

Supporting Information

Direct construction of alkenyl iodides *via* indium-catalyzed iodoalkylation of alkynes with alcohols and aqueous HI

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1. General Remarks

All experiments were carried out under an inert atmosphere of nitrogen. All commercially available reagent grade chemicals were purchased from Aldrich, Acros and Alfa Aesar Chemical Company and used as received without further purification unless otherwise stated. All solvents were used after drying and distilling process. NMR spectra were recorded in CDCl₃ on a Bruker Avance 600 spectrometer with TMS as internal standard (¹H: 600 MHz, ¹³C: 150 MHz) at room temperature, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations are used to indicate the multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m) or broad (br). Mass analyses and HRMS were obtained on an Agilent 5973N MSD mass spectrometer and a Waters Micromass GCT Premier mass spectrometer by the EI method, respectively. Column chromatography was performed on silica gel (100-200 mesh).

2. General Experimental Procedure

To a stirred solution of InI₃ (2.5 mol%), alcohol **1** (0.5 mmol), and 47% aqueous HI (1.5 equiv) in DBE (1.0 mL) was added alkyne **2** (0.75 mmol). The mixture was heated at 60°C and stirred for 6 h. Upon completion of the reaction, the mixture was filtered through a short column of silica gel and washed with ethyl acetate, and the solvents were removed by rotary evaporation to provide raw product. Then the raw product was purified on silica gel using petroleum ether as the eluent to afford desired product **4**.

3. Spectral Data for All the Compounds

(3-iodoprop-2-ene-1,1,3-triyl)tribenzene (4a) *E:Z* (90:10); ¹H NMR (CDCl₃, 600 MHz, ppm): (*E*)-**4a**: δ= 7.11-7.52 (m, 15H), 6.96 (d, *J* = 10.7 Hz, 1H), 4.68 (d, *J* = 10.7 Hz, 1H); (*Z*)-**4a**: δ= 7.11-7.52 (m, 15H), 6.38 (d, *J* = 9.2 Hz, 1H), 5.20 (d, *J* = 9.2 Hz, 1H). ¹³C NMR (CDCl₃, 150 MHz, ppm): δ= 144.1, 142.9, 141.6, 128.7, 128.5, 128.4, 128.2, 126.7, 95.9, 52.8; MS (EI): *m/z*=396; HRMS (EI) calcd for C₂₁H₁₇I 396.0375; found 396.0376.

(1-iodo-3-*p*-tolylprop-1-ene-1,3-diyl)dibenzene (4b) *E:Z* (91:9); ¹H NMR (CDCl₃, 600 MHz, ppm): (*E*)-**4b**: δ= 6.99-7.50 (m, 14 H), 6.93 (d, *J* = 10.8 Hz, 1H), 4.63 (d, *J* = 10.8 Hz, 1H), 2.33 (s, 3H); (*Z*)-**4b**: δ= 6.99-7.50 (m, 14 H), 6.35 (d, *J* = 9.2 Hz, 1H), 5.14 (d, *J* = 9.2 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (CDCl₃, 150 MHz, ppm): δ= 144.2, 143.0, 141.5, 139.8, 136.2, 129.4, 128.6, 128.5, 128.3, 128.1, 128.0, 126.5, 95.6, 52.4, 21.0; MS (EI): *m/z*=410; HRMS (EI) calcd for C₂₂H₁₉I 410.0532; found 410.0535.

(3-(4-chlorophenyl)-1-iodoprop-1-ene-1,3-diyl)dibenzene (4c) *E:Z* (85:15); ¹H NMR (CDCl₃, 600 MHz, ppm): (*E*)-**4c**: δ= 7.04-7.51 (m, 14H), 6.91 (d, *J* = 10.7 Hz, 1H), 4.65 (d, *J* = 10.8 Hz, 1H); (*Z*)-**4c**: δ= 7.04-7.51 (m, 14H), 6.33 (d, *J* = 9.2 Hz, 1H), 5.17 (d, *J* = 9.2 Hz, 1H). ¹³C NMR (CDCl₃, 150 MHz, ppm): δ= 143.4, 142.3, 141.3, 129.8, 128.5, 128.3, 128.2, 128.1, 128.0, 126.8, 96.2, 52.1; MS (EI): *m/z*=430; HRMS (EI) calcd for C₂₁H₁₆ClI 429.9985; found 429.9987.

5-(2-iodo-2-phenylvinyl)-10,11-dihydro-5H-dibenzo[*a,d*][7]annulene (4d) *E:Z* (92:8); ¹H NMR (CDCl₃, 600 MHz, ppm): (*E*)-**4d**: δ= 6.95-7.47 (m, 14H), 4.79 (d, *J* = 10.1 Hz, 1H), 3.31 (m, 2H), 3.00 (m, 2H); (*Z*)-**4d**: δ= 6.95-7.47 (m, 13H), 6.66 (d, *J* = 9.1 Hz, 1H), 5.28 (d, *J* = 9.1 Hz, 1H), 3.34 (m, 2H), 3.11 (m, 2H). ¹³C NMR (CDCl₃, 150 MHz, ppm): δ= 144.0, 142.1, 139.9, 139.2, 130.5, 129.2, 128.5, 128.4, 127.0, 126.3, 95.4, 53.5, 33.2; MS (EI): *m/z*= 422; HRMS (EI) calcd for C₂₃H₁₉I 422.0532; found 422.0526.

(1-iodobut-1-ene-1,3-diyl)dibenzene (4e) *E:Z* (89:11); ¹H NMR (CDCl₃, 600 MHz, ppm): (*E*)-**4e**: δ= 7.16-7.48 (m, 10H), 6.65 (d, *J* = 10.5 Hz, 1H), 3.49 (m, 1H), 1.35 (d, *J* = 6.9 Hz, 3H); (*Z*)-**4e**: δ= 7.16-7.48 (m, 10H), 6.01 (d, *J* = 9.1 Hz, 1H), 3.95 (m, 1H), 1.50 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (CDCl₃, 150 MHz, ppm): δ= 147.2, 144.5, 143.1, 142.0, 128.7, 128.5, 128.4, 128.2, 126.9, 126.5, 94.3, 42.0, 21.7; MS (EI): *m/z*= 334; HRMS (EI) calcd for C₁₆H₁₅I 334.0219; found 334.0222.

1-(4-iodo-4-phenylbut-3-en-2-yl)-4-methylbenzene (4f) *E:Z* (88:12); ^1H NMR (CDCl_3 , 600 MHz, ppm): (*E*)-**4f**: δ = 7.09-7.49 (m, 9H), 6.67 (d, J = 10.6 Hz, 1H), 3.50 (m, 1H), 2.38 (s, 3H), 1.36 (d, J = 6.9 Hz, 3H); (*Z*)-**4f**: δ = 7.09-7.49 (m, 9H), 6.03 (d, J = 9.0 Hz, 1H), 3.96 (m, 1H), 2.39 (s, 3H), 1.51 (d, J = 7.0 Hz, 3H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 147.5, 142.0, 141.5, 136.0, 129.4, 128.8, 128.5, 128.4, 128.2, 126.7, 94.1, 41.6, 21.8, 21.1; MS (EI): m/z =348; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{17}\text{I}$ 348.0375; found 348.0376.

1-chloro-4-(4-iodo-4-phenylbut-3-en-2-yl)benzene (4g) *E:Z* (88:12); ^1H NMR (CDCl_3 , 600 MHz, ppm): (*E*)-**4g**: δ = 7.05-7.43 (m, 9H), 6.56 (d, J = 10.4 Hz, 1H), 3.44 (m, 1H), 1.31 (d, J = 7.0 Hz, 3H); (*Z*)-**4g**: δ = 7.05-7.43 (m, 9H), 5.94 (d, J = 8.9 Hz, 1H), 3.91 (m, 1H), 1.46 (d, J = 7.0 Hz, 3H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 146.5, 142.9, 141.8, 132.1, 128.8, 128.4, 128.3, 128.1, 94.7, 41.3, 21.6; MS (EI): m/z =368; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{ClI}$ 367.9829; found 367.9834.

(1-iodohept-1-ene-1,3-diyl)dibenzene (4h) *E:Z* (87:13); ^1H NMR (CDCl_3 , 600 MHz, ppm): (*E*)-**4h**: δ = 7.11-7.47 (m, 10H), 6.65 (d, J = 10.7 Hz, 1H), 3.28 (m, 1H), 1.67 (m, 2H), 1.11-1.23 (m, 4H), 0.85 (t, J = 7.3 Hz, 3H); (*Z*)-**4h**: δ = 7.11-7.47 (m, 10H), 6.02 (d, J = 9.2 Hz, 1H), 3.79 (m, 1H), 1.87 (m, 2H), 1.28 (m, 4H), 0.94 (t, J = 7.5 Hz, 3H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 146.5, 143.7, 142.0, 128.7, 128.5, 128.2, 128.1, 127.2, 126.4, 94.6, 48.0, 36.3, 29.4, 22.5, 13.9; MS (EI): m/z =376; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{21}\text{I}$ 376.0688; found 376.0683.

(2-(cyclohex-2-enyl)-1-iodovinyl)benzene (4i) *E:Z* (82:18); ^1H NMR (CDCl_3 , 600 MHz, ppm): (*E*)-**4i**: δ = 7.24-7.53 (m, 5H), 6.36 (d, J = 10.5 Hz, 1H), 5.75 (m, 1H), 5.45 (d, J = 10.0 Hz, 1H), 2.82 (brs, 1H), 1.96 (m, 2H), 1.72 (m, 2H), 1.43 (m, 2H); (*Z*)-**4i**: δ = 7.24-7.53 (m, 5H), 5.82 (m, 1H), 5.76 (d, J = 9.2 Hz, 1H), 5.61 (m, 1H), 3.22 (brs, 1H), 2.04 (m, 2H), 1.78 (m, 2H), 1.46-1.53 (m, 2H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 146.8, 142.0, 128.53, 128.51, 128.4, 128.3, 128.2, 128.1, 94.6, 38.7, 28.8, 24.7, 20.6; MS (EI): m/z = 310; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{15}\text{I}$ 310.0219; found 310.0222.

(4E)-1-iodopenta-1,4-diene-1,3,5-triyltribenzene (4j) *E:Z* (84:16); ^1H NMR (CDCl_3 , 600 MHz, ppm): (1*E*)-**4j**: δ = 7.20-7.51 (m, 15H), 6.74 (d, J = 10.3 Hz, 1H), 6.44 (d, J = 15.9 Hz, 1H), 6.31 (dd, J = 15.9, 6.5 Hz, 1H), 4.23 (dd, J = 10.1, 6.6 Hz, 1H); (1*Z*)-**4j**: δ =

7.20-7.51 (m, 15H), 6.62 (d, J = 15.9 Hz, 1H), 6.45 (dd, J = 15.8, 6.6 Hz, 1H), 6.16 (d, J = 9.0 Hz, 1H), 4.75 (m, 1H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 143.1, 141.9, 141.7, 137.1, 130.9, 130.8, 128.9, 128.6, 128.5, 128.4, 127.7, 127.6, 126.9, 126.4, 95.8, 50.6; MS (EI): m/z = 422; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{19}\text{I}$ 422.0532; found 422.0528.

(3-iodo-3-*o*-tolylprop-2-ene-1,1-diyl)dibenzene (4l) *E:Z* (90:10); ^1H NMR (CDCl_3 , 600 MHz, ppm): (*E*)-**4l**: δ = 7.08-7.38 (m, 14H), 7.02 (d, J = 10.6 Hz, 1H), 4.43 (d, J = 10.6 Hz, 1H), 2.18 (s, 3H); (*Z*)-**4l**: δ = 7.08-7.38 (m, 14H), 6.10 (d, J = 9.2 Hz, 1H), 5.19 (d, J = 9.2 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 144.5, 142.9, 142.5, 140.6, 135.8, 130.6, 129.4, 128.7, 128.6, 128.4, 128.20, 128.15, 128.1, 126.64, 126.60, 126.0, 95.5, 52.9, 19.5; MS (EI): m/z = 410; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{19}\text{I}$ 410.0532; found 410.0527.

(3-iodo-3-*m*-tolylprop-2-ene-1,1-diyl)dibenzene (4m) *E:Z* (87:13); ^1H NMR (CDCl_3 , 600 MHz, ppm): (*E*)-**4m**: δ = 7.11-7.37 (m, 14H), 6.98 (d, J = 10.6 Hz, 1H), 4.71 (d, J = 10.6 Hz, 1H), 2.35 (s, 3H); (*Z*)-**4m**: δ = 7.11-7.37 (m, 14H), 6.39 (d, J = 9.2 Hz, 1H), 5.22 (d, J = 9.2 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 143.8, 142.9, 141.4, 138.0, 129.2, 129.1, 128.7, 128.5, 128.2, 126.6, 125.5, 96.2, 52.8, 21.4; MS (EI): m/z = 410; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{19}\text{I}$ 410.0532; found 410.0536.

(3-(4-fluorophenyl)-3-iodoprop-2-ene-1,1-diyl)dibenzene (4n) *E:Z* (90:10); ^1H NMR (CDCl_3 , 600 MHz, ppm): (*E*)-**4n**: δ = 7.00-7.48 (m, 14H), 6.97 (d, J = 10.7 Hz, 1H), 4.63 (d, J = 10.7 Hz, 1H); (*Z*)-**4n**: δ = 7.00-7.48 (m, 14H), 6.32 (d, J = 9.2 Hz, 1H), 5.16 (d, J = 9.3 Hz, 1H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 163.2, 161.5, 144.6, 142.7, 142.5, 137.6, 130.4, 128.8, 128.1, 126.7, 115.5, 115.3, 115.2, 94.4, 52.8; MS (EI): m/z = 414; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{16}\text{IF}$ 414.0281; found 414.0279.

(3-(3-chlorophenyl)-3-iodoprop-2-ene-1,1-diyl)dibenzene (4o) *E:Z* (87:13); ^1H NMR (CDCl_3 , 600 MHz, ppm): (*E*)-**4o**: δ = 7.13-7.51 (m, 14H), 7.02 (d, J = 10.7 Hz, 1H), 4.67 (d, J = 10.7 Hz, 1H); (*Z*)-**4o**: δ = 7.13-7.51 (m, 14H), 6.43 (d, J = 9.2 Hz, 1H), 5.21 (d, J = 9.2 Hz, 1H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 145.0, 143.1, 142.5, 134.1, 129.6, 128.8, 128.6, 128.4, 128.1, 127.3, 126.9, 126.8, 126.6, 93.3, 52.9; MS (EI): m/z = 430; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{16}\text{ClI}$ 429.9985; found 429.9988.

3-(1-iodo-3,3-diphenylprop-1-enyl)thiophene (4p) *E:Z* (76:24); ^1H NMR (CDCl_3 , 600

MHz, ppm): (*E*)-**4p**: δ = 7.11-7.44 (m, 13H), 6.95 (d, J = 10.4 Hz, 1H), 4.86 (d, J = 10.4 Hz, 1H); (*Z*)-**4p**: δ = 7.11-7.44 (m, 13H), 6.50 (d, J = 9.2 Hz, 1H), 5.20 (d, J = 9.2 Hz, 1H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 144.7, 143.0, 141.3, 128.8, 128.7, 128.5, 128.2, 126.7, 125.4, 124.0, 89.5, 53.2; MS (EI): m/z = 402; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{15}\text{IS}$ 401.9933; found 401.9936.

(3-cyclohexenyl-3-iodoprop-2-ene-1,1-diyl)dibenzene (4q) *E:Z* (85:15); ^1H NMR (CDCl_3 , 600 MHz, ppm): (*E*)-**4q**: δ = 7.15-7.33 (m, 10H), 6.61 (d, J = 10.3 Hz, 1H), 5.77 (s, 1H), 4.95 (d, J = 10.3 Hz, 1H), 2.18 (m, 2H), 2.02 (m, 2H), 1.72 (m, 2H), 1.61 (m, 2H); (*Z*)-**4q**: δ = 7.15-7.33 (m, 10H), 6.18 (s, 1H), 6.17 (d, J = 9.2 Hz, 1H), 5.24 (d, J = 9.2 Hz, 1H), 2.18 (m, 2H), 2.02 (m, 2H), 1.72 (m, 2H), 1.61 (m, 2H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 143.4, 141.7, 138.4, 128.6, 128.5, 128.2, 127.0, 126.5, 103.0, 52.7, 28.0, 25.2, 22.4, 21.9; MS (EI): m/z = 400; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{21}\text{I}$ 400.0688; found 400.0689.

(3-iodo-2-methyl-3-phenylprop-2-ene-1,1-diyl)dibenzene (4r) *E:Z* (78:22); ^1H NMR (CDCl_3 , 600 MHz, ppm): (*E*)-**4r**: δ = 7.11-7.54 (m, 15H), 5.30 (s, 1H), 2.08 (s, 3H); (*Z*)-**4r**: δ = 7.11-7.54 (m, 15H), 4.51 (s, 1H), 1.98 (s, 3H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 144.9, 143.8, 142.1, 129.4, 129.1, 128.8, 128.7, 128.2, 127.8, 126.9, 100.7, 53.6, 27.1; MS (EI): m/z = 410; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{19}\text{I}$ 410.0532; found 410.0535.

(2-(iodo(phenyl)methylene)butane-1,1-diyl)dibenzene (4s) *E:Z* (90:10); ^1H NMR (CDCl_3 , 600 MHz, ppm): (*E*)-**4s**: δ = 7.07-7.47 (m, 15H), 5.23 (s, 1H), 2.49 (q, J = 7.4 Hz, 2H), 0.51 (t, J = 7.4 Hz, 3H); (*Z*)-**4s**: δ = 7.07-7.47 (m, 15H), 4.63 (s, 1H), 2.17 (q, J = 7.4 Hz, 2H), 0.20 (t, J = 7.6 Hz, 3H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 148.4, 144.7, 141.9, 129.3, 128.8, 128.3, 128.2, 128.1, 127.7, 126.5, 99.3, 53.2, 32.4, 12.6; MS (EI): m/z =424; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{21}\text{I}$ 424.0688; found 424.0684.

Oxybis(methanetriyl)tetrabenzene ^1H NMR (CDCl_3 , 600 MHz, ppm): δ = 7.35 (d, J = 7.7 Hz, 8H), 7.30 (t, J = 7.7 Hz, 8H), 7.24 (t, J = 7.4 Hz, 4H), 5.40 (s, 2H); ^{13}C NMR (CDCl_3 , 150 MHz, ppm): δ = 142.2, 128.4, 127.4, 127.3, 80.0; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{22}\text{NaO}$ 373.1563. Found: 373.1554.

4. Stereochemical elucidation

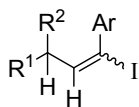


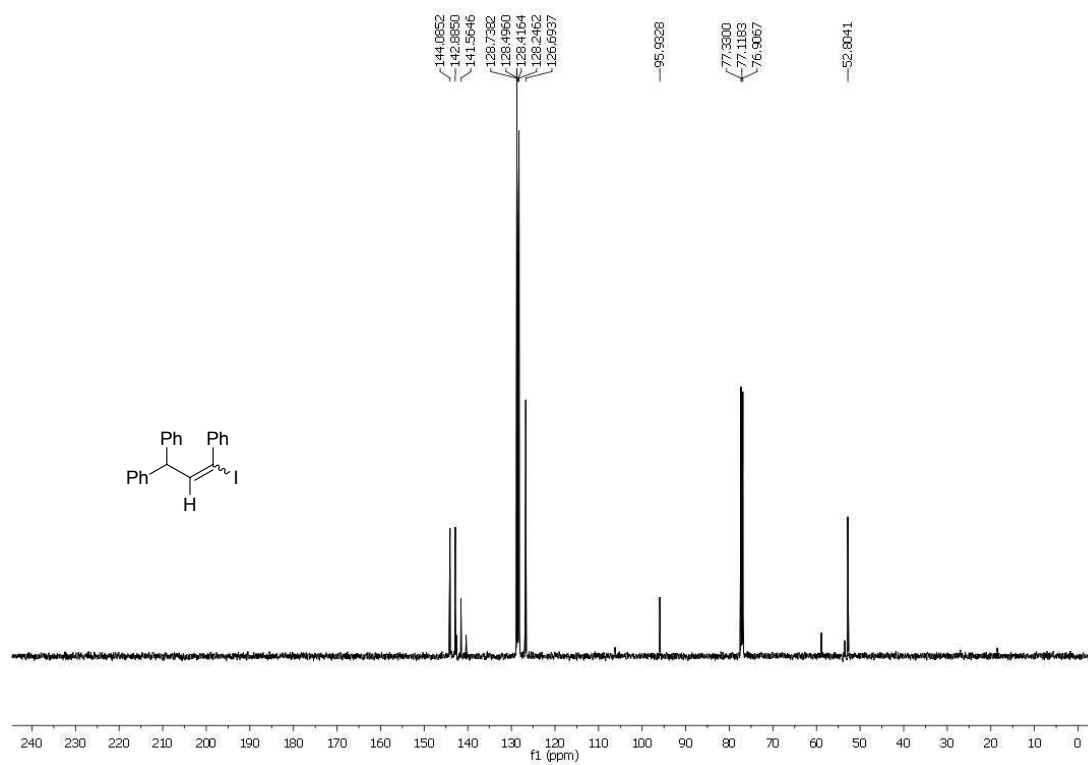
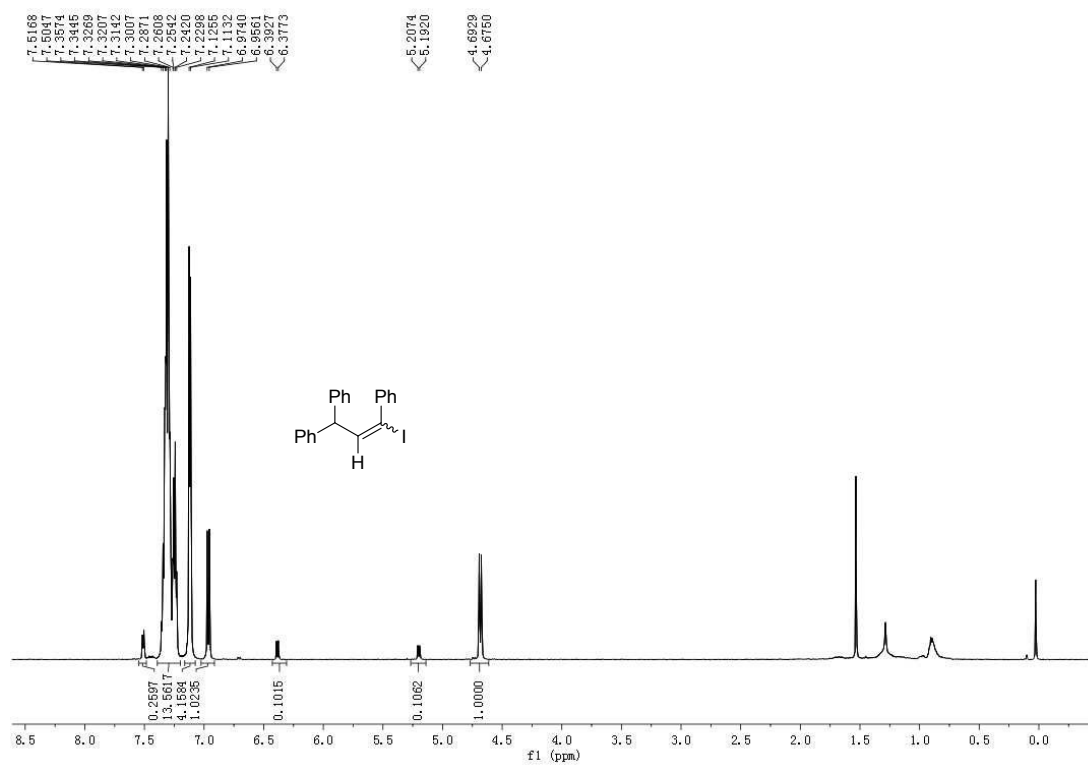
Fig. 1

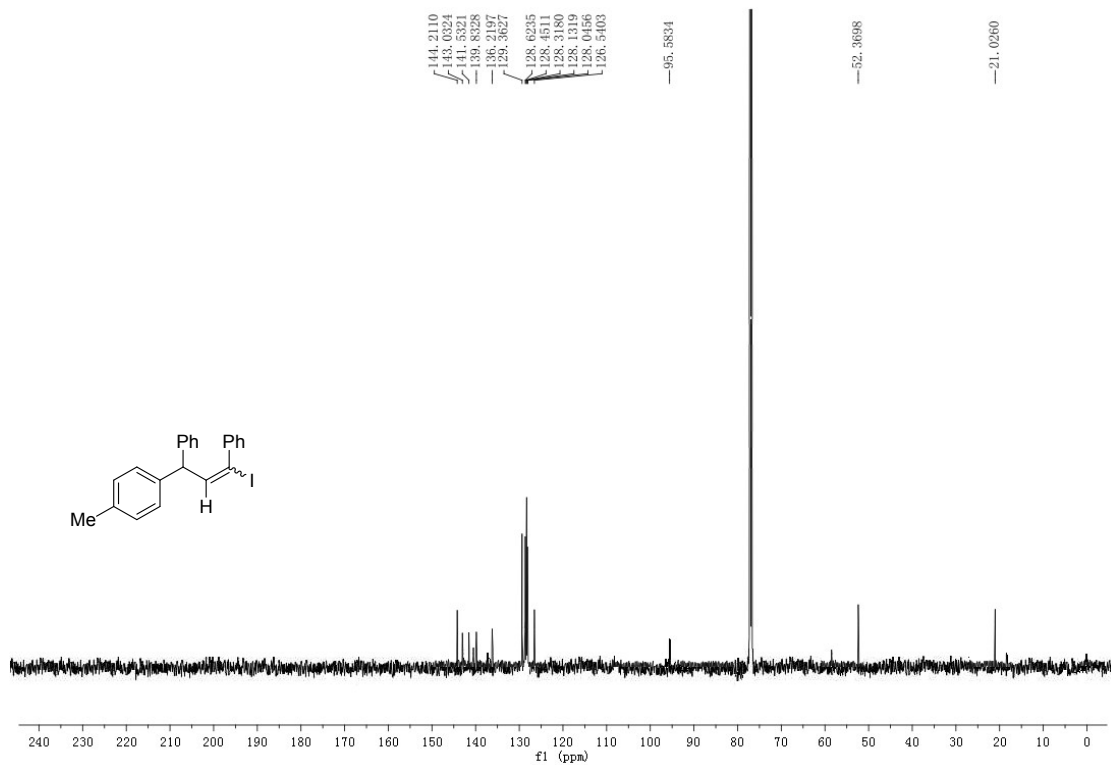
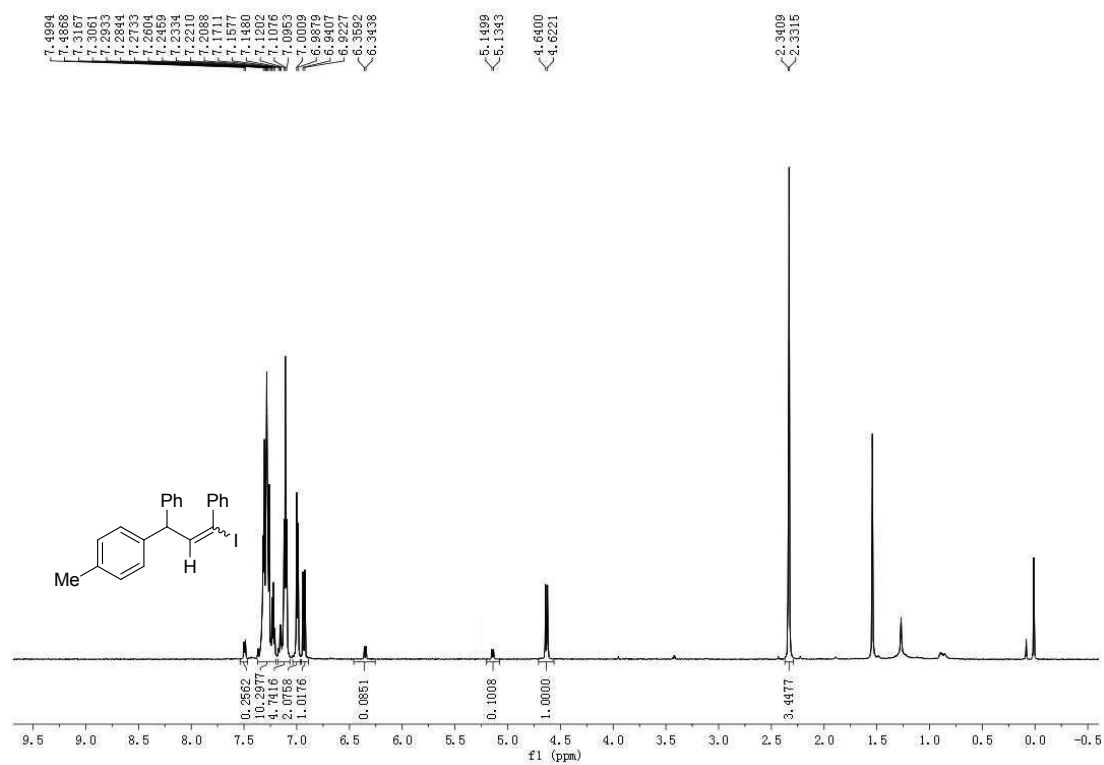
The configuration of alkenyl iodides (the products of the reactions of aromatic terminal alkynes with alcohols) can be readily determined using ¹H NMR since the coupling constants between vinyl protons and methine protons in the *E*-isomer and *Z*-isomer are quite different. Generally, the coupling constant in the *E*-isomer is near 10.6 Hz, while in the *Z*-isomer is near 9.2 Hz.¹⁻⁵

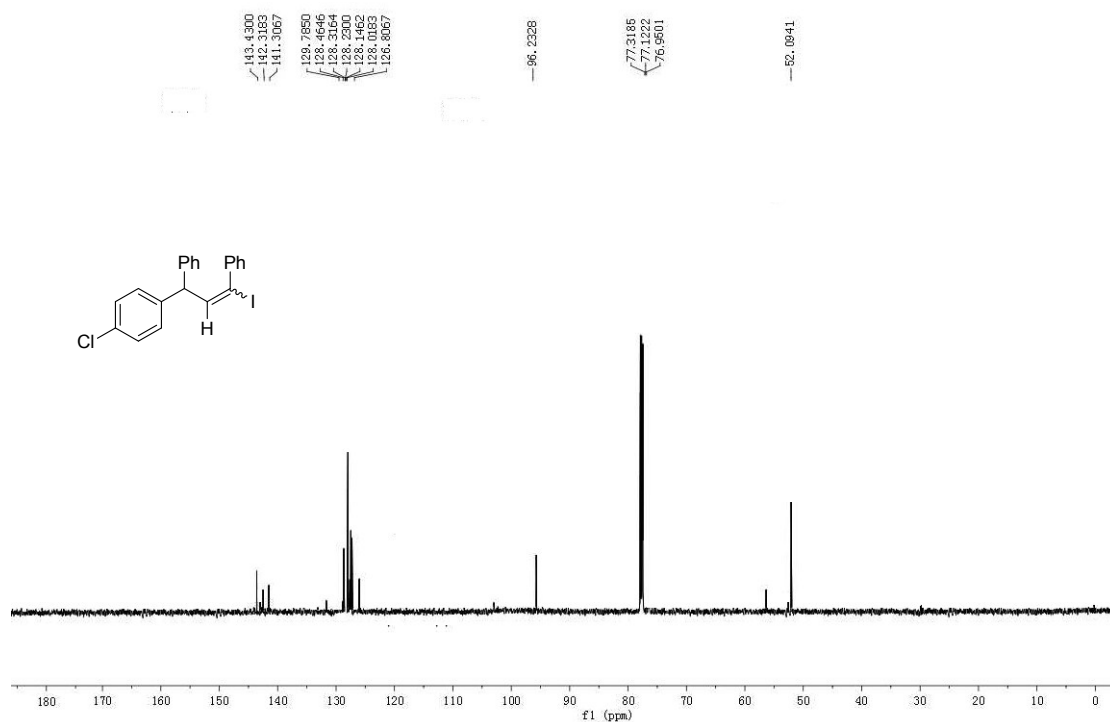
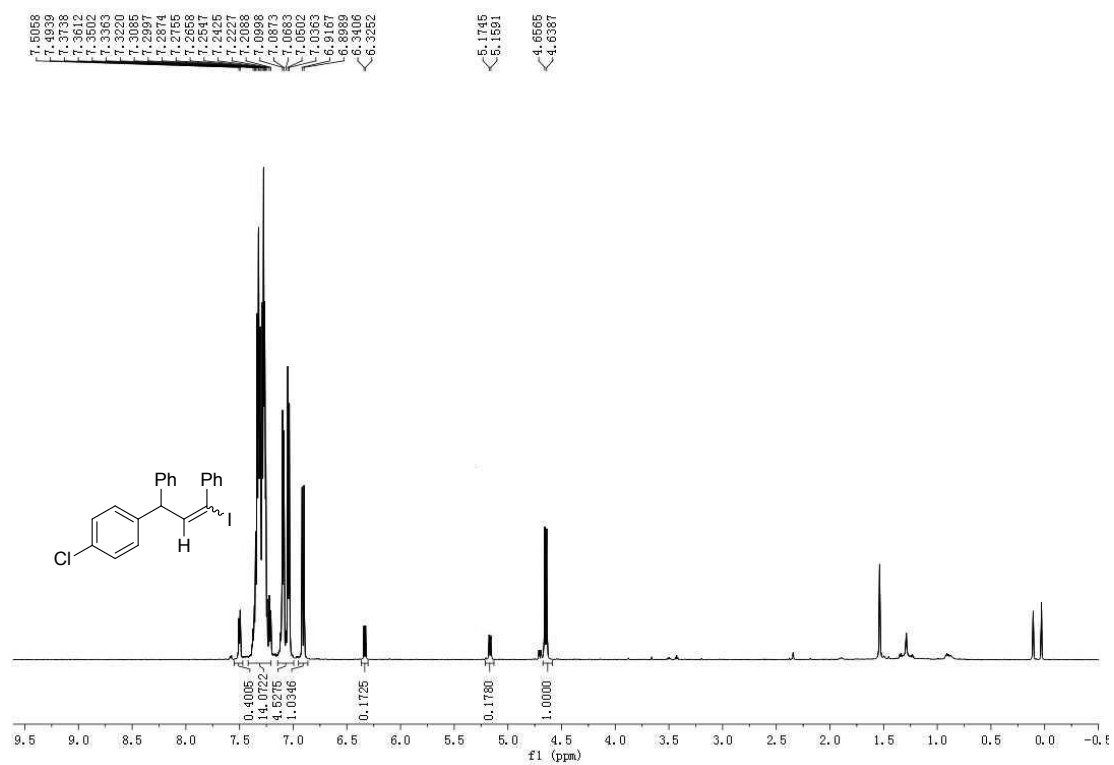
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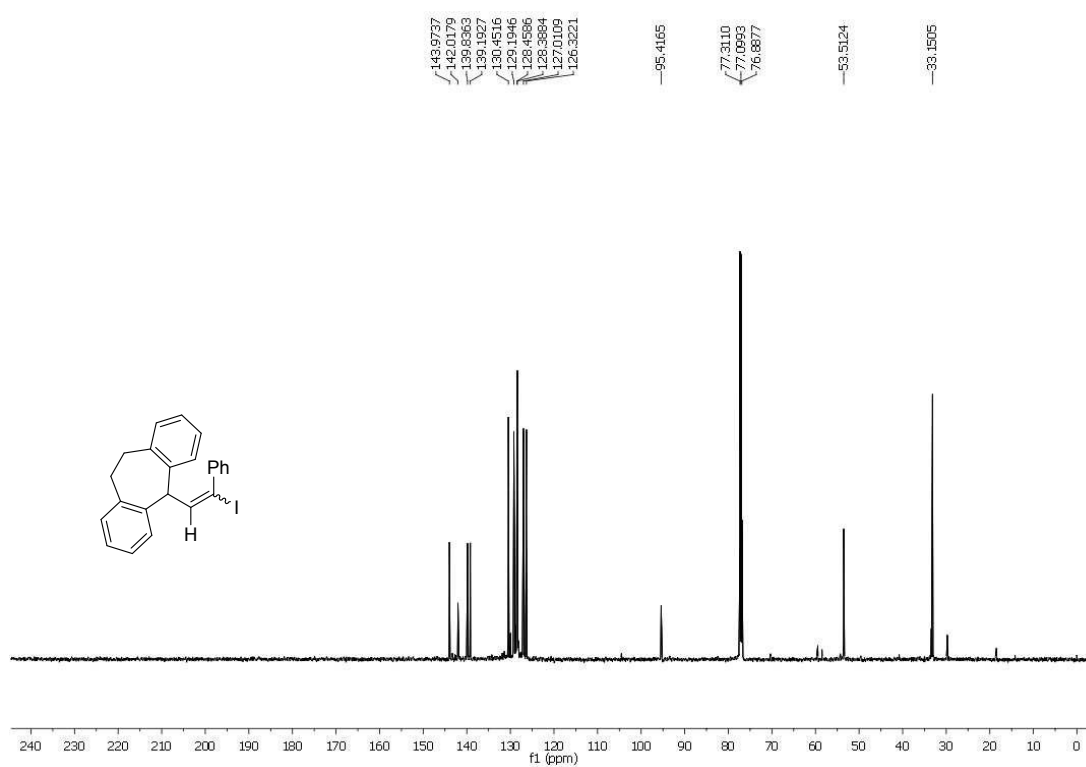
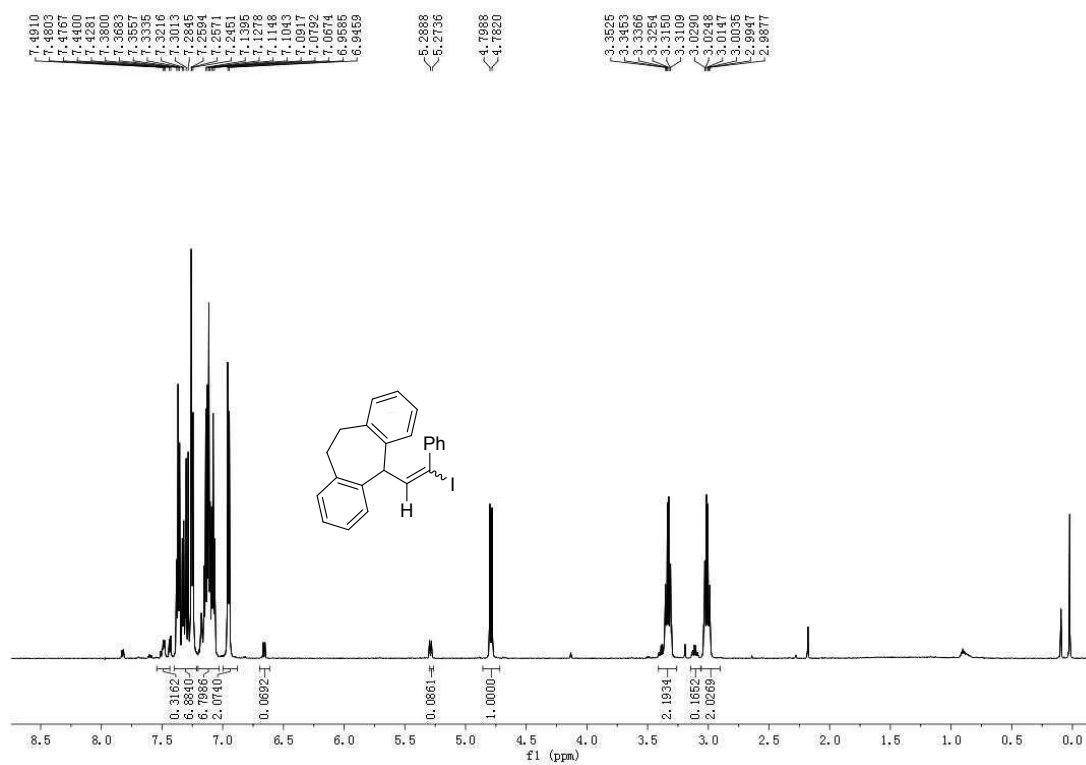
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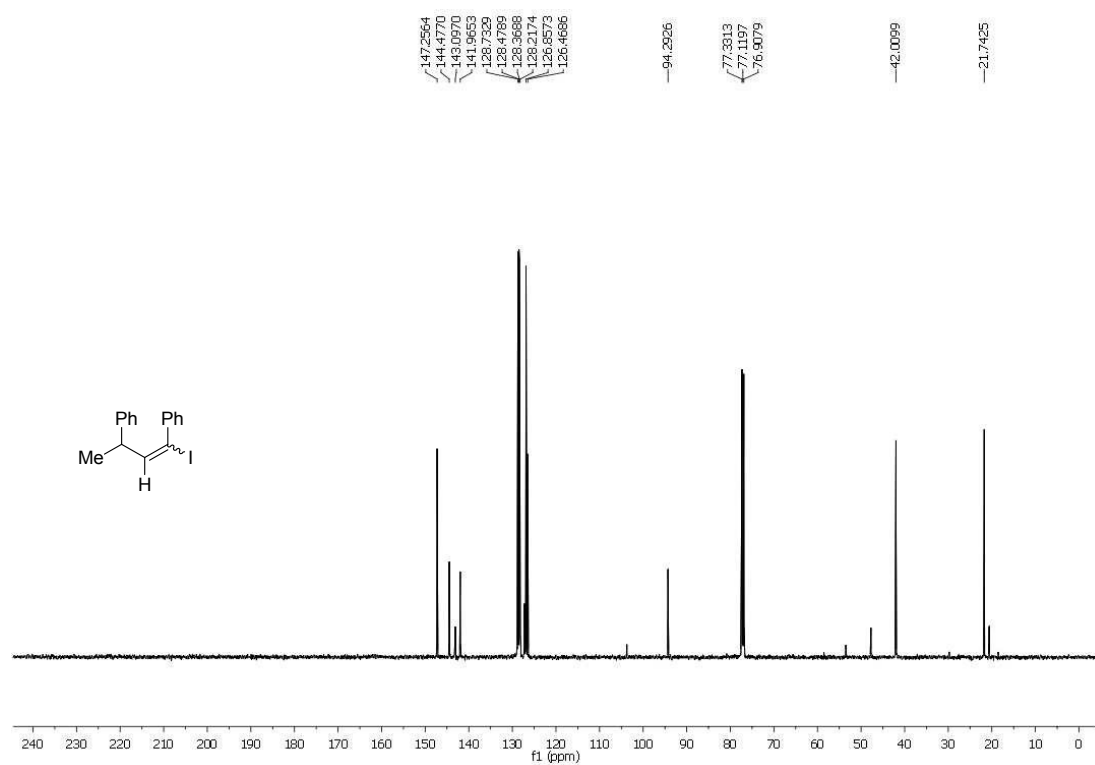
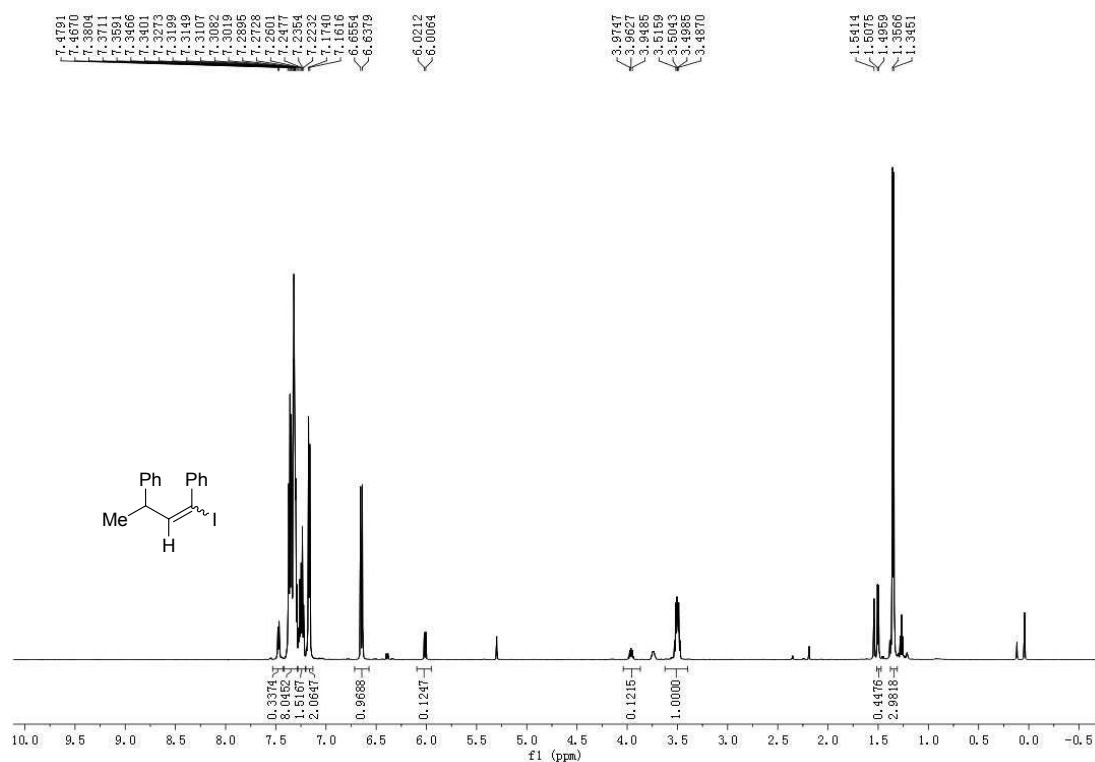
5. Copies of ^1H NMR and ^{13}C NMR Spectra for all the compounds

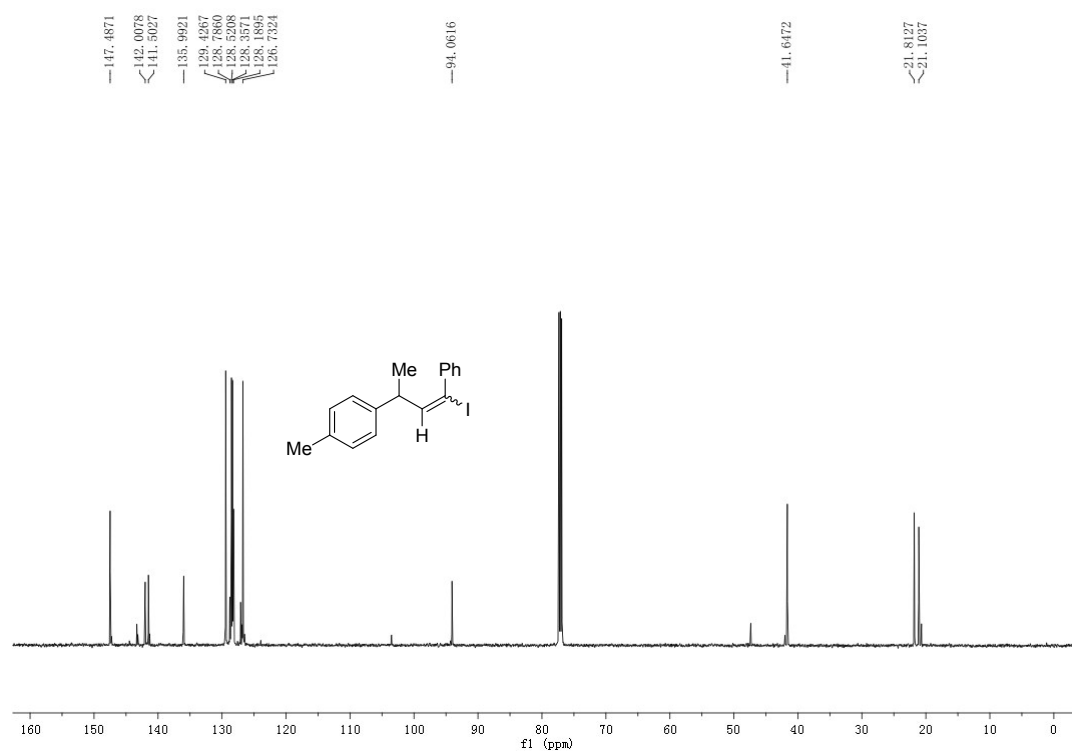
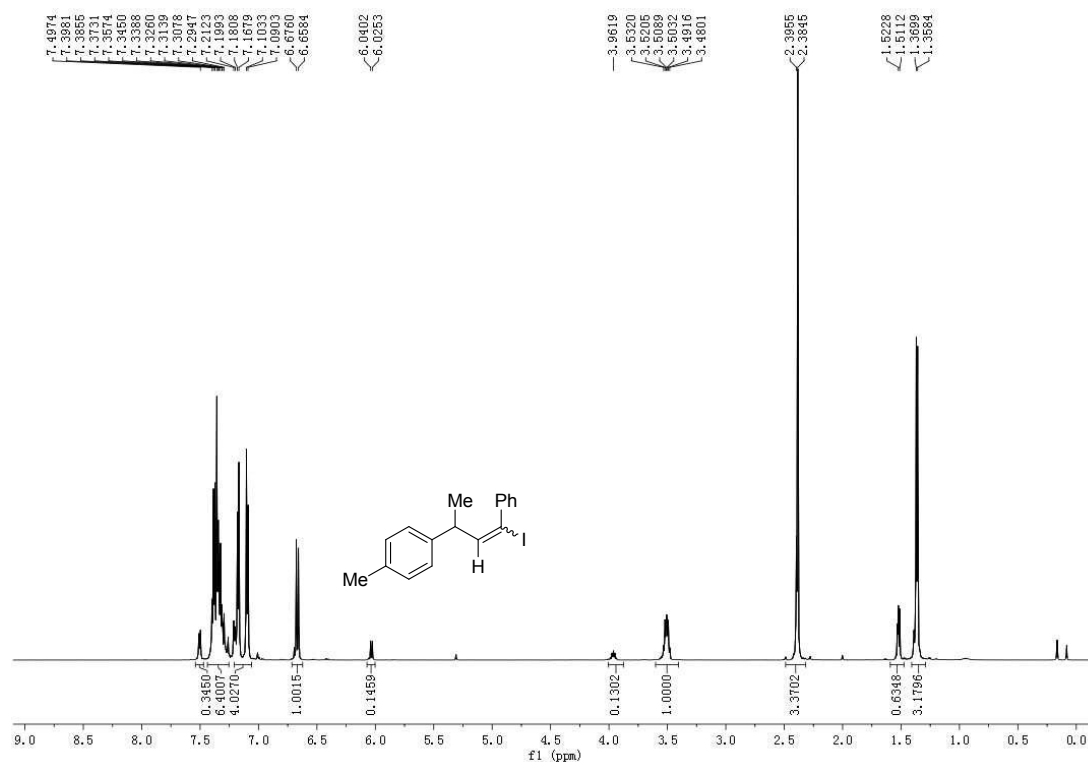


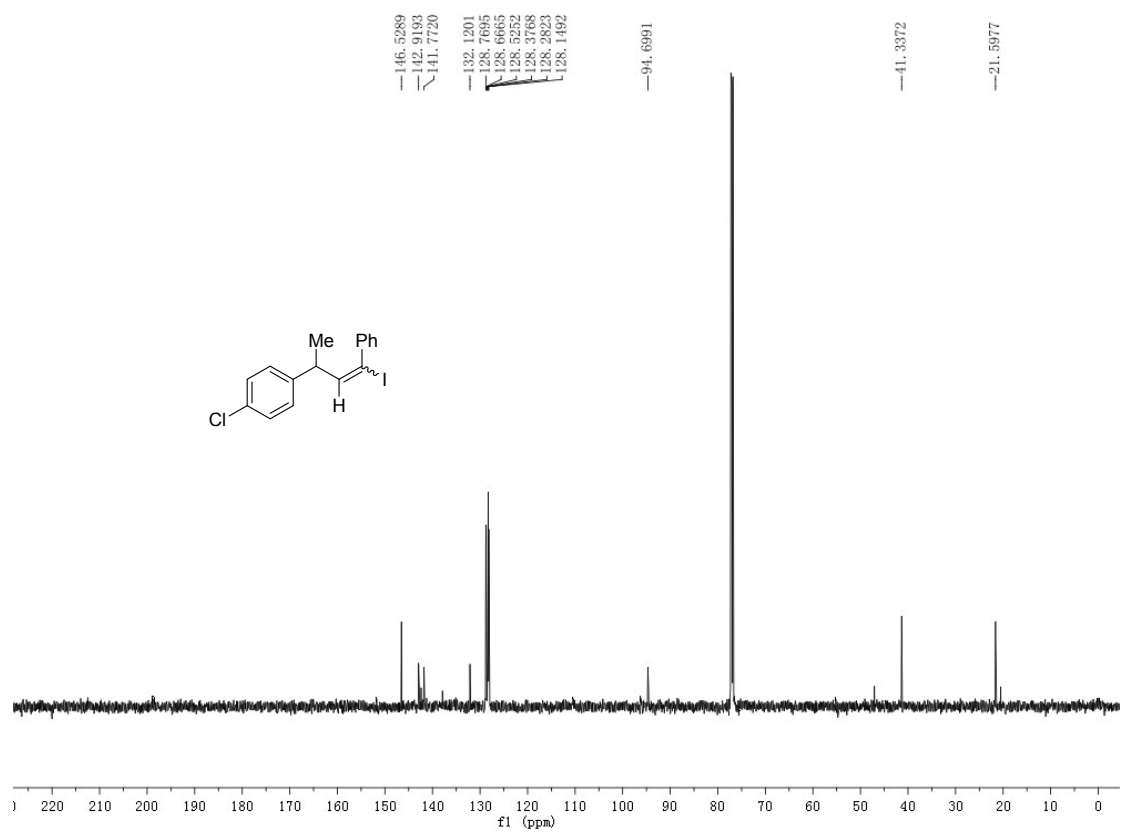
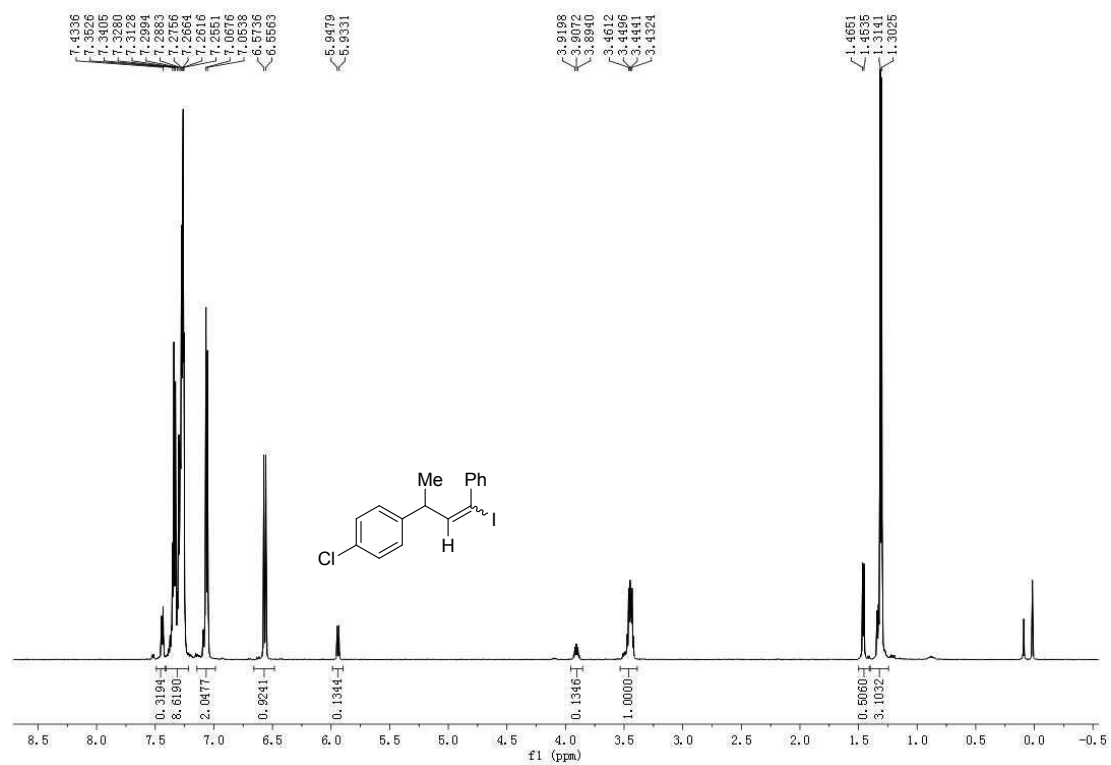


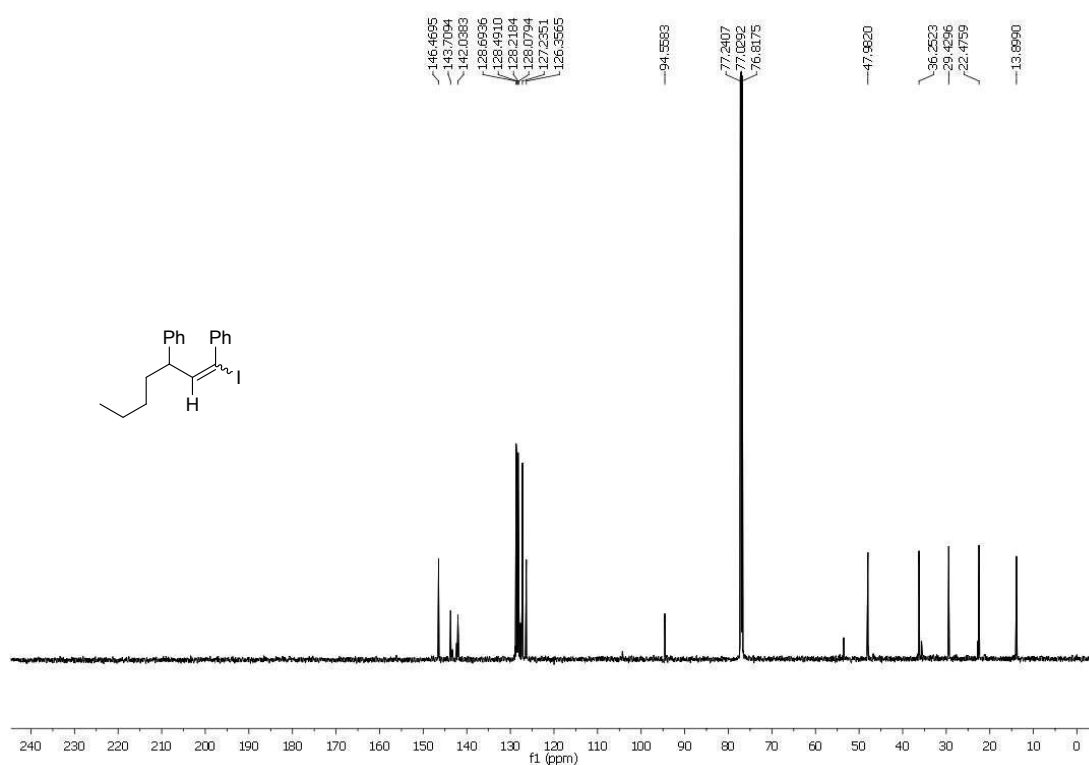
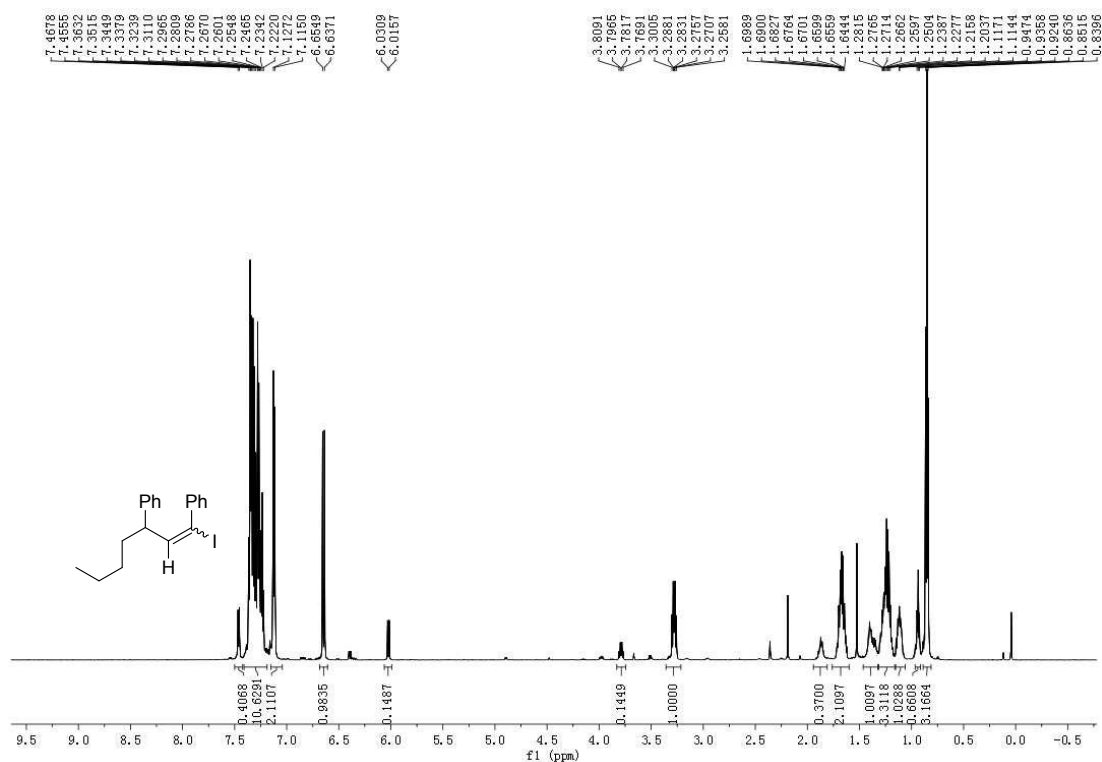


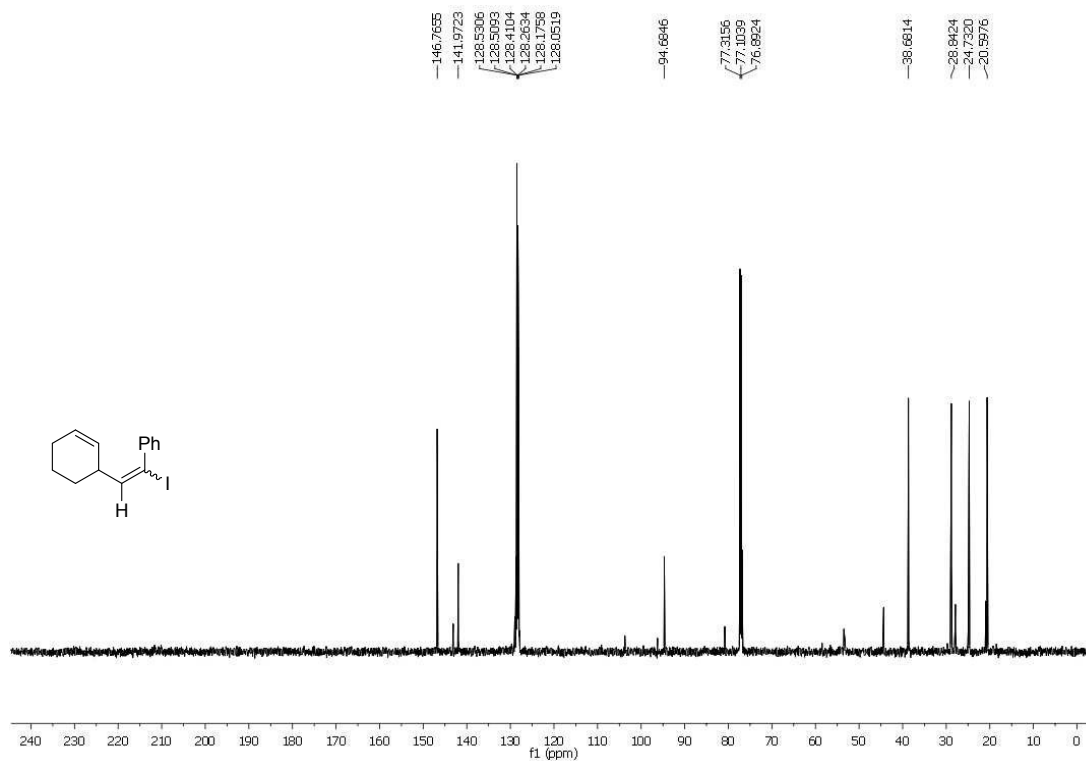
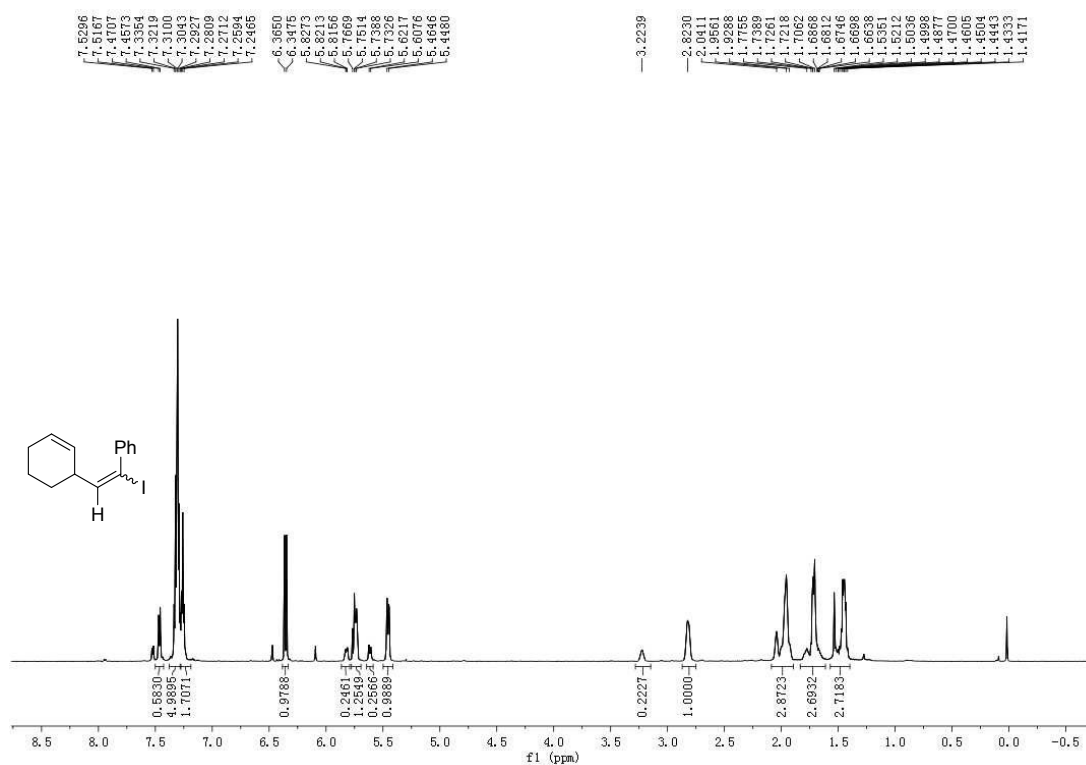


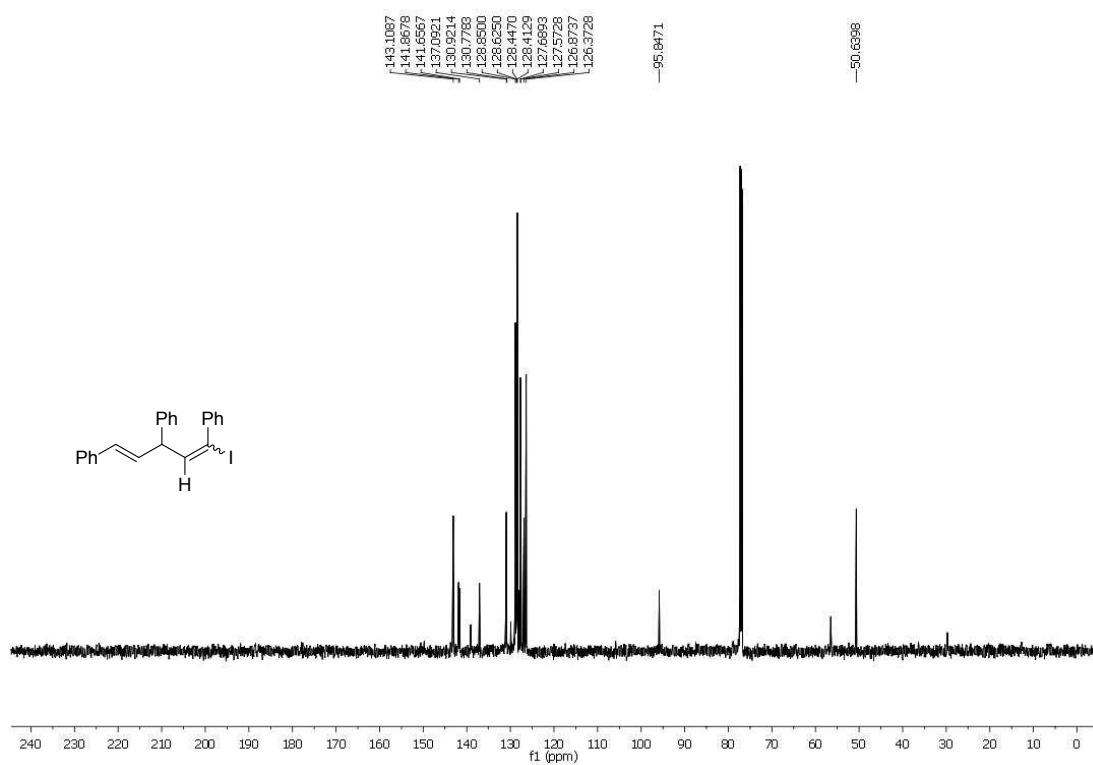
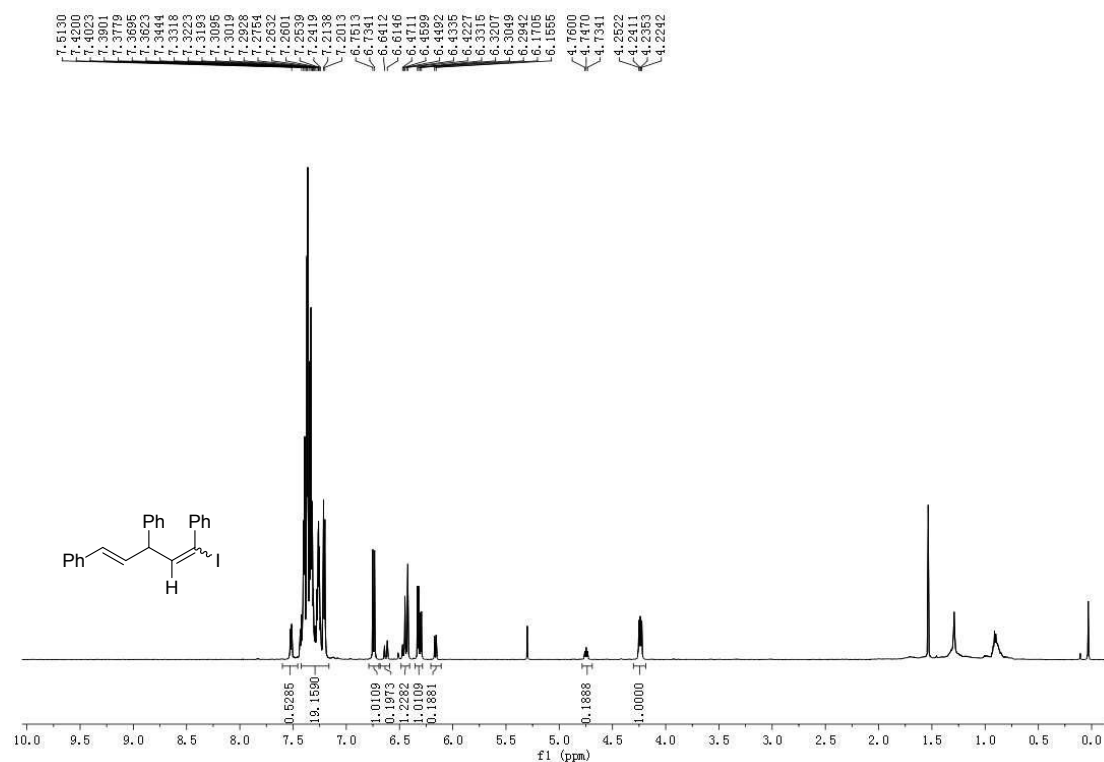


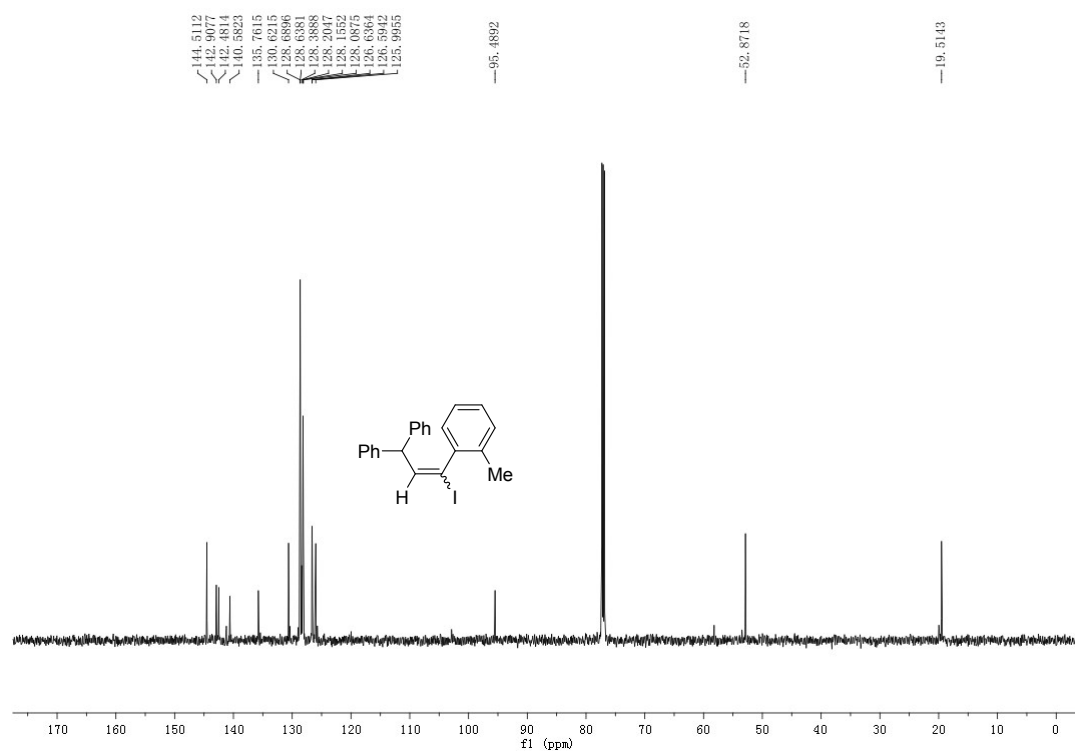
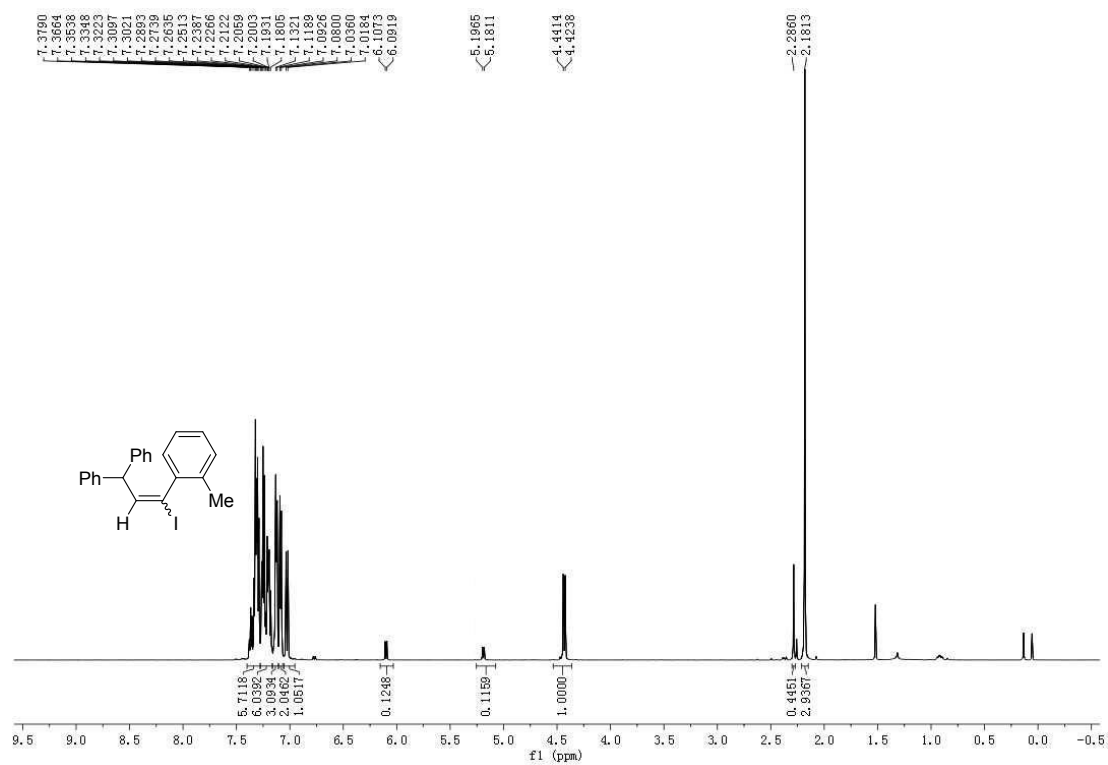


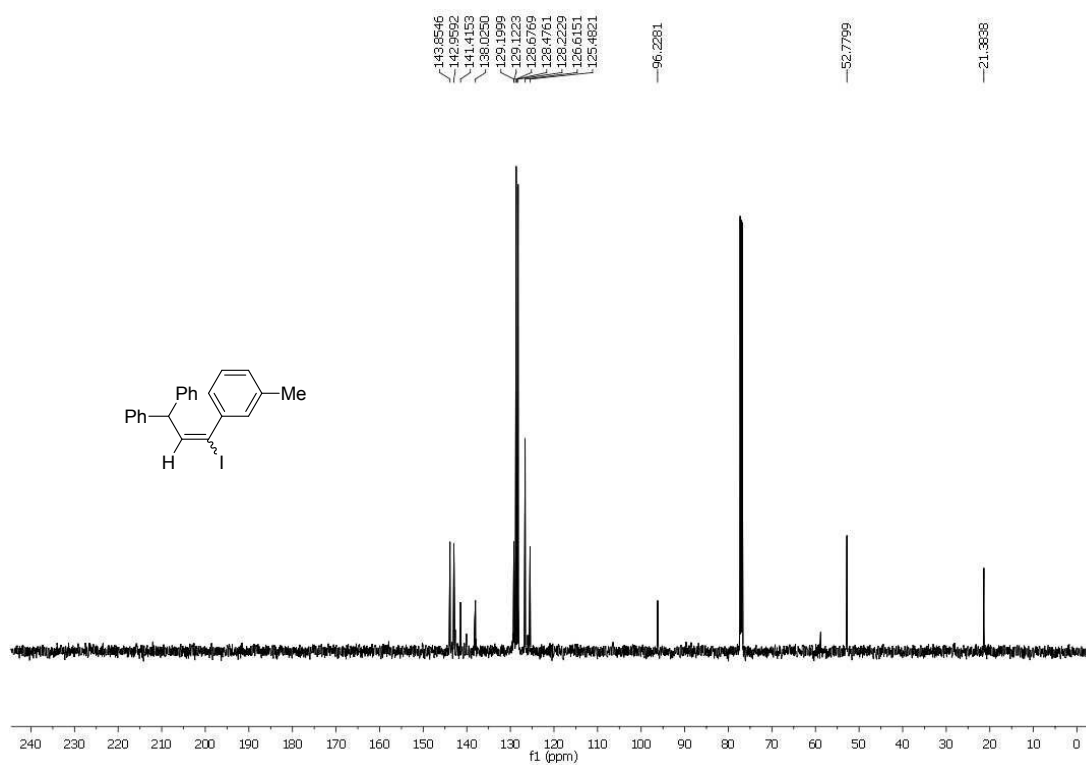
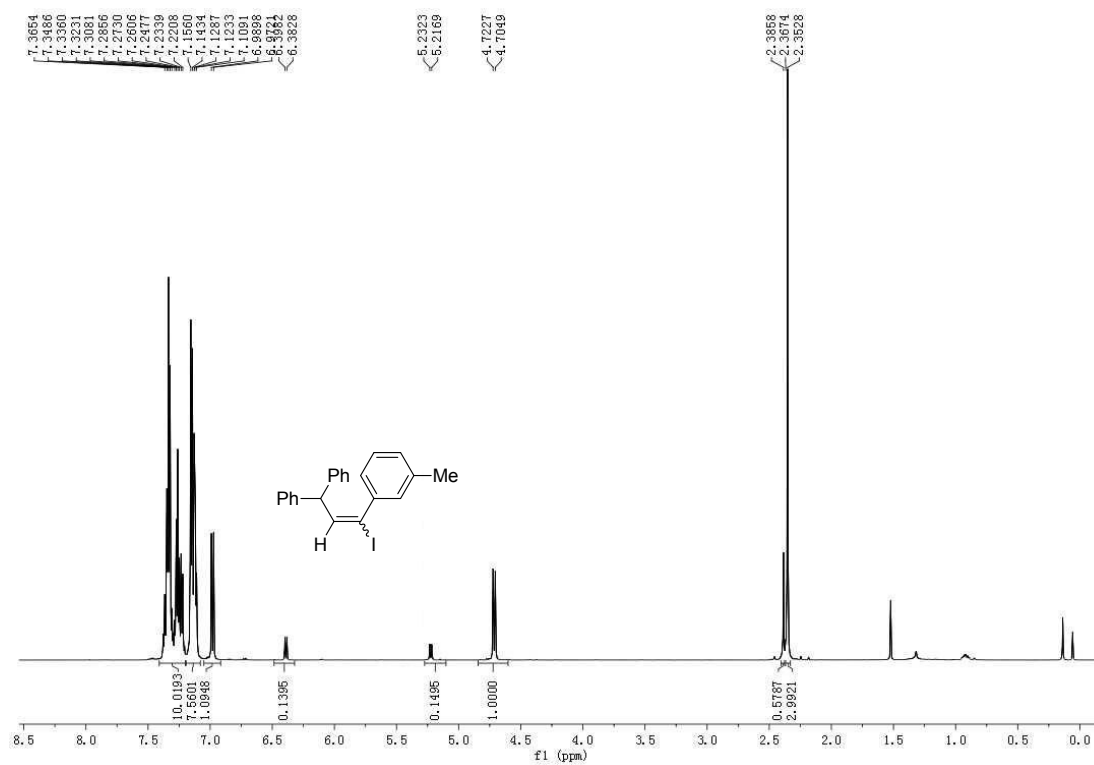


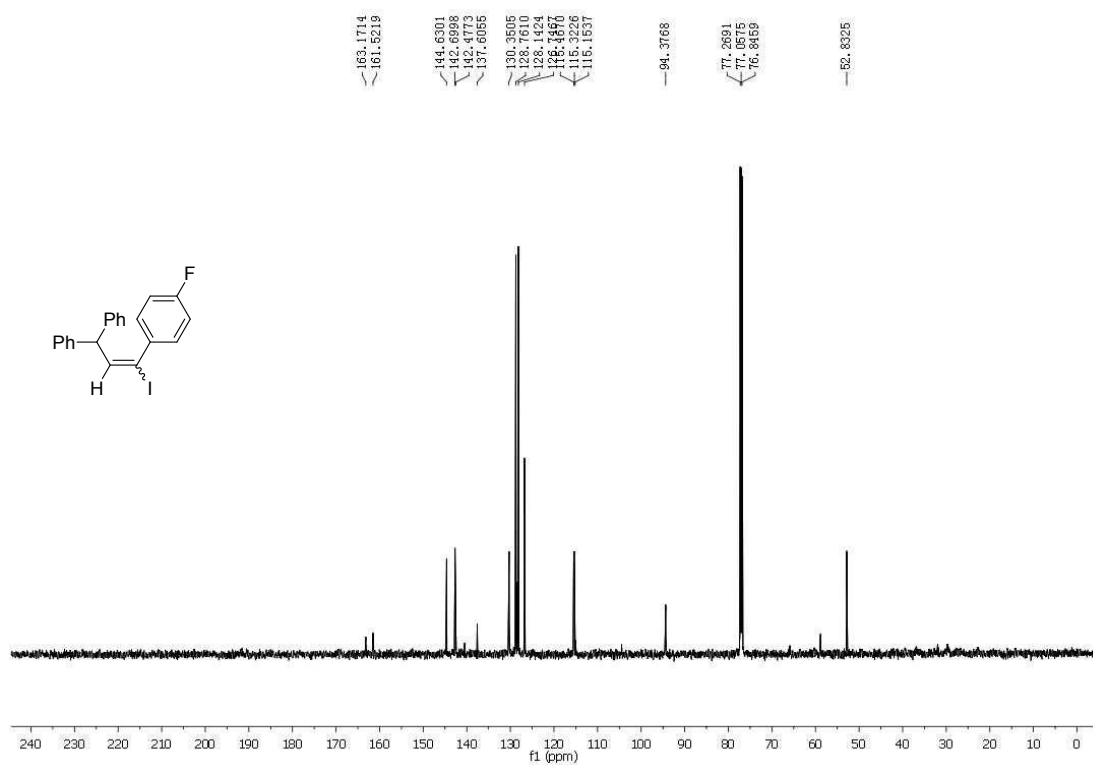
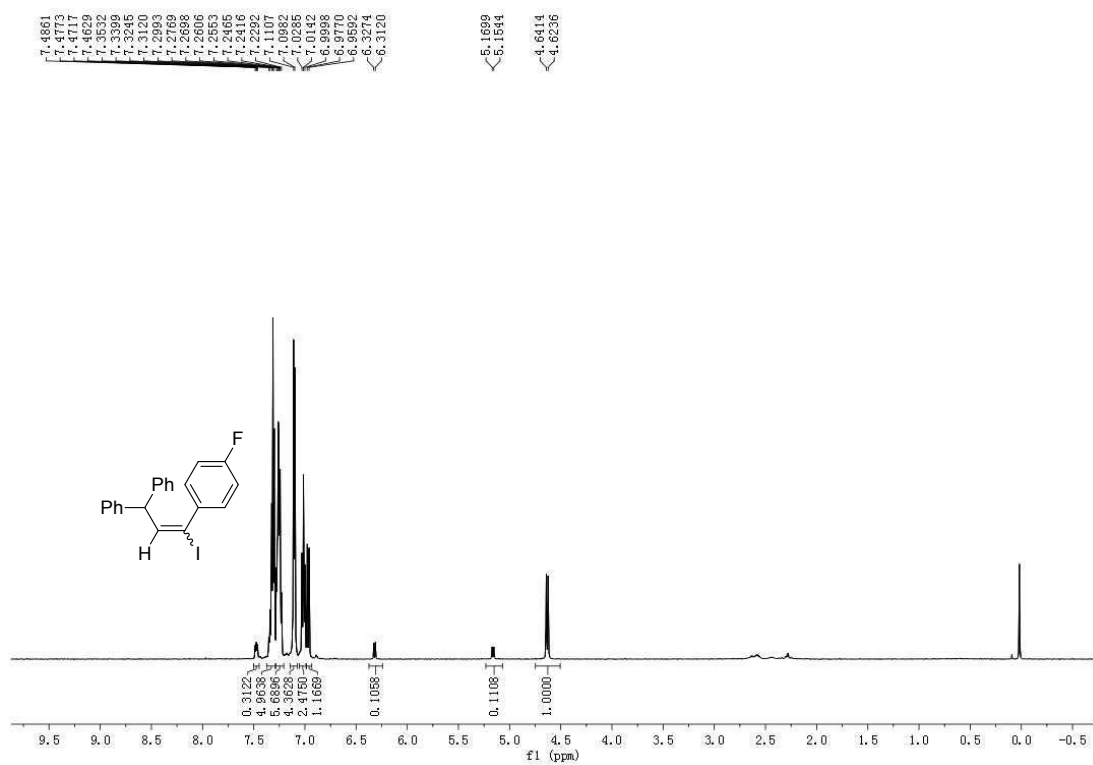


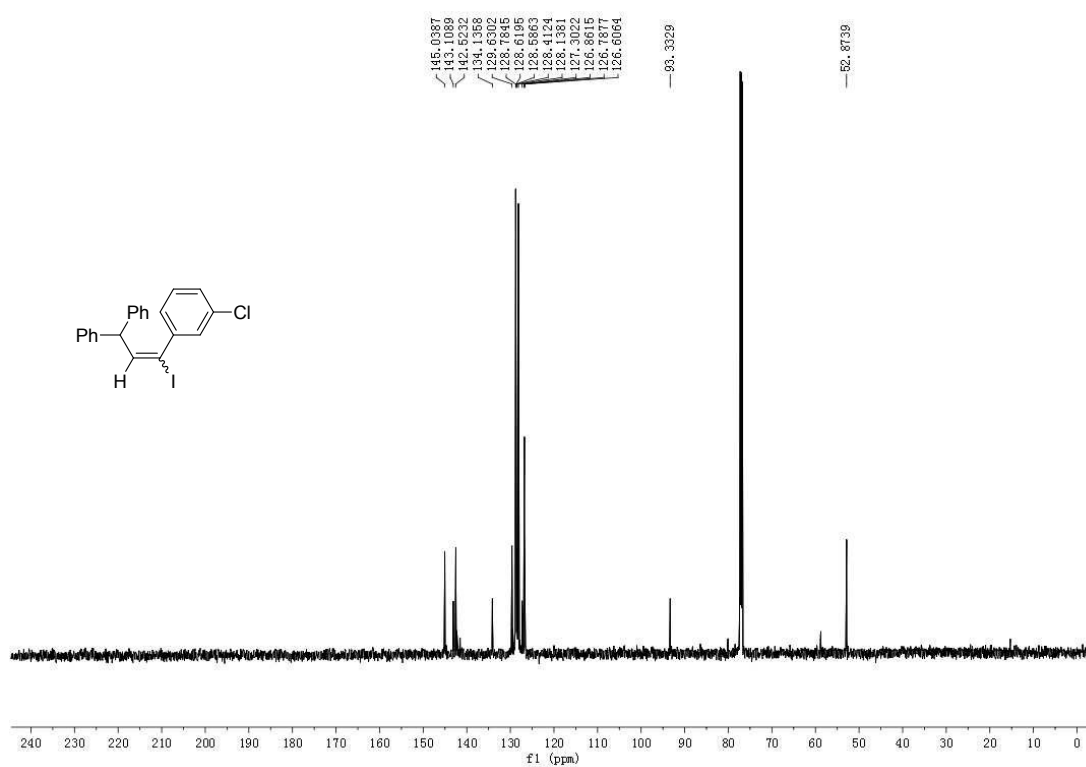
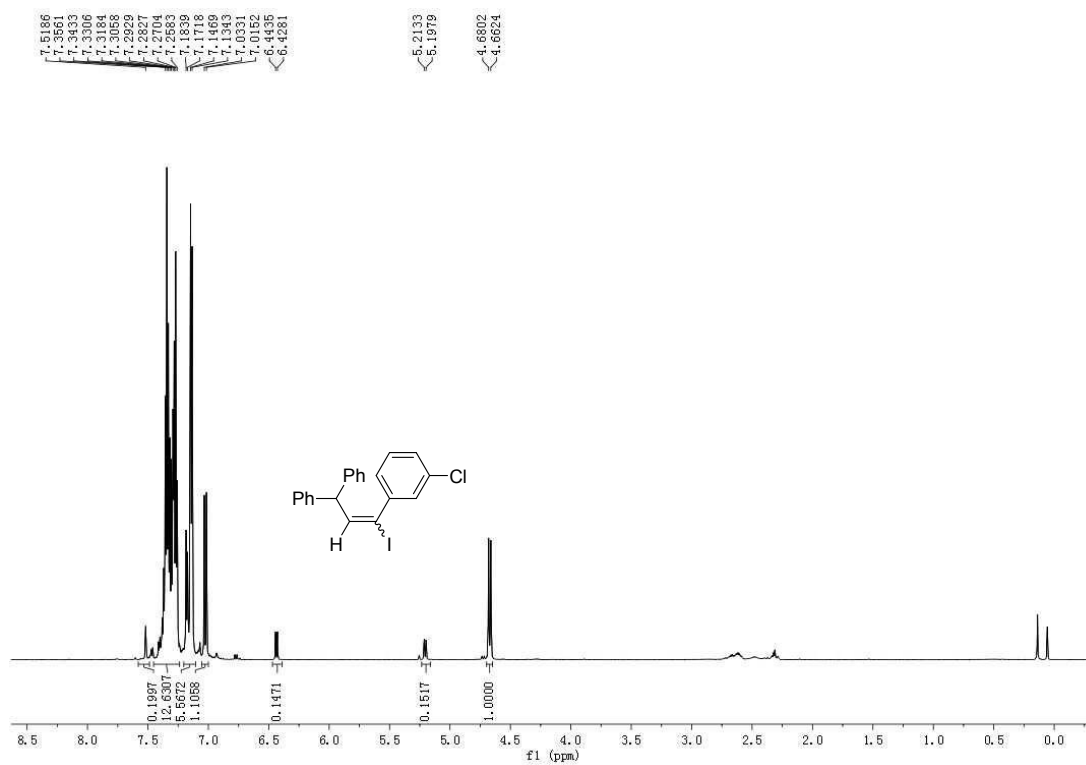


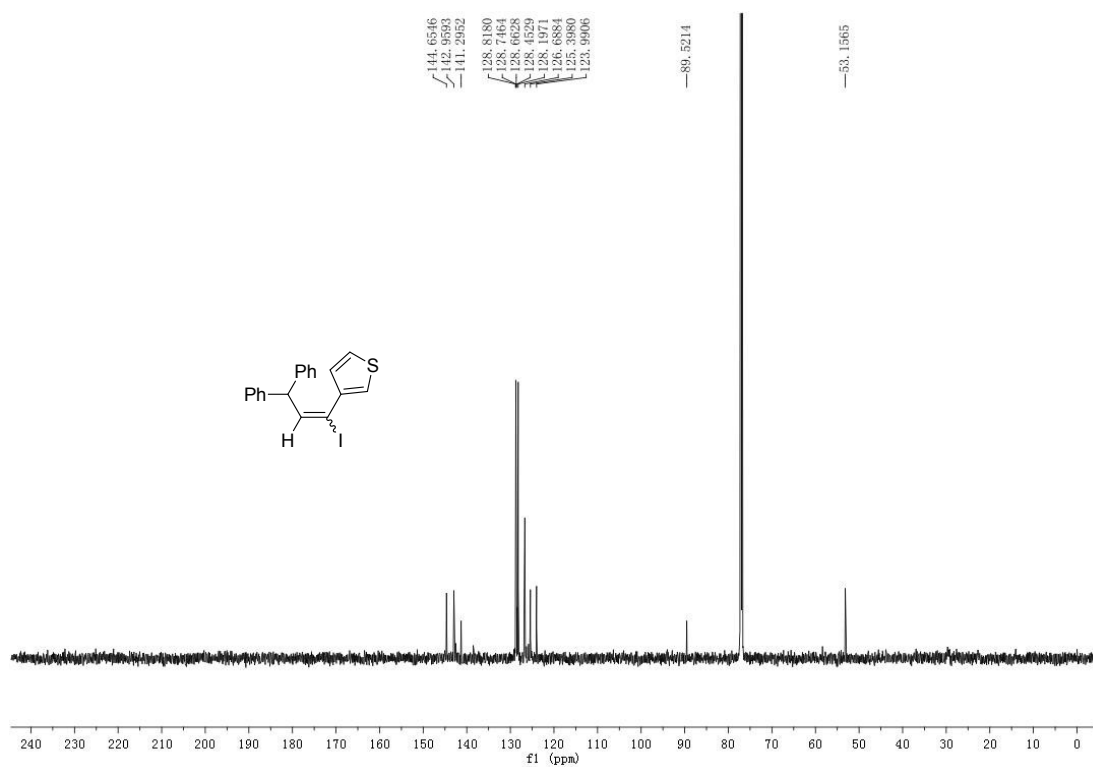
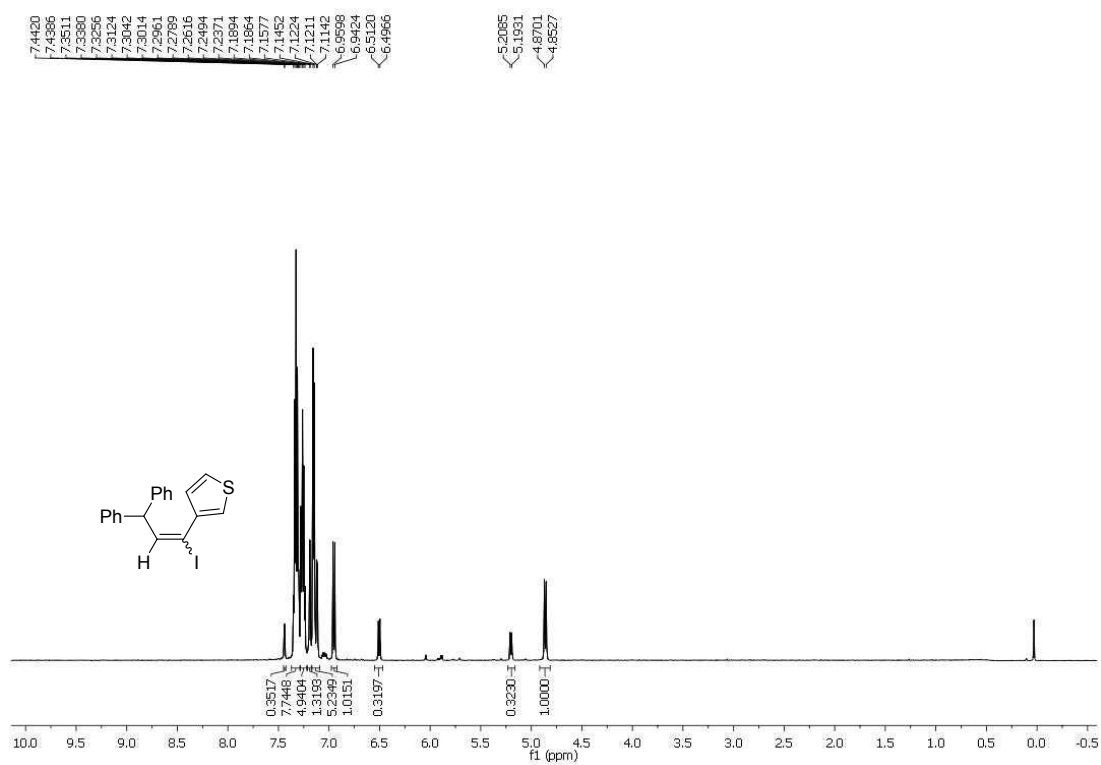


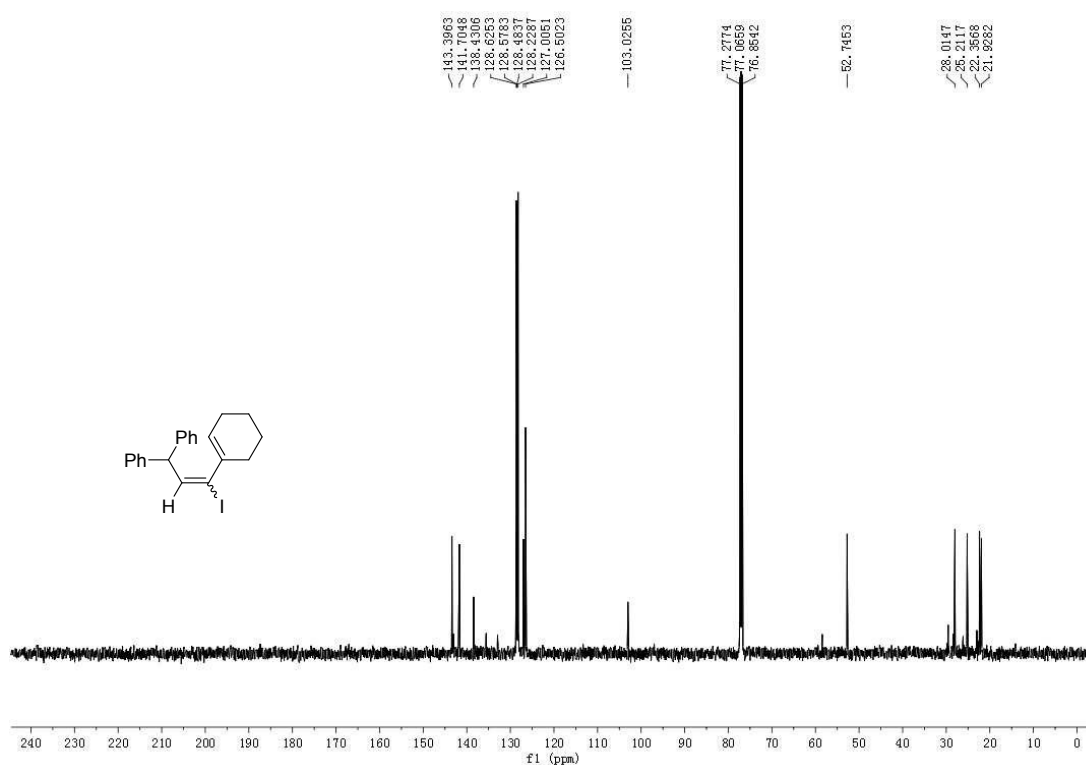
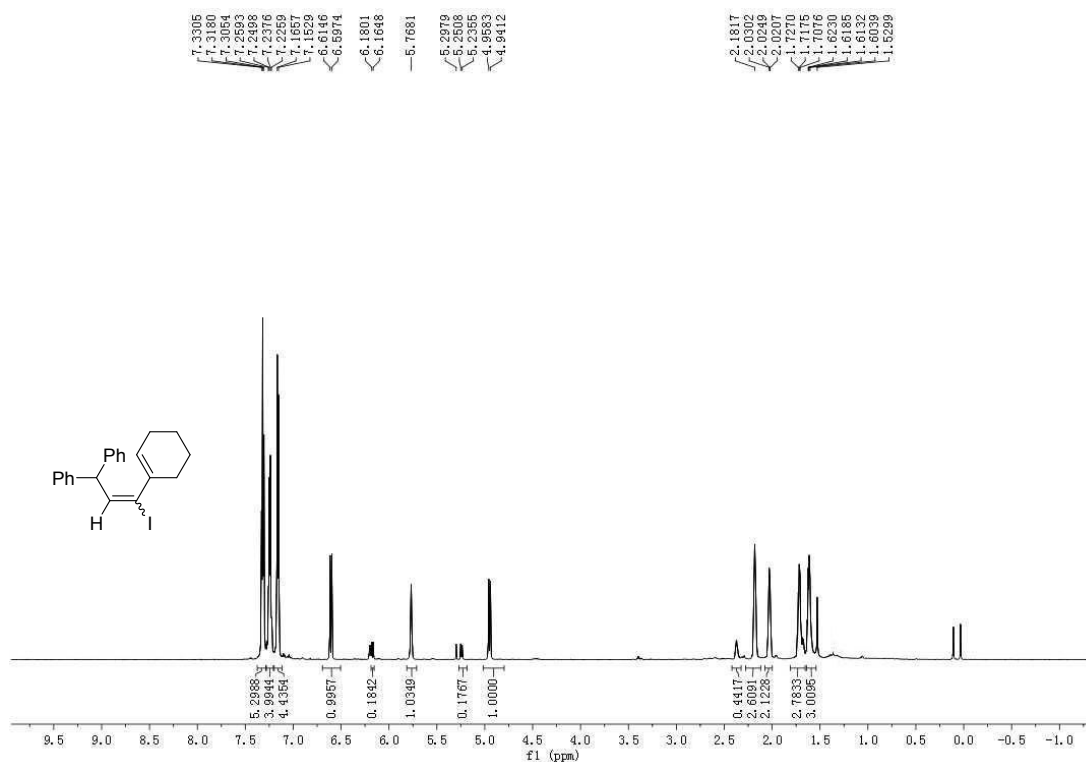


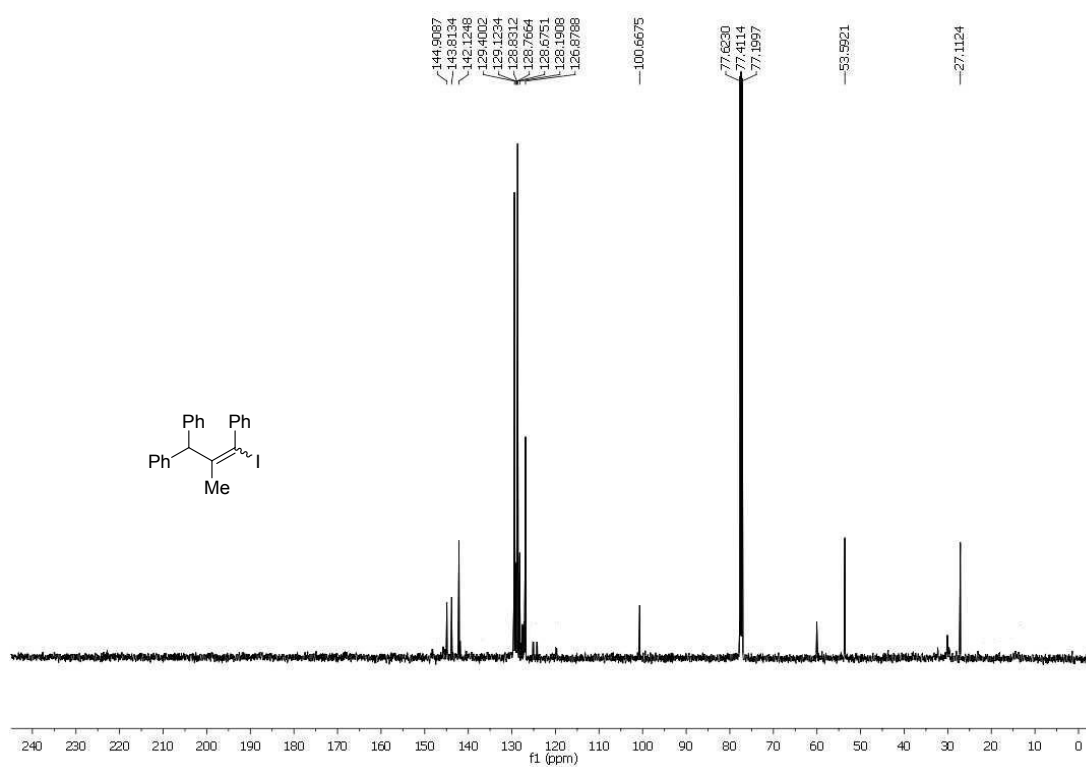
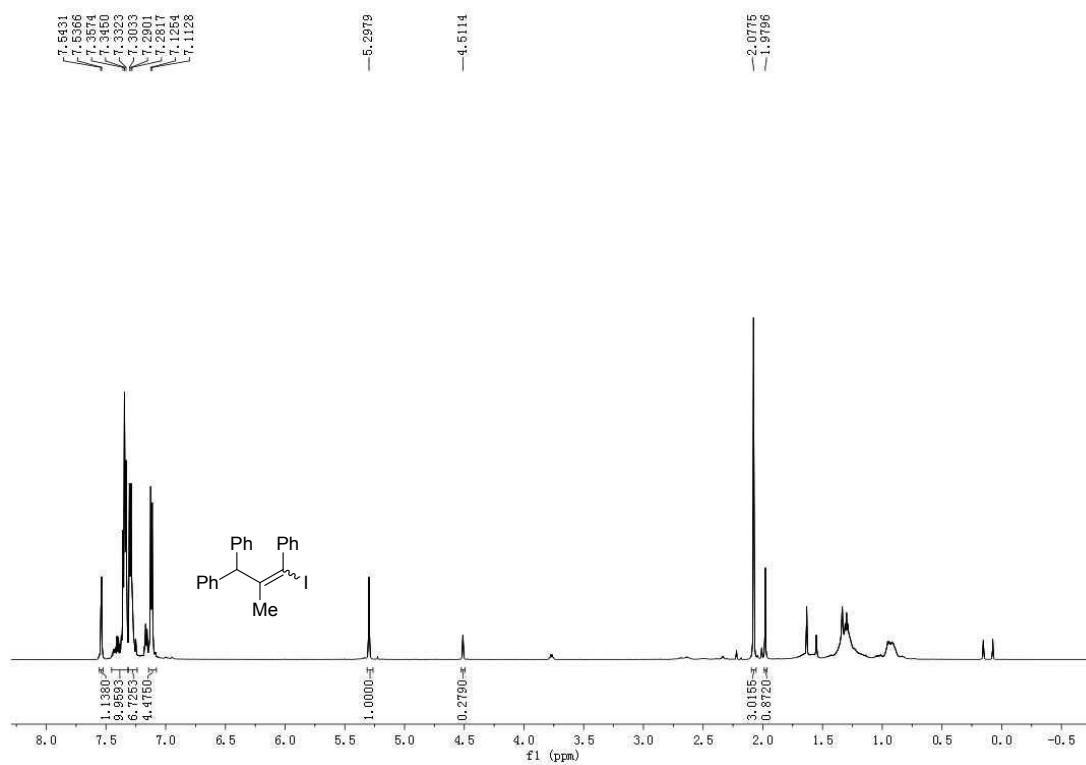


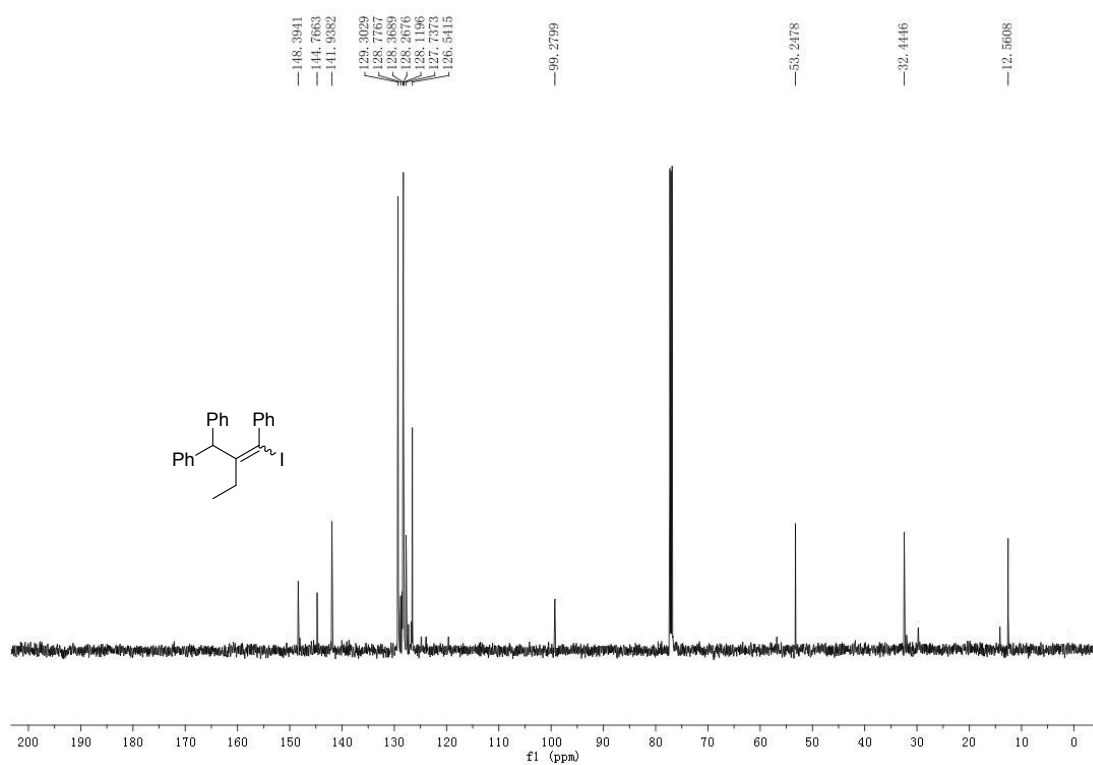
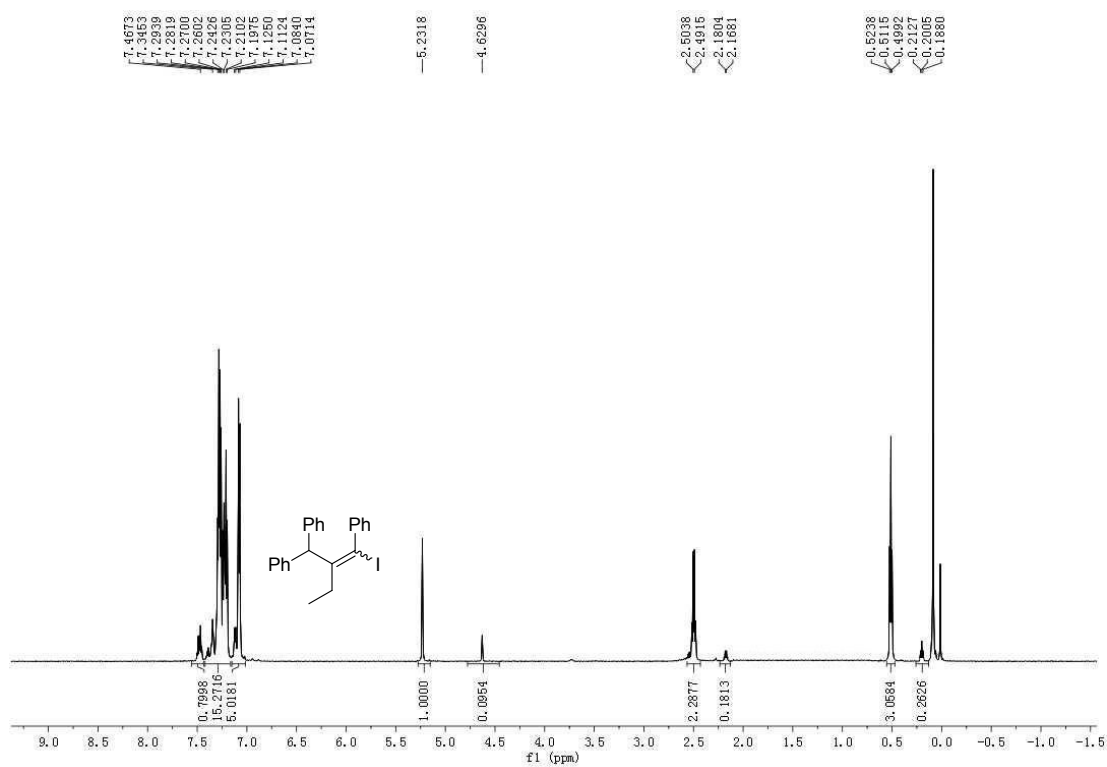












Copies of ¹H NMR and ¹³C NMR Spectra for the Intermediate 4a

