

Synthesis of *Tri*-substituted Allyl Alcohols *via* Copper/Iron co-Catalyzed Cascade Perfluoroalkylation/Rearrangement of Aryl Propynyl Ethers

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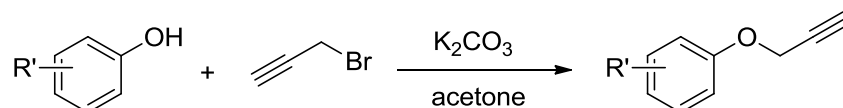
Table of Contents		
I	General Remarks	S1
II	Preparation of Starting Materials	S1
III	Preparation of products 3 and 4.	S2
IV	Deuteration labelling experiment	S2-3
V	X-ray Crystal Diffraction Data for 3ah and 5a	S4-S7
VI	Date of products 3, 4, 5, 6, 7 and 8	S8-S28
VII	¹ H NMR, ¹³ C NMR and ¹⁹ F NMR spectra of compound 3, 4, 5, 6, 7 and 8	S28-S122

I. General Remarks.

Column chromatography was carried out on silica gel. Unless noted ^1H NMR spectra were recorded on 400 MHz in CDCl_3 , ^{13}C NMR spectra were recorded on 100 MHz in CDCl_3 , ^{19}F NMR spectra were recorded on 376 MHz in CDCl_3 . IR spectra were recorded on an FT-IR spectrometer and only major peaks are reported in cm^{-1} . Melting points were determined on a microscopic apparatus and were uncorrected. All new products were further characterized by HRMS (high resolution mass spectra), high resolution mass spectrometry (HRMS) spectra was obtained on a micrOTOF-Q instrument equipped with an ESI source; copies of their ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra are provided. Iodoperfluoroalkanes, FeBr_2 , FeCl_2 , $\text{Fe}(\text{acac})_2$, $\text{Fe}(\text{acac})_3$, $\text{Cu}(\text{OTf})_2$, CuBr , CuI , $\text{Cu}(\text{acac})_2$, CuBr_2 , AcOH and DCM (dry) were purchased from Sigma-Aldrich. All reagents or catalysts were directly used from purchased without further purification.

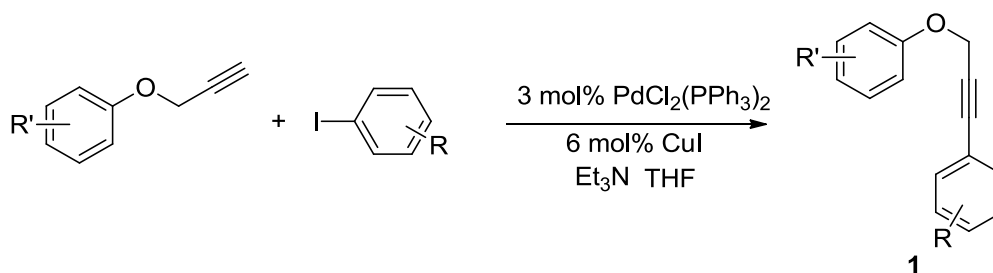
II. Preparation of Starting Materials

Preparation of (prop-2-yn-1-yloxy) benzene



Phenol (10.0 mmol, 1.0 eq.) was suspended in acetone (20 mL), followed by addition of K_2CO_3 (20.0 mmol, 2.0 eq.). The suspension was stirred for 10 min, and then propargyl bromide (30.0 mmol, 1.5 eq.) was added *via* syringe at room temperature. The reaction mixture was stirred for 5 h at room temperature. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography to give the desired product.

Preparation of (3-phenoxyprop-1-yn-1-yl) benzene



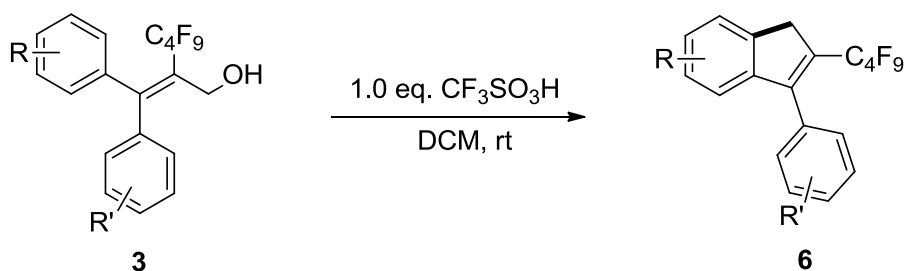
To a dried schlenk flask was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (3 mol%), CuI (6 mol%), iodobenzene (12.0 mmol, 1.2 eq.), (prop-2-yn-1-yloxy) benzene (10.0 mmol, 1.0 eq.) and freshly distilled Et_3N with THF under argon. The resulting mixture was stirred for overnight at room temperature. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography to give the desired product **1**.

III. Preparation of products 3 and 4.



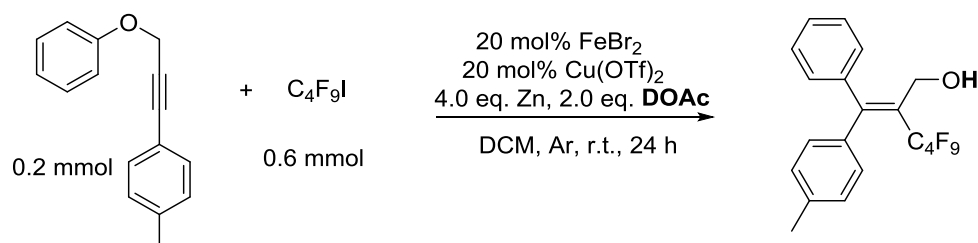
The mixture of **1** (0.20 mmol, 1.0 eq.) with perfluoroiodobutane (0.60 mmol, 3.0 eq.), FeBr₂ (20 mmol%), Cu(OTf)₂ (20 mmol%), Zinc powder (0.8 mmol, 4.0 eq.) and AcOH (0.4 mmol, 2.0 eq.) were combined in dry DCM (4.0 mL) at room temperature for 24 h under argon atmosphere. After the reaction, 15 mL water was added to quench the reaction, and the resulting mixture was extracted twice with DCM (2 × 15 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄ and concentrated. Purification of the crude product by flash column chromatography afforded the desired product (petroleum ether/ethyl acetate as eluent (25:1-20:1)).

Preparation of indenenes 6.

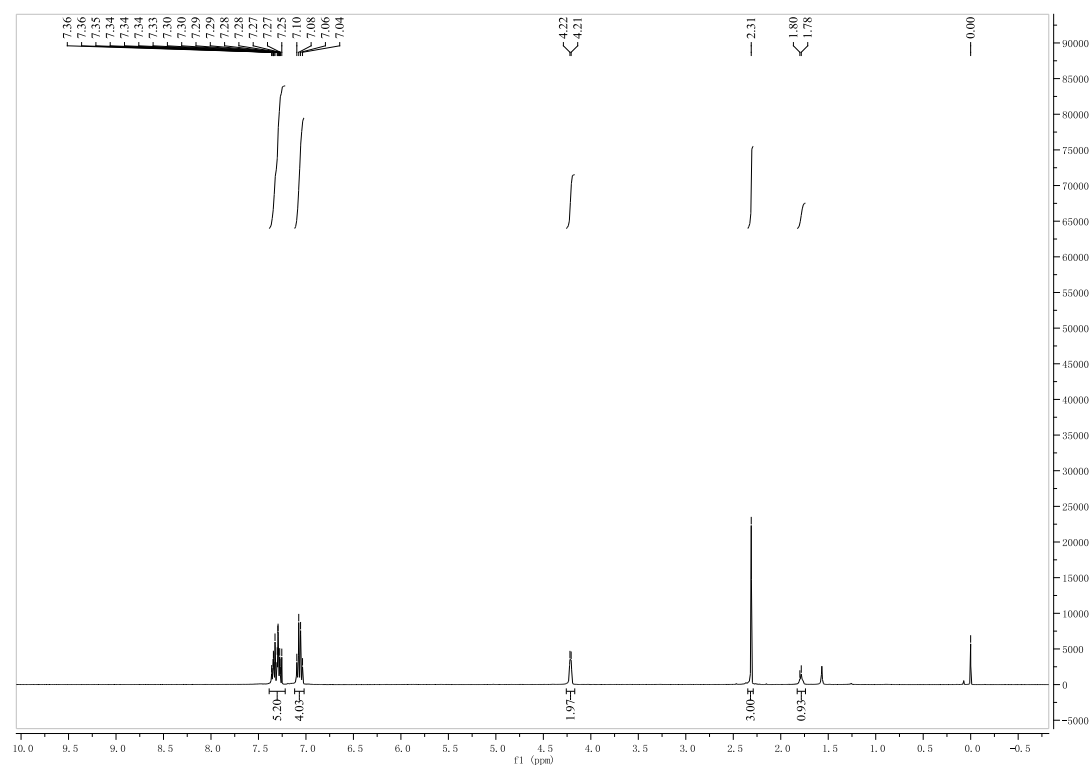


The mixture of **3** (0.1 mmol, 1.0 eq.) and CF₃SO₂OH (0.1 mmol, 1.0 eq.) were combined in dry DCM (2.0 mL) at room temperature for 5 min. After the reaction, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with DCM (2 × 10 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄ and concentrated. Purification of the crude product by flash column chromatography afforded the desired product (petroleum ether/ethyl acetate as eluent (200:1)).

IV. Deuteration labelling experiment

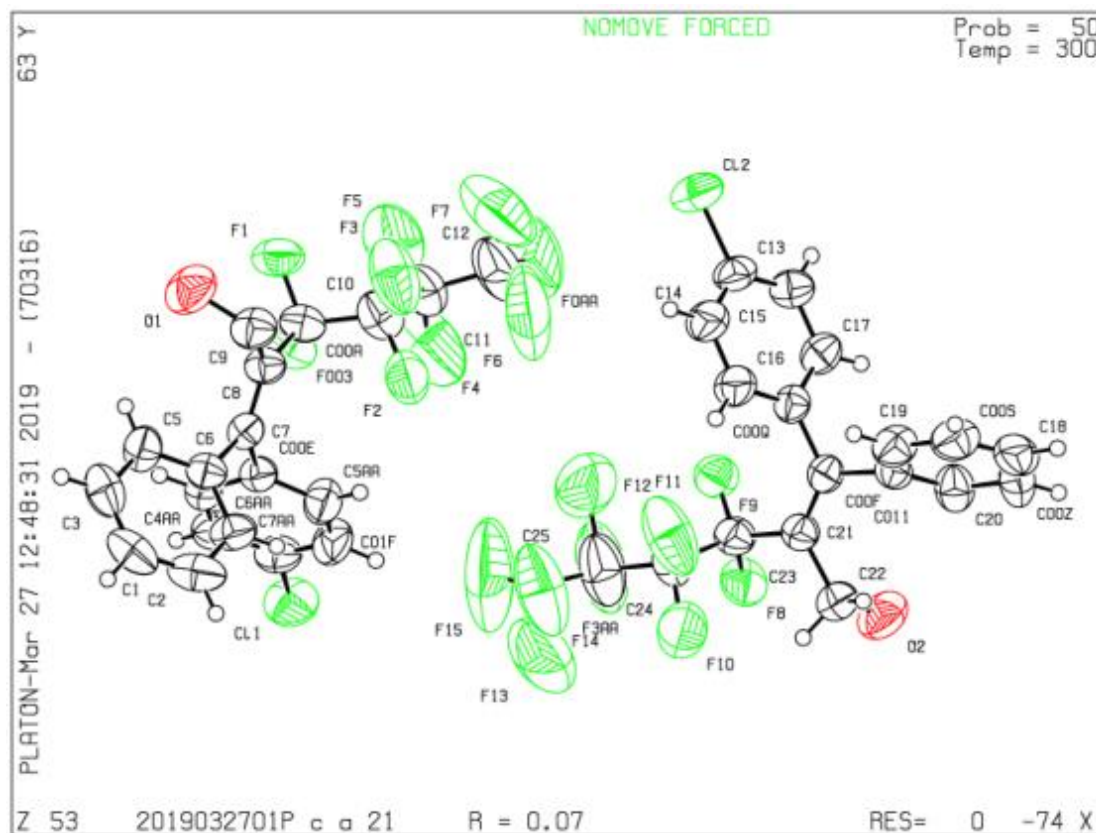


There is no any deuteration signal in NMR spectra, see below.



V. X-ray Crystal Diffraction Data for 3ah and 5a

Crystal Structure and Data of compound **3ah** (CCDC: 1914039)

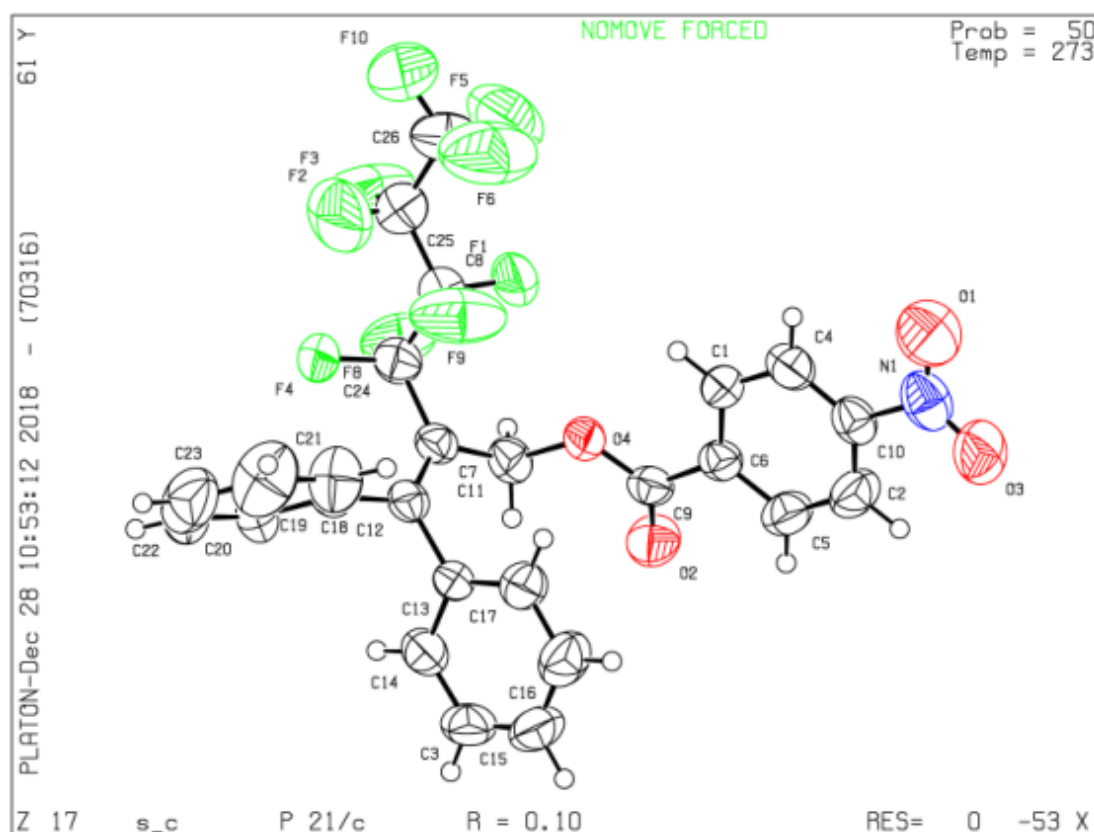


Datablock: 2019032701_0m_a

Bond precision:	C-C = 0.0118 Å		Wavelength=1.54178
Cell:	a=11.543(5)	b=10.400(2)	c=32.618(6)
	alpha=90	beta=90	gamma=90
Temperature:	300 K		
	Calculated	Reported	
Volume	3916(2)	3915.8(19)	
Space group	P c a 21	P c a 21	
Hall group	P 2c -2ac	P 2c -2ac	
Moiety formula	C19 H9 Cl F9 O, C19 H11 Cl	0.09(C19 H9 Cl F9 O),	
	F9 O	0.09(C19 H11 Cl F9 O)	
Sum formula	C38 H20 Cl2 F18 O2	C3.38 H1.96 Cl0.18 F1.60	

		N0 O0.18
Mr	921.44	82.08
Dx,g cm-3	1.563	1.566
Z	4	45
Mu (mm-1)	2.603	2.603
F000	1840.0	1848.0
F000'	1851.15	
h,k,lmax	13,12,39	13,12,39
Nref	7188[3665]	6902
Tmin,Tmax		0.573, 0.753
Tmin'		
Correction method = # Reported T Limits: Tmin=0.573 Tmax=0.753		
AbsCorr = MULTI-SCAN		
Data completeness= 1.88/0.96	Theta(max)= 68.285	
R(reflections)= 0.0712(5377)	wR2(reflections)= 0.2395(6902)	
S = 1.065	Npar= 541	

Crystal Structure and Data of compound **5a** (CCDC: 1887714)



Bond precision:	C-C = 0.0091 Å	Wavelength=0.71073
Cell:	a=6.1329(8)	b=40.065(5) c=10.6098(15)
	alpha=90	beta=103.811(4) gamma=90
Temperature:	273 K	
	Calculated	Reported
Volume	2531.6(6)	2531.6(6)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C ₂₆ H ₁₆ F ₉ N O ₄	?
Sum formula	C ₂₆ H ₁₆ F ₉ N O ₄	C ₂₆ H ₁₆ F ₉ N O ₄
Mr	577.40	577.40
D _x , g cm ⁻³	1.515	1.515
Z	4	4

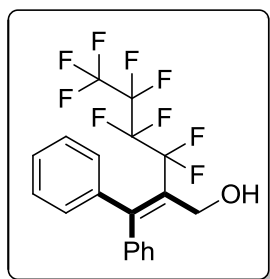
Mu (mm-1)	0.146	0.146
F000	1168.0	1168.0
F000'	1169.01	
h,k,lmax	7,48,12	7,48,12
Nref	4853	4816
Tmin,Tmax		0.639,0.745
Tmin'		

Correction method = # Reported T Limits: Tmin= 0.639 Tmax= 0.745

AbsCorr = MULTI-SCAN

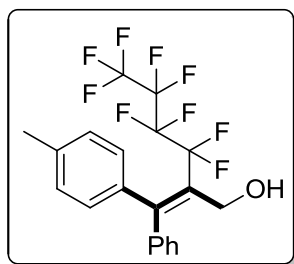
Data completeness= 0.992	Theta(max)= 25.753
R(reflections)= 0.0971(2244)	wR2(reflections)= 0.3040(4816)
S = 1.026	Npar= 362

VI. Date of products 3, 4, 5, 6, 7 and 8



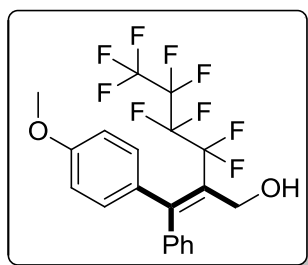
2-(diphenylmethylene)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol **3aa**, 66%, oil.

^1H NMR (400 MHz, CDCl_3): 7.37 (ddd, $J = 15.5, 7.9, 2.8$ Hz, 5H), 7.32 – 7.26 (m, 3H), 7.20 (d, $J = 7.0$ Hz, 2H), 4.26 (d, $J = 5.1$ Hz, 2H), 1.87 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): 156.8 (t, $J = 5.0$ Hz), 140.7, 139.9, 128.6, 128.3, 127.6, 126.5, 126.3 (t, $J = 19$ Hz), 126.1, 118.9, 117.4 (t, $J = 144$ Hz), 116.0, 59.4. ^{19}F NMR (376 MHz, CDCl_3): -80.90 (t, 3F), -103.05 – -103.35 (m, 2F), -119.76 (d, 2F), -125.86 – -126.28 (m, 2F). IR (cm^{-1}): 3422, 3060, 3024, 2964, 2908, 1952, 1809, 1629, 1599, 1578, 1491, 1445, 1351, 1309, 1235, 1202, 1135, 1102, 1078, 1031, 1016, 1001, 921, 891, 873, 848, 801, 743, 703, 643, 621, 610. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{12}\text{F}_9^+$ (M-OH) $^+$: 411.07898, found 411.07877.



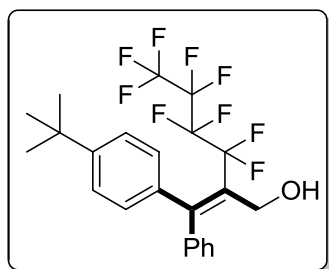
(Z)-3,3,4,4,5,5,6,6,6-nonafluoro-2-(phenyl(p-tolyl)methylene)hexan-1-ol **3ab**, 61%, oil

^1H NMR (400 MHz, CDCl_3): 7.42 – 7.28 (m, 5H), 7.10 (q, $J = 8.2$ Hz, 4H), 4.25 (s, 2H), 2.34 (s, 3H), 1.85 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): 157.0 (t, $J = 4.5$ Hz), 141.0, 137.3, 137.0, 128.6, 128.4, 128.2, 127.8, 127.4, 126.3, 126.1 (t, $J = 19$ Hz), 124.4, 124.0 (t, $J = 45$ Hz), 123.5, 118.9, 117.4, 59.5, 21.1. ^{19}F NMR (376 MHz, CDCl_3): -80.88 (t, 3F), -102.89 – -103.14 (m, 2F), -119.72 (d, 2F), -125.78 – -126.26 (m, 2F). IR (cm^{-1}): 3426, 3059, 3023, 2963, 2923, 1628, 1602, 1584, 1492, 1485, 1444, 1382, 1351, 1310, 1291, 1234, 1171, 1135, 1102, 1029, 1016, 1001, 941, 892, 873, 850, 823, 792, 773, 746, 737, 710, 663, 646, 624, 615. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{15}\text{F}_9^+$ (M-OH) $^+$: 425.09792, found 425.09802.



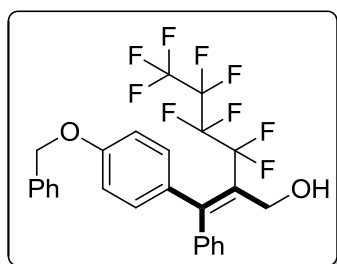
(Z)-3,3,4,4,5,5,6,6,6-nonafluoro-2-((4-methoxyphenyl)(phenyl)methylene)hexan-1-ol **3ac**, 55%, oil.

^1H NMR (400 MHz, CDCl_3): 7.41 – 7.35 (m, 2H), 7.35 – 7.28 (m, 3H), 7.11 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.25 (d, J = 5.9 Hz, 2H), 3.81 (s, 3H), 1.89 (t, J = 6.3 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 159.0, 156.8 (t, J = 4.5 Hz), 141.2, 132.3, 129.0, 128.5, 128.3, 127.9, 126.2, 126.0 (t, J = 20 Hz), 125.8, 118.9, 117.4 (t, J = 14.5 Hz), 116.0, 113.1, 59.6, 55.1. ^{19}F NMR (376 MHz, CDCl_3): -80.91 (t, 3F), -102.50 – -102.80 (m, 2F), -119.71 (dt, 2F), -125.63 – -126.12 (m, 2F). IR (cm^{-1}): 3456, 3060, 3003, 2960, 2938, 2909, 2840, 1607, 1576, 1509, 1465, 1444, 1412, 1386, 1350, 1306, 1288, 1236, 1178, 1134, 1101, 1034, 1017, 922, 902, 890, 873, 850, 832, 796, 782, 745, 701, 650, 624, 612. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{14}\text{F}_9\text{O}^+(\text{M}-\text{OH})^+$: 441.08955, found 441.08975.



(Z)-2-((4-(tert-butyl)phenyl)(phenyl)methylene)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol **3ad**, 58%, M.P. = 48–50 °C, pale yellow solid.

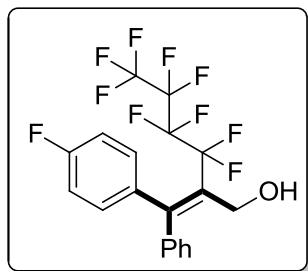
^1H NMR (400 MHz, CDCl_3): 7.41 – 7.36 (m, 2H), 7.36 – 7.30 (m, 5H), 7.13 (d, J = 8.2 Hz, 2H), 4.25 (s, 2H), 1.90 (s, 1H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): 157.1 (t, J = 4.5 Hz), 150.4, 141.1, 136.8, 128.5, 128.2, 127.8, 127.1, 126.3, 126.1 (t, J = 19 Hz), 125.9, 124.5, 118.9, 117.4 (t, J = 14.4 Hz), 116.0, 59.4, 34.5, 31.2. ^{19}F NMR (376 MHz, CDCl_3): -80.93 (t, 3F), -103.00 (t, 2F), -119.71 (m, 2F), -124.84 – -127.60 (m, 2F). IR (cm^{-1}): 3425, 3059, 3031, 2966, 2906, 2871, 1626, 1576, 1510, 1493, 1463, 1444, 1396, 1364, 1350, 1309, 1235, 1135, 1103, 1020, 922, 905, 891, 873, 852, 787, 744, 732, 702, 614. HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{20}\text{F}_9^+(\text{M}-\text{OH})^+$: 467.14158, found 467.14197.



(Z)-2-((4-(benzyloxy)phenyl)(phenyl)methylene)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol **3ae**, 34%, M.P. = 96–98 °C, pale yellow solid.

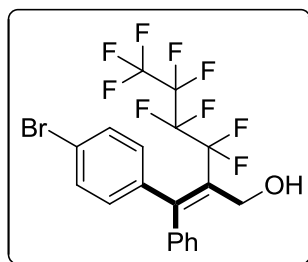
^1H NMR (400 MHz, CDCl_3): 7.47 – 7.42 (m, 3H), 7.42 – 7.35 (m, 5H), 7.34 – 7.30 (m, 2H), 7.12 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 5.06 (s, 2H), 4.25 (s, 2H), 1.85 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): 158.4, 156.7 (t, J = 5.0 Hz), 141.2, 136.8, 132.6, 130.0, 129.0, 128.6, 128.3, 128.0, 127.6, 126.3, 126.1 (t, J = 19 Hz), 125.9, 114.0, 70.0, 59.6. ^{19}F NMR (376 MHz, CDCl_3): -80.85 (t, 3F), -102.49 – -102.81 (m, 2F), -119.67 (d, 2F), -125.72 – -127.03 (m, 2F). IR (cm^{-1}): 3440, 3064, 3035, 2908, 1606, 1575, 1507, 1455, 1444, 1382, 1350, 1308, 1236, 1176, 1134, 1101, 1017, 890,

873, 850, 831, 783, 740, 698. HRMS (ESI) m/z calcd for $C_{26}H_{18}F_9O^+$ (M-OH) $^+$: 517.12085, found 517.12091.



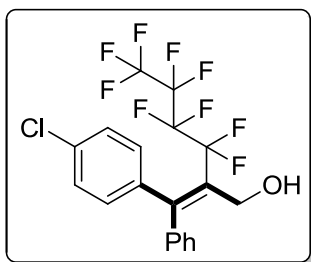
(Z)-3,3,4,4,5,5,6,6,6-nonafluoro-2-((4-fluorophenyl)(phenyl)methylene)hexan-1-ol
3af, 61%, oil.

1H NMR (400 MHz, $CDCl_3$): 7.42 – 7.33 (m, 3H), 7.30 (dd, J = 10.3, 3.8 Hz, 2H), 7.17 (dd, J = 8.3, 5.5 Hz, 2H), 7.01 (t, J = 8.7 Hz, 2H), 4.25 (d, J = 6.4 Hz, 2H), 1.87 (t, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 163.5, 161.0, 155.4, 140.3, 139.9, 135.7 (d, J = 3.0 Hz), 129.5 (d, J = 9.0 Hz), 128.7, 127.2, 115.0 (d, J = 22 Hz), 59.5. ^{19}F NMR (376 MHz, $CDCl_3$): -80.90 (t, J = 9.8, 3F), -102.85 – -103.15 (m, 2F), -114.27 (s, 1F), -119.82 (q, 2F), -125.80 – -126.07 (m, 2F). IR (cm^{-1}): 3629, 3426, 3033, 2926, 2392, 1708, 1603, 1507, 1393, 1350, 1299, 1135, 1102, 1016, 1005, 893, 874, 853, 824, 769, 746, 706, 694. HRMS (ESI) m/z calcd for $C_{19}H_{11}F_{10}^+$ (M-OH) $^+$: 429.06956, found 429.06956.



(Z)-2-((4-bromophenyl)(phenyl)methylene)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol
3ag, 57%, oil.

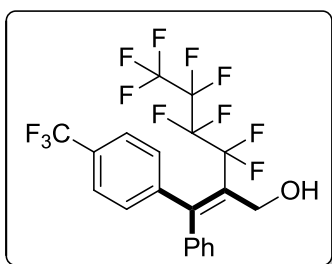
1H NMR (400 MHz, $CDCl_3$): 7.48 – 7.43 (m, 2H), 7.42 – 7.34 (m, 3H), 7.33 – 7.29 (m, 2H), 7.08 (d, J = 8.3 Hz, 2H), 4.25 (d, J = 6.3 Hz, 2H), 1.92 (t, J = 6.5 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): 155.5 (t, J = 5.0 Hz), 140.2, 138.8, 130.9, 129.1, 128.6, 127.8, 127.0, 126.9 (t, J = 19 Hz), 126.7, 121.9, 118.8, 117.2 (t, J = 144 Hz), 116.0, 59.3. ^{19}F NMR (376 MHz, $CDCl_3$): -80.89 (t, 3F), -103.09 – -103.39 (m, 2F), -119.89 (d, 2F), -125.84 – -126.26 (m, 2F). IR (cm^{-1}): 3596, 3430, 3083, 3060, 3028, 2966, 2910, 1952, 1903, 1629, 1598, 1585, 1486, 1444, 1393, 1350, 1313, 1288, 1235, 1135, 1103, 1073, 1031, 1013, 921, 893, 874, 851, 826, 777, 757, 746, 725, 701, 669, 617, 608. HRMS (ESI) m/z calcd for $C_{19}H_{11}BrF_9^+$ (M-OH) $^+$: 488.98949, found 488.98923.



(Z)-2-((4-chlorophenyl)(phenyl)methylene)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol

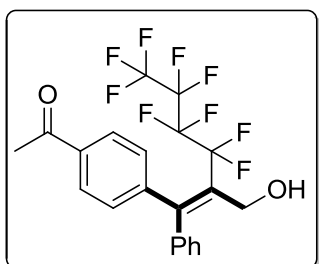
3ah, 61%, M.P.= 85-87 °C, pale yellow solid.

^1H NMR (400 MHz, CDCl_3): 7.43 – 7.34 (m, 3H), 7.34 – 7.27 (m, 4H), 7.14 (d, J = 8.4 Hz, 2H), 4.25 (d, J = 6.3 Hz, 2H), 1.93 (t, J = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 155.5 (t, J = 4.5 Hz), 140.3, 138.3, 133.7, 128.7, 128.0, 127.8, 127.1, 126.9 (t, J = 19 Hz), 126.7, 118.8, 117.3 (t, J = 143 Hz), 116.0, 59.31. ^{19}F NMR (376 MHz, CDCl_3): -80.91 (t, 3F), -103.19 (d, 2F), -119.87 (m, 2F), -125.79 – -126.07 (m, 2F). IR (cm^{-1}): 3426, 3061, 3030, 2968, 2909, 1903, 1630, 1592, 1576, 1489, 1444, 1397, 1351, 1310, 1235, 1202, 1135, 1091, 1016, 922, 904, 890, 873, 851, 829, 784, 759, 746, 731, 722, 701, 637, 611. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{11}\text{ClF}_9(\text{M}-\text{OH})^+$: 445.04001, found 445.04037.



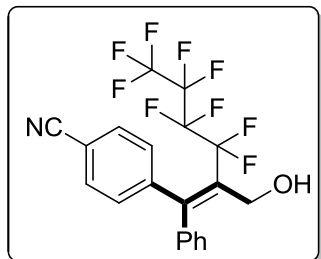
(Z)-3,3,4,4,5,5,6,6,6-nonafluoro-2(phenyl((trifluoromethyl)phenyl)methylene)hexan-1-ol **3ai**, 47%, oil.

^1H NMR (400 MHz, CDCl_3): 7.59 (d, J = 8.1 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.35 (ddd, J = 8.1, 6.6, 1.6 Hz, 5H), 4.27 (d, J = 5.9 Hz, 2H), 1.92 (t, J = 6.3 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 148.2 (t, J = 4.5 Hz), 136.5, 132.8, 122.9 (q, J = 32 Hz), 121.8, 120.8, 120.5, 120.3 (t, J = 19 Hz), 120.1, 118.3, 117.8 (t, J = 4.0 Hz), 112.9, 111.8, 110.2 (t, J = 143 Hz), 108.9, 52.2. ^{19}F NMR (376 MHz, CDCl_3): -62.73 (s, 3F), -80.95 (t, 3F), -103.39 – -103.70 (m, 2F), -119.97 (m, 2F), -125.89 – -126.64 (m, 2F). IR (cm^{-1}): 3425, 3062, 3025, 2971, 2910, 1616, 1578, 1509, 1493, 1444, 1407, 1351, 1327, 1237, 1170, 1133, 1110, 1068, 1020, 922, 906, 891, 855, 790, 779, 740, 701, 674, 616, 601. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{11}\text{F}_{12}(\text{M}-\text{OH})^+$: 479.06637, found 479.06616.



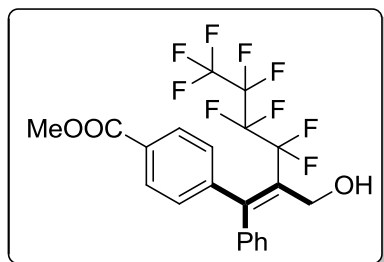
(Z)-1-(4-(3,3,4,4,5,5,6,6,6-nonafluoro-2-(hydroxymethyl)-1-phenylhex-1-en-1-yl)phenyl)ethanone **3aj**, 46%, oil.

^1H NMR (400 MHz, CDCl_3): 7.91 (d, $J = 8.5$ Hz, 2H), 7.41 – 7.36 (m, 2H), 7.32 (m, $J = 14.9$, 5.5 Hz, 5H), 4.26 (s, 2H), 2.59 (s, 3H), 2.01 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): 197.6, 155.5 (t, $J = 5.0$ Hz), 144.7, 139.7, 136.0, 128.7, 127.8, 127.7, 127.2, 127.0 (t, $J = 19$ Hz), 126.8, 117.3, 59.1, 26.5. ^{19}F NMR (376 MHz, CDCl_3): -80.92 (t, 3F), -102.96 – -104.02 (m, 2F), -119.93 (m, 2F), -125.56 – -126.24 (m, 2F). IR (cm^{-1}): 3451, 3060, 2969, 2908, 1684, 1636, 1603, 1576, 1561, 1490, 1444, 1427, 1403, 1351, 1307, 1267, 1235, 1134, 1103, 1075, 1017, 960, 922, 906, 891, 874, 854, 787, 767, 747, 738, 723, 703, 640, 624, 613, 600. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{16}\text{F}_9\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$: 471.10011, found 471.10037.



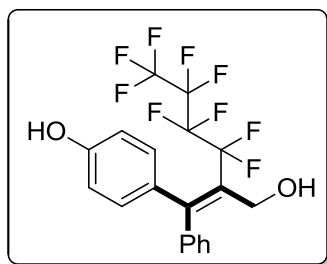
(Z)-4-(3,3,4,4,5,5,6,6,6-nonafluoro-2-(hydroxymethyl)-1-phenylhex-1-enyl)benzonitrile **3ak**, 56%, oil.

^1H NMR (400 MHz, CDCl_3): 7.64 – 7.59 (m, 2H), 7.43 – 7.35 (m, 3H), 7.35 – 7.29 (m, 4H), 4.26 (s, 2H), 2.07 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): 154.4 (t, $J = 5.0$ Hz), 144.6, 139.3, 131.6, 128.9, 128.2, 127.8, 127.6, 127.4, 118.7, 118.4, 117.1 (t, $J = 125$ Hz), 115.9, 111.5, 59.0. ^{19}F NMR (376 MHz, CDCl_3): -80.96 (d, 3F), -103.47 – -103.75 (m, 2F), -120.01 (dt, 2F), -125.83 – -126.55 (m, 2F). IR (cm^{-1}): 3473, 3061, 2969, 2908, 2232, 1636, 1605, 1577, 1501, 1444, 1403, 1351, 1309, 1235, 1135, 1103, 1016, 922, 906, 891, 874, 855, 777, 747, 702, 641, 612. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{11}\text{F}_9\text{N}^+$ ($\text{M}-\text{OH}$) $^+$: 436.07423, found 436.07455.



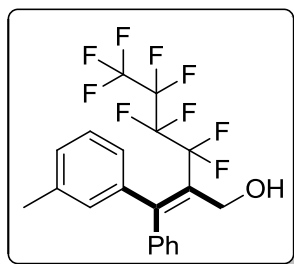
(Z)-methyl 4-(3,3,4,4,5,5,6,6,6-nonafluoro-2-(hydroxymethyl)-1-phenylhex-1-en-1-yl)benzoate **3al**, 60%, oil.

^1H NMR (400 MHz, CDCl_3): 7.99 (d, $J = 8.5$ Hz, 2H), 7.40 – 7.31 (m, 5H), 7.31 – 7.27 (m, 2H), 4.26 (s, 2H), 3.91 (s, 3H), 2.13 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): 166.7, 155.5 (t, $J = 4.5$ Hz), 144.6, 139.8, 129.3, 129.0, 128.6, 127.8, 127.5, 127.1, 127.0 (t, $J = 19$ Hz), 126.8, 118.8, 117.2 (t, $J = 143$ Hz), 115.9, 59.1, 52.1. ^{19}F NMR (376 MHz, CDCl_3): -80.96 (t, 3F), -103.50 (t, 2F), -119.92 (m, 2F), -125.27 – -127.09 (m, 2F). IR (cm^{-1}): 3487, 3060, 2999, 2956, 2907, 1935, 1725, 1607, 1567, 1491, 1439, 1404, 1351, 1289, 1235, 1201, 1135, 1116, 1105, 1021, 922, 907, 892, 873, 862, 845, 764, 745, 727, 711, 700, 647, 634, 624, 612. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{14}\text{F}_9\text{O}_2^+$ ($\text{M}-\text{OH}$) $^+$: 469.08446, found 469.08469.



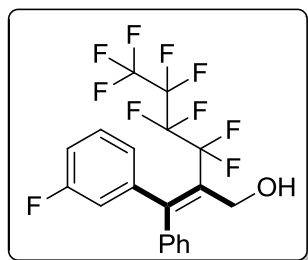
(Z)-4-(3,3,4,4,5,5,6,6,6-nonafluoro-2-(hydroxymethyl)-1-phenylhex-1-en-1-yl)phenol **3am**, 38%, oil.

^1H NMR (400 MHz, CDCl_3): 7.28-7.38 (m, 5H), 7.03 (d, $J = 8.0$ Hz, 2H), 6.76 (d, $J = 8.0$ Hz, 2H), 6.12 (s, 1H), 4.24 (s, 2H), 1.86 (s, 1H). ^{13}C NMR (100 MHz, DMSO): 157.1, 156.0 (t, $J = 4.5$ Hz), 142.0, 131.3, 129.3, 128.6, 128.3, 126.2, 126.0 (t, $J = 19$ Hz), 125.8, 119.0, 117.6 (t, $J = 143$ Hz), 116.1, 114.9, 58.3. ^{19}F NMR (376 MHz, DMSO): -80.51 (s, 3F), -101.39 (t, 2F), -119.33 (d, 2F), -125.73 (t, 2F). IR (cm^{-1}): 3253, 1611, 1590, 1511, 1493, 1444, 1350, 1311, 1235, 1173, 1134, 1103, 1048, 1025, 1008, 922, 891, 873, 851, 835, 782, 744, 729, 701, 626. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{12}\text{F}_9\text{O}^+$ (M-OH) $^+$: 427.07390, found 427.07394.



(Z)-3,3,4,4,5,5,6,6,6-nonafluoro-2-(phenyl(m-tolyl)methylene)hexan-1-ol **3an**, 70%, oil.

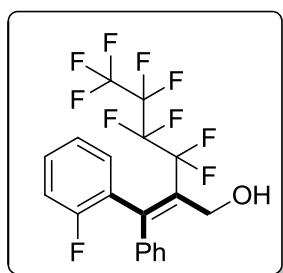
^1H NMR (400 MHz, CDCl_3): 7.42 – 7.32 (m, 5H), 7.21 (t, $J = 8.0$ Hz, 1H), 7.10 (d, $J = 7.9$ Hz, 1H), 7.02 (d, $J = 7.2$ Hz, 2H), 4.25 (d, $J = 6.5$ Hz, 2H), 2.34 (s, 3H), 1.93 (t, $J = 6.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 157.0 (t, $J = 4.5$ Hz), 140.8, 139.8, 137.3, 128.6, 128.2, 128.0, 127.8, 127.5, 126.3, 126.1 (t, $J = 19$ Hz), 125.9, 124.4, 118.9, 117.4 (t, $J = 143$ Hz), 116.0, 59.3, 21.3. ^{19}F NMR (376 MHz, CDCl_3): -80.94 (t, 3F), -103.22 (t, 2F), -119.63 (m, 2F), -124.30 – -128.06 (m, 2F). IR (cm^{-1}): 3426, 3059, 3023, 2963, 2923, 1628, 1602, 1584, 1492, 1485, 1444, 1382, 1351, 1310, 1291, 1234, 1171, 1135, 1102, 1029, 1016, 1001, 941, 892, 873, 850, 823, 792, 773, 746, 737, 710, 663, 646, 624, 615. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{14}\text{F}_9^+$ (M-OH) $^+$: 425.09463, found 425.09439.



(Z)-3,3,4,4,5,5,6,6,6-nonafluoro-2-((3-fluorophenyl)(phenyl)methylene)hexan-1-ol **3ao**, 65%, oil.

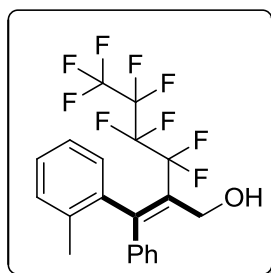
^1H NMR (400 MHz, CDCl_3): 7.46 – 7.35 (m, 3H), 7.35 – 7.32 (m, 2H), 7.31 – 7.26

(m, 1H), 7.02 – 6.95 (m, 2H), 6.93 (d, $J = 9.4$ Hz, 1H), 4.25 (d, $J = 6.3$ Hz, 2H), 1.92 (t, $J = 6.5$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 163.3, 160.8, 155.2 (t, $J = 5.0$ Hz), 141.8 (d, $J = 8.0$ Hz), 141.7, 140.1, 129.4 (d, $J = 8.0$ Hz), 129.3, 128.7, 128.6, 127.8, 127.1, 126.9 (t, $J = 19$ Hz), 126.7, 123.2, 118.8, 117.2 (t, $J = 144$ Hz), 116.0, 114.8 (d, $J = 22$ Hz), 114.7, 114.6, 114.4, 59.2. ^{19}F NMR (376 MHz, CDCl_3): -80.93 (t, 3F), -103.36 – -103.66 (m, 2F), -113.34 (s, 1F), -119.81 (d, 2F), -125.83 – -126.16 (m, 2F). IR (cm^{-1}): 3423, 3063, 3032, 2969, 2910, 1610, 1586, 1483, 1444, 1435, 1351, 1311, 1290, 1235, 1135, 1102, 1078, 1016, 1003, 953, 892, 876, 849, 833, 777, 738, 706, 649, 623. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{11}\text{F}_{10}^+$ (M-OH) $^+$: 429.06956, found 429.06924.



(Z)-3,3,4,4,5,5,6,6,6-nonafluoro-2-((2-fluorophenyl)(phenyl)methylene)hexan-1-ol **3ap**, 66%, oil.

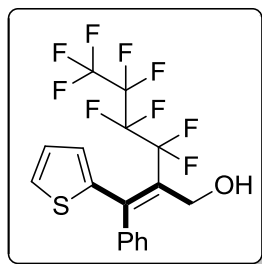
^1H NMR (400 MHz, CDCl_3): 7.44 – 7.32 (m, 5H), 7.31 – 7.22 (m, 2H), 7.12 (td, $J = 7.6, 1.1$ Hz, 1H), 7.04 (ddd, $J = 9.4, 8.3, 0.9$ Hz, 1H), 4.28 (dd, $J = 13.3, 5.1$ Hz, 2H), 1.93 (t, $J = 6.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 159.6, 157.1, 150.6 (t, $J = 5.0$ Hz), 139.5, 129.7, 129.2, 128.9, 128.6, 128.5, 127.7, 127.5, 123.4 (d, $J = 3.0$ Hz), 123.4, 118.9, 117.0 (t, $J = 143$ Hz), 116.0, 115.5, 115.3, 59.0. ^{19}F NMR (376 MHz, CDCl_3): -80.99 (t, 3F), -104.42 (d, 1F), -107.32 (d, 1F), -113.66 (d, 1F), -118.29 – -123.11 (m, 2F), -125.85 – -126.29 (m, 2F). IR (cm^{-1}): 3587, 3429, 3067, 3035, 2969, 2909, 1636, 1610, 1599, 1580, 1488, 1451, 1386, 1351, 1312, 1233, 1135, 1103, 1032, 1016, 943, 924, 905, 892, 874, 847, 815, 786, 756, 743, 699, 657, 640, 621, 613. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{11}\text{F}_{10}^+$ (M-OH) $^+$: 429.06956, found 429.06998.



(Z)-3,3,4,4,5,5,6,6,6-nonafluoro-2-(phenyl(o-tolyl)methylene)hexan-1-ol **3aq**, 57%, oil.

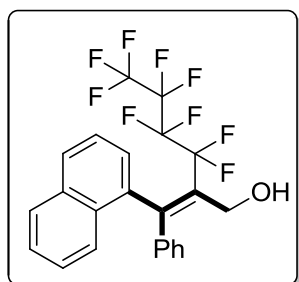
^1H NMR (400 MHz, CDCl_3): 7.45 (dd, $J = 8.1, 1.5$ Hz, 2H), 7.40 – 7.31 (m, 3H), 7.22 (dd, $J = 5.7, 2.8$ Hz, 3H), 7.13 (t, $J = 4.0$ Hz, 1H), 4.42 (d, $J = 12.9$ Hz, 1H), 4.20 (dd, $J = 12.9, 2.8$ Hz, 1H), 2.20 (s, 3H), 2.10 – 1.92 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): 156.0 (q, $J = 3.0$ Hz), 156.0, 139.2 (d, $J = 22$ Hz), 139.0, 135.0, 129.9, 128.7, 128.5, 128.2, 127.8, 127.4, 127.3 (q, $J = 3.0$ Hz), 127.3, 126.8, 126.6 (t, $J = 19$ Hz), 126.4, 124.9, 118.9, 117.6 (t, $J = 144$ Hz), 116.0, 59.3, 19.7. ^{19}F NMR (376 MHz, CDCl_3): -80.91 (t, 3F), -105.37 (d, 2F), -117.56 – -123.09 (m, 2F), -125.04 – -128.40 (m, 2F).

IR (cm⁻¹): 3440, 3063, 3022, 2967, 2926, 1624, 1600, 1576, 1492, 1457, 1444, 1383, 1351, 1235, 1135, 1100, 1016, 924, 891, 873, 848, 782, 737, 701, 625. HRMS (ESI) *m/z* calcd for C₂₀H₁₄F₉⁺ (M-OH)⁺: 425.09463, found 425.09451.



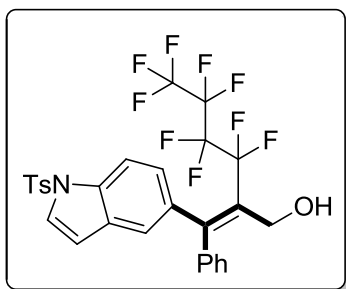
(Z)-3,3,4,4,5,5,6,6,6-nonafluoro-2-(phenyl(thiophen-2-yl)methylene)hexan-1-ol
3ar, 30%, oil.

¹H NMR (400 MHz, CDCl₃): 7.44 – 7.31 (m, 6H), 7.07 (d, *J* = 3.1 Hz, 1H), 6.97 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.22 (s, 2H), 1.83 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): 149.9 (t, *J* = 4.0 Hz), 141.0 (d, *J* = 19 Hz), 140.8, 129.7, 128.7, 128.6, 127.9, 127.7, 126.3, 59.7. ¹⁹F NMR (376 MHz, CDCl₃): -80.75 – -80.97 (t, 3F), -102.85 (t, 2F), -119.44 (m, 2F), -125.78 – -125.93 (m, 2F). IR (cm⁻¹): 3414, 3063, 2968, 2908, 1599, 1495, 1444, 1428, 1351, 1235, 1135, 1102, 1016, 893, 876, 852, 780, 745, 701. HRMS (ESI) *m/z* calcd for C₁₇H₁₀F₉S⁺ (M-OH)⁺: 417.03540, found 417.03592.



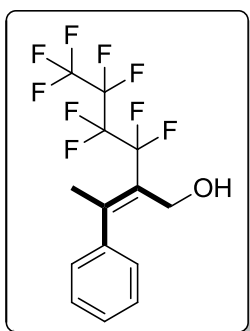
(Z)-3,3,4,4,5,5,6,6,6-nonafluoro-2-(naphthalen-1-yl(phenyl)methylene)hexan-1-ol
3as, 28%, oil.

¹H NMR (400 MHz, CDCl₃): 7.96 (d, *J* = 9.1 Hz, 1H), 7.82 (t, *J* = 8.7 Hz, 2H), 7.56 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.48 (td, *J* = 7.0, 3.8 Hz, 3H), 7.39 – 7.36 (m, 1H), 7.31 (dd, *J* = 13.0, 7.8 Hz, 3H), 4.53 – 4.33 (m, 2H), 2.15 – 2.03 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): 155.0 (t, *J* = 5.0 Hz), 139.5, 137.1, 133.3, 130.8, 128.6, 128.4, 128.3, 128.2, 128.1, 126.3, 125.8, 125.7, 124.6, 124.5 (d, *J* = 5.0 Hz), 124.4, 121.6, 115.0, 59.4. ¹⁹F NMR (376 MHz, CDCl₃): -80.90 (t, 3F), -104.94 – -105.16 (m, 2F), -118.06 – -121.64 (m, 2F), -126.04 (d, 2F). IR (cm⁻¹): 3431, 3061, 2966, 2908, 1597, 1576, 1507, 1494, 1444, 1392, 1351, 1235, 1135, 1100, 1017, 892, 874, 848, 800, 783, 772, 748, 727, 701, 656, 623. HRMS (ESI) *m/z* calcd for C₂₃H₁₄F₉⁺ (M-OH)⁺: 461.09463, found 461.09479.



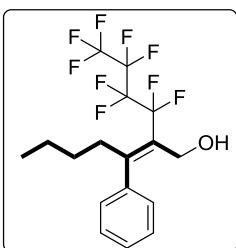
(Z)-3,3,4,4,5,5,6,6,6-nonafluoro-2-(phenyl(1-tosyl-1H-indol-5-yl)methylene)hexan-1-ol **3at**, 30%, oil.

^1H NMR (400 MHz, CDCl_3): 7.92 (d, $J = 8.6$ Hz, 1H), 7.76 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 3.7$ Hz, 1H), 7.33 (dd, $J = 13.0, 6.6$ Hz, 6H), 7.23 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 8.5$ Hz, 1H), 6.62 (d, $J = 3.4$ Hz, 1H), 4.25 (s, 2H), 2.36 (s, 3H), 1.84 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): 156.8 (t, $J = 4.5$ Hz), 145.0, 140.9, 135.1, 134.1, 130.1, 129.8, 128.6, 128.3, 127.8, 126.8, 126.5, 124.3, 120.3, 112.8, 109.1, 59.5, 21.5. ^{19}F NMR (376 MHz, CDCl_3): -80.89 (t, 3F), -102.84 (t, 2F), -119.60 (m, 2F), -125.81 – -126.11 (m, 2F). IR (cm^{-1}): 3566, 3425, 3060, 2926, 2597, 1494, 1456, 1444, 1372, 1351, 1307, 1290, 1235, 1189, 1173, 1133, 1094, 1017, 996, 952, 897, 873, 848, 812, 768, 744, 727, 703, 676, 634. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{19}\text{F}_9\text{NO}_2\text{S}^+$ (M-OH) $^+$: 604.09873, found 604.09888.



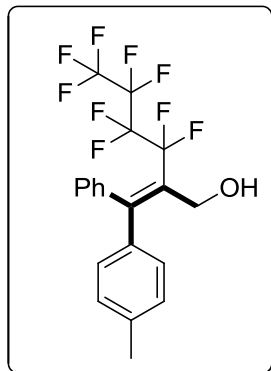
(E)-3,3,4,4,5,5,6,6,6-nonafluoro-2-(1-phenylethylidene)hexan-1-ol **3au**, 32%, oil.

^1H NMR (400 MHz, CDCl_3): 7.40 (dq, $J = 14.6, 7.1$ Hz, 3H), 7.28 (d, $J = 6.8$ Hz, 2H), 3.99 (d, $J = 5.9$ Hz, 2H), 2.25 (s, 3H), 1.65 (t, $J = 6.5$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 150.5 (t, $J = 5.0$ Hz), 142.1, 128.6, 128.0, 126.7, 125.2, 125.0 (t, $J = 20$ Hz), 124.8, 119.0, 117.8 (t, $J = 144$ Hz), 116.1, 59.7, 23.3. ^{19}F NMR (376 MHz, CDCl_3): -80.92 (t, 3F), -105.78 (m, 2F), -121.83 – -122.38 (m, 2F), -125.79 – -126.16 (m, 2F). IR (cm^{-1}): 3407, 3059, 2960, 2909, 1640, 1601, 1577, 1492, 1443, 1384, 1350, 1309, 1288, 1234, 1204, 1170, 1134, 1065, 1027, 1008, 932, 884, 869, 842, 764, 745, 727, 702, 653. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{11}\text{F}_9^+$ (M-OH) $^+$: 349.06333, found 349.06369.



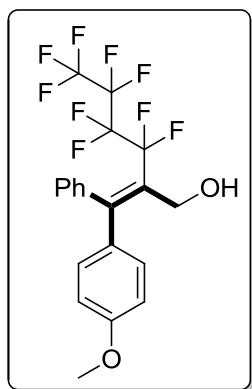
(E)-2-(perfluorobutyl)-3-phenylhept-2-en-1-ol, **3av**, oil, 30%.

^1H NMR (400 MHz, CDCl_3): 7.36-7.43 (m, 3 H), 7.23-7.25 (m, 2 H), 3.92 (s, 2 H), 2.52-2.54 (m, 2 H), 1.61 (s, 1 H, OH), 1.24-1.26 (m, 4 H), 0.82 (t, $J = 8.0$ Hz, 3 H); ^{19}F NMR (376 MHz, CDCl_3): -80.90 (m, 3 F), -105.12 (m, 2 F), -122.04 (m, 2 F), -125.93 (m, 2 F); ^{13}C NMR (100 MHz, CDCl_3): 159.2 (t, $J = 5.0$ Hz), 140.4, 128.4, 127.9, 127.4, 124.8, 124.6 (t, $J = 20$ Hz), 124.4, 118.9, 117.9, 116.1, 111.1, 59.8, 35.8, 30.2, 22.6, 13.7; IR (cm^{-1}): 3420, 3023, 2962, 2934, 2875, 1633, 1490, 1470, 1443, 1381, 1350, 1312, 1235, 1134, 1092, 1015, 925, 886, 870, 845, 776, 745, 702, 654; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{16}\text{F}_9^+$ (M-OH) $^+$: 391.11028, found 391.11099.



(E)-3,3,4,4,5,5,6,6,6-nonafluoro-2-(phenyl(p-tolyl)methylene)hexan-1-ol **3ba**, 63%, oil.

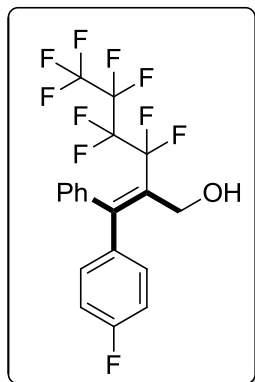
^1H NMR (400 MHz, CDCl_3): 7.31 (dd, $J = 15.2, 7.3$ Hz, 3H), 7.26 (dd, $J = 8.0, 1.9$ Hz, 2H), 7.21 (t, $J = 6.1$ Hz, 4H), 4.29 (d, $J = 5.9$ Hz, 2H), 2.37 (s, 3H), 2.00 – 1.91 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): 156.9 (t, $J = 5.0$ Hz), 140.1, 138.3, 137.9, 129.2, 127.8, 127.5, 126.1, 125.9 (t, $J = 19$ Hz), 125.7, 118.9, 117.4 (t, $J = 143$ Hz), 116.0, 59.4, 21.1. ^{19}F NMR (376 MHz, CDCl_3): -80.98 (d, 3F), -102.91 – -103.19 (m, 2F), -119.74 (d, 2F), -125.86 – -126.28 (m, 2F). IR (cm^{-1}): 3426, 3083, 3057, 3027, 2968, 2925, 1905, 1806, 1762, 1611, 1598, 1578, 1510, 1492, 1444, 1406, 1382, 1350, 1306, 1290, 1234, 1135, 1101, 1075, 1016, 1001, 921, 892, 873, 851, 821, 798, 774, 748, 724, 701, 637, 620, 609. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{14}\text{F}_9^+$ (M-OH) $^+$: 425.09463, found 425.09473.



(E)-3,3,4,4,5,5,6,6,6-nonafluoro-2-((4-methoxyphenyl)(phenyl)methylene)hexan-1-ol **3bb**, 57%, oil.

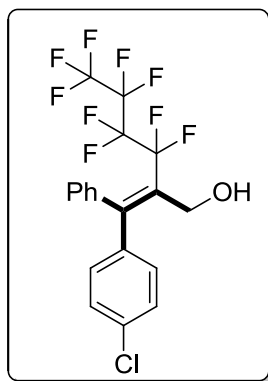
^1H NMR (400 MHz, CDCl_3): 7.30 (t, $J = 7.5$ Hz, 5H), 7.17 (d, $J = 7.1$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 4.30 (d, $J = 5.7$ Hz, 2H), 3.82 (s, 3H), 1.94 (t, $J = 5.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 159.7, 156.6 (t, $J = 4.5$ Hz), 140.3, 133.0, 129.7, 127.6, 125.5, 125.4 (t, $J = 19$ Hz), 125.2, 118.9, 117.5 (t, $J = 143$ Hz), 116.0, 113.8, 59.6,

55.2. ^{19}F NMR (376 MHz, CDCl_3): -80.91 (t, 3F), -102.60 (d, 2F), -119.49 (d, 2F), -125.81 – -126.12 (m, 2F). IR (cm^{-1}): 3446, 2960, 2908, 2840, 2360, 1606, 1574, 1510, 1465, 1444, 1350, 1306, 1288, 1236, 1181, 1134, 1101, 1075, 1032, 1017, 922, 892, 873, 851, 833, 799, 778, 749, 729, 702, 668, 619, 608. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{14}\text{F}_9\text{O}^+$ (M-OH) $^+$: 441.08955, found 441.08942.



(E)-3,3,4,4,5,5,6,6,6-nonafluoro-2-((4-fluorophenyl)(phenyl)methylene)hexan-1-ol **3bc**, 62%, oil.

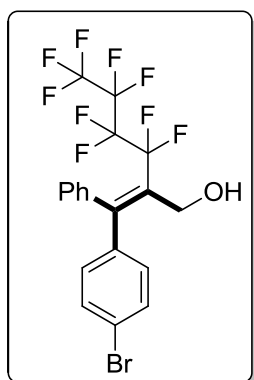
^1H NMR (400 MHz, CDCl_3): 7.41–7.30 (m, 5H), 7.18 (d, J = 7.0 Hz, 2H), 7.07 (t, J = 8.7 Hz, 2H), 4.26 (d, J = 4.3 Hz, 2H), 1.99 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): 163.9, 161.4, 155.9 (t, J = 5.0 Hz), 139.8, 136.6, 130.2 (d, J = 8.0 Hz), 130.1, 127.7, 127.5, 126.5, 126.3 (t, J = 19 Hz), 126.1, 118.8, 117.4 (t, J = 144 Hz), 116.0, 115.6, 115.4, 59.4. ^{19}F NMR (376 MHz, CDCl_3): -80.92 (t, 3F), -102.90 – -103.07 (m, 2F), -112.83 (s, 1F), -119.54 (m, 2F), -125.90 – -126.05 (m, 2F). IR (cm^{-1}): 3426, 3059, 2971, 2909, 1603, 1507, 1492, 1444, 1351, 1313, 1290, 1235, 1160, 1135, 1099, 1075, 1016, 1001, 922, 892, 873, 854, 837, 815, 778, 748, 726, 701, 618, 608. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{11}\text{F}_{10}^+$ (M-OH) $^+$: 429.06956, found 429.06967.



(E)-2-((4-chlorophenyl)(phenyl)methylene)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol **3bd**, 61%, M.P. = 50–52 °C, pale yellow solid.

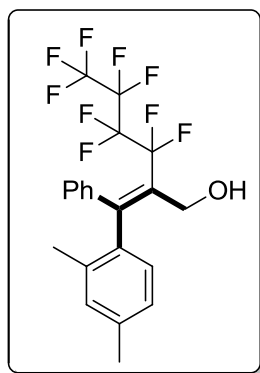
^1H NMR (400 MHz, CDCl_3): 7.38–7.34 (m, 2H), 7.31 (ddd, J = 10.6, 5.9, 3.7 Hz, 5H), 7.18 (d, J = 7.5 Hz, 2H), 4.25 (d, J = 6.1 Hz, 2H), 1.97 (t, J = 6.3 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 155.7 (t, J = 4.5 Hz), 139.5, 139.0, 134.6, 129.5, 128.7, 127.8, 127.4, 126.7, 126.5 (t, J = 19 Hz), 126.4, 118.8, 117.3 (t, J = 144 Hz), 116.0, 59.3. ^{19}F NMR (376 MHz, CDCl_3): -80.94 (t, 3F), -103.04 – -103.32 (m, 2F), -119.61 (d, 2F), -125.84 – -126.19 (m, 2F). IR (cm^{-1}): 3424, 3060, 2969, 2909, 1630, 1591, 1490, 1444, 1398, 1351, 1313, 1288, 1235, 1135, 1103, 1091, 1016, 1001, 922, 893, 874, 852, 830, 780, 761, 747, 730, 701. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{11}\text{ClF}_9^+$ (M-OH) $^+$:

445.04001, found 445.04041.



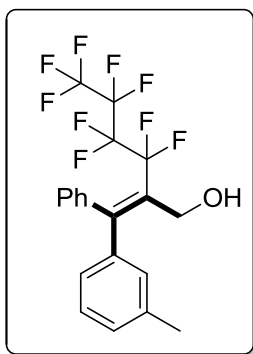
(E)-2-((4-bromophenyl)(phenyl)methylene)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol **3be**, 57%, M.P. = 65-67 °C, pale yellow solid.

^1H NMR (400 MHz, CDCl_3): 7.51 (d, J = 8.5 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.28 – 7.22 (m, 2H), 7.18 (d, J = 7.5 Hz, 2H), 4.25 (d, J = 6.2 Hz, 2H), 1.97 (t, J = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 155.7 (t, J = 5.0 Hz), 139.4, 131.7, 129.8, 127.8, 127.4, 126.7, 126.5 (t, J = 19 Hz), 126.3, 122.8, 118.8, 117.3 (t, J = 143 Hz), 115.9, 59.3. ^{19}F NMR (376 MHz, CDCl_3): -80.92 (t, 3F), -103.18 (d, 2F), -119.60 (m, 2F), -125.85 – -126.08 (m, 2F). IR (cm^{-1}): 3425, 3060, 3028, 2969, 2908, 1629, 1598, 1585, 1486, 1444, 1393, 1350, 1313, 1288, 1235, 1135, 1102, 1073, 1031, 1012, 921, 893, 874, 851, 826, 777, 757, 746, 725, 701, 669, 608. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{11}\text{BrF}_9^+$ (M-OH) $^+$: 488.98949, found 488.98962.



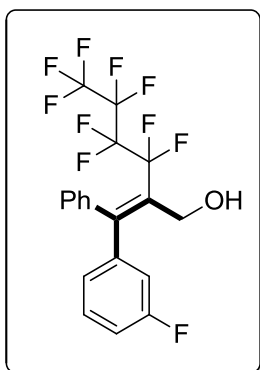
(E)-2-((2,4-dimethylphenyl)(phenyl)methylene)-3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol **3bf**, 62%, oil.

^1H NMR (400 MHz, CDCl_3): 7.28 (d, J = 3.8 Hz, 5H), 7.15 (d, J = 7.7 Hz, 1H), 7.09 – 7.03 (m, 2H), 4.23 (d, J = 12.7 Hz, 1H), 4.09 (d, J = 12.7 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 1.65 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): 156.1 (t, J = 4.5 Hz), 138.9, 138.0, 137.5, 133.8, 131.7, 127.5, 127.0, 118.9, 117.1 (t, J = 144 Hz), 116.0, 59.4, 21.0, 19.7. ^{19}F NMR (376 MHz, CDCl_3): -80.94 (t, 3F), -102.45 – -104.11 (m, 2F), -119.91 – -120.11 (m, 2F), -125.92 – -125.99 (t, 2F). IR (cm^{-1}): 3426, 3057, 3020, 2960, 2924, 1613, 1599, 1492, 1444, 1381, 1350, 1309, 1235, 1134, 1096, 1076, 1032, 1015, 937, 917, 889, 873, 848, 820, 783, 742, 730, 700, 620. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{16}\text{F}_9^+$ (M-OH) $^+$: 439.11028, found 439.11057.



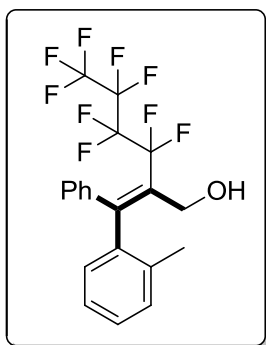
(E)-3,3,4,4,5,5,6,6,6-nonafluoro-2-(phenyl(m-tolyl)methylene)hexan-1-ol **3bg**, 57%, oil.

^1H NMR (400 MHz, CDCl_3): 7.33–7.25 (m, 4H), 7.21 (d, $J = 7.1$ Hz, 2H), 7.14 (d, $J = 7.9$ Hz, 3H), 4.26 (d, $J = 6.5$ Hz, 2H), 2.36 (s, 3H), 1.84 (t, $J = 6.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 156.9 (t, $J = 4.5$ Hz), 140.7, 139.9, 138.4, 129.1, 128.5, 128.1, 127.0, 126.4, 126.2 (t, $J = 19$ Hz), 126.0, 124.7, 118.9, 117.3 (t, $J = 143$ Hz), 116.0, 59.4, 21.4. ^{19}F NMR (376 MHz, CDCl_3): -80.92 (t, 3F), -103.23 (t, 2F), -119.84 (m, 2F), -125.84 – -126.08 (m, 2F). IR (cm^{-1}): 3416, 3063, 3032, 2909, 1610, 1584, 1508, 1483, 1444, 1435, 1351, 1313, 1236, 1152, 1135, 1100, 1076, 1031, 1017, 1002, 950, 878, 852, 833, 793, 774, 747, 706, 627. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{14}\text{F}_9^+$ (M-OH) $^+$: 425.09463, found 425.09485.



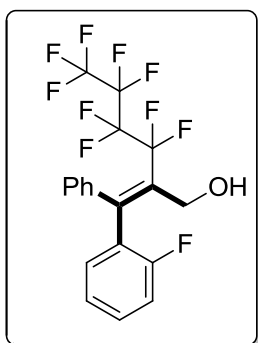
(E)-3,3,4,4,5,5,6,6,6-nonafluoro-2-((3-fluorophenyl)(phenyl)methylene)hexan-1-ol **3bh**, 45%, oil.

^1H NMR (400 MHz, CDCl_3): 7.39 – 7.29 (m, 4H), 7.23 – 7.13 (m, 3H), 7.11 – 6.97 (m, 2H), 4.25 (d, $J = 6.2$ Hz, 2H), 1.88 (t, $J = 6.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 163.7, 161.3, 155.4 (t, $J = 4.5$ Hz), 142.6 (d, $J = 7.0$ Hz), 139.2, 130.2 (d, $J = 8.0$ Hz), 127.8, 127.3, 127.0, 126.8 (t, $J = 19$ Hz), 126.7, 123.7, 117.3 (t, $J = 143$ Hz), 115.5, 115.2, 115.1, 59.3. ^{19}F NMR (376 MHz, CDCl_3): -80.90 (t, $J = 9.8$, 2.7 Hz, 3 F), -103.25 – -103.45 (m, 1F), -111.78 (s, 2F), -119.70 (m, 2F), -125.85 – -126.05 (m, 2F). IR (cm^{-1}): 3430, 3059, 3023, 2962, 2923, 1949, 1881, 1806, 1627, 1601, 1583, 1492, 1444, 1382, 1350, 1311, 1291, 1235, 1135, 1103, 1075, 1031, 1018, 1001, 940, 916, 890, 873, 853, 825, 793, 770, 747, 710, 664, 646, 624, 614. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{11}\text{F}_{10}^+$ (M-OH) $^+$: 429.06956, found 429.06940.



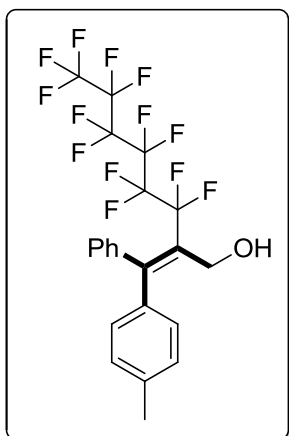
(E)-3,3,4,4,5,5,6,6,6-nonafluoro-2-(phenyl(o-tolyl)methylene)hexan-1-ol **3bi**, 48%, oil.

^1H NMR (400 MHz, CDCl_3): 7.34 – 7.27 (m, 5H), 7.27 – 7.18 (m, 4H), 4.15 (ddd, J = 54.8, 12.7, 5.9 Hz, 2H), 2.34 (s, 3H), 1.61 (d, J = 8.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 155.9 (t, J = 5.0 Hz), 140.4, 138.7, 134.1, 131.0, 128.2, 127.6, 127.3, 126.2, 118.9, 117.1 (t, J = 143 Hz), 116.0, 59.5, 19.8. ^{19}F NMR (376 MHz, CDCl_3): -80.91 (t, 3F), -102.13 – -104.45 (m, 2F), -118.33 – -121.99 (m, 2F), -124.58 – -127.34 (m, 2F). IR (cm^{-1}): 3425, 3061, 3021, 2962, 2908, 1629, 1599, 1578, 1501, 1458, 1444, 1383, 1351, 1310, 1235, 1134, 1097, 1077, 1032, 1015, 921, 891, 874, 849, 802, 747, 728, 700, 642. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{14}\text{F}_9^+$ (M-OH) $^+$: 425.09463, found 425.09482.



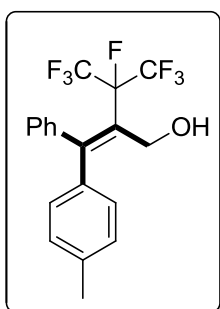
(E)-3,3,4,4,5,5,6,6,6-nonafluoro-2-((2-fluorophenyl)(phenyl)methylene)hexan-1-ol **3bj**, 40%, oil.

^1H NMR (400 MHz, CDCl_3): 7.34 (d, J = 6.5 Hz, 1H), 7.29 (dt, J = 7.1, 3.4 Hz, 6H), 7.19 (dd, J = 10.9, 4.1 Hz, 1H), 7.12 (t, J = 9.0 Hz, 1H), 4.22 (d, J = 8.0 Hz, 2H), 1.74 (t, J = 6.1 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 159.0, 156.5, 150.3 (t, J = 5.0 Hz), 138.7, 130.2 (d, J = 8.0 Hz), 129.4 (t, J = 2.0 Hz), 129.0 (q, J = 18 Hz), 127.7, 127.3, 124.6 (d, J = 3.0 Hz), 116.3, 116.1, 59.7, 18.4. ^{19}F NMR (376 MHz, CDCl_3): -80.92 (t, 3F), -102.60 – 105.19 (m, 2F), -120.30 (d, 2F), -126.00 (t, 2F). IR (cm^{-1}): 3425, 3062, 2968, 1640, 1611, 1599, 1577, 1488, 1451, 1391, 1351, 1314, 1236, 1135, 1112, 1096, 1075, 1031, 1016, 943, 923, 892, 875, 862, 849, 816, 784, 757, 732, 700, 661. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{11}\text{F}_{10}^+$ (M-OH) $^+$: 429.06956, found 429.06992.



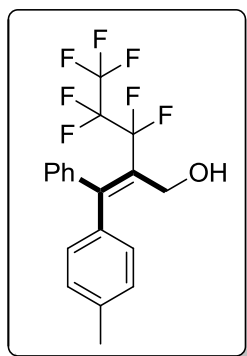
(E)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-2-(phenyl(p-tolyl)methylene)octan-1-ol
4a, 64%, M.P.= 73-75 °C, white solid.

^1H NMR (400 MHz, CDCl_3): 7.35 – 7.27 (m, 3H), 7.25 (d, J = 8.1 Hz, 2H), 7.23 – 7.13 (m, 4H), 4.28 (s, 2H), 2.36 (s, 3H), 1.91 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): 156.9 (t, J = 5.0 Hz), 140.2, 138.3, 137.9, 129.3, 127.8, 127.2, 126.3, 126.1 (t, J = 19 Hz), 125.9, 118.6, 117.6 (t, J = 143 Hz), 115.8, 59.5, 21.1. ^{19}F NMR (376 MHz, CDCl_3): -80.89 (t, 3F), -102.79 – -102.98 (m, 2F), -118.80 (d, 2F), -121.86 (s, 2F), -122.72 (s, 2F), -126.16 (t, 2F). IR (cm^{-1}): 3416, 3058, 3027, 2967, 2925, 1610, 1598, 1577, 1510, 1492, 1444, 1363, 1300, 1239, 1199, 1145, 1101, 1075, 1048, 1023, 1001, 952, 899, 826, 809, 780, 746, 737, 722, 701, 676, 650, 633. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{14}\text{F}_{13}^+$ (M-OH) $^+$: 525.08824, found 525.08868.

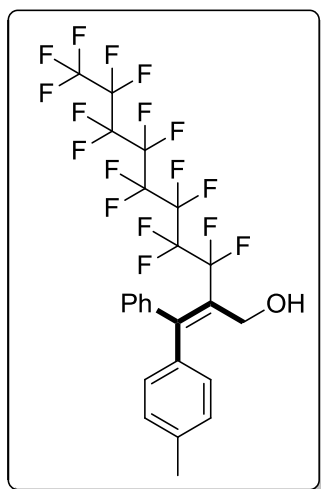


(E)-3,4,4,4-tetrafluoro-2-(phenyl(p-tolyl)methylene)-3-(trifluoromethyl)butan-1-ol
4b, 32%, oil.

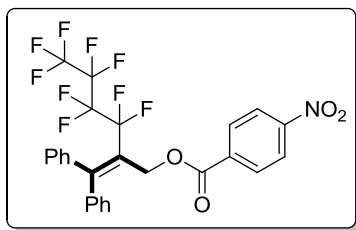
^1H NMR (400 MHz, CDCl_3): 7.32 – 7.28 (m, 2H), 7.25 (d, J = 7.2 Hz, 1H), 7.20 (s, 4H), 7.19 – 7.15 (m, 2H), 4.25 (d, J = 5.8 Hz, 2H), 2.35 (s, 3H), 1.61 (t, J = 6.3 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 156.4 (d, J = 5.0 Hz), 141.3 (d, J = 5.0 Hz), 138.5, 138.0, 129.6, 127.8, 127.1, 126.3 (d, J = 5.0 Hz), 124.0 (d, J = 13 Hz), 120.6, 122.2 (d, J = 29 Hz), 119.3 (d, J = 27 Hz), 58.0, 21.1. ^{19}F NMR (376 MHz, CDCl_3): -73.55 (d, 6F), -170.22 (m, 1F). IR (cm^{-1}): 3462, 3055, 3025, 2924, 2869, 1597, 1577, 1509, 1491, 1444, 1405, 1302, 1287, 1263, 1228, 1183, 1165, 1135, 1102, 1074, 1031, 999, 970, 899, 823, 796, 773, 756, 746, 724, 698, 669, 660, 625. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{14}\text{F}_7^+$ (M-OH) $^+$: 375.09782, found 375.09787.



(E)-3,3,4,4,5,5,5-heptafluoro-2-(phenyl(p-tolyl)methylene)pentan-1-ol **4c**, 61%, oil.
 ^1H NMR (400 MHz, CDCl_3): 7.33 – 7.27 (m, 3H), 7.24 (d, $J = 8.3$ Hz, 2H), 7.22 – 7.14 (m, 4H), 4.28 (s, 2H), 2.36 (s, 3H), 1.89 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): 156.3 (t, $J = 5.0$ Hz), 141.3, 138.5, 138.0, 129.6, 127.8, 127.1, 126.3, 125.8 (t, $J = 19$ Hz), 119.4, 116.8 (d, $J = 23$ Hz), 114.3, 59.5, 21.1. ^{19}F NMR (376 MHz, CDCl_3): -80.38 (t, 3F), -103.35 – -103.62 (m, 2F), -123.07 – -123.22 (m, 2F). IR (cm^{-1}): 3425, 3026, 2966, 2924, 1610, 1598, 1578, 1510, 1491, 1444, 1380, 1346, 1302, 1230, 1179, 1111, 1075, 1058, 1032, 1022, 1001, 949, 926, 910, 824, 798, 775, 752, 724, 701, 681, 654, 638, 621. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{14}\text{F}_7^+$ (M-OH) $^+$: 375.09782, found 375.09796.

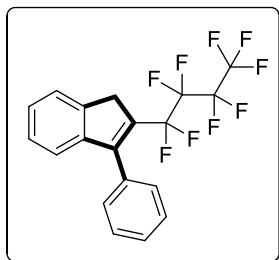


(E)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-2-(phenyl(p-tolyl)methylene)decan-1-ol **4d**, 55%, M.P.= 78-80 °C, white solid.
 ^1H NMR (400 MHz, CDCl_3): 7.33 – 7.27 (m, 3H), 7.24 (d, $J = 8.2$ Hz, 2H), 7.23 – 7.15 (m, 4H), 4.28 (d, $J = 4.4$ Hz, 2H), 2.36 (s, 3H), 1.90 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): 156.9, 140.2, 138.1, 137.4, 129.3, 129.1, 129.0, 126.9, 126.1, 59.5, 21.1. ^{19}F NMR (376 MHz, CDCl_3): -80.87 (t, 3F), -102.90 (t, 2F), -118.75 (s, 2F), -121.85 (d, 6F), -122.78 (s, 2F), -126.19 (t, 2F). IR (cm^{-1}): 3438, 3082, 3057, 3025, 2962, 2924, 1630, 1610, 1598, 1577, 1509, 1491, 1444, 1369, 1352, 1303, 1241, 1212, 1148, 1134, 1112, 1074, 1032, 1022, 1001, 960, 935, 900, 873, 818, 776, 738, 723, 701, 679, 661, 626, 605. HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{14}\text{F}_{17}^+$ (M-OH) $^+$: 625.08186, found 625.08160.

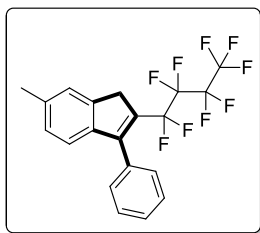


2-(diphenylmethylene)-3,3,4,4,5,5,6,6,6-nonafluorohexyl 4-nitrobenzoate **5a**, 70%, M.P. = 123-125 °C, pale yellow solid.

^1H NMR (400 MHz, CDCl_3): 8.36 (d, $J = 8.8$ Hz, 2H), 8.23 (d, $J = 8.8$ Hz, 2H), 7.36 – 7.31 (m, 5H), 7.25 (dd, $J = 12.3, 7.7$ Hz, 5H), 4.99 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): 155.7 (t, $J = 4.5$ Hz), 139.5, 139.0, 134.6, 129.5, 128.7, 127.8, 127.4, 126.7, 126.5 (t, $J = 19$ Hz), 126.4, 118.8, 117.3 (t, $J = 143$ Hz), 116.0, 59.3. ^{19}F NMR (376 MHz, CDCl_3): -80.88 (d, 3F), -102.92 (t, 2F), -119.88 (m, 2F), -125.78 – -126.03 (m, 2F). IR (cm^{-1}): 3083, 3058, 3024, 2864, 1731, 1609, 1578, 1530, 1491, 1468, 1446, 1412, 1351, 1319, 1270, 1236, 1203, 1135, 1115, 1100, 1016, 957, 923, 873, 850, 783, 741, 719, 704, 601.



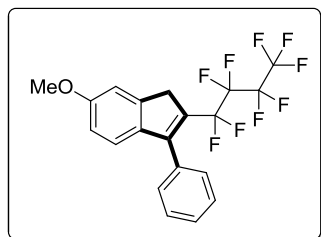
2-(perfluorobutyl)-3-phenyl-1H-indene **6a**, 75%, M.P. = 40-42 °C, pale yellow solid. ^1H NMR (400 MHz, CDCl_3): 7.60 (d, $J = 7.3$ Hz, 1H), 7.54 – 7.44 (m, 3H), 7.43 – 7.32 (m, 4H), 7.16 (d, $J = 7.5$ Hz, 1H), 3.85 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): 149.6 (t, $J = 5.0$ Hz), 142.4, 134.3, 131.6, 130.0, 128.4, 128.2, 128.0, 127.6, 127.1, 123.9, 122.2, 38.8. ^{19}F NMR (376 MHz, CDCl_3): -80.99 (t, 3F), -103.25 (td, 2F), -121.27 – -121.76 (m, 2F), -125.72 – -125.96 (m, 2F). IR (cm^{-1}): 3058, 3029, 2927, 1952, 1807, 1625, 1596, 1581, 1493, 1463, 1445, 1397, 1355, 1296, 1235, 1205, 1133, 1102, 1084, 1074, 1014, 929, 945, 920, 885, 846, 838, 826, 773, 743, 732, 700, 658, 638, 603. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{12}\text{F}_9$ ⁺ ($\text{M}+\text{H}$)⁺: 411.07898, found 411.07849.



6-methyl-2-(perfluorobutyl)-3-phenyl-1H-indene **6b**, 81%, oil.

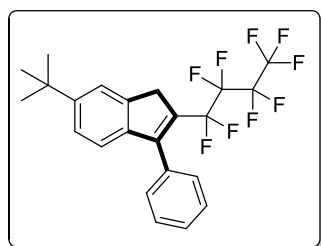
^1H NMR (400 MHz, CDCl_3): 7.46 (t, $J = 6.5$ Hz, 3H), 7.41 (s, 1H), 7.38 – 7.35 (m, 2H), 7.16 (d, $J = 7.9$ Hz, 1H), 7.04 (d, $J = 7.8$ Hz, 1H), 3.80 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 150.7 (t, $J = 5.0$ Hz), 142.8 (d, $J = 32$ Hz), 142.5, 137.6, 133.4, 128.6, 128.0, 127.7, 127.3, 126.9, 126.1 (t, $J = 23$ Hz), 124.6, 123.8, 122.4, 122.1, 38.5, 21.5. ^{19}F NMR (376 MHz, CDCl_3): -81.00 (t, 3F), -102.96 – -103.18 (m, 2F), -121.46 – -121.67 (m, 2F), -125.77 – -125.94 (m, 2F). IR (cm^{-1}): 3058, 3029, 2926, 2865, 1951, 1621, 1597, 1579, 1510, 1493, 1445, 1400, 1354, 1235, 1213, 1170,

1133, 1108, 1083, 1015, 949, 932, 921, 890, 873, 821, 785, 761, 742, 722, 700, 658, 615. HRMS (ESI) m/z calcd for $C_{20}H_{14}F_9^+$ ($M+H$) $^+$: 425.09463, found 425.09494.



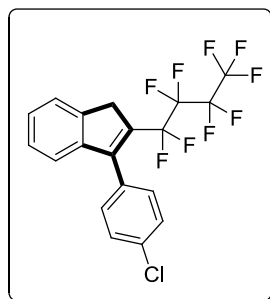
6-methoxy-2-(perfluorobutyl)-3-phenyl-1H-indene **6c**, 77%, oil.

1H NMR (400 MHz, $CDCl_3$): 7.51 – 7.43 (m, 3H), 7.36 (d, J = 7.7 Hz, 2H), 7.15 (d, J = 2.0 Hz, 1H), 7.05 (d, J = 8.5 Hz, 1H), 6.88 (dd, J = 8.5, 2.3 Hz, 1H), 3.88 (s, 3H), 3.80 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.9, 150.6 (t, J = 5.0 Hz), 144.5, 138.1, 133.5, 128.5, 128.1, 128.0, 124.7 (t, J = 23 Hz), 123.1, 118.9 (d, J = 23 Hz), 118.6, 116.4, 116.0 (t, J = 35 Hz), 115.7, 113.5, 113.1, 55.6, 38.7. ^{19}F NMR (376 MHz, $CDCl_3$): -81.01 (t, 3F), -102.88 – -103.16 (m, 2F), -121.54 (d, 2F), -125.62 – -125.95 (m, 2F). IR (cm^{-1}): 3052, 2940, 2838, 1610, 1596, 1580, 1483, 1468, 1444, 1437, 1399, 1354, 1288, 1231, 1170, 1133, 1108, 1082, 1034, 1014, 949, 932, 920, 876, 839, 813, 785, 762, 742, 724, 700, 662, 618. HRMS (ESI) m/z calcd for $C_{20}H_{14}F_9O^+$ ($M+H$) $^+$: 441.08955, found 441.08963.



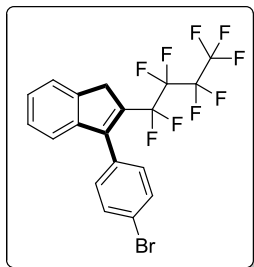
6-(tert-butyl)-2-(perfluorobutyl)-3-phenyl-1H-indene **6d**, 81%, oil.

1H NMR (400 MHz, $CDCl_3$): 7.66 (s, 1H), 7.47 (t, J = 6.4 Hz, 3H), 7.43 – 7.36 (m, 3H), 7.11 (d, J = 8.1 Hz, 1H), 3.85 (s, 2H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.1, 150.7 (t, J = 5.0 Hz), 142.5 (d, J = 6.0 Hz), 133.5, 130.1, 128.6, 128.3, 128.1, 128.0, 126.8, 126.6, 126.3, 124.9, 124.1, 123.8, 122.6, 121.9, 120.9, 118.9, 116.1 (t, J = 260 Hz), 113.6, 38.8, 34.9, 31.3. ^{19}F NMR (376 MHz, $CDCl_3$): -80.77 – -81.06 (m, 3F), -102.95 – -103.32 (m, 2F), -121.16 – -121.78 (m, 2F), -125.67 – -125.93 (m, 2F). IR (cm^{-1}): 3058, 3032, 2965, 2906, 2871, 1950, 1625, 1596, 1576, 1493, 1463, 1445, 1426, 1401, 1398, 1354, 1293, 1235, 1217, 1204, 1133, 1093, 1076, 1015, 947, 933, 921, 889, 875, 830, 779, 765, 744, 730, 716, 700, 674, 617. HRMS (ESI) m/z calcd for $C_{23}H_{20}F_9^+$ ($M+H$) $^+$: 467.14158, found 467.14166.



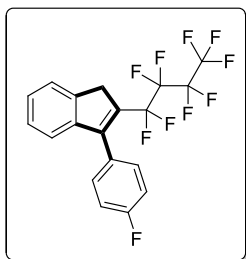
3-(4-chlorophenyl)-2-(perfluorobutyl)-1H-indene **6e**, 60%, M.P. = 48-50 °C, pale yellow solid.

¹H NMR (400 MHz, CDCl₃): 7.60 (d, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.41 (td, *J* = 7.4, 1.1 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 3.85 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): 149.6 (t, *J* = 4.5 Hz), 144.5, 142.4, 134.3, 131.6, 130.0, 128.4, 128.1, 127.9, 127.6, 127.1, 123.9, 122.2, 38.8. ¹⁹F NMR (376 MHz, CDCl₃): -80.97 (t, 3F), -103.16 – -103.47 (m, 2F), -121.55 (m, 2F), -125.71 – -125.99 (m, 2F). IR (cm⁻¹): 3073, 2927, 1624, 1581, 1490, 1463, 1398, 1354, 1295, 1235, 1205, 1133, 1102, 1090, 1017, 943, 921, 889, 837, 771, 733, 717, 700, 645, 605. HRMS (ESI) *m/z* calcd for C₁₉H₁₁ClF₉⁺ (M+H)⁺: 445.04001, found 445.03958.



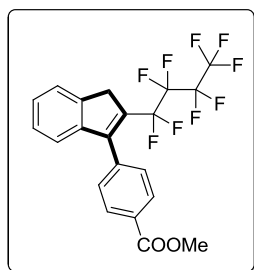
3-(4-bromophenyl)-2-(perfluorobutyl)-1H-indene **6f**, 78%, M.P. = 72-74 °C, yellow solid.

¹H NMR (400 MHz, CDCl₃): 7.61 (t, *J* = 9.0 Hz, 3H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 3.85 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): 149.6 (t, *J* = 5.0 Hz), 144.5, 142.4, 132.1, 131.4, 130.3, 128.5, 128.2, 127.9, 127.6, 127.1, 123.9, 122.5, 122.2, 118.8, 115.9 (t, *J* = 273 Hz), 113.4, 38.8. ¹⁹F NMR (376 MHz, CDCl₃): -80.98 (t, 3F), -103.17 – -103.45 (m, 2F), -121.29 – -121.81 (m, 2F), -125.70 – -126.09 (m, 2F). IR (cm⁻¹): 3072, 3028, 2928, 1752, 1735, 1719, 1701, 1685, 1654, 1625, 1579, 1561, 1483, 1463, 1394, 1355, 1295, 1235, 1205, 1133, 1102, 1083, 1072, 1013, 942, 921, 889, 836, 771, 744, 734, 712, 699, 669, 661, 618, 604. HRMS (ESI) *m/z* calcd for C₁₉H₁₁BrF₉⁺ (M+H)⁺: 488.98949, found 488.98940.



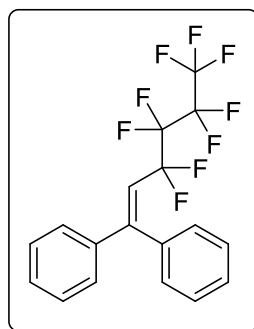
3-(4-fluorophenyl)-2-(perfluorobutyl)-1H-indene **6g**, 75%, oil.

¹H NMR (400 MHz, CDCl₃): 7.60 (d, *J* = 7.3 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.38 – 7.32 (m, 3H), 7.21 – 7.12 (m, 3H), 3.84 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): 163.9, 161.4, 149.9 (t, *J* = 5.0 Hz), 144.7, 142.4, 130.5 (d, *J* = 8.0 Hz), 129.0 (d, *J* = 4.0 Hz), 128.5, 128.3, 128.1, 128.0, 127.6, 127.0, 123.9, 122.2, 118.4, 116.0, 115.3, 115.1, 38.8. ¹⁹F NMR (376 MHz, CDCl₃): -81.00 (t, 3F), -103.11 – -103.41 (m, 2F), -113.53 (s, 1F), -121.29 – -121.76 (m, 2F), -125.62 – -125.97 (m, 2F). IR (cm⁻¹): 2928, 1652, 1625, 1593, 1581, 1490, 1463, 1398, 1354, 1295, 1235, 1205, 1153, 1133, 1103, 1090, 1017, 943, 921, 889, 837, 771, 733, 717, 700, 645, 619, 604. HRMS (ESI) *m/z* calcd for C₁₉H₁₁F₁₀⁺ (M+H)⁺: 429.06956, found 429.06955.



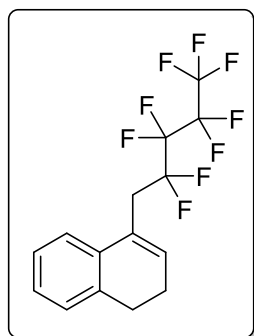
methyl 4-(2-(perfluorobutyl)-1H-inden-3-yl)benzoate **6h**, 65%, M.P.= 62-64 °C, pale yellow solid.

^1H NMR (400 MHz, CDCl_3): 8.16 (d, $J = 8.4$ Hz, 2H), 7.60 (d, $J = 7.4$ Hz, 1H), 7.43 (dd, $J = 15.8, 7.9$ Hz, 3H), 7.34 (t, $J = 7.3$ Hz, 1H), 7.09 (d, $J = 7.6$ Hz, 1H), 3.99 (s, 3H), 3.87 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): 166.8, 149.9 (t, $J = 5.0$ Hz), 144.4, 142.4, 138.1, 130.0, 129.4, 128.8, 128.1 (t, $J = 23$ Hz), 127.7, 127.1, 123.9, 122.2, 118.8, 115.9 (t, $J = 273$ Hz), 113.4, 52.2, 38.9. ^{19}F NMR (376 MHz, CDCl_3): -81.00 (t, 3F), -103.23 – -103.53 (m, 2F), -121.26 – -121.81 (m, 2F), -125.68 – -125.94 (m, 2F). IR (cm^{-1}): 3027, 2954, 1728, 1628, 1604, 1582, 1507, 1463, 1437, 1404, 1356, 1311, 1285, 1235, 1204, 1133, 1113, 1101, 1083, 1022, 968, 945, 923, 893, 857, 824, 774, 761, 744, 733, 711, 669, 663, 606. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{14}\text{F}_9\text{O}_2^+(\text{M}+\text{H})^+$: 469.08446, found 469.08426.



(3,3,4,4,5,5,6,6,6-nonafluorohex-1-ene-1,1-diyl)dibenzene **7**, 21%, oil

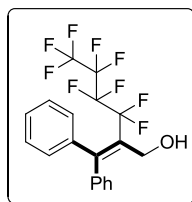
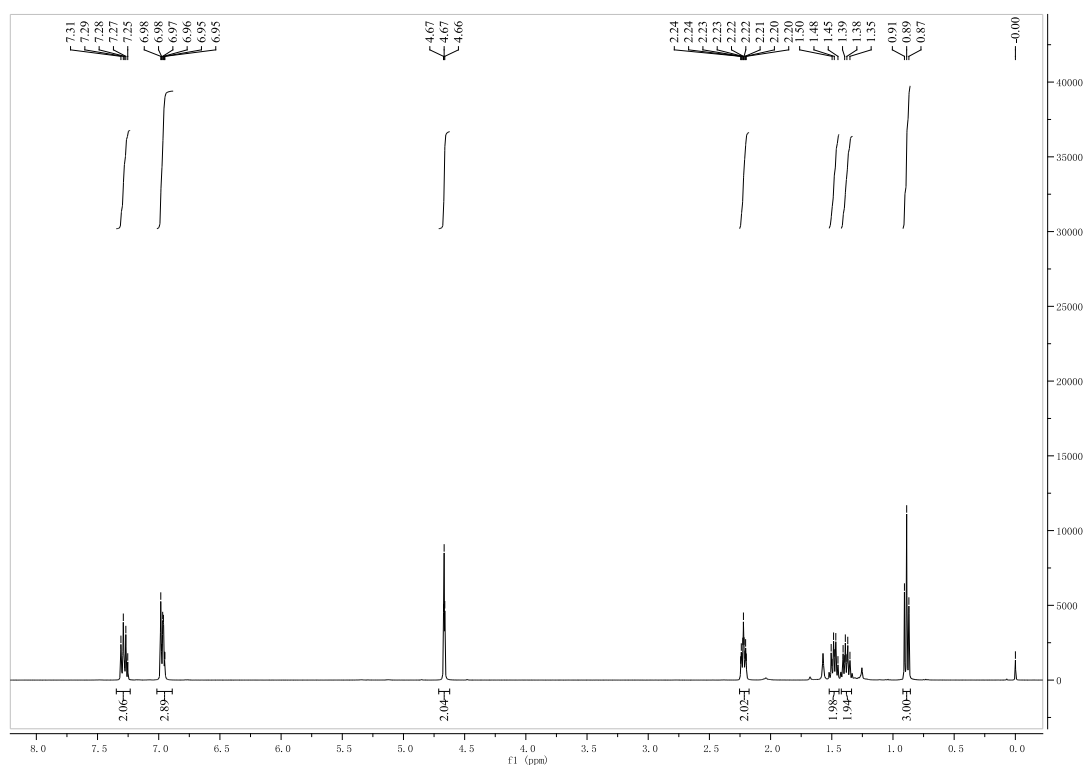
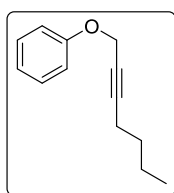
^1H NMR (400 MHz, CDCl_3): 7.30-7.36 (m, 6H), 7.21-7.24 (m, 4H), 6.08 (t, $J = 16$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 154.4, 141.9, 140.7, 137.4, 129.5, 129.0, 128.4 (d, $J = 18.0$ Hz), 128.1, 127.6, 112.8, 112.6, 112.4, 43.5, 35.6. ^{19}F NMR (376 MHz, CDCl_3): -81.01 (tt, 3F), -103.65 – -103.87 (m, 2F), -123.64 – -124.08 (m, 2F), -125.07 – -126.16 (m, 2F). IR (cm^{-1}): 2956, 2923, 2852, 1636, 1448, 1375, 1352, 1230, 1131, 1096, 1025, 908, 879, 759, 740, 698.



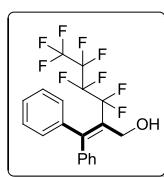
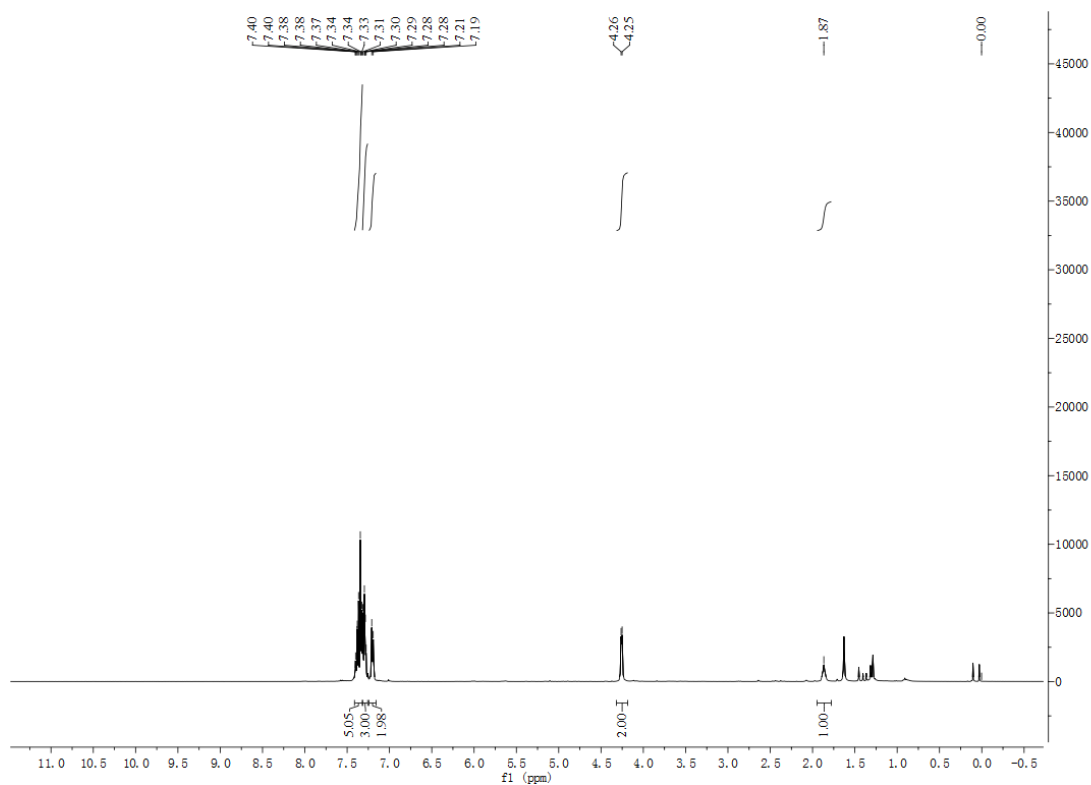
4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1,2-dihydronaphthalene **8**, 73%, oil

^1H NMR (400 MHz, CDCl_3): 7.30-7.36 (m, 4H), 5.98 (t, $J = 7.3$ Hz, 1H), 3.32 (d, $J = 18.7$ Hz, 2H), 3.26 (t, $J = 6.9$ Hz, 2H), 2.83 (q, $J = 7.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): 141.9, 134.9, 130.7, 128.5, 127.6, 126.4, 33.0, 31.7, 31.5 (t, $J = 25$ Hz), 31.2, 4.0. ^{19}F NMR (376 MHz, CDCl_3): -81.08 (tt, 3F), -111.55 (td, 2F), -123.79 – -124.32 (m, 2F), -125.89 (tt, 2F). IR (cm^{-1}): 2957, 2924, 2367, 1456, 1349, 1230, 1216, 1131, 1103, 1027, 879, 843, 805, 750, 696. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{F}_9^+$ ($\text{M}+\text{H}$) $^+$: 363.07898, found 363.07010.

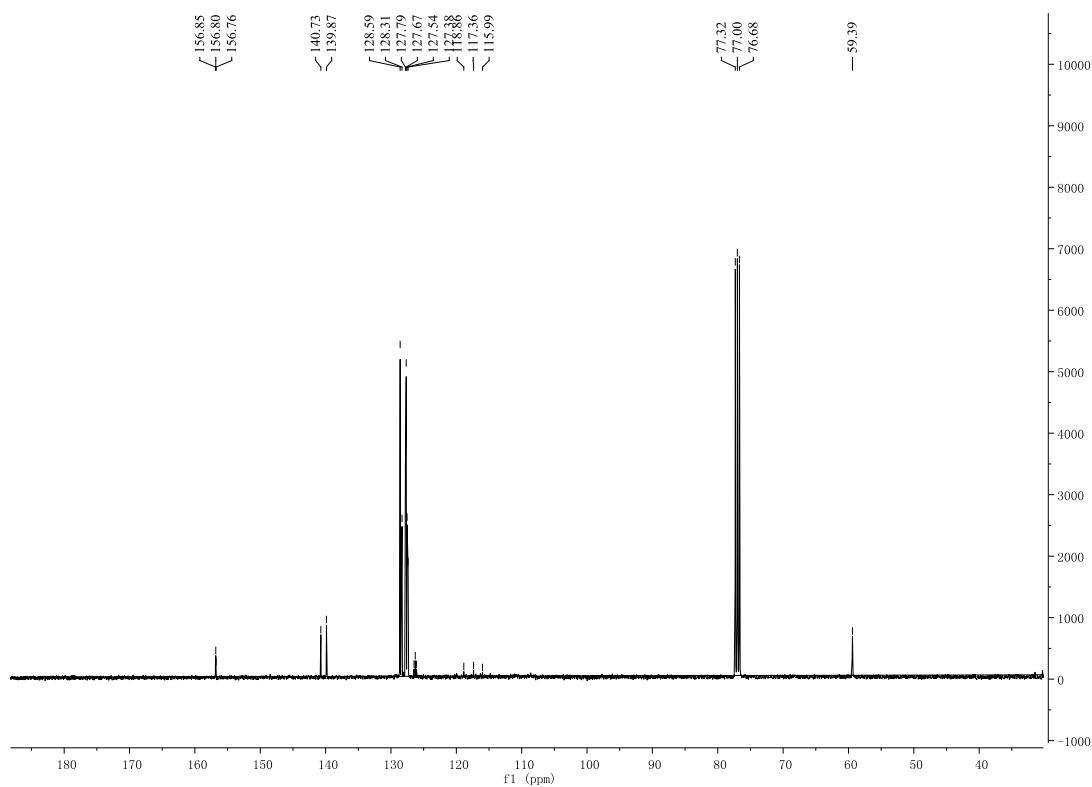
V. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra for compounds 3, 4, 5, 6, 7 and 8

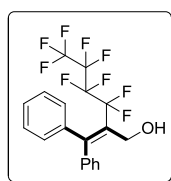


3aa

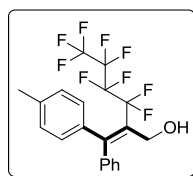
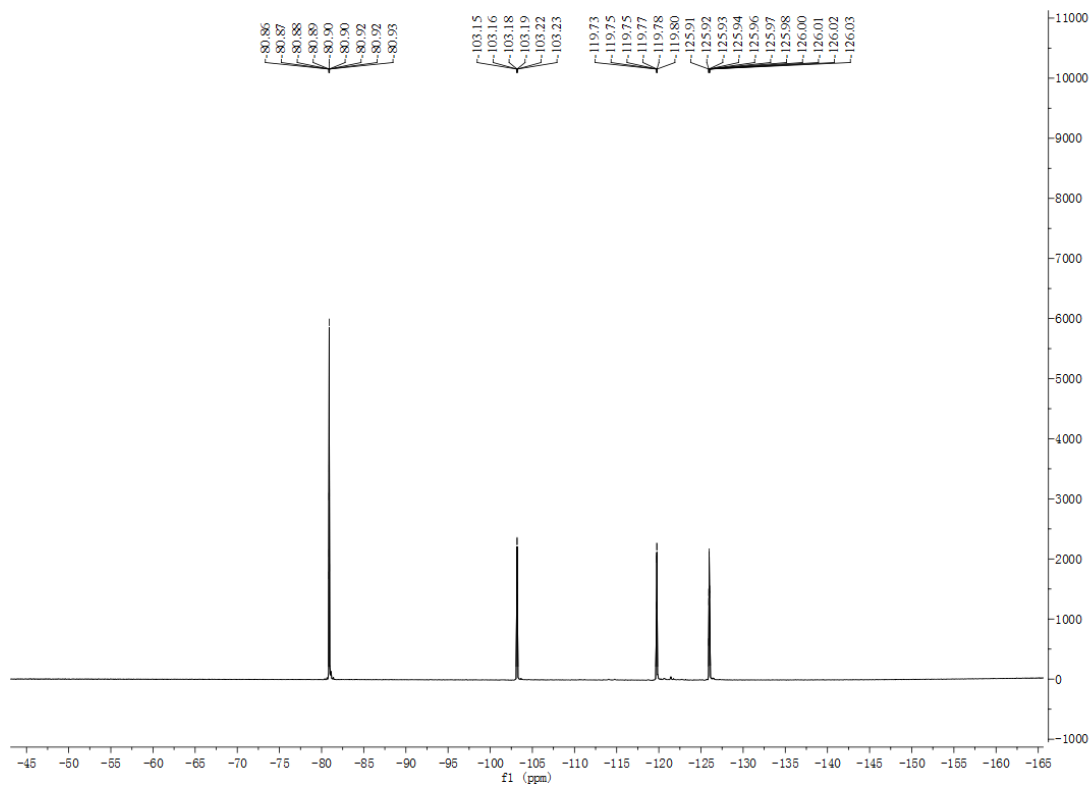


3aa

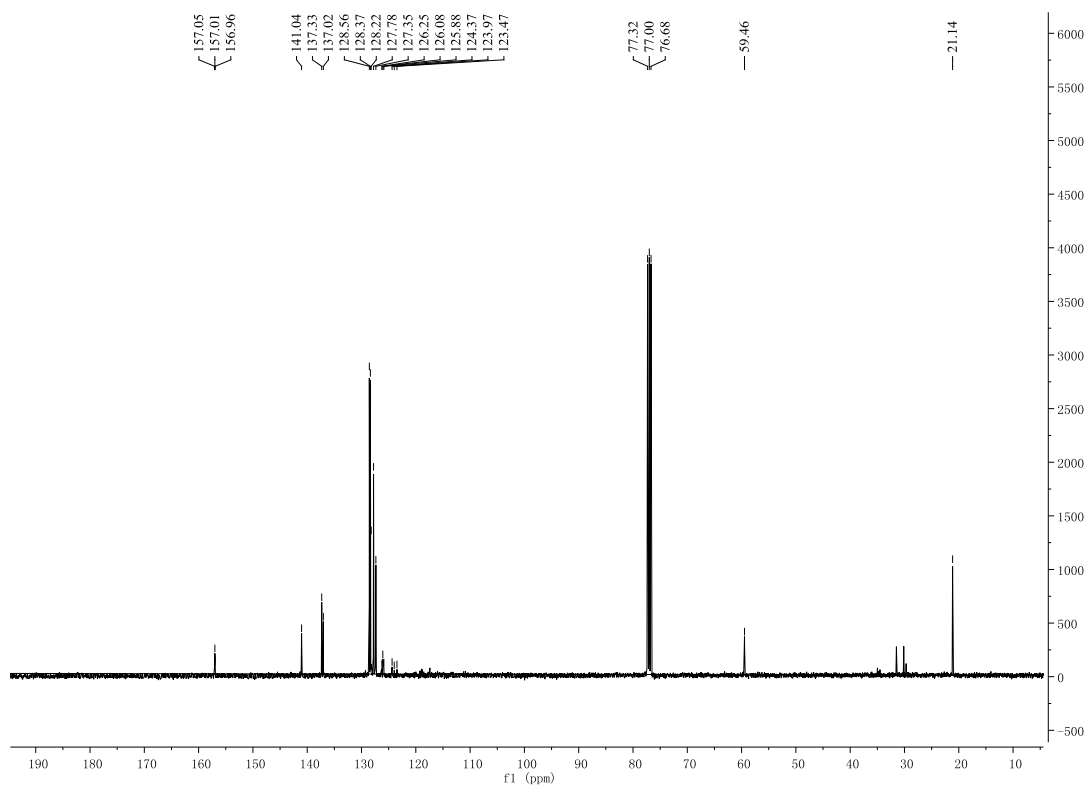
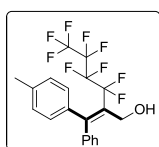


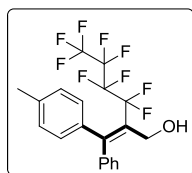


3aa

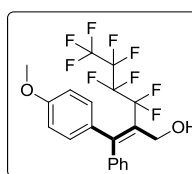
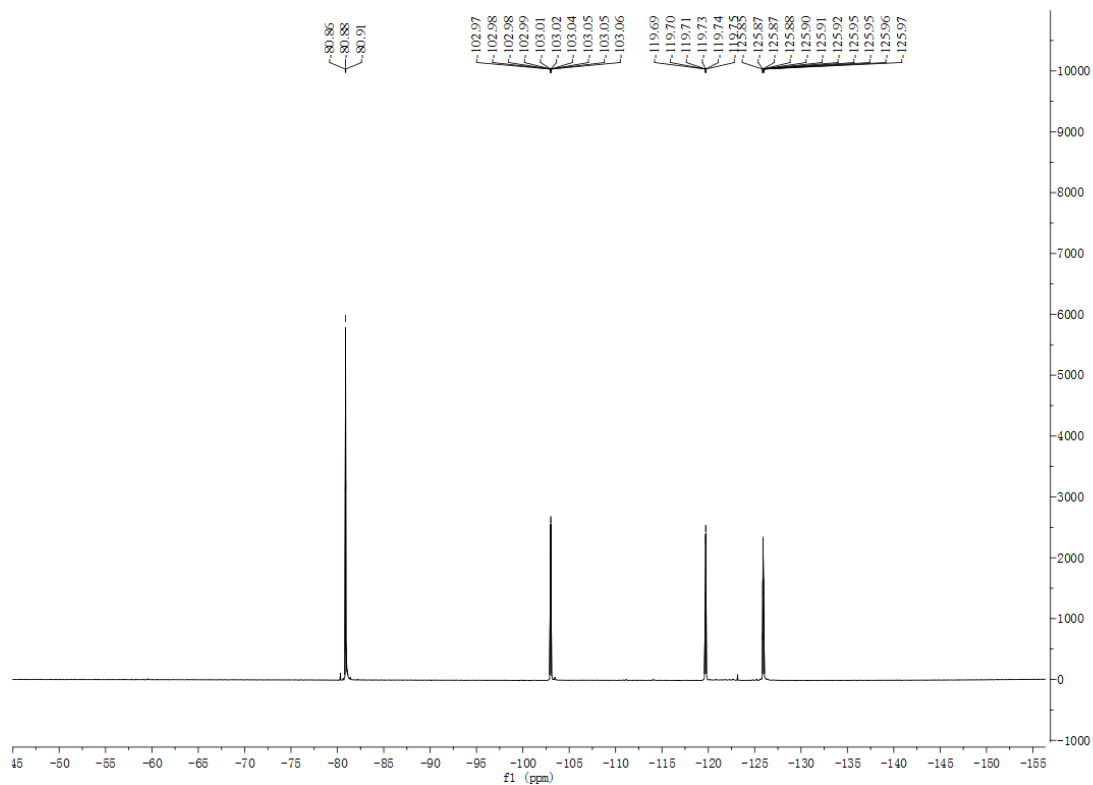


3ab

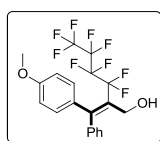
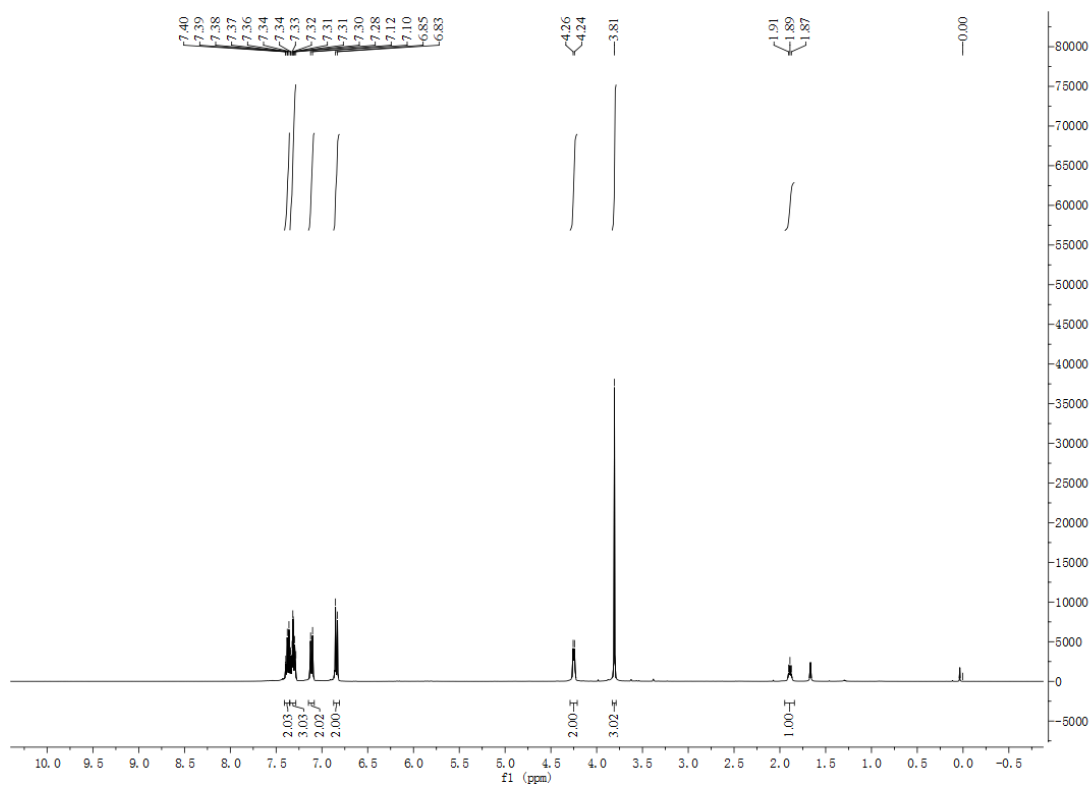




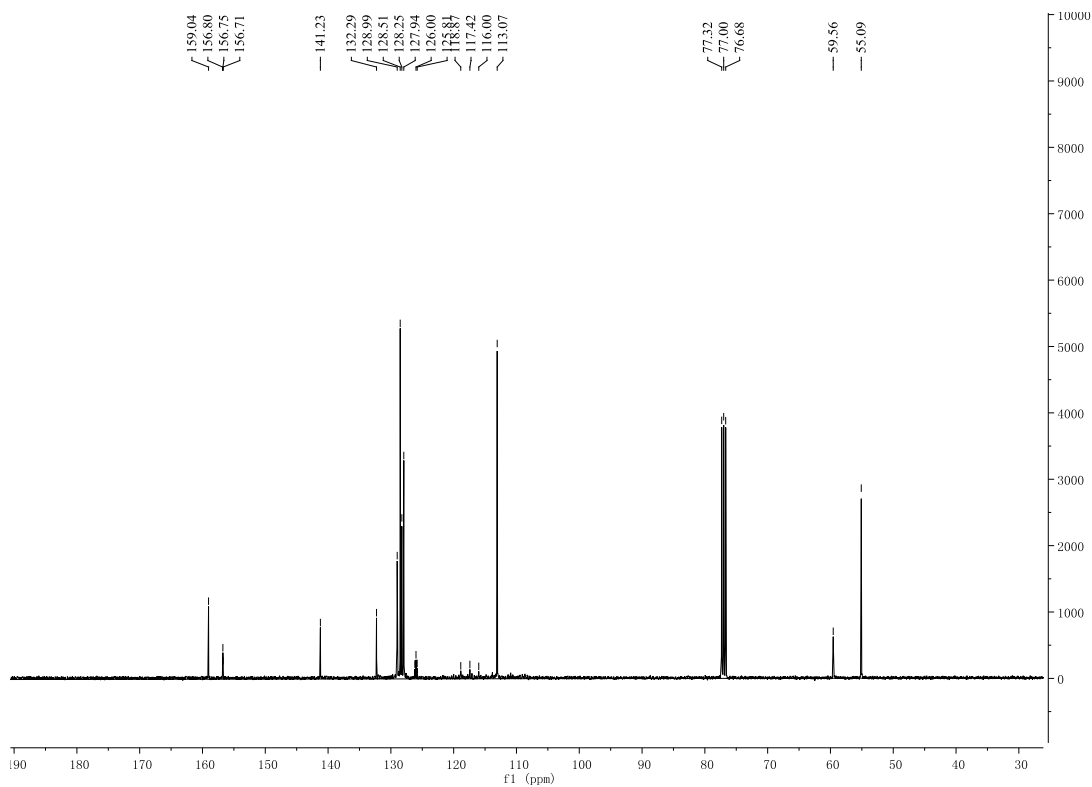
3ab

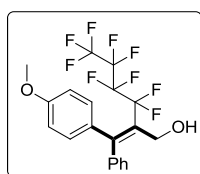


3ac

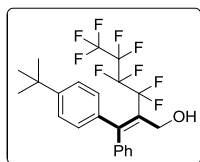
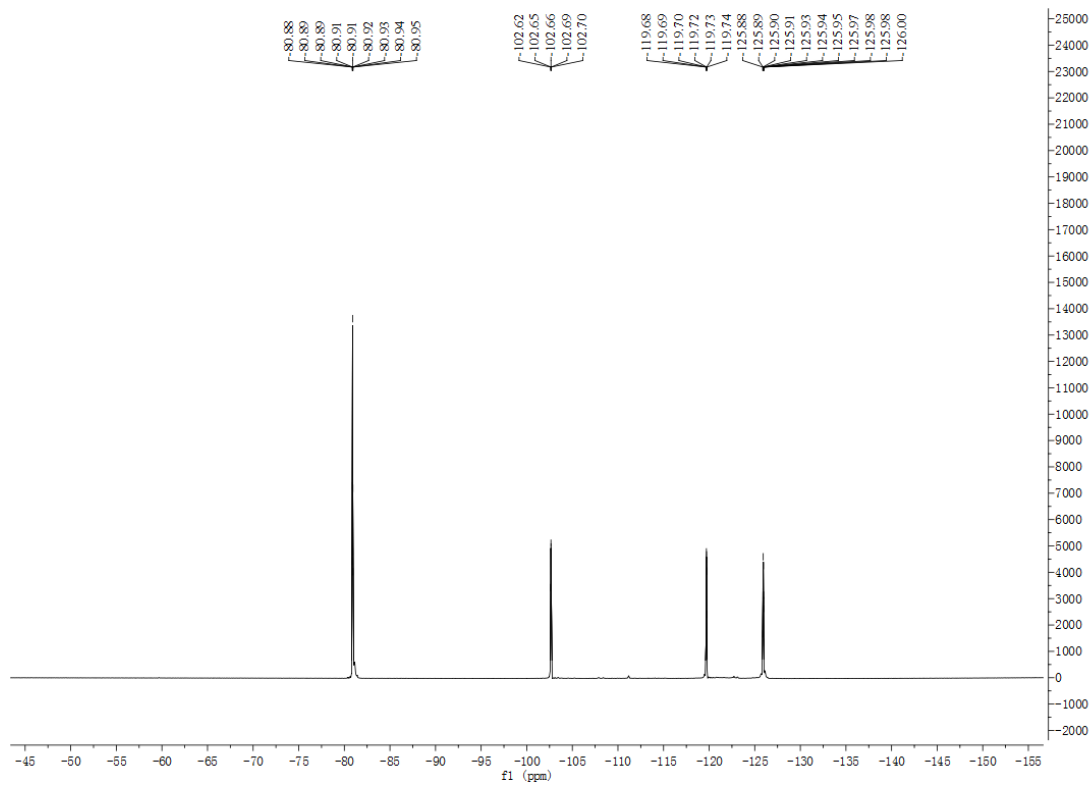


3ac

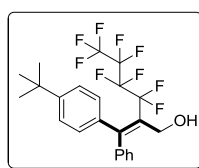
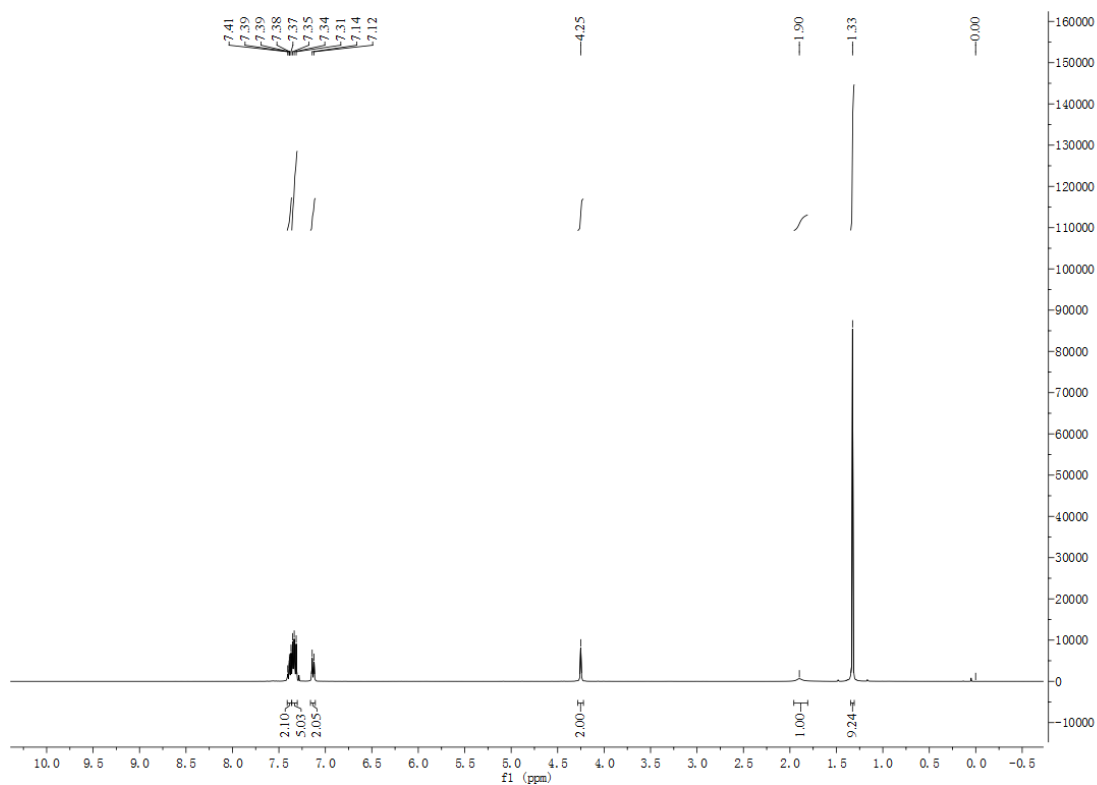




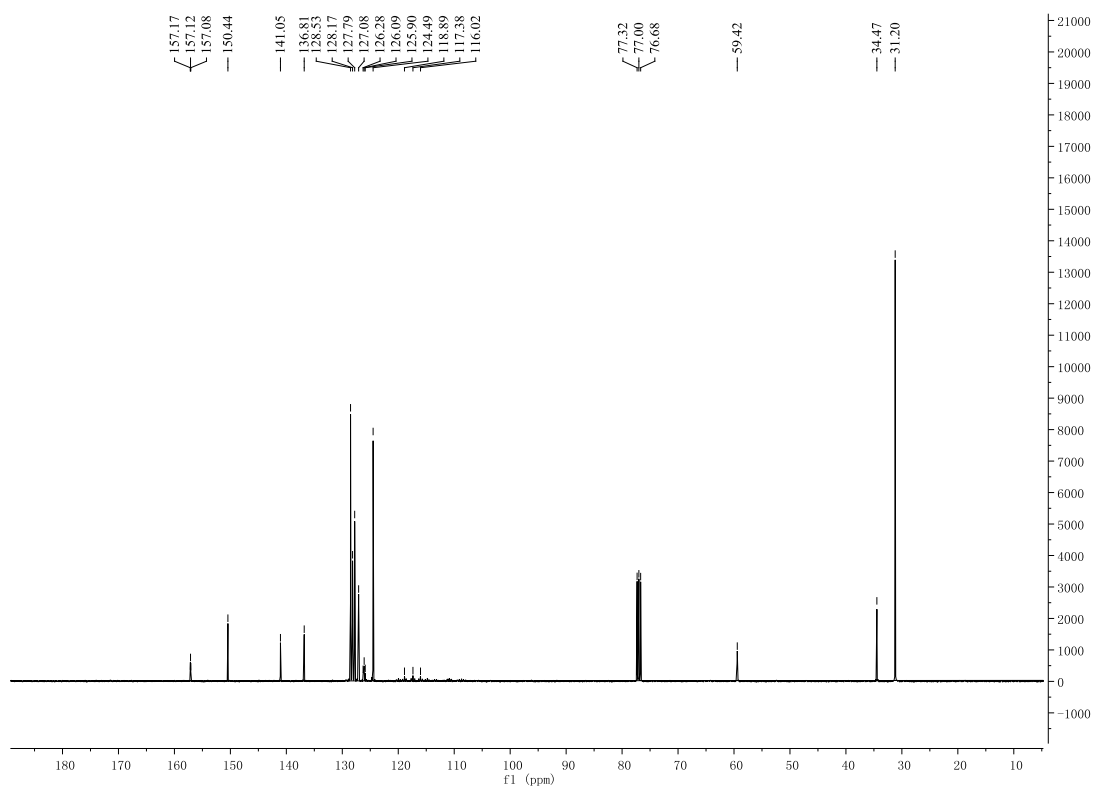
3ac

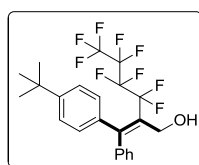


3ad

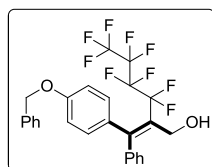
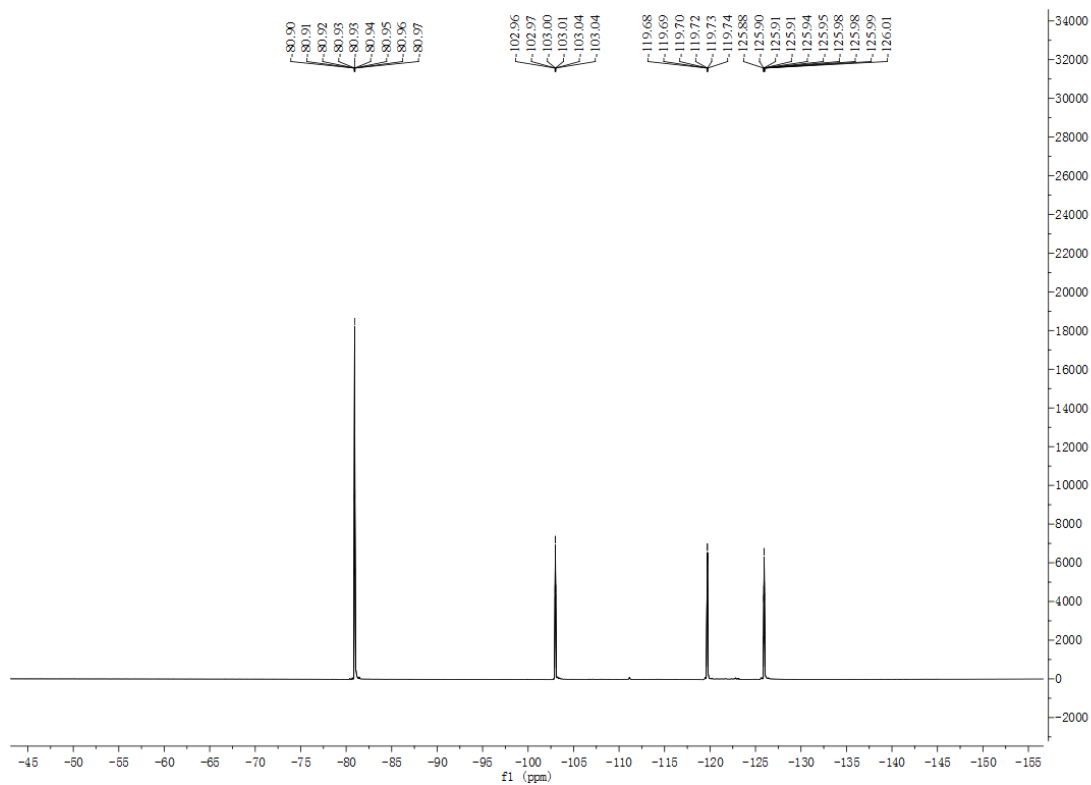


3ad

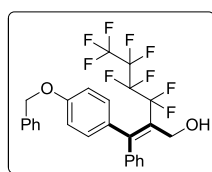




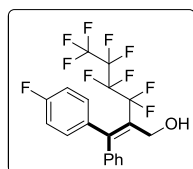
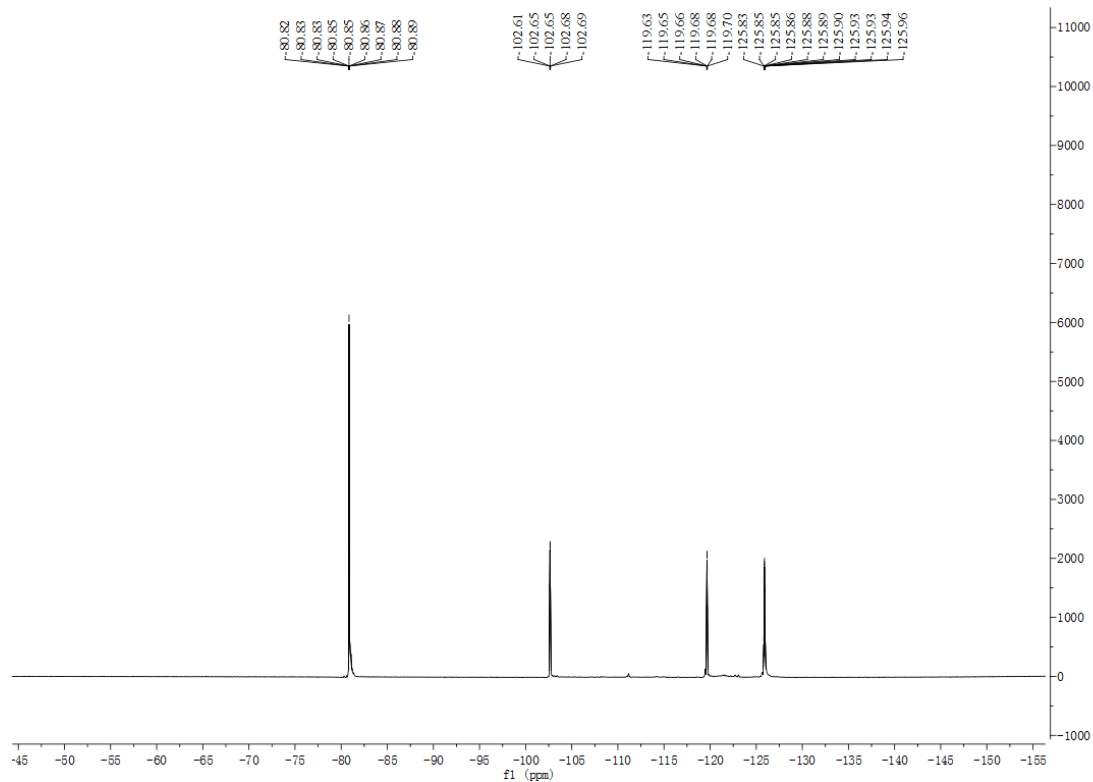
3ad



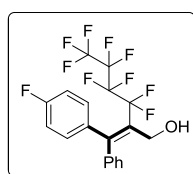
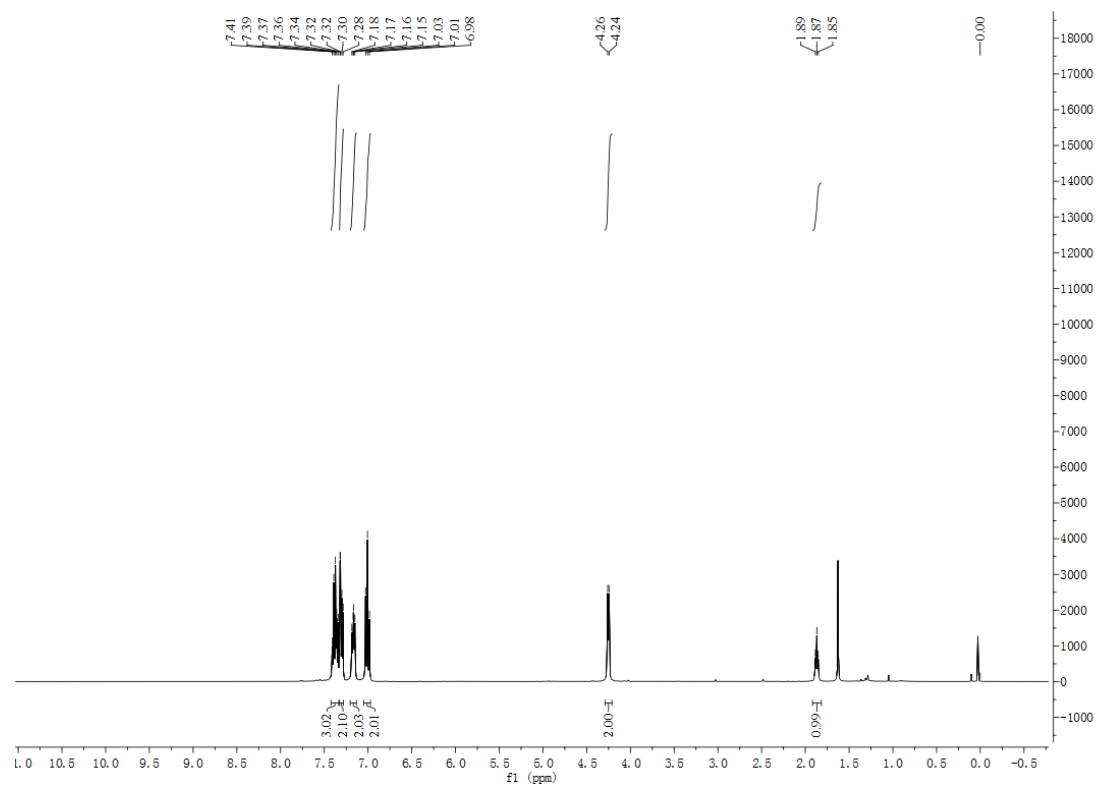
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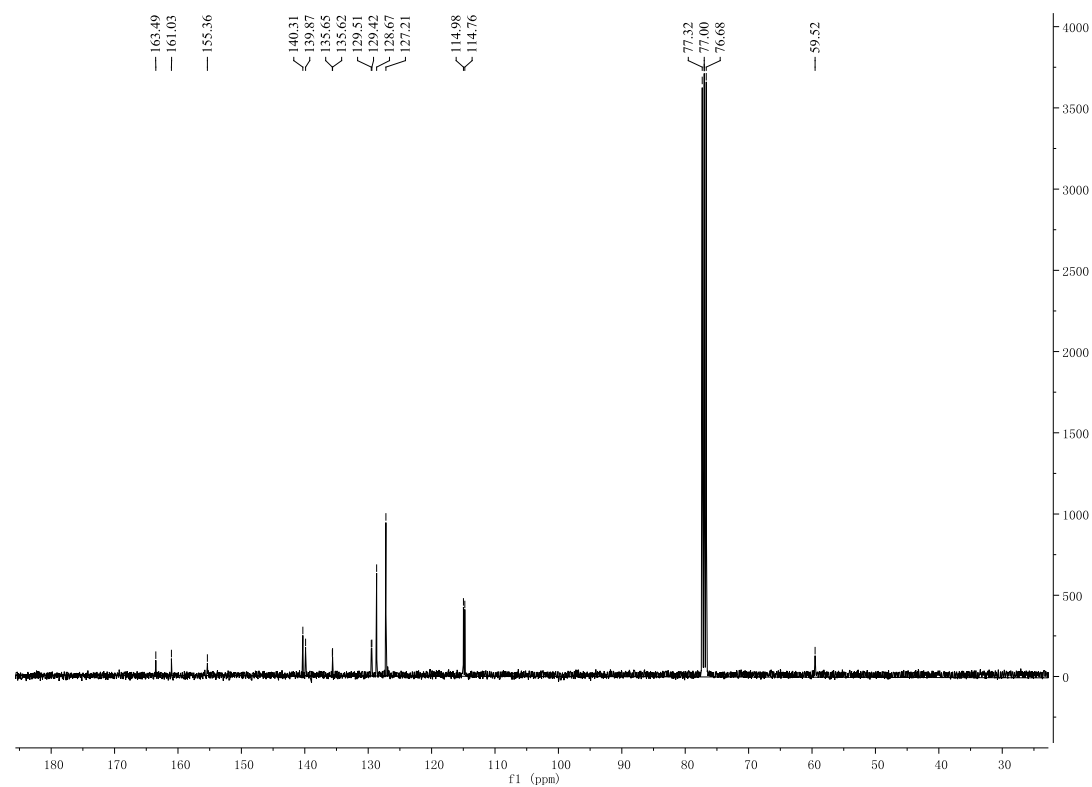
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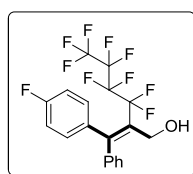


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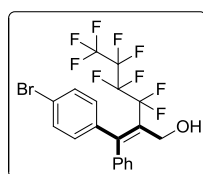
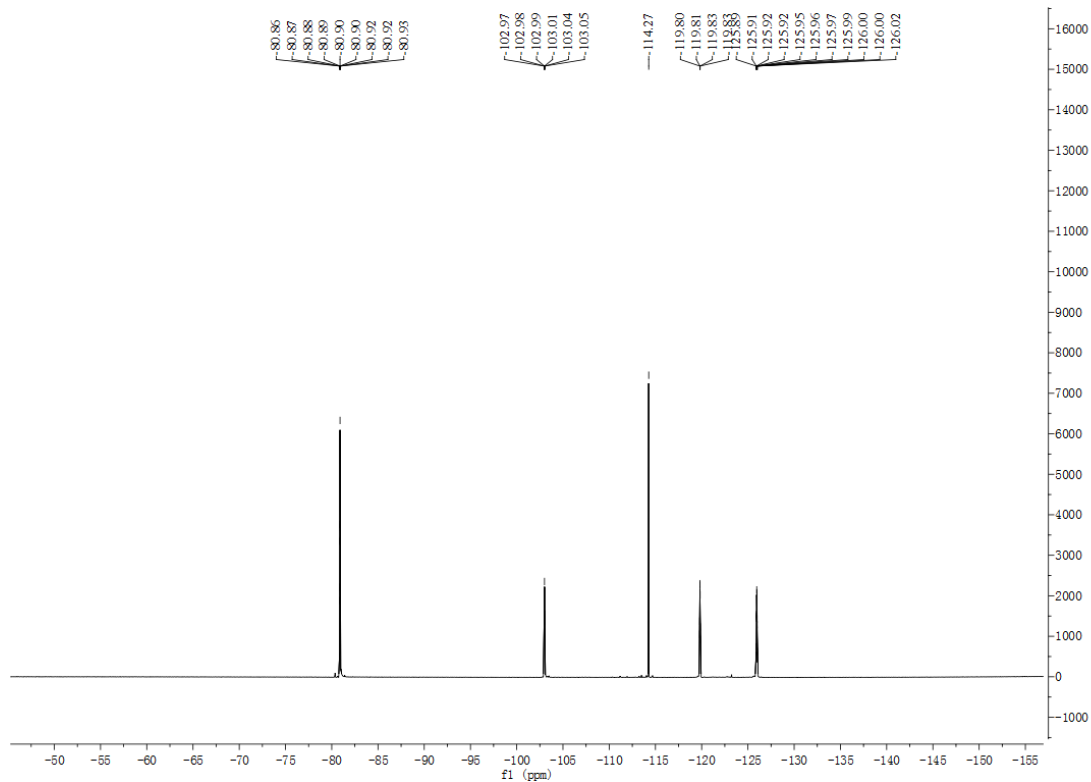


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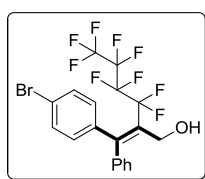
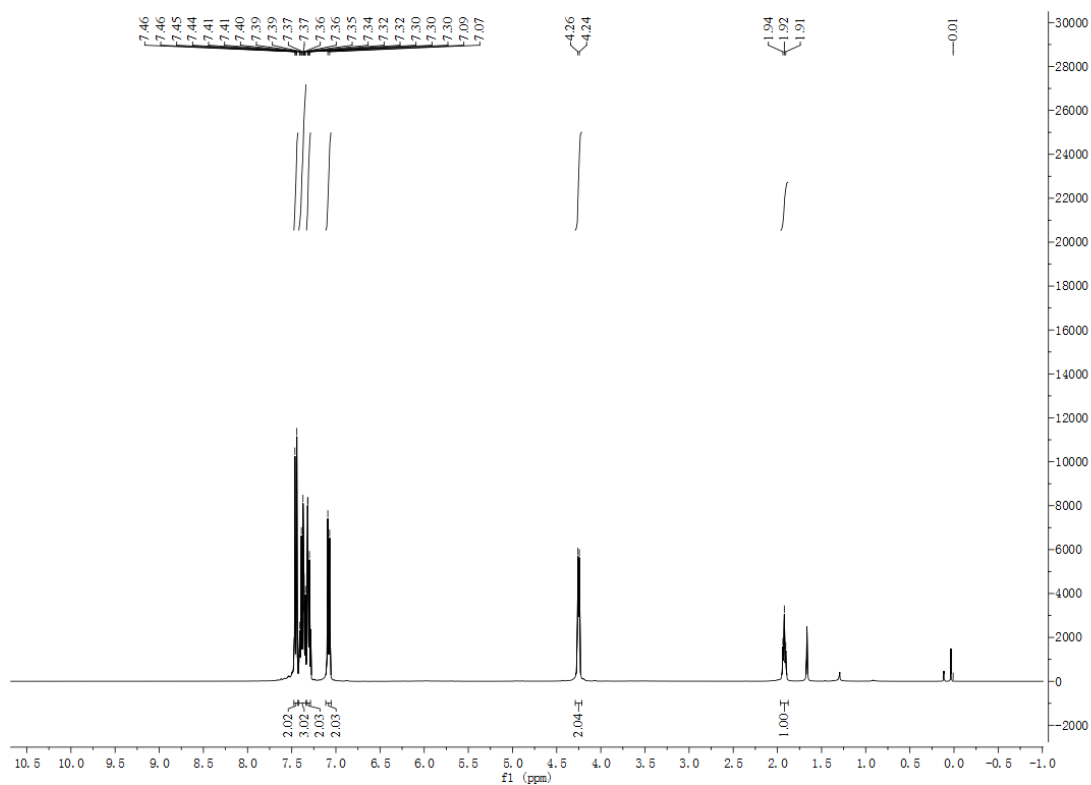




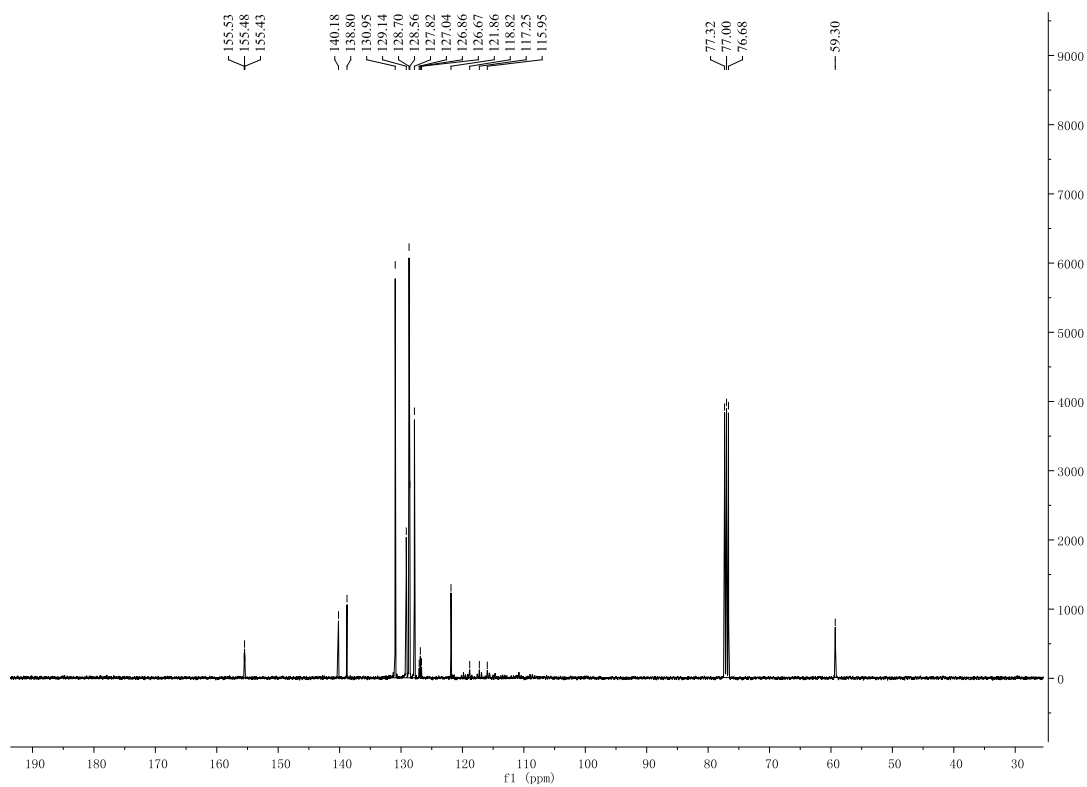
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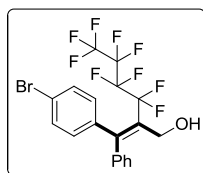


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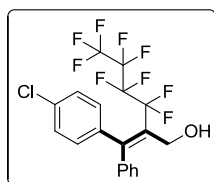
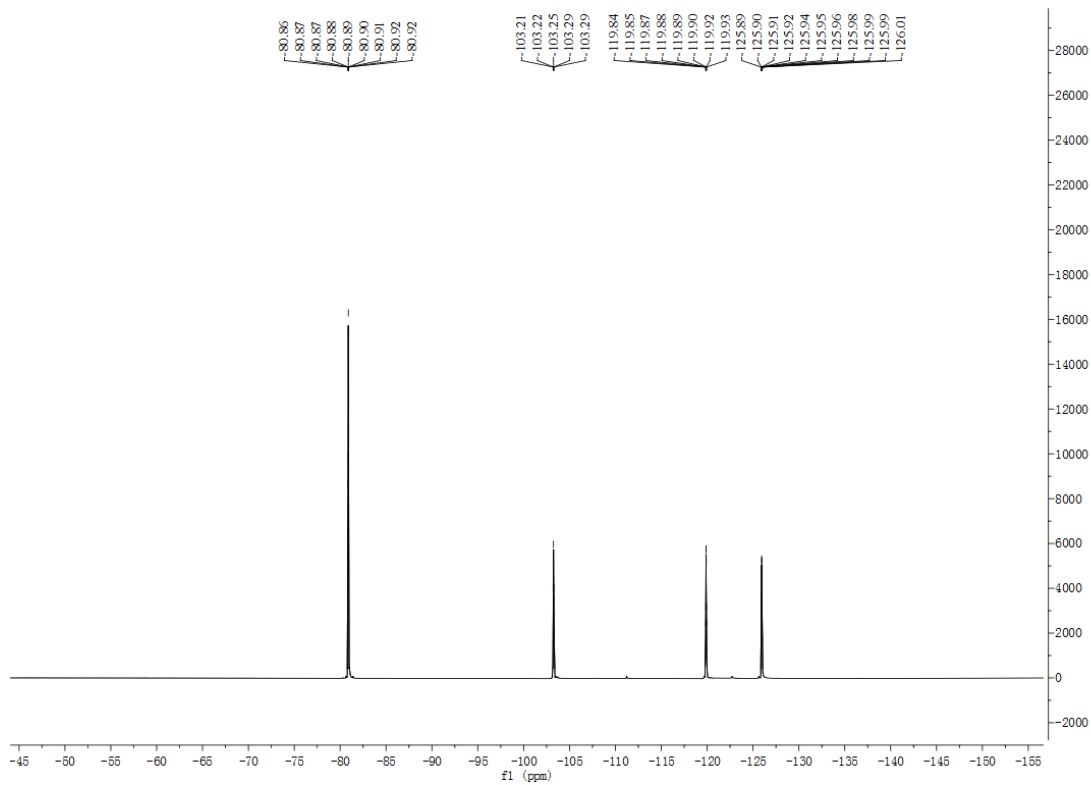


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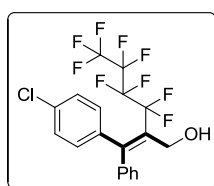
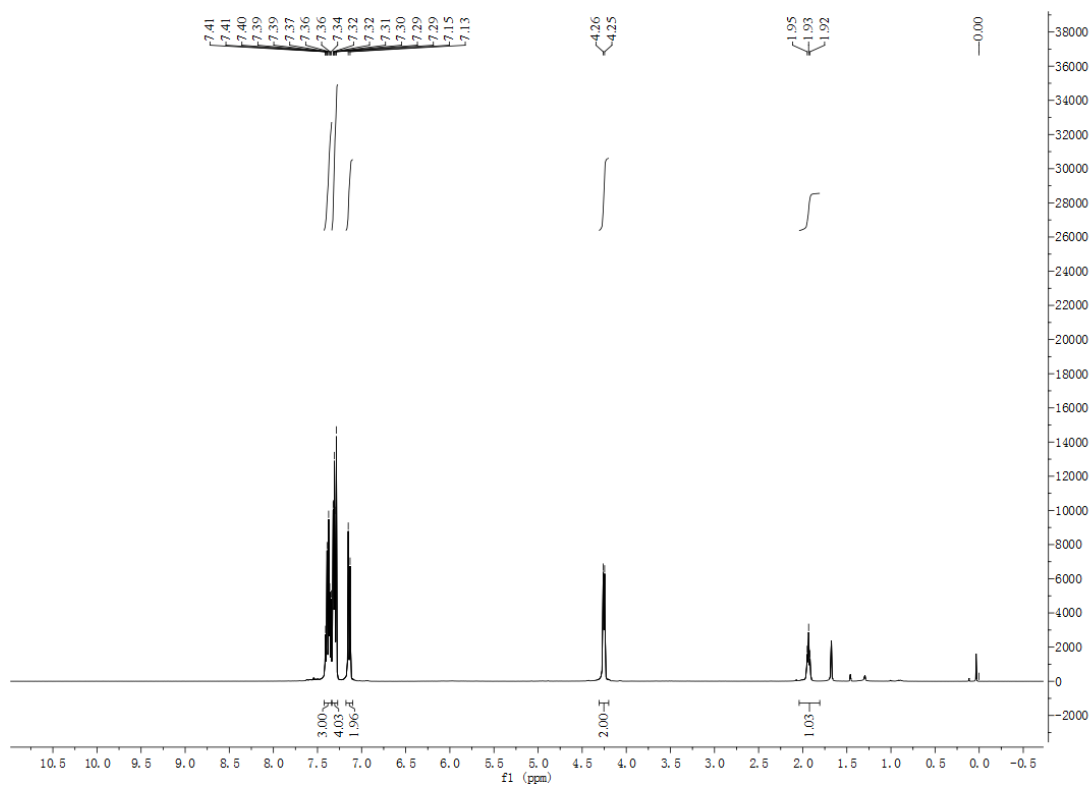




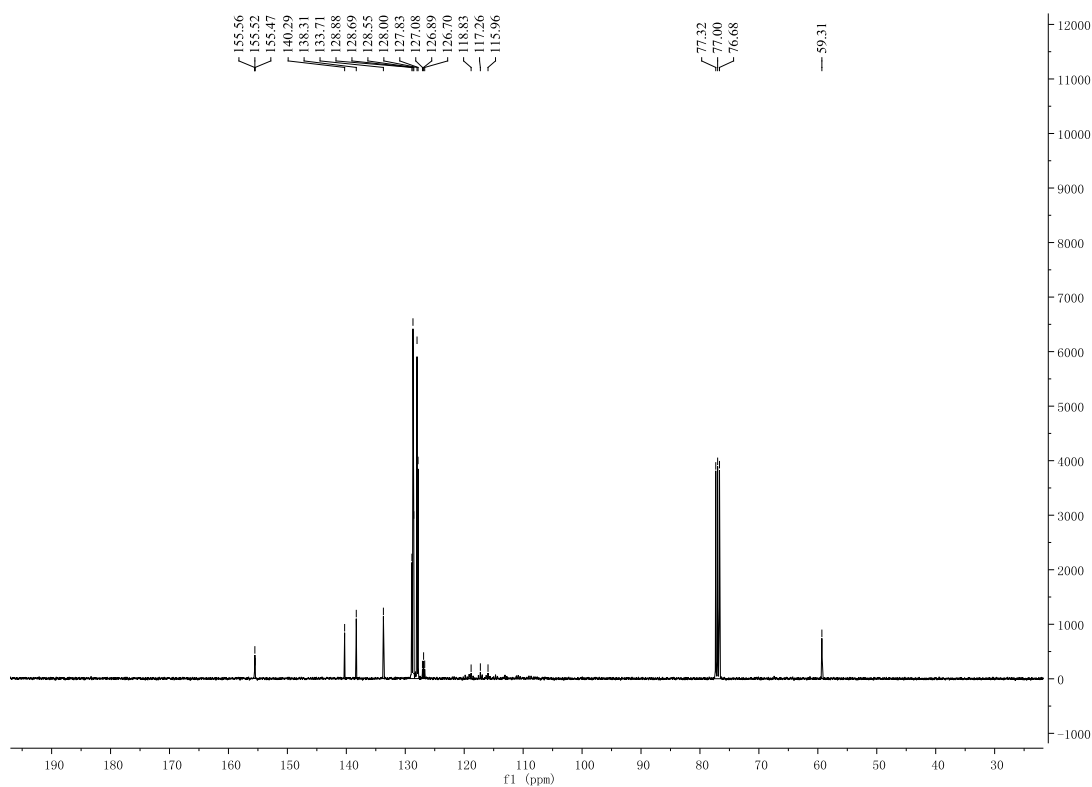
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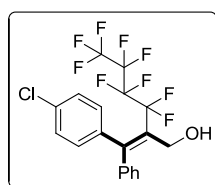


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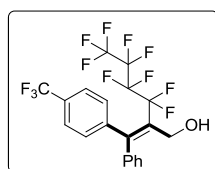
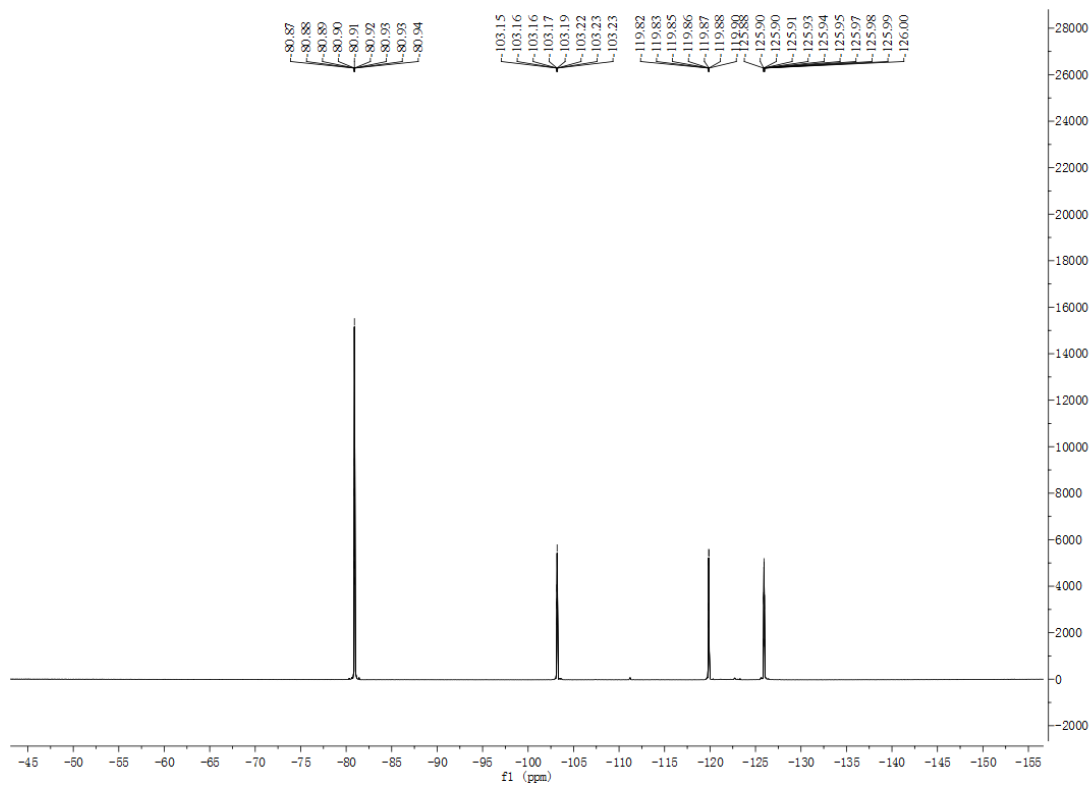


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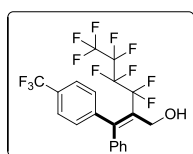
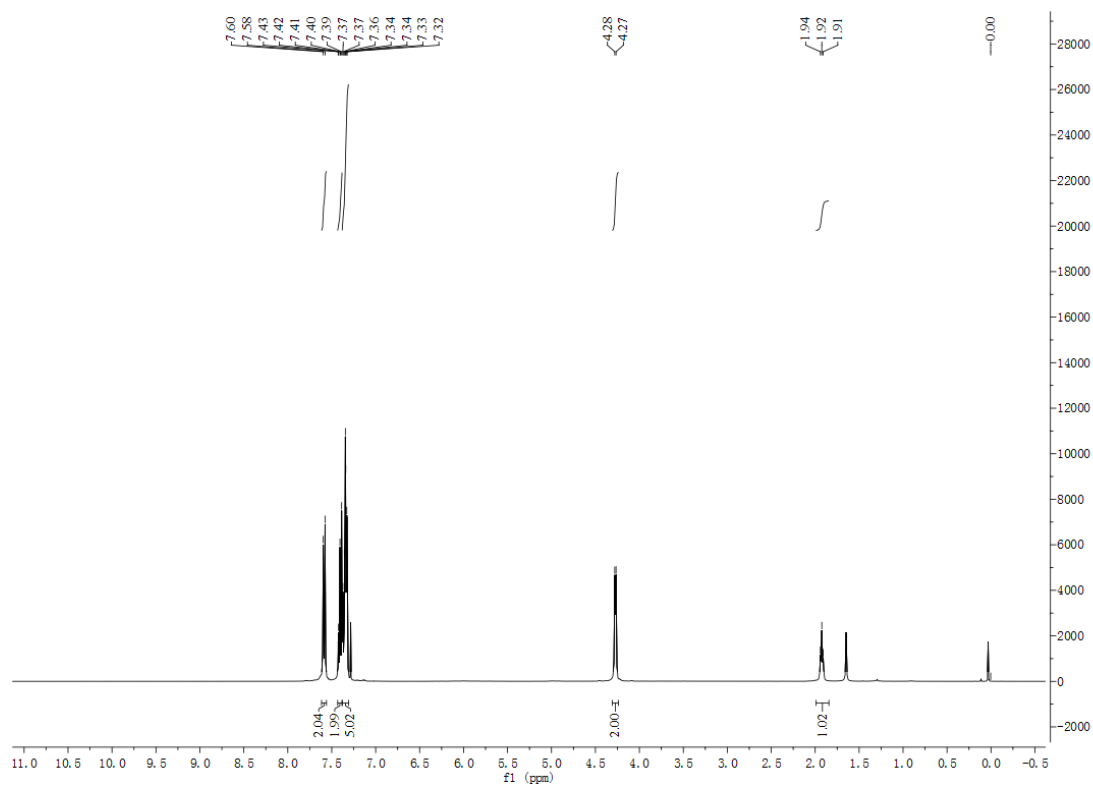




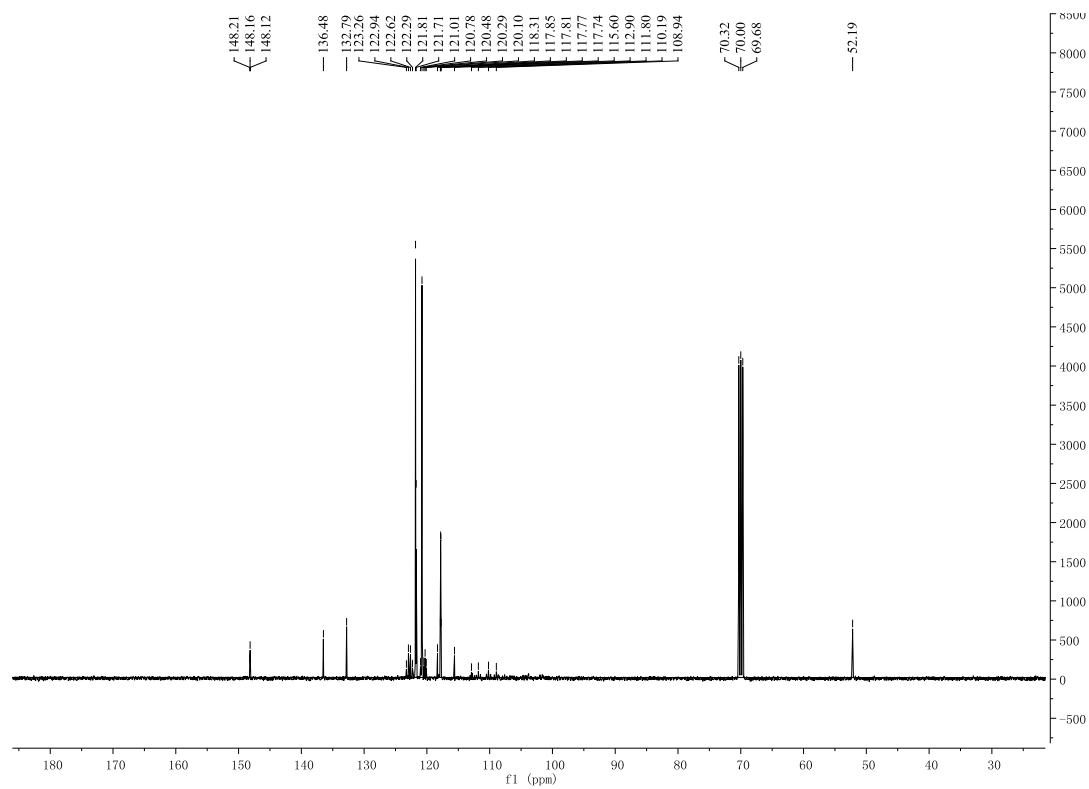
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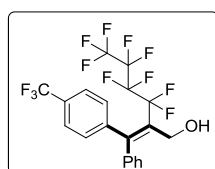


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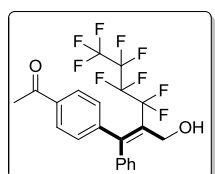
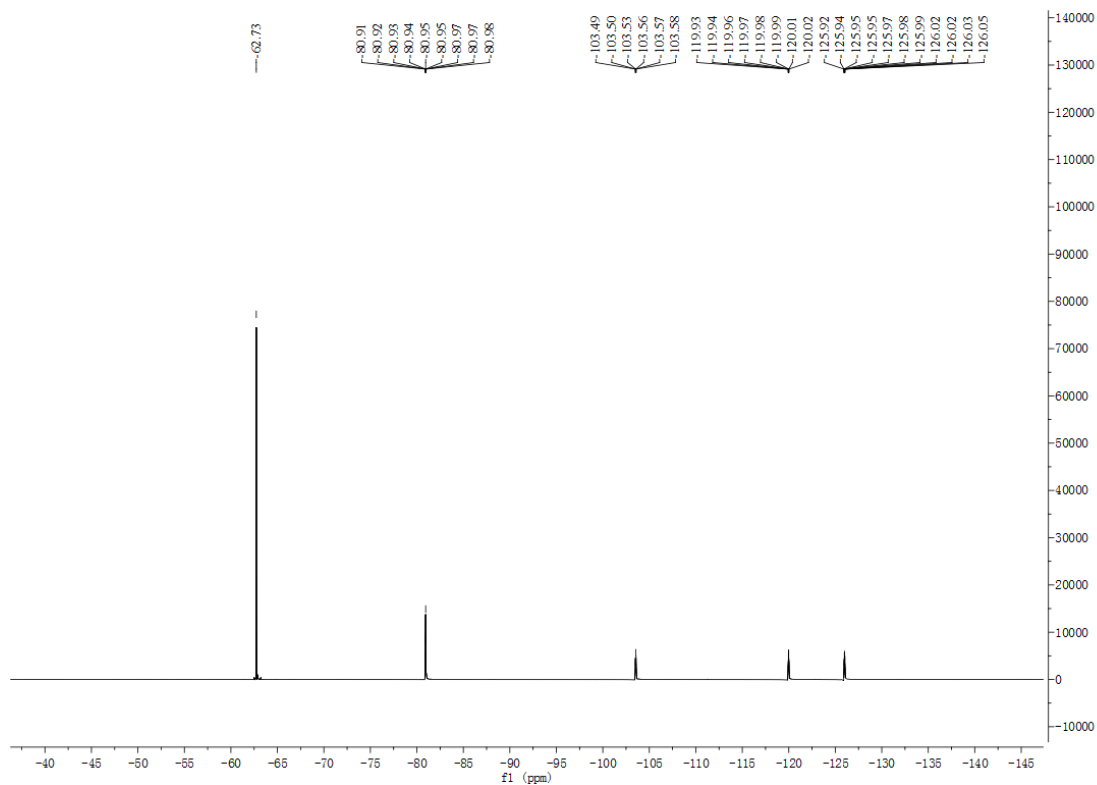


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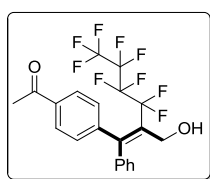
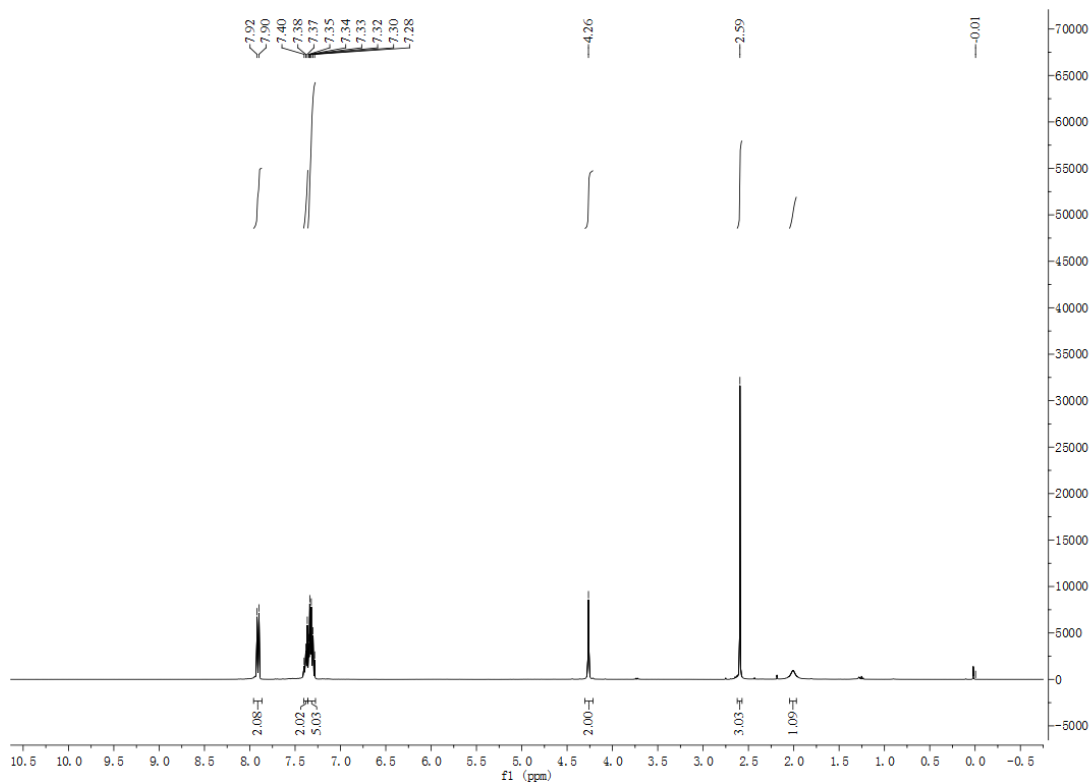




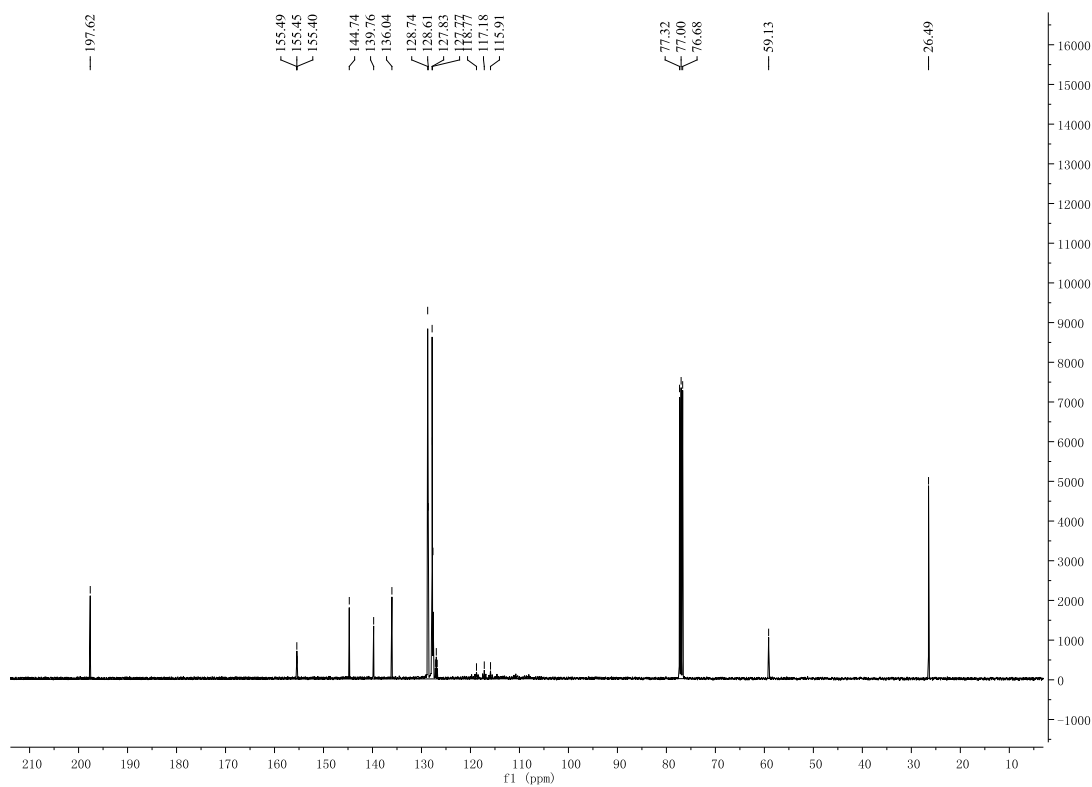
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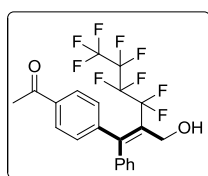


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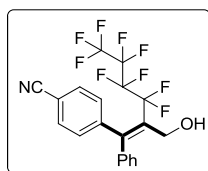
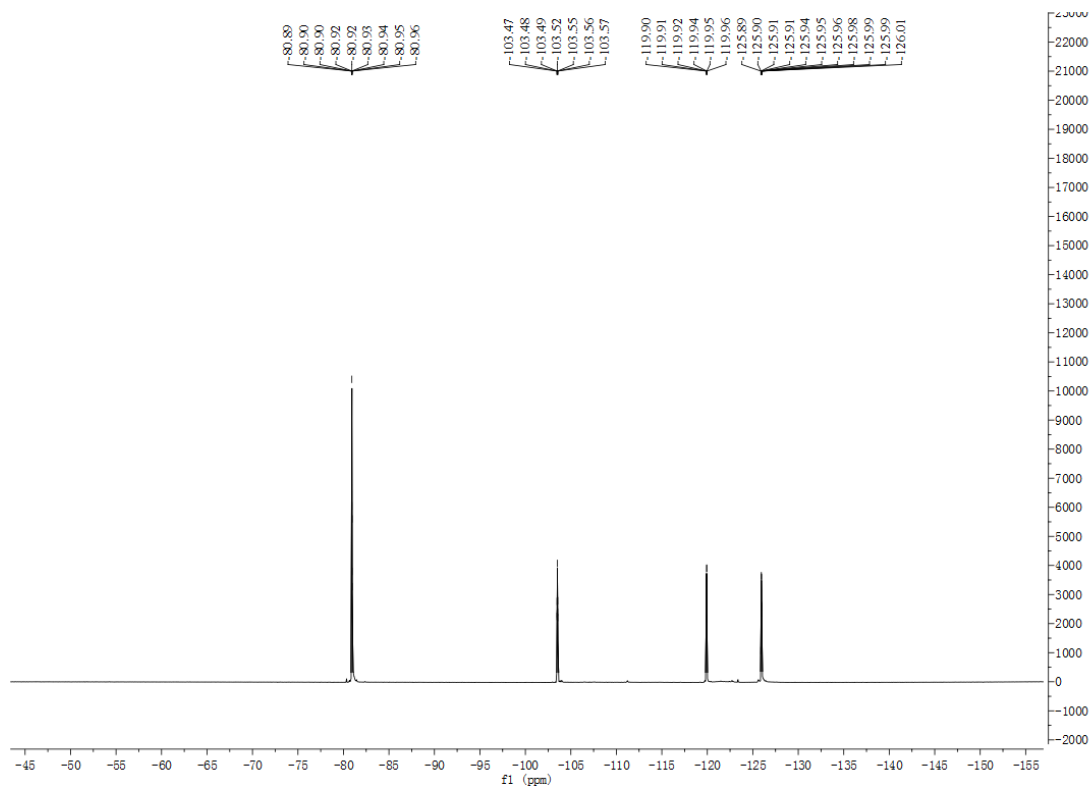


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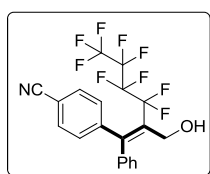
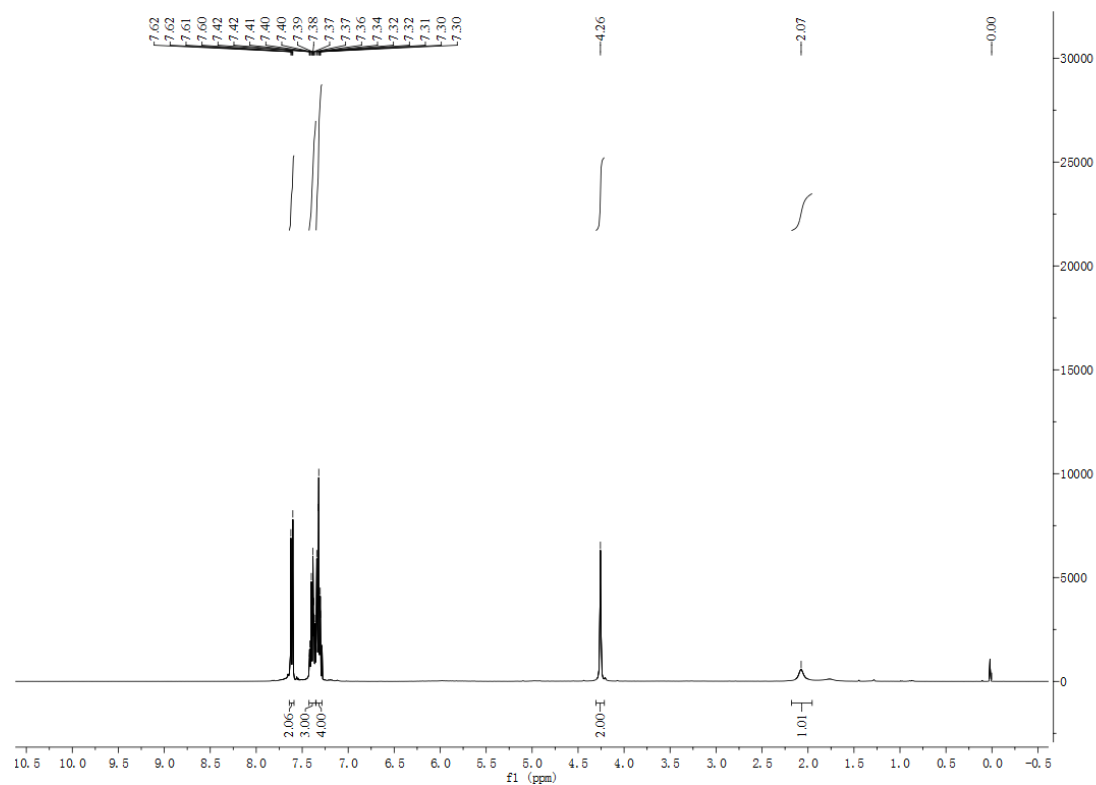




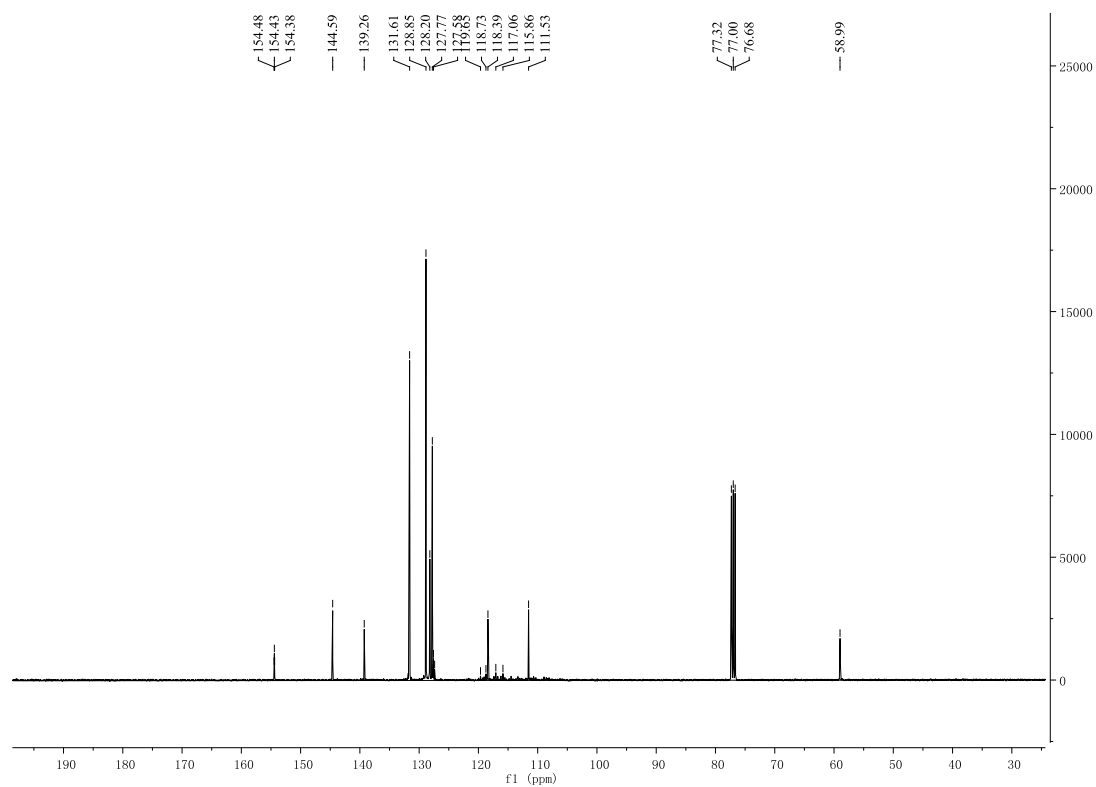
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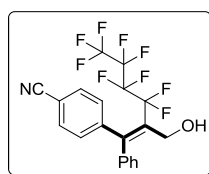


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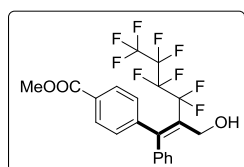
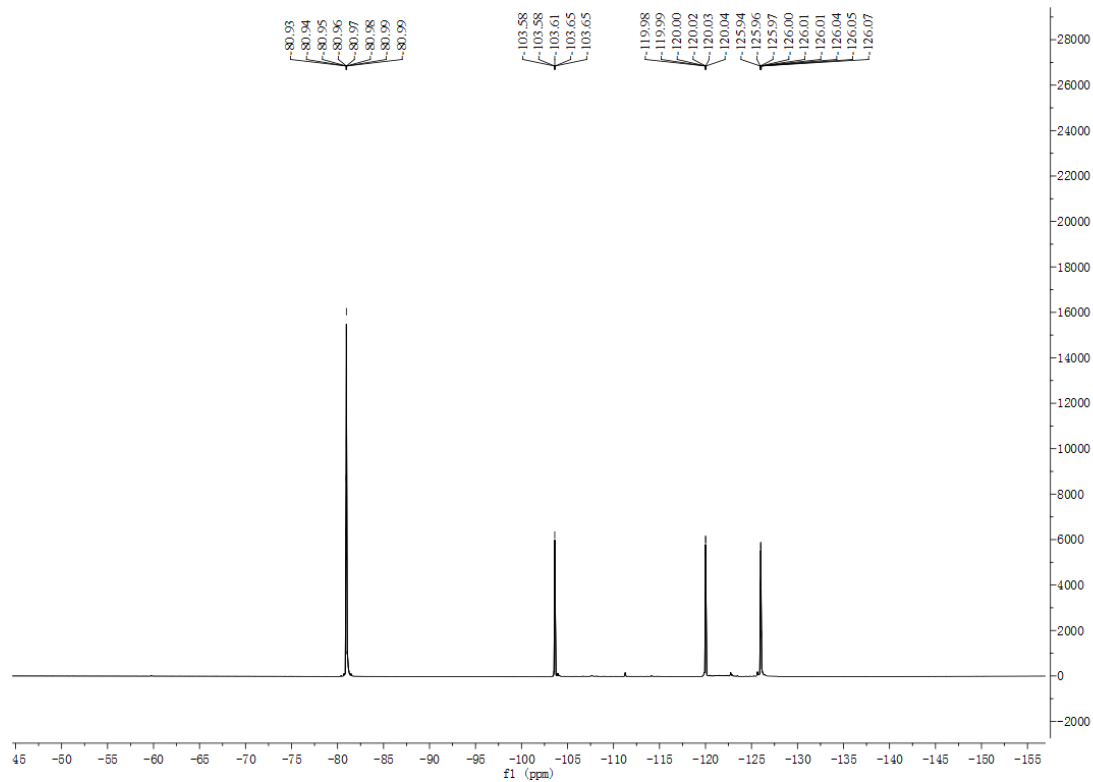


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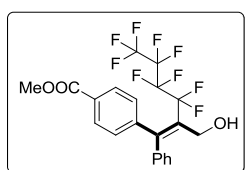
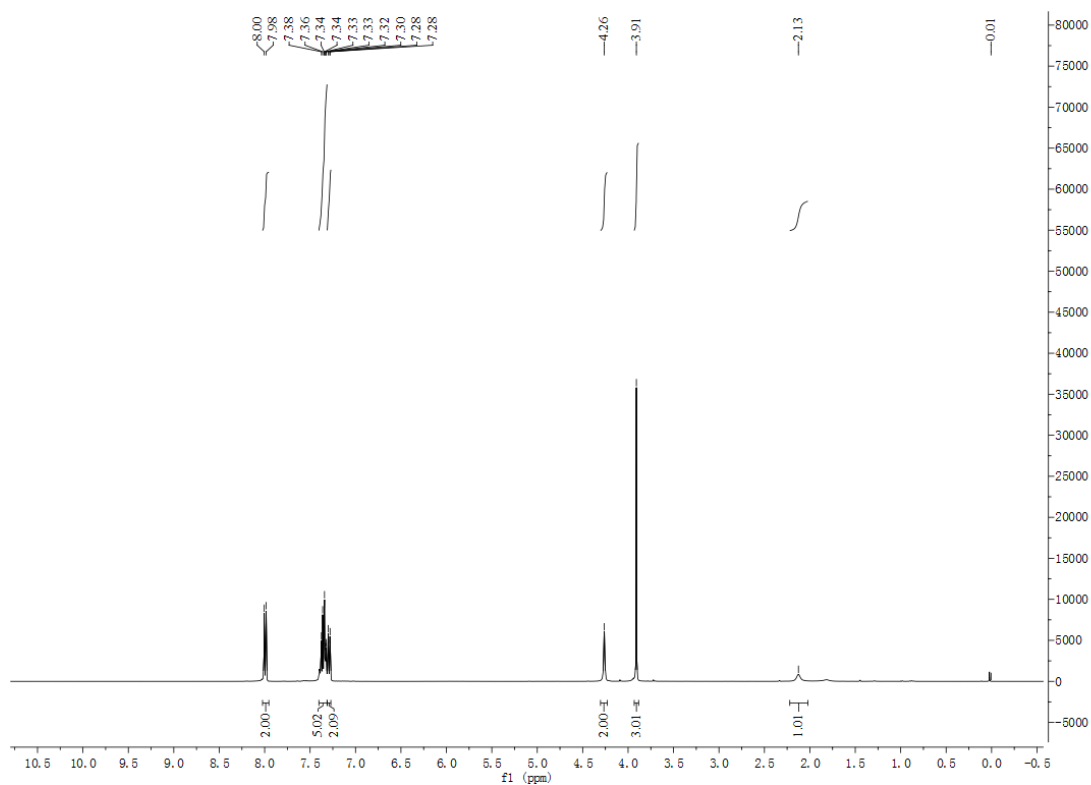




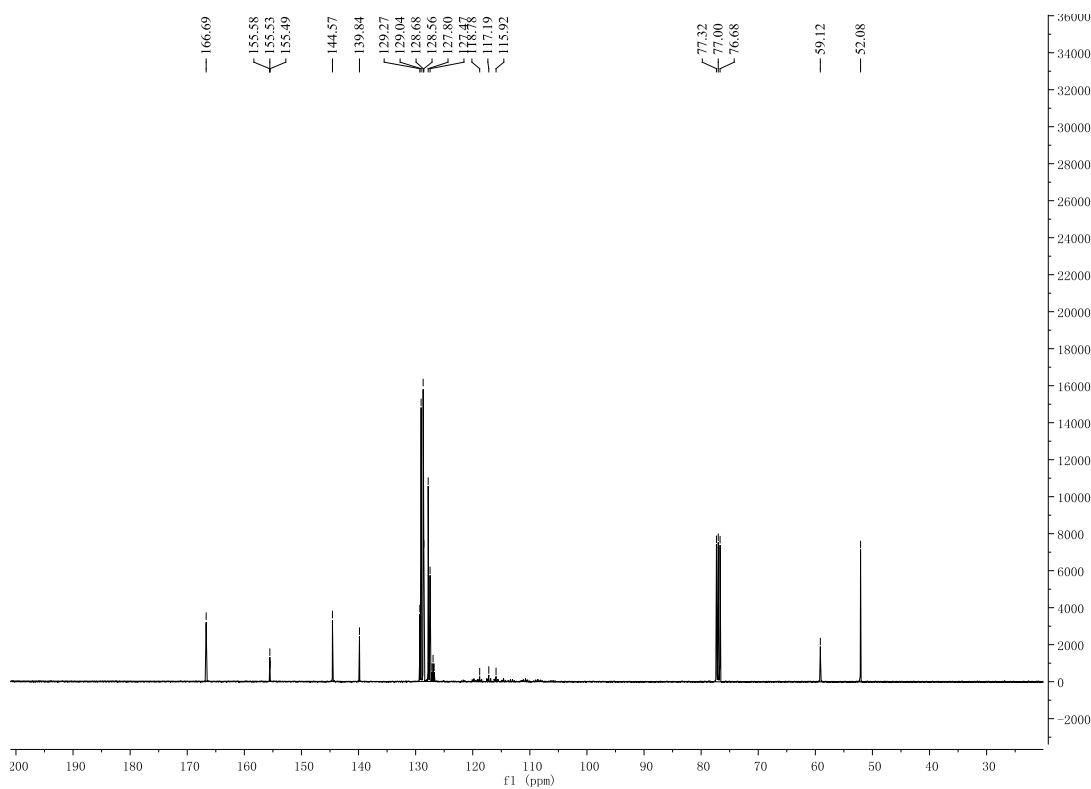
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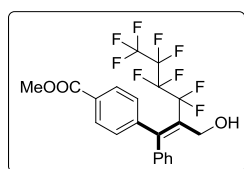


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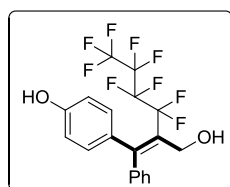
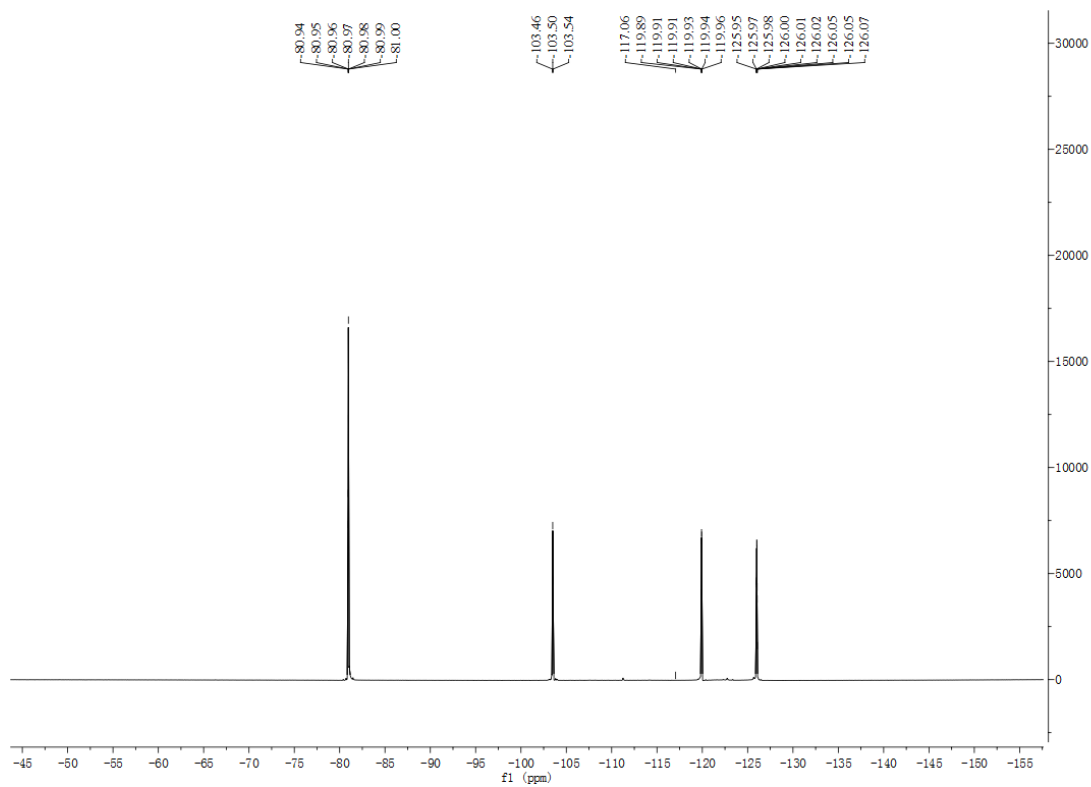


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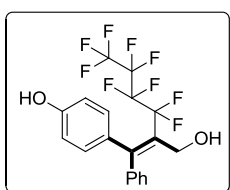
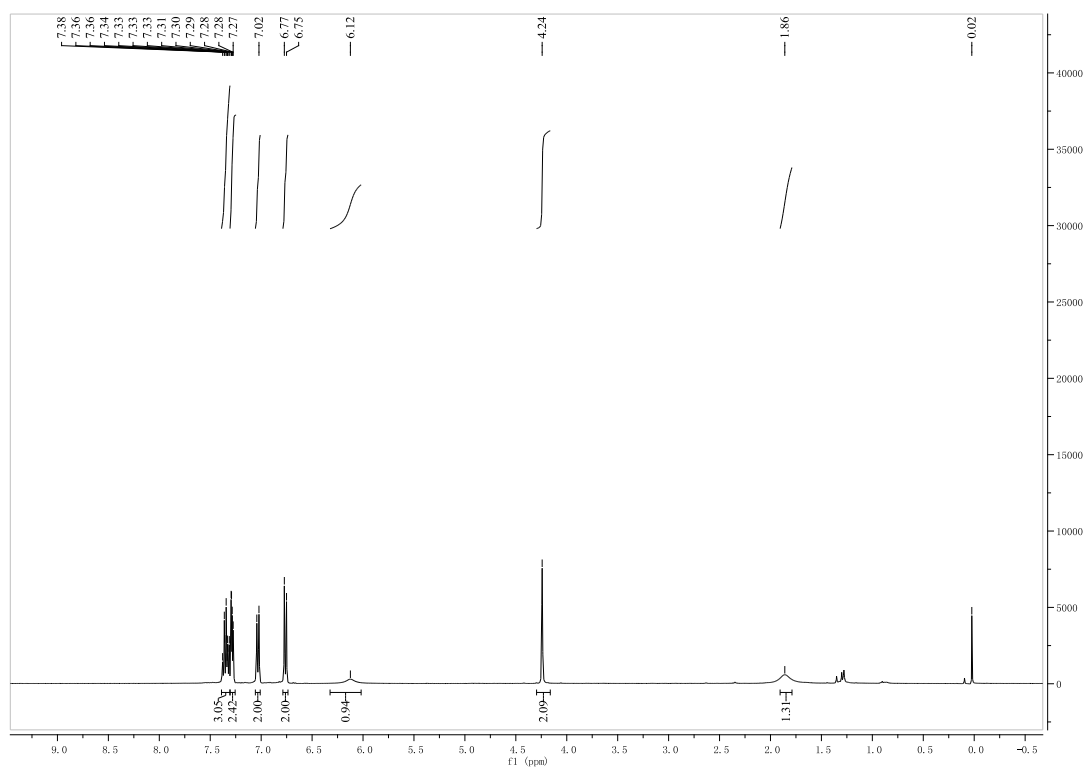




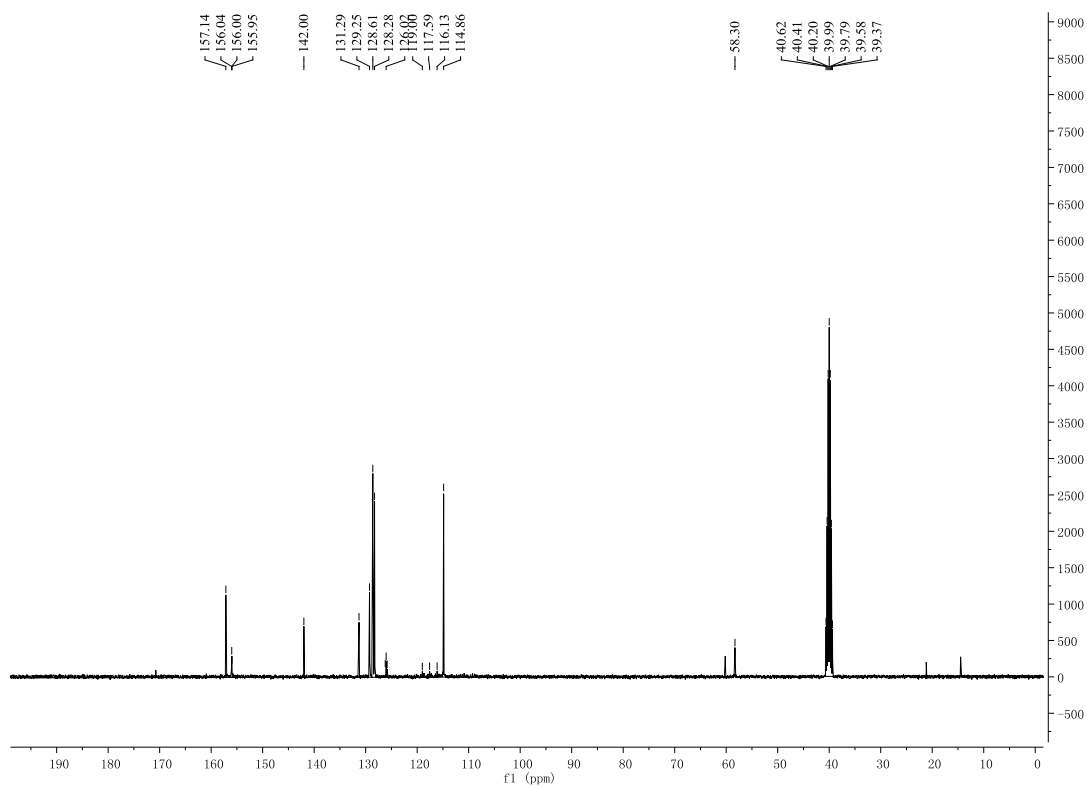
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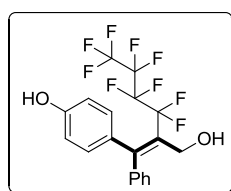


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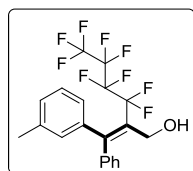
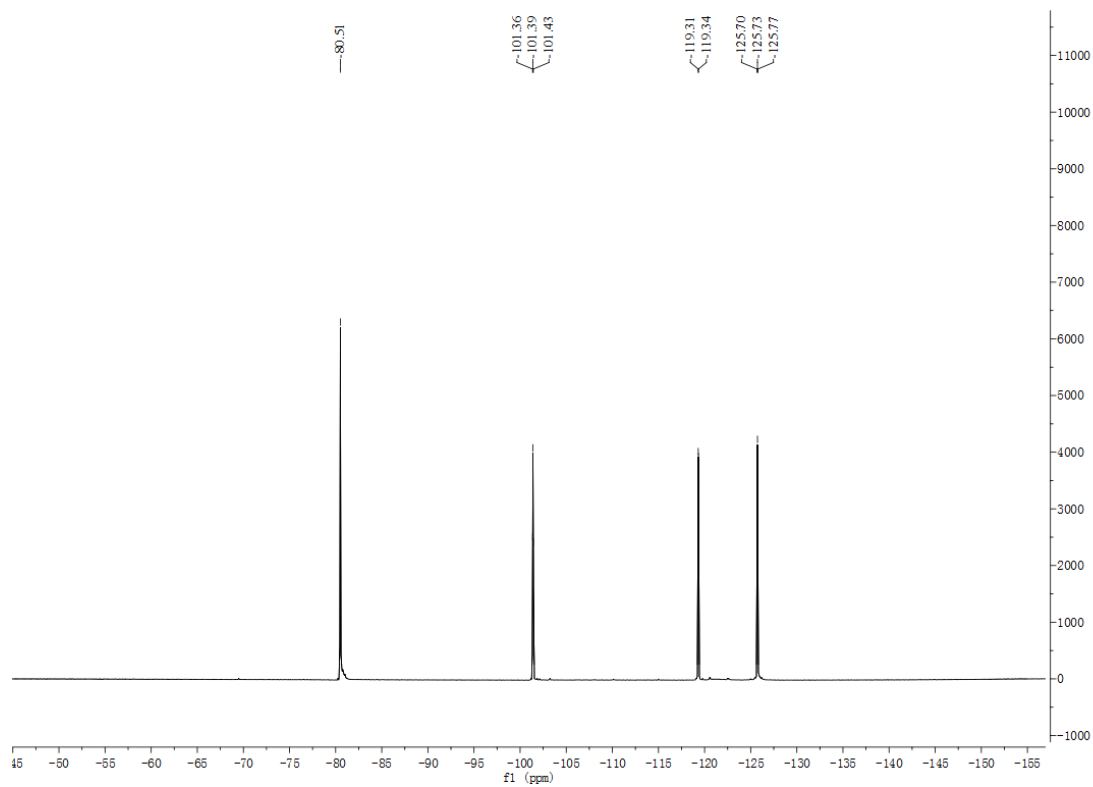


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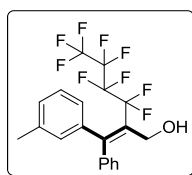
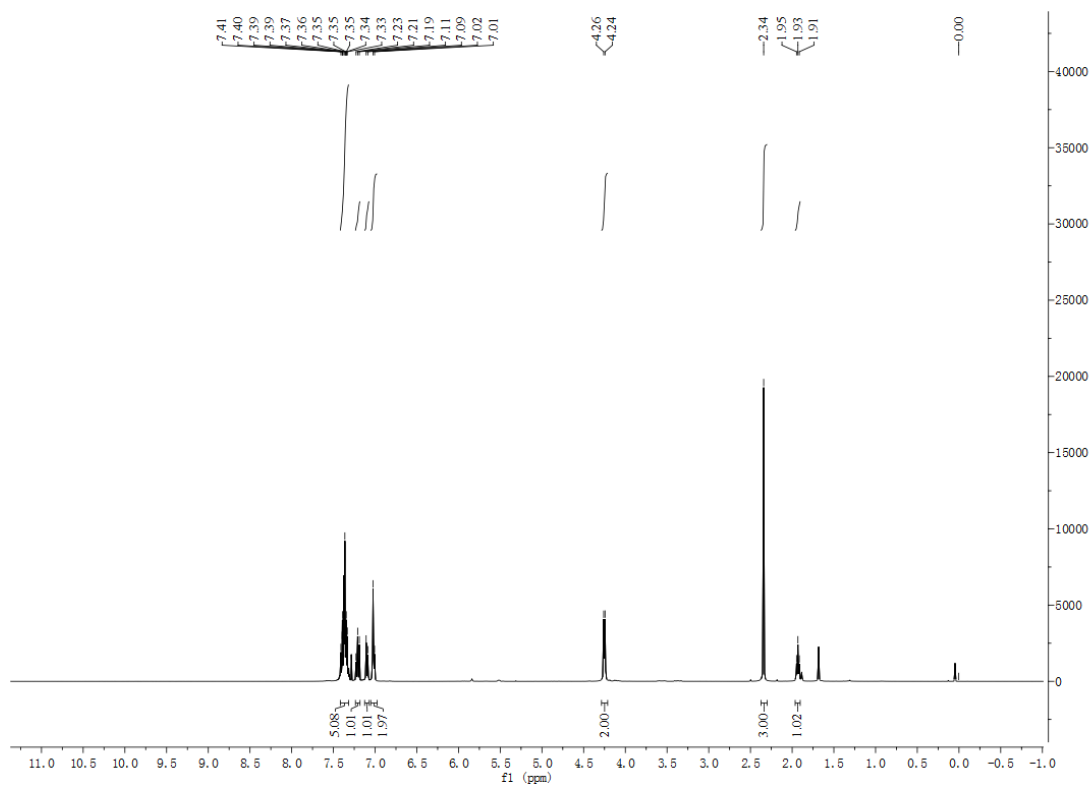




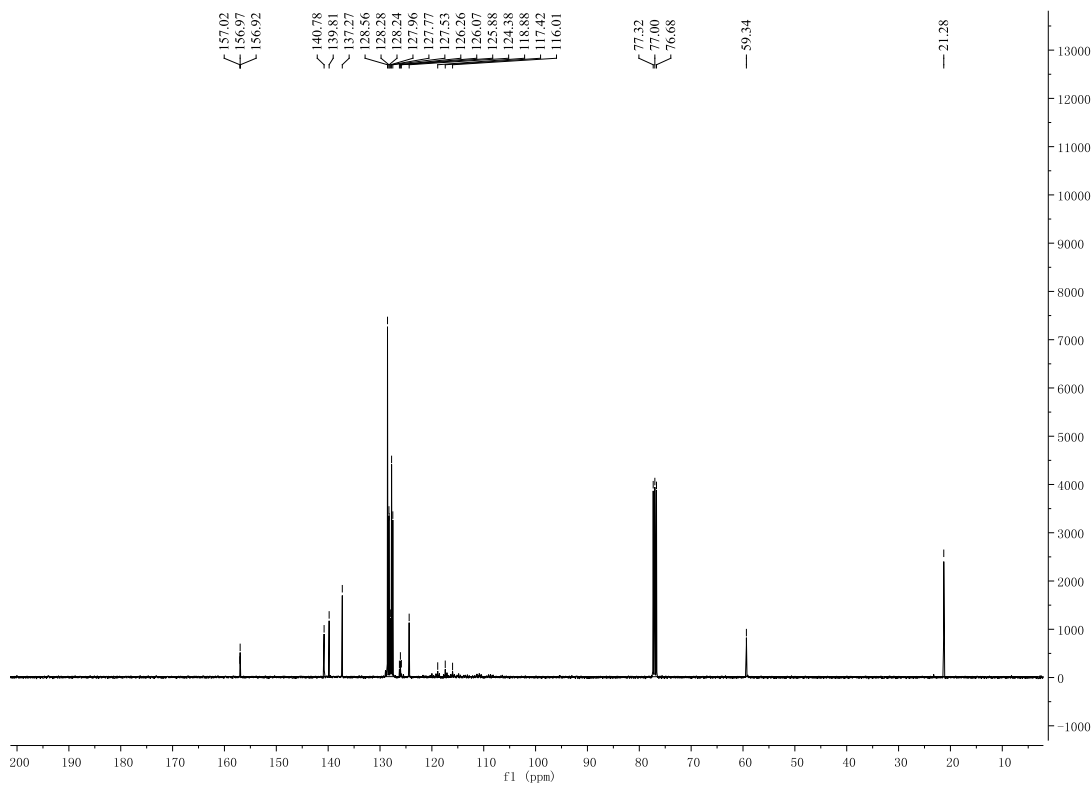
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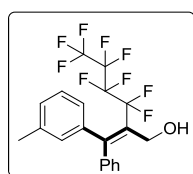


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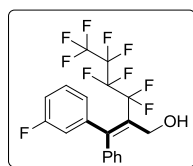
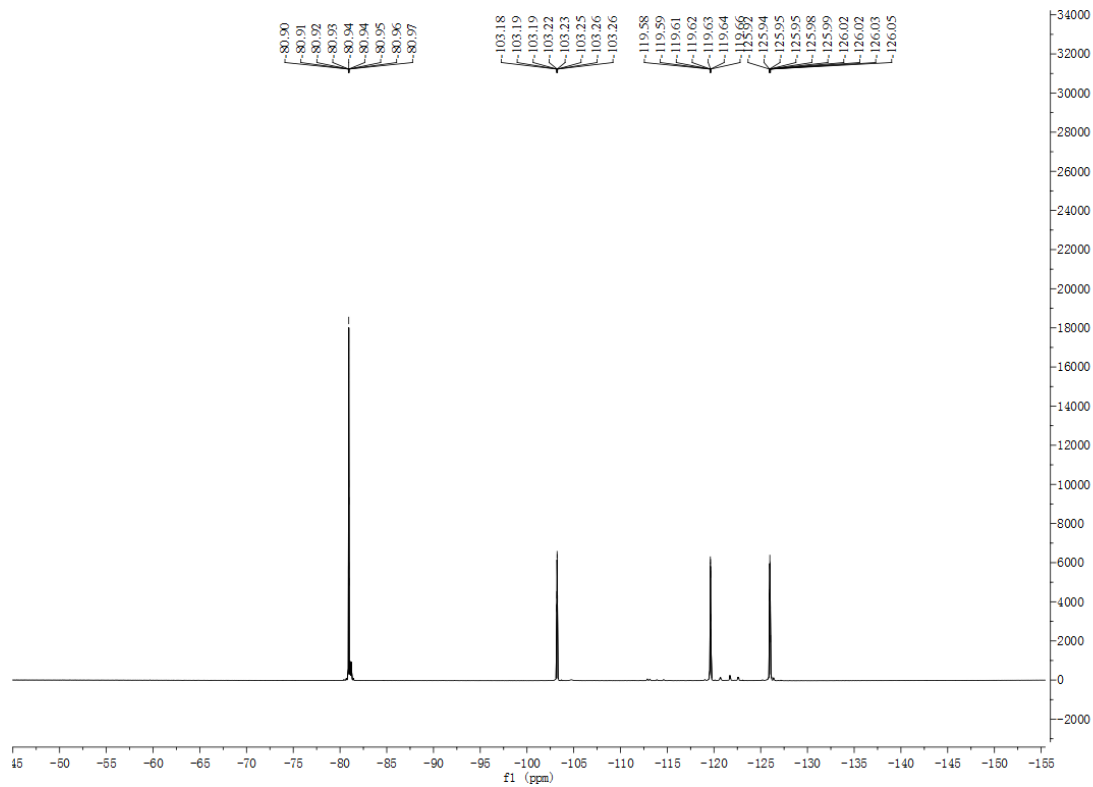


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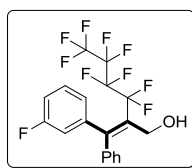
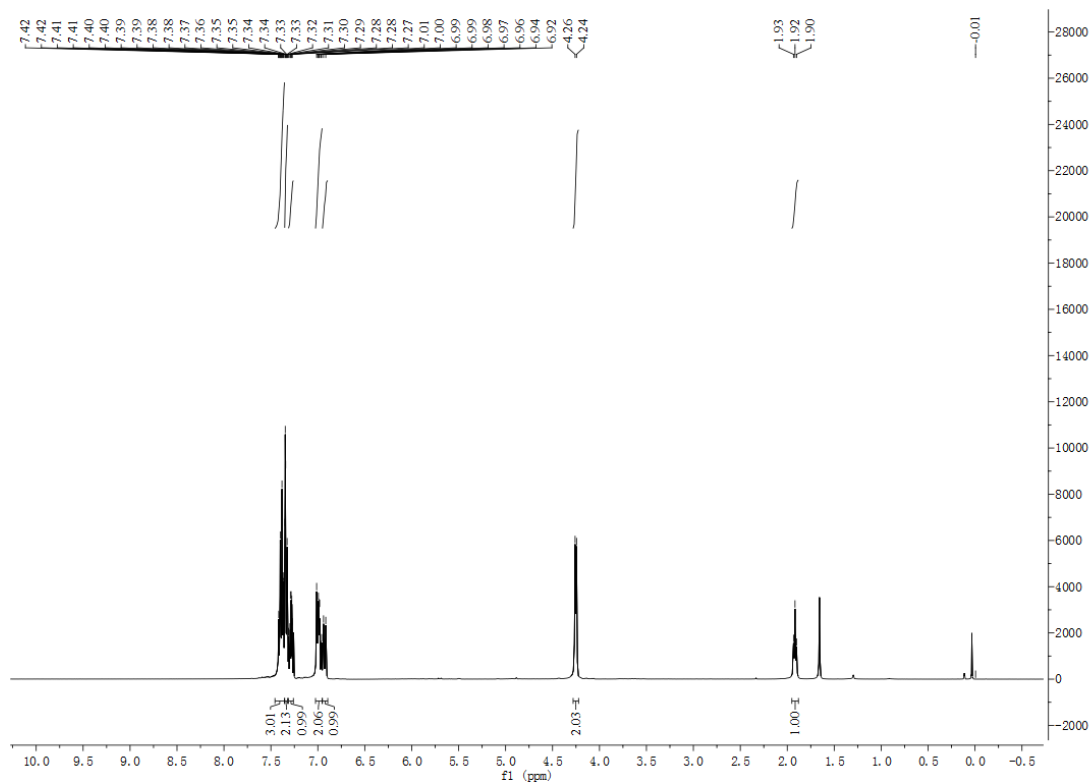




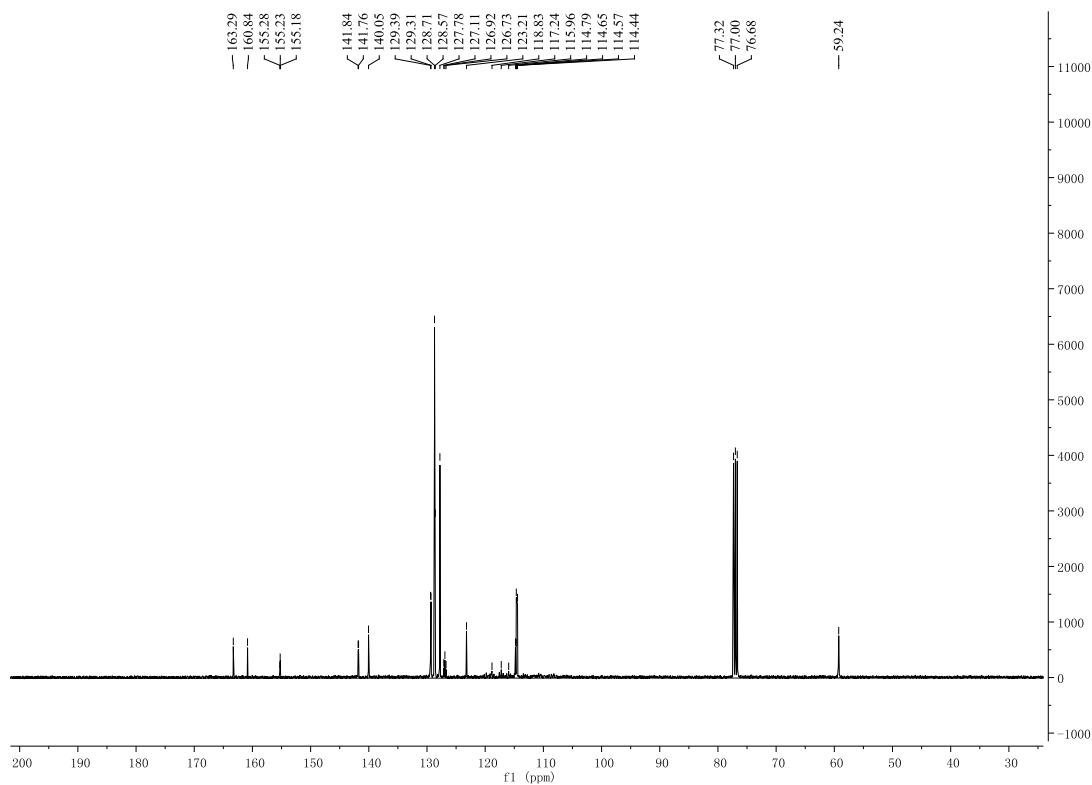
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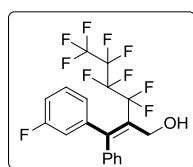


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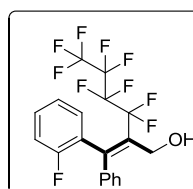
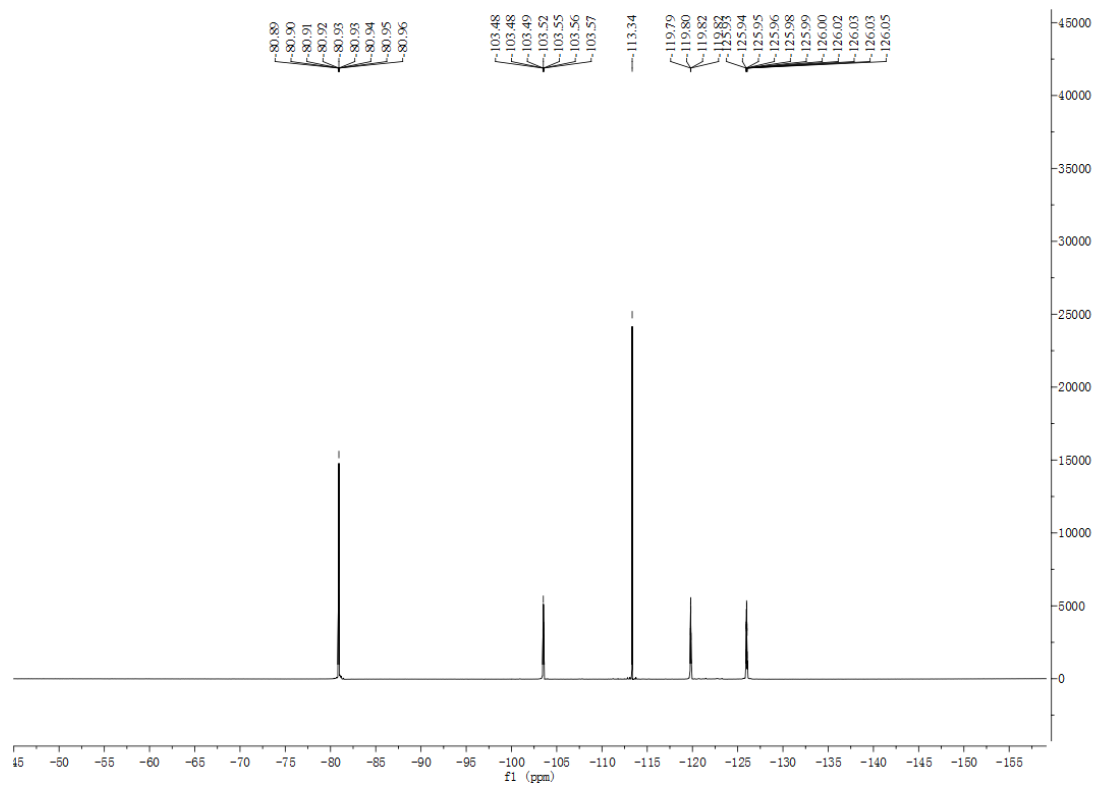


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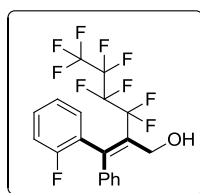
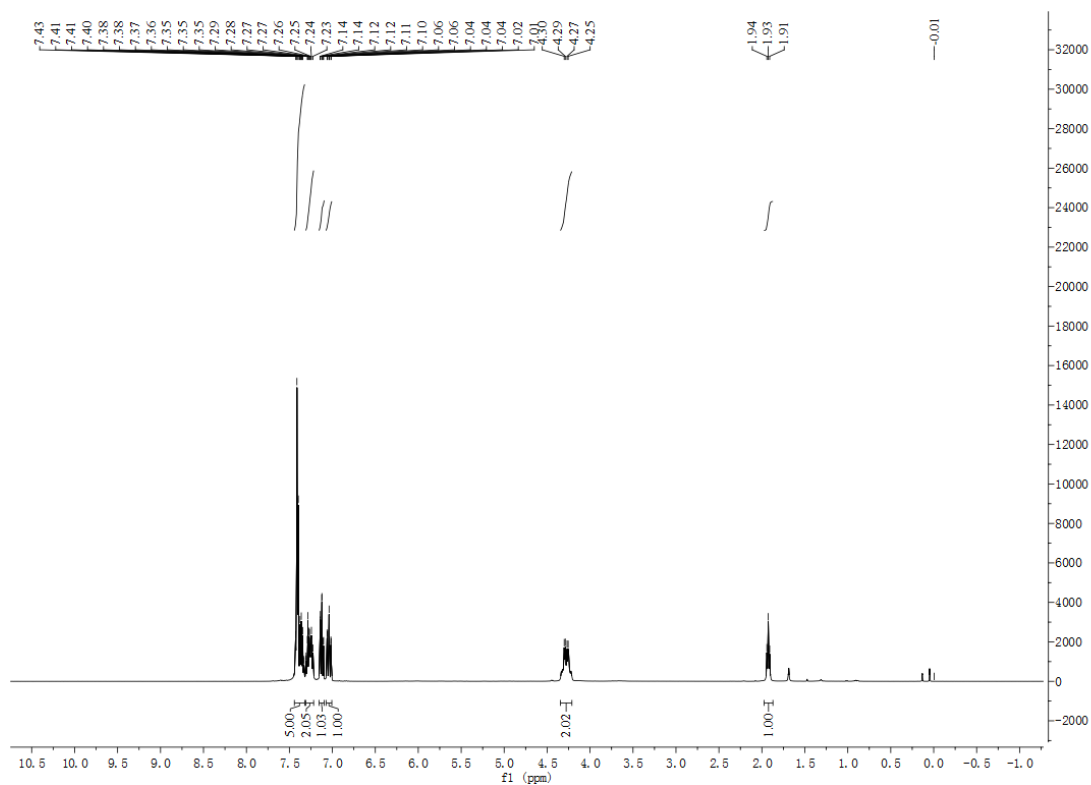




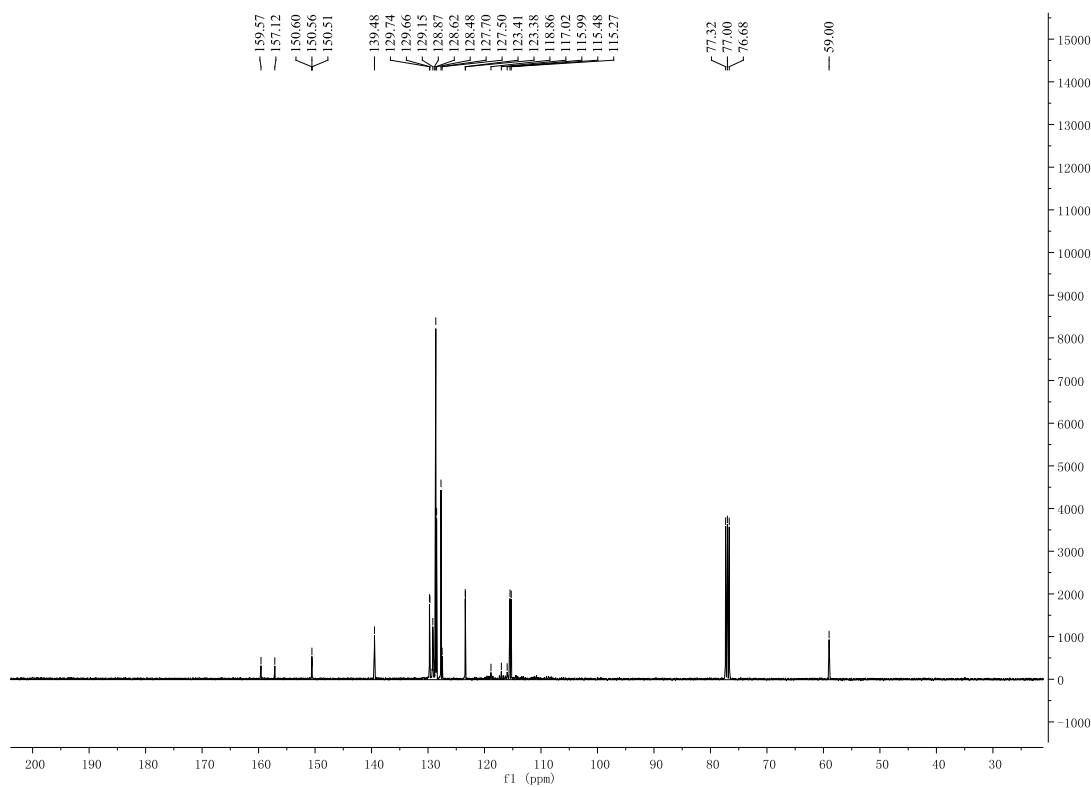
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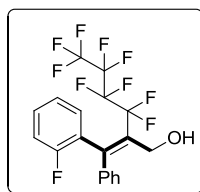


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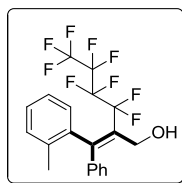
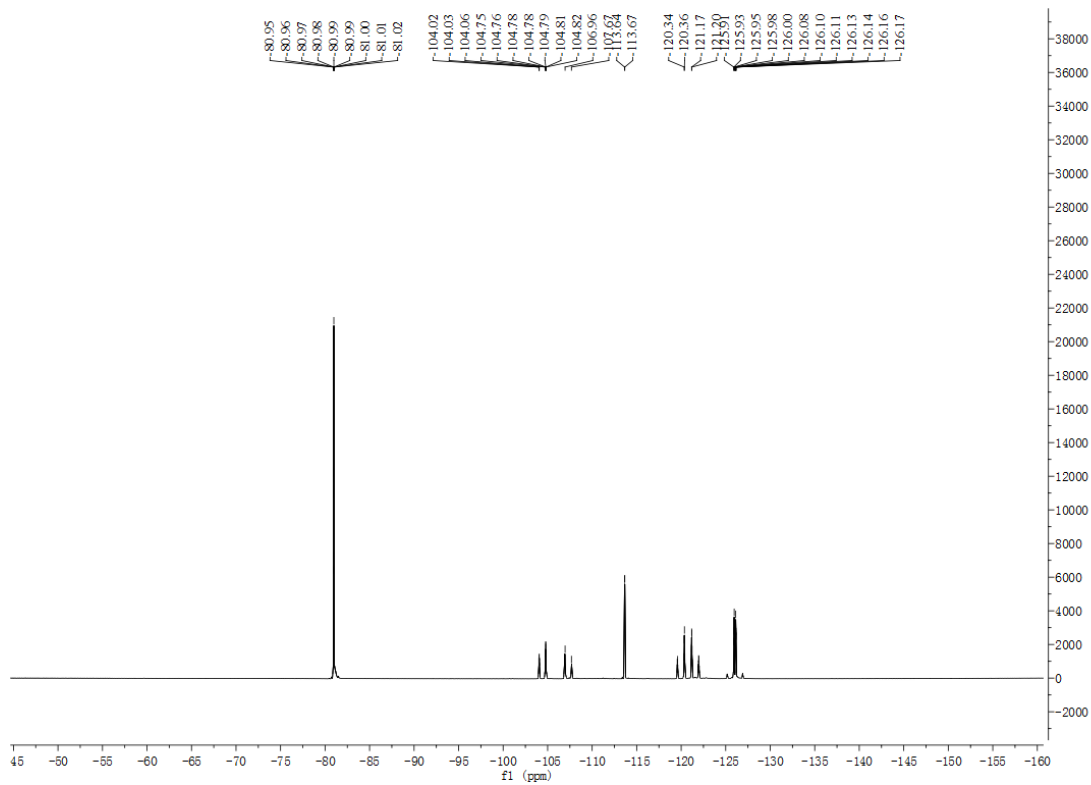


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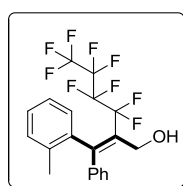
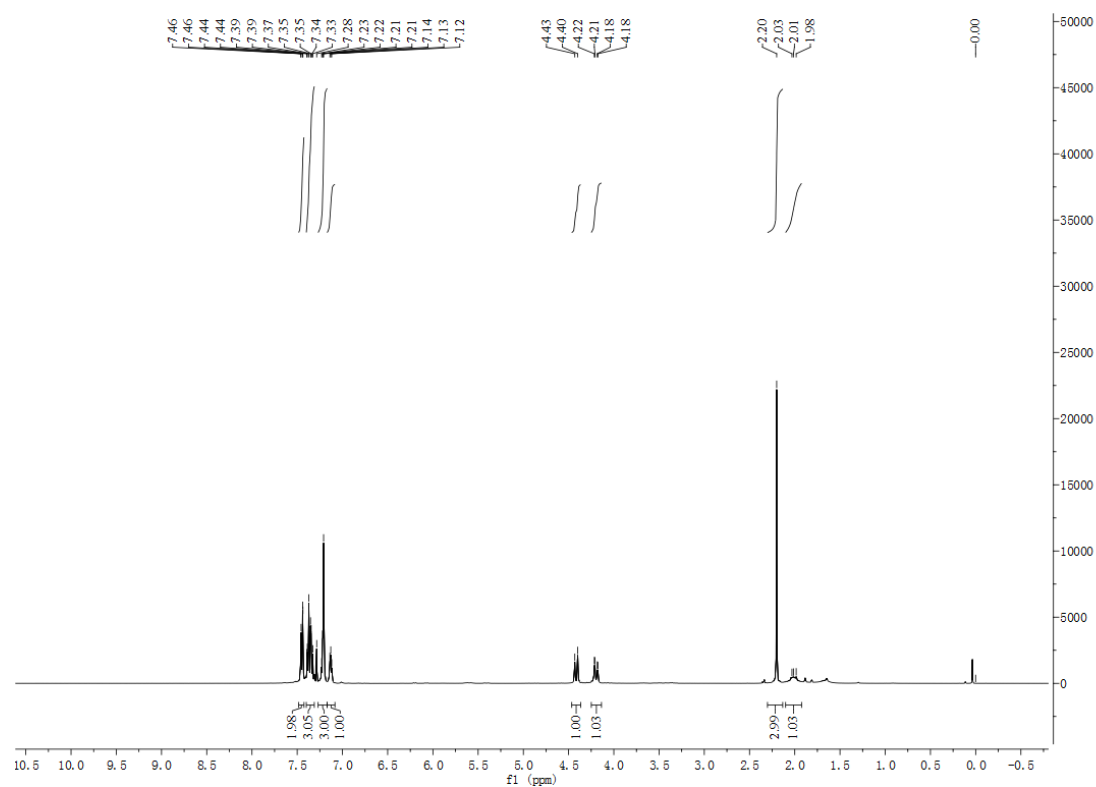




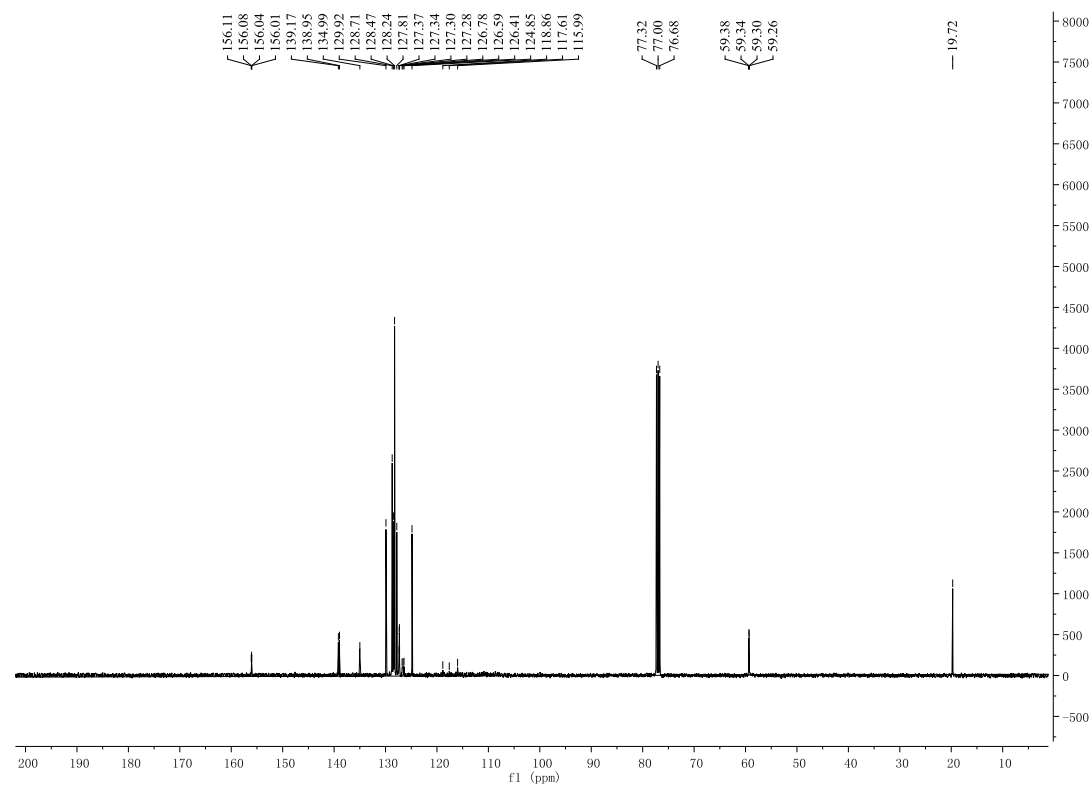
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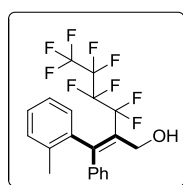


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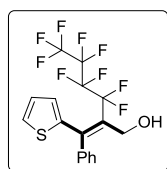
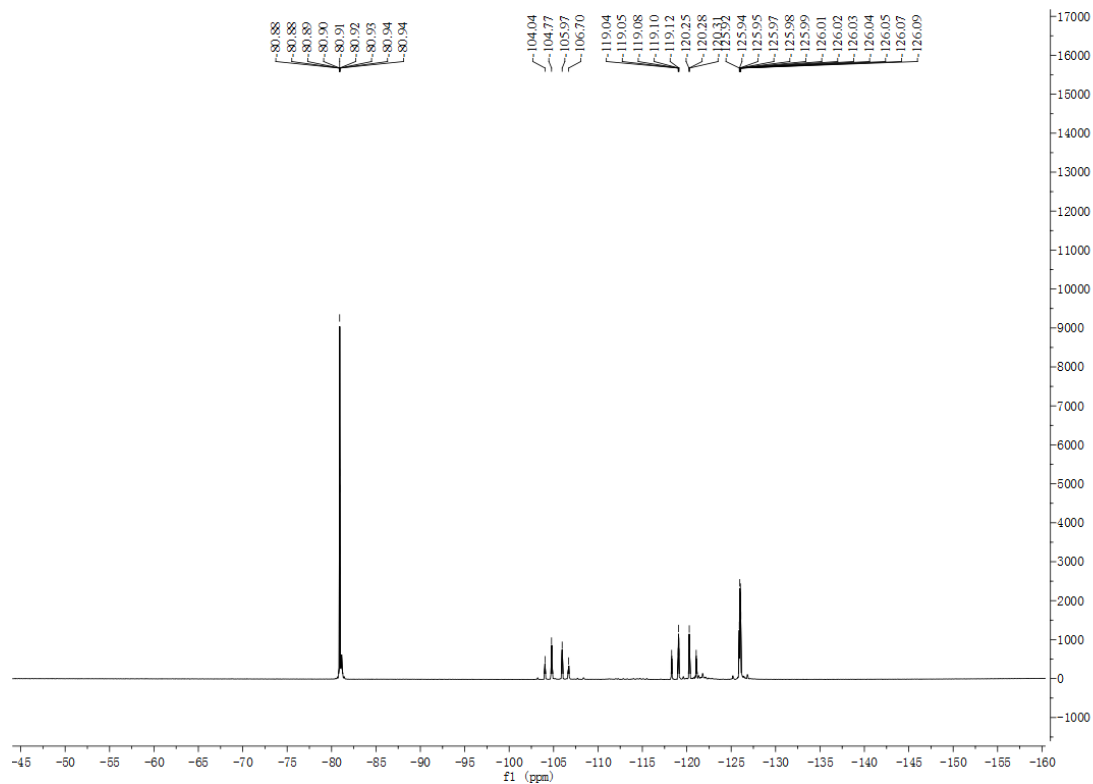


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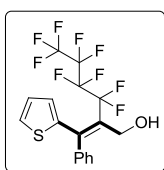
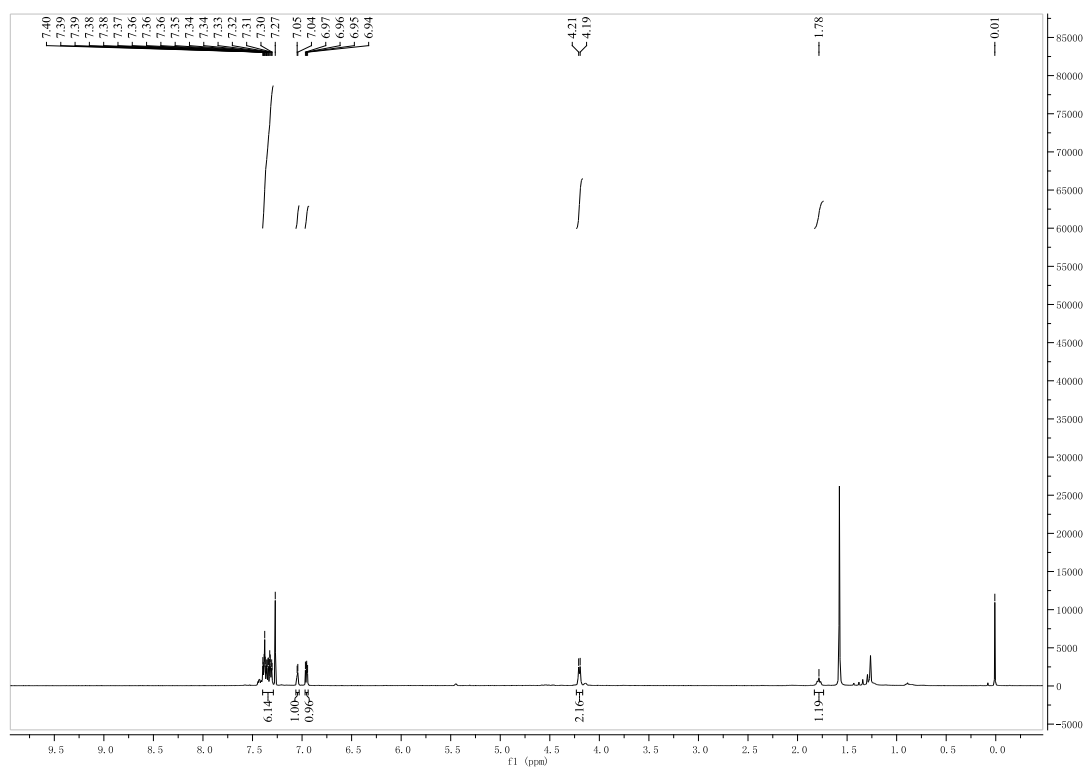




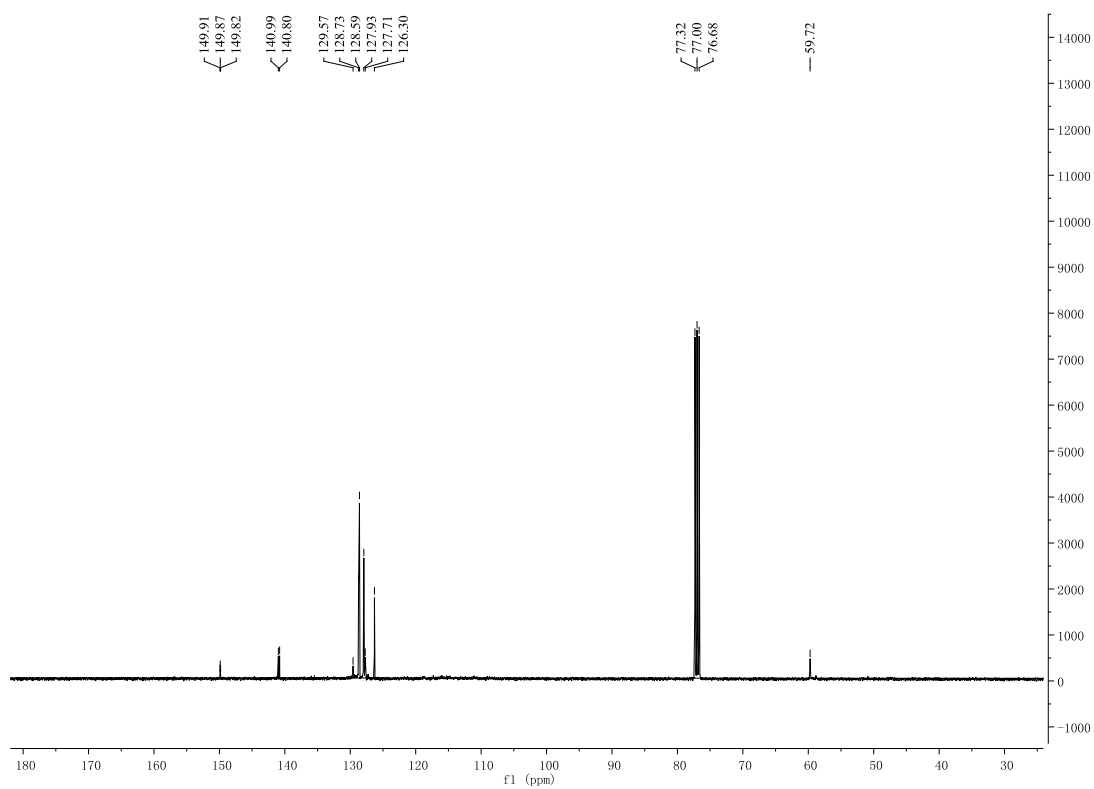
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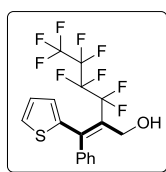


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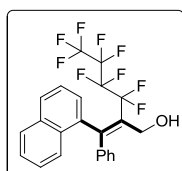
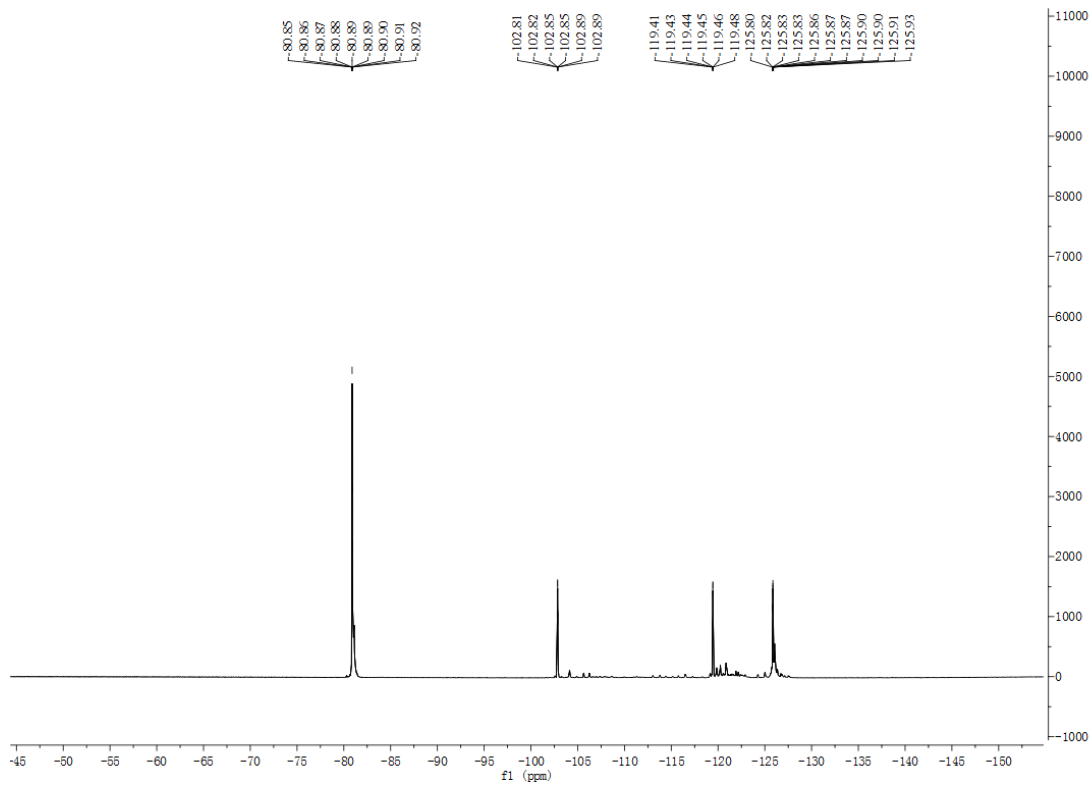


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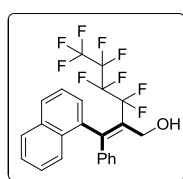
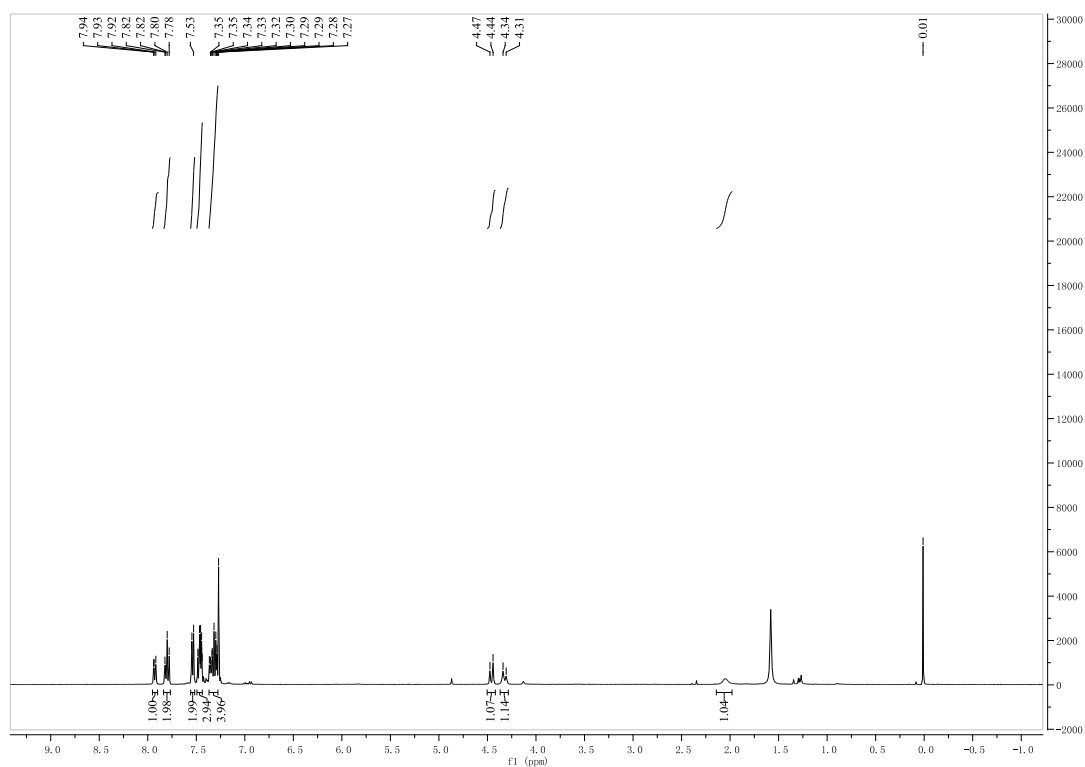




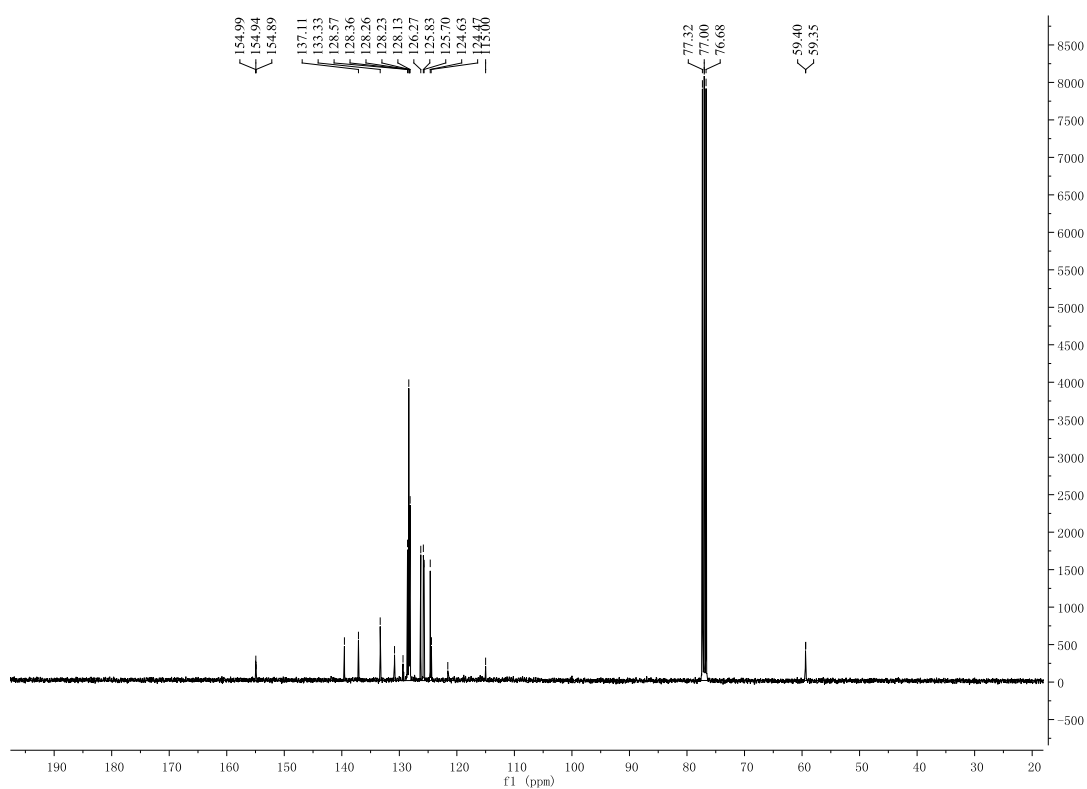
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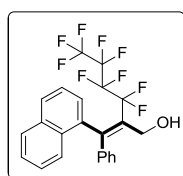


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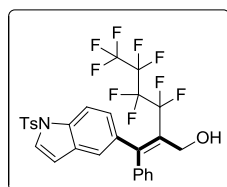
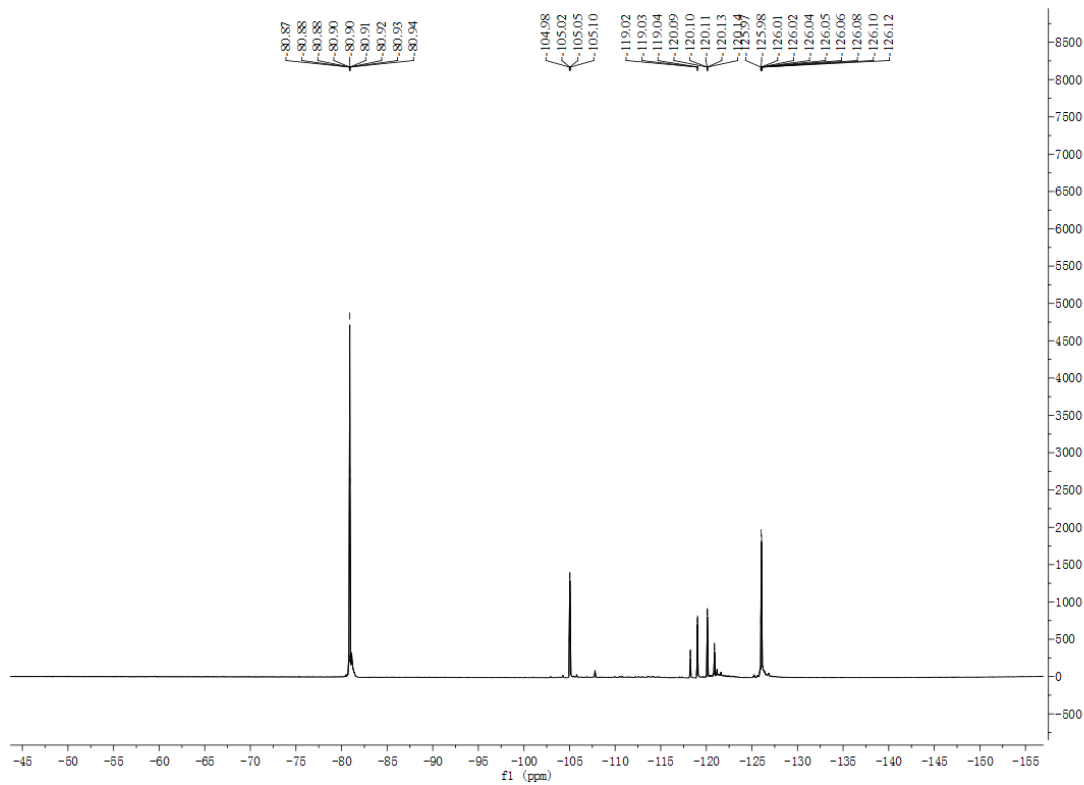


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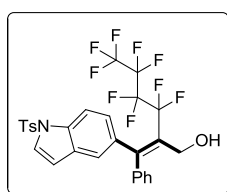
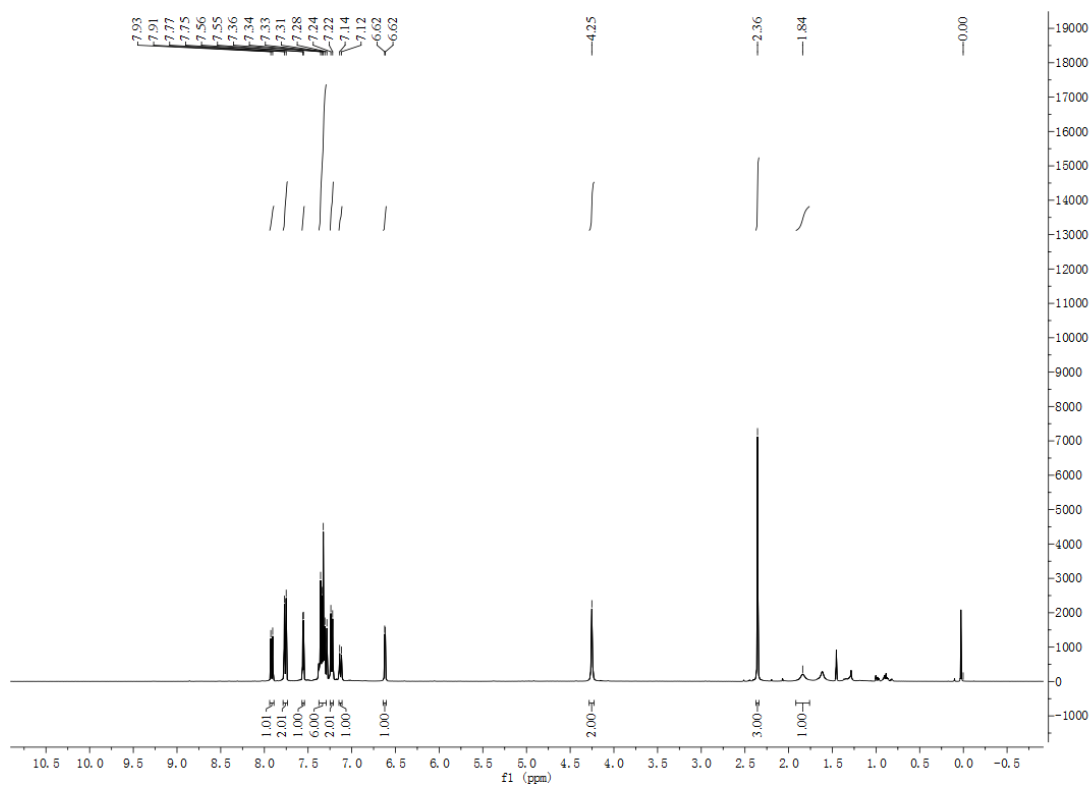




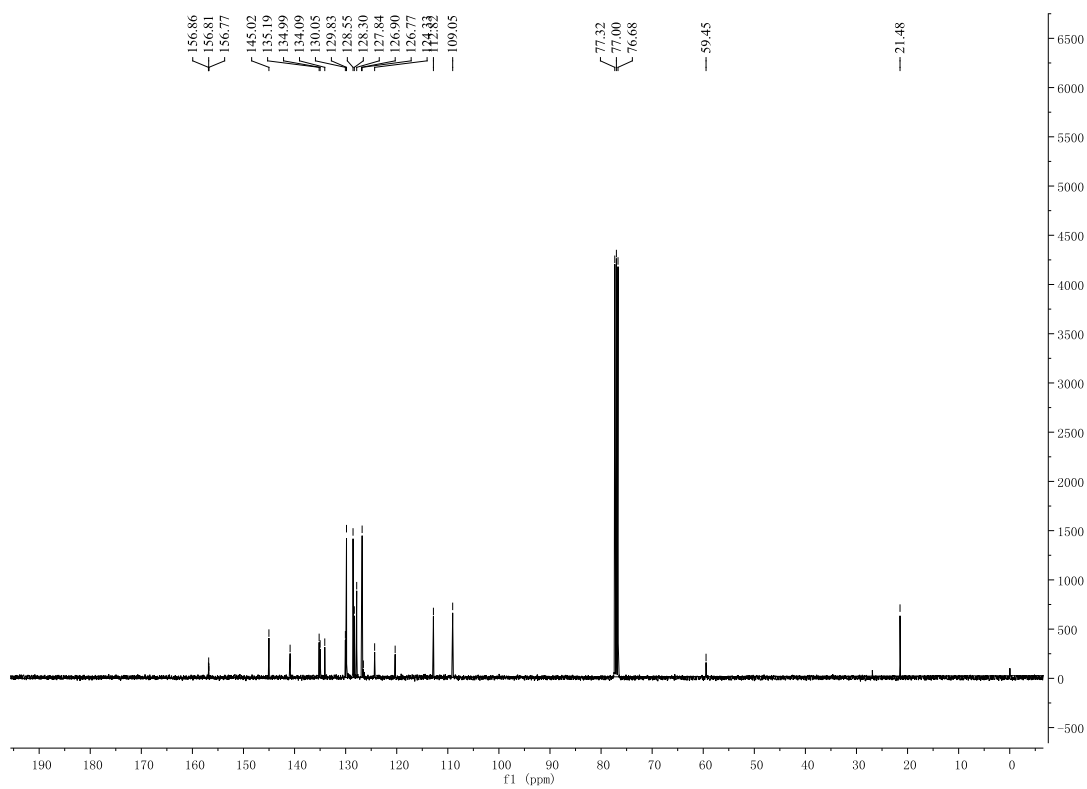
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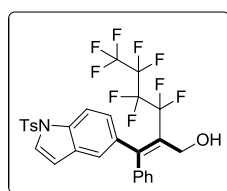


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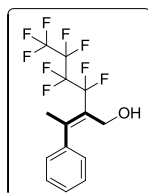
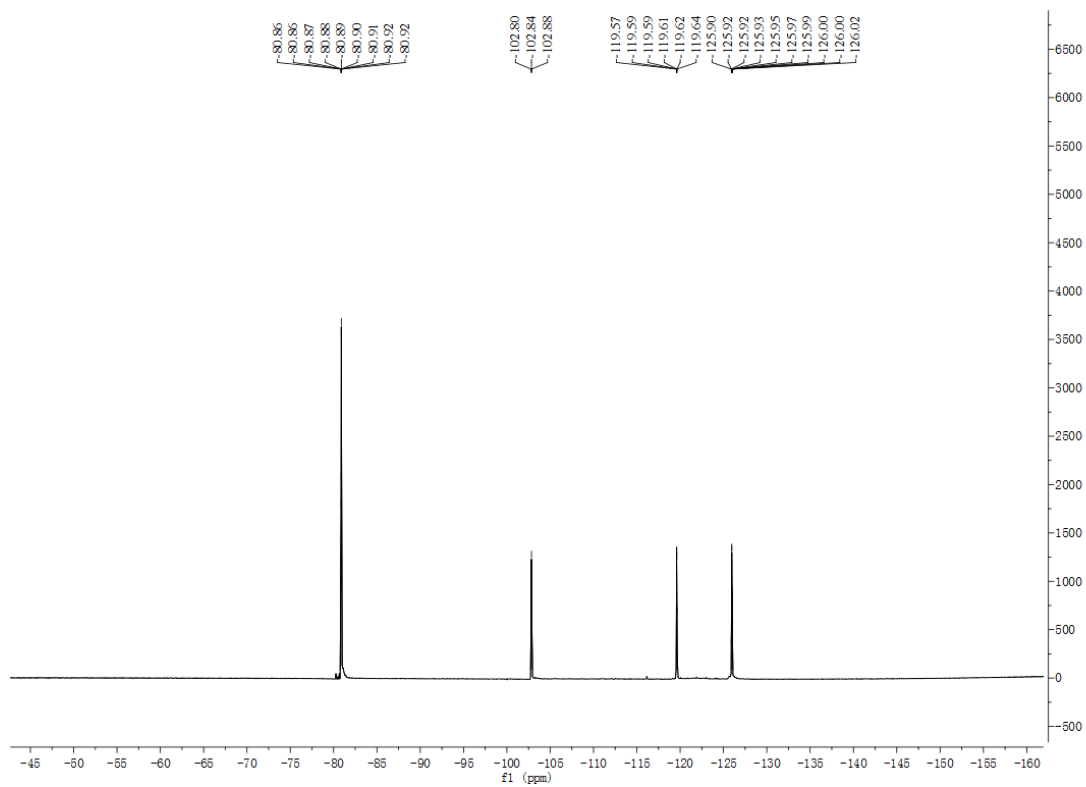


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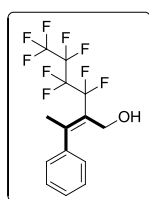
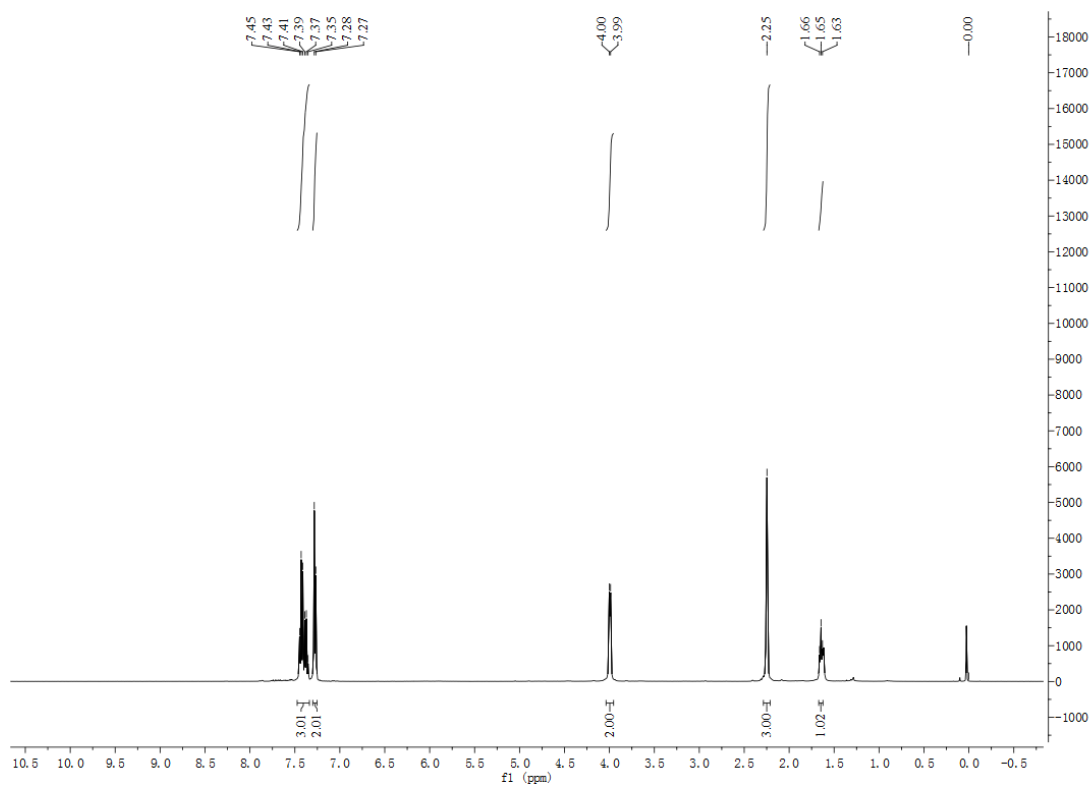




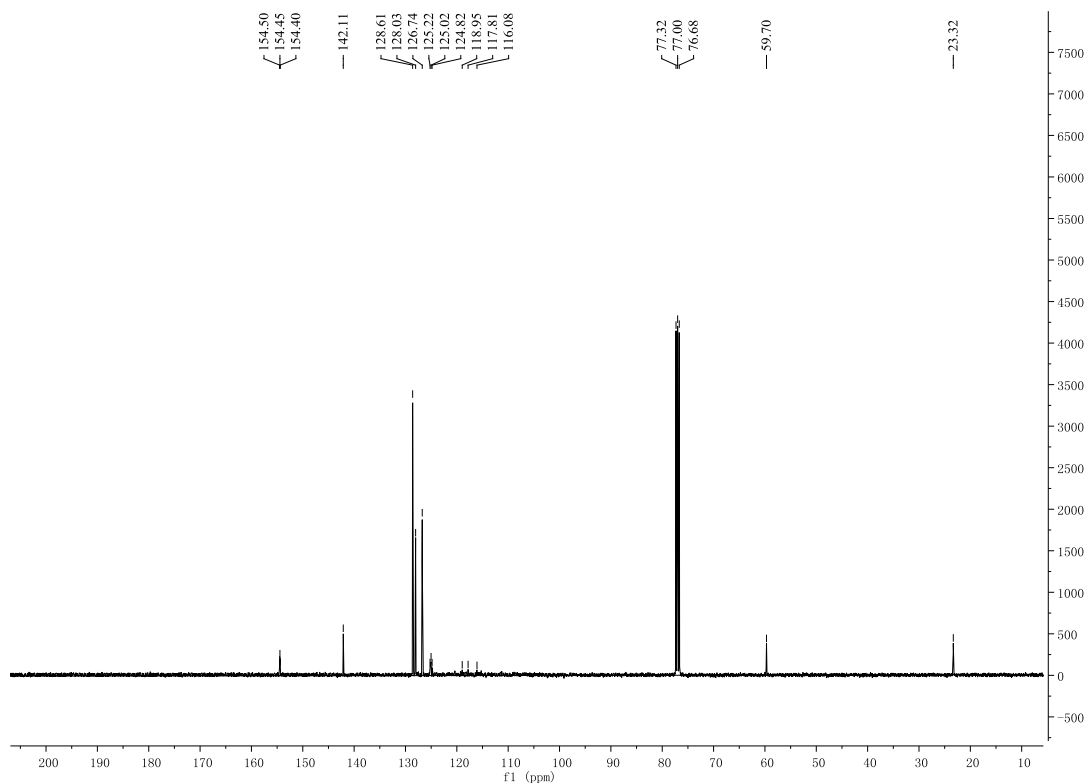
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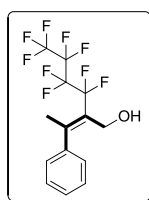


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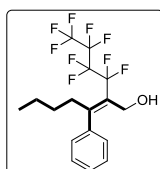
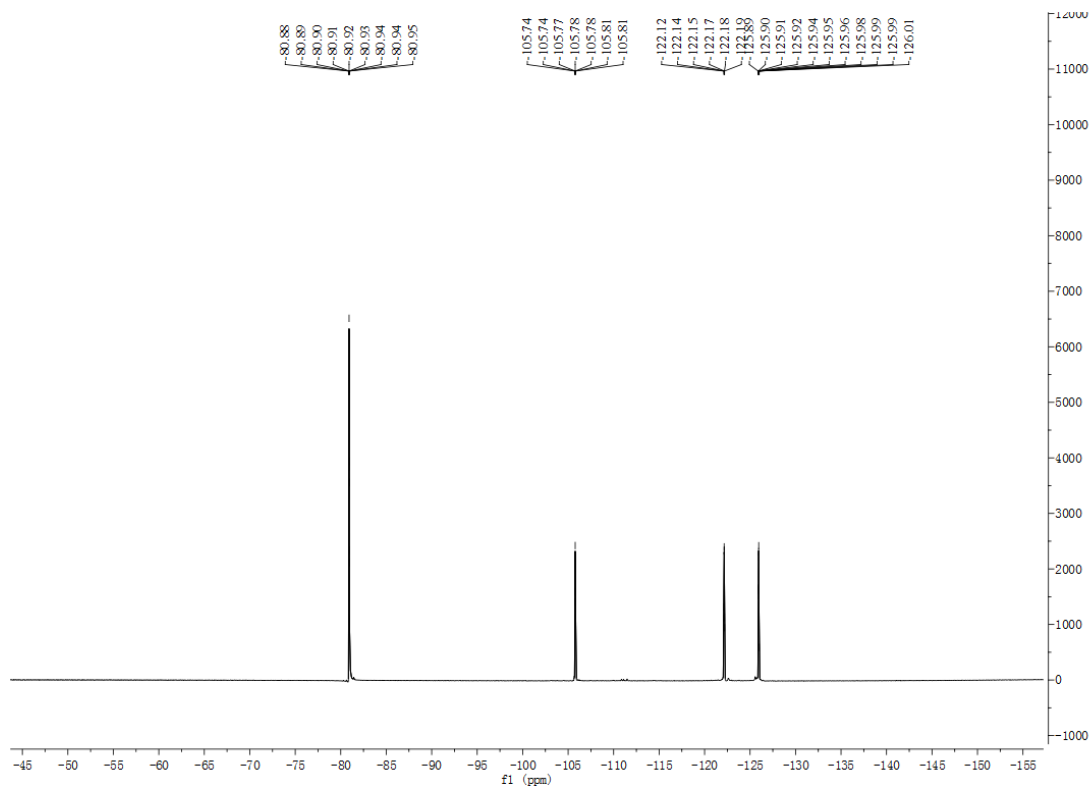


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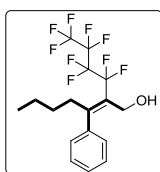
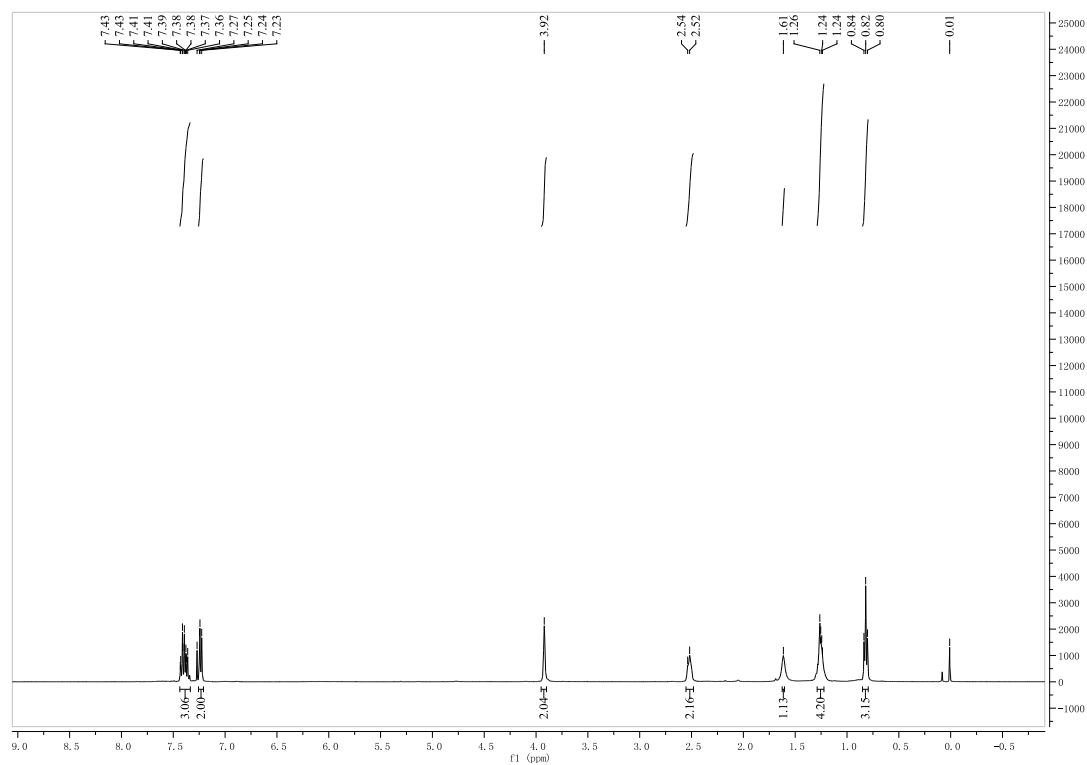




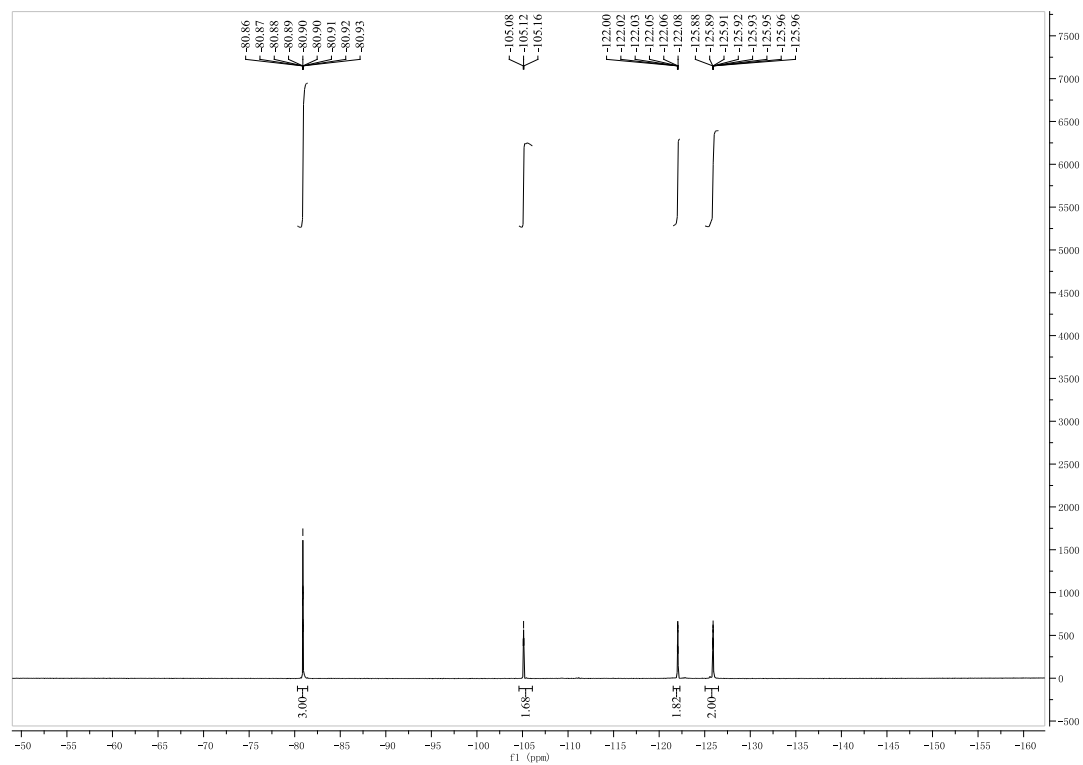
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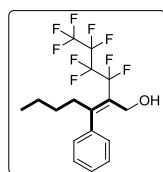


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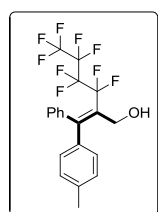
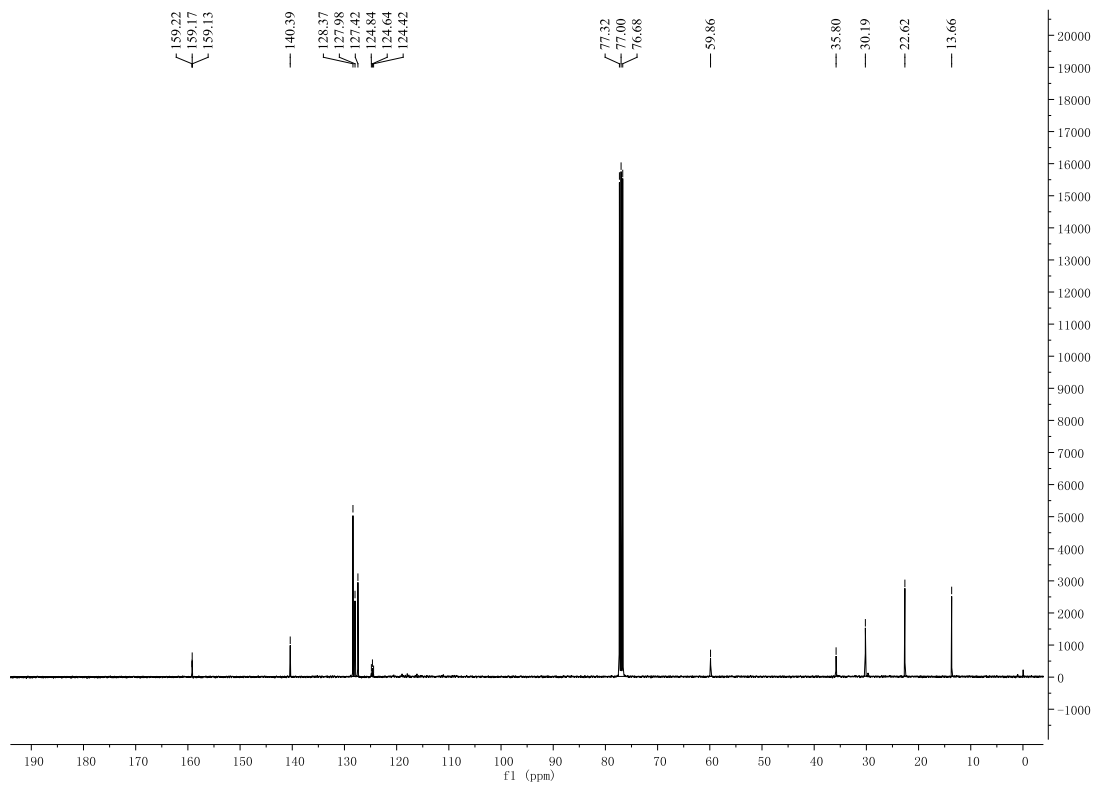


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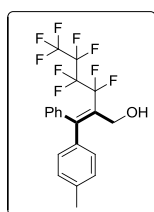
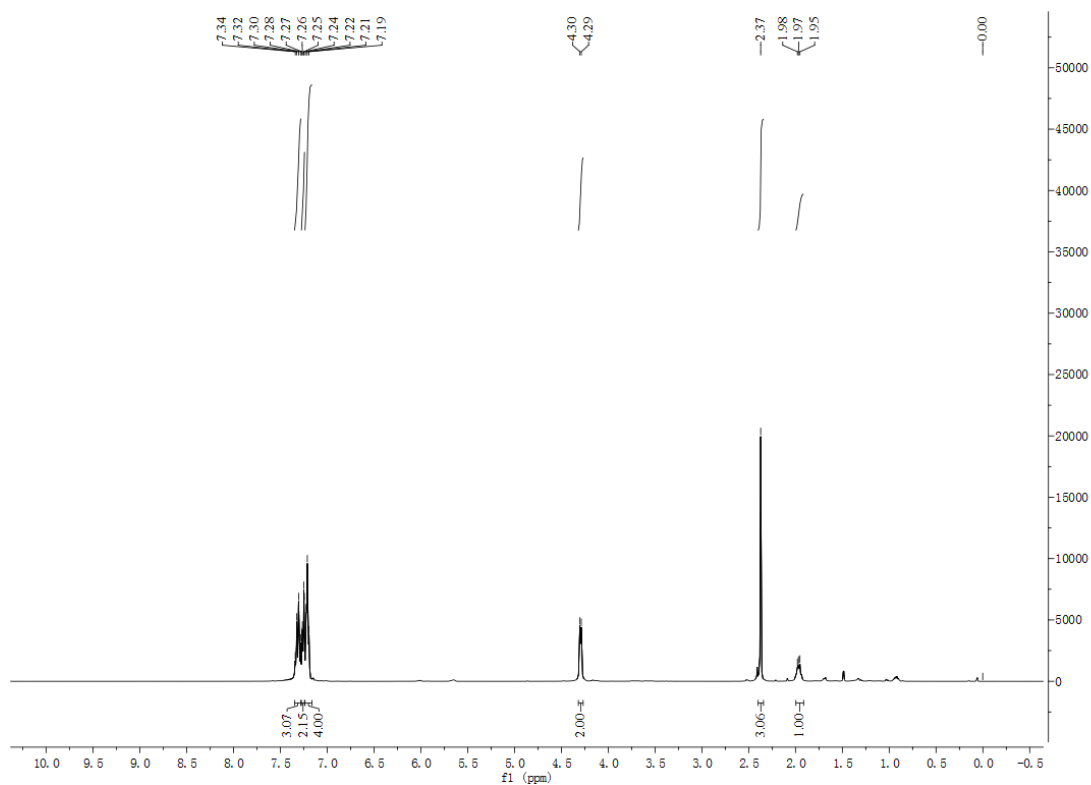




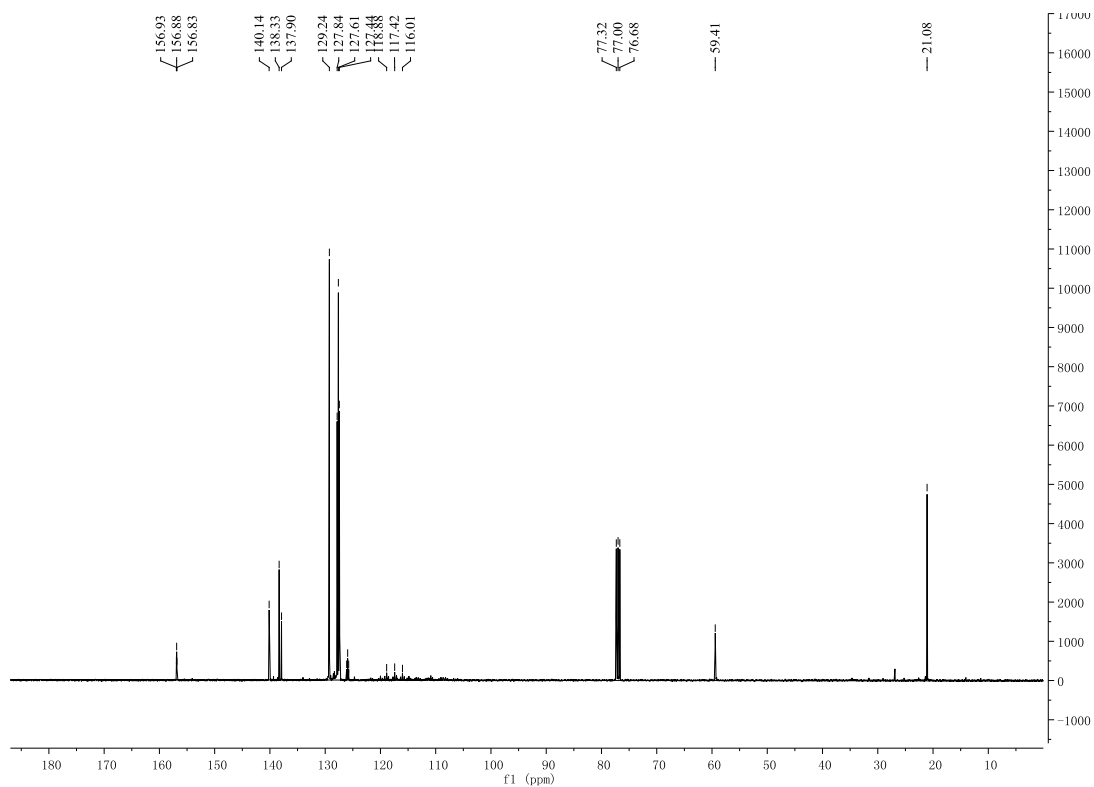
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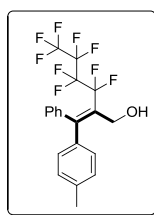


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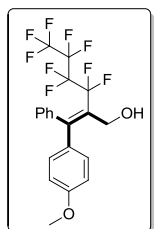
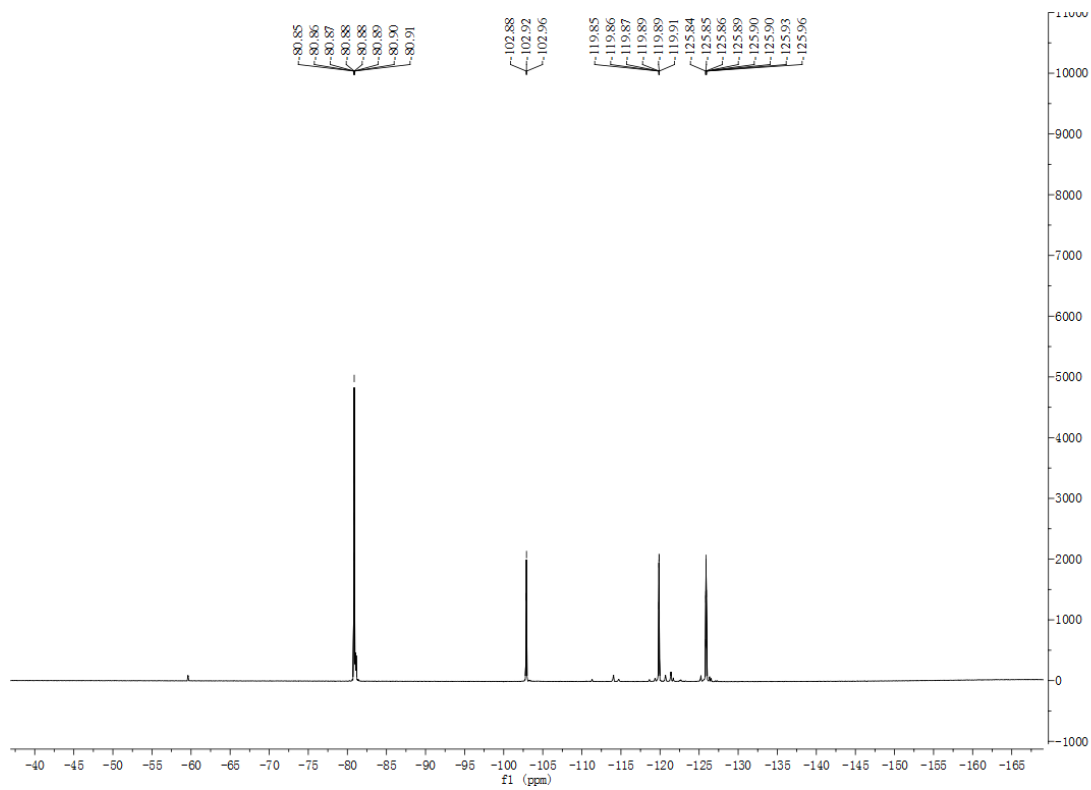


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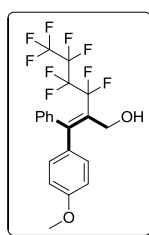
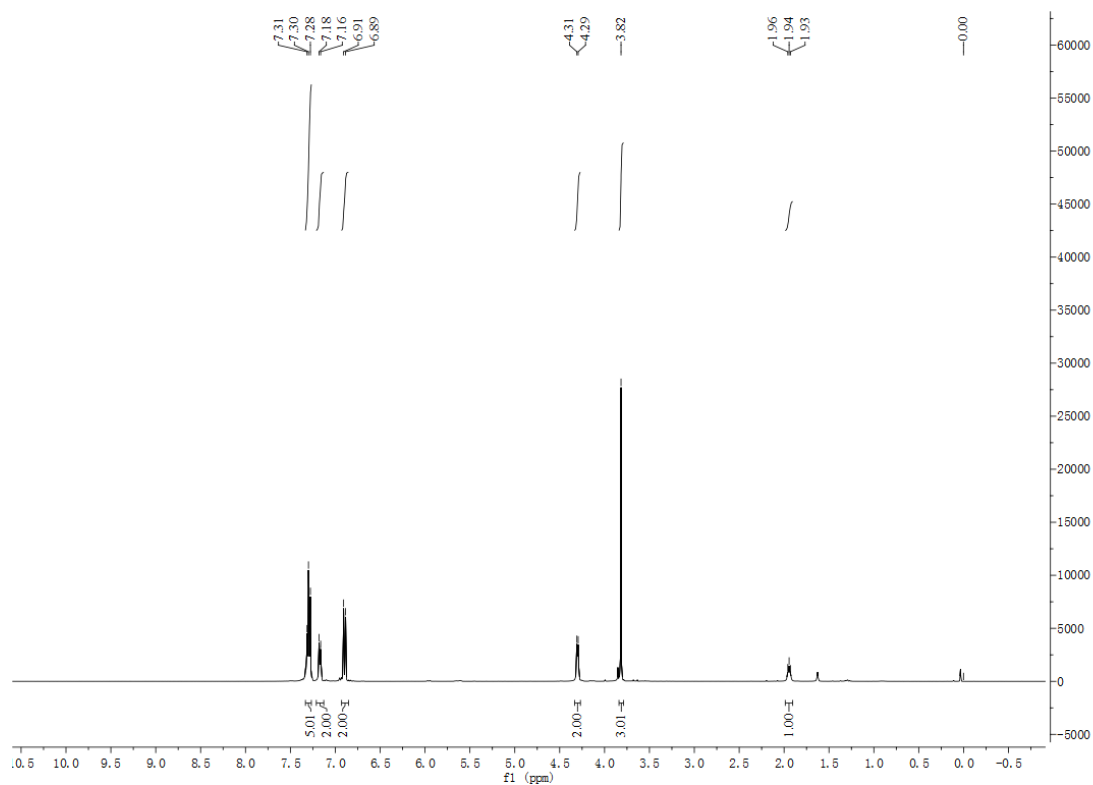




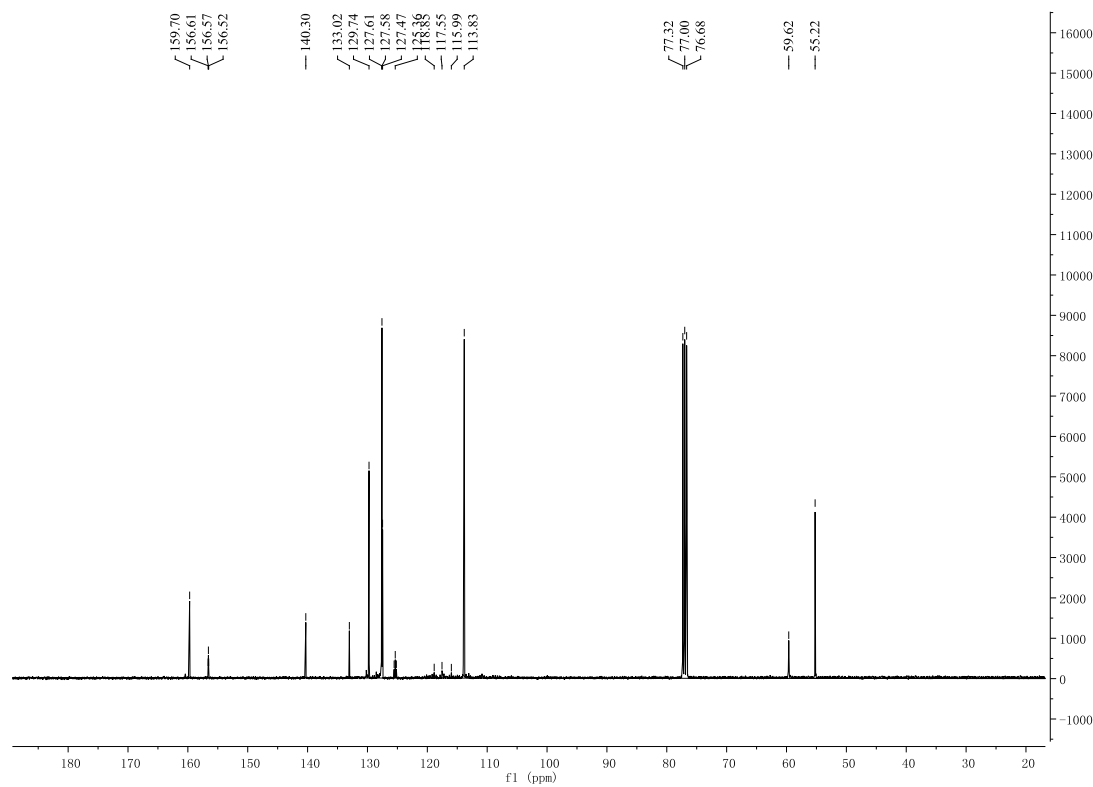
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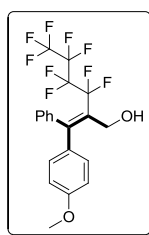


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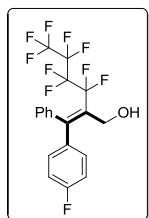
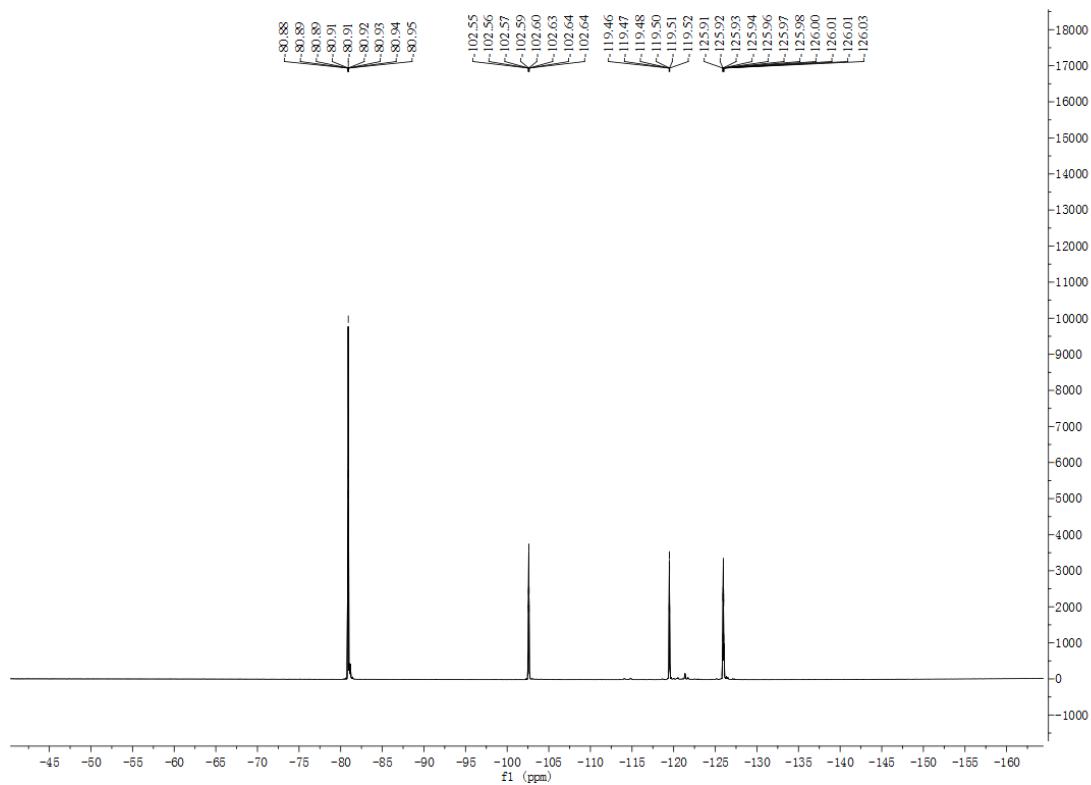


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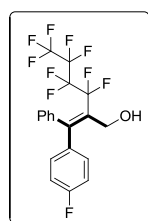
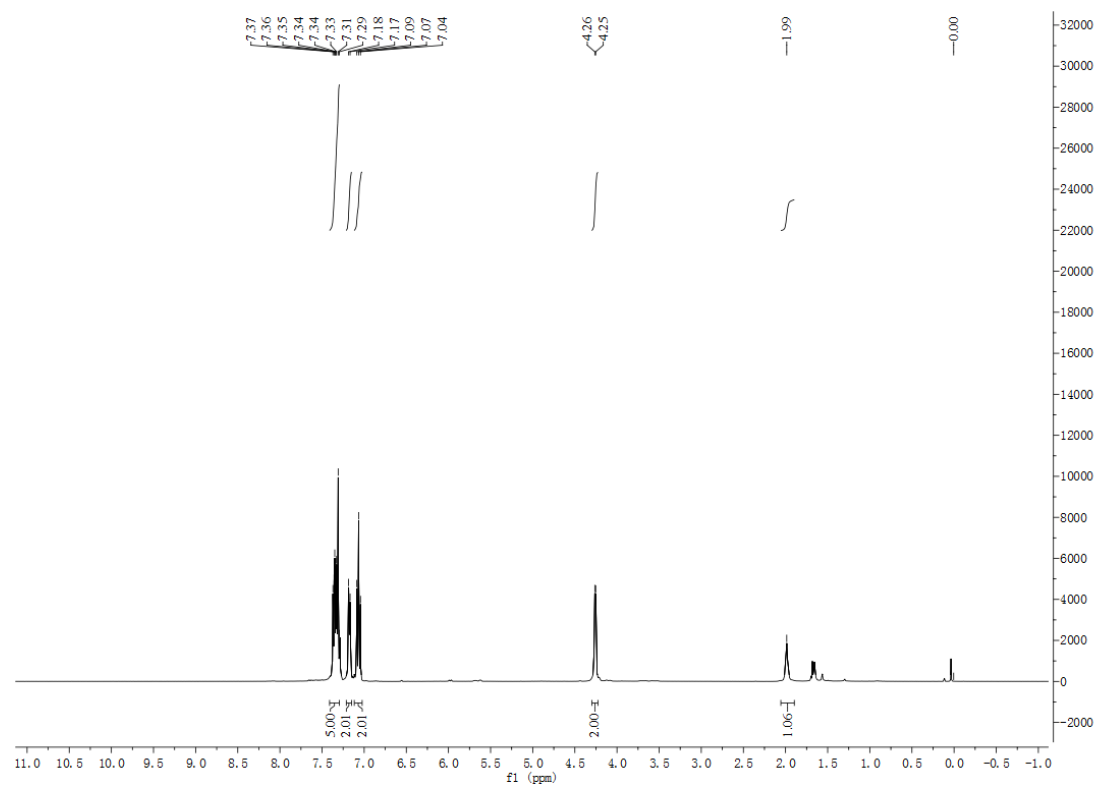




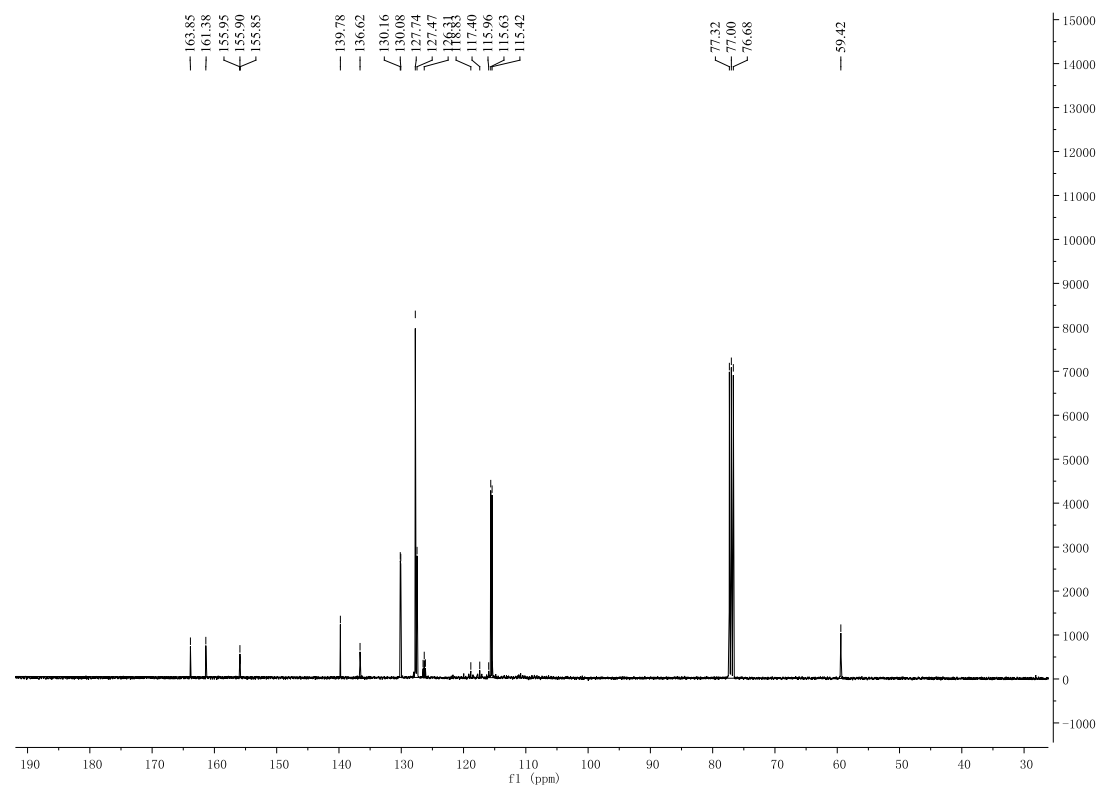
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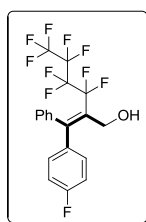


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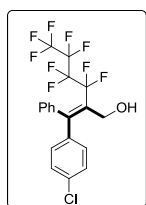
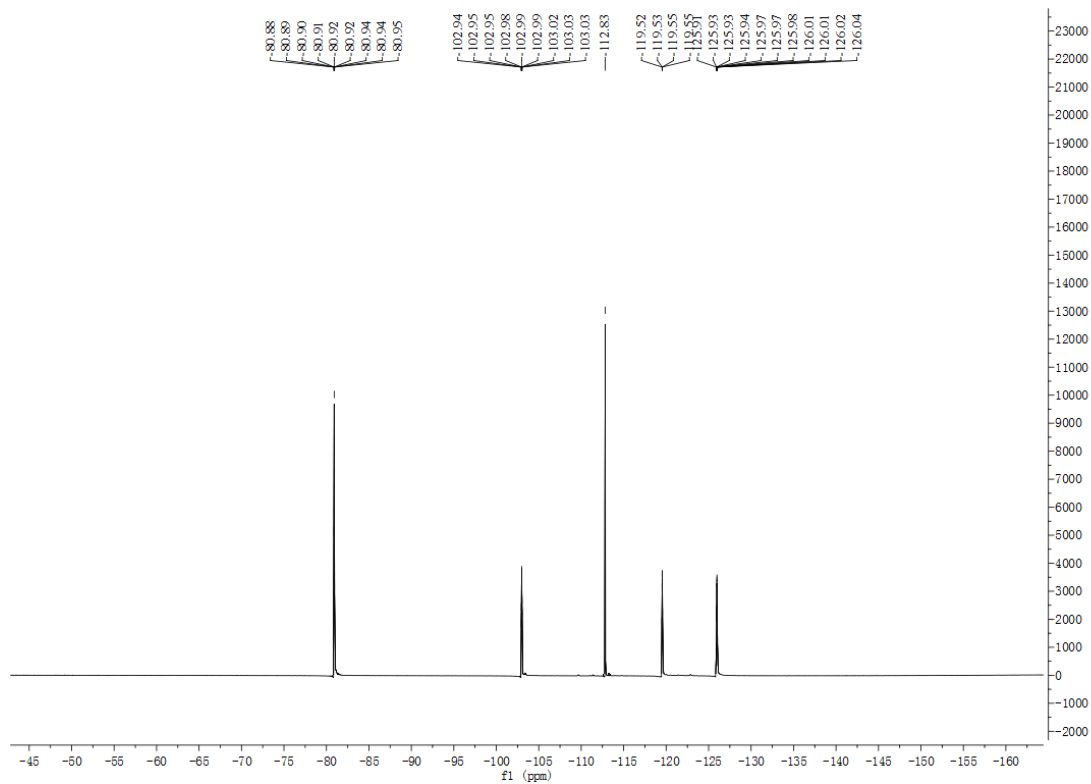


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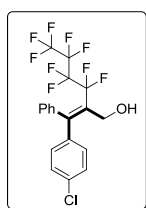
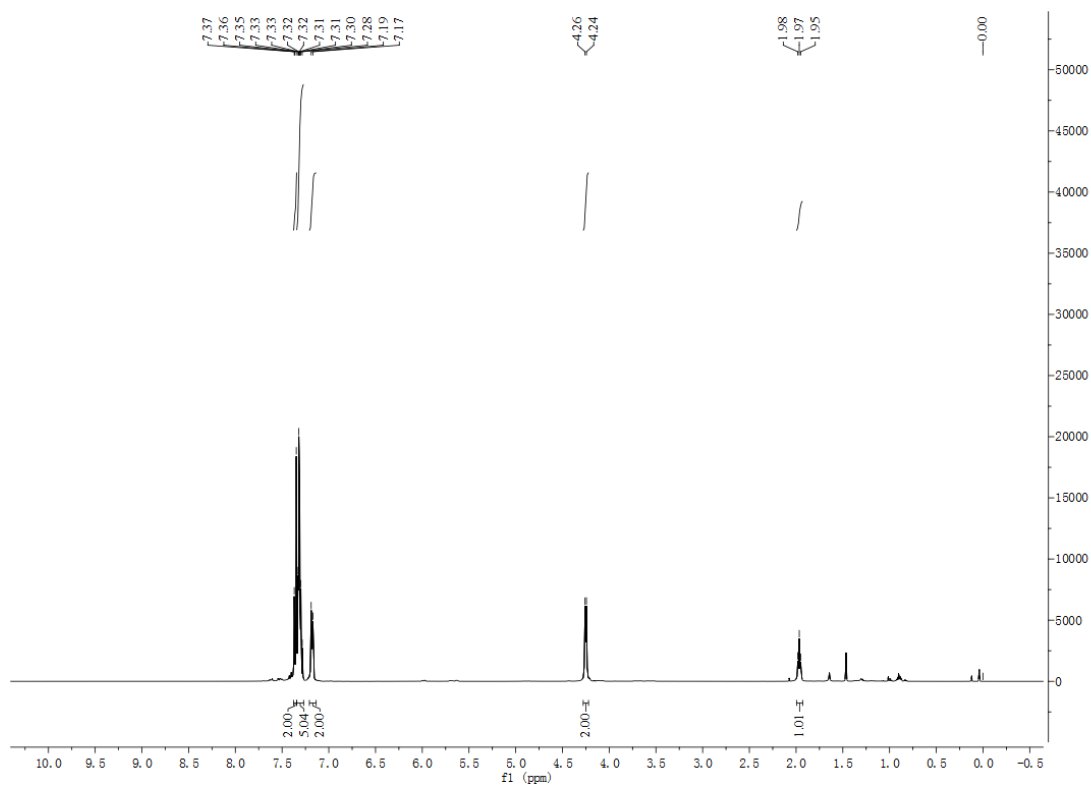




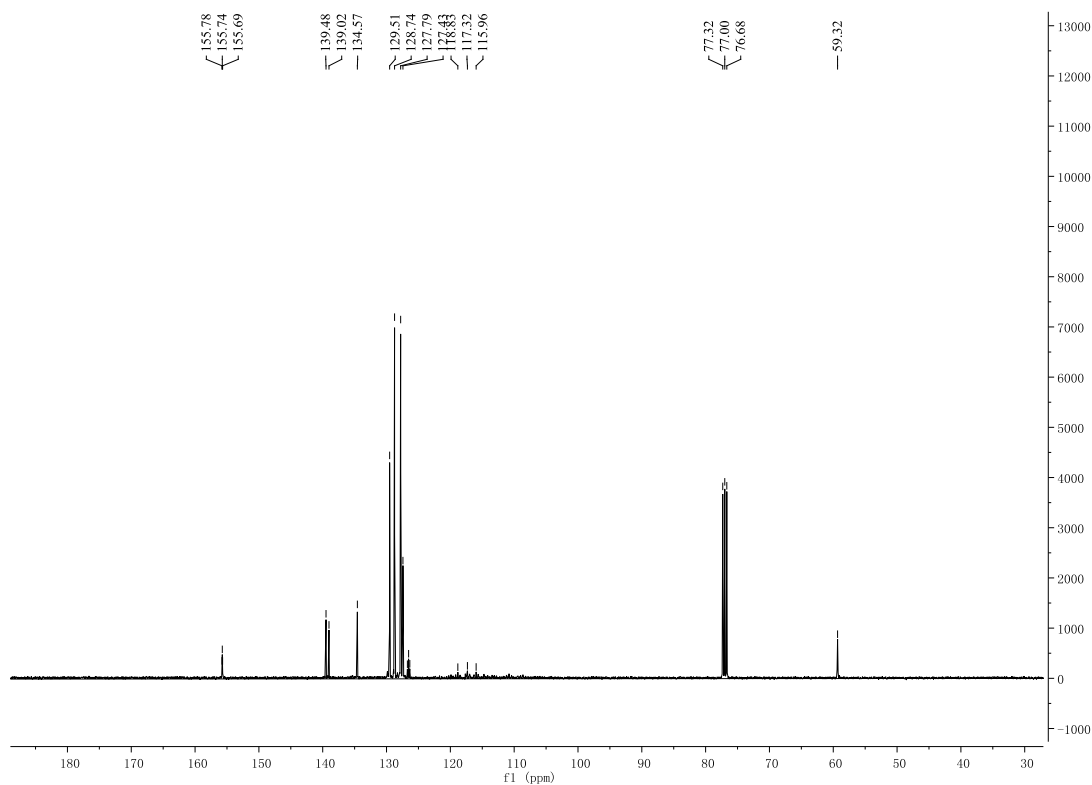
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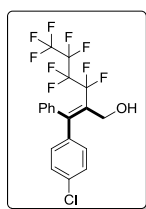


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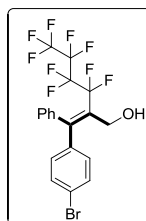
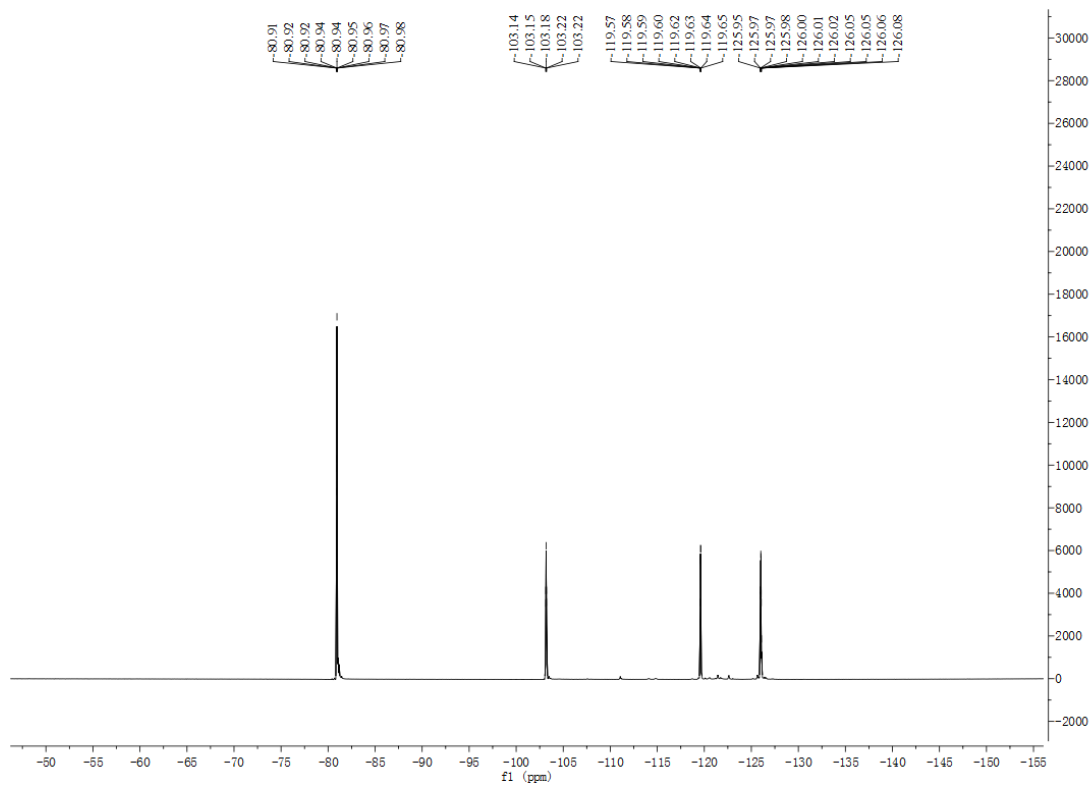


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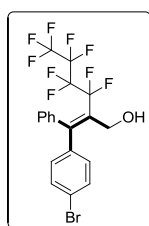
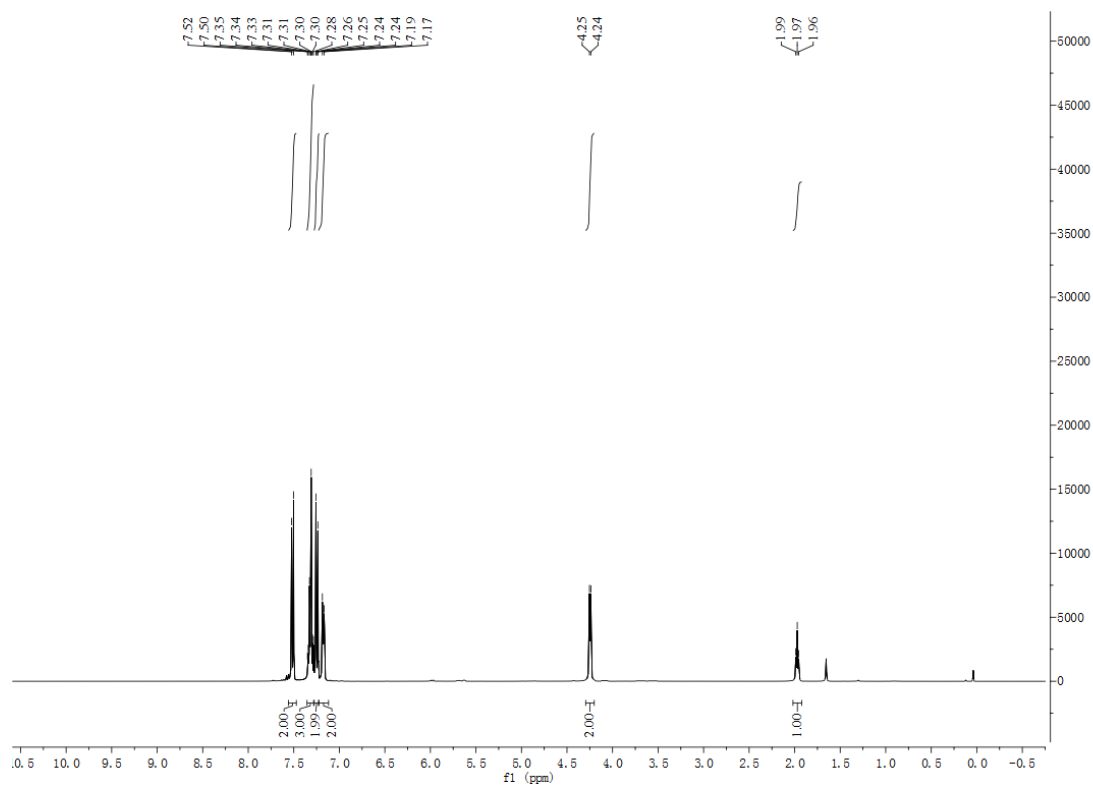




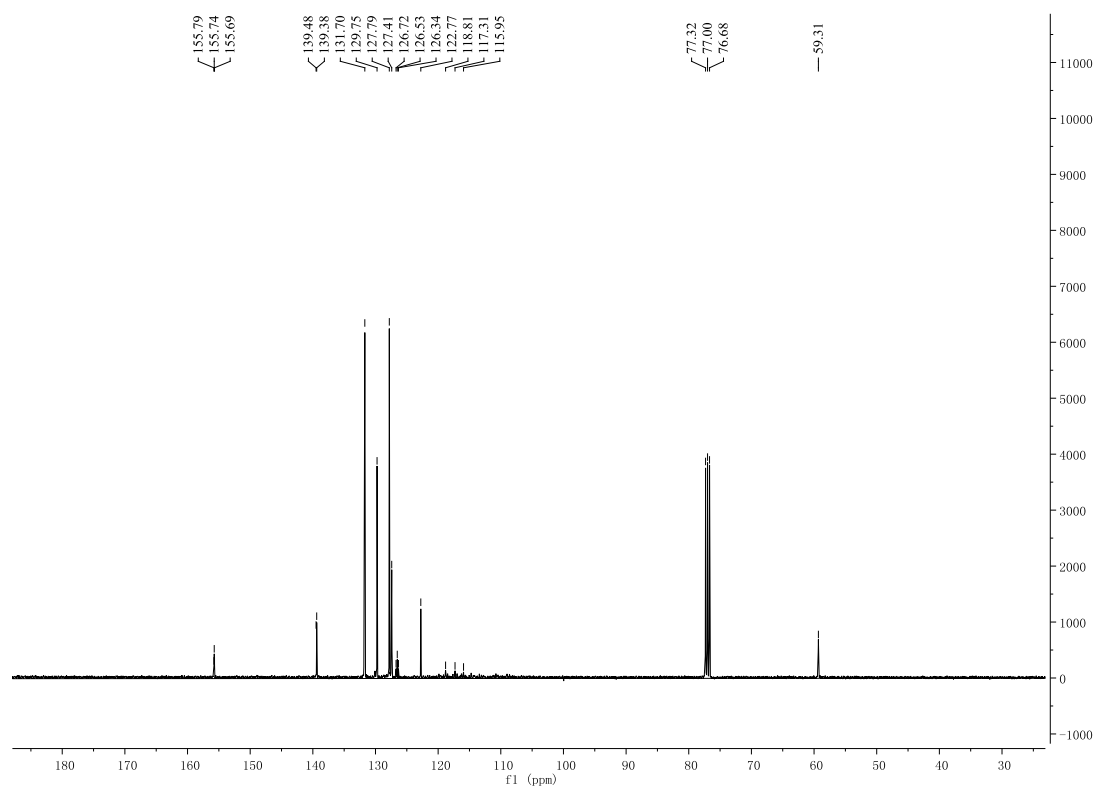
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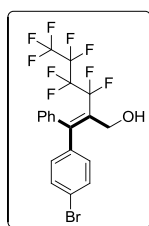


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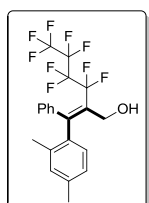
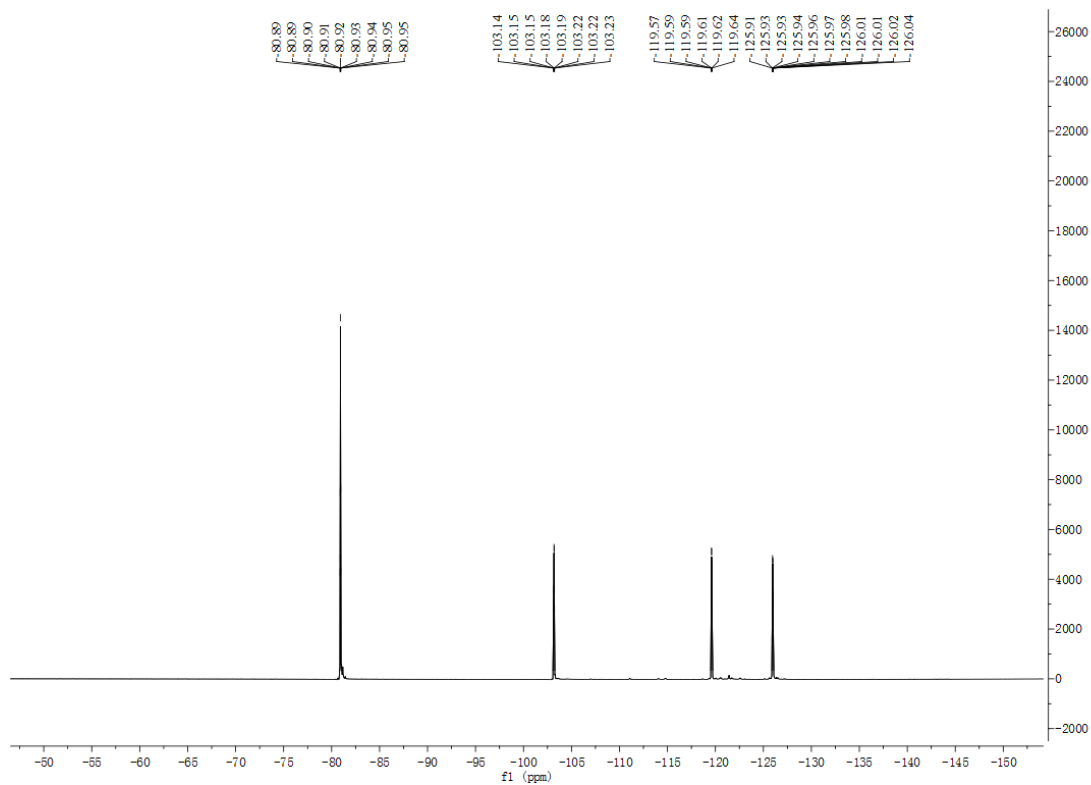


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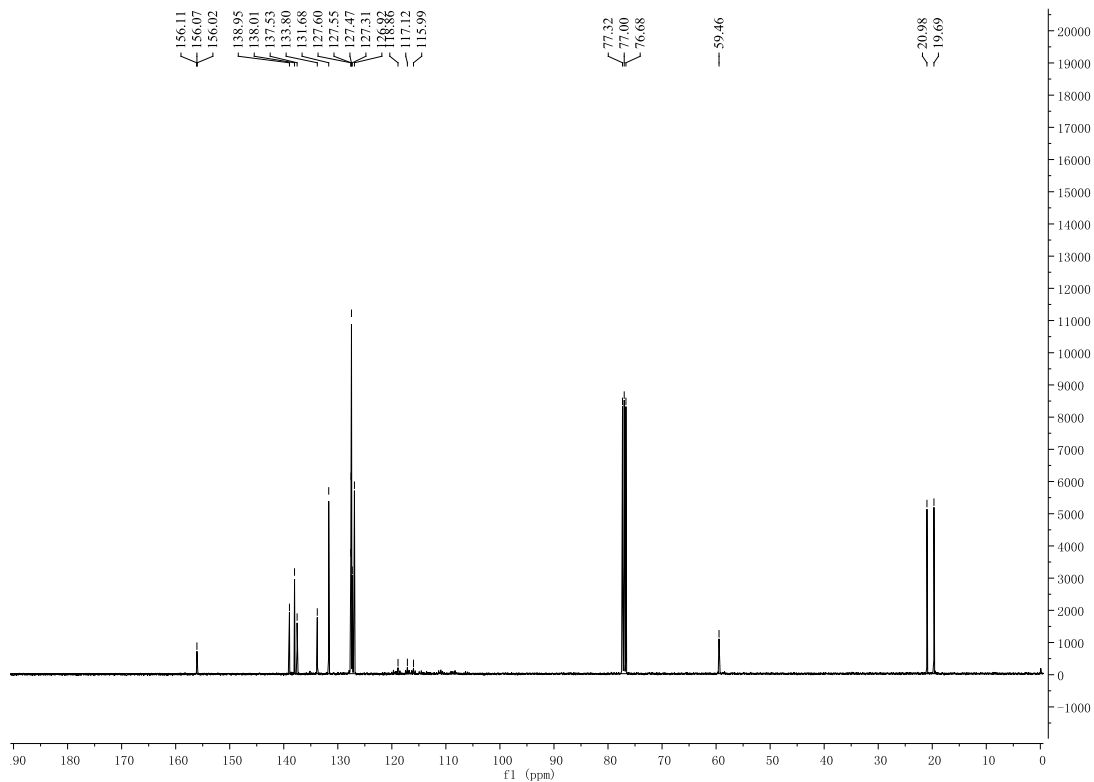
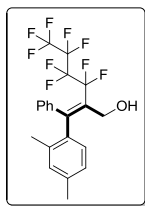


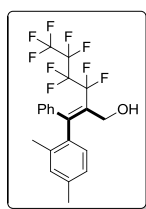


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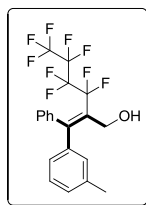
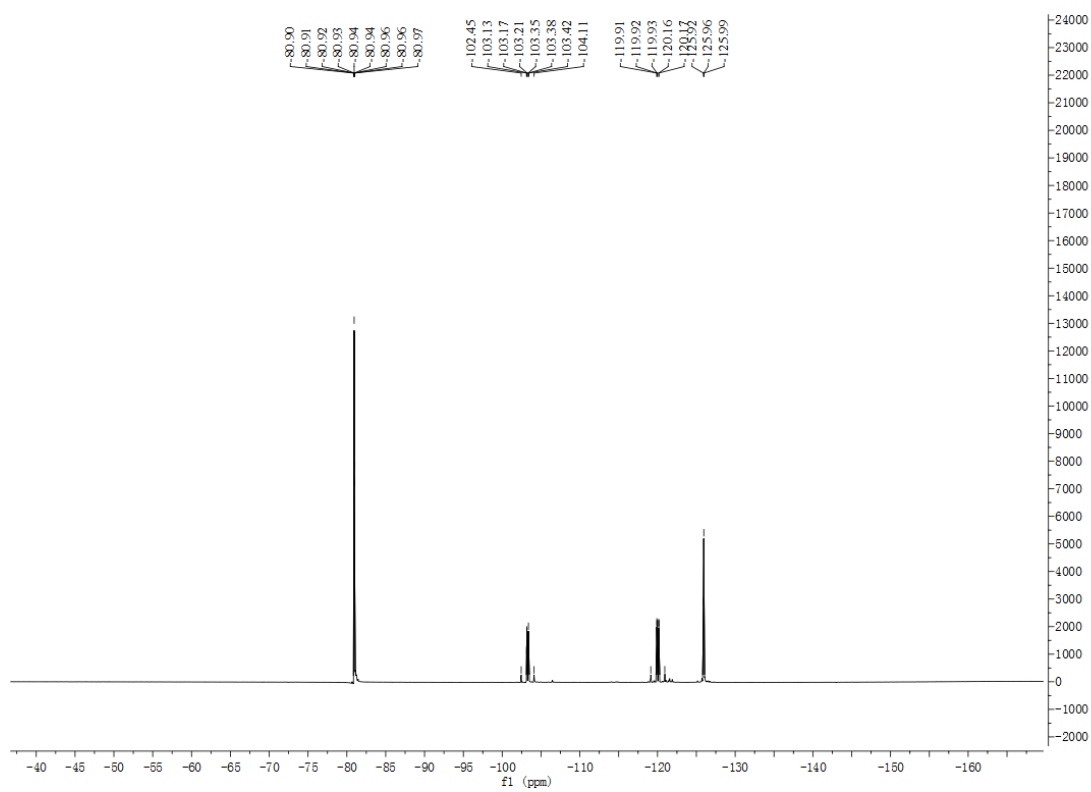


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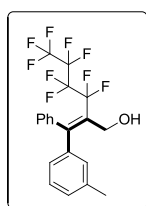
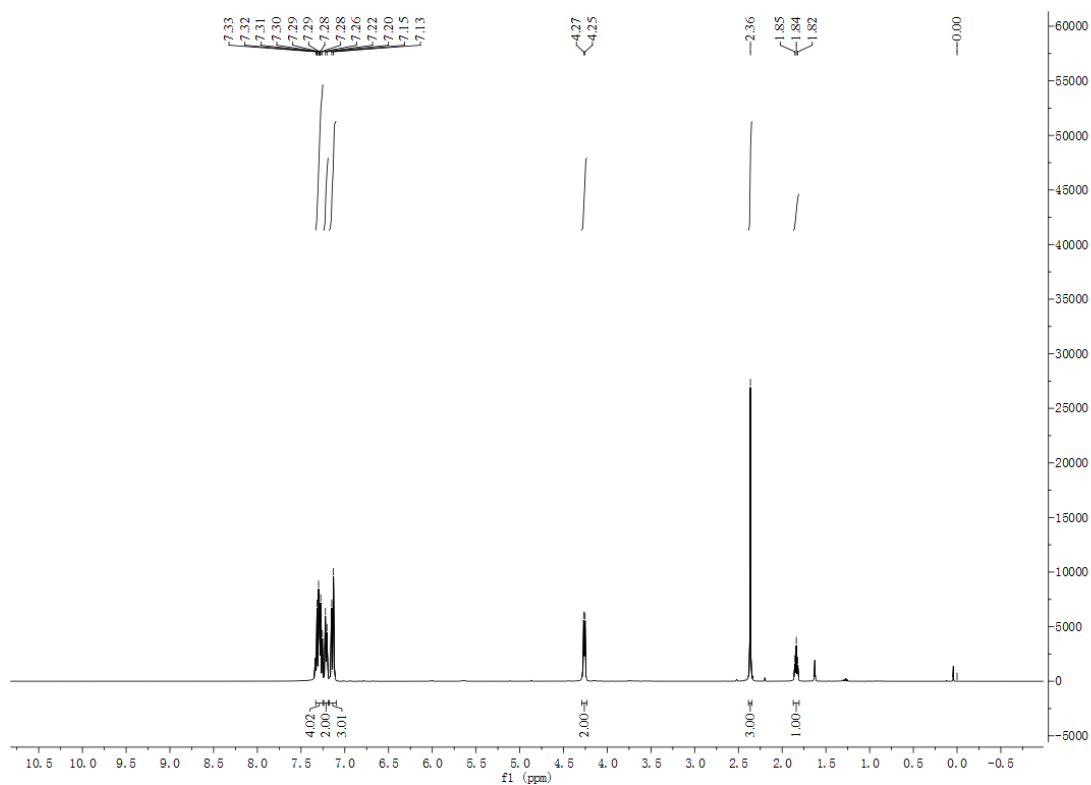




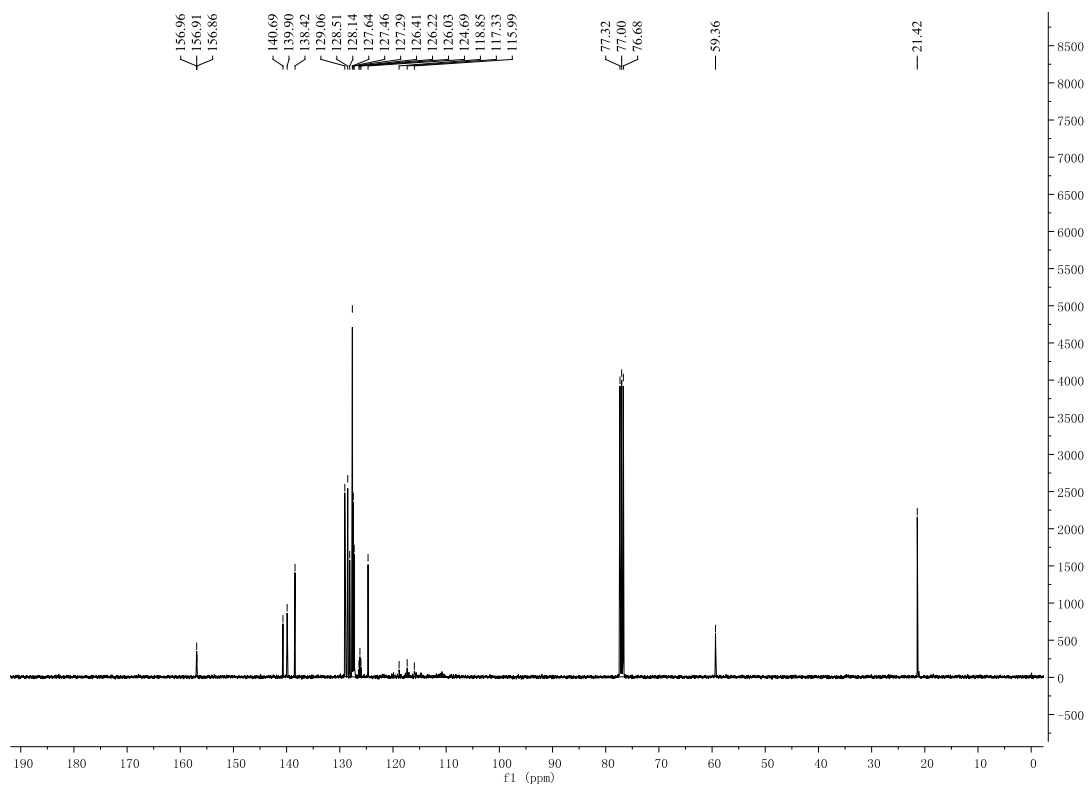
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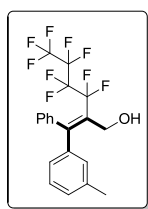


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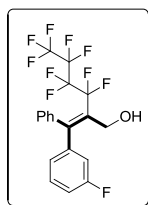
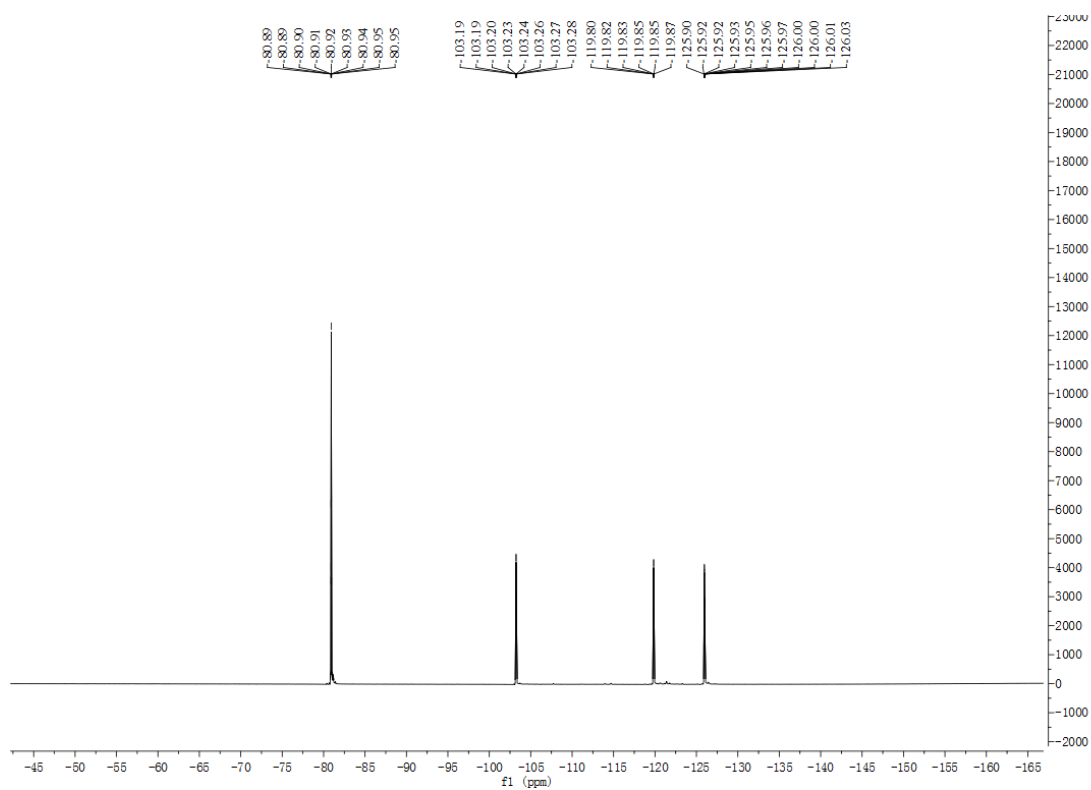


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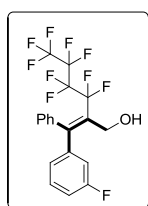
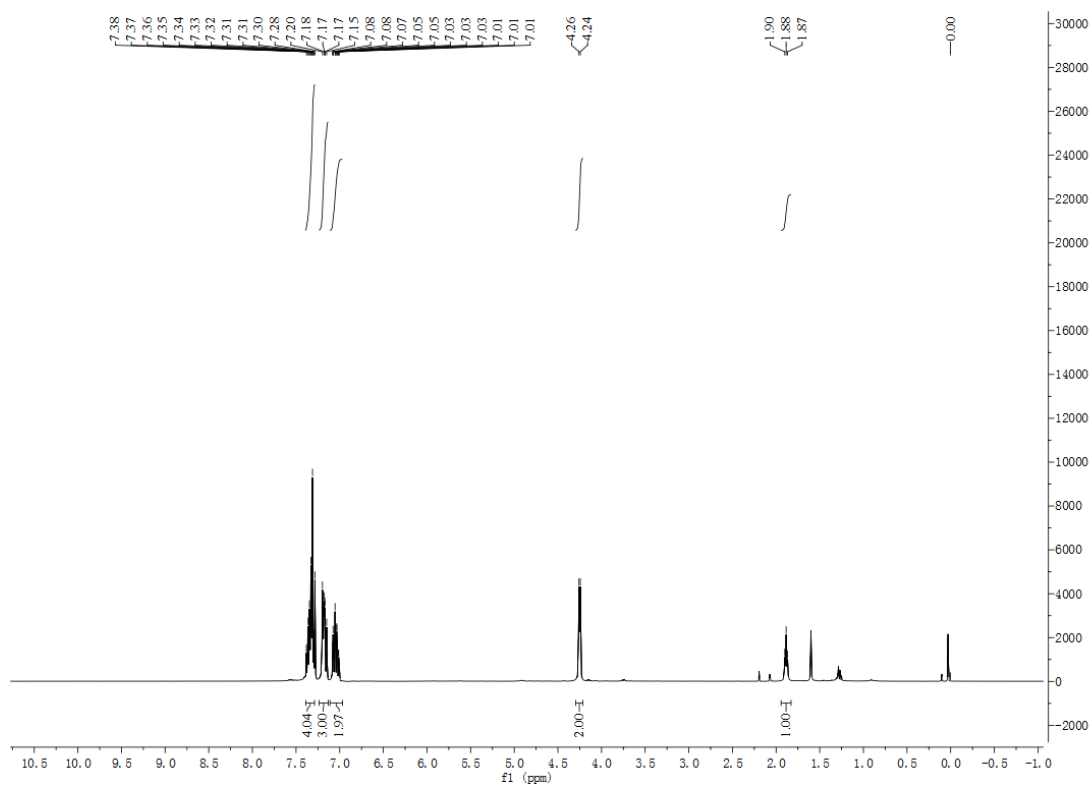




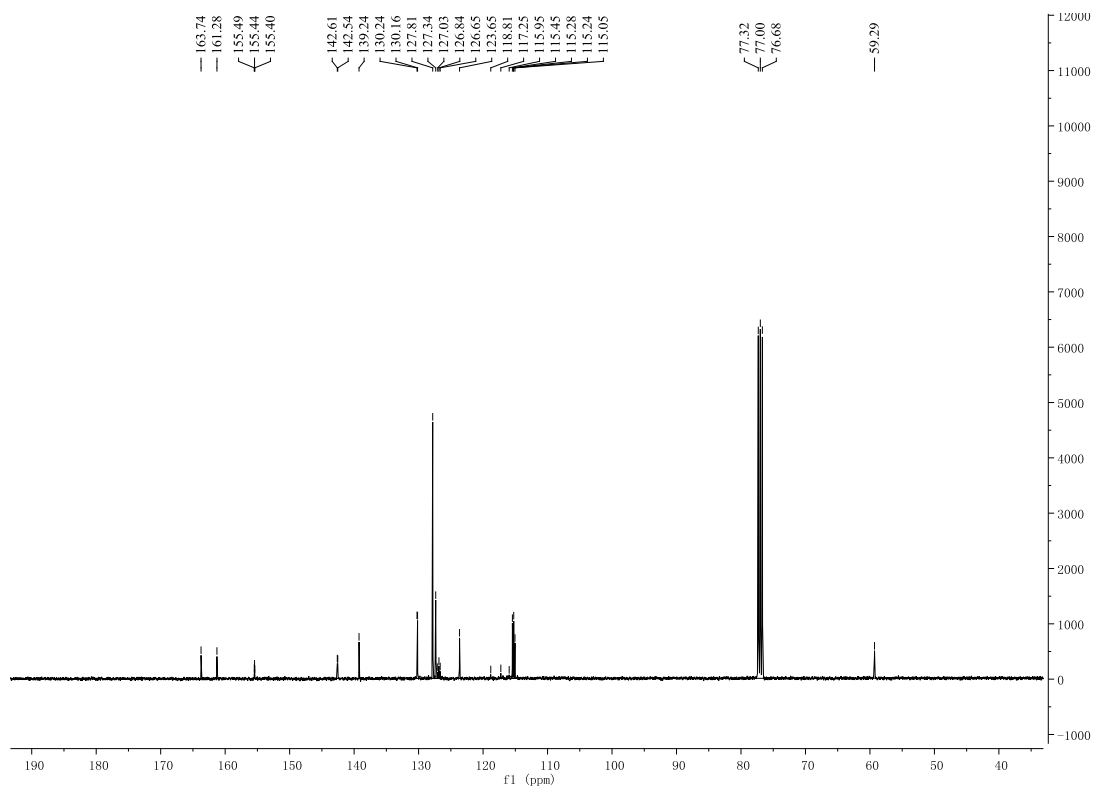
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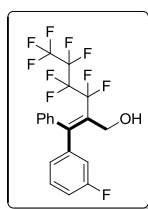


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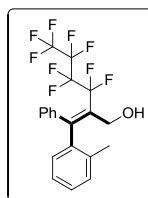
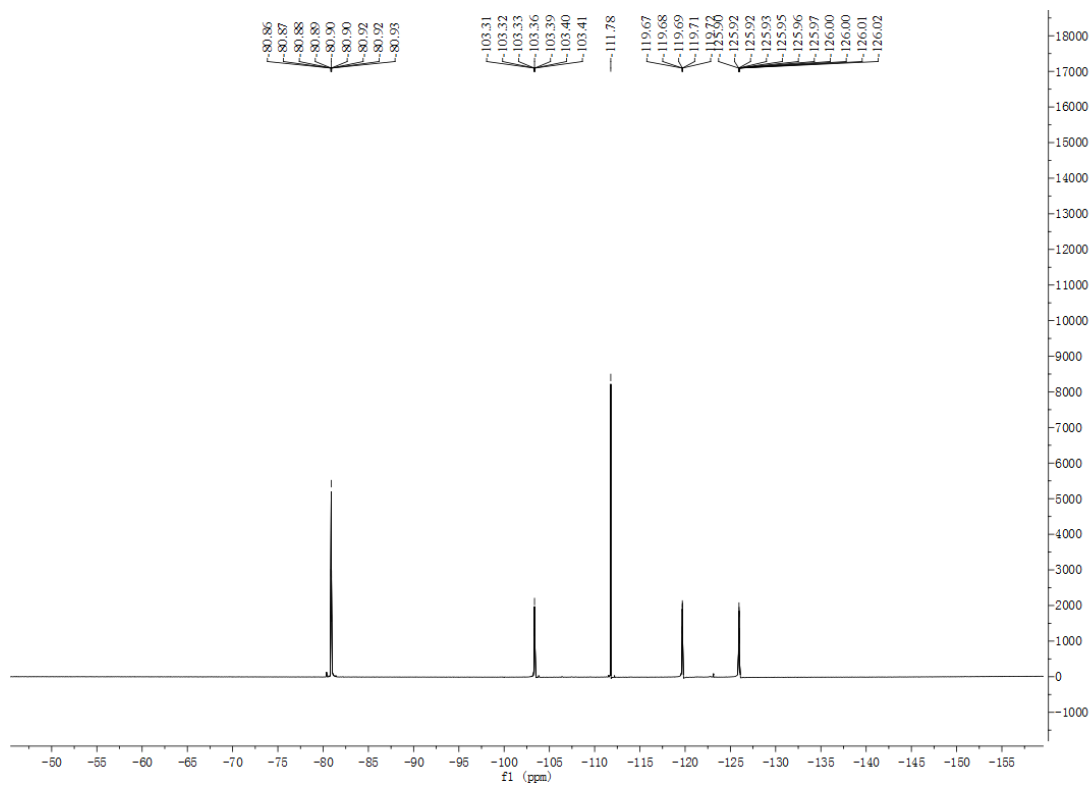


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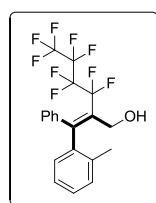
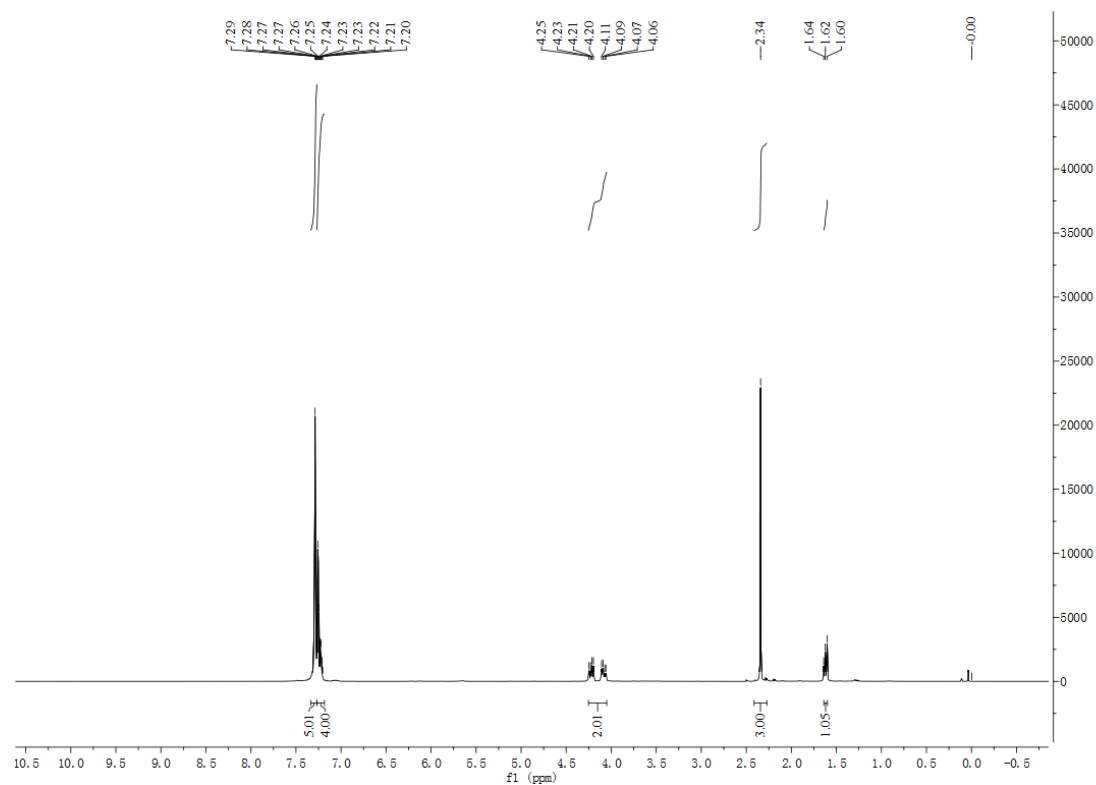




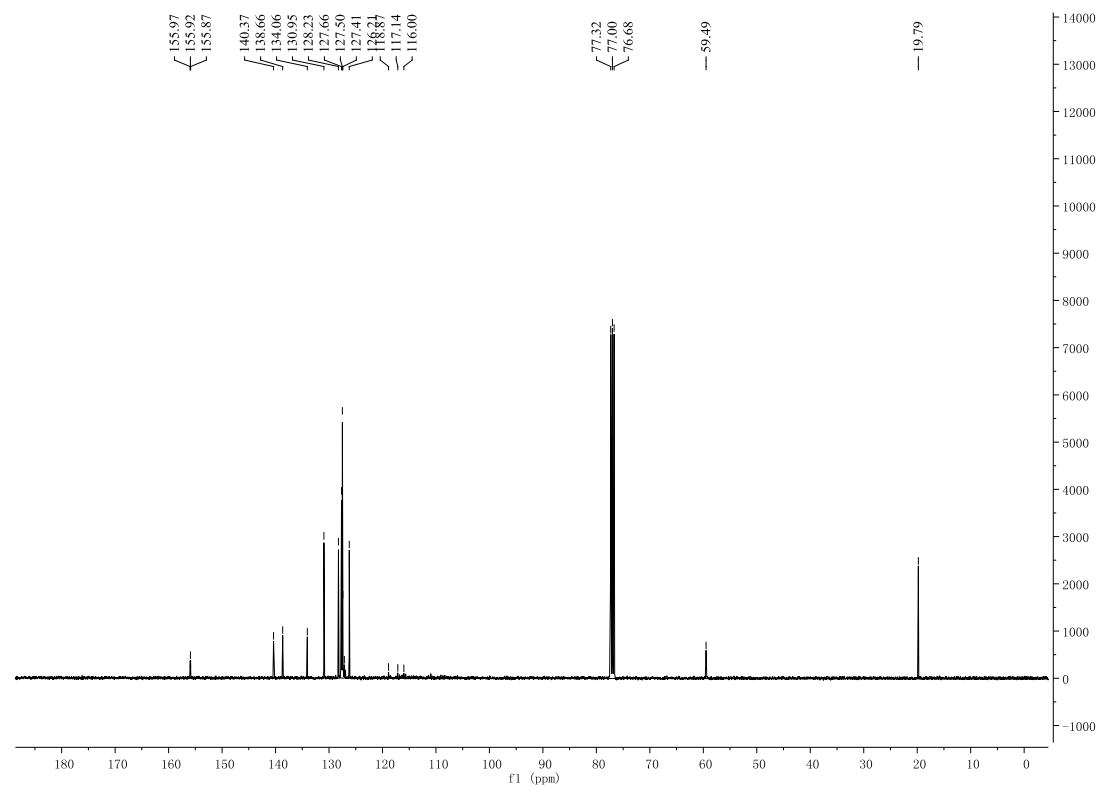
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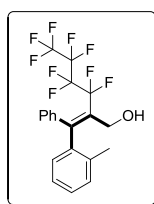


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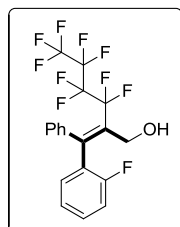
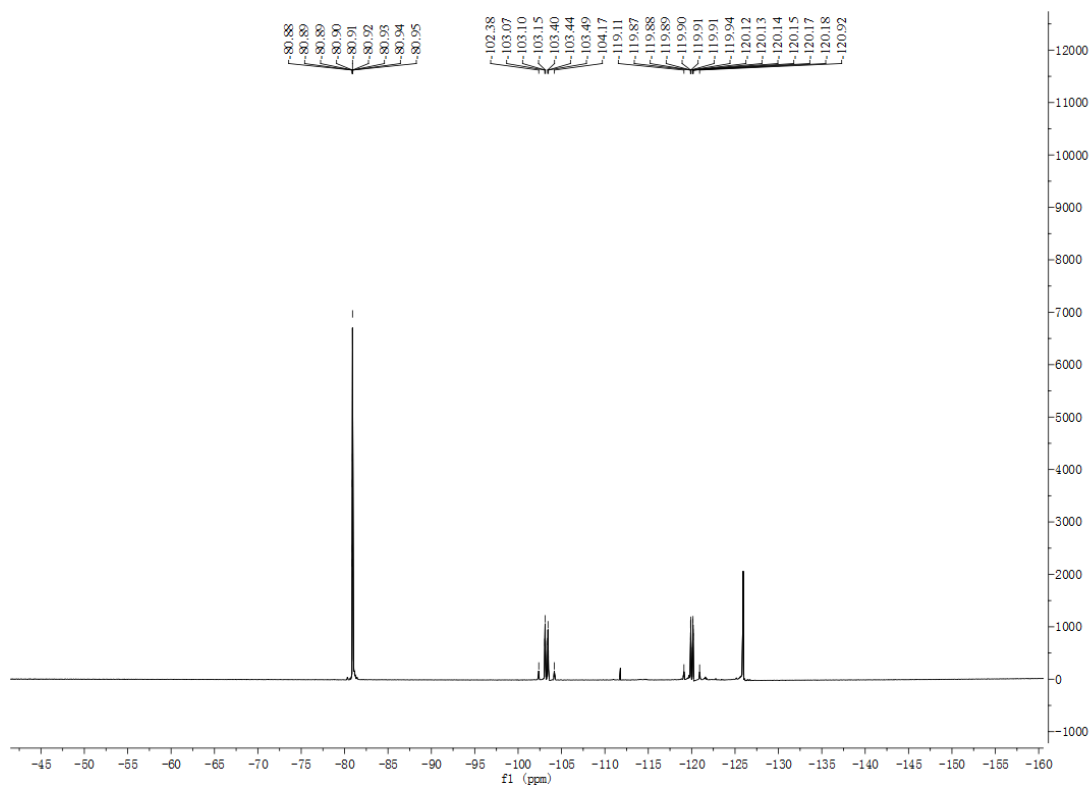


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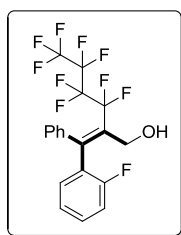
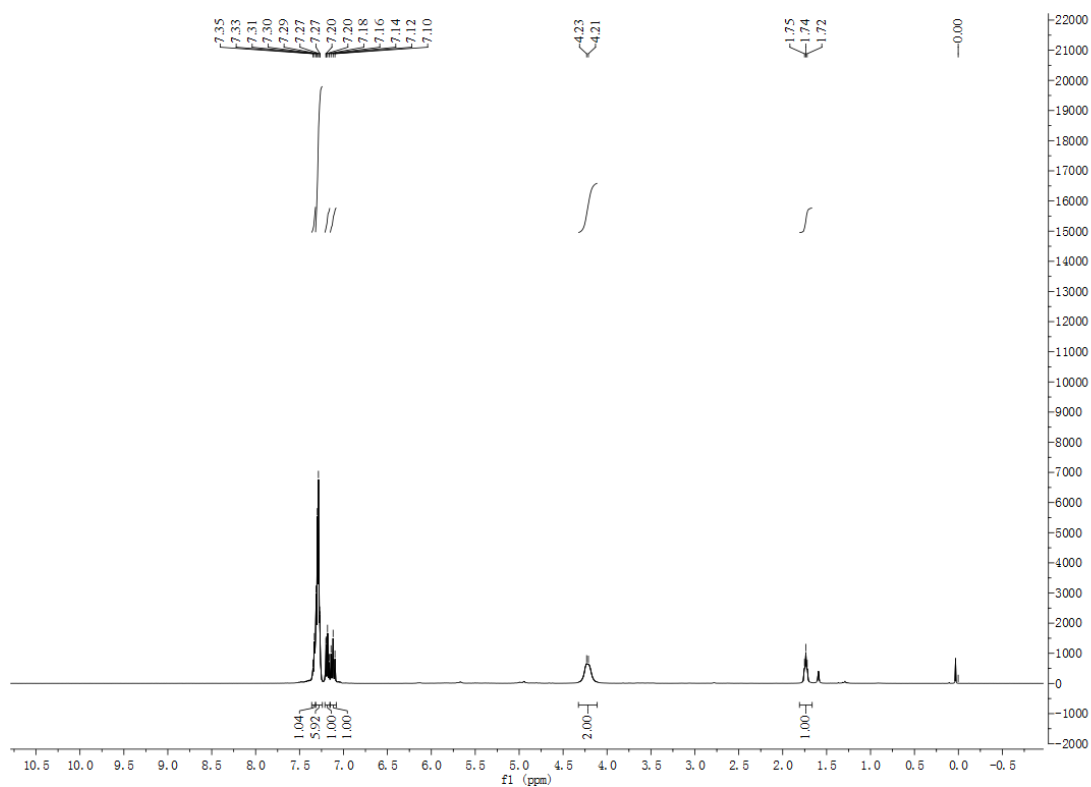




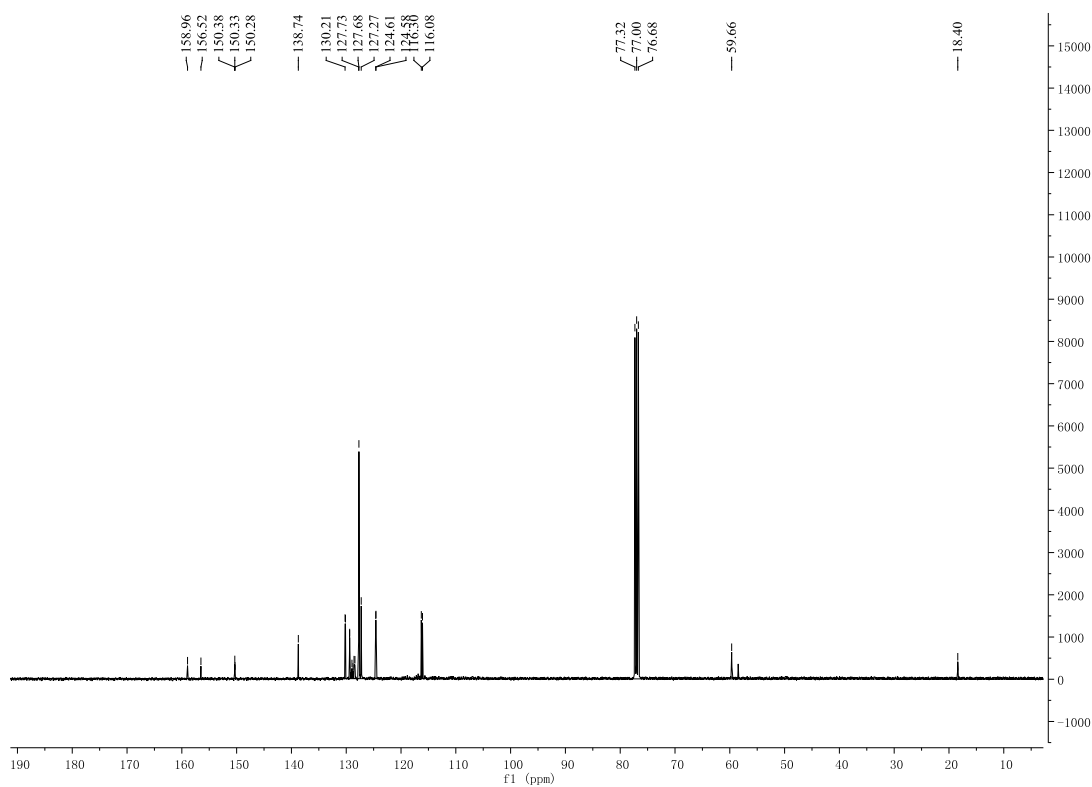
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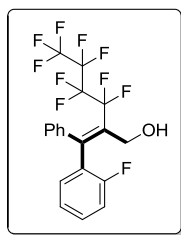


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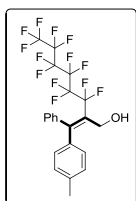
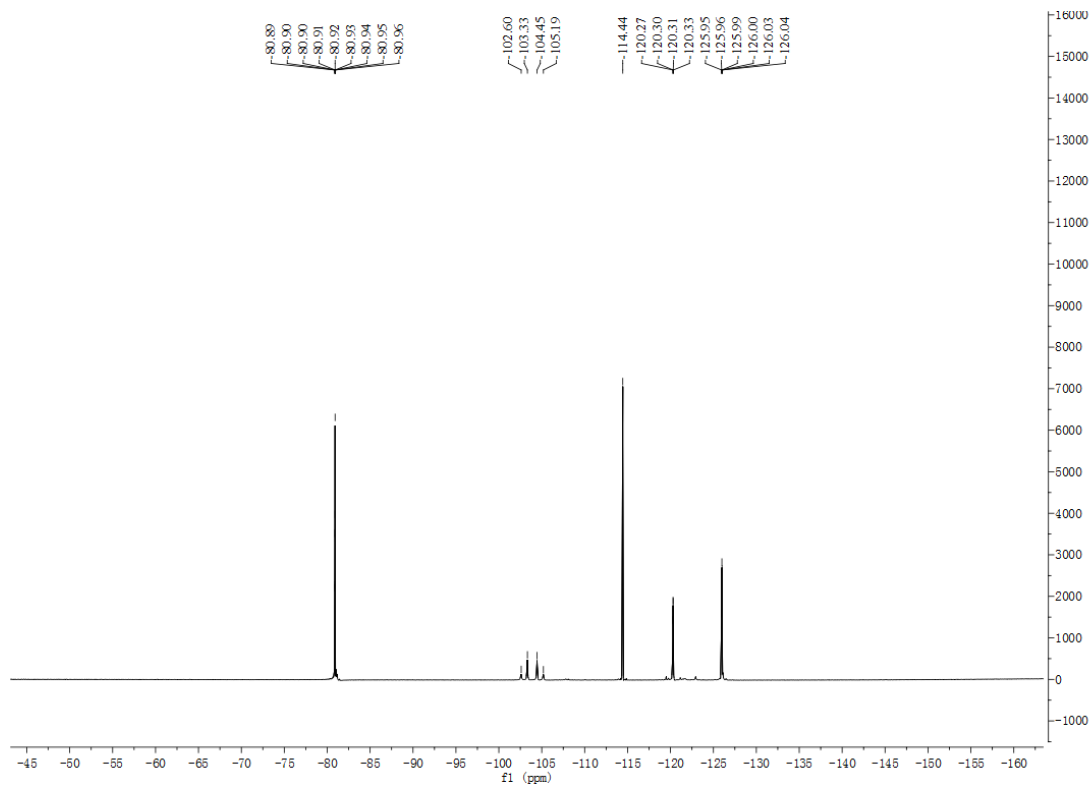


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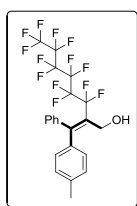
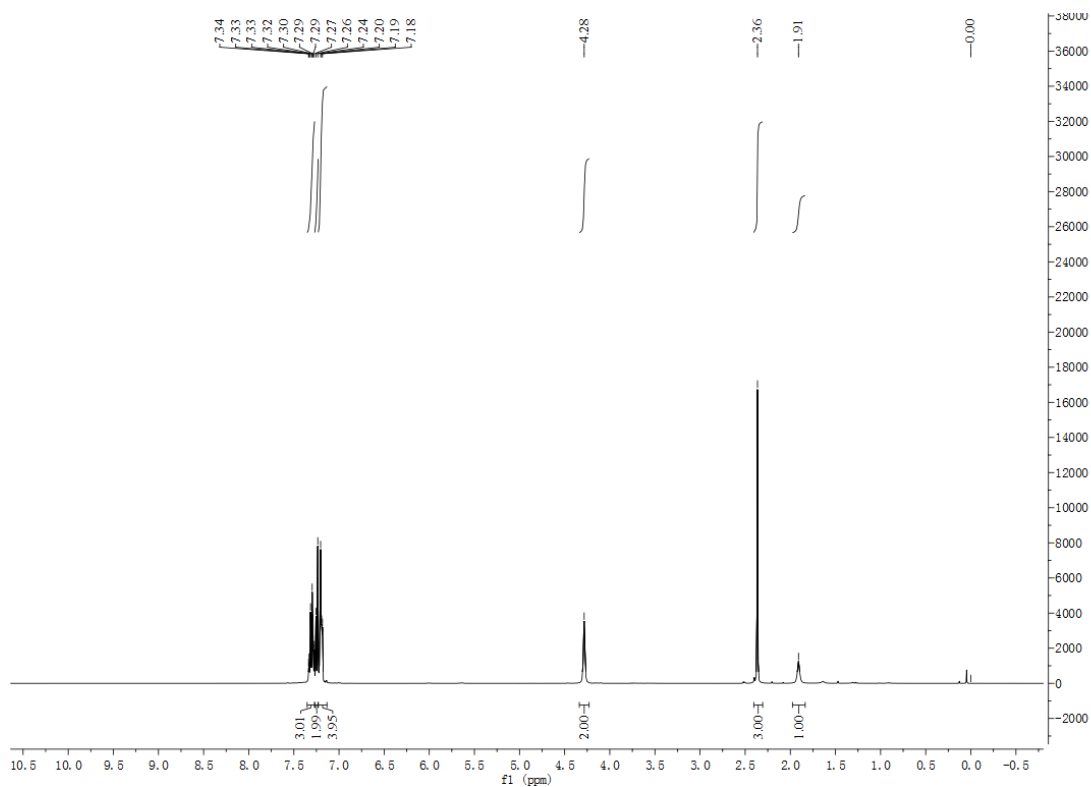




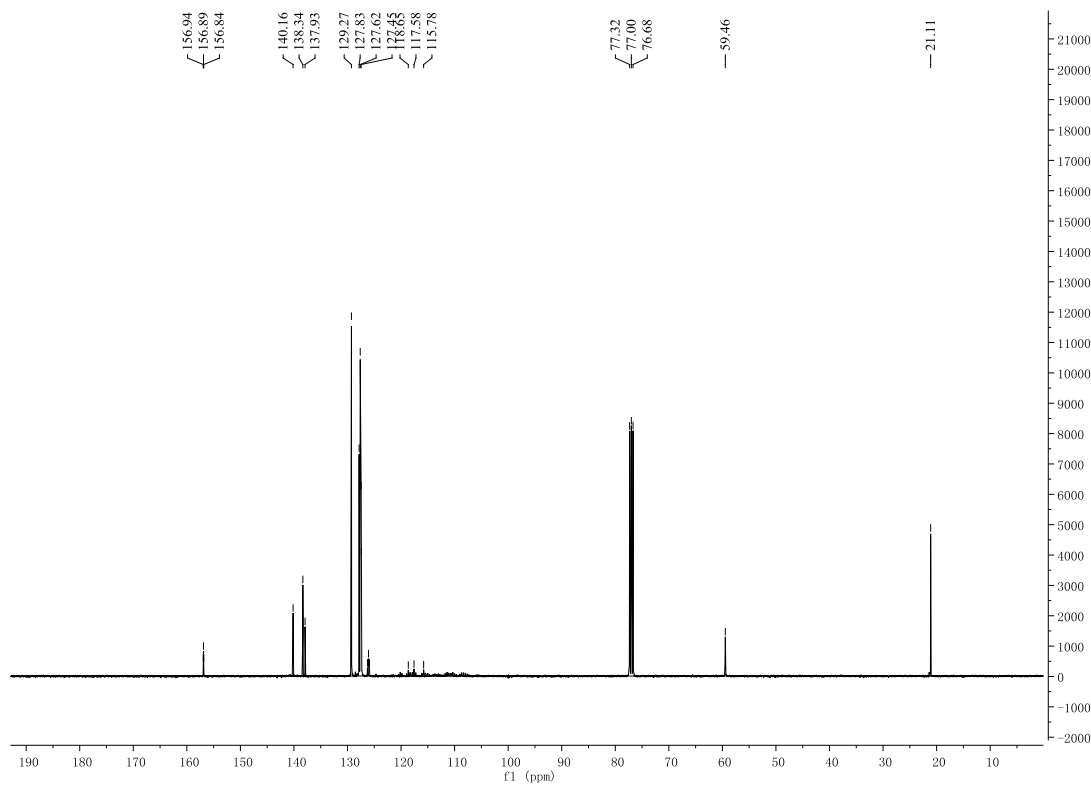
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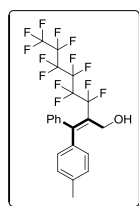


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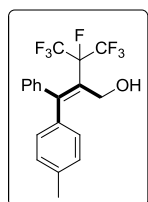
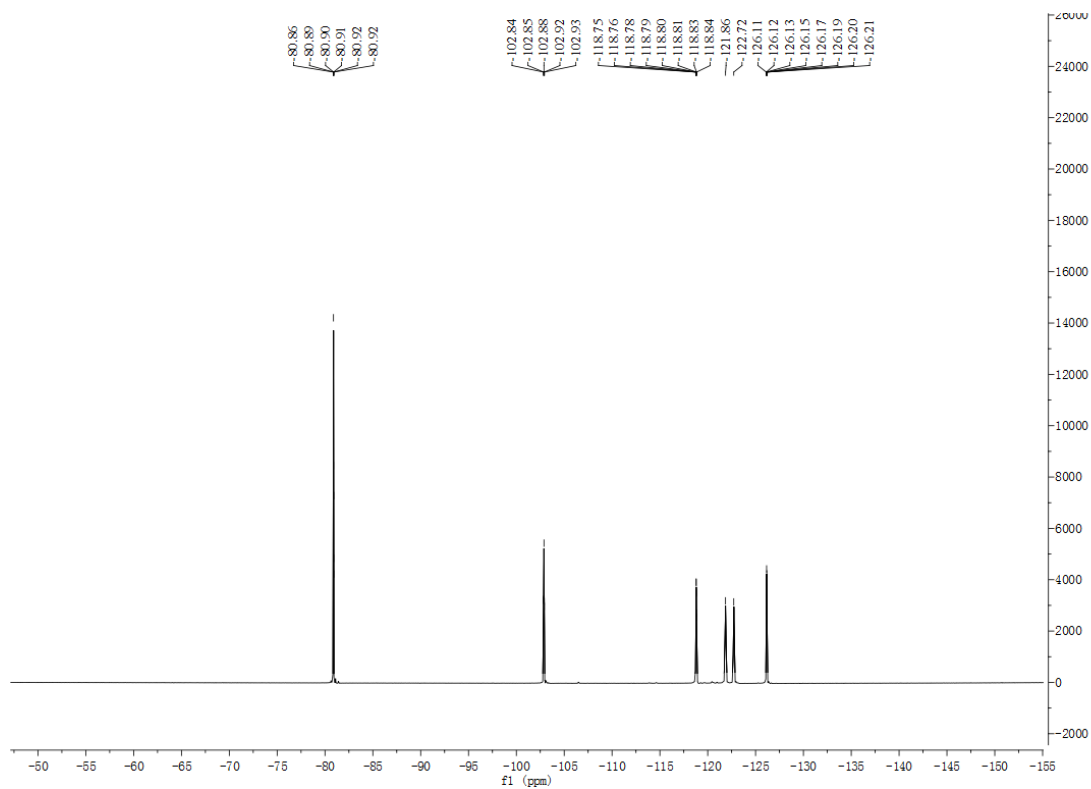


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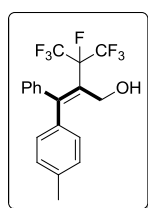
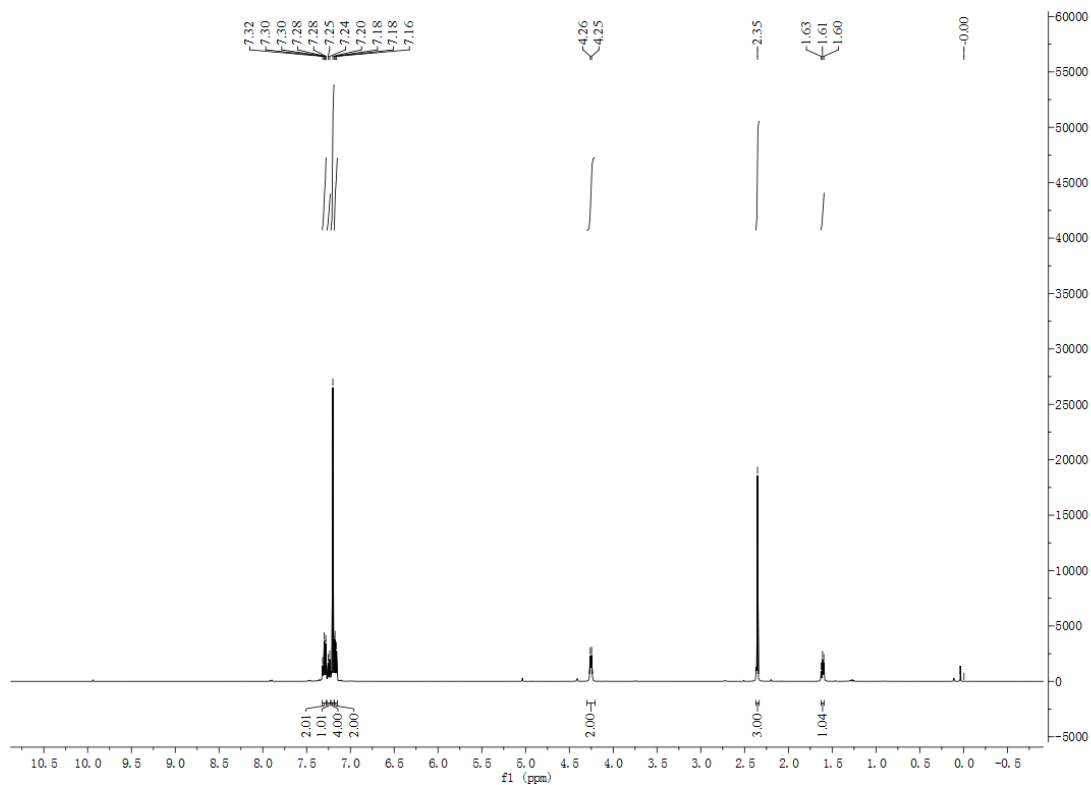




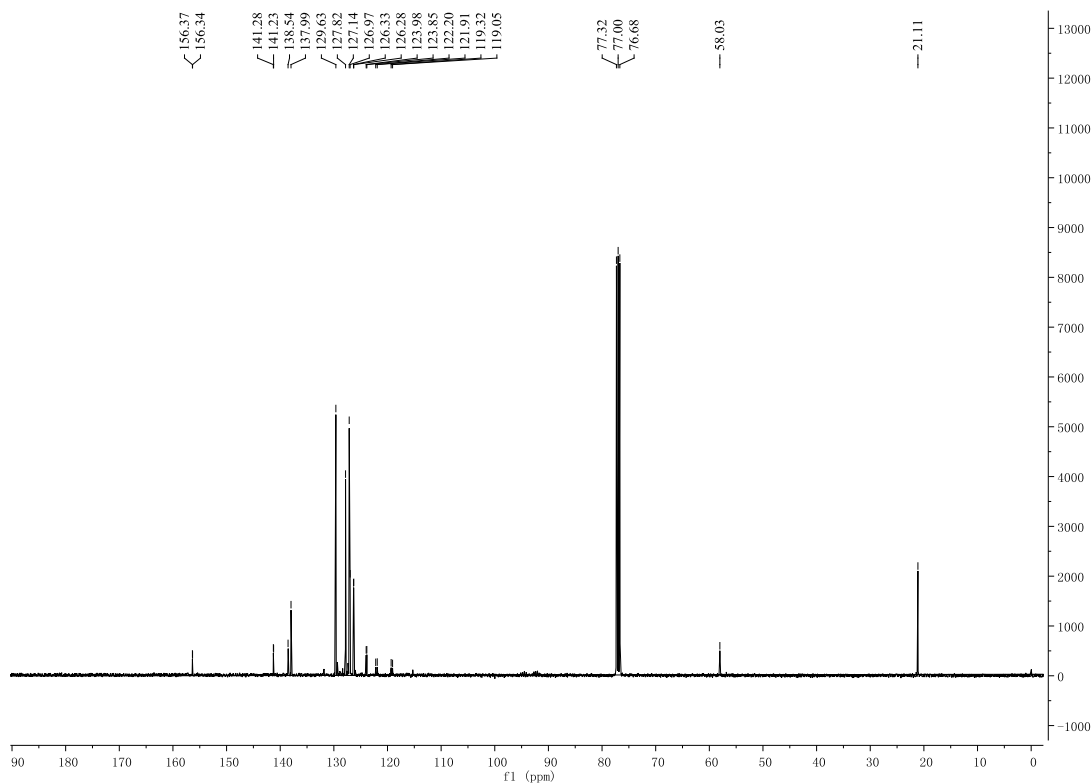
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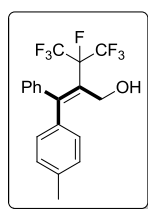


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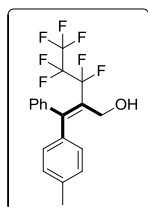
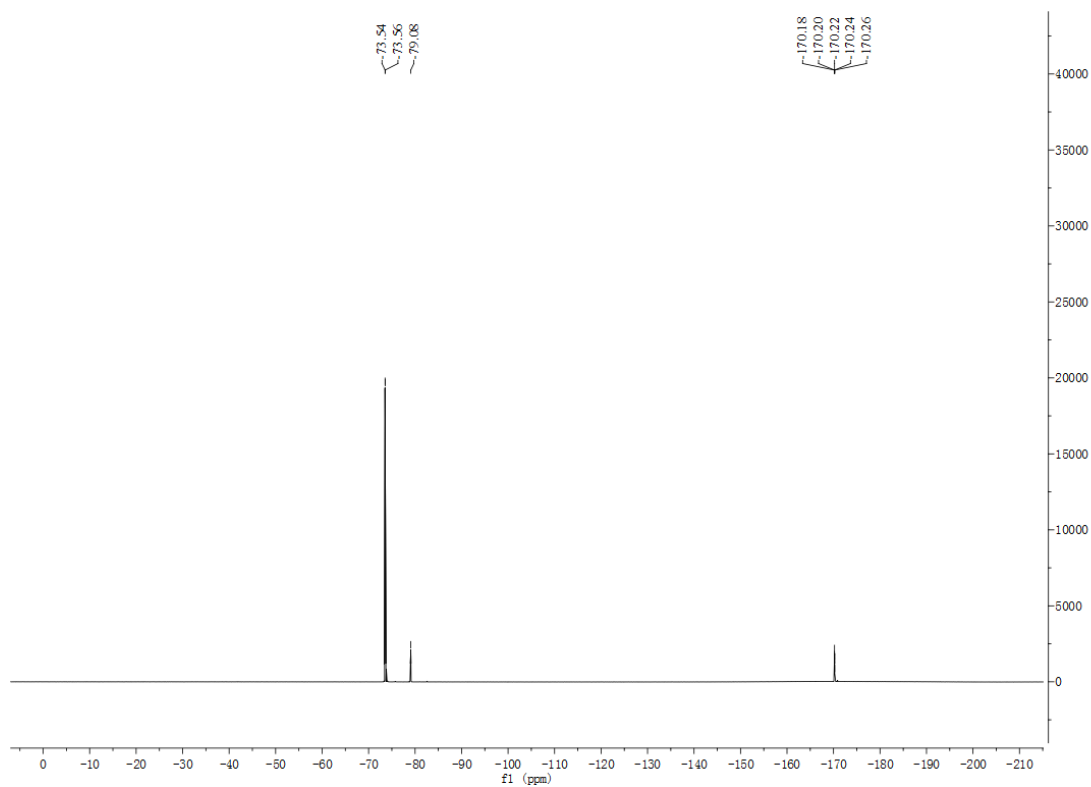


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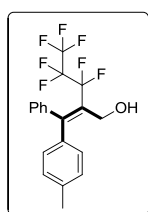
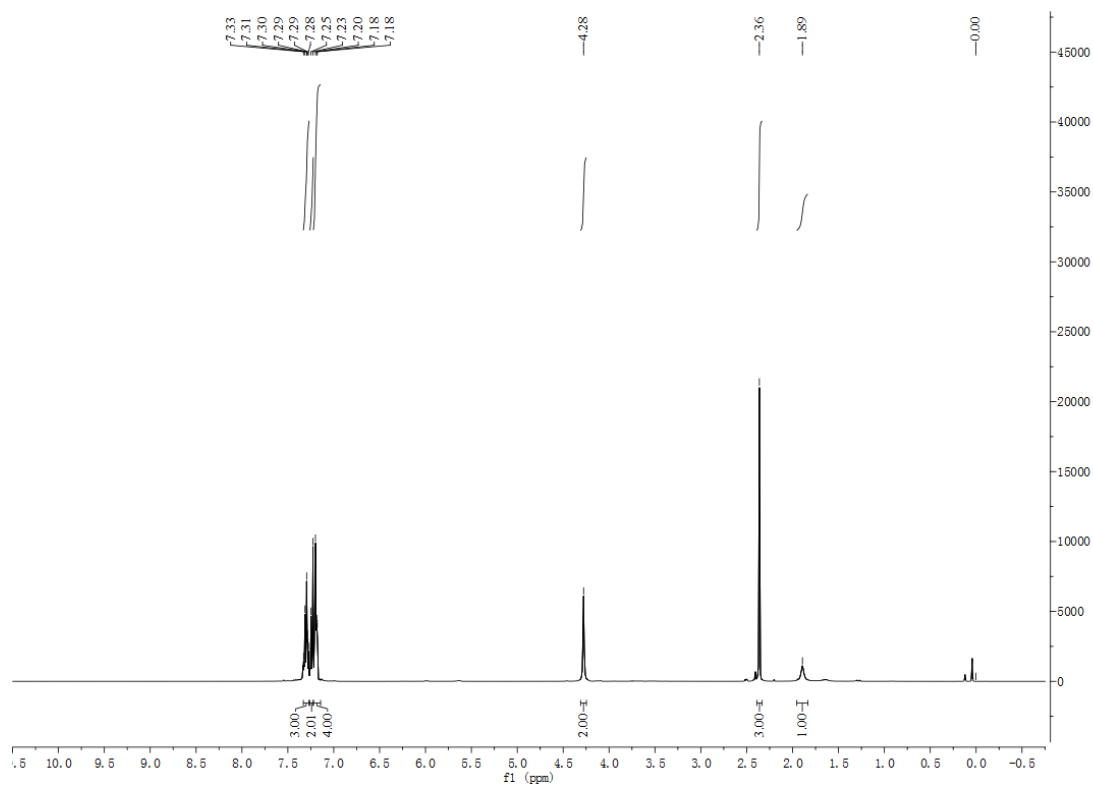




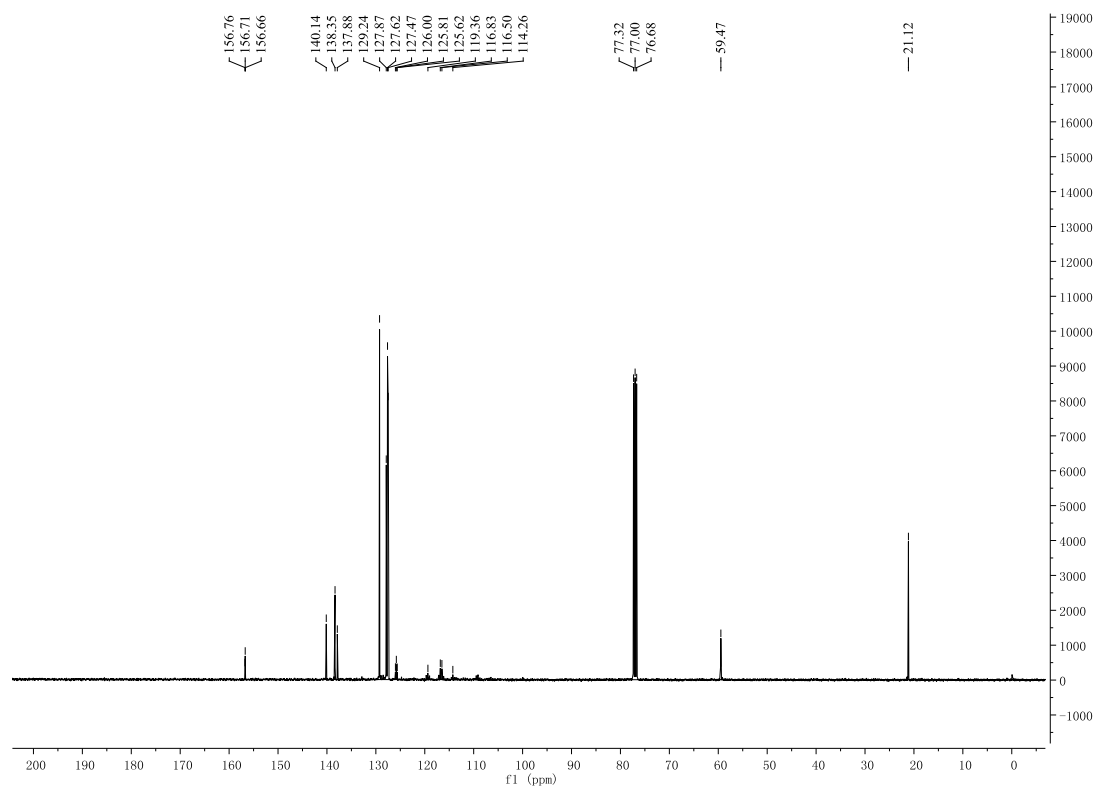
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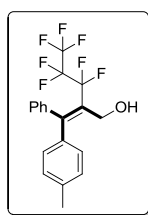


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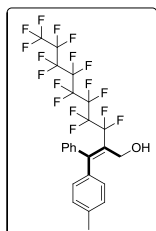
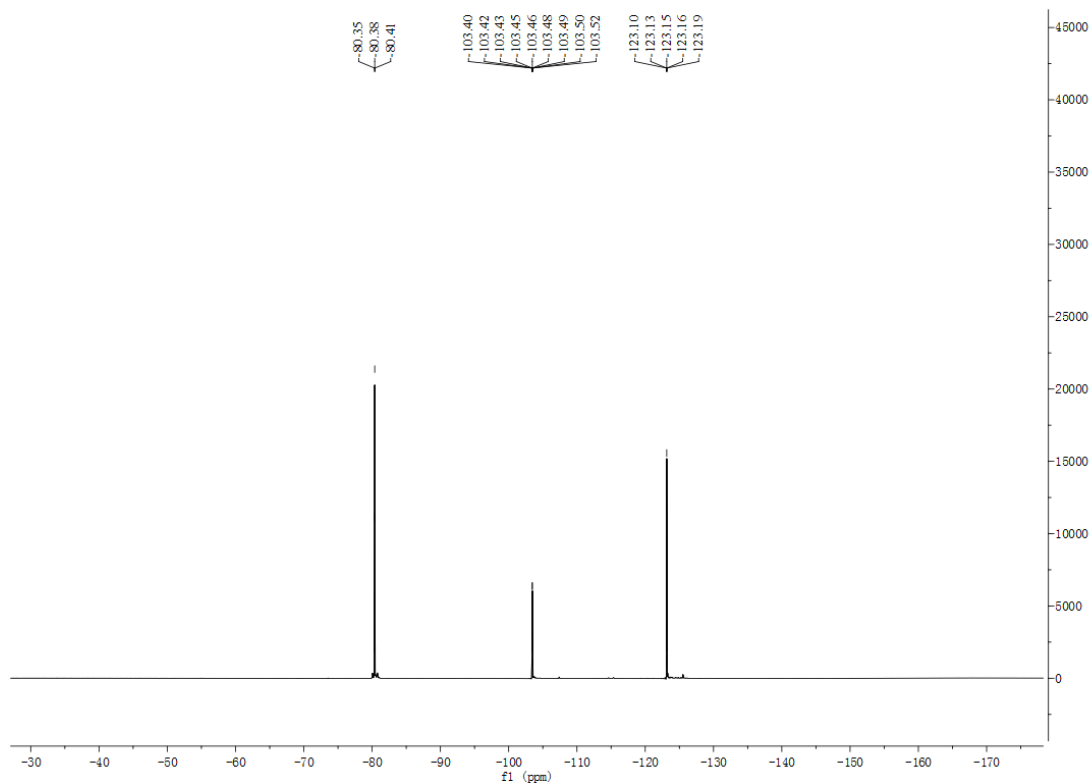


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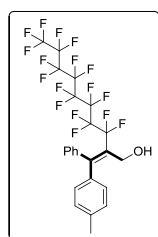
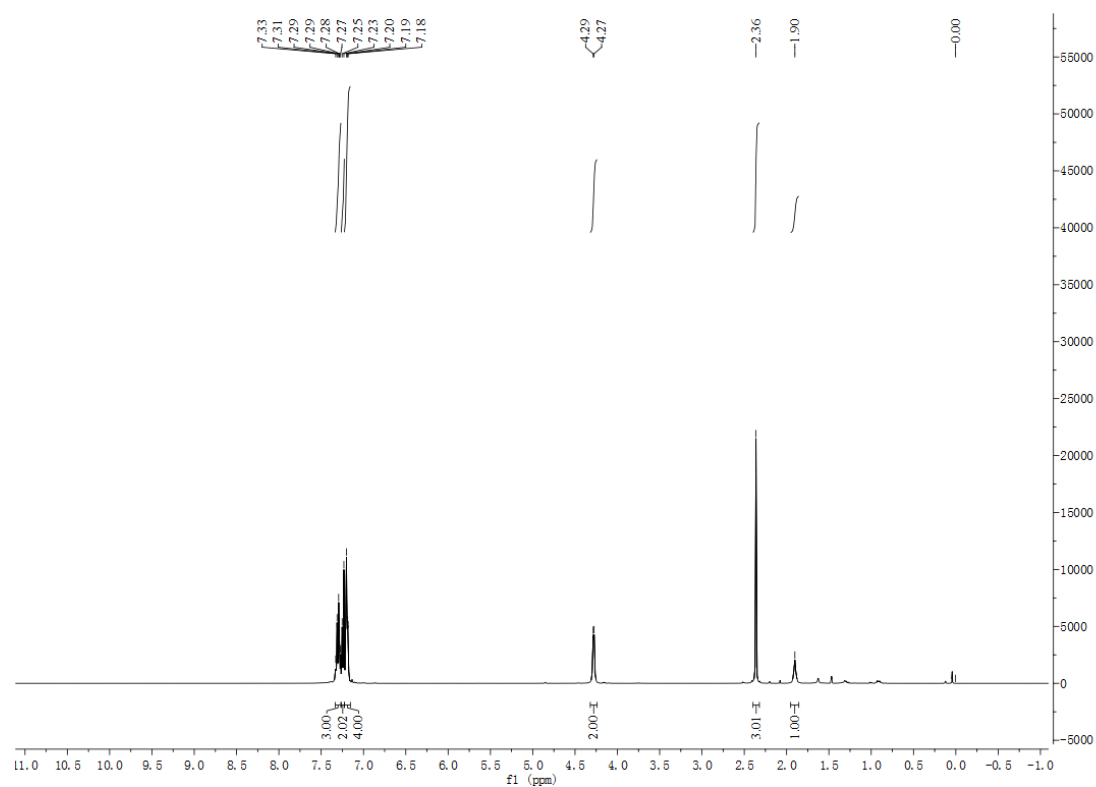




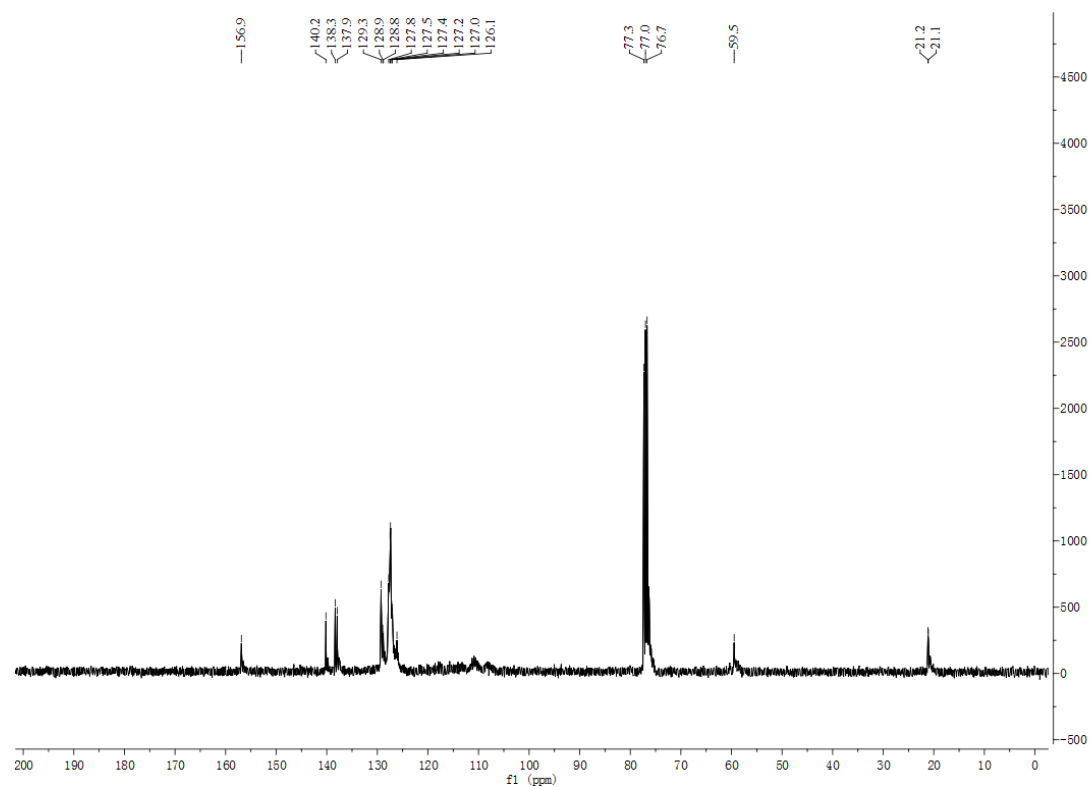
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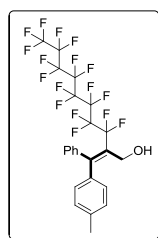
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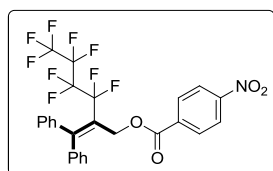
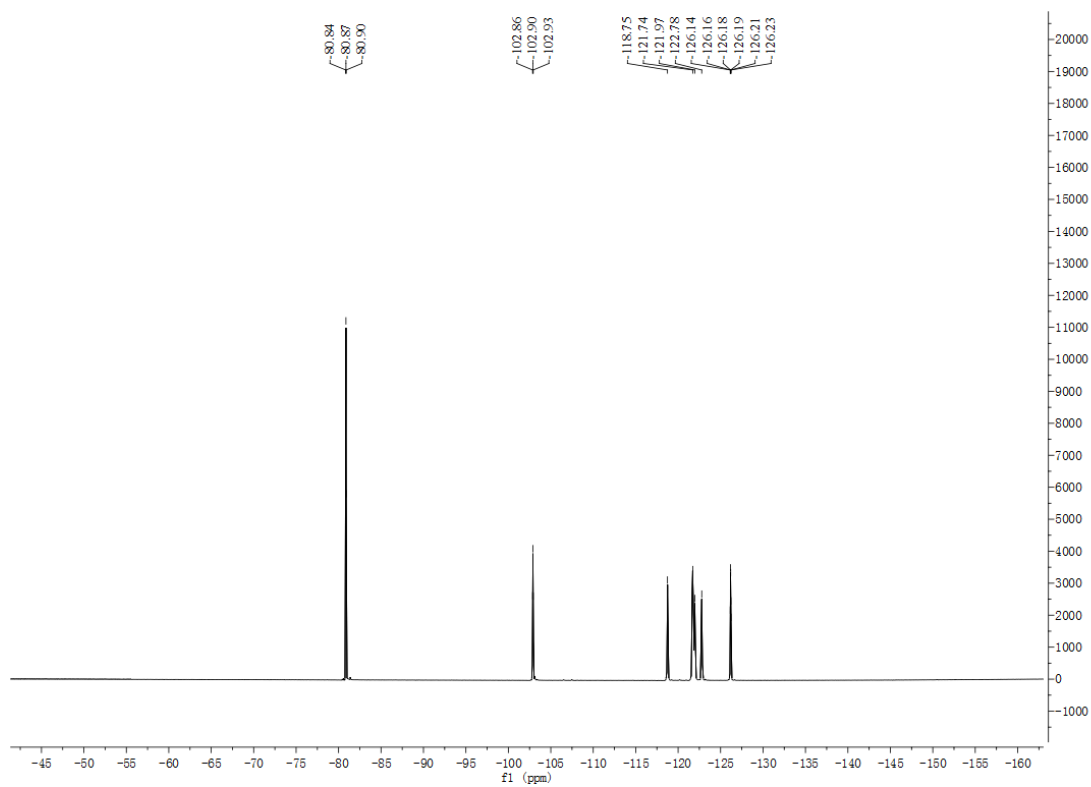
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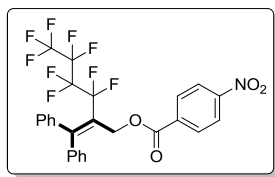
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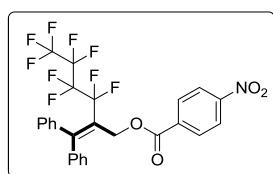


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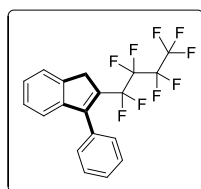
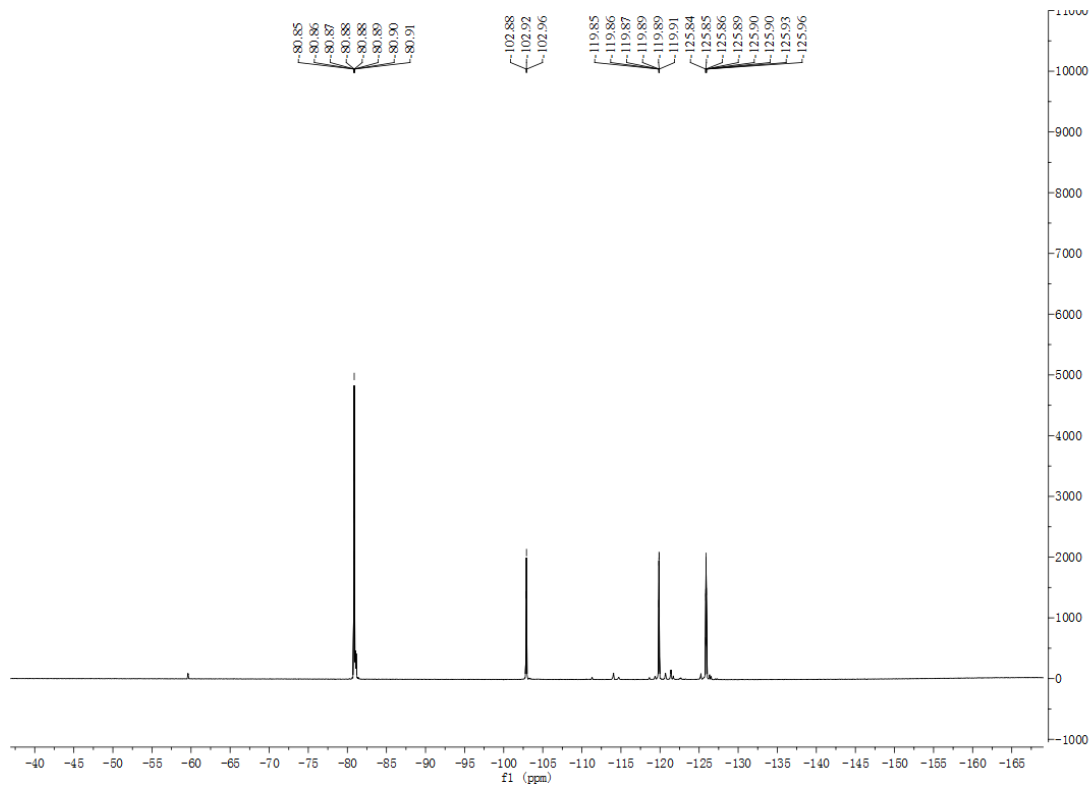


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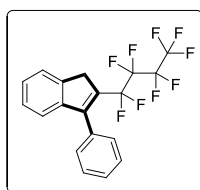
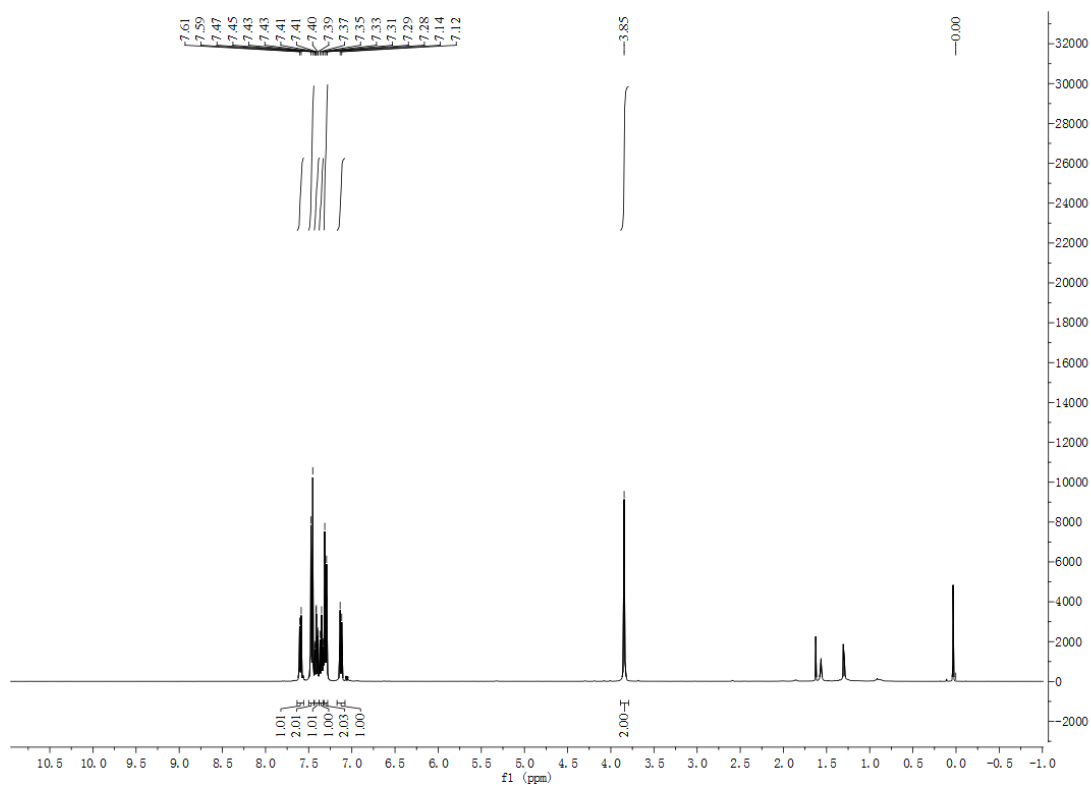




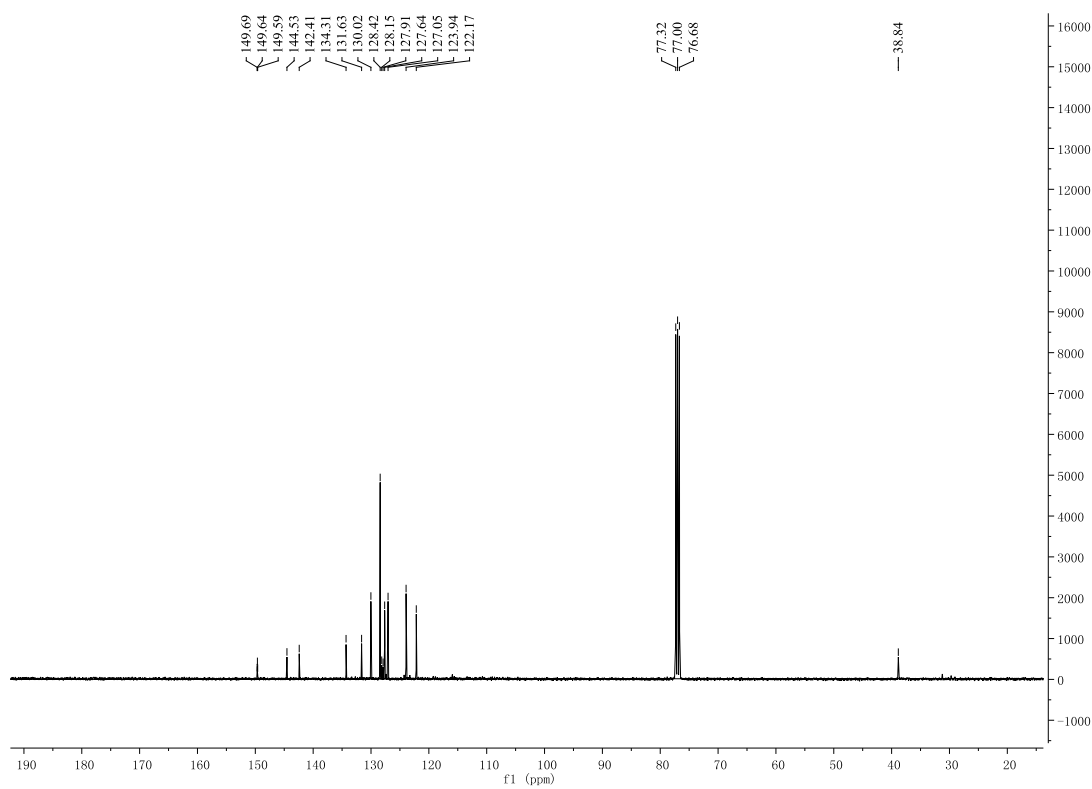
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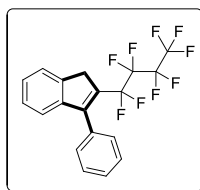


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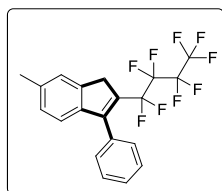
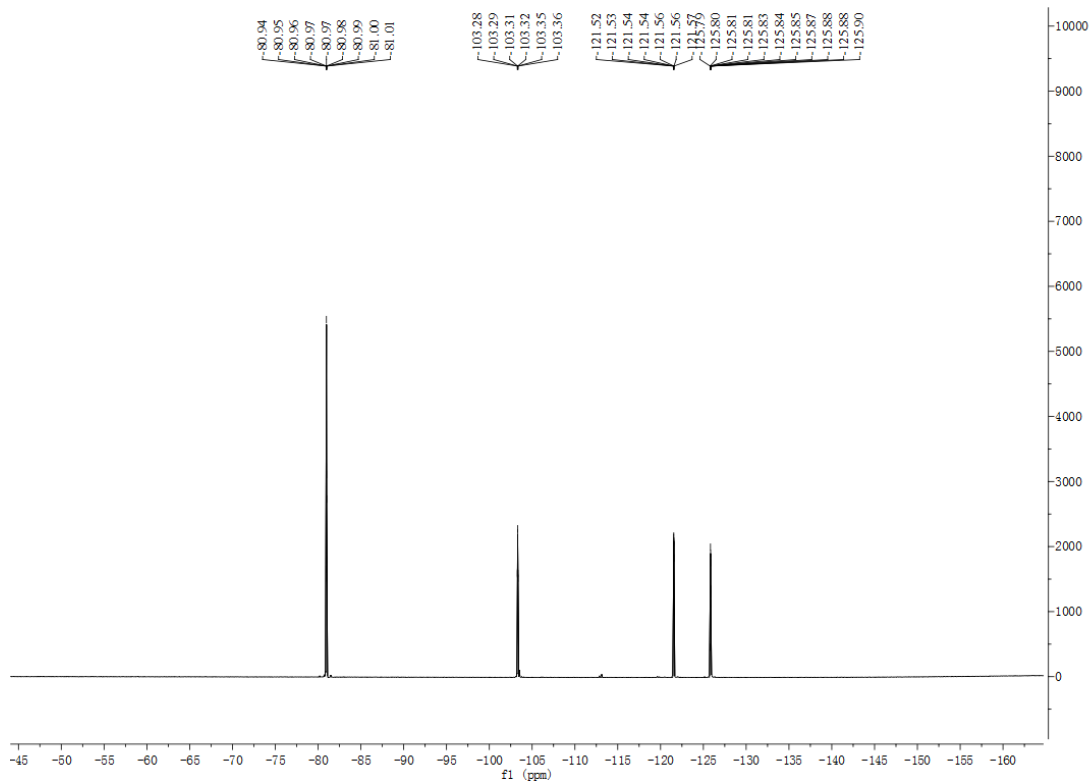


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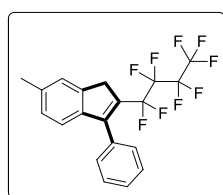
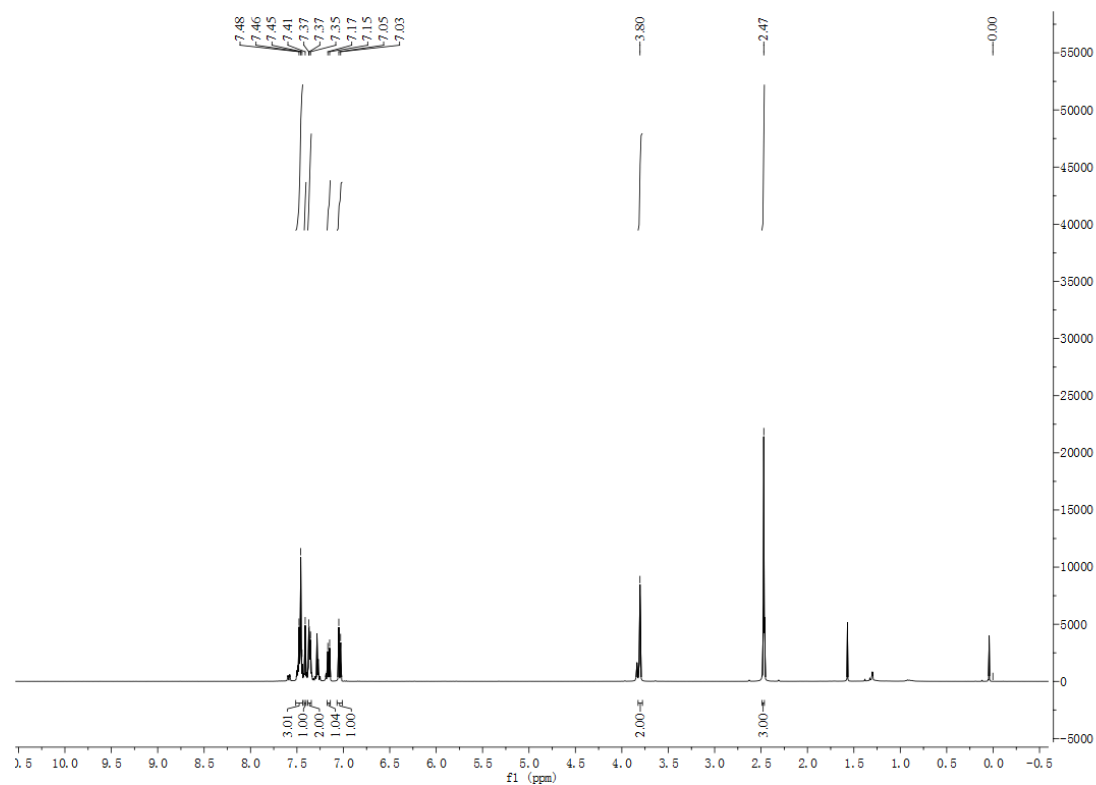




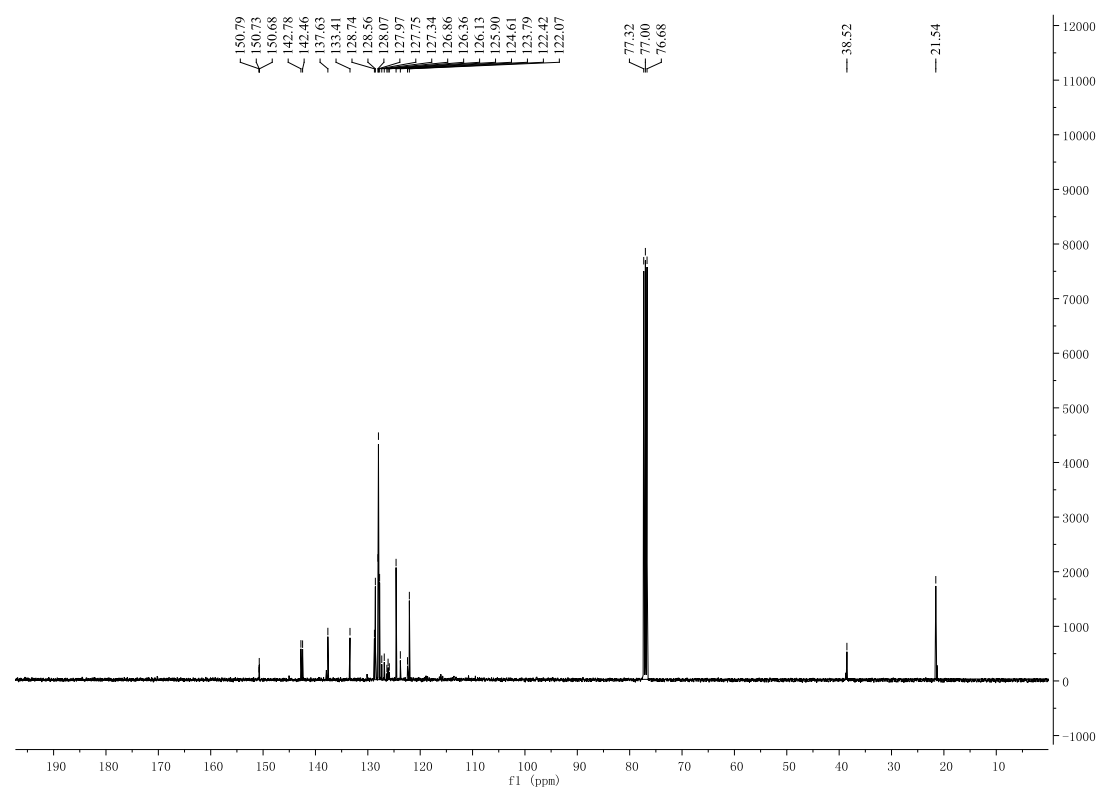
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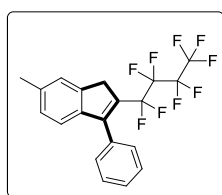


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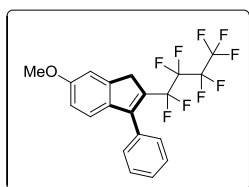
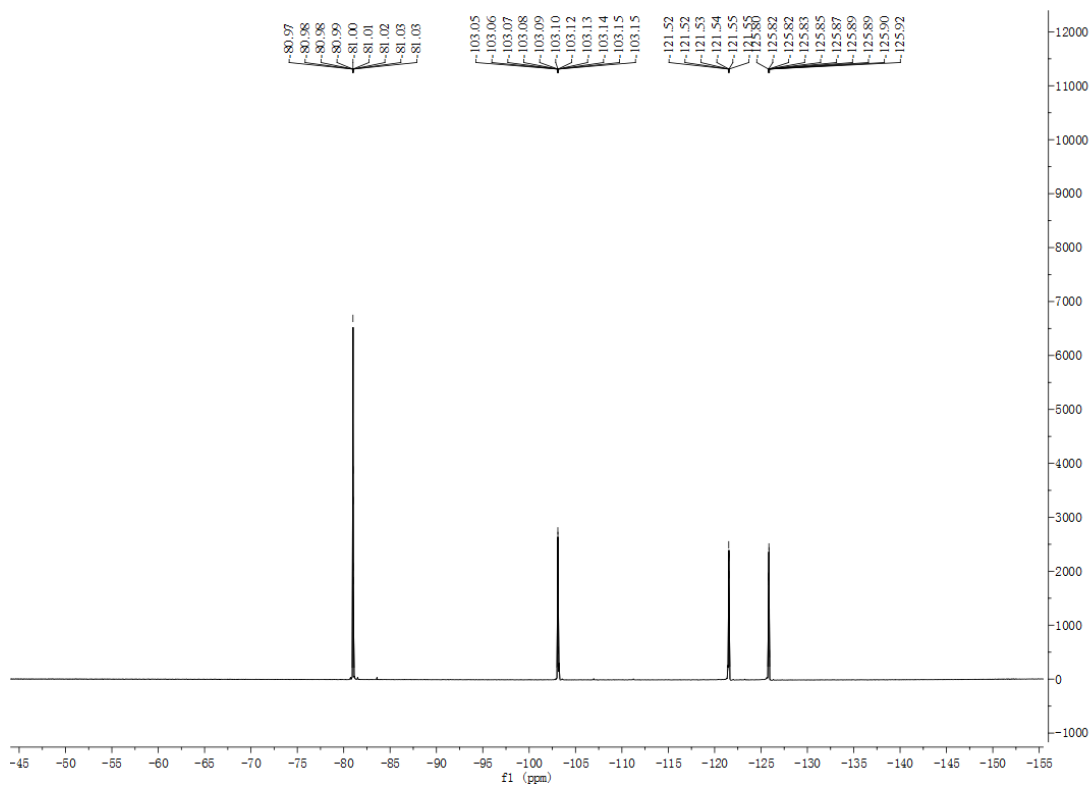


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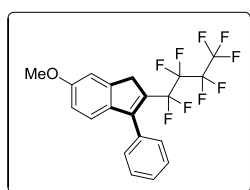
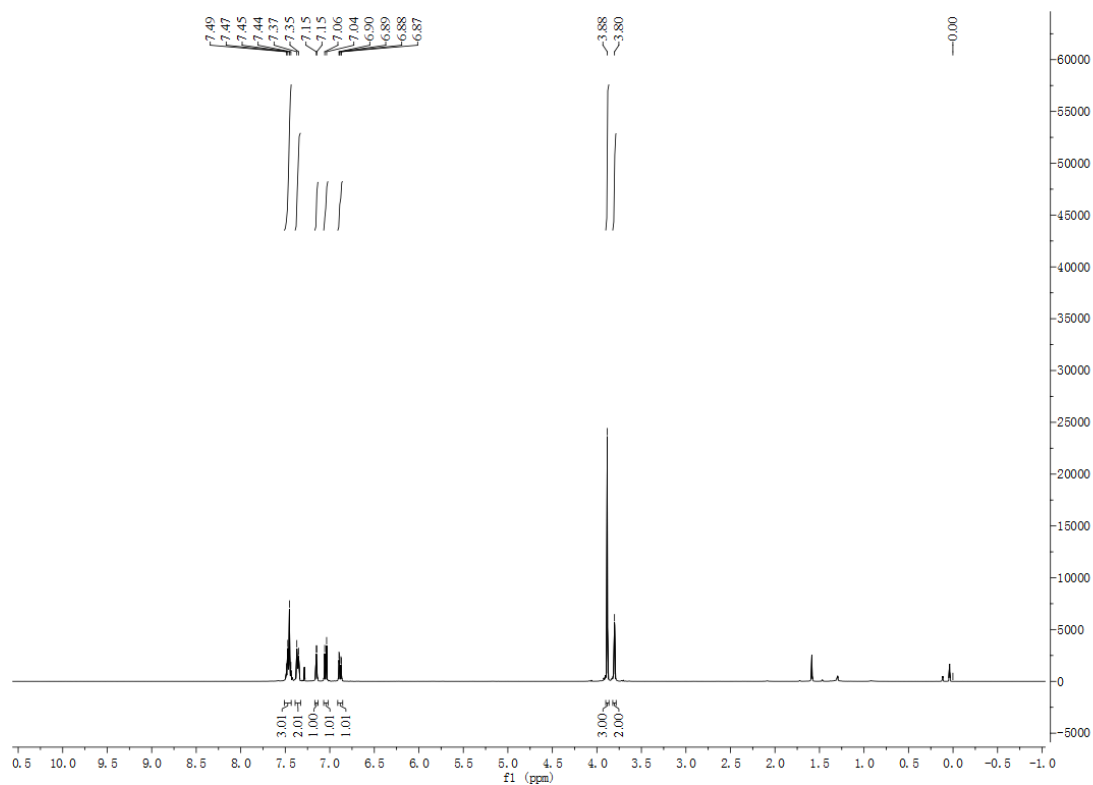




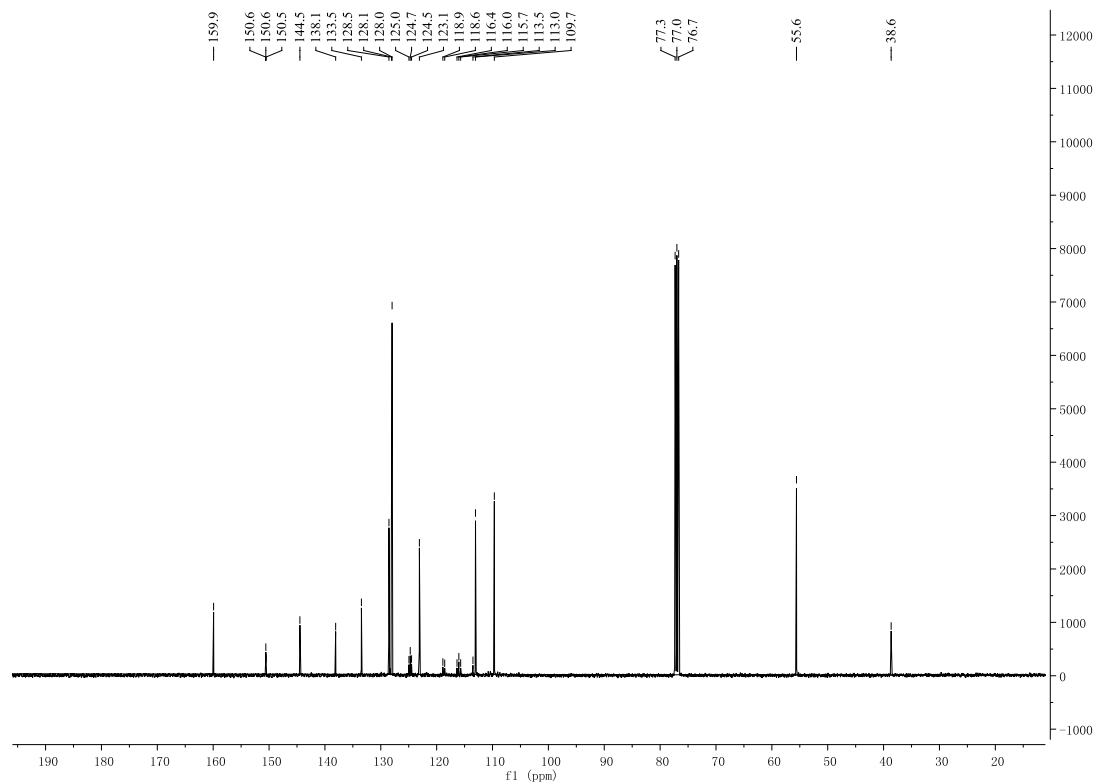
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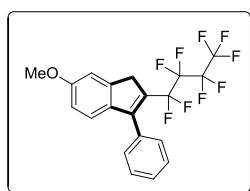


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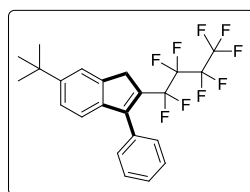
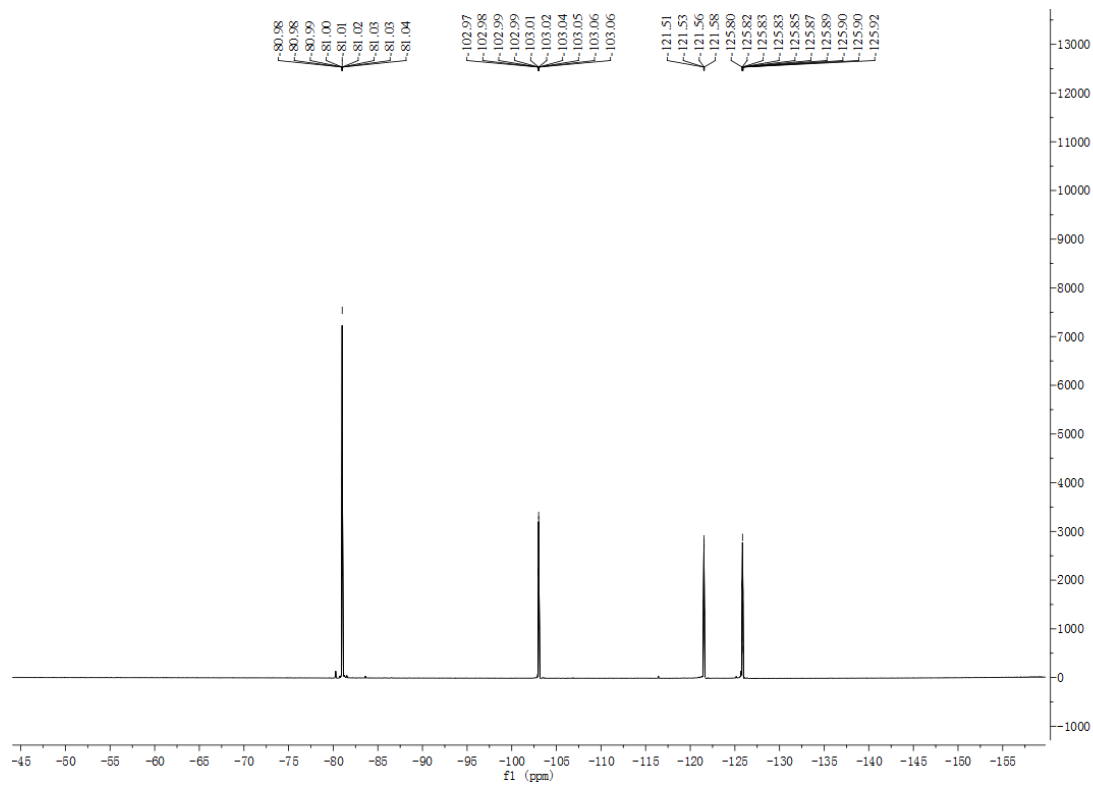


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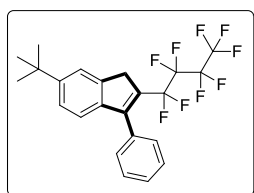
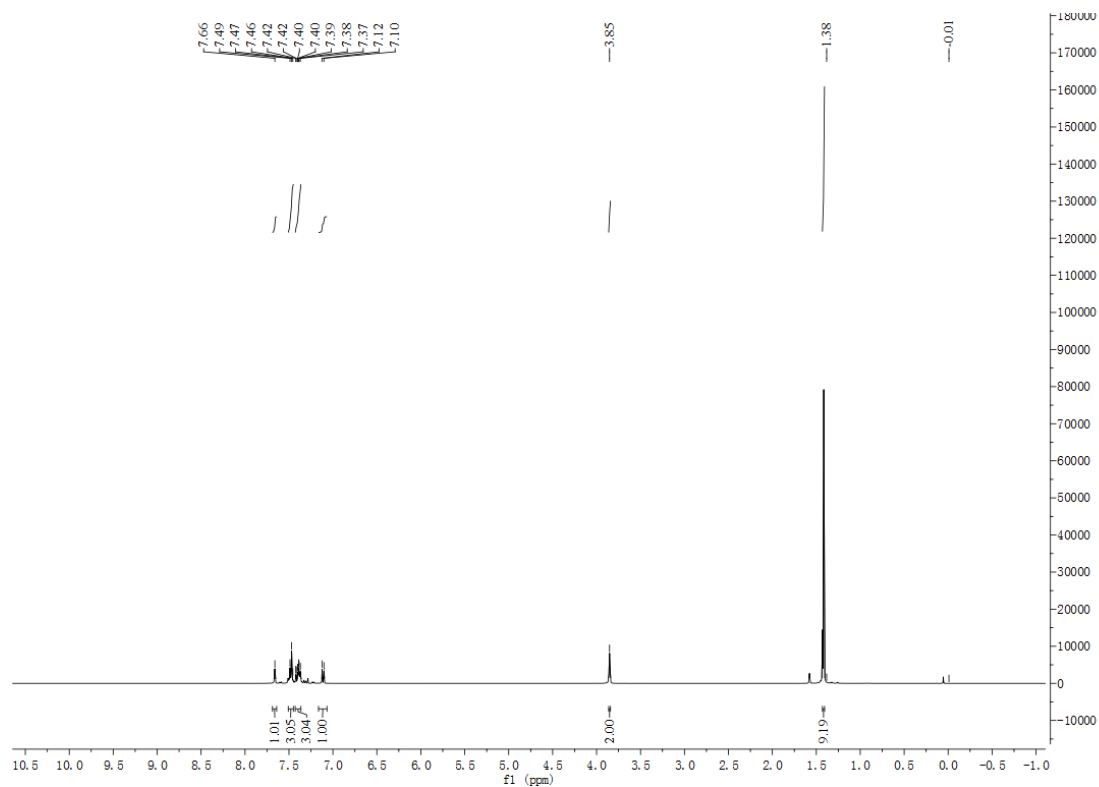




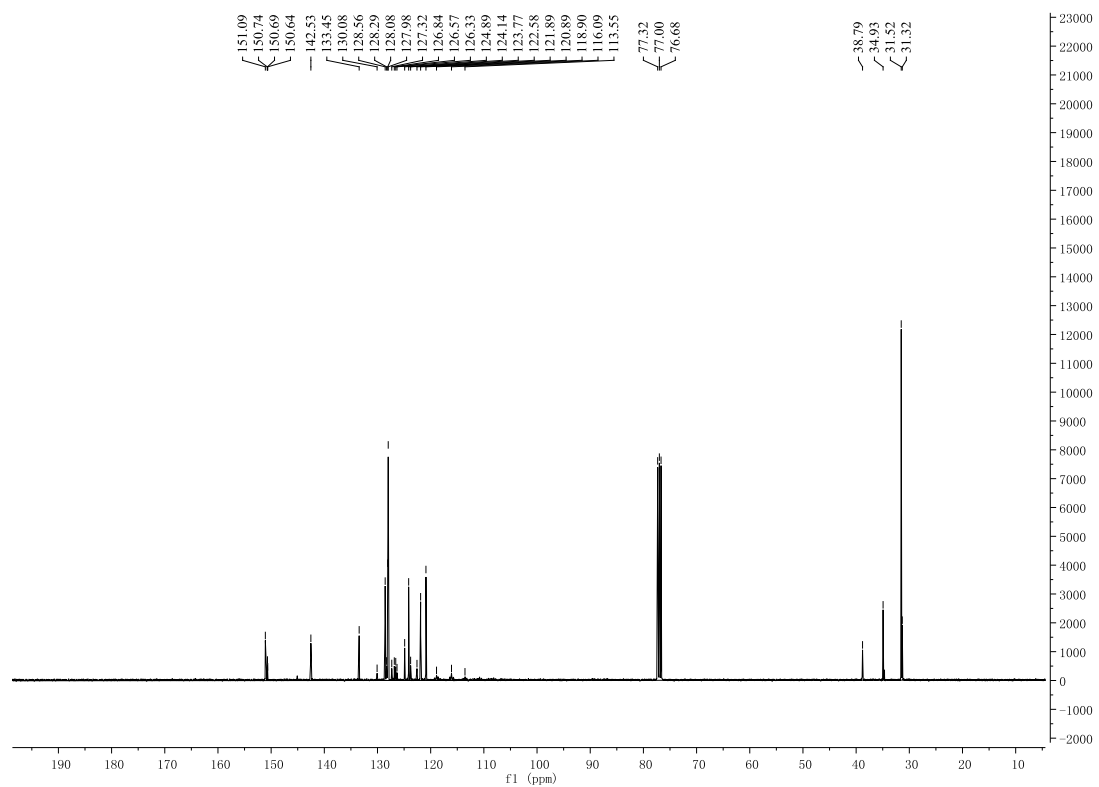
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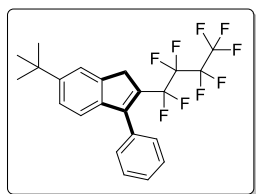


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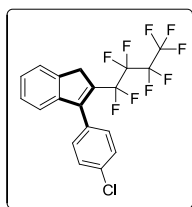
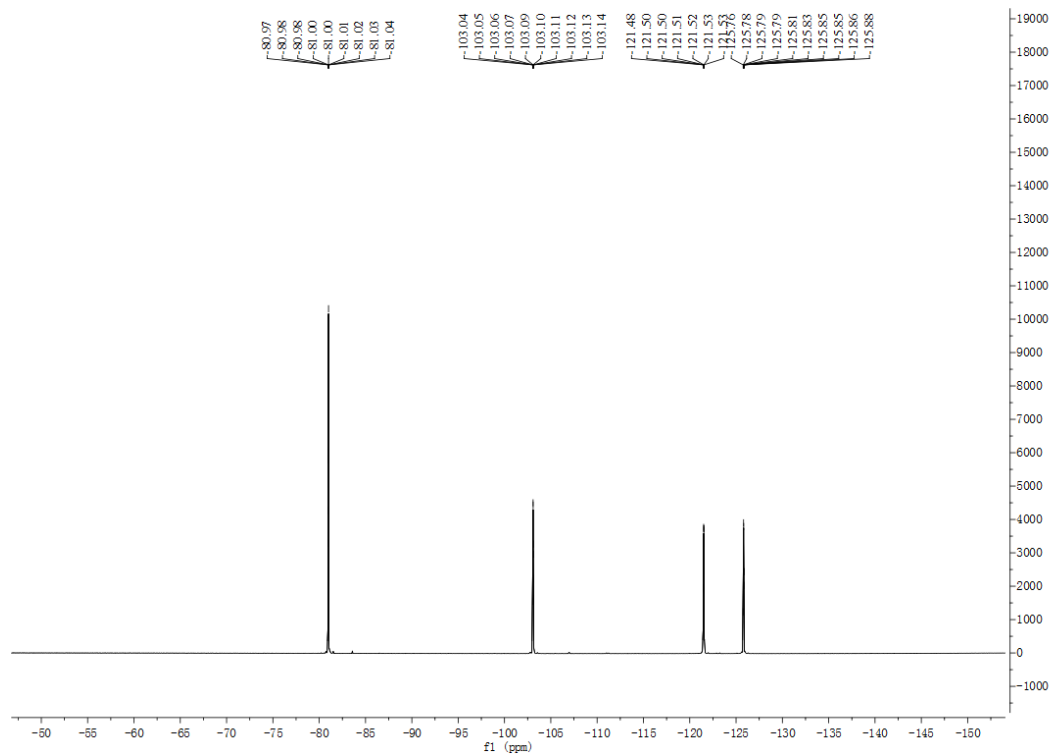


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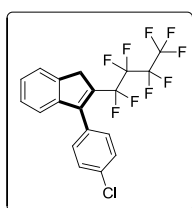
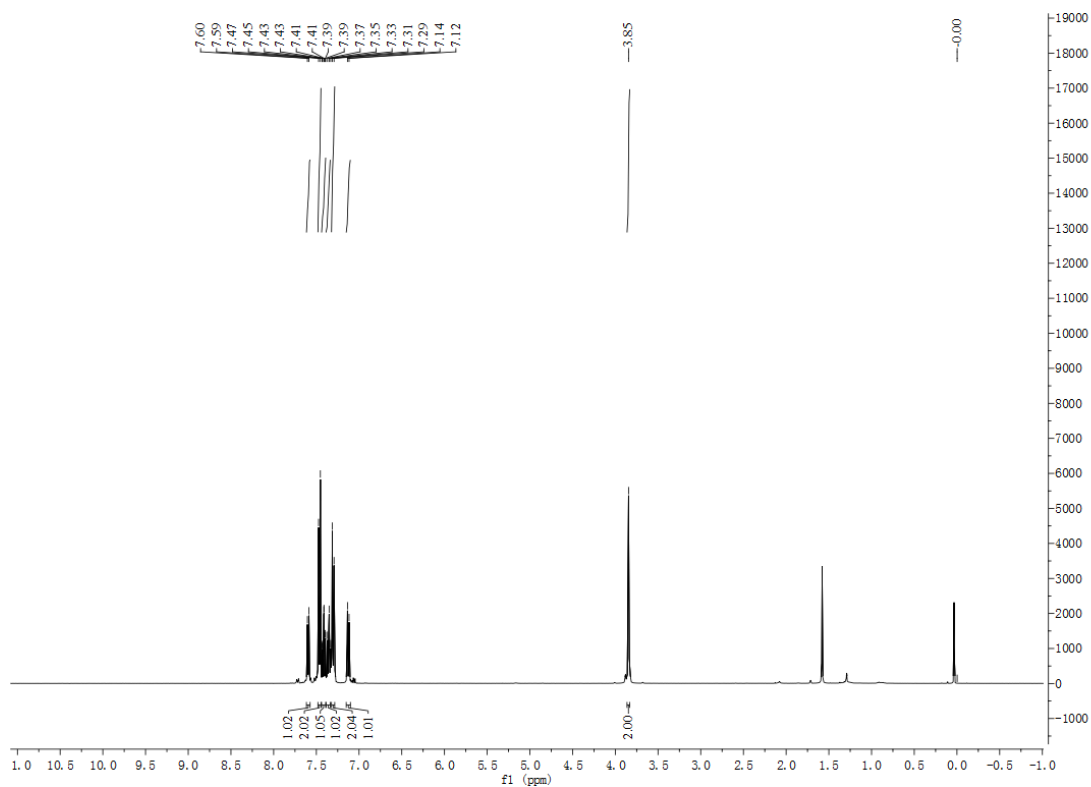




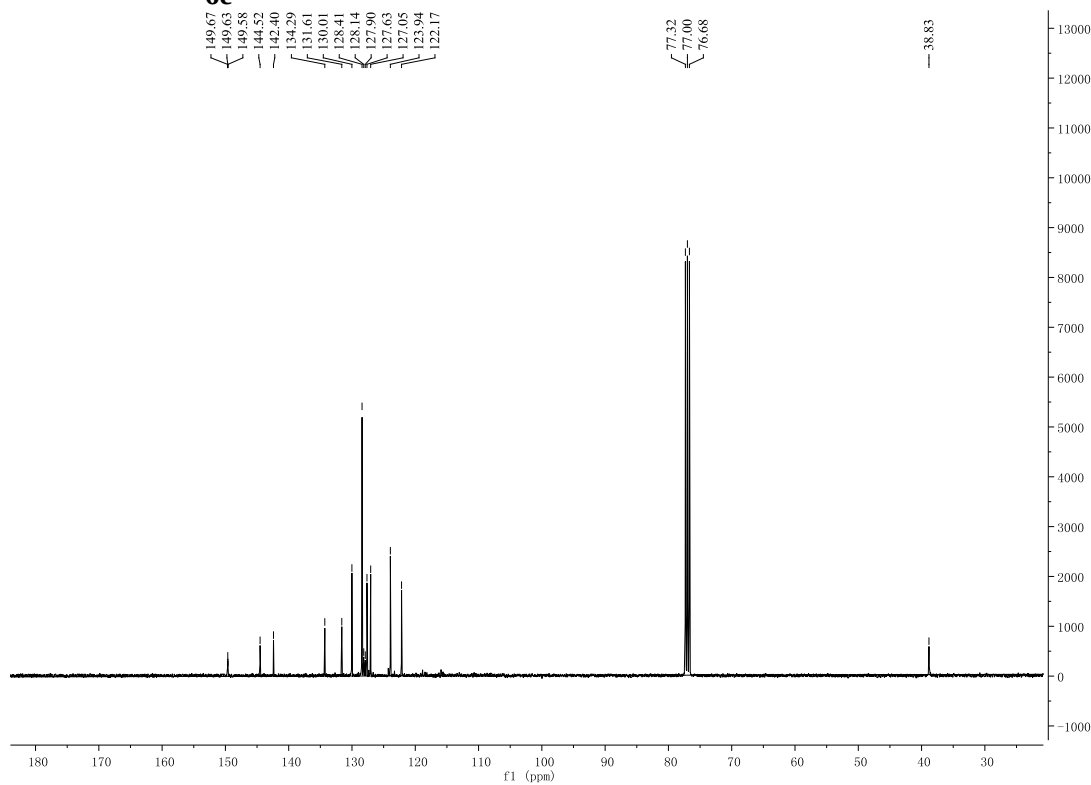
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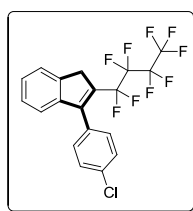


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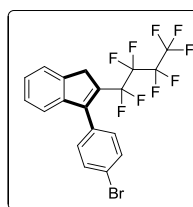
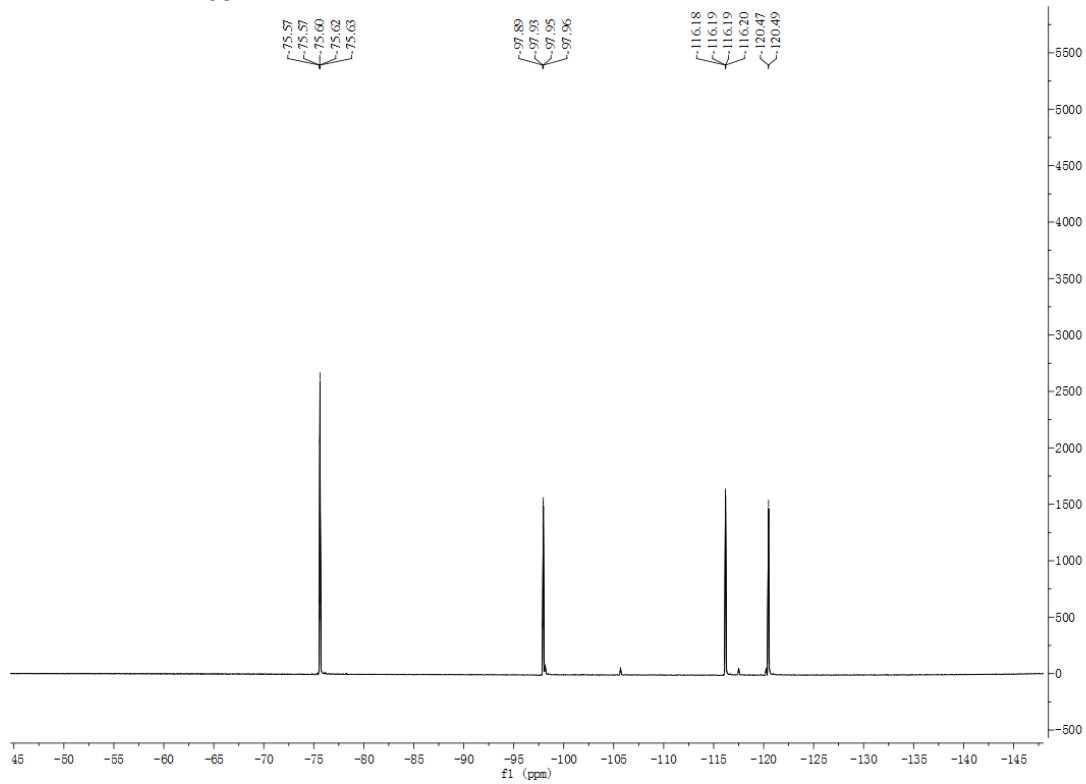


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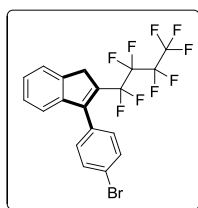
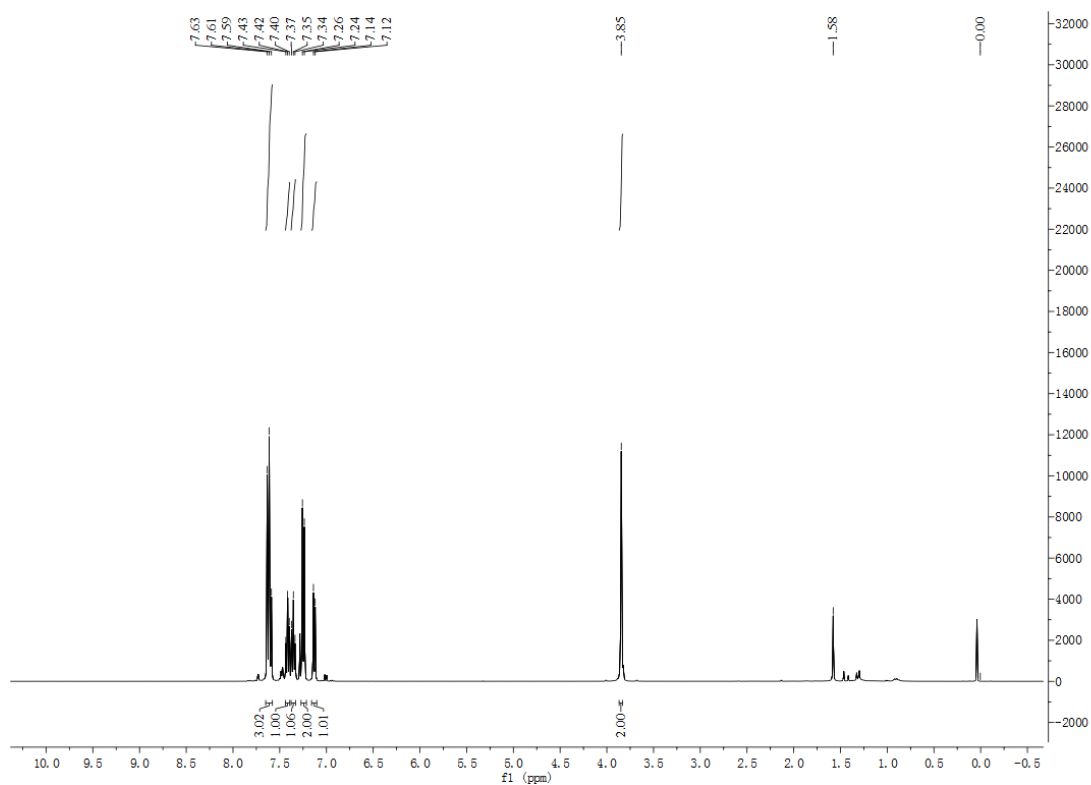




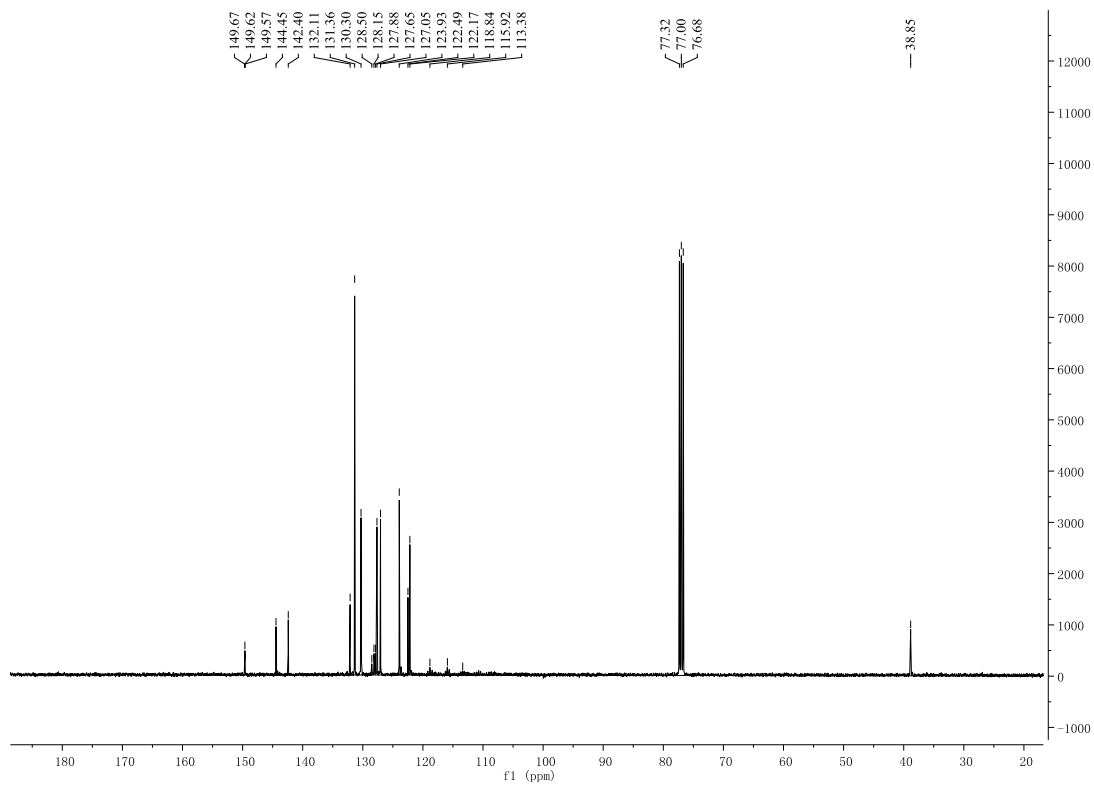
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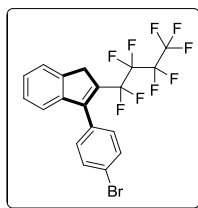


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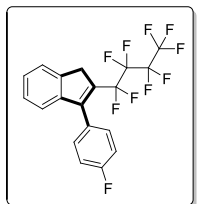
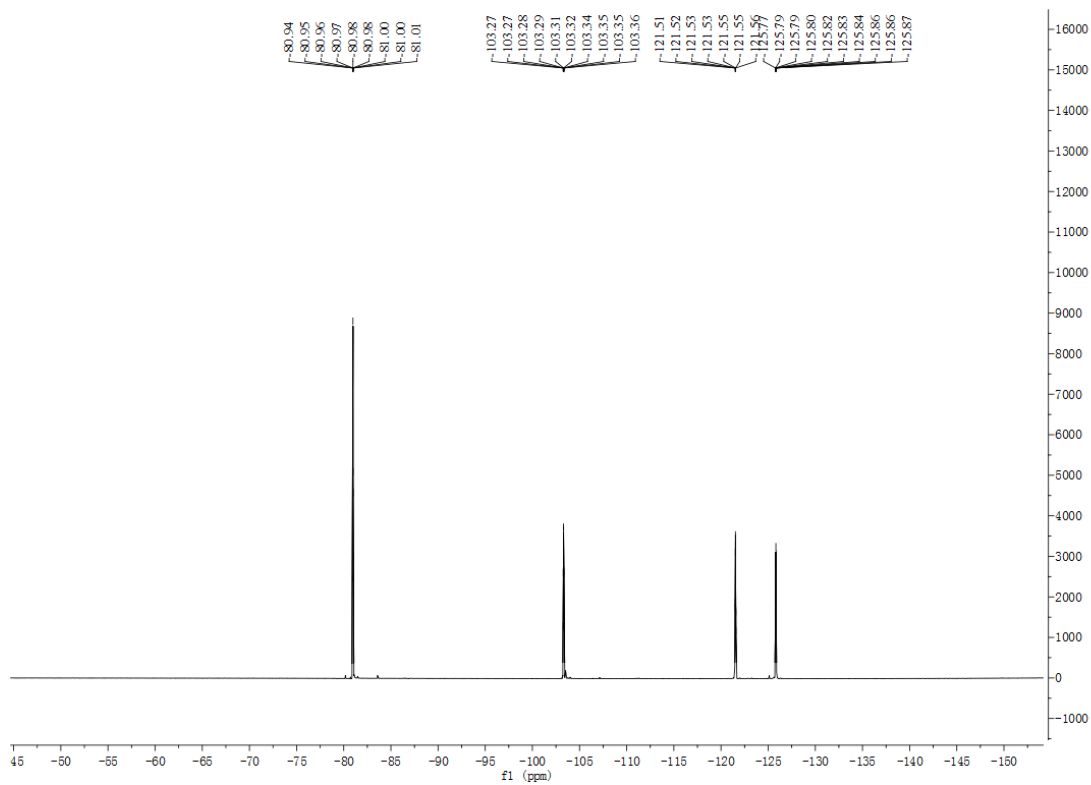


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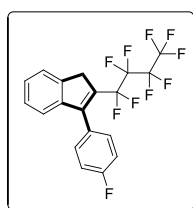
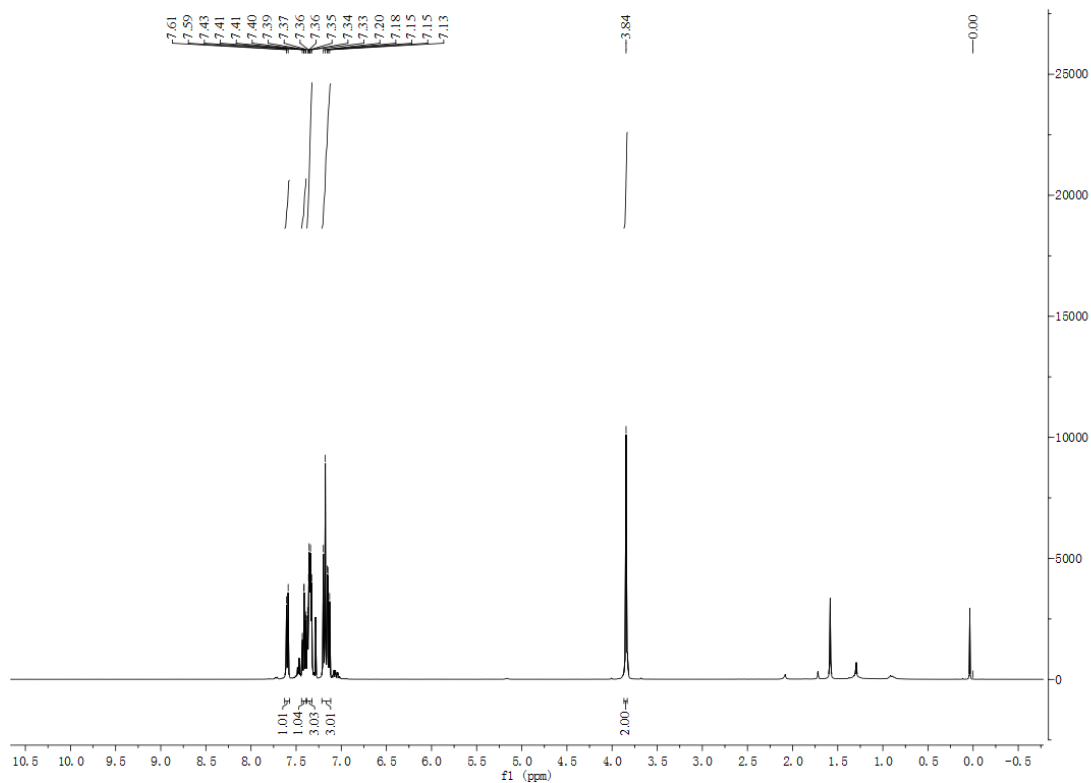




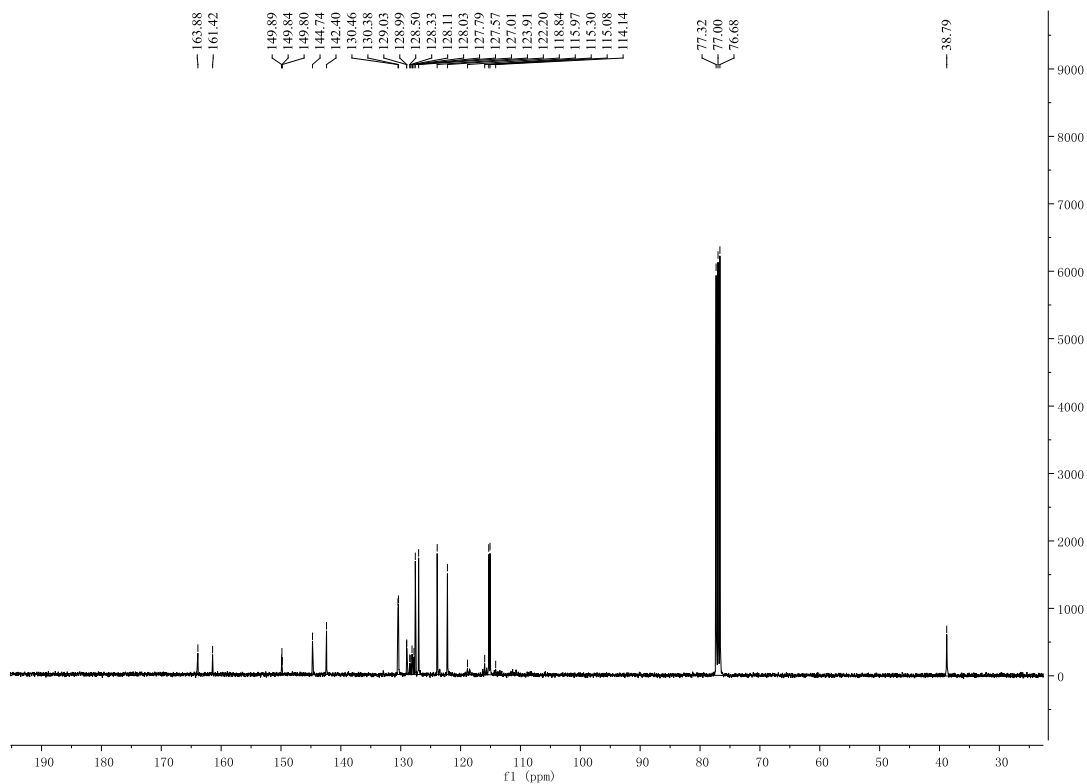
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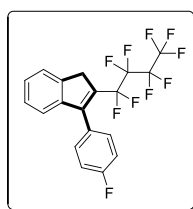


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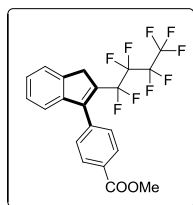
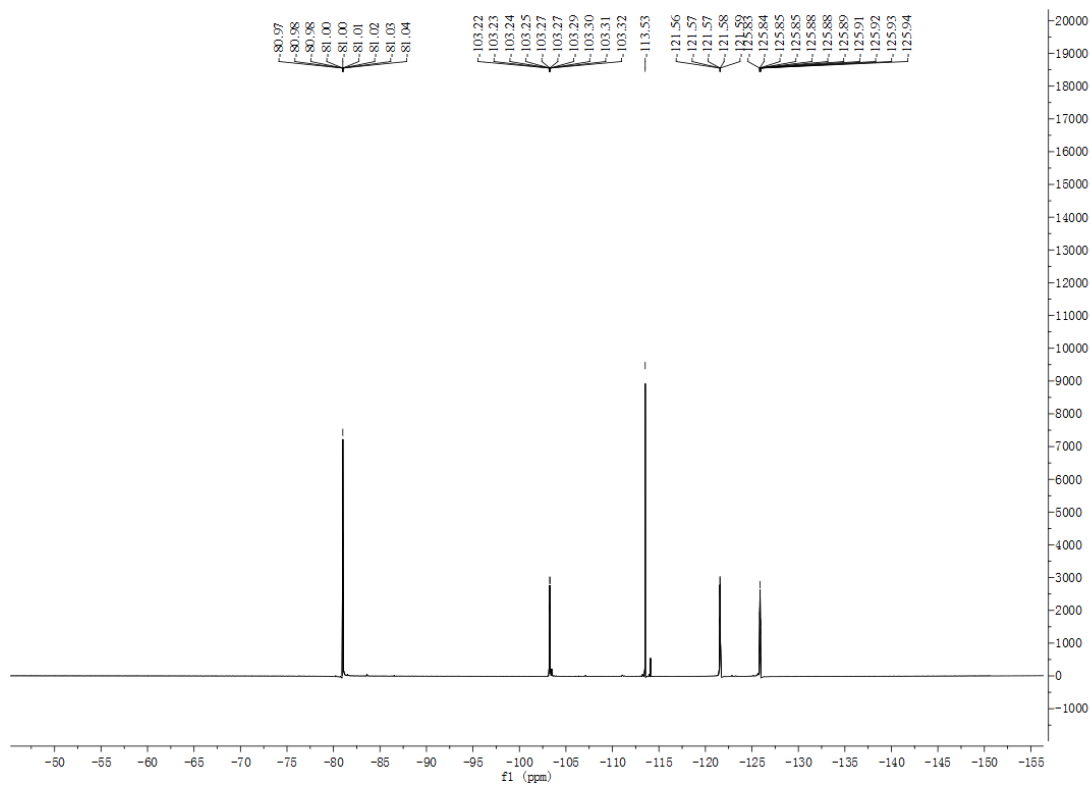


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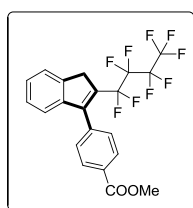
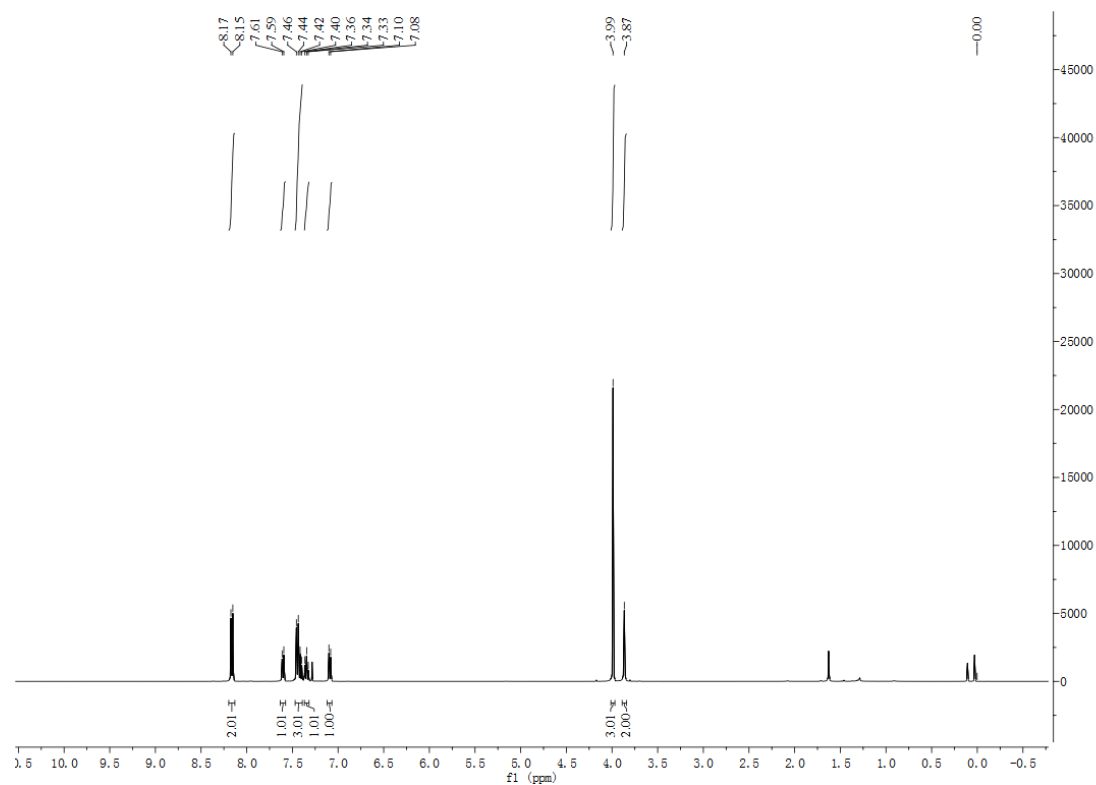




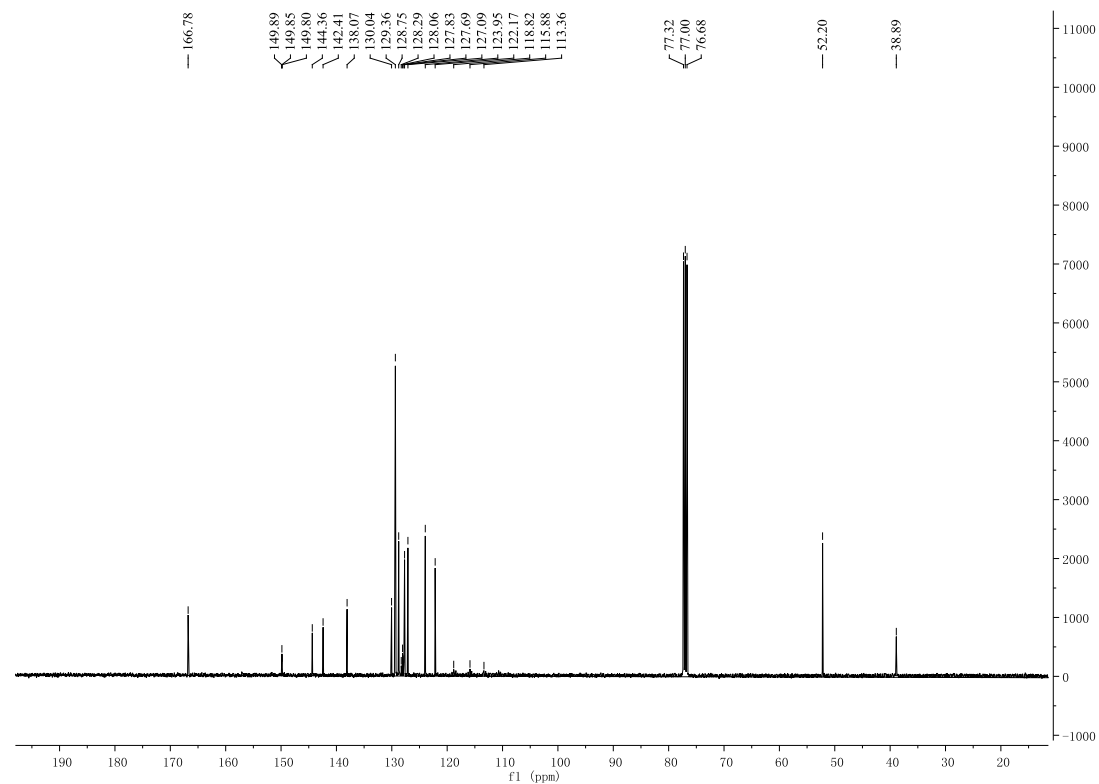
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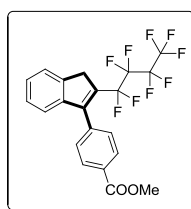


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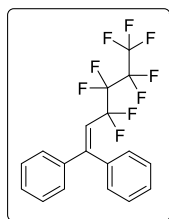
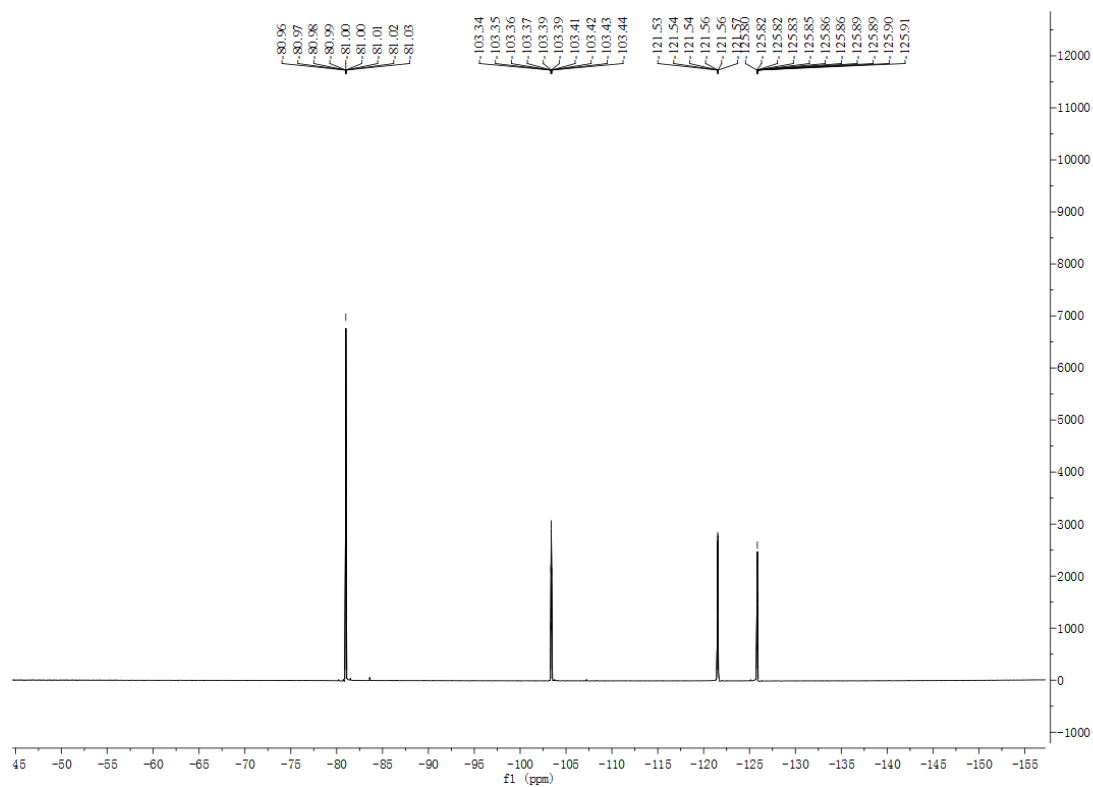


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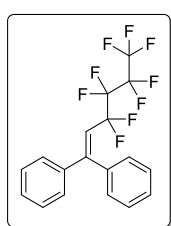
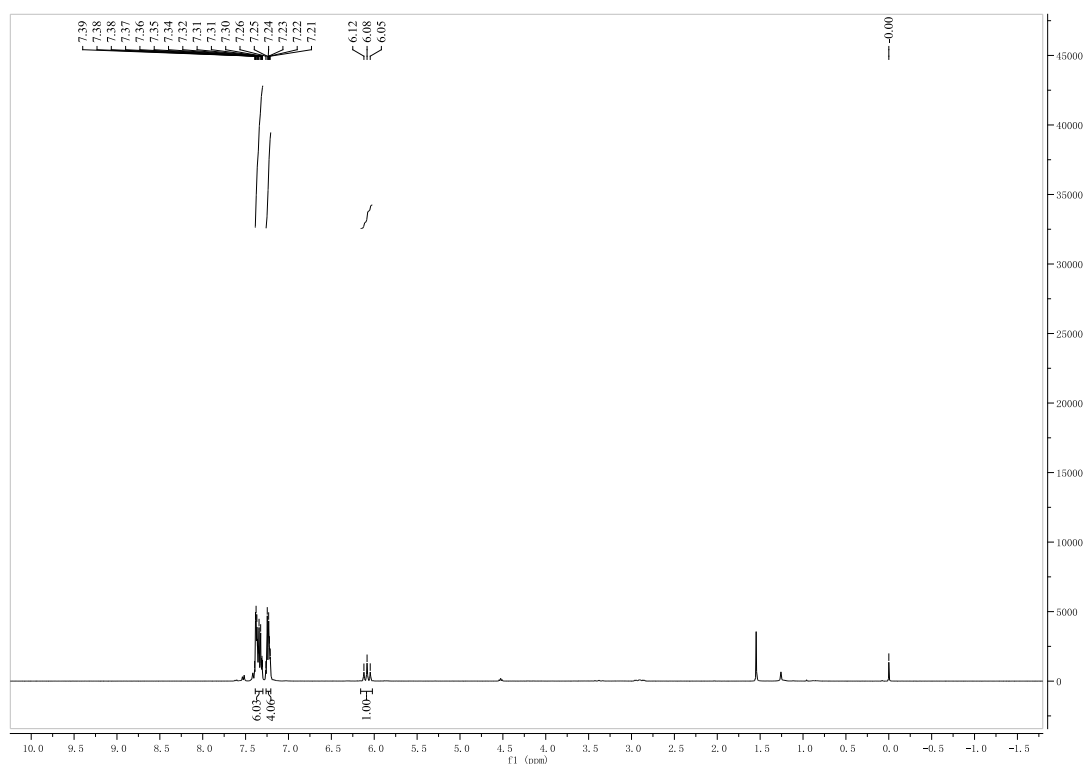




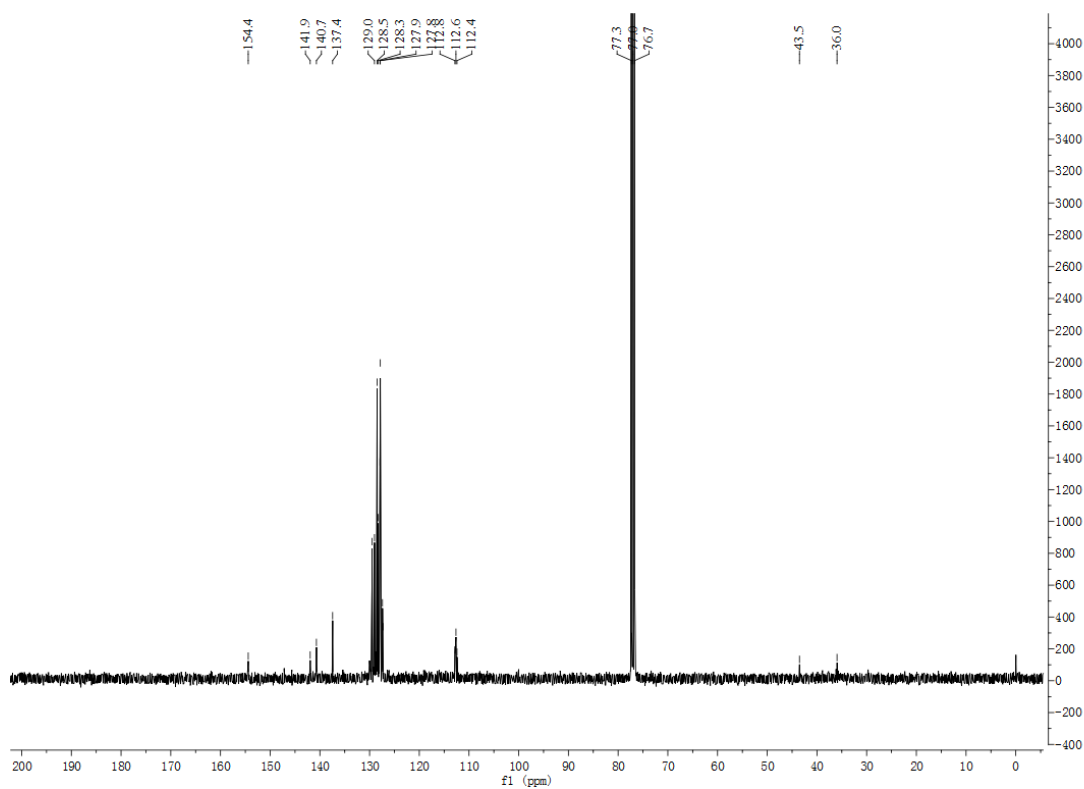
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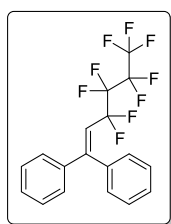
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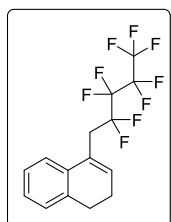
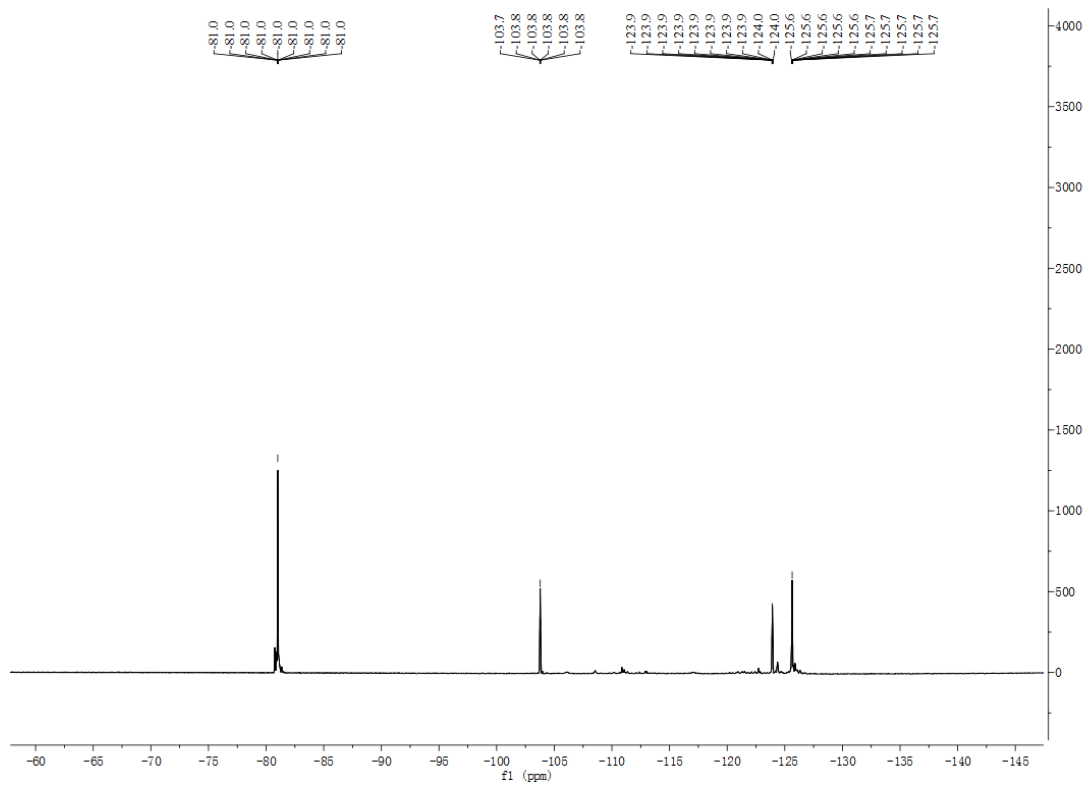
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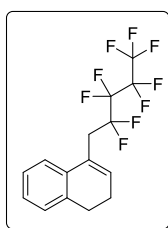
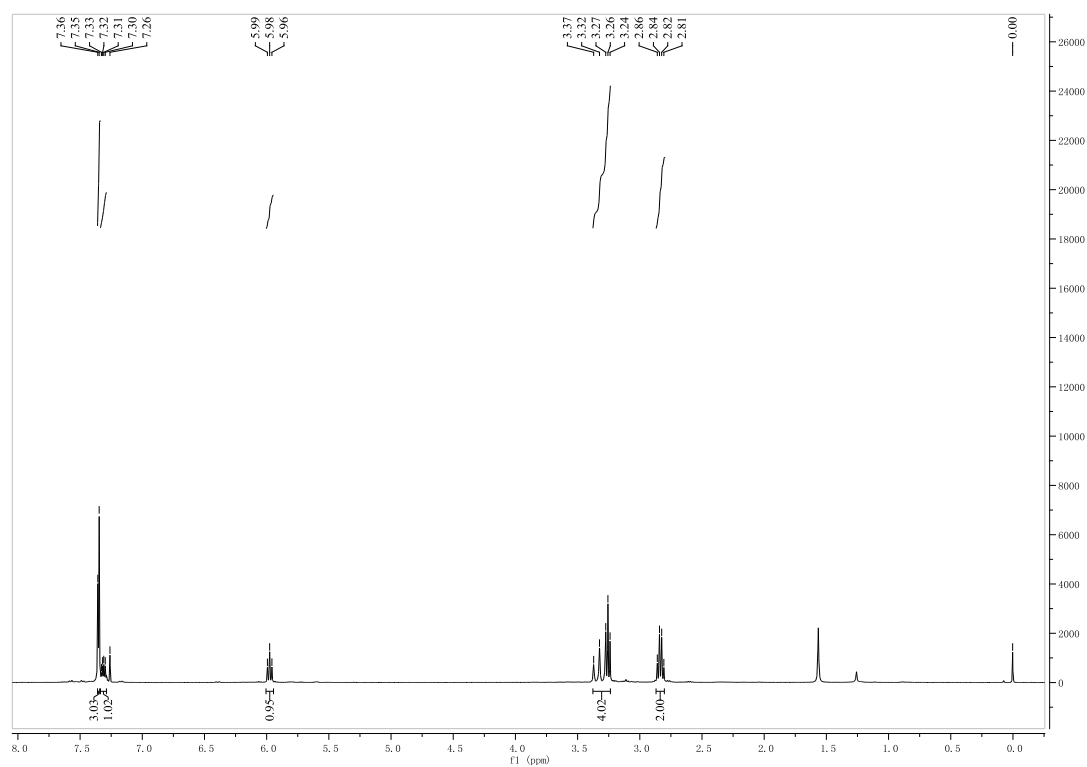
S119



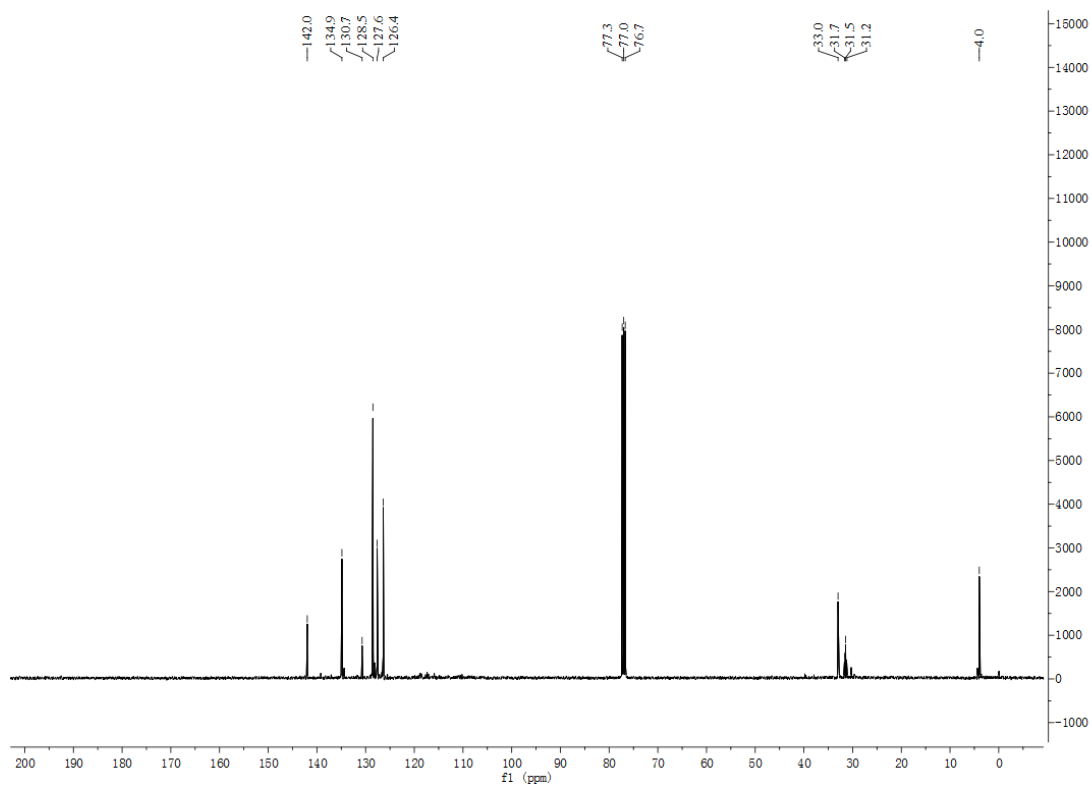
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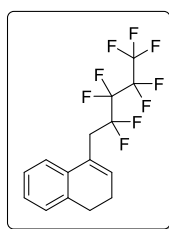
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S121



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