Supporting Information

Au/Ag-Catalyzed Intramolecular Ring Opening of Vinylidenecyclopropanes (VDCPs): an easy Access to Functional Tetrahydropyrans

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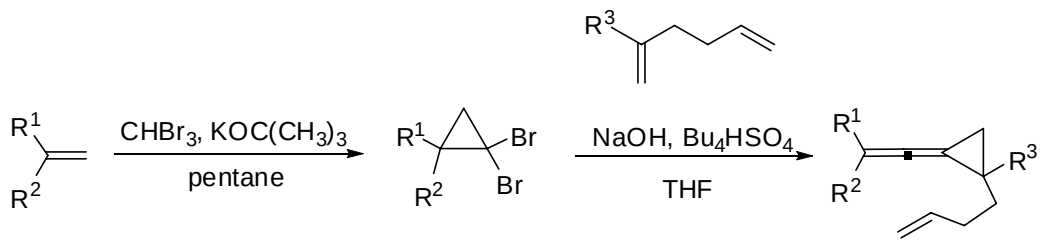
General remarks. ^{1}H-NMR spectra were recorded on a 300 MHz or 400MHz spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard. Infrared spectra were measured on a spectrometer. Mass spectra were recorded by EI method, and HRMS was measured on Kratos Analytical Concept mass spectrometer (EI), and IonSpec 4.7 Tesla FFMS (MALDI). Satisfactory CHN microanalyses were obtained with an analyzer. Melting points are uncorrected. All reactions were monitored by TLC with silica gel coated plates. Flash Column Chromatography was carried out using 300-400 mesh silica gel at increased pressure.

Preparation of Starting Materials 1a-1l.



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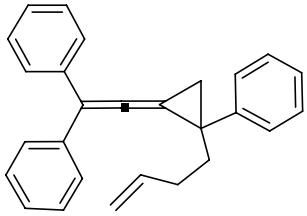
1a, $R^1 = R^2 = C_6H_5$, $R^3 = C_6H_5$
1b, $R^1 = R^2 = C_6H_5$, $R^3 = p\text{-}MeC_6H_4$
1c, $R^1 = R^2 = C_6H_5$, $R^3 = p\text{-}MeOC_6H_4$
1d, $R^1 = R^2 = C_6H_5$, $R^3 = p\text{-}FC_6H_4$
1e, $R^1 = R^2 = C_6H_5$, $R^3 = p\text{-}ClC_6H_4$
1f, $R^1 = R^2 = C_6H_5$, $R^3 = p\text{-}BrC_6H_4$
1g, $R^1 = R^2 = C_6H_5$, $R^3 = m\text{-}BrC_6H_4$
1h, $R^1 = R^2 = p\text{-}MeC_6H_4$, $R^3 = C_6H_5$
1i, $R^1 = R^2 = p\text{-}MeOC_6H_4$, $R^3 = C_6H_5$
1j, $R^1 = R^2 = p\text{-}ClC_6H_4$, $R^3 = C_6H_5$
1k, $R^1 = p\text{-}ClC_6H_4$, $R^2 = R^3 = C_6H_5$

Representative procedure for the preparation of diarylvinylidenecyclopropanes (VDCPs):[1]

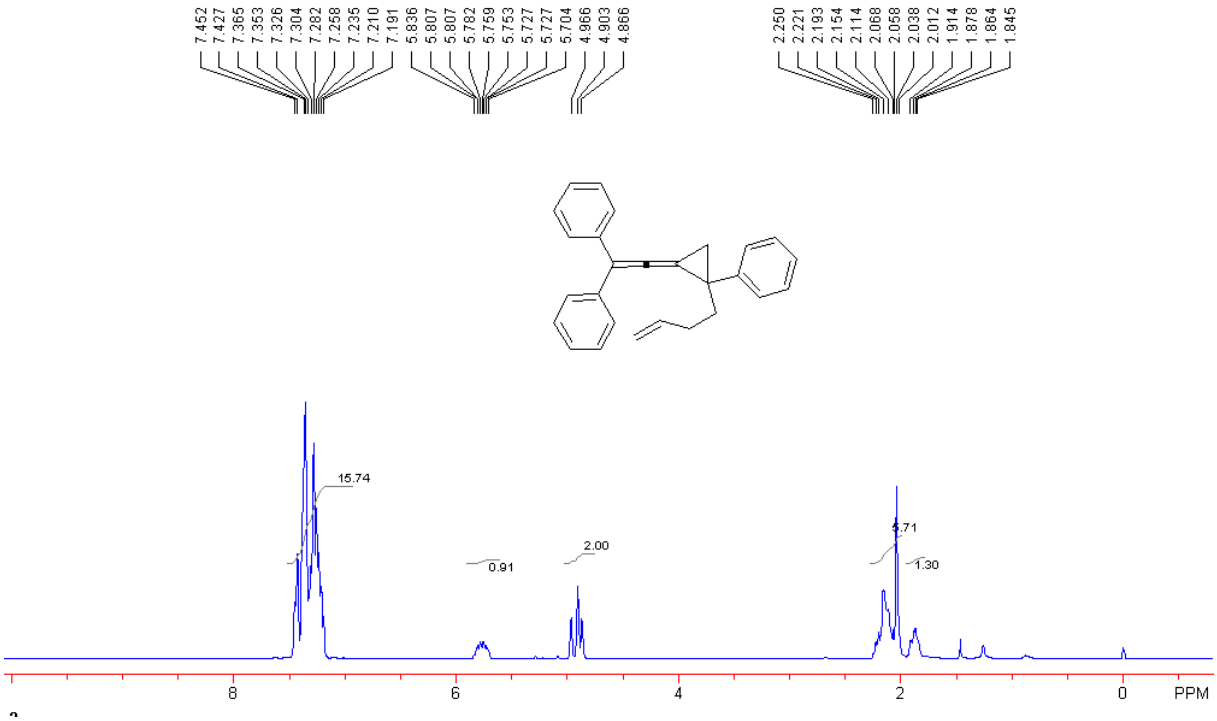
To the solution of 1,1-dibromocyclopropane (5.0 mmol) in THF (30 mL) was added 2-aryl-hexa-1,5-diene[2] (10 mmol), NaOH powder (4.0 g, 100 mmol) and $Bu_4N^+HSO_4^-$ (3.4 g, 10 mmol) as a phase-transfer reagent. The resulting mixture was stirred at room temperature for 36 h. After this period, the resulting dark mixture was poured into 100 mL of petroleum ether, and the solid was filtrated. The organic phase was concentrated under reduced pressure

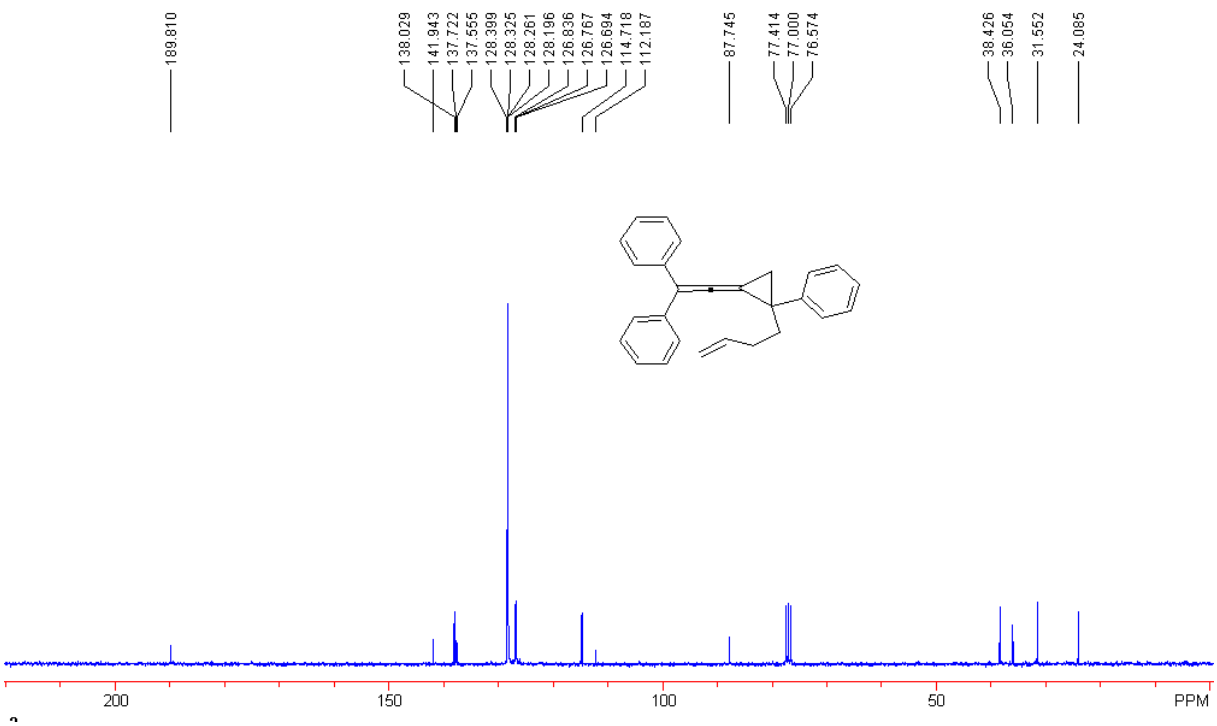
and the residue was purified by column chromatography on silica gel.

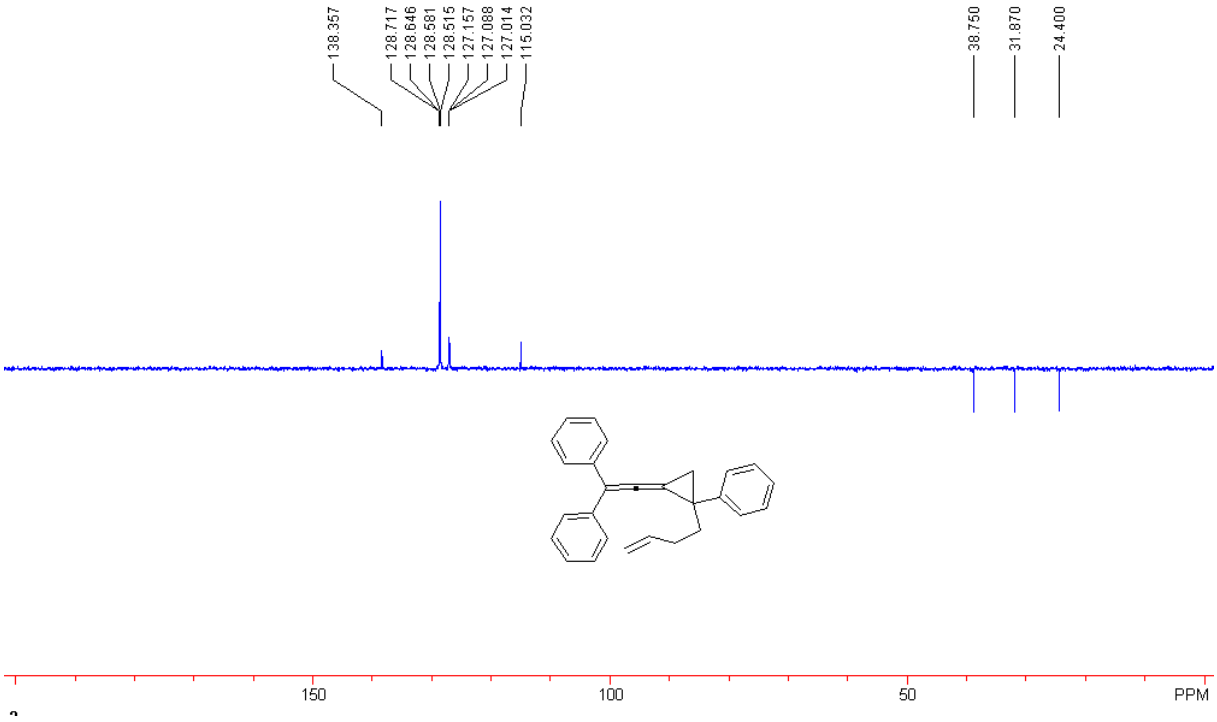


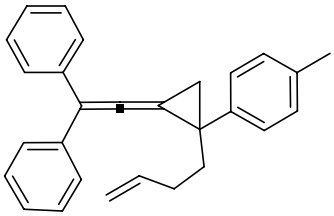
1-(2-(2-(but-3-enyl)-2-phenylcyclopropylidene)-1-phenylvinyl)benzene 1a

A light green oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.85-1.91 (m, 1H), 2.01-2.22 (m, 5H), 4.87-4.97 (m, 2H), 5.73-5.81 (m, 1H), 7.19-7.45 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 24.1, 31.5, 36.0, 38.4, 87.7, 112.2, 114.7, 126.7, 126.78, 126.84, 128.3, 128.4, 137.6, 137.7, 138.0, 141.9, 189.8. IR (CH_2Cl_2) ν 3057, 3025, 2926, 2848, 1992, 1639, 1598, 1492, 1470, 1444, 1028, 995, 913, 766, 696, 627, 610 cm^{-1}. MS (%) m/e 348 (M^+, 12), 291 (20), 229 (42), 215 (100), 204 (35), 165 (24), 115 (34), 91 (44), 77 (24). HRMS (EI) for $C_{27}H_{24}$: 348.1878; Found: 348.1877.



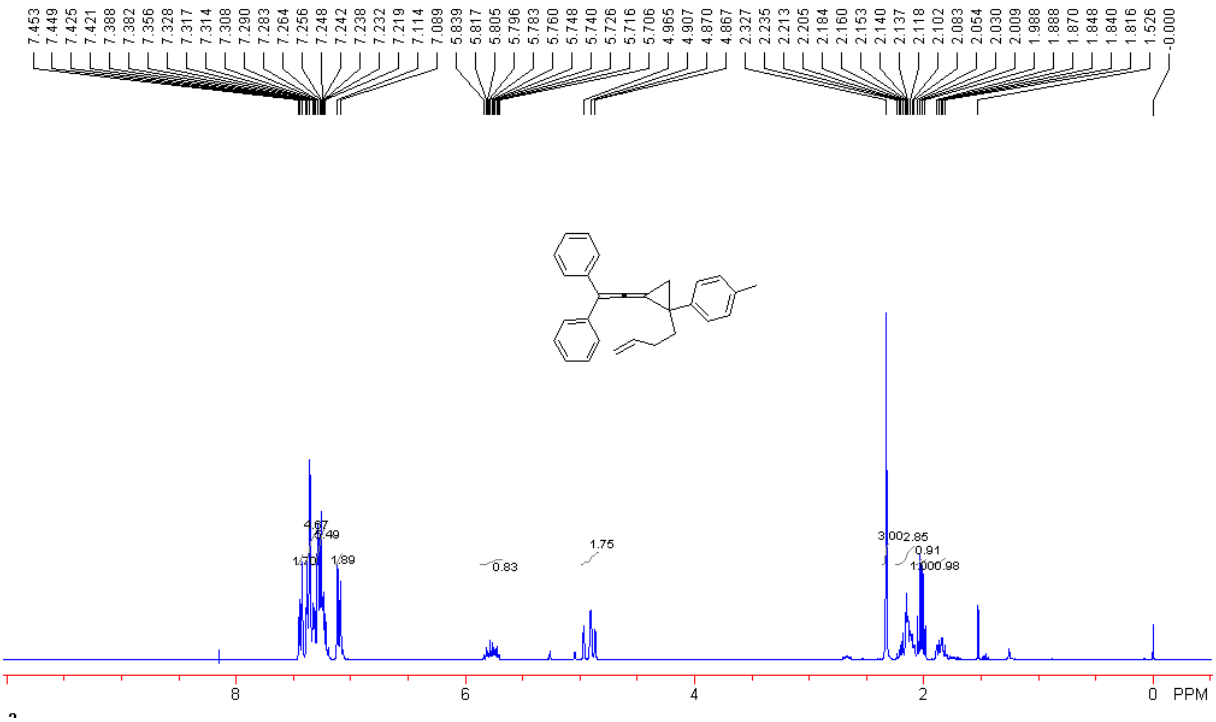


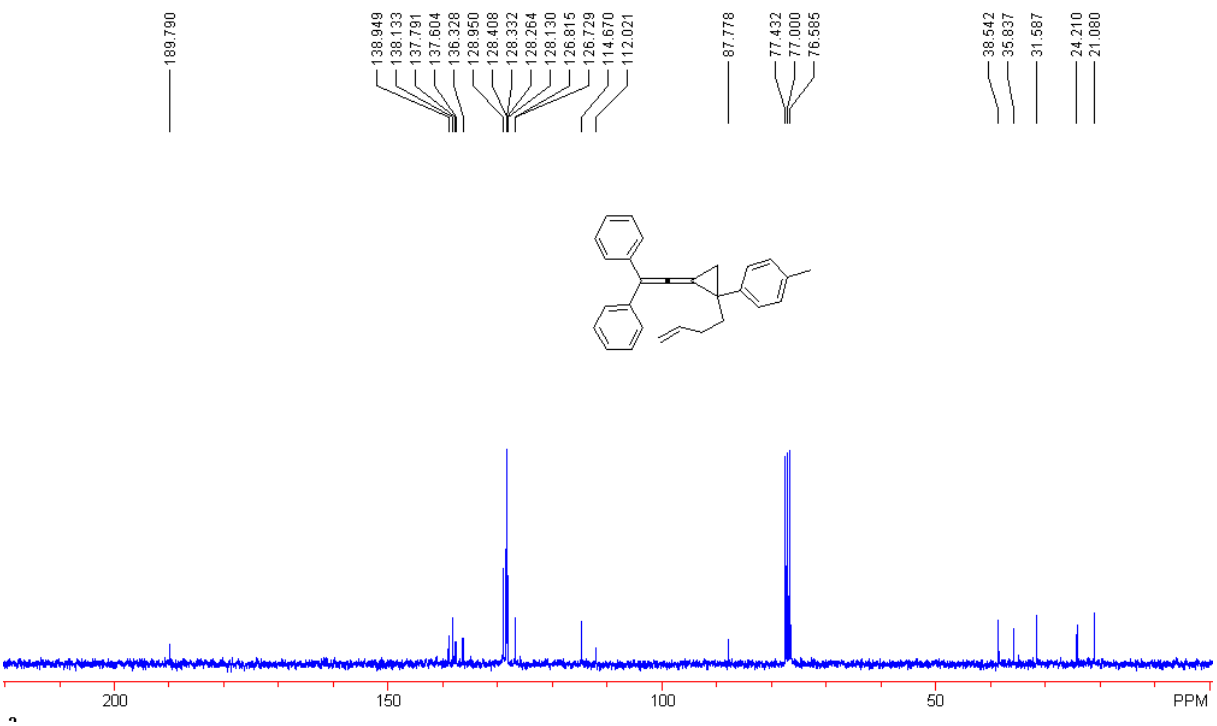


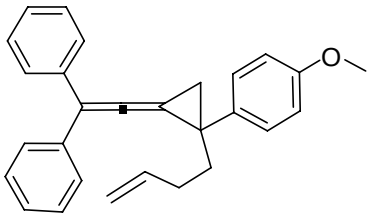


1-(1-(but-3-enyl)-2-(2,2-diphenylvinylidene)cyclopropyl)-4-methylbenzene 1b

A light green oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.82-1.89 (m, 1H), 2.00 (d, *J* = 6.6 Hz, 1H), 2.04 (d, *J* = 6.6 Hz, 1H), 2.08-2.24 (m, 3H), 2.33 (s, 3H, CH_3), 4.87-4.97 (m, 2H), 5.71-5.84 (m, 1H), 7.10 (d, *J* = 7.2 Hz, 2H, Ar), 7.22-7.29 (m, 5H, Ar), 7.31-7.32 (m, 1H, Ar), 7.33-7.39 (m, 4H, Ar), 7.42-7.45 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.1, 24.2, 31.6, 35.8, 38.5, 87.8, 112.0, 114.7, 126.7, 126.8, 128.1, 128.26, 128.33, 128.4, 129.0, 136.3, 137.6, 137.8, 138.1, 138.9, 189.8. IR (CH_2Cl_2) ν 3057, 3024, 2922, 2858, 1991, 1736, 1640, 1597, 1492, 1446, 1277, 1180, 1030, 912, 818, 767, 634 cm^{-1}. MS (%) m/e 362 (M^+, 23), 305 (29), 291 (27), 229 (100), 215 (31), 165 (19), 115 (19), 105 (16), 91 (24). HRMS (EI) for $C_{28}H_{26}$: 362.2035; Found: 362.2039.

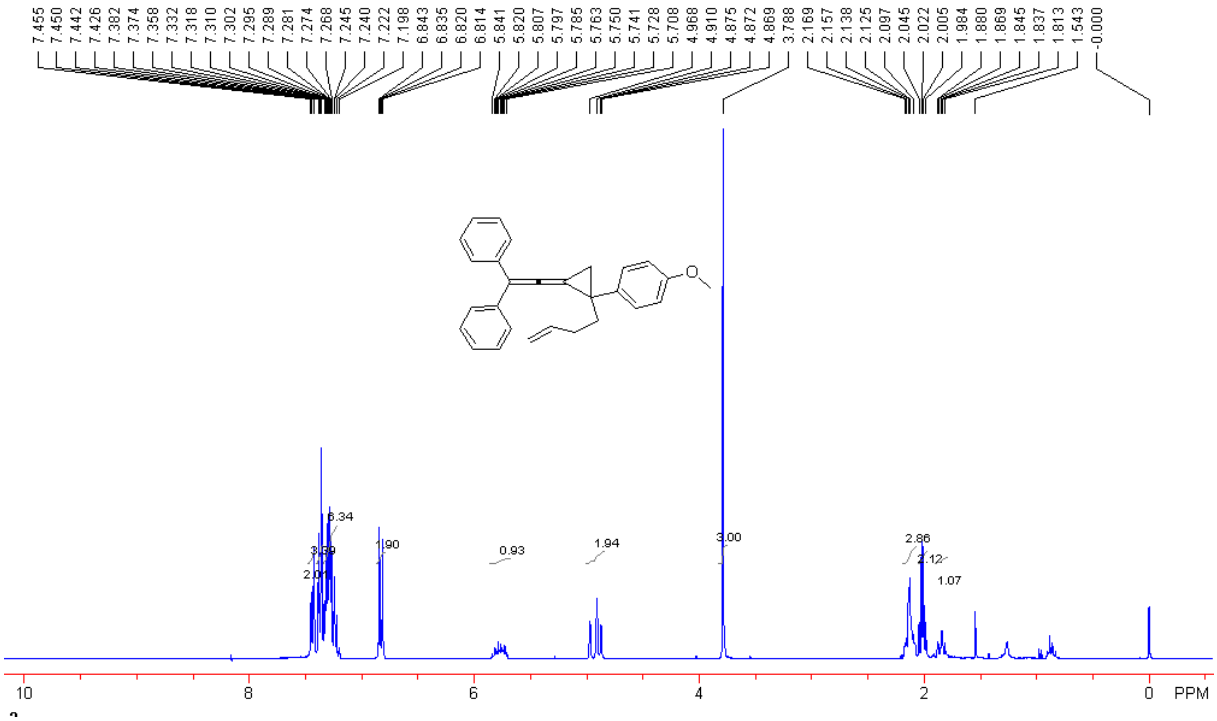


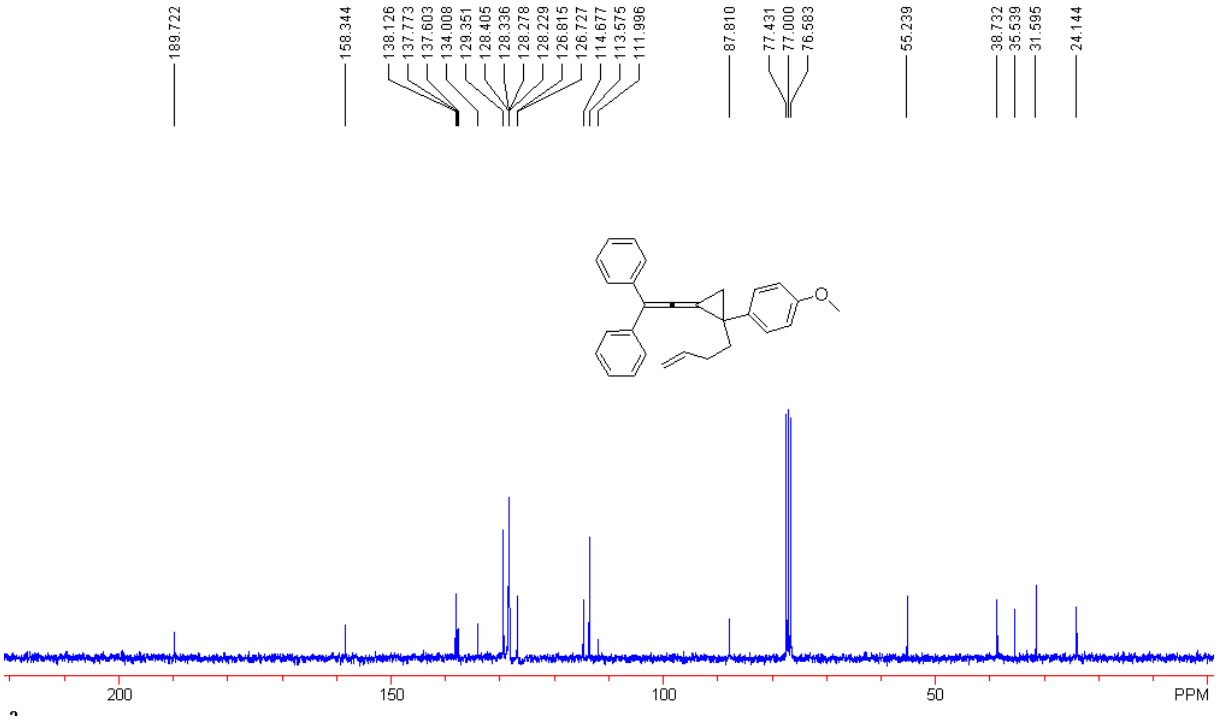


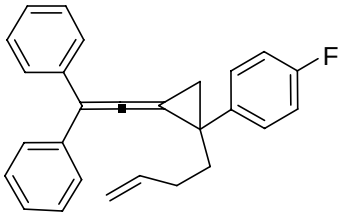


1-(1-(but-3-enyl)-2-(2,2-diphenylvinylidene)cyclopropyl)-4-methoxybenzene 1c

A light green oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.81-1.88 (m, 1H), 2.00 (d, *J* = 6.3 Hz, 1H), 2.03 (d, *J* = 6.3 Hz, 1H), 2.08-2.17 (m, 3H), 3.79 (s, 3H, OCH_3), 4.87-4.97 (m, 2H), 5.71-5.84 (m, 1H), 6.83 (dd, *J* = 2.1 Hz, *J* = 6.6 Hz, 2H, Ar), 7.20-7.45 (m, 12H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 24.1, 31.6, 35.5, 38.7, 55.2, 87.8, 112.0, 113.6, 114.7, 126.7, 126.8, 128.2, 128.28, 128.34, 128.4, 129.4, 134.0, 137.6, 137.8, 138.1, 158.3, 189.7. IR (CH_2Cl_2) ν 3059, 2999, 2931, 2835, 1991, 1609, 1512, 1442, 1295, 1247, 1176, 1032, 912, 833, 767, 696, 552, 516 cm^{-1}. MS (%) m/e 378 (M^+, 51), 337 (50), 323 (50), 291 (38), 259 (34), 245 (100), 215 (72), 202 (90), 121 (80). HRMS (EI) for $C_{28}H_{26}O$: 378.1984; Found: 378.1986.

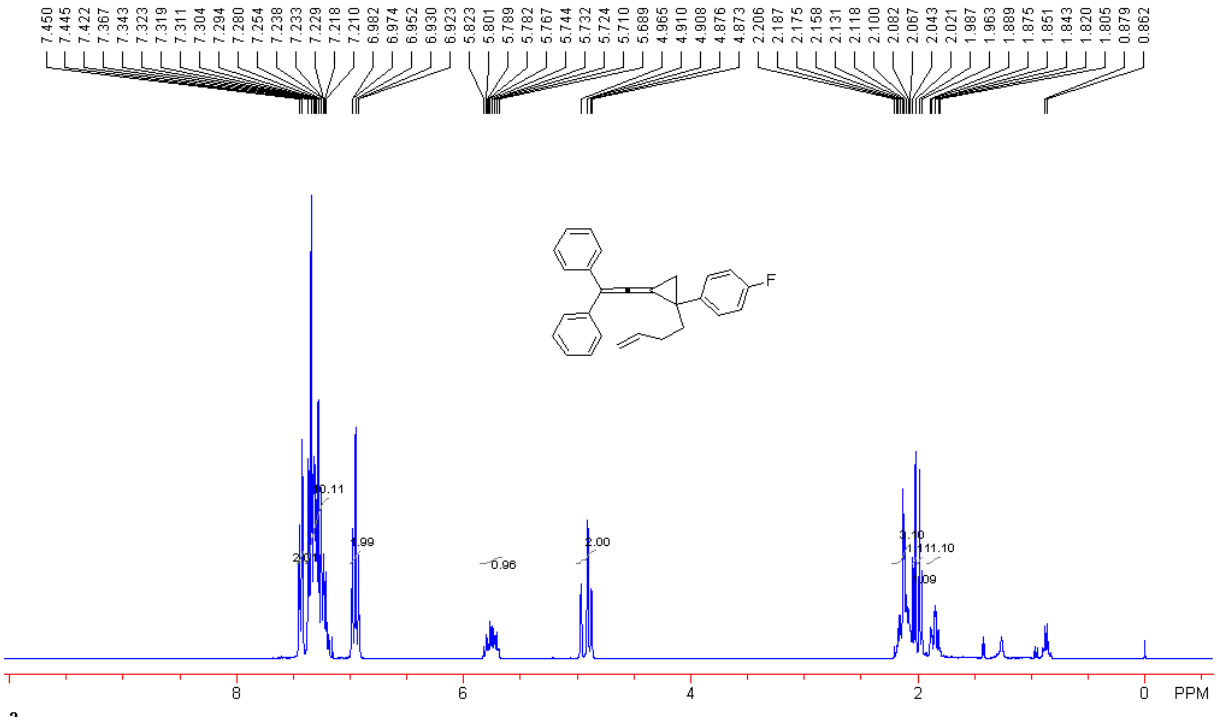


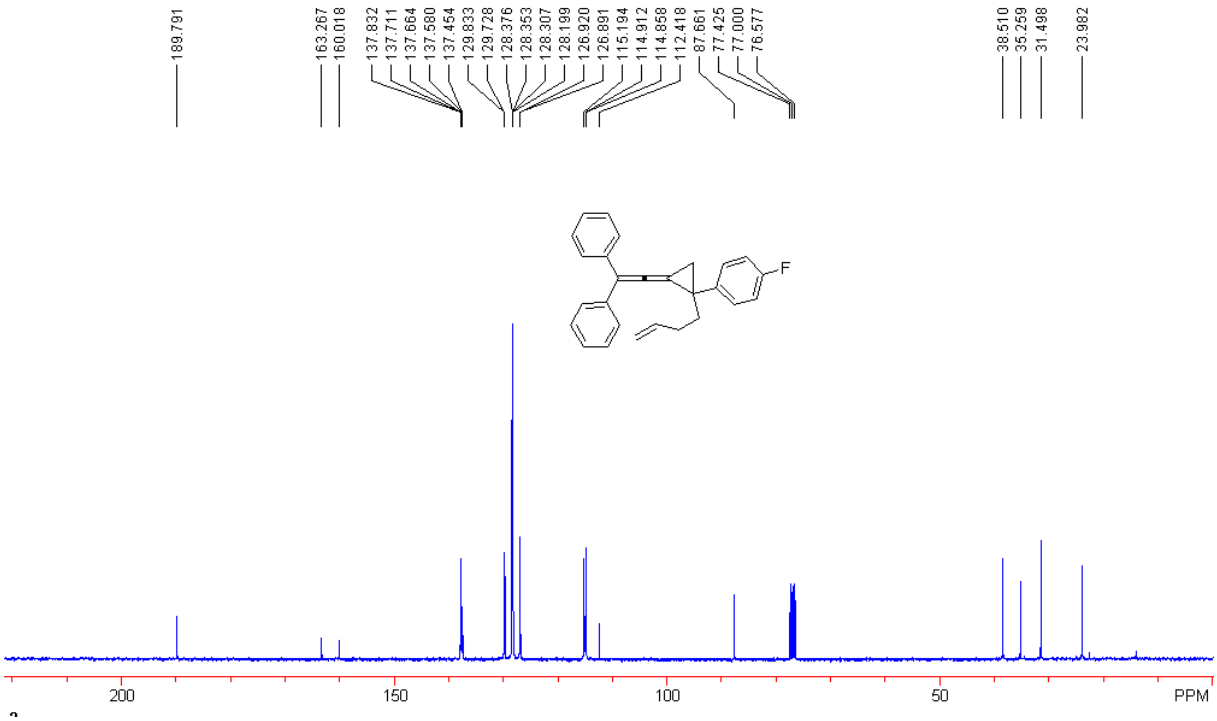


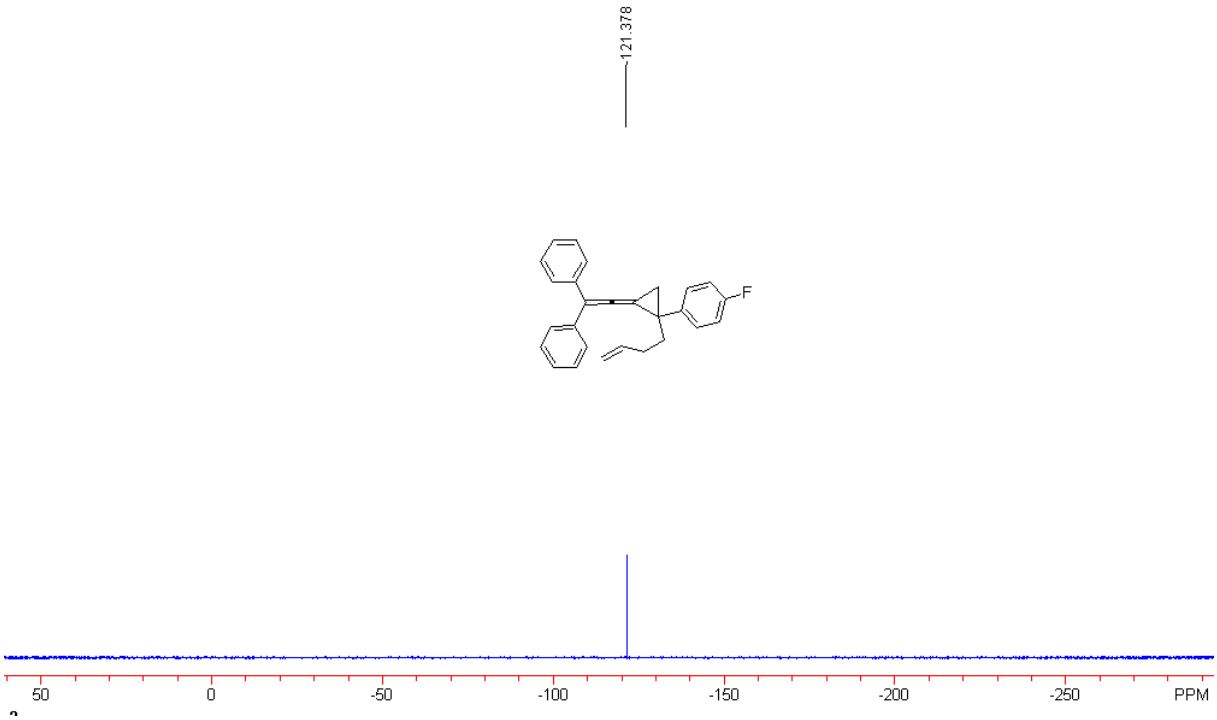


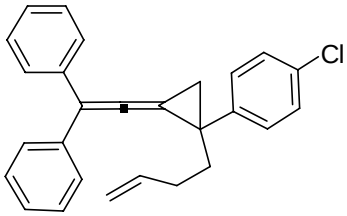
1-(1-(but-3-enyl)-2-(2,2-diphenylvinylidene)cyclopropyl)-4-fluorobenzene 1d

A light green oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.82-1.89 (m, 1H), 1.98 (d, J = 6.9 Hz, 1H), 2.03 (d, J = 6.9 Hz, 1H), 2.07-2.21 (m, 3H), 4.87-4.97 (m, 2H), 5.69-5.82 (m, 1H), 6.92-6.98 (m, 2H, Ar), 7.19-7.37 (m, 10H, Ar), 7.42-7.45 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 24.0, 31.5, 34.5, 35.3, 38.5, 87.6, 112.4, 114.9, 115.1 (d, $J_{C\text{-}F}$ = 21.2 Hz), 126.9 (d, $J_{C\text{-}F}$ = 2.2 Hz), 128.2, 128.3, 128.35, 128.38, 129.8 (d, $J_{C\text{-}F}$ = 7.9 Hz), 137.5, 137.6, 137.66, 137.71, 137.8, 161.6 (d, $J_{C\text{-}F}$ = 243.7 Hz), 189.8. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$) δ -121.4. IR (CH_2Cl_2) ν 3059, 2929, 2849, 1992, 1640, 1597, 1509, 1493, 1443, 1222, 1157, 1030, 913, 838, 767, 696, 542 cm^{-1}. MS (%) m/e 366 (M^+, 11), 338 (18), 309 (25), 247 (28), 233 (100), 204 (64), 165 (24), 133 (24), 91 (25). HRMS (EI) for $C_{27}H_{23}F$: 366.1784; Found: 366.1783.



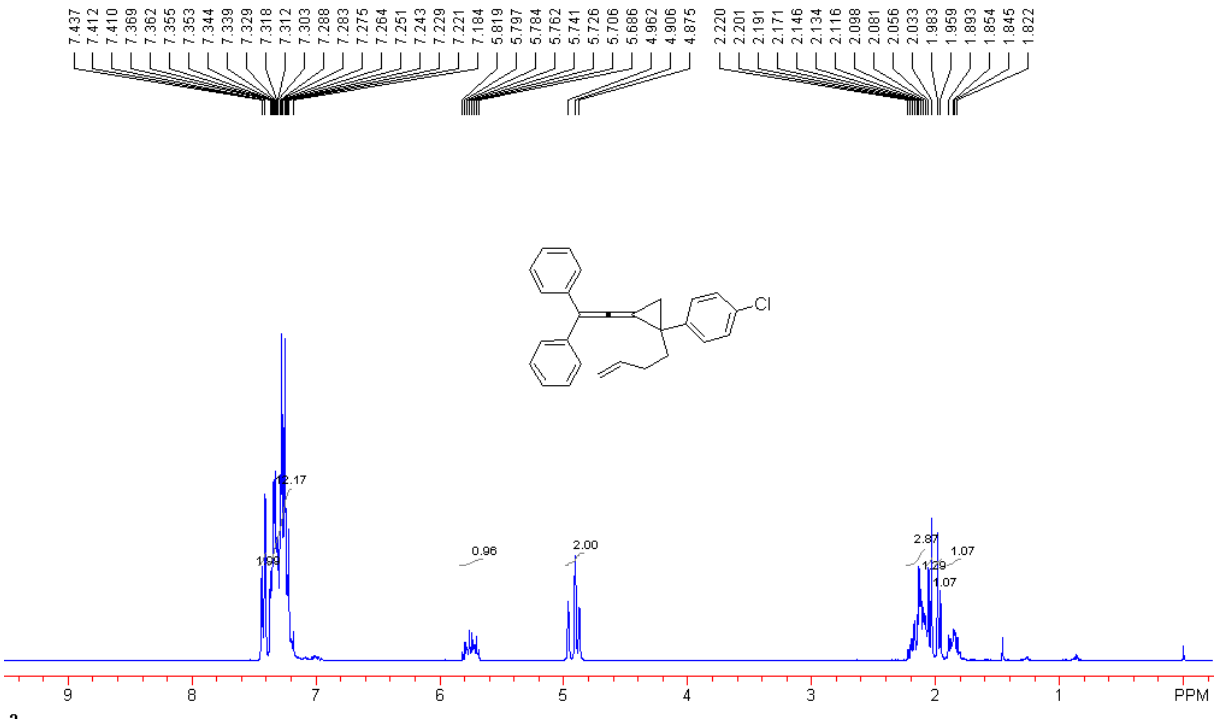


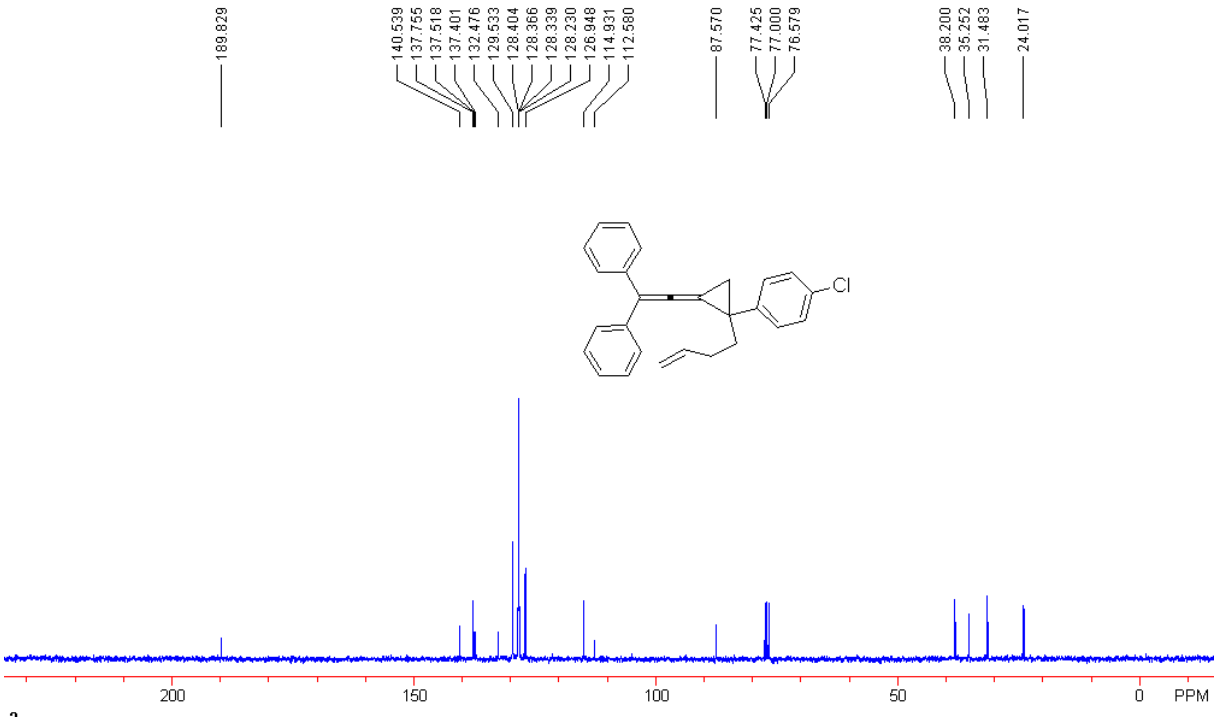


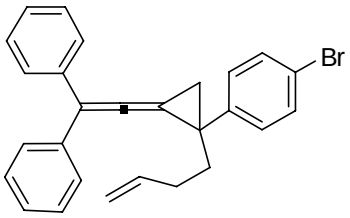


1-(1-(but-3-enyl)-2-(2,2-diphenylvinylidene)cyclopropyl)-4-chlorobenzene 1e

A light green oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.80-1.85 (m, 1H), 1.97 (d, *J* = 6.9 Hz, 1H), 2.04 (d, *J* = 6.9 Hz, 1H), 2.08-2.22 (m, 3H), 4.88-4.97 (m, 2H), 5.69-5.82 (m, 1H), 7.22-7.41 (m, 12H, Ar), 7.42 (d, *J* = 7.5 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 24.0, 31.5, 35.3, 38.2, 87.6, 112.6, 114.9, 126.9, 128.2, 128.3, 128.4, 129.5, 132.5, 137.4, 137.5, 137.8, 140.5, 189.8. IR (CH_2Cl_2) ν 3059, 2924, 2850, 1992, 1596, 1492, 1471, 1442, 1398, 1277, 1092, 1013, 913, 833, 767, 696, 518 cm^{-1}. MS (%) m/e 382 (M^+, 14), 291 (68), 249 (71), 215 (62), 204 (100), 191 (49), 165 (55), 115 (34), 91 (56). HRMS (EI) for $C_{27}H_{23}Cl$: 382.1488; Found: 382.1489.

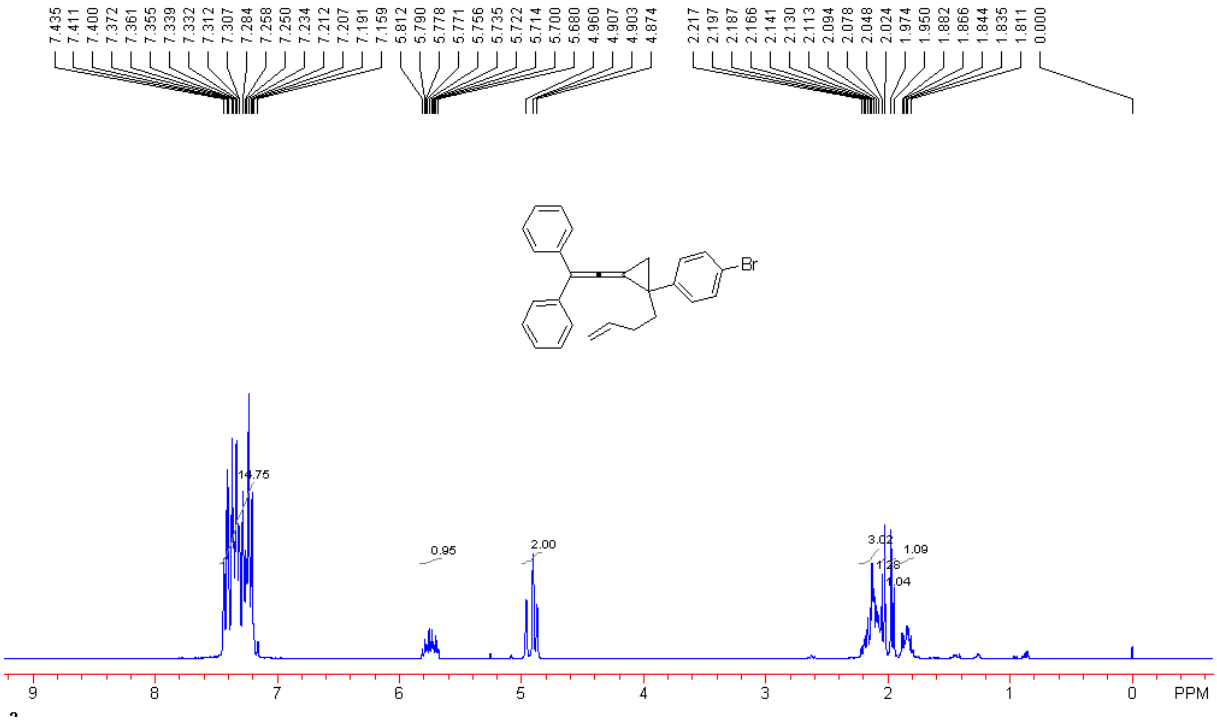


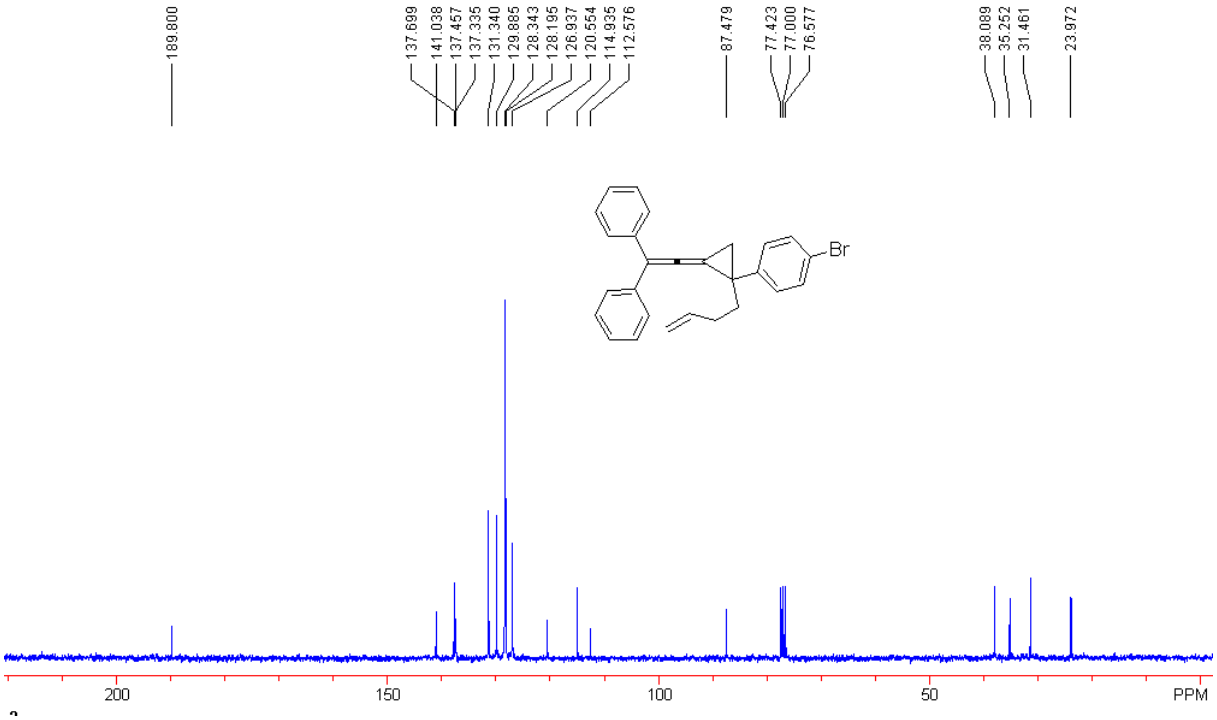


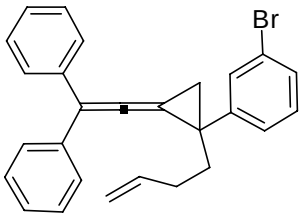


1-bromo-4-(1-(but-3-enyl)-2-(2,2-diphenylvinylidene)cyclopropyl)benzene 1f.

A light green oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.81-1.88 (m, 1H), 1.96 (d, *J* = 7.2 Hz, 1H), 2.04 (d, *J* = 7.2 Hz, 1H), 2.08-2.22 (m, 3H), 4.87-4.96 (m, 2H), 5.68-5.81 (m, 1H), 7.16-7.44 (m, 14H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 24.0, 31.5, 35.3, 38.2, 87.5, 112.6, 114.9, 120.6, 127.0, 128.2, 128.3, 128.38, 128.39, 129.2, 129.9, 131.4, 137.4, 137.5, 137.8, 141.1, 189.8. IR (CH_2Cl_2) ν 3058, 3026, 2929, 2849, 1992, 1735, 1639, 1596, 1490, 1471, 1442, 1393, 1072, 1009, 913, 767, 696, 627 cm^{-1}. MS (%) m/e 428 (M^+, 9), 426 (M^+, 9), 291 (91), 228 (46), 215 (78), 204 (98), 191 (100), 165 (72), 115 (46), 91 (59). HRMS (EI) for $C_{27}H_{23}Br$: 426.0983; Found: 426.0991.

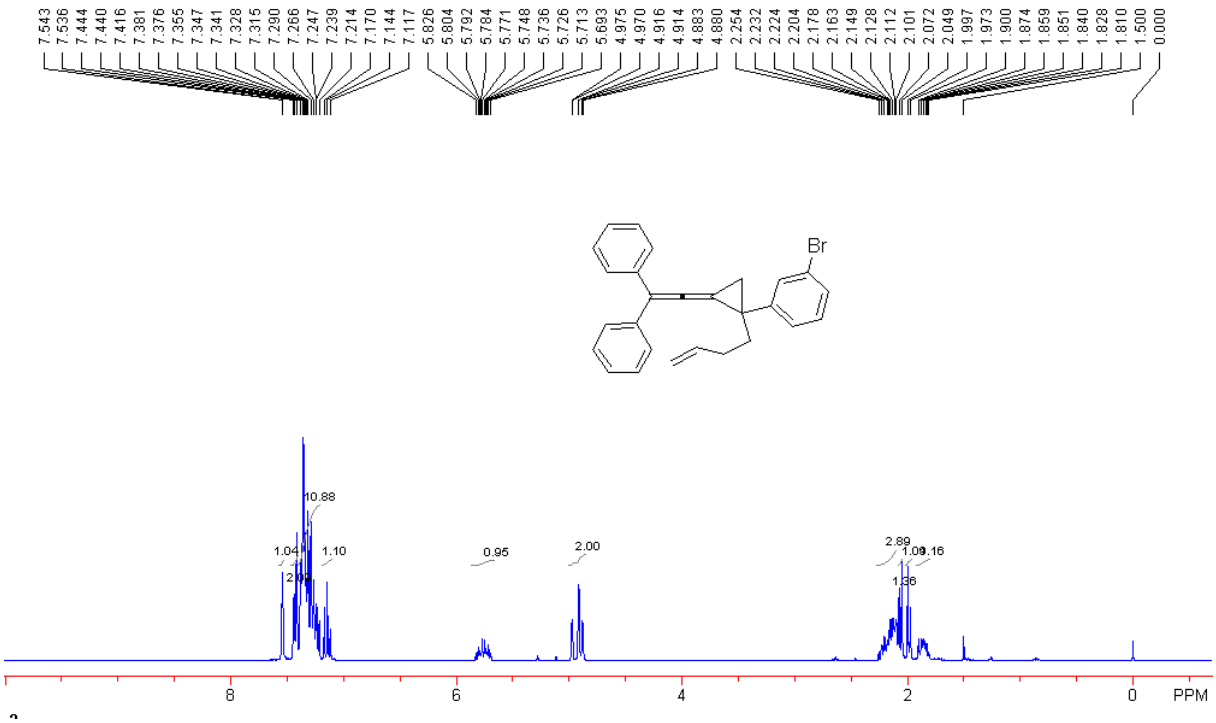


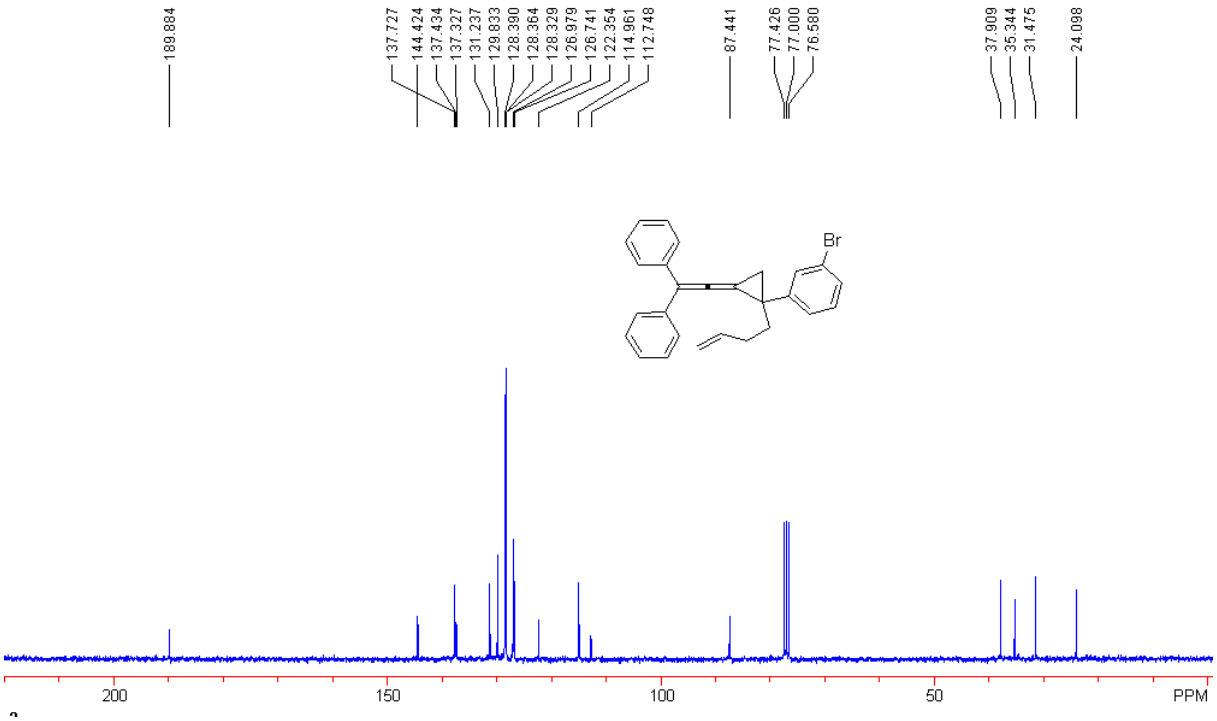


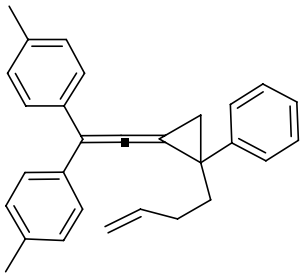


1-bromo-3-(1-(but-3-enyl)-2-(2,2-diphenylvinylidene)cyclopropyl)benzene 1g

A light green oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.81-1.90 (m, 1H), 1.98 (d, *J* = 7.2 Hz, 1H), 2.06 (d, *J* = 7.2 Hz, 1H), 2.10-2.25 (m, 3H), 4.87-4.96 (m, 2H), 5.69-5.83 (m, 1H), 7.12-7.17 (m, 1H, Ar), 7.21-7.42 (m, 10H, Ar), 7.42-7.44 (m, 2H, Ar), 7.54 (d, *J* = 2.7 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 24.1, 31.5, 35.3, 37.9, 87.4, 112.7, 115.0, 122.4, 126.7, 127.0, 128.36, 128.39, 129.8, 131.2, 137.3, 137.4, 137.7, 144.4, 189.9. IR (CH_2Cl_2) ν 3059, 2929, 2851, 1992, 1640, 1593, 1492, 1442, 1415, 1073, 996, 913, 767, 695, 516 cm^{-1}. MS (%) m/e 428 (M^+, 1), 426 (M^+, 1), 373 (6), 291 (41), 215 (35), 204 (52), 191 (100), 165 (46), 115 (20), 91 (28). HRMS (EI) for $C_{27}H_{23}Br$: 426.0983; Found: 426.0985.

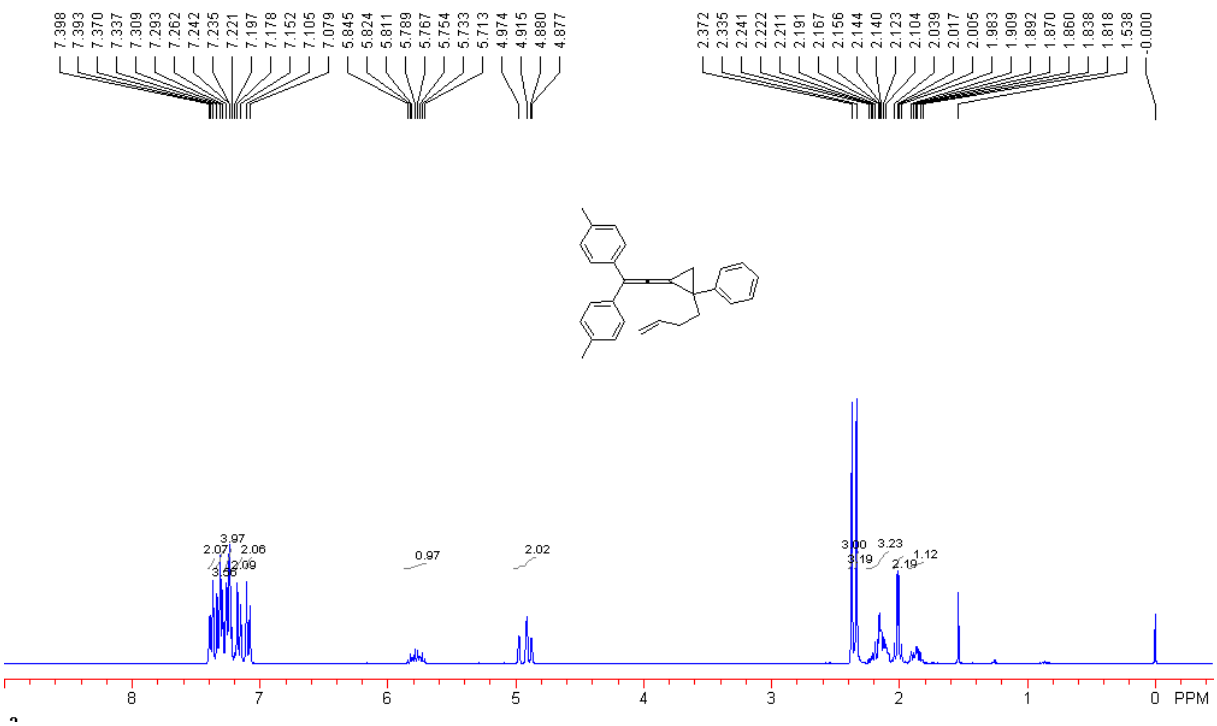






1-(2-(2-(but-3-enyl)-2-phenylcyclopropylidene)-1-*p*-tolylvinyl)-4-methylbenzene 1h

A light green oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.82-1.91 (m, 1H), 1.99 (d, *J* = 6.9 Hz, 1H), 2.03 (d, *J* = 6.9 Hz, 1H), 2.10-2.24 (m, 3H), 2.34 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 4.88-4.97 (m, 2H), 5.71-5.85 (m, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.22-7.26 (m, 4H, Ar), 7.29-7.34 (m, 3H, Ar), 7.38 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.12, 21.16, 23.9, 31.6, 35.7, 38.4, 87.6, 112.0, 114.7, 126.6, 128.1, 128.2, 128.3, 128.9, 128.96, 129.01, 129.1, 134.7, 134.9, 136.4, 136.5, 138.1, 142.1, 189.4. IR (CH_2Cl_2) ν 3023, 2920, 2862, 1990, 1601, 1509, 1445, 1180, 1111, 1021, 822, 700, 580 cm^{-1}. MS (%) m/e 376 (M^+, 24), 321 (30), 305 (27), 232 (100), 219 (49), 202 (34), 105 (52), 91 (33). HRMS (EI) for $C_{29}H_{28}$: 376.2191; Found: 376.2194.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4.880
4.877
2.372
2.335
2.241
2.222
2.211
2.191
2.167
2.156
2.144
2.140
2.123
2.104
2.039
2.017
2.005
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1.870
1.860
1.838
1.818
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2.06
2.09
3.06
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5
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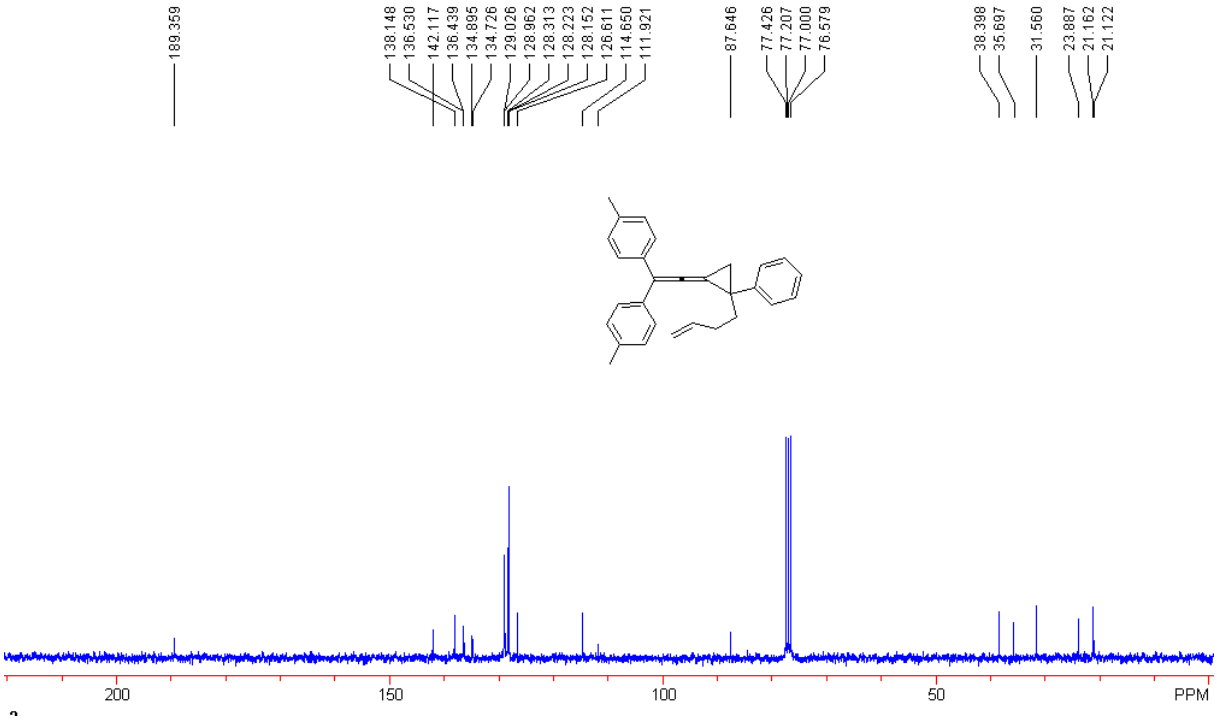
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87.646
77.426
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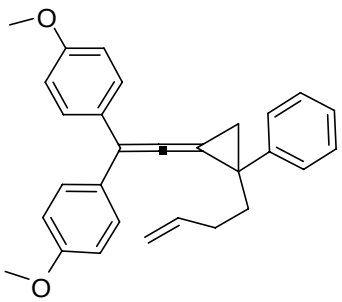
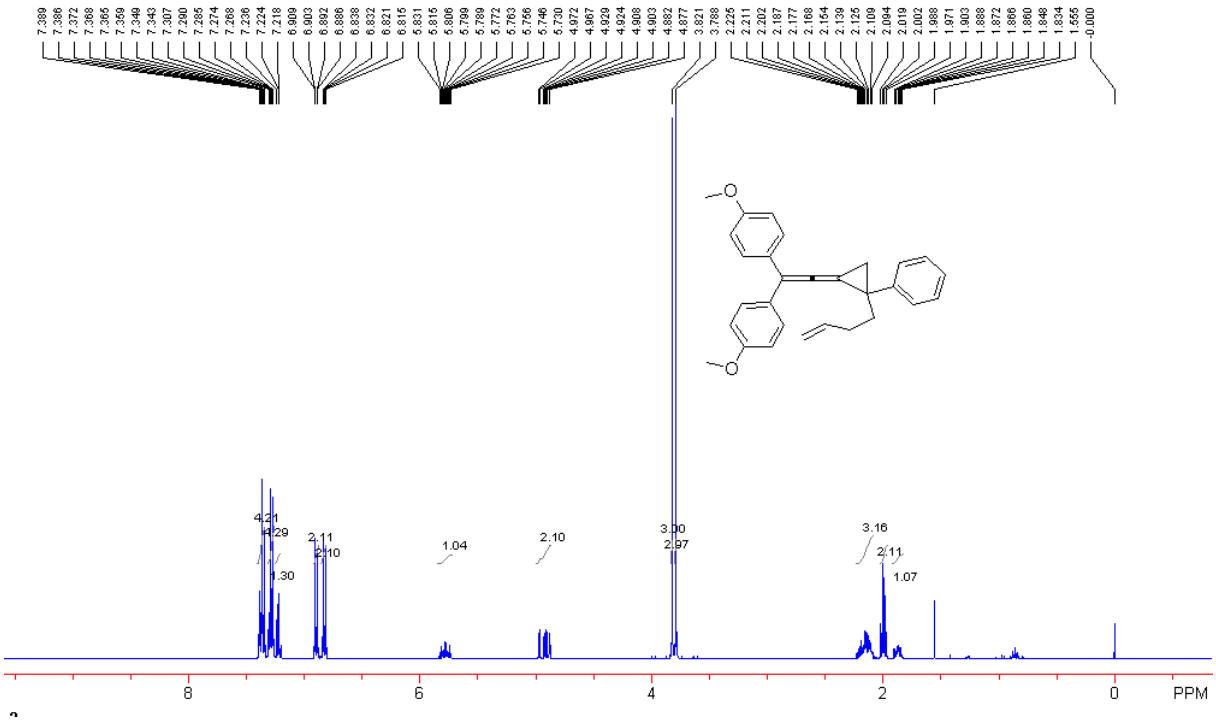
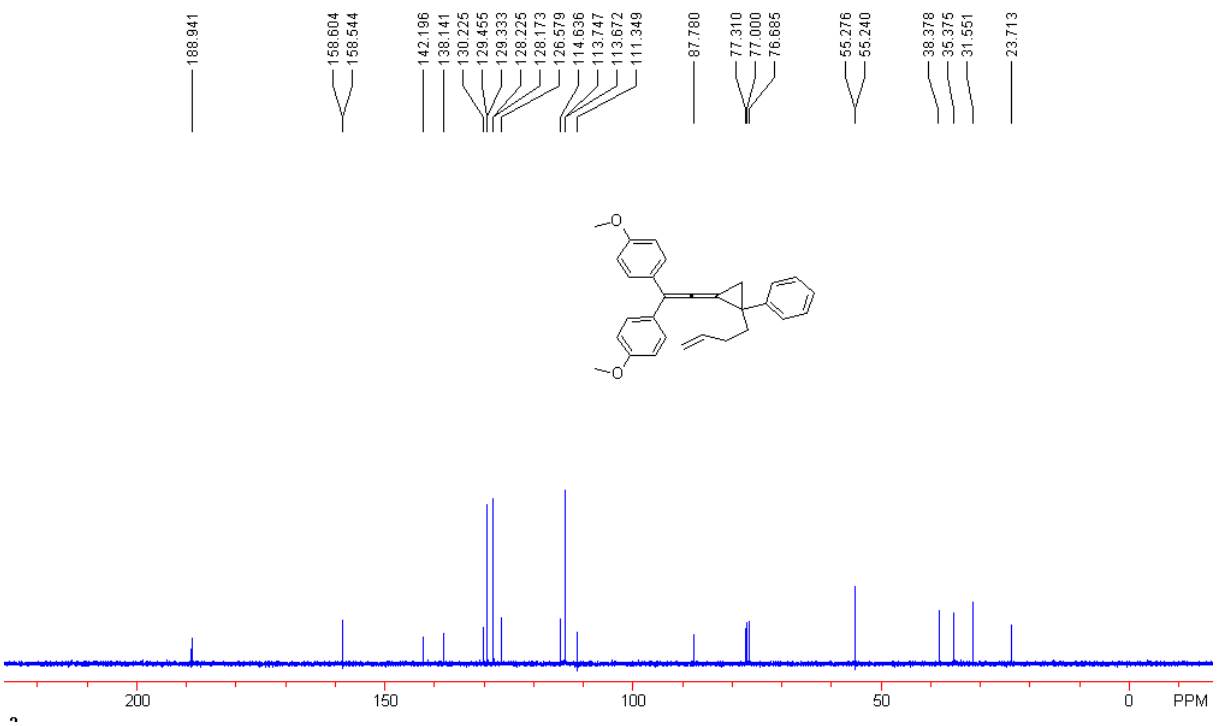
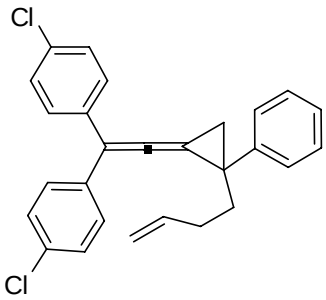


1-(2-(2-(but-3-enyl)-2-phenylcyclopropylidene)-1-(4-methoxyphenyl)vinyl)-4-methoxybenzene 1i

A light green oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.85-1.90 (m, 1H), 1.98 (d, *J* = 6.8 Hz, 1H), 2.01 (d, *J* = 6.8 Hz, 1H), 2.09-2.23 (m, 3H), 3.79 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 4.88-4.97 (m, 2H), 5.73-5.83 (m, 1H), 6.81-6.85 (m, 2H, Ar), 6.88-6.92 (m, 2H, Ar), 7.22-7.24 (m, 1H, Ar), 7.27-7.31 (m, 4H, Ar), 7.34-7.39 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 23.7, 31.6, 35.4, 38.4, 55.2, 55.3, 87.8, 111.3, 113.7, 113.8, 114.6, 126.6, 128.17, 128.22, 129.3, 129.4, 130.1, 130.2, 138.1, 142.2, 158.5, 158.6, 188.9. IR (CH_2Cl_2) ν 3058, 2999, 2933, 2835, 1990, 1734, 1604, 1509, 1463, 1293, 1247, 1173, 1034, 834, 701, 585, 516 cm^{-1}. MS (%) m/e 408 (M^+, 11), 367 (9), 311 (14), 264 (58), 239 (65), 182 (42), 135 (100), 105 (69). HRMS (EI) for $C_{29}H_{28}O_2$: 408.2089; Found: 408.2083.

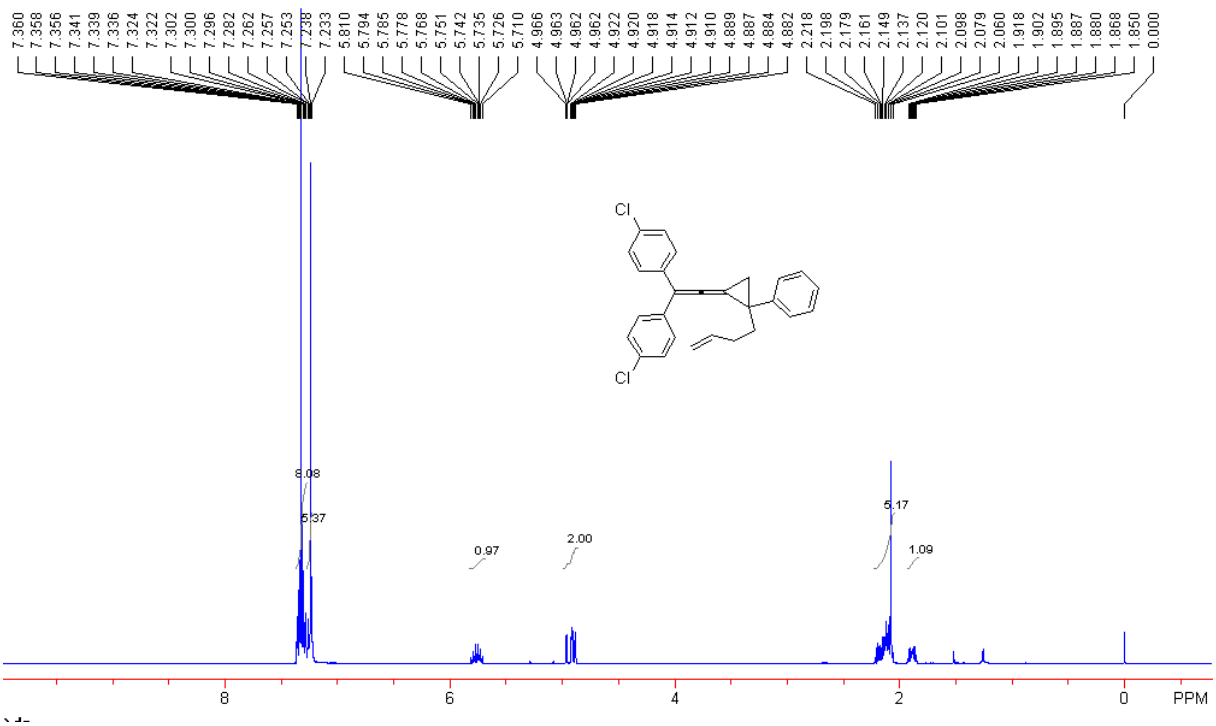






1-(2-(2-(but-3-enyl)-2-phenylcyclopropylidene)-1-(4-chlorophenyl)vinyl)-4-chlorobenzene 1j

A light green oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.85-1.92 (m, 1H), 2.06-2.22 (m, 5H), 4.88-4.97 (m, 2H), 5.71-5.81 (m, 1H), 7.23-7.26 (m, 5H, Ar), 7.28-7.36 (m, 8H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 24.2, 31.5, 36.6, 38.4, 88.3, 110.3, 114.9, 126.9, 128.1, 128.4, 128.5, 128.6, 129.4, 129.5, 132.7, 132.8, 135.8, 135.9, 137.8, 141.6, 189.6. IR (CH_2Cl_2) ν 3060, 2974, 2927, 2854, 1991, 1714, 1640, 1590, 1490, 1446, 1396, 1218, 1092, 1014, 909, 832, 700, 530 cm^{-1}. MS (%) m/e 416 (M^+, 4), 361 (9), 325 (18), 289 (18), 250 (39), 215 (29), 139 (100), 105 (61). HRMS (EI) for $C_{27}H_{22}Cl_2$: 416.1099; Found: 416.1101.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7.257
7.253
7.238
7.233
5.810
5.794
5.785
5.778
5.768
5.751
5.742
5.735
5.726
5.710
4.966
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4.914
4.912
4.910
4.889
4.887
4.884
4.882
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2.198
2.179
2.161
2.149
2.137
2.120
2.101
2.098
2.079
2.060
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1.895
1.887
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1.868
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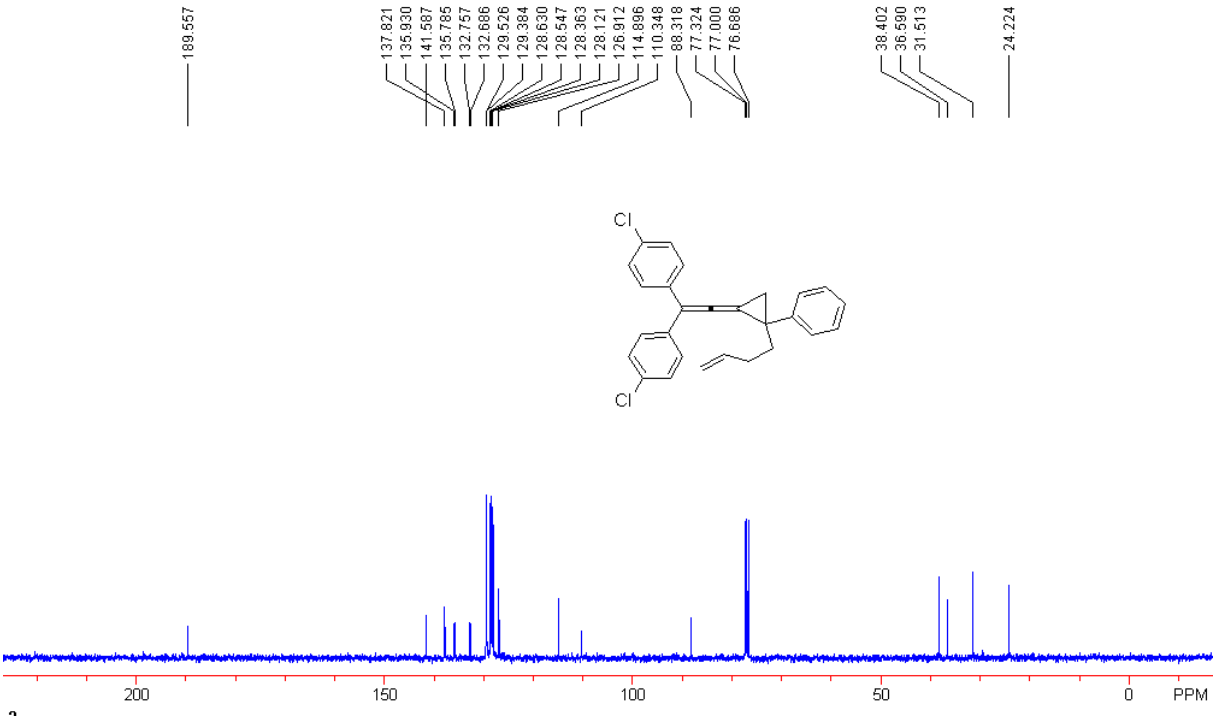
PPM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126.912
114.896
110.348
88.318
77.324
77.000
76.686
38.402
36.590
31.513
24.224
Cl
Cl
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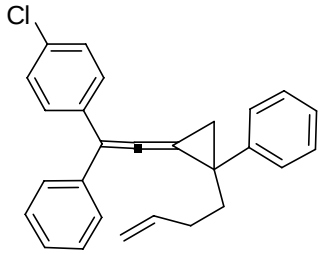
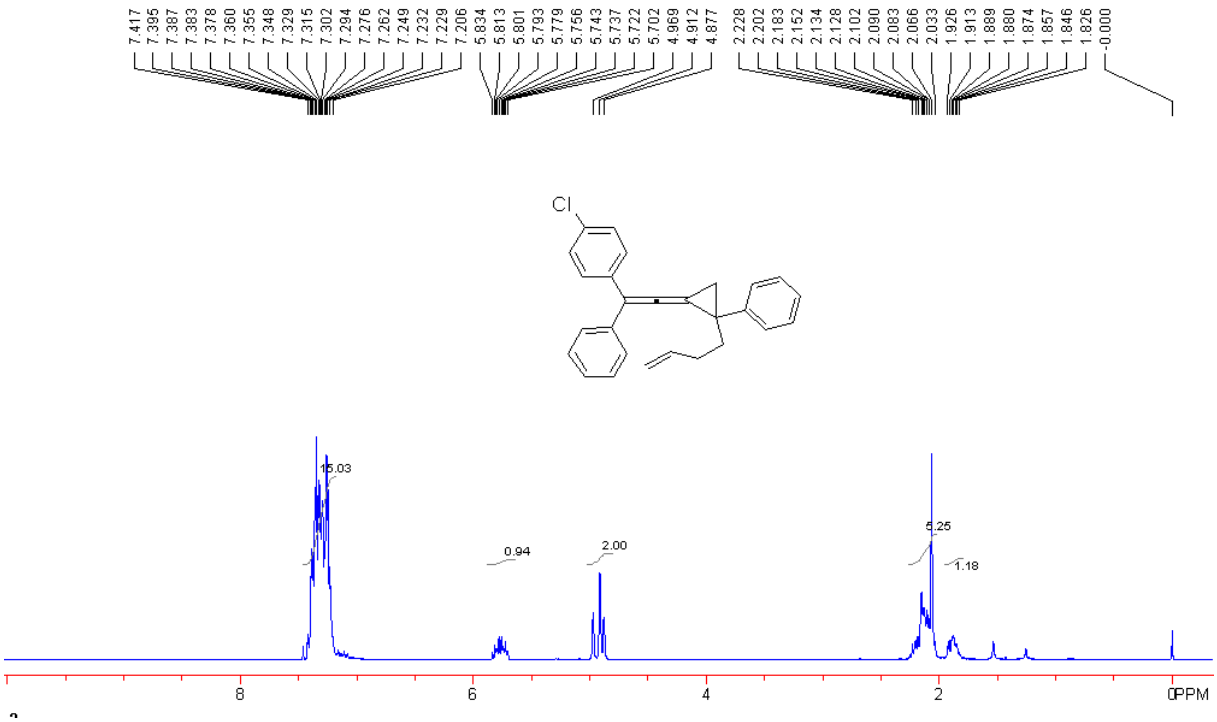
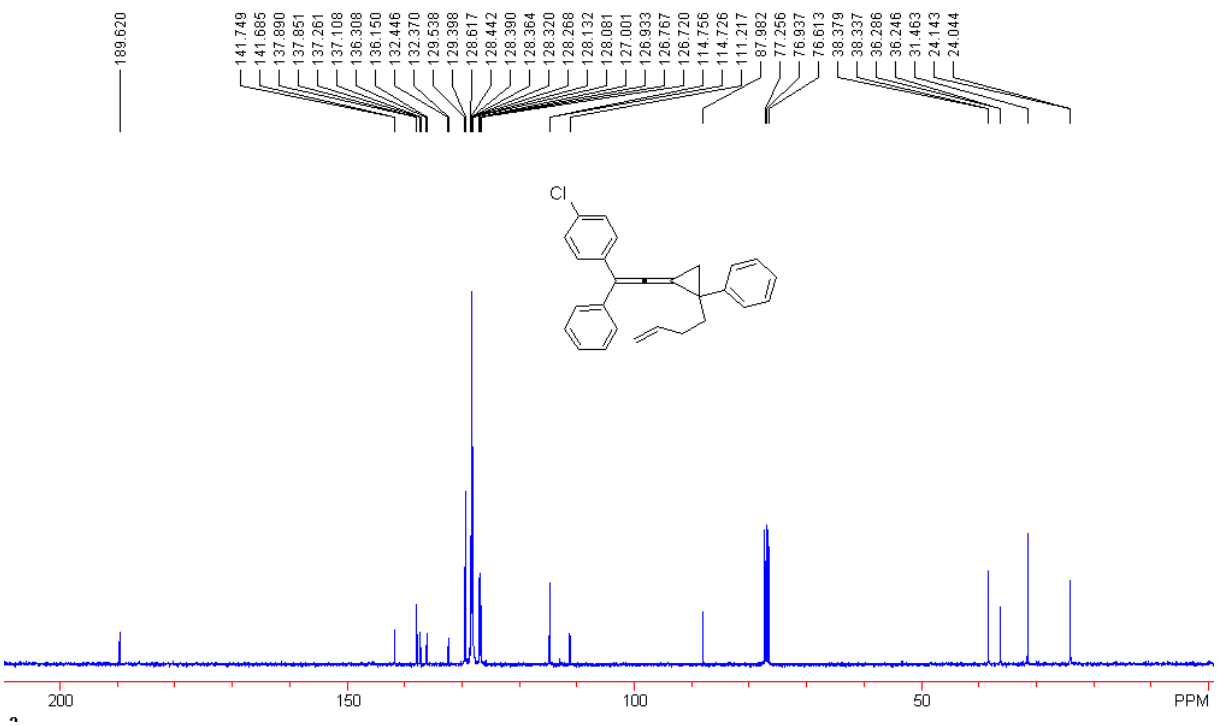
150
100
50
0
PPM

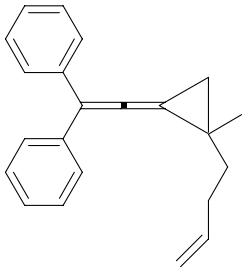

Cl

1-(1-(but-3-enyl)-2-(2-(4-chlorophenyl)-2-phenylvinylidene)cyclopropyl)benzene 1k

A light green oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.85-1.92 (m, 1H), 2.06-2.25 (m, 5H), 4.88-4.97 (m, 2H), 5.70-5.84 (m, 1H), 7.23-7.42 (m, 14H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 24.1, 24.2, 31.5, 36.31, 36.35, 38.40, 38.44, 88.0, 111.3, 114.79, 114.82, 126.78, 126.83, 127.0, 127.1, 128.1, 128.2, 128.3, 128.38, 128.43, 128.45, 128.5, 128.7, 129.5, 129.6, 132.4, 132.5, 136.2, 136.4, 137.2, 137.3, 137.9, 138.0, 141.7, 141.8, 189.6. IR (CH_2Cl_2) ν 3059, 2974, 2926, 2851, 1992, 1640, 1598, 1489, 1468, 1445, 1090, 1013, 912, 833, 762, 697, 502 cm^{-1}. MS (%) m/e 382 (M^+, 21), 327 (24), 291 (61), 278 (28), 238 (47), 228 (46), 215 (100), 202 (52), 115 (39). HRMS (EI) for $C_{27}H_{23}Cl$: 382.1488; Found: 382.1490.

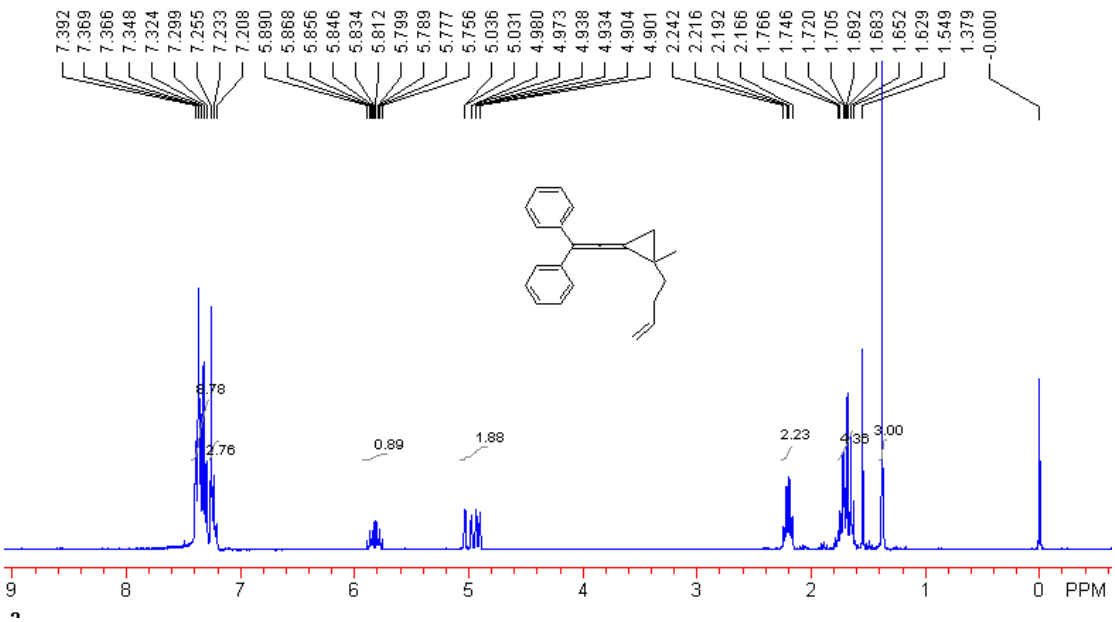


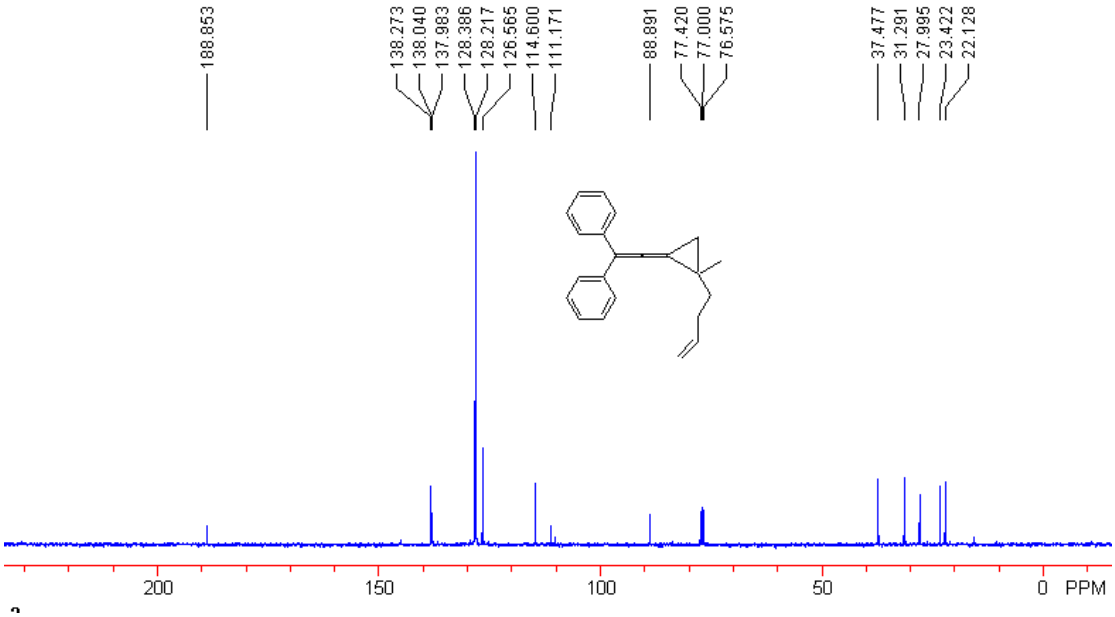




1-(2-(2-(but-3-enyl)-2-methylcyclopropylidene)-1-phenylvinyl)benzene 1l

A light green oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.38 (s, 3H, CH_3), 1.63-1.77 (m, 4H), 2.18 (d, *J* = 7.8 Hz, 1H), 2.23 (d, *J* = 7.8 Hz, 1H), 4.90-5.04 (m, 2H), 5.76-5.89 (m, 1H), 7.21-7.39 (m, 10H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 22.1, 23.4, 28.0, 31.3, 37.5, 88.9, 111.2, 114.6, 126.6, 128.2, 128.4, 138.0, 138.3, 188.9. IR (CH_2Cl_2) ν 3446, 3059, 3026, 2968, 2923, 1991, 1732, 1663, 1640, 1597, 1492, 1446, 1277, 1074, 1030, 912, 767, 697, 627 cm^{-1}. MS (%) m/e 286 (M^+, 8), 243 (28), 231 (51), 215 (68), 204 (100), 189 (15), 165 (38), 152 (21), 115 (14). HRMS (EI) for $C_{22}H_{22}$: 286.1722; Found: 286.1724.

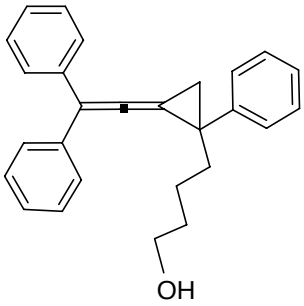




General procedure for the synthesis of diarylvinylidenecyclopropanes 2 containing hydroxyl groups.

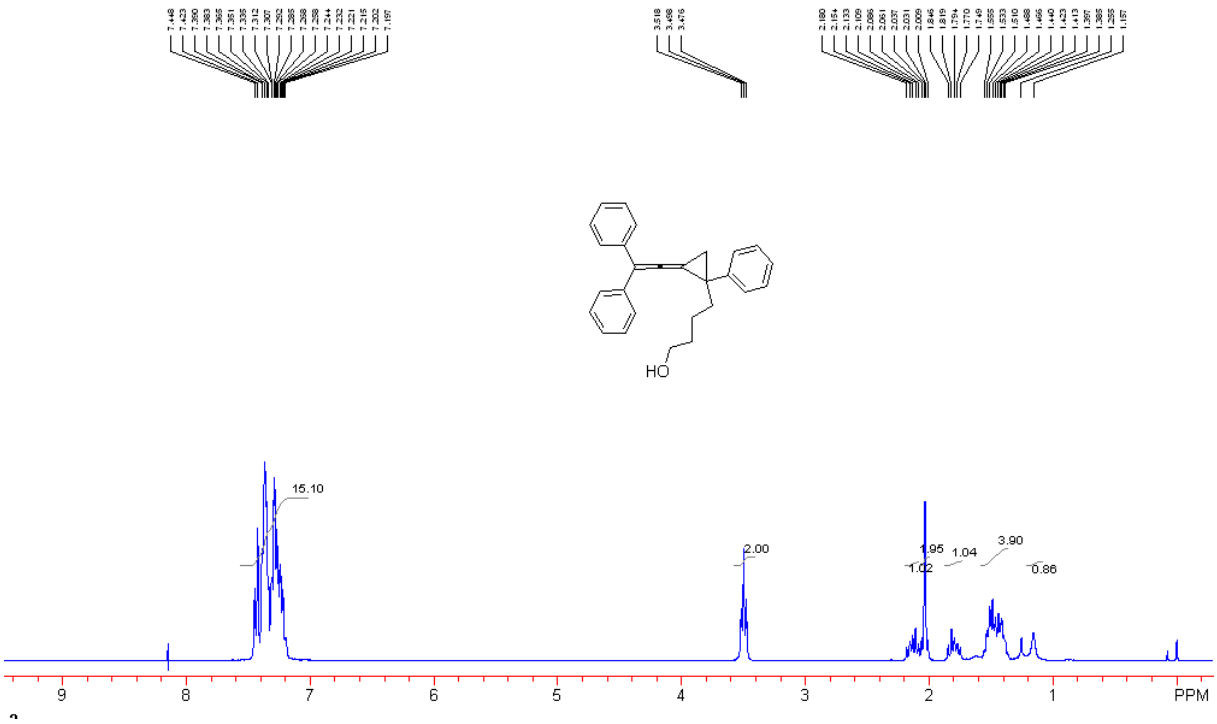
Diarylvinylidenecyclopropanes (VDCPs) **1** (0.3 mmol) was dissolved in THF (3.0 mL), subsequently the solution was cooled to 0 ^{o}C by an ice-bath. BH_3 in THF (0.36 mL, 1.0 N) was dropped into the cooled system and the resulting mixture was stirred for another 15 minutes at 0 ^{o}C. Afterwards, aqueous NaOH (0.3 mL, 1 N) was dropped into the mixture carefully, followed aqueous H_2O_2 (30%, 0.5 mL) added in one portion, and then the mixture was stirred for 2 to 5 minutes at 0 ^{o}C, which was extracted by ether (20 mL x 3). The combined organic phase was washed by Brine (20 mL x 1) and dried over anhydrous $MgSO_4$.

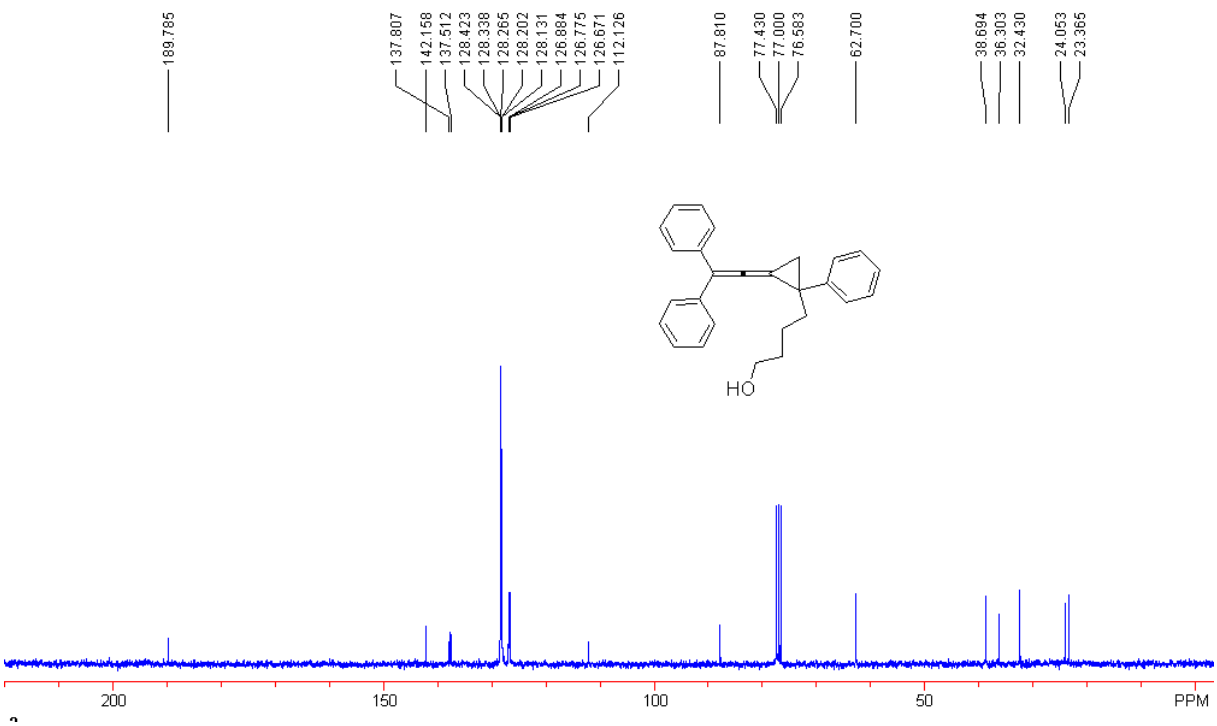
The solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel column with petroleum ether-EtOAc (20:1) as an eluent.

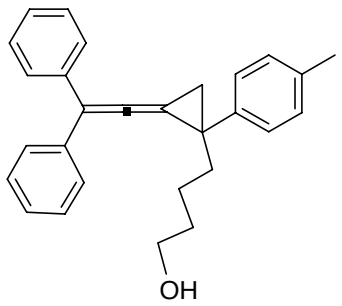


4-(2-(2,2-diphenylvinylidene)-1-phenylcyclopropyl)butan-1-ol 2a

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.16 (brs, 1H, OH), 1.39-1.56 (m, 4H), 1.75-1.85 (m, 1H), 2.02 (d, *J* = 6.9 Hz, 1H), 2.05 (d, *J* = 6.9 Hz, 1H), 2.09-2.18 (m, 1H), 3.50 (t, *J* = 6.3 Hz, 2H), 7.20-7.31 (m, 7H, Ar), 7.34-7.39 (m, 6H, Ar), 7.44 (d, *J* = 7.5 Hz, 2H Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 23.4, 24.1, 32.4, 36.3, 38.7, 62.7, 87.8, 112.1, 126.7, 126.8, 126.9, 128.1, 128.2, 128.27, 128.34, 128.4, 137.5, 137.8, 142.2, 189.8. IR (CH_2Cl_2) ν 3412, 3056, 2935, 2863, 1991, 1598, 1492, 1444, 1073, 1029, 921, 767, 697, 628, 516 cm^{-1}. MS (%) m/e 366 (M^+, 9), 293 (35), 229 (16), 215 (83), 167 (52), 115 (32), 105 (100), 91 (45). HRMS (EI) for $C_{27}H_{26}O$: 366.1984; Found: 366.1987.

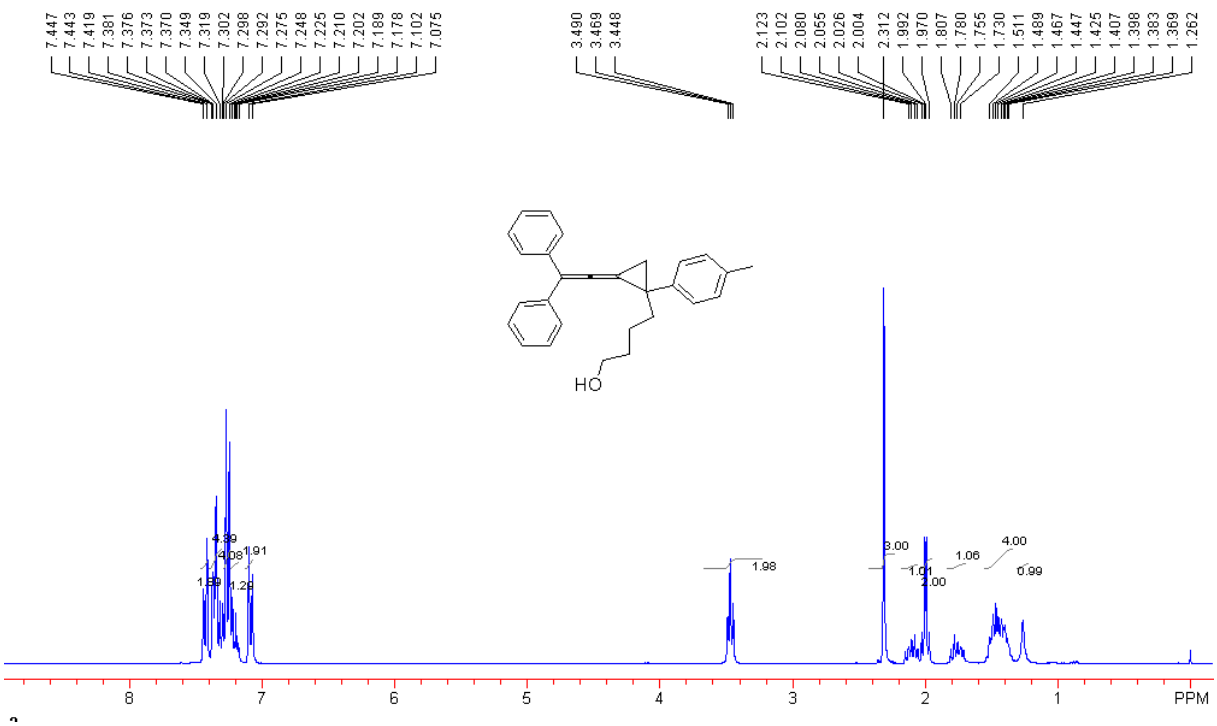






4-(2-(2,2-diphenylvinylidene)-1-*p*-tolylcyclopropyl)butan-1-ol 2b

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.26 (brs, 1H, OH), 1.38-1.53 (m, 4H), 1.71-1.81 (m, 1H), 2.00 (d, *J* = 6.6 Hz, 1H), 2.01 (d, *J* = 6.6 Hz, 1H), 2.06-2.15 (m, 1H), 2.31 (s, 3H, CH_3), 3.47 (t, *J* = 6.3 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H, Ar), 7.19-7.23 (m, 1H, Ar), 7.26 (d, *J* = 8.1 Hz, 4H, Ar), 7.32-7.38 (m, 5H, Ar), 7.43 (d, *J* = 8.1 Hz, 2H Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.0, 23.3, 24.1, 32.4, 36.0, 38.8, 62.6, 87.8, 111.9, 126.7, 126.8, 128.0, 128.1, 128.2, 128.3, 128.4, 128.9, 136.2, 137.5, 137.8, 139.1, 189.7. IR (CH_2Cl_2) ν 3434, 3055, 2936, 2863, 1991, 1727, 1597, 1512, 1492, 1442, 1277, 1223, 1074, 1031, 767, 696, 528 cm^{-1}. MS (%) m/e 380 (M^+, 18), 307 (51), 291 (23), 229 (100), 215 (27), 167 (53), 115 (16), 91 (23). HRMS (EI) for $C_{28}H_{28}O$: 380.2140; Found: 380.2127.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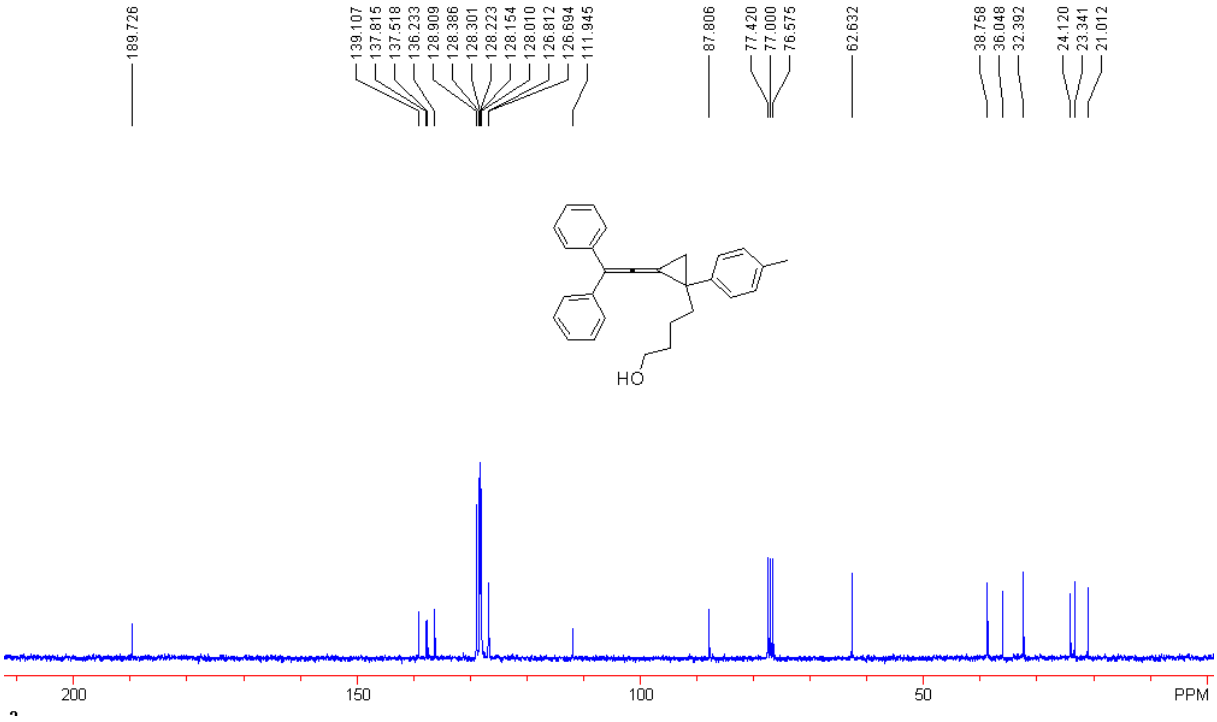
PPM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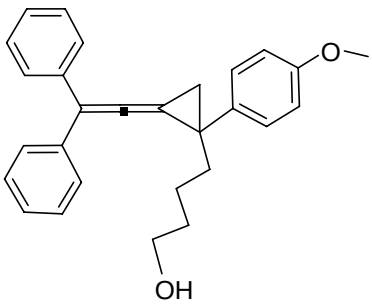
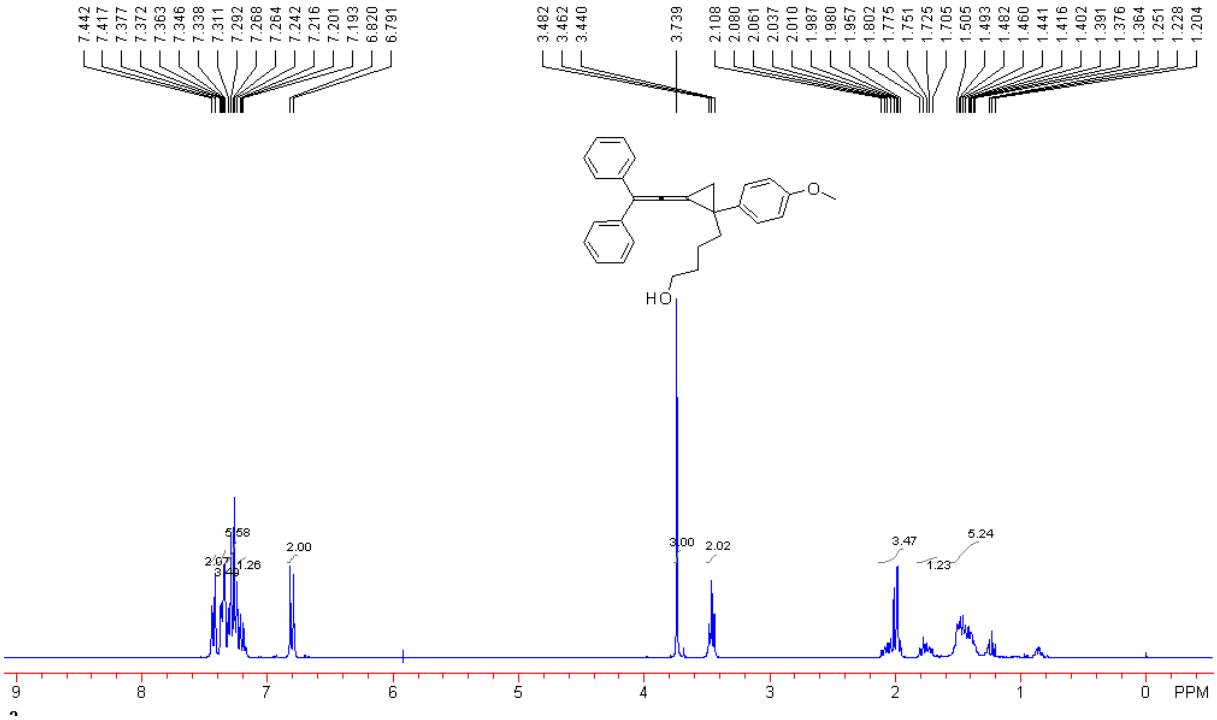
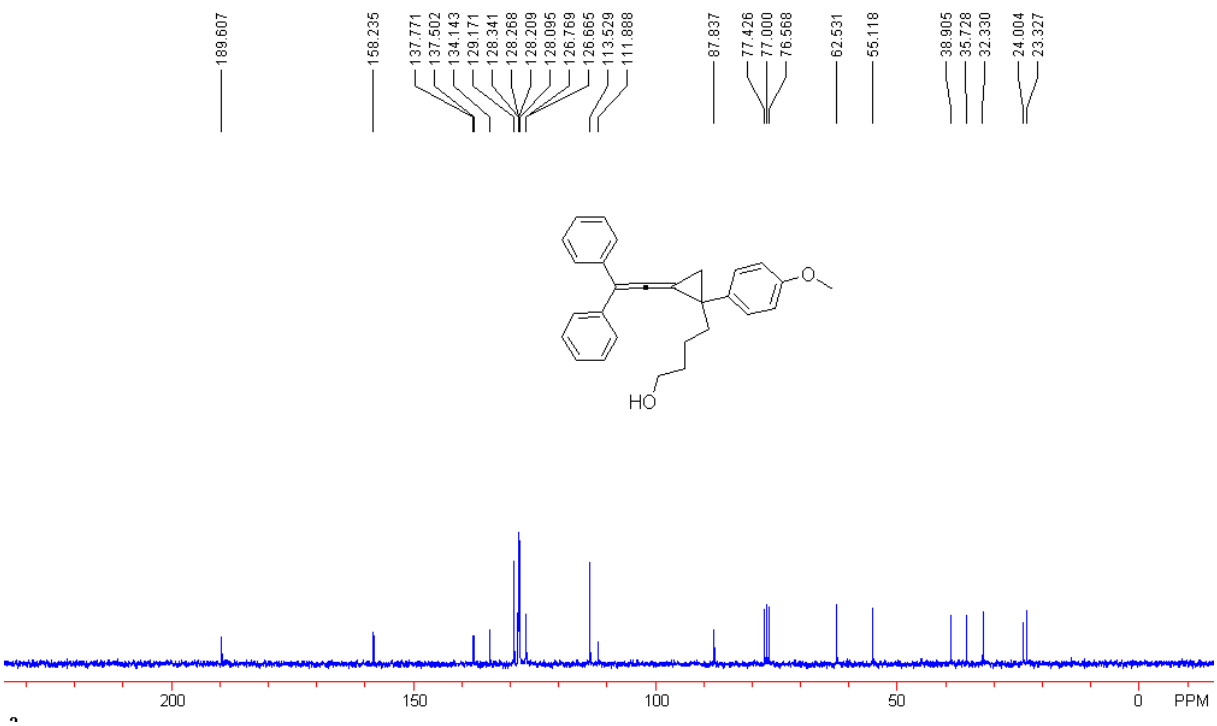
PPM

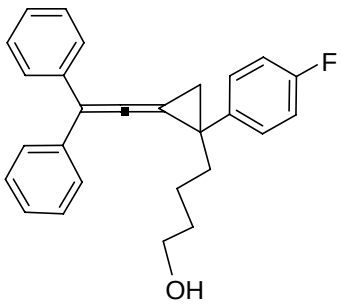


4-(2-(2,2-diphenylvinylidene)-1-(4-methoxyphenyl)cyclopropyl)butan-1-ol 2c

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.38-1.51 (m, 5H), 1.71-1.80 (m, 1H), 1.96-2.11 (m, 4H), 3.46 (t, *J* = 6.3 Hz, 2H), 3.74 (s, 3H, OCH_3), 6.80 (d, *J* = 8.7 Hz, 2H, Ar), 7.19-7.31 (m, 7H, Ar), 7.34-7.38 (m, 3H, Ar), 7.43 (d, *J* = 7.5 Hz, 2H Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 23.3, 24.0, 32.3, 35.7, 38.9, 55.1, 62.5, 87.8, 111.9, 113.5, 126.7, 126.8, 128.1, 128.2, 128.3, 128.34, 129.2, 134.1, 137.5, 137.8, 158.2, 189.6. IR (CH_2Cl_2) ν 3472, 2935, 2862, 1990, 1726, 1608, 1512, 1443, 1247, 1178, 1034, 698 cm^{-1}. MS (%) m/e 396 (M^+, 16), 323 (30), 311 (60), 245 (25), 215 (19), 191 (100), 167 (51), 135 (61). HRMS (EI) for $C_{28}H_{28}O_2$: 396.2089; Found: 396.2082.

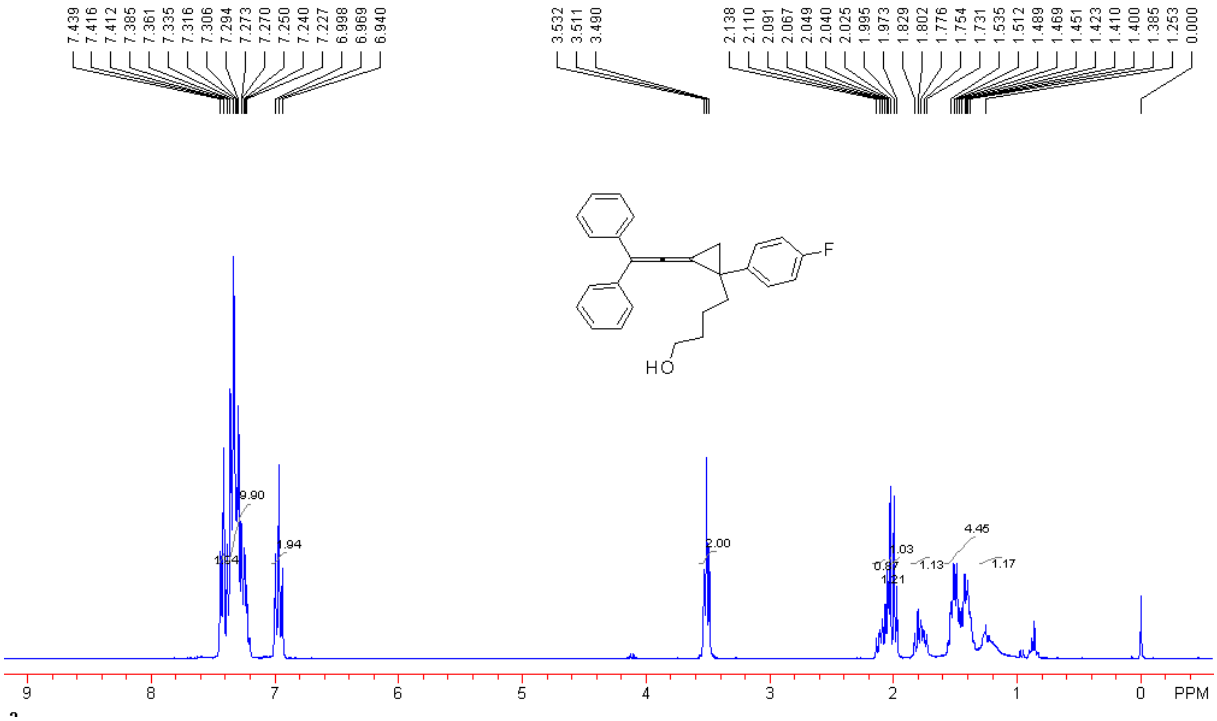






4-(2-(2,2-diphenylvinylidene)-1-(4-fluorophenyl)cyclopropyl)butan-1-ol 2d

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.25 (brs, 1H, OH), 1.39-1.54 (m, 4H), 1.73-1.83 (m, 1H), 1.99 (d, J = 6.6 Hz, 1H), 2.03 (d, J = 6.6 Hz, 1H), 2.07-2.14 (m, 1H), 3.51 (t, J = 6.3 Hz, 2H), 6.97 (dd, J = 8.7 Hz, 2H, Ar), 7.23-7.39 (m, 10H, Ar), 7.43 (d, J = 8.1 Hz, 2H Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 23.3, 24.0, 32.4, 35.5, 38.8, 62.7, 87.7, 112.3, 115.1 (d, $J_{C\text{-}F}$ = 21.2 Hz), 126.9 (d, $J_{C\text{-}F}$ = 5.0 Hz), 128.1, 128.3, 128.36, 128.4, 129.7 (d, $J_{C\text{-}F}$ = 7.4 Hz), 137.4, 137.6, 137.89, 137.92, 161.6 (d, $J_{C\text{-}F}$ = 244.0 Hz), 189.7. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$) δ -121.5. IR (CH_2Cl_2) ν 3416, 2935, 2862, 1991, 1597, 1509, 1493, 1470, 1221, 1157, 1030, 838, 768, 696 cm^{-1}. MS (%) m/e 384 (M^+, 16), 311 (37), 233 (100), 202 (29), 179 (39), 167 (58), 133 (22), 109 (20). HRMS (EI) for $C_{27}H_{25}OF$: 384.1889; Found: 384.1893.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6.940
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2.049
2.040
2.025
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1.754
1.731
1.535
1.512
1.489
1.469
1.451
1.423
1.410
1.400
1.385
1.253
0.000
F
HO
9.90
1.94
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1.13
1.17
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6
5
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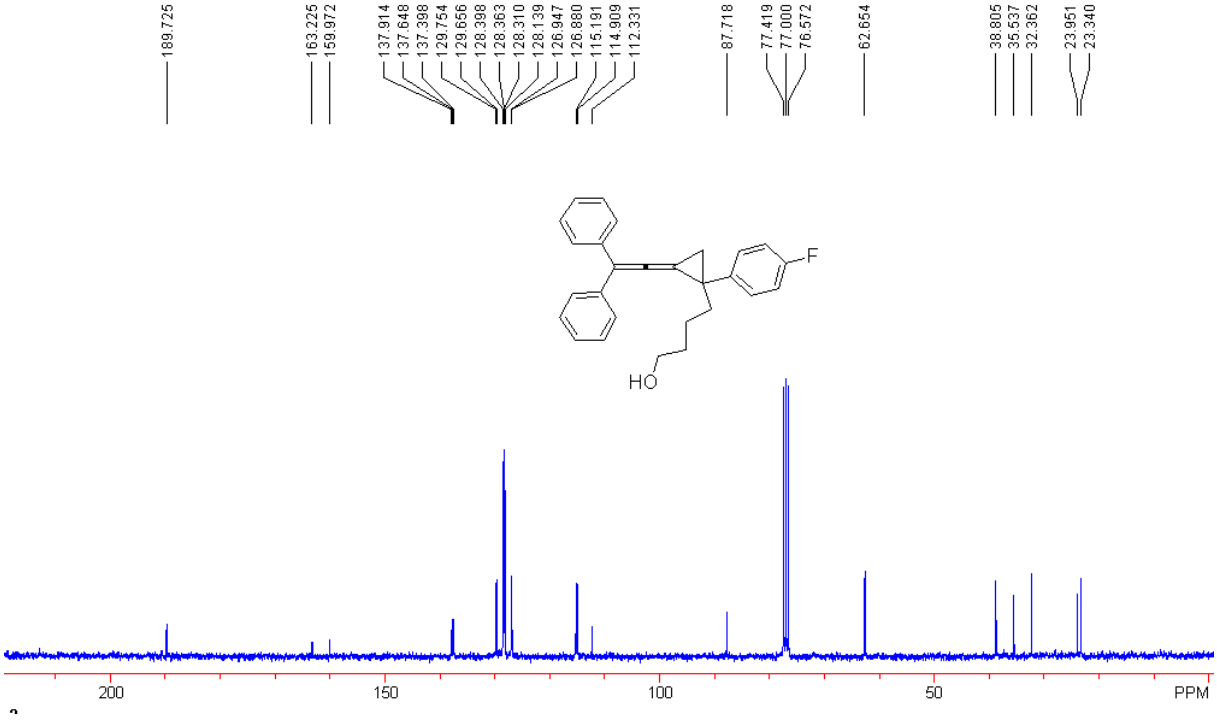
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128.139
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126.880
115.191
114.909
112.331
87.718
77.419
77.000
76.572
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38.805
35.537
32.362
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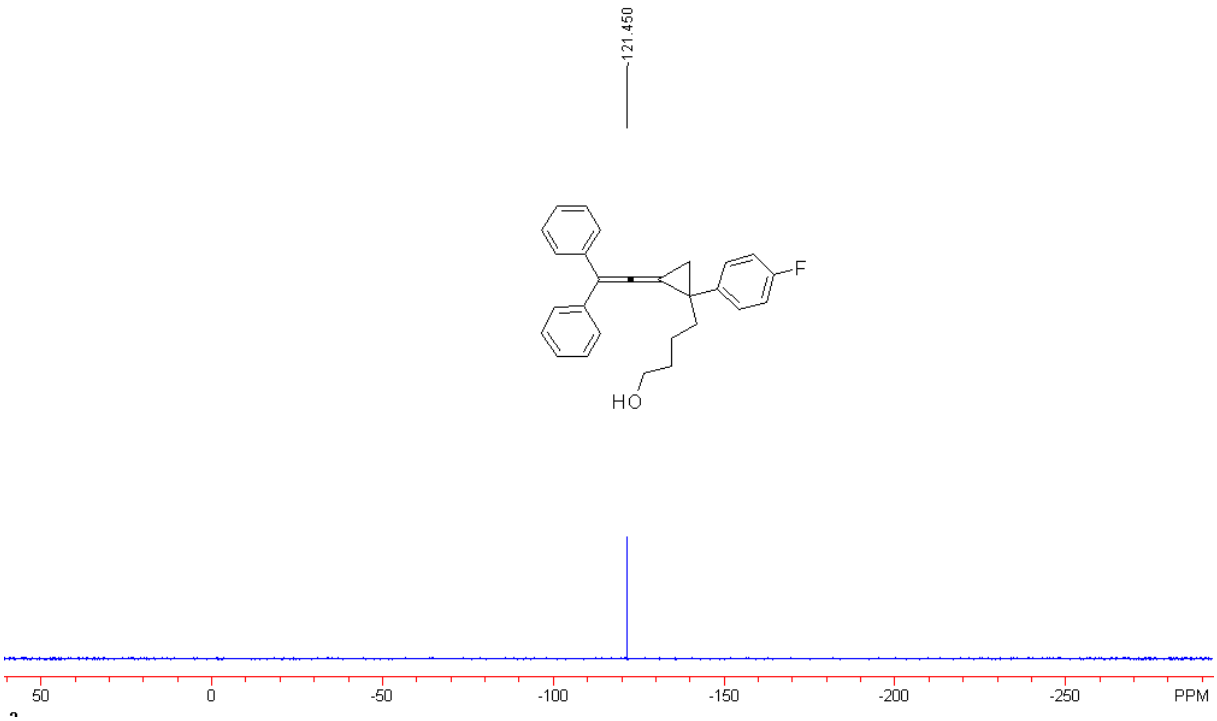
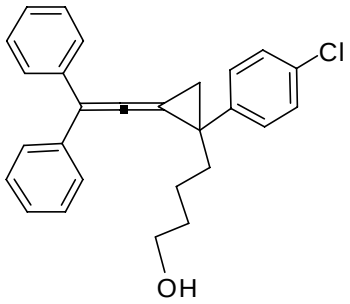
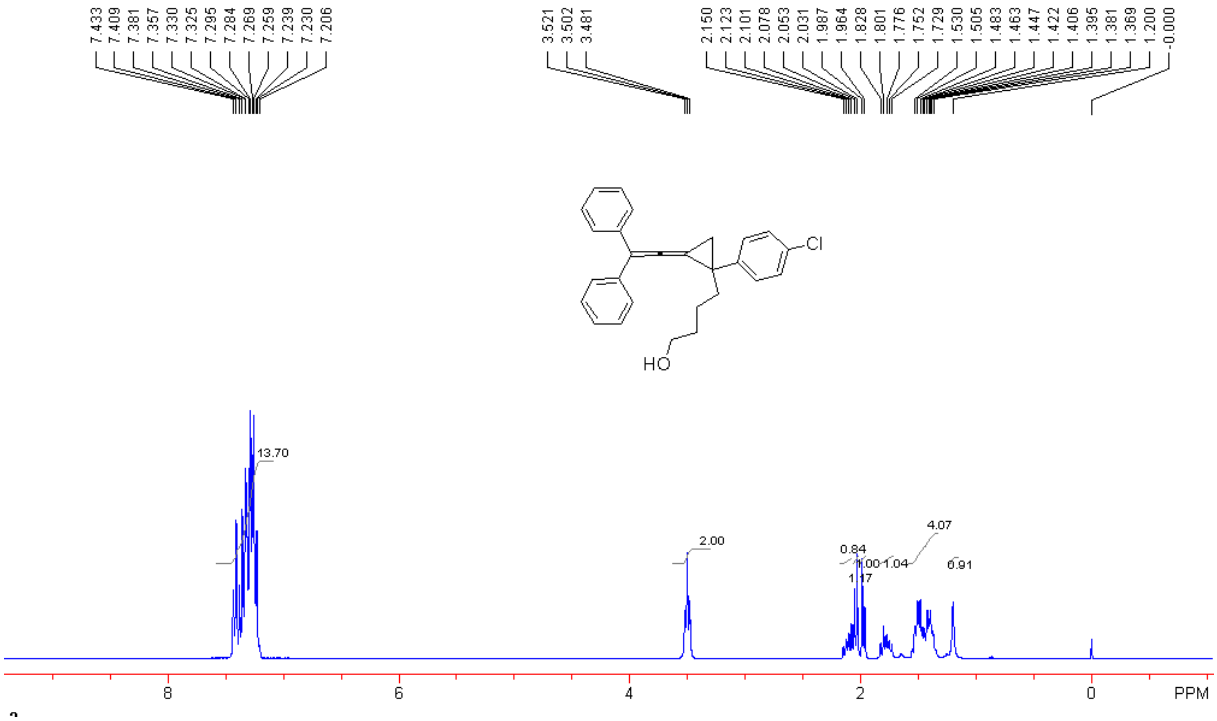
23.340
F
HO
200
150
100
50
PPM





4-(1-(4-chlorophenyl)-2-(2,2-diphenylvinylidene)cyclopropyl)butan-1-ol 2e

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.20 (brs, 1H, OH), 1.37-1.53 (m, 4H), 1.73-1.83 (m, 1H), 1.97 (d, *J* = 6.9 Hz, 1H), 2.04 (d, *J* = 6.9 Hz, 1H), 2.08-2.15 (m, 1H), 3.50 (t, *J* = 6.0 Hz, 2H), 7.21-7.43 (m, 14H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 23.3, 24.0, 32.3, 35.5, 38.5, 62.6, 87.6, 112.5, 126.92, 126.98, 128.2, 128.3, 128.4, 129.5, 132.4, 137.3, 137.6, 140.7, 189.8. IR (CH_2Cl_2) ν 3441, 3057, 2935, 2863, 1992, 1712, 1597, 1492, 1443, 1361, 1221, 1092, 1014, 832, 768, 698 cm^{-1}. MS (%) m/e 400 (M^+, 15), 327 (33), 315 (31), 291 (52), 249 (72), 195 (58), 167 (100), 139 (69). HRMS (EI) for $C_{27}H_{25}OCl$: 400.1594; Found: 400.1595.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7.206
3.521
3.502
3.481
2.150
2.123
2.101
2.078
2.053
2.031
1.987
1.964
1.828
1.801
1.776
1.752
1.729
1.530
1.505
1.483
1.463
1.447
1.422
1.406
1.395
1.381
1.369
1.200
-0.000
Cl
HO
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1.00
1.04
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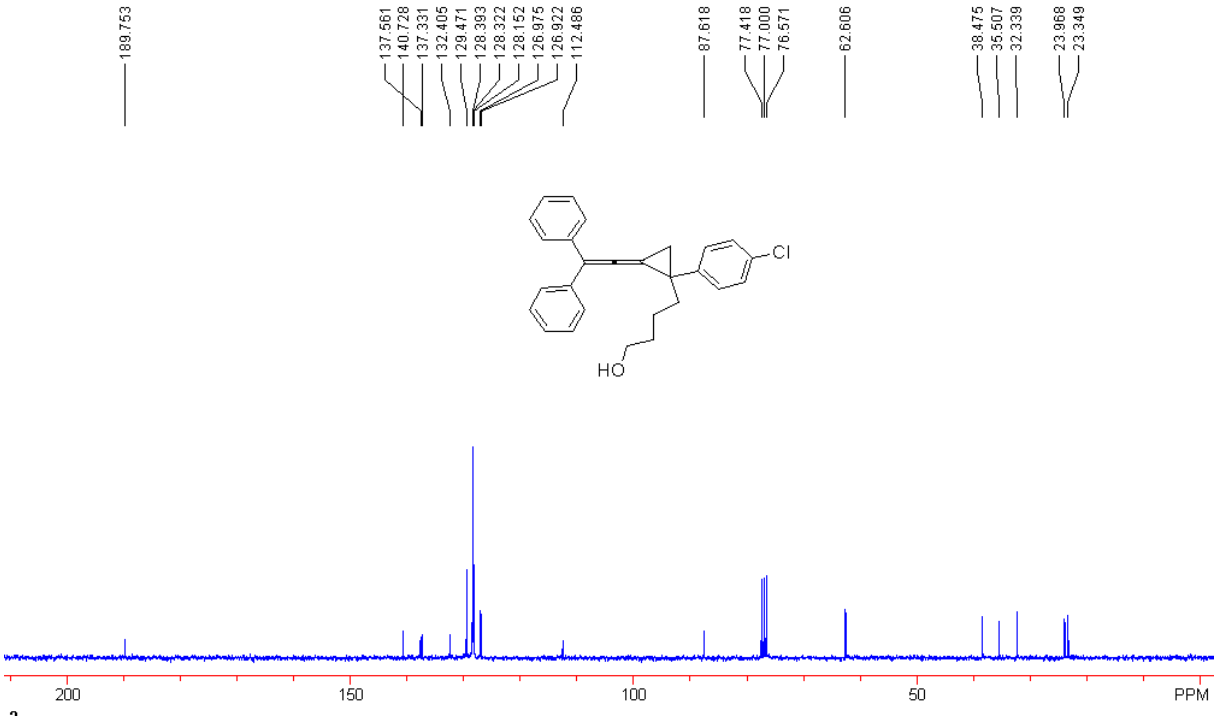
0.91
8
6
4
2
0
PPM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128.152
126.975
126.922
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87.618
77.418
77.000
76.571
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38.475
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32.339
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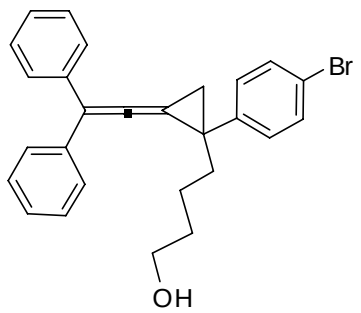
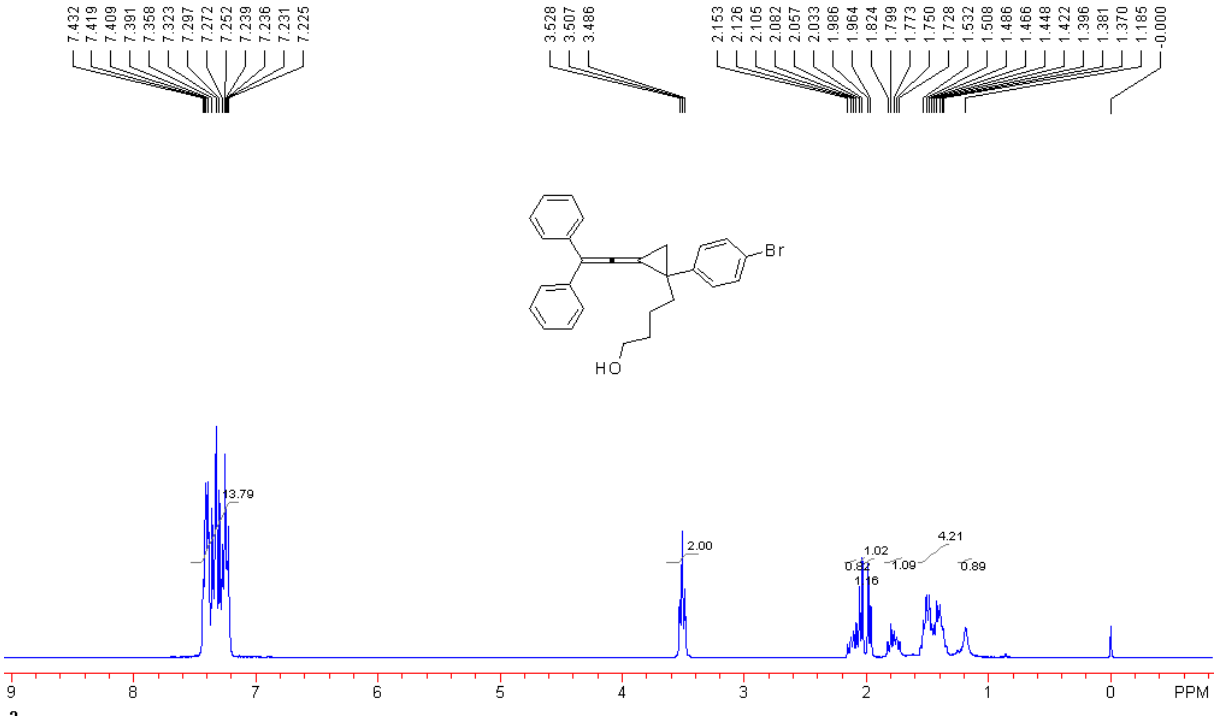
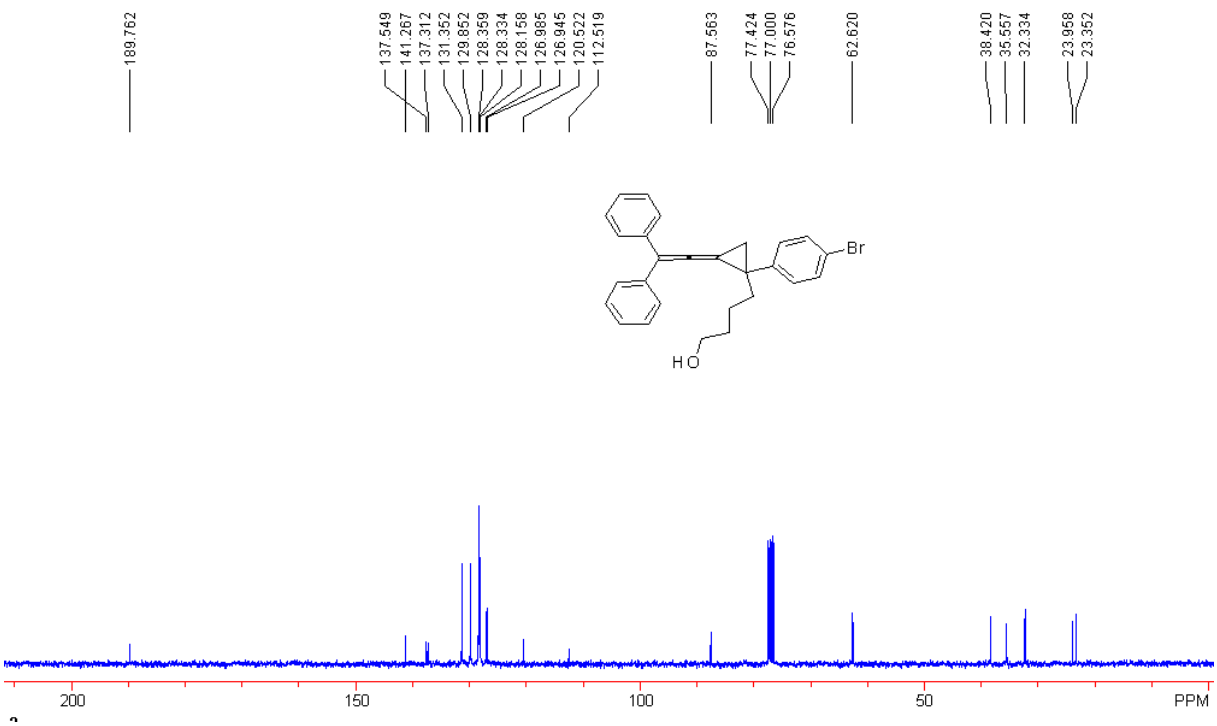
Cl
HO
200
150
100
50
PPM

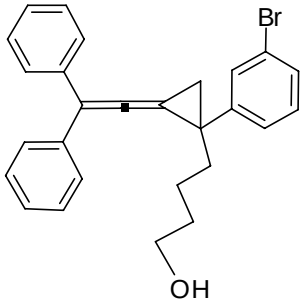


4-(1-(4-bromophenyl)-2-(2,2-diphenylvinylidene)cyclopropyl)butan-1-ol 2f

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.19 (brs, 1H, OH), 1.34-1.53 (m, 4H), 1.73-1.82 (m, 1H), 1.97 (d, *J* = 6.9 Hz, 1H), 2.04 (d, *J* = 6.9 Hz, 1H), 2.08-2.15 (m, 1H), 3.51 (t, *J* = 6.3 Hz, 2H), 7.23-7.43 (m, 14H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 23.4, 24.0, 32.3, 35.6, 38.4, 62.6, 87.6, 112.5, 120.5, 126.95, 126.99, 128.2, 128.3, 128.4, 129.9, 131.4, 137.3, 137.5, 141.3, 189.8. IR (CH_2Cl_2) ν 3456, 3056, 3000, 2925, 1713, 1592, 1560, 1491, 1443, 1360, 1219, 1156, 1076, 773, 701 cm^{-1}. MS (%) m/e 442 (M^+, 7), 426 (13), 398 (11), 229 (37), 205 (57), 191 (100), 165 (74), 115 (40). HRMS (EI) for $C_{27}H_{25}OBr$: 444.1089; Found: 444.1082.

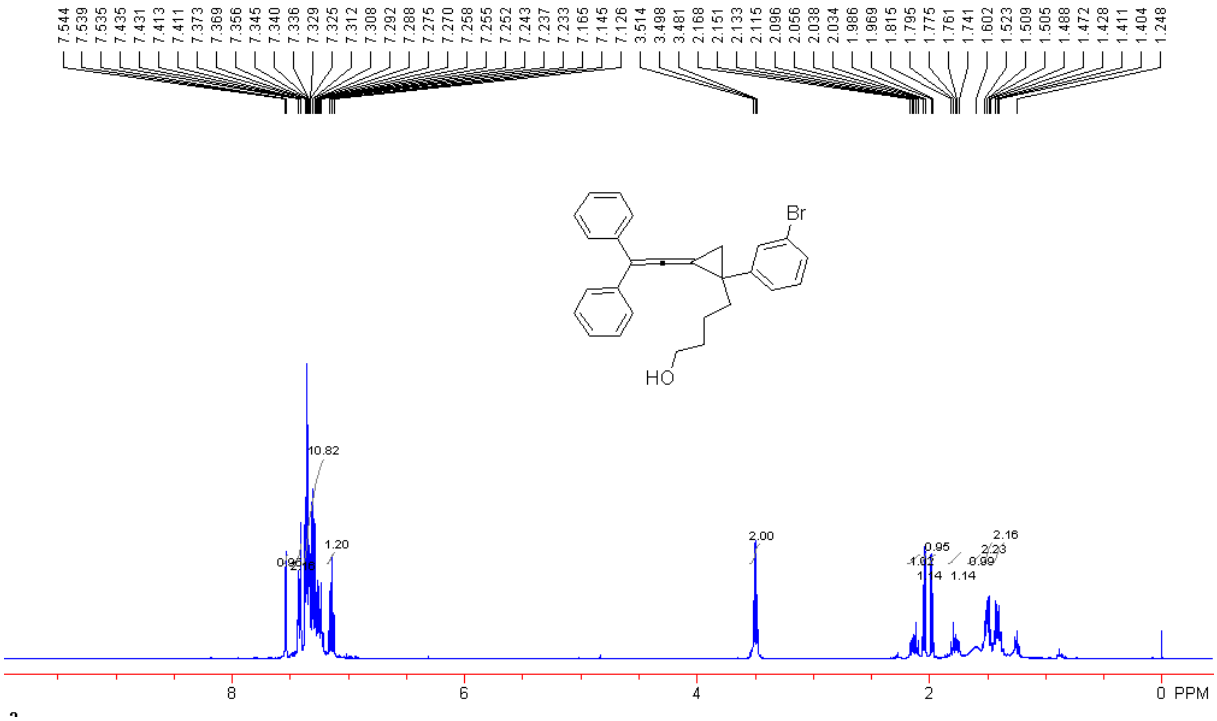






4-(1-(3-bromophenyl)-2-(2,2-diphenylvinylidene)cyclopropyl)butan-1-ol 2g

A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.36-1.44 (m, 2H), 1.47-1.54 (m, 2H), 1.60 (brs, 1H, OH), 1.74-1.82 (m, 1H), 1.98 (d, *J* = 6.8 Hz, 1H), 2.04 (d, *J* = 6.8 Hz, 1H), 2.10-2.17 (m, 1H), 3.50 (t, *J* = 6.8 Hz, 2H), 7.15 (dd, *J* = 7.6 Hz, *J* = 8.0 Hz, 1H), 7.23-7.38 (m, 10H, Ar), 7.42 (dd, *J* = 1.2 Hz, *J* = 8.0 Hz, 2H), 7.54 (dd, *J* = 1.6 Hz, *J* = 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 23.4, 24.1, 32.3, 35.6, 38.2, 62.6, 87.5, 112.7, 122.4, 126.7, 126.98, 127.0, 128.2, 128.36, 128.38, 129.76, 129.83, 131.1, 137.3, 137.5, 144.6, 189.8. IR (CH_2Cl_2) ν 3418, 3057, 3026, 2935, 1991, 1593, 1563, 1492, 1442, 1408, 1072, 1030, 909, 769, 695 cm^{-1}. MS (%) m/e 444 (M^+, 7), 371 (23), 291 (67), 239 (64), 215 (57), 167 (100), 105 (84), 91 (57). HRMS (EI) for $C_{27}H_{25}OBr$: 444.1089; Found: 444.1088.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HO
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2.23
1.14
8
6
4
2
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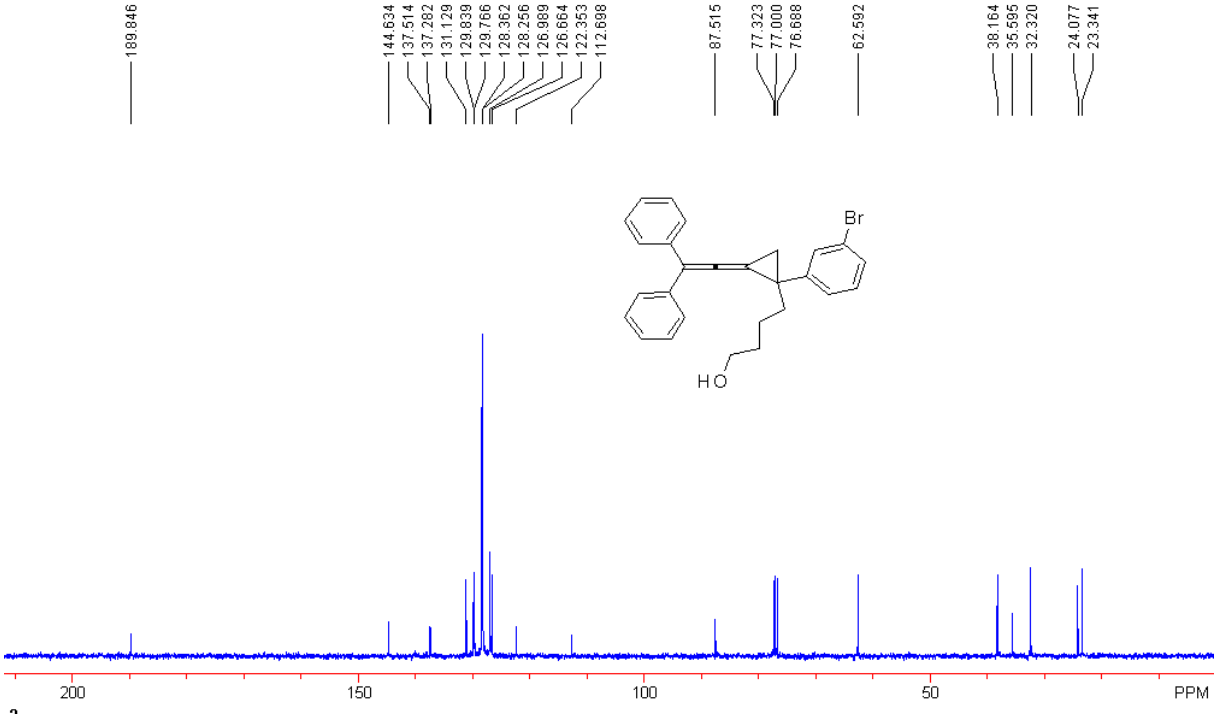
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87.515
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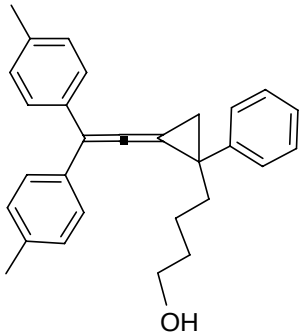
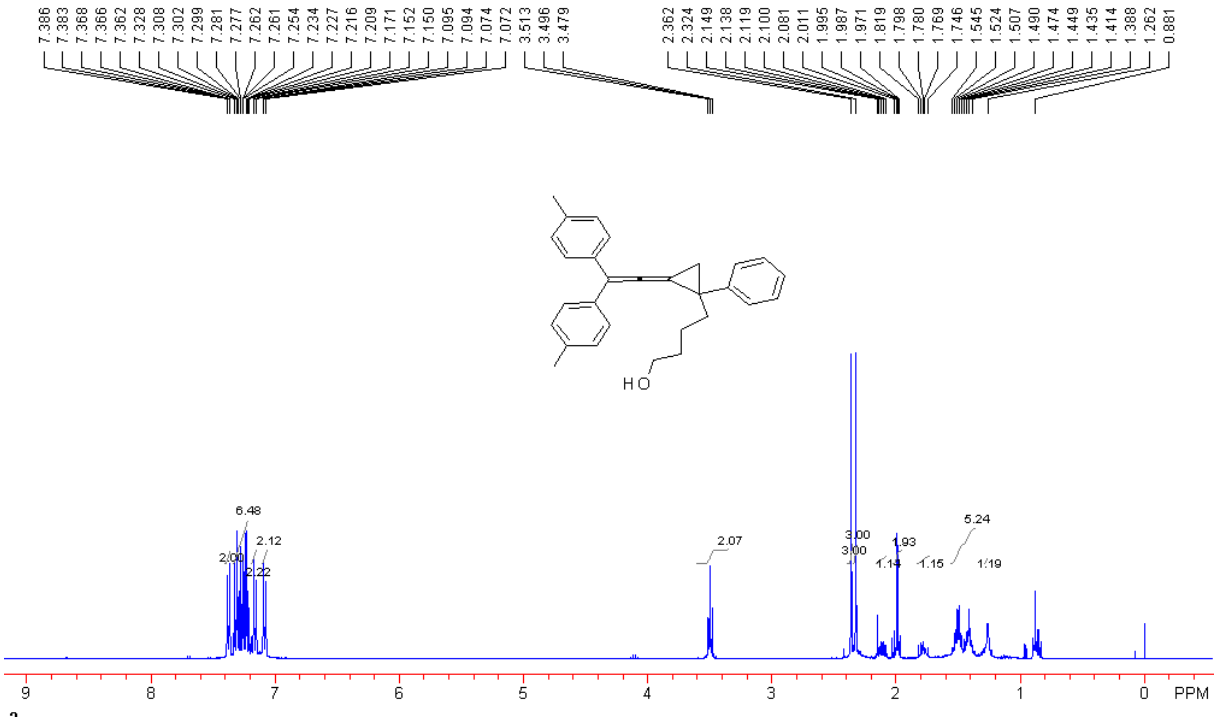
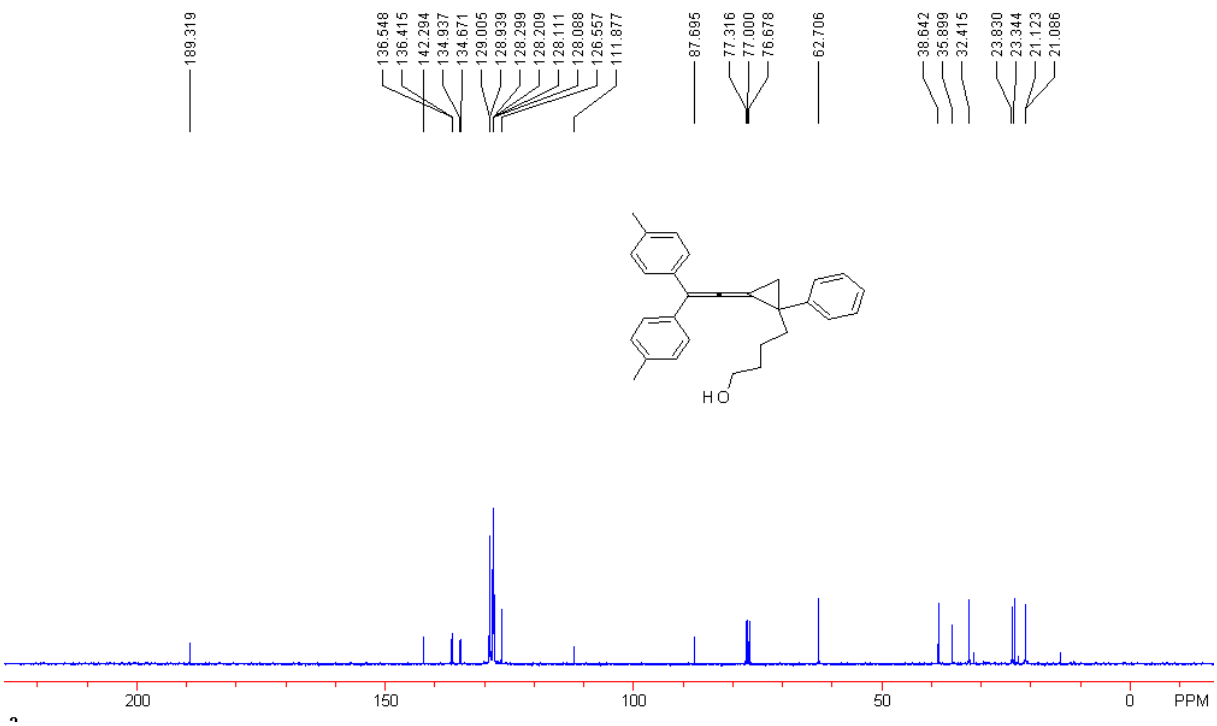
62.592
38.164 35.595 32.320
24.077 23.341
Br
HO
200
150
100
50
PPM

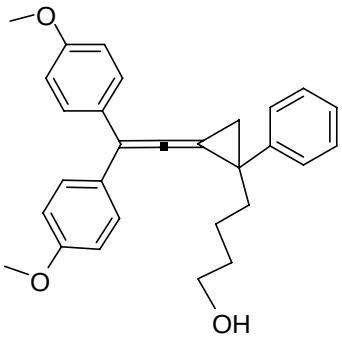


4-(2-(2,2-dip-tolylvinylidene)-1-phenylcyclopropyl)butan-1-ol 2h

A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.26 (brs, 1H, OH), 1.39-1.53 (m, 4H), 1.75-1.82 (m, 1H), 1.98 (d, *J* = 6.4 Hz, 1H), 2.01 (d, *J* = 6.4 Hz, 1H), 2.08-2.15 (m, 1H), 2.32 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.50 (t, *J* = 7.2 Hz, 2H), 7.08 (dd, *J* = 0.8 Hz, *J* = 8.8 Hz, 2H, Ar), 7.16 (d, *J* = 8.0 Hz, 2H, Ar), 7.21-7.33 (m, 7H, Ar), 7.36-7.39 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.09, 21.13, 23.3, 23.8, 32.4, 35.9, 38.6, 62.7, 87.7, 111.9, 126.6, 128.09, 128.12, 128.2, 128.3, 128.9, 129.0, 134.7, 134.9, 136.4, 136.5, 142.3, 189.3. IR (CH_2Cl_2) ν 3417, 3022, 2934, 2862, 1990, 1600, 1508, 1445, 1410, 1181, 1071, 1032, 910, 822, 700, 580 cm^{-1}. MS (%) m/e 394 (M^+, 20), 321 (78), 229 (100), 195 (78), 161 (45), 115 (30), 105 (47), 91 (35). HRMS (EI) for $C_{29}H_{30}O$: 394.2297; Found: 394.2300.

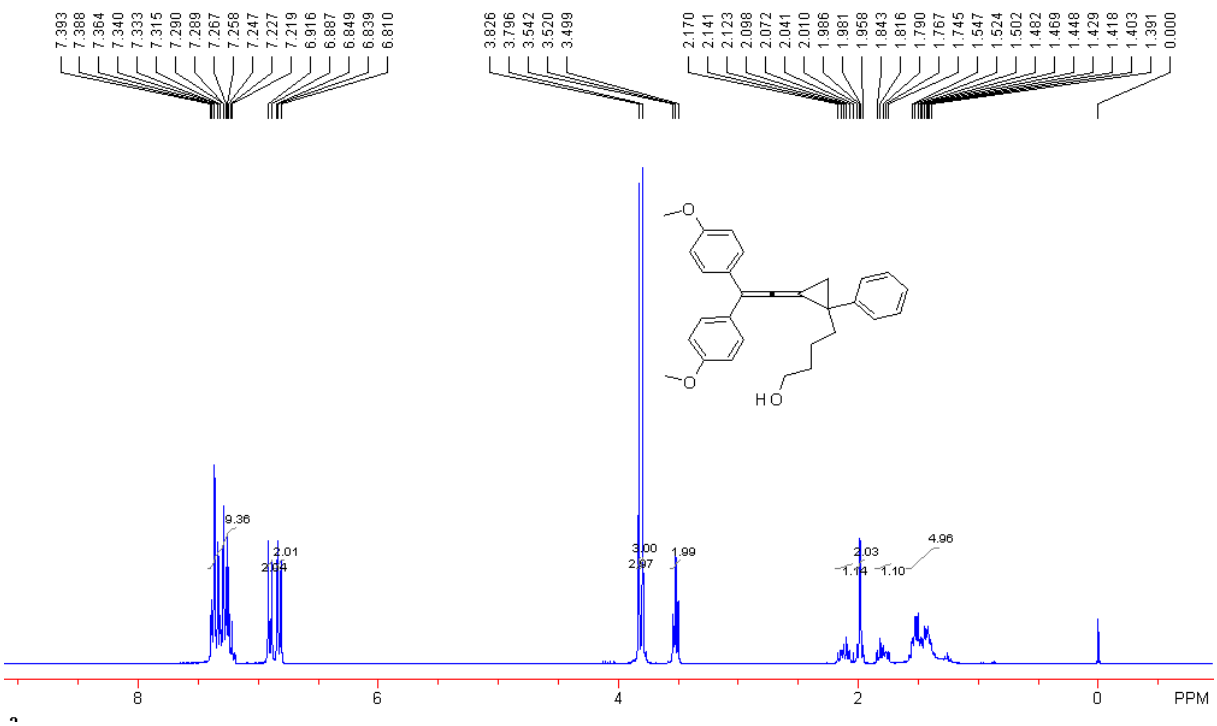






4-(2-(2,2-bis(4-methoxyphenyl)vinylidene)-1-phenylcyclopropyl)butan-1-ol 2i

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.39-1.57 (m, 4H), 1.75-1.84 (m, 1H), 1.97 (d, *J* = 6.9 Hz, 1H), 2.00 (d, *J* = 6.9 Hz, 1H), 2.04-2.17 (m, 1H), 3.52 (t, *J* = 6.3 Hz, 2H), 3.80 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.82 (d, *J* = 8.7 Hz, 2H, Ar), 6.90 (d, *J* = 8.7 Hz, 2H, Ar), 7.21-7.39 (m, 9H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 23.4, 23.7, 32.5, 35.6, 38.7, 55.26, 55.30, 62.7, 87.8, 111.3, 113.7, 113.8, 126.5, 128.1, 128.2, 129.3, 129.5, 130.1, 130.3, 142.4, 158.5, 158.6, 188.9. IR (CH_2Cl_2) ν 3455, 2999, 2934, 2836, 1989, 1604, 1509, 1463, 1444, 1292, 1247, 1173, 1033, 834, 701 cm^{-1}. MS (%) m/e 426 (M^+, 15), 353 (38), 341 (15), 227 (52), 161 (50), 135 (73), 105 (100), 77 (46). HRMS (EI) for $C_{29}H_{30}O_3$: 426.2195; Found: 426.2202.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HO
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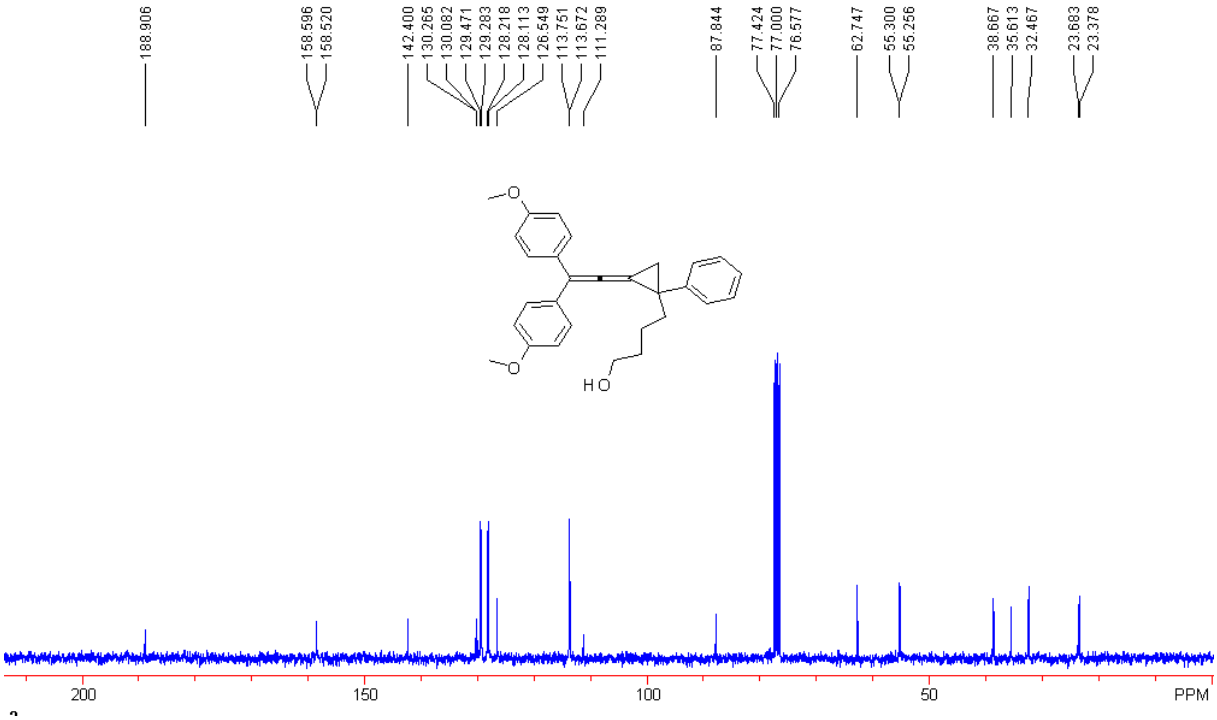
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111.289
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77.424
77.000
76.577
62.747
55.300
55.256
38.667
35.613
32.467
23.683
23.378
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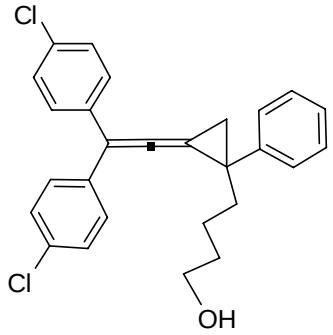
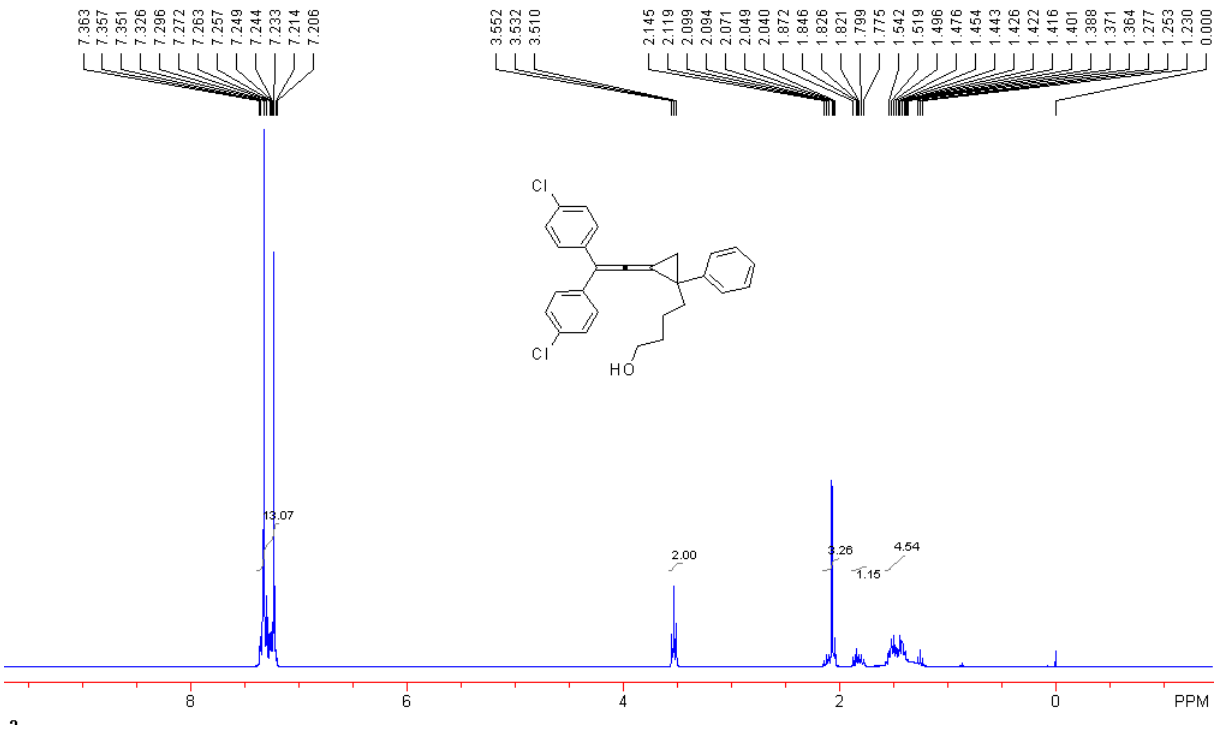
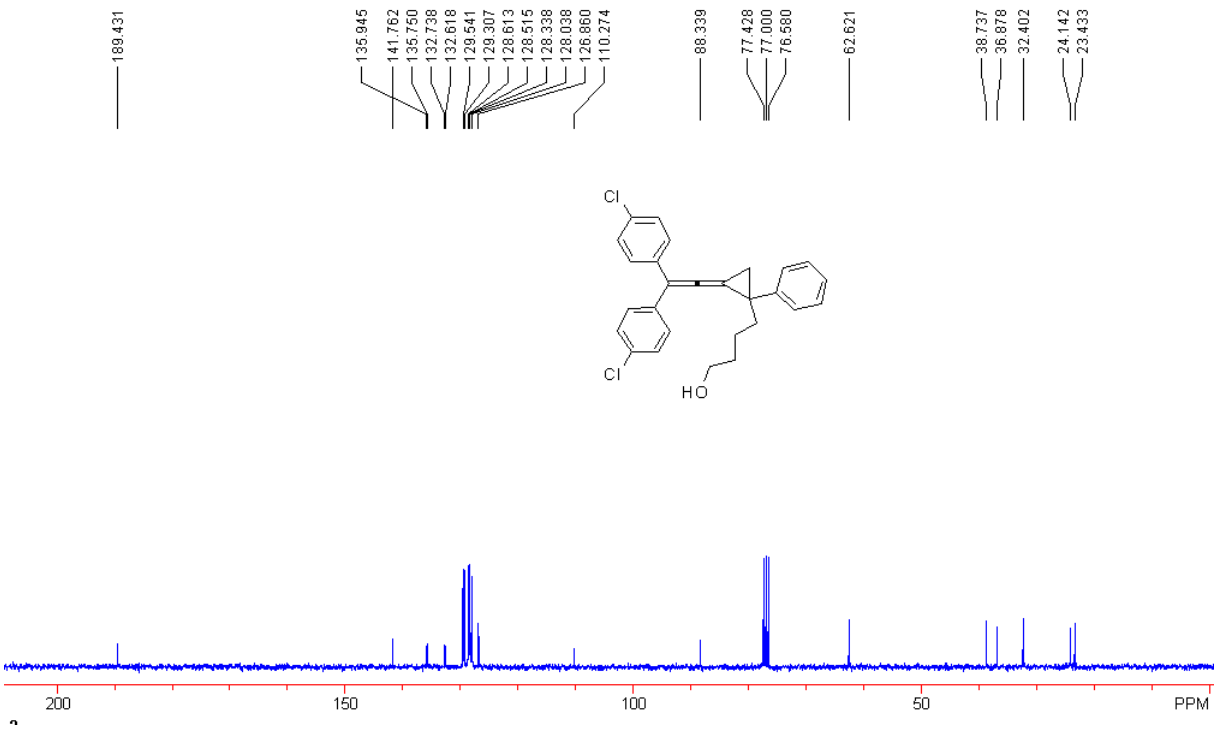
O
HO
200
150
100
50
PPM

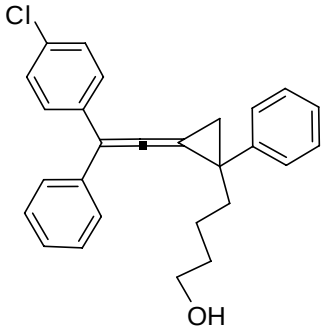


4-(2-(2,2-bis(4-chlorophenyl)vinylidene)-1-phenylcyclopropyl)butan-1-ol 2j

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.40-1.58 (m, 4H), 1.79-1.89 (m, 1H), 2.06-2.16 (m, 3H), 3.55 (t, *J* = 6.3 Hz, 2H), 7.23-7.38 (m, 13H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 23.4, 24.1, 32.4, 36.9, 38.7, 62.6, 88.3, 110.3, 126.9, 128.0, 128.3, 128.5, 128.6, 129.3, 129.5, 132.6, 132.7, 135.8, 135.9, 141.8, 189.4. IR (CH_2Cl_2) ν 3413, 3056, 2936, 2862, 1991, 1710, 1600, 1489, 1465, 1396, 1091, 1013, 908, 832, 700 cm^{-1}. MS (%) m/e 434 (M^+, 21), 361 (73), 326 (58), 289 (67), 249 (100), 235 (90), 202 (73), 161 (90). HRMS (EI) for $C_{27}H_{24}OCl_2$: 434.1204; Found: 434.1205.

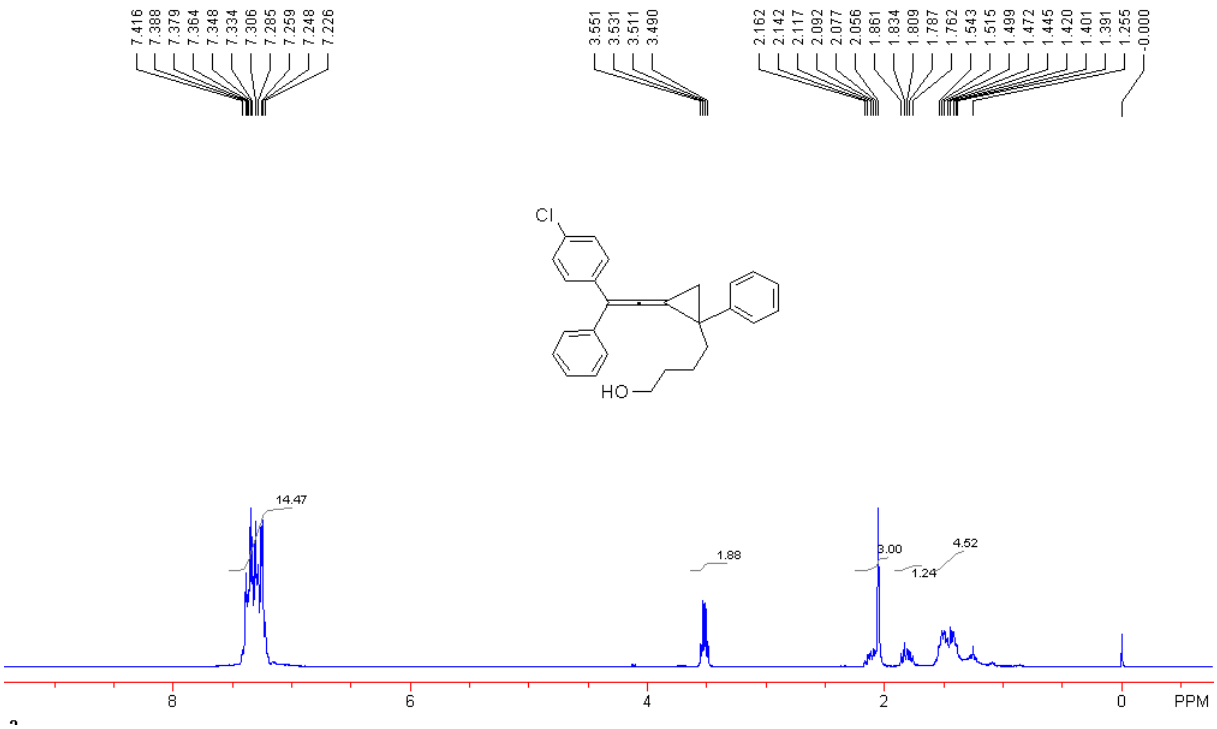






4-(2-(2-(4-chlorophenyl)-2-phenylvinylidene)-1-phenylcyclopropyl)butan-1-ol 2k

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.18-1.26 (m, 2H), 1.39-1.54 (m, 4H), 1.79-1.86 (m, 1H), 2.06-2.14 (m, 3H), 3.50 (d, *J* = 6.0 Hz, 1H), 3.54 (d, *J* = 6.0 Hz, 1H), 7.23-7.42 (m, 14H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 23.4, 24.1, 32.4, 36.6, 38.8, 62.7, 88.1, 111.2, 126.7, 127.0, 128.10, 128.13, 128.36, 128.45, 128.5, 129.6, 132.5, 136.4, 137.1, 141.9, 189.6. IR (CH_2Cl_2) ν 3384, 3057, 2935, 2861, 1991, 1598, 1489, 1468, 1445, 1393, 1090, 1013, 833, 762, 698 cm^{-1}. MS (%) m/e 400 (M^+, 17), 327 (59), 291 (54), 249 (37), 215 (100), 201 (76), 161 (49), 115 (40). HRMS (EI) for $C_{27}H_{25}OCl$: 400.1594; Found: 400.1593.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7.334
7.306
7.285
7.259
7.248
7.226
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3.531
3.511
3.490
2.162
2.142
2.117
2.092
2.077
2.056
1.861
1.834
1.809
1.787
1.762
1.543
1.515
1.499
1.472
1.445
1.420
1.401
1.391
1.255
-0.000
Cl
HO
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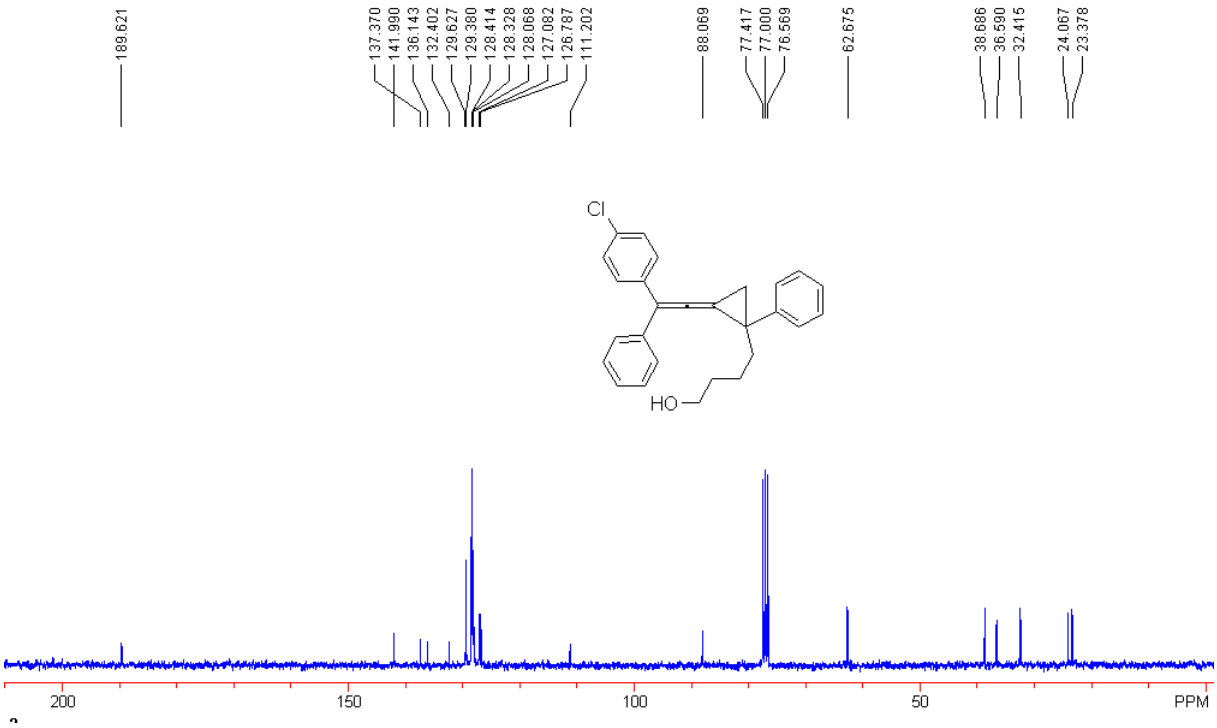
1.88
3.00
1.24
4.52
8
6
4
2
0
PPM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141.990
136.143
132.402
129.627
129.380
128.414
128.328
128.068
127.082
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111.202
88.069
77.417
77.000
76.569
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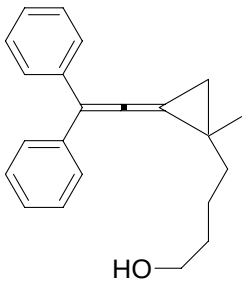
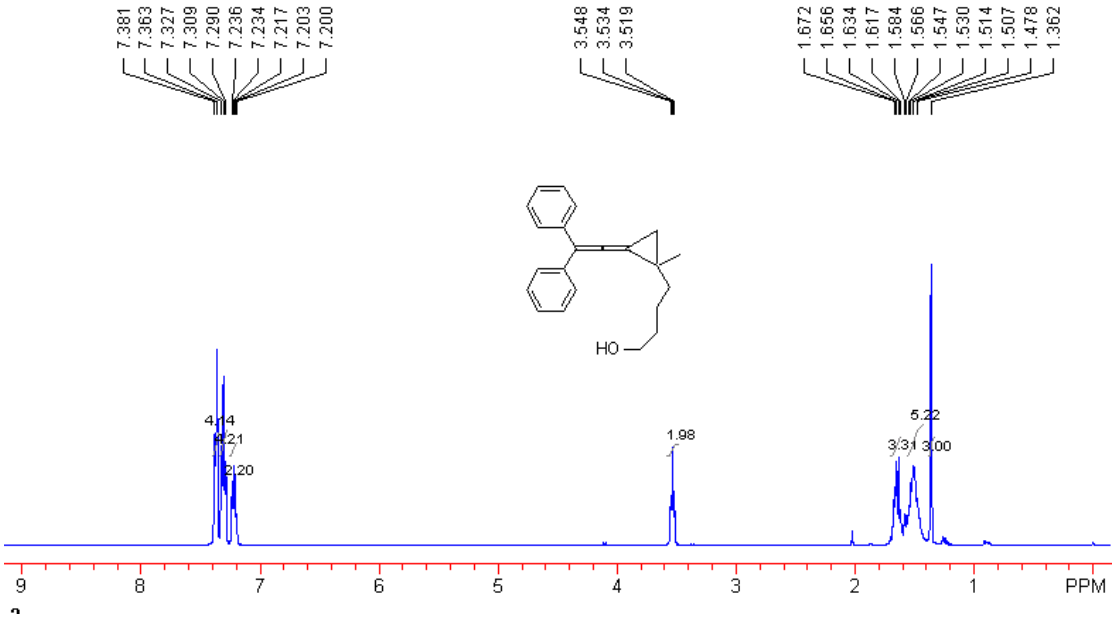
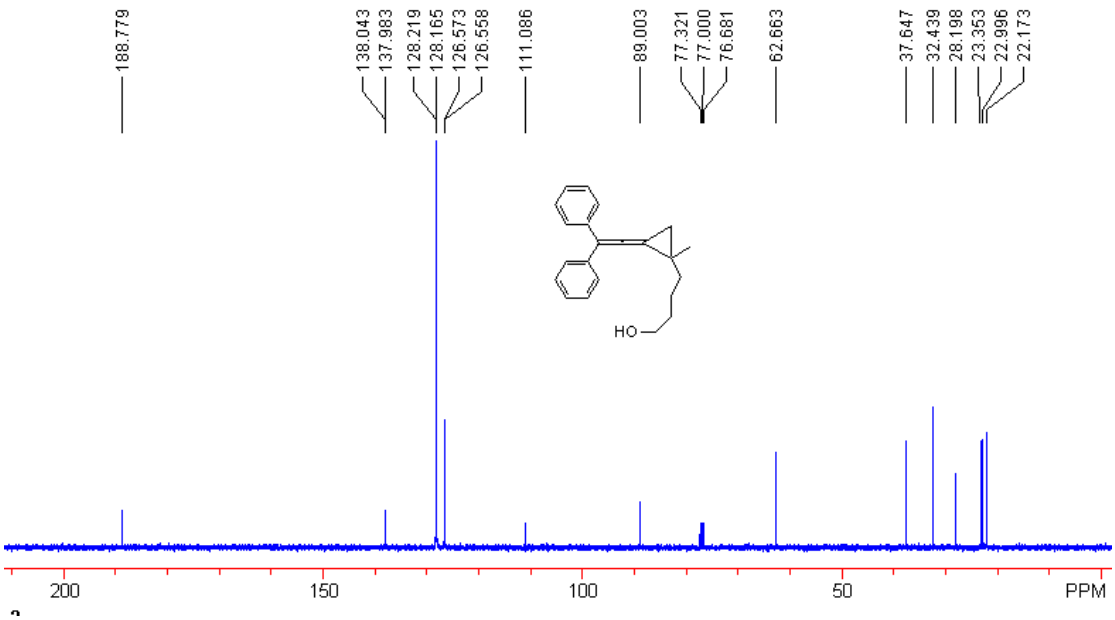
38.686
36.590
32.415
24.067
23.378
Cl
HO
200
150
100
50
PPM


HO

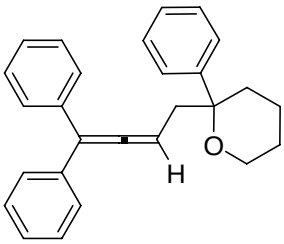
Compound 2l. A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.36 (s, 3H), 1.48-1.58 (m, 5H), 1.62-1.67 (m, 3H), 3.53 (t, *J* = 5.6 Hz, 1H), 7.20-7.24 (m, 2H, Ar), 7.29-7.33 (m, 4H, Ar), 7.37 (d, *J* = 7.2 Hz, 4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 22.2, 23.0, 23.4, 28.2, 32.4, 37.6, 62.7, 89.0, 111.1, 126.56, 126.57, 128.17, 128.22, 137.98, 138.04, 188.8. IR (CH_2Cl_2) ν 3404, 3055, 2934, 2862, 1989, 1597, 1492, 1442, 1376, 1278, 1073, 1030, 767, 696,626, 608 cm^{-1}. MS (%) m/e 304 (M^+, 9), 245 (22), 231 (78), 215 (74), 202 (76), 191 (31), 178 (29), 167 (73), 99 (100), 91 (46). HRMS (EI) for $C_{22}H_{24}O$: 304.1827; Found: 304.1830.





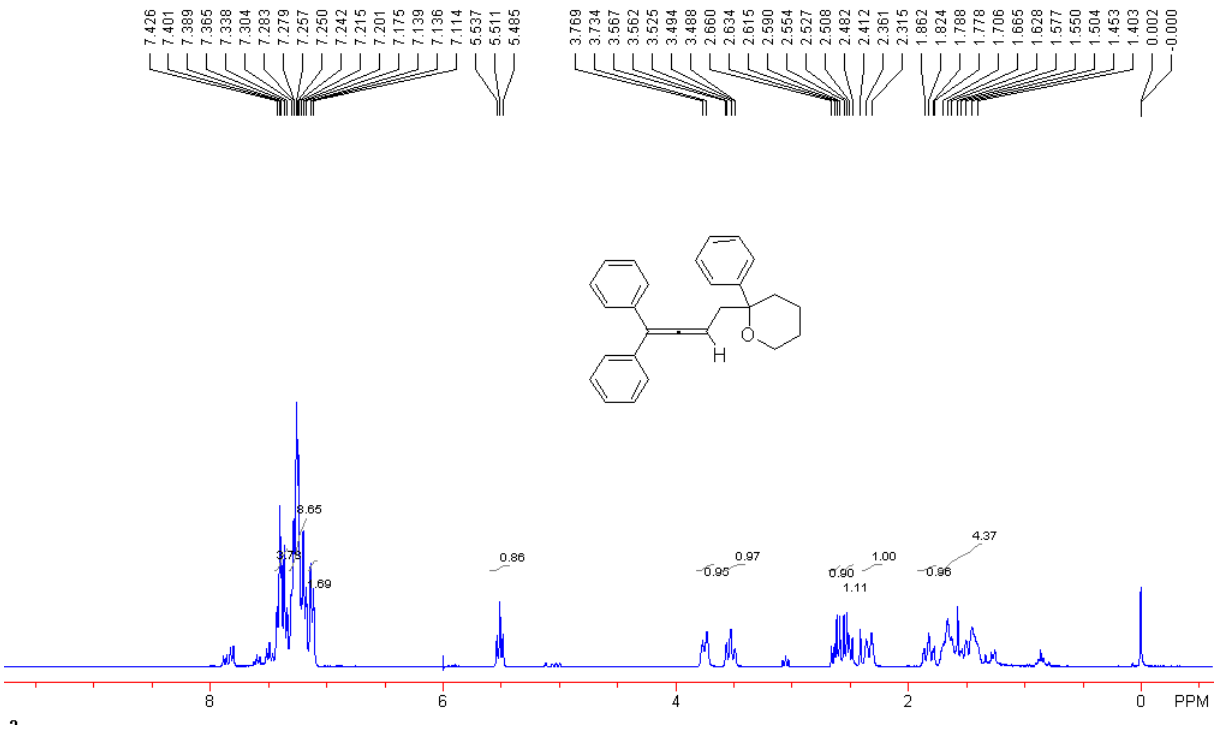
General procedure for the intramolecular cycloaddition of diarylvinylidenecyclopropanes 1 catalyzed by Au(I).

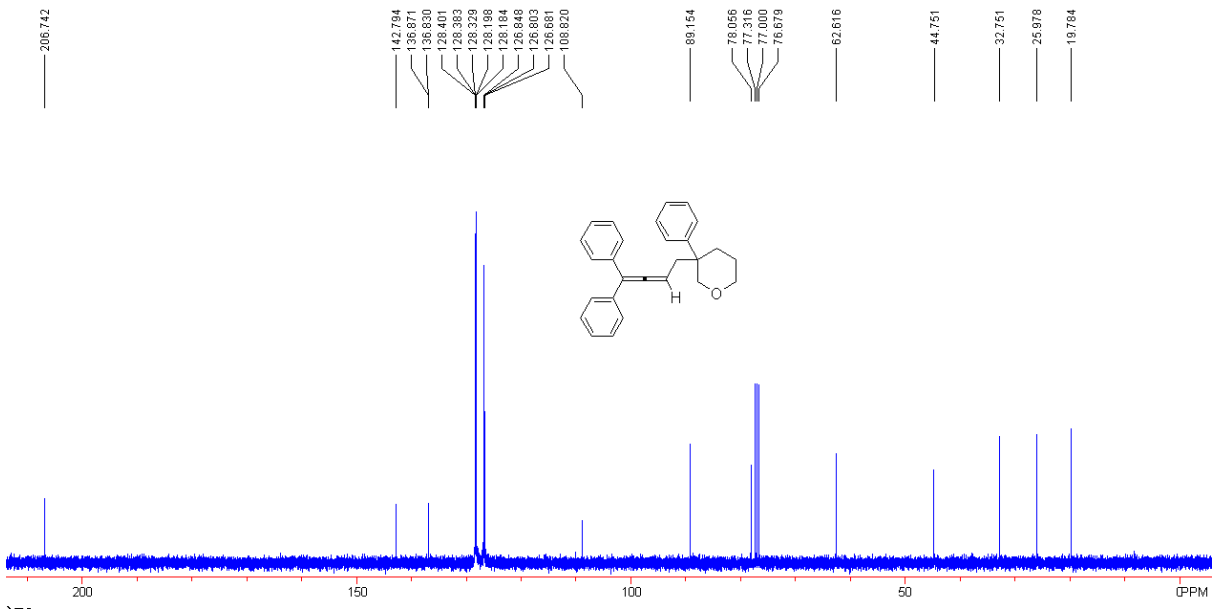
Diarylvinylidenecyclopropanes (VDCPs) **1** (0.1 mmol) was dissolved in 1,4-dioxane (3.0 mL), and then $(Ph_3PAu)_3OBF_4$ (6.0 mg, 4 mol %) and AgOTf (1.0 mg, 4 mol %) was added at 60 ^oC. The mixture was stirred for another 10-30 minutes under this temperature. The solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel column with petroleum ether-EtOAc (80:1) as an eluent.

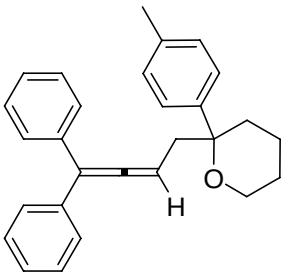


2-(4,4-diphenylbuta-2,3-dienyl)-2-phenyl-tetrahydro-2H-pyran.

A colorless oil; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.40-1.71 (m, 4H), 1.83 (dt, *J* = 3.3 Hz, *J* = 13.5 Hz, 1H), 2.33 (d, *J* = 13.2 Hz, 1H), 2.51 (dd, *J* = 8.1 Hz, *J* = 13.8 Hz, 1H), 2.60 (dd, *J* = 8.1 Hz, *J* = 13.8 Hz, 1H), 3.53 (dt, *J* = 2.1 Hz, *J* = 11.1 Hz, 1H), 3.75 (d, *J* = 10.8 Hz, 1H), 5.51 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 6.3 Hz, 2H, Ar), 7.14-7.33 (m, 9H, Ar), 7.36-7.42 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.8, 26.0, 32.7, 44.8, 62.6, 78.1, 89.2, 108.8, 126.7, 126.9, 128.2, 128.3, 128.4, 130.1, 132.4, 136.8, 136.9, 142.7, 206.7. IR (CH_2Cl_2) ν 3081, 3026, 2939, 2863, 1944, 1661, 1598, 1492, 1447, 1317, 1277, 1176, 1081, 1043, 941, 764, 699, 638 cm^{-1}. MS (%) m/e 366 (M^+, 2), 307 (2), 182 (33), 161 (13), 105 (91), 84 (100), 77 (48), 47 (20). HRMS (EI) for $C_{27}H_{26}O$: 366.1984; Found: 366.1986.



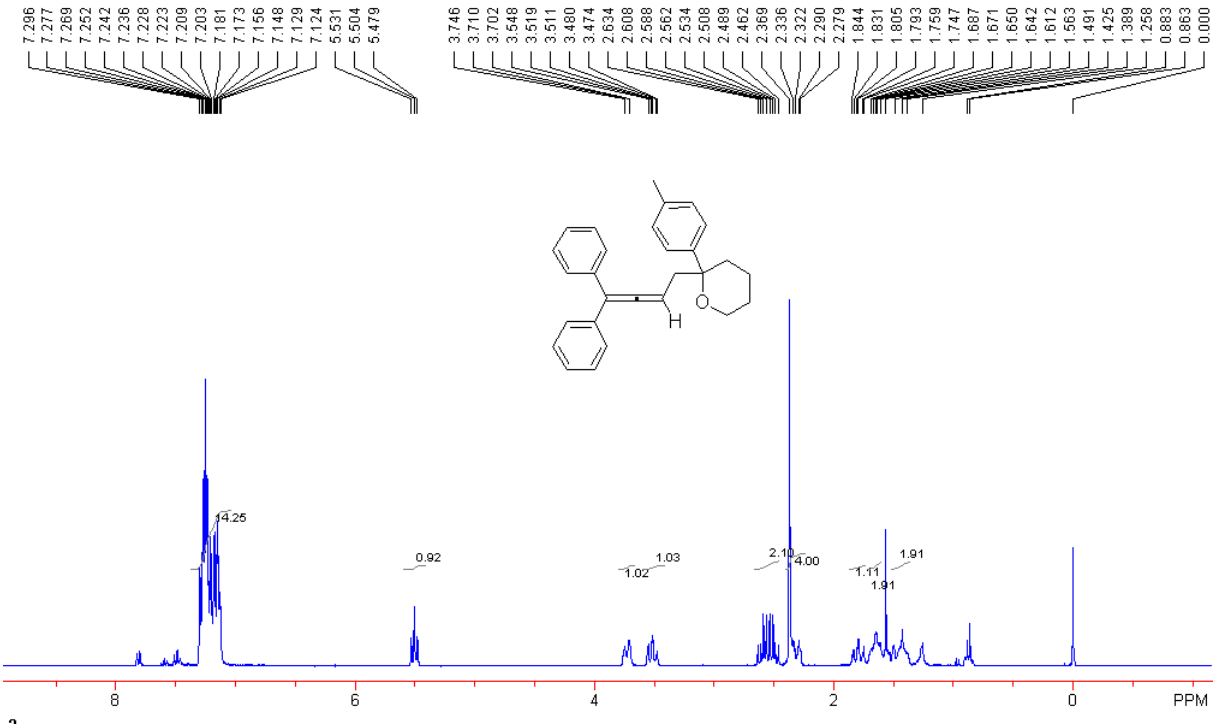


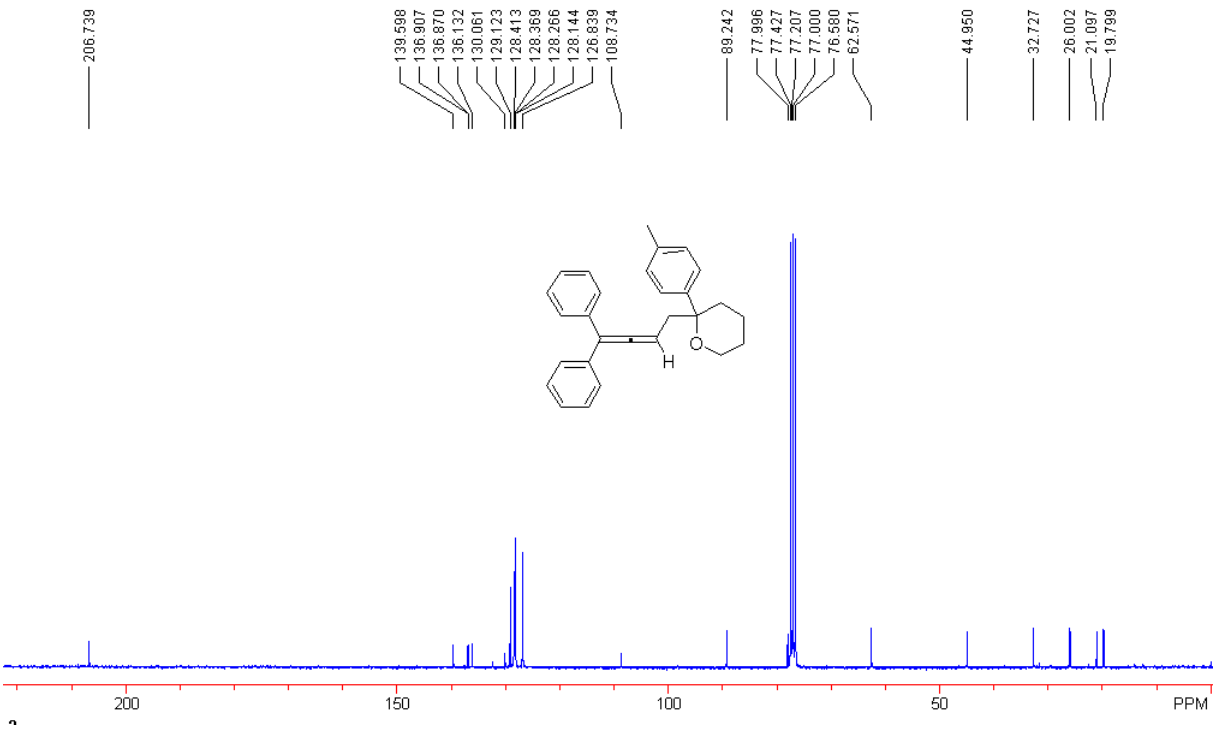


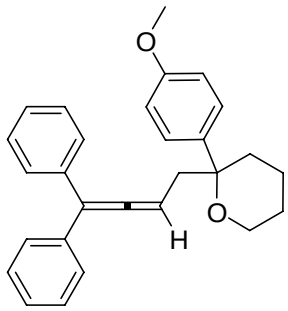
2-(4,4-diphenylbuta-2,3-dienyl)-2-p-tolyl-tetrahydro-2H-pyran.

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.38-1.45 (m, 2H), 1.61-1.69 (m, 1H),

1.80 (dt, *J* = 3.3 Hz, *J* = 13.5 Hz, 1H), 2.31 (dd, *J* = 3.3 Hz, *J* = 13.5 Hz, 1H), 2.37 (s, 3H, CH_3), 2.50 (dd, *J* = 8.1 Hz, *J* = 13.8 Hz, 1H), 2.60 (dd, *J* = 8.1 Hz, *J* = 13.8 Hz, 1H), 3.52 (dt, *J* = 2.4 Hz, *J* = 11.1 Hz, 1H), 3.73 (d, *J* = 10.8 Hz, 1H), 5.50 (t, *J* = 7.8 Hz, 1H), 7.12-7.30 (m, 14H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.8, 21.1, 26.0, 32.7, 45.0, 62.6, 78.0, 89.2, 108.7, 126.8, 128.1, 128.3, 128.37, 128.41, 129.1, 130.1, 136.1, 136.87, 136.91, 139.6, 206.7. IR (CH_2Cl_2) ν 3055, 2939, 2882, 1944, 1715, 1662, 1598, 1511, 1492, 1443, 1276, 1177, 1081, 1042, 814, 768, 697, 638 cm^{-1}. MS (%) m/e 380 (M^+, 10), 307 (17), 282 (7), 262 (5), 229 (6), 175 (100), 119 (63), 91 (22). HRMS (EI) for $C_{28}H_{28}O$: 380.2140; Found: 380.2145.

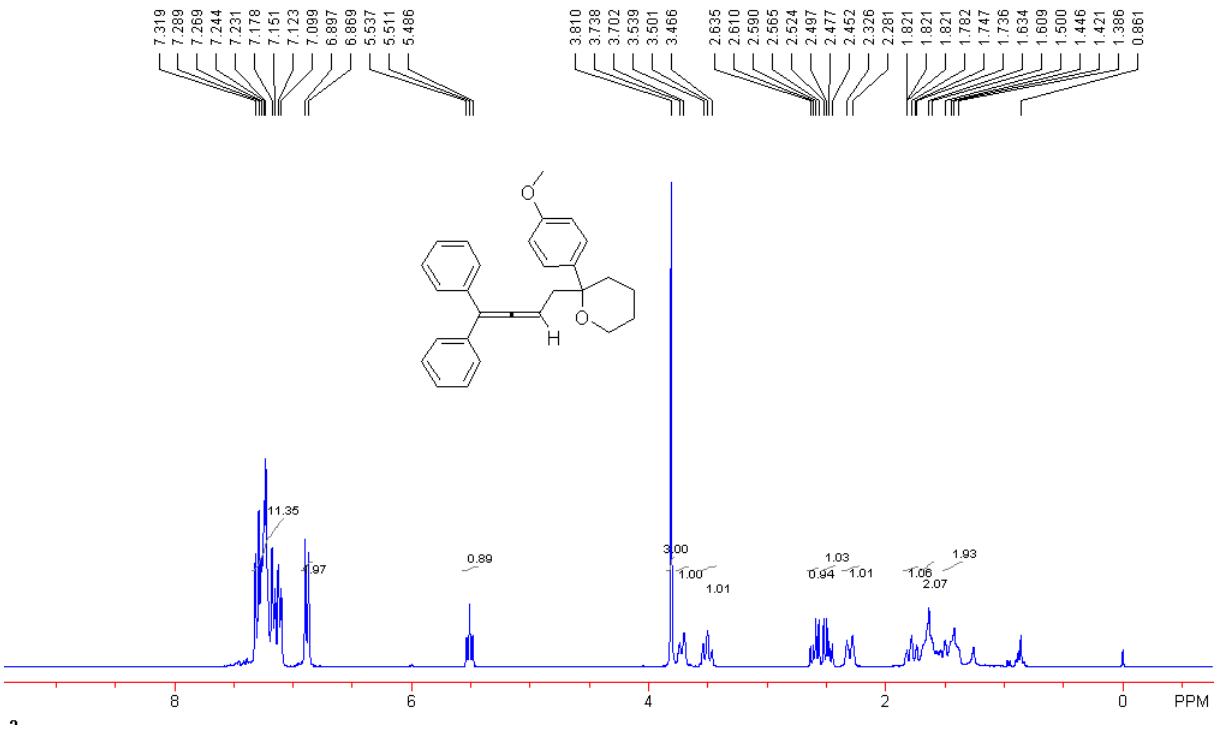






2-(4,4-diphenylbuta-2,3-dienyl)-2-(4-methoxyphenyl)-tetrahydro-2H-pyran.

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.40-1.50 (m, 2H), 1.61-1.63 (m, 2H), 1.76 (t, *J* = 13.5 Hz, 1H), 2.30 (d, *J* = 13.5 Hz, 1H), 2.49 (dd, *J* = 7.5 Hz, *J* = 13.5 Hz, 1H), 2.60 (dd, *J* = 7.5 Hz, *J* = 13.5 Hz, 1H), 3.50 (t, *J* = 11.4 Hz, 1H), 3.72 (d, *J* = 10.8 Hz, 1H), 3.81 (s, 3H, OCH_3), 5.50 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 2H, Ar), 7.11 (d, *J* = 7.2 Hz, 2H, Ar), 7.16 (d, *J* = 8.1 Hz, 2H, Ar), 7.23-7.32 (m, 8H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.7, 26.0, 32.8, 45.1, 55.1, 62.4, 77.8, 89.2, 108.7, 113.7, 126.8, 128.09, 128.12, 128.3, 128.4, 134.5, 136.77, 136.80, 158.2, 206.7. IR (CH_2Cl_2) ν 3056, 2999, 2938, 2862, 1943, 1714, 1608, 1510, 1492, 1442, 1359, 1298, 1247, 1219, 1177, 1080, 1040, 831, 769, 698, 636, 551 cm^{-1}. MS (%) m/e 396 (M^+, 49), 323 (5), 298 (10), 229 (8), 191 (100), 167 (5), 135 (72), 77 (10). HRMS (EI) for $C_{28}H_{28}O_2$: 396.2089; Found: 396.2093.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5.486
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3.738
3.702
3.539
3.501
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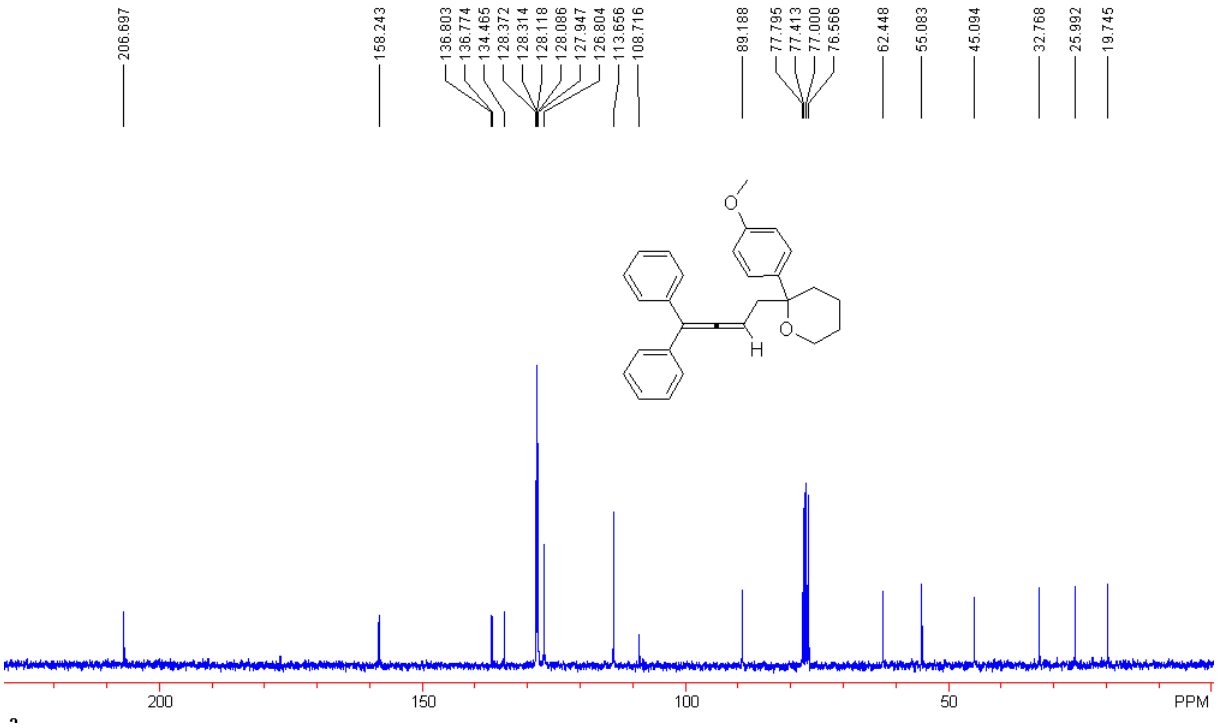
PPM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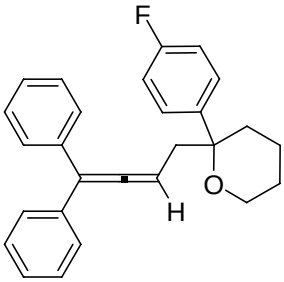
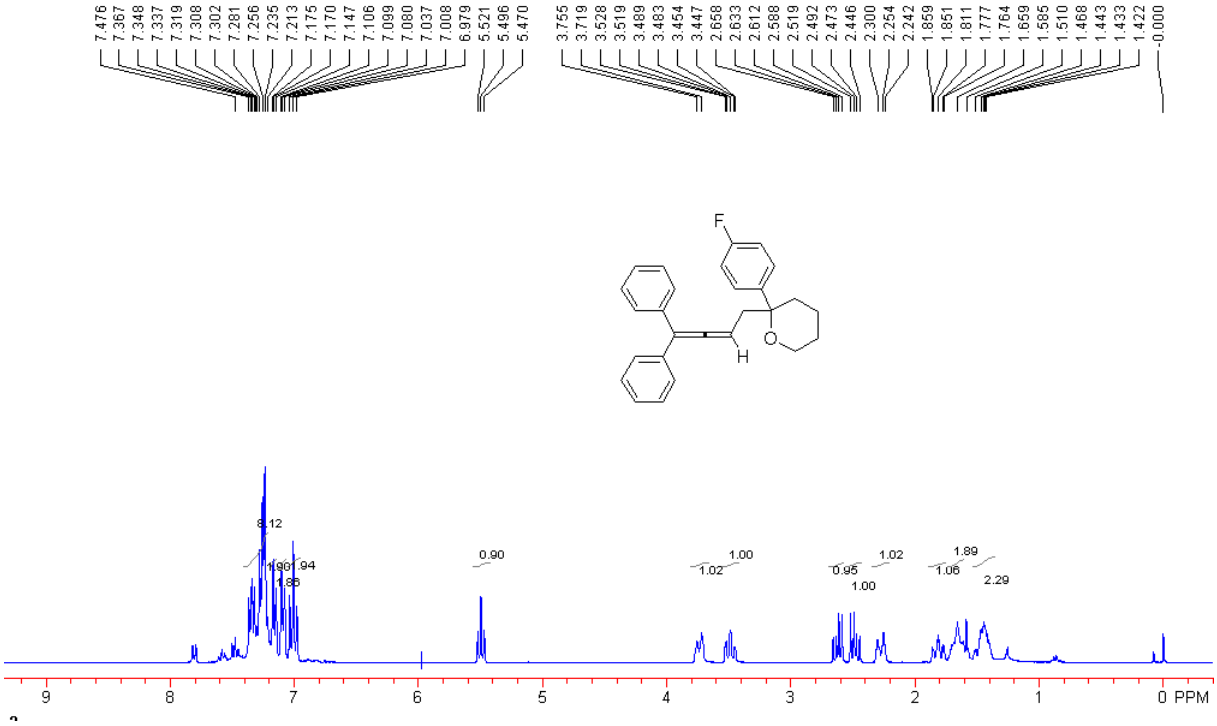
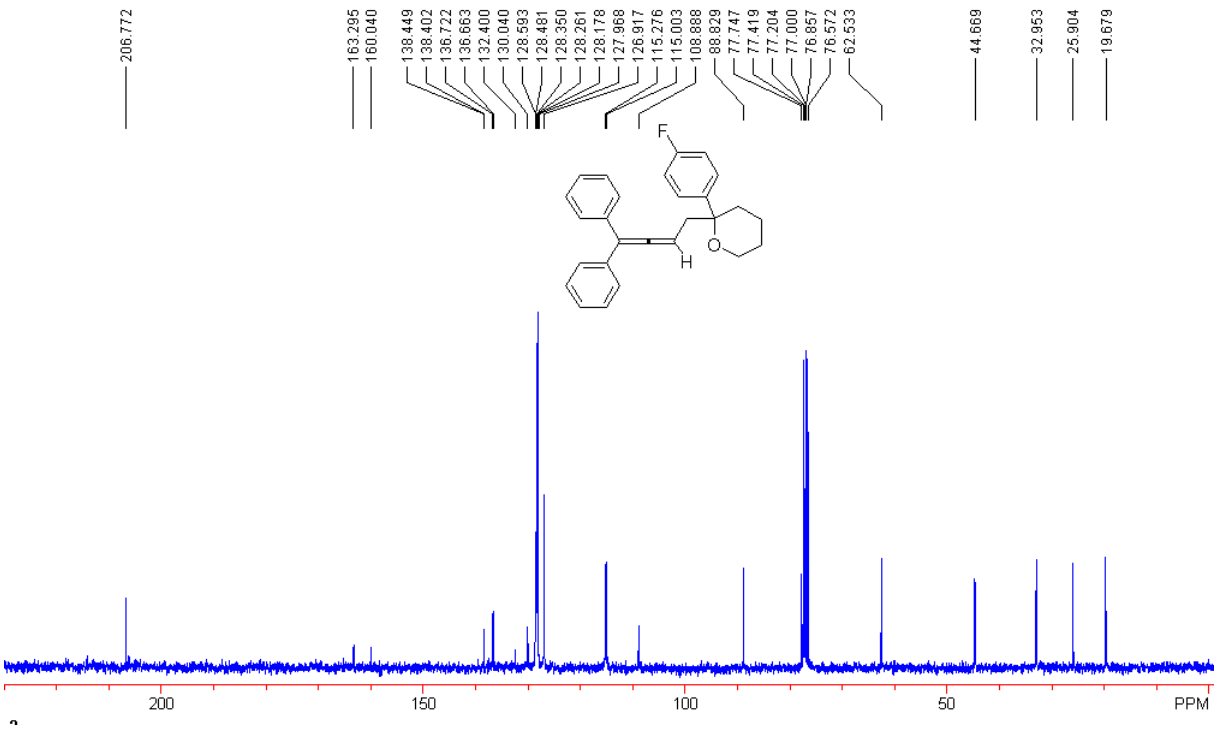
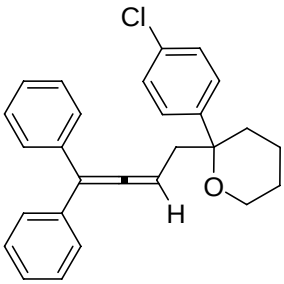

F
O
H

2-(4,4-diphenylbuta-2,3-dienyl)-2-(4-fluorophenyl)-tetrahydro-2H-pyran.

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.41-1.44 (m, 2H), 1.59-1.70 (m, 2H), 1.81 (dt, *J* = 3.6 Hz, *J* = 13.5 Hz, 1H), 2.28 (dd, *J* = 3.6 Hz, *J* = 13.5 Hz, 1H), 2.48 (dd, *J* = 8.1 Hz, *J* = 13.8 Hz, 1H), 2.62 (dd, *J* = 8.1 Hz, *J* = 13.8 Hz, 1H), 3.48 (dt, *J* = 2.1 Hz, *J* = 10.8 Hz, 1H), 3.73 (d, *J* = 10.8 Hz, 1H), 5.50 (t, *J* = 7.8 Hz, 1H), 6.98-7.04 (m, 2H, Ar), 7.10 (dd, *J* = 2.1 Hz, *J* = 7.8 Hz, 2H, Ar), 7.16 (dd, *J* = 1.5 Hz, *J* = 6.9 Hz, 2H, Ar), 7.21-7.37 (m, 8H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.7, 25.9, 33.0, 44.7, 62.5, 77.7, 88.8, 115.1 (d, J_{C-F} = 20.5 Hz), 126.9, 128.0, 128.2, 128.3, 128.4, 128.5 (d, J_{C-F} = 8.4 Hz), 130.0, 132.4, 136.66, 136.72, 138.4 (d, J_{C-F} = 3.5 Hz), 161.7 (d, J_{C-F} = 244.1 Hz), 206.8. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$) δ -122.0. IR (CH_2Cl_2) ν 3057, 2940, 2863, 1944, 1714, 1602, 1507, 1493, 1443, 1277, 1224, 1081, 1043, 835, 768, 735, 698, 638, 545 cm^{-1}. MS (%) m/e 384 (M^+, 23), 311 (5), 262 (14), 179 (100), 123 (74), 105 (82), 77 (41), 41 (88). HRMS (EI) for $C_{27}H_{25}OF$: 384.1889; Found: 384.1886.

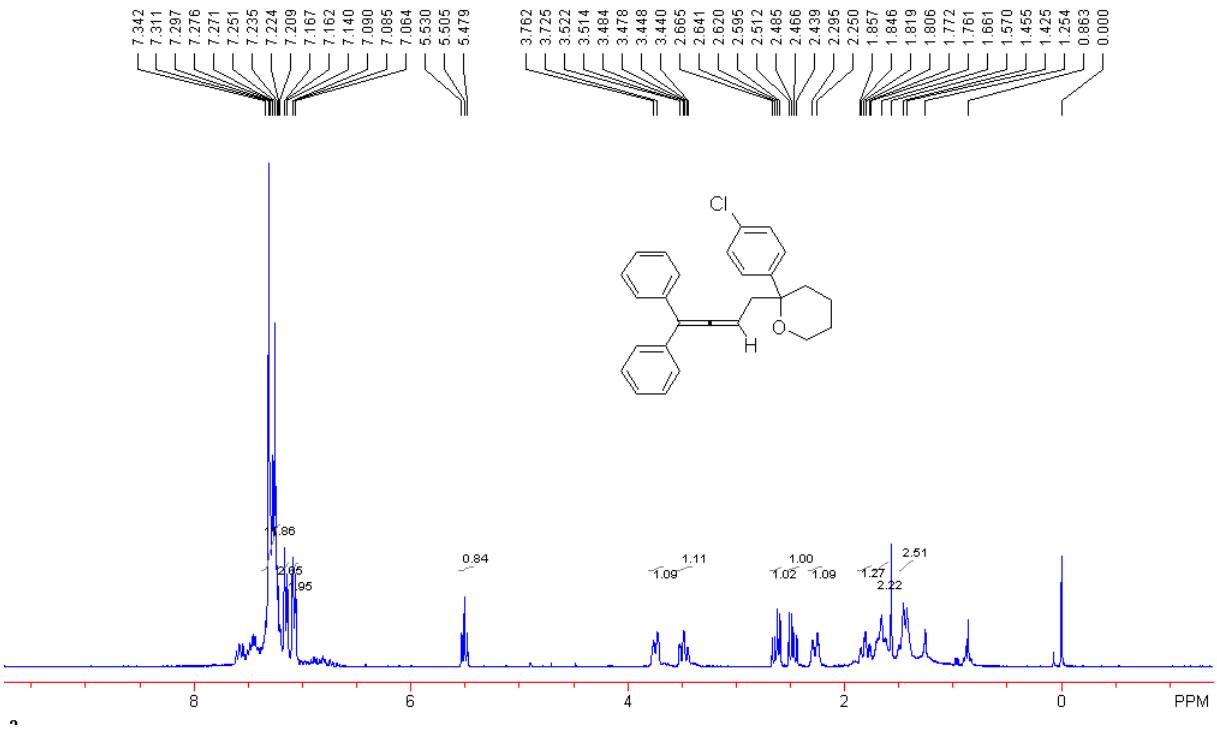






2-(4-chlorophenyl)-2-(4,4-diphenylbuta-2,3-dienyl)-tetrahydro-2H-pyran.

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.43-1.46 (m, 2H), 1.57-1.71 (m, 2H), 1.81 (dt, *J* = 3.3 Hz, *J* = 13.5 Hz, 1H), 2.28 (dd, *J* = 3.6 Hz, *J* = 13.5 Hz, 1H), 2.48 (dd, *J* = 8.1 Hz, *J* = 13.8 Hz, 1H), 2.63 (dd, *J* = 8.1 Hz, *J* = 13.8 Hz, 1H), 3.48 (dt, *J* = 2.4 Hz, *J* = 11.1 Hz, 1H), 3.74 (d, *J* = 11.1 Hz, 1H), 5.50 (t, *J* = 7.8 Hz, 1H), 7.07 (dd, *J* = 1.5 Hz, *J* = 7.8 Hz, 2H, Ar), 7.15 (dd, *J* = 1.5 Hz, *J* = 7.8 Hz, 2H, Ar), 7.21-7.34 (m, 10H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.8, 22.7, 26.0, 31.6, 33.0, 44.6, 62.7, 78.0, 88.9, 107.1, 126.77, 126.83, 128.4, 128.8, 129.5, 129.6, 131.3, 132.7, 132.8, 134.9, 135.0, 142.6, 206.6. IR (CH_2Cl_2) ν 3056, 3028, 2939, 2863, 2381, 1715, 1597, 1491, 1443, 1399, 1354, 1290, 1178, 1081, 1042, 1013, 829, 739, 699 cm^{-1}. MS (%) m/e 400 (M^+, 13), 327 (4), 277 (6), 262 (23), 197 (33), 195 (100), 139 (59), 111 (11). HRMS (EI) for $C_{27}H_{25}OCl$: 400.1594; Found: 400.1588.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7.140
7.090
7.085
7.064
5.530
5.505
5.479
3.762
3.725
3.522
3.514
3.484
3.478
3.448
3.440
2.665
2.641
2.620
2.595
2.512
2.485
2.466
2.439
2.295
2.250
1.857
1.846
1.819
1.806
1.772
1.761
1.661
1.570
1.455
1.425
1.254
0.863
0.000
Cl
O
H
1.86
2.05
1.95
0.84
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1.02
1.00
1.09
1.27
2.22
2.51
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2
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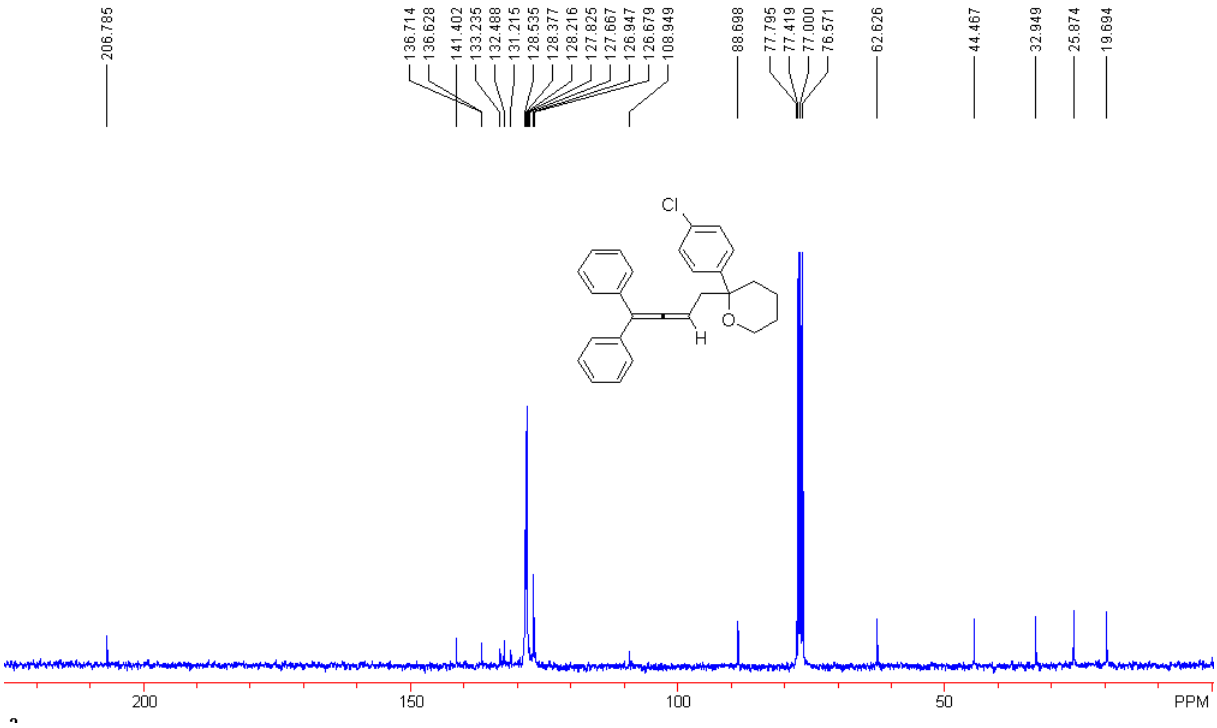
PPM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128.377
128.216
127.825
127.667
126.947
126.679
108.949
88.698
77.795
77.419
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25.874
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Cl
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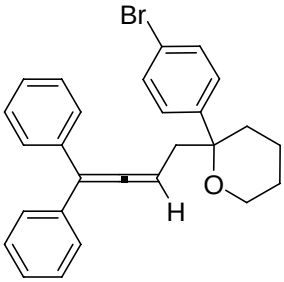
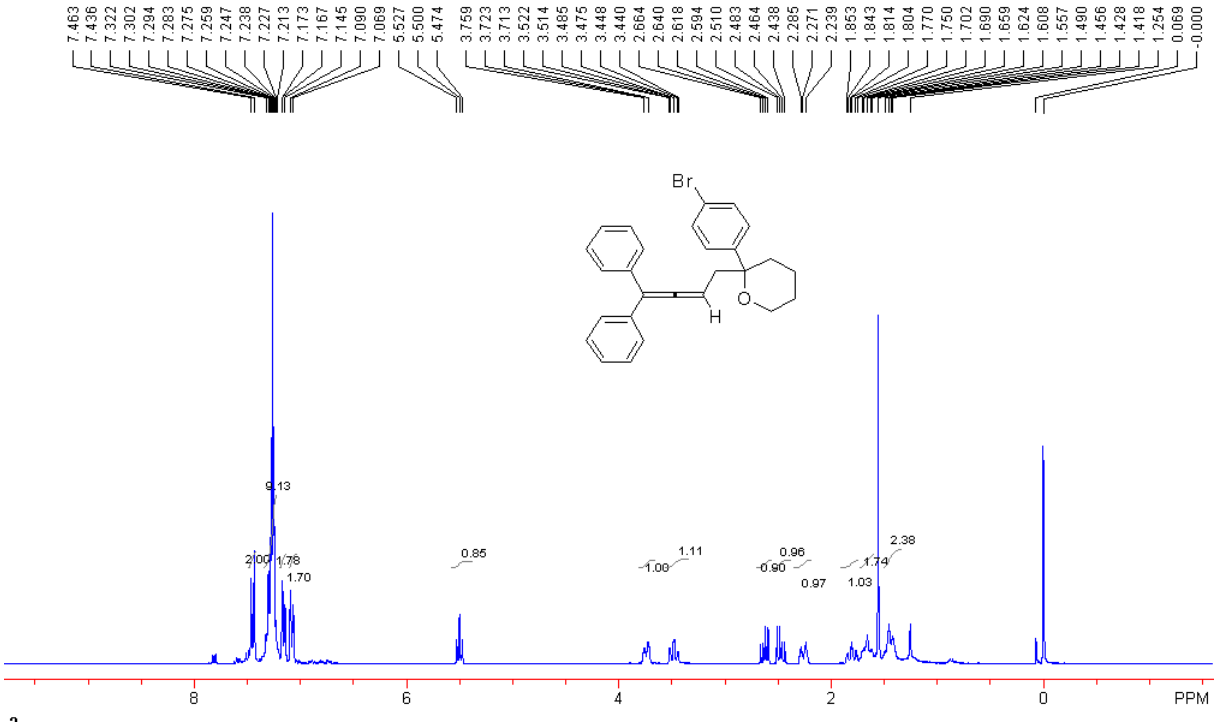
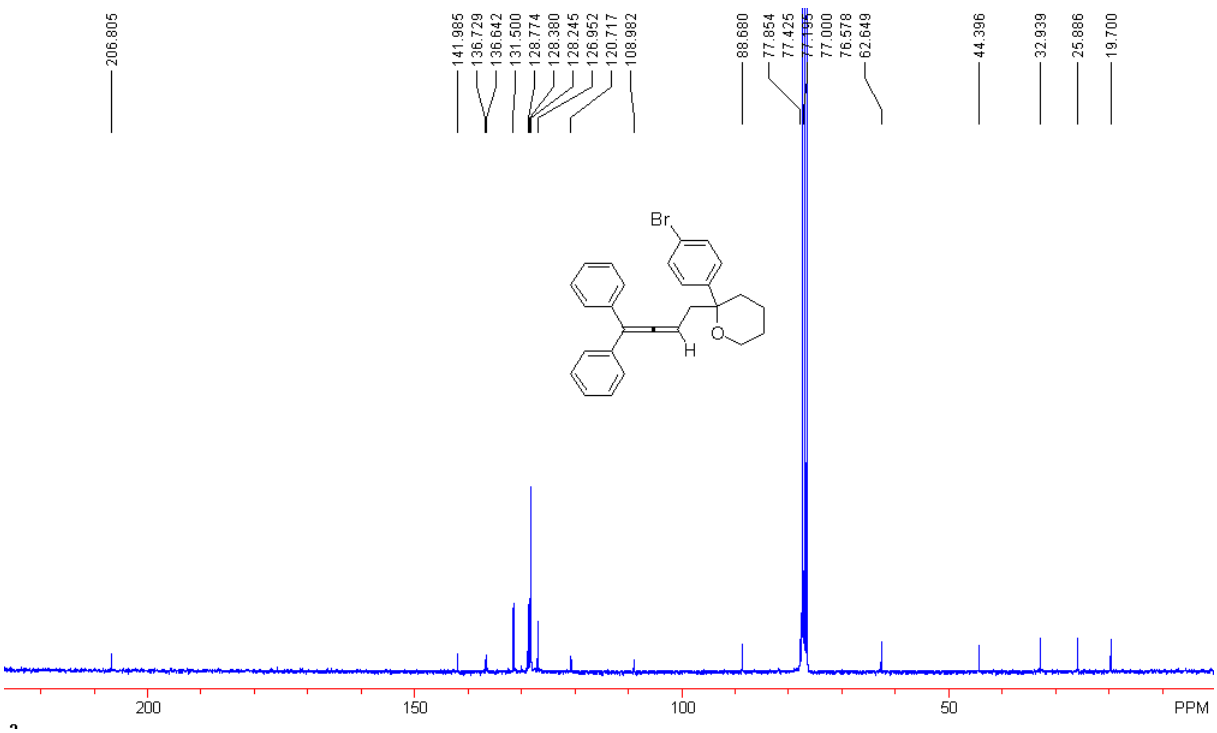
H
200
150
100
50
PPM

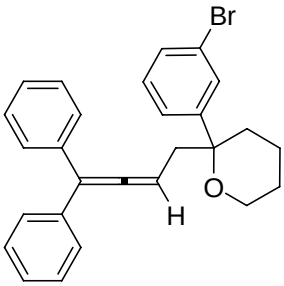

Br
O
H

2-(4-bromophenyl)-2-(4,4-diphenylbuta-2,3-dienyl)-tetrahydro-2H-pyran.

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.43-1.49 (m, 2H), 1.61-1.75 (m, 2H), 1.81 (dt, *J* = 6.0 Hz, *J* = 16.2 Hz, 1H), 2.25 (dd, *J* = 6.9 Hz, *J* = 9.6 Hz, 1H), 2.47 (dd, *J* = 7.8 Hz, *J* = 13.5 Hz, 1H), 2.63 (dd, *J* = 7.8 Hz, *J* = 13.5 Hz, 1H), 3.48 (dt, *J* = 2.4 Hz, *J* = 10.5 Hz, 1H), 3.74 (dd, *J* = 3.3 Hz, *J* = 13.8 Hz, 1H), 5.50 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 6.3 Hz, 2H, Ar), 7.15 (d, *J* = 6.9 Hz, 2H, Ar), 7.21-7.32 (m, 8H, Ar), 7.45 (d, *J* = 8.1 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.7, 25.9, 32.9, 44.4, 62.6, 77.9, 88.7, 109.0, 120.7, 127.0, 128.2, 128.4, 128.8, 131.5, 136.6, 136.7, 142.0, 206.8. IR (CH_2Cl_2) ν 3057, 2939, 2862, 1944, 1597, 1491, 1452, 1080, 1044, 1009, 768, 696 cm^{-1}. MS (%) m/e 446 (M^+, 16), 446 (M^+, 16), 373 (5), 277 (10), 262 (22), 239 (100), 203 (14), 183 (65), 167 (12). HRMS (EI) for $C_{27}H_{25}OBr$: 444.1089; Found: 404.1084.

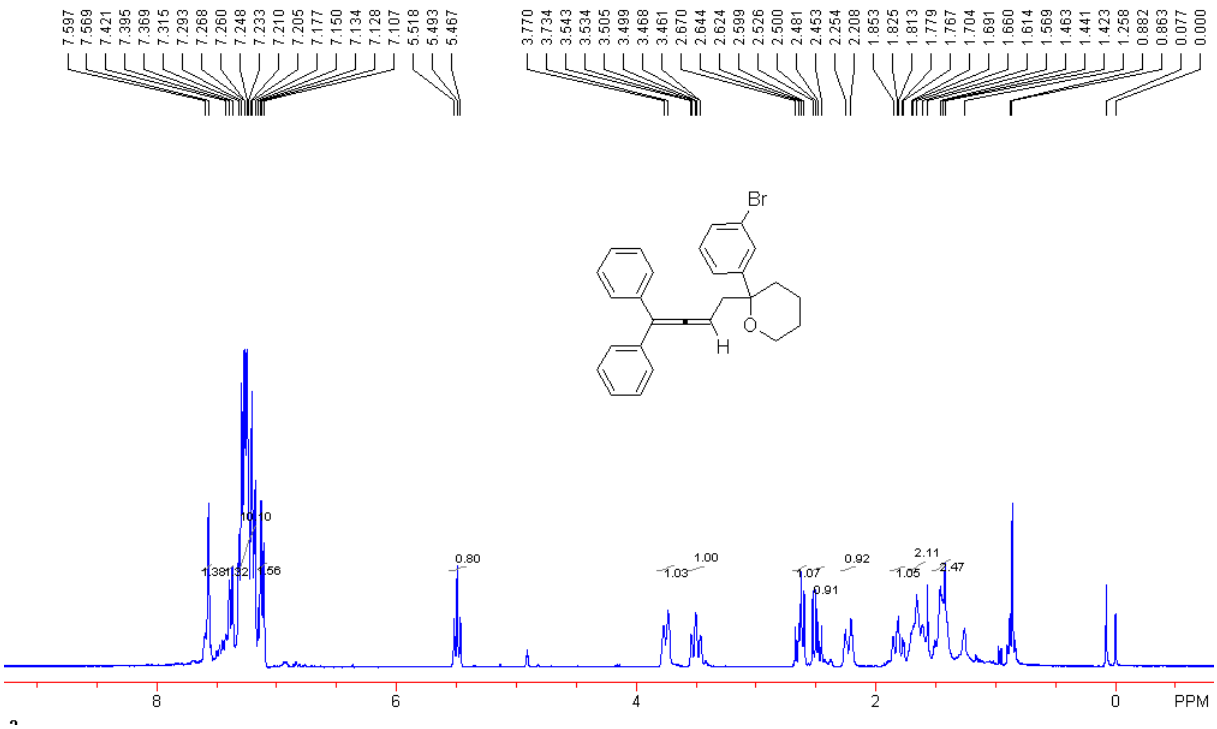






2-(3-bromophenyl)-2-(4,4-diphenylbuta-2,3-dienyl)-tetrahydro-2H-pyran.

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.43-1.47 (m, 2H), 1.61-1.71 (m, 2H), 1.83 (dt, *J* = 3.3 Hz, *J* = 10.8 Hz, 1H), 2.25 (dt, *J* = 3.6 Hz, *J* = 13.2 Hz, 1H), 2.49 (dd, *J* = 8.4 Hz, *J* = 13.5 Hz, 1H), 2.64 (dd, *J* = 8.4 Hz, *J* = 13.5 Hz, 1H), 3.51 (dt, *J* = 3.0 Hz, *J* = 10.8 Hz, 1H), 3.75 (d, *J* = 10.8 Hz, 1H), 5.49 (t, *J* = 7.8 Hz, 1H), 7.11-7.15 (m, 2H, Ar), 7.18-7.32 (m, 10H, Ar), 7.38 (d, *J* = 7.8 Hz, 1H, Ar), 7.56-7.57 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.7, 25.8, 32.9, 44.2, 62.7, 77.8, 88.7, 109.0, 122.8, 125.5, 126.92, 126.94, 128.2, 128.4, 129.8, 130.0, 136.68, 136.73, 145.7, 206.8. IR (CH_2Cl_2) ν 3060, 2937, 2862, 1660, 1598, 1578, 1447, 1317, 1277, 1075, 1043, 941, 807, 700, 638 cm^{-1}. MS (%) m/e 446 (M^+, 7), 444 (M^+, 7), 371 (6), 277 (8), 241 (100), 239 (100), 203 (9), 185 (52), 183 (60). HRMS (EI) for $C_{27}H_{25}OBr$: 444.1089; Found: 404.1093.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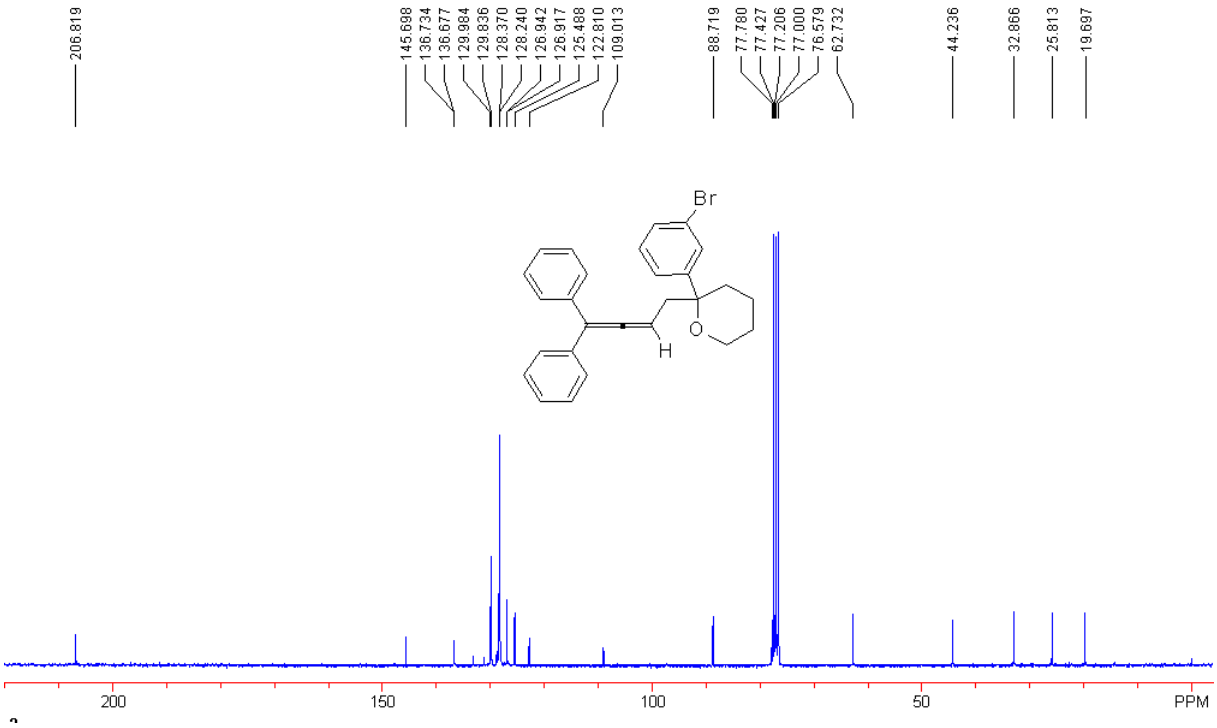
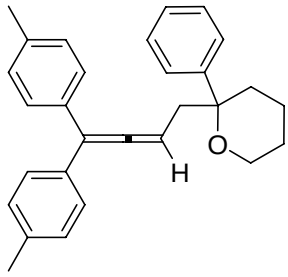
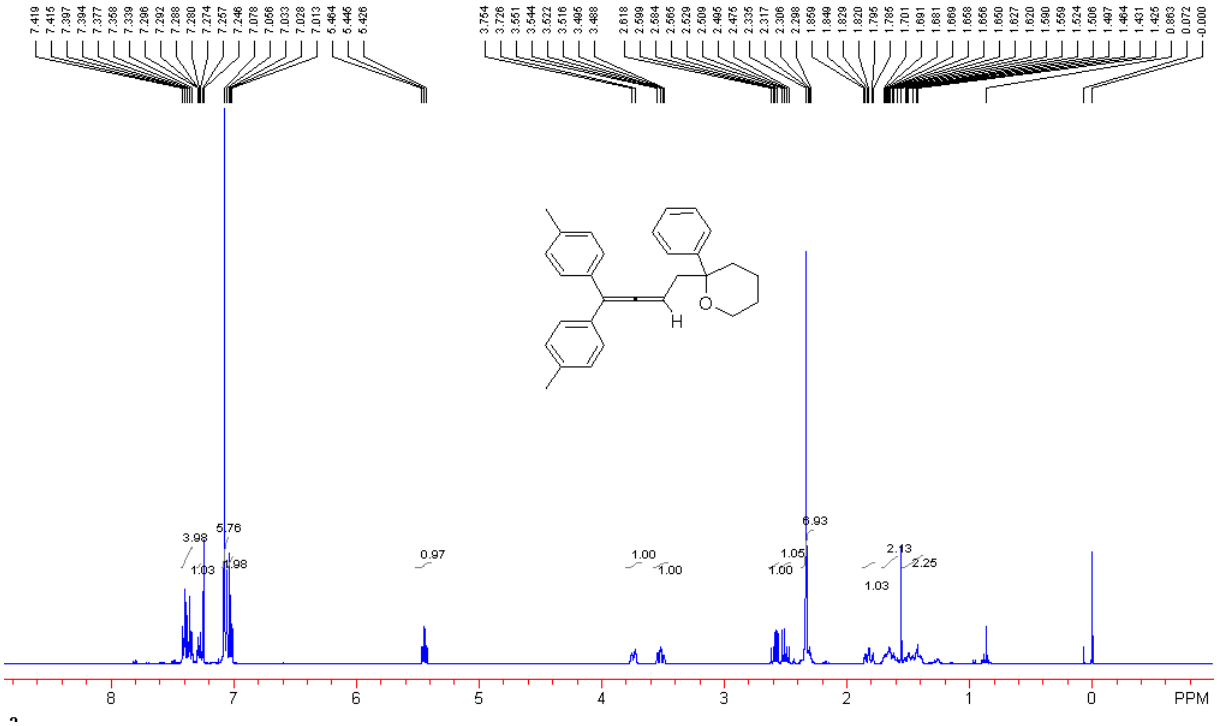
3.770 3.734 3.543 3.534 3.505 3.499 3.468 3.461 2.670 2.644 2.624 2.599 2.526 2.500 2.481 2.453 2.254 2.208 1.853 1.825 1.813 1.779 1.767 1.704 1.691 1.660 1.614 1.569 1.463 1.441 1.423 1.258 0.882 0.863 0.077 0.000
Br
O
H
0.80
1.03
1.00
1.07
0.91
0.92
1.05
2.11
2.47
8
6
4
2
0
PPM

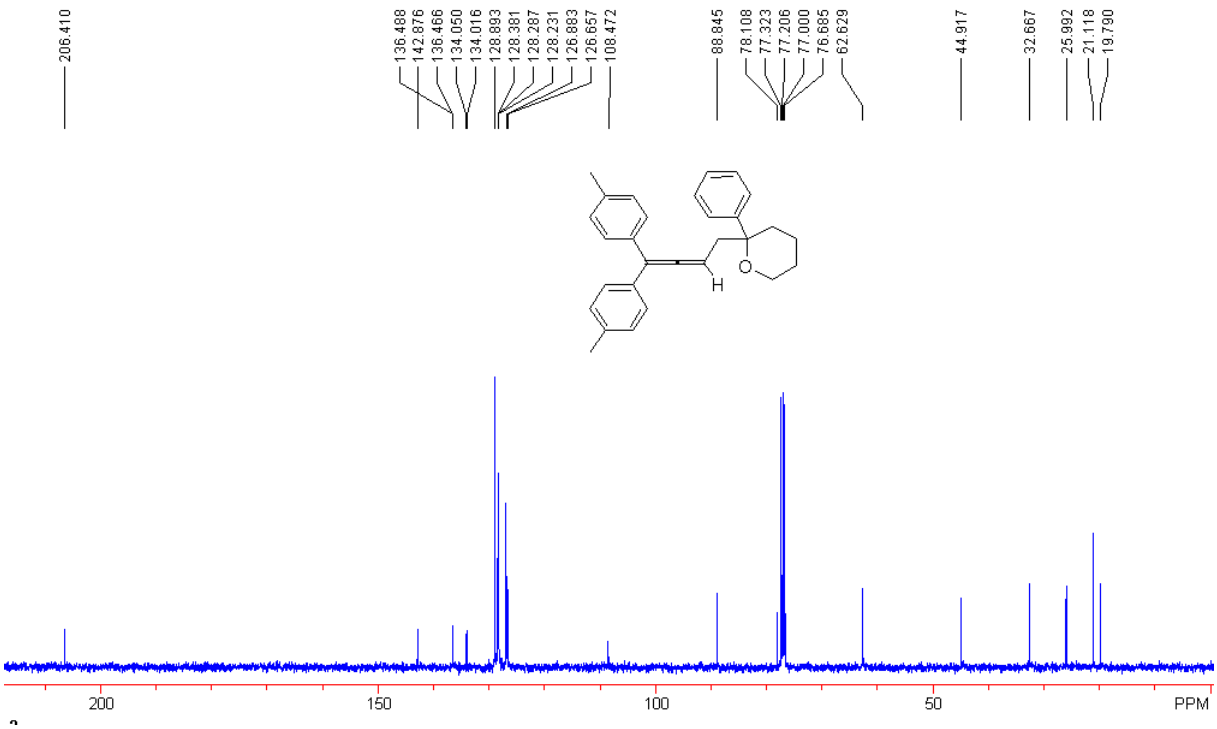

206.819
145.698 136.734 136.677 129.984 129.836 128.370 128.240 126.942 126.917 125.488 122.810 109.013
88.719
77.780 77.427 77.206 77.000 76.579 62.732
44.236
32.866
25.813
19.697
Br
O
H
200
150
100
50
PPM

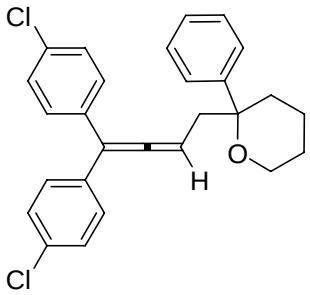

O
H

2-(4,4-dip-tolylbuta-2,3-dienyl)-2-phenyl-tetrahydro-2H-pyran.

A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.43-1.59 (m, 2H), 1.62-1.70 (m, 2H), 1.82 (dt, *J* = 4.0 Hz, *J* = 12.0 Hz, 1H), 2.31 (t, *J* = 4.0 Hz, 1H), 2.34 (s, 6H, $2CH_3$), 2.50 (dd, *J* = 8.0 Hz, *J* = 14.4 Hz, 1H), 2.59 (dd, *J* = 8.0 Hz, *J* = 14.4 Hz, 1H), 3.52 (dt, *J* = 2.8 Hz, *J* = 11.2 Hz, 1H), 3.74 (d, *J* = 11.2 Hz, 1H), 5.45 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H, Ar), 7.07 (d, *J* = 8.0 Hz, 6H, Ar), 7.26-7.30 (m, 1H, Ar), 7.34-7.42 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.8, 21.1, 26.0, 32.7, 44.9, 62.6, 78.1, 88.8, 108.5, 126.7, 126.9, 128.2, 128.3, 128.4, 128.9, 134.0, 134.1, 136.47, 136.49, 142.9, 206.4. IR (CH_2Cl_2) ν 3023, 2938, 2863, 1715, 1659, 1608, 1510, 1445, 1360, 1218, 1081, 1041, 820, 764, 702 cm^{-1}. MS (%) m/e 394 (M^+, 27), 321 (32), 296 (8), 229 (7), 195 (18), 161 (100), 119 (19), 105 (80), 77 (21). HRMS (EI) for $C_{29}H_{30}O$: 394.2297; Found: 394.2295.







2-(4,4-bis(4-chlorophenyl)buta-2,3-dienyl)-2-phenyl-tetrahydro-2H-pyran.

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.46-1.50 (m, 2H), 1.61-1.70 (m, 2H), 1.80 (dt, *J* = 3.3 Hz, *J* = 12.3 Hz, 1H), 2.32 (dd, *J* = 3.6 Hz, *J* = 13.8 Hz, 1H), 2.48 (dd, *J* = 8.1 Hz, *J* = 13.5 Hz, 1H), 2.63 (dd, *J* = 8.1 Hz, *J* = 13.5 Hz, 1H), 3.53 (dt, *J* = 2.7 Hz, *J* = 10.8 Hz, 1H), 3.75 (d, *J* = 10.8 Hz, 1H), 5.55 (t, *J* = 8.1 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H, Ar), 7.06 (d, *J* = 8.4 Hz, 1H, Ar), 7.19-7.26 (m, 4H, Ar), 7.29-7.33 (m, 2H, Ar), 7.37 (d, *J* = 6.6 Hz, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.8, 22.7, 26.0, 31.6, 33.0, 44.6, 62.7, 78.0, 89.9, 107.1, 126.8, 128.4, 128.8, 129.5, 129.6, 131.3, 132.7, 132.8, 134.9, 135.0, 142.6, 206.6. IR (CH_2Cl_2) ν 3058, 3029, 2939, 2864, 1942, 1715, 1664, 1589, 1489, 1445, 1398, 1286, 1218, 1175, 1090, 1041, 1014, 926, 887, 832, 762, 703 cm^{-1}. MS (%) m/e 434 (M^+, 3), 361 (2), 277 (3), 250 (8), 202 (5), 161 (100), 139 (22), 105 (48), 77 (12). HRMS (EI) for $C_{27}H_{24}OCl_2$:

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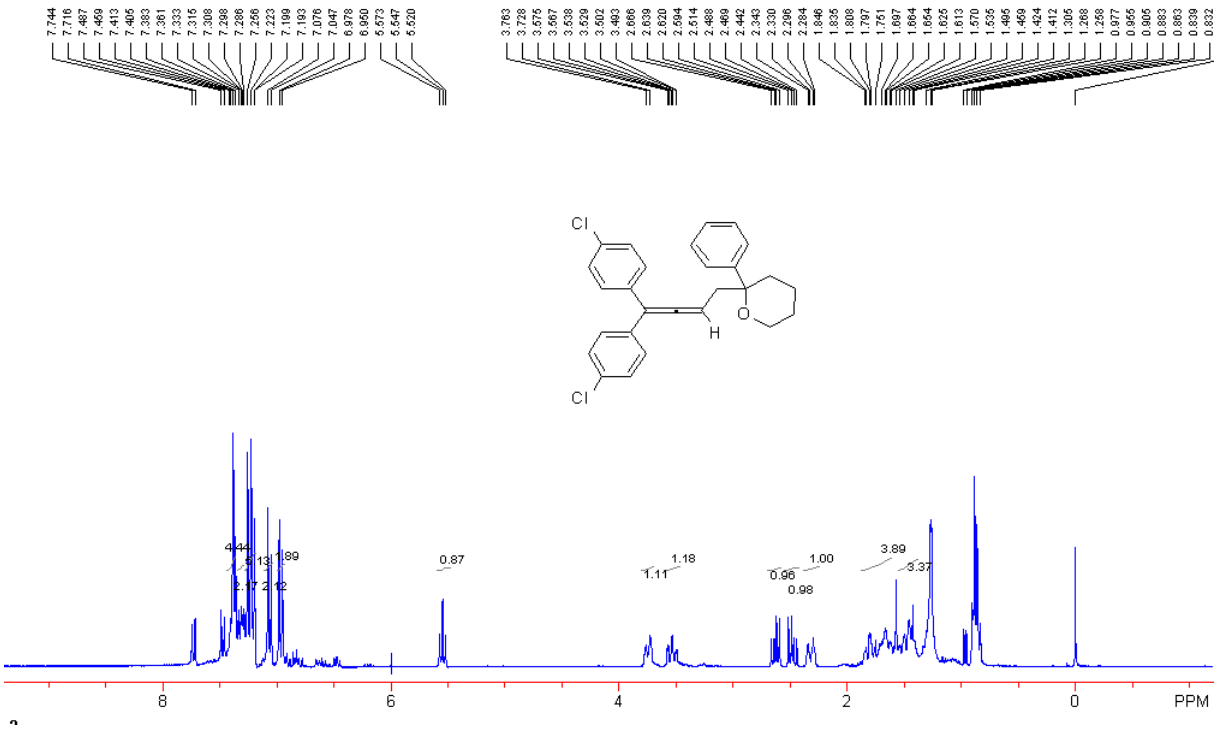
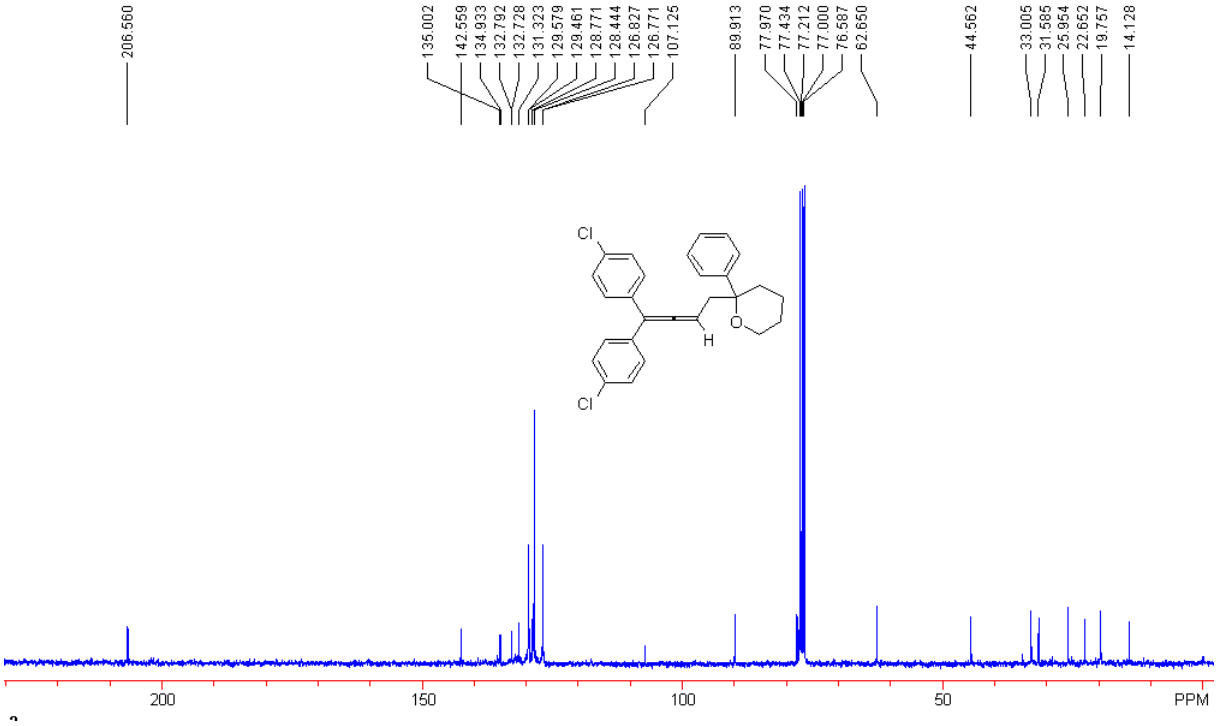
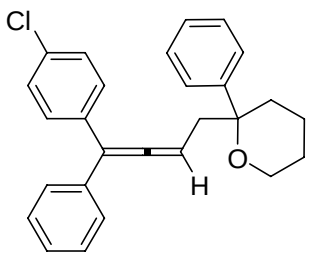
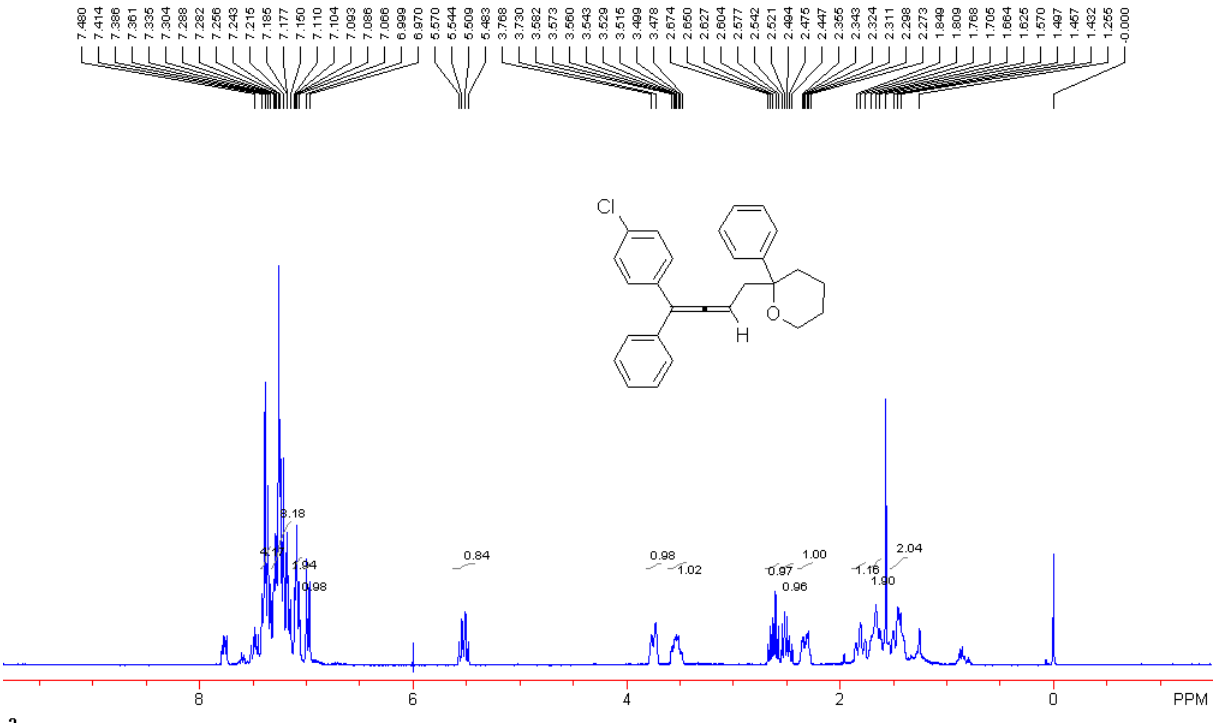


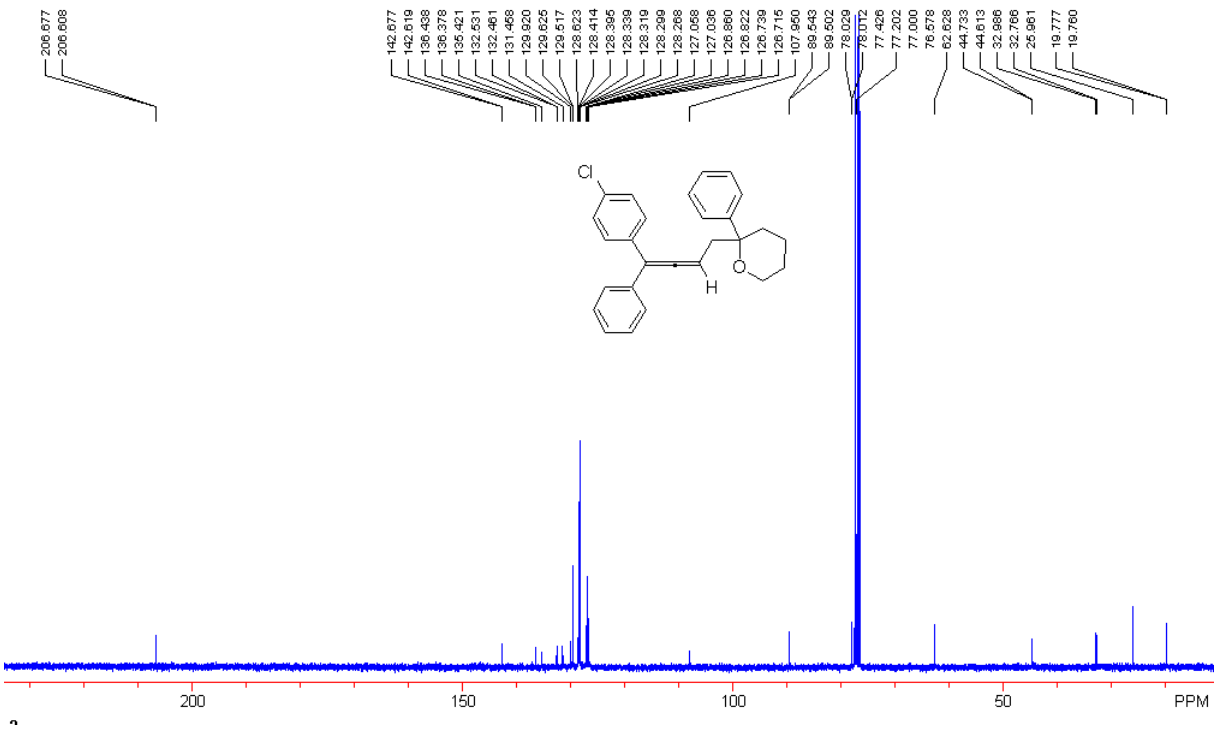




2-(4-(4-chlorophenyl)-4-phenylbuta-2,3-dienyl)-2-phenyl-tetrahydro-2H-pyran.

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.43-1.50 (m, 2H), 1.63-1.66 (m, 2H), 1.80 (t, *J* = 15.0 Hz, 1H), 2.30-2.36 (m, 1H), 2.45-2.67 (m, 2H), 3.48-3.58 (m, 1H), 3.75 (d, *J* = 9.3 Hz, 1H), 5.48-5.57 (m, 1H), 6.99 (d, *J* = 8.7 Hz, 1H, Ar), 7.07-7.11 (m, 2H, Ar), 7.18-7.30 (m, 7H, Ar), 7.34-7.41 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.8, 26.0, 32.8, 33.0, 44.6, 44.7, 62.6, 78.0, 89.51, 89.55, 107.9, 126.7, 126.8, 126.9, 127.1, 128.26, 128.32, 128.4, 128.6, 129.5, 129.6, 129.9, 131.5, 132.46, 132.53, 132.6, 135.37, 135.41, 136.38, 136.44, 142.6, 142.7, 206.6, 206.7. IR (CH_2Cl_2) ν 3058, 2938, 2863, 1945, 1663, 1598, 1489, 1446, 1273, 1082, 1043, 1014, 832, 762, 699 cm^{-1}. MS (%) m/e 400 (M^+, 11), 327 (9), 216 (7), 202 (8), 161 (100), 139 (7), 105 (64), 91 (6), 77 (19). HRMS (EI) for $C_{27}H_{25}OCl$: 400.1594; Found: 400.1591.

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128.299
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62.628
44.733
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Cl
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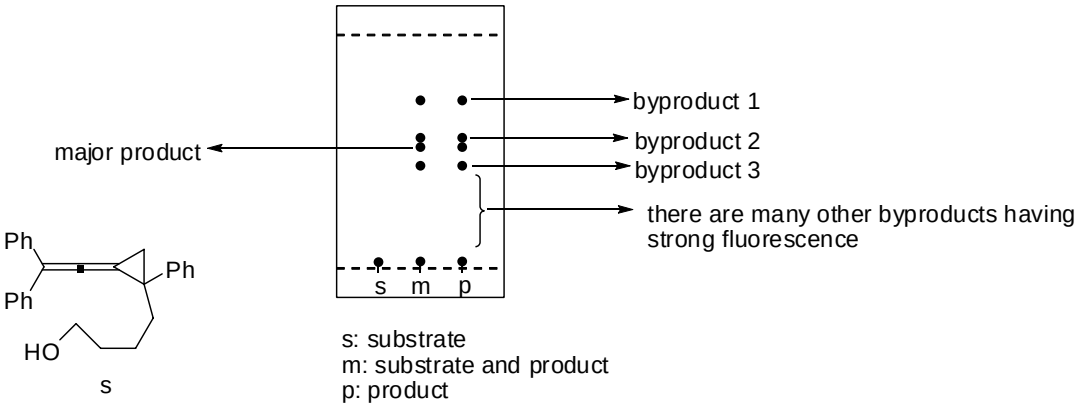
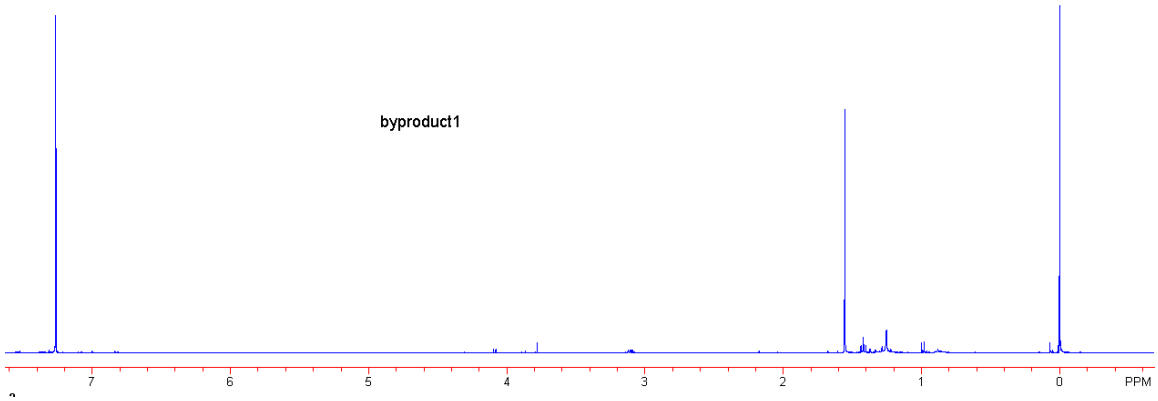
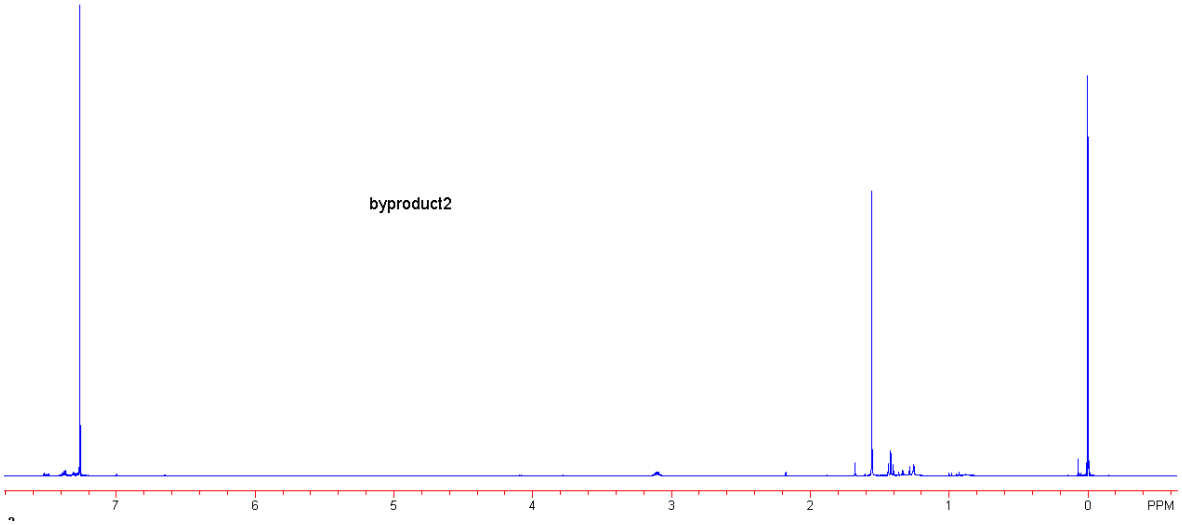


eluent: Petroleum ether:ethyl acetate = 40:1, twice

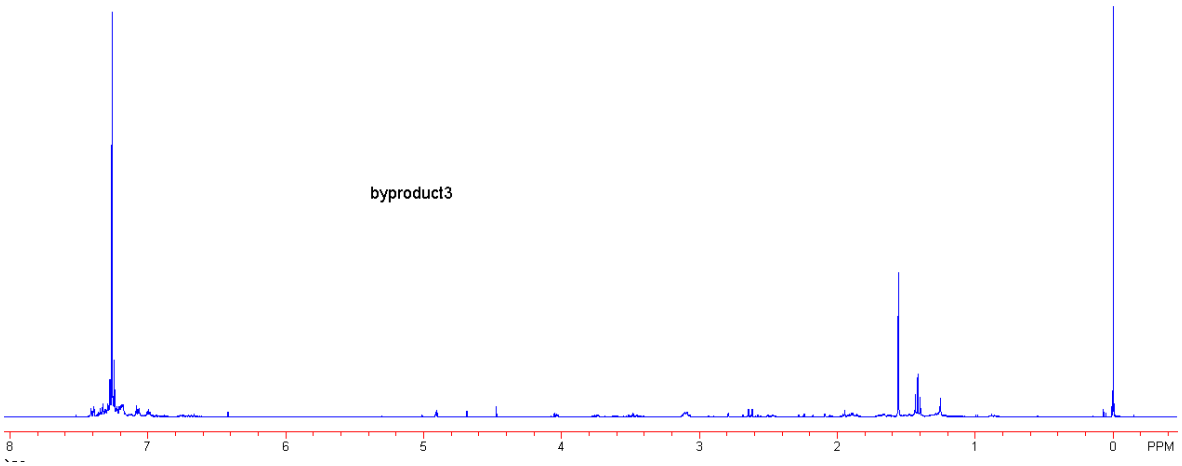
^{1}H NMR spectrum of byproduct 1



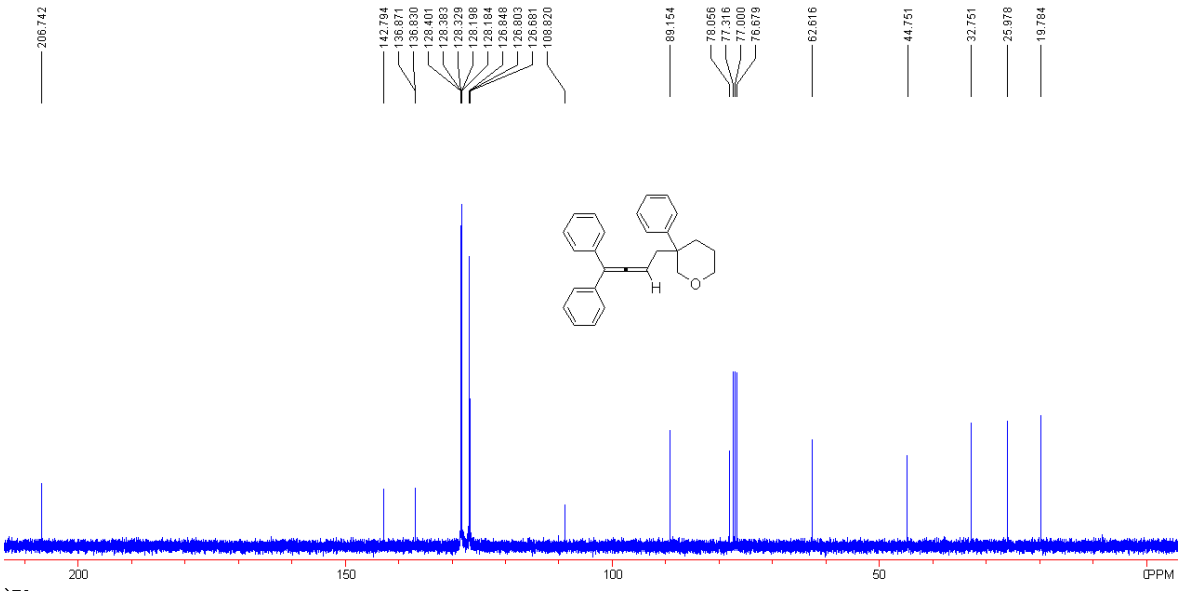
^{1}H NMR spectrum of byproduct 2



^{1}H NMR spectrum of byproduct 3



^{13}C NMR spectrum of the major product: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128.184
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126.803
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89.154
78.056
77.316
77.000
76.679
62.616
44.751
32.751
25.978
19.784
H
O
200
150
100
50
0PPM

References

(1) (a) Isagawa, K.; Mizuno, K.; Sugita, H.; Otsuji, Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2283-2285. (b) Li, W.; Shi, M. *J. Org. Chem.* **2009**, *74*, 856-860.

(2) Imai, M.; Tanaka, M.; Tanaka, K.; Yamamoto, Y.; Imai-Ogata, N.; Shimowatari, M.; Nagumo, S.; Kawahara, N.; Suemune, H. *J. Org. Chem.* **2004**, *69*, 1144-1150.