Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION FOR:

Visible light-driven cross-coupling reactions of alkyl halides with phenylacetylene derivatives for C(sp^3)-C(sp) bond formation catalyzed by B_{12} complex

Li Chen, Y. Kametani, K. Imamura, T. Abe, Y. Shiota, Yoshio Hisaeda* and Hisashi Shimakoshi*

Department of Chemistry and Biochemistry, Graduate School of Engineering,

Kyushu University, Fukuoka 819-0395, Japan

Chemicals

All solvents and chemicals used in this study were obtained from commercial sources of reagent grade and used as received unless otherwise noted. The cobalamin derivative, heptamethyl cobyrinate perchlorate (**C1**), was synthesized by a previously reported method.[S1] The cobalt complex, Co(III){(C_2C_3)(DO)(DOH)pn}Br_2 (**C2**), (C_2C_3)(DO)(DOH)pn is a deprotonated form of 4,10-dipropyl-5,9-diazatrideca-4,9-diene-3,10-dione dioxime) was prepared according to the literature.[S2] Structure of all substrate, alkynes and organic halides, are summarized in Chart S1.

Measurements

The ^{1}H NMR and ^{13}C NMR spectra were recorded by a Bruker Avance 500 spectrometer at the Centre of Advanced Instrumental Analysis, Kyushu University, and the chemical shifts (in ppm) were referenced relative to the residual solvent peak of $CDCl_3$ at 7.27 ppm. The gas chromatography-mass spectra (GC-MS) were obtained using a Shimadzu GCMS-QP5050A equipped with a J&W Scientific DB-1 column (length: 30m; ID: 0.25 mm, film: 0.25 □m) and helium as the carrier gas. For the measurement, the injector and detector temperatures were 250 ^{o}C, the oven temperature was initially held at 100 ^{o}C for 2 min, then increased to 240 ^{o}C at the rate of 10 ^{o}C/min. Hydrogen gas was analyzed by a Shimadzu 14-B gas chromatograph equipped with SHINCARBON ST packed column (Shimadzu GLC). The UV-vis absorption spectra were obtained by a Hitachi U-3300 spectrophotometer at room temperature. The ESR spectra were measured using a Bruker EMX-Plus X-band spectrometer at room temperature. The settings for the ESR measurements were a frequency of 9.87 GHz, power of 1.0 mW, center field of 3515 G, sweep width of 150 G, modulation amplitude of 1.0 G, time constant of 40 ms, and sweep time of 20 s. The light emitting diode (LED PER-AMP, λ=448 nm) purchased from TechnoSigma were used as the light source for the light irradiation experiments. The high resolution-mass spectra of new compounds (**1e**, **2c**, **2e**, **2g**, **2h**, and **2i**) were obtained on a JEOL JMS-700 using *m*-nitrobenzylalcohol as a matrix.

General procedure for catalytic reaction by the B_{12}

A 10 mL methanol solution of the B_{12} complex (**C1**) (1.0×10^{-4} M) (1 mol%), [Ir(dtbbpy)$(ppy)_3$][PF_6] (**P1**) (1.0×10^{-5} M), *i*-Pr_2NEt (0.1 M), R-X substrate (2.0×10^{-2} M), alkyne substrate (1.5×10^{-1} M) and diphenyl as the internal standard was degassed by N_2

gas, then irradiated using an LED (λ=448 nm) as the light source with stirring. After a 6 hour irradiation, the resulting solution was passed through a short silica-gel column to remove the B_{12} complex then analyzed by GC-MS. The yields of the products were calculated by comparison to the peak area ratio of the internal standard. All the products were isolated by silica gel column chromatography (Kanto Chemicals, 60N) with the CH_2Cl_2/hexane eluent and identified by GC-MS, and ^1H and ^{13}C NMR.

ESR spin-trapping experiment

The ESR spectra for the DMPO spin-adducts were observed after 4 hours of VIS-light irradiation of reaction solution, [B_{12} complex (**C1**)]=1.0 × 10^{-4} M; [Ir PS(**P1**)]=1.0×10^{-5} M; [*i*-Pr_2NEt]=0.1 M; [phenethyl bromide]=2.0×10^{-2} M; [phenylacetylene]=1.5×10^{-1} M; [DMPO]=6.0×10^{-1} M under N_2 at room temperature. The settings for the ESR measurements were a frequency of 9.78 GHz, power of 1.0 mW, a center field of 3515 G, a sweep width of 150 G, a modulation amplitude of 3.0 G, a time constant of 40 ms, and a sweep time of 20 s.

Control reaction using *n*-Bu_3SnH/AIBN

The control experiment using *n*-Bu_3SnH/AIBN was performed. A 1ml benzene solution of *n*-Bu_3SnH (1.4×10^{-3} M)/AIBN (1.2×10^{-4} M) was added dropwise to a 9 mL benzene solution of phenethyl bromide (1.4 × 10^{-2} M), phenylacetylene (1.4 × 10^{-1} M), and diphenyl as the internal standard. Subsequently, the mixture was refluxed for 75 min under N_2. After cooling to room temperature, the resulting solution was passed through a short silica-gel column, then analyzed by GC-MS. The yields of the products were calculated by comparison to the peak area ratio of the internal standard.

Catalyst recovery

After the photocatalytic reaction, small amount of KCN was added to form the dicyano form of B_{12} catalyst, and determined the concentration of B_{12} complex using the absorbance at 590 nm ascribed to α-band of the B_{12} complex.

Theoretical calculations.

Geometry optimizations were performed using the hybrid (Hartree-Fock/DFT) B3LYP functional[S4,S5] combined with the 6-31G** basis set.[S6] The RB3LYP functional was used

for the closed-shell molecules. Solvent effects are estimated for methanol by using the PCM method. The Gaussian 09 program[S6] was used for all calculations.

References

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S3. D. J. Becke, *Chem. Phys.* 1993, **98**, 5648-5652.

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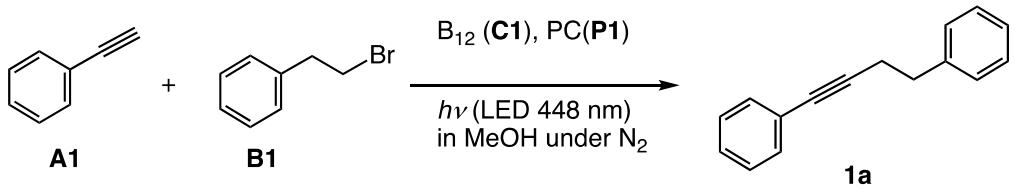
S5. W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* 1972, **56,** 2257-2261.

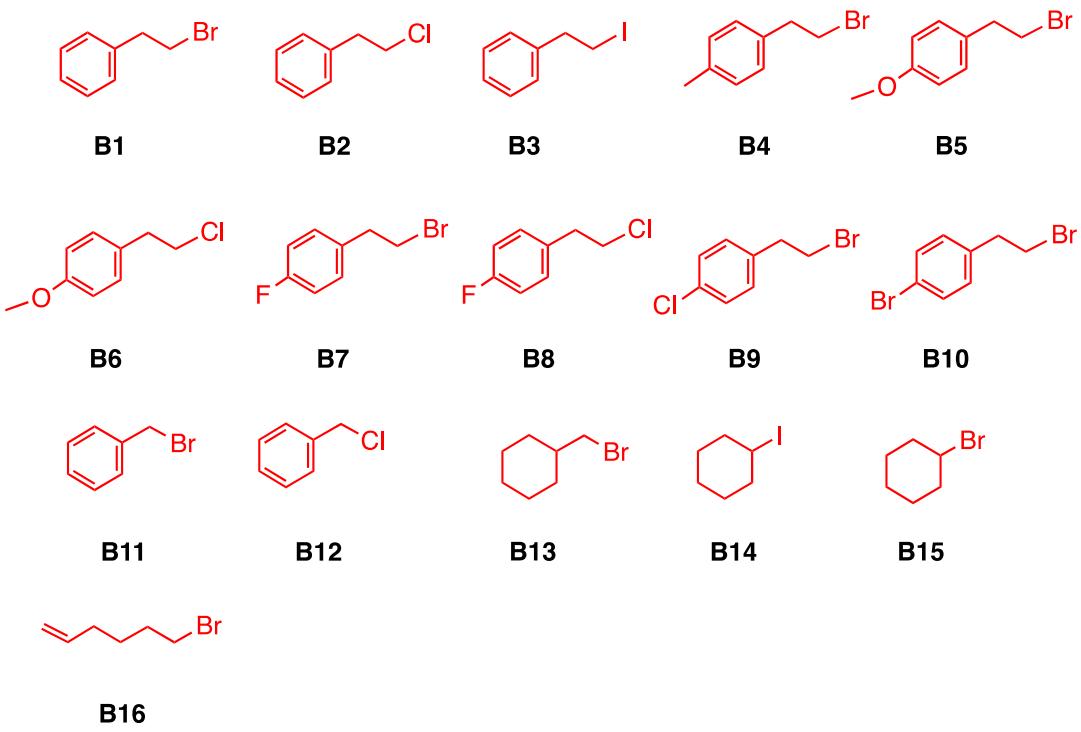
S6. Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016. Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; 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, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009

Table S1 Optimization of reaction conditions



A1 **B1** **1a**

Entry	**C1**/10^{-4} M	PC/10^{-4} M	*i*-Pr_2NEt/M	**A1**/10^{-2} M	**B1**/10^{-2} M	Reaction time	Yield of **1a**/%
1	1	0.1	0.1	15	2	6	89
2	1.5	0.2	0.1	10	1.5	6	68
3	1.5	0.5	0.1	10	1.5	6	50
4	1.5	1.0	0.1	10	1.5	6	37
5	1.5	1.5	0.1	10	1.5	6	24
6	1	0.1	0.05	15	2	6	75
7	1	0.1	0.1	20	2	6	91
8	1	0.1	0.1	10	2	6	71
9	1	0.13	0.1	10	1.5	6	87
10	1	0.1	0.1	15	2	11	67



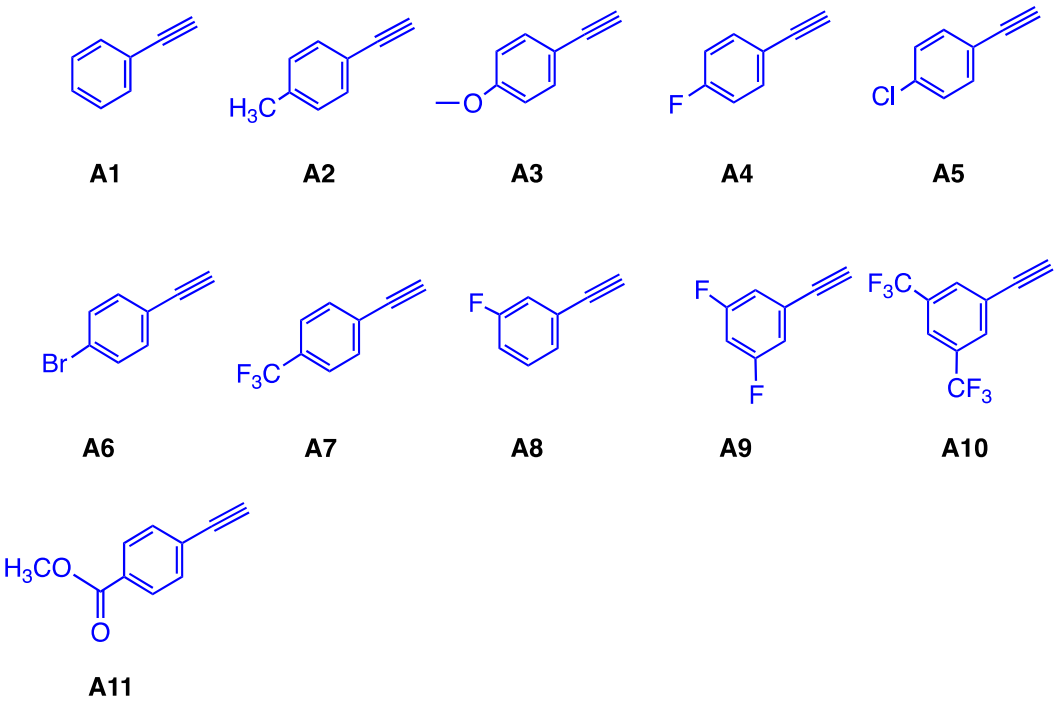


Chart S1. Structure of substrate phenylacetylenes and organic halides.

Figure S1. Experiment set-up image of photo-driven the B_{12} derivative (**C1**)-catalyzed the alkynylation.

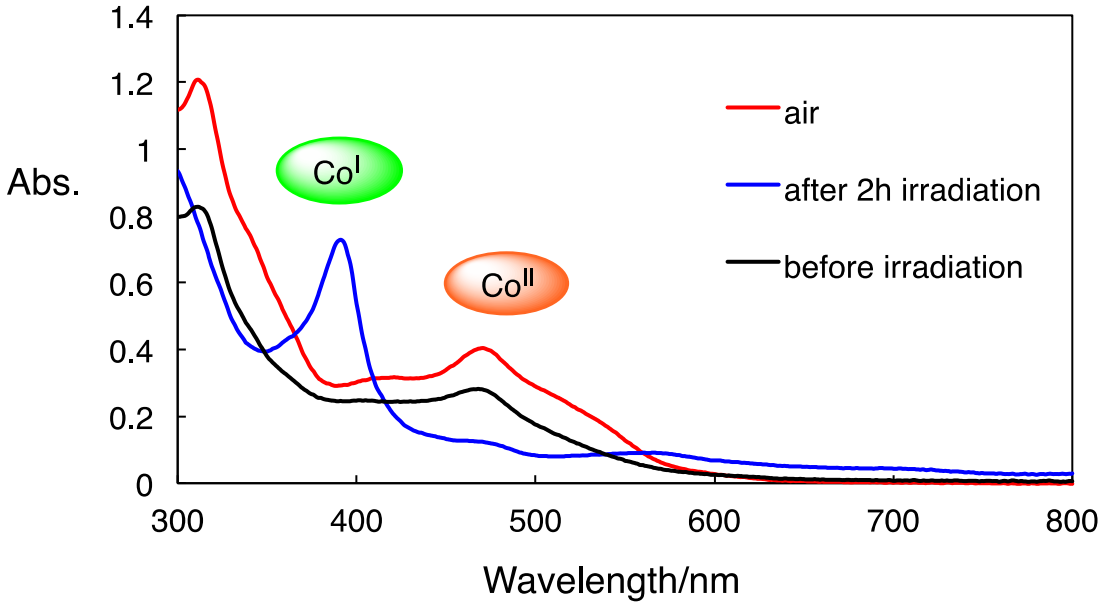


Figure S2. UV-vis spectral change of the B_{12} derivative (**C1**) during visible light irradiation in the presence of $[Ir(dtbbpy)(ppy)_2]PF_6$ (**P1**) and *i*-Pr_2NEt in MeOH under N_2.

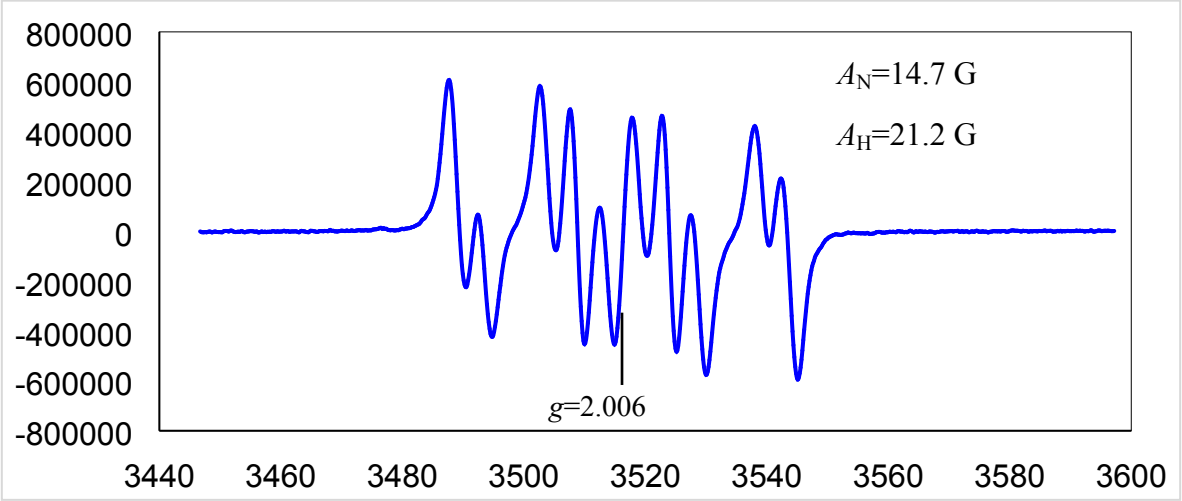


Figure S3. ESR spectrum observed during the photo-catalytic reaction in MeOH: [B_{12} complex (**C1**)]=1.0 × 10^{-4} M; [Ir PS(**P1**)]=1.0×10^{-5} M; [*i*-Pr_2NEt]=0.1 M; [phenethyl bromide]=2.0×10^{-2} M; [phenylacetylene]=1.5×10^{-1} M; [DMPO]=6.0×10^{-1} M, 4h, under N_2.

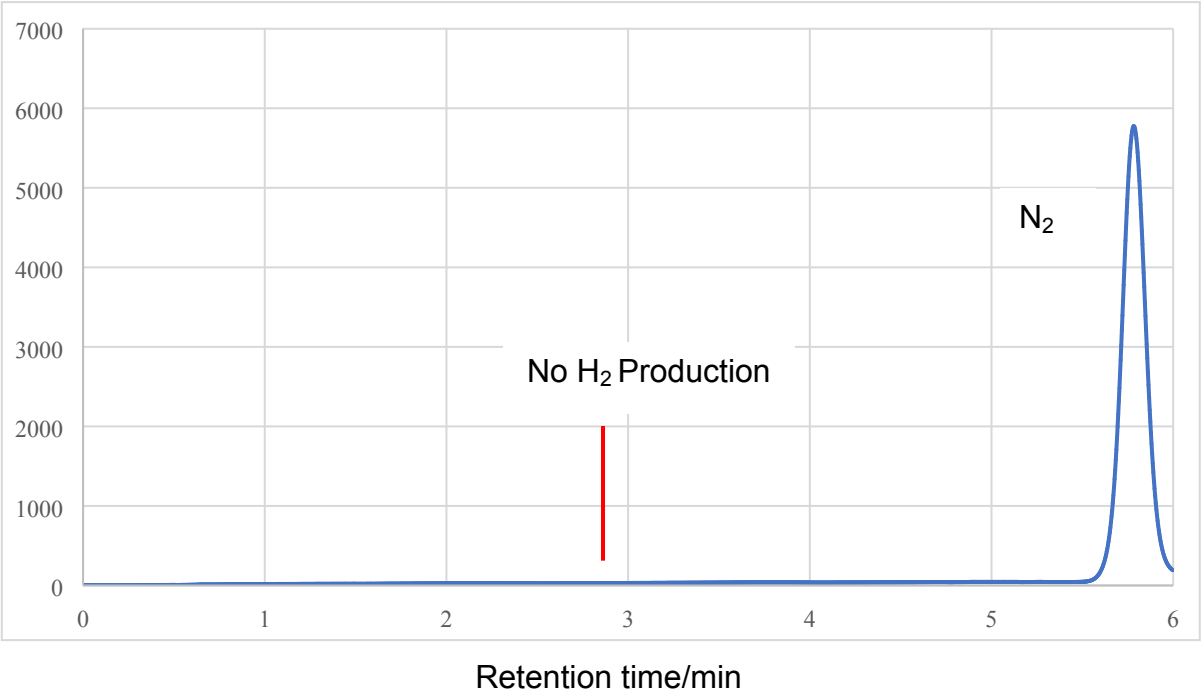
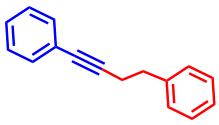


Figure S4. GC of photocatalytic reaction catalyzed by the B_{12} complex (**C1**) under N_2 at room temperature after 6 hours visible light irradiation.

Product data

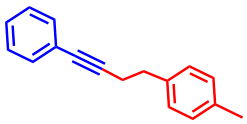
1,4-Diphenyl-1-butyne (1a)



Compound **1a** was prepared according to the general procedure using phenethyl bromide and phenylacetylene as reactant.

Colorless oil, yield (89%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.68 (t, 2H), 2.91 (t, 2H), 7.23-7.36 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.67, 35.18, 81.30, 89.48, 123.84, 126.29, 127.59, 128.17, 128.36, 128.52, 131.51, 140.69; GC-MS: M^+=206.

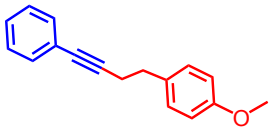
1-Methyl-4-(4-phenylbut-3-yn-1-yl)benzene (1b)



Compound **1b** was prepared according to the general procedure using 4-methylphenethyl bromide and ethynylbenzene as reactant.

Colorless oil, yield (75%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.34 (s, 3H), 2.67 (t, 2H), 2.89 (t, 2H), 7.13 (d, 2H), 7.16 (d, 2H), 7.23-7.28 (m, 2H), 7.39 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=20.99, 21.78, 34.79, 81.26, 89.65, 123.97, 127.54, 128.15, 128.37, 129.04, 131.52, 135.74, 137.67; GC-MS: M^+=220.

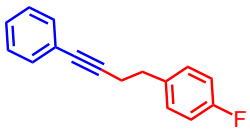
1-Methoxy-4-(4-phenylbut-3-yn-1-yl)benzene (1c)



Compound **1c** was prepared according to the general procedure using 4-methoxyphenethyl bromide and ethynylbenzene as reactant.

Colorless oil, yield (77%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.67 (t, 2H), 2.88 (t, 2H), 3.81 (s, 3H), 6.86 (d, 2H), 7.20 (d, 2H), 7.26-7.29 (m, 2H), 7.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.94, 34.32, 55.24, 81.31, 89.63, 113.82, 123.93, 127.55, 128.16, 129.45, 131.52, 132.88, 158.18; GC-MS: M^+=236.

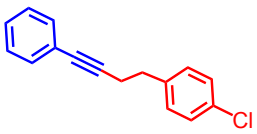
1-Fluoro-4-(4-phenylbut-3-yn-1-yl)benzene (1d)



Compound **1d** was prepared according to the general procedure using 4-fluorophenethyl bromide and ethynylbenzene as reactant.

Colorless oil, yield (72%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.67 (t, 2H), 2.89 (t, 2H), 7.00 (t, 2H), 7.23-7.27 (m, 4H), 7.36 (t, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.50, 34.07, 81.37, 88.69, 114.77, 123.55, 127.41, 127.95, 129.73, 131.25, 136.09, 160.41, 162.35; GC-MS: M^+=224.

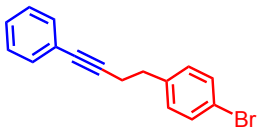
1-Chloro-4-(4-phenylbut-3-yn-1-yl)benzene (1e)



Compound **1e** was prepared according to the general procedure using 4-chlorophenethyl bromide and ethynylbenzene as reactant.

White solid, yield (50%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.69 (t, 2H), 2.90 (t, 2H), 7.23 (t, 2H), 7.27-7.30 (m, 4H), 7.37 (t, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.25, 34.19, 81.43, 88.71, 123.49, 127.44, 127.95, 128.21, 129.66, 131.25, 131.88, 138.83; GC-MS: M^+=240; HR-MS (EI, *m*/*z*): 240.0708.

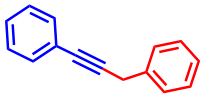
1-Bromo-4-(4-phenylbut-3-yn-1-yl)benzene (1f)



Compound **1f** was prepared according to the general procedure using 4-bromophenethyl bromide and ethynylbenzene as reactant.

White solid, yield (32%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.67 (t, 2H), 2.87 (t, 2H), 7.16 (t, 2H), 7.24-7.36 (m, 4H), 7.43 (t, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.44, 34.51, 81.69, 88.93, 120.17, 123.72, 127.71, 128.21, 130.32, 131.43, 131.51, 139.60; GC-MS: M^+=284.

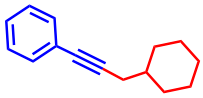
1,3-Diphenyl-1-propyne (1g)



Compound **1g** was prepared according to the general procedure using benzyl bromide and ethynylbenzene as reactant.

Colorless oil, yield (46%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=3.86 (s, 2H), 7.27-7.37 (m, 5H), 7.43-7.47 (m, 5H),; ^{13}C NMR (125 MHz, $CDCl_3$): δ=26.01, 82.95, 87.78, 124.00, 126.88, 128.05, 128.22, 128.47, 128.80, 131.90, 137.06; GC-MS: M^+=192.

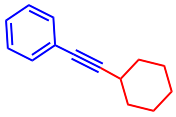
(3-Cyclohexylprop-1-yn-1-yl)benzene (1h)



Compound **1h** was prepared according to the general procedure using (Bromomethyl)cyclohexane and ethynylbenzene as reactant.

Colorless oil, yield (60%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.03-1.32 (m, 5H), 1.57 (m, 1H), 1.66-1.76 (m, 3H), 1.86 (d, 2H), 2.30 (d, 2H), 7.25-7.29 (m, 3H), 7.39-7.41 (m, 2H),; ^{13}C NMR (125 MHz, $CDCl_3$): δ=25.93, 26.07, 26.96, 32.55, 37.30, 81.23, 89.08, 123.96, 127.13, 127.89, 131.30; GC-MS: M^+=198.

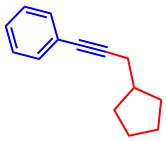
(Cyclohexylethynyl)benzene (1i)



Compound **1i** was prepared according to the general procedure using Bromocyclohexane and ethynylbenzene as reactant.

Colorless oil, yield (31%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.36 (m, 3H), 1.55 (m, 3H), 1.77 (m, 2H), 1.89 (m, 2H), 2.59 (m, 1H), 7.26-7.28 (m, 3H), 7.39-7.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=25.16, 26.22, 29.95, 33.01, 80.84, 94.69, 124.48, 127.61, 128.37, 131.83; GC-MS: M^+=184.

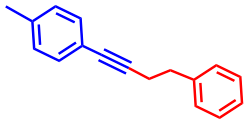
(3-Cyclopentylprop-1-yn-1-yl)benzene (1j)



Compound **1j** was prepared according to the general procedure using 1-bromo-6-hexene and ethynylbenzene as reactant.

Colorless oil, yield (61%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.34-1.38 (m, 2H), 1.67 (m, 4H), 1.85 (m, 2H), 2.16 (m, 1H), 2.41 (d, 2H), 7.27-7.29 (m, 4H), 7.39-7.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=25.06, 29.44, 31.80, 38.93, 123.97, 125.73, 127.14, 127.90, 131.31; GC-MS: M^+=184.

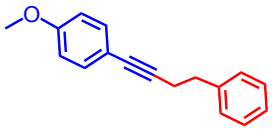
1-Methyl-4-(4-phenylbut-1-yn-1-yl)benzene (2a)



Compound **2a** was prepared according to the general procedure using phenethyl bromide and 4-ethynyltoluene as reactant.

Colorless oil, yield (73%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.31 (s, 3H), 2.67 (t, 2H), 2.91 (t, 2H), 7.07 (d, 2H), 7.19-7.31 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.35, 21.67, 35.29, 81.37, 88.68, 120.84, 126.26, 128.35, 128.52, 128.93, 131.40, 137.56, 140.79; GC-MS: M^+ = 220.

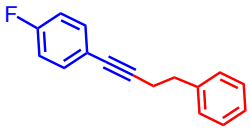
1-Methoxy-4-(4-phenylbut-1-yn-1-yl)benzene (2b)



Compound **2b** was prepared according to the general procedure using phenethyl bromide and 4-ethynylanisole as reactant.

Colorless oil, yield (70%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.65 (t, 2H), 2.89 (t, 2H), 3.77 (s, 1H), 6.77 (d, 2H), 7.18-7.28 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.91, 35.60, 55.50, 81.32, 88.14, 114.12, 116.36, 126.51, 128.61, 128.78, 133.11, 141.10, 159.41; GC-MS: M^+=236.

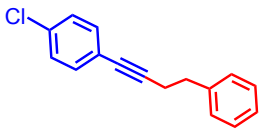
1-Fluoro-4-(4-phenylbut-1-yn-1-yl)benzene (2c)



Compound **2c** was prepared according to the general procedure using phenethyl bromide and 1-ethynyl-4-fluorobenzene as reactant.

Colorless oil, yield (83%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.67 (t, 2H), 2.91 (t, 2H), 6.96 (d, 2H), 7.21-7.34 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.30, 34.90, 80.07, 88.88, 115.03, 119.71, 126.08, 128.14, 133.08, 140.40, 160.91, 162.89; GC-MS: M^+=224; HR-MS (EI, *m*/*z*): 224.0998.

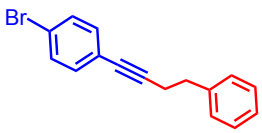
1-Chloro-4-(4-phenylbut-1-yn-1-yl)benzene (2d)



Compound **2d** was prepared according to the general procedure using phenethyl bromide and 1-chloro-4-ethynylbenzene as reactant.

Colorless oil, yield (82%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.70 (t, 2H), 2.93 (t, 2H), 7.26-7.32 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.62, 35.05, 80.32, 90.56, 122.39, 126.36, 128.39, 128.49, 132.74, 133.57, 140.56; GC-MS: M^+=240.

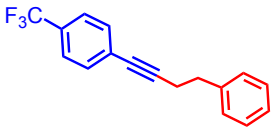
1-Bromo-4-(4-phenylbut-1-yn-1-yl)benzene (2e)



Compound **2e** was prepared according to the general procedure using phenethyl bromide and 1-ethynyl-4-bromobenzene as reactant.

Colorless oil, yield (85%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.70 (t, 2H), 2.93 (t, 2H), 7.23-7.32 (m, 7H), 7.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.65, 35.04, 80.40, 90.79, 121.72, 122.87, 126.37, 128.41, 128.50, 131.44, 133.00, 140.56; GC-MS: M^+=284; HR-MS (EI, *m*/*z*): 284.0188.

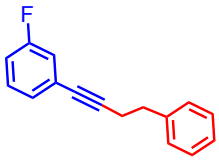
1-Trifluoromethyl-4-(4-phenylbut-1-yn-1-yl)benzene (2f)



Compound **2f** was prepared according to the general procedure using phenethyl bromide and 4-ethynyl-α,α,α-trifluorotoluene as reactant.

White solid, yield (79%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.72 (t, 2H), 2.94 (t, 2H), 7.23-7.35 (m, 5H), 7.46 (d, 2H), 7.53 (d, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.62, 34.94, 80.32, 92.33, 125.10, 126.43, 127.76, 128.43, 128.50, 129.32, 129.59, 131.75, 140.44; GC-MS: M^+ = 274.

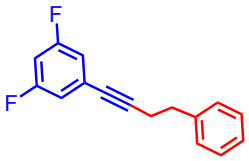
1-Fluoro-3-(4-phenylbut-1-yn-1-yl)benzene (2g)



Compound **2g** was prepared according to the general procedure using phenethyl bromide and 1-ethynyl-3-fluorobenzene as reactant.

Colorless oil, yield (77%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.69 (t, 2H), 2.92 (t, 2H), 6.97 (m, 1H), 7.06 (m, 1H), 7.14 (m, 1H), 7.20-7.33 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.56, 35.00, 80.31, 90.64, 114.82, 118.42, 125.75, 126.36, 127.37, 128.40, 129.63, 140.52, 161.41, 163.37; GC-MS: M^+=224; HR-MS (EI, *m*/*z*): 224.1000.

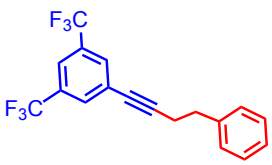
1, 3-Difluoro-5-(4-phenylbut-1-yn-1-yl)benzene (2h)



Compound **2h** was prepared according to the general procedure using phenethyl bromide and 1-ethynyl-3,5-difluorobenzene as reactant.

Colorless oil, yield (90%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.72 (t, 2H), 2.94 (t, 2H), 6.76 (m, 1H), 6.88 (m, 2H), 7.28-7.37 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.23, 34.57, 79.26, 91.66, 103.50, 114.09, 126.18, 128.17, 140.07, 161.37, 163.35; GC-MS: M^+=242; HR-MS (EI, *m*/*z*): 242.0907.

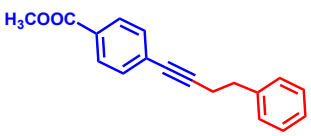
3,5-Trifluoromethyl-4-(4-phenylbut-1-yn-1-yl)benzene (2i)



Compound **2i** was prepared according to the general procedure using phenethyl bromide and 1-ethynyl-3,5-(trifluoromethyl)benzene as reactant.

Colorless oil, yield (88%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.74 (t, 2H), 2.95 (t, 2H), 7.25-7.36 (m, 5H), 7.78 (d, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.78, 34.99, 79.21, 93.91, 121.23, 122.20, 124.37, 126.47, 126.82, 128.75, 131.72, 131.94, 132.20, 140.44; GC-MS: M^+=342; HR-MS (EI, *m*/*z*): 342.0836.

Methyl 4-(4-phenyl-1-butynyl)benzoate (2j)



Compound **2j** was prepared according to the general procedure using phenethyl bromide and methyl 4-ethynylbenzonate as reactant.

White solid, yield (86%); ^{1}H NMR (500 MHz, $CDCl_3$): δ=3.21 (t, 2H), 3.62 (t, 2H), 3.98 (s, 3H), 7.26-7.39 (m, 5H), 7.65 (d, 2H), 8.08 (d, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=32.98, 39.64, 52.48, 82.10, 91.60, 126.34, 127.11, 128.83, 129.78, 130.84, 131.84, 132.66, 139.12, 166.39; GC-MS: M^+=264.

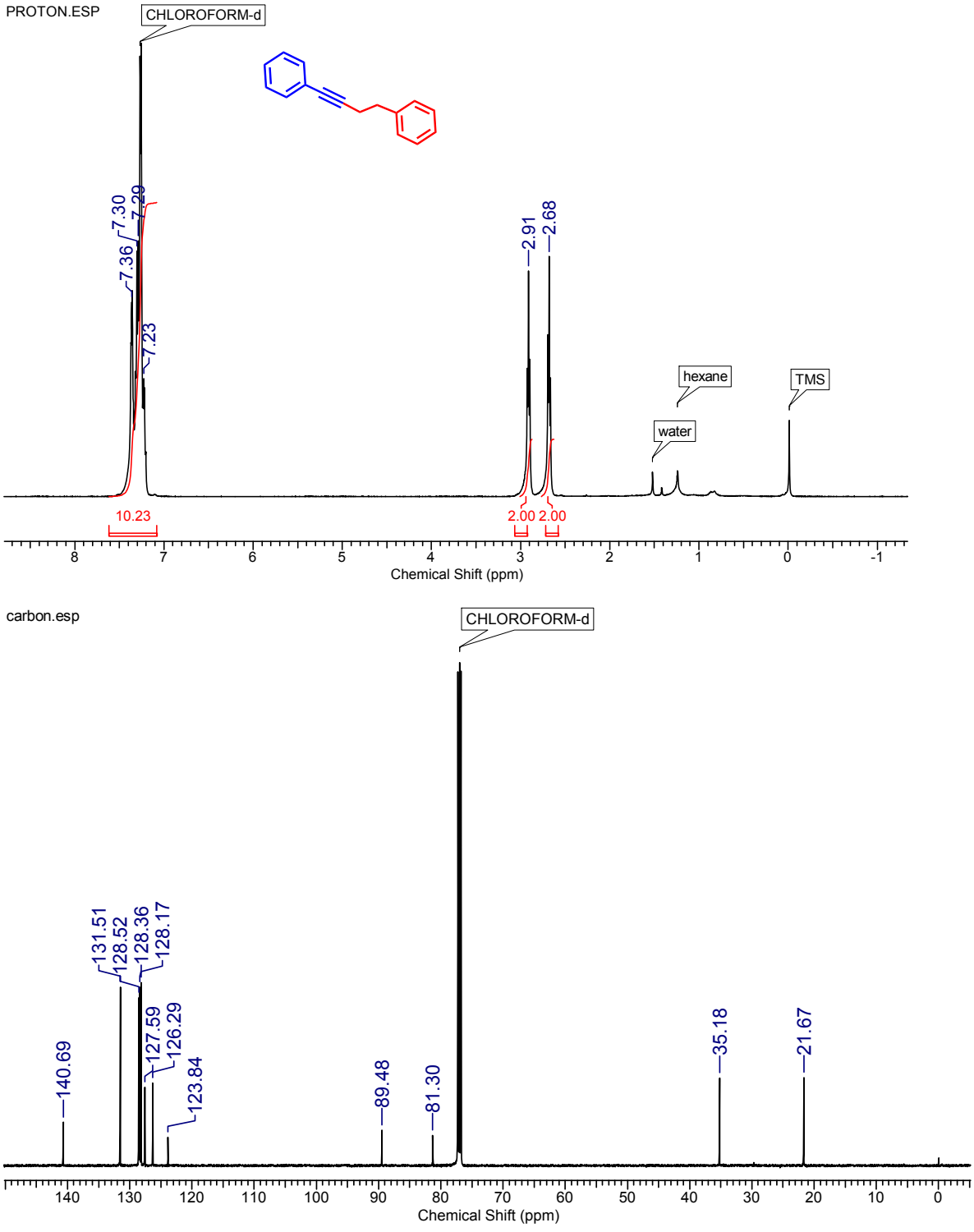


Figure S5. ^{1}H and ^{13}C NMR spectra of **1a** in $CDCl_3$.

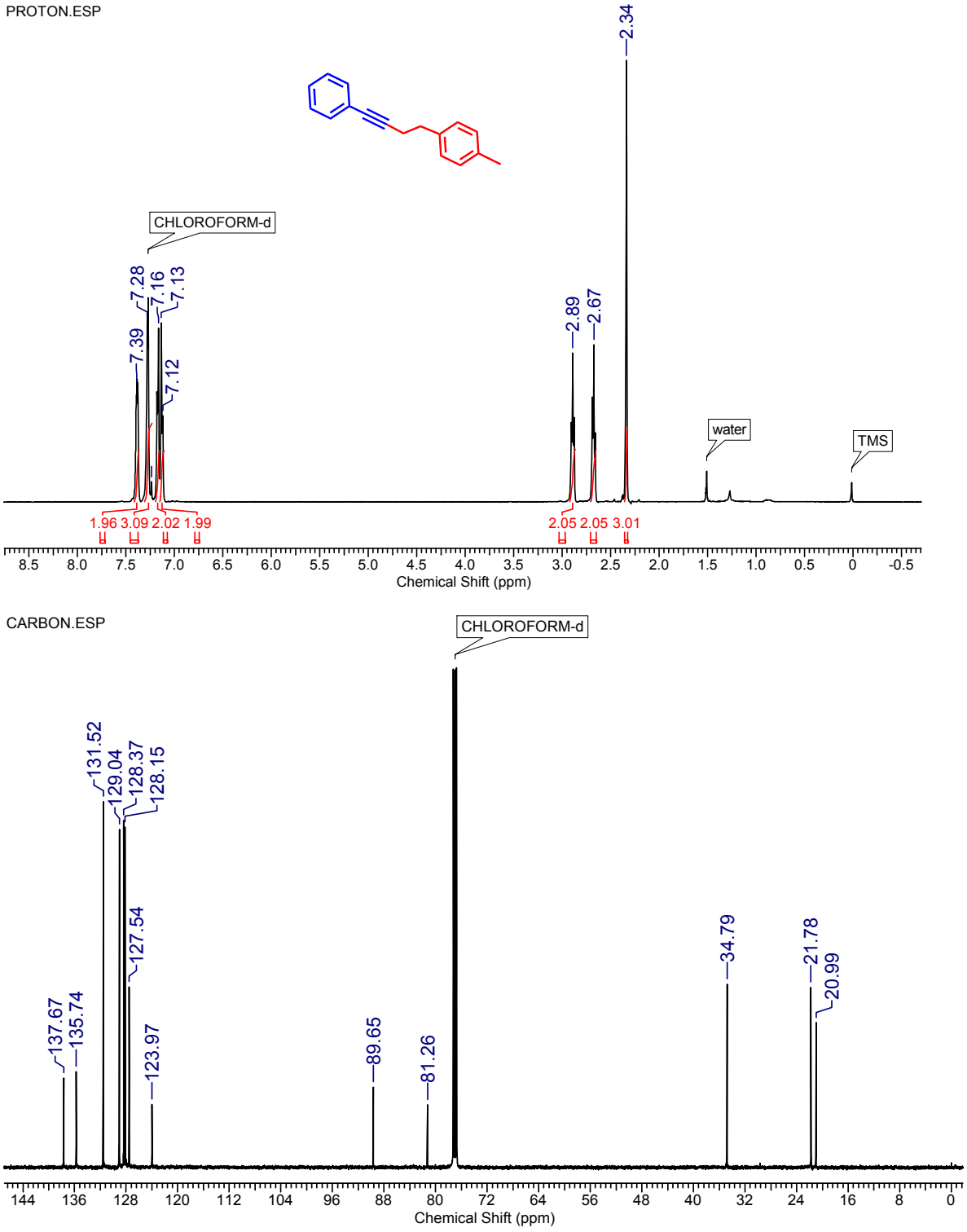


Figure S6. ^{1}H and ^{13}C NMR spectra of **1b** in $CDCl_3$.

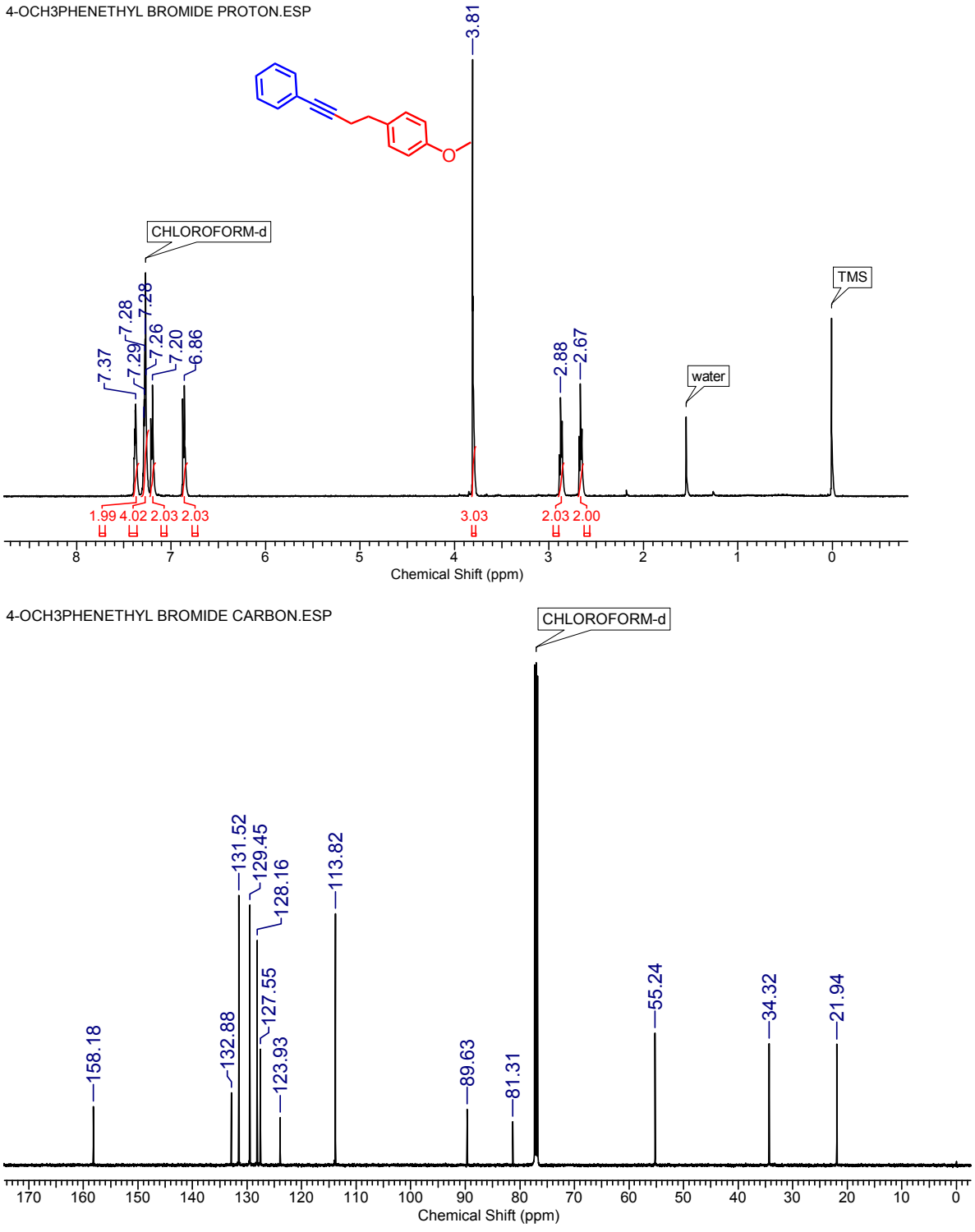


Figure S7. ^{1}H and ^{13}C NMR spectra of **1c** in $CDCl_3$.

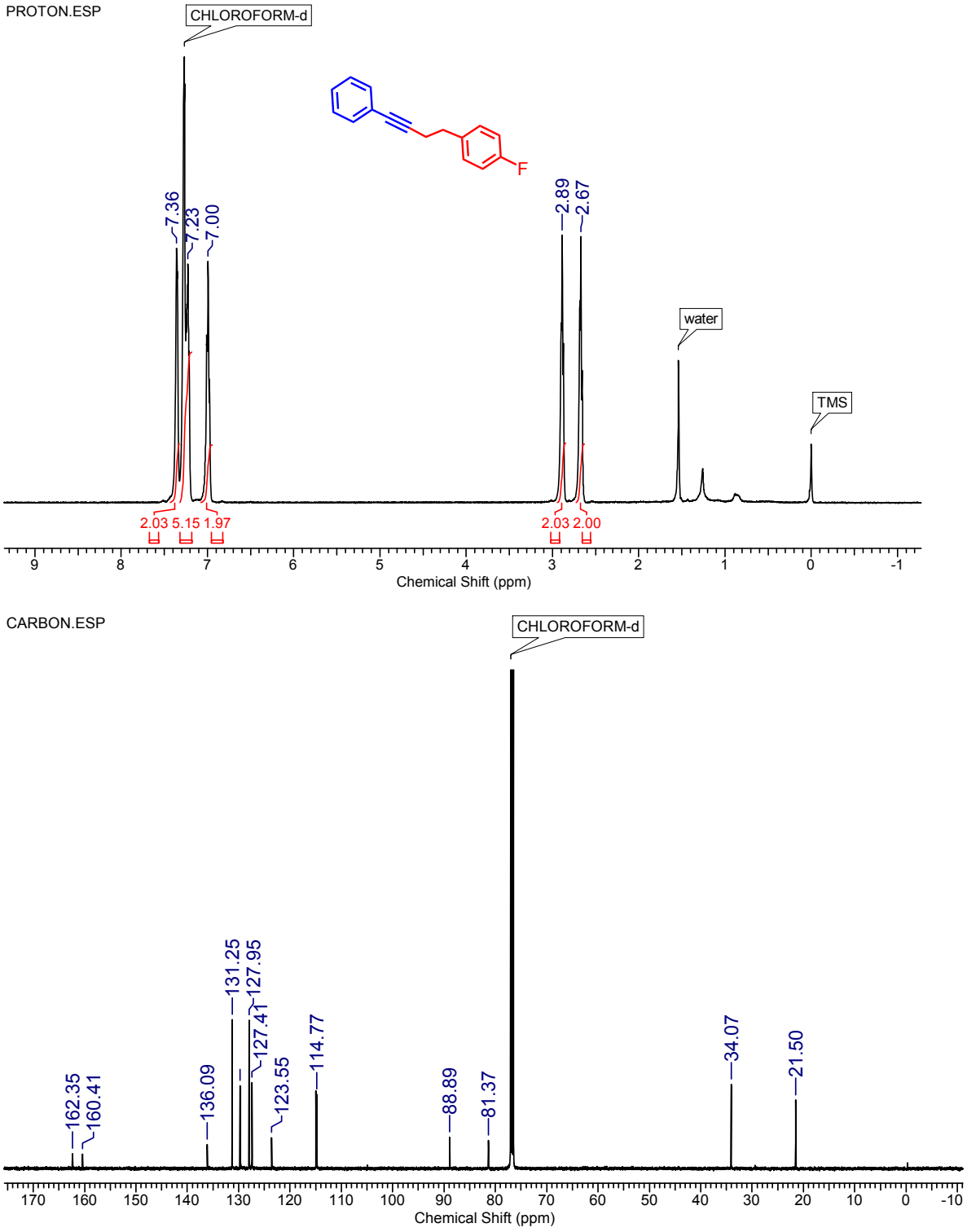


Figure S8. ^{1}H and ^{13}C NMR spectra of **1d** in $CDCl_3$.

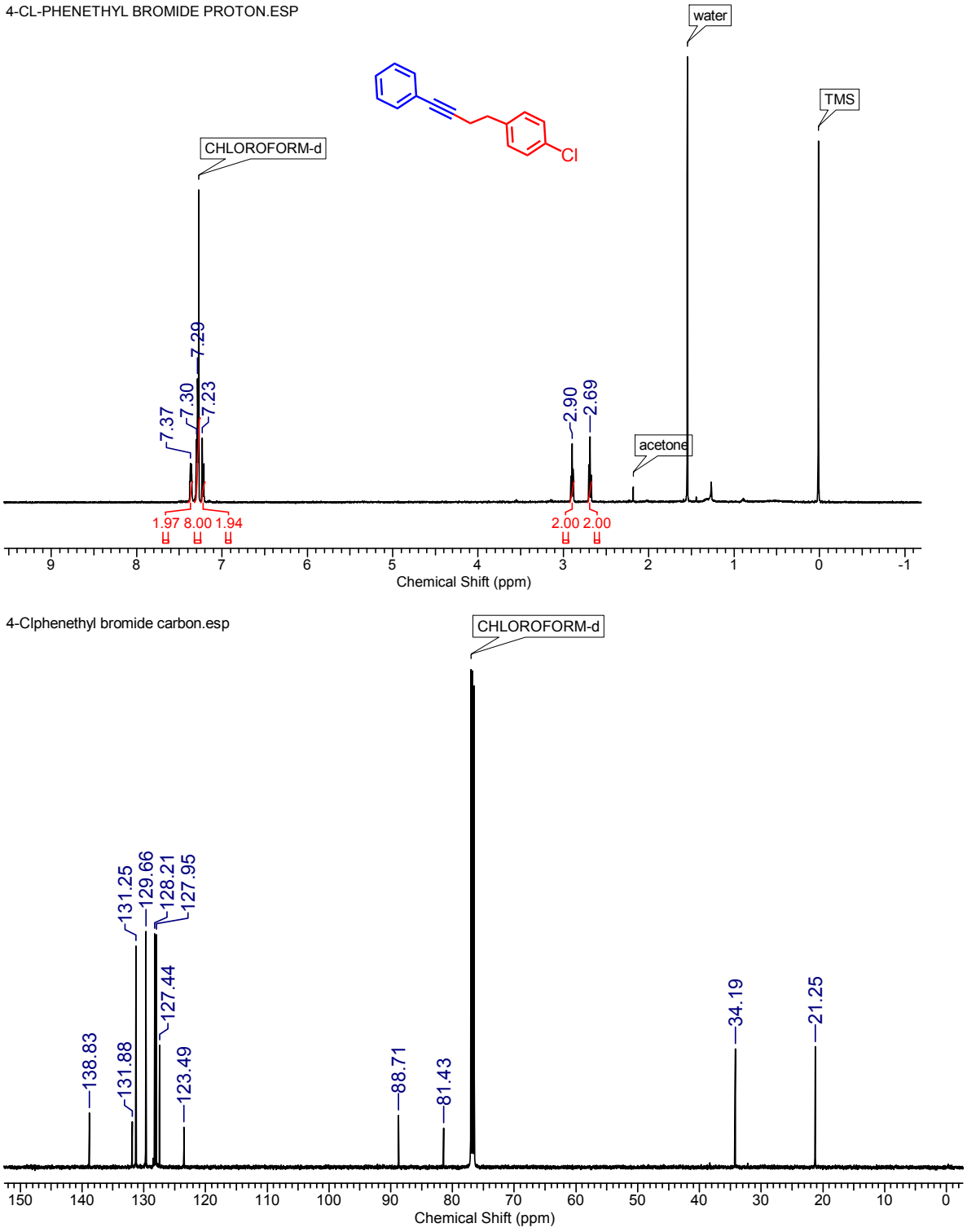


Figure S9. ^{1}H and ^{13}C NMR spectra of **1e** in $CDCl_3$.

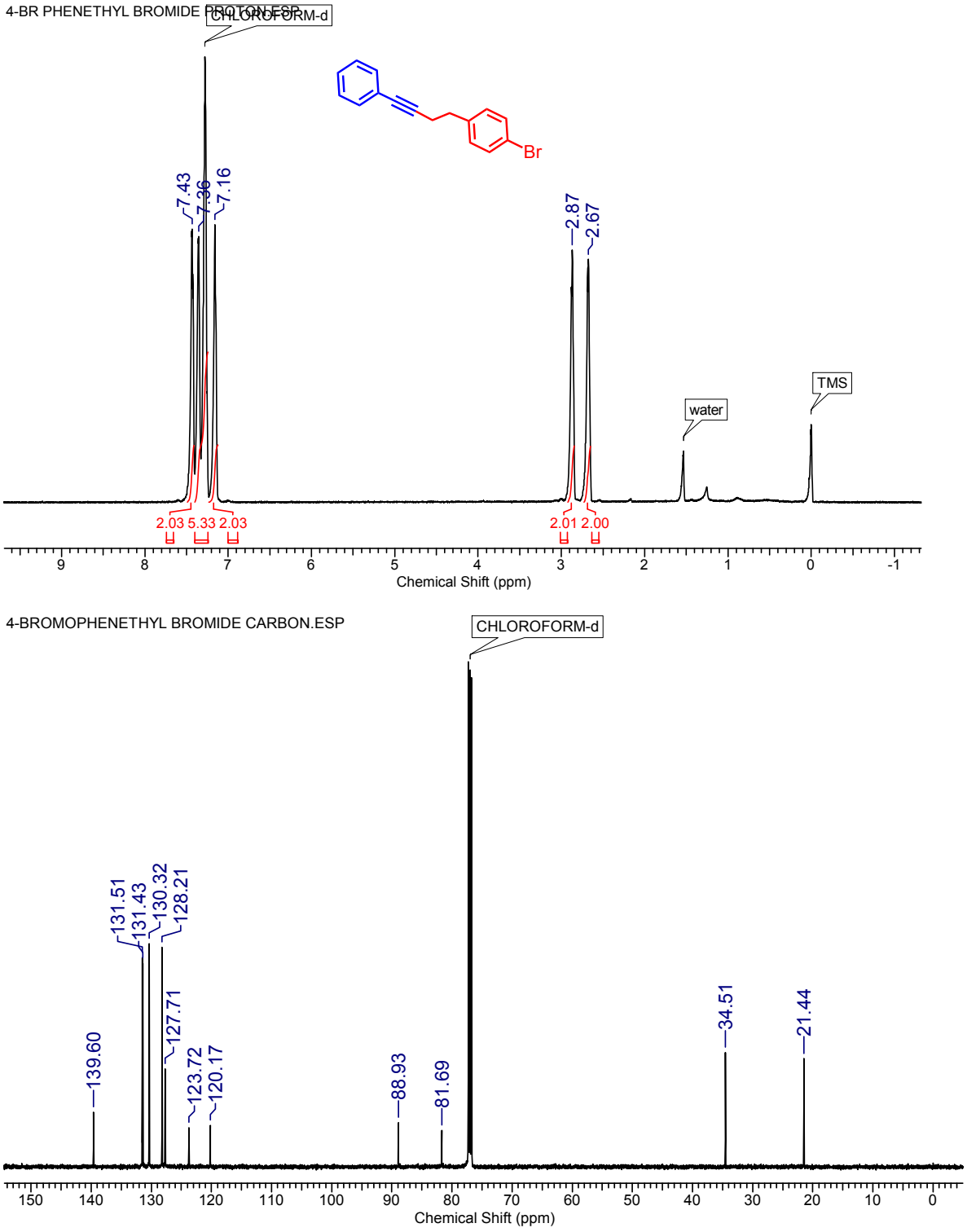


Figure S10. ^{1}H and ^{13}C NMR spectra of **1f** in $CDCl_3$.

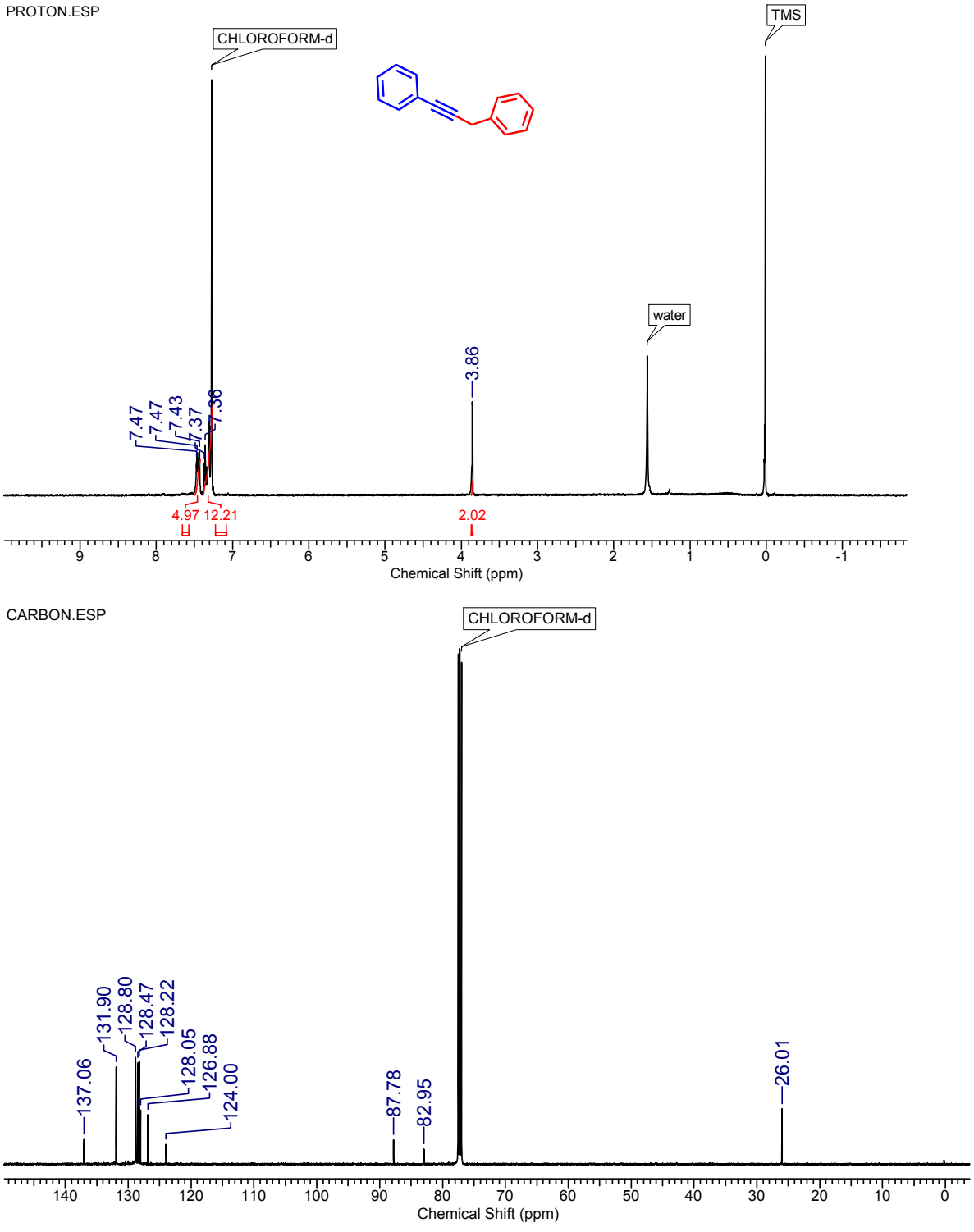


Figure S11. ^{1}H and ^{13}C NMR spectra of **1g** in $CDCl_3$.

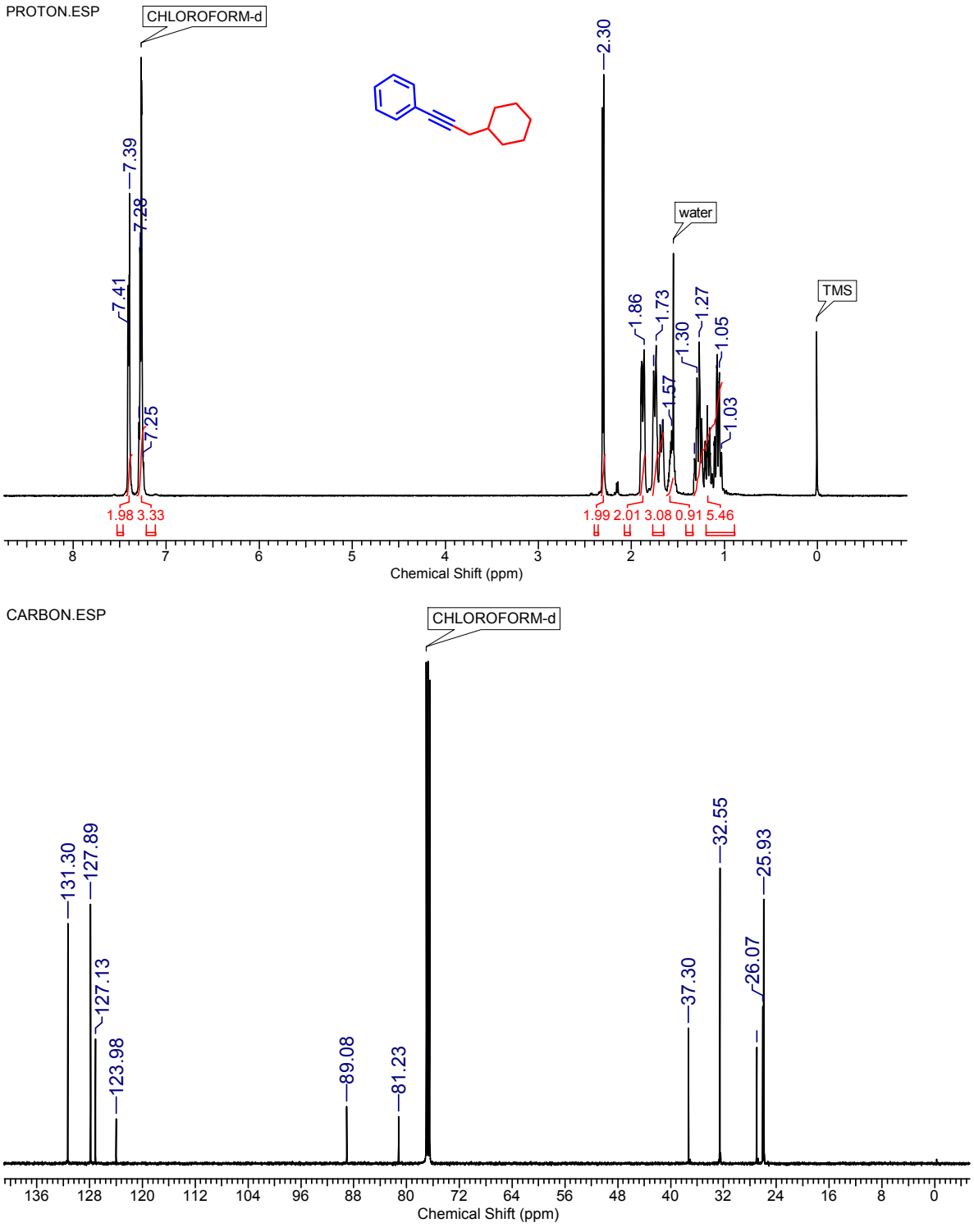


Figure S12. ^{1}H and ^{13}C NMR spectra of **1h** in $CDCl_3$.

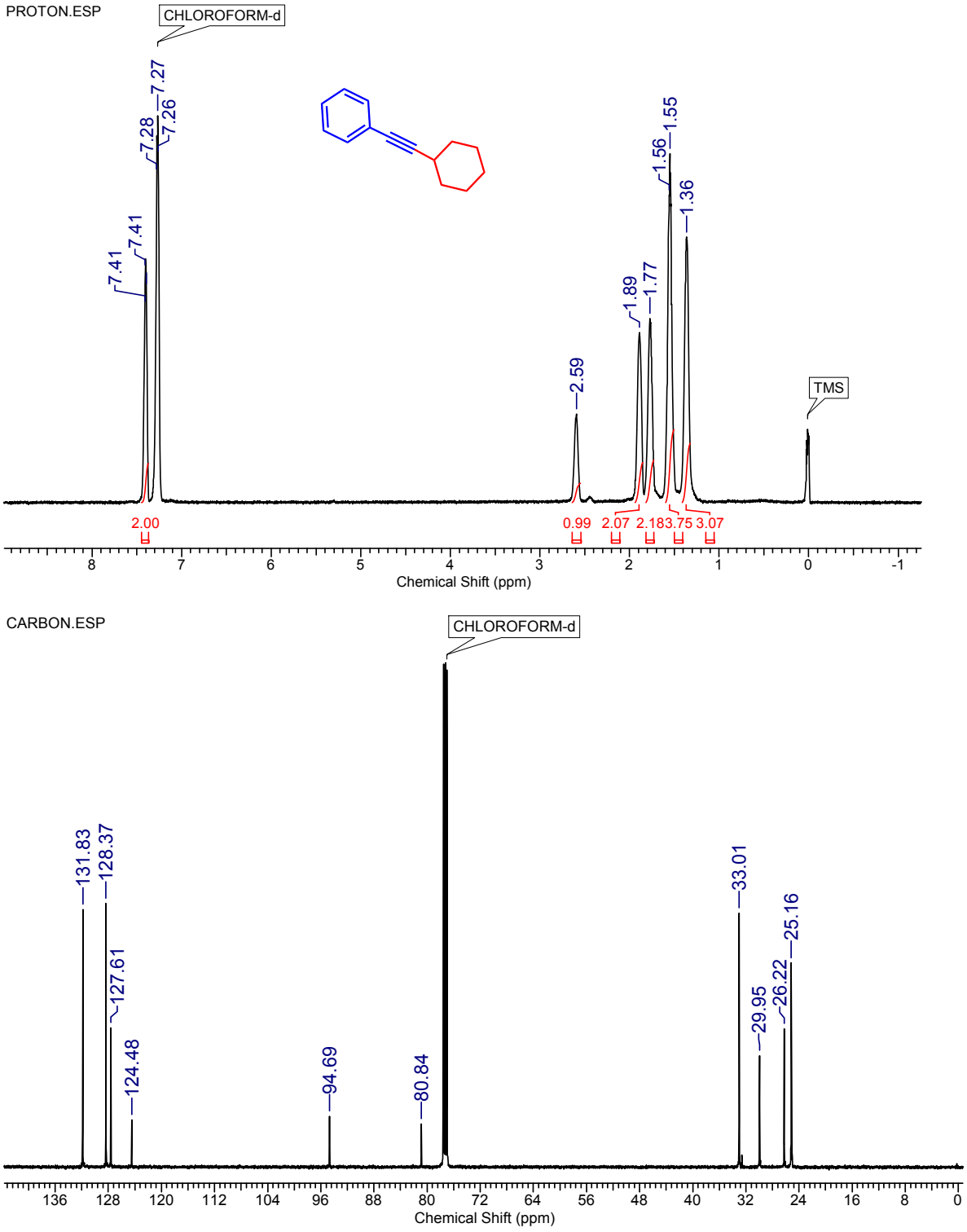


Figure S13. ^{1}H and ^{13}C NMR spectra of **1i** in $CDCl_3$.

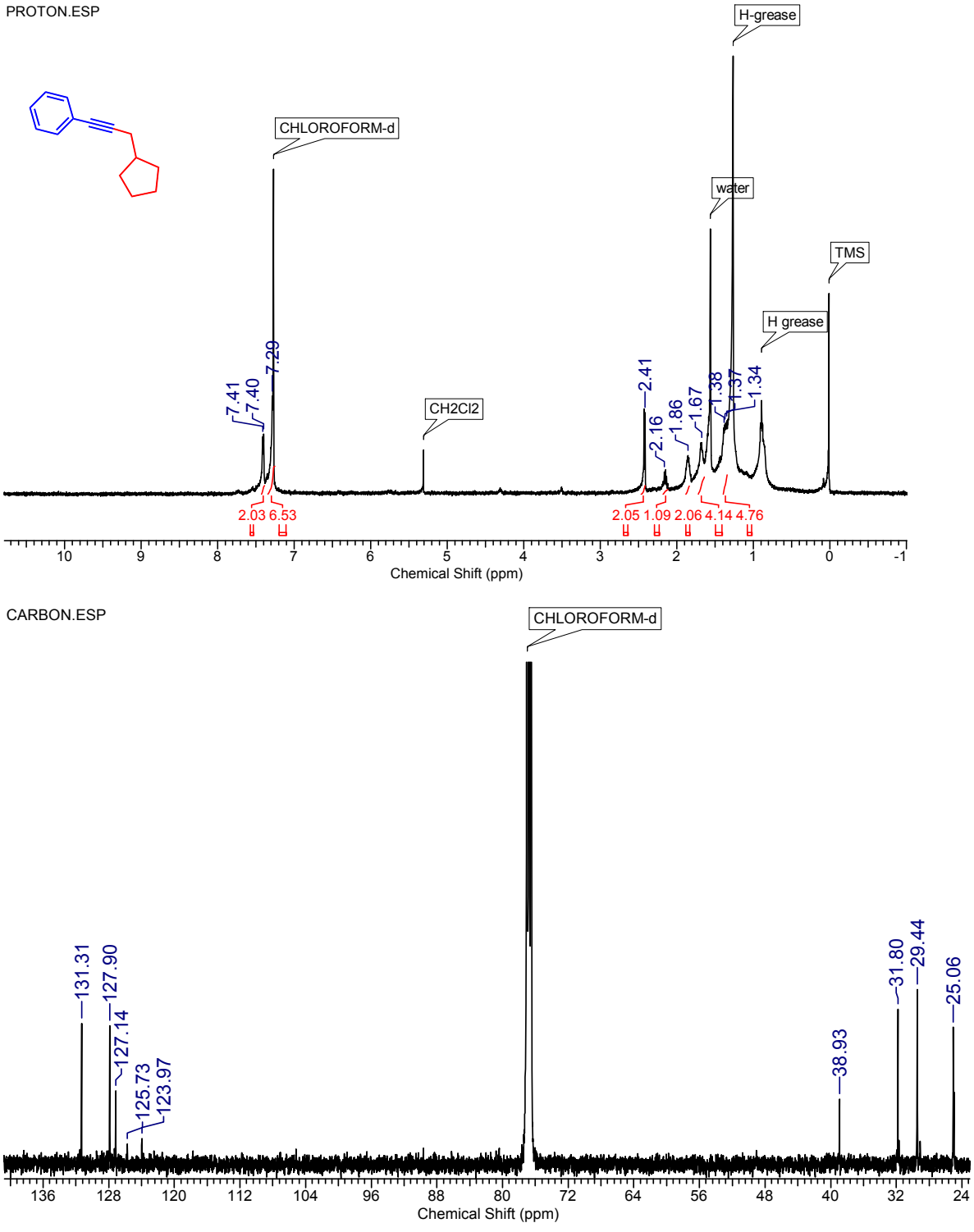


Figure S14. ^{1}H and ^{13}C NMR spectra of **1j** in $CDCl_3$.

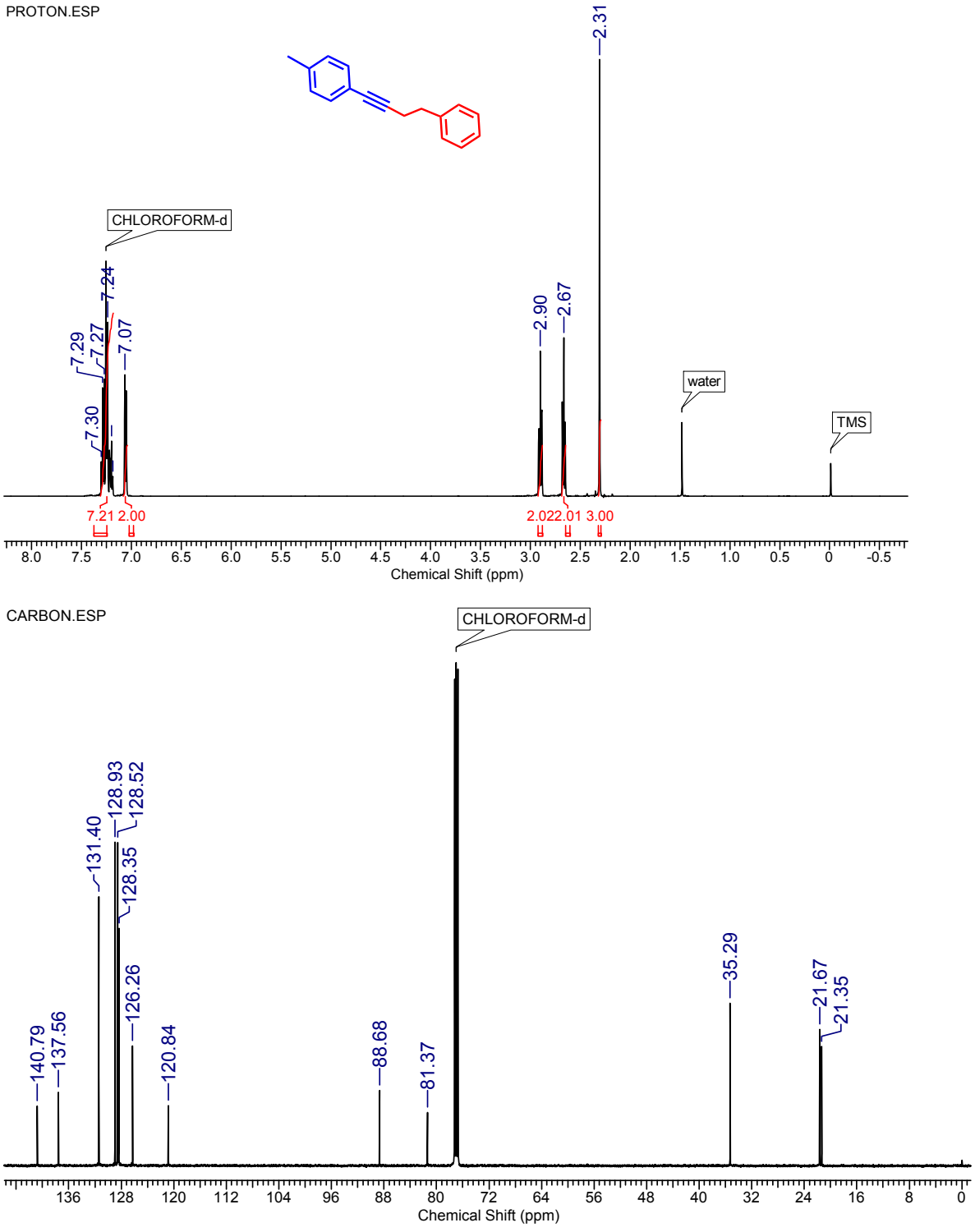


Figure S15. ^{1}H and ^{13}C NMR spectra of **2a** in $CDCl_3$.

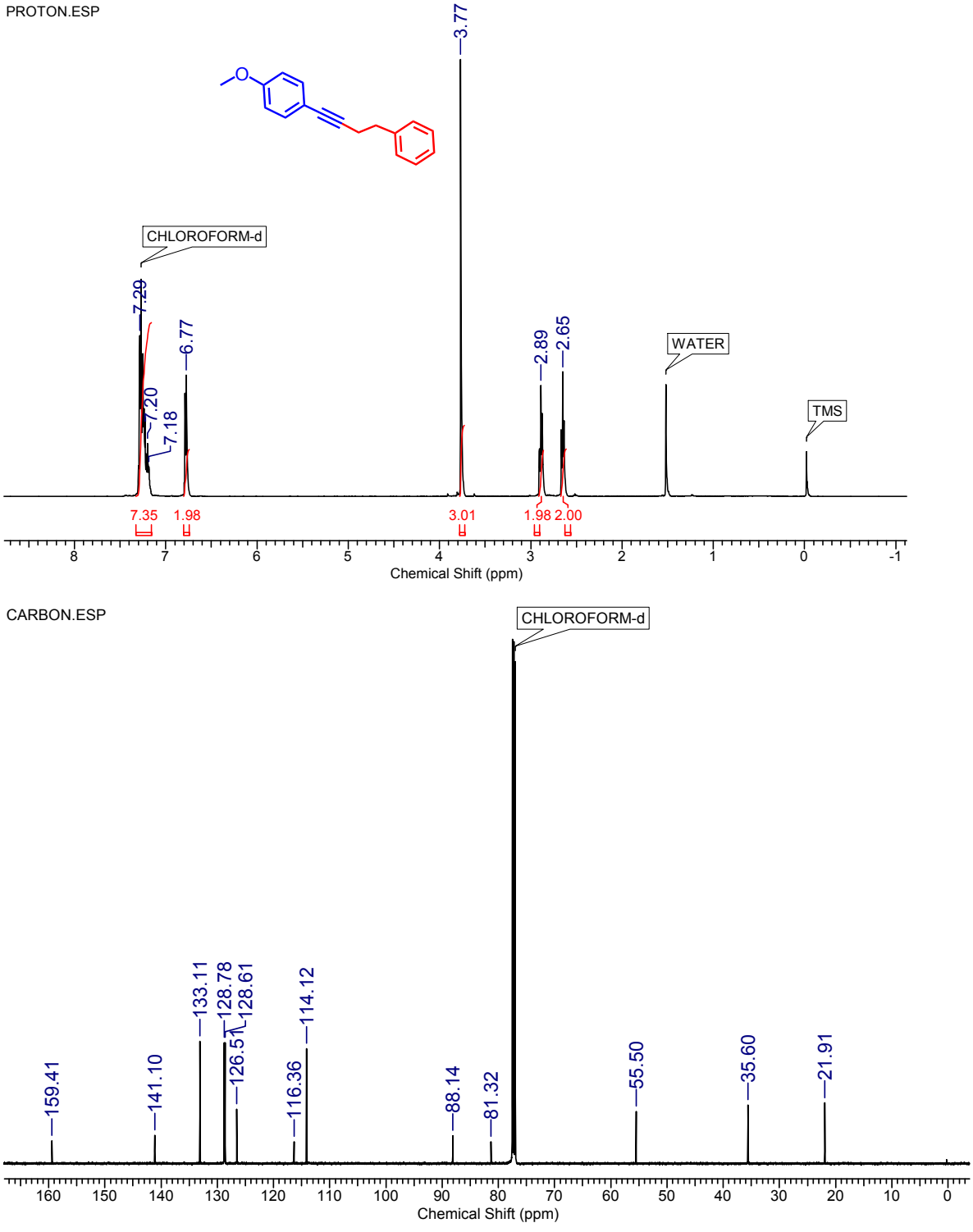


Figure S16. ^{1}H and ^{13}C NMR spectra of **2b** in $CDCl_3$.

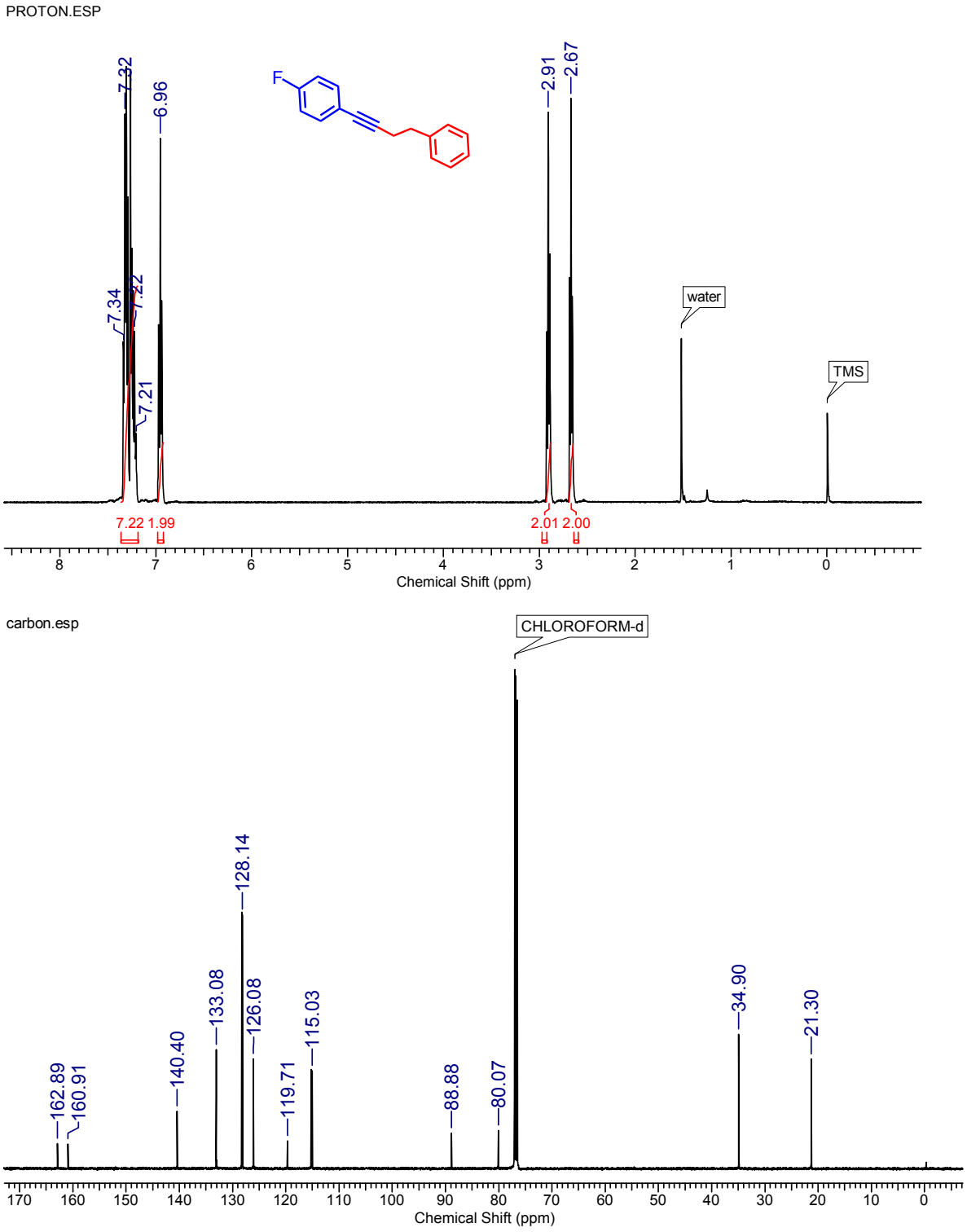


Figure S17. ^{1}H and ^{13}C NMR spectra of **2c** in $CDCl_3$.

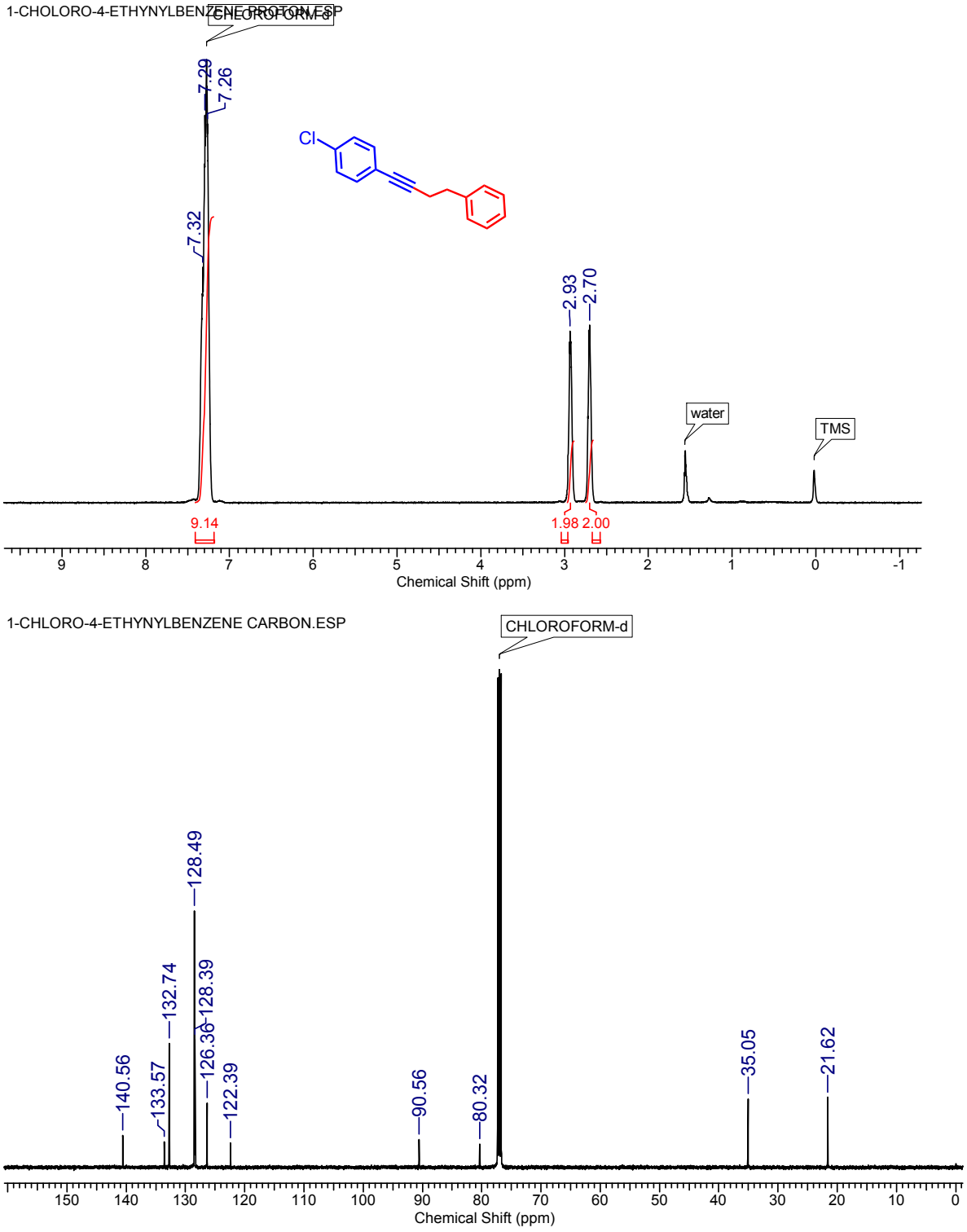


Figure S18. ^{1}H and ^{13}C NMR spectra of **2d** in $CDCl_3$.

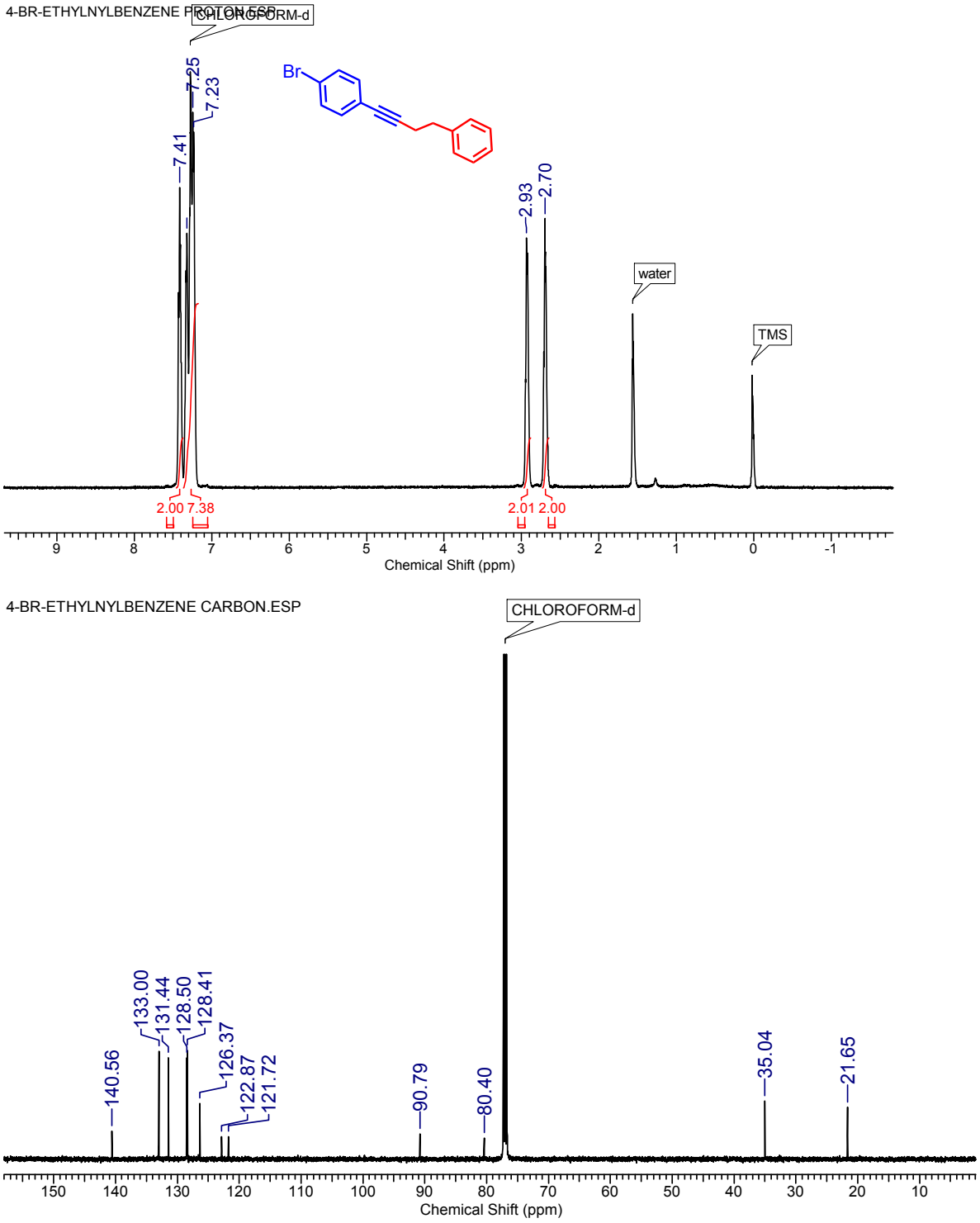


Figure S19. ^{1}H and ^{13}C NMR spectra of **2e** in $CDCl_3$.

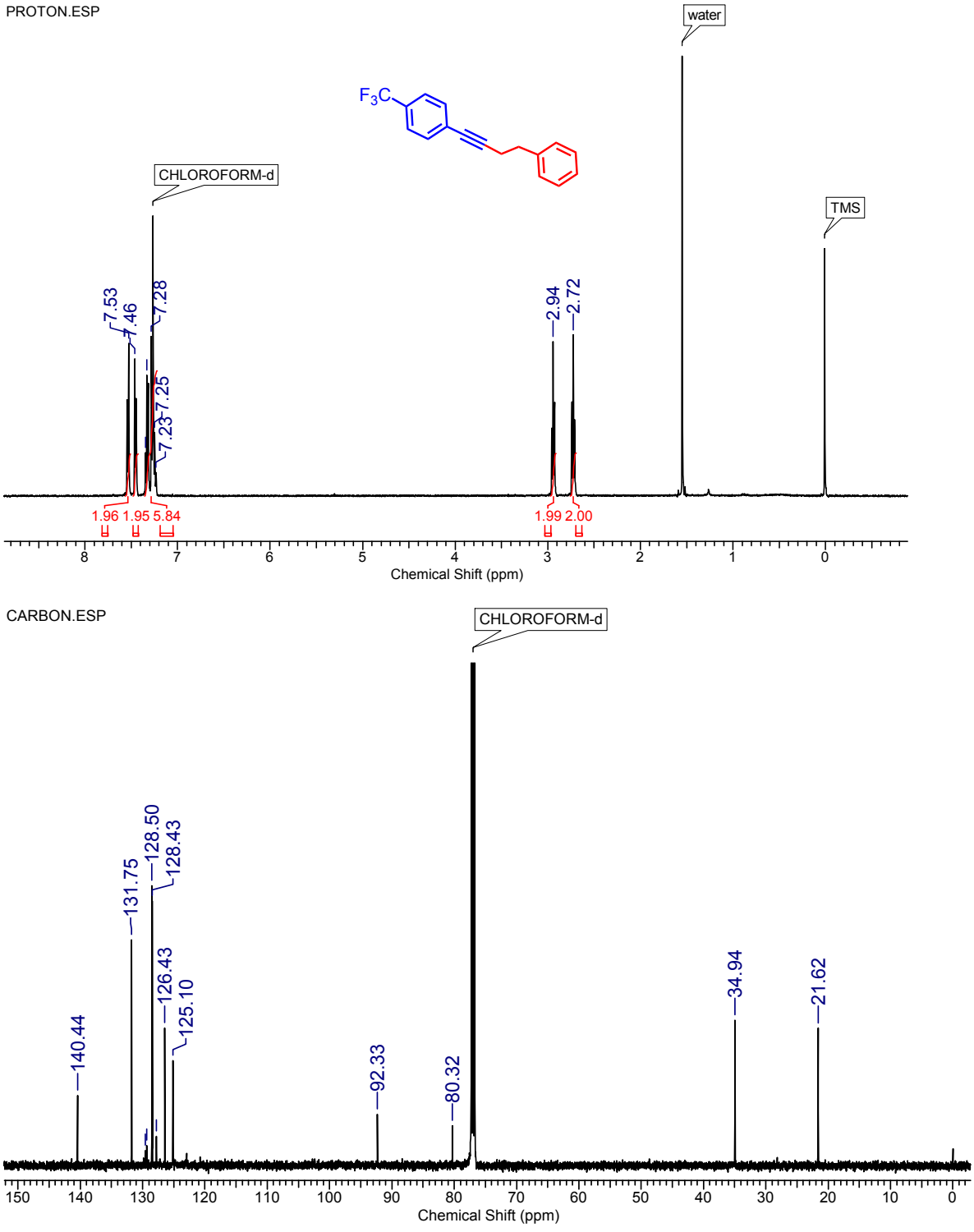


Figure S20. ^{1}H and ^{13}C NMR spectra of **2f** in $CDCl_3$.

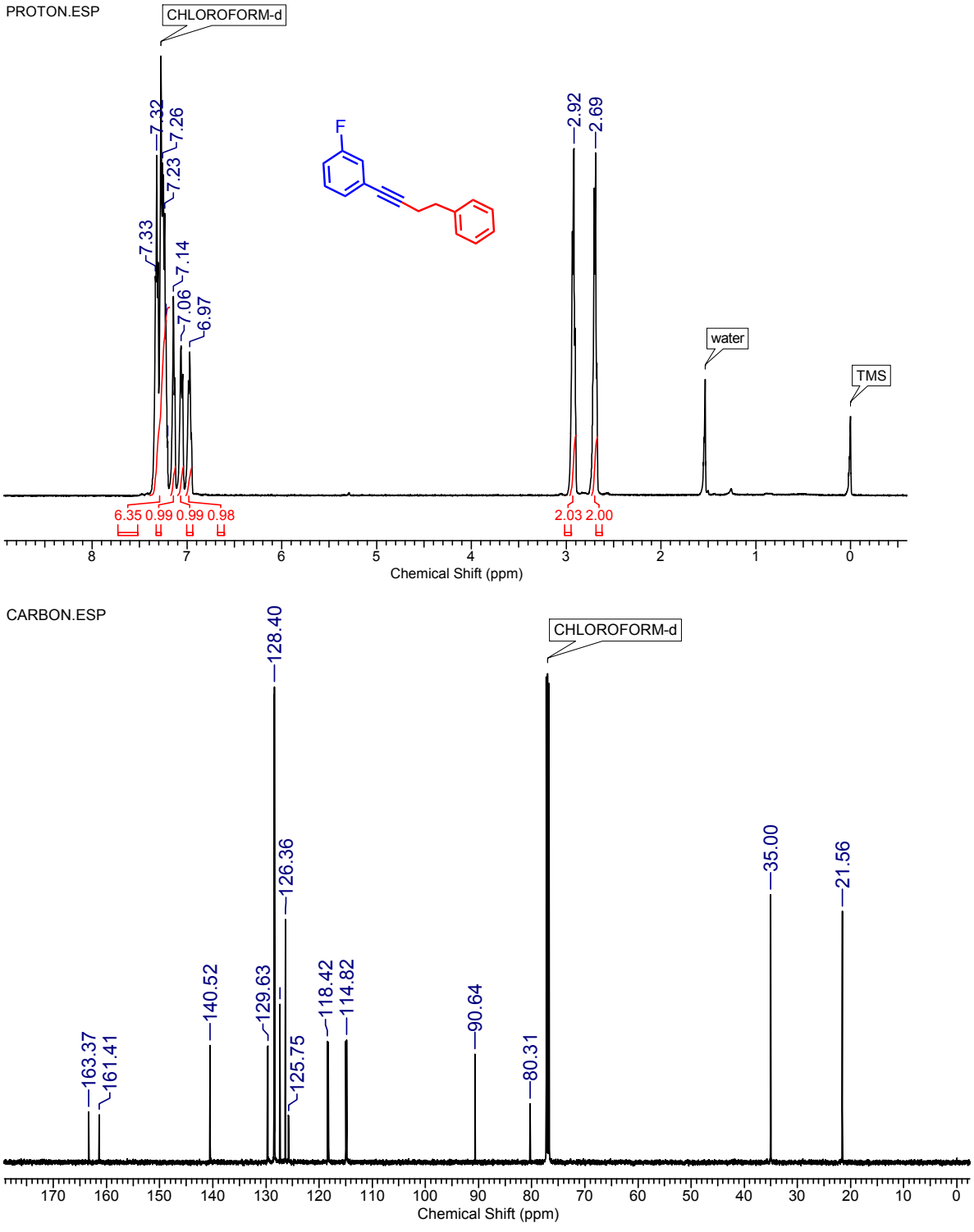


Figure S21. ^{1}H and ^{13}C NMR spectra of **2g** in $CDCl_3$.

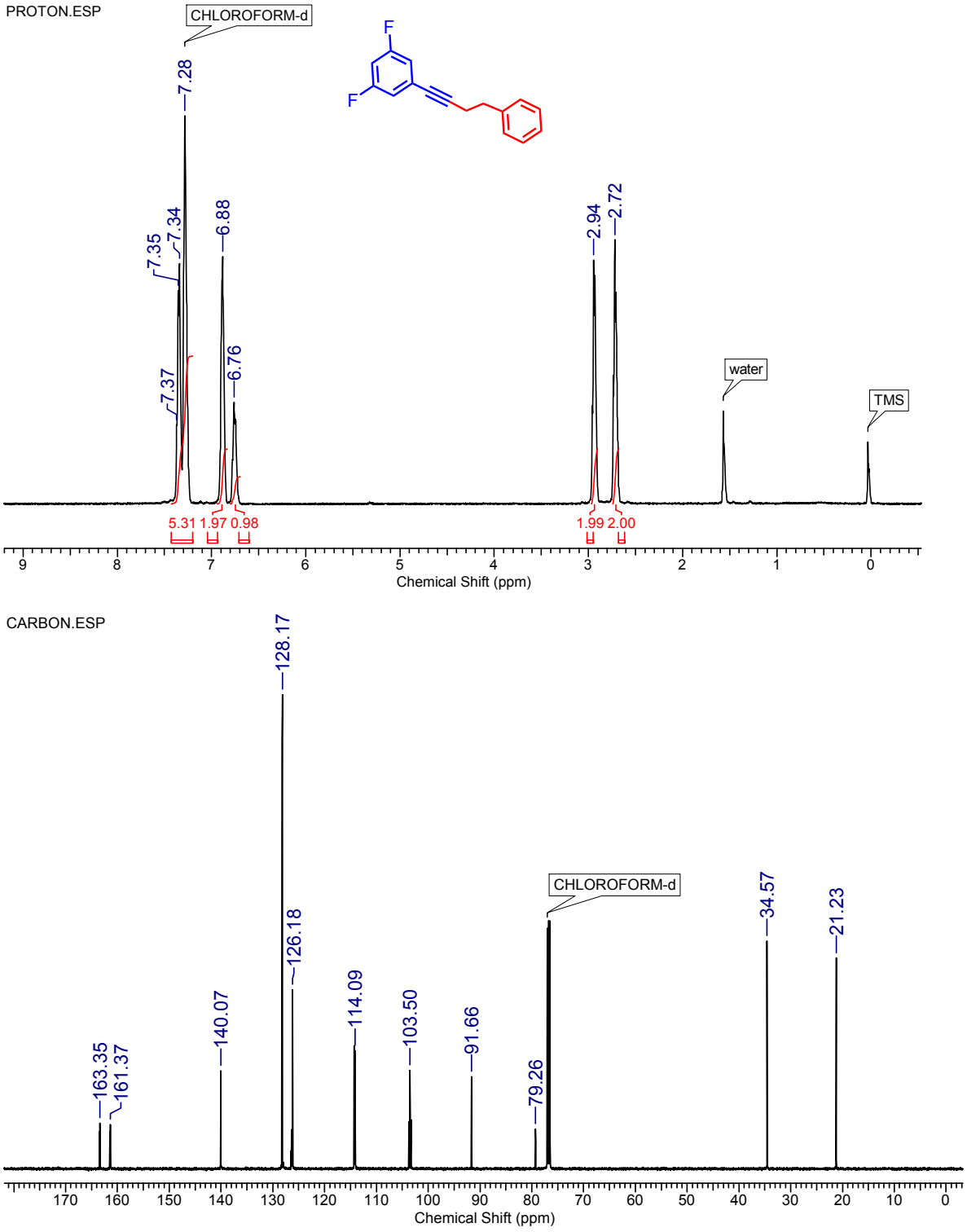


Figure S22. ^{1}H and ^{13}C NMR spectra of **2h** in $CDCl_3$.

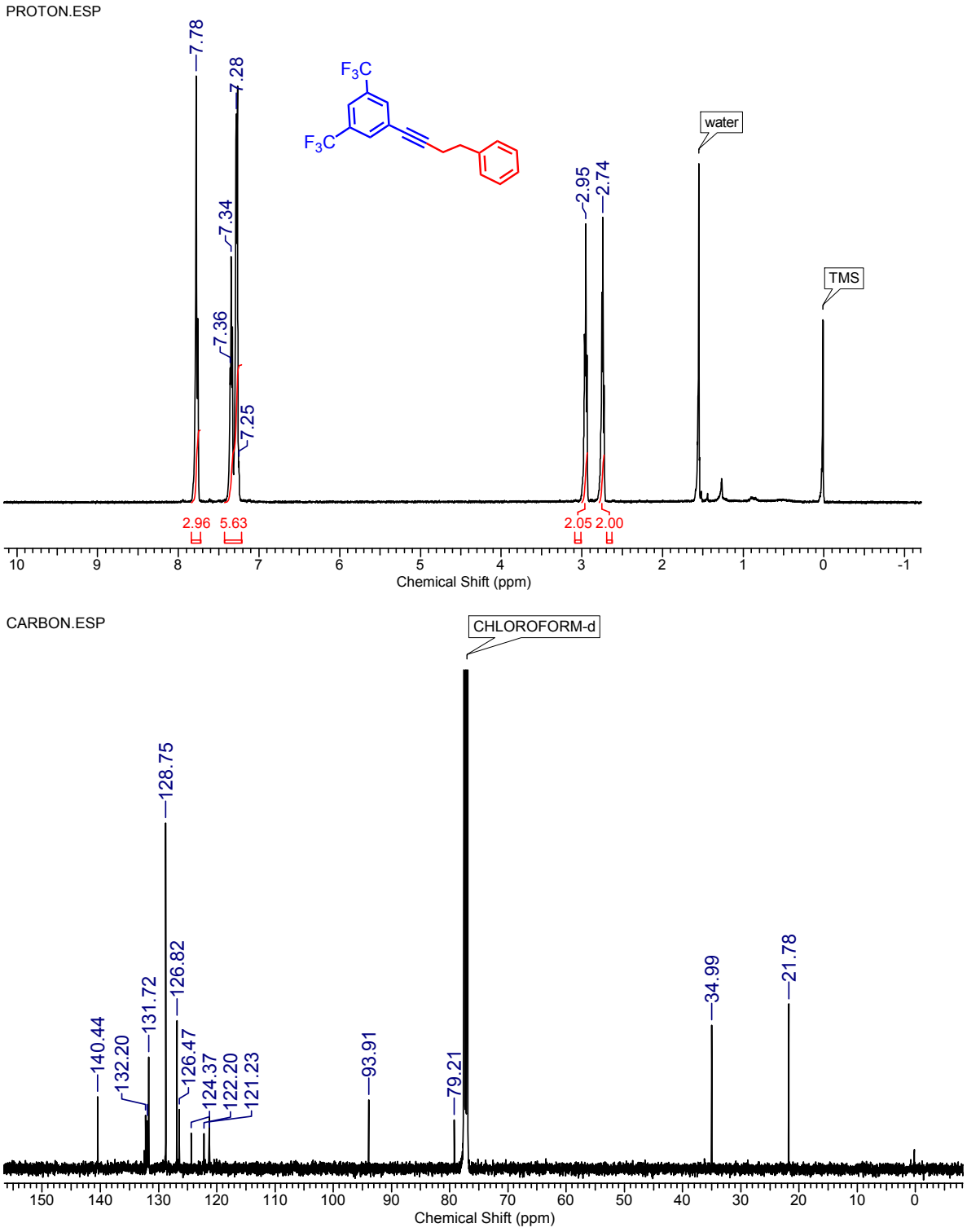


Figure S23. ^{1}H and ^{13}C NMR spectra of **2i** in $CDCl_3$.

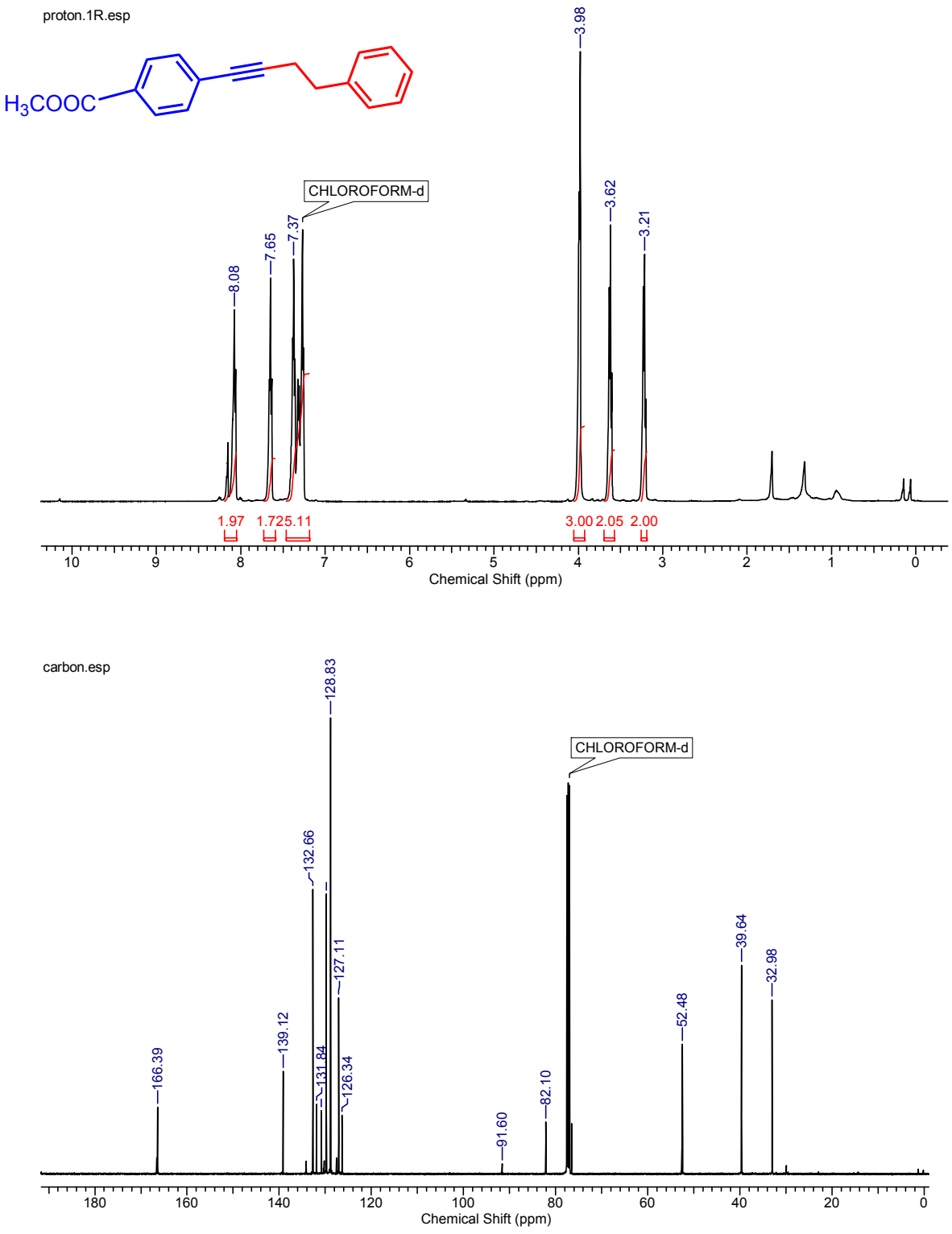


Figure S24. ^{1}H and ^{13}C NMR spectra of **2j** in $CDCl_3$.

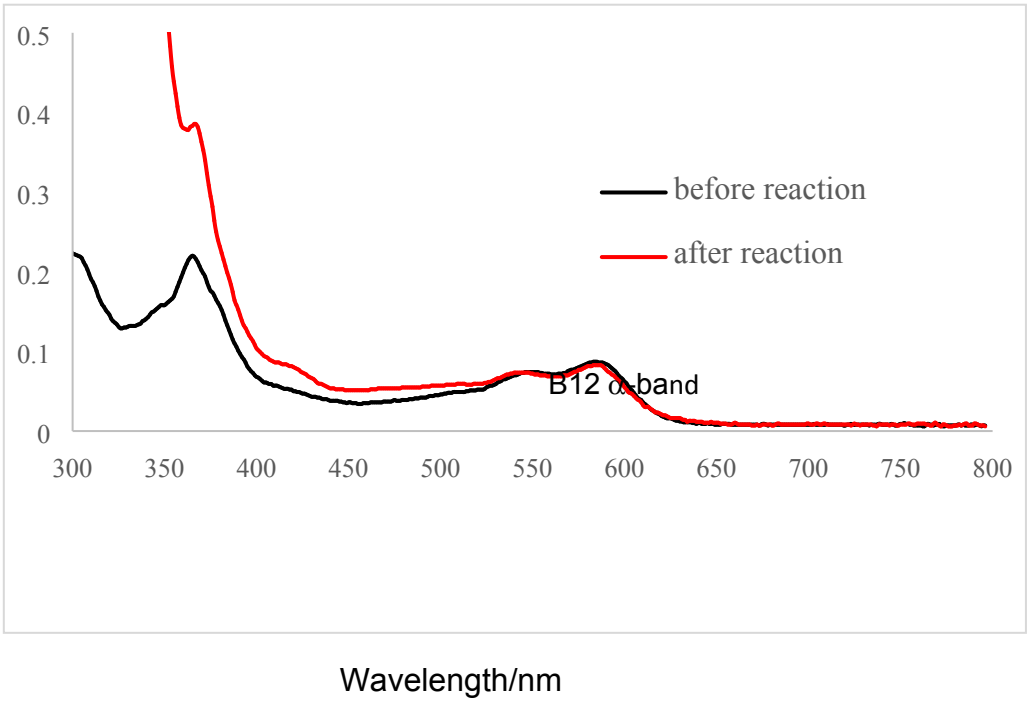


Figure S25. UV-vis spectra of the B_{12} catalyst (**C1**) before (black line) and after (red line) the photo reaction; Absorbance at 590 nm ascribed to α-band of the B_{12} complex (before reaction)=0.084 and 0.079 (after reaction). Recovery of the B_{12} catalyst is 94% based on these absorbances. Spectra were measured by adding KCN to change the B_{12} catalyst to dicyano form for quantification.

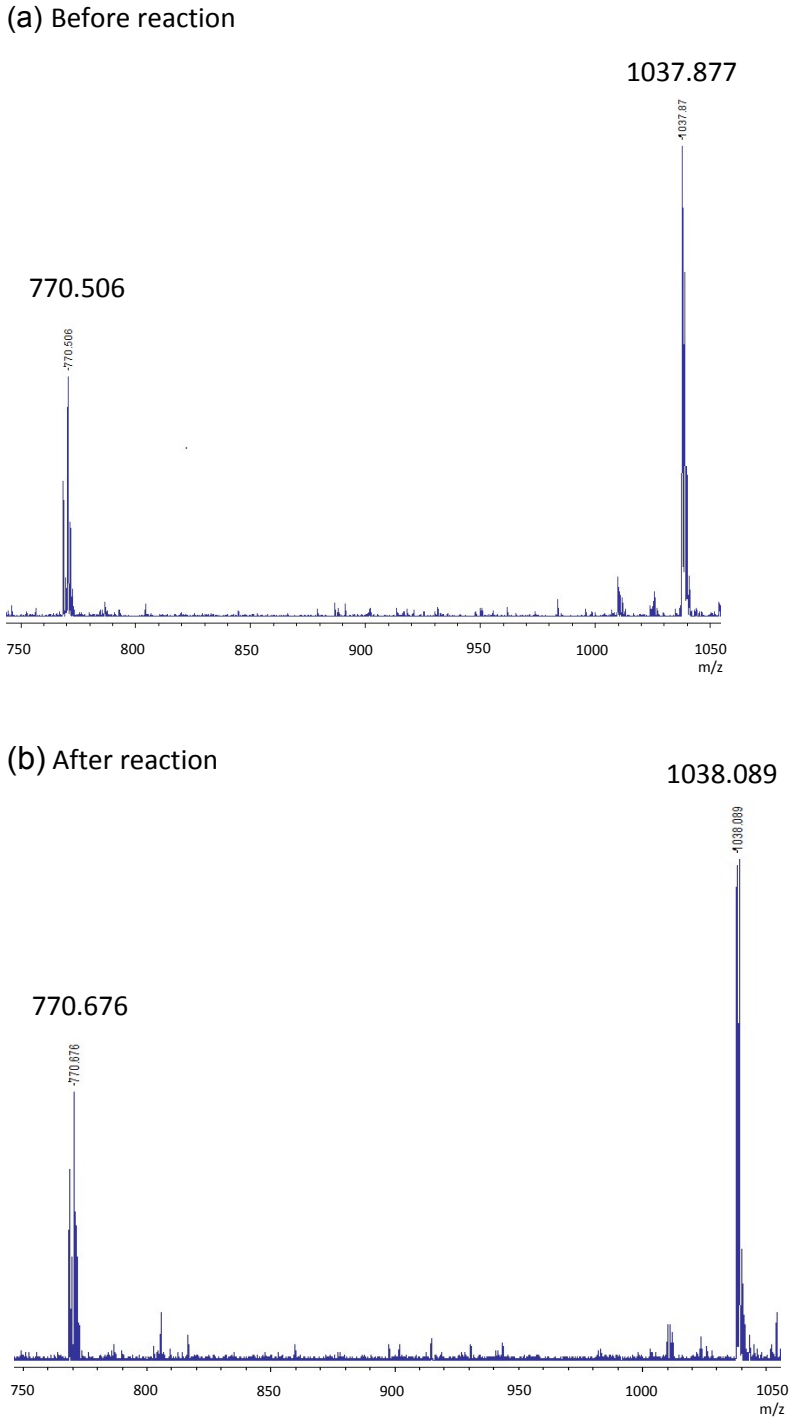


Figure S26. MALDI-MS of the B_{12} catalyst (**C1**) before (a) and after (b) the photo reaction; peaks at 1038 (*m*/*z*) and 770 (*m*/*z*) are ascribed to **C1** and $[Ir(dtbbpy)(ppy)_2]^+$ (**P1**), respectively.

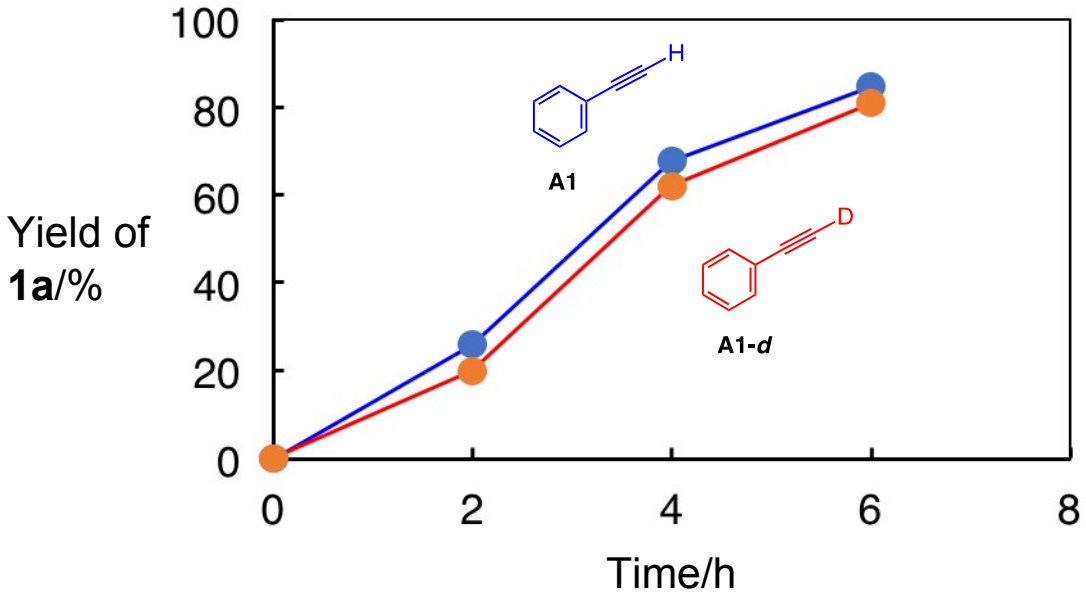


Fig. S27. Time-courses of reactions using **A1** (blue) and deuterated alkyne **A1-*d*** (red).

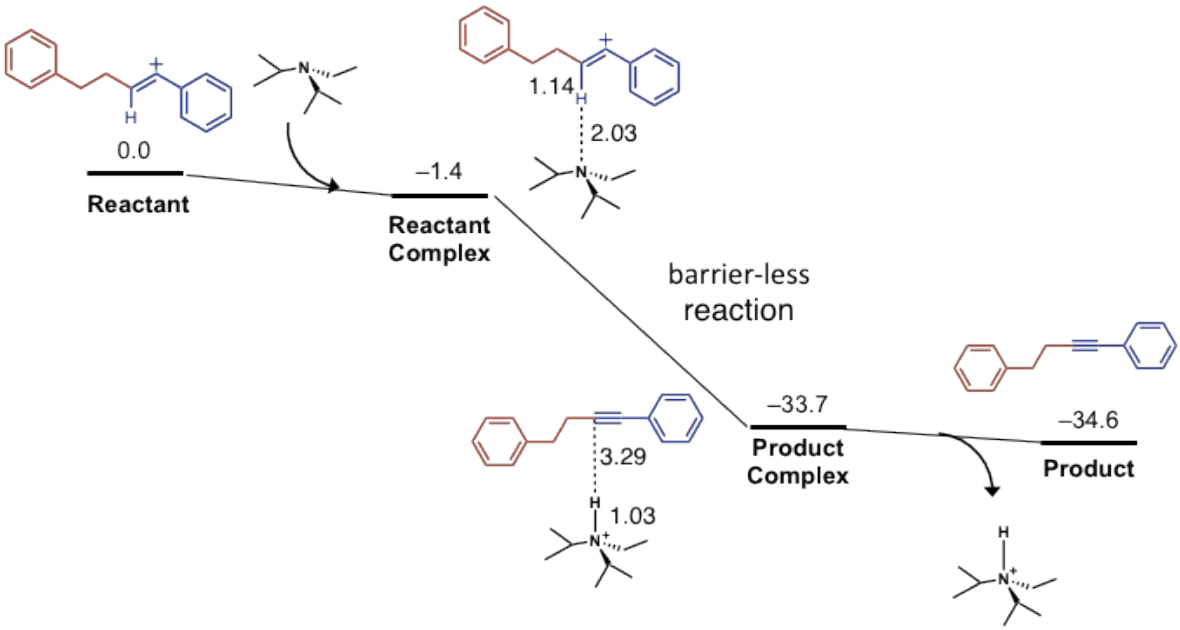


Fig. S28. Optimized structures and computed energy diagrams for deprotonation step in alkyne formation. Units are in kcal/mol**.**