanone (3j): Compound **2j** (189 mg, 0.5 mmol) and anhydrous $FeCl_3$ (12.0 mg, 0.075 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **3a** for 9 h to afford **3j** (114 mg, 0.30 mmol, 60%) as a brown white solid. IR (KBr) 3034, 1697, 1235 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 3H), 6.98–7.04 (m, 1H), 7.15–7.21 (m, 3H), 7.28–7.33 (m, 5H), 7.7–7.43 (m, 1H), 7.77 (t, *J* = 9.1 Hz, 2H), 8.01 (dd, *J* = 8.6 Hz, 1.6Hz, 1H), 8.40 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4, 105.7, 119.7, 121.2, 121.8, 125.1, 125.1, 126.2, 127.1, 127.7, 129.2, 129.3, 130.5, 131.2, 131.3, 132.3, 132.4, 133.9, 137.3, 140.3, 158.0, 158.3, 159.9, 196.6 ppm. HRMS: calcd. for $C_{26}H_{19}O_3$ [M+H] 379.1334; found 379.1330.

General Experimental Procedure for the Synthesis of Benzo[*b*]oxepines.

Representative Experimental Procedure for the synthesis of (7,9-dichloro-2,3-dihydrobenzo[*b*]oxepin-4-yl)(phenyl)methanone (5a): Compound **4a** (160 mg, 0.5 mmol) was taken in a 10 mL round bottom flask containing 3 mL of dry 1,2-dichloroethane. Anhydrous $FeCl_3$ (12.0 mg, 0.075 mmol) was added to it and the reaction mixture was heated to reflux for 10 h under an Ar-atmosphere. After completion of the reaction (TLC), dichloroethane was distilled out under reduced pressure and the residue was purified by silica gel (mesh 100-200) column chromatography (petroleum ether/EtOAc) to afford **5a** (111 mg, 0.35 mmol, 70%) as a white solid. m.p. 126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.18 (t, *J* = 4.1 Hz, 2H), 4.44 (t, *J* =

4.6 Hz, 2H), 6.95 (s, 1H), 7.05 (s, 1H), 7.36 (s, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.71 (d, *J* = 6.9 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 33.1, 70.1, 111.7, 126.0, 126.4, 126.9, 128.6, 129.5, 130.7, 132.3, 132.6, 137.8, 138.9, 141.7, 154.6, 197.6 ppm. HRMS: calcd. for $C_{17}H_{13}Cl_2O_2$ [M+H] 319.0293; found 319.0289.

(9-Methoxy-2,3-dihydrobenzo[*b*]oxepin-4-yl)(*p*-tolyl)methanone (5b):

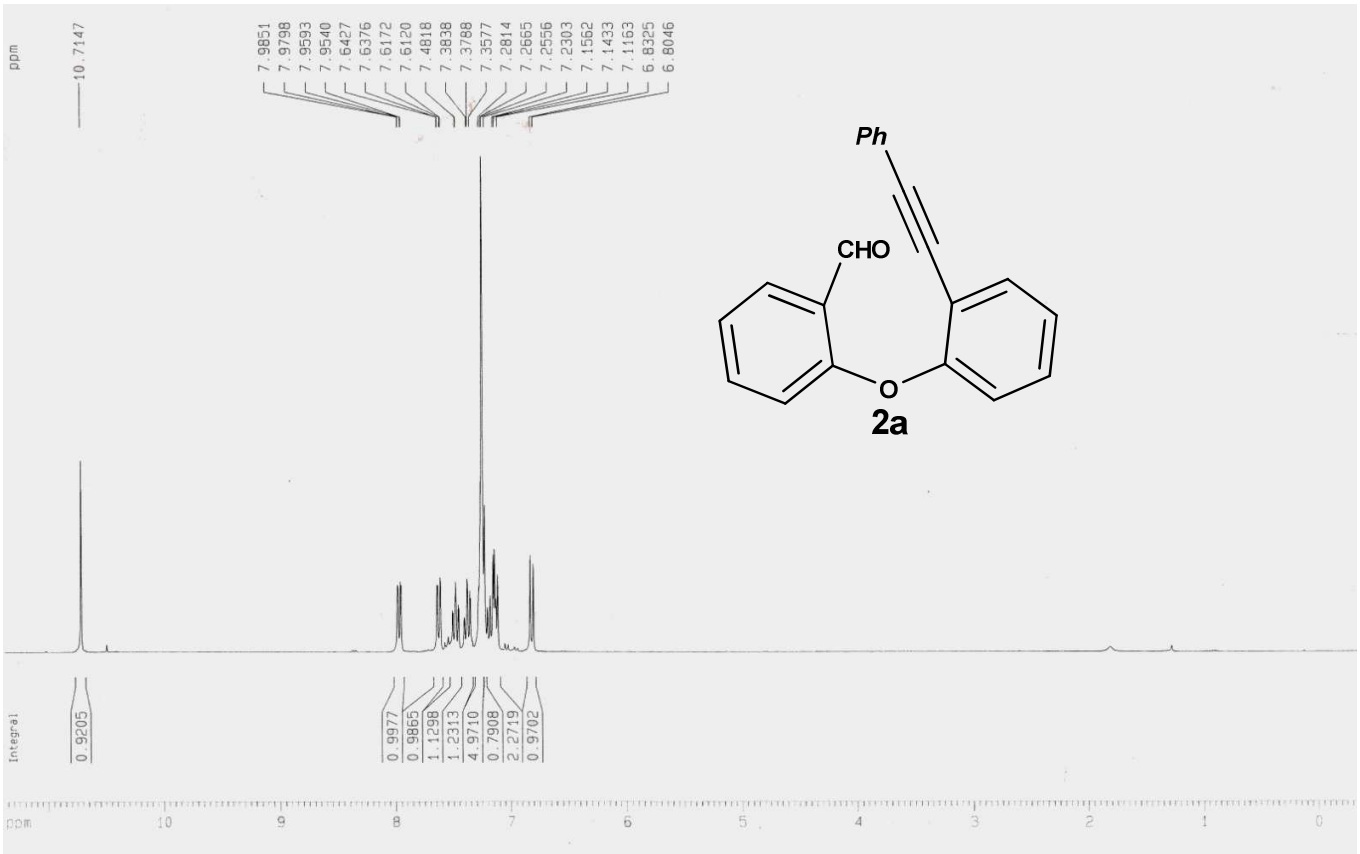
Compound **4b** (147 mg, 0.5 mmol) and anhydrous $FeCl_3$ (12.0 mg, 0.075 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **5a** for 20 h to afford **5b** (85 mg, 0.29 mmol, 58%) as a yellow solid, m.p. 110 °C. IR (KBr) 2920, 1622, 1257, 1245, 1089, 1072 $cm^{-1.}$ ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3H), 3.15 (t, *J* = 3.6 Hz, 2H), 3.90 (s, 3H), 4.44 (t, *J* = 4.3 Hz, 2H), 6.74–6.77 (m, 1H), 6.90–6.92 (m, 2H), 7.67 (s, 1H), 7.26 (d, *J* = 7.7 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 33.3, 56.3, 69.7, 112.8, 121.7, 124.0, 126.6, 128.9, 129.6, 135.4, 139.8, 140.9, 142.4, 149.9, 150.5, 197.6 ppm. HRMS: calcd. for $C_{19}H_{19}O_3$ [M+H] 295.1334; found 295.1331.

(7-Bromo-2,3-dihydrobenzo[*b*]oxepin-4-yl)(4-methoxyphenyl)methanone (5c):

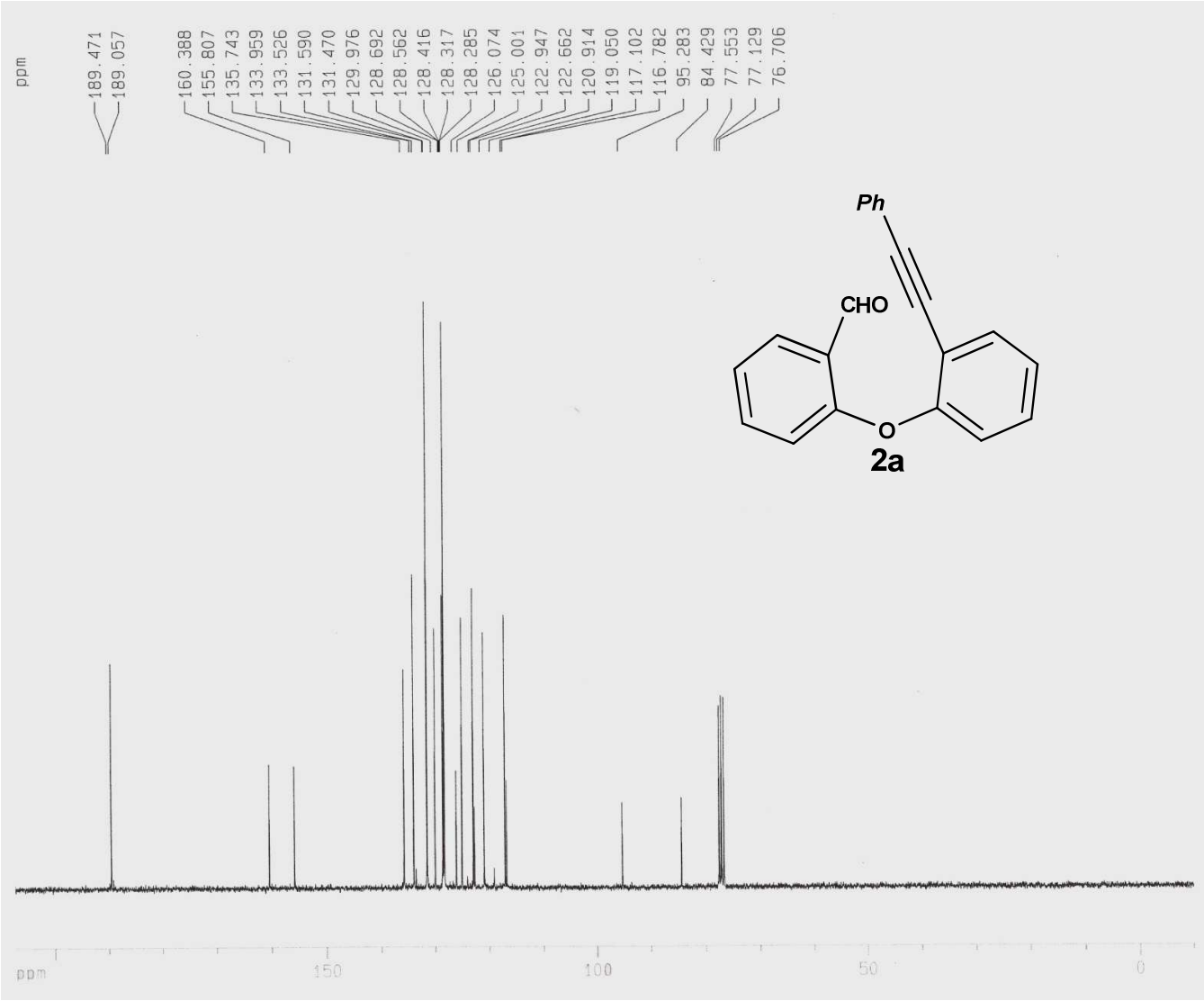
Compound **4c** (180 mg, 0.5 mmol) and anhydrous $FeCl_3$ (12.0 mg, 0.075 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **5a** for 12 h to afford **5c** (120 mg, 0.34 mmol, 67%) as a orange solid, m.p. 100 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.11 (t, *J* = 4.5 Hz, 2H), 3.89 (s, 3H), 4.32 (t, *J* = 4.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.96 (d, *J* = 9.0 Hz, 2H), 7.26–7.32 (m, 3H), 7.75 (d, *J* = 8.5 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.7, 55.6, 69.2, 113.8, 114.4, 122.3, 125.5, 127.2, 129.7, 130.3, 132.0, 133.2, 136.8, 137.6, 138.3, 159.3, 163.1, 196.6 ppm. HRMS: calcd. for $C_{18}H_{15}BrNaO_3$ [M+Na] 381.0102; found 381.0198.

Reference: (1) G. W. Yeage, D. N. Schissel, *Synthesis* 1995, **1**, 2830.

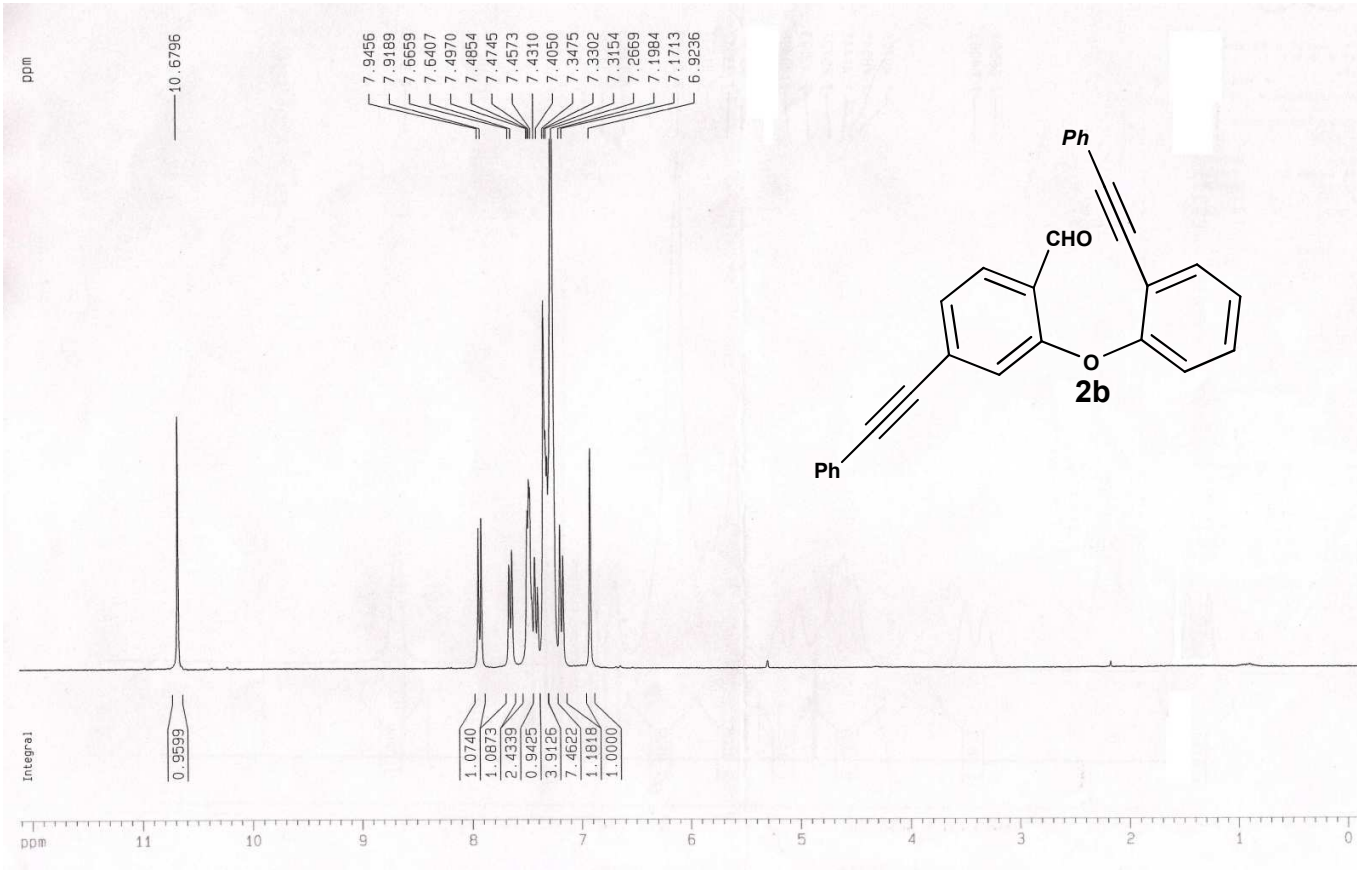
^{1}H NMR, $CDCl_3$, 300 MHz



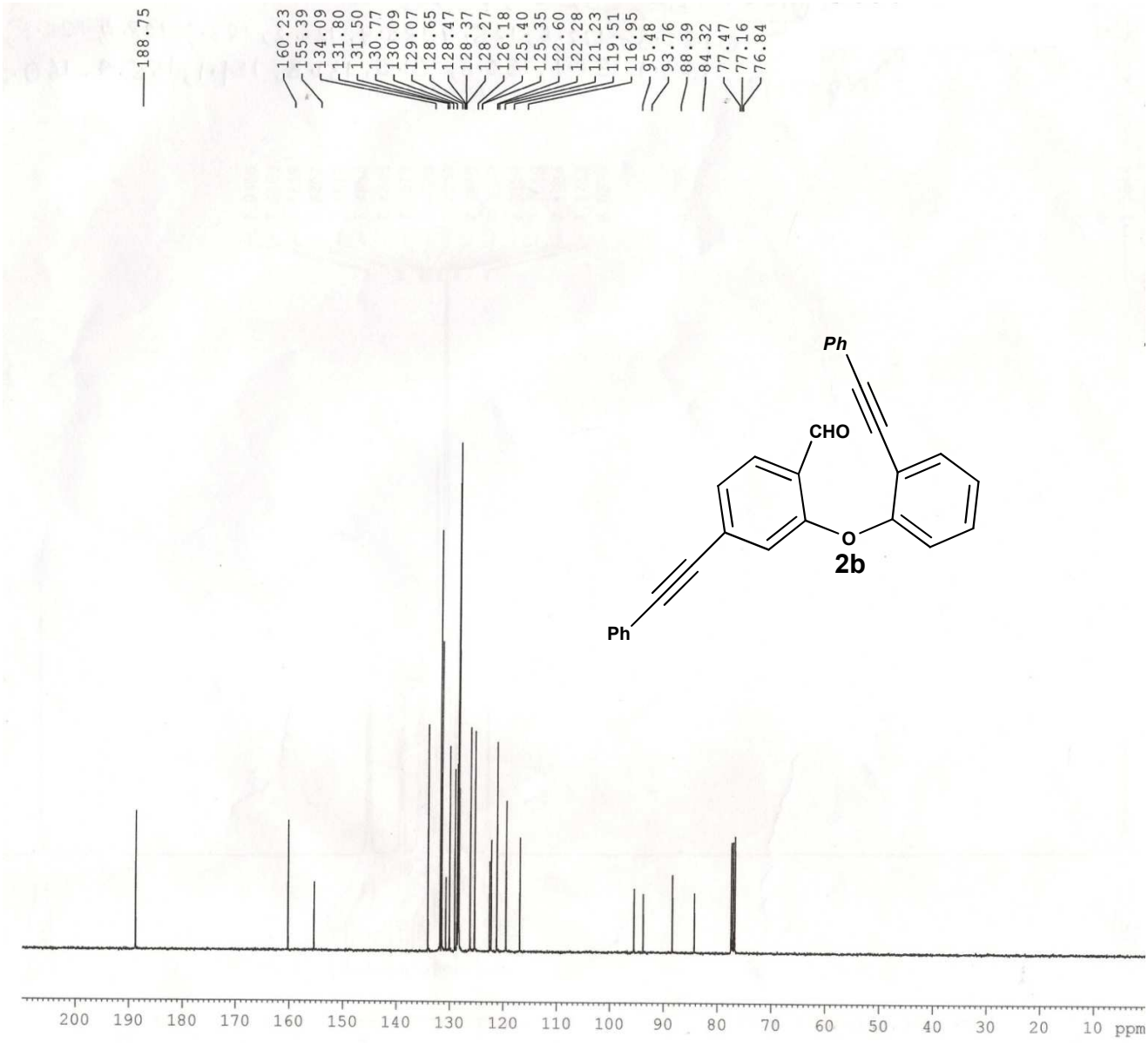
^{13}C NMR, $CDCl_3$, 125 MHz



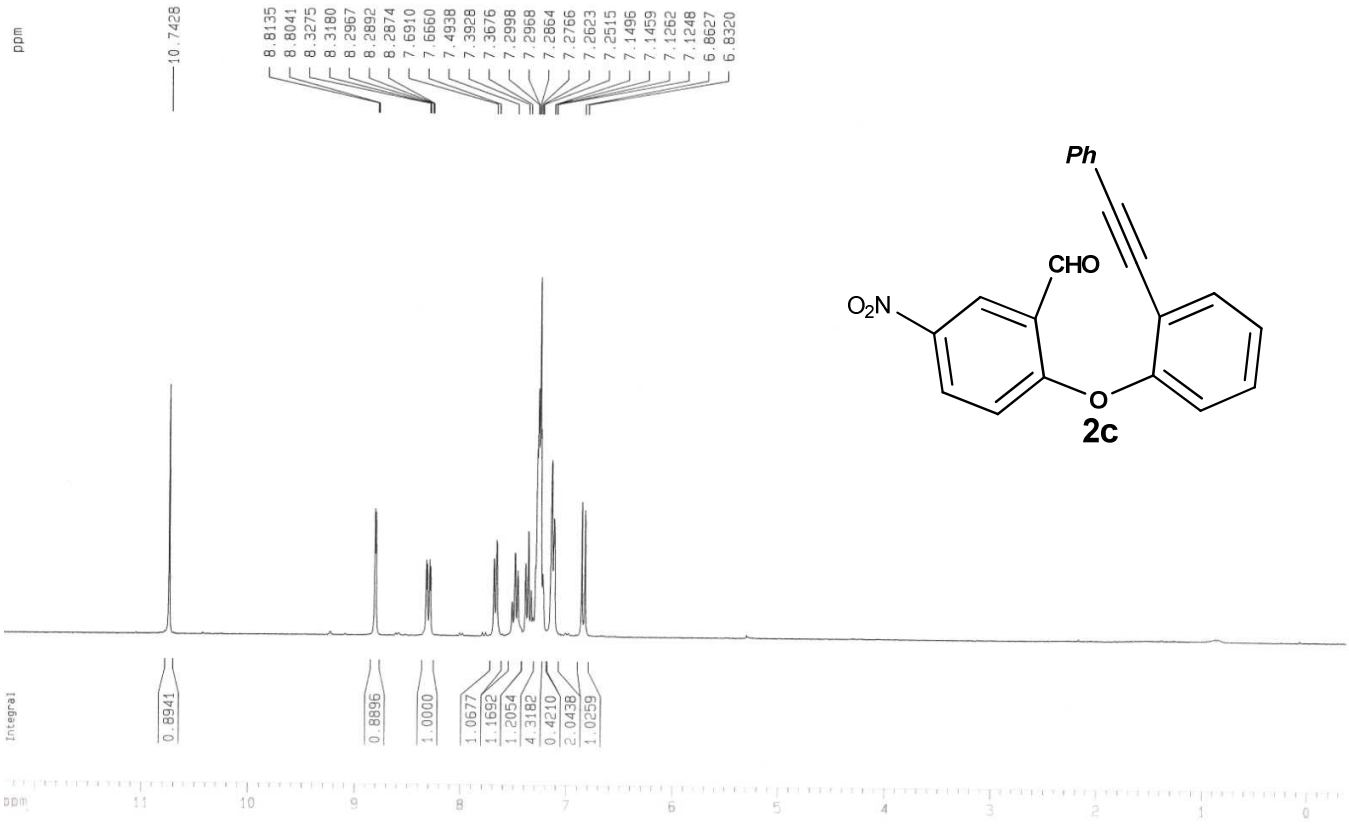
^{1}H NMR, $CDCl_3$, 300 MHz



^{13}C NMR, $CDCl_3$, 75 MHz

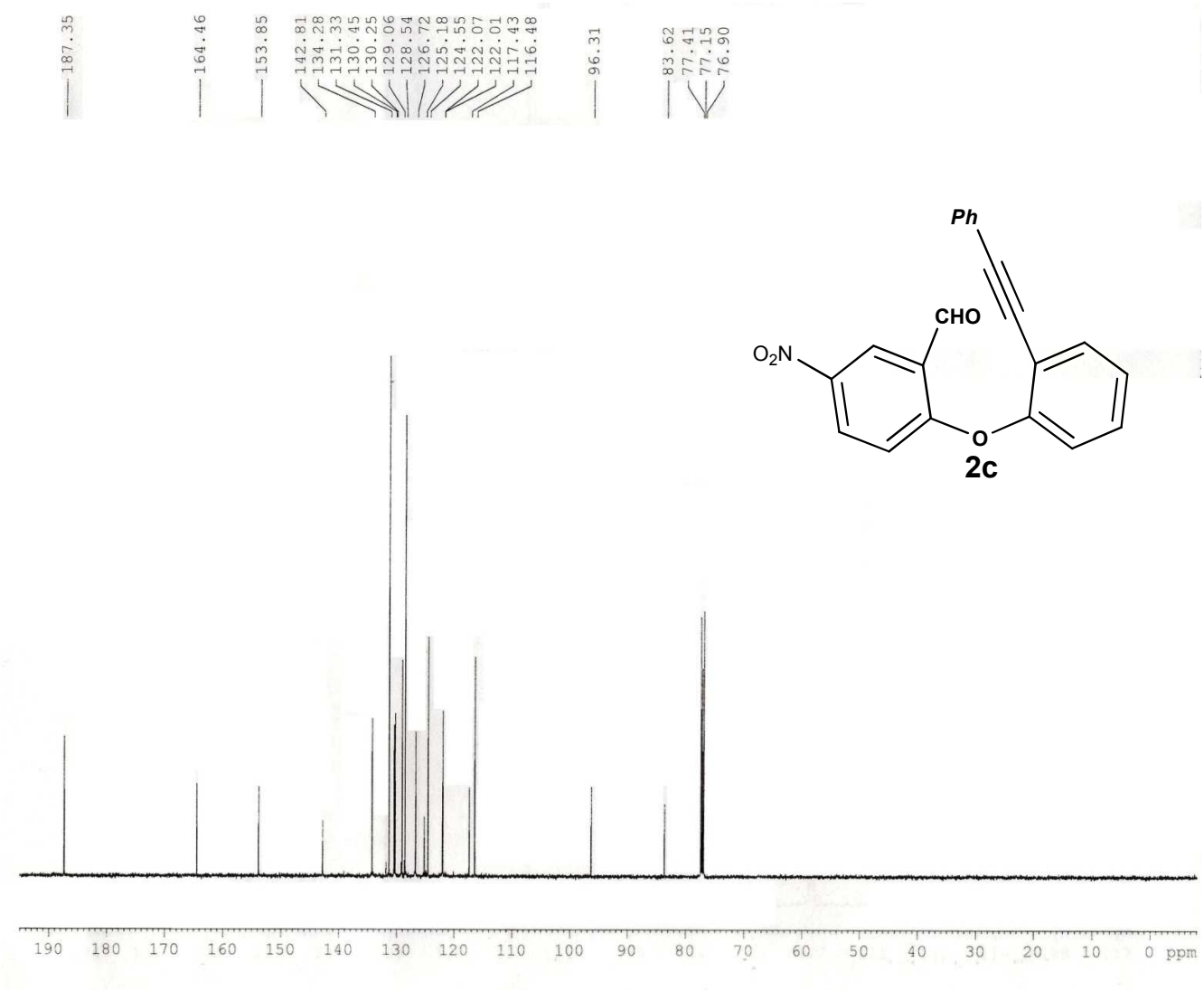


^{1}H NMR, $CDCl_3$, 300 MHz

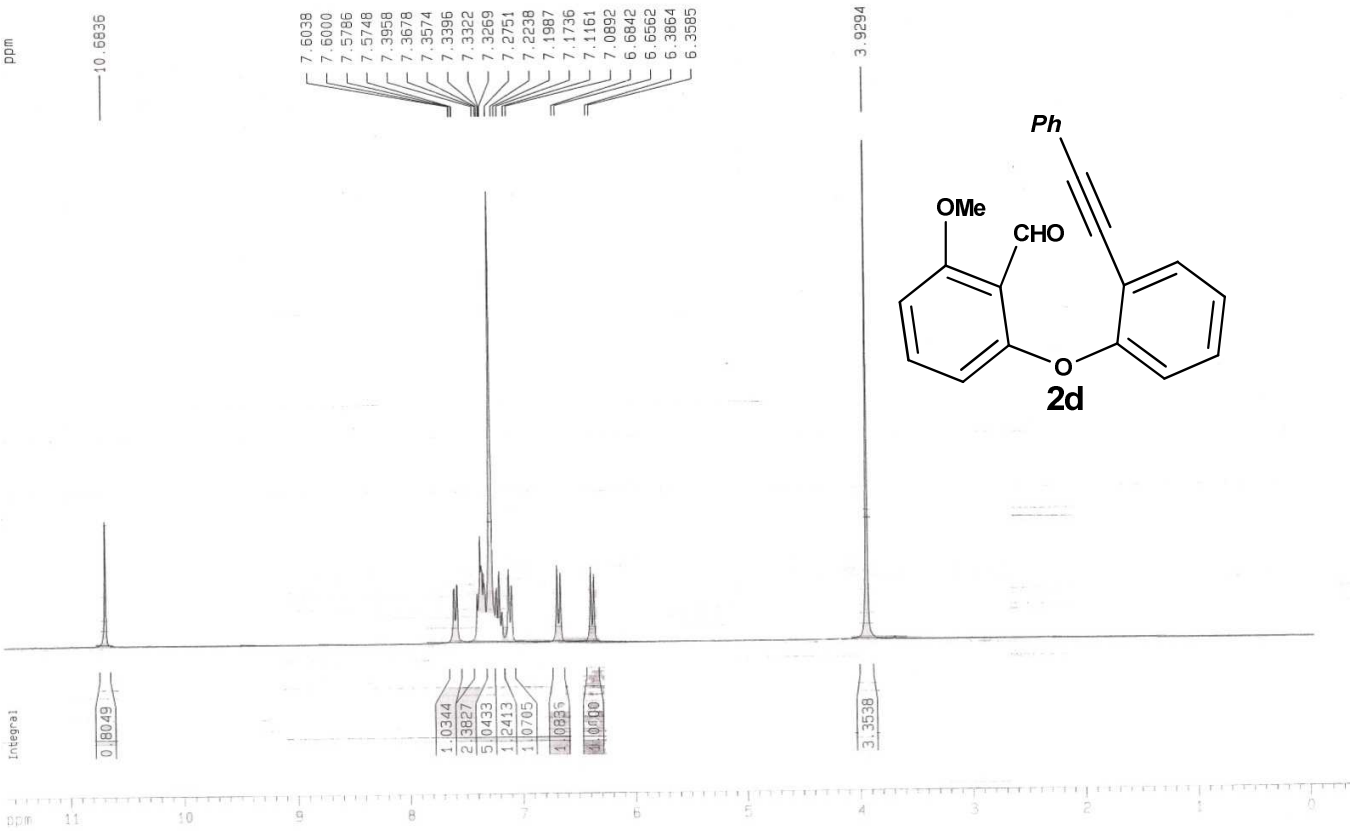


2c

^{13}C NMR, $CDCl_3$, 125 MHz

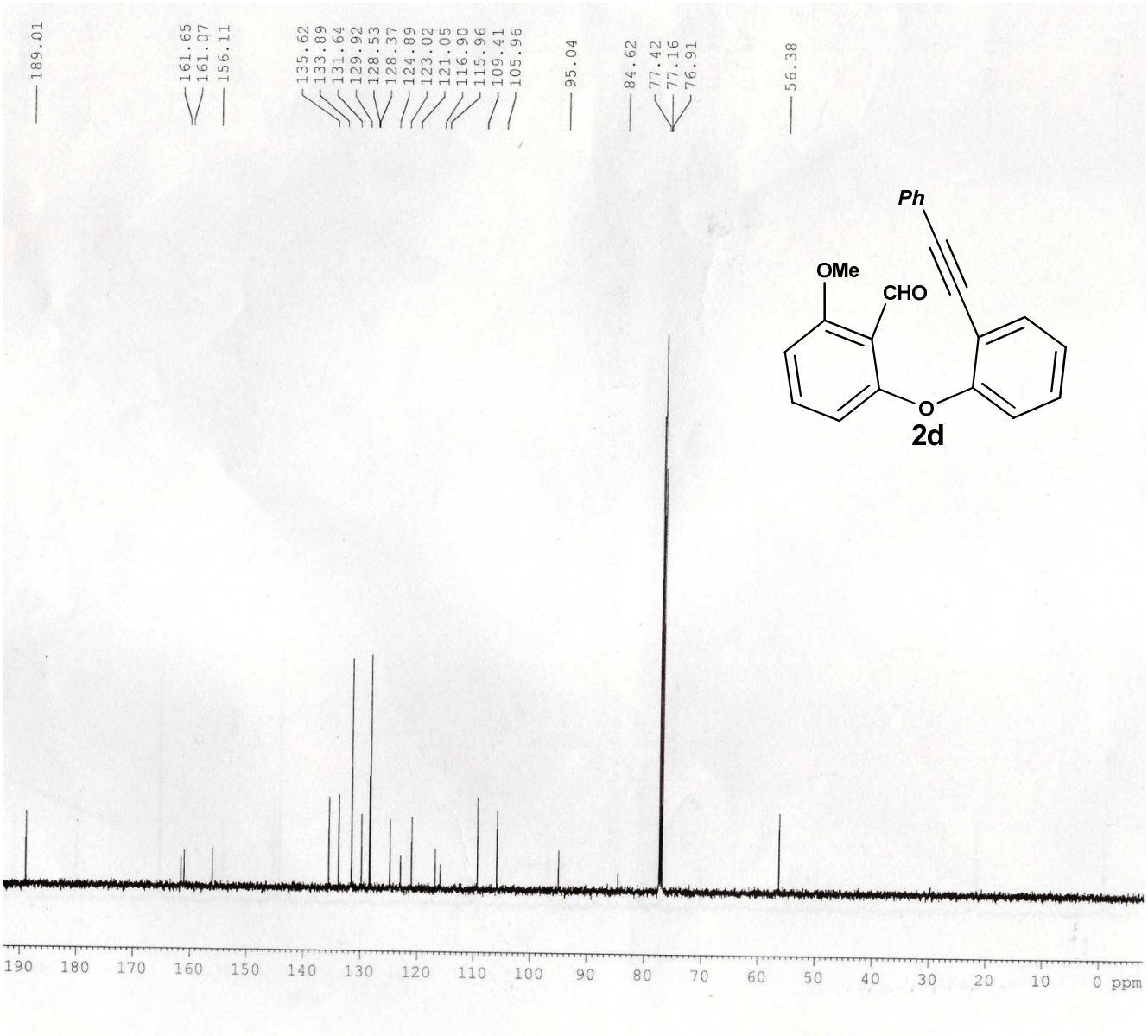


^{1}H NMR, $CDCl_3$, 300 MHz

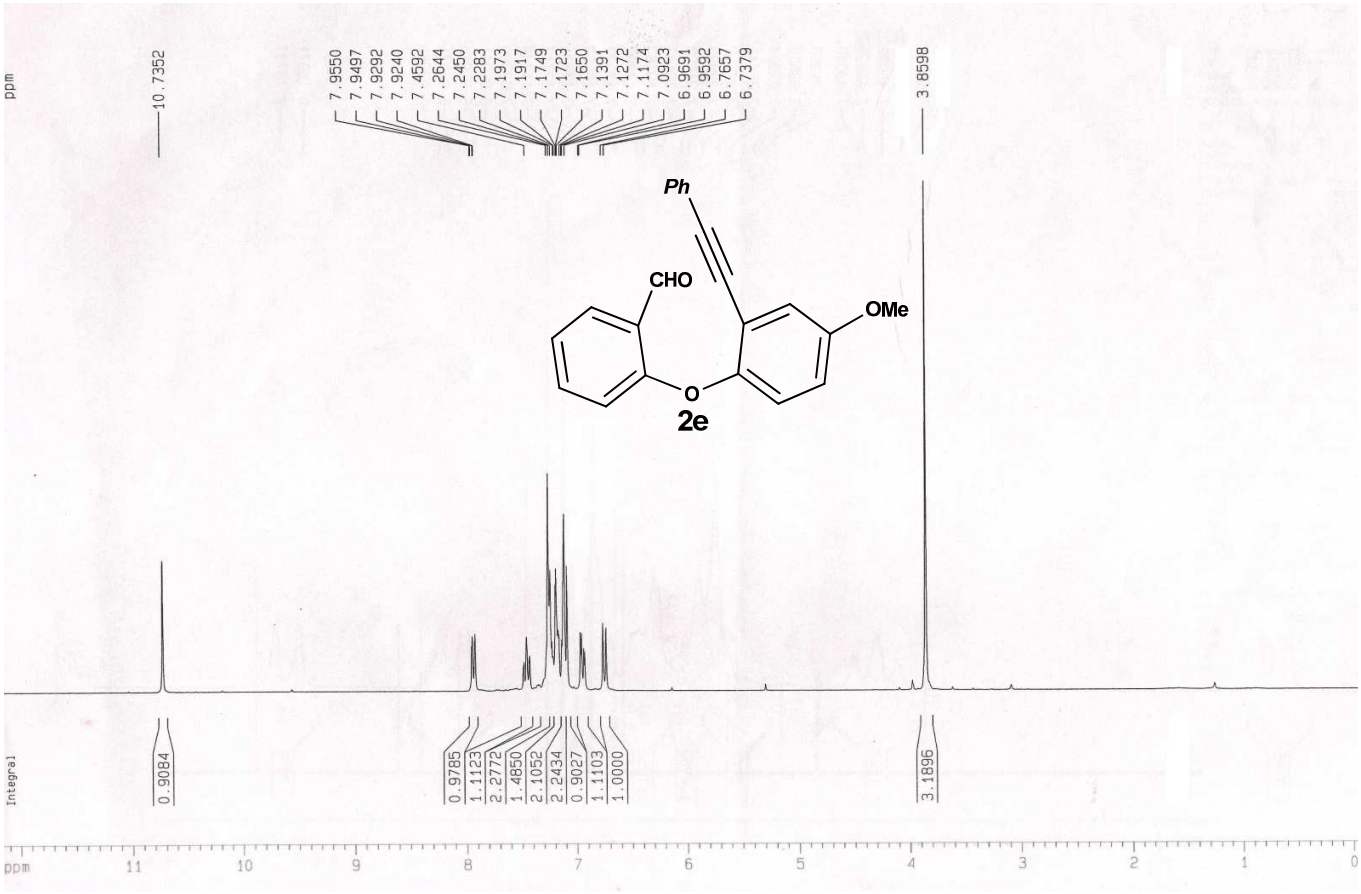


2d

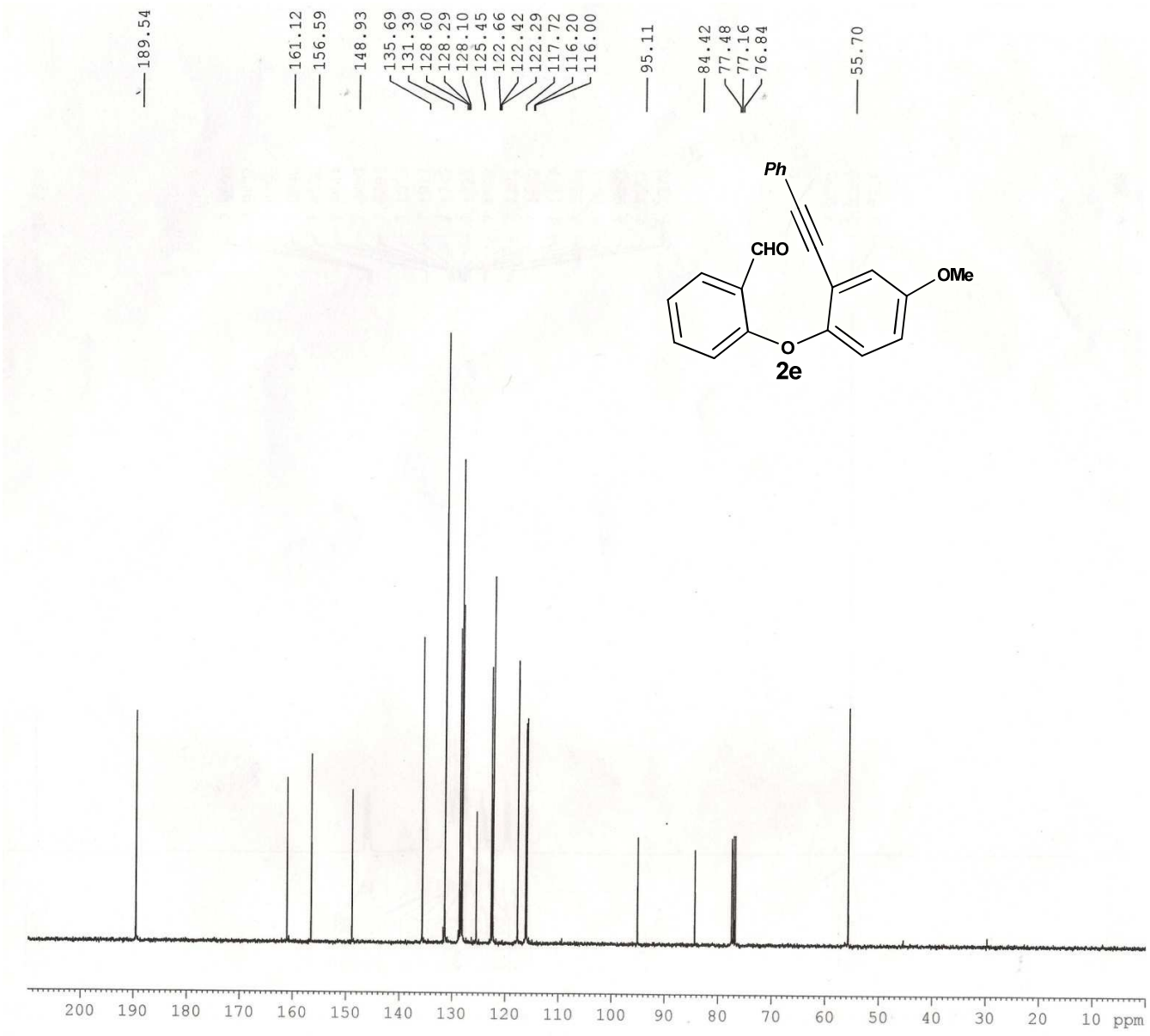
^{13}C NMR, $CDCl_3$, 125 MHz



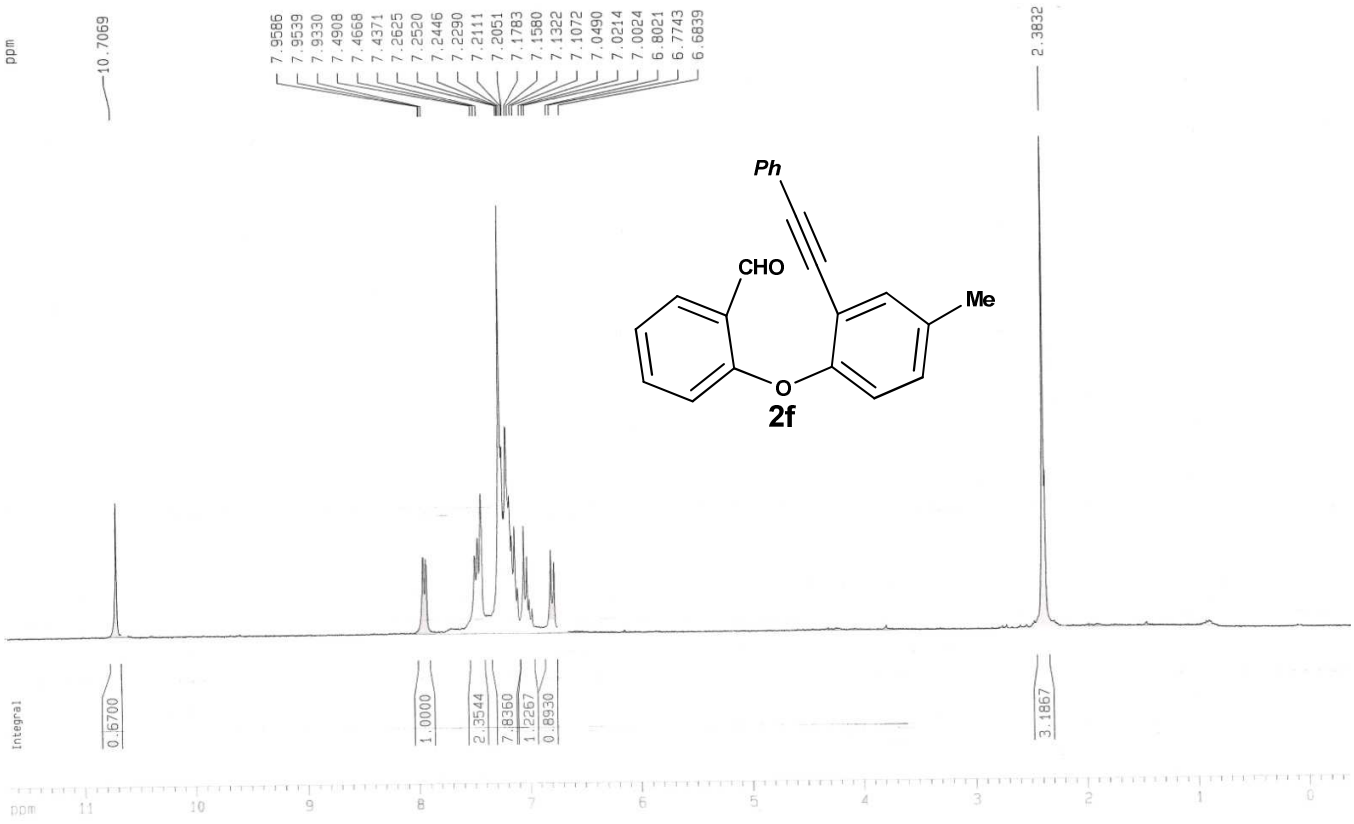
^{1}H NMR, $CDCl_3$, 300 MHz



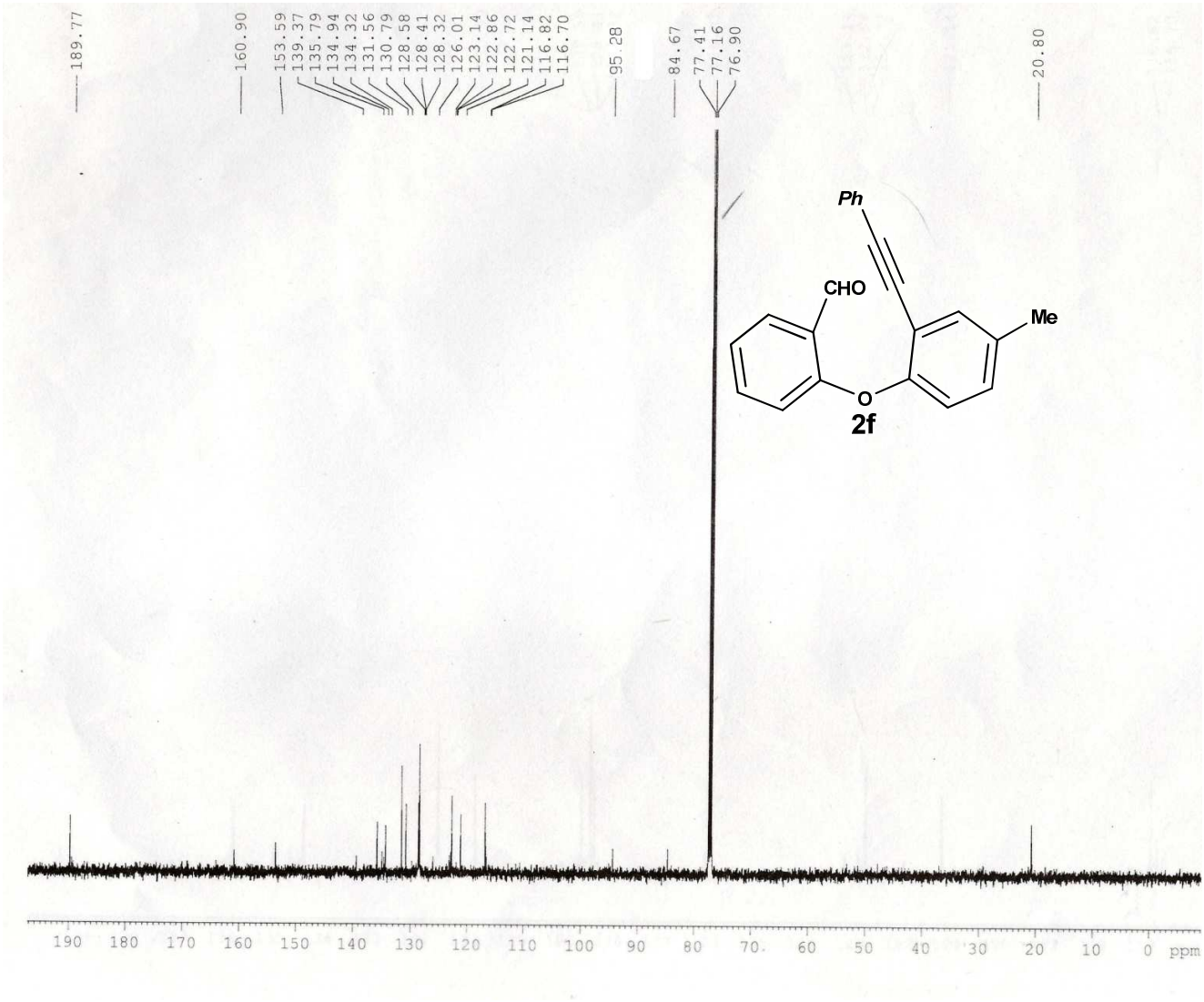
^{13}C NMR, $CDCl_3$, 125 MHz



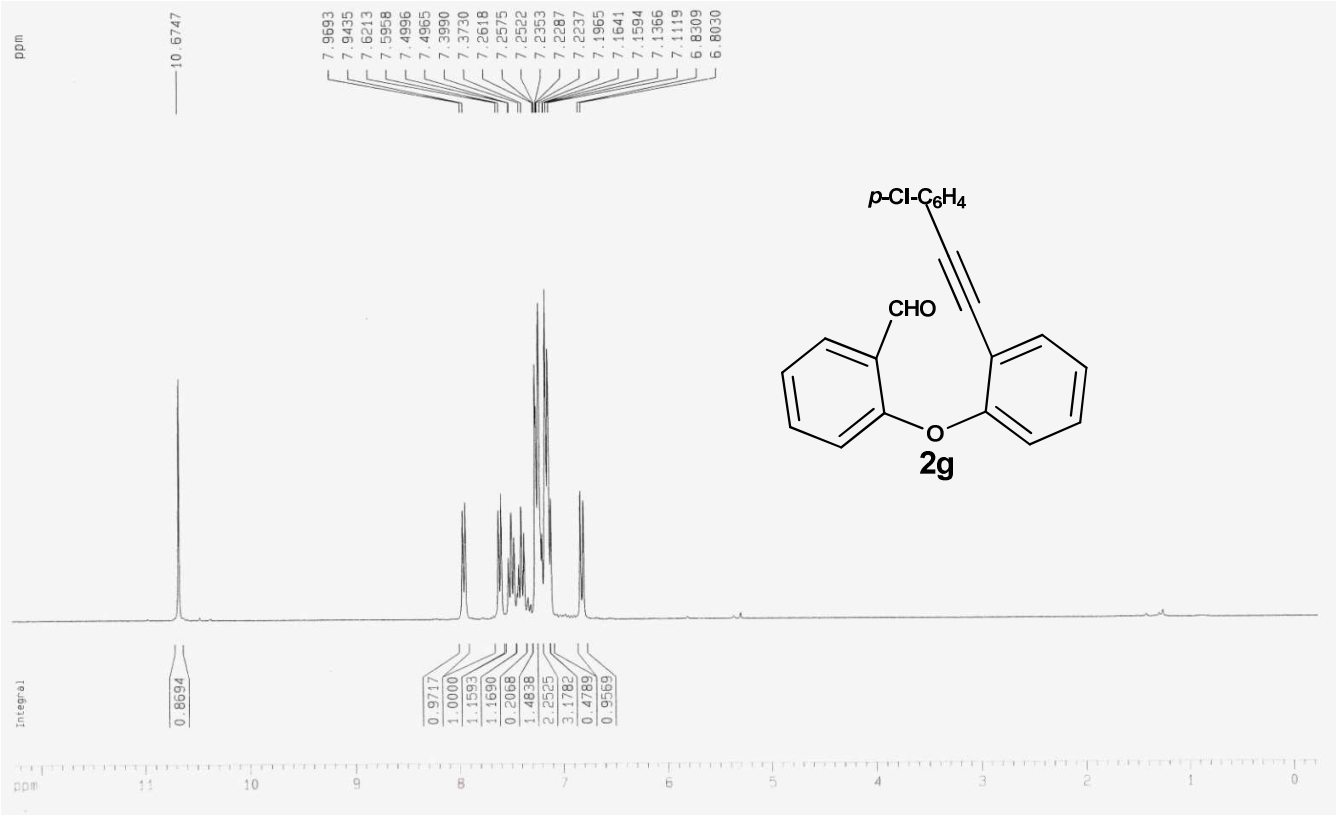
^{1}H NMR, $CDCl_3$, 300 MHz



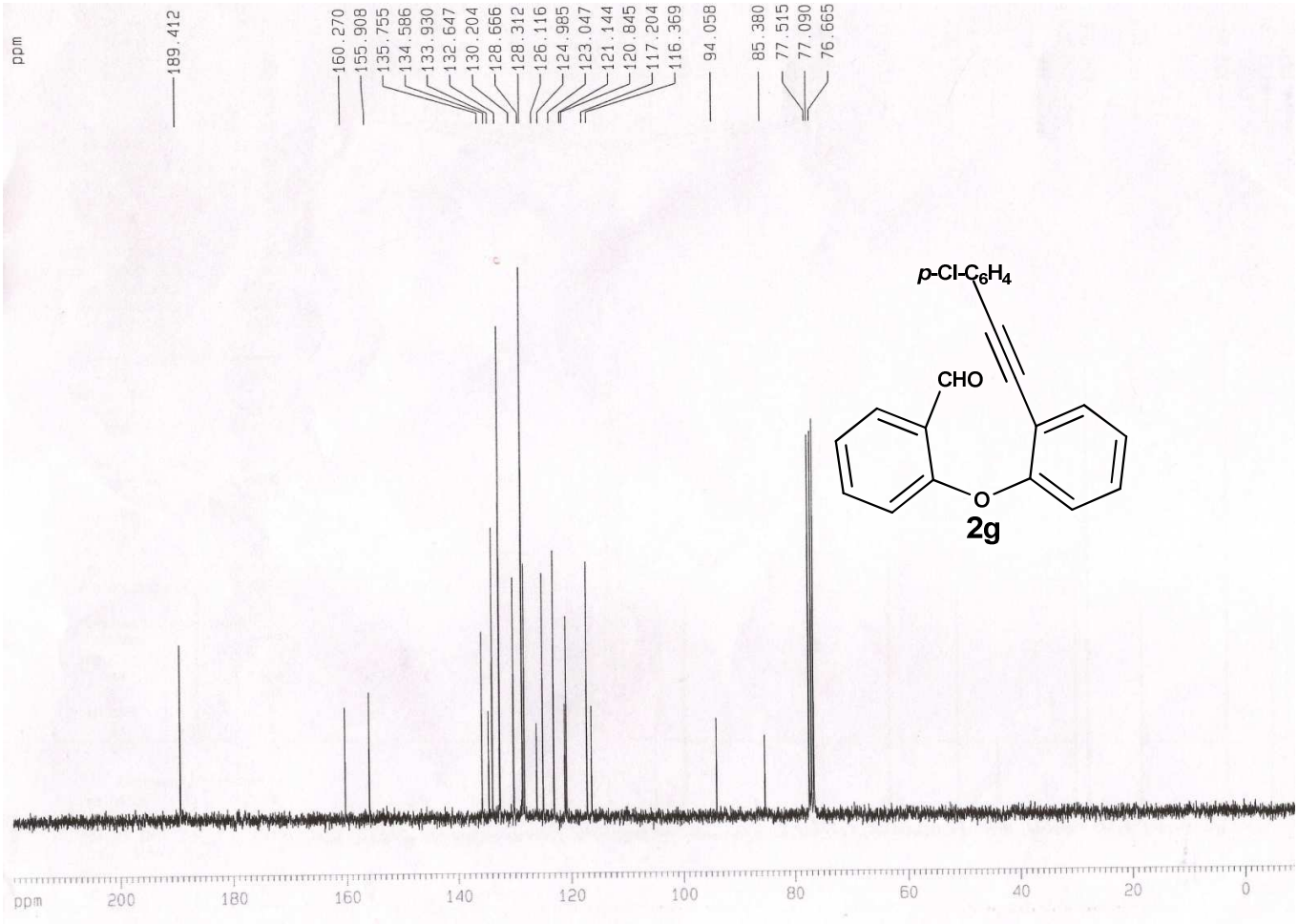
^{13}C NMR, $CDCl_3$, 125 MHz



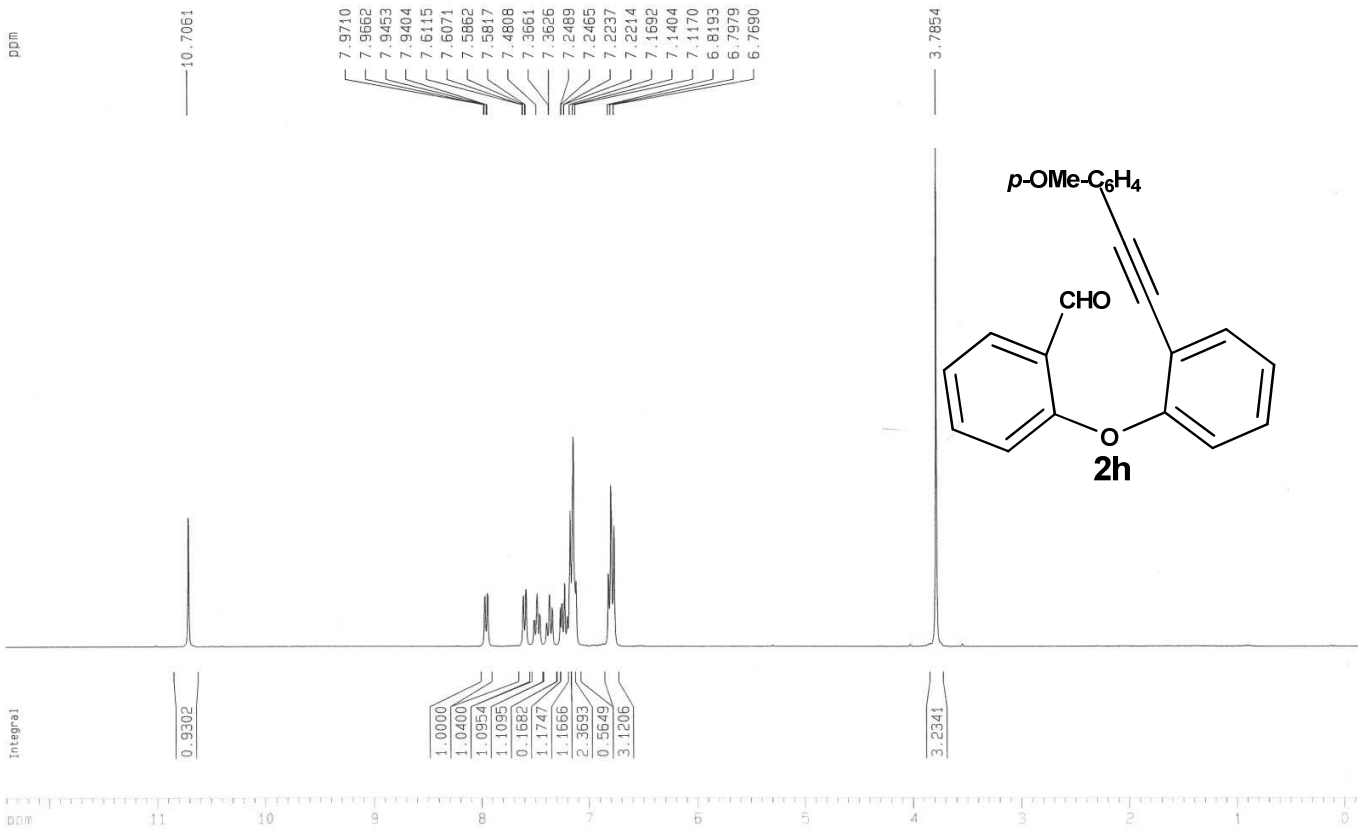
^{1}H NMR, $CDCl_3$, 300 MHz



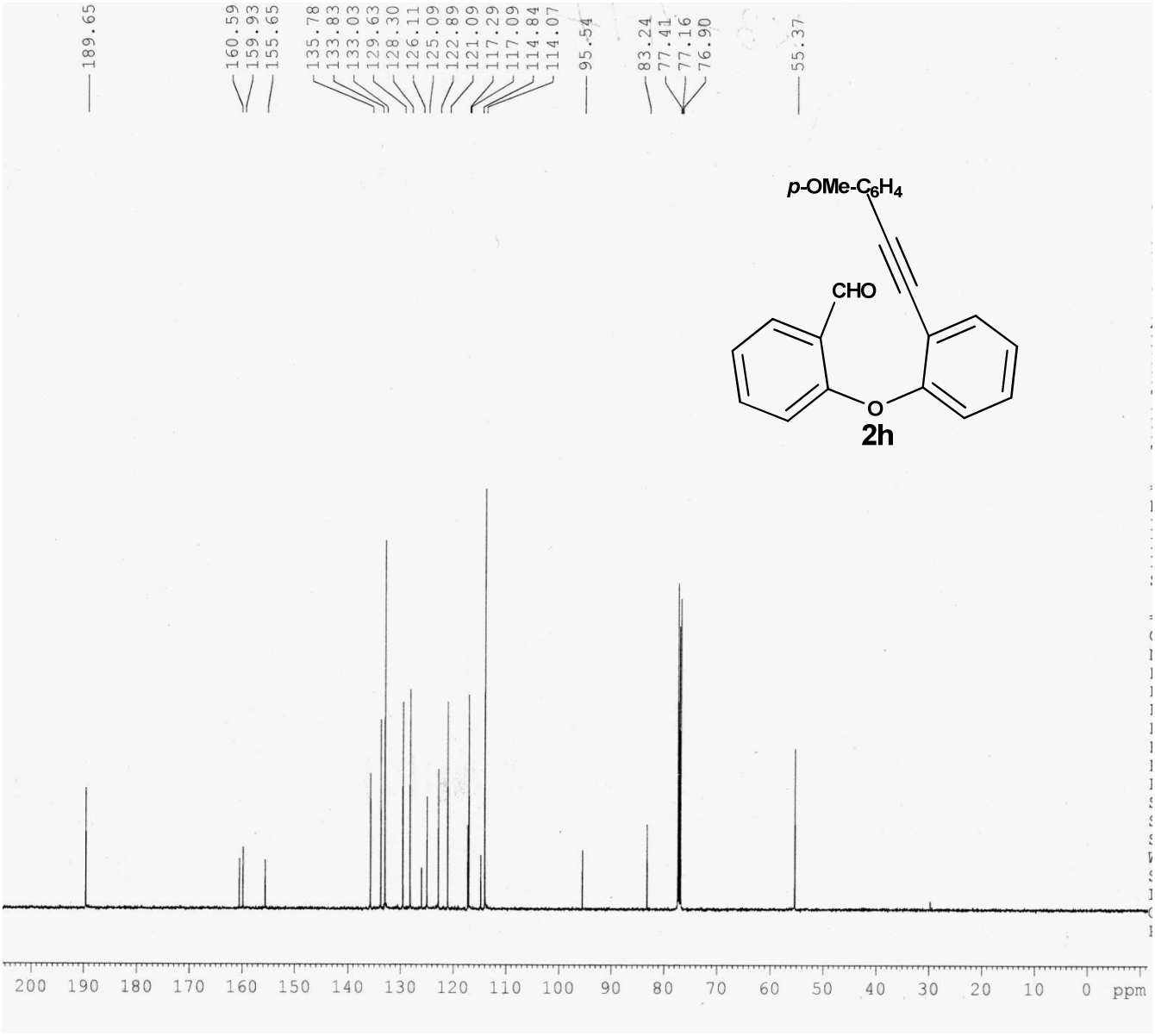
^{13}C NMR, $CDCl_3$, 75 MHz



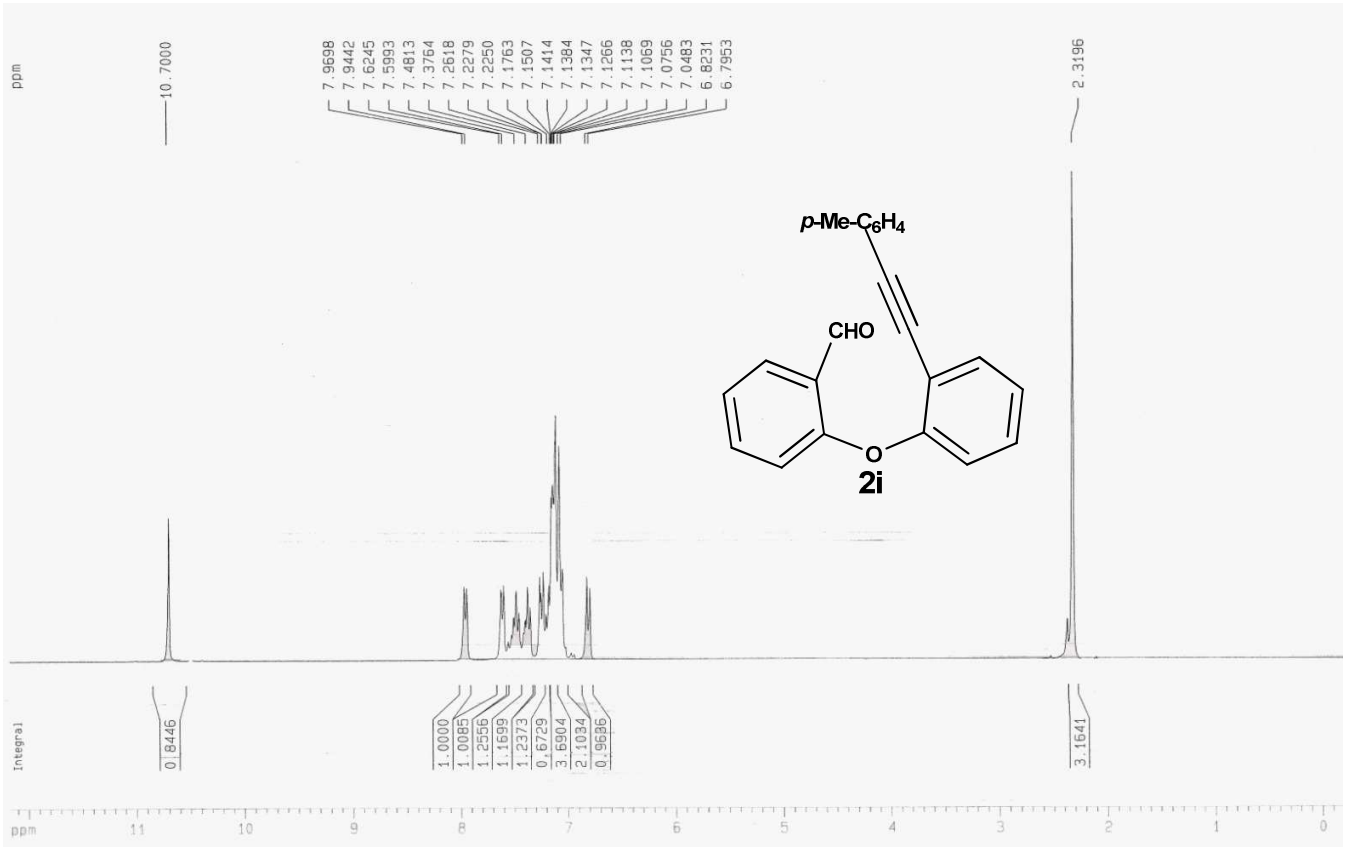
^{1}H NMR, $CDCl_3$, 300 MHz



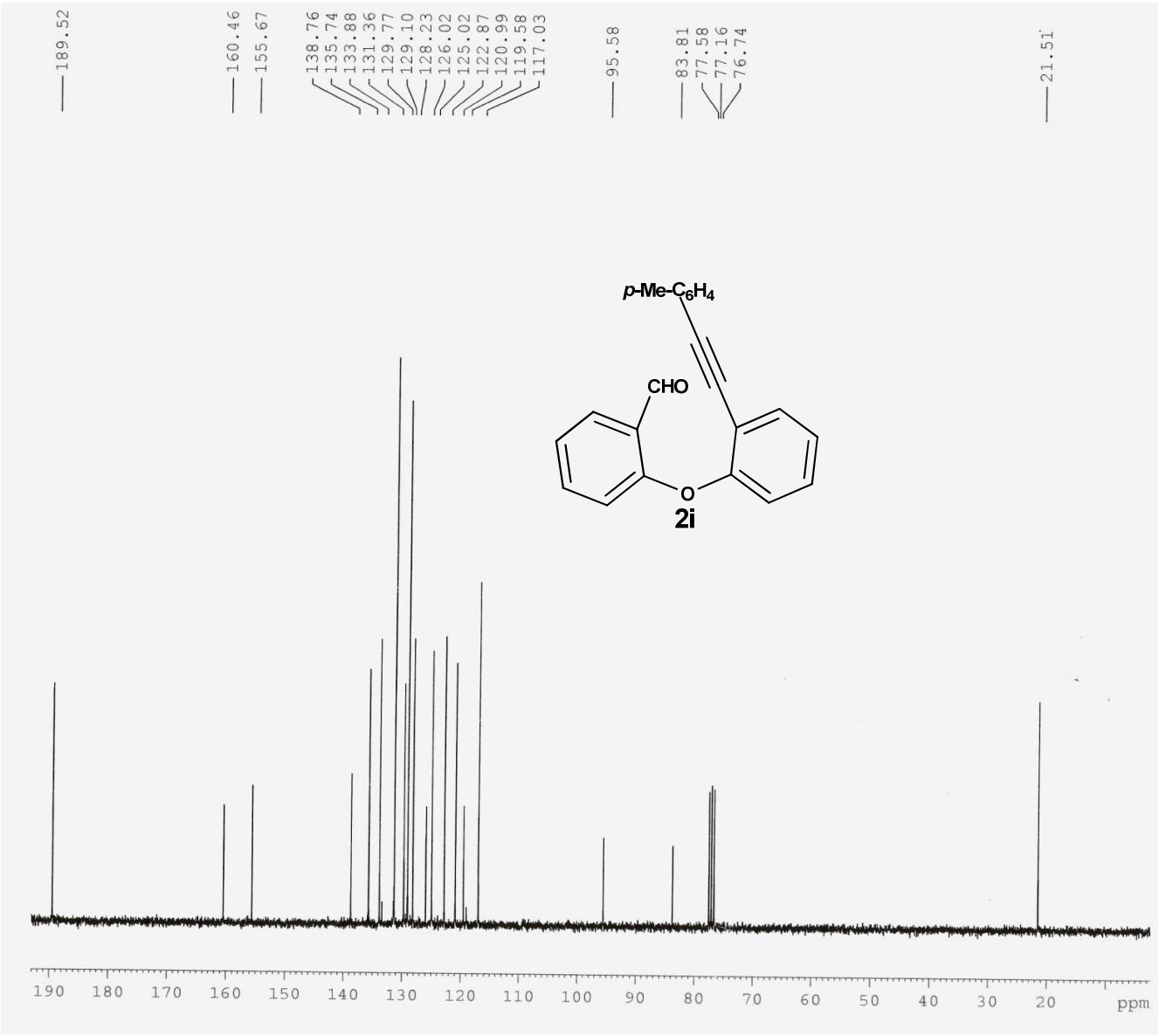
^{13}C NMR, $CDCl_3$, 125 MHz



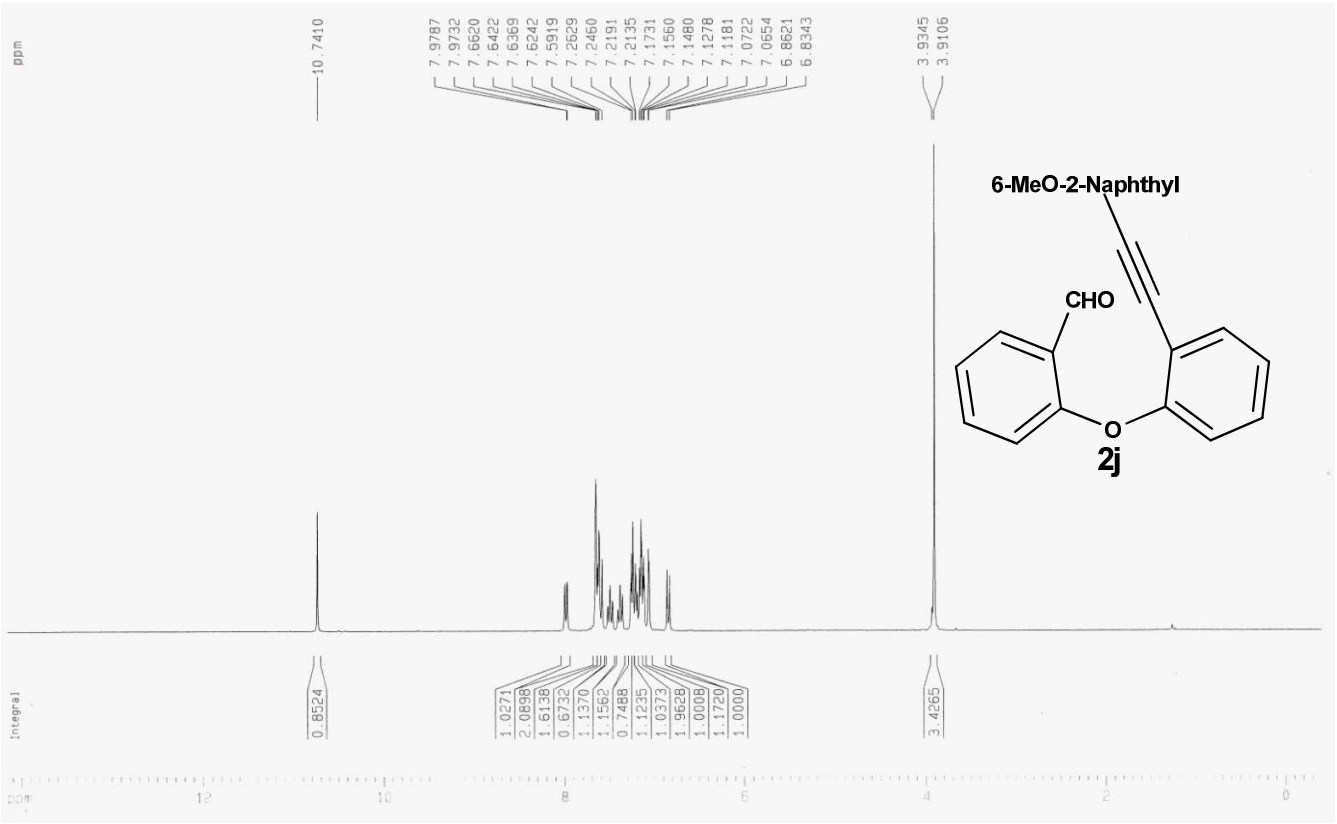
^{1}H NMR, $CDCl_3$, 300 MHz



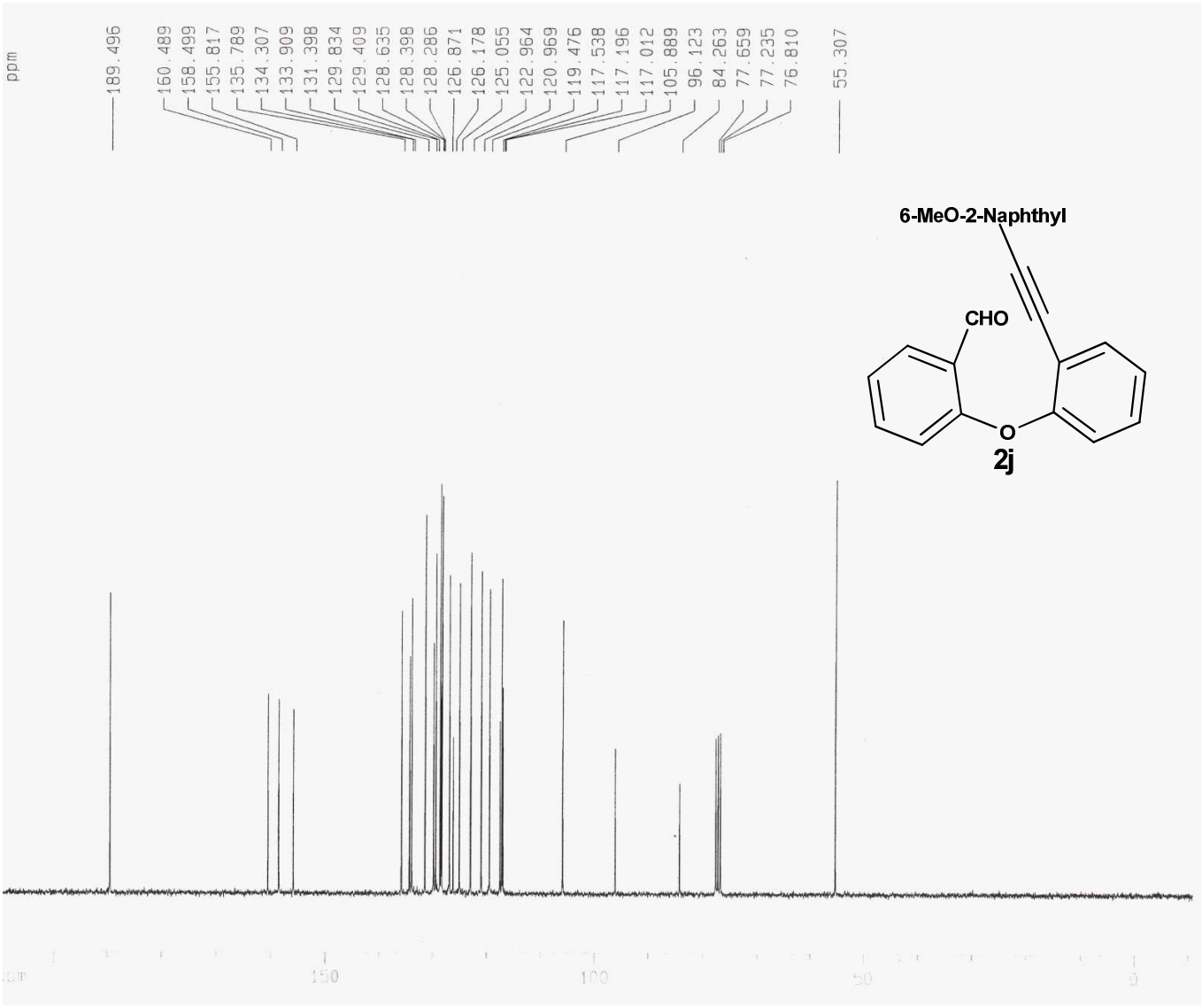
^{13}C NMR, $CDCl_3$, 75 MHz



^{1}H NMR, $CDCl_3$, 300 MHz

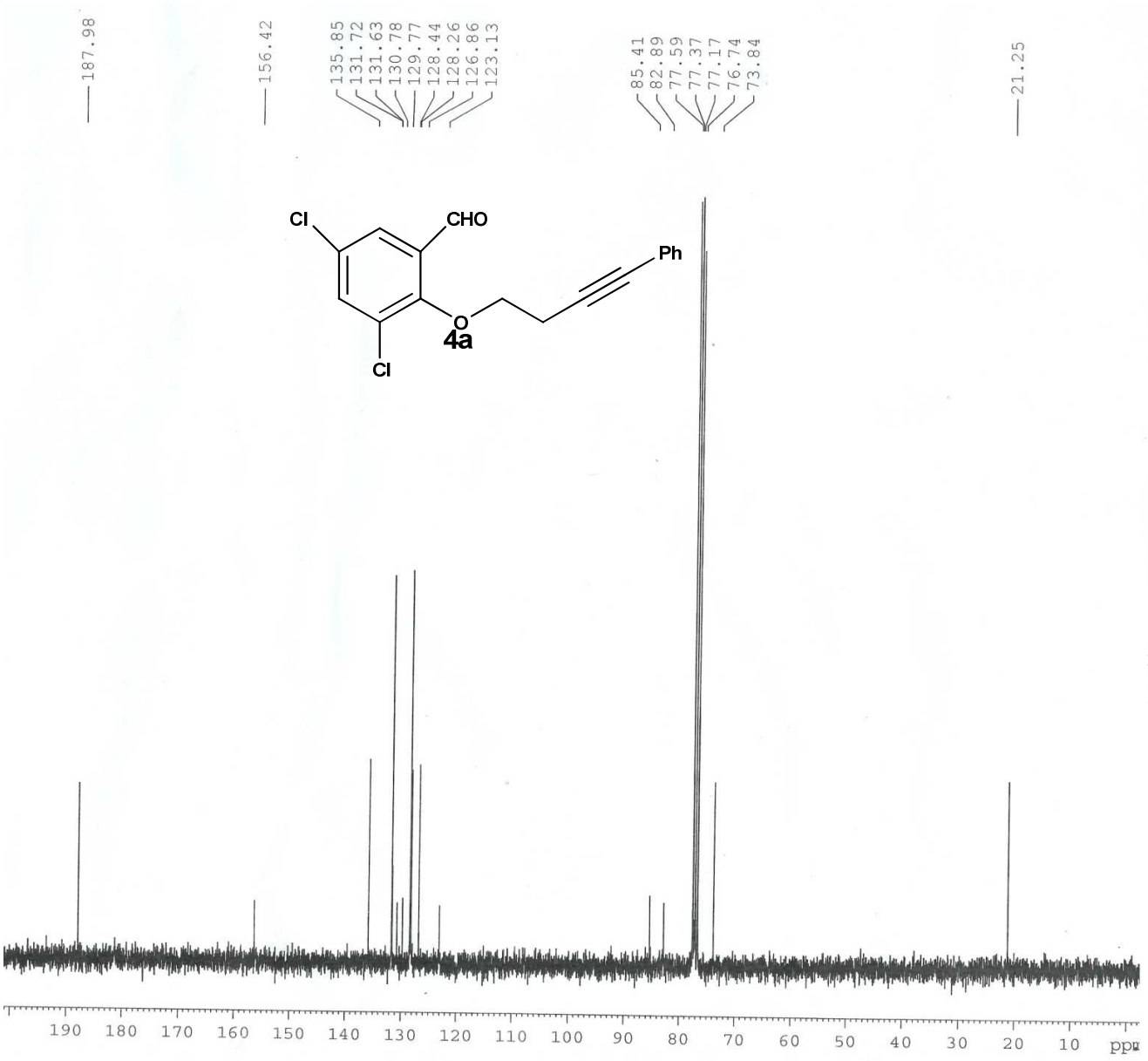


^{13}C NMR, $CDCl_3$, 75 MHz

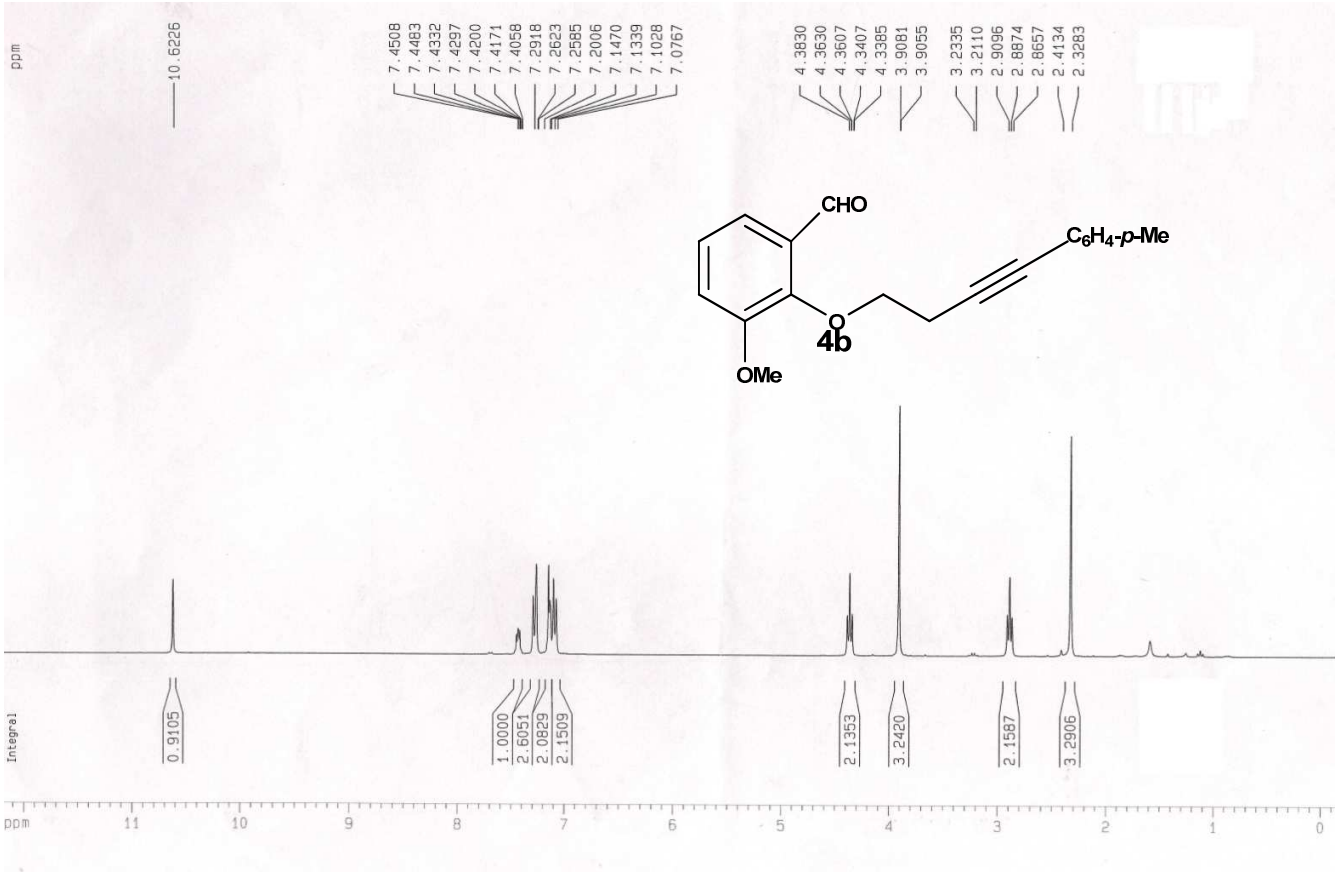


^{1}H NMR, $CDCl_3$, 300 MHz

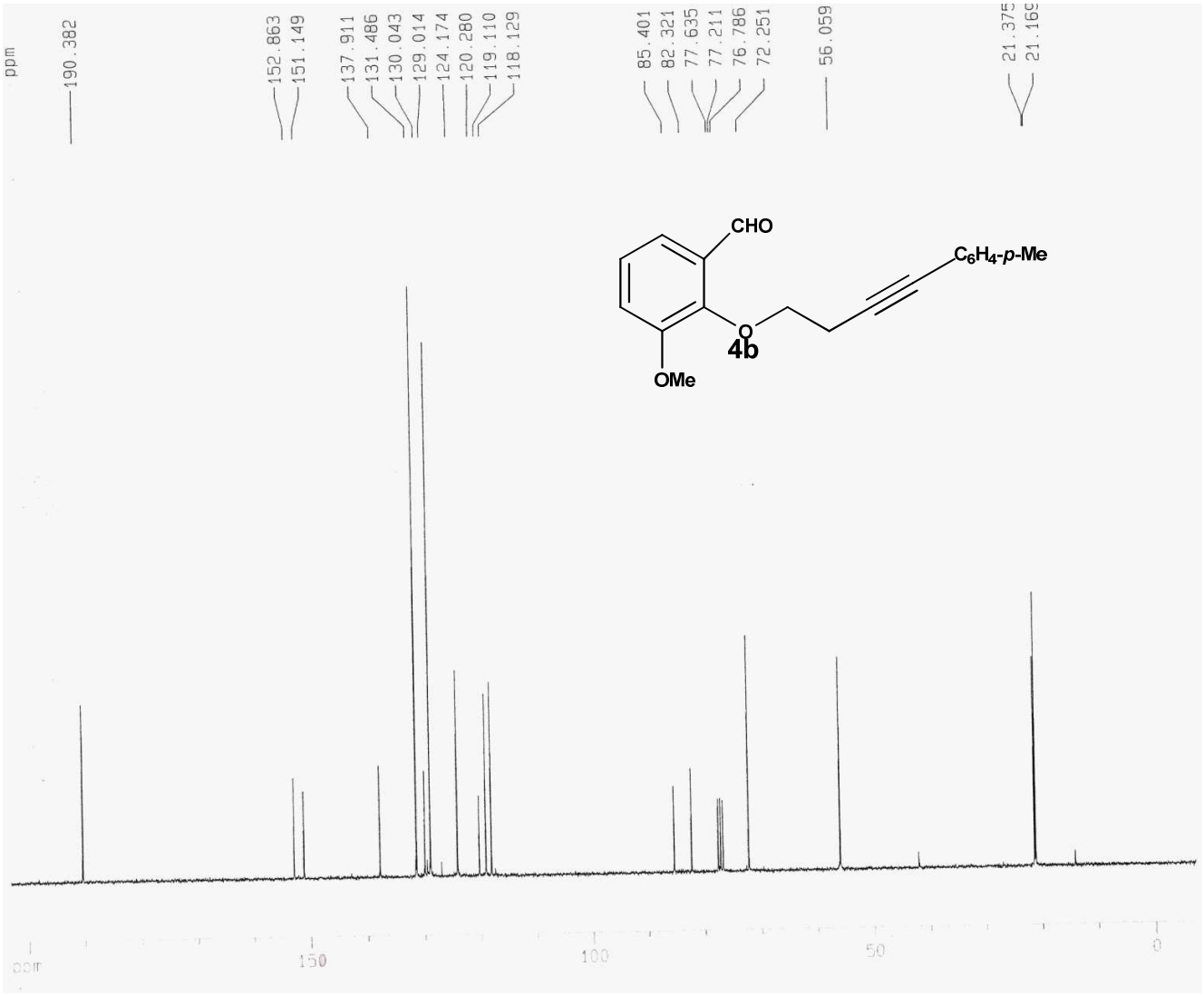
^{13}C NMR, $CDCl_3$, 75 MHz



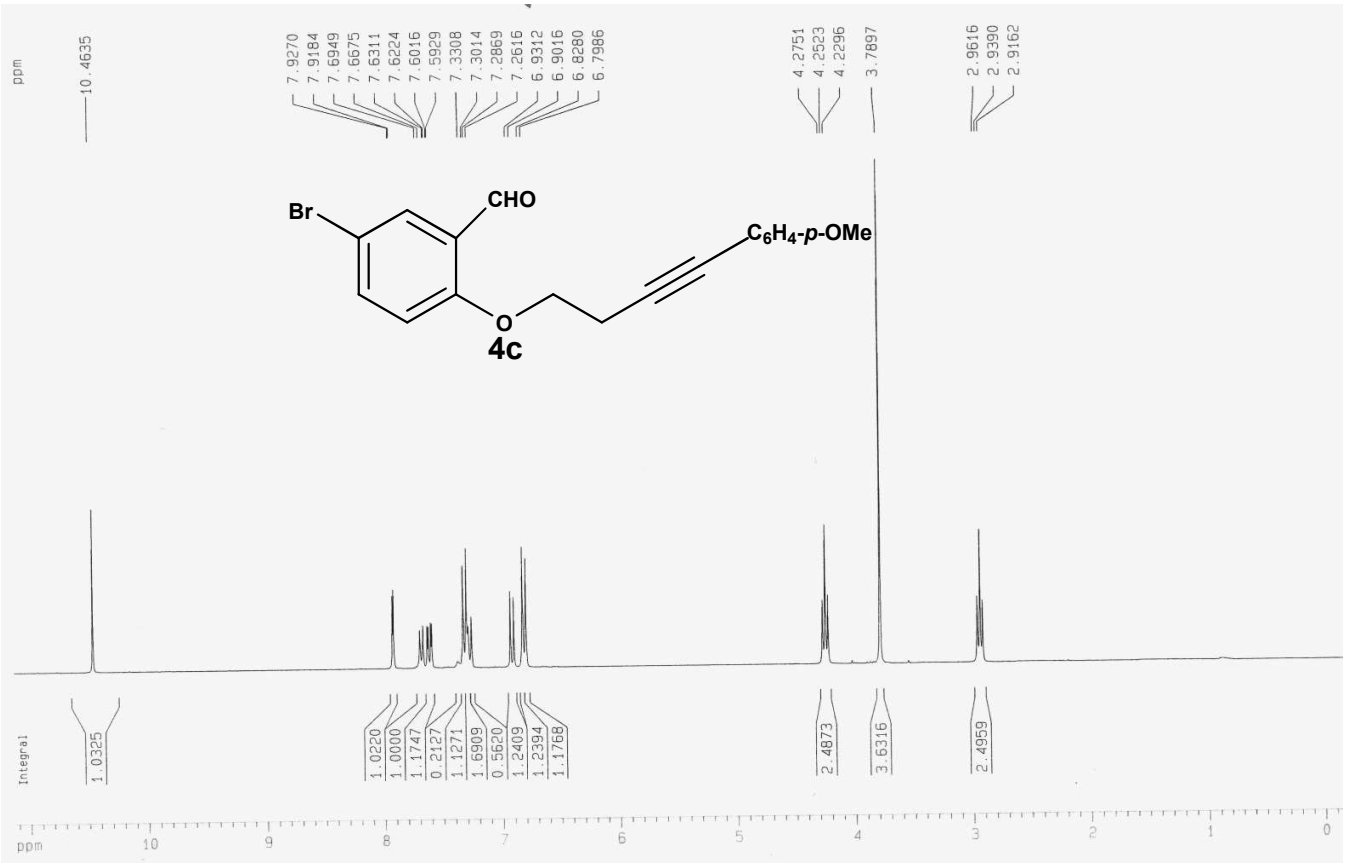
^{1}H NMR, $CDCl_3$, 300 MHz



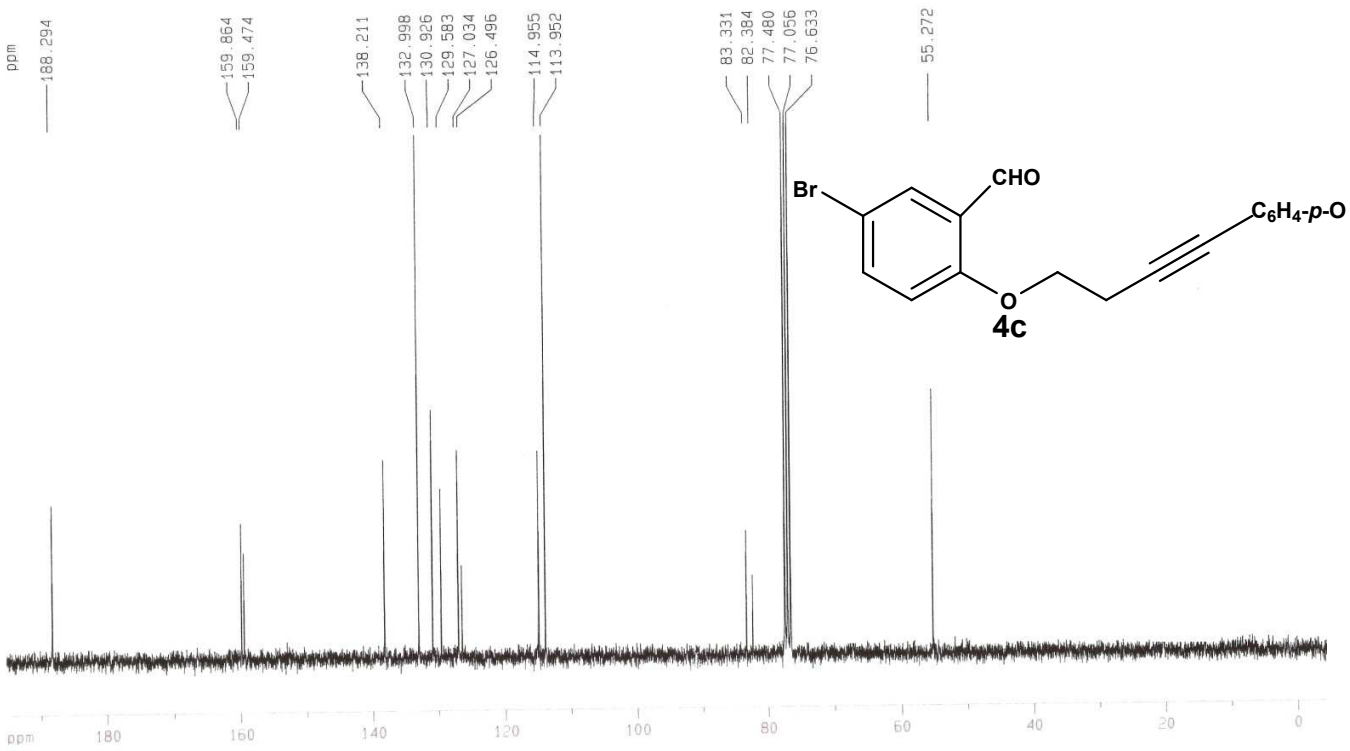
^{13}C NMR, $CDCl_3$, 75 MHz



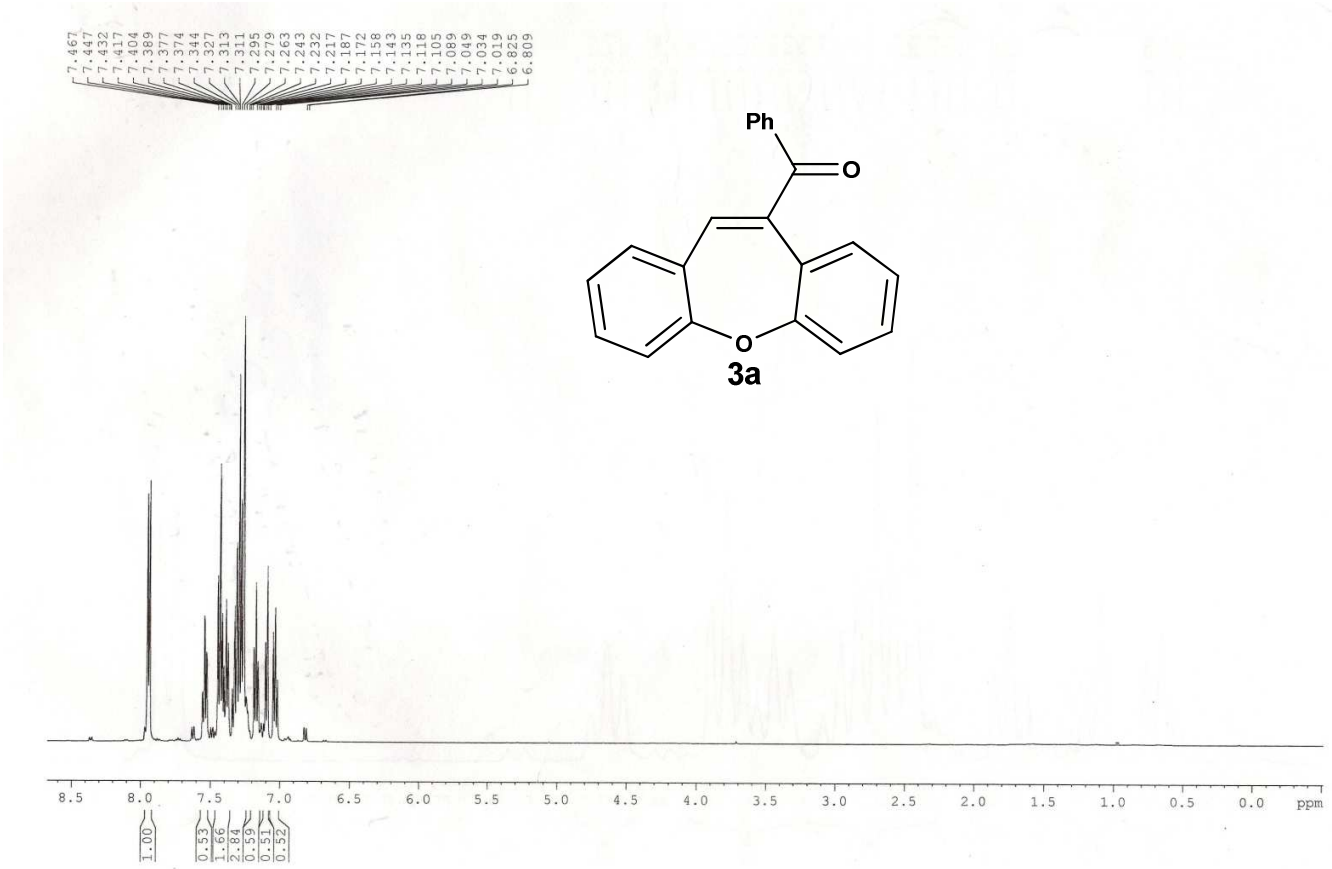
^{1}H NMR, $CDCl_3$, 300 MHz



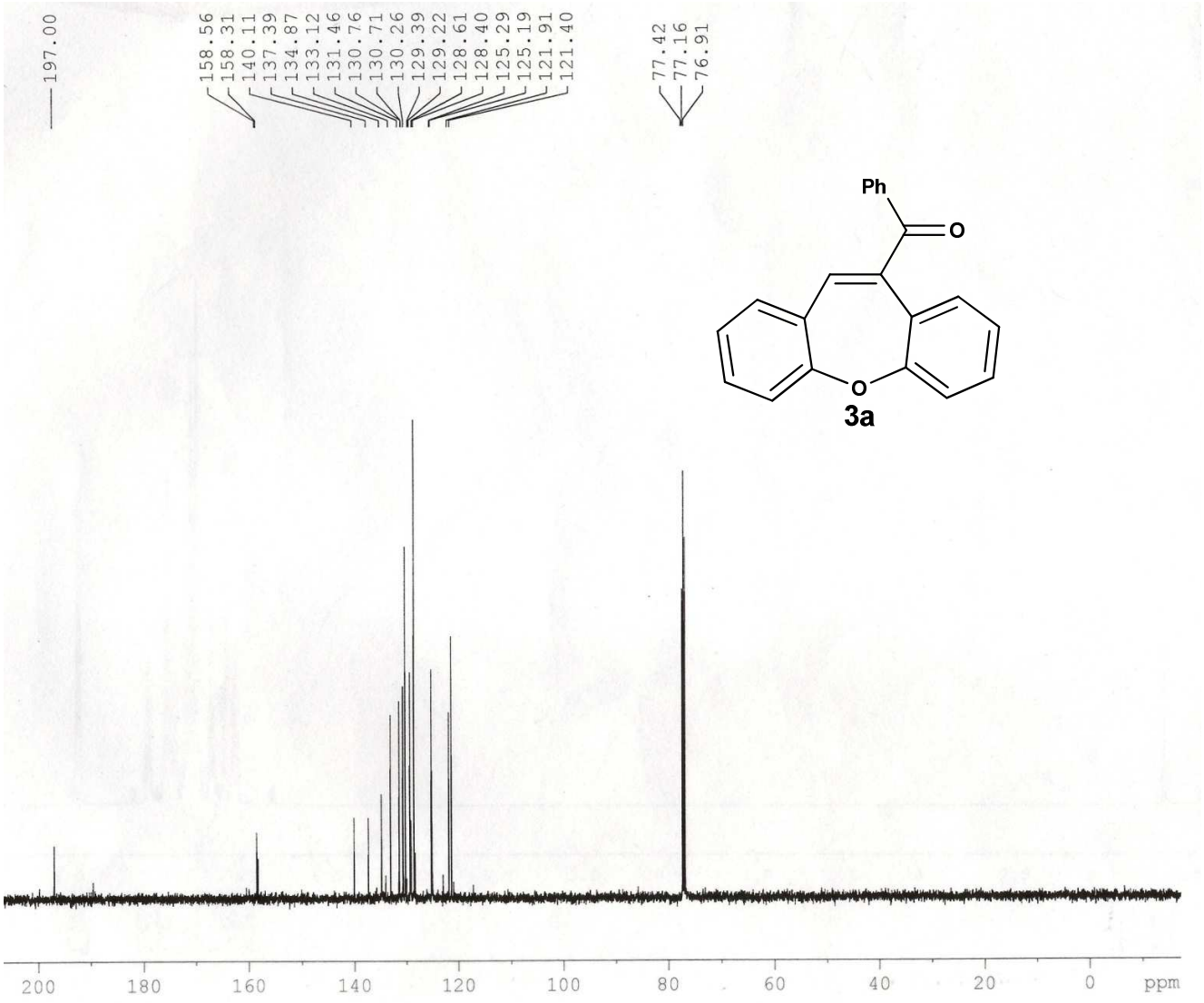
^{13}C NMR, $CDCl_3$, 75 MHz



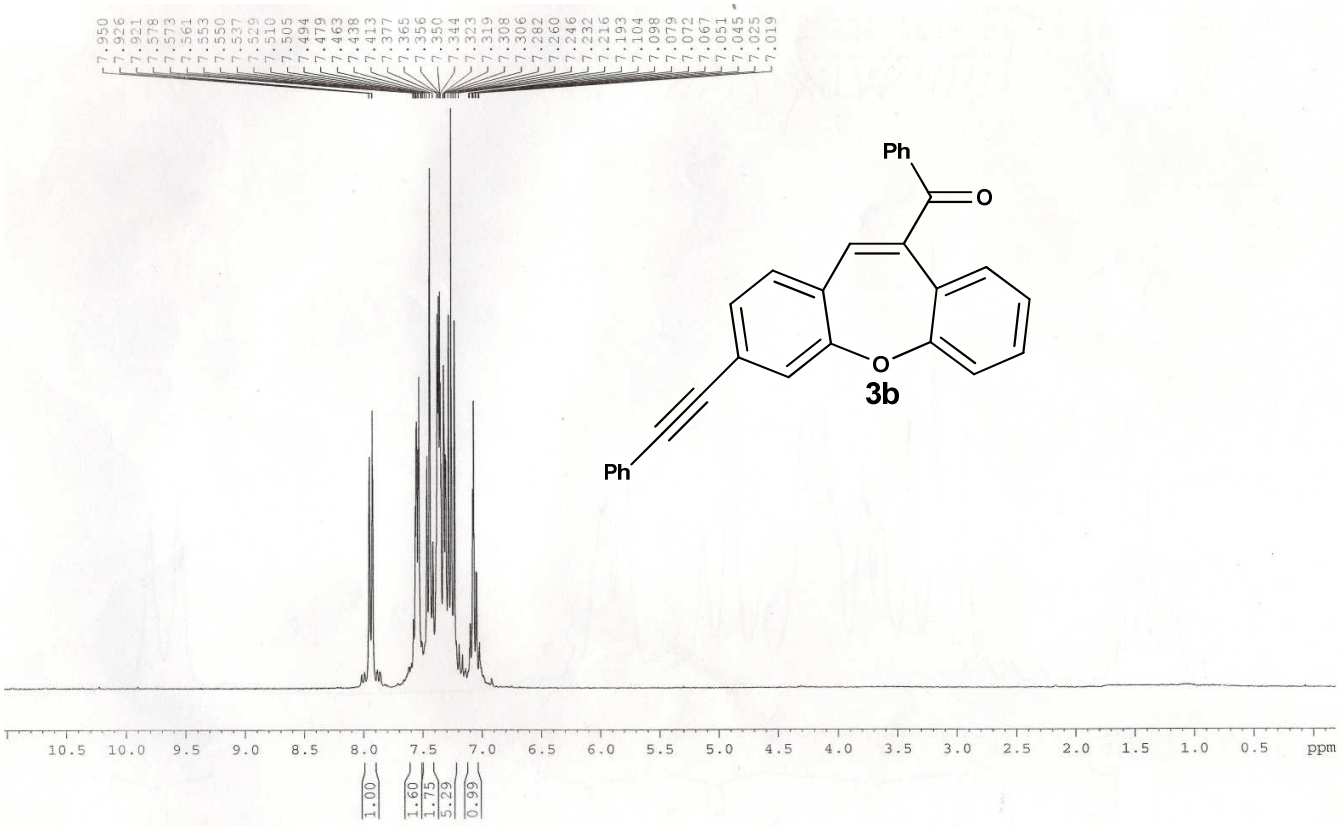
^{1}H NMR, $CDCl_3$, 500 MHz



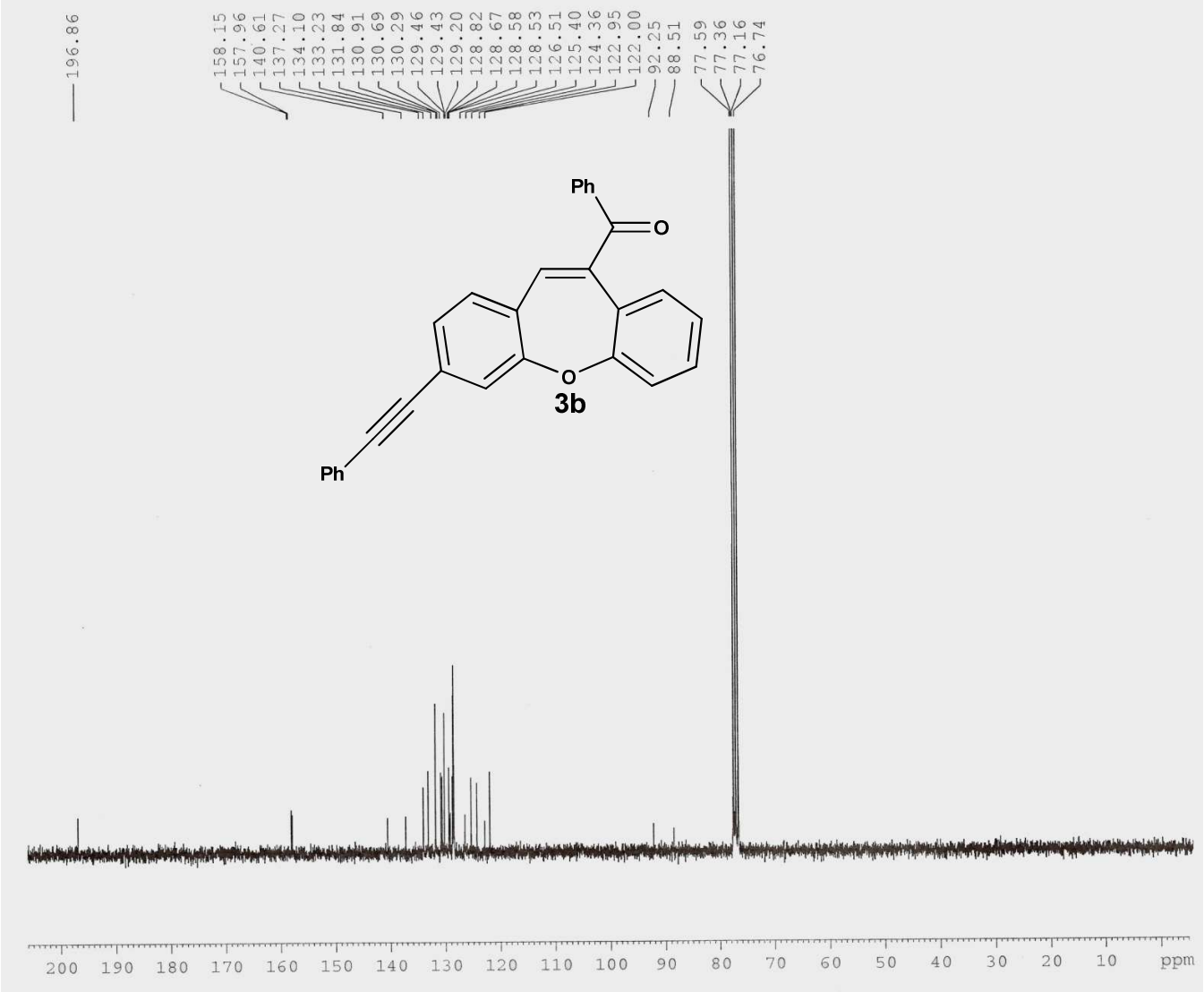
^{13}C NMR, $CDCl_3$, 125 MHz



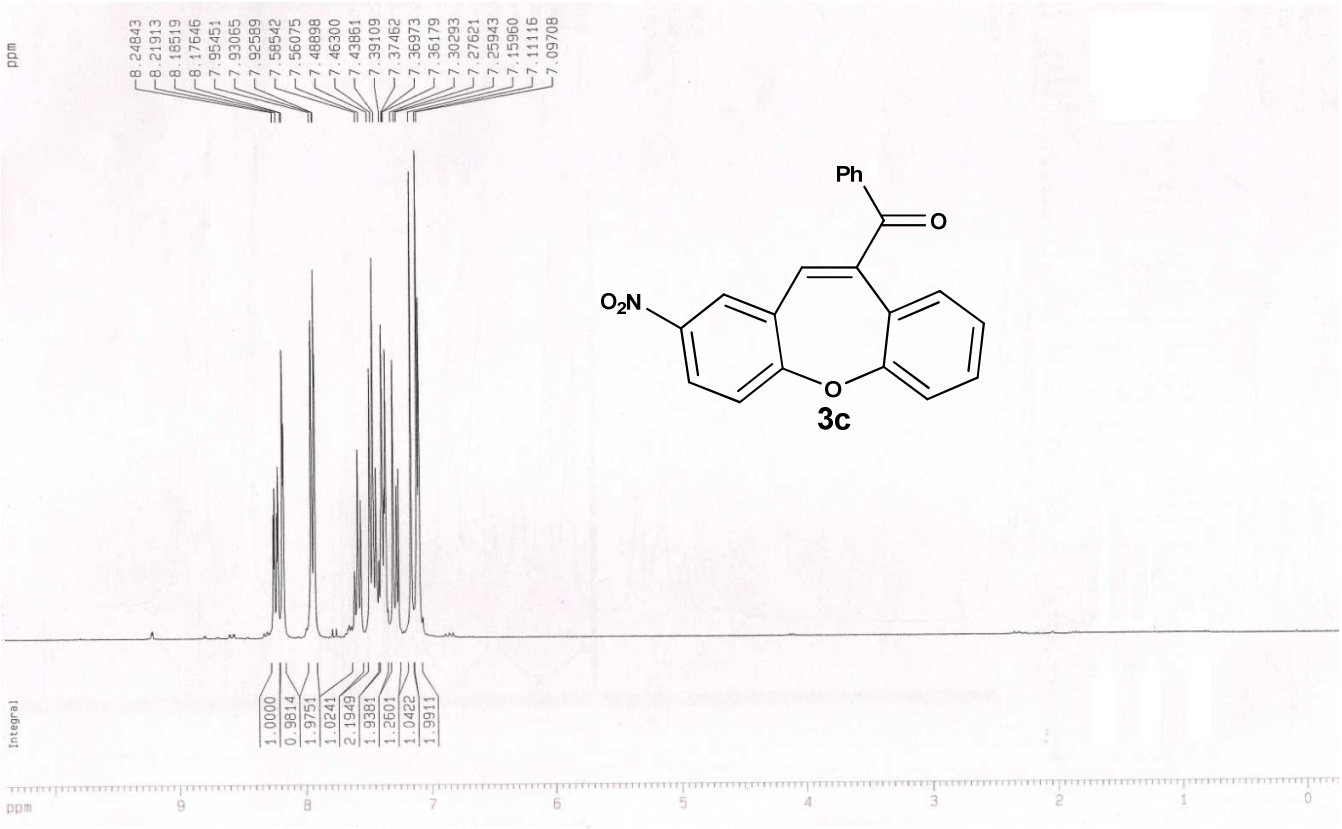
^{1}H NMR, $CDCl_3$, 300 MHz



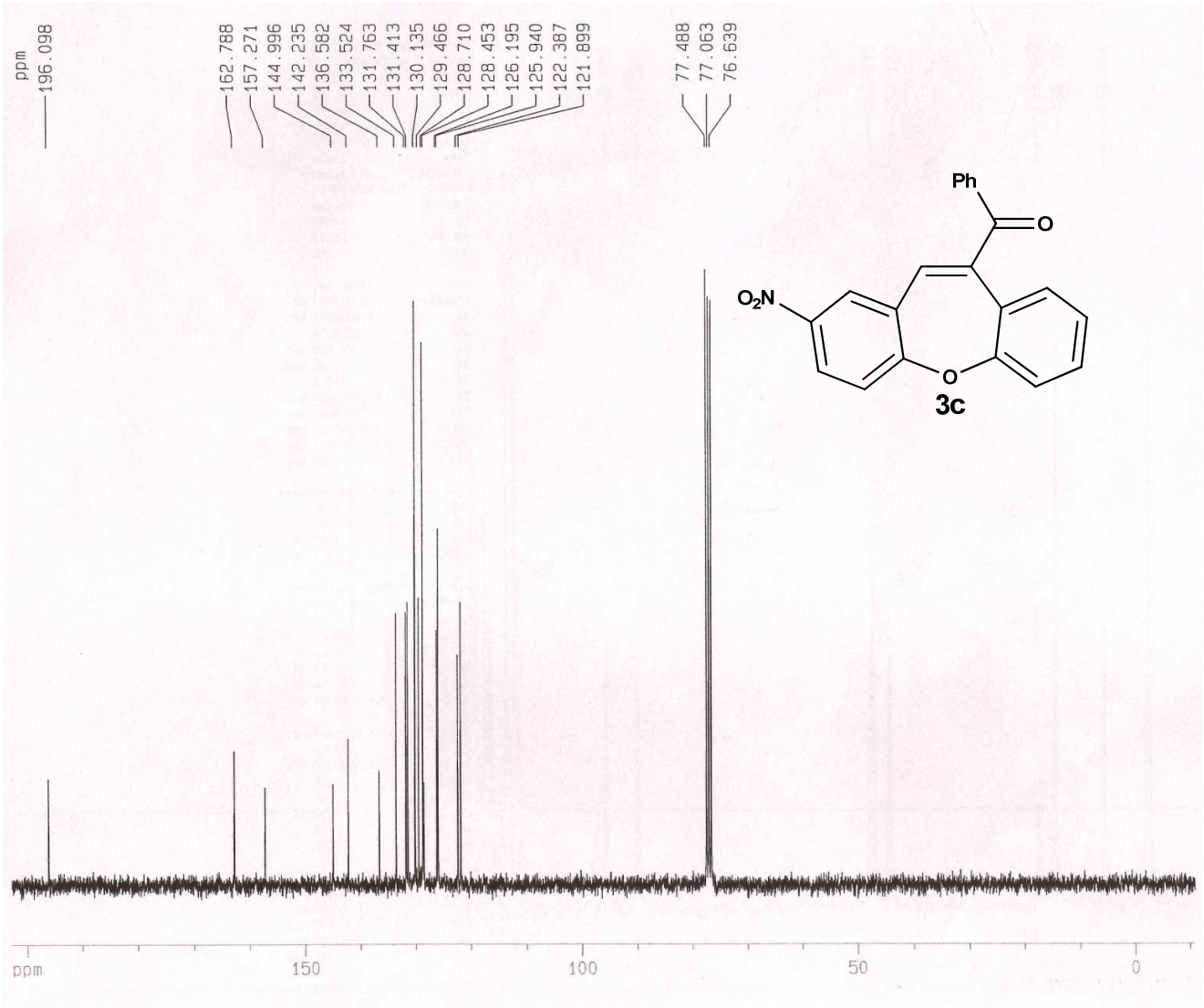
^{13}C NMR, $CDCl_3$, 75 MHz



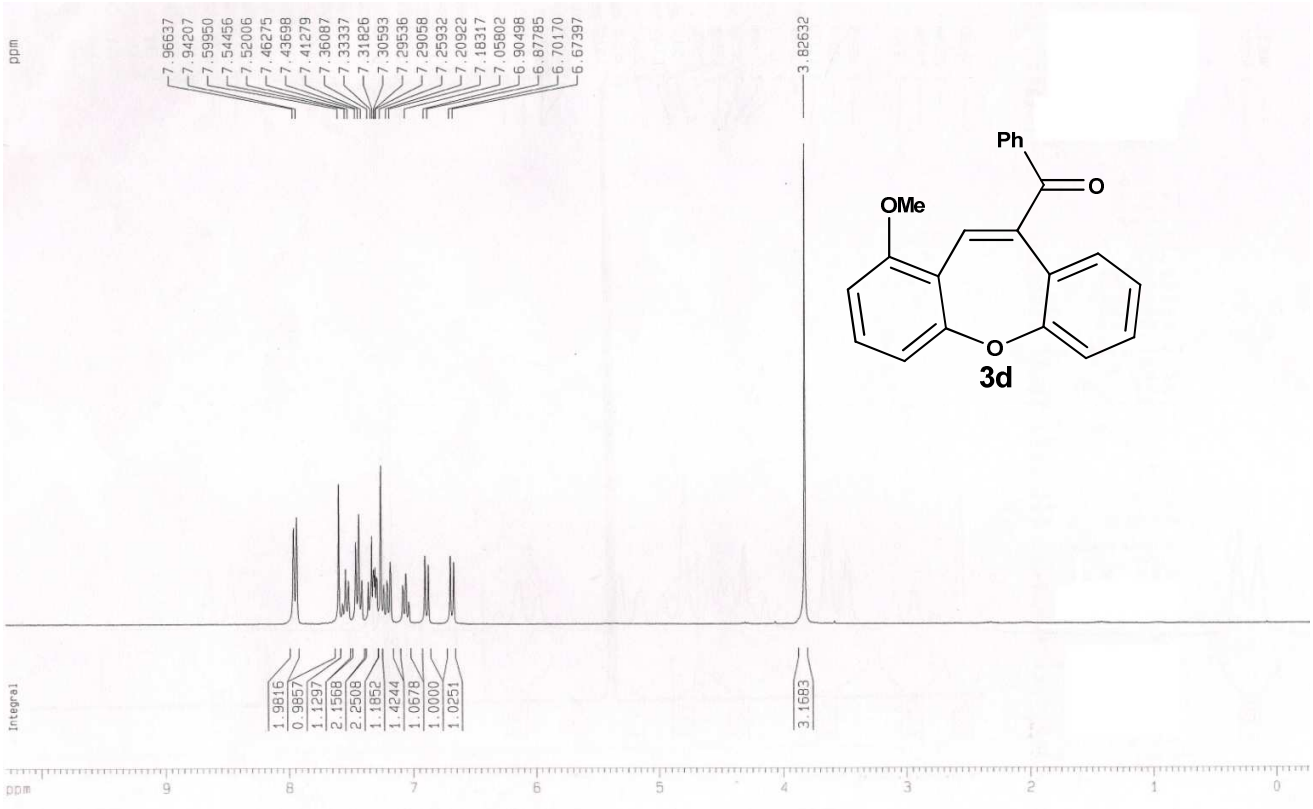
^{1}H NMR, $CDCl_3$, 300 MHz



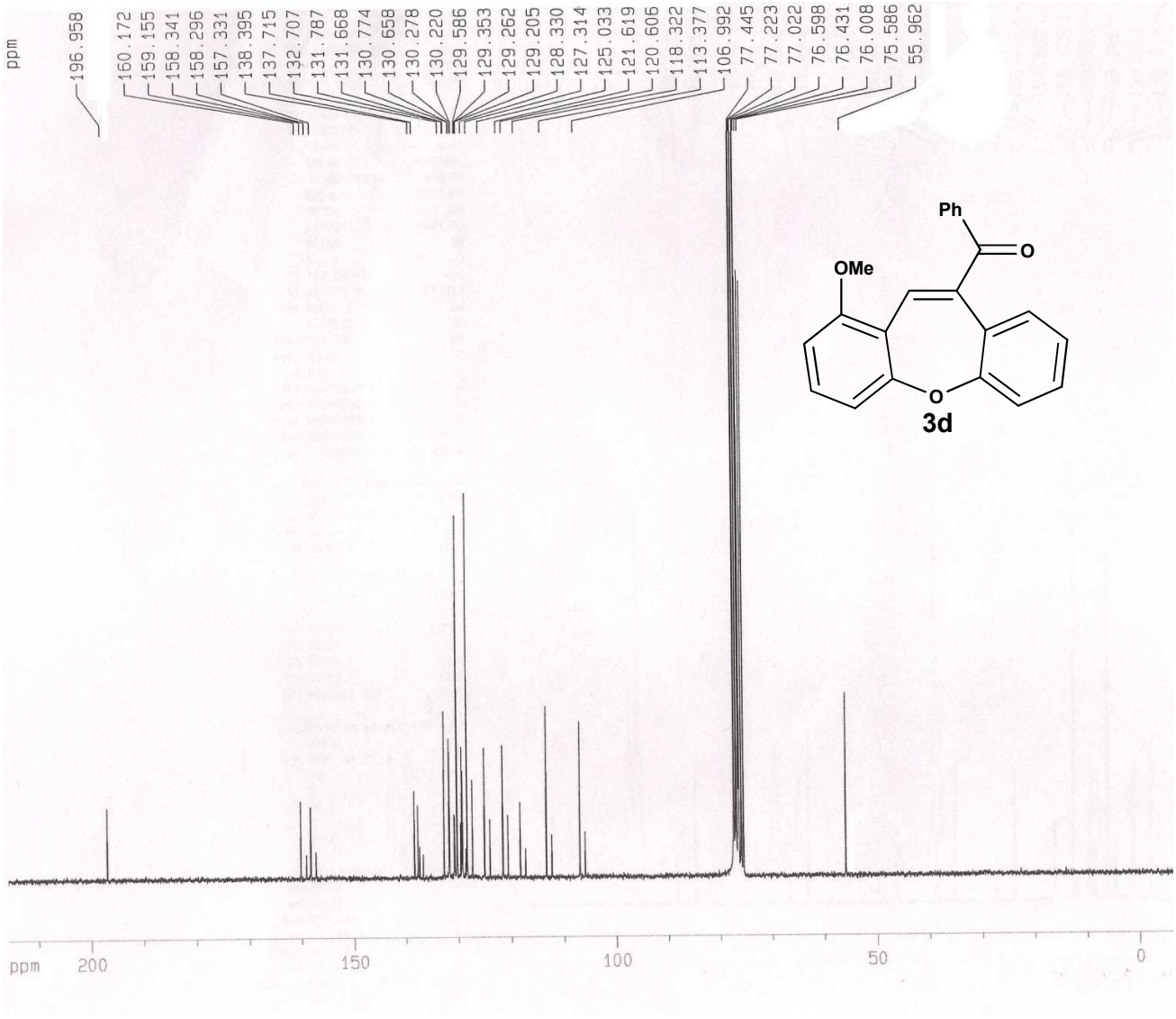
^{13}C NMR, $CDCl_3$, 75 MHz



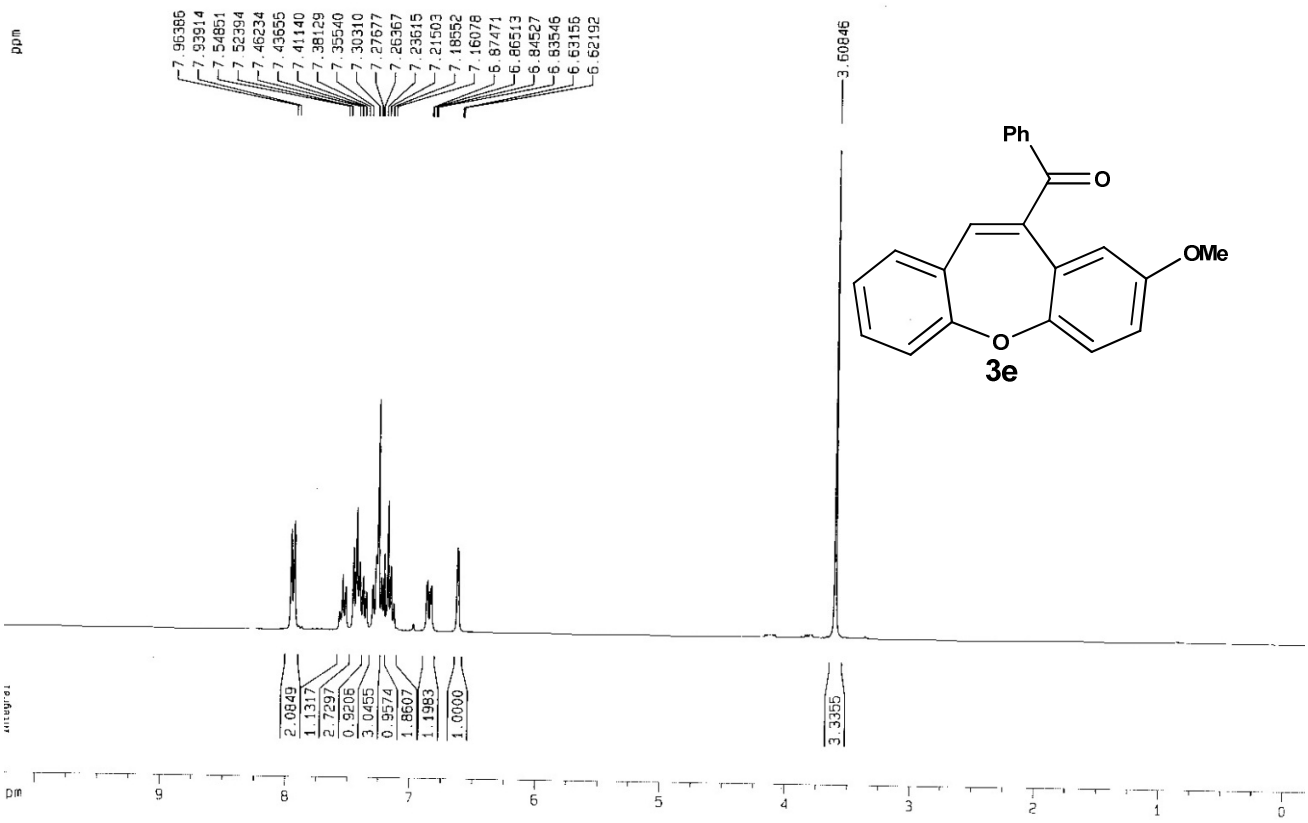
^{1}H NMR, $CDCl_3$, 300 MHz



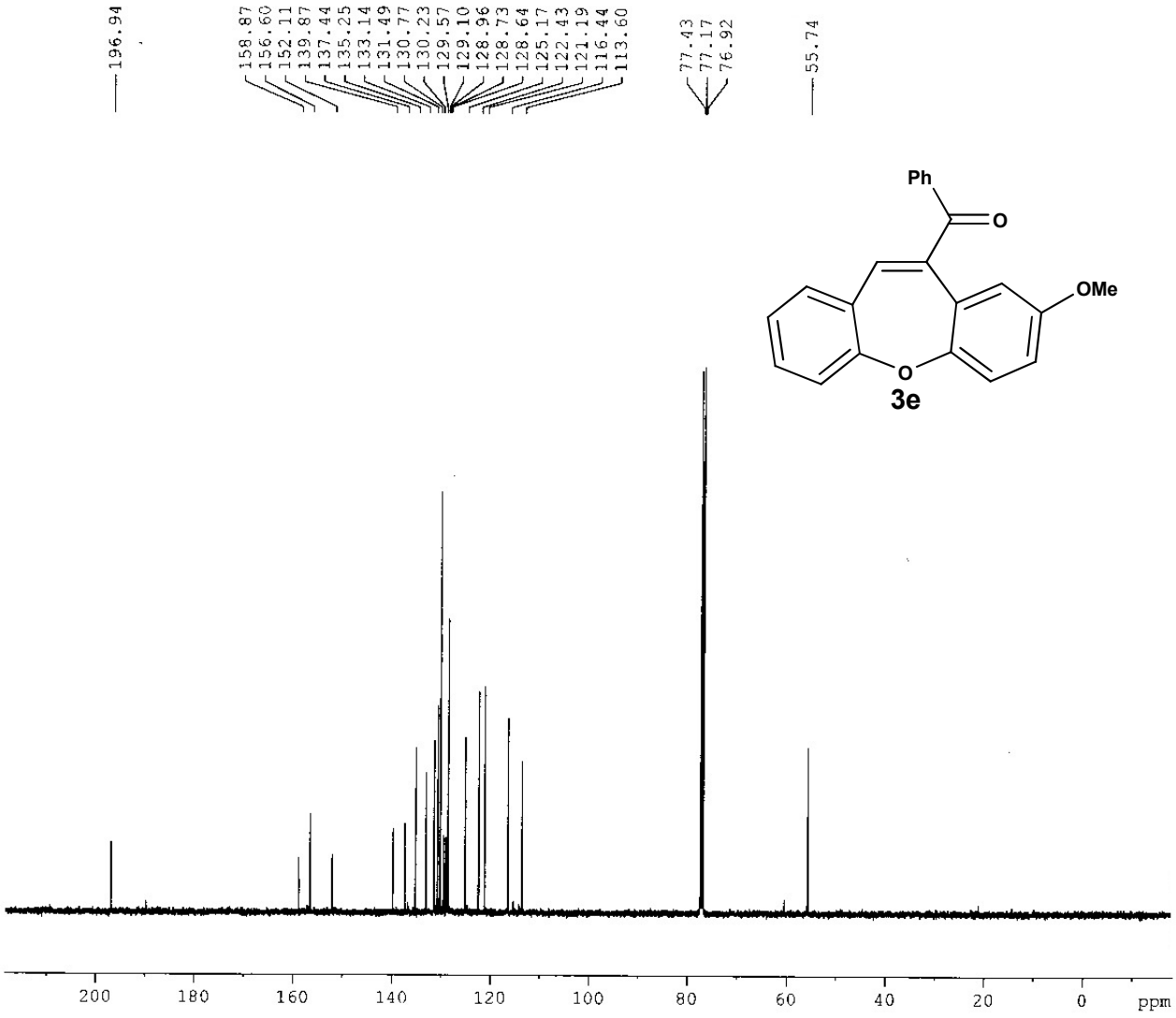
^{13}C NMR, $CDCl_3$, 75 MHz



^{1}H NMR, $CDCl_3$, 300 MHz

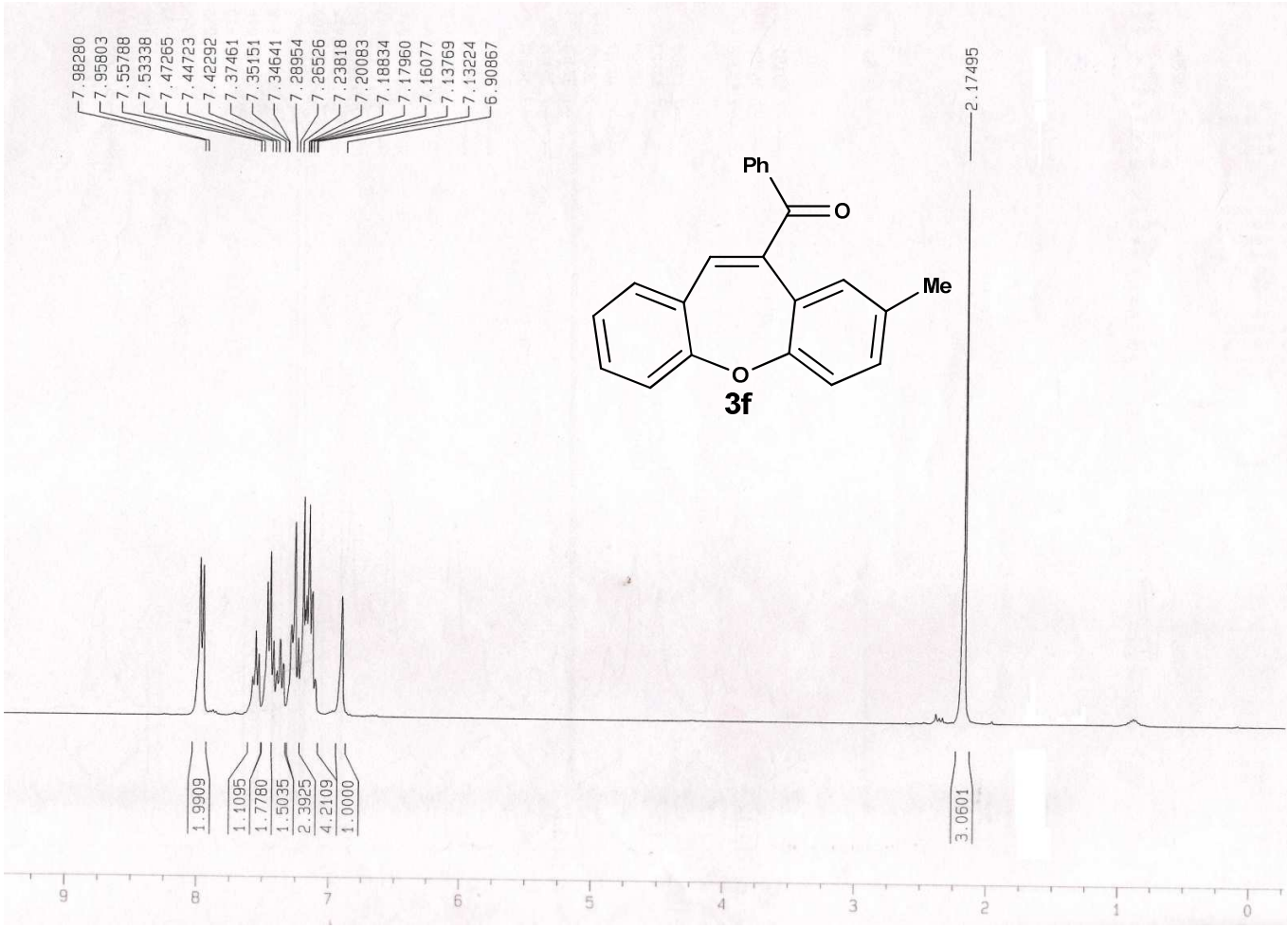


^{13}C NMR, $CDCl_3$, 75 MHz

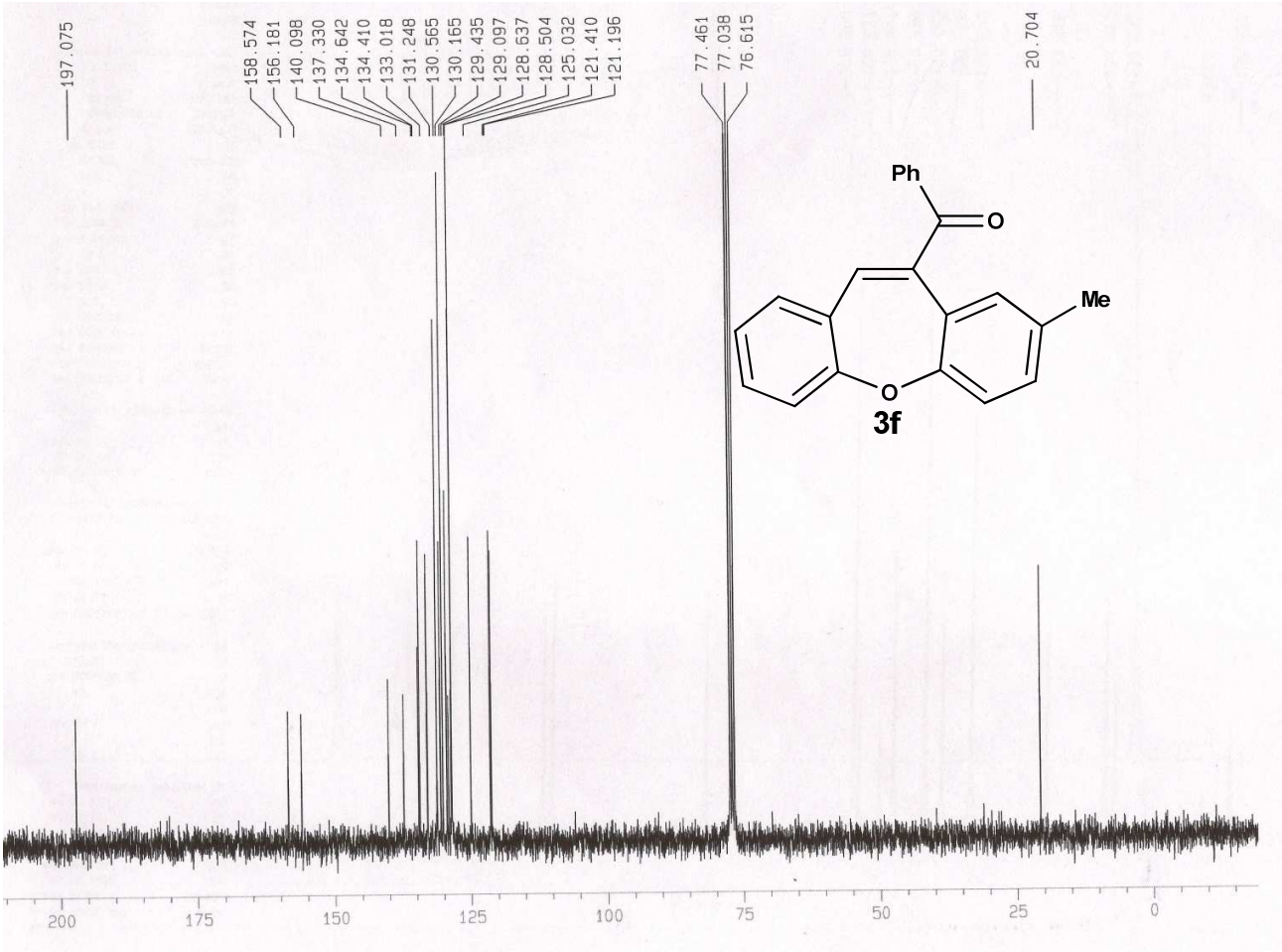


3e

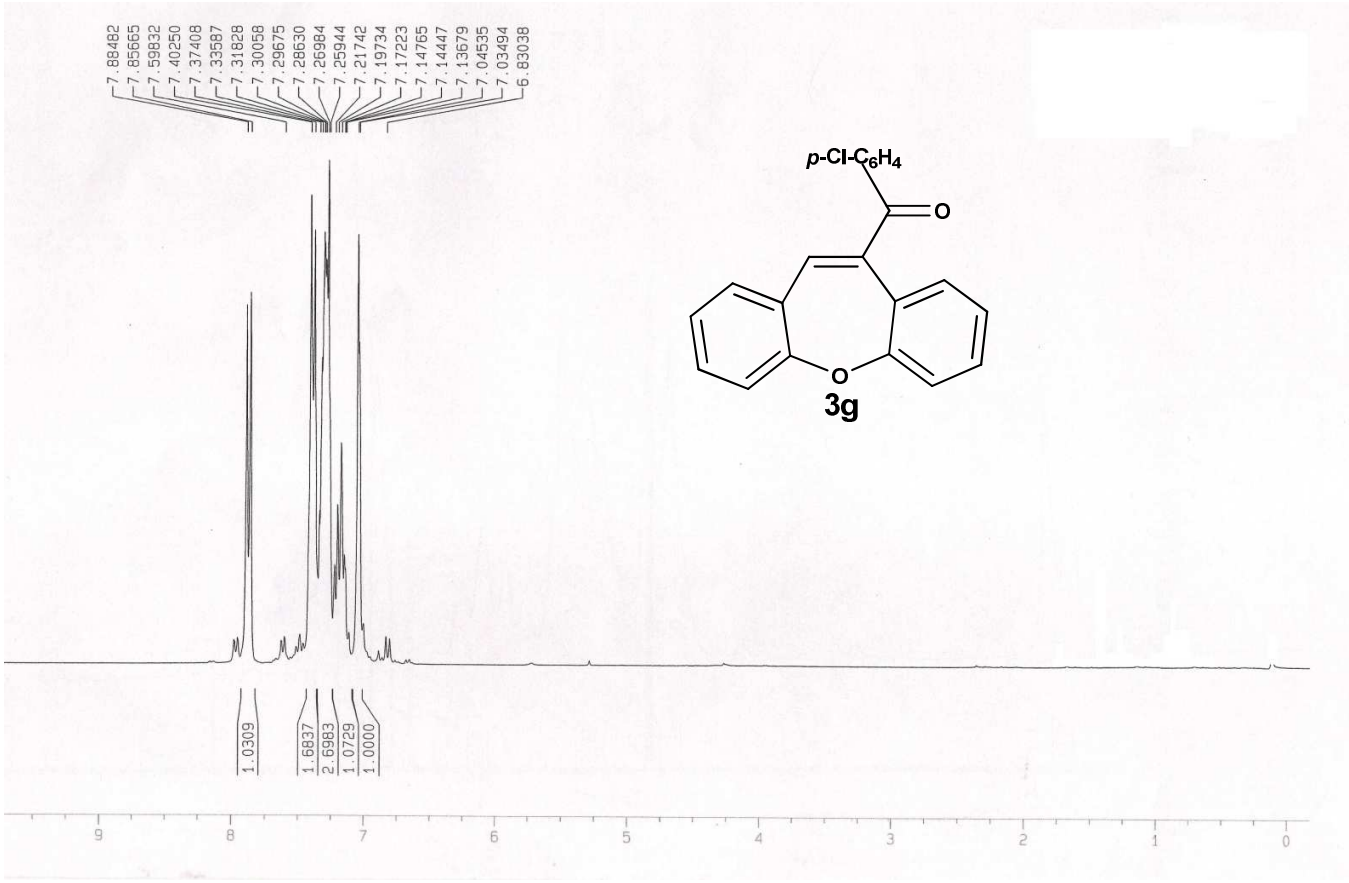
^{1}H NMR, $CDCl_3$, 300 MHz



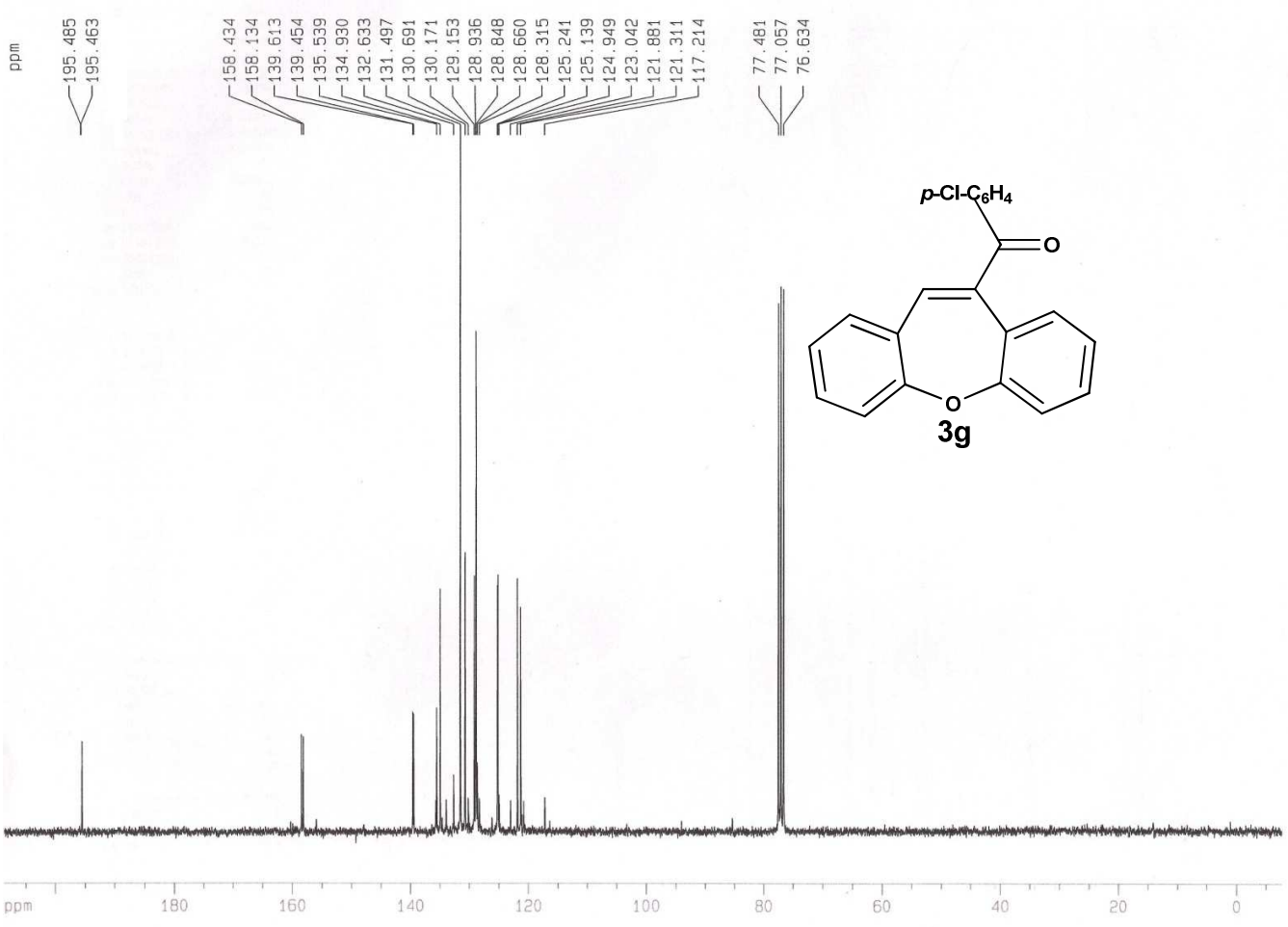
^{13}C NMR, $CDCl_3$, 75 MHz



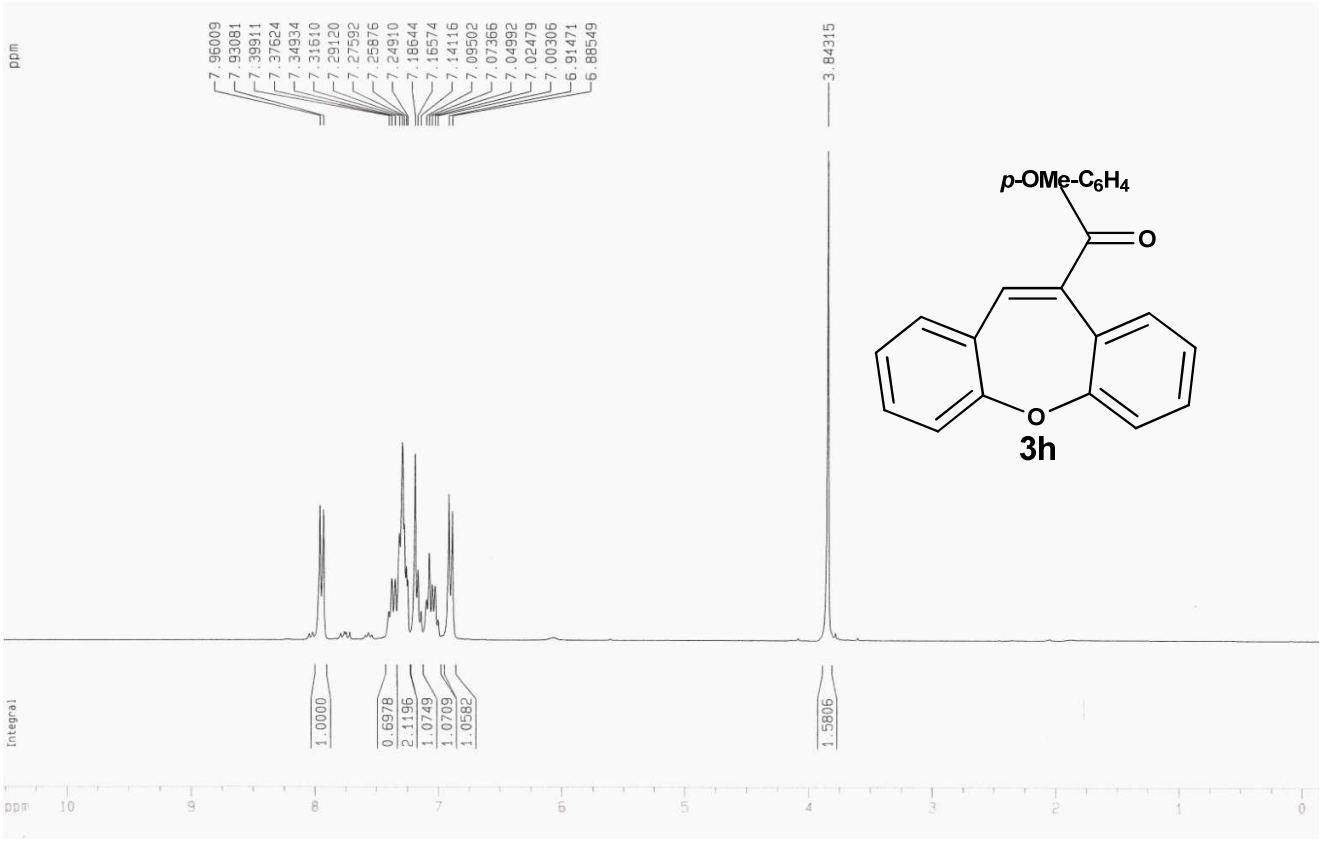
^{1}H NMR, $CDCl_3$, 300 MHz



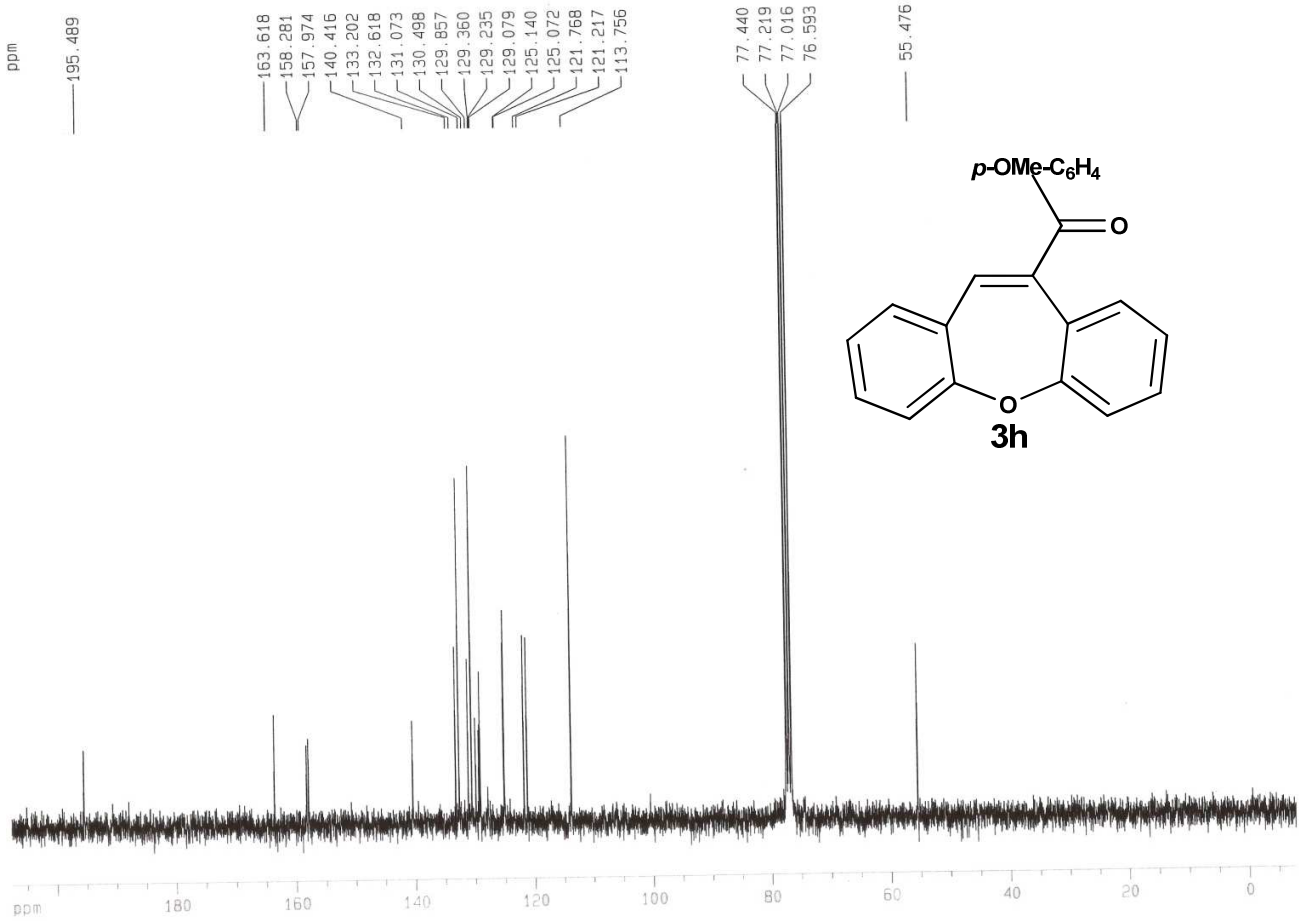
^{13}C NMR, $CDCl_3$, 75 MHz



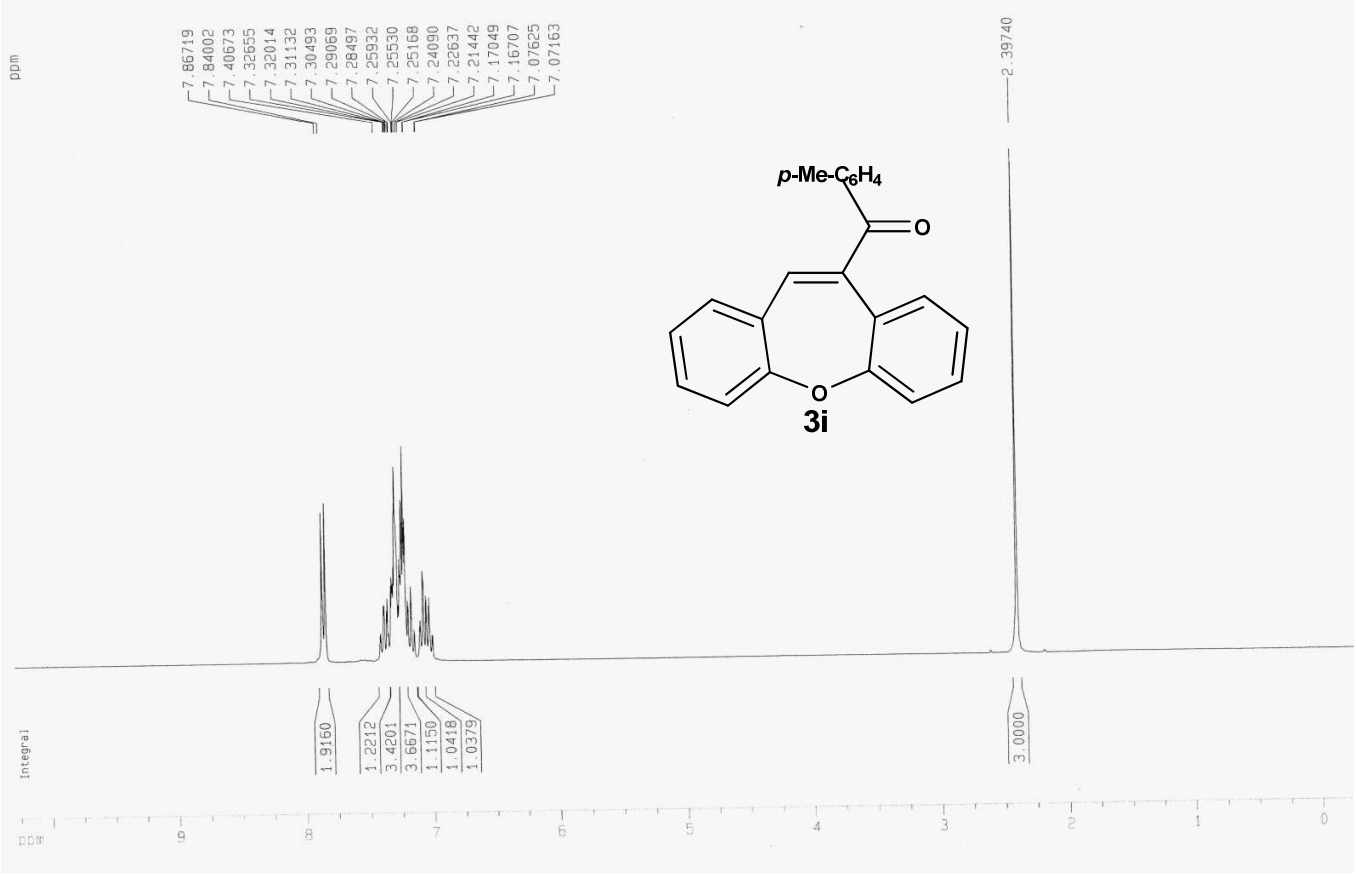
^{1}H NMR, $CDCl_3$, 300 MHz



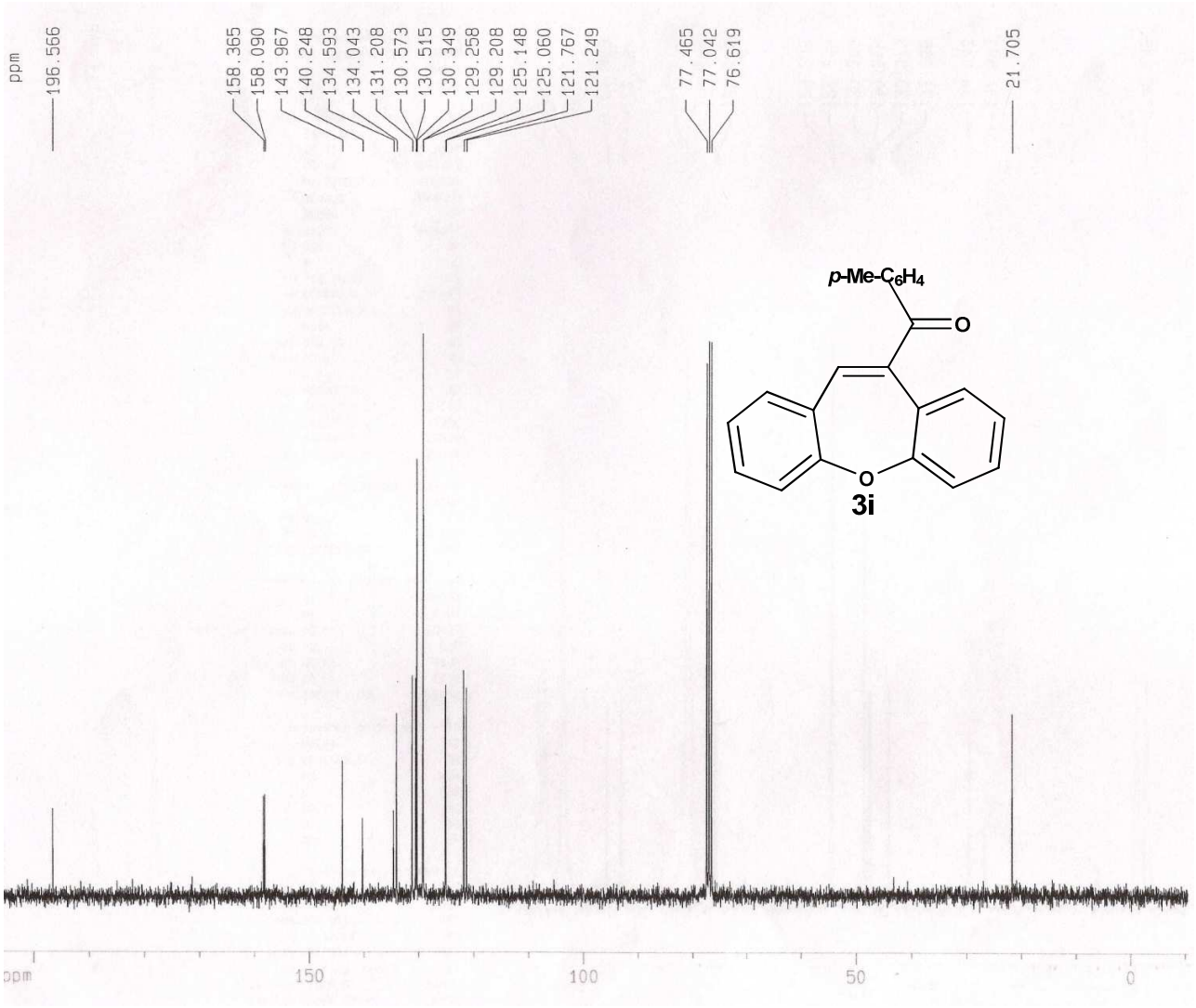
^{13}C NMR, $CDCl_3$, 75 MHz



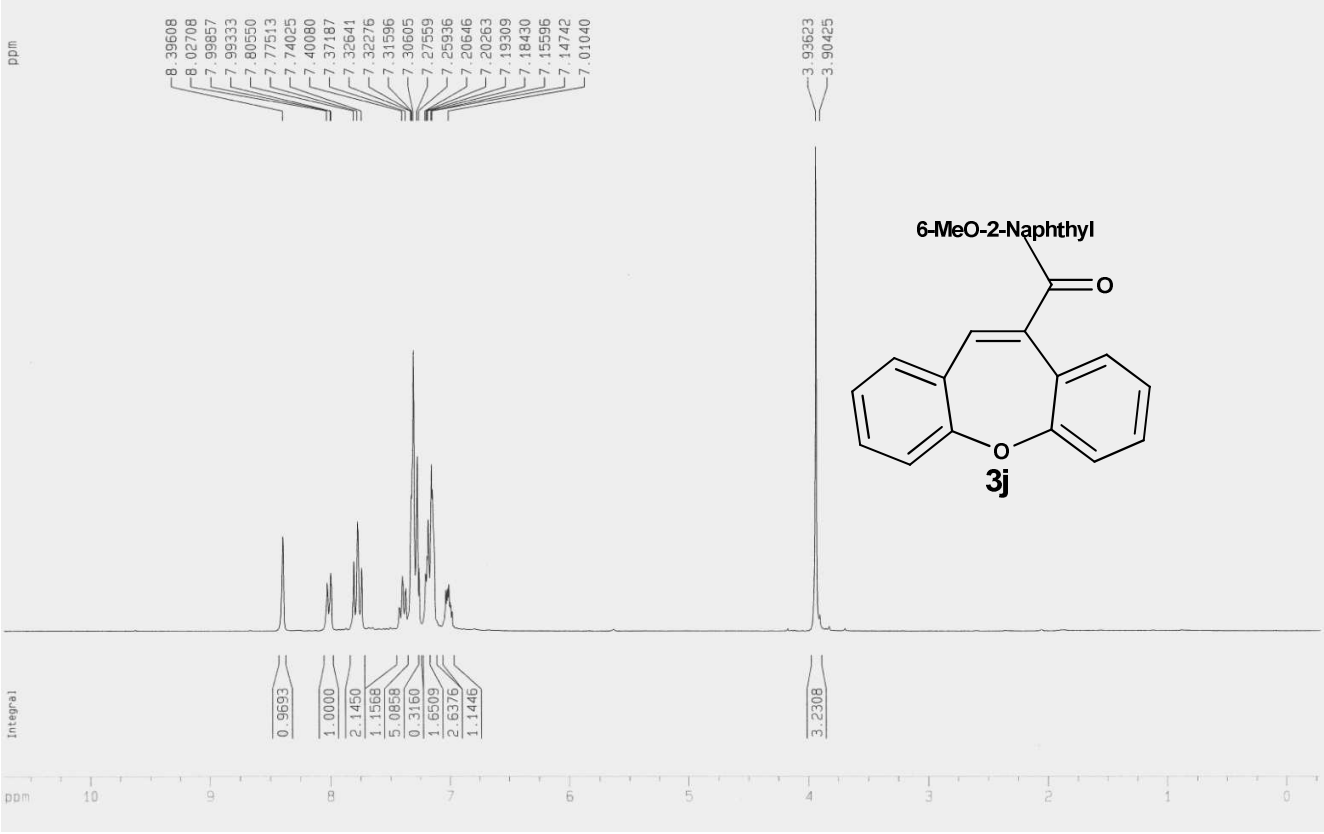
^{1}H NMR, $CDCl_3$, 300 MHz



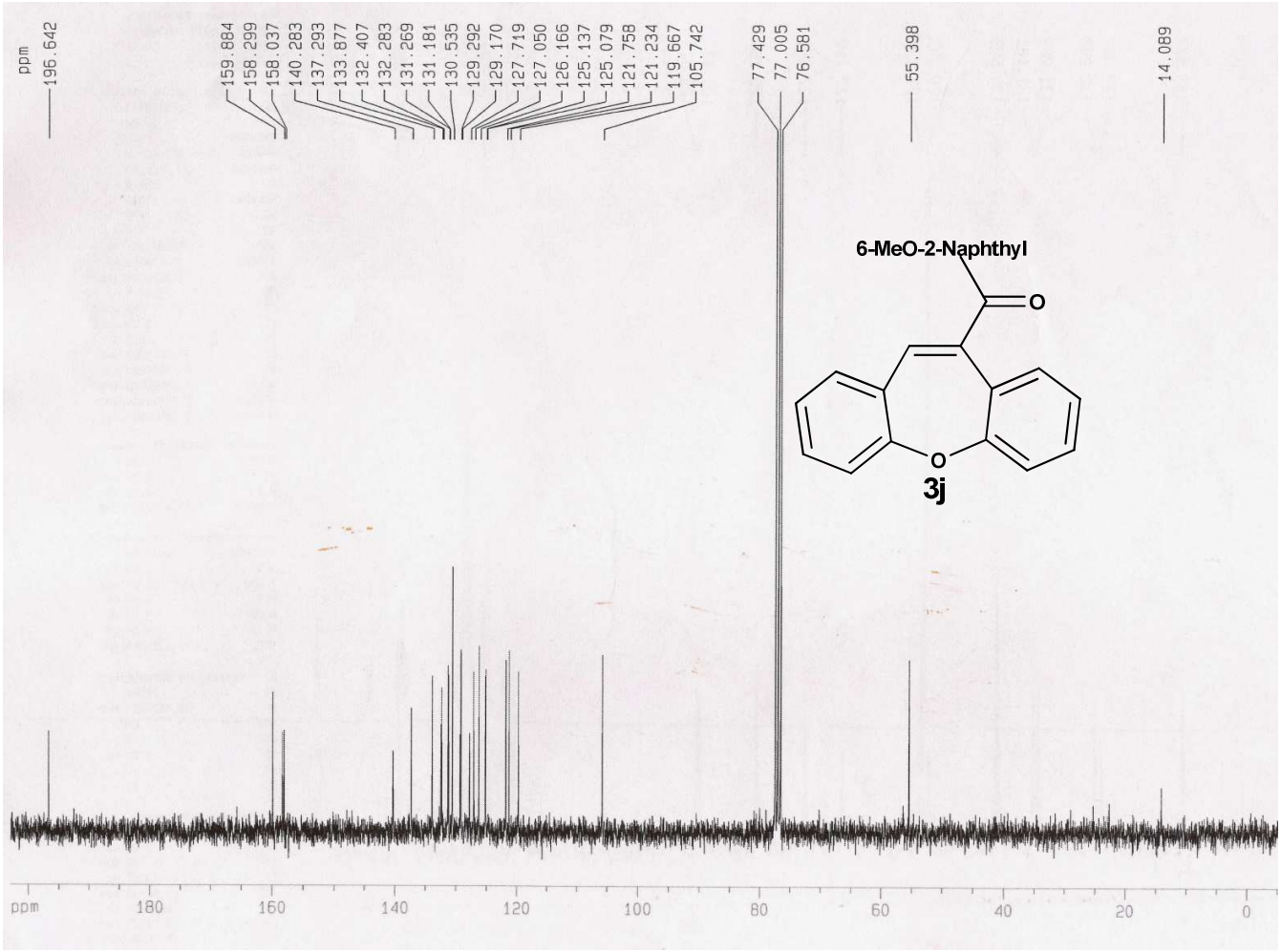
^{13}C NMR, $CDCl_3$, 75 MHz



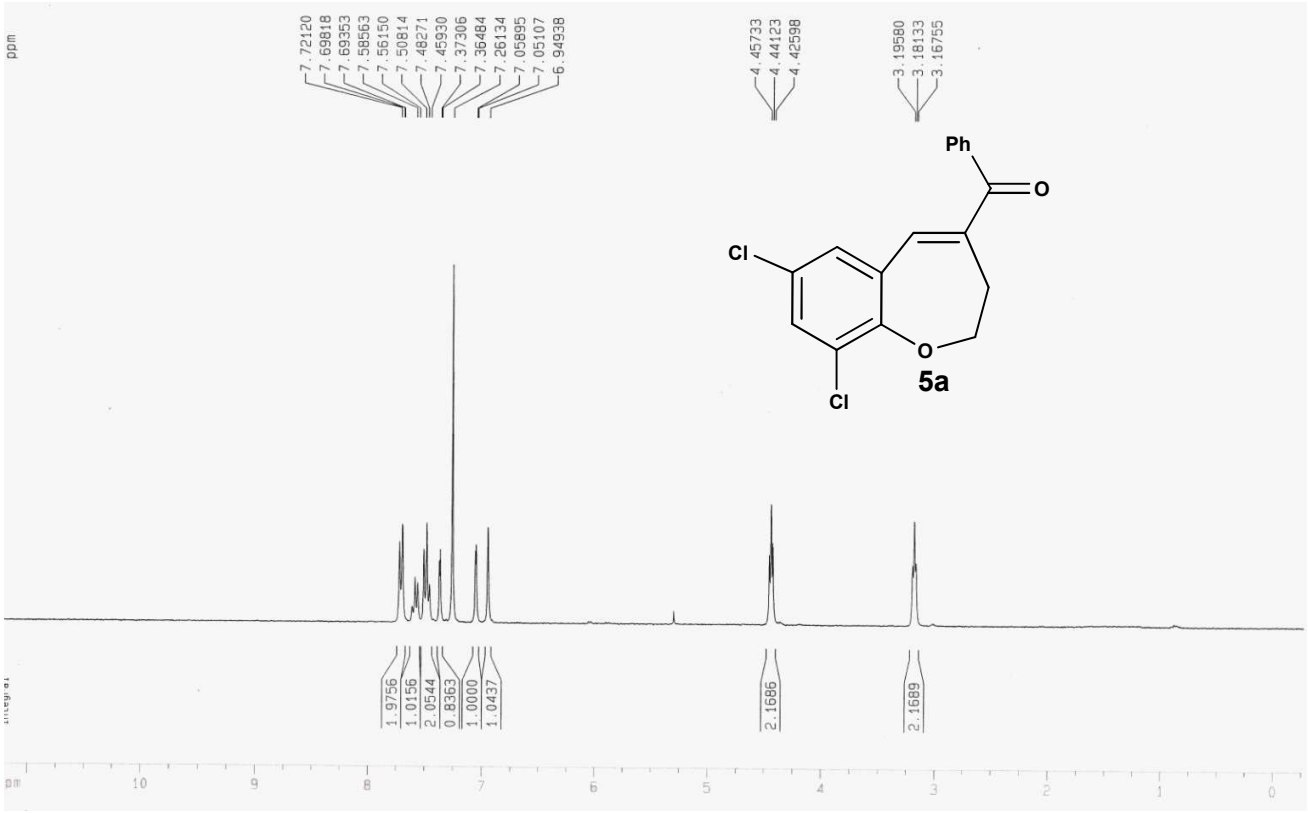
^{1}H NMR, $CDCl_3$, 300 MHz



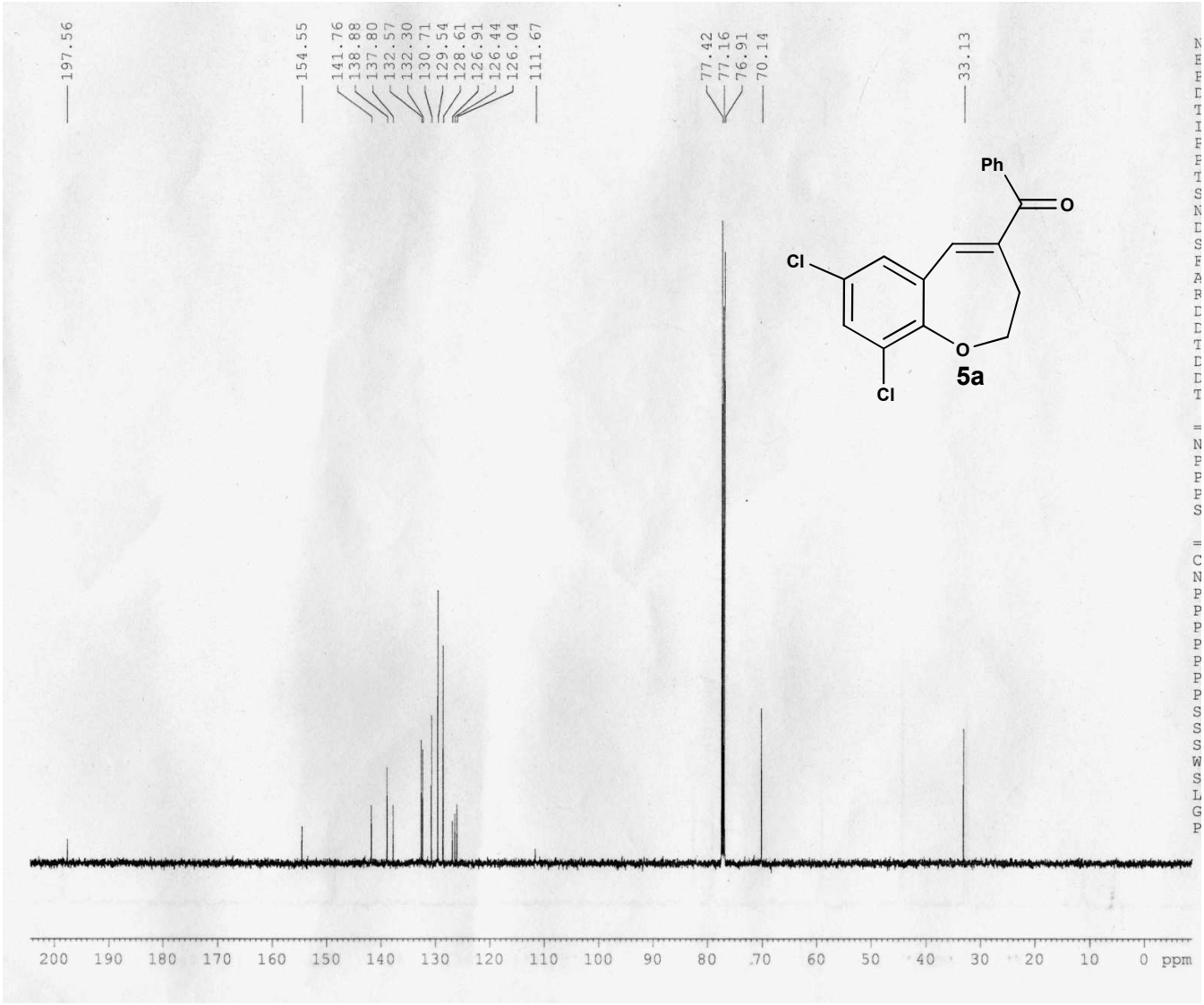
^{13}C NMR, $CDCl_3$, 75 MHz



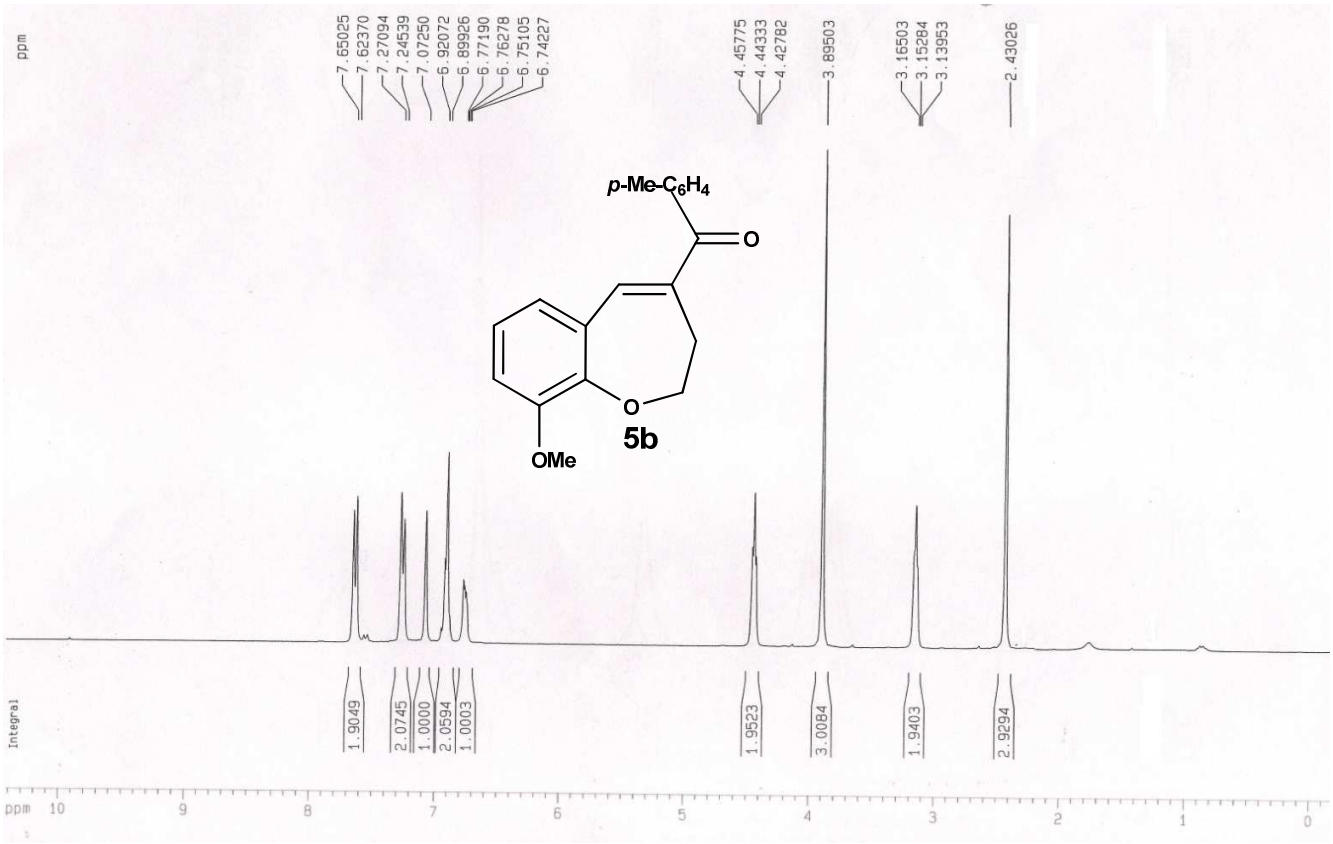
^{1}H NMR, $CDCl_3$, 300 MHz



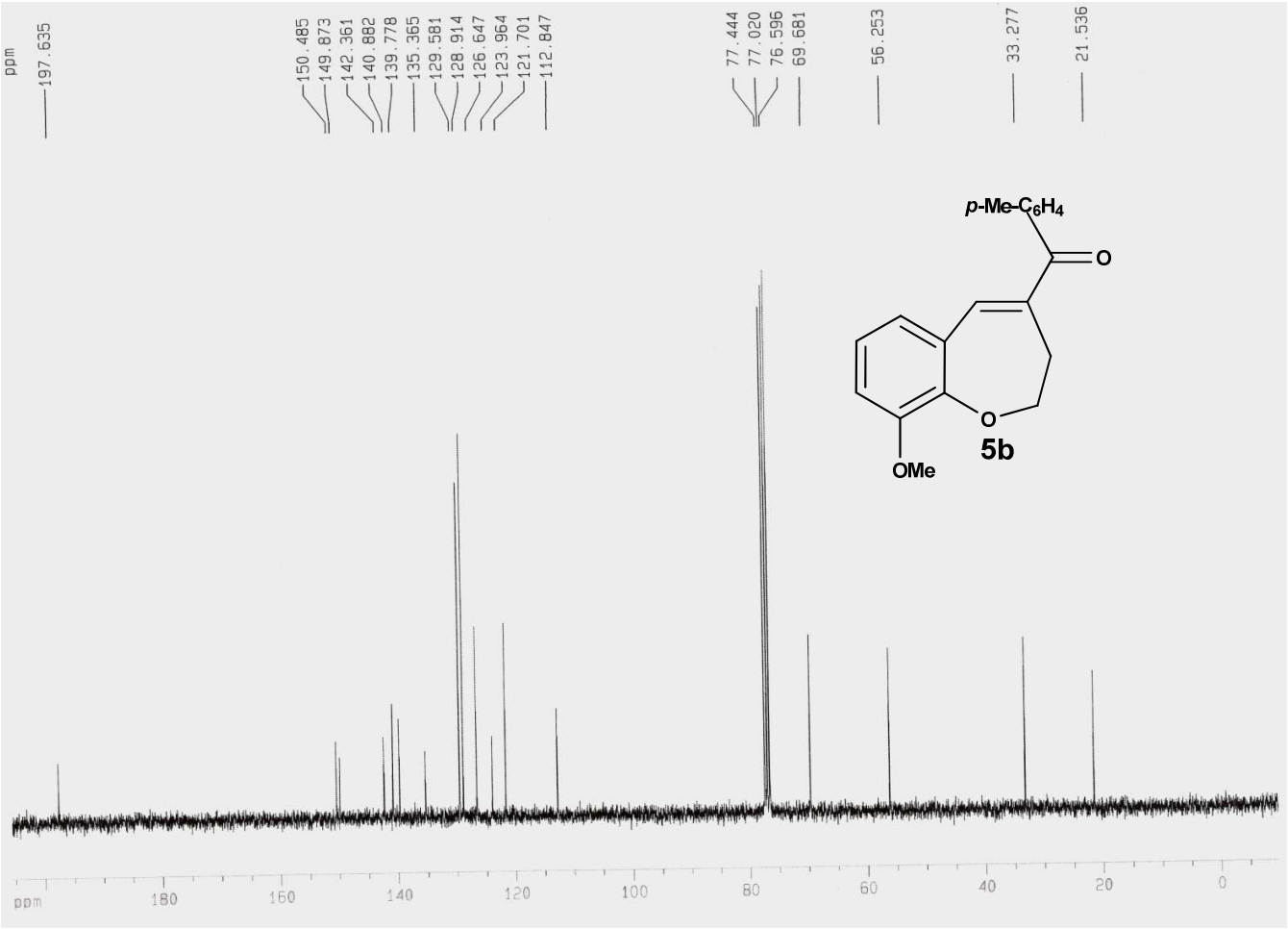
^{13}C NMR, $CDCl_3$, 125 MHz



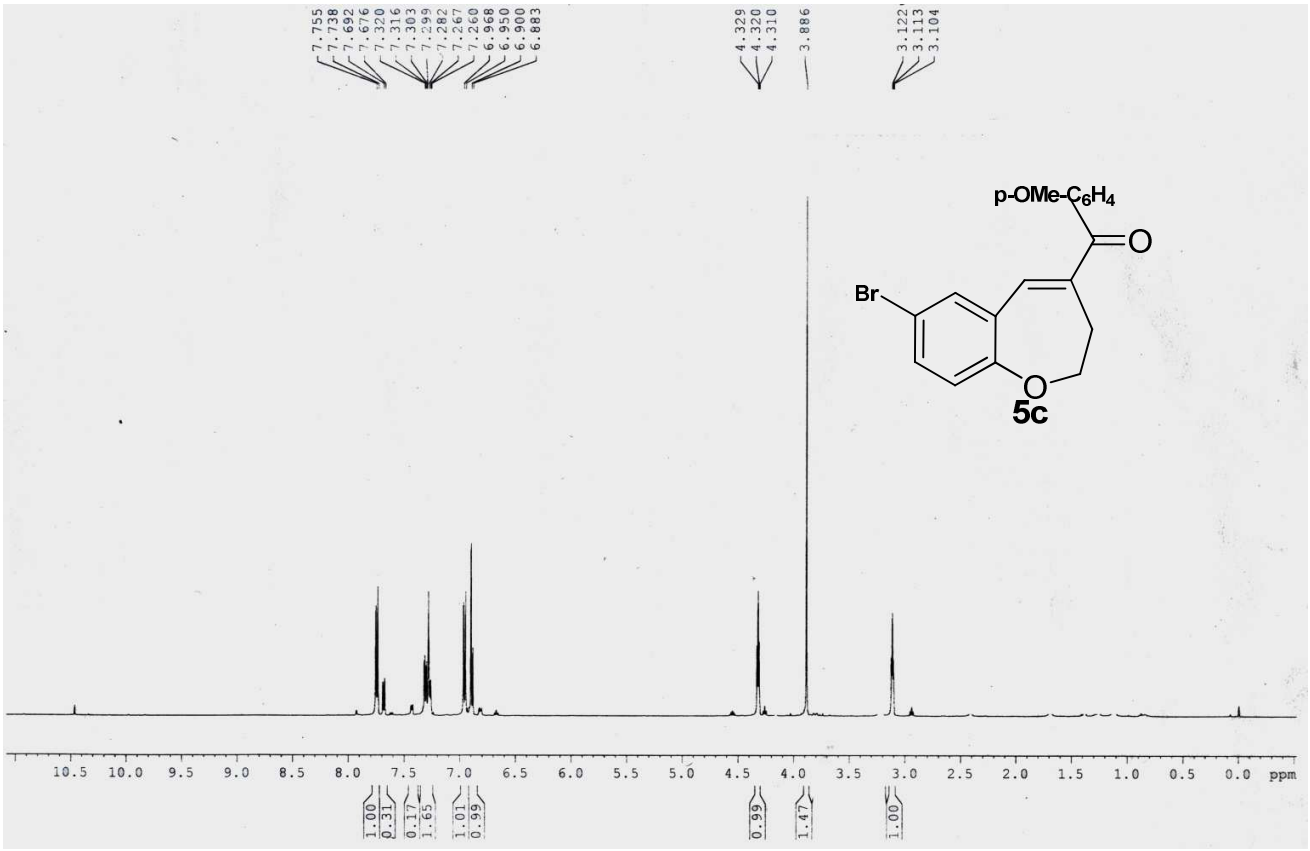
^{1}H NMR, $CDCl_3$, 300 MHz



^{13}C NMR, $CDCl_3$, 75 MHz



^{1}H NMR, $CDCl_3$, 500 MHz



^{13}C NMR, $CDCl_3$,100 MHz