

Supporting Information

Water promoted allylic nucleophilic substitution reactions of (*E*)-1,3 diphenylallyl acetate

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1. General information:

All reactions were carried out under air atmosphere. Thin-layer chromatography (TLC) was performed on silica coated glass plates (silica gel 60) with detection by irradiation of 254 nm UV light. Product was purified by Flash column chromatography on silica gel (60-120) mesh using solvent combination of hexan and ethyl acetate. All yields reported in Table 4 referred to isolated yields and pure as determined by NMR and GCMS analysis. While yields reported in Table 1-3 are GC yields referenced to diglyme as internal standard. GS-MS analysis was performed on a Agilent Agilent 7890A GC System with Agilent 5975C XL EI/CI MSD with Triple Axis Detector. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV-400 spectrometer at 295 K. in CDCl₃. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS) as internal standard or to the used solvent (in case of product **3a** and **3l** additional TMS externally added). *J* (coupling constant) were reported in Hz, splitting patterns of proton are described as s (singlet), d (doublet), t (triplet), m (multiplet) etc. All products obtained and discussed in this work have been previously reported except compound **3h** and characterized by suitable technique such as ¹H NMR, ¹³C NMR, GC-MS, and were compared with previously reported data.

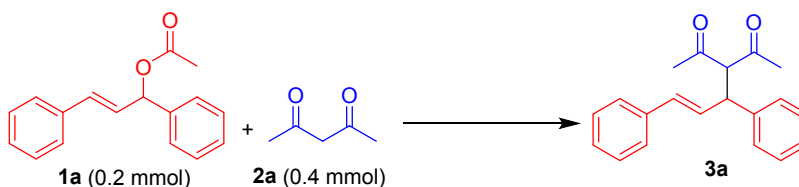
2. General experimental procedure for allylic alkylation.

In 10 mL round bottom flask water (2 mL) is added then sodium ter-butoxide (**2**, 0.40 mmol) added then acetylacetone (**2a**, 0.40 mmol) is added and reaction mixture stirred for 10 minutes at room temperature. Finally (*E*)-1,3-diphenylallyl acetate (**1a**, 0.20 mmol) is added and after addition the round bottom flask was placed in oil bath and magnetically stirred at 50 °C for 24 hours under air atmosphere. After 24 hours, the reaction mixture was cooled to room temperature. Then the product was extracted with ethyl acetate (4 x 10 mL). The combined organic layers were dried over Na₂SO₄ and evaporated to afford the crude product. Finally, product was purified by column chromatography on silica gel to afford the pure product **3a**. The product was confirmed by at least two or one of the analytical techniques among GC-MS, ¹H NMR, ¹³C NMR, spectroscopic analysis.

3. General experimental procedure for *O*-allylation and allylic amination

In 10 mL round bottom flask water (2 mL) is added then corresponding nucleophile (**2**, 0.40 mmol) is added and stirred reaction mixture for 10 minutes at room temperature. Finally (*E*)-1,3-diphenylallyl acetate (**1a**, 0.20 mmol) is added and after addition the round bottom flask was placed in oil bath and magnetically stirred at 50 °C for 24 h (for amines 16 h) under air atmosphere. After completion, the reaction mixture was cooled to room temperature. Then the product was extracted with ethyl acetate (4 x 10 mL). The combined organic layers were dried over Na₂SO₄ and evaporated to afford the crude product. Finally, product was purified by column chromatography on silica gel to afford the pure product **3**. The product was confirmed by at least two or one of the analytical techniques among GC-MS, ¹H NMR, ¹³C NMR, spectroscopic analysis.

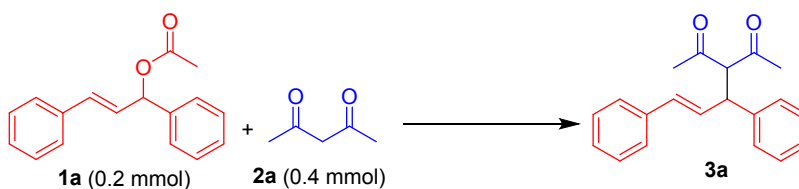
Table 1. Time Study^a



Entry	Time (h)	3a Yield (%) ^b
1	3	9
2	6	21
3	9	35
4	12	58
5	15	64
6	18	70
7	21	89
8	24	94
9	27	98

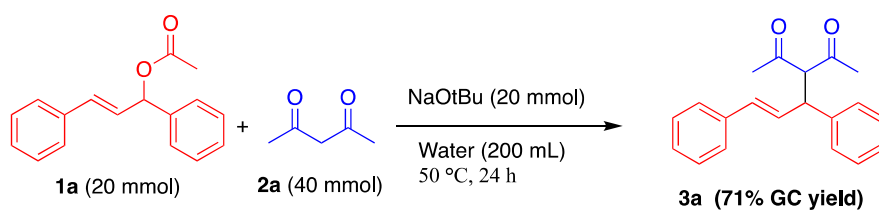
^aReaction Conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), NaOtBu (0.20 mmol), water (2 mL), 50 °C, under air atmosphere. ^bGC yield.

Table 2 Effect of Water volume^a



Entry	Water (mL)	3a Yield (%) ^b
1	0.5	38
2	1	57
3	2	94
4	4	97

^aReaction Conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), NaOtBu (0.20 mmol), Water, 50 °C, 24 h, under air atmosphere. ^bGC yield.

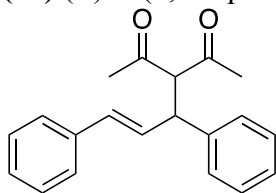


Product separates by simple extraction without any solvent

Scheme 1: Scale up of allylic alkylation to 20 mmol scale.

4. Spectroscopic data of product:

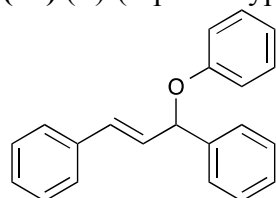
(3a) (*E*)-3-(1,3-diphenylallyl)pentane-2,4-dione¹



¹H NMR (400 MHz, Chloroform-*d*): δ 1.92 (s, 3 H), 2.25 (s, 3 H), 4.33–4.34 (m, 2 H), 6.19 (dd, $J = 5.2, 15.8$ Hz, 1 H), 6.48 (d, $J = 15.8$ Hz, 1 H), 7.18–7.33 (m, 10 H).

¹³C NMR (100 MHz, Chloroform-*d*): δ 29.71, 30.00, 49.17, 74.54, 126.36, 127.27, 127.71, 127.92, 128.52, 129.02, 131.68, 136.55, 140.10, 202.66, 202.82.

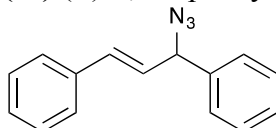
(3b) (*E*)-(3-phenoxyprop-1-ene-1,3-diyl)dibenzene²



¹H NMR (400 MHz, Chloroform-*d*): δ 5.71 (d, $J = 6.3$ Hz, 1H), 6.35 (dd, $J = 15.9, 6.3$ Hz, 1H), 6.58 (d, $J = 16.0$ Hz, 1H), 6.82 (t, $J = 7.3$ Hz, 1H), 6.89 (d, $J = 7.8$ Hz, 2H), 7.24 – 7.08 (m, 6H), 7.32 – 7.23 (m, 5H), 7.41 – 7.33 (m, 2H).

¹³C NMR (100 MHz, Chloroform-*d*): δ 80.84, 116.37, 121.17, 126.78, 126.79, 127.99, 128.00, 128.66, 128.83, 129.44, 129.50, 131.63, 136.47, 140.48, 158.06.

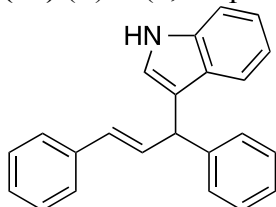
(3c) (*E*)-1,3-diphenyl-N-(prop-2-yn-1-yl)prop-2-en-1-amine³



GC-MS m/z (% relative intensity): 208 (10), 207 (67), 206 (100), 130 (57), 103 (18), 102 (10), 91 (10), 89 (11), 77 (27), 51 (10).

¹H NMR (400 MHz, Chloroform-*d*): δ 5.14 (d, $J = 7.2$ Hz, 1H), 6.22 (dd, $J = 15.7, 7.3$ Hz, 1H), 6.64 (d, $J = 15.7$ Hz, 1H), 7.36 – 7.16 (m, 10H).

(3d) (*E*)-3-(1,3-diphenylallyl)-1*H*-indole⁴

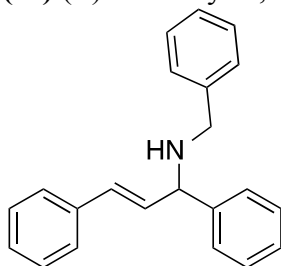


GC-MS m/z (% relative intensity): 309 (M^+ , 100), 308 (39), 232 (34), 206 (28), 204 (21), 192 (20), 191 (20), 130 (21), 115 (19).

¹H NMR (400 MHz, Chloroform-*d*): δ 5.20 (d, $J = 7.3$ Hz, 1H), 6.52 (d, $J = 15.9$ Hz,

1H), 6.81 (dd, $J = 15.8, 7.4$ Hz, 1H), 6.96 (s, 1H), 7.10 (t, $J = 7.1$ Hz, 1H), 7.19-7.57 (m, 13H), 8.07 (s, 1H).

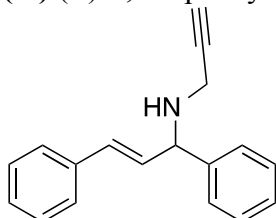
(3e) (*E*)-*N*-benzyl-1,3-diphenylprop-2-en-1-amine⁵



¹H NMR (400 MHz, Chloroform-*d*): δ 3.79 (s, 2H), 4.40 (d, $J = 7.5$ Hz, 1H), 6.35 (dd, $J = 15.8, 7.5$ Hz, 1H), 6.57 (d, $J = 15.8$ Hz, 1H), 7.16-7.49 (15 H).

¹³C NMR (100 MHz, Chloroform-*d*): δ 51.31, 64.58, 126.57, 127.18, 127.52, 127.57, 127.63, 128.43, 128.57, 128.62, 128.78, 130.82, 132.22, 136.96, 139.93, 142.51.

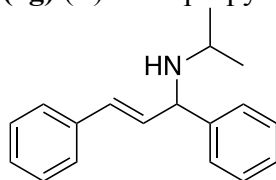
(3f) (*E*)-1,3-diphenyl-*N*-(prop-2-yn-1-yl)prop-2-en-1-amine⁶



GC-MS *m/z* (% relative intensity): 247 (M^+ , 15), 246 (23), 207 (39), 206 (100), 156 (14), 130 (16), 128 (16), 115 (27), 104 (24), 103 (17), 77 (27).

¹H NMR (400 MHz, Chloroform-*d*): δ 2.36 (t, $J = 2.3$ Hz, 1H), 3.31 (d, $J = 16.8$ Hz, 1H), 3.47 (d, $J = 16.8$ Hz, 1H), 4.86 (d, $J = 8.1$ Hz, 1H), 6.47 (dd, $J = 15.8, 8.1$ Hz, 1H), 6.62 (s, 1H), 7.33 – 7.18 (m, 10 H).

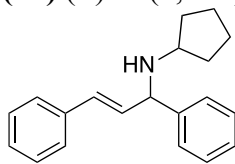
(3g) (*E*)-*N*-isopropyl-1,3-diphenylprop-2-en-1-amine⁷



GC-MS *m/z* (% relative intensity): 251 (M^+ , 46), 208 (39), 193 (69), 192 (40), 191 (36), 174 (36), 160 (74), 115 (100), 104 (40), 91 (32)

¹H NMR (400 MHz, Chloroform-*d*): δ 1.05 (dd, $J = 18.2, 6.3$ Hz, 6H), 2.79 (hept, $J = 6.3$ Hz, 1H), 4.53 (d, $J = 7.1$ Hz, 1H), 6.57 – 6.19 (m, 2H), 7.45 – 7.13 (m, 10H).

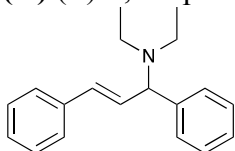
(3h) (*E*)-*N*-(1,3-diphenylallyl)cyclopentanamine



GC-MS m/z (% relative intensity): 277 (M^+ , 22), 208 (27), 200 (18), 193 (65), 192 (30), 191 (262), 186 (67), 178 (26), 91 (28).

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 1.35 (d, $J = 9.4$ Hz, 4H), 1.65 – 1.50 (m, 2H), 1.85 – 1.73 (m, 2H), 4.39 (d, $J = 7.5$ Hz, 1H), 3.00 (p, $J = 7.1$ Hz, 1H), 6.30 (dd, $J = 15.8, 7.5$ Hz, 1H), 6.48 (d, $J = 15.8$ Hz, 1H), δ 7.40 – 7.09 (m, 10H).

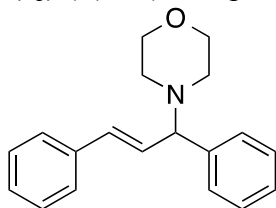
(3i) (*E*)-1,3-diphenyl-*N*-(prop-2-yn-1-yl)prop-2-en-1-amine²



GC-MS m/z (% relative intensity): 265 (M^+ , 18), 264 (23), 193 (100), 192 (29), 191 (24), 188 (35), 178 (24), 174 (22), 115 (88), 91 (25).

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 0.98 (t, $J = 6.9$ Hz, 6H), 2.64 (s, 4H), 4.25 (d, $J = 8.4$ Hz, 1H), 6.31 (dd, $J = 15.8, 6.5$ Hz, 1H), 6.48 (d, $J = 15.7$ Hz, 1H), 7.34 – 7.11 (m, 10H).

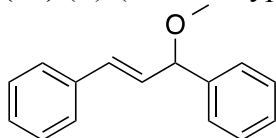
(3j) (*E*)-4-(1,3-diphenylallyl)morpholine⁷



GC-MS m/z (% relative intensity): 279 (M^+ , 18), 202 (15), 194 (18), 193 (100), 192 (19), 191 (18), 188 (18), 178 (22), 115 (83), 91 (24).

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 2.25-2.58 (m, 4H), 3.63-3.85 (m, 5H), 6.36-6.16 (m, 1H), 6.50 (d, $J = 15.8$ Hz, 1H), 7.11-7.37 (m, 10 H).

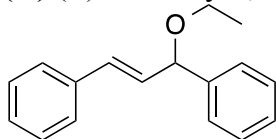
(3k) (*E*)-(3-methoxyprop-1-ene-1,3-diyl)dibenzene⁴



GC-MS m/z (% relative intensity): 224 (M^+ , 100), 223 (76), 193 (45), 192 (86), 191 (59), 178 (30), 115 (94), 105 (55), 91 (37), 77 (47).

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 3.38 (s, 3 H), 4.80 (d, $J = 7.0$ Hz, 1 H), 6.28 (dd, $J = 7.0, 15.8$ Hz, 1 H), 6.60 (d, $J = 15.8$ Hz, 1 H), 7.19-7.46 (m, 10 H).

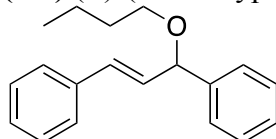
(3l) (*E*)-3-ethoxy-1, 3-diphenylprop-1-ene²⁴



GC-MS m/z (% relative intensity): 238 (M⁺, 91), 237 (44), 194 (28), 193 (46), 192 (44), 191 (34), 178 (28), 115 (55), 105 (100), 77 (29).

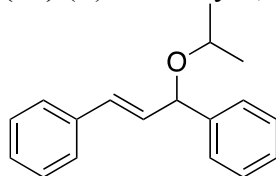
¹H NMR (400 MHz, Chloroform-*d*): δ 1.19 (t, *J* = 7.0 Hz, 3H), 3.55 – 3.37 (m, 2H), 4.85 (d, *J* = 7.0 Hz, 1H), 6.23 (d, *J* = 15.9 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 7.39 – 7.11 (m, 10H).

(3m) (*E*)-(3-butoxyprop-1-ene-1,3-diyl)dibenzene⁸



GC-MS m/z (% relative intensity): 266 (M⁺, 42), 210 (18), 194 (22), 193 (35), 192 (32), 191 (26), 178 (21), 115 (47), 105 (100), 91 (19).

(3n) (*E*)-3-ethoxy-1, 3-diphenylprop-1-ene²⁴

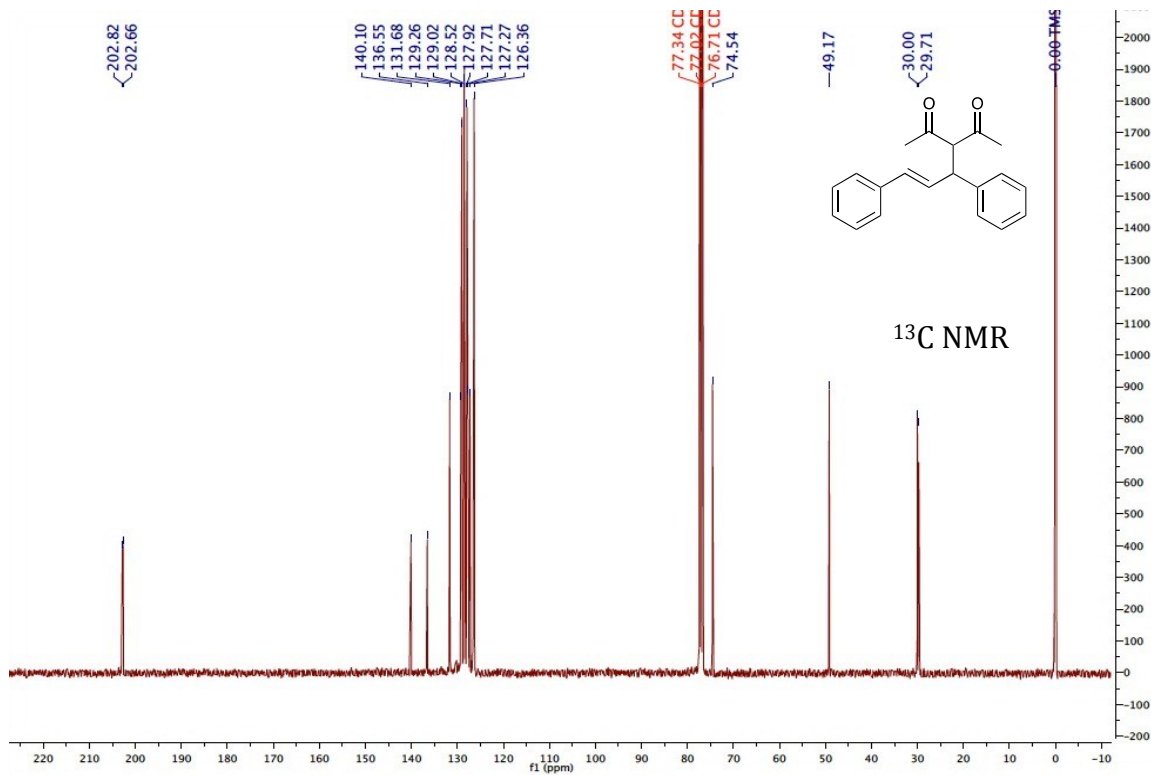
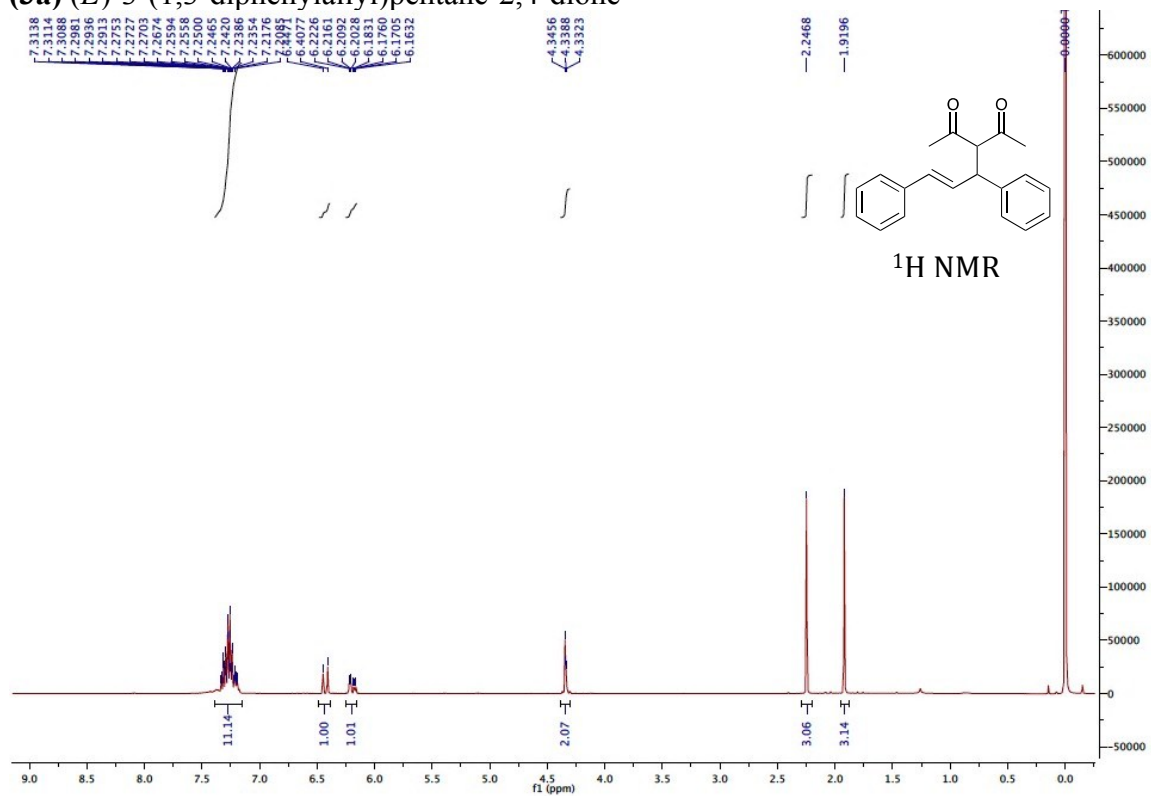


GC-MS m/z (% relative intensity): 252 (M⁺), 210, 193, 181, 165, 152.

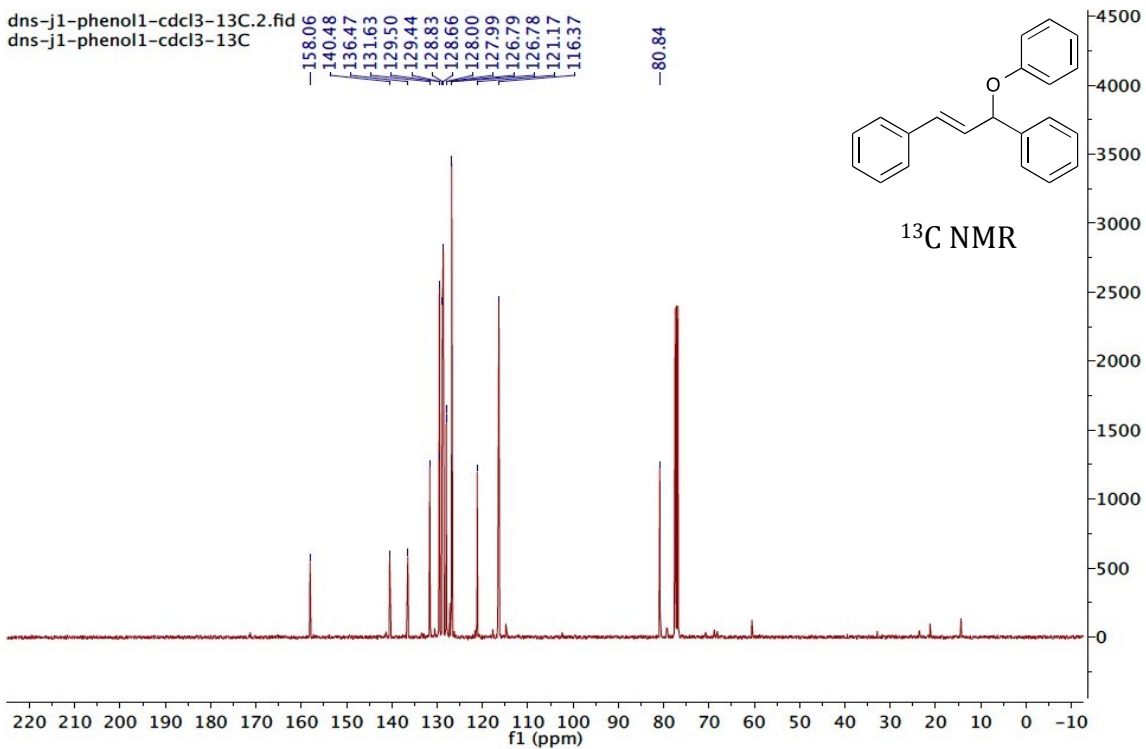
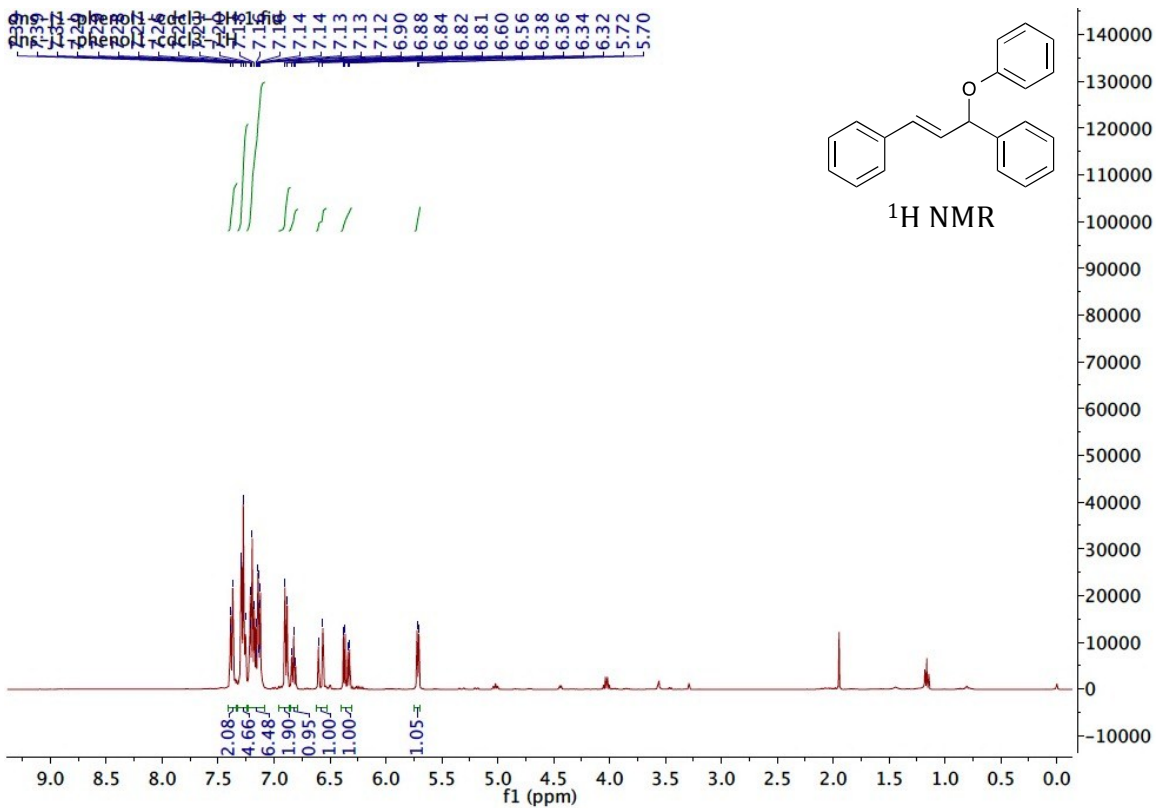
5. References:

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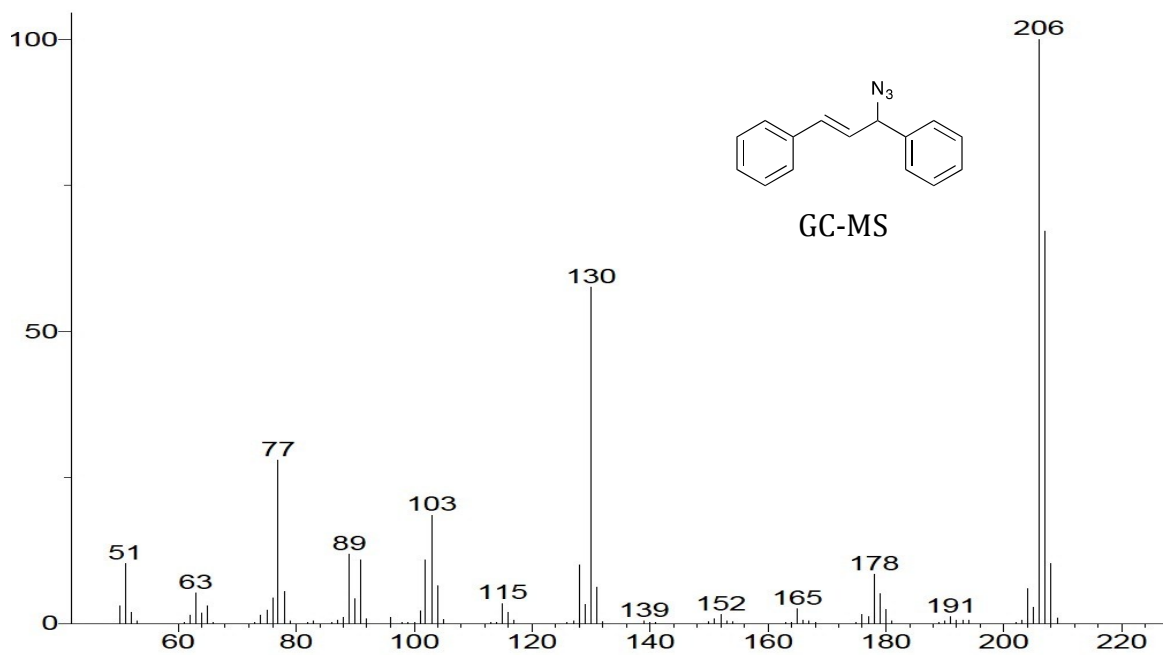
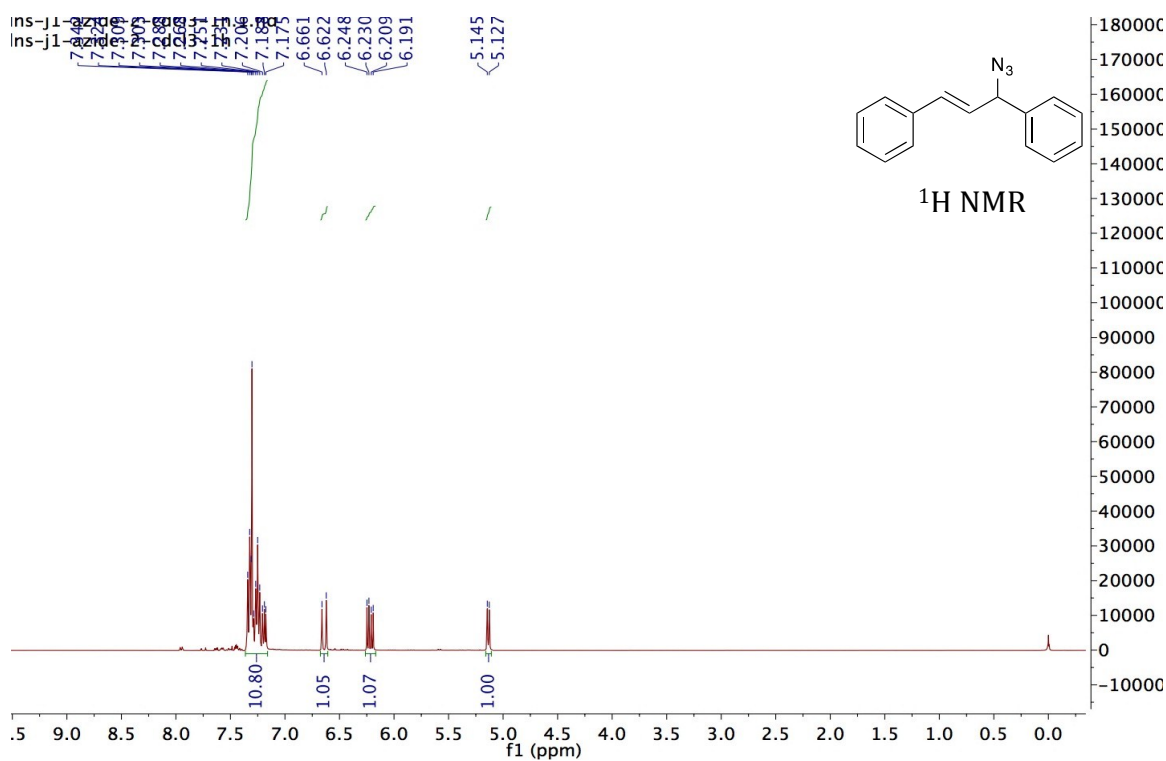
Analytical Spectra's
(3a) (*E*)-3-(1,3-diphenylallyl)pentane-2,4-dione



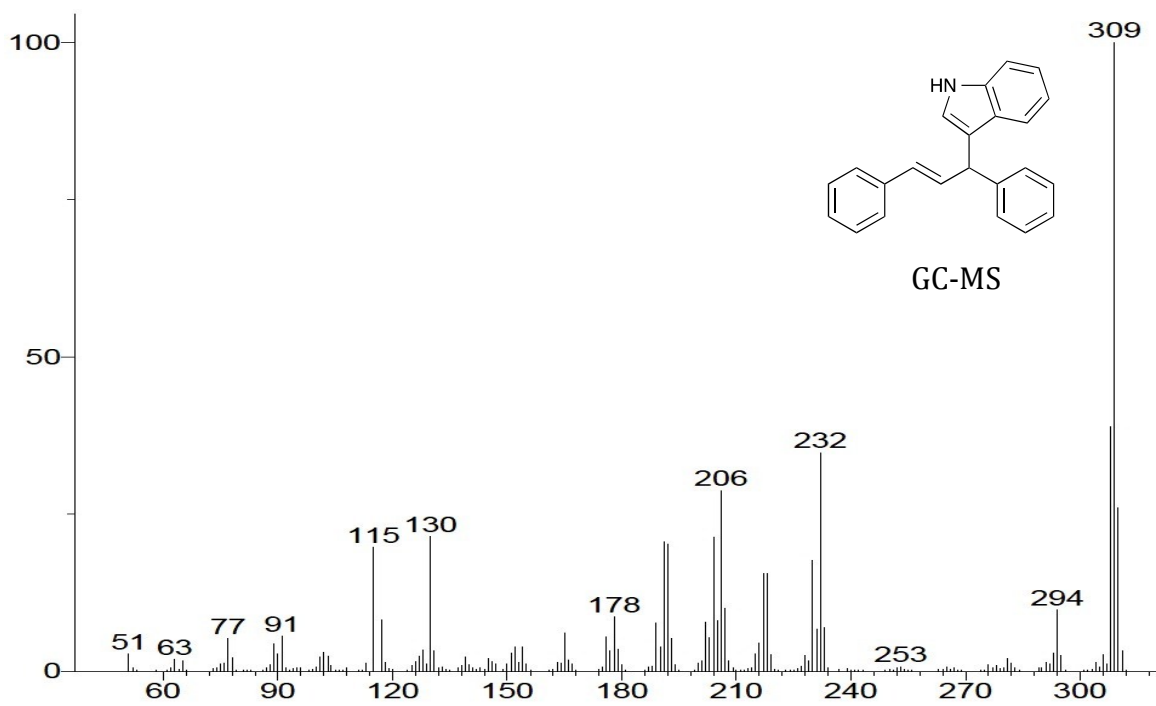
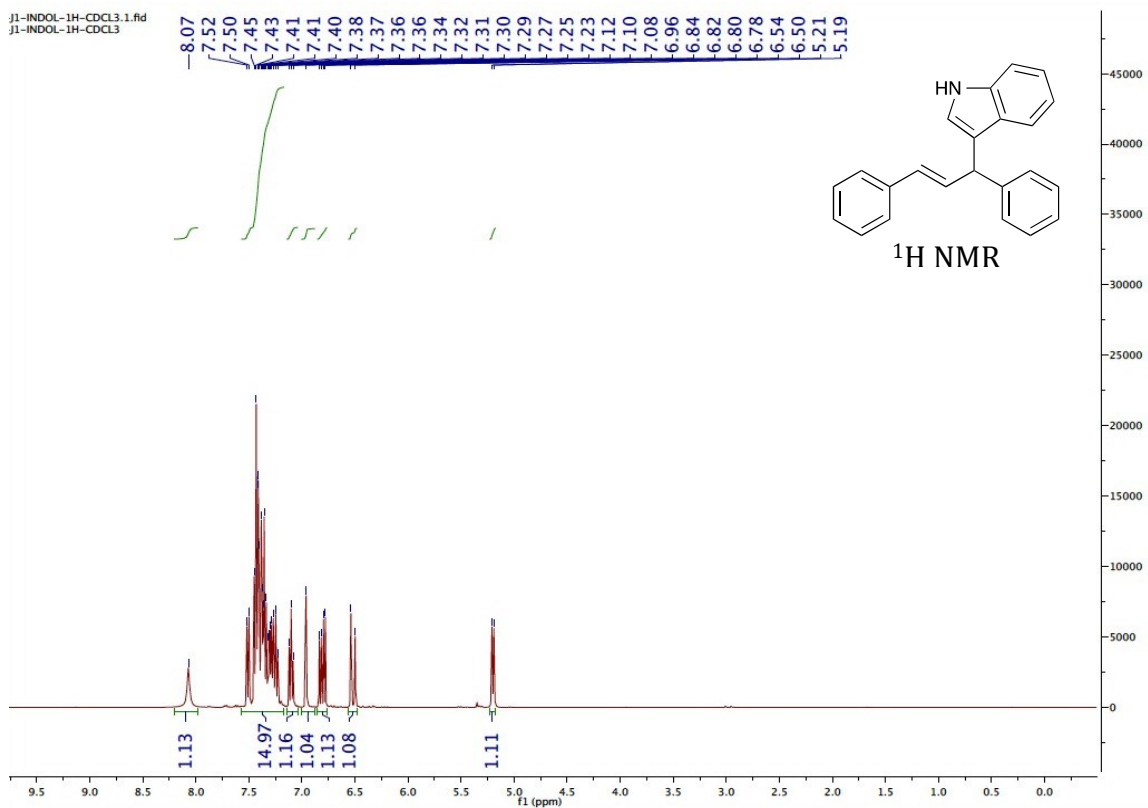
(3b) (*E*)-(3-phenoxyprop-1-ene-1,3-diyl)dibenzene



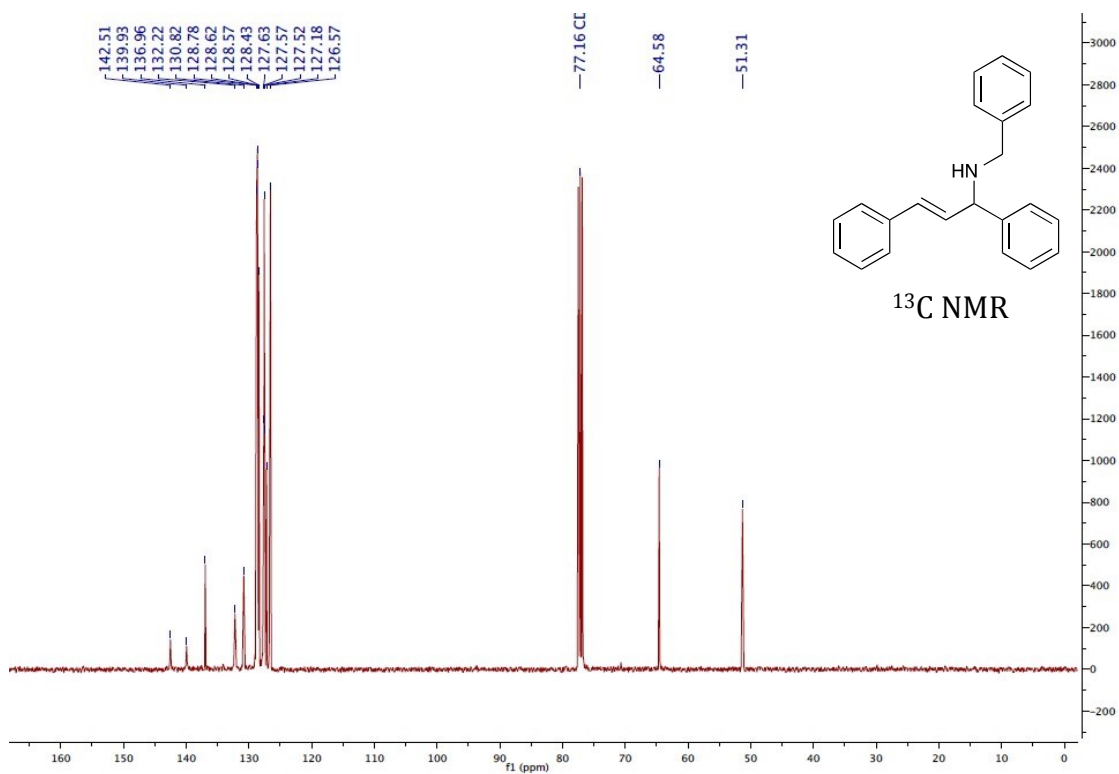
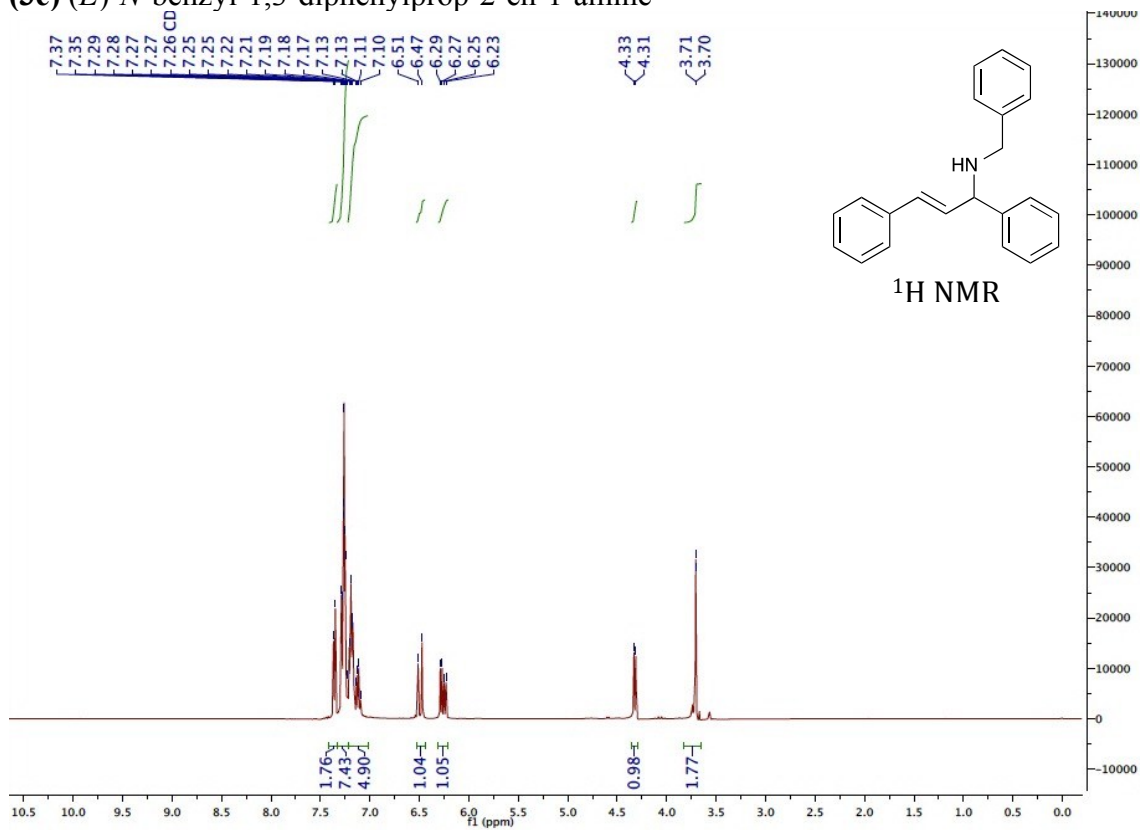
(3c) *(E)*-1,3-diphenyl-*N*-(prop-2-yn-1-yl)prop-2-en-1-amine



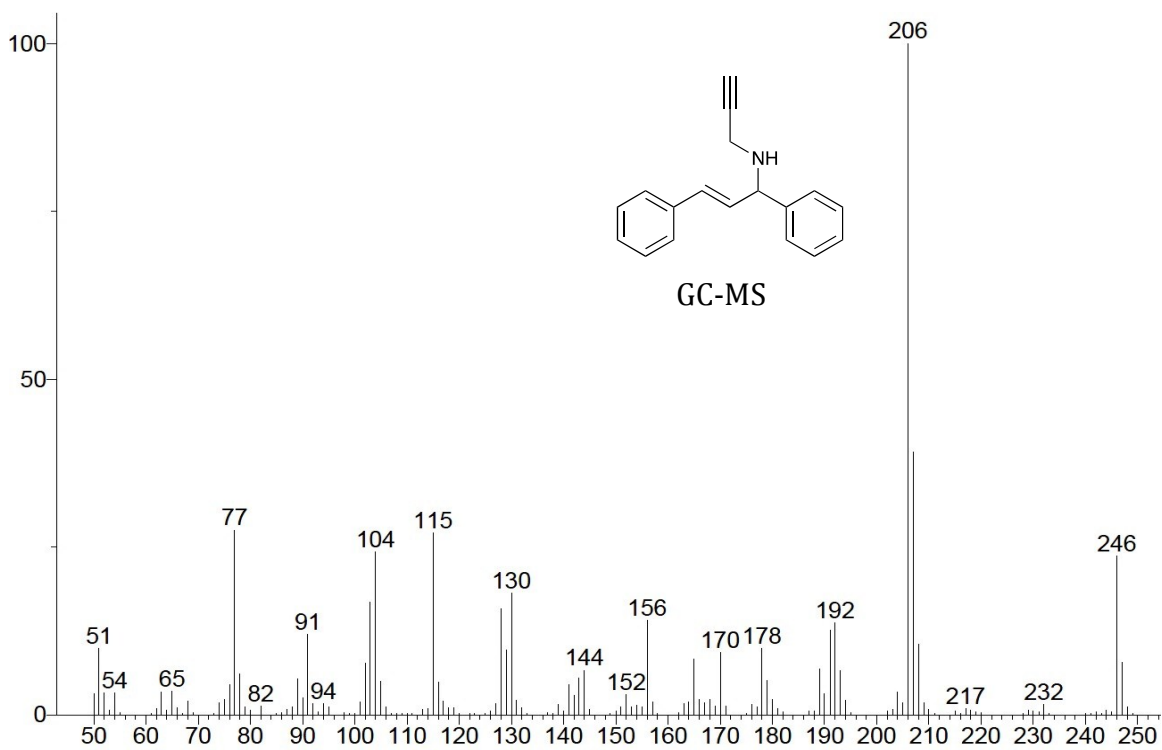
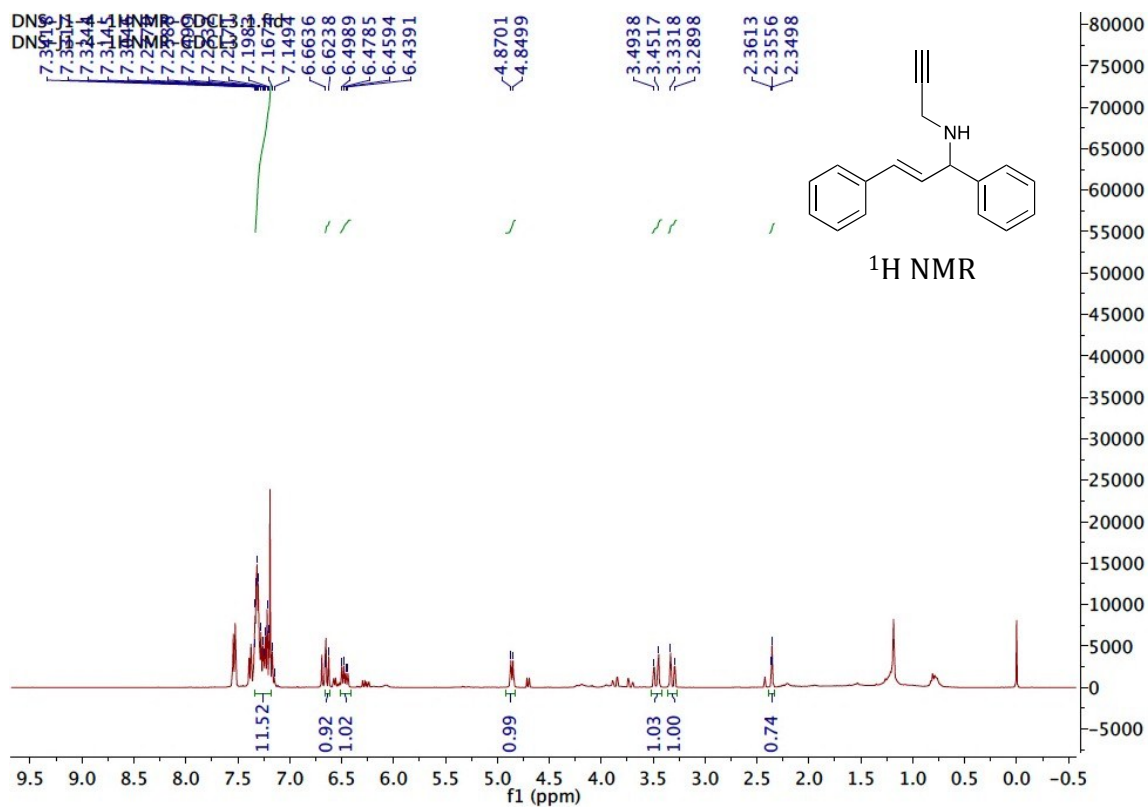
(3d) (*E*)-3-(1,3-diphenylallyl)-1*H*-indole



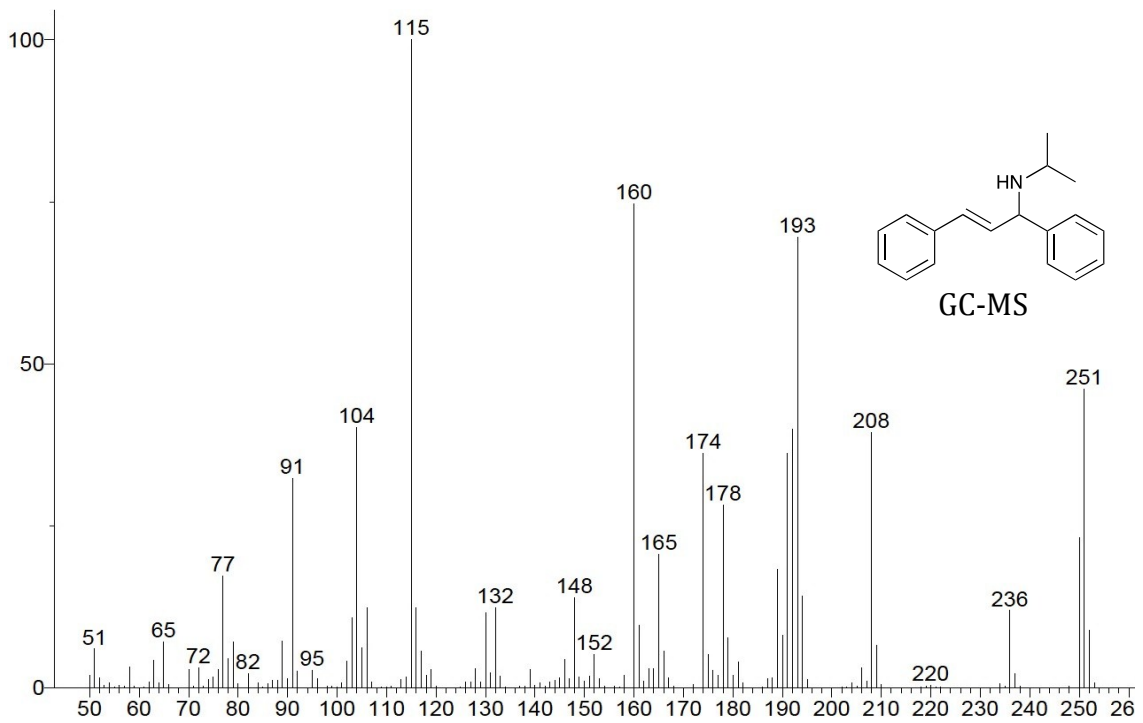
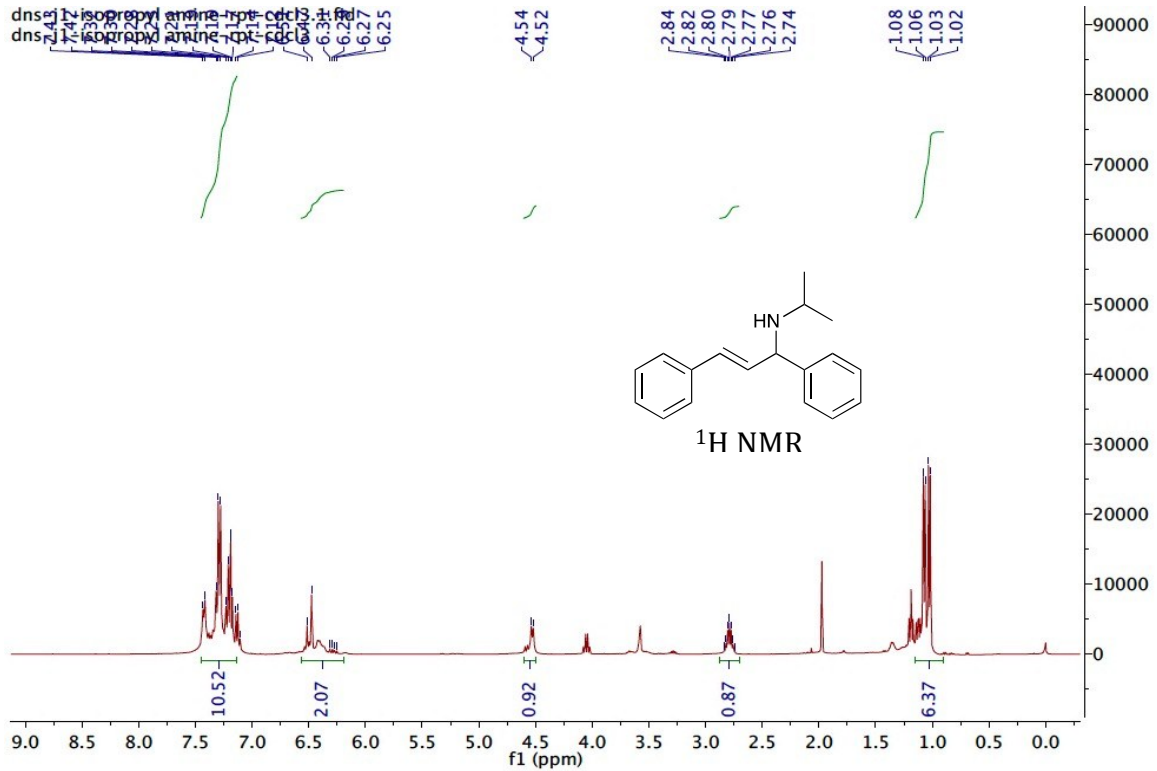
(3e) (*E*)-*N*-benzyl-1,3-diphenylprop-2-en-1-amine



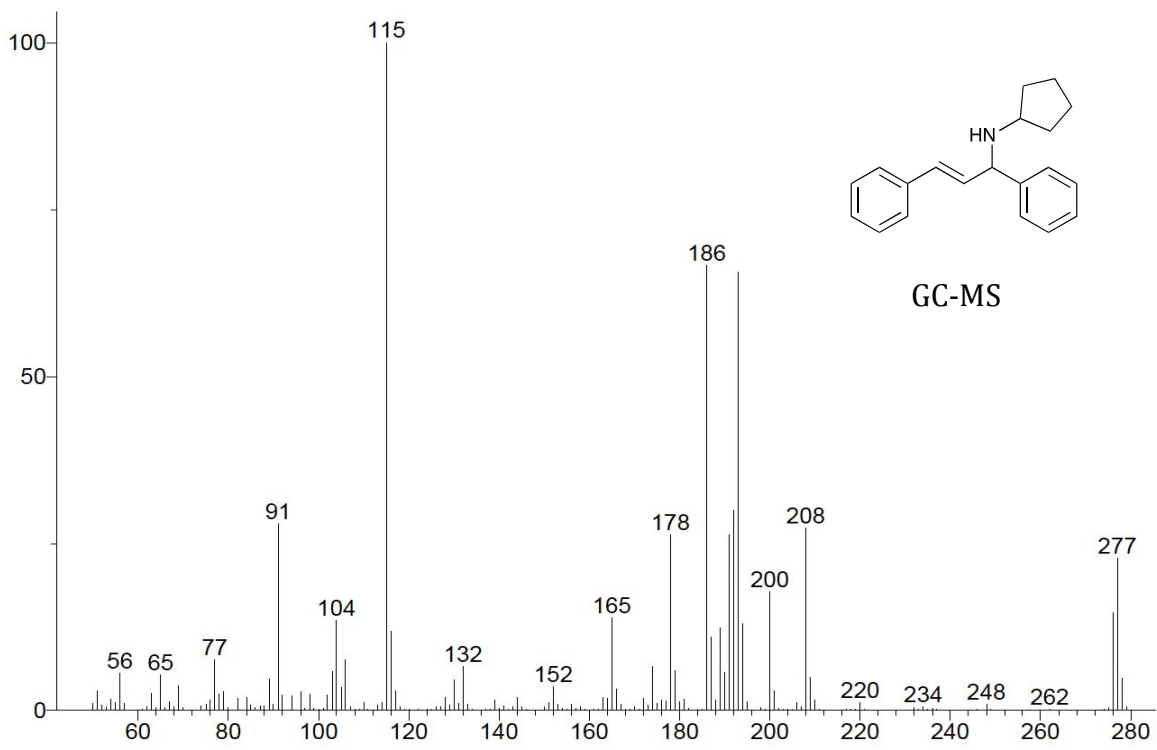
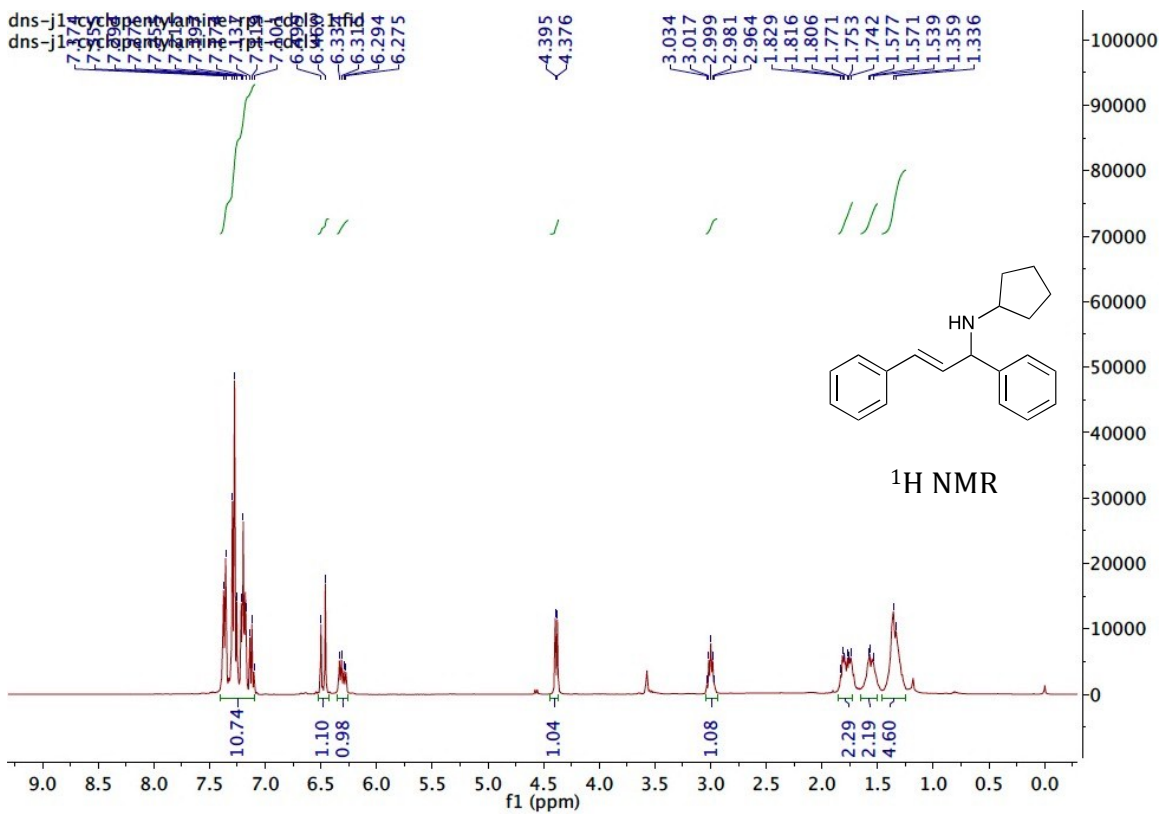
(3f) (*E*)-1,3-diphenyl-*N*-(prop-2-yn-1-yl)prop-2-en-1-amine



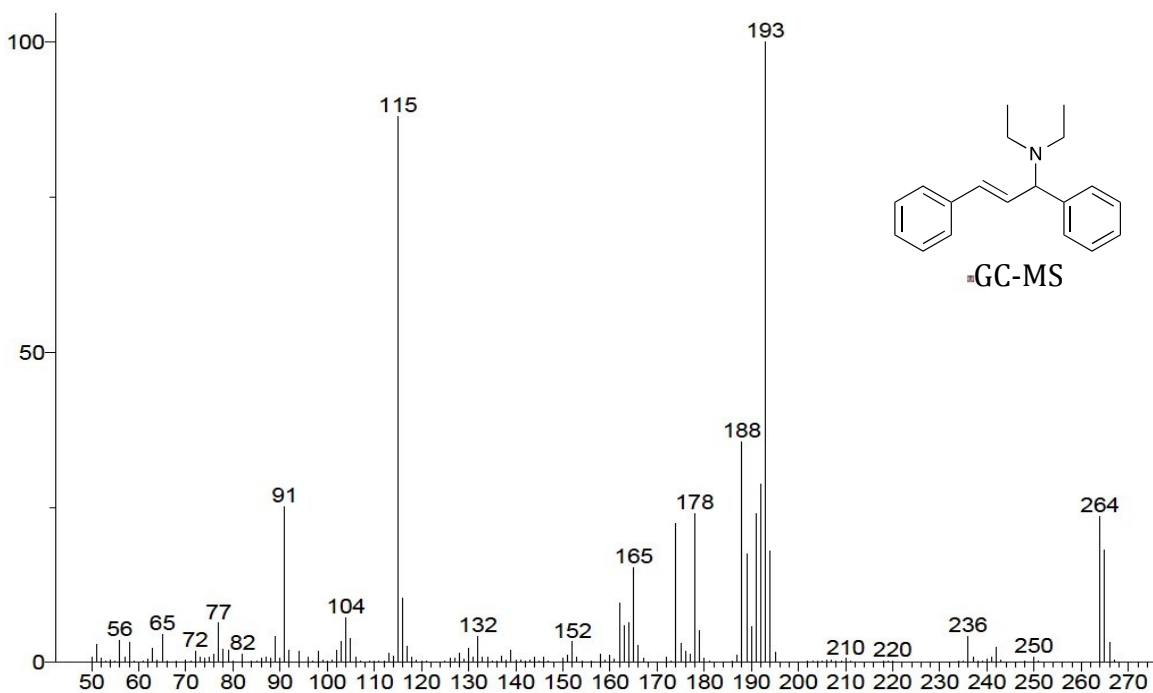
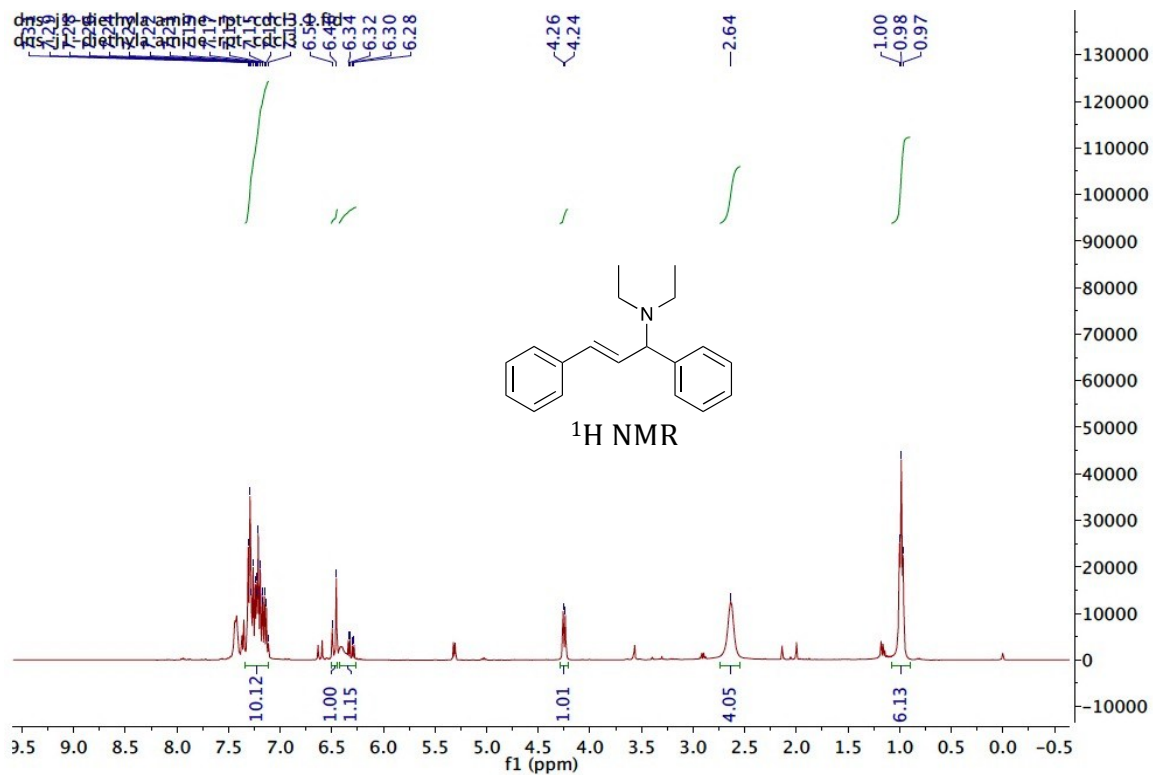
(3g) (*E*)-*N*-isopropyl-1,3-diphenylprop-2-en-1-amine



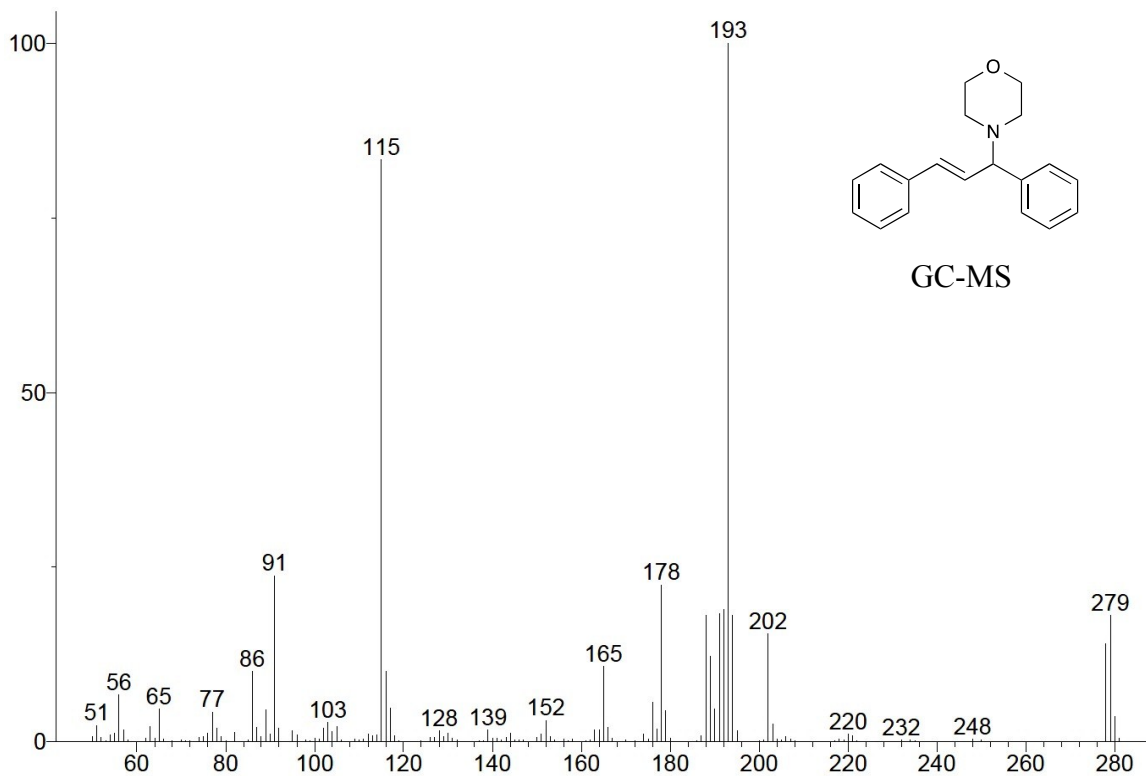
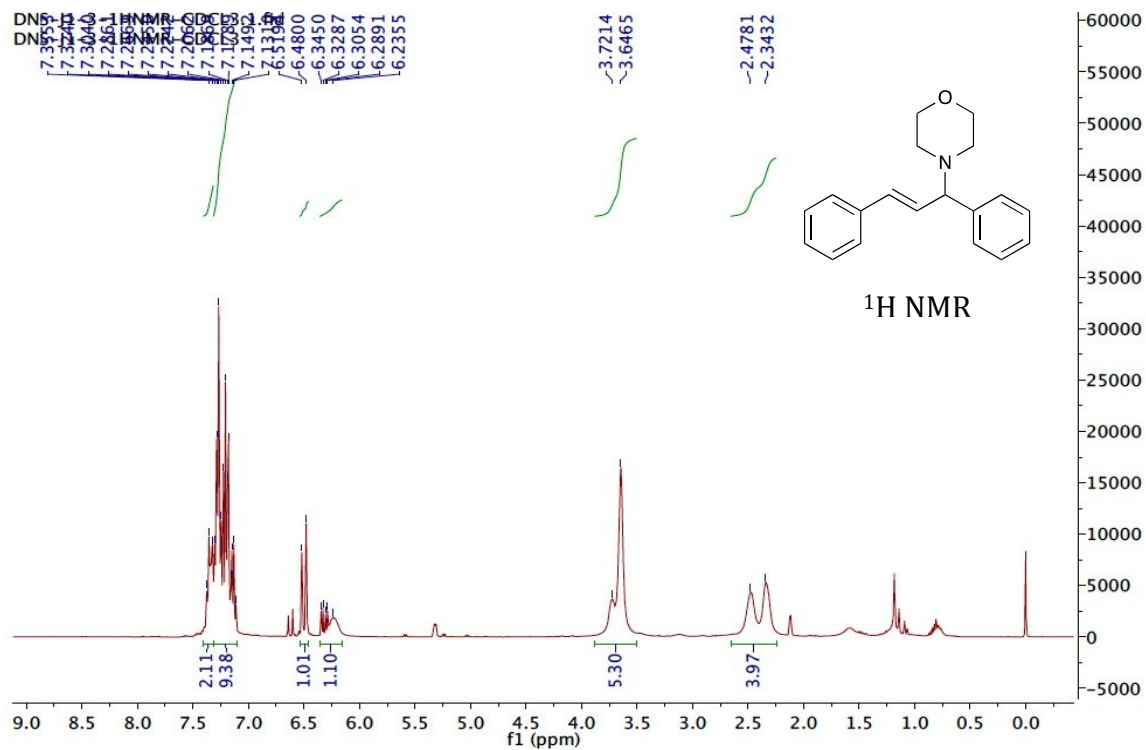
(3h) (*E*)-*N*-(1,3-diphenylallyl)cyclopentanamine



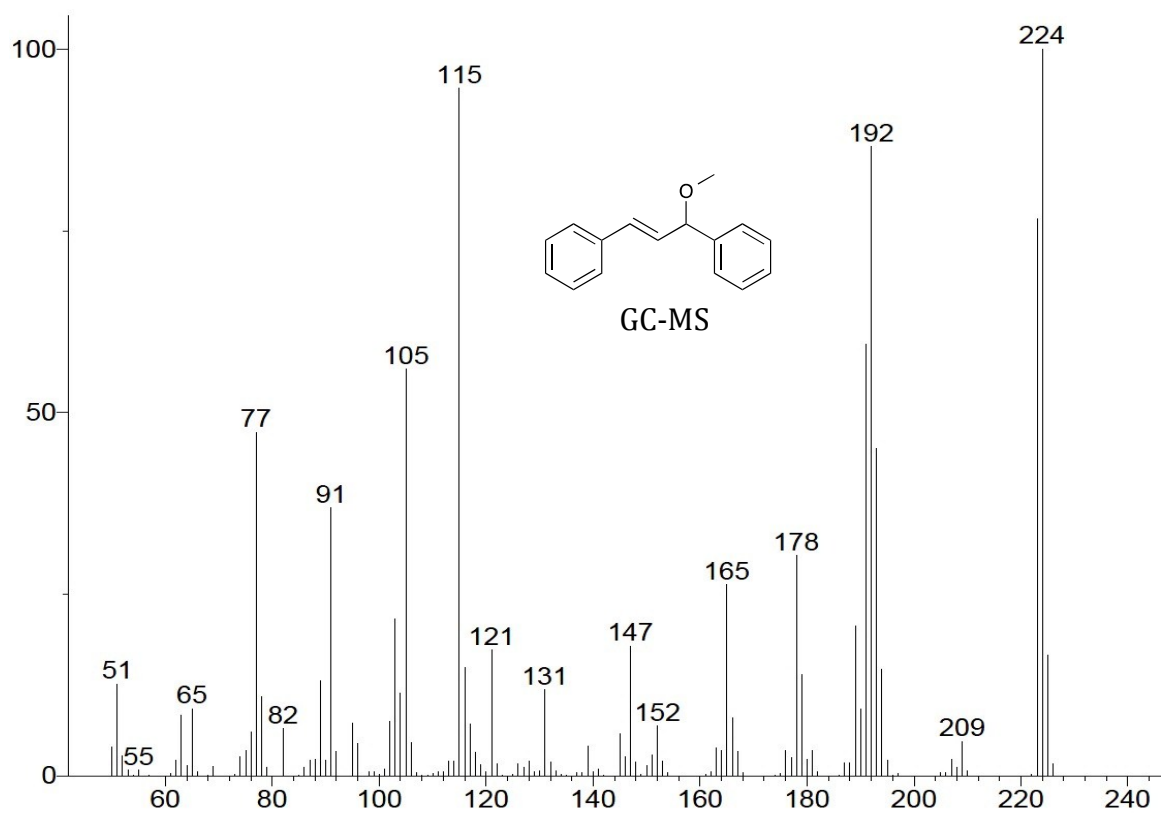
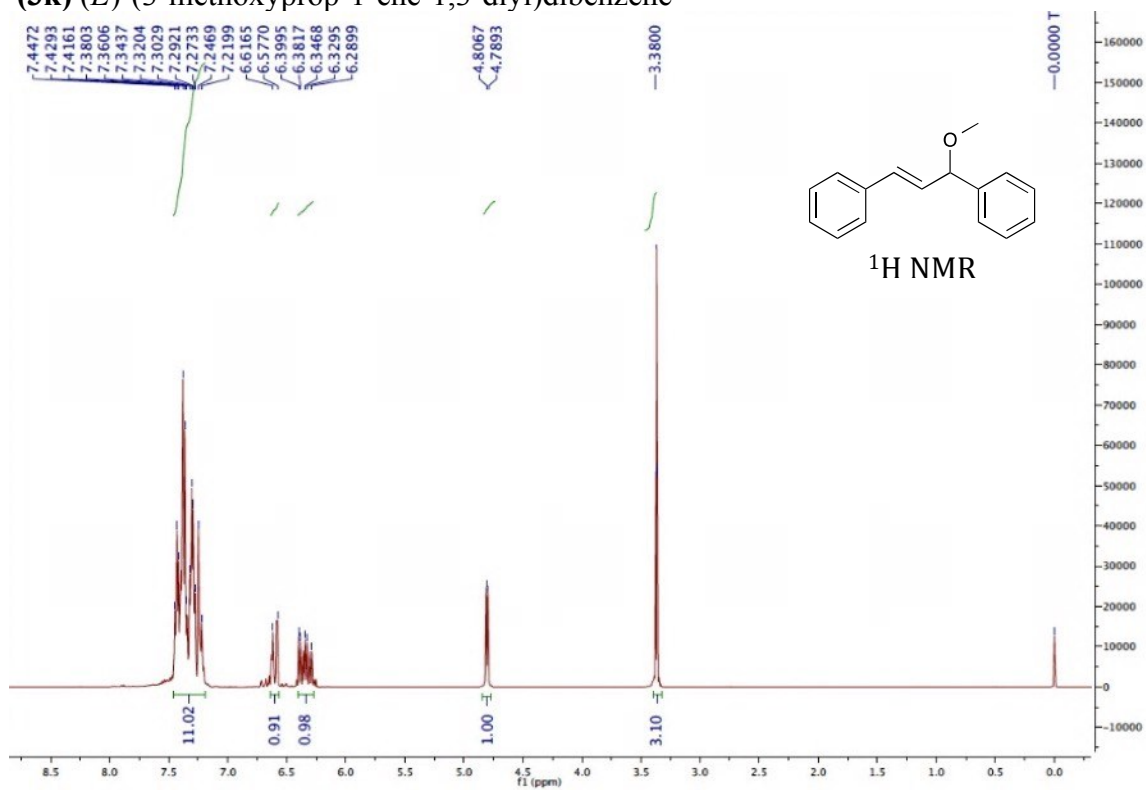
(3i) (*E*)-1,3-diphenyl-*N*-(prop-2-yn-1-yl)prop-2-en-1-amine



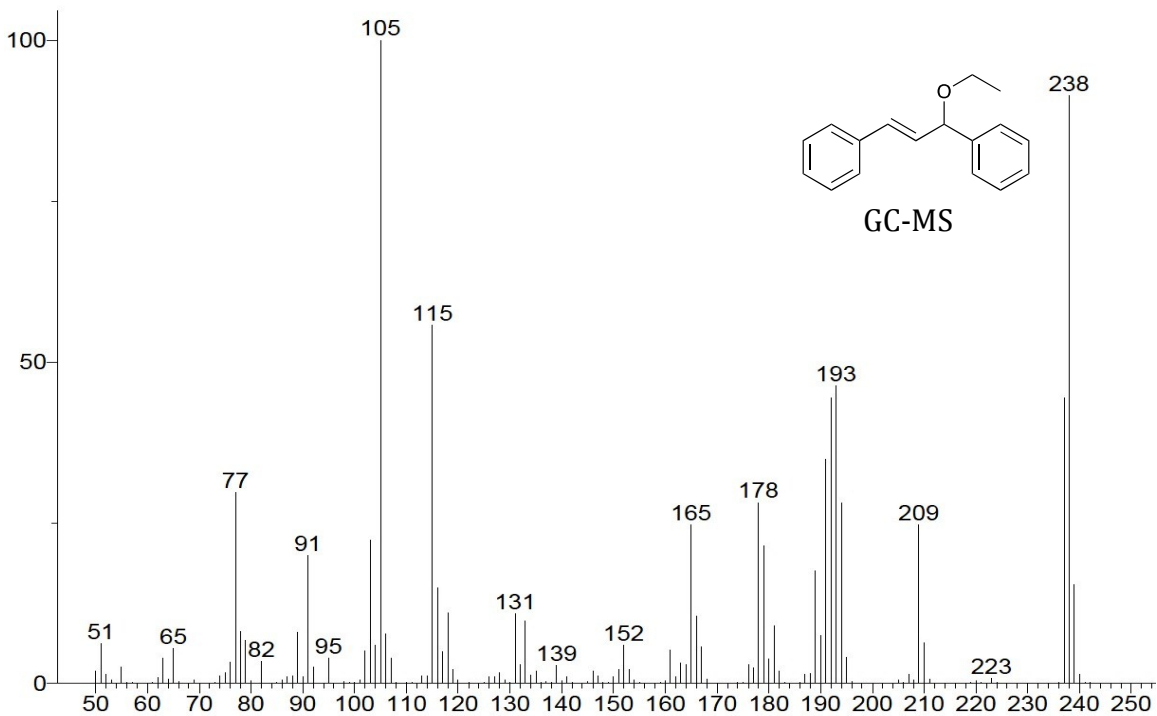
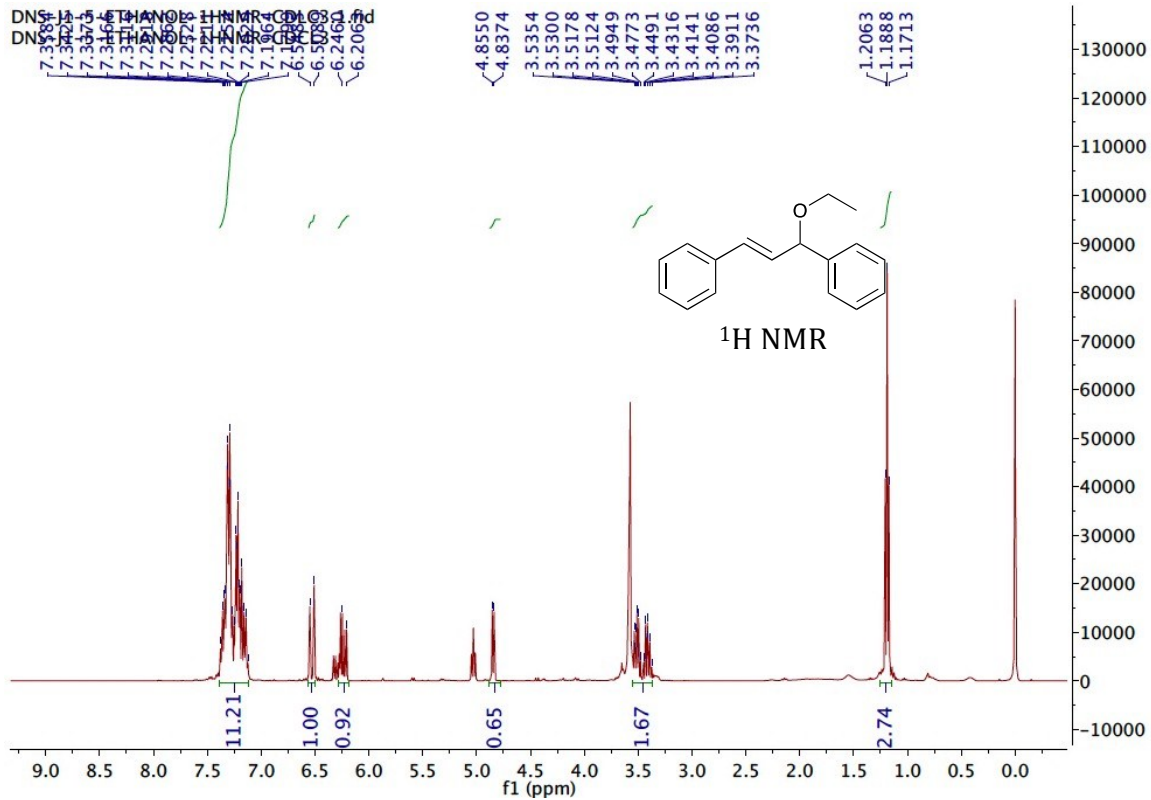
(3j) (*E*)-4-(1,3-diphenylallyl)morpholine



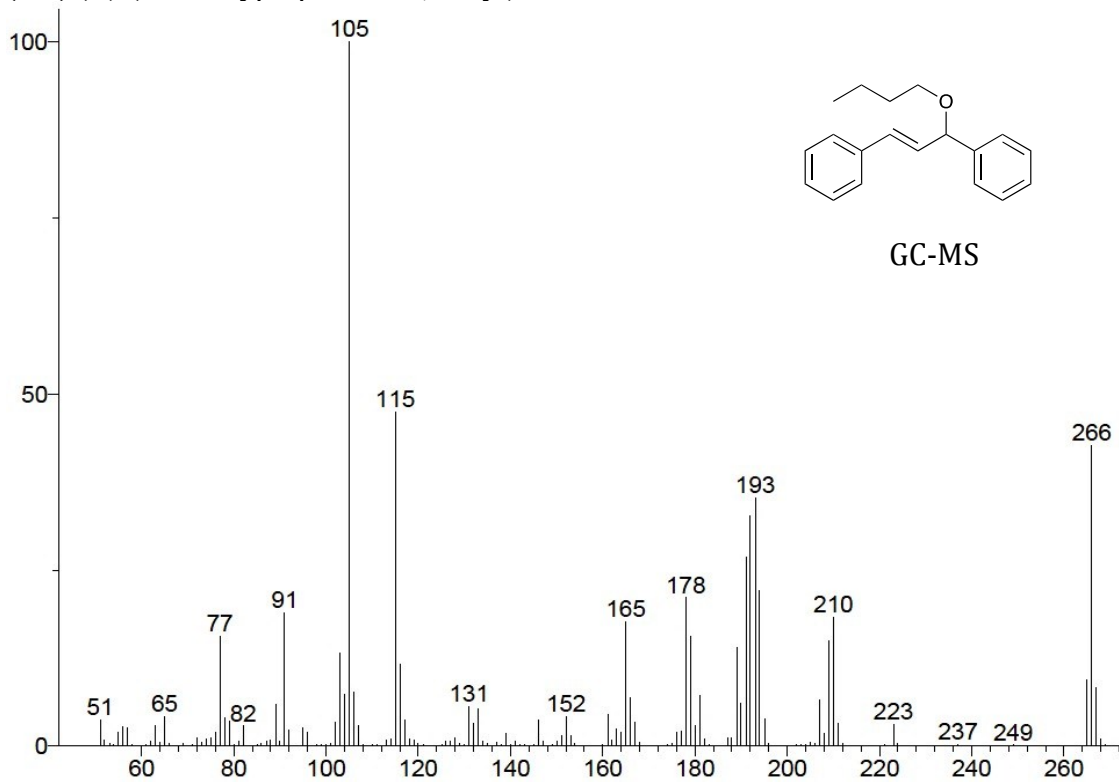
(3k) (*E*)-(3-methoxyprop-1-ene-1,3-diyl)dibenzene



(3) *(E)*-3-ethoxy-1,3-diphenylprop-1-ene



(3m) (*E*)-(3-butoxyprop-1-ene-1,3-diyl)dibenzene



(3n) (*E*)-(3-isopropoxyprop-1-ene-1,3-diyl)dibenzene

