Supporting Information for

Oxetane intermediate during a direct aldol reaction: Stereoselective [5+1] annulation affording tetralines

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Contents of the Supporting Information

Experimental Section

General. Proton NMR, $^{13}C\{^{1}H\}$NMR, and $^{13}C\{^{1}H,^{19}F\}$NMR spectra were measured on a JEOL JNM-ECZ600R spectrometer as solutions in $CDCl_3$. Proton NMR spectra were recorded using the residual $CHCl_3$ as an internal reference (7.24 ppm) and ^{13}C NMR using $CDCl_3$ as an internal reference (77.00 ppm). For mass spectra measurements was used JEOL JMS-T100LC.

Material. Unless otherwise noted, the reagents were commercially available and were used without further purification. Dichloromethane was purified by distillation over calcium hydride. The ^{18}O-labeled benzaldehyde was prepared by nucleophilic substitution of benzyl chloride with $^{18}OH_2$ and subsequent oxidation with Dess-Martin periodinane according to the reported procedures.[S1]

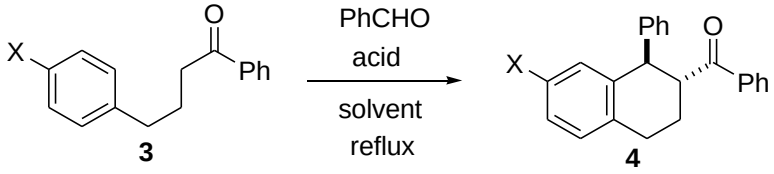
Preparation of Substrates 3a–e. Substrate **3b** was prepared by the reaction of acetoacetate with phenethyl bromide according to the literature.[S2] Substrates **3a** and **3d** were prepared by Grignard reaction of *N*-methoxy-*N*-methyl-4-arylbutanamide with phenylmagnesium bromide according to the literature.[S3] Similarly, substrate **3e** was prepared from 4-(4-(trifluoromethyl)phenyl)butanenitrile[S4] with phenylmagnesium bromide. Selected data for **3e**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.08 (quint, *J* = 7.6 Hz, 2H); $^{13}C\{^{1}H,^{19}F\}$NMR (150 MHz, $CDCl_3$) δ 199.7, 145.8, 136.9, 133.1, 128.8, 128.6, 128.0, 125.3, 125.3, 37.4, 35.0, 25.3; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{15}F_3NaO$ $(M + Na)^+$ 315.0973, found 315.0980.

Substrate **3c** was also prepared from *N*-methoxy-*N*-methyl-4-phenylbutanamide as follows. To a stirred solution of *N*-methyl imidazole (1.23 g, 15 mmol) in THF (25 mL) at −78 °C was added n-BuLi (2.6 M in hexane, 5.2 mL, 14 mmol). After the mixture was refluxed for 30 min, *N*-methoxy-*N*-methyl-4-phenylbutanamide (1.04 g, 5 mmol) was added to the mixture at −78 °C. After the mixture was refluxed for 9 h, the reaction mixture was then quenched by aqueous acetic acid, and extracted by ethyl acetate. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by SiO_2 column (eluent: 5% ethyl acetate in hexane) to give **3c** (1.09 g, 96% yield) as an oil. Rf: 0.34 (10% ethyl acetate in hexane), Selected data for **3c**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 6.99 (s, 1H), 3.96 (s, 3H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.03 (quint, *J* = 7.6

(S1) Du, C.; Wang, X.; Jin, S.; Shi, H.; Li, Y.; Pang, Y.; Liu, Y.; Cheng, M.; Guo, C.; Liu, Y. *Asian J. Org. Chem*. **2016**, *5*, 755.
(S2) Harikrishna, M.; Mohan, H. R.; Dubey, P. K.; Shankar, M.; Subbaraju, G. V. *Synth. Commun*. **2012**, *42*, 1288–1305.
(S3) Torres-Ochoa, R. O.; Wang, Q.; Zhu, J. *Chem. Eur. J*. **2019**, *25*, 9477–9484.
(S4) Shimogaki, M.; Fujita, M.; Sugimura, T. *Angew. Chem. Int. Ed*. **2016**, *55*, 15797–1580

Hz, 2H); $^{13}C\{^{1}H\}$NMR (150 MHz, $CDCl_3$) δ 192.8, 142.9, 141.8, 128.8, 128.5, 128.3, 126.8, 125.8, 38.5, 36.2, 35.3, 25.8; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{16}N_2NaO$ $(M + Na)^+$ 251.1160, found 251.1155.

Table S1. Effect of substituent of the substrate **3**



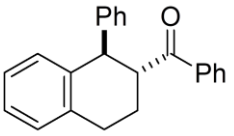
3 **4**

a: X = H, **d**: X = CH_3, **e**: X = CF_3

entry	substrate	acid	time / h	yield / %
1	**3a**	$BF_3{\cdot}OEt_2$	2	89[a]
2	**3a**	Me_3SiOTf	2	88[a]
3	**3b**	$BF_3{\cdot}OEt_2$	1.5	94[b]
4	**3c**	Me_3SiOTf	18	74[b]

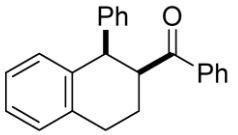
[a] The data has been described in Table 1. [b] The data has been described in Table 2.

***trans*-(1,2,3,4-Tetrahydro-1-phenylnaphthalen-2-yl)(phenyl)methanone (4aa)**



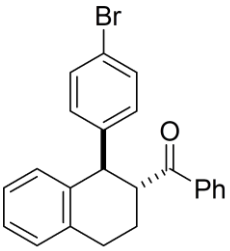
To a stirred solution of **3a** (112 mg, 0.5 mmol) and benzaldehyde (63 mg, 0.6 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 2 mL) was added $BF_3{\cdot}OEt_2$ (50 μL, 0.4 mmol). The mixture was refluxed with an oil bath for 2 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 5% ethyl acetate in hexane) to give **4aa** (180 mg, 0.44 mmol, 88% yield); Rf: 0.41 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.14–7.09 (m, 5H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 4.67 (d, *J* = 9.0 Hz, 1H), 3.91 (td, *J* = 10.2, 3.0 Hz, 1H), 3.07 (ddd, *J* = 16.5, 11.7, 5.5 Hz, 1H), 2.90 (dt, *J* = 16.5, 4.3 Hz, 1H), 2.15 (m, 1H), 1.96 (m, 1H); $^{13}C\{^{1}H\}$NMR (150 MHz, $CDCl_3$) δ 202.5, 145.4, 139.2, 136.7, 136.0, 132.8, 130.1, 129.3, 128.4, 128.4, 128.1, 126.3, 126.1, 125.8, 50.9, 47.2, 29.2, 26.9; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{20}NaO$ $(M + Na)^+$ 335.1412, found 335.1409.

***cis*-(1,2,3,4-Tetrahydro-1-phenylnaphthalen-2-yl)(phenyl)methanone (*cis*-4aa)**



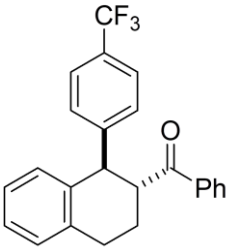
To a stirred solution of **3a** (112 mg, 0.5 mmol) and benzaldehyde (63 mg, 0.6 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 2 mL) was added $BF_3 \cdot OEt_2$ (50 μL, 0.4 mmol). The mixture was refluxed with an oil bath for 2 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture containing **3aa** as major *trans*-isomer and *cis*-isomer of **3aa** (9 : 1) was purified by SiO_2 column (eluent: 5% ethyl acetate in hexane) to elute **4aa.** Continued column chromatography with 30% ethyl acetate in hexane as an eluent gave *cis*-**4aa** (15.5 mg, 9 % yield). Rf: 0.41 (10% ethyl acetate in hexane). The Rf value of *cis*-**4aa** is same as that of **4aa**, but the successful separation of these isomers may be owing to difference in solubility in the eluent used. Selected data for *cis*-**4aa**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.09-7.05 (m, 4H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 2H), 4.68 (d, *J* = 5.5 Hz, 1H), 4.01 (ddd, *J* = 12.4, 5.5, 2.7 Hz, 1H), 3.13 (dd, *J* = 17.2, 5.5 Hz, 1H), 2.99 (ddd, *J* = 18.6, 12.4, 6.2 Hz, 1H), 2.20 (m, 1H), 1.93 (m, 1H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 201.3, 141.8, 138.2, 137.2, 136.5, 132.9, 130.5, 129.6, 129.0, 128.9, 128.4, 127.6, 126.7, 126.6, 126.1, 47.8, 47.4, 28.5, 19.0; HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{20}NaO$ $(M + Na)^+$ 335.1412, found 335.1411.

(1-(4-Bromophenyl)-1,2,3,4-tetrahydronaphthalen-2-yl)(phenyl)methanone (4ab).



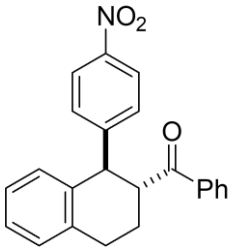
To a stirred solution of **3a** (56 mg, 0.25 mmol) and 4-bromobenzaldehyde (56 mg, 0.3 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 1 mL) was added $BF_3 \cdot OEt_2$ (25 μL, 0.2 mmol). The mixture was refluxed with an oil bath for 2 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 5% ethyl acetate in hexane) to give **4ab** (70.4 mg, 0.18 mmol, 72% yield); Rf: 0.46 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.14–7.10 (m, 2H), 7.05–7.02 (m, 3H), 6.77 (d, *J* = 7.6 Hz, 1H), 4.66 (d, *J* = 9.6 Hz, 1H), 3.85 (td, *J* = 10.3, 2.3 Hz, 1H), 3.07 (m, 1H), 2.91 (dt, *J* = 16.5, 4.1 Hz, 1H), 2.16 (m, 1H), 1.93 (m, 1H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 201.9, 144.5, 138.6, 136.3, 135.9, 133.0, 131.4, 131.0, 130.0, 128.6, 128.1, 126.1, 126.0, 120.2, 50.8, 46.5, 29.2, 27.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{19}BrNaO$ $(M + Na)^+$ 413.0517, found 413.0513.

1-(4-(Trifluoromethyl)phenyl)-1,2,3,4-tetrahydronaphthalen-2-yl)(phenyl)methanone (4ac).



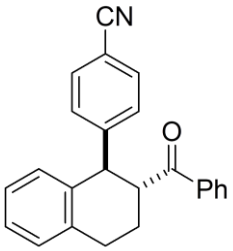
To a stirred solution of **3a** (112 mg, 0.5 mmol) and 4-trifluorobenzaldehyde (0.13 mL, 1.0 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 2 mL) was added $BF_3{\cdot}OEt_2$ (180 μL, 1.4 mmol). The mixture was refluxed with an oil bath for 1 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 5% ethyl acetate in hexane) to give **4ac** (177.2 mg, 0.47 mmol. 93% yield); Rf: 0.5 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.16–7.12 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 4.77 (d, J = 9.6 Hz, 1H), 3.88 (m, 1H), 3.10 (ddd, *J* = 16.5, 11.0, 4.8, Hz, 1H), 2.93 (dt, *J* = 16.5, 4.1 Hz, 1H), 2.19 (m, 1H), 1.95 (m, 1H); ^{13}C{^{1}H, ^{19}F}NMR (150 MHz, $CDCl_3$) δ 201.8, 149.7, 138.3, 136.3, 136.0, 133.1, 130.0, 129.7, 128.7, 128.6, 128.1, 126.3, 126.2, 125.4, 124.2, 50.8, 46.9, 29.3, 27.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{19}F_3NaO$ $(M + Na)^+$ 403.1286, found 403.1284.

(1,2,3,4-Tetrahydro-1-(4-nitrophenyl)naphthalen-2-yl)(phenyl)meth anone (4ad).



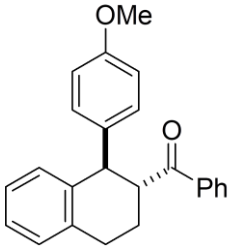
To a stirred solution of **3a** (56 mg, 0.25 mmol) and 4-nitroaldehyde (45 mg, 0.3 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 1 mL) was added $BF_3{\cdot}OEt_2$ (25 μL, 0.2 mmol). The mixture was refluxed with an oil bath for 2 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture purified by column chromatography (SiO_2, eluent: 5% ethyl acetate in hexane) to give **4ad** (72.5 mg, 0.20 mmol, 81% yield); Rf: 0.34 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.18–7.13 (m, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 4.85 (d, *J* = 9.6 Hz, 1H), 3.88 (m, 1H), 3.12 (ddd, *J* = 16.5, 11.7, 5.5 Hz, 1H), 2.95 (dt, *J* = 16.5, 4.1 Hz, 1H), 2.22 (m, 1H), 1.95 (m, 1H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 201.3, 153.3, 146.5, 137.7, 136.0, 136.0, 133.3, 130.3, 129.9, 128.9, 128.7, 128.1, 126.5, 126.4, 123.7, 50.8, 46.8, 29.3, 27.2; HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{19}NNaO_3$ $(M + Na)^+$ 380.1263, found 380.1268.

(1-(4-Cyanophenyl)-1,2,3,4-tetrahydronaphthalen-2-yl)(phenyl)methanone (4ae).



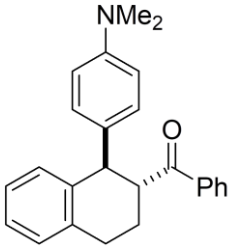
To a stirred solution of **3a** (112 mg, 0.5 mmol) and 4-cyanobenzaldehyde (131 mg, 1.0 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 2 mL) was added $BF_3{\cdot}OEt_2$ (180 μL, 1.4 mmol). The mixture was refluxed with an oil bath for 1 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 10% ethyl acetate in hexane) to give **4ae** (164.5 mg, 0.49 mmol, 97% yield); Rf: 0.26 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.52–7.47 (m, 3H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.29–7.26 (m, 2H), 7.14 (m, 2H), 7.04 (m, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 4.78 (d, *J* = 9.6 Hz, 1H), 3.85 (td, *J* = 10.3, 3.0 Hz, 1H), 3.10 (m, 1H), 2.93 (dt, *J* = 17.2, 4.1 Hz, 1H), 2.21-2.17 (m, 1H), 1.94 (m, 1H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 201.5, 151.2, 137.8, 136.1, 136.0, 133.3, 132.2, 130.2, 129.9, 128.8, 128.7, 128.0, 126.4, 126.3, 118.8, 110.3, 50.8, 47.1, 29.3, 27.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{19}NNaO$ $(M + Na)^+$ 360.1364, found 360.1363.

(1,2,3,4-Tetrahydro-1-(4-methoxyphenyl)naphthalen-2-yl)(phenyl)methanone (4af).



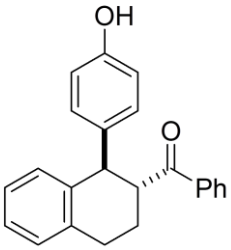
To a stirred solution of **3a** (112 mg, 0.5 mmol) and 4-methoxybenzaldehyde (75 mg, 0.55 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 2 mL) was added $BF_3{\cdot}OEt_2$ (50 μL, 0.4 mmol). The mixture was refluxed with an oil bath for 2 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 10% ethyl acetate in hexane) to give **4af** (82.9 mg, 0.24 mmol, 48% yield); Rf: 0.39 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 6.9 Hz, 2H), 7.13–7.09 (m, 2H), 7.06–7.02 (m, 3H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 2H), 4.61 (d, *J* = 9.6 Hz, 1H), 3.88 (m, 1H), 3.71 (s, 3H), 3.06 (m, 1H), 2.90 (m, 1H), 2.14 (m, 1H), 1.96 (m, 1H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 202.7, 158.0, 139.6, 137.5, 136.7, 135.9, 132.8, 130.2, 130.1, 128.5, 128.4, 128.1, 126.0, 125.8, 113.7, 55.1, 51.0, 46.4, 29.3, 27.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{22}NaO_2$ $(M + Na)^+$ 365.1517, found 365.1516.

(1-(4-(Dimethylamino)phenyl)-1,2,3,4-tetrahydronaphthalen-2-yl)(phenyl)methanone (4ag).



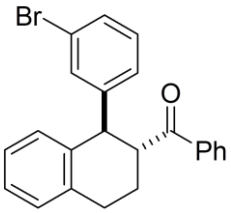
To a stirred solution of **3a** (56 mg, 0.25 mmol) and 4-dimethylaminobenzaldehyde (45 mg, 0.3 mmol) in dichloromethane (1 mL) was added TMSOTf (90 μL, 0.5 mmol). The mixture was refluxed with an oil bath for 4 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 20% ethyl acetate in hexane) to give **4ag** (26.7 mg, 0.075 mmol, 30% yield); Rf: 0.35 (20% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.11–7.08 (m, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 9.0 Hz, 2H), 4.57 (d, *J* = 8.3 Hz, 1H), 3.89 (td, *J* = 10.3, 3.4 Hz, 1H), 3.04 (ddd, *J* = 16.5, 11.0, 5.5 Hz, 1H), 2.88 (dt, *J* = 16.5, 4.1 Hz, 1H), 2.84 (s, 6H), 2.14 (m, 1H), 1.95 (m, 1H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 202.9, 148.9, 139.9, 136.8, 135.9, 132.7, 130.1, 129.8, 128.4, 128.3, 128.2, 125.9, 125.6, 112.7, 50.9, 46.1, 40.7, 29.2, 26.9; HRMS (ESI-TOF) *m*/*z* calcd for $C_{25}H_{25}NNaO$ $(M + Na)^+$ 378.1834, found 378.1828.

(1,2,3,4-Tetrahydro-1-(4-hydroxyphenyl)naphthalen-2-yl)(phenyl)methanone (4ah).



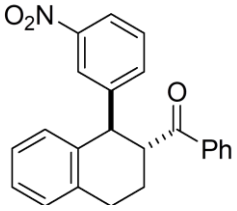
To a stirred solution of **3a** (56 mg, 0.25 mmol) and 4-hydroxybenzaldehyde (37 mg, 0.3 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 1 mL) was added $BF_3{\cdot}OEt_2$ (50 μL, 0.4 mmol). The mixture was refluxed with an oil bath for 4 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 10–20% ethyl acetate in hexane) to give **4ah** (61.0 mg, 0.19 mmol, 74% yield); Rf: 0.26 (20% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.13–7.09 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* =9.0 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 9.0 Hz, 2H), 4.60 (d, *J* = 9.6 Hz, 1H), 3.87 (m, 1H), 3.06 (m, 1H), 2.90 (dt, *J* = 17.2, 4.8 Hz, 1H), 2.13 (m, 1H), 1.95 (m, 1H) ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 202.8, 153.9, 139.5, 137.6, 136.7, 135.9, 132.9, 130.4, 130.0, 128.6, 128.5, 128.1, 126.0, 125.8, 115.2, 51.0, 46.4, 29.3, 27.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{20}NaO_2$ $(M + Na)^+$ 351.1361, found 351.1354.

(1-(3-Bromophenyl)-1,2,3,4-tetrahydronaphthalen-2-yl)(phenyl)methanone (4ai).



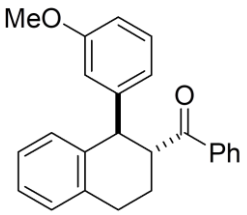
To a stirred solution of **3a** (56 mg, 0.25 mmol) and 3-bromobenzaldehyde (56 mg, 0.3 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 1 mL) was added $BF_3{\cdot}OEt_2$ (25 μL, 0.2 mmol). The mixture was refluxed with an oil bath for 2h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 5% ethyl acetate in hexane) to give **4ai** (75.2 mg, 0.19 mmol, 77% yield); Rf: 0.52 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.27 (s, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.14–7.11 (m, 2H), 7.09–7.03 (m, 3H), 6.78 (d, *J* = 7.6 Hz, 1H), 4.65 (d, *J* = 9.6 Hz, 1H), 3.86 (m, 1H), 3.06 (m, 1H), 2.90 (dt, *J* = 16.5, 4.1 Hz, 1H), 2.16 (m, 1H), 1.93 (m, 1H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 201.9, 147.9, 138.3, 136.4, 135.9, 133.0, 132.1, 130.0, 129.9, 129.5, 128.6, 128.6, 128.2, 128.1, 126.2, 126.1, 122.5, 50.7, 46.8, 29.1, 27.0; HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{19}BrNaO$ $(M + Na)^+$ 413.0517, found 413.0514.

(1,2,3,4-Tetrahydro-1-(3-nitrophenyl)naphthalen-2-yl)(phenyl)methanone (4aj).



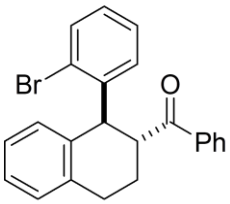
To a stirred solution of **3a** (112 mg, 0.5 mmol) and 3-nitroaldehyde (83.1 mg, 0.55 mmol) in a mixed solvent of hexane and dichloromethane (4 : 1 (v/v), 2 mL) was added $BF_3{\cdot}OEt_2$ (50 μL, 0.4 mmol). The mixture was stirred refluxed with an oil bath for 2 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 5% ethyl acetate in hexane) to give **4aj** (171.6 mg, 0.46 mmol, 96% yield); Rf: 0.31 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00–7.97 (m, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.39–7.35 (m, 3H), 7.18–7.13 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 4.84 (d, *J* = 10.3 Hz, 1H), 3.90 (t, *J* = 10.3 Hz, 1H), 3.14 (m, 1H), 2.95 (m, 1H), 2.22 (m, 1H), 1.95 (m, 1H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 201.4, 148.4, 147.6, 137.7, 136.04, 136.02, 133.3, 129.8, 129.2, 128.9, 128.7, 128.1, 126.5, 126.4, 123.9, 121.6, 50.8, 46.7, 29.3, 27.2; HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{19}NNaO_3$ $(M + Na)^+$ 380.1263, found 380.1269.

(1,2,3,4-Tetrahydro-1-(3-methoxyphenyl)naphthalen-2-yl)(phenyl)methanone (4ak).



To a stirred solution of **3a** (112 mg, 0.5 mmol) and 3-methoxybenzaldehyde (75 mg, 0.55 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 2 mL) was added $BF_3{\cdot}OEt_2$ (50 μL, 0.4 mmol). The mixture was refluxed with an oil bath for 2 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 10% ethyl acetate in hexane) to give **4ak** (103.1 mg, 0.29 mmol. 58% yield); Rf: 0.38 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.13–7.08 (m, 3H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.67 (t, *J* = 2.1 Hz, 1H), 6.64 (dd, *J* = 8.3, 2.1 Hz, 1H), 4.64 (d, *J* = 9.0 Hz, 1H), 3.91 (td, *J* = 10.3, 2.8 Hz, 1H), 3.69 (s, 3H), 3.05 (ddd, *J* = 16.8, 11.0, 4.8 Hz, 1H), 2.89 (dt, *J* = 16.8, 4.5 Hz, 1H), 2.15 (m, 1H), 1.95 (m, 1H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 202.5, 159.8, 147.2, 139.1, 137.1, 136.0, 132.7, 130.2, 129.3, 128.5, 128.1, 126.1, 125.9, 121.8, 115.4, 111.8, 55.2, 50.9, 47.4, 29.2, 27.0; HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{22}NaO_2$ $(M + Na)^+$ 365.1517, found 365.1514.

(1-(2-Bromophenyl)-1,2,3,4-tetrahydronaphthalen-2-yl)(phenyl)methanone (4al).



To a stirred solution of **3a** (56 mg, 0.25 mmol) and 2-bromobenzaldehyde (56 mg, 0.3 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 1 mL) was added $BF_3{\cdot}OEt_2$ (25 μL, 0.2 mmol). The mixture was refluxed with an oil bath for 2 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 5% ethyl acetate in hexane) to give **4al** (85.1 mg, 0.22 mmol, 87% yield) as a white solid; Rf: 0.6 (10% ethyl acetate in hexane); mp = 129.1–131.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.50–7.46 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.14–7.11 (m, 3H), 7.06–6.98 (m, 3H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.06 (d, *J* = 6.9 Hz, 1H), 4.15 (m, 1H), 3.00 (m, 1H), 2.81 (dt, *J* = 17.2, 5.5 Hz, 1H), 2.15 (m, 1H), 2.03 (m, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, at 50 °C) δ 201.9, 144.5, 137.9, 136.7, 136.1, 133.4, 132.8, 132.0, 129.5, 128.5, 128.3, 128.2, 128.0, 127.4, 126.3, 126.0, 124.7, 47.9, 46.3, 28.2, 25.6; HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{19}BrNaO$ $(M + Na)^+$ 413.0517, found 413.0526.

Table S2. Crystal data and structure refinement for **4al**.

Formula	$C_{23}H_{19}OBr$	V (Å^3)	1808.49 (7)
Fw	391.29	Z	4
Crystal system	monoclinic	D_{calcd} (g/cm^{-3})	1.437
Space group	$P2_1/n$	μ (mm^{-1})	2.28
a (Å)	9.8918 (2)	θ_{max} (°)	30.51
b (Å)	10.5226 (2)	no. of data collected	5385
c (Å)	17.7799 (4)	no. of parameters	226
α (°)	90.000	R	0.0584
β (°)	102.256 (2)	Rw	0.1857
γ (°)	90.000		

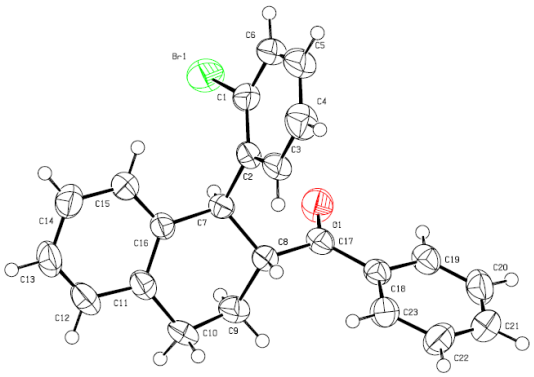
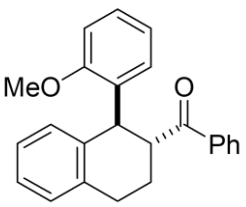


Figure S1. An ORTEP view (50% probability level) of **4al**

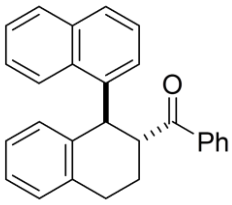
(1,2,3,4-Tetrahydro-1-(2-methoxyphenyl)naphthalen-2-yl)(phenyl)methanone (4am).



To stirred solution of **3a** (112 mg, 0.5 mmol) and 2-methoxybenzaldehyde (75 mg, 0.55 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 2 mL) was added $BF_3{\cdot}OEt_2$ (50 μL, 0.4 mmol). The mixture was refluxed with an oil bath for 2 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 30% ethyl acetate in hexane) to give **4am** (119.9 mg, 0.35 mmol. 70% yield) as a colorless oil; Rf: 0.39 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.13–7.07 (m, 3H), 7.01 (t, J = 7.2 Hz, 1H), 6.89 (d, J = 7.6 Hz, 1H), 6.82 (d, J = 8.3

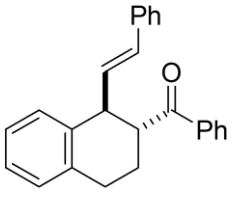
Hz, 1H), 6.79–6.76 (m, 2H), 4.89 (d, *J* = 7.6 Hz, 1H), 4.07 (m, 1H), 3.63 (s, 3H), 2.96 (ddd, *J* = 16.5, 9.0, 4.8 Hz, 1H), 2.83 (dt, *J* = 16.5, 5.5 Hz, 1H), 2.11 (m, 1H), 1.98 (m, 1H); $^{13}C\{^{1}H\}$NMR (150 MHz, $CDCl_3$ at 50 ℃) δ 202.9, 157.4, 139.2, 137.2, 136.3, 134.1, 132.5, 131.0, 129.3, 128.4, 128.3, 128.2, 127.6, 126.0, 125.5, 120.7, 111.5, 55.5, 47.9, 42.2, 28.7, 26.2; HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{22}NaO_2$ $(M + Na)^+$ 365.1517, found 365.1522.

(1,2,3,4-Tetrahydro-1-(naphthalen-1-yl)naphthalen-2-yl)(phenyl)methanone (4an).



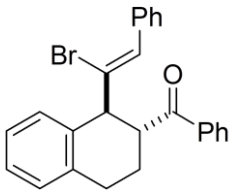
To a stirred solution of **3a** (56 mg, 0.25 mmol) and 1-naphthaldehyde (47 mg, 0.3 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 1 mL) was added $BF_3{\cdot}OEt_2$ (25 μL, 0.2 mmol). The mixture was refluxed with an oil bath for 2 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture purified by column chromatography (SiO_2, eluent: 5% ethyl acetate in hexane) to give **4an** (62.2 mg, 0.17 mmol, 69% yield); Rf: 0.51 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$ at 50 ℃) δ 7.99 (m, 1H), 7.79 (m, 1H), 7.64–7.59 (m, 3H), 7.41–7.37 (m, 3H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.24–7.22 (m, 2H), 7.18–7.16 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.38 (d, *J* = 6.9 Hz, 1H), 4.23 (m, 1H), 3.10 (m, 1H), 2.92 (dt, *J* = 16.5, 4.8 Hz, 1H), 2.21 (m, 1H), 2.11 (m, 1H); $^{13}C\{^{1}H\}$NMR (150 MHz, $CDCl_3$ at 50 ℃) δ 202.7, 139.4, 136.8, 135.7, 134.3, 132.6, 131.7, 129.8, 129.0, 128.6, 128.4, 128.0, 127.9, 127.3, 126.4, 126.0, 125.9, 125.4, 125.3, 124.2, 49.1, 29.7, 28.6, 26.5; HRMS (ESI-TOF) *m*/*z* calcd for $C_{27}H_{22}NaO$ $(M + Na)^+$ 385.1568, found 385.1571.

(1,2,3,4-Tetrahydro-1-styrylnaphthalen-2-yl)(phenyl)methanone (4ao).



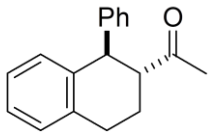
To a stirred solution of **3a** (112 mg, 0.5 mmol) and *trans*-cinnamilaldehyde (0.19 mL, 1.5 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v), 2 mL) was added $BF_3{\cdot}OEt_2$ (0.15 mL, 1.5 mmol). The mixture was stirred refluxed with an oil bath for 6 h. The reaction mixture was then quenched by water, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 5–10% ethyl acetate in hexane) to give **4ao** (89.7 mg, 53% yield) as an oil; Rf: 0.39, 10% ethyl acetate in hexane; ^{1}H NMR (600 MHz, $CDCl_3$)δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.29–7.13 (m, 9H), 6.50 (d, *J* = 15.1 Hz, 1H), 6.07 (dd, *J* = 15.1, 9.0 Hz, 1H), 4.20 (t, *J* = 9.0 Hz, 1H), 3.74 (t, *J* = 9.0 Hz, 1H), 2.98 (m, 1H), 2.89 (m, 1H), 2.16 (m, 1H), 1.95 (m, 1H); $^{13}C\{^{1}H\}$NMR (150 MHz, $CDCl_3$) δ 202.3, 137.6, 137.1, 136.8, 135.5, 133.0, 132.8, 131.8, 129.4, 128.8, 128.7, 128.4, 128.3, 127.2, 126.2, 126.1, 47.8, 44.7, 29.0, 26.5; HRMS (ESI-TOF) *m*/*z* calcd for $C_{25}H_{22}NaO$ $(M + Na)^+$ 361.1568, found 361.1574.

(1-(1-Bromo-2-phenylvinyl)-1,2,3,4-tetrahydronaphthalen-2-yl)(phenyl)methanone (4ap).



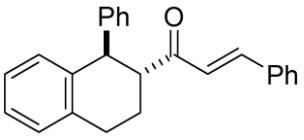
To a stirred solution of **3a** (112 mg, 0.5 mmol) and α-bromocinnamaldehyde (211 mg, 1.0 mmol) in dichloromethane (2 mL) was added Me_3SiOTf (0.18 mL, 1.0 mmol). The mixture was refluxed with an oil bath for 3 h. The reaction mixture was then quenched by water, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 3% ethyl acetate in hexane) to give **4ap** (135 mg, 65% yield) as an oil; Rf: 0.4 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.48–7.43 (m, 4H), 7.33 (m, 1H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.24–7.18 (m, 3H), 7.14 (m, 1H), 7.01 (s, 1H), 4.60 (d, *J* = 9.6 Hz, 1H), 4.22 (td, *J* = 9.6, 3.4 Hz, 1H), 3.01 (ddd, *J* = 16.5, 12.4, 4.8 Hz, 1H), 2.87 (dt, *J* = 16.5, 3.4 Hz, 1H), 2.18 (m, 1H), 1.93 (qd, *J* = 12.4, 4.8 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 202.2, 136.7, 136.4, 135.6, 135.5, 133.3, 132.3, 129.2, 129.0, 128.9, 128.7, 128.4, 128.0, 127.8, 126.6, 126.4, 52.7, 46.3, 29.2, 26.5; HRMS (ESI-TOF) *m/z* calcd for $C_{25}H_{21}BrNaO$ $(M + Na)^+$ 439.0673, found 439.0668.

1-(1,2,3,4-Tetrahydro-1-phenylnaphthalen-2-yl)ethanone (4b).



To a stirred solution of **3b** (81 mg, 0.5 mmol) and benzaldehyde (90 mg, 0.85 mmol) in hexane (2 mL) was added $BF_3{\cdot}OEt_2$ (50 μL, 0.4 mmol). The mixture was refluxed with an oil bath for 4 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 5% ethyl acetate in hexane) to give **4b+4b'** (100.2 mg); Rf **4b**: 0.31 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27–7.24 (m, 2H), 7.21–7.18 (m, 1H), 7.10–7.07 (m, 4H), 7.01–6.99 (m, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 4.37 (d, *J* = 9.6 Hz, 1H), 3.06–2.97 (m, 2H), 2.90 (dt, *J* = 16.5, 4.8 Hz, 1H), 2.09 (m, 1H), 1.93 (s, 3H), 1.93–1.88 (m, 1H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 211.0, 145.1, 138.7, 135.8, 129.9, 129.2, 128.8 128.5, 126.5, 126.0, 125.9, 56.4, 47.3, 30.0, 29.0, 25.4; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{18}NaO$ $(M + Na)^+$ 273.1255, found 273.1264.

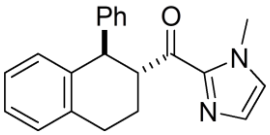
1-(1,2,3,4-Tetrahydro-1-phenylnaphthalen-2-yl)-3-phenylprop-2-en-1-one (4b').



To a stirred solution of **3b** (41 mg, 0.25 mmol) and benzaldehyde (80 mg, 0.75 mmol) in dichloromethane (1 mL) was added TMSOTf (45 μL, 0.25 mmol). The mixture was refluxed with an oil bath for 6 h. The reaction mixture was then quenched by Na_2CO_3

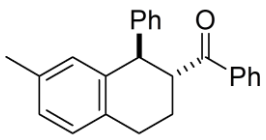
aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 4% ethyl acetate in hexane) to give **4b'** (63.2 mg, 0.19 mmol, 75% yield); Rf **4b'**: 0.32 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41–7.37 (m, 3H), 7.35–7.30 (m, 3H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.15–7.09 (m, 5H), 7.03–7.00 (m, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.56 (d, *J* = 15.8 Hz, 1H), 4.51 (d, *J* = 9.6 Hz, 1H), 3.33 (ddd, *J* = 11.0, 9.6, 2.8 Hz, 1H), 3.05 (ddd, *J* = 16.5, 11.0, 4.1 Hz, 1H), 2.93 (dt, *J* = 16.5, 4.5 Hz, 1H), 2.17–2.13 (m, 1H), 2.01–1.92 (m, 1H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 201.7, 145.4, 142.7, 139.1, 136.1, 134.5, 130.4, 130.1, 129.3, 128.8, 128.5, 128.4, 128.3, 126.4, 126.1, 125.9, 125.4, 54.4, 47.3, 29.2, 26.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{25}H_{22}NaO$ $(M + Na)^+$ 361.1568, found 361.1566.

(1,2,3,4-Tetrahydro-1-phenylnaphthalen-2-yl)(1-methyl-1H-imidazol-2-yl)methanone (4c)



To a stirred solution of **3c** (114 mg, 0.5 mmol) and benzaldehyde (160 mg, 1.5 mmol) in dichloromethane (2 mL) was added TMSOTf (270 μL, 1.5 mmol). The mixture was refluxed with an oil bath for 48 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: dichloromethane) to give **4c** (143.5 mg, 0.45 mmol, 90% yield). Rf: 0.61 (dichloromethane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21–7.15 (m, 4H), 7.12–7.07 (m, 3H), 7.04 (s, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.91 (s, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 4.59 (d, *J* = 10.3 Hz, 1H), 4.39 (td, *J* = 10.3, 2.8 Hz, 1H), 3.87 (s, 3H), 3.18 (ddd, *J* = 16.5, 11.0, 5.5 Hz, 1H), 2.90 (dt, *J* = 16.5, 4.1 Hz, 1H), 2.30 (m, 1H), 1.94 (m, 1H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 194.3, 145.2, 142.5, 139.3, 136.1, 129.9, 129.5, 128.8, 128.5, 128.2, 126.9, 126.1, 125.9, 125.7, 50.7, 46.6, 36.2, 29.2, 27.0; HRMS (ESI-TOF) *m*/*z* calcd for $C_{21}H_{20}N_2NaO$ $(M + Na)^+$ 339.1473, found 339.1472.

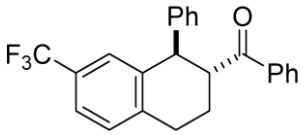
(1,2,3,4-Tetrahydro-7-methyl-1-phenylnaphthalen-2-yl)(phenyl)methanone (4d).



To a stirred solution of **3d** (119 mg, 0.5 mmol) and benzaldehyde (63 mg, 0.6 mmol) in hexane (2 mL) was added $BF_3{\cdot}OEt_2$ (50 μL, 0.4 mmol). The mixture was refluxed with an oil bath for 1.5 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 5% ethyl acetate in hexane) to give **4d** (154.2 mg, 0.47 mmol, 94% yield); Rf: 0.49 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.21–7.16 (m, 2H), 7.14–7.08 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.63 (s, 1H), 4.62 (d, *J* =

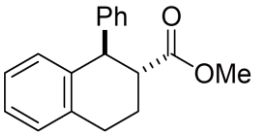
8.9 Hz, 1H), 3.88 (td, *J* = 10.3, 3.4 Hz, 1H), 3.00 (ddd, *J* = 16.5, 10.3, 4.8 Hz, 1H), 2.84 (dt, *J* = 16.5, 4.8 Hz, 1H), 2.15 (s, 3H), 2.15–2.11 (m, 1H), 1.97–1.90 (m, 1H); $^{13}C\{^{1}H\}$NMR (150 MHz, $CDCl_3$) δ 202.7, 145.6, 138.8, 136.7, 135.5, 133.0 132.8, 130.5, 129.3, 128.5, 128.4, 128.1, 126.8, 126.2, 51.1, 47.1, 28.8, 26.9, 21.0; HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{22}NaO$ $(M + Na)^+$ 349.1568, found 349.1563.

(7-(Trifluoromethyl)-1,2,3,4-tetrahydro-1-phenylnaphthalen-2-yl)(phenyl)methanone (4e).



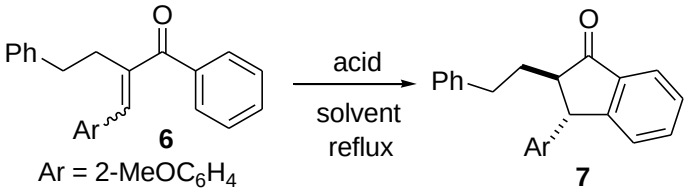
To a stirred solution of **3e** (119 mg, 0.5 mmol) and benzaldehyde (106 mg, 1.0 mmol) in dichloromethane (2 mL) was added TMSOTf (90 μL, 0.5 mmol). The mixture was refluxed with an oil bath for 18 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 5% ethyl acetate in hexane) to give **4e** (140 mg, 0.37 mmol, 74% yield); Rf: 0.35 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 3H), 7.23–7.19 (m, 3H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.10–7.09 (m, 3H), 4.68 (d, *J* = 8.3 Hz, 1H), 3.91 (ddd, *J* = 10.3, 8.3, 3.4 Hz, 1H), 3.06 (ddd, *J* = 17.2, 10.3, 4.8 Hz, 1H), 2.92 (dt, *J* = 17.2, 4.8 Hz, 1H), 2.16 (m, 1H), 1.98 (m, 1H); $^{13}C\{^{1}H, ^{19}F\}$NMR (150 MHz, $CDCl_3$) δ 202.1, 144.5, 140.0, 139.8, 136.4, 133.0, 129.1, 129.0, 128.6, 128.6, 128.5, 128.1, 127.0, 126.7, 124.2, 122.6, 50.4, 46.9, 28.8, 26.0; HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{19}F_3NaO$ $(M + Na)^+$ 403.1286, found 403.1295.

Methyl 1,2,3,4-tetrahydro-1-phenylnaphthalene-2-carboxylate (5).



The dichloromethane solution (1 mL) containing **4c** (31 mg, 0.1 mmol) and MS4A (70 mg) was stirred at room temperature under nitrogen for 1.5 h. To the mixture was added MeOTf (53 μL, 0.5 mmol) at 0 ℃, and resulting mixture was stirred at room temperature until consumption of **4c** monitored by TLC. Upon consumption of **4c**, DBU (50 μL, 0.33 mmol) and MeOH (1 mL) add to the solution. After 1 h the reaction mixture was quenched by HCl aq, and solids were removed by filtration. The filtrate was extracted with dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent: 15% ethyl acetate in hexane) to give **5** (22 mg, 0.083 mmol, 83% yield) as a colorless oil; Rf **5**: 0.35 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.6 Hz, 2H), 7.20 (m, 1H), 7.12–7.09 (m, 4H), 7.02 (m, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 4.43 (d, *J* = 9.0 Hz, 1H), 3.55 (s, 3H), 3.00 (m, 1H), 2.95–2.89 (m, 2H), 2.16 (m, 1H), 2.03 (m, 1H); $^{13}C\{^{1}H\}$NMR (150 MHz, $CDCl_3$) δ 175.2, 144.8, 138.2, 135.9, 130.0, 129.1, 128.6, 128.4, 126.5, 126.0, 126.0, 51.6, 49.3, 47.8, 28.7, 25.7; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{18}NaO_2$ $(M + Na)^+$ 289.1204, found 289.1208.

Mechanistic investigation: Examination of a reaction pathway via the aldol condensation product. As a preliminary examination for the reaction pathway, we subjected the aldol condensation product to the acidic reaction conditions for the [5 + 1] annulation as follows. Enone **6** was separately prepared by the base-catalyzed aldol reaction, and treated with $BF_3 \cdot OEt_2$. The Nazarov cyclization product, **7**, was obtained instead of the tetraline product, **4ae**. This suggests that the conventional aldol condensation is not involved in the reaction pathway of the [5 + 1] annulation.



Enone **6** was prepared by aldol condensation reaction of **3a** with 2-methoxyabenzaldehyde as follows. To a stirred solution of **3a** (673 mg, 3 mmol) and 2-methoxybenzaldehyde (1.23 g, 4.5 mmol) in ethanol (5 mL) was added NaOH (2.4 g 6 mmol). The mixture was refluxed with an oil bath for 12 h. The reaction mixture was then quenched by HCl aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by SiO_2 column (eluent: 5% ethyl acetate in hexane) to give **6** (294 mg, 29% yield) as a mixture of *E/Z* isomers (8 : 2). Rf: 0.45 (10% ethyl acetate in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) of the major isomer δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.25 (s, 1H), 7.23–7.20 (m,2H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.74 (s, 3H) 2.95 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H); selected ^{1}H NMR (600 MHz, $CDCl_3$) of the minor isomer δ 7.34 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.58 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 2.88–2.86 (m, 2H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) of the mixture δ 200.3, 199.0, 157.2, 156.4, 141.6, 141.3, 140.5, 140.0, 138.72, 138.67, 136.4, 132.7, 131.8, 130.2, 129.92, 129.88, 129.4, 129.2, 129.0, 128.5, 128.30, 128.28, 128.1, 127.6, 125.93, 125.88, 125.2, 124.6, 120.2, 120.1, 110.5, 110.0, 55.4, 55.1, 38.1, 34.7, 34.4, 29.7; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{15}F_3NaO$ $(M + Na)^+$ 365.1517, found 365.1514.

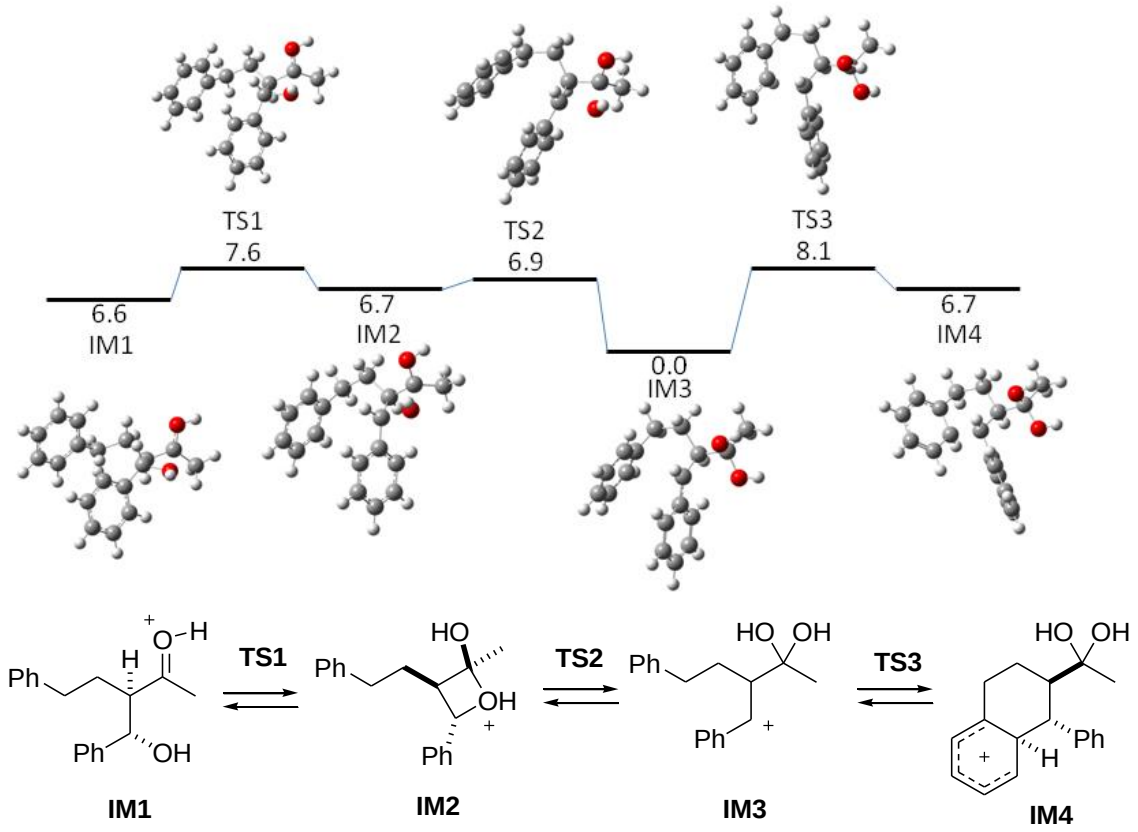
To a stirred solution of **6** (76.6 mg, 0.224 mmol) in a mixed solvent of hexane and dichloromethane (9 : 1 (v/v),2 mL) was added $BF_3 \cdot OEt_2$ (30 μL, 0.269 mmol). The mixture was refluxed with an oil bath for 12 h. The reaction mixture was then quenched by Na_2CO_3 aqueous solution, and extracted by dichloromethane. The extracts were dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by SiO_2 column (eluent: 5% ethyl acetate in hexane) to give **7** (66.9 mg, 87% yield) as an oil. Rf: 0.34 (10% ethyl acetate in hexane), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* =

7.6 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 2H), 6,94 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 4.63 (s, 1H), 3.71 (s, 3H), 2.77–2.71 (m, 3H), 2.25 (m, 1H), 2.00 (m, 1H); $^{13}C\{^{1}H\}$NMR (150 MHz, $CDCl_3$) δ 208.0, 157.5, 157.1, 141.9, 136.6, 134.7, 131.7, 129.2, 128.5, 128.2, 128.1, 127.4, 126.2, 125.7, 123.4, 121.0, 111.2, 56.0, 55.4, 46.3, 33.2, 33.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{15}F_3NaO$ $(M + Na)^+$ 365.1517, found 365.1524.

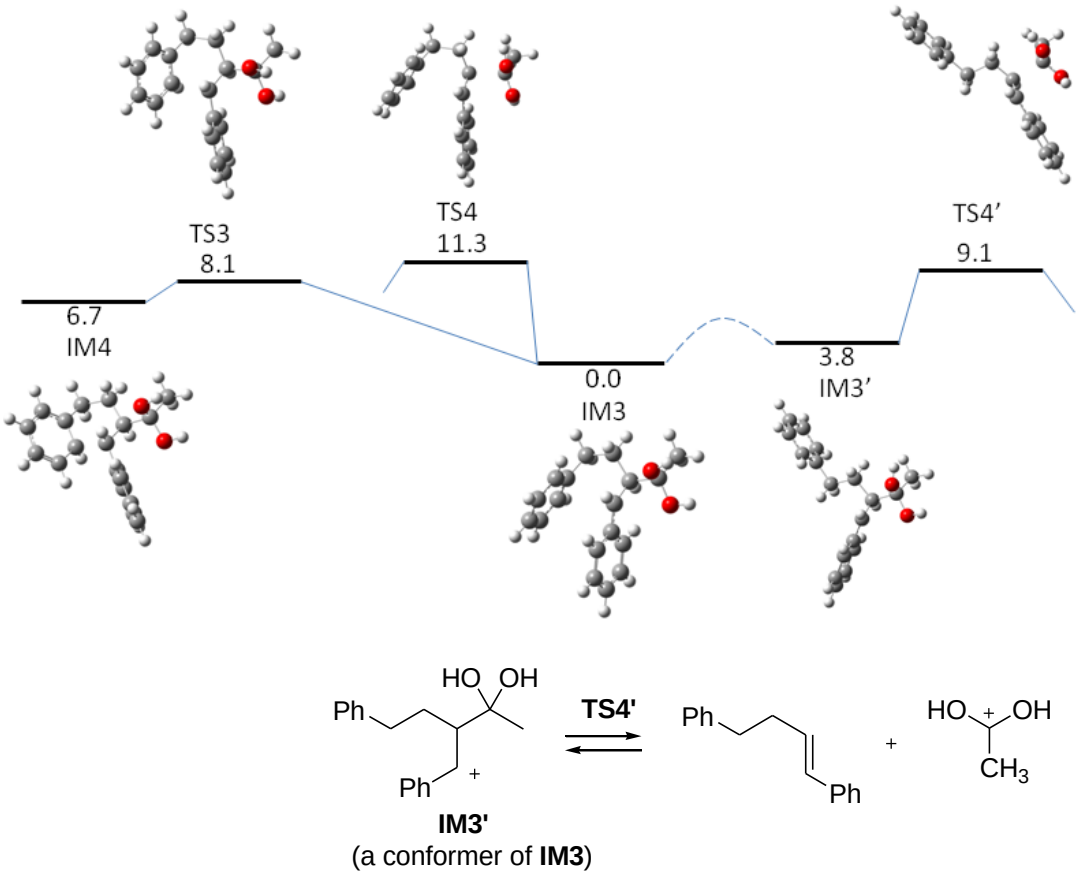
Theoretical Calculations. All geometrical parameters of the reaction intermediates and the transition states were fully optimized at the level of the hybrid exchange-correlation functional B3LYP[S5] with the 6-31G(d) basis set. All calculations were carried out using the Gaussian 09, Revision C.01 package.[S6]

(S5) (a) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 1372–1377. (b) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648–5652. (c) Becke, A. D. *Phys. Rev*. **1998**, *A38*, 3098–3100.

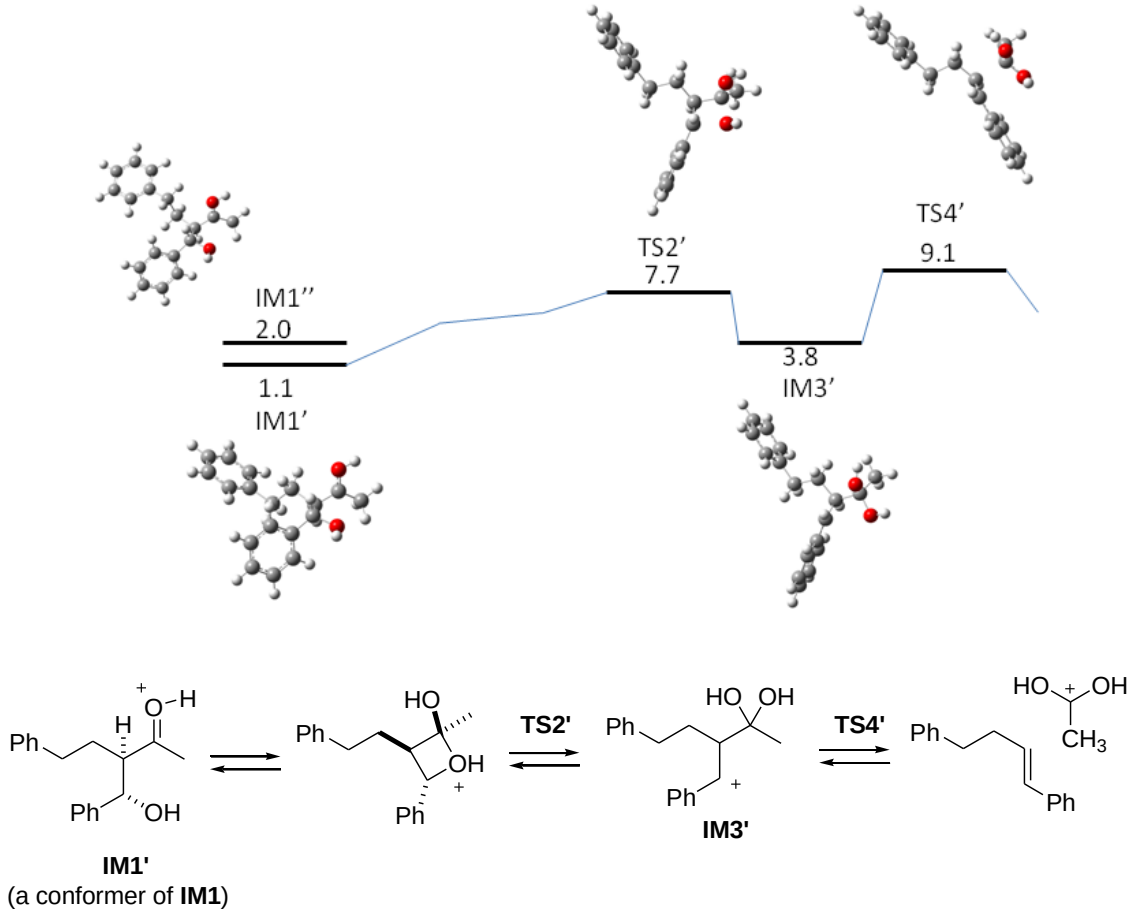
(S6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc., Wallingford CT, 2010.



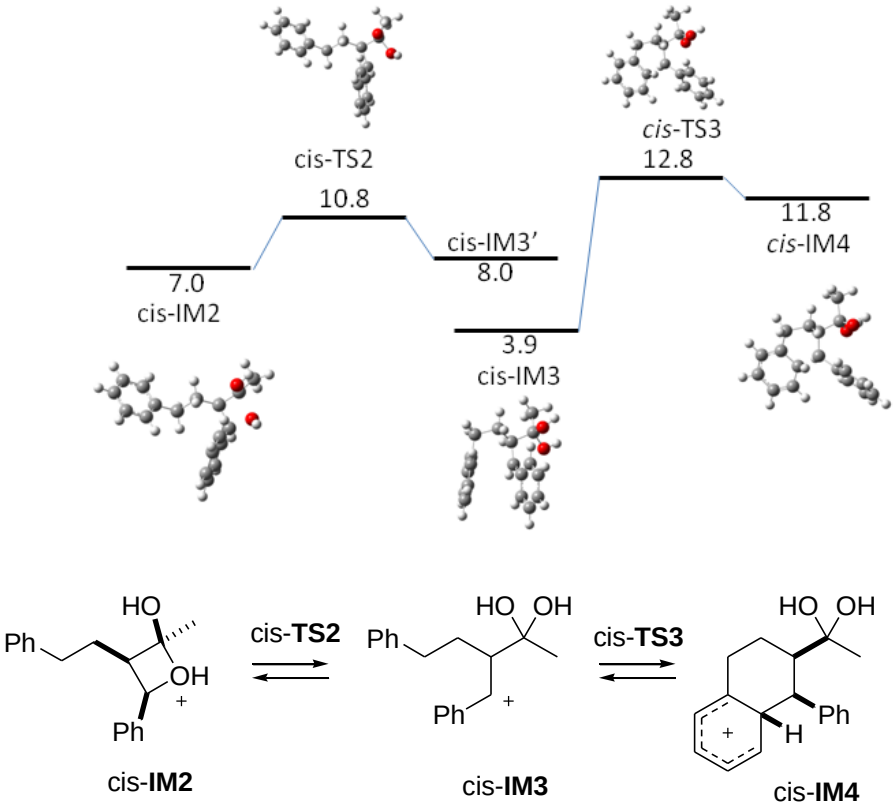
Scheme S1. Energy profile (in kcal/mol) for formation of *trans* tetraline product



Scheme S2. Comparison of energy profiles (in kcal/mol) for the *trans* tetraline formation and Grob elimination



Scheme S3. Energy profile (in kcal/mol) for Grob elimination



Scheme S4. Energy profile (in kcal/mol) for formation of *cis* tetraline product

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Spin = Singlet
E(RB3LYP) = -848.73993792 a.u.
RMS Gradient Norm = 0.00000505 a.u.
Imaginary Freq =
Dipole Moment = 10.9202 Debye
1 1

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H	1.76356600	-2.39431100	1.44658000
C	1.86551200	-0.50255700	0.44244700
H	1.96316000	0.13219700	1.32906100
C	3.24808400	-0.84047700	-0.01131800
C	1.28418400	0.38166100	-0.72651700
C	0.26205700	1.42059400	-0.35347300
C	0.59926200	2.46146600	0.52897600
C	-0.99642800	1.42409100	-0.96797300
C	-0.31175900	3.47848100	0.79862000
H	1.58433700	2.48887800	0.98839300
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H	-1.27192200	0.61993900	-1.64462900
C	-1.56612500	3.47445300	0.17923300
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H	-2.27429600	4.27175600	0.38503000
O	2.48811000	1.00978700	-1.22759700
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H	4.25692500	-1.96631500	-1.16589700
C	4.46122200	-0.21742100	0.56096400
H	4.54363500	-0.52966400	1.61285000
H	5.37938400	-0.49180800	0.03258200
H	4.33532000	0.86928000	0.55433500
H	2.25014600	1.61919900	-1.94785400
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C	-0.24120400	-1.63493400	1.55296900
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H	-0.34215400	-2.51603400	2.20138100
C	-1.50849100	-1.52035000	0.71994200
C	-2.55501000	-0.70603600	1.17270000
C	-1.71216100	-2.27784400	-0.44196300
C	-3.76546000	-0.64025500	0.48290600
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C	-2.91801700	-2.20538300	-1.14332800
H	-0.94022900	-2.95345400	-0.80299800
C	-3.94932500	-1.38490400	-0.68369300
H	-4.56424700	-0.00592100	0.85690900
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H	-4.89072100	-1.33556100	-1.22320500

IM1'
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Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
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RMS Gradient Norm = 0.00000305 a.u.
Imaginary Freq =
Dipole Moment = 6.8061 Debye
1 1

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C	-3.96101700	-2.43411900	-0.99690000
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O	-0.75437600	2.93233400	-1.35066600
H	0.04872900	3.47397800	-1.40132300
C	-0.42161100	3.64778400	0.95699000
H	0.67099900	3.66123900	0.88344900
H	-0.79092500	4.65174600	0.71750800
H	-0.69775100	3.42141100	1.99015100
H	-2.80400600	3.48099500	-0.19426100
H	-1.52137100	0.61963200	-1.59275200
C	1.26253500	-0.59322100	0.34928900
H	0.99734900	-0.82518600	1.38903200
H	0.71281500	-1.30389800	-0.28313300
C	2.75295900	-0.76901700	0.14934200
C	3.63816300	-0.65898600	1.23021100
C	3.27694600	-1.00491500	-1.12993800
C	5.01481100	-0.77954100	1.03844900
H	3.24707300	-0.48628000	2.23086100
C	4.65215700	-1.12705400	-1.32470100
H	2.60299500	-1.10595000	-1.97868700
C	5.52491700	-1.01255900	-0.24003900
H	5.68763400	-0.69777200	1.88730200

H	5.04253000	-1.31780600	-2.32032700
H	6.59605700	-1.11116400	-0.39002200

IM1”
Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.74713035 a.u.
RMS Gradient Norm = 0.00000581 a.u.
Imaginary Freq =
Dipole Moment = 9.8520 Debye
1 1

C	-0.41405000	-0.75568800	0.61452400
H	-0.90022900	-1.30641900	1.42863800
C	1.04400000	-1.29536600	0.46165600
H	1.54842600	-1.14944200	1.42209700
C	1.14783100	-2.73666100	0.14732100
C	1.92123100	-0.54514000	-0.61073000
H	1.42043700	-0.63911800	-1.58273400
C	2.14048800	0.90615800	-0.27646200
C	1.50517000	1.90868900	-1.02342600
C	2.99338300	1.26932400	0.77855800
C	1.71227400	3.25368300	-0.71671000
H	0.86247100	1.63834200	-1.85806000
C	3.20072000	2.61320800	1.08165200
H	3.50807200	0.49893000	1.34668100
C	2.55755800	3.60651800	0.33725800
H	1.22402600	4.02388100	-1.30614300
H	3.86595300	2.88740800	1.89494100
H	2.72139600	4.65347400	0.57445300
O	3.12994600	-1.31537500	-0.60405900
O	0.59278800	-3.13313700	-0.94910300
H	0.72413200	-4.08806600	-1.12463100
C	1.87223700	-3.68712300	1.01684600
H	1.48431900	-3.62109000	2.04129300
H	1.82861300	-4.72353600	0.66918200
H	2.91767000	-3.34961300	1.05413000
H	-0.29016000	0.27102100	0.97697500
H	3.78982700	-0.86121400	-1.15521800
C	-1.33684000	-0.75231600	-0.61931700
H	-1.50236500	-1.77317900	-0.97897500
H	-0.86378900	-0.20134500	-1.44057500
C	-2.67178600	-0.11586300	-0.27846500
C	-2.80306400	1.27877000	-0.22788800
C	-3.78606300	-0.90875600	0.02142500
C	-4.02091300	1.86672900	0.11292900
H	-1.94832500	1.90997800	-0.46398800
C	-5.00634200	-0.32358500	0.36273200
H	-3.70368500	-1.99307700	-0.02235900
C	-5.12586600	1.06601800	0.41005100

H	-4.10927400	2.94908700	0.14100100
H	-5.86354100	-0.95266400	0.58520200
H	-6.07565800	1.52315100	0.67166400

TS1

Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.73829934 a.u.
RMS Gradient Norm = 0.00000359 a.u.
Imaginary Freq = 1
Dipole Moment = 10.2650 Debye
1 1

C	1.20755700	-1.90493900	0.84850400
H	1.15888600	-2.51776400	-0.05682600
H	1.94652700	-2.38810700	1.50068900
C	1.76411700	-0.51190100	0.49198200
H	1.83966200	0.09763000	1.39866400
C	3.15534800	-0.58260500	-0.13214000
C	1.07885000	0.31346700	-0.62770000
C	0.13473700	1.42622600	-0.30161600
C	0.49129900	2.43114000	0.61242500
C	-1.09512100	1.50878200	-0.96676700
C	-0.37135100	3.49502300	0.85881700
H	1.45178300	2.39593000	1.12081300
C	-1.95937000	2.57500000	-0.71833900
H	-1.38815500	0.72827100	-1.66374700
C	-1.59906600	3.56802100	0.19268000
H	-0.08761600	4.26941300	1.56512500
H	-2.91239000	2.62701200	-1.23559800
H	-2.27090800	4.39924500	0.38537600
O	2.36130500	0.87173400	-1.18002800
O	3.33891900	-1.59193200	-0.94492900
H	4.26014400	-1.64824400	-1.26661000
C	4.34325400	0.09303600	0.46210100
H	4.67153700	-0.51228800	1.31996400
H	5.17342300	0.16614900	-0.24889900
H	4.08851600	1.08935200	0.82383200
H	2.33079100	0.94246200	-2.15360700
H	0.64949300	-0.36203000	-1.37208800
C	-0.14879900	-1.92027000	1.58188100
H	-0.12882800	-1.19461000	2.40446700
H	-0.22973600	-2.90558600	2.06071900
C	-1.38966200	-1.69231400	0.73428100
C	-2.42151400	-0.87499800	1.21291800
C	-1.57614400	-2.34865600	-0.49210100
C	-3.60320000	-0.71030700	0.48924700
H	-2.30169800	-0.36467800	2.16569900
C	-2.75247900	-2.17811800	-1.22507300
H	-0.81392200	-3.02472800	-0.87371600

C	-3.77097600	-1.35700000	-0.73629100
H	-4.39255800	-0.07728400	0.88467900
H	-2.88031700	-2.70236000	-2.16825000
H	-4.69131400	-1.23371300	-1.29988500

IM2

Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.73971640 a.u.
RMS Gradient Norm = 0.00000248 a.u.
Imaginary Freq =
Dipole Moment = 8.3079 Debye
1 1

C	1.32772100	-1.99790100	0.74196400
H	1.32437400	-2.53347900	-0.21268000
H	2.13980400	-2.43935200	1.33303400
C	1.69078500	-0.52587700	0.50003700
H	1.69889100	0.01039200	1.45347000
C	3.03979800	-0.29568700	-0.21976500
C	0.88544400	0.25962600	-0.55226000
C	0.01001700	1.40802600	-0.24861600
C	0.28176500	2.29325300	0.80957000
C	-1.10272700	1.64230400	-1.07322300
C	-0.54482500	3.38870100	1.03529400
H	1.14241900	2.13715000	1.45392700
C	-1.93271700	2.73652300	-0.84093100
H	-1.33171700	0.95207500	-1.88073200
C	-1.65272800	3.61103100	0.21044700
H	-0.32884100	4.07017500	1.85228400
H	-2.79568800	2.90515900	-1.47740700
H	-2.29754400	4.46600100	0.39098500
O	2.29361200	0.80099500	-1.16223000
O	3.40252400	-1.33595400	-1.00662000
H	4.34644600	-1.28519100	-1.24130600
C	4.15877200	0.42254100	0.48489200
H	4.57197900	-0.24184300	1.25260900
H	4.95834400	0.69332400	-0.21458900
H	3.80004900	1.33334600	0.96775100
H	2.39637400	0.58108200	-2.11227800
H	0.47947600	-0.38257100	-1.33378500
C	-0.00057700	-2.22610400	1.48992200
H	0.00840900	-1.66315900	2.43159700
H	-0.02783200	-3.28606500	1.77467300
C	-1.25781600	-1.88703500	0.70819200
C	-2.22705400	-1.03368800	1.25043600
C	-1.50277600	-2.45890500	-0.55128800
C	-3.40600200	-0.75240000	0.55720100
H	-2.06273700	-0.59202500	2.23065000

C	-2.67631500	-2.17421100	-1.25120000
H	-0.78708100	-3.15820800	-0.97935700
C	-3.63235100	-1.31800500	-0.69825800
H	-4.14833300	-0.09539900	1.00148400
H	-2.85400700	-2.63746300	-2.21796400
H	-4.55235400	-1.10742100	-1.23605100

TS2

Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.73938596 a.u.
RMS Gradient Norm = 0.00000777 a.u.
Imaginary Freq = 1
Dipole Moment = 6.9178 Debye
1 1

C	1.50324700	-1.90114200	0.70509000
H	1.55007000	-2.41356200	-0.26055300
H	2.35268100	-2.27806800	1.28830500
C	1.73235300	-0.39676500	0.49109800
H	1.70392400	0.11721900	1.45631000
C	3.04800100	-0.02675100	-0.23476400
C	0.82203400	0.31437500	-0.51122100
C	-0.14275900	1.35715300	-0.21973600
C	-0.06275900	2.16307400	0.93579200
C	-1.17886500	1.58627300	-1.14896500
C	-0.99691900	3.16715500	1.15129900
H	0.73316800	2.01322100	1.65843900
C	-2.11604200	2.58861800	-0.92537900
H	-1.25607800	0.95837200	-2.03214100
C	-2.02331600	3.38023500	0.22215400
H	-0.93080300	3.78743700	2.03958000
H	-2.91601300	2.75354300	-1.64000600
H	-2.75219600	4.16626400	0.39672000
O	2.35078900	1.07976600	-1.06105000
O	3.44009500	-1.01359600	-1.10585800
H	4.39314700	-0.94884900	-1.28885500
C	4.16731100	0.59934800	0.56071400
H	4.58045300	-0.14331900	1.25202200
H	4.96795000	0.94896600	-0.10215900
H	3.80687800	1.45375800	1.13735800
H	2.53156200	0.92910200	-2.01216600
H	0.58381200	-0.28564400	-1.38762700
C	0.19933000	-2.25969500	1.44217900
H	0.17195800	-1.74661200	2.41148400
H	0.24273300	-3.33252100	1.67168300
C	-1.07681700	-1.96125900	0.67516200
C	-2.10746200	-1.21764300	1.26539000
C	-1.27602800	-2.46197900	-0.62271900

C	-3.29863100	-0.97066500	0.58126600
H	-1.98005700	-0.83636200	2.27599300
C	-2.46353800	-2.21247600	-1.31268300
H	-0.51159500	-3.07942600	-1.09011600
C	-3.47879100	-1.46329800	-0.71260100
H	-4.08774000	-0.39923600	1.06182000
H	-2.60438100	-2.62078100	-2.30981400
H	-4.40863600	-1.28020500	-1.24348000

TS2’

Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.73811476 a.u.
RMS Gradient Norm = 0.00000252 a.u.
Imaginary Freq = 1
Dipole Moment = 8.7818 Debye
1 1

C	0.87337400	0.95634300	0.04872900
H	1.09746900	1.14333600	-1.00667400
H	1.43891200	1.70307900	0.61968600
C	-0.62223200	1.19222100	0.30960700
H	-0.84641000	1.00430000	1.36391900
C	-1.18940400	2.57854800	-0.06513900
C	-1.57155800	0.39957000	-0.57206400
C	-2.36675700	-0.73872400	-0.20400300
C	-2.65777200	-1.06465300	1.14200600
C	-2.86215900	-1.56969700	-1.23784400
C	-3.41167100	-2.19085300	1.43682900
H	-2.29918500	-0.43491000	1.94930100
C	-3.60999600	-2.69928300	-0.93584800
H	-2.64178300	-1.32455400	-2.27372800
C	-3.88484700	-3.00797900	0.40097500
H	-3.63400400	-2.44052700	2.46925700
H	-3.97860900	-3.33873600	-1.73129000
H	-4.47108400	-3.89066200	0.63937800
O	-2.55118500	2.00008300	-0.46113100
O	-0.59044500	3.06014800	-1.21026900
H	-0.63975400	4.03055100	-1.23910600
C	-1.37900800	3.60469500	1.02610400
H	-0.40107400	3.92307100	1.40311300
H	-1.91198800	4.48335400	0.64311300
H	-1.95827600	3.19149600	1.85447000
H	-2.80829600	2.36827600	-1.33113300
H	-1.33005800	0.46432600	-1.63270600
C	1.35059100	-0.45520700	0.45007600
H	1.11160300	-0.63071800	1.50732600
H	0.79449100	-1.20850000	-0.12425000
C	2.83760200	-0.63423800	0.22148600
C	3.75660200	-0.33327900	1.23485900

C	3.32242900	-1.06776000	-1.01925900
C	5.12855600	-0.45927800	1.01348500
H	3.39676400	-0.00674900	2.20870700
C	4.69342900	-1.19480900	-1.24455800
H	2.62196900	-1.31765400	-1.81413600
C	5.60017400	-0.88922300	-0.22801900
H	5.82782400	-0.22836400	1.81216200
H	5.05280300	-1.53848000	-2.21048500
H	6.66761000	-0.99213100	-0.40025400

IM3

Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.75037659 a.u.
RMS Gradient Norm = 0.00000344 a.u.
Imaginary Freq =
Dipole Moment = 3.2044 Debye
1 1

C	1.73977400	-1.85417000	0.38544800
H	1.82059100	-2.20235700	-0.64918400
H	2.66439900	-2.14971500	0.88982700
C	1.64458400	-0.30775000	0.38258800
H	1.58015600	0.06191400	1.40958600
C	2.92785100	0.36220900	-0.24590100
C	0.49520500	0.16530700	-0.43446500
C	-0.41964300	1.19263700	-0.15443300
C	-0.40092400	1.94590500	1.05714300
C	-1.38406400	1.52207600	-1.15392600
C	-1.29167800	2.98493100	1.24058300
H	0.33075000	1.71915400	1.82334100
C	-2.27603900	2.56322400	-0.95680100
H	-1.40134700	0.94972400	-2.07595600
C	-2.22766600	3.29361100	0.23693400
H	-1.26937300	3.56852200	2.15518600
H	-3.00248900	2.81607100	-1.72207600
H	-2.92261500	4.11437900	0.39096300
O	2.65234500	1.74797000	-0.15175800
O	2.96044000	-0.07891300	-1.58773300
H	3.84420300	0.07425100	-1.95988900
C	4.22201000	0.02157600	0.49113500
H	4.48188800	-1.03499500	0.39686700
H	5.04626200	0.60518300	0.05776000
H	4.15365300	0.28401900	1.55065500
H	3.45765900	2.24970400	-0.36141600
H	0.45113600	-0.25514000	-1.43499300
C	0.55285200	-2.52522800	1.10109700
H	0.57393500	-2.26884000	2.16695000
H	0.69868900	-3.61226000	1.04553800

C	-0.79614400	-2.15760600	0.52426800
C	-1.79445900	-1.58684200	1.33319600
C	-1.09957300	-2.41310600	-0.83042900
C	-3.03553300	-1.24636900	0.80431800
H	-1.58964100	-1.41064900	2.38636600
C	-2.34543500	-2.07968200	-1.36150300
H	-0.36152200	-2.90012000	-1.46367600
C	-3.31288600	-1.48486800	-0.54844400
H	-3.79466000	-0.80574800	1.44411700
H	-2.56592100	-2.29814800	-2.40252100
H	-4.28741900	-1.23252400	-0.95636400

IM3'

Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.74426356 a.u.
RMS Gradient Norm = 0.00000305 a.u.
Imaginary Freq =
Dipole Moment = 6.8061 Debye
1 1

C	0.82290200	0.84430800	0.01588500
H	1.02427100	1.06408900	-1.03762700
H	1.41816700	1.54558700	0.61169600
C	-0.68093100	1.14687300	0.32206400
H	-0.87509100	0.96619200	1.38289500
C	-1.05616000	2.64200300	0.00094600
C	-1.55644500	0.33519300	-0.54059100
C	-2.39270600	-0.73510400	-0.20943300
C	-2.55564400	-1.21385900	1.12807500
C	-3.11976200	-1.37100700	-1.26520600
C	-3.39934800	-2.27612100	1.38377400
H	-2.01970800	-0.73865500	1.94165800
C	-3.96101700	-2.43411900	-0.99690000
H	-3.00097600	-1.00443300	-2.28088400
C	-4.09871600	-2.88436200	0.32527200
H	-3.52794600	-2.64254300	2.39684100
H	-4.51210400	-2.91683400	-1.79702300
H	-4.76115000	-3.71907200	0.53730400
O	-2.46511100	2.62353300	0.11896700
O	-0.75437600	2.93233400	-1.35066600
H	0.04872900	3.47397800	-1.40132300
C	-0.42161100	3.64778400	0.95699000
H	0.67099900	3.66123900	0.88344900
H	-0.79092500	4.65174600	0.71750800
H	-0.69775100	3.42141100	1.99015100
H	-2.80400600	3.48099500	-0.19426100
H	-1.52137100	0.61963200	-1.59275200
C	1.26253500	-0.59322100	0.34928900
H	0.99734900	-0.82518600	1.38903200

H	0.71281500	-1.30389800	-0.28313300
C	2.75295900	-0.76901700	0.14934200
C	3.63816300	-0.65898600	1.23021100
C	3.27694600	-1.00491500	-1.12993800
C	5.01481100	-0.77954100	1.03844900
H	3.24707300	-0.48628000	2.23086100
C	4.65215700	-1.12705400	-1.32470100
H	2.60299500	-1.10595000	-1.97868700
C	5.52491700	-1.01255900	-0.24003900
H	5.68763400	-0.69777200	1.88730200
H	5.04253000	-1.31780600	-2.32032700
H	6.59605700	-1.11116400	-0.39002200

TS3

Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.73743777 a.u.
RMS Gradient Norm = 0.00000363 a.u.
Imaginary Freq = 1
Dipole Moment = 1.7713 Debye
1 1

C	-1.49856300	2.06285600	-0.49798200
H	-1.84610800	2.22324400	0.52816500
H	-1.45958700	3.04140000	-0.98301800
C	-0.08869900	1.44750400	-0.46286800
H	0.34046700	1.45591800	-1.47151800
C	-0.02642300	0.03657100	0.11109200
H	-0.45008500	-0.01904800	1.11097500
C	1.18539700	-0.77641000	-0.05026800
C	1.64730300	-1.52277900	1.05154600
H	1.09490000	-1.49206400	1.98693400
C	1.90881100	-0.83045500	-1.25878400
H	1.56096100	-0.28231300	-2.13043600
C	3.06754200	-1.59147000	-1.35362200
H	3.61580000	-1.62942200	-2.29001100
C	3.52758800	-2.30835800	-0.24274000
H	4.43497700	-2.90016100	-0.31856000
C	2.81756100	-2.26937300	0.96065400
H	3.17591600	-2.82216800	1.82357200
C	-2.53200300	1.19661400	-1.26184600
H	-2.24346400	1.12150600	-2.31726000
H	-3.51133400	1.68276500	-1.21783900
C	-2.57059500	-0.15302500	-0.62927000
C	-1.45256300	-1.02320300	-0.85269400
H	-0.93527500	-0.92692200	-1.80461600
C	-1.44898800	-2.32099500	-0.23879100
H	-0.63775100	-3.00578600	-0.46427800
C	-3.54726100	-0.52376400	0.29567300

H	-4.37045100	0.15113500	0.51118100
C	-3.48462100	-1.76823100	0.92187500
H	-4.26118000	-2.04852300	1.62833500
C	-2.43649900	-2.67462900	0.65165200
H	-2.42481200	-3.64650500	1.13431900
C	0.87096700	2.35674100	0.42803900
C	0.87620500	3.82260600	-0.02614200
H	-0.08553600	4.30503000	0.15434700
H	1.63474600	4.36152700	0.55320600
H	1.12352500	3.91913900	-1.09021400
O	0.38236400	2.21921800	1.73987700
H	1.03872100	2.61761200	2.33632600
O	2.19108600	1.85279300	0.41785800
H	2.72701500	2.35634800	-0.21463700

IM4

Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.73970475 a.u.
RMS Gradient Norm = 0.00000534 a.u.
Imaginary Freq =
Dipole Moment = 5.0366 Debye
1 1

C	1.46921200	-2.10020200	-0.46266300
H	1.78621600	-2.28229000	0.57010800
H	1.43023700	-3.06954000	-0.96592700
C	0.07972900	-1.44385000	-0.46186100
H	-0.30950600	-1.41681600	-1.48645800
C	-0.92235300	-2.32190900	0.36301200
C	0.09850800	0.00511400	0.10892700
C	-1.17054000	0.80776900	-0.04592400
C	-1.74111300	1.05385500	-1.30360500
C	-1.78512600	1.34767700	1.09267200
C	-2.90948800	1.80381100	-1.41864300
H	-1.28498900	0.64832600	-2.20487600
C	-2.95644600	2.09560000	0.97998100
H	-1.35644700	1.15916000	2.07383900
C	-3.52083500	2.32684000	-0.27608300
H	-3.34371800	1.97973500	-2.39838000
H	-3.42844300	2.49613600	1.87239900
H	-4.42987100	2.91412000	-0.36605400
O	-2.19906000	-1.77257600	0.13173100
O	-0.51607600	-2.17743600	1.71766400
H	-0.99730500	-2.82066300	2.26298200
C	-0.92230600	-3.80091200	-0.04423200
H	0.01495100	-4.30186000	0.20788700
H	-1.72596400	-4.32057800	0.49561400
H	-1.11899500	-3.91595800	-1.11453300

H	-2.87441300	-2.38990300	0.45716300
H	0.37109500	-0.04949600	1.16444800
C	2.54122900	-1.24824200	-1.19120200
H	2.26445500	-1.15121700	-2.24937900
H	3.51564800	-1.74253400	-1.14320800
C	2.58029000	0.09049600	-0.54966200
C	1.34560400	0.88457200	-0.61559300
C	3.66209700	0.54330000	0.19127100
C	1.39687700	2.22100500	-0.00854400
H	0.97642700	0.94426600	-1.64775300
C	3.62109200	1.80583300	0.79109900
H	4.55316700	-0.07005100	0.28497100
C	2.49520200	2.65629600	0.68126200
H	0.51056800	2.84190600	-0.08917900
H	4.48522700	2.14766300	1.35573700
H	2.51293100	3.63736700	1.14416200

TS4

Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.73240128 a.u.
RMS Gradient Norm = 0.00000528 a.u.
Imaginary Freq = 1
Dipole Moment = 6.2177 Debye
1 1

C	0.48223200	-2.36221100	-0.43387000
H	0.71883200	-2.55901800	0.61967300
H	0.07901000	-3.28765100	-0.86282600
C	-0.53795700	-1.24105200	-0.52452100
H	-0.98173700	-1.10586400	-1.51201200
C	-2.25177700	-1.94390000	0.44577300
C	-0.33252800	-0.08639800	0.23253500
C	-0.93340300	1.20177600	0.05156800
C	-1.64435800	1.56871200	-1.12009900
C	-0.82665500	2.14400800	1.10343600
C	-2.23999000	2.81682700	-1.21730200
H	-1.69478300	0.88652400	-1.96400100
C	-1.42569300	3.39304000	1.00117000
H	-0.27575700	1.87516500	2.00030200
C	-2.13512500	3.72888300	-0.15588900
H	-2.77441400	3.09632100	-2.11999900
H	-1.34227700	4.10528500	1.81578100
H	-2.59990600	4.70687000	-0.23989100
O	-3.01543200	-0.89058800	0.76185800
O	-1.79368500	-2.48824700	1.58118500
H	-1.38382100	-3.35067500	1.40318900
C	-2.78677300	-2.87601000	-0.62407500
H	-2.06565000	-3.64806200	-0.89784200

H	-3.68317000	-3.36000400	-0.21567100
H	-3.06602300	-2.32991300	-1.52868700
H	-3.47161600	-0.54402400	-0.02239800
H	0.25081200	-0.20337700	1.14485700
C	1.80496300	-2.02376100	-1.17906300
H	1.58305800	-1.82469800	-2.23401000
H	2.43213800	-2.92333100	-1.15622200
C	2.54934000	-0.85568300	-0.57194400
C	2.54553300	0.40585000	-1.18601200
C	3.24670300	-1.00873600	0.63796500
C	3.21926500	1.48611100	-0.60989600
H	2.03030000	0.53725600	-2.13494200
C	3.91683500	0.06739900	1.21680000
H	3.28098900	-1.98410500	1.11941800
C	3.90317700	1.31998600	0.59389600
H	3.21725400	2.45151300	-1.10802200
H	4.46211400	-0.07197500	2.14597800
H	4.43485700	2.15539900	1.04014500

TS4’

Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.73586636 a.u.
RMS Gradient Norm = 0.00000275 a.u.
Imaginary Freq = 1
Dipole Moment = 7.1721 Debye
1 1

C	-1.04637800	0.49353000	0.01029300
H	-1.20512600	0.45676300	1.09651600
H	-1.54066000	1.39743600	-0.35867000
C	0.44791300	0.52920100	-0.29039600
H	0.70245700	0.70095800	-1.33662800
C	1.17425200	2.26172500	0.38291100
C	1.26178000	-0.38181000	0.40018000
C	2.57253600	-0.83445100	0.07724600
C	3.22208200	-0.52802400	-1.15082300
C	3.26135000	-1.63278700	1.03268000
C	4.50380000	-0.99174800	-1.39680800
H	2.71106800	0.06101500	-1.90396400
C	4.54204400	-2.09575800	0.77681400
H	2.76959900	-1.87887400	1.97011200
C	5.16362300	-1.77429400	-0.43723000
H	4.99513200	-0.75828800	-2.33584900
H	5.05996500	-2.70557500	1.50991600
H	6.16553700	-2.14067700	-0.64139200
O	2.49807500	2.23551800	0.16153900
O	0.88455000	2.31030000	1.70740400
H	-0.04741700	2.54725300	1.85063500

C	0.49382900	3.26698200	-0.52272700
H	-0.59195400	3.24611900	-0.42469200
H	0.85850400	4.25710100	-0.22487400
H	0.76904000	3.09808900	-1.56485500
H	2.96024700	1.86832600	0.93781900
H	0.88224400	-0.72176200	1.36568900
C	-1.75034000	-0.72875200	-0.63564500
H	-1.57037300	-0.71153600	-1.71779300
H	-1.28566900	-1.64720500	-0.25370300
C	-3.23693300	-0.73419400	-0.35356900
C	-4.13399100	-0.11334900	-1.23302400
C	-3.73941300	-1.32725400	0.81279200
C	-5.50064200	-0.08349800	-0.95358600
H	-3.76245100	0.33940900	-2.15029300
C	-5.10536200	-1.30066300	1.09463300
H	-3.05867500	-1.82699600	1.49969200
C	-5.98923100	-0.67637600	0.21210600
H	-6.18411000	0.39423100	-1.64982200
H	-5.48026900	-1.77374900	1.99785900
H	-7.05359600	-0.65945400	0.42766800

cis-TS3
Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.72997920 a.u.
RMS Gradient Norm = 0.00000096 a.u.
Imaginary Freq = 1
Dipole Moment = 2.9101 Debye
1 1

C	-0.74740900	1.78978300	1.26524800
H	-0.15701900	1.28914500	2.03670200
H	-0.63695200	2.85981600	1.45436100
C	-0.22415200	1.42920500	-0.14054000
H	-0.99064800	1.75164100	-0.85571000
C	1.05239200	2.22352200	-0.55378000
C	-0.07281700	-0.08684300	-0.39733500
C	-2.24294700	1.41153900	1.36854000
H	-2.87379500	2.21108200	0.96442400
H	-2.52289000	1.30223900	2.42672100
C	-2.53248900	0.12981100	0.64396300

C	-3.67955200	-0.06908100	-0.11879400
C	-1.51962400	-0.89350800	0.66530600
C	-3.88616700	-1.28645200	-0.77369800
C	-1.79343700	-2.15550200	0.03117000
C	-2.94703700	-2.33629200	-0.69733500
H	-4.79203700	-1.42647800	-1.35747200
H	-1.05341200	-2.94668400	0.10514300
H	-3.14368000	-3.27588400	-1.20325400
H	-4.42552700	0.71705900	-0.19155300
H	-0.90143600	-0.92716000	1.55897100
C	1.11873500	-0.88687700	-0.05966300
H	-0.43847600	-0.33868900	-1.38937300
C	1.52131500	-1.87281400	-0.98487800
H	0.95749500	-2.00277000	-1.90544600
C	2.64399600	-2.65910600	-0.74978300
H	2.95030000	-3.39977200	-1.48208600
C	3.37174200	-2.49319300	0.43182600
H	4.24250500	-3.11278500	0.62514900
C	2.97610600	-1.53192800	1.36804500
H	3.54165100	-1.40294900	2.28582900
C	1.86253000	-0.73482700	1.12817500
H	1.58547700	0.01797000	1.85523300
C	0.73140200	3.68718100	-0.88112300
H	0.31926100	4.21721400	-0.01897400
H	1.65658200	4.20585800	-1.16712000
H	0.03077200	3.76118400	-1.71820500
O	1.54736100	1.56901900	-1.70886700
H	2.11577200	2.17909700	-2.20636900
O	1.94968400	2.14474900	0.53427200
H	2.76416400	2.62300000	0.30772500

cis-IM4
Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.73156176 a.u.
RMS Gradient Norm = 0.00000941 a.u.
Imaginary Freq =
Dipole Moment = 5.6811 Debye
1 1

C	-0.74313000	1.84598400	1.21297100
H	-0.20404900	1.32790300	2.01136100
H	-0.61572900	2.91257700	1.41151200
C	-0.16693600	1.46476600	-0.16093400
H	-0.86238500	1.85403900	-0.91714300
C	1.18660200	2.14832400	-0.48260400
C	-0.15177600	-0.08410800	-0.40070400
O	1.63101500	1.53089700	-1.67957400
O	2.03770800	1.89261900	0.61479200

H	2.86637500	2.38529600	0.49818200
C	1.04305500	3.65933200	-0.71051200
H	0.69090400	4.17895100	0.18431300
H	2.02465300	4.08220500	-0.96526100
H	0.36444300	3.87118100	-1.54195200
H	2.36708500	2.04486900	-2.04934000
C	-2.25017400	1.51779200	1.23832600
H	-2.84251600	2.33296700	0.80475700
H	-2.60103200	1.41790900	2.27799700
C	-2.56031900	0.24436100	0.51595800
C	-3.79085200	-0.02240100	-0.06383900
C	-1.47229300	-0.73719400	0.41229300
C	-4.02223300	-1.26254300	-0.67075700
C	-1.80001700	-2.03063900	-0.19326300
C	-3.03554700	-2.27520400	-0.72989900
H	-4.99714800	-1.45479300	-1.11239800
H	-1.00817900	-2.77269700	-0.24495800
H	-3.26464900	-3.22407700	-1.20338400
H	-4.58507900	0.71777800	-0.03118600
H	-1.02666100	-0.87943400	1.40647700
C	1.05985100	-0.91995600	-0.04857500
C	1.55049500	-1.05369800	1.25962000
C	1.70003900	-1.62775300	-1.07711500
C	2.65628600	-1.85646000	1.52736600
H	1.08574200	-0.51664700	2.08236100
C	2.80988500	-2.43032900	-0.81297900
H	1.33959400	-1.53024400	-2.09794200
C	3.28990400	-2.54882100	0.49139400
H	3.02516100	-1.94164000	2.54523700
H	3.29505700	-2.96306300	-1.62557100
H	4.14830300	-3.17952400	0.70303200
H	-0.36671200	-0.24040800	-1.45832100

cis-IM3

Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.74420318 a.u.
RMS Gradient Norm = 0.00000871 a.u.
Imaginary Freq =
Dipole Moment = 3.2540 Debye
1 1

C	1.29838000	1.41821200	1.15603900
H	0.97411800	0.65397400	1.86608600
H	2.23322800	1.83009000	1.54883900
C	1.57846400	0.79054800	-0.23261400
H	1.72914000	1.61286200	-0.93965900
C	2.91455900	-0.02893600	-0.30068400

C	0.44904000	-0.02327200	-0.80525300
O	2.81174800	-0.72134700	-1.53541600
O	2.91853100	-0.91166700	0.80053700
H	3.81301200	-1.26832800	0.92657200
C	4.15331900	0.86749900	-0.28770000
H	4.23761600	1.43516400	0.64247600
H	5.05380300	0.24383900	-0.37640200
H	4.14442500	1.56020000	-1.13338300
H	3.66915000	-1.12061100	-1.75906900
C	0.24596000	2.54467700	1.07035200
H	0.64251700	3.36419900	0.45905700
H	0.09718000	2.94913600	2.07865100
C	-1.07279200	2.07213800	0.50417200
C	-1.40126200	2.29669700	-0.84759000
C	-1.99494700	1.37979500	1.30789600
C	-2.60594300	1.83027300	-1.38484100
C	-3.18856400	0.90627600	0.77397400
C	-3.49660300	1.12582200	-0.57818200
H	-2.85100700	2.03614900	-2.42297700
H	-3.89454100	0.38008300	1.41017200
H	-4.43974400	0.77178700	-0.98418700
H	-0.72549500	2.87942400	-1.47012800
C	-0.22919300	-1.15334100	-0.32000800
C	0.05561200	-1.80928500	0.91815200
C	-1.26019100	-1.68973800	-1.15521700
C	-0.64867000	-2.94204700	1.27738100
H	0.85999500	-1.44569900	1.54209200
C	-1.96283900	-2.82087000	-0.77888900
H	-1.48242400	-1.19734600	-2.09671300
C	-1.65580100	-3.44657300	0.43605300
H	-0.42133100	-3.44961100	2.20928200
H	-2.73933600	-3.22407000	-1.42054200
H	-2.20125100	-4.33846100	0.73197100
H	0.16082400	0.26402700	-1.81185400
H	-1.77328100	1.22005200	2.36051000

cis-IM3’
Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.73769943 a.u.
RMS Gradient Norm = 0.00000177 a.u.
Imaginary Freq =
Dipole Moment = 6.4775 Debye
1 1

C	-0.62534900	0.92066000	-0.07488700
H	-0.46358700	0.29007900	0.80350800
H	-1.18929400	1.79654900	0.26611100
C	0.72712300	1.42122400	-0.64733100

H	0.50643900	2.04192000	-1.52195900
C	1.50960300	2.37769500	0.34860300
C	1.64760100	0.35252500	-1.13130100
O	2.81314900	2.39767100	-0.18508600
O	1.58897000	1.81967200	1.64576600
H	0.91865100	2.22992700	2.21570300
C	0.89281700	3.77657500	0.38952700
H	-0.14135400	3.76610900	0.75006100
H	1.48292700	4.40664400	1.06532100
H	0.90986700	4.23068600	-0.60402400
H	3.38084300	2.91682900	0.41134300
C	-1.47574400	0.16123400	-1.11347700
H	-1.62910300	0.80145100	-1.99147700
H	-0.92075500	-0.72174000	-1.46163000
C	-2.81178500	-0.26156900	-0.54331600
C	-3.95449500	0.52637500	-0.73692700
C	-2.92323700	-1.43300200	0.21953100
C	-5.17858200	0.15511100	-0.18013100
H	-3.88779500	1.43178900	-1.33657900
C	-4.14545300	-1.80844600	0.77572400
H	-2.04858000	-2.06421500	0.36740400
C	-5.27668100	-1.01319200	0.57805900
H	-6.05650800	0.77319500	-0.34483300
H	-4.21807800	-2.72384700	1.35621700
H	-6.23055500	-1.30644500	1.00664600
C	2.15766500	-0.79039500	-0.50839800
C	1.94778000	-1.12832400	0.86813300
C	2.94501700	-1.67244900	-1.32133500
C	2.49203400	-2.28862000	1.38256200
H	1.41018700	-0.43991300	1.50590400
C	3.46793700	-2.83752800	-0.79701800
H	3.11797500	-1.41453900	-2.36234700
C	3.23898400	-3.14461700	0.55396400
H	2.34644200	-2.54214400	2.42746100
H	4.05499100	-3.50687600	-1.41686800
H	3.65295700	-4.05935400	0.96943700
H	1.97596300	0.47561300	-2.16273700

cis-TS2
Calculation Method = RB3LYP
Basis Set = 6-31G(d)
Charge = 1
Spin = Singlet
E(RB3LYP) = -848.73332119 a.u.
RMS Gradient Norm = 0.00000445 a.u.
Imaginary Freq = 1
Dipole Moment = 8.2933 Debye
1 1

C	0.57816200	-1.04159100	-0.02672000
H	0.47251900	-0.42076200	0.86547700

H	1.11355500	-1.94414000	0.29354400
C	-0.78846200	-1.48638700	-0.56551300
H	-0.60971800	-2.09575500	-1.45883600
C	-1.69176000	-2.32490400	0.36505400
C	-1.81380900	-0.43247100	-0.99214800
O	-2.99467700	-1.86805800	-0.23266500
O	-1.62516400	-1.85715900	1.67033200
H	-1.79609400	-2.58100800	2.29584700
C	-1.59212700	-3.83075900	0.25553200
H	-0.59974100	-4.16526300	0.57613600
H	-2.34922900	-4.31008800	0.88785900
H	-1.75841500	-4.15666800	-0.77355000
H	-3.55949800	-1.54595400	0.49696300
C	1.42919700	-0.30335800	-1.08202800
H	1.54591300	-0.94754700	-1.96367200
H	0.89512500	0.59569900	-1.41836100
C	2.79065600	0.08534500	-0.54384700
C	3.87429300	-0.79735900	-0.63972600
C	2.98265600	1.31922300	0.09100800
C	5.11962100	-0.45740200	-0.11021700
H	3.74651100	-1.75407400	-1.14249700
C	4.22662200	1.66321600	0.62111600
H	2.15453200	2.02224700	0.16170800
C	5.29816900	0.77389800	0.52303500
H	5.95158700	-1.15024500	-0.19931500
H	4.36133000	2.62747300	1.10326100
H	6.26864700	1.04198400	0.93042500
C	-2.10561700	0.84396000	-0.42348700
C	-1.73748100	1.24006000	0.89197500
C	-2.79506200	1.77127400	-1.25274700
C	-2.03208200	2.51857000	1.33624600
H	-1.26222600	0.53034200	1.55692400
C	-3.07061200	3.05359500	-0.80345500
H	-3.09020600	1.47227800	-2.25489000
C	-2.68813300	3.42627300	0.49043700
H	-1.75581900	2.81932600	2.34175500
H	-3.58279100	3.76049300	-1.44785500
H	-2.90730400	4.42850900	0.84743300
H	-2.18534300	-0.55220900	-2.00676900

cis-IM2

Calculation Method = RB3LYP

Basis Set = 6-31G(d)

Charge = 1

Spin = Singlet

E(RB3LYP) = -848.73916701 a.u.

RMS Gradient Norm = 0.00000729 a.u.

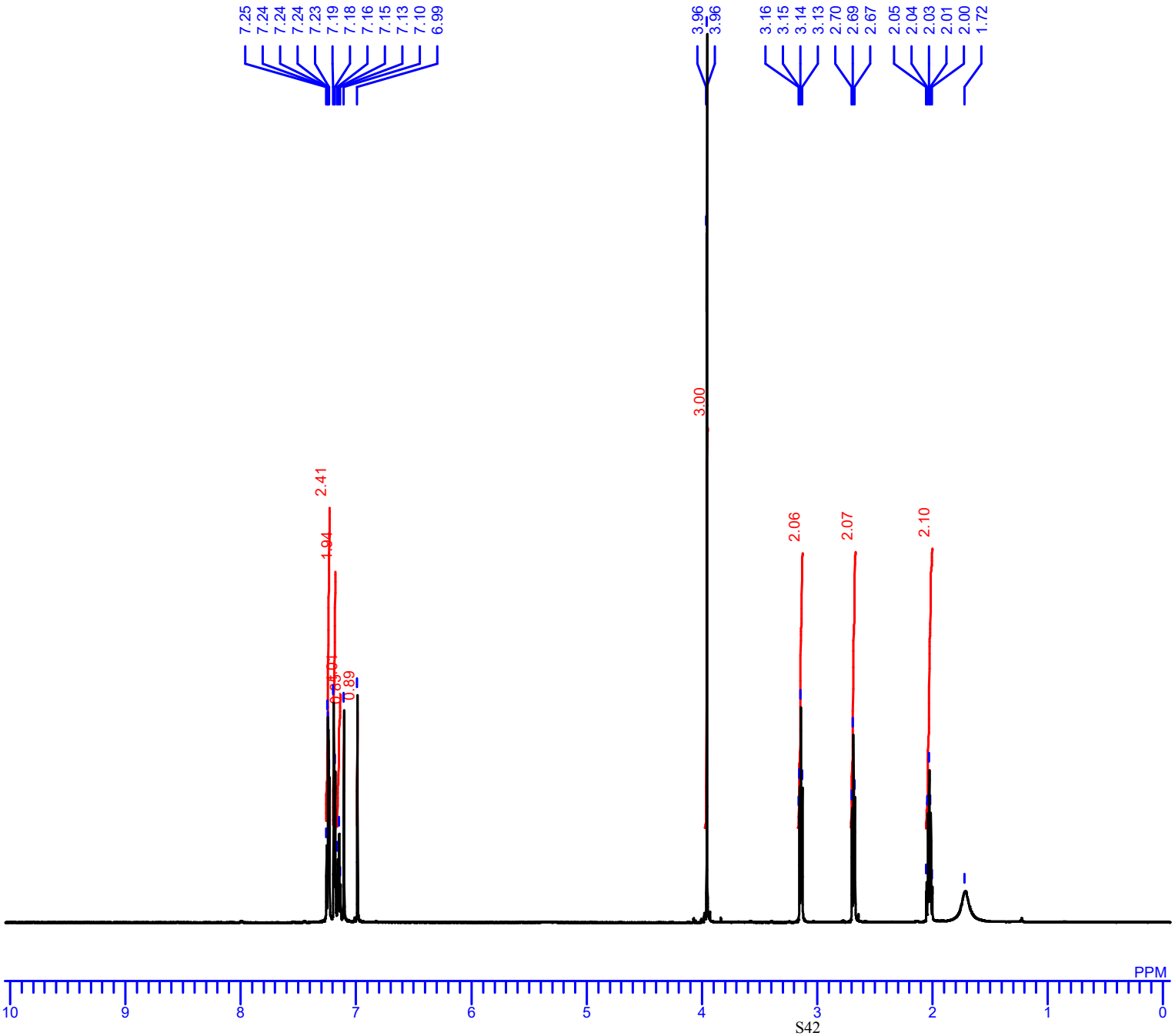
Imaginary Freq =

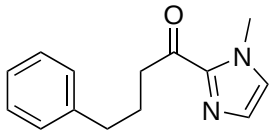
Dipole Moment = 10.1280 Debye

1 1

C	-0.29622400	1.17089100	-0.00646000
H	-0.24198300	0.48612800	0.84377900
H	-0.72175600	2.10772200	0.37424400
C	1.10358100	1.46236200	-0.56160600
H	0.99806400	2.08851800	-1.45472200
C	2.07375200	2.18620700	0.38325700
C	2.06782000	0.28705200	-0.90060000
O	3.26231900	0.94593400	-0.22183300
O	1.86609600	1.95705000	1.66985400
H	2.40119900	2.54481500	2.23714700
C	2.71325200	3.48403500	0.00088300
H	1.95747900	4.27389100	0.10813100
H	3.56378100	3.72272000	0.64910500
H	3.05114000	3.46869400	-1.03609300
H	3.61490100	0.34238000	0.46565700
C	-1.24270300	0.59276000	-1.08078400
H	-1.30553100	1.29733500	-1.92080200
H	-0.81793400	-0.33769900	-1.47763000
C	-2.62681600	0.32677200	-0.52515800
C	-3.61466000	1.31910100	-0.56296100
C	-2.93183200	-0.90487800	0.06878000
C	-4.87815800	1.08825200	-0.01761900
H	-3.39852500	2.27669900	-1.03292200
C	-4.19420200	-1.13919800	0.61487300
H	-2.17833100	-1.68975800	0.09588100
C	-5.17031000	-0.14187400	0.57405500
H	-5.63582100	1.86554300	-0.06196700
H	-4.41813000	-2.10236900	1.06495500
H	-6.15520300	-0.32498000	0.99379600
C	1.84308200	-1.10254700	-0.39061500
C	1.69326700	-1.38773900	0.97933400
C	1.81813200	-2.15728800	-1.31584300

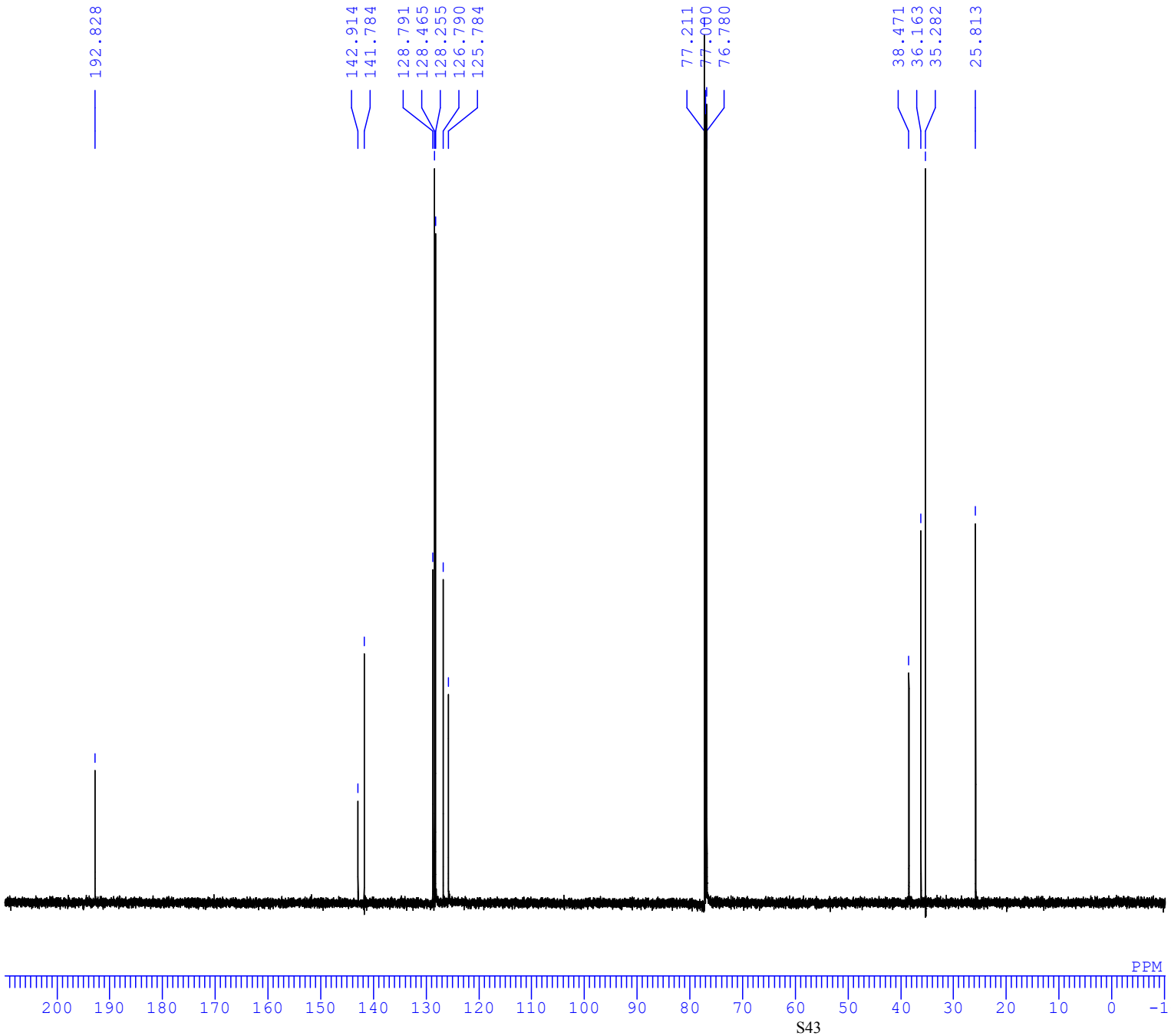
C	1.51909400	-2.70329500	1.40589300
H	1.70286600	-0.58924000	1.71668900
C	1.62909500	-3.47014200	-0.88626100
H	1.94780500	-1.95012800	-2.37514900
C	1.48199300	-3.74442900	0.47456300
H	1.40593000	-2.91507000	2.46472400
H	1.60824600	-4.27701200	-1.61217800
H	1.34243400	-4.76749100	0.81043900
H	2.32307600	0.25918700	-1.95965200

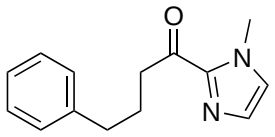




3c

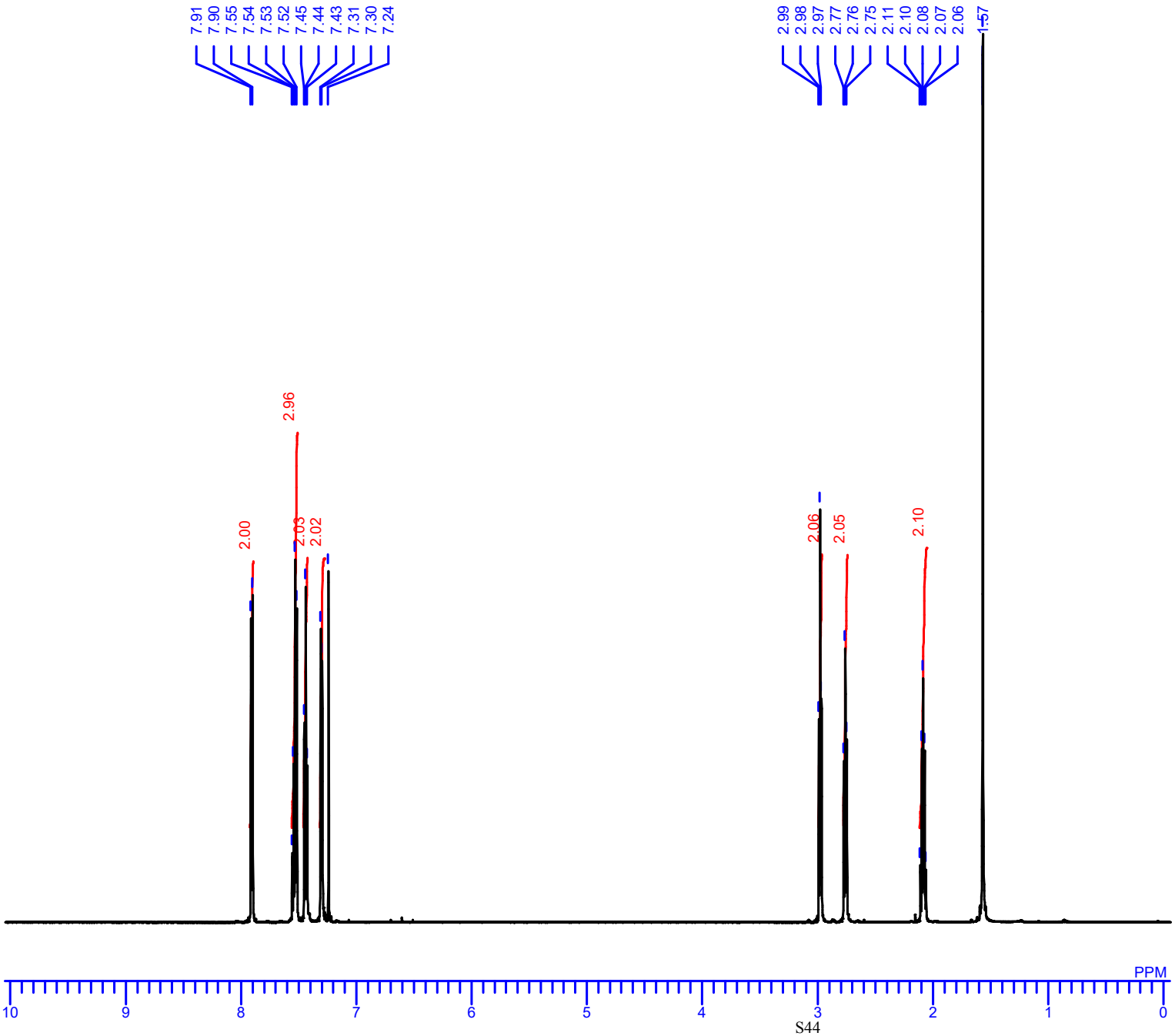
^{1}H NMR
(600 MHz, $CDCl_3$)

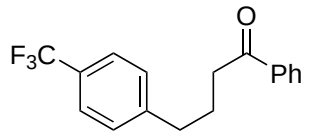




3c

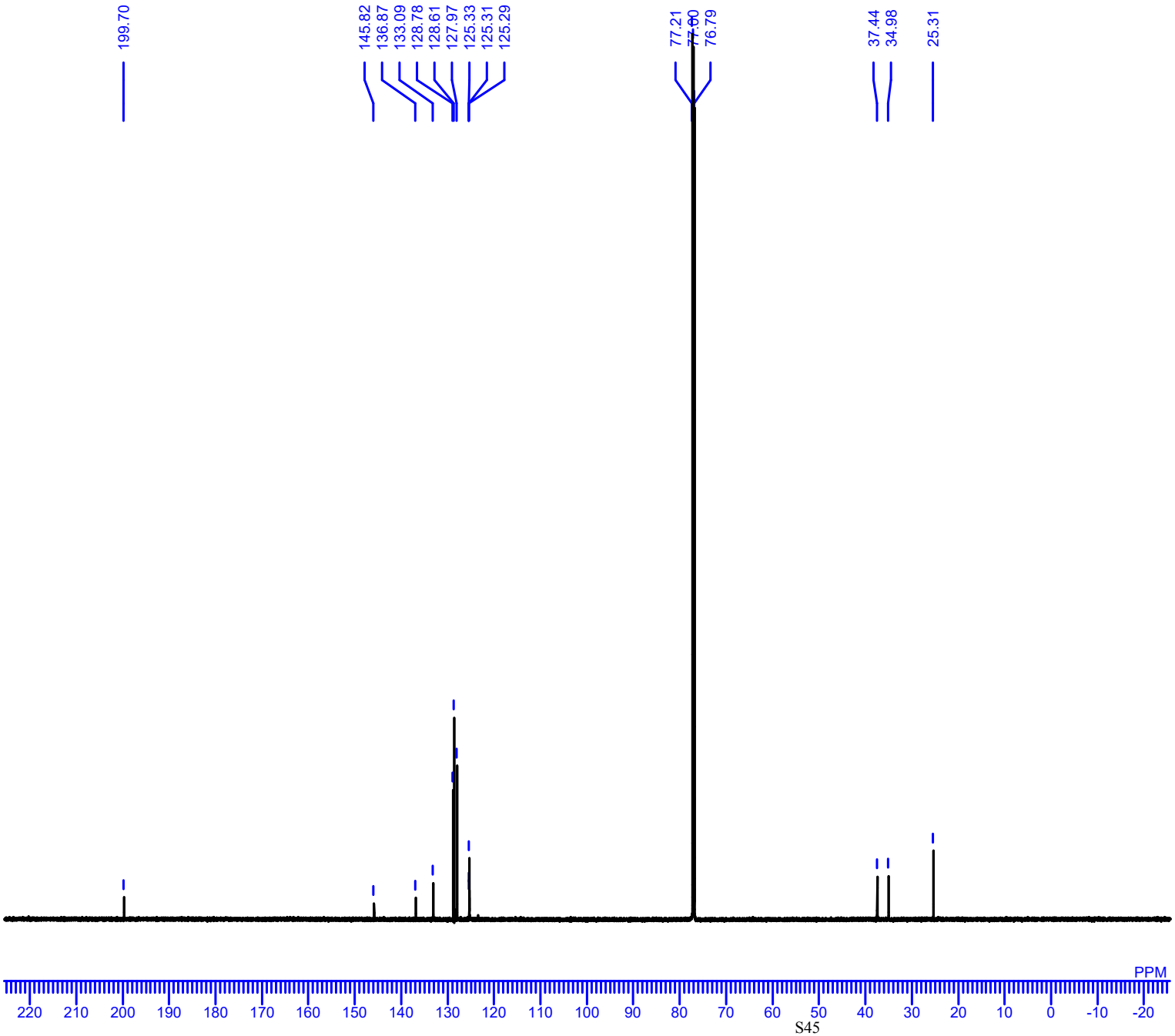
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

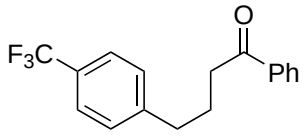




3e

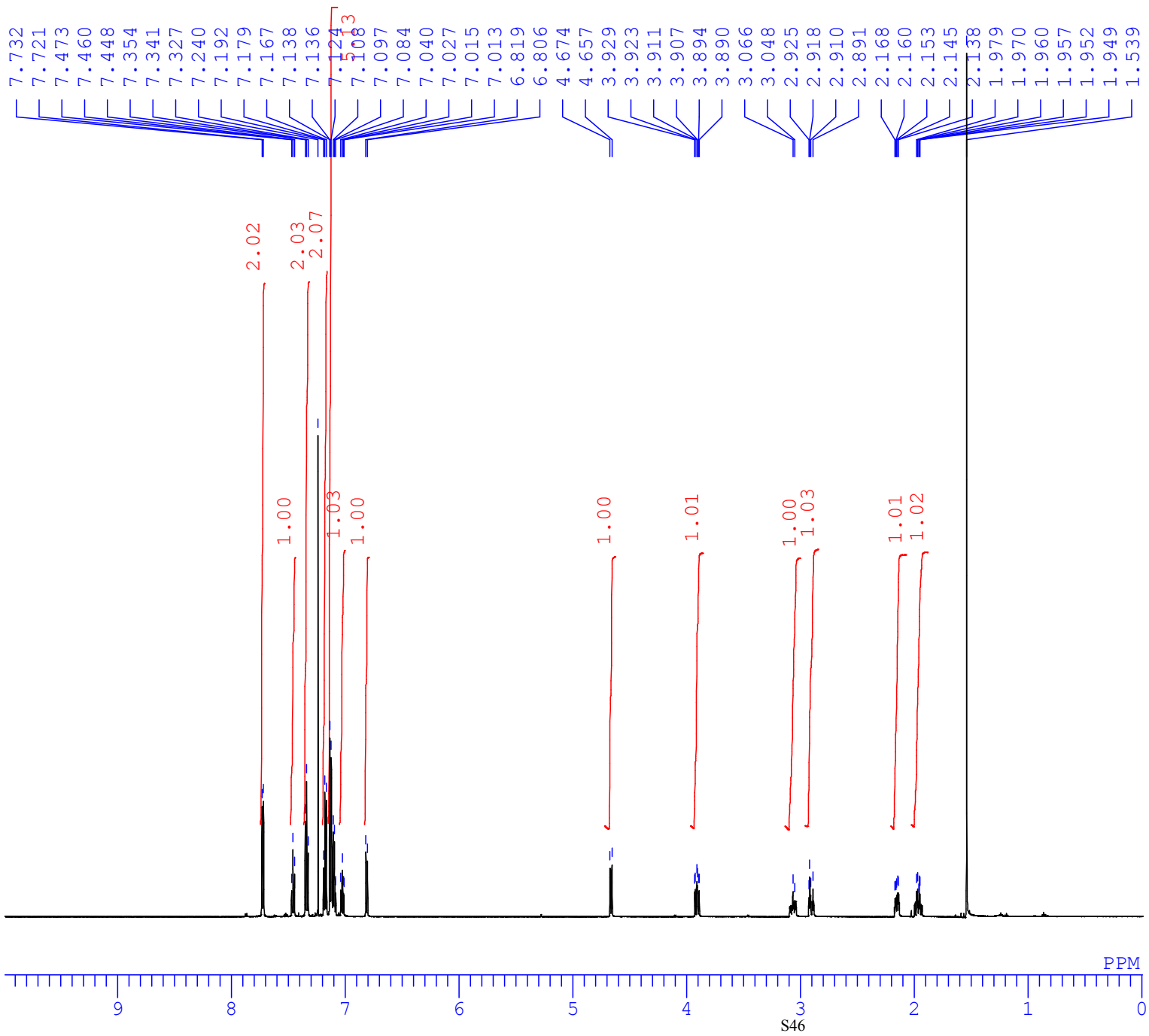
^{1}H NMR
(600 MHz, $CDCl_3$)

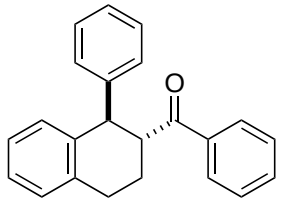




3e

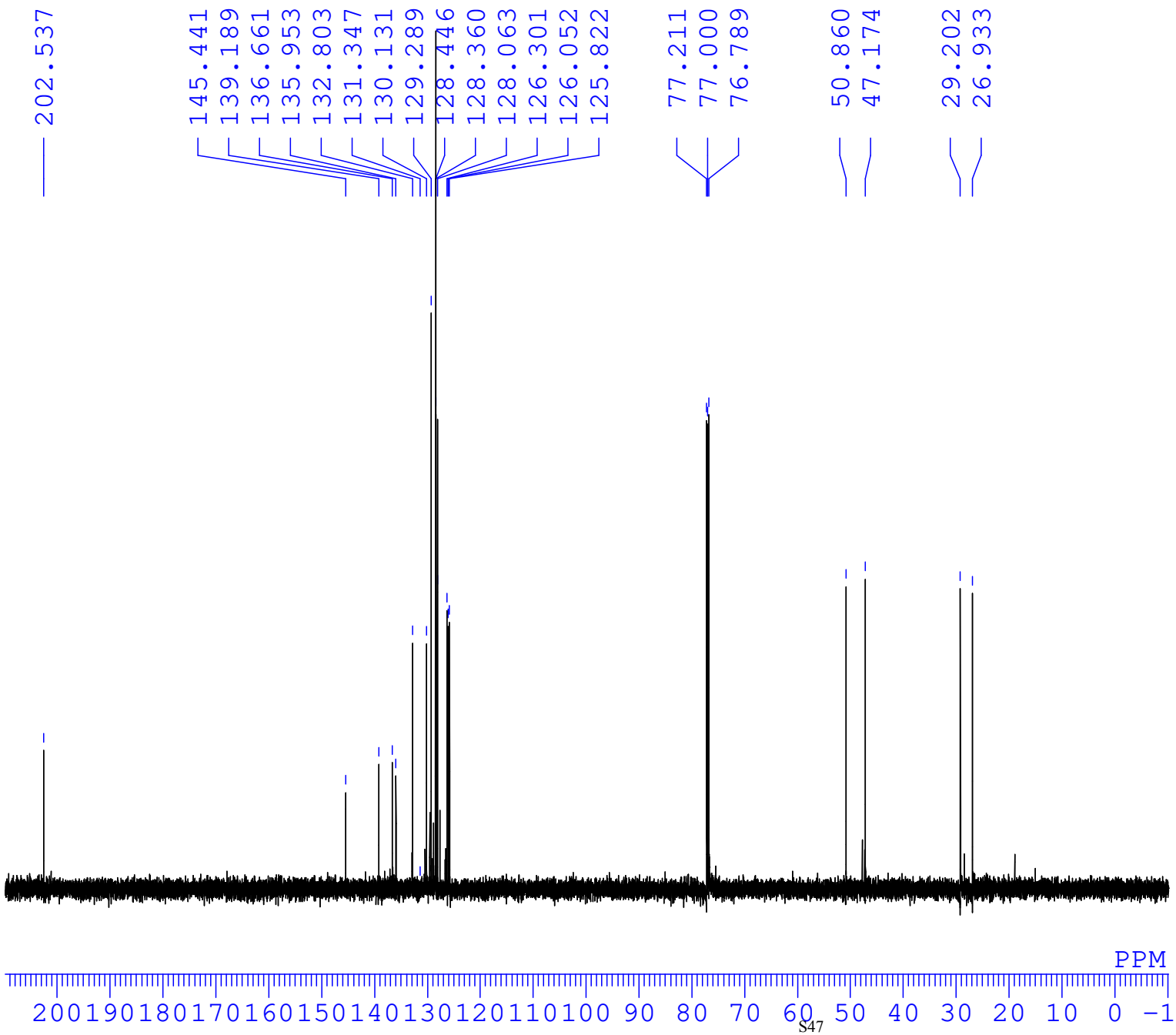
$^{13}C\{^{1}H,^{19}F\}$ NMR
(150 MHz, $CDCl_3$)

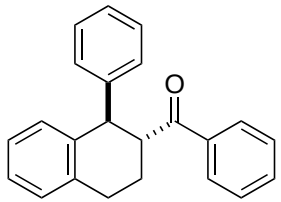




4aa

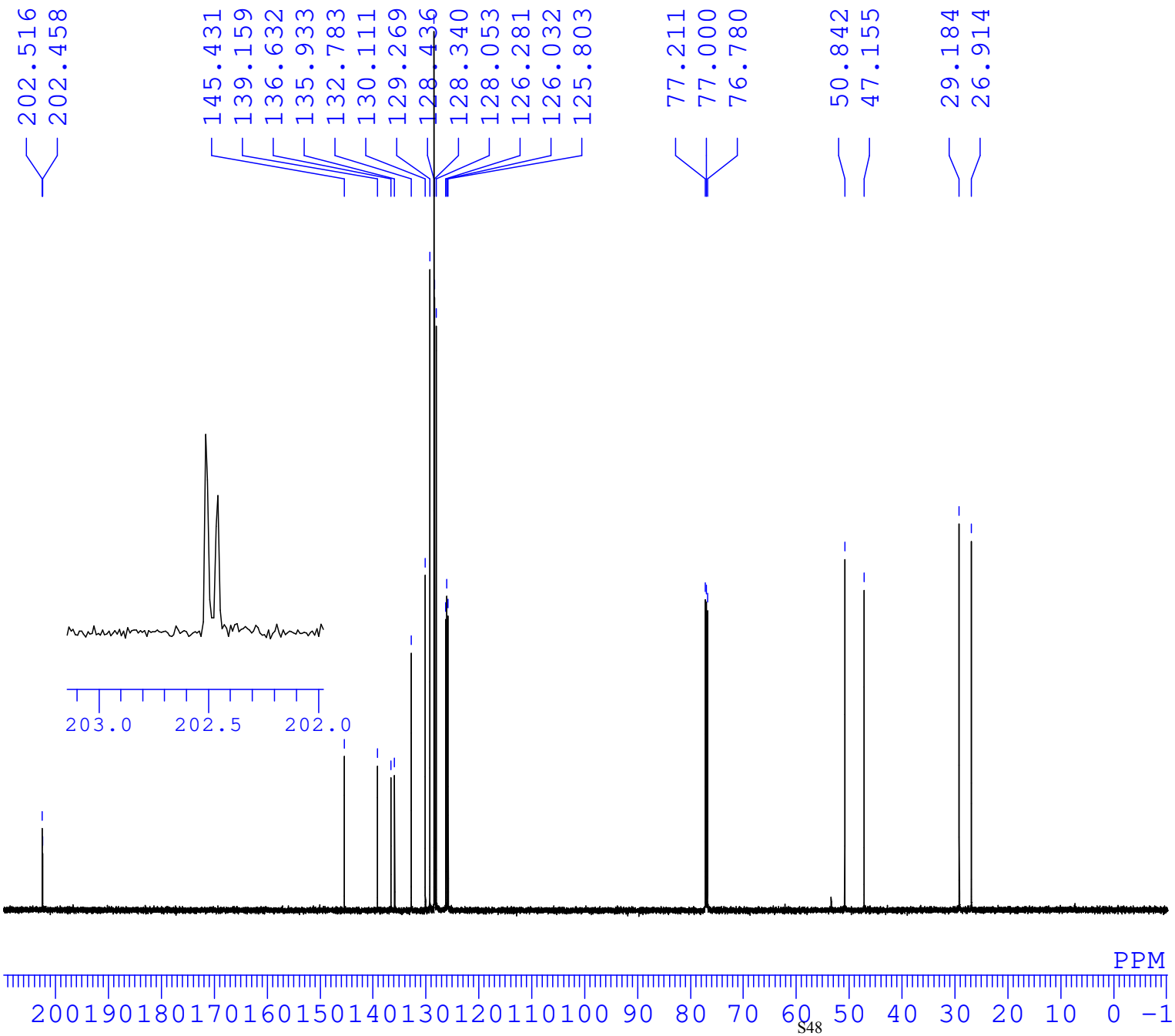
^{1}H NMR
(600 MHz, $CDCl_3$)

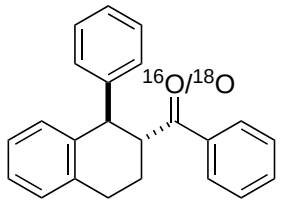




4aa

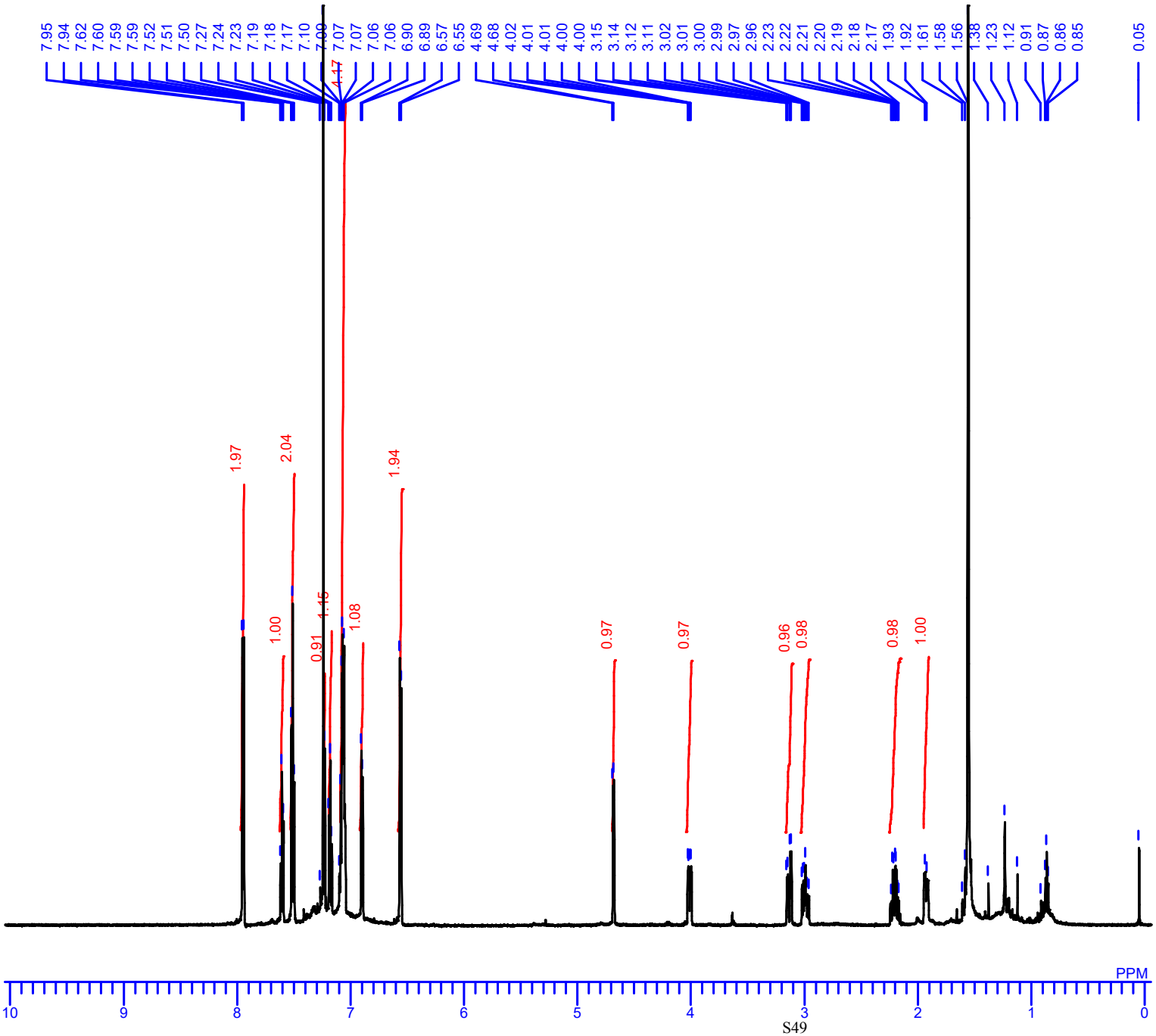
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

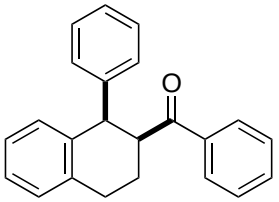




4aa + 4aa-^{18}O

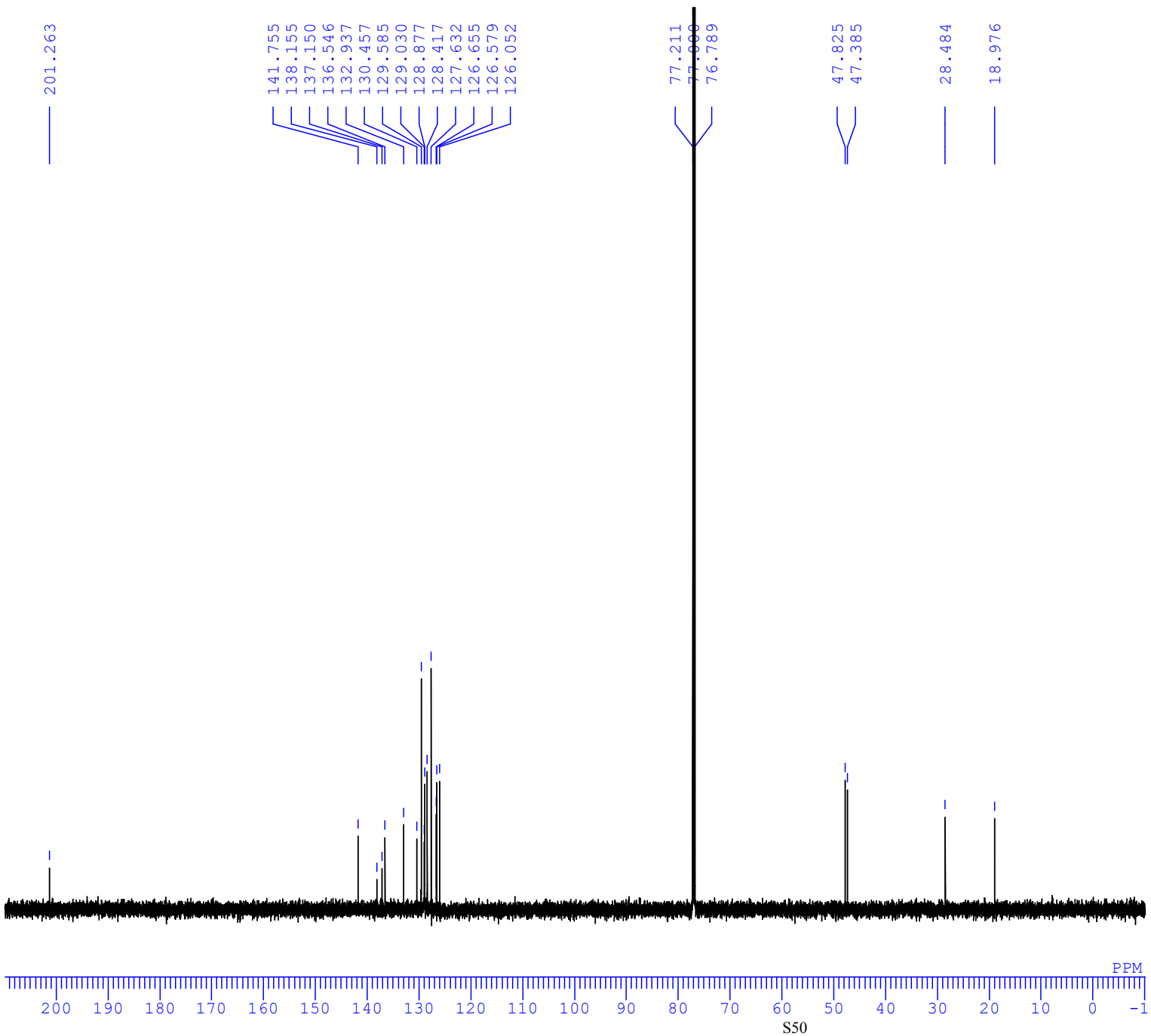
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

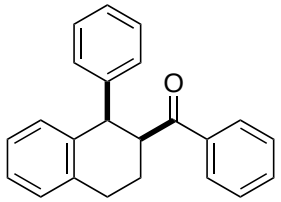




***cis*-4aa**

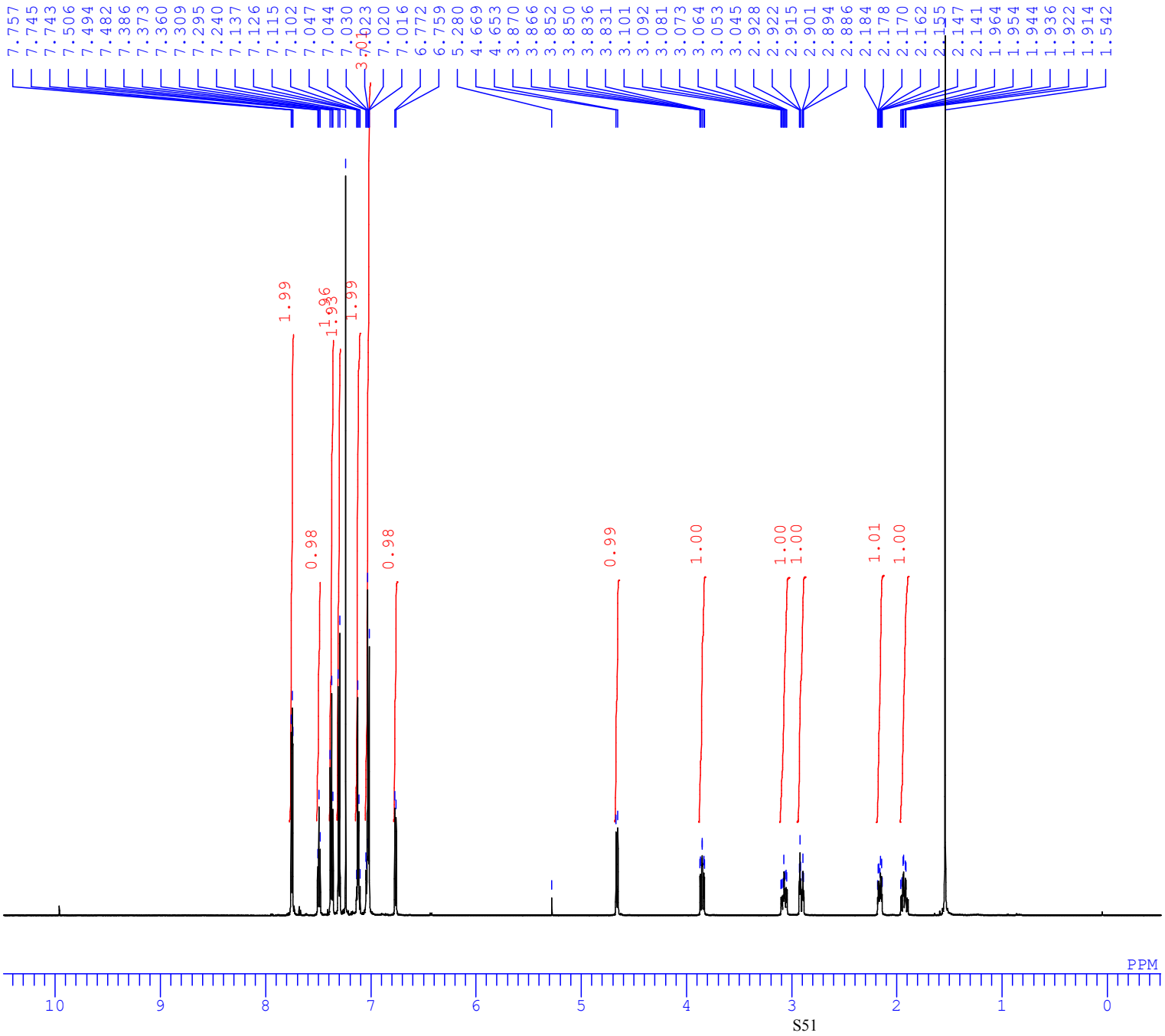
^{1}H NMR
(600 MHz, $CDCl_3$)

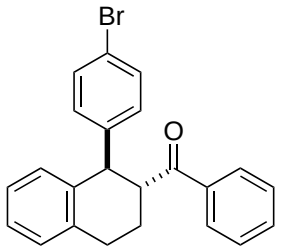




***cis*-4aa**

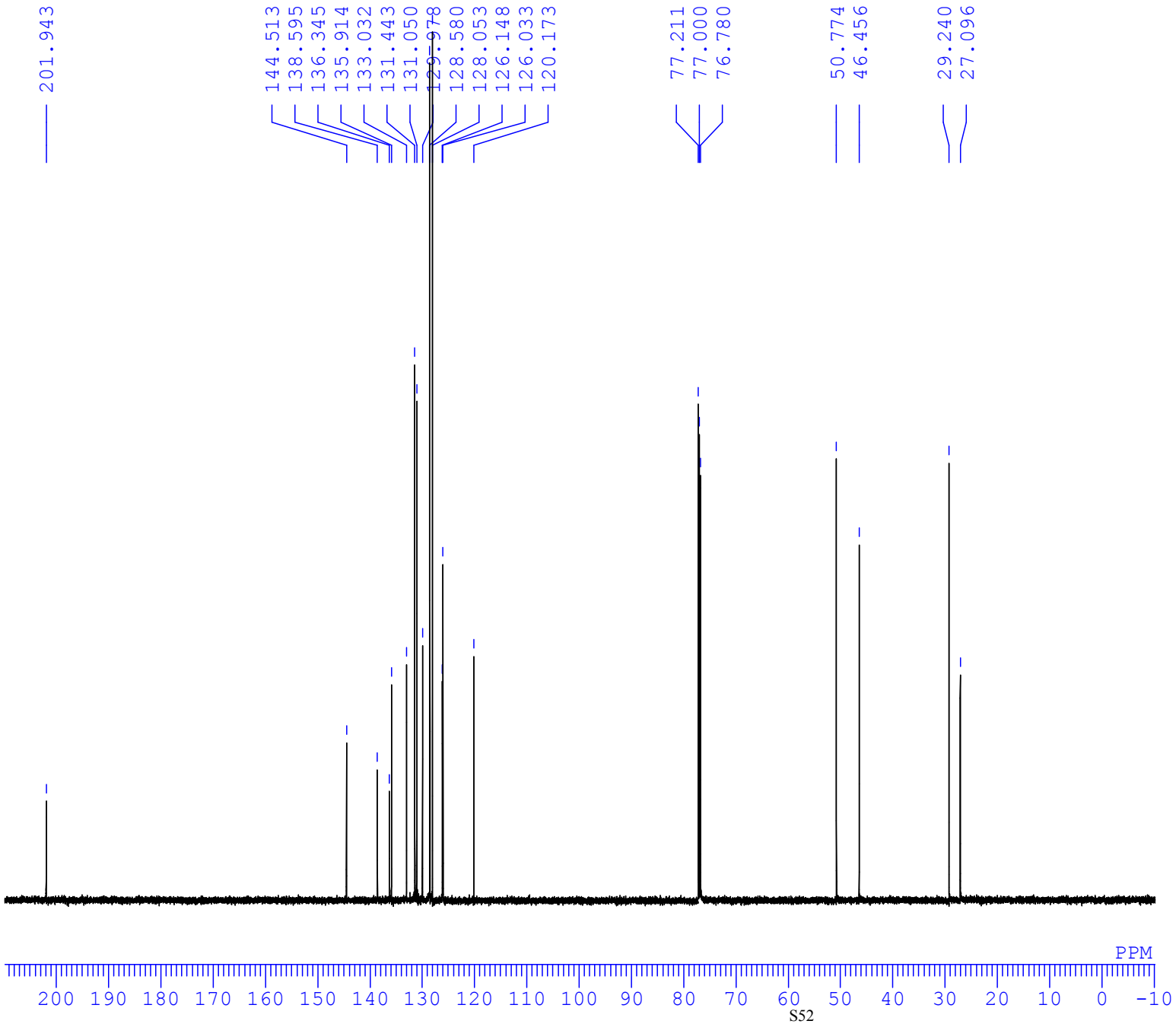
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

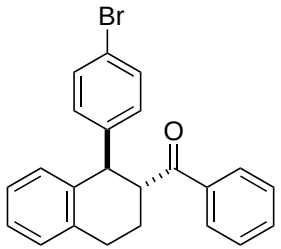




4ab

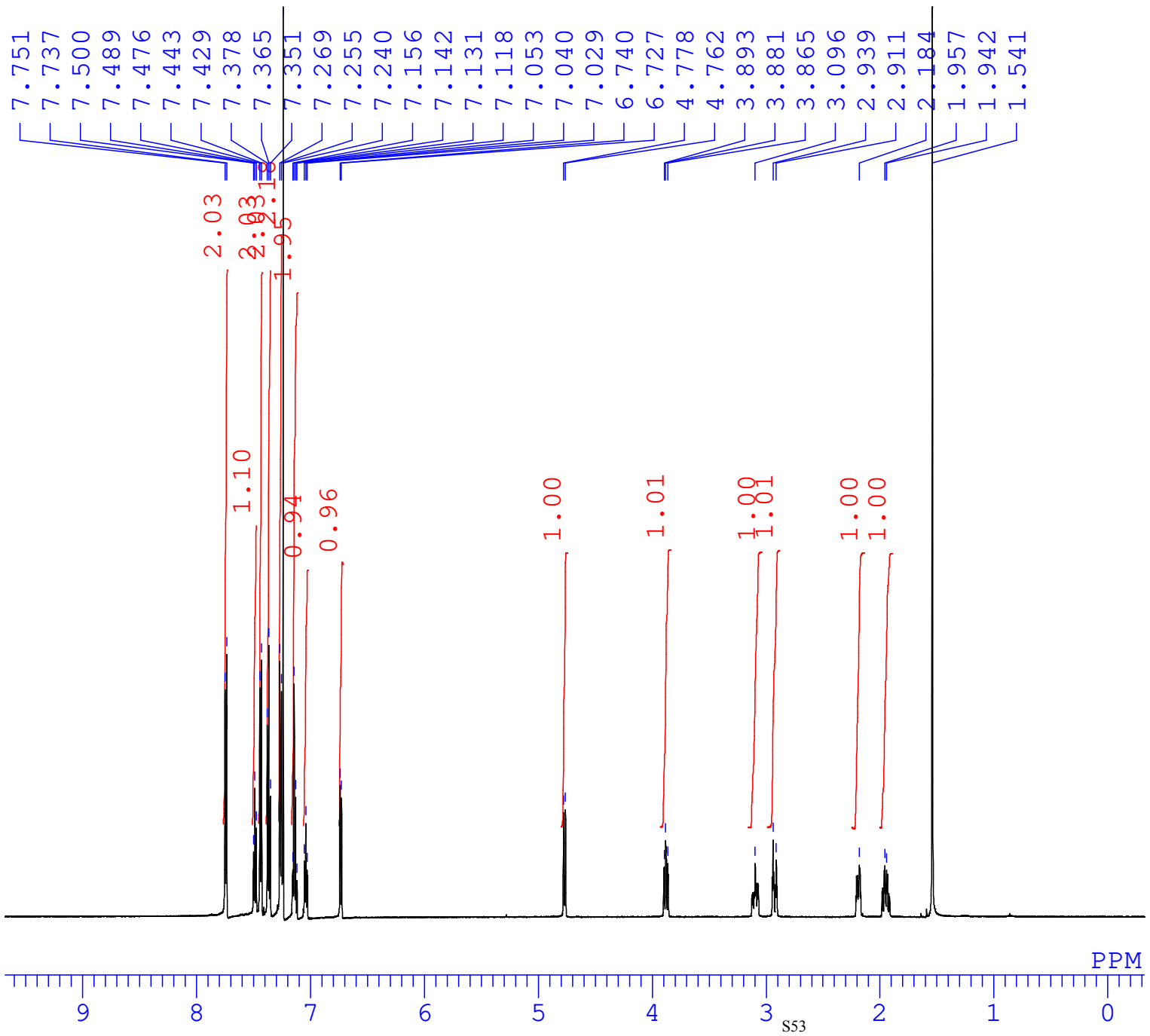
^{1}H NMR
(600 MHz, $CDCl_3$)

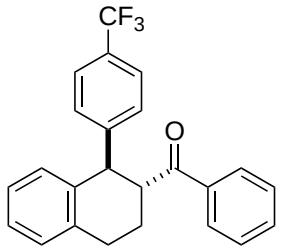




4ab

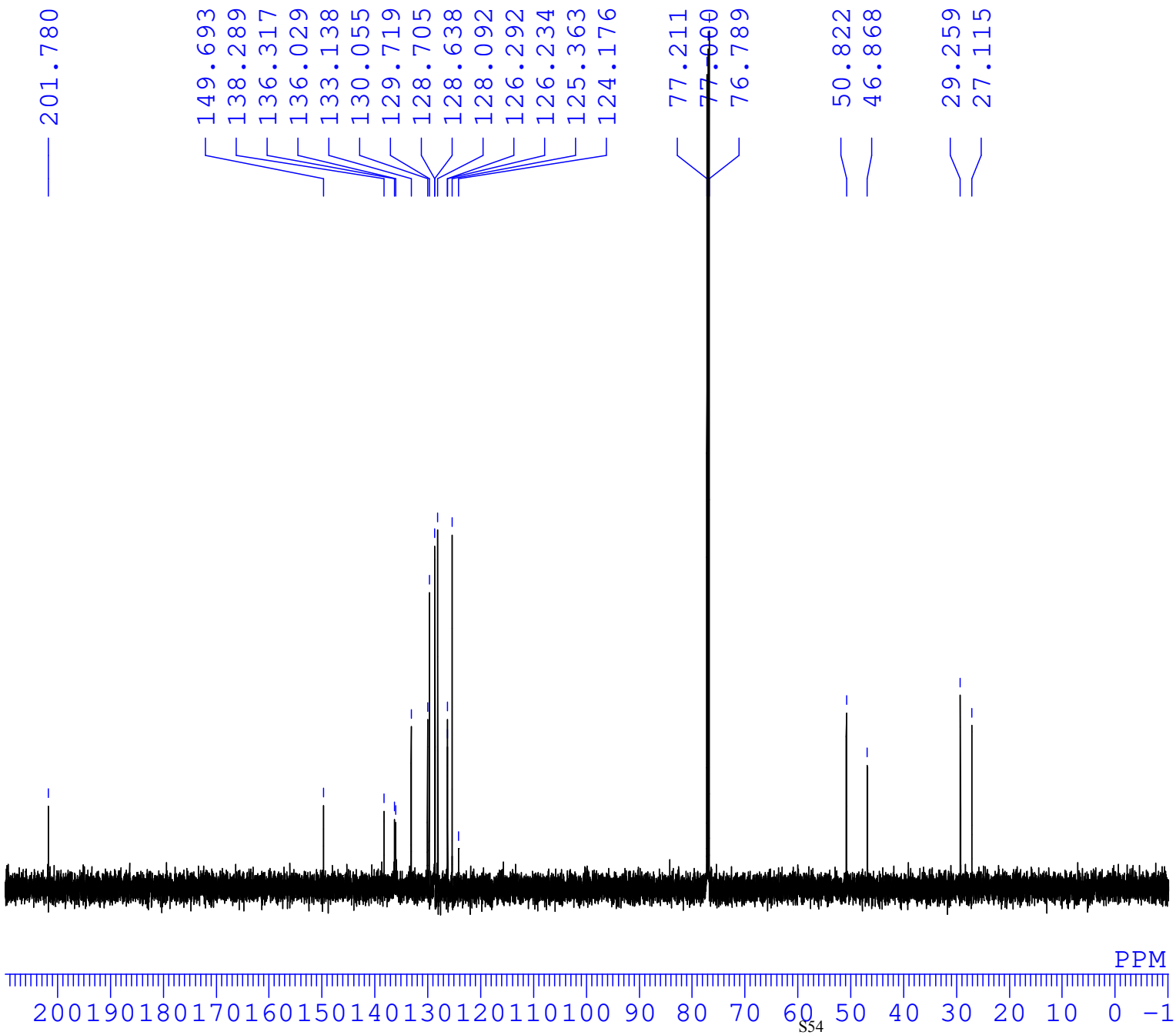
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

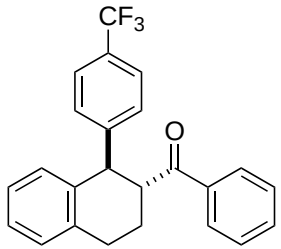




4ac

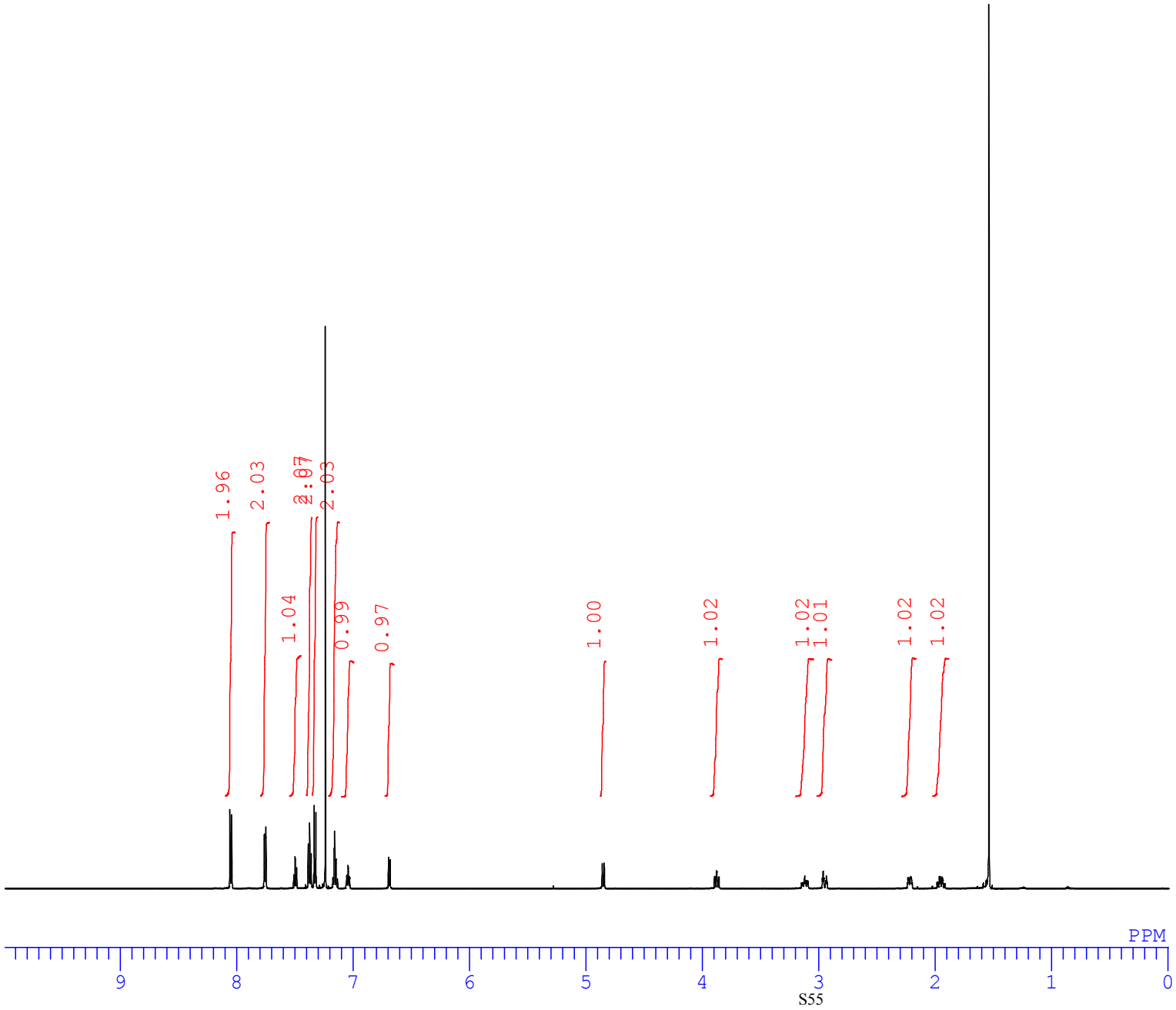
^{1}H NMR
(600 MHz, $CDCl_3$)

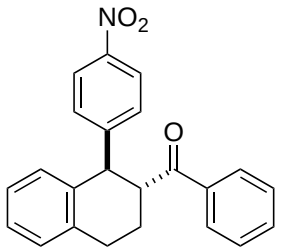




4ac

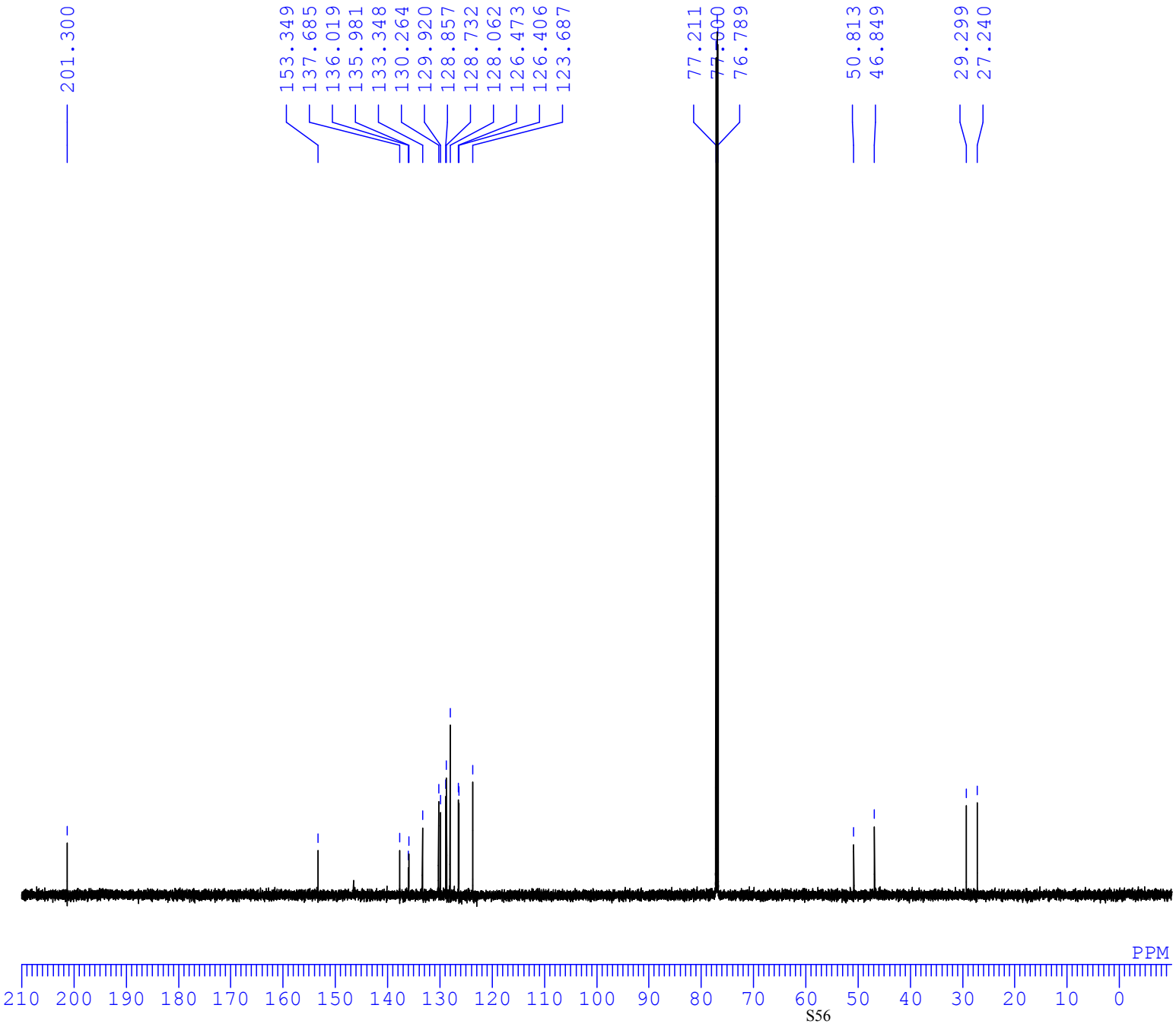
$^{13}C\{^{1}H,^{19}F\}$ NMR
(150 MHz, $CDCl_3$)

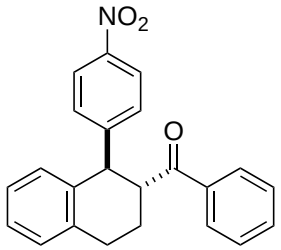




4ad

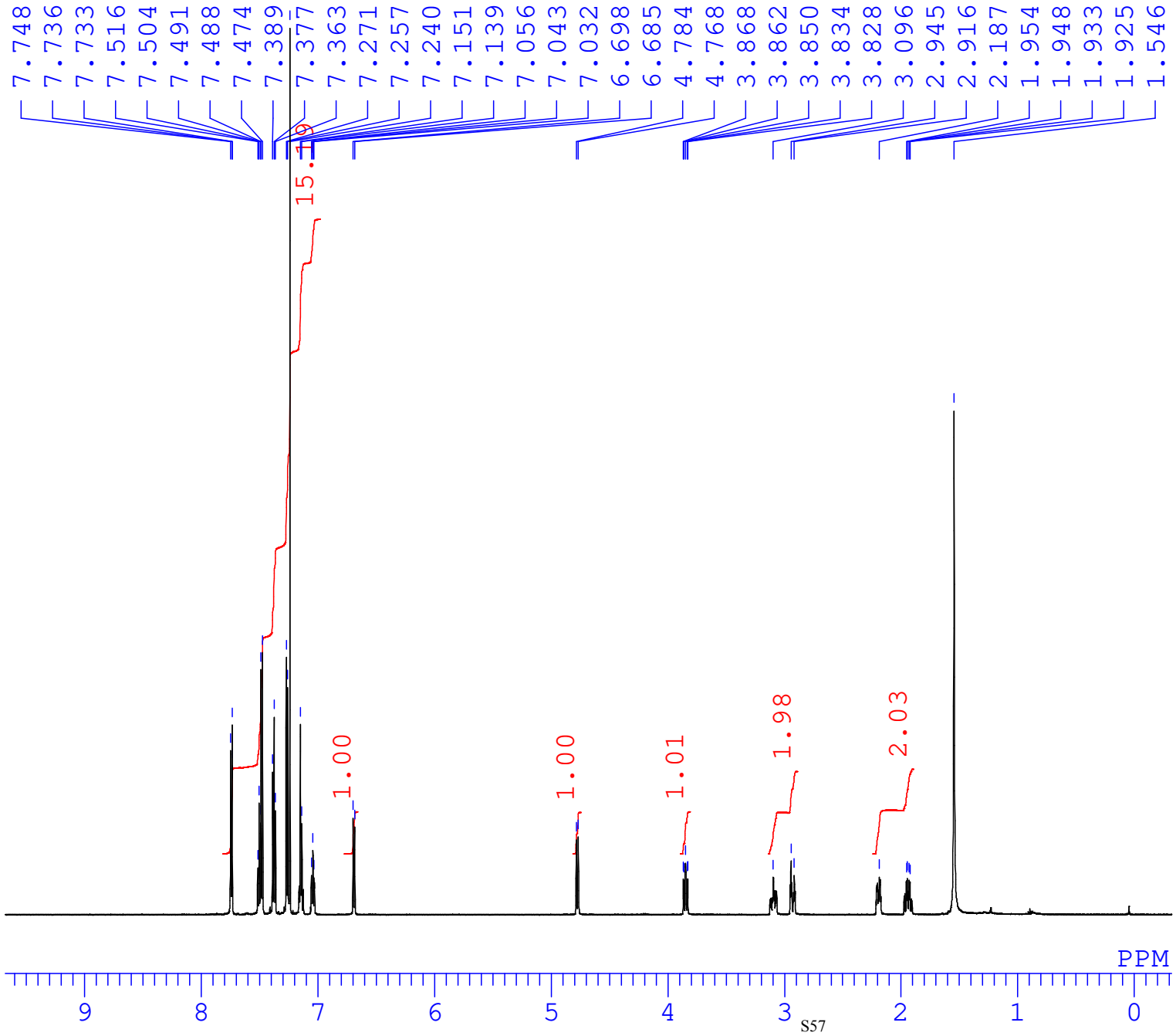
^{1}H NMR
(600 MHz, $CDCl_3$)

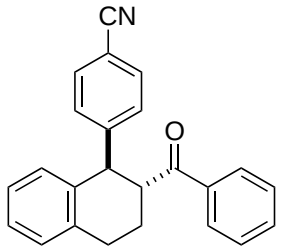




4ad

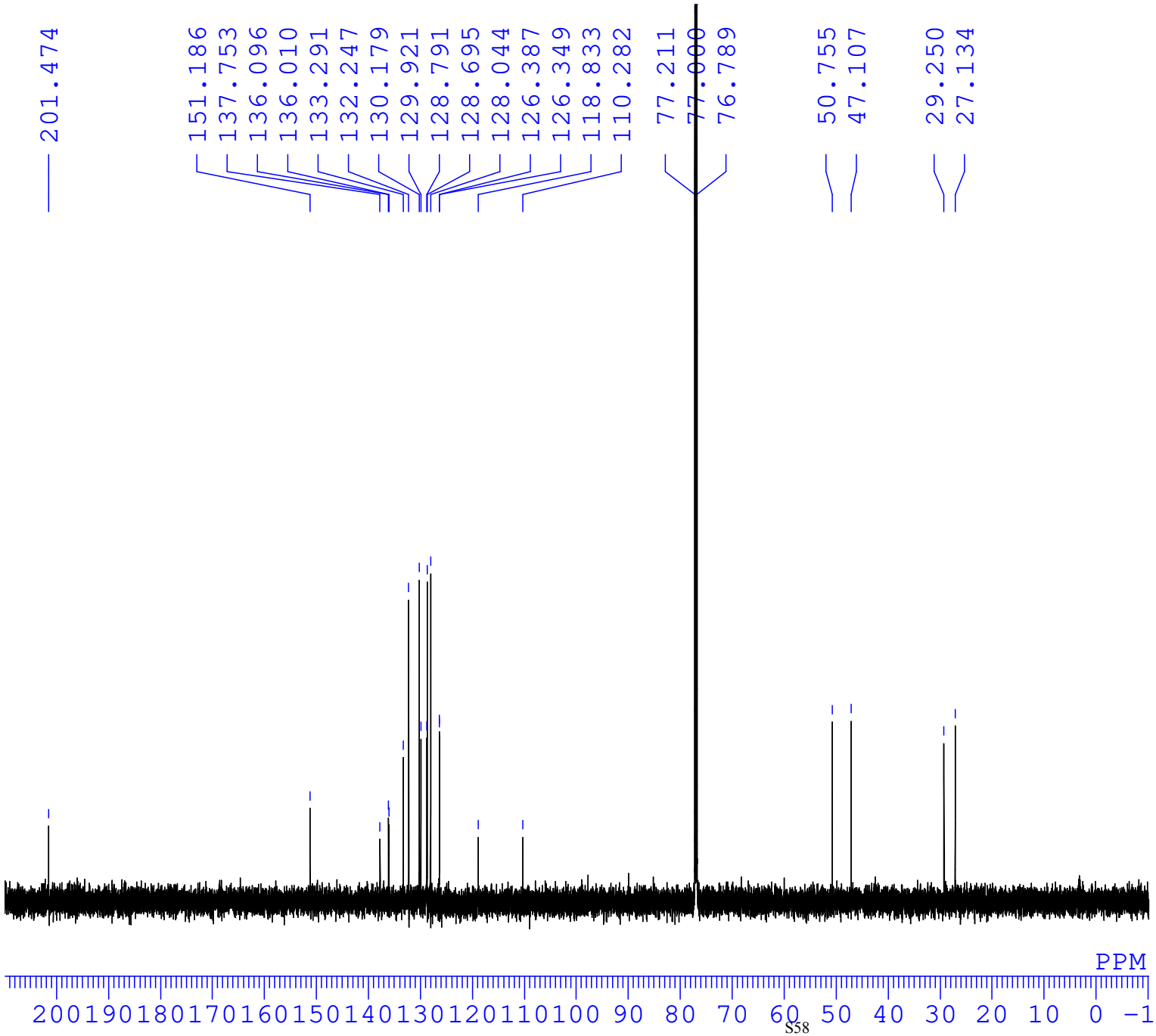
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

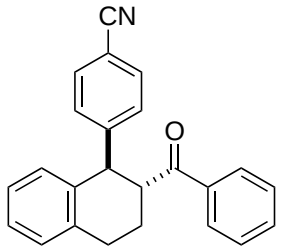




4ae

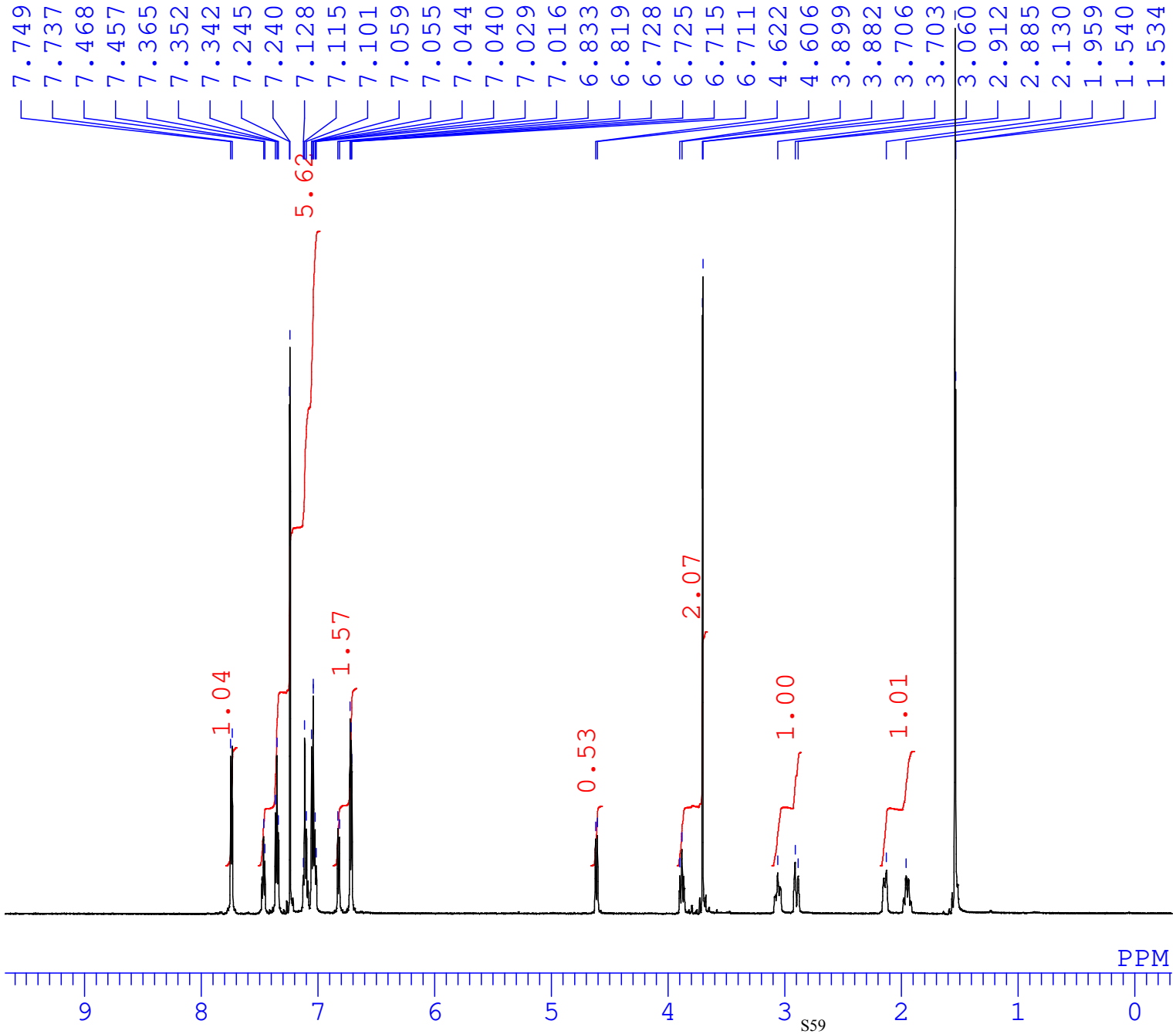
^{1}H NMR
(600 MHz, $CDCl_3$)

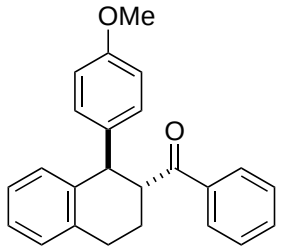




4ae

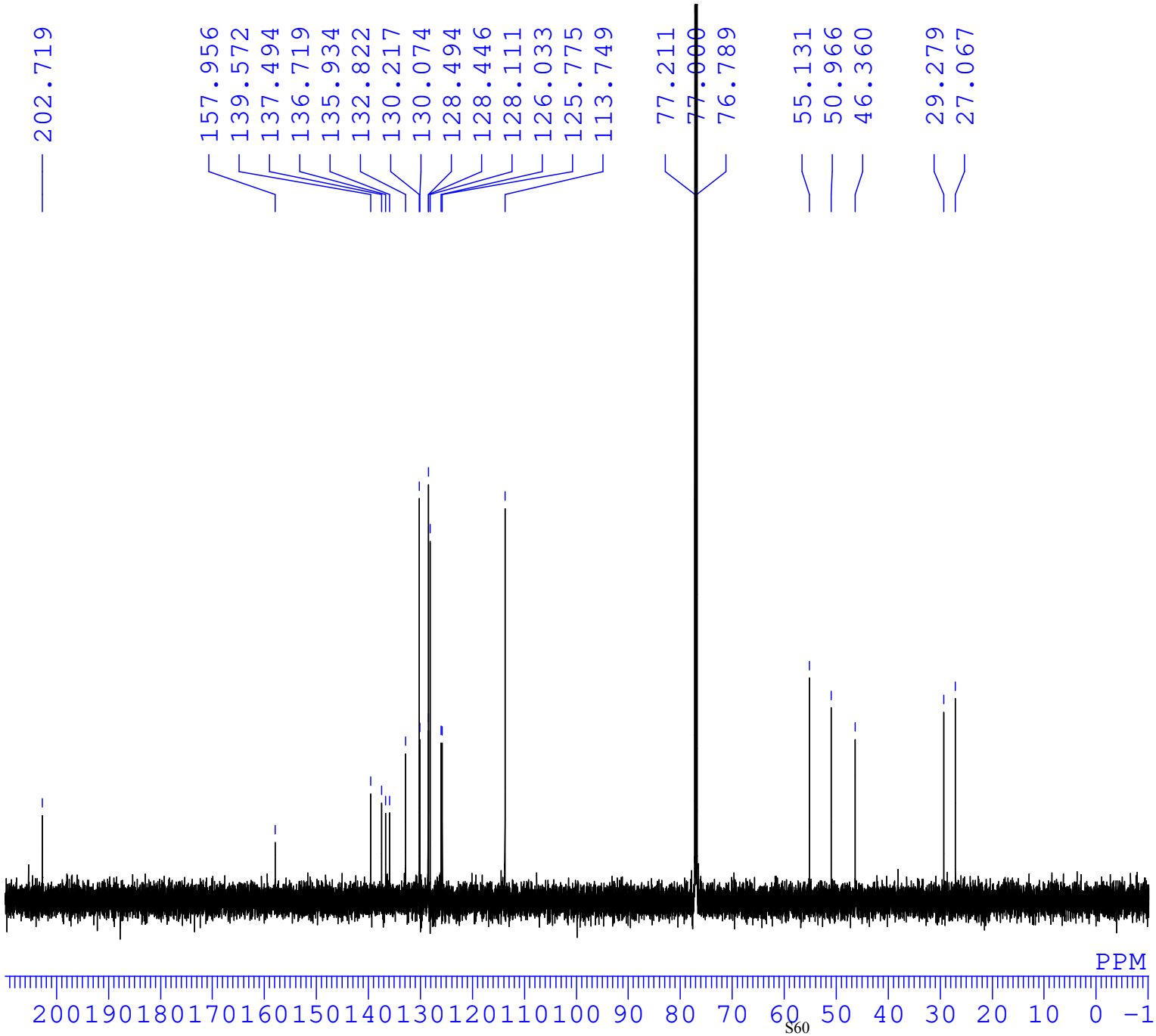
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

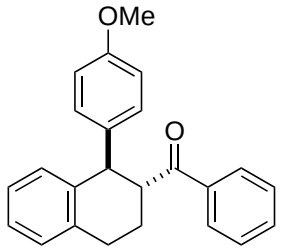




4af

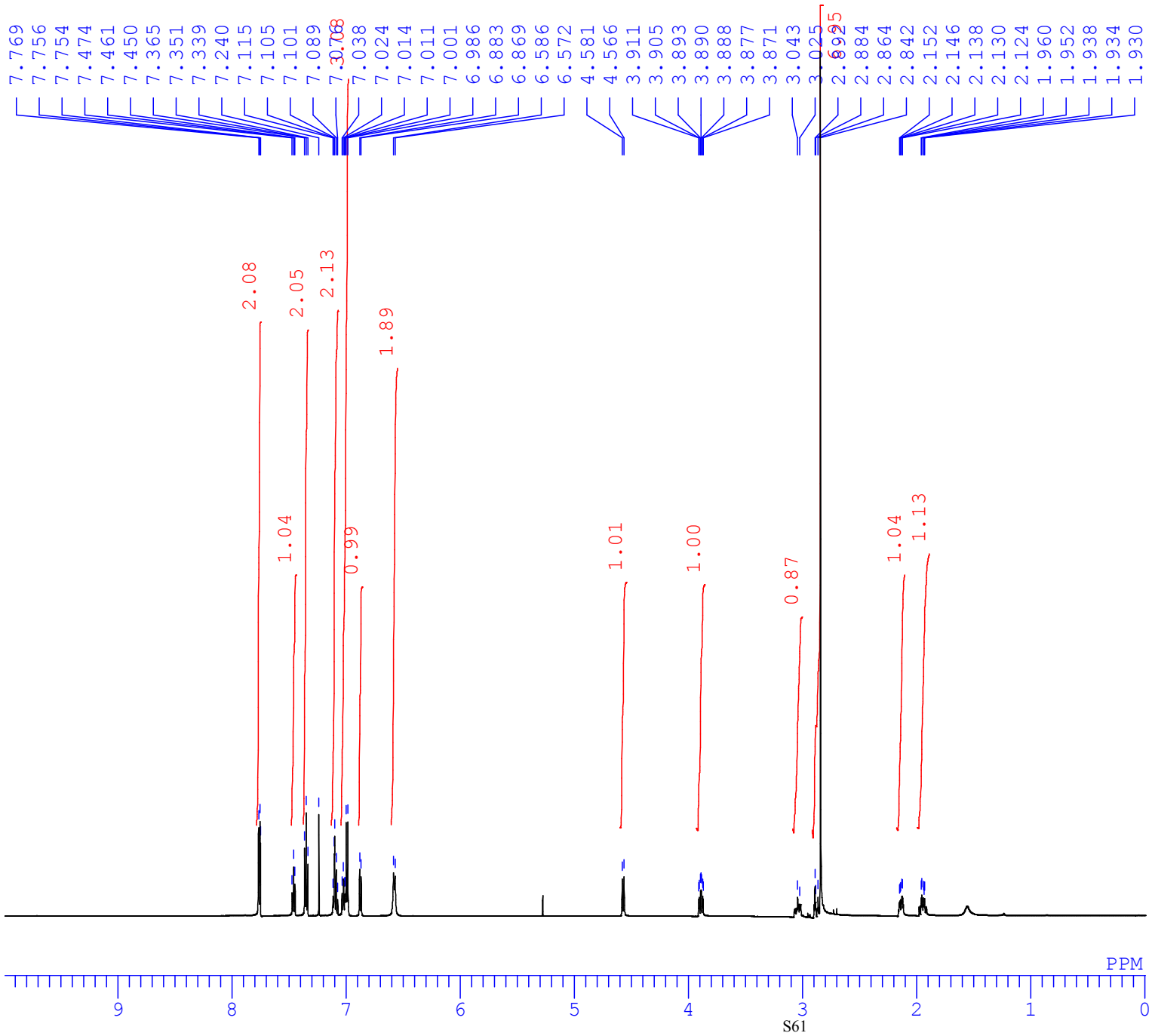
^{1}H NMR
(600 MHz, $CDCl_3$)

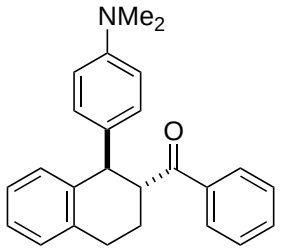




4af

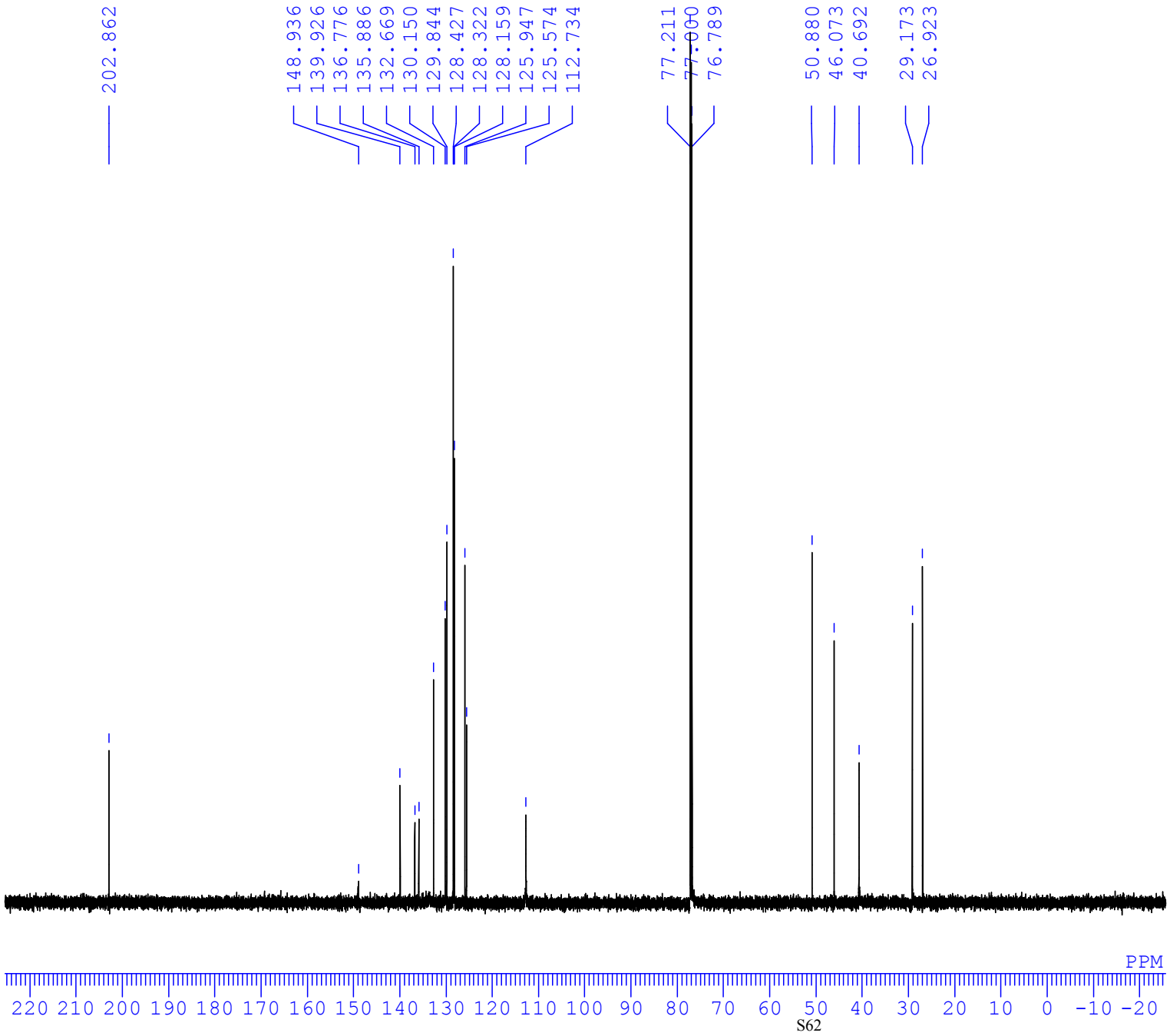
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

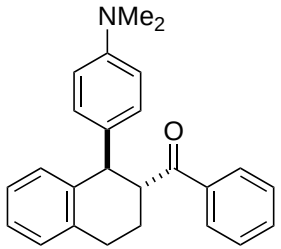




4ag

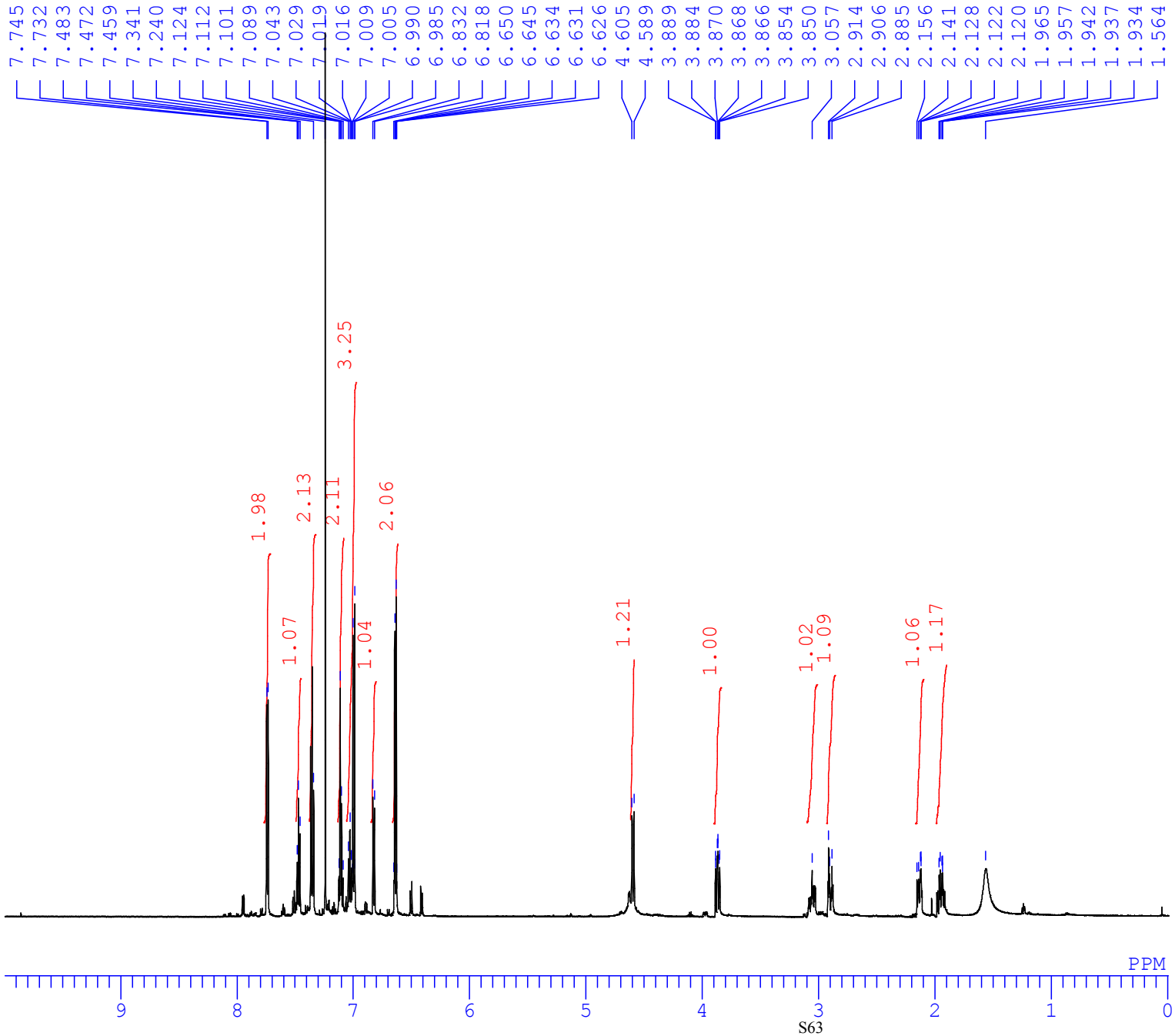
^{1}H NMR
(600 MHz, $CDCl_3$)

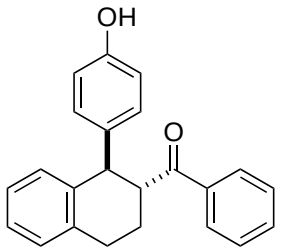




4ag

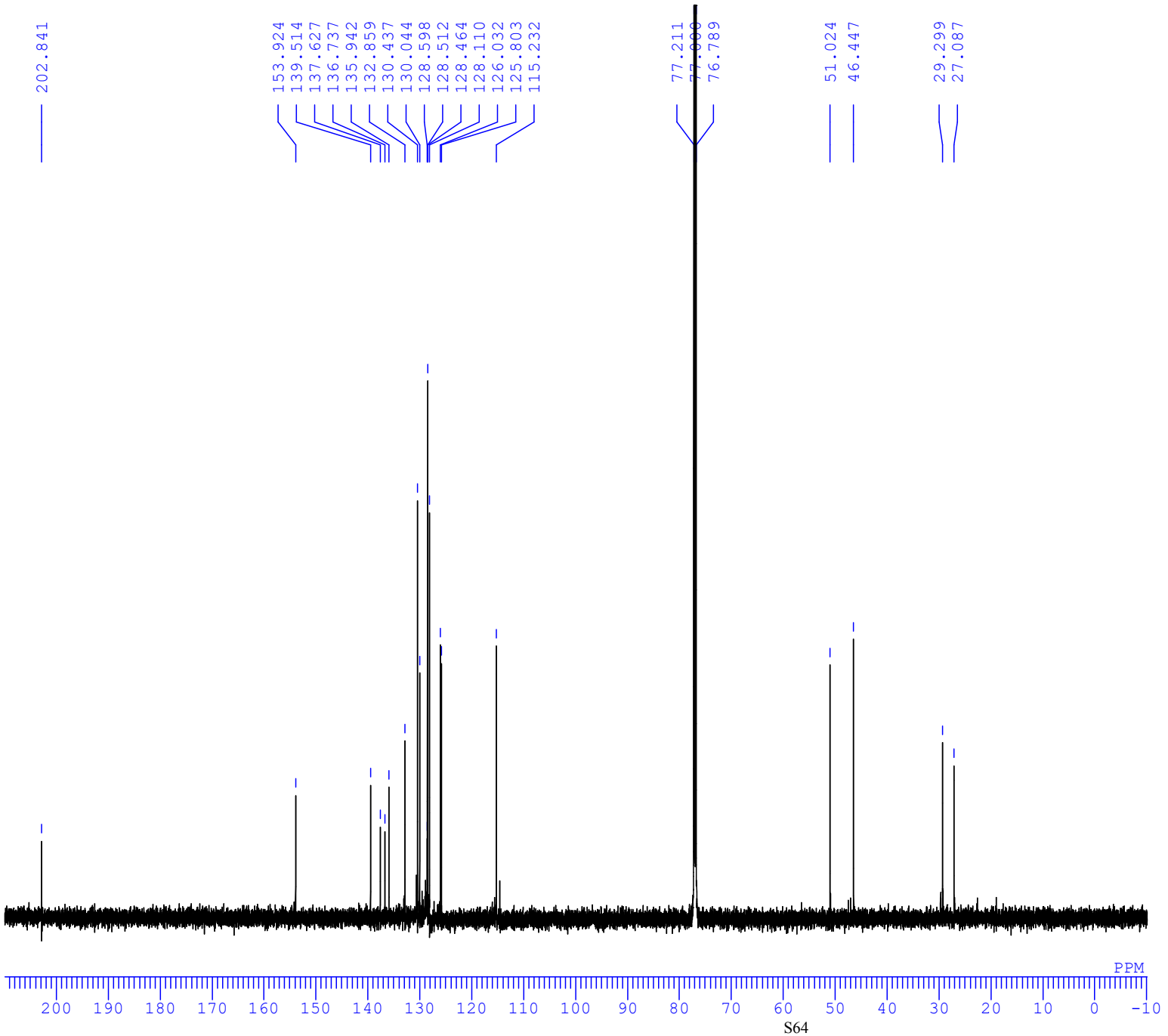
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

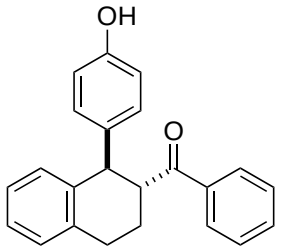




4ah

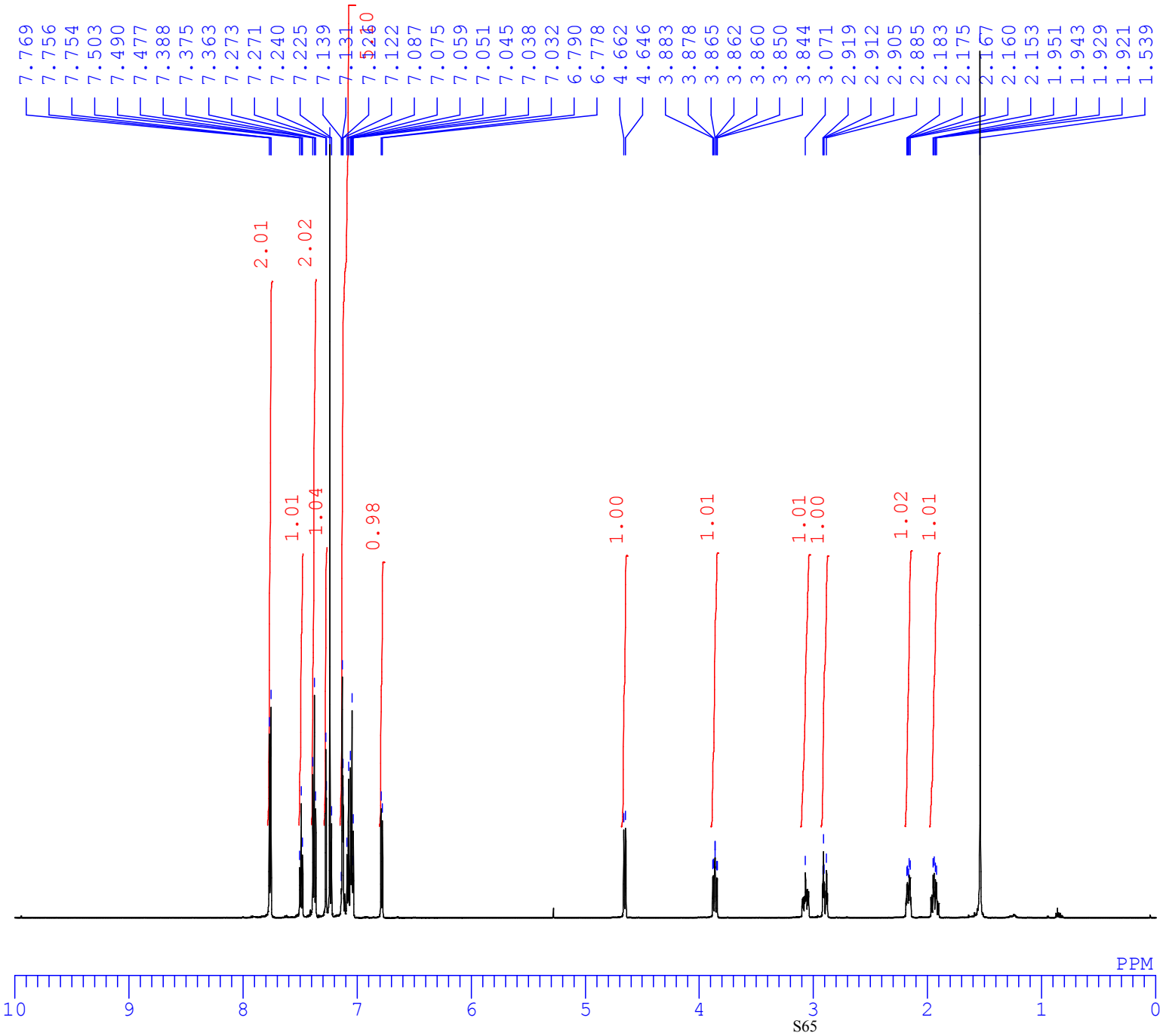
^{1}H NMR
(600 MHz, $CDCl_3$)

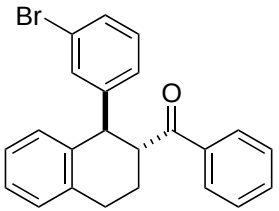




4ah

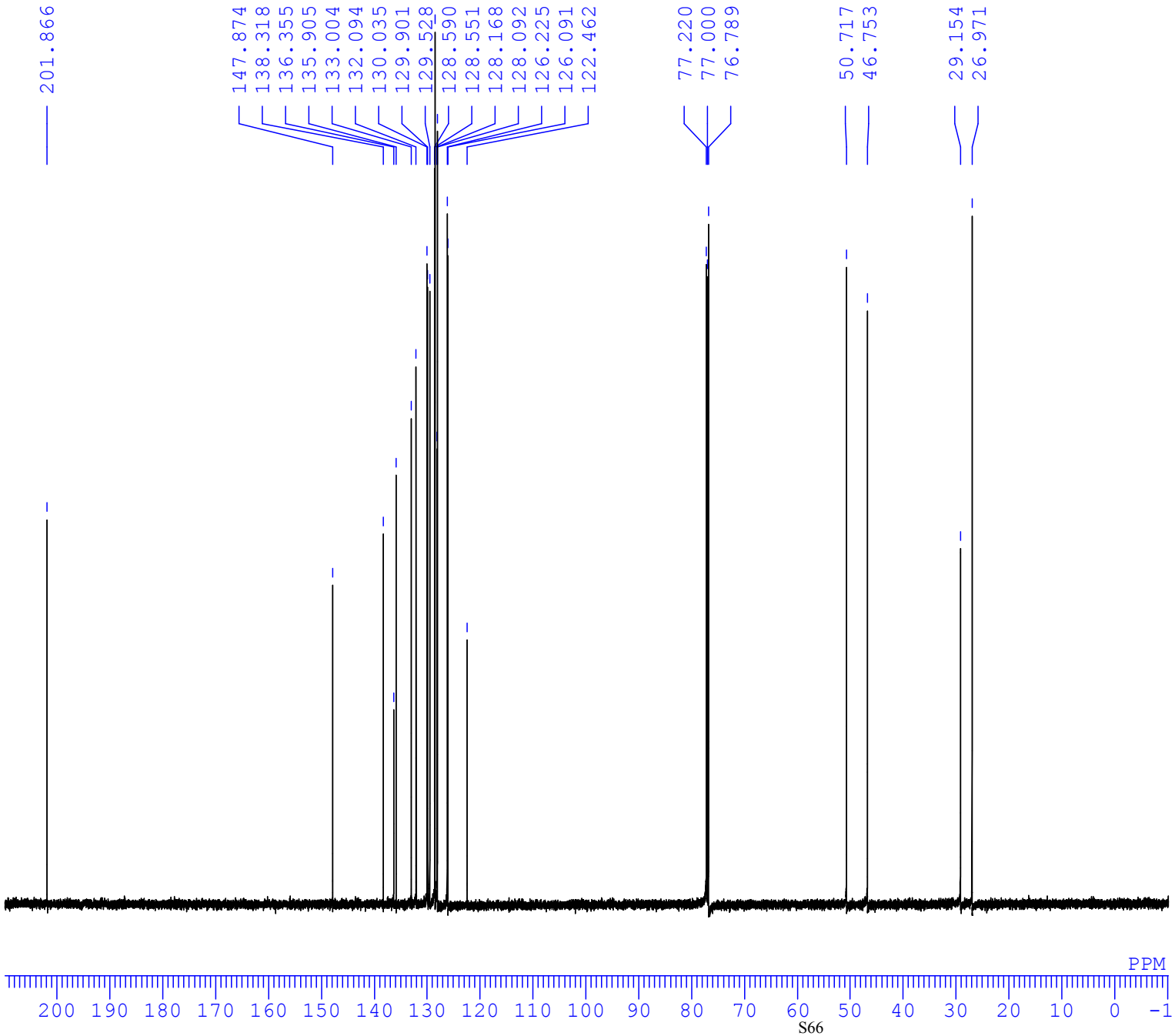
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

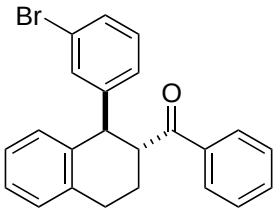




4ai

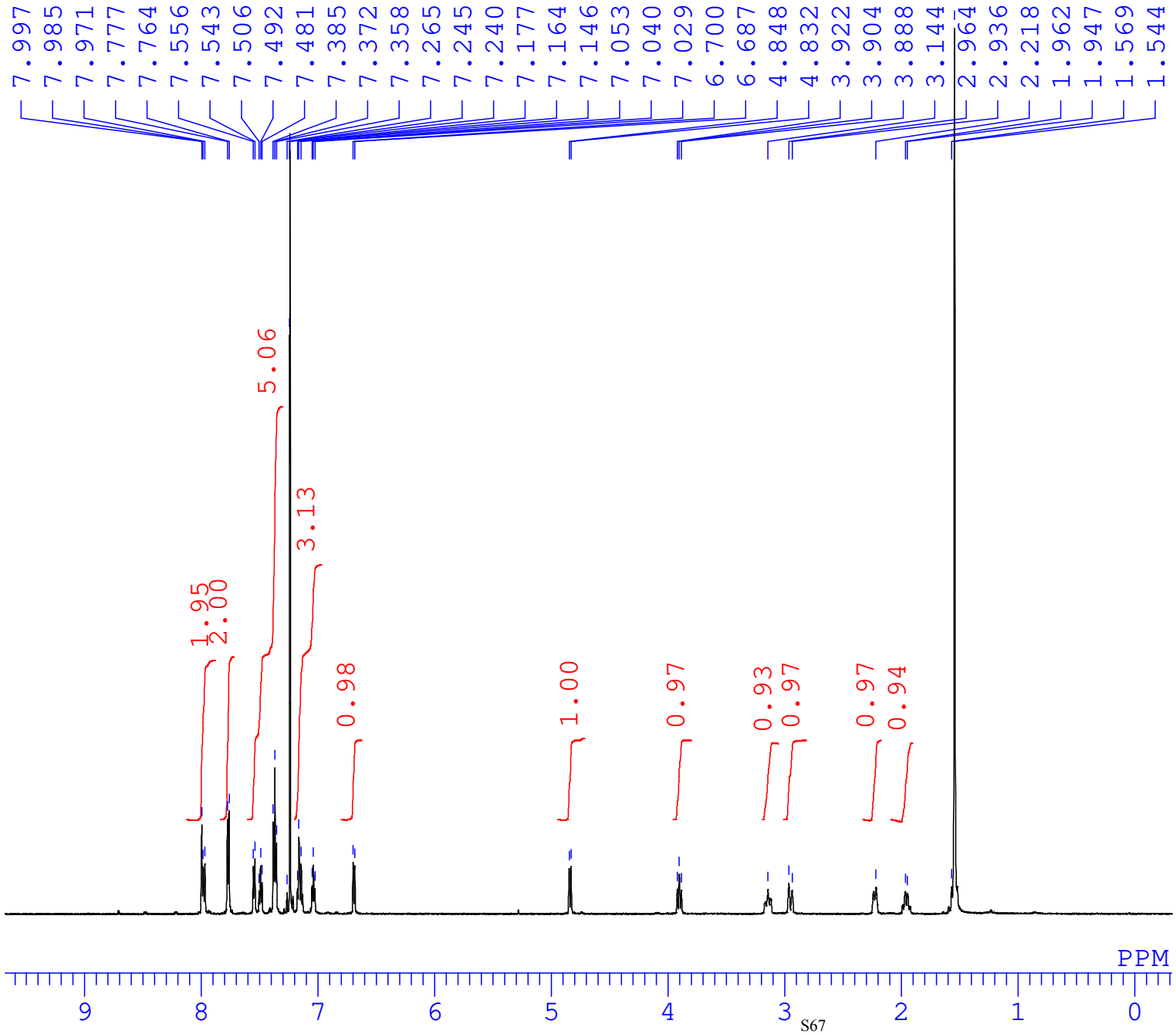
^{1}H NMR
(600 MHz, $CDCl_3$)

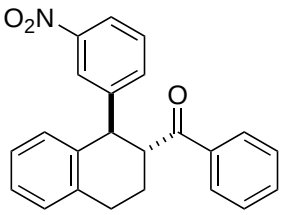




4ai

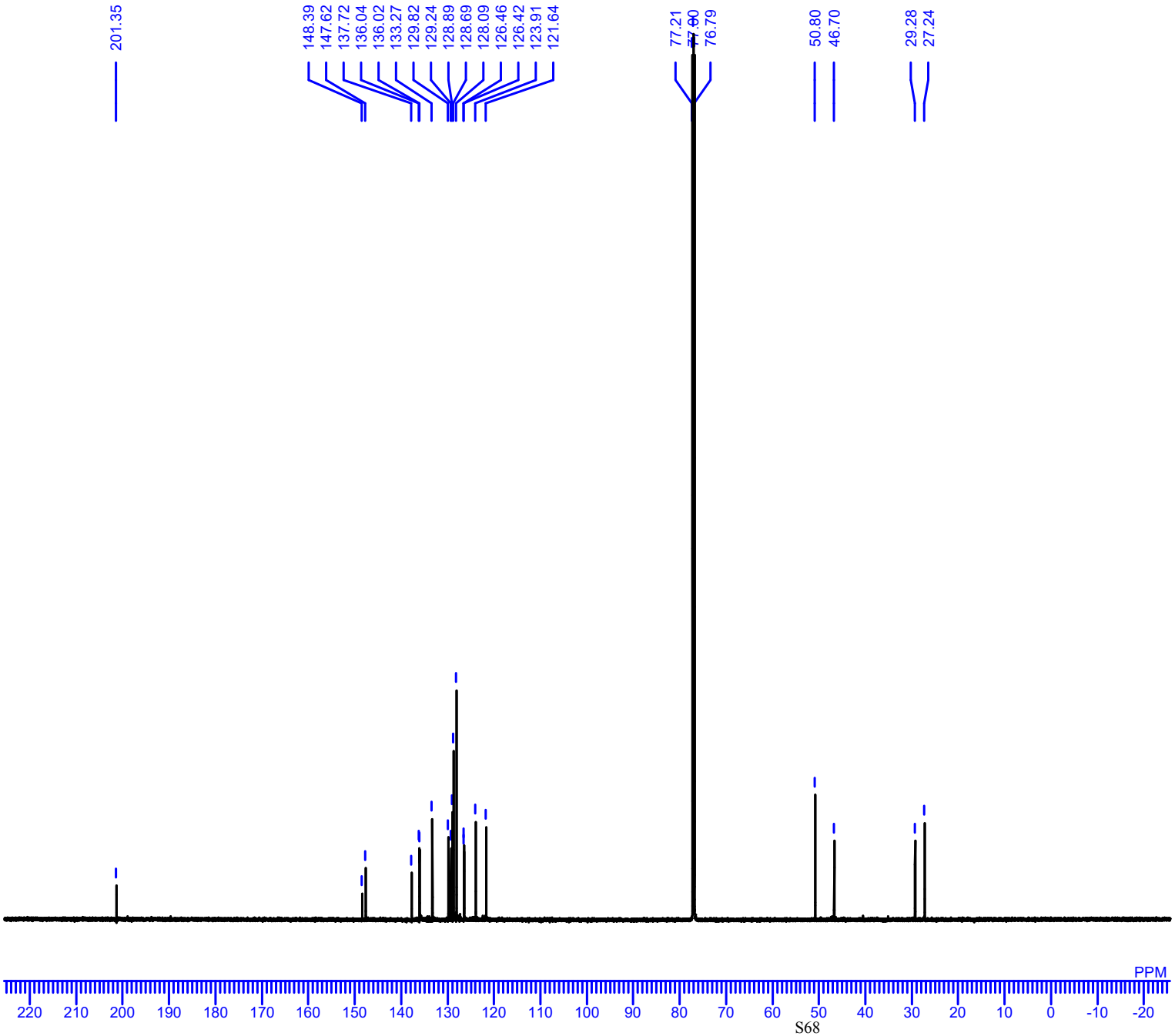
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

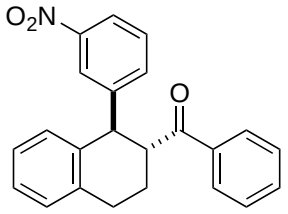




4aj

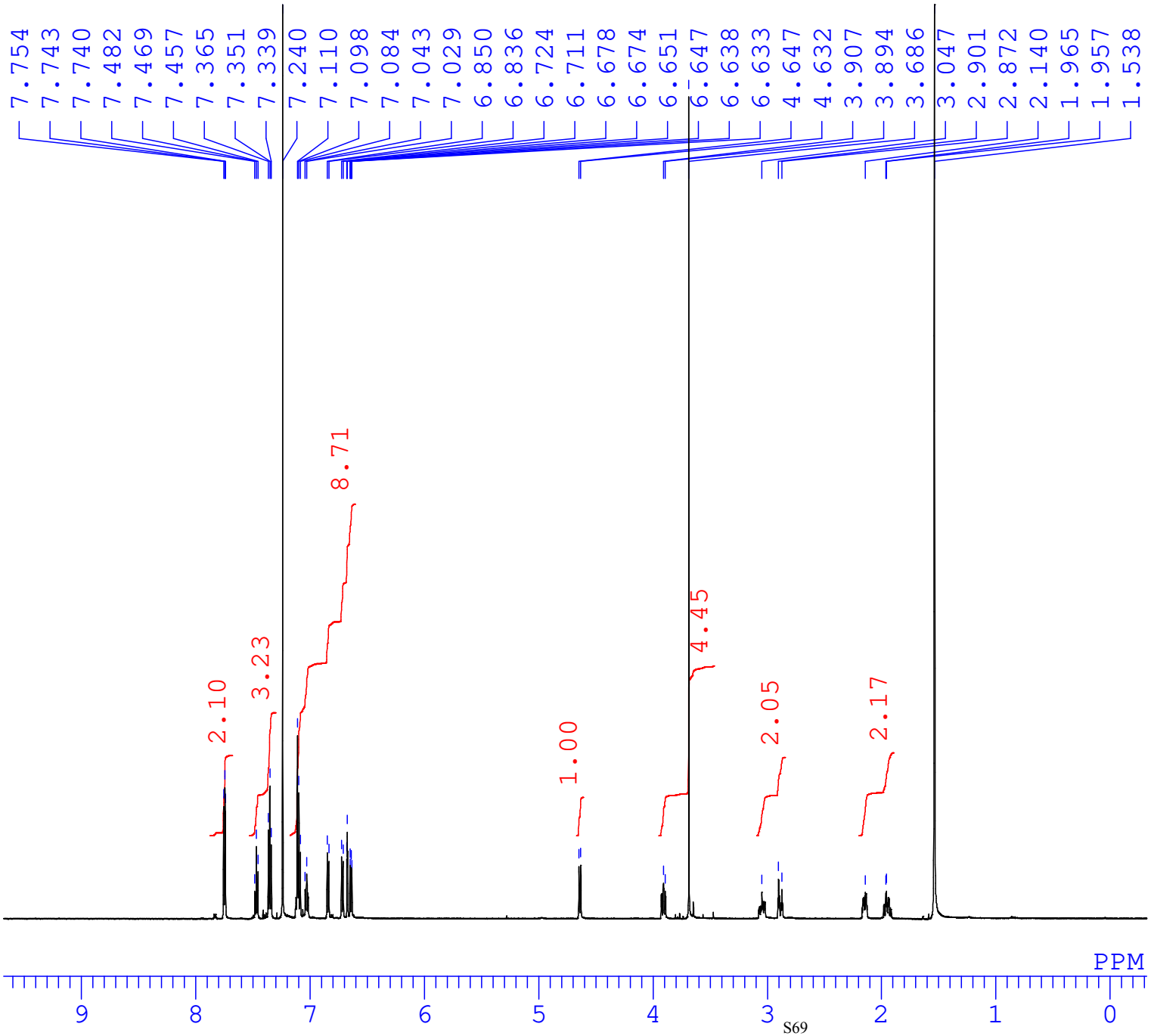
^{1}H NMR
(600 MHz, $CDCl_3$)

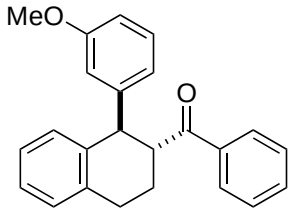




4aj

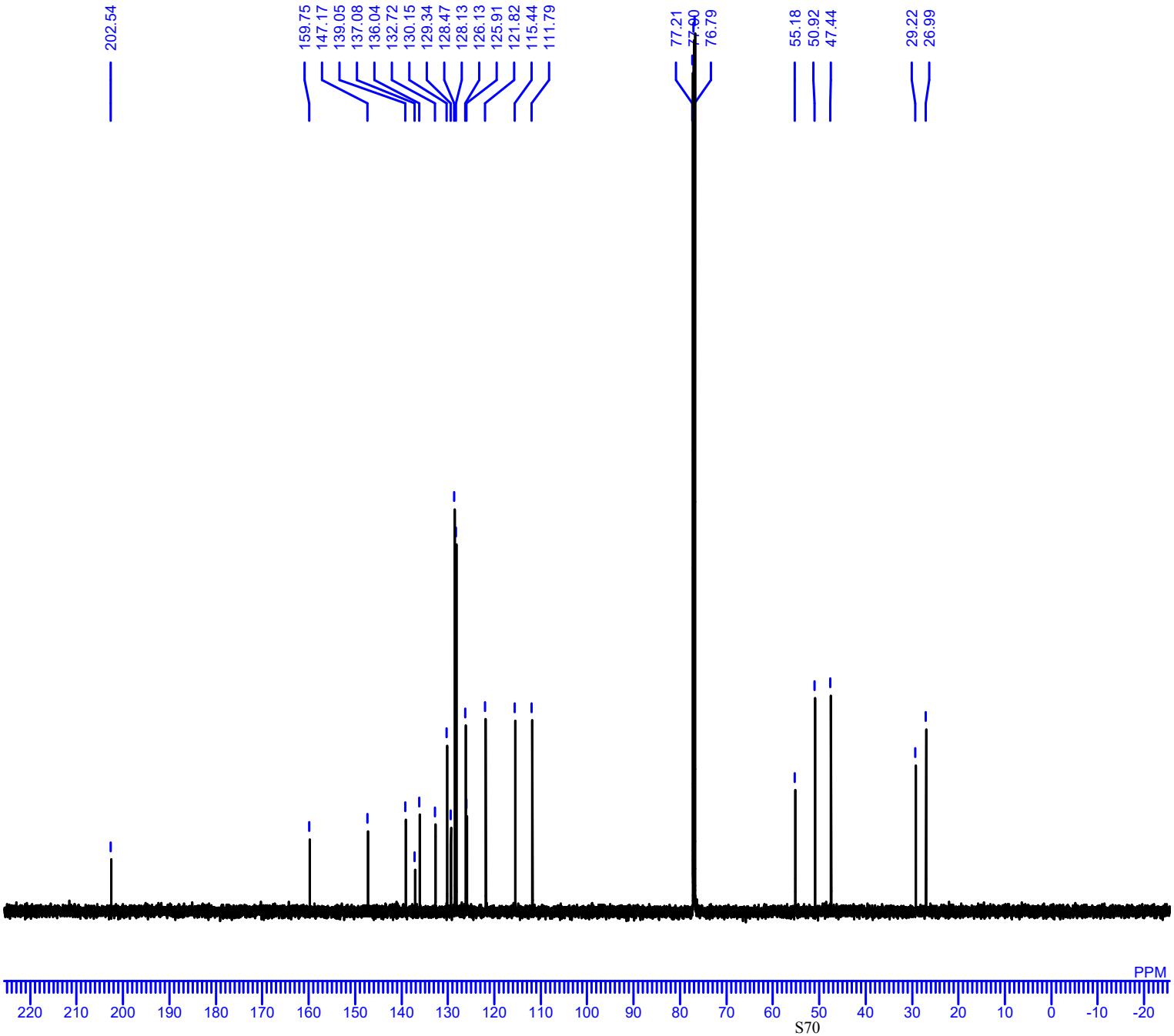
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

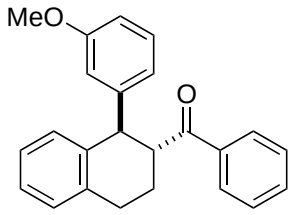




4ak

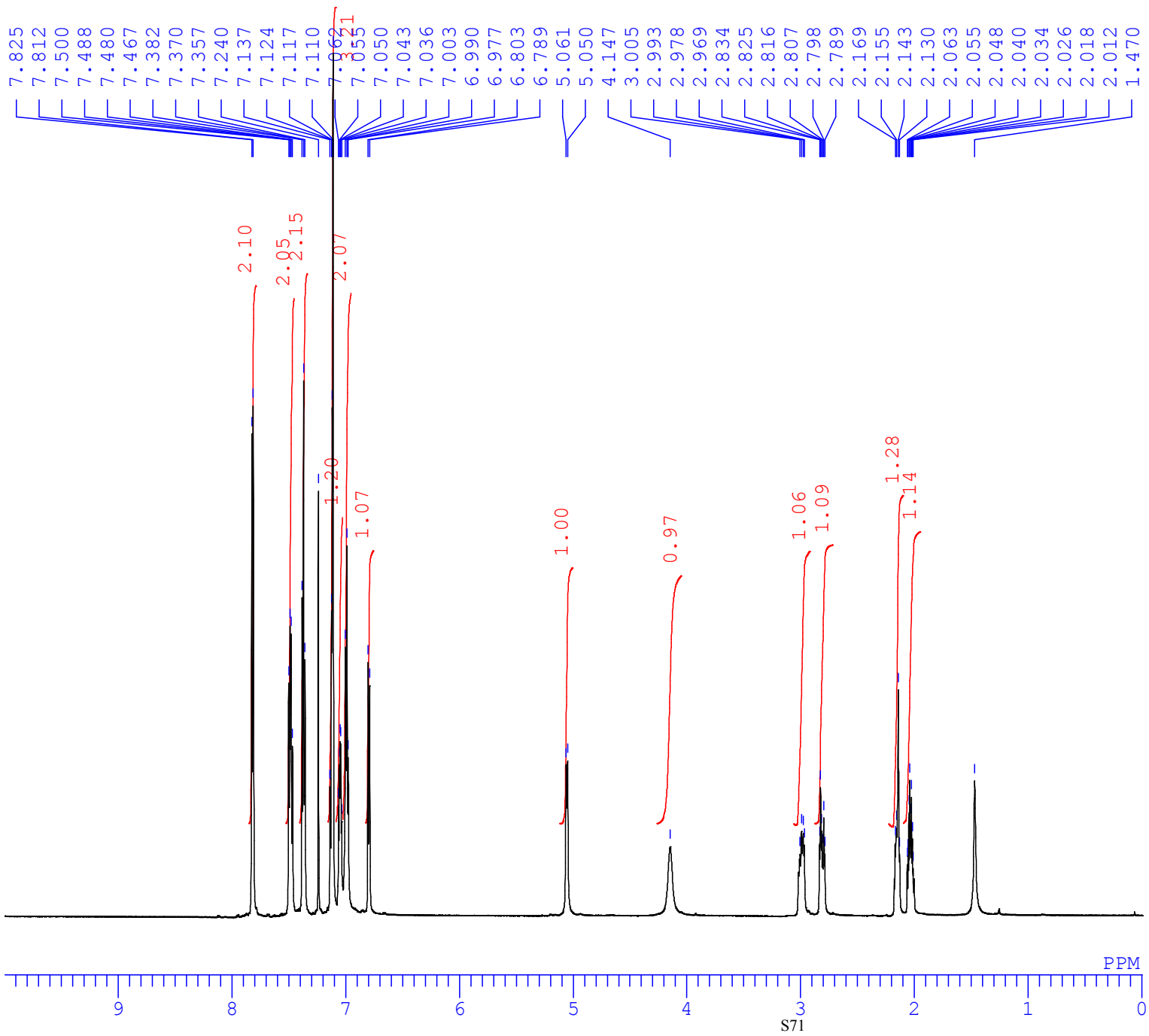
^{1}H NMR
(600 MHz, $CDCl_3$)

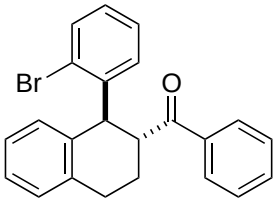




4ak

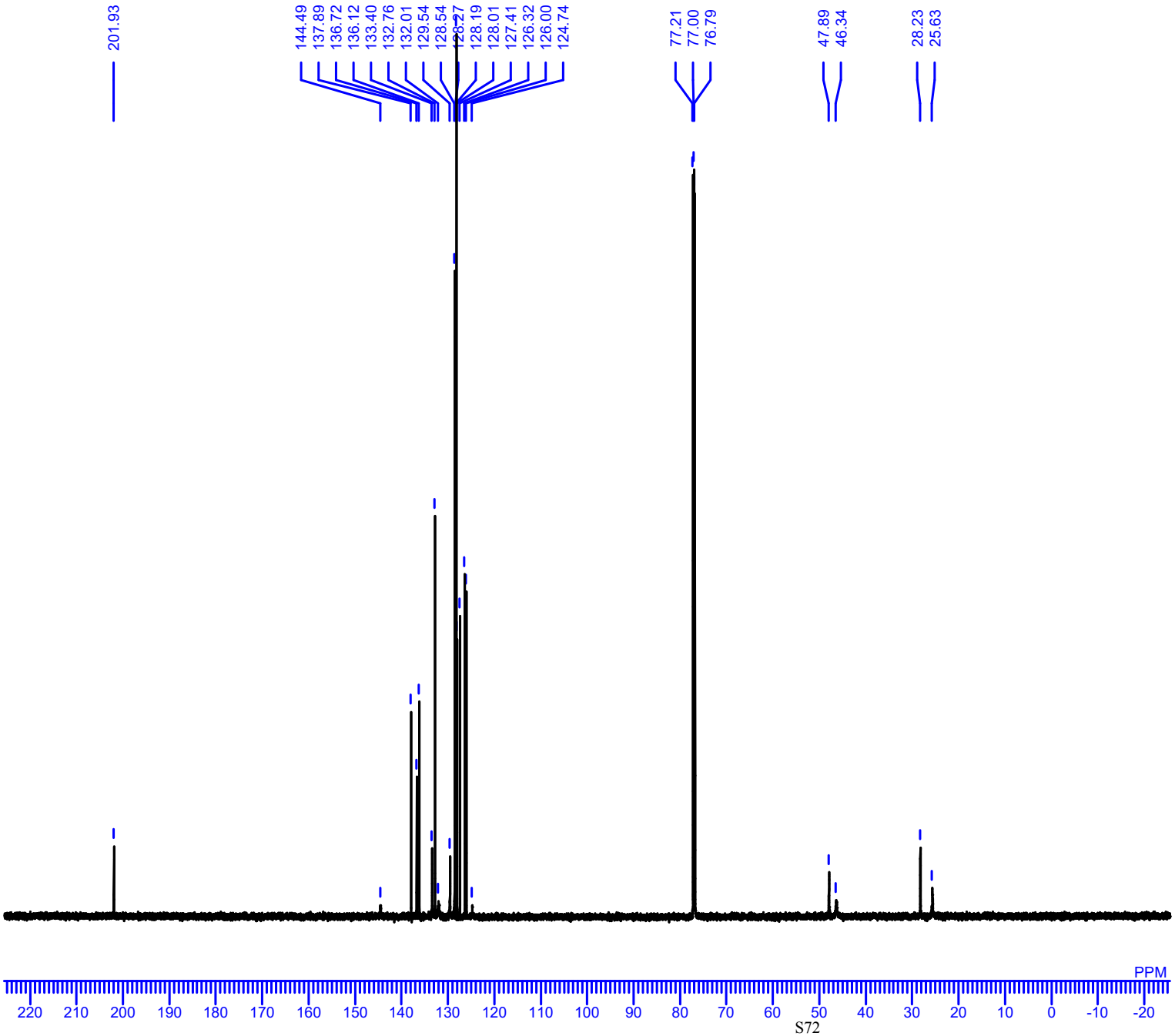
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

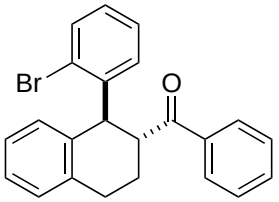




4al

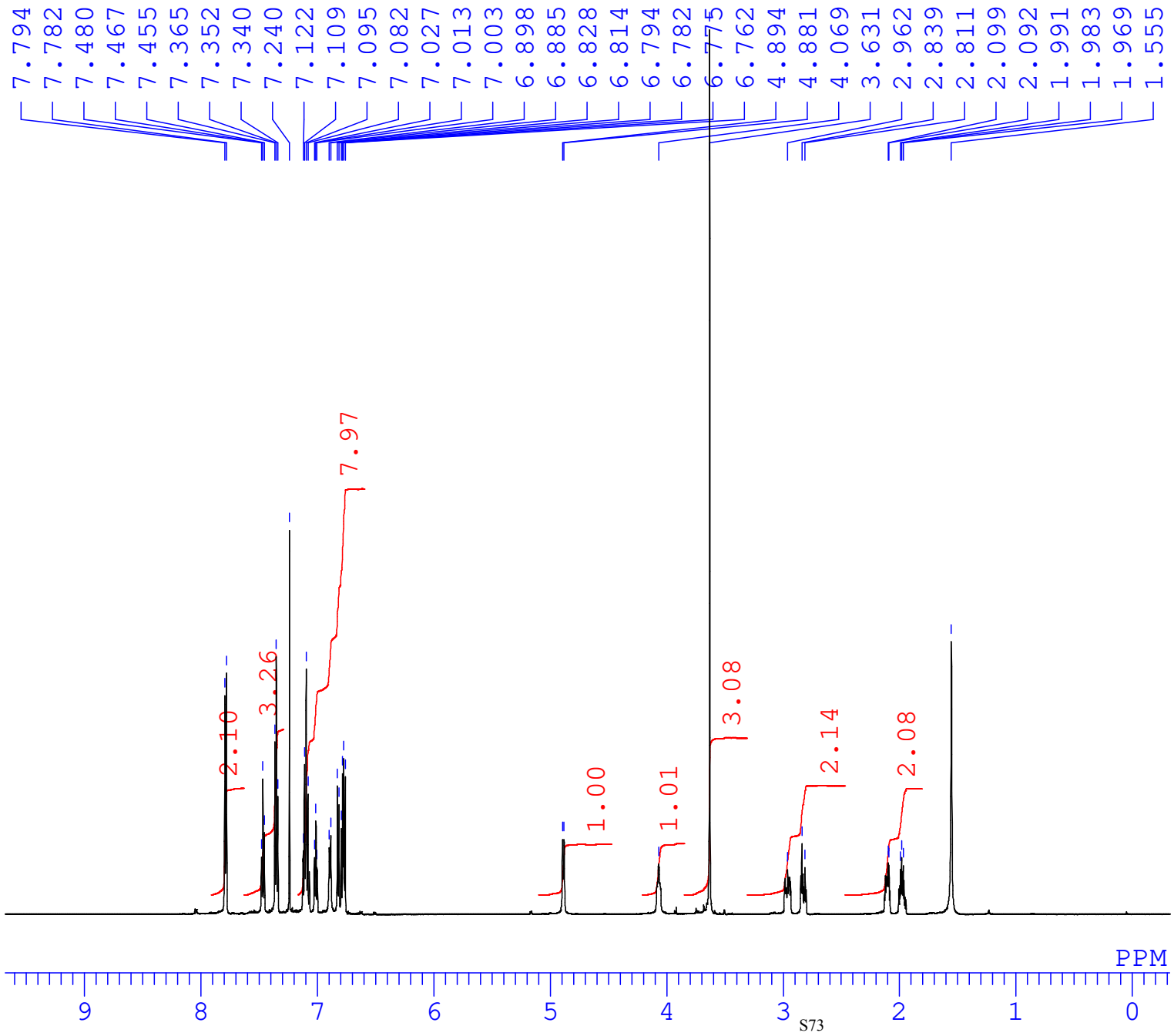
^{1}H NMR
(600 MHz, $CDCl_3$)

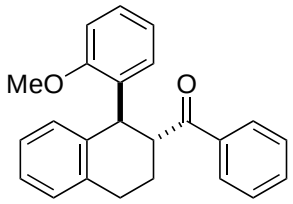




4al

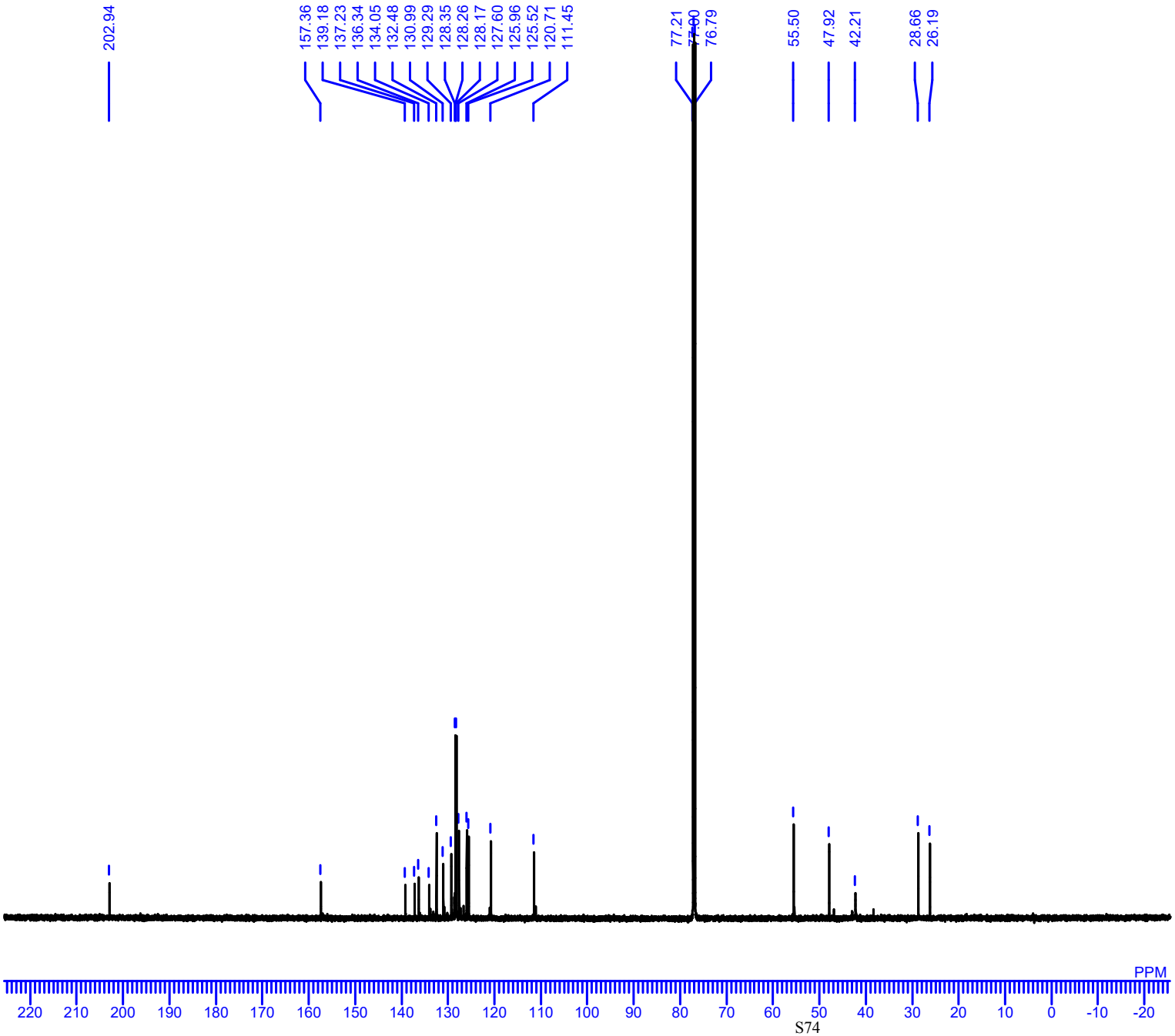
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)
at 50 ^{o}C

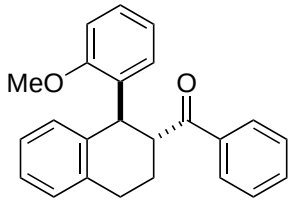




4am

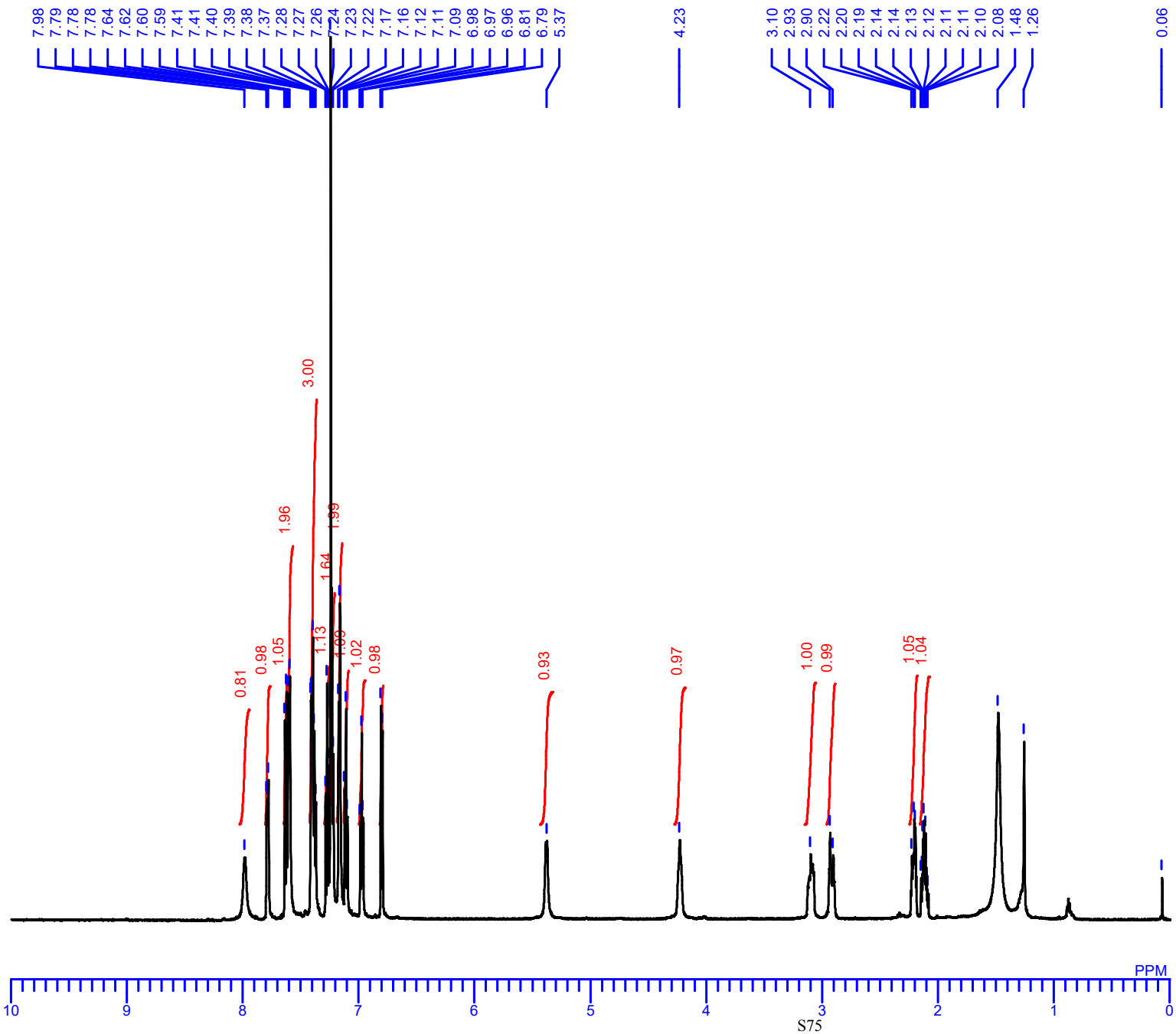
^{1}H NMR
(600 MHz, $CDCl_3$)

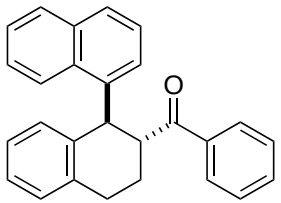




4am

$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)
at 50 ^{o}C

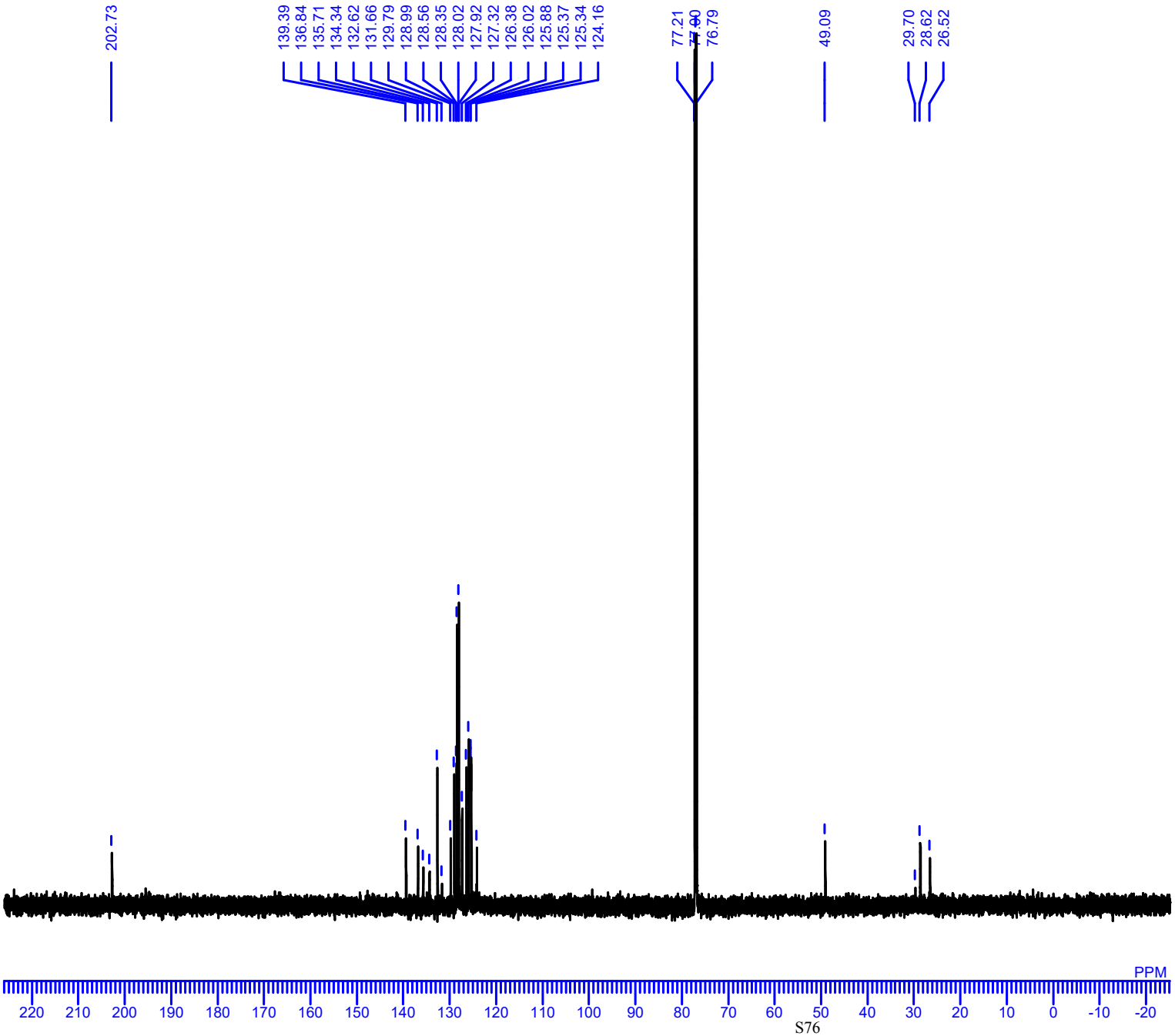


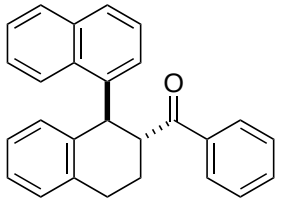


4an

^{1}H NMR
(600 MHz, $CDCl_3$)

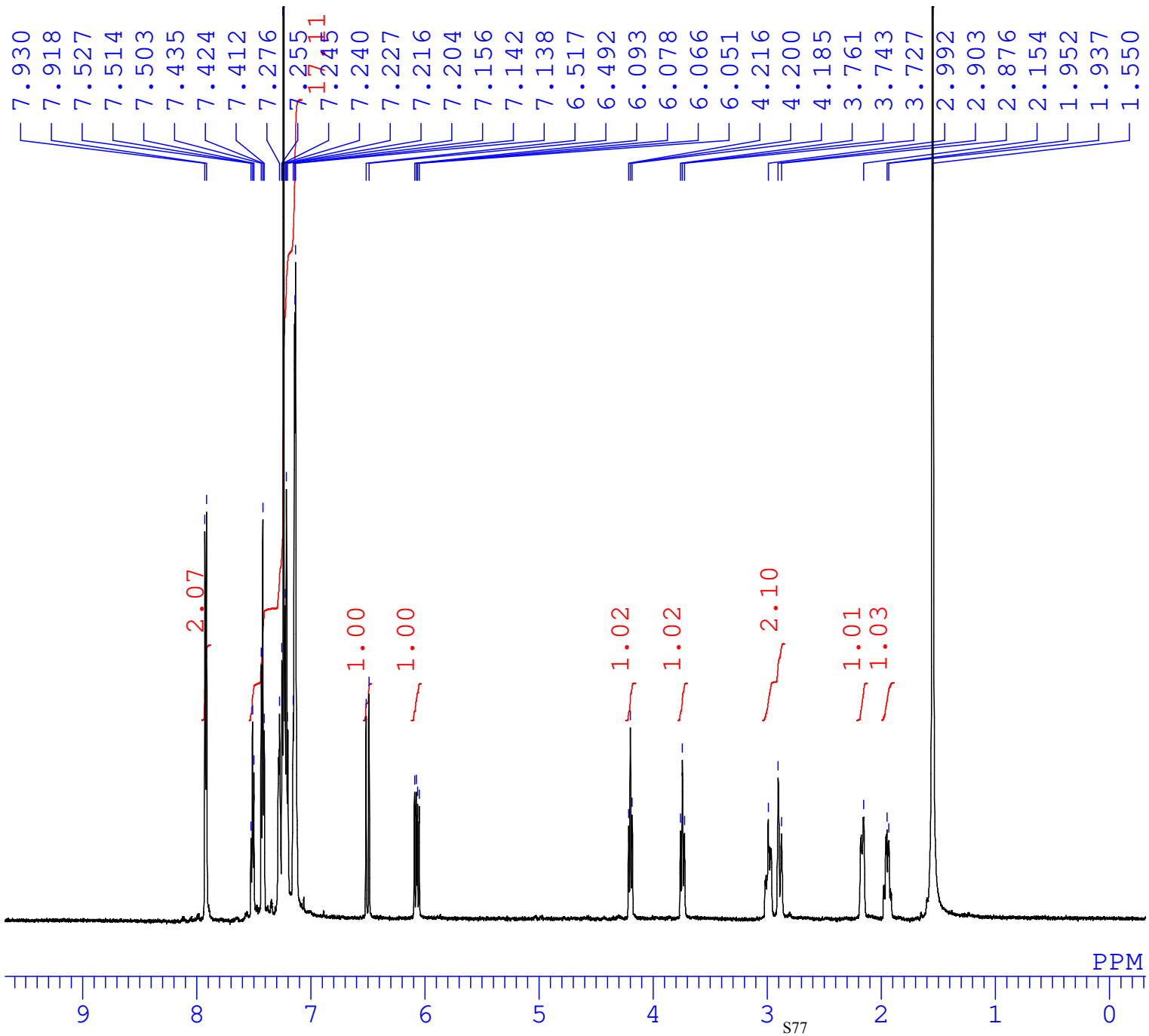
at 50 ^{o}C

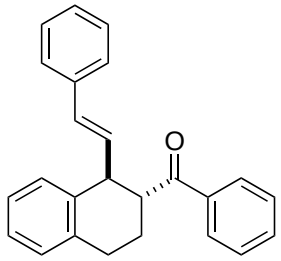




4an

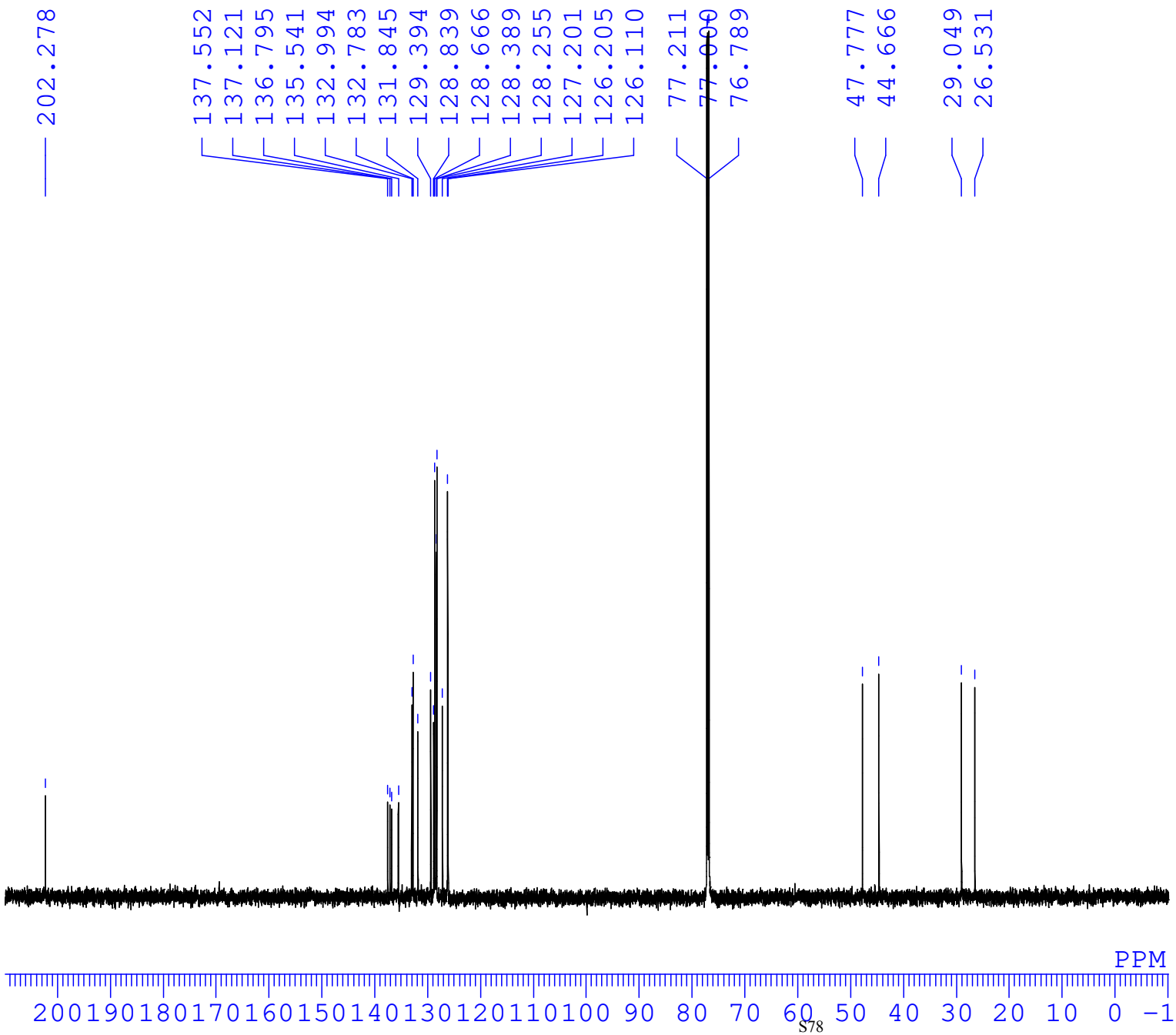
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)
at 50 ^{o}C

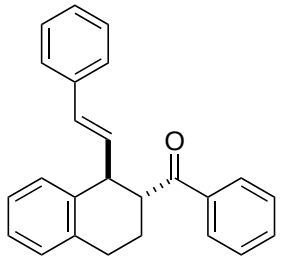




4ao

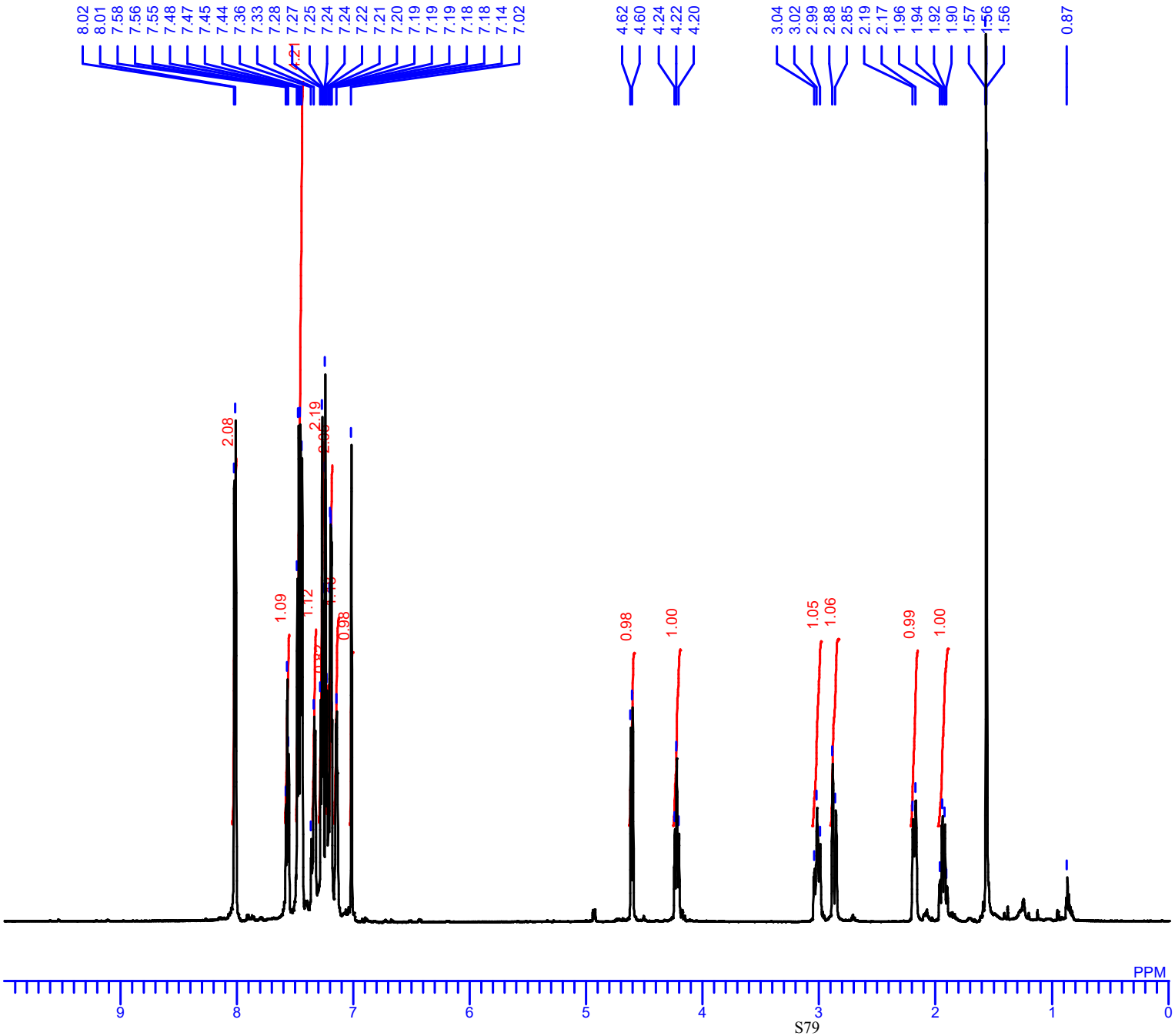
^{1}H NMR
(600 MHz, $CDCl_3$)

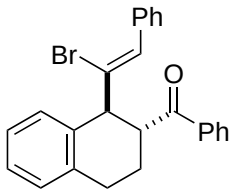




4ao

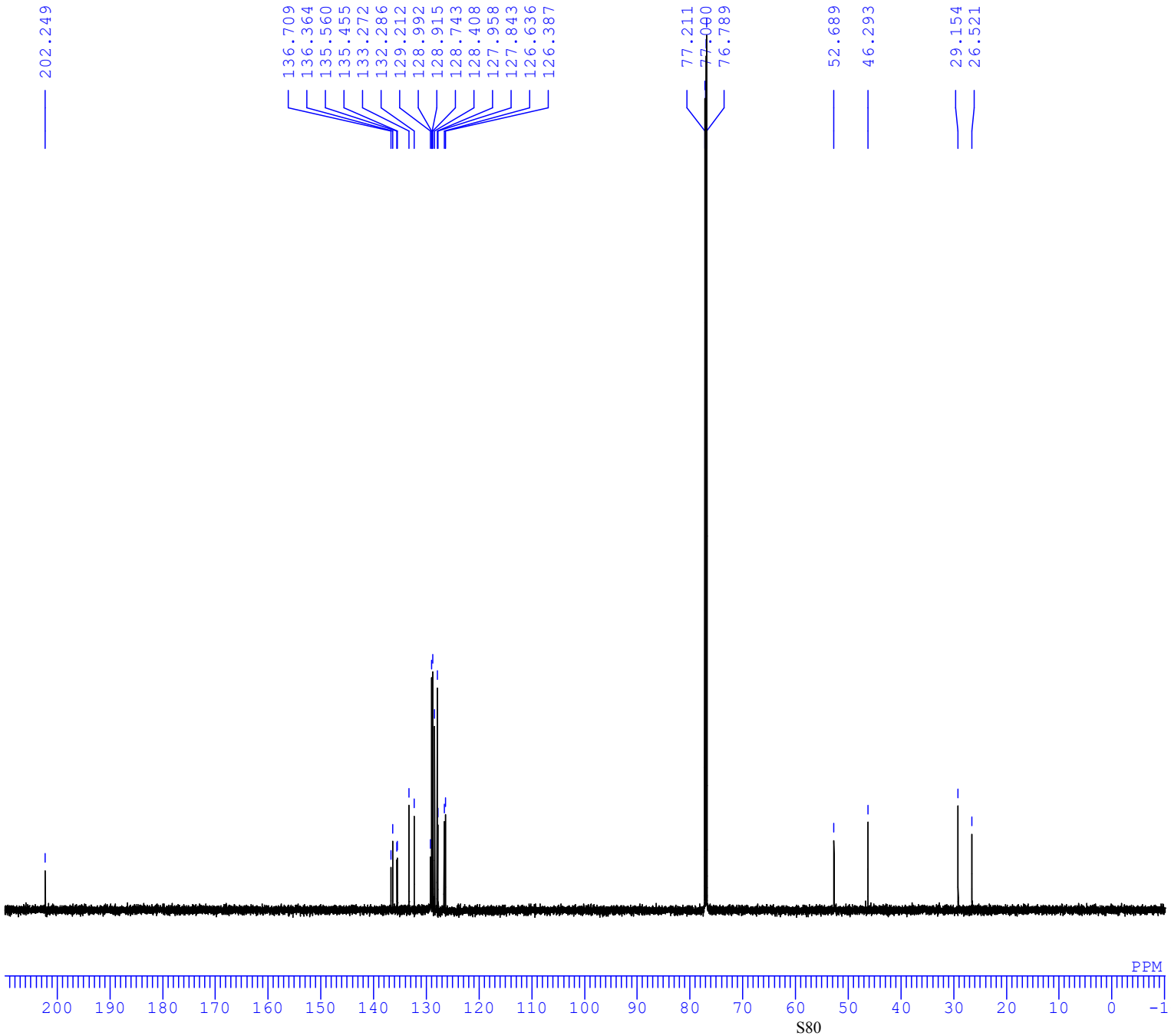
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

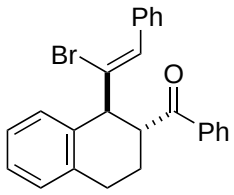




4ap

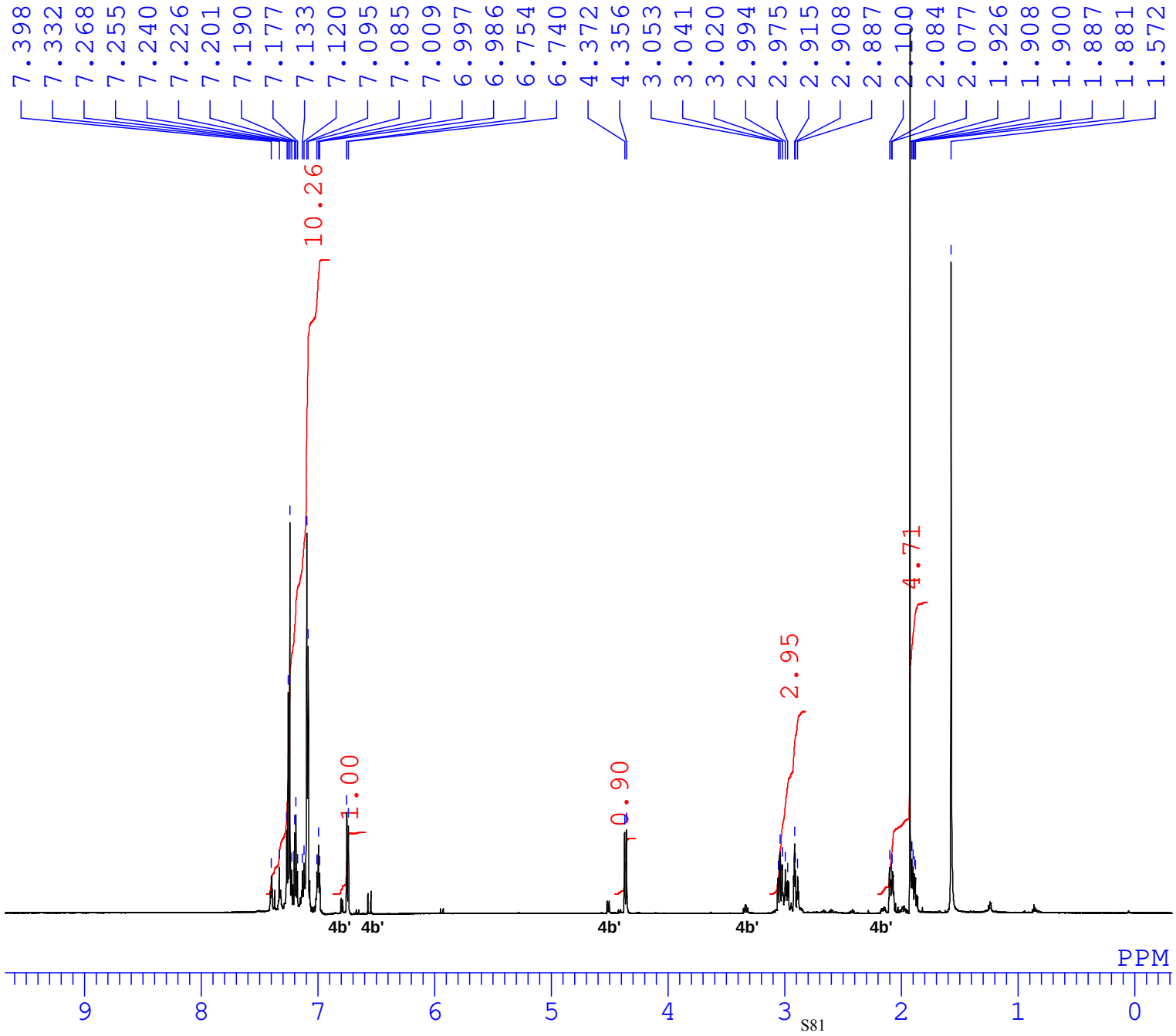
^{1}H NMR
(600 MHz, $CDCl_3$)

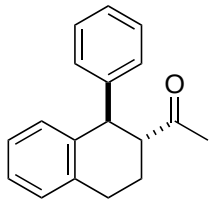




4ap

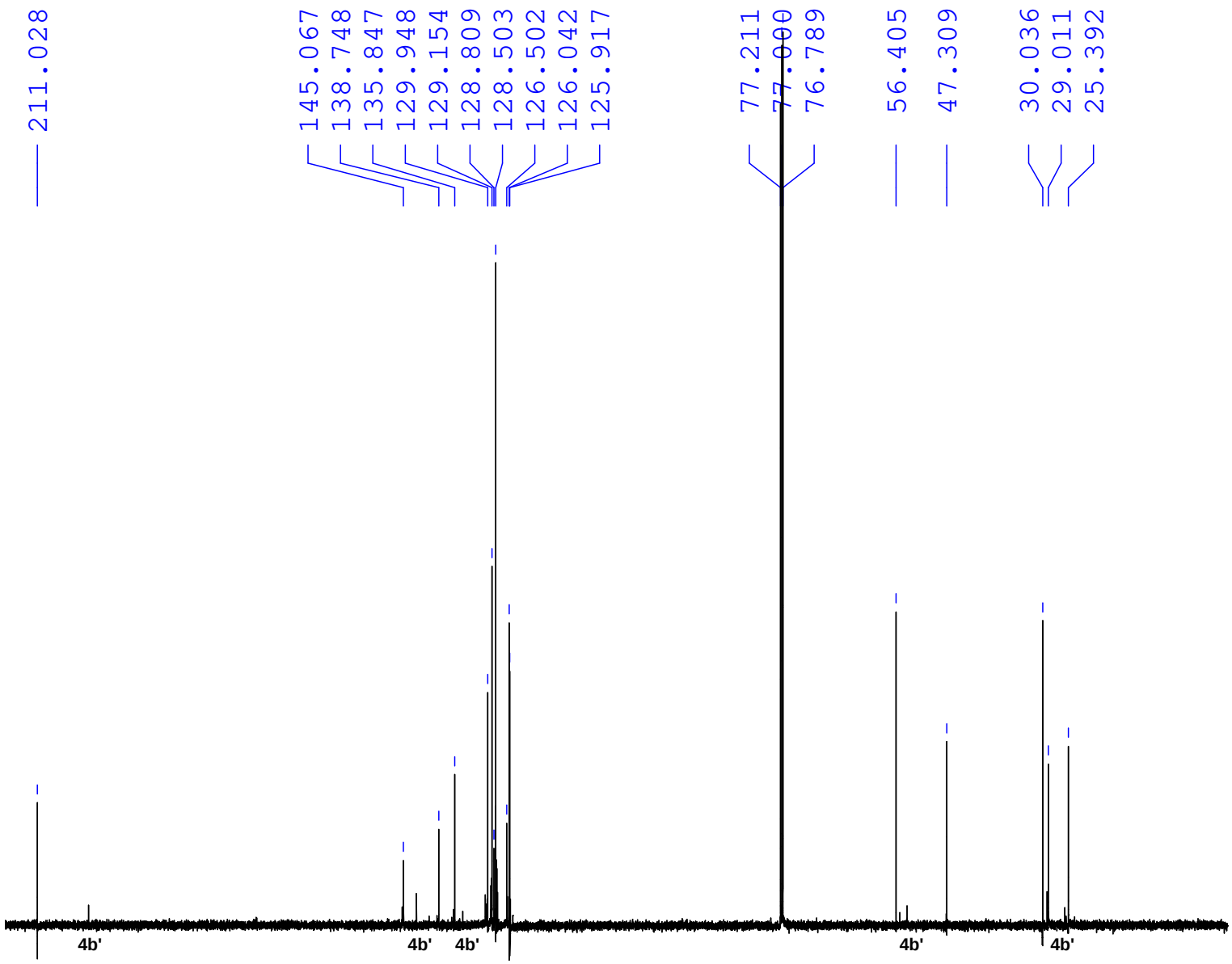
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

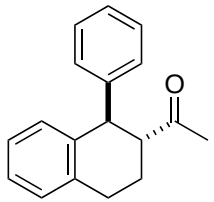




4b

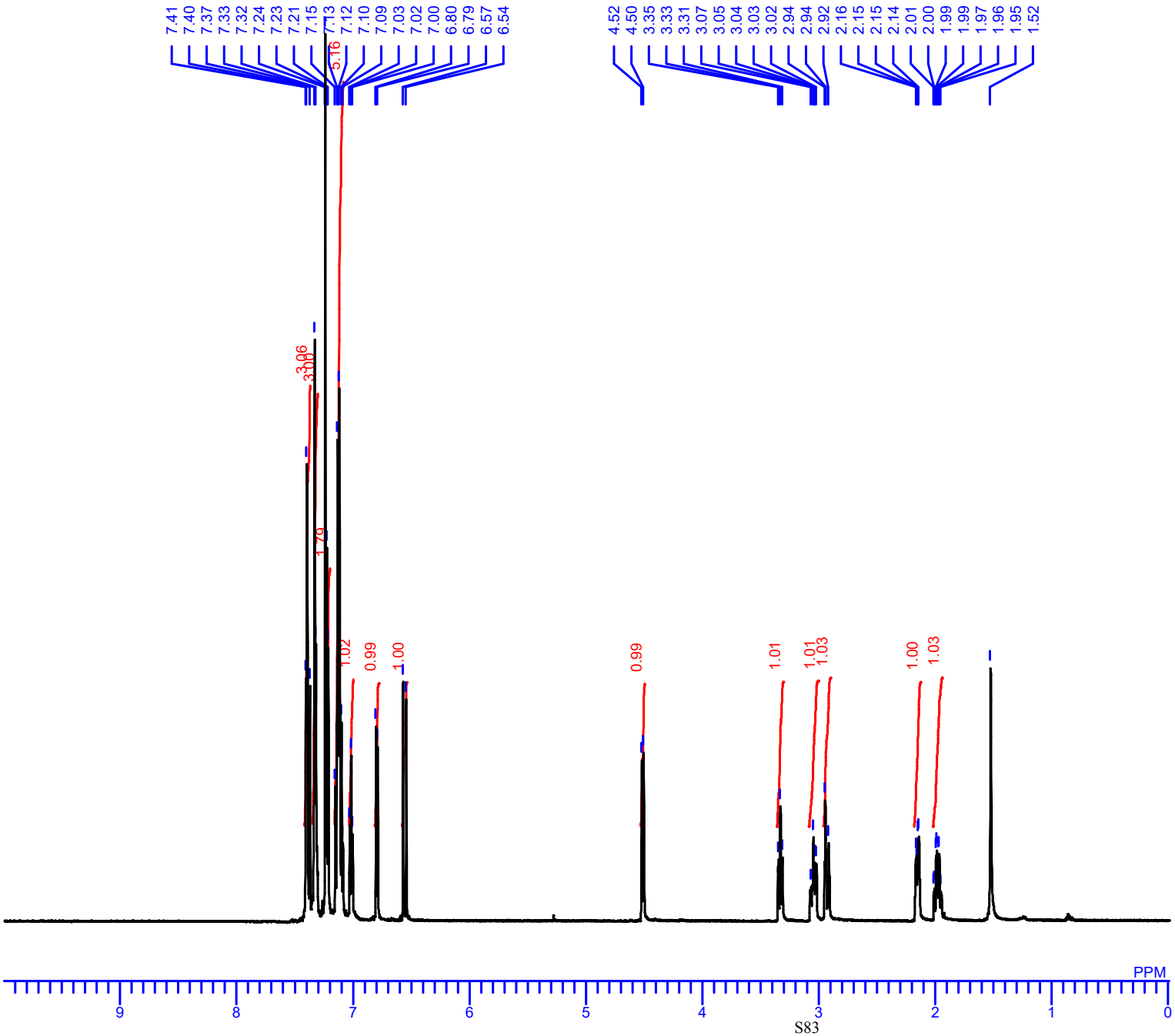
^{1}H NMR
(600 MHz, $CDCl_3$)

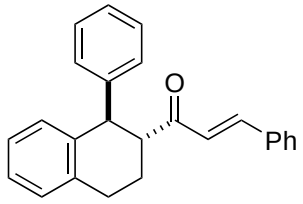




4b

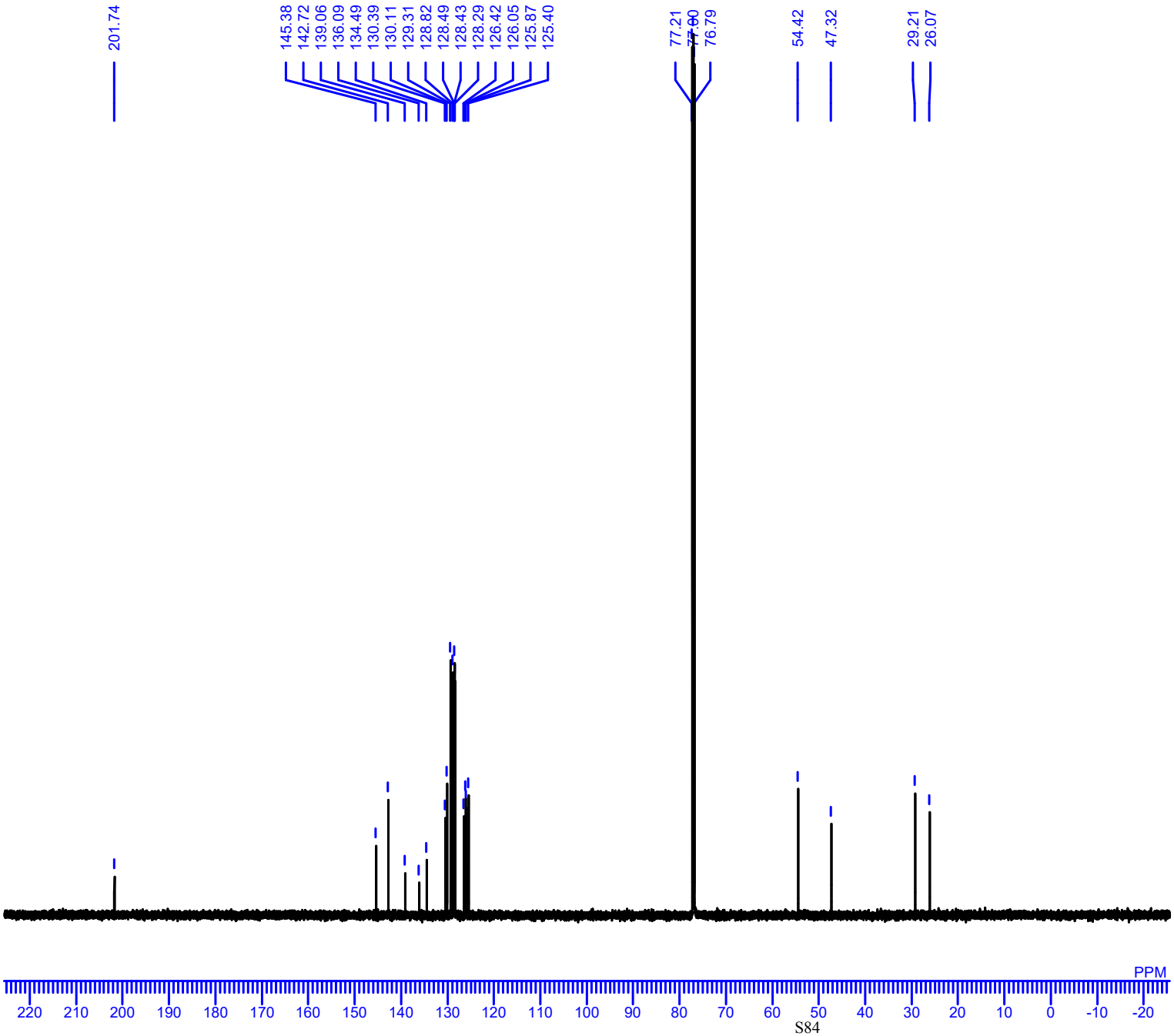
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

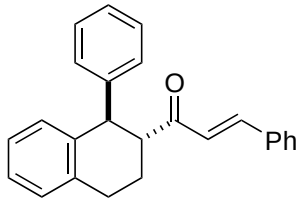




4b'

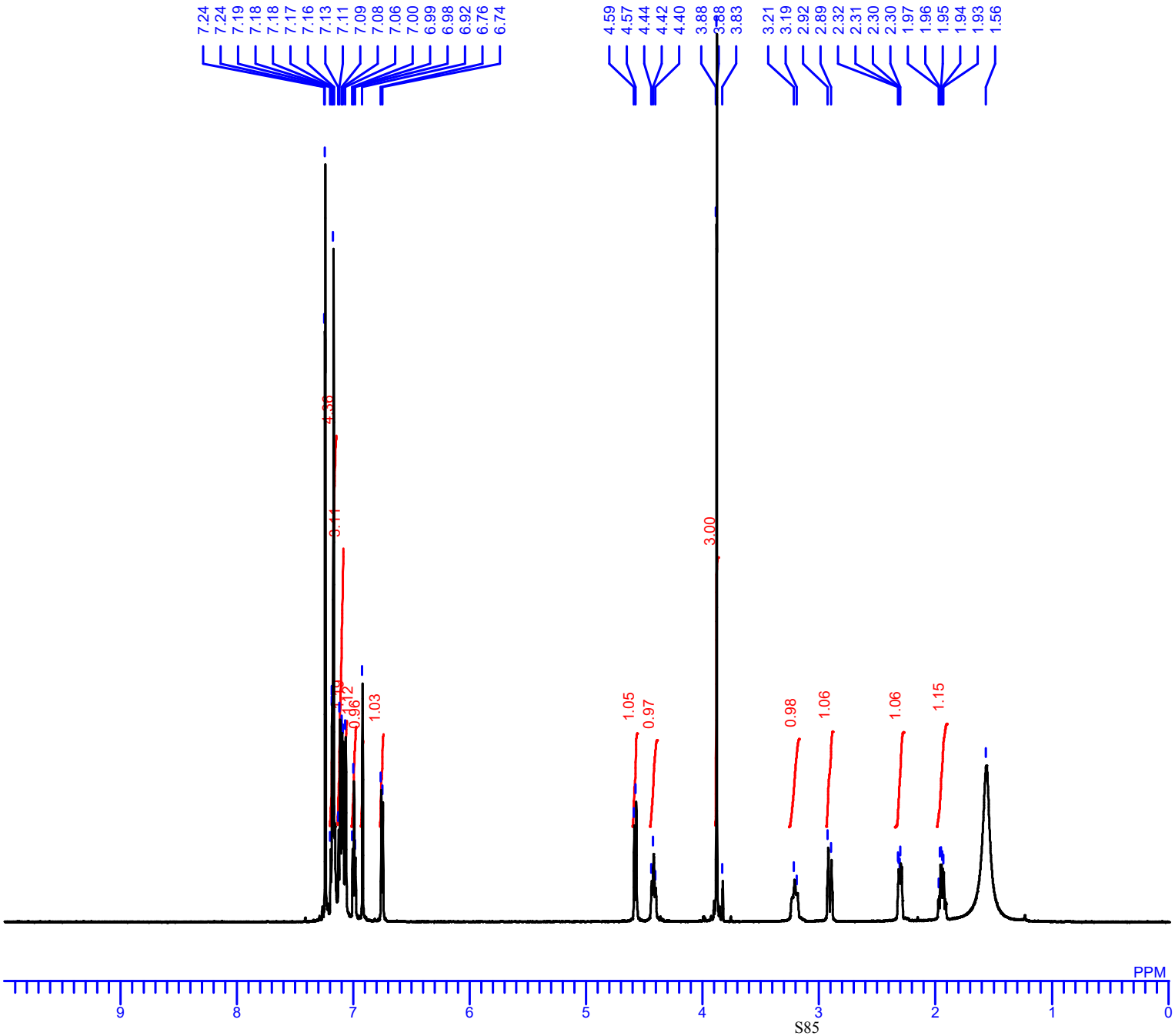
^{1}H NMR
(600 MHz, $CDCl_3$)

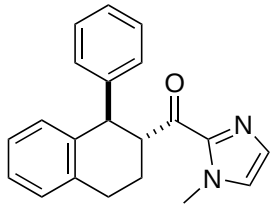




4b'

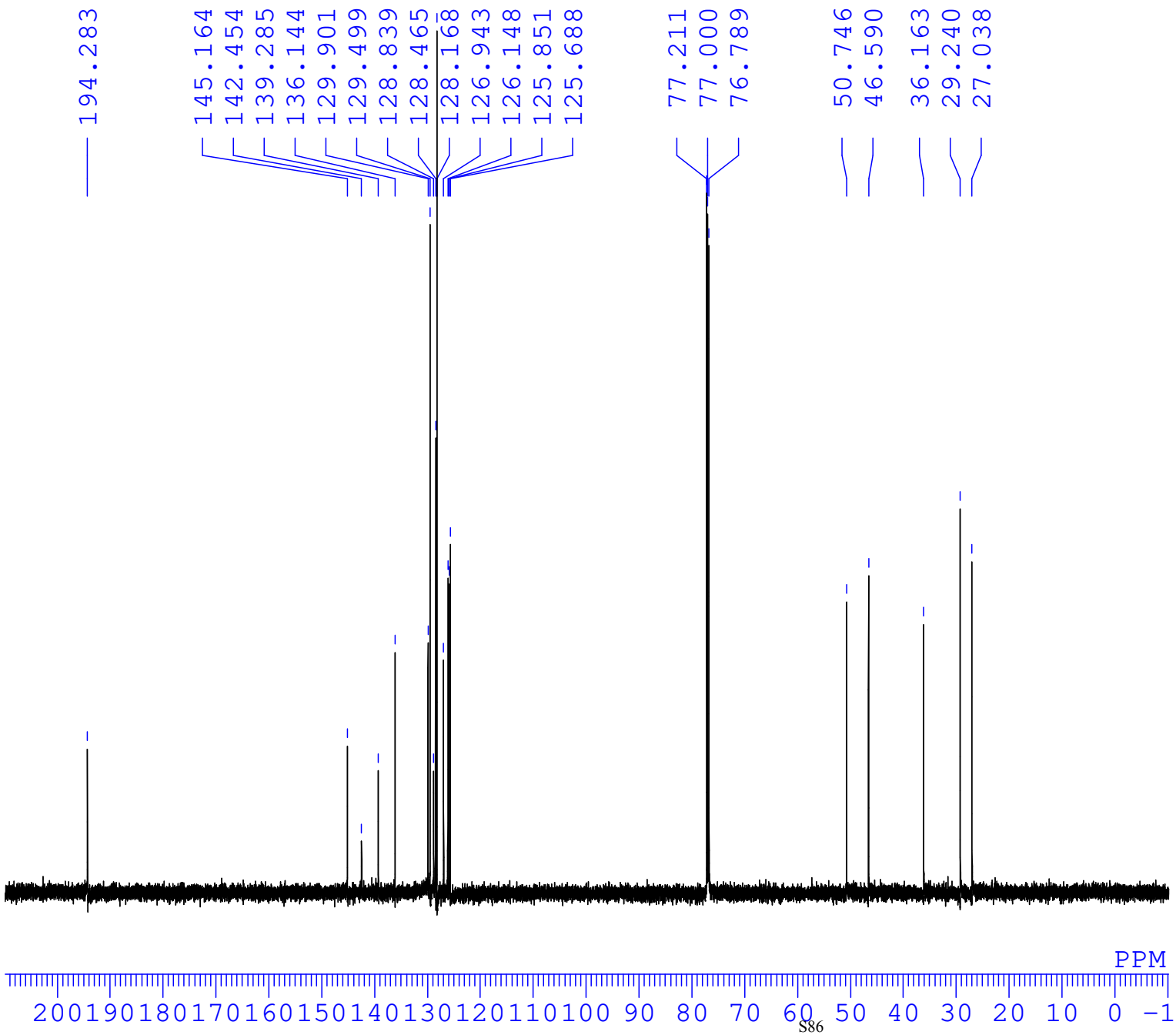
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

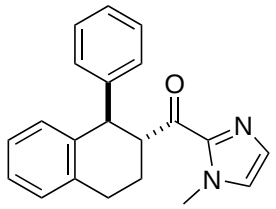




4c

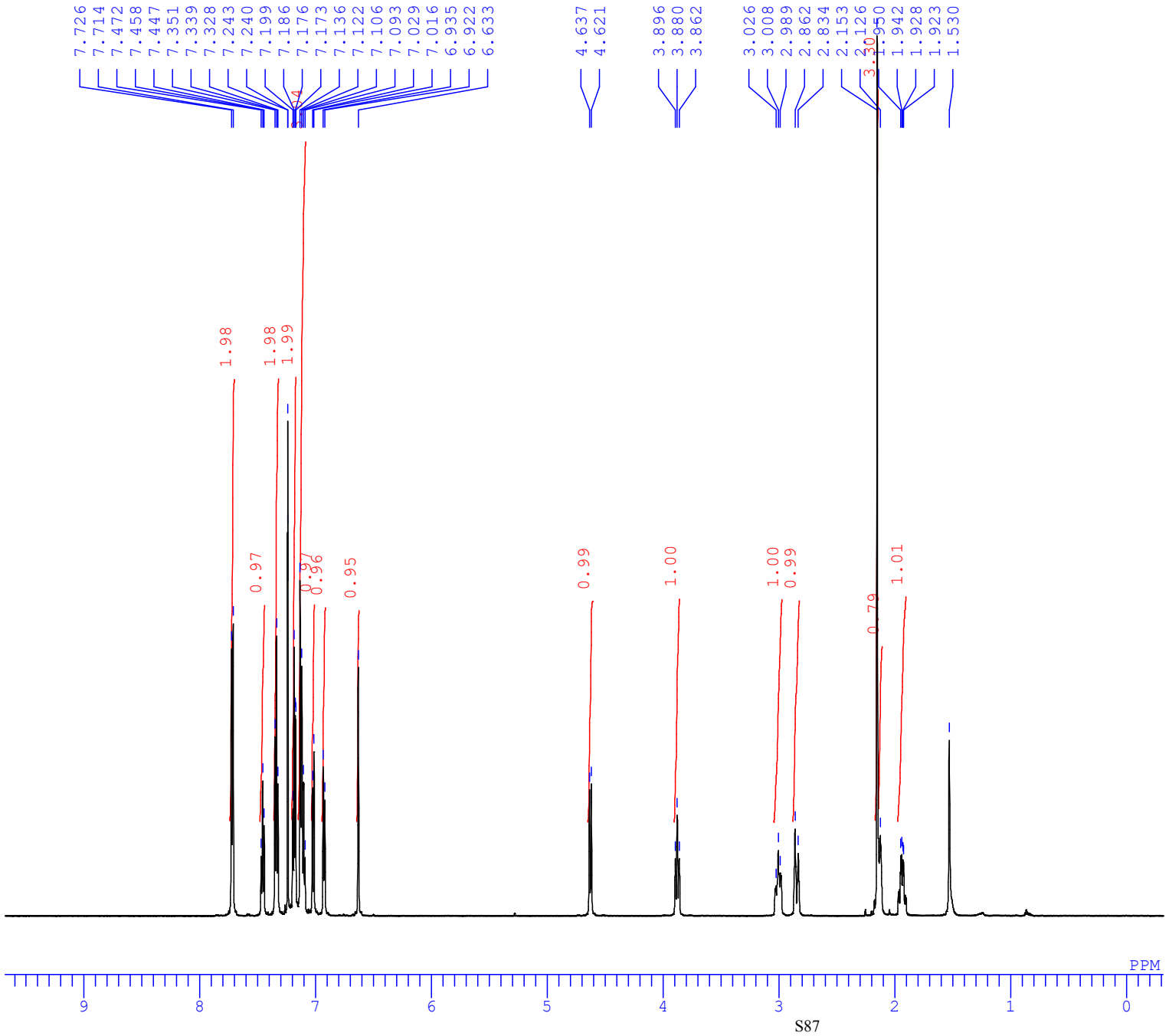
^{1}H NMR
(600 MHz, $CDCl_3$)

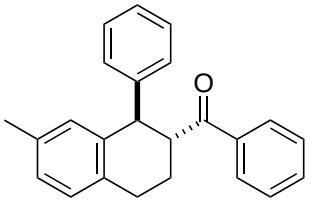




4c

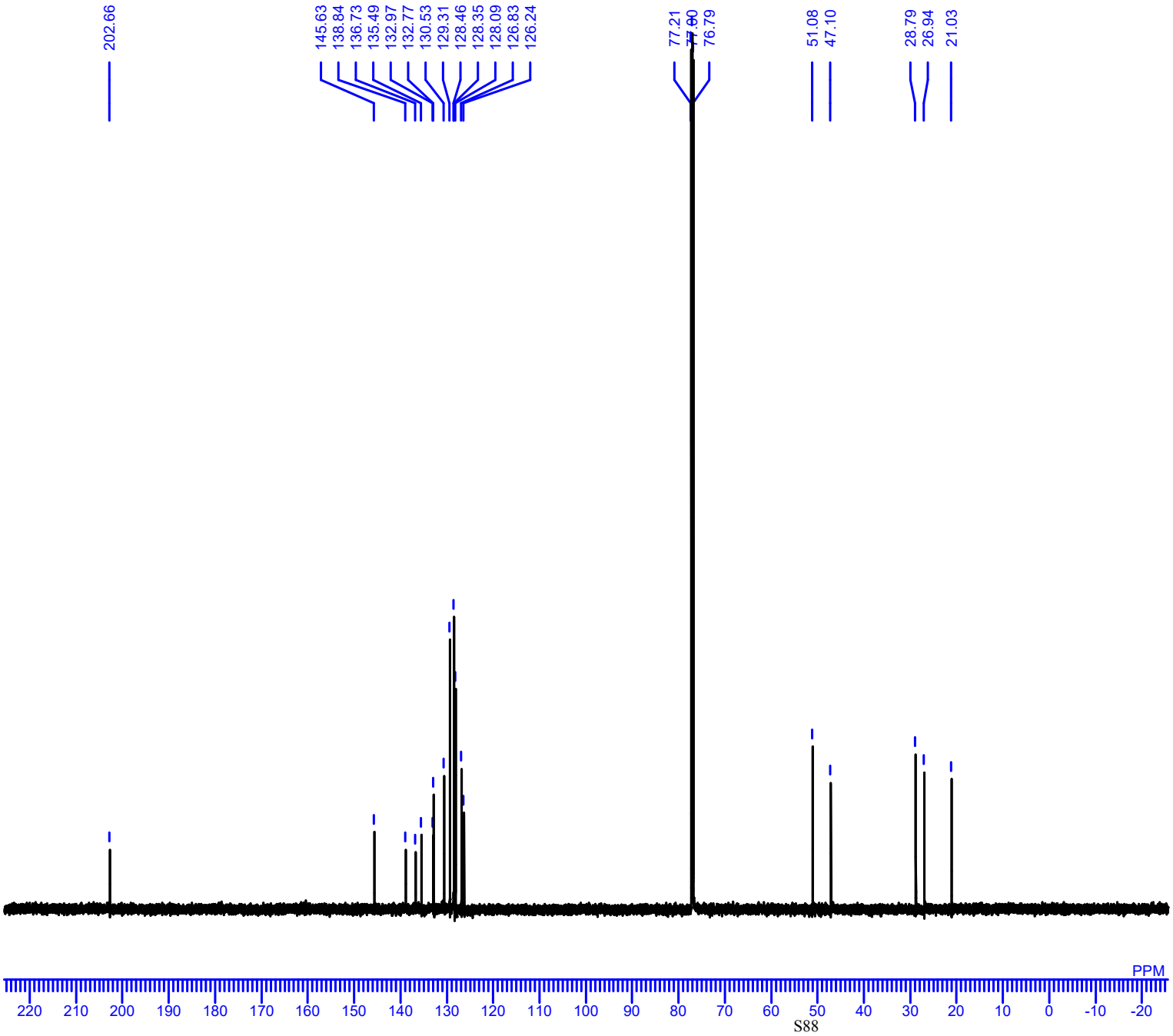
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

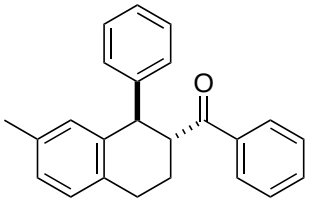




4d

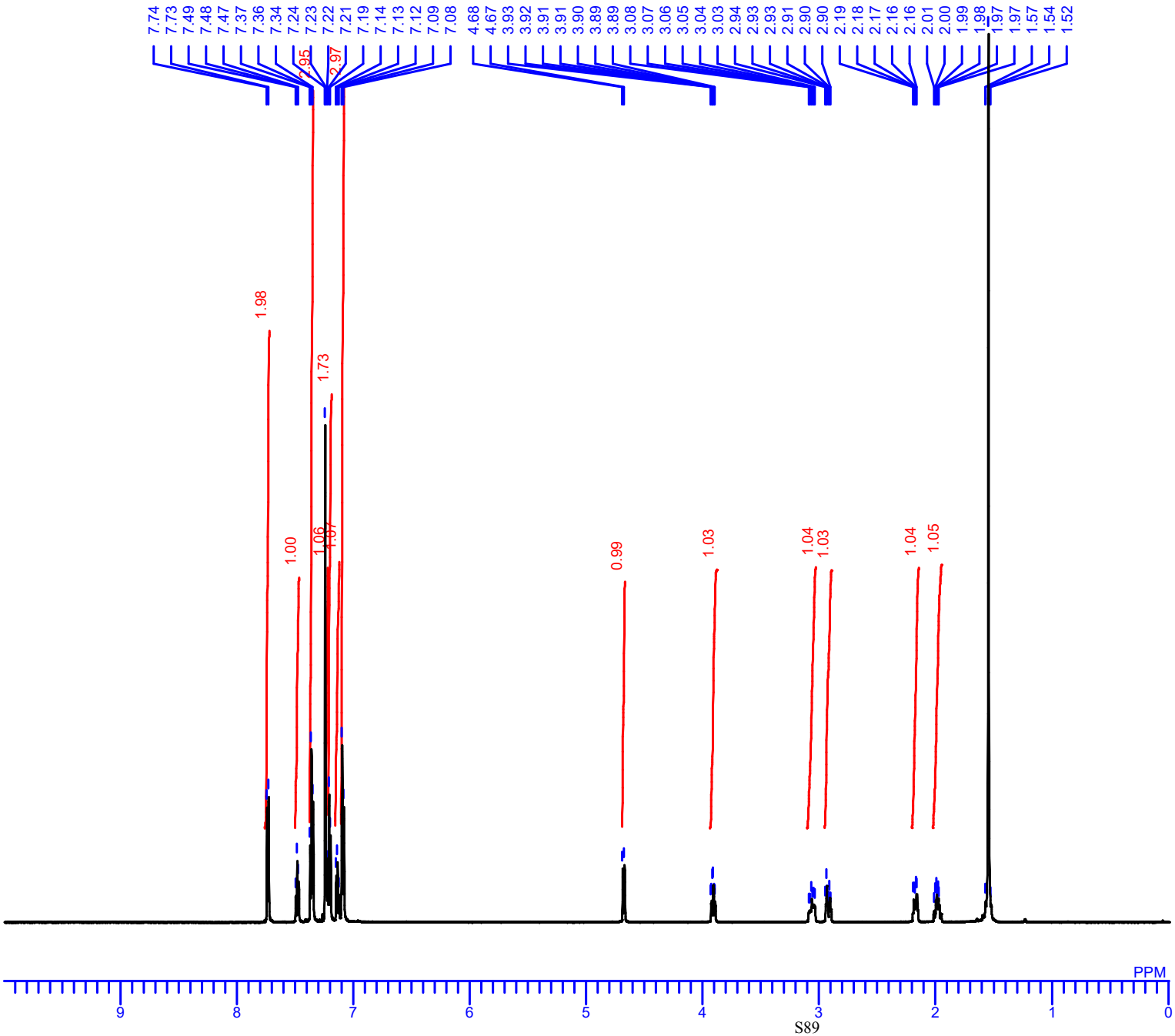
^{1}H NMR
(600 MHz, $CDCl_3$)

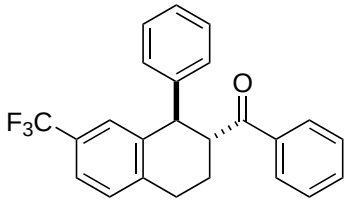




4d

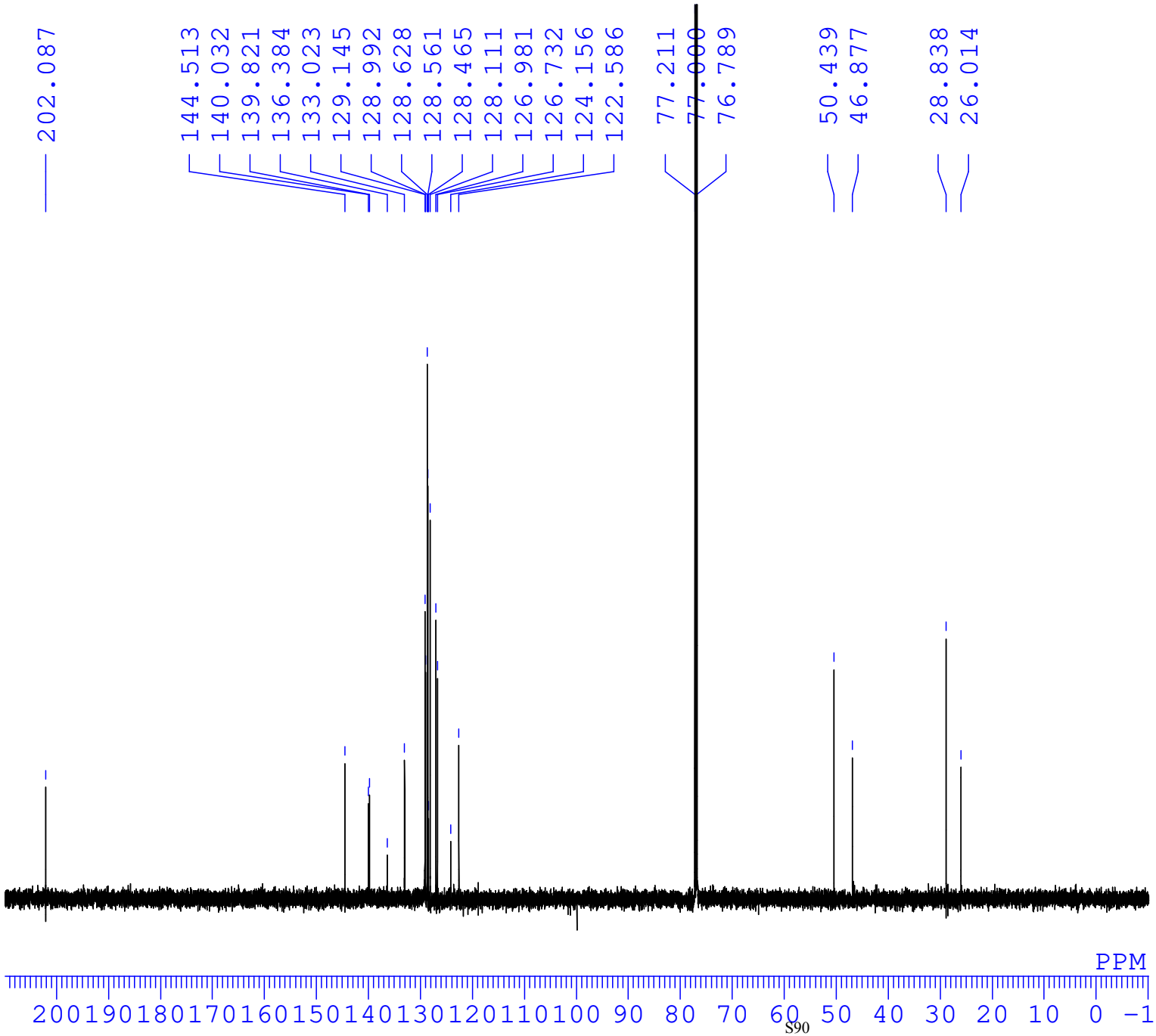
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

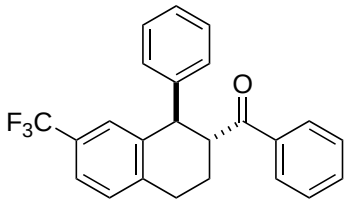




4e

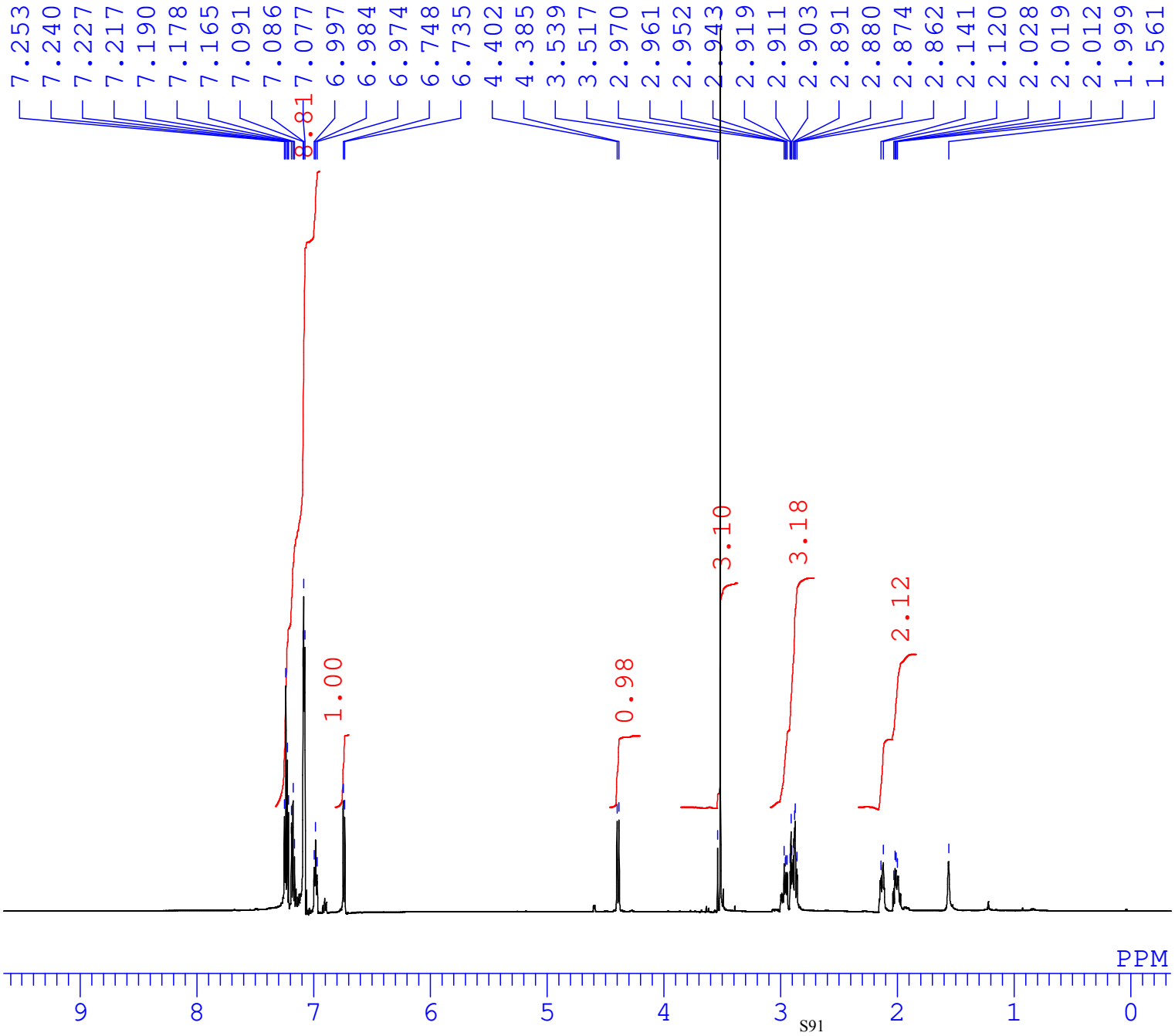
^{1}H NMR
(600 MHz, $CDCl_3$)

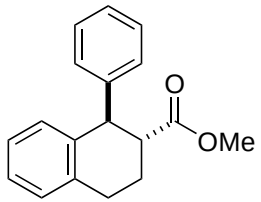




4e

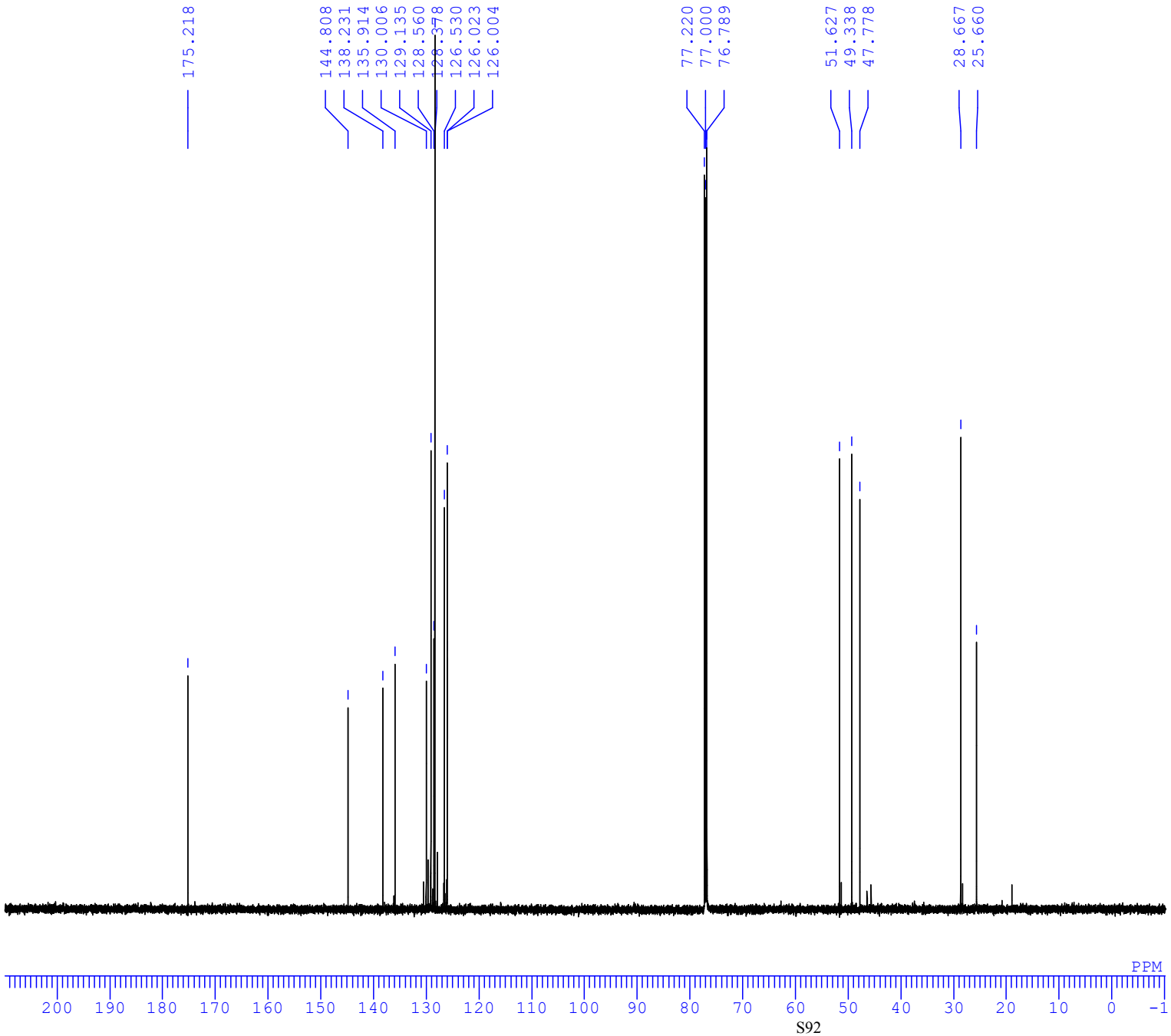
$^{13}C\{^{1}H,^{19}F\}$ NMR
(150 MHz, $CDCl_3$)

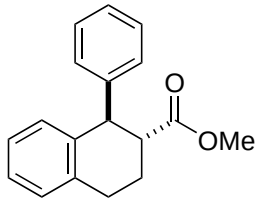




5

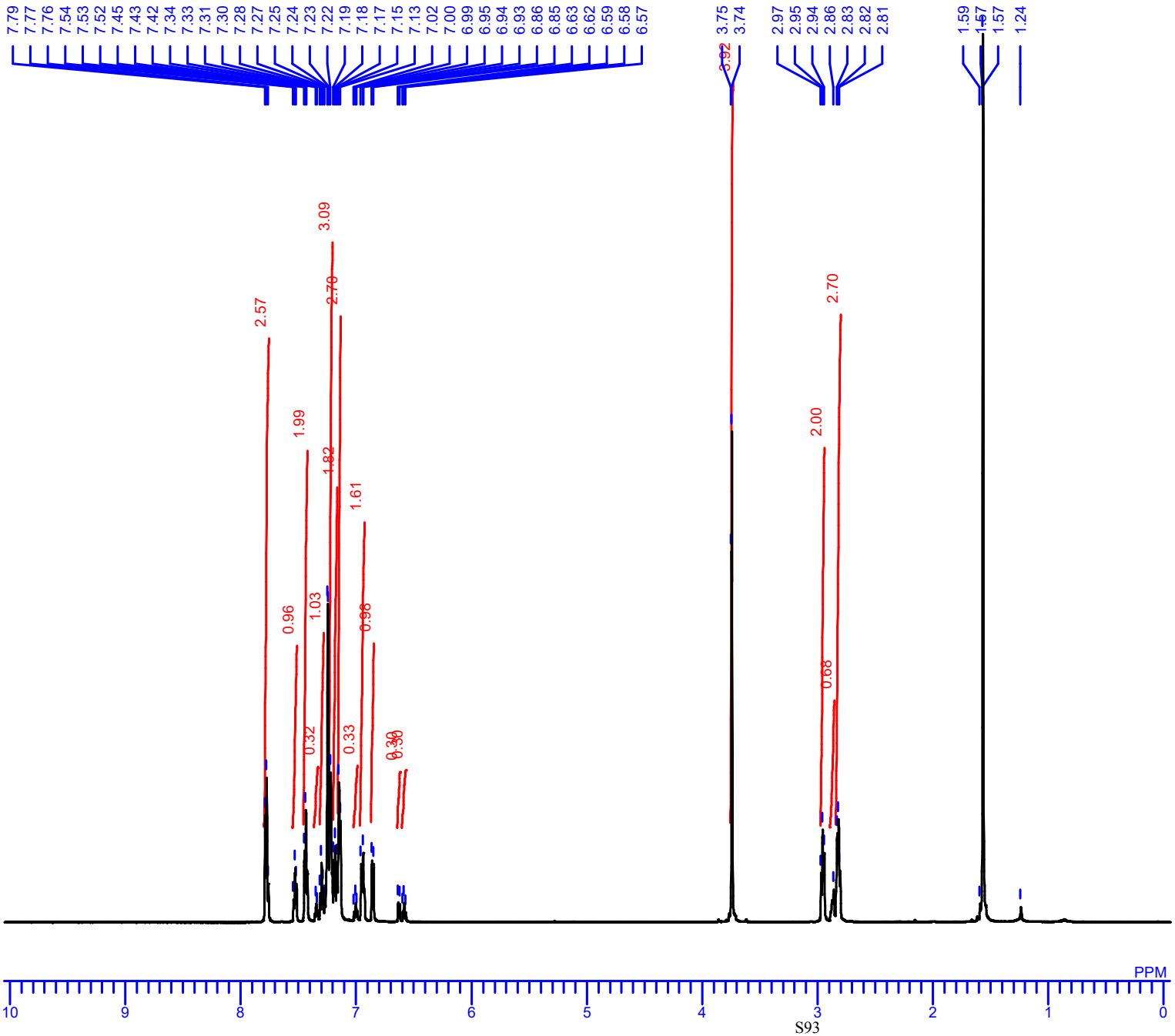
^{1}H NMR
(600 MHz, $CDCl_3$)

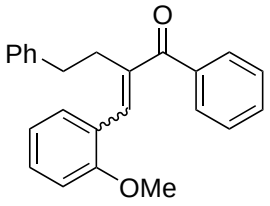




5

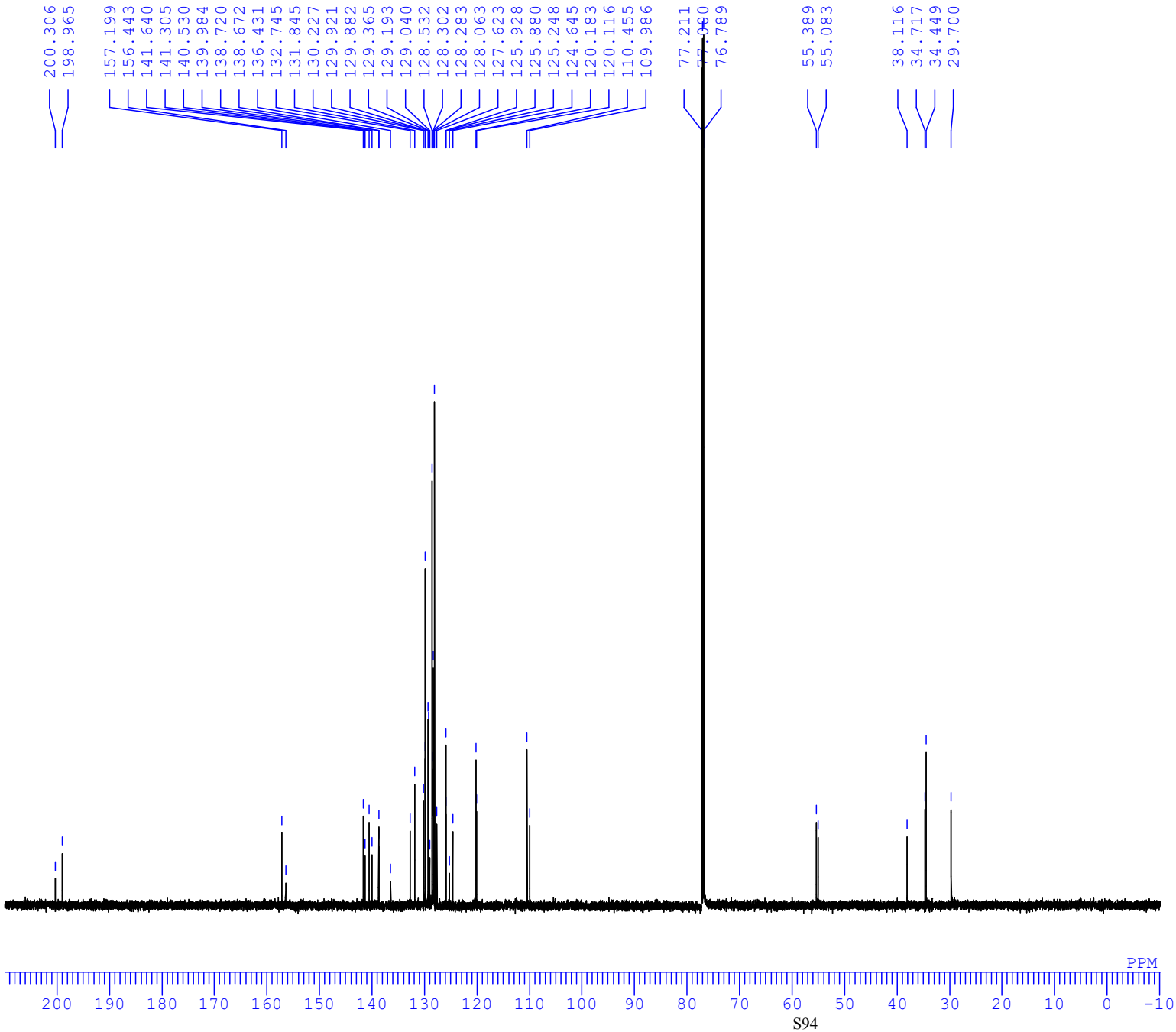
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

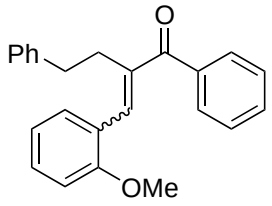




6

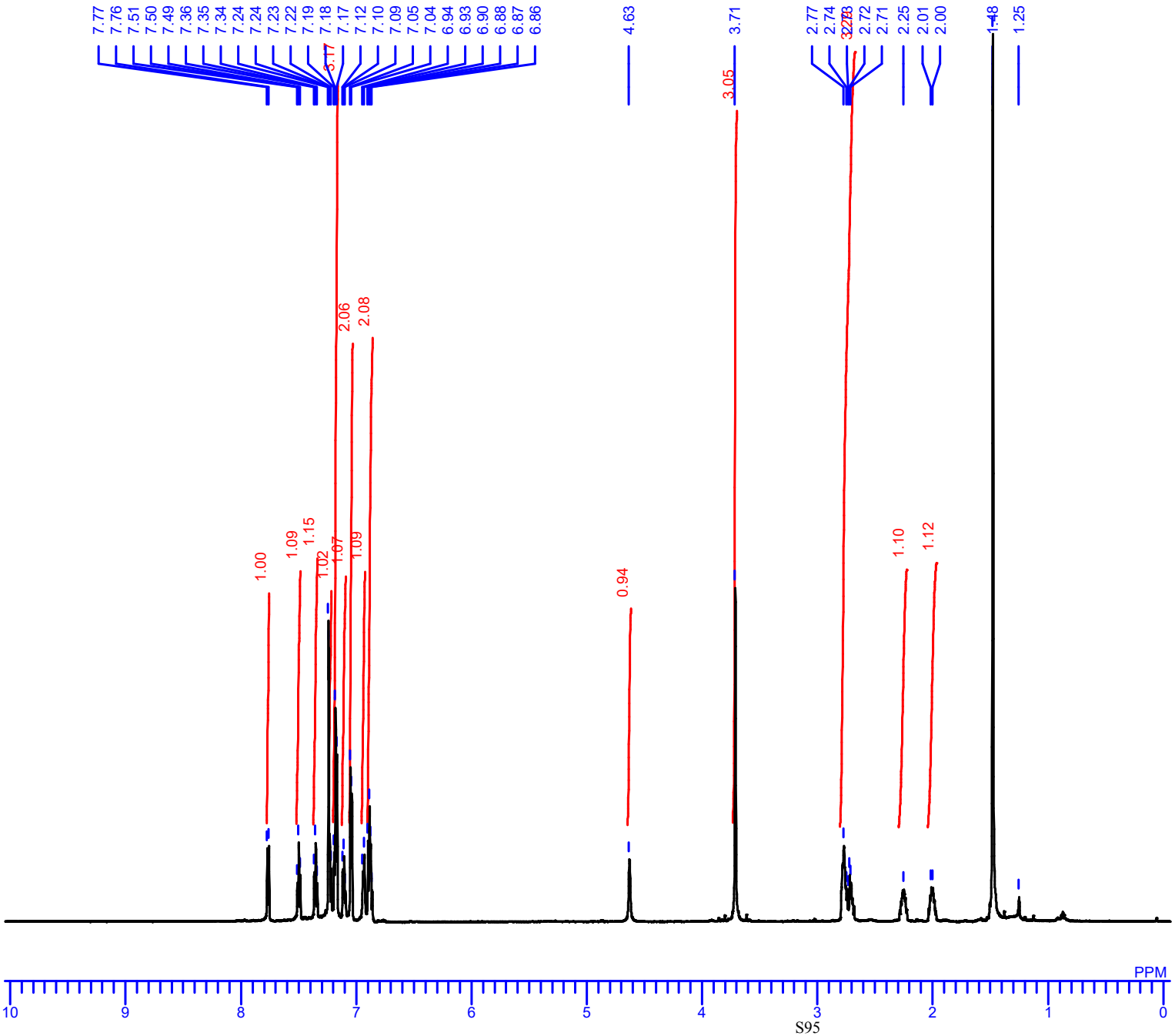
^{1}H NMR
(600 MHz, $CDCl_3$)

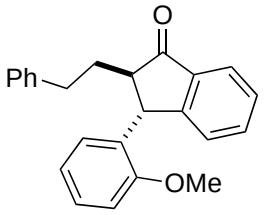




6

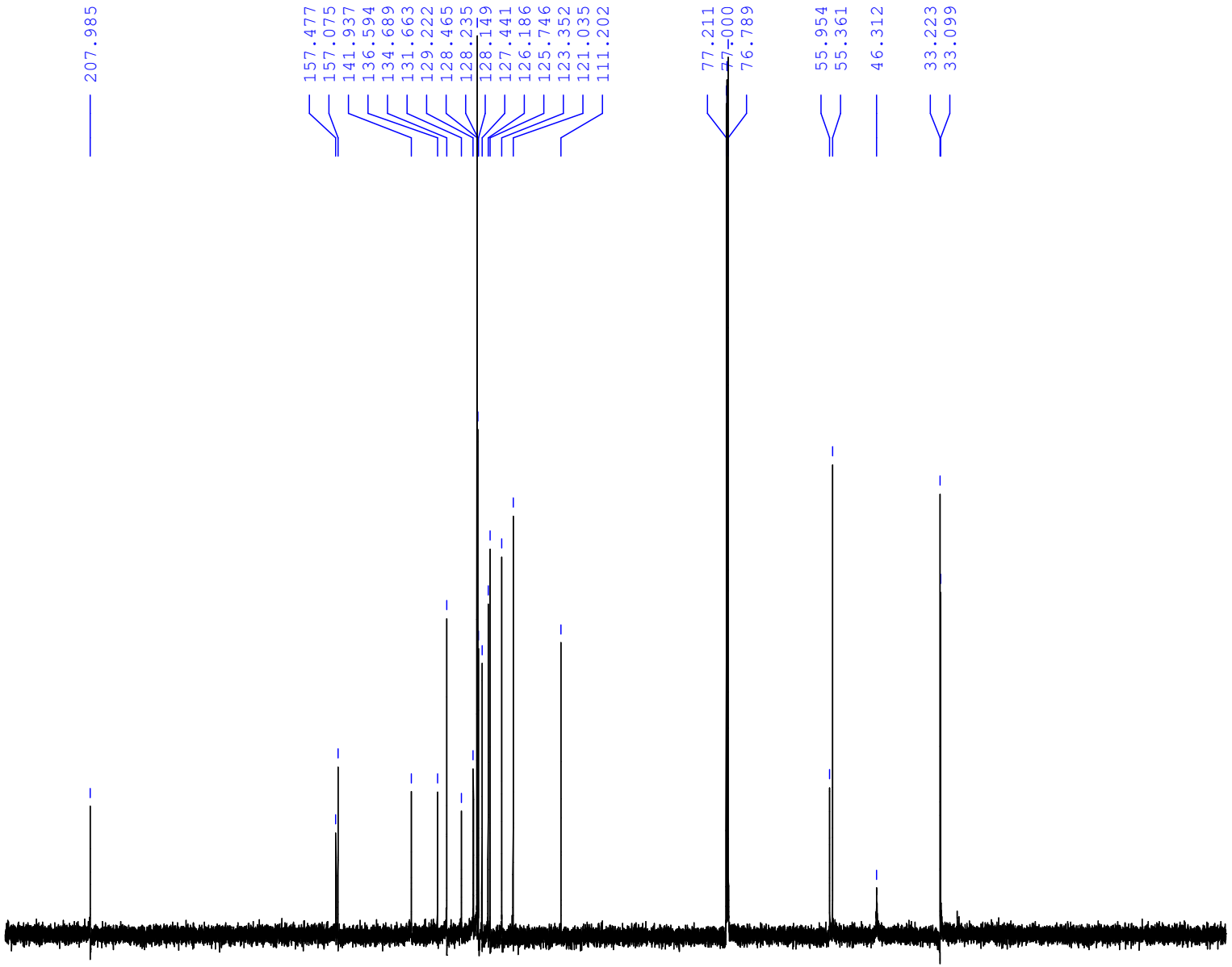
$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)

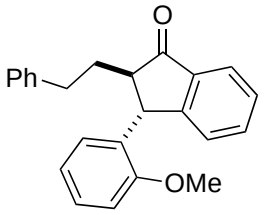




7

^{1}H NMR
(600 MHz, $CDCl_3$)





7

$^{13}C\{^{1}H\}$ NMR
(150 MHz, $CDCl_3$)