Supporting Information

Irradiation-Induced Heck Reaction of Unactivated Alkyl Halides at Room Temperature

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1. General Information

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity≥99.999%) unless otherwise mentioned. Commercial reagents were purchased from Adamas, TCI and Aldrich. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

^{1}H-NMR，^{19}F-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for ^{1}H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for ^{13}C- NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. ESI-mass data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software.

2. Preparation of Substrates

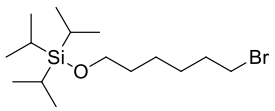
General Procedure A: **Bromination of Secondary Alcohols.** The alcohol (10 mmol) (neat or a solution in CH_2Cl_2) was added to a solution of Ph_3PBr_2 (1.2 equiv.) and imidazole (1.2 equiv.) in dry CH_2Cl_2 (0.2 M) at 0 °C. The reaction mixture was allowed to warm to r.t., and it was stirred overnight. Next, the solvent was removed on a rotary evaporator. The residue was diluted with hexanes/Et_2O (4:1), and the resulting solution was filtered and concentrated. The residue was purified by flash column chromatography with petroleum ether or petroleum ether/ethyl acetate.

General Procedure B: Bromination of Tertiary Alcohols. The alcohol (neat or a solution in a minimal amount of CH_2Cl_2) was added to a solution of LiBr (2.0 equiv.) in 48 wt% aqueous HBr at 0 °C. The reaction mixture was allowed to warm to r.t., and it was stirred for 3–12 h. Next, the reaction mixture was diluted with Et_2O, washed with water, saturated $NaHCO_3$, and brine, dried over Na_2SO_4, and

concentrated on a rotary evaporator. The residue was purified by flash column chromatography with petroleum ether or petroleum ether/ethyl acetate.

General Procedure C: Bromination of Tertiary Alcohols. PBr_3 (0.42 equiv.) was added dropwise to a solution of the tertiary alcohol and pyridine (0.42 equiv.) in anhydrous hexanes (0.5 M in alcohol) at 0 °C. After stirring at 0 °C for 2 h, the reaction mixture was allowed to warm to r.t., and it was stirred for an additional 3 h. Next, the reaction mixture was diluted with Et_2O, washed with water, saturated $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated on a rotary evaporator. The residue was purified by flash column chromatography with petroleum ether or petroleum ether/ethyl acetate.

General Procedure D for the Preparation of Styrenes. Ph_3PMeBr (4.29 g, 12.0 mmol, 1.20 equiv.) was added to an oven-dried transparent Schlenk tube (100 mL) equipped with a stirring bar. The tube was evacuated and filled with argon (three times). Anhydrous Tetrahydrofuran (40.0 mL) was added to the tube under the argon atmosphere, and then ^{n}BuLi (2.5 M, 4.8 mL, 12.0 mmol, 1.20 equiv.) was added dropwise to a solution at 0 °C. The mixture was stirred at 0 °C for 15 min, after which, a solution of a aldehyde (10 mmol, 1.0 equiv.) was added at 0 °C. The reaction mixture was stirred at r.t. for 48 h. The resulting solution was quenched with aq. NH_4Cl and the mixture was extracted with ethyl acetate (3 x 40 mL). The combined organic phases were dried over $MgSO_4$, concentrated in vacuo, and the residue was purified by column chromatography on silica gel to give styrene.

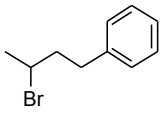


((6-bromohexyl)oxy)triisopropylsilane (S-1): 6-bromohexan-1-ol (10 mmol) was added to a solution of triisopropylsilyl chloride (20 mmol) and imidazole (1.2 equiv.) in dry CH_2Cl_2 (0.2 M) at room temperature and then stirred overnight. Next, the reaction mixture was diluted with Et_2O, washed with water, saturated $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated on a rotary evaporator. The residue was purified by flash column chromatography with petroleum ether. (Colorless liquid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (t, *J* = 6.4 Hz, 2H), 3.41 (t, *J* = 6.8 Hz, 2H), 1.87 (dt, *J* = 6.9 Hz, 2H), 1.61 – 1.51 (m, 2H), 1.48 – 1.37 (m, 4H), 1.08 – 1.05 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) 63.2, 33.9, 32.8, 28.1, 26.9, 25.1, 18.0, 12.0.

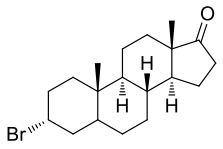
HRMS (ESI) Calcd for $C_{15}H_{34}BrSiO^+$ $[M+H]^+$: 337.1557, found: 337.1545.



(3-bromobutyl)benzene (S-2): The bromide was prepared according to General Procedure A from the corresponding alcohol, *4-phenylbutan-2-ol*. The product was purified by flash column chromatography on silica gel (eluent: petroleum ether). (Colorless liquid) (Ref: *Nature Chem*. **2011**, *2*, 140–145)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.08 (m, 5H), 4.18 – 3.95 (m, 1H), 2.95 – 2.66 (m, 2H), 2.23 – 1.95 (m, 2H), 1.82 – 1.62 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 128.5, 128.4, 126.0, 50.8, 42.6, 33.9, 26.5.

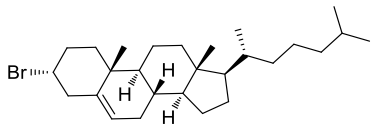


(3R,8R,9S,10S,13S,14S)-3-bromo-10,13-dimethyltetradecahydro-1H-cyclopenta [a]phenanthren-17(2H)-one (S-3): The bromide was prepared according to General Procedure A from the corresponding alcohol, *(3S,8R,9S,10S,13S,14S)-3-hydroxy -10,13-dimethyltetradecahydro-1H-cyclopenta[a]phenanthren-17(2H)-one*. The product was purified by flash column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20 : 1). (White solid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03 (tt, *J* = 12.0, 4.8 Hz, 1H), 2.44 (dd, *J* = 19.3, 8.7 Hz, 1H), 2.17 – 1.87 (m, 5H), 1.86 – 1.70 (m, 4H), 1.65 – 1.45 (m, 3H), 1.36 – 1.15 (m, 6H), 1.12 – 0.94 (m, 2H), 0.88 – 0.86 (m, 6H), 0.70 (td, *J* = 11.7, 4.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.2, 54.3, 52.2, 51.3, 47.9, 47.7, 40.4, 39.7, 35.8, 35.5, 34.9, 34.0, 31.5, 30.7, 28.1, 21.7, 20.3, 13.8, 12.3.

HRMS (ESI) Calcd for $C_{19}H_{30}BrO^+$ $[M+H]^+$: 353.1475, found: 353.1469.

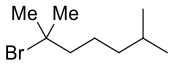


(3R,8S,9S,10R,13R,14S,17R)-3-bromo-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (S-4): The bromide was prepared according to General Procedure A from the corresponding alcohol, *(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol*. The product purified by flash column chromatography on silica gel (eluent: petroleum ether). (White solid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 – 5.27 (m, 1H), 3.96 – 3.88 (m, 1H), 2.91 – 2.48 (m, 2H), 2.23 – 2.12 (m, 1H), 2.08 – 1.93 (m, 3H), 1.88 – 1.82 (m 2H), 1.60 – 1.27 (m, 11H), 1.19 – 1.01 (m, 11H), 0.93 – 0.85 (m, 10H), 0.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 122.3, 56.7, 56.1, 52.7, 50.1, 44.3, 42.3, 40.3, 39.7, 39.5, 36.4, 36.2, 35.8, 34.3, 31.8, 31.7, 28.2, 28.0, 24.3, 23.8, 22.8, 22.6, 20.9, 19.2, 18.7, 11.8.

HRMS (ESI) Calcd for $C_{27}H_{46}BrO^+$ $[M+H]^+$: 449.2777, found: 449.2588

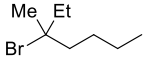


2-bromo-2,6-dimethylheptane (S-5): The bromide was prepared according to General Procedure B from the corresponding alcohol, *2,6-dimethylheptan-2-ol*. The product was purified by flash column chromatography on silica gel (eluent: petroleum ether). (Colorless liquid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 – 1.73 (m, 8H), 1.62 – 1.44 (m, 3H), 1.20 (dd, J = 15.5, 7.0 Hz, 2H), 0.89 (d, J = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 68.6, 47.7, 38.8, 34.3, 27.8, 24.1, 22.6.

HRMS (EI) Calcd for $C_9H_{19}Br^+$ $[M]^+$: 206.0670, found: 206.0664

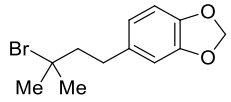


3-bromo-3-methylheptane (S-6): The bromide was prepared according to General Procedure B from the corresponding alcohol, *3-methylheptan-3-ol*. The product was purified by flash column chromatography on silica gel (eluent: petroleum ether). (Colorless liquid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 – 1.74 (m, 4H), 1.72 – 1.54 (m, 3H), 1.51 – 1.27 (m, 4H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) 75.1, 44.8, 38.1, 31.0, 27.9, 22.8, 14.1, 10.3.

HRMS (EI) Calcd for $C_8H_{17}Br^+$ $[M]^+$: 192.0514, found: 192.0509

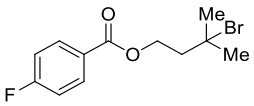


5-(3-bromo-3-methylbutyl)benzo[d][1,3]dioxole (S-7): The bromide was prepared according to General Procedure B from the corresponding alcohol, *5-(3-bromo-3-methylbutyl)benzo[d][1,3]dioxole*. The product was purified by flash column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20 : 1). (Colorless liquid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 – 6.69 (m, 2H), 6.66 (d, *J* = 7.9 Hz, 1H), 5.92 (s, 2H), 2.82 – 2.72 (m, 2H), 2.09 – 2.00 (m, 2H), 1.81 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.7, 135.4, 121.1, 108.9, 108.2, 100.8, 67.5, 49.7, 34.3, 32.6.

HRMS (EI) Calcd for $C_{12}H_{15}BrO_2^+$ $[M]^+$: 270.0255, found: 270.0252.

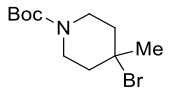


3-bromo-3-methylbutyl 4-fluorobenzoate (S-8): The bromide was prepared according to General Procedure C from the corresponding alcohol, *3-hydroxy-3-methylbutyl 4-fluorobenzoate*. The product was purified by flash column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10 : 1). (Colorless liquid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (t, *J* = 5.9 Hz, 2H), 7.11 (t, *J* = 8.4 Hz, 2H), 4.58 (t, *J* = 6.1 Hz, 2H), 2.30 (t, *J* = 6.7 Hz, 2H), 1.86 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (d, *J* = 254.0 Hz), 165.5, 132.1 (d, *J* = 9.3 Hz), 126.4, 115.6 (d, *J* = 22.0 Hz), 64.1, 63.2, 45.4, 34.7.

HRMS (ESI) Calcd for $C_{12}H_{15}BrFO_2^+$ $[M+H]^+$: 289.0234, found: 289.0052.

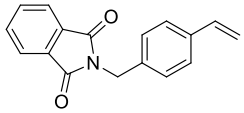


tert-butyl 4-bromo-4-methylpiperidine-1-carboxylate (S-9): The bromide was prepared according to General Procedure C from the corresponding alcohol, *tert-butyl 4-hydroxy-4-methylpiperidine-1-carboxylate.* The product was purified by flash column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10 : 1). (White solid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 – 3.85 (m, 2H), 3.18 – 3.15(m, 2H), 2.01 (t, *J* = 14.3 Hz, 2H), 1.86 (s, 3H), 1.61 – 1.50 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 79.7, 67.9, 41.5, 35.0, 28.4. (one carbon signal is overlapped)

HRMS (ESI) Calcd for $C_{11}H_{21}BrNO_2^+$ $[M+H]^+$: 278.0750, found: 278.0742.

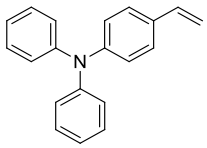


2-(4-vinylbenzyl)isoindoline-1,3-dione (S-10): 1-(chloromethyl)-4-vinylbenzene (10 mmol) was added to a solution of phthalimide (10 mmol) and K_2CO_3 (1.2 equiv.) in DMF (0.2 M) at room temperature and then stirred overnight. Next, the reaction mixture was diluted with Et_2O, washed with water, saturated $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated on a rotary evaporator. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20 : 1). (White solid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 4.0 Hz, 2H), 7.71 (d, *J* = 4.0 Hz, 2H), 7.37 (dd, *J* = 18.3, 8.0 Hz, 4H), 6.67 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.71 (d, *J* = 17.5 Hz, 1H), 5.22 (d, *J* = 11.1 Hz, 1H), 4.83 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 137.2, 136.3, 135.8, 134.0, 132.1, 128.9, 126.5, 123.4, 114.2, 41.3.

HRMS (ESI) Calcd for $C_{17}H_{14}NO_2^+$ $[M+H]^+$: 264.1019, found: 264.1011.

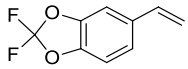


N,N-diphenyl-4-vinylaniline (S-11): The styrene was prepared according to General Procedure D from the corresponding aldehyde, *4-(diphenylamino)benzaldehyde*. The product was purified by flash column chromatography on silica gel (eluent: petroleum ether). (White solid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 6H), 7.15 – 6.97 (m, 8H), 6.66 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.64 (d, *J* = 17.6 Hz, 1H), 5.15 (d, *J* = 10.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 147.5, 136.2, 131.9, 129.3, 127.1, 124.4, 123.6, 122.9, 112.2.

HRMS (ESI) Calcd for $C_{20}H_{18}N^+$ $[M+H]^+$: 272.1434, found: 272.1424.

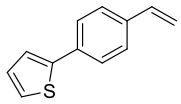


2,2-difluoro-5-vinylbenzo[d][1,3]dioxole (S-12): The styrene was prepared according to General Procedure D from the corresponding aldehyde, *2,2-difluorobenzo[d][1,3]dioxole-5-carbaldehyde*. The product was purified by flash column chromatography on silica gel (eluent: petroleum ether). (White solid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.55 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.55 (d, *J* = 17.5 Hz, 1H), 5.15 (d, *J* = 10.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 143.3, 135.6, 134.2, 129.74 (t, *J* = 254.6 Hz), 122.4, 114.2, 109.3, 106.5.

HRMS (EI) Calcd for $C_9H_6F_2O_2^+$ $[M]^+$: 184.0336, found: 184.0332.

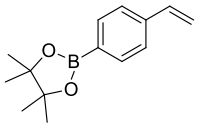


2-(4-vinylphenyl)thiophene (S-13): The styrene was prepared according to General Procedure D from the corresponding aldehyde, *4-(thiophen-2-yl)benzaldehyde*. The product was purified by flash column chromatography on silica gel (eluent: petroleum ether). (White solid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 6.9 Hz, 2H), 7.34 – 7.25 (m, 2H), 7.08 (s, 1H), 6.72 (dd, *J* = 19.3, 10.8 Hz, 1H), 5.77 (d, *J* = 15.6 Hz, 1H), 5.26 (d, *J* = 10.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 136.7, 136.3, 133.8, 128.1, 126.7, 126.0, 124.8, 123.0, 113.9.

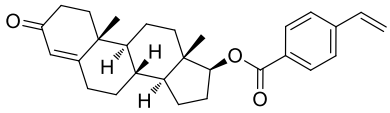
HRMS (EI) Calcd for $C_{12}H_{10}S^+$ $[M]^+$: 186.0503, found: 186.0506.



4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (S-14): (4-vinylphenyl)boronic acid (20 mmol) was added to a solution of 2,3-dimethylbutane-2,3-diol (20 mmol), anhydrous $MgSO_4$ (20 mmol) in Et_2O (0.2 M) at room temperature and then stirred overnight. Next, the reaction mixture was filted, concentrated on a rotary evaporator. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20 : 1). (White solid) (Ref: *Macromolecules,* **2005**, *38*, 8987–8990)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.72 (m, 2H), 7.41 (t, J = 6.8 Hz, 2H), 6.82 – 6.65 (m, 1H), 5.81 (dd, J = 17.6, 4.9 Hz, 1H), 5.28 (dd, J = 10.8, 4.1 Hz, 1H), 1.34 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 136.9, 135.0, 125.5, 114.9, 83.7, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



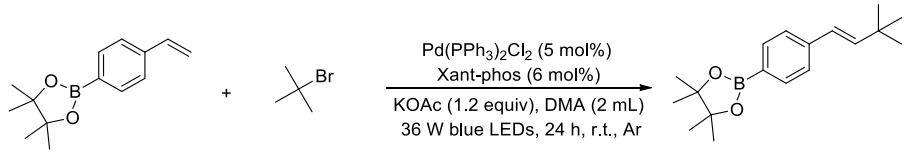
(8R,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl (S-15): 4-vinylbenzoic acid (20 mmol), was added to a solution of 4-vinylbenzoate (8R,9S,10R,13S,14S,17S)-17-hydroxy-10,13-dimethyl-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one (20 mmol), DMAP (20 mmol), DCC (20 mmol), in CH_2Cl_2 (0.2 M) at room temperature and then stirred overnight. Next, the reaction mixture was filted, concentrated on a rotary evaporator. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20 : 1). (White solid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.85 (d, *J* = 17.6 Hz, 1H), 5.73 (s, 1H), 5.37 (d, *J* = 10.9 Hz, 1H), 4.83 (t, *J* = 8.3 Hz, 1H), 2.47 – 2.22 (m, 5H), 2.01 (d, *J* = 12.7 Hz, 1H), 1.86 (d, *J* = 12.7 Hz, 2H), 1.72 – 1.56 (m, 5H), 1.49 – 1.35 (m, 2H), 1.29 – 0.99 (m, 7H), 0.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 170.9, 166.1, 141.7, 135.9, 129.7, 129.6, 126.0, 123.9, 116.4, 82.8, 53.6, 50.2, 42.8, 38.5, 36.6, 35.6, 35.3, 33.8, 32.7, 31.4, 27.6, 23.5, 20.5, 17.3, 12.2.

HRMS (ESI) Calcd for $C_{28}H_{35}O_3^+$ $[M+H]^+$: 419.2581, found: 419.2566.

3. Investigation of the Key Reaction Parameters[a]



0.2 mmol 0.3 mmol **1**

entry	Variations from standard conditions	1[b]	Conv[b]

1	**None**	**92%**	**100%**
2	$Pd(PPh_3)_4$ instead of $Pd(PPh_3)_2Cl_2$	82%	92%
3	$Pd_2(dba)_3$ instead of $Pd(PPh_3)_2Cl_2$	N.R	<5%
4	$PdCl_2$ instead of $Pd(PPh_3)_2Cl_2$	N.R	<5%
5	$Pd(OAc)_2$ instead of $Pd(PPh_3)_2Cl_2$	N.R	<5%
6	$Pd(dppf)_2Cl_2$ instead of $Pd(PPh_3)_2Cl_2$	N.R	<5%
7	$Pd(allyl)_2Cl_2$ instead of $Pd(PPh_3)_2Cl_2$	N.R	<5%
8	$Pd(OAc)_2$ + PPh_3 (10 mol%)instead of $Pd(PPh_3)_2Cl_2$	33%	35%
9	$PdCl_2$ (5 mol%) + PPh_3 (10 mol%) instead of $Pd(PPh_3)_2Cl_2$	82%	>99%
10	$PdCl_2$ (5 mol%) + PPh_3 (5 mol%) instead of $Pd(PPh_3)_2Cl_2$	Trace	<10%
11	$PdCl_2$ (5 mol%) + PPh_3 (20 mol%) instead of $Pd(PPh_3)_2Cl_2$	93%	96%
12	$PdCl_2$ (5 mol%) + PPh_2Cy (10 mol%) instead of $Pd(PPh_3)_2Cl_2$	73%	90%
13	$PdCl_2$ (5 mol%) + PCy_3 (10 mol%) instead of $Pd(PPh_3)_2Cl_2$	38%	55%
14	$PdCl_2$ (5 mol%) + $P(^tBu)_3$ (10 mol%) instead of $Pd(PPh_3)_2Cl_2$	28%	35%
15	$PdCl_2$ (5 mol%) + P(3-OMe-Ph)$_3$ (10 mol%) instead of $Pd(PPh_3)_2Cl_2$	21%	25%
16	$PdCl_2$ (5 mol%) + P(4-OMe-Ph)$_3$ (10 mol%) instead of $Pd(PPh_3)_2Cl_2$	65%	80%
17	$PdCl_2$ (5 mol%) + P(2,4-Me-C_6H_4)$_3$ (10 mol%) instead of $Pd(PPh_3)_2Cl_2$	12%	20%
18	$PdCl_2$ (5 mol%) + P(furan)$_3$ (10 mol%) instead of $Pd(PPh_3)_2Cl_2$	N.R	<10%
19	$PdCl_2$ (5 mol%) + P(perfluorophenyl)$_3$ (10 mol%) instead of $Pd(PPh_3)_2Cl_2$	15%	25%
20	$PdCl_2$ (5 mol%) + PPh_2Py (10 mol%) instead of $Pd(PPh_3)_2Cl_2$	27%	45%
21	Cyxant-phos instead of Xant-phos	9%	15%
22	Nixant-phos instead of Xant-phos	81%	90%
23	DPE-phos instead of Xant-phos	34%	55%
24	DPPP instead of Xant-phos	Trace	<10%
25	BINAP instead of Xant-phos	Trace	<10%
26	Dtbpy instead of Xant-phos	38%	56%
27	X-phos instead of Xant-phos	Trace	<5%
28	Tri-phos instead of Xant-phos	N.R	<5%
29	DMF instead of DMA	57%	65%
30	CH_3CN instead of DMA	Trace	<5%
31	THF instead of DMA	47%	64%
32	DCE instead of DMA	N.R	<5%
33	**K_2CO_3 instead of KOAc**	**73% (93%[c])**	**100%[c]**
34	K_3PO_4 instead of KOAc	63%	90%
35	Et_3N instead of KOAc	Trace	<10%
36	K_2HPO_4 instead of KOAc	N.R	<5%
37	$[Ir(ppy)_2(dtbbpy)]PF_6$ (1 mol %) instead of (Pd + Ligand)	N.R	<5%
38	$[Ru(bpy)_3]Cl_2$ (1 mol %) instead of (Pd + Ligand)	N.R	<5%
39	*fac*-Ir(ppy)$_3$ (1 mol %) instead of (Pd + Ligand)	N.R	<5%
40	T = 100 ^oC without irradiation	N.R	<5%
41	In the dark	N.R	<5%
42	36W White-LEDs instead of Blue-LEDs	21%	30%
43	36W Green-LEDs instead of Blue-LEDs	19%	25%

44	36W Purple-LEDs instead of Blue-LEDs	82%	87%
45	15W UV (254 nm) instead of Blue-LEDs	N.R	85%
46	Without the Xant-phos	N.R	<5%
47	Without the base	N.R	<5%
48	Without the $Pd(PPh_3)_2Cl_2$	N.R	<5%
49	In the air	N.R	<5%

[a]Reaction condition: **4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane** (0.2 mmol), [t]**Bu-Br** (0.3 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%), Xant-phos (6 mol%), KOAc (120 mol%) in DMA (2 mL), irradiation by 36W blue LEDs at 23 ^oC for 24 h under Ar atmosphere. [b]Yield determined by ^1H NMR using diphenylmethane as an internal standard. [c]With 1 equiv. H_2O

As one referee suggested, we tested to use Pd(0)(Xantphos) complex as catalysts to further verity that "dual phosphine ligand system" is essential. We have tested the pre-reduction of $Pd(Xantphos)Cl_2$ by catalytic amount of hydrazine (a method to generate Pd(0)(Xantphos)). The result showed that the reaction did not proceed with only Pd(0)(Xantphos) as catalyst.

4. General Procedure and Spectral Data

4.1 General procedure 1

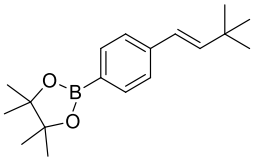
Styrene (1.0 equiv., 0.2 mmol) (if solid), alkyl halide (1.5 equiv., 0.3 mmol) (if solid), $Pd(PPh_3)_2Cl_2$ (5 mol%, 7 mg) and Xantphos (6 mol%, 6.9 mg), K_2CO_3 (0.24 mmol, 33 mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids, styrene (1.0 equiv., 0.2 mmol) (if liquid), halide (1.5 equiv., 0.3 mmol) (if liquid), anhydrous DMA (2.0 mL), and H_2O (1 equiv.) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under the irradiation of 36 W blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 24 h-36 h. The mixture was quenched with saturated NaCl solution and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel with petroleum ether or a mixture of petroleum ether / ethyl acetate.

4.2 General procedure 2

Alkyl Halide (1.5 equiv., 7.5 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%) and Xantphos (6 mol%), K_2CO_3 (1.2 equiv.) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids,

styrene (1.0 equiv., 5 mmol), anhydrous DMA (50 mL), H_2O (1 equiv.) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under the irradiation of 36 W blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 36 h. After reaction completed, the mixture was quenched with saturated NaCl solution and extracted with ethyl acetate (3 × 50 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel with petroleum ether or a mixture of petroleum ether/ethyl acetate as eluent.

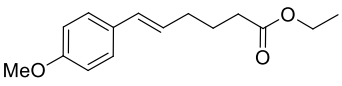
4.3 Spectral Data



(E)-2-(4-(3,3-dimethylbut-1-en-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1): Following the general procedure 1 (t = 24 h), obtained in 91% yield as a colorless liquid (52.0 mg, eluent: petroleum ether:ethyl acetate = 20:1). (Ref: *Macromolecules,* **2005**, *38*, 8987–8990)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.6 Hz, 2H), 7.36 (d, J = 7.7 Hz, 2H), 6.40 – 6.23 (m, 2H), 1.34 (s, 12H), 1.12 (s, 9H).

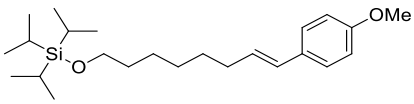
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 140.9, 135.0, 125.3, 124.6, 83.7, 77.3, 77.0, 76.7, 33.5, 29.5, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



***(E)*-ethyl 6-(4-methoxyphenyl)hex-5-enoate (2):** Following the general procedure 1(t = 36 h), obtained in 83% yield as a colorless liquid (41.2 mg, eluent: petroleum ether:ethyl acetate = 20:1). (Ref: *Bioorg. Med. Chem.* **1997**, *5*, 1649–1674)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.03 (dt, *J* = 15.8, 7.0 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 2.43 – 2.17 (m, 4H), 1.80 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 158.8, 130.4, 130.1, 127.4, 127.1, 113.9, 60.3, 55.3, 33.7, 32.4, 24.7, 14.3.

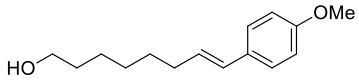


***(E)*-triisopropyl((8-(4-methoxyphenyl)oct-7-en-1-yl)oxy)silane (3):** Following the general procedure 1 (t = 36 h), obtained in 65% yield as a colorless liquid (50.8 mg, eluent: petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.08 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.79 (s, 3H), 3.67 (t, *J* = 6.6 Hz, 2H), 2.18 (q, *J* = 6.8 Hz, 2H), 1.59 – 1.34 (m, 8H), 1.08 – 1.02 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 130.8, 129.9, 129.0, 126.9, 113.9, 63.5, 55.3, 33.0, 29.7, 29.5, 29.1, 25.7, 18.0, 12.0.

HRMS (ESI) Calcd for $C_{24}H_{43}SiO_2^+$ $[M+H]^+$: 391.3027, found: 391.3014.

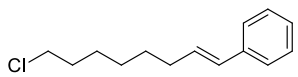


***(E)*-8-(4-methoxyphenyl)oct-7-en-1-ol (4):** Following the general procedure 1(t = 36 h), obtained in 77% yield as a colorless liquid (36.2 mg, eluent: petroleum ether:ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.07 (dt, *J* = 15.7, 6.9 Hz, 1H), 3.79 (s, 3H), 3.63 (t, *J* = 6.6 Hz, 2H), 2.16-2.21 (m, 2H), 1.55-1.59 (m, 2H), 1.45 – 1.48 (m, 2H), 1.35-1.38 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 130.7, 129.1, 128.9, 127.0, 113.9, 63.1, 55.3, 32.9, 32.8, 29.5, 29.0, 25.6.

HRMS (ESI) Calcd for $C_{15}H_{23}O_2^+$ $[M+H]^+$: 235.1693, found: 235.1685.



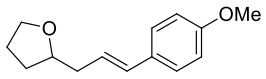
***(E)*-1-(8-chlorooct-1-en-1-yl)-4-methoxybenzene1 (5):** Following the general procedure 1 (t = 36 h), obtained in 55% yield as a colorless liquid (24.5 mg, eluent:

petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 4H), 7.11 (t, *J* = 7.1 Hz, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 6.21 – 6.09 (m, 1H), 3.46 (t, *J* = 6.7 Hz, 2H), 2.14 (q, *J* = 7.0 Hz, 2H), 1.77 – 1.65 (m, 2H), 1.45 – 1.28 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 130.9, 129.9, 128.5, 126.8, 125.9, 45.2, 32.9, 32.6, 29.2, 28.5, 26.8.

HRMS (ESI) Calcd for $C_{15}H_{20}ClO^+$ $[M+H]^+$: 223.1248, found: 223.1254

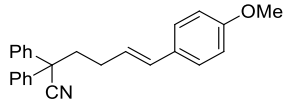


***(E)*-2-(3-(4-methoxyphenyl)allyl)tetrahydrofuran (6):** Following the general procedure 1 (t = 36 h), obtained in 80% yield as a colorless liquid (35.0 mg, eluent: petroleum ether:ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.10 (dd, *J* = 15.4, 7.5 Hz, 1H), 3.99 – 3.86 (m, 2H), 3.80 (s, 3H), 3.77 – 3.72 (m, 1H), 2.49 – 2.36 (m, 2H), 2.04 – 1.83 (m, 3H), 1.61 – 1.52 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 131.3, 130.4, 127.2, 124.5, 113.9, 78.9, 68.0, 55.3, 39.2, 30.8, 25.7.

HRMS (ESI) Calcd for $C_{14}H_{19}O_2$ $[M+H]^+$: 219.1380, found: 219.1387.

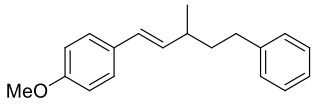


***(E)*-6-(4-methoxyphenyl)-2,2-diphenylhex-5-enenitrile (7):** Following the general procedure 1(t = 36 h), obtained in 72% yield as a colorless liquid (54.1 mg, eluent: petroleum ether:ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 8H), 7.32 – 7.27 (m, 2H), 7.26 – 7.19 (m, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.03 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.78 (s, 3H), 2.57 – 2.49 (m, 2H), 2.36 – 2.26 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 140.1, 130.5, 130.1, 129.0, 128.0, 127.1, 126.9, 126.1, 122.3, 114.0, 55.3, 51.5, 39.5, 29.3.

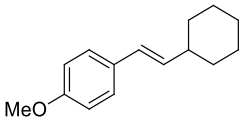
HRMS (ESI) Calcd for $C_{25}H_{23}NNaO^+$ $[M+Na]^+$: 376.1672, found: 376.1657.



***(E)*-1-methoxy-4-(3-methyl-5-phenylpent-1-en-1-yl)benzene (8):** Following the general procedure 1(t = 36 h), obtained in 81% yield as a colorless liquid (43.1 mg, eluent: petroleum ether). (Ref: *Chem. Commun.* **2012**, *48*, 7847–7849)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 14.3, 8.9 Hz, 4H), 7.11 (d, *J* = 7.5 Hz, 3H), 6.77 (d, *J* = 8.3 Hz, 2H), 6.24 (d, *J* = 15.9 Hz, 1H), 5.90 (dd, *J* = 15.9, 8.0 Hz, 1H), 3.73 (s, 3H), 2.65 – 2.48 (m, 2H), 2.31 – 2.16 (m, 1H), 1.63 (dd, *J* = 15.3, 7.6 Hz, 2H), 1.04 (d, *J* = 6.7 Hz, 3H).

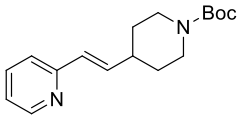
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 142.7, 134.3, 130.6, 128.4, 128.3, 127.9, 127.0, 125.6, 113.9, 55.3, 38.9, 36.9, 33.7, 20.9.



***(E)*-1-(2-cyclohexylvinyl)-4-methoxybenzene (9):** Following the general procedure 1(t = 24 h), obtained in 96% yield as a colorless liquid (41.5 mg, eluent: petroleum ether). (Ref: *Angew. Chem. Int. Ed.* **2014**, *53*, 5974–5977)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.28 (d, *J* = 16.0 Hz, 1H), 6.03 (dd, *J* = 16.0, 7.0 Hz, 1H), 3.79 (s, 3H), 2.13 – 2.06 (m, 1H), 1.84 – 1.64 (m, 5H), 1.38 – 1.11 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 134.8, 130.8, 127.0, 126.5, 113.9, 55.3, 41.1, 33.1, 26.2, 26.1.

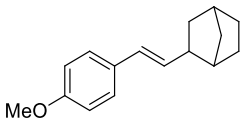


***(E)*-tert-butyl 4-(2-(pyridin-2-yl)vinyl)piperidine-1-carboxylate (10):** Following the general procedure 2, obtained in 81% yield as a colorless liquid (1.17g, eluent: petroleum ether:ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.4 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.31 – 7.20 (m, 1H), 7.11 (t, *J* = 5.5 Hz, 1H), 6.70 (dd, *J* = 15.8, 8.2 Hz, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 4.14 (s, 2H), 2.79 (t, *J* = 11.5 Hz, 2H), 2.35 (dd, *J* = 16.0, 10.1 Hz, 1H), 1.79 (d, *J* = 13.0 Hz, 2H), 1.49 – 1.39 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 154.9, 149.3, 139.0, 136.6, 128.4, 121.9, 121.4, 79.4, 43.7, 39.2, 31.5, 28.5.

HRMS (ESI) Calcd for $C_{17}H_{24}N_2NaO_2^+$ $[M+Na]^+$: 311.1730, found: 311.1722.

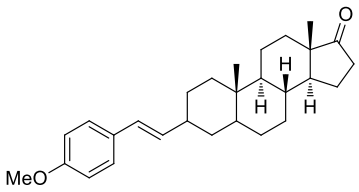


***(E)*-2-(4-methoxystyryl)bicyclo[2.2.1]heptane (11):** Following the general procedure 1 (t = 36 h), obtained in 78% yield as a white solid (35.7 mg, eluent: petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.0 Hz, 2H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.24 (d, *J* = 15.8 Hz, 1H), 5.98 (dd, *J* = 15.8, 8.1 Hz, 1H), 3.79 (s, 3H), 2.23 (dd, *J* = 14.3, 9.1 Hz, 2H), 2.11 (s, 1H), 1.60 – 1.50 (m, 3H), 1.43 (d, *J* = 9.8 Hz, 1H), 1.35 (d, *J* = 12.6 Hz, 1H), 1.26 (t, *J* = 9.1 Hz, 1H), 1.21 – 1.14 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 134.4, 130.8, 127.0, 126.6, 113.9, 55.3, 45.4, 42.8, 38.0, 36.6, 35.8, 29.8, 29.0.

HRMS (ESI) Calcd for $C_{16}H_{21}O^+$ $[M+H]^+$: 229.1587, found: 229.1577.



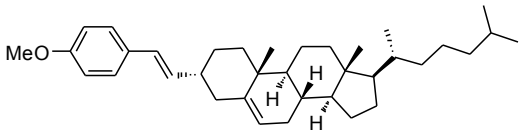
(8R,9S,10S,13S,14S)-3-((E)-4-methoxystyryl)-10,13-dimethyltetradecahydro-1H-cyclopenta[a]phenanthren-17(2H)-one (12): Following the general procedure 2, obtained in 72% yield as a white solid (1.46g, eluent: petroleum ether:ethyl acetate = 10:1). (**A** : **B** = 6.7:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.7 Hz, 2H, **A**+**B**), 6.89 – 6.79 (m, 2H, **A**+**B**), 6.40 – 6.22 (m, 1.83 H, **A**), 6.03 (dd, *J* = 16.0, 6.9 Hz, 0.26 H, **B**), 3.80 (s, 3H,

A+**B**), 2.68 – 2.35 (m, 2H, **A**+**B**), 2.13 – 2.00 (m, 1H, **A**+**B**), 1.97 – 1.89 (m, 1H, **A**+**B**), 1.84 – 1.74 (m, 3H, **A**+**B**), 1.68 – 1.45 (m, 6H, **A**+**B**), 1.35 – 1.18 (m, 8H, **A**+**B**), 1.05 – 0.94 (m, 1H, **A**+**B**), 0.87 – 0.82 (m, 6H, **A**+**B**), 0.80 – 0.70 (m, 1H, **A**+**B**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.7, 158.6, 132.7, 130.8, 128.1, 126.9, 113.9, 55.3, 54.6, 51.5, 47.9, 41.0, 36.5, 35.9, 35.8, 35.0, 33.9, 33.7, 31.6, 30.8, 28.6, 26.1, 21.7, 20.0, 13.8, 11.9.

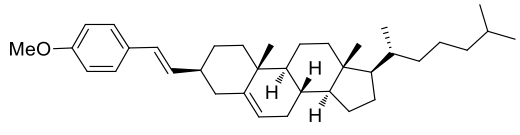
HRMS (ESI) Calcd for $C_{28}H_{38}NaO_2^+$ $[M+Na]^+$: 429.2764, found: 429.2747.



(3R,8S,9S,10R,13R,14S,17R)-3-((E)-4-methoxystyryl)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (13): Following the general procedure 1 (t = 36 h), obtained in 72% yield as a white solid (72.4 mg, eluent: petroleum ether). (**A** : **B** = 1.8:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H, **A**), 6.83 (d, *J* = 8.7 Hz, 2H, **A**), 6.34 (d, *J* = 16.0 Hz, 1H, **A**), 6.19 (dd, *J* = 16.0, 7.2 Hz, 1H, **A**), 5.32 (d, *J* = 4.7 Hz, 1H, **A**), 3.79 (s, 3H, **A**), 2.62 (d, *J* = 12.3 Hz, 2H, **A**), 2.04 – 1.89 (m, 4H, **A**), 1.65 – 1.25 (m, 14H, **A**), 1.18 – 0.98 (m, 12H, **A**), 0.91 (d, *J* = 6.5 Hz, 3H, **A**), 0.87 (dd, *J* = 6.6, 1.8 Hz, 6H, **A**), 0.68 (s, 3H, **A**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 140.5, 132.0, 131.0, 128.4, 127.1, 121.4, 113.9, 56.8, 56.2, 55.3, 50.3, 42.3, 39.9, 39.6, 37.9, 37.4, 37.3, 36.2, 35.9, 34.4, 32.0, 31.9, 28.3, 28.1, 28.0, 24.3, 23.9, 22.9, 22.6, 20.8, 19.5, 18.7, 11.9.

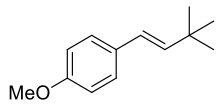


(3S,8S,9S,10R,13R,14S,17R)-3-((E)-4-methoxystyryl)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H, **B**), 6.83 (d, *J* = 8.7 Hz, 2H, **B**), 6.31 (d, *J* = 15.9 Hz, 1H, **B**), 6.04 (dd, *J* = 15.9 Hz, 6.4 Hz, 1H, **B**), 5.34 (d, *J* = 5.1 Hz, 1H, **B**), 3.79 (s, 3H, **B**), 2.19 – 1.88 (m, 6H, **B**), 1.75 – 1.23 (m, 14H, **B**), 1.18 – 0.98 (m, 12H, **B**), 0.92 (d, *J* = 6.5 Hz, 3H, **B**), 0.87 (dd, *J* = 6.6, 1.8 Hz, 6H, **B**), 0.68 (s, 3H, **B**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 142.6, 134.0, 130.7, 127.0, 126.9, 119.9, 113.9, 56.9, 56.2, 55.3, 50.5, 42.9, 42.3, 39.9, 39.5, 39.3, 39.2, 36.9, 36.2, 35.8, 32.0, 31.9, 29.0, 28.3, 28.1, 24.3, 23.8, 22.9, 22.6, 21.0, 19.5, 18.8, 11.9.

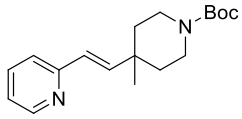
HRMS (ESI) Calcd for $C_{36}H_{55}O^+$ $[M+H]^+$: 503.4247, found: 503.4236.



***(E)*-1-(3,3-dimethylbut-1-en-1-yl)-4-methoxybenzene (14):** Following the general procedure 1(t = 24 h), obtained in 94% yield as a colorless liquid (35.7 mg, eluent: petroleum ether). (Ref: *J. Am. Chem. Soc.* **2011**, *133*, 8478–8481)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.17 (d, *J* = 16.2 Hz, 1H), 6.04 (d, *J* = 16.2 Hz, 1H), 3.72 (s, 3H), 1.03 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 139.8, 130.8, 127.0, 123.88, 113.9, 55.2, 33.2, 29.7.

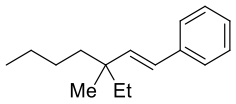


***(E)*-tert-butyl-4-methyl-4-(2-(pyridin-2-yl)vinyl)piperidine-1-carboxylate (15):** Following the general procedure 1 (t = 36 h), obtained in 55% yield as a colorless liquid (35.7 mg, eluent: petroleum ether:ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 4.5 Hz, 1H), 7.63 (t, J = 8.4 Hz, 1H), 7.28 (d, J = 3.7 Hz, 1H), 7.18 – 7.07 (m, 1H), 6.73 (d, J = 16.2 Hz, 1H), 6.46 (d, J = 16.2 Hz, 1H), 3.51 (d, J = 3.1 Hz, 2H), 3.45 – 3.34 (m, 2H), 1.83 – 1.68 (m, 2H), 1.54 – 1.44 (m, 11H), 1.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 155.0, 149.3, 143.2, 136.7, 127.3, 121.9, 121.4, 79.3, 40.4, 36.7, 35.0, 28.5, 26.5.

HRMS (ESI) Calcd for $C_{18}H_{26}N_2NaO_2^+$ $[M+H]^+$: 325.1886, found: 325.1875.

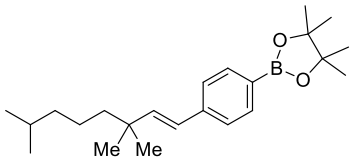


***(E)*-(3-ethyl-3-methylhept-1-en-1-yl)benzene (16):** Following the general procedure 1 (t = 36 h), obtained in 62% yield as a colorless liquid (26.8 mg, eluent: petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.24 (d, *J* = 16.3 Hz, 1H), 6.10 (d, *J* = 16.3 Hz, 1H), 1.48 – 1.33 (m, 4H), 1.29 – 1.17 (m, 4H), 1.03 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 138.2, 128.5, 126.8, 126.7, 126.0, 40.8, 39.3, 33.7, 26.5, 23.6, 22.6, 14.2, 8.6.

HRMS (EI) Calcd for $C_{16}H_{24}^+$ $[M]^+$: 216.1878, found: 216.1874.

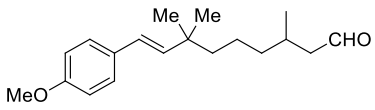


***(E)*-4,4,5,5-tetramethyl-2-(4-(3,3,7-trimethyloct-1-en-1-yl)phenyl)-1,3,2-dioxaborolane (17):** Following the general procedure 1 (t = 36 h), obtained in 85% yield as a colorless liquid (55.4 mg, eluent: petroleum ether:ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.23 – 6.13 (m, 2H), 1.44 (dt, *J* = 13.2, 6.7 Hz, 1H), 1.31 – 1.23 (m, 16H), 1.09 – 1.04 (m, 2H), 1.01 (s, 6H), 0.77 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 141.0, 135.0, 125.6, 125.3, 83.7, 43.4, 39.7, 36.4, 27.9, 27.2, 24.9, 22.7, 22.4. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

HRMS (EI) Calcd for $C_{23}H_{37}BO_2^+$ $[M]^+$: 356.2887, found: 356.2884.

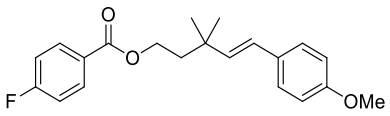


***(E)*-9-(4-methoxyphenyl)-3,7,7-trimethylnon-8-enal (18):** Following the general procedure 1 (t = 36 h), obtained in 45% yield as a colorless liquid (26.0 mg, eluent: petroleum ether:ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (t, *J* = 2.3 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.21 (d, *J* = 16.2 Hz, 1H), 6.02 (d, *J* = 16.2 Hz, 1H), 3.80 (s, 3H), 2.38 (ddd, *J* = 16.0, 5.6, 2.0 Hz, 1H), 2.27 – 2.16 (m, 1H), 2.10 – 1.99 (m, 1H), 1.37 – 1.20 (m, 6H), 1.07 (s, 6H), 0.94 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 158.5, 130.8, 129.1, 129.0, 126.9, 113.8, 63.4, 55.2, 33.0, 29.5, 29.0, 25.7, 18.0, 12.0. (one carbon signal is overlapped)

HRMS (ESI) Calcd for $C_{19}H_{29}O_2^+$ $[M+H]^+$: 289.2162, found: 289.2157.



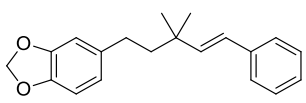
***(E)*-3,3-dimethyl-5-phenylpent-4-en-1-yl 4-fluorobenzoate (19):** Following the general procedure 1 (t = 36 h), obtained in 82% yield as a colorless liquid (56.3 mg, eluent: petroleum ether:ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.27 (d, *J* = 9.0 Hz, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.28 (d, *J* = 16.2 Hz, 1H), 6.09 (d, *J* = 16.2 Hz, 1H), 4.35 (t, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.88 (t, *J* = 7.1 Hz, 2H), 1.19 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 165.65 (d, *J* = 253.5 Hz), 158.8, 137.2, 132.07 (d, *J* = 9.3 Hz), 130.4, 127.2, 126.6, 125.7, 115.40 (d, *J* = 21.9 Hz), 113.9, 62.7, 55.3, 41.3, 35.4, 27.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -106.1.

HRMS (ESI) Calcd for $C_{21}H_{24}FO_3^+$ $[M+H]^+$: 343.1704, found: 343.1705.

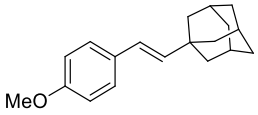


***(E)*-5-(3,3-dimethyl-5-phenylpent-4-en-1-yl)benzo[d][1,3]dioxole (20):** Following the general procedure 1 (t = 36 h), obtained in 76% yield as a colorless liquid (44.8 mg, eluent: petroleum ether:ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.3 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.13 (dd, *J* = 15.0, 7.8 Hz, 1H), 6.68 – 6.50 (m, 3H), 6.25 (d, *J* = 16.2 Hz, 1H), 6.14 (d, *J* = 16.2 Hz, 1H), 5.81 (s, 2H), 2.49 – 2.33 (m, 2H), 1.62 – 1.52 (m, 2H), 1.08 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 145.4, 140.1, 137.9, 136.9, 128.5, 126.8, 126.2, 126.1, 120.8, 108.8, 108.1, 100.7, 45.6, 36.4, 31.1, 27.2.

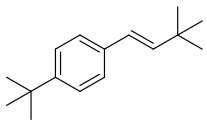
HRMS (ESI) Calcd for $C_{20}H_{23}O_2^+$ $[M+H]^+$: 295.1693, found: 295.1687.



(3r,5r,7r)-1-((E)-4-methoxystyryl)adamantane (21): Following the general procedure 1(t = 24 h), obtained in 76% yield as a white solid (40.7 mg, eluent: petroleum ether). (Ref: *J. Org. Chem.* **2004**, *69*, 3961–3963)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.18 (d, *J* = 16.2 Hz, 1H), 5.97 (d, *J* = 16.2 Hz, 1H), 3.80 (s, 3H), 2.02 (s, 3H), 1.80 – 1.63 (m, 12H).

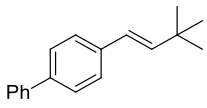
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 140.1, 131.0, 127.0, 123.8, 113.9, 55.3, 42.3, 36.9, 35.0, 28.5.



***(E)*-1-(tert-butyl)-4-(3,3-dimethylbut-1-en-1-yl)benzene (22):** Following the general procedure 1(t = 24 h), obtained in 95% yield as a colorless liquid (41.0 mg, eluent: petroleum ether). (Ref: *Org. Lett.* **2009**, *11*, 2862–2854)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 4H), 6.30 – 6.19 (m, 2H), 1.31 (s, 9H), 1.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 141.1, 135.2, 125.7, 125.4, 124.2, 34.5, 33.3, 31.3, 29.6.

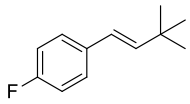


***(E)*-4-(3,3-dimethylbut-1-en-1-yl)-1,1'-biphenyl (23):** Following the general procedure 1(t = 24 h), obtained in 85% yield as a white solid (40.1 mg, eluent: petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.1 Hz, 4H), 7.32 (t, *J* = 7.2 Hz, 1H), 6.38 – 6.26 (m, 2H), 1.14 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 140.9, 139.5, 137.1, 128.7, 127.2, 127.1, 126.9, 126.4, 124.1, 33.4, 29.6.

HRMS (EI) Calcd for $C_{18}H_{20}^{+}$ $[M]^{+}$: 236.1565, found: 236.1560.

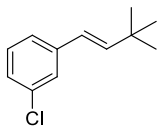


***(E)*-1-(3,3-dimethylbut-1-en-1-yl)-4-fluorobenzene (24):** Following the general procedure 1(t = 24 h), obtained in 85% yield as a colorless liquid (30.3 mg, eluent: petroleum ether). (Ref: *RSC Adv.* **2013**, *3*, 19264–19267)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.7, 5.5 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 6.26 (d, *J* = 16.2 Hz, 1H), 6.16 (d, *J* = 16.2 Hz, 1H), 1.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.83 (d, *J* = 245.3 Hz), 141.6, 134.1, 127.37 (d, *J* = 7.8 Hz), 123.4, 115.27 (d, *J* = 21.5 Hz), 33.3, 29.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.1.

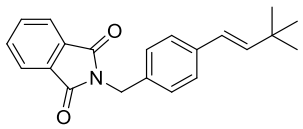


***(E)*-1-chloro-3-(3,3-dimethylbut-1-en-1-yl)benzene (25):** Following the general procedure 1(t = 24 h), obtained in 82% yield as a colorless liquid (31.8 mg, eluent: petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.21 – 7.19 (m, 2H), 7.18 – 7.11 (m, 1H), 6.31 – 6.19 (m, 2H), 1.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 140.0, 134.4, 129.6, 126.6, 125.9, 124.3, 123.4, 33.5, 29.5.

HRMS (EI) Calcd for $C_{12}H_{15}Cl^+$ $[M]^+$: 194.0862, found: 194.0857.

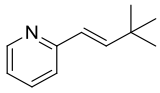


***(E)*-2-(4-(3,3-dimethylbut-1-en-1-yl)benzyl)isoindoline-1,3-dione (26):** Following the general procedure 1 (t = 36 h), obtained in 72% yield as a white solid (49.2 mg, eluent: petroleum ether:ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.33 (dd, *J* = 27.3, 8.2 Hz, 4H), 6.29 – 6.16 (m, 2H), 4.81 (s, 2H), 1.09 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 142.3, 137.8, 134.8, 134.0, 132.1, 128.9, 126.3, 124.0, 123.3, 41.4, 33.4, 29.6.

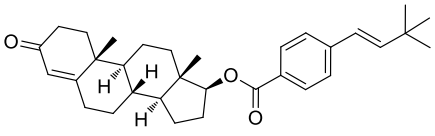
HRMS (ESI) Calcd for $C_{21}H_{21}NNaO_2^+$ $[M+Na]^+$: 342.1465, found: 342.1453.



***(E)*-2-(3,3-dimethylbut-1-en-1-yl)pyridine (27):** Following the general procedure 1 (t = 36 h), obtained in 81% yield as a pale yellow liquid (26.1 mg, eluent: petroleum ether:ethyl acetate = 10:1). (Ref: *Chem. Commun*. **2011**, *47*, 2943–2945)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.3 Hz, 1H), 7.60 (dd, *J* = 11.6, 5.6 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.08 (dd, *J* = 6.6, 5.7 Hz, 1H), 6.78 (d, *J* = 16.0 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 1.15 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 149.3, 146.4, 136.5, 124.8, 121.5, 121.2, 33.5, 29.4.

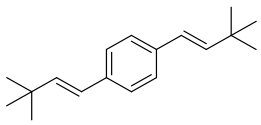


(8R,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl4-((E)-3,3-dimethylbut-1-en-1-yl)benzoate (28) : Following the general procedure 1 (t = 36 h), obtained in 85% yield as a white solid. (84.5 mg, eluent: petroleum ether:ethyl acetate = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 6.43 – 6.32 (m, 2H), 5.76 (s, 1H), 4.86 (t, *J* = 8.4 Hz, 1H), 2.53 – 2.25 (m, 5H), 2.05 (dt, *J* = 7.8, 4.9 Hz, 1H), 1.90 (d, *J* = 10.1 Hz, 2H), 1.80 – 1.59 (m, 5H), 1.53 – 1.37 (m, 2H), 1.32 – 0.98 (m, 19H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 171.0, 166.4, 144.6, 142.6, 129.8, 128.7, 125.9, 124.0, 82.8, 53.7, 50.3, 42.9, 38.6, 36.8, 35.7, 35.4, 34.0, 33.6, 32.8, 31.5, 29.4, 27.7, 23.6, 20.6, 17.4, 12.3.

HRMS (ESI) Calcd for $C_{32}H_{42}NaO_3^+$ $[M+Na]^+$: 497.3026, found: 497.3005.

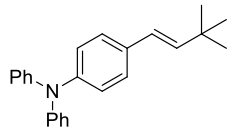


1,4-bis((E)-3,3-dimethylbut-1-en-1-yl)benzene (29) : $Pd(PPh_3)_2Cl_2$ (10 mol%, 14 mg) and Xant-phos (12 mol%, 13.8 mg), K_2CO_3 (2.4 equiv., 66 mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids, Styrene (1.0 equiv., 0.2 mmol) (if liquid), Halide (3 equiv., 0.6 mmol) (if liquid) and anhydrous DMA (3.0 mL), H_2O (2 equiv.) was added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under the irradiation of a 36 W blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 36 h, obtained in 71% yield as a colorless liquid (34.4 mg, eluent: petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 4H), 6.32 – 6.18 (m, 4H), 1.11 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 136.6, 126.1, 124.3, 33.4, 29.6.

HRMS (EI) Calcd for $C_{18}H_{26}^+$ $[M]^+$: 242.2035, found: 242.2030.

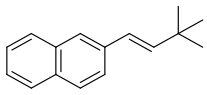


***(E)*-4-(3,3-dimethylbut-1-en-1-yl)-N,N-diphenylaniline (30) :** Following the general procedure 1 (t = 36 h), obtained in 87% yield as a white solid (57.1 mg, eluent: petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 6H), 7.07 (d, *J* = 8.6 Hz, 4H), 7.00 (dd, *J* = 16.6, 8.4 Hz, 4H), 6.28 – 6.15 (m, 2H), 1.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.5, 140.6, 132.7, 129.2, 126.8, 124.4, 124.02, 123.9, 122.6, 33.3, 29.7.

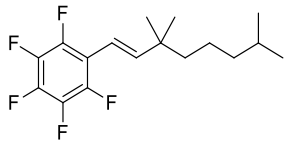
HRMS (ESI) Calcd for $C_{24}H_{26}N^+$ $[M+H]^+$: 328.2060, found: 328.2051.



***(E)*-2-(3,3-dimethylbut-1-en-1-yl)naphthalene (31) :** Following the general procedure 1 (t = 24 h), obtained in 91% yield as a white solid (38.2 mg, eluent: petroleum ether). (Ref: *RSC Adv.* **2013**, *3*, 19264–19267)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 7.5 Hz, 3H), 7.70 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.49 – 7.36 (m, 2H), 6.43 (m, 2H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 135.5, 133.7, 132.6, 128.0, 127.8，127.6, 126.1, 125.5, 125.4, 124.7, 123.6, 33.5, 29.6.



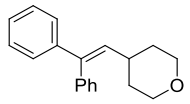
***(E)*-1,2,3,4,5-pentafluoro-6-(3,3,7-trimethyloct-1-en-1-yl)benzene (32):** Following the general procedure 1 (t = 36 h), obtained in 81% yield as a colorless liquid (51.8 mg, eluent: petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (d, *J* = 16.7 Hz, 1H), 6.05 (d, *J* = 16.7 Hz, 1H), 1.45 (dt, *J* = 13.2, 6.6 Hz, 1H), 1.28 (dd, *J* = 8.9, 6.4 Hz, 2H), 1.19 – 1.12 (m, 2H), 1.07 (t, *J* = 7.3 Hz, 2H), 1.02 (s, 6H), 0.78 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.63 (td, *J* = 6.9, 1.8 Hz), δ 144.50 (dm, *J* = 252.9 Hz), 139.18 (dm, *J* = 252.6 Hz), 137.62 (dm, *J* = 250.6 Hz), 112.9 (m), 110.2, 43.1, 39.6, 37.5, 29.7, 27.8, 26.7, 22.6, 22.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.8 (dd, *J* = 21.8, 7.8 Hz), -158.2 (t, *J* = 20.9 Hz), -163.2 – -164.1 (m).

HRMS (EI) Calcd for $C_{17}H_{21}F_5^+$ $[M]^+$: 320.1563, found: 320.1559.

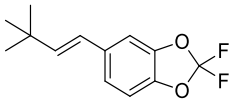


4-(2,2-diphenylvinyl)tetrahydro-2H-pyran (33): Following the general procedure 1 (t = 36 h), obtained in 72% yield as a white solid (38.1 mg, eluent: petroleum ether:ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 3H), 7.26 – 7.16 (m, 7H), 5.89 (d, *J* = 9.8 Hz, 1H), 3.94 – 3.89 (m, 2H), 3.35 – 3.24 (m, 2H), 2.38 (qd, *J* = 9.9, 5.3 Hz, 1H), 1.62 – 1.52 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 139.8, 130.8, 127.0, 123.8, 113.9, 55.3, 33.2, 29.7.

HRMS (ESI) Calcd for $C_{19}H_{21}O^+$ $[M+H]^+$: 265.1587, found: 265.1581.



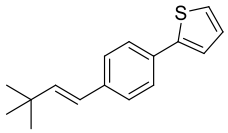
***(E)*-5-(3,3-dimethylbut-1-en-1-yl)-2,2-difluorobenzo[d][1,3]dioxole (34):** Following the general procedure 1 (t = 36 h), obtained in 65% yield as a colorless liquid (31.3 mg, eluent: petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 1.6 Hz, 1H), 7.00 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.24 (d, *J* = 16.1 Hz, 1H), 6.15 (d, *J* = 16.1 Hz, 1H), 1.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 142.5, 142.3, 134.7, 131.63 (t, *J* = 254.6 Hz), 123.5, 121.8, 109.2, 106.4, 33.4, 29.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -50.3.

HRMS (ESI) Calcd for $C_{13}H_{15}F_2O_2^+$ [M+H]$^+$: 241.1035, found: 241.1034.

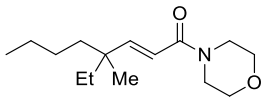


***(E)*-2-(4-(3,3-dimethylbut-1-en-1-yl)phenyl)thiophene (35):** Following the general procedure 1 (t = 36 h), obtained in 95% yield as a white solid (46.0 mg, eluent: petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.26 (dd, *J* = 18.3, 4.3 Hz, 2H), 7.06 (t, *J* = 4.2 Hz, 1H), 6.34 – 6.23 (m, 2H), 1.13 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 142.1, 137.3, 132.8, 128.0, 126.5, 126.0, 124.5, 124.1, 122.8, 33.5, 29.6.

HRMS (EI) Calcd for $C_{16}H_{18}S^+$ [M]$^+$: 242.1129, found: 242.1124.

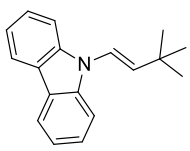


***(E)*-4-ethyl-4-methyl-1-morpholinooct-2-en-1-one (36):** Following the general procedure 1 (t = 24 h), obtained in 58% yield as a white solid (29.5 mg, eluent: petroleum ether:ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (d, *J* = 15.5 Hz, 1H), 6.04 (d, *J* = 15.5 Hz, 1H), 3.70 – 3.58 (m, 8H), 1.45 – 1.12 (m, 8H), 0.99 (s, 3H), 0.87 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 155.8, 116.4, 66.8, 46.1, 42.2, 39.9, 32.8, 26.3, 23.4, 22.1, 14.0, 8.5.

HRMS (ESI) Calcd for $C_{15}H_{28}NO_2^+$ [M+H]$^+$: 254.2115, found: 254.2119.

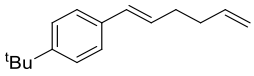


***(E)*-9-(3,3-dimethylbut-1-en-1-yl)-9H-carbazole (37):** Following the general procedure 1 (t = 24 h), obtained in 61% yield as a white solid (30.5 mg, eluent: petroleum ether).

^{1}H NMR (400 MHz, CD_3COCD_3) δ 8.15 (d, J = 7.8 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.47 (t, J = 8.3 Hz, 2H), 7.26 (t, J = 7.5 Hz, 2H), 7.05 (d, J = 14.5 Hz, 1H), 6.30 (d, J = 14.5 Hz, 1H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, CD_3COCD_3) δ141.1, 136.2, 127.4, 124.7, 121.4, 121.3, 121.2, 111.5, 33.8, 30.6.

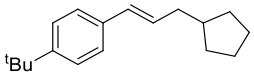
MS (ESI) Calcd for $C_{18}H_{20}N_2^+$ $[M+H]^+$: 250.1590, found: 250.1596.



***(E)*-1-(tert-butyl)-4-(hexa-1,5-dien-1-yl)benzene (38):** Following the general procedure 1 (t = 36 h), obtained in 55% yield as a colorless liquid (23.5 mg, eluent: petroleum ether). (Ref: *Chem. Commun.* **2012**, *48*, 8709–8711)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 4H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.27 – 6.12 (m, 1H), 5.91 – 5.81 (m, 1H), 5.07 – 4.97 (m, 2H), 2.33 – 2.19 (m, 4H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 138.2, 135.0, 129.9, 129.4, 125.7, 125.4, 114.9, 34.5, 33.7, 32.5, 31.3.

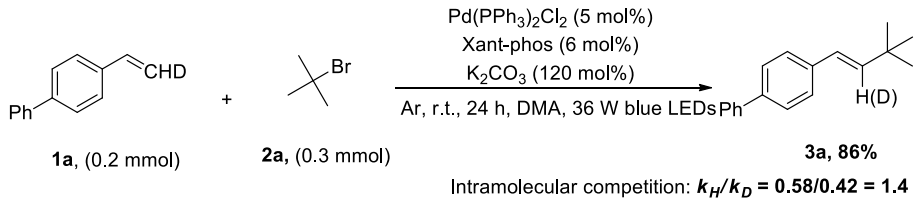


***(E)*-1-(tert-butyl)-4-(3-cyclopentylprop-1-en-1-yl)benzene (39):** Following the general procedure 1 (t = 36 h), obtained in 62% yield as a colorless liquid (30.0 mg, eluent: petroleum ether:ethyl acetate = 10:1). (Ref: *J. Am. Chem. Soc.* **2015**, *137*, 4932−4935)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (q, *J* = 8.6 Hz, 4H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.19 (dt, *J* = 15.7, 7.1 Hz, 1H), 2.19 (t, *J* = 7.1 Hz, 2H), 1.93 (dt, *J* = 15.0, 7.6 Hz, 1H), 1.78 – 1.74 (m, 2H), 1.64 – 1.49 (m, 4H), 1.31 (s, 9H), 1.24 – 1.11 (m, 2H).

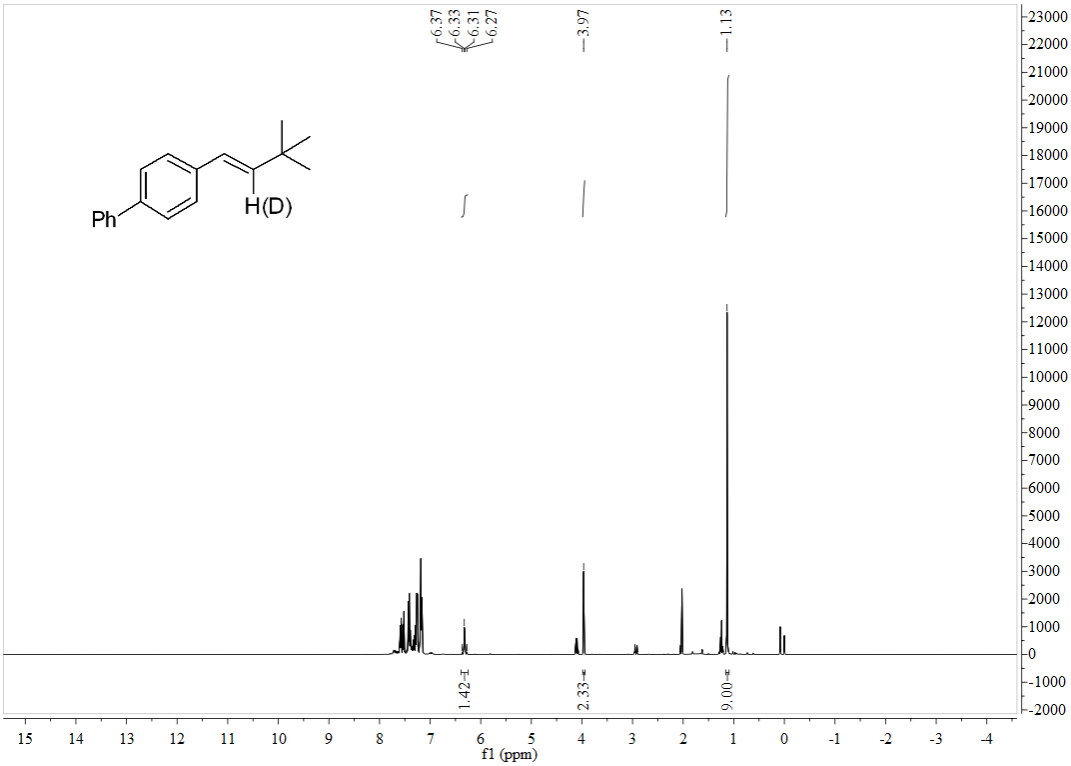
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 135.3, 129.8, 128.6, 125.6, 125.4, 40.1, 39.5, 34.5, 32.3, 31.4, 25.2.

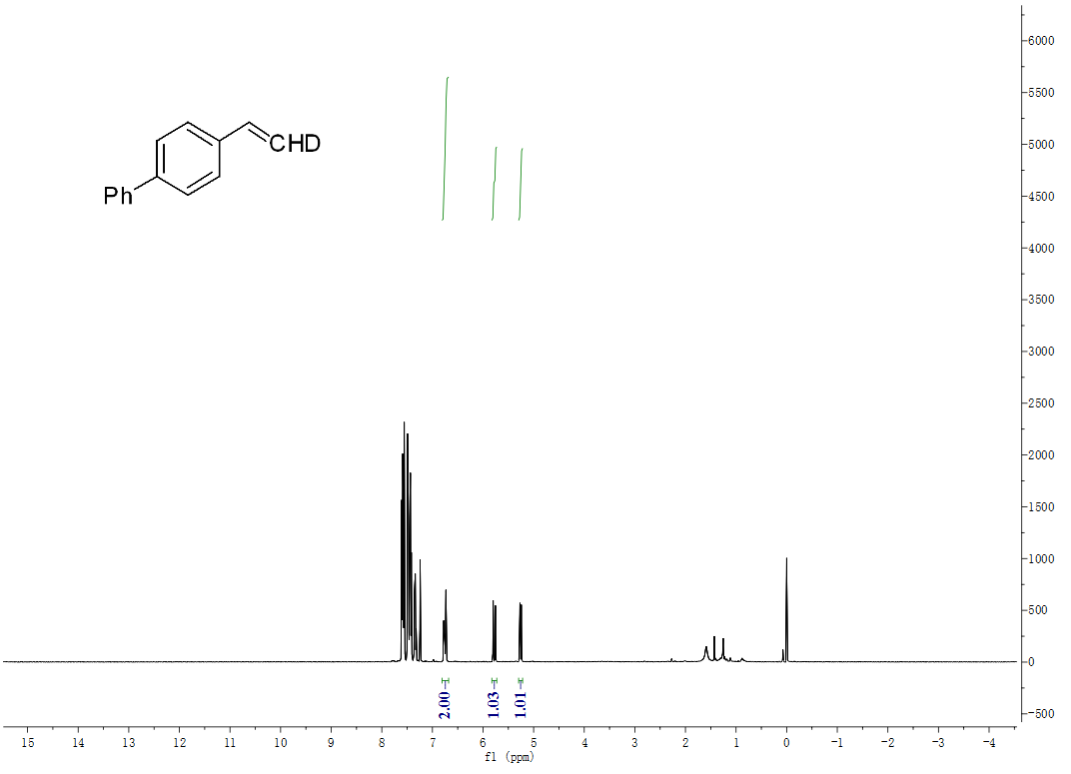
Investigation of the Mechanism



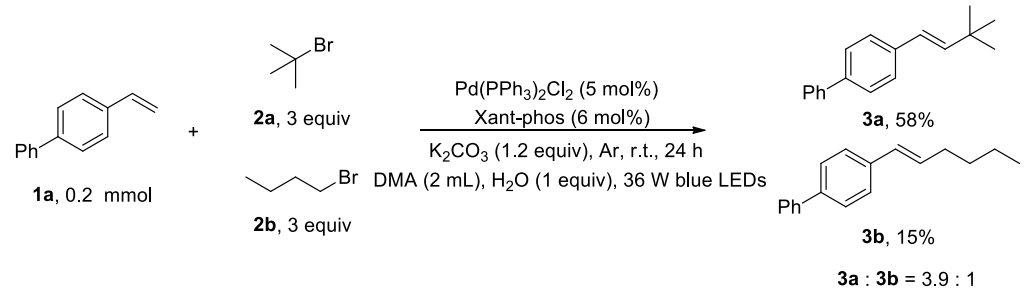
Intramolecular competition: k_H/k_D = 0.58/0.42 = 1.4

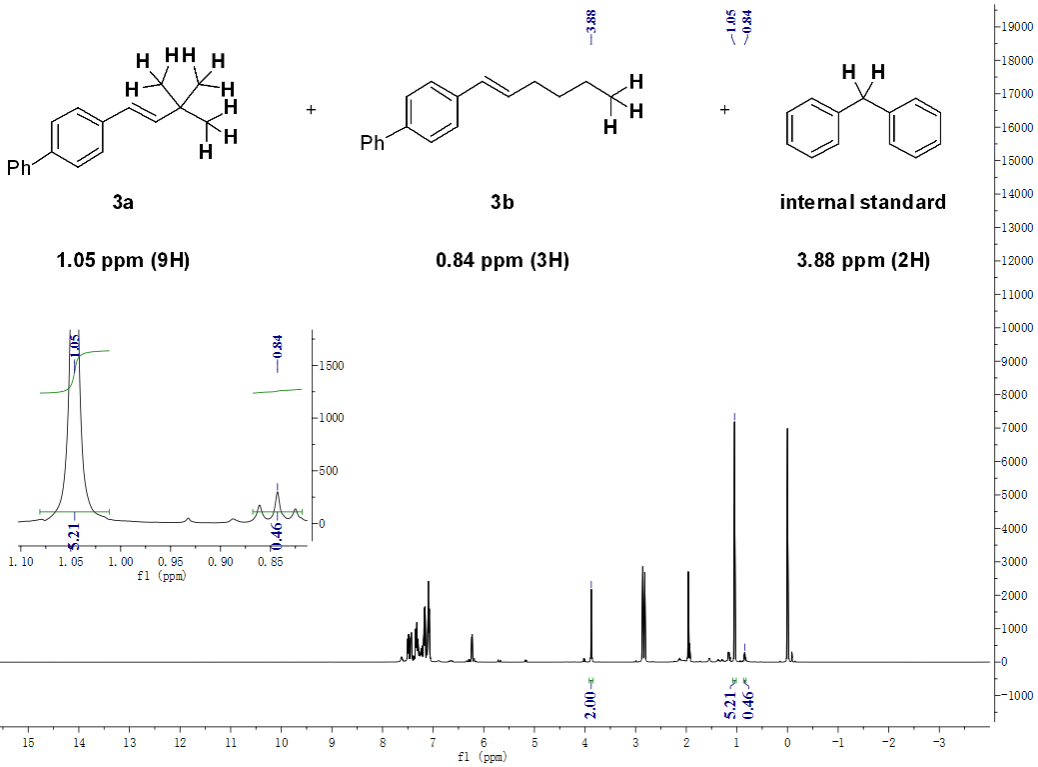
1a (1.0 equiv., 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol %, 7 mg) and Xant-phos (6 mol %, 6.9 mg), K_2CO_3 (0.24 mmol, 33mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids, **2a** (1.5 equiv., 0.3 mmol), and anhydrous DMA (2.0 mL) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under the irradiation of a 36 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 24 h. After reaction completed, the mixture was quenched with saturated NaCl solution and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. Yield determined by ^1H NMR using diphenylmethane as an internal standard.


6.37
6.33
6.31
6.27
3.97
1.13
Ph
H(D)
1.42
2.33
9.00
f1 (ppm)


CHD
Ph
2.00
1.03
1.01
f1 (ppm)

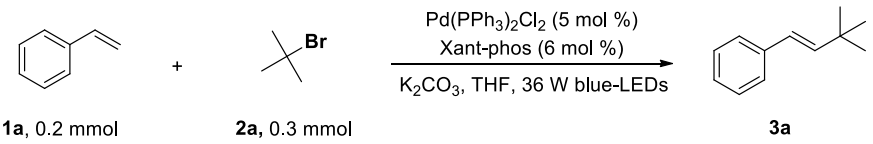
5. Competitive Reaction





1a (1.0 equiv., 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol %, 7 mg) and Xant-phos (6 mol %, 6.9 mg), K_2CO_3 (0.24 mmol, 33mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids, **2a** (3 equiv., 0.6 mmol), **3a** (3 equiv., 0.6 mmol) and anhydrous DMA (2.0 mL) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under the irradiation of a 36 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 24 h. After reaction completed, the mixture was quenched with saturated NaCl solution and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. Yield determined by ^1H NMR using diphenylmethane as an internal standard

6. X-ray Photoelectron Spectroscopy (XPS) Data



1a, 0.2 mmol **2a,** 0.3 mmol **3a**

$Pd(PPh_3)_2Cl_2$ (5 mol %, 7 mg) and Xant-phos (6 mol %, 6.9 mg), K_2CO_3 (1.2 equiv., 0.24 mmol) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids, **1a** (1.0 equiv., 0.2 mmol), **2a** (1.5 equiv., 0.3 mmol), anhydrous Tetrahydrofuran (THF, 2.0 mL) was added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under the irradiation of a 36 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 12 h. After 12 h, the reaction was concentrated under N_2. The resulting powder was analyzed by synchrotron radiation induced photoemission spectroscopy (SRPES) in National Synchrotron Radiation Laboratory with VG-Scienta R3000 as the Electron energy analyzer. (Note: all the XPS experiments were carried out under vacuum atmosphere)

The XPS showed that peak corresponding to $\mathbf{Pd^{II}}$ was observed with the binding energy at **337.3 eV**，which were negatively shifted by **0.2 eV** compared with free $Pd(PPh_3)_2Cl_2$ (***Pd^{II} at 337.5 eV***). (shown in Figure S1)

The XPS showed that peak corresponding to $\mathbf{Pd^{I}}$ was observed with the binding energy at **336.3 eV**. (shown in Figure S1)

The XPS showed that peak corresponding to $\mathbf{Pd^{0}}$ was observed with the binding energy at **335.3 eV** which were negatively shifted by **0.2 eV** compared with the standard value (***Pd^{0} at 335.1 eV***). (shown in Figure S1)

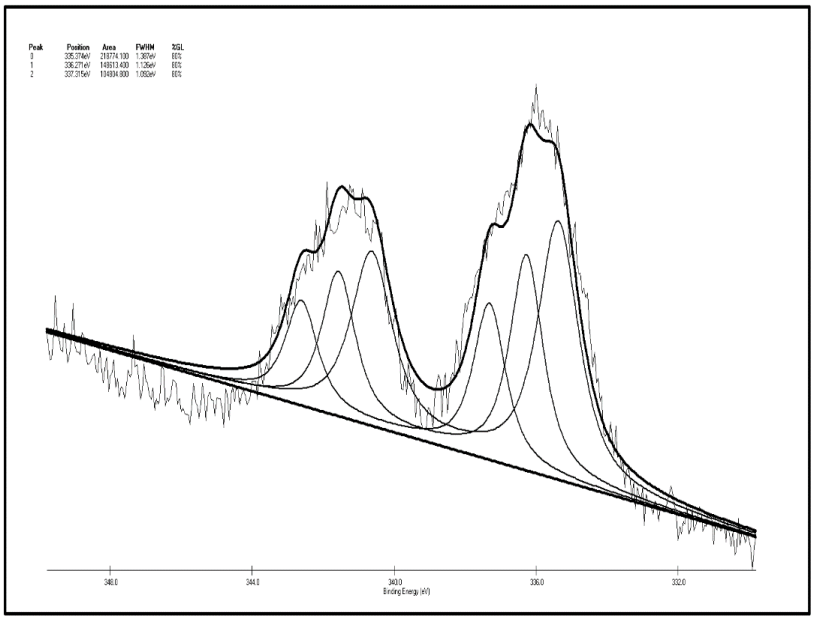
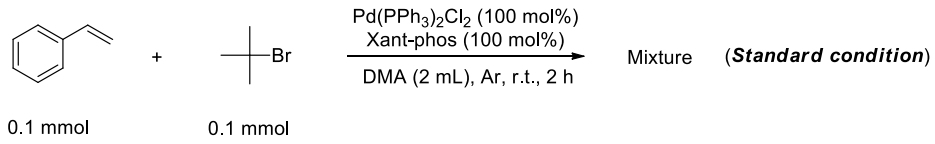


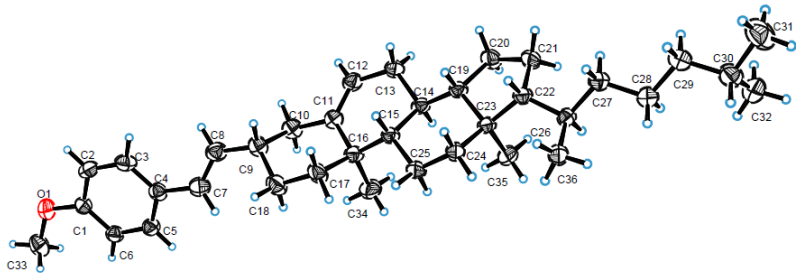
Figure S1 The X-ray Photoelectron Spectroscopy (XPS) Data of the Reaction Mixture

7. UV-vis. Data



UV/Vis measurements were conducted with a mixture of stoichiometric amounts of palladium salts and ligands. It was observed that the reaction mixture exhibits a clear absorption peak centered at 350 nm with absorption onset that overlaps with the blue LED wavelength (460 nm). This absorption onset explains the best performance of the blue LED among other irradiation sources. Removing styrene from the reaction mixture did not change the absorption wavelength or intensity, whereas removing tert-butyl bromide and removing Xantphos caused a reduction in the absorption intensity and a hypochromic absorption shift of about 5 nm. An important observation is that when $Pd(PPh_3)_2Cl_2$ was removed from the reaction mixture, the absorption peak at around 350 nm disappeared, revealing that the absorption peak of lmax = 350 nm with an onset around 460 nm originates from the palladium intermediate form in the reaction mixture. To verify this conclusion, we also measured the absorption spectrum of $Pd(PPh_3)_2Cl_2$ and an absorption peak around 350 nm was observed. The measurement of UV/Vis absorption of $Pd(PPh_3)_4$ gives a broadened absorption band extending from the visible region to the UV region, revealing that irradiation by blue LEDs can also excite the Pd(0) phosphine complex, which may facilitate single-electron oxidative addition. Irradiation with suitable wavelengths is crucial for the reaction as demonstrated in optimization studies because low-energy irradiation (such as green LEDs) does not excite the palladium complex, and higher energy irradiation (in the UV region) may cause decomposition of the intermediate and destroy the desired reaction process. We may conceive that an irradiation wavelength between that of purple and blue light may offer the best efficiency for this reaction, although this is currently limited by the irradiation sources available. Based on the absorption spectrum, these studies suggest that irradiation at different wavelengths should be considered as a parameter when optimizing palladium-catalyzed reactions induced by irradiation.

9. X-Ray Crystallographic Data



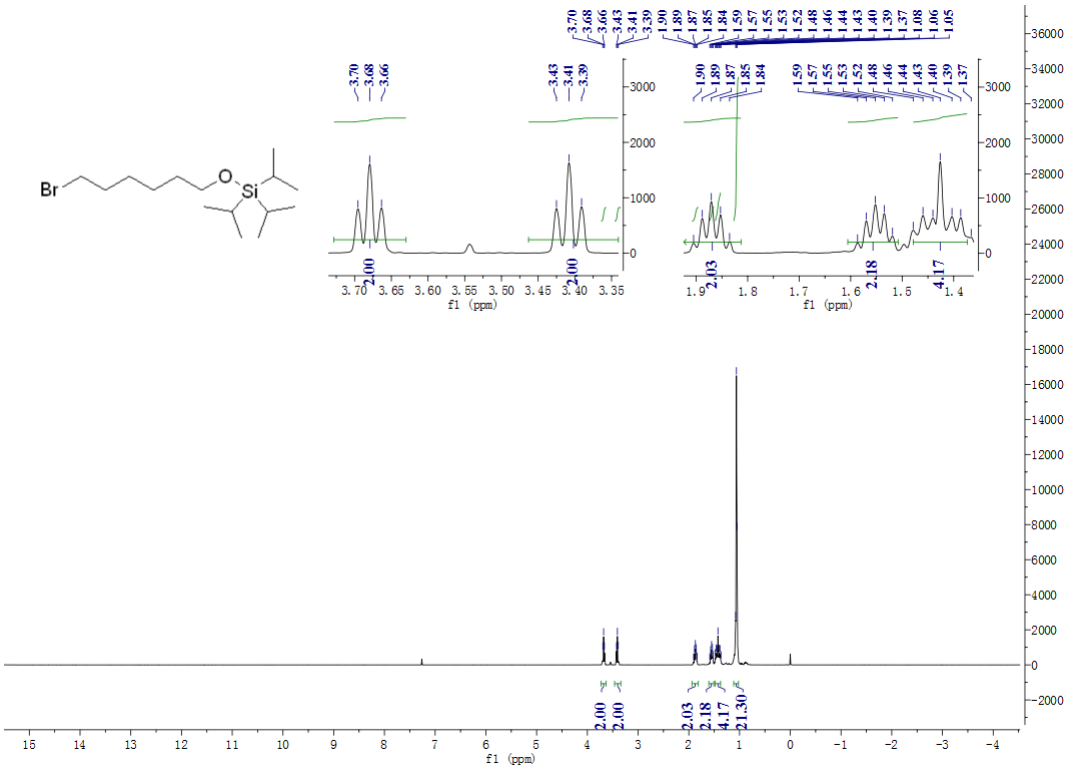
Crystal data and structure refinement for compound 13

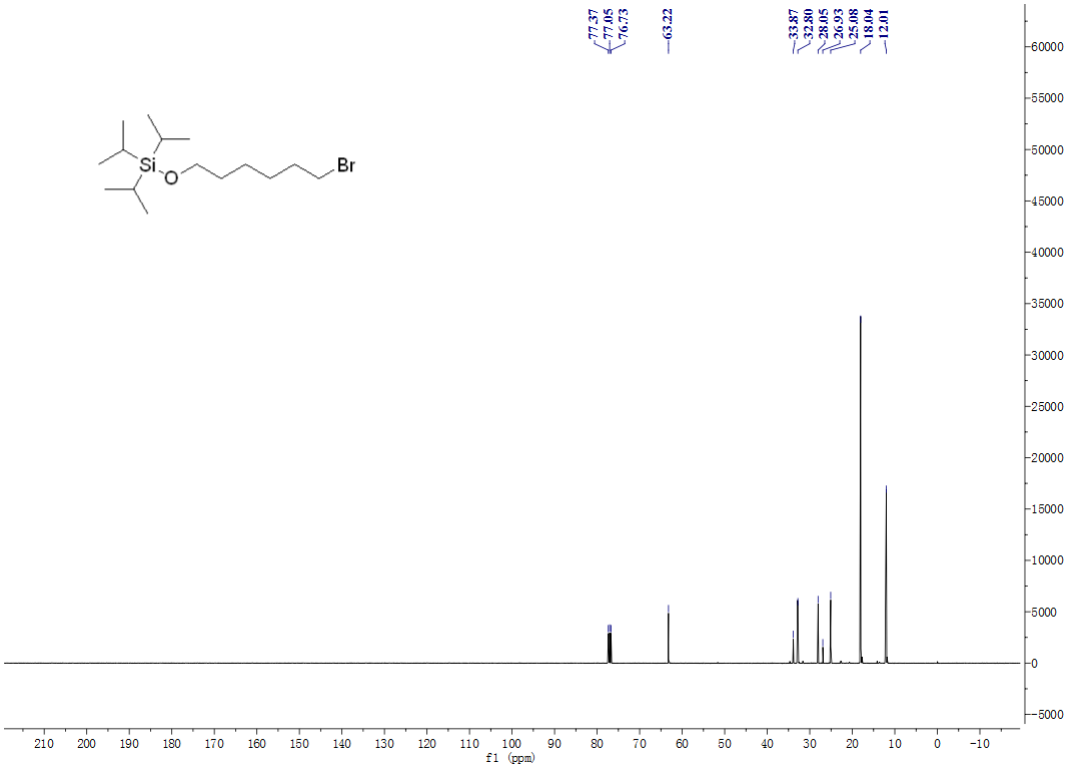
Empirical formula	$C_{36}H_{54}O$
Formula weight	502.79
Temperature/K	291(2)
Crystal system	triclinic
Space group	P1
a/Å	7.73350(10)
b/Å	14.1534(2)
c/Å	14.5834(2)
α/°	77.0050(10)
β/°	87.5840(10)
γ/°	89.6900(10)
Volume/Å^3	1553.95(4)
Z	2
ρ_{calc}g/cm^3	1.075
μ/mm^{-1}	0.460
F(000)	556.0
Crystal size/mm^3	0.280 × 0.250 × 0.220
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.87 to 142.658
Index ranges	$-9 \le h \le 9$, $-17 \le k \le 15$, $-17 \le l \le 17$
Reflections collected	41658
Independent reflections	11228 [R_{int} = 0.0235, R_{sigma} = 0.0145]
Data/restraints/parameters	11228/25/679
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0517, wR_2 = 0.1471
Final R indexes [all data]	R_1 = 0.0550, wR_2 = 0.1517

The CCDC number of this compound is 1560078.

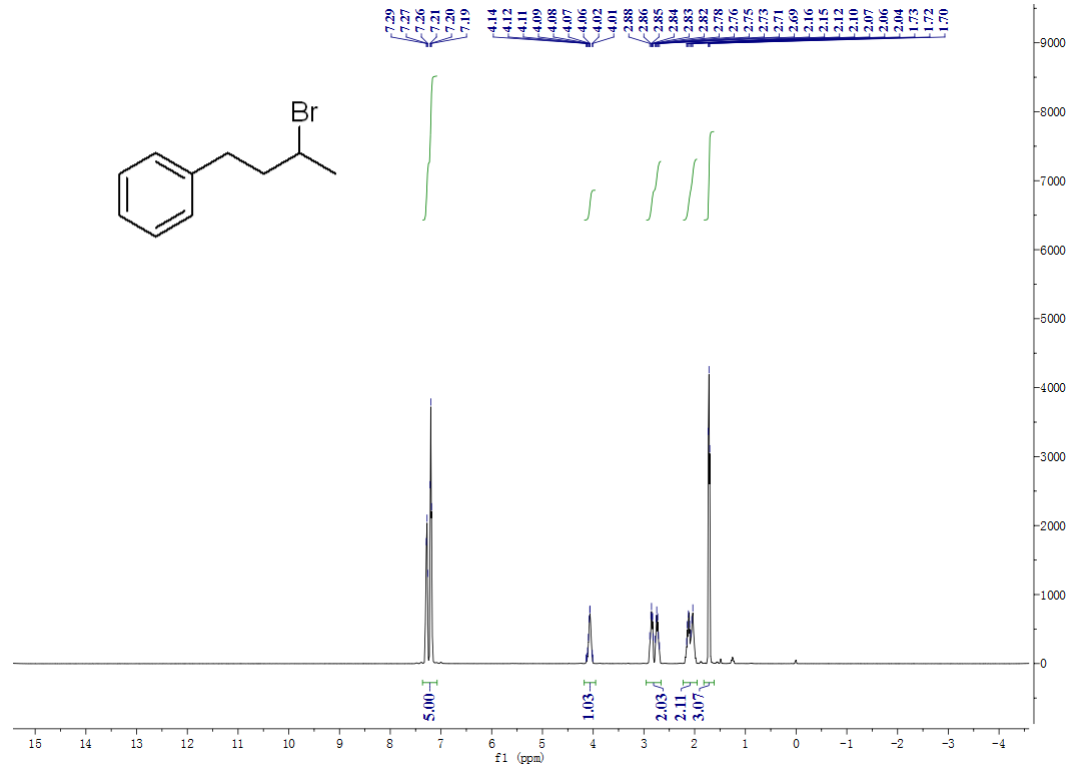
10. NMR Spectra

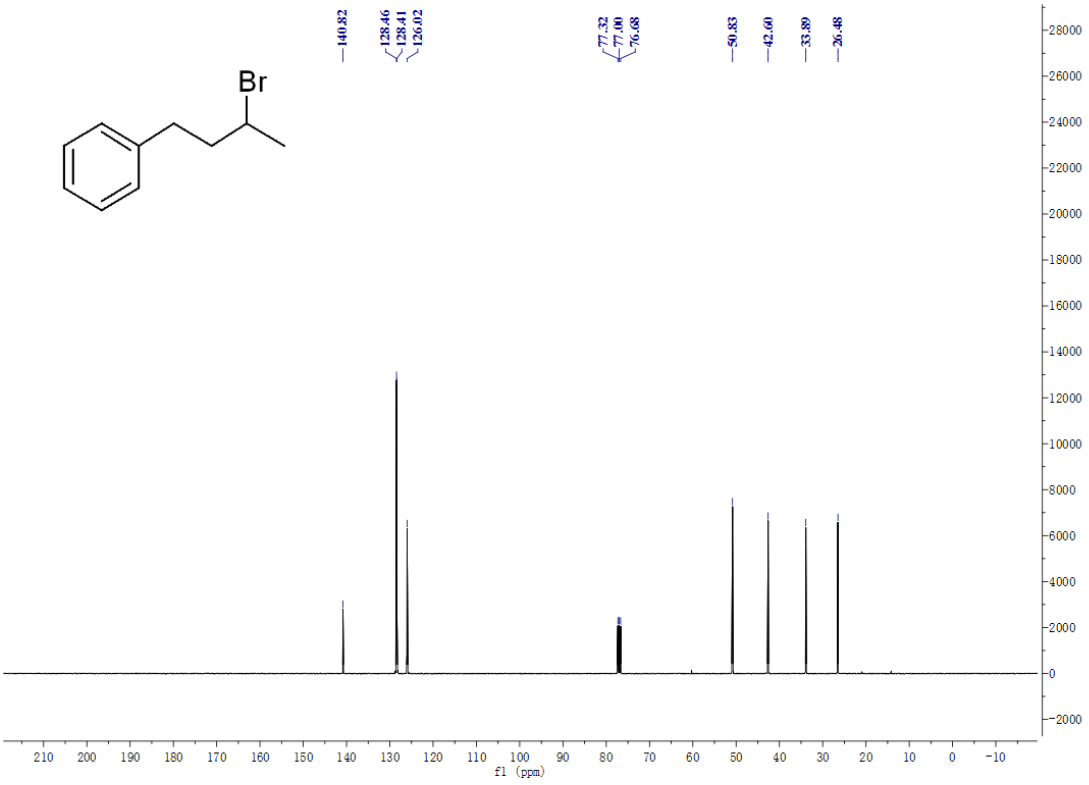
((6-bromohexyl)oxy)triisopropylsilane (S-1)



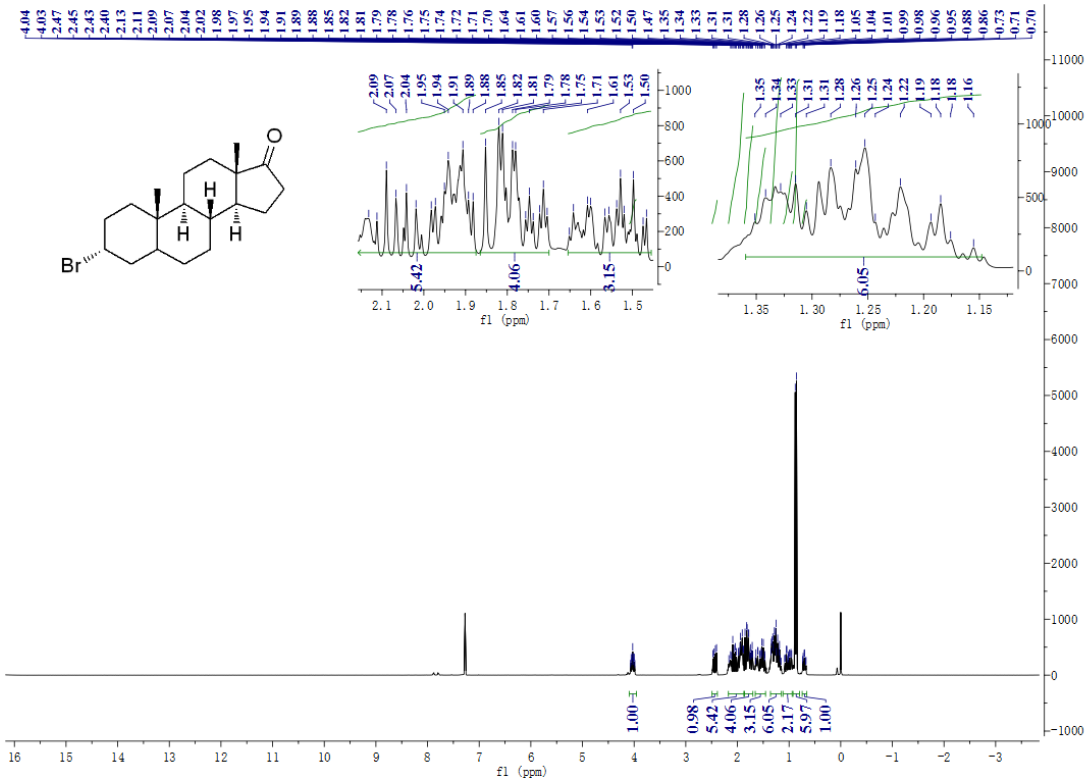


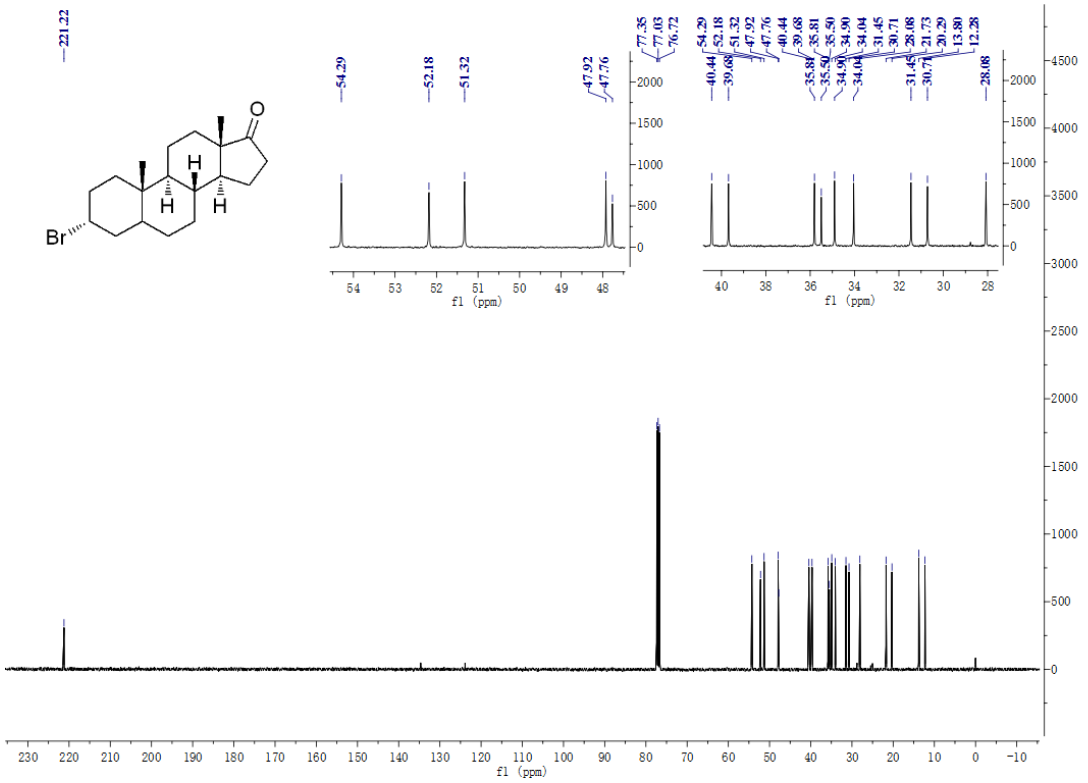
(3-bromobutyl)benzene (S-2)



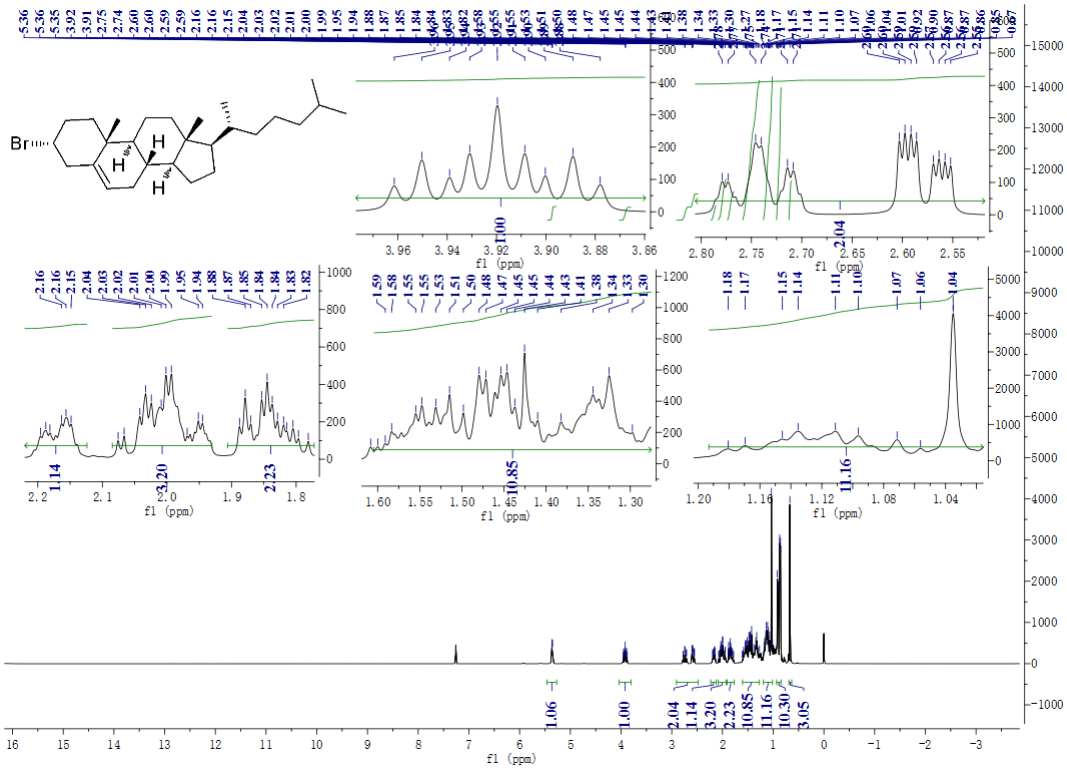


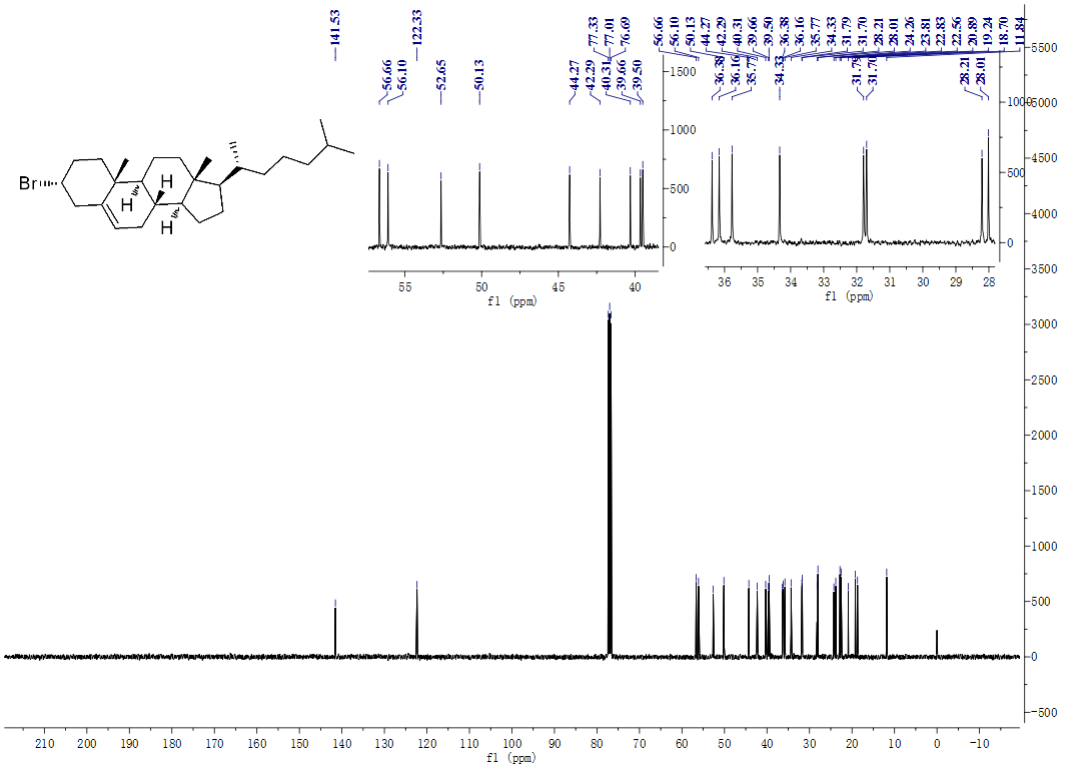
(3R,8R,9S,10S,13S,14S)-3-bromo-10,13-dimethyltetradecahydro-1H-cyclopenta a]phenanthren-17(2H)-one (S-3)



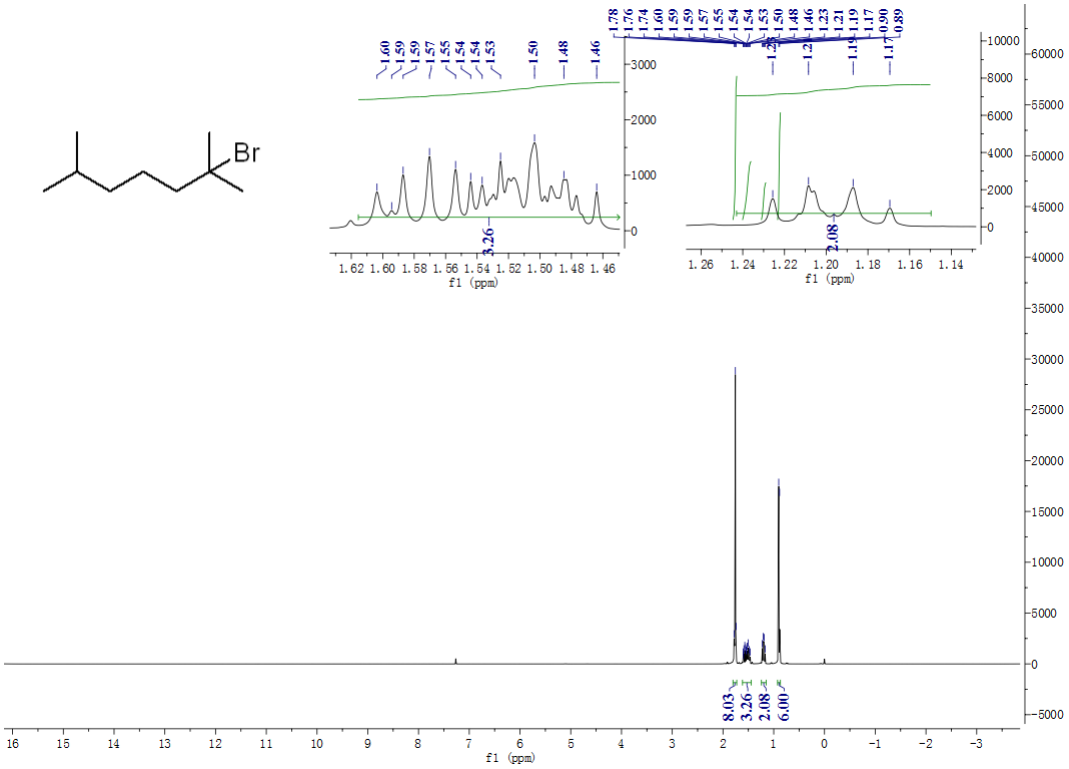


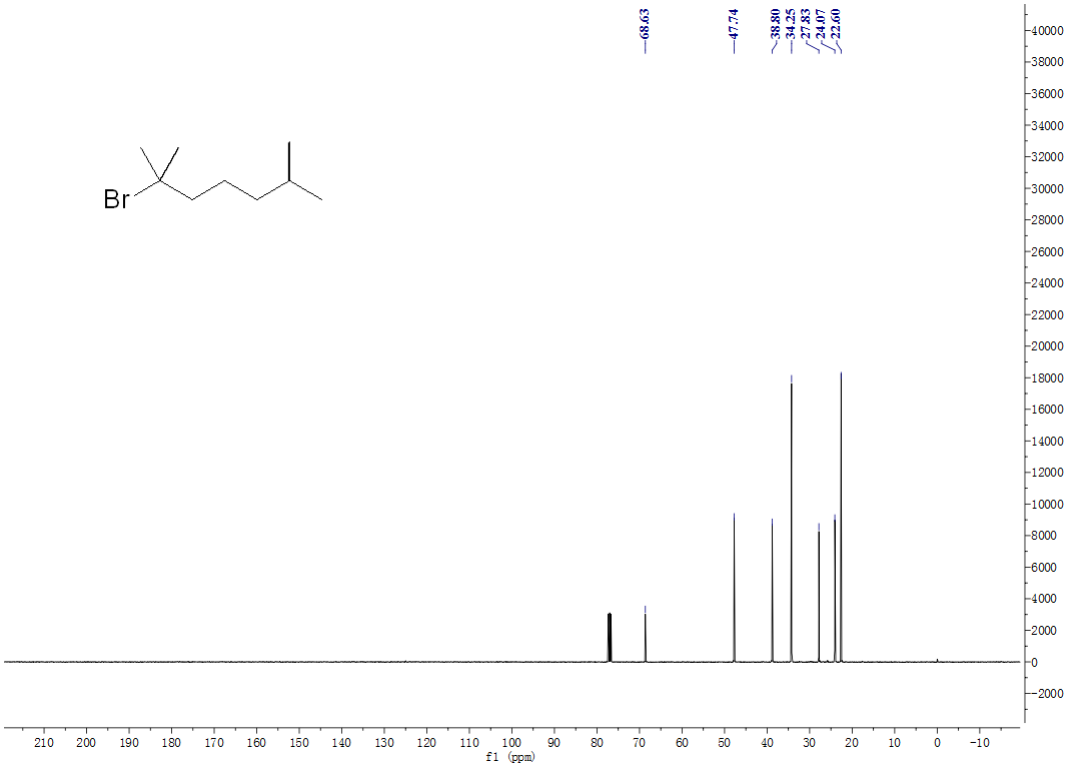
(3R,8S,9S,10R,13R,14S,17R)-3-bromo-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (S-4)



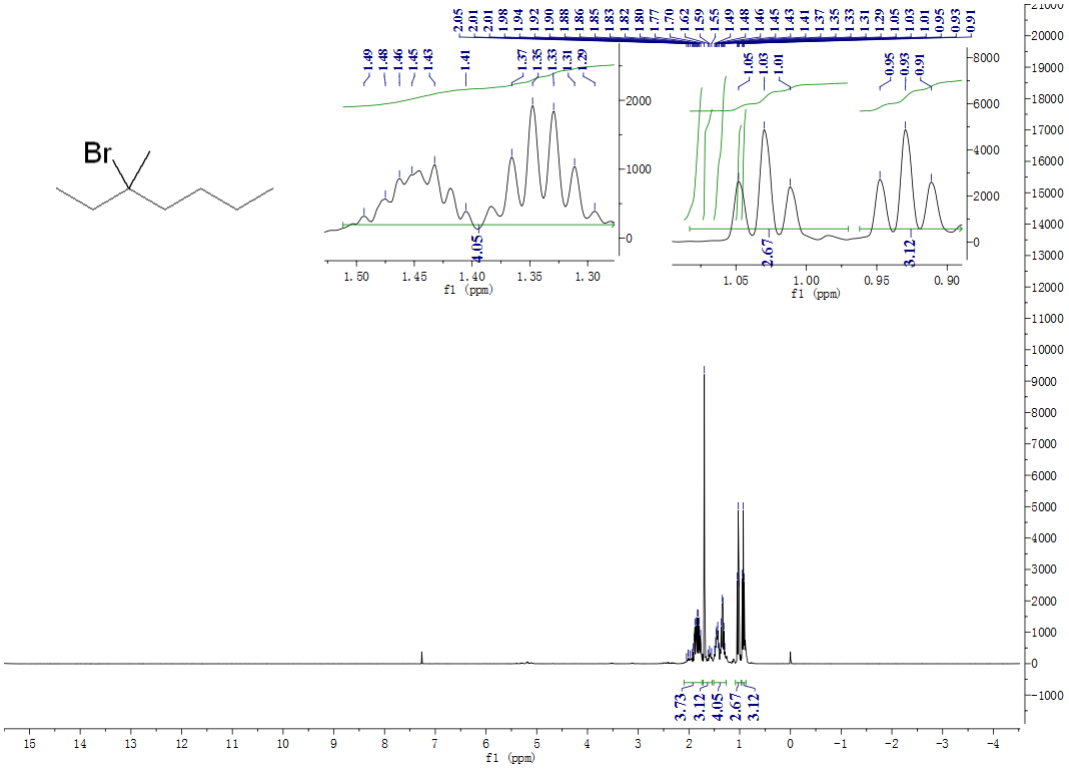


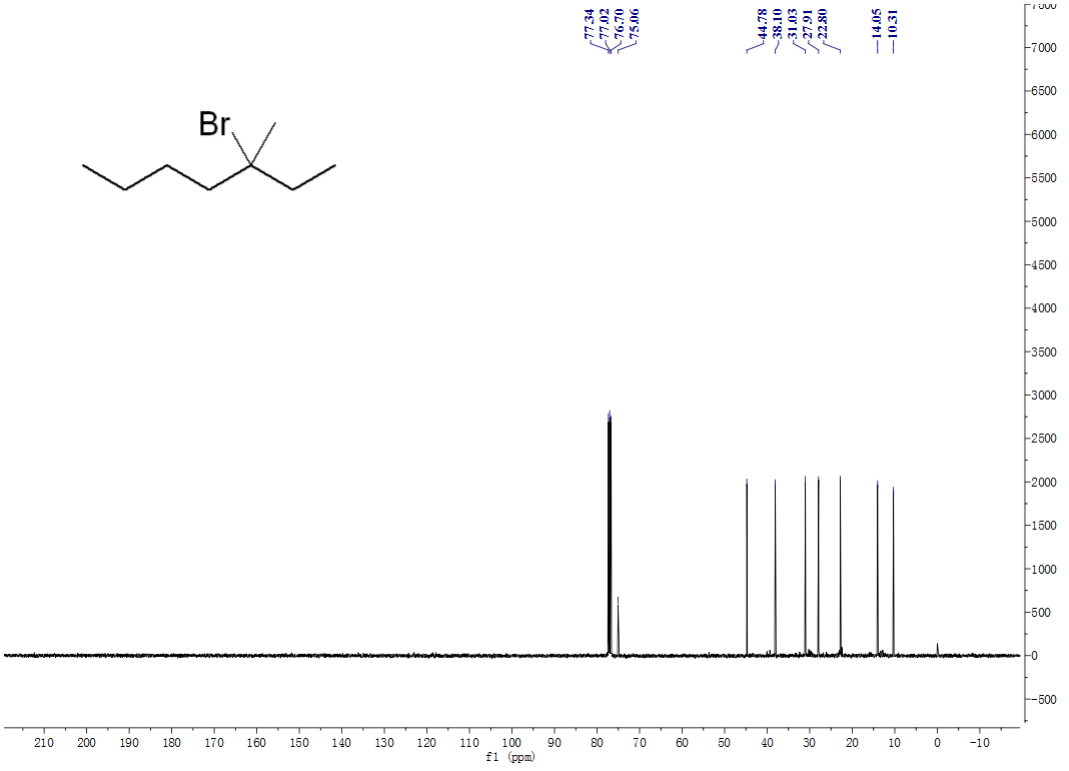
2-bromo-2,6-dimethylheptane (S-5)



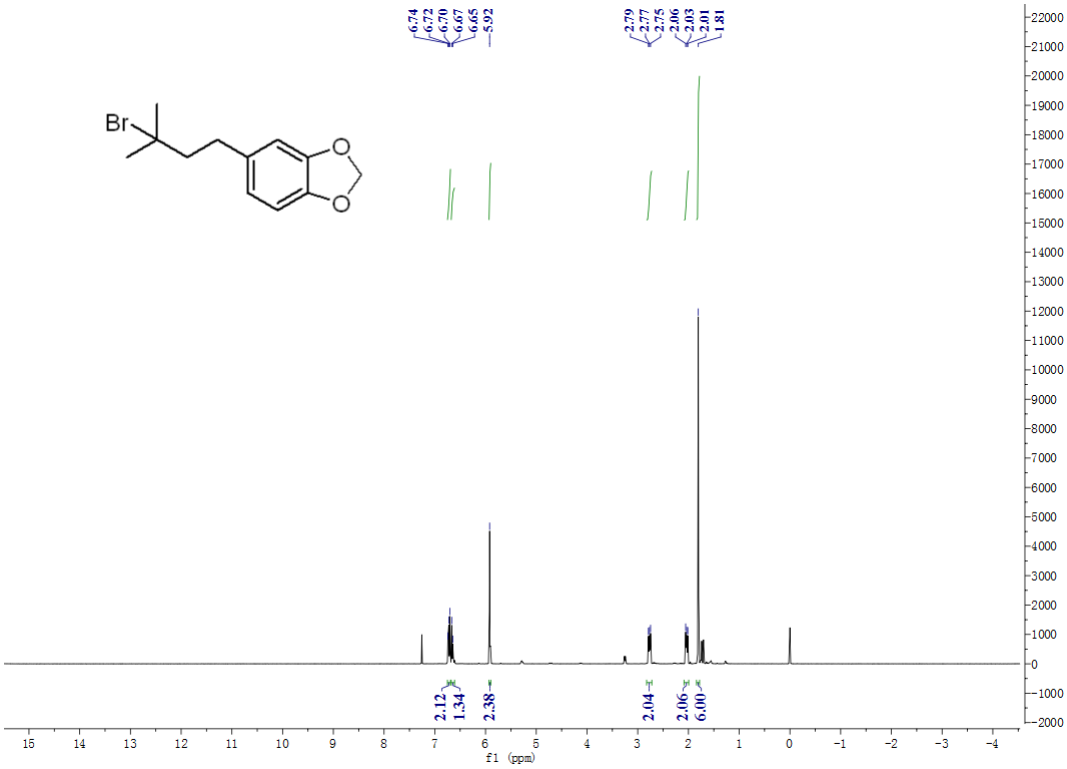


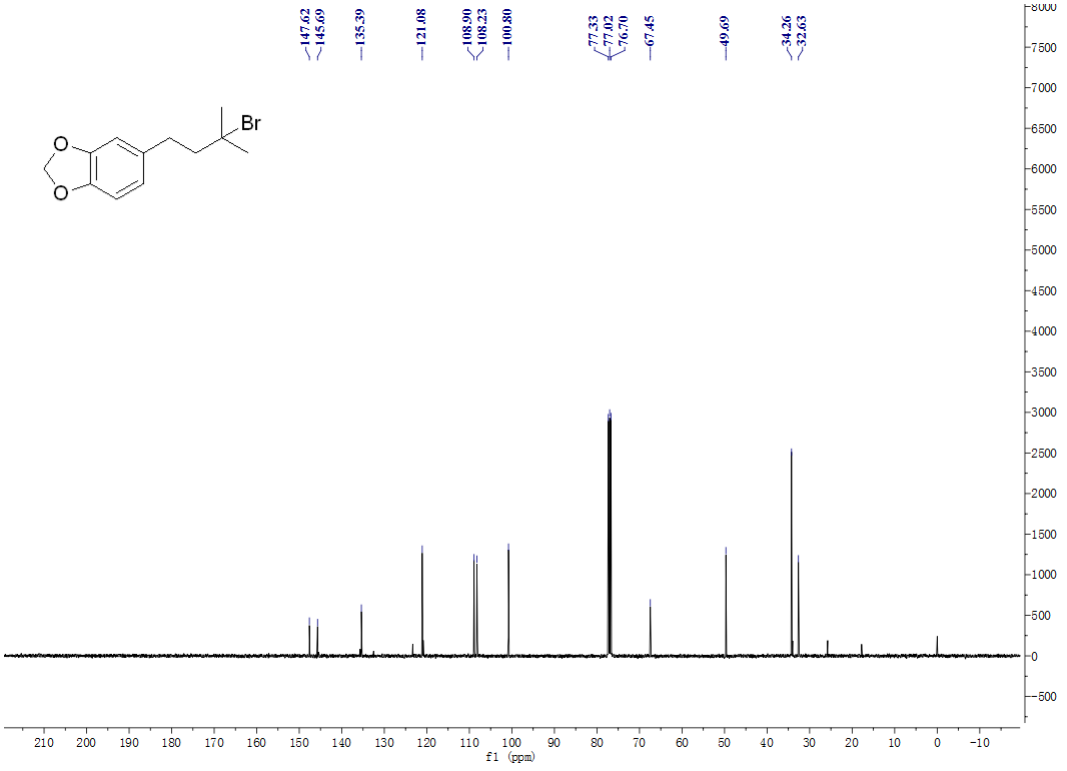
3-bromo-3-methylheptane (S-6)



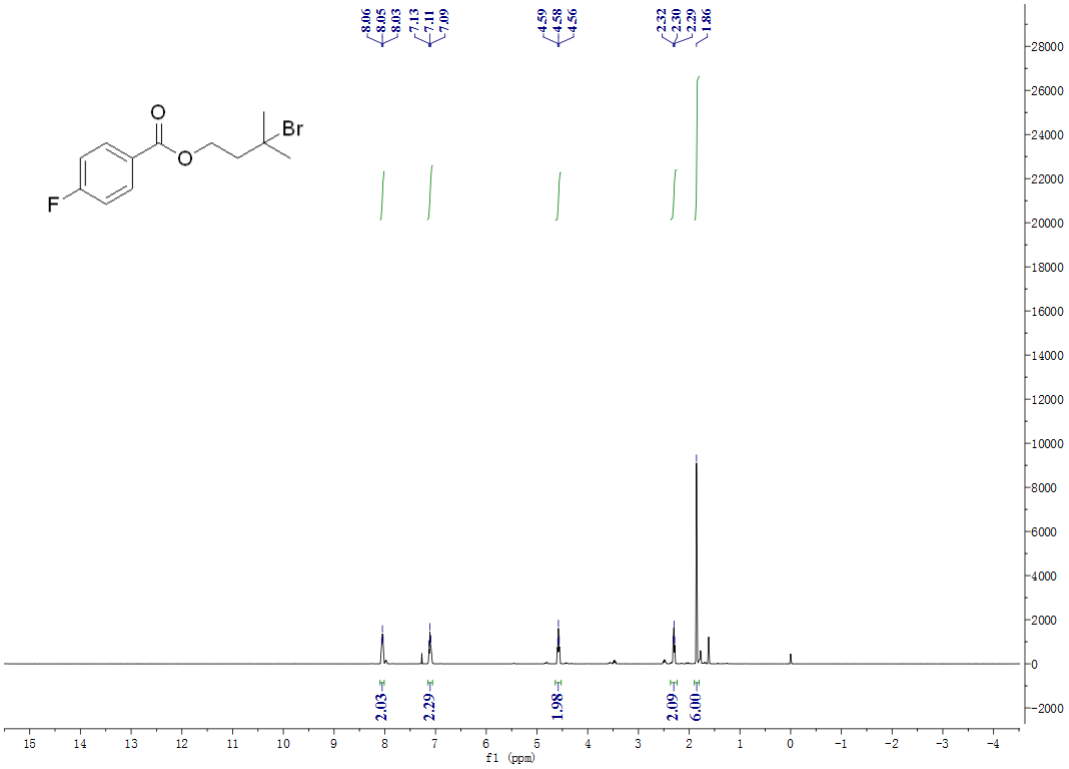


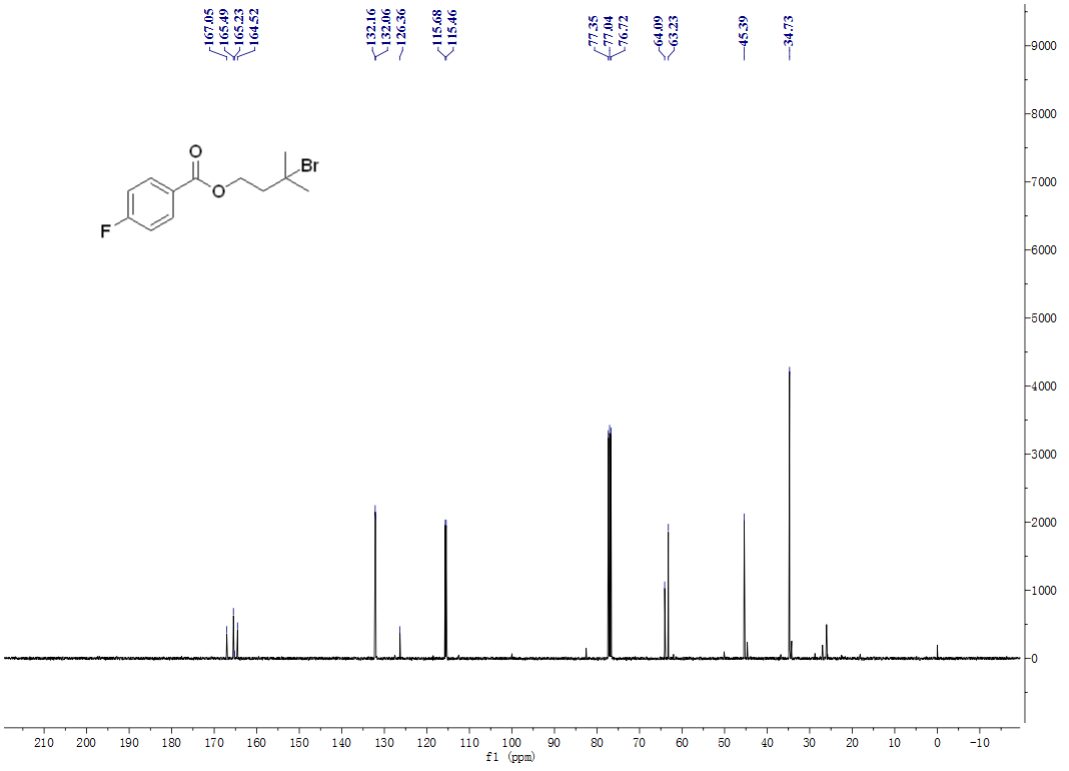
5-(3-bromo-3-methylbutyl)benzo[d][1,3]dioxole (S-7)



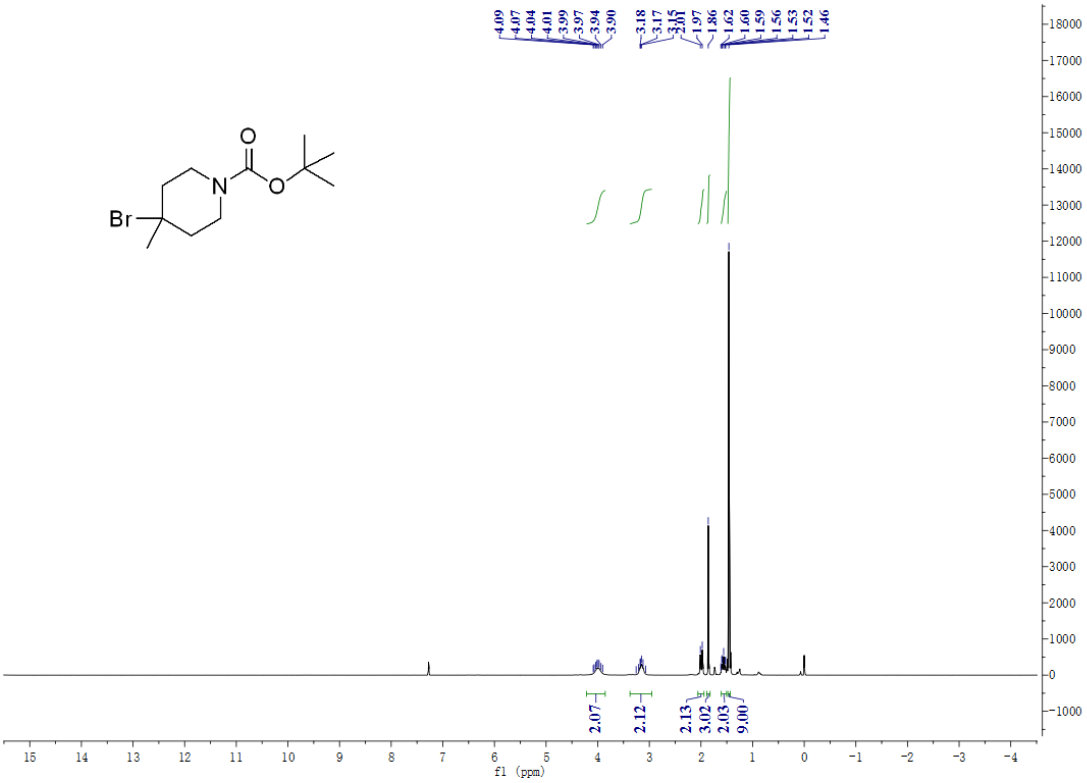


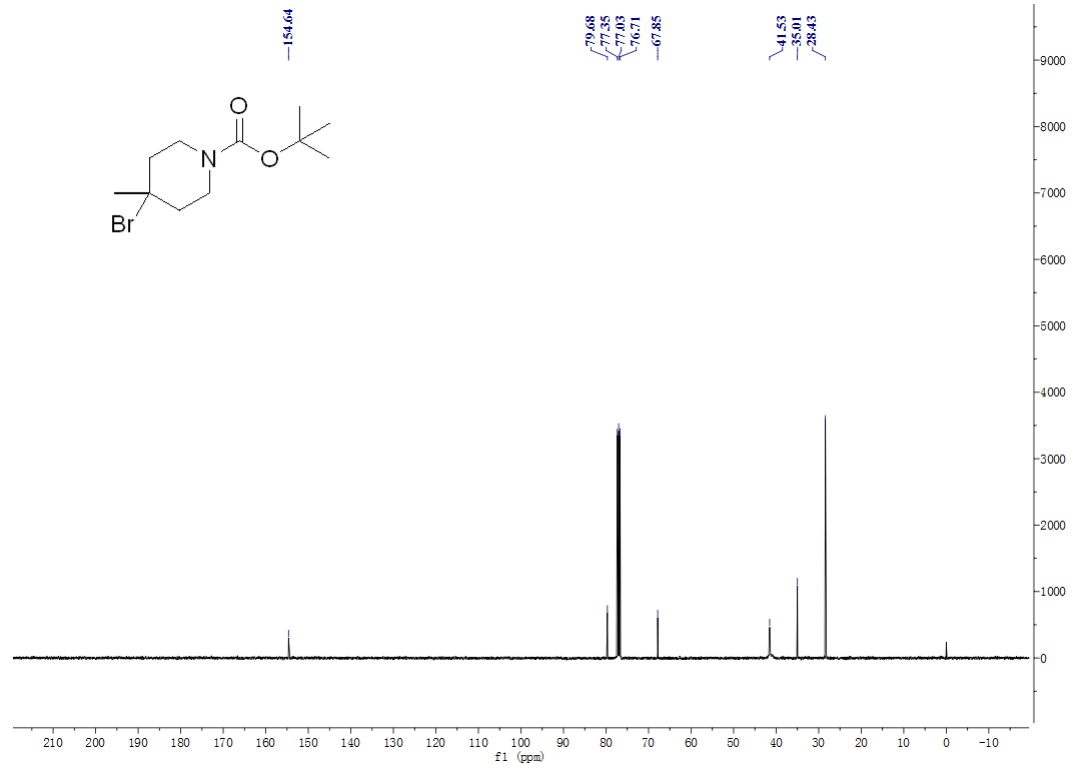
3-bromo-3-methylbutyl 4-fluorobenzoate (S-8)



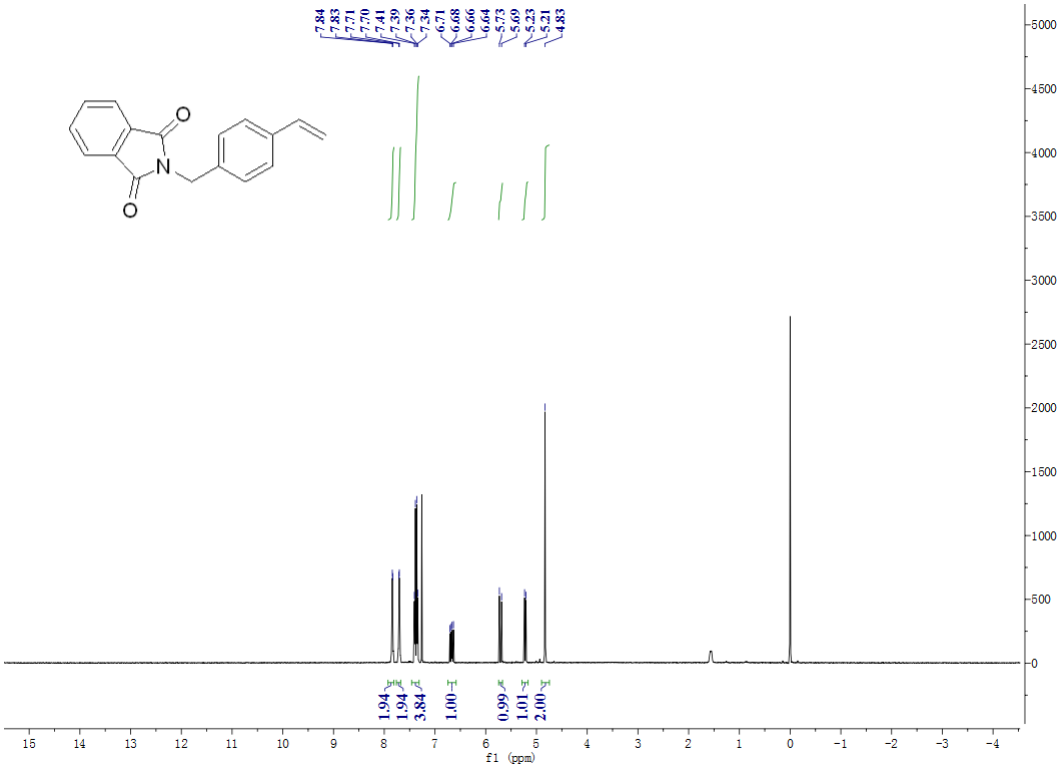


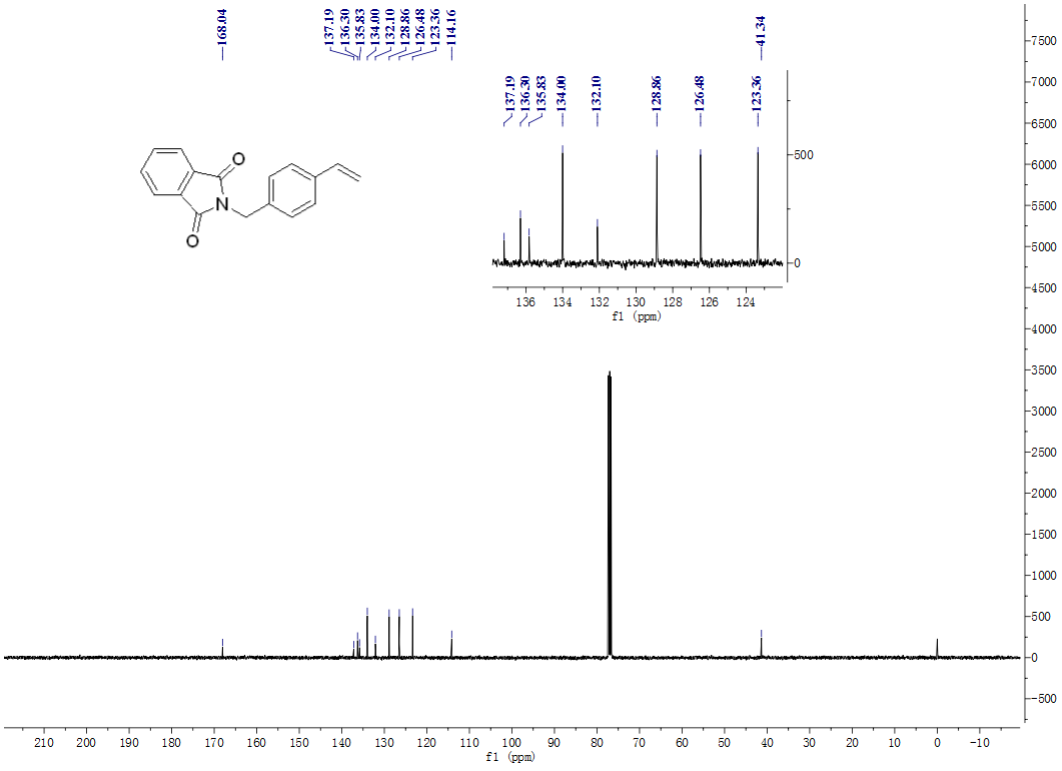
tert-butyl 4-bromo-4-methylpiperidine-1-carboxylate (S-9)



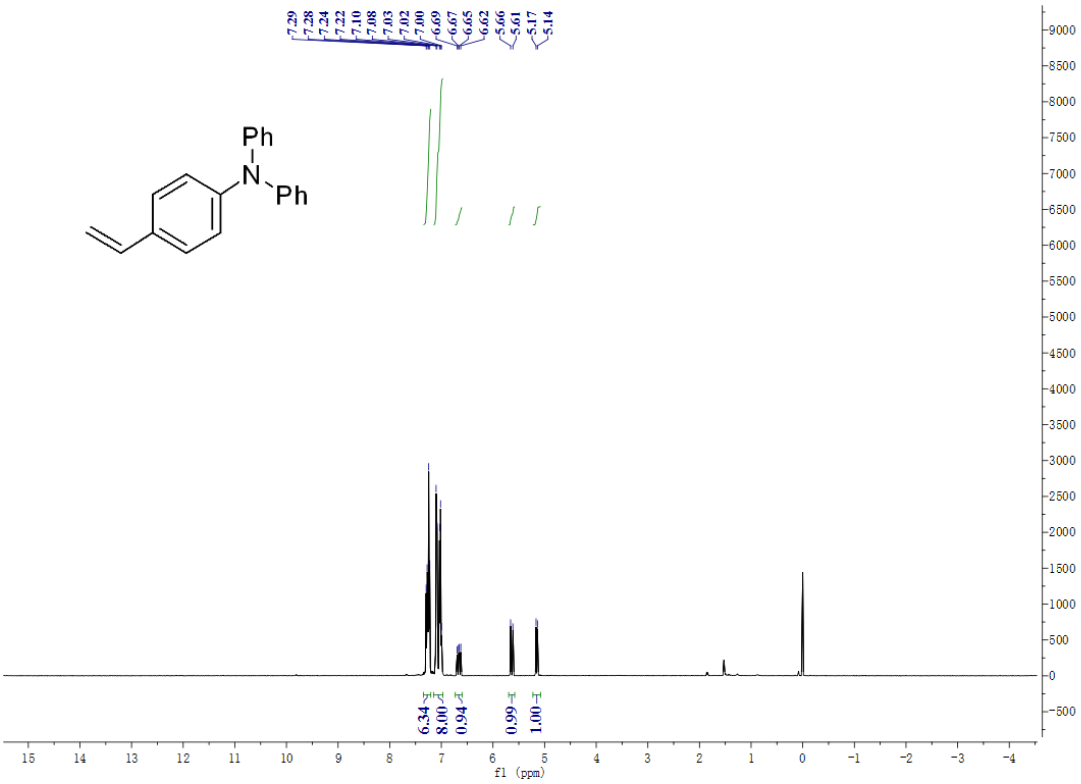


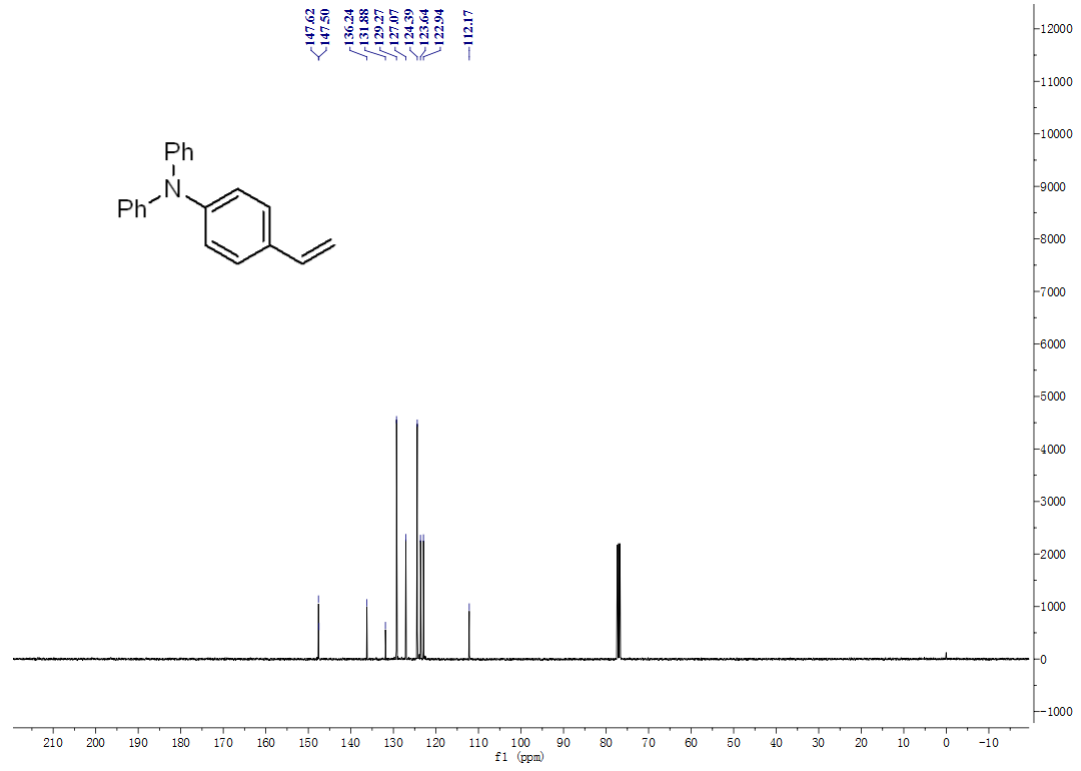
2-(4-vinylbenzyl)isoindoline-1,3-dione (S-10)



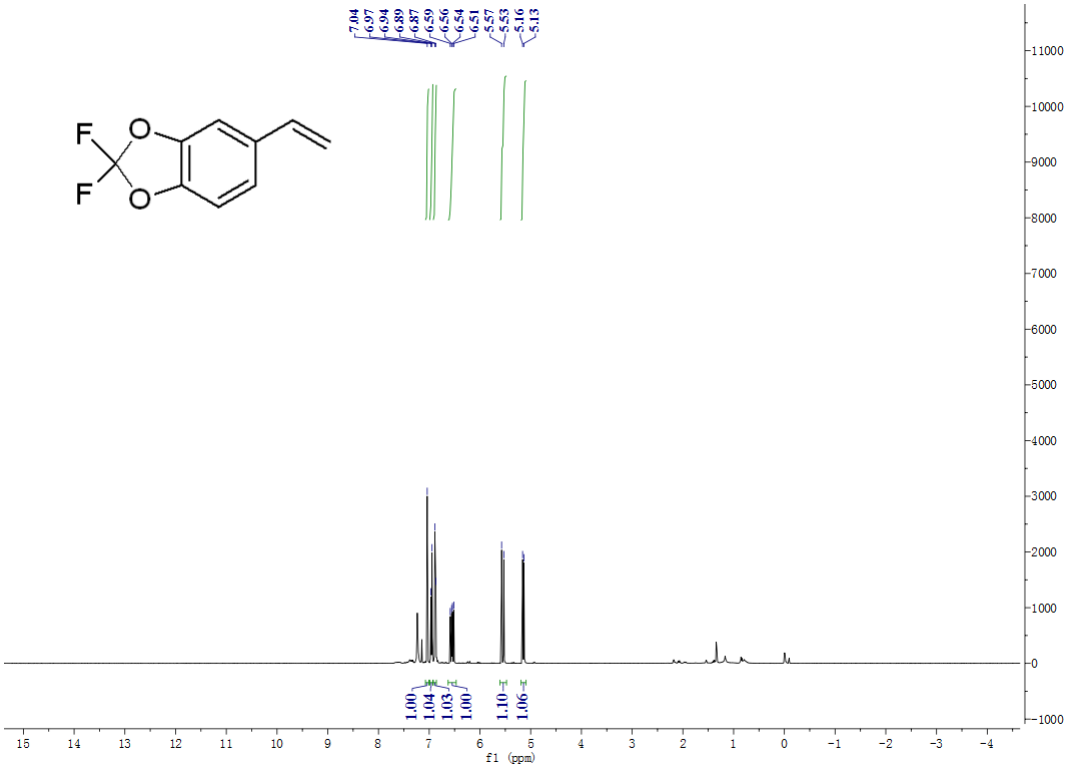


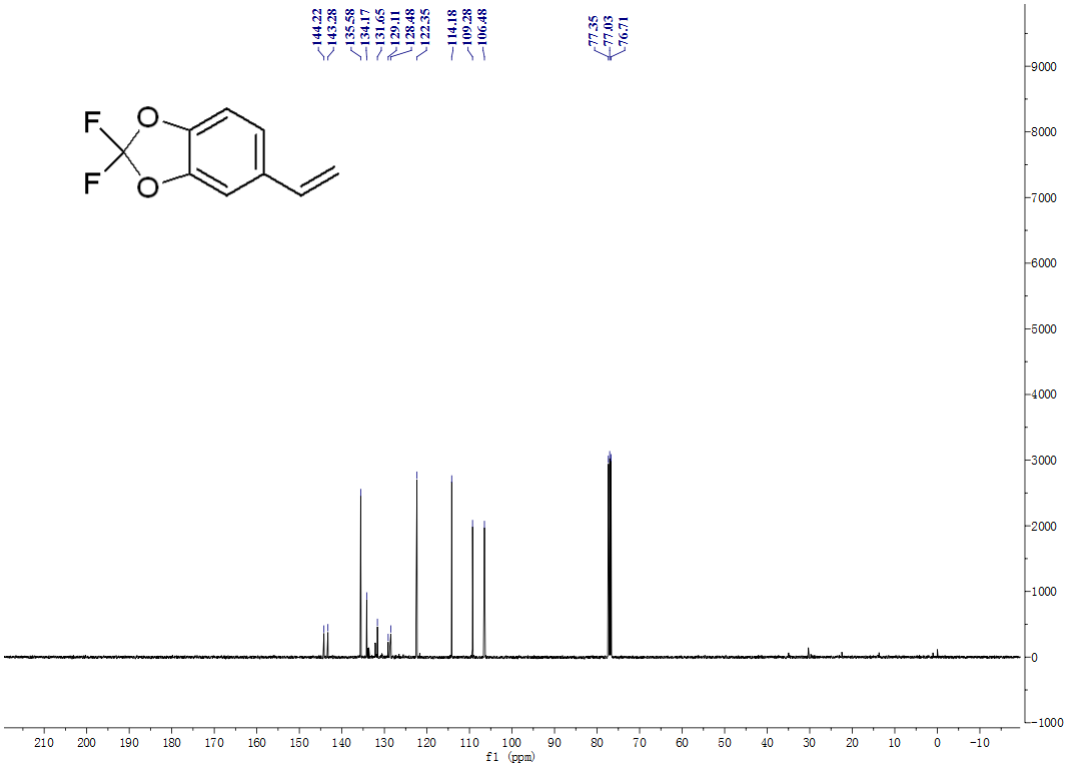
N,N-diphenyl-4-vinylaniline (S-11)



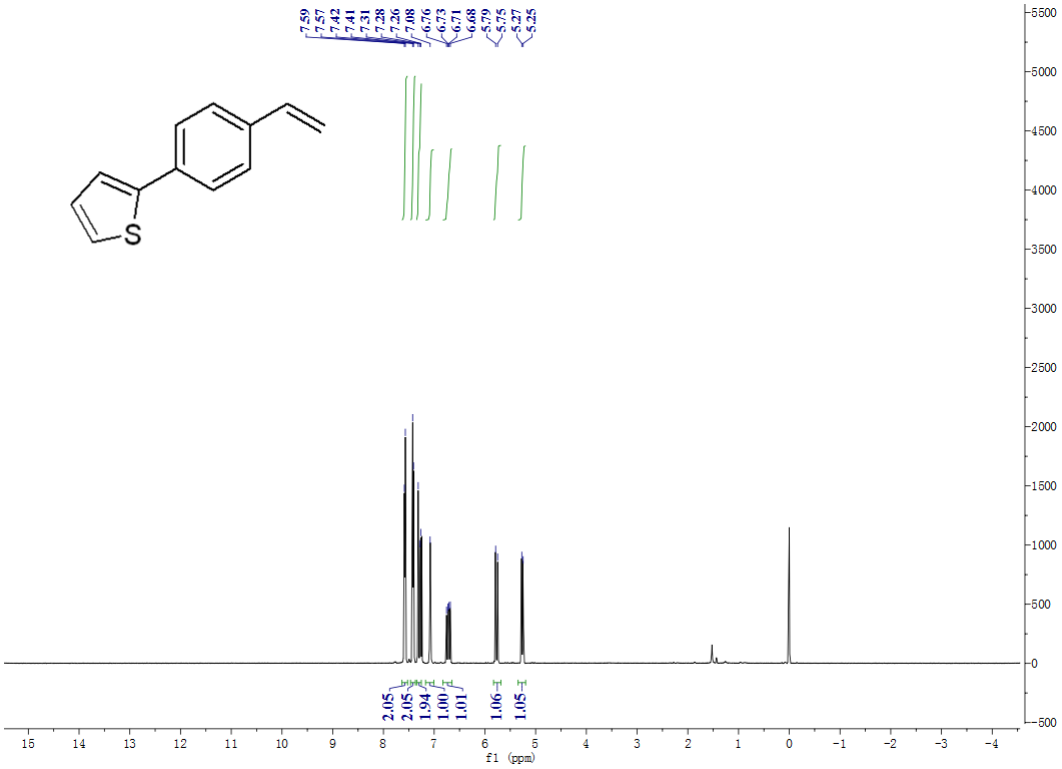


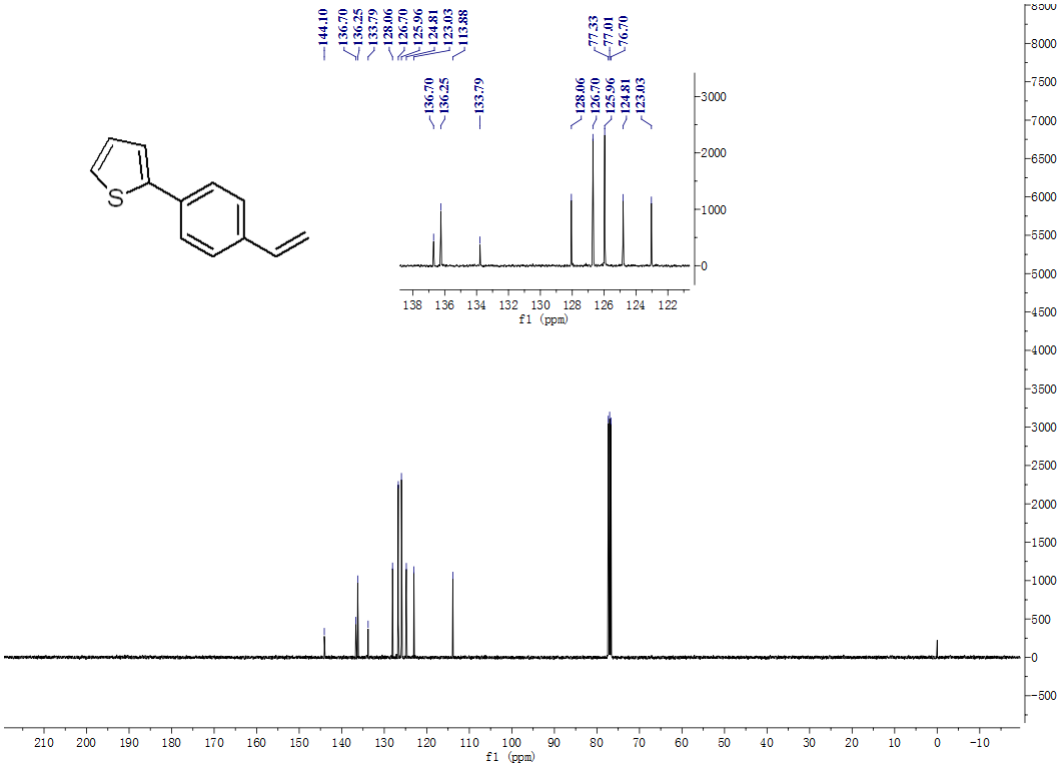
2,2-difluoro-5-vinylbenzo[d][1,3]dioxole (S-12)



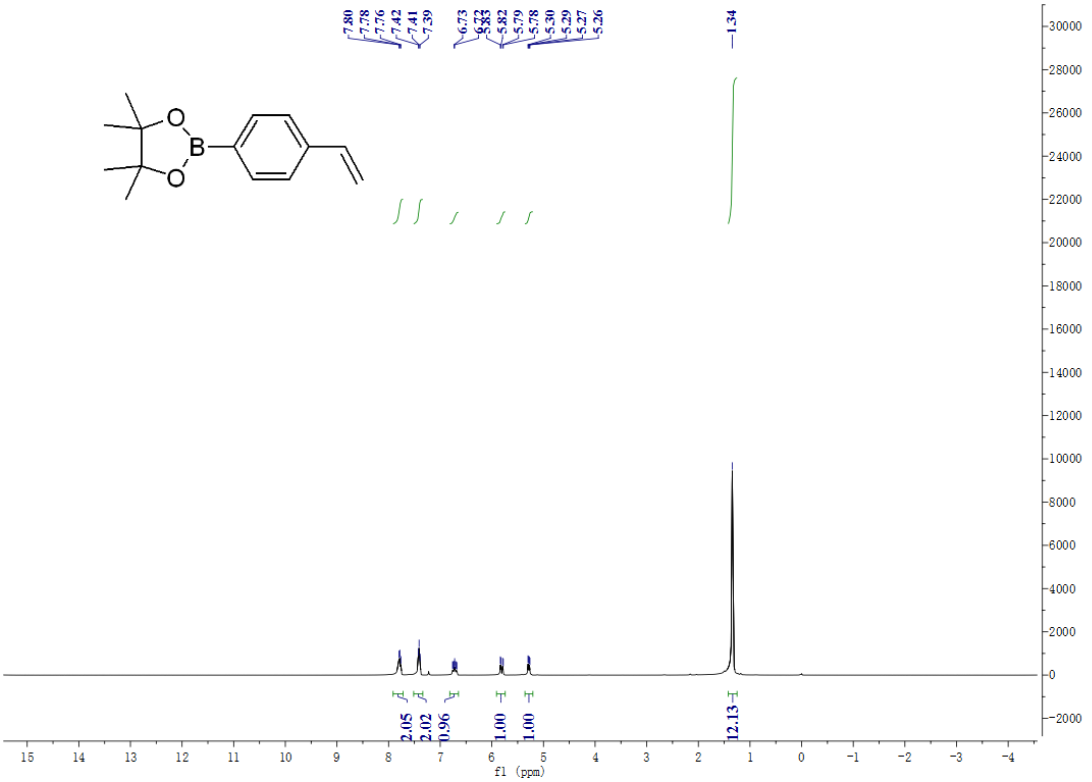


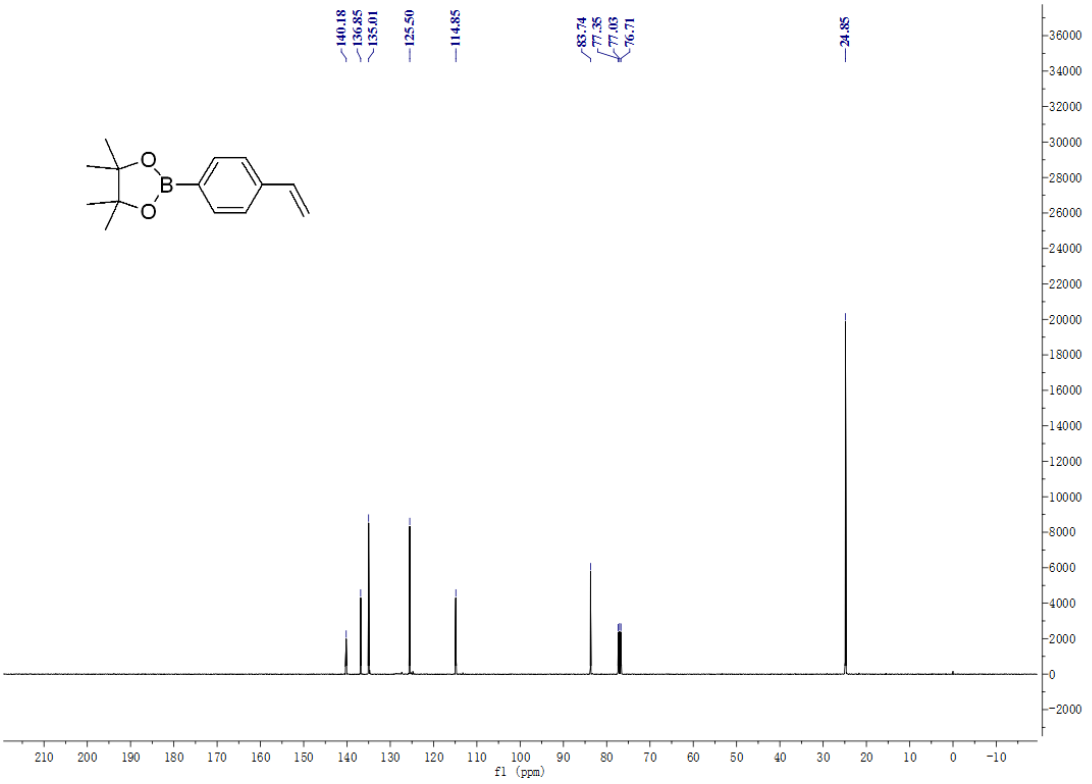
2-(4-vinylphenyl)thiophene (S-13)



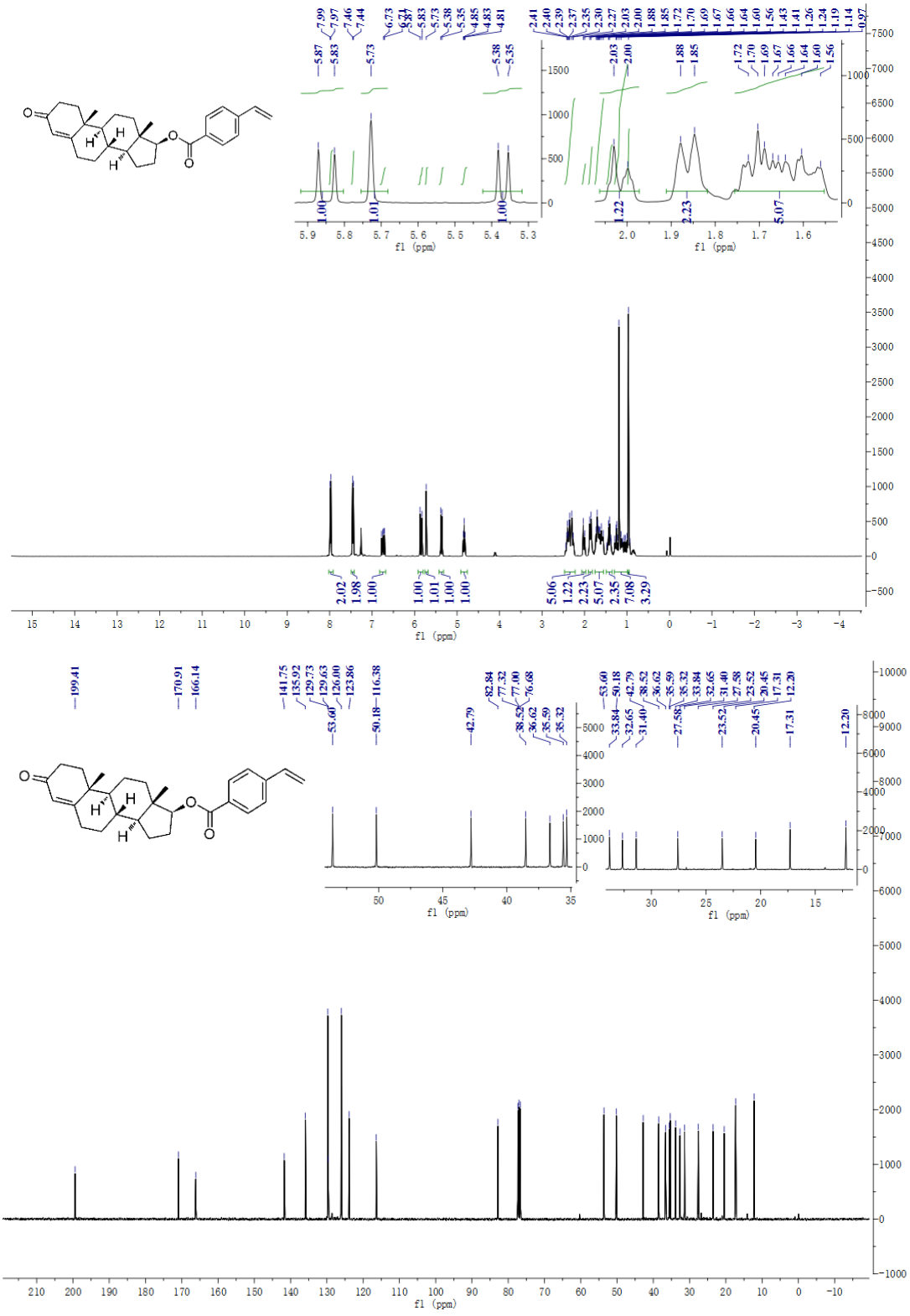


4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (S-14)

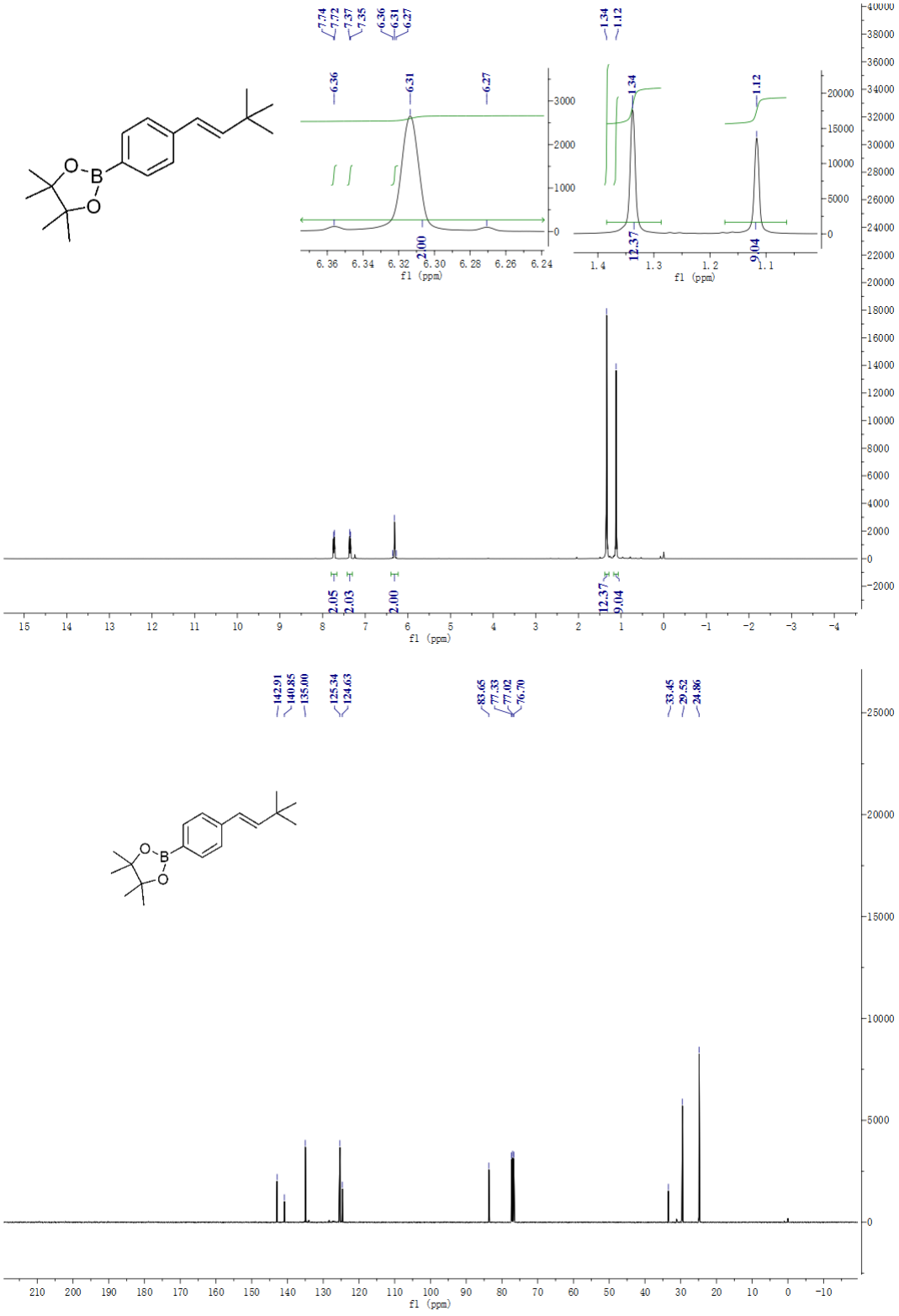




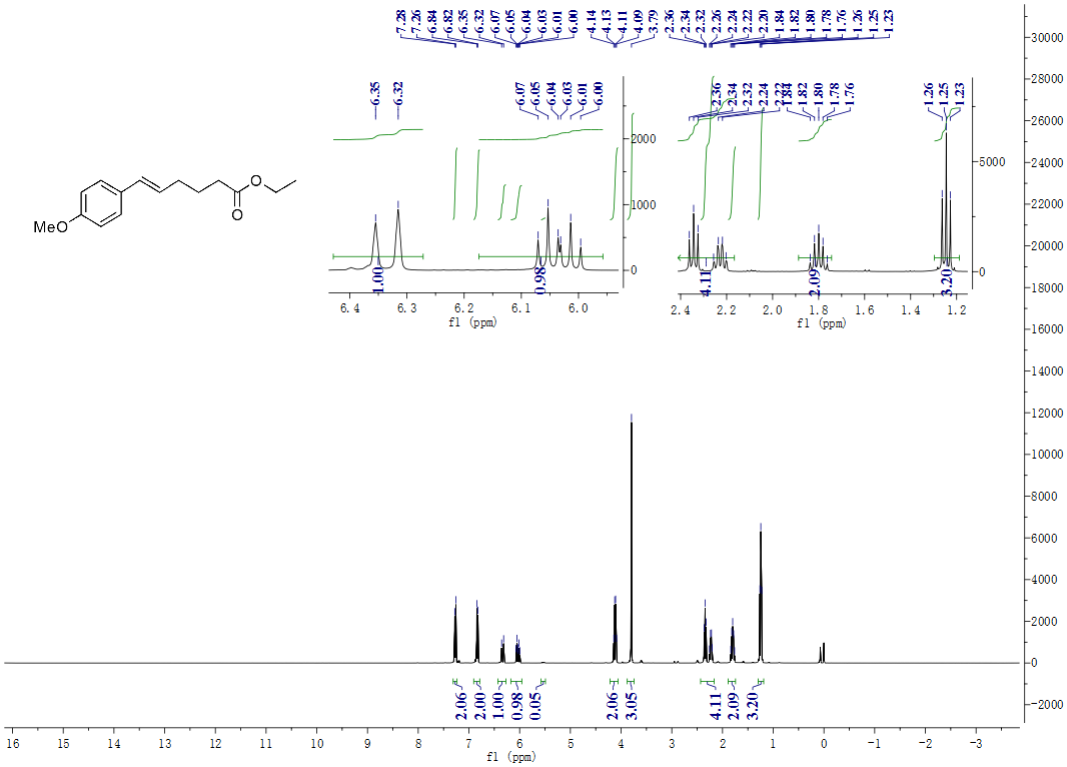
(8R,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl (S-15)

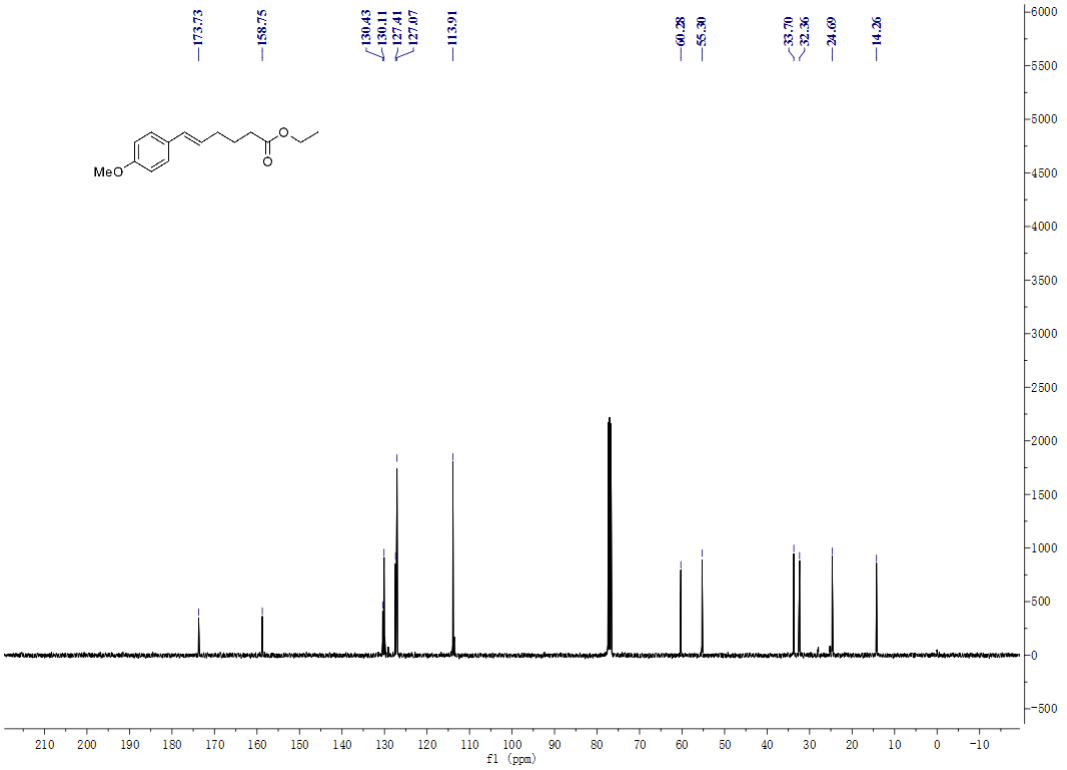


***(E)*-2-(4-(3,3-dimethylbut-1-en-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1)**

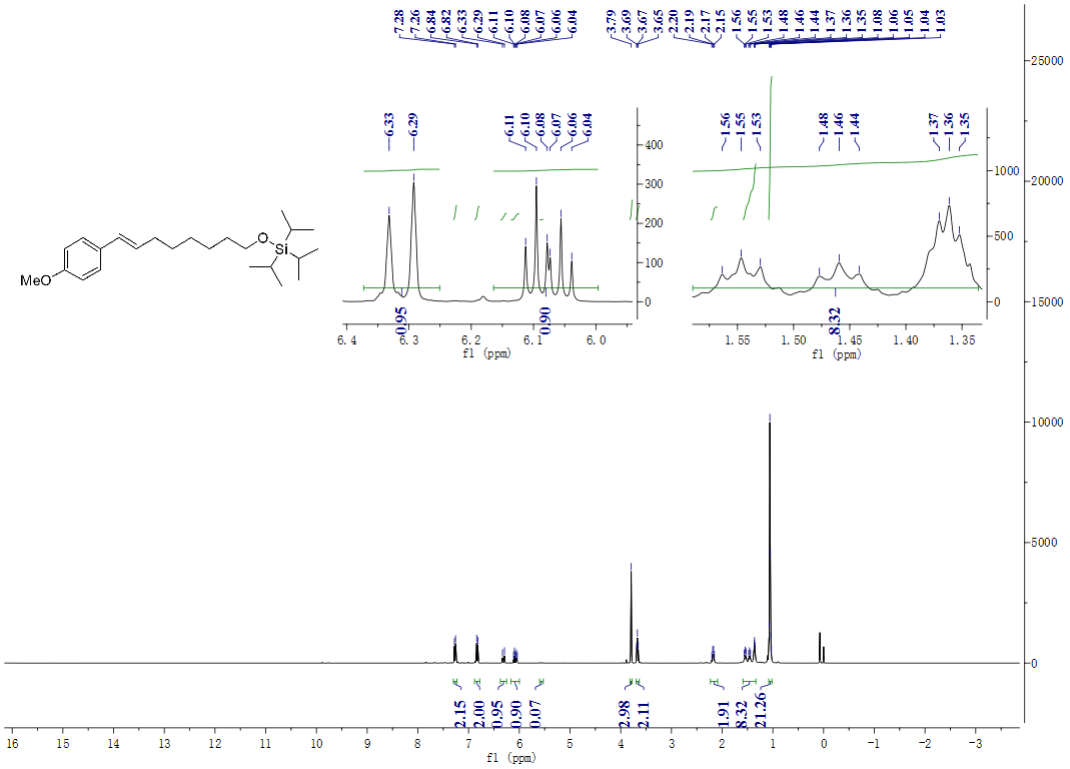


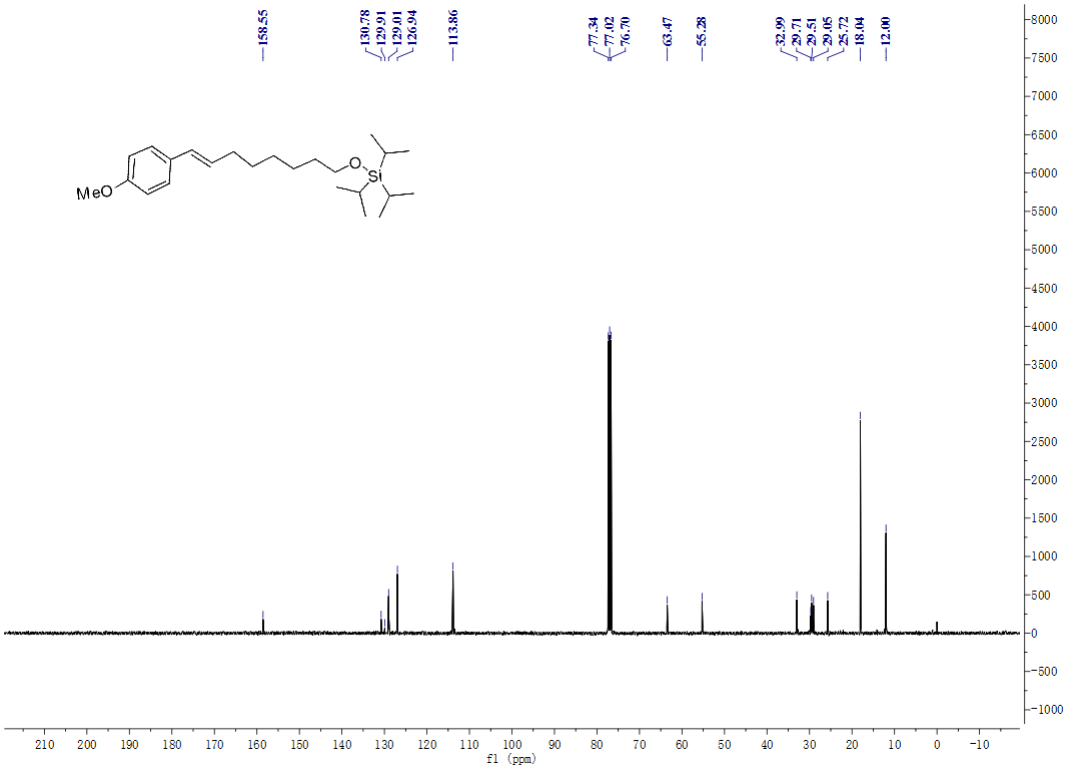
(E)-ethyl 6-(4-methoxyphenyl)hex-5-enoate (2)



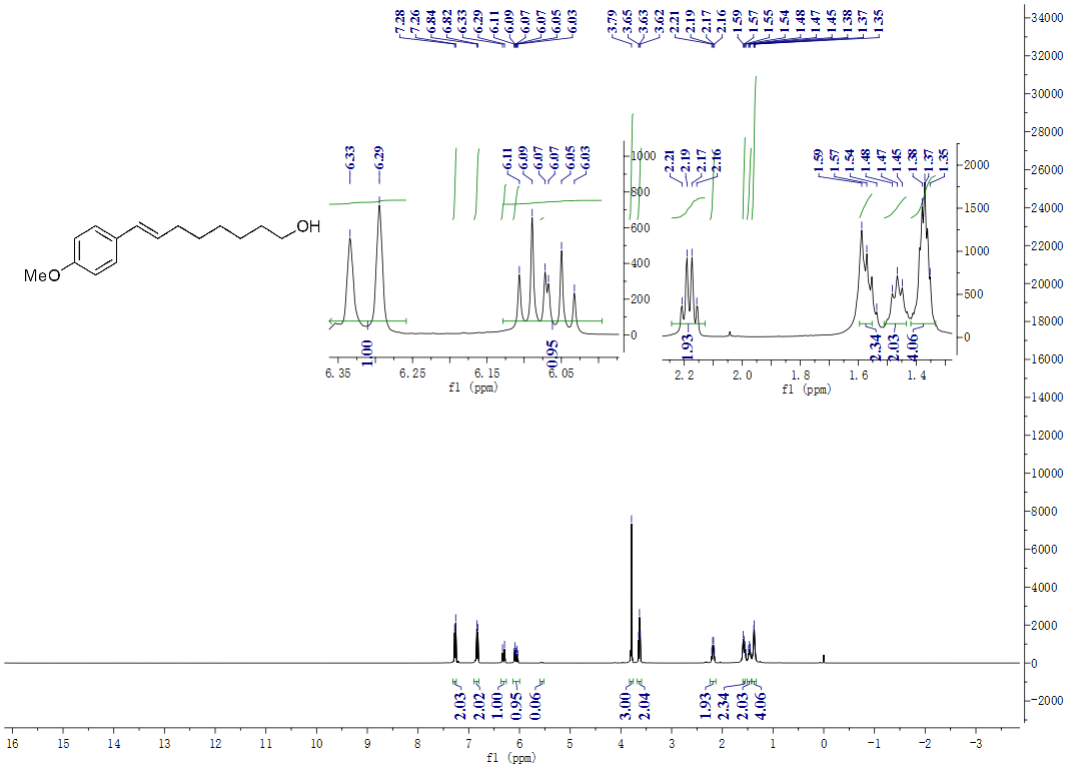


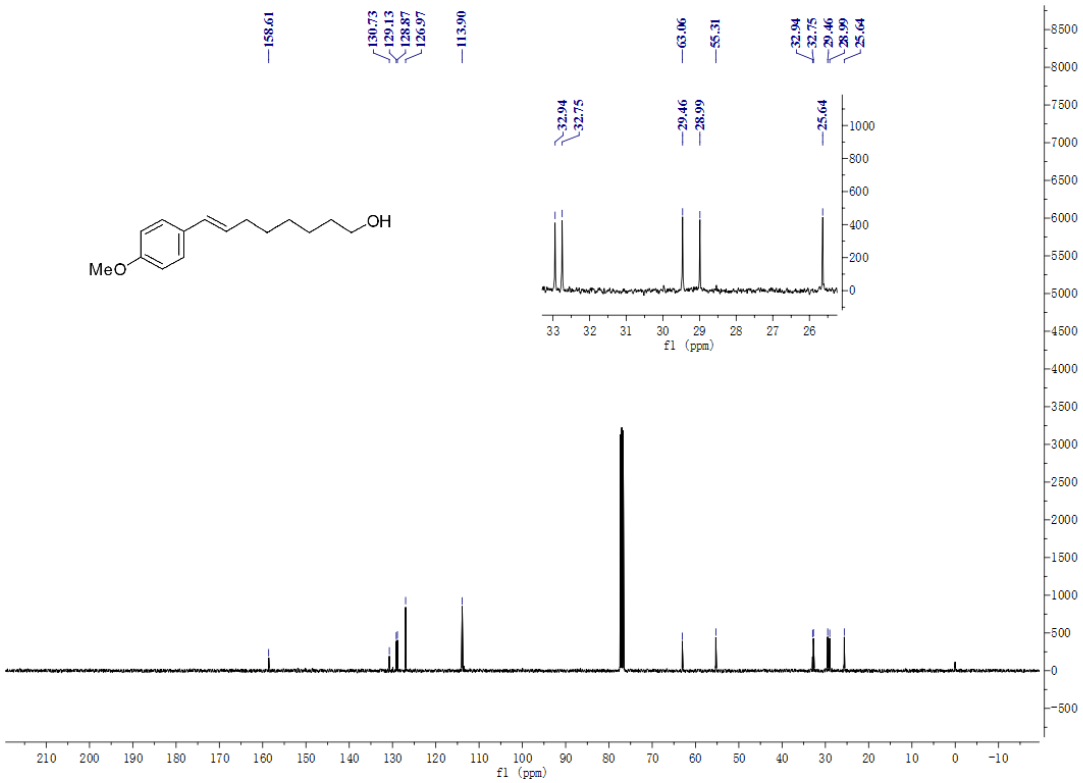
(E)-triisopropyl((8-(4-methoxyphenyl)oct-7-en-1-yl)oxy)silane (3)



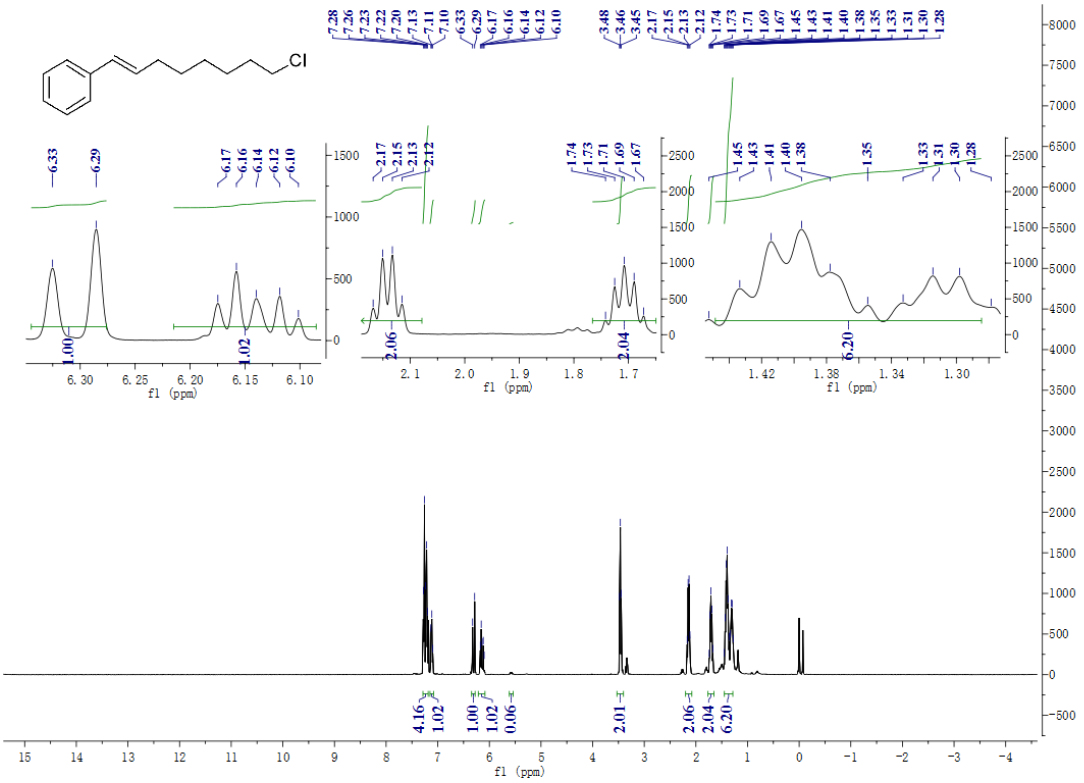


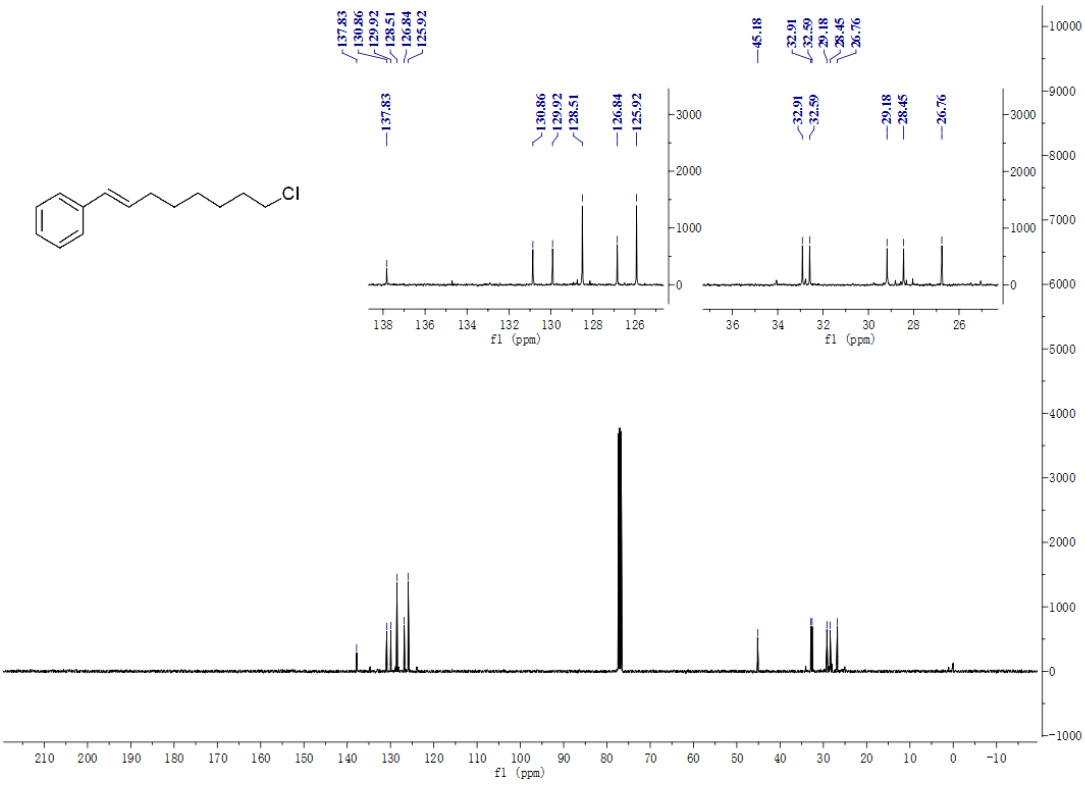
(E)-8-(4-methoxyphenyl)oct-7-en-1-ol (4)



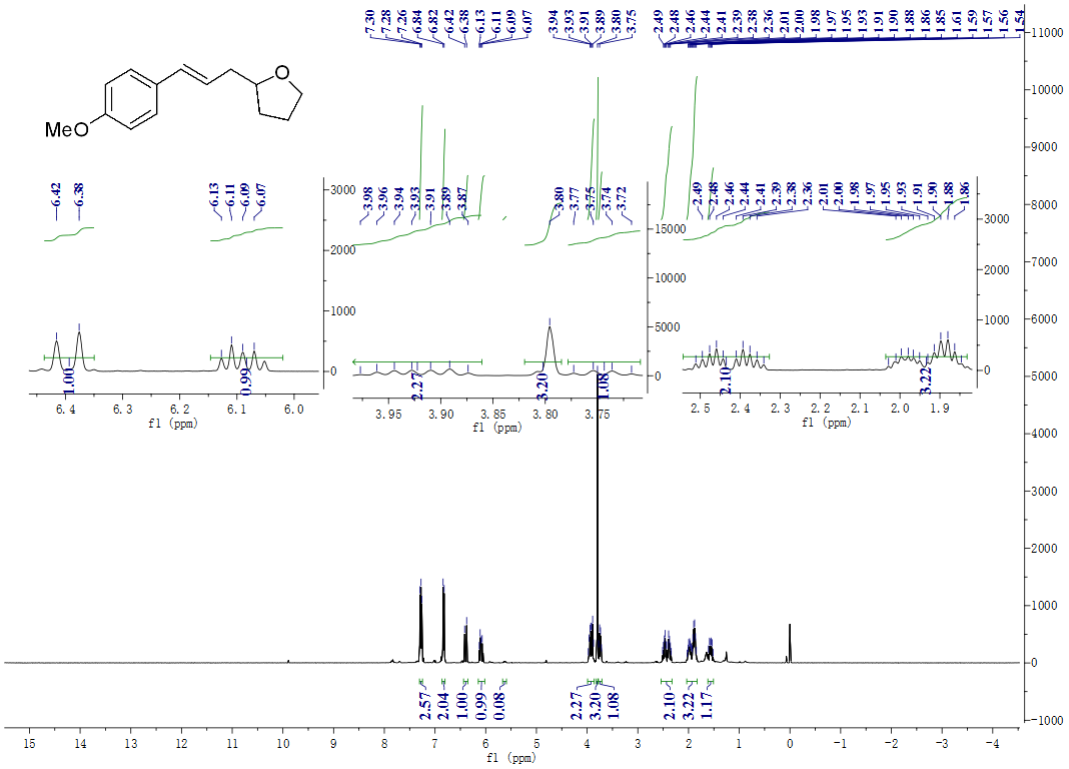


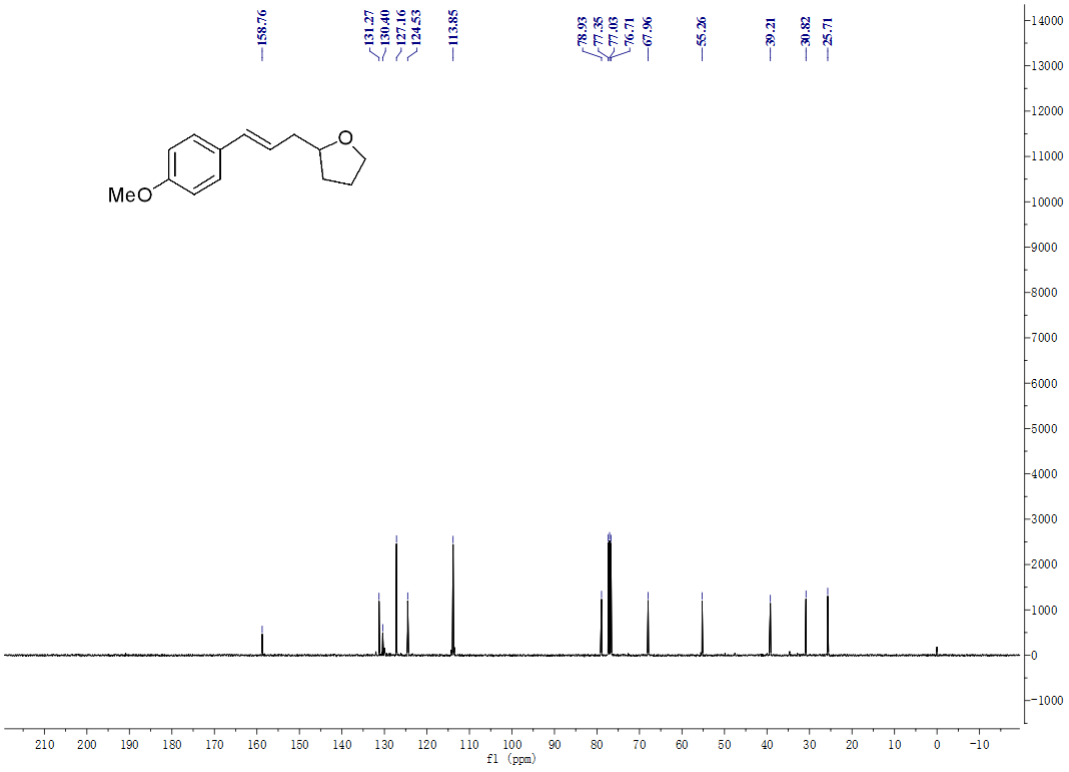
(E)-1-(8-chlorooct-1-en-1-yl)-4-methoxybenzene1 (5)



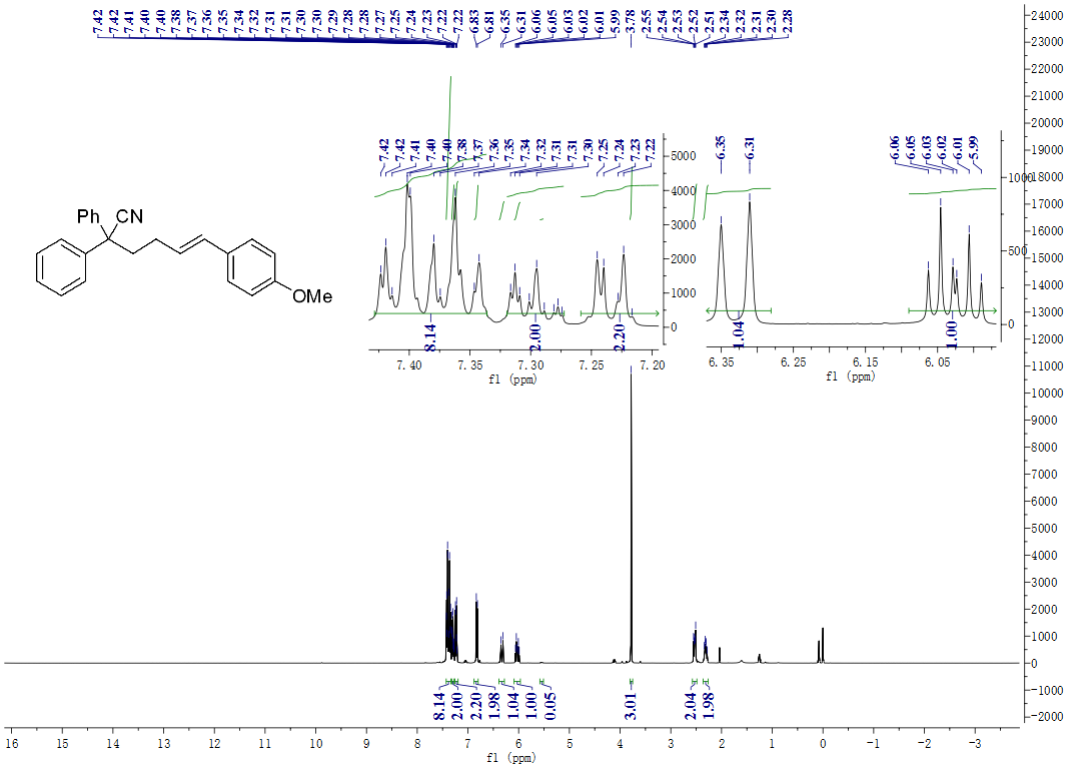


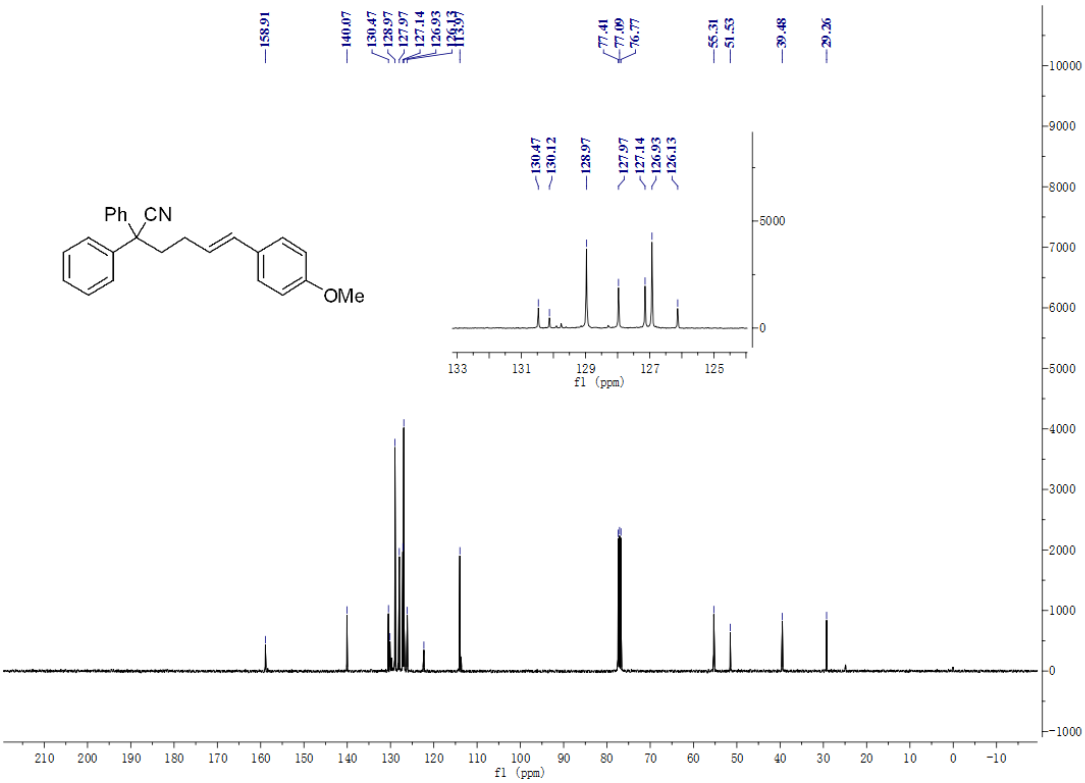
(E)-2-(3-(4-methoxyphenyl)allyl)tetrahydrofuran (6)



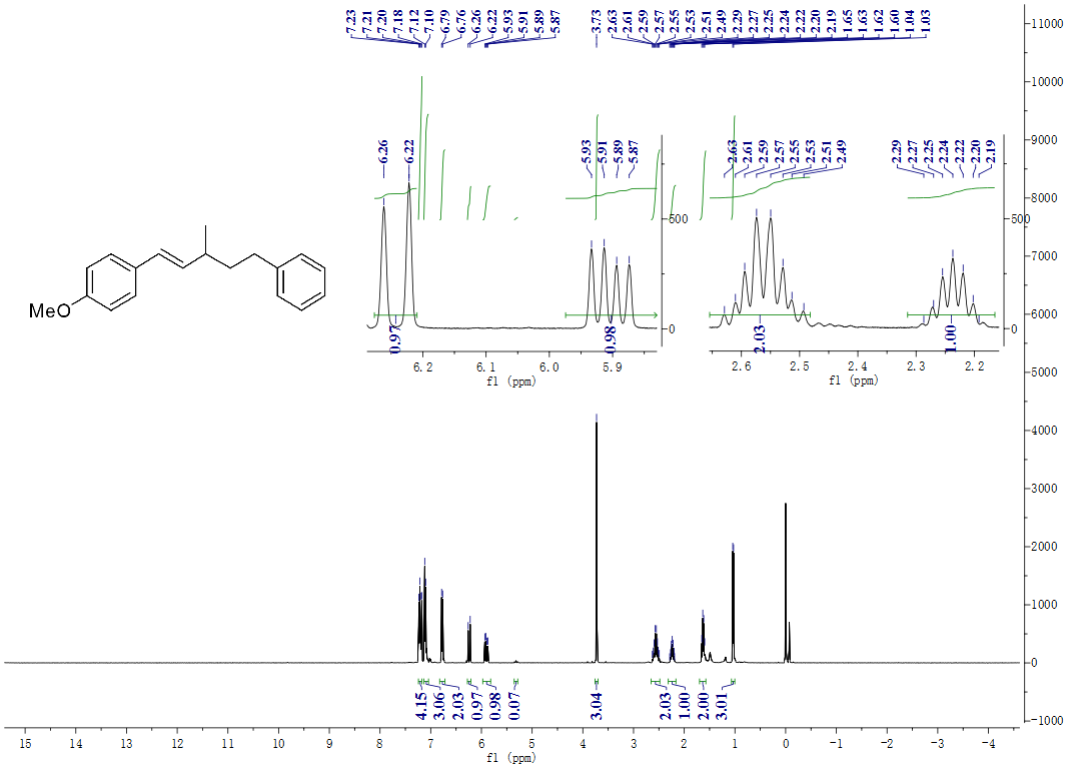


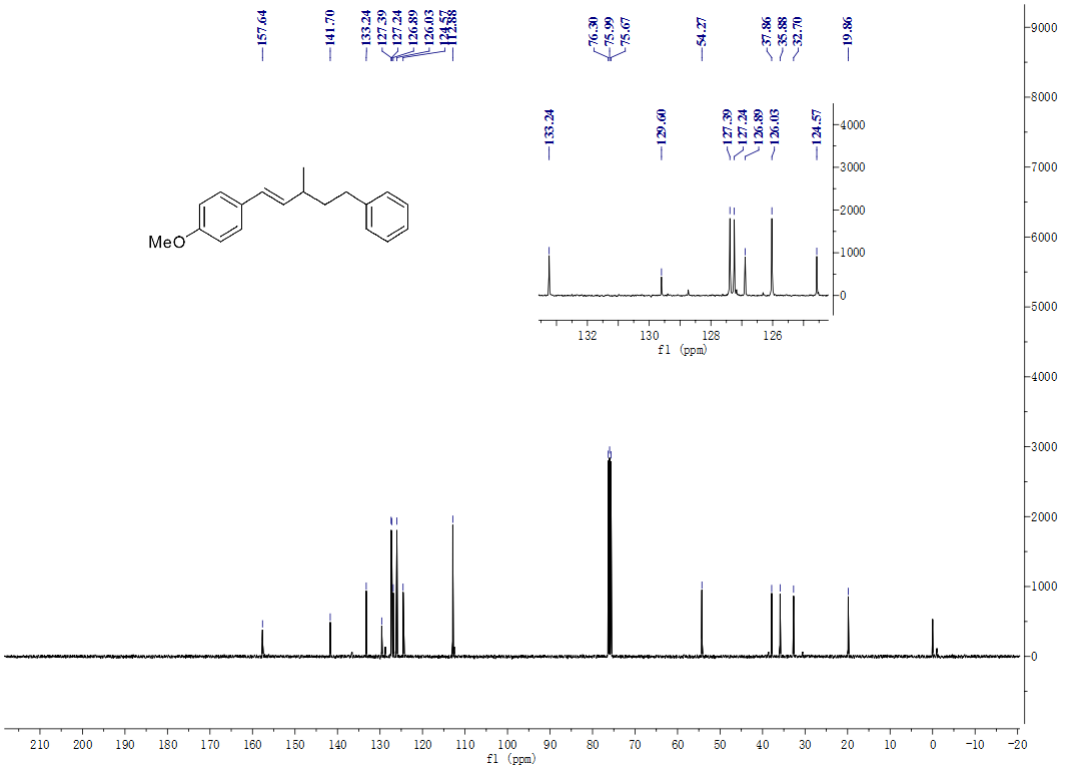
(E)-6-(4-methoxyphenyl)-2,2-diphenylhex-5-enenitrile (7)



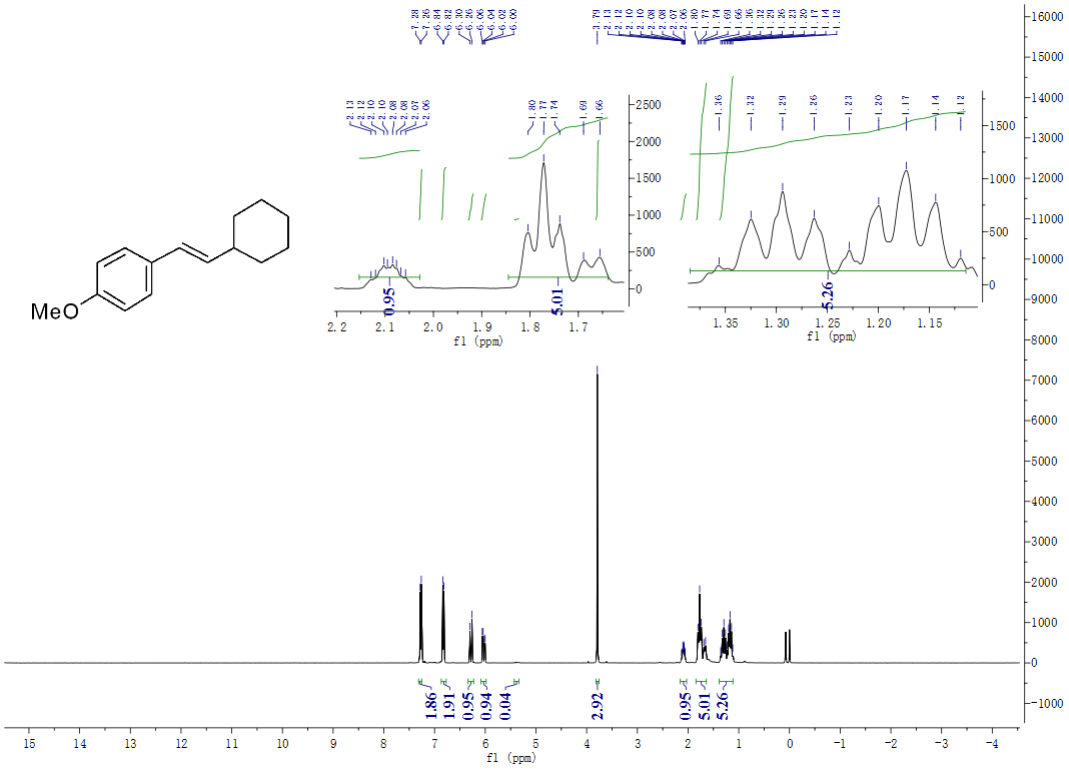


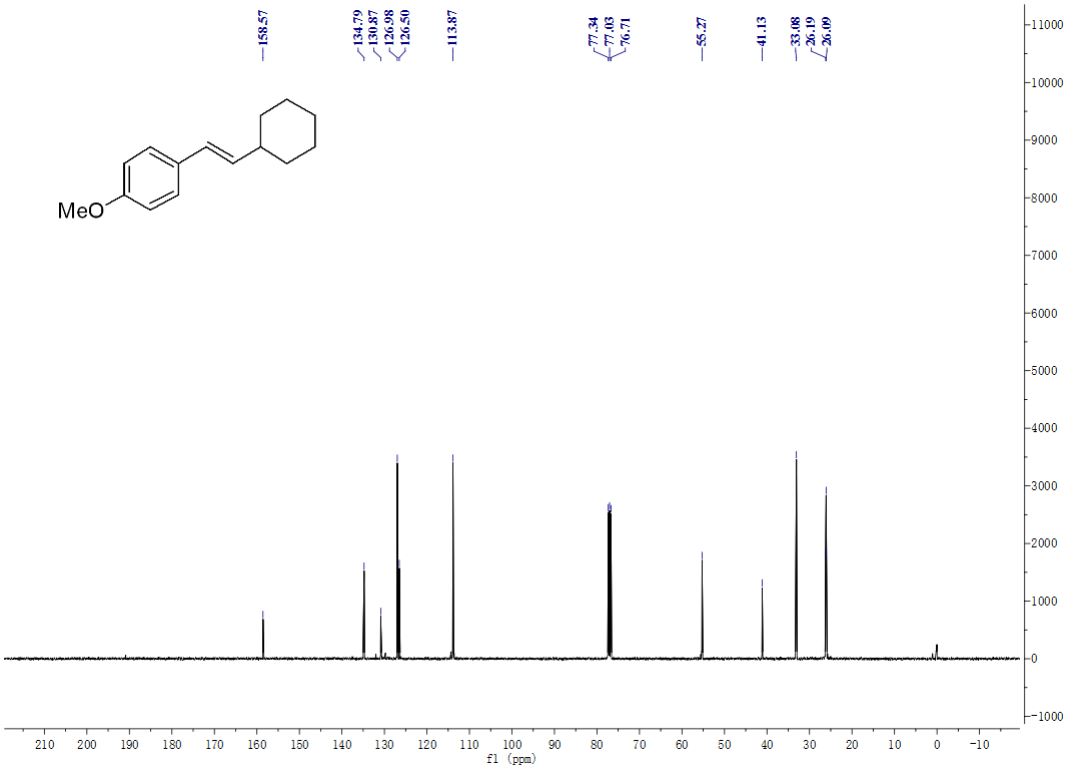
(E)-1-methoxy-4-(3-methyl-5-phenylpent-1-en-1-yl)benzene (8)



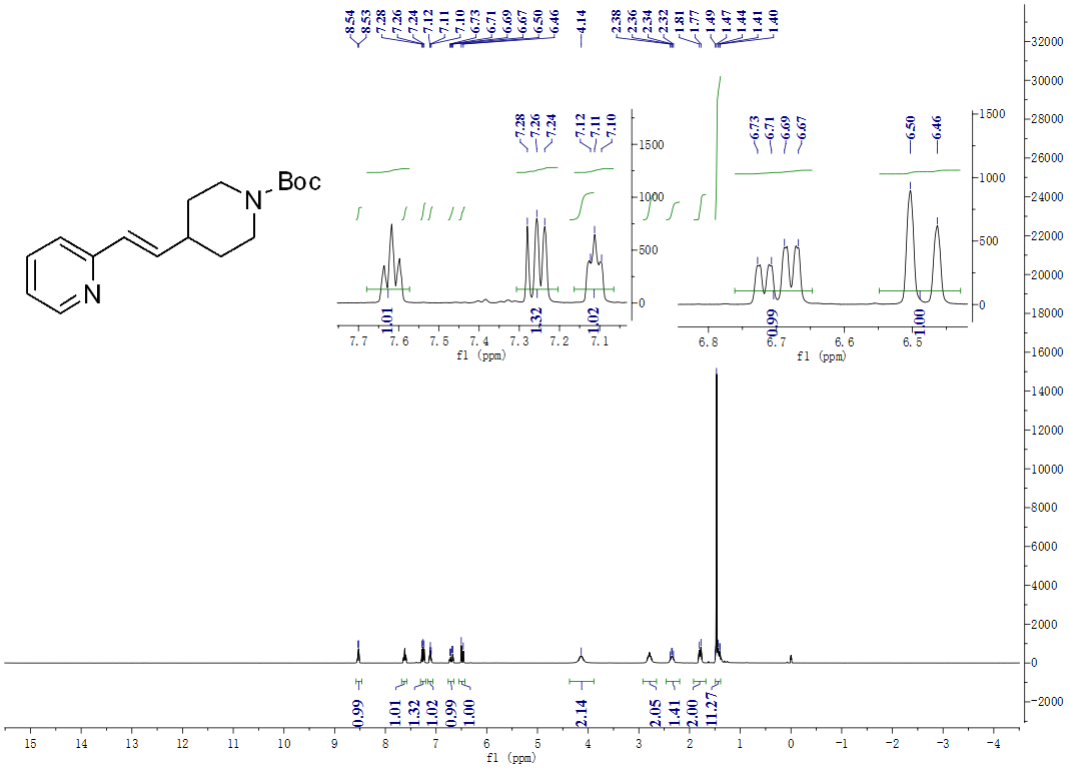


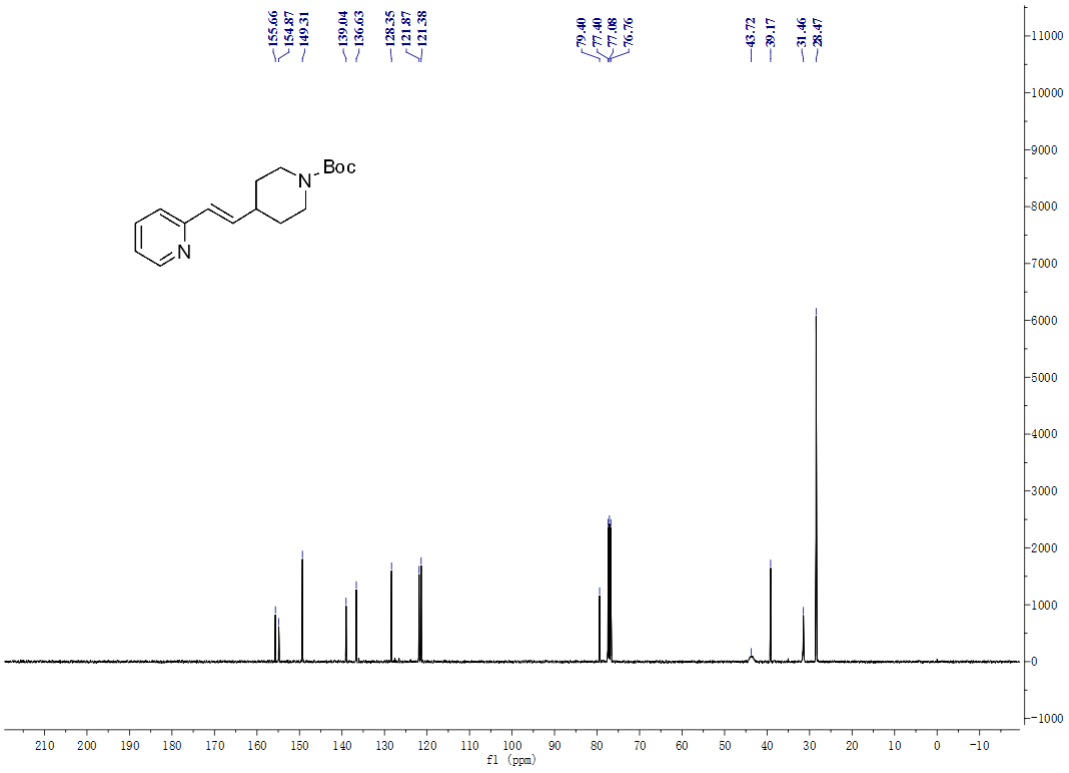
(E)-1-(2-cyclohexylvinyl)-4-methoxybenzene (9)



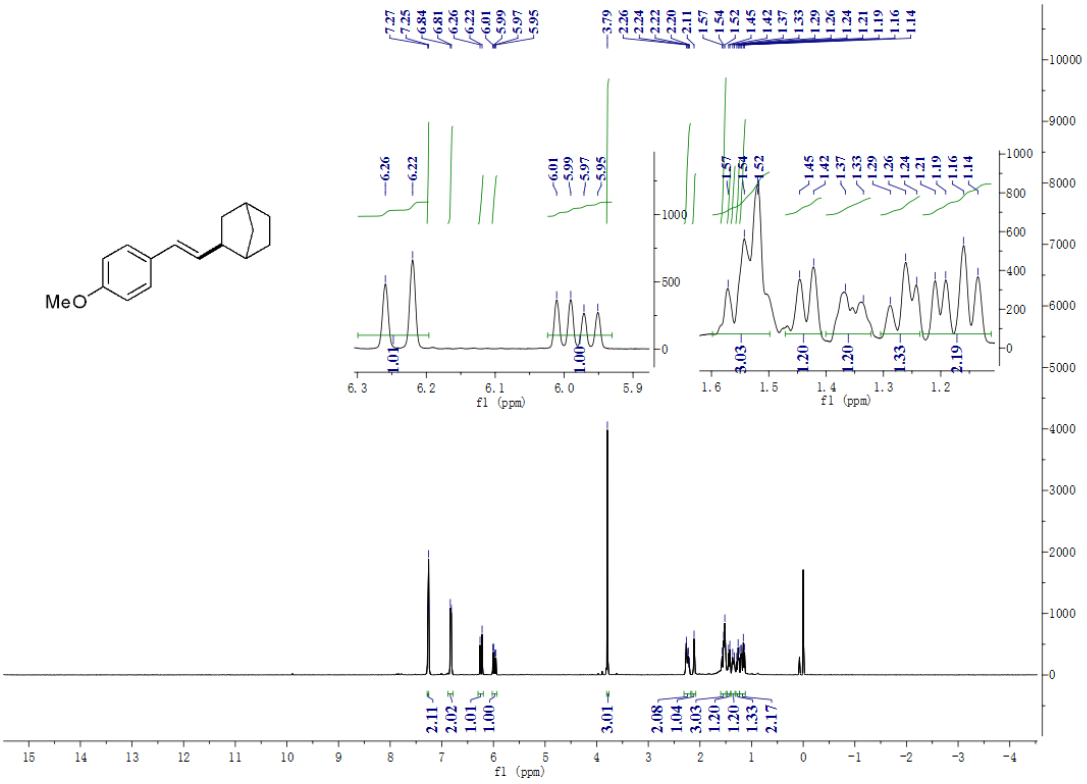


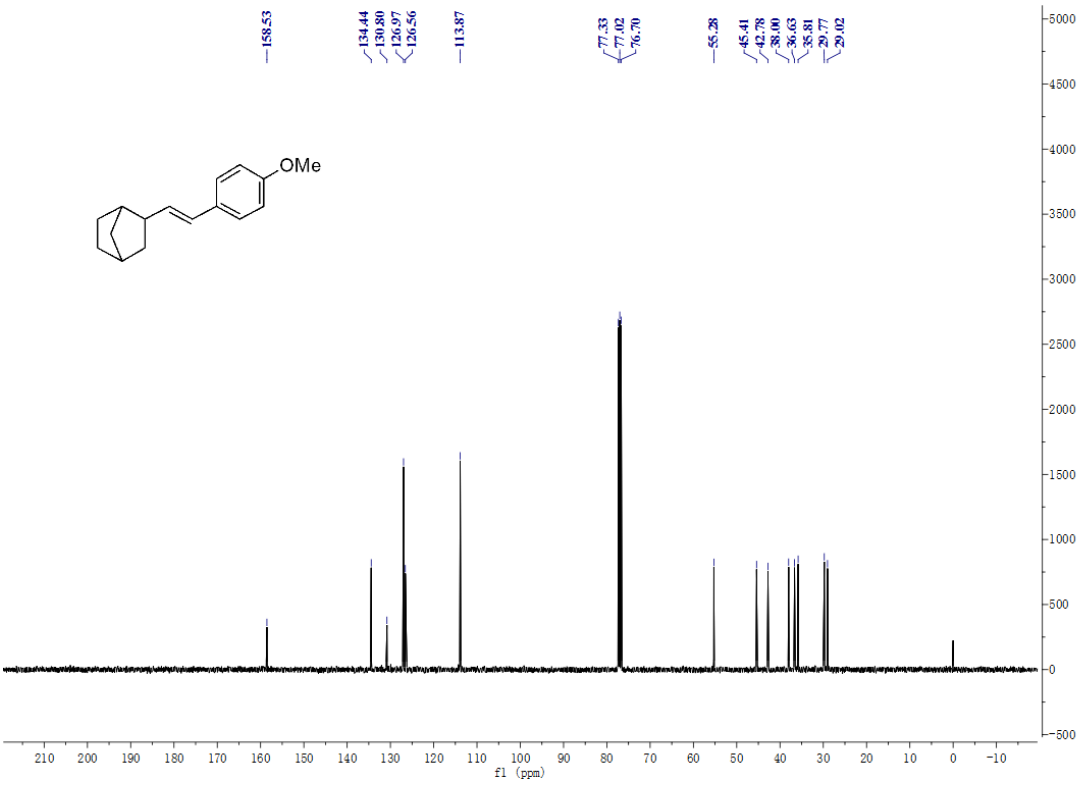
(E)-tert-butyl 4-(2-(pyridin-2-yl)vinyl)piperidine-1-carboxylate (10)



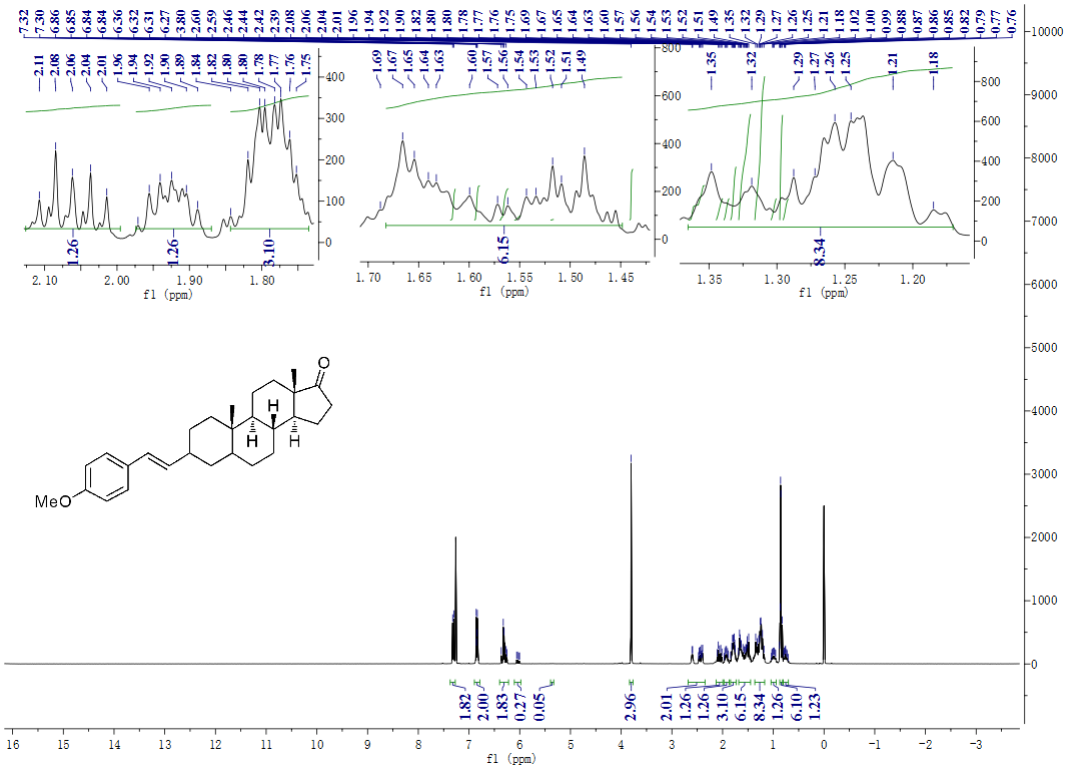


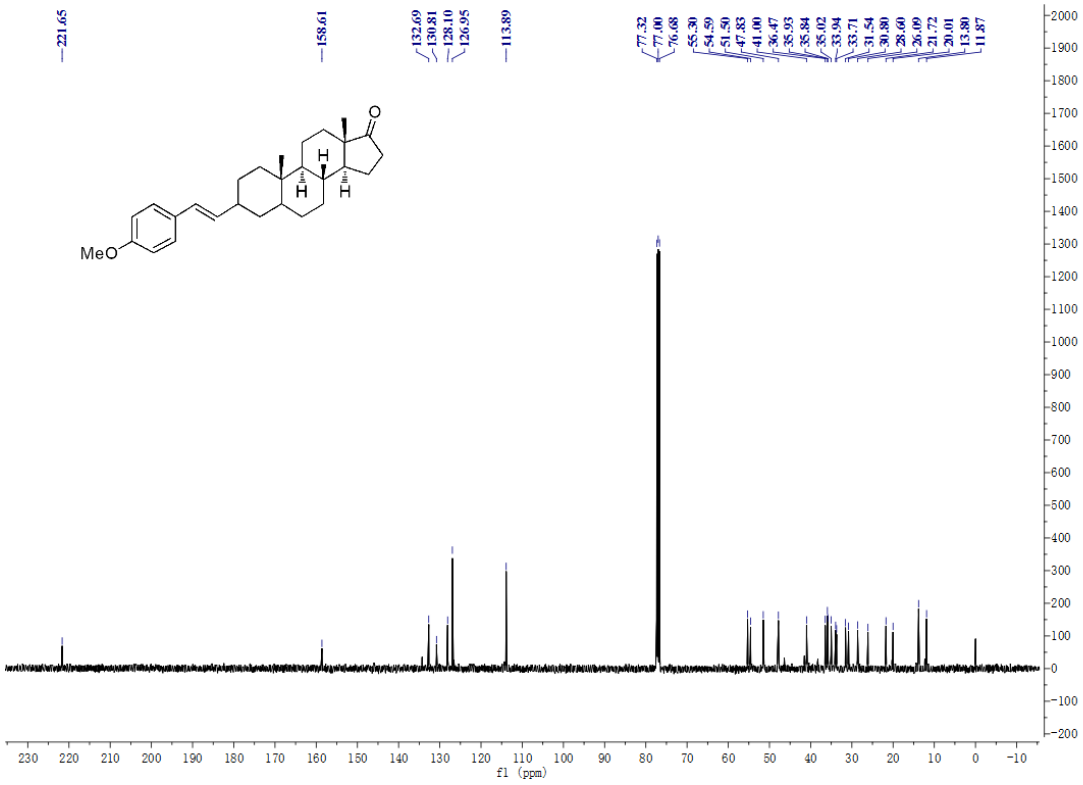
(E)-2-(4-methoxystyryl)bicyclo[2.2.1]heptane (11)



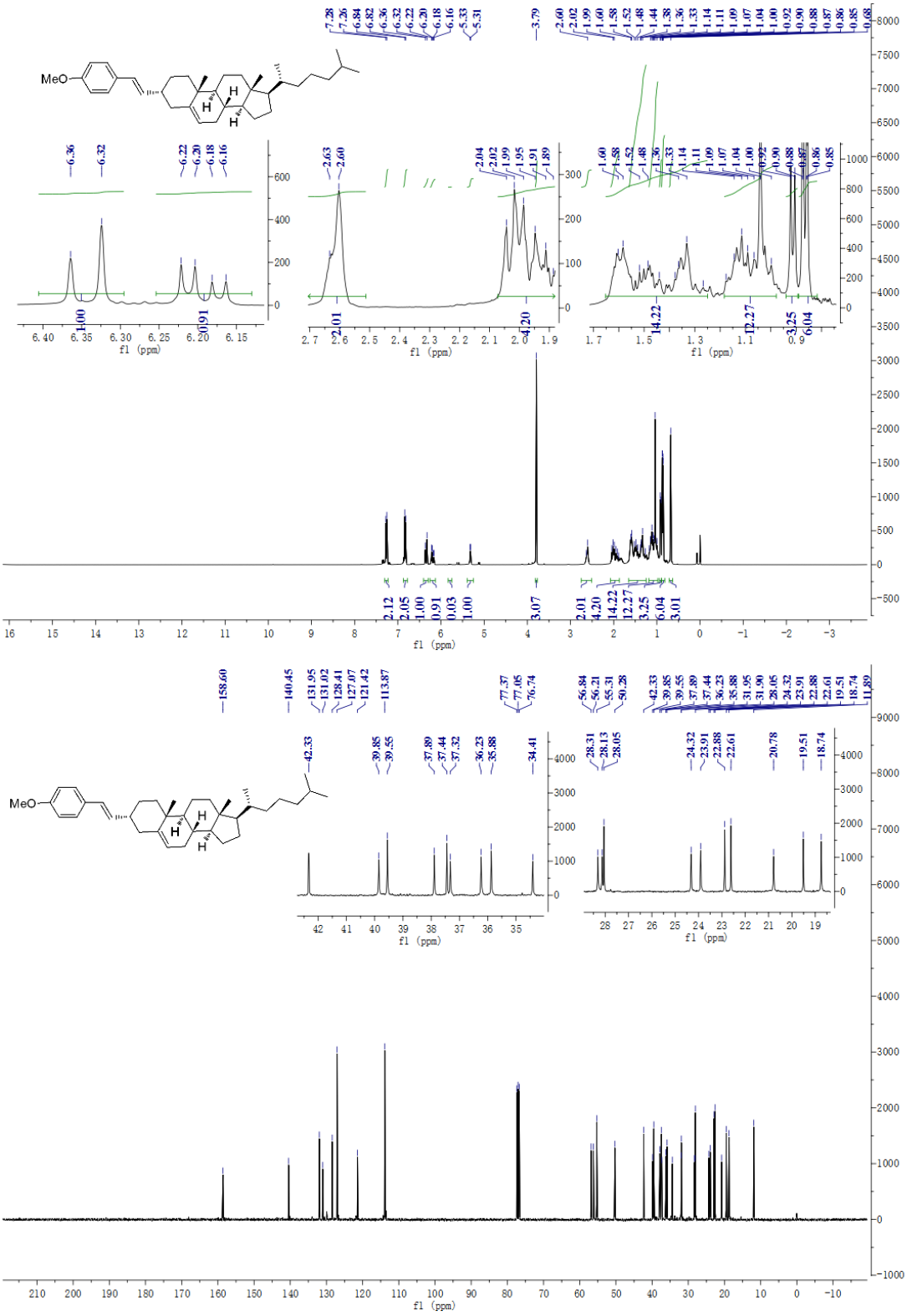


(8R,9S,10S,13S,14S)-3-((*E*)-4-methoxystyryl)-10,13-dimethyltetradecahydro-1H-cyclopenta[a]phenanthren-17(2H)-one (12)

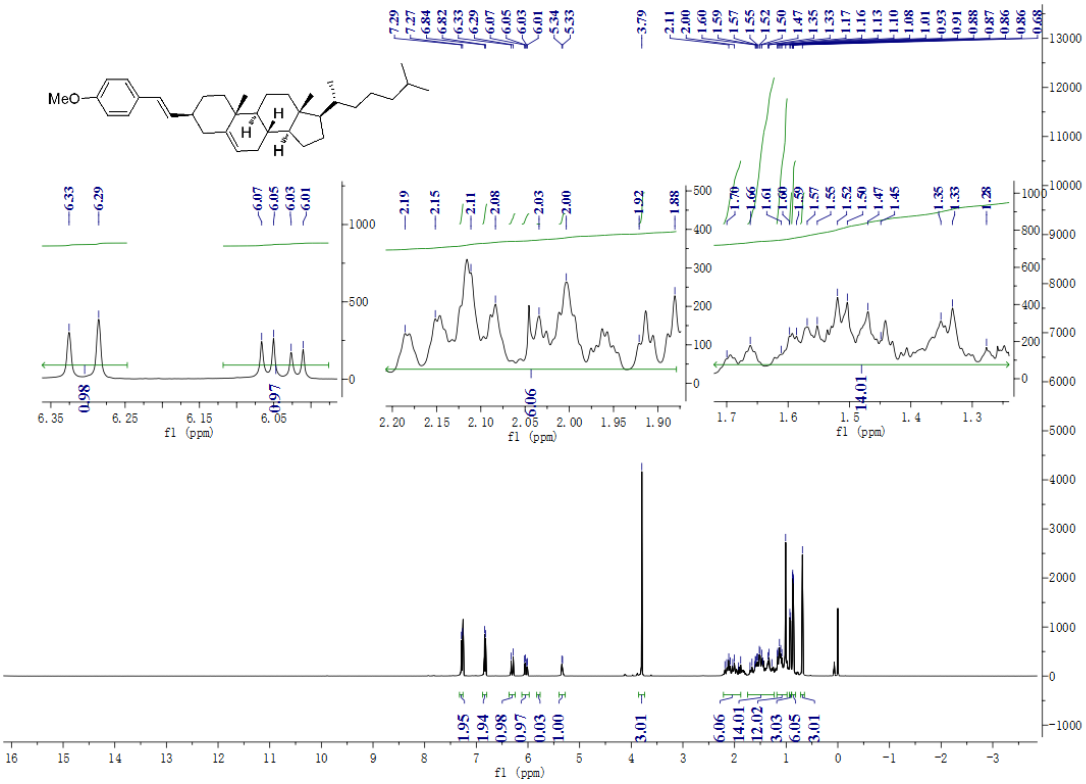


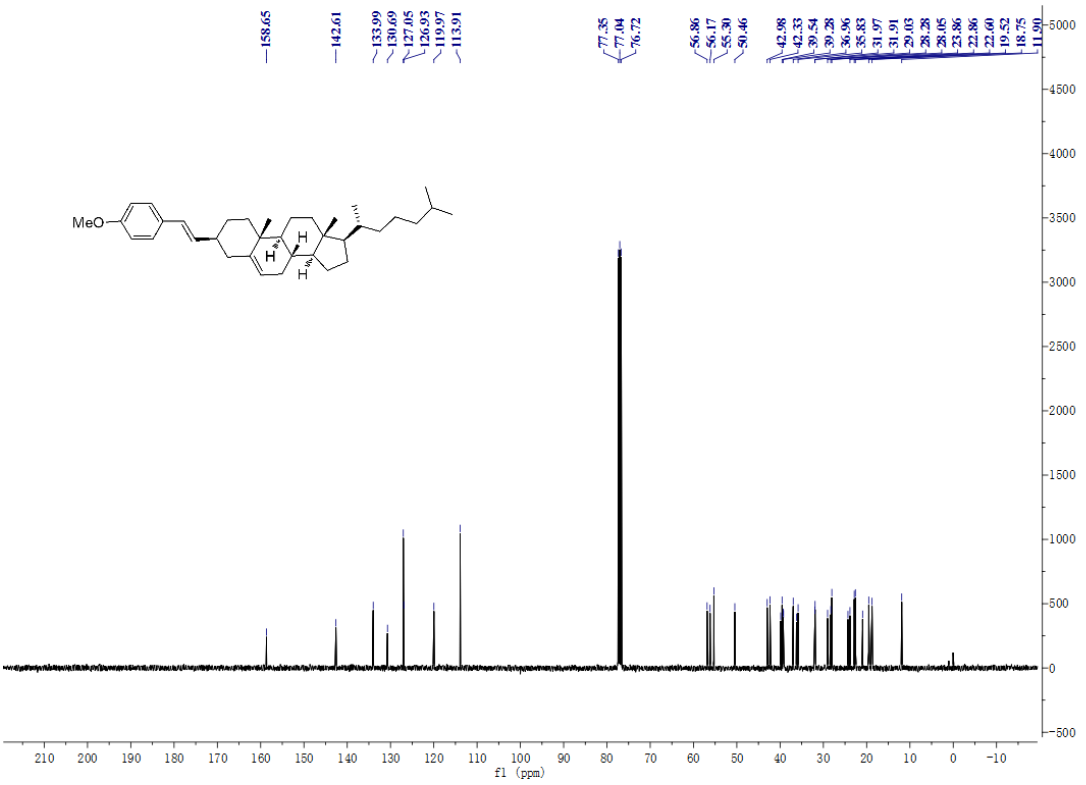


(3R,8S,9S,10R,13R,14S,17R)-3-((*E*)-4-methoxystyryl)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (13)

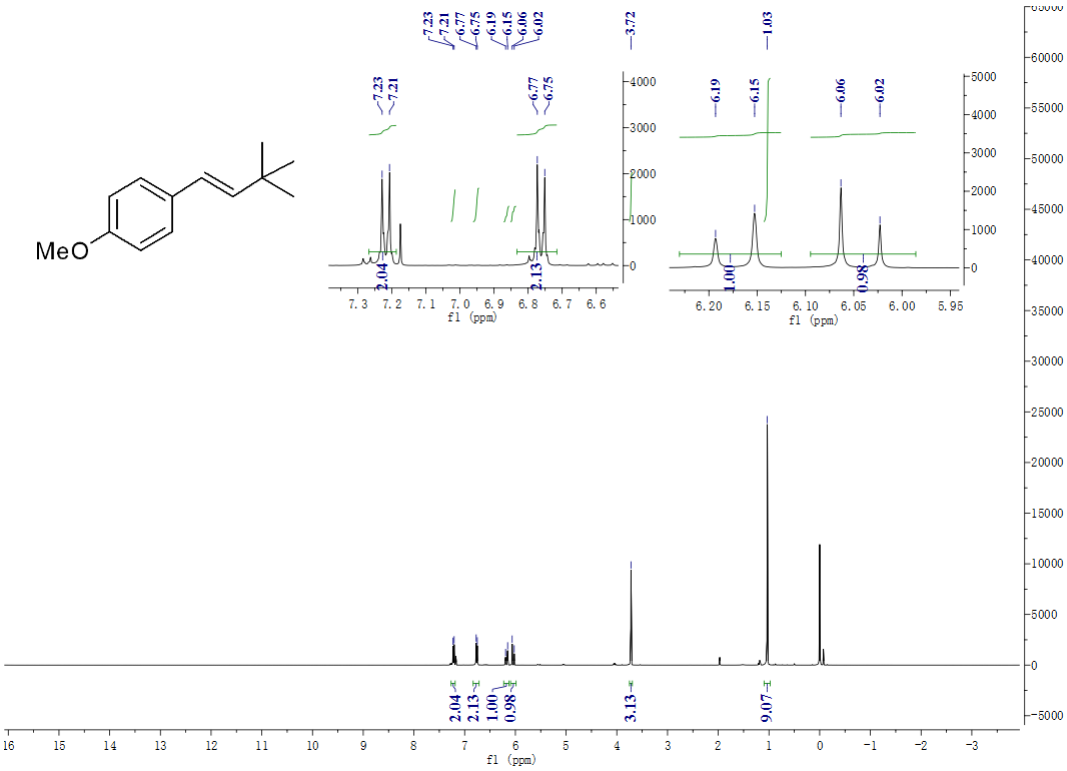


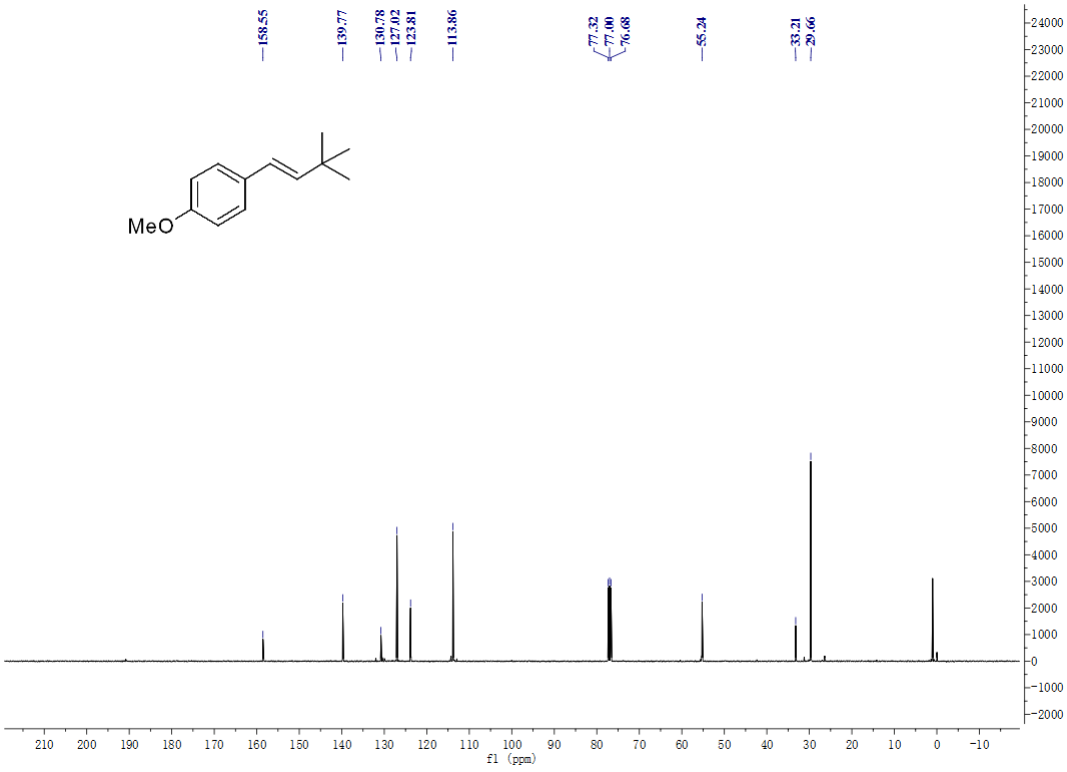
(3S,8S,9S,10R,13R,14S,17R)-3-((*E*)-4-methoxystyryl)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (13)



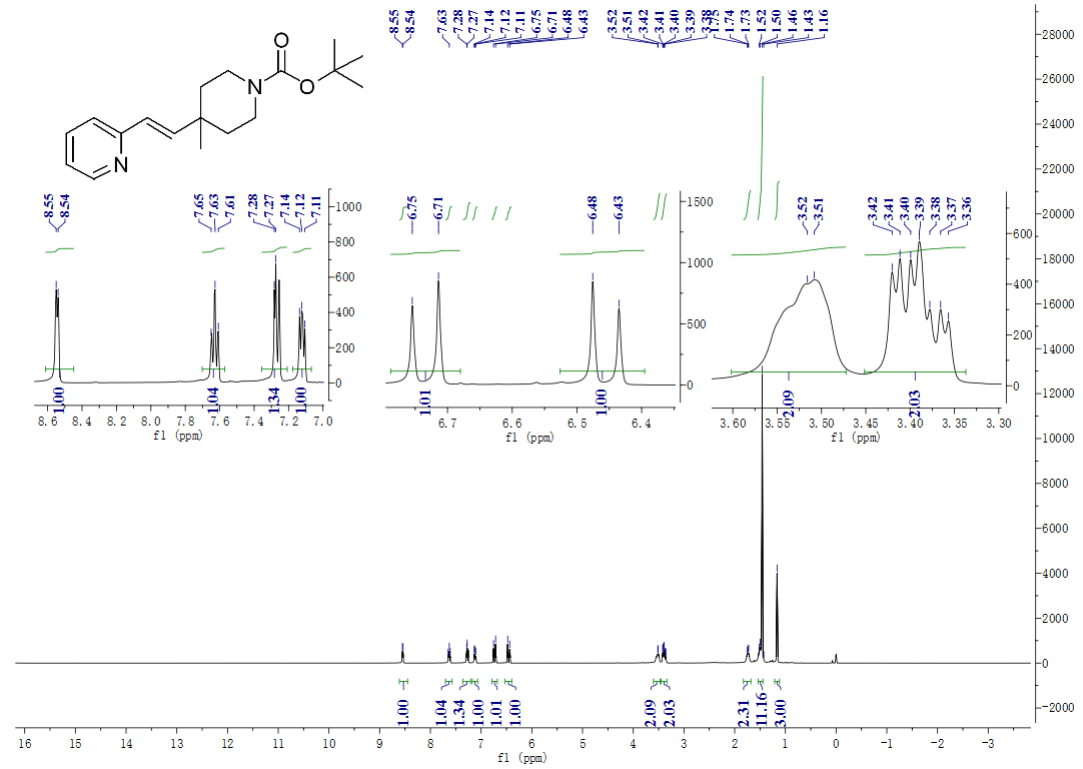


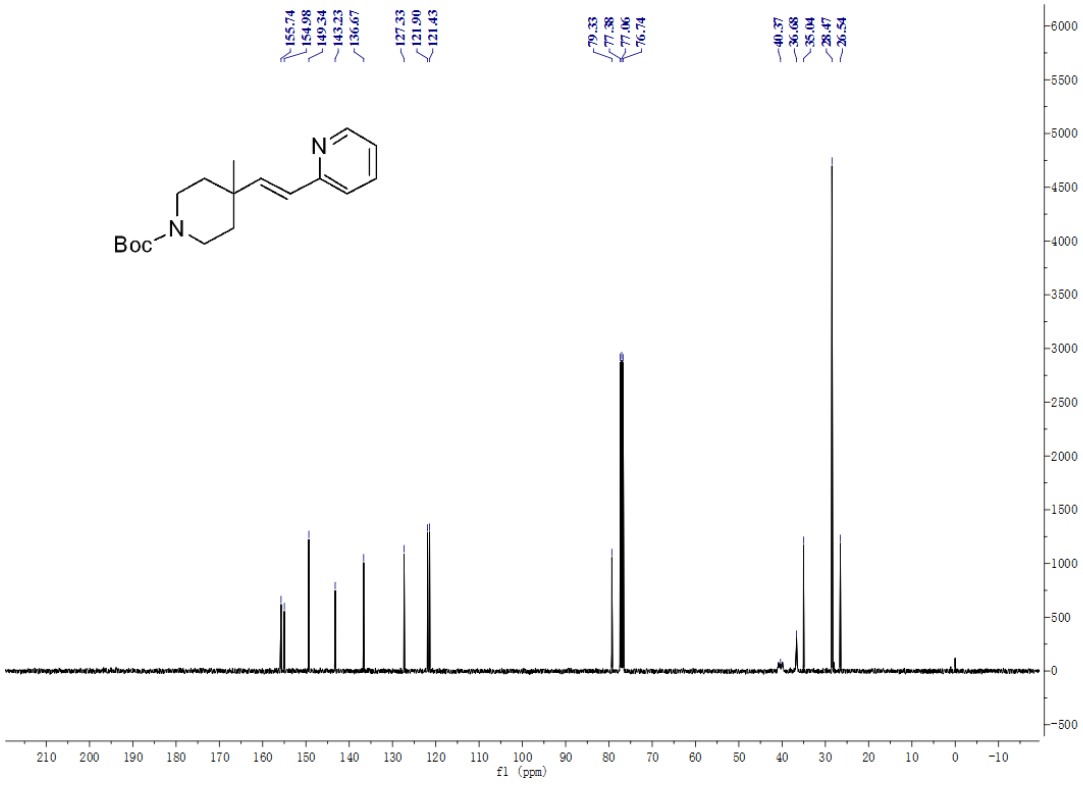
(E)-1-(3,3-dimethylbut-1-en-1-yl)-4-methoxybenzene (14)



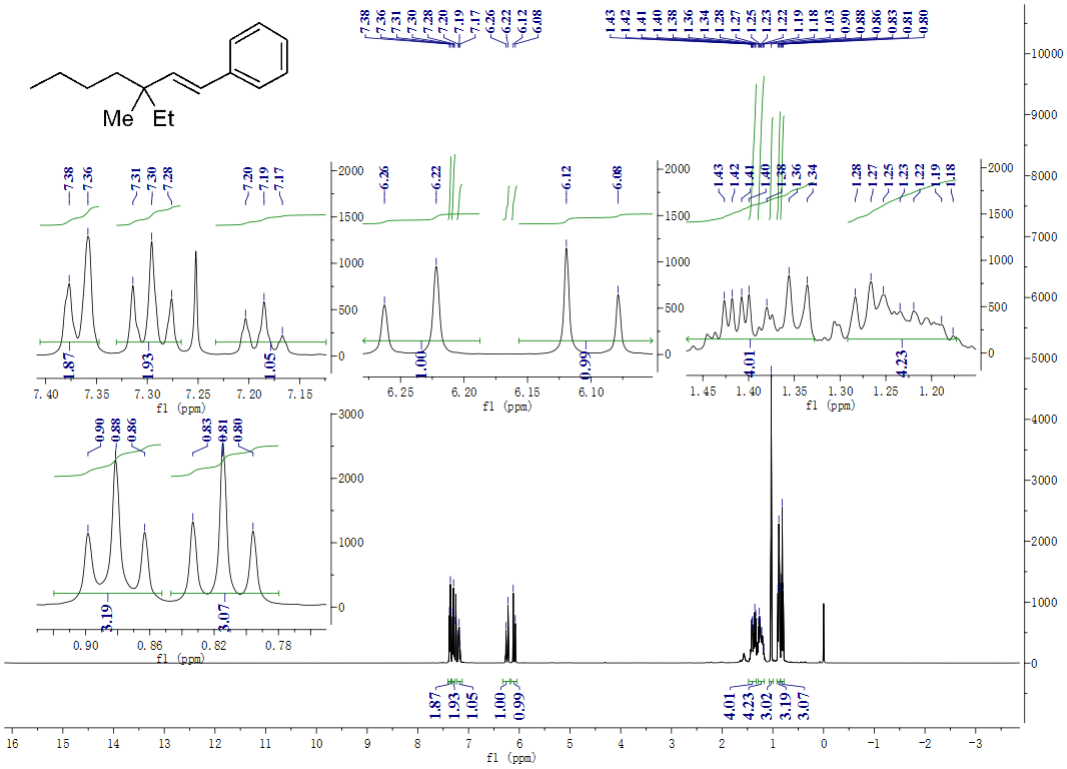


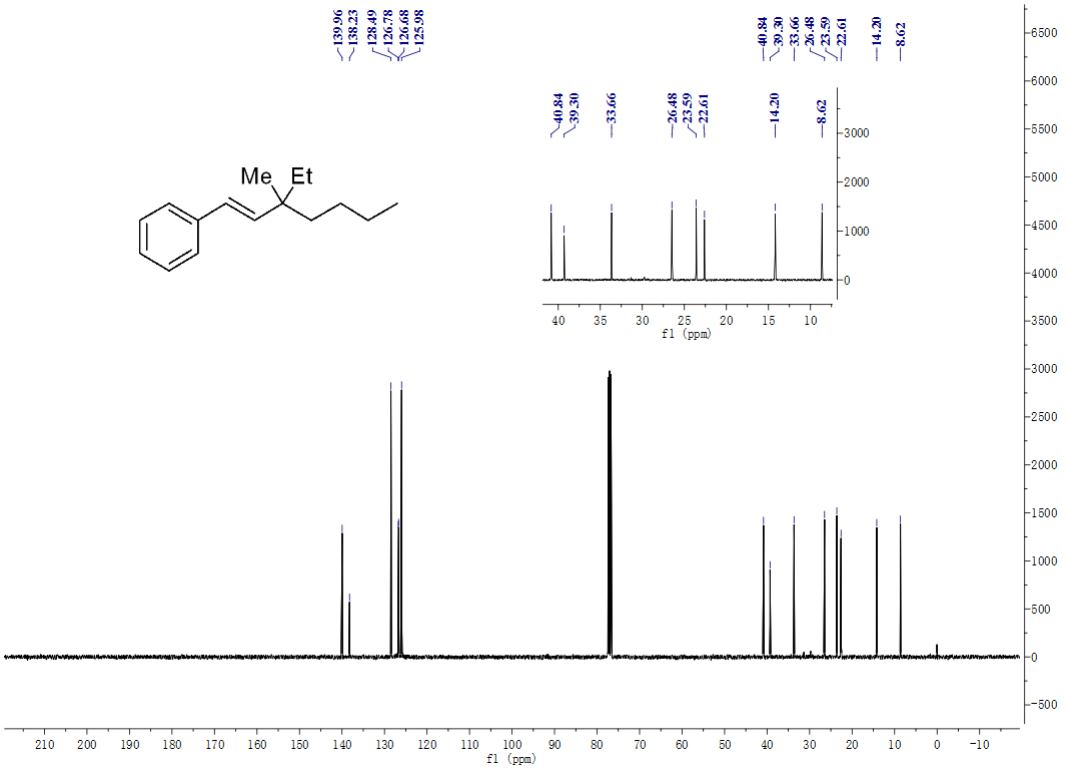
(E)-tert-butyl-4-methyl-4-(2-(pyridin-2-yl)vinyl)piperidine-1-carboxylate (15)



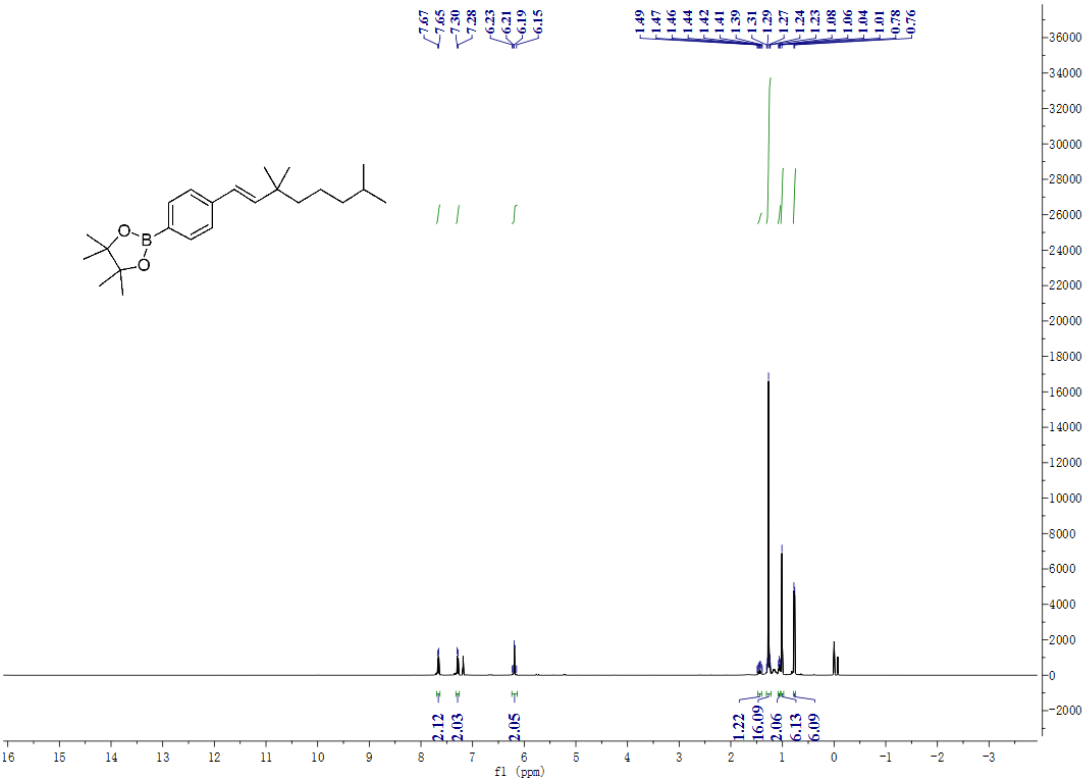


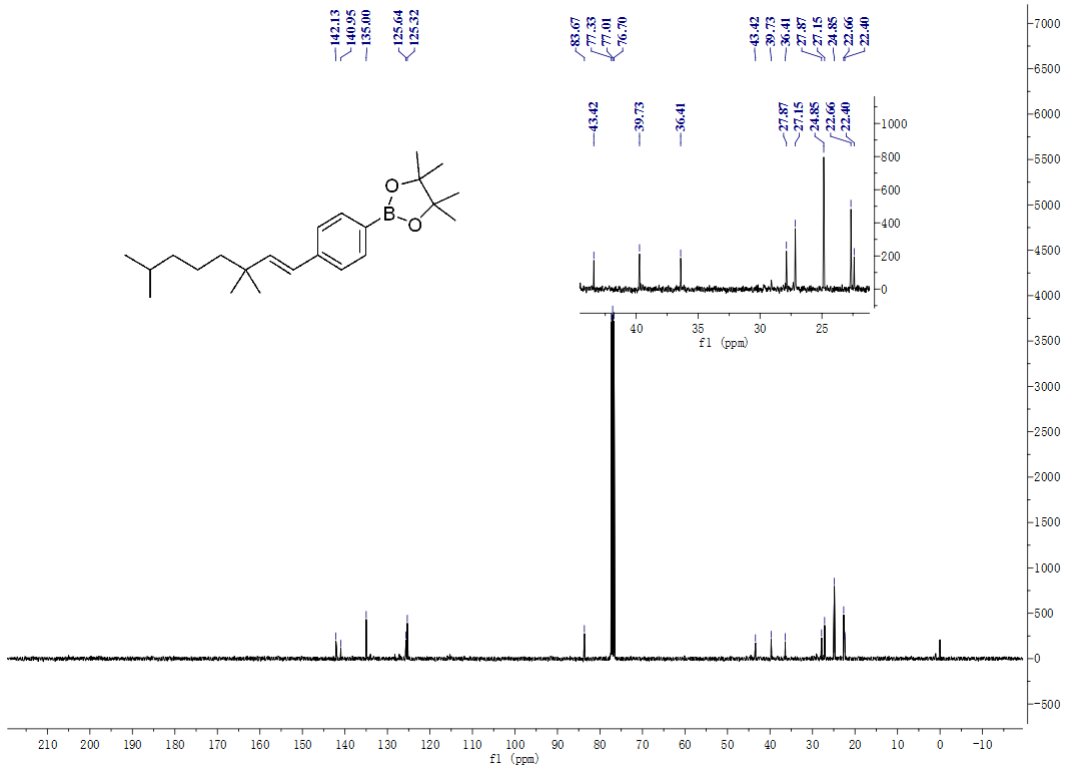
(E)-(3-ethyl-3-methylhept-1-en-1-yl)benzene (16)



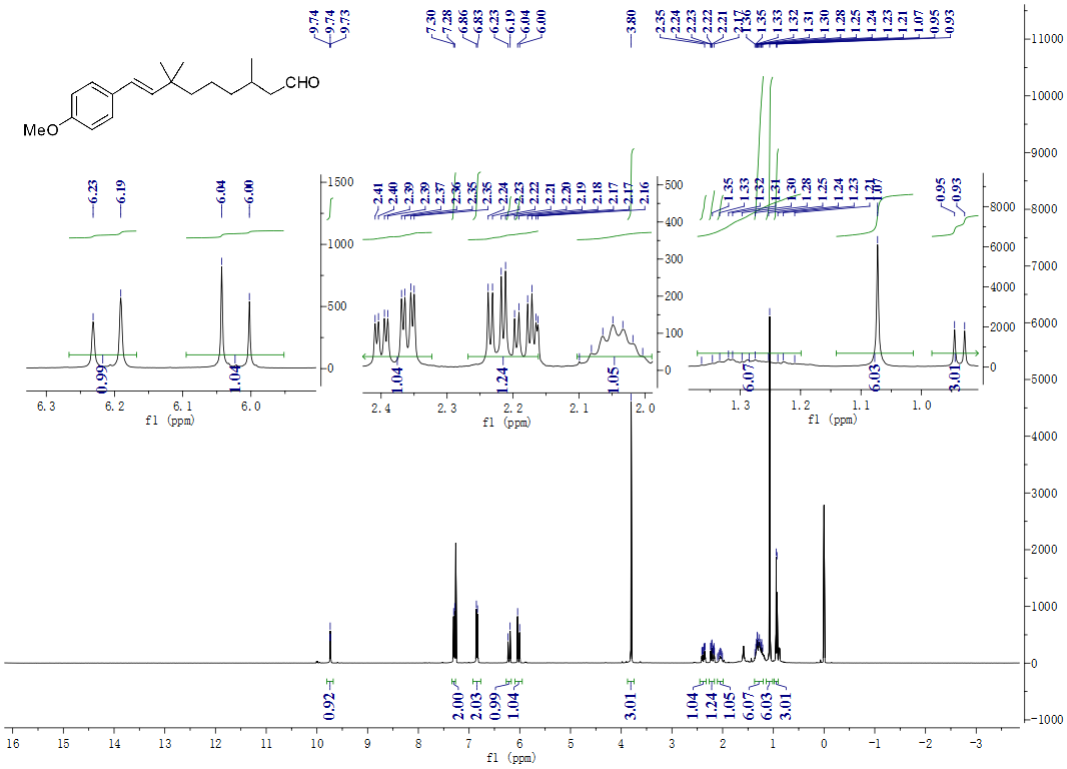


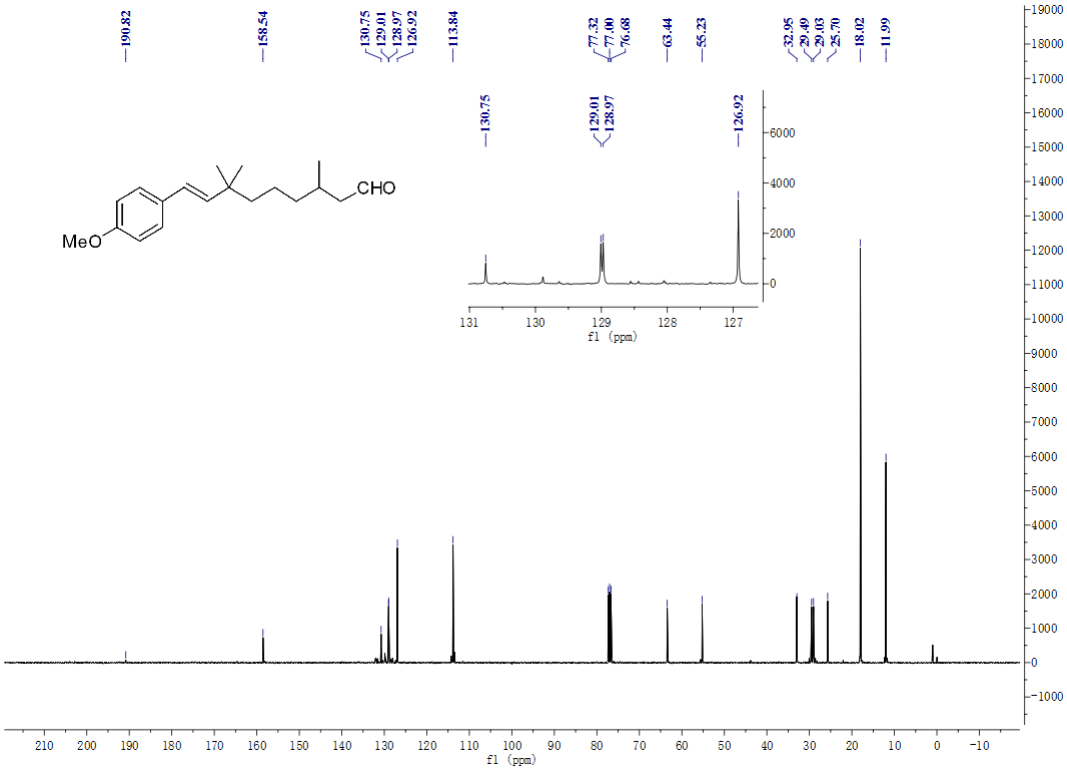
_(E)_-4,4,5,5-tetramethyl-2-(4-(3,3,7-trimethyloct-1-en-1-yl)phenyl)-1,3,2-dioxaborolane (17)



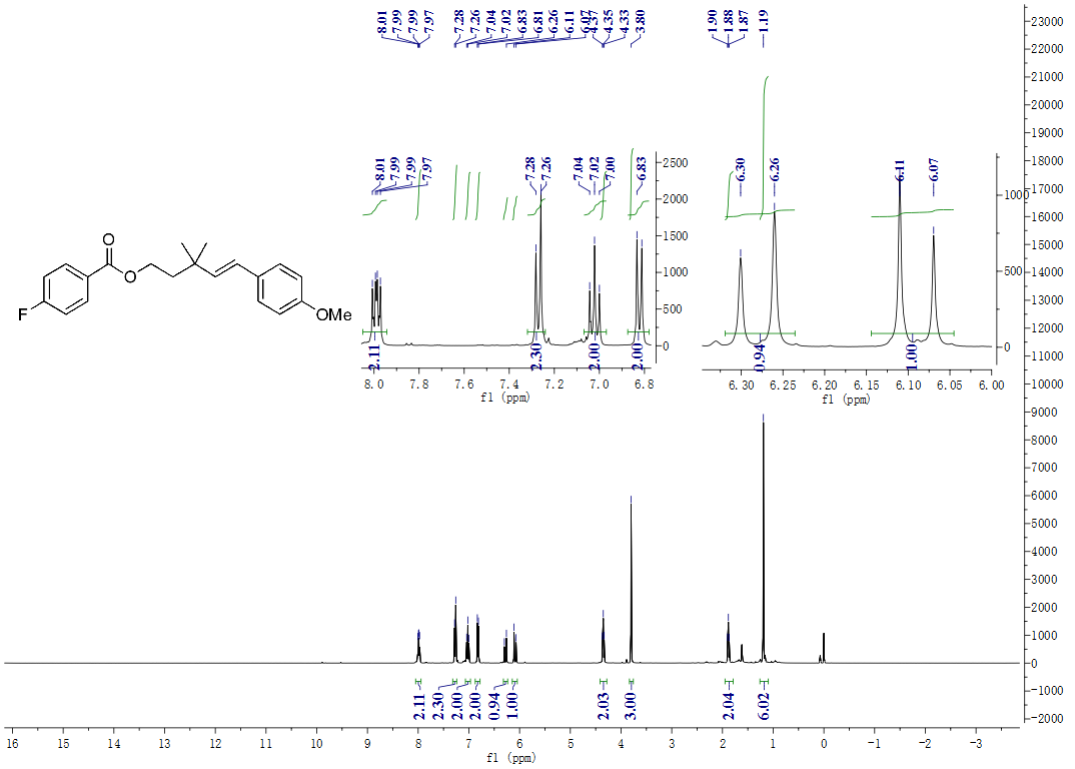


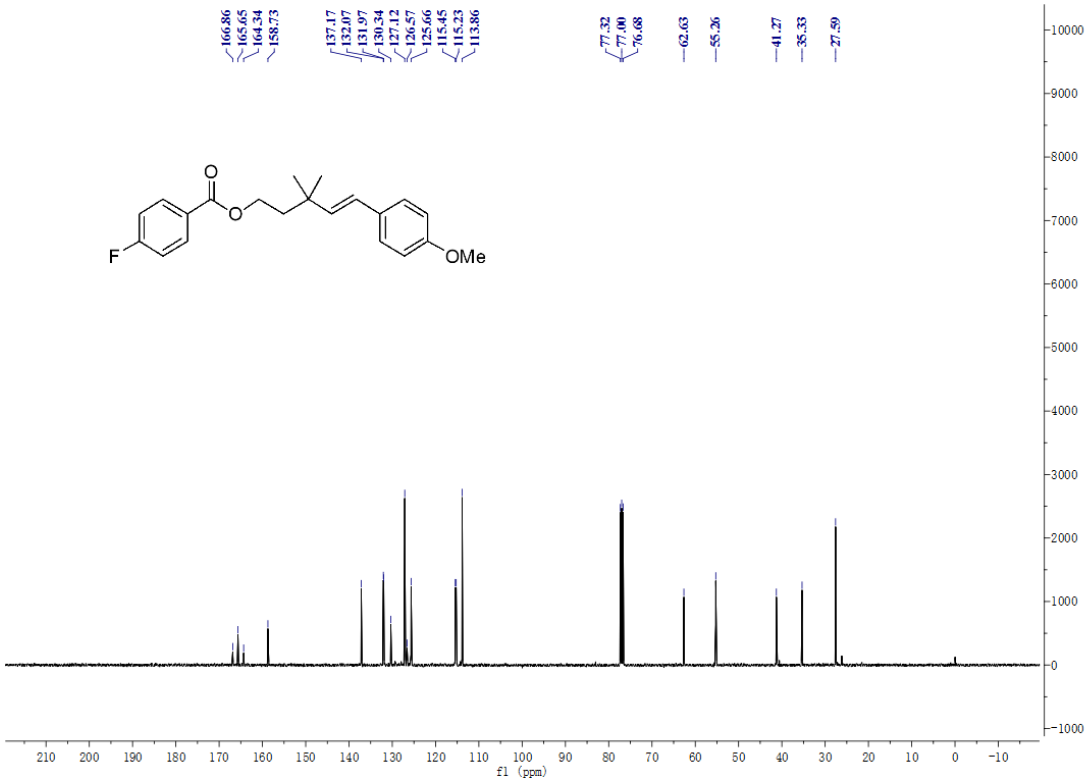
(E)-9-(4-methoxyphenyl)-3,7,7-trimethylnon-8-enal (18)

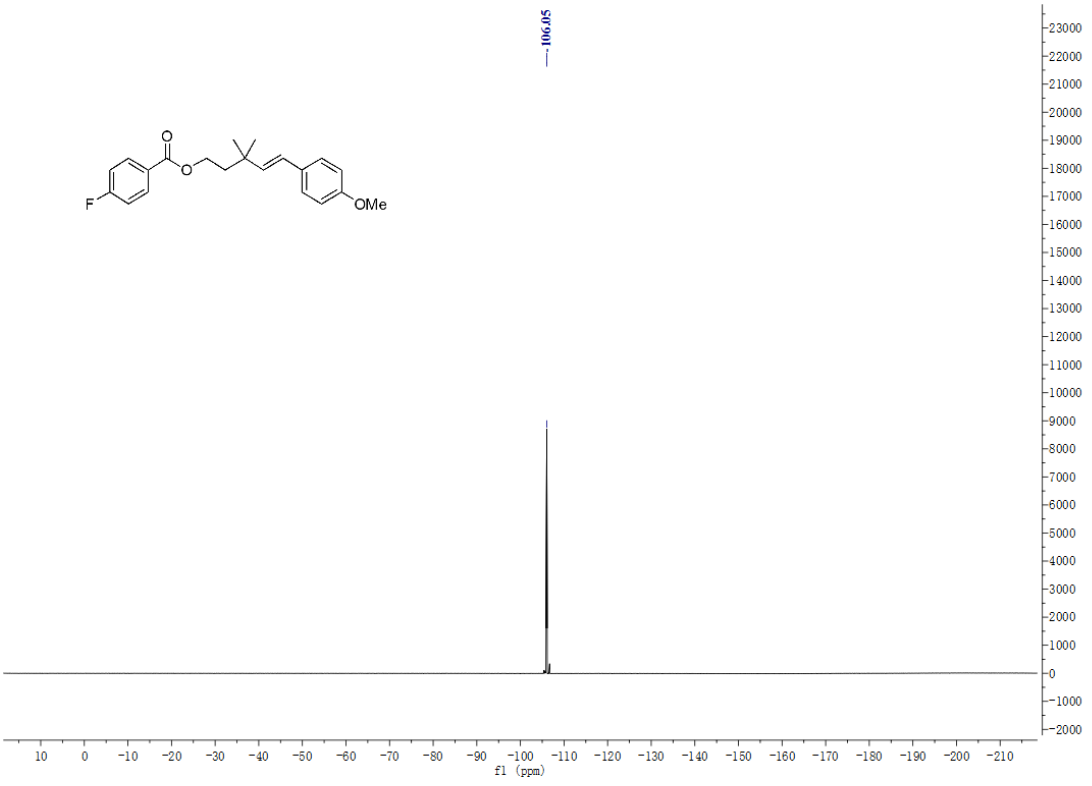




(E)-3,3-dimethyl-5-phenylpent-4-en-1-yl 4-fluorobenzoate (19)



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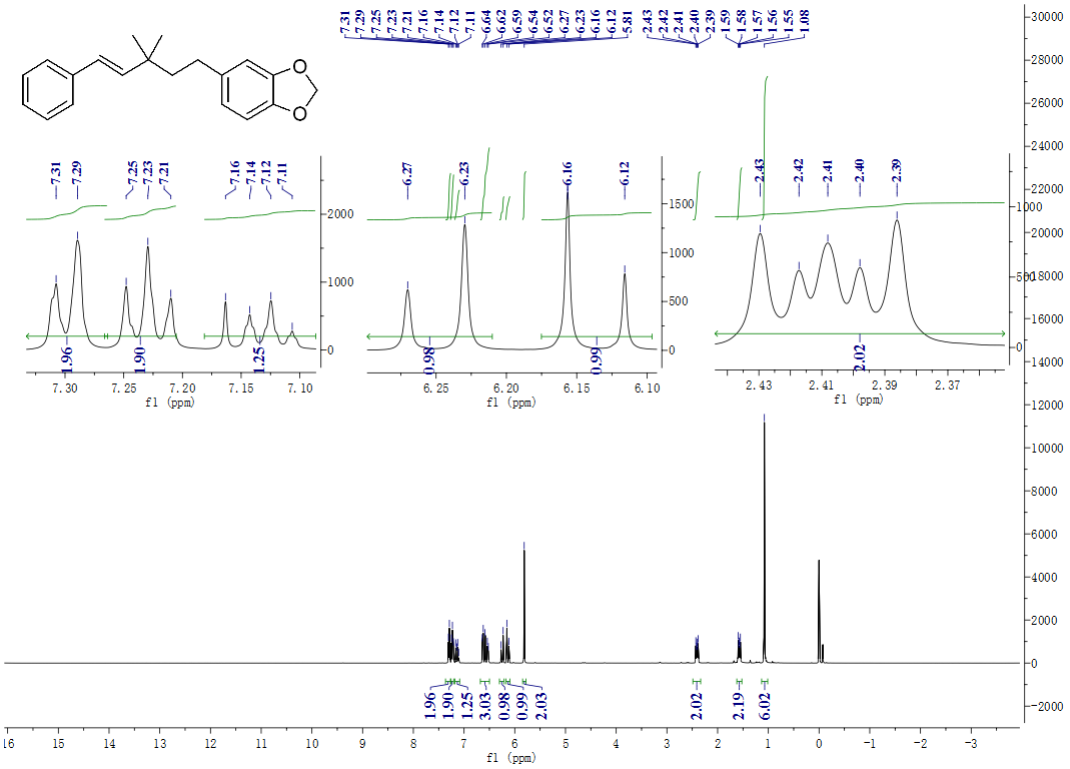
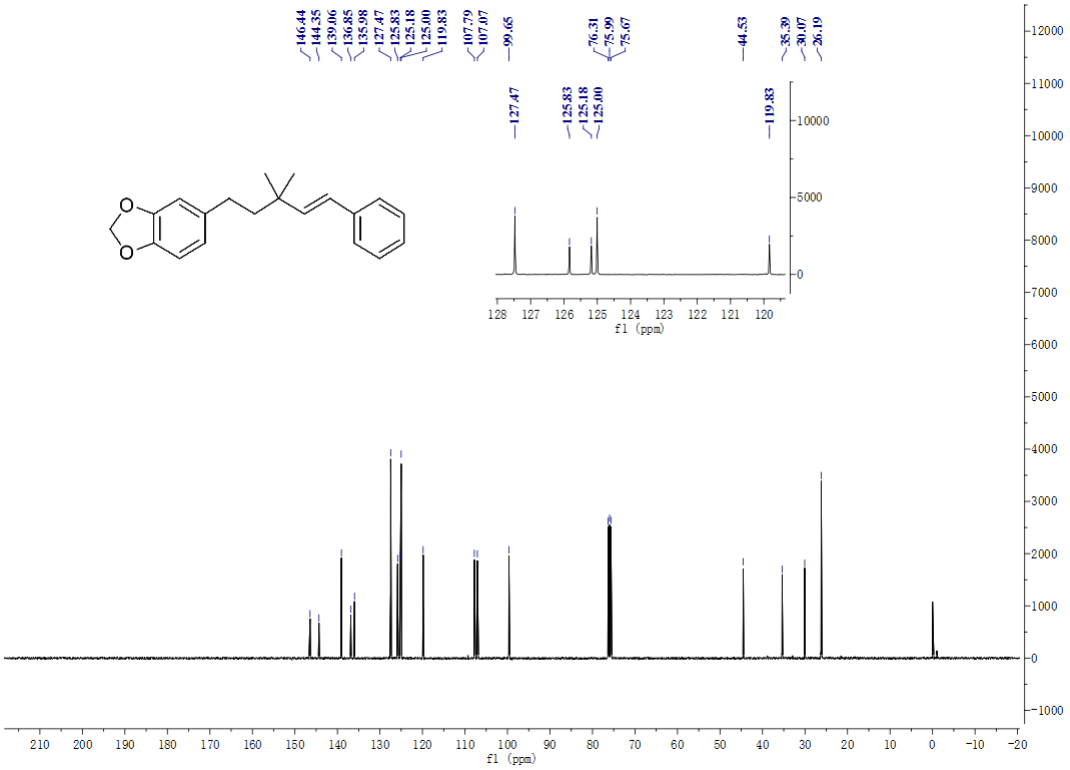
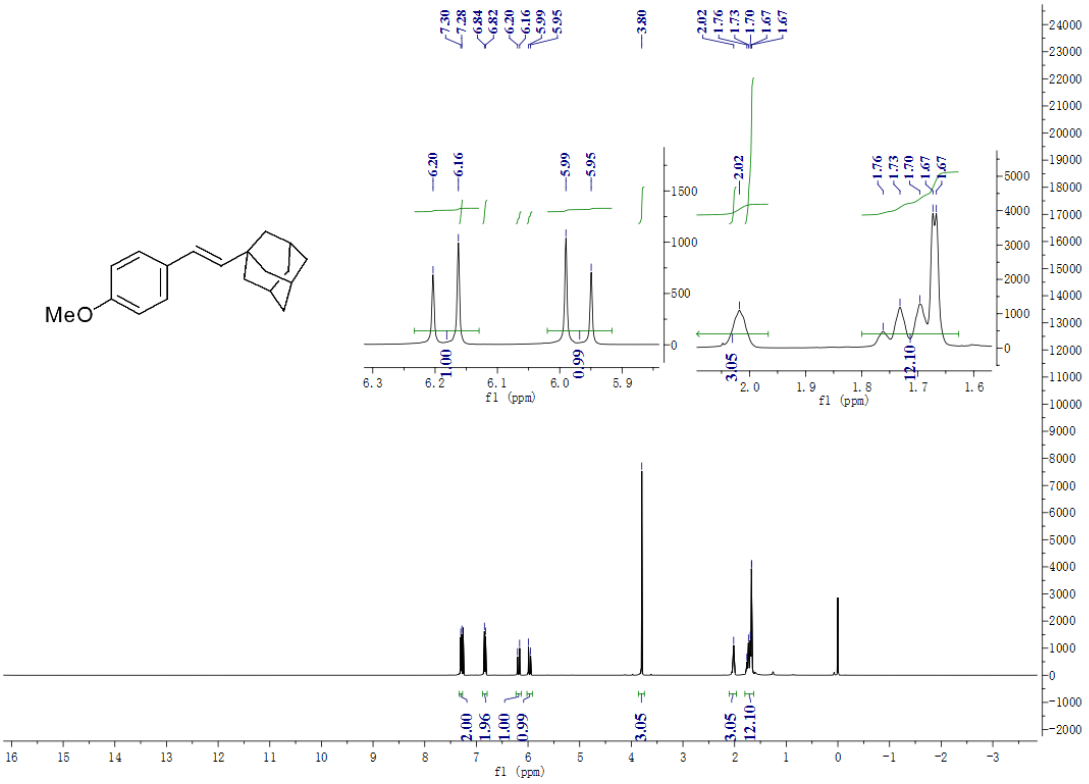
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

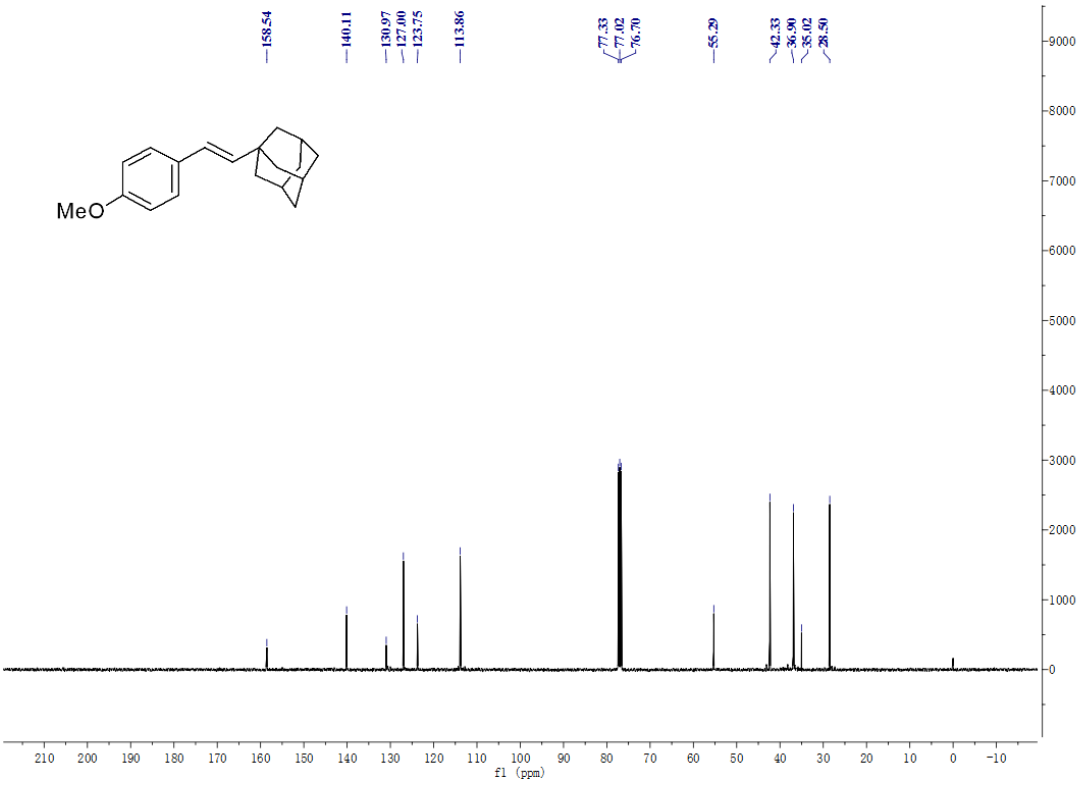
(E)-5-(3,3-dimethyl-5-phenylpent-4-en-1-yl)benzo[d][1,3]dioxole (20)



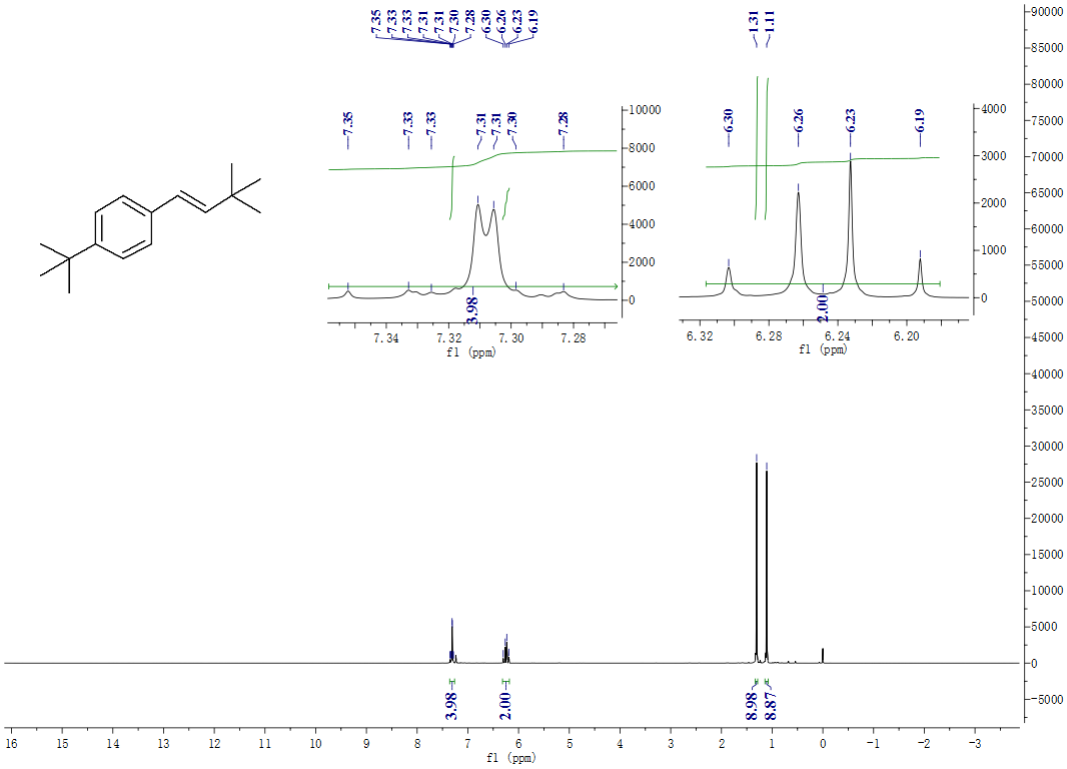


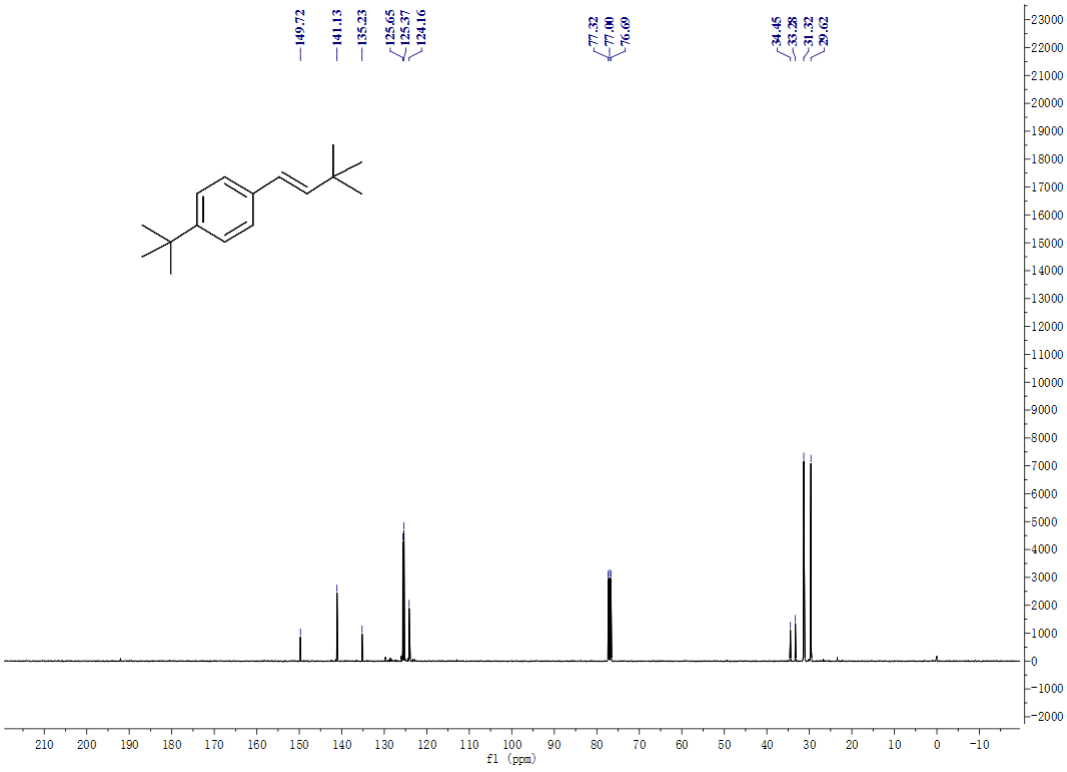
(3r,5r,7r)-1-((*E*)-4-methoxystyryl)adamantane (21)



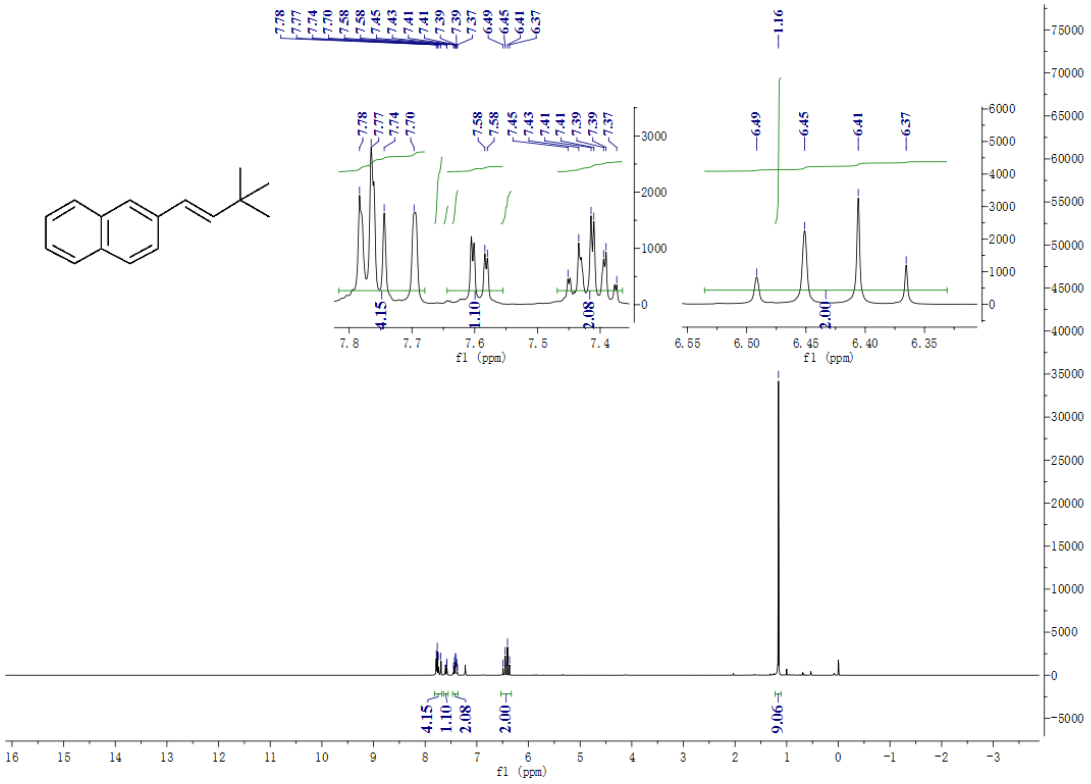


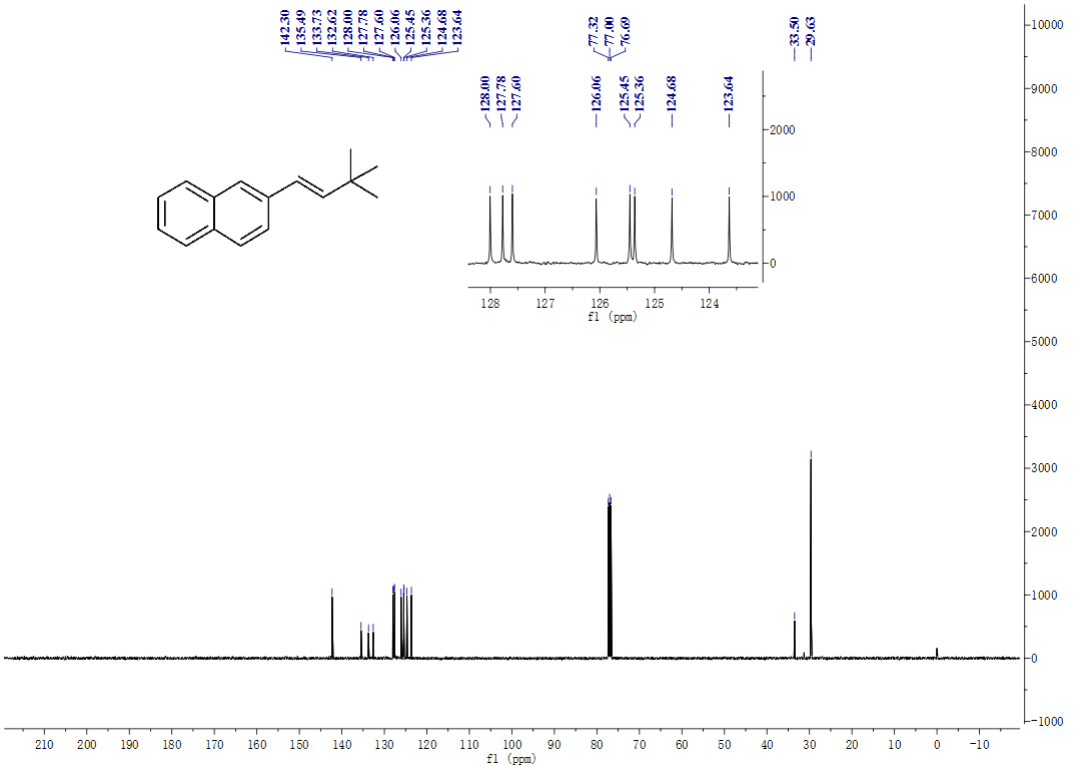
(E)-1-(tert-butyl)-4-(3,3-dimethylbut-1-en-1-yl)benzene (22)



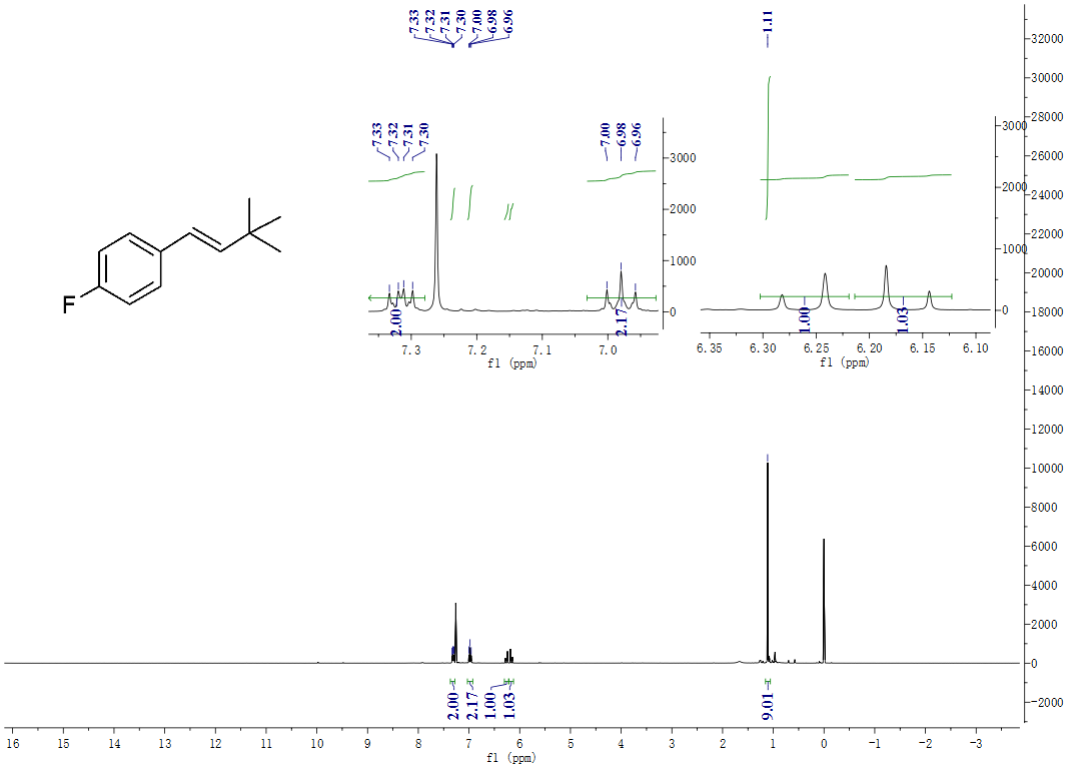


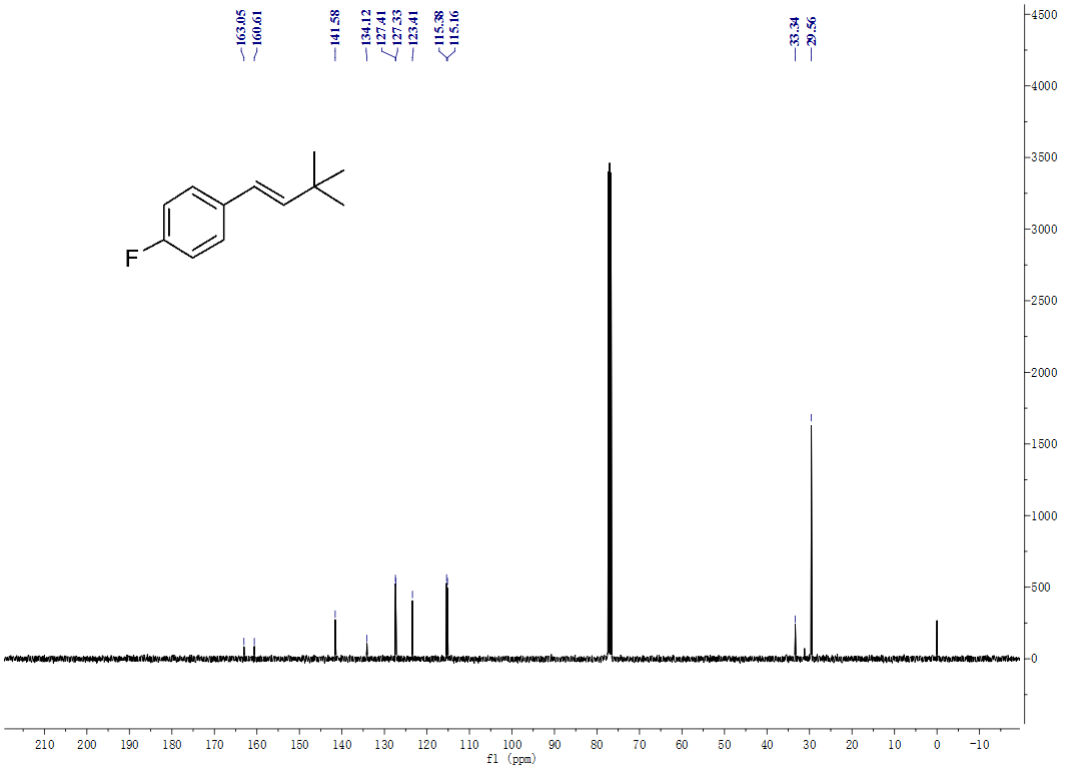
(E)-4-(3,3-dimethylbut-1-en-1-yl)-1,1'-biphenyl (23)

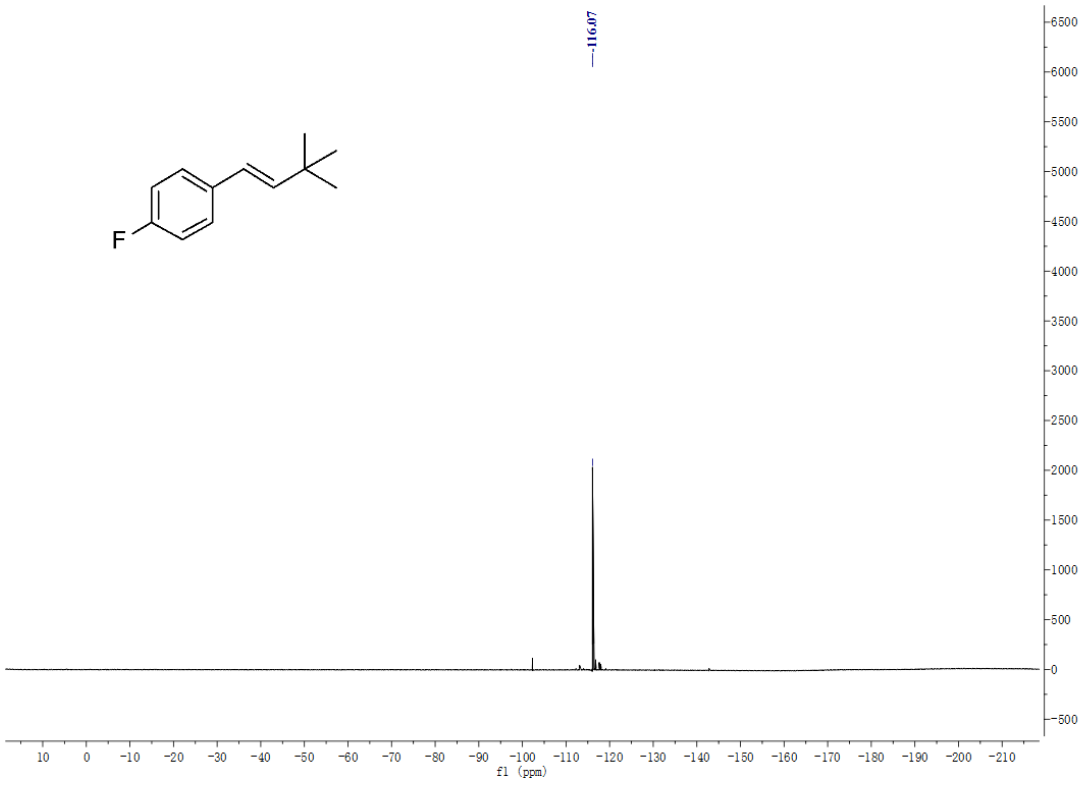




(E)-1-(3,3-dimethylbut-1-en-1-yl)-4-fluorobenzene (24)



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1500
1000
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-500
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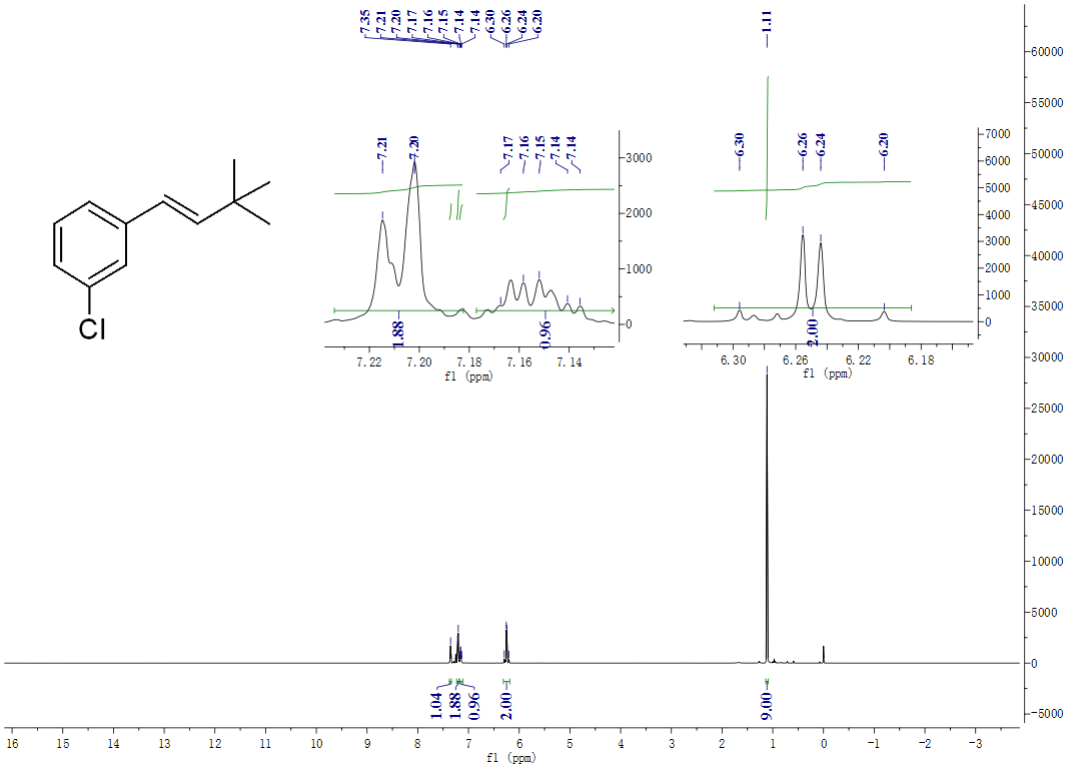
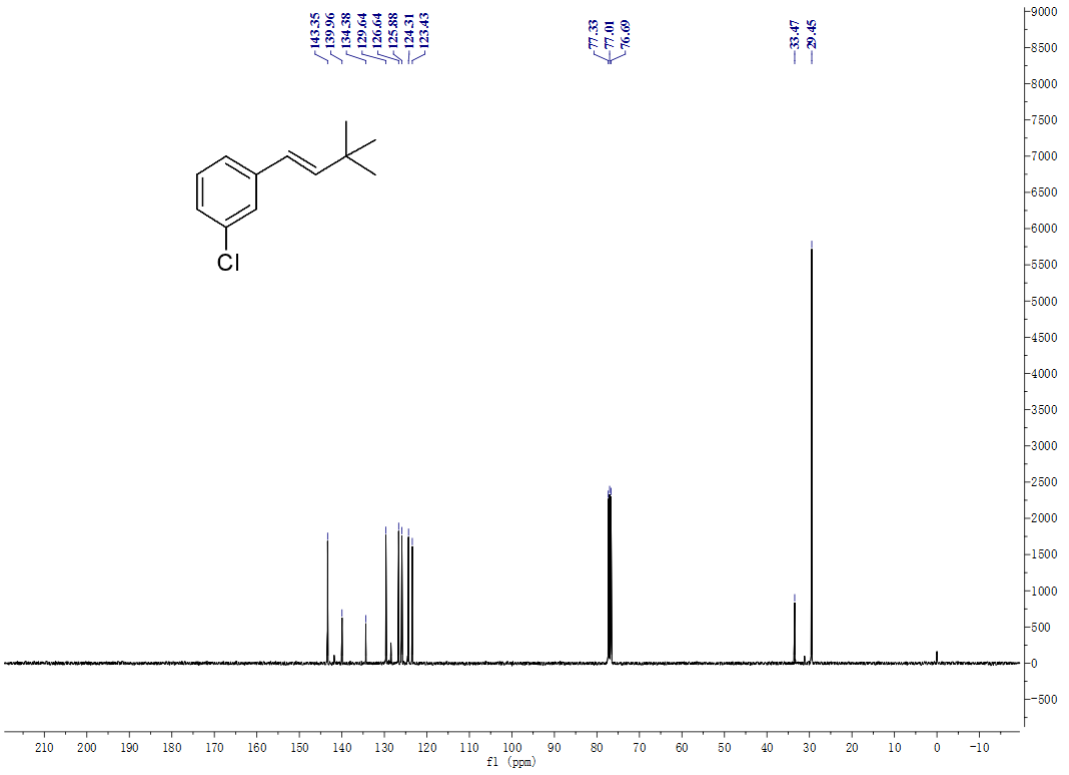
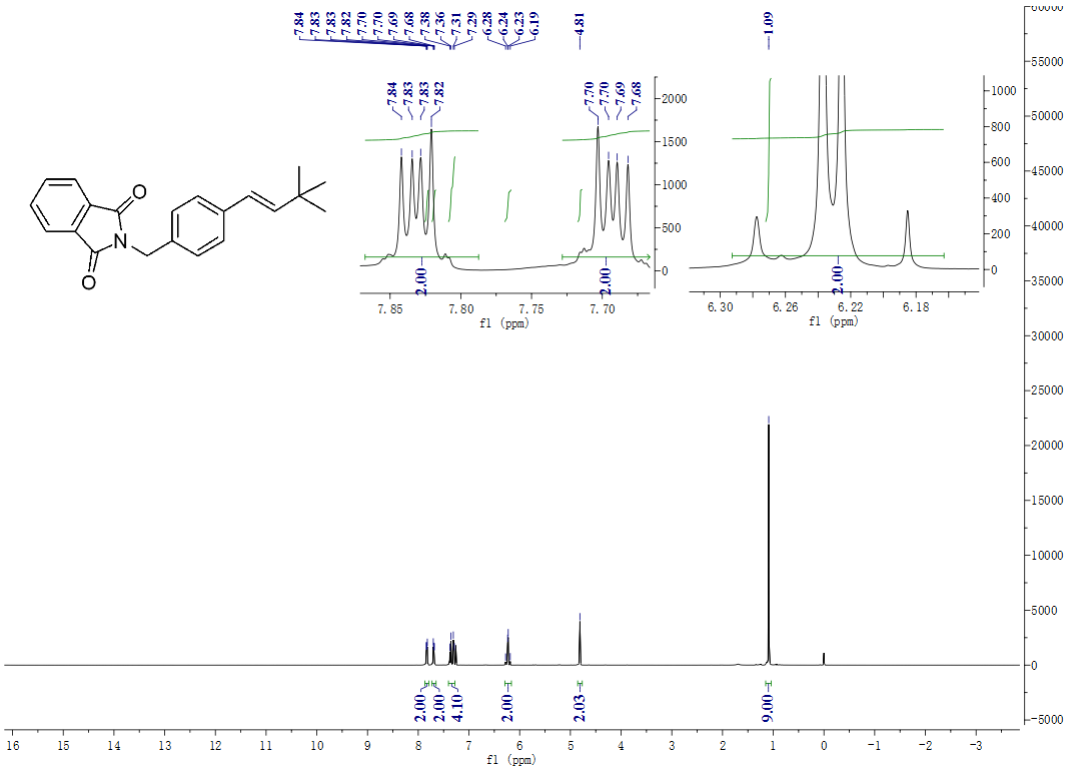
f1 (ppm)

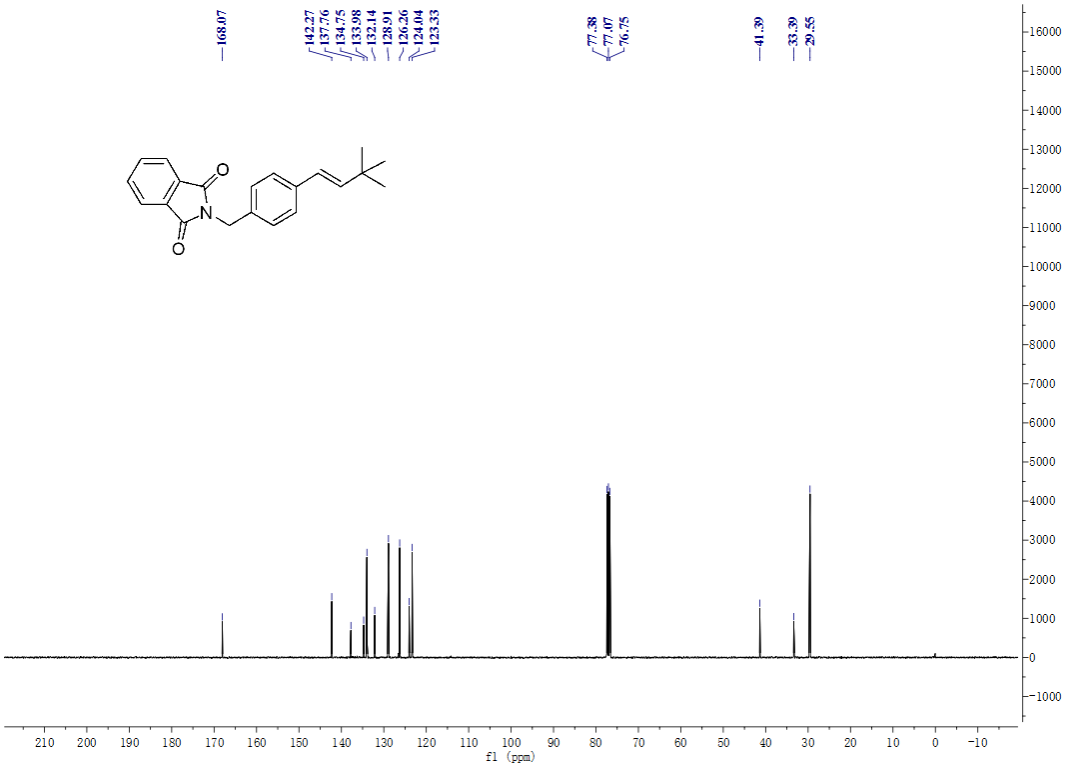
(E)-1-chloro-3-(3,3-dimethylbut-1-en-1-yl)benzene (25)



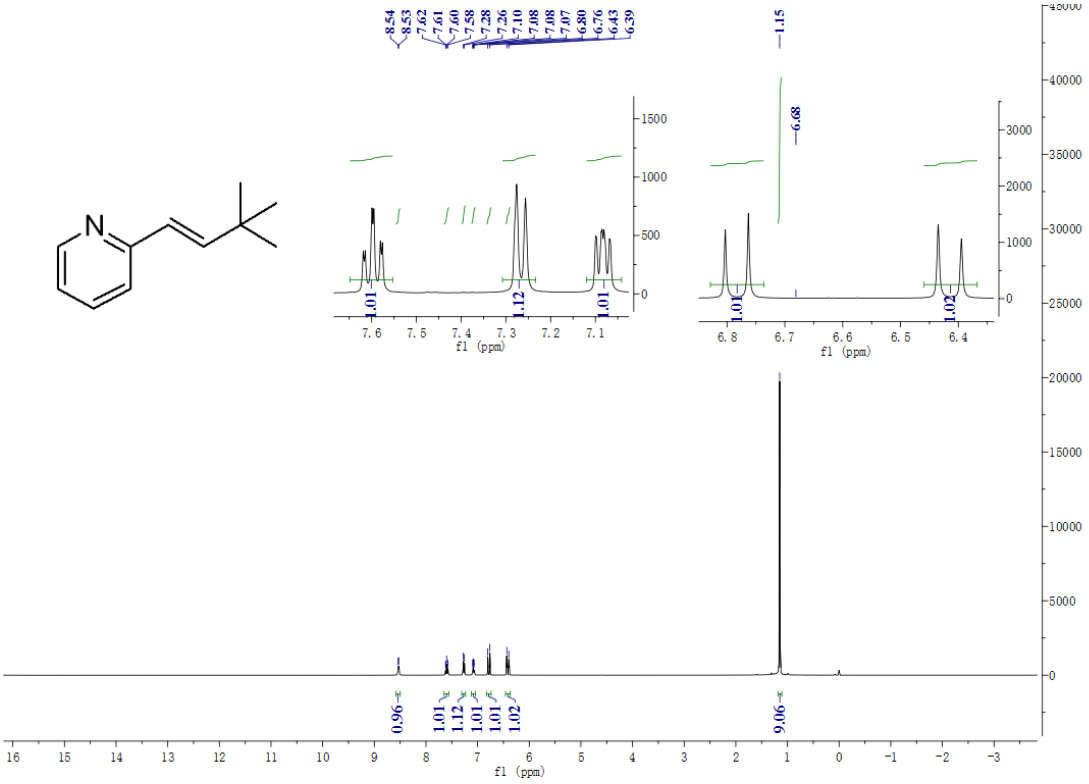


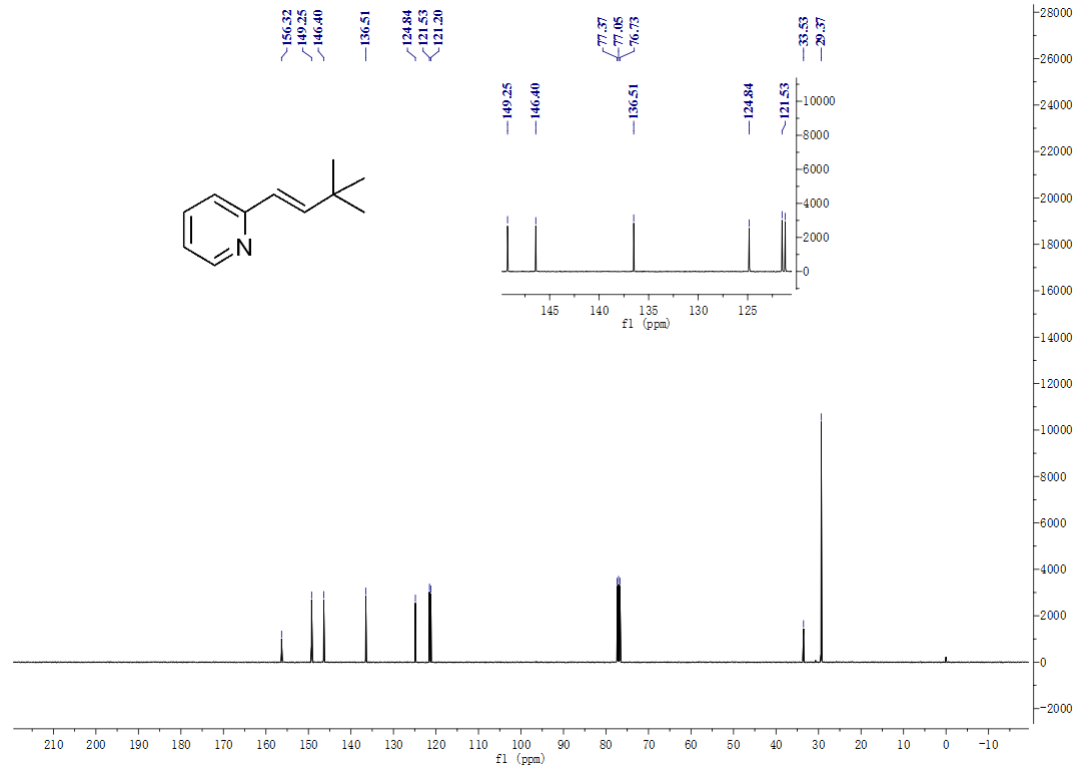
(E)-2-(4-(3,3-dimethylbut-1-en-1-yl)benzyl)isoindoline-1,3-dione (26)



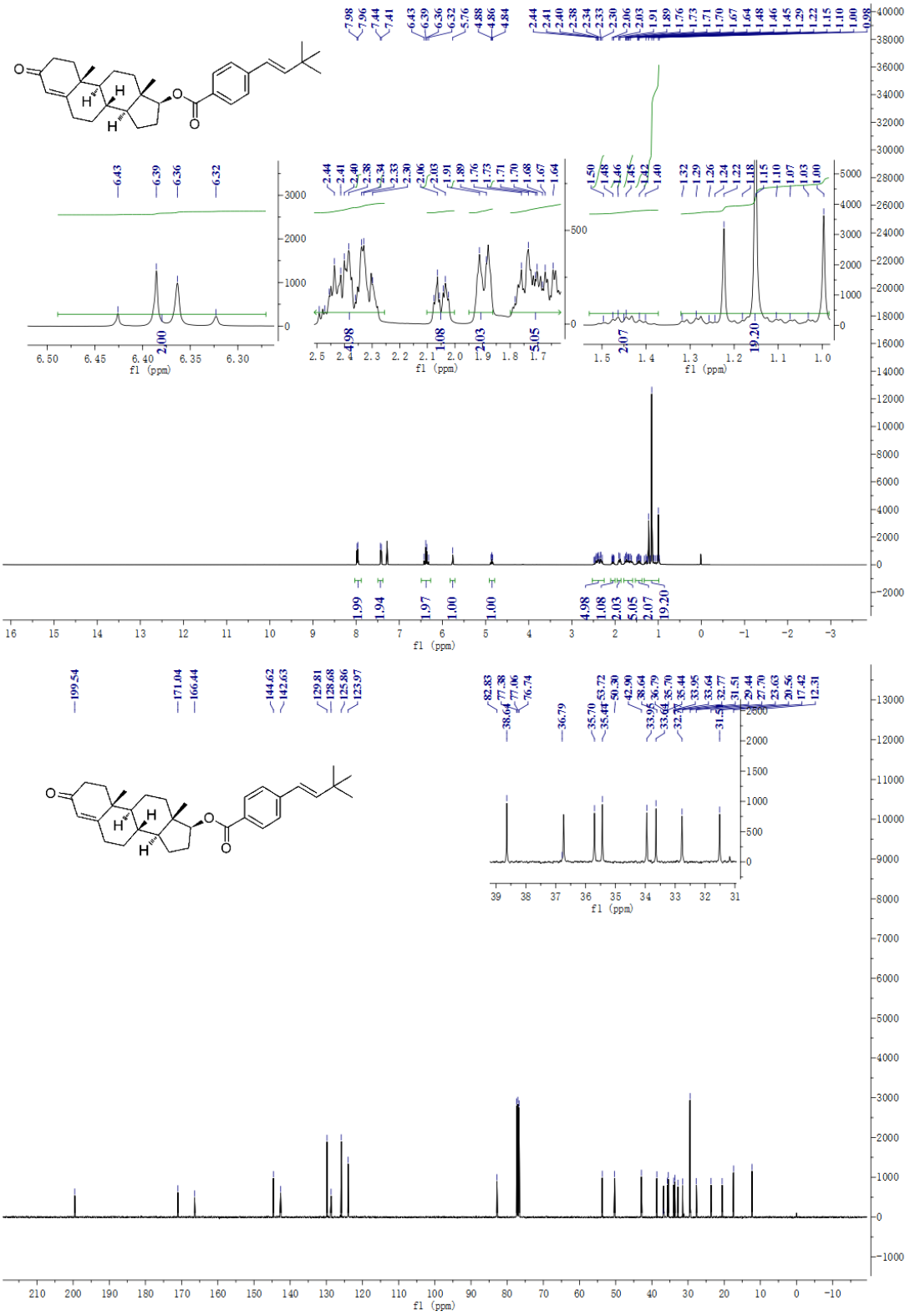


(E)-2-(3,3-dimethylbut-1-en-1-yl)pyridine (27)

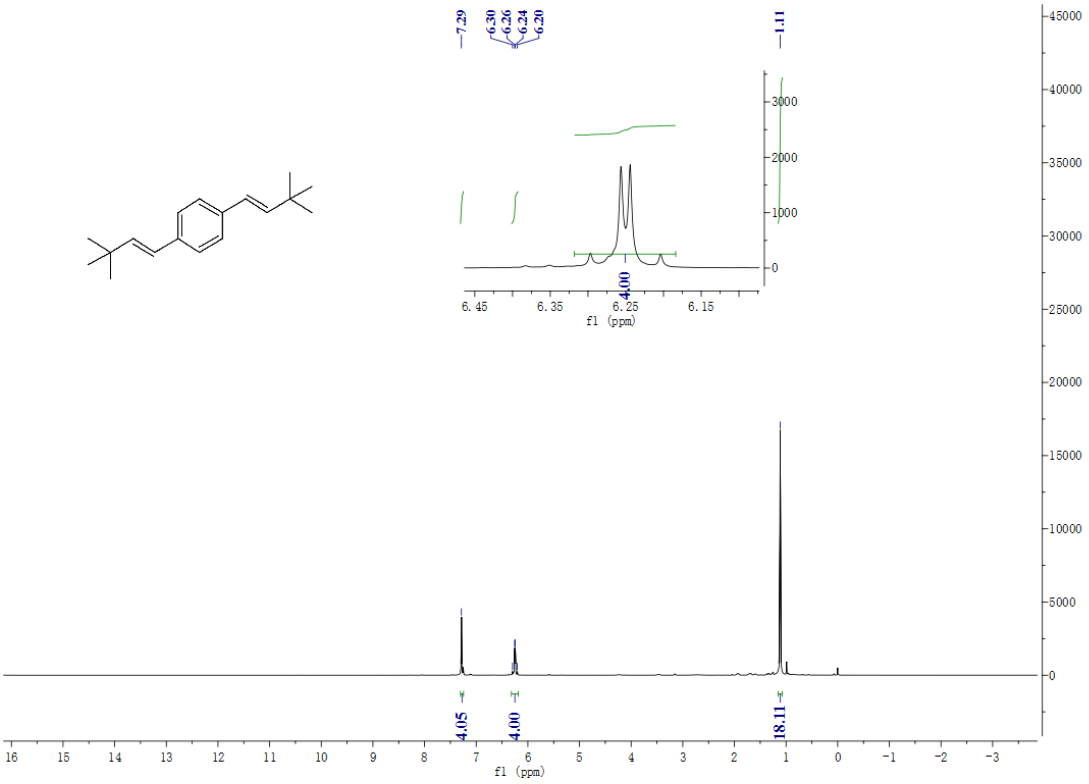


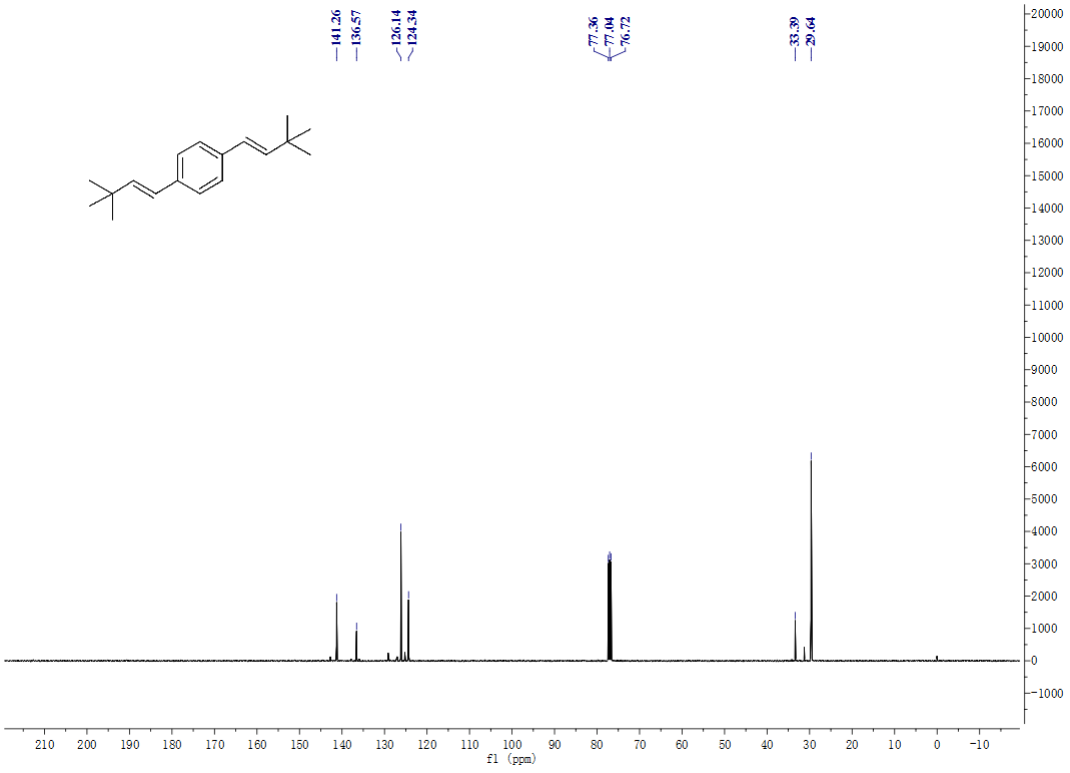


(8R,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl4-((*E*)-3,3-dimethylbut-1-en-1-yl)benzoate (28)

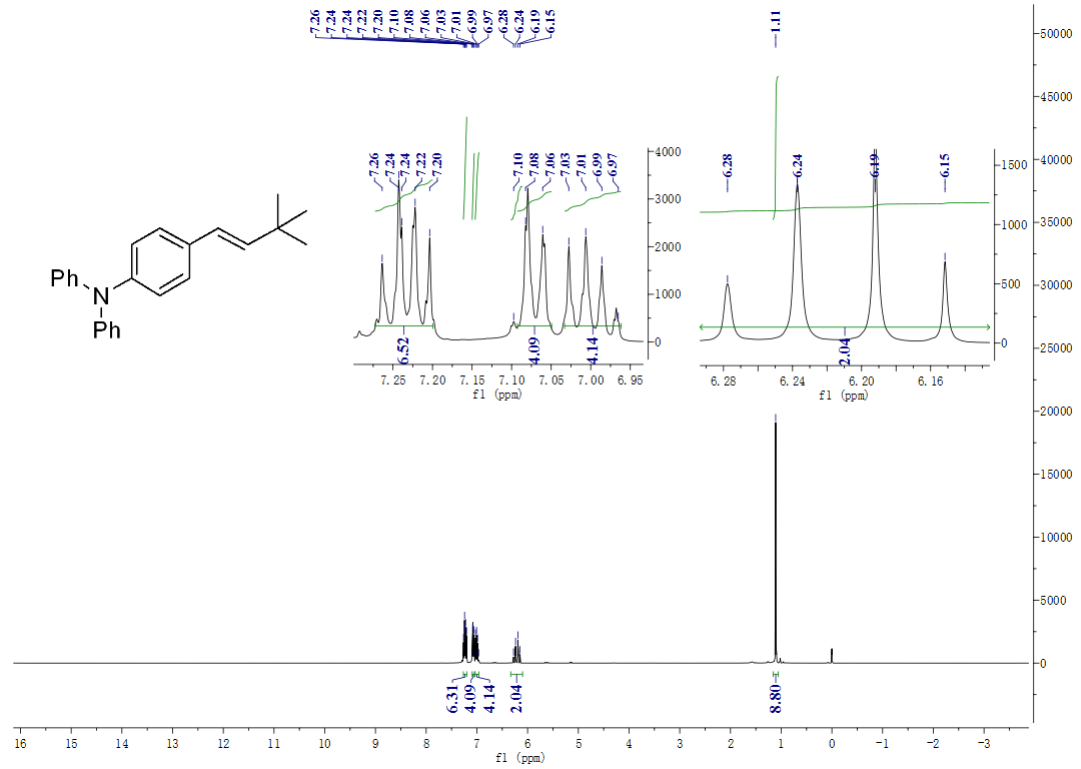


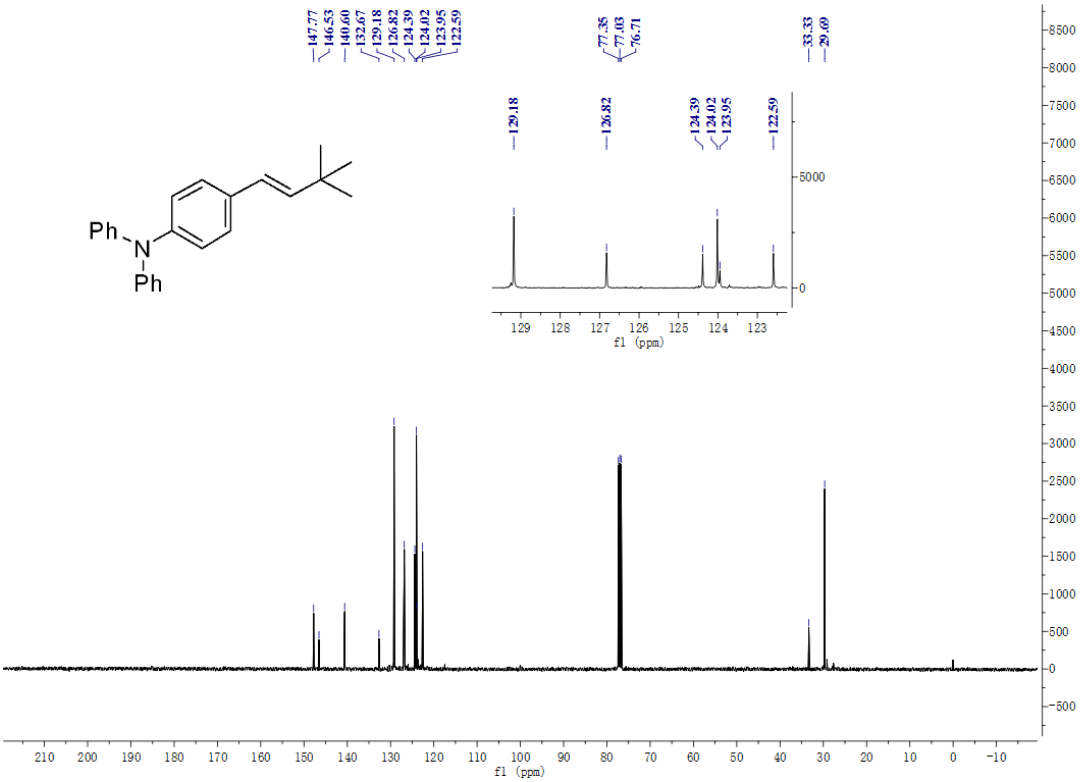
1,4-bis((*E*)-3,3-dimethylbut-1-en-1-yl)benzene (29)



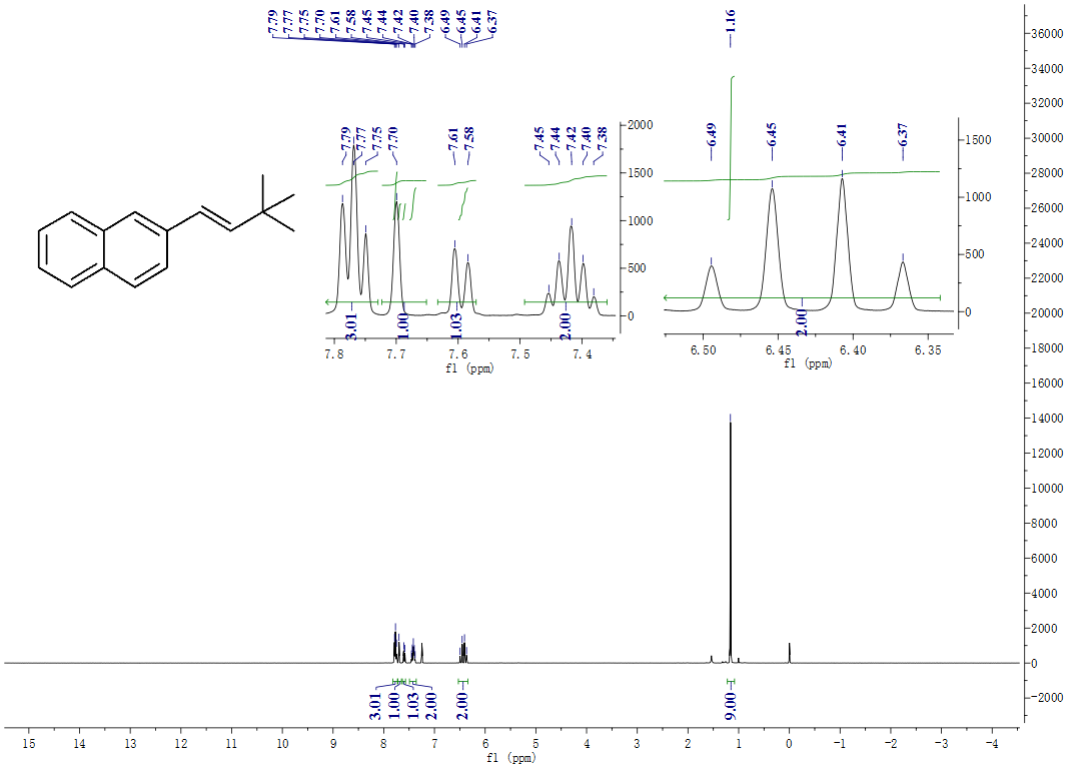


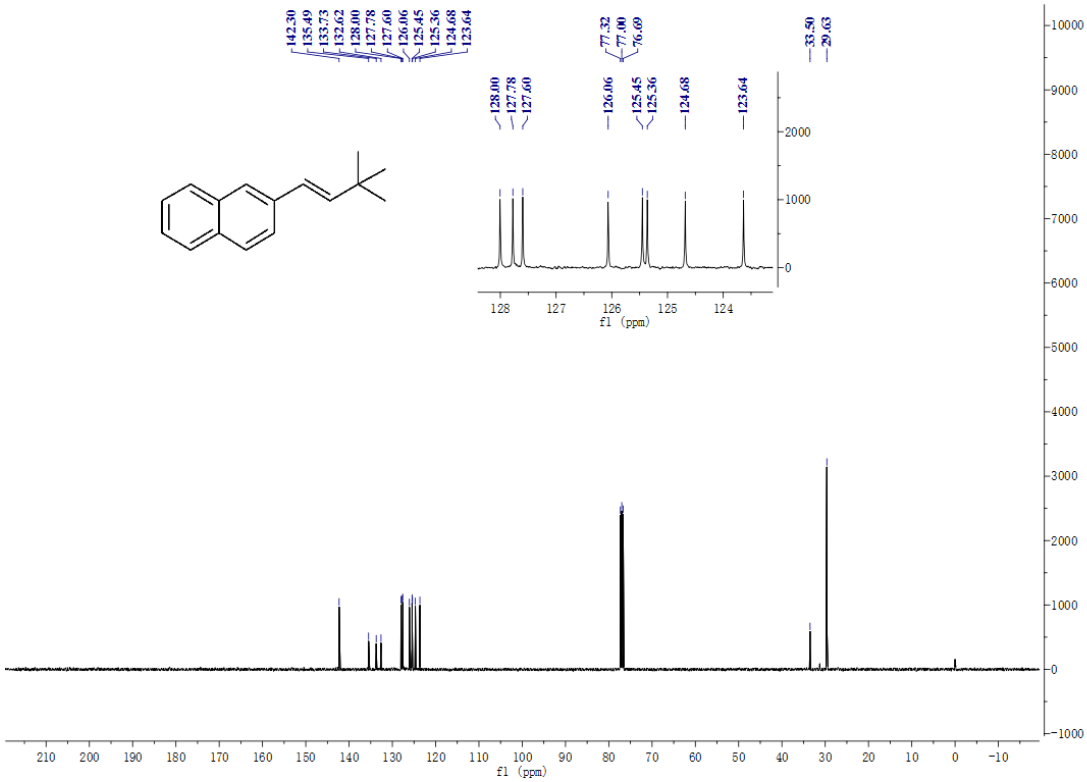
(E)-4-(3,3-dimethylbut-1-en-1-yl)-N,N-diphenylaniline (30)



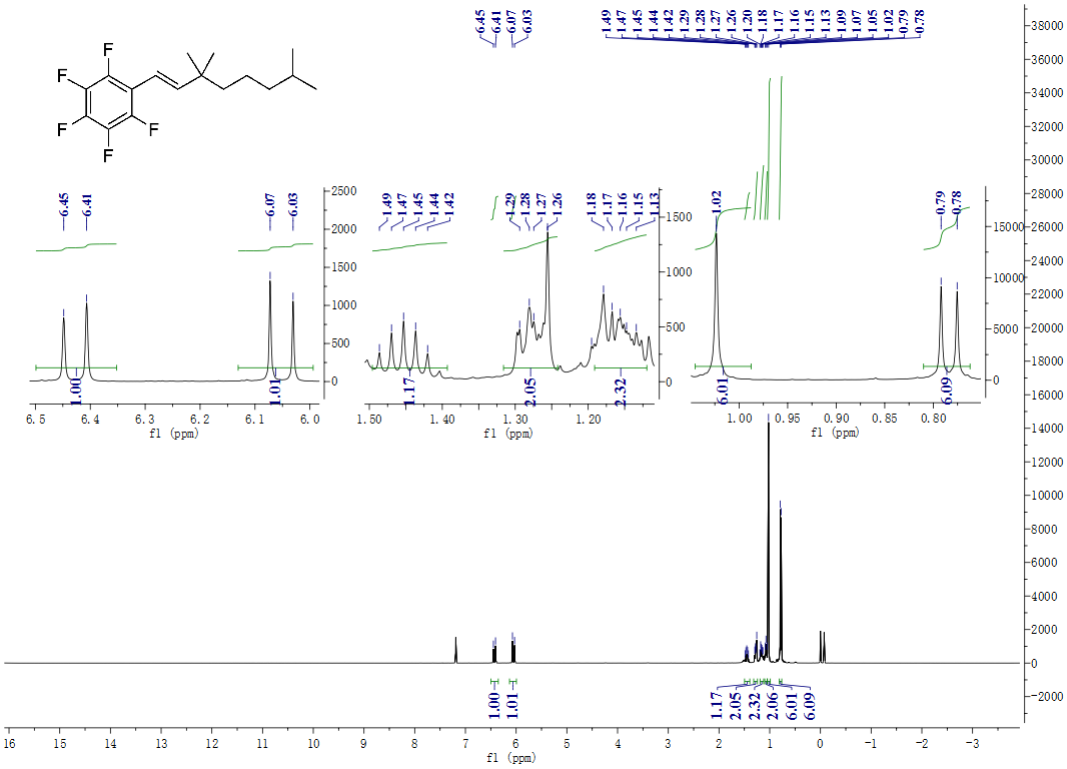


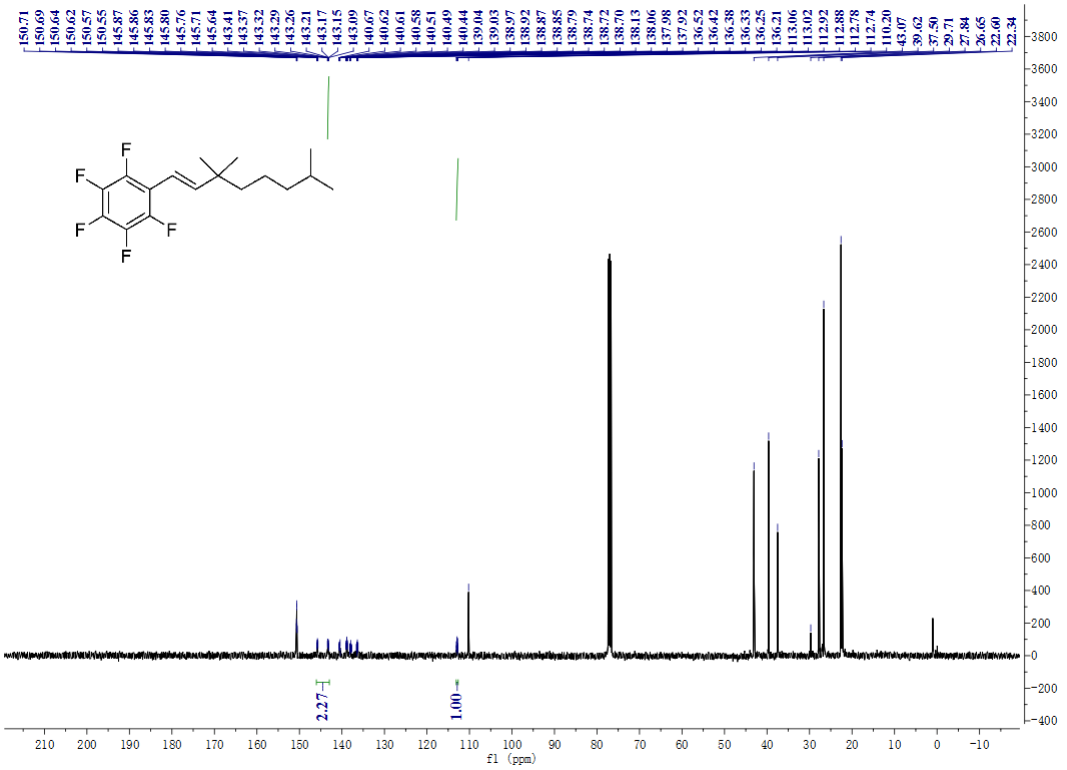
(E)-2-(3,3-dimethylbut-1-en-1-yl)naphthalene (31)

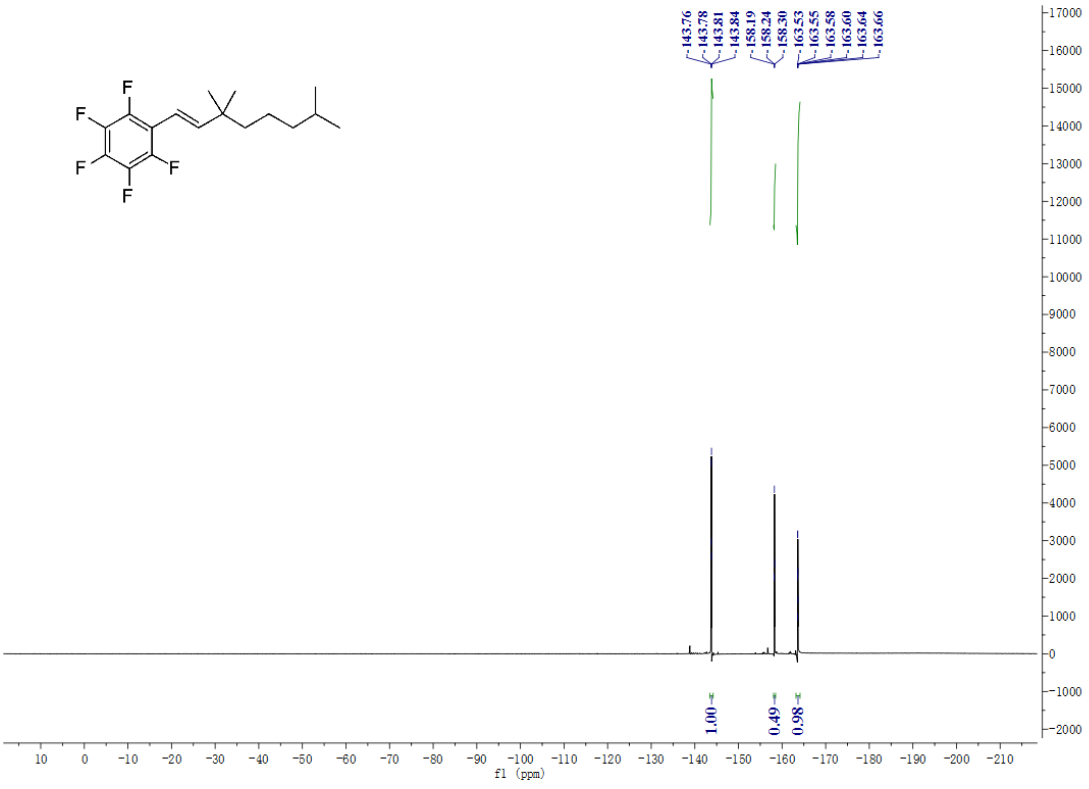




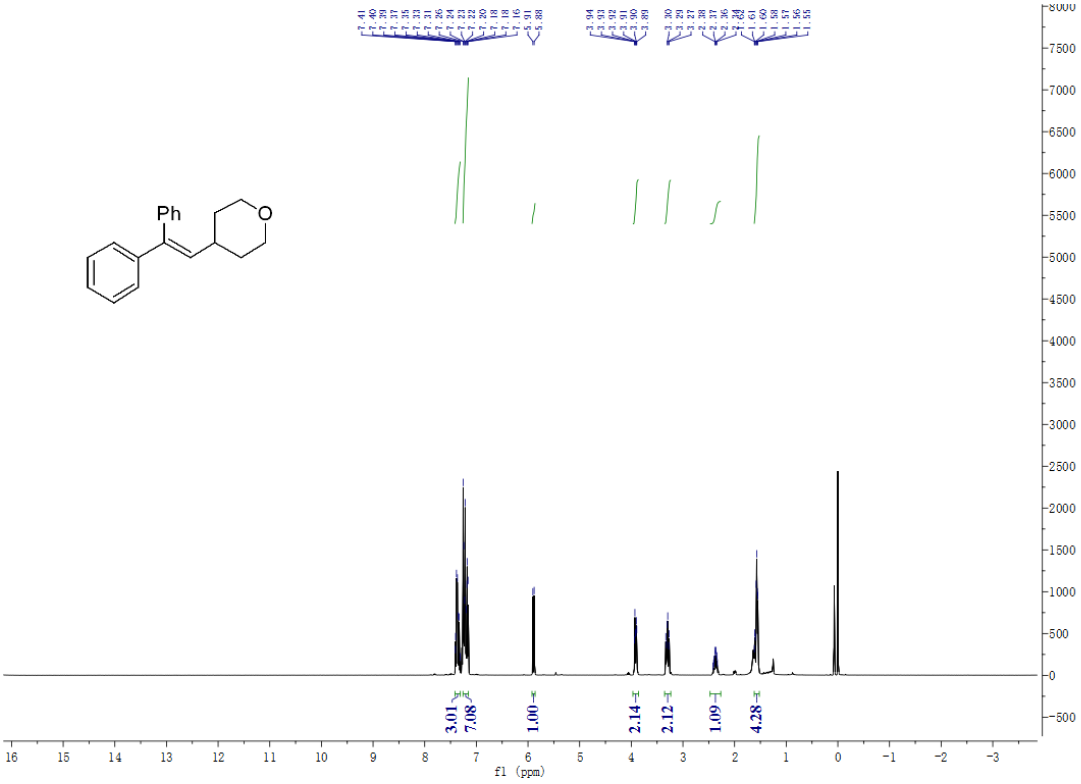
(E)-1,2,3,4,5-pentafluoro-6-(3,3,7-trimethyloct-1-en-1-yl)benzene (32)

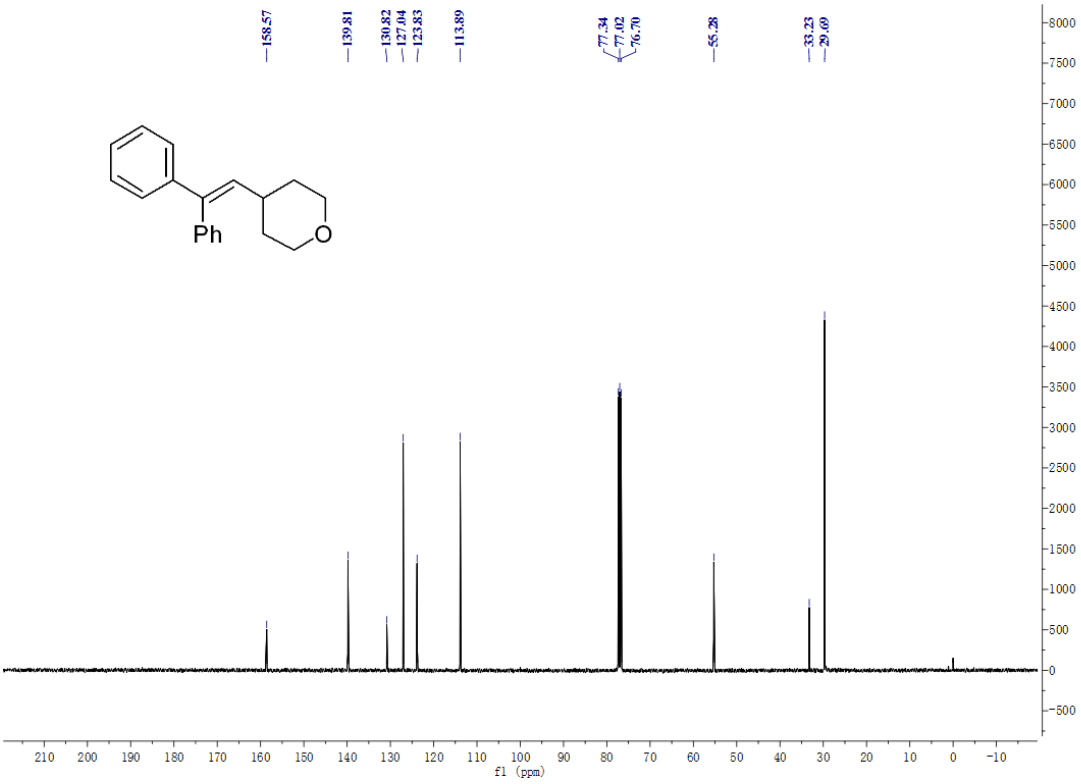




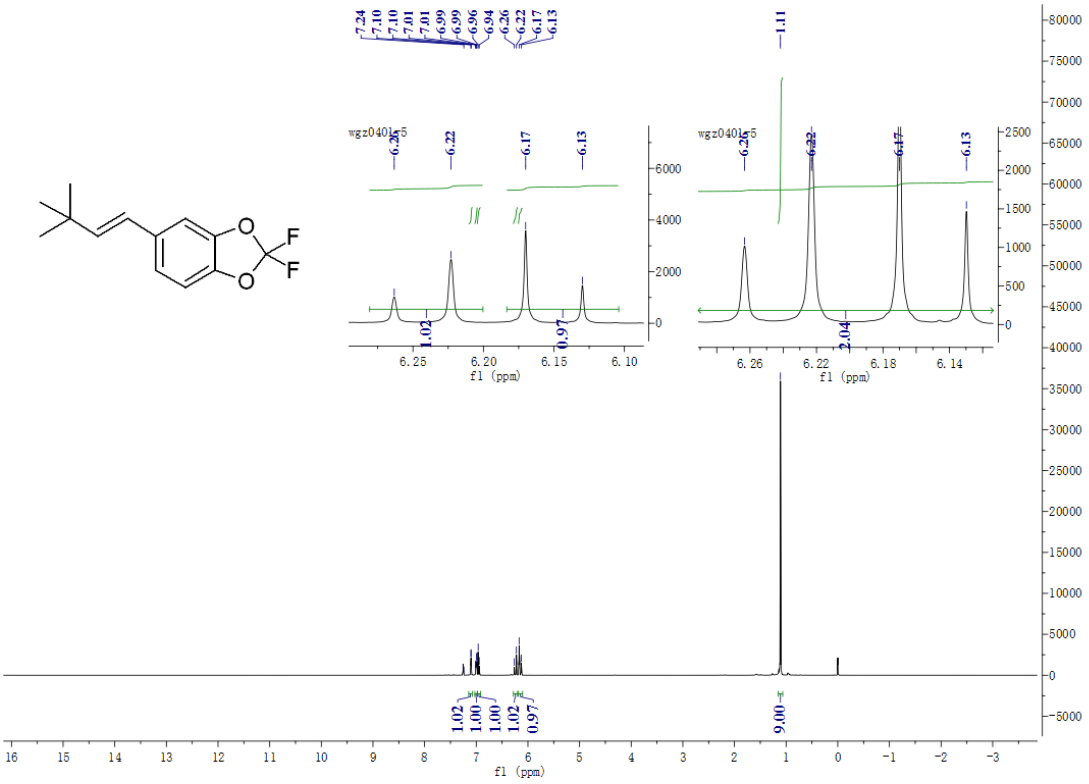

F
F
F
F
F
-143.76
-143.78
-143.81
-143.84
-158.19
-158.24
-158.30
-163.53
-163.55
-163.58
-163.60
-163.64
-163.66
1.00
0.49
0.98
f1 (ppm)

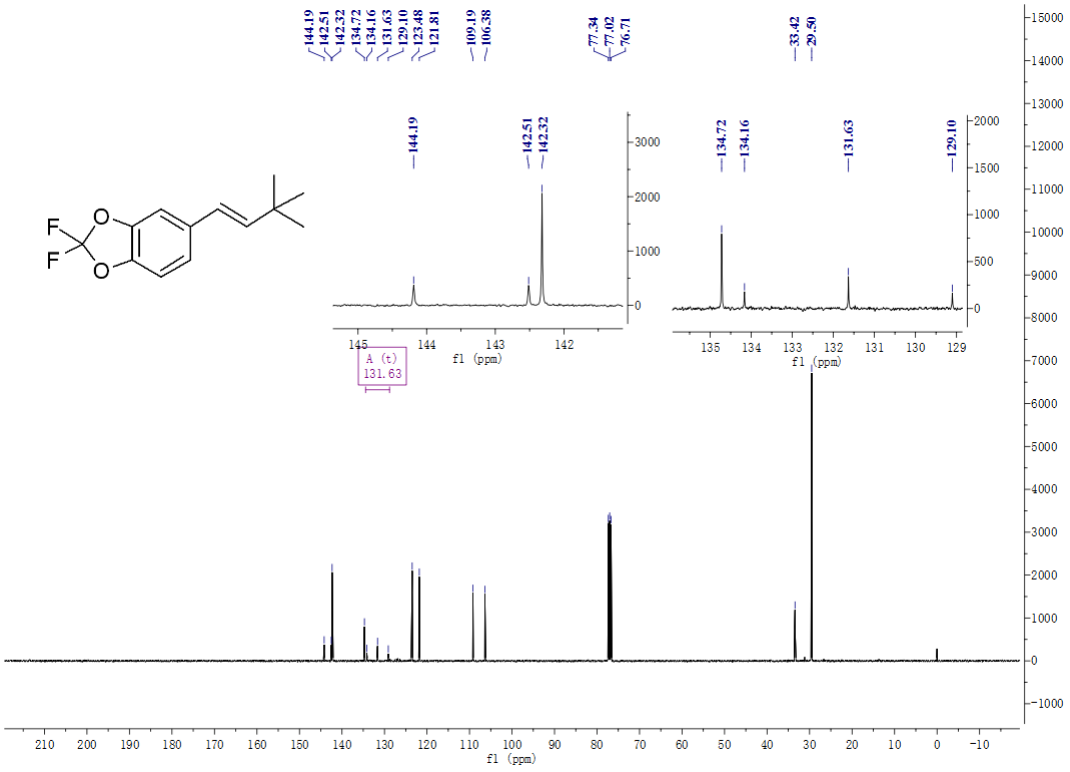
4-(2,2-diphenylvinyl)tetrahydro-2H-pyran (33)

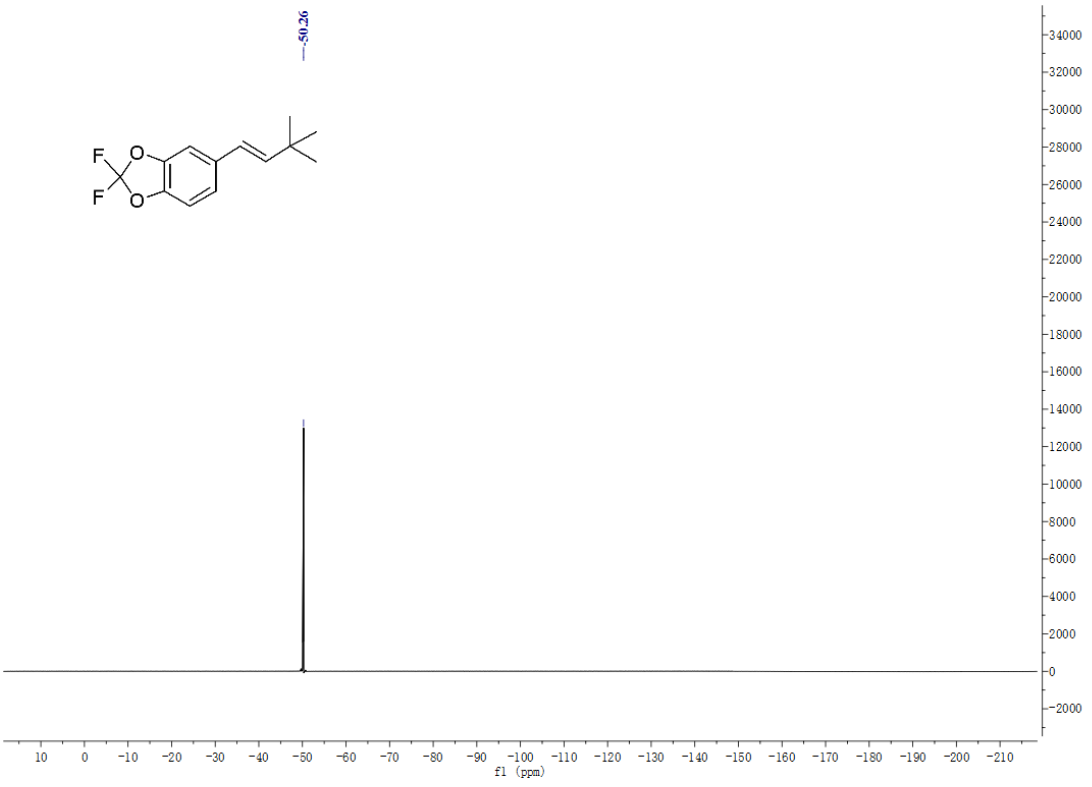




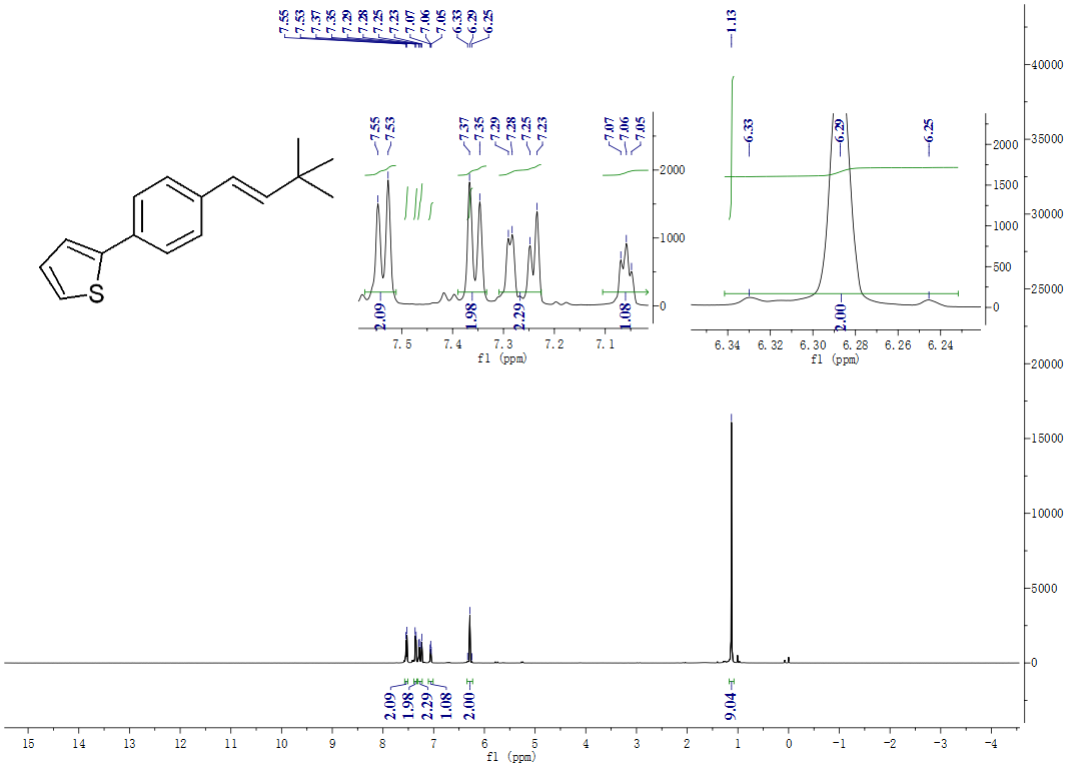
(E)-5-(3,3-dimethylbut-1-en-1-yl)-2,2-difluorobenzo[d][1,3]dioxole (34)

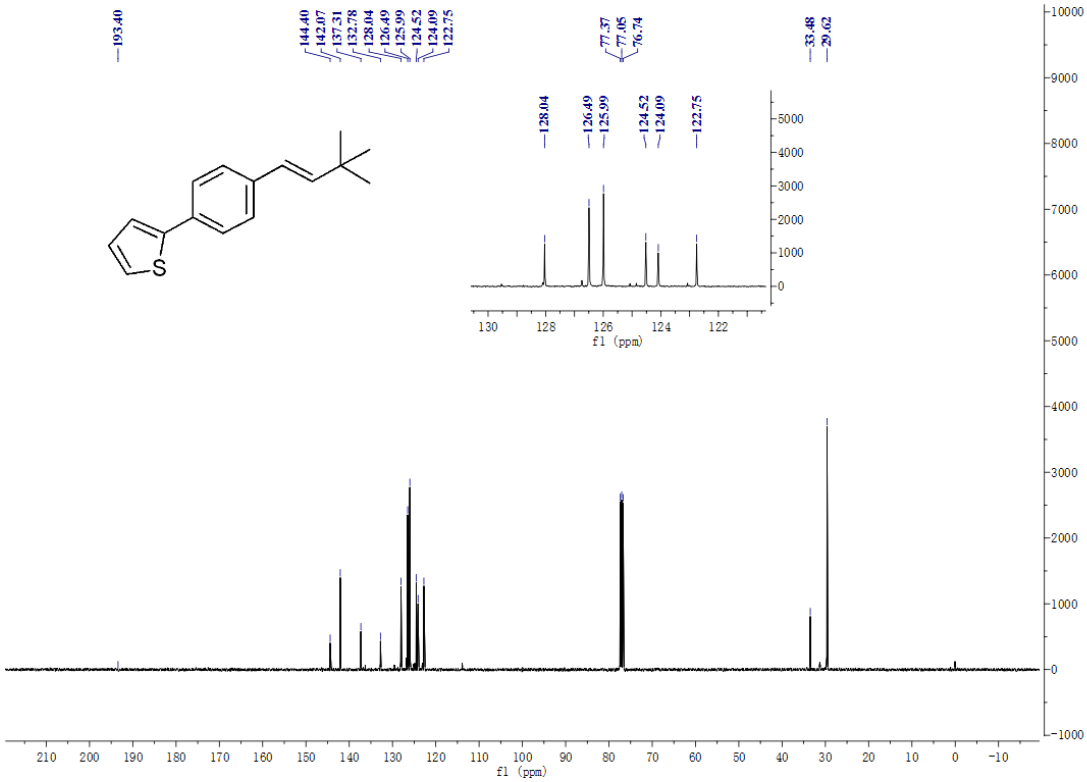




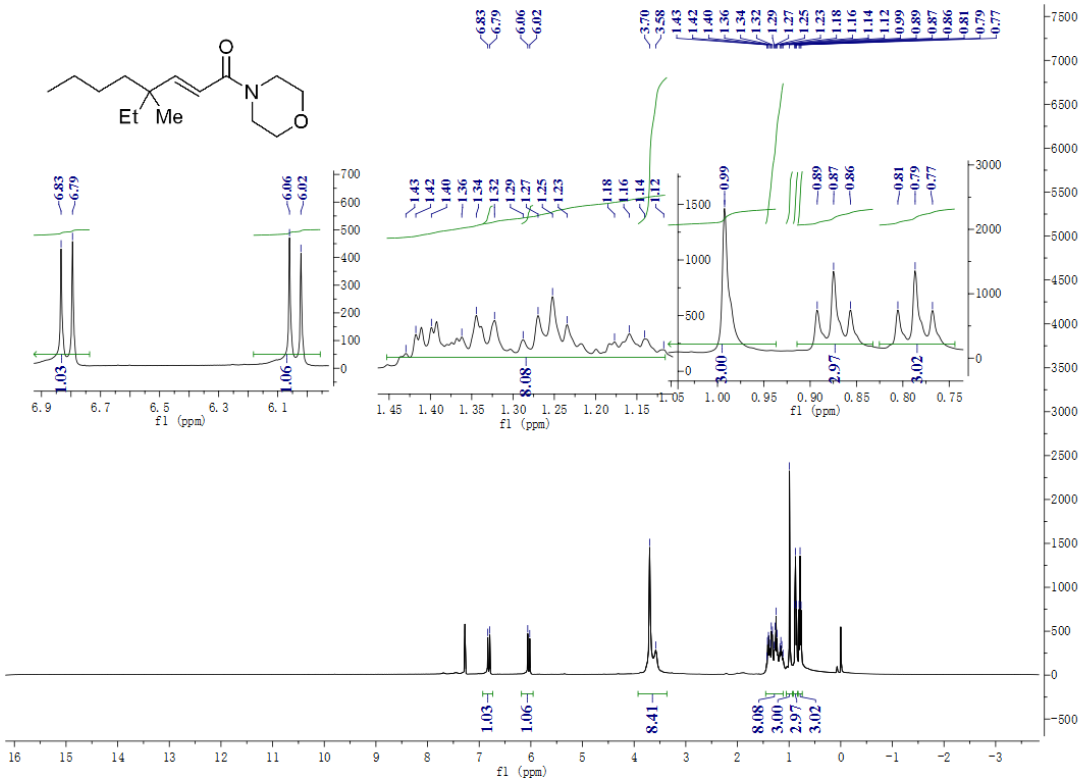

-50.26
F
O
F
O
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

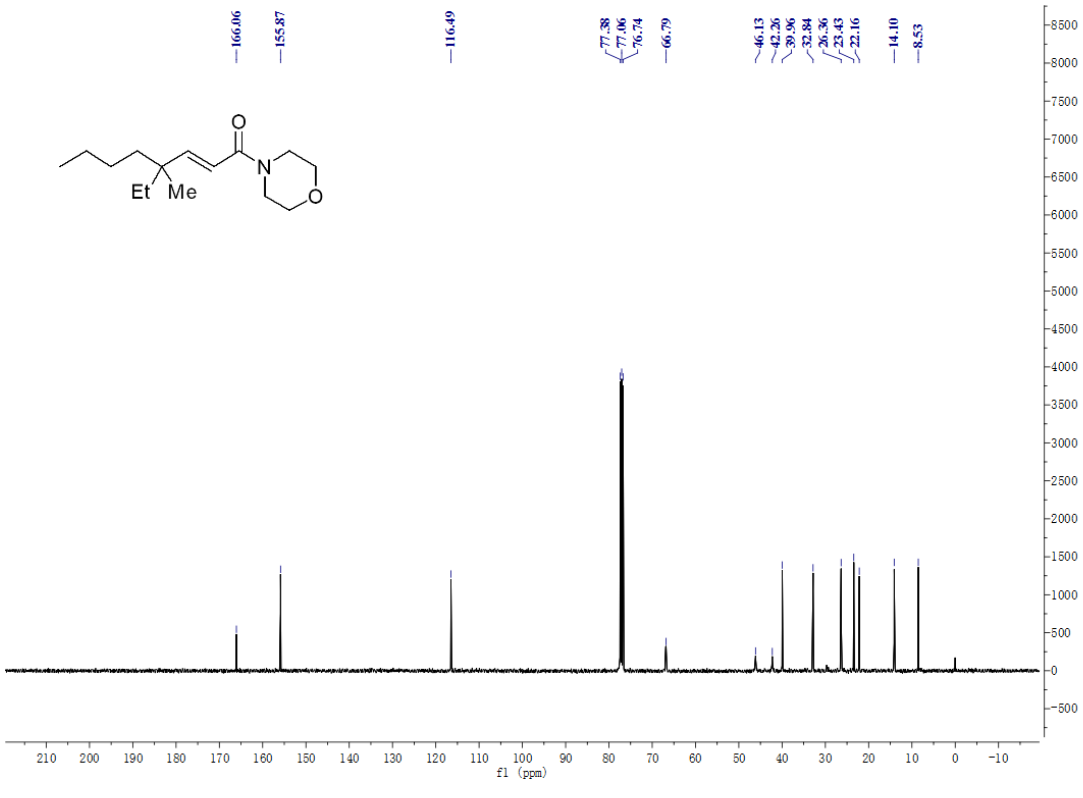
(E)-2-(4-(3,3-dimethylbut-1-en-1-yl)phenyl)thiophene (35)



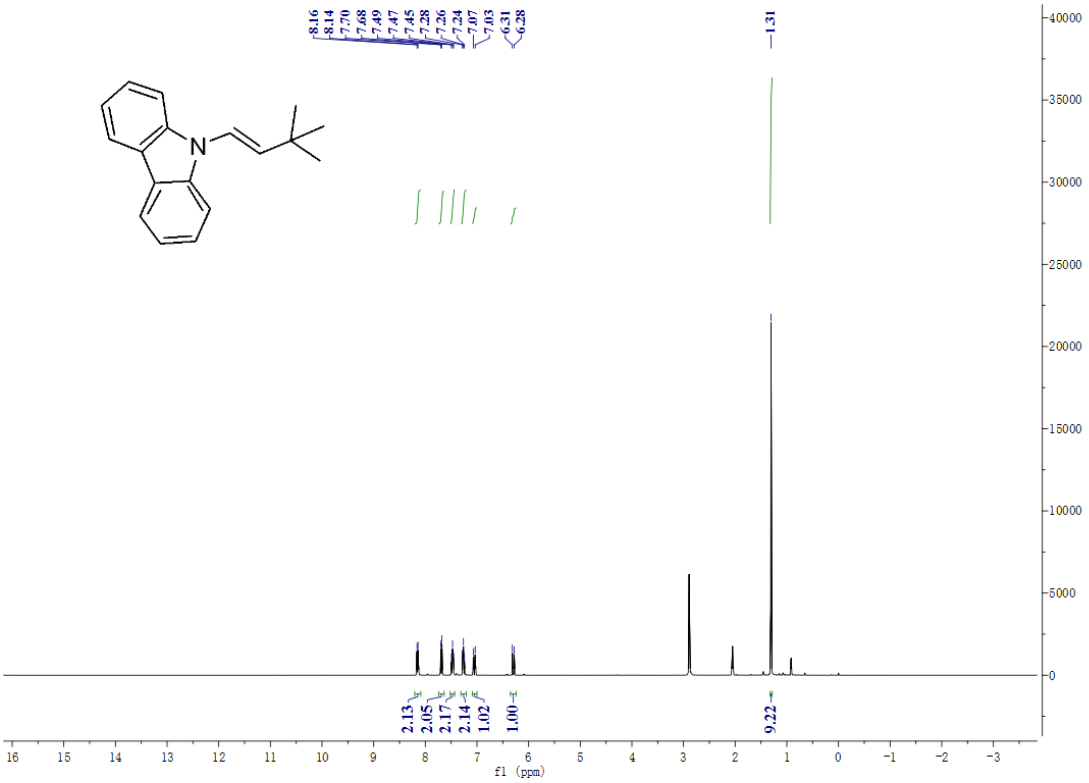


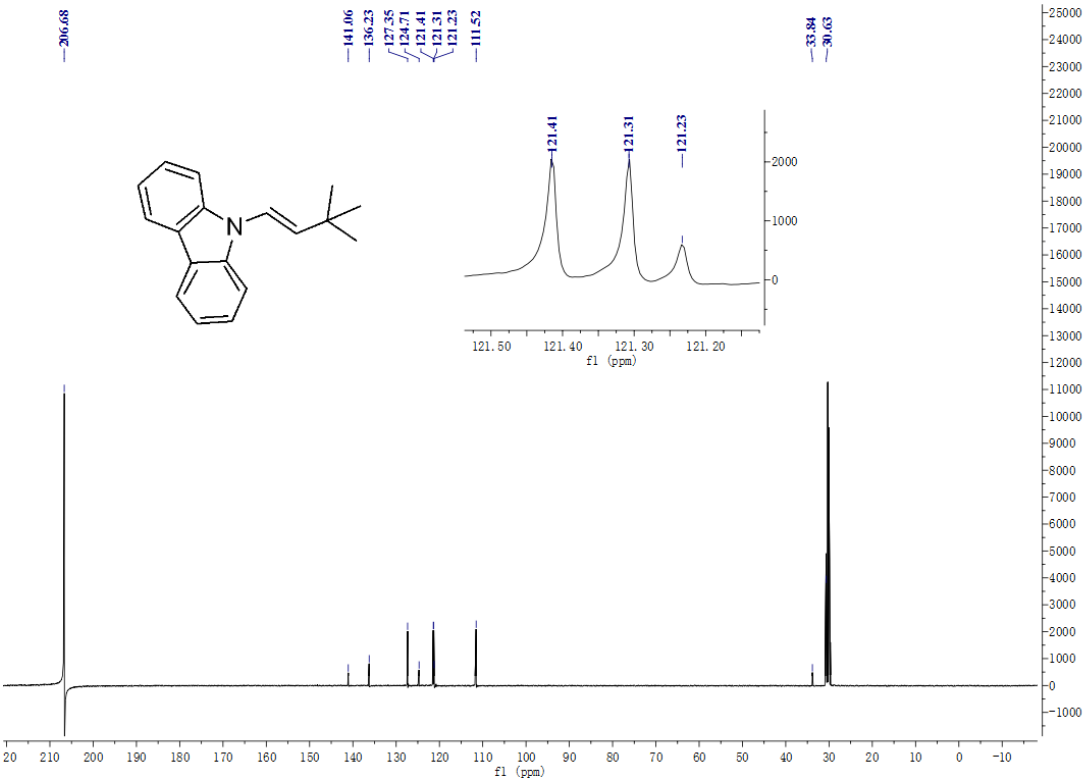
(E)-4-ethyl-4-methyl-1-morpholinooct-2-en-1-one (36)



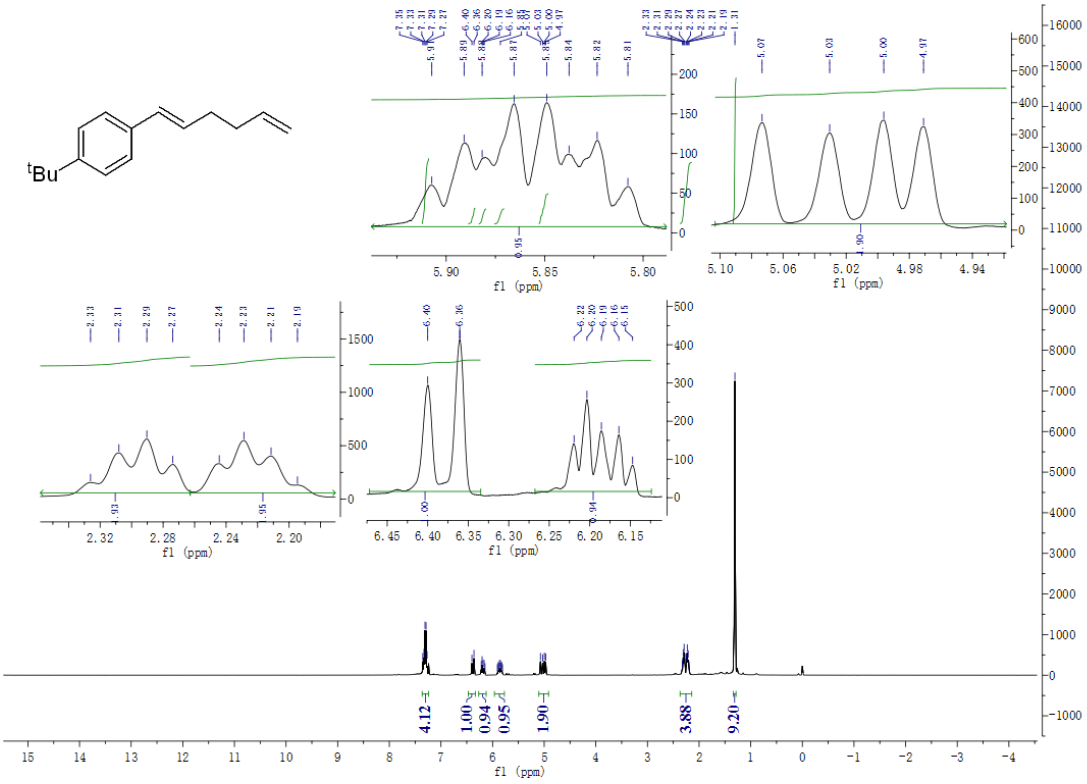


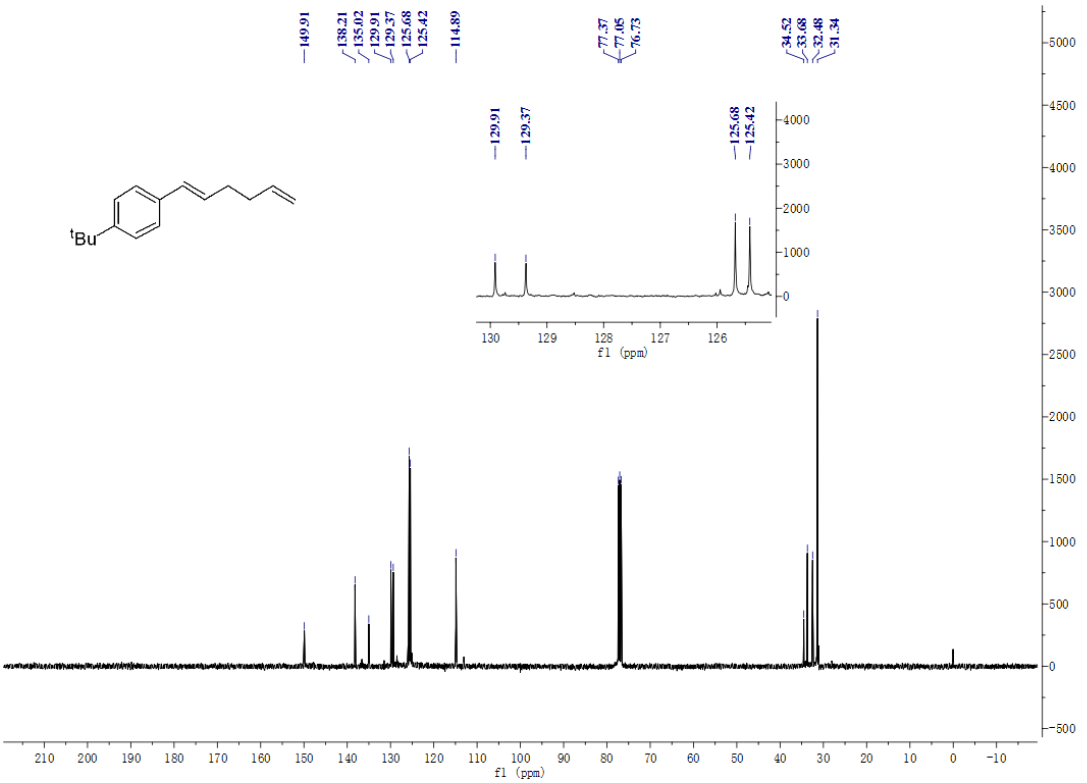
(E)-9-(3,3-dimethylbut-1-en-1-yl)-9H-carbazole (37)





(E)-1-(tert-butyl)-4-(hexa-1,5-dien-1-yl)benzene (38)





(E)-1-(tert-butyl)-4-(3-cyclopentylprop-1-en-1-yl)benzene (39)