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SUPPORTING INFORMATION

Steady-state photochemistry (Pschorr cyclization) and nanosecond transient absorption spectroscopy of *twisted* 2-bromoaryl ketones

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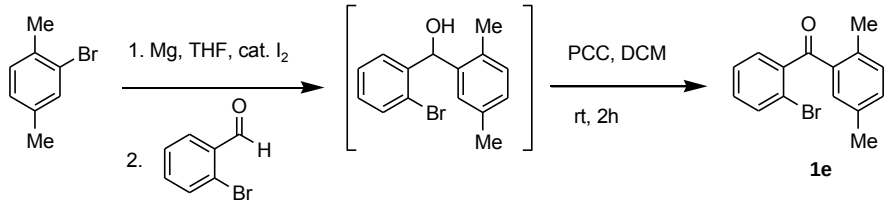
EXPERIMENTAL SECTION

General Aspects. Anhydrous tetrahydrofuran (THF) was freshly distilled over sodium prior to use. Acetonitrile and dichloromethane (DCM) were stored over anhyd $CaCl_2$ and distilled over CaH_2 prior to use as all other solvents. The progress of reactions was monitored by GC (PerkinElmer^{TM} Clarus 500) and/or by analytical thin layer chromatography (TLC) using aluminum sheets pre-coated with silica-gel (Merck). Preparative photolyses were carried out in a Luzchem photoreactor fitted with $\lambda \approx 350$ nm lamps. Column chromatography was conducted with silica-gel of 60-120 μ particle size. NMR spectra were recorded on JEOL-Lambda (400 MHz and 500 MHz) spectrometers. The melting points were determined with a Perfit Melting Point apparatus (Perfit India) and are uncorrected. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrophotometer. UV-vis absorption spectra were recorded using a Cary 4000 UV-vis spectrophotometer. Mass spectral analyses were carried out with Waters ESI-Q^{TOF} Instrument.

Synthesis of 2-Bromo-2′,5′-dimethylbenzophenone 1e.

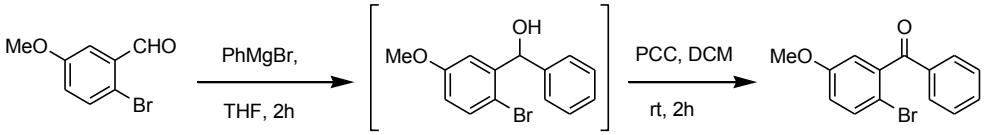


To an ice-cold solution of 2,5-dimethylphenylmagnesium bromide prepared from Mg turnings (3.2 mmol), 2-bromo-1,4-dimethylbenzene (2.6 mmol) and catalytic amount of I_2 in dry THF (3 mL) was added a solution of 2-bromobenzaldehyde (2.2 mmol) in dry THF (3 mL) under N_2 atmosphere. The resulting reaction mixture was stirred at room temperature for 2 h and then

quenched with saturated NH_4Cl. The solvent was removed in vacuo and the resulting reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine solution, dried over anhyd Na_2SO_4, filtered and the solvent was removed in vacuo. The residue was subjected to a short pad silica-gel column chromatography to obtain the corresponding alcohol in 90% yield.

To the solution of above alcohol (1.9 mmol) in dry DCM (10 mL) at 5-10 °C was added 4-Å molecular sieves followed by PCC (2.9 mmol). The reaction mixture was stirred at room temperature for 2 h. Subsequently, the reaction mixture was filtered over a short pad of silica-gel with 50% chloroform/pet. ether to obtain 2-bromo-2′,5′-dimethylbenzophenone **1e** as colorless liquid. Yield 89%. IR (neat) cm^{-1} 2924, 2853, 1671, 1430, 1304; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.27 (s, 3H), 2.52 (s, 3H), 7.11 (s, 1H), 7.19 (d, J = 7.7 Hz, 1H), 7.23 (d, J = 7.7 Hz, 1H), 7.32-7.41 (m, 3H), 7.63 (d, J = 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.8, 120.1, 127.2, 129.8, 131.4, 131.8, 132.0, 132.9, 133.4, 135.1, 136.3, 136.8, 141.7, 198.1; ESI-MS^+ *m/z* Calcd for $C_{15}H_{13}BrO$ 289.0228 [M+H], found 289.0228.

Preparation of 2-Bromo-5-methoxybenzophenone 3a.

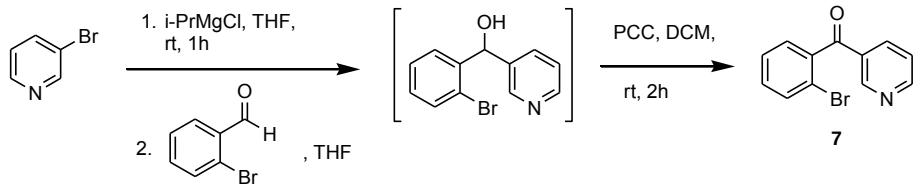


3a

To an ice-cold solution of phenylmagnesium bromide prepared from Mg turnings (0.7 mmol), bromobenzene (0.6 mmol) and catalytic amount of I_2 in dry THF (2 mL) was added a solution of 2-bromo-5-methoxybenzaldehyde (0.5 mmol) in dry THF (2 mL). The reaction mixture was stirred at room temperature for 2 h and then quenched with saturated NH_4Cl. Usual workup followed by a short pad silica-gel column chromatography afforded the corresponding

alcohol as a colorless oil (91%), which was further subjected to PCC oxidation, as described above, to yield 2-bromo-5-methoxybenzophenone (87%) as a colorless solid. Mp 43-45 ^{o}C (lit.[2] 42-44 ^{o}C); IR (KBr) cm^{-1} 3063, 2937, 2838; 1673, 1588, 1467; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.79 (s, 3H), 6.87 (d, J = 3.0 Hz, 1H), 6.91 (dd, J_1 = 8.8 Hz, J_2 = 3.0 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.84 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.6, 109.6, 114.1, 117.3, 128.6, 130.2, 133.8, 133.9, 135.8, 141.3, 158.7, 195.6.

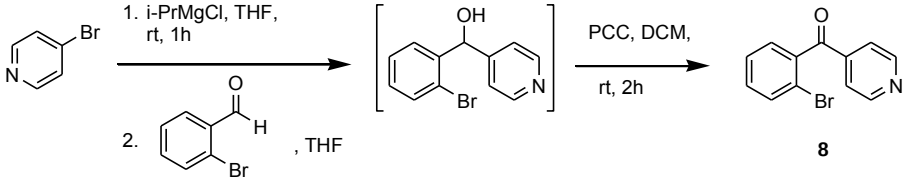
Preparation of (2-Bromophenyl)(3-pyridinyl)methanone 7.



To an ice-cold THF solution of *i*-PrMgCl (6.3 mmol, 0.73 M) contained in a round bottom flask under a nitrogen gas atmosphere was added 3-bromopyridine (6.3 mmol). The resulting reaction was allowed to stir at 20-25 ^{o}C over a period of 1 h. Into this reaction mixture was introduced a solution of 2-bromobenzaldehyde (6.3 mmol) in THF (5 mL) and the contents were stirred at room temperature for 2 h. Subsequently, the reaction was quenched with saturated NH_4Cl. The organic solvent was removed in vacuo and the reaction product was extracted with ethyl acetate. The organic layer was washed with brine, dried over anhyd Na_2SO_4, filtered and the solvent removed in vacuo. The residue was subjected to a short pad silica-gel column chromatography to obtain the corresponding alcohol (80 %), which was further subjected to PCC oxidation as described above to afford the (2-bromophenyl)(3-pyridinyl)methanone as colorless liquid. Yield 70%. IR (neat) cm^{-1} 3053, 2924, 1675, 1584, 1292; ^{1}H NMR ($CDCl_3$, 400 MHz) δ

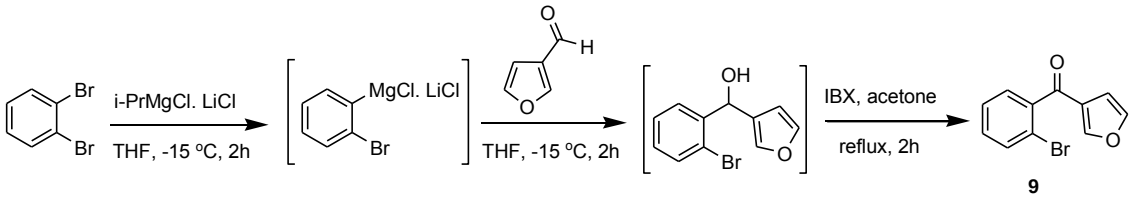
7.39-7.51 (m, 3H), 7.60 (dd, J_1 = 8.0 Hz, J_2 = 5.0 Hz, 1H), 7.69 (d, J = 7.3 Hz, 1H), 8.33 (dt, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 8.85 (dd, J_1 = 5.0 Hz, J_2 = 1.5 Hz, 1H), 8.92 (d, J = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 119.5, 124.6, 127.8, 129.4, 132.3, 132.6, 133.6, 138.8, 139.0, 149.3, 151.3, 193.5; ESI-MS$^+$ *m/z* Calcd for $C_{12}H_8BrNO$ 261.9867 [M+H], found 261.9867.

Synthesis of (2-Bromophenyl)(4-pyridinyl)methanone 8.



4-Bromopyridine hydrochloride was first washed with 2M K_2CO_3 solution in water and then reacted with *i*-PrMgCl and 2-bromobenzaldehyde as described above for the synthesis of ketone **7** to afford 2-bromophenyl-4-pyridylmethanol (yield 65%), which was further subjected to PCC oxidation to yield (2-bromophenyl)(4-pyridinyl)methanone **8,** as a colorless oil. Yield 72%. IR (neat) cm^{-1} 3048, 1682, 1587, 1557, 1407, 1288; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37 (dd, J_1 = 7.4 Hz, J_2 = 1.7 Hz, 1H), 7.41 (td, J_1 = 8.0 Hz, J_2 = 1.7 Hz, 1H), 7.46 (td, J_1 = 7.4 Hz, J_2 = 1.1 Hz, 1H), 7.59 (dd, J_1 = 4.0 Hz, J_2 = 1.7 Hz, 2H), 7.68 (dd, J_1 = 8.0 Hz, J_2 = 1.1 Hz, 1H), 8.81 (dd, J_1 = 4.0 Hz, J_2 = 1.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 119.6, 122.6, 127.5, 129.4, 132.1, 133.5, 139.0, 142.2, 150.9, 195.1; ESI-MS$^+$ *m/z* Calcd for $C_{12}H_8BrNO$ 261.9867 [M+H], found 261.9868.

Synthesis of (2-Bromophenyl)(3-furanyl)methanone 9.

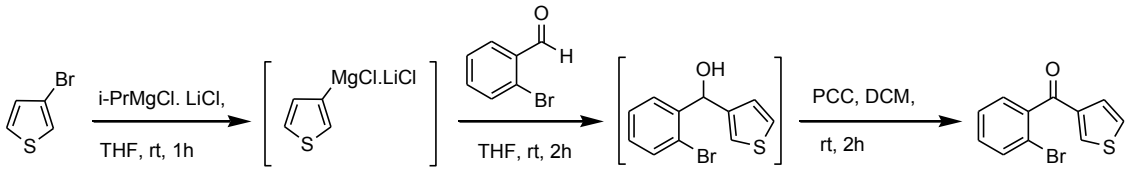


9

To a THF solution of *i*-PrMgCl.LiCl (5.7 mmol, 1M in THF) contained in a round bottom flask and colled to -15 ^{o}C was added dropwise a solution of 1,2-dibromobenzene (5.7 mmol) in THF (2.0 mL) under a nitrogen gas atmosphere. The resulting reaction was allowed to stir at -15 ^{o}C over a period of 2h. Then, a solution of 3-formylfuran (5.2 mmol) in THF (3 mL) was added and the reaction was stirred at the same temperature for 2h. Subsequently, the reaction was quenched with saturated NH_4Cl. The solvent was removed in vacuo and the resulting reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over anhyd Na_2SO_4, filtered and the solvent removed in vacuo. The residue thus obtained was subjected to a short pad silica-gel column chromatography to obtain the corresponding alcohol (76%), which was oxidized with IBX as described below.

To a solution of above alcohol (8.5 mmol) in acetone (20 mL) was added IBX (12.5 mmol), and the resulting heterogeneous solution was heated at reflux for 2h. The crude reaction mixture was filtered over a short pad of silica-gel to obtain a colorless liquid of (2-bromophenyl)(3-furanyl)methanone, yield 57%. IR (neat) cm^{-1} 1332, 1664, 1587, 1558, 1509, 1315; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.88 (d, J = 1.6 Hz, 1H), 7.32-7.36 (m, 1H), 7.38-7.40 (m, 2H), 7.49 (t, J = 1.7 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 0.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 109.1, 119.2, 127.1, 127.3, 128.5, 131.3, 133.5, 141.0, 144.6, 150.4, 189.2; ESI-MS^{+} *m/z* Calcd for $C_{11}H_7BrO_2$ 250.9707 [M+H], found 250.9708.

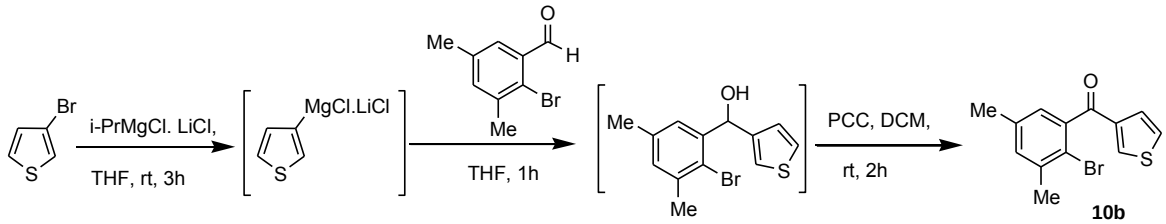
Synthesis of (2-Bromophenyl)(3-thionyl)methanone 10a.



10a

To a solution of *i*-PrMgCl.LiCl (3.9 mmol, 1M in THF) contained in a round bottom flask was added dropwise a solution of 3-bromothiophene (3.6 mmol) in THF (2.0 mL) at cold-water condition under nitrogen gas atmosphere. The resulting reaction was allowed to stir at 20-25 ^{o}C over a period of 1h. Later, a solution of 2-bromobenzaldehyde (3.8 mmol) in THF (5 mL) was added and the reaction was stirred at rt for further 2h. Subsequently, the reaction mixture was quenched with saturated NH_4Cl. Usual workup procedure and a short pad silica-gel column chromatography of crude reaction mixture afforded the corresponding alcohol (80%), which was further subjected to PCC oxidation as described below to obtain a colorless liquid of (2-bromophenyl)(3-thionyl)methanone, yield 64%. IR (neat) cm^{-1} 3105, 2924, 2853, 1662, 1587, 1508, 1410, 1284; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32-7.43 (m, 4H), 7.58 (dd, J_1 = 5.0 Hz, J_2 = 1.2 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.80 (dd, J_1 = 2.9 Hz, J_2 = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 119.3, 126.7, 127.1, 127.7, 128.6, 131.2, 133.3, 136.0, 141.2, 141.5, 189.3; ESI-MS^{+} *m/z* Calcd for $C_{11}H_7BrOS$ 266.9479 [M+H], found 266.9479.

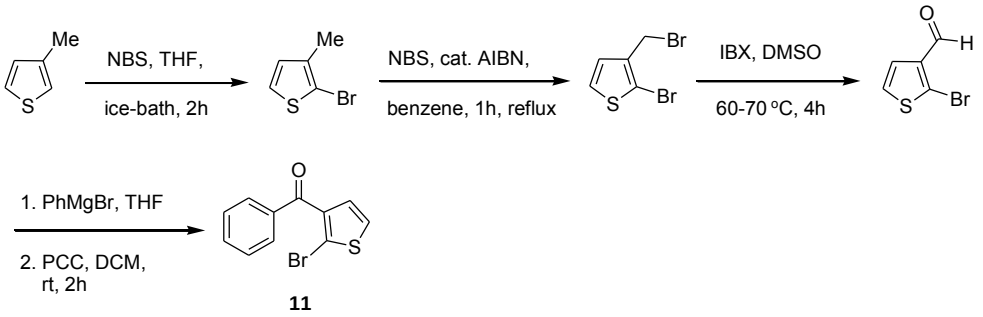
Synthesis of (2-Bromo-3,5-dimethylphenyl)(3-thionyl)methanone 10b.



10b

3-Bromothiophene (4.3 mmol) was reacted with *i*-PrMgCl.LiCl (4.7 mmol, 1M in THF) and 2-bromo-3,5-dimethylbenzaldehyde (4.3 mmol), as described above for the synthesis of ketone **10a**, to afford the corresponding alcohol (yield 79%), which was further subjected to PCC oxidation to yield (2-bromo-3,5-dimethylphenyl)(3-thionyl)methanone (81%) as colorless solid. Mp 88-90 ^{o}C; IR (KBr) cm^{-1} 3105, 2922, 1653, 1505, 1408, 1313; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.30 (s, 3H), 2.42 (s, 3H), 6.97 (s, 1H), 7.16 (s, 1H), 7.34 (dd, J_1 = 5.1 Hz, J_2 = 2.9 Hz, 1H), 7.56 (d, J = 5.1 Hz, 1H), 7.80 (d, J = 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.7, 23.0, 117.8, 126.3, 126.5, 127.6, 132.7, 135.9, 137.0, 138.8, 141.7, 141.8, 190.1; ESI-MS^{+} *m/z* Calcd for $C_{13}H_{11}BrOS$ 294.9792 [M+H], found 294.9798.

Synthesis of (2-Bromothiophen-3-yl)phenylmethanone 11.



11

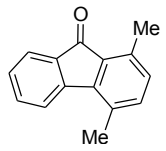
To an ice-cold solution of 3-methylthiophene (4.1 mmol) in THF (30 mL) was added NBS (4.5 mmol). The resulting solution was stirred at ice-cold condition over a period of 2 h and then poured into water. Aqueous solution was extracted with pet. ether, dried over anhyd Na_2SO_4, filtered and the solvent removed in vacuo. The residue obtained was subjected to a short pad silica-gel column chromatography to obtain 2-bromo-3-methylthiophene[3] as colorless liquid (60%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.20 (s, 3H), 6.64 (d, J = 5.6 Hz, 1H), 7.17 (d, J = 5.6 Hz, 1H).

To a solution of 2-bromo-3-methylthiophene (1.71 mmol) in dry benzene (10 mL) were added NBS (1.69 mmol) and catalytic amount of AIBN. The resulting suspension was heated to reflux for 1h. The crude reaction mixture was cooled to -40 ^{o}C to precipitate some of the succinimide, and this was filtered off. The solvent was removed from the filtrate under vacuo and the crude oil obtained was subjected to a flash column chromatography on silica-gel to yield 2-bromo-3-(bromomethyl)thiophene[4] as colorless liquid (yield 75%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.46 (s, 2H), 7.00 (d, J = 5.6 Hz, 1H), 7.26 (d, J = 5.6 Hz, 1H).

To a solution of 2-bromo-3-(bromomethyl)thiophene (1.0 mmol) in dry DMSO (3 mL) was added IBX (1.6 mmol) and the resulting solution was heated at 60-70 ^{o}C for 4h. The reaction was quenched with water and extracted with dichloromethane. The organic layer was thoroughly washed with water, dried over anhyd Na_2SO_4, filtered and the solvent was removed in vacuo. The crude oil obtained was further purified by a silica-gel column chromatography to afford 2-bromo-3-formylthiophene[5] as pale yellow liquid. Yield 60%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (d, J = 5.6 Hz, 1H), 7.36 (d, J = 5.6 Hz, 1H), 9.94 (s, 1H).

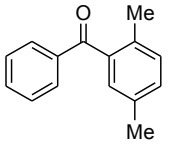
To a solution of phenylmagnesium bromide prepared from Mg turnings (0.7 mmol) and bromobenzene (0.6 mmol) in dry THF (2 mL) was added a solution of 2-bromo-3-formylthiophene (0.3 mmol) in 2 mL of anhyd THF under nitrogen gas atmosphere. The reaction mixture was stirred at room temperature for 2 h and then quenched with saturated NH_4Cl. Usual workup followed by a short pad silica-gel column chromatography afforded the corresponding alcohol as colorless liquid (91%), which was further subjected to PCC oxidation to yield the (2-bromophenyl)(3-thionyl)methanone (87%) as colorless liquid. IR (neat) cm^{-1} 3106, 2919, 2850, 1658, 1511, 1402, 1260; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.12 (d, J = 5.6 Hz, 1H), 7.31 (d, J = 5.6 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.84 (d, J = 7.8 Hz, 2H); ^{13}C NMR

($CDCl_3$, 125 MHz) δ 116.7, 126.2, 128.5, 129.4, 129.9, 133.2, 137.2, 139.3, 190.6; ESI-MS^+ *m/z* Calcd for $C_{11}H_7BrOS$ 266.9479 [M+H], found 266.9479.

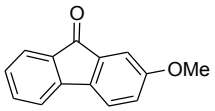


1,4-Dimethylfluoren-9-one (1e-Fl). Yellow solid, mp 85-87 ^oC; IR (KBr) cm^{-1} 2957, 2923, 2864, 1698, 1601, 1450; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.54 (s, 3H), 2.59 (s, 3H), 6.94 (d, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.65 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.7, 20.1, 123.2, 123.8, 128.2, 131.0, 131.6, 134.2, 134.7, 136.8, 136.9, 142.4, 144.6, 195.4; ESI-MS^+ *m/z* Calcd for $C_{15}H_{12}O$ 209.0966 [M+H], found 209.0966.

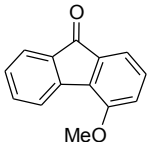
2,5-Dimethylbenzophenone (1e-Bp). Colorless oil, IR (neat) cm^{-1} 2924, 1665, 1598, 1448, 1315, 1294, 1268; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.27 (s, 3H), 2.33 (s, 3H), 7.12 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.4, 20.8, 128.4, 128.9, 130.1, 130.8, 130.9, 133.0, 133.4, 134.7, 137.8, 138.6, 198.9.



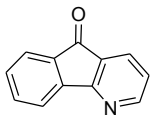
2-Methoxyfluoren-9-one (3e-Fl-1).[1] Yellow solid; IR (KBr) cm^{-1} 1712, 1602; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.85 (s, 3H), 6.98 (dd, J_1 = 8.2 Hz, J_2 = 2.4 Hz, 1H), 7.17- 7.21 (m, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.41-7.46 (m, 2H), 7.60 (d, *J* = 7.2 Hz, 1H).



4-Methoxyfluoren-9-one (3e-Fl-2).[6] Yellow solid, mp 106-108 ^oC; IR (neat) cm^{-1} 2919, 2848, 1711, 1594, 1273; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.98 (s, 3H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.21- 7.30 (m, 3H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.82 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.6, 116.5, 117.8, 124.0, 124.2, 128.0, 130.4, 131.2, 133.5, 134.8, 135.7, 143.8, 155.4, 194.3.

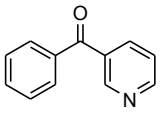


Indeno[1,2-*b*]pyridin-5-one (7-Fl). Pale yellow solid, mp 128-130 °C ; IR (KBr) cm^{-1} 3052,



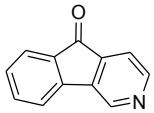
2924, 1721, 1593, 1564, 1405; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.21 (dd, J_1 = 7.4 Hz, J_2 = 5.1 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.73 (d, J = 7.4 Hz, 1H), 7.86 (d, J = 7.4 Hz, 1H), 7.89 (dd, J_1 = 7.4 Hz, J_2 = 1.7 Hz, 1H), 8.62 (dd, J_1 = 5.1 Hz, J_2 = 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 120.9, 123.3, 124.2, 128.3, 131.0, 131.4, 134.7, 135.4, 143.5, 154.0, 165.1, 191.8; ESI-MS$^+$ *m/z* Calcd for $C_{12}H_7NO$ 182.0605 [M+H], found 182.0608.

3-Benzoylpyridine (7-Bp).[7] Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 (dd, J_1 = 7.8



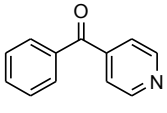
Hz, J_2 = 4.8 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.63 (t, J = 7.8 Hz, 1H), 7.81 (d, J = 8.3 Hz, 2H), 8.11 (d, J = 7.8 Hz, 1H), 8.80 (d, J = 4.8 Hz, 1H), 8.99 (d, J = 1.6 Hz, 1H).

3-Azafluoren-9-one (8-Fl). Greenish yellow solid, 116-118 °C (lit.[8] 118-119 °C) ; IR (KBr) cm^{-1}



2924, 1725, 1601, 1409; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38 (t, J = 7.4 Hz, 1H), 7.51 (d, J = 4.6 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.65 (d, J = 7.4 Hz, 1H), 7.74 (d, J = 7.4 Hz, 1H), 8.71 (br s, 1H), 8.91 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 117.3, 121.2, 125.3, 129.9, 133.3, 135.5, 137.5, 140.2, 142.1, 143.2, 151.7, 193.1.

4-Benzoylpyridine (8-Bp). Colorless solid, mp 66-68 °C (lit[9] 70-71 °C) ; ^{1}H NMR ($CDCl_3$, 400



MHz) δ 7.50 (t, J = 7.3 Hz, 2H), 7.57 (dd, J_1 = 4.4 Hz, J_2 = 1.7 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.80 (d, J = 7.3 Hz, 2H), 8.80 (dd, J_1 = 4.4 Hz, J_2 = 1.7 Hz, 2H).

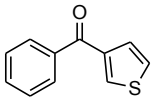
Indeno[1,2-*b*]furan-4-one (9-Fl). Orange liquid; IR (neat) cm^{-1} 2924, 2854, 1712, 1426; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.50 (d, *J* = 1.7 Hz, 1H), 7.11 (d, *J* = 6.8 Hz, 1H), 7.17 (t, *J* = 6.8 Hz, 1H), 7.29 (t, *J* = 6.8 Hz, 1H), 7.41 (d, *J* = 1.7 Hz, 1H), 7.43 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 106.8, 117.1, 123.5, 123.8, 129.1, 132.9, 134.1, 138.5, 148.3, 175.4, 185.2; ESI-MS^+ *m/z* Calcd for $C_{11}H_6O_2$ 171.0446 [M+H], found 171.0448.

3-Benzoylfuran (9-Bp).[10] Colorless liquid; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.91 (d, *J* = 1.7 Hz, 1H), 7.48-7.51 (m, 3H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.86 (d, *J* = 7.1 Hz, 2H), 7.93 (br s, 1H).

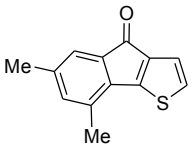
3-Thiacyclopenta[*a*]inden-8-one (10a-Fl-1). Chrome yellow solid, 92-94 ^oC; IR (neat) cm^{-1} 3102, 3079, 2924, 1730, 1604, 1453, 1350; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.12 (d, *J* = 5.1 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.17 (td, J_1 = 7.4 Hz, J_2 = 1.1 Hz, 1H), 7.18 (d, *J* = 5.1 Hz, 1H), 7.33 (td, J_1 = 7.4 Hz, J_2 = 1.1 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 119.3, 121.4, 123.6, 128.5, 129.1, 133.9, 136.4, 138.8, 142.0, 159.0, 187.3; ESI-MS^+ *m/z* Calcd for $C_{11}H_6OS$ 187.0217 [M+H], found 187.0219.

2-Thiacyclopenta[*a*]inden-8-one (10a-Fl-2). Yellow solid, mp 82-84 ^oC; IR (KBr) cm^{-1} 3085, 2924, 1720, 1602, 1505; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.13 (d, *J* = 2.0 Hz, 1H), 7.26 (td, J_1 = 7.4 Hz, J_2 = 1.1 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.47 (td, J_1 = 7.4 Hz, J_2 = 1.1 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.75 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 115.7, 121.2, 125.1, 127.1, 128.4, 134.5, 141.0, 141.2, 142.1, 146.1, 185.9; ESI-MS^+ *m/z* Calcd for $C_{11}H_6OS$ 187.0217 [M+H], found 187.0218.

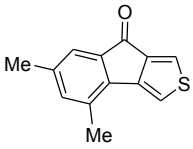
3-Benzoylthiophene (10a-Bp).[7] Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.8 (dd, J_1 = 4.9 Hz, J_2 = 2.9 Hz, 1H), 7.49 (t, J = 7.3 Hz, 2H), 7.47-7.61 (m, 2H), 7.84 (d, J = 7.3 Hz, 2H), 7.91 (d, J = 2.9 Hz, 1H).



4,6-Dimethyl-3-thiacyclopenta[*a*]inden-8-one (10b-Fl-1). Orange crystalline solid, mp 121-123 °C; IR (KBr) cm^{-1} 2920, 1698, 1603, 1411; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.28 (s, 3H), 2.32 (s, 3H), 6.95 (s, 1H), 7.11 (s, 1H), 7.13 (d, J = 5.1 Hz, 1H), 7.16 (d, J = 5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.5, 21.2, 121.3, 122.5, 128.7, 129.6, 134.7, 135.7, 136.8, 138.8, 141.1, 159.0, 187.9; ESI-MS$^+$ *m/z* Calcd for $C_{13}H_{10}OS$ 215.0530 [M+H], found 215.0534.



4,6-Dimethyl-2-thiacyclopenta[*a*]inden-8-one (10b-Fl-2). Chrome yellow solid, mp 150-152 °C; IR (KBr) cm^{-1} 3078, 2922, 1699, 1506; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.33 (s, 3H), 2.44 (s, 3H), 7.02 (d, J = 2.0 Hz, 1H), 7.10 (s, 1H), 7.33 (s, 1H), 7.74 (d, J = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.2, 21.2, 116.1, 123.1, 126.6, 132.5, 136.7, 137.4, 138.5, 141.4, 142.7, 146.0, 186.5; ESI-MS$^+$ *m/z* Calcd for $C_{13}H_{10}OS$ 215.0530 [M+H], found 215.0537.



X-Ray crystal structure data

Table: 1 Crystal data for **1b**, **1c** and **2a**.

Property	**1b**	**1c**	**2a**
Chemical formula	$C_{14}H_{11}BrO_2$	$C_{14}H_{11}BrO_2$	$C_{14}H_{11}BrO_2$
Formula weight	291.14	291.14	291.14
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P* $2_1/c$	*P* $2_1/n$	*P*$2_1/c$
a (Å)	11.015 (5)	9.450(3)	9.193(5)
b (Å)	10.540 (5)	12.177(4)	9.861(5)
c (Å)	10.353(5)	10.170(4)	13.394(5)
α (°)	90.000(5)	90.00	90.000(5)
β (°)	99.880(5)	96.052(6)	97.068(5)

γ (°)	90.000(5)	90.00	90.000(5)
Volume (Å^3)	1184.2(3)	1163.8(7)	1205.0(10)
Z	4	4	4
T (K)	100(2)	100(2)	100(2)
ρ_{calc} (g cm^{-3})	1.633	1.662	1.605
μ (mm^{-1})	3.457	3.517	3.397
F (000)	584	584	584
Reflections collected	7600	7361	7578
Unique reflections	2929	2841	2945
Reflections with $I > 2\sigma(I)$	2258	2147	2304
Goodness-of-fit	1.165	1.152	1.165
Final R_1 [$I > 2\sigma(I)$]	0.0415	0.0553	0.0394
Final wR_2	0.0873	0.1322	0.0904

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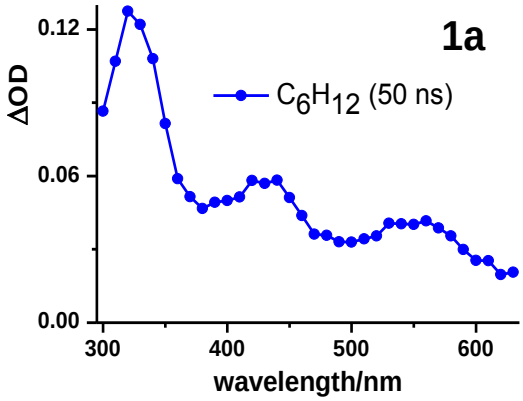
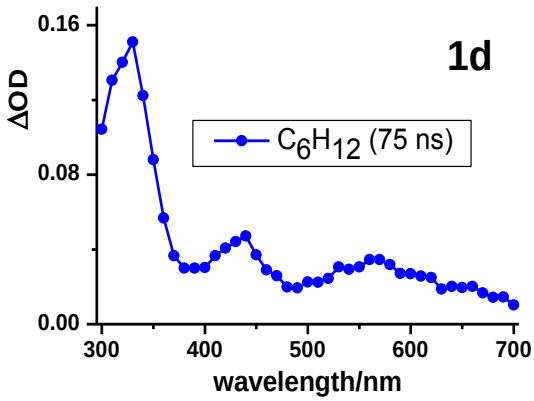
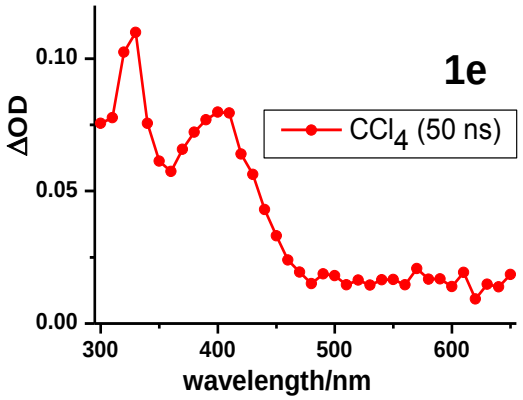
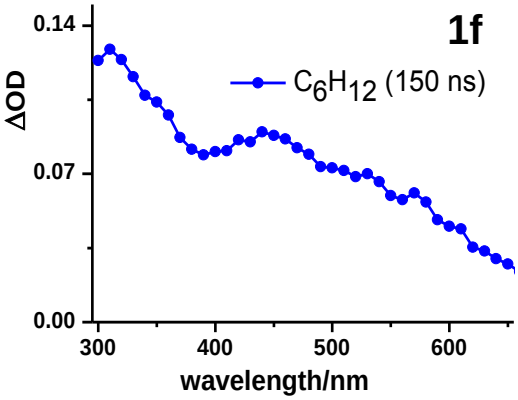
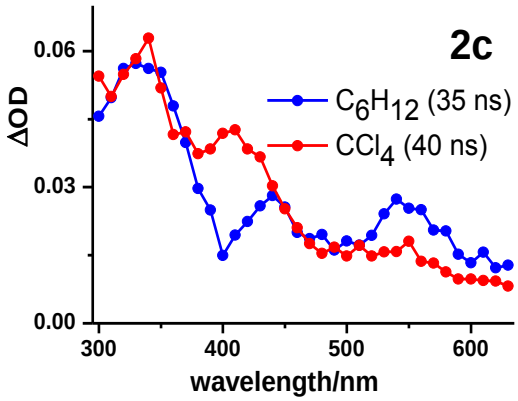
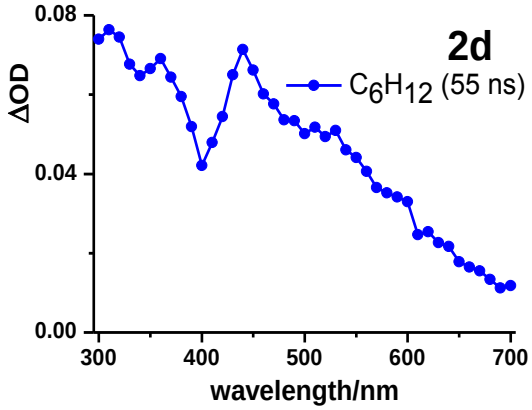


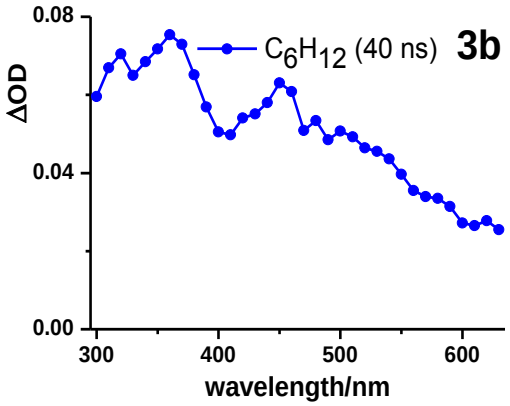


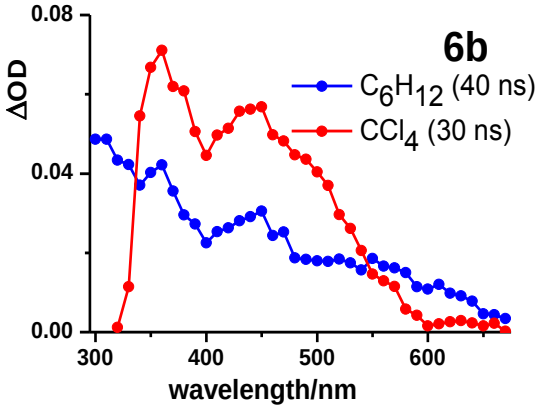


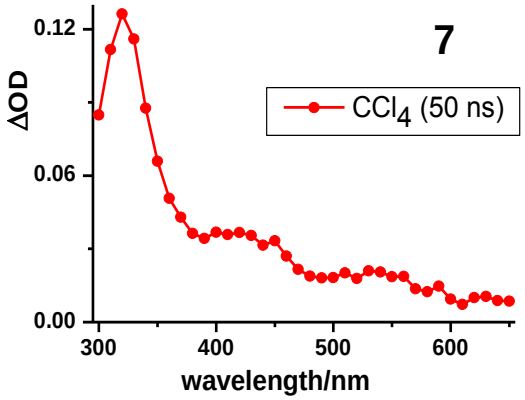


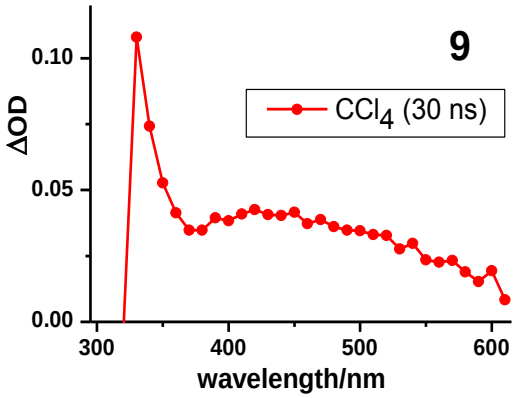

2c
C6H12 (35 ns)
CCl4 (40 ns)
ΔOD
wavelength/nm


2d
C6H12 (55 ns)
ΔOD
wavelength/nm


3b
C6H12 (40 ns)
ΔOD
wavelength/nm


6b
C6H12 (40 ns)
CCl4 (30 ns)
ΔOD
wavelength/nm


7
CCl4 (50 ns)
ΔOD
wavelength/nm


9
CCl4 (30 ns)
ΔOD
wavelength/nm

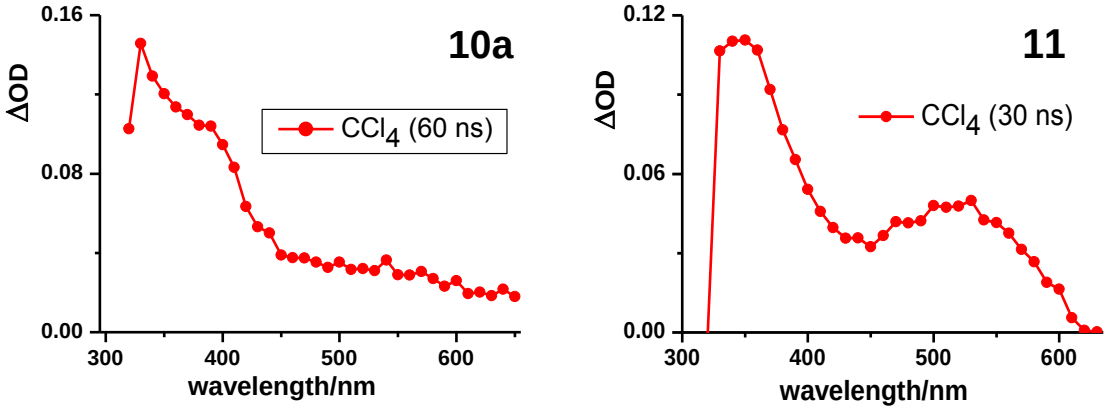


Figure S1. Triplet-triplet transient absorptions spectra of ketones **1a**, **1d**, **1e-f**, **2c-d**, **3b**, **6d**, **7**, **9**, **10a** and **11**.

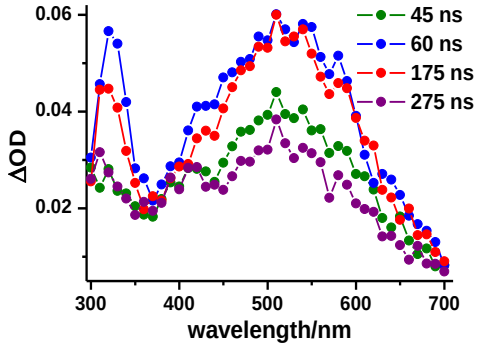


Fig. S2 The transient absorption spectra of benzene–Br• complex formed upon nanosecond flash photolysis of **1a** in benzene at different delay times.

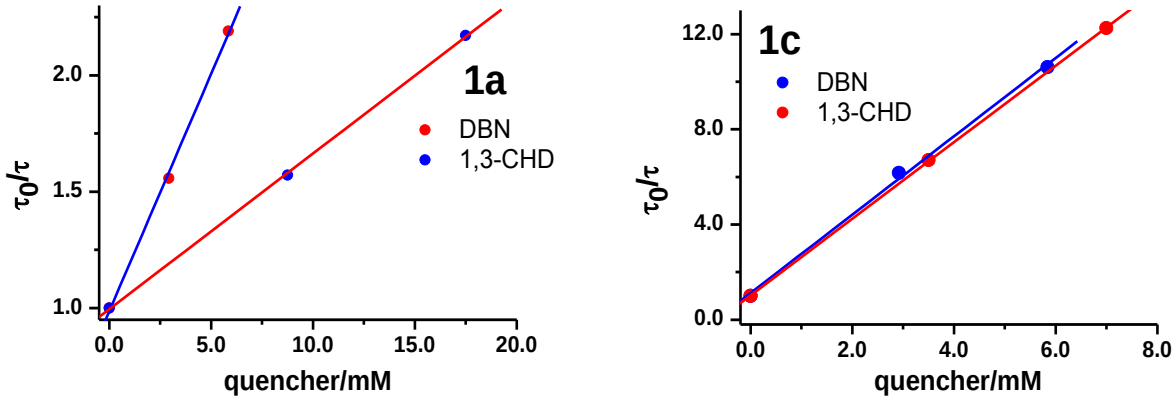
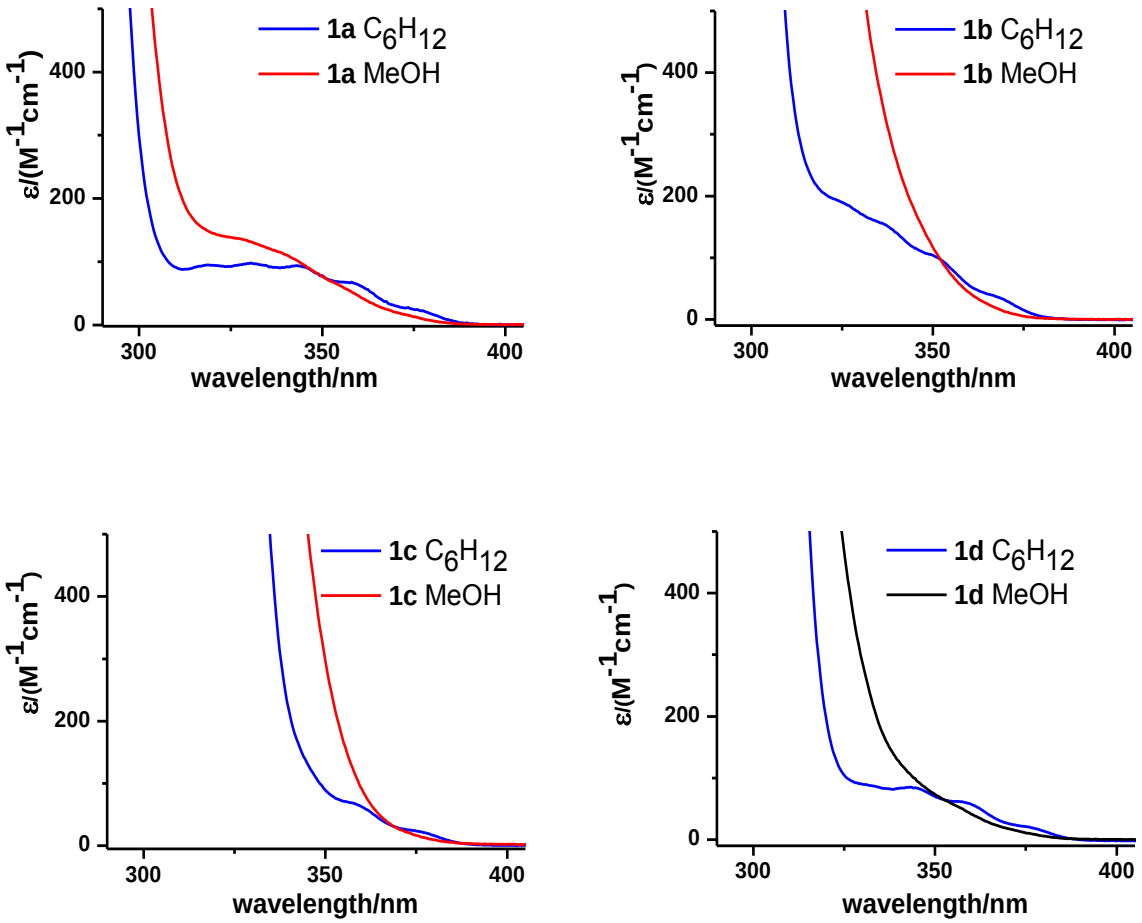
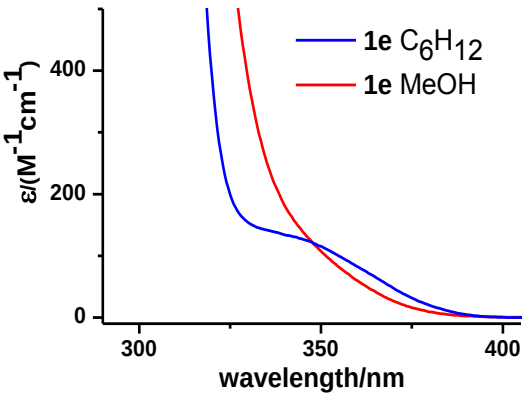
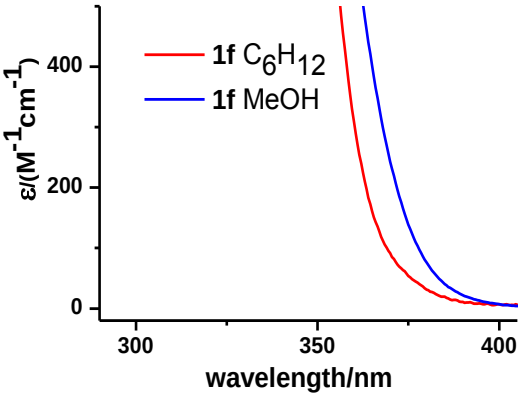
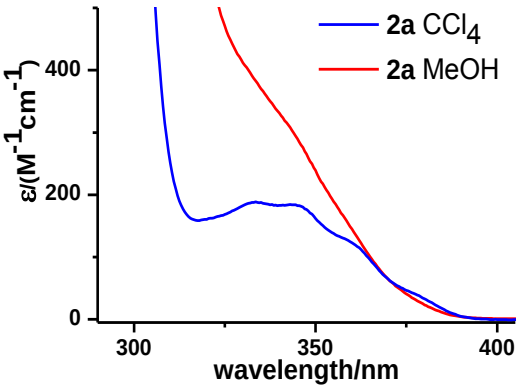


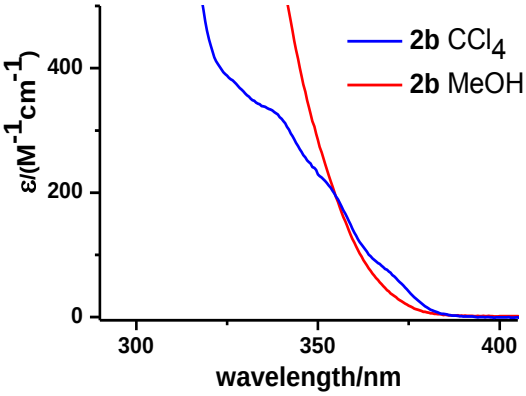
Figure S3.The Stern-Volmer quenching plots for the quenching of the triplets of **1a** and **1c** with diazabicyclononene (DBN) and 1,3-cyclohexadiene.

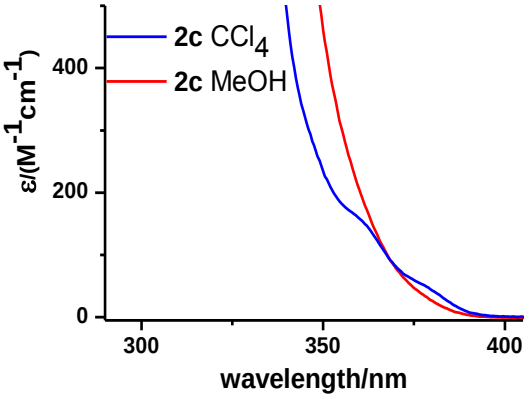



1e C_6H_{12}
1e MeOH
ε/(M^{-1}cm^{-1})
wavelength/nm


1f C_6H_{12}
1f MeOH
ε/(M^{-1}cm^{-1})
wavelength/nm


2a CCl_4
2a MeOH
ε/(M^{-1}cm^{-1})
wavelength/nm


2b CCl_4
2b MeOH
ε/(M^{-1}cm^{-1})
wavelength/nm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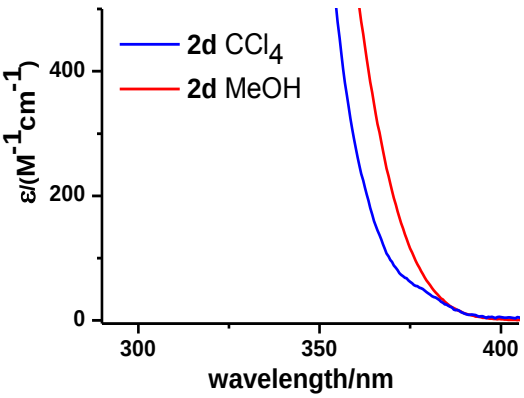
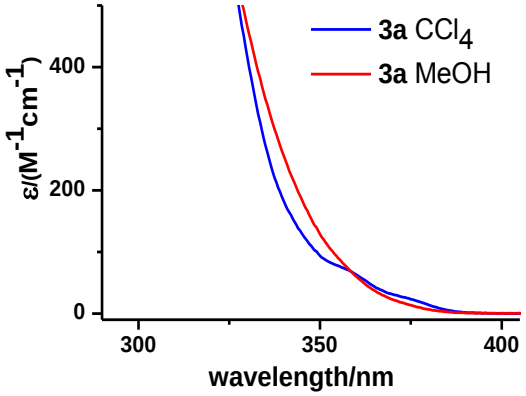
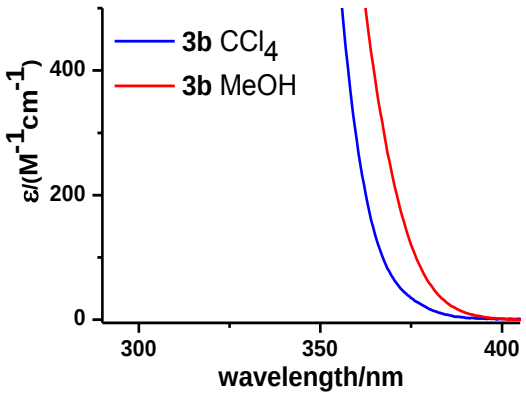
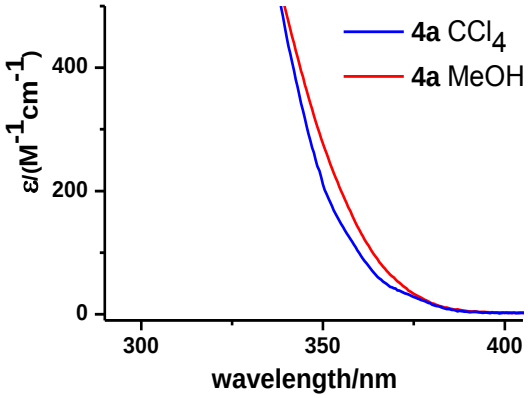
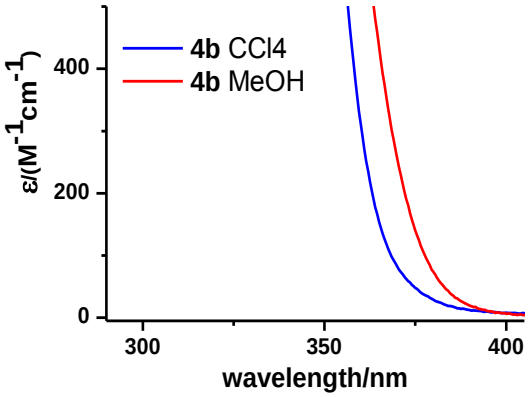
2c MeOH
ε/(M^{-1}cm^{-1})
wavelength/nm

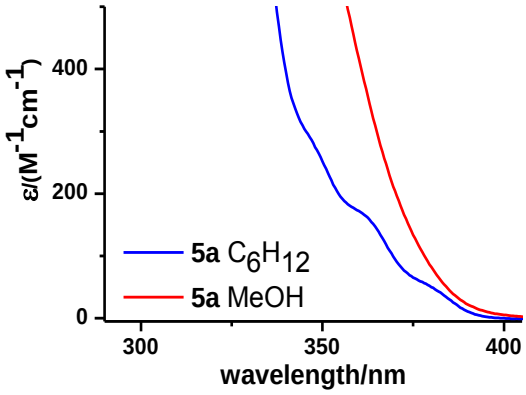

2d CCl_4
2d MeOH
ε/(M^{-1}cm^{-1})
wavelength/nm

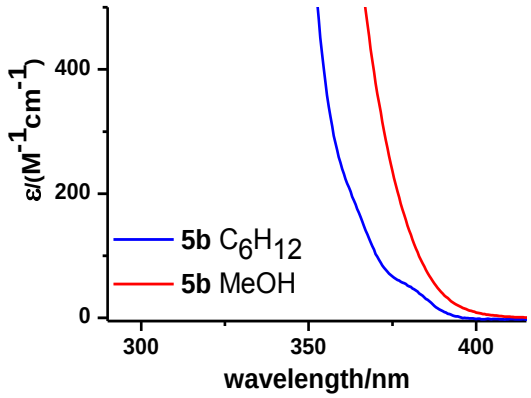

3a CCl4
3a MeOH
ε/(M-1cm-1)
wavelength/nm

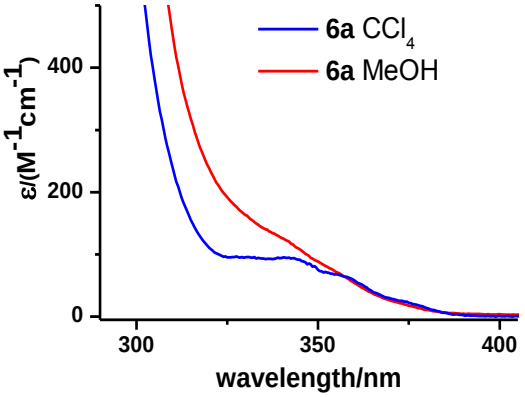

3b CCl4
3b MeOH
ε/(M-1cm-1)
wavelength/nm

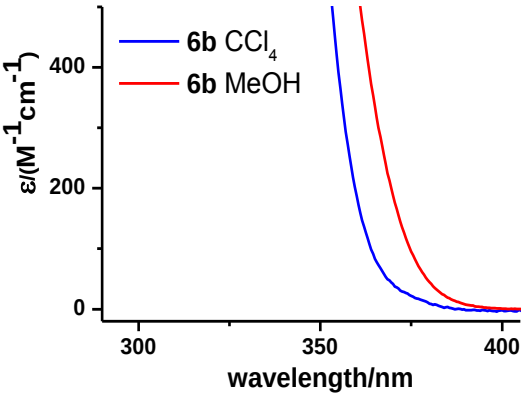

4a CCl4
4a MeOH
ε/(M-1cm-1)
wavelength/nm

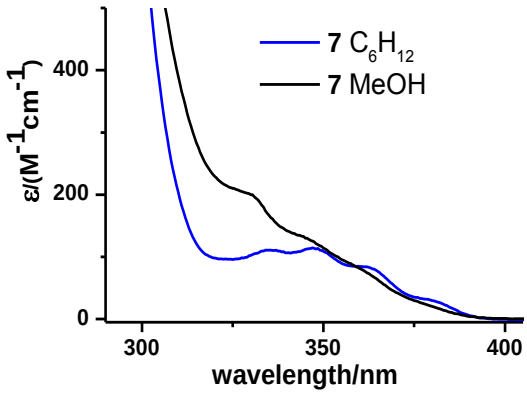

4b CCl4
4b MeOH
ε/(M-1cm-1)
wavelength/nm

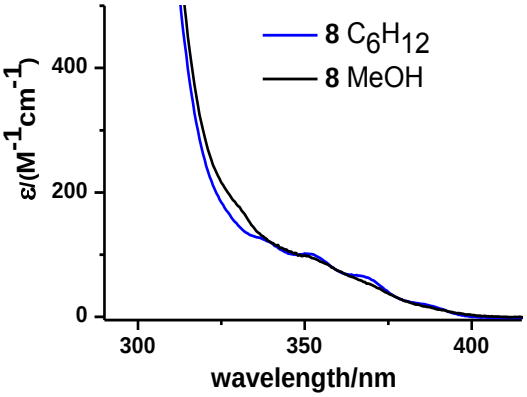

5a C6H12
5a MeOH
ε/(M-1cm-1)
wavelength/nm

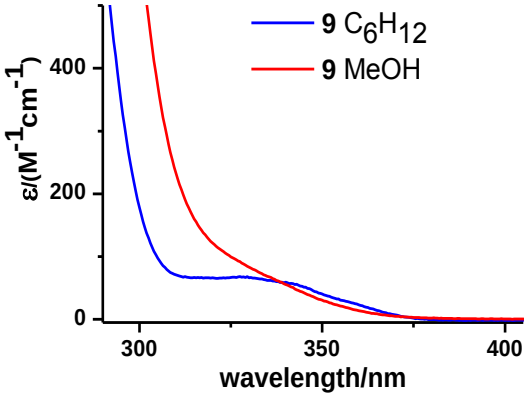

5b C6H12
5b MeOH
ε/(M-1cm-1)
wavelength/nm

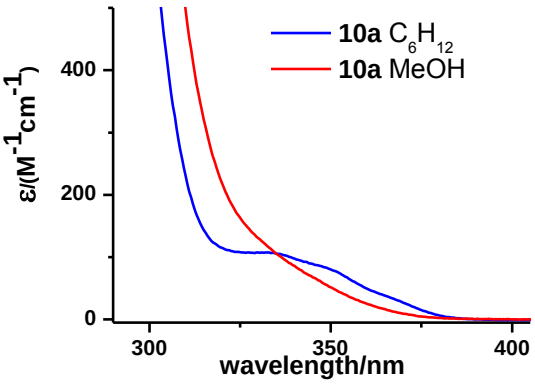

6a CCl4
6a MeOH
ε/(M-1cm-1)
0
200
400
300
350
400
wavelength/nm


6b CCl4
6b MeOH
ε/(M-1cm-1)
0
200
400
300
350
400
wavelength/nm


7 C6H12
7 MeOH
ε/(M-1cm-1)
0
200
400
300
350
400
wavelength/nm


8 C6H12
8 MeOH
ε/(M-1cm-1)
0
200
400
300
350
400
wavelength/nm


9 C6H12
9 MeOH
ε/(M-1cm-1)
0
200
400
300
350
400
wavelength/nm


10a C6H12
10a MeOH
ε/(M-1cm-1)
0
200
400
300
350
400
wavelength/nm

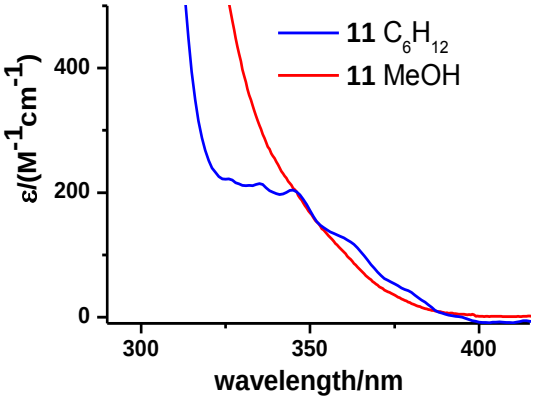


Figure S4. UV-Vis absorption spectra of ketones **1**-**10a** and **11** in cyclohexane and methanol.

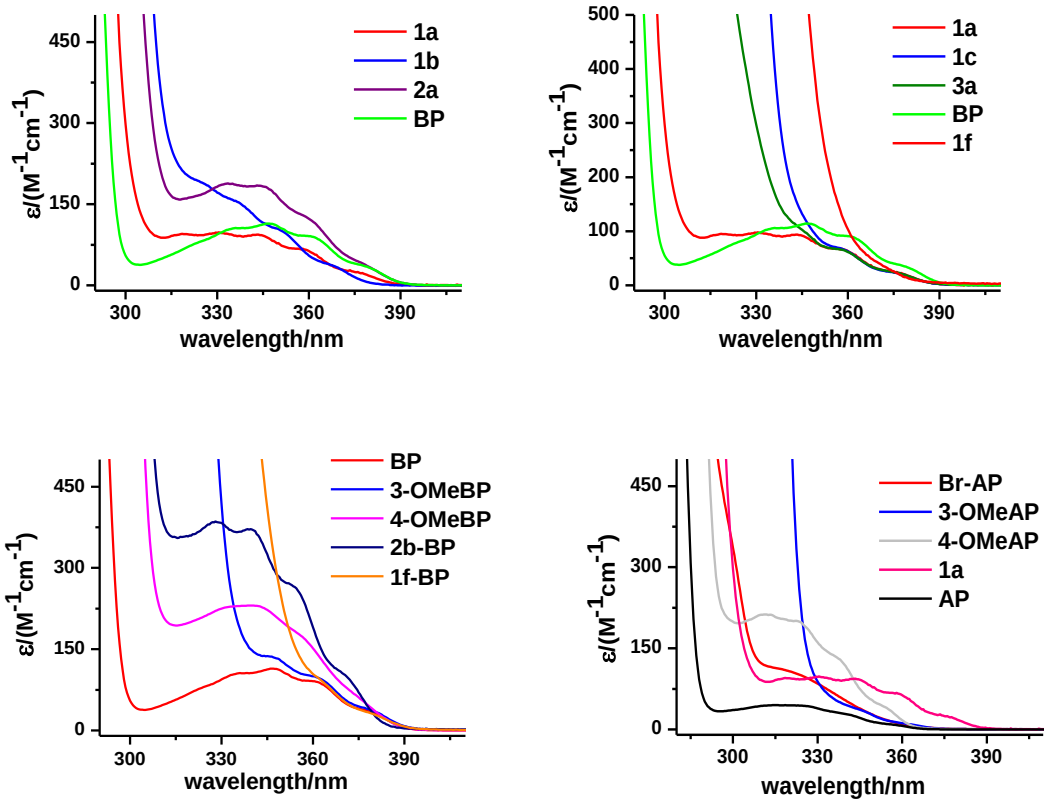


Fig. S5 Comparative UV-Vis ground-state absorption spectra of acetophenones, benzophenones and their substituted 2-bromo analogs in cyclohexane solvent; BP = benzophenone, AP = acetophenone.

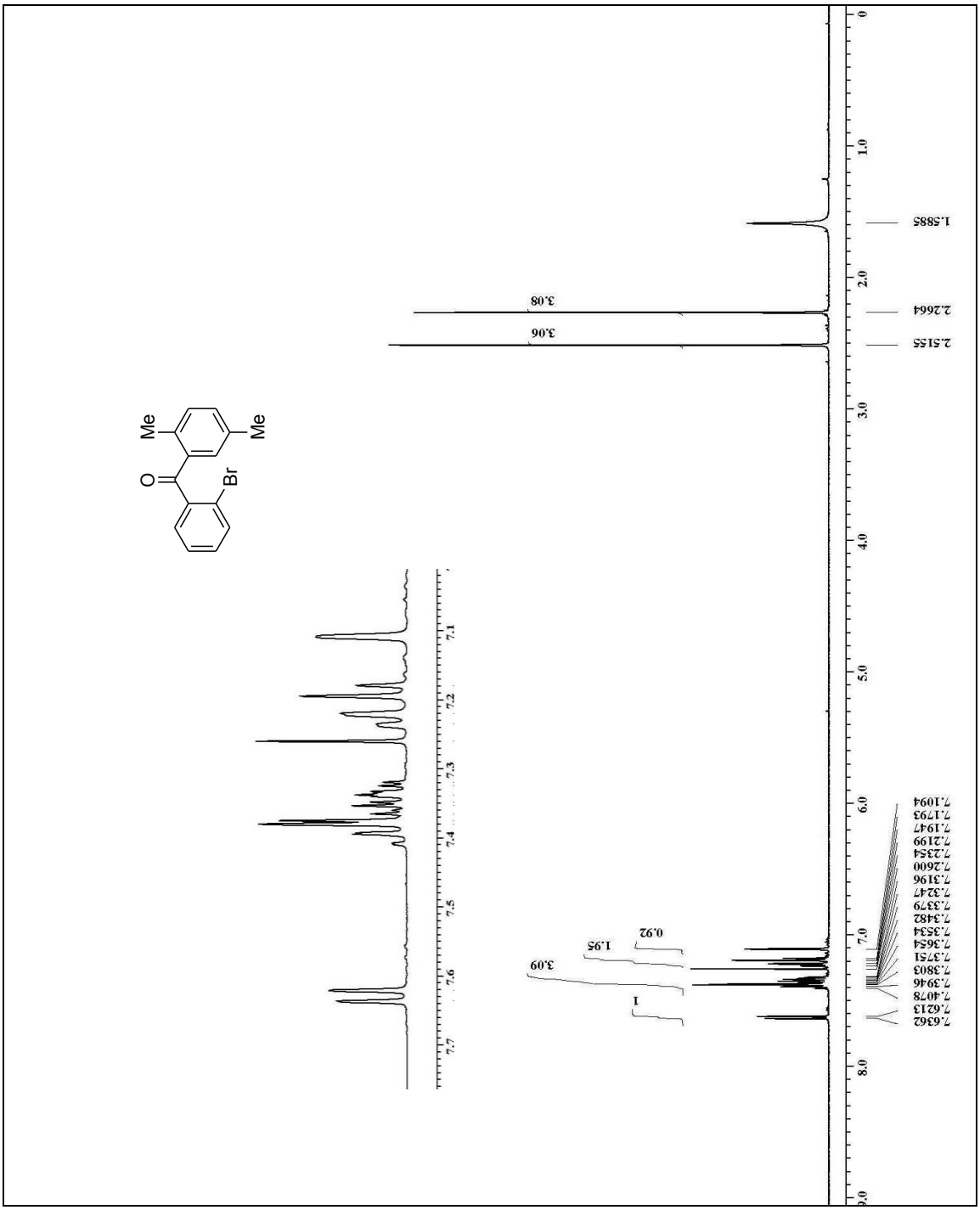


Figure S6. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-bromo-2′,5′-dimethylbenzophenone **1e**.

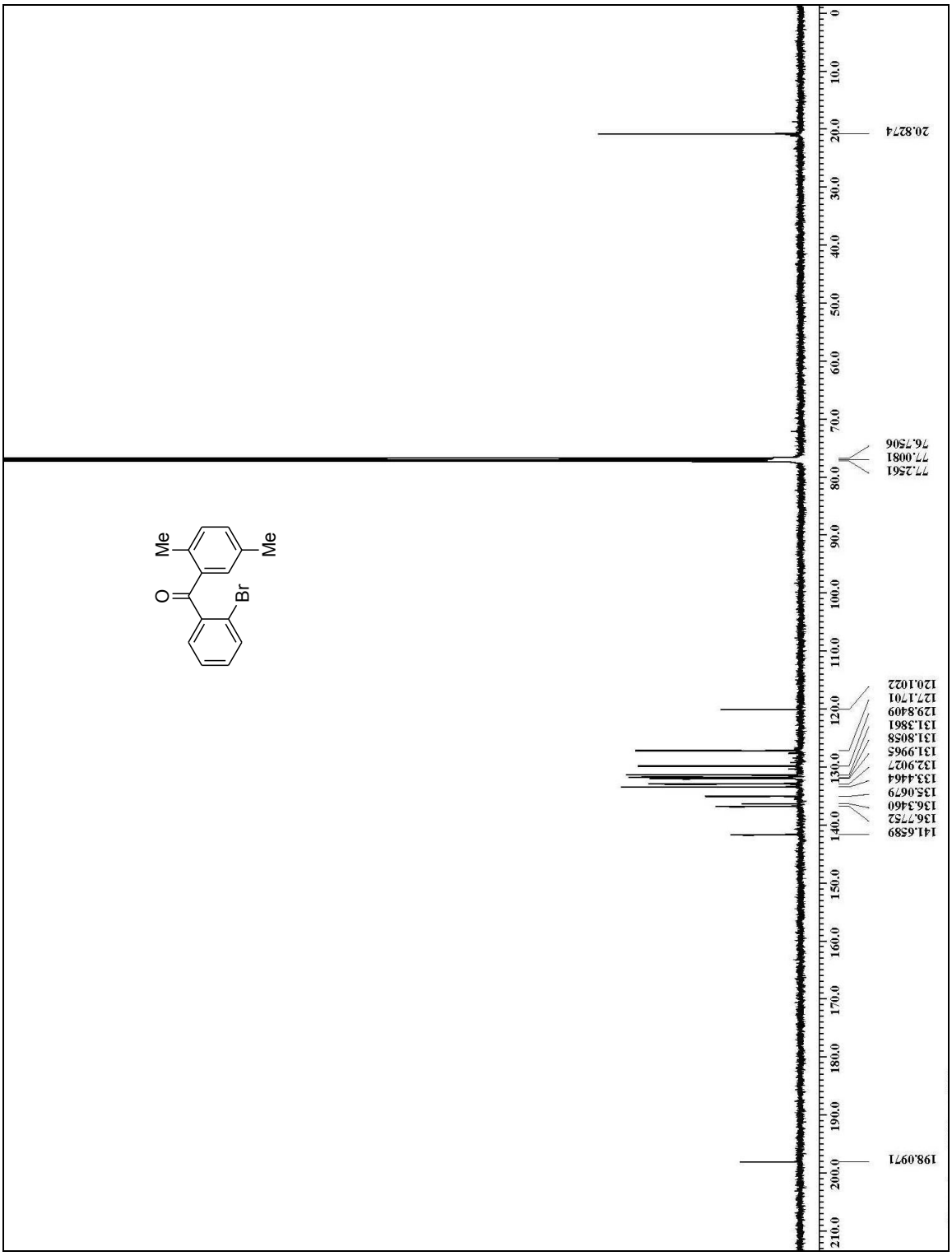


Figure S7. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of 2-bromo-2′,5′-dimethylbenzophenone **1e**.

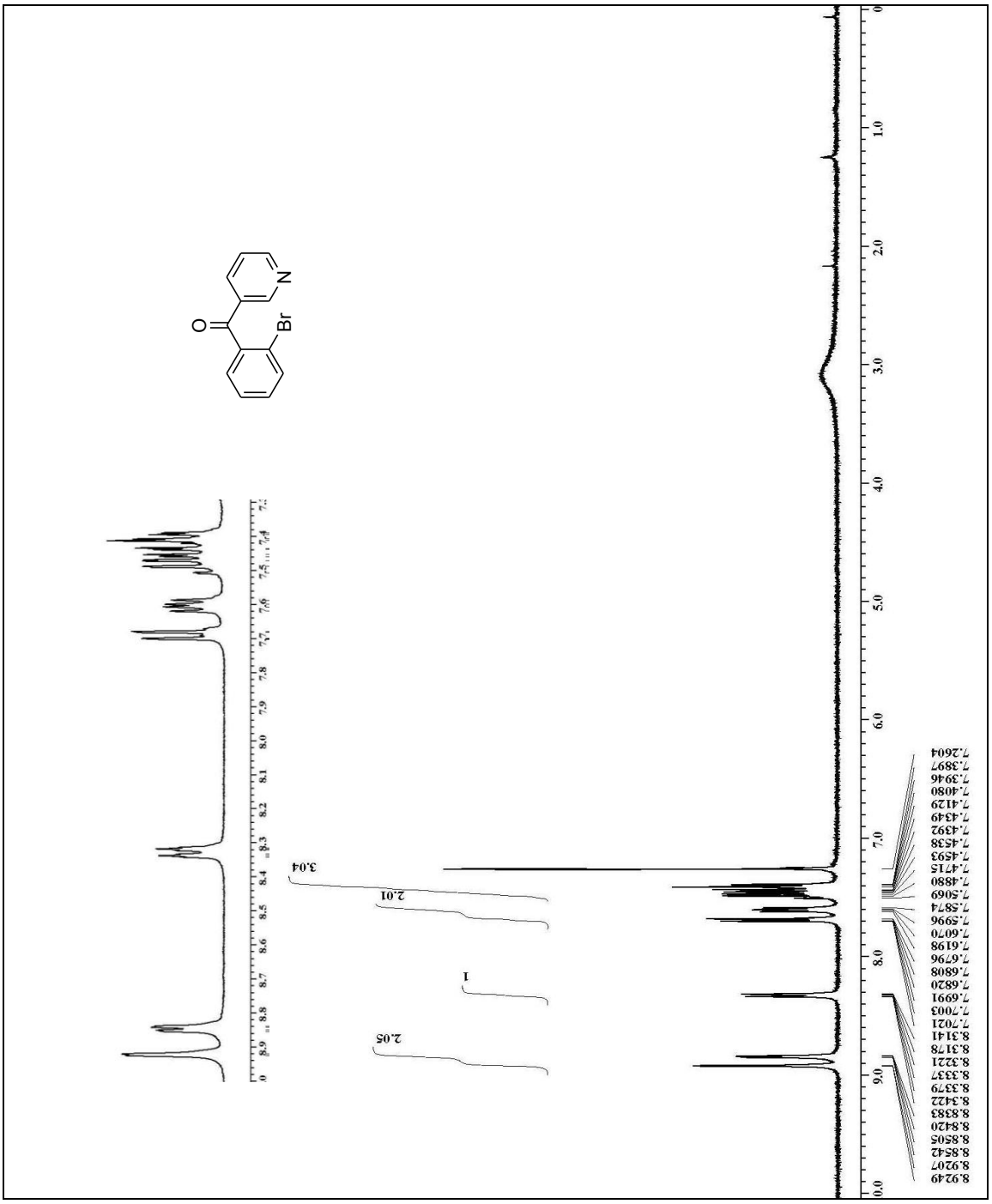


Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (2-bromophenyl)(3-pyridinyl)methanone **7**.

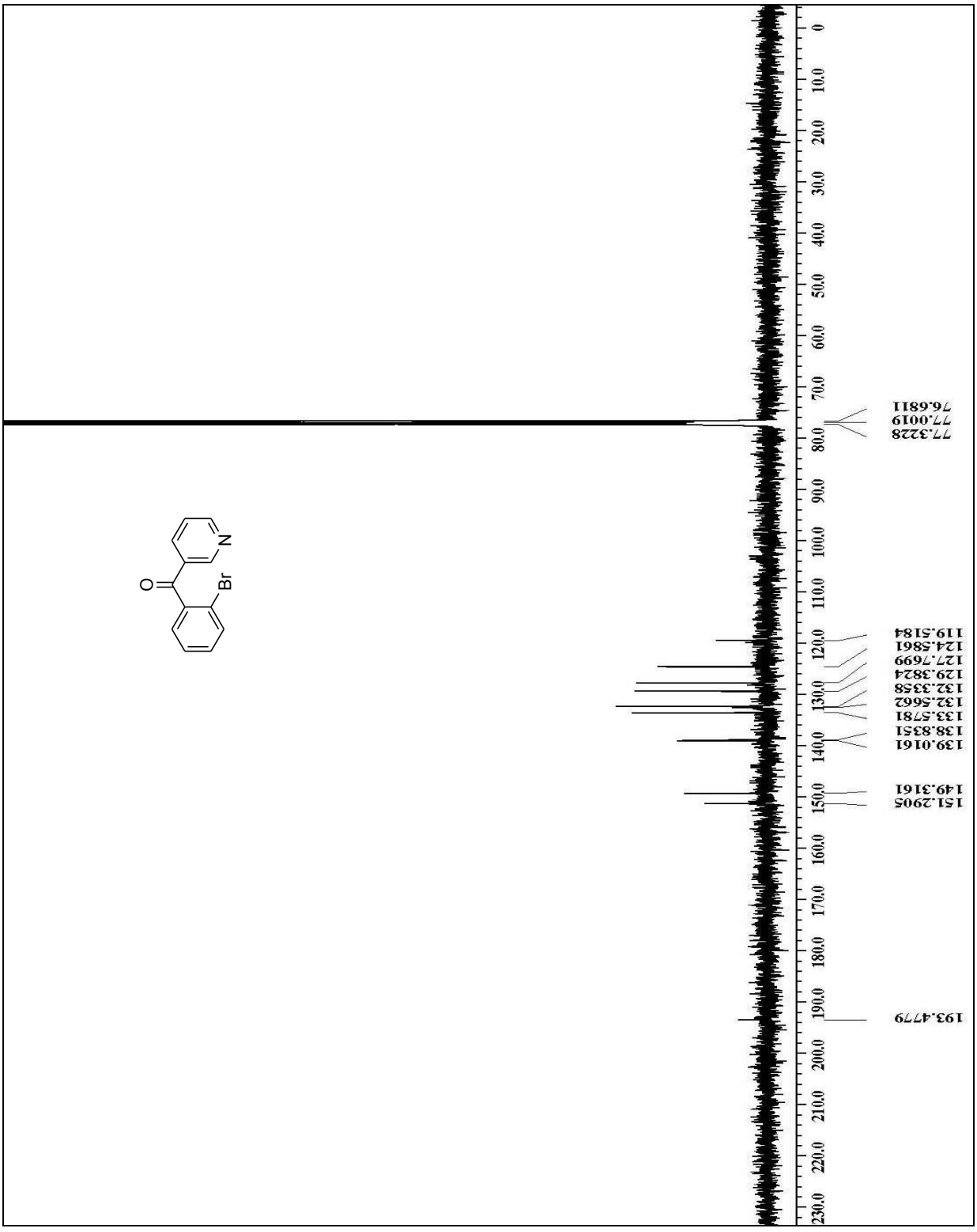


Figure S9. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (2-bromophenyl)(3-pyridinyl)methanone **7**.

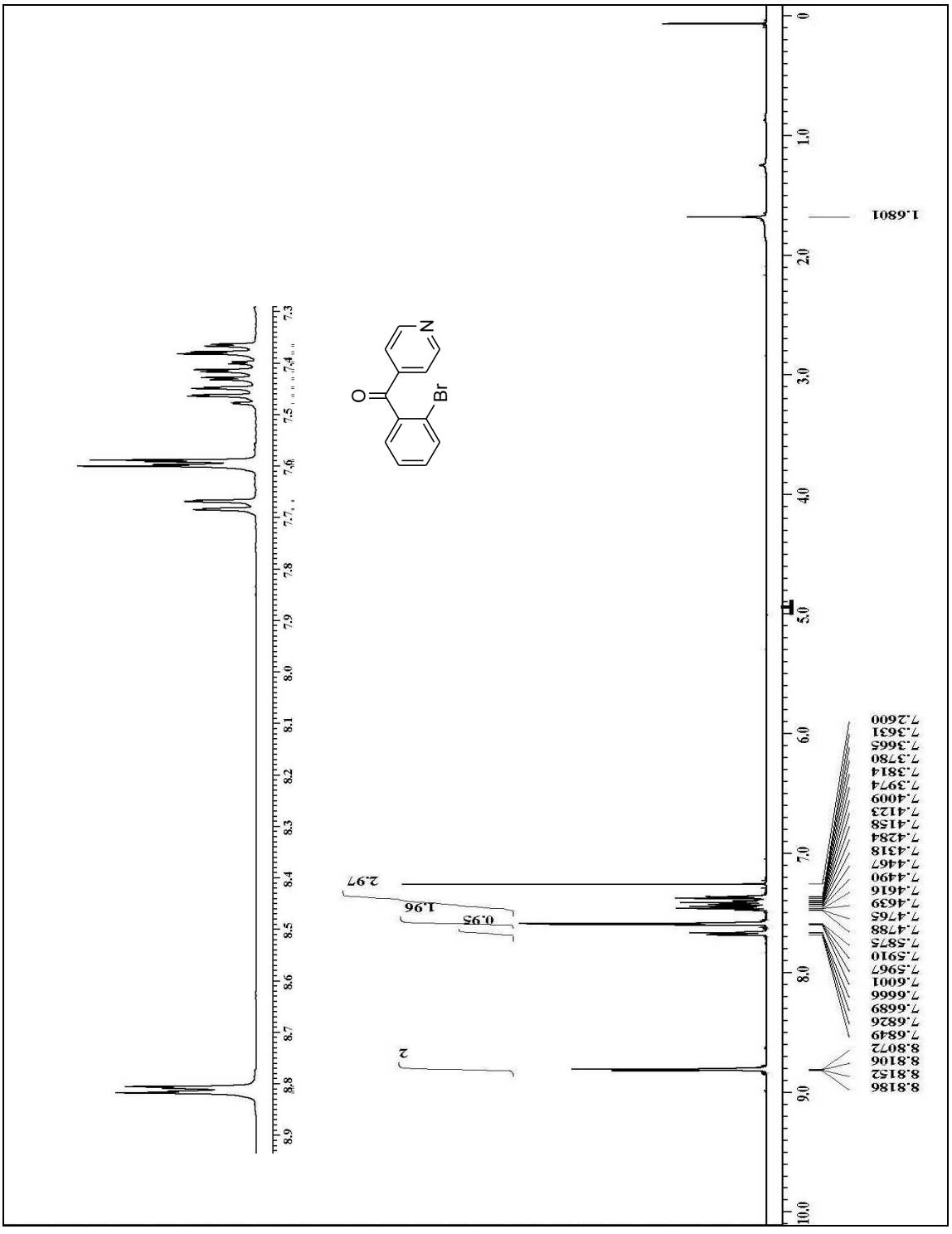


Figure S10. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (2-bromophenyl)(4-pyridinyl)methanone **8**.

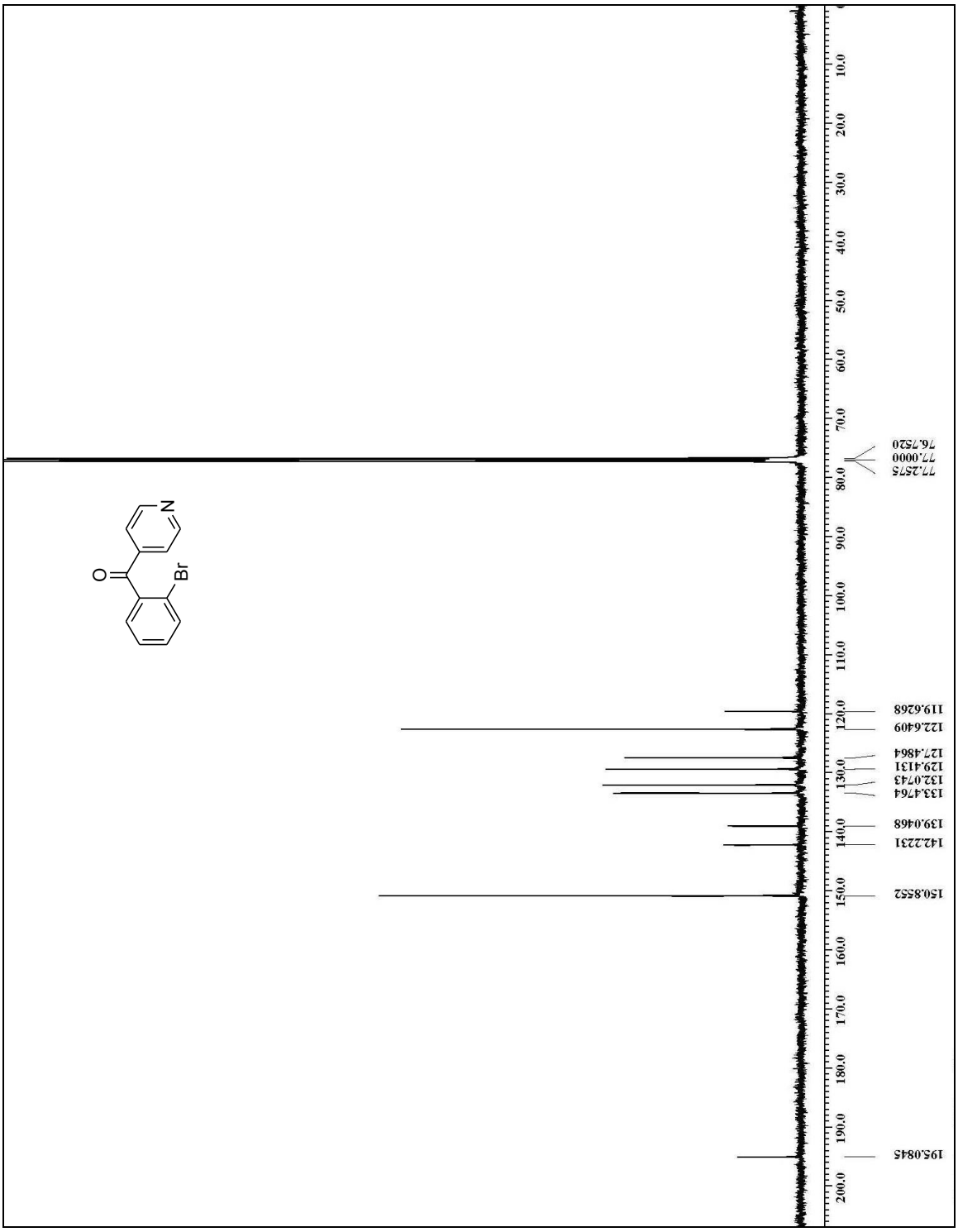


Figure S11. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of (2-bromophenyl)(4-pyridinyl)methanone **8.**

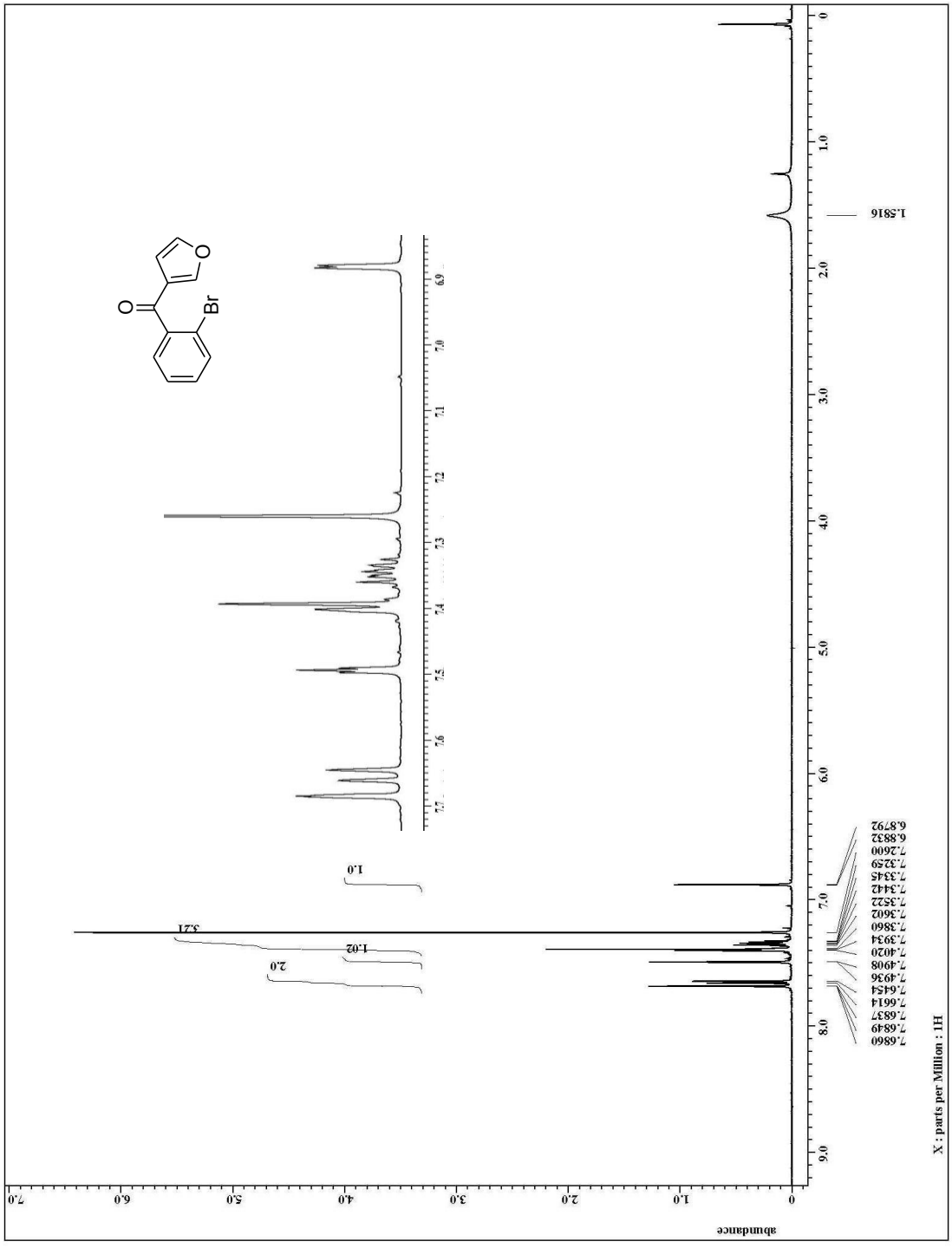


Figure S12. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (2-bromophenyl)(3-furanyl)methanone **9**.

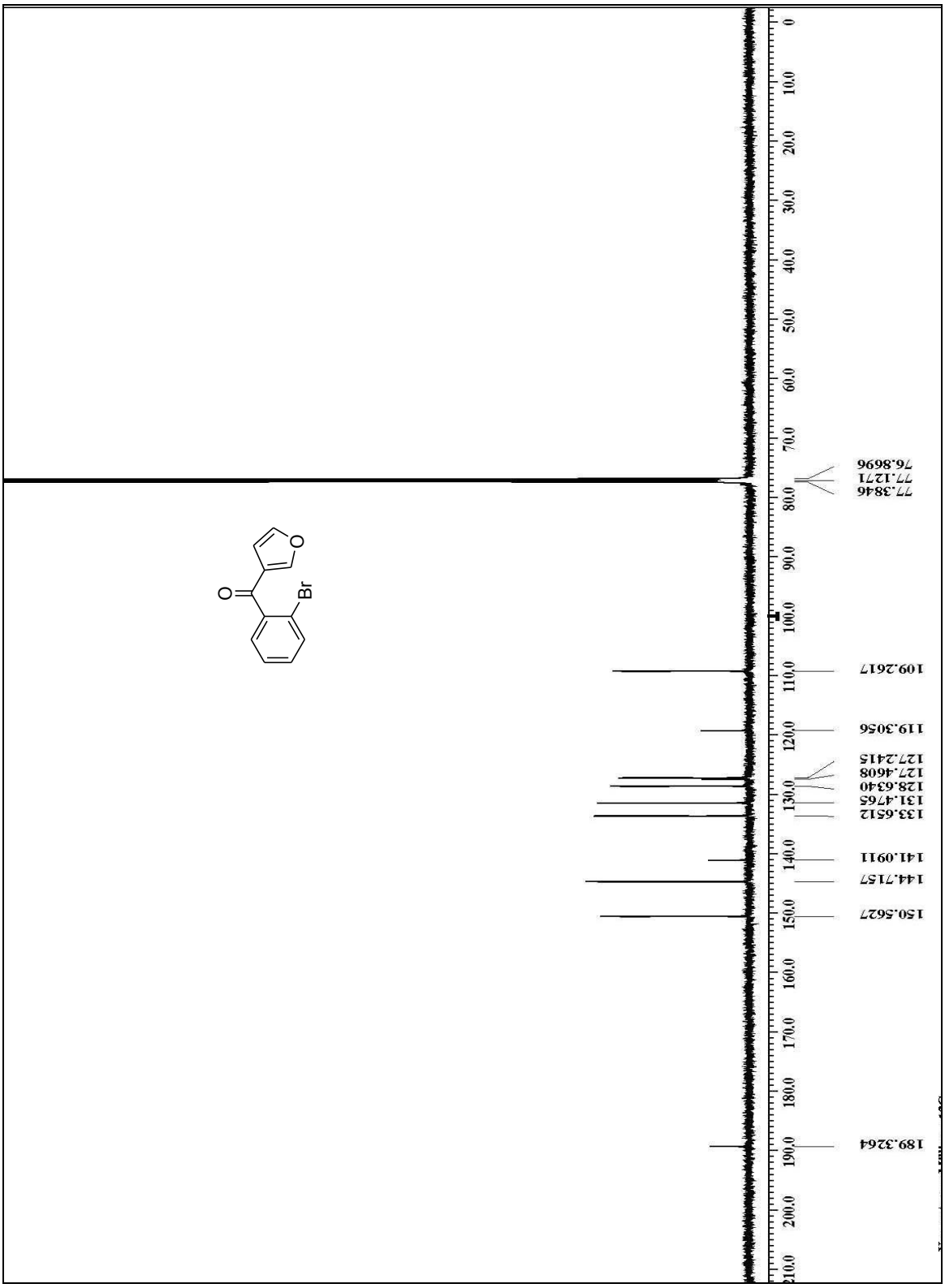


Figure S13. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of (2-bromophenyl)(3-furanyl)methanone **9**.

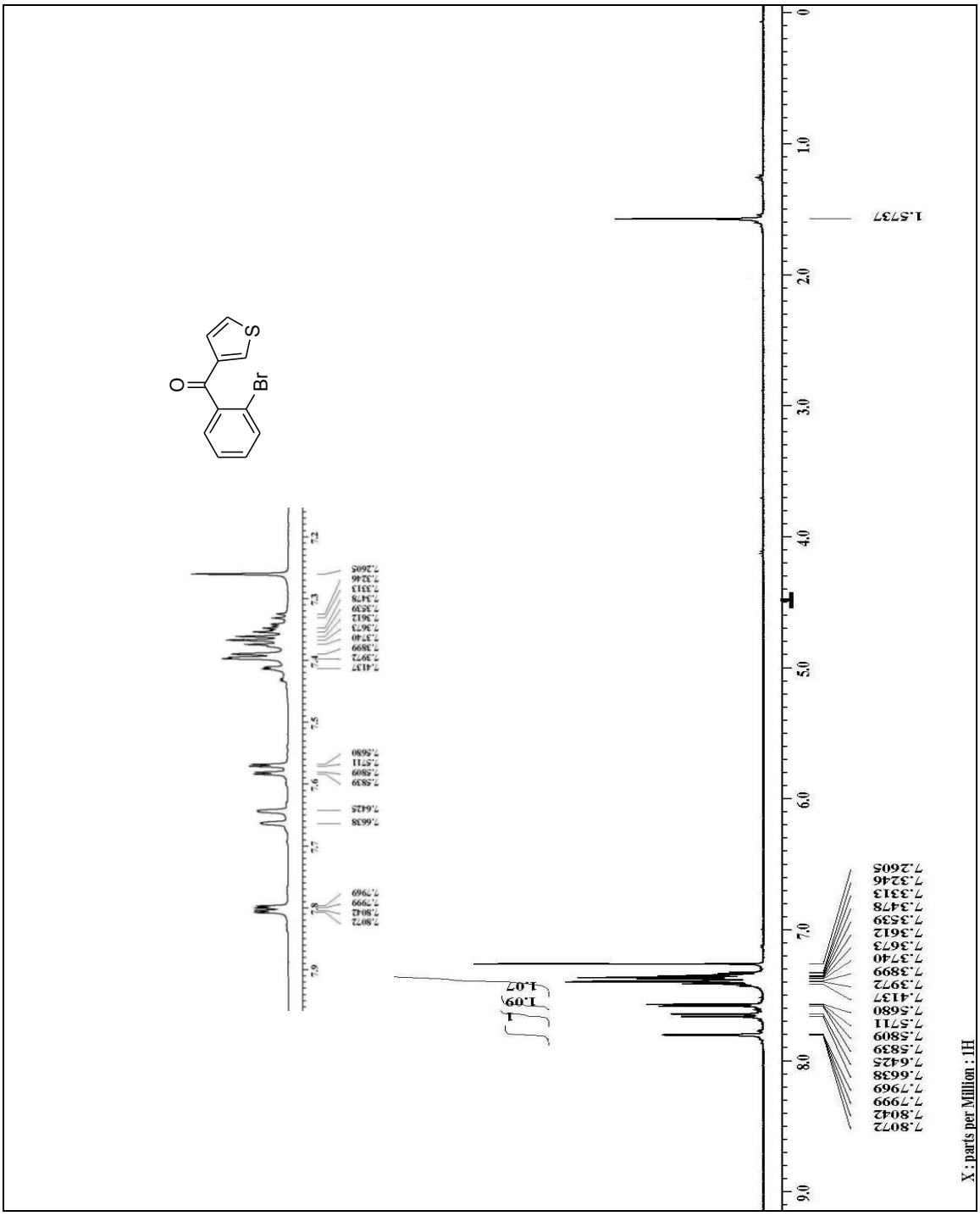


Figure S14. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (2-bromophenyl)(3-thionyl)methanone **10a**.

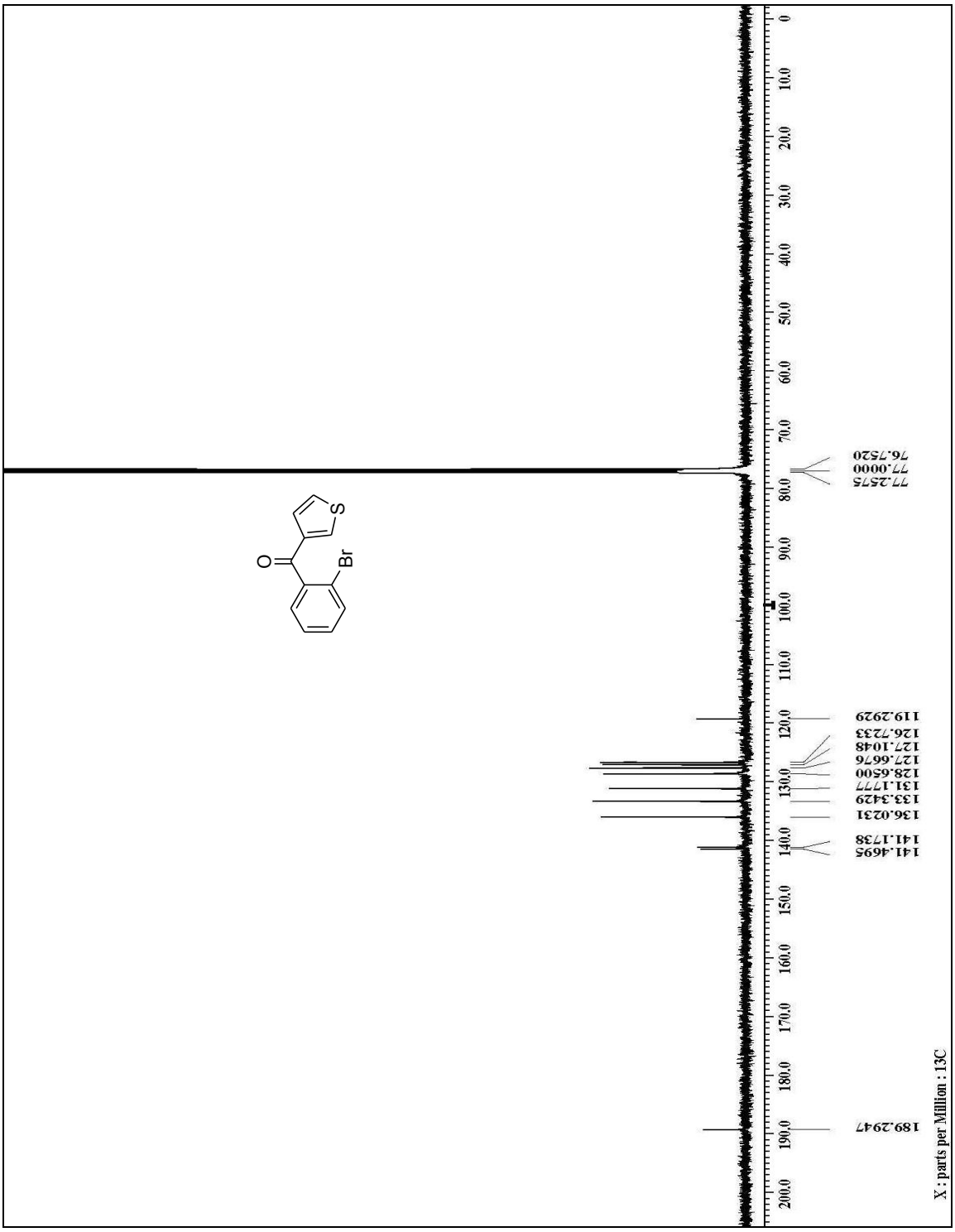


Figure S15. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of (2-bromophenyl)(3-thionyl)methanone **10a**.

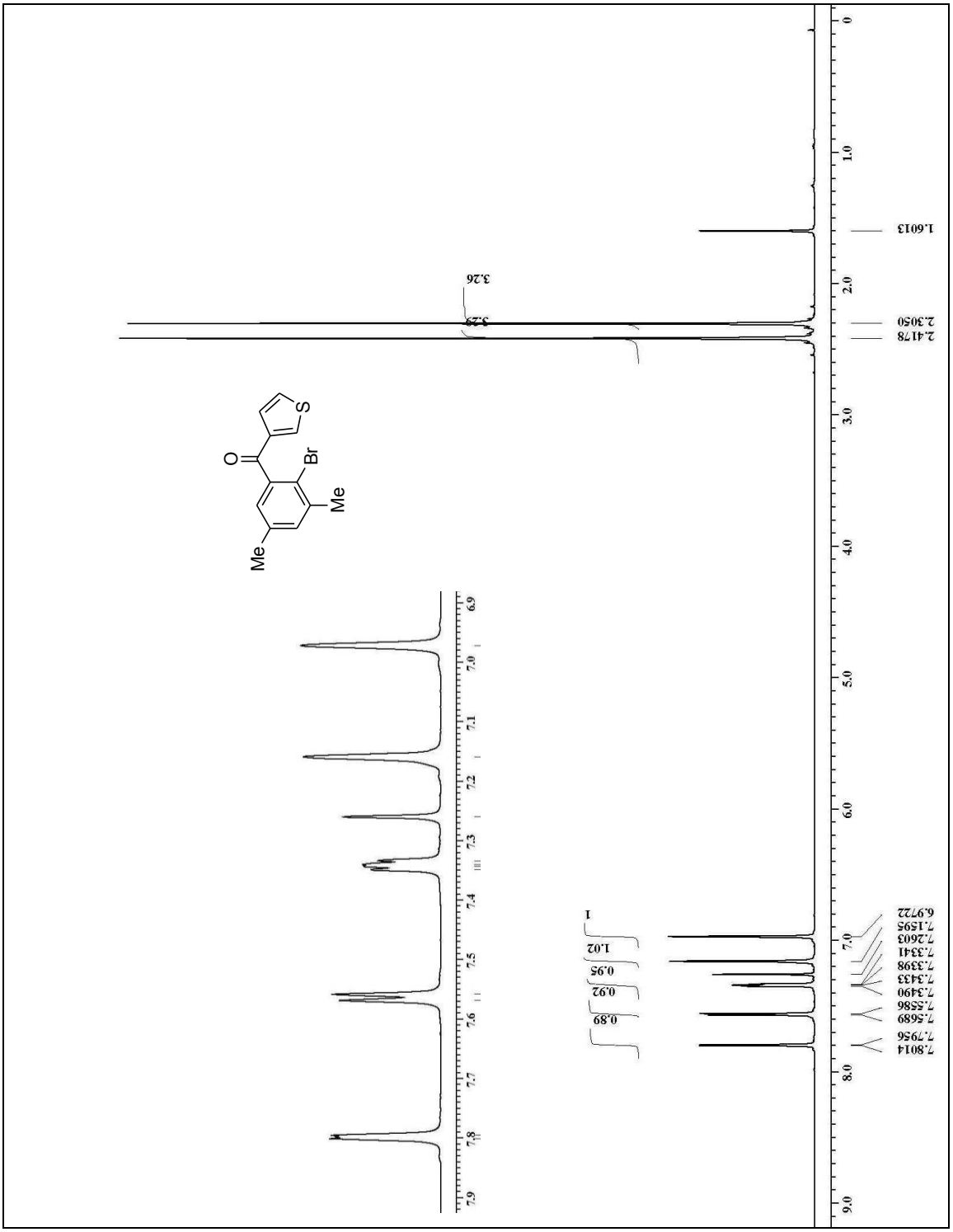


Figure S16. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (2-bromo-3,5-dimethylphenyl)(3-thionyl)methanone **10b**.

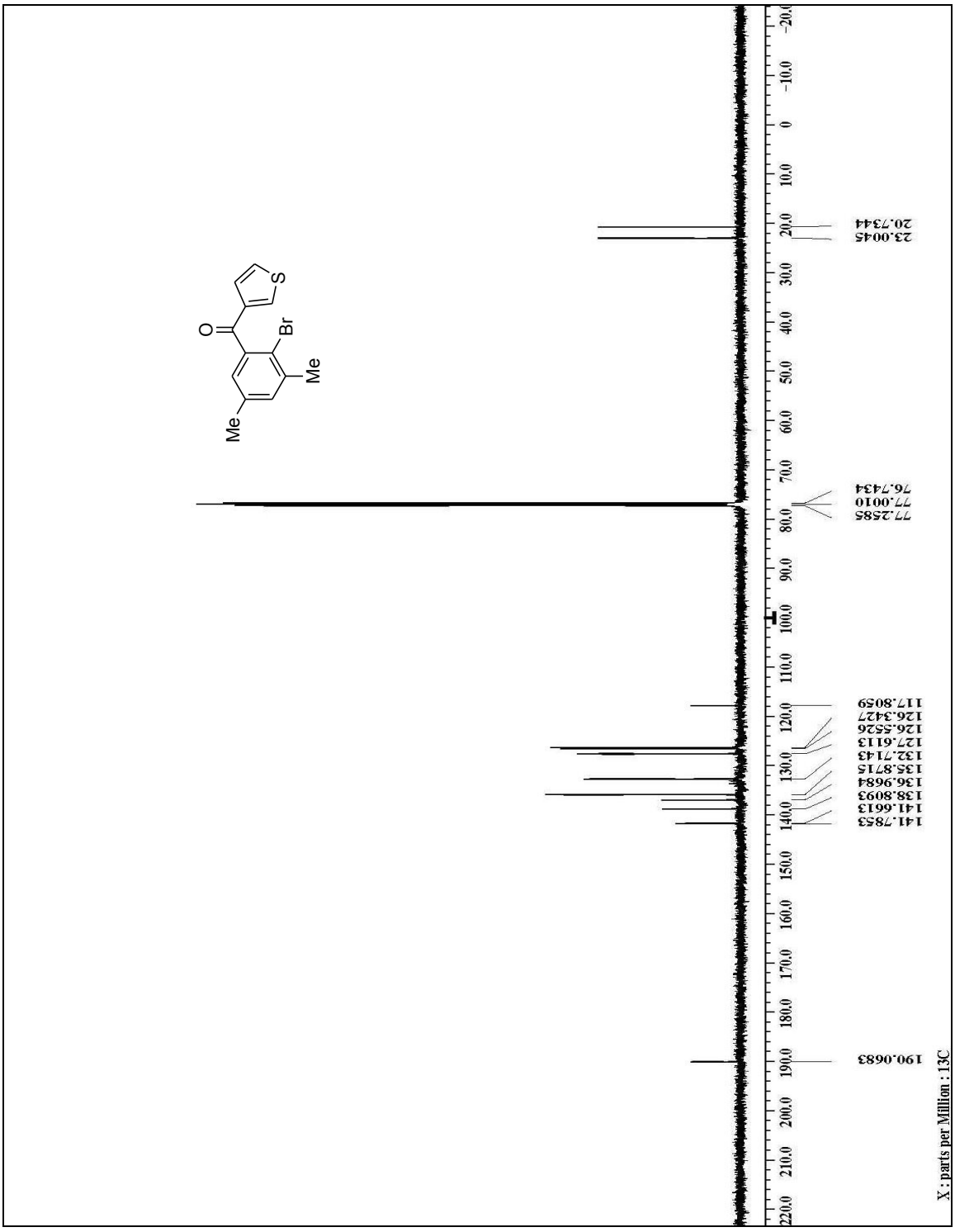


Figure S17. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of (2-bromo-3,5-dimethylphenyl)(3-thionyl)methanone **10b**.

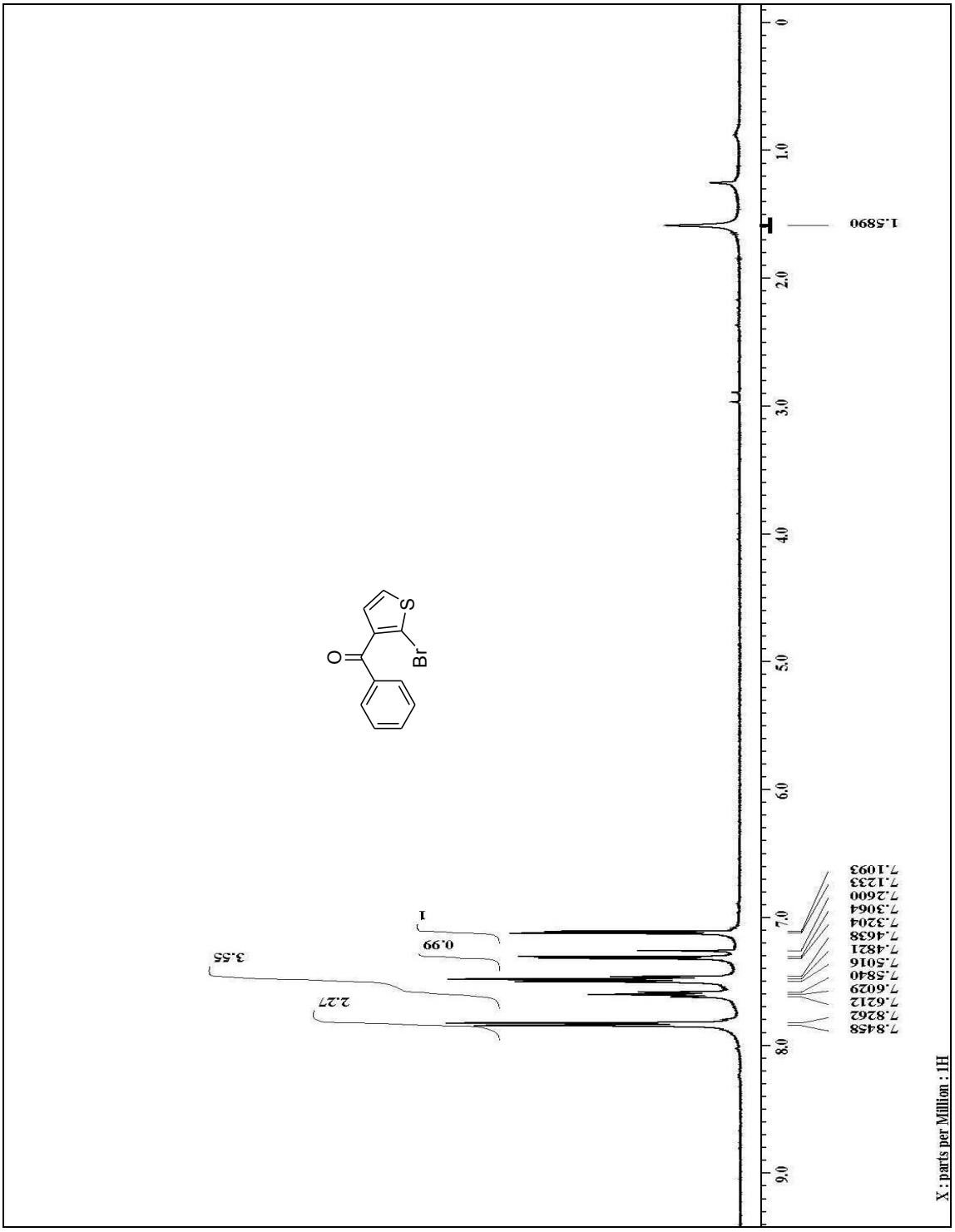


Figure S18. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (2-bromophenyl)(3-thionyl)methanone **11**.

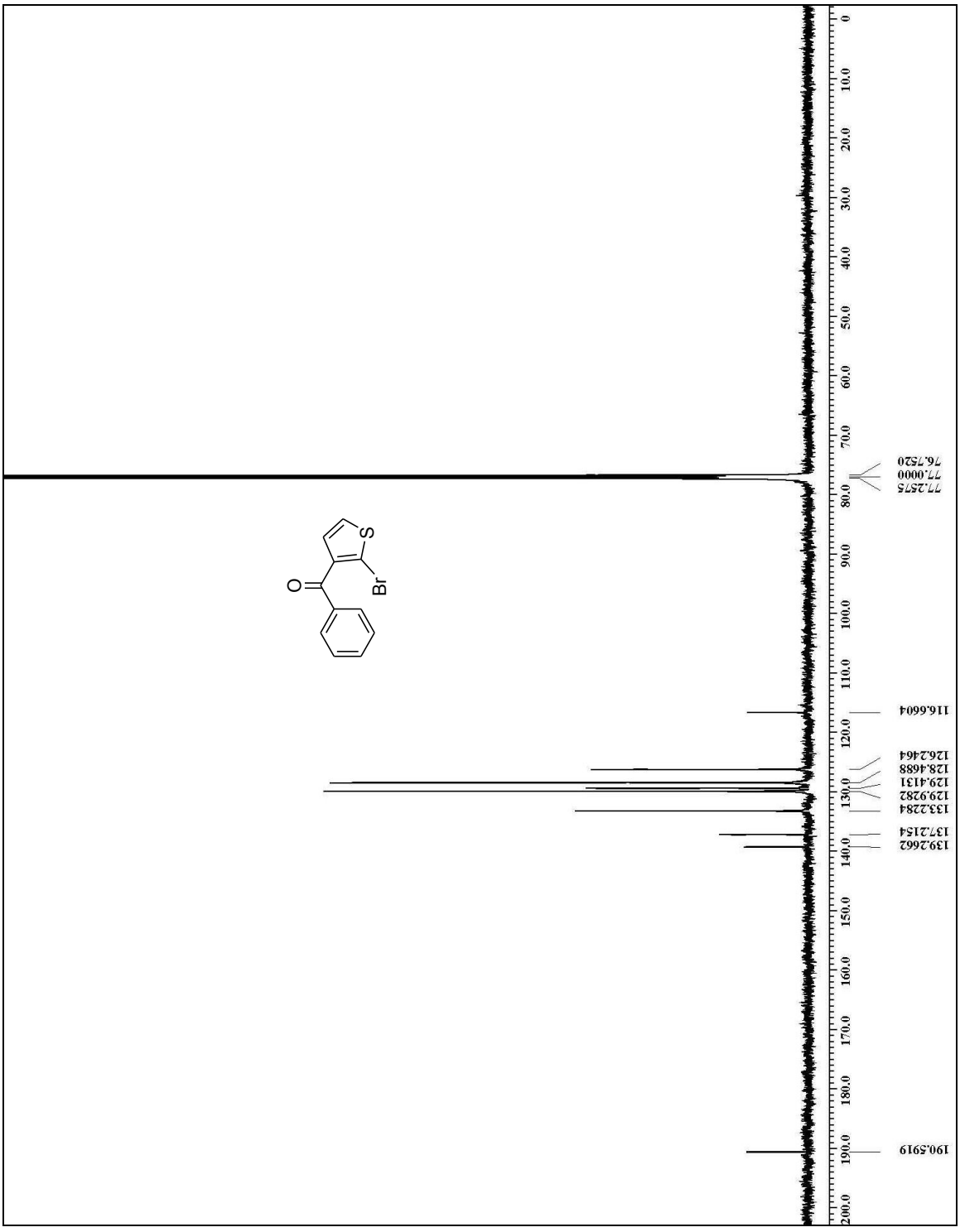


Figure S19. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of (2-bromophenyl)(3-thionyl)methanone **11**.

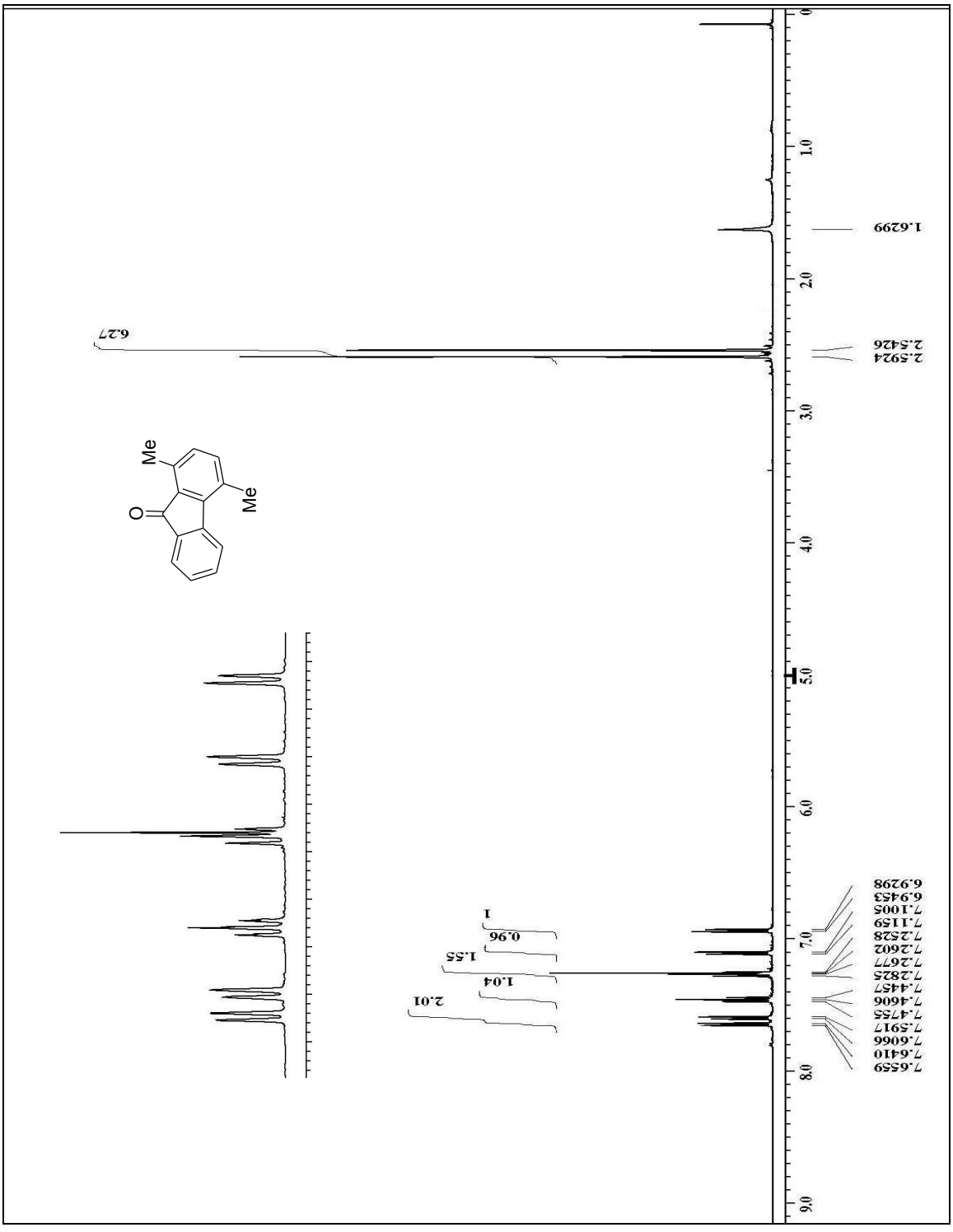


Figure S20. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 1,4-dimethylfluoren-9-one (**1e-Fl**).

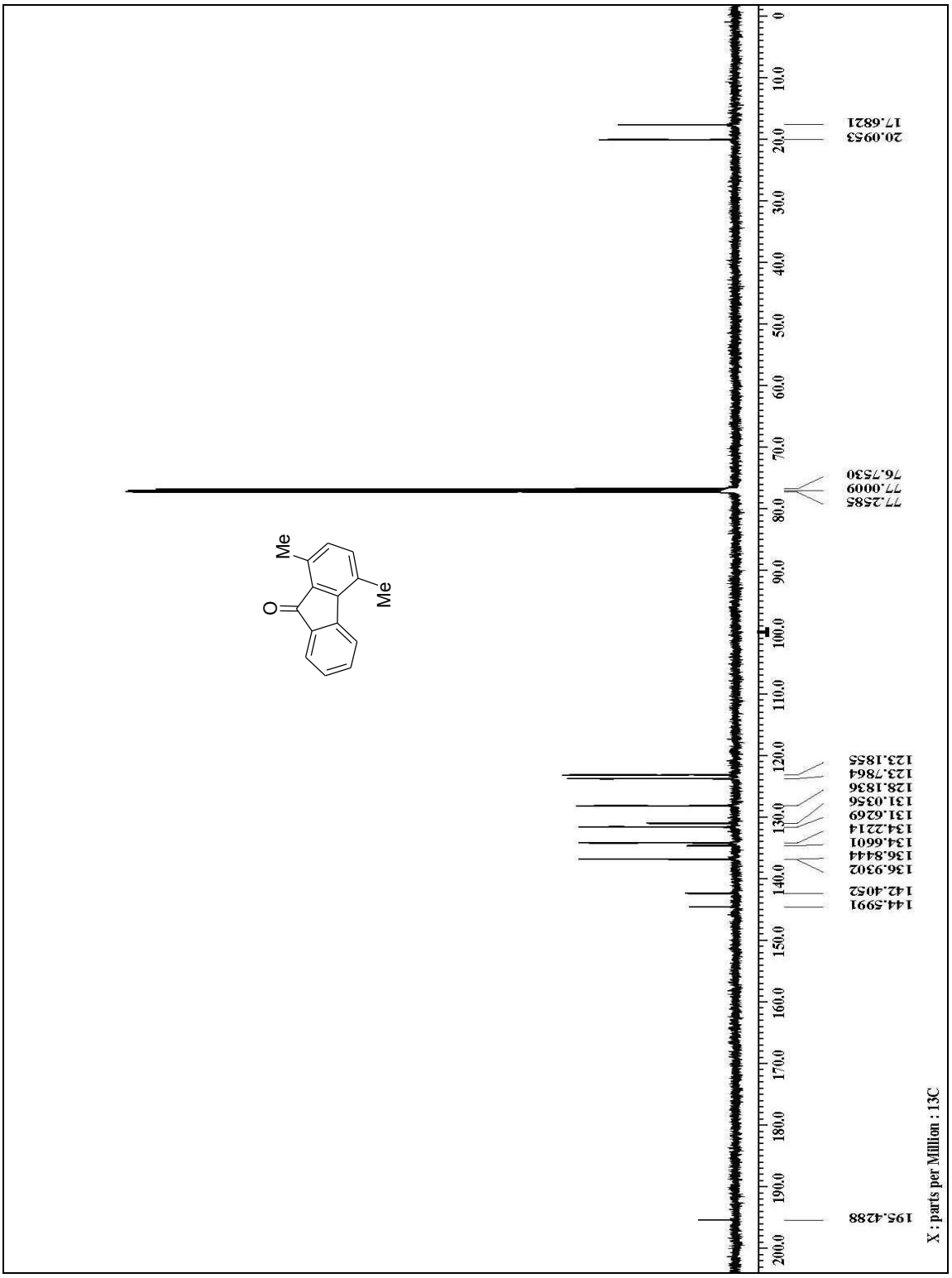


Figure S21. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of 1,4-dimethylfluoren-9-one (**1e-Fl**).

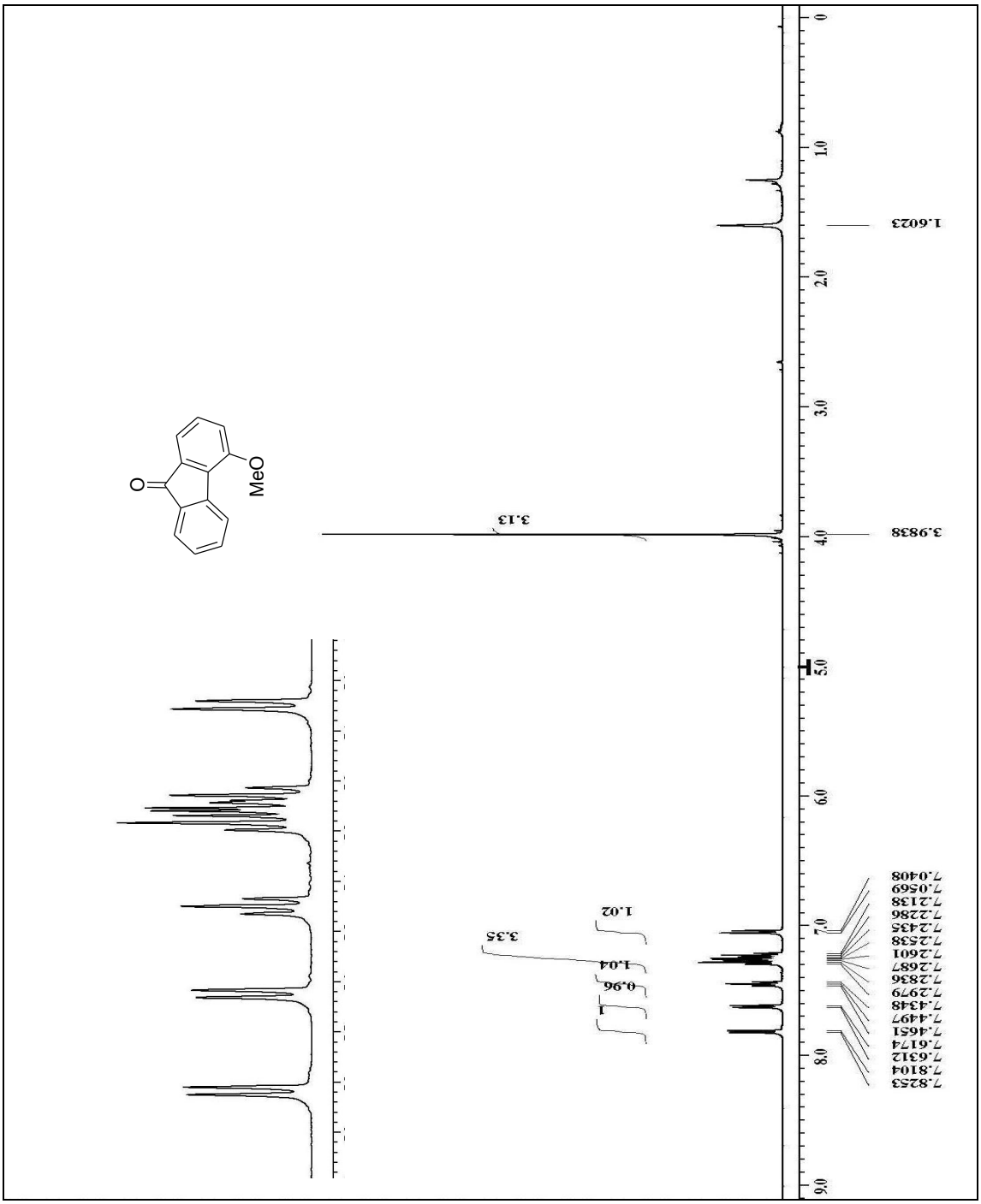


Figure S22. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 4-methoxyfluoren-9-one (**3e-Fl-2**).

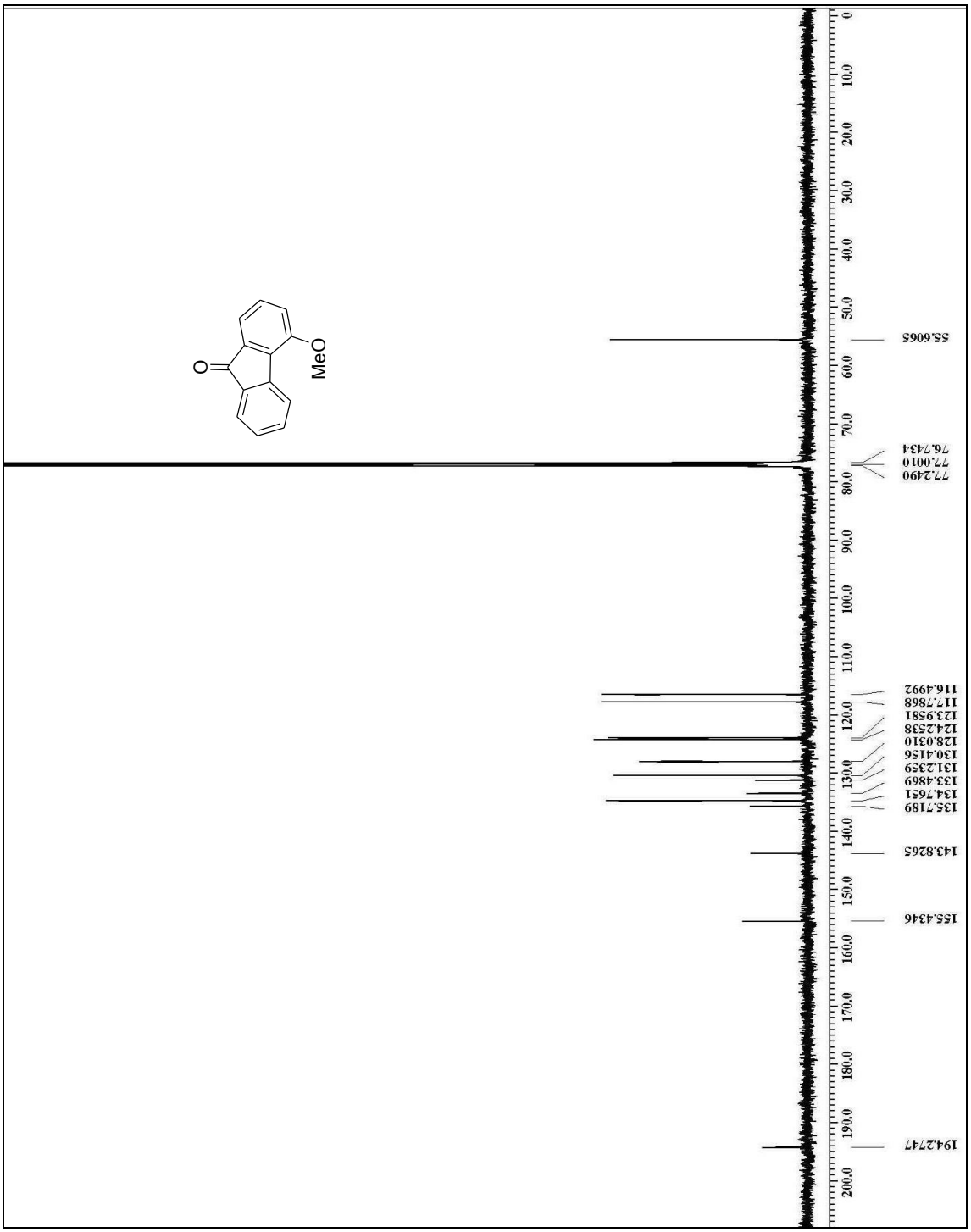


Figure S23. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of 4-methoxyfluoren-9-one (**3e-Fl-2**).

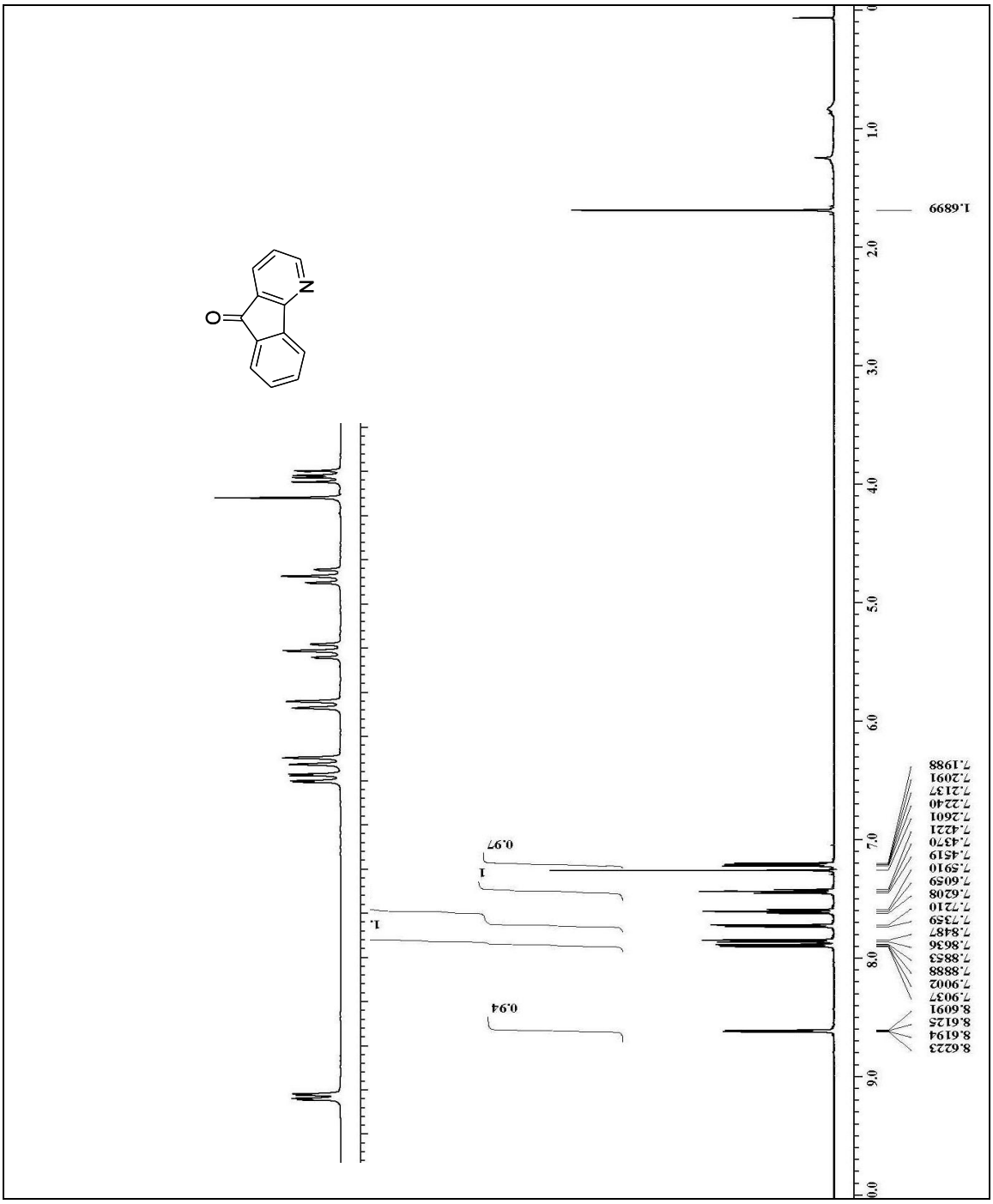


Figure S24. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of indeno[1,2-*b*]pyridin-5-one (**7-Fl**).

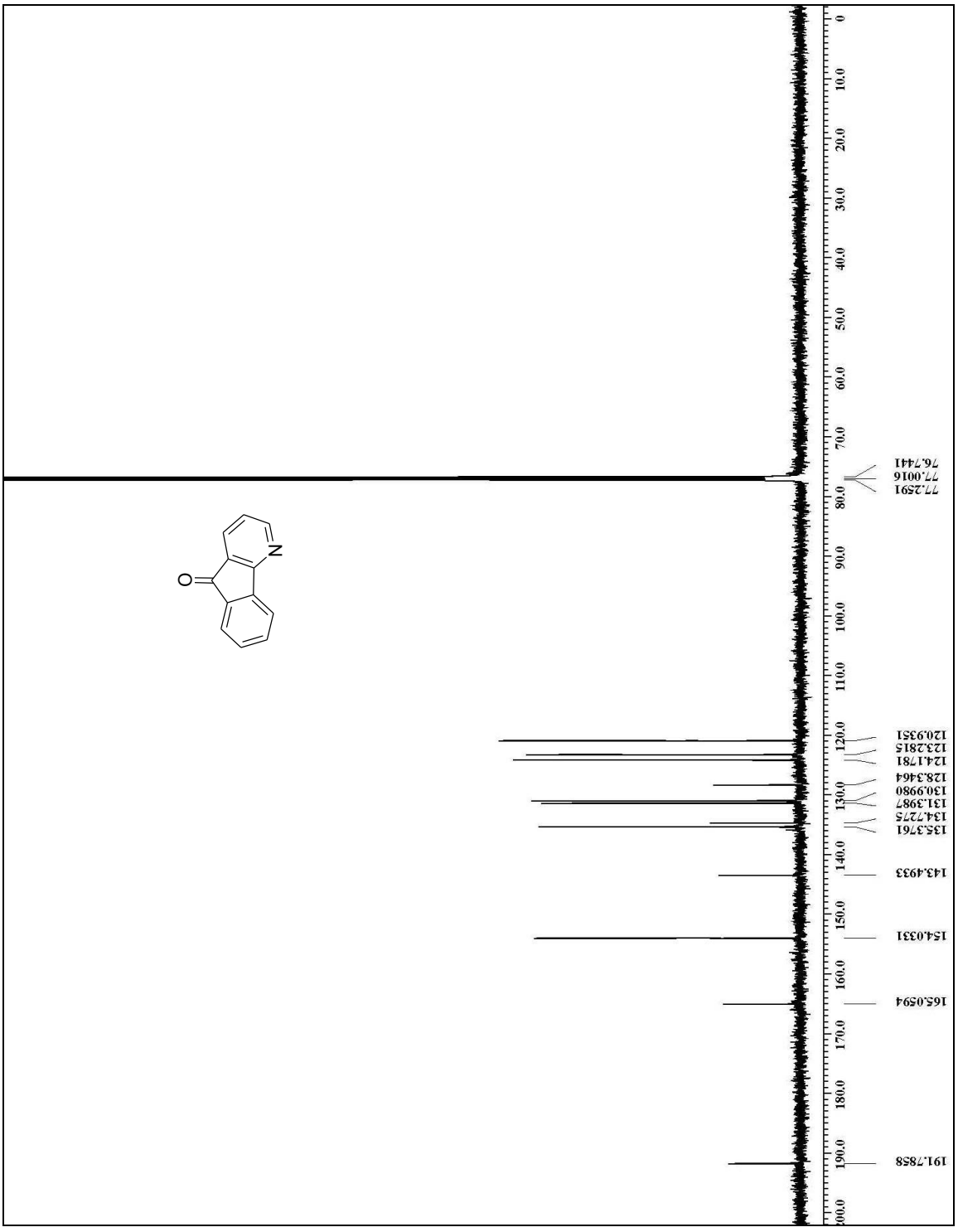


Figure S25. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of indeno[1,2-*b*]pyridin-5-one (**7-Fl**).

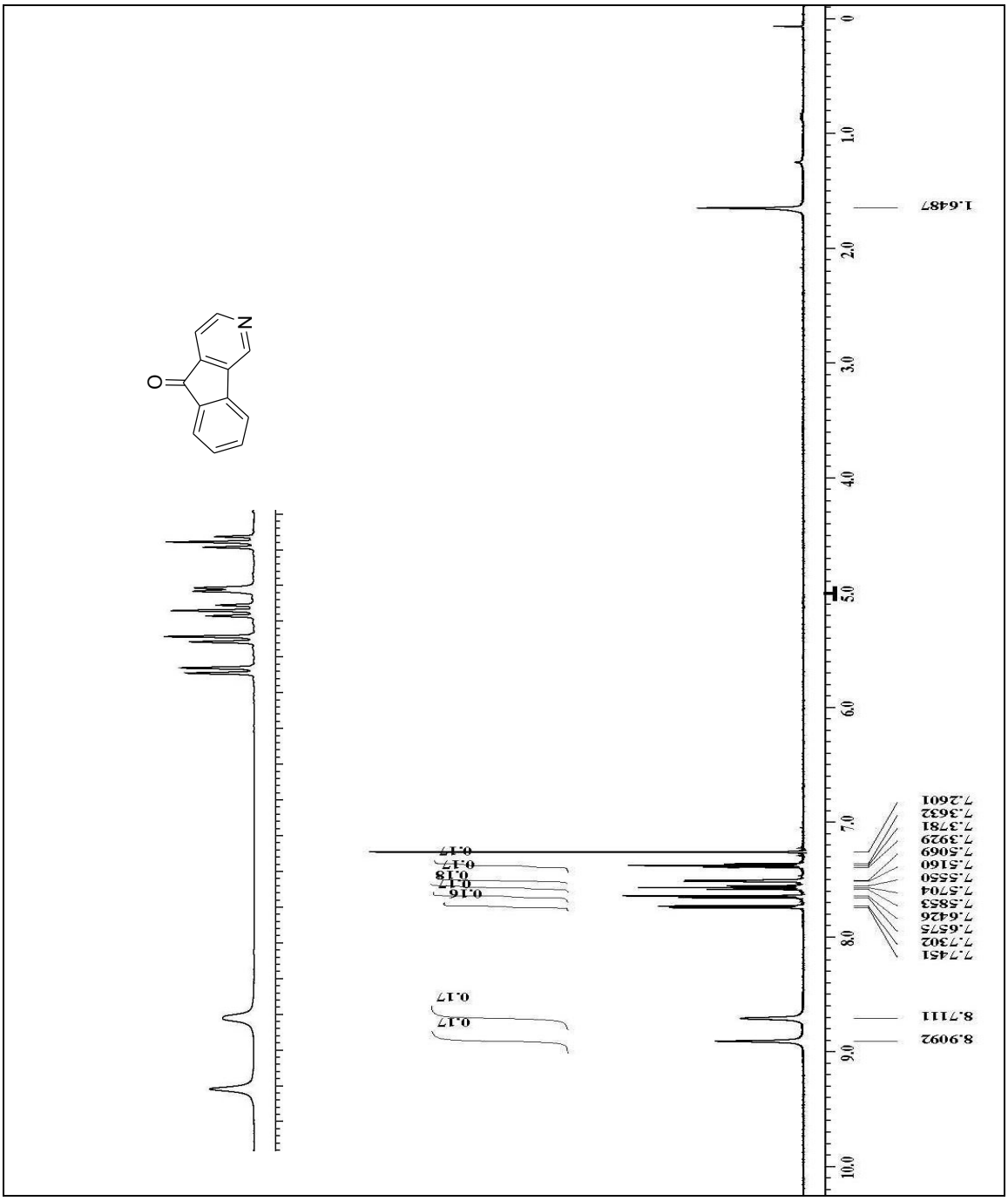


Figure S26. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 3-azafluoren-9-one (**8-Fl**).

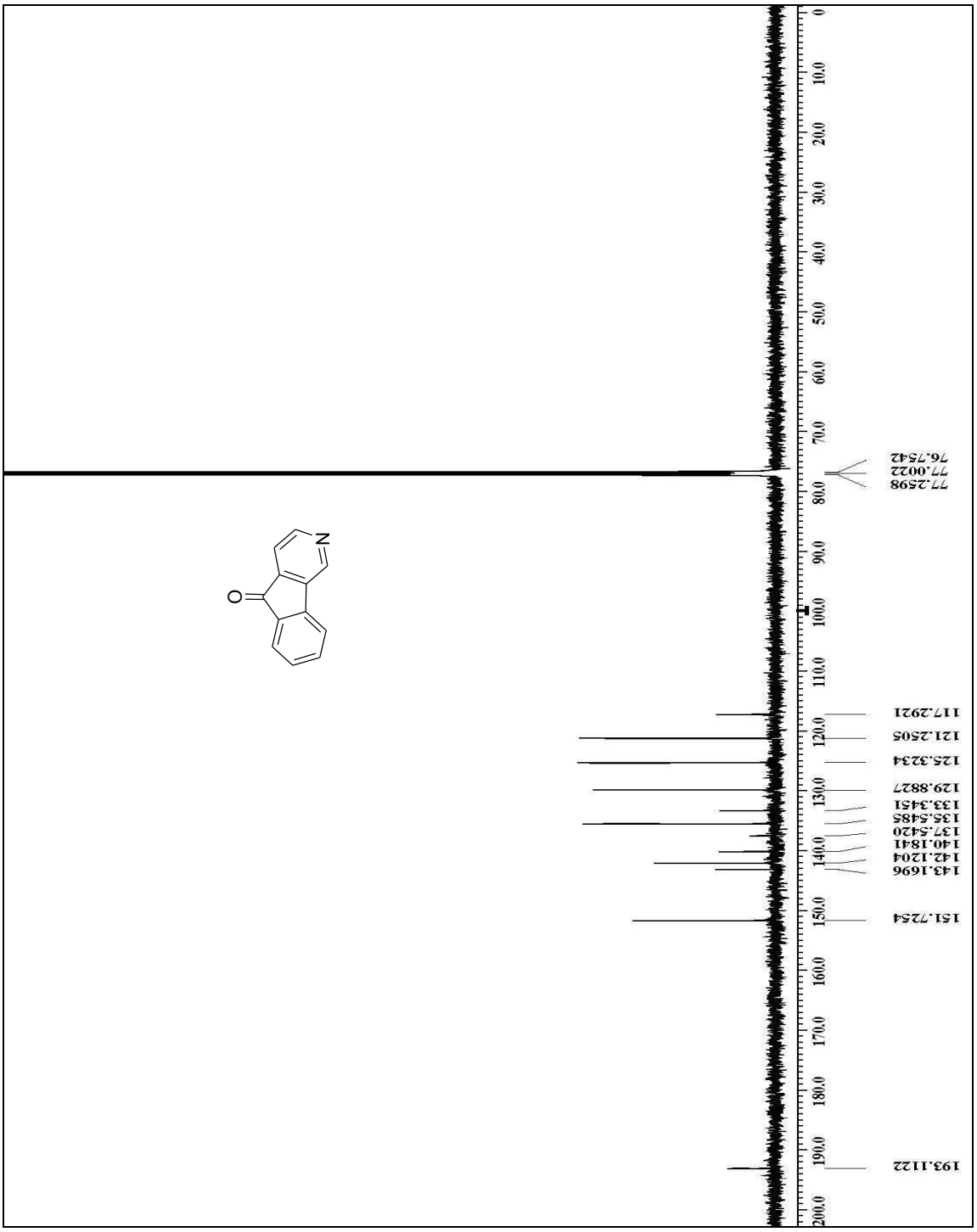


Figure S27. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of 3-azafluoren-9-one (**8-Fl**).

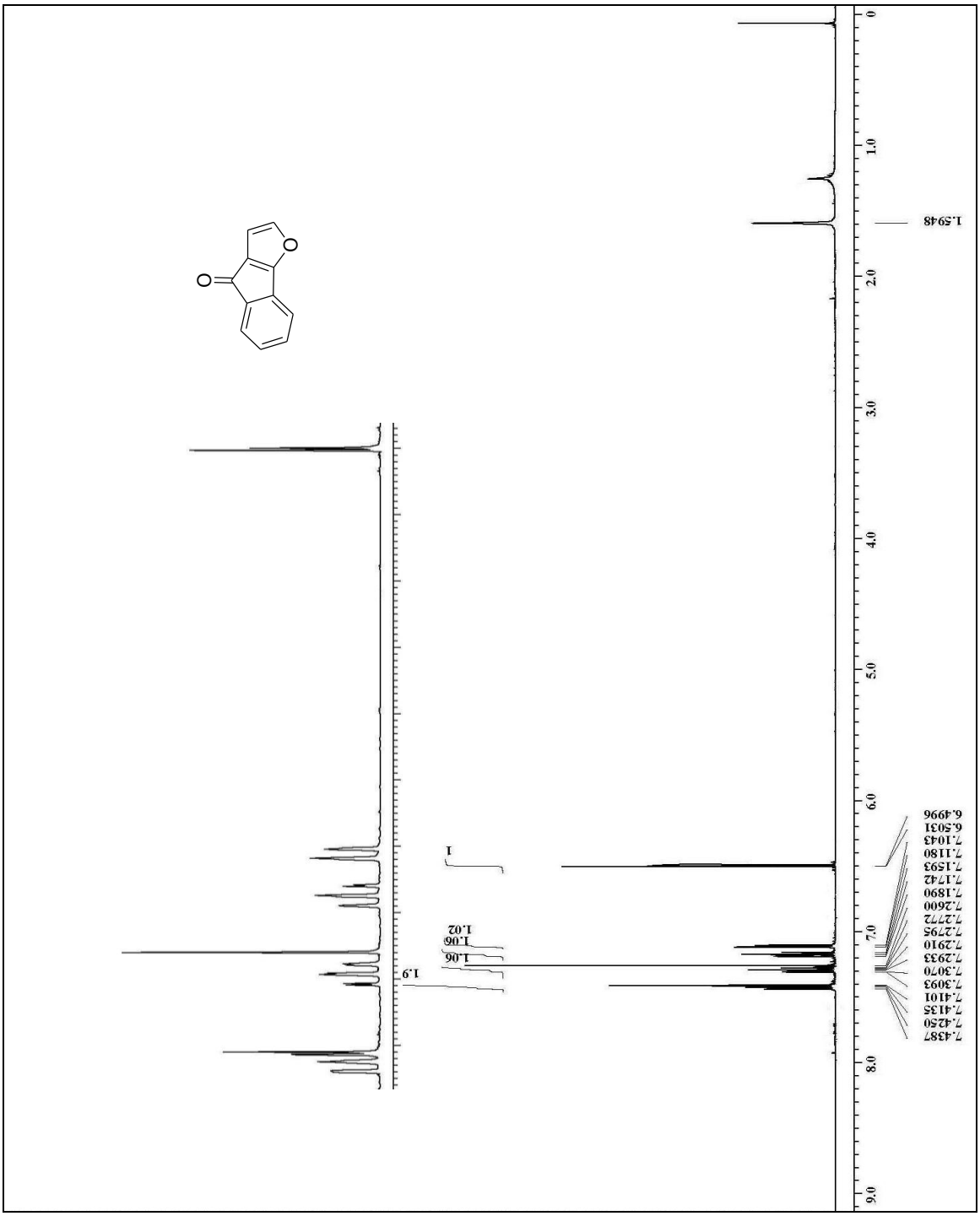


Figure S28. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of indeno[1,2-*b*]furan-4-one (**9-Fl**).

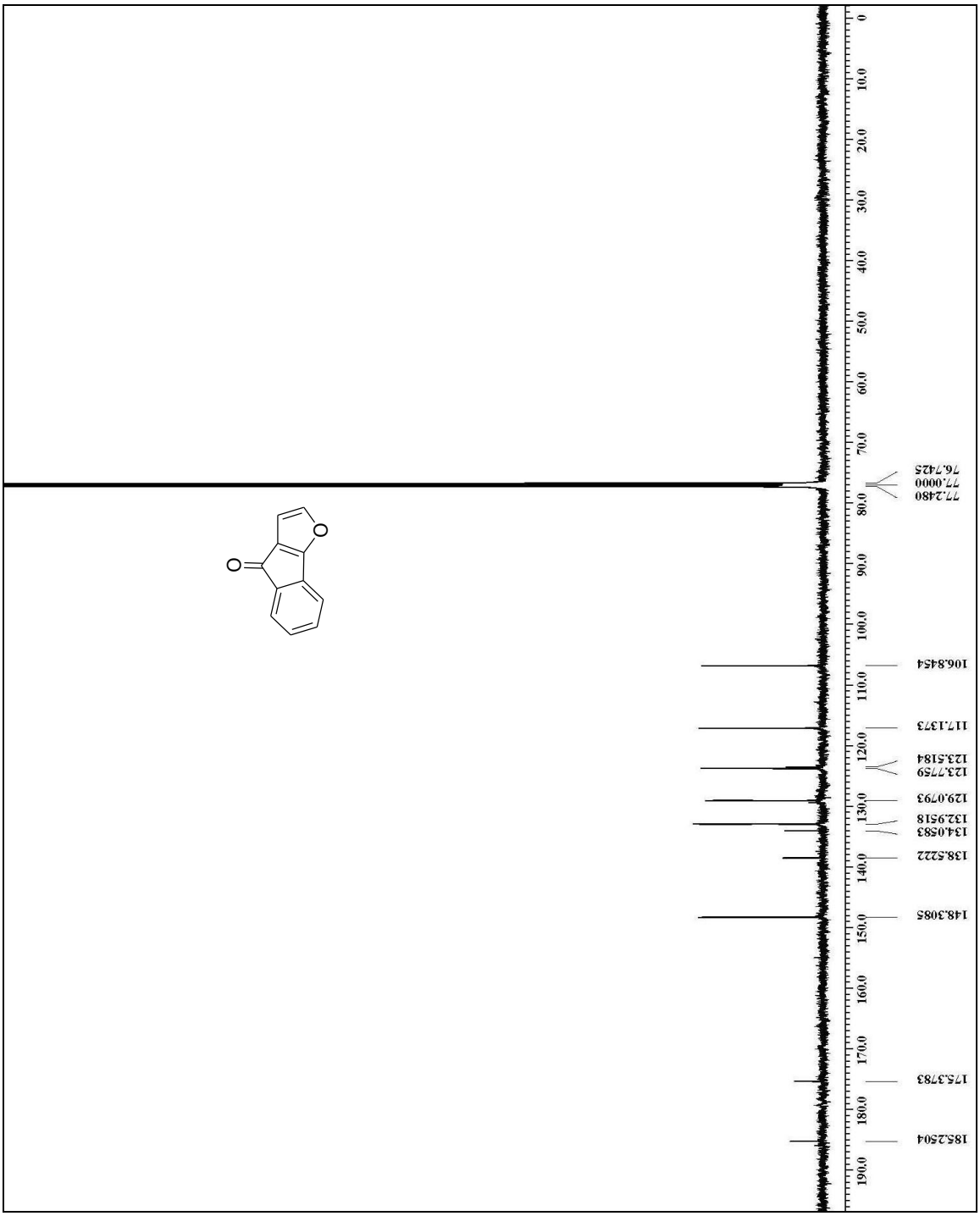


Figure S29. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of indeno[1,2-*b*]furan-4-one (**9-Fl**).

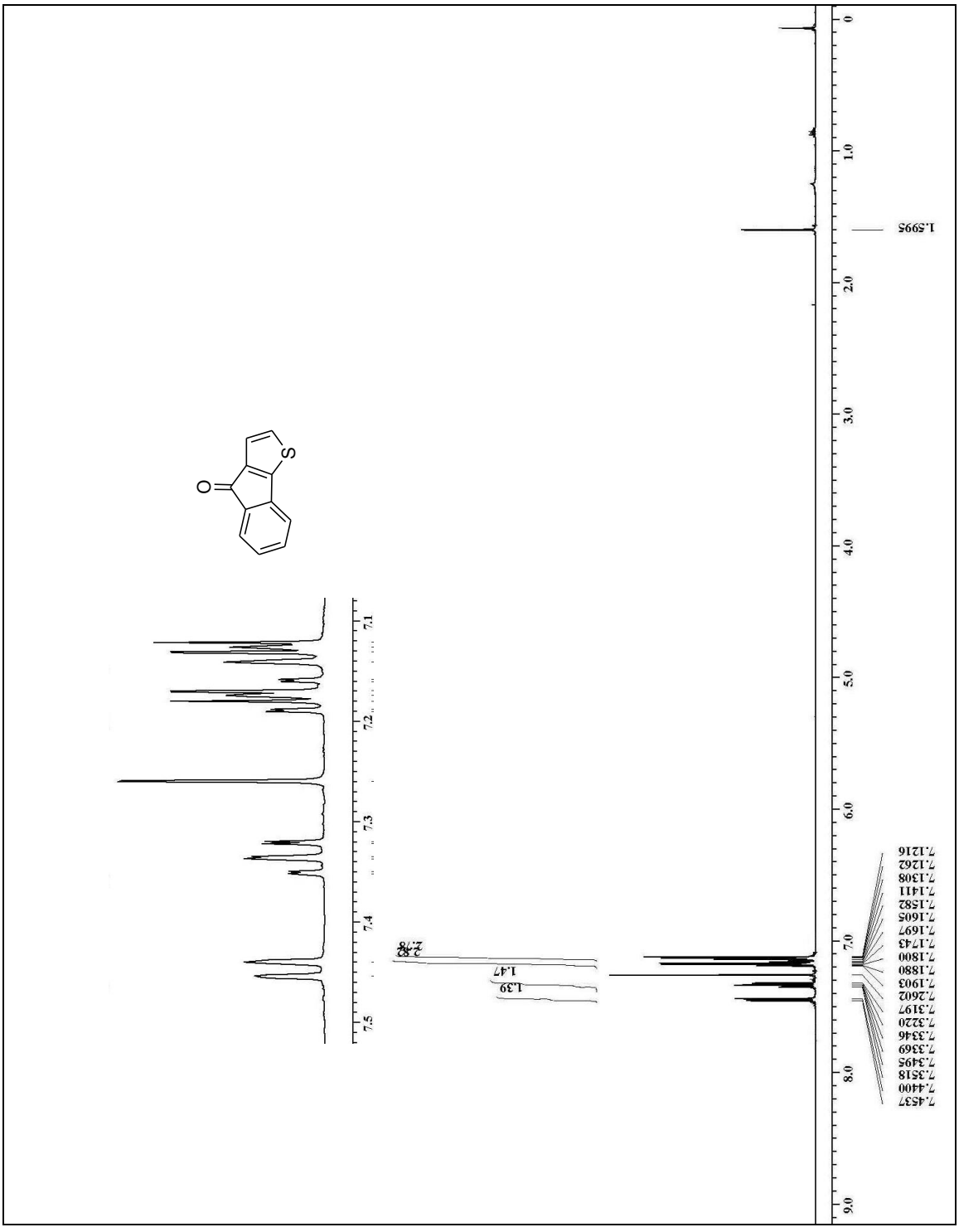


Figure S30. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 3-thiacyclopenta[*a*]inden-8-one (**10a-Fl-1**).

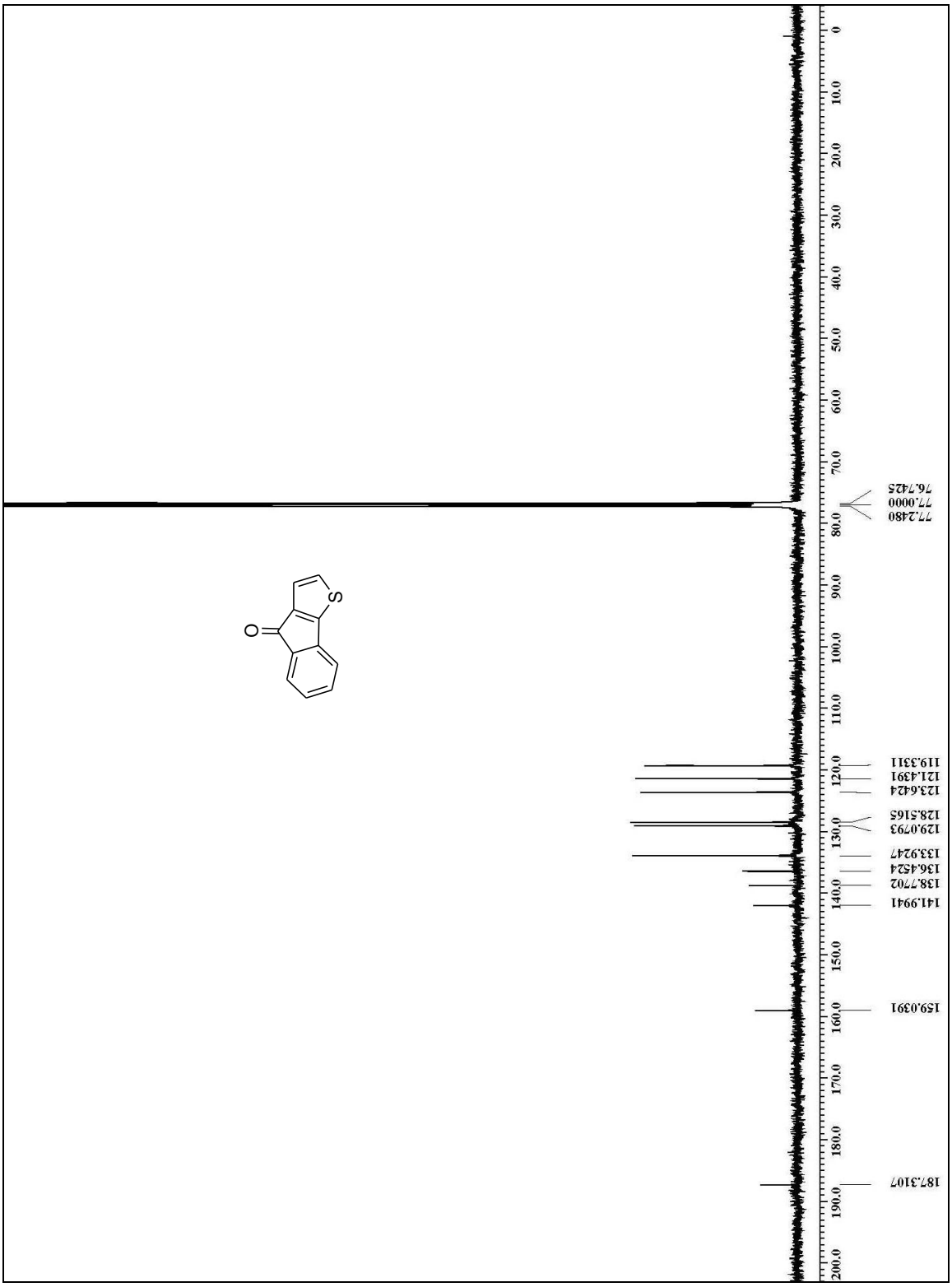


Figure S31. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of 3-thiacyclopenta[*a*]inden-8-one (**10a-Fl-1**).

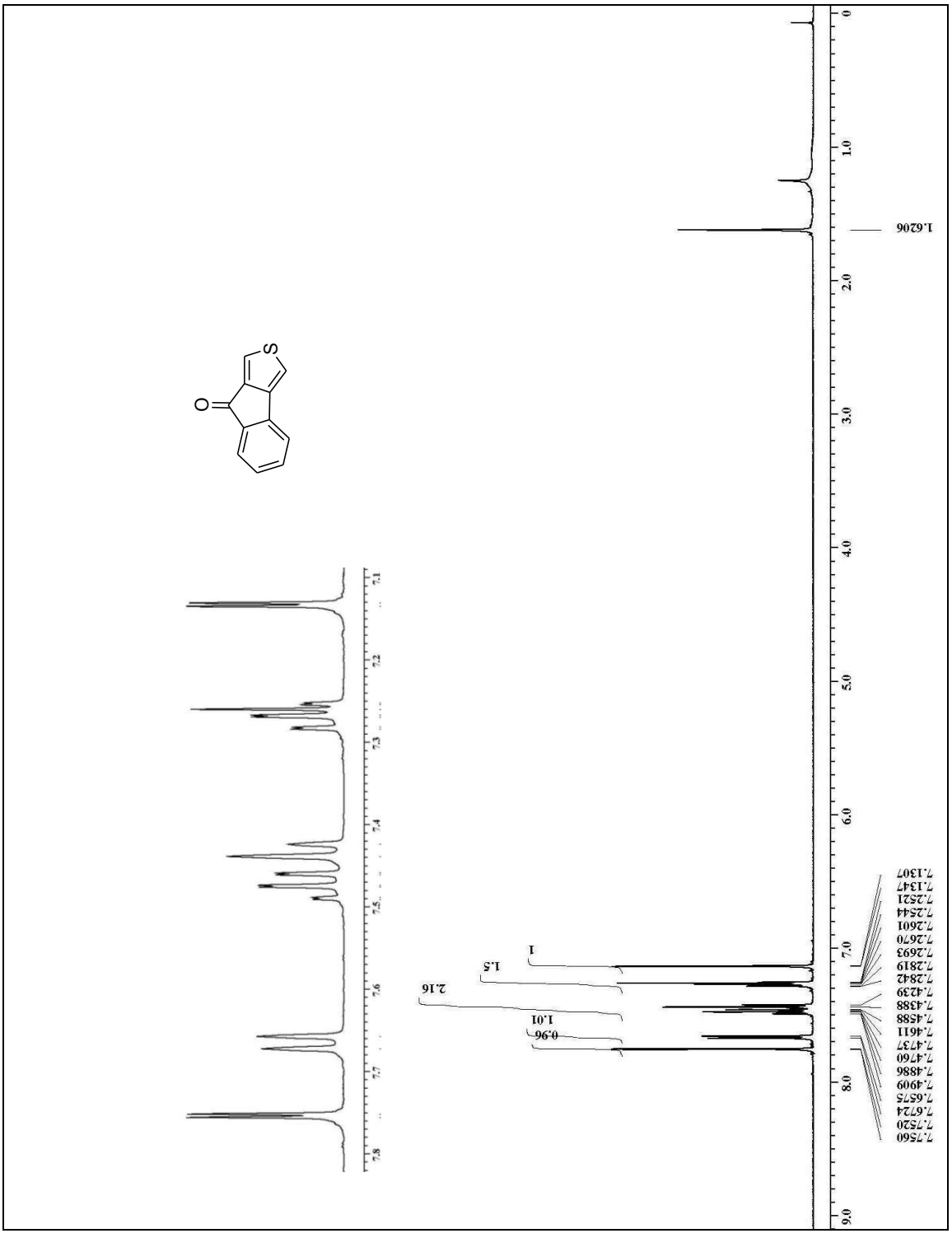


Figure S32. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-thiacyclopenta[*a*]inden-8-one (**10a-Fl-2**).

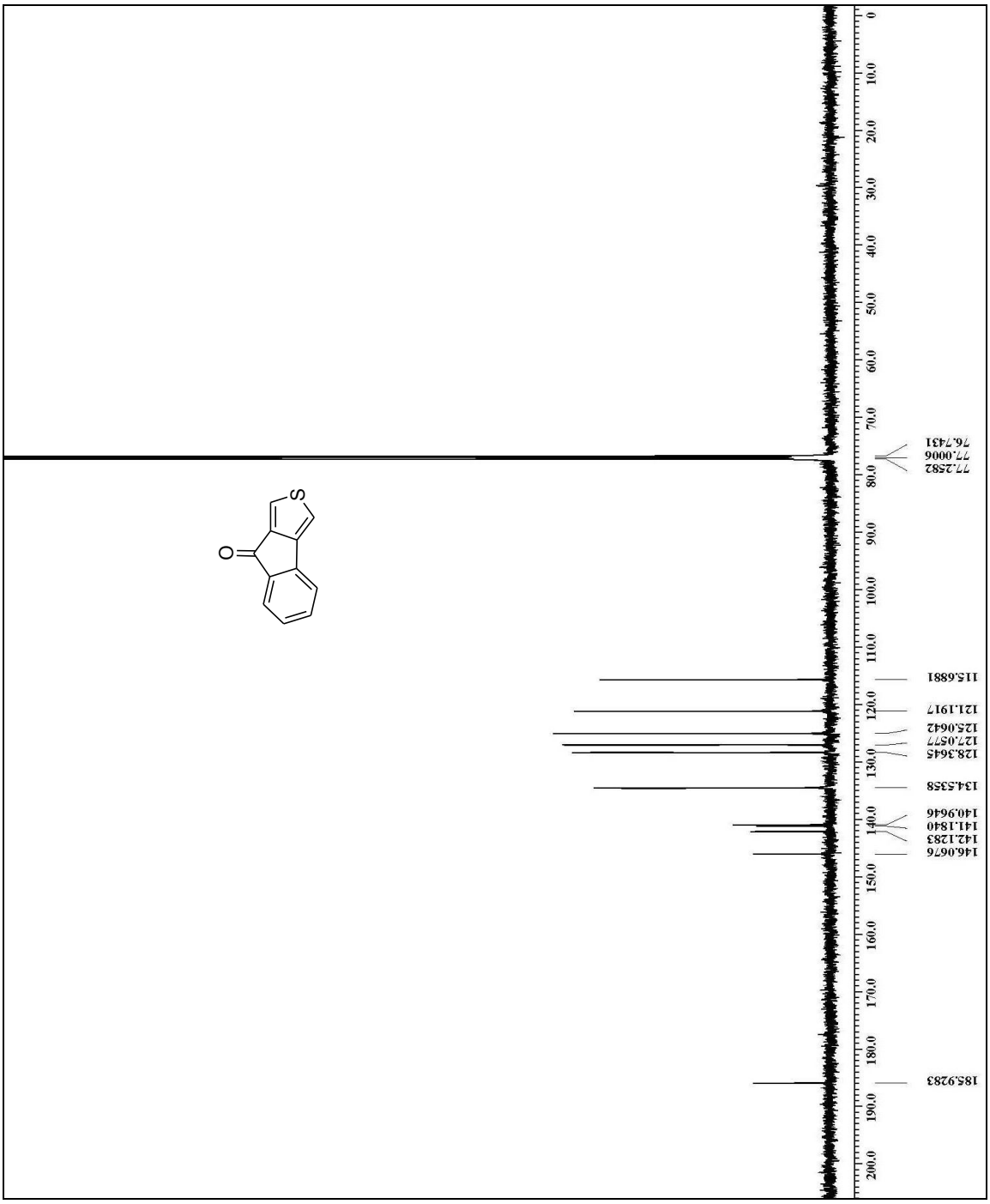


Figure S33. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of 2-thiacyclopenta[*a*]inden-8-one (**10a-Fl-2**).

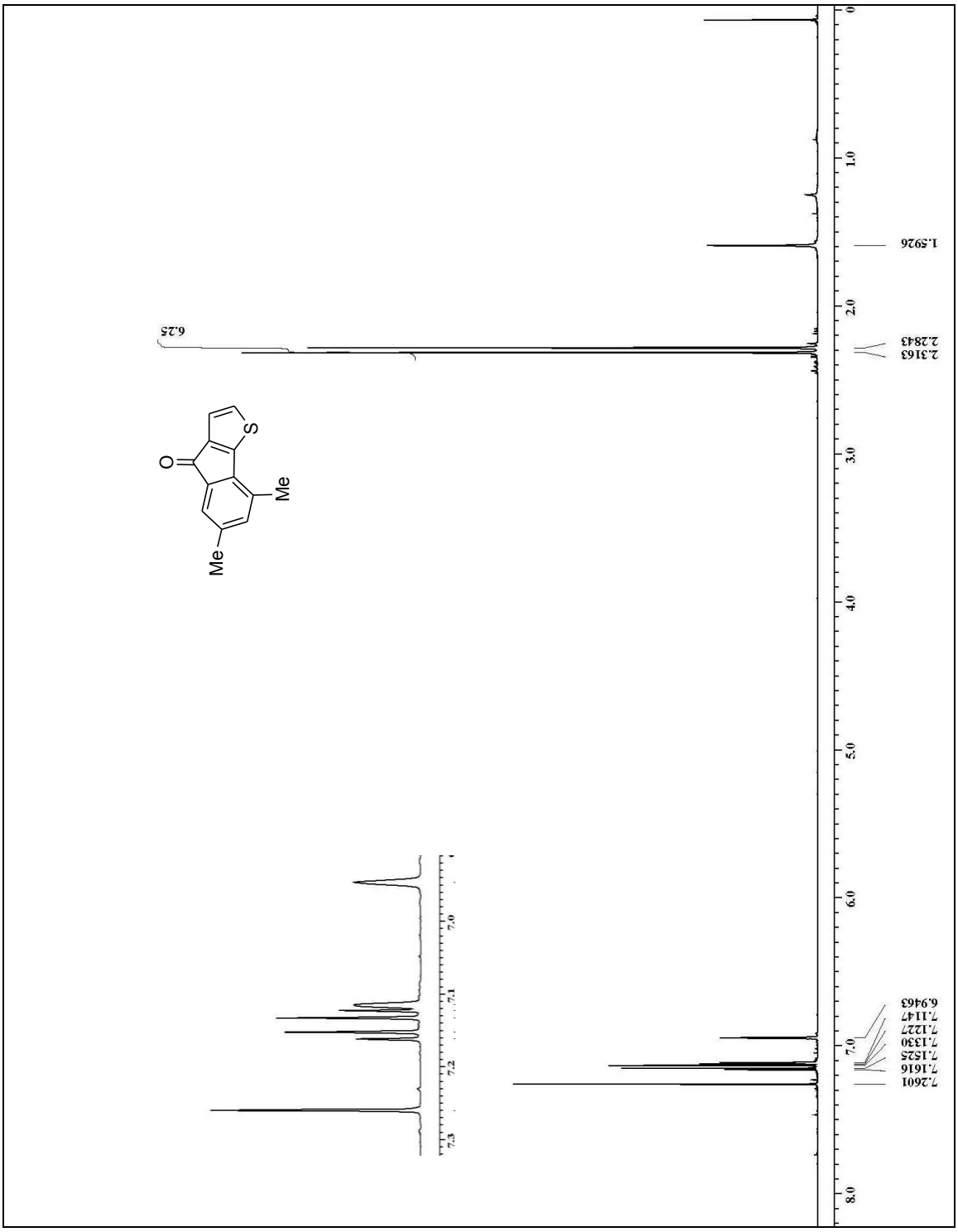


Figure S34. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 4,6-dimethyl-3-thiacyclopenta[*a*]inden-8-one (**10b-Fl-1**).

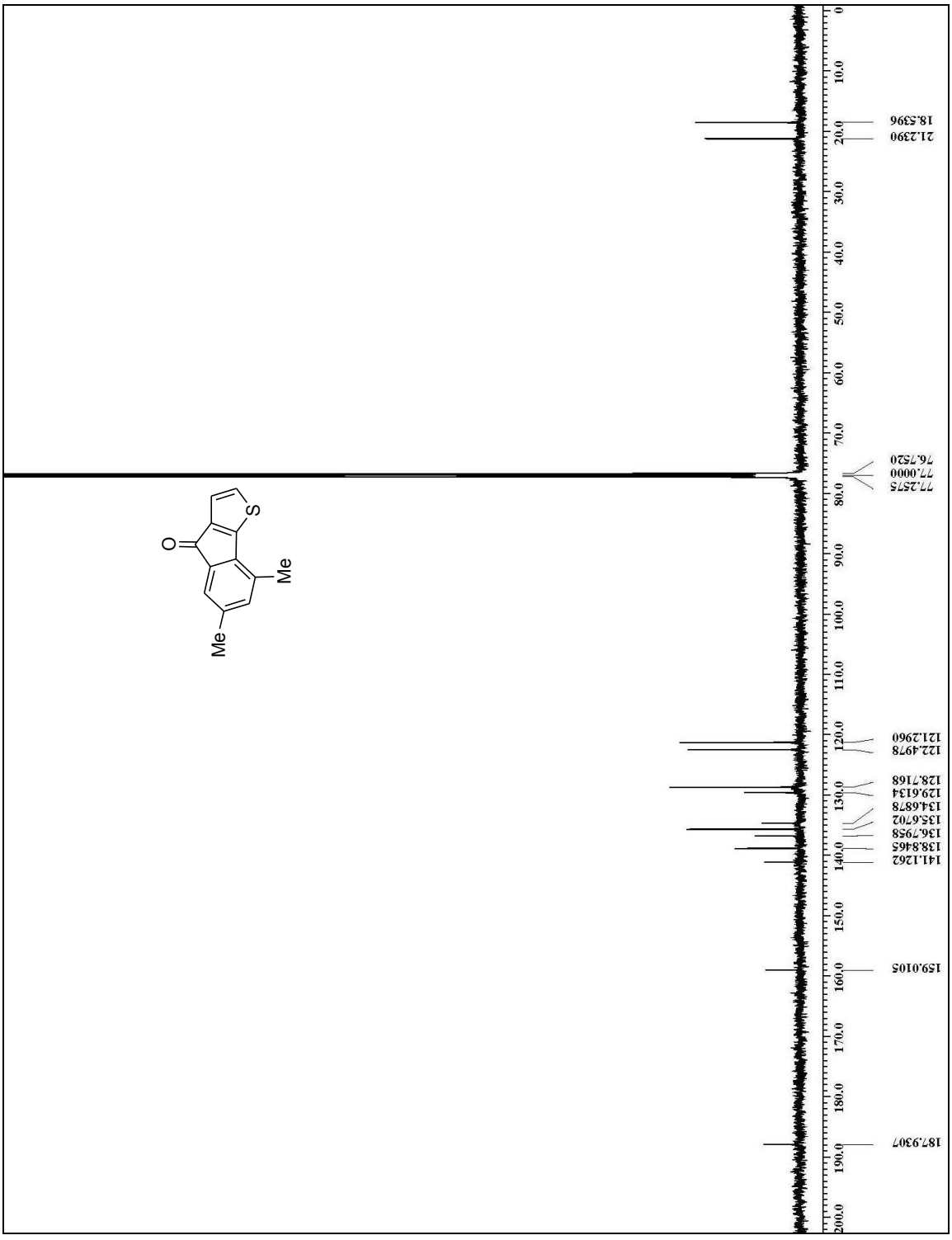


Figure S35. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of 4,6-dimethyl-3-thiacyclopenta[*a*]inden-8-one (**10b-Fl-1**).

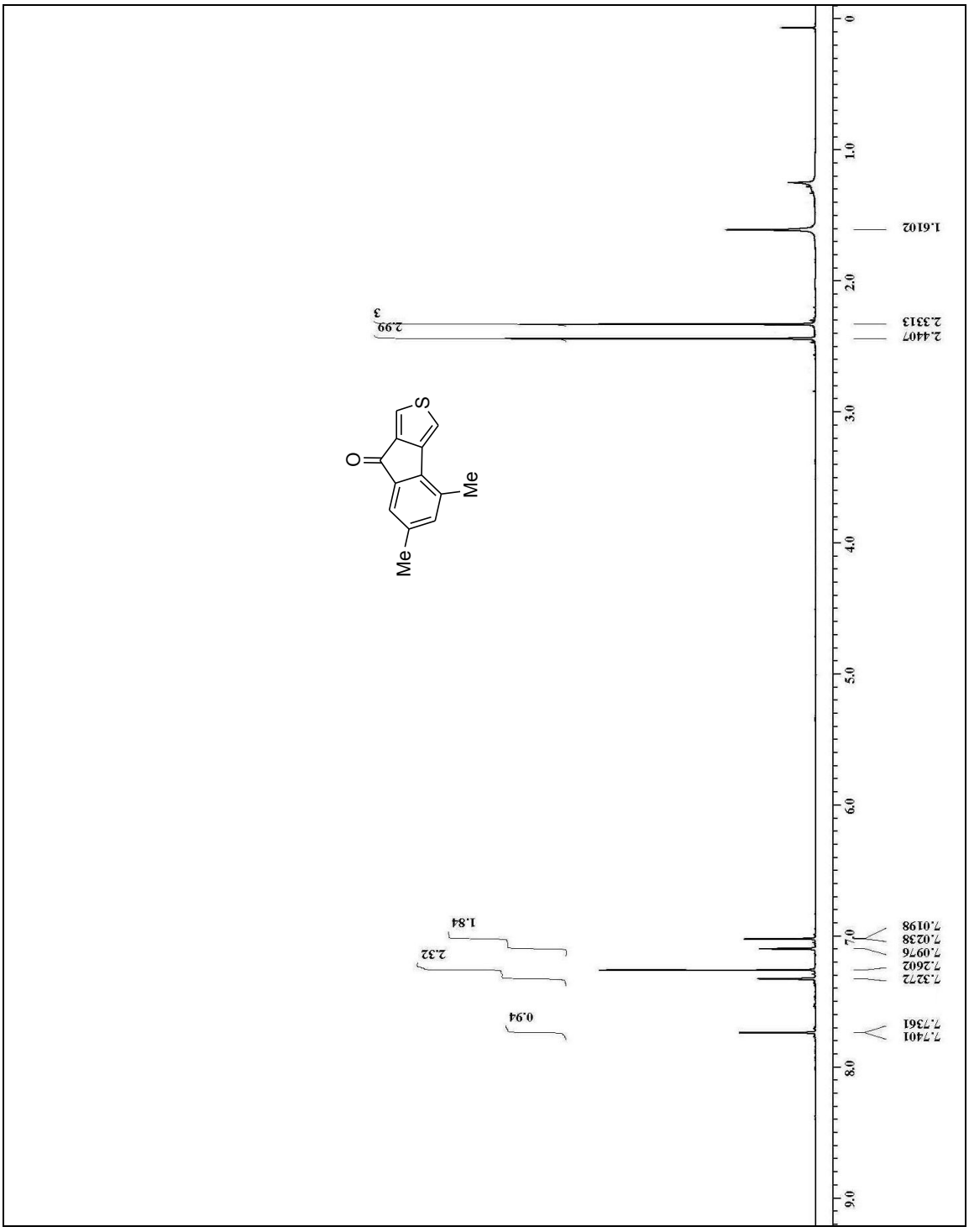


Figure S36. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 4,6-dimethyl-2-thiacyclopenta[*a*]inden-8-one (**10b-Fl-2**).

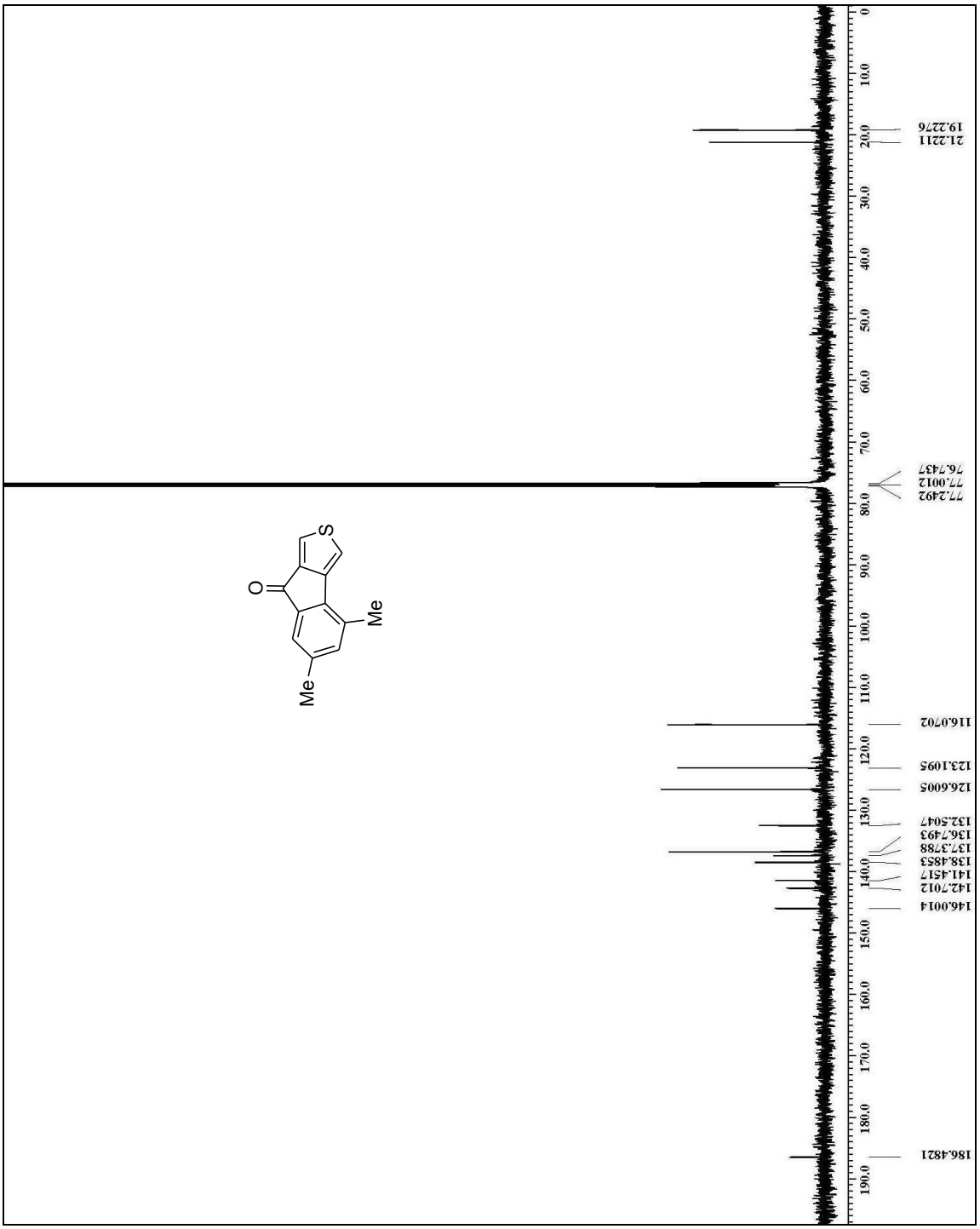


Figure S37. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of 4,6-dimethyl-2-thiacyclopenta[*a*]inden-8-one (**10b-Fl-2**).