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Supporting Information

Recyclable Cu@C_2N Nano-catalyst Applied in the Transformation of Alkynes: pH Switchable Access to Ketones and 1,3-Diynes

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Experimental Section

Chemicals

Hexaketocyclohexane octahydrate (HKH·8H_2O (≥95%)) was purchased from HEOWNS (Tianjin, China), copper chloride dihydrate ($CuCl_2$·2H_2O (≥99%)) was purchased from Energy Chemical Company (Shanghai, China). Alkynes (≥98%) were purchased from Bidepharm Company (Shanghai, China). Formic acid, acetic acid, trifluoroacetic acid, sulfuric acid, propanoic acid, methanol, ethanol, 2,2,2-trifluoroethanol, ethyl acetate, tetrahydrofuran (THF), triethylamine, ethylenediamine, pyridine, aqueous ammonia, tert-butylamine, 4-dimethylaminopyridine (DMAP), isopropanol (IPA) and dichloromethane were purchased from Tianjin Med. Co. Ltd (Tianjin, China, analytical reagent (AR)). Hexaketocyclohexane octahydrate (HTB) was purchased from Tianjin HEOWNS Co. Ltd (Tianjin, China, analytical reagent (AR)). All chemicals were commercial purchased and used without further purification. Hexaaminobenzene (HAB) was prepared according to the literature: **Reference:** Mahmood, J. Kim, D. Jeon, I.-Y. Lah, M. Baek, J.-B. *Synthesis.* **2013**, *24,* 246. 1-Methyl-4-(prop-1-yn-1-yl)benzene, 1-chloro-4-(prop-1-yn-1-yl)benzene, but-1-yn-1-ylbenzene and pent-1-yn-1-ylbenzene were prepared according to the literature: **Reference:** Briones, J. F. Davies, H. M. L. *Org. Lett.* **2011**, *13*, 3984.

Instrumentation

Transmission electron microscopy (TEM), dark-field scanning transmission electron microscopy (dark-field STEM), and energy dispersive spectrometer (EDS) characterizations were all carried out with a TECNAI G^2 TF20 instrument (200 kV, USA). The field-emission scanning electron microscopy (SEM) were performed on a Hitachi SU8010 instrument (10 kV, Japan). The X-ray photoelectron spectroscopy (XPS) were recorded at ESCALab250Xi spectrometer (USA). Crystalline patterns of the materials were identified by powder X-ray diffraction (PXRD) using Cu Kα radiation (λ = 1.5418 Å) (Bruker D8 Advance). The loading amount of Cu elements were determined by inductively coupled plasma optical emission spectrum (ICP-OES) (Agilent ICPOES730, USA). Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectroscopy was performed on a Shimadzu UV2600 (Shimadzu, Japan). The NH_3/CO_2-TPD were measured by Xianquan TP-5080 (Tianjing Xianquan, China). ^1H-NMR (400 MHz), ^{13}C-NMR (100 MHz) and ^{19}F-NMR (376 MHz) spectra were determined on Bruker Avance III 400 MHz NMR.

Synthesis of Cu@C_2N

For the preparation of Cu@C_2N, HAB·3HCl (2 mmol), HTB·$8H_2O$ (2 mmol) and $CuCl_2·2H_2O$ (4 mmol) were mixed in 20 mL of acetic acid/ethanol (1:1) and refluxed at 120 °C for 4 h. After cooled to room temperature, the precipitate was removed by centrifugation. Afterward, 100 mL of H_2O was added to the supernatant and allowed to stand overnight. The resulting precipitate was centrifugated, washed with H_2O/ethanol (1/1), and then freeze-dried at -50 °C under reduced pressure (<100 Pa) for 24 h.

Catalytic activity evaluation

Hydration Reaction

Method a: 10 mg as-prepared heterogeneous catalyst (the containing Cu amount was confirmed by ICP-OES) were mixed with 0.5 mmol alkynes and 0.5 mL H_2O in 2 mL HCOOH. After stirring at 60 °C for 2 h, the catalyst was removed by centrifugation. The product was purified by flash chromatography (silica gel, hexane/EtOAc, 5:1, R_f = 0.5) to give ketones compounds **2**.

Method b: 10 mg as-prepared heterogeneous catalyst (the containing Cu amount was confirmed by ICP-OES) were mixed with 0.5 mmol alkynes, 0.5 mL H_2O and 0.5 mL concentrated H_2SO_4 in 2 mL CF_3CH_2OH. After stirring at 90 °C for 2 h, the catalyst was removed by centrifugation. The product was purified by flash chromatography (silica gel, hexane/EtOAc, 5:1, $R_f = 0.5$) to give ketones compounds **2**.

Homo-coupling Reaction

Method a: 20 mg as-prepared heterogeneous catalyst (the containing Cu amount was confirmed by ICP-OES) were mixed with 0.5 mmol alkynes and 1 mol% Et_3N in 1 mL H_2O. After stirring at 80 °C for 4 h, the catalyst was removed by centrifugation. The product was purified by flash chromatography (silica gel, hexane, $R_f = 0.6$) to give symmetrical 1,3-diyne compounds **3**.

Method b: 20 mg as-prepared heterogeneous catalyst (the containing Cu amount was confirmed by ICP-OES) were mixed with 0.5 mmol alkynes and 1 mol% Et_3N in 1 mL IPA/H_2O (1:1). After stirring at 80 °C for 4 h, the catalyst was removed by centrifugation. The product was purified by flash chromatography (silica gel, hexane, $R_f = 0.6$) to give symmetrical 1,3-diyne compounds **3**.

Hetero-coupling Reaction

20 mg as-prepared heterogeneous catalyst (the containing Cu amount was confirmed by ICP-OES) were mixed with 0.5 mmol phenylacetylene, 0.1mmol alkynes and 1 mol% Et_3N in 1 mL IPA/H_2O (1:1). After stirring at 80 °C for 4 h, the catalyst was removed by centrifugation. The product was purified by flash chromatography (silica gel, hexane, $R_f = 0.6$) to give unsymmetrical 1,3-diyne compounds **4**.

Supporting Figures

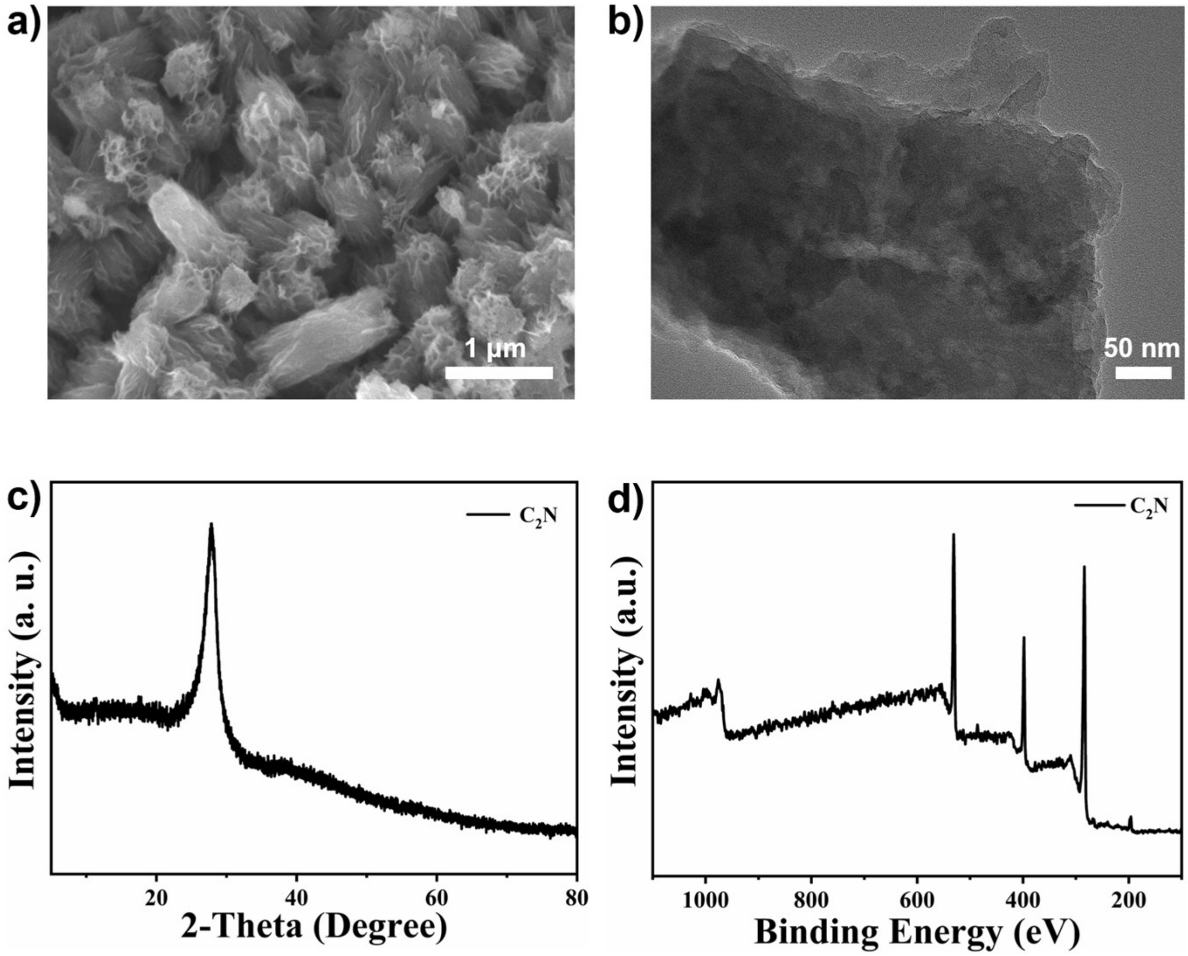


Figure S1. (a) The SEM images of C_2N. (b) The dark-field TEM image of C_2N. (c) Powder XRD patterns of C_2N. (d) XPS surveys of C_2N.

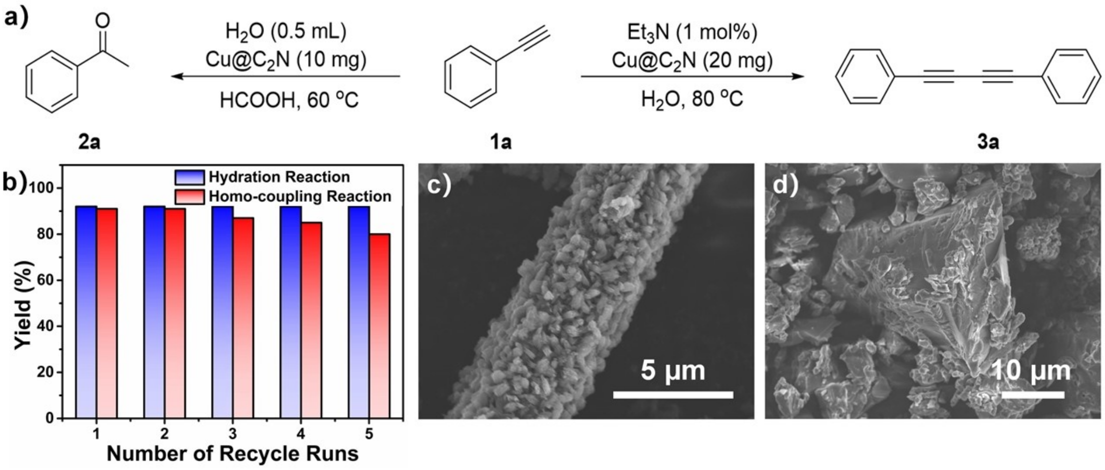


Figure S2. (a) The cyclic model reaction. (b) Catalytic performance of Cu@C_2N catalyst during five cycles. (c) The SEM image of Cu@C_2N after five recycling hydration reactions. (d) The SEM image of Cu@C_2N after five recycling homo-coupling reactions.

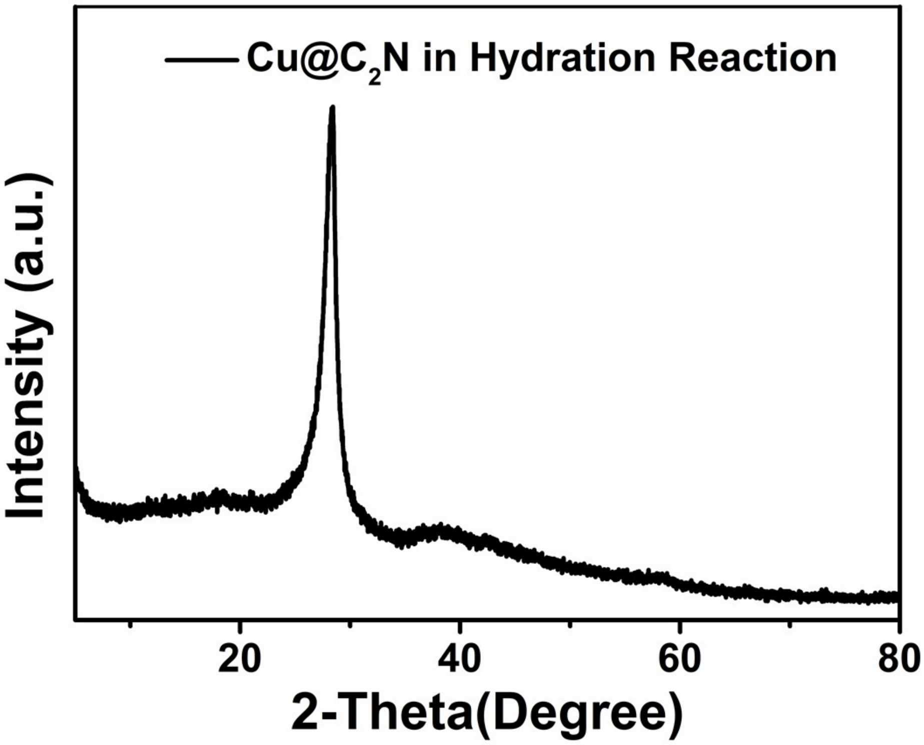


Figure S3. Powder XRD patterns of Cu@C$_2$N after five catalytic cycles (Hydration Reaction).

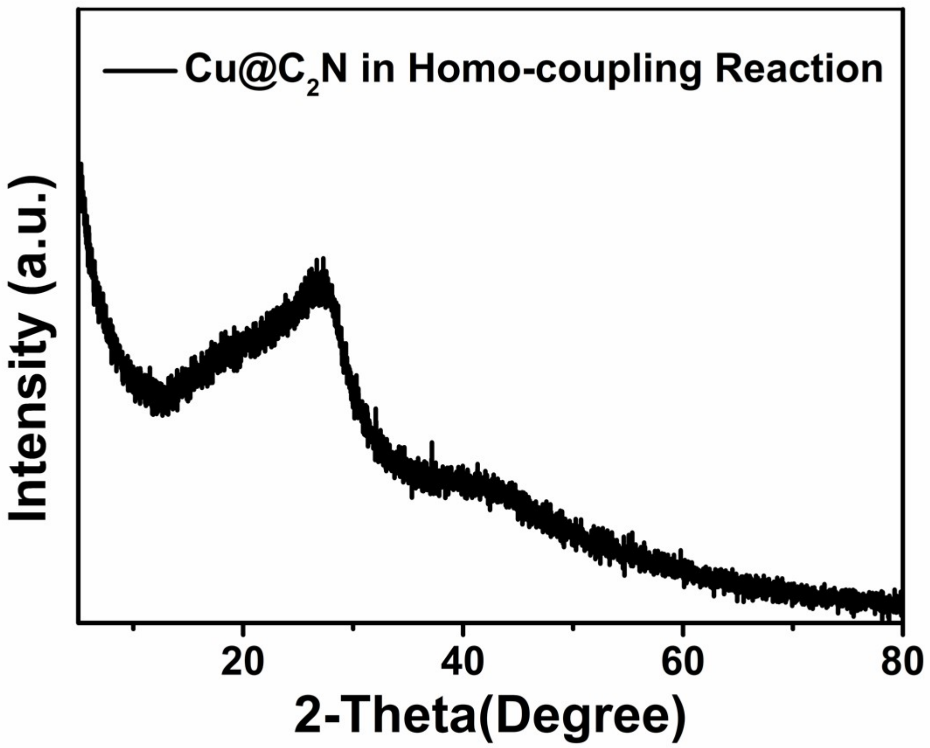


Figure S4. Powder XRD patterns of Cu@C_2N after five catalytic cycles (Homo-coupling Reaction).

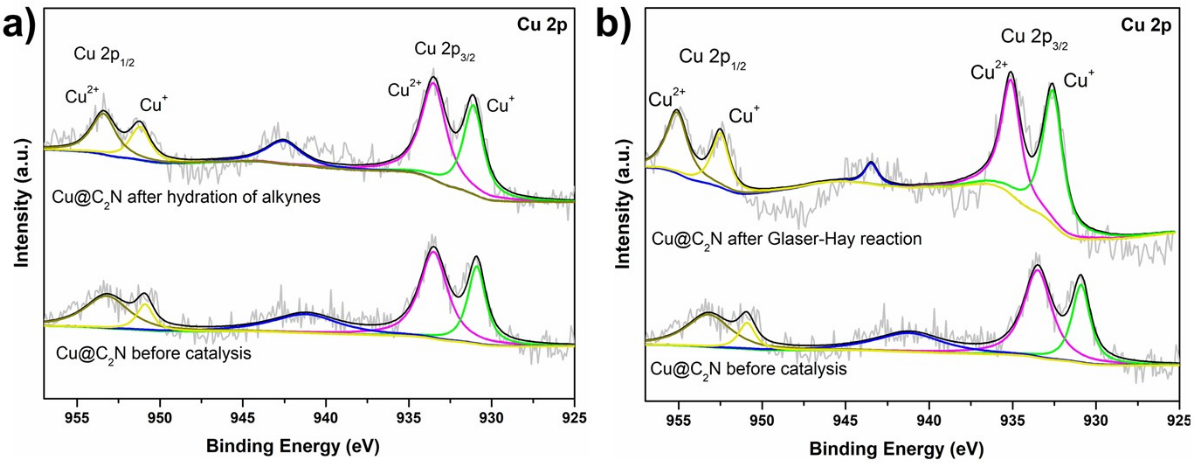


Figure S5. (a) XPS Cu 2p spectra of Cu@C$_2$N before and after hydration reaction. (b) XPS Cu 2p spectra of Cu@C2N before and after Glaser-Hay reaction.

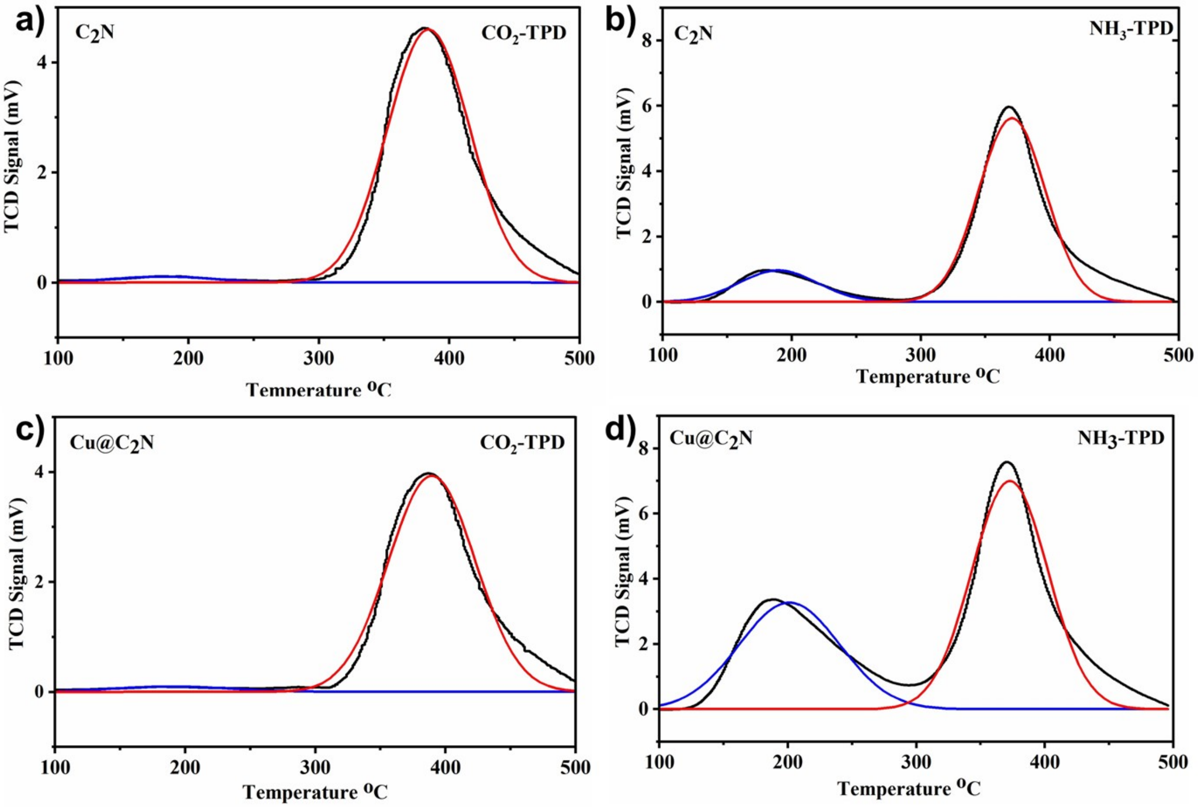


Figure S6. (a-b) Temperature-programmed desorption of CO_2 (a) and NH_3 (b) on C_2N. (c-d) Temperature-programmed desorption of CO_2 (c) and NH_3 (d) on Cu@C_2N.

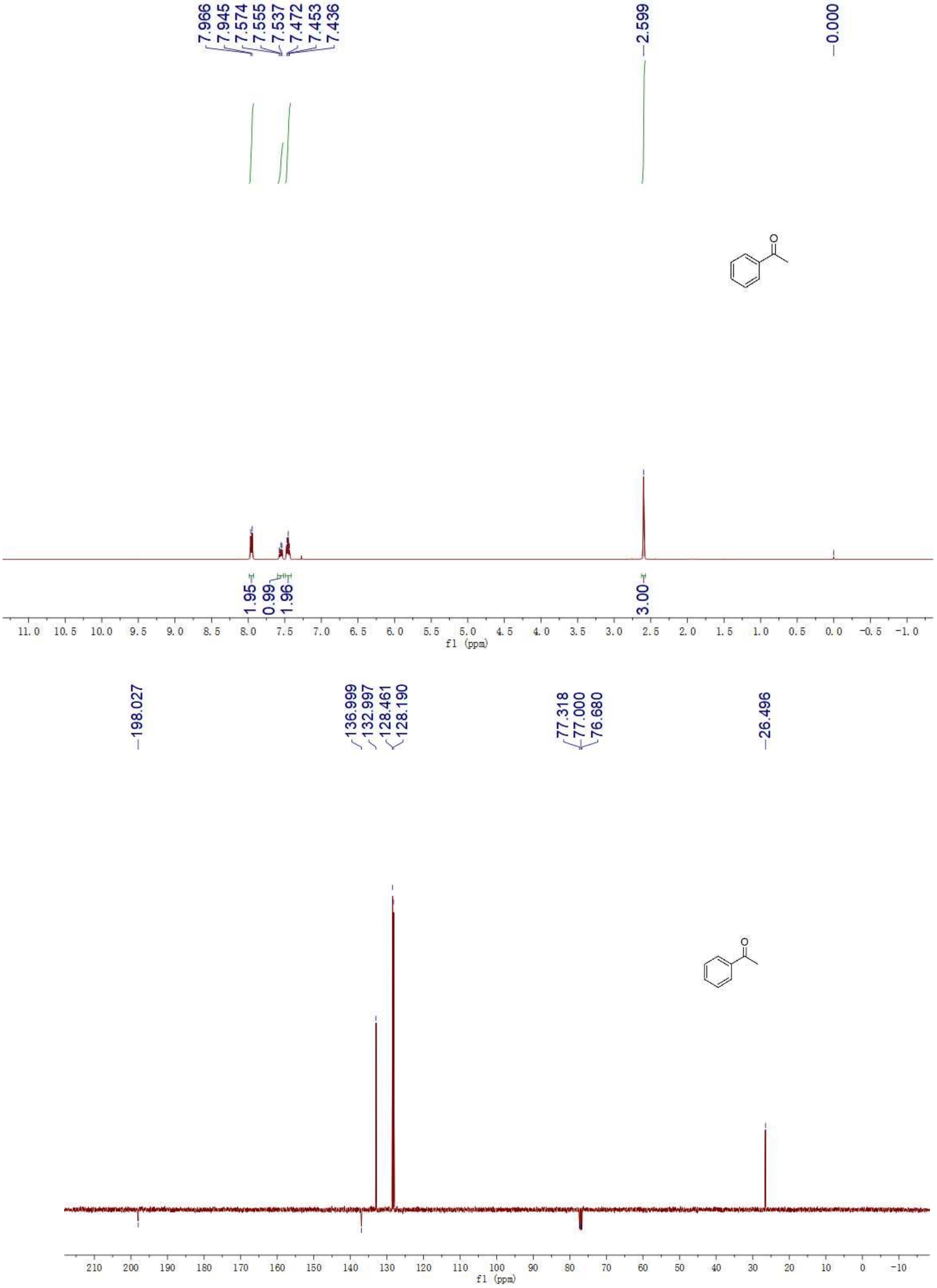


Figure S7. ^{1}H and ^{13}C NMR spectra of acetophenone (**2a**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0,137.0, 133.0, 128.5, 128.1, 26.5.

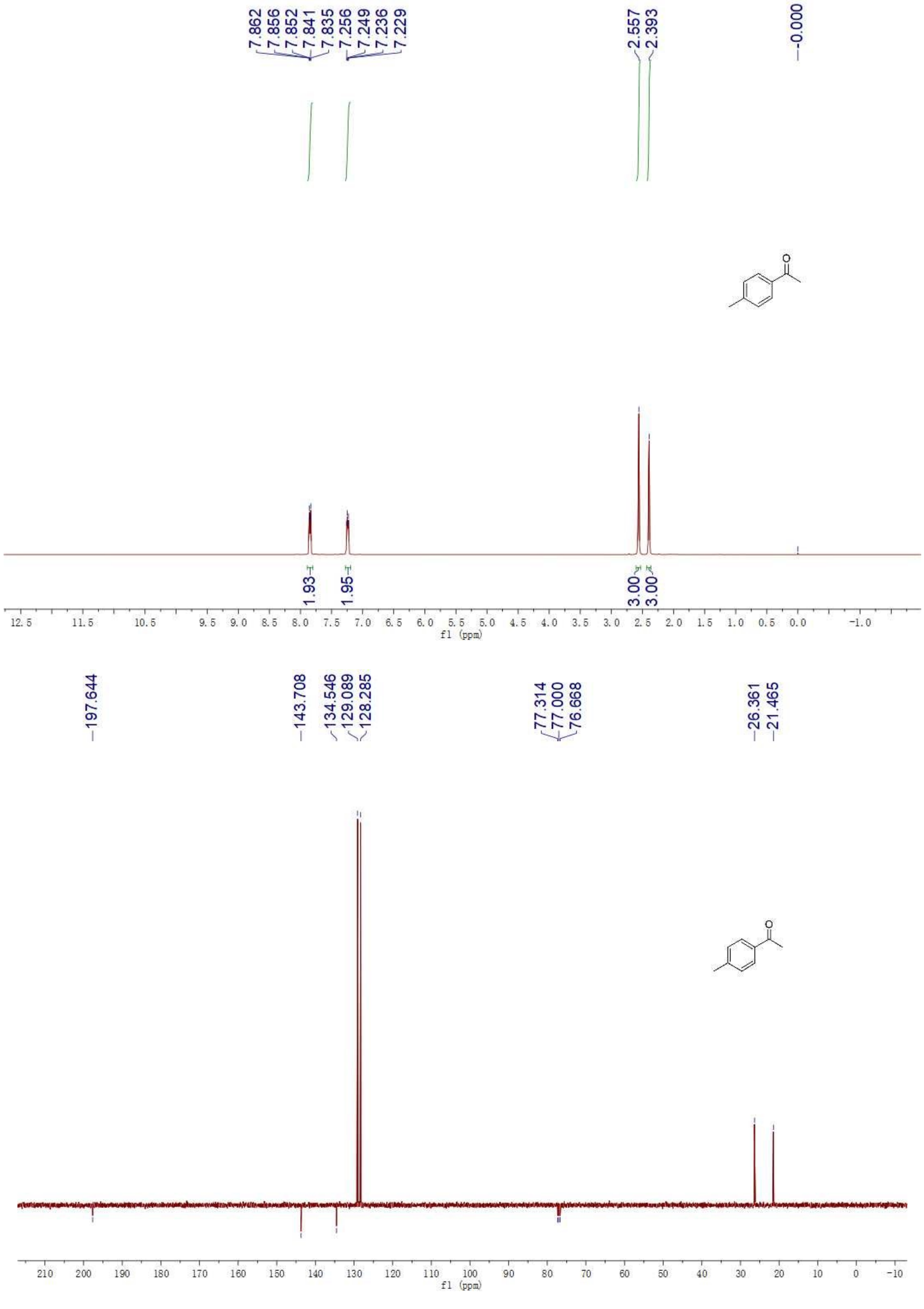


Figure S8. ^{1}H and ^{13}C NMR spectra of 1-(*p*-tolyl)ethan-1-one (**2b**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.84 (m, 2H), 7.26-7.23 (m, 2H), 2.56 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 143.7, 134.5, 129.1, 128.2, 26.4, 21.5.

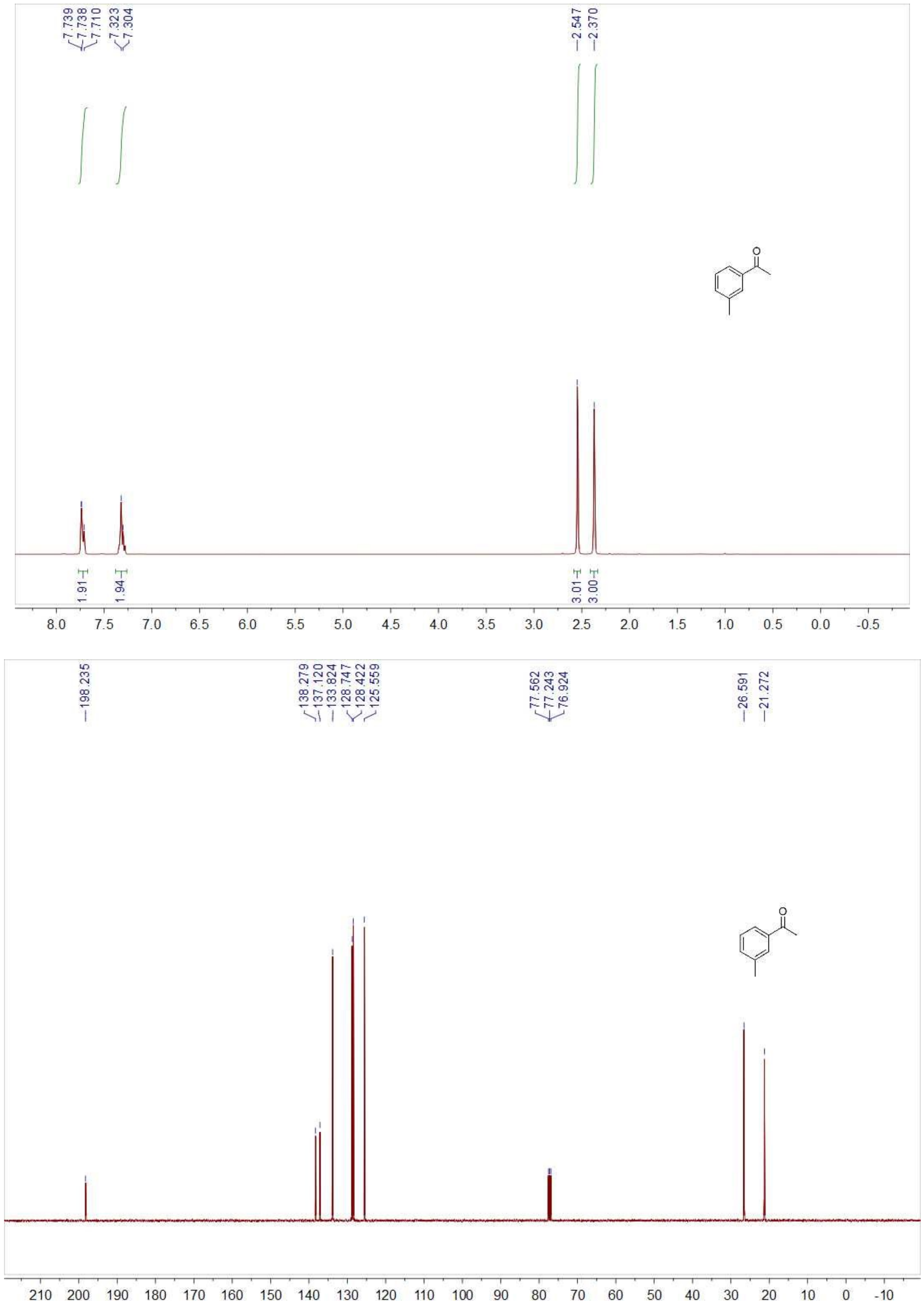


Figure S9. ^{1}H and ^{13}C NMR spectra of 1-(*m*-tolyl)ethan-1-one (**2c**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.71 (m, 2H), 7.32-7.30 (m, 2H), 2.55 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.24, 138.28, 137.12, 133.82, 128.75, 128.42, 125.56, 26.59, 21.27.

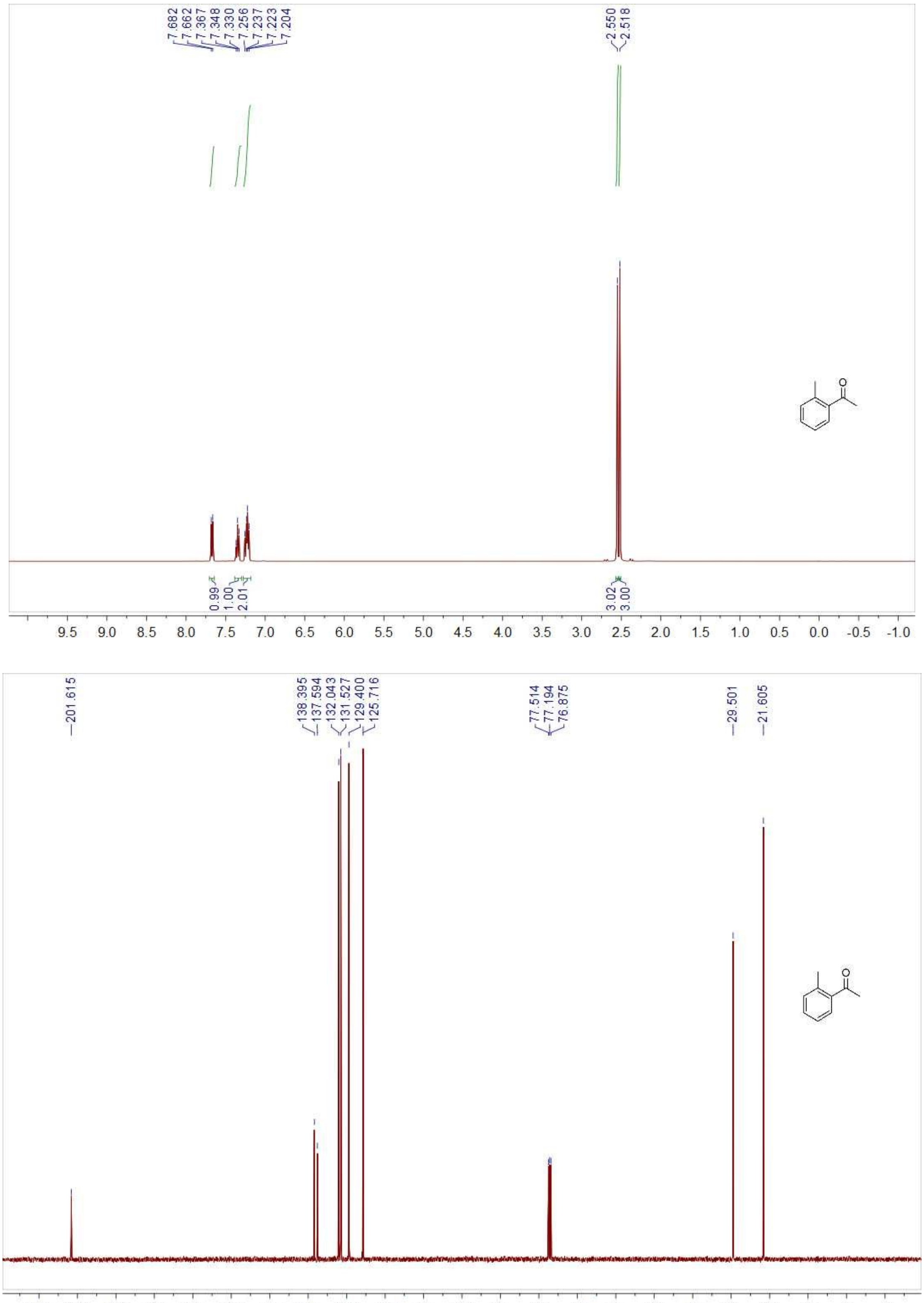


Figure S10. ^{1}H and ^{13}C NMR spectra of 1-(*o*-tolyl)ethan-1-one (**2d**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.23 (q, J = 5.6 Hz, 2H), 2.55 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.62, 138.40, 137.59, 132.04, 131.53, 129.40, 125.72, 29.50, 21.61.

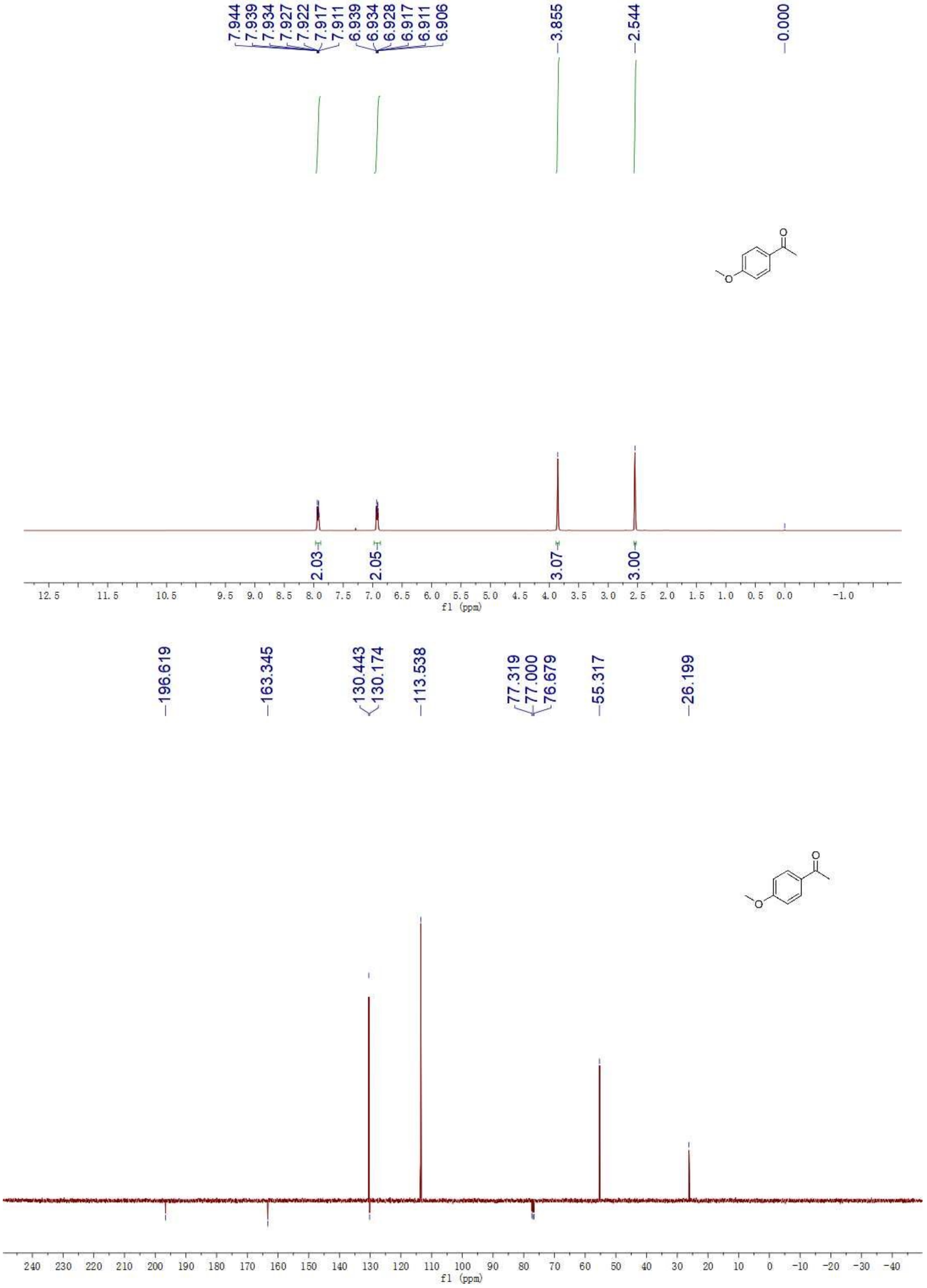


Figure S11. ^{1}H and ^{13}C NMR spectra of 1-(4-methoxyphenyl)ethan-1-one (**2e**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.91 (m, 2H), 6.94-6.91 (m, 2H), 3.86 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 163.3, 130.4, 130.1, 113.5, 55.3, 26.2.

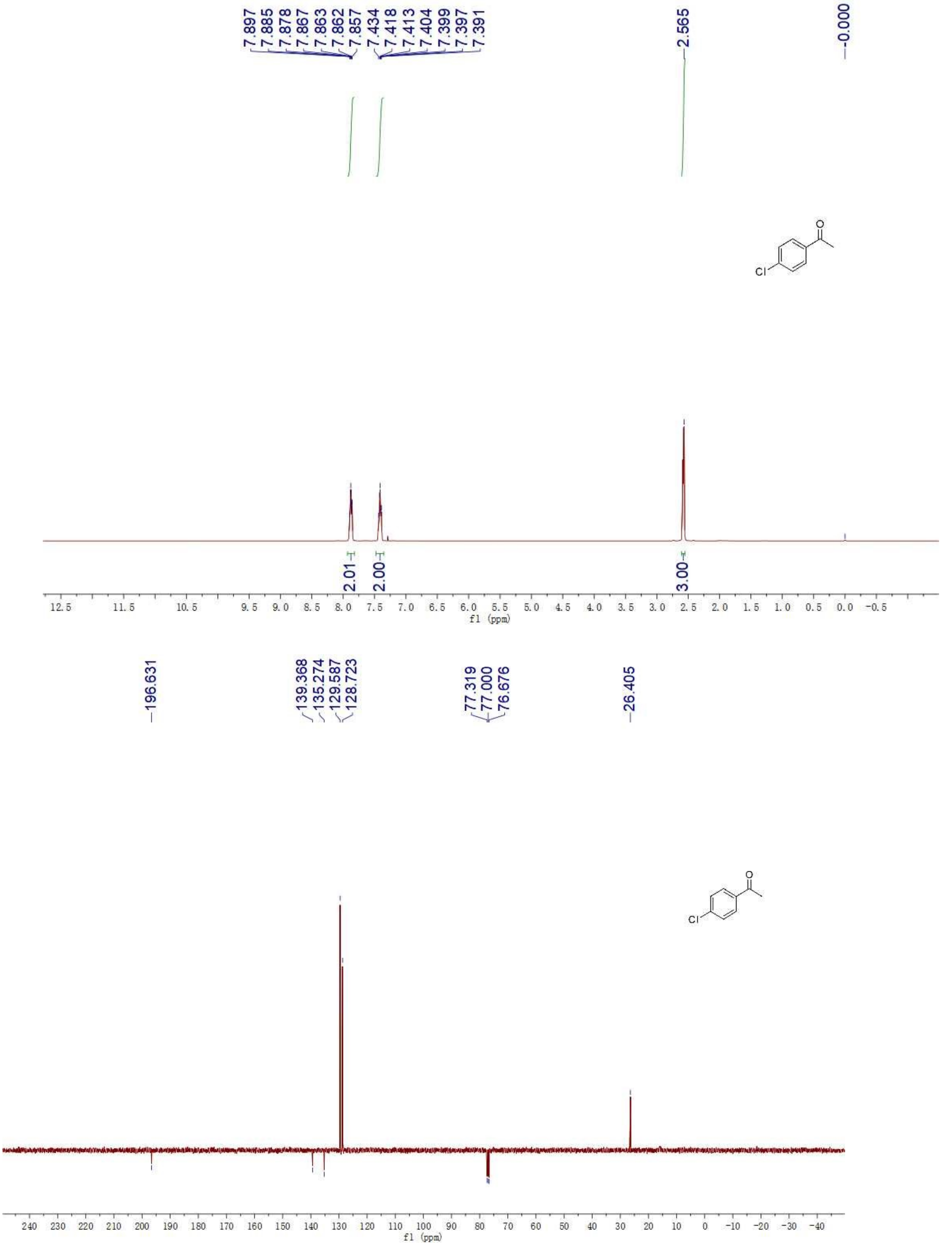


Figure S12. ^{1}H and ^{13}C NMR spectra of 1-(4-chlorophenyl)ethan-1-one (**2f**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.86 (m, 2H), 7.43-7.39 (m, 1H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 139.4, 135.3, 129.6, 128.7, 26.4.

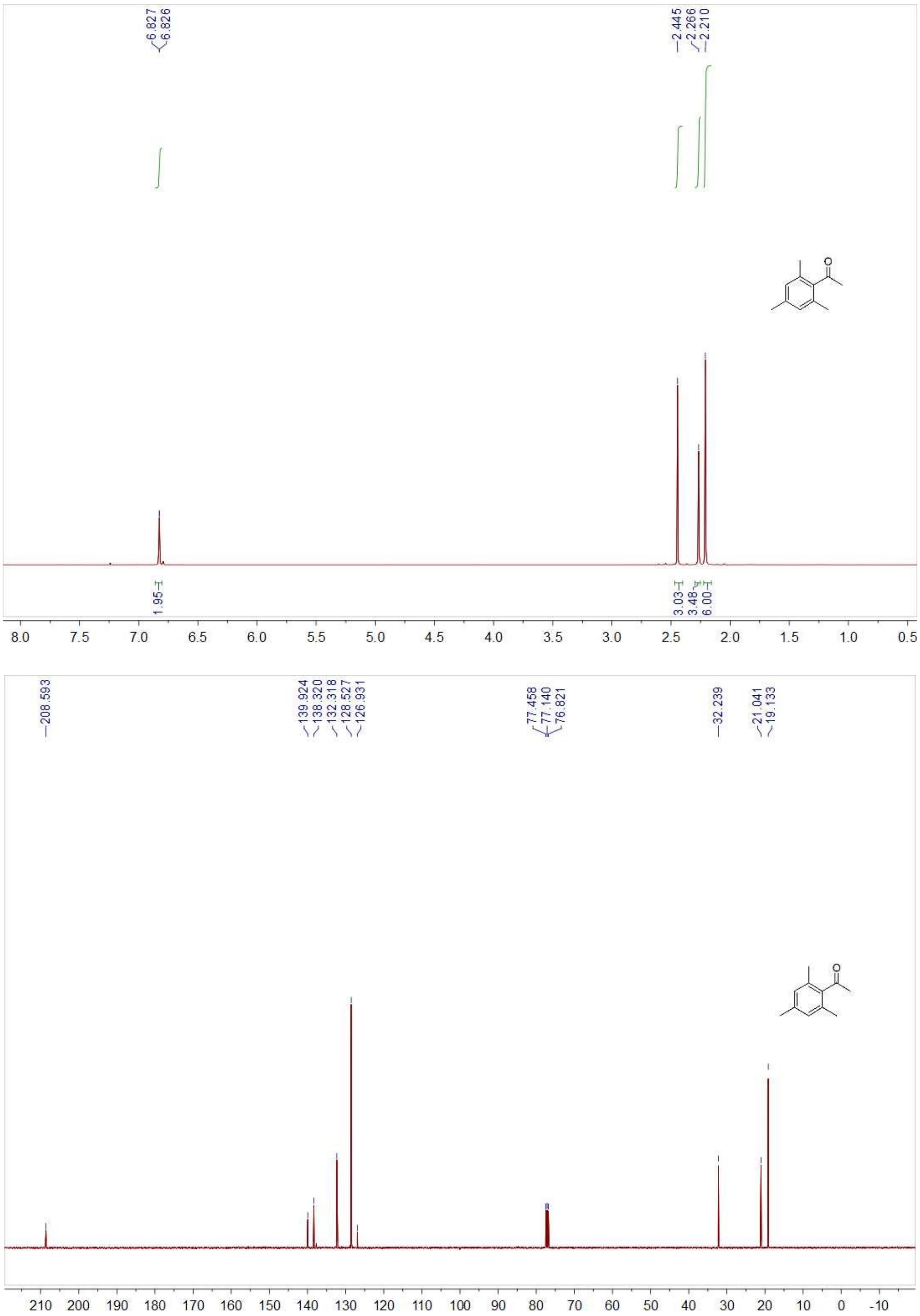


Figure S13. ^{1}H and ^{13}C NMR spectra of 1-(naphthalen-1-yl)ethan-1-one (**2g**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (s, 2H), 2.45 (s, 3H), 2.27 (s, 3H), 2.21 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.6, 139.9, 138.3, 132.3, 128.5, 126.9, 32.2, 21.0, 19.1.

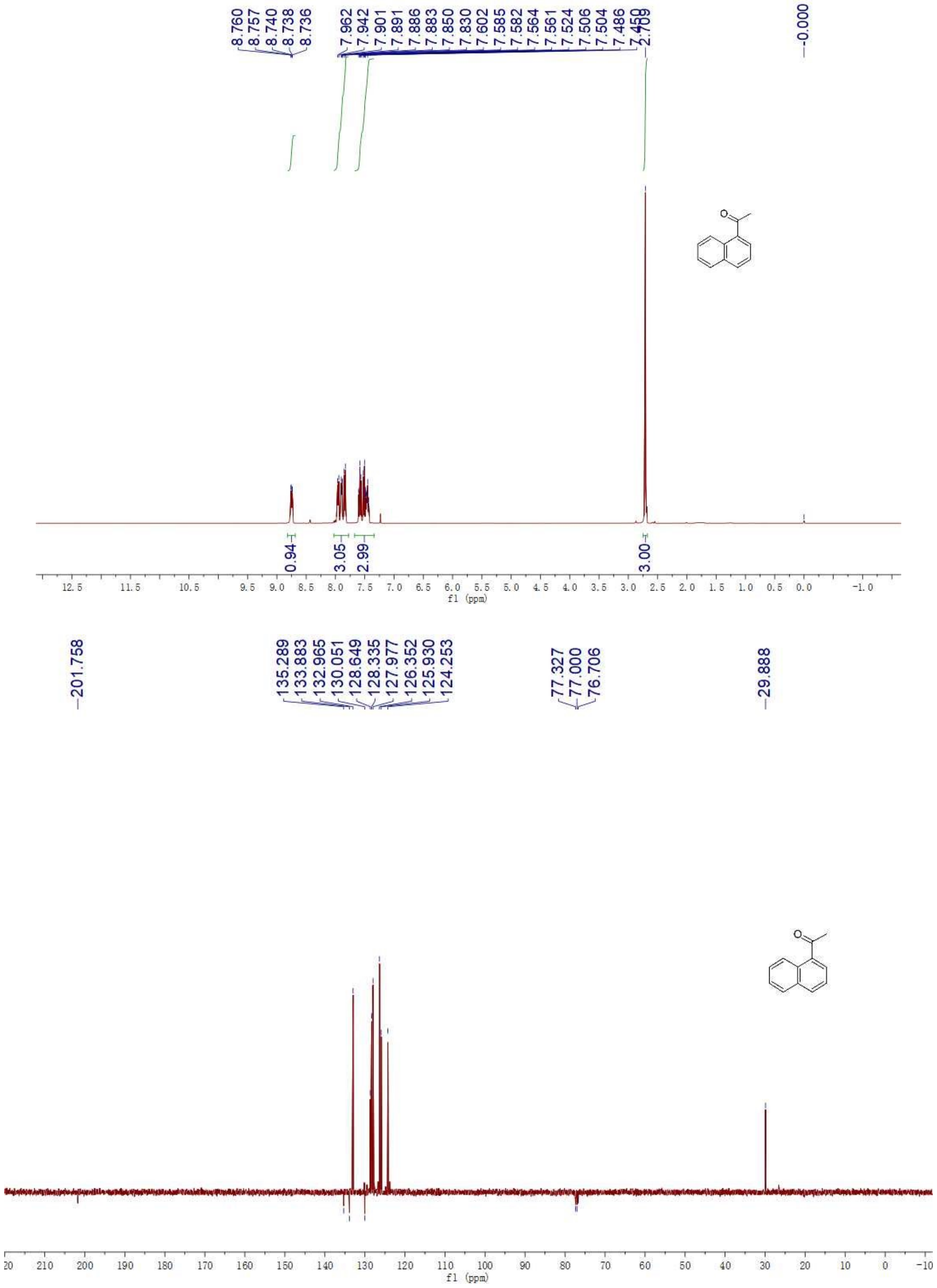


Figure S14. ^{1}H and ^{13}C NMR spectra of 1-mesitylethan-1-one (**2h**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76-8.74 (m, 1H), 7.96-7.83 (m, 3H), 7.60-7.43 (m, 3H), 2.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 135.3, 133.9, 133.0, 130.1, 128.6, 128.3, 128.0, 126.4, 125.9, 124.2, 29.9.

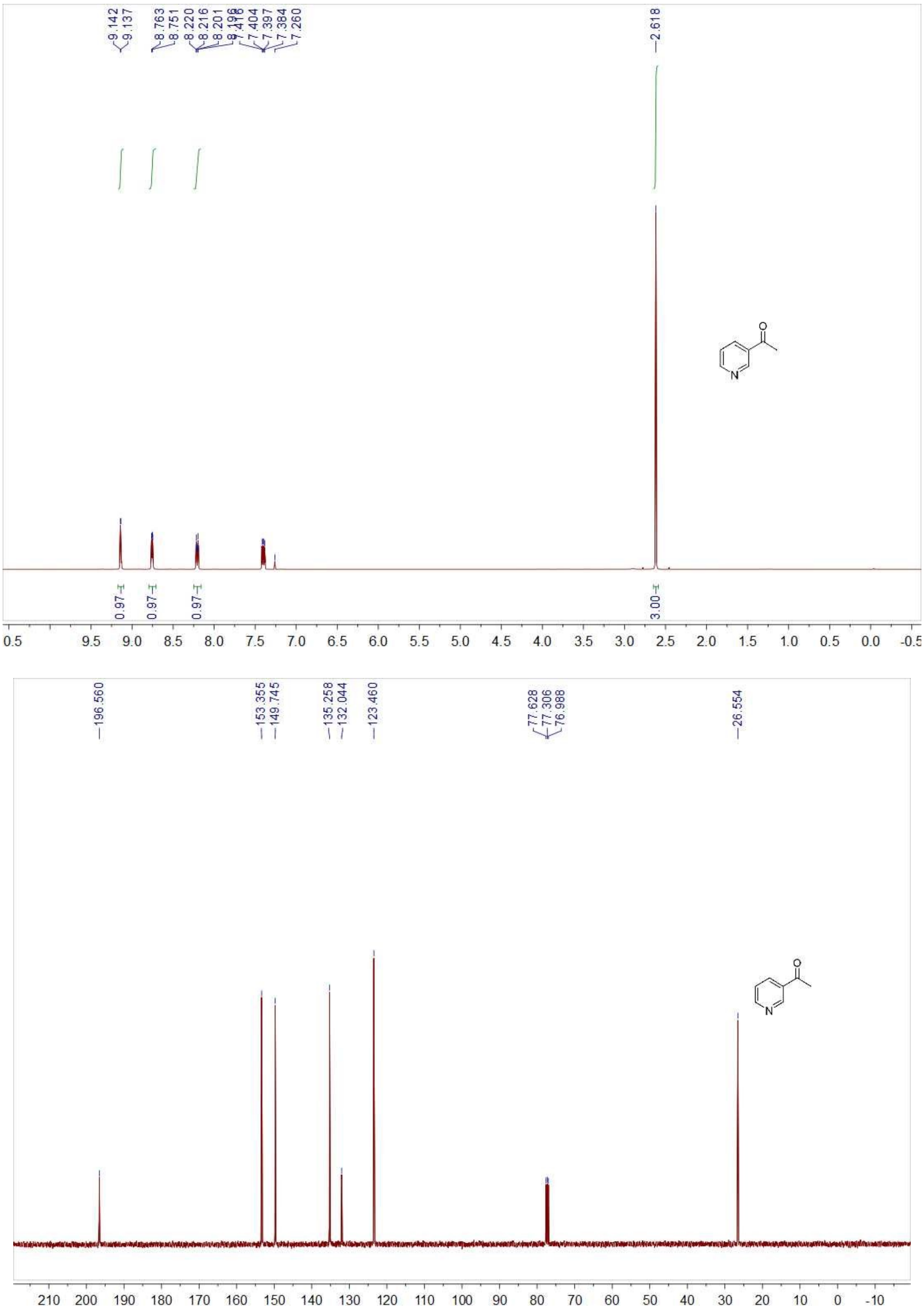


Figure S15. ^{1}H and ^{13}C NMR spectra of 1-(pyridin-3-yl)ethan-1-one (**2h**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (m, *J* = 2.0 Hz, 1H), 8.76, 8.75 (dd, *J* = 1.6, 1.6 Hz, 1H), 8.22, 8.20 (tt, *J* = 1.6, 2.0 Hz, 1H), 7.40 (q, *J* = 2.8 Hz, 1H), 2.62 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.56, 153.36, 149.75, 135.26, 132.04, 123.46, 26.55.

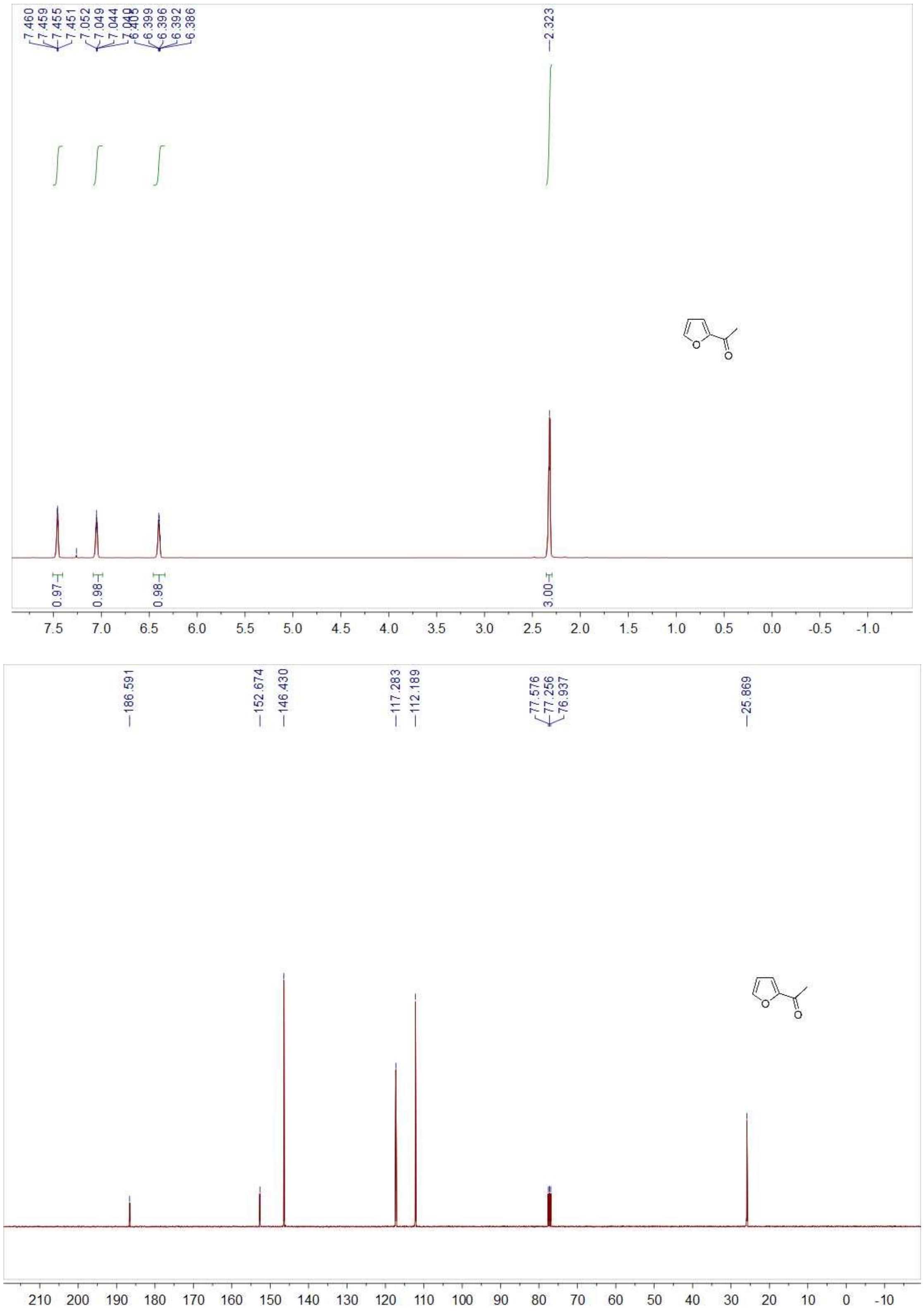


Figure S16. ^{1}H and ^{13}C NMR spectra of 1-(furan-2-yl)ethan-1-one (**2j**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.45 (m, 1H), 7.06-7.04 (m, 1H), 8.41-8.39 (m, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.59, 152.67, 146.43, 117.28, 112.19, 25.87.

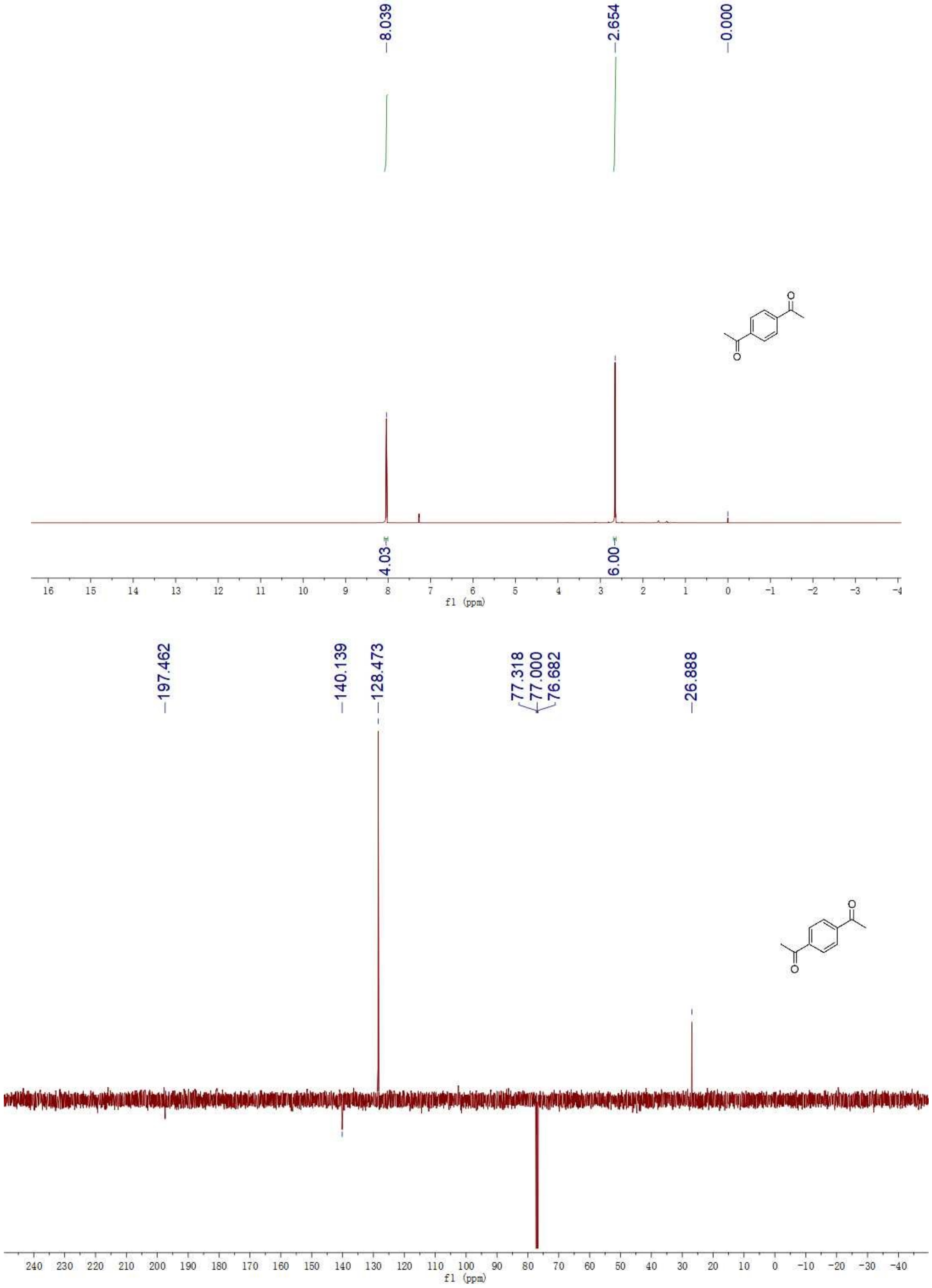


Figure S17. ^{1}H and ^{13}C NMR spectra of 1,1'-(1,4-phenylene)bis(ethan-1-one) (**2k**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 4H), 2.65 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 140.1, 128.5, 26.9.

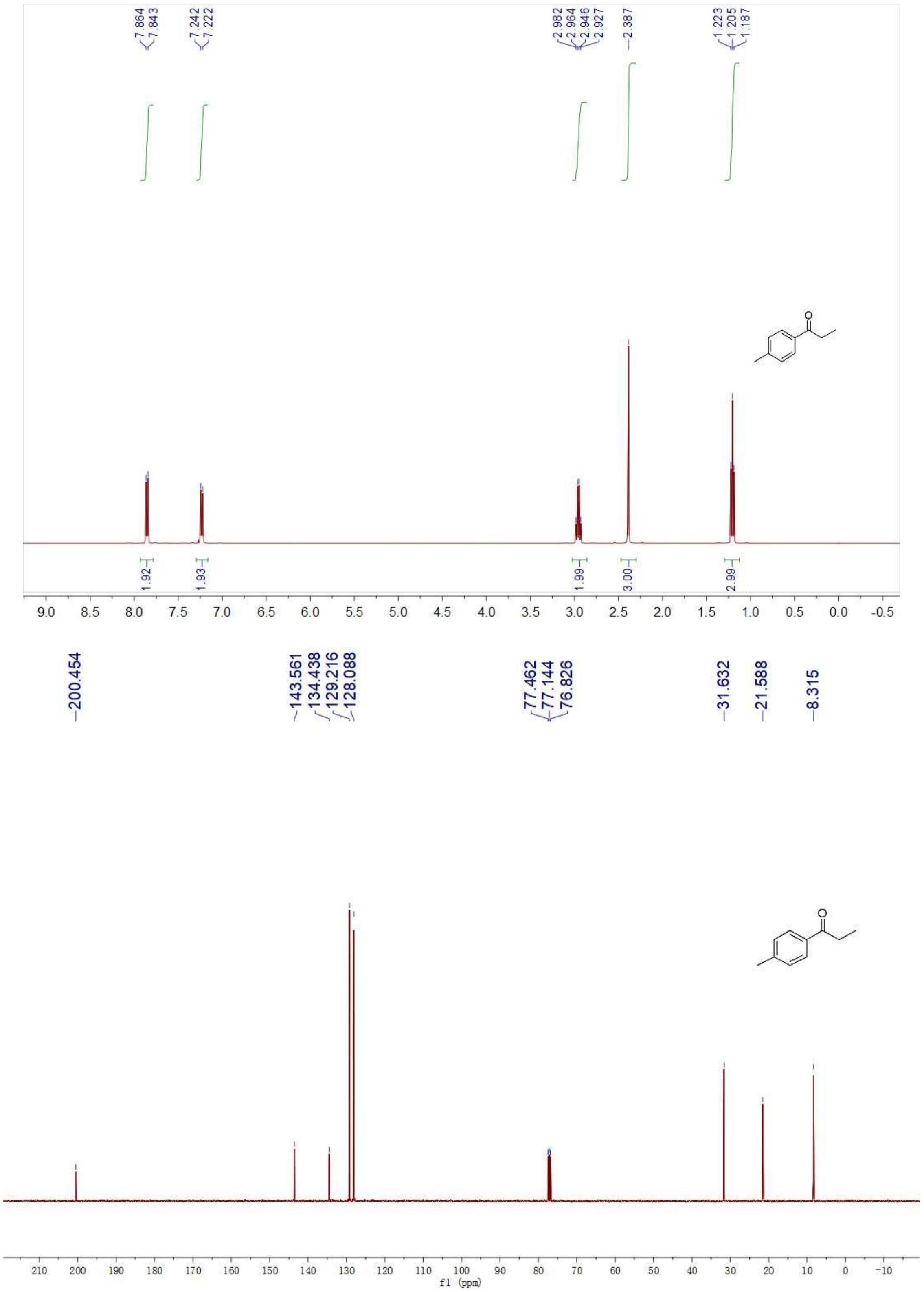


Figure S18. ^{1}H and ^{13}C NMR spectra of 1,1'-(1,4-phenylene)bis(ethan-1-one) (**2l**). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.96 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 200.45, 143.56, 134.44, 129.22, 128.09, 31.63, 21.59, 8.32.

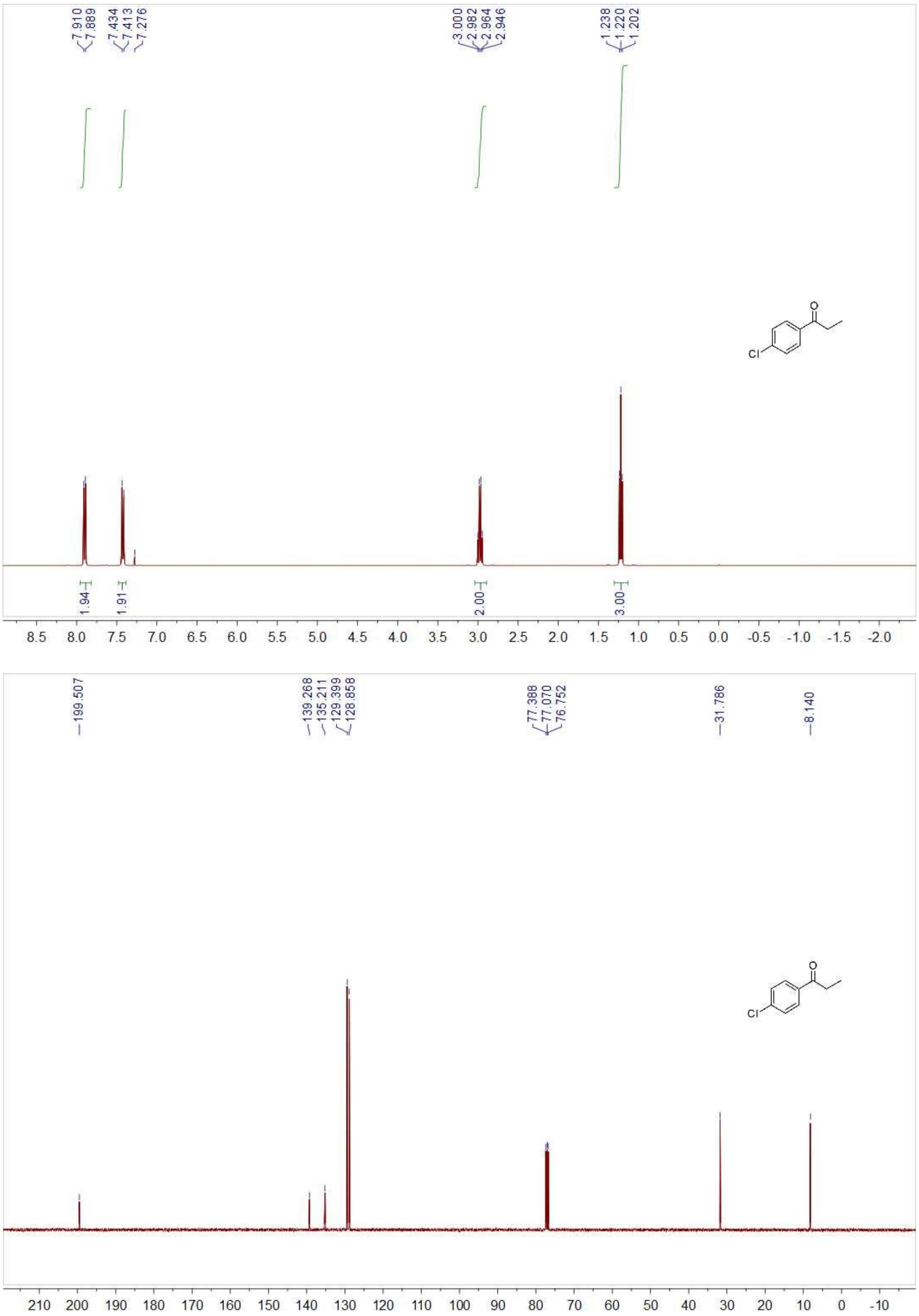


Figure S19. ^{1}H and ^{13}C NMR spectra of 1-(4-chlorophenyl)propan-1-one (**2m**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 2.97 (q, J = 7.2 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.51, 139.27, 135.21, 129.40, 128.86, 31.79, 8.14.

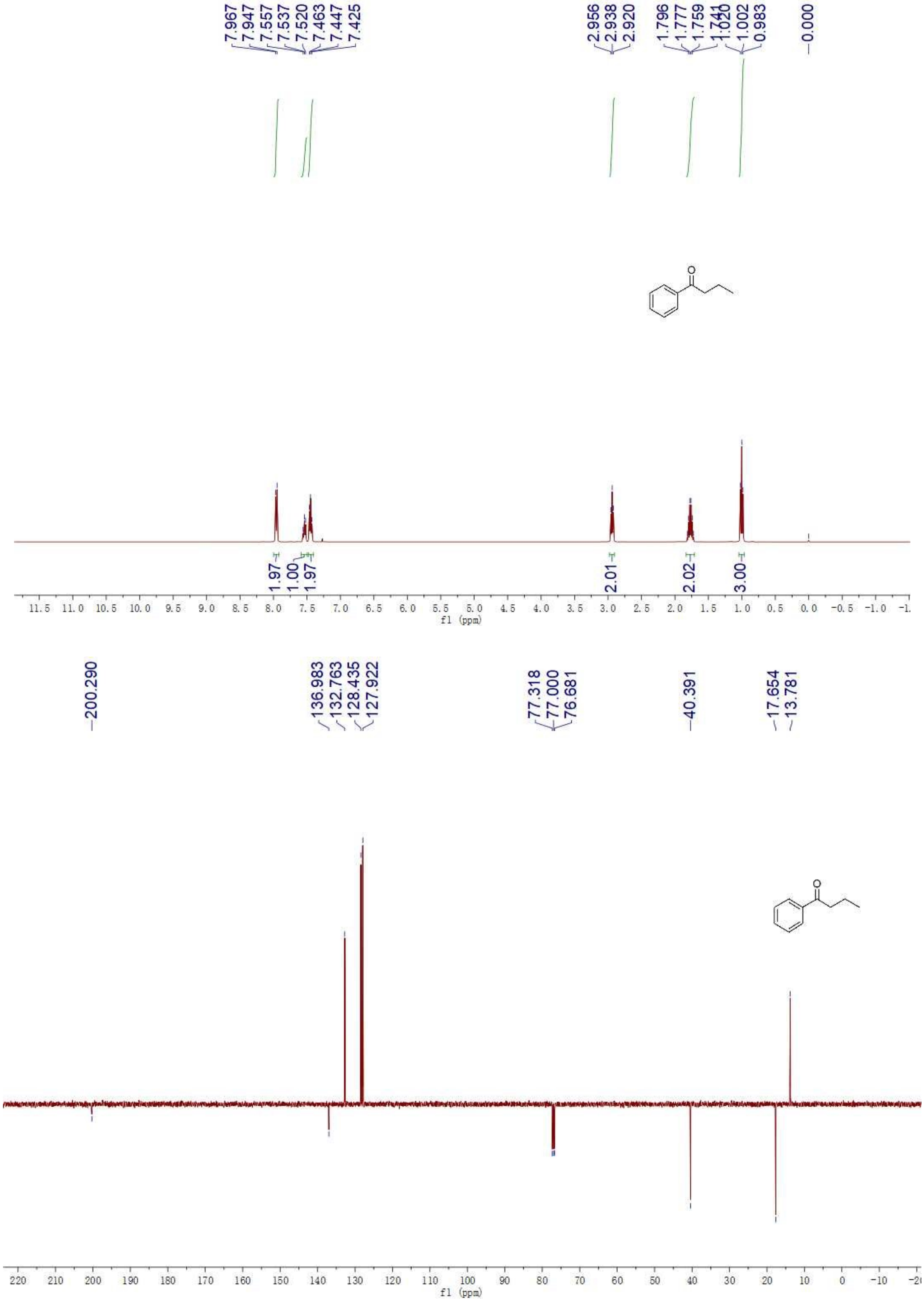


Figure S20. ^{1}H and ^{13}C NMR spectra of 1-phenylbutan-1-one (**2n**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.0 Hz, 2H), 7.54 (t, J = 8.0 Hz, 1H), 7.45 (t, J = 6.4 Hz, 2H), 2.94 (t, J = 7.2 Hz, 2H), 1.81-1.72 (m, 2H), 1.00 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 136.9, 132.8, 128.4, 127.9, 40.4, 17.7, 13.8.

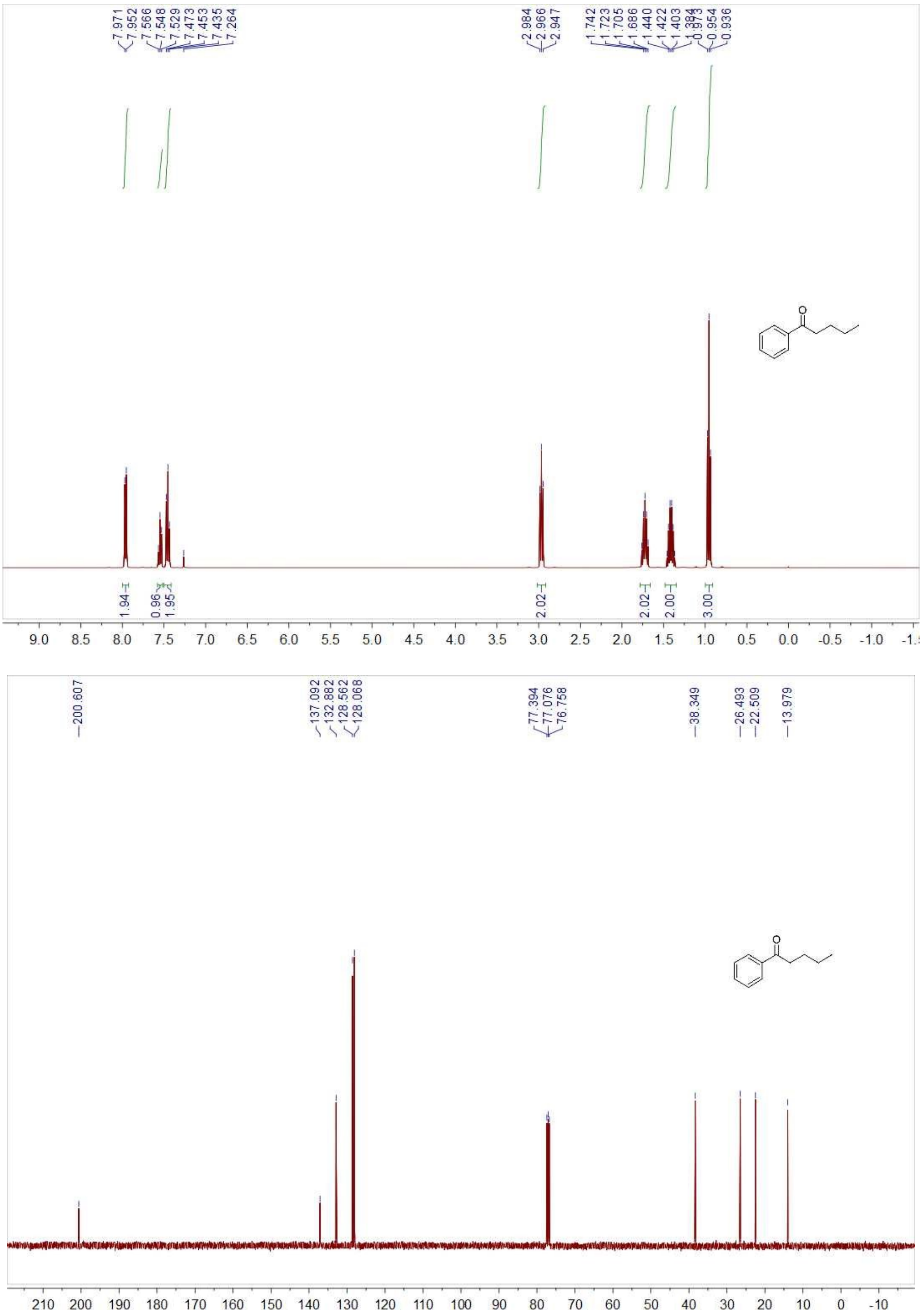
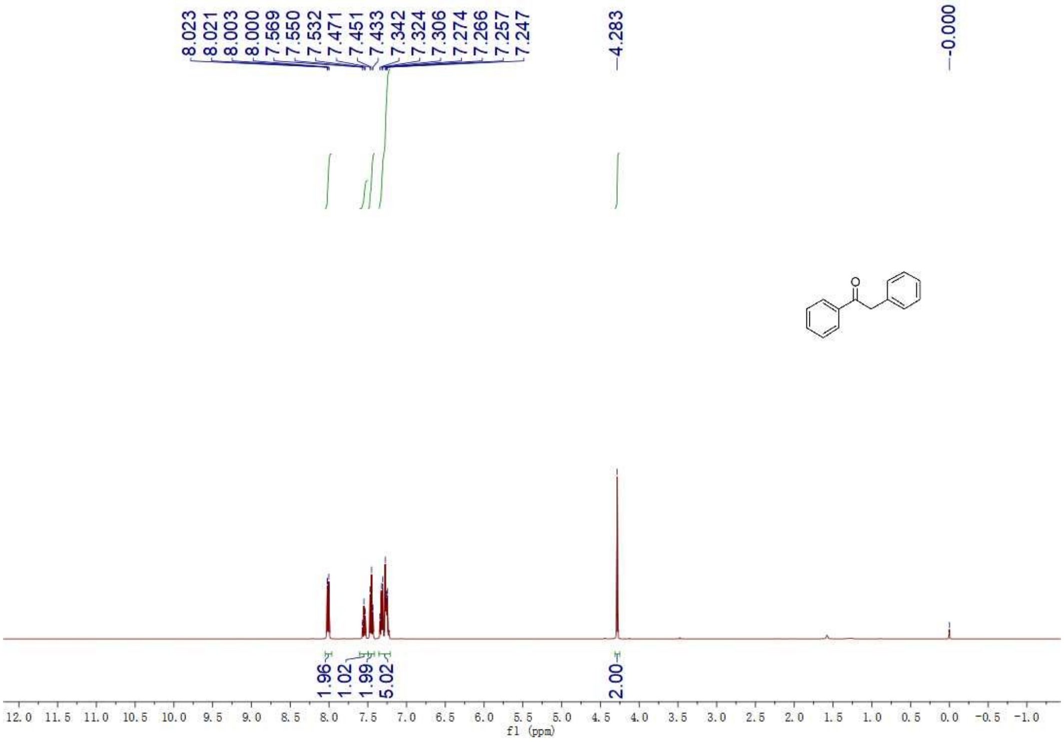


Figure S21. ^{1}H and ^{13}C NMR spectra of 1-phenylpentan-1-one (**2o**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 2.97 (t, J = 7.2 Hz, 2H), 1.72 (quint, J = 7.6 Hz, 2H), 1.41 (sext, J = 7.6 Hz, 2H), 0.954 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 137.1, 132.9, 128.6, 128.1, 38.3, 26.5, 22.5, 13.9.



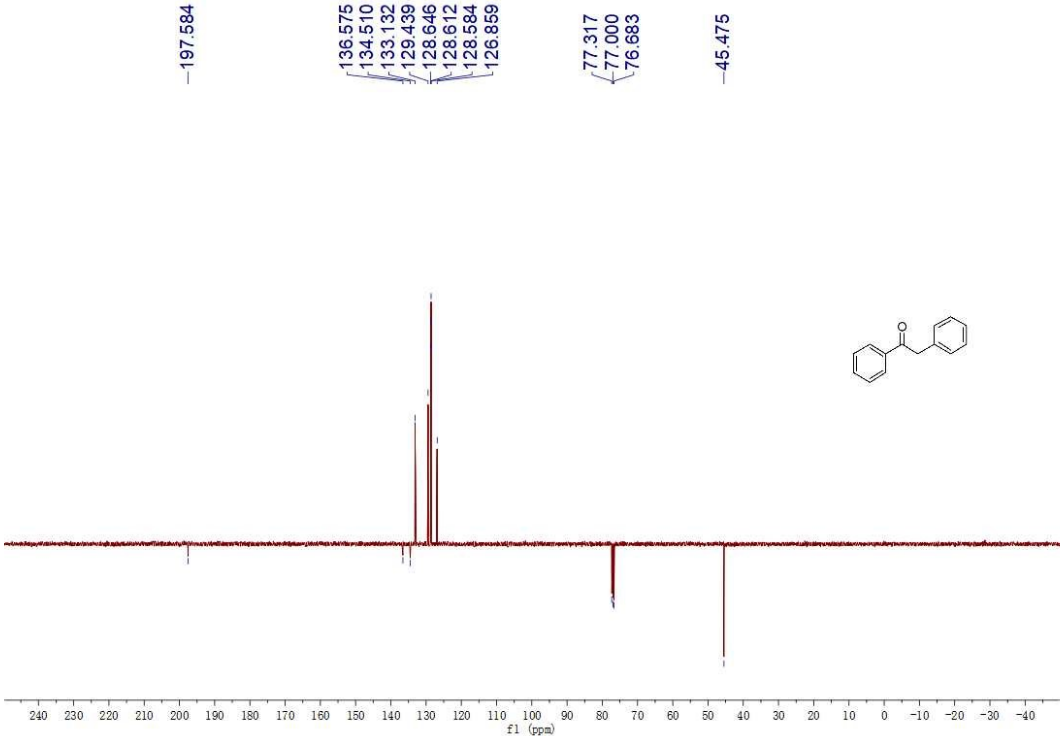


Figure S22. ^{1}H and ^{13}C NMR spectra of 1,2-diphenylethan-1-one (**2p**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.98 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.34-7.25 (m, 5H), 4.28 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 136.6, 134.5, 133.1, 129.4, 128.6, 128.6, 128.5, 126.9, 45.5.

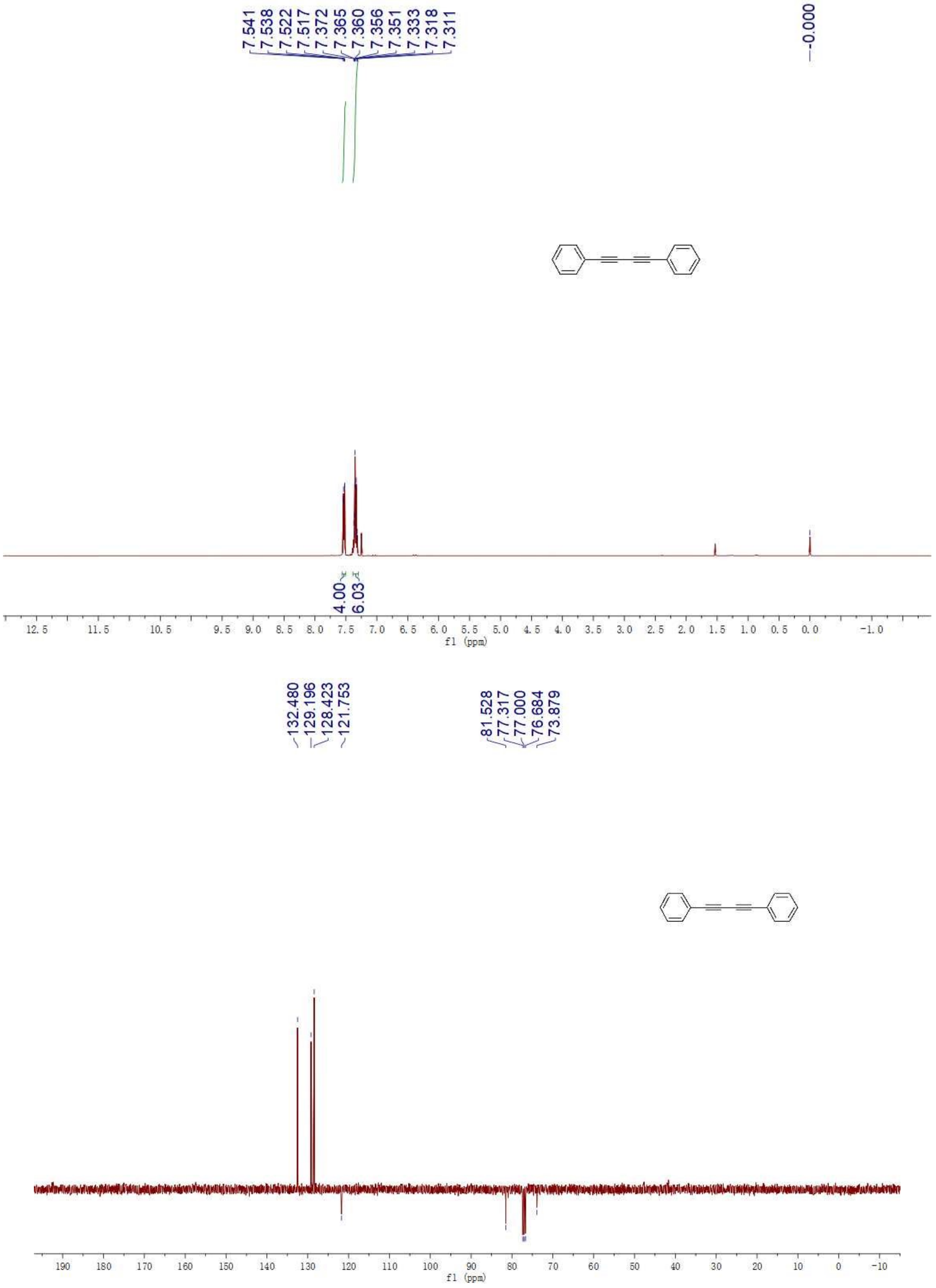


Figure S23. ^{1}H and ^{13}C NMR spectra of 1,4-diphenylbuta-1,3-diyne (**3a**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.52 (m, 4H), 7.37-7.31 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.5, 129.2, 128.4, 121.8, 81.5, 73.9.

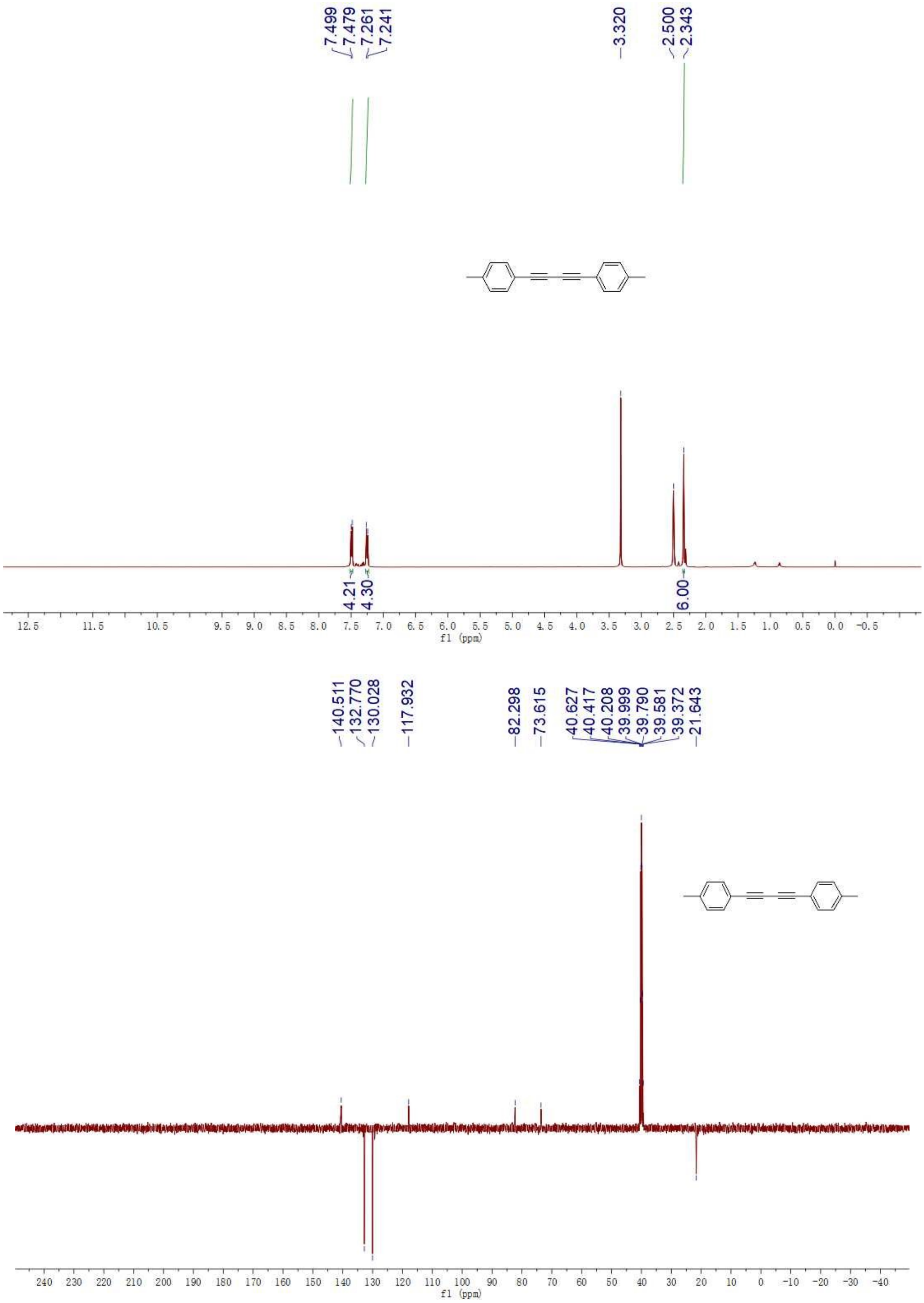


Figure S24. ^{1}H and ^{13}C NMR spectra of 1,4-di-p-tolylbuta-1,3-diyne (**3b**). ^{1}H NMR (400 MHz, DMSO-*d6*): δ 7.49 (d, *J* = 8.0 Hz, 4H), 7.25 (d, *J* = 8.0 Hz, 4H), 2.34 (s, 6H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 140.5, 132.8, 130.1, 117.9, 82.3, 73.6, 21.6.

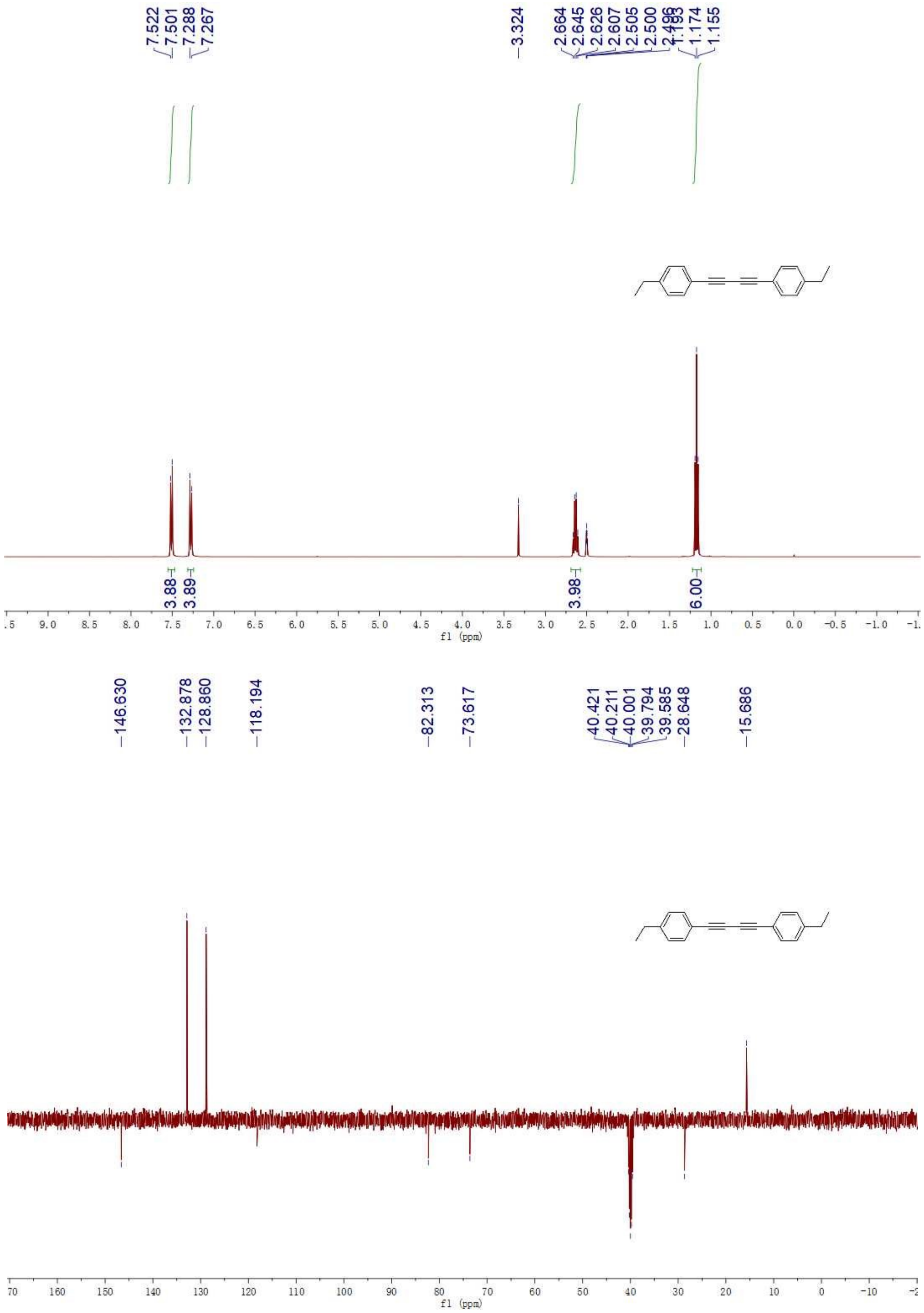


Figure S25. ^{1}H and ^{13}C NMR spectra of 1,4-bis(4-ethylphenyl)buta-1,3-diyne (**3c**). ^{1}H NMR (400 MHz, DMSO-*d6*): δ 7.51 (d, *J* = 8.4 Hz, 4H), 7.28 (d, *J* = 8.4 Hz, 4H), 2.64 (q, *J* = 7.6 Hz, 4H), 1.17 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 146.6, 132.9, 128.9, 118.2, 82.3, 73.6, 28.6, 15.7.

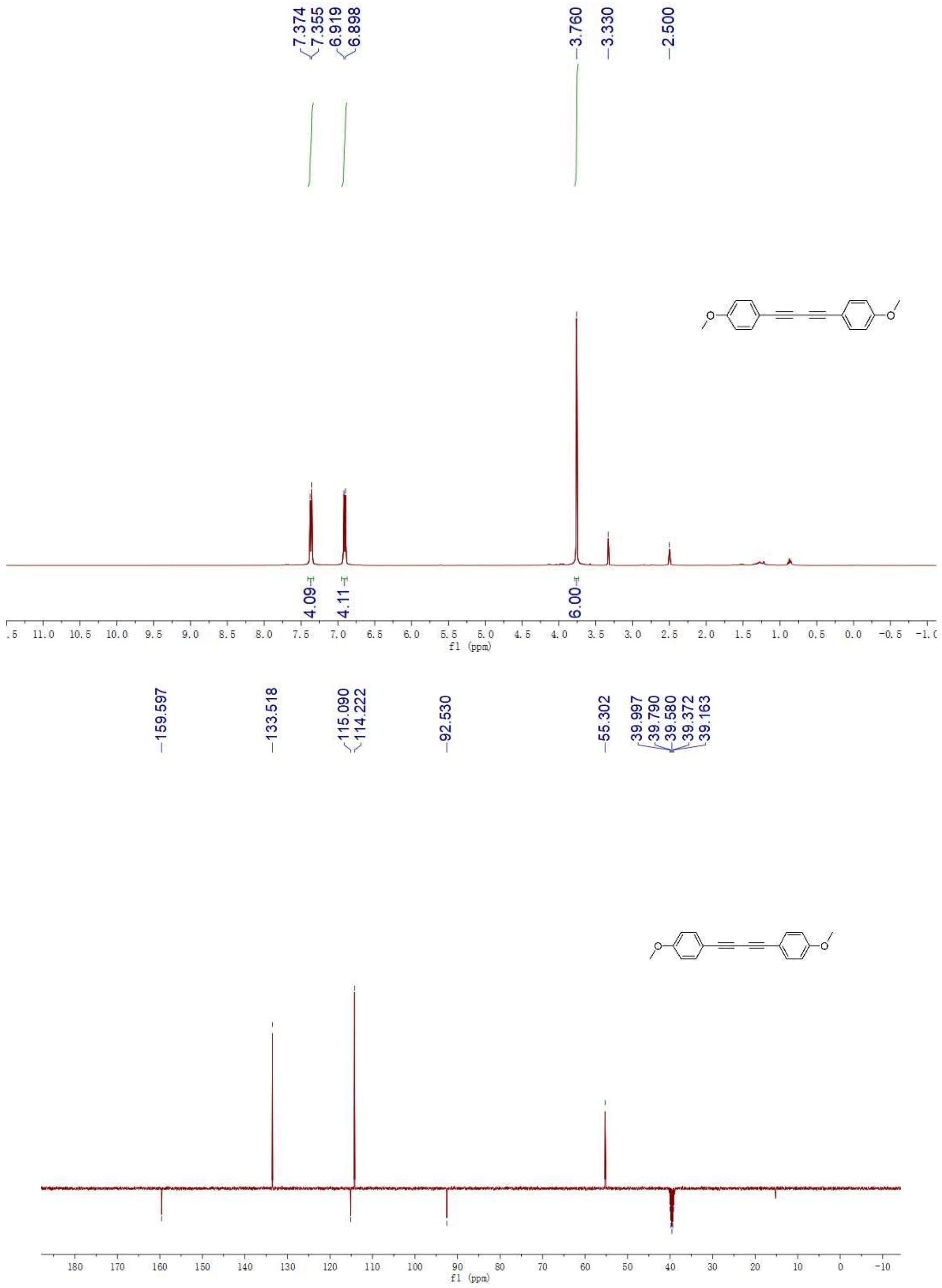


Figure S26. ^{1}H and ^{13}C NMR spectra of 1,4-bis(4-methoxyphenyl)buta-1,3-diyne (**3d**). ^{1}H NMR (400 MHz, DMSO-*d*6): δ 7.36 (d, *J* = 7.6 Hz, 4H), 6.91 (d, *J* = 8.4 Hz, 4H), 3.76 (s, 6H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 159.6, 133.5, 115.1, 114.2, 92.5, 55.3.

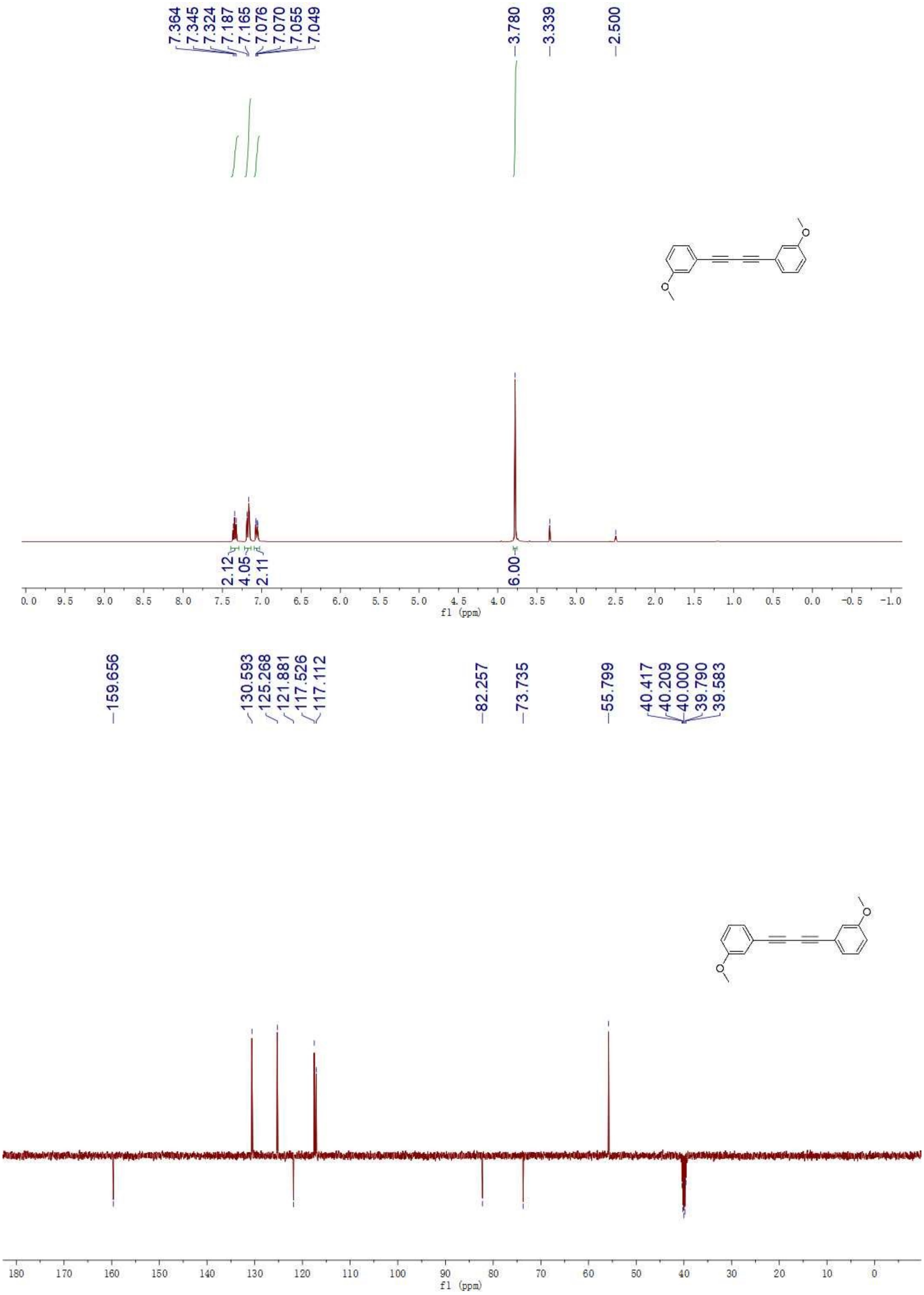


Figure S27. ^{1}H and ^{13}C NMR spectra of 1,4-bis(3-methoxyphenyl)buta-1,3-diyne (**3e**). ^{1}H NMR (400 MHz, DMSO-*d*6): δ 7.35 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 4H), 7.08-7.05 (m, 2H), 3.78 (s, 6H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 159.7, 130.6, 125.3, 121.9, 117.5, 117.1, 82.3, 73.7, 55.8.

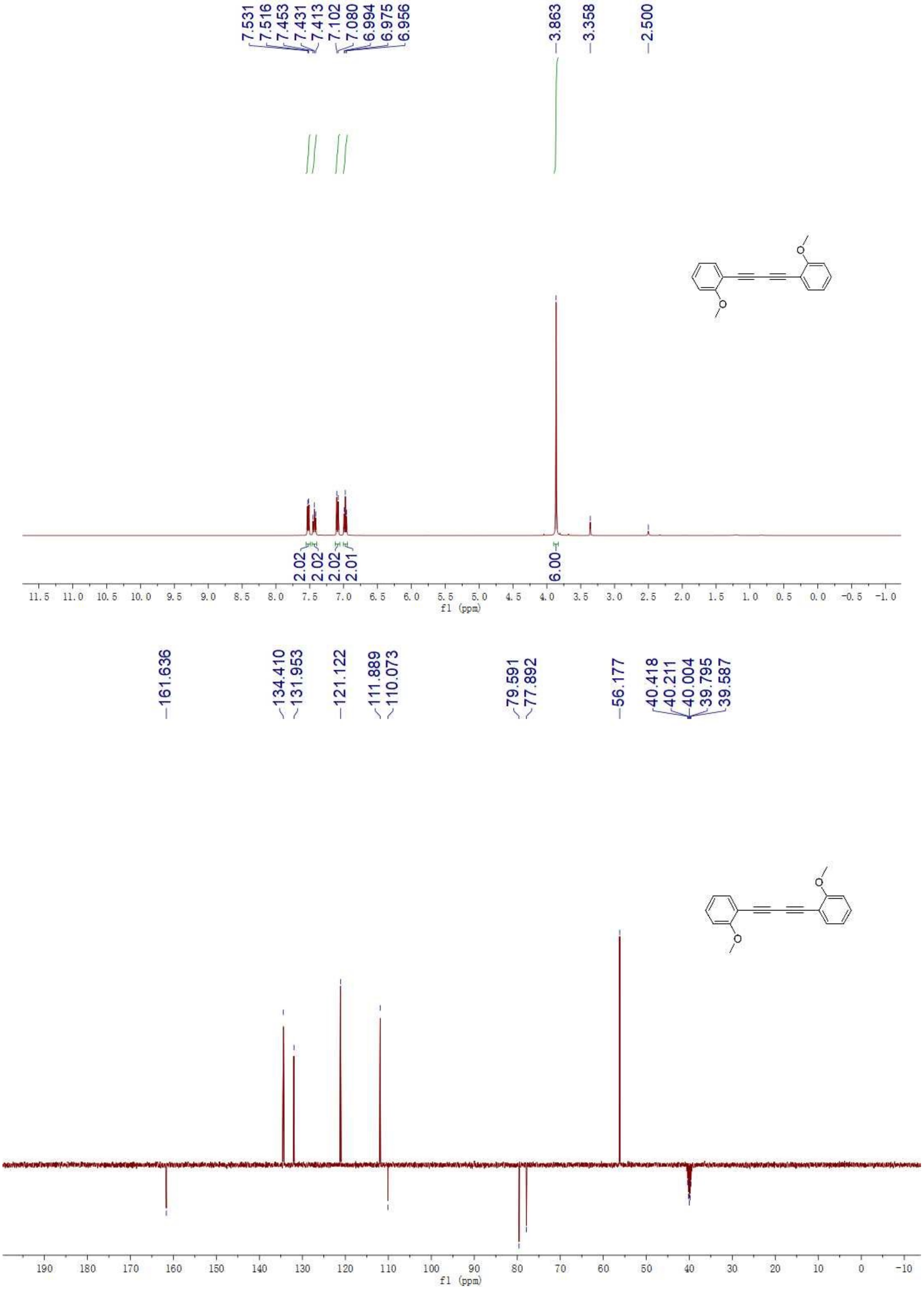
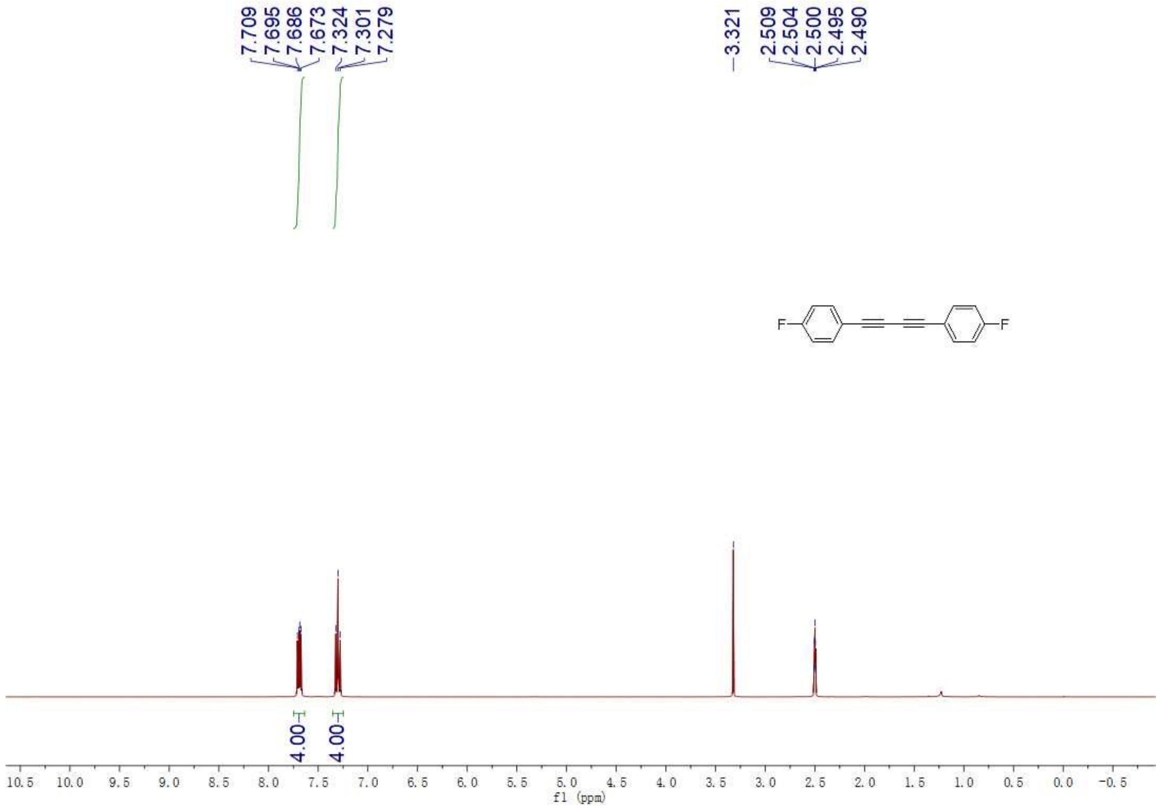
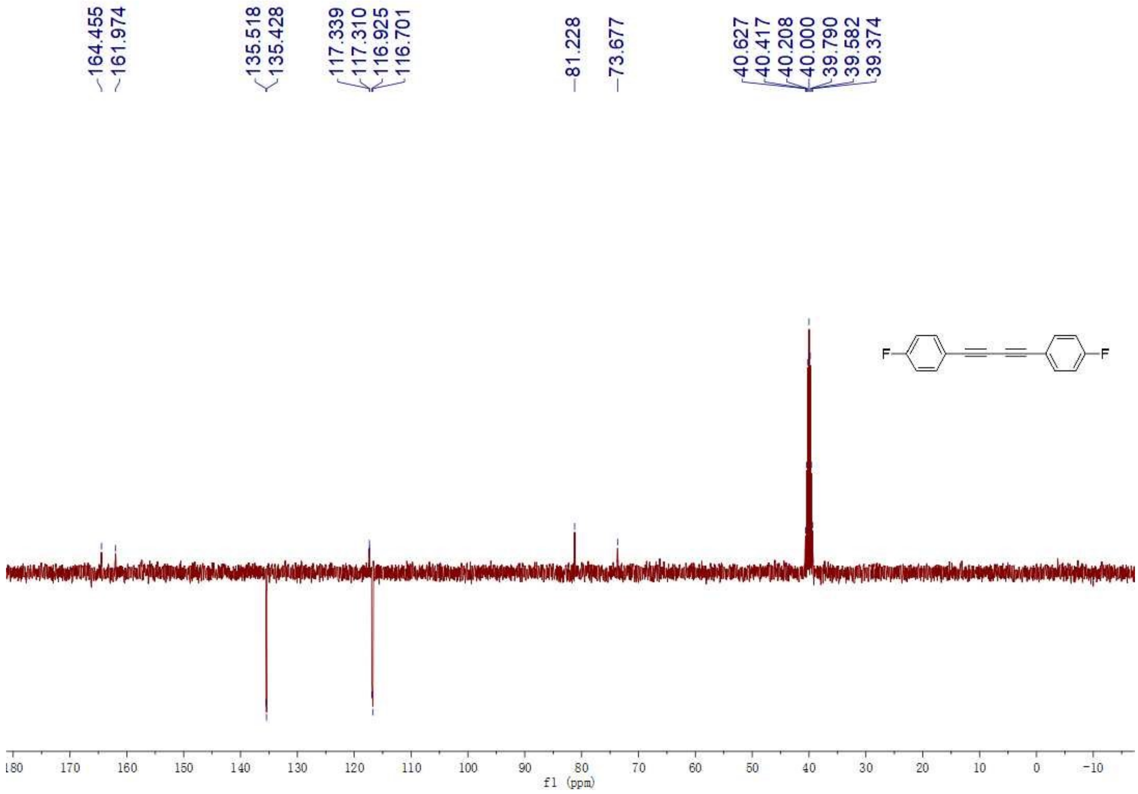


Figure S28. ^{1}H and ^{13}C NMR spectra of 1,4-bis(2-methoxyphenyl)buta-1,3-diyne (**3f**). ^{1}H NMR (400 MHz, DMSO-*d*6): δ 7.52 (d, *J* = 6.0 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 3.86 (s, 6H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 161.6, 134.4, 132.0, 121.1, 112.0, 110.1, 79.6, 78.0, 56.2.


7.709
7.695
7.686
7.673
7.324
7.301
7.279
3.321
2.509
2.504
2.500
2.495
2.490
F
F
4.00
4.00
10.5 10.0 9.5 9.0 8.5 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 -0.5
f1 (ppm)


164.455
161.974
135.518
135.428
117.339
117.310
116.925
116.701
81.228
73.677
40.627
40.417
40.208
40.000
39.790
39.582
39.374
F
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

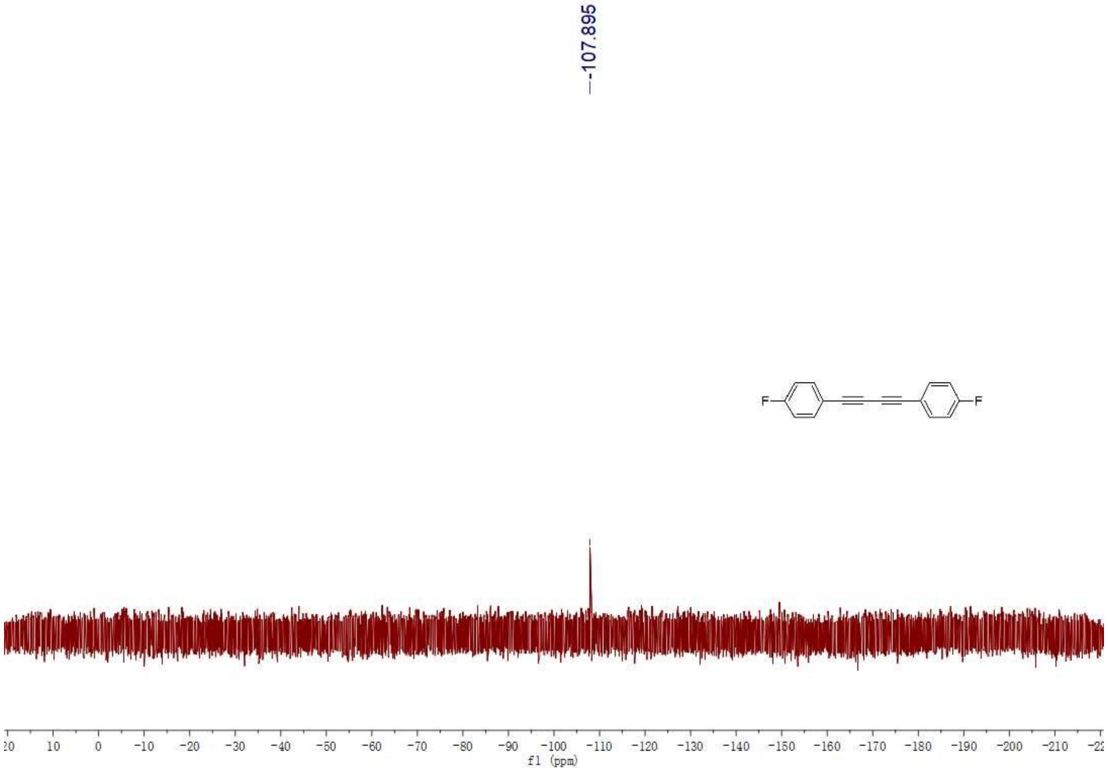
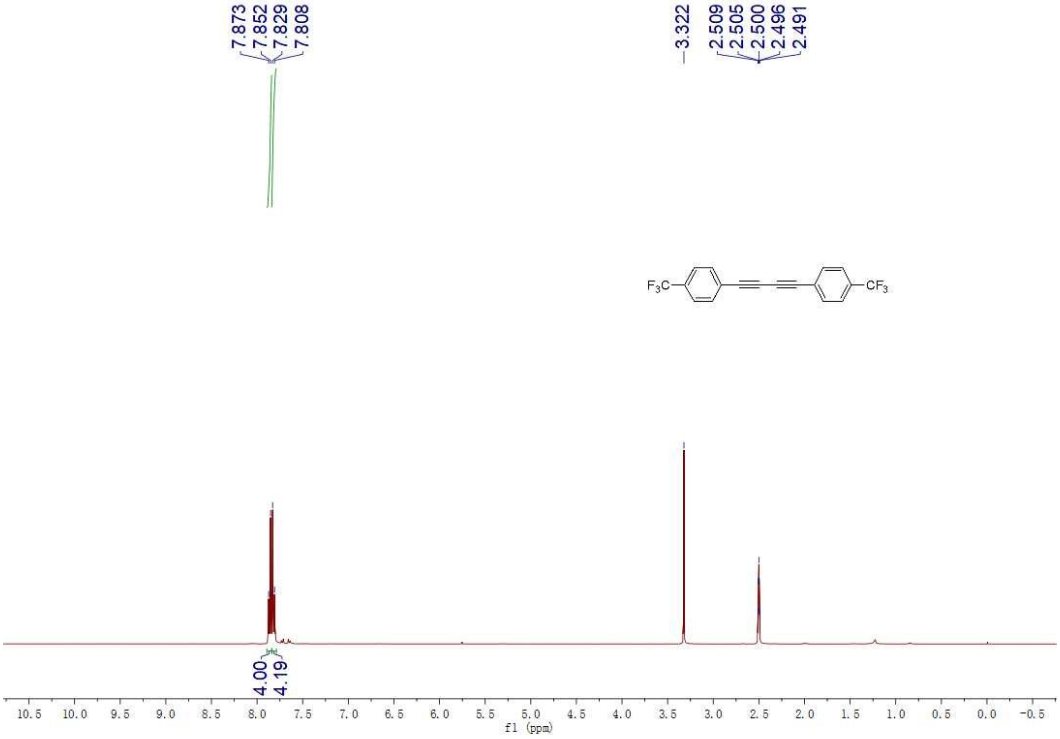
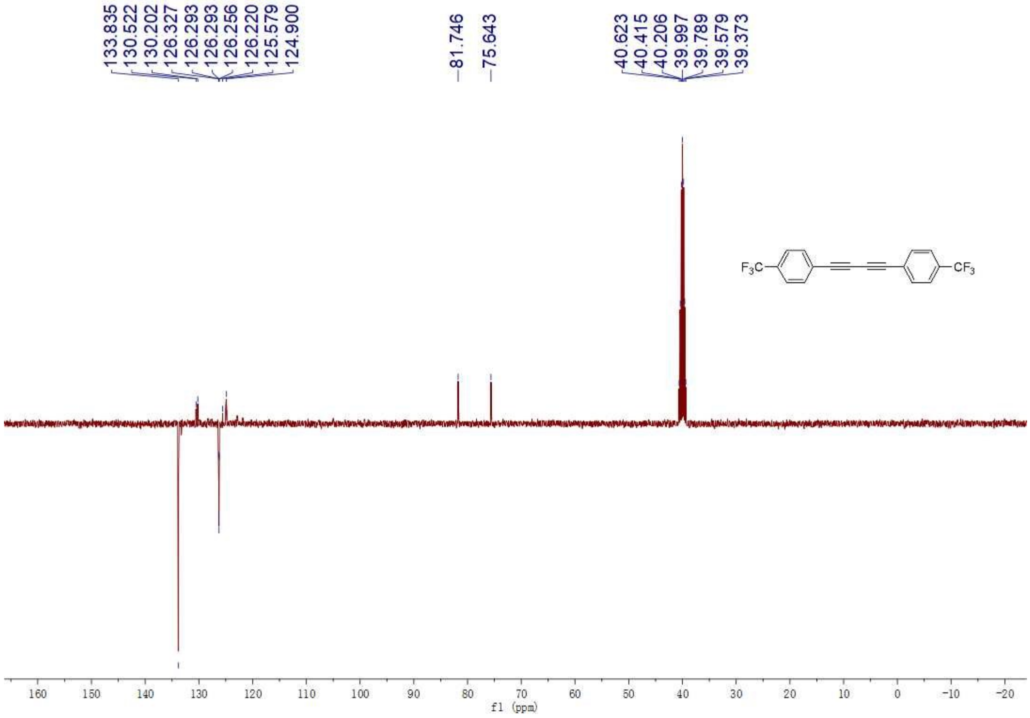


Figure S29. ^{1}H, ^{13}C and ^{19}F NMR spectra of 1,4-bis(4-fluorophenyl)buta-1,3-diyne (**3g**). ^{1}H NMR (400 MHz, DMSO-*d*6): δ 7.69 (q, *J* = 3.6 Hz, 4H), 7.30 (d, *J* = 9.2 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 164.5, 162.0 135.5 (d, *J* = 9.0 Hz), 117.3 (d, *J* = 2.9 Hz), 116.8 (d, *J* = 22.4 Hz), 81.2, 73.7. ^{19}F NMR (376 MHz, DMSO-*d*6): δ -107.90


7.873
7.852
7.829
7.808
3.322
2.509
2.505
2.500
2.496
2.491
F3C
CF3
4.00
4.19
10.5 10.0 9.5 9.0 8.5 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 -0.5
f1 (ppm)


133.835
130.522
130.202
126.327
126.293
126.293
126.256
126.220
125.579
124.900
81.746
75.643
40.623
40.415
40.206
39.997
39.789
39.579
39.373
F3C
CF3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

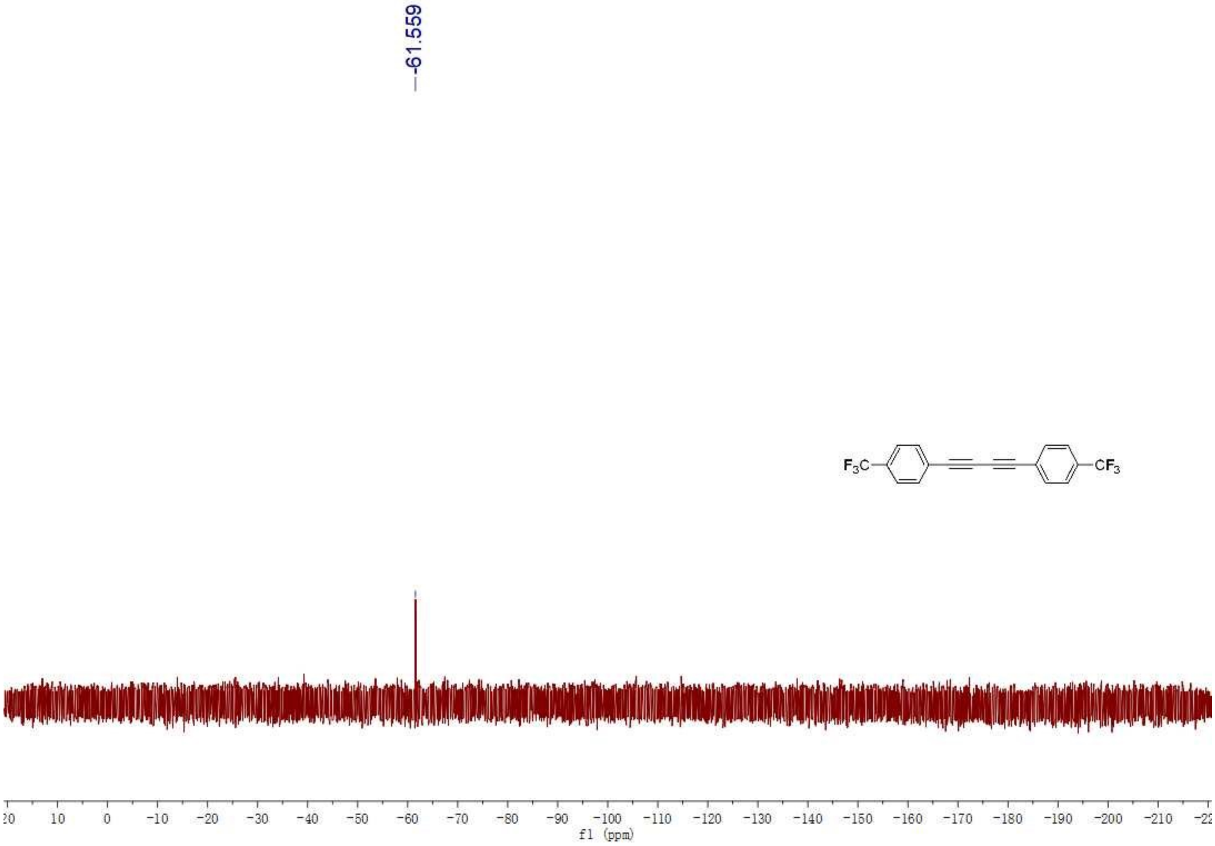


Figure S30. ^{1}H, ^{13}C and ^{19}F NMR spectra of 1,4-bis(4-(trifluoromethyl)phenyl)buta-1,3-diyne (**3h**). ^{1}H NMR (400 MHz, DMSO-*d6*): δ 7.86, 7.82 (dd, J = 8.4, 8.4 Hz, 8H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 133.8, 130.5, 130.2, 126.3 (q, J = 3.7 Hz), 81.7, 75.6. ^{19}F NMR (376 MHz, DMSO-*d6*): δ -61.56

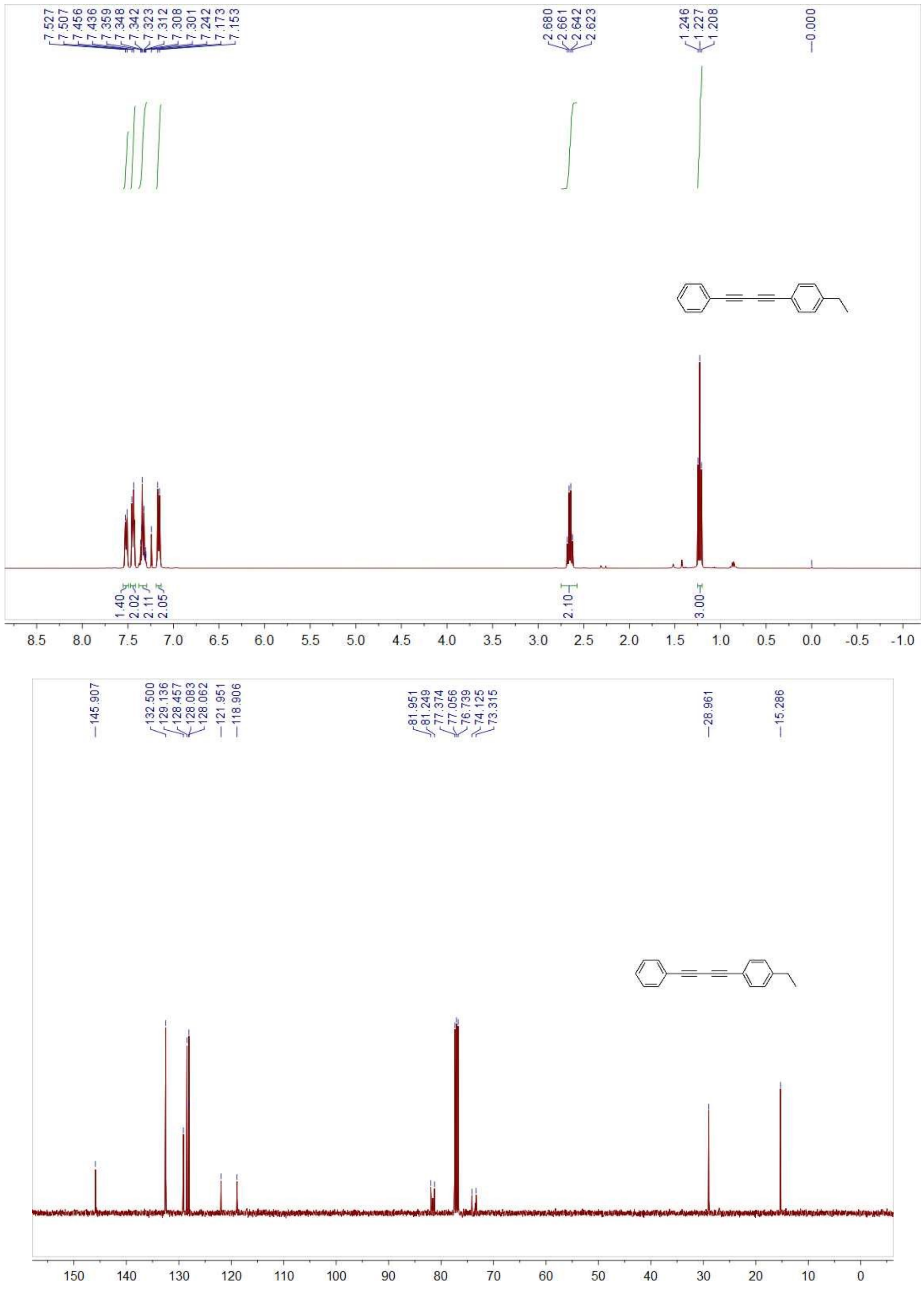


Figure S31. ^{1}H and^{13}C NMR spectra of 1-ethyl-4-(phenylbuta-1,3-diyn-1-yl)benzene (**4a**).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.36-7.30 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 145.9, 132.5, 129.1, 128.5, 128.1, 128.1, 122.0, 118.9, 82.0, 81.2, 74.1, 73.3, 29.0, 15.3.

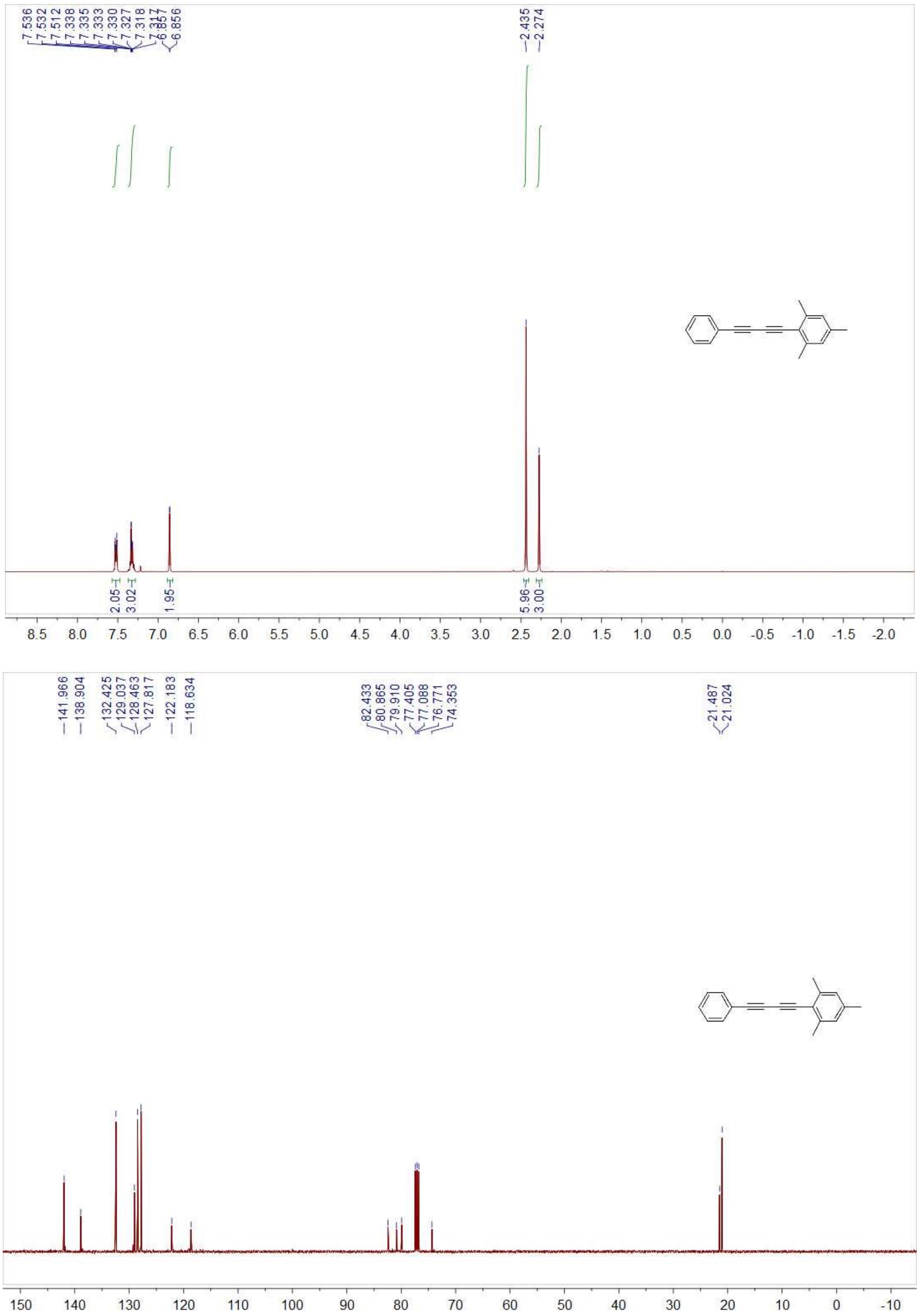


Figure S32. ^{1}H and^{13}C NMR spectra of 1,3,5-trimethyl-2-(phenylbuta-1,3-diyn-1-yl)benzene (**4b**). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.54-7.51 (m, 2H), 7.34-7.32 (m, 2H), 6.86 (s, 2H), 2.44 (s, 6H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 142.0, 138.9, 132.4, 129.0, 128.5, 127.8, 122.2, 118.6, 82.4, 80.9, 79.9, 74.4, 21.5, 21.0.

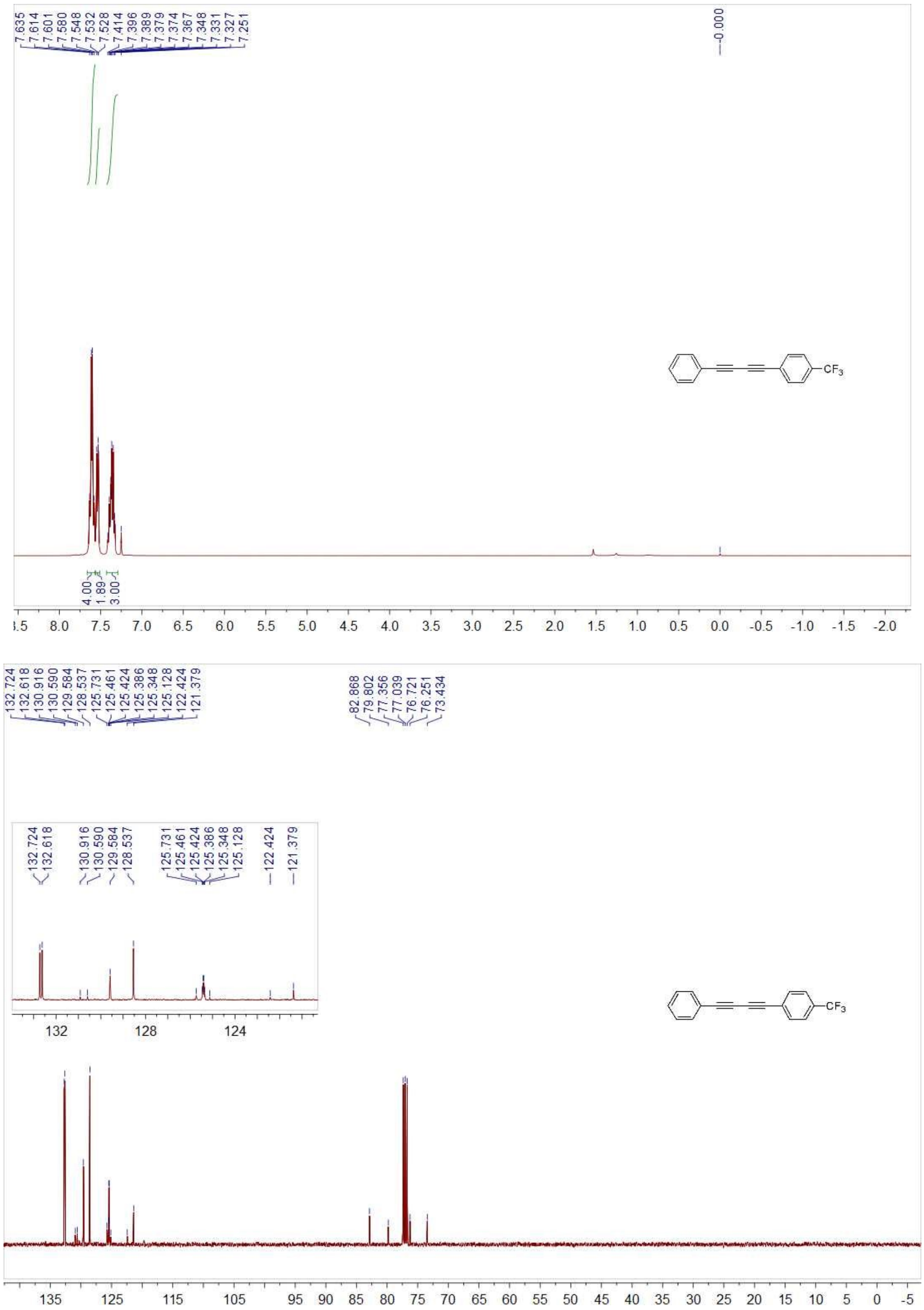


Figure S33. ^{1}H and ^{13}C NMR spectra of 1-(phenylbuta-1,3-diyn-1-yl)-4-(trifluoromethyl)benzene (**4c**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.53 (m, 6H), 7.40-7.33 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.7, 132.6, 130.9, 130.6, 129.6, 128.5, 125.7, 125.4 (q, J = 3.8 Hz), 125.1, 122.4, 121.4, 82.9, 79.8, 76.3, 73.4 .

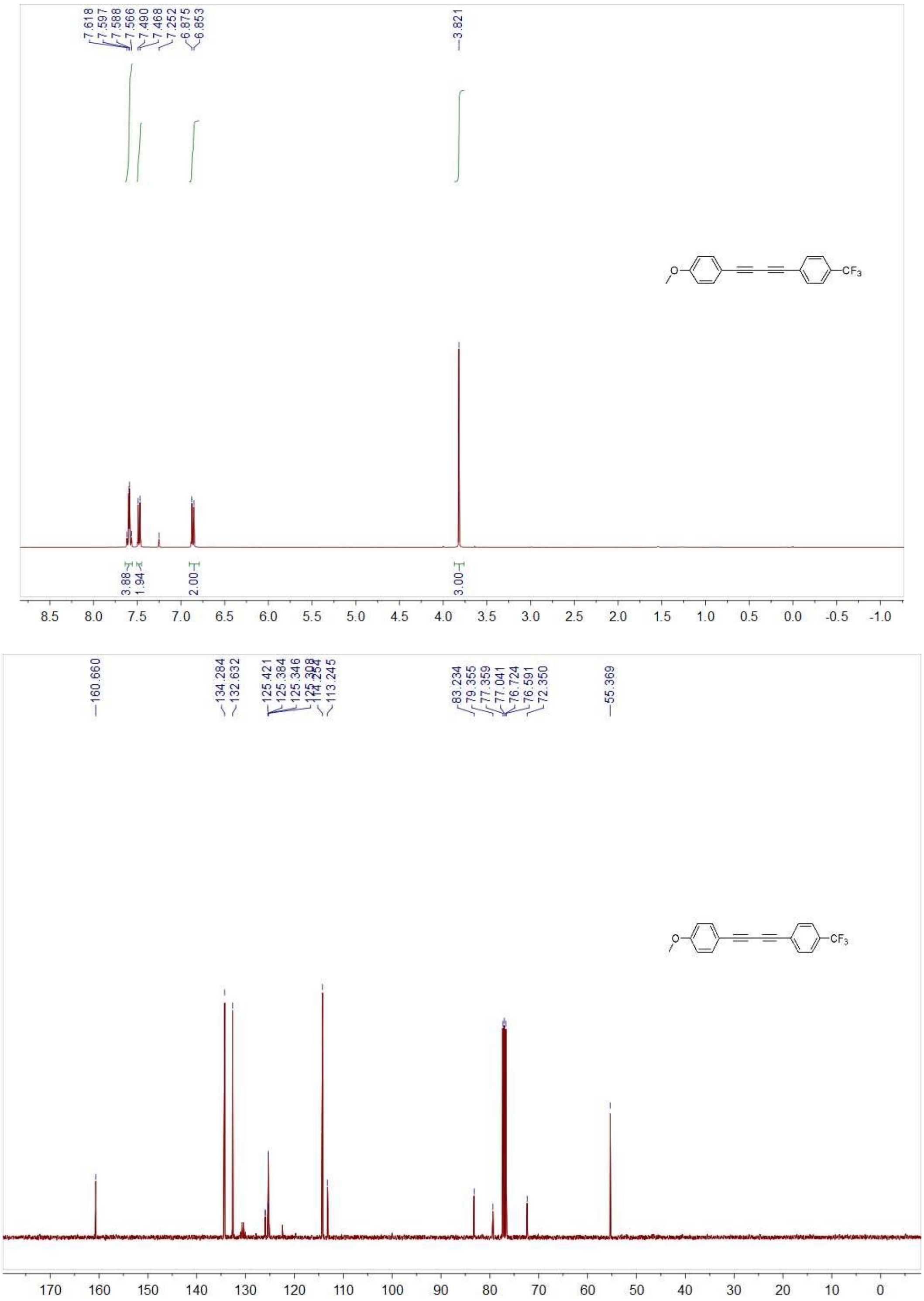
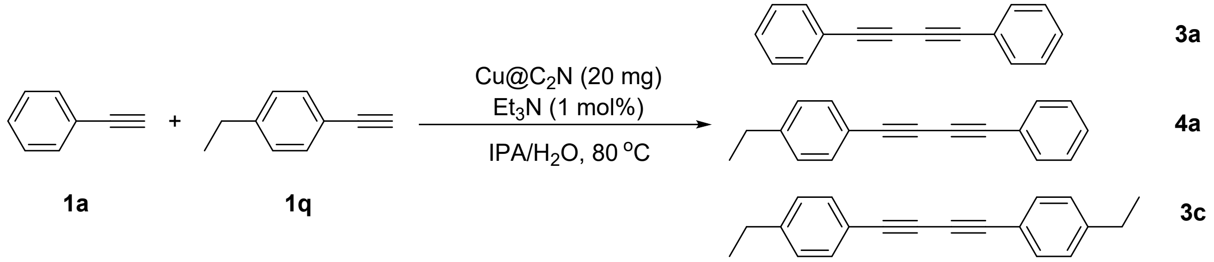


Figure S34. ^{1}H and ^{13}C NMR spectra of 1-methoxy-4-((4-(trifluoromethyl)phenyl)buta-1,3-diyn-1-yl)benzene (**4d**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61, 7.58 (dd, *J* = 8.4, 8.8 Hz, 4H), 7.48 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 134.3, 132.6, 130.5 (q, *J* = 32.5 Hz), 126.0, 125.4 (q, *J* = 3.8 Hz), 123.8, 114.3, 113.2, 83.2, 79.4, 76.6, 72.4, 55.4.

Table S1. The ICP-OES results of Cu in the samples of Cu@C_2N

		Cu (mg·Kg^{-1})	**Cu wt%**
Before five cycles		65100.0	6.51%
After five cycles	Hydration Reaction	65163.6	6.51%
	Homo-coupling Reaction	60938.3	6.09%

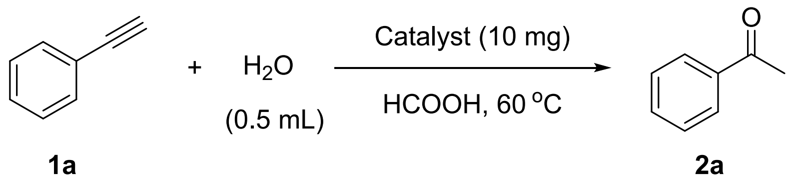
Table S2. Optimization of reaction conditions for the hetero-coupling.[a,b]



Entry	**1a** (mmol)	**1q** (mmol)	**3a** yield%	**4a** yield%	**3c** yield%
1[c]	0.1	0.1	48	trace	42
2	0.1	0.1	42	12	35
3	0.1	0.2	32	35	27
4	0.1	0.3	25	58	trace

[a] Reaction conditions: The mixture of **1a** (0.1 mmol), **1q** (0.1-0.3 mmol) and catalysts (20 mg) with 1 mol% Et_3N was stirred at 80 °C in solvent (1 mL) under an air atmosphere. [b] Isolated yields. [c] H_2O as solvent.

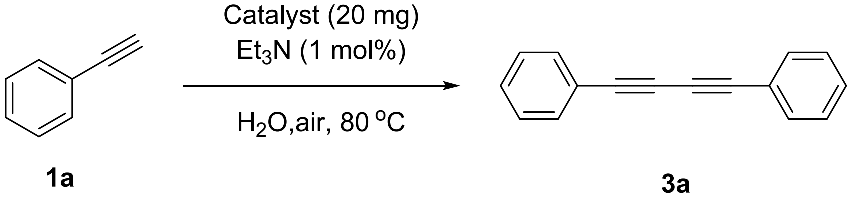
Table S3 Mechanistic studies of hydration of alkynes.[a,b]



Entry	Catalyst	**1a** Conversion%	**2a** Yield%
1	-	-	n.r.[c]
2	C_2N	-	n.r.
3	$CuCl_2$	-	n.r.
4	CuI	-	n.r.
5	$C_2N+CuCl_2$	30	26
6	C_2N+CuI	-	n.r.

[a]Reaction conditions: The mixture of **1a** (0.5 mmol) and catalysts (10 mg) was stirred at 60 °C in HCOOH (2 mL) under an air atmosphere. [b]Isolated yields. [c]n.r. = no reaction.

Table S4 Mechanistic studies of Glaser-Hay reaction.[a,b]



Entry	Catalyst	**1a** Conversion%	**3a** Yield%
1	-	-	n.r.[c]
2	C_2N	-	n.r.
3	$CuCl_2$	13	11
4	CuI	17	15
5	C_2N+$CuCl_2$	16	13
6	C_2N+CuI	22	18

[a]Reaction conditions: The mixture of **1a** (0.5 mmol) and catalysts (20 mg) was stirred at 80 °C in H_2O (1 mL) with 1mol% Et_3N under an air atmosphere. [b]Isolated yields. [c]n.r. = no reaction.