Supporting Information

Highly Crystallized Pd/Cu Nanoparticles on Activated Carbon: An Efficient Heterogenous Catalyst for Sonogashira Cross-Coupling Reaction

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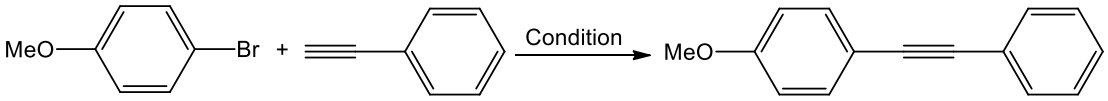
Characterization

The structures of the Pd/Cu bimetallic nanoparticles were investigated by X-ray diffraction (XRD) data, which are collected on a D/Max2550 X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å). SEM was carried out on a field-emission scanning electron microscopy (SU-8020 Hitachi FE-SEM). Transmission electron microscopy (TEM) analysis was performed on a Tecnai G2 F20 TEM. X-ray photoelectron spectroscopy (XPS) was studied using a Kratos AXIS ULTRA surface analysis system with a monochromatic Al Kα radiation as the excitation source. Collected XPS spectra were analyzed using Casa XPS and calibrated using the adventitious C1 speak with a fixed value of 284.6eV. Inductively coupled plasma (ICP) analysis was performed on a Bruker-M90 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Brucker EQUINX55 spectrometer, $CDCl_3$ as solvent, TMS as internal standard.

Optimizations for Pd/Cu@AC catalyzed Sonogashira coupling reaction of aryl bromide and phenylacetylene.

Table S1 The reaction results between 4-Bromoanisole and phenylacetylene.



Entry	Ligand	T（℃）	NMR Yield (%)
1	PPh_3	80	N.D
2	PPh_3	100	<5%
3	Xant-Phos	100	N.D
4	D(t-Bu)PF	100	<5%
5	dppf	100	N.D
6	S-Phos	100	6%
7	X-Phos	100	94%
8	t-Butyl XPhos	100	39%

Condition: 4-bromoanisole (0.5 mmol), phenylacetylene (0.6 mmol), K_2CO_3 (2 equiv), Ligand (5 mol%), EtOH (5 ml), Pd/Cu@AC (3 mol%), 24h, stirred in N_2.

The XRD patterns of the AC and Pd/Cu@AC Cat 5

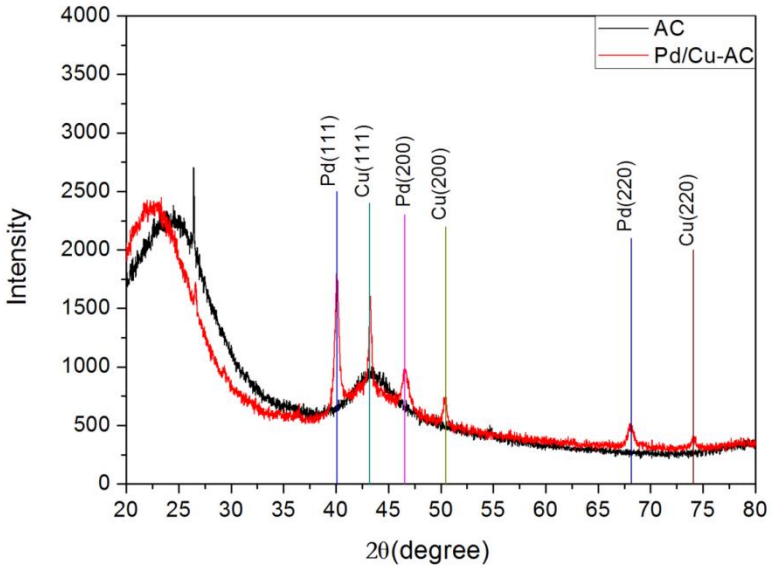
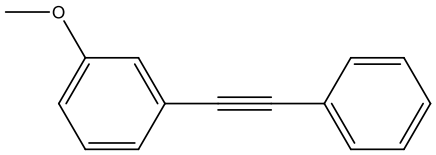


Figure S1 The XRD patterns of the activated carbon (AC) and Pd/Cu@AC Cat 5.

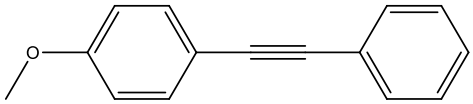
NMR spectra data for the Sonogashira-cross coupling products

Entry 1:

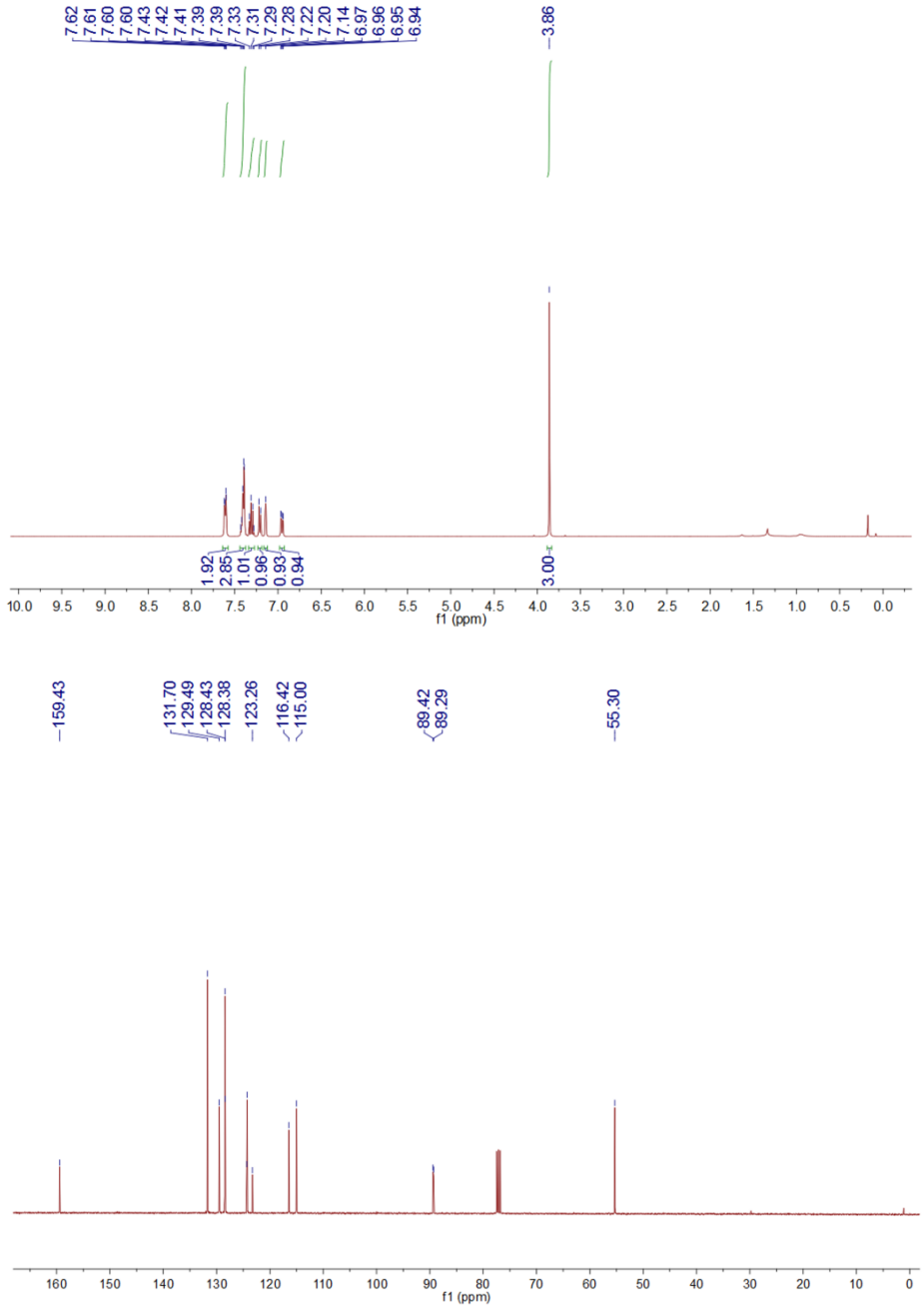


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.62-7.60 (m, 2H), 7.43-7.39 (m, 3H), 7.33-7.32 (m, 1H), 7.22-7.20 (d, 1H), 7.14 (s, 1H), 6.97-6.94 (dd, 1H), 3.86 (s, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.43, 131.70, 129.49, 128.43, 124.33, 124.25, 123.26, 116.42, 115.00, 89.42, 89.29, 55.30.

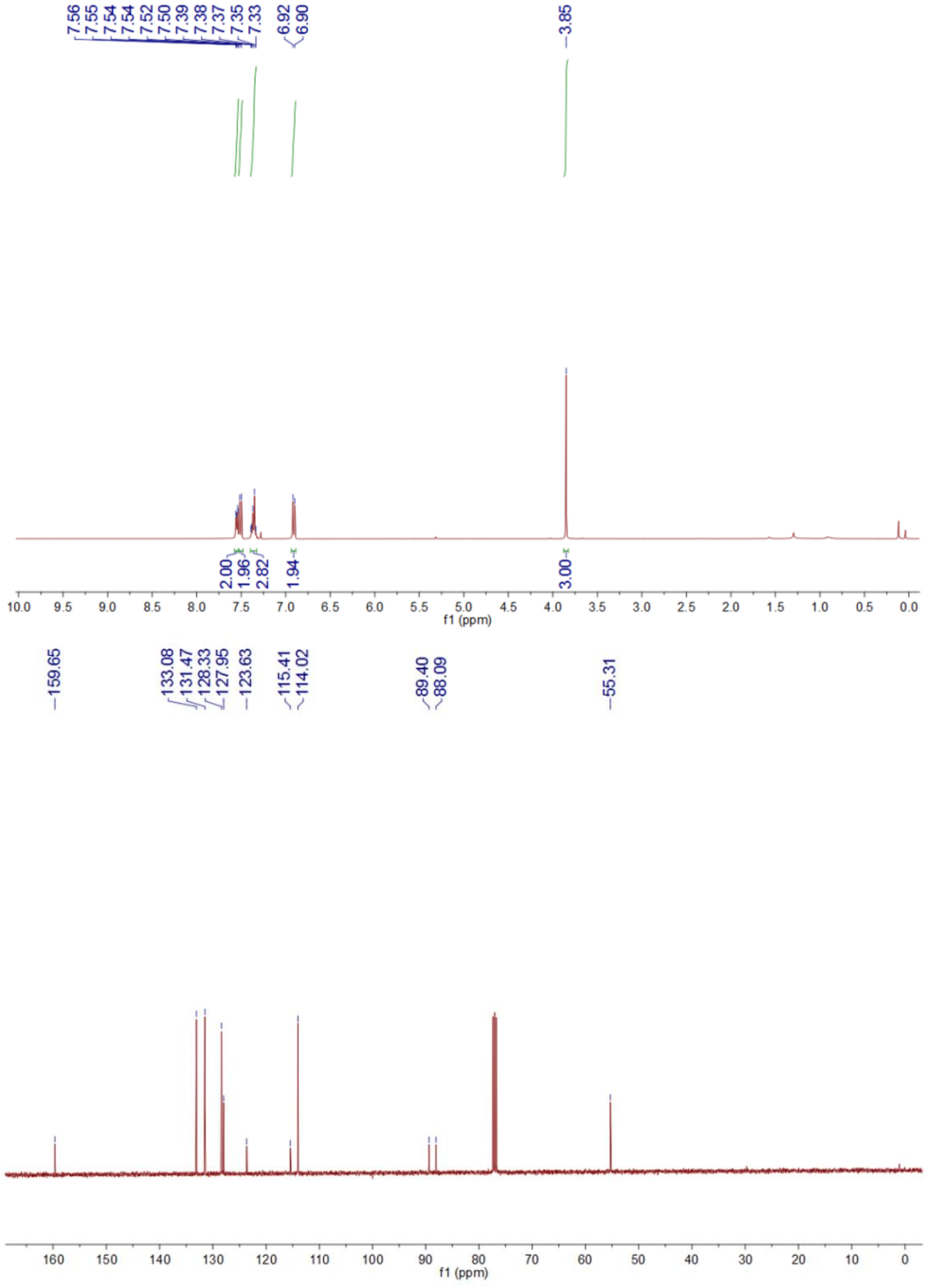
Entry 2:



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (dd, 2H), 7.52-7.50 (d, 2H), 7.39-7.33 (m, 3H), 6.92-6.90 (d, 2H), 3.85 (s, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.65, 133.08, 131.47, 128.33, 127.95, 123.63, 115.41, 114.02,



89.40, 88.09, 55.31.



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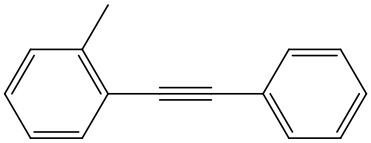
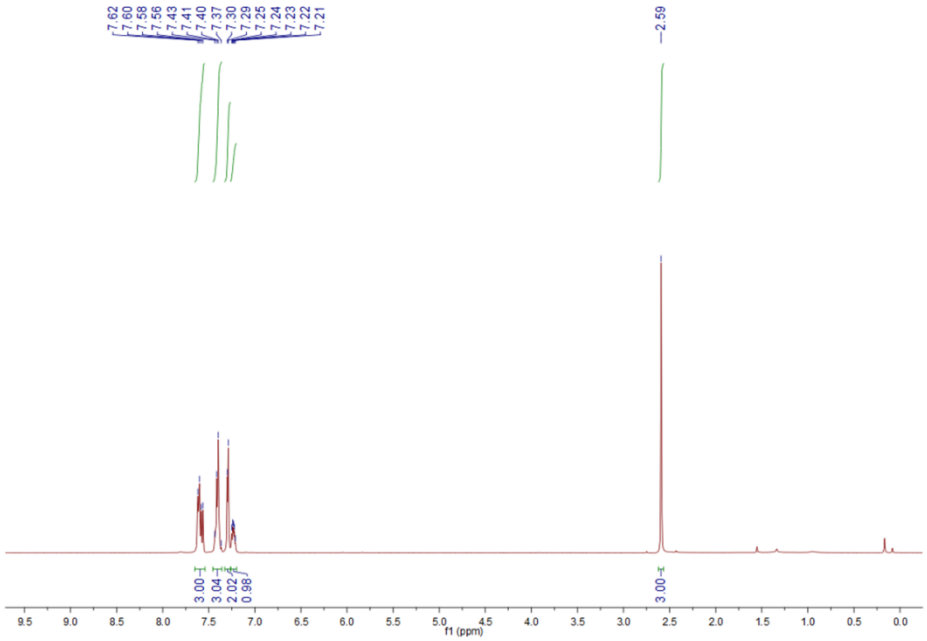
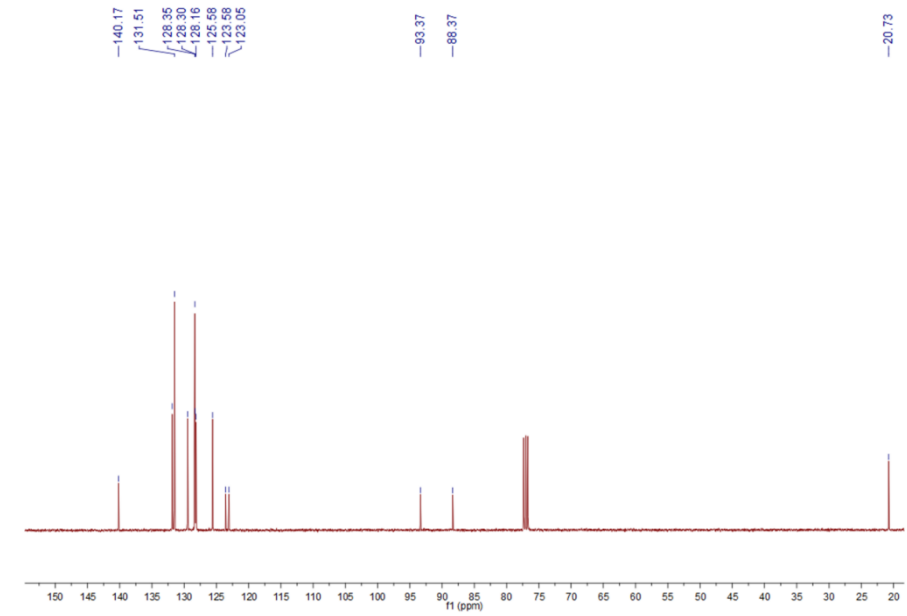


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.62-7.58 (m, 3H), 7.43-7.37 (m, 3H), 7.30-7.29 (d, 2H), 7.25-7.21 (m, 1H), 2.59 (s, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 140.17, 131.84, 131.51, 129.46, 128.35, 128.30, 128.16, 125.58, 123.58, 123.05, 93.37, 88.37, 20.73.





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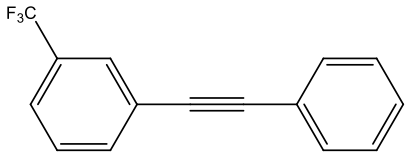
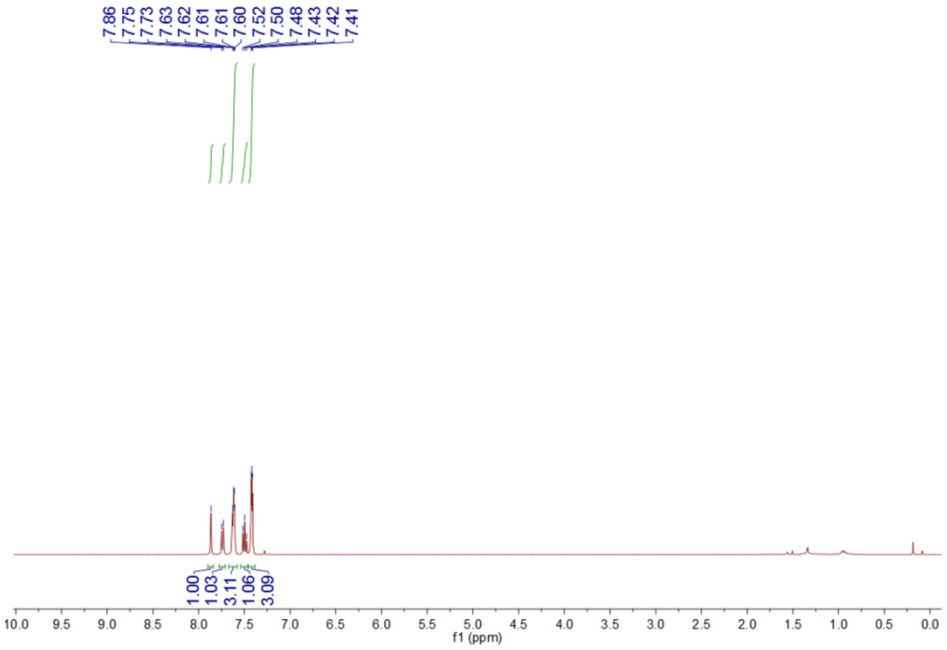
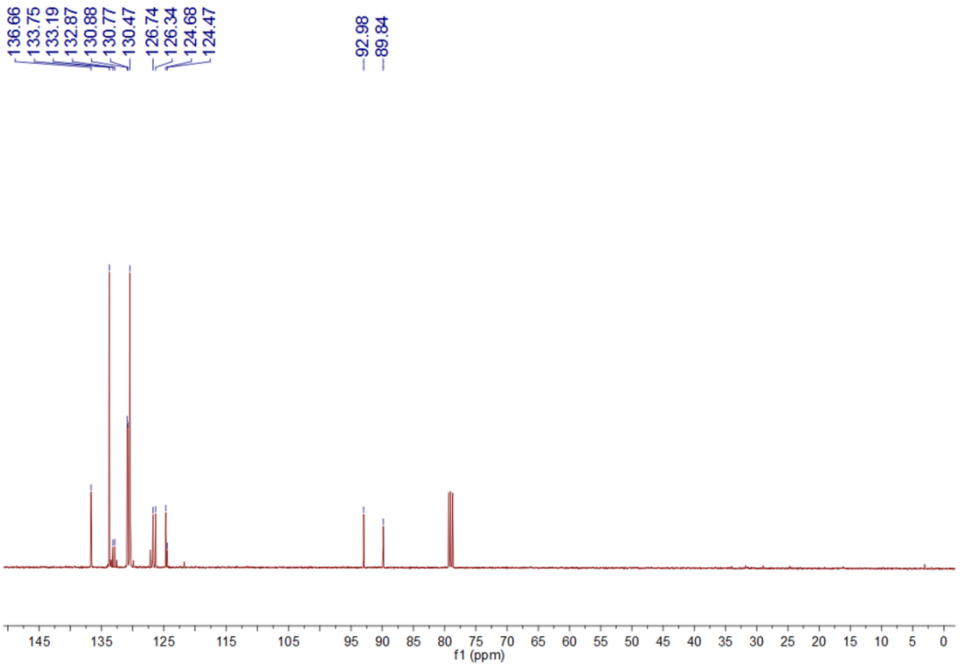


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.75-7.73 (d, 2H), 7.63-7.60 (m, 3H), 7.52-7.48 (t, 1H), 7.43-7.41 (m, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 136.66, 133.75, 133.19, 132.87, 130.88, 130.77, 130.47, 126.74, 126.34,



124.68, 124.47, 92.98, 89.84.



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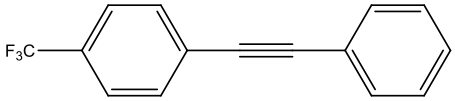
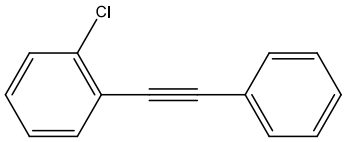
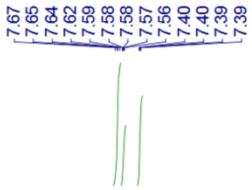


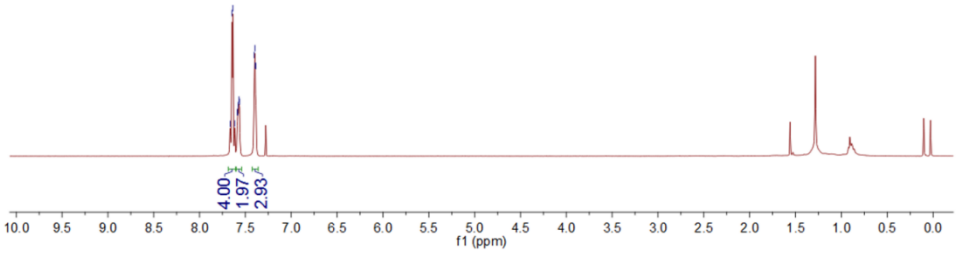
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67-7.62 (q, 4H), 7.59-7.56 (m, 2H), 7.40-7.39 (m, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 134.66, 131.75, 128.89, 128.78, 128.48, 124.74, 124.34, 122.68, 90.98, 87.85.

Entry 6:

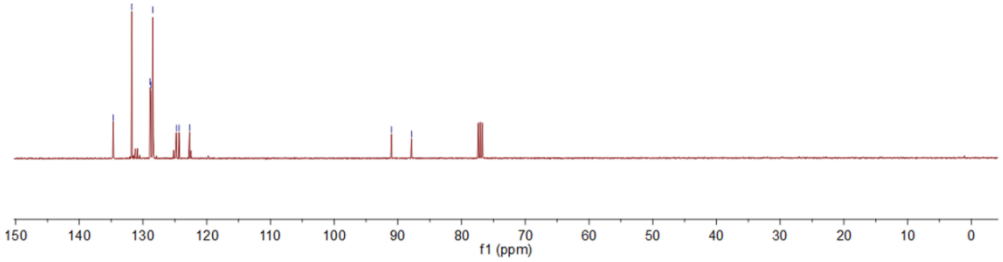


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63-7.56 (m, 3H), 7.48-7.45 (m, 1H), 7.40-7.37 (m, 3H), 7.31-7.25 (m, 2H).

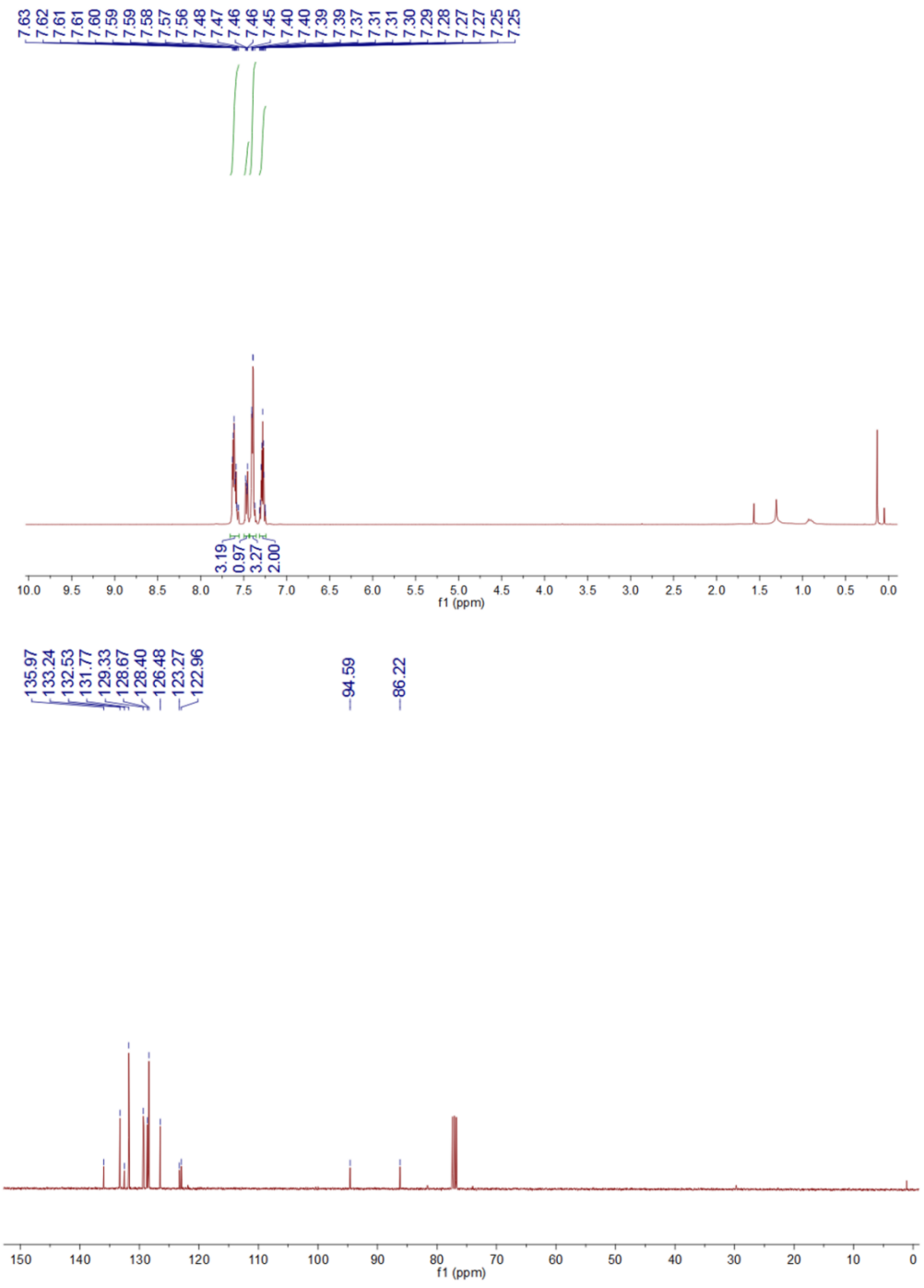




^{13}C-NMR (400 MHz, $CDCl_3$): δ 135.97, 133.24, 132.53, 131.77, 129.33, 128.67,



128.40, 126.48, 123.27, 122.96, 94.59, 86.22.



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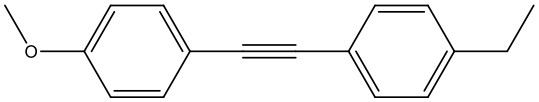
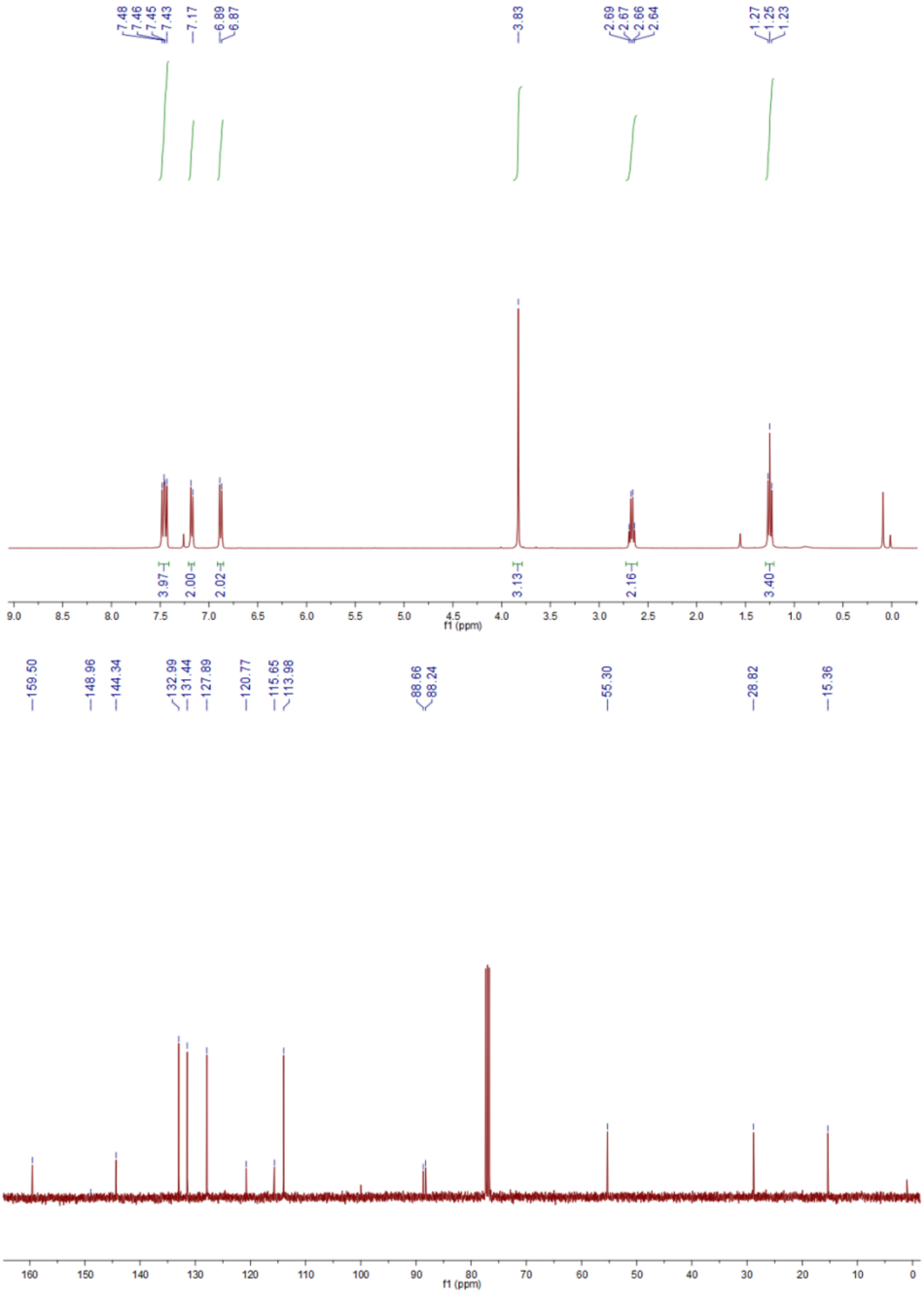


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.48-7.43 (m, 4H), 7.19-7.17 (d, 2H), 6.98-6.87 (d, 2H), 3.83 (s, 3H), 2.69-2.64 (q, 2H), 1.27-1.23 (t, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.50, 148.96, 144.34, 132.99, 131.44, 127.89, 120.77, 115.65, 113.98, 88.66, 88.24, 55.30, 28.82, 15.36.



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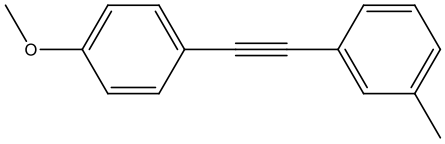
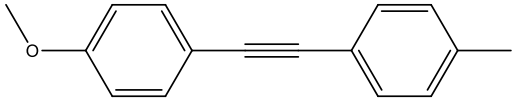
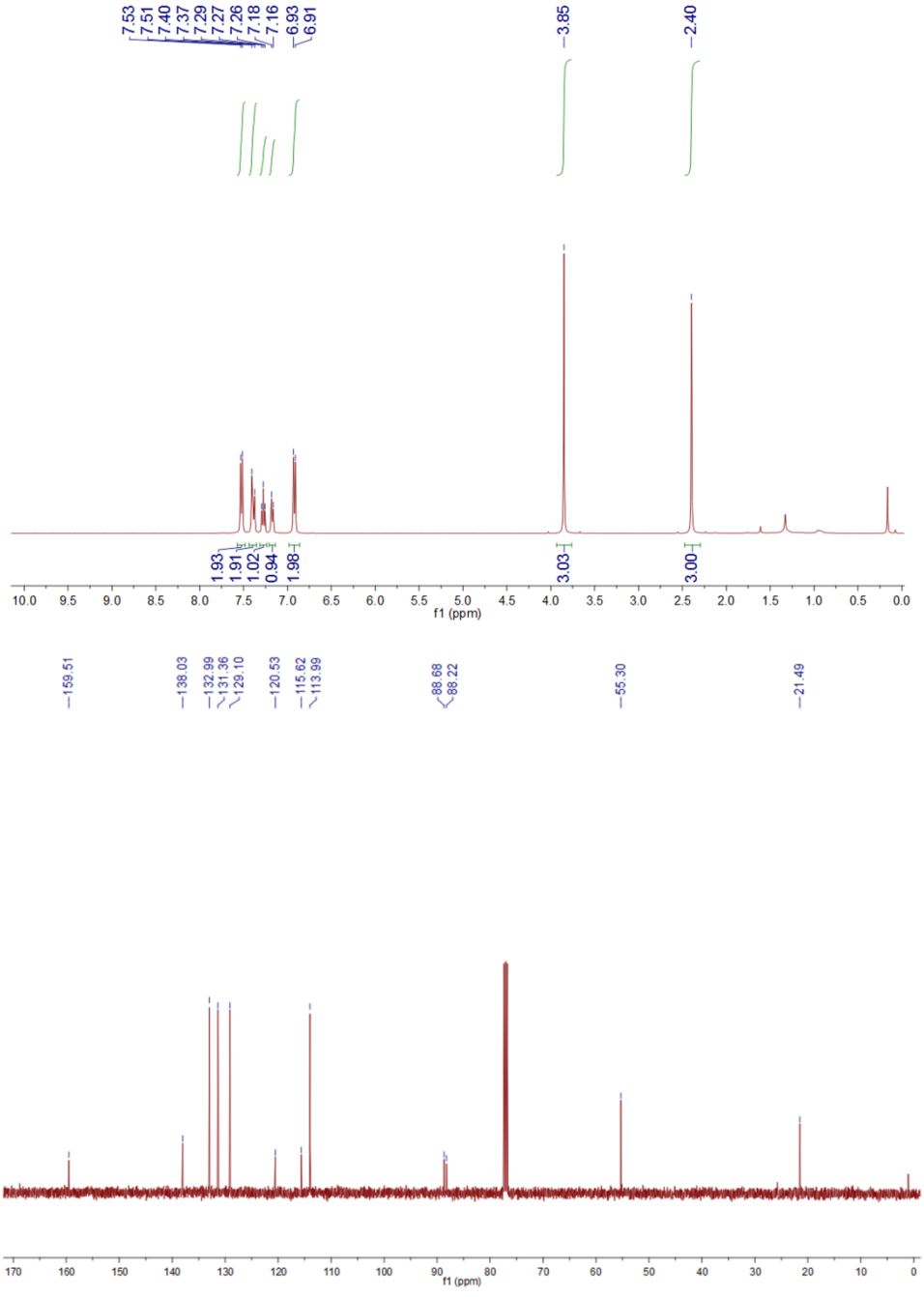


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.53-7.51 (d, 2H), 7.40-7.37 (d, 2H), 7.27-7.26 (m, 1H), 7.18-7.16 (d, 1H), 3.85 (s, 3H), 2.40 (s, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.58, 137.97, 133.04, 132.05, 128.85, 128.53, 128.22, 123.41, 115.52, 114.00, 89.03, 88.25, 55.30, 21.25.

Entry 9:

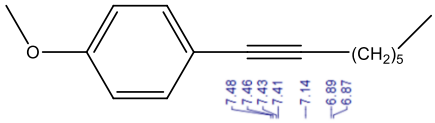


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.48-7.46 (d, 2H), 7.43-7.41 (d, 2H), 7.16-7.14 (d, 2H), 6.89-6.87 (d, 2H), 3.83 (s, 3H), 2.37 (s, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.51,

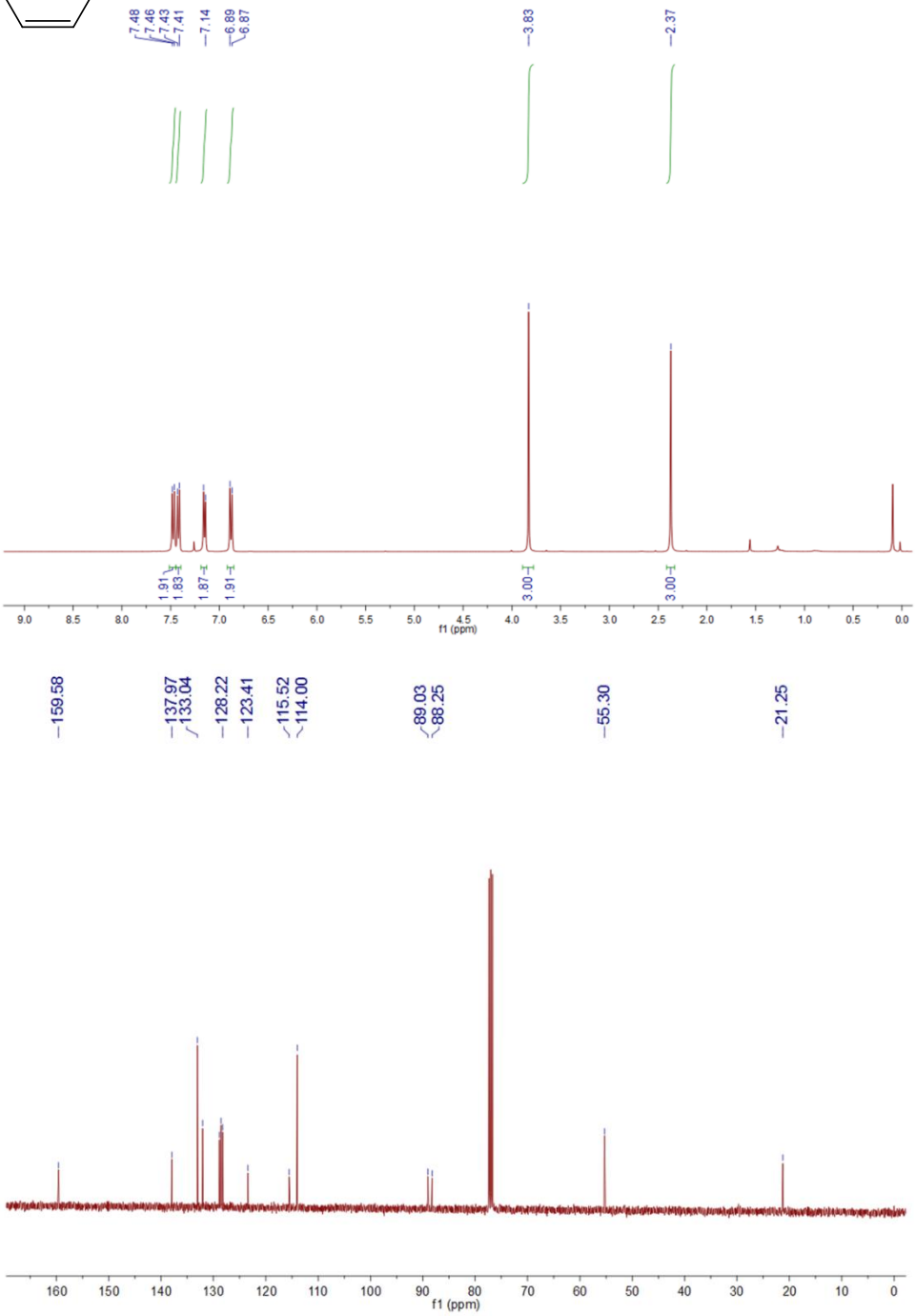


138.03, 132.99, 131.36, 129.10, 120.53, 115.62, 113.99, 88.68, 88.22, 55.30, 21.49.

Entry 10:



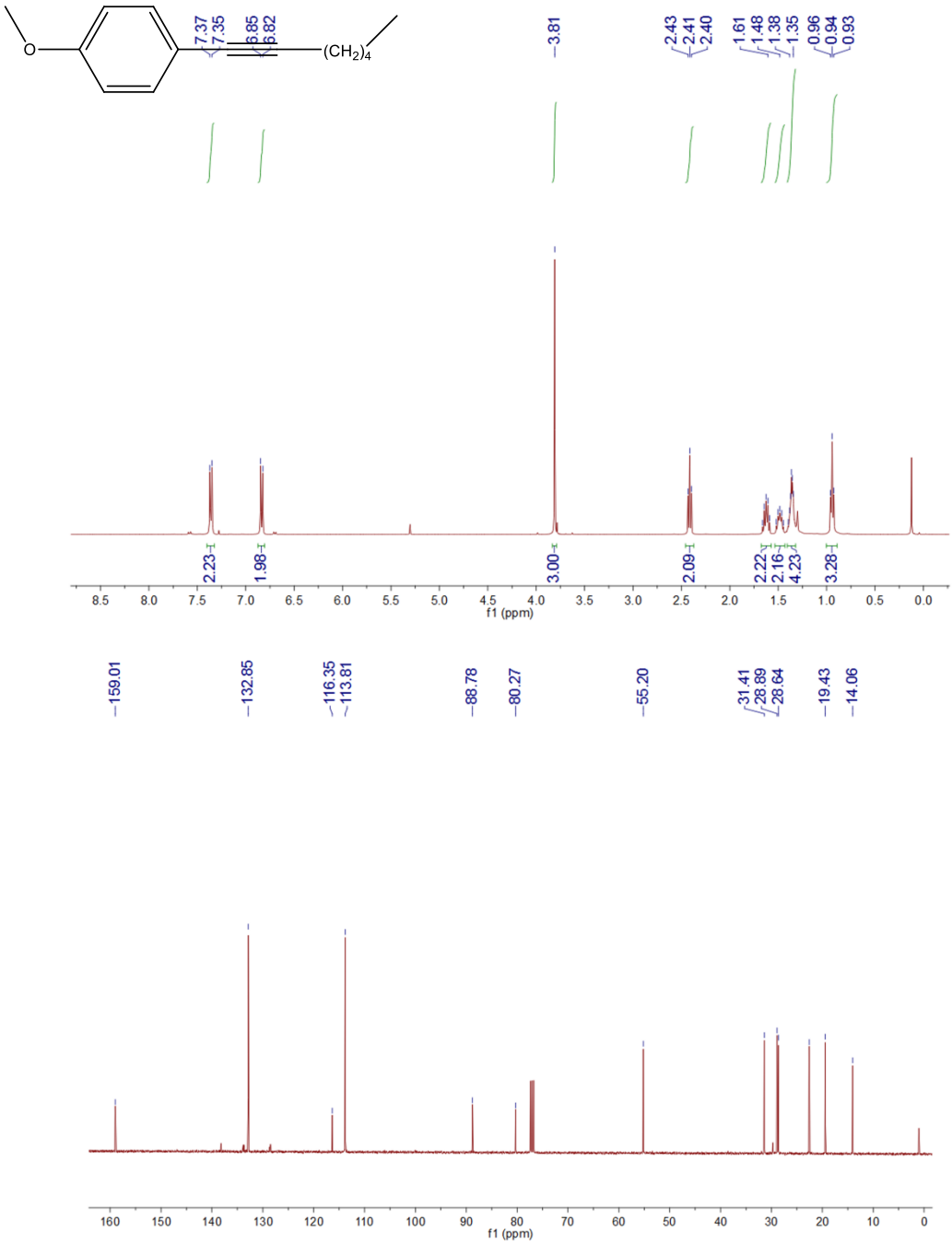
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37-7.35 (d, 2H),



6.85-6.82 (d, 2H), 3.81 (s, 3H), 2.43-2.40 (t, 2H), 1.66-1.59 (m, 2H), 1.50-1.45 (m,

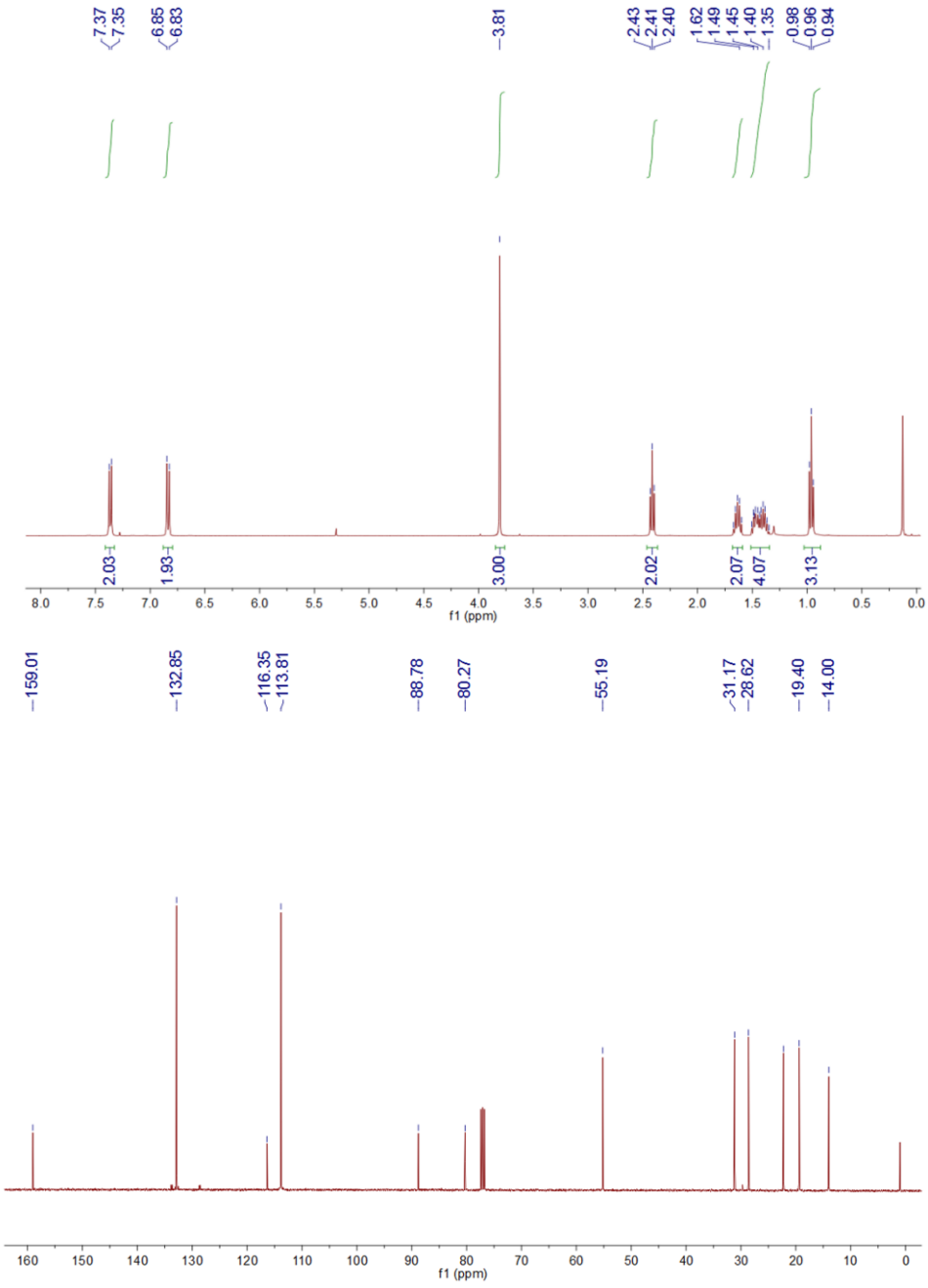
2H), 1.4-1.35 (m, 4H), 0.96-0.93 (t, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.01, 132.85, 116.35, 113.81, 88.78, 88.27, 55.20, 31.41, 28.89, 28.64, 22.59, 19.43, 14.06.

Entry 11:

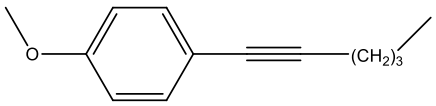


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37-7.35 (d, 2H), 6.85-6.82 (d, 2H), 3.81 (s, 3H),

2.43-2.40 (t, 2H), 1.64-1.60 (m, 2H), 1.50-1.35 (m, 4H), 0.98-0.94 (t, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.01, 132.85, 116.35, 113.81, 88.78, 88.27, 55.19, 31.17, 28.62, 22.27, 19.40, 14.00.

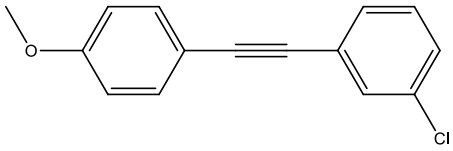


Entry 12:



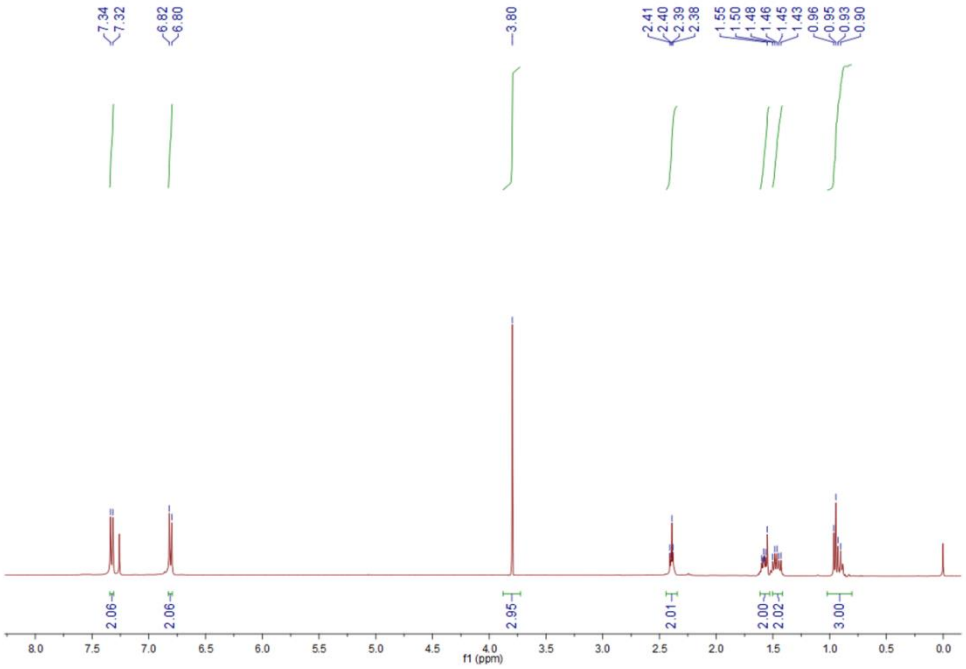
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.34-7.32 (d, 2H), 6.82-6.80 (d, 2H), 3.80 (s, 3H), 2.41-2.38 (m, 2H), 1.60-1.55 (m, 2H), 1.50-1.43 (m, 2H), 0.96-0.90 (m, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.00, 132.84, 116.34, 113.81, 88.72, 80.27, 55.19, 31.00, 22.03, 19.10, 13.64.

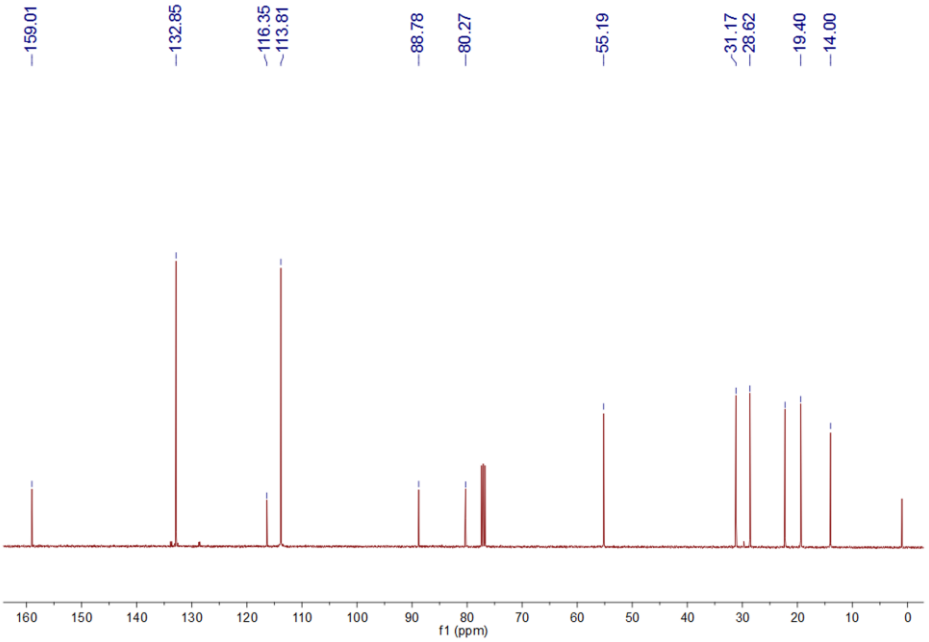
Entry 13:



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.50-7.48 (d, 2H), 7.42-7.40 (m, 1H), 7.31-7.28 (m, 2H), 6.92-6.90 (d, 2H), 3.85 (s, 3H).

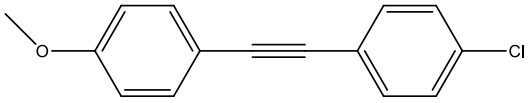
^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.90, 134.15, 133.18, 131.29, 129.55, 129.53,



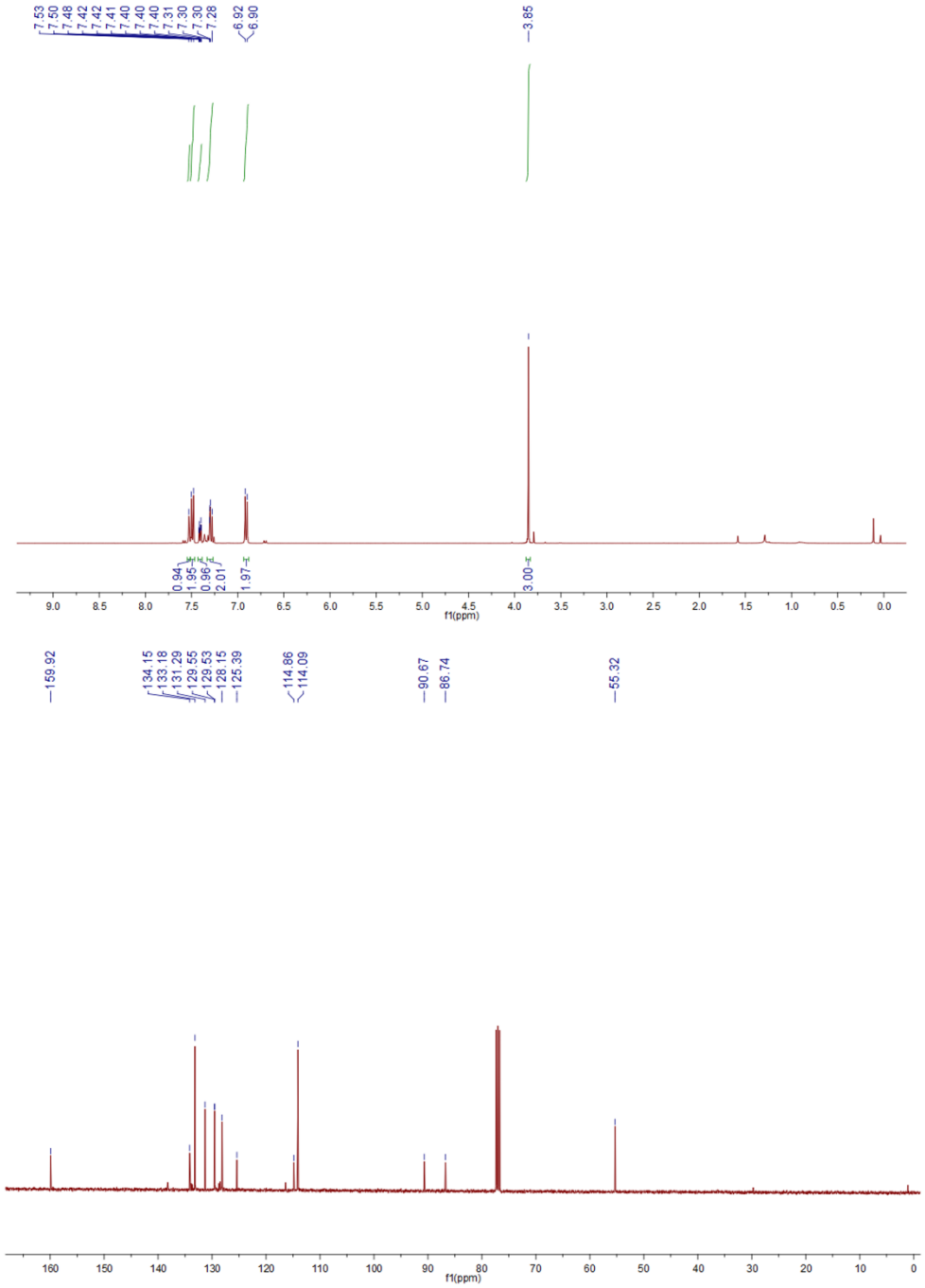


128.15, 125.39, 114.86, 114.09, 90.67, 86.75, 55.32.

Entry 14:



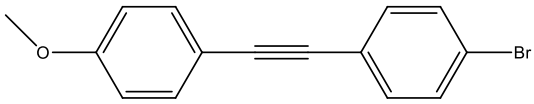
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.49-7.44 (m, 4H), 7.34-7.32 (d, 2H), 6.91-6.89 (d,



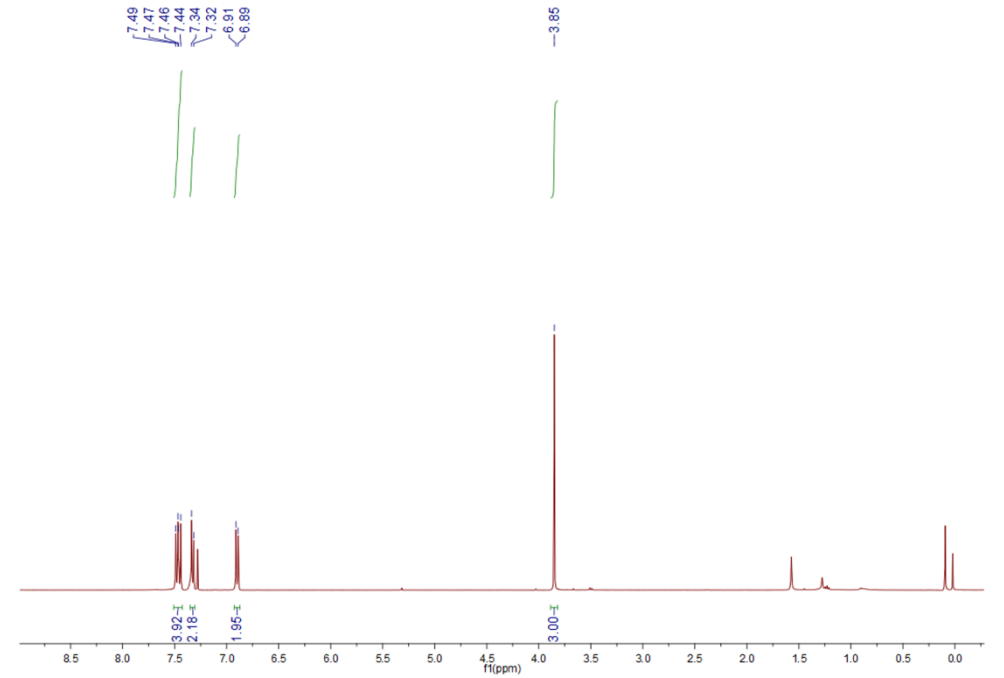
2H), 3.85 (s, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.80, 133.88, 133.07, 132.64,

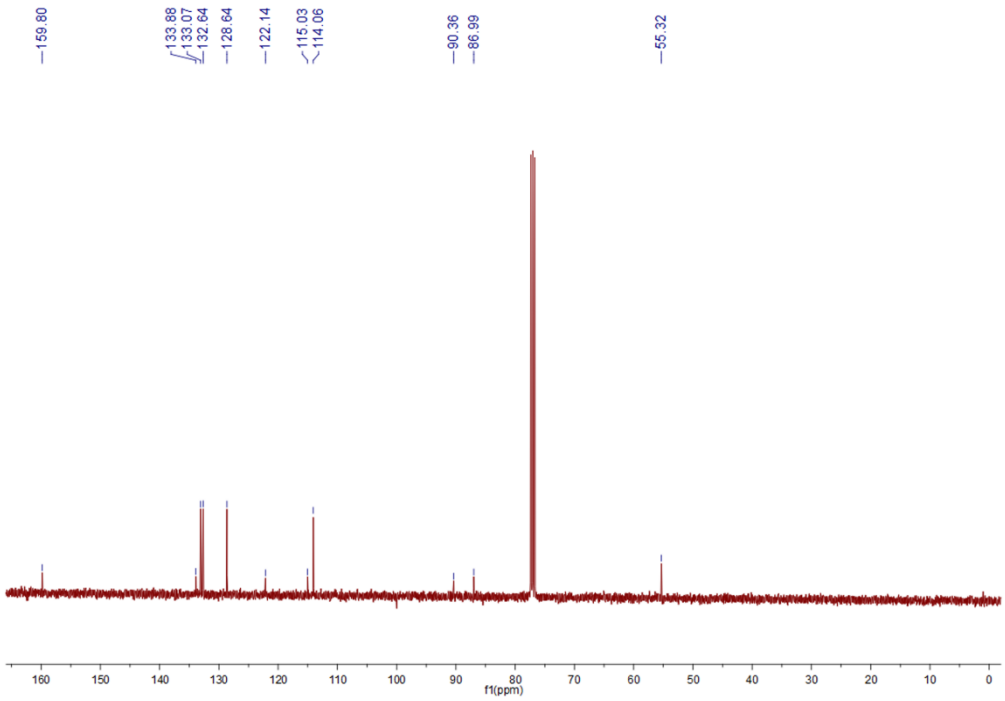
128.64, 122.14, 128.15, 115.03, 114.06, 90.36, 86.99, 55.32.

Entry 15:



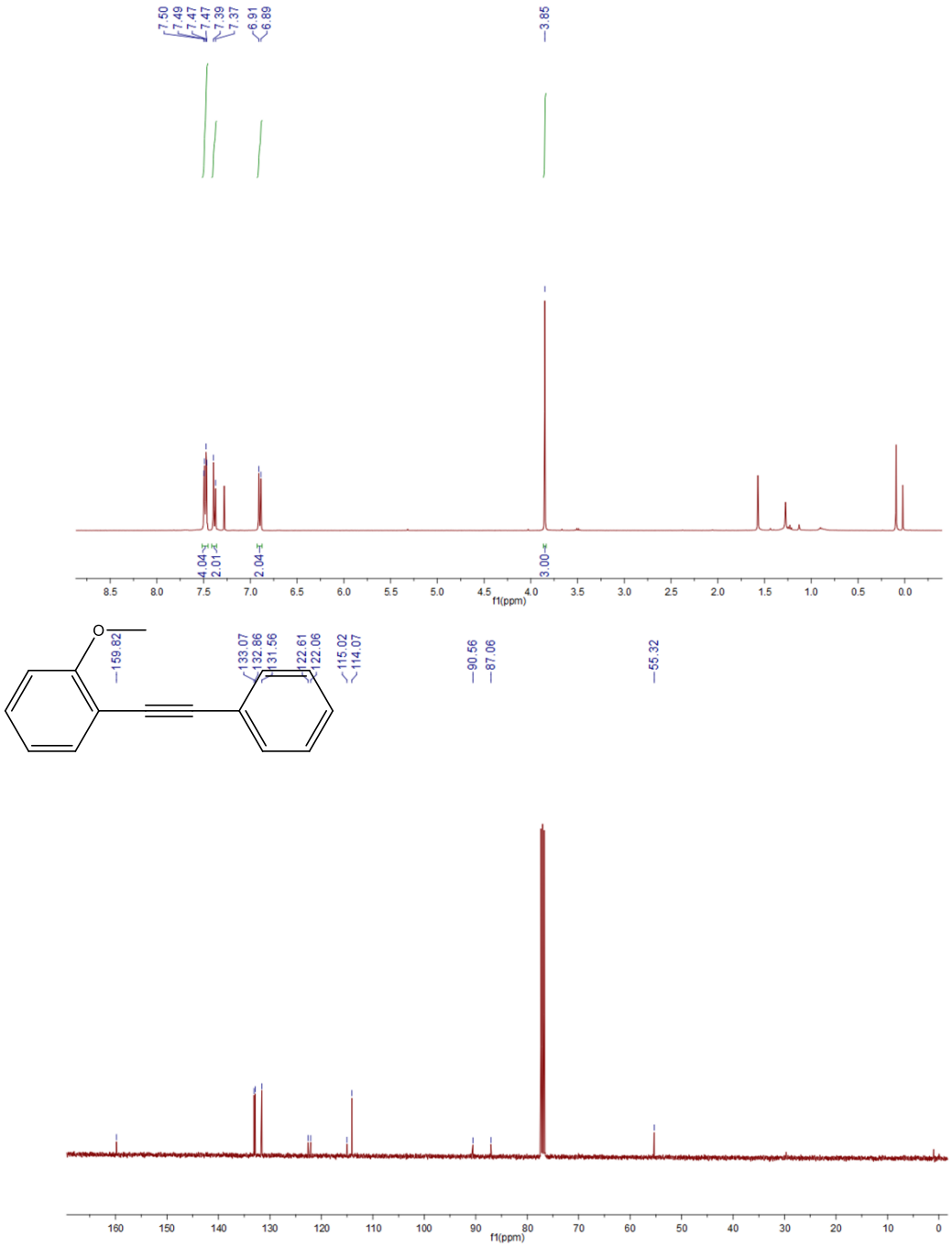
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50-7.47 (m, 4H), 7.39-7.37 (d, 2H), 6.91-6.89 (d,





2H), 3.85 (s, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.82, 133.07, 132.86, 131.56, 122.61, 122.06, 115.02, 114.07, 90.56, 87.06, 55.32.

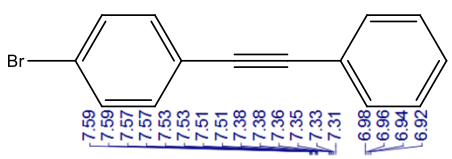
Entry 16:



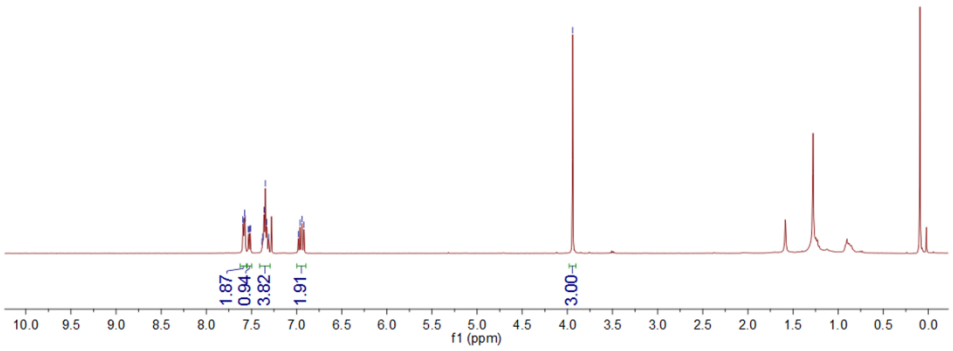
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.59-7.57 (m, 2H), 7.53-7.51 (m, 1H), 7.38-7.31 (m,

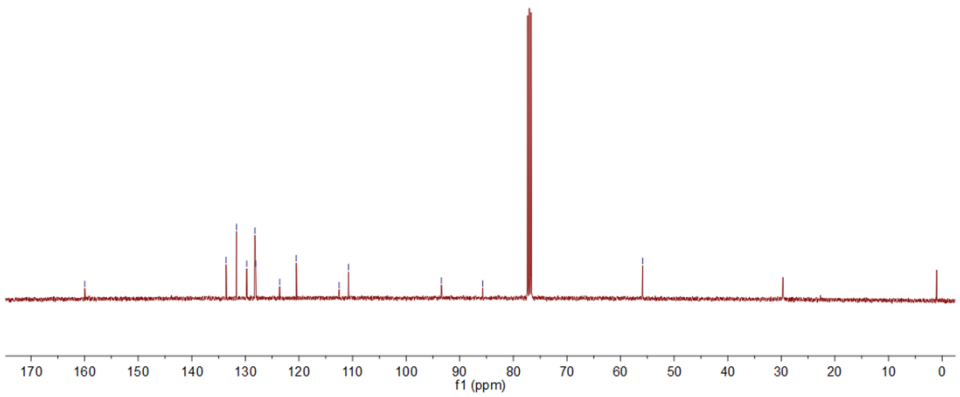
4H), 6.98-6.92 (m, 2H), 3.94 (s, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.96, 133.59, 131.67, 129.74, 128.23, 128.09, 123.60, 120.50, 112.51, 110.75, 93.43, 85.72, 55.86.

Entry 17:

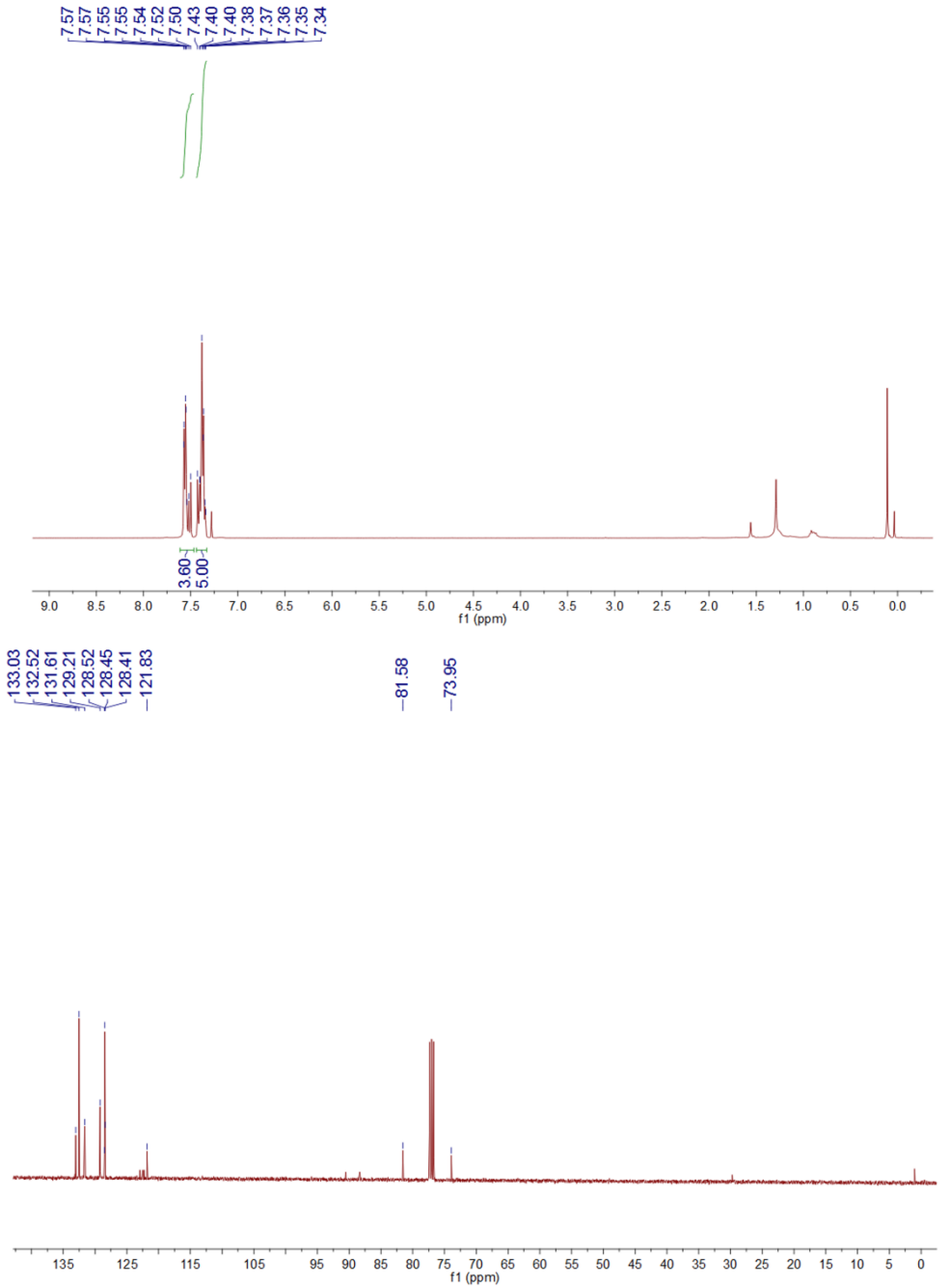


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.57-7.50 (m,

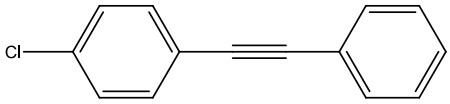




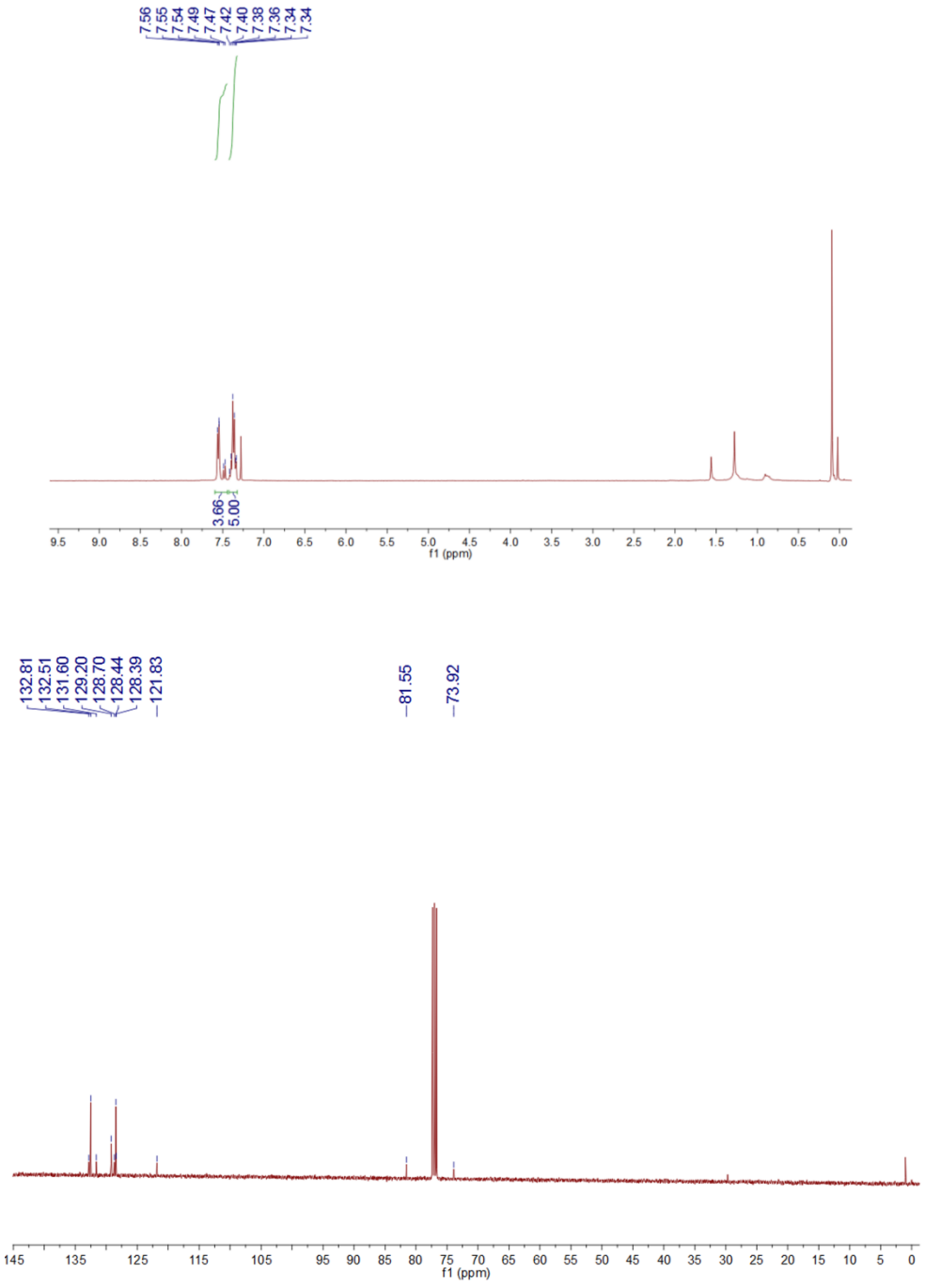
4H), 7.43-7.34 (m, 5H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 133.03, 132.52, 131.61, 129.21, 128.52, 128.45, 128.41, 121.83, 81.58, 73.95.



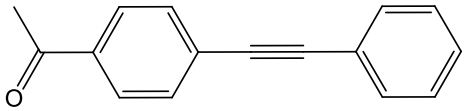
Entry 18:



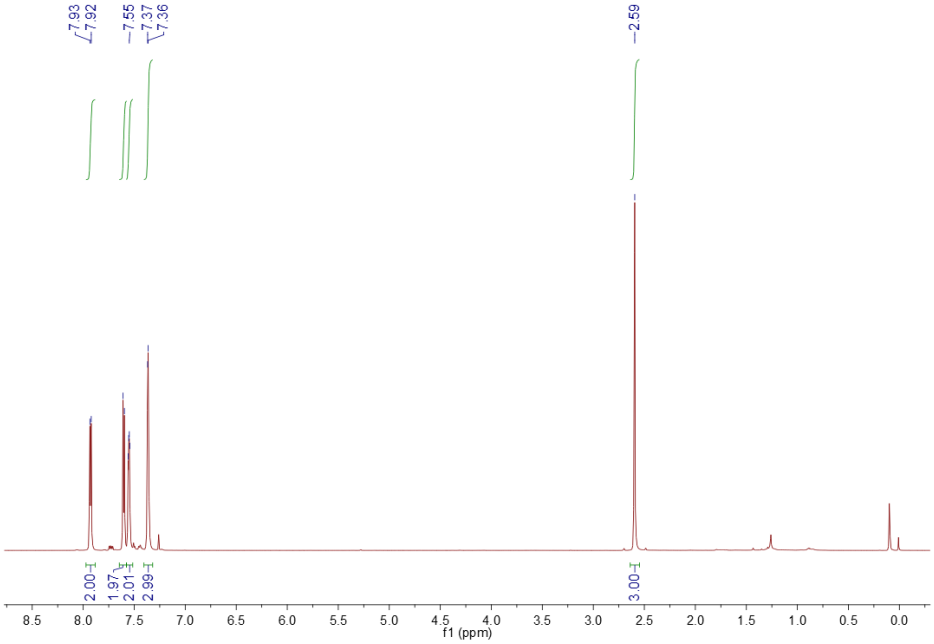
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.56-7.47 (m, 4H), 7.42-7.34 (m, 5H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 132.81, 132.51, 131.60, 129.60, 128.70, 128.44, 128.39, 121.83, 81.55, 73.92.

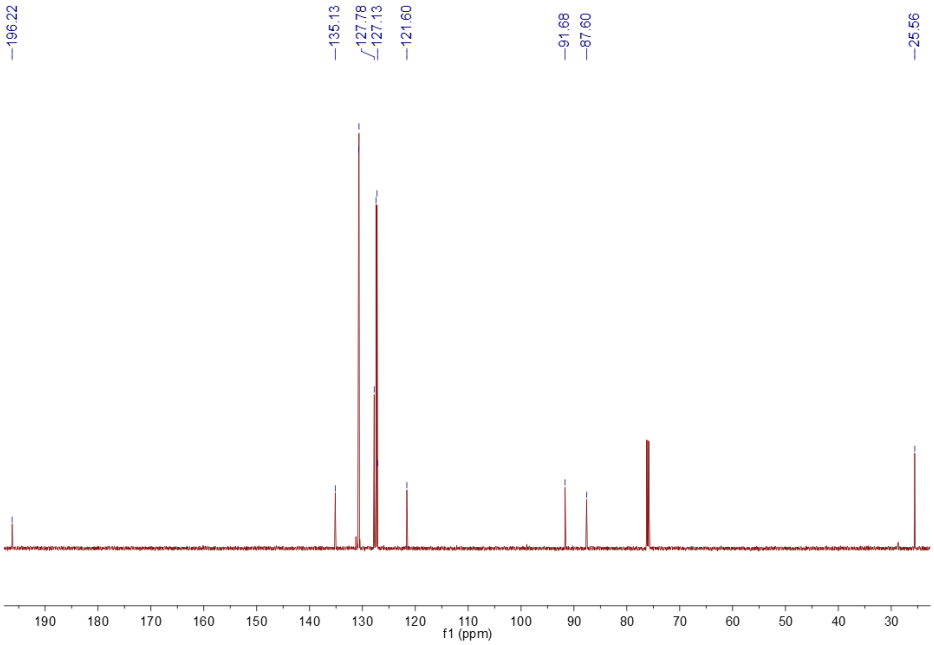


Entry 18:

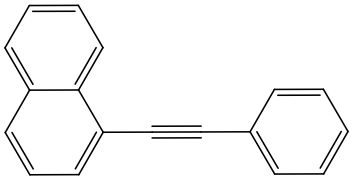


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.93-7.92 (d, 2H), 7.61-7.60 (d, 2H), 7.56-7.54 (m, 2H), 7.37-7.36 (m, 3H), 2.59 (s, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 196.22, 135.13, 130.70, 130.65, 127.78, 127.41, 127.23, 127.13, 91.68, 87.60, 25.56.



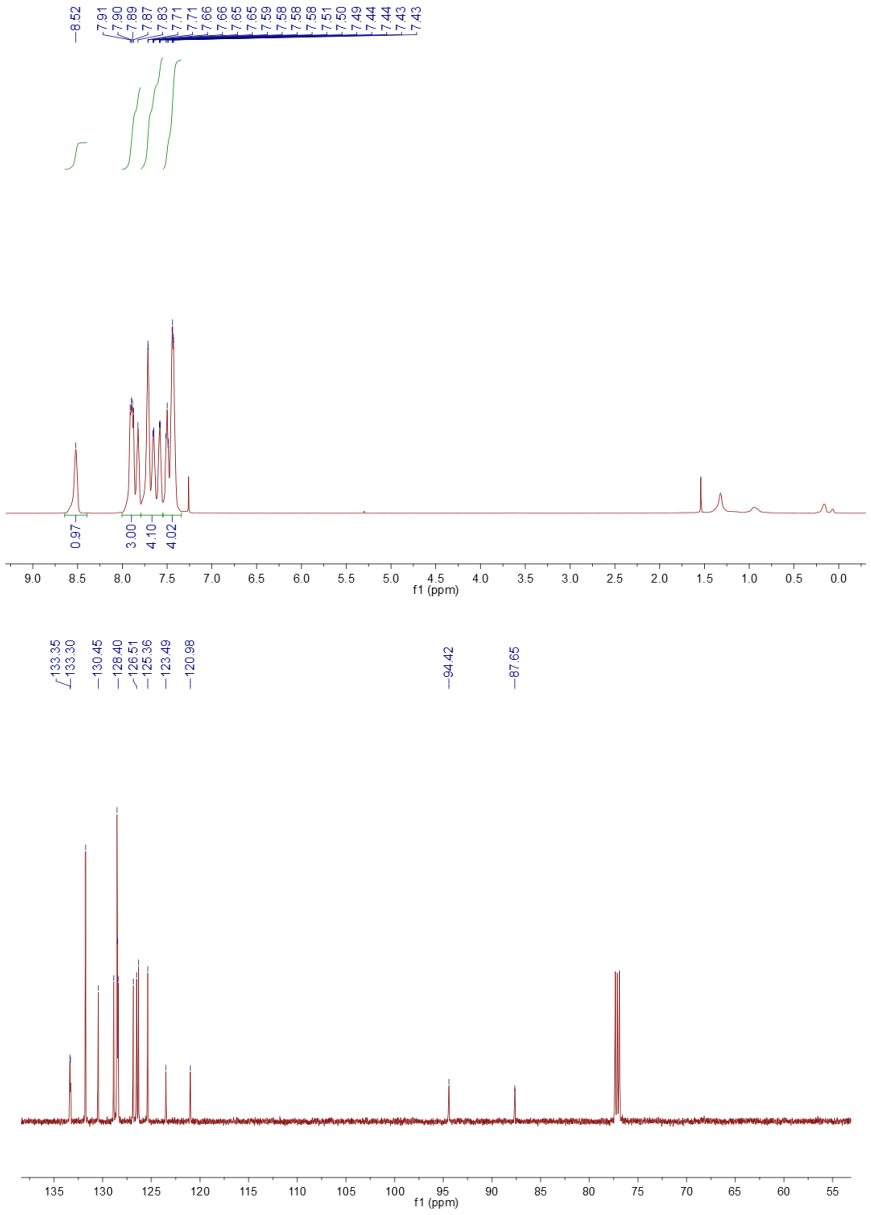


Entry 18:



^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.52 (m, 1H), 7.91-7.83 (m, 3H), 7.71-7.58 (m, 4H), 7.50-7.43 (m, 4H).

^{13}C-NMR (400 MHz, $CDCl_3$): δ 133.35, 133.30, 131.75, 130.45, 128.85, 128.52, 128.47, 128.40, 126.86, 126.51, 126.30, 125.36, 123.49, 120.98, 94.42, 87.65.



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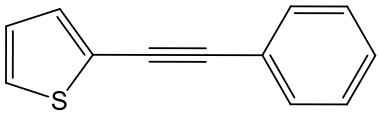

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.53-7.52 (m, 2H), 7.47-7.45 (d, 2H), 7.36-7.32 (m, 5H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 133.24, 131.79, 130.58, 127.67, 127.46, 127.37, 121.91, 120.77, 89.29, 87.21.