Supplementary Information

Interplay of diruthenium catalyst in controlling enantioselective propargylic substitution reactions with visible light-generated alkyl radicals

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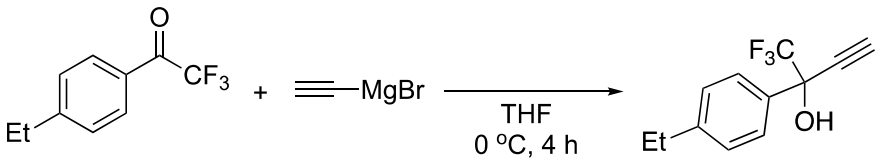
S1. General methods

All reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques. **1**,[S1] **2**,[S2] **3a**,[S3] **3b**,[S4] **3d**,[S5] **3e**,[S6] **3f**,[S6] **3g**,[S7] **3i**,[S8] **3j**,[S6] **3n**,[S6] **4a**,[S9] **4b**,[S9] **4c**,[S9] **4d**,[S9] **4e**,[S10] **4f**,[S9] **4g**,[S11] **4j**,[S12] **4k**,[S13] **4l**,[S12] **4m**,[S10] **4n**,[S14] **4p**,[S12] **4q**,[S9] **4r**,[S15] **4t**,[S16] **4u**,[S17] **4v**,[S11] **14**$^+$BF$_4^-$,[S5] **16**$^+$BF$_4^-$,[S18] **[Ru]-1**,[S19] and **[Ru]-2**[S19] were prepared according to the literature procedures. Other reagents include starting materials for the preparation of **1**, **2**, **3a**−**3n**, **4a**−**4v**, **5**, **8**, **14**$^+$BF$_4^-$, **16**$^+$BF$_4^-$, **[Ru]-1**, and **[Ru]-2**, *fac*-[Ir(ppy)$_3$] (ppy = 2-(pyridyl)phenyl), *fac*-[Ir(Fppy)$_3$] (Fppy = 3,5-difluoro-2-(pyridyl)phenyl), [Ir(ppy)$_2$(dtbbpy)]PF$_6$ (dtbbpy = 4,4′-di-tert-butyl-2,2′-bipyridine), NH$_4$BF$_4$, Lewis acids, TEMPO, and solvents were obtained from commercial sources. Solvents were dried by general methods and degassed before use. Flash column chromatography was carried out on a Yamazen YFLC-AI-580 system. Gas chromatography−mass spectroscopy (GC−MS) was performed on a Shimadzu GCMS-QP2010 PLUS instrument. HPLC analyses were performed on Hitachi L-7100 and GL-7410 apparatuses equipped with a UV detector using 25 cm x 4.6 mm DAICEL Chiralpak columns. Specific rotations were measured on a JASCO DIP-1000 polarimeter. X-ray analysis was performed by a Rigaku XtaLAB Synergy-S diffractometer. Photoluminescence spectra were measured on a Shimadzu RF-5300PC spectrophotometer. Melting points were measured by using a Stanford Research Systems OptiMelt MPA100. High-resolution FAB mass spectra were measured on a JEOL JMS-700 mass spectrometer. Specific rotations were measured on a JASCO DIP-1000 polarimeter. ^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (100 MHz), and ^{19}F NMR (376 MHz, referenced to $CF_3C_6H_5$ in $CDCl_3$ at δ –64.0) spectra were measured in $CDCl_3$, $(CD_3)_2CO$ or CD_3CN on a JEOL ECS-400 spectrometer with δ values in ^{1}H and ^{13}C{^{1}H} NMR calibrated by using residual peaks of $CHCl_3$ (^{1}H: 7.26; ^{13}C: 77.0), $(CD_2H)_2CO$ (^{1}H, 2.09; ^{13}C: 206.0), CD_2HCN (^{1}H, 1.93; ^{13}C: 117.7) respectively.

S2. General procedure for the preparation of propargylic alcohol substrates (3 and 8) (taking 1,1,1-trifluoro-2-(4-ethylphenyl)but-3-yn-2-ol (3c) as a typical example)

Scheme S1. Preparation of Propargylic Alcohol Substrates **3c**



3c

To a solution of 2,2,2-trifluoro-1-(4-ethylphenyl)ethan-1-one (3.00 mmol, 607 mg) in anhydrous THF (15 mL) was added ethynylmagnesium bromide (0.5 M in THF, 9.0 mL, 4.5 mmol) at 0 °C. After stirring for 4 h, the mixture was quenched by saturated NH$_4$Cl aq. (4 mL), and the solution was extracted with Et$_2$O (10 ml × 2). The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated under

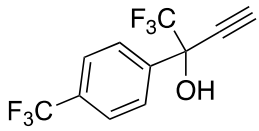
reduced pressure. The residue was purified by column chromatography with hexane/EtOAc (95:5-90:10) to give 1,1,1-trifluoro-2-(4-ethylphenyl)but-3-yn-2-ol as a pale yellow oil (588.8 mg, 2.58 mmol, 86% isolated yield based on the amount of 2,2,2-trifluoro-1-(4-ethylphenyl)ethan-1-one) (Scheme S1).

^{1}H NMR ($(CD_3)_2CO$, 400 MHz): δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.67 (s, 1H), 3.49 (s, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR ($(CD_3)_2CO$, 100 MHz): δ 145.7, 133.8, 127.7, 127.4, 124.1 (q, $^1J_{CF}$ = 283.7 Hz), 80.3, 77.1, 72.4 (q, $^2J_{CF}$ = 31.6 Hz), 28.4, 15.2.

^{19}F NMR ($(CD_3)_2CO$, 376 MHz): δ –82.4 (s).

HRMS (FAB+): Calcd. for $C_{12}H_{11}F_3O$ $[M]^+$: 228.0762. Found: 228.0763.



3h

1,1,1-Trifluoro-2-(4-(trifluoromethyl)phenyl)but-3-yn-2-ol (**3h**). A pale yellow oil (683.8 mg, 2.55 mmol, 85% isolated yield based on the amount of 2,2,2-trifluoro-1-(4-(trifluoromethyl)phenyl)ethan-1-one).

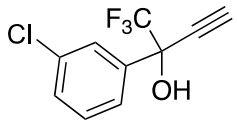
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 8.4 Hz, 2H), 3.37 (s, 1H), 2.87 (s, 1H).

^{13}C{^{1}H} NMR ($(CD_3)_2CO$), 100 MHz): δ 141.3, 131.7 (q, $^1J_{CF}$ = 32.2 Hz), 128.8, 125.9 (q, $^3J_{CF}$ = 3.5 Hz), 124.9 (q, $^2J_{CF}$ = 270.2 Hz), 124.2 (q, $^3J_{CF}$ = 284.0 Hz), 79.7, 78.7, 72.6 (q, $^2J_{CF}$ = 31.9 Hz).

^{13}C NMR spectrum of this compound was measured in acetone-d_6 because some peaks of this compound overlapped with those of $CDCl_3$.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –62.9 (s), –80.4 (s).

HRMS (FAB+): Calcd. for $C_{11}H_7F_6O$ $[M+H]^+$: 269.0401. Found: 269.0401.



3k

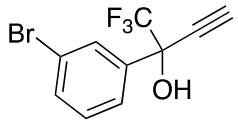
1,1,1-Trifluoro-2-(3-chloromophenyl)but-3-yn-2-ol (**3k**). A pale yellow oil (667.1 mg, 2.49 mmol, 83% isolated yield based on the amount of 1-(3-chlorophenyl)-2,2,2-trifluoroethan-1-one).

^{1}H NMR ($(CD_3)_2CO$, 400 MHz): δ 7.75 (br, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.41 (dq, *J* = 8.1, 1.1 Hz, 1H), 7.36 (pseudo t, *J* = 7.8 Hz, 1H), 3.26 (s, 1H), 2.85 (s, 1H).

^{13}C{^{1}H} NMR ($(CD_3)_2CO$, 100 MHz): δ 136.4, 134.3, 129.9, 129.5, 127.4, 125.3, 122.8 (q, $^1J_{CF}$ = 284.3 Hz), 78.8, 77.2, 72.3 (q, $^2J_{CF}$ = 32.6 Hz).

^{19}F NMR ($(CD_3)_2CO$, 376 MHz): δ –82.0 (s).

HRMS (FAB+): Calcd. for $C_{10}H_6ClF_3O$ $[M]^+$: 234.0059. Found: 234.0068.



3l

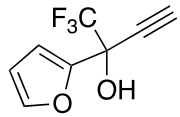
1,1,1-Trifluoro-2-(3-bromophenyl)but-3-yn-2-ol (**3l**). A pale yellow oil (667.1 mg, 2.40 mmol, 80% isolated yield based on the amount of 1-(3-bromophenyl)-2,2,2-trifluoroethan-1-one).

^{1}H NMR ($(CD_3)_2CO$, 400 MHz): δ 8.09 (br, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.76 (dq, *J* = 8.0, 1.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.09 (s, 1H), 3.68 (s, 1H).

^{13}C{^{1}H} NMR ($(CD_3)_2CO$, 100 MHz): δ 138.6, 132.3, 130.0, 129.9, 126.1, 123.4 (q, $^{1}J_{CF}$ = 284.0 Hz) 121.6, 79.0, 77.6, 71.6 (q, $^{2}J_{CF}$ = 31.9 Hz).

^{19}F NMR ($(CD_3)_2CO$, 376 MHz): δ –80.7 (s).

HRMS (FAB+): Calcd. for $C_{10}H_6BrF_3O$ $[M]^+$: 277.9554. Found: 277.9565.



3m

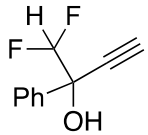
1,1,1-Trifluoro-2-(furan-2-yl)but-3-yn-2-ol (**3m**). A pale yellow oil (427.7 mg, 2.25 mmol, 75% isolated yield based on the mount of 2,2,2-trifluoro-1-(furan-2-yl)ethan-1-one).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, *J* = 2.0, 1H), 6.69 (dd, *J* = 3.3, 0.9 Hz, 1H), 6.42 (dd, *J* = 3.3, 2.0 Hz, 1H), 3.52 (br, 1H), 2.77 (s, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 146.8, 144.2, 122.4 (q, $^{1}J_{CF}$ = 284.6 Hz), 111.1, 110.8, 76.7, 76.3, 69.0 (q, $^{2}J_{CF}$ = 34.5 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz): δ –81.5 (s).

HRMS (FAB+): Calcd. for $C_8H_6F_3O_2$ $[M+H]^+$: 191.0320. Found: 191.0318.



8

1,1-Difluoro-2-phenylbut-3-yn-2-ol (**8**). A pale yellow oil (477.3 mg, 2.61 mmol, 87% isolated yield based on the amount of 2,2-difluoro-1-phenylethan-1-one).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.47–7.38 (m, 3H), 5.72 (t, *J* = 56.0 Hz, 1H), 3.02(s, 1H), 2.80 (s, 1H).

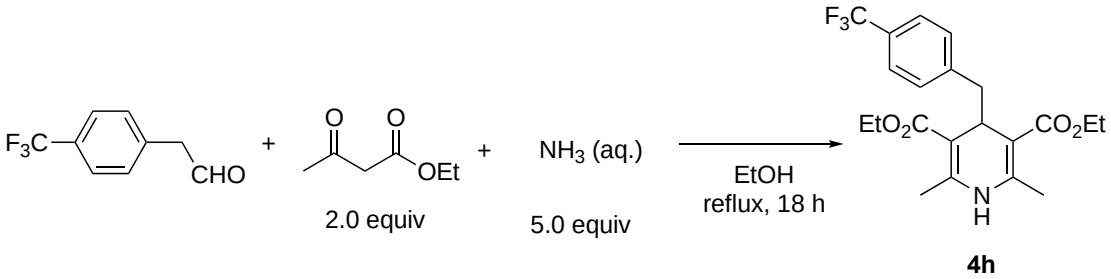
^{13}C{^{1}H} NMR ($(CD_3)_2CO$, 100 MHz): δ 137.8, 128.8, 128.1, 127.0, 115.4 (t, $^{1}J_{CF}$ = 249.6 Hz), 81.2, 76.9, 72.3 (t, $^{2}J_{CF}$ = 23.5 Hz).

^{13}C NMR spectrum of this compound was measured in acetone-d_6 because some peaks of this compound overlapped with those of $CDCl_3$.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –129.3 (dd, $^2J_{FF}$ = 276 Hz, $^2J_{HF}$ = 60 Hz), –129.2 (dd, $^2J_{FF}$ = 276 Hz, $^2J_{HF}$ = 60 Hz).
HRMS (FAB+): Calcd. for $C_{10}H_8F_2O$ $[M]^+$: 182.0543. Found: 182.0548.

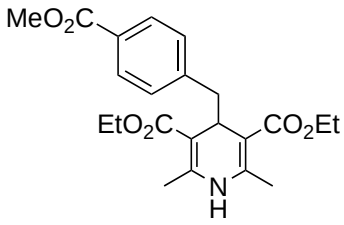
S3. General procedure for the preparation of 4-alkyl-1,4-dihydropyridine derivatives (4) (taking diethyl 2,6-dimethyl-4-(4-(trifluoromethyl)benzyl)-1,4-dihydropyridine-3,5-dicarboxylate (4h) as a typical example)

Scheme 2. Preparation of diethyl 2,6-dimethyl-4-(4-(trifluoromethyl)benzyl)-1,4-dihydropyridine-3,5-dicarboxylate **4h**



4h

In a 50 mL Schlenk flask were placed 2-(4-(trifluoromethyl)phenyl)acetaldehyde (940.8 mg, 5.00 mmol), ethyl acetoacetate (1301.4 mg, 10.00 mmol), and ethanol (20 mL) at room temperature under N_2, where an aqueous solution of 28 *wt* % NH_3 (1.5 mL, *ca.* 25 mmol) was added. The reaction mixture was stirred and refluxed for 18 h by using an oil bath, then was dried in vacuo. The residue was further purified by column chromatography (SiO_2) with a mixture of *n*-hexane/ethyl acetate (7:3) as an eluent to afford diethyl 2,6-dimethyl-4-(4-(trifluoromethyl)benzyl)-1,4-dihydropyridine-3,5-dicarboxylate (**4h**) as a white solid (1070.1 mg, 2.60 mmol, 52% yield based on the amount of 2-(4-(trifluoromethyl)phenyl)acetaldehyde).
m.p.: 129.0–130.2 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.8 Hz, 2H,), 7.11 (d, *J* = 7.8 Hz, 2H,), 6.02 (s, 1H), 4.18 (t, *J* = 5.7 Hz, 1H), 4.08–3.92 (m, 4H), 2.60 (d, *J* = 5.7 Hz, 2H), 2.16 (s, 6H), 1.17 (t, *J* = 7.2 Hz, 6H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.6, 145.9, 143.6, 130.1, 127.8 (q, $^2J_{CF}$ = 31.9 Hz), 124.4 (q, $^1J_{CF}$ = 270.2 Hz), 124.0 (q, $^3J_{CF}$ = 2.9 Hz), 101.2, 59.6, 42.1, 35.3, 18.9, 14.1.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –63.7 (s).
HRMS (FAB+): Calcd. for $C_{21}H_{24}F_3NO_4$ $[M]^+$: 411.1657. Found: 411.1653.



4i

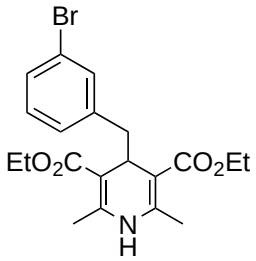
Diethyl 4-(4-(methoxycarbonyl)benzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4i**). A white solid (762.2 mg, 1.90 mmol, 38% isolated yield, based on the amount of methyl 4-(2-oxoethyl)benzoate).

m.p.: 86.5–88.0 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 5.20 (s, 1H), 4.24 (t, *J* = 5.5 Hz, 1H), 4.15–4.02 (m, 4H), 3.89 (s, 1H), 2.65 (d, *J* = 5.5 Hz, 2H), 2.15 (s, 6H), 1.24 (t, *J* = 7.4 Hz, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.6, 167.4, 145.5, 145.2, 130.1, 128.5, 127.6, 101.4, 59.7, 51.9, 42.2, 35.4, 19.2, 14.3.

HRMS (FAB+): Calcd. for $C_{22}H_{28}NO_6$ $[M+H]^+$: 402.1917. Found: 402.1936.



4o

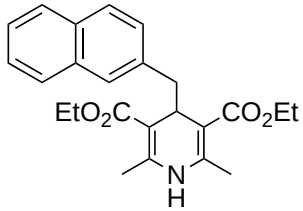
Diethyl 4-(3-bromobenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4o**). A white solid (971.3 mg, 2.30 mmol, 46% isolated yield, based on the amount of 2-(3-bromobenzyl)acetaldehyde).

m.p.: 88.3–89.5 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (ddd, *J* = 7.8, 2.0, 0.9 Hz1H,), 7.20 (t, *J* = 2.0 Hz, 1H,), 7.03 (t, *J* = 7.8 Hz, 1H), 6.91 (d of pseudo t, *J* = 7.8, 1.6 Hz, 1H), 5.36 (s, 1H), 4.19 (t, *J* = 5.6 Hz, 1H), 4.15–4.04 (m, 4H), 2.54 (d, *J* = 5.6 Hz, 2H), 2.18 (s, 6H), 1.26 (t, *J* = 7.2 Hz, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.6, 145.7, 141.7, 133.0, 128.8, 128.7, 128.6, 121.3, 101.4, 59.7, 41.9, 35.4, 19.2, 14.3.

HRMS (FAB+): Calcd. for $C_{20}H_{25}BrNO_4$ $[M+H]^+$: 422.0967. Found: 422.0946.



4s

Diethyl 2,6-dimethyl-4-(naphthalen-2-ylmethyl)-1,4-dihydropyridine-3,5-dicarboxylate (**4s**). A white solid (846.0 mg, 2.15 mmol, 43% isolated yield, based on the amount of 2-(4-(naphthalen-2-ylmethyl))acetaldehyde).

m.p.: 119.0–120.6 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.71 (m, 2H), 7.65 (d, *J* = 8.8 Hz, 1H,), 7.43 (s, 1H), 7.41-7.36 (m, 2H), 7.20 (dd, *J* = 8.0 Hz, 1.2Hz, 1H), 5.09 (s, 1H), 4.28 (t, *J* = 5.4

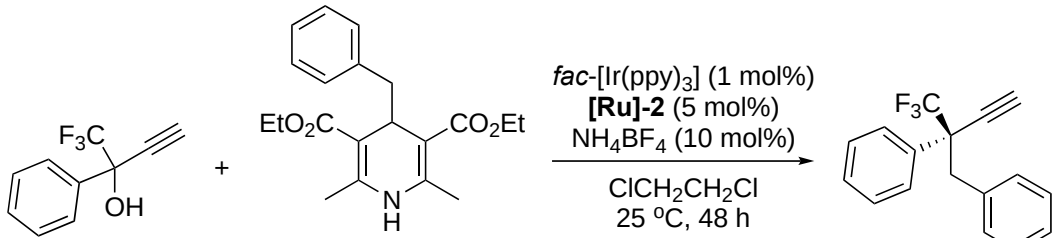
Hz, 1H), 4.10-3.95 (m, 4H), 2.75 (d, J = 5.2 Hz, 2H), 2.12 (s, 6H), 1.19 (t, J = 7.2 Hz, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.8, 145.4, 137.0, 133.2, 131.9, 129.1, 128.2, 127.4 (overlapping), 126.3, 125.5, 124.9, 101.8, 59.6, 42.4, 35.6, 19.2, 14.3.

HRMS (FAB+): Calcd. for $C_{24}H_{27}NO_4$ $[M]^+$: 393.1940. Found: 393.1951.

S4. General procedure for the preparation of chiral propargylic alkylation products (5, 7, and 9) (taking (*R*)-(2-(trifluoromethyl)but-3-yne-1,2-diyl)dibenzene (7aa) as a typical example)

Scheme 3. Preparation of Chiral Propargylic Alkylation Products **7**



3a **4a** 1.2 equiv **7aa**

In an oven dried 20 mL Schlenk flask were placed **[Ru]-2** (6.3 mg, 0.0050 mmol) and NH_4BF_4 (1.1 mg, 0.010 mmol) under N_2. Anhydrous $ClCH_2CCH_2Cl$ (2.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 30 min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg. 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), and *fac*-[Ir(ppy)$_3$] (0.7 mg, 0.0011 mmol) were added under N_2 at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 48 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography (SiO_2) with *n*-hexane as an eluent to afford (*R*)-(2-(trifluoromethyl)but-3-yne-1,2-diyl)dibenzene (**7aa**) as a colorless oil (22.2 mg, 0.081 mmol, 81% yield based on the amount of **3a**).

$[\alpha]_D^{20}$: –12.2 (c = 0.5 in $CHCl_3$).

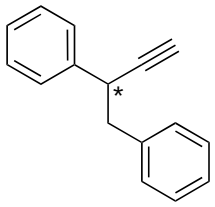
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68–7.64 (m, 2H), 7.39–7.33 (m, 3H), 7.22–7.09 (m, 3H), 7.00–6.97 (m, 2H), 3.52 (d, J = 13.2 Hz, 1H), 3.42 (d, J = 13.2 Hz, 1H), 2.66 (s, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 134.4, 133.3, 130.8, 128.5, 128.5, 128.3, 127.6, 127.0, 125.7 (q, $^{1}J_{CF}$ = 282.7 Hz), 79.0 (q, $^{3}J_{CF}$ = 1.9 Hz), 78.1, 53.0 (q, $^{2}J_{CF}$ = 26.5 Hz), 40.7.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.5 (s).

HRMS (FAB+): Calcd. for $C_{17}H_{13}F_3$ $[M]^+$: 274.0969. Found: 274.0964.

The enantiomeric excess of **7aa** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 14.6 min (major) and 19.9 min (minor), 94% ee.



5

But-3-yne-1,2-diyldibenzene (5). A colorless oil (15.1 mg, 0.073 mmol, 73% yield based on the amount of **1**).

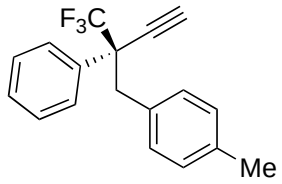
[α]$_D^{20}$: –14.8 (c = 0.5 in $CHCl_3$).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33–7.19 (m, 8H), 7.13 (d, *J* = 7.2 Hz, 2H), 3.88 (ddd, *J* = 7.8, 6.8, 2.5 Hz, 1H), 3.06 (dd, *J* = 13.2, 7.8 Hz, 1H), 3.04 (dd, *J* = 13.2, 6.8 Hz, 1H), 2.28 (d, *J* = 2.5 Hz, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 140.7, 138.6, 129.4, 128.4, 128.1, 127.6, 126.9, 126.5, 85.3, 71.9, 44.7, 39.8.

HRMS (FAB+): Calcd. for $C_{16}H_{15}$ $[M+H]^+$: 207.1174. Found: 207.1173.

The enantiomeric excess of **5** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 21.8 min (minor) and 44.7 min (major), 48% ee.



7ab

(*R*)-1-Methyl-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7ab). A colorless oil (22.5 mg, 0.078 mmol, 78% yield based on the amount of **3a**).

[α]$_D^{20}$: +21.9 (c = 0.5 in $CHCl_3$).

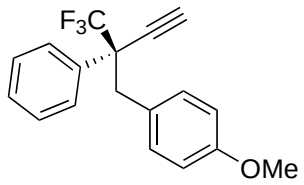
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68–7.64 (m, 2H), 7.39–7.33 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 3.48 (d, *J* = 13.6 Hz, 1H), 3.38 (d, *J* = 13.6 Hz, 1H), 2.65 (s, 1H), 2.24 (s, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 136.5, 133.4, 131.2, 130.6, 128.5 (overlapping), 128.3, 128.2, 125.7 (q, $^1J_{CF}$ = 282.7 Hz), 79.1, 78.0, 53.0 (q, $^2J_{CF}$ = 26.2 Hz), 40.3, 21.0.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.5 (s).

HRMS (FAB+): Calcd. for $C_{18}H_{15}F_3$ $[M]^+$: 288.1126. Found: 288.1128.

The enantiomeric excess of **7ab** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 13.7 min (major) and 18.9 min (minor), 94% ee.



7ac

(*R*)-1-Methyl-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7ac). A colorless oil (24.0 mg, 0.079 mmol, 79% yield based on the amount of **3a**).

$[\alpha]_D^{20}$: +66.9 (c = 0.5 in $CHCl_3$).

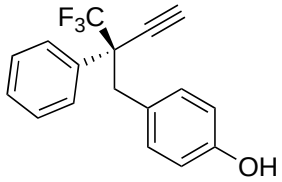
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68–7.64 (m, 2H), 7.40–7.33 (m, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 3.72 (s, 3H), 3.46 (d, *J* = 13.6 Hz, 1H), 3.37 (d, *J* = 13.6 Hz, 1H), 2.65 (s, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 158.5, 133.4, 131.7, 128.5 (overlapping), 128.3, 126.3, 125.7 (q, $^1J_{CF}$ = 282.7 Hz), 113.0, 79.1 (q, $^3J_{CF}$ = 1.9 Hz), 78.0, 55.0, 53.1 (q, $^2J_{CF}$ = 26.2 Hz), 39.9.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –71.7 (s).

HRMS (FAB+): Calcd. for $C_{18}H_{15}F_3O$ $[M]^+$: 304.1075. Found: 304.1088.

The enantiomeric excess of **7ac** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 20.1 min (major) and 23.7 min (minor), 92% ee.



7ad

(*R*)-4-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)phenol (7ad). A colorless oil (20.3 mg, 0.070 mmol, 70% yield based on the amount of **3a**).

$[\alpha]_D^{20}$: –40.9 (c = 0.5 in $CHCl_3$).

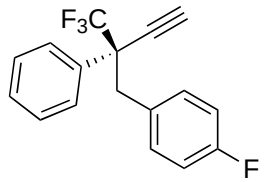
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66–7.62 (m, 2H), 7.39–7.33 (m, 3H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 3.44 (d, *J* = 13.8 Hz, 1H), 3.35 (d, *J* = 13.8 Hz, 1H), 2.65 (s, 1H), 2.1–1.3 (br, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 154.5, 133.4, 131.9, 128.5, 128.5, 128.3, 126.6, 125.7 (q, $^1J_{CF}$ = 282.7 Hz), 114.5, 79.1 (q, $^3J_{CF}$ = 1.9 Hz), 78.0, 53.2 (q, $^2J_{CF}$ = 26.2 Hz), 40.0.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.3 (s).

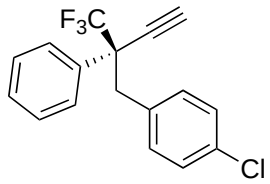
HRMS (FAB+): Calcd. for $C_{17}H_{13}F_3O$ $[M]^+$: 290.0918. Found: 290.0912.

The enantiomeric excess of **7ad** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 80/20, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 19.8 min (major) and 31.3 min (minor), 92% ee.



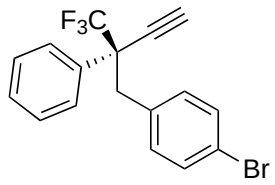
7ae

(*R*)-1-Fluoro-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7ae). A colorless oil (23.4 mg, 0.080 mmol, 80% yield based on the amount of **3a**).
[α]$_D^{20}$: –17.1 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65–7.61 (m, 2H), 7.39–7.34 (m, 3H), 6.93 (dd, *J* = 8.8, 5.6 Hz, 2H), 6.80 (pseudo t, *J* = 8.8 Hz, 2H), 3.47 (d, *J* = 13.2 Hz, 1H), 3.39 (d, *J* = 13.2 Hz, 1H), 2.66 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 162.0 (d, $^1J_{CF}$ = 244.4 Hz), 133.2, 132.2 (d, $^3J_{CF}$ = 7.6 Hz), 130.0 (d, $^4J_{CF}$ = 2.8 Hz), 128.7, 128.4, 128.4, 125.6 (q, $^1J_{CF}$ = 279.5 Hz), 114.5 (d, $^2J_{CF}$ = 21.0 Hz), 78.8 (q, $^3J_{CF}$ = 1.9 Hz), 78.2, 53.0 (q, $^2J_{CF}$ = 26.8 Hz), 40.0.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.4 (s), –117.3 (s).
HRMS (FAB+): Calcd. for $C_{17}H_{13}F_4$ $[M+H]^+$: 293.0953. Found: 293.0962.
The enantiomeric excess of **7ae** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.3 mL/min, λ = 220 nm, retention time: 32.2 min (major) and 35.0 min (minor), 92% ee.



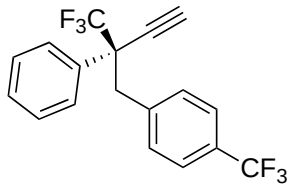
7af

(*R*)-1-Chloro-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7af). A white solid (22.8 mg, 0.074 mmol, 74% yield based on the amount of **3a**).
m.p.: 56.4–57.8 °C
[α]$_D^{20}$: –19.5 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.61 (m, 2H), 7.40–7.34 (m, 3H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 3.47 (d, *J* = 13.6 Hz, 1H), 3.38 (d, *J* = 13.6 Hz, 1H), 2.67 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 133.0, 132.8, 132.0, 128.7, 128.4 (overlapping), 127.8, 125.6 (q, $^1J_{CF}$ = 282.7 Hz), 78.7 (q, $^3J_{CF}$ = 1.9 Hz), 78.3, 52.9 (q, $^2J_{CF}$ = 26.2 Hz), 40.1.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.5 (s).
HRMS (FAB+): Calcd. for $C_{17}H_{12}ClF_3$ $[M]^+$: 308.0580. Found: 308.0570.
The enantiomeric excess of **7af** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 17.3 min (major) and 25.4 min (minor), 90% ee.



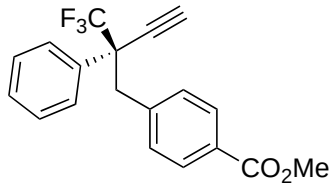
7ag

(*R*)-1-Bromo-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7ag). A colorless oil (24.0 mg, 0.068 mmol, 68% yield based on the amount of **3a**).
[α]$_D^{20}$: –49.5 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65–7.61 (m, 2H), 7.38–7.34 (m, 3H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.45 (d, *J* = 13.6 Hz, 1H), 3.36 (d, *J* = 13.6 Hz, 1H), 2.67 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 133.3, 133.0, 132.4, 130.7, 128.7, 128.4 (overlapping), 125.6 (q, $^1J_{CF}$ = 282.7 Hz), 121.2, 78.7 (q, $^3J_{CF}$ = 2.4 Hz), 78.4, 52.8 (q, $^2J_{CF}$ = 26.8 Hz), 40.2.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.5.
HRMS (FAB+): Calcd. for $C_{17}H_{12}BrF_3$ $[M]^+$: 352.0074. Found: 352.0083.
The enantiomeric excess of **7ag** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 15.4 min (major) and 23.7 min (minor), 94% ee.



7ah

(*R*)-1-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)-4-(trifluoromethyl)benzene (7ah). A white solid (25.3 mg, 0.074 mmol, 74% yield based on the amount of **3a**).
m.p.: 54.5–55.5 °C
[α]$_D^{20}$: –49.1 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66–7.62 (m, 2H), 7.39–7.35 (m, 5H), 7.08 (d, 2H, *J* = 8.4 Hz), 3.56 (d, *J* = 13.4 Hz, 1H), 3.46 (d, *J* = 13.4 Hz, 1H), 2.68 (s, 1H).
^{13}C{^{1}H} NMR ($(CD_3)_2CO$, 100 MHz): δ 140.1, 133.6, 132.3, 129.6, 129.5 (q, $^2J_{CF}$ = 31.6 Hz), 129.4, 129.2, 126.6 (q, $^1J_{CF}$ = 282.4 Hz), 125.2 (q, $^1J_{CF}$ = 269.8 Hz), 125.0 (q, $^3J_{CF}$ = 2.8 Hz), 80.8, 79.1, 53.4 (q, $^2J_{CF}$ = 27.2 Hz), 40.2.
^{13}C NMR spectrum of this compound was measured in acetone-d_6 because some peaks of this compound overlapped with those of $CDCl_3$.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –64.1 (s), –73.6 (s).
HRMS (FAB+): Calcd. for $C_{18}H_{12}F_6$ $[M]^+$: 342.0843. Found: 342.0856.
The enantiomeric excess of **7ah** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 11.4 min (major) and 15.6 min (minor), 91% ee.



7ai

Methyl (*R*)-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzoate (7ai). A pale yellow solid (24.9 mg, 0.075 mmol, 75% yield based on the amount of **3a**).

m.p.: 74.0–75.5 °C

[α]$_D^{20}$: –45.6 (c = 0.5 in $CHCl_3$).

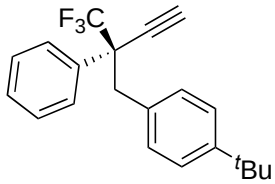
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.65–7.62 (m, 2H), 7.38–7.33 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H), 3.56 (d, *J* = 14.0 Hz, 1H), 3.47 (d, *J* = 14.0 Hz, 1H), 2.67 (s, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 166.9, 139.7, 133.0, 130.8, 128.9, 128.8, 128.7, 128.4, 125.6 (q, $^1J_{CF}$ = 282.7 Hz), 78.6 (q, $^3J_{CF}$ = 1.9 Hz), 78.4, 52.8 (q, $^2J_{CF}$ = 26.8 Hz), 52.0, 40.7.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.5 (s).

HRMS (FAB+): Calcd. for $C_{19}H_{16}F_3O_2$ $[M+H]^+$: 333.1102. Found: 333.1107.

The enantiomeric excess of **7ai** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 18.9 min (major) and 31.1 min (minor), 96% ee.



7aj

(*R*)-1-(*tert*-Butyl)-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7aj). A white solid (23.1 mg, 0.070 mmol, 70% yield based on the amount of **3a**).

m.p.: 88.7–89.9 °C

[α]$_D^{20}$: –13.2 (c = 0.5 in $CHCl_3$).

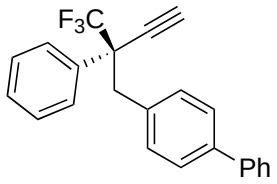
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69–7.66 (m, 2H), 7.39–7.33 (m, 3H,), 7.13 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 3.50 (d, *J* = 13.6 Hz, 1H), 3.39 (d, *J* = 13.6 Hz, 1H), 2.65 (s, 1H), 1.24 (s, 9H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 149.6, 133.5, 131.3, 130.3, 128.5, 128.5, 128.2, 125.7 (q, $^1J_{CF}$ = 282.7 Hz), 124.5, 79.2 (q, $^3J_{CF}$ = 1.9 Hz), 77.8, 52.9 (q, $^2J_{CF}$ = 26.2 Hz), 40.0, 34.3, 31.3.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –72.0 (s).

HRMS (FAB+): Calcd. for $C_{21}H_{21}F_3$ $[M]^+$: 330.1595. Found: 330.1594.

The enantiomeric excess of **7aj** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 9.9 min (major) and 17.9 min (minor), 84% ee.



7ak

(*R*)-4-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)-1,1'-biphenyl (7ak). A white solid (24.9 mg, 0.071 mmol, 71% yield based on the amount of **3a**).

m.p.: 102.6–103.7 °C

[α]$_D^{20}$: –46.4 (c = 0.5 in $CHCl_3$).

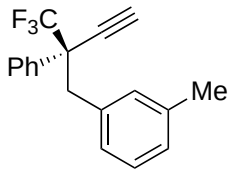
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71–7.67 (m, 2H), 7.52 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.42–7.34 (m, 7H), 7.30 (tt, *J* = 7.4, 1.6 Hz,1H), 7.05 (d, *J* = 8.0 Hz, 2H), 3.56 (d, *J* = 13.2 Hz, 1H), 3.47 (d, *J* = 13.2 Hz, 1H), 2.69 (s, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 140.6, 139.7, 133.4, 133.3, 131.1, 128.7, 128.6, 128.5, 128.3, 127.2, 126.9, 126.2, 125.7 (q, $^1J_{CF}$ = 283.7 Hz), 79.0, 78.1, 53.0 (q, $^2J_{CF}$ = 26.5 Hz), 40.3.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –71.8 (s).

HRMS (FAB+): Calcd. for $C_{23}H_{17}F_3$ $[M]^+$: 350.1282. Found: 350.1270.

The enantiomeric excess of **7ak** was determined by HPLC analysis; DAICEL Chiralpak OD, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 11.4 min (minor) and 12.4 min (major), 83% ee.



7al

(*R*)-1-Methyl-3-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7al). A colorless oil (21.0 mg, 0.073 mmol, 73% yield based on the amount of **3a**).

[α]$_D^{20}$: –14.9 (c = 0.5 in $CHCl_3$).

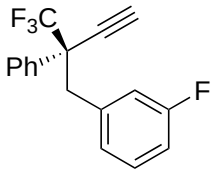
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67–7.64 (m, 2H), 7.38–7.33 (m, 3H), 7.00 (pseudo t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.79 (br, 1H), 6.76 (d, *J* = 6.8 Hz, 1H), 3.47 (d, *J* = 13.4 Hz, 1H), 3.38 (d, *J* = 13.4 Hz, 1H), 2.65 (s, 1H), 2.19 (s, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 137.0, 134.2, 133.4, 131.7, 128.5, 128.2, 127.7, 127.7, 127.4, 127.2, 125.7 (q, $^1J_{CF}$ = 282.7 Hz), 79.0 (q, $^3J_{CF}$ = 1.9 Hz), 78.0, 53.0 (q, $^2J_{CF}$ = 26.2 Hz), 40.7, 21.3.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –72.0 (s).

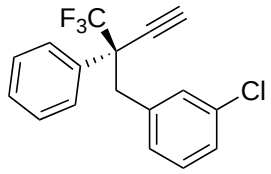
HRMS (FAB+): Calcd. for $C_{18}H_{15}F_3$ $[M]^+$: 288.1126. Found: 288.1137.

The enantiomeric excess of **7al** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 13.6 min (major) and 17.7 min (minor), 90% ee.



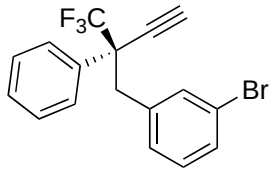
7am

(*R*)-1-Fluoro-3-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7am). A colorless oil (23.4 mg, 0.080 mmol, 80% yield based on the amount of **3a**).
[α]$_D^{20}$: –48.0 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67–7.62 (m, 2H), 7.42–7.34 (m, 3H), 7.07 (dd, *J* = 14.0, 8.6 Hz, 1H), 6.85 (ddd, *J* = 8.6, 7.6, 2.8 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.72 (dd, *J* = 7.6, 2.4 Hz, 1H), 3.50 (d, *J* = 13.2 Hz, 1H), 3.41 (d, *J* = 13.2 Hz, 1H), 2.69 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 162.1 (d, $^1J_{CF}$ = 243.4 Hz), 136.8 (d, $^3J_{CF}$ = 7.7 Hz), 133.0, 128.9 (d, ^3J = 8.6 Hz), 128.7, 128.4 (overlapping), 126.5 (d, $^4J_{CF}$ = 1.9 Hz), 125.5 (q, $^1J_{CF}$ = 283.0 Hz), 117.6 (d, $^2J_{CF}$ = 22.0 Hz), 114.0 (d, $^2J_{CF}$ = 20.1 Hz), 78.7 (q, $^3J_{CF}$ = 1.9 Hz), 78.3, 52.8 (q, $^2J_{CF}$ = 26.8 Hz), 40.4.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.6 (s), –115.7 (s).
HRMS (FAB+): Calcd. for $C_{17}H_{12}F_4$ $[M]^+$: 292.0875. Found: 292.0872.
The enantiomeric excess of **7am** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 11.9 min (major) and 16.0 min (minor), 90% ee.



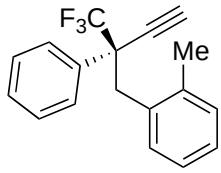
7an

(*R*)-1-Chloro-3-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7an). A colorless oil (23.8 mg, 0.077 mmol, 77% yield based on the amount of **3a**).
[α]$_D^{20}$: –13.5 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66–7.61 (m, 2H), 7.40–7.34 (m, 3H), 7.13 (ddd, *J* = 8.0, 2.1, 0.9 Hz, 1H), 7.03 (t, *J* = 8.0, Hz, 1H), 7.00 (pseudo t, *J* = 2.0 Hz, 1H), 6.82 (d of pseudo t, *J* = 8.0, 1.4 Hz, 1H), 3.47 (d, *J* = 13.8 Hz, 1H), 3.38 (d, *J* = 13.8 Hz, 1H), 2.70 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 136.3, 133.3, 133.0, 130.9, 128.8, 128.8, 128.4 (overlapping), 127.2, 125.5 (q, $^1J_{CF}$ = 282.7 Hz), 78.6 (q, $^3J_{CF}$ = 1.9 Hz), 78.4, 52.8 (q, $^2J_{CF}$ = 26.8 Hz), 40.4.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.5 (s).
HRMS (FAB+): Calcd. for $C_{17}H_{12}ClF_3$ $[M]^+$: 308.0580. Found: 308.0578.
The enantiomeric excess of **7an** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 22.4 min (major) and 33.0 min (minor), 91% ee.



7ao

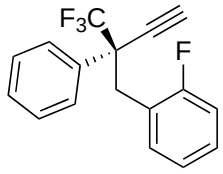
(*R*)-1-Bromo-3-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7ao). A colorless oil (25.4 mg, 0.072 mmol, 72% yield based on the amount of **3a**).
$[\alpha]_D^{20}$: –44.5 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.65–7.61 (m, 2H), 7.39–7.35 (m, 3H,), 7.29 (ddd, *J* = 8.0, 2.0, 0.9 Hz, 1H), 7.16 (t, *J* = 2.0 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.86 (d of pseudo t, *J* = 8.0, 1.4 Hz, 1H), 3.46 (d, *J* = 13.6 Hz, 1H), 3.37 (d, *J* = 13.6 Hz, 1H), 2.70 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) : δ 136.6, 133.8, 133.0, 130.1, 129.3, 129.1, 128.8, 128.4, 128.4, 125.5 (q, $^1J_{C\text{-}F}$ = 282.7 Hz), 121.5, 78.6 (q, $^3J_{CF}$ = 1.9 Hz), 78.5, 52.9 (q, $^2J_{CF}$ = 26.8 Hz), 40.4.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.4 (s).
HRMS (FAB+): Calcd. for $C_{17}H_{12}BrF_3$ $[M]^+$: 352.0074. Found: 352.0073.
The enantiomeric excess of **7ao** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 19.5 min (major) and 27.8 min (minor), 93% ee.



7ap

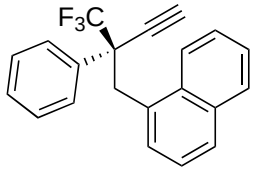
(*R*)-1-Methyl-2-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7ap). A colorless oil (21.3 mg, 0.074 mmol, 74% yield based on the amount of **3a**).
$[\alpha]_D^{20}$: –50.8 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68–7.64 (m, 2H), 7.39–7.35 (m, 3H), 7.10 (dd, *J* = 8.0, 2.0 Hz,1H), 7.07 (pseudo t of d *J* = 7.8, 1.5 Hz, 1H), 6.88 (pseudo t of d, *J* = 7.2, 2.0 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 3.61 (d, *J* = 14.4 Hz, 1H), 3.44 (d, *J* = 14.4 Hz, 1H), 2.55 (s, 1H), 2.25 (s, 3H).
^{13}C{^{1}H} NMR ($(CD_3)_2CO$, 100 MHz): δ 138.3, 134.6, 133.6, 130.7, 130.6, 129.2, 129.1, 128.9, 127.3, 126.7 (q, $^1J_{CF}$ = 282.1 Hz), 125.4, 79.4, 79.2 (q, $^3J_{CF}$ = 1.9 Hz), 52.9 (q, $^2J_{CF}$ = 26.9 Hz), 36.7, 19.9.
^{13}C NMR spectrum of this compound was measured in acetone-d_6 because some peaks of this compound overlapped with those of $CDCl_3$.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.5 (s).
HRMS (FAB+): Calcd. for $C_{18}H_{15}F_3$ $[M]^+$: 288.1126. Found: 288.1112.

The enantiomeric excess of **7ap** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 14.4 min (major) and 20.0 min (minor), 90% ee.



7aq

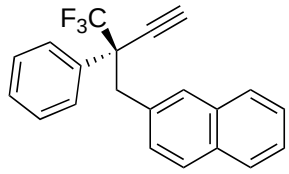
(*R*)-1-Fluoro-2-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7aq). A colorless oil (22.8 mg, 0.078 mmol, 78% yield based on the amount of **3a**).
[α]$_D^{20}$: –47.0 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71–7.67 (m, 2H), 7.38–7.33 (m, 3H), 7.18–7.11 (m, 1H), 7.02–6.85 (m, 3H), 3.62 (d, *J* = 13.6 Hz, 1H), 3.51 (d, *J* = 13.6 Hz, 1H), 2.64 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 161.4 (d, $^1J_{CF}$ = 245.3 Hz), 133.4, 132.0 (d, $^3J_{CF}$ = 3.8 Hz), 128.8 (d, $^3J_{CF}$ = 8.6 Hz), 128.6, 128.4, 128.2, 125.6 (q, $^1J_{CF}$ = 282.7 Hz), 123.2 (d, $^4J_{CF}$ = 3.8 Hz), 121.8 (d, $^2J_{CF}$ = 14.4 Hz), 115.0 (d, $^2J_{CF}$ = 23.0 Hz), 78.8 (q, $^3J_{CF}$ = 1.9 Hz), 77.6, 52.3 (q, $^2J_{CF}$ = 26.8 Hz), 33.1.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.4 (s), –116.8 (s).
HRMS (FAB+): Calcd. for $C_{17}H_{12}F_4$ $[M]^+$: 292.0875. Found: 292.0865.
The enantiomeric excess of **7aq** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 15.6 min (major) and 18.7 min (minor), 93% ee.



7ar

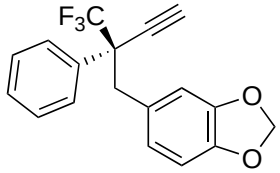
(*R*)-1-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)naphthalene (7ar). A white solid (22.4 mg, 0.069 mmol, 69% yield based on the amount of **3a**).
m.p.: 83.6–84.2 °C
[α]$_D^{20}$: +26.9 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11–8.06 (m, 1H), 7.82–7.77 (m, 1H), 7.70–7.66 (m, 3H), 7.47–7.41 (m, 2H), 7.37–7.33 (m, 2H), 7.17 (pseudo t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 6,8 Hz, 1H), 4.16 (d, *J* = 14.4 Hz, 1H), 3.89 (d, *J* = 14.4 Hz, 1H), 2.41 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 134.0, 133.5, 133.0, 130.5, 128.6, 128.5, 128.4 (overlapping), 128.3, 127.6, 125.9 (q, $^1J_{CF}$ = 283.0 Hz), 125.5, 125.3, 124.7, 124.2, 79.2 (q, $^3J_{CF}$ = 2.0 Hz), 78.0, 52.4 (q, $^2J_{CF}$ = 26.5 Hz), 36.1.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –71.9 (s).
HRMS (FAB+): Calcd. for $C_{21}H_{15}F_3$ $[M]^+$: 324.1126. Found: 324.1132.

The enantiomeric excess of **7ar** was determined by HPLC analysis; DAICEL Chiralpak OD, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 10.4 min (minor) and 12.9 min (major), 91% ee.



7as

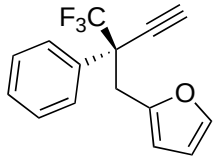
(*R*)-2-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)naphthalene (7as). A colorless oil (23.0 mg, 0.071 mmol, 71% yield based on the amount of **3a**).
[α]$_D^{20}$: +37.9 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (dd, J = 5.6, 3.3 Hz, 1H), 7.71–7.67 (m, 2H), 7.65 (dd, J = 6.3, 3.3 Hz, 1H), 7.75–7.62 (m, 4H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.47 (br, 1H), 7.41 (d, *J* = 5.6 H, 1H), 7.40 (d, *J* = 6.3 Hz, 1H), 7.38–7.33 (m, 3H), 7.07 (dd, *J* = 8.3, 1.8 Hz, 1H), 3.69 (d, *J* = 13.4 Hz, 1H), 3.60 (d, *J* = 13.4 Hz, 1H), 2.66 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 133.4, 132.9, 132.4, 131.9, 129.9, 128.7, 128.6, 128.5, 128.3, 127.7, 127.4, 126.9, 125.7, 125.7 (q, $^1J_{CF}$ = 282.7 Hz), 125.7, 79.0 (q, $^3J_{CF}$ = 1.9 Hz), 78.2, 53.1 (q, $^2J_{CF}$ = 26.5 Hz), 40.9.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.4 (s).
HRMS (FAB+): Calcd. for $C_{21}H_{15}F_3$ $[M]^+$: 324.1126. Found: 324.1115.
The enantiomeric excess of **7as** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 22.3 min (minor) and 26.3 min (major), 95% ee.



7at

(*R*)-5-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzo[d][1,3]dioxole (7at). A colorless oil (21.0 mg, 0.066 mmol, 66% yield based on the amount of **3a**).
[α]$_D^{20}$: +52.5 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67–7.64 (m, 2H), 7.40–7.34 (m, 3H), 6.57 (d, *J* = 8.1 Hz, 1H), 6.49 (d, *J* = 1.3 Hz, 1H), 6.44 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.86 (dd, *J* = 2.2, 1.3 Hz, 1H), 3.43 (d, *J* = 13.6 Hz, 1H), 3.34 (d, *J* = 13.6 Hz, 1H), 2.68 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 146.8, 146.5, 133.3, 128.6, 128.4, 128.3, 127.9, 125.6 (q, $^1J_{CF}$ = 283.0 Hz), 124.2, 111.0, 107.5, 100.8, 79.0, 78.1, 53.1 (q, $^2J_{CF}$ = 26.2 Hz), 40.5.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.4 (s).
HRMS (FAB+): Calcd. for $C_{18}H_{13}F_3O_2$ $[M]^+$: 318.0868. Found: 318.0865.

The enantiomeric excess of **7at** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 90/10, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 22.7 min (minor) and 48.1 min (major), 91% ee.



7au

(*R*)-2-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)furan (7au). A colorless oil (19.7 mg, 0.080 mmol, 80% yield based on the amount of **3a**).

[α]$_D^{20}$: –16.2 (c = 0.5 in $CHCl_3$).

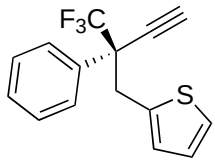
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64–7.60 (m, 2H), 7.44–7.35 (m, 4H,), 6.42 (d, *J* = 3.2 Hz, 1H), 6.00-5.99 (m, 1H), 6.73-6.72 (m, 1H), 6.42 (d, *J* = 3.2 Hz, 1H), 6.00 (ddd, *J* = 3.2, 2.4, 0.8Hz, 1H), 2.74 (s, 1H), 2.29 (d, *J* = 0.8 Hz, 2H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 153.3, 146.0, 134.2, 128.8, 128.5, 128.3, 124.1 (q, $^1J_{CF}$ = 284.6 Hz), 111.0, 106.4, 78.2 (q, $^3J_{CF}$ = 1.9 Hz), 75.7, 52.3 (q, $^2J_{CF}$ = 29.7 Hz), 13.6.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –72.2 (s).

HRMS (FAB+): Calcd. for $C_{15}H_{11}F_3O$ $[M]^+$: 264.0762. Found: 264.0752.

The enantiomeric excess of **7au** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 21.0 min (major) and 27.2 min (minor), 90% ee.



7av

(*R*)-2-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)thiophene (7av). A colorless oil (21.0 mg, 0.075 mmol, 75% yield based on the amount of **3a**).

[α]$_D^{20}$: –12.5 (c = 0.5 in $CHCl_3$).

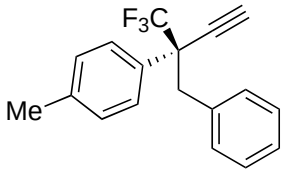
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71–7.67 (m, 2H), 7.42–7.36 (m, 3H,), 7.03 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.80 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.72 (d, *J* = 3.7 Hz, 1H), 3.80 (d, *J* = 14.8 Hz, 1H), 3.68 (d, *J* = 14.8 Hz, 1H), 2.66 (s, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 135.8, 132.8, 128.8, 128.6, 128.4, 128.2, 126.0, 125.3 (q, $^1J_{CF}$ = 282.7 Hz), 124.9, 78.9 (q, $^3J_{CF}$ = 1.9 Hz), 77.7, 52.9 (q, $^2J_{CF}$ = 27.2 Hz), 35.4.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –74.1 (s).

HRMS (FAB+): Calcd. for $C_{15}H_{11}F_3S$ $[M]^+$: 280.0534. Found: 280.0522.

The enantiomeric excess of **7av** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 15.4 min (major) and 22.9 min (minor), 94% ee.



7ba

(*R*)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-methylbenzene (7ba). A colorless oil (23.4 mg, 0.081 mmol, 81% yield based on the amount of **3b**).

[α]$_D^{20}$: –44.6 (c = 0.5 in $CHCl_3$).

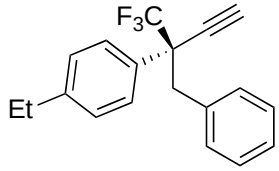
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.18–7.10 (m, 5H), 7.00 (d, *J* = 8.0, 1.6 Hz, 2H), 3.50 (d, *J* = 13.4 Hz, 1H), 3.40 (d, *J* = 13.4 Hz, 1H), 2.63 (s, 1H), 2.35 (s, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 138.4, 134.5, 130.8, 130.3, 129.0, 128.3, 127.5, 126.9, 125.7 (q, $^1J_{CF}$ = 282.7 Hz), 79.1 (q, $^3J_{CF}$ = 2.0 Hz), 77.8, 52.6 (q, $^2J_{CF}$ = 26.5 Hz), 40.6, 21.0.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –72.1 (s).

HRMS (FAB+): Calcd. for $C_{18}H_{15}F_3$ $[M]^+$: 288.1126. Found: 288.1123.

The enantiomeric excess of **7ba** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 15.1 min (major) and 22.2 min (minor), 90% ee.



7ca

(*R*)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-ethylbenzene (7ca). A colorless oil (23.0 mg, 0.076 mmol, 76% yield based on the amount of **3c**).

[α]$_D^{20}$: –47.4 (c = 0.5 in $CHCl_3$).

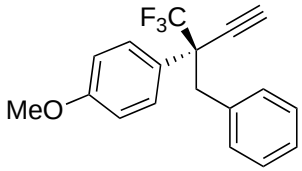
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.21–7.10 (m, 5H), 7.01 (dd, *J* = 8.0, 1.6 Hz, 2H), 3.51 (d, *J* = 13.2 Hz, 1H), 3.41 (d, *J* = 13.2 Hz, 1H), 2.66 (q, *J* = 7.7 Hz, 2H), 2.63 (s, 1H), 1.25 (t, *J* = 7.7 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 144.6, 134.6, 130.8, 130.6, 128.4, 127.7, 127.5, 126.9, 125.7 (q, $^1J_{CF}$ = 282.7 Hz), 79.2 (q, $^3J_{CF}$ = 2.9 Hz), 77.8, 52.6 (q, $^2J_{CF}$ = 26.5 Hz), 40.7, 28.3, 15.2.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.6 (s).

HRMS (FAB+): Calcd. for $C_{19}H_{17}F_3$ $[M]^+$: 302.1282. Found: 302.1280.

The enantiomeric excess of **7ca** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 11.7 min (major) and 14.6 min (minor), 90% ee.



7da

(*R*)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-methylbenzene (7da). A colorless oil (21.6 mg, 0.071 mmol, 71% yield based on the amount of **3d**).

[α]$_D^{20}$: –43.6 (c = 0.5 in $CHCl_3$).

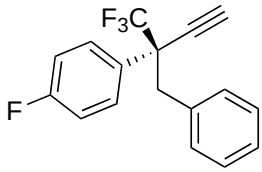
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, *J* = 9.0 Hz, 2H), 7.20–7.11 (m, 3H), 7.01 (dd, *J* = 7.6, 1.6 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 3.50 (d, *J* = 13.4 Hz, 1H), 3.40 (d, *J* = 13.4 Hz, 1H), 2.63 (s, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 159.6, 134.5, 130.8, 129.7, 127.6, 126.9, 125.7 (q, $^1J_{CF}$ = 282.7 Hz), 125.2, 113.5, 79.2 (q, $^3J_{CF}$ = 2.0 Hz), 77.8, 55.2, 52.3 (q, $^2J_{CF}$ = 26.5 Hz), 40.6.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –74.0 (s).

HRMS (FAB+): Calcd. for $C_{18}H_{16}F_3O$ $[M+H]^+$: 304.1153. Found: 305.1140.

The enantiomeric excess of **7da** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 23.2 min (major) and 34.6 min (minor), 91% ee.



7ea

(*R*)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-fluorobenzene (7ea). A colorless oil (22.5 mg, 0.077 mmol, 77% yield based on the amount of **3e**).

[α]$_D^{20}$: –58.8 (c = 0.5 in $CHCl_3$).

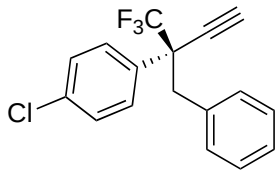
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (dd, *J* = 8.6, 5.0 Hz, 2H), 7.20–7.10 (m, 3H), 7.04 (pseudo t, *J* = 8.4 Hz, 2H), 6.98 (dd, *J* = 8.0, 1.6 Hz, 2H), 3.46 (d, *J* = 13.2 Hz, 1H), 3.41 (d, *J* = 13.2 Hz, 1H), 2.67 (s, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 162.7 (d, $^1J_{CF}$ = 247.3 Hz), 134.1, 130.7, 130.4 (d, $^3J_{CF}$ = 7.7 Hz), 129.1 (d, $^4J_{CF}$ = 2.9 Hz), 127.7, 127.1, 125.6 (q, $^1J_{CF}$ = 282.7 Hz), 115.2 (d, $^2J_{CF}$ = 21.1 Hz), 78.8 (q, $^3J_{CF}$ = 2.9 Hz), 78.2, 52.5 (q, $^2J_{CF}$ = 26.7 Hz), 40.8.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.8 (s), –115.1 (s).

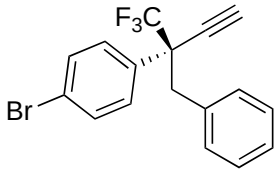
HRMS (FAB+): Calcd. for $C_{17}H_{13}F_4$ $[M+H]^+$: 293.0953. Found: 293.0945.

The enantiomeric excess of **7ea** was determined by HPLC analysis; DAICEL Chiralpak OD, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 9.0 min (major) and 10.0 min (minor), 94% ee.



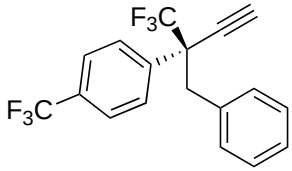
7fa

(*R*)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-chlorobenzene (7fa). A colorless oil (22.8 mg, 0.074 mmol, 74% yield based on the amount of **3f**).
[α]$_D^{20}$: –54.2 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.21–7.11 (m, 3H), 6.99 (dd, *J* = 8.0, 1.6 Hz, 2H), 3.47 (d, *J* = 13.6 Hz, 1H), 3.42 (d, *J* = 13.6 Hz, 1H), 2.68 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 134.7, 134.0, 131.9, 130.7, 129.9, 128.5, 127.7, 127.1, 125.5 (q, $^1J_{CF}$ = 282.7 Hz), 78.6 (q, $^3J_{CF}$ = 1.9 Hz), 78.4, 52.6 (q, $^2J_{CF}$ = 26.8 Hz), 40.6.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –72.0 (s).
HRMS (FAB+): Calcd. for $C_{17}H_{12}ClF_3$ $[M]^+$: 308.0580. Found: 308.0590.
The enantiomeric excess of **7fa** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 15.2 min (major) and 16.6 min (minor), 90% ee.



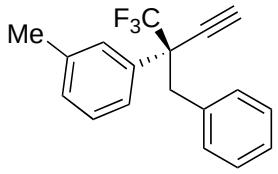
7ga

(*R*)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-bromobenzene (7ga). A white solid (24.7 mg, 0.070 mmol, 70% yield based on the amount of **3g**).
m.p.: 49.2–59.3 °C
[α]$_D^{20}$: –20.3 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53–7.46 (m, 4H), 7.20–7.11 (m, 3H), 6.98 (dd, *J* = 8.0, 1.6 Hz, 2H), 3.46 (d, *J* = 13.2 Hz, 1H), 3.41 (d, *J* = 13.2 Hz, 1H), 2.67 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 133.9, 132.5, 131.4, 130.7, 130.3, 127.7, 127.2, 125.4 (q, $^1J_{CF}$ = 283.0 Hz), 123.0, 78.5 (q, $^3J_{CF}$ = 1.9 Hz), 78.4, 52.7 (q, $^2J_{CF}$ = 26.8 Hz), 40.6.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.7 (s).
HRMS (FAB+): Calcd. for $C_{17}H_{12}BrF_3$ $[M]^+$: 352.0074. Found: 352.0083.
The enantiomeric excess of **7ga** was determined by HPLC analysis; DAICEL Chiralpak OD, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 8.8 min (major) and 9.8 min (minor), 92% ee.



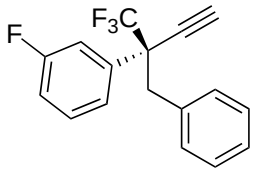
7ha

(*R*)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-(trifluoromethyl)benzene (7ha). A colorless oil (28.4 mg, 0.083 mmol, 83% yield based on the amount of **3h**).
[α]$_D^{20}$: –50.2 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.21–7.10 (m, 3H), 6.97 (dd, *J* = 7.6, 1.4 Hz, 2H), 3.50 (d, *J* = 13.6 Hz, 1H), 3.46 (d, *J* = 13.6 Hz, 1H), 2.72 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 137.5, 133.7, 130.7, 129.0 128.4 (q, $^2J_{CF}$ = 12.8 Hz), 127.8, 127.3, 125.4 (q, $^1J_{CF}$ = 283.0 Hz), 125.2 (q, $^3J_{CF}$ = 3.5 Hz), 123.8 (q, $^1J_{CF}$ = 270.9 Hz), 78.8, 78.3 (q, $^3J_{CF}$ = 1.9 Hz), 53.0 (q, $^2J_{CF}$ = 26.8 Hz), 40.7.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –64.3 (s), –73.3 (s).
HRMS (FAB+): Calcd. for $C_{18}H_{12}F_6$ $[M]^+$: 342.0843. Found: 342.0847.
The enantiomeric excess of **7ha** was determined by HPLC analysis; DAICEL Chiralpak OD, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 9.7 min (major) and 10.7 min (minor), 93% ee.



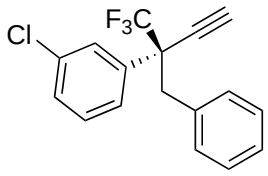
7ia

(*R*)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-3-methylbenzene (7ia). A colorless oil (19.3 mg, 0.067 mmol, 67% yield based on the amount of **3i**).
[α]$_D^{20}$: –49.4 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47–7.44 (br, 2H), 7.25 (pseudo t, *J* = 8.0 Hz, 1H), 7.21–7.10 (m, 4H), 6.99 (dd, *J* = 8.0, 1.6 Hz, 2H), 3.51 (d, *J* = 13.6 Hz, 1H), 3.40 (d, *J* = 13.6 Hz, 1H), 2.64 (s, 1H), 2.36 (s, 3H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 137.9, 134.5, 133.2, 130.8, 129.3, 129.2, 128.1, 127.5, 126.9, 125.7 (q, $^1J_{CF}$ = 282.7 Hz), 125.4, 79.1 (q, $^3J_{CF}$ = 2.0 Hz), 78.0, 52.9 (q, $^2J_{CF}$ = 26.2 Hz), 40.7, 21.6.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.4 (s).
HRMS (FAB+) Calcd. for $C_{18}H_{16}F_3$ $[M+H]^+$: 289.1204. Found: 289.1203.
The enantiomeric excess of **7ia** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 13.9 min (major) and 15.4 min (minor), 90% ee.



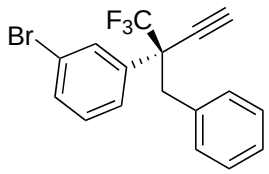
7ja

(*R*)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-3-fluorobenzene (7ja). A colorless oil (21.0 mg, 0.072 mmol, 72% yield based on the amount of **3j**).
[α]$_D^{20}$: –18.5 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (br d, *J* = 8.0 Hz, 1H), 7.40–7.30 (m, 2H), 7.20–7.10 (m, 3H), 7.05 (pseudo t of dd, *J* = 8.3, 2.8, 0.9 Hz, 1H), 6.98 (d, *J* = 8.0, 1.6 Hz, 2H), 3.47 (d, *J* = 13.4 Hz, 1H, 3.42 (d, *J* = 13.4 Hz, 1H), 2.68 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 162.5 (d, $^1J_{CF}$ = 245.3 Hz), 136.0 (d, $^3J_{CF}$ = 7.7 Hz), 133.9, 130.7, 129.7 (d, $^3J_{CF}$ = 7.7 Hz), 127.7, 127.2, 125.0 (q, $^1J_{CF}$ = 282.7 Hz), 124.1, 116.1 (d, $^2J_{CF}$ = 24.0 Hz), 115.6 (d, $^2J_{CF}$ = 21.1 Hz), 78.4, 77.2, 52.9 (q, $^2J_{CF}$ = 27.1 Hz), 40.8.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.4 (s), –113.8 (s).
HRMS (FAB+): Calcd. for $C_{17}H_{12}F_4$ $[M]^+$: 292.0875. Found: 292.0878.
The enantiomeric excess of **7ja** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 11.9 min (major) and 16.0 min (minor), 90% ee.



7ka

(*R*)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-3-chlorobenzene (7ka). A colorless oil (20.1 mg, 0.065 mmol, 65% yield based on the amount of **3k**).
[α]$_D^{20}$: –50.0 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (br, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.33 (dt, *J* = 8.0, 1.8 Hz, 1H), 7.29 (pseudo t, *J* = 7.4 Hz, 1H), 7.21–7.11 (m, 3H), 6.99 (dd, *J* = 7.6, 1.2 Hz, 1H), 3.47 (d, *J* = 13.6 Hz, 1H), 3.42 (d, *J* = 13.6 Hz, 1H), 2.69 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 135.5, 134.3, 133.9, 130.7, 129.4, 128.9, 128.8, 127.7, 127.2, 126.6, 125.4 (q, $^1J_{CF}$ = 283.0 Hz,), 78.6, 78.4 (q, $^3J_{CF}$ = 2.0 Hz), 52.9 (q, $^2J_{CF}$ = 24.8 Hz), 40.7.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.4 (s).
HRMS (FAB+): Calcd. for $C_{17}H_{12}ClF_3$ $[M]^+$: 308.0580. Found: 308.0576.
The enantiomeric excess of **7ka** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 27.9 min (major) and 35.2 min (minor), 95% ee.



7la

(*R*)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-3-bromobenzene (7la). A colorless oil (24.7 mg, 0.070 mmol, 70% yield based on the amount of **3l**).

[α]$_D^{20}$: –45.9 (c = 0.5 in $CHCl_3$).

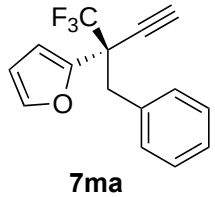
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (br, 1H), 7.58(d of pseudo quint, *J* = 8.0, 0.9 Hz, 1H), 7.49 (ddd, *J* = 8.0, 1.8, 0.9 Hz, 1H,), 7.23 (t, *J* = 8.0 Hz, 1H), 7.19–7.11 (m, 3H), 6.99 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.46 (d, *J* = 13.4 Hz, 1H), 3.41 (d, *J* = 13.4 Hz, 1H), 2.69 (s, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 135.7, 133.8, 131.8, 131.7, 130.7, 129.7, 127.7, 127.2, 127.1, 125.4 (q, $^1J_{CF}$ = 283.0 Hz,), 122.5, 78.7, 78.3 (q, $^3J_{CF}$ = 1.9 Hz), 52.8 (q, $^2J_{CF}$ = 26.5 Hz), 40.7.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.4 (s).

HRMS (FAB+) Calcd. for $C_{17}H_{12}BrF_3$ $[M]^+$: 352.0074. Found: 352.0070.

The enantiomeric excess of **7la** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 14.1 min (minor) and 18.4 min (major), 90% ee.



7ma

(*R*)-2-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)furan (7ma). A colorless oil (20.1 mg, 0.076 mmol, 76% yield based on the amount of **3m**).

[α]$_D^{20}$: –11.0 (c = 0.5 in $CHCl_3$).

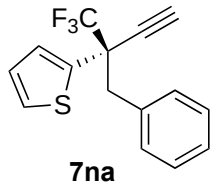
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (dd, *J* = 2.0, 0.8 Hz, 1H), 7.21–7.15 (m, 3H,), 6.97 (dd, *J* = 7.6, 1.8 Hz, 2H), 6.40 (dd, *J* = 3.6, 0.8, Hz, 1H), 6.32 (dd, *J* = 3.6 Hz, 2.0 Hz, 1H), 3.61 (d, *J* = 12.8 Hz, 1H), 3.22 (d, *J* = 12.8 Hz, 1H), 2.47 (s, 1H).

^{13}C{^{1}H} NMR (CD_3CN, 100 MHz): δ 147.2, 144.4, 134.6, 130.9, 128.2, 127.7, 125.2 (q, $^1J_{CF}$ = 282.7 Hz), 112.8, 111.2, 77.5, 76.9 (q, $^3J_{CF}$ = 1.9 Hz), 49.7 (q, $^2J_{CF}$ = 28.1 Hz), 38.7.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –74.7 (s).

HRMS (FAB+): Calcd. for $C_{15}H_{11}F_3O$ $[M]^+$: 264.0762. Found: 264.0758.

The enantiomeric excess of **7ma** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 13.2 min (minor) and 16.0 min (major), 96% ee.



7na

(*S*)-2-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)thiophene (7na). A colorless oil (18.2 mg, 0.065 mmol, 65% yield based on the amount of **3n**).

[α]$_D^{20}$: –51.6 (c = 0.5 in $CHCl_3$).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.22–7.14 (m, 4H,), 7.04 (dd, *J* = 8.0 1.6 Hz, 1H), 6.98 (dd, *J* = 4.9, 3.6 Hz, 1H), 3.41 (d, *J* = 12.8 Hz, 1H), 3.36 (d, *J* = 12.8 Hz, 1H), 2.60 (s, 1H).

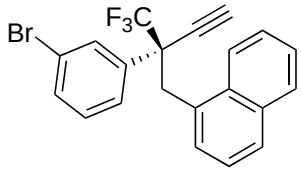
^{13}C{^{1}H} NMR (CD_3CN, 100 MHz): δ 137.3, 134.0, 130.6, 128.3, 127.6, 127.2, 126.8, 126.3, 125.1 (q, $^1J_{CF}$ = 282.7 Hz), 78.5, 76.8, 50.5 (q, $^2J_{CF}$ = 28.1 Hz), 42.6.

^{13}C NMR spectrum of this compound was measured in acetonitrile-d_6 because some peaks of this compound overlapped with those of $CDCl_3$.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –75.1 (s).

HRMS (FAB+): Calcd. for $C_{15}H_{11}F_3S$ $[M]^+$: 280.0534. Found: 280.0527.

The enantiomeric excess of **7na** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 18.4 min (minor) and 23.6 min (major), 90% ee.



7lr

(*R*)-1-(2-(3-Bromophenyl)-2-(trifluoromethyl)but-3-yn-1-yl)naphthalene (7lr). A white solid (24.6 mg, 0.061 mmol, 61% yield based on the amount of **3l**).

m.p.: 95.2–96.4 °C

[α]$_D^{20}$: +36.9 (c = 0.5 in $CHCl_3$).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08–8.02 (m, 1H), 7.85–7.79 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.51–7.41 (m, 3H), 7.22 (pseudo t, *J* = 7.0 Hz, 1H), 7.20 (pseudo t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 4.14 (d, *J* = 14.4 Hz, 1H), 3.85 (d, *J* = 14.4 Hz, 1H), 2.45 (s, 1H).

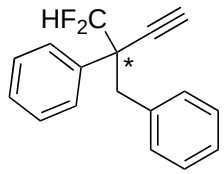
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 136.3, 133.6, 132.9, 131.8, 131.6, 130.0, 129.8, 128.6, 128.4, 127.9, 126.9, 125.6 (q, $^1J_{CF}$ = 283.0 Hz), 125.5, 125.4, 124.7, 124.1, 122.6, 78.7, 78.5 (q, $^3J_{CF}$ = 1.9 Hz), 52.3 (q, $^2J_{CF}$ = 26.8 Hz), 36.2.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –71.6 (s).

HRMS (FAB+): Calcd. for $C_{21}H_{14}BrF_3$ $[M]^+$: 402.0231. Found: 402.0240.

The enantiomeric excess of **7lr** was determined by HPLC analysis; DAICEL Chiralpak OD, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 13.6 min (minor) and 18.9 min (major), 91% ee.

Colorless needle crystals suitable for X-ray analysis were obtained by recrystallization from Et_2O, after additional purification of (*R*)-isomer by HPLC.



9

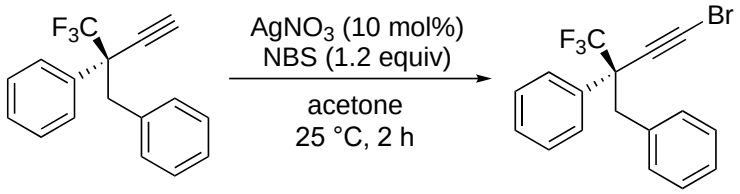
(*R*)-(2-(Difluoromethyl)but-3-yne-1,2-diyl)dibenzene (9). A colorless oil (19.2 mg, 0.075 mmol, 75% yield based on the amount of **8**).
[α]$_D^{20}$: –32.7 (c = 0.5 in $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.40–7.31 (m, 3H), 7.22–7.15 (m, 3H), 7.07 (dd, *J* = 7.2, 2.4 Hz, 2H), 5.95 (t, *J* = 56.2 Hz, 1H), 3.39 (d, *J* = 13.2 Hz, 1H), 3.31 (dd, *J* = 13.2, 0.8 Hz, 1H), 2.62 (s, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 135.2, 134.9, 130.7, 128.3, 128.2, 128.1, 127.7, 126.9, 116.5 (t, $^1J_{CF}$ = 250.1 Hz), 80.8 (dd, $^3J_{CF}$ = 5.7, 3.8 Hz), 77.5, 51.1 (t, $^2J_{CF}$ = 20.1 Hz), 41.2 (t, $^3J_{CF}$ = 2.9 Hz).
^{19}F NMR ($CDCl_3$, 376 MHz): δ –123.3 (dd, $^2J_{FF}$ = 268 Hz, $^2J_{HF}$ = 54 Hz), -126.5 (dd, dd, $^2J_{FF}$ = 268 Hz, $^2J_{HF}$ = 54 Hz).
HRMS (FAB+): Calcd. for $C_{17}H_{15}F_2$ $[M+H]^+$: 257.1142. Found: 257.1137.
The enantiomeric excess of **9** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 19.4 min (major) and 30.4 min (minor), 63% ee.

S5. Large-Scale Preparation of 7aa

In an oven dried 100 mL Schlenk flask were placed **[Ru]-2** (63.0 mg, 0.050 mmol) and NH_4BF_4 (11.0 mg, 0.10 mmol) under N_2. Anhydrous $ClCH_2CCH_2Cl$ (20 mL) was added, and then the mixture was magnetically stirred at room temperature for 60 min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (200 mg. 1.0 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (412.1 mg, 1.2 mmol), *fac*-[Ir(ppy)$_3$] (6.4 mg, 0.01 mmol) were added under N_2 at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 48 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography (SiO_2) with *n*-hexane as an eluent to afford (*R*)-(2-(trifluoromethyl)but-3-yne-1,2-diyl)dibenzene (**7aa**) as a colorless oil (205.5 mg, 0.75 mmol, 75% yield based on the amount of **3a**) with 93% ee.

S6. Preparation of (*S*)-(4-bromo-2-(trifluoromethyl)but-3-yne-1,2-diyl)dibenzene (10)

Scheme 4.



7aa
93% ee

10
95%, 93% ee

In a 20 mL Schlenk flask were placed **(*R*)-7aa** (27.4 mg. 0.10 mmol, 93% ee), *N*-bromosuccinimide (NBS) (21.4 mg, 0.12 mmol) and $AgNO_3$ (1.7 mg, 0.010 mmol) under N_2, where acetone (5.0 mL) was added at room temperature. And the mixture was stirred at room temperature for 2 h. The volatiles were then removed *in vacuo*, and the residue was purified by column chromatography (SiO_2) with *n*-hexane as an eluent to afford (*S*)-(4-bromo-2-(trifluoromethyl)but-3-yne-1,2-diyl)dibenzene (**10**) as a colorless oil (33.6 mg, 0.95 mmol, 95% yield based on the amount of **7aa**).

$[\alpha]_D^{20}$: –41.3 (c = 0.5 in $CHCl_3$).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60–7.56 (m, 2H), 7.38–7.33 (m, 3H), 7.19–7.11 (m, 3H), 6.95 (dd, *J* = 7.8, 1.4 Hz, 2H), 3.49 (d, *J* = 13.4 Hz, 1H), 3.42 (d, *J* = 13.4 Hz, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 134.3, 133.5, 130.7, 128.6, 128.4, 128.3, 127.6, 127.0, 125.5 (q, $^1J_{CF}$ = 283.0 Hz), 75.5, 54.2 (q, $^2J_{CF}$ = 26.5 Hz), 49.6, 41.0.

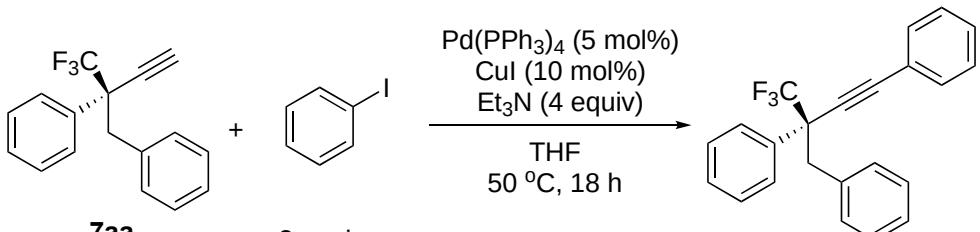
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.2 (s).

HRMS (FAB+): Calcd. for $C_{17}H_{12}BrF_3$ $[M]^+$: 352.0074. Found: 352.0080.

The enantiomeric excess of **10** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 100/0, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 16.0 min (major) and 19.4 min (minor), 93% ee.

S7. Preparation of (*S*)-(2-(trifluoromethyl)but-3-yne-1,2,4-triyl)tribenzene (11)

Scheme 5.



7aa
93% ee

2 equiv

11
93%, 93% ee

In a 20 mL Schlenk flask were placed **(*R*)-7aa** (27.4 mg. 0.10 mmol, 93% ee), iodobenzene (40.8 mg, 0.20 mmol), Pd(PPh3)4 (5.8 mg, 0.0050 mmol), CuI (1.9 mg, 0.010 mmol), and Et_3N (56 μL, 0.40 mmol) under N_2, where THF (2.0 mL) was added at room temperature. And the mixture was stirred at 50 °C for 18 h. The volatiles

were then removed *in vacuo*, and the residue was purified by column chromatography (SiO_2) with *n*-hexane as an eluent to afford (*S*)-(2-(trifluoromethyl)but-3-yne-1,2,4-triyl)tribenzene (**11**) as a white solid. (32.6 mg, 0.93 mmol, 93% yield based on the amount of **7aa**).

m.p.= 57.0-58.5 °C.

$[\alpha]_D^{20}$: –53.5 (c = 0.5 in $CHCl_3$).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (br d, *J* = 8.0 Hz,2H), 7.45 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.40–7.33 (m, 6H), 7.19–7.10 (m, 3H), 7.04 (dd, *J* = 7.6, 1.6 Hz, 2H), 3.58 (d, *J* = 13.2 Hz, 1H), 3.50 (d, *J* = 13.2 Hz, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 134.8, 134.3, 131.7, 130.8, 128.7, 128.6, 128.4, 128.3, 128.3, 127.5, 126.9, 125.9 (q, $^1J_{CF}$ = 283.3 Hz), 122.2, 89.6, 84.5, 53.6 (q, $^2J_{CF}$ = 26.5 Hz), 41.2.

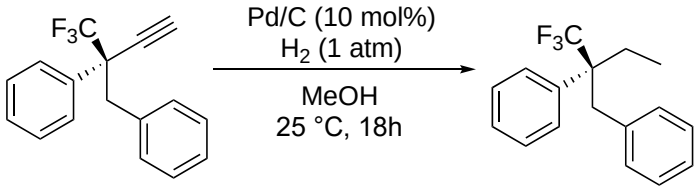
^{19}F NMR ($CDCl_3$, 376 MHz): δ –73.2.

HRMS (FAB+): Calcd. for $C_{23}H_{17}F_3$ $[M]^+$: 350.1282. Found: 350.1289.

The enantiomeric excess of **11** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 8.0 min (major) and 9.5 min (minor), 93% ee.

S8. Preparation of (*S*)-(2-(trifluoromethyl)butane-1,2-diyl)dibenzene (12).

Scheme 6.



7aa
93% ee

12
96%, 92% ee

In a 20 mL Schlenk flask were placed **(*R*)-7aa** (27.4 mg. 0.10 mmol, 93% ee), and Pd/C (10.6 mg, 0.01 mmol, Palladium 10% on Carbon) under N_2, where MeOH (4.0 mL) was added at room temperature. After substitution of N_2 atmosphere to H_2 atmosphere by a hydrogen balloon, the mixture was stirred at room temperature for 18 h. The volatiles were then removed *in vacuo*, and the residue was purified by column chromatography (SiO_2) with *n*-hexane as an eluent to afford (*S*)-(2-(trifluoromethyl)butane-1,2-diyl)dibenzene (**12**) as a colorless oil. (26.7 mg, 0.96 mmol, 96% yield based on the amount of **7aa**).

$[\alpha]_D^{20}$: –50.3 (c = 0.5 in $CHCl_3$).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41–7.29 (m, 5H), 7.20–7.09 (m, 3H), 6.80 (dd, *J* = 7.6, 1.6 Hz, 2H), 3.22 (s, 2H), 2.01 (qq, *J* = 7.5, 0.7, Hz, 2H), 0.96 (tq, *J* = 7.5, 1.4 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 137.1, 135.7, 130.7, 128.6 (q, $^1J_{C\text{-}F}$ = 284.6 Hz), 128.2 (overlapping), 127.7, 127.4, 126.6, 52.6 (q, $^2J_{CF}$ = 21.7 Hz), 42.0, 25.0, 8.9.

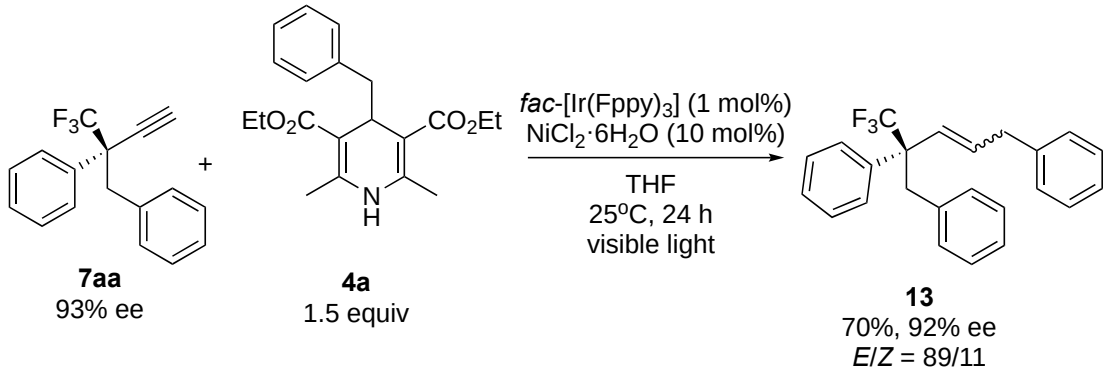
^{19}F NMR ($CDCl_3$, 376 MHz): δ –68.4.

HRMS (FAB+): Calcd. for $C_{17}H_{17}F_3$ $[M]^+$: 278.1282. Found: 278.1293.

The enantiomeric excess of **12** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 11.5 min (minor) and 36.1 min (major), 92% ee.

S9. Preparation of (*R*)-(2-(trifluoromethyl)pent-3-ene-1,2,5-triyl)tribenzene (13)

Scheme 7.



In a 20 mL Schlenk flask were placed **(*R*)-7aa** (27.4 mg. 0.10 mmol, 93% ee), **4a** (51.5 mg, 0.375mmol), *fac*-[Ir(Fppy)$_3$] (0.8 mg, 0.0011 mmol), and $NiCl_2{\cdot}6H_2O$ (2.4 mg, 0.020 mmol) under N_2, where THF (2.0 mL) was added at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 24 h. *E*/*Z* ratio of (*R*)-(2-(trifluoromethyl)pent-3-ene-1,2,5-triyl)tribenzene in the crude mixture was determined to be 55/45 by quantitative measurement of GC-MS. The volatiles were then removed *in vacuo*, and the residue was purified by column chromatography (SiO_2) with *n*-hexane as an eluent to afford a mixture of (*R*,*E*)-(2-(trifluoromethyl)pent-3-ene-1,2,5-triyl)tribenzene ((*E*)-**13**) and (*R*,*Z*)-(2-(trifluoromethyl)pent-3-ene-1,2,5-triyl)tribenzene ((*Z*)-**13**) as a colorless oil (*E*/*Z* = 89/11, 25.6 mg, 0.70 mmol, 70% yield based on the amount of **7aa**).

[α]$_D^{20}$: –26.5 (c = 0.5 in $CHCl_3$).

^{1}H NMR ($CDCl_3$, 400 MHz)*

((*E*)-**13**): δ 7.48–7.44 (m, 2H), 7.36–7.27 (m, 5H), 7.22 (t of pseudo t, *J* = 7.2, 1.7Hz, 1H), 7.18–7.07(m, 5H), 6.86 (dd, *J* = 8.0, 1.6 Hz, 2H), 5.93 (dtq, *J* = 16.0, 6.9, 1.6 Hz, 1H), 5.65 (dq, *J* = 16.0, 1.3 Hz,1H), 3.50 (d, *J* = 14.2 Hz, 1H), 3.47 (d, *J* = 6.9 Hz, 2H), 3.37 (d, *J* = 14.2 Hz, 1H).

((*Z*)-**13** (^{1}H NMR resonances due to 11H of aromatic CH, 1H of CH=C*H*CH_2, and 3H of CH_2 overlapping with those of (*E*)-**13** (δ 7.48–7.06, 5.97–5.88, and 3.53–3.49, respectively)): 6.95 (dd, *J* = 7.6, 1.6Hz, 2H), 6.90 (dd, *J* = 8.2, 1.4 Hz, 2H), 5.83 (dq, *J* = 12.0, 1.8 Hz, 1H), (m, 3H, 3H of two CH_2 resonances overlapping with those of (*E*)-**13**), 3.33 (d, *J* = 13.6 Hz, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)*

((*E*)-**13**): δ 139.6, 137.4, 135.6, 133.3, 131.0, 129.2, 129.1, 128.6, 128.5, 128.0, 127.7, 127.6, 127.3 (q, $^1J_{CF}$ = 283.3 Hz), 126.5, 126.2, 55.2 (q, $^2J_{CF}$ = 23.0 Hz), 40.7, 39.5.

((*Z*)-**13**: δ 139.7, 137.9, 136.2, 136.0, 131.3, 129.3, 128.8, 128.3, 128.1, 126.8, 126.6, 126.6 (q, $^{1}J_{CF}$ = 277.9 Hz), 126.0, 55.1 (q, $^{2}J_{CF}$ = 23.0 Hz), 42.9, 35.6.
^{19}F NMR ($CDCl_3$, 376 MHz): δ –69.9.
HRMS (FAB+) Calcd. for $C_{24}H_{21}F_3$ $[M]^+$: 366.1595. Found: 366.1605.
The enantiomeric excess of **13** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: ((*E*)-**13**): 13.8 min (minor) and 15.8 min (major), 92% ee; ((*Z*)-**13**): 11.9 min (minor) and 18.3 min (major), 92% ee.

S10. Stoichiometric reaction of 14 with 4a

In an oven dried 20 mL Schlenk flask were placed **14** (138 mg, 0.10 mmol) and under N_2. Anhydrous $ClCH_2CCH_2Cl$ (2.0 mL) was added and then, 1,1,1-trifluoro-2-(*p*-tolyl)but-3-yn-2-ol (**3b**) (21.4 mg, 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), *fac*-$[Ir(ppy)_3]$ (0.7 mg, 0.0011 mmol) were added under N_2 at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 48 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography (SiO_2) with *n*-hexane as an eluent to afford (*R*)-(2-(trifluoromethyl)but-3-yne-1,2-diyl)dibenzene (**7aa**) as a colorless oil (18.1 mg, 0.066 mmol, 66% yield based on the amount of **3a**) with 88% ee (Fig. 4a).

S11. Catalytic reaction of 3a with 4a by using 14 as a catalyst

In an oven dried 20 mL Schlenk flask were placed **14** (6.9 mg, 0.0050 mmol) and under N_2. Anhydrous $ClCH_2CCH_2Cl$ (2.0 mL) was added, and then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg. 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), *fac*-$[Ir(ppy)_3]$ (0.7 mg, 0.0011 mmol) were added under N_2 at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 48 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography (SiO_2) with *n*-hexane as an eluent to afford (*R*)-(2-(trifluoromethyl)but-3-yne-1,2-diyl)dibenzene (**7aa**) as a colorless oil (23.3 mg, 0.085 mmol, 85% yield based on the amount of **3a**) with 85% ee (Fig. 4b).

S12. Reactions in the presence of TEMPO

In an oven dried 20 mL Schlenk flask were placed **[Ru]-2** (6.3 mg, 0.0050 mmol) and NH_4BF_4 (1.1 mg, 0.010 mmol) under N_2. Anhydrous $ClCH_2CCH_2Cl$ (2.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 30

min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg. 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), *fac*-[Ir(ppy)$_3$] (0.7 mg, 0.0011 mmol) were added under N_2 at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 48 h. The volatiles were removed in vacuo, and the crude yield of 1-(benzyloxy)-2,2,6,6-tetramethylpiperidine (**15**)[S20] (34% NMR yield) was determined by ^{1}H NMR in $CDCl_3$, where 1,1,2,2-tetrachloroethane (16.8 mg, 0.100 mmol) was added as an internal standard (Fig. 4c).

S13. Deuterium labeling reaction

In an oven dried 20 mL Schlenk flask were placed **[Ru]-2** (6.3 mg, 0.0050 mmol) and NH_4BF_4 (1.1 mg, 0.010 mmol) under N_2. Anhydrous $ClCH_2CCH_2Cl$ (2.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 30 min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg. 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1-deuterium-4-hydropyridine-3,5-dicarboxylate (**4a**-d_1) (41.2 mg, 0.12 mmol), *fac*-[Ir(ppy)$_3$] (0.7 mg, 0.0011 mmol) were added under N_2 at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 48 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography (SiO_2) with *n*-hexane as an eluent to afford (*R*)-(2-(trifluoromethyl)but-3-yne-1,2-diyl)dibenzene (**7aa**) as a colorless oil (21.1 mg, 0.077 mmol, 77% yield based on the amount of **3a**) with 93% ee. The ratio of H/D is determined by ^{1}H NMR to be 70/30 at δ 2.66 (Fig. 4d).

S14. Stern–Volmer analysis

Luminescence quenching experiments for the THF solution of *fac*-[Ir(ppy)$_3$] (2.0 μmol/L, prepared by stepwise dilutions of *fac*-[Ir(ppy)$_3$] (1.3 mg, 2.0 μmol) with $ClCH_2CH_2Cl$) with **3a**, **4a** or **16** in selected concentrations were performed on a Shimadzu RF-5300PC spectrophotometer, where the solutions containing *fac*-[Ir(ppy)$_3$] and **3a**, **4a** or **16** were excited at λ_{max} = 440 nm, and emissions were measured at λ = 494 nm.

From the slopes (100.5 for **3a**, 208.3 for **4a** and 32.6 for **16**,) obtained by the plot and the excited-state lifetime of *fac*-[Ir(ppy)$_3$] (τ = 1.9 μs),[S21] the rate constants were calculated to be at, $k_{\mathbf{3a}} = (5.3 \pm 0.2) \times 10^7$ M^{-1} s^{-1} (**3a**), $k_{\mathbf{4a}} = (1.10 \pm 0.05) \times 10^8$ M^{-1} s^{-1} (**4a**) and $k_{\mathbf{16}} = (1.72 \pm 0.07) \times 10^7$ M^{-1} s^{-1} (**16**) respectively (Fig. 4e).

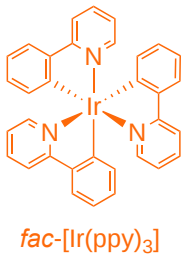
S15. Light on/off experiments

In an oven dried 20 mL Schlenk flask were placed **[Ru]-2** (6.3 mg, 0.0050 mmol) and NH_4BF_4 (1.1 mg, 0.010 mmol) under N_2. Anhydrous $ClCH_2CCH_2Cl$ (2.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 30 min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg. 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), *fac*-[Ir(ppy)$_3$] (0.7 mg, 0.0011 mmol) were added under N_2 at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C. The reaction was conducted for 32 h under alternating periods of (1) irradiation from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source, and (2) darkness with the reaction vessel wrapped with aluminum foil, where yields of **7aa** were determined every 4 hours by quantitative measurements of gas chromatography–mass spectroscopy (GC-MS) recorded on a Shimadzu GCMS-QP2010 PLUS instrument, where *n*-octane was added as an internal standard (Fig. 4f).

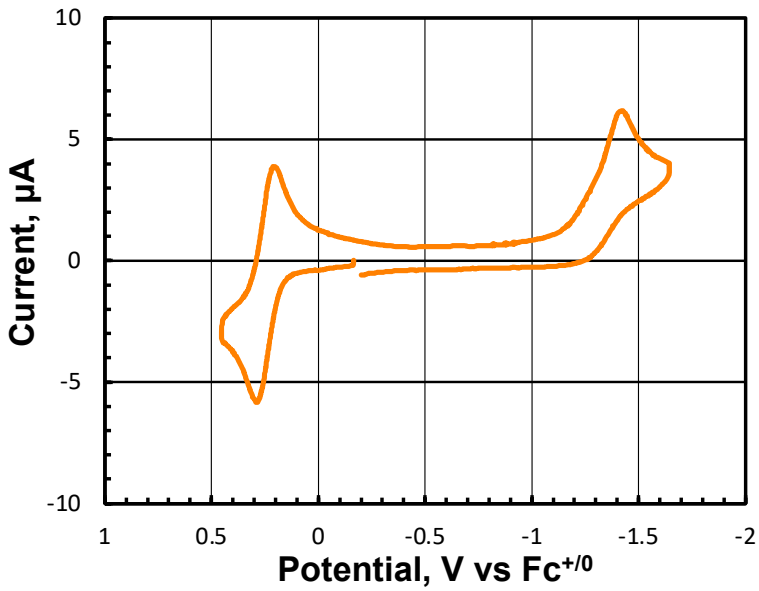
S16. Cyclic voltammetric studies

Cyclic voltammograms were recorded on an ALS/Chi model 610C electrochemical analyzer in $ClCH_2CH_2Cl$ containing 1 mM of sample and 0.1 M of $^nBu_4NPF_6$ as a supporting electrolyte using glassy carbon working electrode and platinum wire counter electrode at a scan rate of 0.1 V/s at room temperature. All potentials were measured against $Ag/AgNO_3$ reference electrode (0.01 M $AgNO_3$, 0.1 M $^nNBu_4ClO_4$, MeCN) and converted to the values vs $FeCp_2^{+/0}$ (Cp = η^5-C_5H_5). The cyclic voltammograms of *fac*-[Ir(ppy)$_3$], **4a**, and **3a** in $ClCH_2CH_2Cl$ are shown in Fig. S1.

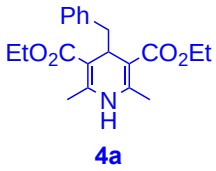
a)



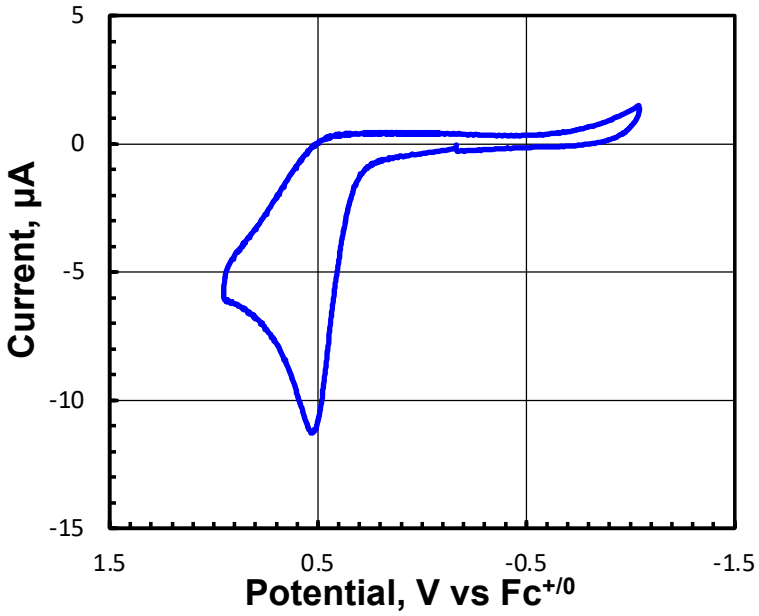
fac-[Ir(ppy)$_3$]



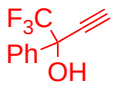
b)



4a



c)



3a

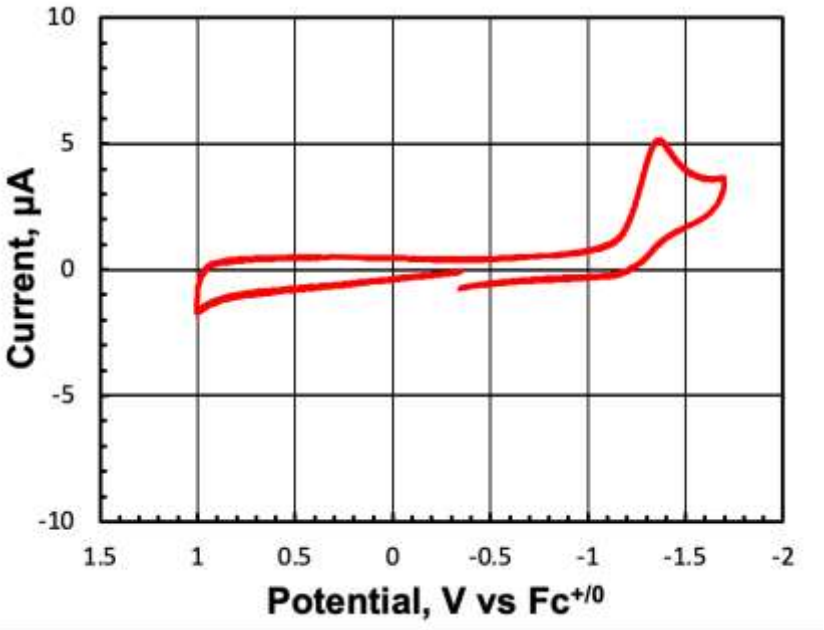


Fig. S1. | Cyclic voltammetric studies. (a) Cyclic voltammogram of *fac*-[Ir(ppy)$_3$] in $ClCH_2CH_2Cl$. $E_{1/2}(Ir/Ir^-)$ = –1.60 V vs $FeCp_2^{+/0}$, $E_{pa}(Ir/Ir^+)$ = +0.25 V vs $FeCp_2^{+/0}$. Therefore, $E_{pc}(Ir^*/Ir^-)$ = +0.90 V vs $FeCp_2^{+/0}$, $E_{1/2}(Ir^{*/+})$ = –2.25 V vs $FeCp_2^{+/0}$, based on the emission energy of *fac*-[Ir(ppy)$_3$] at 2.50 eV.[S22] (b) Cyclic voltammogram of **4a** in THF. E_{pa}(**4a**/**4a**$^{+\bullet}$) = +0.53 V vs $FeCp_2^{+/0}$. (c) Cyclic voltammogram of **3a** in $ClCH_2CH_2Cl$. E_{pc}(**3a**/**3a**$^{-\bullet}$) = –1.36 V vs $FeCp_2^{+/0}$.

S17. Time profile experiment

In an oven dried 20 mL Schlenk flask were placed **[Ru]-2** (6.3 mg, 0.0050 mmol) and NH_4BF_4 (1.1 mg, 0.010 mmol) under N_2. Anhydrous $ClCH_2CCH_2Cl$ (2.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 30 min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg. 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), *fac*-[Ir(ppy)$_3$] (0.7 mg, 0.0011 mmol) were added under N_2 at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source. Yields of **7aa** at selected times (2, 4, 8, 12, 24 and 48 h) were determined by quantitative measurements of gas chromatography–mass spectroscopy (GC-MS) recorded on a Shimadzu GCMS-QP2010 PLUS instrument, where *n*-octane was added as an internal standard (Fig. S2). The reaction rate was calculated as $k_{\mathbf{7aa}} = (2.33 \pm 0.04) \times 10^{-7}\ M^{-1}\ s^{-1}$.

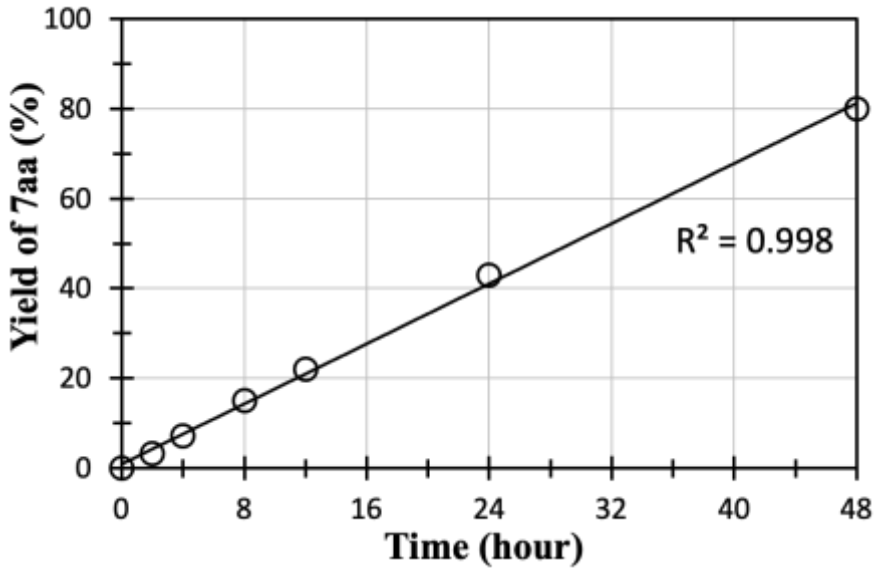


Fig. S2. | Time profile experiment.

S18. Determination of quantum yields

In an oven dried 20 mL Schlenk flask were placed **[Ru]-2** (6.3 mg, 0.0050 mmol) and NH_4BF_4 (1.1 mg, 0.010 mmol) under N_2. Anhydrous $ClCH_2CCH_2Cl$ (2.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 30 min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg. 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), *fac*-[Ir(ppy)$_3$] (0.7 mg, 0.0011 mmol) were added under N_2 at room temperature. The reaction flask was illuminated from the side with an Ushio SX-U1251HQ ultrahigh pressure 250 W Hg lamp equipped with a 440-nm band pass filter (Kenko B440) at a distance of approximately 2 cm from the light source for 6 h. The volatiles were

removed in vacuo, and the crude yield of **7aa** (0.00920 mmol, 9.2% NMR yield based on the amount of **3a** was determined by ^{1}H NMR in $CDCl_3$, where 1,1,2,2-tetrachloroethane (16.8 mg, 0.100 mmol) was added as an internal standard. Independently, the yields of **7aa** were determined by terminating the reactions at 2 and 4 h, which clarified a zero-order reaction rate at 4.26×10^{-8} mol s^{-1}. The irradiated light intensity to a 2.5 mL solution in 50-mL Schlenk was estimated to be 8.50×10^{-7} E s^{-1} at 440 nm by using $K_3[Fe(C_2O_4)_3]$ as a chemical actinometer.[S23] Thus, the quantum yield of the photoredox- and ruthenium-catalyzed reaction of **3a** with **4a** to afford propargylic alkylated product **7aa** is given as $\Phi = 0.0502 \pm 0.0003$ (Fig. S3).

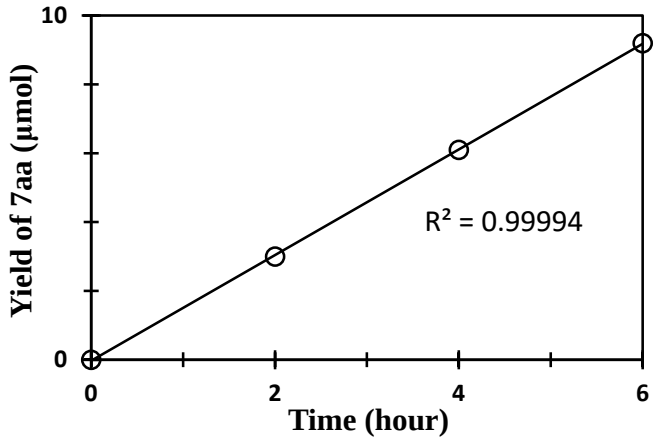


Fig. S3. | Quantum yield determination.

S19. X-ray crystallographic study of (*R*)-1-(2-(3-bromophenyl)-1,1,1-trifluorobut-3-yn-2-yl)naphthalene (7lr)

Diffraction data for a crystal of **7lr** were collected for the 2θ range of 4.5° to 62.2° at –180 °C on a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector and VariMax optics using multi-layer mirror monochromated Mo-Kα (λ = 0.71073 Å) radiation, and VariMax optics. Intensity data were corrected for Lorentz and polarization effect and for empirical absorptions (CrysAlisPro),[S24] while structure solutions and refinements were carried out by using CrystalStructure package.[S25] Positions of non-hydrogen atoms were determined by direct methods (SHELXT Version 2014/5),[S26] and subsequent Fourier syntheses (SHELXL Version 2016/6),[S27] and were refined on F_o^2 with all the unique reflections by full-matrix least squares with anisotropic thermal parameters. All the hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Anomalous dispersion effects were included in F_c,[S28] and mass attenuation coefficients, values for $\Delta f'$ and $\Delta f''$, and neutral atom scattering factors were taken from references.[S29-S31] The absolute configuration of **7lr** with a chiral center at the C(1) atom was determined to be (*R*), with the Flack parameter refined to be –0.005(5). Details of the crystal and data collection parameters of (*R*)-**7lr** are summarized in Table S1. An ORTEP drawing of (*R*)-**7lr** is shown in Fig. S4.

Table S1. Crystallographic Data for (*R*)-**7Ir**.

compound	(*R*)-**7Ir**
chemical formula	$C_{21}H_{14}BrF_3$
CCDC number	2172478
formula weight	403.24
crystal size, mm^3	0.131 × 0.066 × 0.037
crystal color, habit	colorless, needle
temperature, °C	–180
crystal system	monoclinic
space group	$P2_1$ (no. 4)
a, Å	9.1554(4)
b, Å	7.1034(3)
c, Å	13.5438(6)
α, deg	90
β, deg	103.113(4)
γ, deg	90
V, $Å^3$	857.85(7)
Z	2
d_{calcd}, g, cm^{-3}	1.561
F(000)	404
μ, cm^{-1}	24.327
transmission factors range	0.847 – 0.914
number of measured reflections	13715
number of unique reflections	4344
number of refined parameters	226
R_{int}	0.0457
*R*1 ($I > 2\ \sigma(I)$) [a]	0.0297
*wR*2 (all data) [b]	0.0564
GOF [c]	1.000
maximum residual peak / hole, e $Å^{-3}$	+0.30 / –0.33
Flack parameter	–0.005(5)

[a] $R1 = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + rP]$, $P = (\mathrm{Max}(F_o^2, 0) + 2\ F_c^2)/3$ [$r = 3.65$]. [c] $\mathrm{GOF} = [\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_{params})]^{1/2}$.

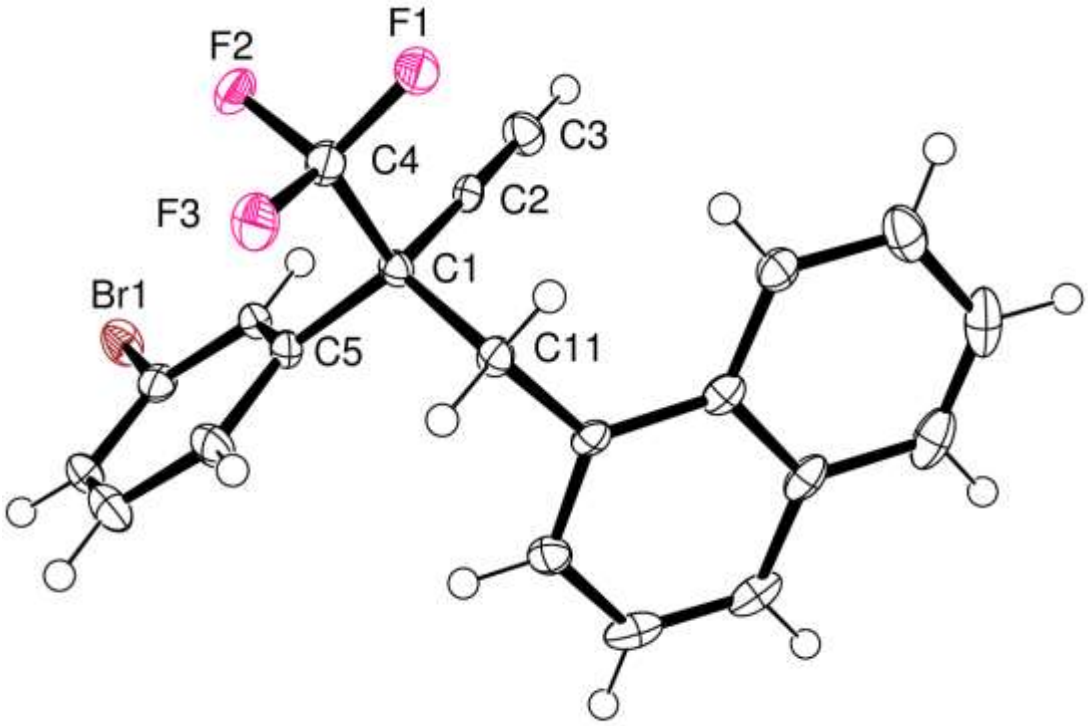


Fig. S4. | ORTEP drawing of (*R*)-7Ir. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): C(1)–C(2): 1.468(4), C(1)–C(4): 1.535(4), C(1)–C(5): 1.548(4), C(1)–C(11): 1.556(4), C(2)–C(3): 1.188(5); C(2)–C(1)–C(4):106.6(2), C(2)–C(1)–C(5): 111.3(2), C(4)–C1)–C(5): 106.9(2), C(2)–C1)–C(11): 110.4(3), C(4)–C1)–C(11): 108.1(2), C(5)–C1)–C(11): 113.2(2), C(3)–C2)–C(1): 178.4(3).

S20. DFT calculations

DFT calculations were carried out with the Gaussian16 (Revision A.03) program package.[S32] Geometry optimization and analytical vibrational frequency analysis were performed by ωB97XD Kohn-Sham DFT [S33,S34] (restricted KS method for singlet state and unrestricted KS method for doublet and triplet states).[S34] In the numerical integration, a larger grid (*superfinegrid*) was used.[S32] Pople's 6-311G** basis set[S35] for C, H, S, and Cl atoms and the SDD basis set [S36] with the effective core potential for Ru atom were used for the Gaussian basis functions (5d-type). The solvent effects of dichloroethane were estimated by the IEF-PCM method[S37,S38] for the gas phase optimized structures. For the IEF-PCM calculations, the ωB97XD functional was used with the larger basis set (Pople's 6-311++G** basis set[S35] for C, H, N, O, S, and Cl atoms (5d-type) and the SDD basis set for Ru atom; ωB97XD(IEFPCM)/(SDD, 6-311++G**)//ωB97XD(IEFPCM)/(SDD, 6-311G**)). The Gibbs free energy at 298K was estimated by the IEF-PCM energy and the gas-phase thermal correction term.

Table S2. Total Electronic Energy *E* and Gibbs Free Energy $G^{298.15K}$ (au).

	ωB97XD/(SDD, 6-311G)**		**ωB97XD(IEFPCM)/(SDD, 6-311++G**) //ωB97XD/(SDD, 6-311G**)**	
	E	***thermal correction***	***E***	$G^{298.15K}$
I	-2652.931215	0.577572	-2652.987526	-2652.409954
Bn·	-270.878749	0.085445	-270.884482	-270.799037
II	-2923.827178	0.683276	-2923.885964	-2923.202688
TS_{II-III}	-2923.824805	0.685582	-2923.882584	-2923.197002
III	-2923.871077	0.688734	-2923.937231	-2923.248497
IV	-2924.089301	0.688499	-2924.116165	-2923.427666
V	-2924.502562	0.703703	-2924.566060	-2923.862357
VI	-2924.163164	0.701287	-2924.351071	-2923.649784
$^2[Ir(ppy)_3]^-$	-1540.585524	0.417328	-1540.672281	-1540.254953
$^1[Ir(ppy)_3]$	-1540.580980	0.424514	-1540.608779	-1540.184265
PyH^+	-861.641565	0.252167	-861.717414	-861.465247
Py	-861.257404	0.238104	-861.277723	-861.039619

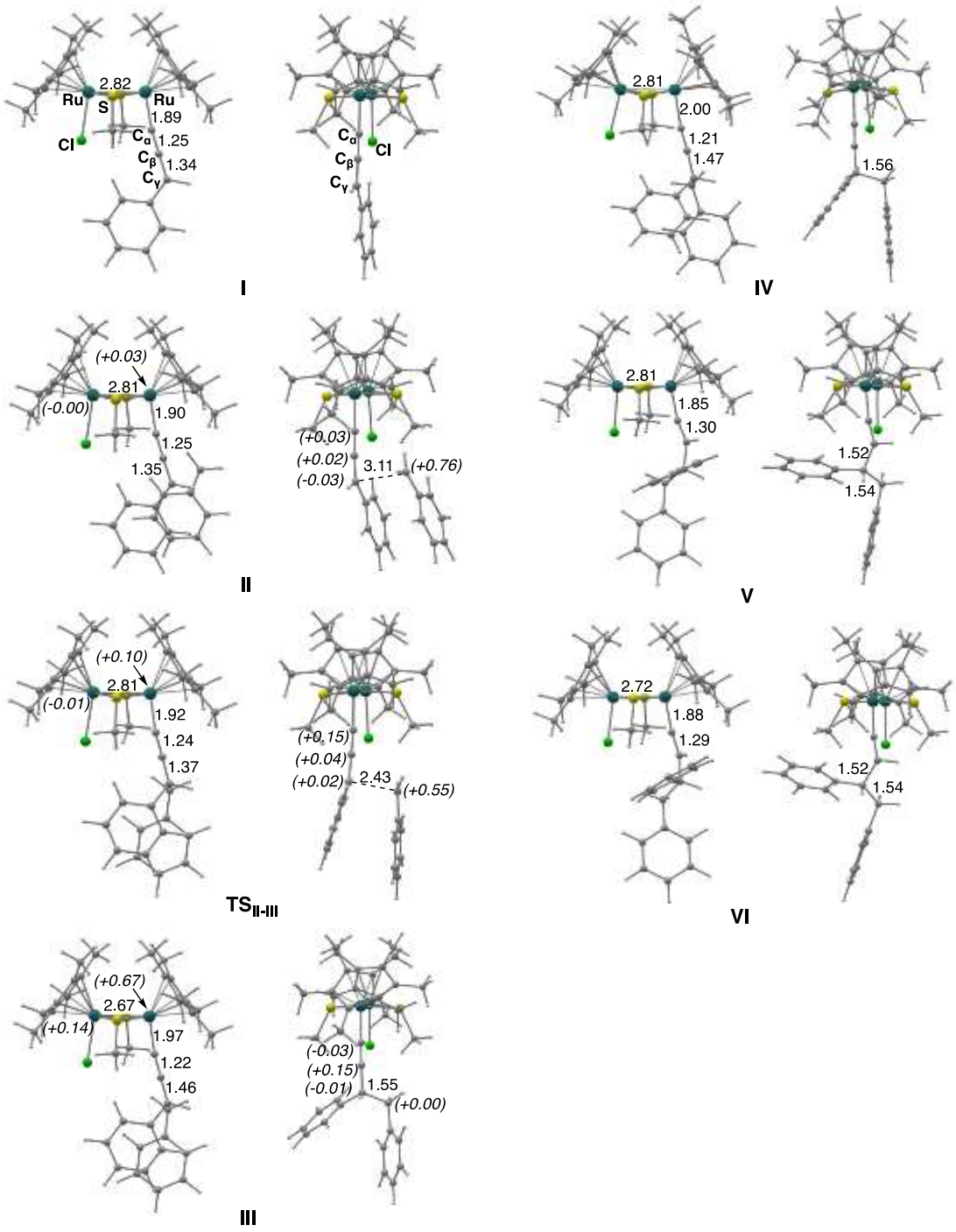


Fig. S5. | Structures optimized at ωB97X-D/(SDD, 6-311G) level of theory.** Bond lengths are given in Å.

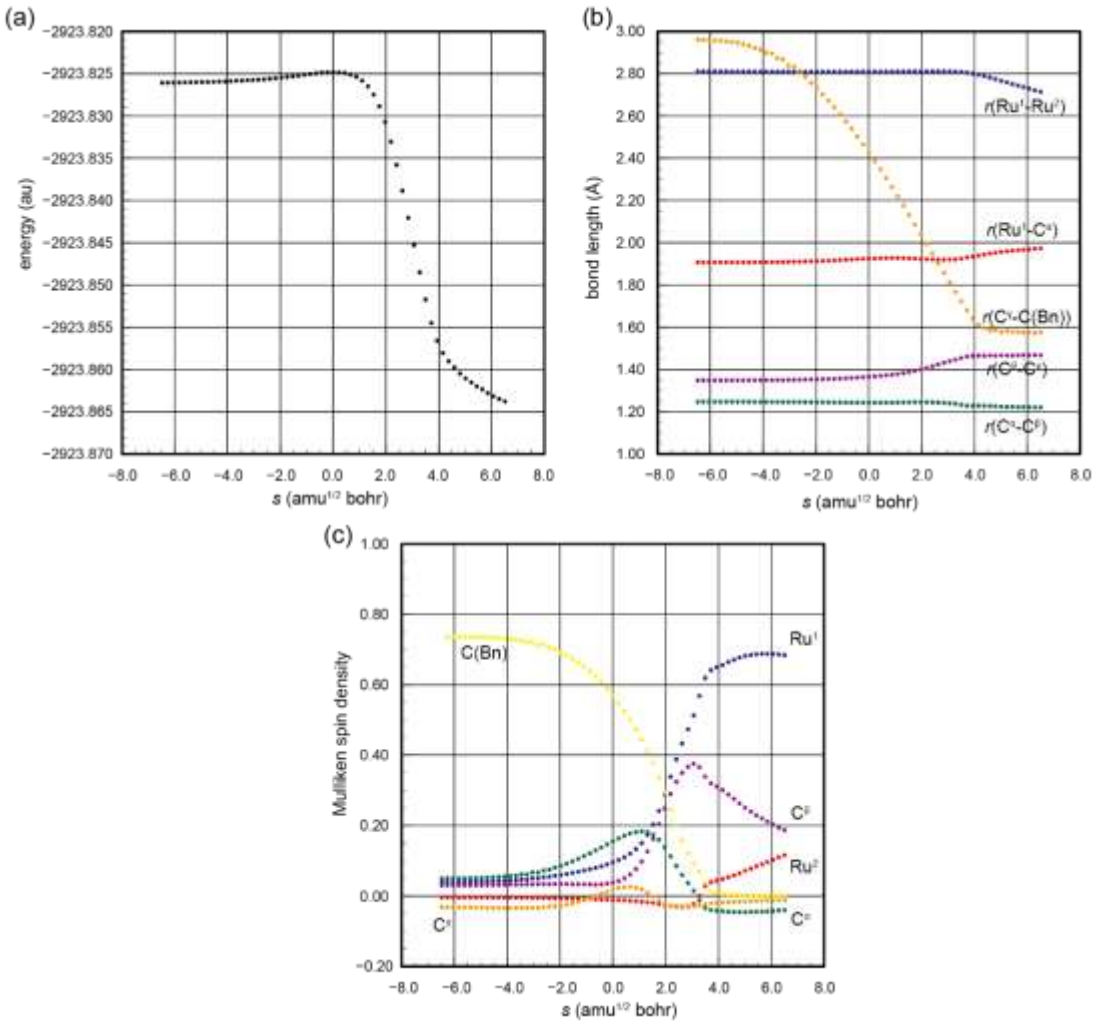


Fig. S6. | Profiles for $TS_{II\text{-}III}$. (a) Potential energy profile along IRC for $TS_{II\text{-}III}$. (b) Changes in bond lengths along the IRC for $TS_{II\text{-}III}$. (c) Changes in Mulliken spin density along the IRC for $TS_{II\text{-}III}$.

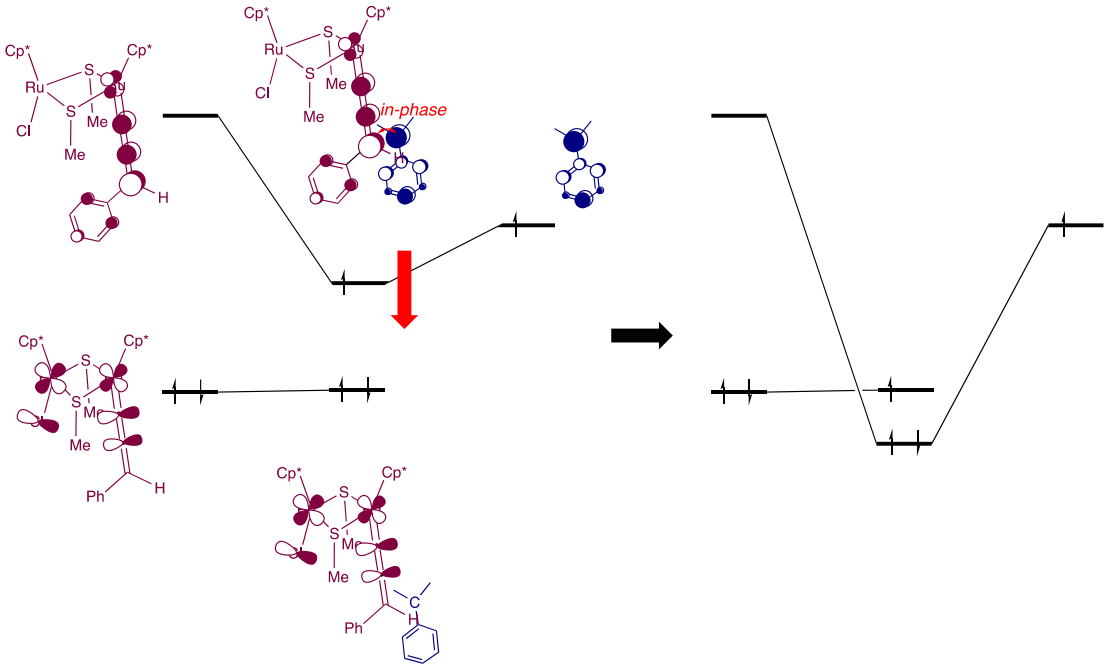


Fig. S7. | Change in SOMO along the reaction.

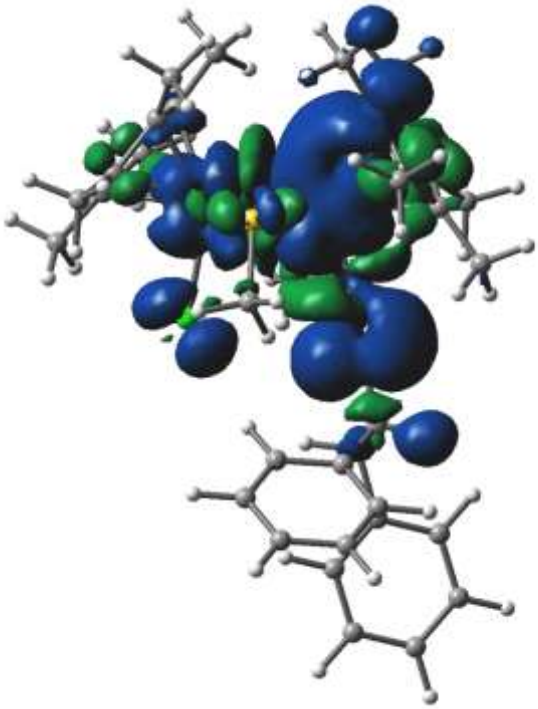


Fig. S8. | Spin density in III.

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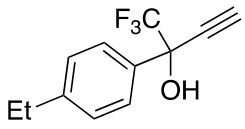
S22. NMR charts



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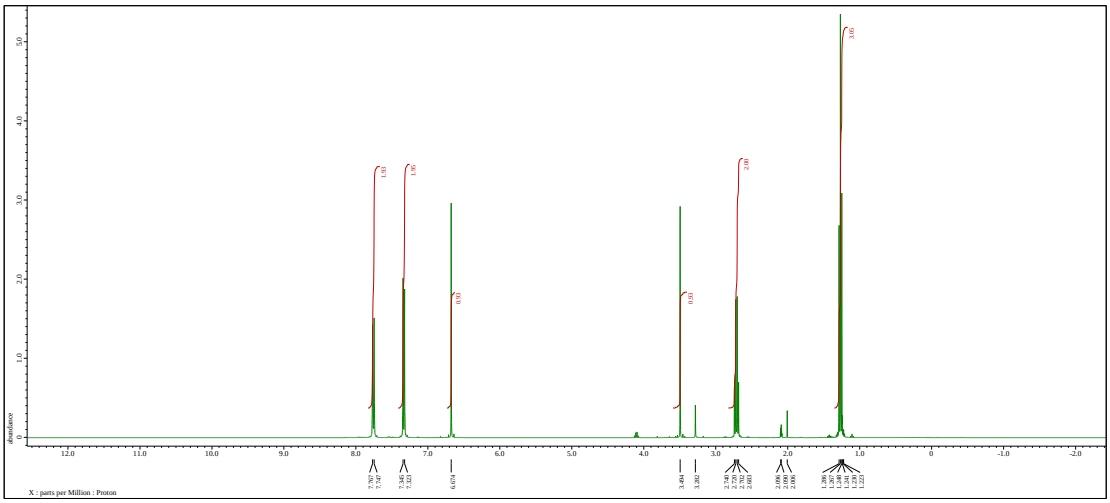
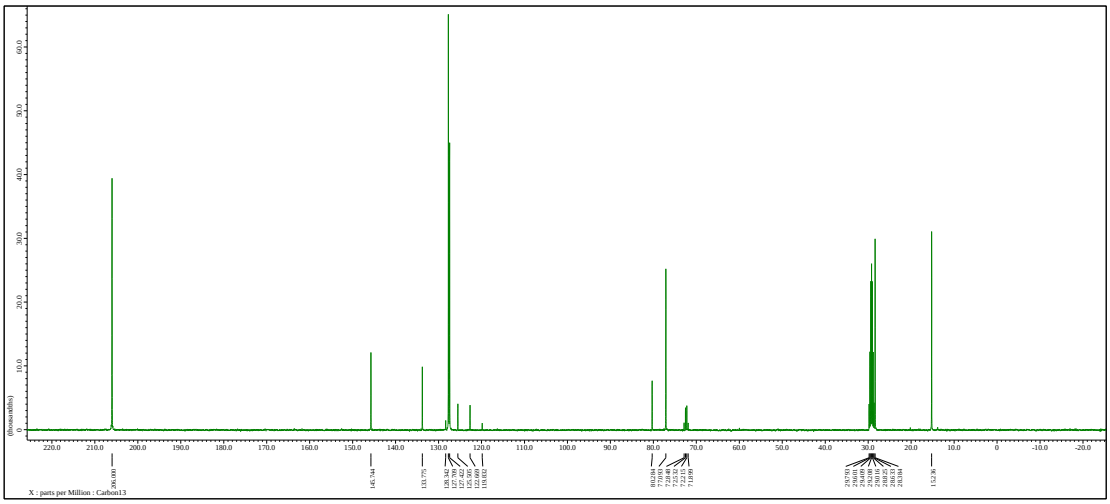
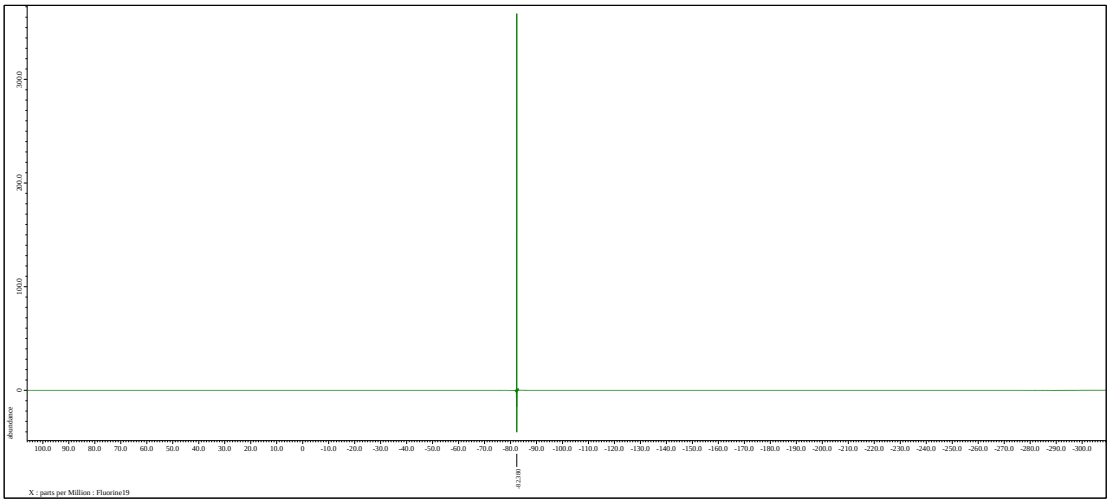
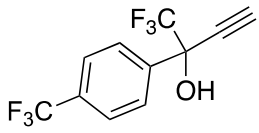
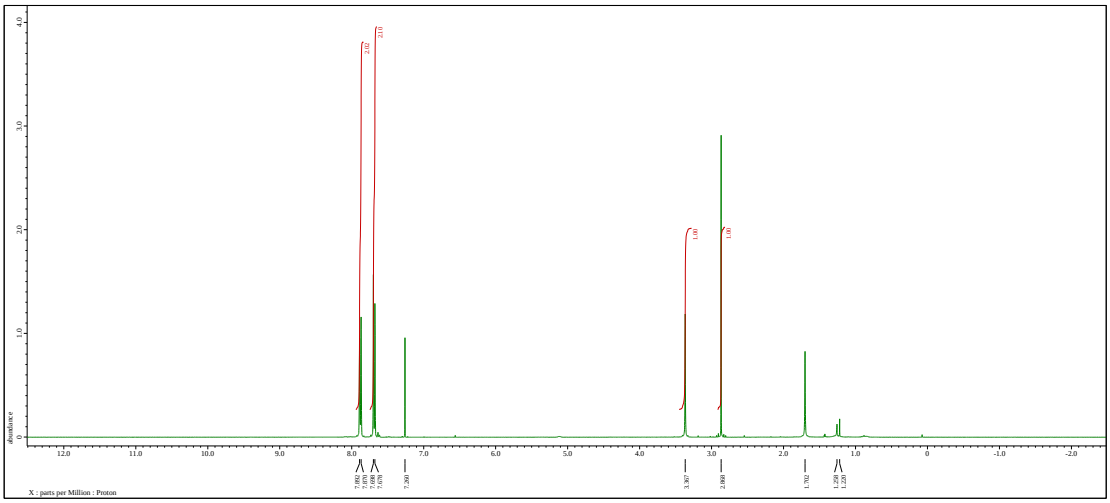


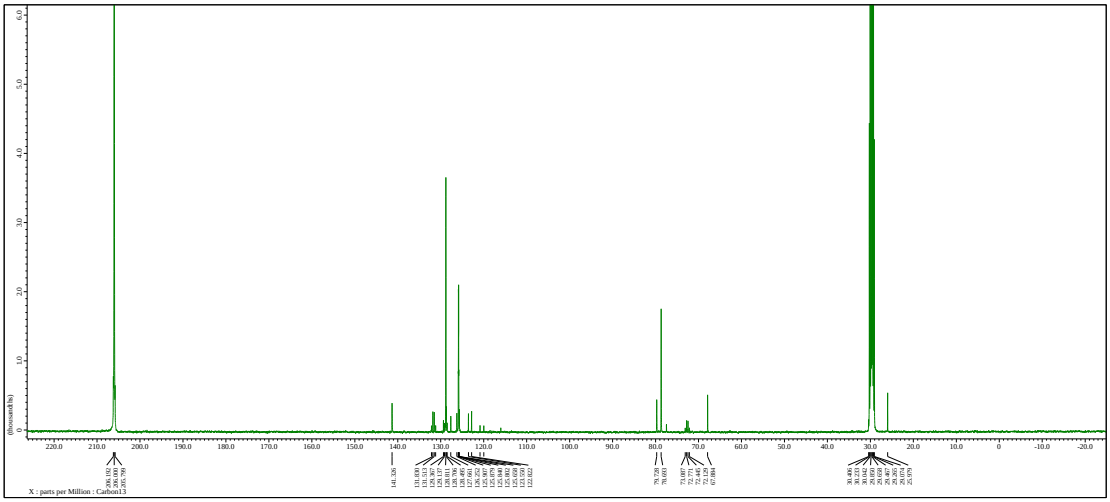


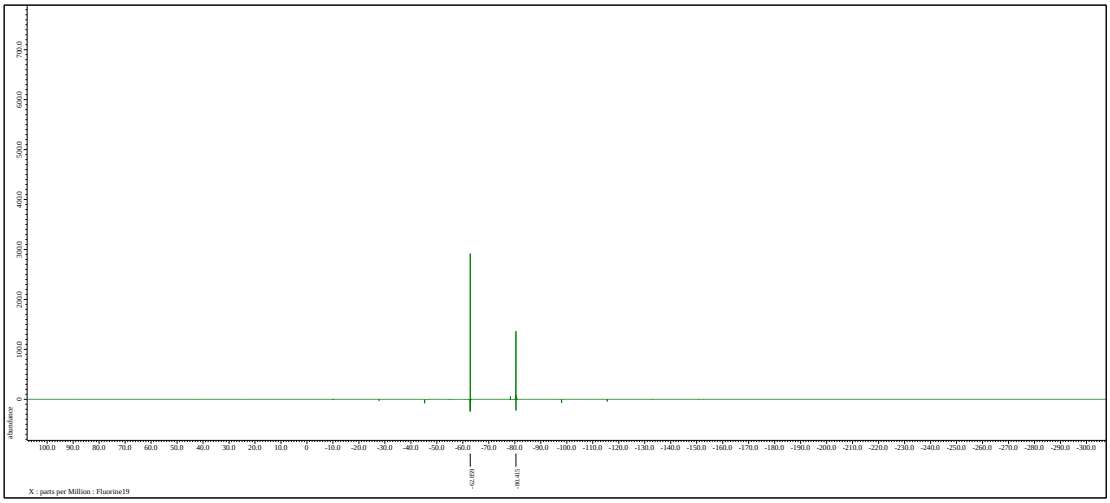



F3C
OH
F3C

3h


X : parts per Million : Proton


X : parts per Million : Carbon13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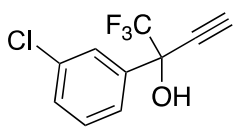
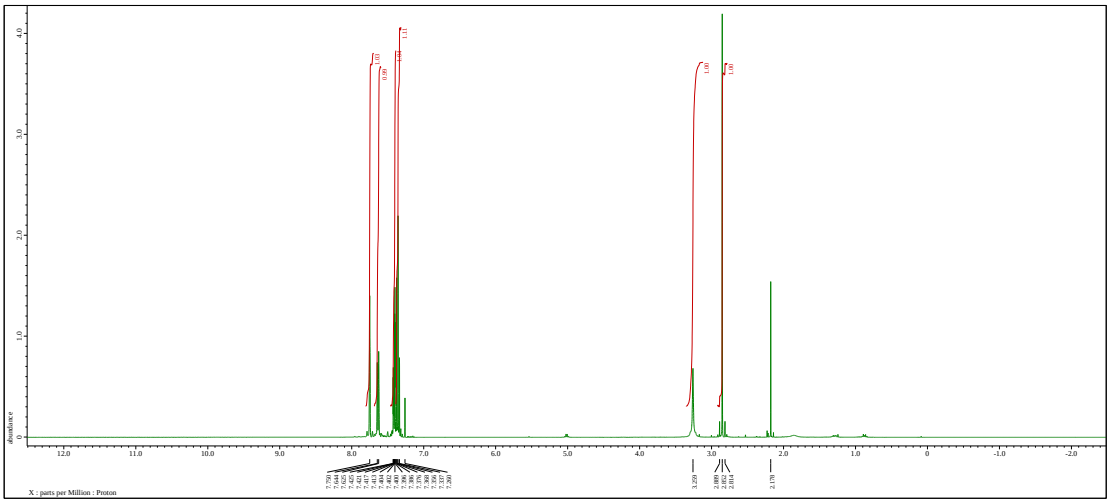

Cl
F3C
OH

3k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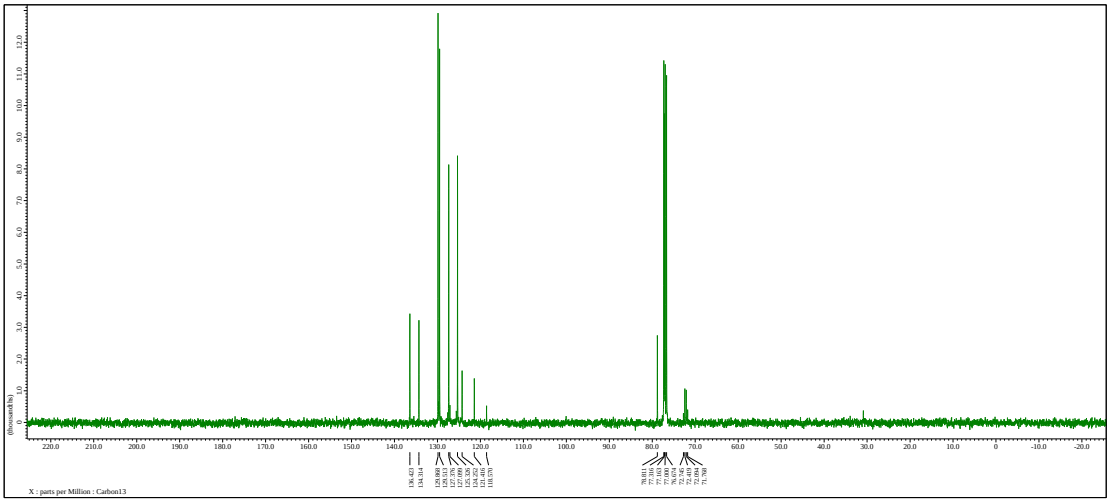
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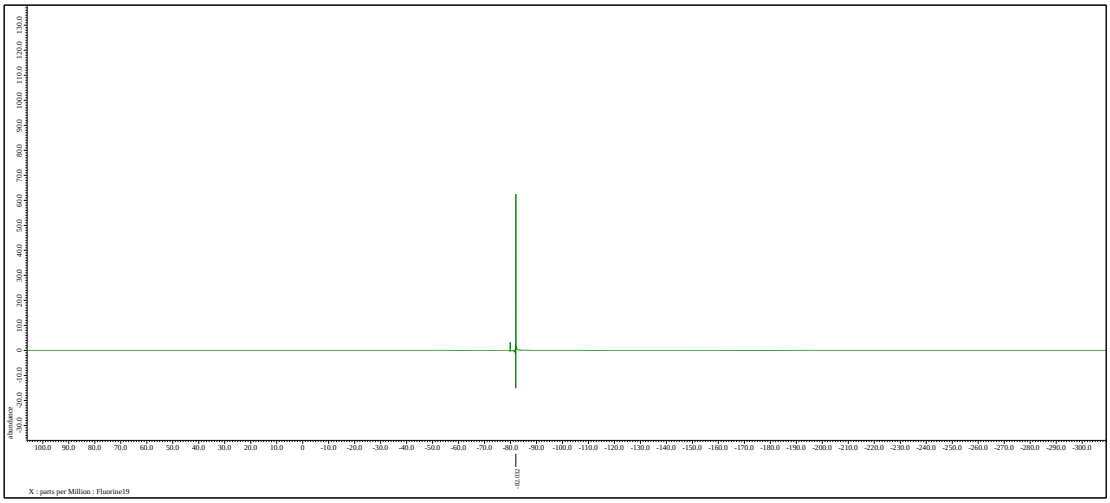
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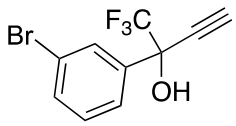
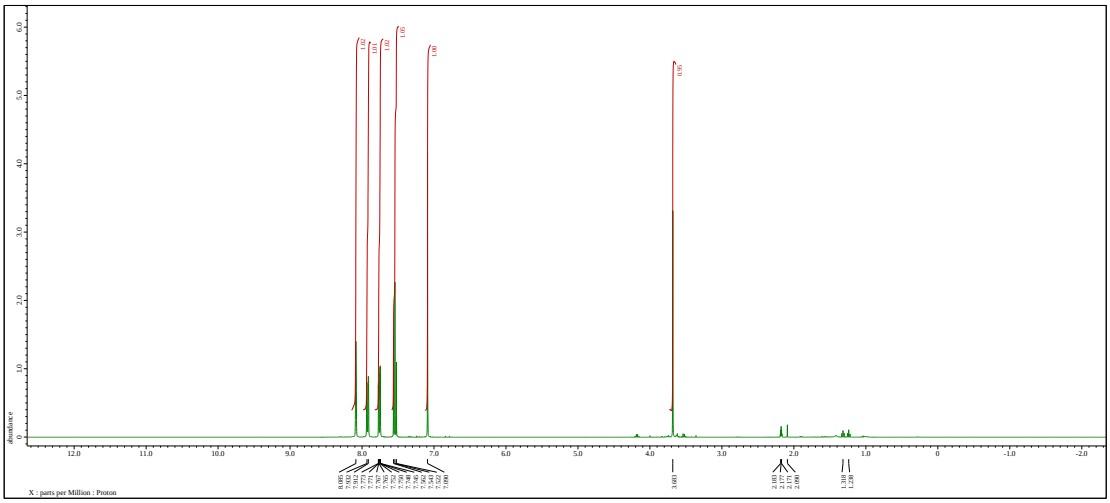

Br
F3C
OH

3l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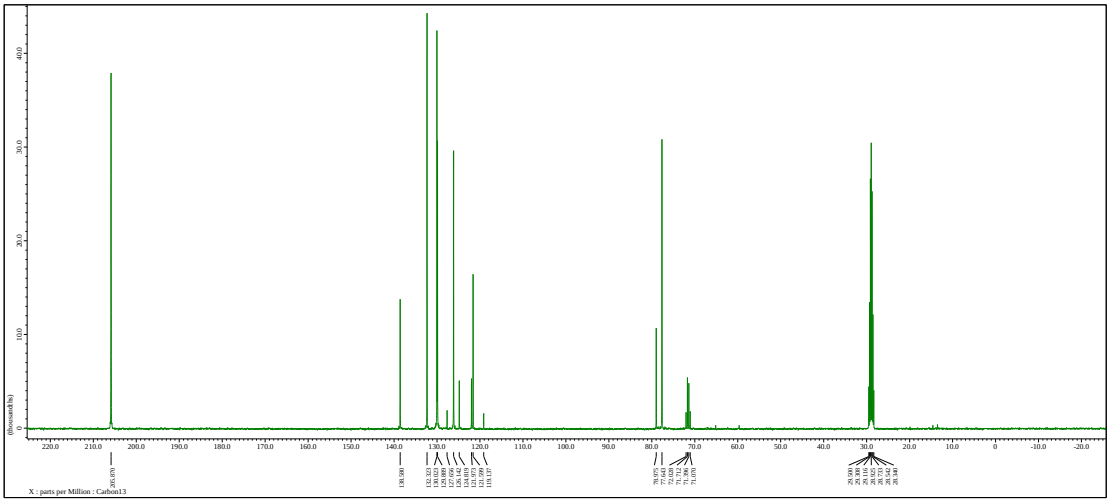
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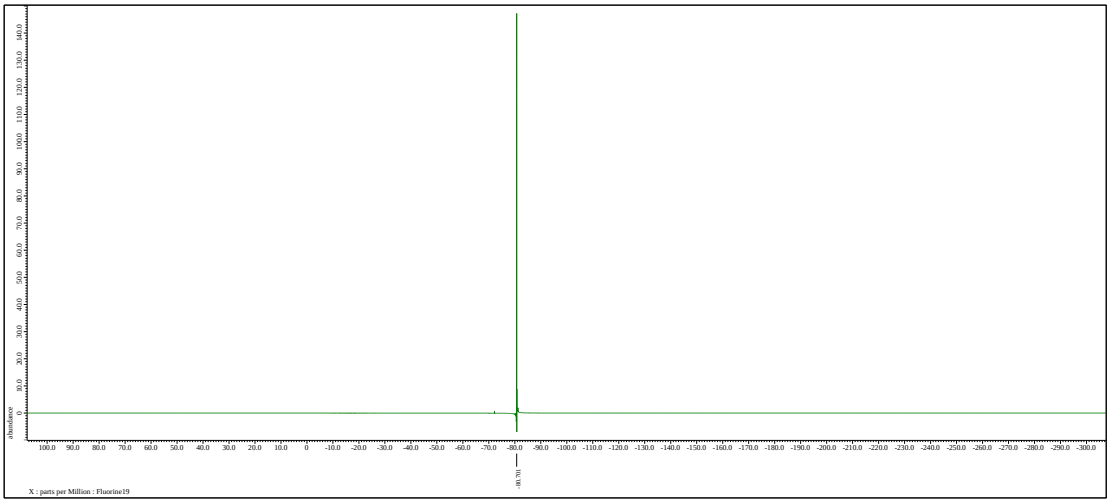
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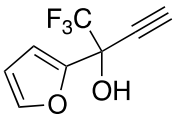
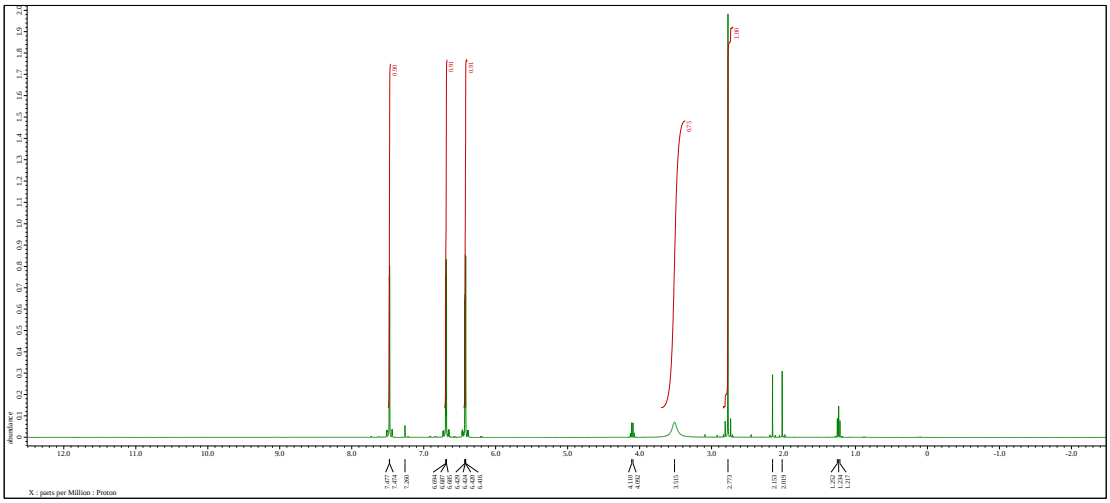

F3C
OH
O

3m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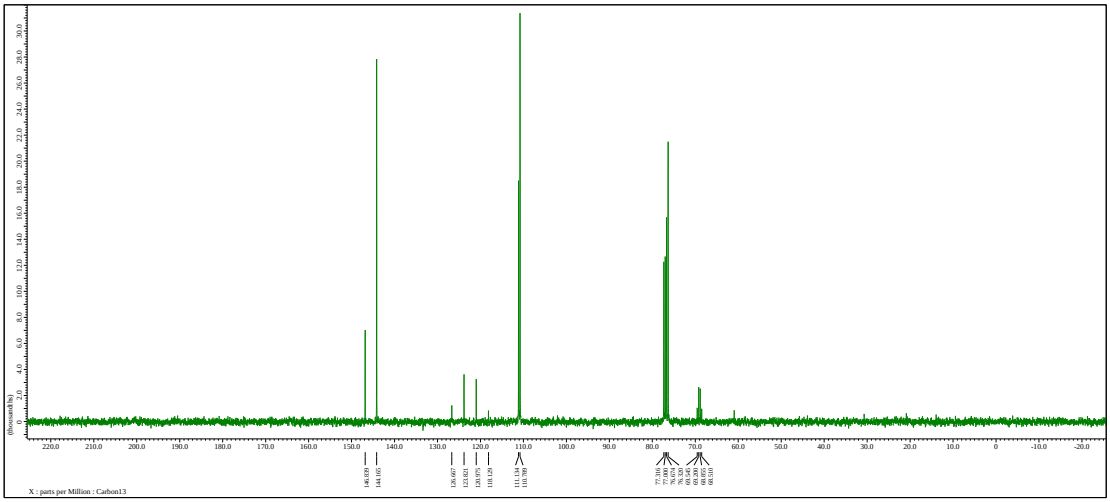
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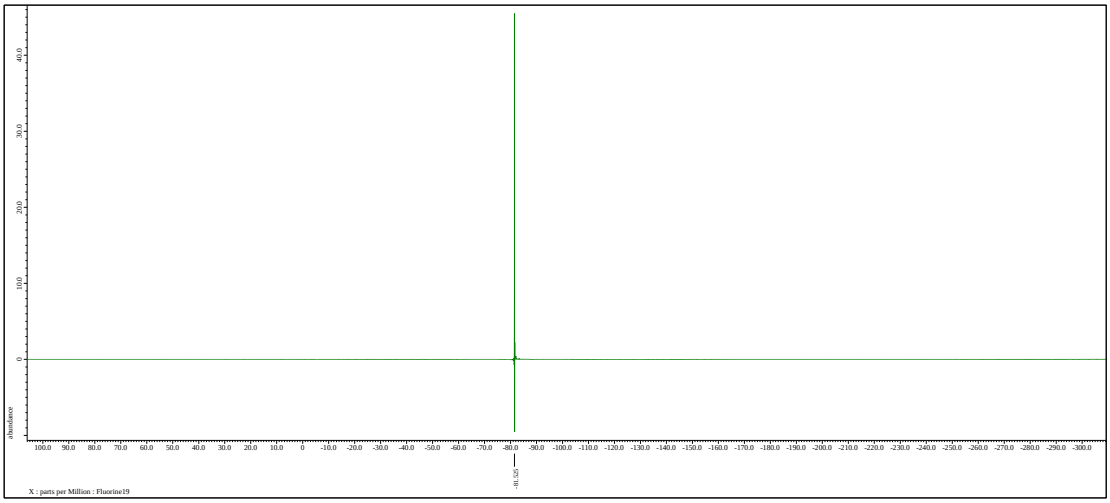
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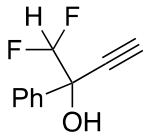
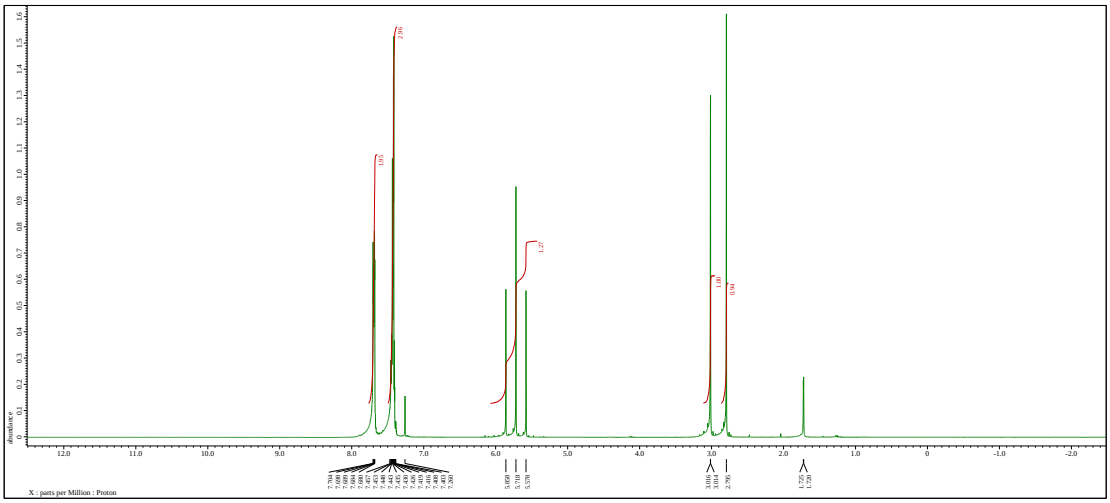
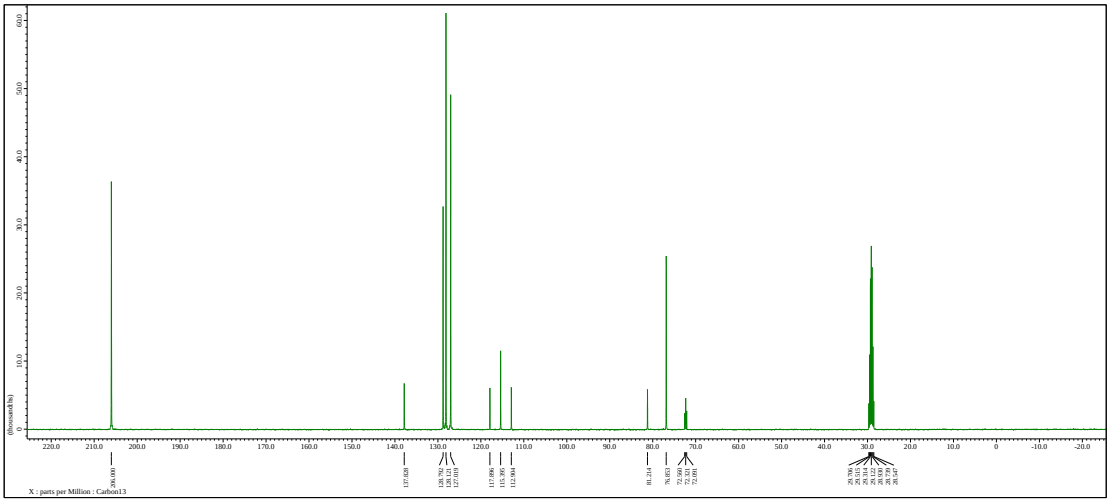

H
F
F
Ph
OH

8


X : parts per Million : Proton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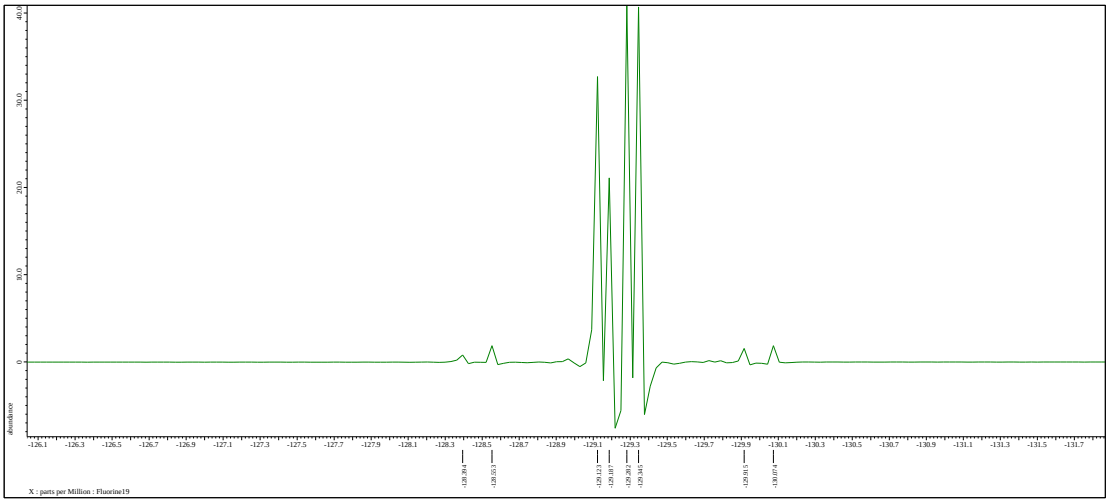
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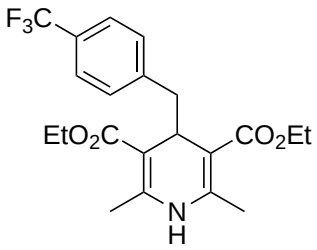
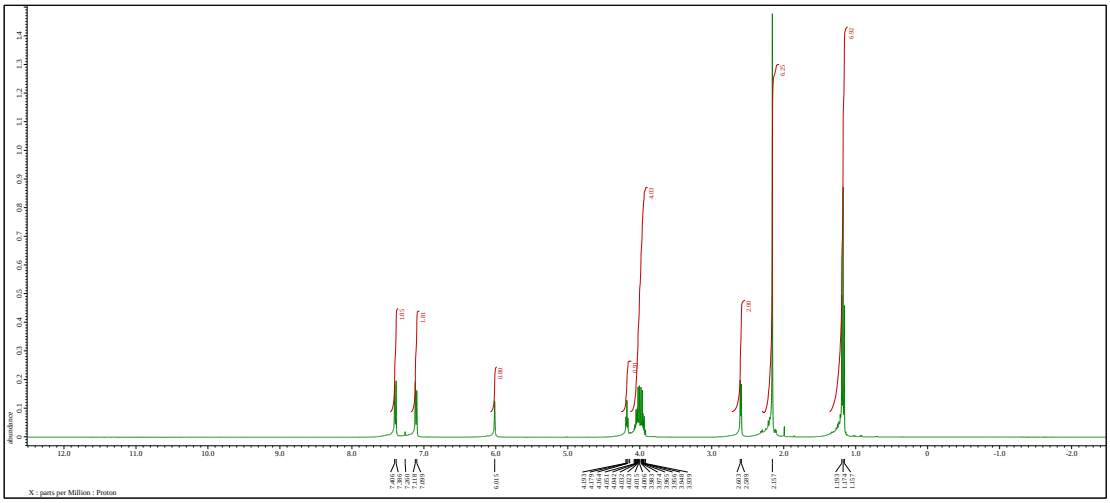

F3C
EtO2C
CO2Et
N
H

4h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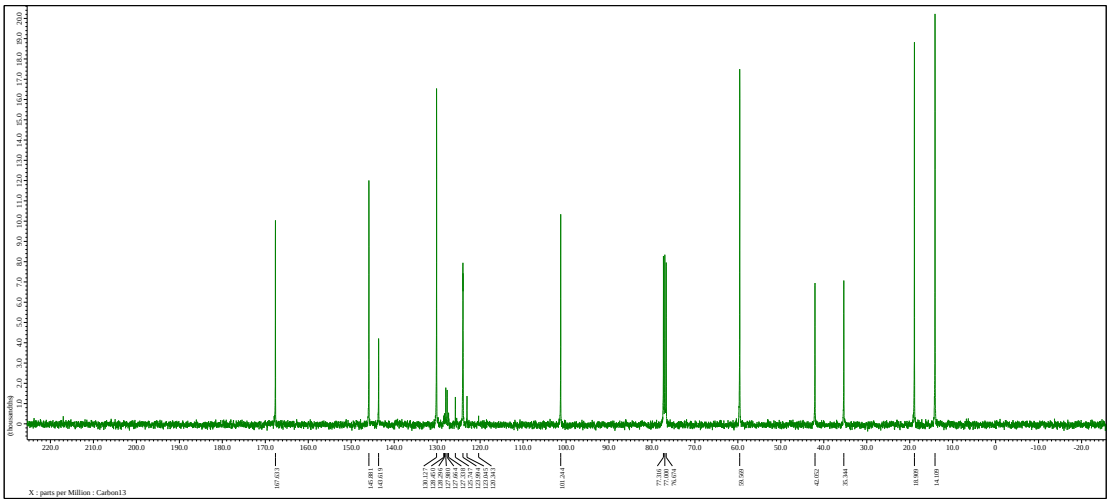
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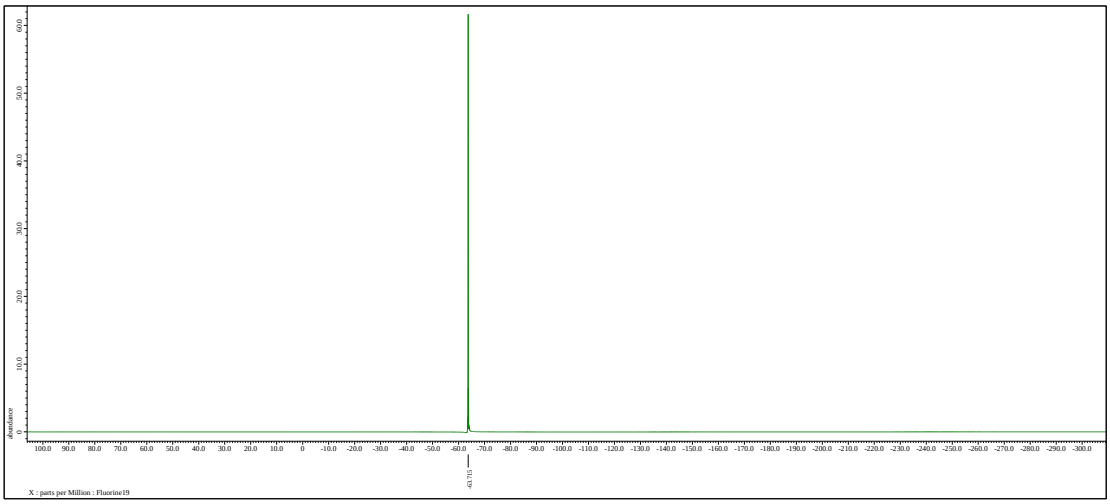
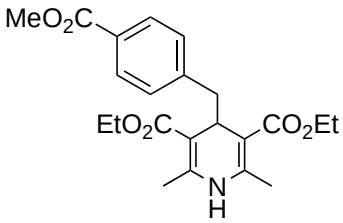
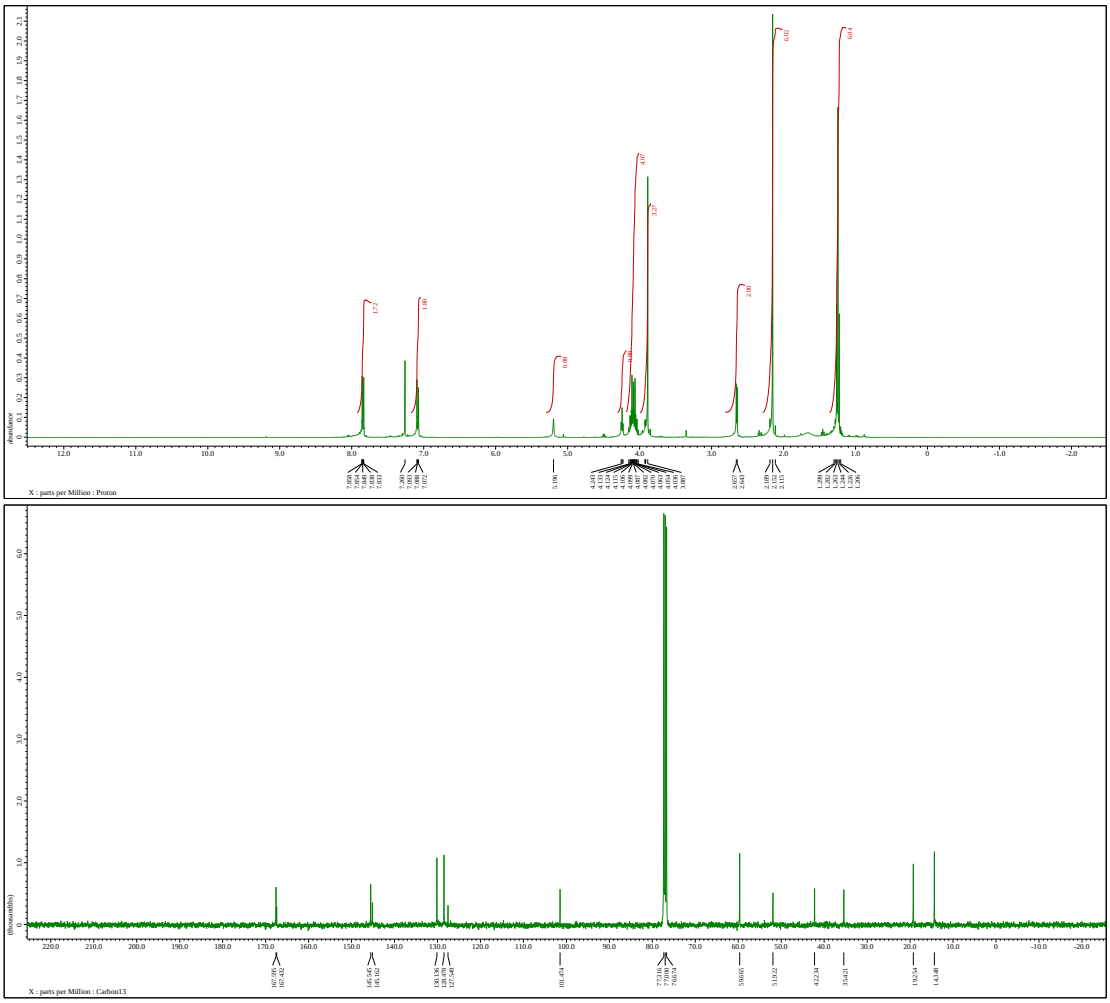
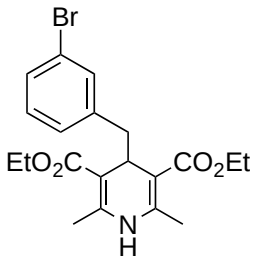

X : parts per Million : Fluorine19

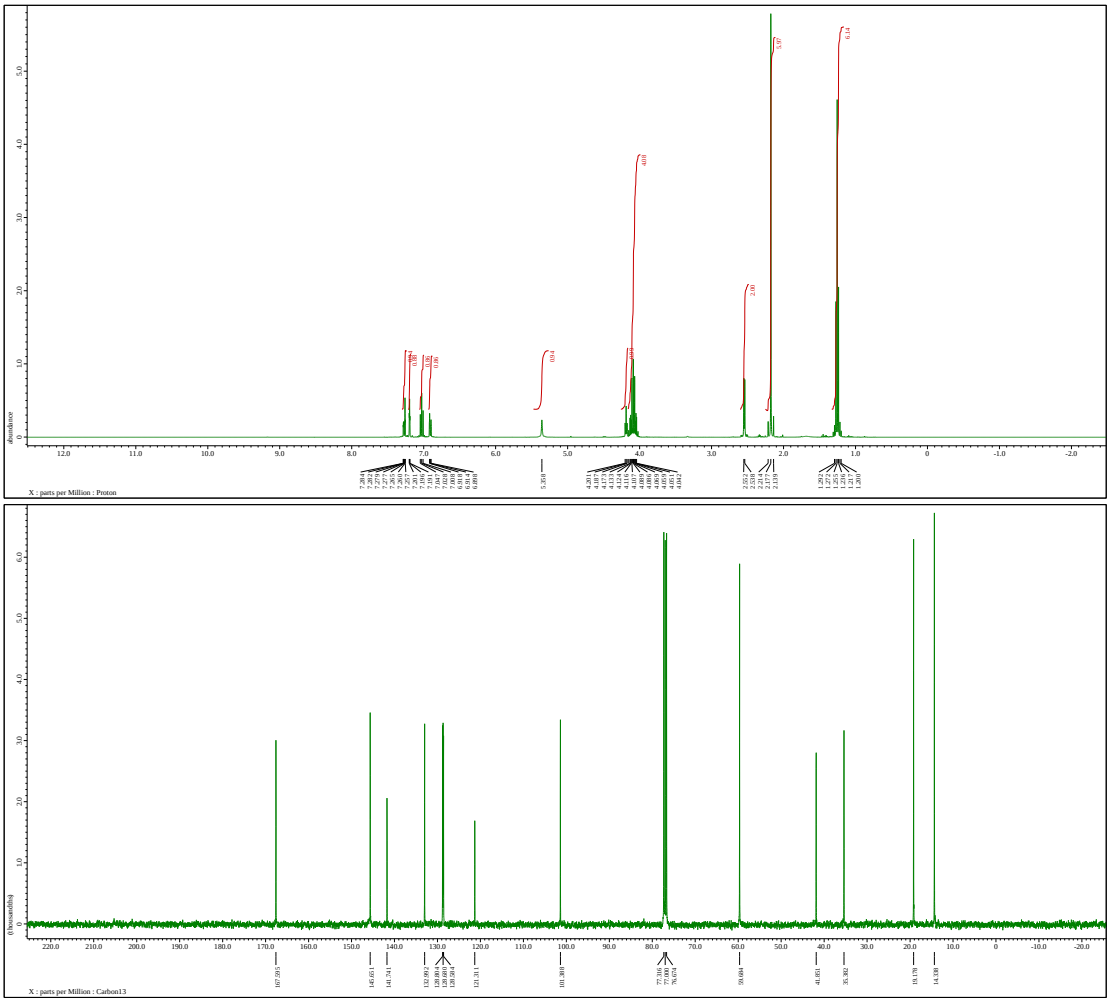

MeO2C
EtO2C
CO2Et
N
H

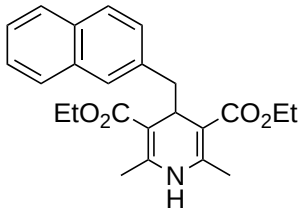
4i


X : parts per Million : Proton
X : parts per Million : Carbon13

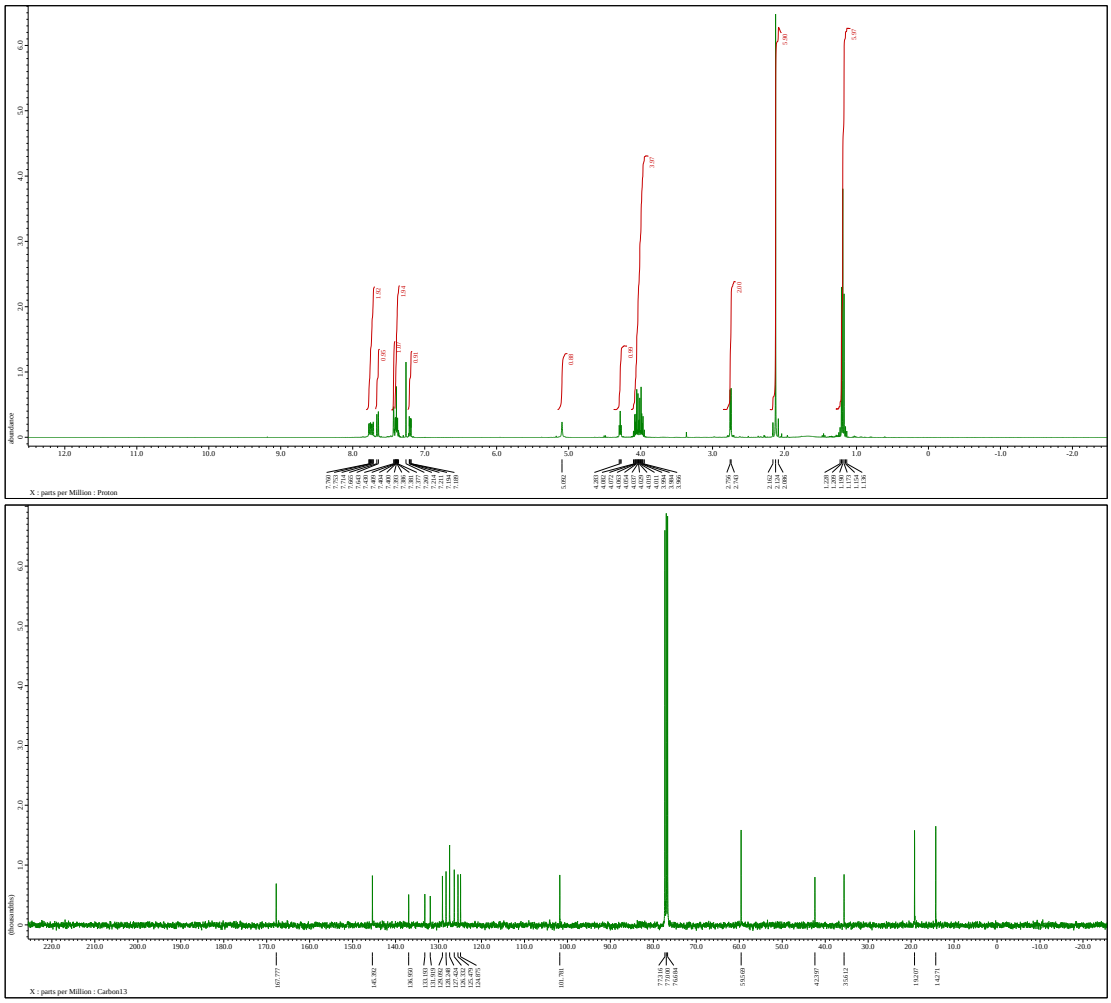

Br
EtO2C
CO2Et
N
H

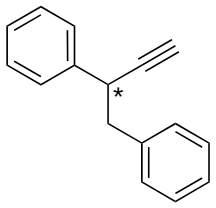
4o


X : parts per Million : Proton
X : parts per Million : Carbon13

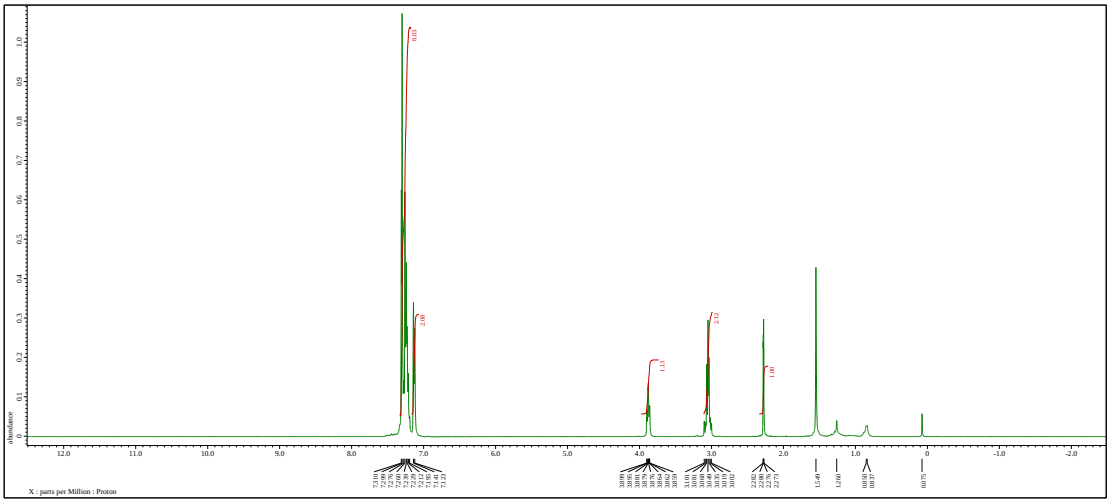


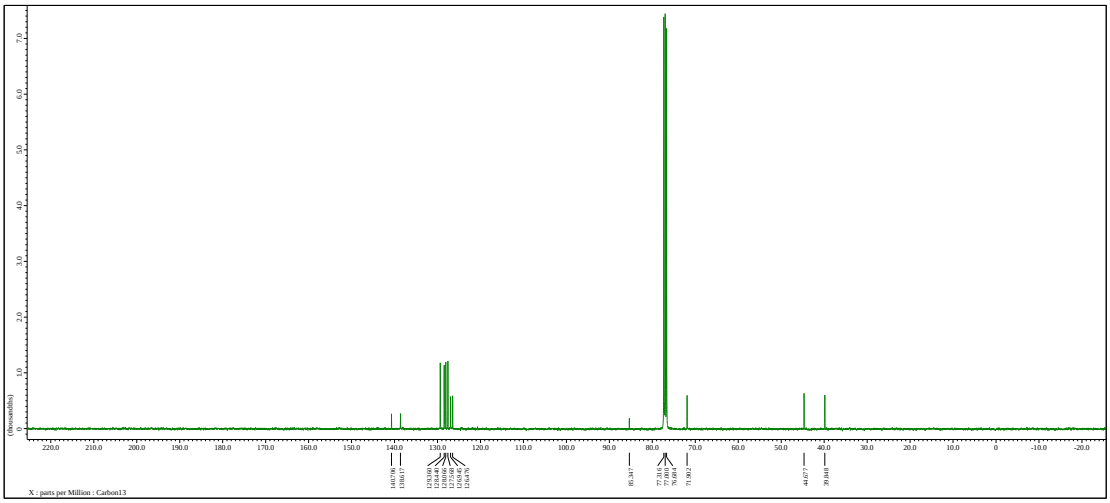
4s

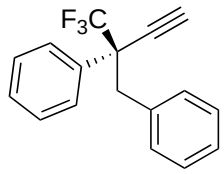




5


abundance
X : parts per Million : Proton


(Arrosantibbs)
X : parts per Million : Carbon13



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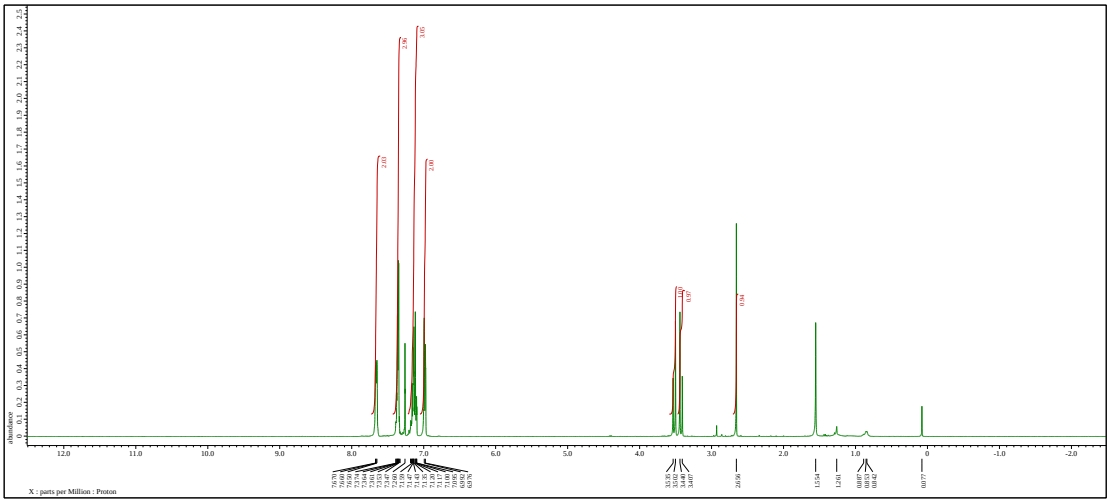
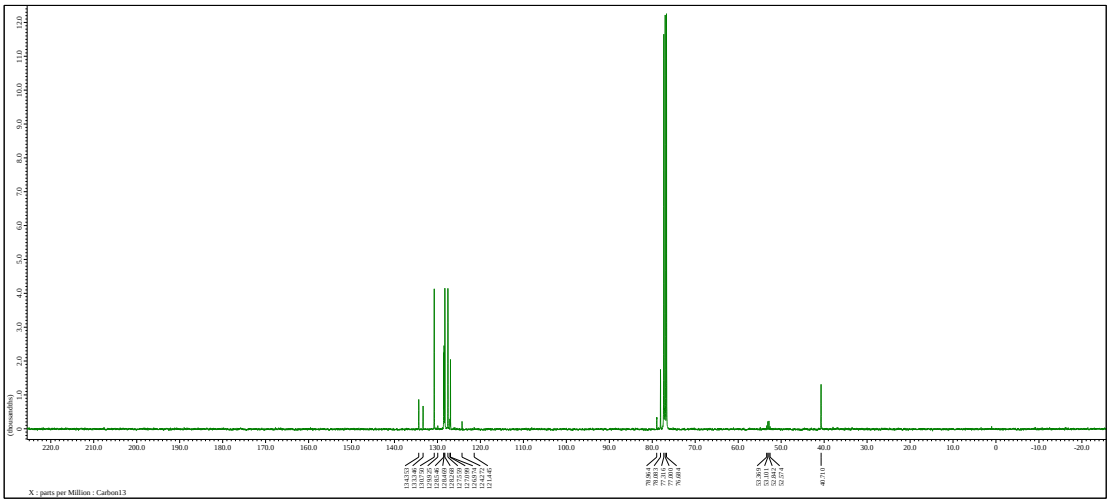
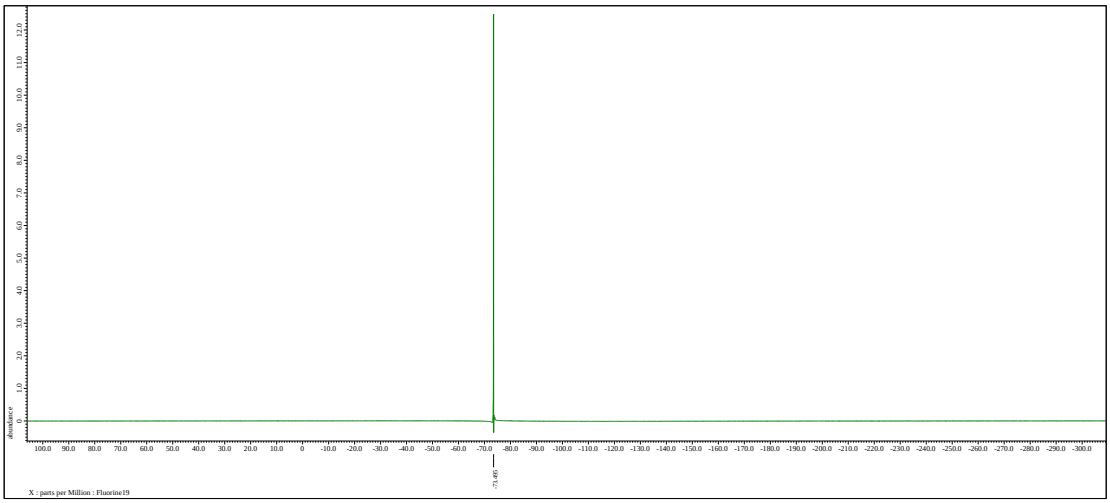
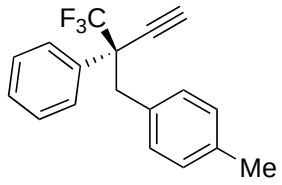
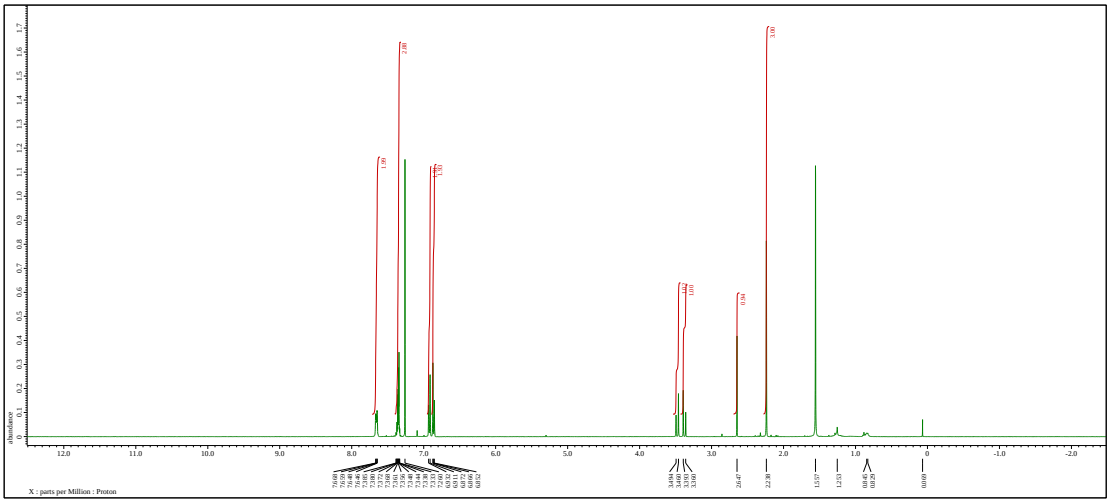


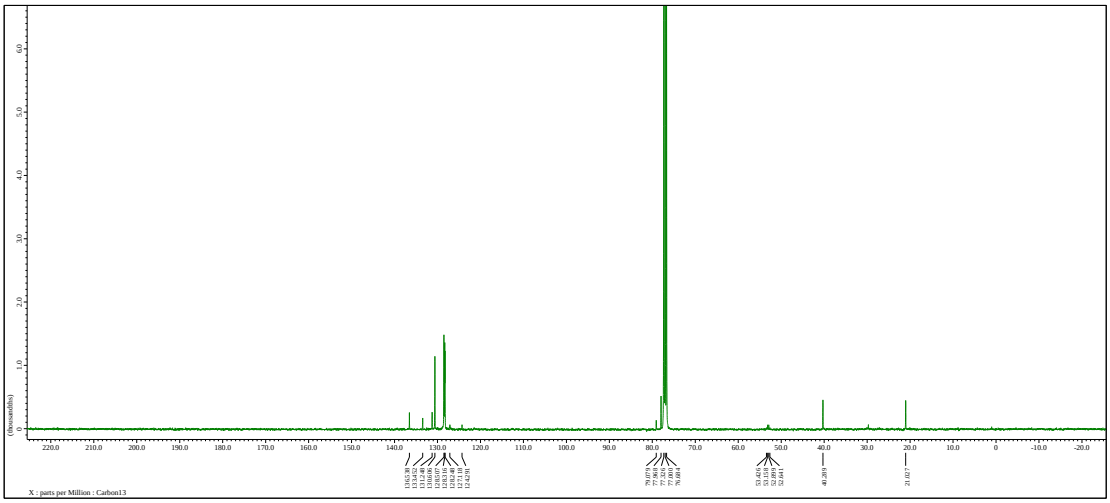


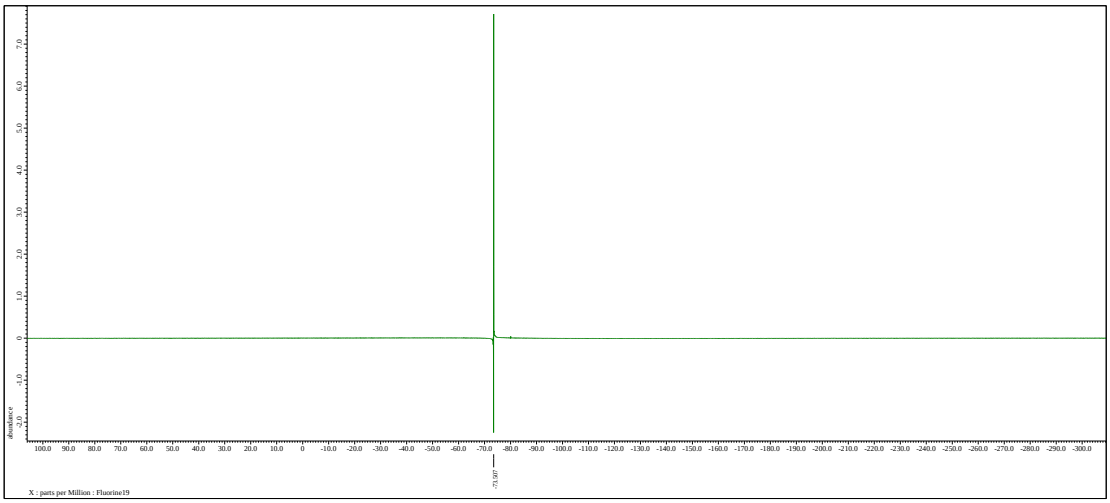


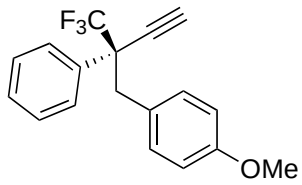

F3C
Me

7ab


X : parts per Million : Proton


X : parts per Million : Carbon13


X : parts per Million : Fluorine19



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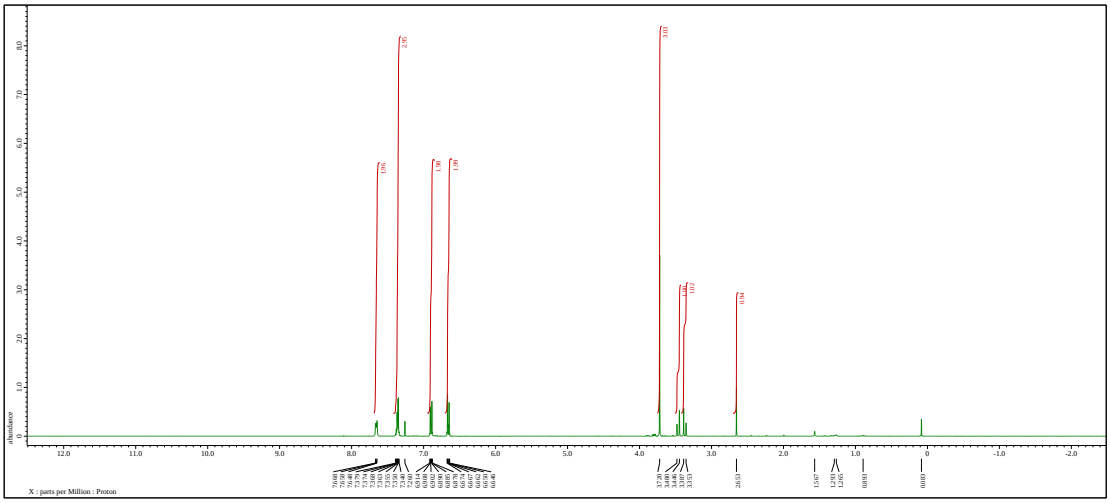

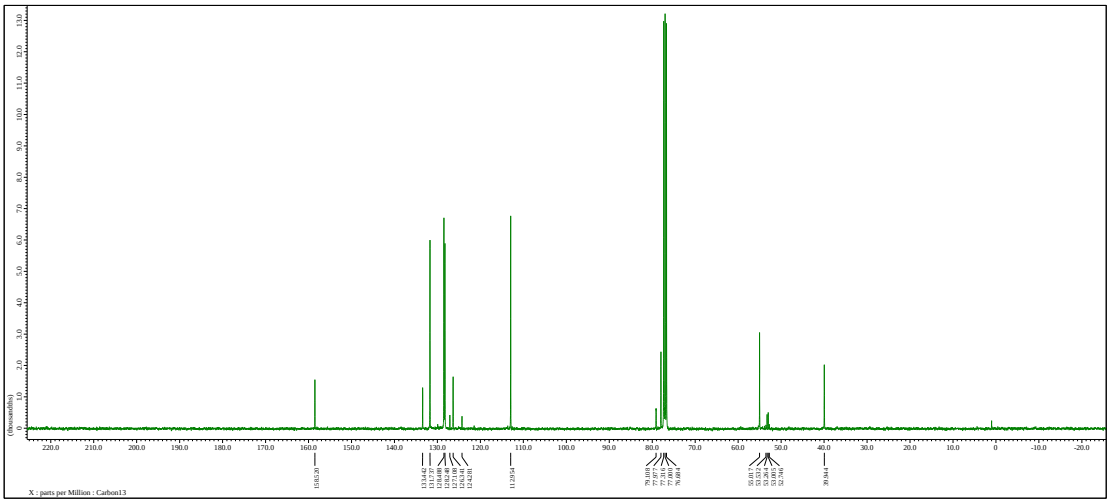

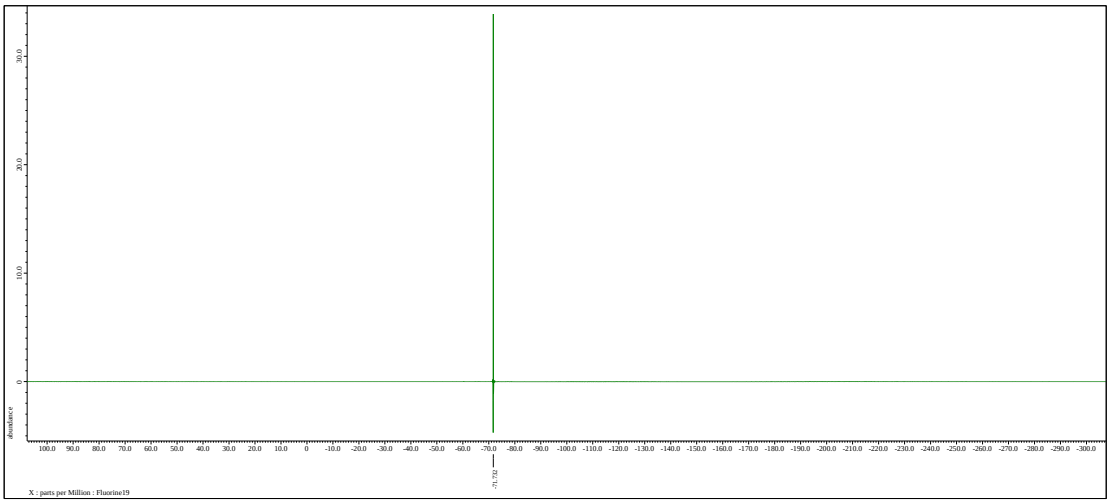

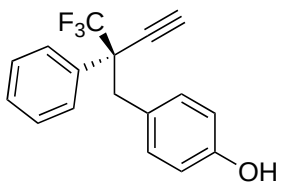

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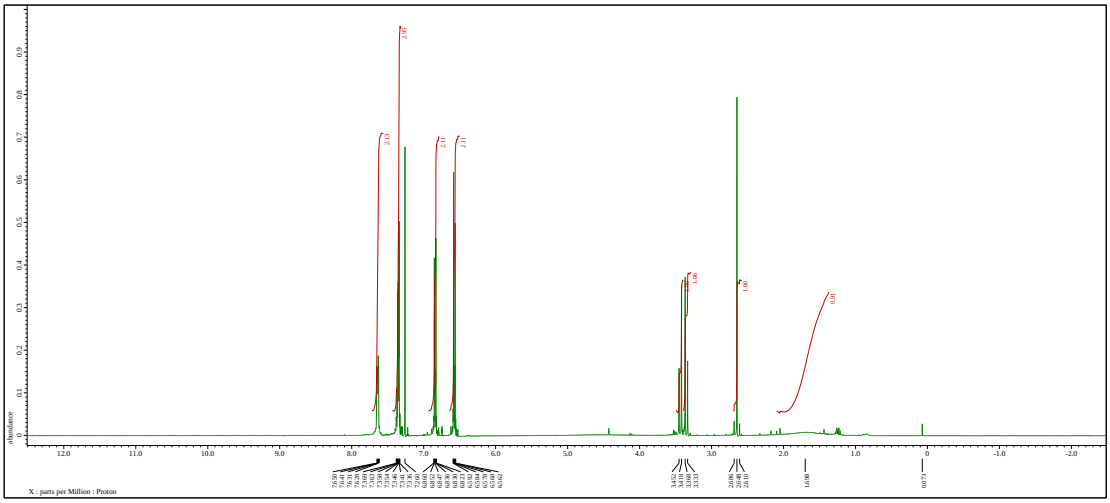

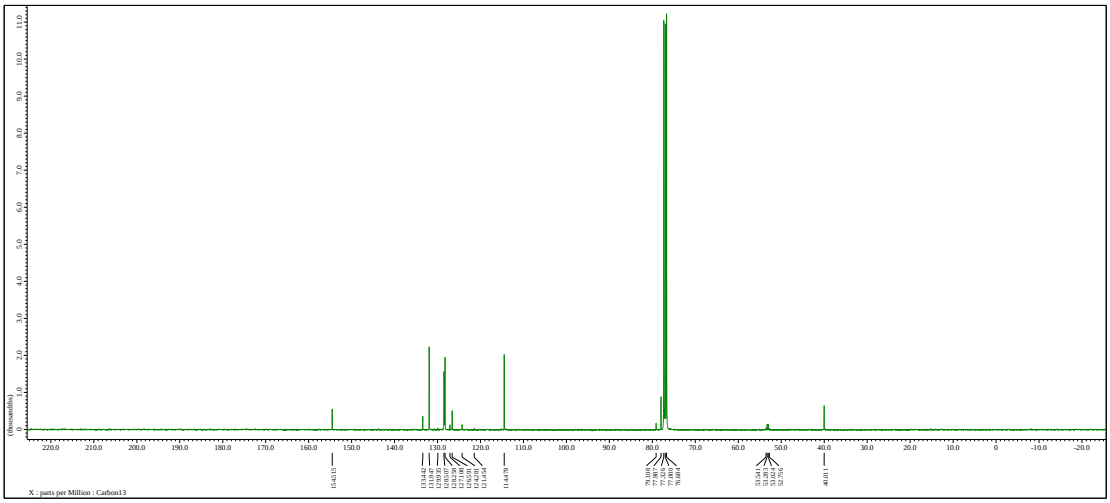

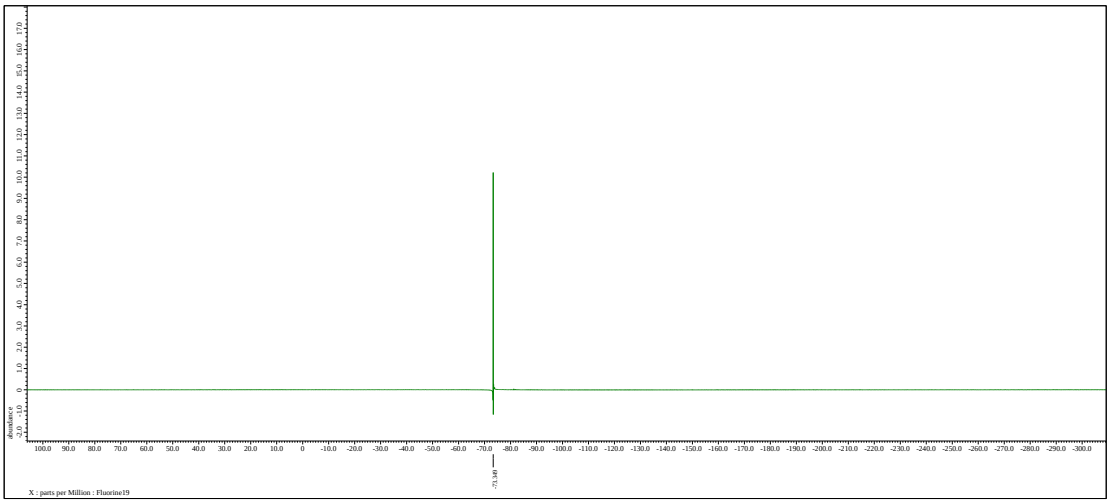

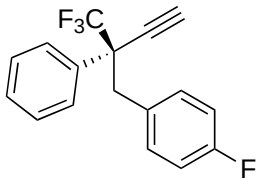

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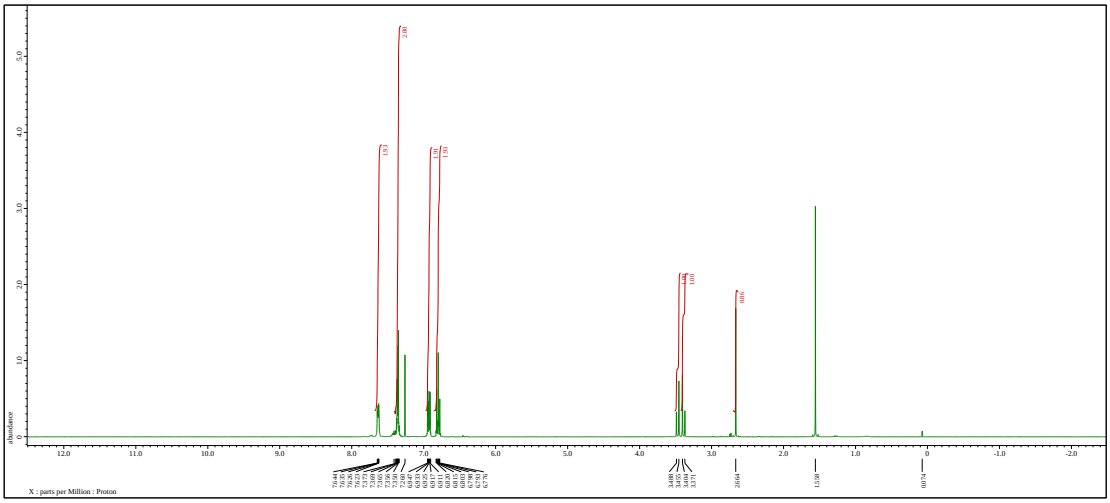

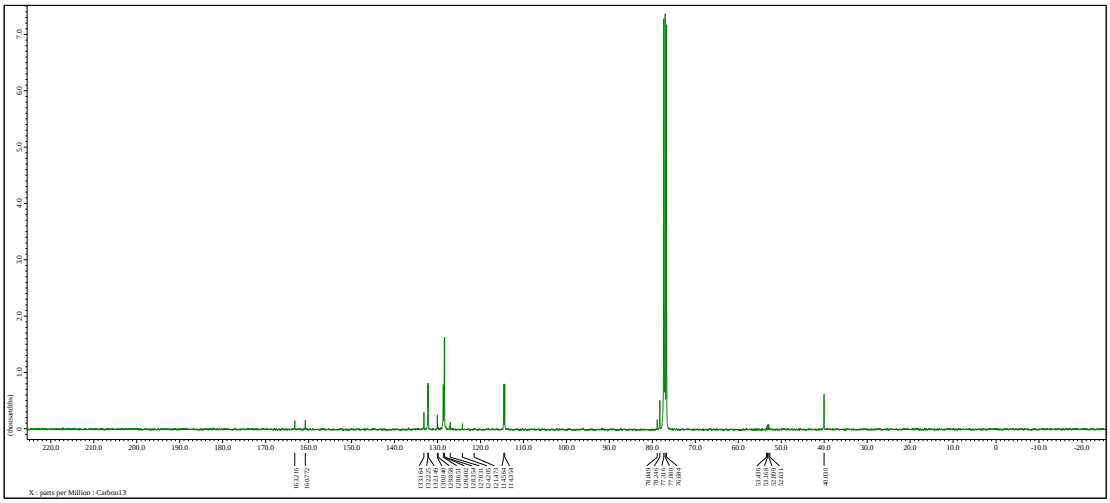

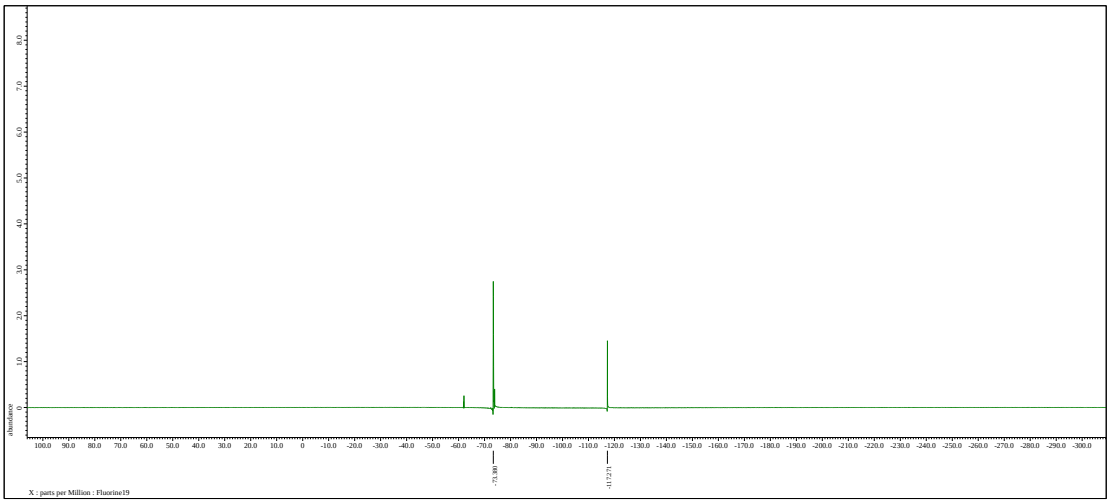

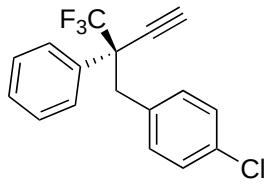

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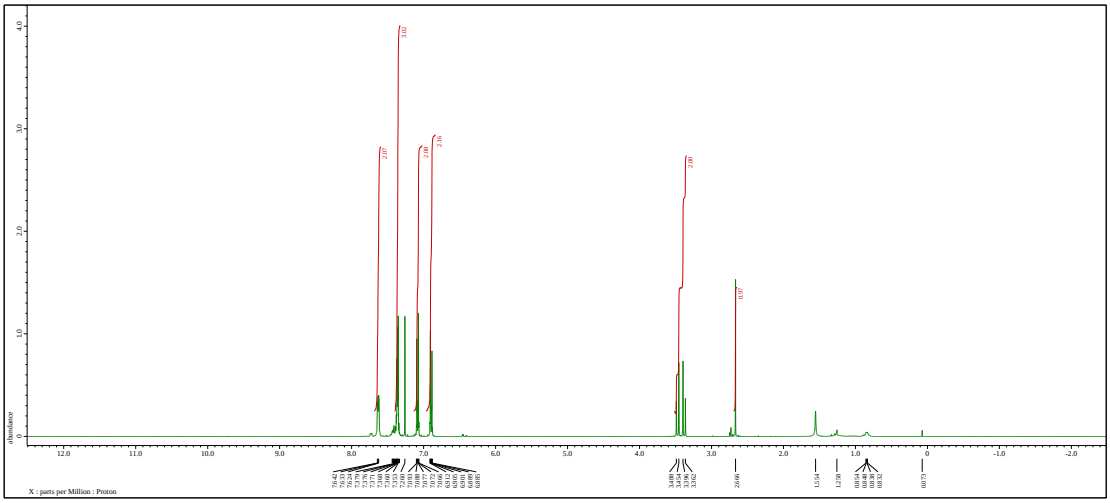

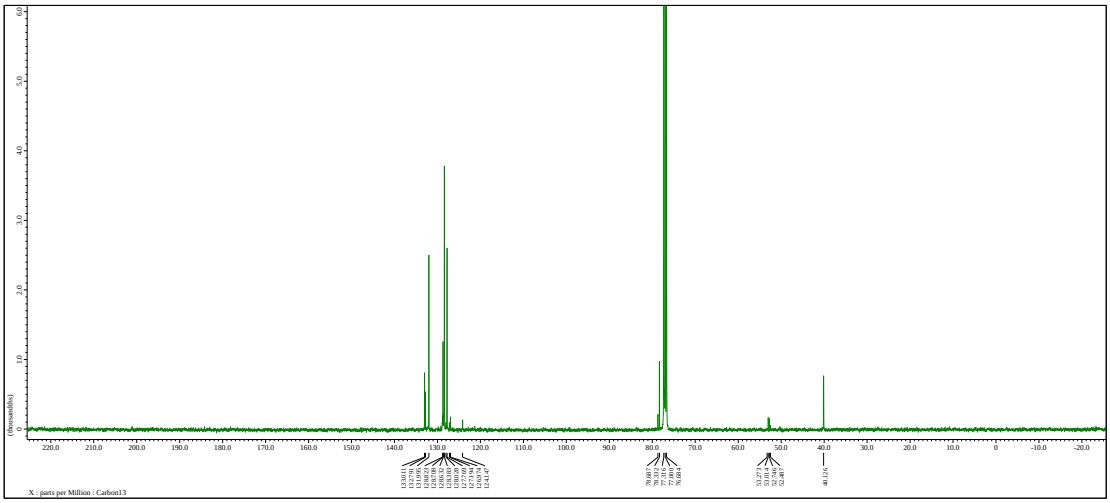

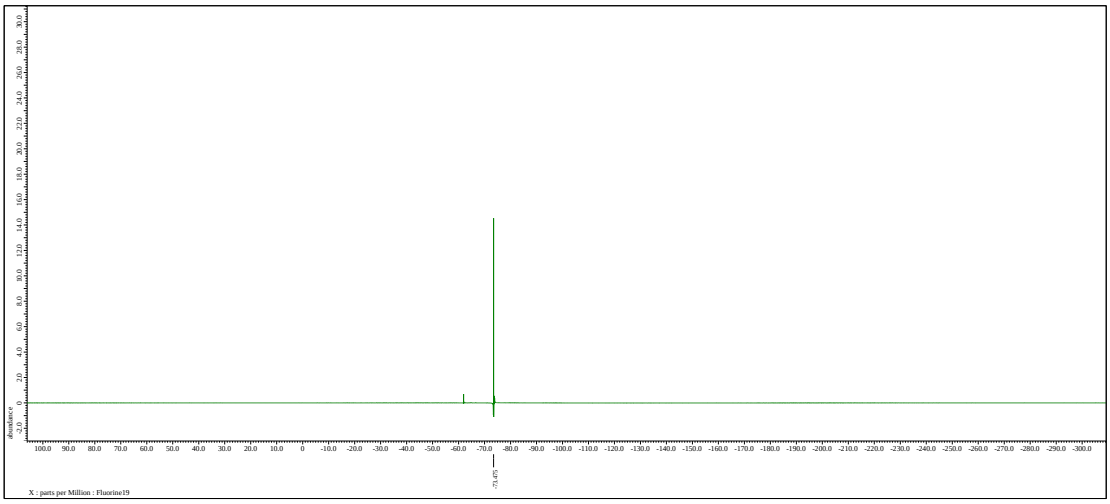

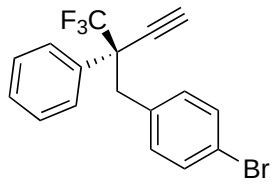

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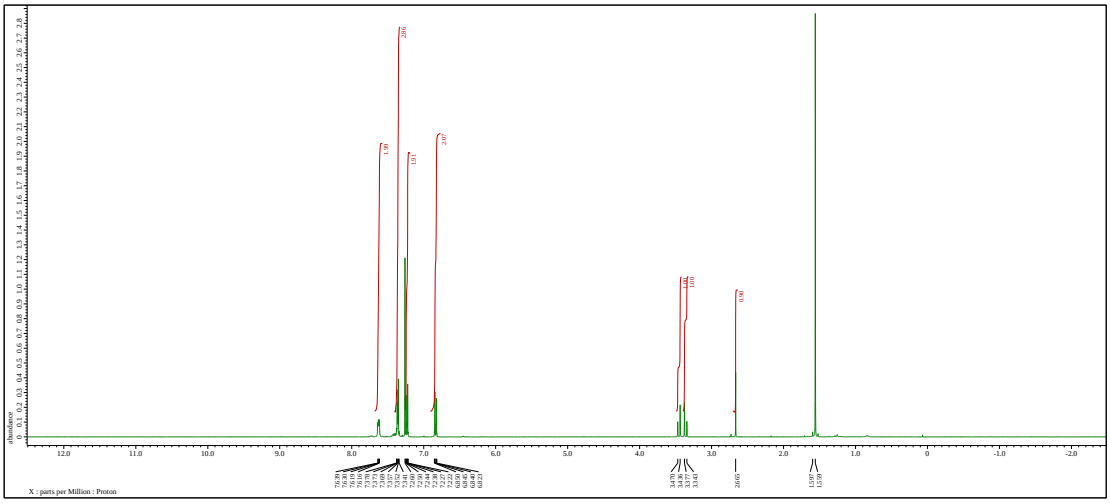

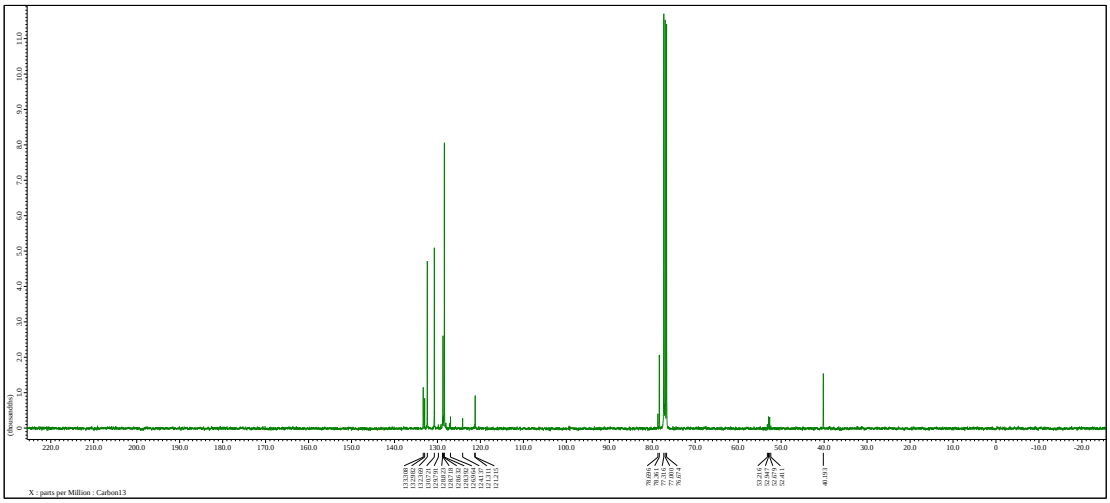

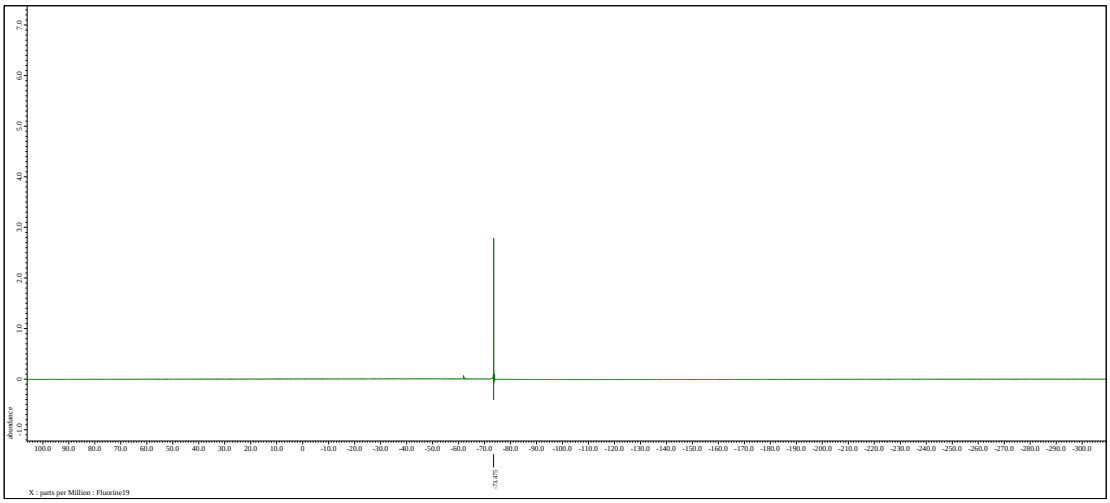

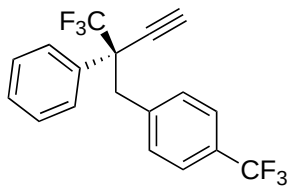

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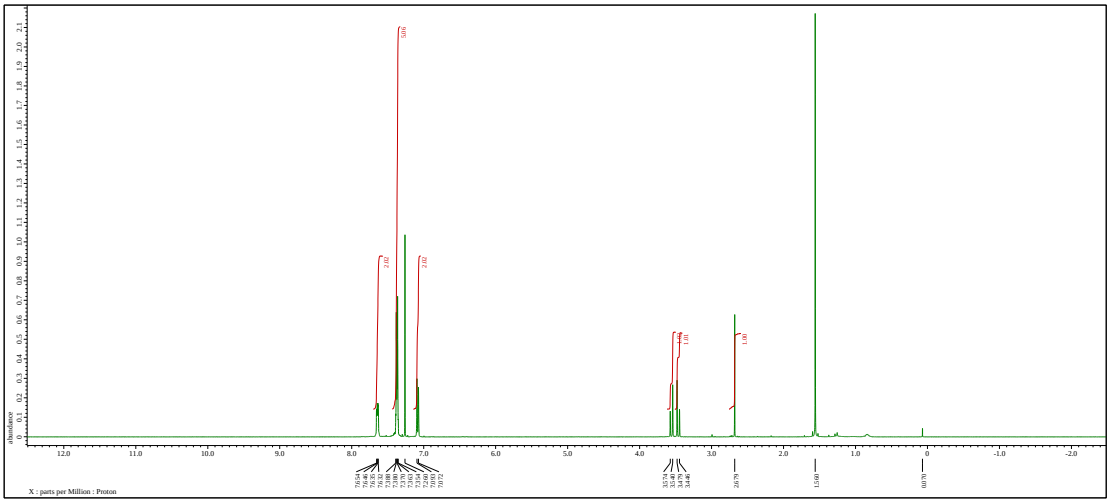

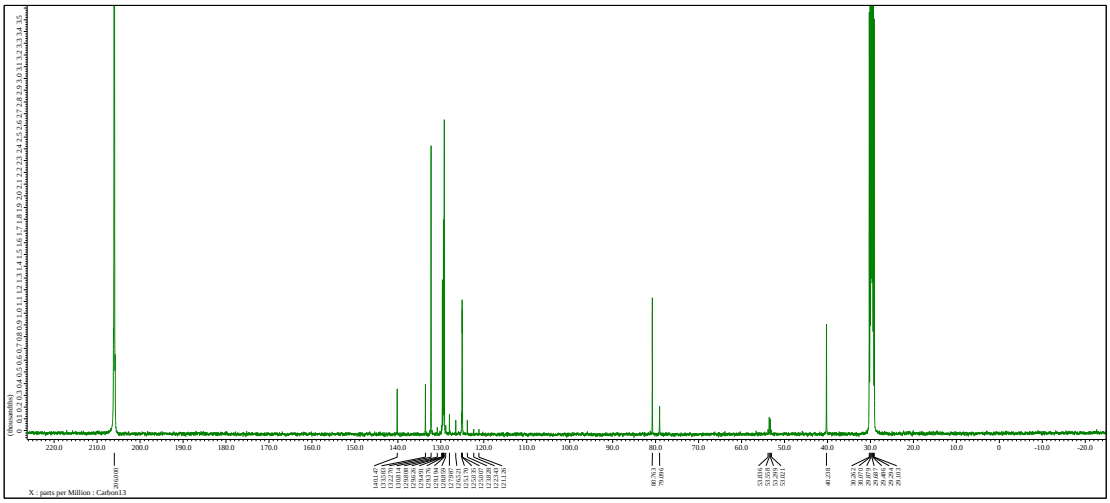

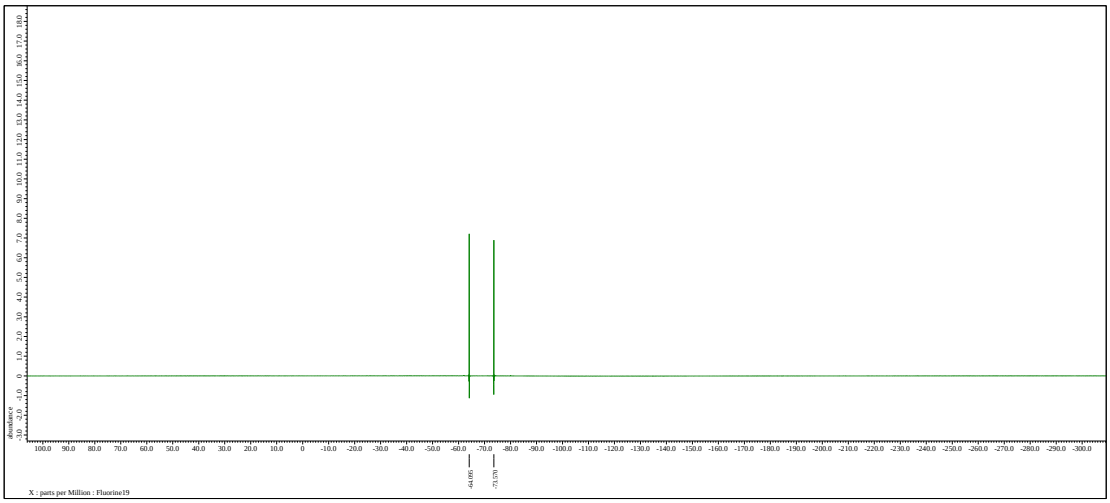

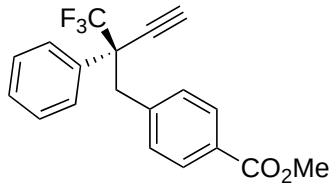

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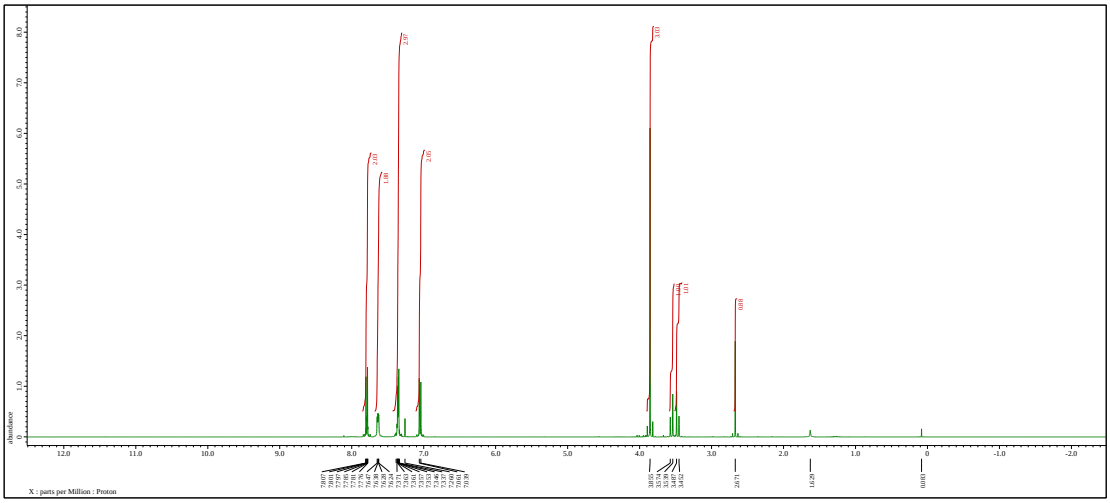

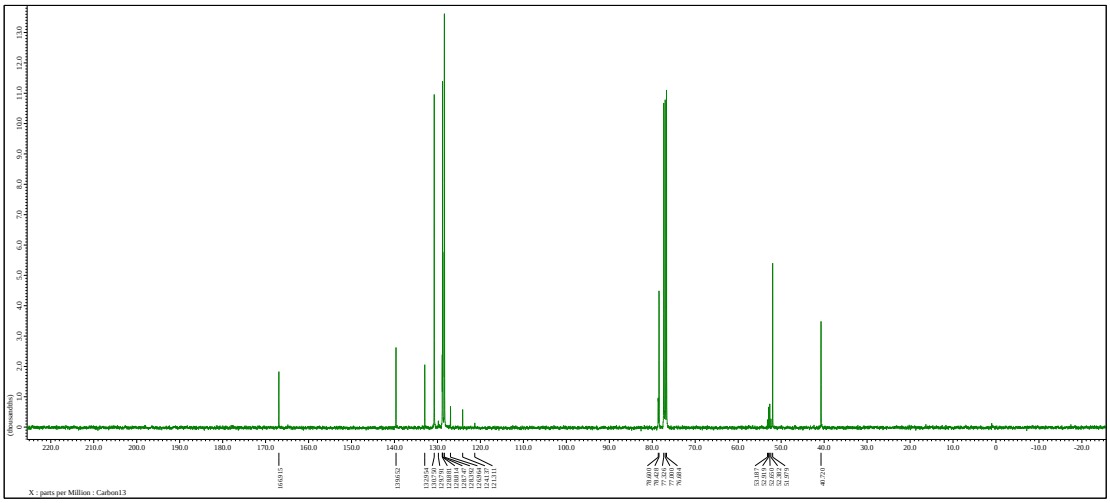

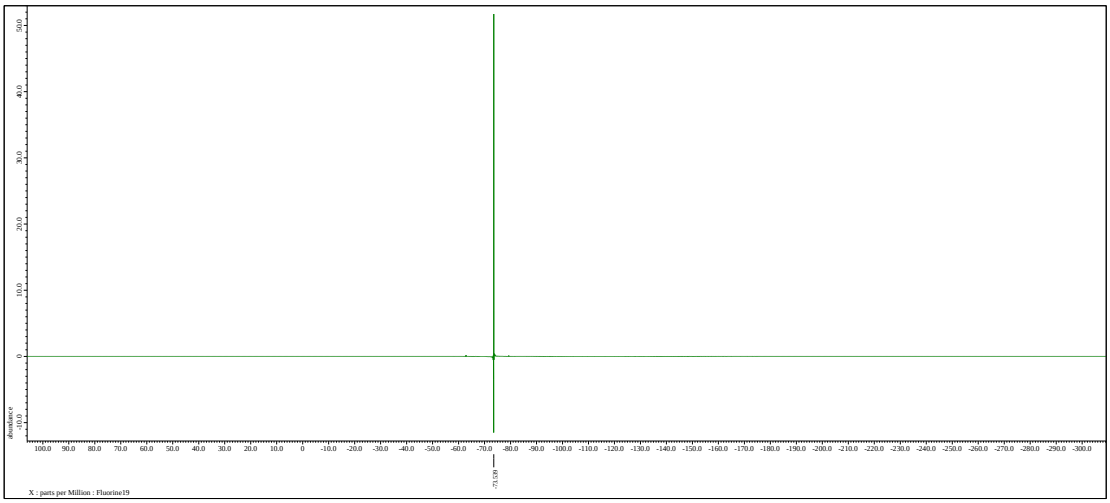

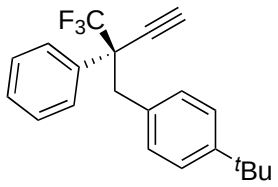

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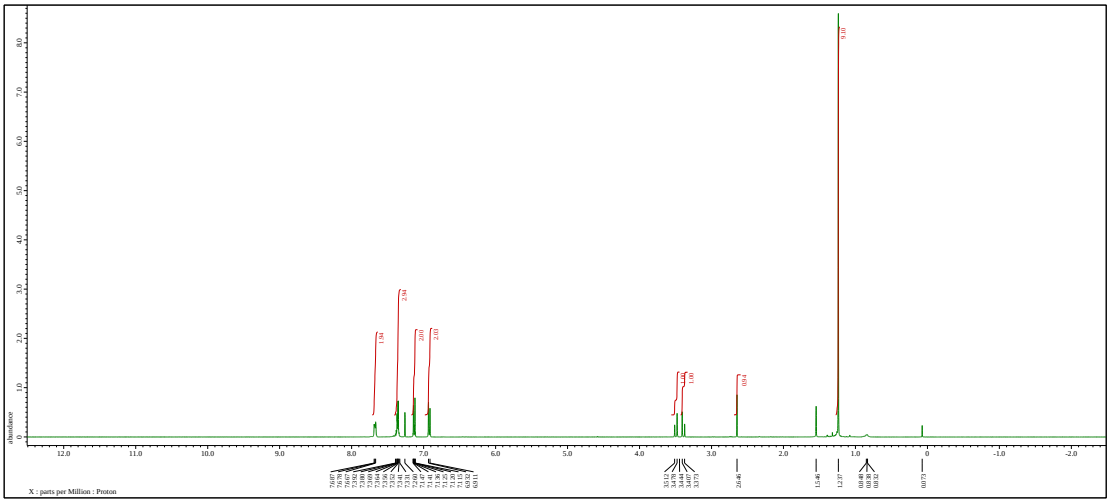

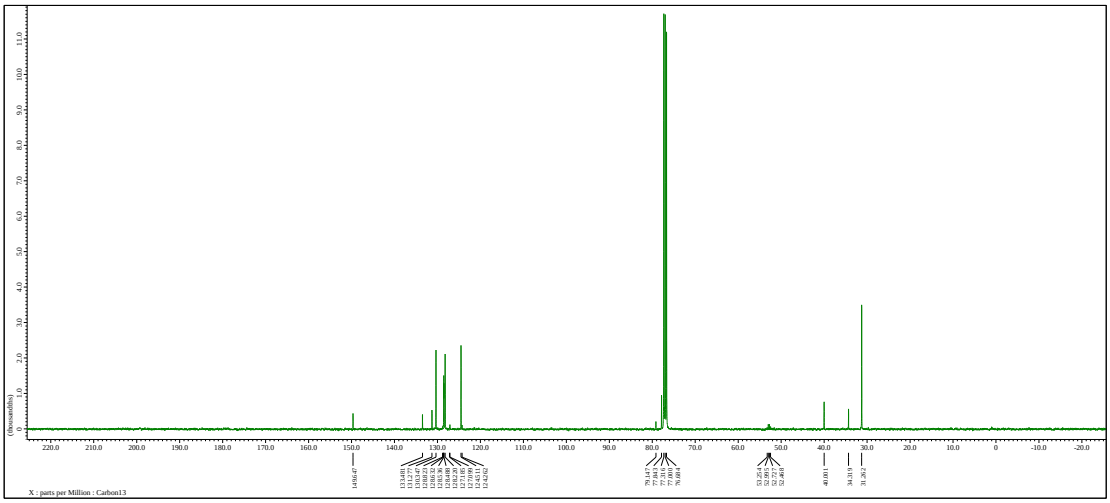

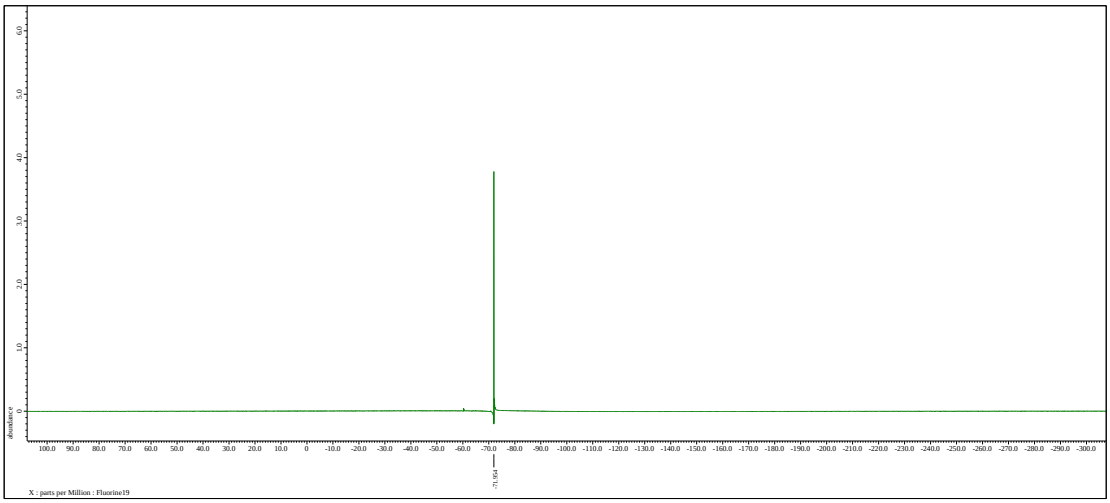

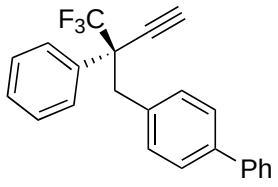

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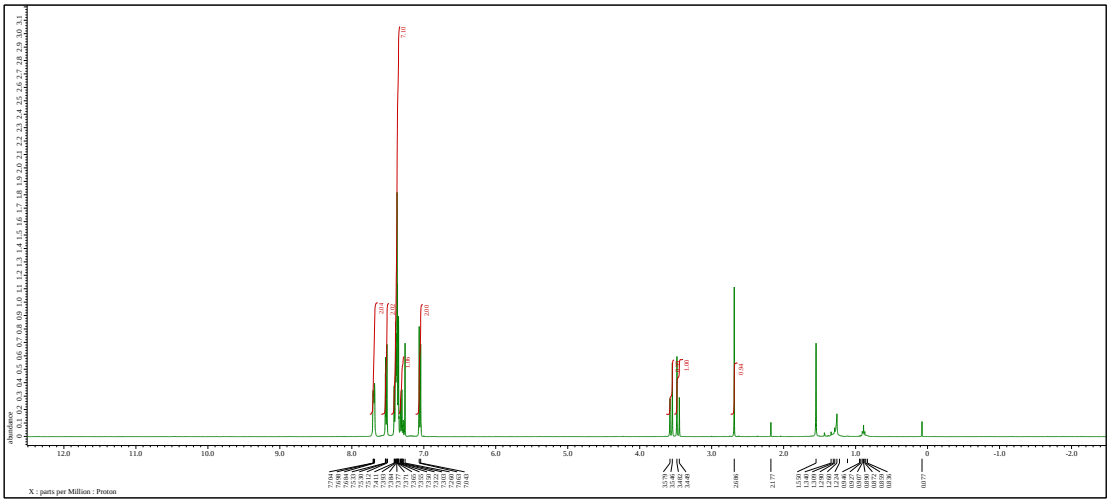

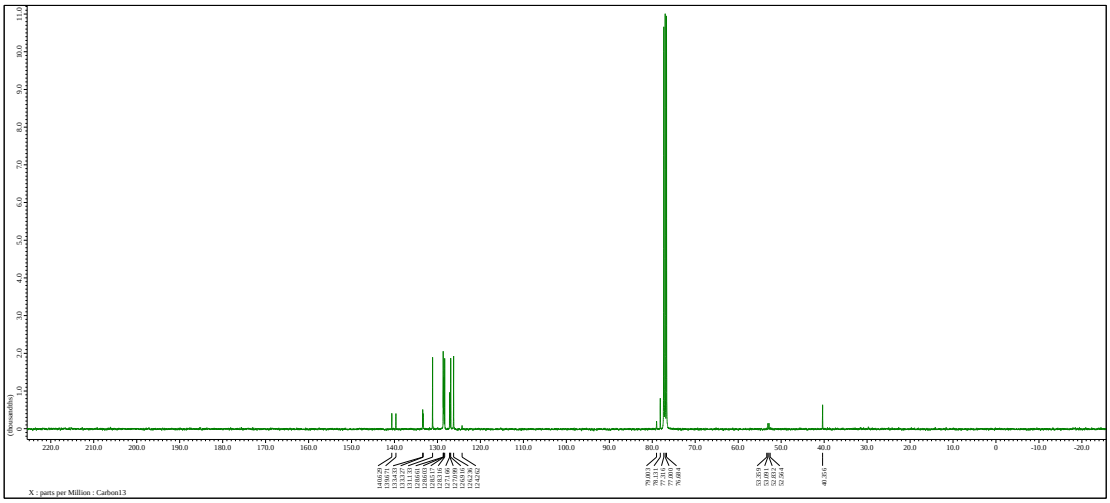

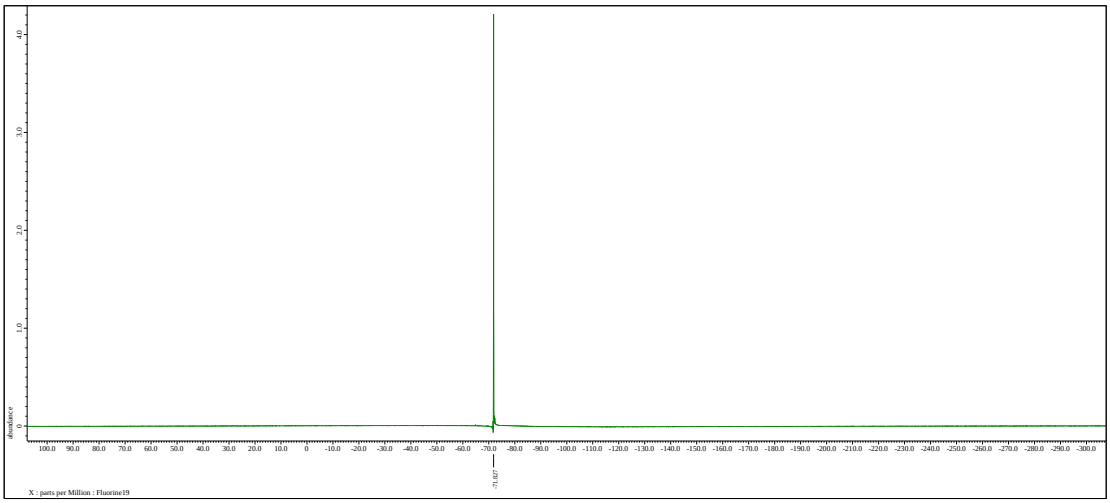

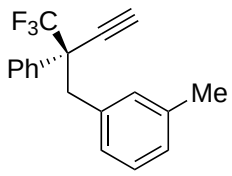

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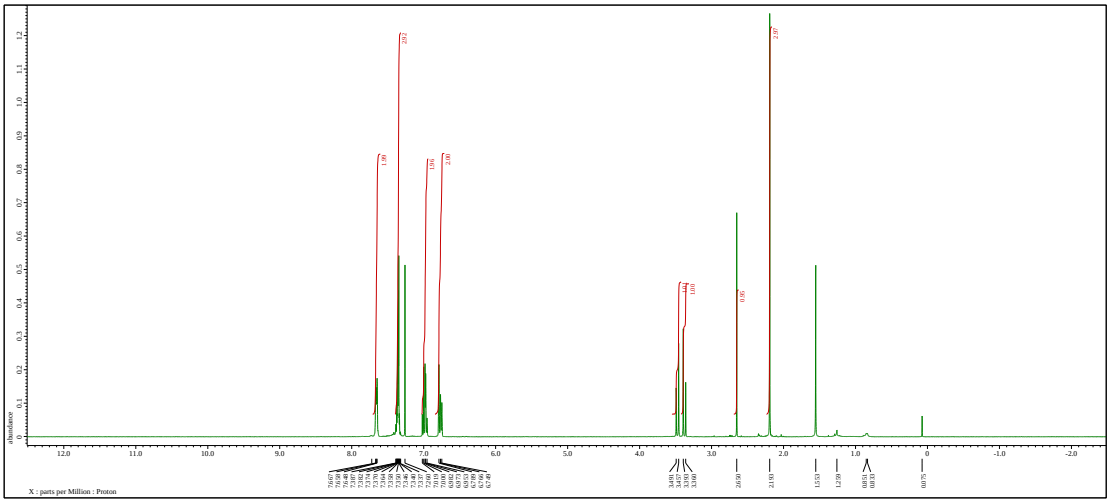

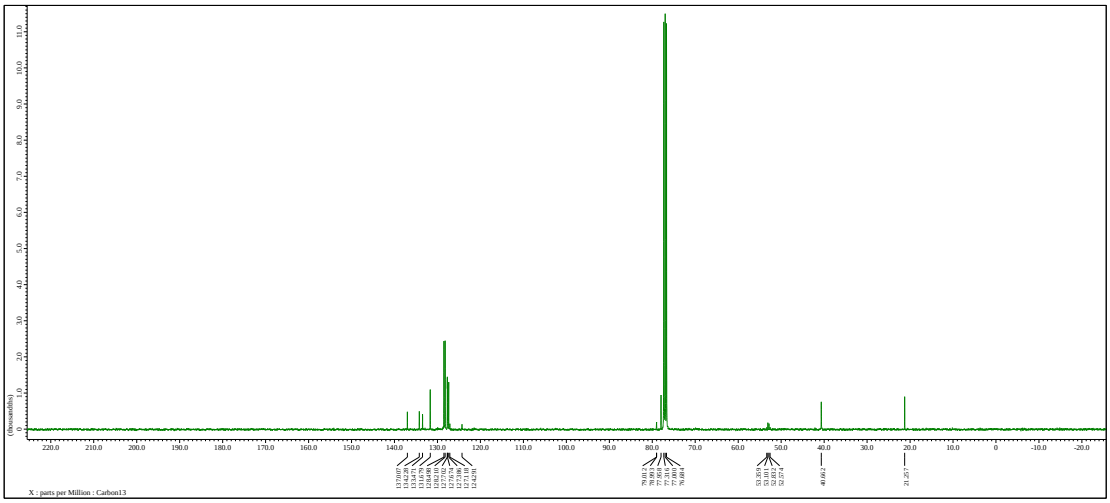

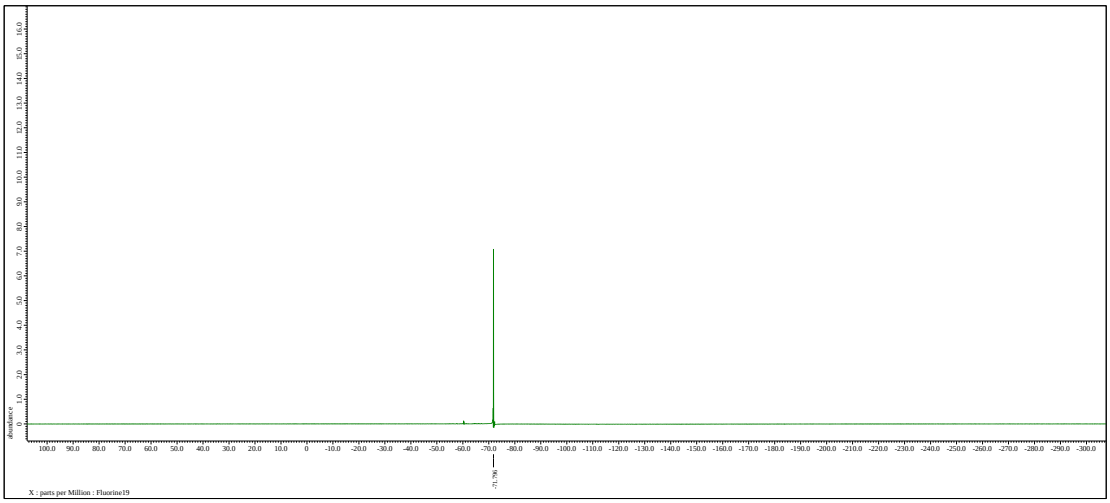

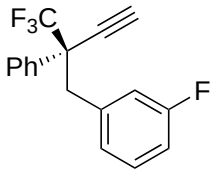

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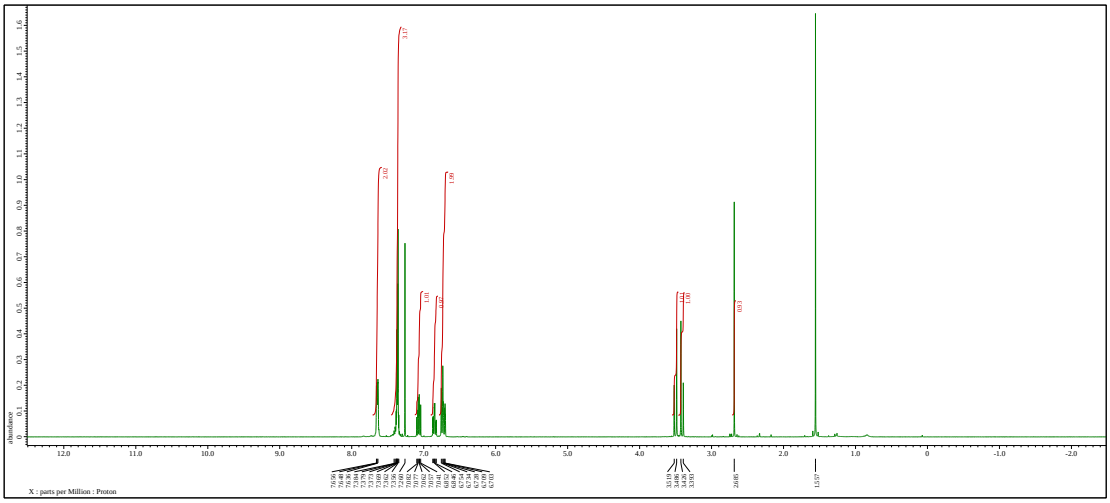

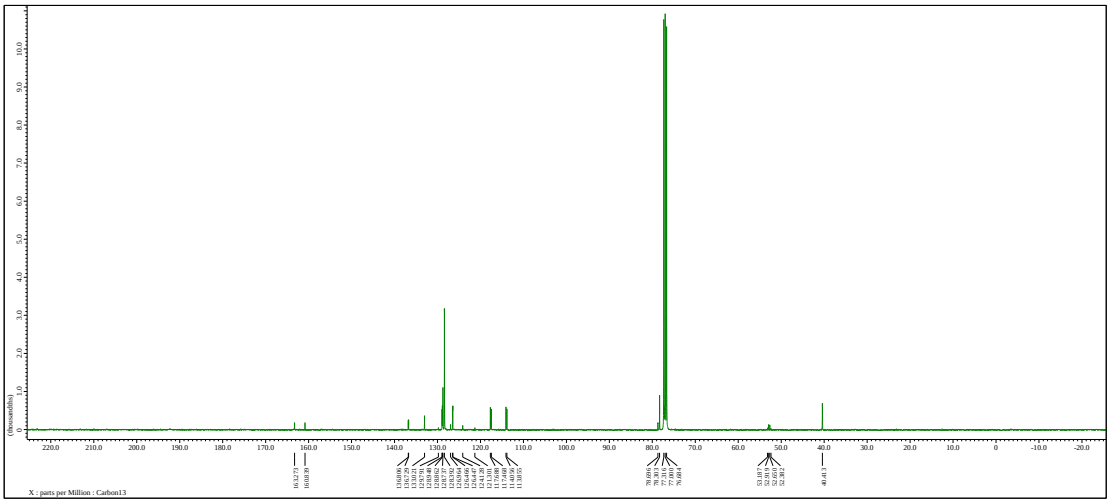

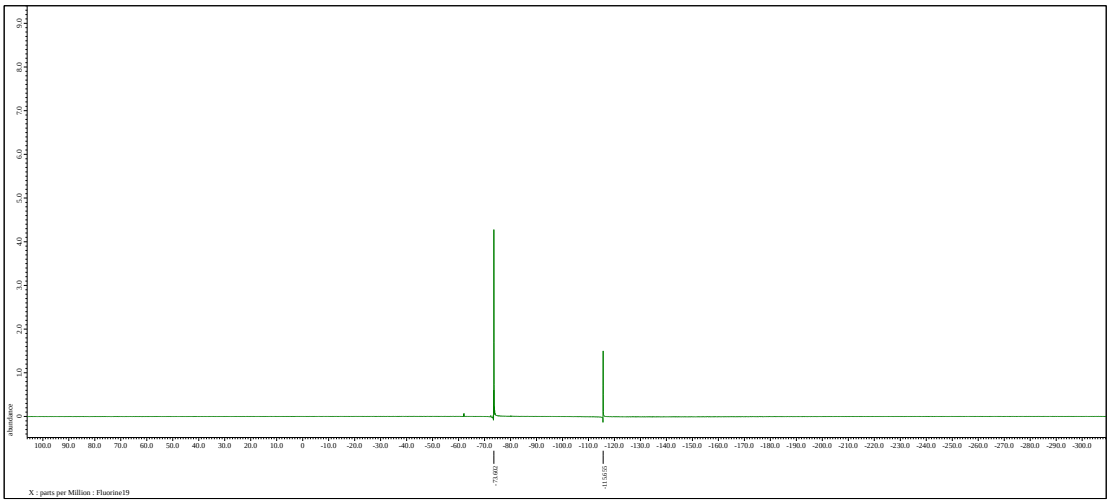

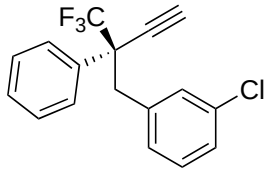

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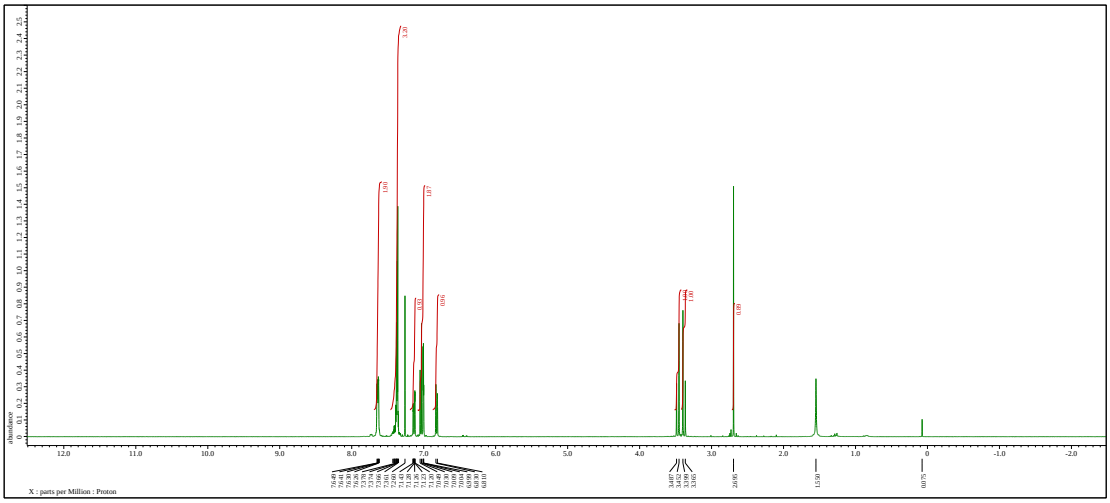

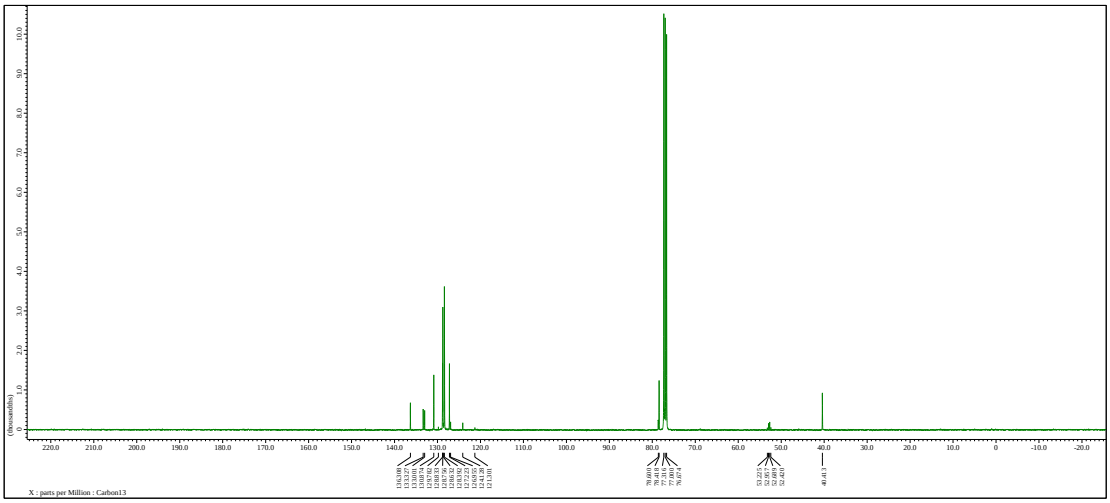

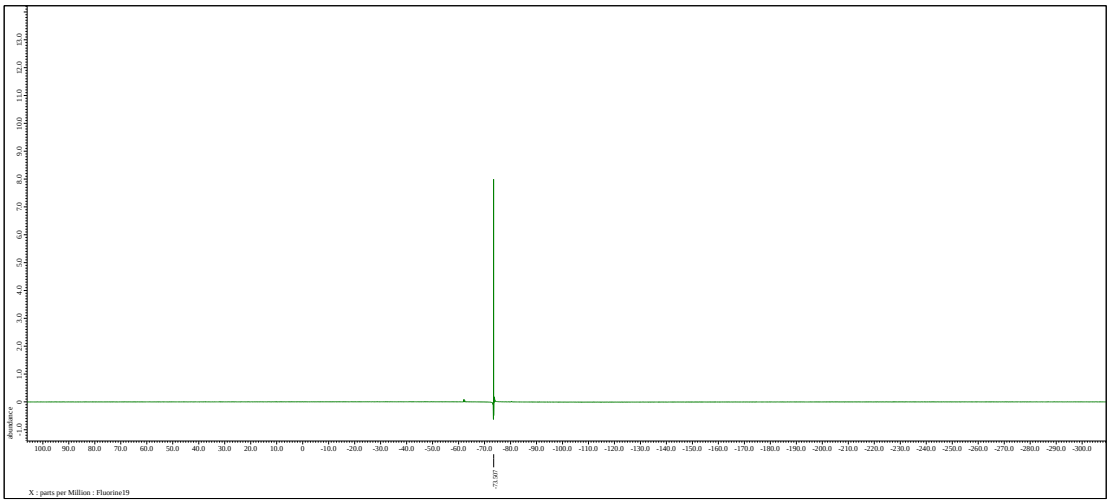

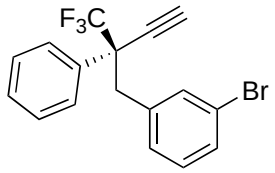
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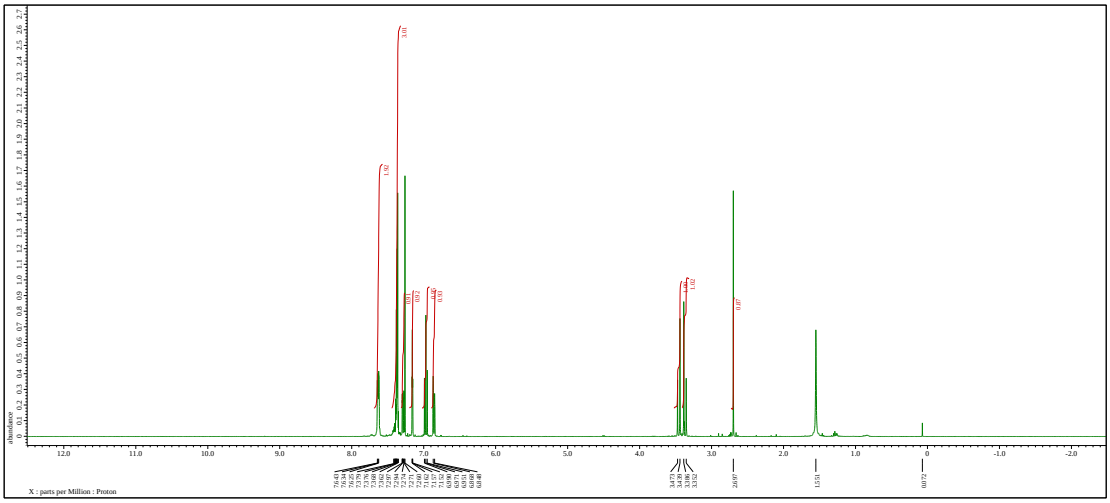
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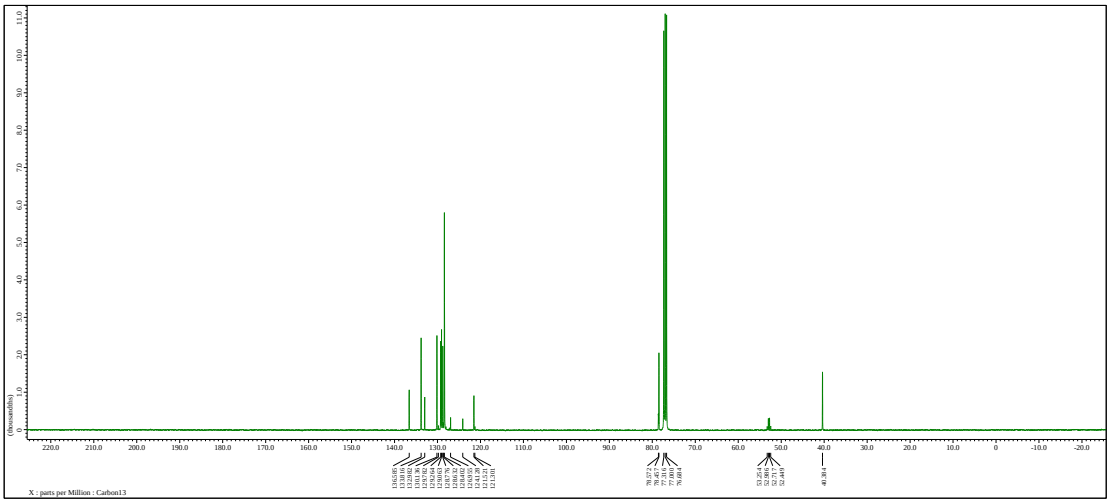
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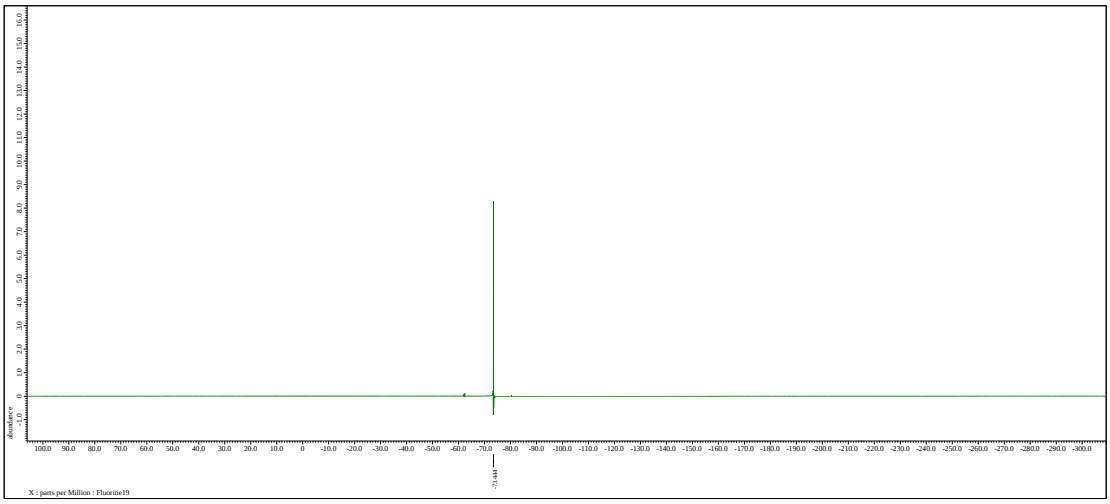
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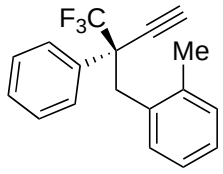

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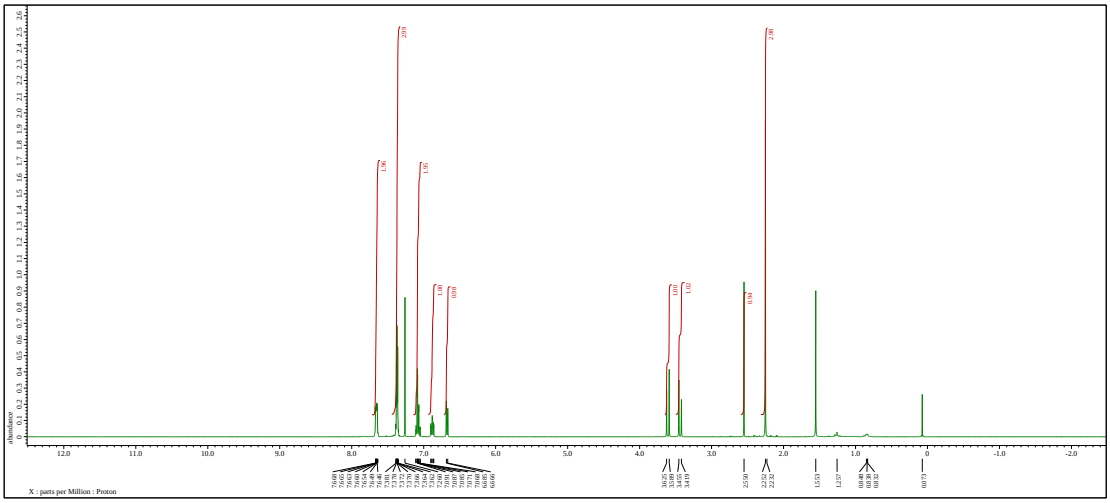

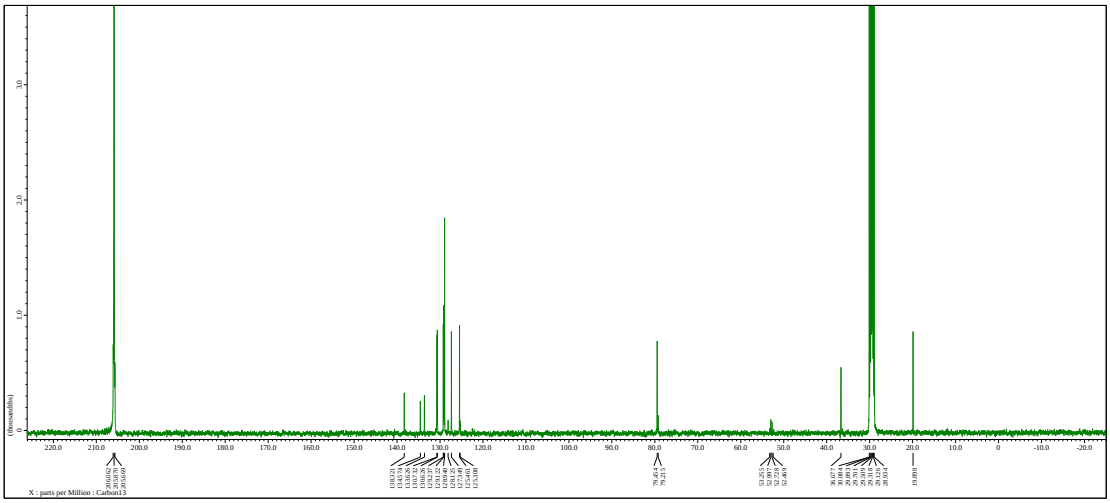

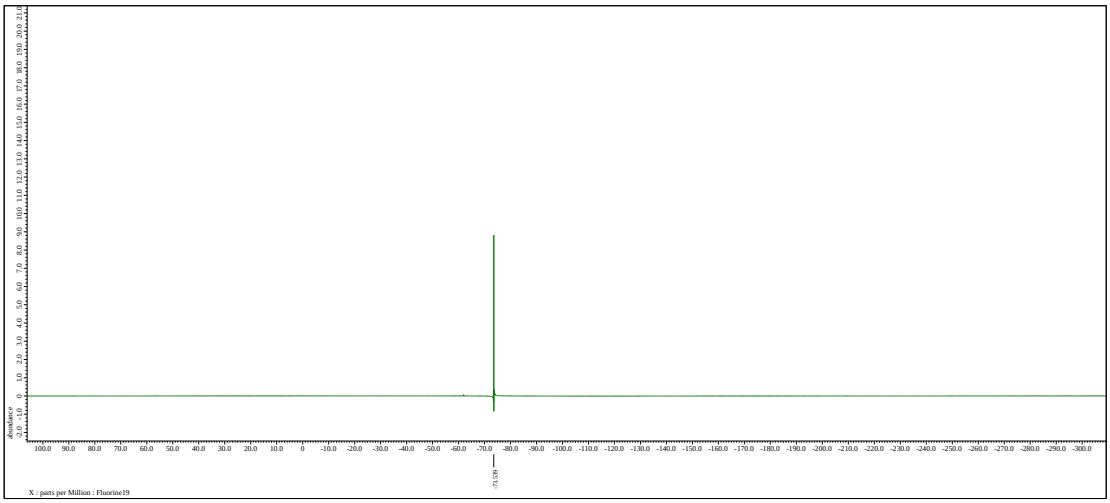

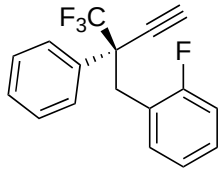
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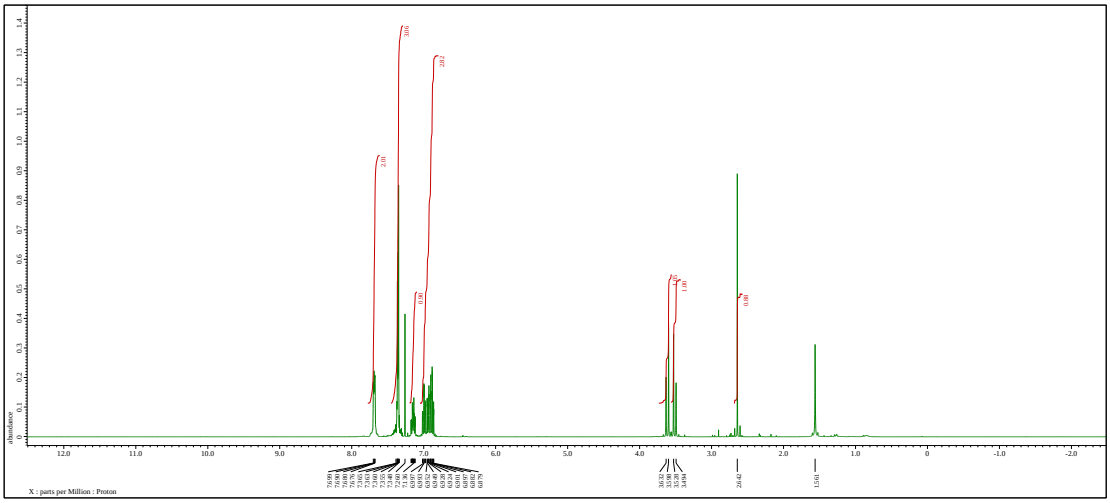
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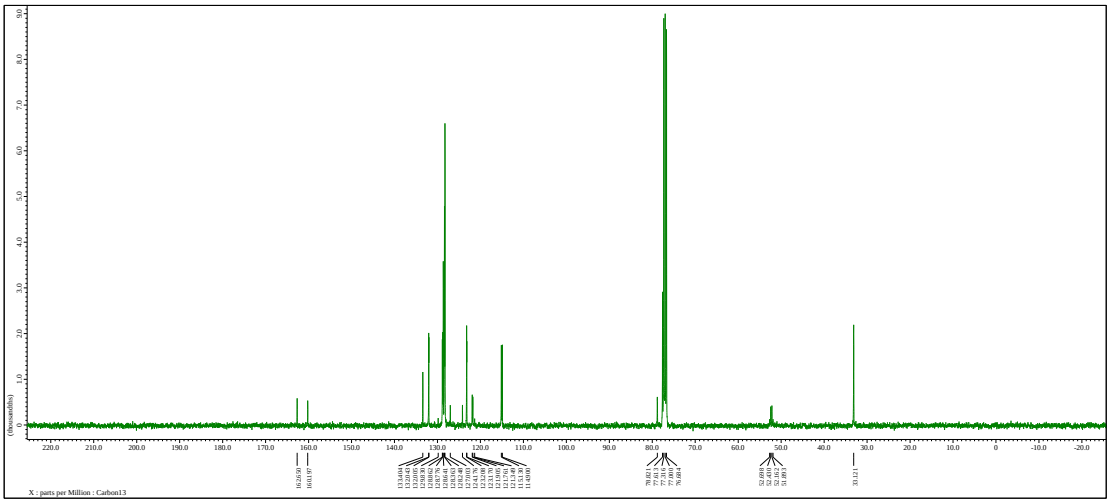
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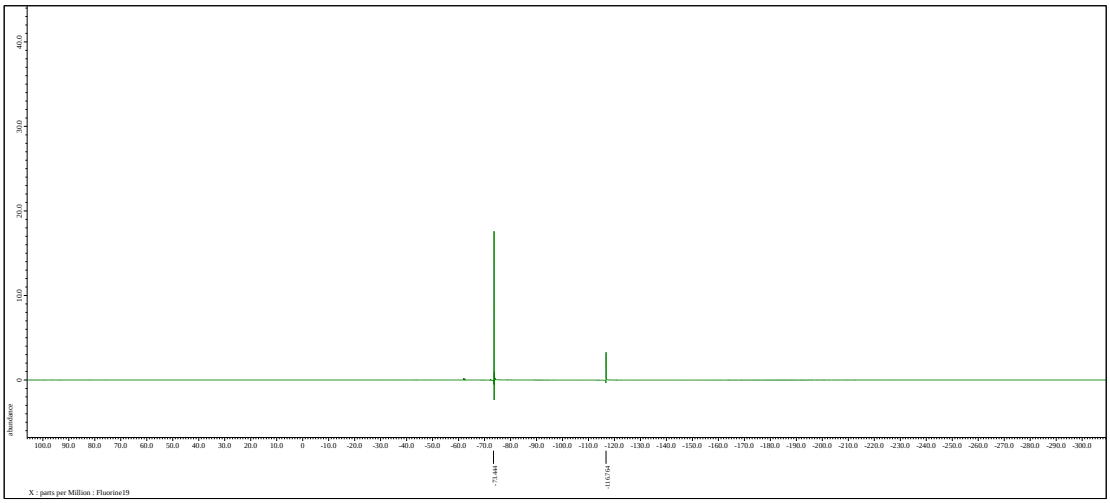
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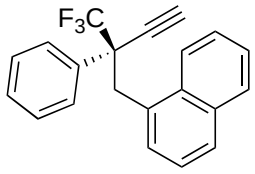

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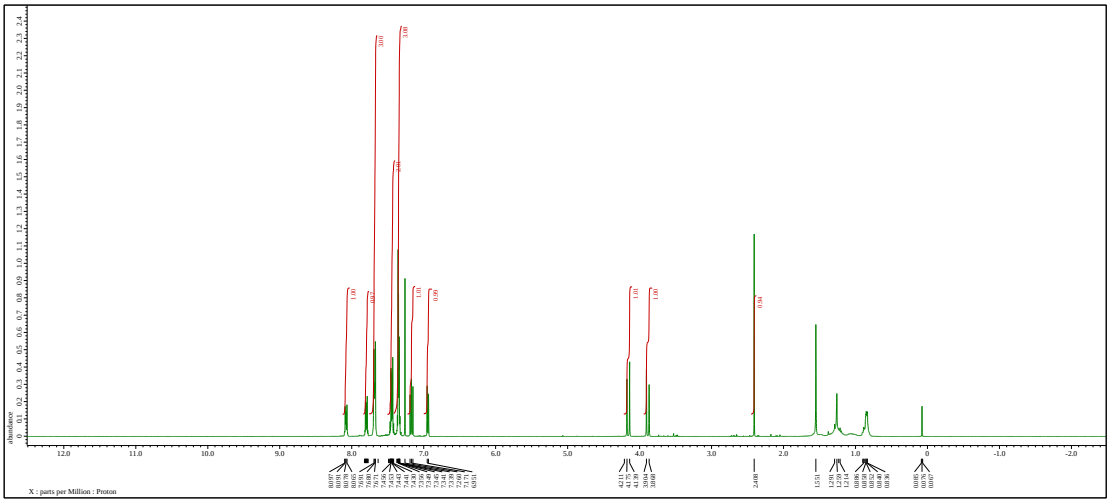

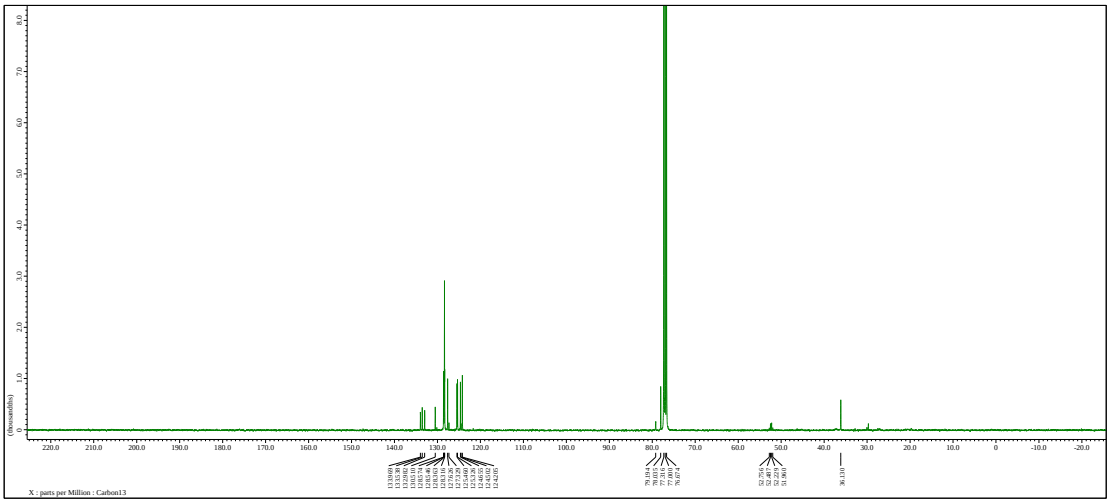

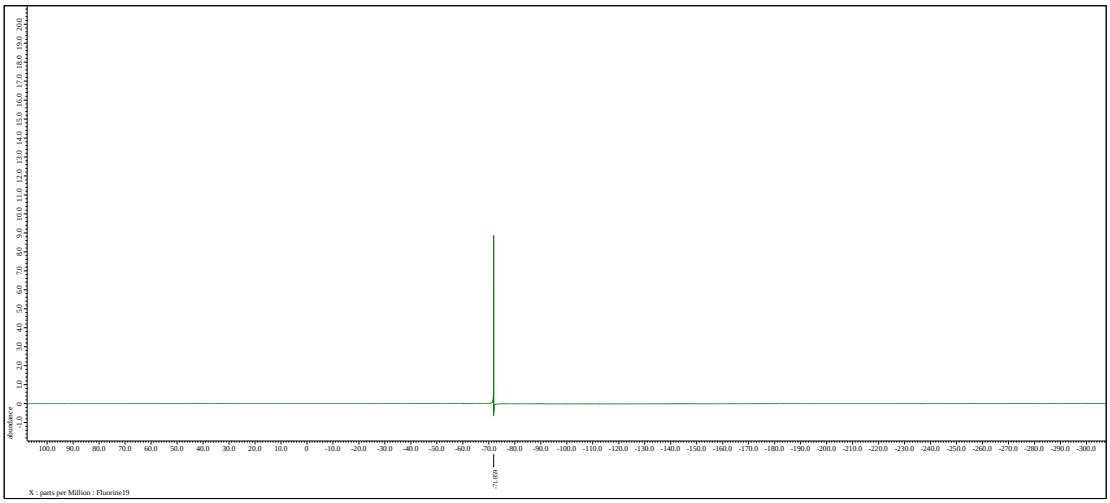

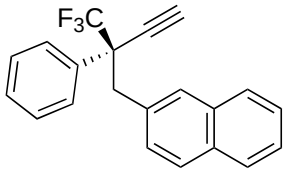

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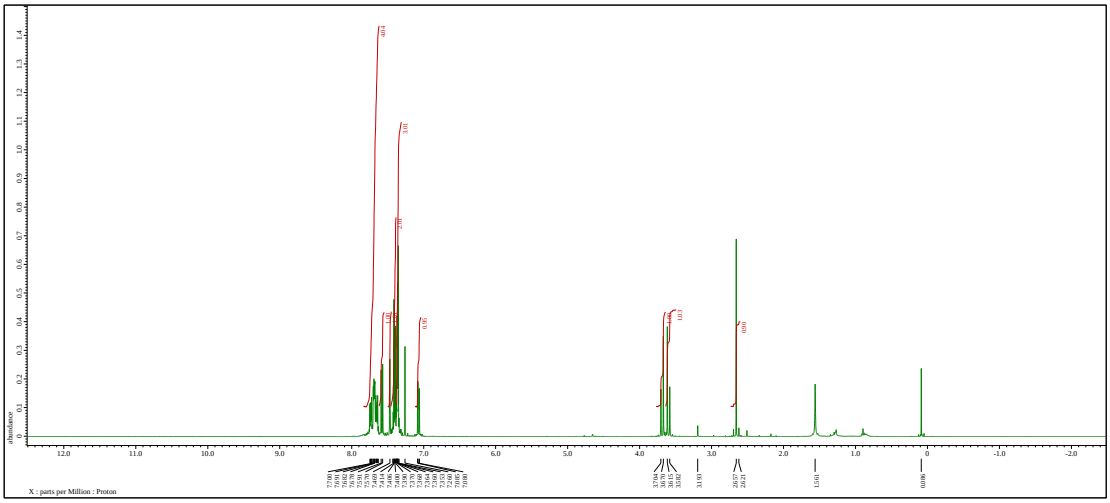

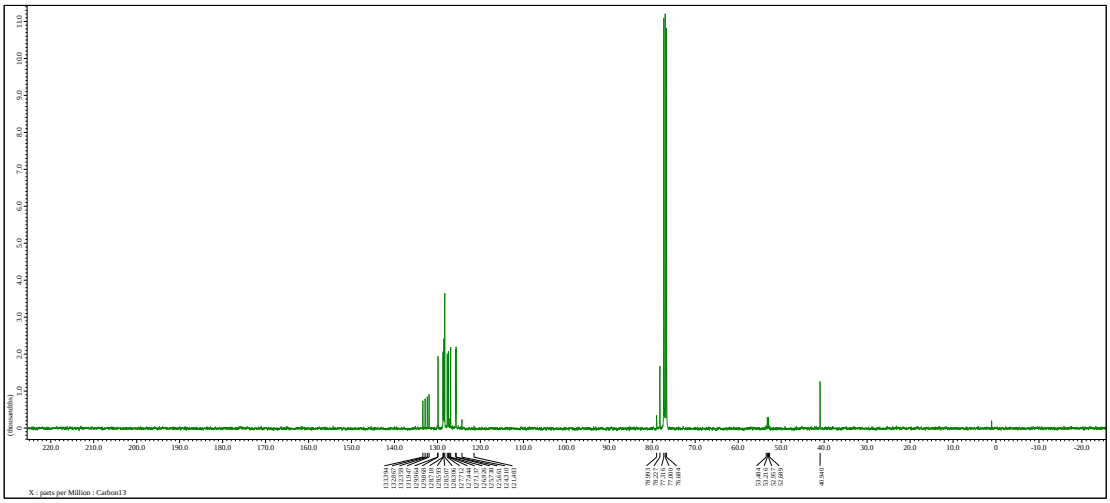

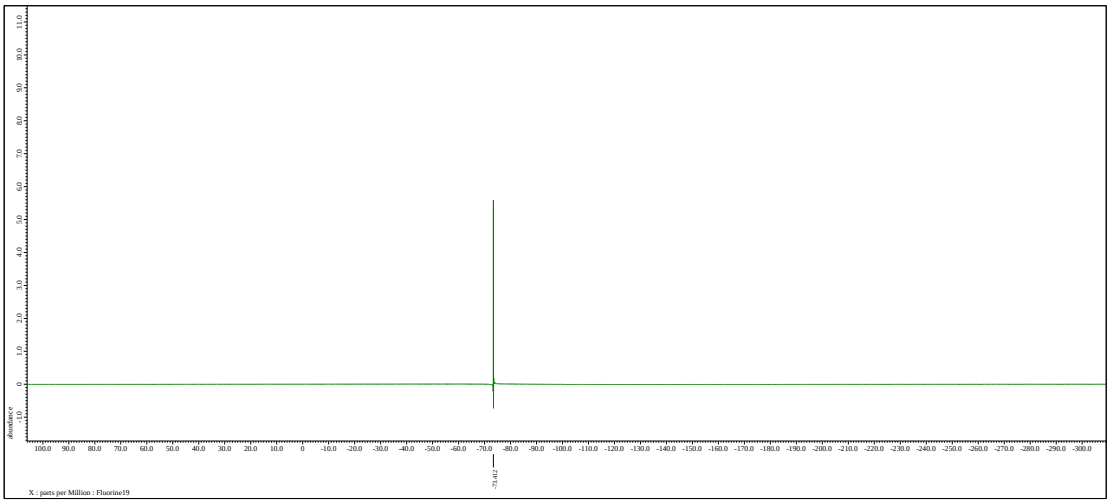

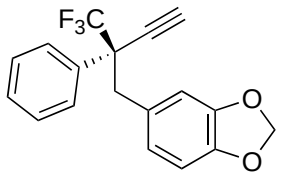

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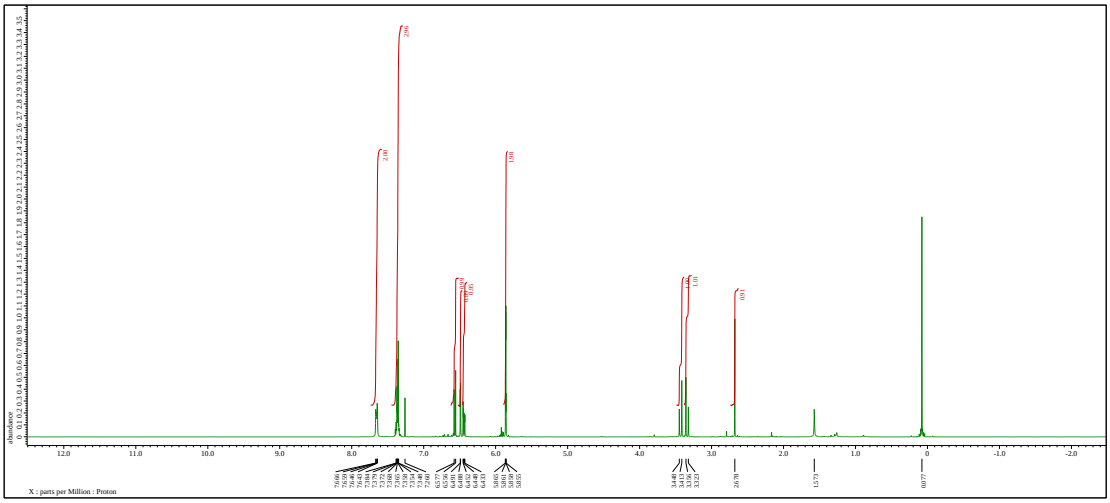

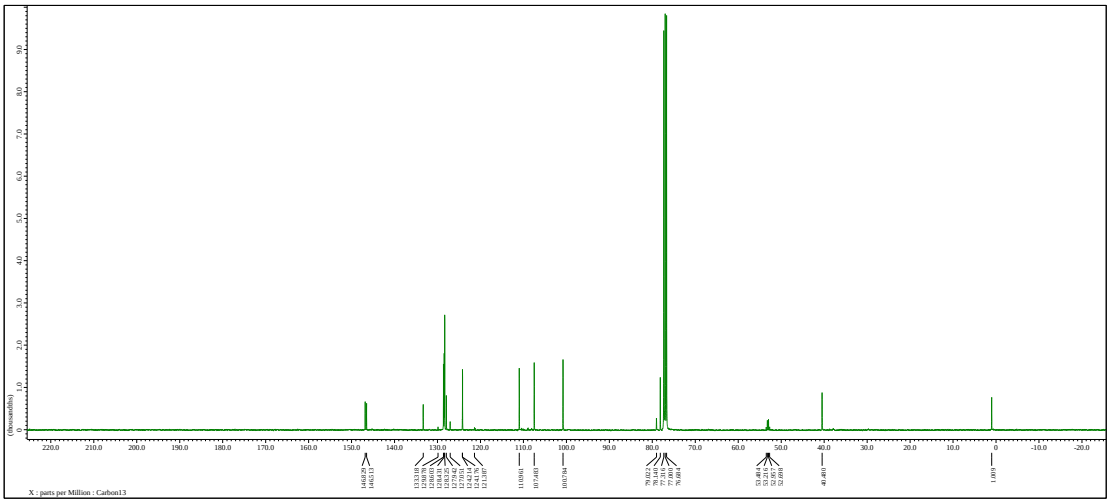

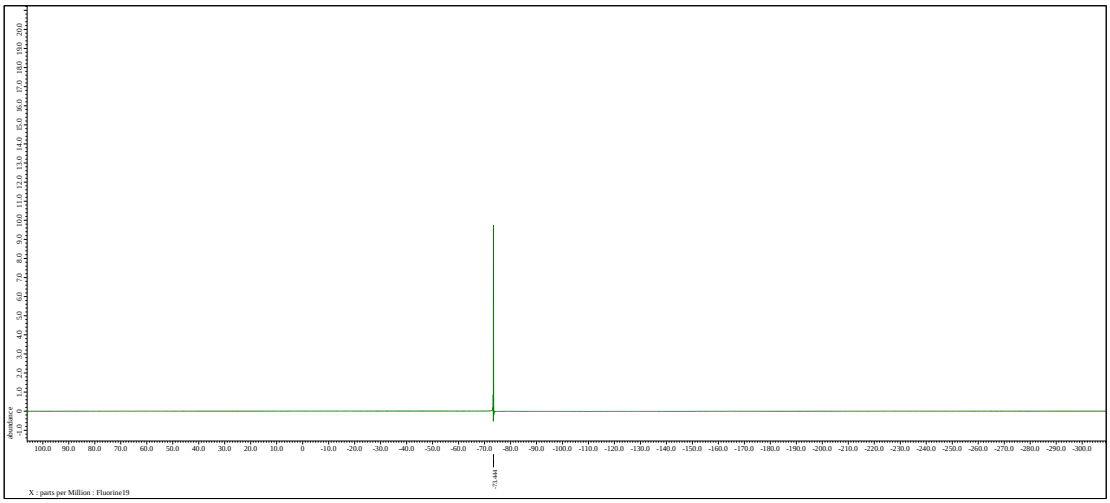

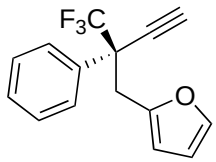
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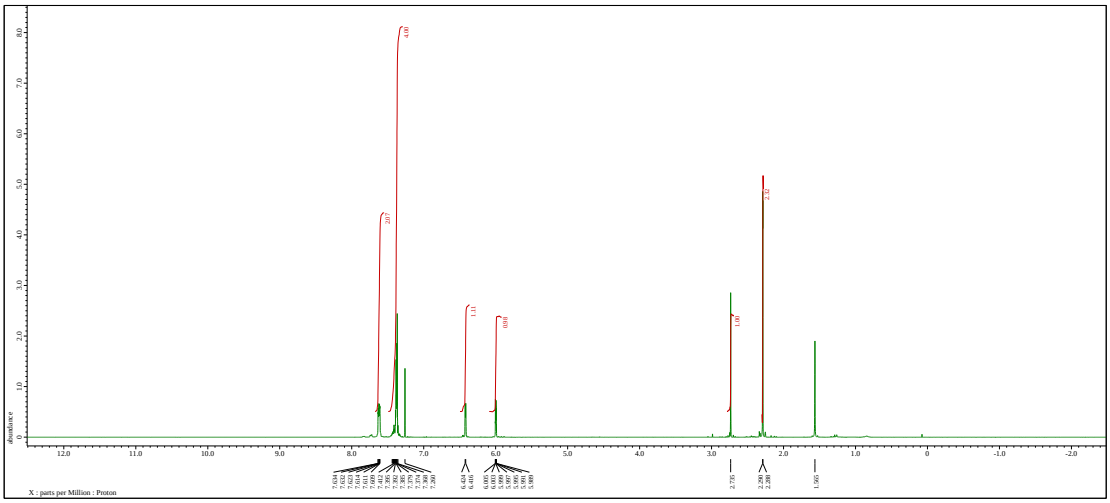
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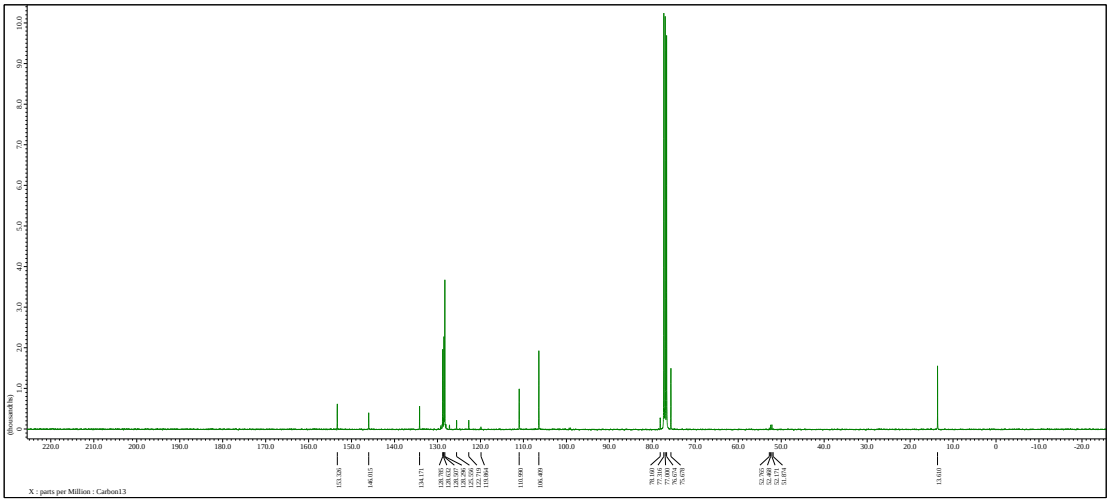
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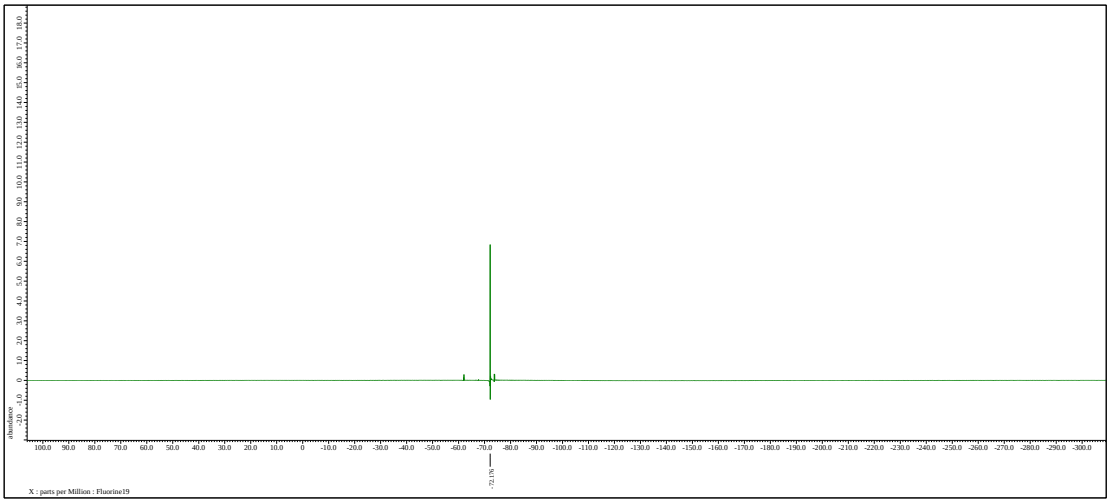
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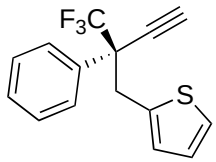

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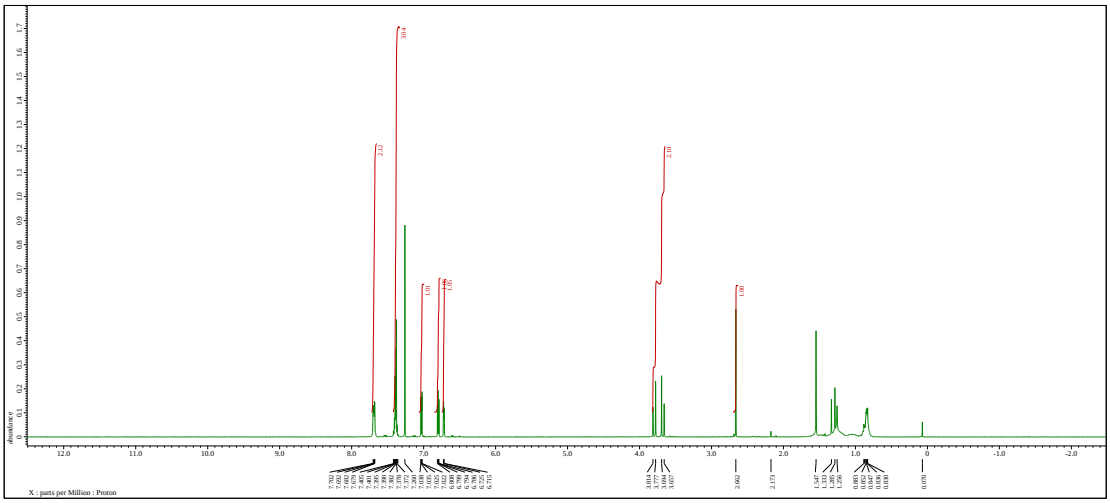

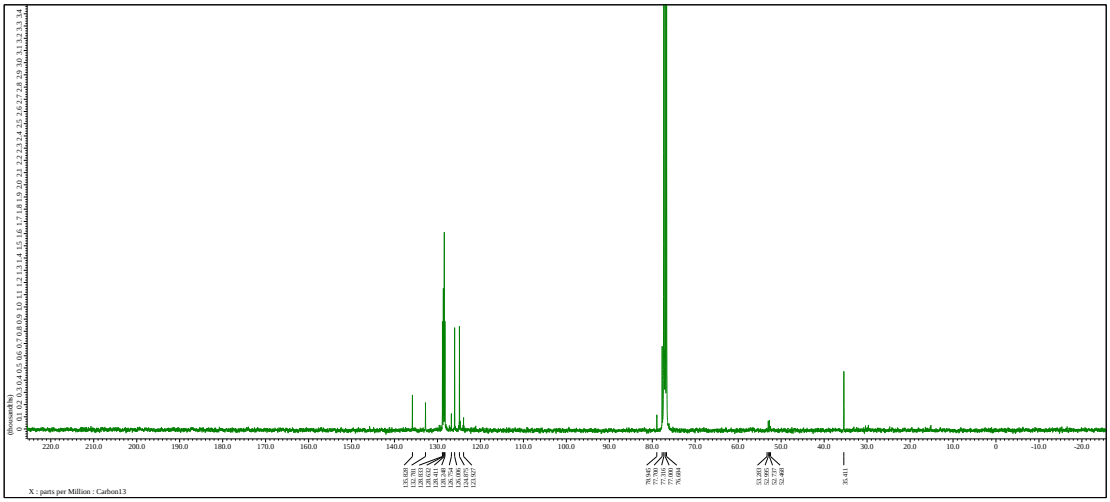

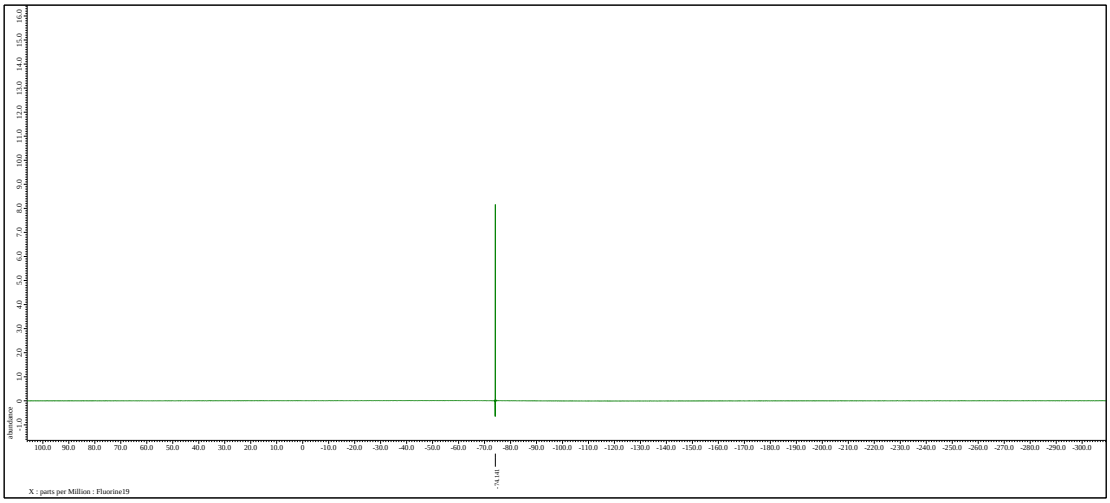

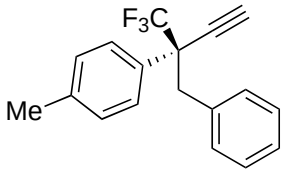

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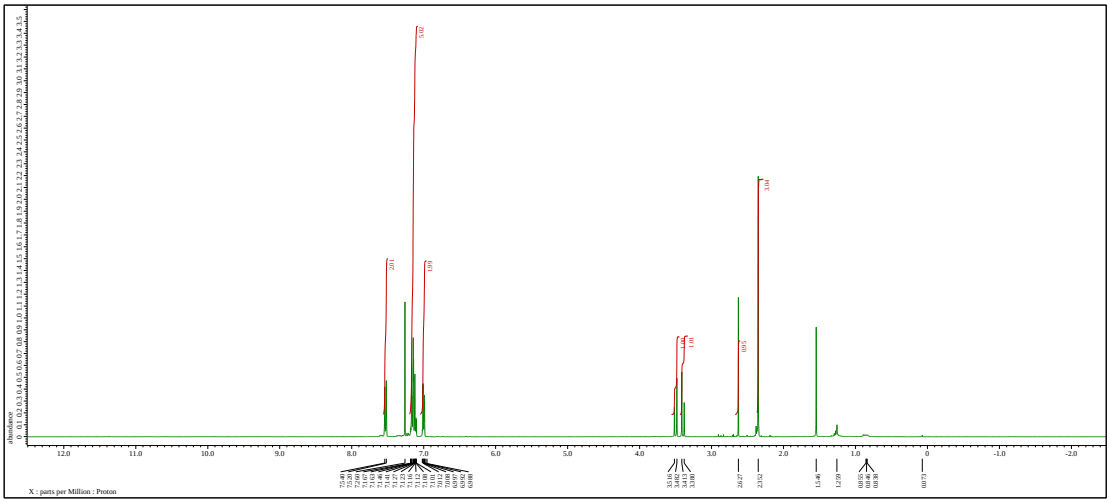

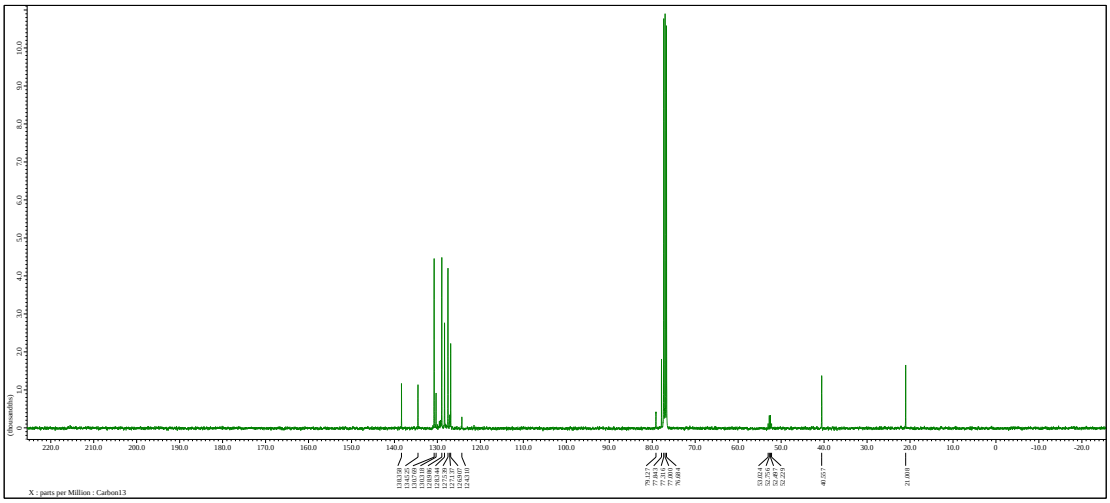

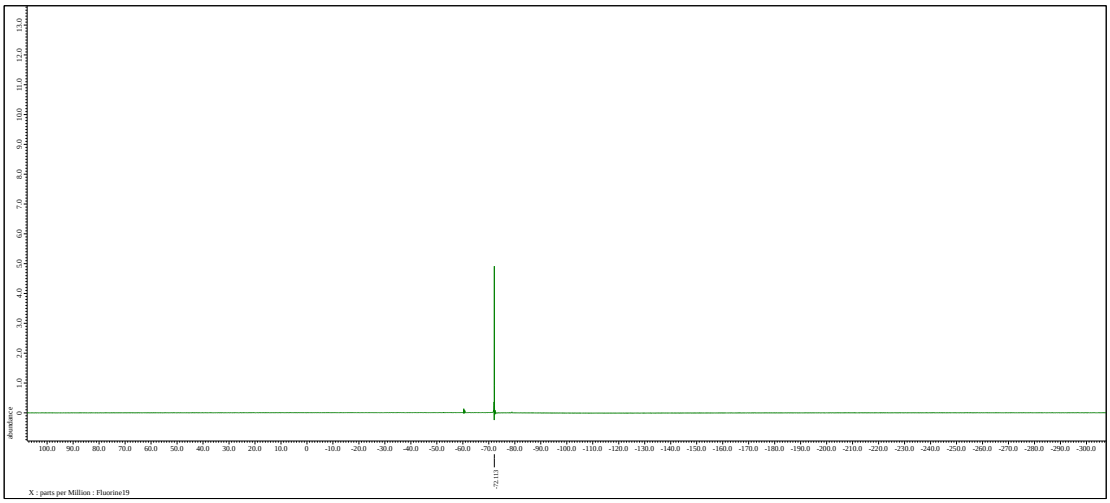

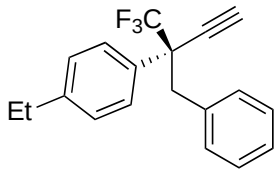

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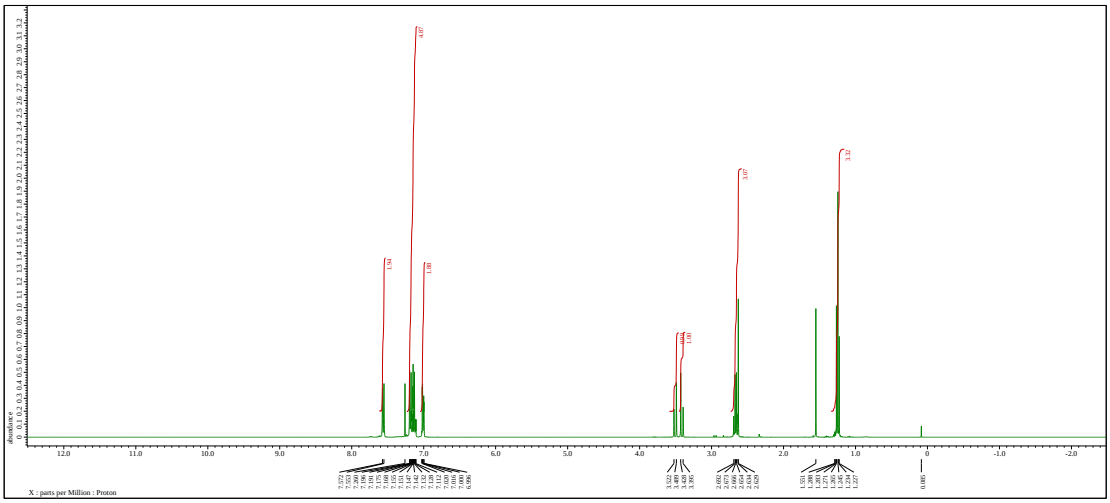

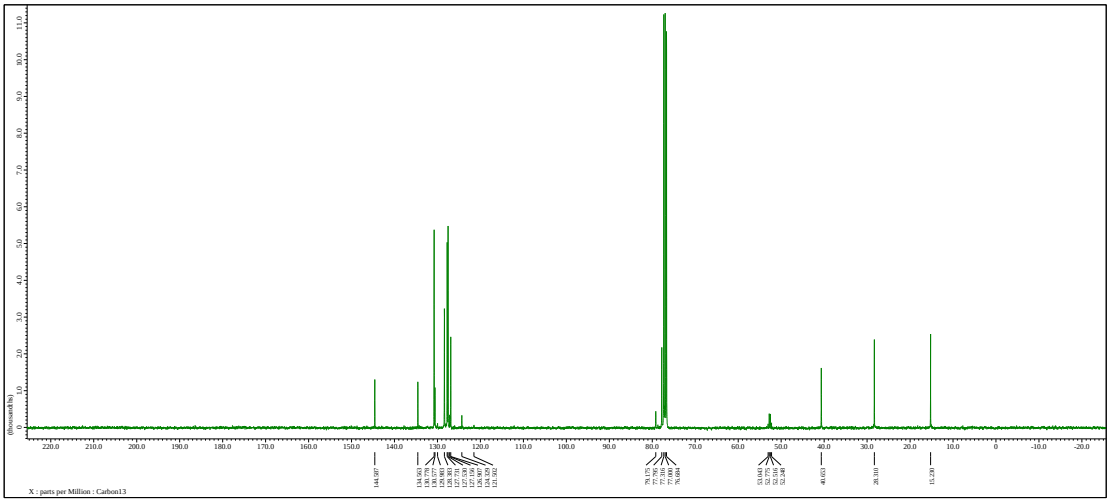

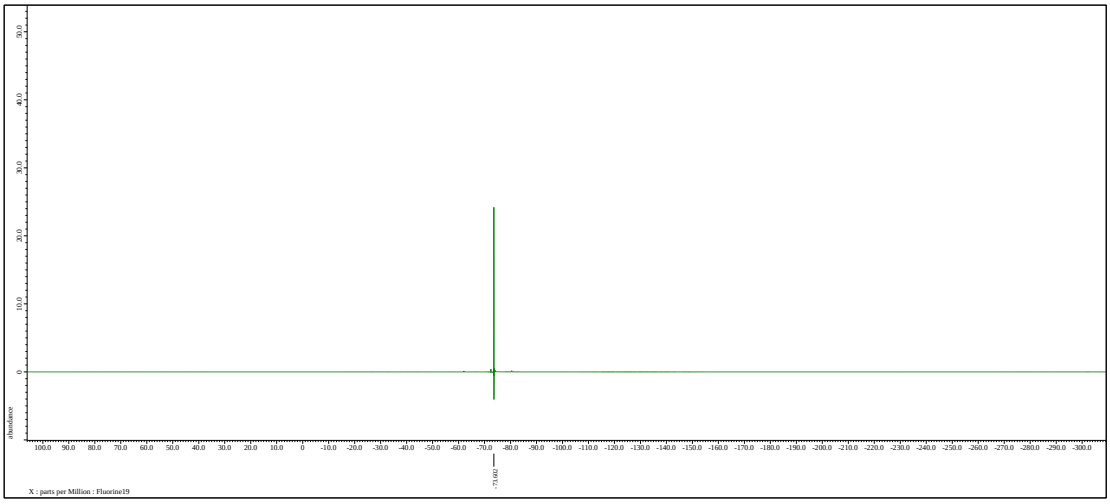

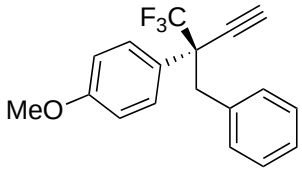

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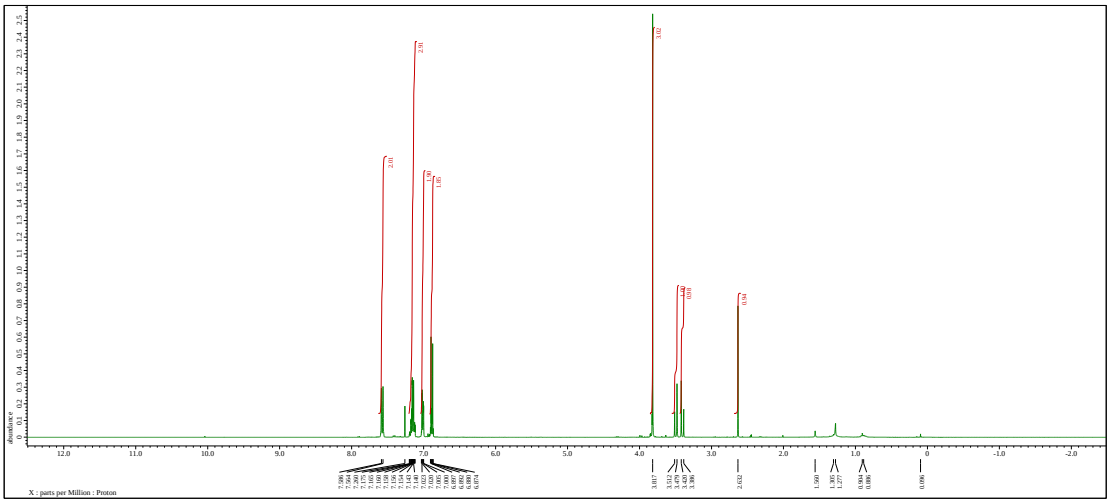

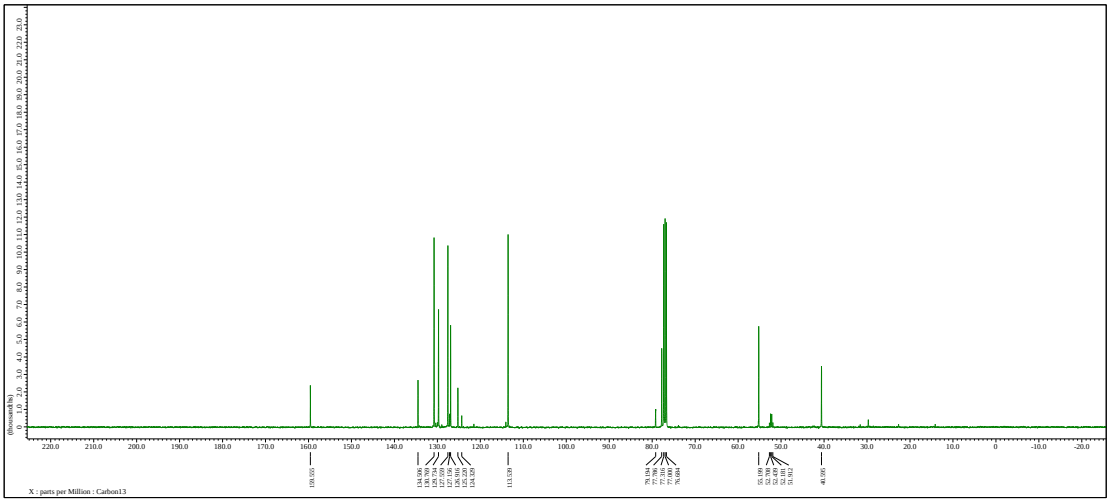

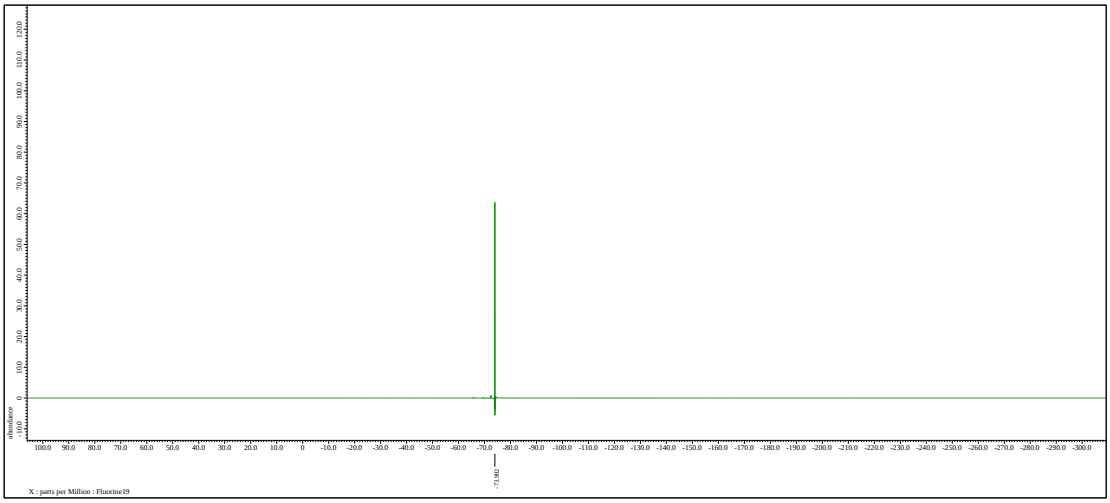

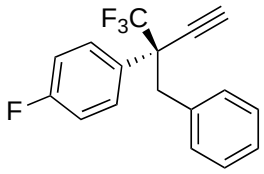
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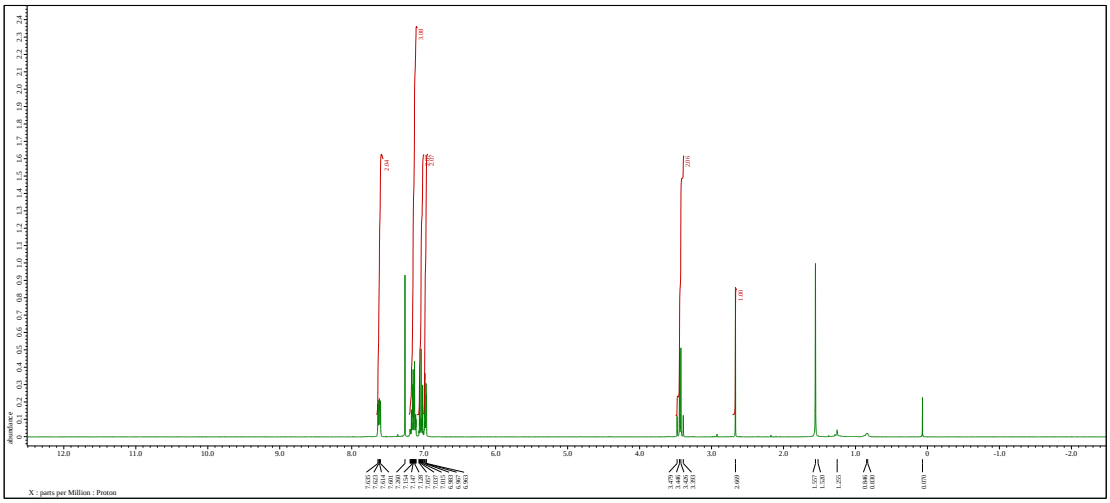
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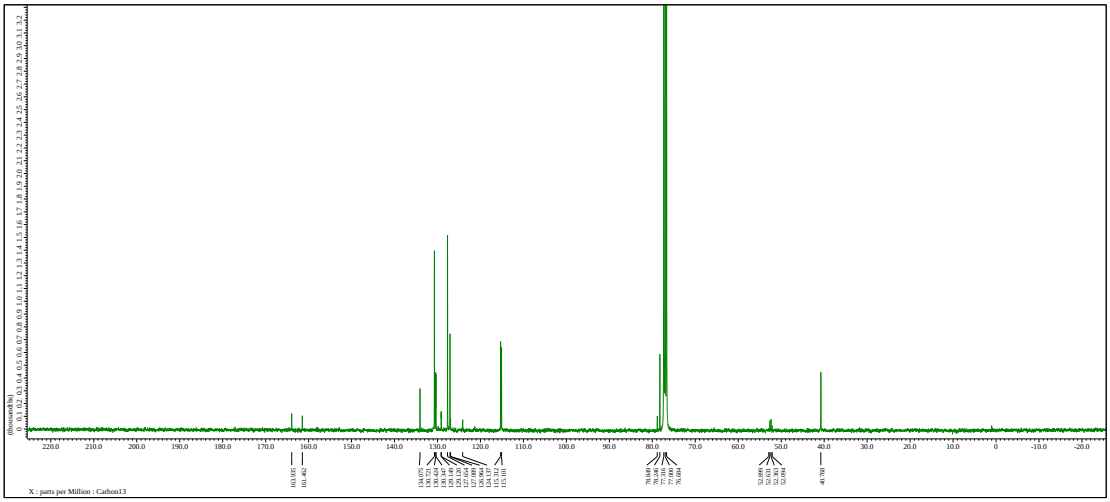
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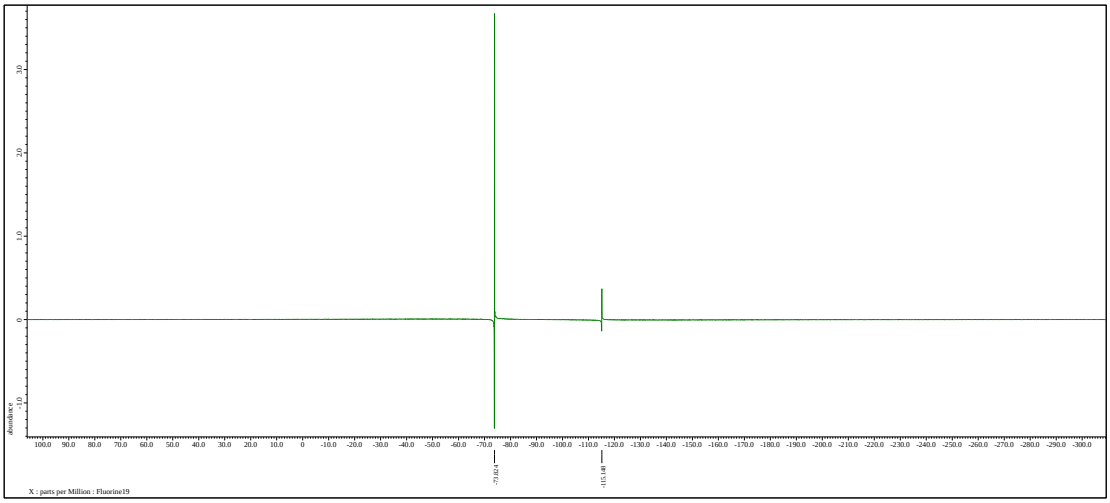
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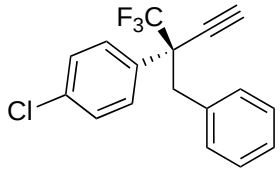

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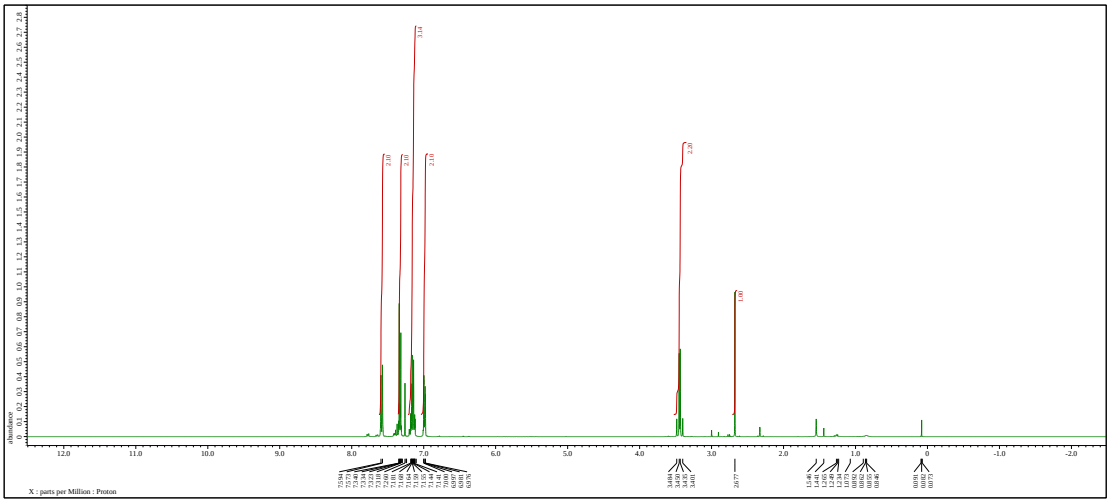

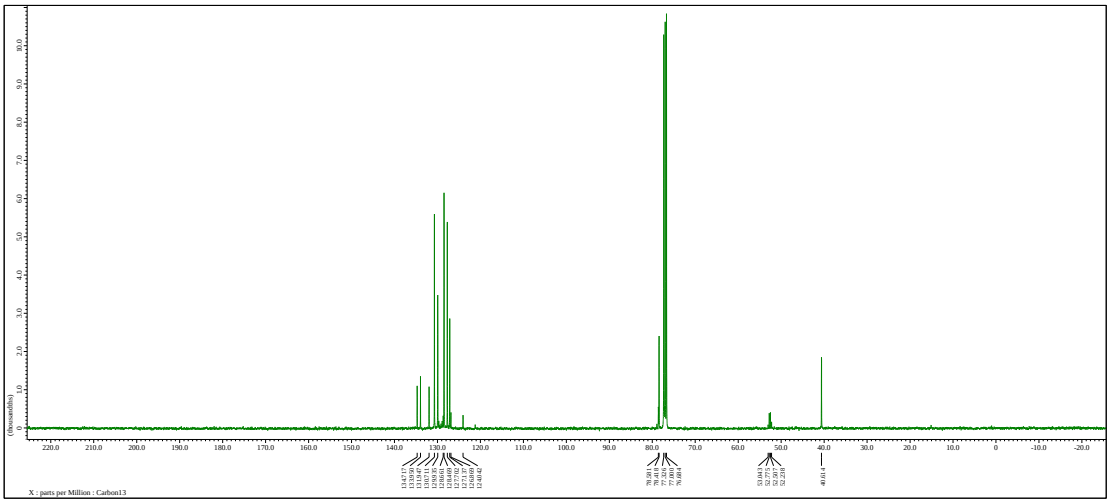

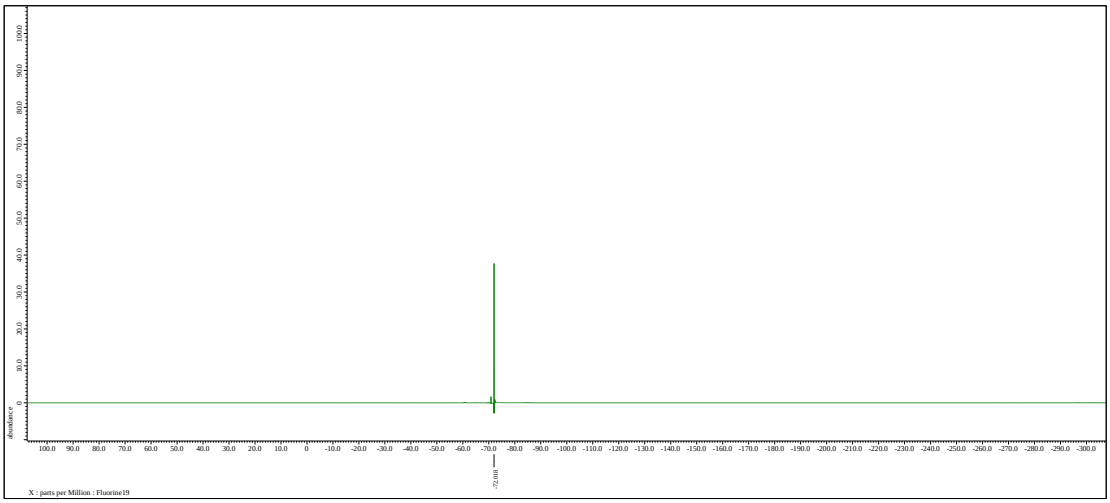

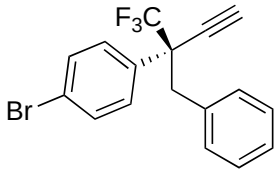

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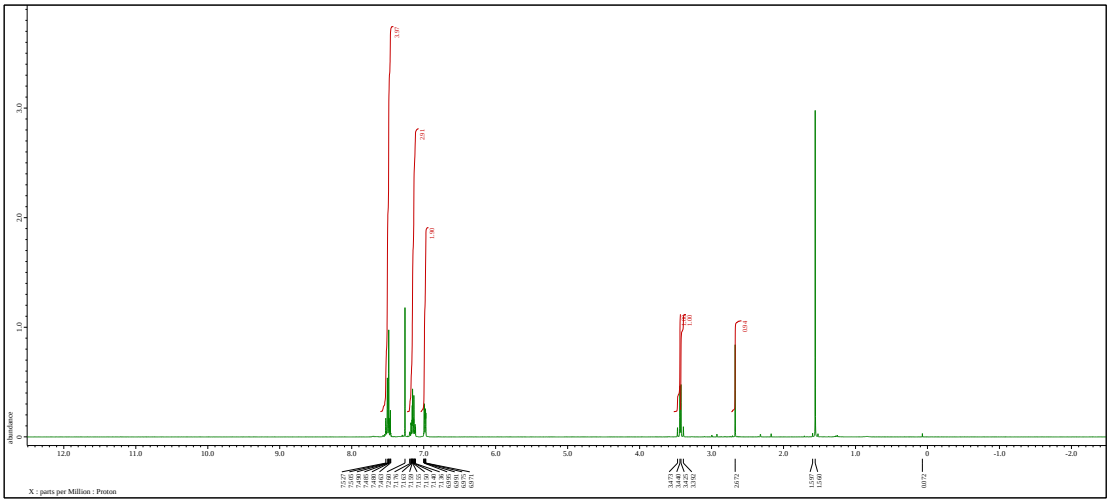

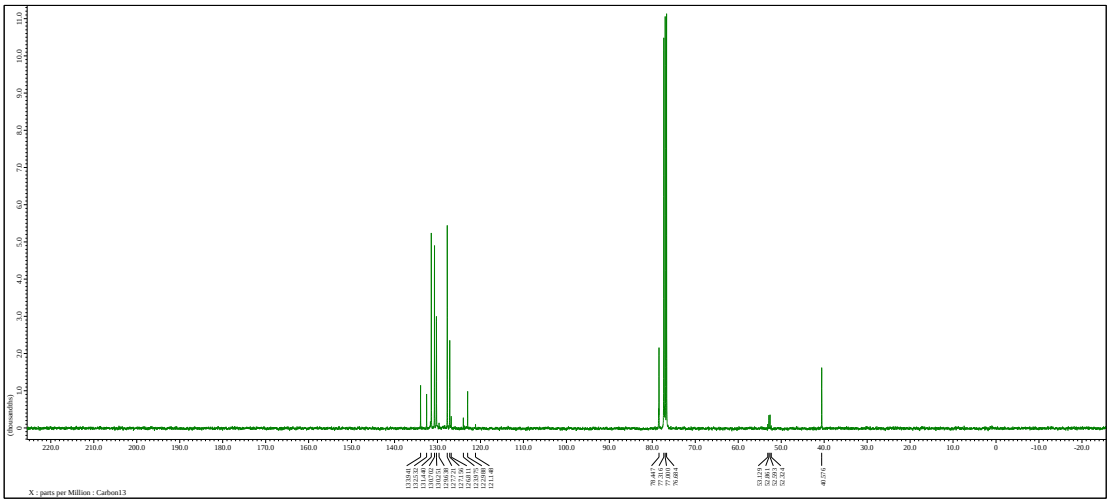

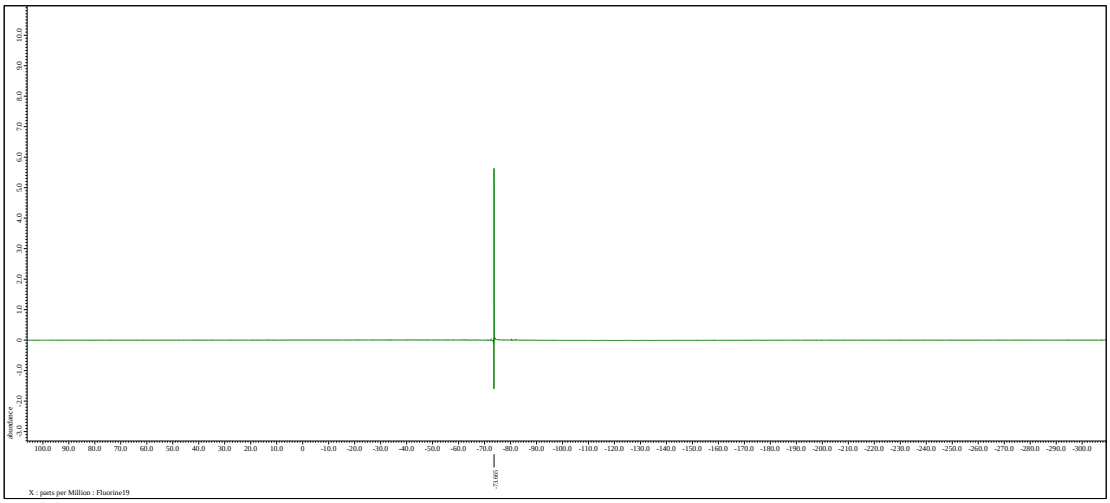

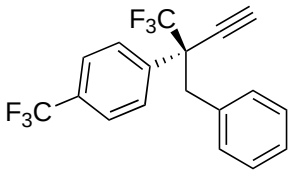

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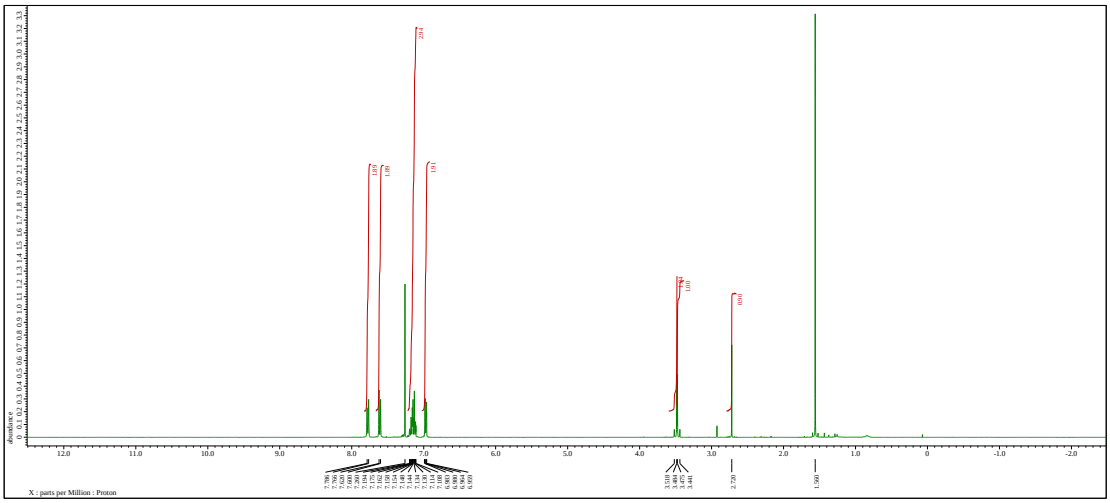

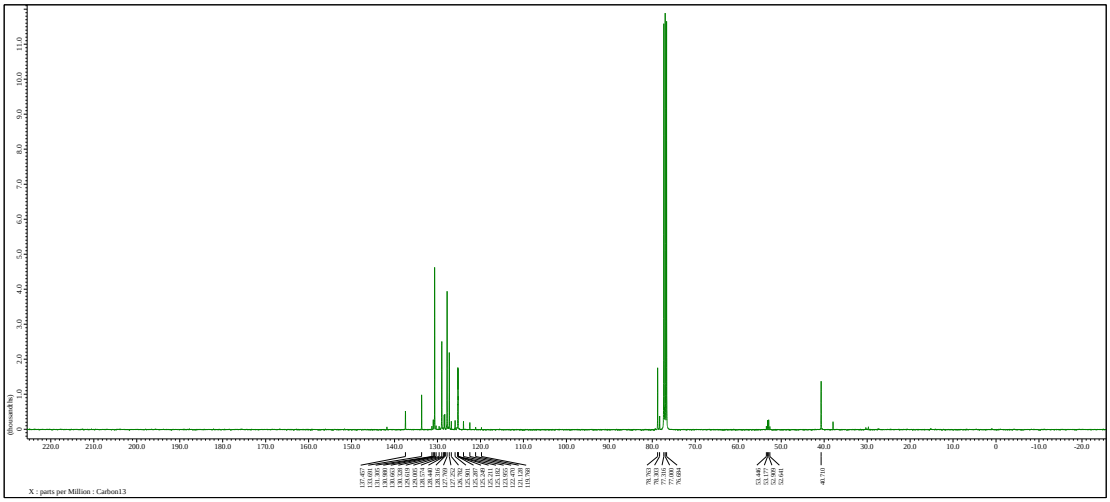

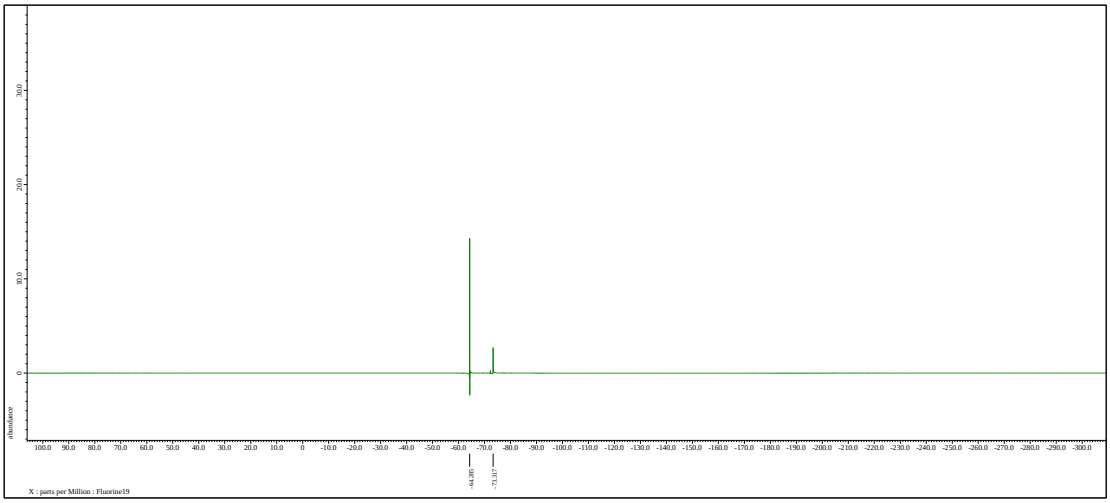

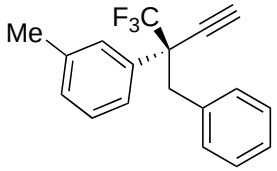

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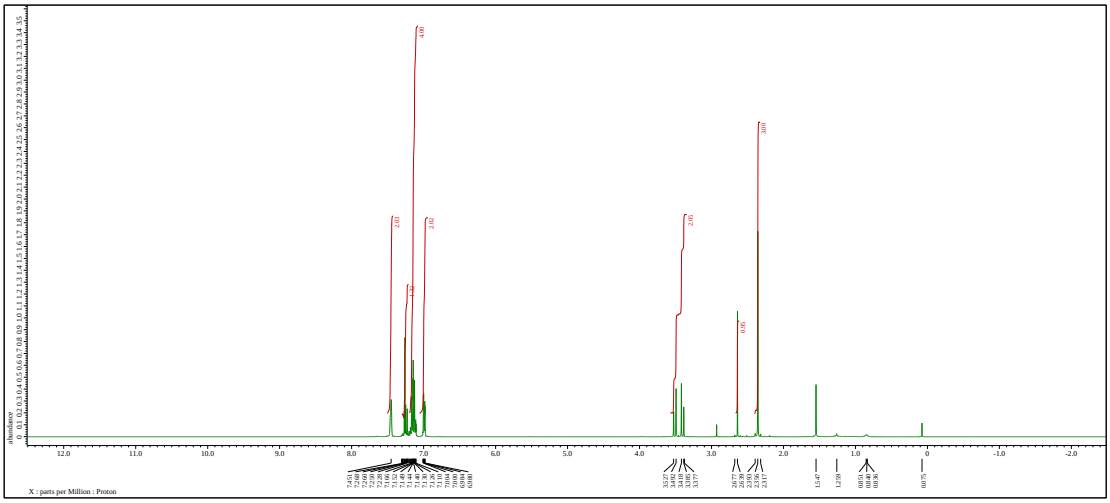

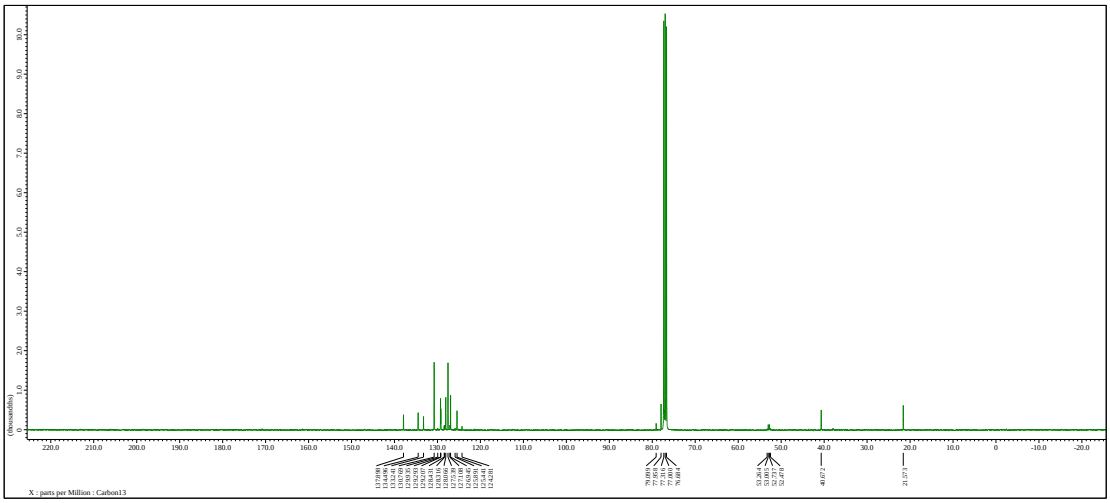

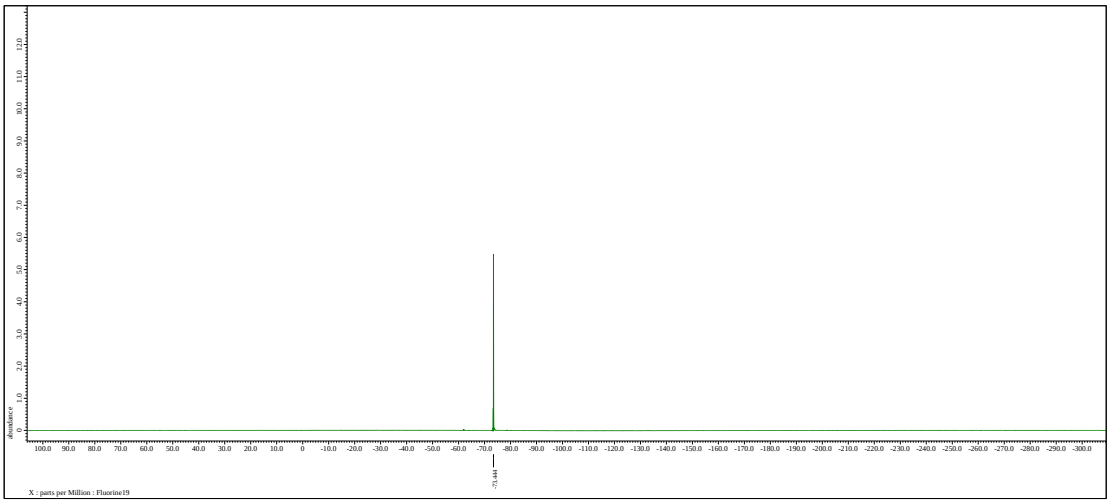

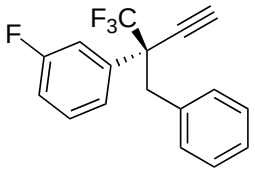
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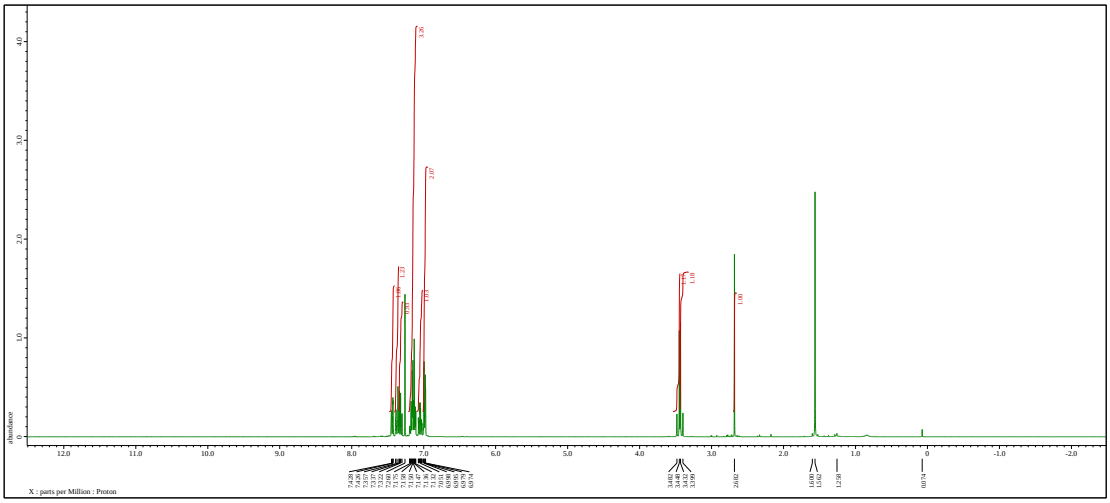
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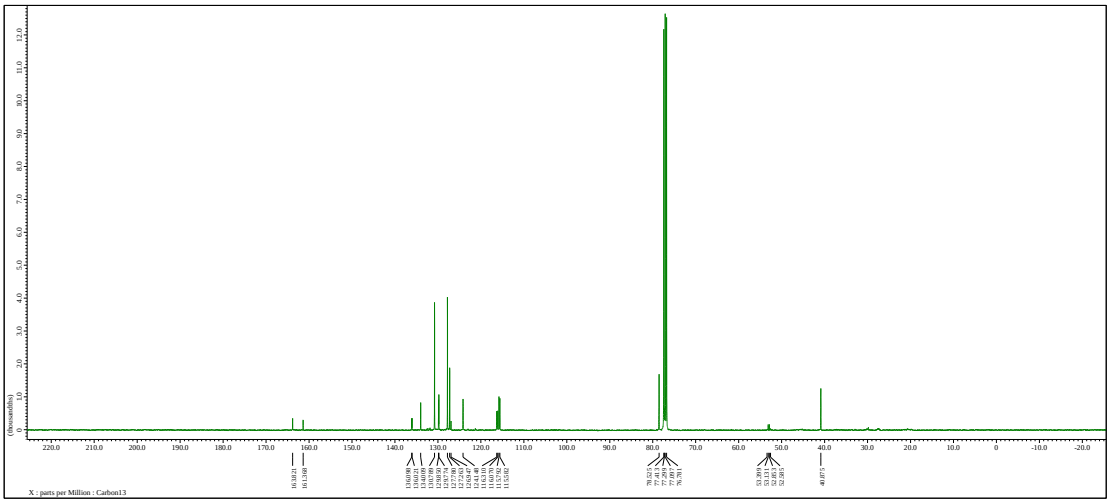
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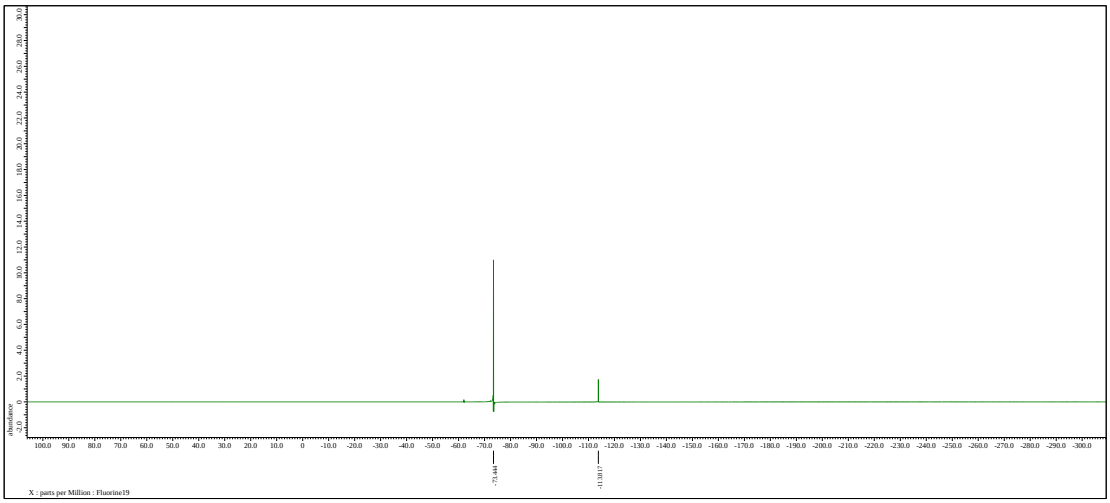
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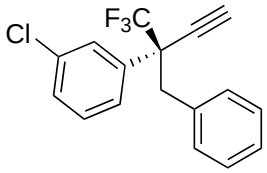

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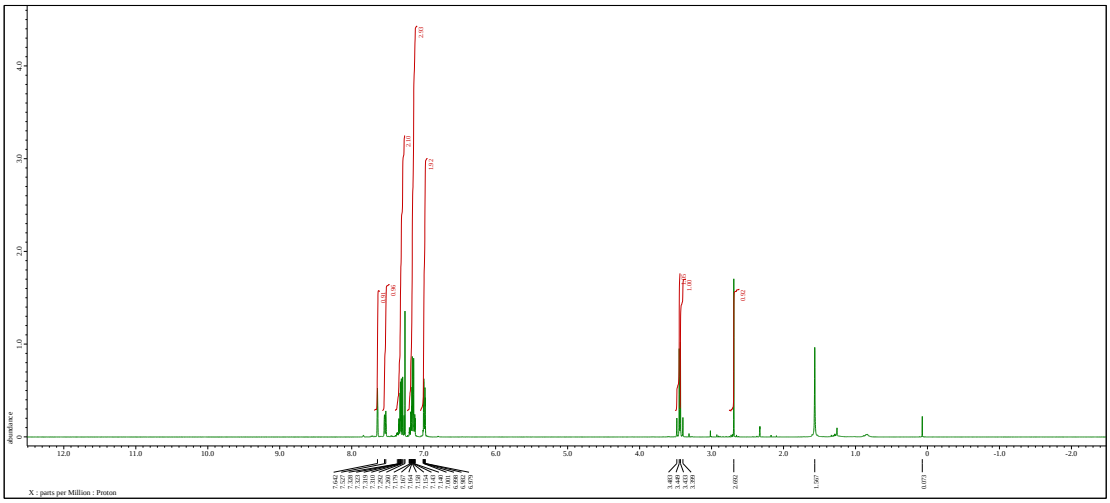

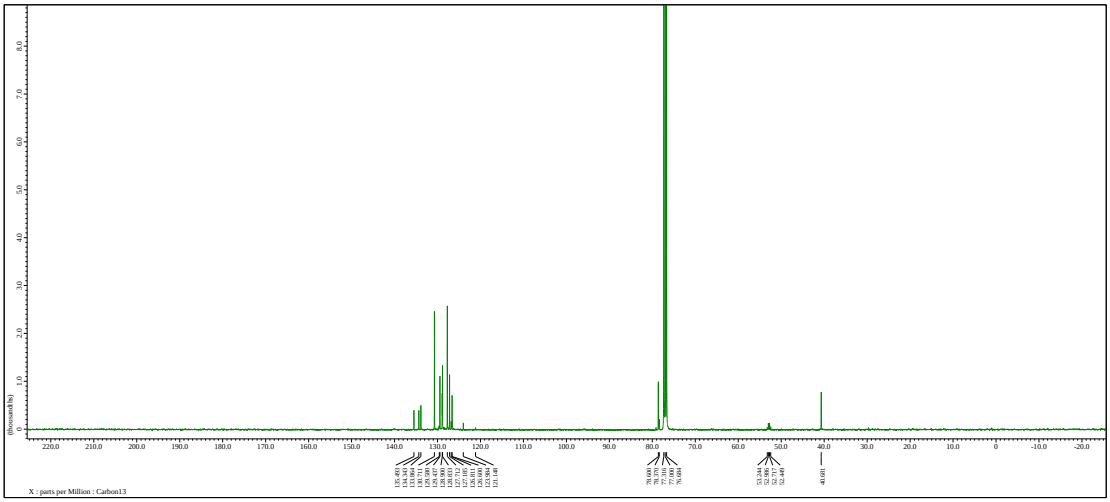

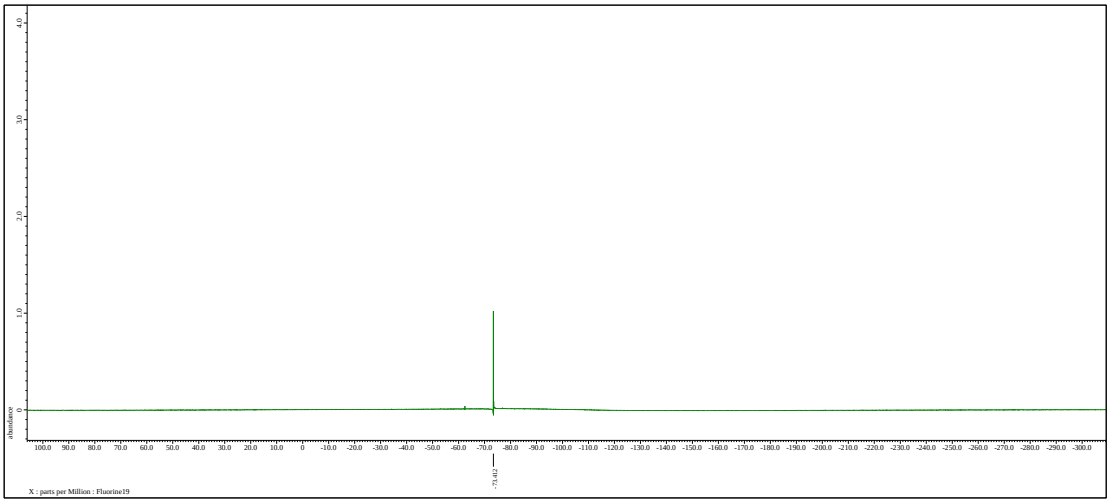

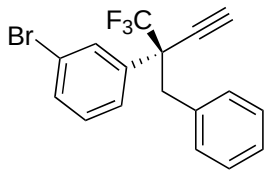

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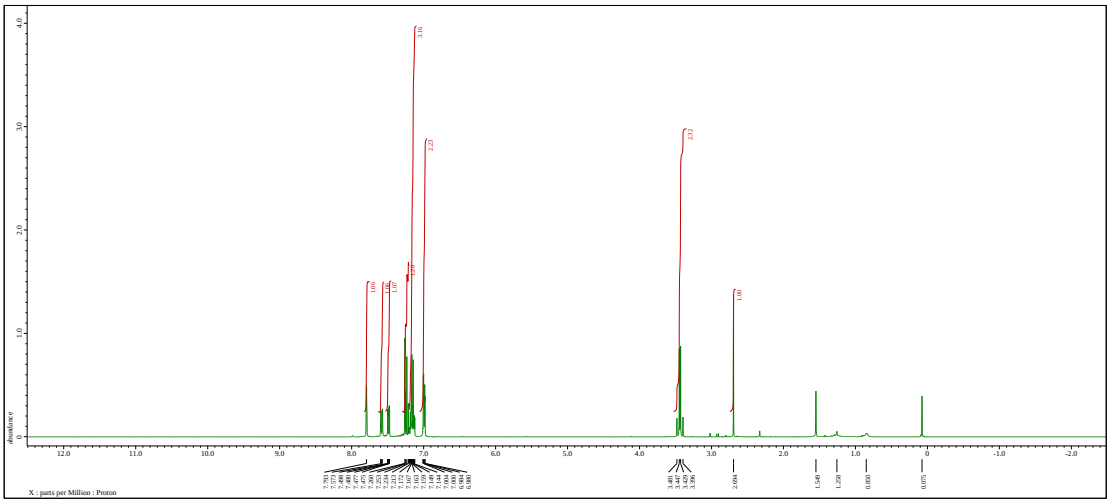

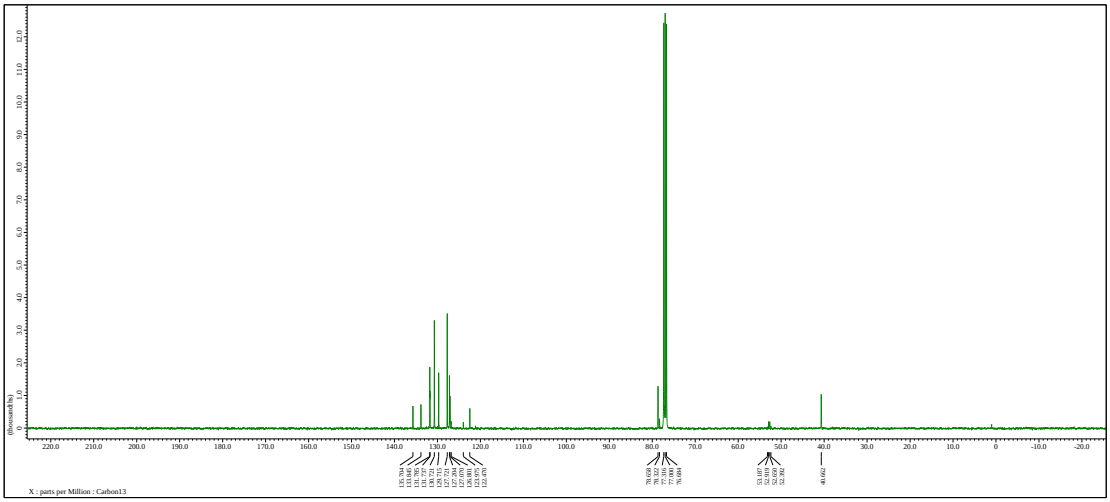

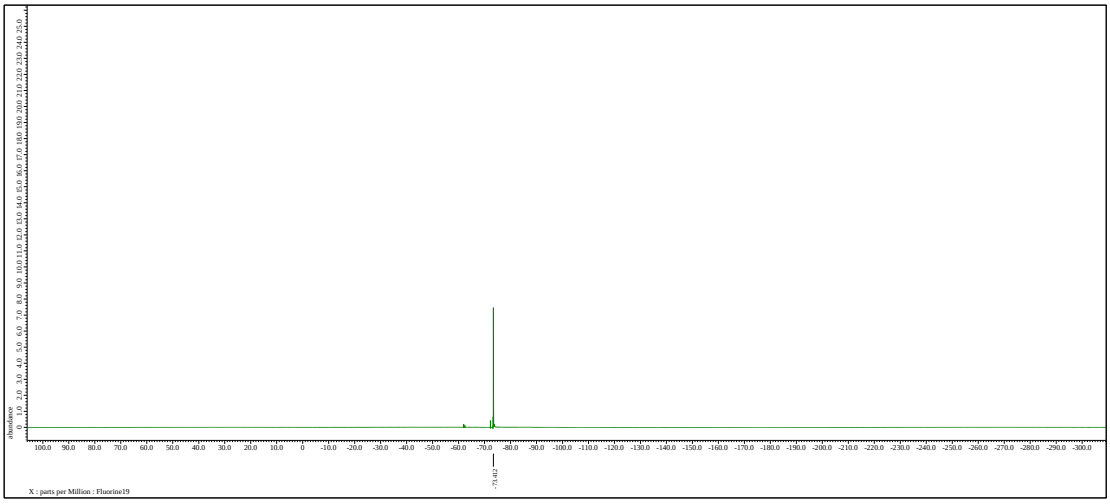

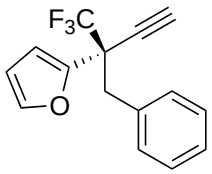

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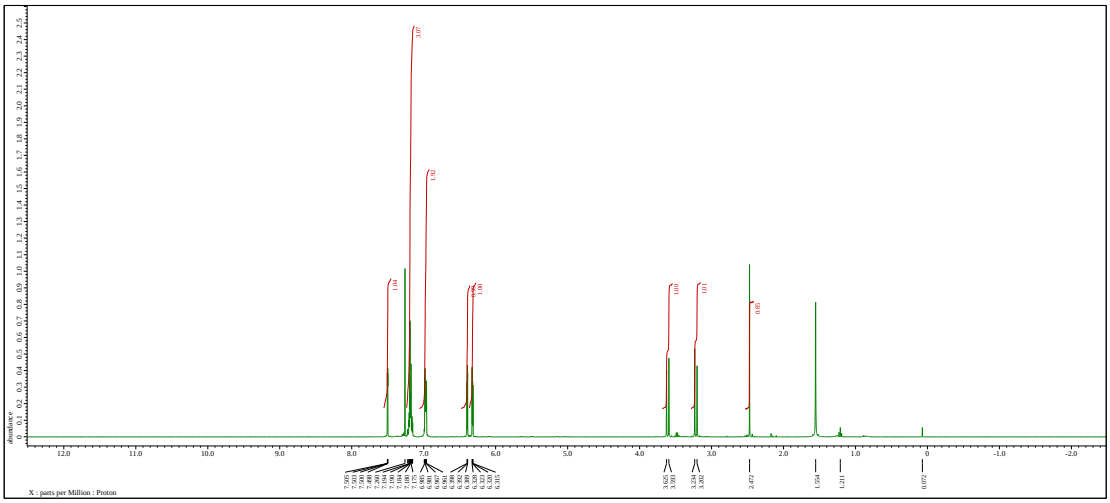

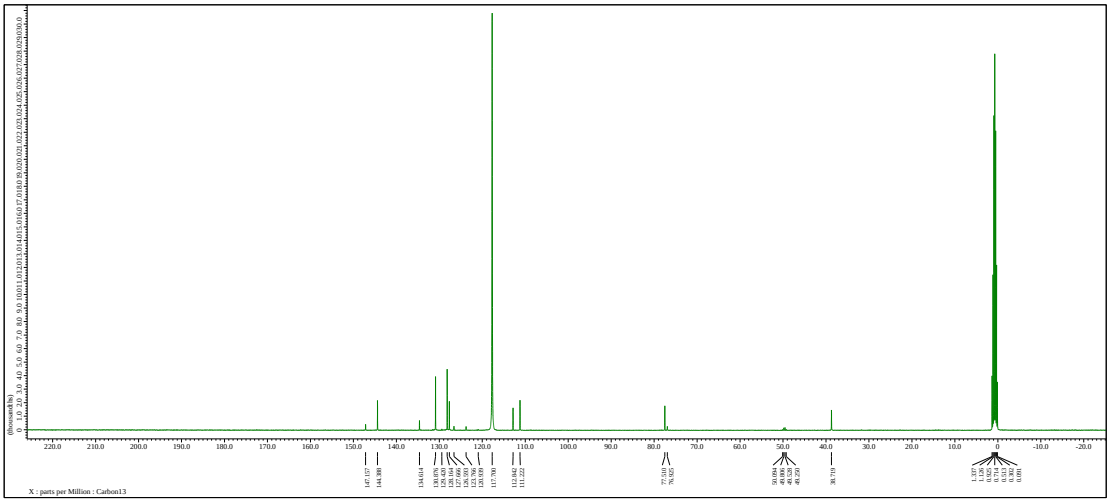

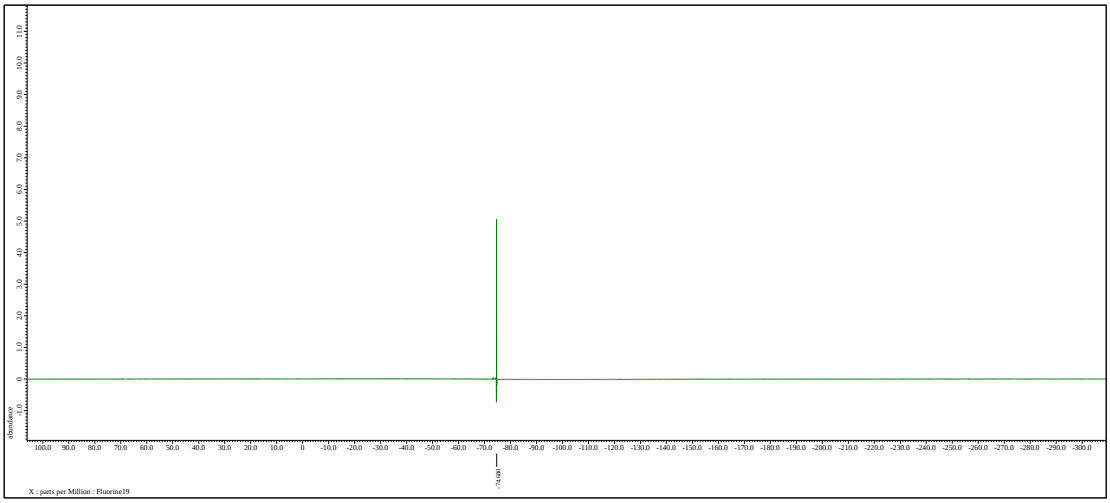

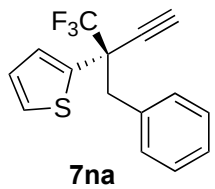

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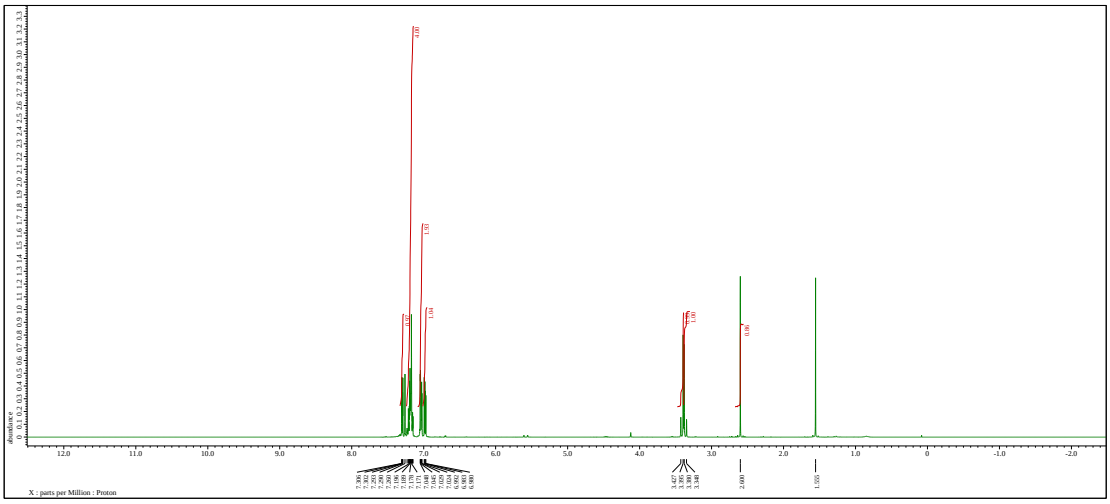

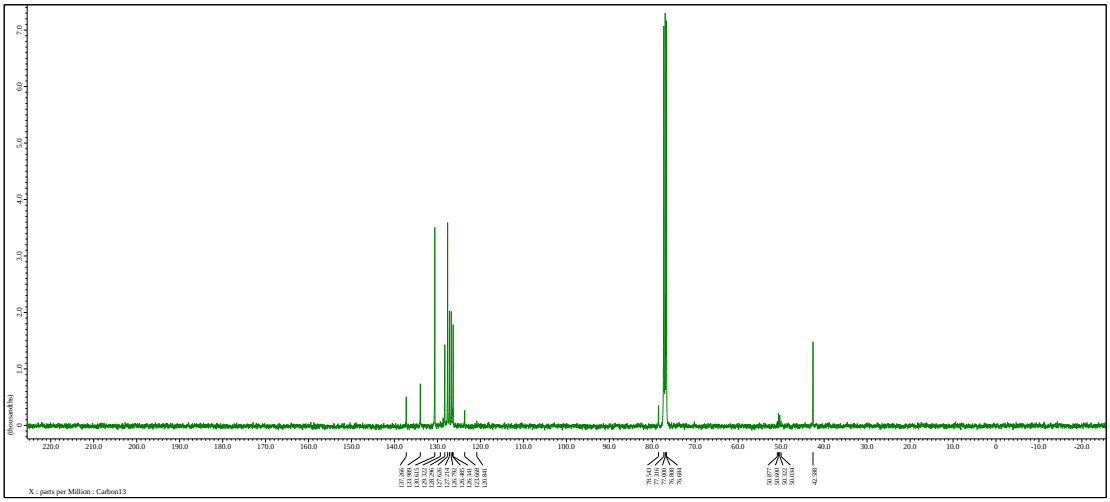

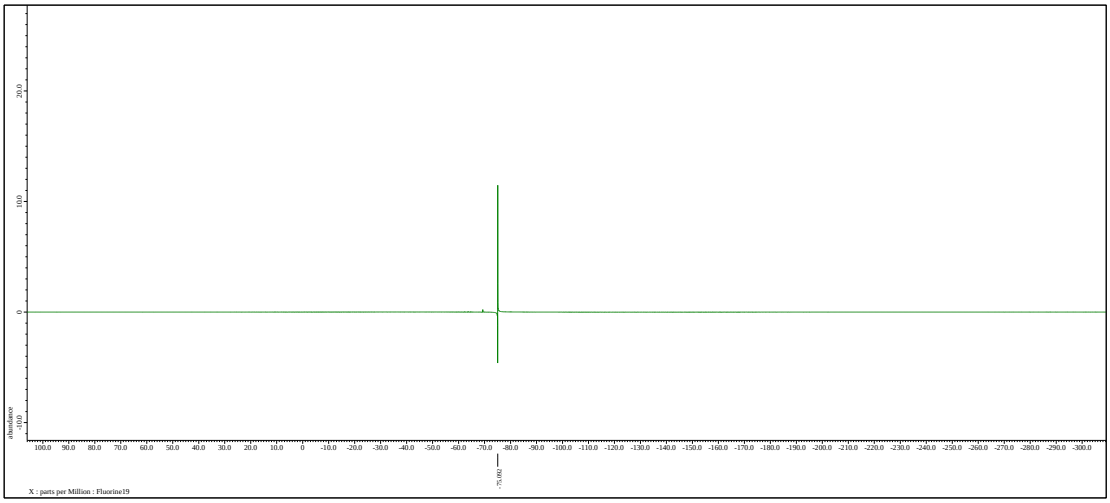

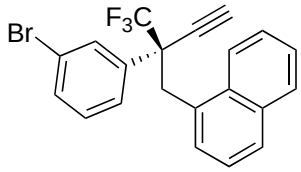

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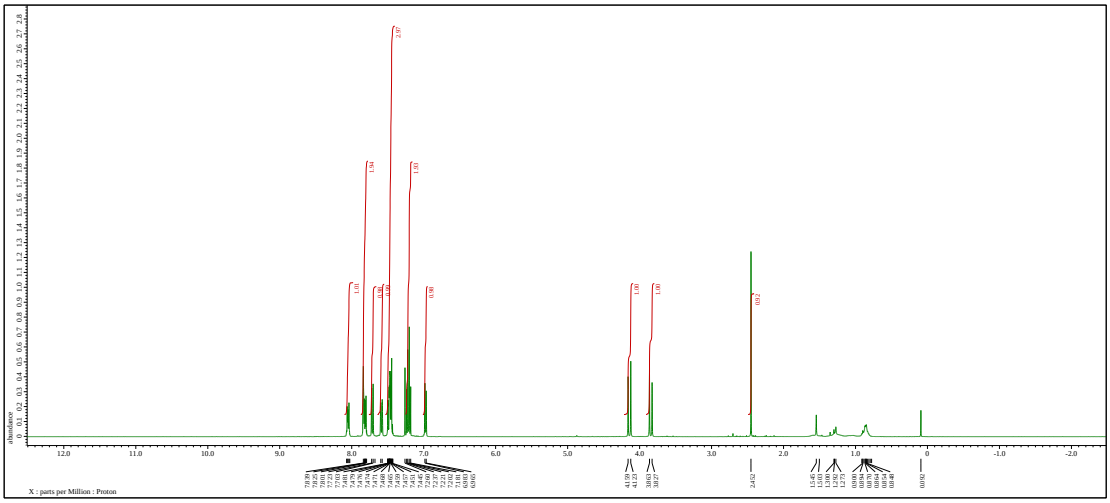

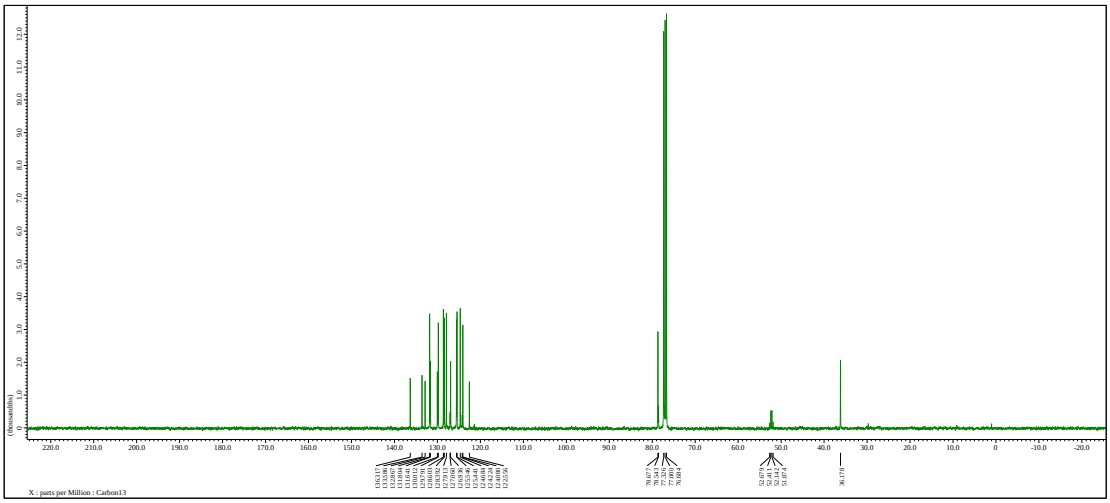

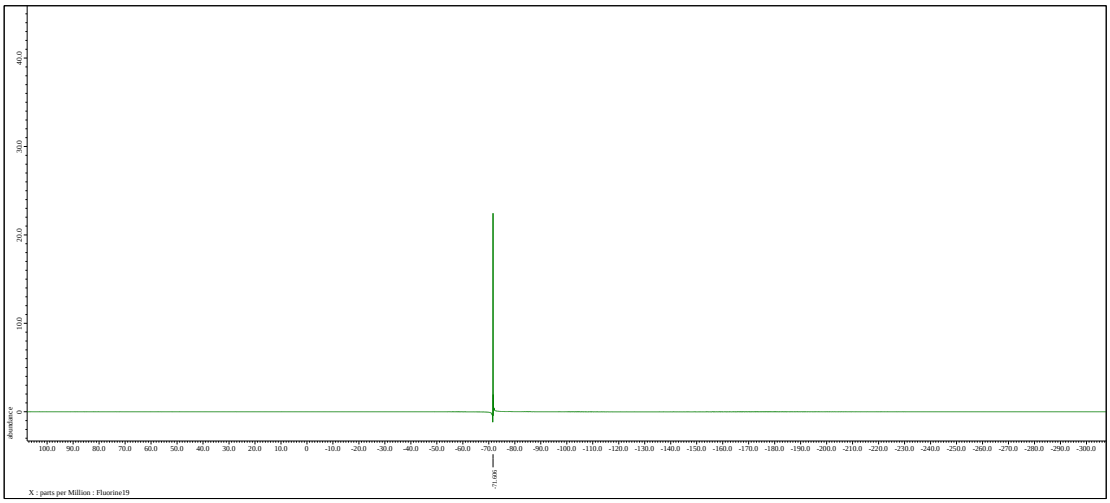

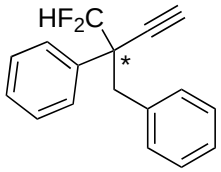
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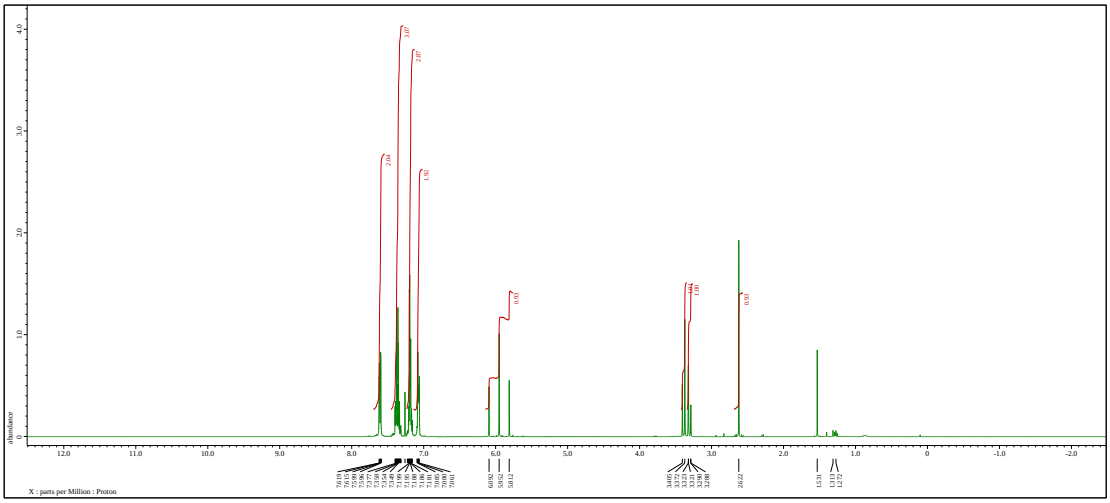
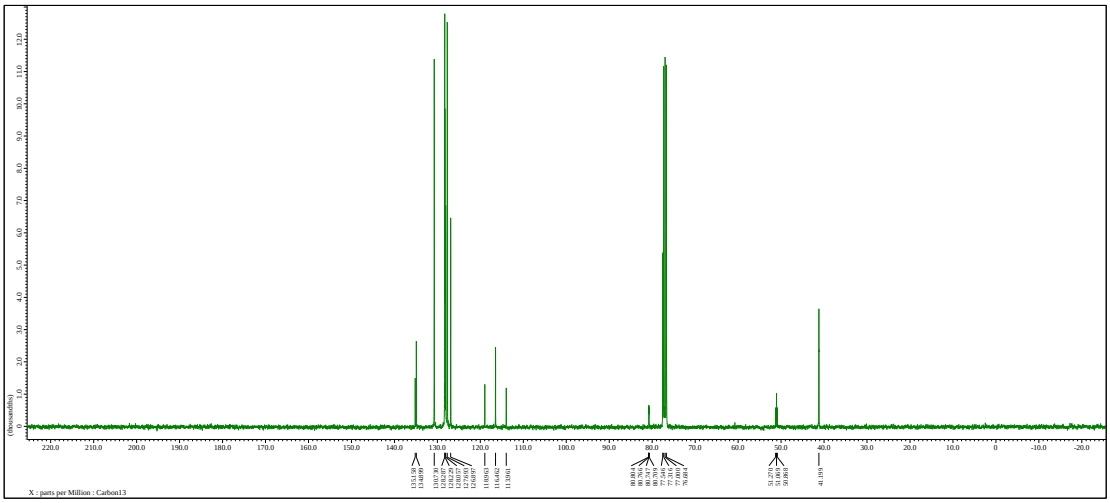
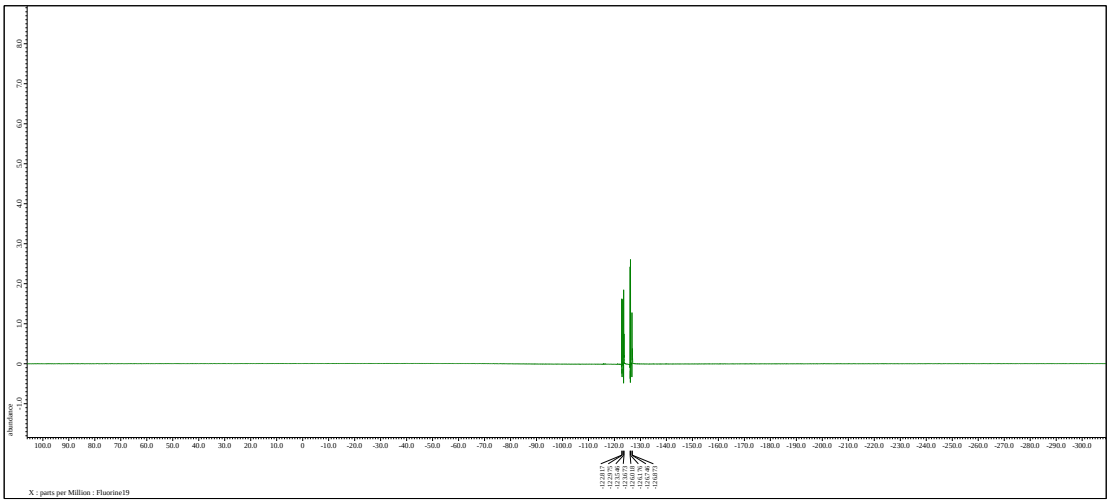
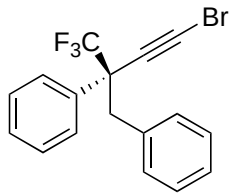
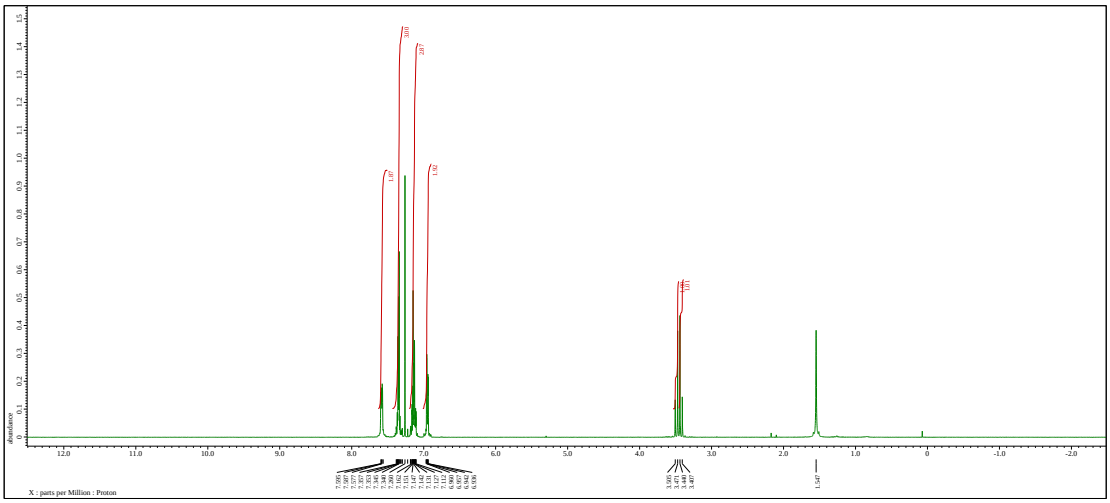

X : parts per Million : Proton

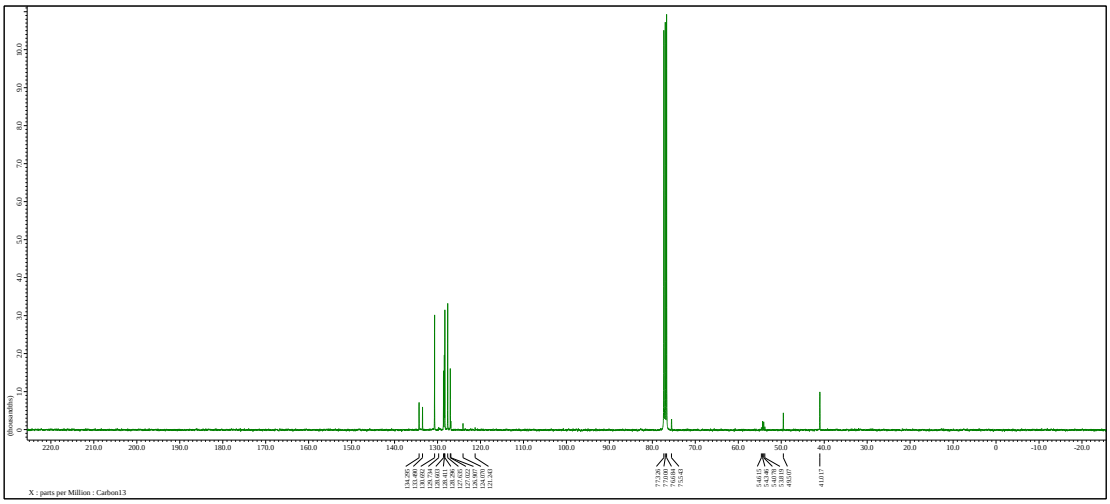

X : parts per Million : Carbon13

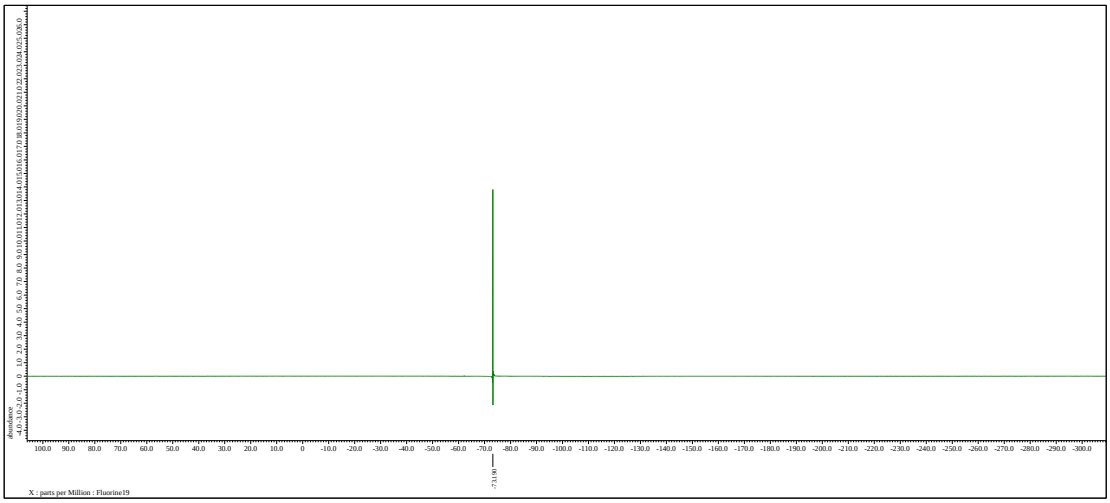

X : parts per Million : Fluorine19

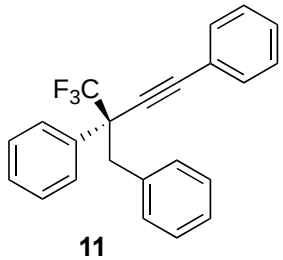

F3C
Br

10

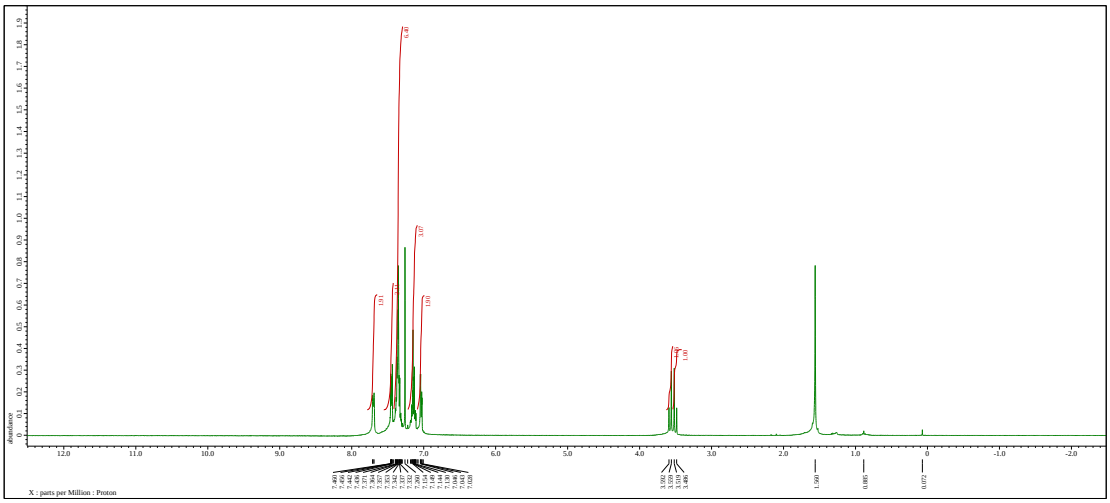

X : parts per Million : Proton

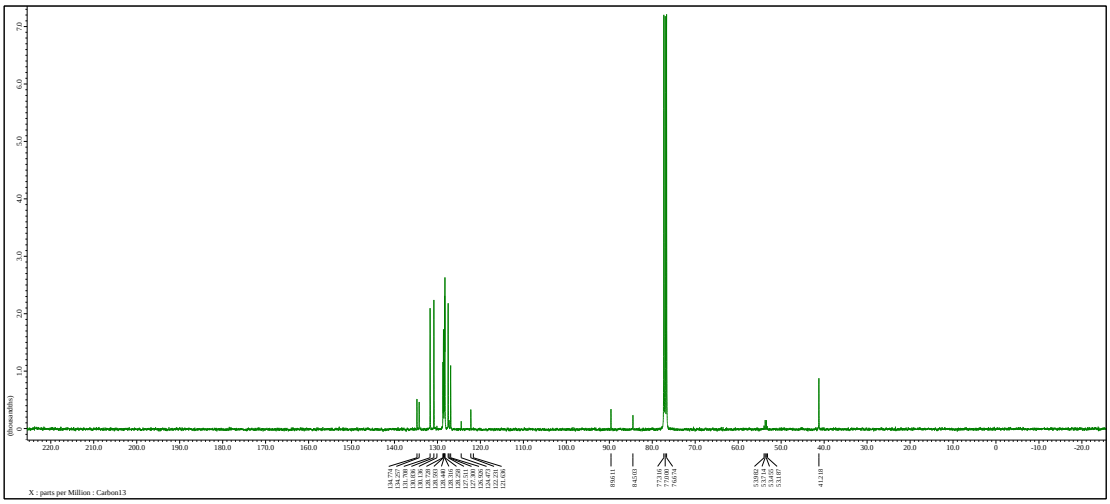

X : parts per Million : Carbon13

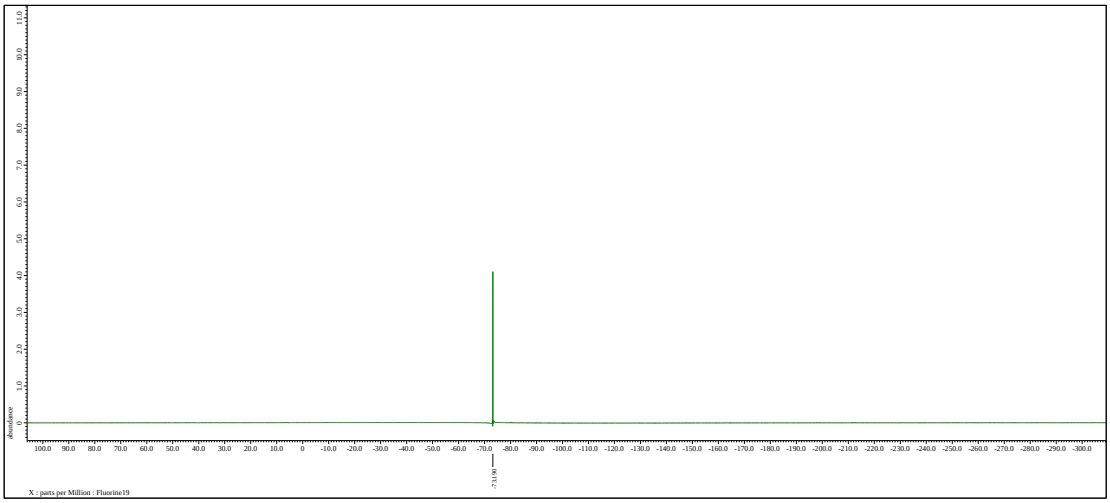

X : parts per Million : Fluorine19

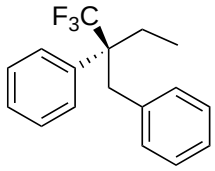


11

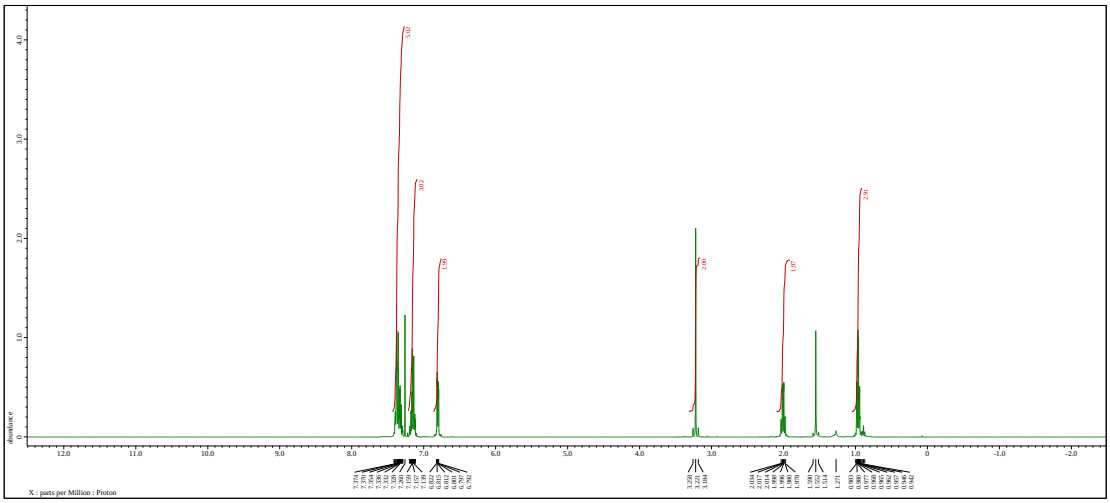


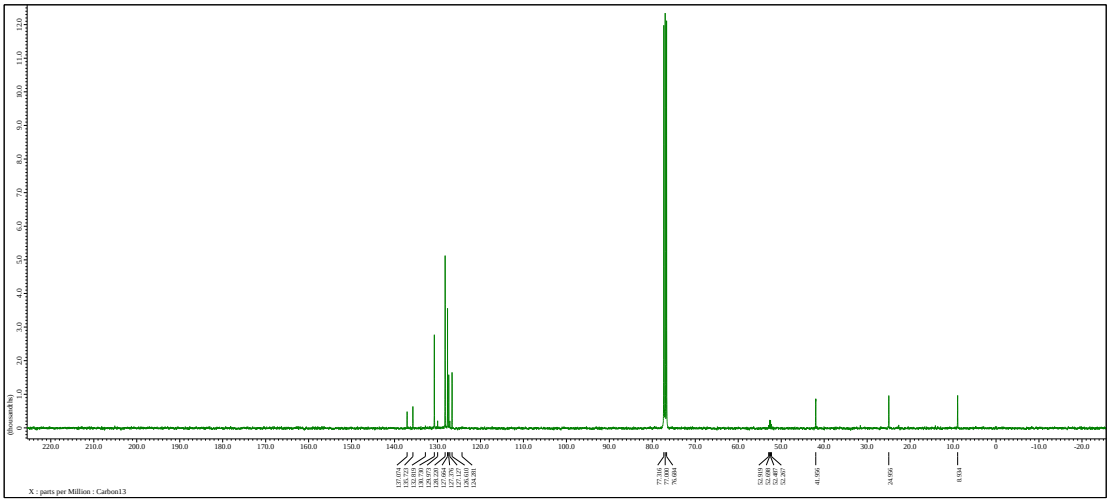


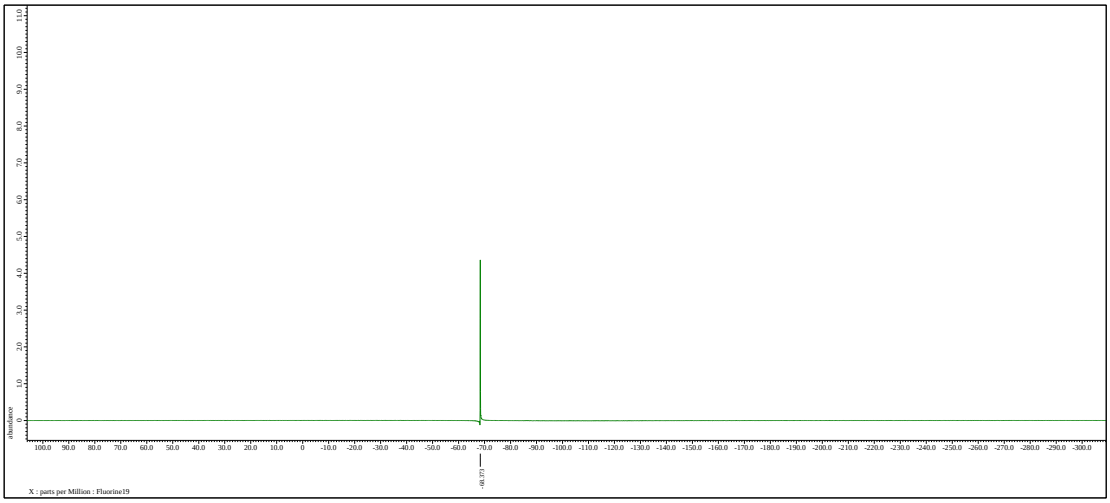


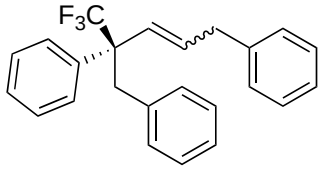

F3C

12

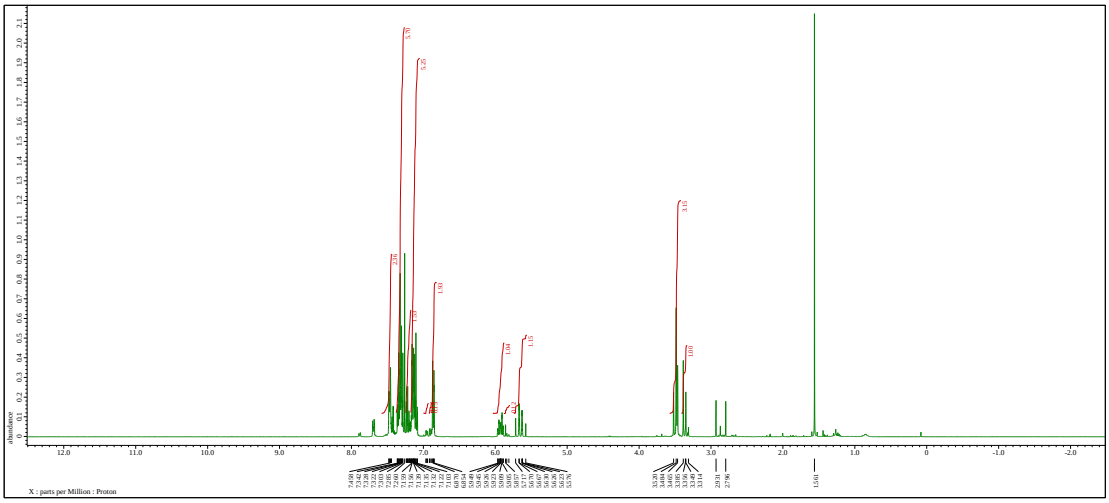

X : parts per Million : Proton

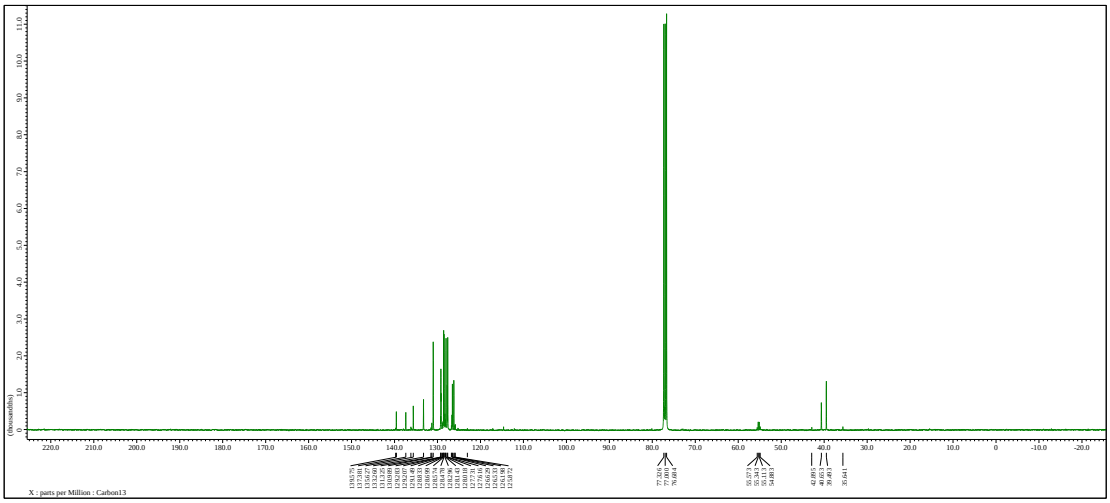

X : parts per Million : Carbon13

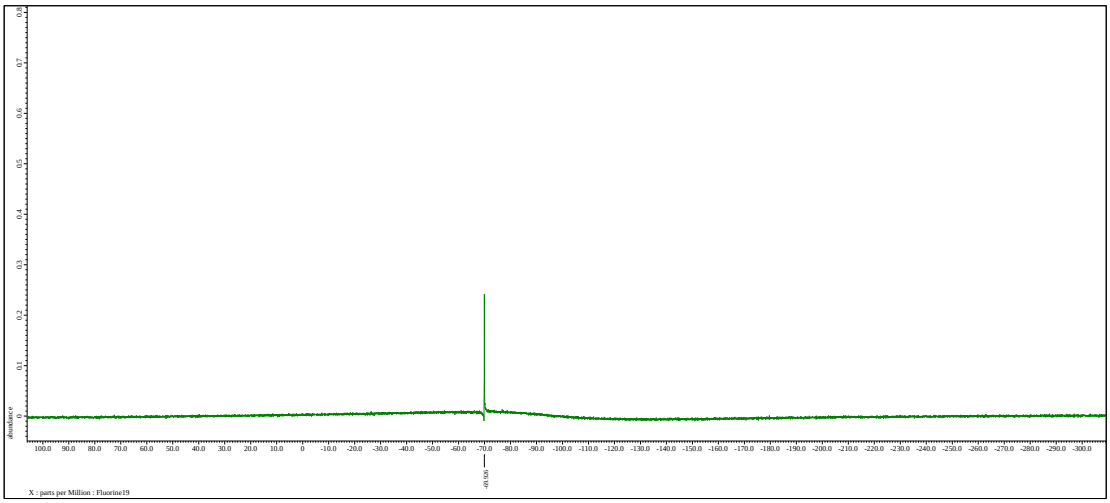

X : parts per Million : Fluorine19


F3C

13

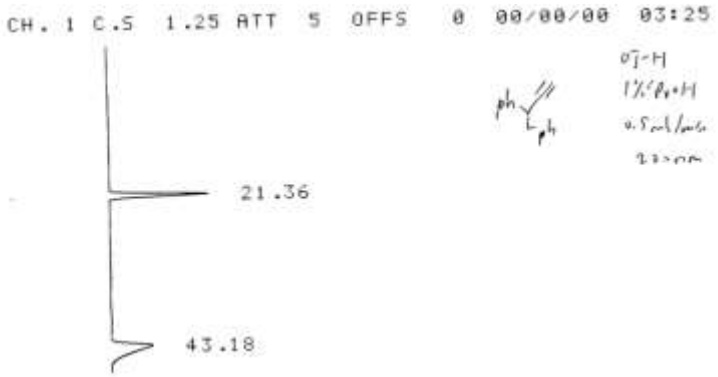

X : parts per Million : Proton


X : parts per Million : Carbon13


X : parts per Million : Fluorine19

S23. HPLC charts

5 (racemate)



D-2500 00/00/00 03:25

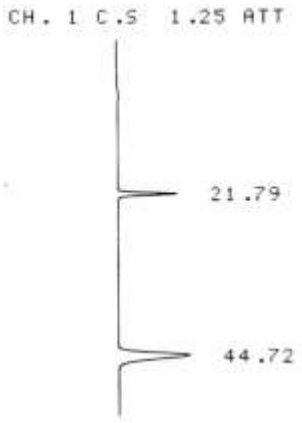
METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	21.36	111322	46.050	BB
2	43.18	130422	53.950	BB
TOTAL		241744	100.000	

PEAK REJ : 0

5 (chiral)



D-2500 00/00/00 02:29

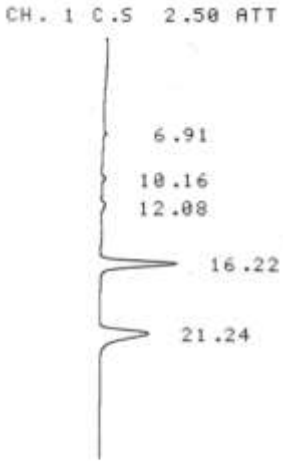
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	21.79	6518	26.234	BB
2	44.72	18328	73.766	BB
TOTAL		24846	100.000	

PEAK REJ : 0

7aa (racemate)



D-2500 00/00/00 00:21

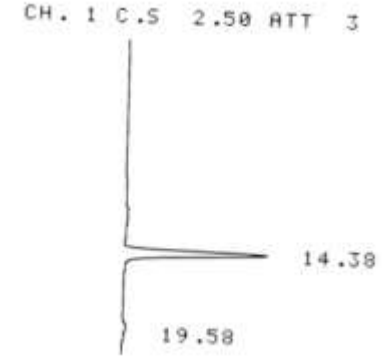
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
4	16.22	20010	49.260	BB
5	21.24	20611	50.740	BB
TOTAL		40621	100.000	

PEAK REJ : 1200

7aa (chiral)



D-2500 00/00/00 00:22

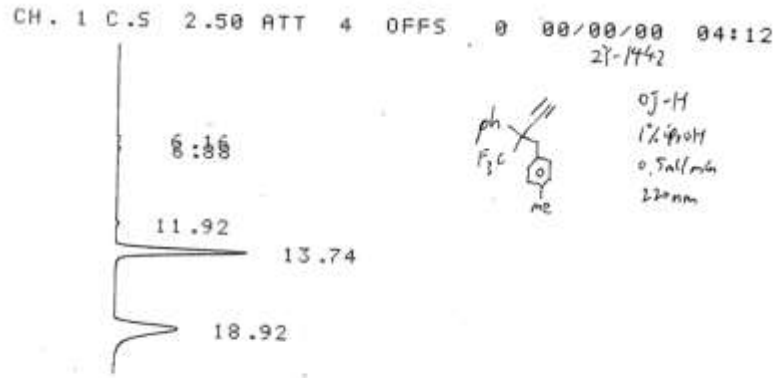
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	14.38	29864	97.002	BB
2	19.58	923	2.998	BB
TOTAL		30787	100.000	

PEAK REJ : 0

7ab (racemate)



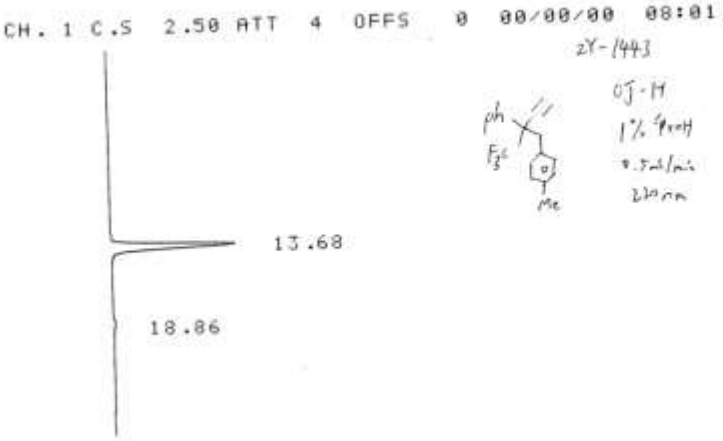
D-2500 00/00/00 04:12

METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
4	13.74	54065	50.596	BB
5	18.92	52792	49.404	BB
TOTAL		106857	100.000	
PEAK REJ :		700		

7ab (chiral)



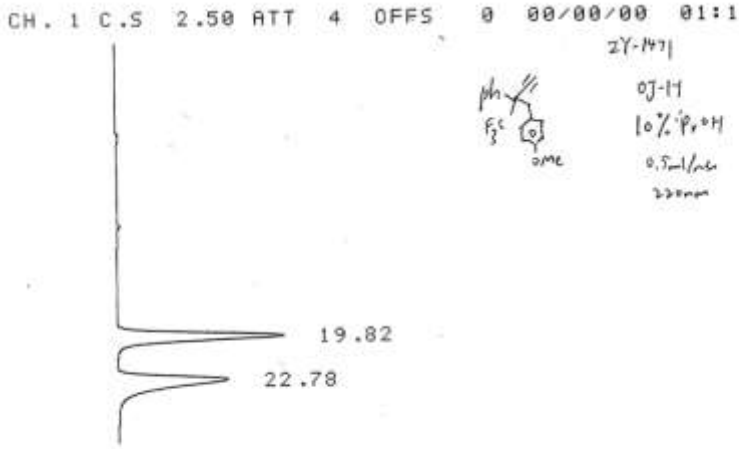
D-2500 00/00/00 08:01

METHOD: TAG: 6 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	13.68	48405	97.242	BB
2	18.86	1373	2.758	BB
TOTAL		49778	100.000	
PEAK REJ :		0		

7ac (racemate)



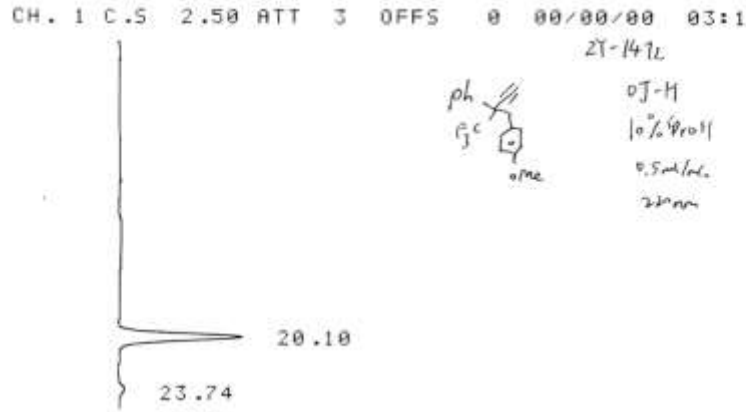
D-2500 00/00/00 01:19

METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	19.82	101021	50.795	BB
2	22.78	97857	49.205	BB
TOTAL		198878	100.000	
PEAK REJ :		0		

7ac (chiral)



D-2500 00/00/00 03:10

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	20.10	35227	96.136	BB
2	23.74	1416	3.864	BB
TOTAL		36643	100.000	
PEAK REJ :		0		

7ad (racemate)

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CH. 1 C.S  1.25 ATT  3  OFFS   0  00/00/00  04:12
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D-2500                                              00/00/00  04:12

METHOD:                TAG:     3  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   19.76        47549     50.141  BB
    2   30.70        47281     49.859  BB
TOTAL
                     94830    100.000
PEAK REJ :            0
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7ad (chiral)

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CH. 1 C.S  1.25 ATT  4  OFFS   0  00/00/00  00:01
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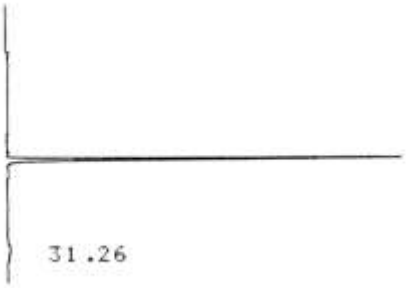


```
D-2500                                              00/00/00  00:01

METHOD:                TAG:     1  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   19.80        71668     95.999  BB
    2   31.26         2987      4.001  BB
TOTAL
                     74655    100.000
PEAK REJ :            0
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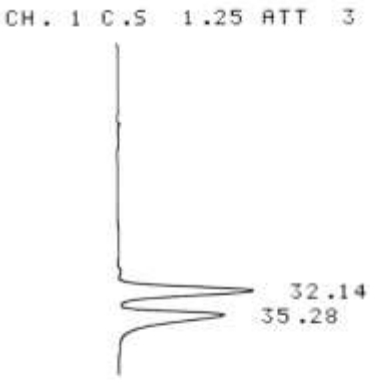
7ae (racemate)



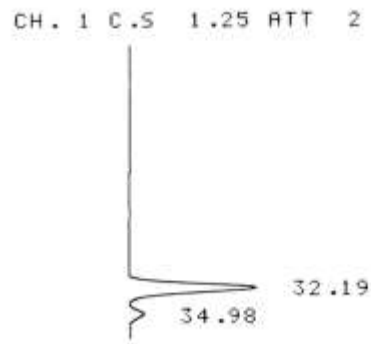
D-2500 00/00/00 00:56

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	32.14	82872	50.214	BB
2	35.28	82166	49.786	BB
TOTAL		165038	100.000	
PEAK REJ :		0		

7ae (chiral)



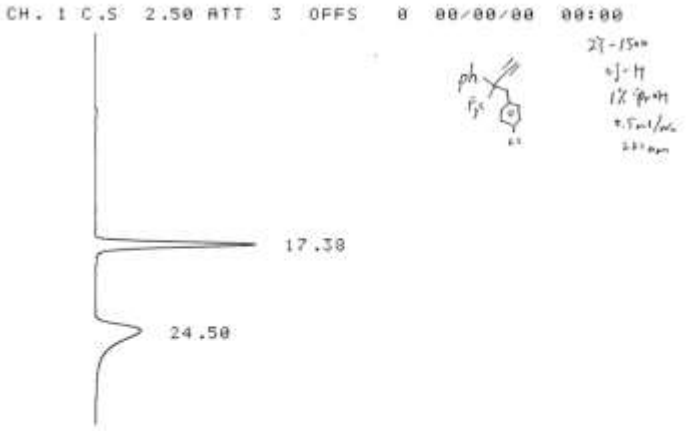
D-2500 00/00/00 00:42

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	32.19	36704	95.833	BB
2	34.98	1596	4.167	BB
TOTAL		38300	100.000	
PEAK REJ :		0		

7af (racemate)



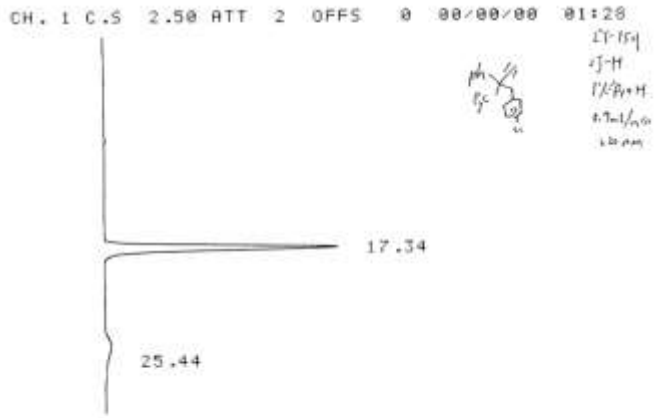
D-2500 00/00/00 00:00

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	17.38	45384	51.277	BB
2	24.50	43123	48.723	BB
TOTAL		88507	100.000	
PEAK REJ :		0		

7af (chiral)



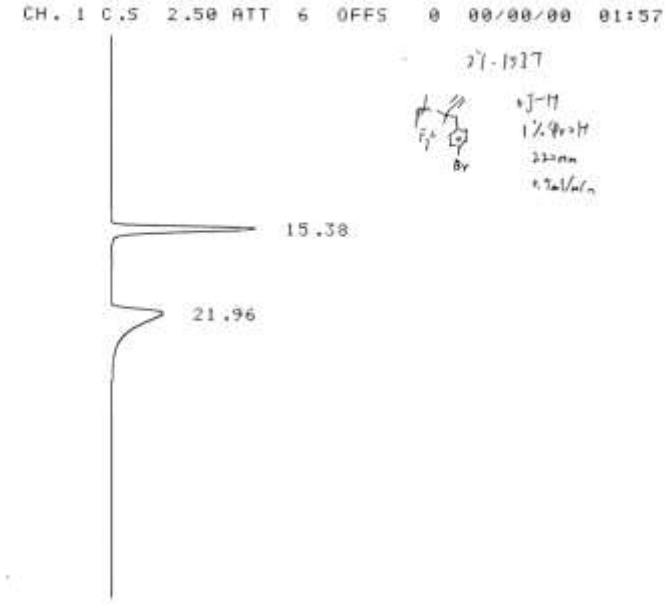
D-2500 00/00/00 01:28

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	17.34	35915	95.094	BB
2	25.44	1853	4.906	BB
TOTAL		37768	100.000	
PEAK REJ :		0		

7ag (racemate)



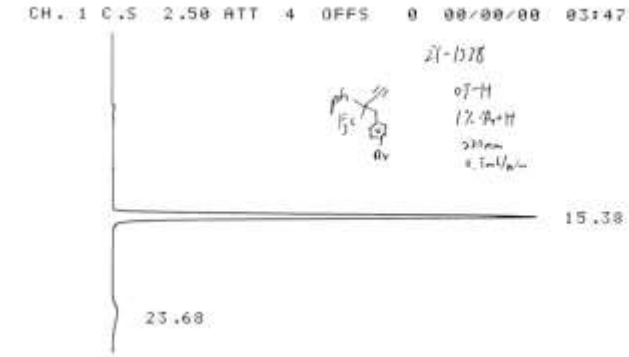
D-2500 00/00/00 01:57

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.38	343806	47.005	BB
2	21.96	387618	52.995	BB
TOTAL		731424	100.000	
PEAK REJ :		0		

7ag (chiral)



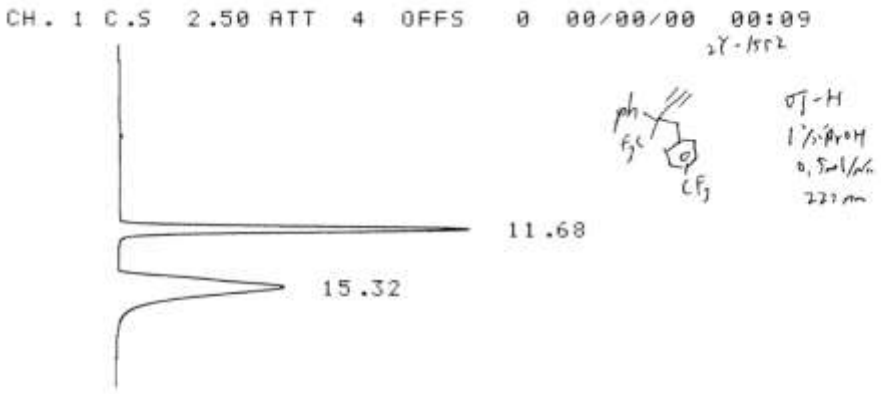
D-2500 00/00/00 03:47

METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.38	227544	97.027	BB
2	23.68	6972	2.973	BB
TOTAL		234516	100.000	
PEAK REJ :		0		

7ah (racemate)



D-2500 00/00/00 00:09

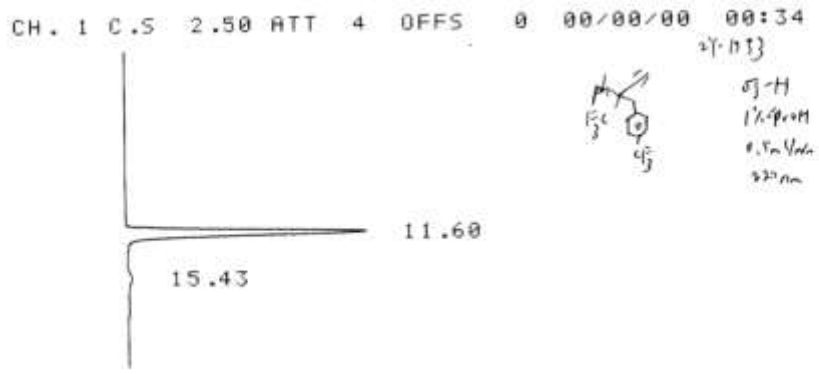
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.68	144051	53.995	BB
2	15.32	122736	46.005	BB
TOTAL		266787	100.000	

PEAK REJ : 0

7ah (chiral)



D-2500 00/00/00 00:34

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.60	91516	95.737	BB
2	15.43	4075	4.263	BB
TOTAL		95591	100.000	

PEAK REJ : 0

7ai (racemate)

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CH. 1 C.S  1.25 ATT  4  OFFS  0  00/00/00  00:44
```


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D-2500                                              00/00/00  00:44

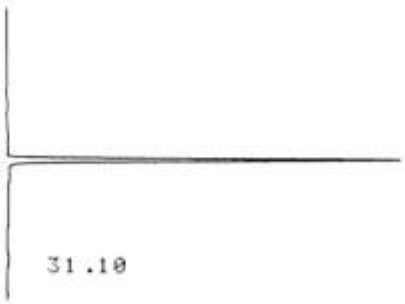
METHOD:                TAG:     2  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   18.58        87848     50.612  BB
    2   29.58        85724     49.388  BB
TOTAL
                    173572    100.000
PEAK REJ :            0
```

7ai (chiral)

```
CH. 1 C.S  1.25 ATT  4  OFFS  0  00/00/00  03:09
```




```
D-2500                                              00/00/00  03:09

METHOD:                TAG:     3  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   18.88       133304     97.798  BB
    2   31.10         3002      2.202  BB
TOTAL
                    136306    100.000
PEAK REJ :            0
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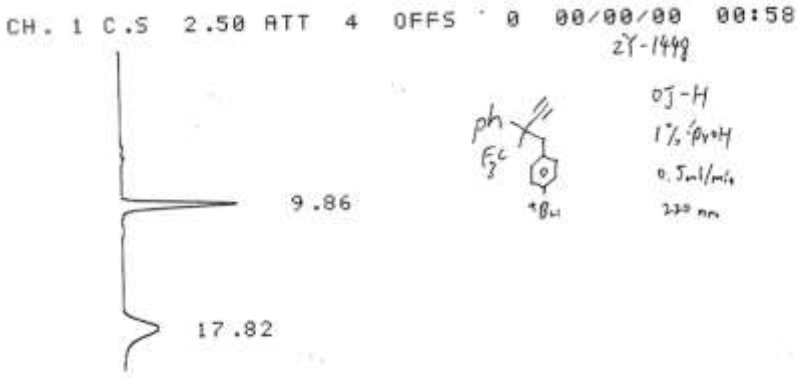
7aj (racemate)



D-2500 00/00/00 00:58

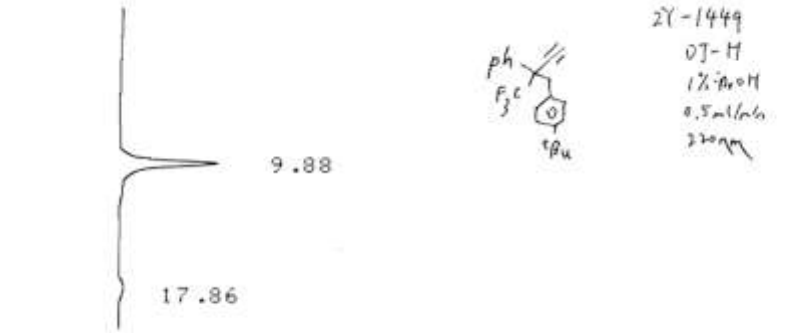
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	9.86	42994	52.497	BB
2	17.82	38904	47.503	BB
TOTAL		81898	100.000	

PEAK REJ : 0

7aj (chiral)



D-2500 00/00/00 00:28

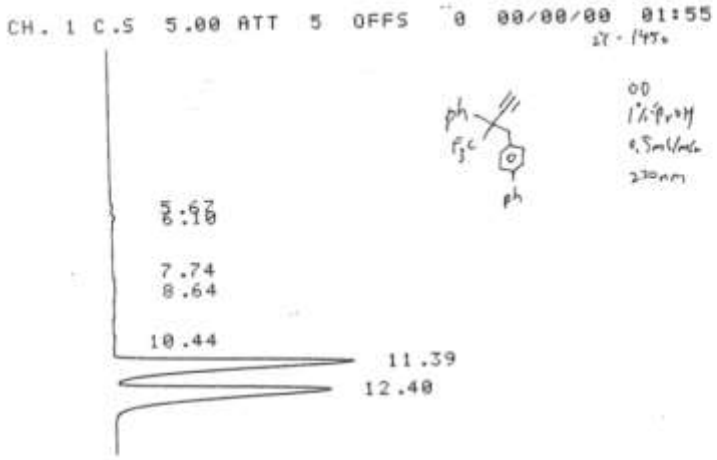
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	9.88	29071	91.802	BB
2	17.86	2596	8.198	BB
TOTAL		31667	100.000	

PEAK REJ : 0

7ak (racemate)



D-2500 00/00/00 01:55

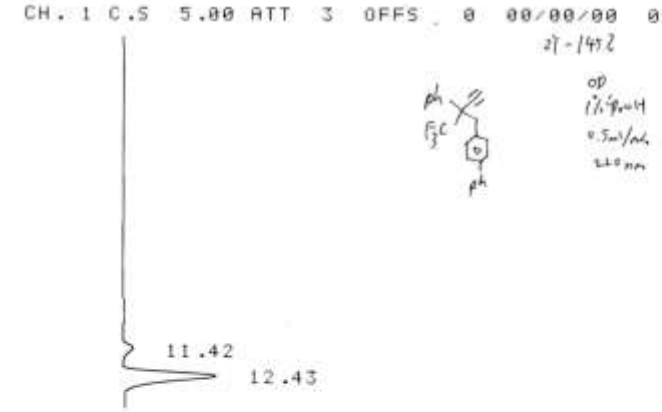
METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
6	11.39	205520	48.976	BV
7	12.40	214118	51.024	VB
TOTAL		419638	100.000	

PEAK REJ : 3500

7ak (chiral)



D-2500 00/00/00 02:23

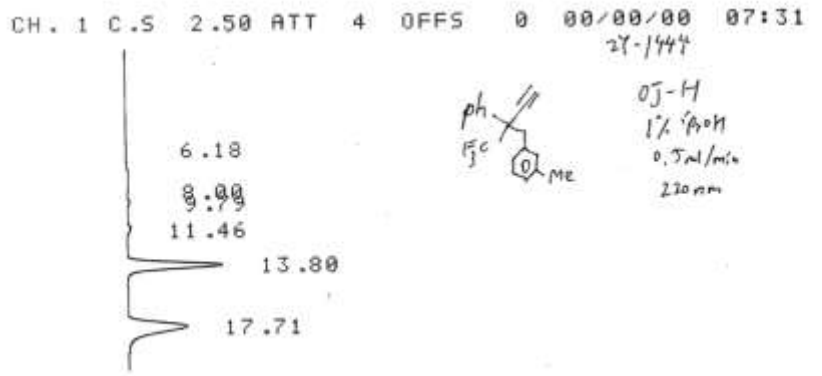
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.42	1818	8.681	BB
2	12.43	19125	91.319	BB
TOTAL		20943	100.000	

PEAK REJ : 0

7al (racemate)



D-2500 00/00/00 07:31

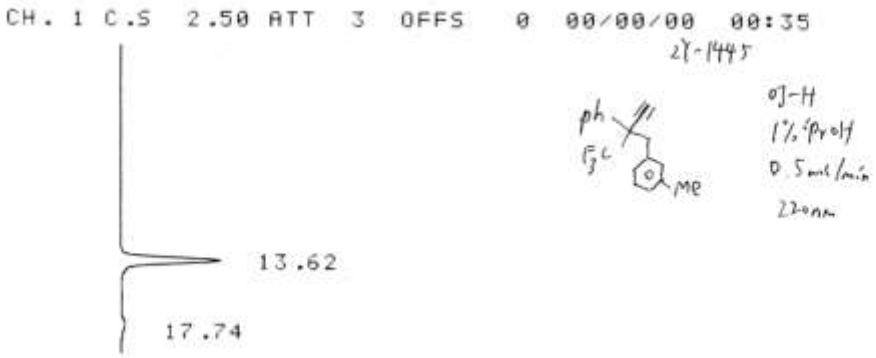
METHOD: TAG: 5 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
5	13.80	41647	49.819	BB
6	17.71	41950	50.181	BB
TOTAL		83597	100.000	

PEAK REJ : 1600

7al (chiral)



D-2500 00/00/00 00:35

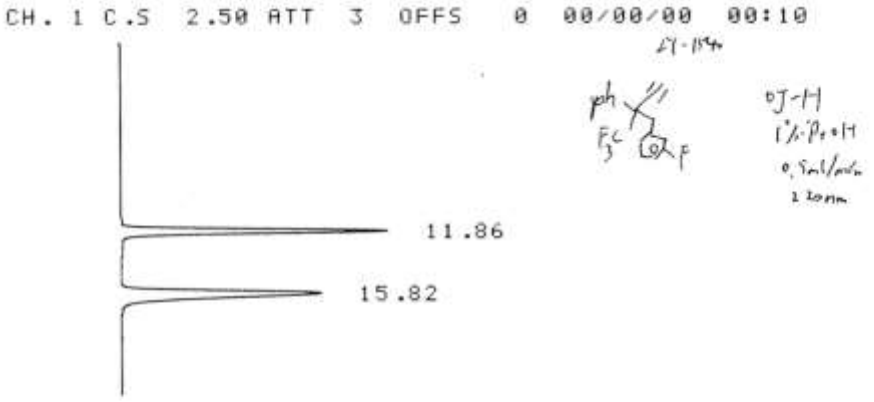
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	13.62	20157	95.080	BB
2	17.74	1043	4.920	BB
TOTAL		21200	100.000	

PEAK REJ : 0

7am (racemate)



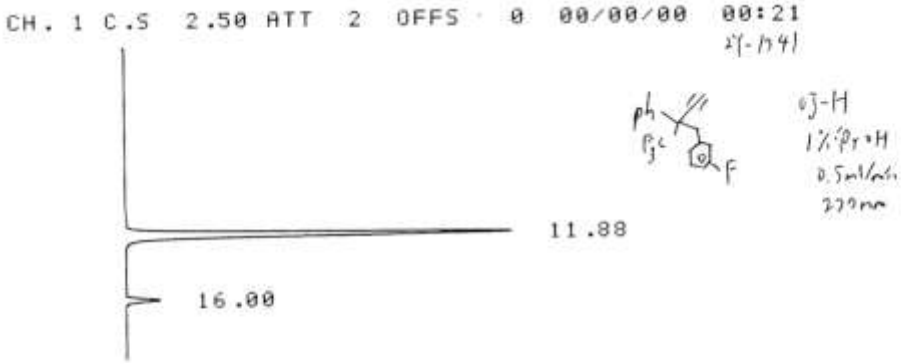
D-2500 00/00/00 00:10

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.86	40194	45.931	BB
2	15.82	47316	54.069	BB
TOTAL		87510	100.000	
PEAK REJ :		0		

7am (chiral)



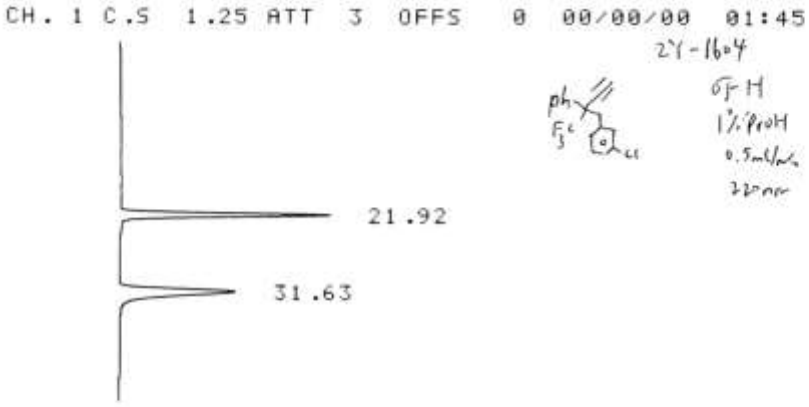
D-2500 00/00/00 00:21

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.88	26913	94.931	BB
2	16.00	1437	5.069	BB
TOTAL		28350	100.000	
PEAK REJ :		0		

7an (racemate)



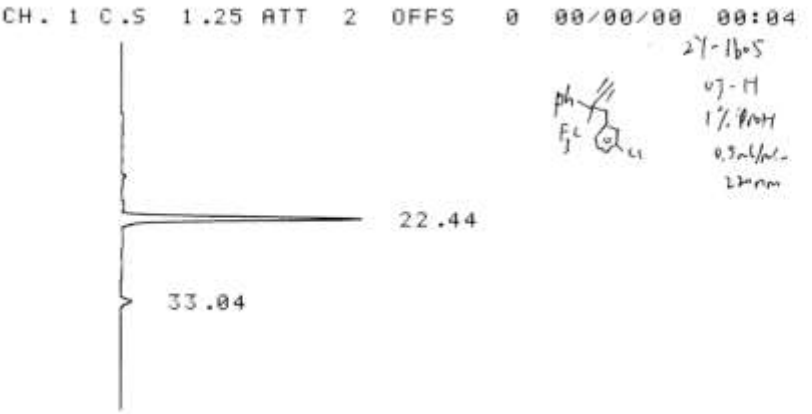
D-2500 00/00/00 01:45

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	21.92	54946	49.620	BB
2	31.63	55788	50.380	BB
TOTAL		110734	100.000	
PEAK REJ :		0		

7an (chiral)



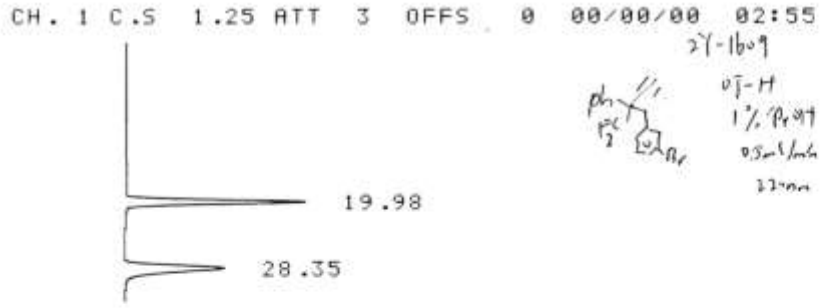
D-2500 00/00/00 00:04

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	22.44	31052	95.642	BB
2	33.04	1415	4.358	BB
TOTAL		32467	100.000	
PEAK REJ :		0		

7ao (racemate)



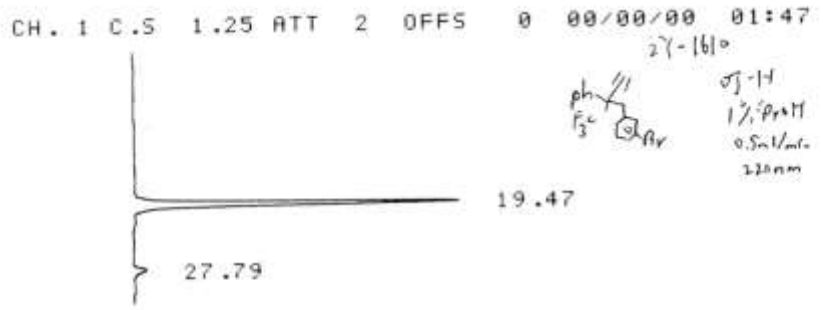
D-2500 00/00/00 02:55

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	19.98	48335	51.028	BB
2	28.35	46387	48.972	BB
TOTAL		94722	100.000	
PEAK REJ :		0		

7ao (chiral)



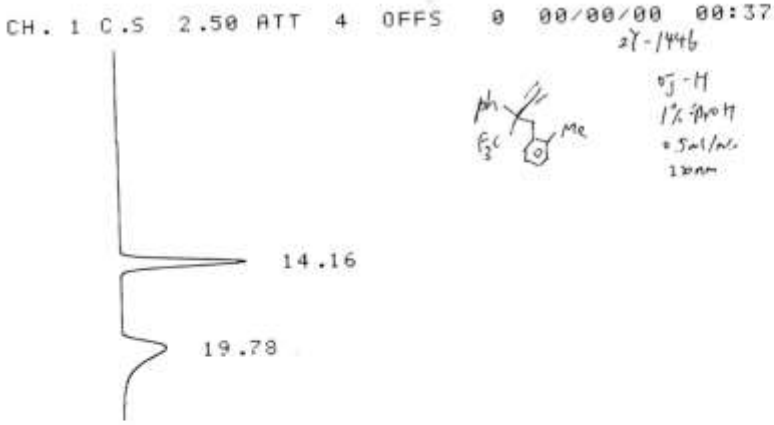
D-2500 00/00/00 01:47

METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	19.47	41257	96.682	BB
2	27.79	1416	3.318	BB
TOTAL		42673	100.000	
PEAK REJ :		0		

7ap (racemate)



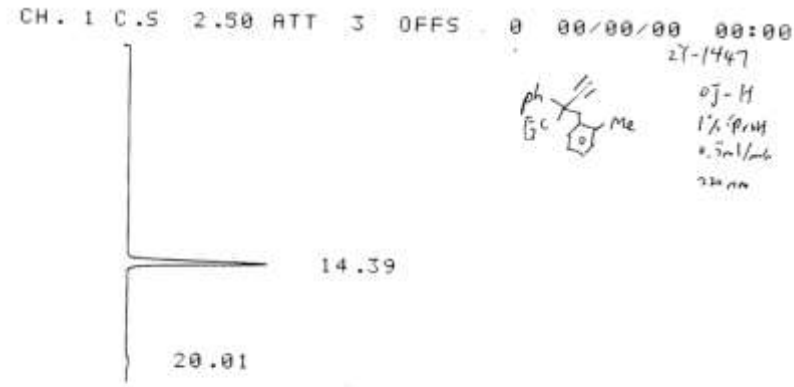
D-2500 00/00/00 00:37

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	14.16	67756	52.148	BB
2	19.78	62173	47.852	BB
TOTAL		129929	100.000	
PEAK REJ :		0		

7ap (chiral)



D-2500 00/00/00 00:00

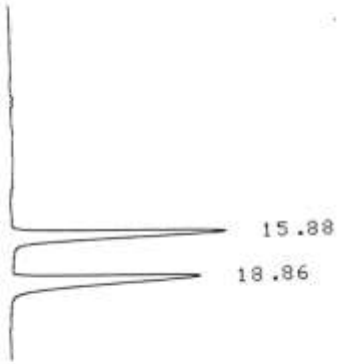
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	14.39	20469	95.085	BB
2	20.01	1058	4.915	BB
TOTAL		21527	100.000	
PEAK REJ :		0		

7aq (racemate)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:36



00/00/00 00:36

D-2500

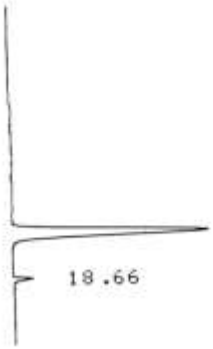
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.88	59573	48.618	BB
2	18.86	62961	51.382	BB
TOTAL		122534	100.000	
PEAK REJ :		0		

7aq (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:35



00/00/00 00:35

D-2500

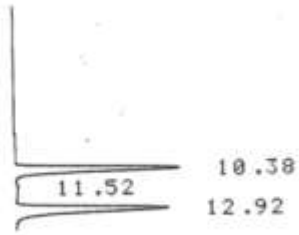
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.56	51528	96.512	BB
2	18.66	1862	3.488	BB
TOTAL		53390	100.000	
PEAK REJ :		0		

7ar (racemate)

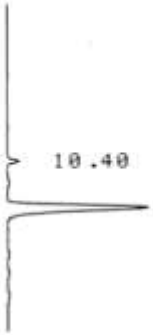
```
CH. 1 C.S  2.50 ATT  6  OFFS   0  00/00/00  03:24
```




```
D-2500                                              00/00/00  03:24

METHOD:                  TAG:      5  CH: 1

FILE: 0  CALC-METHOD: AREA%     TABLE:    0  CONC: AREA

  NO.      RT          AREA       CONC  BC
    1   10.38        220533     47.754  BB
    3   12.92        241279     52.246  BB
TOTAL
                     461812    100.000
PEAK REJ :          3500
```

7ar (chiral)

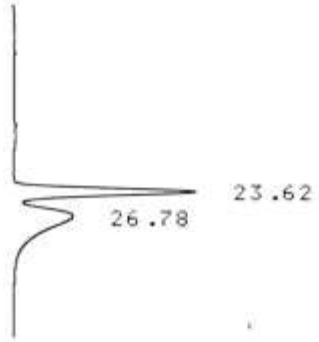
```
CH. 1 C.S  2.50 ATT  6  OFFS   0  00/00/00  01:16
```




```
D-2500                                              00/00/00  01:16

METHOD:                  TAG:      2  CH: 1

FILE: 0  CALC-METHOD: AREA%     TABLE:    0  CONC: AREA

  NO.      RT          AREA       CONC  BC
    1   10.40         12167      4.633  BB
    2   12.92        250443     95.367  BB
TOTAL
                     262610    100.000
PEAK REJ :             0
```

7as (racemate)

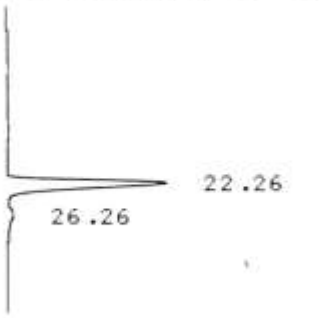
```
CH. 1 C.S  1.25 ATT  4  OFFS   0  00/00/00  02:24
```




```
D-2500                                              00/00/00  02:24

METHOD:                TAG:     3  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   23.62       183168     52.127  BV
    2   26.78       168223     47.873  VB
TOTAL
                    351391    100.000
PEAK REJ :            0
```

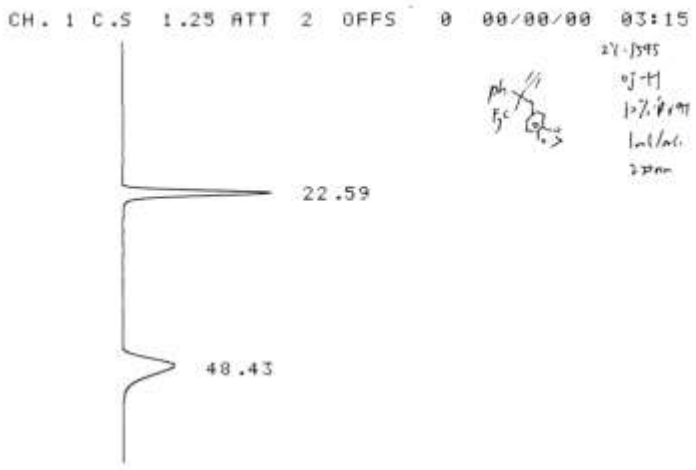
7as (chiral)

```
CH. 1 C.S  1.25 ATT  6  OFFS   0  00/00/00  01:06
```




```
D-2500                                              00/00/00  01:06

METHOD:                TAG:     2  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   22.26       670761     97.442  BB
    2   26.26        17608      2.558  BB
TOTAL
                    688369    100.000
PEAK REJ :            0
```

7at (racemate)



D-2500 00/00/00 03:15

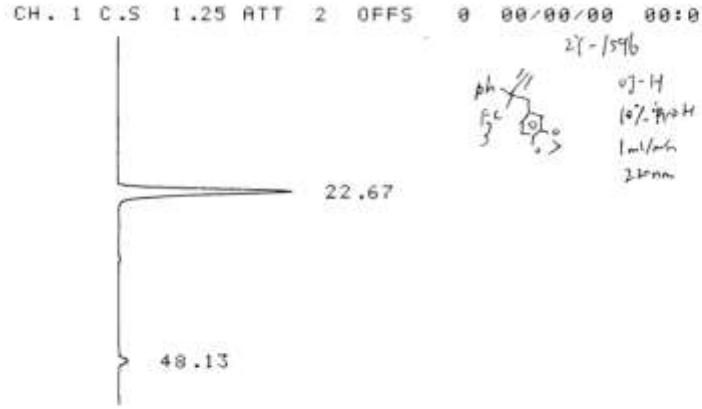
METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	22.59	37910	50.827	BB
2	48.43	36676	49.173	BB
TOTAL		74586	100.000	

PEAK REJ : 0

7at (chiral)



D-2500 00/00/00 00:01

METHOD: TAG: 1 CH 1

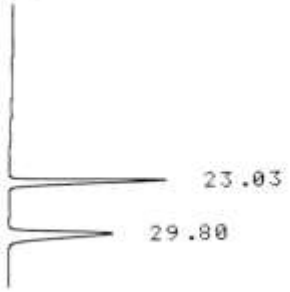
FILE: 0 CALC-M HOD: AREA% TABLE 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	22.67	34983	95.329	BB
2	48.13	1714	4.671	BB
TOTAL		36697	100.000	

PEAK REJ : 0

7au (racemate)

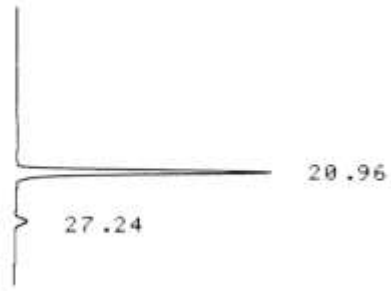
```
CH. 1 C.S  1.25 ATT  5  OFFS   0  00/00/00  00:16
```




```
D-2500                                              00/00/00  00:16

METHOD:                TAG:     1  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   23.03       183632     49.752  BB
    2   29.80       185463     50.248  BB
TOTAL
                    369095    100.000
PEAK REJ :            0
```

7au (chiral)

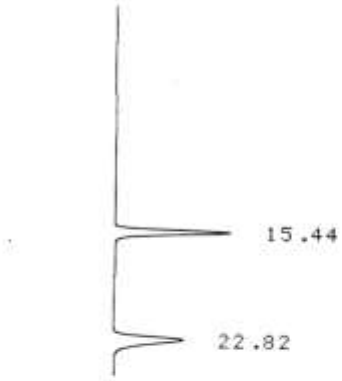
```
CH. 1 C.S  1.25 ATT  2  OFFS   0  00/00/00  00:38
```




```
D-2500                                              00/00/00  00:38

METHOD:                TAG:     2  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   20.96       39608     94.960  BB
    2   27.24        2102      5.040  BB
TOTAL
                    41710    100.000
PEAK REJ :            0
```

7av (racemate)

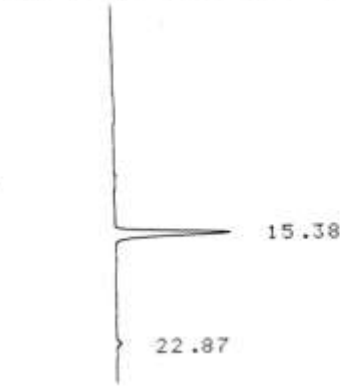
```
CH. 1 C.S  2.50 ATT  4  OFFS   0  00/00/00  00:00
```




```
D-2500                                              00/00/00  00:00

METHOD:                TAG:     1  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   15.44        44780     50.247  BB
    2   22.82        44340     49.753  BB
TOTAL
                     89120    100.000
PEAK REJ :            0
```

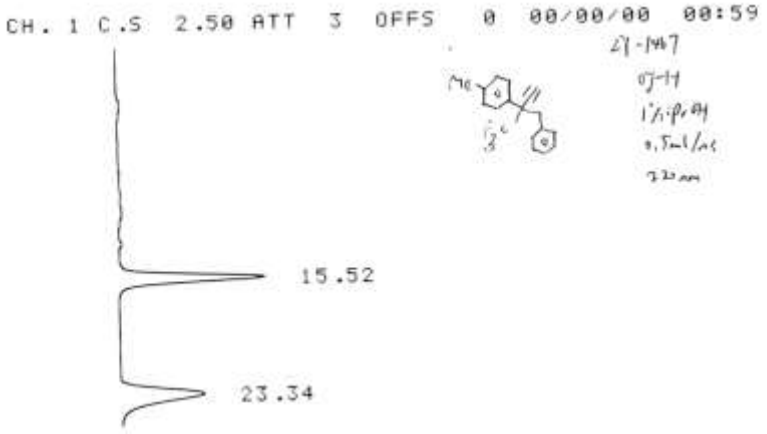
7av (chiral)

```
CH. 1 C.S  2.50 ATT  3  OFFS   0  00/00/00  08:23
```




```
                                                    00/00/00  08:23
D-2500

METHOD:                TAG:     6  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   15.38        22707     97.192  BB
    2   22.87          656      2.808  BB
TOTAL
                     23363    100.000
PEAK REJ :            0
```

7ba (racemate)



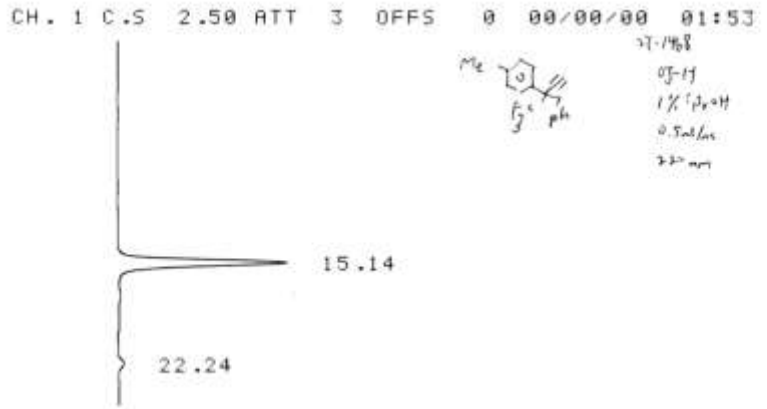
D-2500 00/00/00 00:59

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.52	40652	49.590	BB
2	23.34	41325	50.410	BB
TOTAL		81977	100.000	
PEAK REJ :		0		

7ba (chiral)



D-2500 00/00/00 01:53

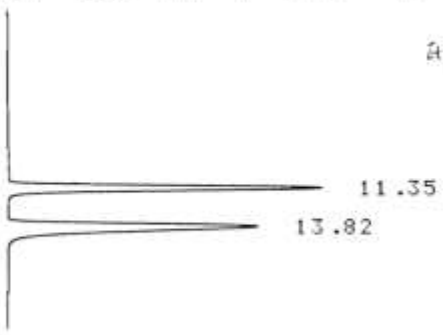
METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.14	44533	95.012	BB
2	22.24	2338	4.988	BB
TOTAL		46871	100.000	
PEAK REJ :		0		

7ca (racemate)

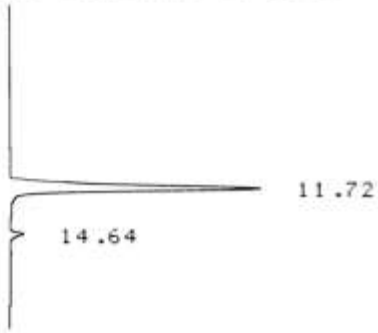
```
CH. 1 C.S  2.50 ATT  5  OFFS   0  00/00/00  00:00
```




```
D-2500                                              00/00/00  00:00

METHOD:                TAG:     1  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   11.35       234656     46.948  BB
    2   13.82       265160     53.052  BB
TOTAL
                    499816    100.000
PEAK REJ :            0
```

7ca (chiral)

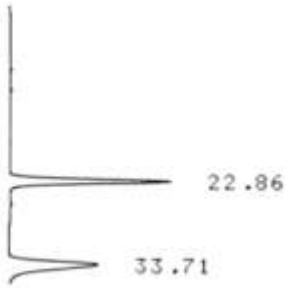
```
CH. 1 C.S  2.50 ATT  2  OFFS   0  00/00/00  00:02
```




```
D-2500                                              00/00/00  00:02

METHOD:                TAG:     1  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   11.72        17448     94.826  BB
    2   14.64          952      5.174  BB
TOTAL
                     18400    100.000
PEAK REJ :            0
```

7da (racemate)

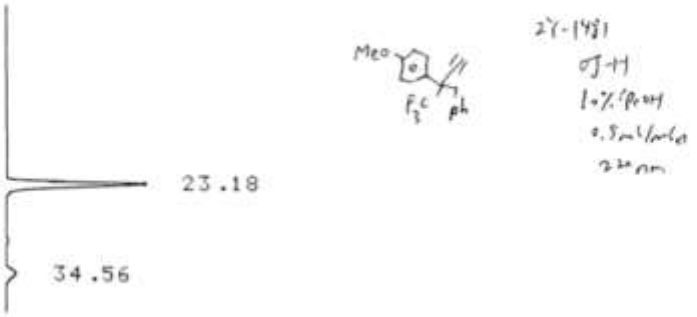
```
CH. 1 C.S  1.25 ATT  3  OFFS   0  00/00/00  02:01
```




```
D-2500                                                  00/00/00  02:01

METHOD:                TAG:     3  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1  22.86        52779     50.450  BB
    2  33.71        51838     49.550  BB
TOTAL
                   104617    100.000
PEAK REJ :           0
```

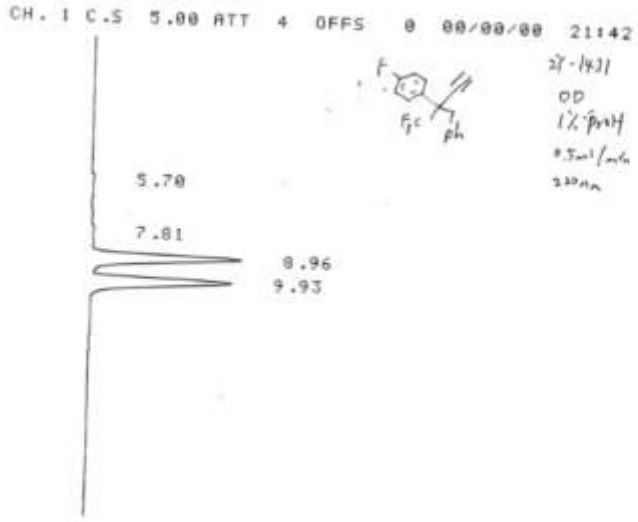
7da (chiral)

```
CH. 1 C.S  1.25 ATT  3  OFFS   0  00/00/00  01:25
```




```
D-2500                                                  00/00/00  01:25

METHOD:                TAG:     3  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1  23.18        53632     95.361  BB
    2  34.56         2609      4.639  BB
TOTAL
                    56241    100.000
PEAK REJ :           0
```

7ea (racemate)



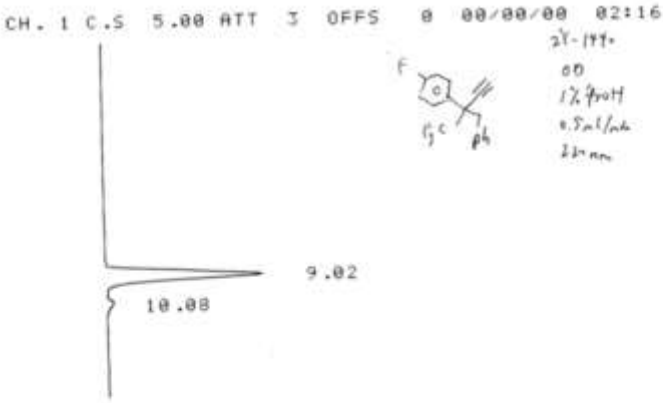
D-2500 00/00/00 21:42

METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
3	8.96	62309	50.026	BV
4	9.93	62243	49.974	VB
TOTAL		124552	100.000	
PEAK REJ :		500		

7ea (chiral)



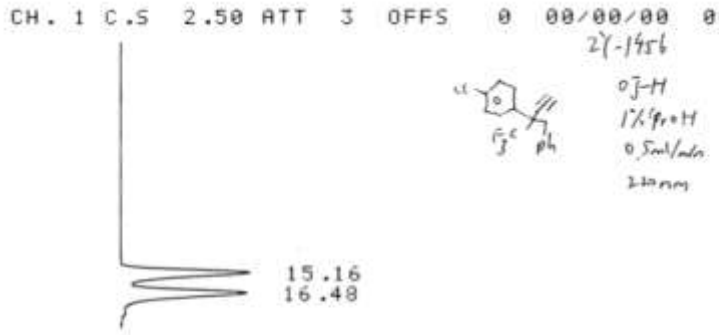
D-2500 00/00/00 02:16

METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	9.02	33123	97.198	BB
2	10.08	955	2.802	TBB
TOTAL		34078	100.000	
PEAK REJ :		0		

7fa (racemate)



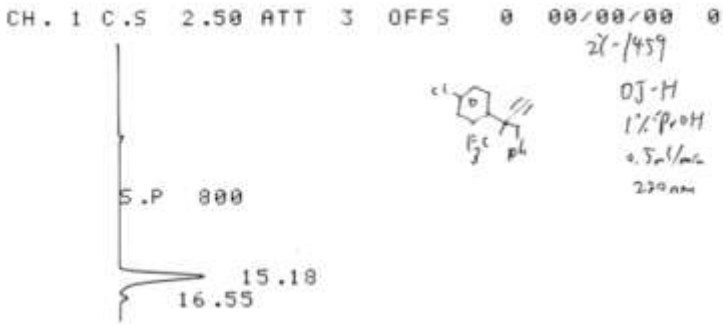
D-2500 00/00/00 00:00

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.16	35691	48.019	BV
2	16.48	38636	51.981	VB
TOTAL		74327	100.000	
PEAK REJ :		0		

7fa (chiral)



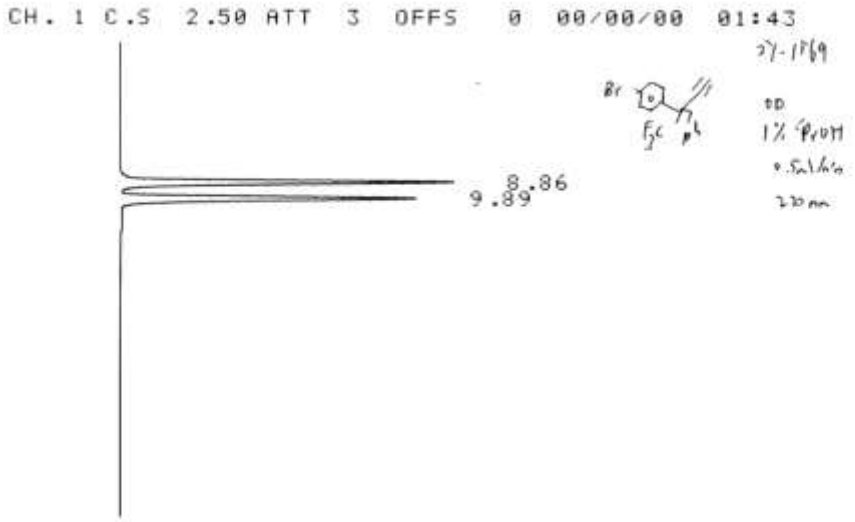
D-2500 00/00/00 00:25

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.18	23828	94.951	BV
2	16.55	1267	5.049	VB
TOTAL		25095	100.000	
PEAK REJ :		0		

7ga (racemate)



D-2500 00/00/00 01:43

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	8.86	43906	51.060	BB
2	9.89	42083	48.940	BB
TOTAL		85989	100.000	
PEAK REJ :		0		

7ga (chiral)

D-2500 00/00/00 00:59

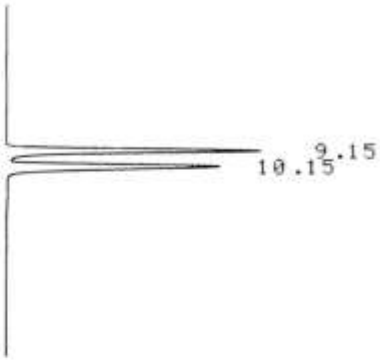
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	8.78	36849	95.983	BB
2	9.77	1542	4.017	BB
TOTAL		38391	100.000	
PEAK REJ :		0		

7ha (racemate)

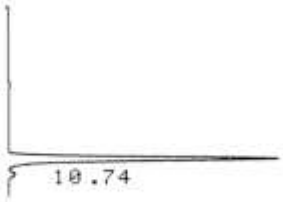
```
CH. 1 C.S  2.50 ATT  5  OFFS   0  00/00/00  00:46
```




```
D-2500                                              00/00/00  00:46

METHOD:                TAG:     1  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1    9.15       152182     50.672  BV
    2   10.15       148144     49.328  VB
TOTAL
                     300326    100.000
PEAK REJ :             0
```

7ha (chiral)

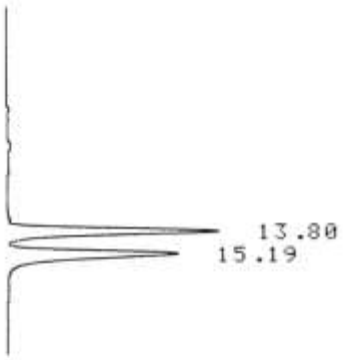
```
CH. 1 C.S  2.50 ATT  3  OFFS   0  00/00/00  01:16
```




```
D-2500                                              00/00/00  01:16

METHOD:                TAG:     1  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1    9.68        32244     96.447  BB
    2   10.74         1188      3.553  BB
TOTAL
                     33432    100.000
PEAK REJ :             0
```

7ia (racemate)

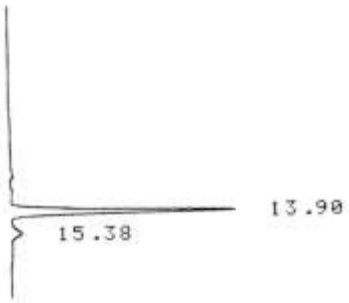
```
CH. 1 C.S  2.50 ATT  3  OFFS   0  00/00/00  00:46
```




```
D-2500                                                  00/00/00  00:46

METHOD:                TAG:     2  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1  13.80        47133     50.424  BV
    2  15.19        46341     49.576  VB
TOTAL
                      93474    100.000
PEAK REJ :             0
```

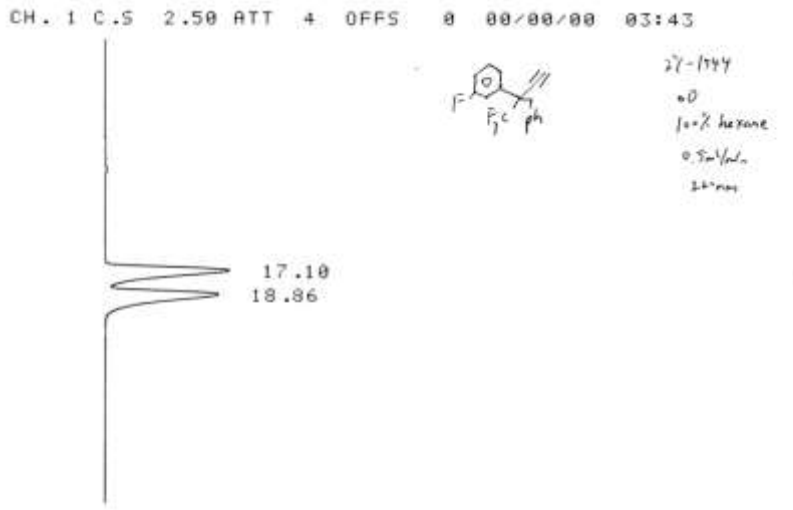
7ia (chiral)

```
CH. 1 C.S  2.50 ATT  3  OFFS   0  00/00/00  03:02
```




```
D-2500                                                  00/00/00  03:02

METHOD:                TAG:     3  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1  13.90        23758     94.635  BB
    2  15.38         1347      5.365  BB
TOTAL
                      25105    100.000
PEAK REJ :             0
```

7ja (racemate)



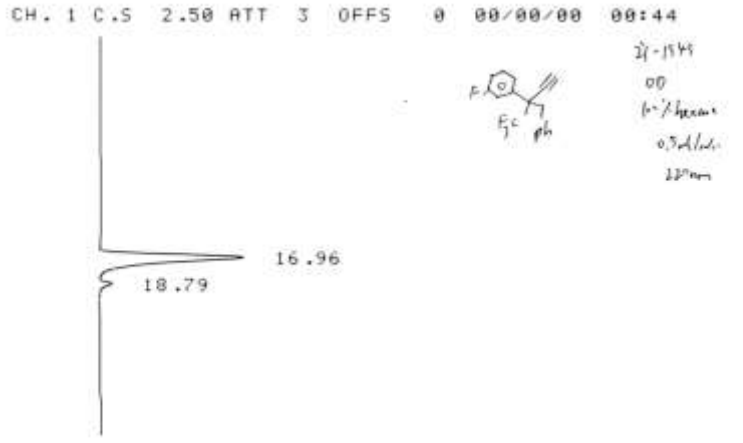
D-2500 00/00/00 03:43

METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	17.10	106167	49.215	BV
2	18.86	109552	50.785	VB
TOTAL		215719	100.000	
PEAK REJ :		0		

7ja (chiral)



D-2500 00/00/00 00:44

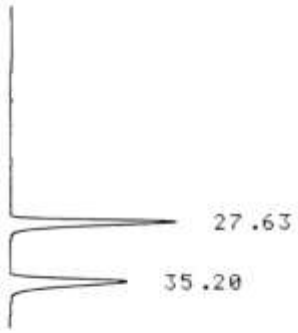
METHOD: TAG: 2 CH: 1

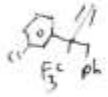
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	16.96	55783	95.432	BB
2	18.79	2670	4.568	BB
TOTAL		58453	100.000	
PEAK REJ :		0		

7ka (racemate)

```
CH. 1 C.S  1.25 ATT  4  OFFS   0  00/00/00  01:05
```



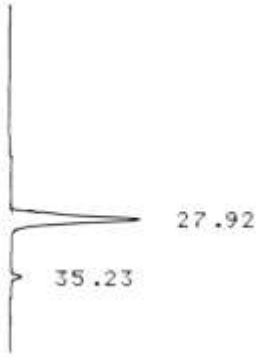


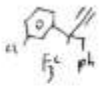
2Y-1600
OJ-H
1% iPrOH
0.5ml/min
220 nm

```
D-2500                                              00/00/00  01:05

METHOD:                TAG:     2  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   27.63       134497     51.212  BB
    2   35.20       128130     48.788  BB
TOTAL
                    262627    100.000
PEAK REJ :            0
```

7ka (chiral)

```
CH. 1 C.S  1.25 ATT  4  OFFS   0  00/00/00  00:17
```



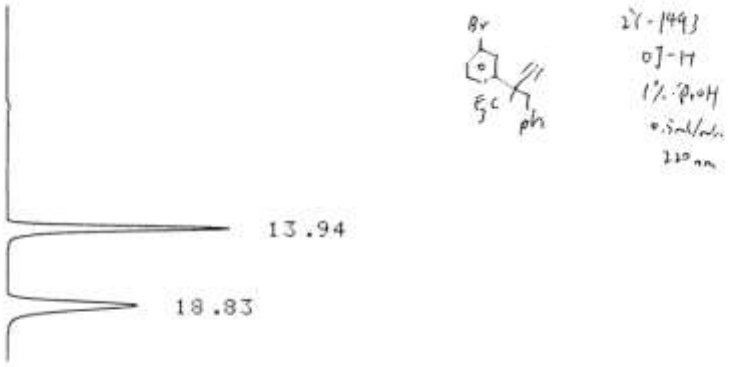


2Y-1601
OJ-H
1% iPrOH
0.5ml/min
220nm

```
D-2500                                              00/00/00  00:17

METHOD:                TAG:     1  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   27.92       147598     97.300  BB
    2   35.23         4096      2.700  BB
TOTAL
                    151694    100.000
PEAK REJ :            0
```

7la (racemate)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 01:02



D-2500 00/00/00 01:02

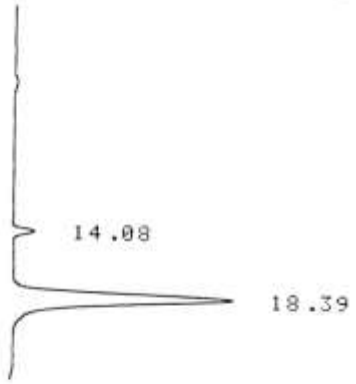
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	13.94	43268	51.048	BB
2	18.83	41492	48.952	BB
TOTAL		84760	100.000	
PEAK REJ :		0		

7la (chiral)

CH. 1 C.S 2.50 ATT 2 OFFS 0 00/00/00 02:28



D-2500 00/00/00 02:28

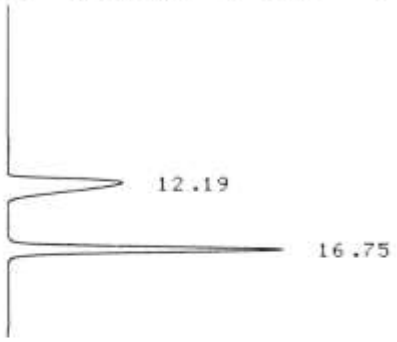
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	14.08	2145	5.120	BB
2	18.39	39748	94.880	BB
TOTAL		41893	100.000	
PEAK REJ :		0		

7ma (racemate)

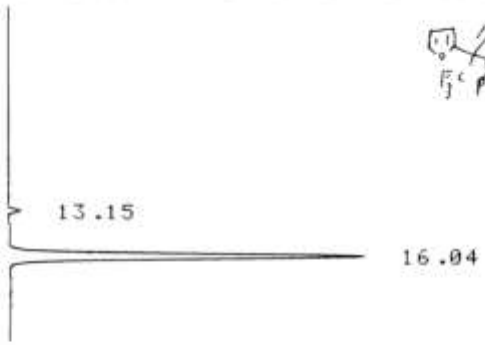
```
CH. 1 C.S  2.50 ATT  4  OFFS   0  00/00/00  01:28
```




```
D-2500                                              00/00/00  01:28

METHOD:                TAG:     1  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1  12.19       111003     46.790  BB
    2  16.75       126236     53.210  BB
TOTAL
                     237239    100.000
PEAK REJ :             0
```

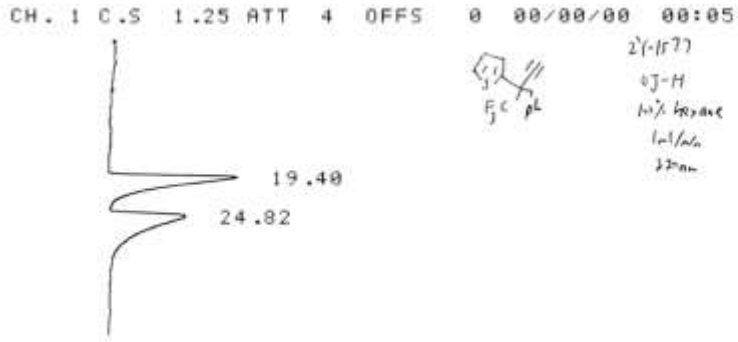
7ma (chiral)

```
CH. 1 C.S  2.50 ATT  2  OFFS   0  00/00/00  04:54
```




```
D-2500                                              00/00/00  04:54

METHOD:                TAG:     3  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1  13.15          616      1.882  BB
    2  16.04        32107     98.118  BB
TOTAL
                     32723    100.000
PEAK REJ :             0
```

7na (racemate)



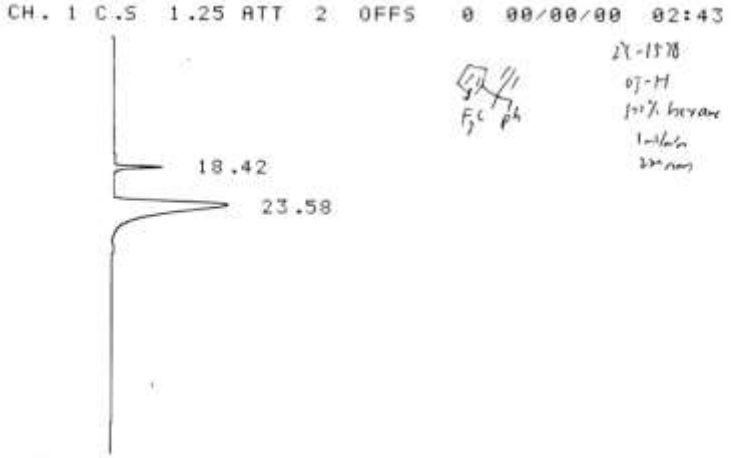
D-2500 00/00/00 00:05

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	19.40	230428	55.847	BB
2	24.82	182180	44.153	BB
TOTAL		412608	100.000	
PEAK REJ :		0		

7na (chiral)



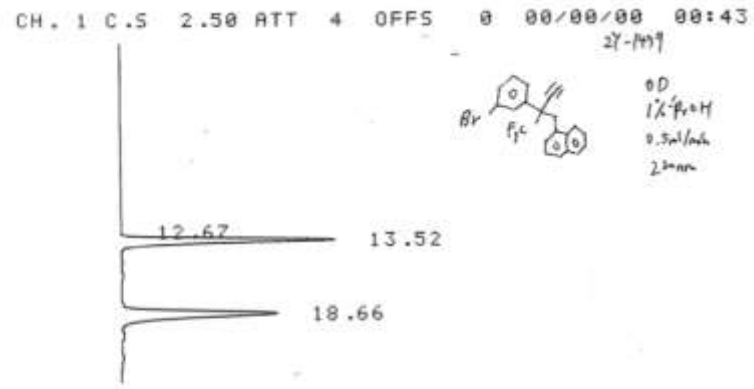
D-2500 00/00/00 02:43

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	18.42	2494	5.083	BB
2	23.58	46571	94.917	BB
TOTAL		49065	100.000	
PEAK REJ :		0		

7lr (racemate)



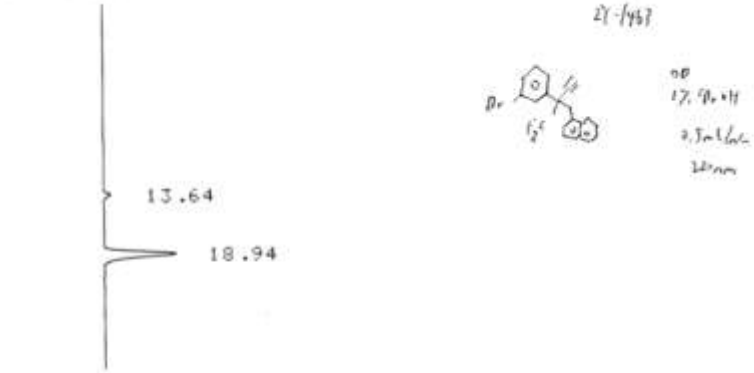
D-2500 00/00/00 00:43

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
2	13.52	84006	49.898	BB
3	18.66	84348	50.102	BB
TOTAL		168354	100.000	
PEAK REJ :		800		

7lr (chiral)



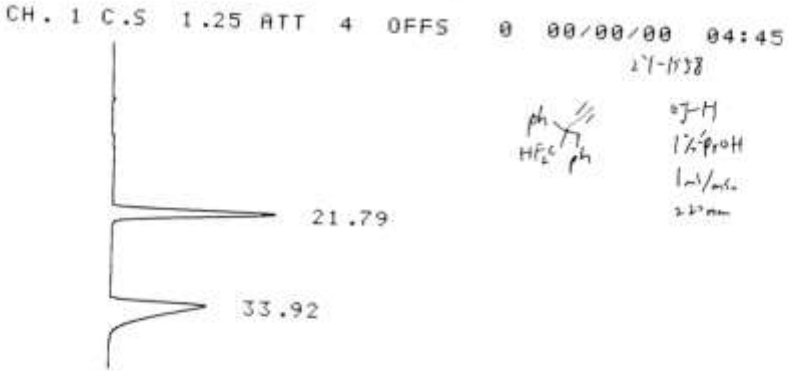
D-2500 00/00/00 01:00

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	13.64	1684	4.439	BB
2	18.94	36255	95.561	BB
TOTAL		37939	100.000	
PEAK REJ :		0		

9 (racemate)



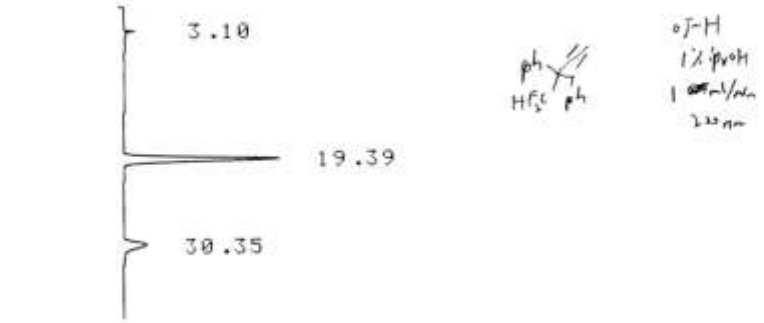
D-2500 00/00/00 04:45

METHOD: TAG: 5 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	21.79	156554	46.727	BB
2	33.92	178488	53.273	BB
TOTAL		335042	100.000	
PEAK REJ :		0		

9 (chiral)



D-2500 00/00/00 00:29

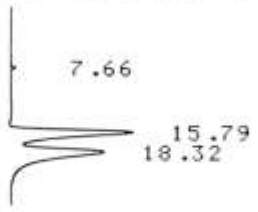
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
2	19.39	19866	81.532	BB
3	30.35	4500	18.468	BB
TOTAL		24366	100.000	
PEAK REJ :		400		

10 (racemate)

```
CH. 1 C.S  1.25 ATT  3  OFFS   0  00/00/00  02:08
```

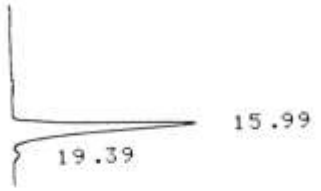


2Y-1645
OJ-H
100% hexane
0.7ml/min
220 nm

```
D-2500                                          00/00/00  02:08

METHOD:                  TAG:     3  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    2  15.79         59580     51.112  BV
    3  18.32         56988     48.888  VB
TOTAL
                     116568    100.000
PEAK REJ :           600
```

10 (chiral)

```
CH. 1 C.S  1.25 ATT  3  OFFS   0  00/00/00  01:15
```

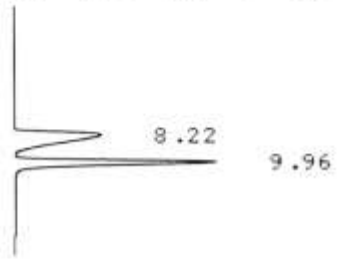


2Y-1631
OJ-H
100% hexane
0.7ml/min
210nm

```
                                                00/00/00  01:15
D-2500

METHOD:                  TAG:     3  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1  15.99        122008     96.492  BB
    2  19.39          4435      3.508  BB
TOTAL
                     126443    100.000
PEAK REJ :           0
```

11 (racemate)

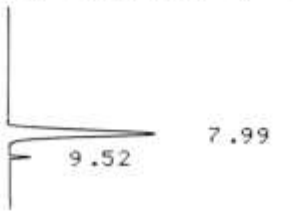
```
CH. 1 C.S  2.50 ATT  5  OFFS   0  00/00/00  01:56
```




```
D-2500                                              00/00/00  01:56

METHOD:                  TAG:     5  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1    8.22       123622     48.472  BB
    2    9.96       131417     51.528  BB
TOTAL
                     255039    100.000
PEAK REJ :             0
```

11 (chiral)

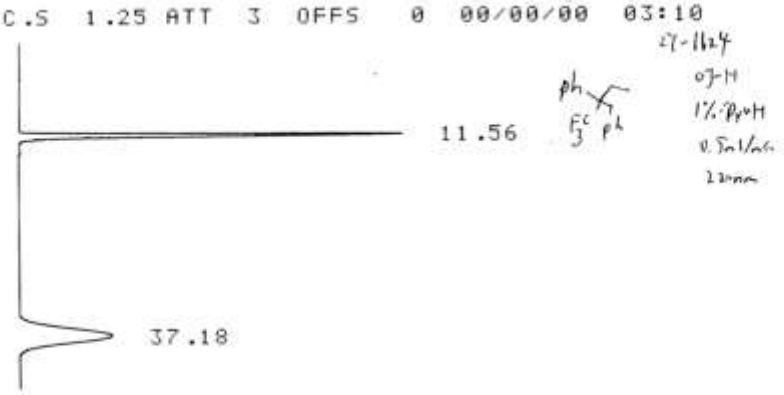
```
CH. 1 C.S  2.50 ATT  4  OFFS   0  00/00/00  07:27
```




```
D-2500                                              00/00/00  07:27

METHOD:                  TAG:    13  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:    0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1    7.99        82751     96.389  BB
    2    9.52         3100      3.611  BB
TOTAL
                     85851    100.000
PEAK REJ :             0
```

12 (racemate)

CH. 1 C.S 1.25 ATT 3 OFFS 0 00/00/00 03:10



D-2500 00/00/00 03:10

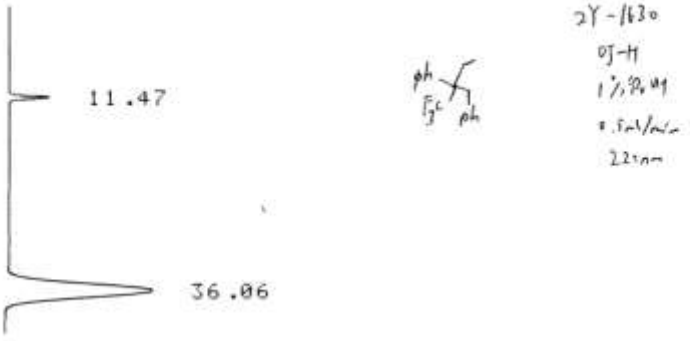
METHOD: TAG: 7 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.56	73777	47.572	BB
2	37.18	81308	52.428	BB
TOTAL		155085	100.000	
PEAK REJ :		0		

12 (chiral)

CH. 1 C.S 1.25 ATT 3 OFFS 0 00/00/00 00:11



D-2500 00/00/00 00:11

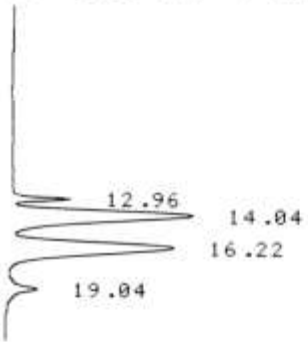
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.47	5916	4.170	BB
2	36.06	135966	95.830	BB
TOTAL		141882	100.000	
PEAK REJ :		0		

13 (racemate)

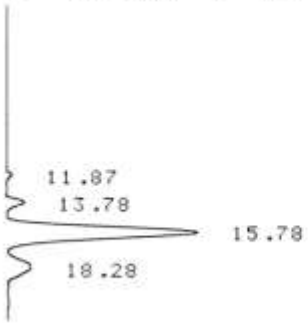
```
CH. 1 C.S  2.50 ATT  4  OFFS   0  00/00/00  00:11
```




```
D-2500                                              00/00/00  00:11

METHOD:                TAG:     1  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    1   12.96        17121      4.871  BV
    2   14.04       159155     45.278  VV
    3   16.22       156901     44.637  VB
    4   19.04        18327      5.214  BB
TOTAL
                    351504    100.000
PEAK REJ :            0
```

13 (chiral)

```
CH. 1 C.S  2.50 ATT  3  OFFS   0  00/00/00  01:38
```




```
D-2500                                              00/00/00  01:38

METHOD:                TAG:     1  CH: 1

FILE: 0  CALC-METHOD: AREA%    TABLE:   0  CONC: AREA

  NO.      RT         AREA       CONC  BC
    2   11.87          481      0.409  BB
    3   13.78         4356      3.706  BB
    4   15.78       100761     85.710  BB
    5   18.28        11962     10.175  BB
TOTAL
                    117560    100.000
PEAK REJ :            0
```

S24. Cartesian coordinates

Cartesian coordinates of stationary points at the ωB97XD(IEFPCM)/(SDD, 6-311G**) level of theory are given below:

I (charge = +1, singlet, NIMAG=0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	0.253720	1.416289	-0.000131
2	44	0	1.023046	-1.293494	-0.022322
3	17	0	-1.182169	-2.302441	-0.118661
4	16	0	0.545321	0.023385	-1.858744
5	16	0	0.441547	-0.019011	1.827880
6	6	0	-1.015557	-0.320087	-2.719102
7	1	0	-1.786882	-0.629070	-2.020709
8	1	0	-0.819029	-1.116491	-3.437319
9	1	0	-1.296403	0.590350	-3.249853
10	6	0	-1.155037	-0.411017	2.597458
11	1	0	-1.866375	-0.763833	1.857107
12	1	0	-0.970582	-1.185244	3.342586
13	1	0	-1.508962	0.494651	3.091218
14	6	0	2.073222	2.789446	-0.498839
15	6	0	0.866652	3.229337	-1.164002
16	6	0	1.848847	2.853512	0.890316
17	6	0	-0.079102	3.612411	-0.169579
18	6	0	0.493734	3.314311	1.106015
19	6	0	1.799673	-3.387281	0.206123
20	6	0	2.169391	-2.836422	-1.062266
21	6	0	2.373506	-2.577576	1.222114
22	6	0	3.045908	-1.714734	-0.818555
23	6	0	3.149481	-1.537645	0.591606
24	6	0	-1.627342	1.199467	-0.033981
25	6	0	-2.879328	1.215921	-0.043282
26	6	0	-4.220944	1.247274	-0.050024
27	1	0	-4.703122	2.225522	-0.082031
28	6	0	3.343786	2.476447	-1.216933
29	1	0	3.777455	3.395197	-1.622771
30	1	0	4.081964	2.024283	-0.555700
31	1	0	3.165649	1.797054	-2.052199
32	6	0	2.826476	2.624386	1.994931
33	1	0	3.788847	2.279802	1.621416
34	1	0	2.991029	3.561031	2.534835

35	1	0	2.450575	1.889982	2.711641
36	6	0	-0.104552	3.635013	2.439619
37	1	0	0.291414	2.978832	3.216062
38	1	0	0.126973	4.667332	2.719862
39	1	0	-1.189582	3.524752	2.424089
40	6	0	-1.382882	4.299414	-0.412784
41	1	0	-2.086826	4.114589	0.398204
42	1	0	-1.214820	5.378176	-0.482174
43	1	0	-1.845497	3.964296	-1.341408
44	6	0	0.728131	3.446087	-2.637259
45	1	0	-0.315270	3.398177	-2.950913
46	1	0	1.113993	4.435052	-2.903509
47	1	0	1.288435	2.701534	-3.203917
48	6	0	3.829235	-1.011476	-1.877619
49	1	0	4.555801	-1.705888	-2.308723
50	1	0	3.185882	-0.655728	-2.685036
51	1	0	4.377278	-0.161461	-1.475634
52	6	0	4.051105	-0.599836	1.322317
53	1	0	4.954659	-1.125185	1.645666
54	1	0	4.354063	0.233192	0.690026
55	1	0	3.562954	-0.195498	2.209913
56	6	0	2.298402	-2.841412	2.691789
57	1	0	3.096921	-3.531156	2.982121
58	1	0	2.417362	-1.924929	3.270430
59	1	0	1.345993	-3.297455	2.964071
60	6	0	1.835938	-3.428582	-2.394763
61	1	0	1.987522	-2.703543	-3.195585
62	1	0	2.472529	-4.295322	-2.596448
63	1	0	0.795163	-3.755029	-2.423286
64	6	0	1.010448	-4.633729	0.420091
65	1	0	1.701856	-5.477657	0.512193
66	1	0	0.409088	-4.576960	1.326869
67	1	0	0.334744	-4.823609	-0.412011
68	6	0	-5.100670	0.109830	-0.017191
69	6	0	-4.596206	-1.201830	0.004827
70	6	0	-6.489998	0.321092	-0.007763
71	6	0	-5.468456	-2.273055	0.037359
72	1	0	-3.523536	-1.367980	-0.009645
73	6	0	-7.356248	-0.756440	0.026219
74	1	0	-6.879418	1.333616	-0.026421
75	6	0	-6.844720	-2.051764	0.048937
76	1	0	-5.078274	-3.283367	0.052370
77	1	0	-8.426959	-0.594272	0.034358
78	1	0	-7.524699	-2.895552	0.074578

Bn (charge = 0, doublet, NIMAG=0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.989362	0.000000	0.000004
2	6	0	-0.251214	-1.213139	0.000003
3	6	0	-0.251214	1.213139	0.000004
4	6	0	1.129085	-1.206776	-0.000000
5	1	0	-0.791368	-2.154199	0.000003
6	6	0	1.129086	1.206776	-0.000001
7	1	0	-0.791367	2.154199	0.000001
8	6	0	1.830962	-0.000000	-0.000002
9	1	0	1.671328	-2.145870	-0.000004
10	1	0	1.671328	2.145870	-0.000005
11	1	0	2.914692	-0.000001	-0.000004
12	6	0	-2.392929	0.000000	-0.000004
13	1	0	-2.950546	-0.928693	-0.000006
14	1	0	-2.950550	0.928690	-0.000008

II (charge = +1, doublet, NIMAG=0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	-0.919213	1.383380	0.210637
2	44	0	-1.917543	-1.231116	-0.081062
3	17	0	0.060544	-2.451429	0.625547
4	16	0	-1.891282	0.031952	1.854385
5	16	0	-0.689441	-0.020541	-1.633496
6	6	0	-0.706769	-0.474424	3.132935
7	1	0	0.194252	-0.885891	2.688620
8	1	0	-1.200397	-1.226992	3.748383
9	1	0	-0.488617	0.406975	3.737018
10	6	0	1.011124	-0.587758	-1.914548
11	1	0	1.482229	-0.888248	-0.983794
12	1	0	0.961182	-1.434733	-2.599466
13	1	0	1.547797	0.233518	-2.392218
14	6	0	-2.644883	2.944280	0.206720
15	6	0	-1.640290	3.257071	1.200069
16	6	0	-2.027282	2.977708	-1.058983

17	6	0	-0.415267	3.530901	0.526666
18	6	0	-0.627171	3.290305	-0.866421
19	6	0	-2.788075	-3.235858	-0.592328
20	6	0	-3.465244	-2.650574	0.524551
21	6	0	-2.950097	-2.371930	-1.707988
22	6	0	-4.115462	-1.445425	0.065164
23	6	0	-3.775179	-1.258820	-1.305790
24	6	0	0.833363	0.961652	0.819775
25	6	0	2.014627	0.849987	1.206211
26	6	0	3.320103	0.765606	1.526156
27	1	0	3.837201	1.687950	1.790701
28	6	0	-4.092690	2.764372	0.522599
29	1	0	-4.532260	3.722378	0.815529
30	1	0	-4.649916	2.390907	-0.335877
31	1	0	-4.230031	2.068674	1.352344
32	6	0	-2.664100	2.852257	-2.403322
33	1	0	-3.722441	2.609045	-2.331539
34	1	0	-2.572967	3.801269	-2.939130
35	1	0	-2.172428	2.083402	-3.004584
36	6	0	0.355761	3.542643	-1.966304
37	1	0	0.152463	2.907774	-2.830006
38	1	0	0.296886	4.585464	-2.293562
39	1	0	1.378011	3.351251	-1.637948
40	6	0	0.833118	4.067677	1.146842
41	1	0	1.715922	3.776750	0.577263
42	1	0	0.783435	5.160265	1.172065
43	1	0	0.960720	3.705918	2.167207
44	6	0	-1.906439	3.461185	2.657633
45	1	0	-1.009216	3.291000	3.253867
46	1	0	-2.237630	4.489288	2.834019
47	1	0	-2.686247	2.788976	3.017494
48	6	0	-5.106994	-0.664452	0.863083
49	1	0	-6.000319	-1.274460	1.024083
50	1	0	-4.708441	-0.388301	1.841355
51	1	0	-5.411325	0.244891	0.348224
52	6	0	-4.322561	-0.233217	-2.241092
53	1	0	-5.139306	-0.661236	-2.829943
54	1	0	-4.712272	0.628155	-1.700773
55	1	0	-3.556788	0.116472	-2.934540
56	6	0	-2.463814	-2.641285	-3.095888
57	1	0	-3.202963	-3.242361	-3.634448
58	1	0	-2.309843	-1.716739	-3.653113
59	1	0	-1.524613	-3.195479	-3.085534
60	6	0	-3.604394	-3.273365	1.877486

61	1	0	-3.917047	-2.536389	2.618487
62	1	0	-4.353268	-4.070792	1.854889
63	1	0	-2.656556	-3.703742	2.204569
64	6	0	-2.093828	-4.555152	-0.599016
65	1	0	-2.800843	-5.324967	-0.924991
66	1	0	-1.241581	-4.556104	-1.277861
67	1	0	-1.725492	-4.814989	0.391868
68	6	0	4.108157	-0.433024	1.545964
69	6	0	3.530534	-1.689231	1.293451
70	6	0	5.488824	-0.336935	1.786936
71	6	0	4.323827	-2.820249	1.286043
72	1	0	2.462443	-1.765725	1.113862
73	6	0	6.276727	-1.471972	1.768427
74	1	0	5.935111	0.634719	1.967549
75	6	0	5.693594	-2.711695	1.519917
76	1	0	3.877305	-3.789204	1.098617
77	1	0	7.343074	-1.396397	1.940095
78	1	0	6.312600	-3.601662	1.508869
79	6	0	5.212156	1.007497	-1.347166
80	6	0	6.576869	1.350431	-1.159661
81	6	0	4.910914	-0.345494	-1.654775
82	6	0	7.569934	0.399219	-1.279019
83	1	0	6.833322	2.379320	-0.929294
84	6	0	5.911451	-1.287235	-1.770108
85	1	0	3.874505	-0.634564	-1.791085
86	6	0	7.246534	-0.923854	-1.584640
87	1	0	8.606922	0.682920	-1.140655
88	1	0	5.658788	-2.315414	-2.001676
89	1	0	8.030094	-1.665957	-1.681300
90	6	0	4.195205	1.962886	-1.205892
91	1	0	4.427072	2.998927	-0.986888
92	1	0	3.157386	1.693884	-1.358651

$TS_{II\text{-}III}$ (charge = +1, doublet, NIMAG=1, 146.5*i* cm^{-1})

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	-1.078420	1.405569	0.114054
2	44	0	-1.838455	-1.288905	-0.117376
3	17	0	0.371968	-2.298954	0.025477
4	16	0	-1.480330	-0.110139	1.841770
5	16	0	-1.155150	0.129178	-1.829138

6	6	0	-0.002166	-0.557544	2.792599
7	1	0	0.837906	-0.766480	2.140800
8	1	0	-0.253193	-1.441076	3.380098
9	1	0	0.214501	0.277271	3.460332
10	6	0	0.487536	-0.208553	-2.521253
11	1	0	1.120639	-0.670163	-1.767836
12	1	0	0.354933	-0.882072	-3.368440
13	1	0	0.895748	0.741669	-2.867864
14	6	0	-2.901826	2.759651	0.589514
15	6	0	-1.741037	3.138584	1.362451
16	6	0	-2.580412	2.917952	-0.774495
17	6	0	-0.726227	3.578955	0.463255
18	6	0	-1.211543	3.380985	-0.864994
19	6	0	-2.597613	-3.361897	-0.525393
20	6	0	-3.049829	-2.890066	0.747550
21	6	0	-3.099813	-2.485858	-1.524085
22	6	0	-3.906677	-1.750090	0.517679
23	6	0	-3.915576	-1.483406	-0.881815
24	6	0	0.821455	1.150557	0.284893
25	6	0	2.054460	1.150367	0.441799
26	6	0	3.405019	1.146953	0.643597
27	1	0	3.921014	2.105172	0.615067
28	6	0	-4.222291	2.413608	1.193734
29	1	0	-4.684705	3.308854	1.619995
30	1	0	-4.909841	2.003909	0.454582
31	1	0	-4.106445	1.684535	1.997464
32	6	0	-3.484578	2.778324	-1.954561
33	1	0	-4.467230	2.405743	-1.671237
34	1	0	-3.618921	3.754916	-2.428078
35	1	0	-3.061646	2.101586	-2.701154
36	6	0	-0.515827	3.783759	-2.127162
37	1	0	-0.875186	3.201026	-2.976710
38	1	0	-0.696886	4.841513	-2.342254
39	1	0	0.562023	3.635007	-2.046596
40	6	0	0.565460	4.225695	0.843811
41	1	0	1.322161	4.083176	0.072863
42	1	0	0.406367	5.300001	0.976662
43	1	0	0.957857	3.818778	1.776018
44	6	0	-1.697062	3.244921	2.853717
45	1	0	-0.677922	3.147958	3.229782
46	1	0	-2.080676	4.220834	3.167391
47	1	0	-2.307692	2.474316	3.325542
48	6	0	-4.755808	-1.109220	1.565460
49	1	0	-5.509210	-1.824739	1.906729

50	1	0	-4.163666	-0.805637	2.431291
51	1	0	-5.275763	-0.233468	1.181709
52	6	0	-4.762502	-0.492382	-1.608273
53	1	0	-5.643232	-0.987611	-2.027892
54	1	0	-5.105473	0.298523	-0.942915
55	1	0	-4.212831	-0.031815	-2.430248
56	6	0	-2.924580	-2.655177	-2.999390
57	1	0	-3.700449	-3.321541	-3.388937
58	1	0	-3.003670	-1.702201	-3.523483
59	1	0	-1.954874	-3.095429	-3.234330
60	6	0	-2.807994	-3.565241	2.060324
61	1	0	-3.001735	-2.885987	2.891719
62	1	0	-3.465217	-4.433132	2.170604
63	1	0	-1.774570	-3.907494	2.134752
64	6	0	-1.793683	-4.594327	-0.765516
65	1	0	-2.474557	-5.427695	-0.967176
66	1	0	-1.125625	-4.476573	-1.618159
67	1	0	-1.181520	-4.843710	0.099486
68	6	0	4.150287	0.045244	1.221579
69	6	0	3.606431	-1.244206	1.293288
70	6	0	5.457835	0.268357	1.672892
71	6	0	4.355527	-2.281823	1.821014
72	1	0	2.605972	-1.429799	0.914841
73	6	0	6.201547	-0.773020	2.201705
74	1	0	5.887802	1.261684	1.603048
75	6	0	5.650531	-2.048226	2.276952
76	1	0	3.929994	-3.276968	1.872513
77	1	0	7.211071	-0.594346	2.551367
78	1	0	6.233654	-2.863734	2.689108
79	6	0	5.367704	0.413306	-1.581680
80	6	0	6.492959	1.260513	-1.471092
81	6	0	5.564677	-0.983061	-1.497956
82	6	0	7.755421	0.731177	-1.291111
83	1	0	6.355612	2.335163	-1.534911
84	6	0	6.830246	-1.503924	-1.312367
85	1	0	4.707035	-1.642535	-1.569860
86	6	0	7.927538	-0.651153	-1.207727
87	1	0	8.613599	1.388373	-1.216375
88	1	0	6.969048	-2.576133	-1.245431
89	1	0	8.919665	-1.062747	-1.064276
90	6	0	4.061619	0.942775	-1.682750
91	1	0	3.908815	1.999397	-1.869604
92	1	0	3.228765	0.282992	-1.886194

III (charge = +1, doublet, NIMAG=0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	-1.048683	-1.332695	-0.077451
2	44	0	-1.915802	1.179851	0.173045
3	17	0	0.158573	2.372865	0.177045
4	16	0	-1.383335	0.167194	-1.835550
5	16	0	-1.254600	-0.190158	1.932352
6	6	0	0.150790	0.712789	-2.632563
7	1	0	0.987478	0.668827	-1.945404
8	1	0	-0.008993	1.735124	-2.975439
9	1	0	0.311352	0.055869	-3.488069
10	6	0	0.324548	0.228084	2.717037
11	1	0	0.969720	0.758341	2.024471
12	1	0	0.088718	0.842644	3.586243
13	1	0	0.785727	-0.706460	3.036999
14	6	0	-2.569260	-2.902212	-0.727415
15	6	0	-1.344435	-3.105547	-1.462614
16	6	0	-2.284423	-3.075374	0.652483
17	6	0	-0.320875	-3.446804	-0.537243
18	6	0	-0.873303	-3.363009	0.781949
19	6	0	-2.872166	3.198125	0.577161
20	6	0	-3.224830	2.706209	-0.718749
21	6	0	-3.328747	2.264082	1.544460
22	6	0	-3.989891	1.492935	-0.538910
23	6	0	-4.029478	1.204392	0.855795
24	6	0	0.890495	-1.005219	-0.050395
25	6	0	2.096632	-0.856620	-0.016827
26	6	0	3.539225	-0.614711	0.038866
27	1	0	4.036115	-1.592750	0.023618
28	6	0	-3.901587	-2.690573	-1.366910
29	1	0	-4.253537	-3.629974	-1.803525
30	1	0	-4.647408	-2.358434	-0.645595
31	1	0	-3.842512	-1.952830	-2.168383
32	6	0	-3.254943	-3.104173	1.786991
33	1	0	-4.242860	-2.762110	1.483788
34	1	0	-3.351302	-4.130440	2.152250
35	1	0	-2.916451	-2.483164	2.618706
36	6	0	-0.153950	-3.705677	2.046546
37	1	0	-0.674466	-3.305139	2.917157
38	1	0	-0.085214	-4.791316	2.161573

39	1	0	0.858421	-3.298024	2.035025
40	6	0	1.052712	-3.906173	-0.890431
41	1	0	1.741203	-3.775484	-0.057504
42	1	0	1.010574	-4.969832	-1.146179
43	1	0	1.451571	-3.358896	-1.743851
44	6	0	-1.215871	-3.132683	-2.950716
45	1	0	-0.210363	-2.852216	-3.265690
46	1	0	-1.413715	-4.144825	-3.316866
47	1	0	-1.926295	-2.456449	-3.426675
48	6	0	-4.734520	0.796476	-1.628624
49	1	0	-5.542883	1.443109	-1.981023
50	1	0	-4.087179	0.575997	-2.479909
51	1	0	-5.177788	-0.134984	-1.281746
52	6	0	-4.802437	0.123704	1.535576
53	1	0	-5.724034	0.533781	1.958479
54	1	0	-5.074153	-0.667659	0.838084
55	1	0	-4.227562	-0.319530	2.350336
56	6	0	-3.231917	2.431659	3.026373
57	1	0	-4.058678	3.056189	3.378361
58	1	0	-3.288819	1.473368	3.542962
59	1	0	-2.298709	2.920023	3.308934
60	6	0	-2.991619	3.422329	-2.010414
61	1	0	-3.096473	2.746890	-2.860217
62	1	0	-3.716279	4.233278	-2.128866
63	1	0	-1.990006	3.854113	-2.038504
64	6	0	-2.192332	4.491610	0.866262
65	1	0	-2.956065	5.252223	1.059156
66	1	0	-1.546401	4.418736	1.740442
67	1	0	-1.579822	4.816924	0.027331
68	6	0	4.031292	0.173823	-1.164103
69	6	0	3.479807	1.419261	-1.461983
70	6	0	5.080569	-0.304495	-1.940533
71	6	0	3.964881	2.166858	-2.525996
72	1	0	2.668873	1.809106	-0.853956
73	6	0	5.568965	0.443605	-3.005987
74	1	0	5.534698	-1.260224	-1.699726
75	6	0	5.011370	1.679936	-3.302388
76	1	0	3.529911	3.135732	-2.744739
77	1	0	6.392241	0.062071	-3.598788
78	1	0	5.394548	2.265607	-4.129963
79	6	0	5.427208	0.199006	1.520087
80	6	0	6.170521	-0.861151	2.036580
81	6	0	6.099616	1.341034	1.089057
82	6	0	7.554799	-0.784827	2.121862

83	1	0	5.659085	-1.755350	2.382221
84	6	0	7.483496	1.421357	1.172391
85	1	0	5.534234	2.168867	0.674034
86	6	0	8.214856	0.358472	1.688172
87	1	0	8.118237	-1.615365	2.531725
88	1	0	7.991994	2.316264	0.832627
89	1	0	9.294718	0.421898	1.755248
90	6	0	3.932751	0.076560	1.373502
91	1	0	3.519660	-0.510366	2.199434
92	1	0	3.459745	1.062338	1.406553

IV (charge = 0, singlet, NIMAG=0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	-0.969863	1.374832	0.195500
2	44	0	-2.003086	-1.197380	-0.252475
3	17	0	-0.009928	-2.596504	-0.281902
4	16	0	-1.361579	-0.264558	1.787087
5	16	0	-1.088173	0.261408	-1.830831
6	6	0	0.110563	-1.011204	2.538555
7	1	0	0.943509	-1.012773	1.845582
8	1	0	-0.147680	-2.030444	2.826272
9	1	0	0.349159	-0.420115	3.424048
10	6	0	0.503689	-0.260489	-2.526086
11	1	0	1.083998	-0.807747	-1.791656
12	1	0	0.282837	-0.887547	-3.391049
13	1	0	1.033155	0.640214	-2.838236
14	6	0	-2.668769	2.996367	0.470352
15	6	0	-1.766343	2.998067	1.575925
16	6	0	-1.908205	3.236256	-0.705213
17	6	0	-0.453046	3.301560	1.100835
18	6	0	-0.532864	3.435887	-0.329753
19	6	0	-3.142399	-3.112162	-0.611685
20	6	0	-3.561660	-2.508571	0.607788
21	6	0	-3.377540	-2.191137	-1.671432
22	6	0	-4.130370	-1.219502	0.296323
23	6	0	-4.012440	-1.020534	-1.113147
24	6	0	0.975585	0.929252	0.237688
25	6	0	2.182574	0.803719	0.262832
26	6	0	3.631462	0.584422	0.234277
27	1	0	4.135347	1.475229	0.630367

28	6	0	-4.157802	3.020139	0.587508
29	1	0	-4.495072	4.051290	0.741841
30	1	0	-4.648064	2.651843	-0.313160
31	1	0	-4.504073	2.432798	1.437090
32	6	0	-2.465946	3.406139	-2.081809
33	1	0	-3.380970	2.827416	-2.213683
34	1	0	-2.698796	4.460267	-2.263799
35	1	0	-1.756926	3.076993	-2.842047
36	6	0	0.582765	3.867693	-1.228672
37	1	0	0.381254	3.589106	-2.264503
38	1	0	0.712307	4.954109	-1.187582
39	1	0	1.517101	3.388805	-0.932113
40	6	0	0.749810	3.581764	1.943791
41	1	0	1.664546	3.345454	1.401890
42	1	0	0.766907	4.638077	2.232181
43	1	0	0.747997	2.975879	2.850807
44	6	0	-2.167374	2.849746	3.008893
45	1	0	-1.321732	2.549669	3.628079
46	1	0	-2.549359	3.802112	3.390955
47	1	0	-2.947218	2.095578	3.127555
48	6	0	-4.856449	-0.366615	1.286361
49	1	0	-5.663516	-0.940475	1.751067
50	1	0	-4.187095	-0.023922	2.080258
51	1	0	-5.299540	0.503752	0.806376
52	6	0	-4.576060	0.096063	-1.930155
53	1	0	-5.439091	-0.253597	-2.505005
54	1	0	-4.902107	0.920425	-1.298434
55	1	0	-3.832049	0.479700	-2.631994
56	6	0	-3.130638	-2.448901	-3.124637
57	1	0	-3.959765	-3.015476	-3.561478
58	1	0	-3.029602	-1.512902	-3.676027
59	1	0	-2.213341	-3.022283	-3.267254
60	6	0	-3.542922	-3.150997	1.958973
61	1	0	-3.552507	-2.397169	2.747739
62	1	0	-4.417080	-3.797420	2.090900
63	1	0	-2.646510	-3.759527	2.088372
64	6	0	-2.589275	-4.489304	-0.760607
65	1	0	-3.412239	-5.186752	-0.951305
66	1	0	-1.881486	-4.544923	-1.586746
67	1	0	-2.062456	-4.804793	0.139043
68	6	0	4.059915	-0.600610	1.084497
69	6	0	3.378422	-1.813322	0.996508
70	6	0	5.180919	-0.516153	1.904507
71	6	0	3.808568	-2.917471	1.719556

72	1	0	2.495374	-1.891591	0.369339
73	6	0	5.614600	-1.620601	2.629107
74	1	0	5.730241	0.418338	1.963356
75	6	0	4.929330	-2.825221	2.538517
76	1	0	3.260351	-3.850098	1.642694
77	1	0	6.491936	-1.539135	3.261471
78	1	0	5.265435	-3.687535	3.103918
79	6	0	5.614080	0.305653	-1.342145
80	6	0	6.393589	1.458775	-1.425312
81	6	0	6.258652	-0.930044	-1.296189
82	6	0	7.780396	1.383265	-1.462954
83	1	0	5.905117	2.428433	-1.462084
84	6	0	7.644327	-1.011173	-1.333507
85	1	0	5.664992	-1.834313	-1.210605
86	6	0	8.410342	0.145486	-1.416875
87	1	0	8.369697	2.291256	-1.531160
88	1	0	8.127317	-1.981113	-1.292220
89	1	0	9.492424	0.082730	-1.446318
90	6	0	4.115645	0.404254	-1.233835
91	1	0	3.749644	1.255469	-1.815452
92	1	0	3.641398	-0.493143	-1.640836

V (charge = +1, singlet, NIMAG=0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	-0.931443	1.329920	-0.326193
2	44	0	-1.615740	-1.358460	0.100601
3	17	0	0.671036	-2.160660	-0.027862
4	16	0	-1.019064	0.170354	1.715312
5	16	0	-1.417807	-0.292551	-1.942524
6	6	0	0.617592	-0.006393	2.462396
7	1	0	1.266486	-0.570667	1.802660
8	1	0	0.483403	-0.525970	3.411635
9	1	0	1.018474	0.991162	2.641546
10	6	0	-0.017840	-0.817076	-2.969219
11	1	0	0.832638	-1.104561	-2.358818
12	1	0	-0.372317	-1.666839	-3.553458
13	1	0	0.227919	0.003845	-3.644066
14	6	0	-2.704332	2.712421	0.352170
15	6	0	-1.417632	3.228663	0.779098
16	6	0	-2.708251	2.658681	-1.051646

17	6	0	-0.657438	3.544639	-0.379940
18	6	0	-1.415094	3.117318	-1.518932
19	6	0	-2.265610	-3.496937	0.181688
20	6	0	-2.498432	-2.843572	1.434156
21	6	0	-3.035692	-2.831043	-0.809354
22	6	0	-3.481484	-1.805690	1.216789
23	6	0	-3.789165	-1.776156	-0.172079
24	6	0	0.867041	1.141099	-0.728728
25	6	0	2.047041	1.208938	-1.268898
26	6	0	3.431466	0.845413	-0.763086
27	1	0	4.095054	1.619436	-1.165263
28	6	0	-3.827323	2.412190	1.287726
29	1	0	-4.223168	3.343143	1.703754
30	1	0	-4.644663	1.896548	0.784679
31	1	0	-3.488106	1.794002	2.121080
32	6	0	-3.838480	2.301795	-1.958528
33	1	0	-4.704413	1.941645	-1.406029
34	1	0	-4.144111	3.185410	-2.525750
35	1	0	-3.543263	1.531799	-2.675424
36	6	0	-1.052949	3.344834	-2.952947
37	1	0	-1.515785	2.598828	-3.600561
38	1	0	-1.397904	4.332002	-3.275557
39	1	0	0.026865	3.304143	-3.101743
40	6	0	0.635690	4.289048	-0.402190
41	1	0	1.244892	4.015444	-1.263009
42	1	0	0.431401	5.362581	-0.452736
43	1	0	1.219045	4.092677	0.497040
44	6	0	-1.045923	3.572333	2.186215
45	1	0	0.030892	3.491772	2.343203
46	1	0	-1.343908	4.602101	2.406078
47	1	0	-1.543361	2.916567	2.901316
48	6	0	-4.158634	-1.040422	2.304910
49	1	0	-4.807452	-1.716625	2.868660
50	1	0	-3.438557	-0.607652	3.001936
51	1	0	-4.776497	-0.236512	1.908729
52	6	0	-4.833253	-0.953371	-0.850784
53	1	0	-5.738167	-1.547687	-1.007475
54	1	0	-5.101637	-0.082693	-0.253570
55	1	0	-4.487361	-0.605471	-1.825413
56	6	0	-3.151327	-3.243087	-2.241752
57	1	0	-3.927443	-4.008407	-2.339007
58	1	0	-3.424772	-2.403381	-2.881386
59	1	0	-2.216436	-3.667456	-2.609473
60	6	0	-1.940959	-3.278464	2.752414

61	1	0	-2.044925	-2.493317	3.502370
62	1	0	-2.470071	-4.165220	3.113885
63	1	0	-0.881989	-3.525131	2.662249
64	6	0	-1.415179	-4.703048	-0.029519
65	1	0	-2.038942	-5.598121	0.061213
66	1	0	-0.953595	-4.699982	-1.016501
67	1	0	-0.615383	-4.757511	0.707044
68	6	0	3.548529	0.931364	0.749655
69	6	0	3.804066	-0.169429	1.559307
70	6	0	3.430304	2.186392	1.352350
71	6	0	3.932215	-0.020932	2.937677
72	1	0	3.906945	-1.155422	1.126701
73	6	0	3.549353	2.338594	2.725703
74	1	0	3.266830	3.058625	0.726635
75	6	0	3.802010	1.228133	3.526521
76	1	0	4.141579	-0.890807	3.549483
77	1	0	3.470884	3.324430	3.170729
78	1	0	3.912736	1.341975	4.598603
79	6	0	5.281347	-0.900528	-1.183141
80	6	0	6.331359	-0.015457	-1.422793
81	6	0	5.586220	-2.193833	-0.762744
82	6	0	7.649903	-0.408843	-1.236202
83	1	0	6.126788	0.994446	-1.764120
84	6	0	6.903871	-2.593105	-0.577869
85	1	0	4.779748	-2.897386	-0.577197
86	6	0	7.940798	-1.699320	-0.811145
87	1	0	8.453130	0.293933	-1.425782
88	1	0	7.120003	-3.603451	-0.249936
89	1	0	8.969721	-2.006268	-0.664972
90	6	0	3.840434	-0.495820	-1.401277
91	1	0	3.656937	-0.414731	-2.479340
92	1	0	3.168829	-1.279322	-1.039362
93	1	0	1.985968	1.520189	-2.316223

VI (charge = +2, doublet, NIMAG=0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	-0.896452	1.309254	-0.311743
2	44	0	-1.744985	-1.243829	0.054448
3	17	0	0.342027	-2.303487	-0.243288
4	16	0	-0.923309	0.167649	1.713409

5	16	0	-1.620506	-0.123236	-1.994015
6	6	0	0.702696	-0.276283	2.361661
7	1	0	1.283112	-0.807417	1.616230
8	1	0	0.538275	-0.894907	3.244241
9	1	0	1.197909	0.651338	2.651465
10	6	0	-0.357347	-0.782032	-3.116239
11	1	0	0.511554	-1.142942	-2.574446
12	1	0	-0.829346	-1.596376	-3.666407
13	1	0	-0.101069	0.014382	-3.816161
14	6	0	-2.463747	2.813448	0.542550
15	6	0	-1.103756	3.238704	0.823749
16	6	0	-2.625914	2.772228	-0.856067
17	6	0	-0.457894	3.511587	-0.417953
18	6	0	-1.364278	3.153754	-1.463526
19	6	0	-2.449561	-3.446576	0.161871
20	6	0	-2.563069	-2.784519	1.431810
21	6	0	-3.230271	-2.731683	-0.788840
22	6	0	-3.523808	-1.720578	1.285099
23	6	0	-3.910862	-1.666602	-0.091881
24	6	0	0.897164	0.986262	-0.769440
25	6	0	2.067399	0.885454	-1.310075
26	6	0	3.470186	0.622642	-0.791826
27	1	0	4.077814	1.430834	-1.215405
28	6	0	-3.503509	2.597073	1.589366
29	1	0	-3.780030	3.557590	2.033037
30	1	0	-4.406943	2.150661	1.174901
31	1	0	-3.131827	1.959204	2.394051
32	6	0	-3.875581	2.522302	-1.629736
33	1	0	-4.692440	2.189386	-0.992490
34	1	0	-4.187837	3.451591	-2.114326
35	1	0	-3.719539	1.780457	-2.416373
36	6	0	-1.143268	3.380628	-2.924061
37	1	0	-1.752393	2.711287	-3.532352
38	1	0	-1.421051	4.408198	-3.177920
39	1	0	-0.096122	3.245038	-3.196566
40	6	0	0.862266	4.179990	-0.594143
41	1	0	1.397850	3.804431	-1.465501
42	1	0	0.693926	5.251852	-0.734776
43	1	0	1.493094	4.049849	0.283172
44	6	0	-0.549853	3.550464	2.176293
45	1	0	0.519664	3.339397	2.227755
46	1	0	-0.695330	4.613711	2.389774
47	1	0	-1.052024	2.980546	2.958108
48	6	0	-4.111579	-0.934461	2.407036

49	1	0	-4.867849	-1.550904	2.902109
50	1	0	-3.362532	-0.662858	3.150879
51	1	0	-4.598599	-0.026500	2.057190
52	6	0	-4.956275	-0.786586	-0.689431
53	1	0	-5.895765	-1.342914	-0.758922
54	1	0	-5.134822	0.095425	-0.076193
55	1	0	-4.684092	-0.464692	-1.695012
56	6	0	-3.441751	-3.128962	-2.212053
57	1	0	-4.220498	-3.896163	-2.259653
58	1	0	-3.765500	-2.286868	-2.823650
59	1	0	-2.534902	-3.551363	-2.646053
60	6	0	-1.940244	-3.258733	2.703406
61	1	0	-1.988961	-2.496775	3.481155
62	1	0	-2.469683	-4.144417	3.066075
63	1	0	-0.895253	-3.530894	2.546579
64	6	0	-1.704478	-4.704461	-0.096846
65	1	0	-2.409906	-5.535842	0.015408
66	1	0	-1.298003	-4.739034	-1.106752
67	1	0	-0.890300	-4.848979	0.610616
68	6	0	3.576141	0.739637	0.719449
69	6	0	3.867905	-0.341277	1.545011
70	6	0	3.424423	2.000249	1.301237
71	6	0	3.992359	-0.167699	2.920803
72	1	0	4.024575	-1.326374	1.126218
73	6	0	3.538773	2.177315	2.673298
74	1	0	3.264160	2.861573	0.660501
75	6	0	3.823346	1.086777	3.490571
76	1	0	4.243241	-1.017264	3.545034
77	1	0	3.448385	3.169041	3.102377
78	1	0	3.941673	1.222154	4.559039
79	6	0	5.431662	-0.989618	-1.172753
80	6	0	6.411617	-0.038937	-1.453072
81	6	0	5.827432	-2.236895	-0.694878
82	6	0	7.754616	-0.324253	-1.246824
83	1	0	6.136872	0.934646	-1.847561
84	6	0	7.170390	-2.527623	-0.490747
85	1	0	5.077946	-2.994837	-0.484887
86	6	0	8.137576	-1.569061	-0.762432
87	1	0	8.504810	0.424959	-1.470386
88	1	0	7.461211	-3.503870	-0.121190
89	1	0	9.185637	-1.791945	-0.603157
90	6	0	3.966755	-0.698645	-1.413240
91	1	0	3.786396	-0.647287	-2.493568
92	1	0	3.352552	-1.525403	-1.042773

93	1	0	1.977846	0.981053	-2.399765

^{2}[Ir(ppy)$_3$]$^-$ (charge = -1, doublet, NIMAG=0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.053584	-0.015146	0.043504
2	7	0	-1.331438	1.214621	-1.077823
3	7	0	-0.600894	-1.788654	-0.949021
4	7	0	1.814706	0.263567	-1.191946
5	6	0	-1.365599	2.511012	-0.696224
6	6	0	-1.773129	-2.338122	-0.393910
7	6	0	2.931520	-0.323528	-0.703289
8	6	0	-2.171020	0.760708	-2.012718
9	6	0	-0.056923	-2.379916	-2.026804
10	6	0	1.862747	0.947048	-2.338004
11	6	0	-2.270353	3.387129	-1.305102
12	6	0	-2.362634	-3.448767	-1.031379
13	6	0	4.134005	-0.220532	-1.414570
14	6	0	-3.086610	1.580180	-2.646574
15	6	0	-0.592070	-3.465388	-2.669333
16	6	0	3.018146	1.083889	-3.082234
17	6	0	-3.129587	2.921506	-2.282176
18	6	0	-1.811770	-4.016861	-2.151018
19	6	0	4.177536	0.480129	-2.602988
20	6	0	0.364530	1.802461	0.890320
21	6	0	-1.527223	-0.517685	1.222816
22	6	0	1.435573	-1.003120	1.106107
23	6	0	-0.413340	2.867621	0.364752
24	6	0	-2.255476	-1.672466	0.784622
25	6	0	2.748565	-1.027695	0.566548
26	6	0	1.271441	2.147787	1.909667
27	6	0	-1.972083	0.140033	2.365049
28	6	0	1.255460	-1.677558	2.329551
29	6	0	-0.286185	4.177908	0.840794
30	6	0	-3.378738	-2.098300	1.525296
31	6	0	3.803991	-1.676254	1.222502
32	6	0	0.615346	4.473088	1.847050
33	6	0	-3.788206	-1.415976	2.659909
34	6	0	3.587125	-2.319873	2.424554
35	6	0	1.395152	3.445177	2.379913
36	6	0	-3.089151	-0.291811	3.089986

37	6	0	2.300466	-2.316544	2.972338
38	1	0	-2.090671	-0.298493	-2.231762
39	1	0	0.866446	-1.930035	-2.383960
40	1	0	0.925611	1.392533	-2.653295
41	1	0	-2.304808	4.424731	-1.000110
42	1	0	-3.280284	-3.856772	-0.619631
43	1	0	5.027744	-0.693075	-1.028977
44	1	0	-3.753327	1.169559	-3.393983
45	1	0	-0.091822	-3.888836	-3.531633
46	1	0	3.007101	1.646571	-4.007009
47	1	0	-3.837515	3.597273	-2.750541
48	1	0	-2.283315	-4.869487	-2.628106
49	1	0	5.108170	0.559084	-3.154856
50	1	0	1.884216	1.364999	2.345597
51	1	0	-1.430464	1.016590	2.709490
52	1	0	0.264942	-1.689541	2.770621
53	1	0	-0.891835	4.979194	0.427407
54	1	0	-3.931806	-2.980324	1.214479
55	1	0	4.802613	-1.681289	0.795176
56	1	0	2.104865	3.665248	3.173109
57	1	0	-3.405146	0.247037	3.978804
58	1	0	2.118223	-2.826308	3.914607
59	1	0	0.711775	5.488747	2.216401
60	1	0	-4.655247	-1.766779	3.213971
61	1	0	4.402932	-2.822814	2.933184

^{1}[Ir(ppy)$_3$] (charge = 0, singlet, NIMAG=0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.000078	-0.000080	0.012173
2	6	0	1.283329	1.164410	1.052245
3	6	0	-1.650095	0.528580	1.052779
4	6	0	0.367181	-1.693952	1.051842
5	6	0	1.435765	2.489549	0.576956
6	6	0	-2.873922	-0.001831	0.577488
7	6	0	1.438736	-2.488111	0.576336
8	6	0	2.044657	0.807577	2.175124
9	6	0	-1.721638	1.365700	2.176151
10	6	0	-0.322256	-2.175347	2.174693
11	6	0	2.301546	3.394820	1.201269
12	6	0	-4.090702	0.294591	1.202316

13	6	0	1.790404	-3.690478	1.200410
14	6	0	3.034977	3.008152	2.307423
15	6	0	-4.122470	1.122398	2.308993
16	6	0	1.089136	-4.132741	2.306595
17	6	0	2.900349	1.707669	2.791791
18	6	0	-2.928895	1.656081	2.793306
19	6	0	0.029921	-3.366401	2.791145
20	6	0	0.621603	2.858134	-0.587213
21	6	0	-2.786274	-0.890308	-0.587372
22	6	0	2.164600	-1.967053	-0.587996
23	7	0	-0.149830	1.862706	-1.080658
24	7	0	-1.538603	-1.060374	-1.081212
25	7	0	1.687702	-0.801492	-1.081500
26	6	0	-0.950736	2.089042	-2.127141
27	6	0	-1.334541	-1.866376	-2.128369
28	6	0	2.283776	-0.221026	-2.128186
29	6	0	0.588756	4.120916	-1.187597
30	6	0	-3.863684	-1.549499	-1.188004
31	6	0	3.274779	-2.569649	-1.188420
32	6	0	-1.023893	3.313061	-2.760834
33	6	0	-2.358227	-2.541143	-2.762332
34	6	0	3.380469	-0.769391	-2.762014
35	6	0	-0.231469	4.348373	-2.274959
36	6	0	-3.650937	-2.372754	-2.276044
37	6	0	3.881456	-1.973020	-2.276008
38	1	0	-1.550607	1.245954	-2.450445
39	1	0	-0.304600	-1.964273	-2.452082
40	1	0	1.853271	0.719841	-2.451589
41	1	0	1.201471	4.920321	-0.793763
42	1	0	-4.862208	-1.418654	-0.793775
43	1	0	3.661091	-3.499734	-0.794344
44	1	0	-1.688000	3.450481	-3.603972
45	1	0	-2.145445	-3.184355	-3.606019
46	1	0	3.831164	-0.262946	-3.605336
47	1	0	-0.260299	5.327511	-2.739273
48	1	0	-4.484651	-2.886809	-2.740585
49	1	0	4.743943	-2.437346	-2.740388
50	1	0	1.954659	-0.196577	2.574725
51	1	0	-0.807011	1.789805	2.575771
52	1	0	-1.147086	-1.595791	2.574515
53	1	0	2.408974	4.408278	0.828646
54	1	0	-5.022052	-0.119197	0.829670
55	1	0	2.614527	-4.289865	0.827513
56	1	0	3.471010	1.396607	3.661368

57	1	0	-2.944744	2.305330	3.663252
58	1	0	-0.524601	-3.705437	3.660708
59	1	0	3.704679	3.709686	2.791477
60	1	0	-5.064781	1.351058	2.793471
61	1	0	1.362240	-5.063451	2.790486

PyH^+ (charge = +1, singlet, NIMAG=0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.743706	-0.000012	0.000000
2	6	0	-2.143860	-0.000008	1.213643
3	6	0	-2.143860	-0.000008	-1.213643
4	6	0	-0.752854	-0.000003	1.219093
5	6	0	-0.752854	-0.000003	-1.219093
6	6	0	-0.082151	-0.000002	0.000000
7	1	0	-3.757709	-0.000018	0.000000
8	6	0	-3.043564	-0.000008	2.403255
9	1	0	-2.842039	0.871473	3.027173
10	1	0	-2.841970	-0.871428	3.027232
11	1	0	-4.093314	-0.000058	2.104548
12	6	0	-3.043564	-0.000008	-2.403255
13	1	0	-2.842039	0.871473	-3.027173
14	1	0	-4.093314	-0.000058	-2.104548
15	1	0	-2.841970	-0.871428	-3.027232
16	1	0	0.999997	-0.000000	-0.000000
17	6	0	0.008474	0.000007	2.518009
18	8	0	-0.524698	0.000029	3.594463
19	8	0	1.310515	-0.000006	2.303254
20	6	0	2.167039	0.000007	3.480012
21	1	0	1.924950	0.884966	4.070956
22	1	0	1.924937	-0.884929	4.070986
23	6	0	3.595843	-0.000012	2.998338
24	1	0	4.265200	-0.000004	3.860701
25	1	0	3.808764	0.888758	2.401650
26	1	0	3.808750	-0.888805	2.401678
27	6	0	0.008474	0.000007	-2.518009
28	8	0	-0.524698	0.000029	-3.594463
29	8	0	1.310515	-0.000006	-2.303254
30	6	0	2.167039	0.000007	-3.480012
31	1	0	1.924950	0.884966	-4.070956
32	1	0	1.924937	-0.884929	-4.070986

33	6	0	3.595843	-0.000012	-2.998338
34	1	0	4.265200	-0.000004	-3.860701
35	1	0	3.808764	0.888758	-2.401650
36	1	0	3.808750	-0.888805	-2.401678

Py (charge = 0, singlet, NIMAG=0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.839569	-0.000039	-0.000000
2	6	0	-2.186460	-0.000022	1.163898
3	6	0	-2.186460	-0.000022	-1.163898
4	6	0	-0.779963	0.000007	1.206802
5	6	0	-0.779963	0.000007	-1.206802
6	6	0	-0.094210	0.000017	-0.000000
7	6	0	-3.059693	-0.000042	2.384027
8	1	0	-2.859276	0.872011	3.009122
9	1	0	-2.859164	-0.872022	3.009184
10	1	0	-4.098982	-0.000116	2.060250
11	6	0	-3.059693	-0.000042	-2.384027
12	1	0	-2.859276	0.872011	-3.009122
13	1	0	-4.098982	-0.000116	-2.060250
14	1	0	-2.859164	-0.872022	-3.009184
15	1	0	0.986006	0.000035	0.000000
16	6	0	-0.027032	0.000032	2.491918
17	8	0	-0.517921	0.000092	3.592160
18	8	0	1.298826	-0.000014	2.289564
19	6	0	2.119590	0.000018	3.467279
20	1	0	1.878964	0.882201	4.065469
21	1	0	1.878908	-0.882092	4.065555
22	6	0	3.560576	-0.000050	3.012498
23	1	0	4.222297	-0.000030	3.881660
24	1	0	3.778043	0.886457	2.413283
25	1	0	3.777985	-0.886628	2.413367
26	6	0	-0.027032	0.000032	-2.491918
27	8	0	-0.517921	0.000092	-3.592160
28	8	0	1.298826	-0.000014	-2.289564
29	6	0	2.119590	0.000018	-3.467279
30	1	0	1.878964	0.882201	-4.065469
31	1	0	1.878908	-0.882092	-4.065555
32	6	0	3.560576	-0.000050	-3.012498
33	1	0	4.222297	-0.000030	-3.881660

34	1	0	3.778043	0.886457	-2.413283
35	1	0	3.777985	-0.886628	-2.413367
