Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information

A PMMA-based heterogeneous photocatalyst for visible light-promoted (4+2) cycloaddition

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Characterization of Photocatalyst cPMMA-BTPh₂

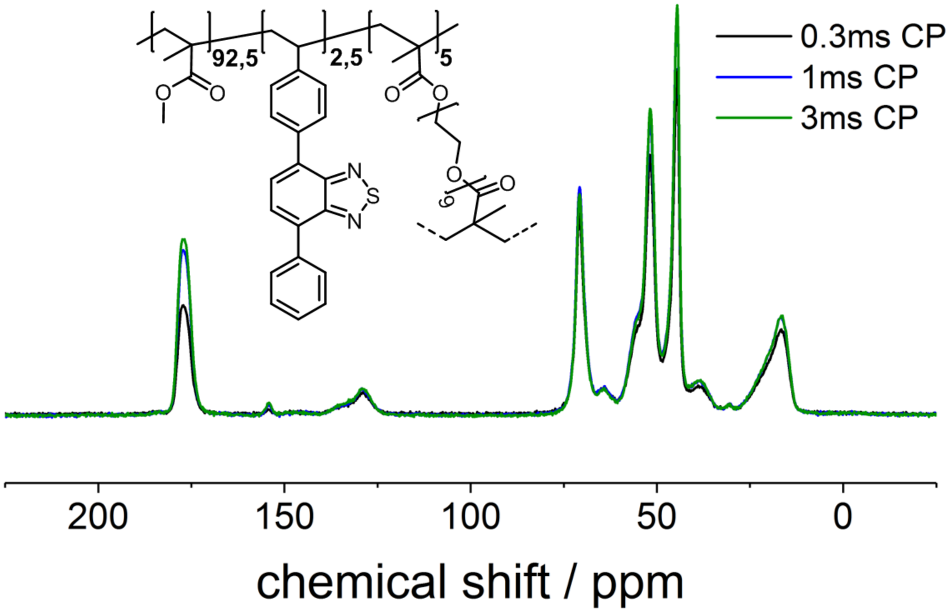


Fig. S1. ^{13}C CP-MAS NMR spectrum for different contact times (0.3 ms, 1 ms, 3 ms) of cPMMA-BTPh$_2$.

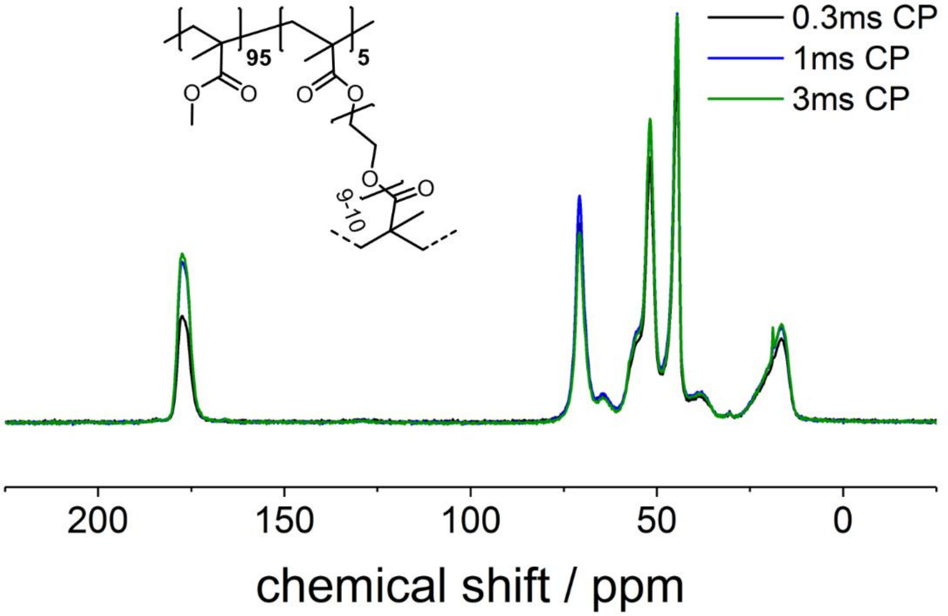


Fig. S2. ^{13}C CP-MAS NMR spectrum for different contact times (0.3 ms, 1 ms, 3 ms) of cPMMA.

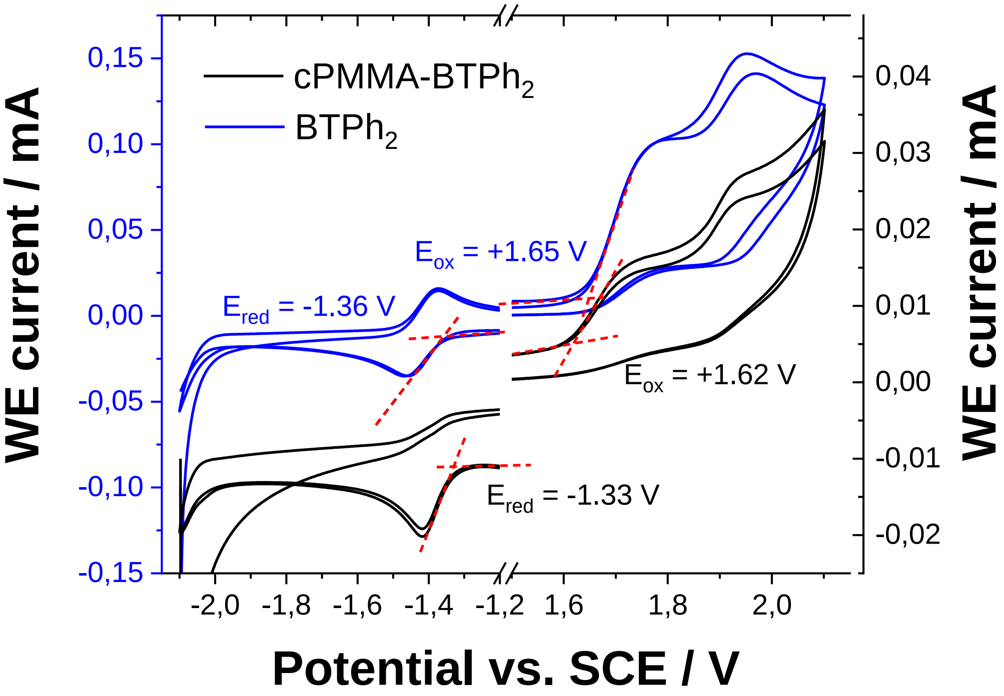
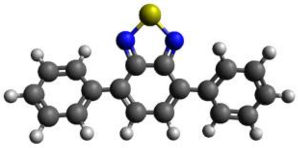
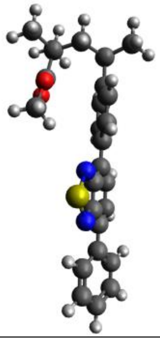
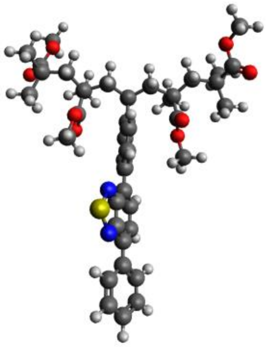


Fig. S3. Cyclic voltammetry of cPMMA-BTPh$_2$ and BTPh$_2$ with a scan rate of 100 mV/s in CH_3CN.

Table S1. DFT and TDDFT-calculated electrooptical parameters of the catalysts (rB3LYP, 6-31+g(d))

	HOMO *vs.* SCE	LUMO *vs.* SCE	Band Gap (electr.)	λ_{max} (calc.)	Band Gap (optic. calc. from λ_{max})
$BTPh_2$ 	+1.64 V	-1.70 V	2.93 eV	480 nm	2.58 eV
cPMMA-$BTPh_2$ analogue 1 	+1.36 V	-1.51 V	2.87 eV	496 nm	2.50 eV
cPMMA-$BTPh_2$ analogue 2 	+1.40 V	-1.47 V	2.87 eV	496 nm	2.50 eV

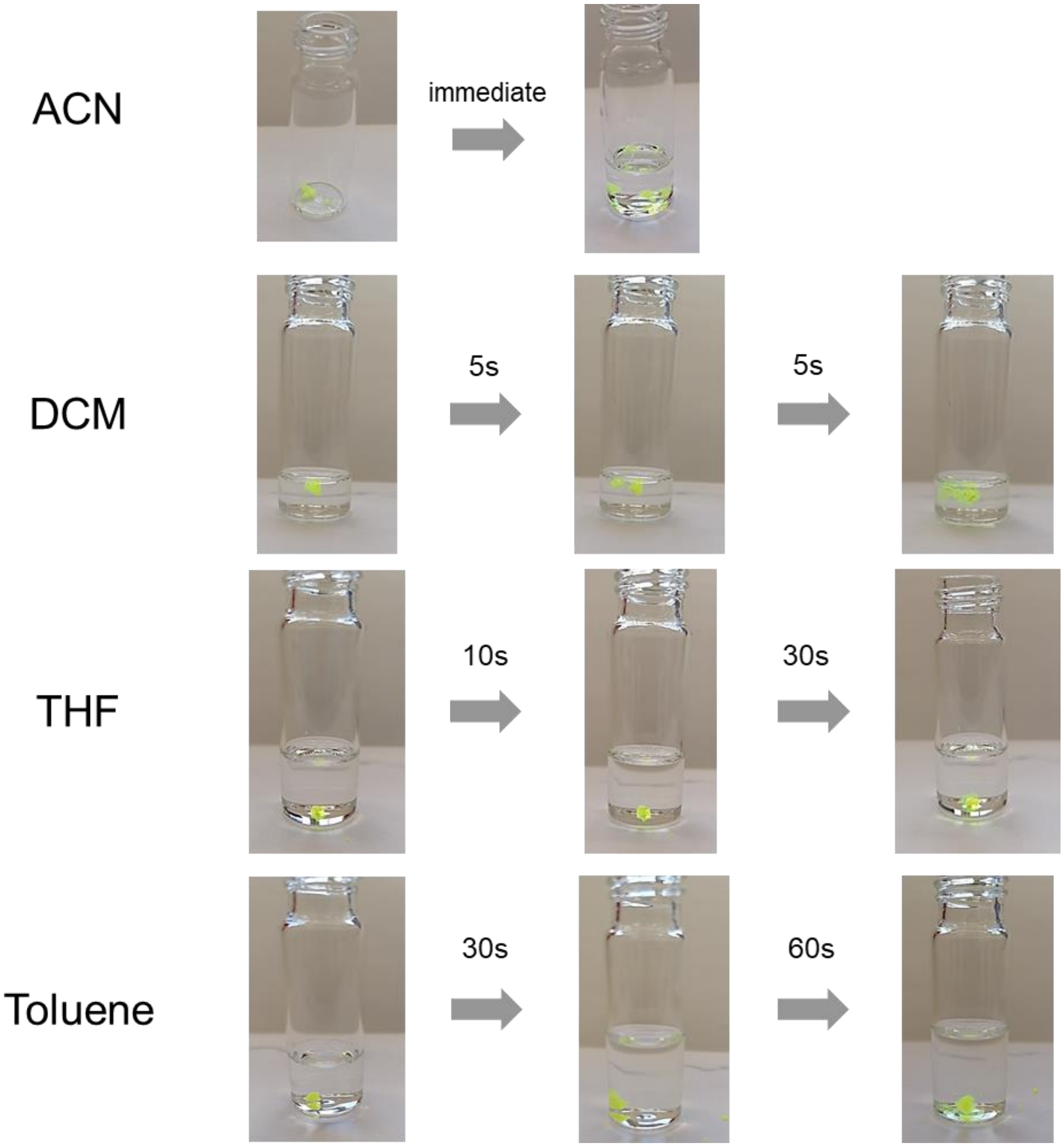


Fig. S4. Swelling experiments in acetonitrile, dichloromethane, THF and toluene. The pictures were taken after the times indicated.

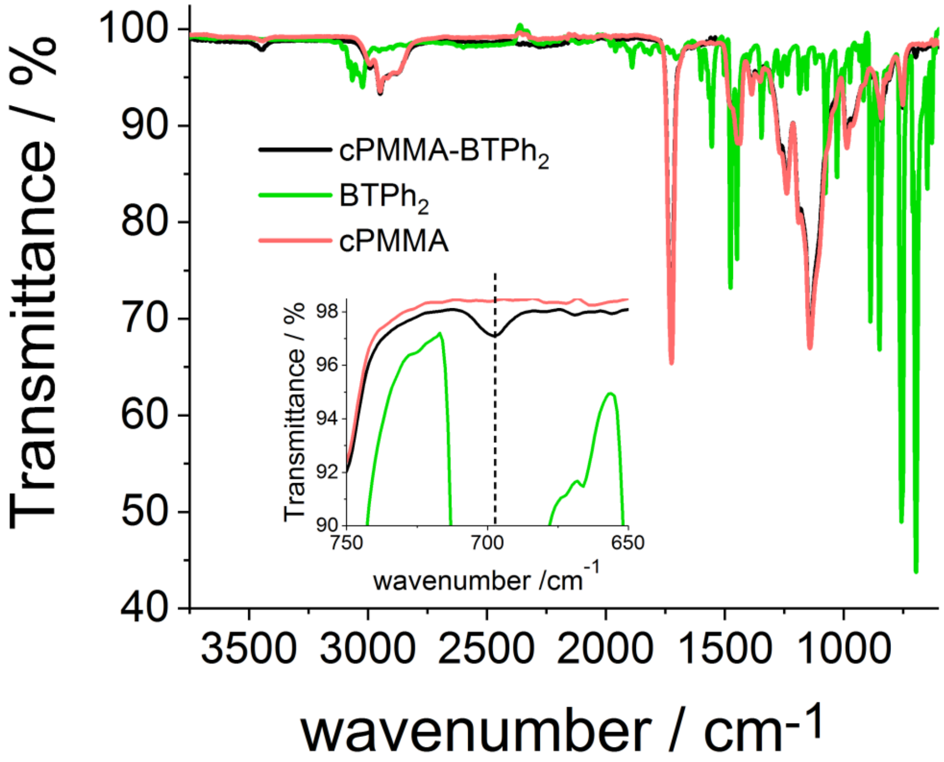


Fig. S5. Comparison of Fourier transform infrared (FTIR) spectra of cPMMA-BTPh$_2$, cPMMA and BTPh$_2$. cPMMA and cPMMA-BTPh$_2$ differ only slightly at 696 cm^{-1}, the major resonance of BTPh$_2$.

Current prices for used chemicals:

MMA – 18€ / 500g (Alfa)

Poly(ethylene glycol) dimethacrylate – 67,80€ / 250g (Sigma)

4,7-Dibromo-2,1,3-benzothiadiazole – 27,30 € / 1g (Alfa Aesar)

Phenylboronic acid – 37€ / 10g (Alfa Aesar)

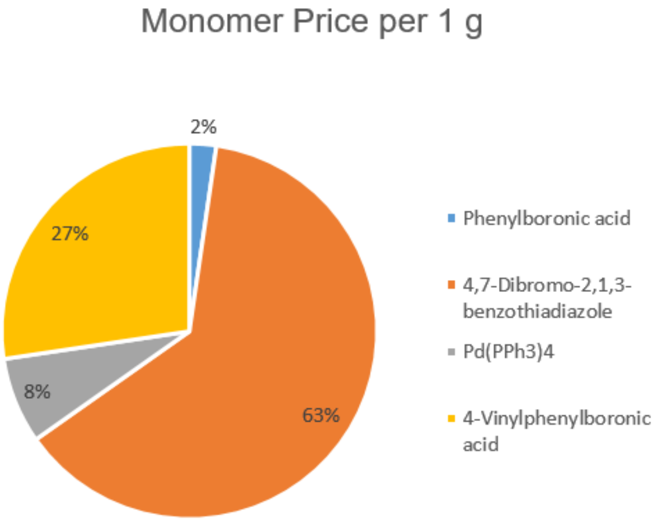
4-Vinylphenylboronic acid – 95€ / 5g (TCI)

$Pd(PPh_3)_4$ – 105€ / 5g (TCI)

AIBN – 42€ / 25g (Sigma)

Cost of material for cPMMA-$BTPh_2$ (solvents not included):

Monomer Synthesis: Phenylboronic acid (509 mg), 4,7-Dibromo-2,1,3-benzothiadiazole (1840 mg), $Pd(PPh_3)_4$ (283 mg), 4-Vinylphenylboronic acid (1150 mg) = 79,91€ for 950 mg of Monomer = 84,11 €/g

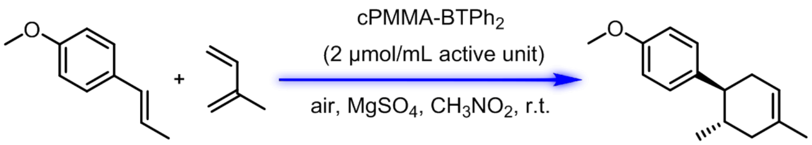


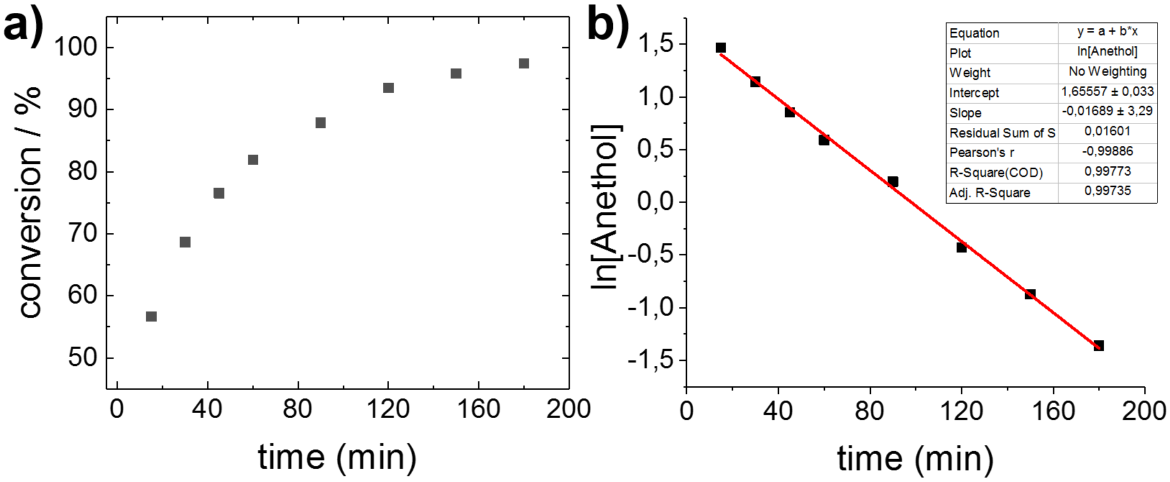
Polymer Synthesis: MMA (294 mg), PEGDMA (93 mg), AIBN (4 mg), Photocatalytic unit (25,5 mg) = 2,07€ for 300 mg of Polymer = 6,92 € / g

Fig. S6. Material cost estimation for the synthesis of 1g of cPMMA-$BTPh_2$

Photocatalysis

Part A: Kinetic Study





Equation	y = a + b*x
Plot	ln[Anethol]
Weight	No Weighting
Intercept	1,65557 ± 0,033
Slope	-0,01689 ± 3,29
Residual Sum of S	0,01601
Pearson's r	-0,99886
R-Square(COD)	0,99773
Adj. R-Square	0,99735

Fig. S7. Monitoring experiment of the photocatalytic Diels-Alder reaction. (a) Reaction conversion and (b) logarithmic plot of the concentration of *trans*-anethole during the reaction. The initial concentration of *trans*-anethole was 0.1 M.

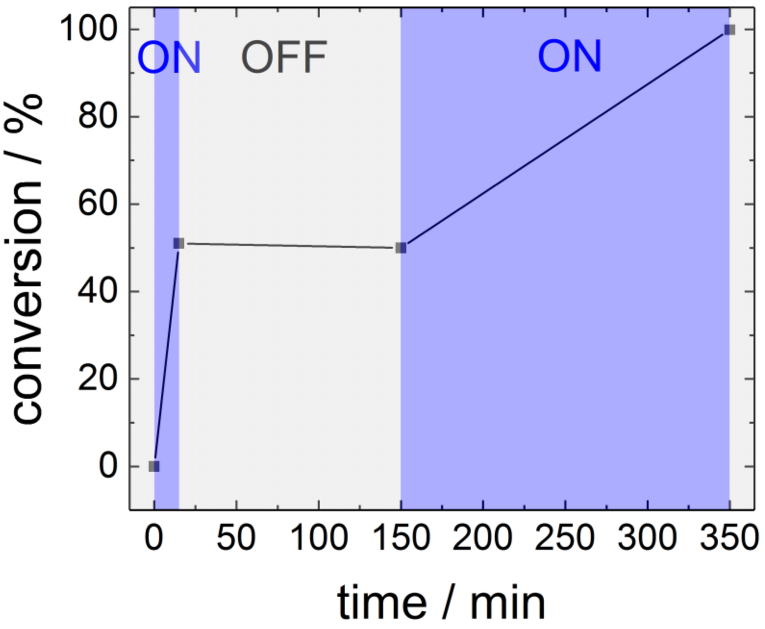


Fig. S8. Reaction conversion change during the light on and off experiment.

Part B: Apparent Quantum Yield Calculation

$$\Phi_{\mathrm{AQY}} = \frac{\text{number of product molecules formed}}{\text{number of incident photons}}$$

$$= \frac{\mathrm{N_e}}{\mathrm{N_p}}$$

$$= \frac{\mathrm{n} * \mathrm{N_A}}{\left(\frac{\mathrm{P} * \mathrm{t}}{\frac{\mathrm{h} * \mathrm{c}}{\lambda}}\right)}$$

$$= \frac{\mathrm{n} * \mathrm{N_A} * \mathrm{h} * \mathrm{c}}{\mathrm{P} * \mathrm{t} * \lambda}$$

$$= \frac{0.125 * 10^{-3}\mathrm{mol} * 6.023 * 10^{23}\mathrm{mol}^{-1} * 6.63 * 10^{-34}\,\frac{\mathrm{m^2kg}}{\mathrm{s}} \times 3 * 10^{8}\,\frac{\mathrm{m}}{\mathrm{s}}}{\left(0.8\mathrm{cm} * 2.3 * 0.065\,\frac{\mathrm{W}}{\mathrm{cm}^2}\right) \times 240 * 60\mathrm{s} \times 460 * 10^{-9}\ \mathrm{m}}$$

$$= 0.0227 = 2.27\%$$

Part C: Recycle Experiment

The recycle experiment was conducted similar to the general procedure. Specifically, a dried vial with a magnetic stir bar was charged with *trans*-anethole (35.6 mg, 0.24 mmol), isoprene (240 µL, 2.4 mmol), cPMMA-BTPh$_2$ (2.4 mg) and nitromethane (2.4 mL). After 4 h of reaction, the conversion was analyzed by GC-MS. The reaction mixture was centrifuged at 1000 rpm for 2 min and the supernatant was replaced by CH_3NO_2. Then, another equivalent of *trans*-anethole (35.6 mg, 0.24 mmol) and isoprene (240 µL, 2.4 mmol) were added into the mixture and the solution was further irradiated under blue light. The catalyst was recycled 4 times.

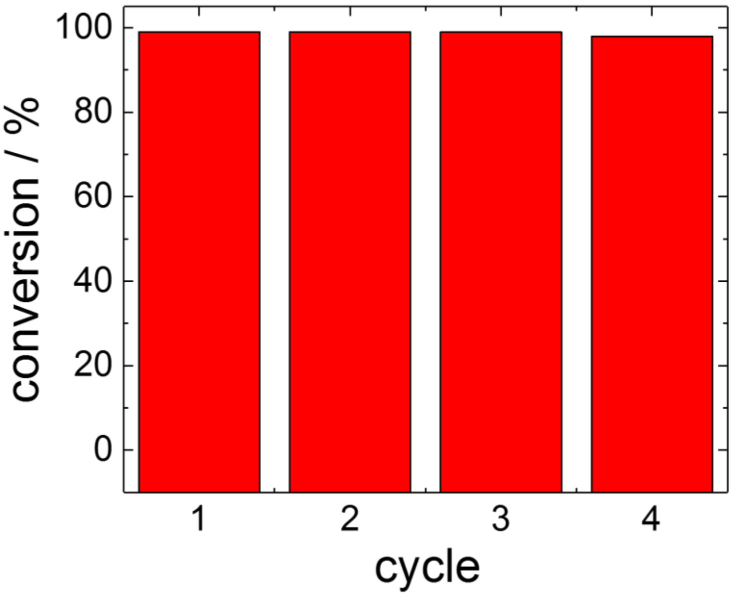


Fig. S9. Repeating experiment of the photocatalytic Diels-Alder reaction with cPMMA-BTPh$_2$.

In the same way, BTPh$_2$ was tested. Without purification process, another equivalent of *trans*-anethol a dried vial with a magnetic stir bar was charged with *trans*-anethole (35.6 mg, 0.24 mmol), isoprene (240 µL, 2.4 mmol), BTPh$_2$ (0.6 mg, 2.0 µmol) and nitromethane (2.4 mL). After 2 h of reaction, the conversion was analyzed by GC-MS. Another equivalent of *trans*-anethole (35.6 mg, 0.24 mmol) and isoprene (240 ul, 2.4 mmol) were added into the mixture and the solution was put under blue light irradiation. The procedure was repeated 3 times.

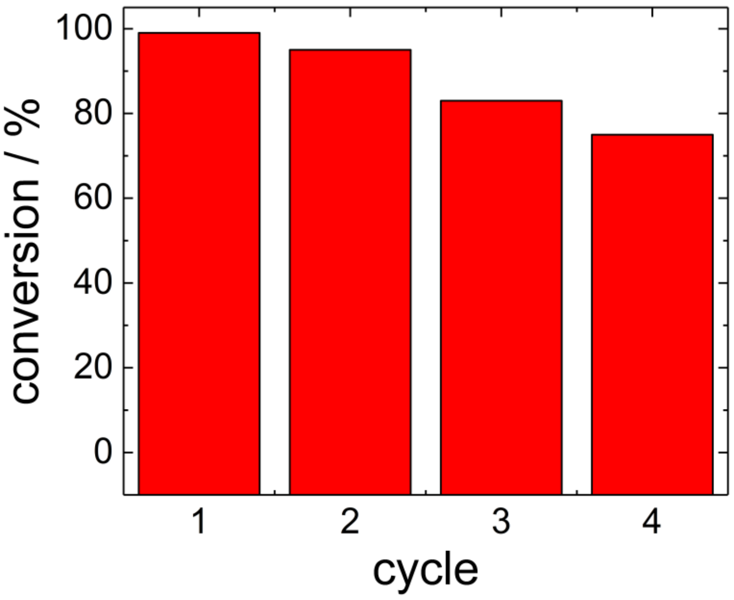


Fig. S10. Repeating experiment of the photocatalytic Diels-Alder reaction with $BTPh_2$.

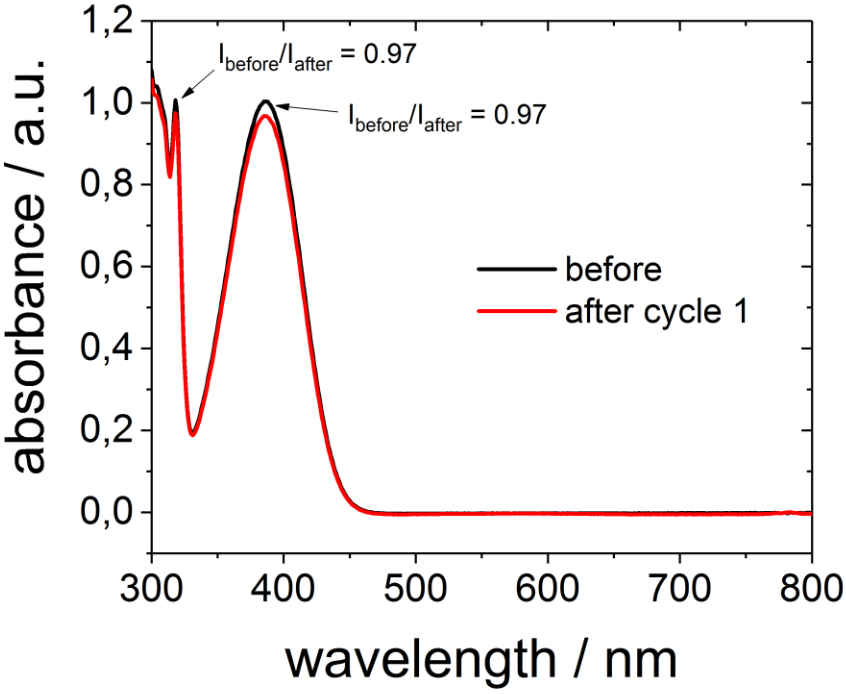


Fig. S11. UV-Vis spectra of cPMMA-$BTPh_2$ before and after the photocatalytic Diels-Alder reaction. The maximum intensities on both peaks show a similar decrease indicating this to be a concentration-related effect.

Part D: Solubility Experiments

In order to prove the heterogeneity of the cPMMA-BTPh$_2$ photocatalyst the catalyst was irradiated with blue light while being stirred in CH_3NO_2 (I), $CDCl_3$ (II) and d_8-THF (III) respectively. For sample I, after 4h the mixture was filtered through a syringe filter. The solution was centrifuged for 10min at 10000 rpm and the supernatant was evaporated to dryness on the rotary evaporator. $CDCl_3$ was added to the round-bottom flask and taken for ^{1}H-NMR analysis. For the setups II and III the mixture was filtered through a syringe filter, centrifuged as above and the supernatant directly taken for ^{1}H-NMR.

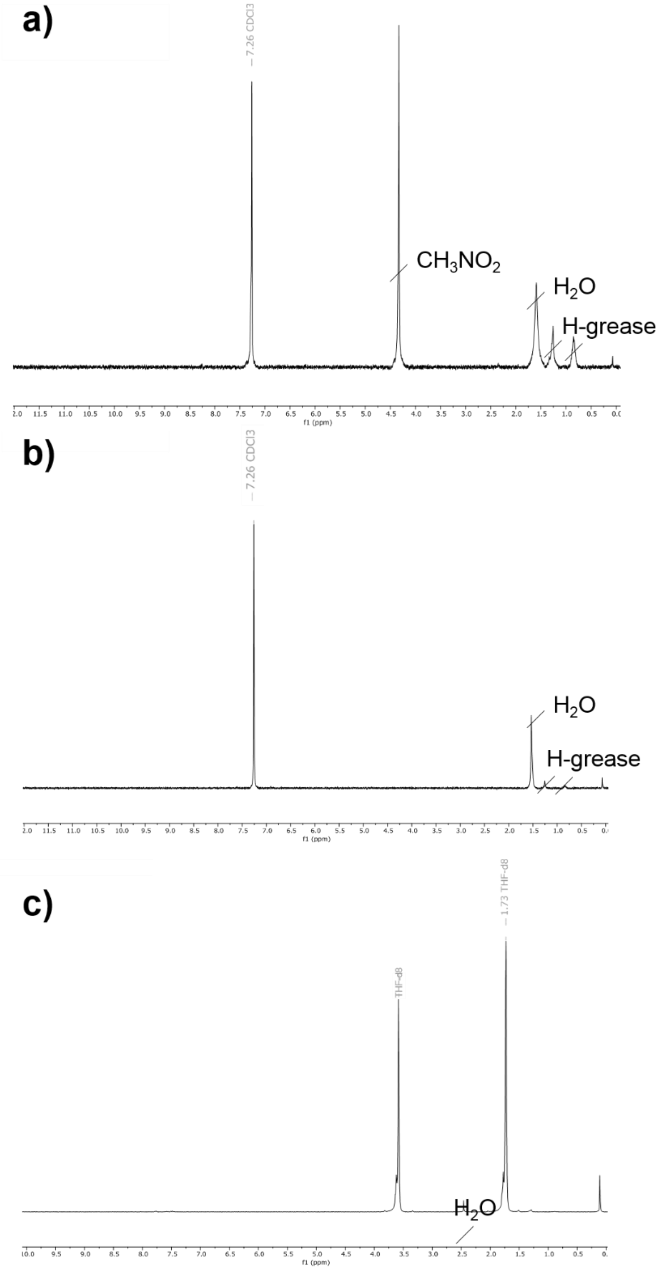


Fig. S12. ^{1}H-NMR spectra of a) experiment I b) experiment II and c) experiment III

Part E: Transient Absorption Spectra

Transient absorption spectra were recorded to further investigate the concrete electron transfer process between the photocatalyst $BTPh_2$ and substrates in the Diels-Alder reaction.

The signal peaking at 660 nm represents the photo-induced absorption (PIA) of $BTPh_2$ in its excited state (Fig. S11). The lifetime of the singlet excited state of $BTPh_2$ in a N_2-purged solution was determined to be 11.1 ns, which is consistent to that obtained from the time-resolved photoluminescence spectroscopy (TRPL). However, the addition of O_2 did not affect the PIA of $BTPh_2$ (Fig. S12). The possible reason might be that the phosphorescence signal for active oxygen species such as $^1O_2$ normally localized on 1270 nm was beyond the detection limit of the transient absorption measurement. In comparison, the PIA curves of $BTPh_2$ under the addition of *trans*-anethole remained first the similar shape as that of pure $BTPh_2$ within the initial time from 1 ns to 3.1 ns, and then a new absorption peak at 610 nm appeared after 9.9 ns pulse irradiation (Fig. S13). This observation indicates that the formation of the radical cation of *trans*-anethole began to occur after 9.9 ns, which is similar as previous report,[1] thus supporting the proposed hole initiation mechanism. By increasing the concentration of *trans*-anethole, the absorption intensity of the mixture decayed faster, demonstrating the active electron transfer from the substrate to the photo-generated holes of the photocatalyst (Fig. S14). The decay profiles of the TA were consistent with the ones of the TRPL (Fig. S16 and Table S2).

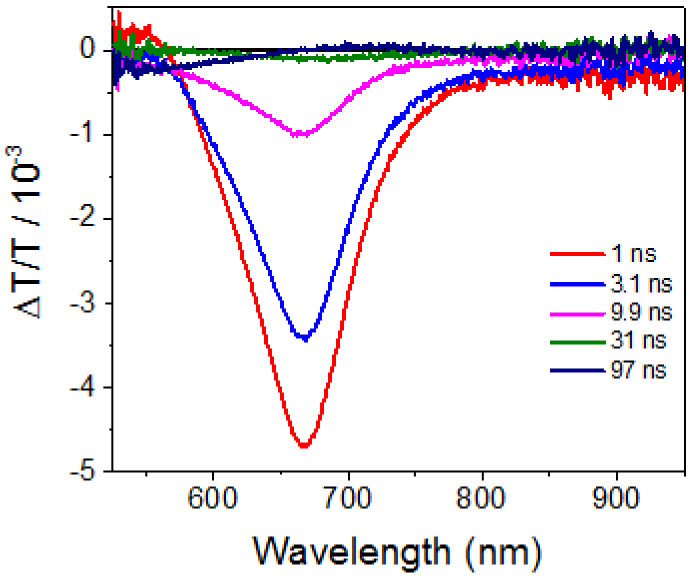


Fig. S13. Transient absorption spectra of $BTPh_2$ (20 mg/L in CH_3CN) under N_2 at different times. Excitation wavelength 355 nm.

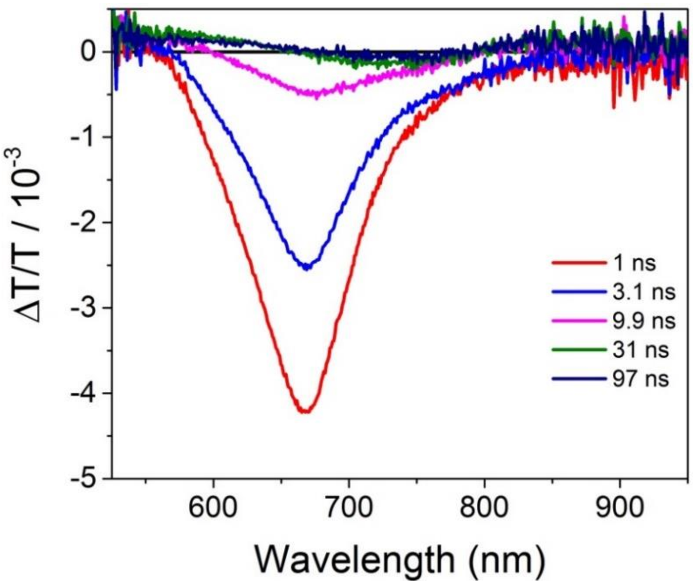


Fig. S14. Transient absorption spectra of $BTPh_2$ (20 mg/L in CH_3CN) under O_2 at different times. Excitation wavelength 355 nm.

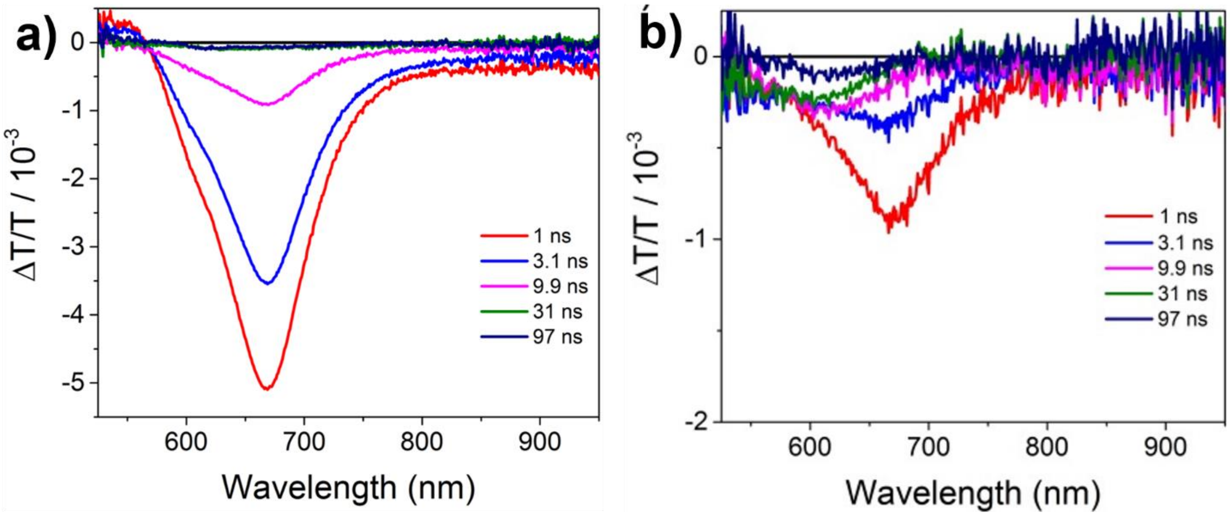


Fig. S15. Transient absorption spectra of $BTPh_2$ (20 mg/L) and *trans*-anethole (2 mM for a) and 20 mM for b)) under N_2 atmosphere in CH_3CN at different times. Excitation wavelength 355 nm.

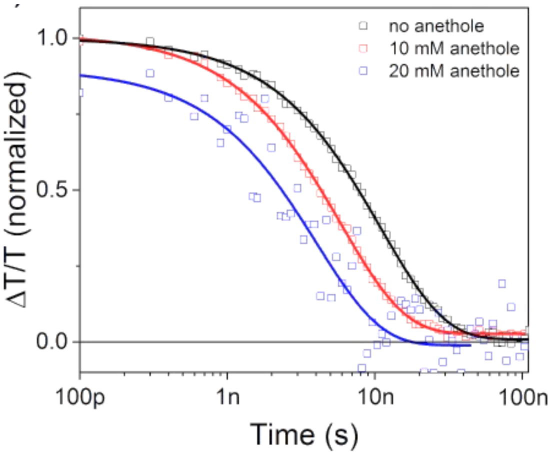


Fig. S16. Time profiles of the absorbance decay at 675 nm of pure $BTPh_2$ (black), with 10 mM trans-anethole (red) and 20 mM trans-anethole (blue) in CH_3CN.

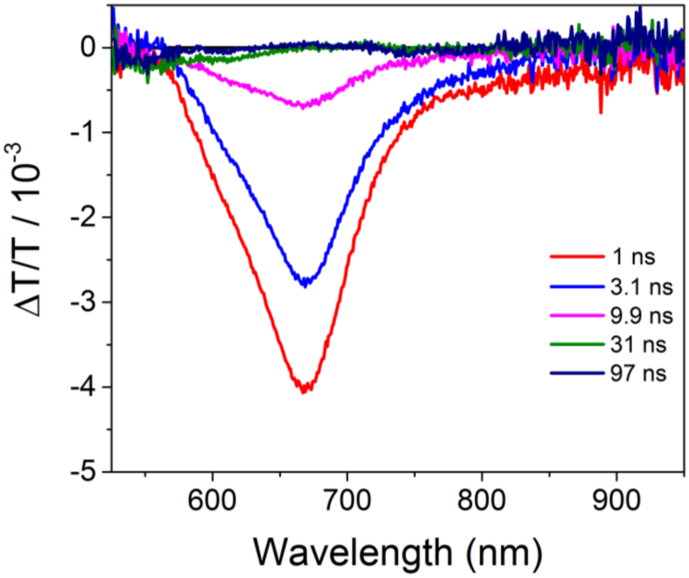


Fig. S17. Transient absorption spectra of $BTPh_2$ (20 mg/L) and *trans*-anethole (2 mM) under O_2 atmosphere in CH_3CN at different times. Excitation wavelength 355 nm.

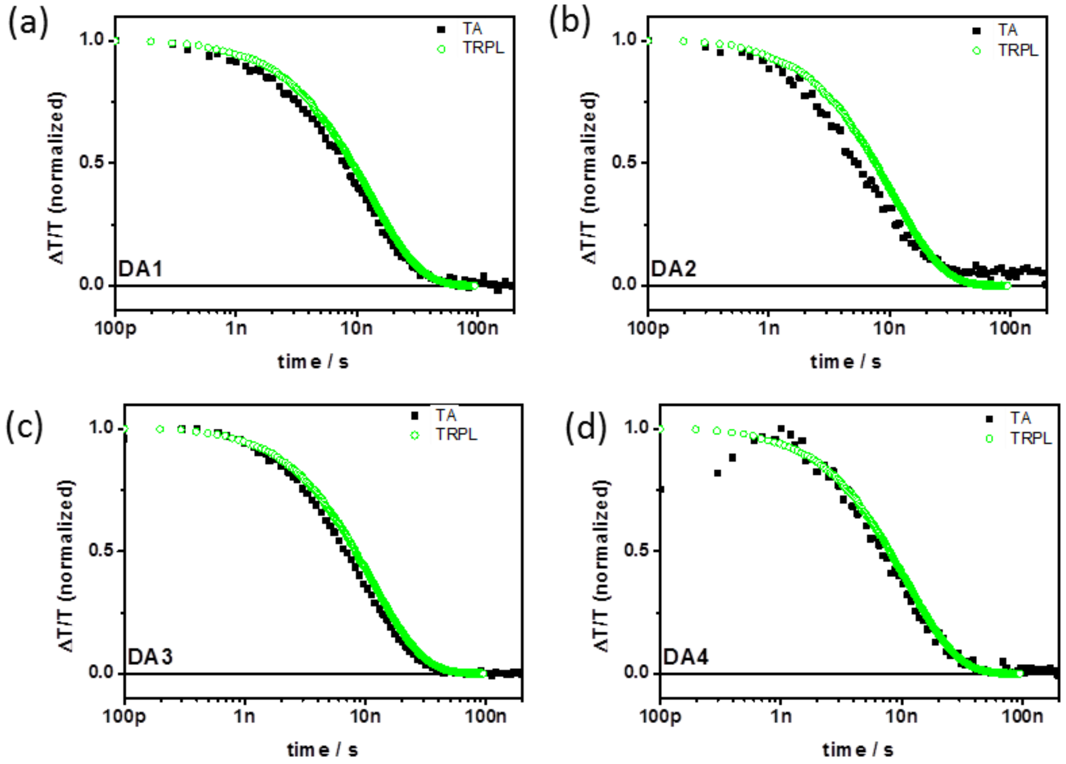
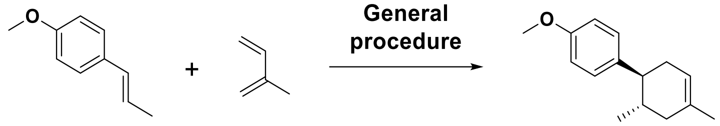


Fig. S18. Comparison of decay profiles of transient absorption (TA) at 660 – 690 nm and time-resolved photoluminescence (TRPL) at 480-520 nm for the Diels-Alder reaction. (a) pure $BTPh_2$ (20 mg/L in CH_3CN) under N_2, (b) pure $BTPh_2$ (20 mg/L in CH_3CN) under O_2, (c) $BTPh_2$ (20 mg/L) and *trans*-anethole (2 mM) under N_2 atmosphere in CH_3CN, (d) $BTPh_2$ (20 mg/L) and *trans*-anethole (2 mM) under O_2 atmosphere in CH_3CN.

Table S2. Excited state life time of the measured mixtures

Entry	Sample name	Fluorescence life time (ns)	Transient life time (ns)
1	$BTPh_2$ (CH_3CN)	12.9	11.1
2	$BTPh_2$ + O_2	10.7	7.5
3	$BTPh_2$ + anethole	11.5	9.1
4	$BTPh_2$ + anethole + O_2	11.2	9.4

Part F: Compound Characterization

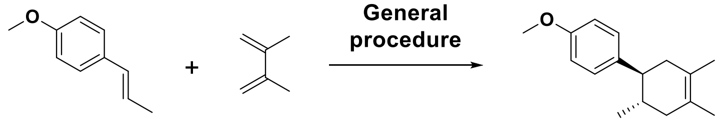


(1S,2S)-4'-methoxy-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl: According to the general procedure, a dried vial with a magnetic stir bar was charged with *trans*-anethole (35.6 mg, 0.24 mmol), isoprene (240 µl, 2.4 mmol), catalyst (2.4 mg), $MgSO_4$ (15mg) and nitromethane (2.4 mL). After the reaction was finished, the mixture was worked up according to the protocol and purified by chromatography on silica with hexane/ethyl acetate (12/1) as the elution to afford the pure cycloadduct as clear oil.

R_f (hexane/ethyl acetate 12/1): 0.76

^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.99 (d, J=9 Hz, 2H), 6.75 (d, J=9 Hz, 2H), 5.36 (bs, 1H), 3.71 (s, 3H), 2.21 (m, 1H), 2.11 (m, 1H), 2.04 (m, 1H), 1.98 (m, 1H), 1.81 (m, 1H), 1.71 (m, 1H), 1.61 (s, 3H), 0.62 (d, J=6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.8, 138.2, 133.8, 128.5, 120.9, 113.7, 55.2, 47.0, 39.9, 35.3, 34.0, 23.4, 20.2.

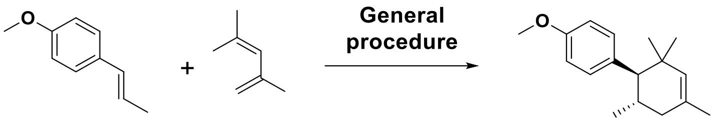


(1S,2S)-4'-methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl: According to the general procedure, a dried vial with a magnetic stir bar was charged with *trans*-anethole (35.6 mg, 0.24 mmol), 2,3-dimethylbuta-1,3-diene (81.5 µL, 0.72 mmol), catalyst (2.4 mg), $MgSO_4$ (15mg) and nitromethane (2.4 mL). After the reaction was finished, the mixture was worked up according to the protocol and purified by chromatography on silica with hexane/dichloromethane (1/1) as the elution to afford the pure cycloadduct as clear oil.

R_f (hexane/dichloromethane 1/1): 0.81

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.02 (d, J=9 Hz, 2H), 6.78 (d, J=12 Hz, 2H), 3.71 (s, 3H), 2.33 (td, J=6, 12 Hz, 1H), 2.07 (m, 1H), 1.98 (m, 2H), 1.77 (m, 2H), 1.56 (s, 3H), 1.54 (s, 3H), 0.63 (d, J=9 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.6, 138.2, 128.5, 125.5, 125.4, 113.7, 55.2, 47.8, 41.9, 41.7, 34.3, 20.1, 18.8, 18.7.

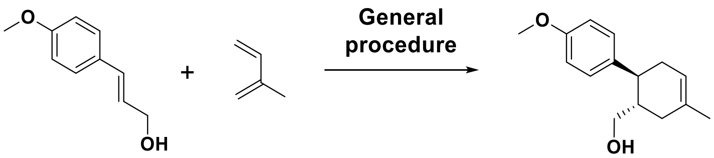


(1R,2S)-4'-methoxy-2,4,6,6-tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl: According to the general procedure, a dried vial with a magnetic stir bar was charged with *trans*-anethole (35.6 mg, 0.24 mmol), 2,4-dimethylpenta-1,3-diene (93.1 µL, 0.72 mmol), catalyst (2.4 mg), $MgSO_4$ (15mg) and nitromethane (2.4 mL). After the reaction was finished, the mixture was worked up according to the protocol and purified by chromatography on silica with hexane/ethyl acetate (25/1) as the elution to afford the pure cycloadduct as clear oil.

R_f (hexane/ethyl acetate 25/1): 0.61

^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.97 (dd, J=6, 18 Hz, 2H), 6.76 (dd, J=9, 18 Hz, 2H), 5.12 (s, 1H), 3.72 (s, 3H), 2.11 (d, 9 Hz, 1H), 2.05 (m, 1H), 1.98 (m, 1H), 1.70 (m, 1H), 1.59 (s, 3H), 0.75 (s, 3H), 0.70 (s, 3H), 0.64 (d, J=6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.7, 133.3, 130.3, 129.3, 113.2, 112.2, 57.4, 56.1, 40.5, 36.3, 30.0, 28.8, 24.6, 23.3, 20.8.



((1S,2S)-4'-methoxy-4-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanol: According to the general procedure, a dried vial with a magnetic stir bar was charged with (E)-3-(4-methoxyphenyl)prop-2-en-1-ol (39.4 mg, 0.24 mmol), isoprene (240 µL, 2.4 mmol), catalyst (2.4 mg), $MgSO_4$ (15mg) and nitromethane (2.4 mL). After the reaction was finished, the mixture was worked up according to the protocol and purified by chromatography on silica with hexane/ethyl acetate (4/1) as the elution to afford the pure cycloadduct as clear oil.

R_f (hexane/ethyl acetate 4/1): 0.56

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.06 (d, J=9 Hz, 2H), 6.78 (d, J=9 Hz, 2H), 5.37 (bs, 1H), 3.70 (s, 3H), 3.33 (dd, J=3, 9 Hz, 1H), 3.22 (dd, 6, 12 Hz, 1H), 2.45 (m, 1H), 2.14 (m, 1H), 2.12 (m, 1H), 2.03 (t, J=12 Hz, 1H), 1.93 (m, 1H), 1.90 (m, 1H), 1.64 (s, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz): δ 158.1, 137.0, 133.4, 128.4, 120.6, 114.1, 65.9, 55.2, 42.2, 41.5, 34.7, 33.9, 23.5.

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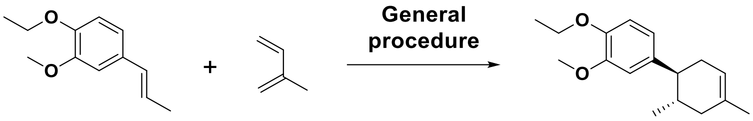
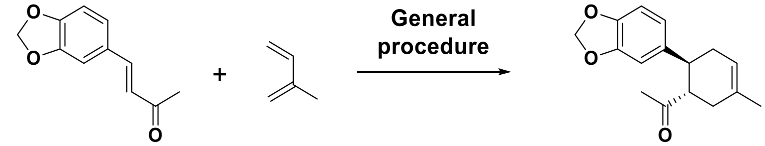


(1S,2S)-4'-ethoxy-3'-methoxy-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl: According to the general procedure, a dried vial with a magnetic stir bar was charged with (E)-1-ethoxy-2-methoxy-4-(prop-1-en-1-yl)benzene (48.1 mg, 0.25 mmol), isoprene (250 µL, 2.5 mmol), catalyst (2.4 mg), $MgSO_4$ (15mg) and nitromethane (2.4 mL). After the reaction was finished, the mixture was worked up according to the protocol and purified by chromatography on silica with hexane/ethyl acetate (12/1) as the elution to afford the pure cycloadduct as clear oil.

R_f (hexane/ethyl acetate 12/1): 0.46

^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.71 (m, 1H), 6.63 (m, 2H), 5.37 (bs, 1H), 4.02 (m, 2H), 3.78 (s, 3H), 2.21 (m, 1H), 2.14 (m, 1H), 2.09 (m, 1H), 1.99 (m, 1H), 1.83 (m, 1H), 1.72 (m, 1H), 1.62 (s, 3H), 1.38 (t, J=6 Hz, 3H), 0.66 (d, J=6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.1, 146.4, 138.8, 133.8, 120.8, 119.6, 112.6, 111.0, 64.3, 55.9, 47.4, 39.8, 35.2, 34.0, 23.4, 20.2, 14.9.

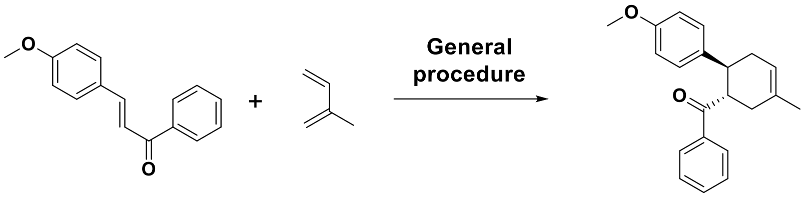


1-((1S,6S)-6-(benzo[d][1,3]dioxol-5-yl)-3-methylcyclohex-3-en-1-yl)ethan-1-one: According to the general procedure, a dried vial with a magnetic stir bar was charged with (E)-4-(benzo[d][1,3]dioxol-5-yl)but-3-en-2-one (45.6 mg, 0.24 mmol), isoprene (240 µL, 2.4 mmol), catalyst (2.4 mg), $MgSO_4$ (15mg) and nitromethane (2.4 mL). After the reaction was finished, the mixture was worked up according to the protocol and purified by chromatography on silica with hexane/ethyl acetate (10/1) as the elution to afford the pure cycloadduct as clear oil.

R_f (hexane/ethyl acetate 10/1): 0.36

^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.72 (d, J=9 Hz, 1H), 6.70 (d, J=1.6 Hz, 1H), 6.67 (dd, J= 3, 9 Hz, 1H), 5.93 (s, 2H), 5.48 (m, 1H), 2.99 (dt, J=5.3, 10.3 Hz, 1H), 2.87 (dt, J=5.4, 11 Hz, 1H), 2.31 (m, 1H), 2.26 (m, 1H), 2.17 (m, 1H), 2.07 (m, 1H), 1.90 (s, 3H), 1.73 (s, 3H);

^{13}C NMR (CDCl$_3$, 75 MHz): δ 212.0, 147.7, 146.1, 138.0, 132.1, 120.6, 120.5, 108.3, 107.7, 100.9, 53.7, 42.5, 34.2, 33.3, 29.8, 23.2.

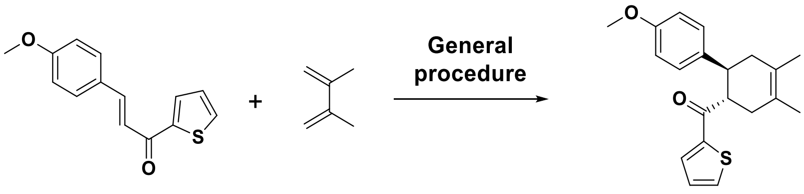


((1S,2S)-4'-methoxy-4-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone: According to the general procedure, a dried vial with a magnetic stir bar was charged with (E)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (57.2 mg, 0.24 mmol), isoprene (240 µL, 2.4 mmol), catalyst (2.4 mg), $MgSO_4$ (15mg) and nitromethane (2.4 mL). After the reaction was finished, the mixture was worked up according to the protocol and purified by chromatography on silica with hexane/dichloromethane (1/1) as the elution to afford the pure cycloadduct as clear oil.

R_f (hexane/dichloromethane 1/1): 0.28

^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.84 (d, J=7.4 Hz, 2H), 7.50 (t, J=6.8 Hz, 1H), 7.39 (t, J=7.5 Hz, 2H), 7.13 (d, J=8.5 Hz, 2H), 6.72 (d, J=8.4 Hz, 2H), 5.56 (bs, 1H), 3.98 (m, 1H), 3.71(s, 3H), 3.22 (m, 1H), 2.34 (m, 4H), 1.74 (s, 3H);

^{13}C NMR (CDCl$_3$, 75 MHz): δ 203.8, 157.8, 137.4, 136.5, 132.7, 132.5, 128.41, 128.38, 128.0, 121.0, 113.7, 55.1, 47.4, 41.6, 35.2, 34.2, 23.2.

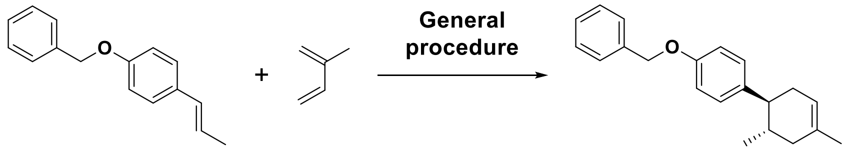


((1S,2S)-4'-methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)(thiophen-2-yl)methanone: According to the general procedure, a dried vial with a magnetic stir bar was charged with (E)-3-(4-methoxyphenyl)-1-(thiophen-2-yl)prop-2-en-1-one (58.6 mg, 0.24 mmol), 2,3-dimethylbuta-1,3-diene (271.6 µL, 2.4 mmol), catalyst (2.4 mg), $MgSO_4$ (15mg) and nitromethane (2.4 mL). After the reaction was finished, the mixture was worked up according to the protocol and purified by chromatography on silica with hexane/ethyl acetate (4/1) as the elution to afford the pure cycloadduct as clear oil.

R_f (hexane/ethyl acetate 4/1): 0.61

^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.54 (d, J=4.1 Hz, 2H), 7.10 (d, J=8.2 Hz, 2H), 7.00 (t, J=4.1 Hz, 1H), 6.79 (d, J=8.5 Hz, 2H), 4.77 (d, J=15 Hz, 2H), 3.92 (m, 2H), 3.72 (s, 3H), 2.41 (t, J=9.7 Hz 1H), 2.02 (t, J=10 Hz, 1H), 1.65 (s, 3H), 1.07 (s, 3H);

^{13}C NMR (CDCl$_3$, 75 MHz): δ 193.4, 158.2, 152.5, 143.8, 133.6, 131.9, 131.7, 129.3, 128.1, 113.5, 108.7, 55.2, 48.7, 45.0, 42.0, 35.0, 21.9, 18.8.

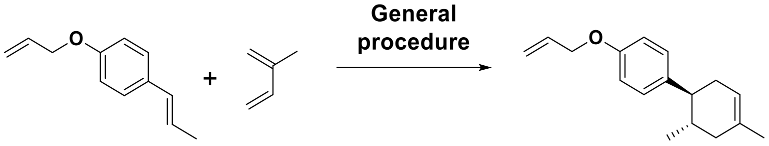


(1S,2S)-4'-(benzyloxy)-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl: According to the general procedure, a dried vial with a magnetic stir bar was charged with (E)-1-(benzyloxy)-4-(prop-1-en-1-yl)benzene (53.8 mg, 0.24 mmol), isoprene (240 µL, 2.4 mmol), catalyst (2.4 mg), MgSO$_4$ (15mg) and nitromethane (2.4 mL). After the reaction was finished, the mixture was worked up according to the protocol and purified by chromatography on silica with hexane/ethyl acetate (8/1) as the elution to afford the pure cycloadduct as clear oil.

R$_f$ (hexane/ethyl acetate 8/1): 0.37

^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.42 (m, 5H), 7.13 (d, 2H), 6.96 (d, 2H), 5.49 (s, 1H), 5.08 (s, 2H), 2.34 (m, 1H), 2.23 (m, 2H), 2.13 (m, 1H), 1.94 (m, 1H), 1.86 (m, 1H), 1.74 (s, 3H), 0.76 (d, 3H).

^{13}C NMR (CDCl$_3$, 75 MHz) δ 157.18, 138.56, 137.39, 133.87, 128.63, 127.97, 127.62, 121.01, 114.73, 70.12, 47.07, 39.94, 35.36, 34.04, 30.99, 23.50, 20.37.

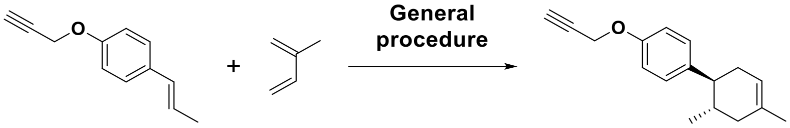


(1S,2S)-4'-(allyloxy)-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl: According to the general procedure, a dried vial with a magnetic stir bar was charged with (E)-1-(allyloxy)-4-(prop-1-en-1-yl)benzene (41.8 mg, 0.24 mmol), isoprene (240 µL, 2.4 mmol), catalyst (2.4 mg), MgSO$_4$ (15mg) and nitromethane (2.4 mL). After the reaction was finished, the mixture was worked up according to the protocol and purified by chromatography on silica with hexane/ethyl acetate (8/1) as the elution to afford the pure cycloadduct as clear oil.

R$_f$ (hexane/ethyl acetate 8/1): 0.32

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.11 (d, 2H), 6.89 (d, 2H), 6.10 (m, 1H), 5.44 (d, 2H), 5.30 (d, 2H), 4.55 (d, 2H), 2.33 (m, 1H), 2.22 (m, 2H), 2.12 (m, 1H), 1.91 (m, 1H), 1.85 (m, 1H), 1.73 (s, 3H), 0.74 (d, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 156.88, 138.37, 133.64, 128.51, 120.96, 117.45, 114.56, 68.85, 47.00, 39.89, 35.29, 34.00, 30.91, 23.43, 20.28.



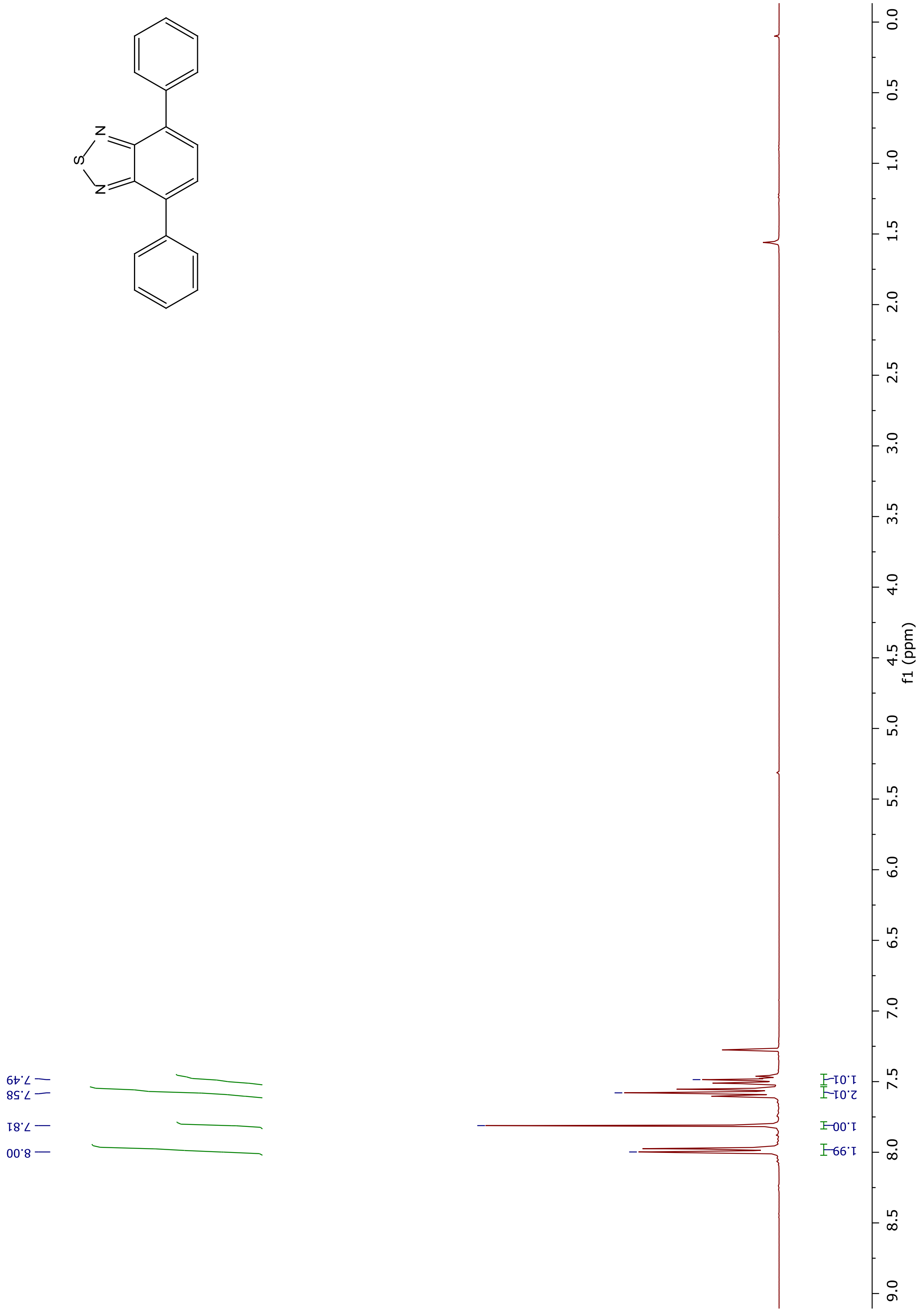
(1S,2S)-2,4-dimethyl-4'-(prop-2-yn-1-yloxy)-1,2,3,6-tetrahydro-1,1'-biphenyl: According to the general procedure, a dried vial with a magnetic stir bar was charged with (E)-1-(prop-1-en-1-yl)-4-(prop-2-yn-1-yloxy)benzene (41.3 mg, 0.24 mmol), isoprene (240 µL, 2.4 mmol), catalyst (2.4 mg), $MgSO_4$ (15mg) and nitromethane (2.4 mL). After the reaction was finished, the mixture was worked up according to the protocol and purified by chromatography on silica with hexane/ethyl acetate (8/1) as the elution to afford the pure cycloadduct as clear oil.

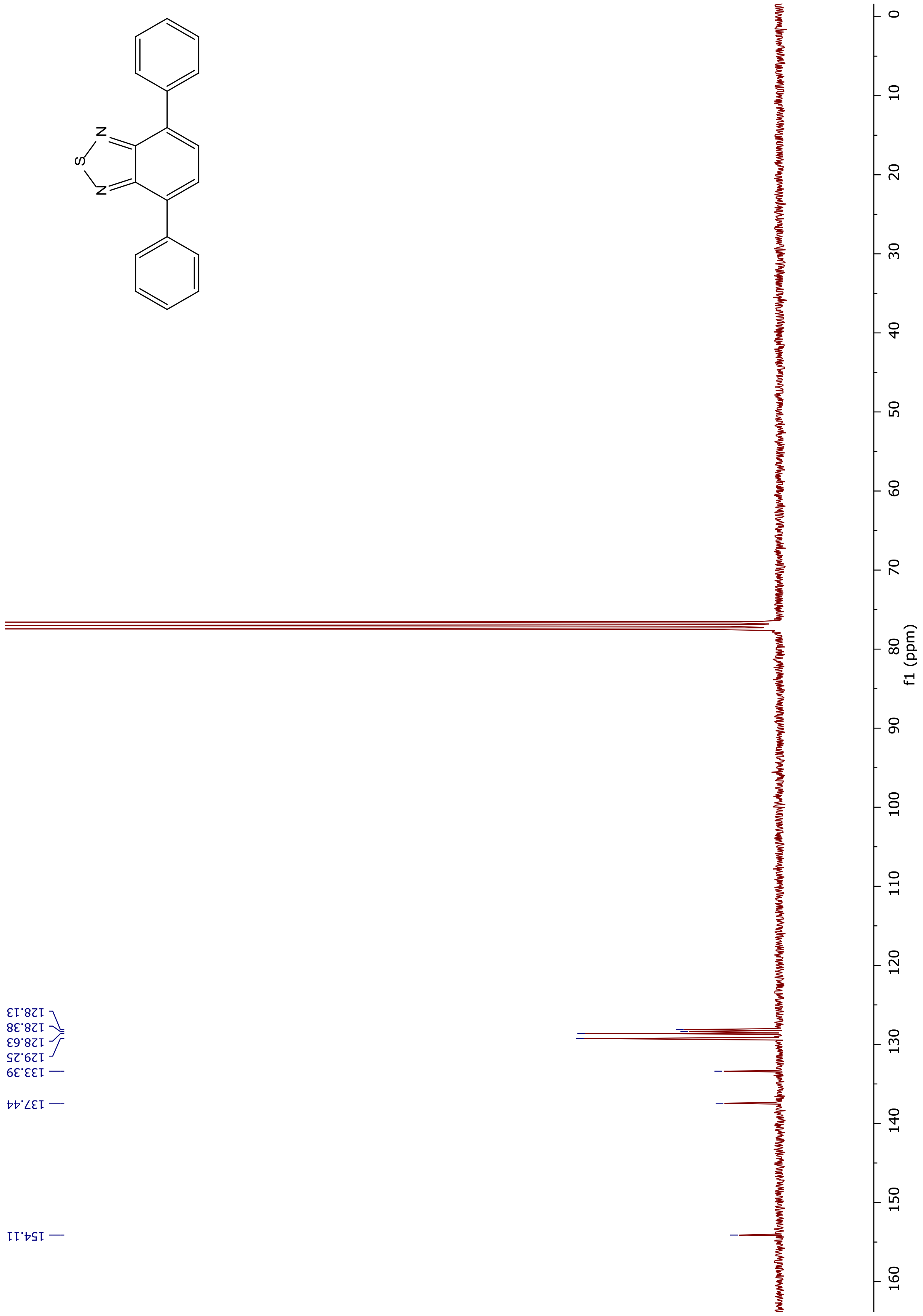
R_f (hexane/ethyl acetate 8/1): 0.30

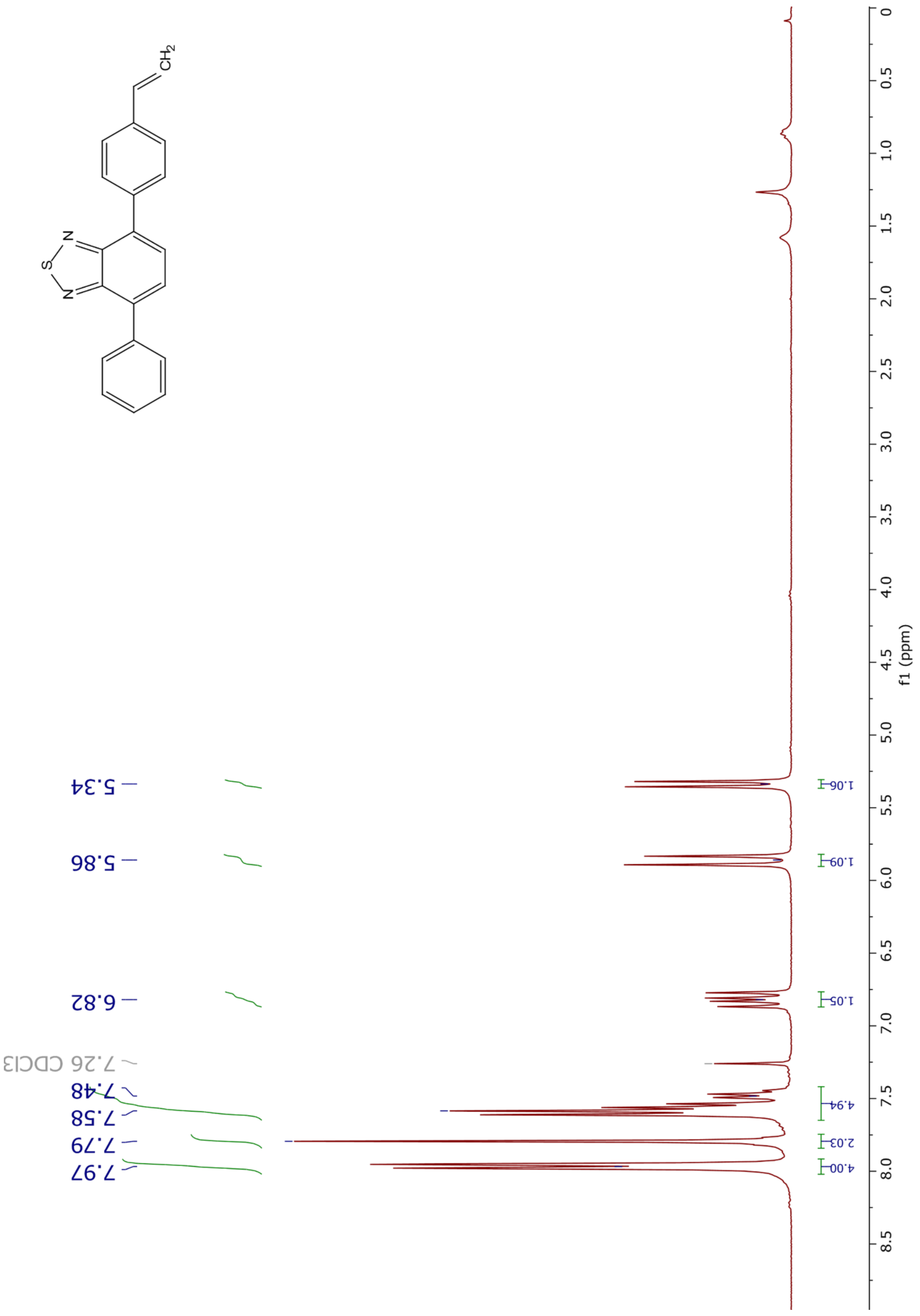
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.10 (d, 2H), 6.92 (d, 2H), 5.45 (s, 1H), 4.68 (d, 2H), 2.52 (s, 1H), 2.31 (m, 1H), 2.20 (m, 2H), 2.10 (m, 1H), 1.91 (m, 1H), 1.82 (m, 1H), 1.70 (s, 3H), 0.72 (d, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.95, 139.28, 133.93, 128.65, 120.98, 114.81, 79.01, 75.44, 55.99, 47.10, 39.93, 35.33, 34.05, 23.51, 20.37.

^{1}H and ^{13}C NMR spectra




N
S
N
154.11
137.44
133.39
129.25
128.63
128.38
128.13
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)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S
N
N
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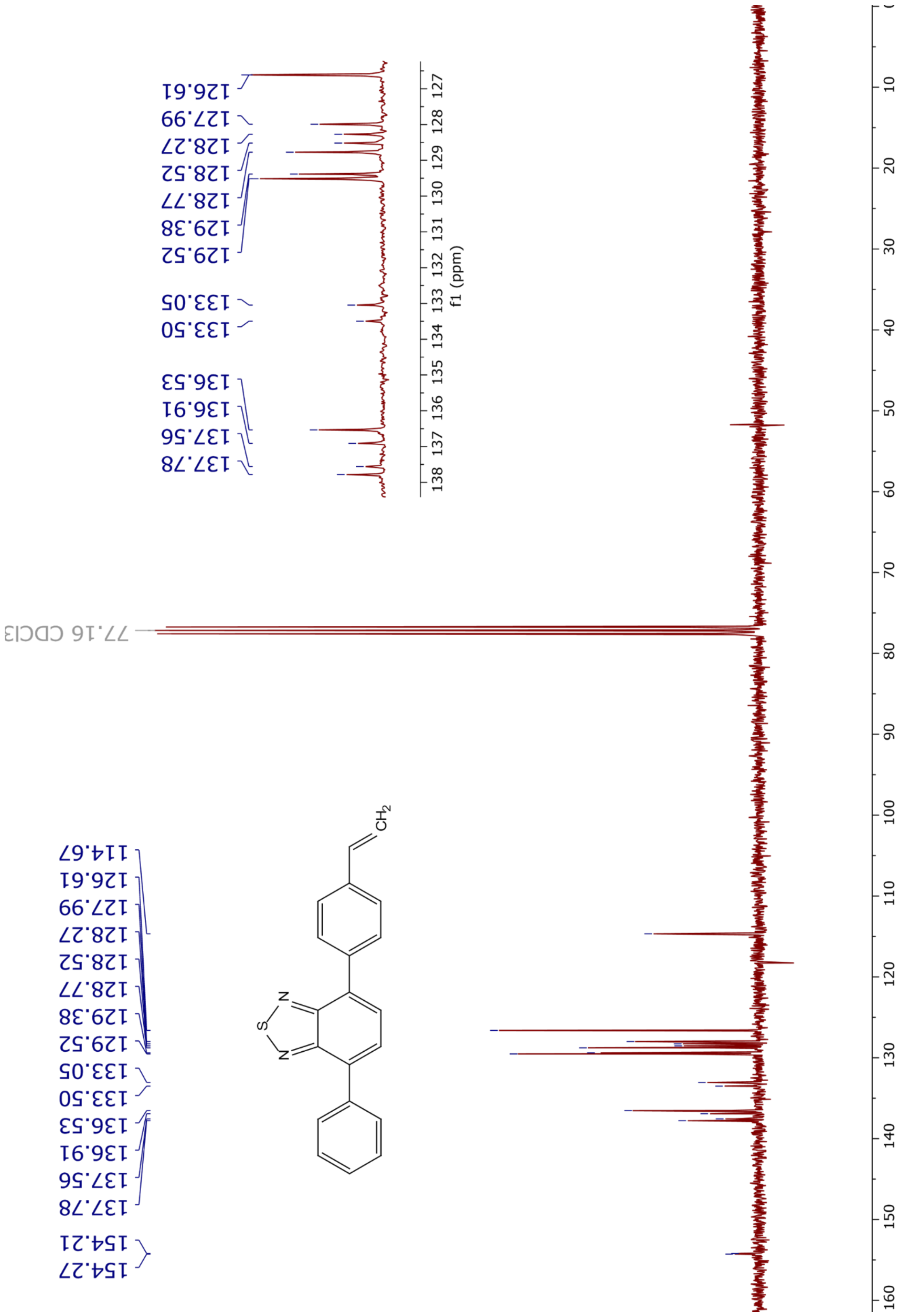
5.86
6.82
7.26 CDCl3
7.48
7.58
7.79
7.97
1.06
1.09
1.05
4.94
2.03
4.00
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
f1 (ppm)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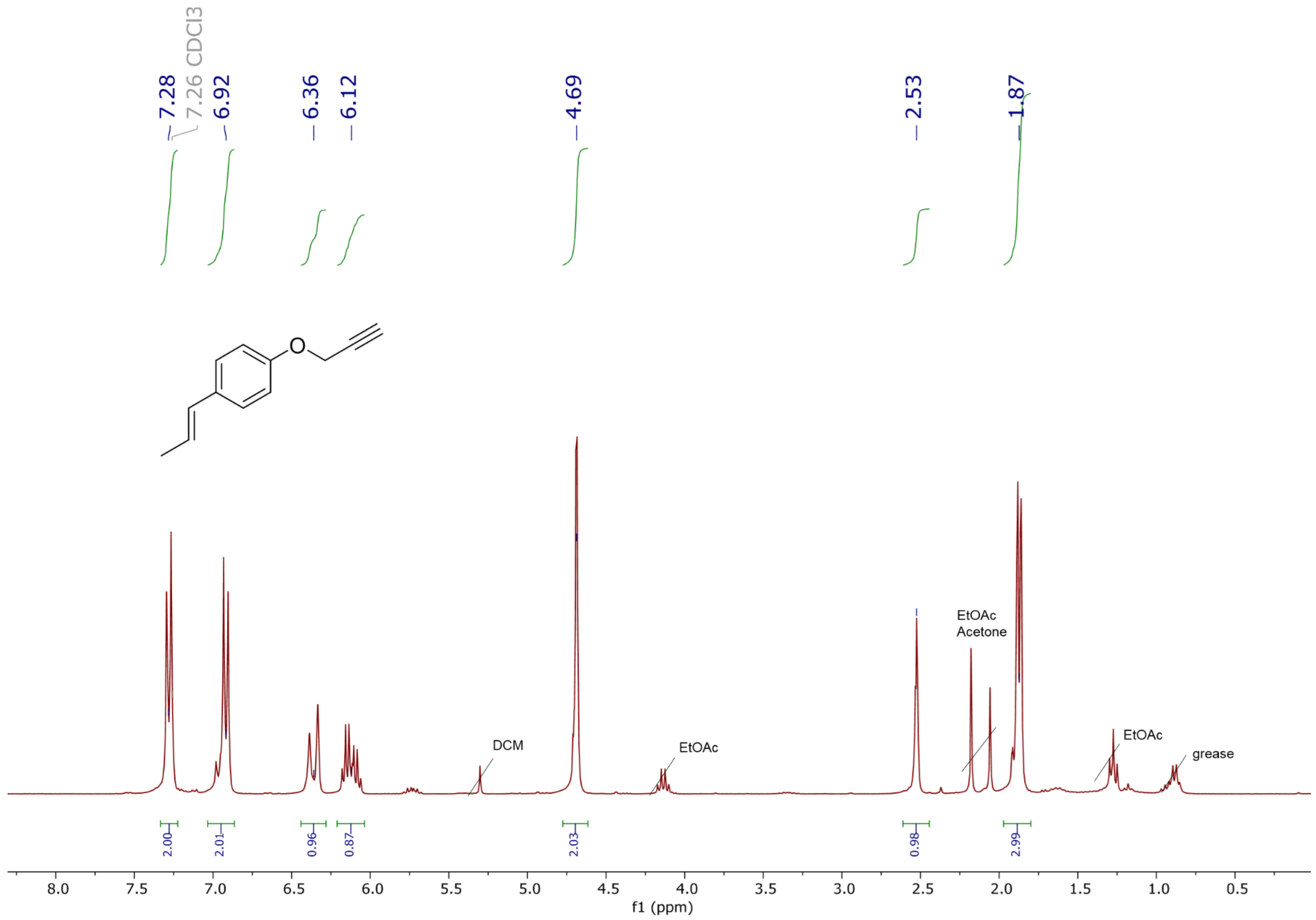
154.21
137.78
137.56
136.91
136.53
133.50
133.05
129.52
129.38
128.77
128.52
128.27
127.99
126.61
114.67
77.16 CDCl3
137.78
137.56
136.91
136.53
133.50
133.05
129.52
129.38
128.77
128.52
128.27
127.99
126.61
N
S
N
CH2
138 137 136 135 134 133 132 131 130 129 128 127
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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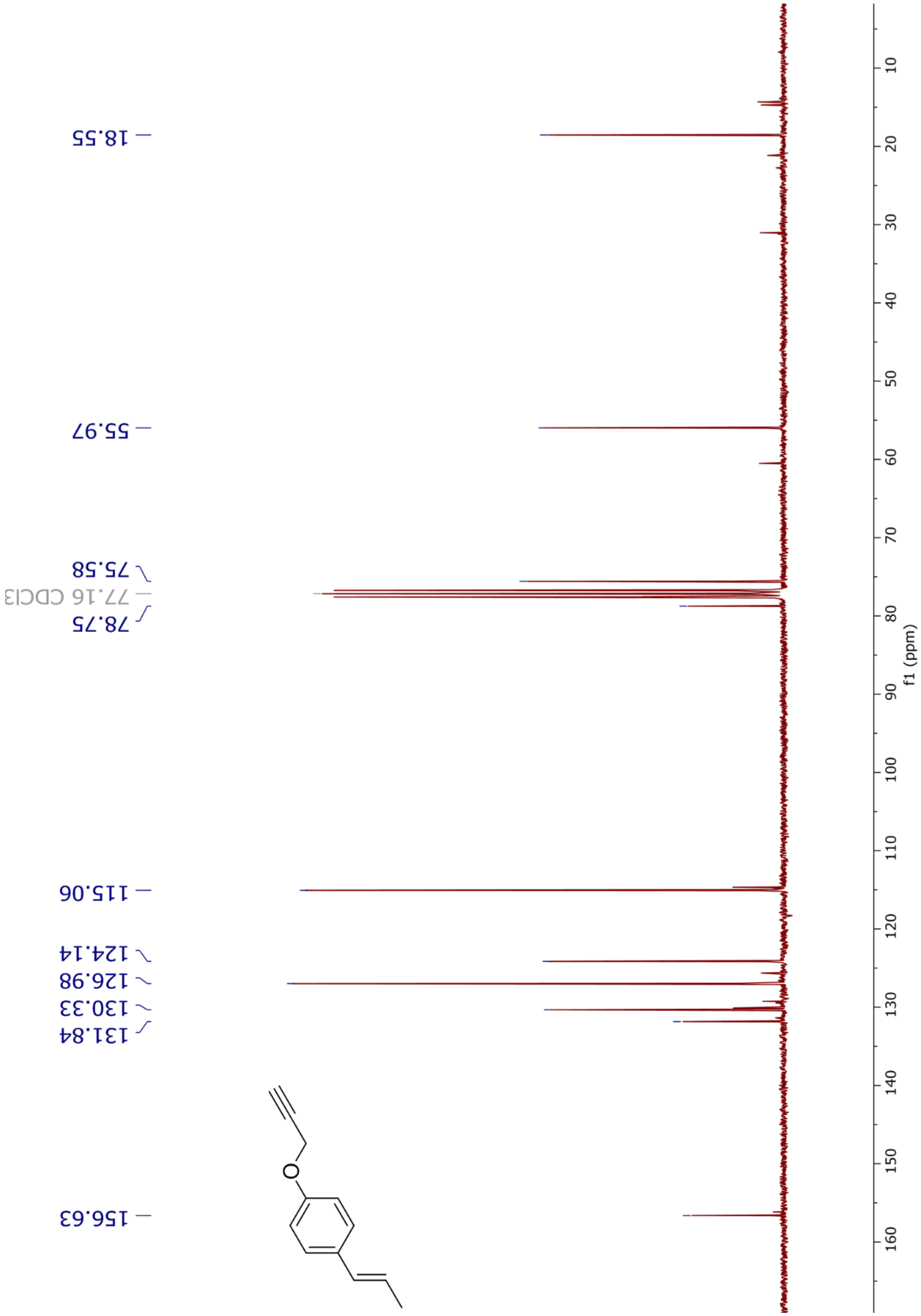
7.26 CDCl3
6.92
6.36
6.12
4.69
2.53
1.87
O
DCM
EtOAc
EtOAc
Acetone
EtOAc
grease
2.00
2.01
0.96
0.87
2.03
0.98
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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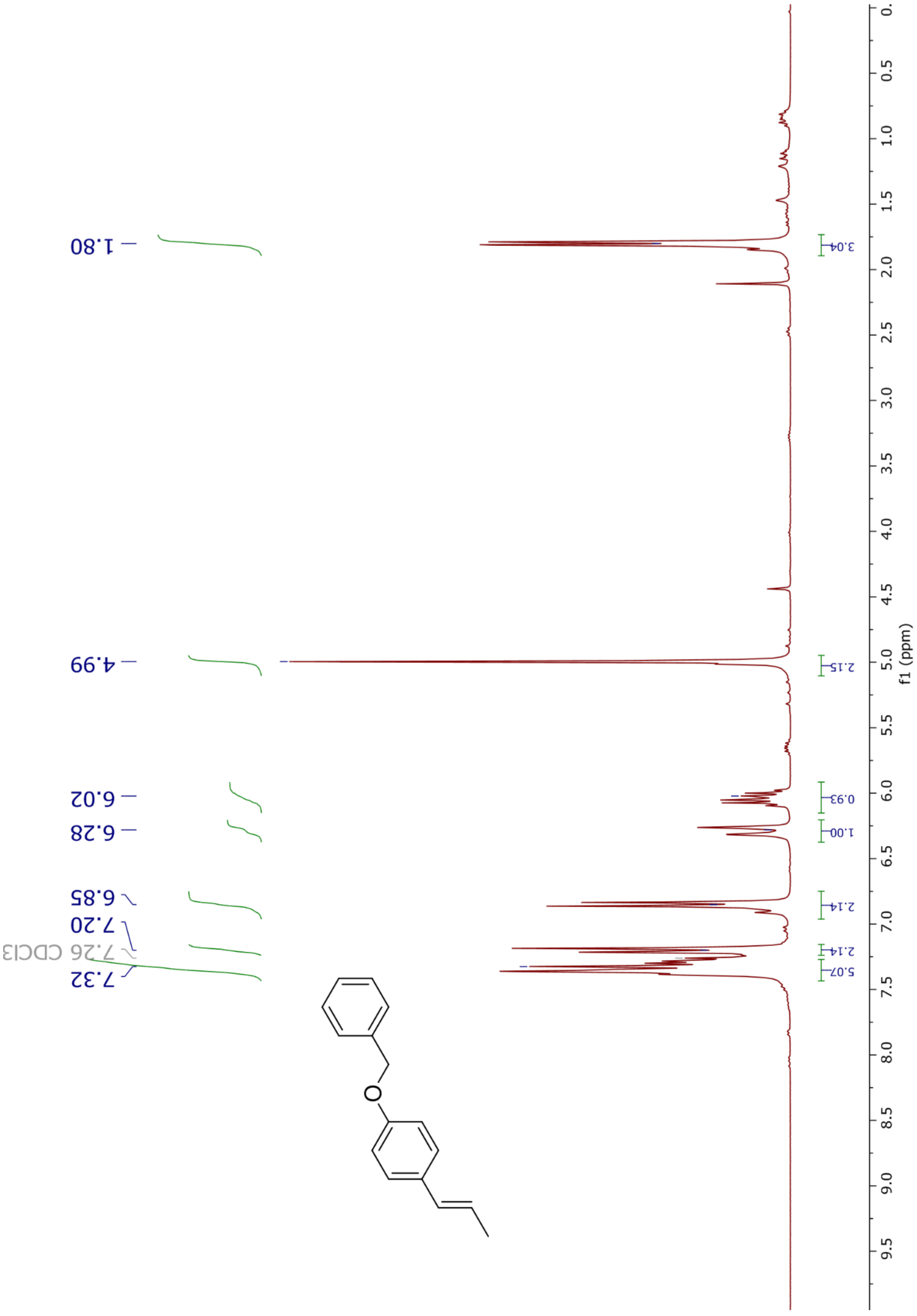
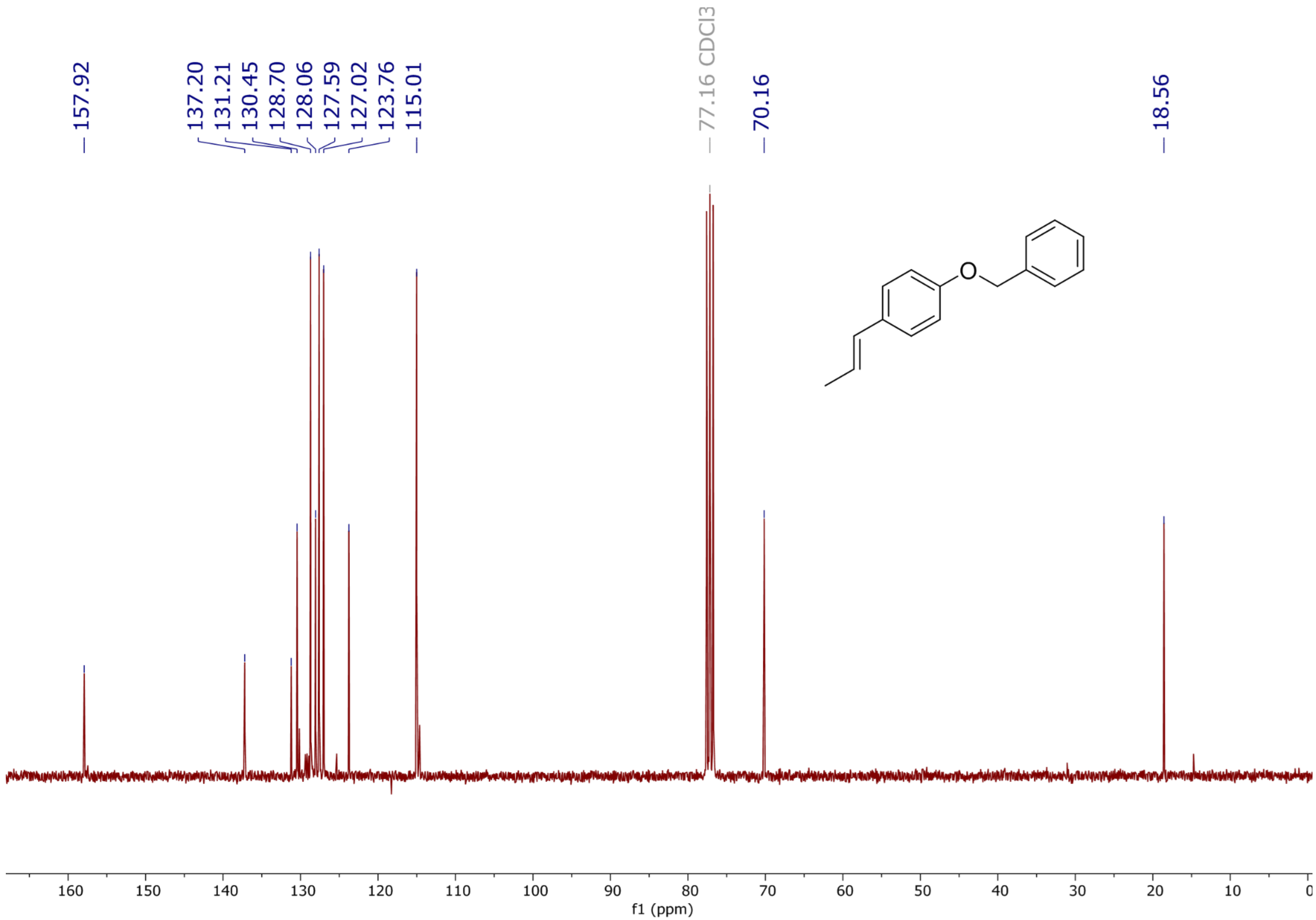
75.58
77.16 CDCl3
78.75
115.06
124.14
126.98
130.33
131.84
156.63
O
f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160



1.80
4.99
6.02
6.28
6.85
7.20
7.26 CDCl3
7.32
3.04
2.15
0.93
1.00
2.14
2.14
5.07
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
f1 (ppm)
O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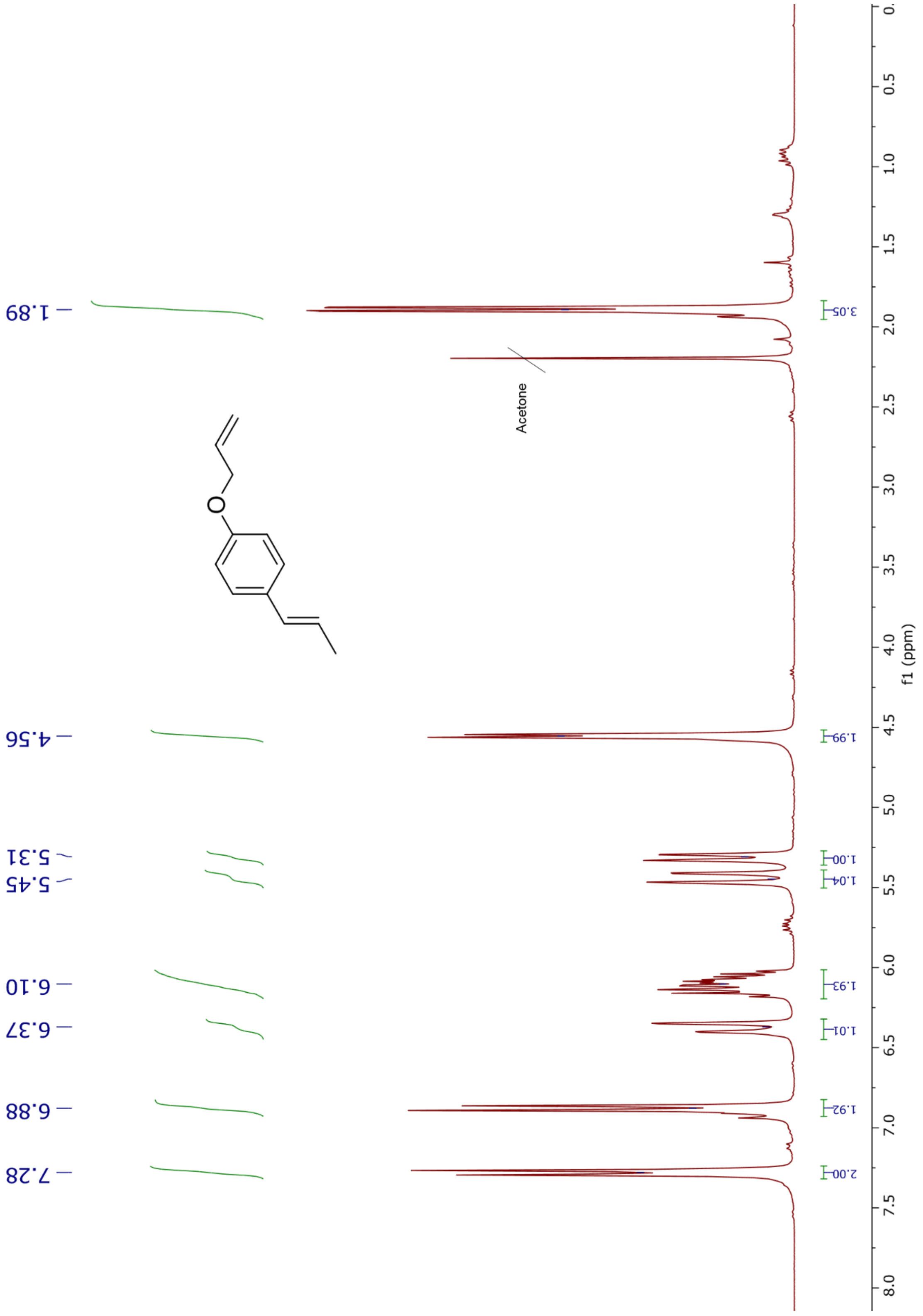
130.45
128.70
128.06
127.59
127.02
123.76
115.01
77.16 CDCl3
70.16
18.56
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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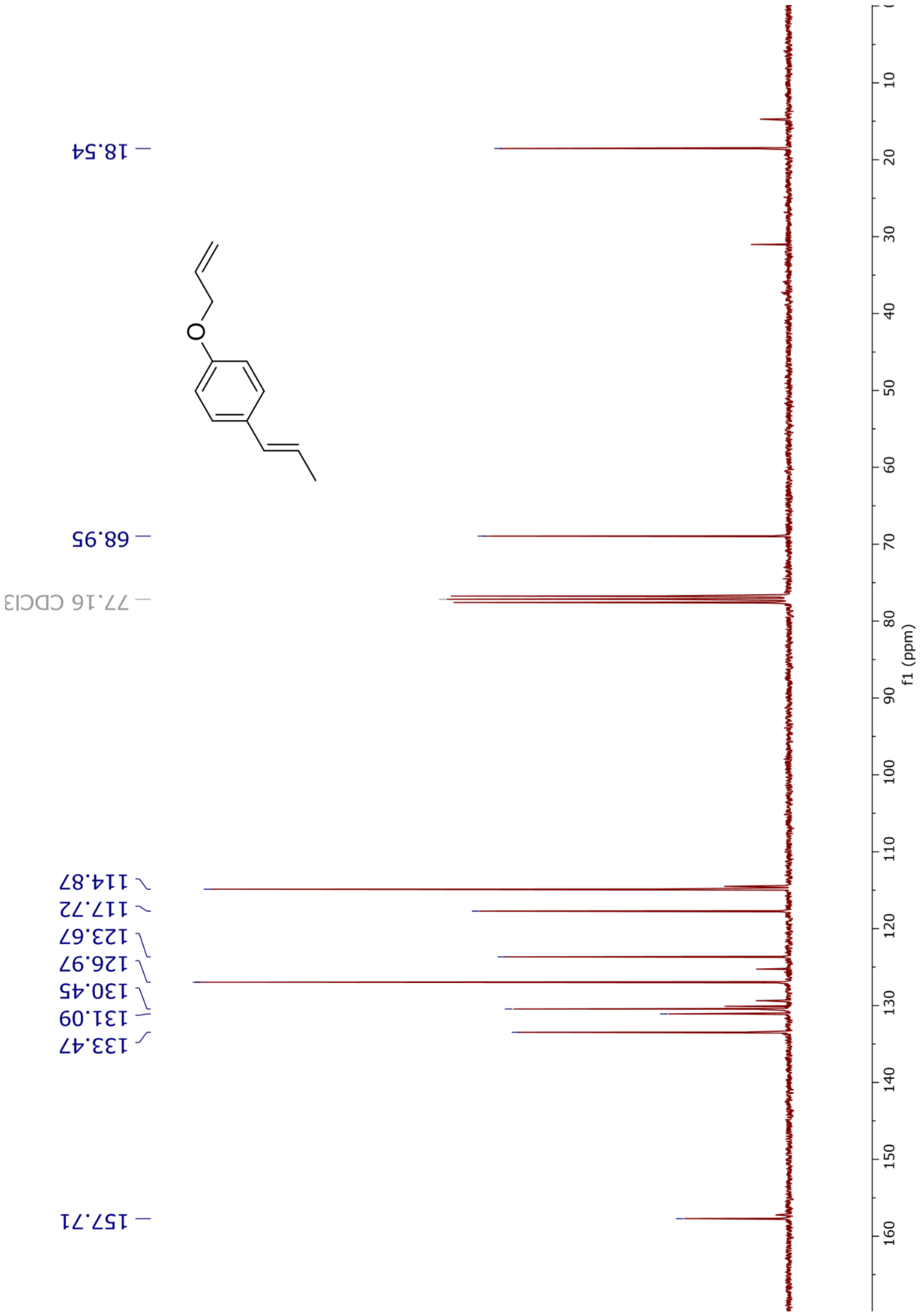
4.56
5.31
5.45
6.10
6.37
6.88
7.28
Acetone
3.05
1.99
1.00
1.04
1.93
1.01
1.92
2.00
0.
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
O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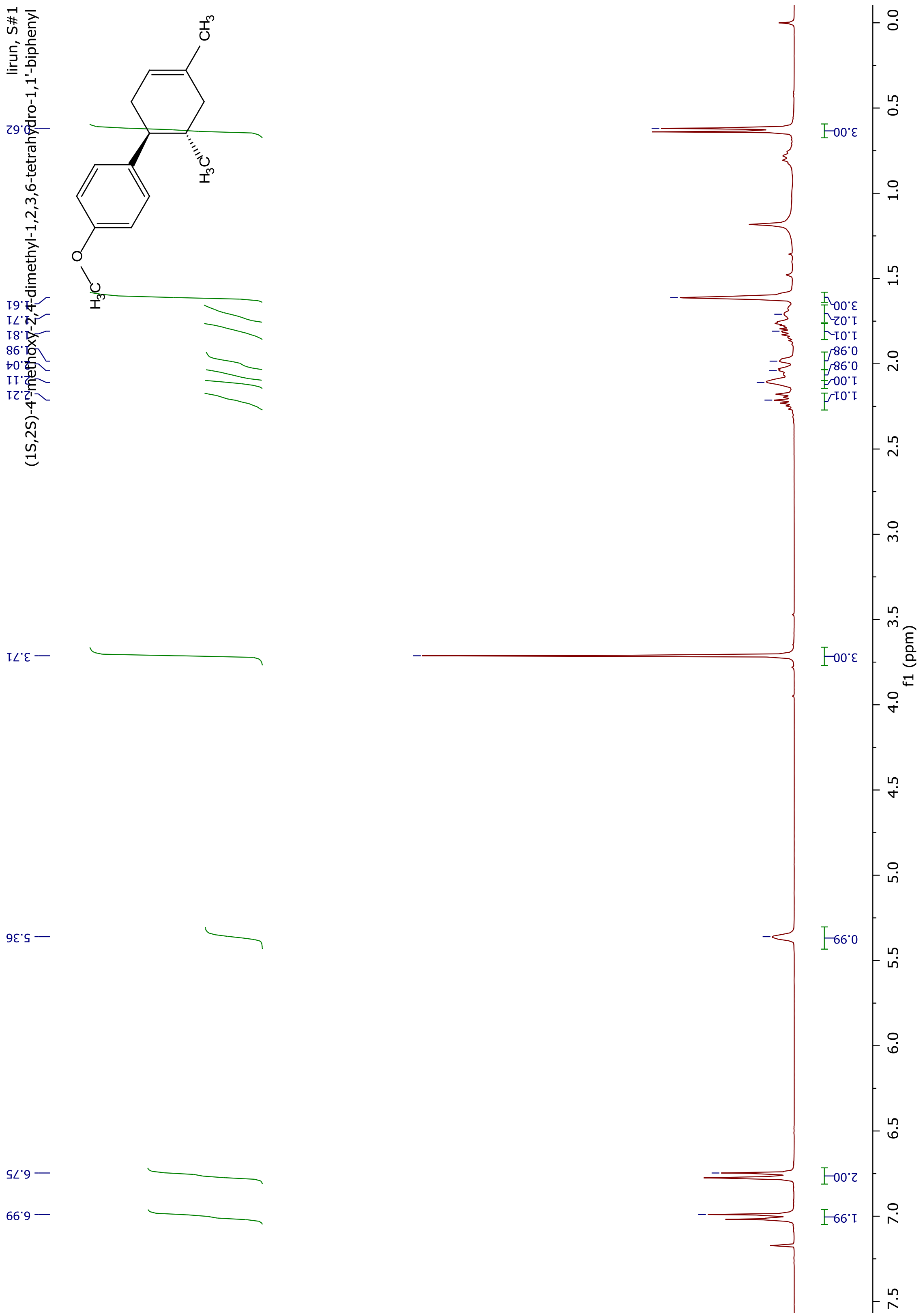
68.95
77.16 CDCl3
114.87
117.72
123.67
126.97
130.45
131.09
133.47
157.71
O
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)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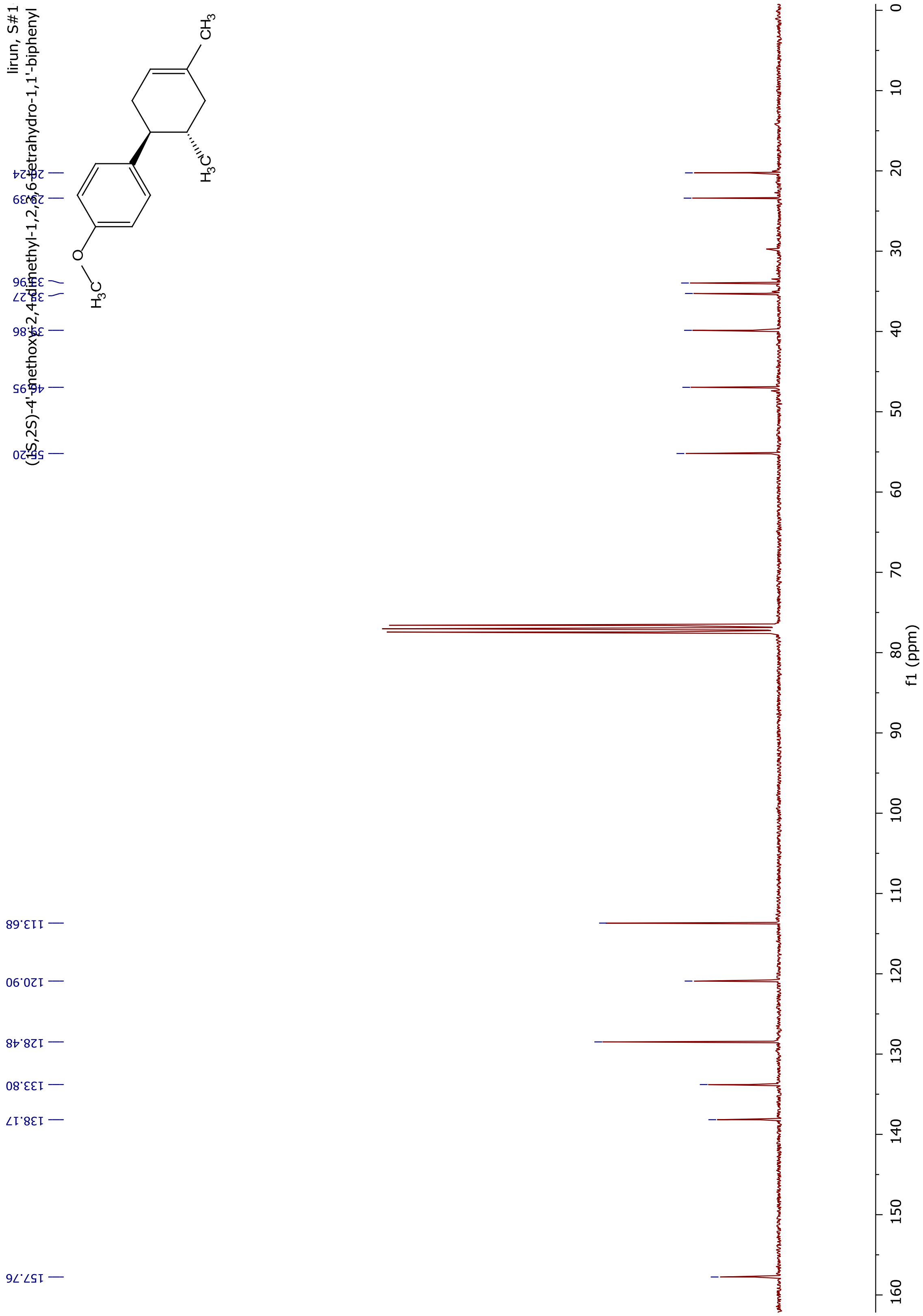
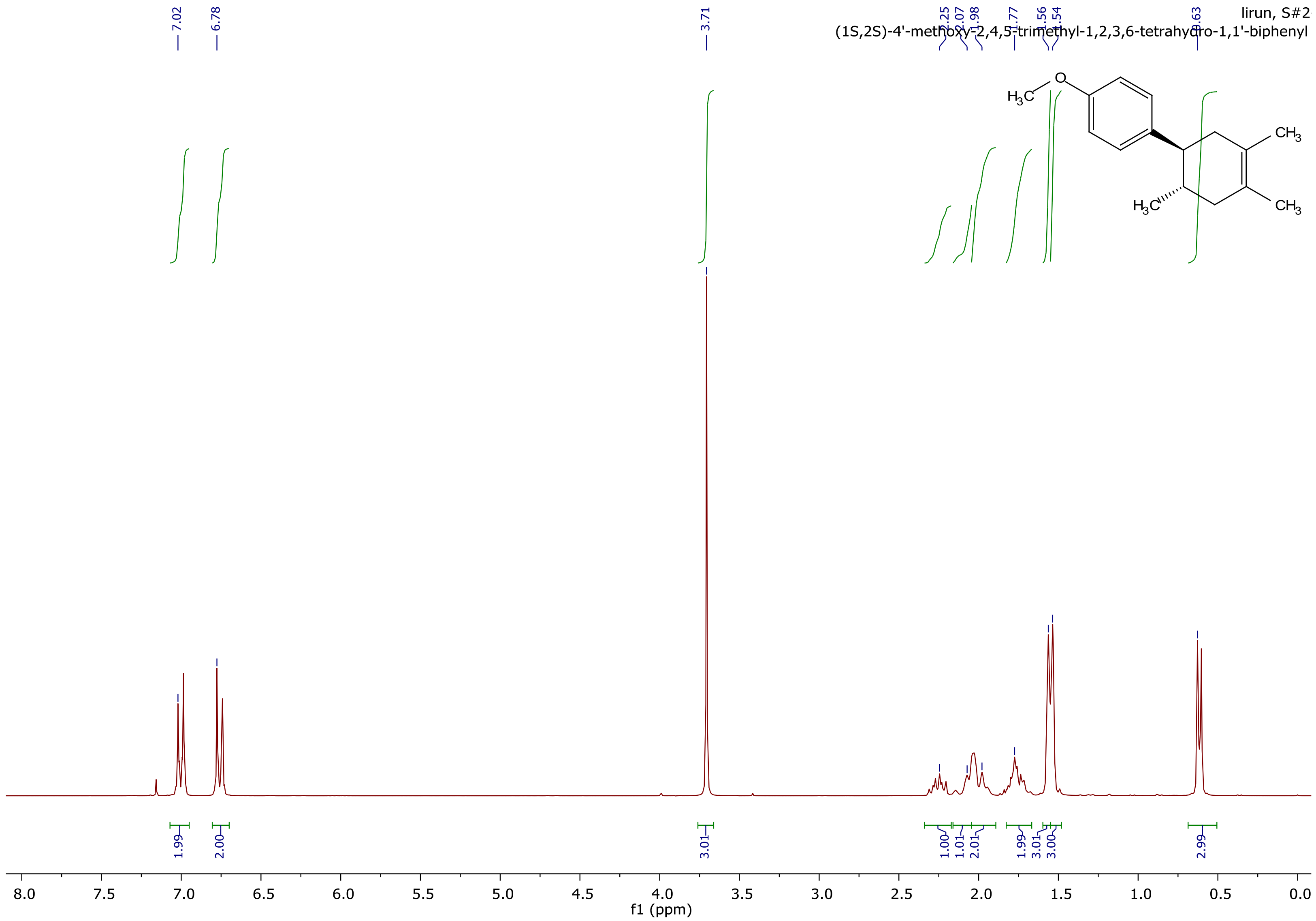
CH3
H3C
0.62
1.61
1.71
1.81
1.98
2.04
2.11
2.21
3.71
5.36
6.75
6.99
3.00
3.00
1.02
1.01
0.98
0.98
1.00
1.01
3.00
0.99
2.00
1.99
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)


lirun, S#1
(1S,2S)-4'-methoxy-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl
CH3
H3C
H3C
O
20.24
23.39
33.96
35.27
39.86
46.95
55.20
113.68
120.90
128.48
133.80
138.17
157.76
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)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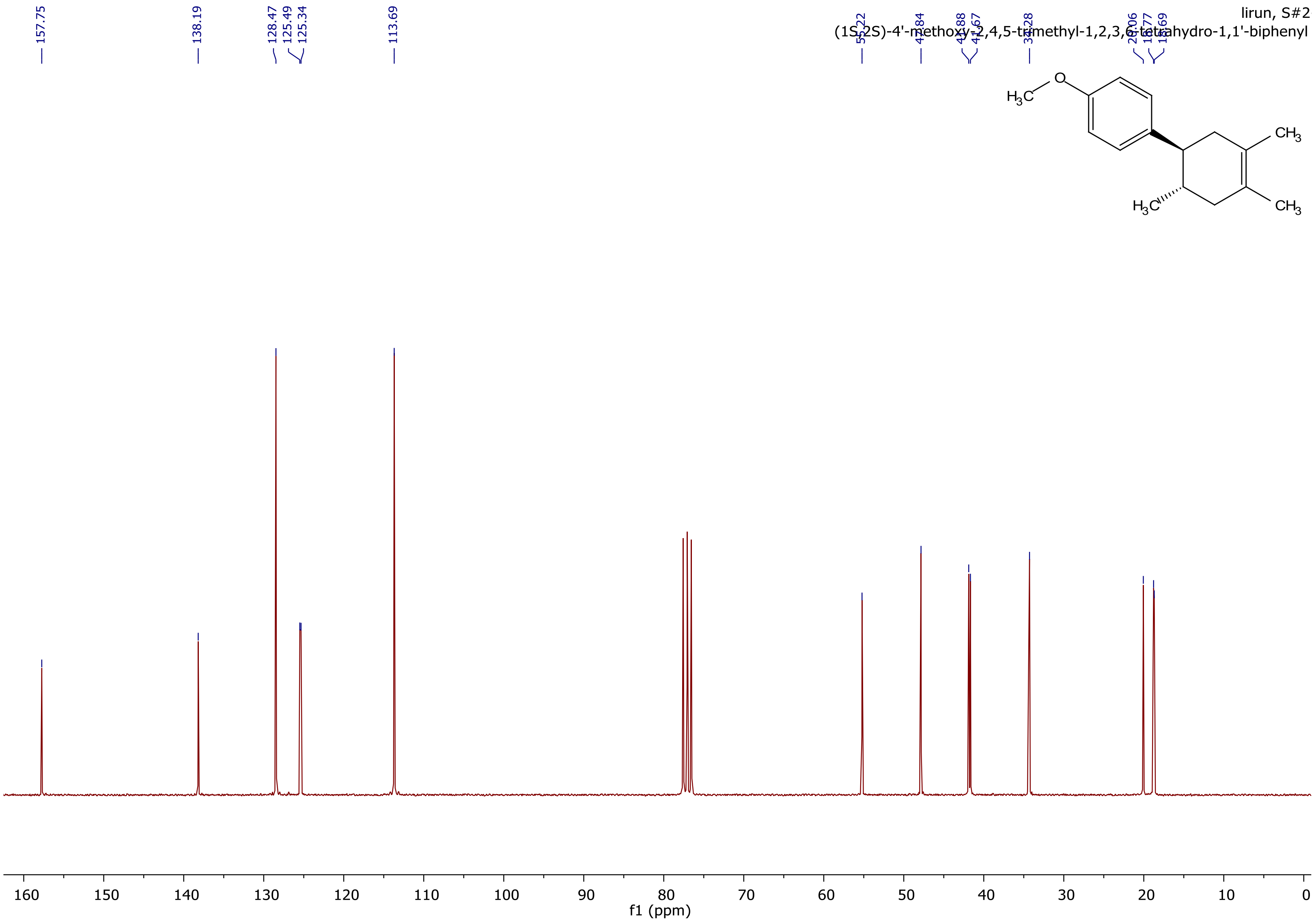
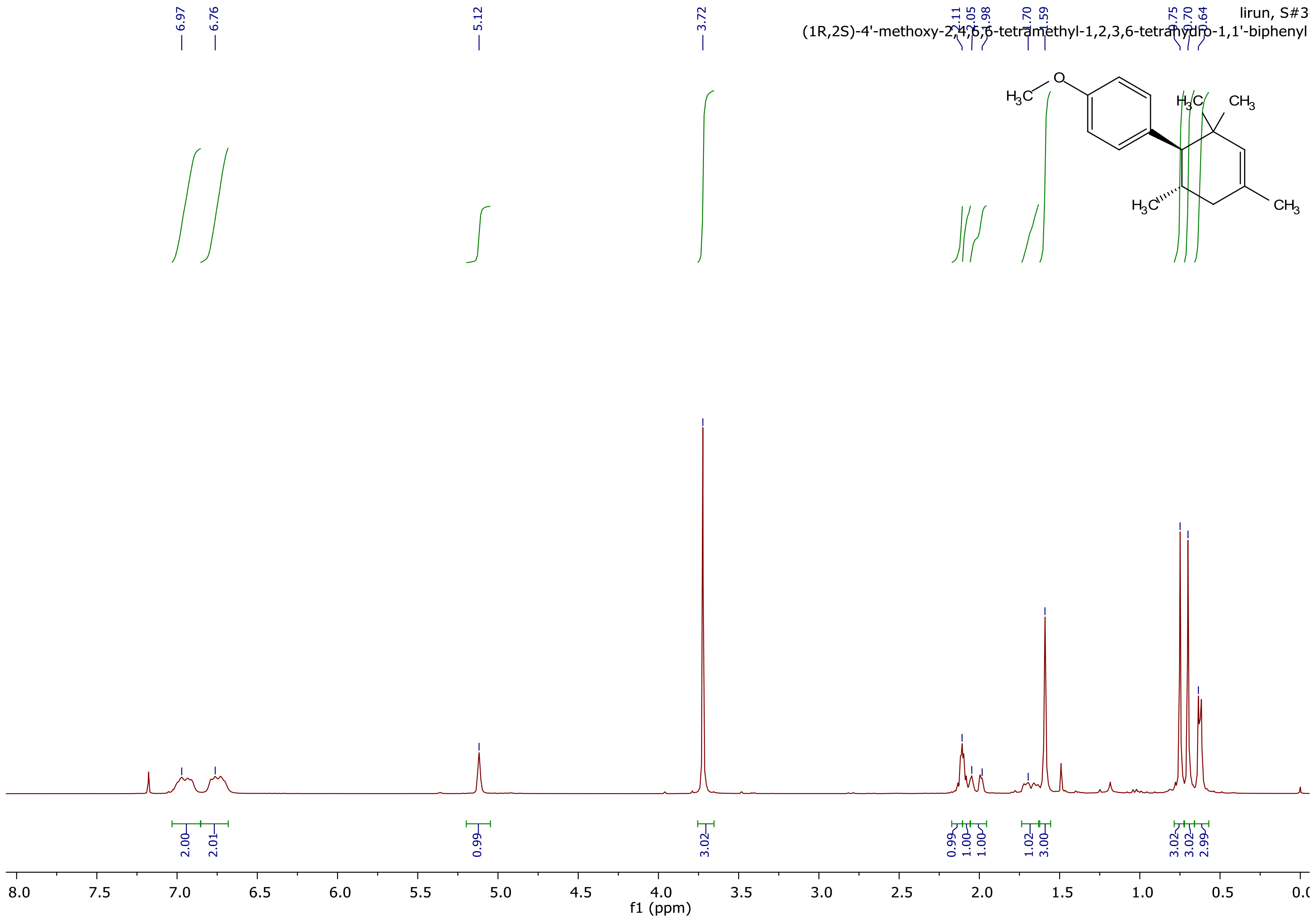
6.78
3.71
2.25
2.07
1.98
1.77
1.56
1.54
0.63
H3C
O
CH3
CH3
H3C
1.99
2.00
3.01
1.00
1.01
2.01
1.99
3.01
3.00
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

lirun, S#2
(1S,2S)-4'-methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl

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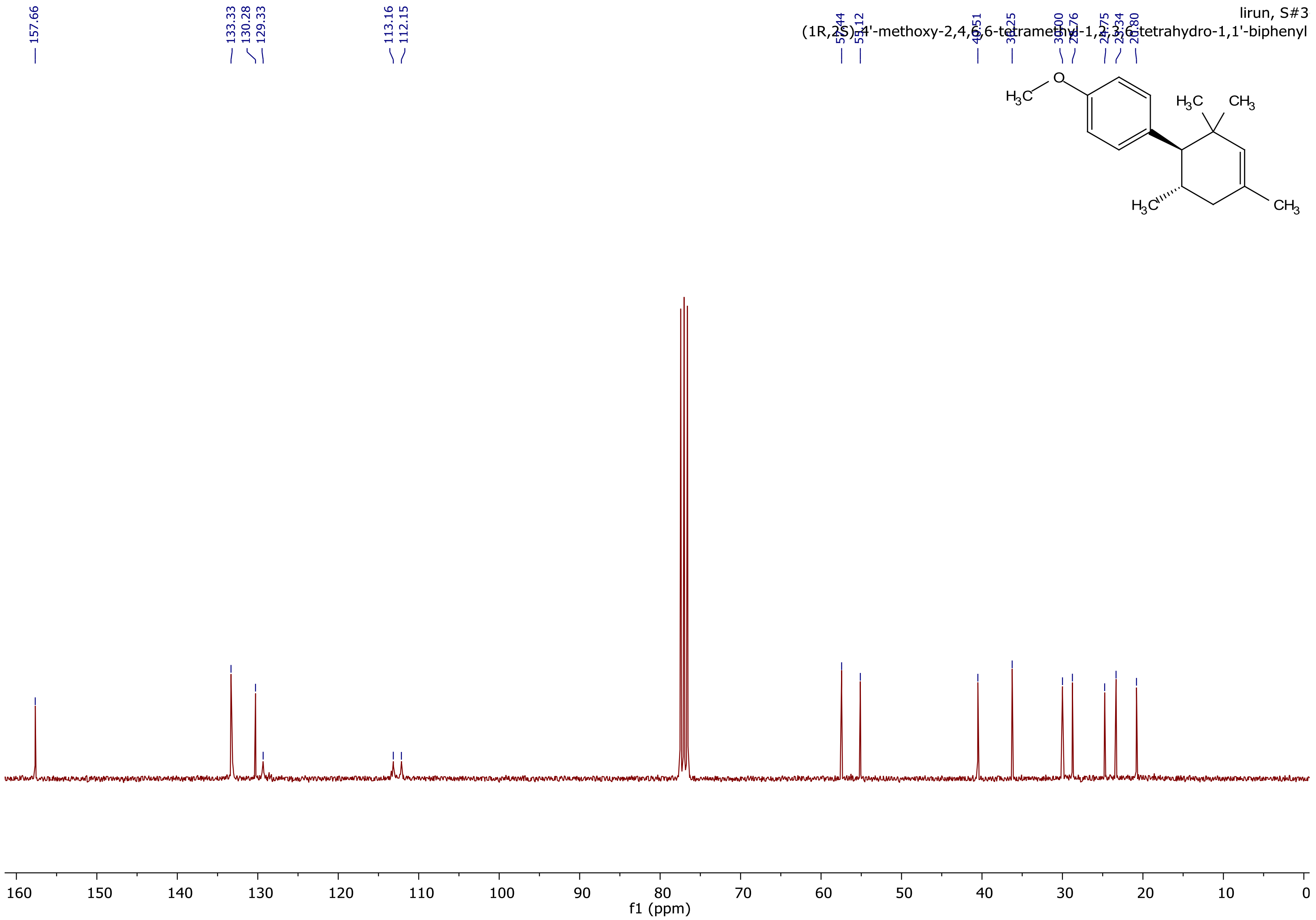
6.76
5.12
3.72
2.11
2.05
1.98
1.70
1.59
0.75
0.70
0.64
H3C
O
H3C
CH3
H3C
CH3
2.00
2.01
0.99
3.02
0.99
1.00
1.00
1.02
3.00
3.02
3.02
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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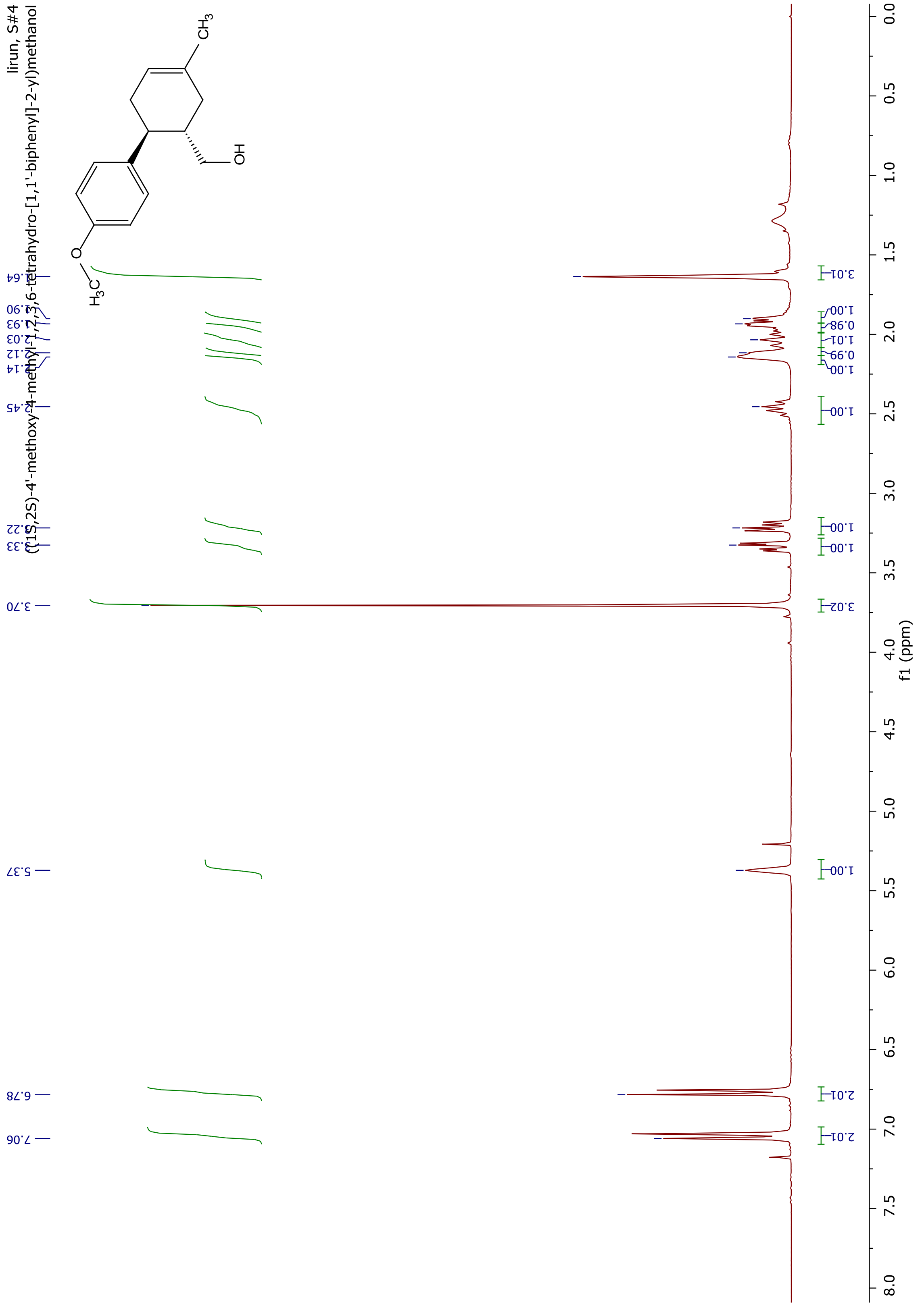
133.33
130.28
129.33
113.16
112.15
57.44
55.12
40.51
36.25
30.00
28.76
24.75
23.34
20.80
H_3C
O
H_3C
CH_3
H_3C
CH_3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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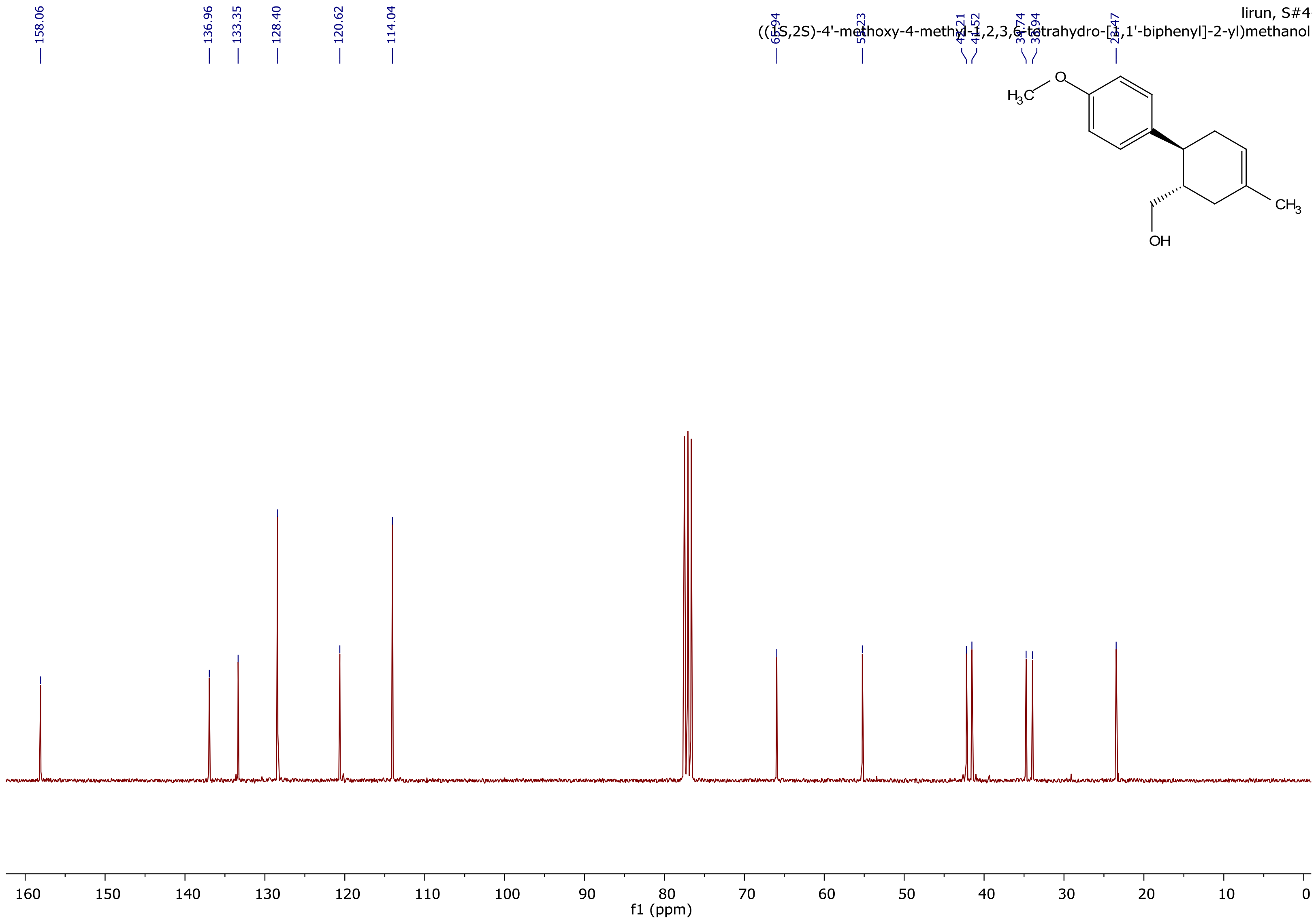
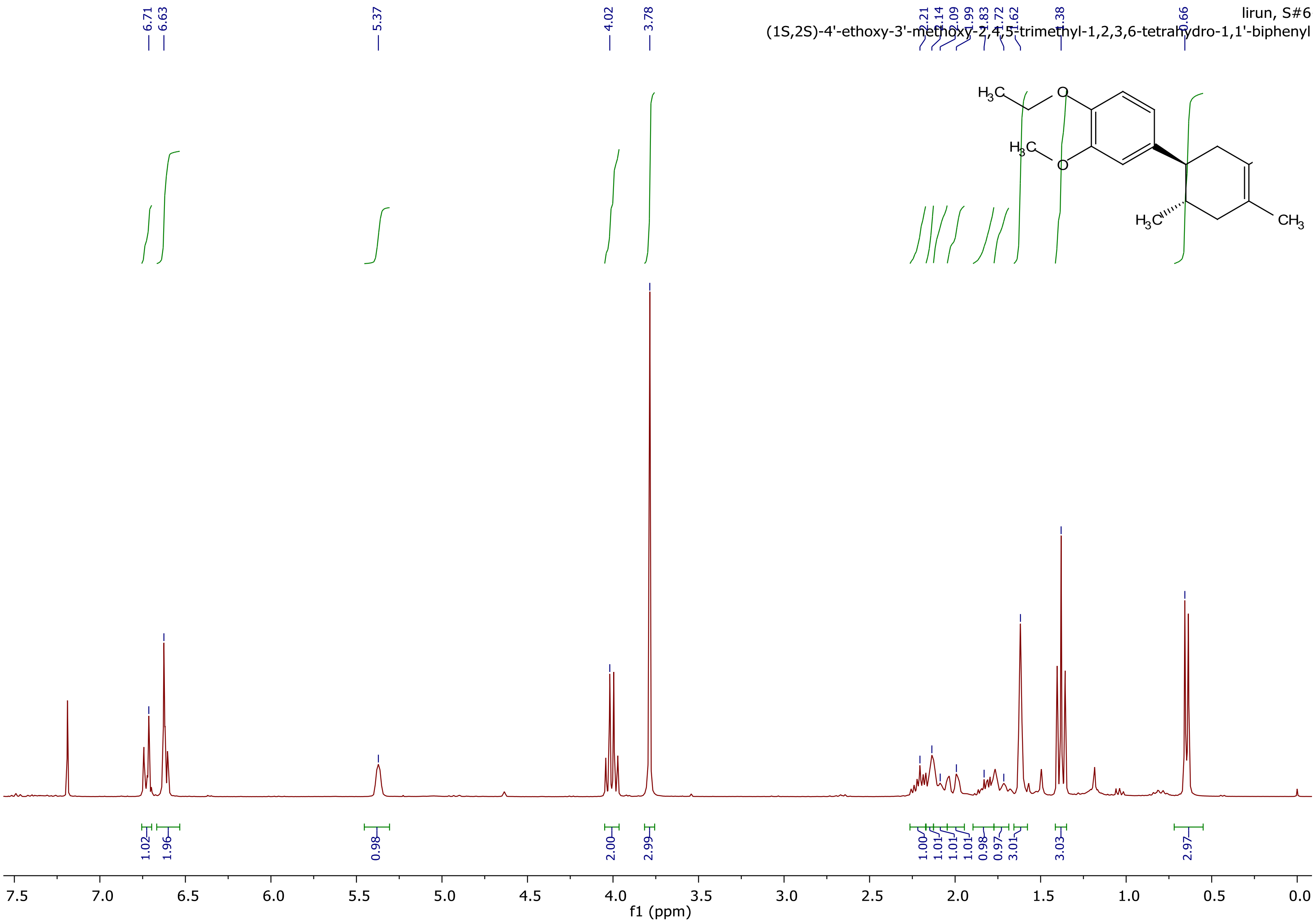
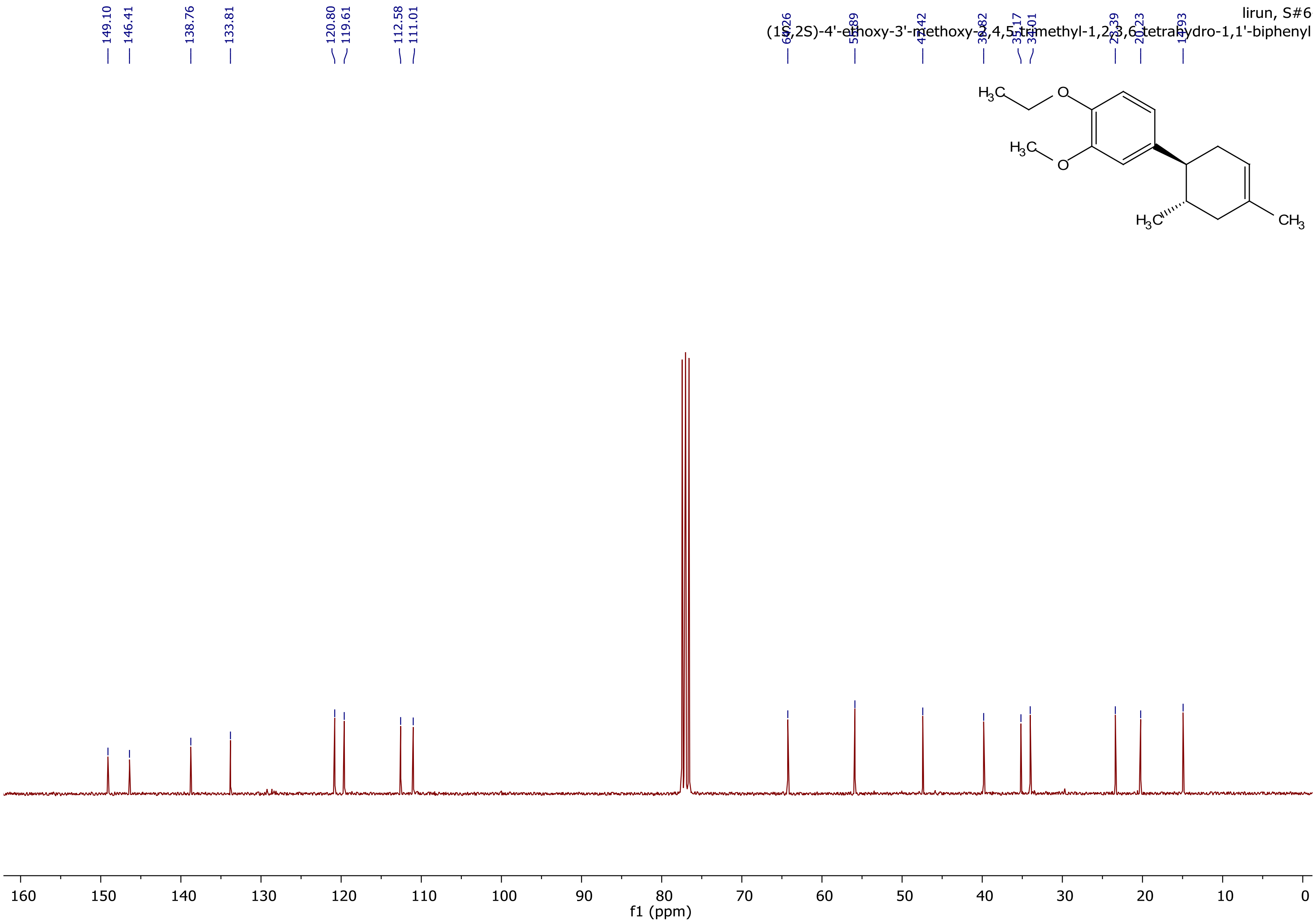
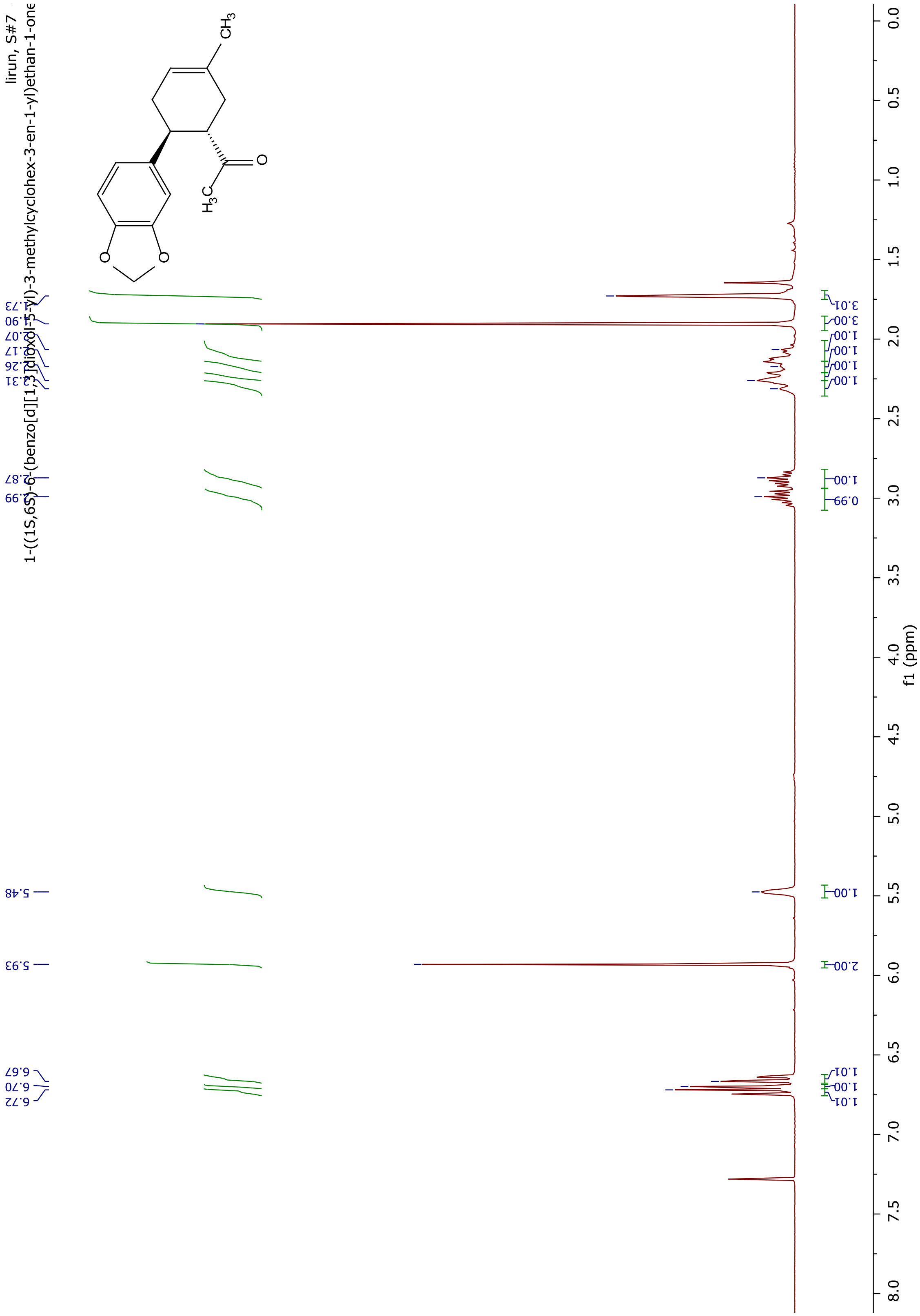
H_3C
O
CH_3
OH
7.06
6.78
5.37
3.70
3.33
3.22
2.45
2.14
2.12
2.03
1.93
1.90
1.64
2.01
2.01
1.00
3.02
1.00
1.00
1.00
1.00
0.99
1.01
0.98
1.00
3.01
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)

lirun, S#4
((1S,2S)-4'-methoxy-4-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanol



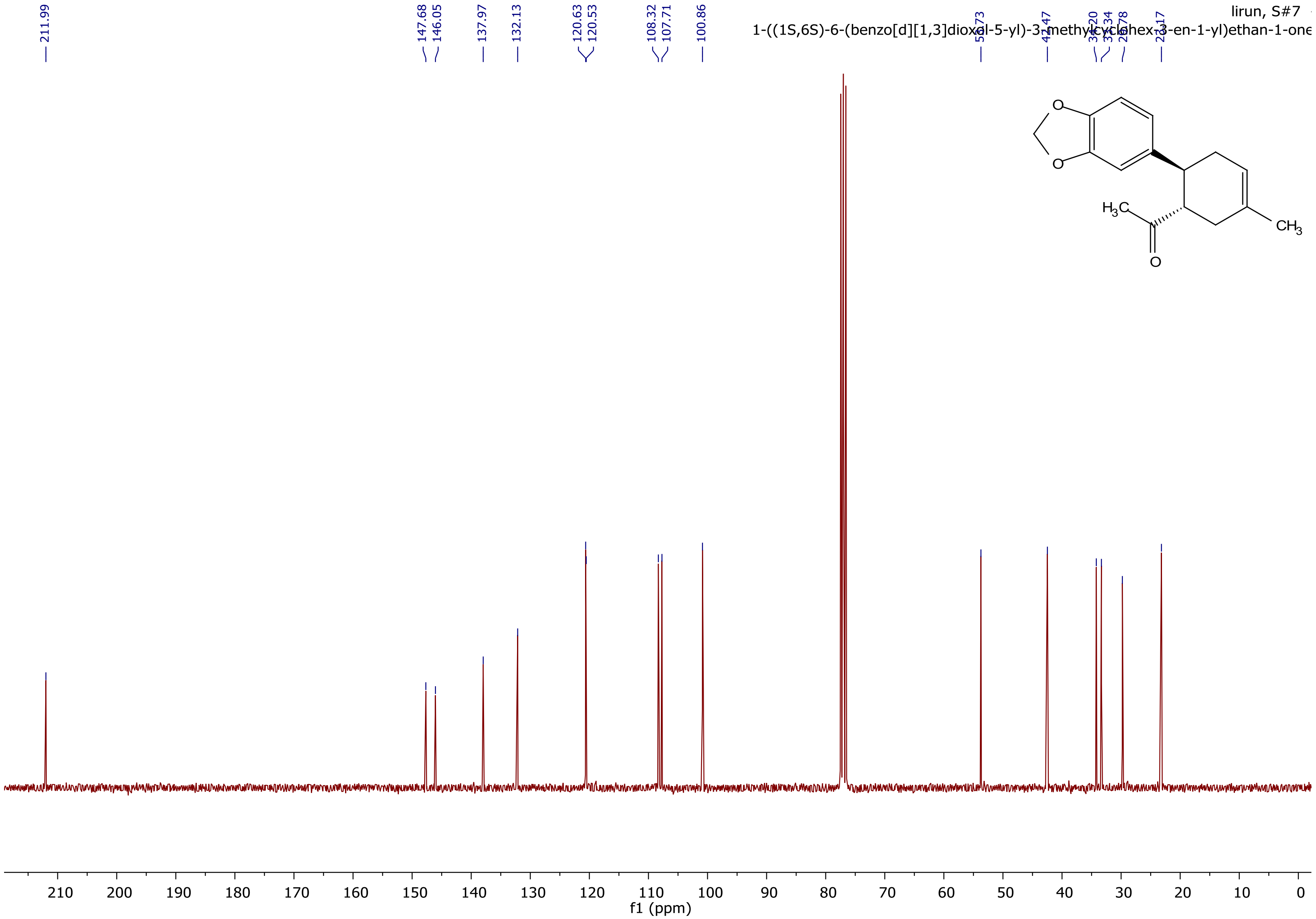

lirun, S#6
(1S,2S)-4'-ethoxy-3'-methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl
6.71
6.63
5.37
4.02
3.78
2.21
2.14
2.09
1.99
1.83
1.72
1.62
1.38
0.66
H_3C
O
H_3C
O
H_3C
CH_3
1.02
1.96
0.98
2.00
2.99
1.00
1.01
1.01
1.01
0.98
0.97
3.01
3.03
2.97
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

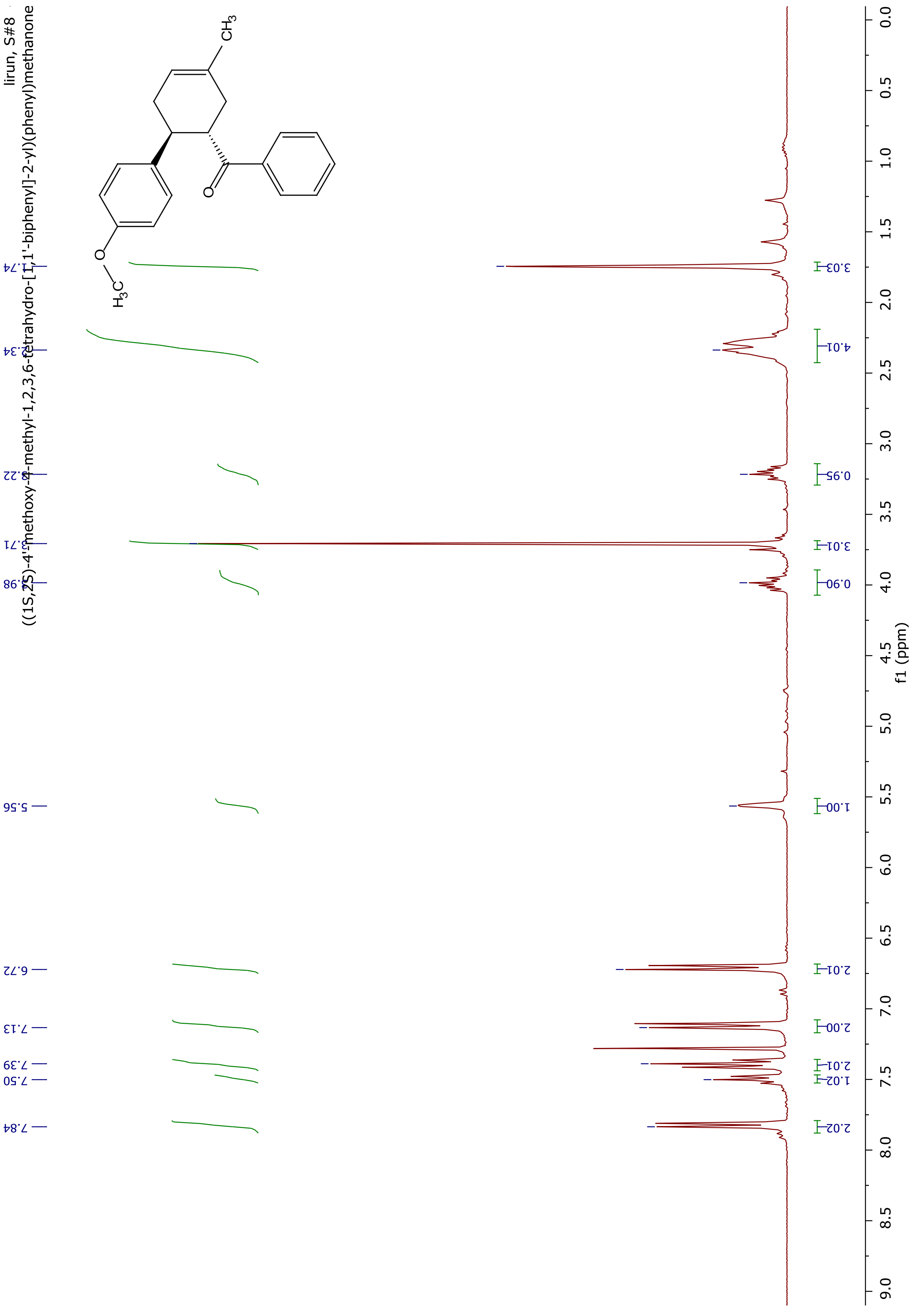

lirun, S#6
(1S,2S)-4'-ethoxy-3'-methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl
149.10
146.41
138.76
133.81
120.80
119.61
112.58
111.01
64.26
55.89
47.42
39.82
35.17
34.01
23.39
20.23
14.93
H_3C
O
H_3C
O
H_3C
CH_3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


lirun, S#7
1-((1S,6S)-6-(benzo[d][1,3]dioxol-5-yl)-3-methylcyclohex-3-en-1-yl)ethan-1-one
CH3
H3C
O
1.73
1.90
2.07
2.17
2.26
2.31
2.87
2.99
5.48
5.93
6.67
6.70
6.72
3.01
3.00
1.00
1.00
1.00
1.00
1.00
0.99
1.00
2.00
1.01
1.00
1.01
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)

lirun, S#7

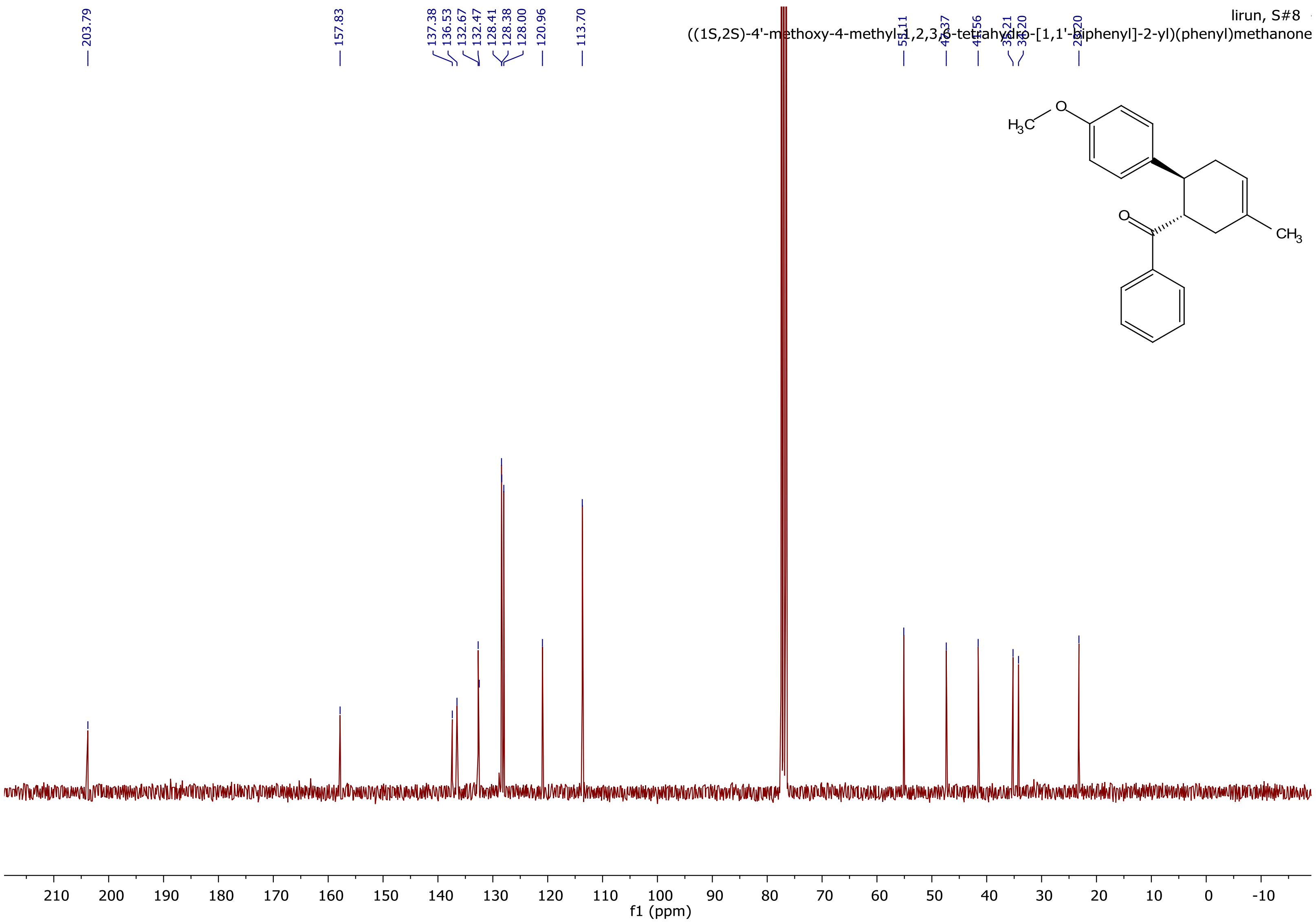
1-((1S,6S)-6-(benzo[d][1,3]dioxol-5-yl)-3-methylcyclohex-3-en-1-yl)ethan-1-one

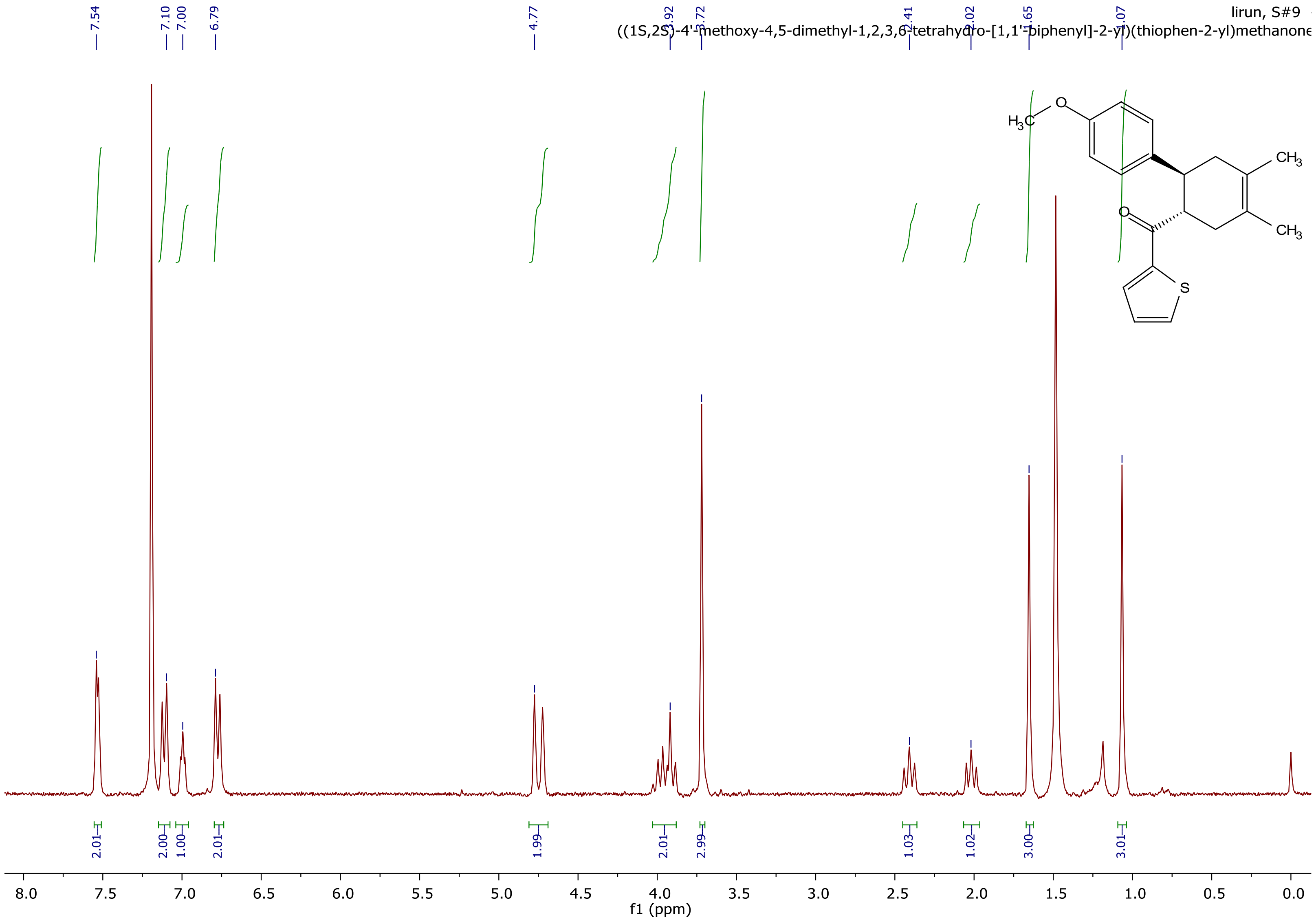



lirun, S#8
((1S,2S)-4'-methoxy-4-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone
CH3
H3C
O
O
1.74
2.34
3.22
3.71
3.98
5.56
6.72
7.13
7.39
7.50
7.84
3.03
4.01
0.95
3.01
0.90
1.00
2.01
2.00
2.01
1.02
2.02
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
f1 (ppm)

lirun, S#8

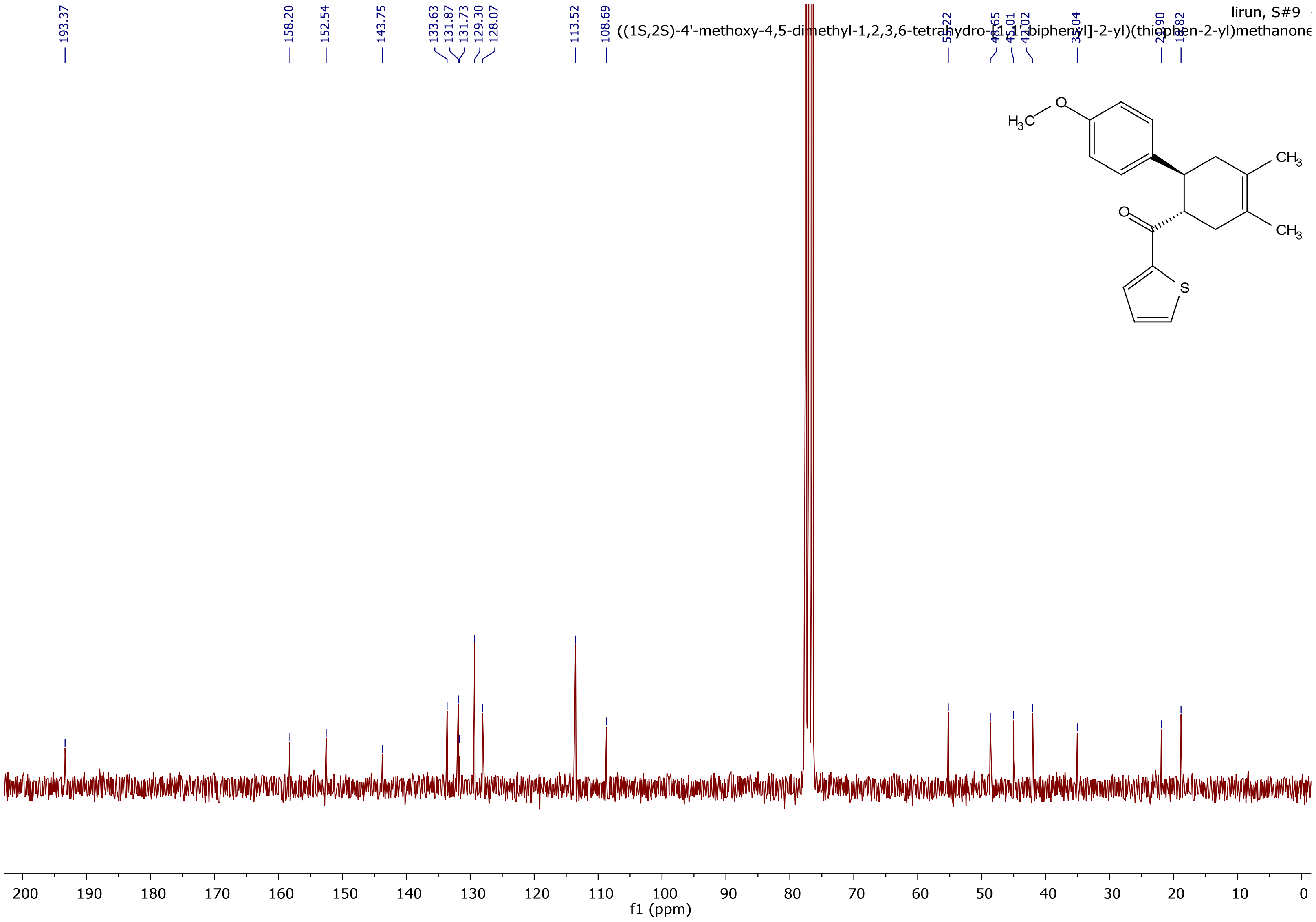
((1S,2S)-4'-methoxy-4-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone

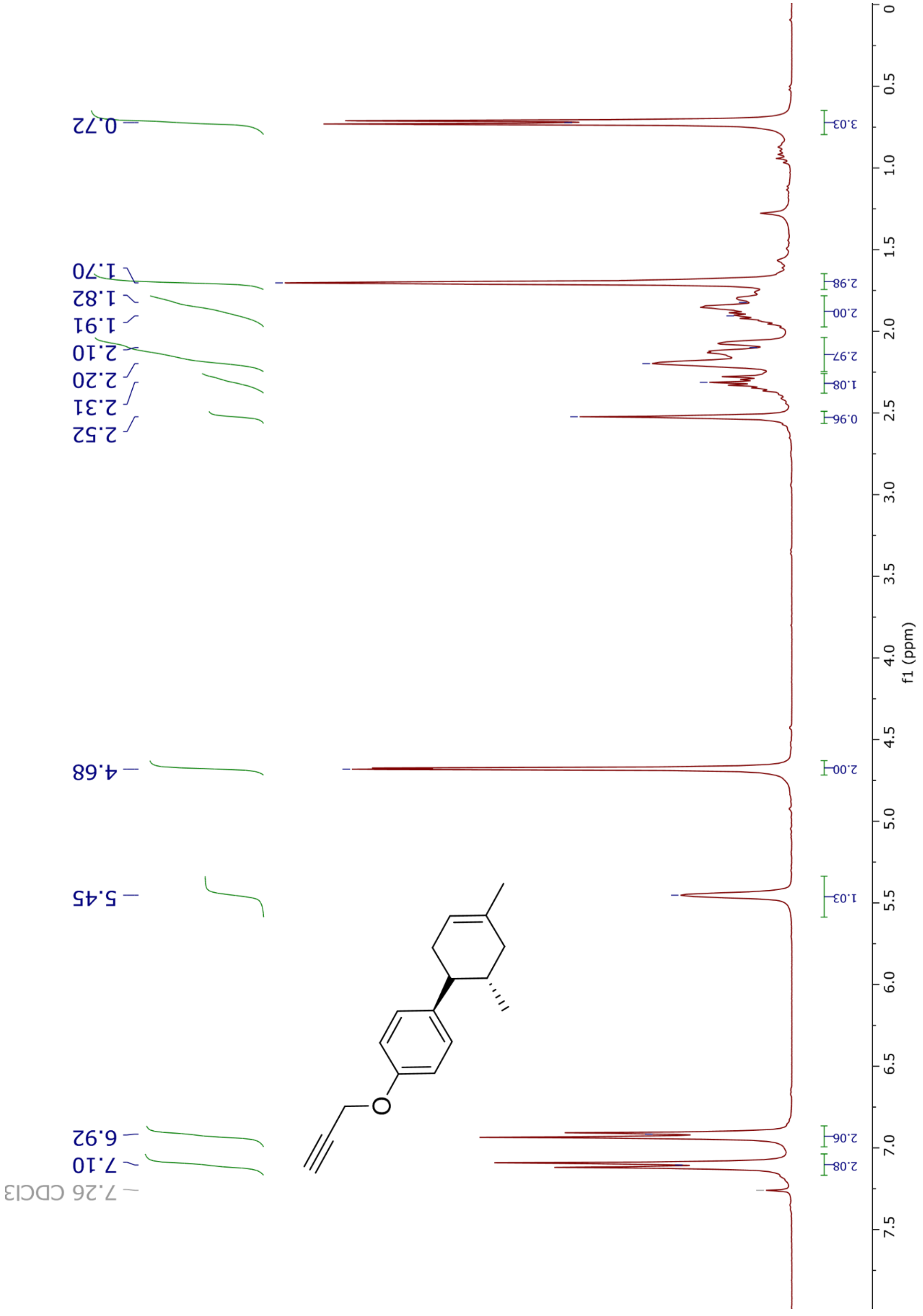



lirun, S#9
((1S,2S)-4'-methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)(thiophen-2-yl)methanone
7.54
7.10
7.00
6.79
4.77
3.92
3.72
2.41
2.02
1.65
1.07
H_3C
O
CH_3
CH_3
O
S
2.01
2.00
1.00
2.01
1.99
2.01
2.99
1.03
1.02
3.00
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

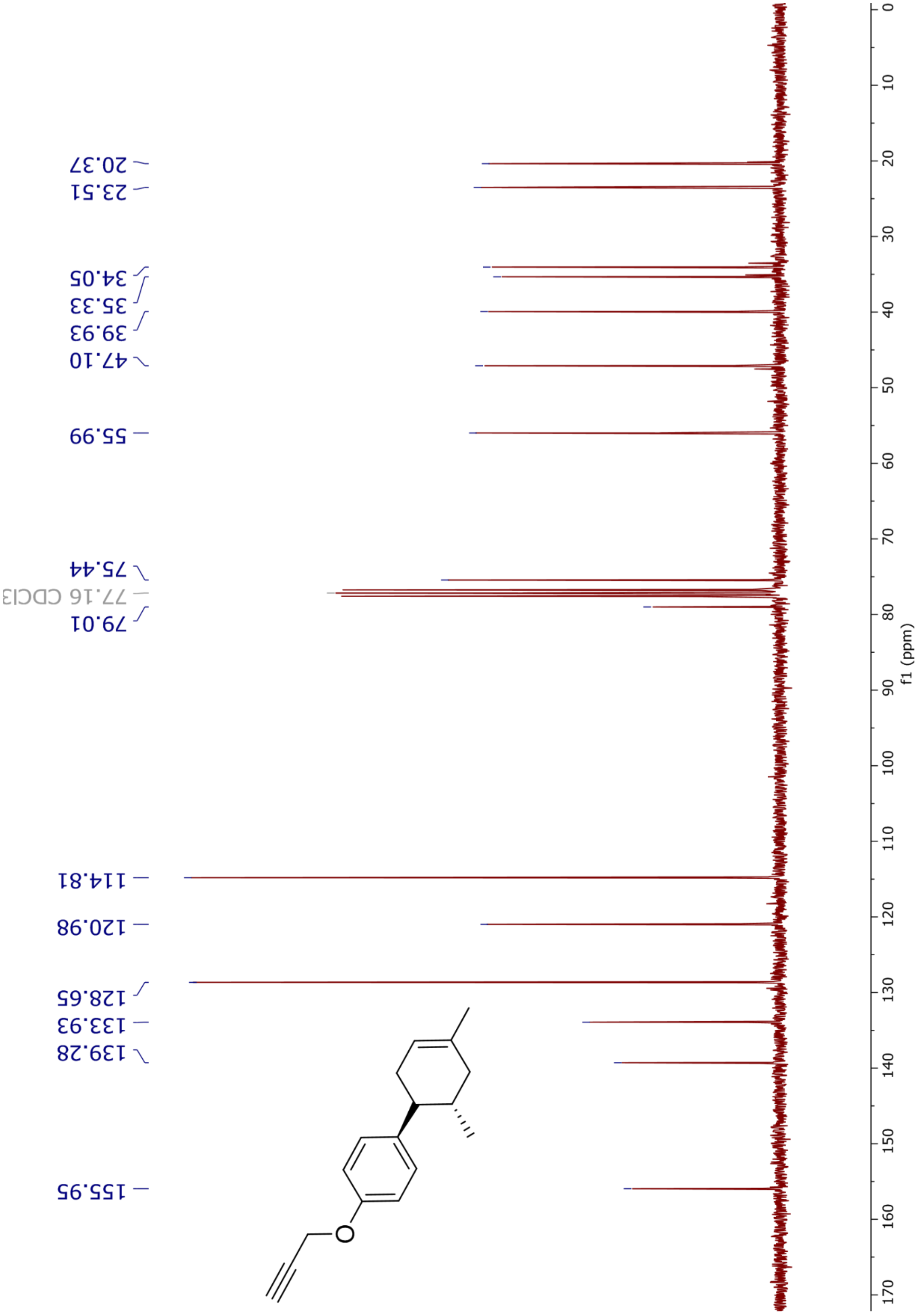
lirun, S#9

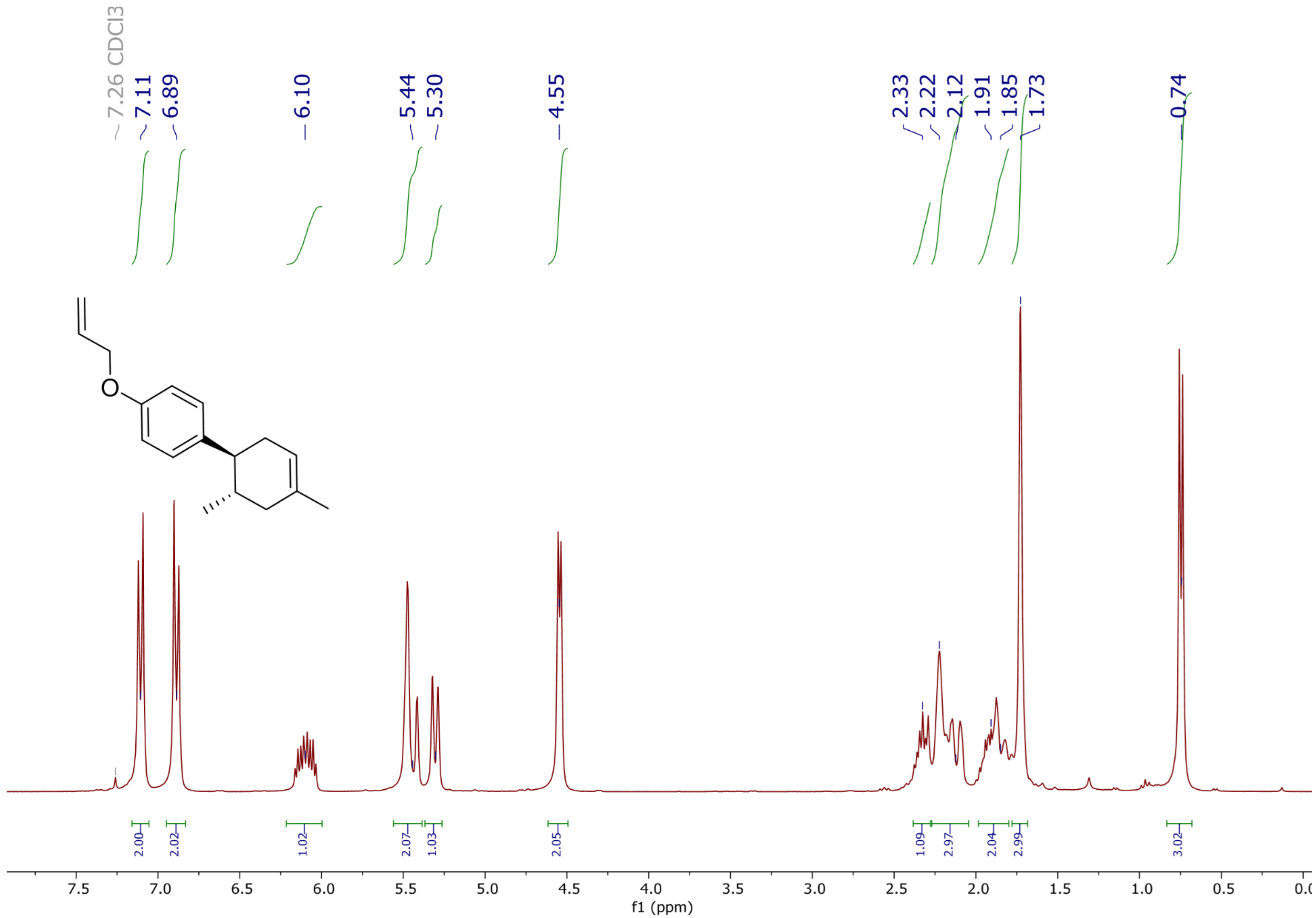
((1S,2S)-4'-methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)(thiophen-2-yl)methanone

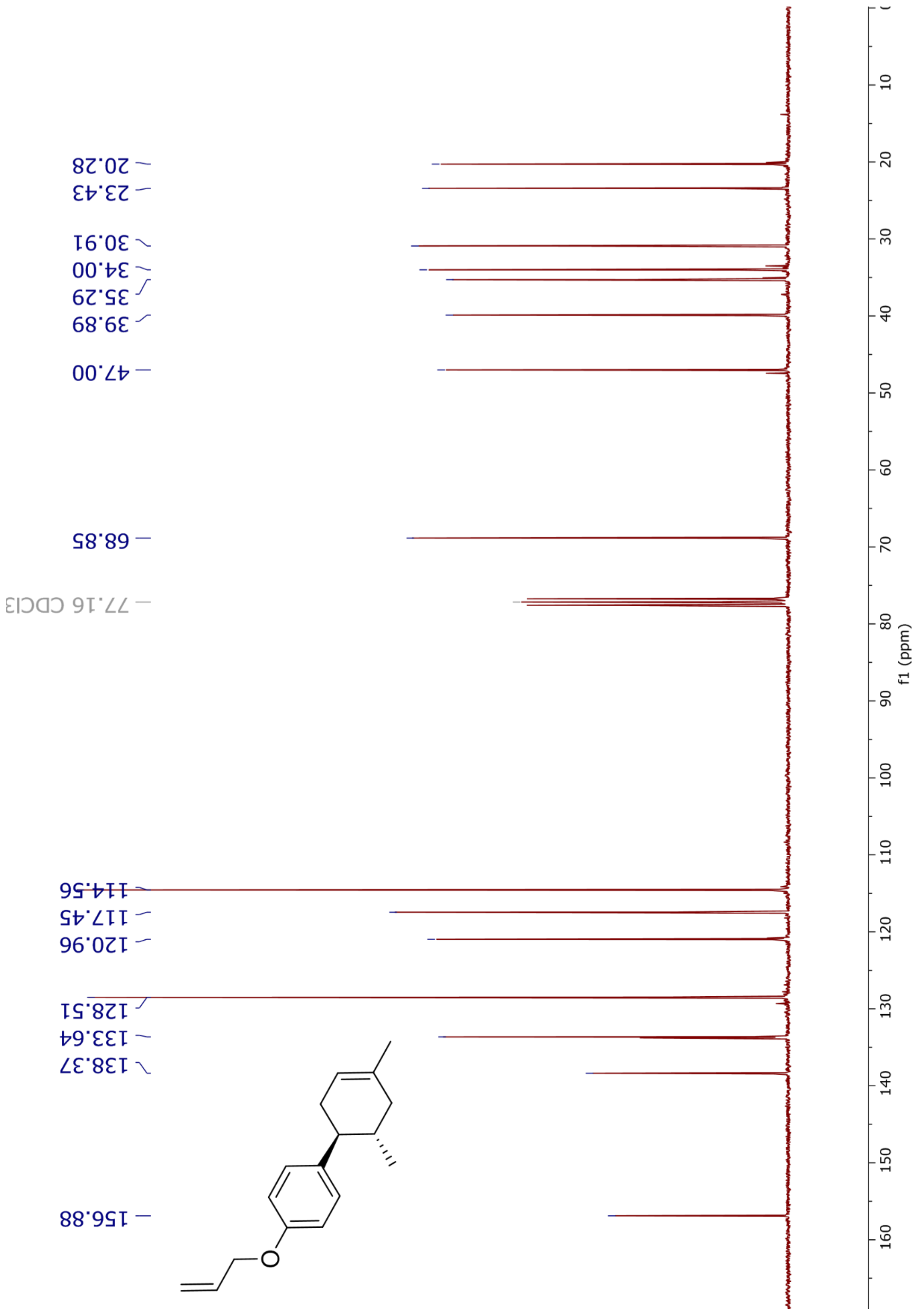


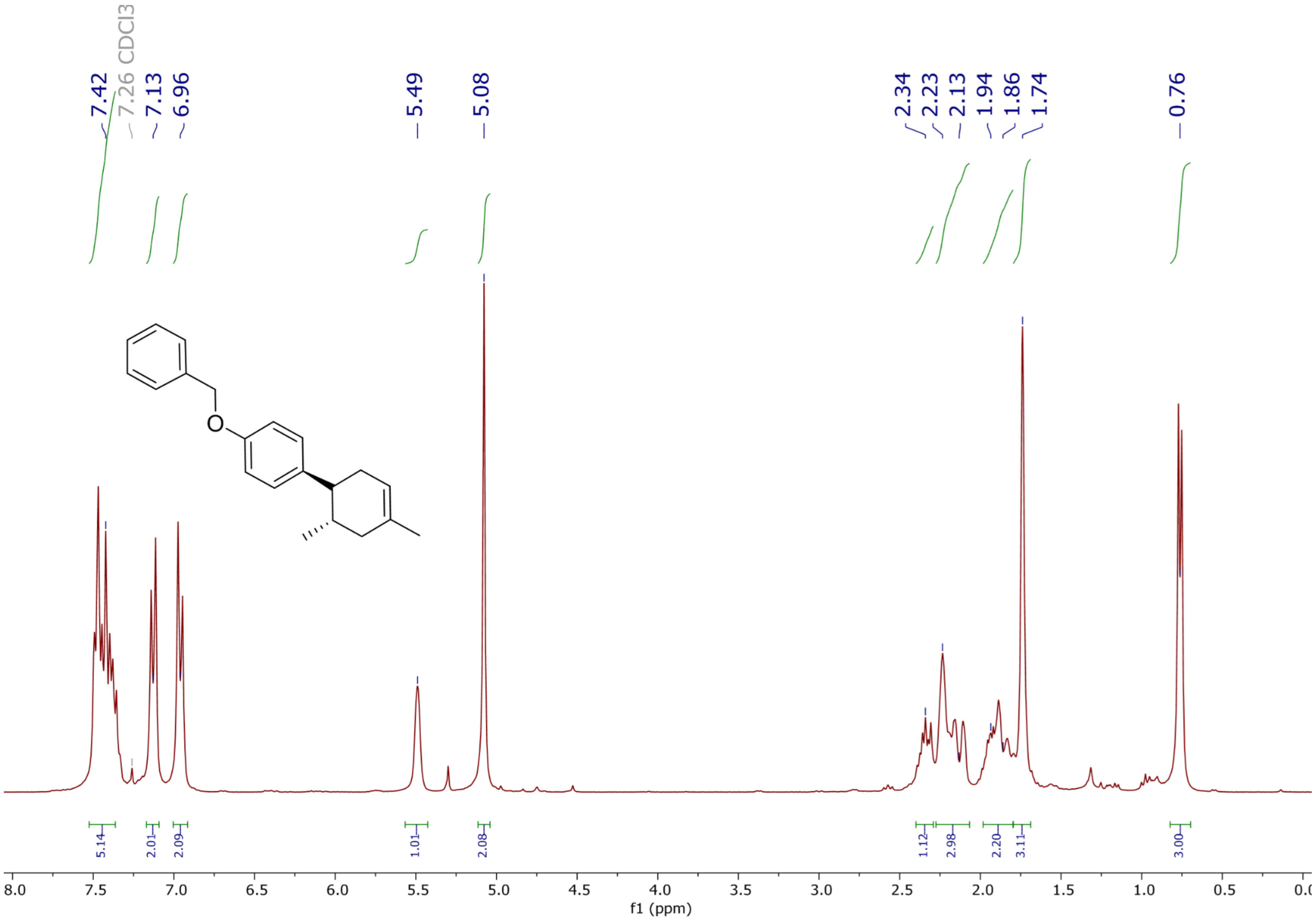


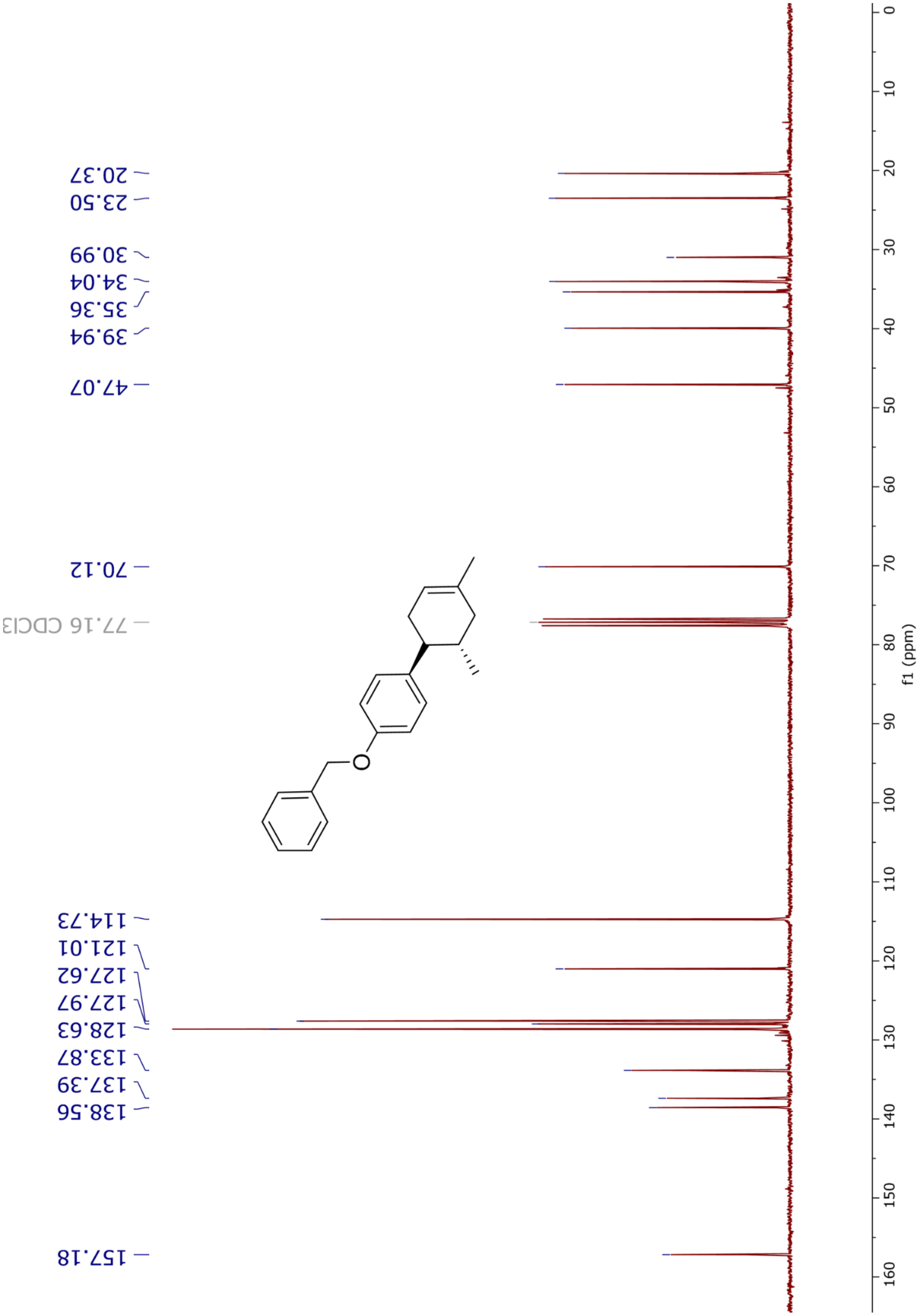
0.72
1.70
1.82
1.91
2.10
2.20
2.31
2.52
4.68
5.45
6.92
7.10
7.26 CDCl3
3.03
2.98
2.00
2.97
1.08
0.96
2.00
1.03
2.06
2.08
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)
O


20.37
23.51
34.05
35.33
39.93
47.10
55.99
75.44
77.16 CDCl3
79.01
114.81
120.98
128.65
133.93
139.28
155.95
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)
O


7.26 CDCl3
7.11
6.89
6.10
5.44
5.30
4.55
2.33
2.22
2.12
1.91
1.85
1.73
0.74
2.00
2.02
1.02
2.07
1.03
2.05
1.09
2.97
2.04
2.99
3.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O


20.28
23.43
30.91
34.00
35.29
39.89
47.00
68.85
77.16 CDCl3
114.56
117.45
120.96
128.51
133.64
138.37
156.88
O
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)


7.42
7.26 CDCl3
7.13
6.96
5.49
5.08
2.34
2.23
2.13
1.94
1.86
1.74
0.76
5.14
2.01
2.09
1.01
2.08
1.12
2.98
2.20
3.11
3.00
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


20.37
23.50
30.99
34.04
35.36
39.94
47.07
70.12
77.16 CDCl3
114.73
121.01
127.62
127.97
128.63
133.87
137.39
138.56
157.18
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

References

1. S. Tojo, S. Toki and S. Takamuku, *J. Org. Chem.*, 1991, **56**, 6240-6243.