**ISCI, Volume *3***

## Supplemental Information

# HOTf-Catalyzed Alkyl-Heck-type Reaction

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## Supplemental Figures for $^{1}$H NMR, $^{13}$C NMR, and $^{19}$F NMR Spectra

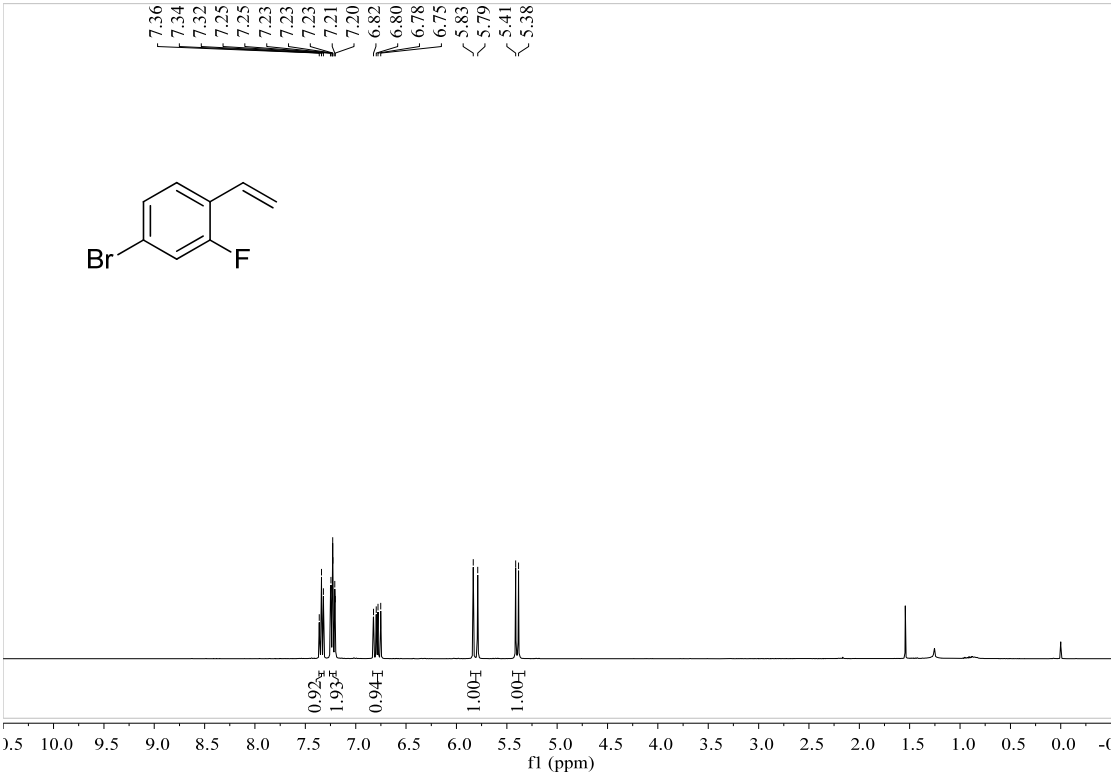



**Figure S1**. $^{1}$H NMR spectrum of 4-bromo-2-fluoro-1-vinylbenzene, Related to **Figure 1**.

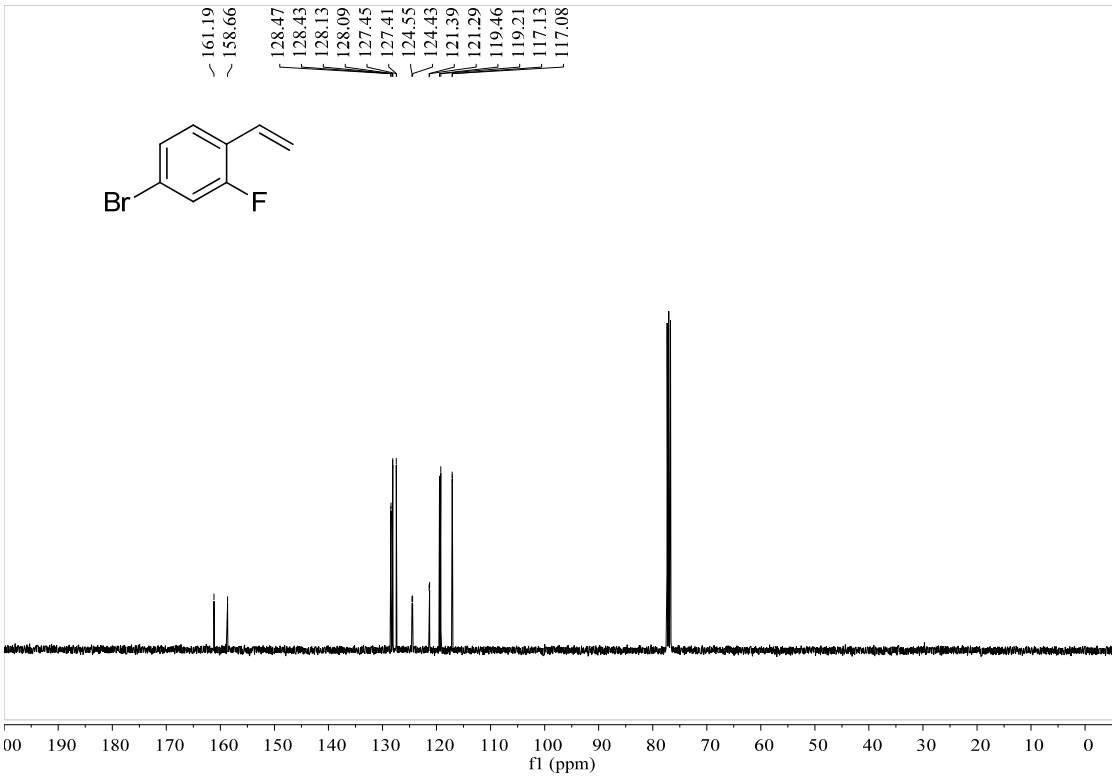



**Figure S2**. $^{13}C$ NMR spectrum of 4-bromo-2-fluoro-1-vinylbenzene, Related to **Figure 1**.

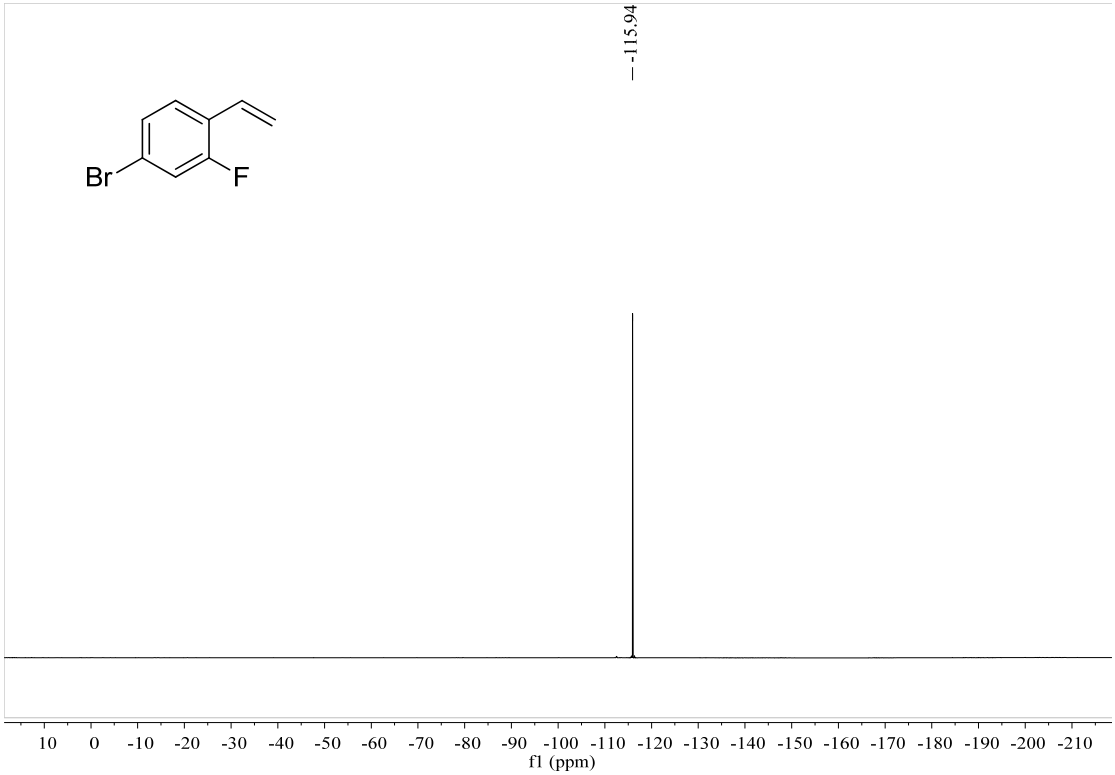



**Figure S3**. $^{19}F$ NMR spectrum of 4-bromo-2-fluoro-1-vinylbenzene, Related to **Figure 1**.

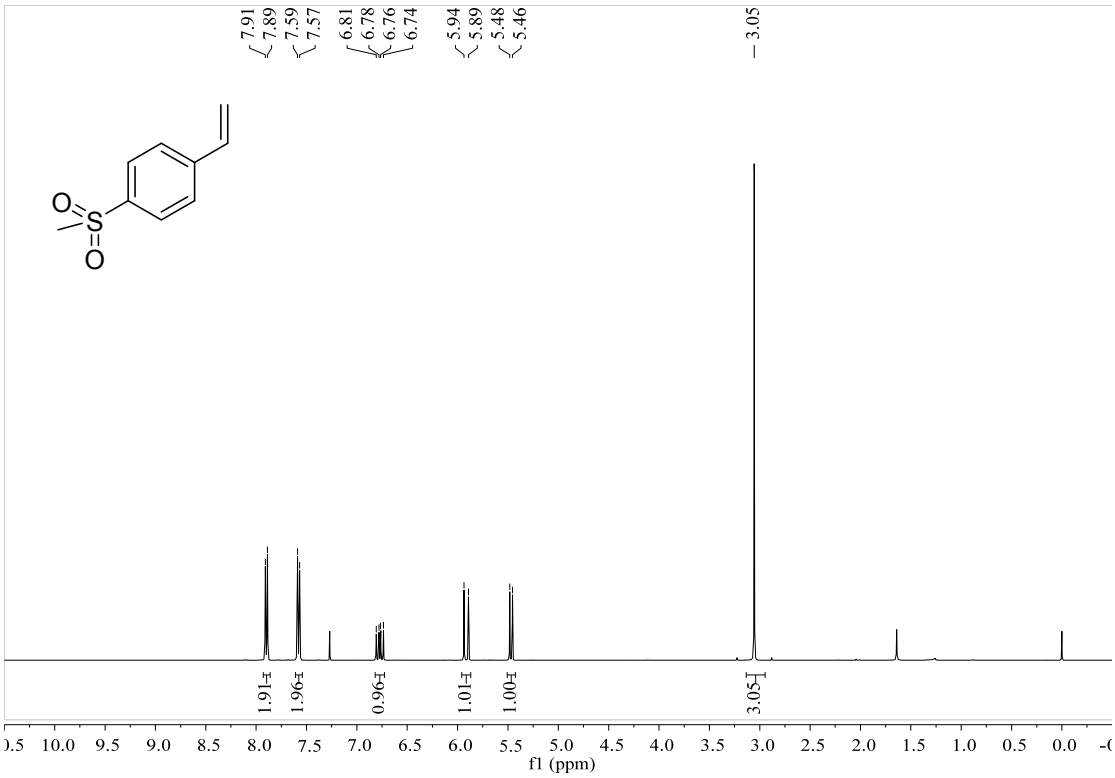



**Figure S4**. [1]H NMR spectrum of 1-(methylsulfonyl)-4-vinylbenzene, Related to **Figure 1**.

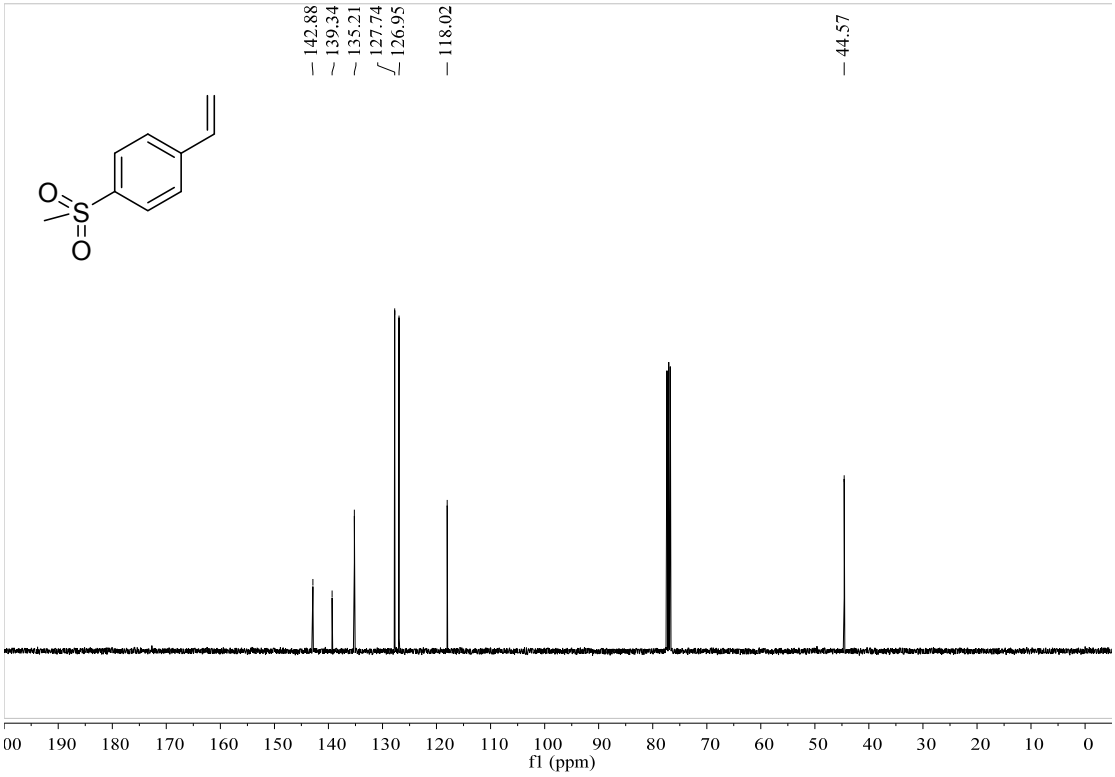



**Figure S5**. [13]C NMR spectrum of 1-(methylsulfonyl)-4-vinylbenzene, Related to **Figure 1**.

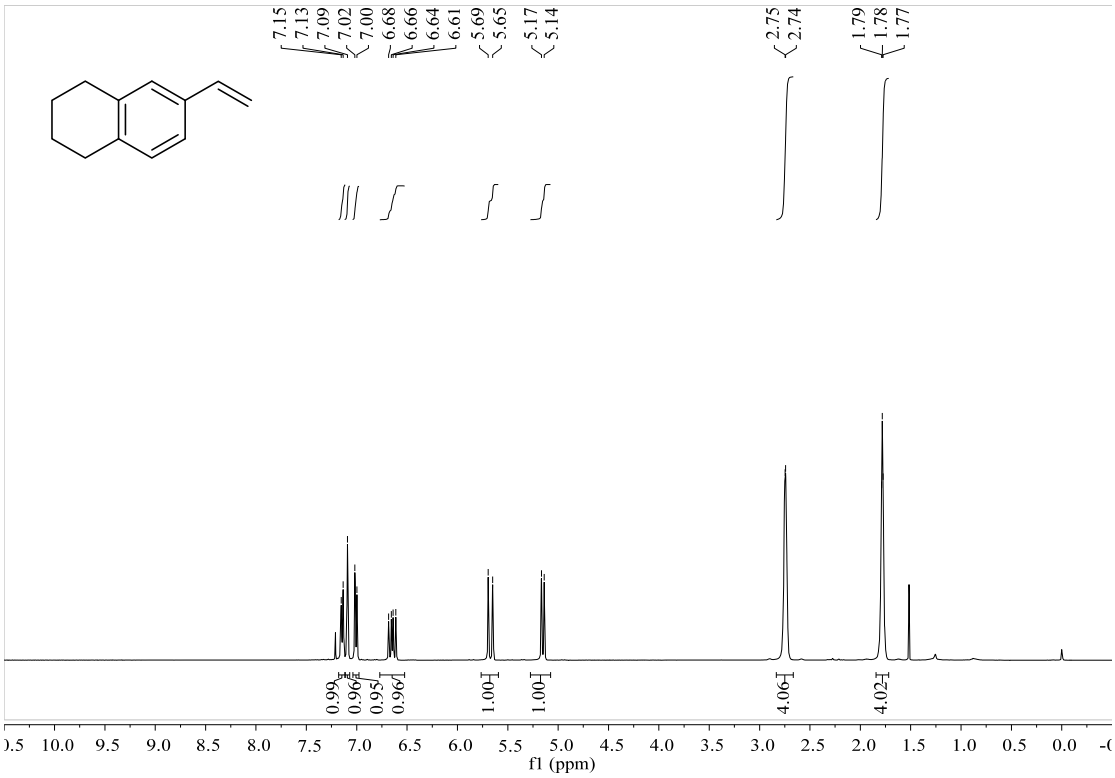



**Figure S6**. [1]H NMR spectrum of 6-vinyl-1,2,3,4-tetrahydronaphthalene, Related to **Figure 1**.

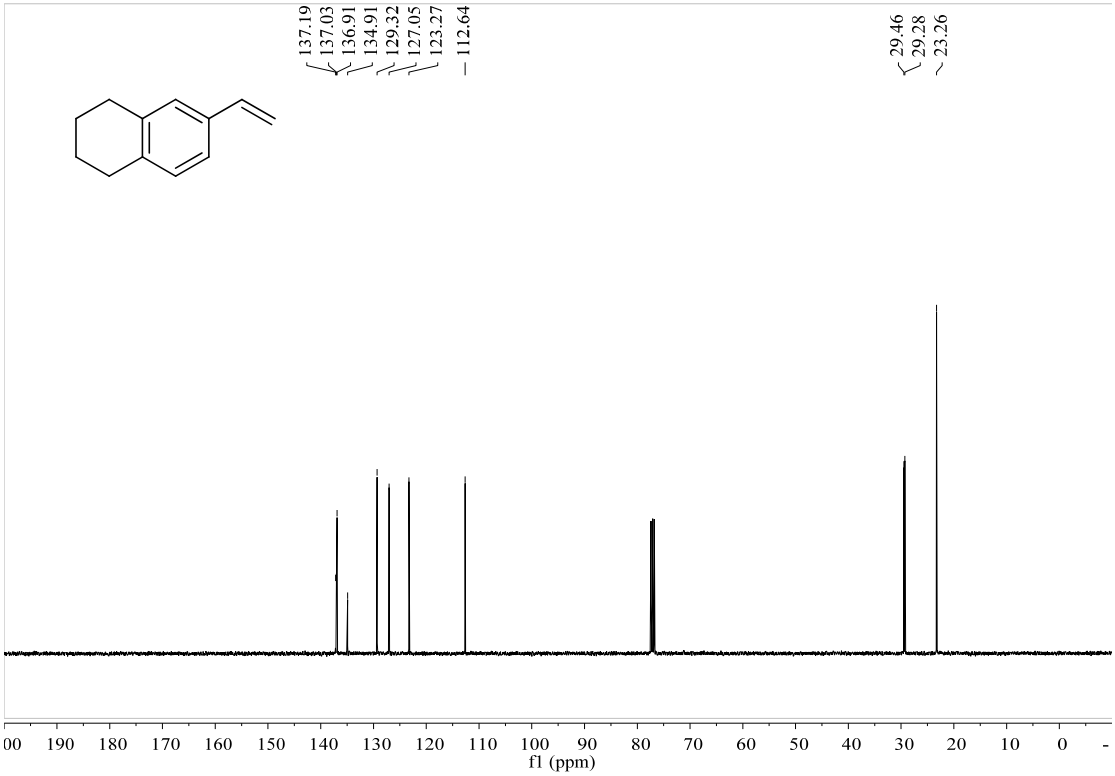



**Figure S7**. [13]C NMR spectrum of 6-vinyl-1,2,3,4-tetrahydronaphthalene, Related to **Figure 1**.

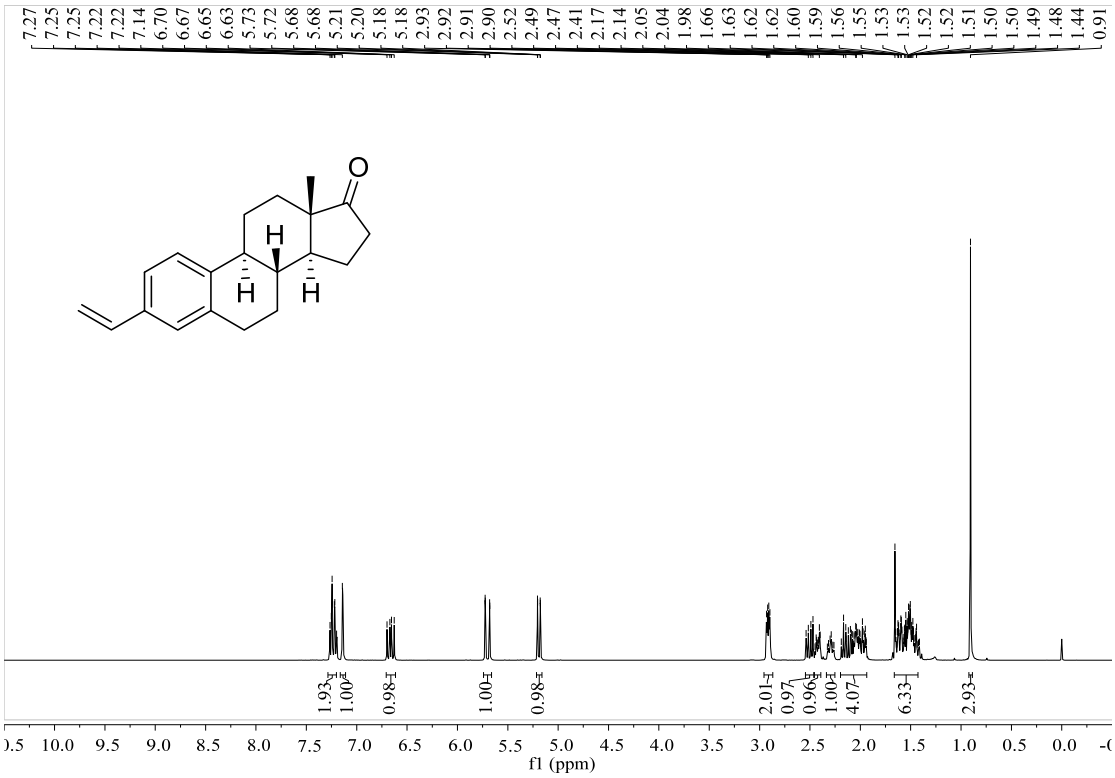



**Figure S8.** [1]H NMR spectrum of compound **57**, related to **scheme 2.**

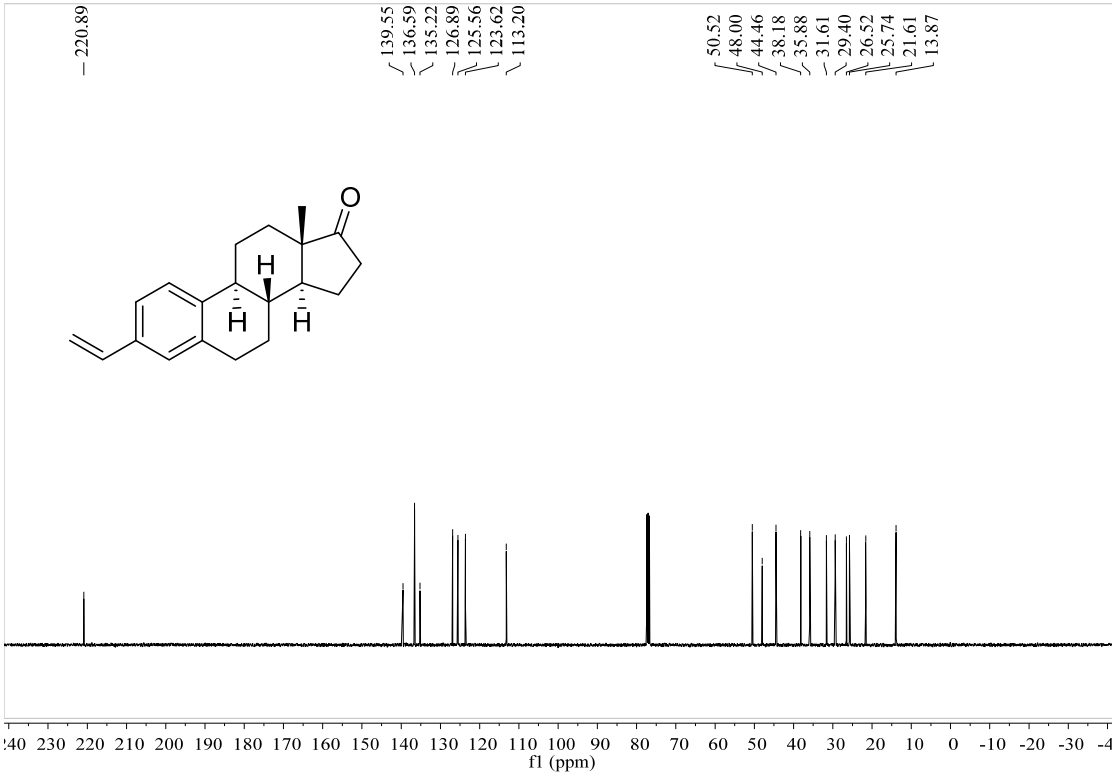



**Figure S9.**[13]C NMR spectrum of compound **57**, related to **Scheme 2.**

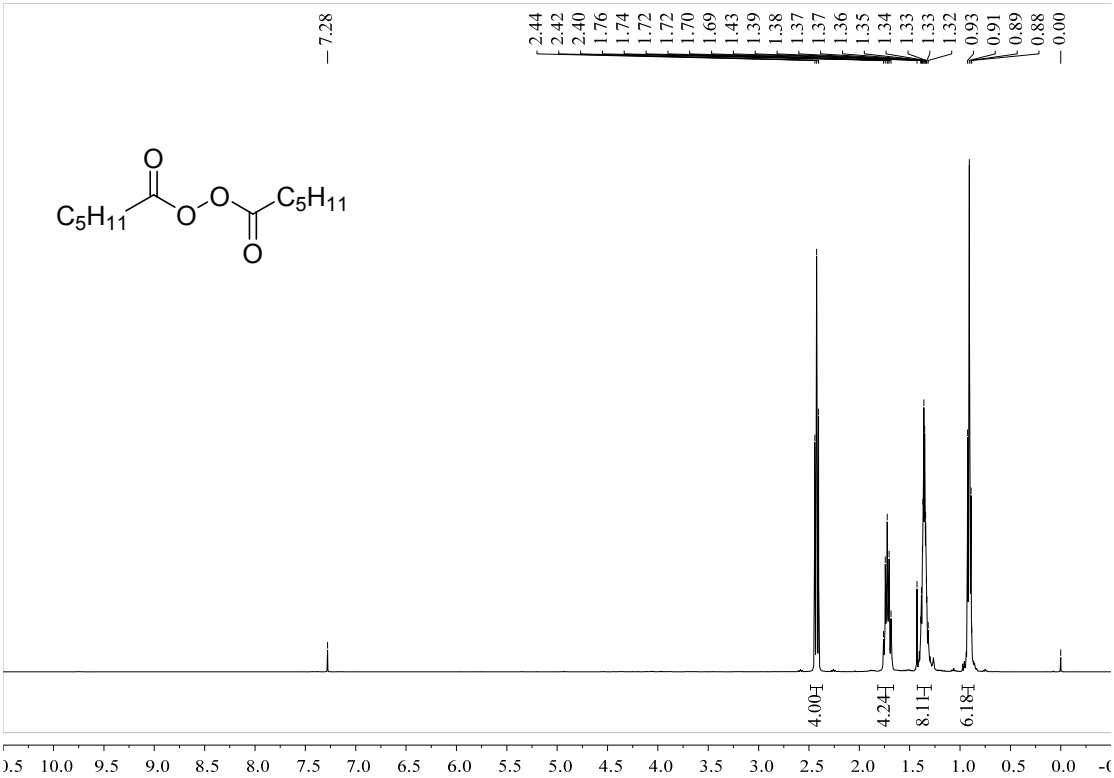



**Figure S10.** $^{1}H$ NMR spectrum of hexanoic peroxyanhydride, related to **Figure 3**.

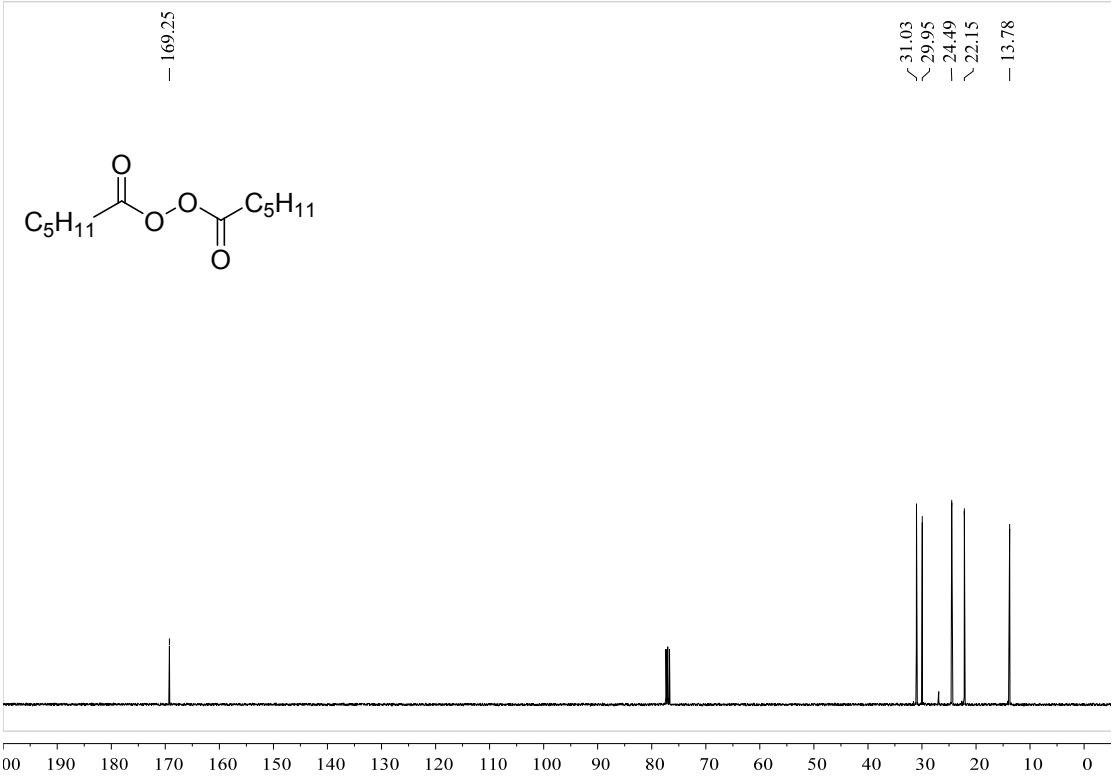



**Figure S11.** $^{13}C$ NMR spectrum of hexanoic peroxyanhydride, related to **Figure 3**.

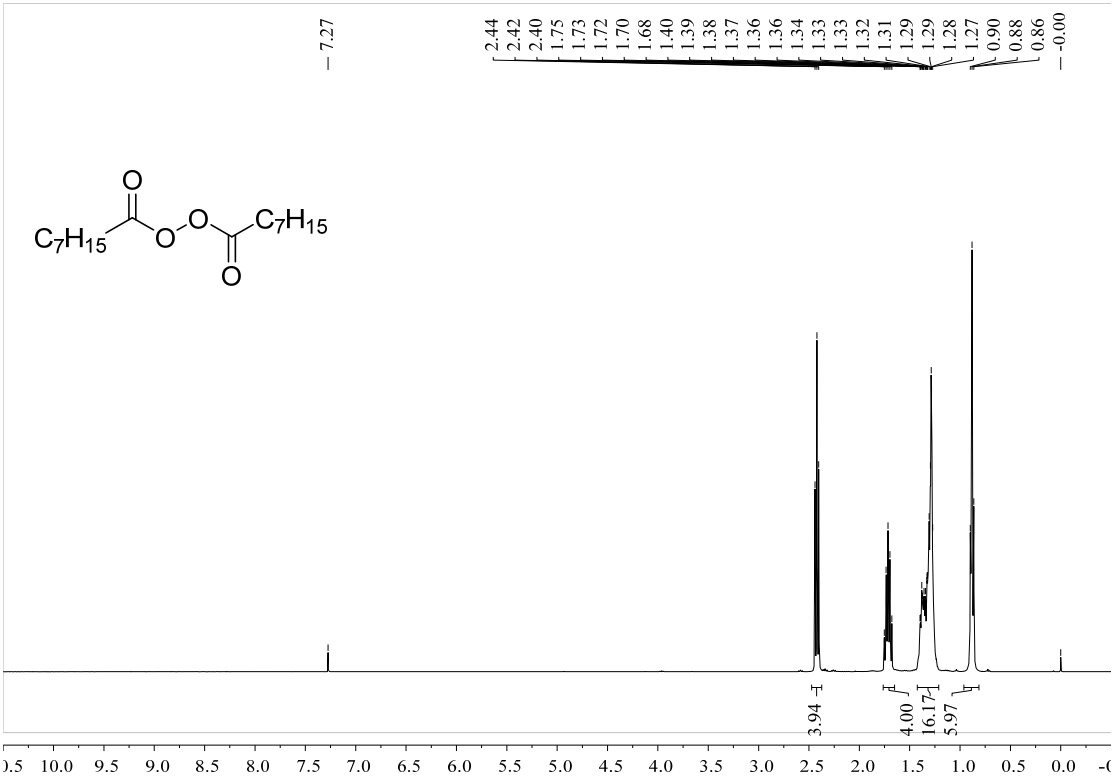



**Figure S12.** $^{1}$H NMR spectrum of octanoic peroxyanhydride, related to **Figure 3**.

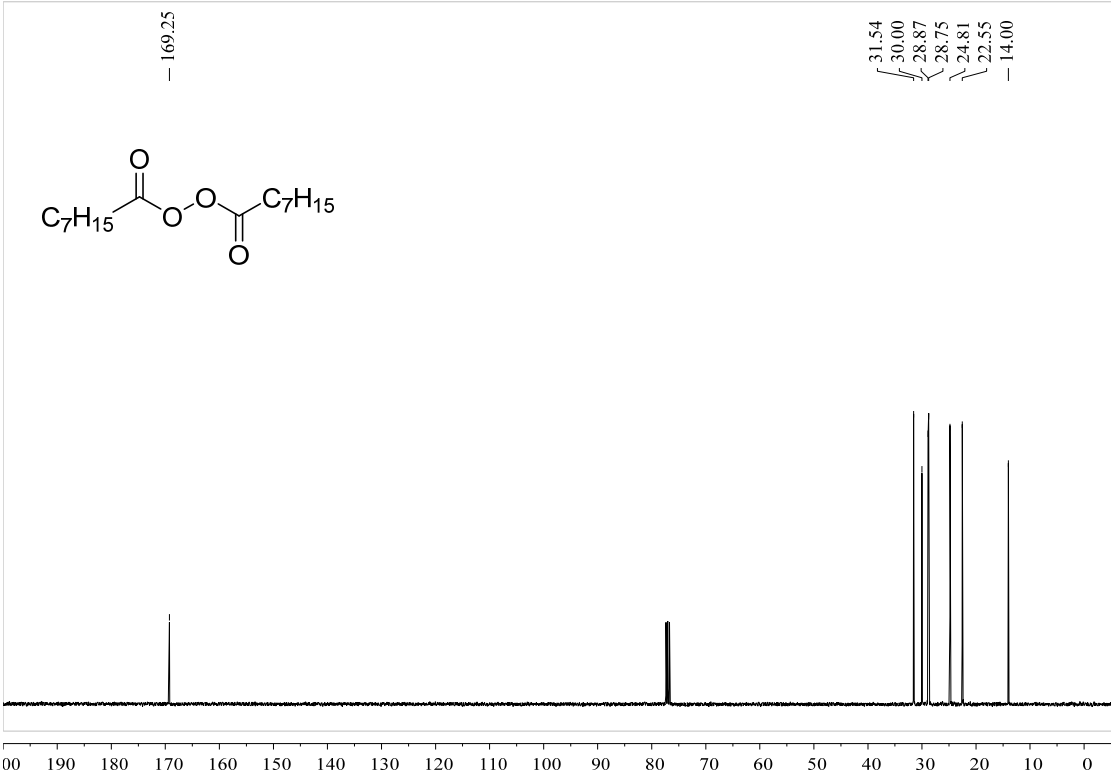



**Figure S13.** $^{13}$C NMR spectrum of octanoic peroxyanhydride, related to **Figure 3**.

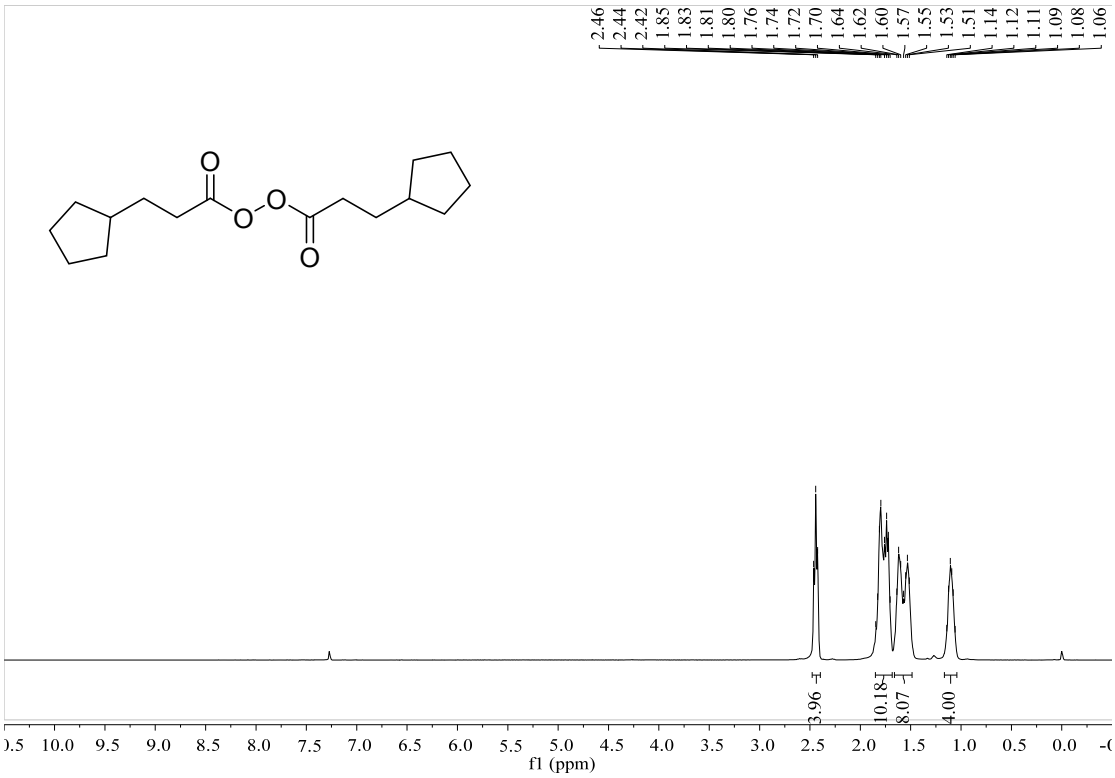



**Figure S14.** $^{1}$H NMR spectrum of 3-cyclopentylpropanoic peroxyanhydride, related to **Figure 3**.

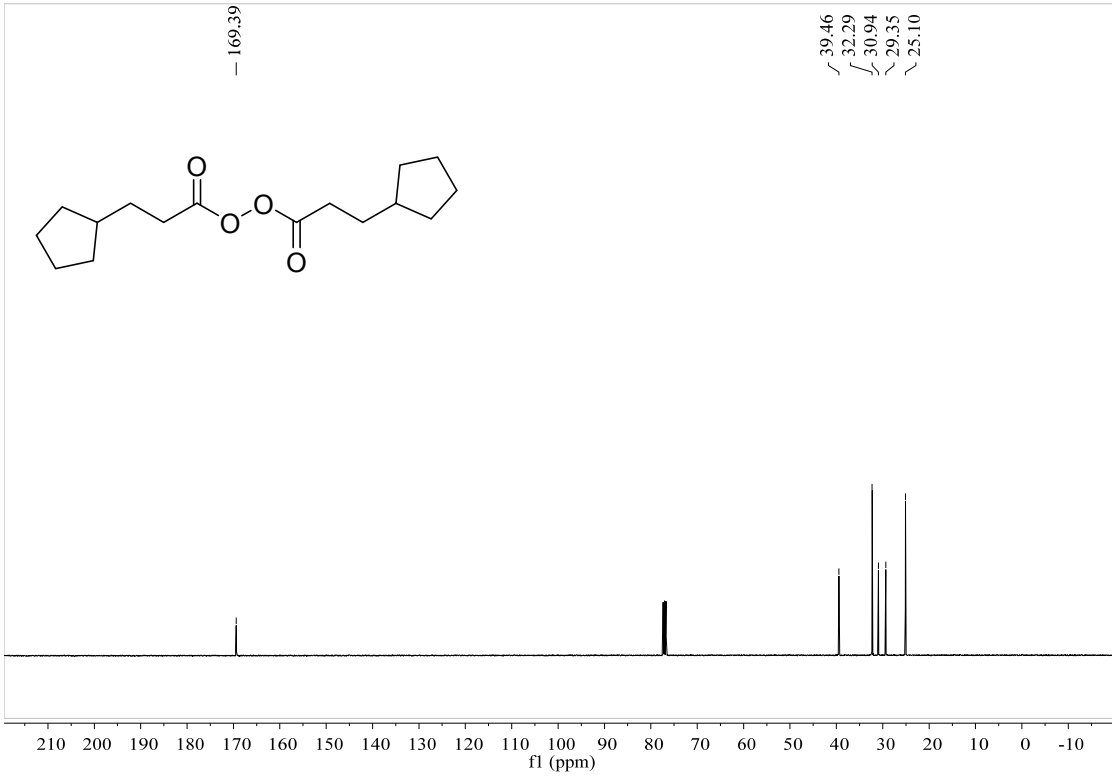



**Figure S15.** $^{13}$C NMR spectrum of 3-cyclopentylpropanoic peroxyanhydride, related to **Figure 3**.

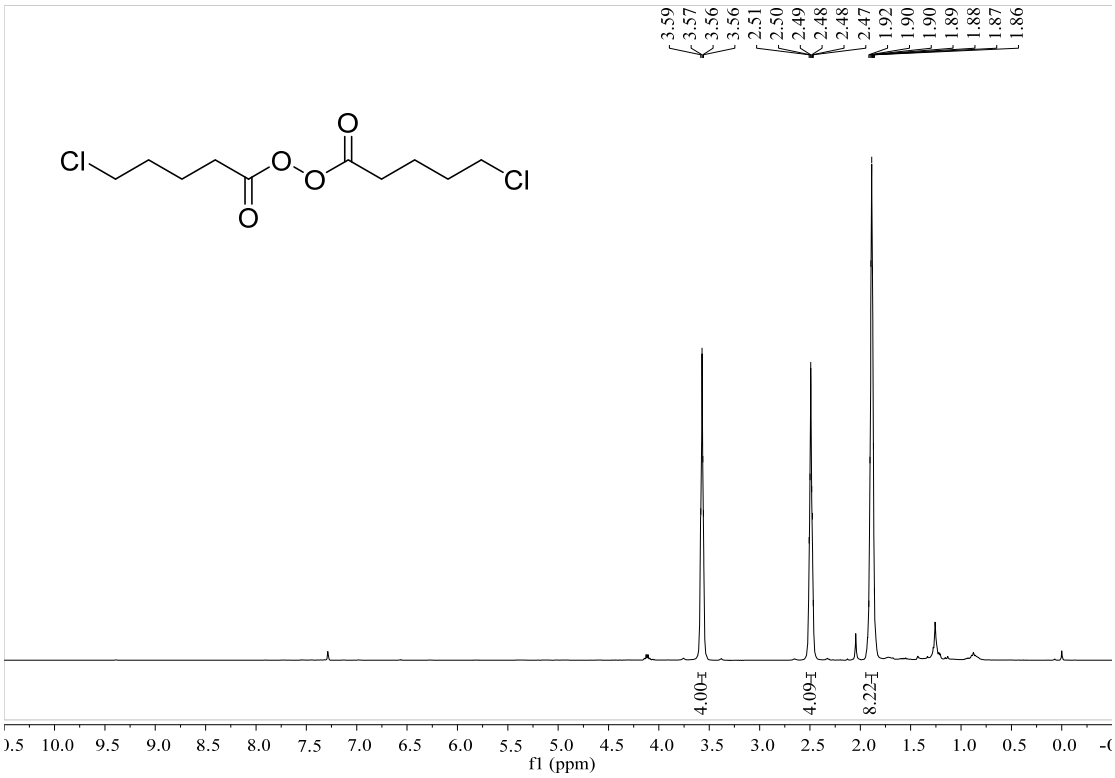



**Figure S16.** $^{1}$H NMR spectrum of 5-chloropentanoic peroxyanhydride, related to **Figure 3**.

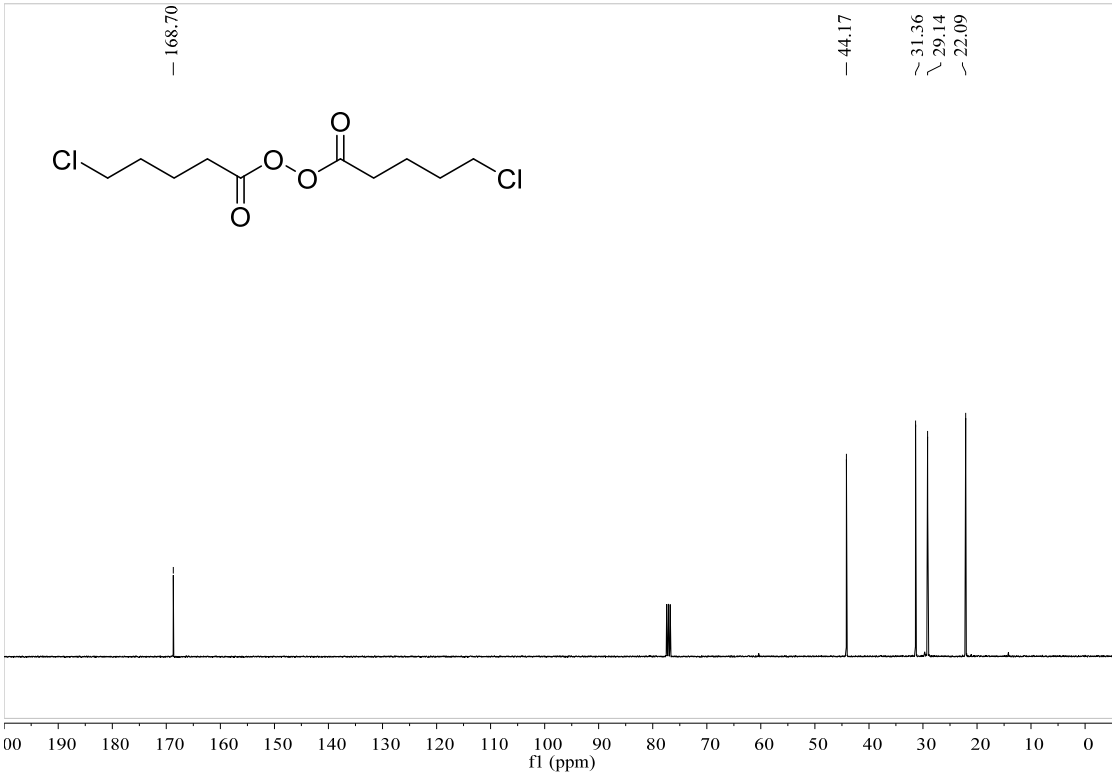



**Figure S17.** $^{13}$C NMR spectrum of 5-chloropentanoic peroxyanhydride, related to **Figure 3**.

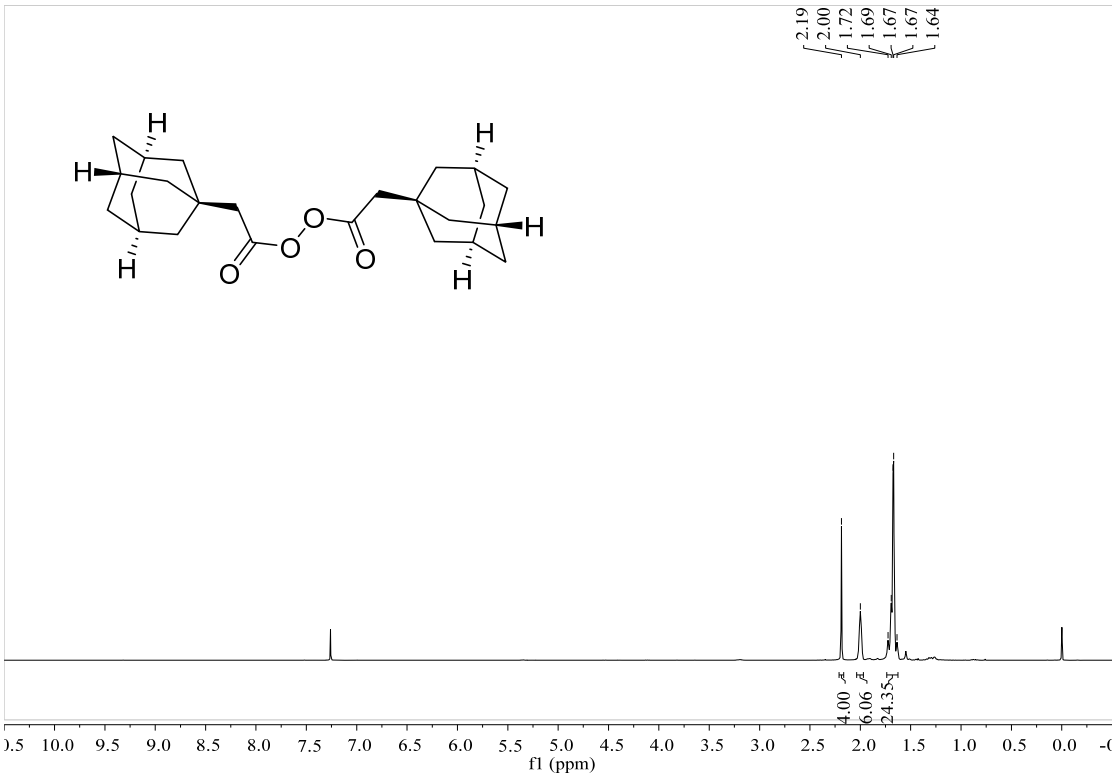



**Figure S18.** $^{1}$H NMR spectrum of 2-((3*r*,5*r*,7*r*)-adamantan-1-yl)acetic peroxyanhydride, related to **Figure 3**.

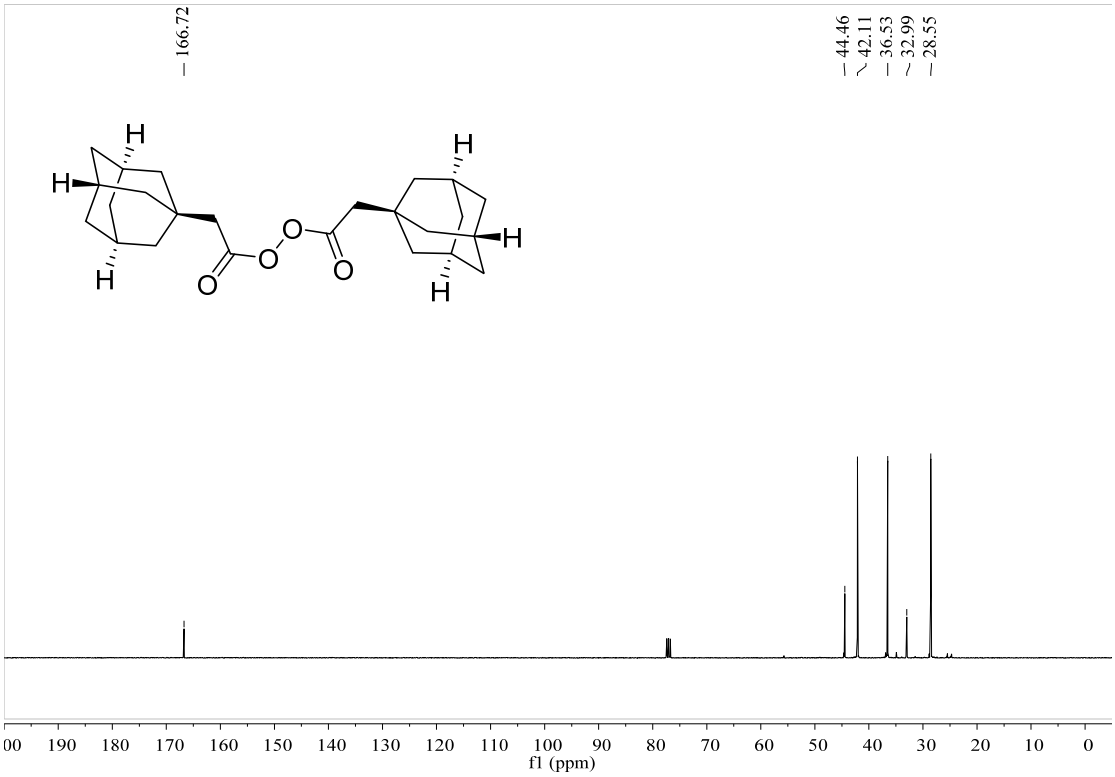



**Figure S19.** $^{13}$C NMR spectrum of 2-((3*r*,5*r*,7*r*)-adamantan-1-yl)acetic peroxyanhydride, related to **Figure 3**.

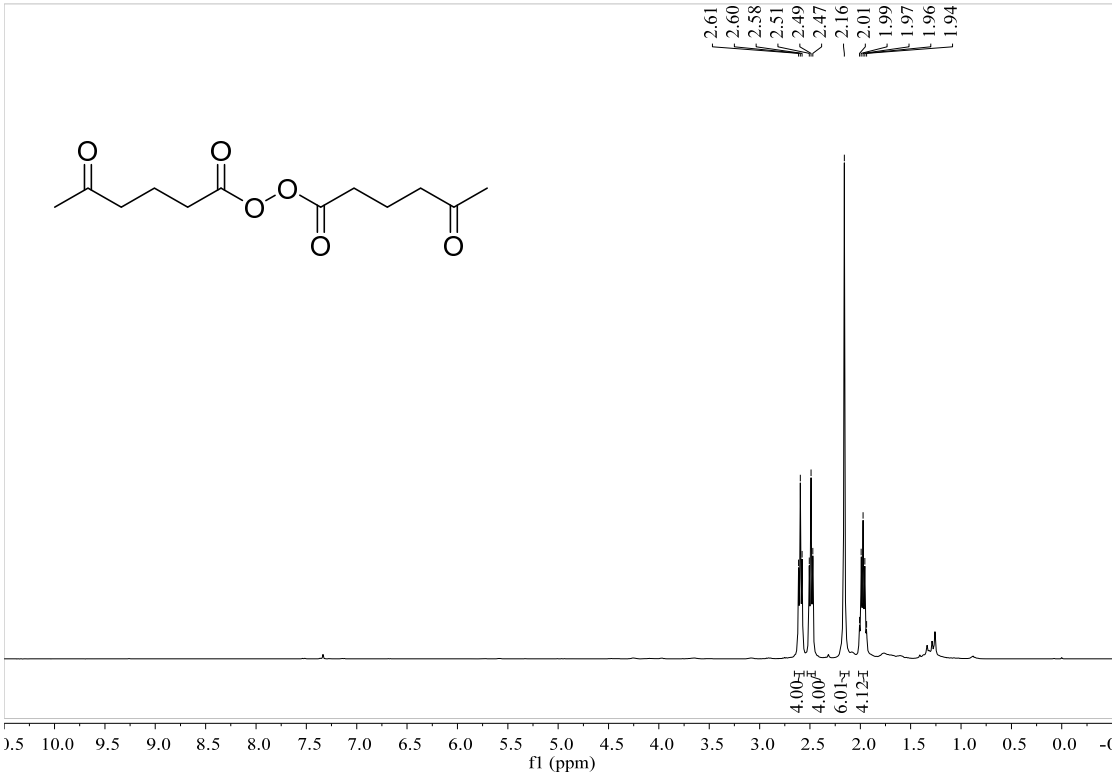



**Figure S20.** $^{1}$H NMR spectrum of 5-oxohexanoic peroxyanhydride, related to **Figure 3**.

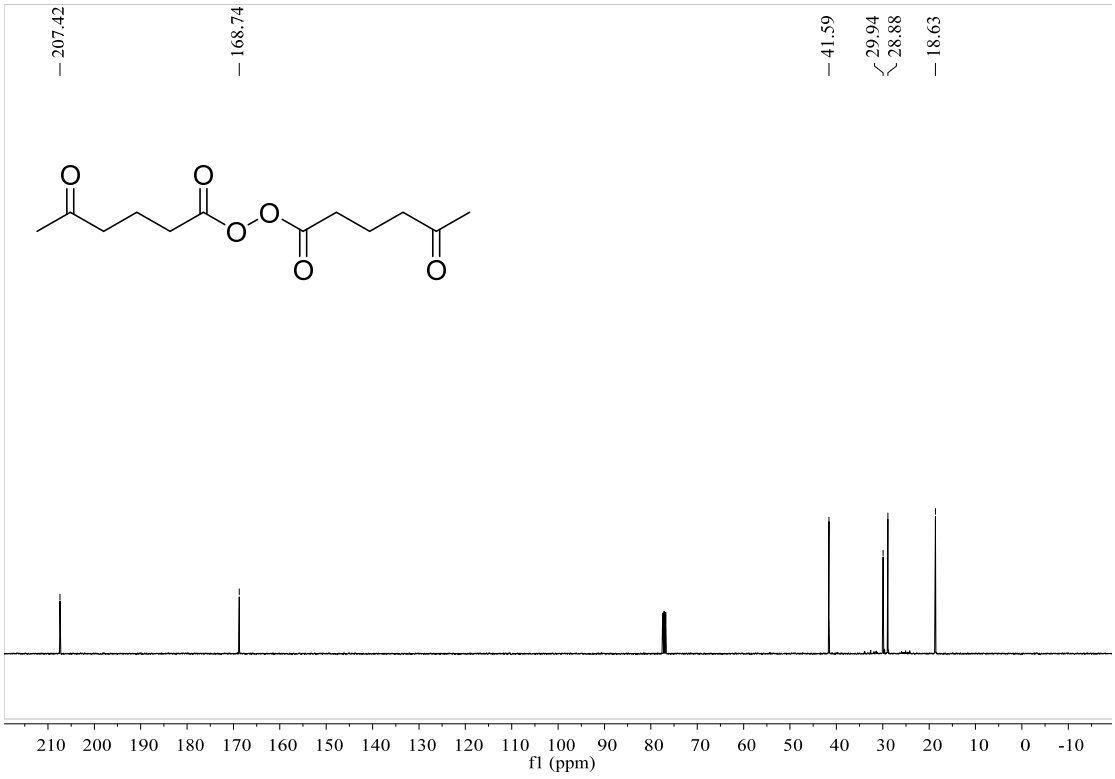



**Figure S21.** $^{13}$C NMR spectrum of 5-oxohexanoic peroxyanhydride, related to **Figure 3**.

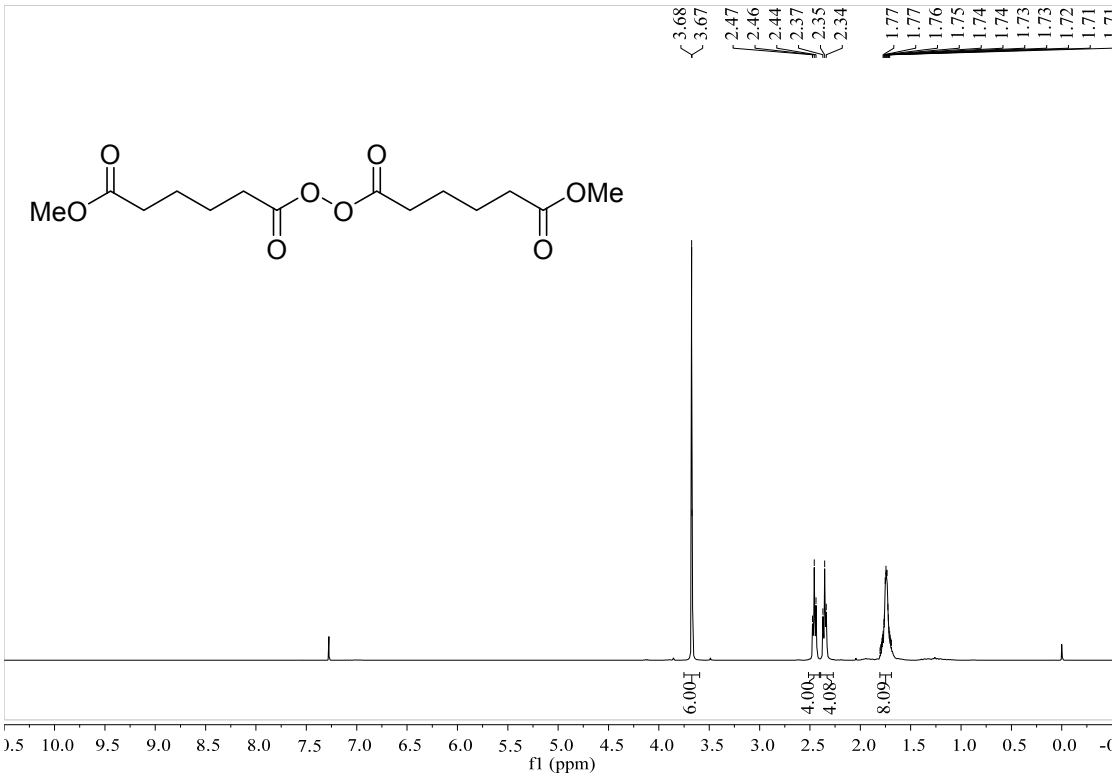



**Figure S22.** $^{1}$H NMR spectrum of 6-methoxy-6-oxohexanoic peroxyanhydride, related to **Figure 3**.

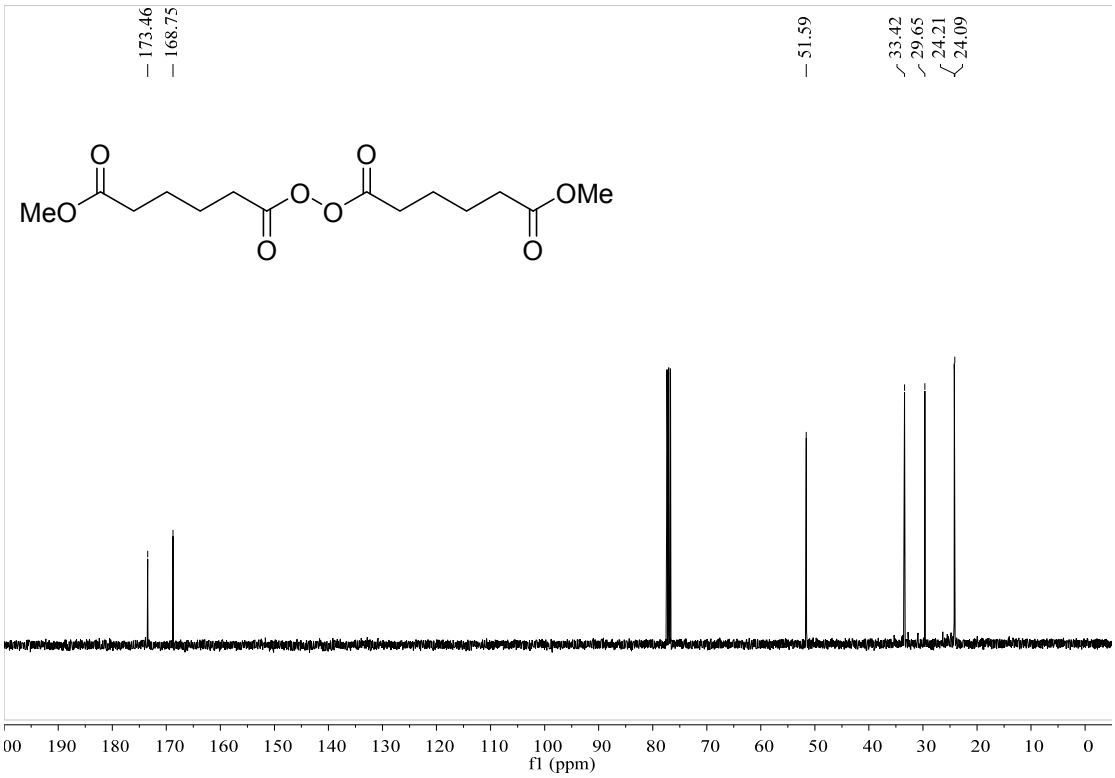



**Figure S23.** $^{13}$C NMR spectrum of 6-methoxy-6-oxohexanoic peroxyanhydride, related to **Figure 3**.

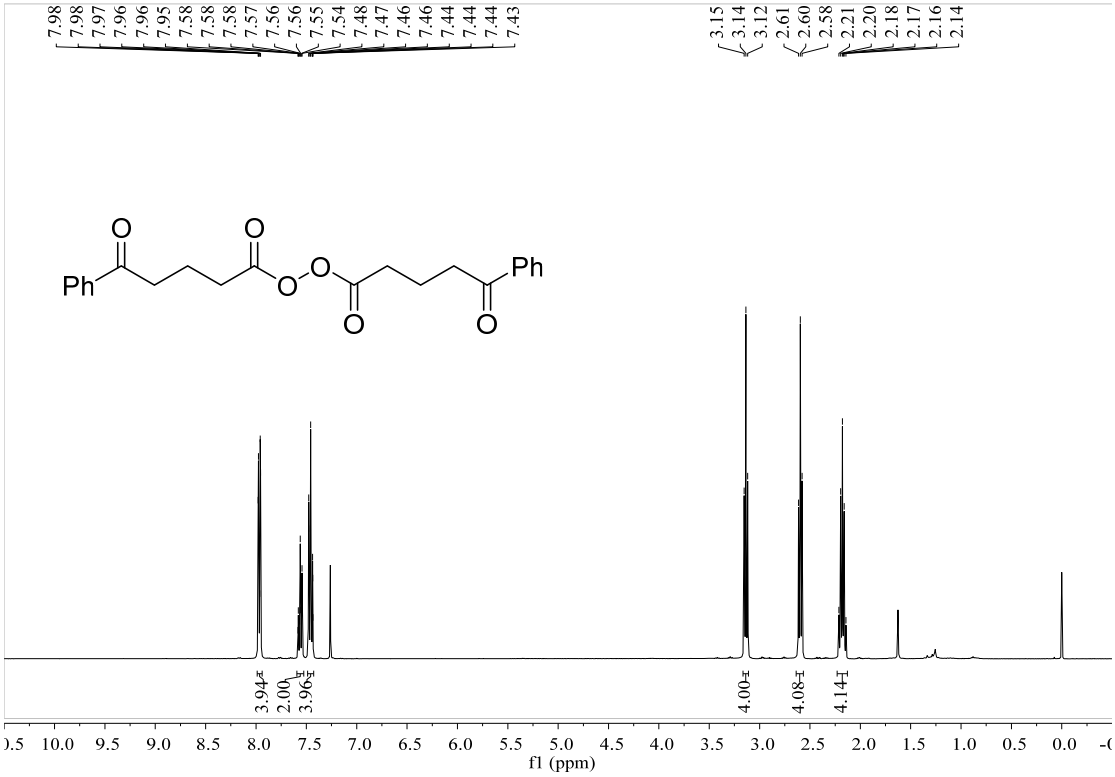



**Figure S24.** $^{1}$H NMR spectrum of 5-oxo-5-phenylpentanoic peroxyanhydride, related to **Figure 3**.

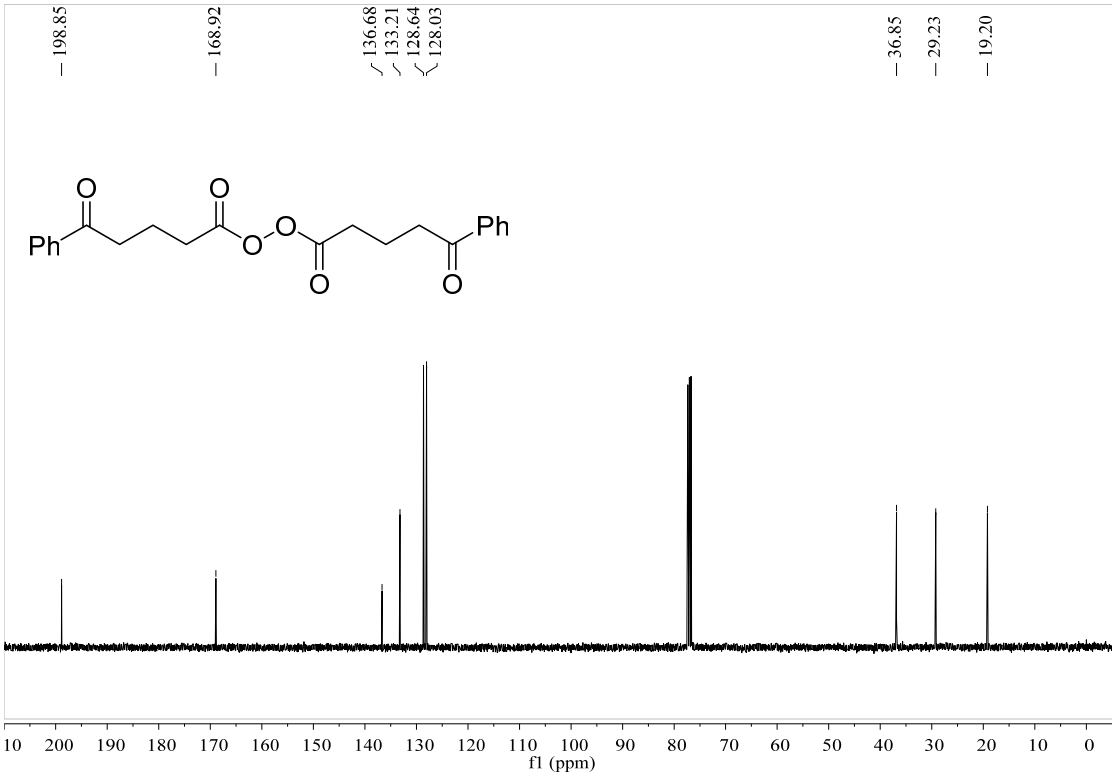



**Figure S25.** $^{13}$C NMR spectrum of 5-oxo-5-phenylpentanoic peroxyanhydride.peroxyanhydride, related to **Figure 3**.

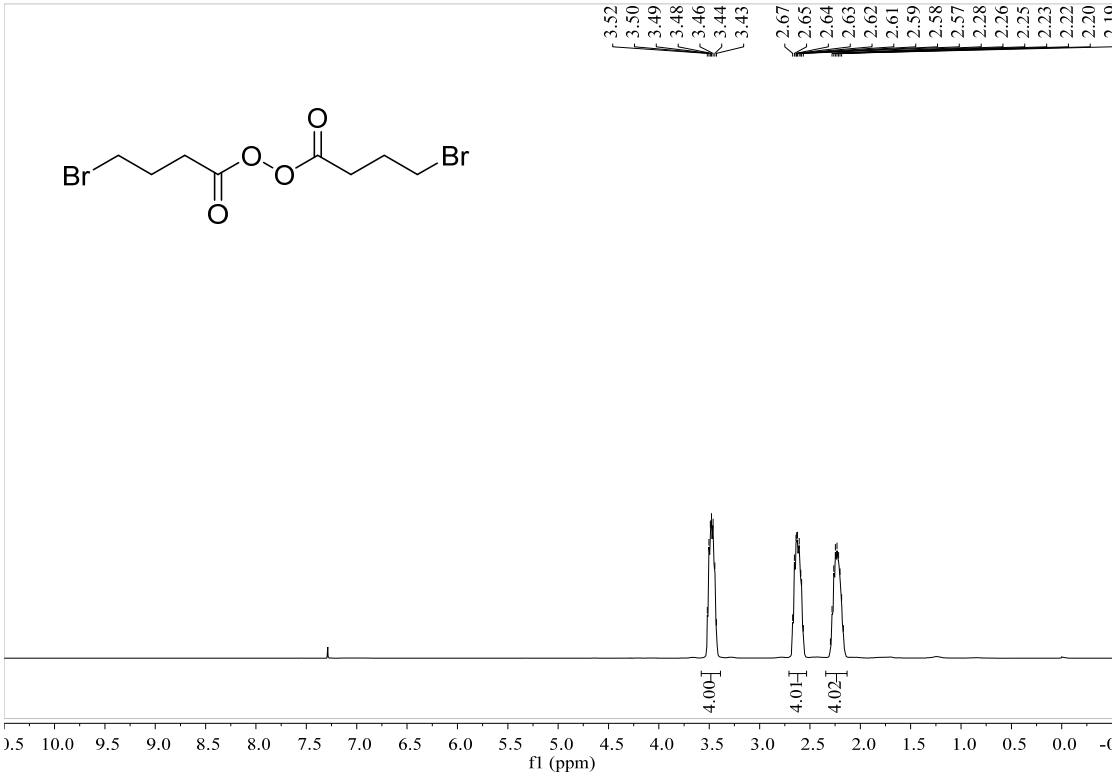



**Figure S26.** [1]H NMR spectrum of 4-bromobutanoic peroxyanhydride, related to **Figure 3**.

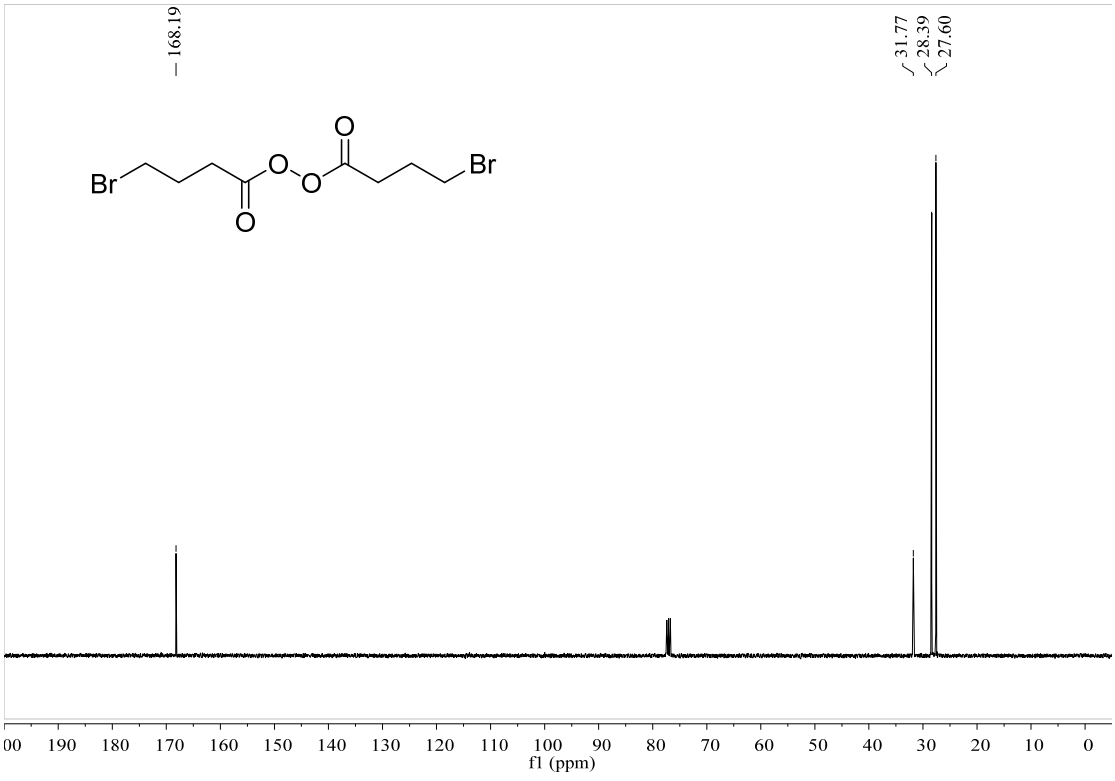



**Figure S27.** [13]C NMR spectrum of 4-bromobutanoic peroxyanhydride, related to **Figure 3**.

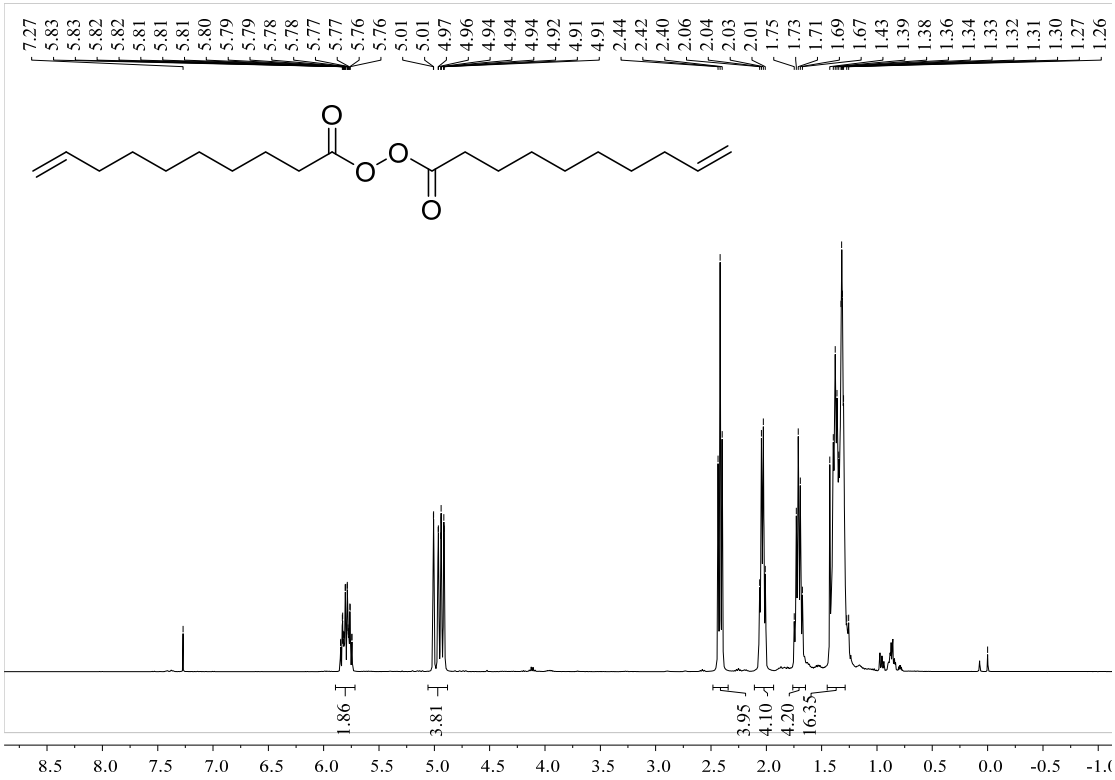



**Figure S28.** $^{1}$H NMR spectrum of dec-9-enoic peroxyanhydride, related to **Figure 3**.

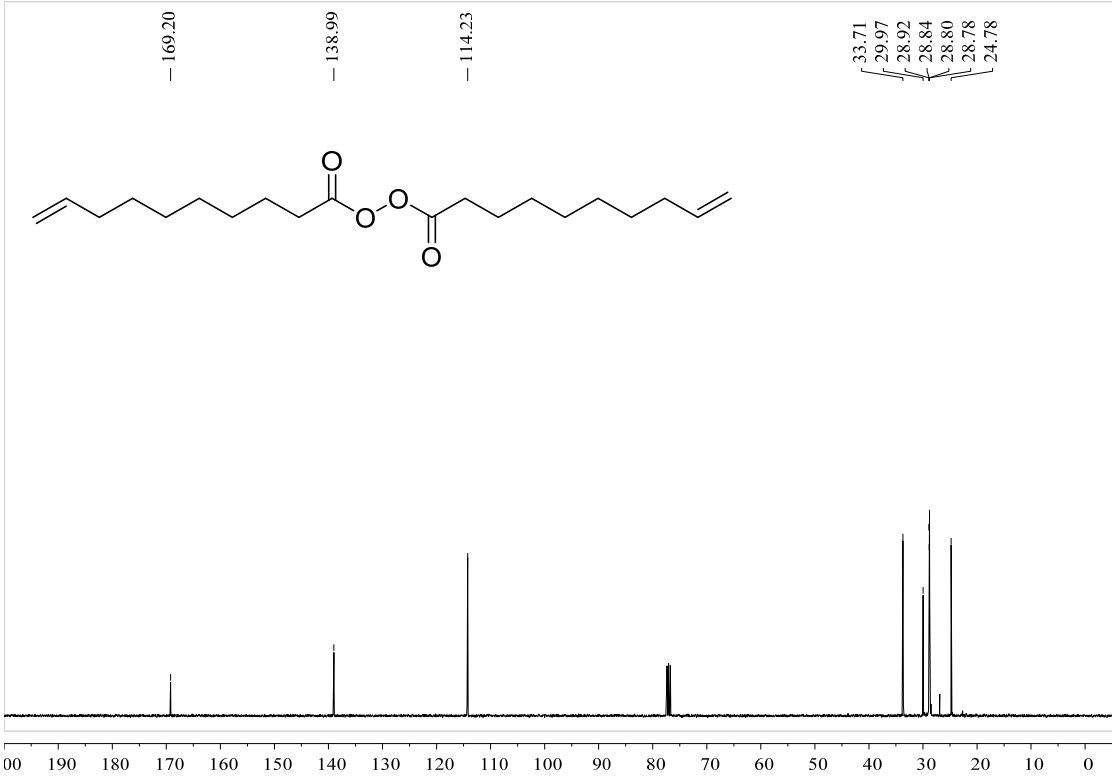



**Figure S29.** $^{13}$C NMR spectrum of dec-9-enoic peroxyanhydride, related to **Figure 3**.

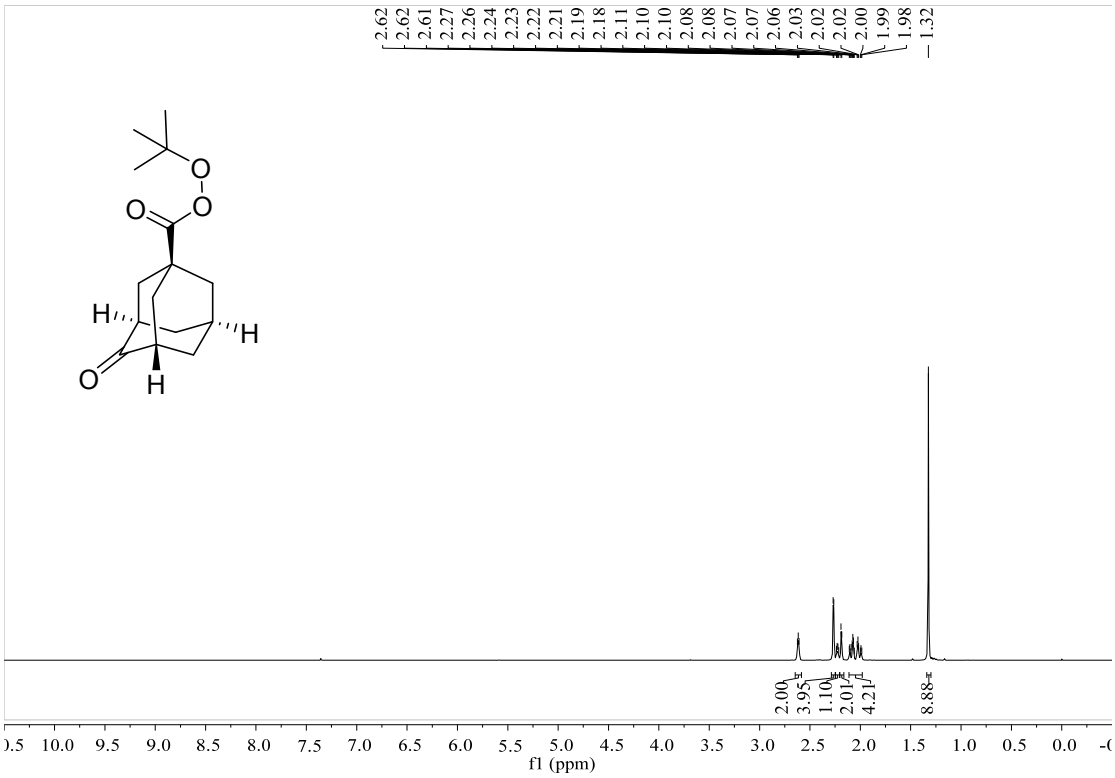



**Figure S30.** $^{1}$H NMR spectrum of *tert*-butyl(1*s*,3*r*,5*s*,7*s*)-4-oxoadamantane-1-carboperoxoate, related to **Figure 2**.

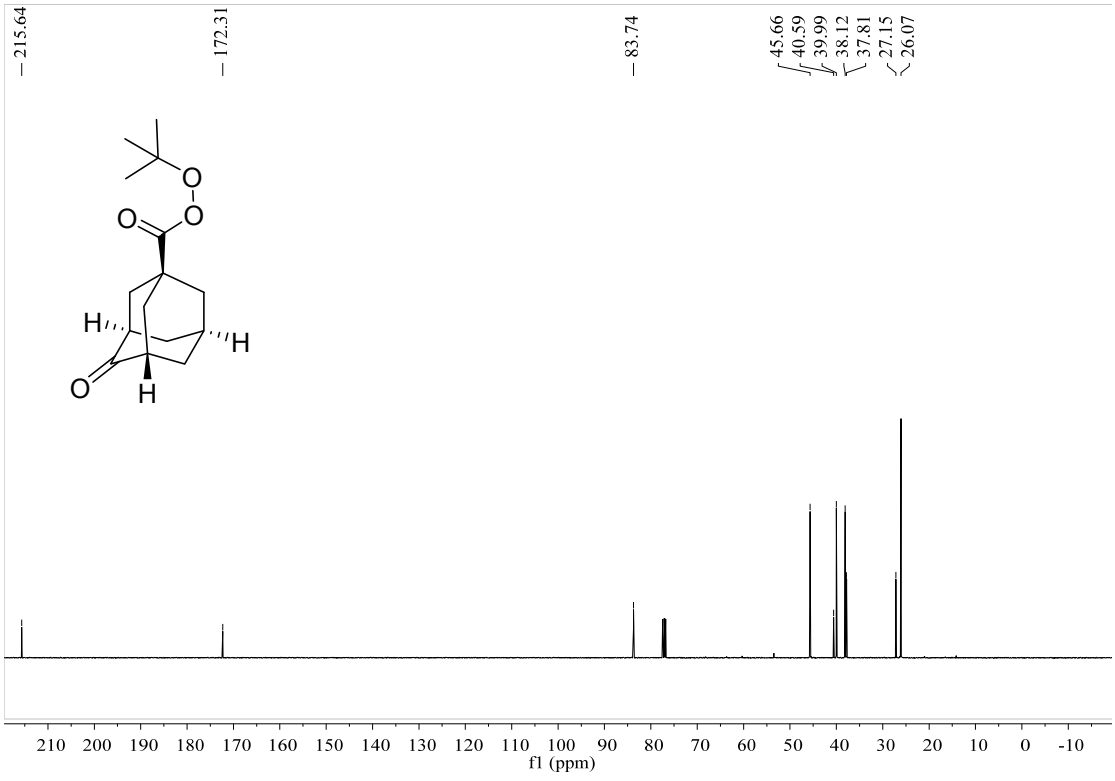



**Figure S31.** $^{13}$C NMR spectrum of *tert*-butyl (1*s*,3*r*,5*s*,7*s*)-4-oxoadamantane-1-carboperoxoate, related to **Figure 2**.

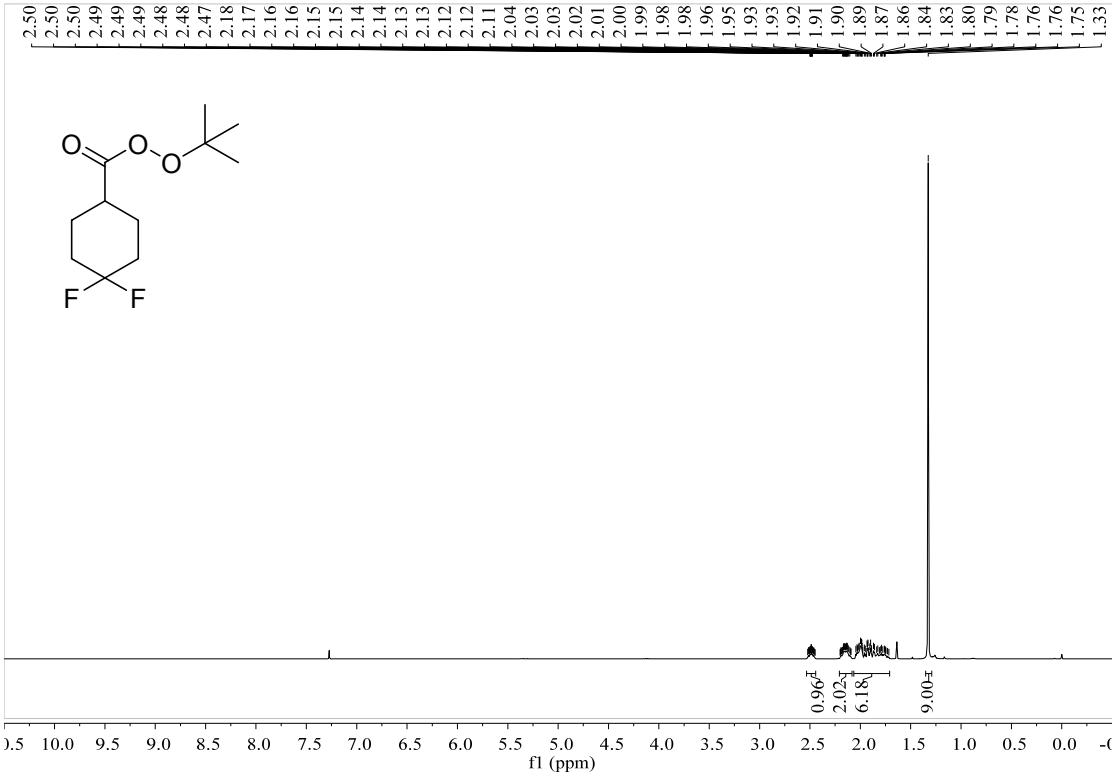



**Figure S32.** $^{1}$H NMR spectrum of *tert*-butyl 4,4-difluorocyclohexane-1-carboperoxoate, related to **Figure 2**.

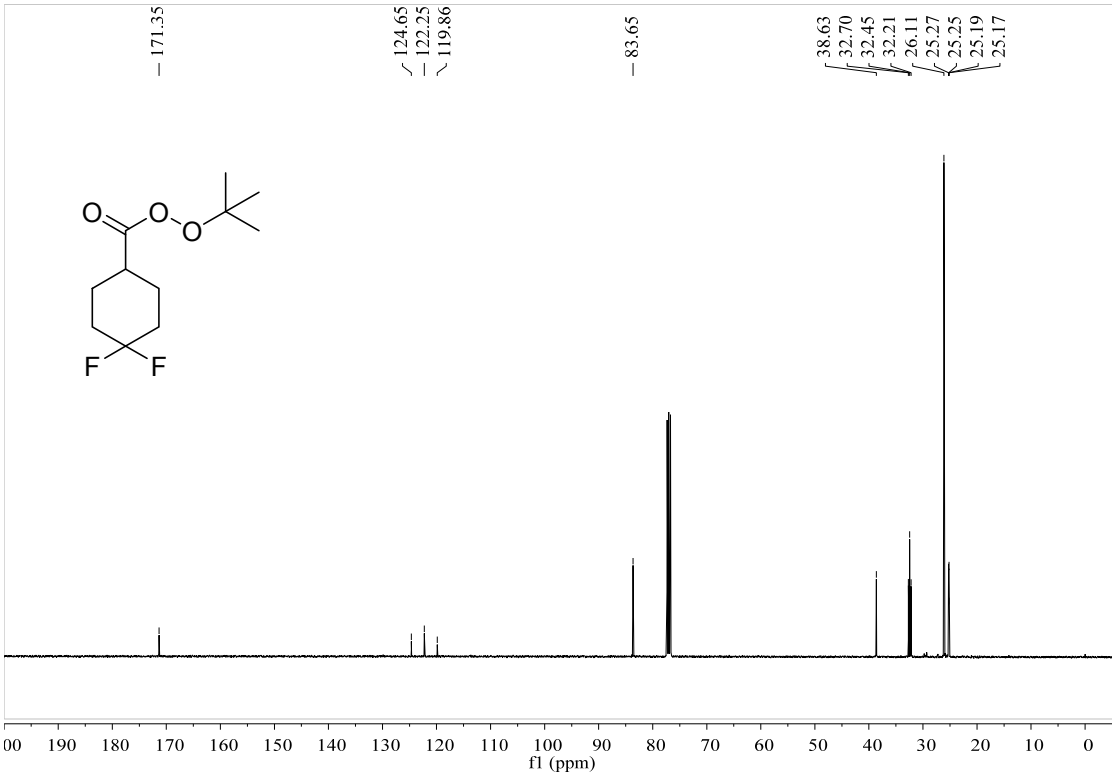



**Figure S33.** $^{13}$C NMR spectrum of *tert*-butyl 4,4-difluorocyclohexane-1-carboperoxoate, related to **Figure 2**.

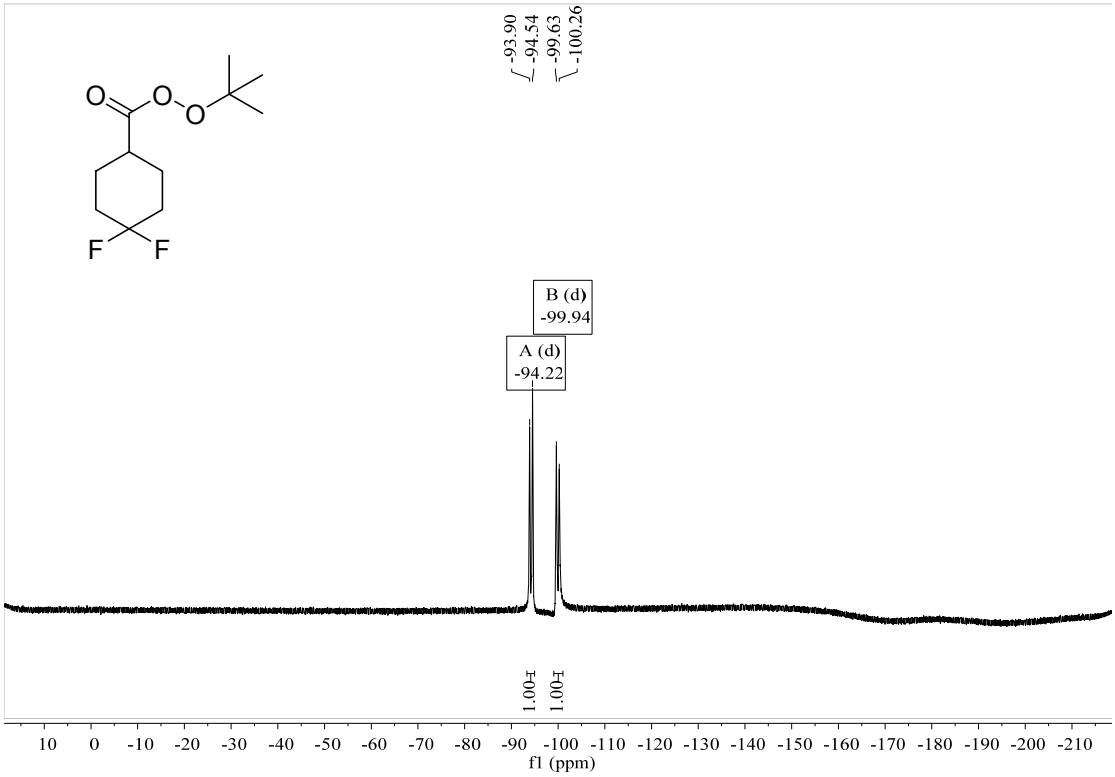



**Figure S34.** $^{19}F$ NMR spectrum of *tert*-butyl 4,4-difluorocyclohexane-1-carboperoxoate, related to **Figure 2**.

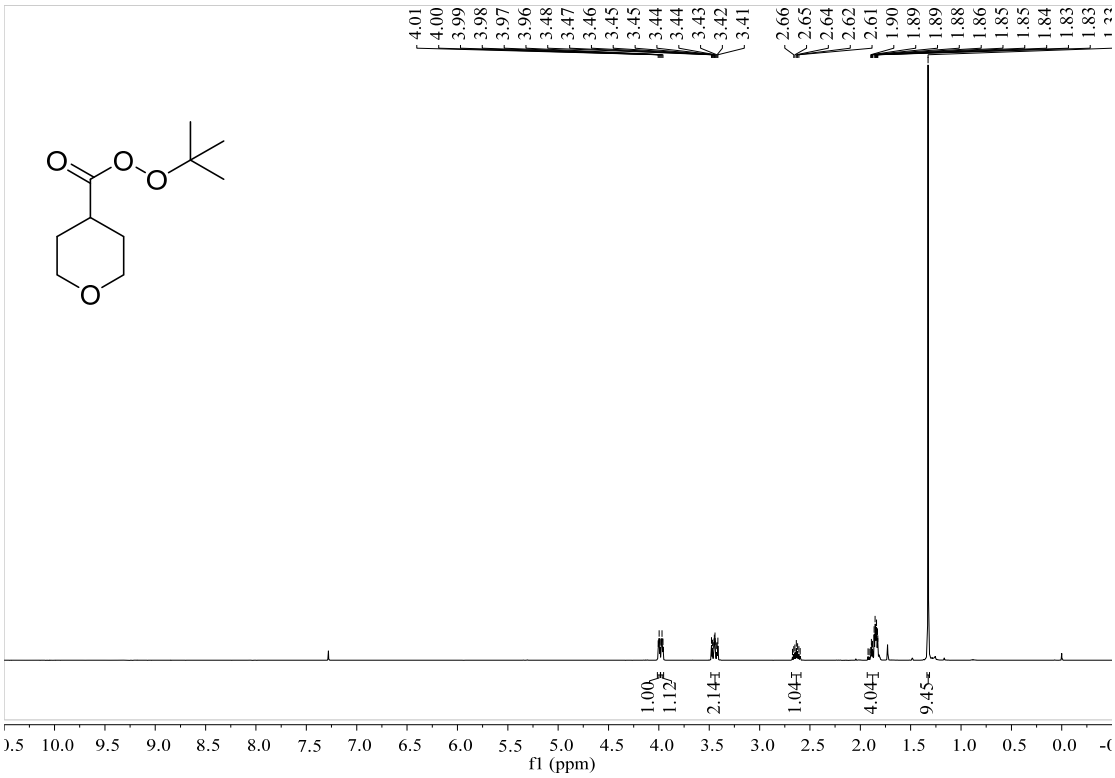



**Figure S35.** $^{1}$H NMR spectrum of *tert*-butyl tetrahydro-2*H*-pyran-4-carboperoxoate, related to **Figure 2**.

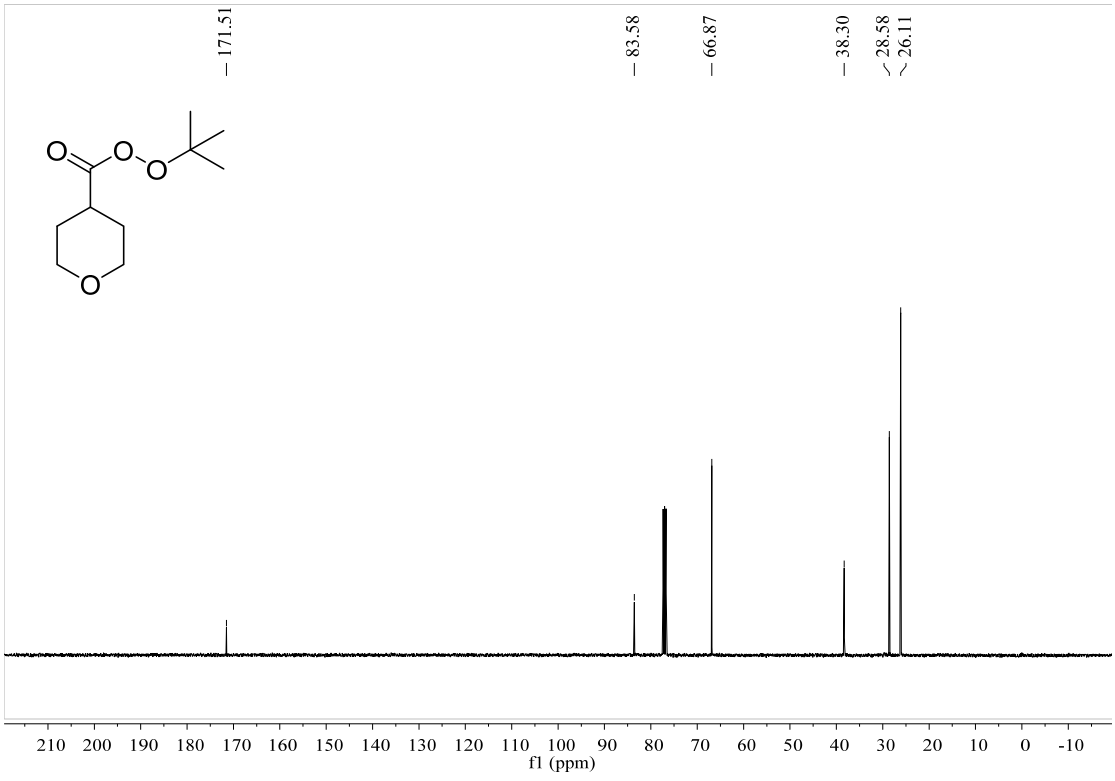



**Figure S36.** $^{13}$C NMR spectrum of *tert*-butyl tetrahydro-2*H*-pyran-4-carboperoxoate, related to **Figure 2**.

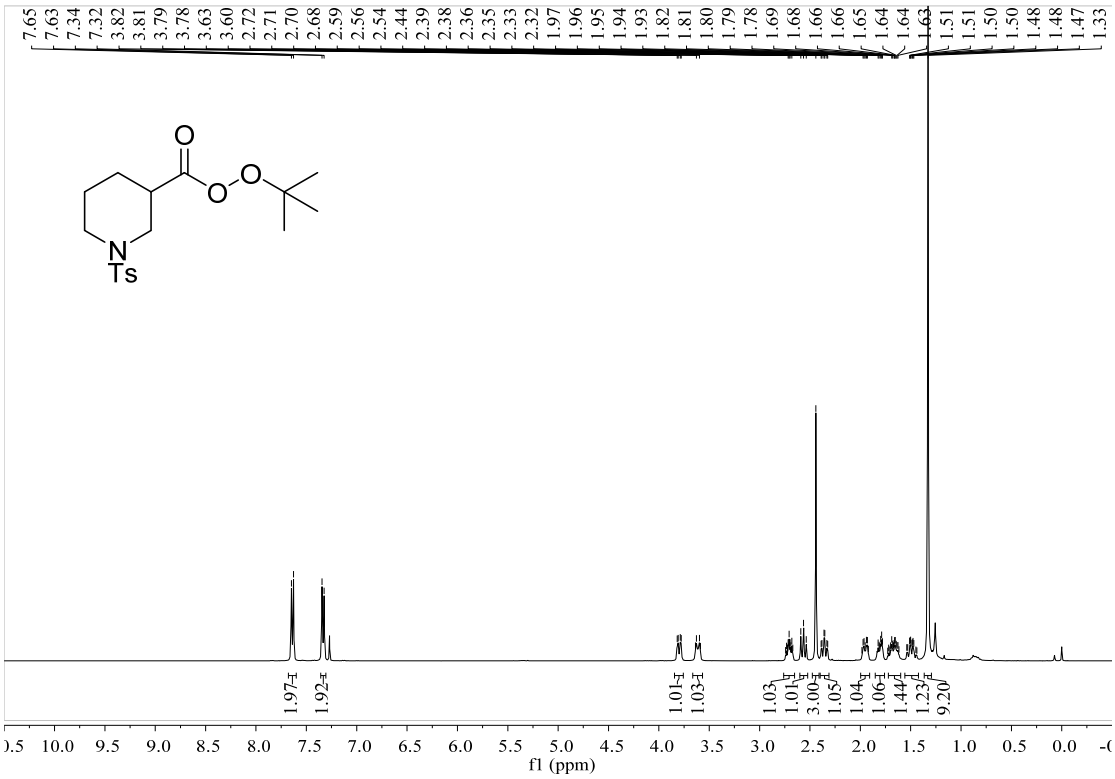



**Figure S37.** [1]H NMR spectrum of *tert*-butyl 1-tosylpiperidine-3-carboperoxoate, related to **Figure 2**.

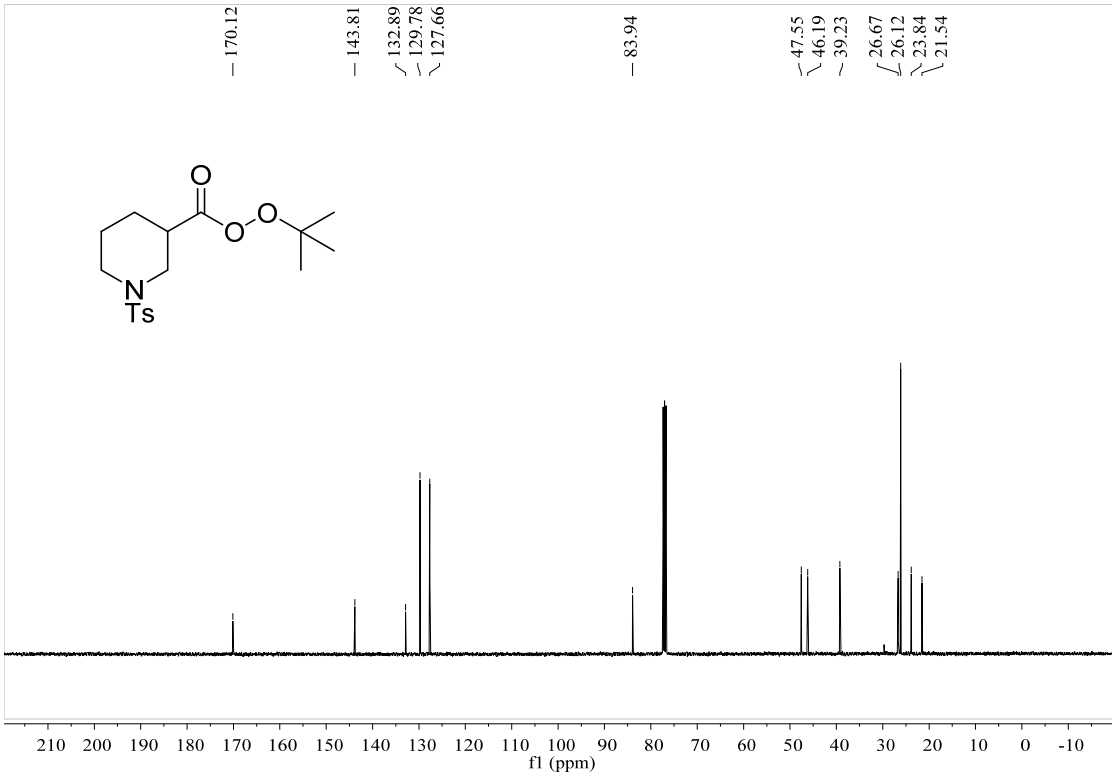



**Figure S38.** [13]C NMR spectrum of *tert*-butyl 1-tosylpiperidine-3-carboperoxoate, related to **Figure 2**.

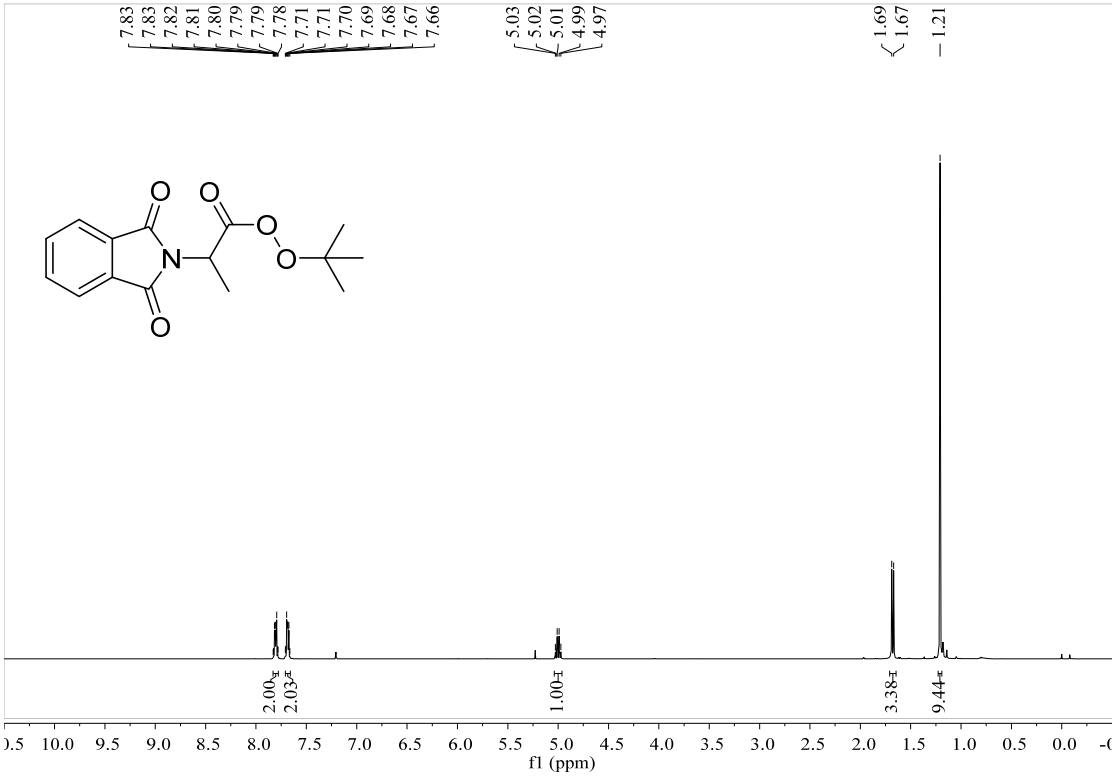



**Figure S39.** [1]H NMR spectrum of *tert*-butyl 2-(1,3-dioxoisoindolin-2-yl)propaneperoxoate, related to **Figure 2**.

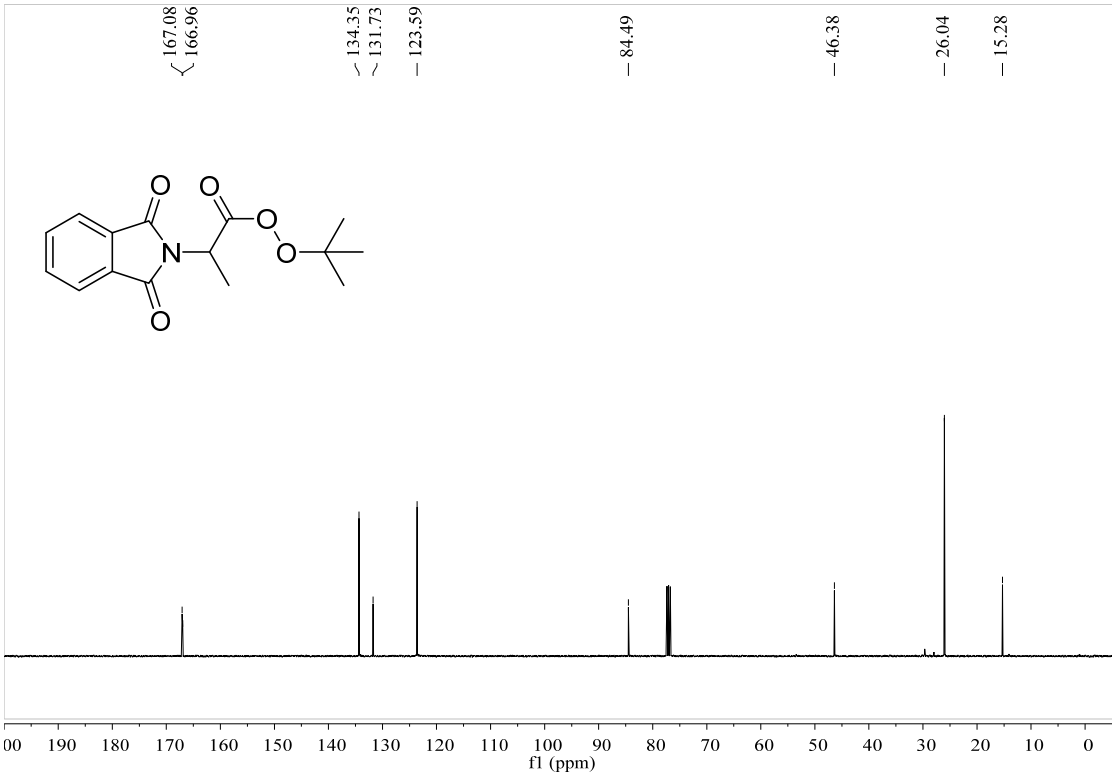



**Figure S40.** [13]C NMR spectrum of *tert*-butyl 2-(1,3-dioxoisoindolin-2-yl)propaneperoxoate, related to **Figure 2**.

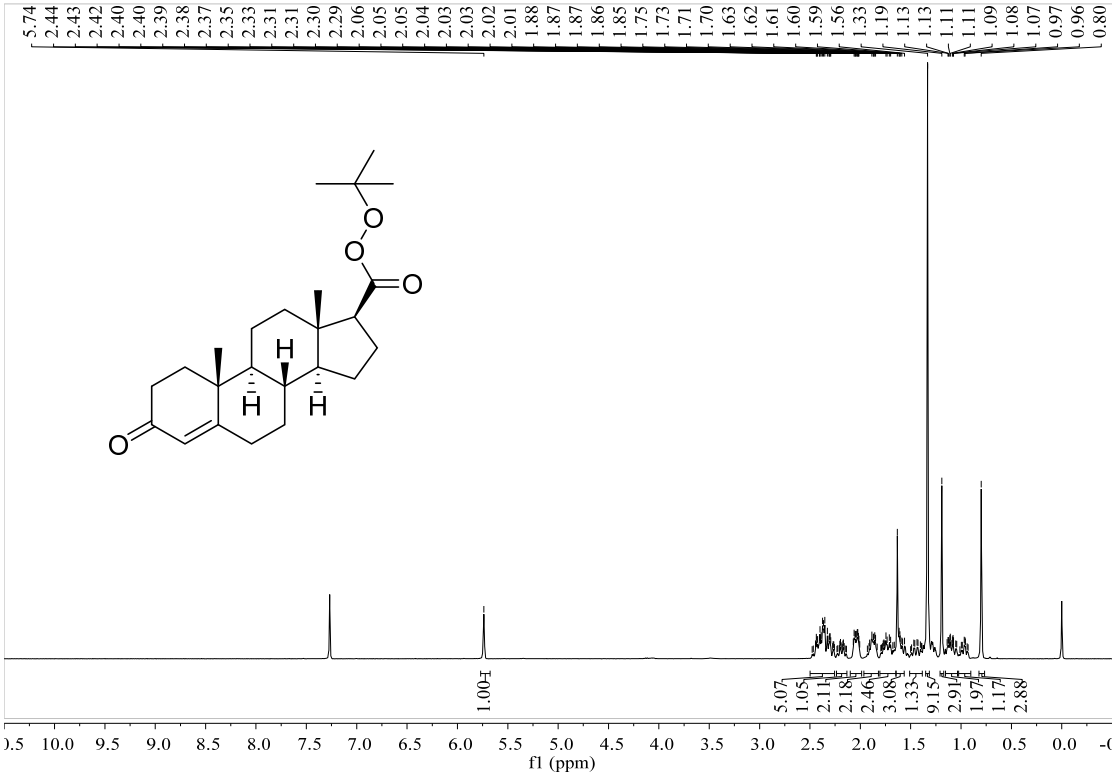



**Figure S41.** $^{1}$H NMR spectrum of compound **55**, related to **scheme 2.**

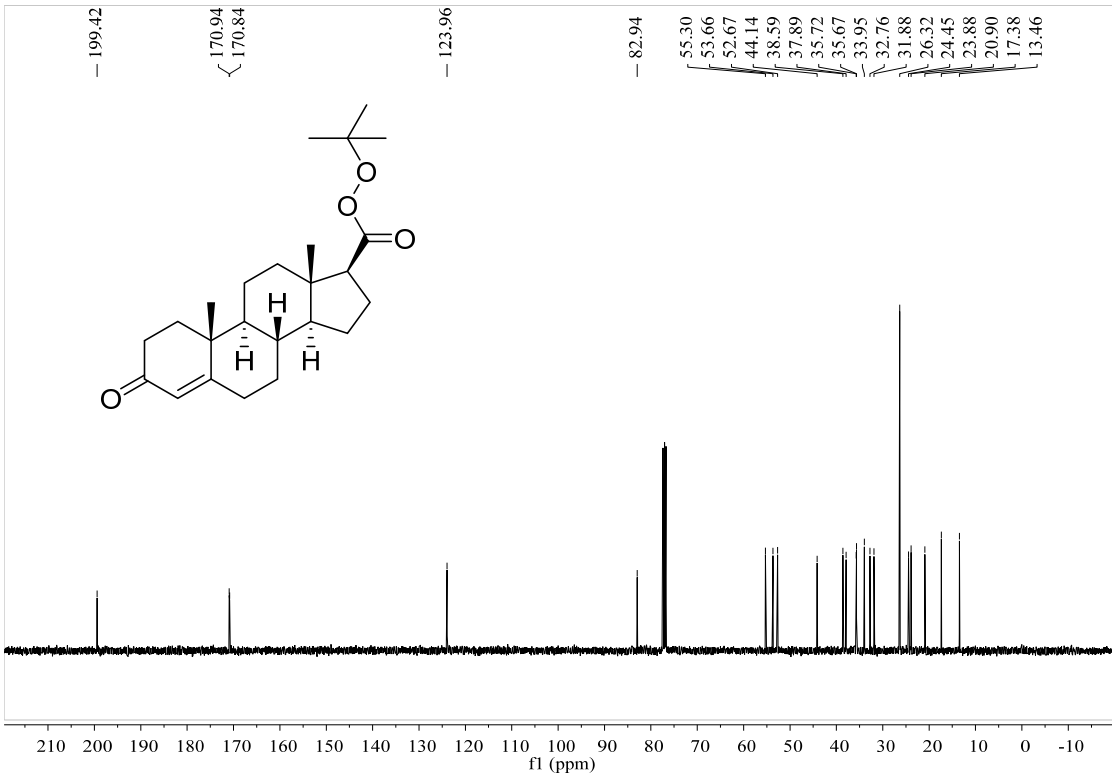



**Figure S42.** $^{13}$C NMR spectrum of compound **55**, related to **scheme 2.**

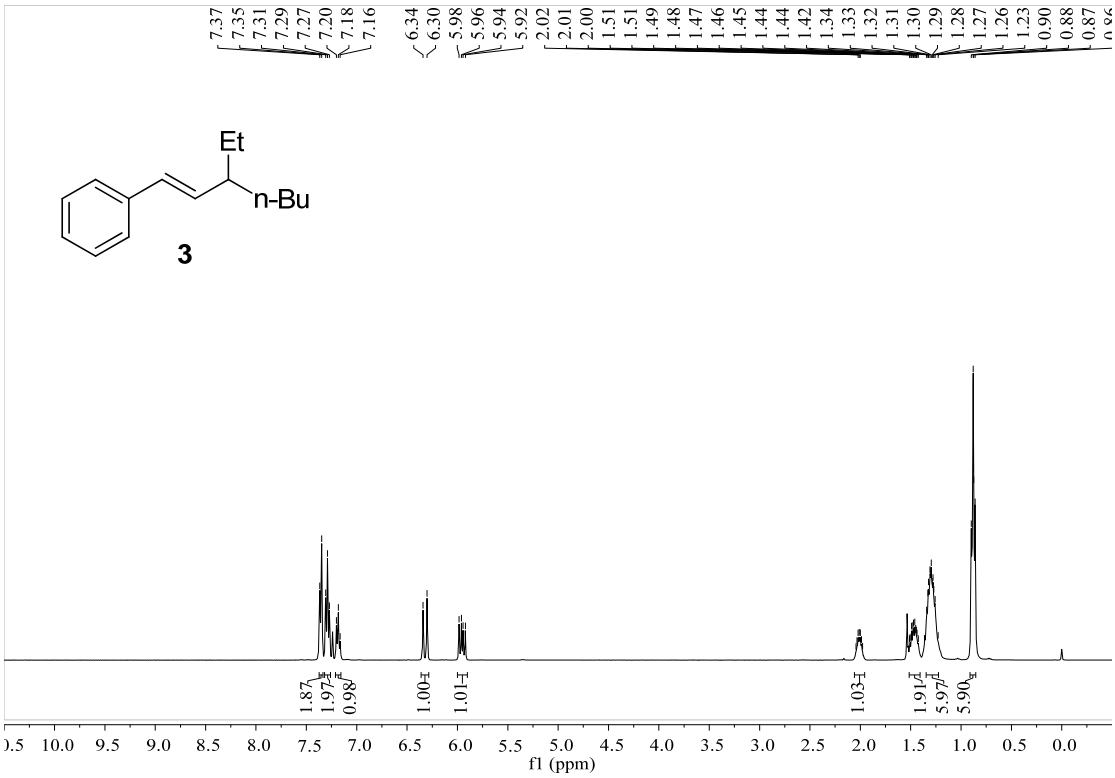



**Figure S43.** $^{1}$H NMR spectrum of compound **3**, **related to Table 1.**

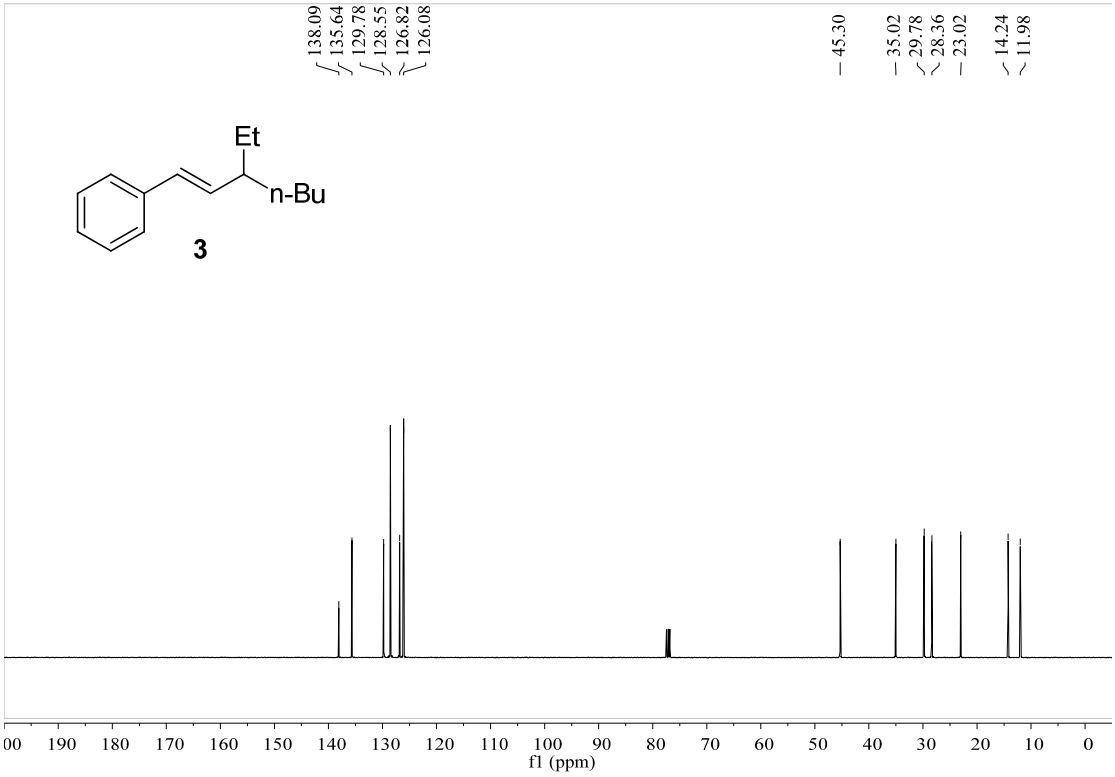



**Figure S44.** $^{13}$C NMR spectrum of compound **3**, **related to Table 1.**

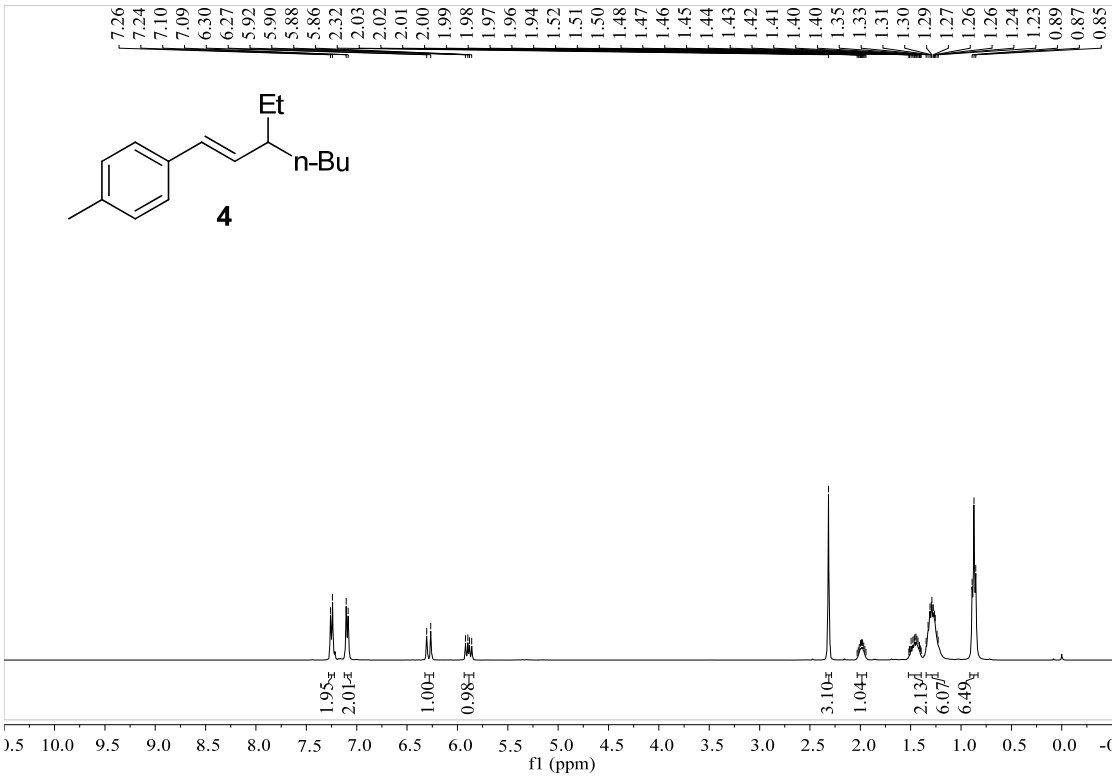



**Figure S45.** $^{1}$H NMR spectrum of compound **4**, related to **Figure 1.**

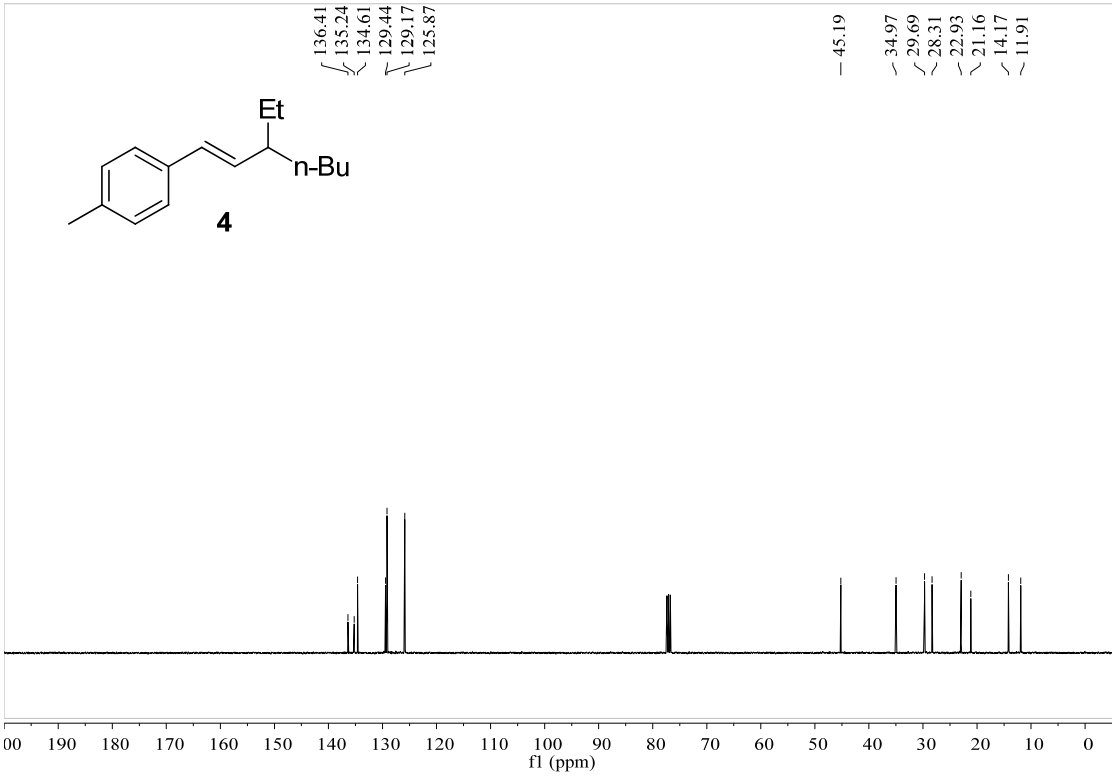



**Figure S46.** $^{13}$C NMR spectrum of compound **4**, related to **Figure 1.**

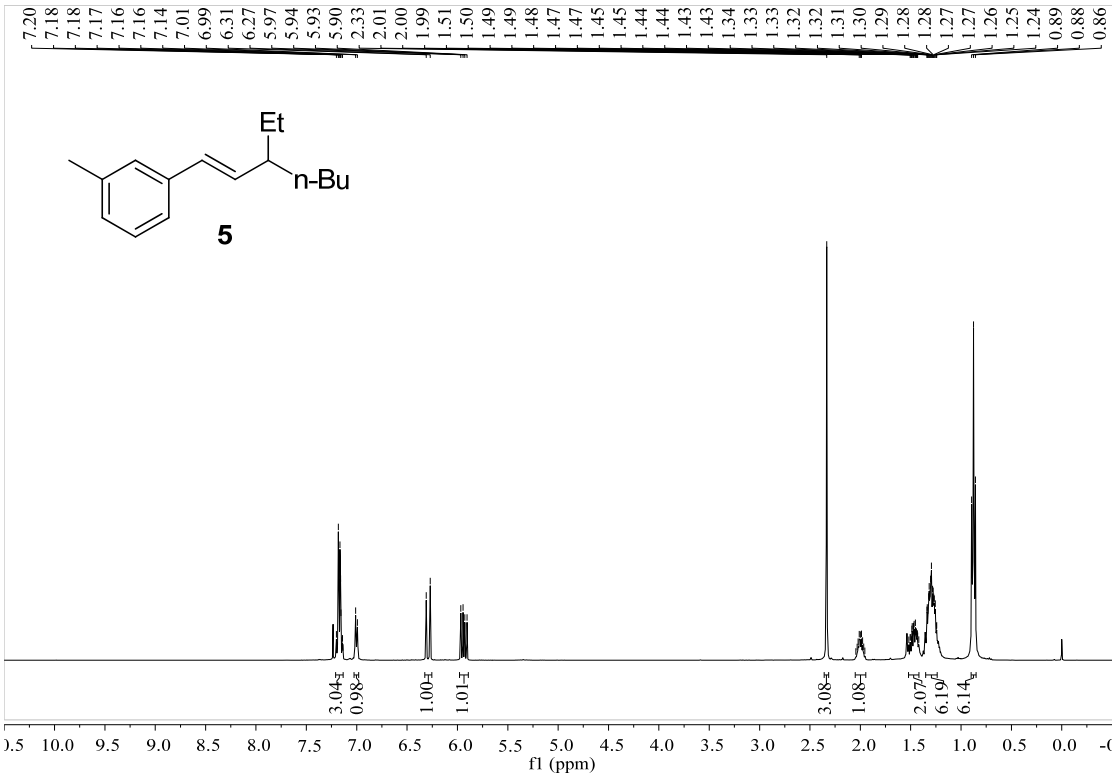



**Figure S47.** $^{1}$H NMR spectrum of compound **5**, related to **Figure 1.**

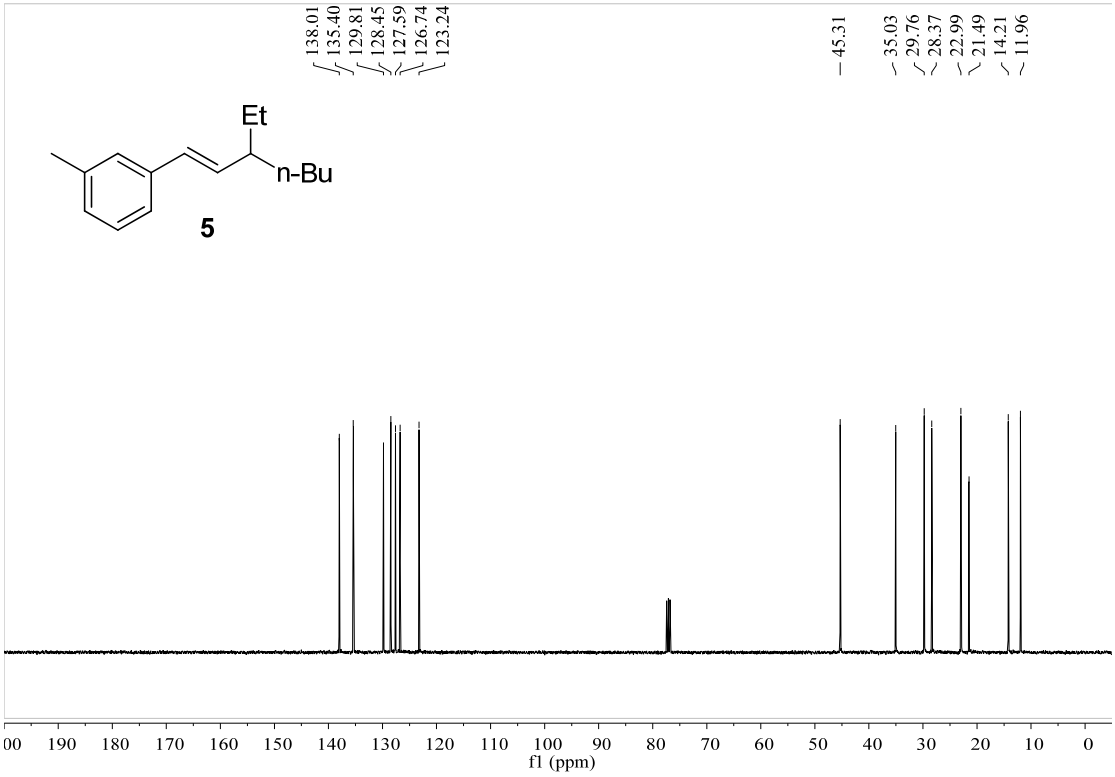



**Figure S48.** $^{13}$C NMR spectrum of compound **5**, related to **Figure 1.**

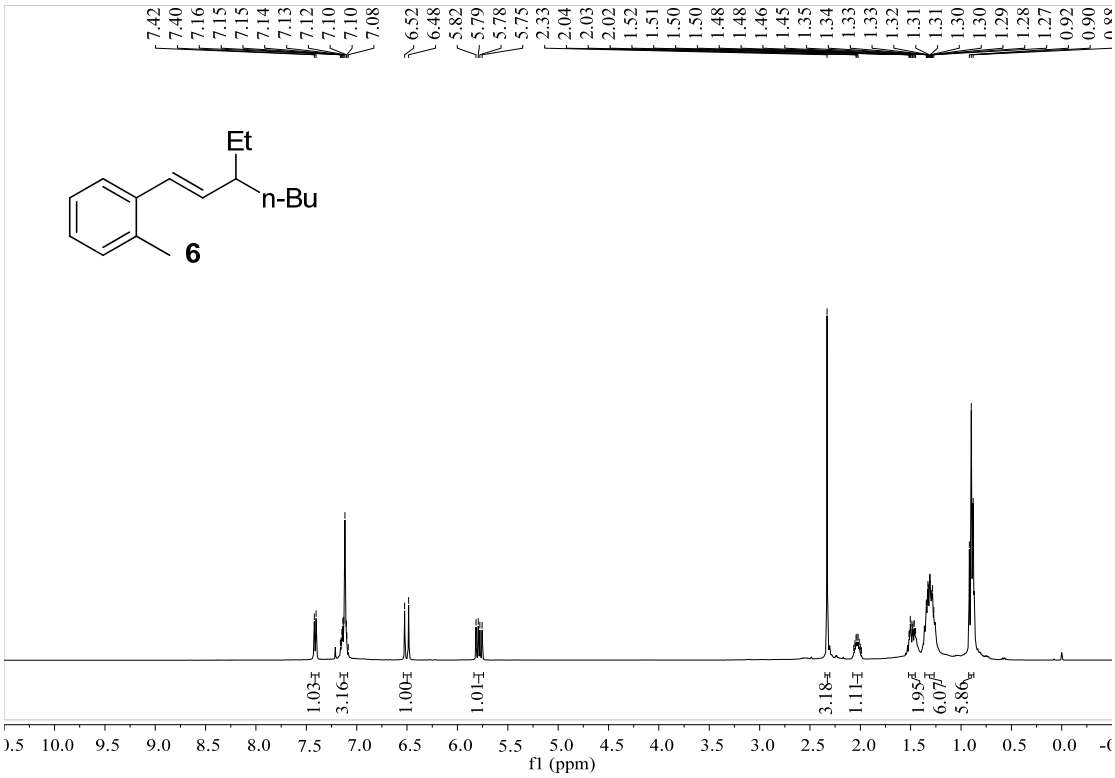



**Figure S49.** $^{1}$H NMR spectrum of compound **6**, related to **Figure 1.**

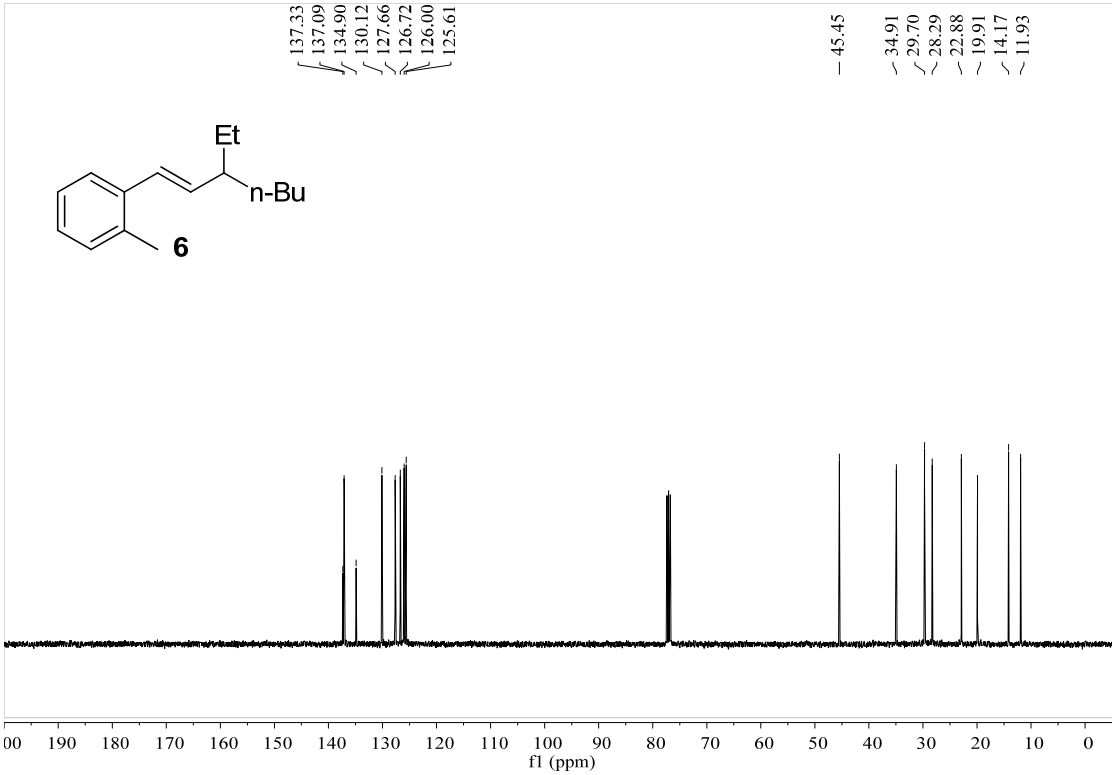



**Figure S50.** $^{13}$C NMR spectrum of compound **6**, related to **Figure 1.**

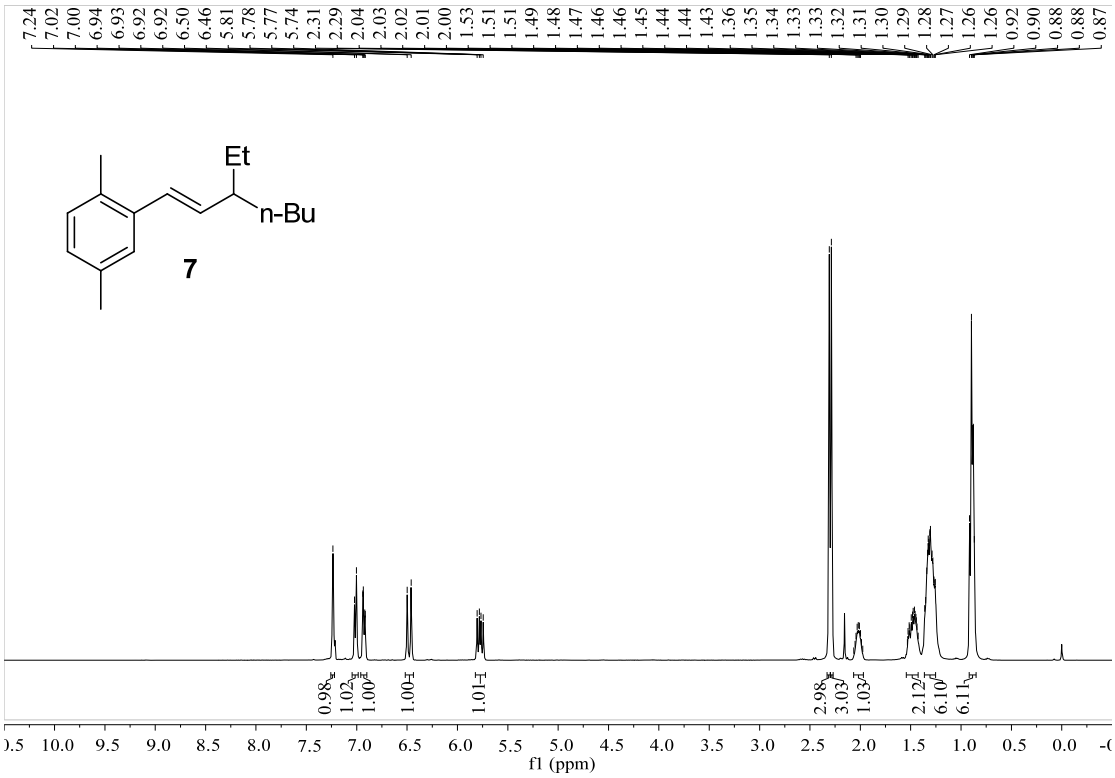



**Figure S51.** $^{1}$H NMR spectrum of compound **7**, related to **Figure 1.**

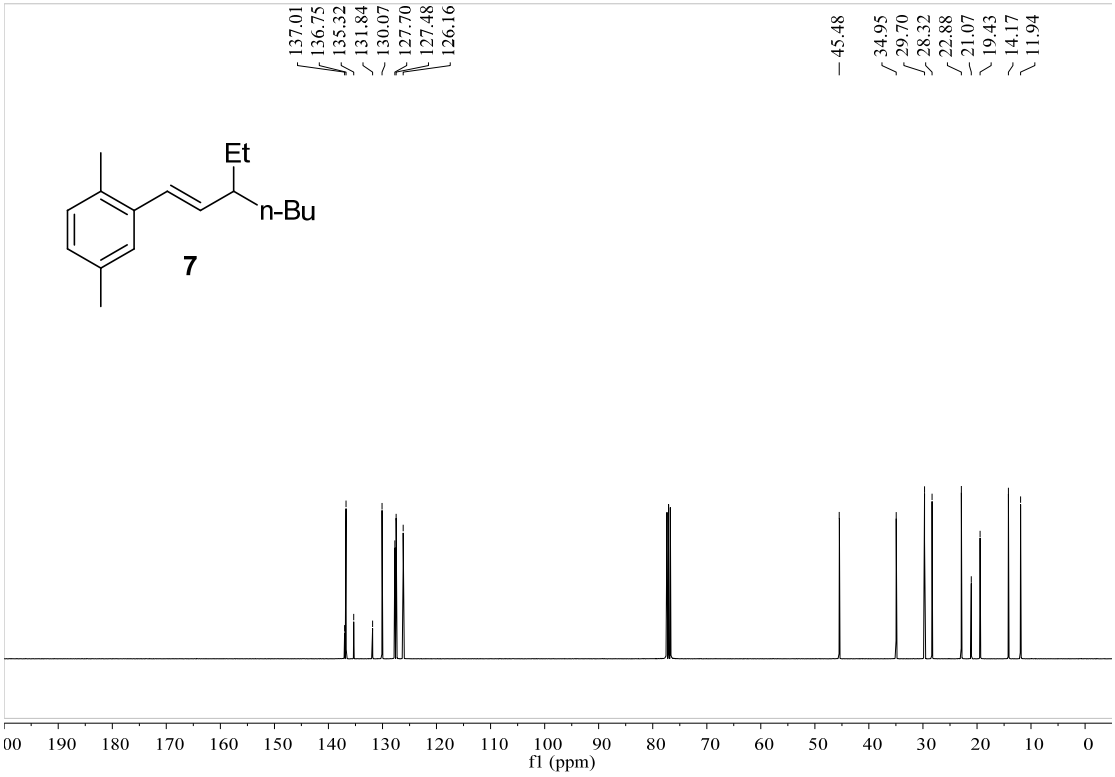



**Figure S52.** $^{13}$C NMR spectrum of compound **7**, related to **Figure 1.**

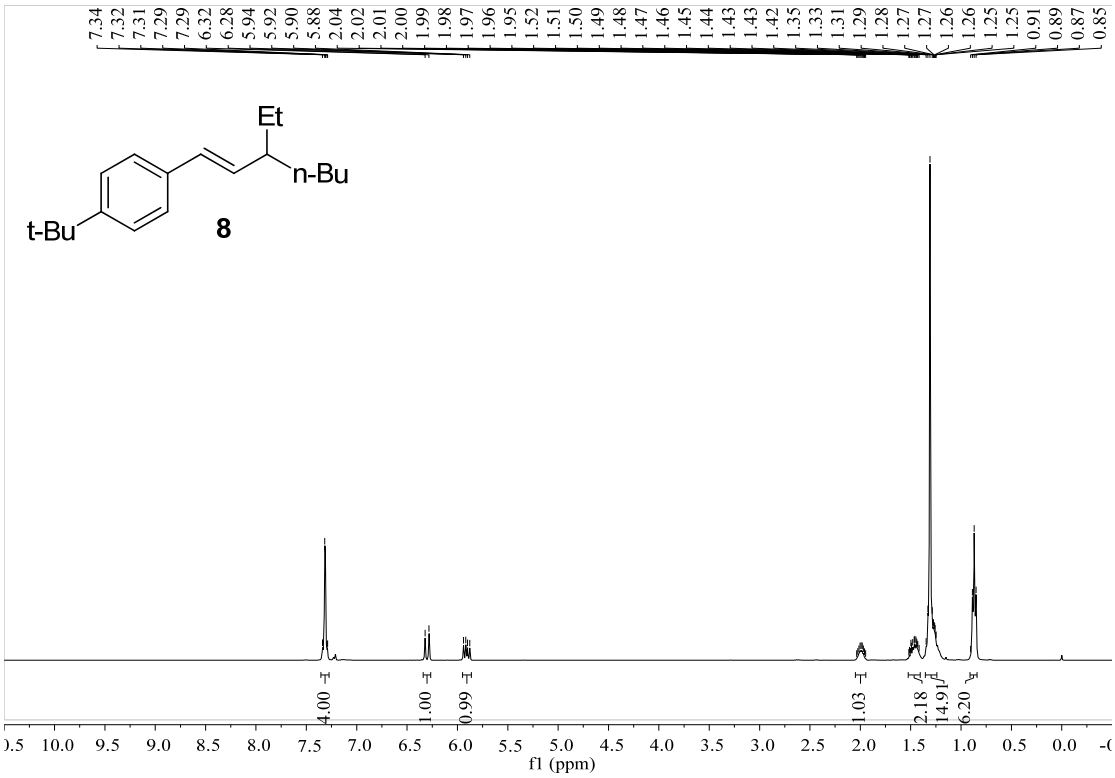



**Figure S53.** $^{1}$H NMR spectrum of compound **8**, related to **Figure 1.**

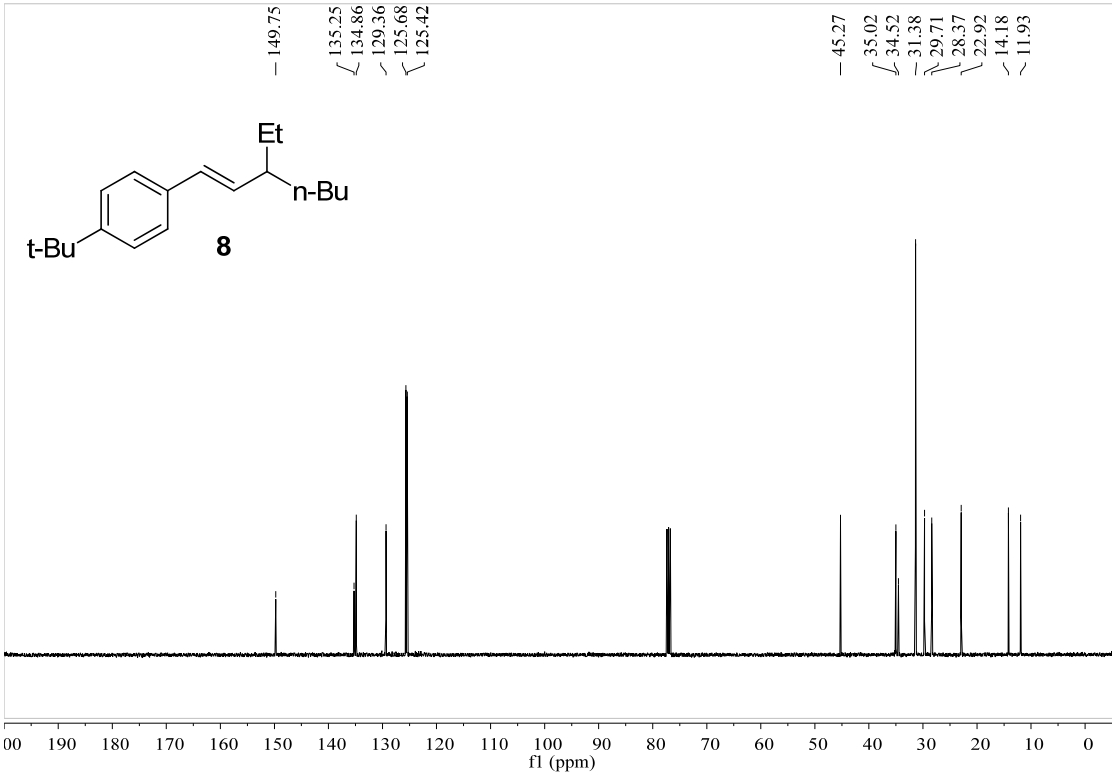



**Figure S54.** $^{13}$C NMR spectrum of compound **8**, related to **Figure 1.**

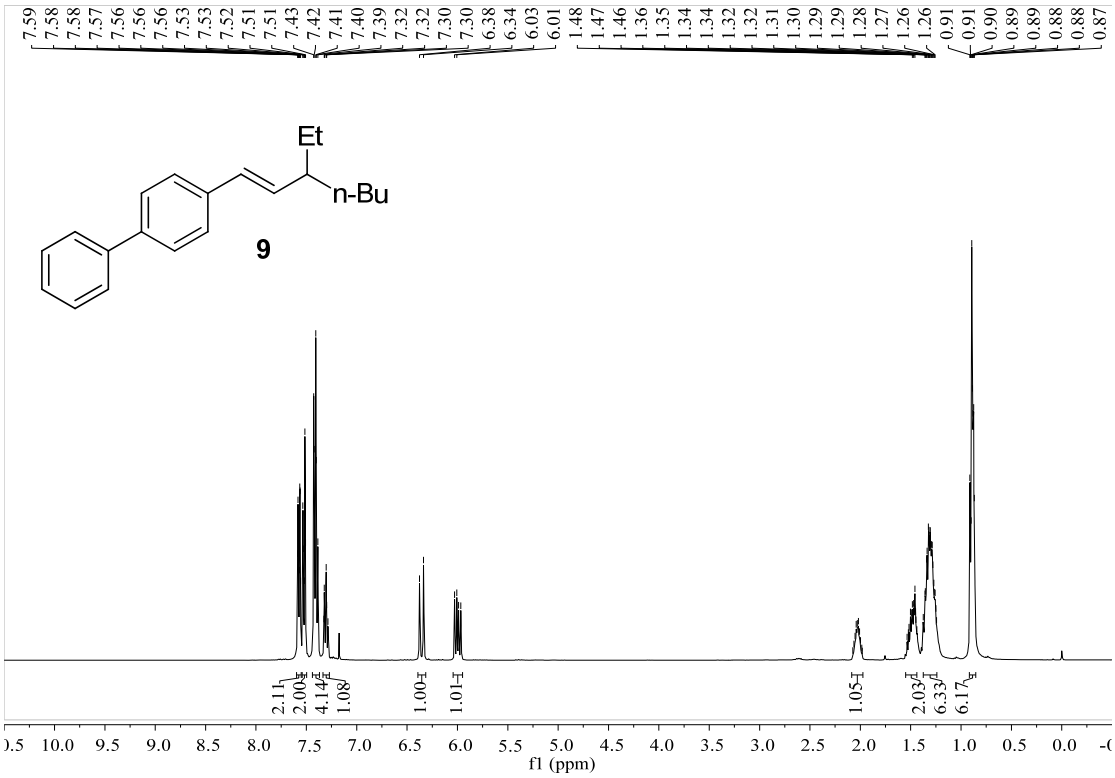



**Figure S55.** $^{1}$H NMR spectrum of compound **9**, related to **Figure 1.**

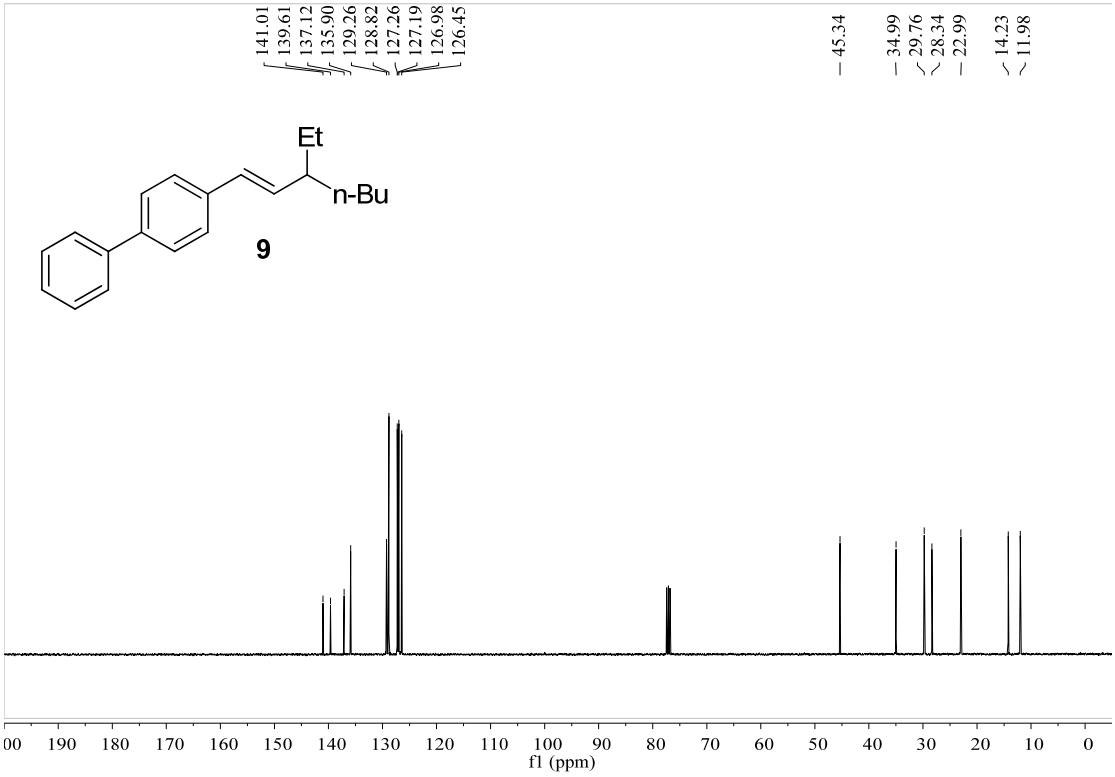



**Figure S56.** $^{13}$C NMR spectrum of compound **9**, related to **Figure 1.**

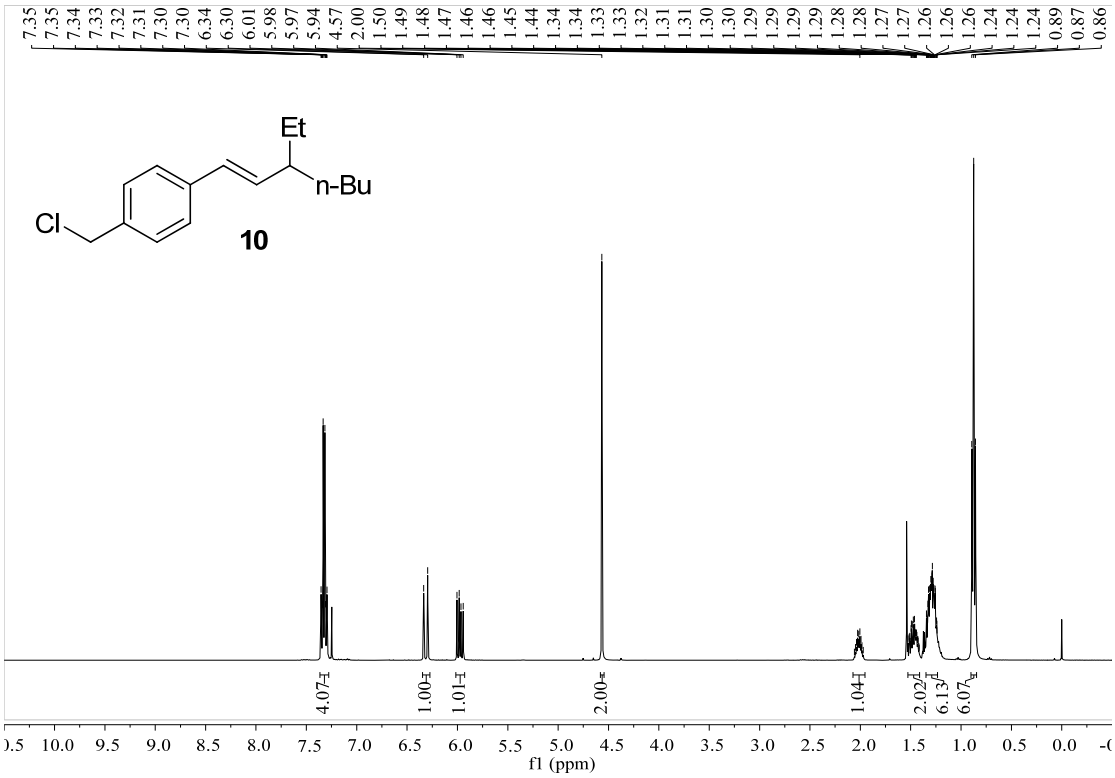



**Figure S57.** $^{1}$H NMR spectrum of compound **10**, related to **Figure 1.**

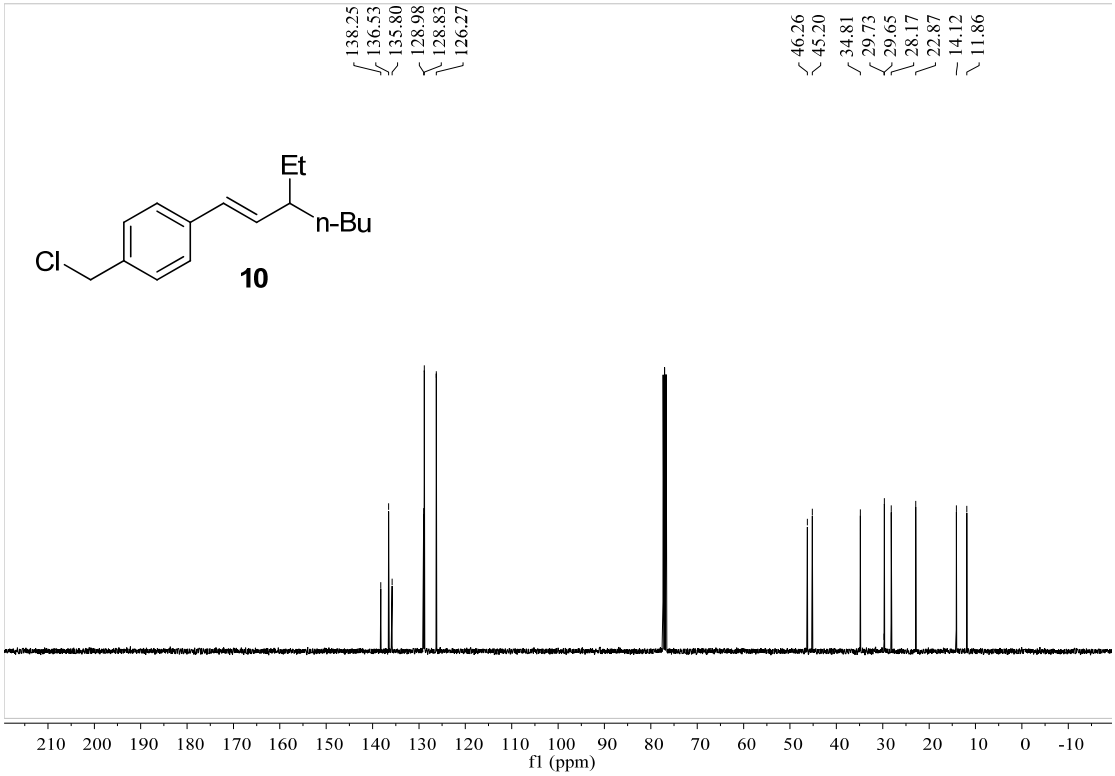



**Figure S58.** $^{13}$C NMR spectrum of compound **10**, related to **Figure 1.**

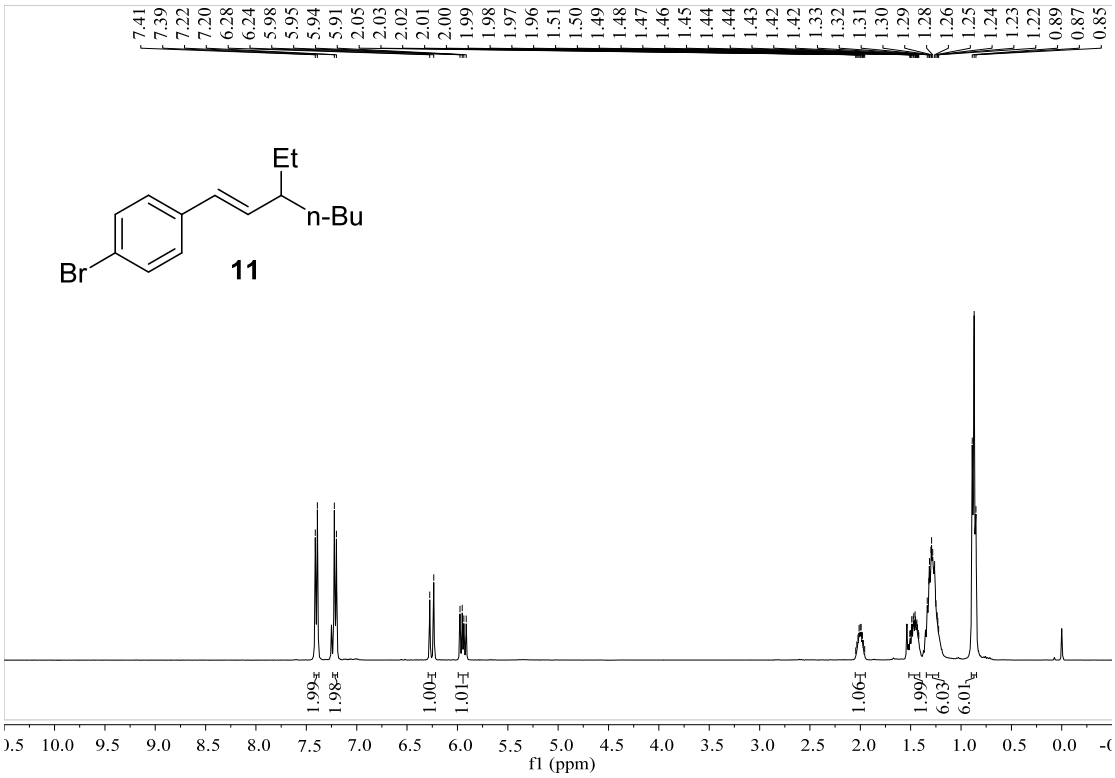



**Figure S59.** $^{1}$H NMR spectrum of compound **11**, related to **Figure 1.**

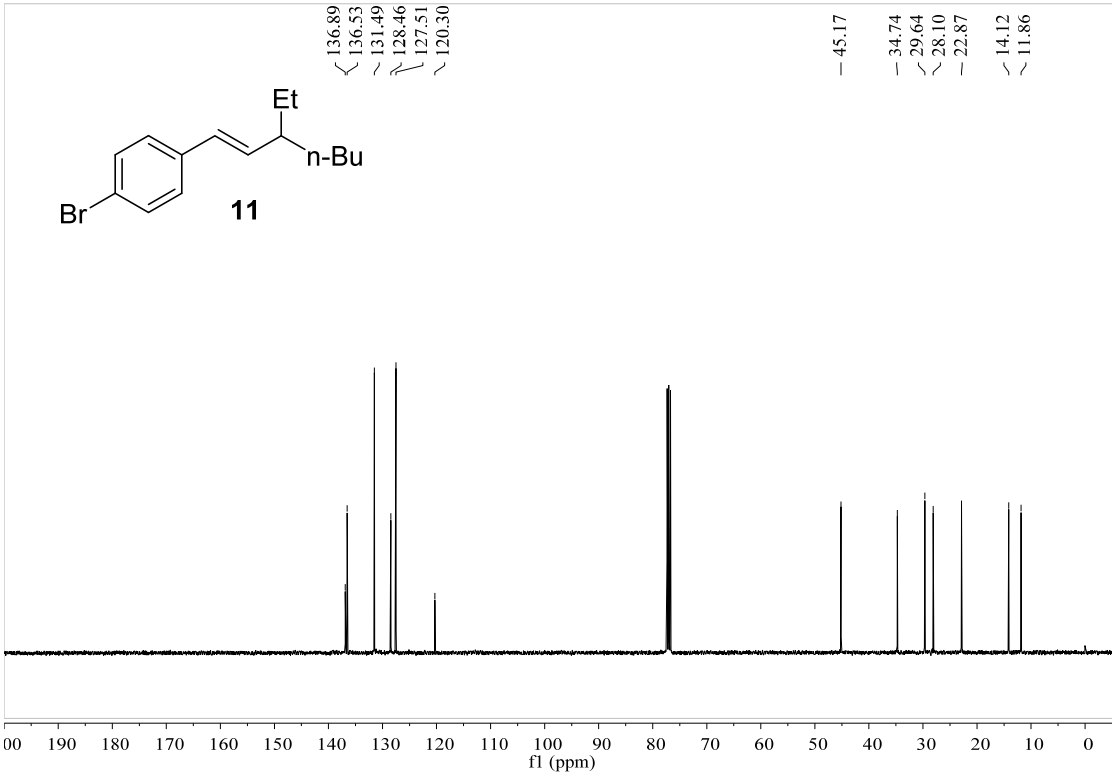



**Figure S60.** $^{13}$C NMR spectrum of compound **11**, related to **Figure 1.**

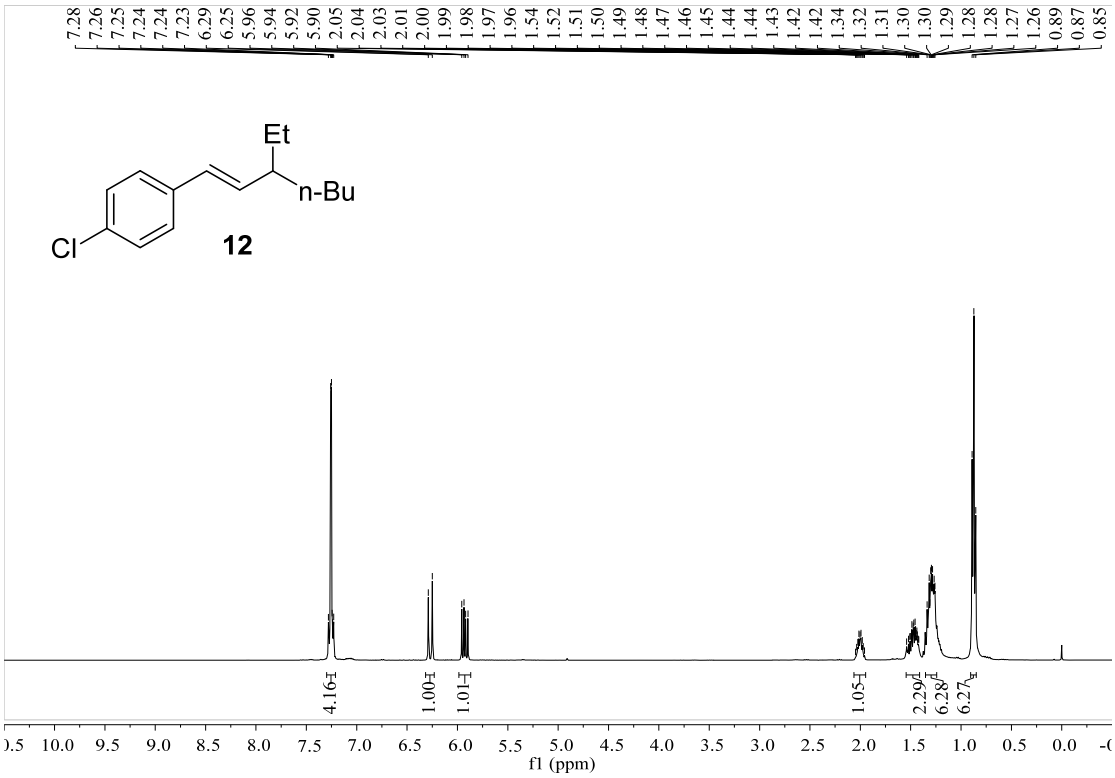



**Figure S61.** $^{1}$H NMR spectrum of compound **12**, related to **Figure 1.**

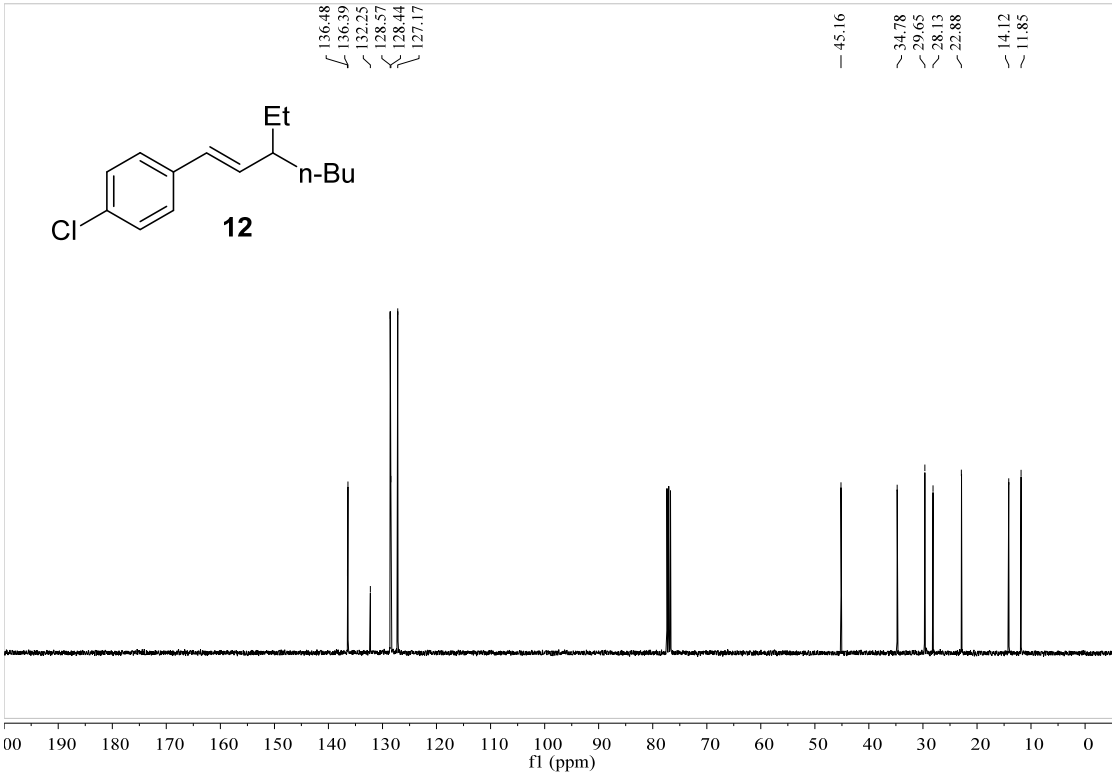



**Figure S62.** $^{13}$C NMR spectrum of compound **12**, related to **Figure 1.**

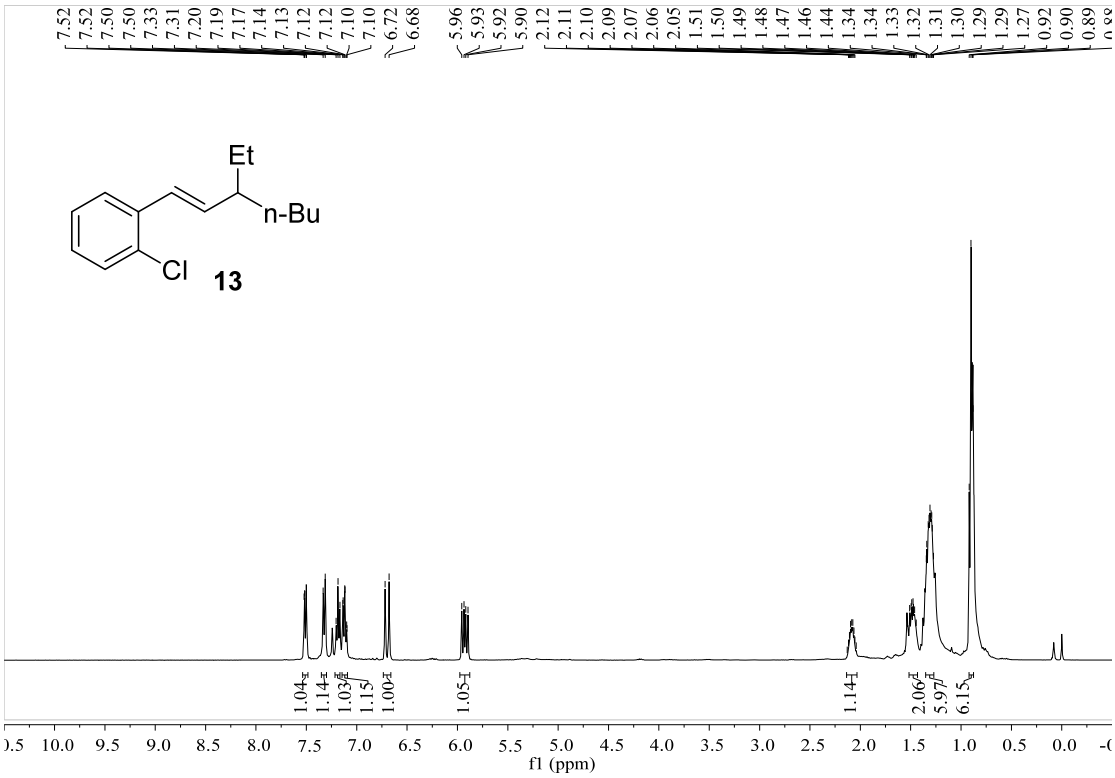



**Figure S63.** $^{1}$H NMR spectrum of compound **13**, related to **Figure 1.**

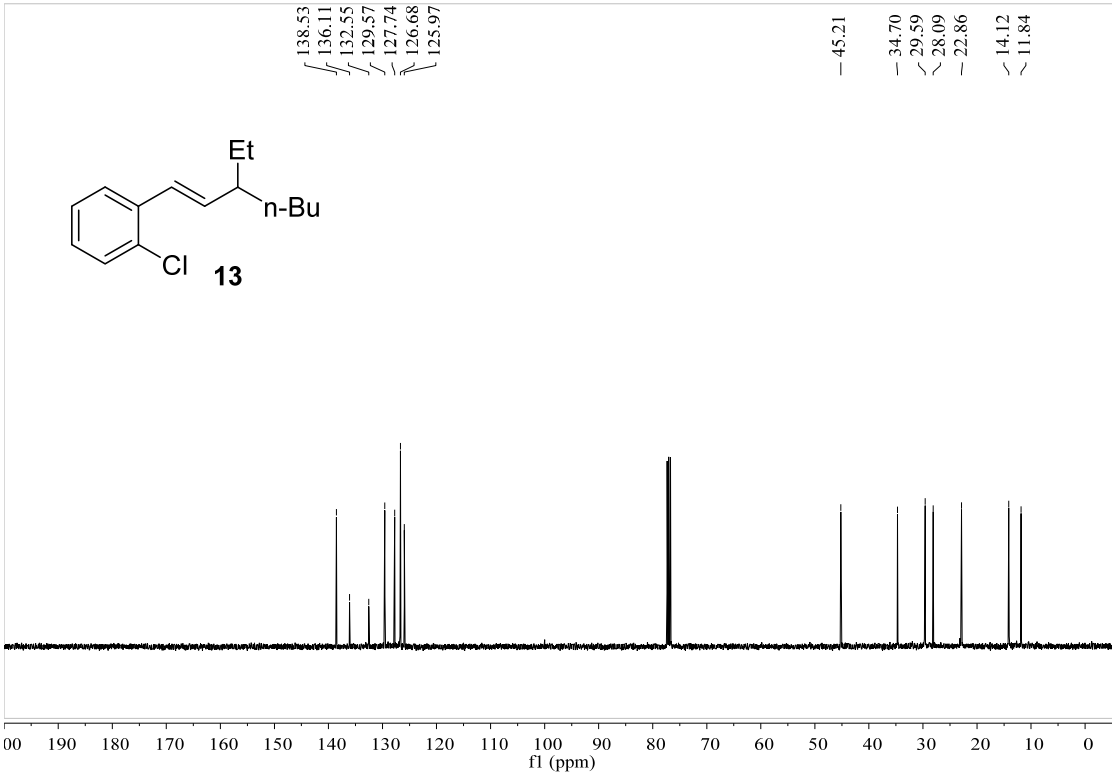



**Figure S64.** $^{13}$C NMR spectrum of compound **13**, related to **Figure 1.**

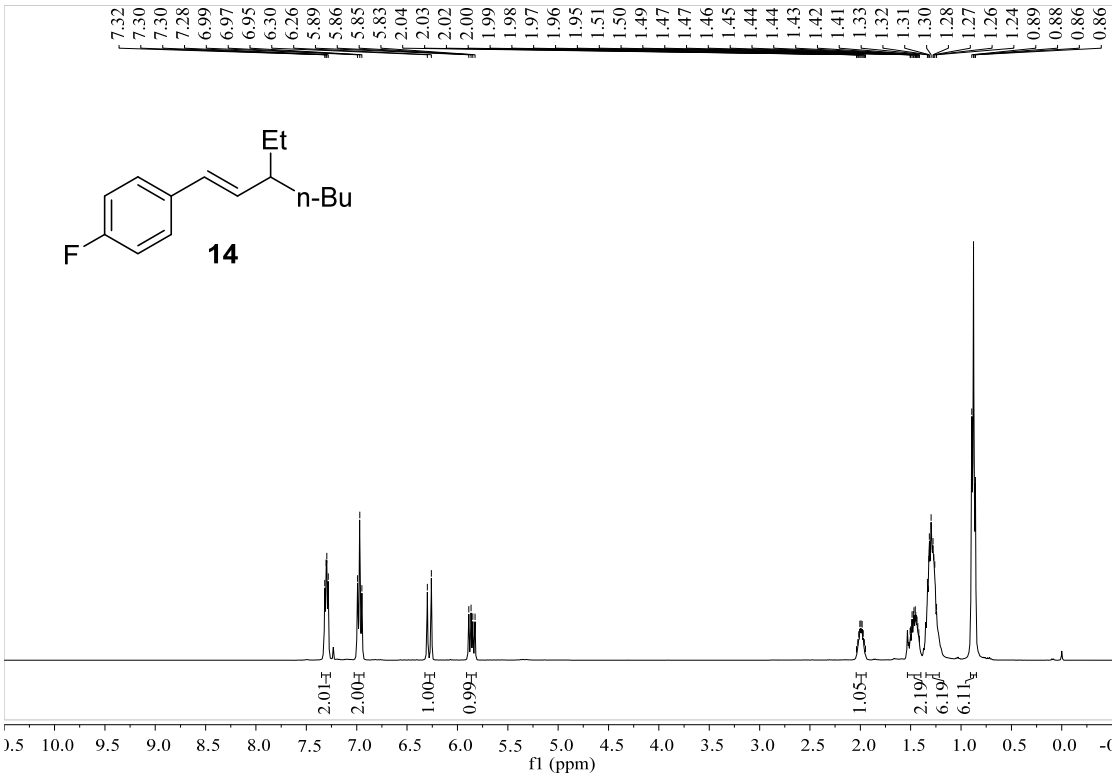



**Figure S65.** $^{1}$H NMR spectrum of compound **14**, related to **Figure 1.**

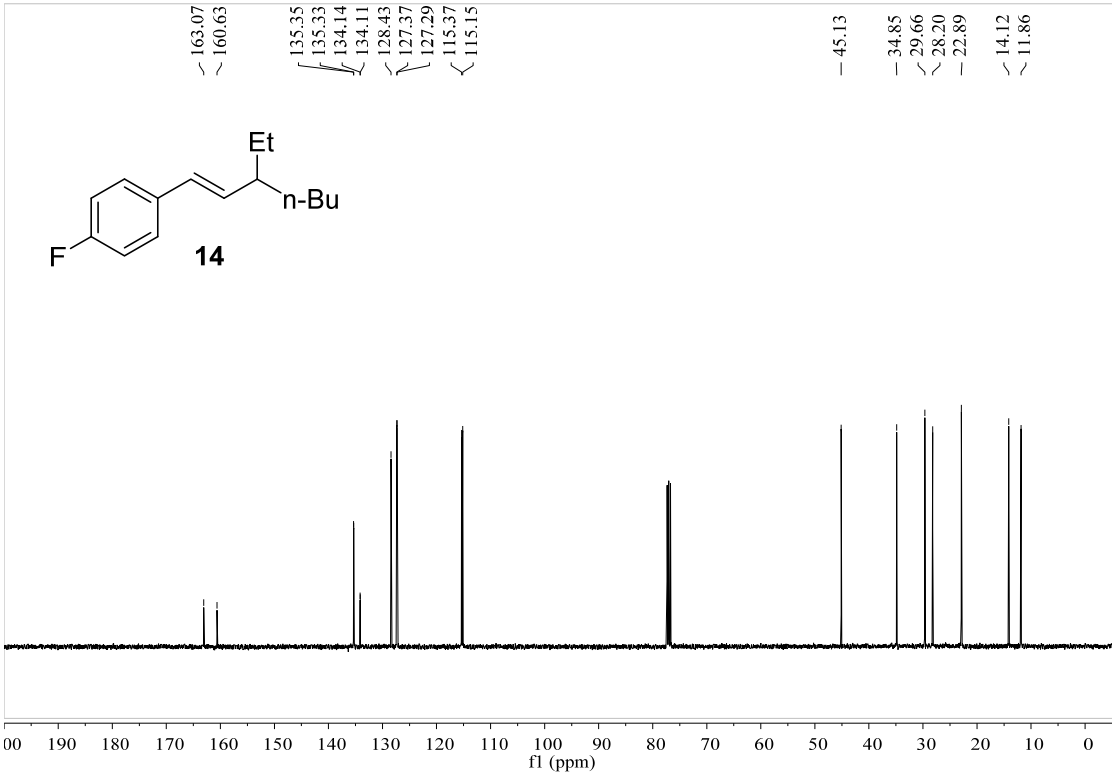



**Figure S66.** $^{13}$C NMR spectrum of compound **14**, related to **Figure 1.**

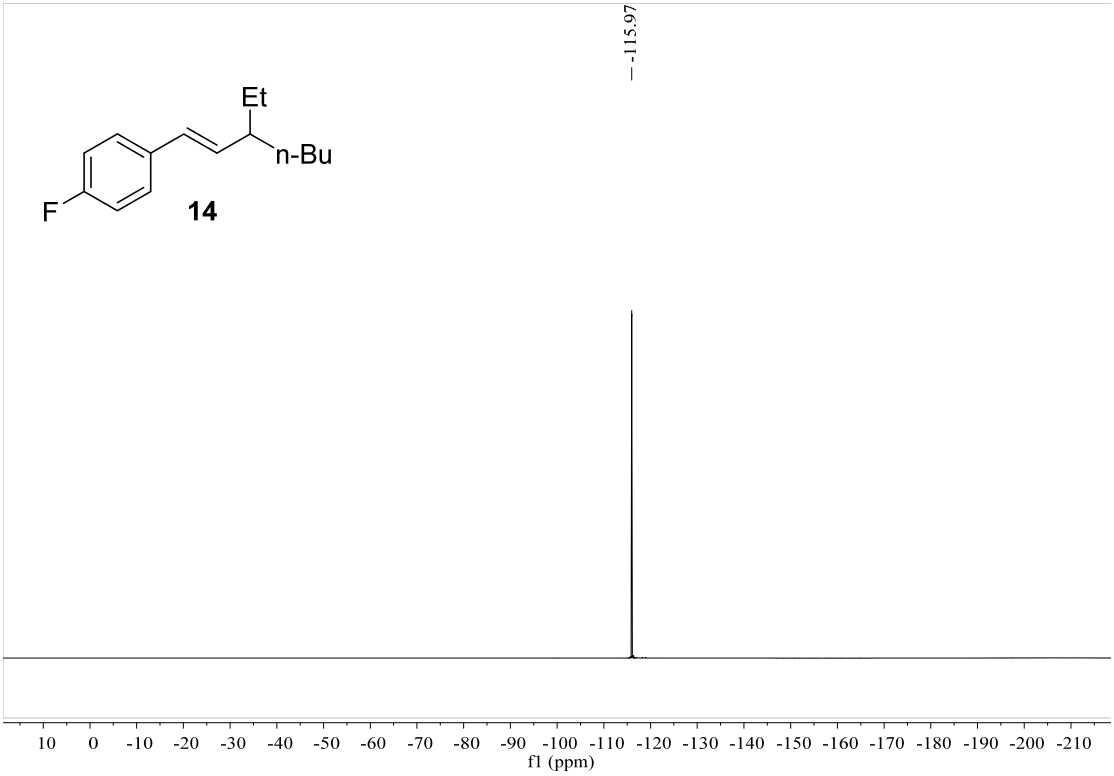



**Figure S67.** $^{19}F$ NMR spectrum of compound **14**, related to **Figure 1.**

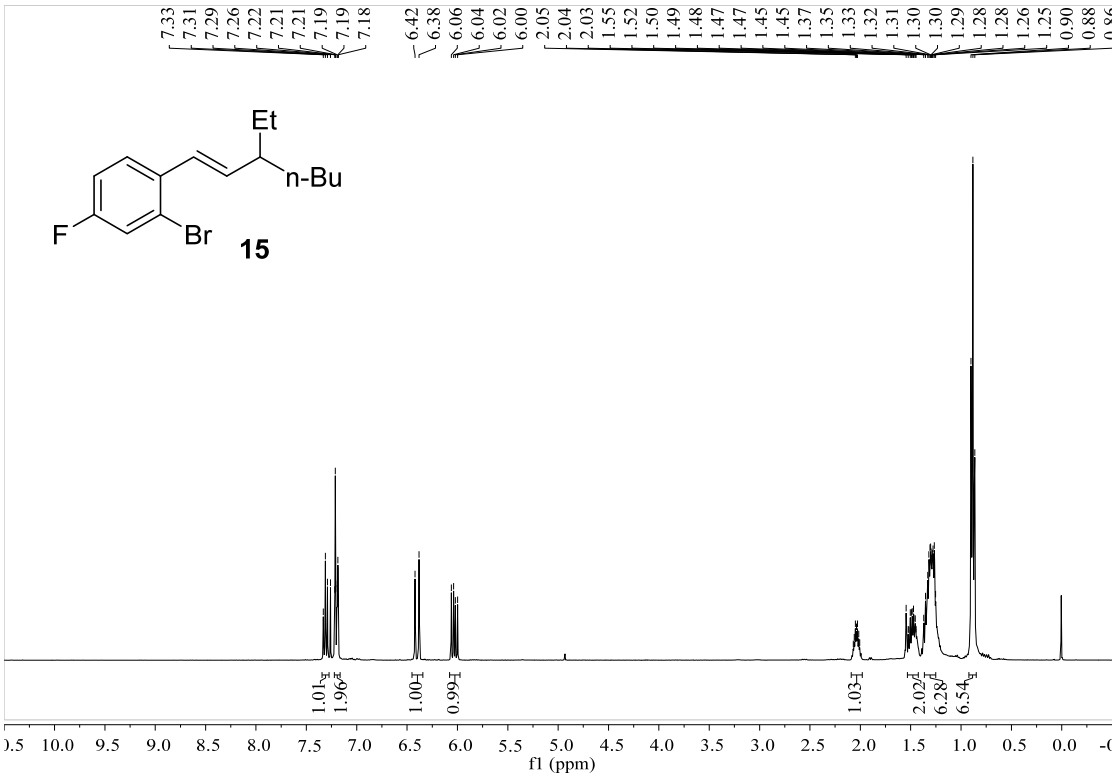



**Figure S68.** $^{1}$H NMR spectrum of compound **15**, related to **Figure 1.**

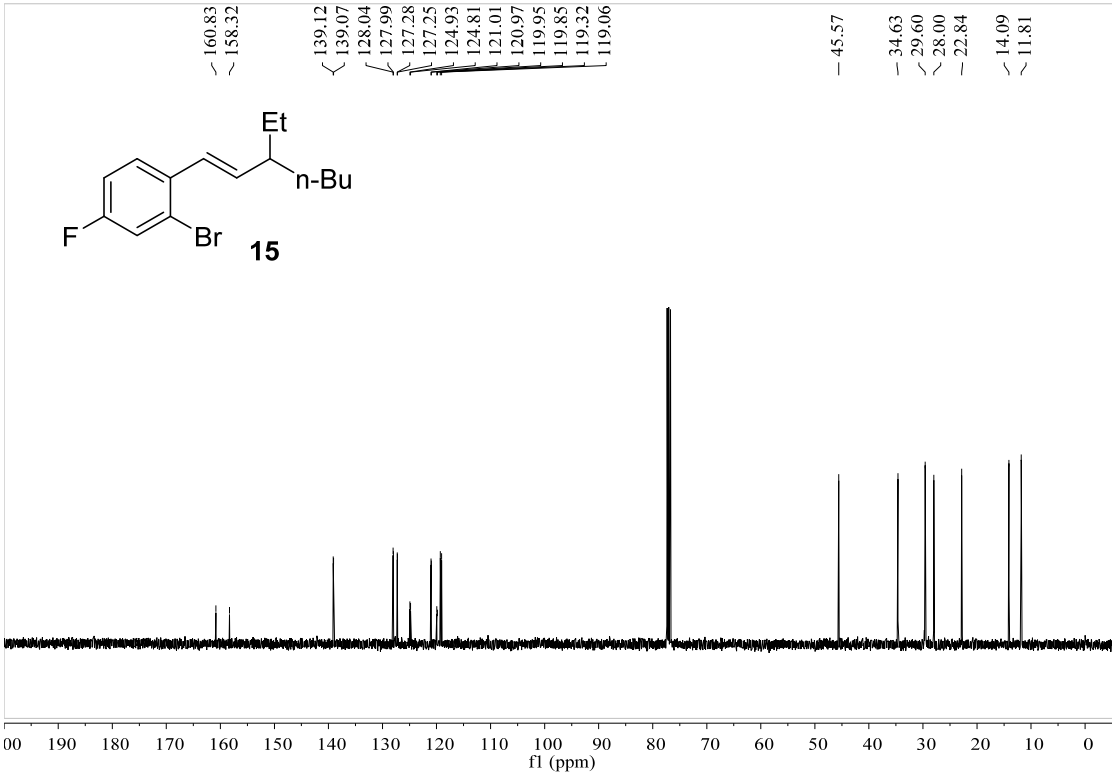



**Figure S69.** $^{13}$C NMR spectrum of compound **15**, related to **Figure 1.**

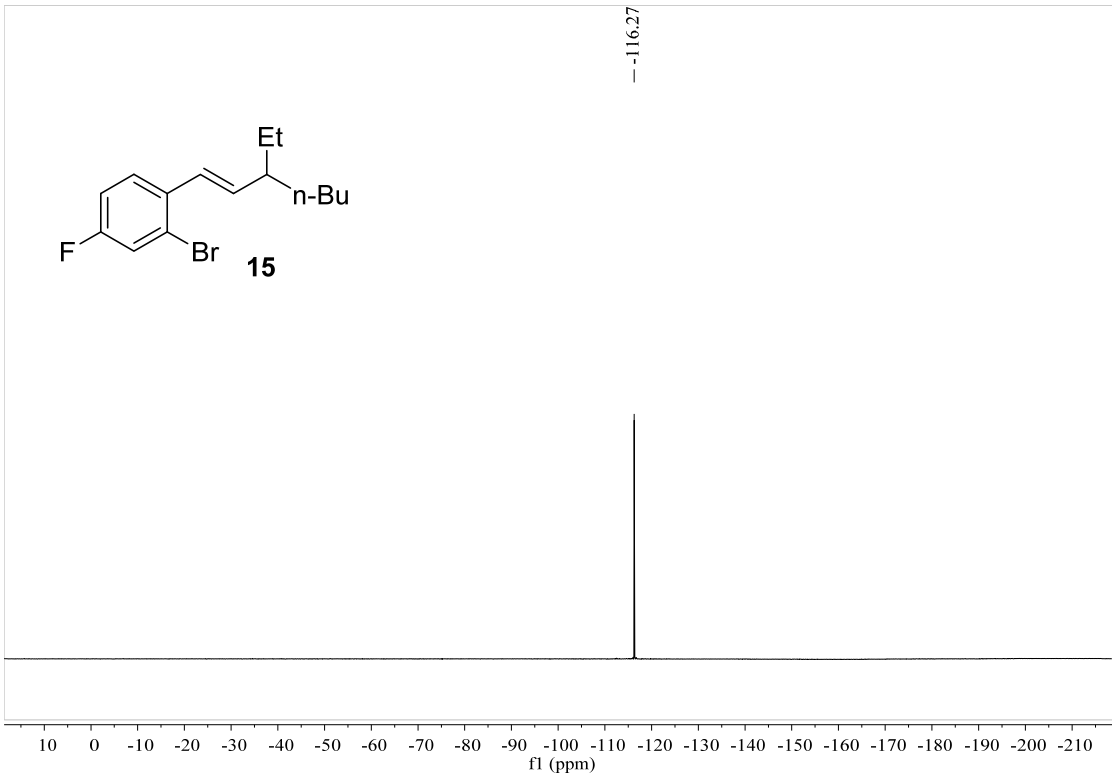



**Figure S70.** $^{19}F$ NMR spectrum of compound **15**, related to **Figure 1.**

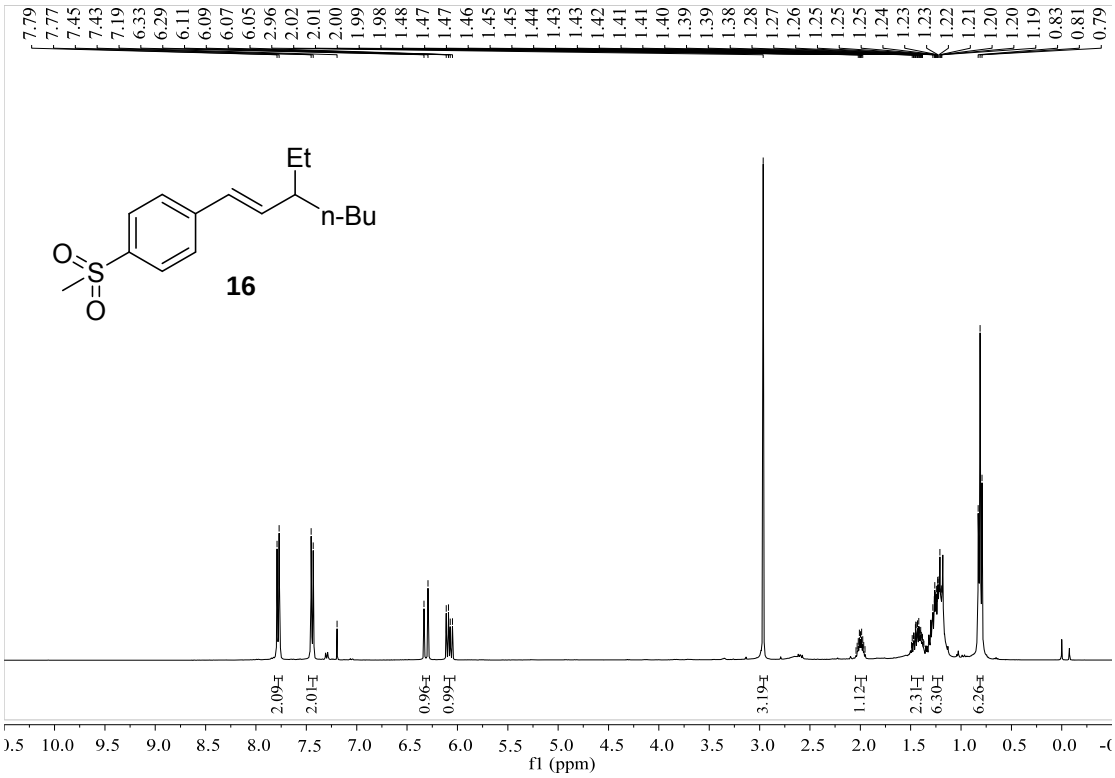



**Figure S71.** $^{1}$H NMR spectrum of compound **16**, related to **Figure 1.**

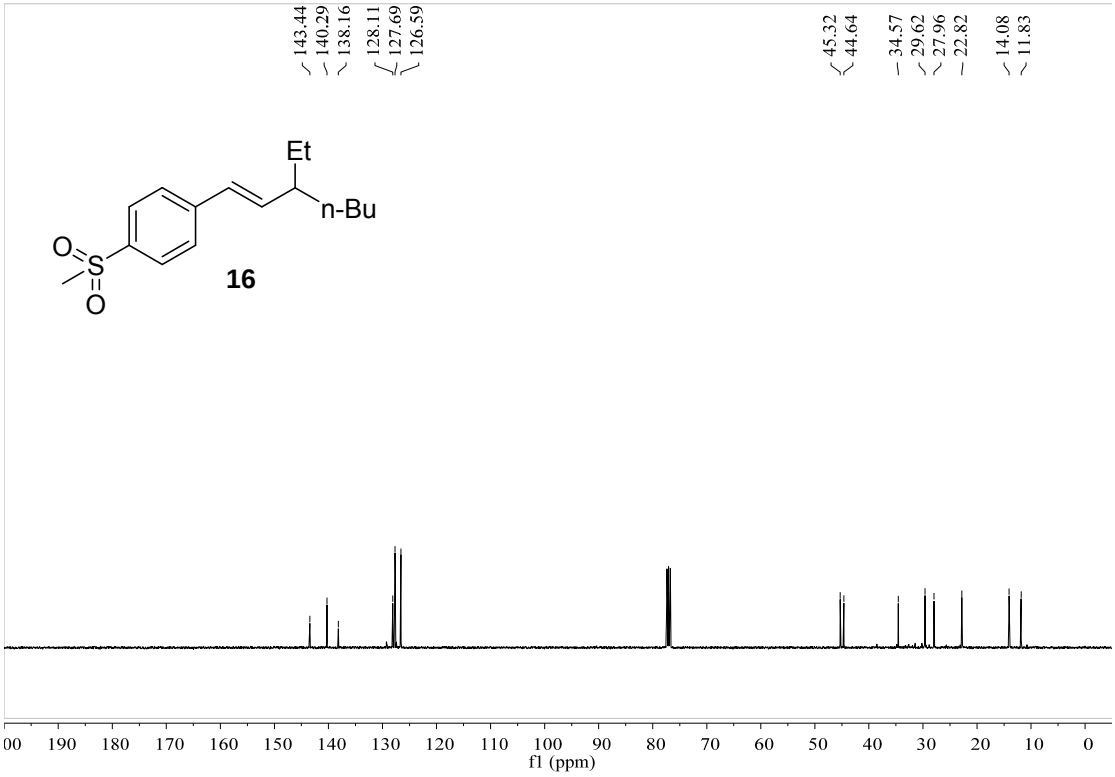



**Figure S72.** $^{13}$C NMR spectrum of compound **16**, related to **Figure 1.**

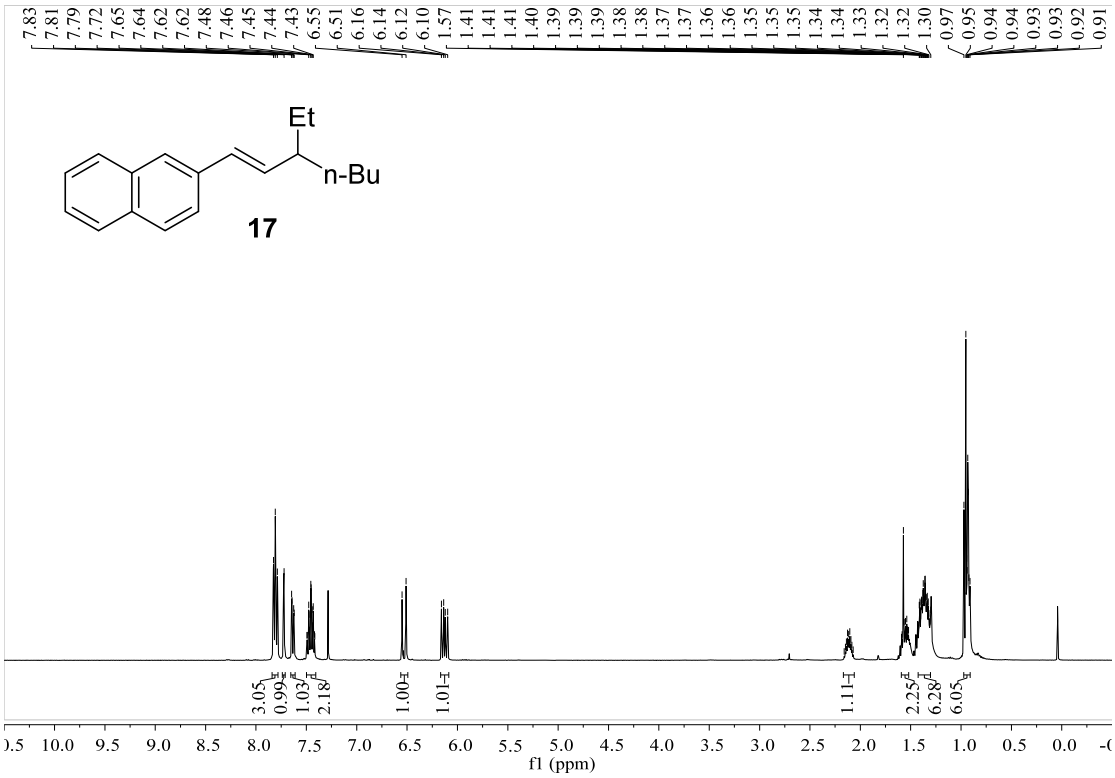



**Figure S73.** $^{1}$H NMR spectrum of compound **17**, related to **Figure 1.**

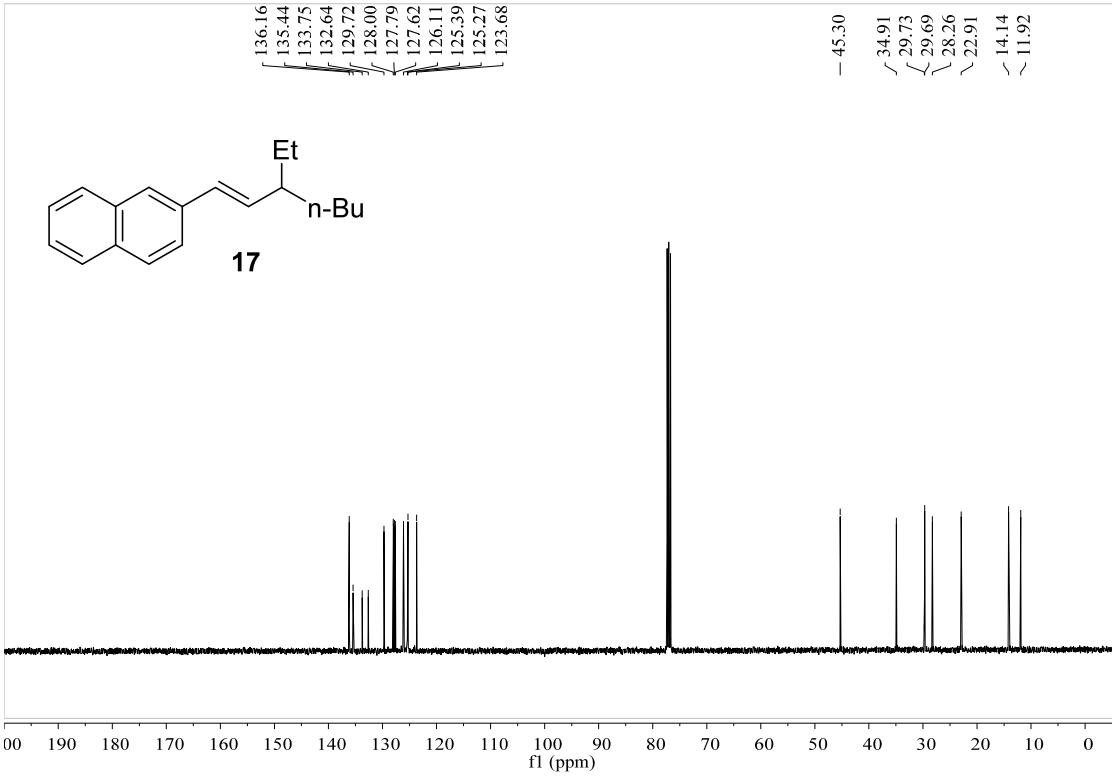



**Figure S74.** $^{13}$C NMR spectrum of compound **17**, related to **Figure 1.**

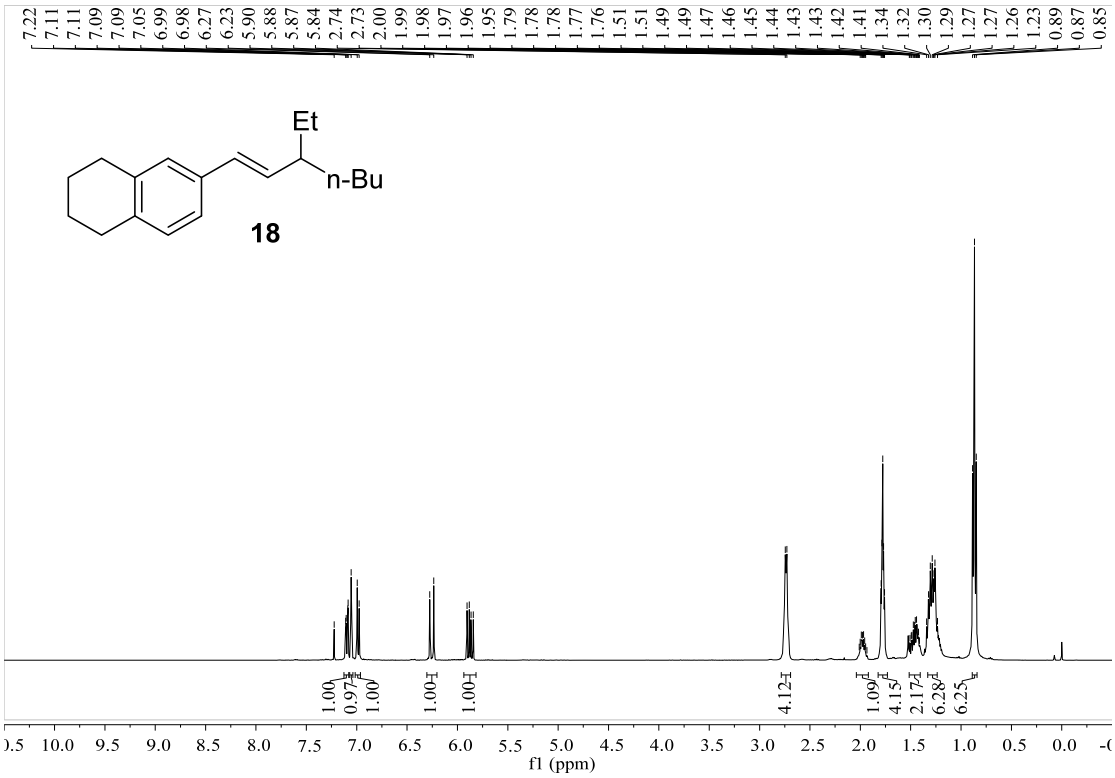



**Figure S75.** $^{1}$H NMR spectrum of compound **18**, related to **Figure 1.**

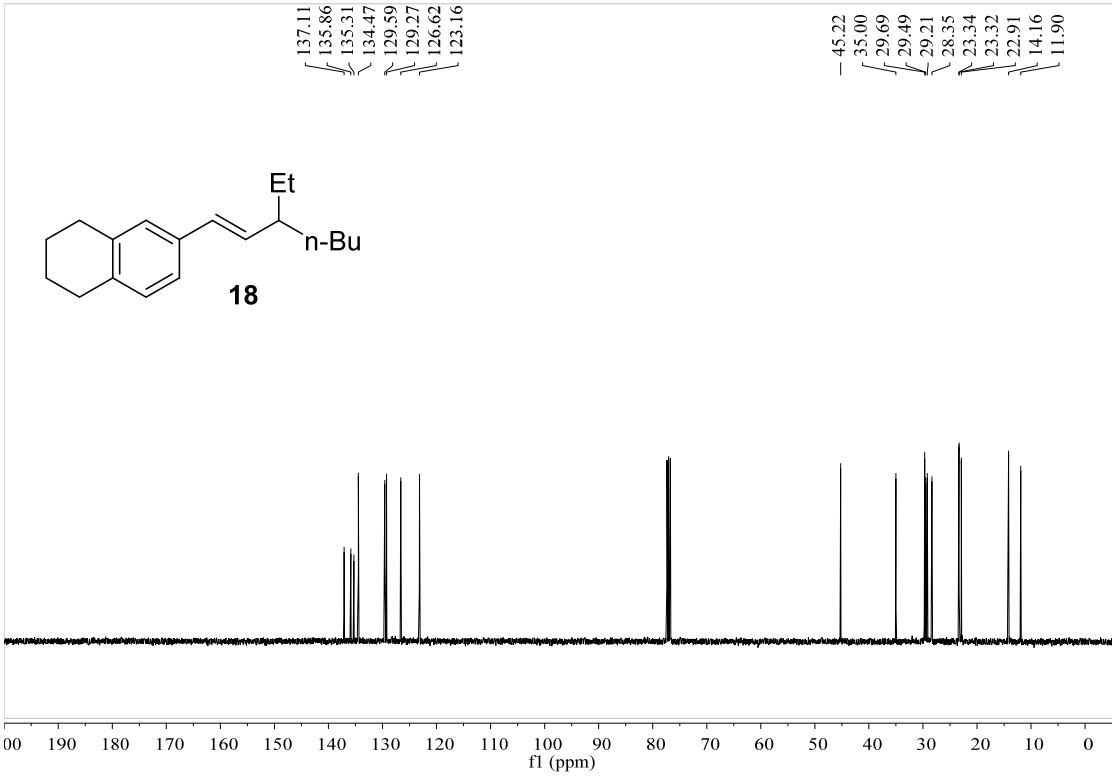



**Figure S76.** $^{13}$C NMR spectrum of compound **18**, related to **Figure 1.**

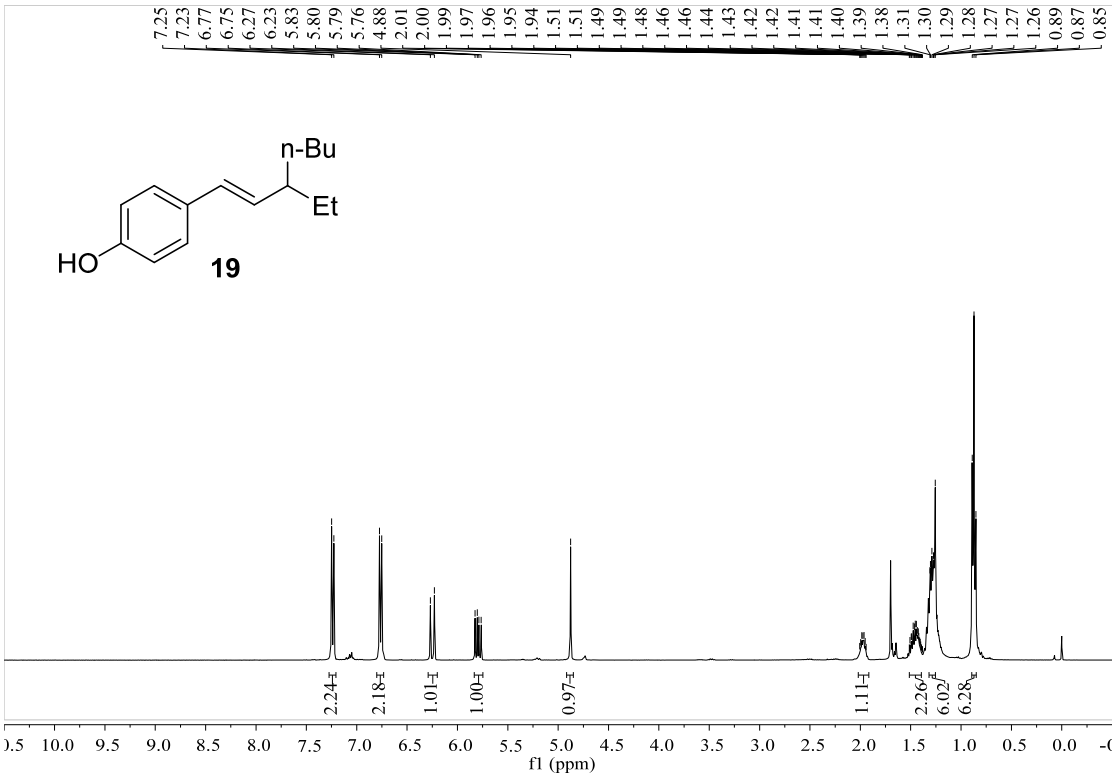



**Figure S77.** $^{1}$H NMR spectrum of compound **19**, related to **Figure 1.**

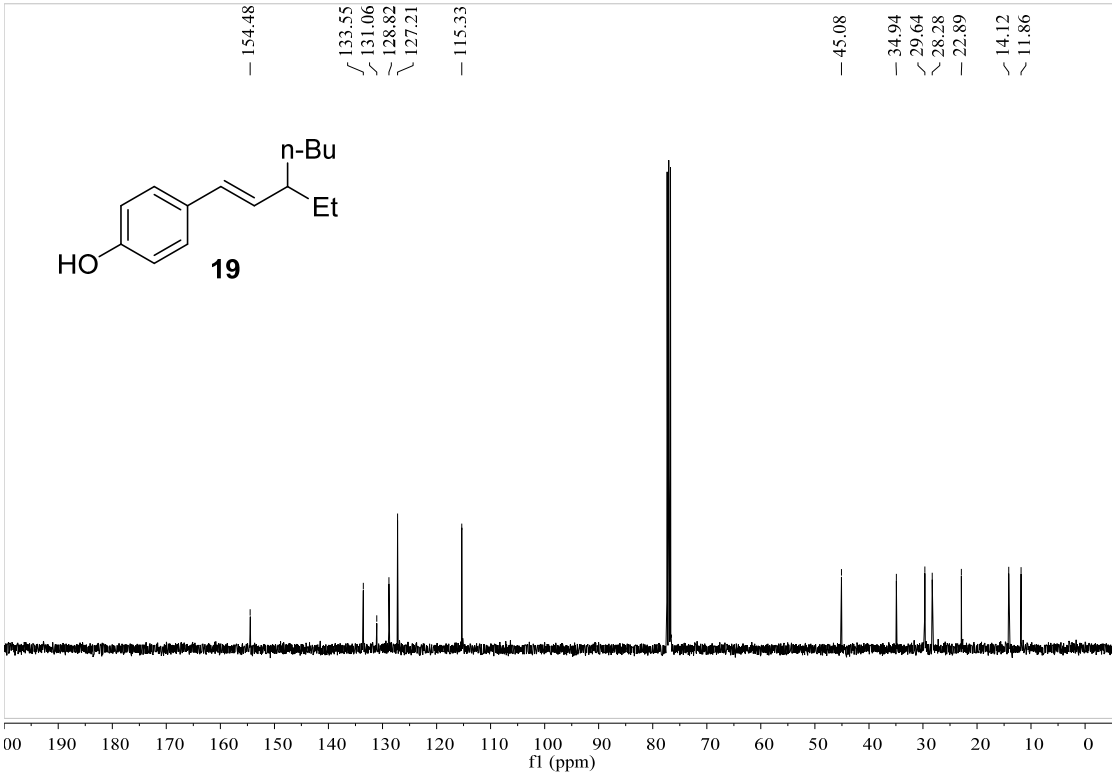



**Figure S78.** $^{13}$C NMR spectrum of compound **19**, related to **Figure 1.**

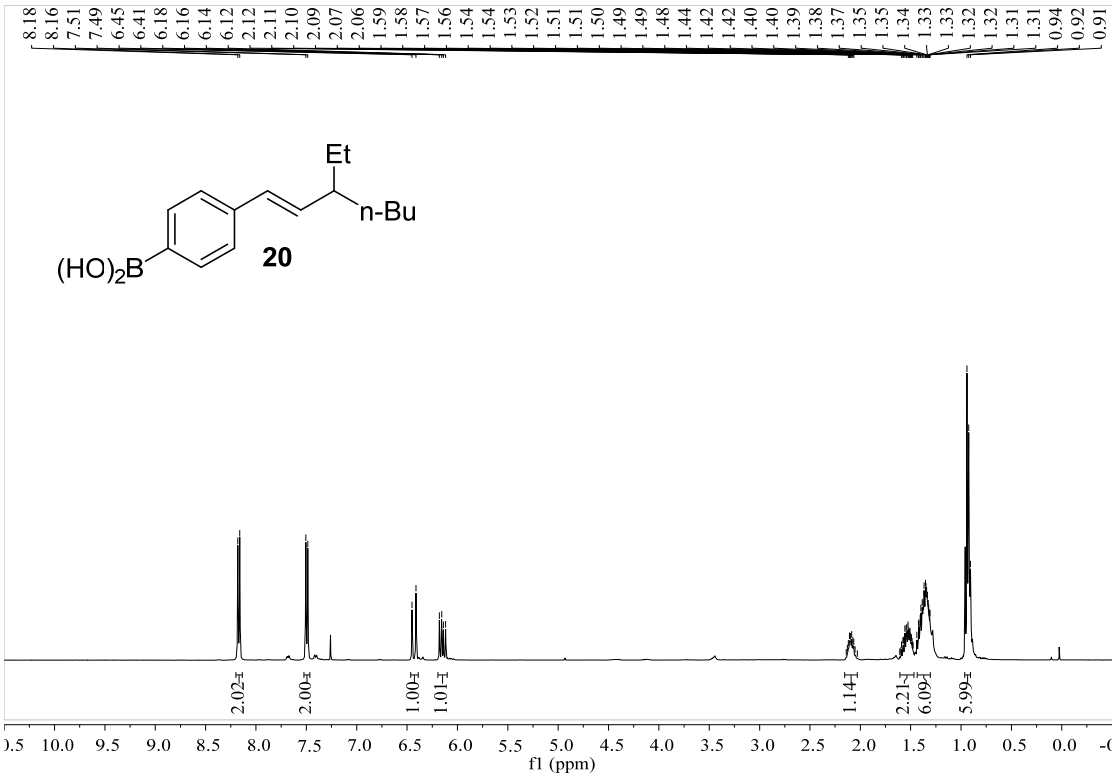



**Figure S79.** $^{1}$H NMR spectrum of compound **20**, related to **Figure 1.**

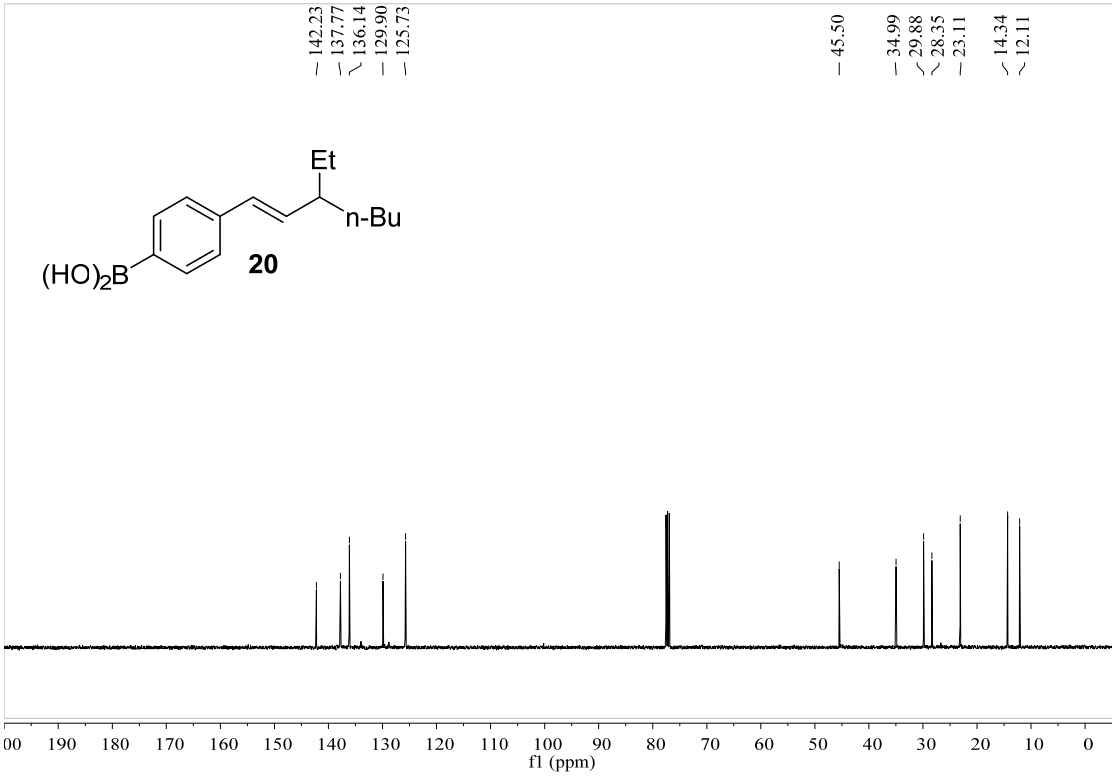



**Figure S80.** $^{13}$C NMR spectrum of compound **20**, related to **Figure 1.**

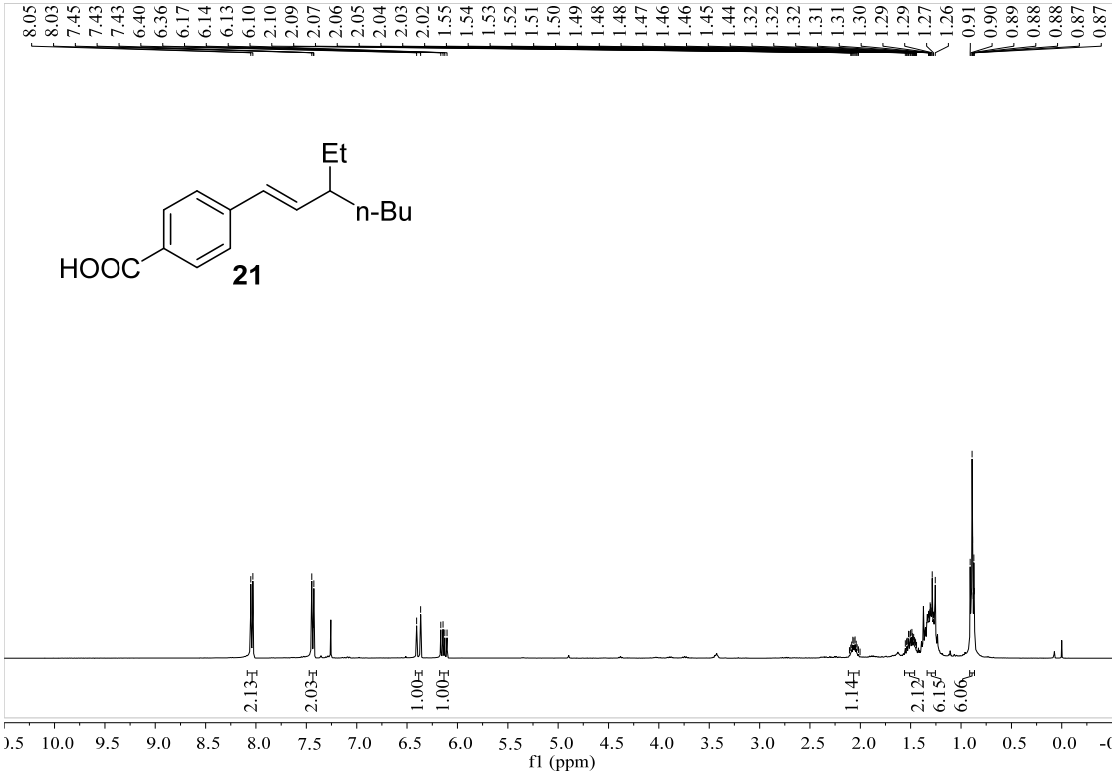



**Figure S81.** $^{1}$H NMR spectrum of compound **21**, related to **Figure 1.**

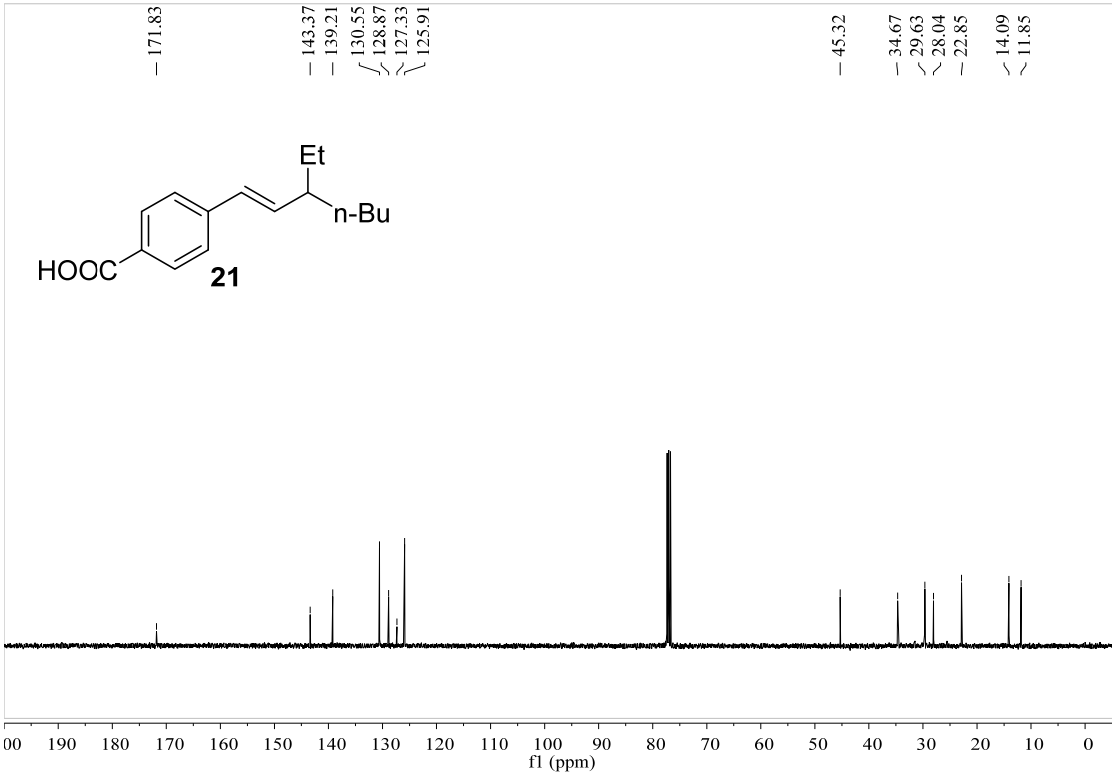



**Figure S82.** $^{13}$C NMR spectrum of compound **21**, related to **Figure 1.**

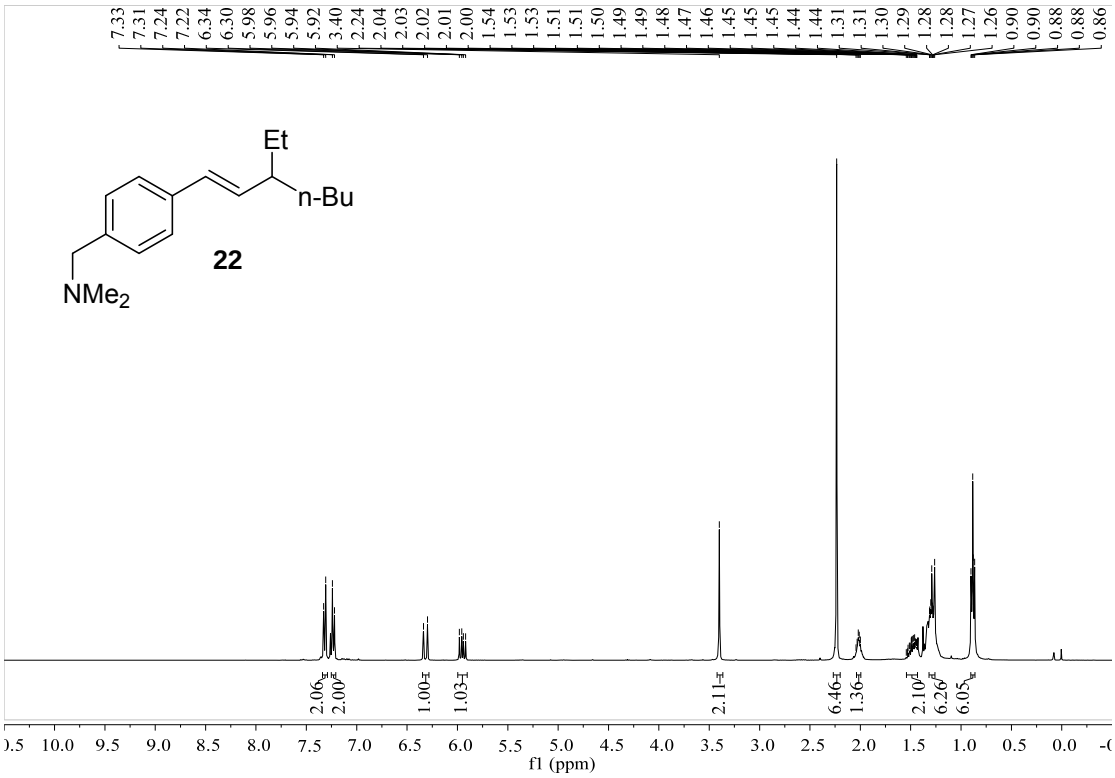



**Figure S83.** $^{1}$H NMR spectrum of compound **22**, related to **Figure 1.**

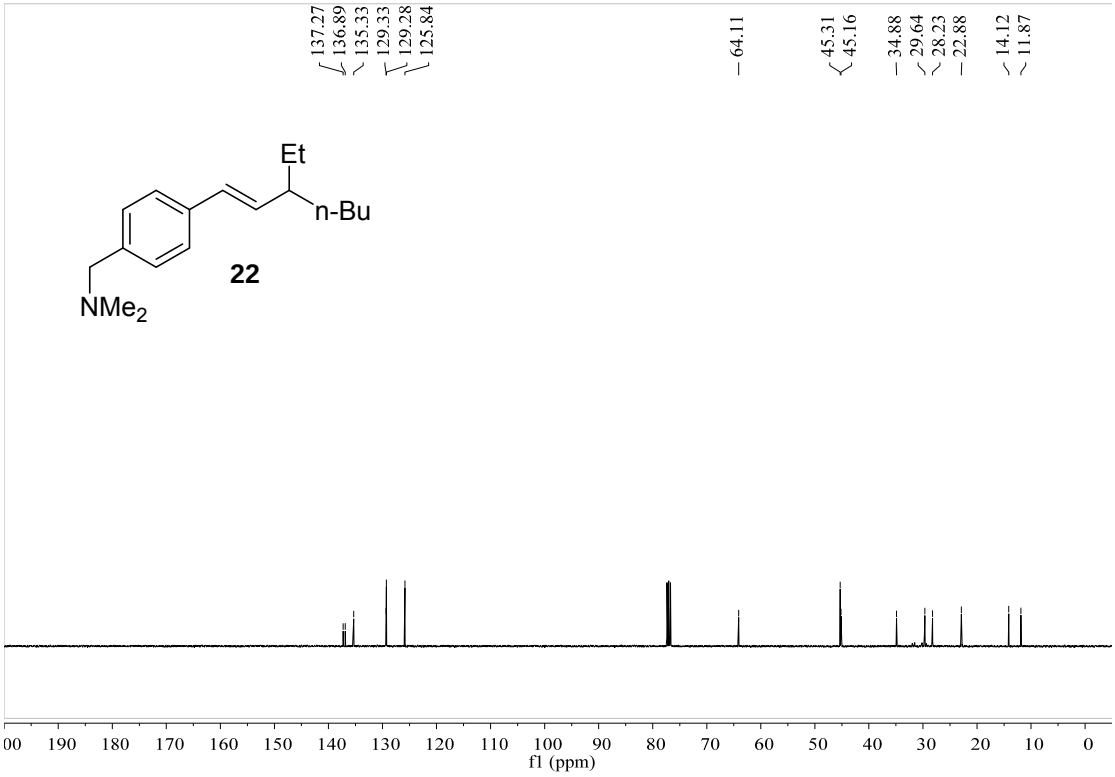



**Figure S84.** $^{13}$C NMR spectrum of compound **22**, related to **Figure 1.**

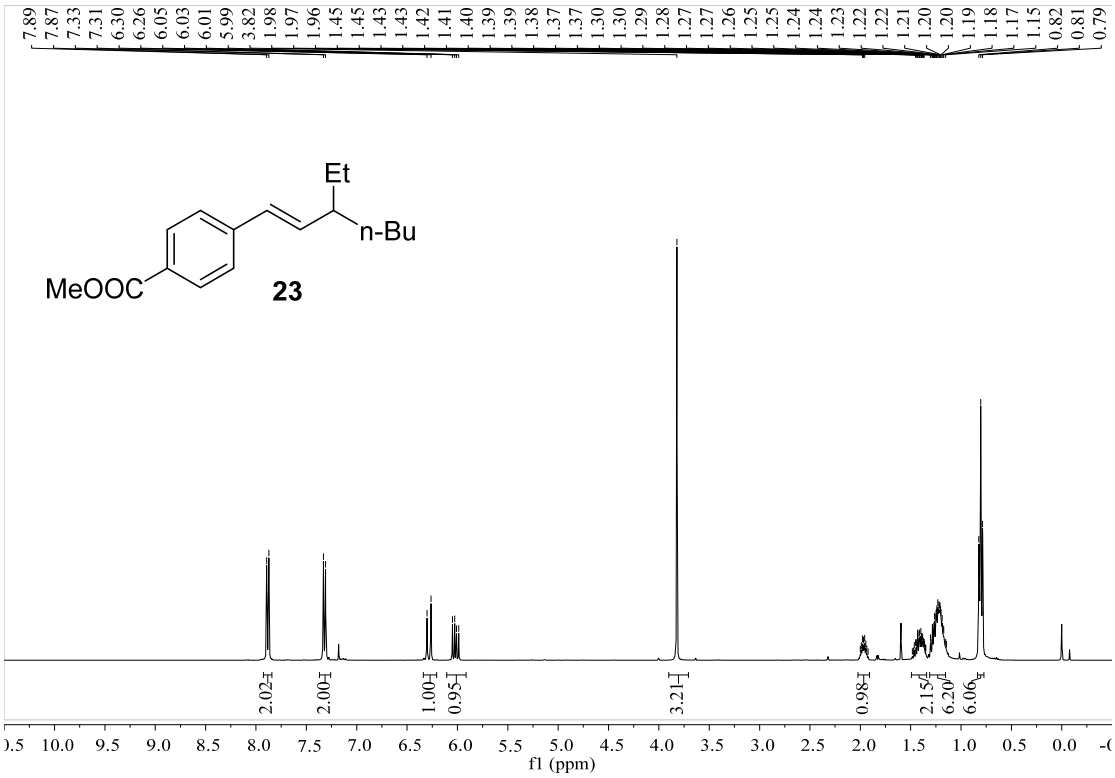



**Figure S85.** $^{1}$H NMR spectrum of compound **23**, related to **Figure 1.**

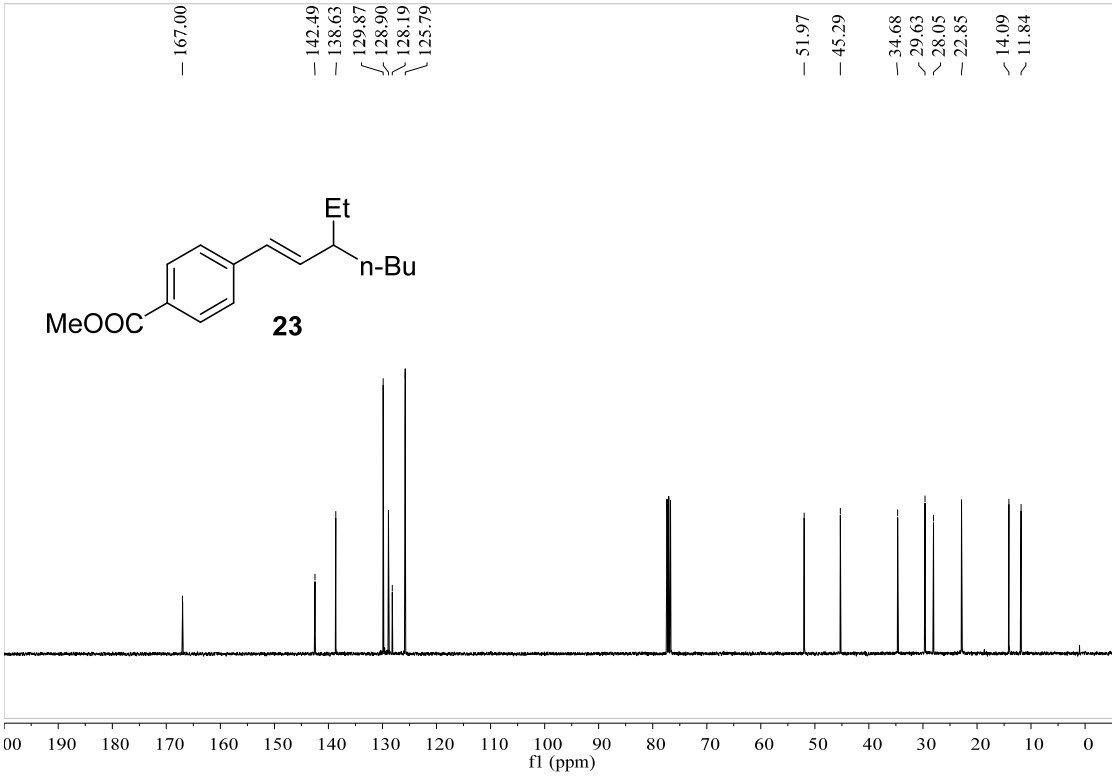



**Figure S86.** $^{13}$C NMR spectrum of compound **23**, related to **Figure 1.**

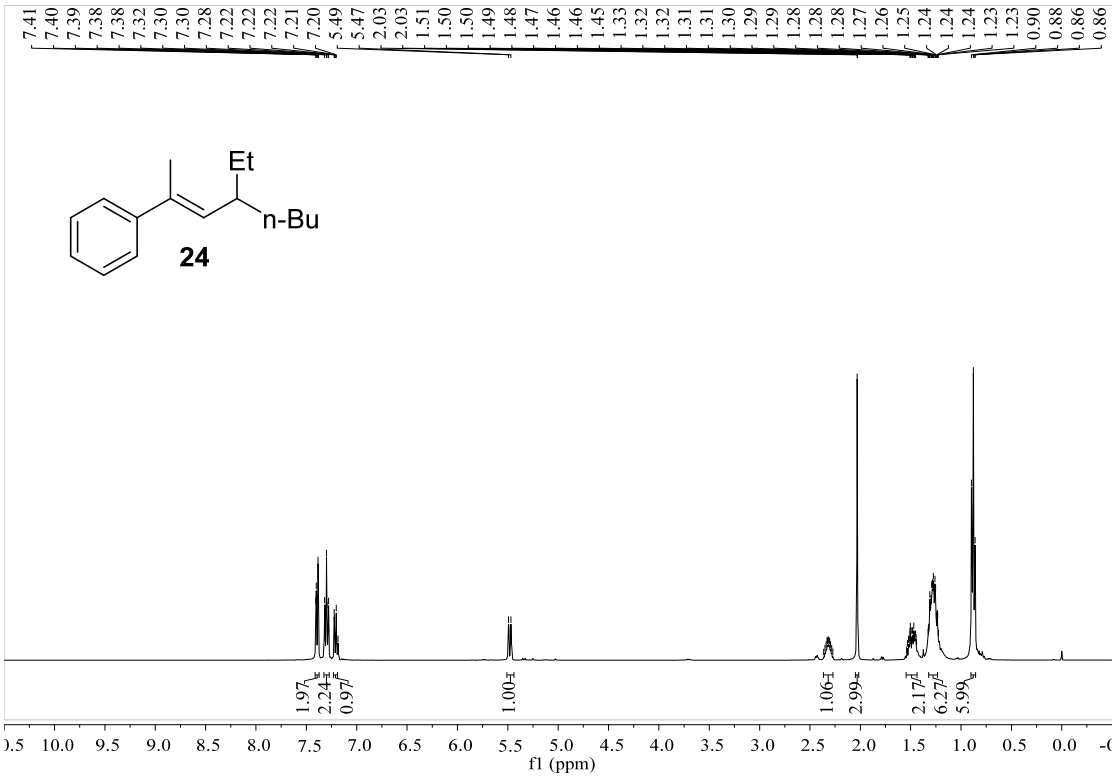



**Figure S87.** $^{1}$H NMR spectrum of compound **24**, related to **Figure 1.**

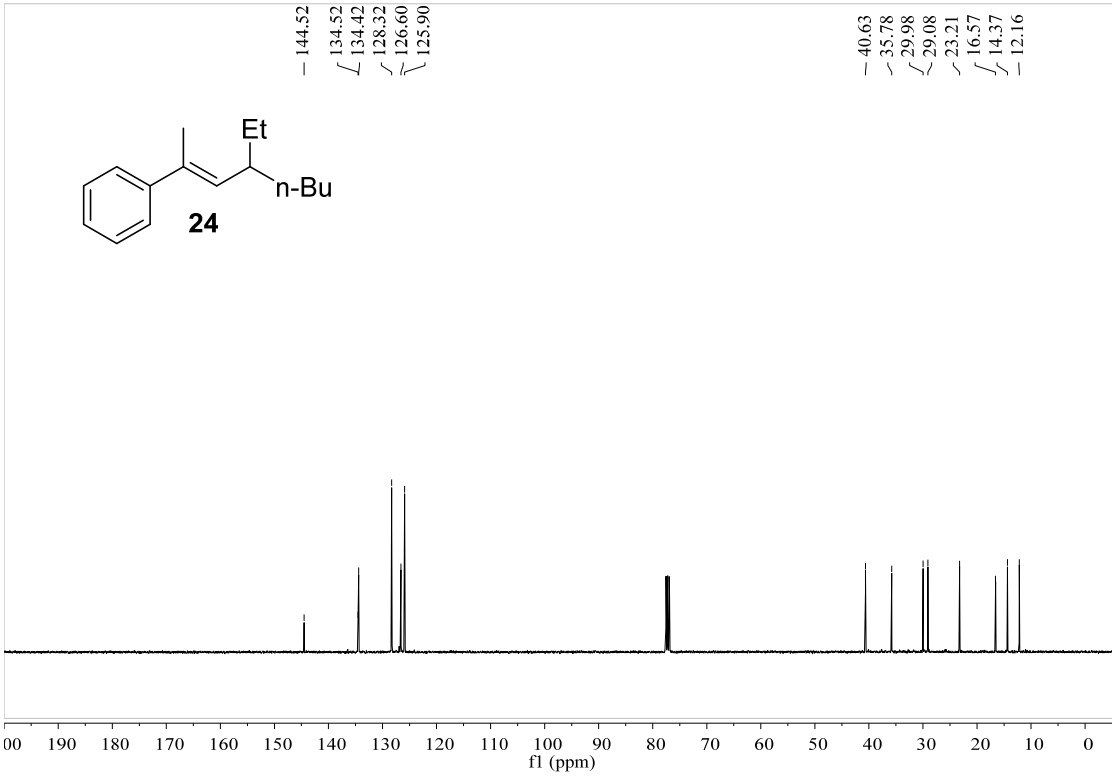



**Figure S88.** $^{13}$C NMR spectrum of compound **24**, related to **Figure 1.**

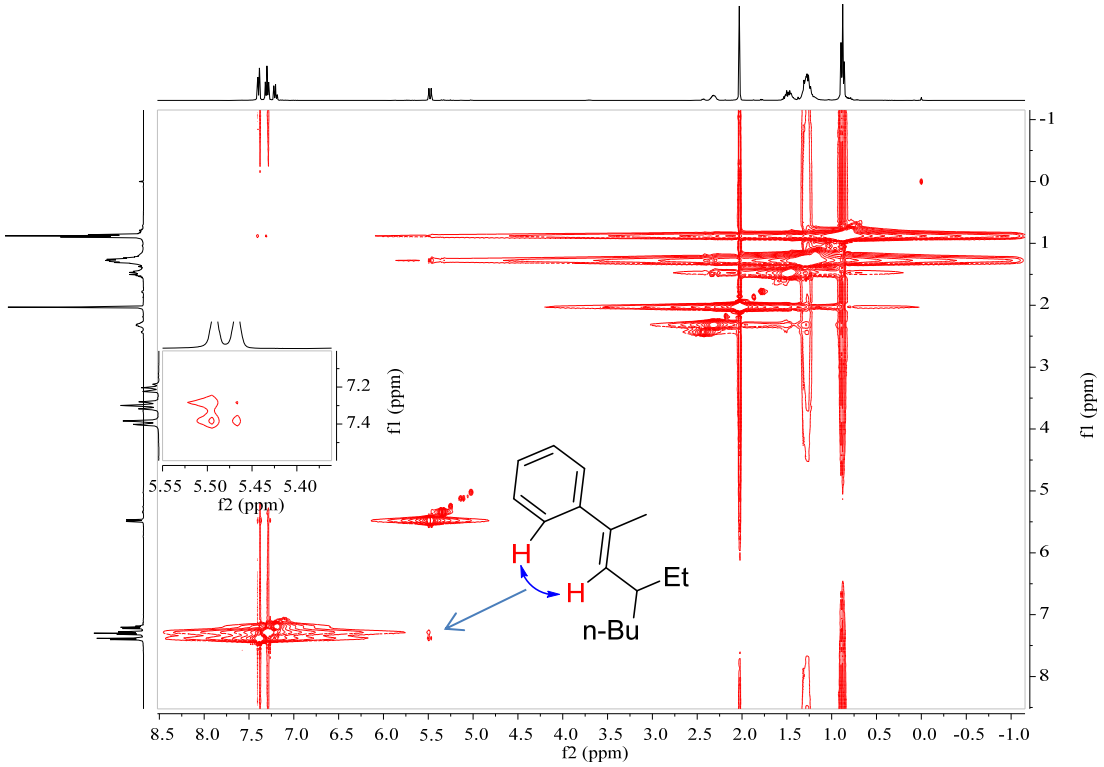



**Figure S89.** NOE spectrum of compound **24**, related to **Figure 1.**

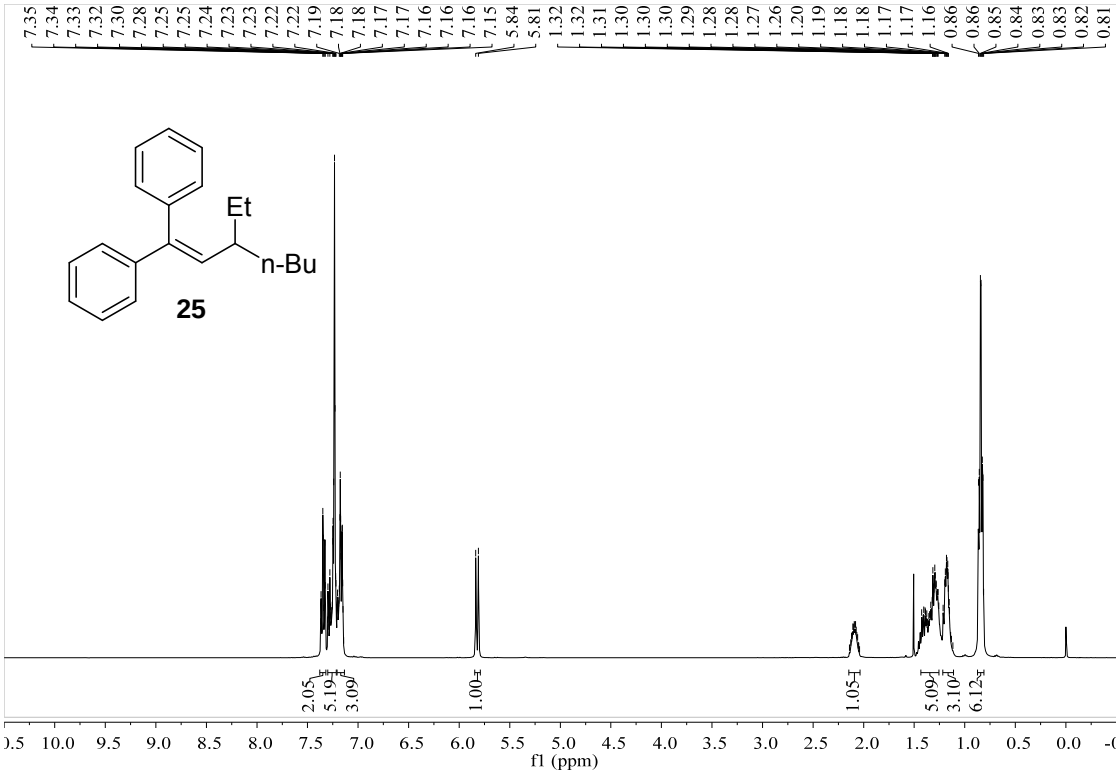



**Figure S90.** $^{1}$H NMR spectrum of compound **25**, related to **Figure 1.**

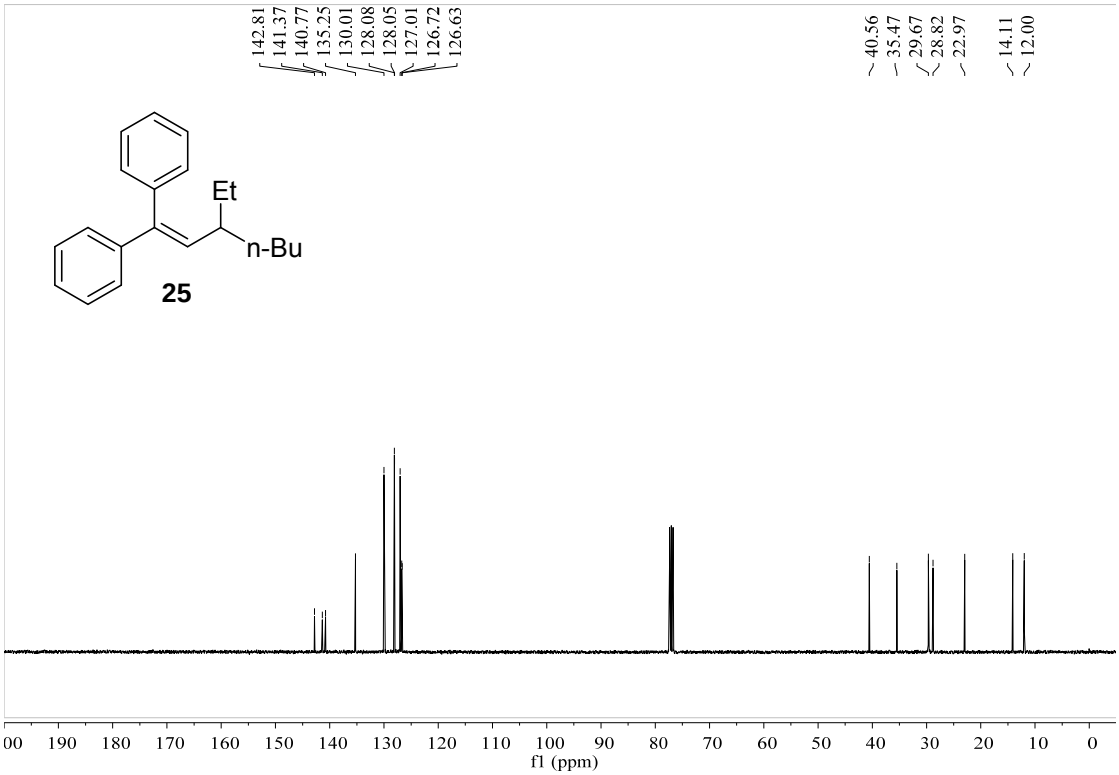



**Figure S91.** $^{13}$C NMR spectrum of compound **25**, related to **Figure 1.**

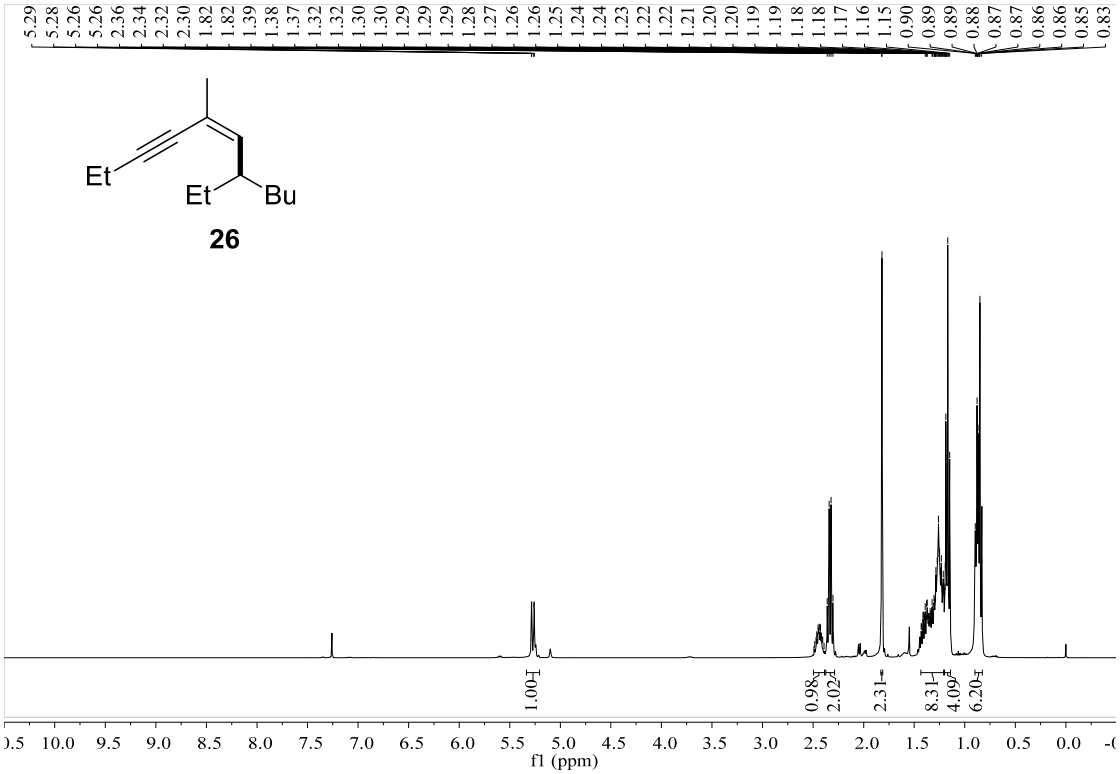



**Figure S92.** $^{1}$H NMR spectrum of compound **26**, related to **Figure 1.**

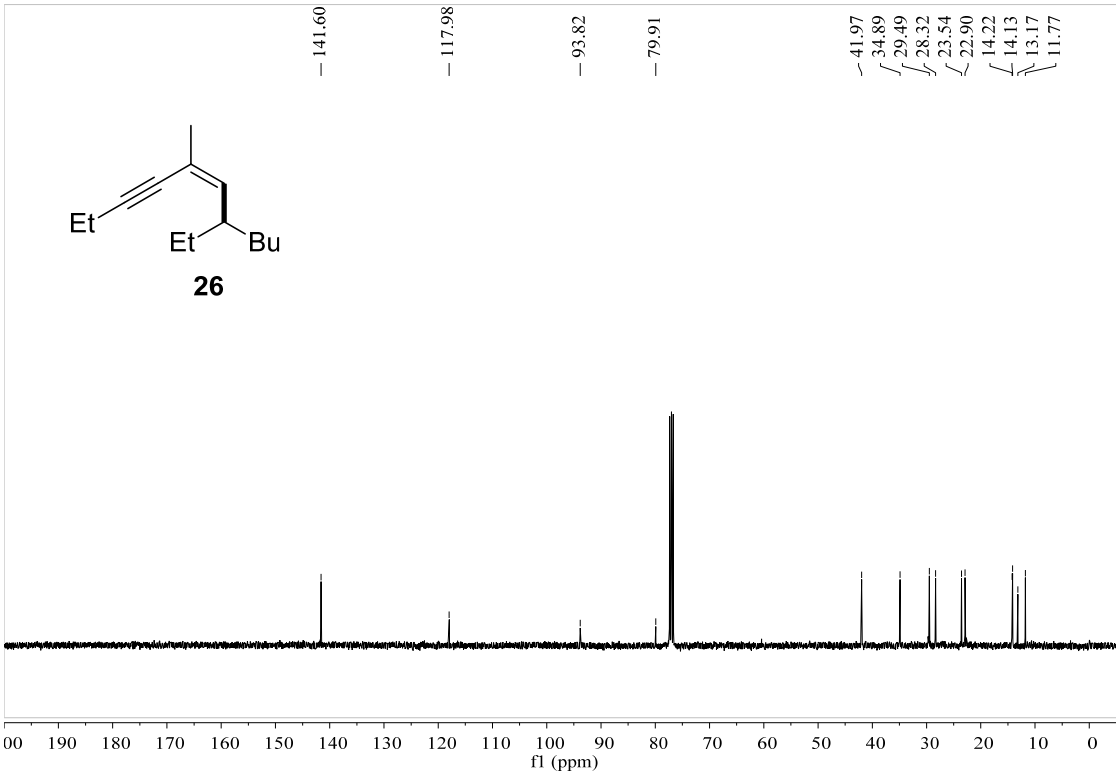



**Figure S93.** $^{13}$C NMR spectrum of compound **26**, related to **Figure 1.**

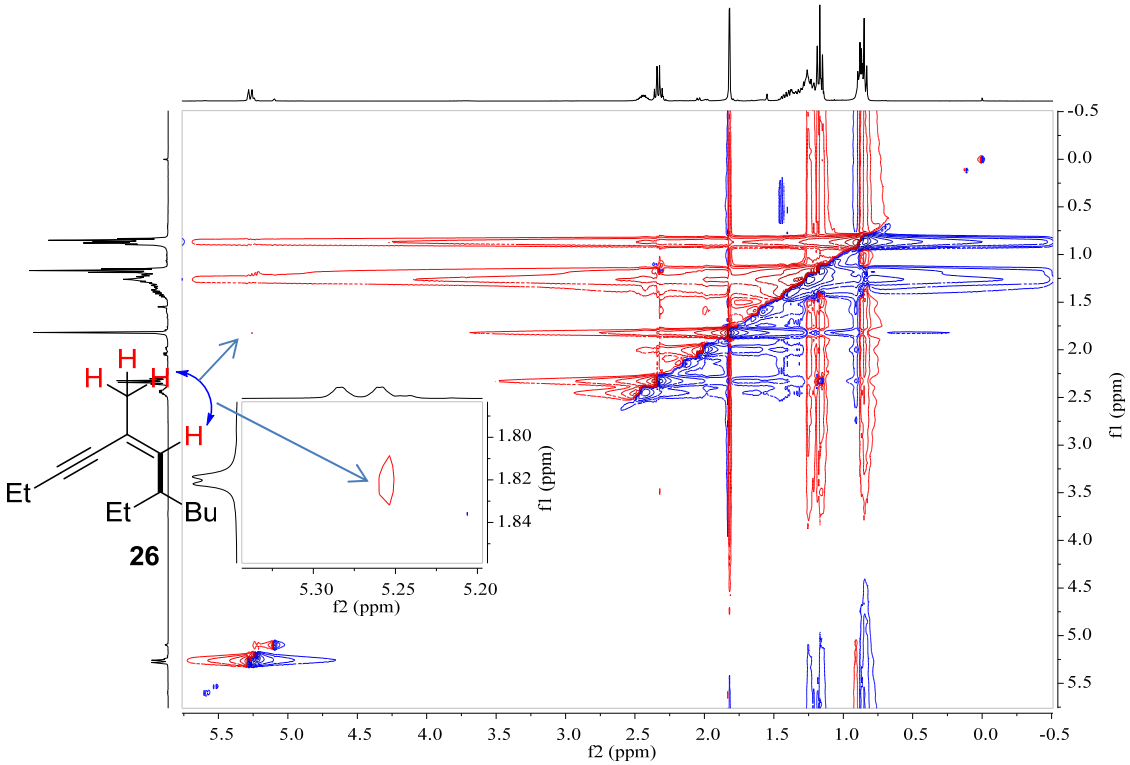



**Figure S94.** NOE spectrum of compound **26**, related to **Figure 1.**

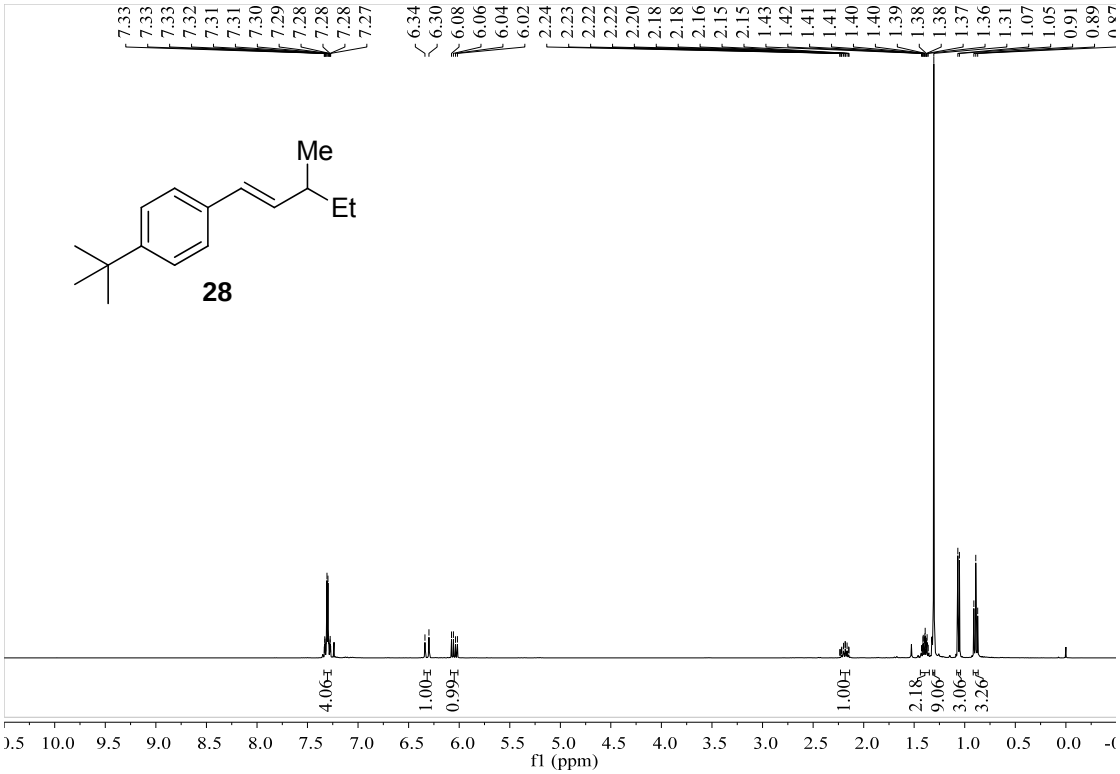



**Figure S95.** $^{1}$H NMR spectrum of compound **28**, related to **Figure 2.**

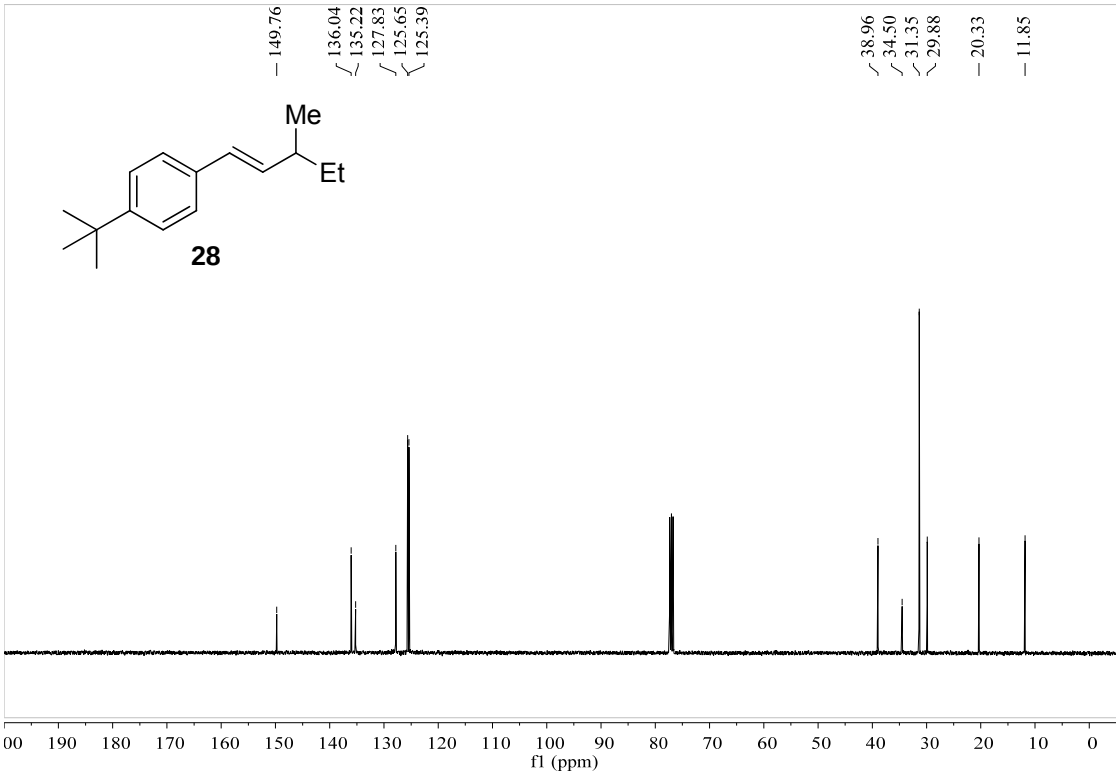



**Figure S96.** $^{13}$C NMR spectrum of compound **28**, related to **Figure 2.**

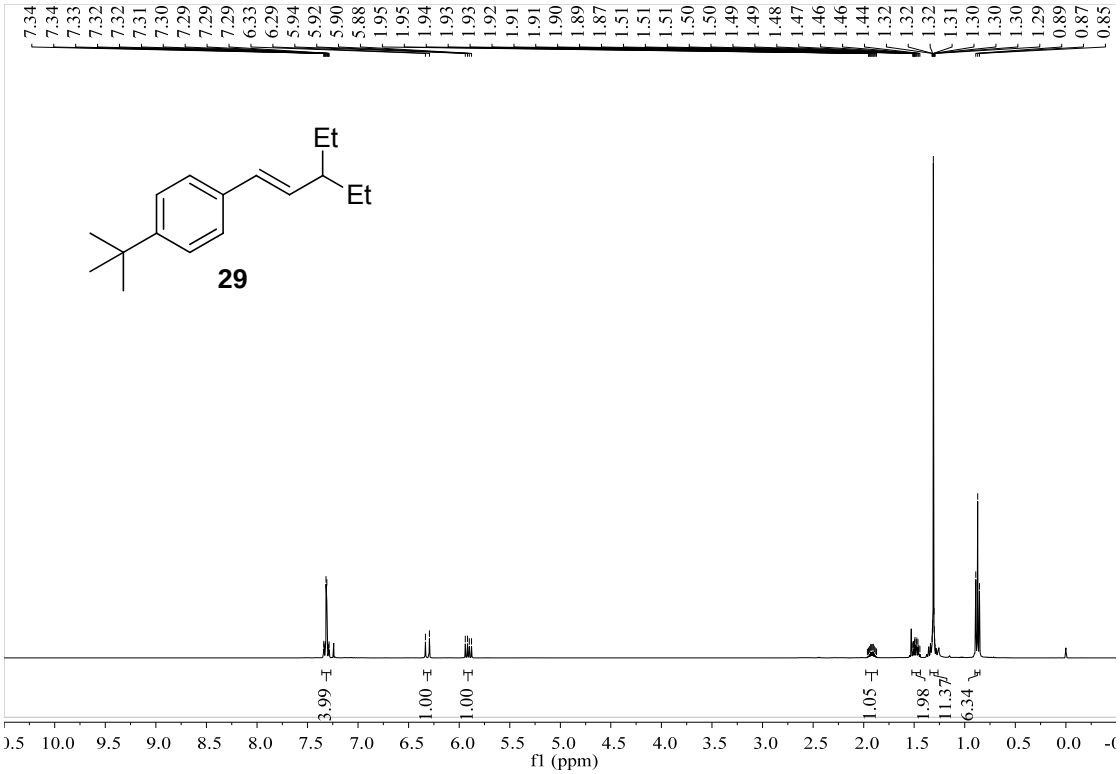



**Figure S97.** $^{1}$H NMR spectrum of compound **29**, related to **Figure 2.**

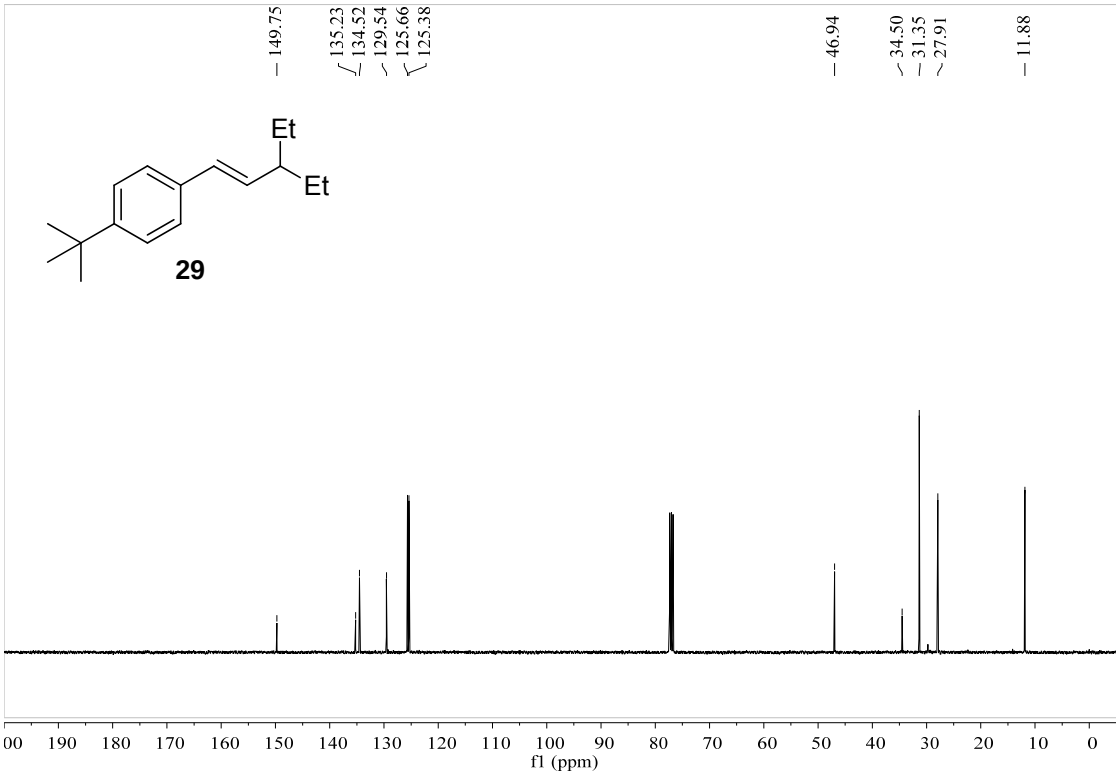



**Figure S98.** $^{13}$C NMR spectrum of compound **29**, related to **Figure 2.**

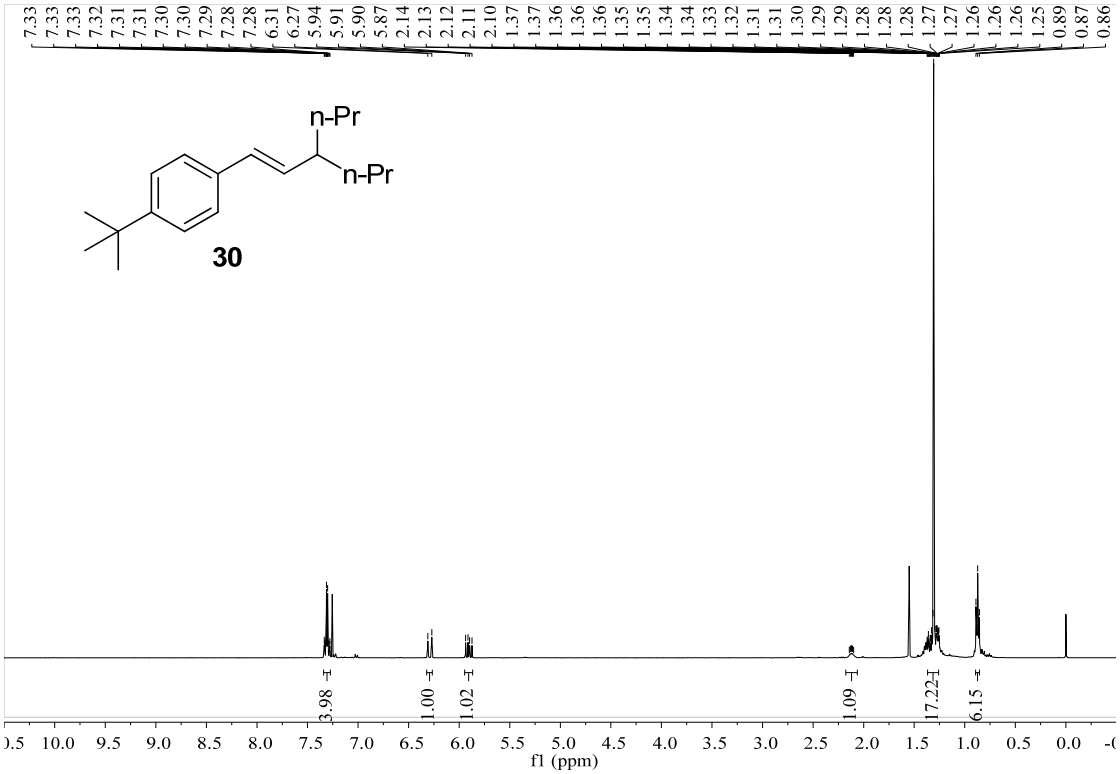



**Figure S99.** $^{1}$H NMR spectrum of compound **30**, related to **Figure 2.**

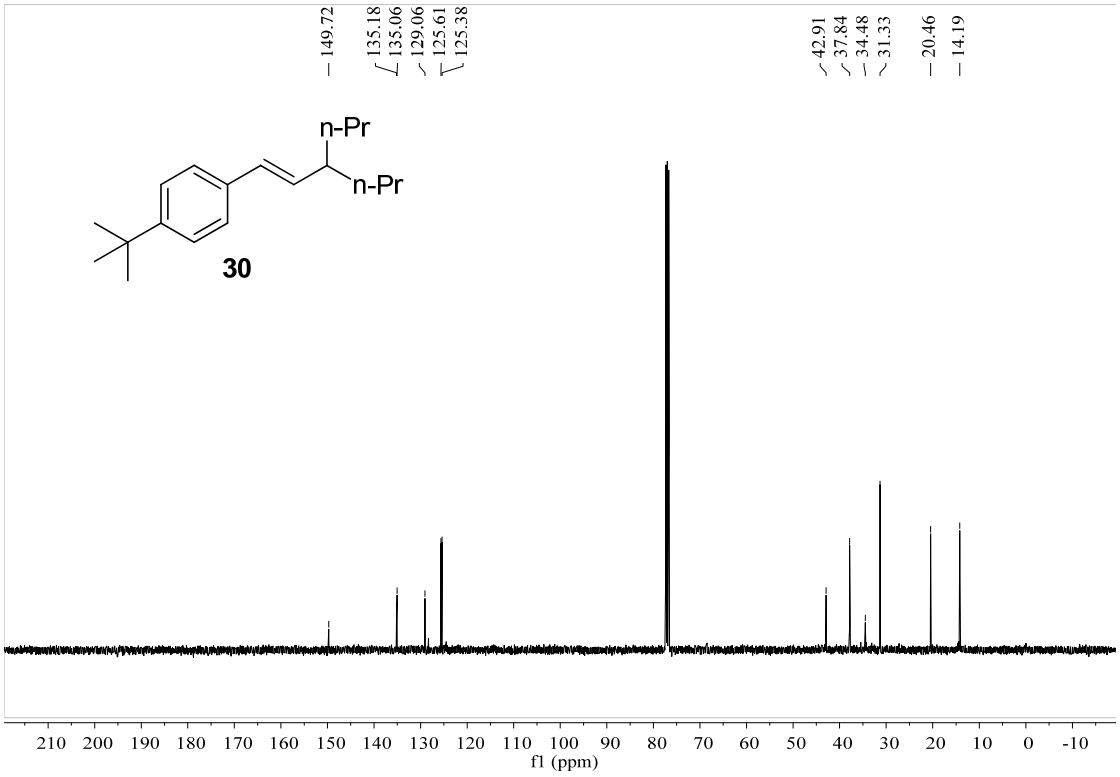



**Figure S100.** $^{13}$C NMR spectrum of compound **30**, related to **Figure 2.**

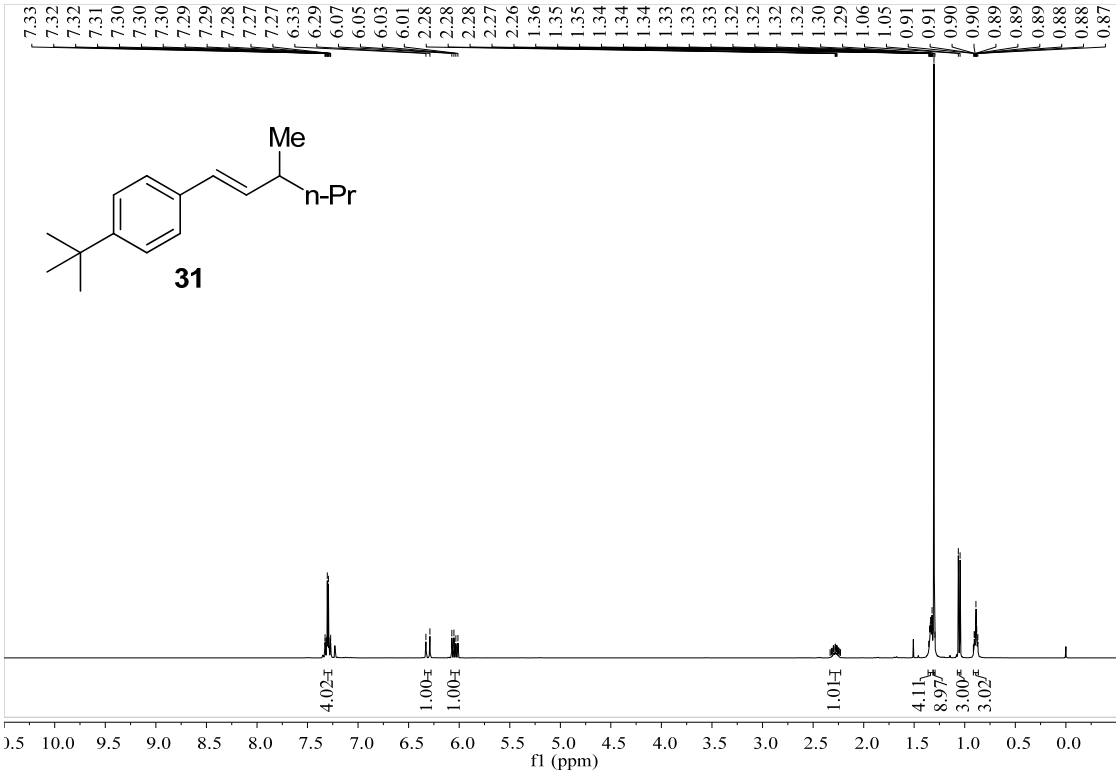



**Figure S101.** $^{1}$H NMR spectrum of compound **31**, related to **Figure 2.**

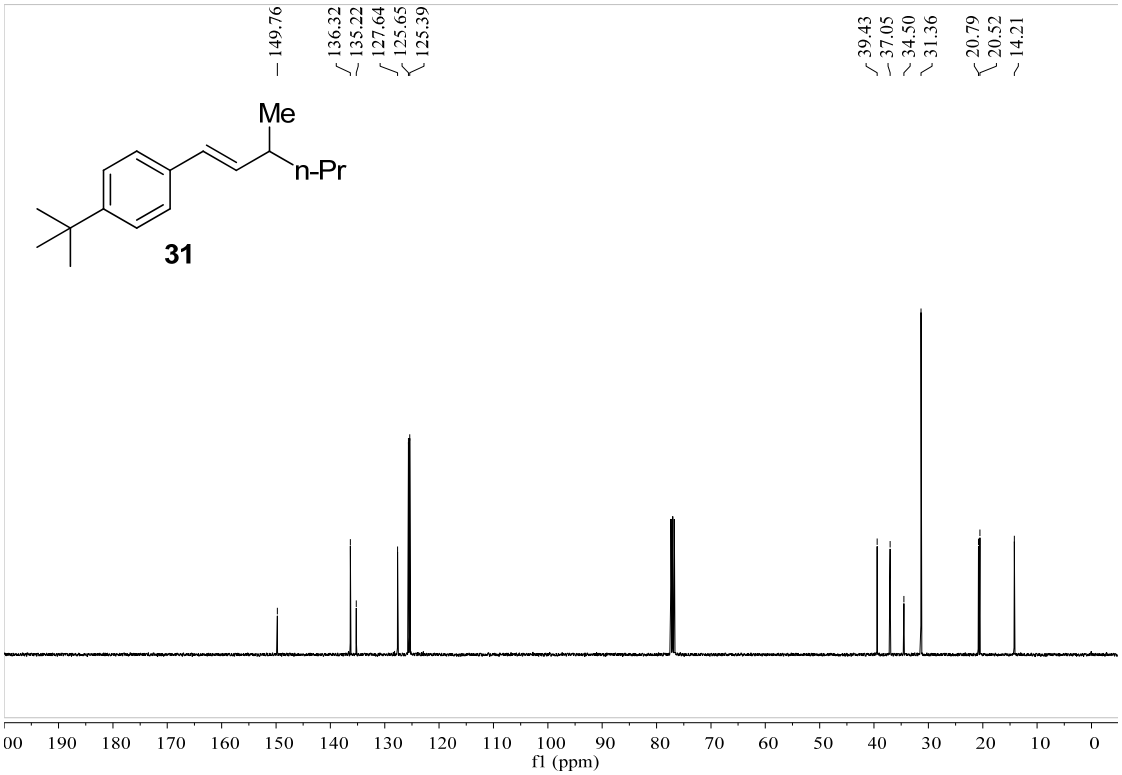



**Figure S102.** $^{13}$C NMR spectrum of compound **31**, related to **Figure 2.**

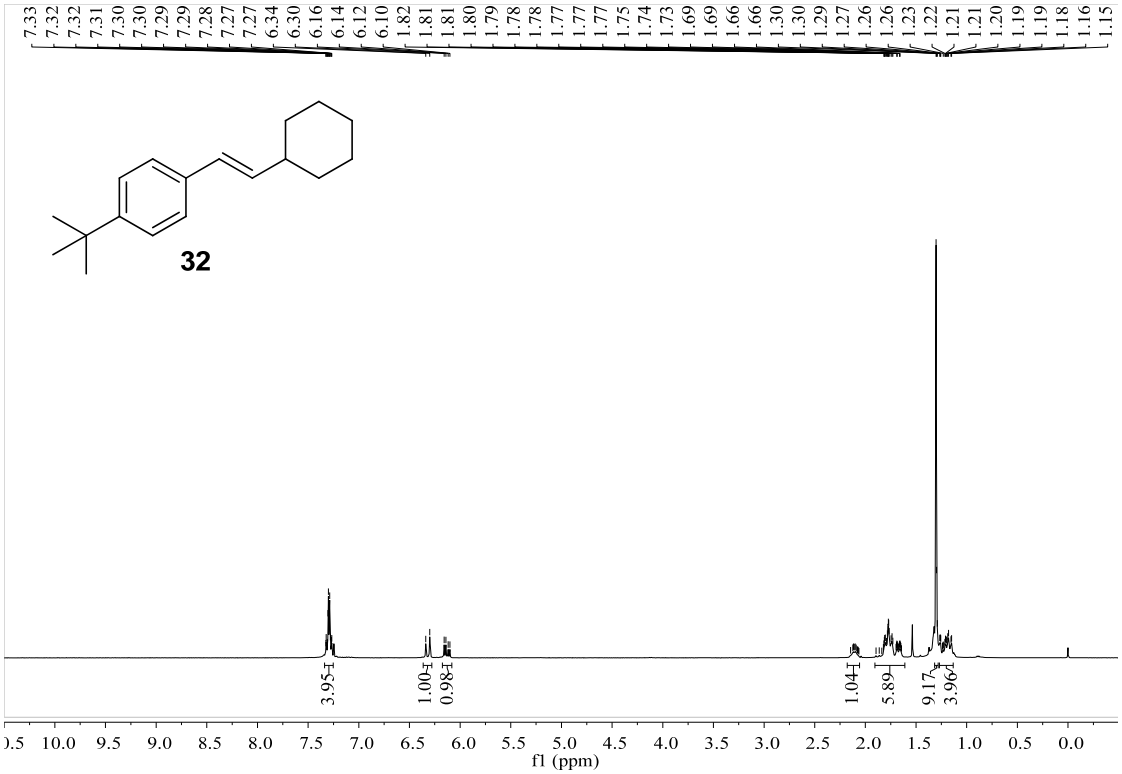



**Figure S103.** $^{1}$H NMR spectrum of compound **32**, related to **Figure 2.**

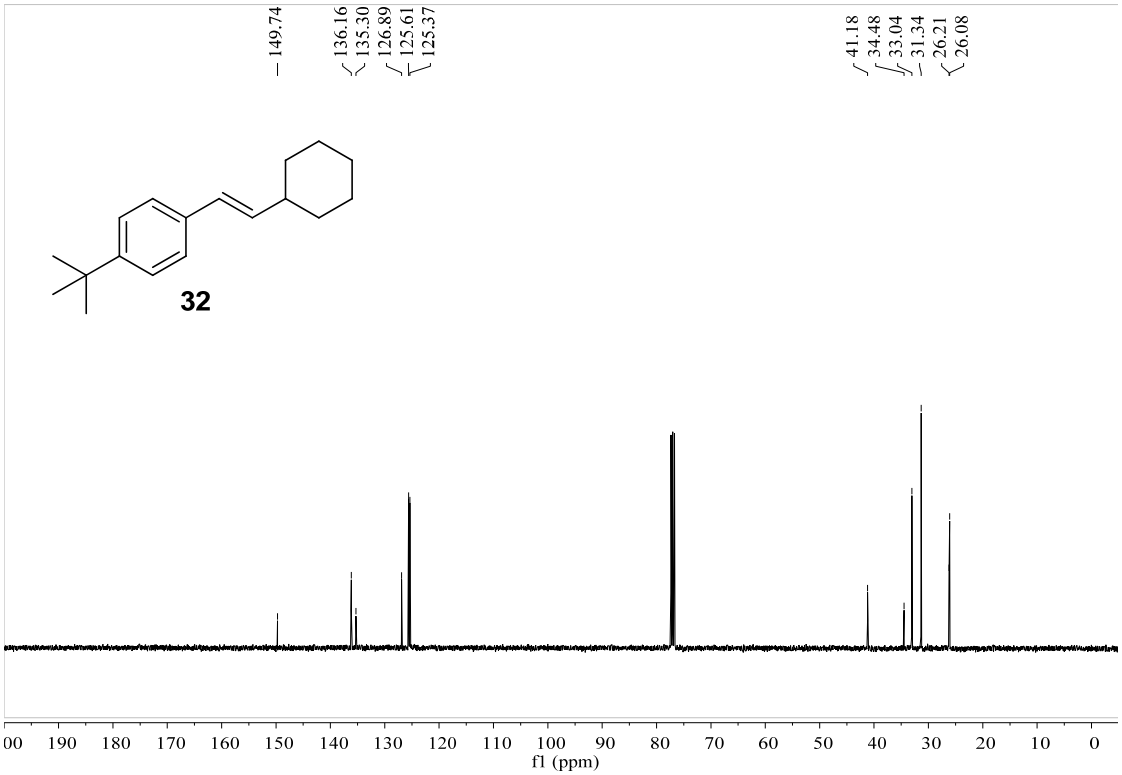



**Figure S104.** $^{13}$C NMR spectrum of compound **32**, related to **Figure 2.**

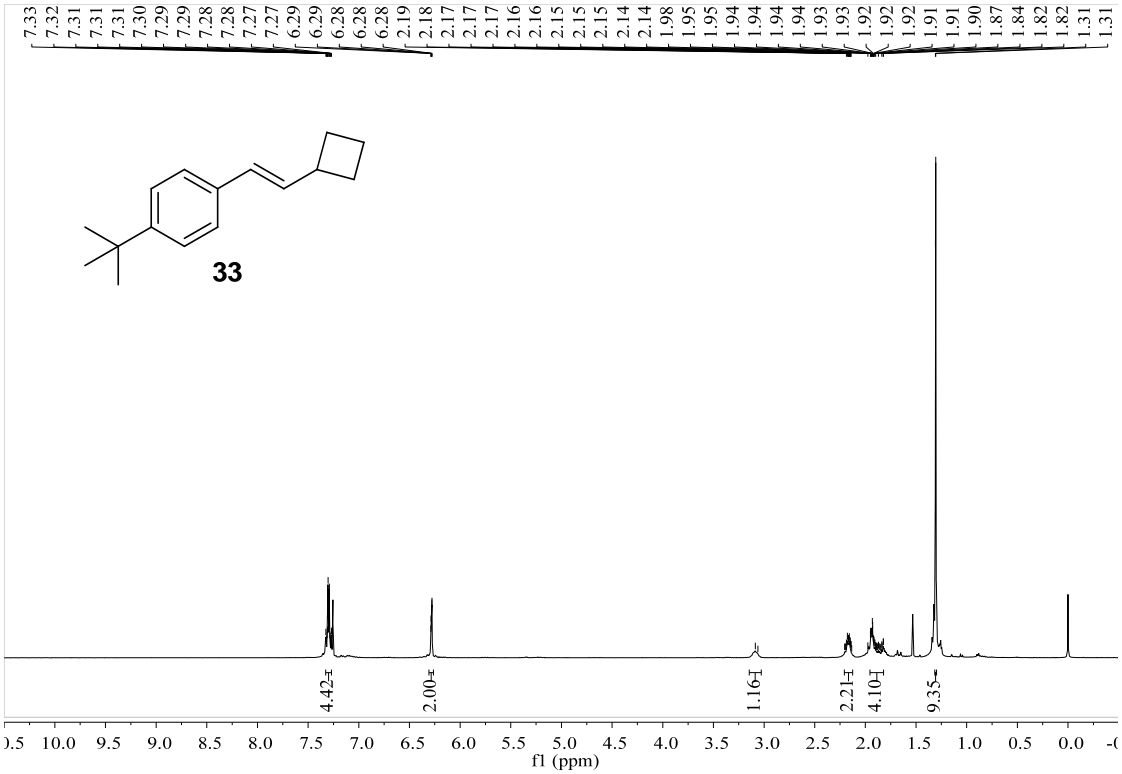



**Figure S105.** $^{1}$H NMR spectrum of compound **33**, related to **Figure 2.**

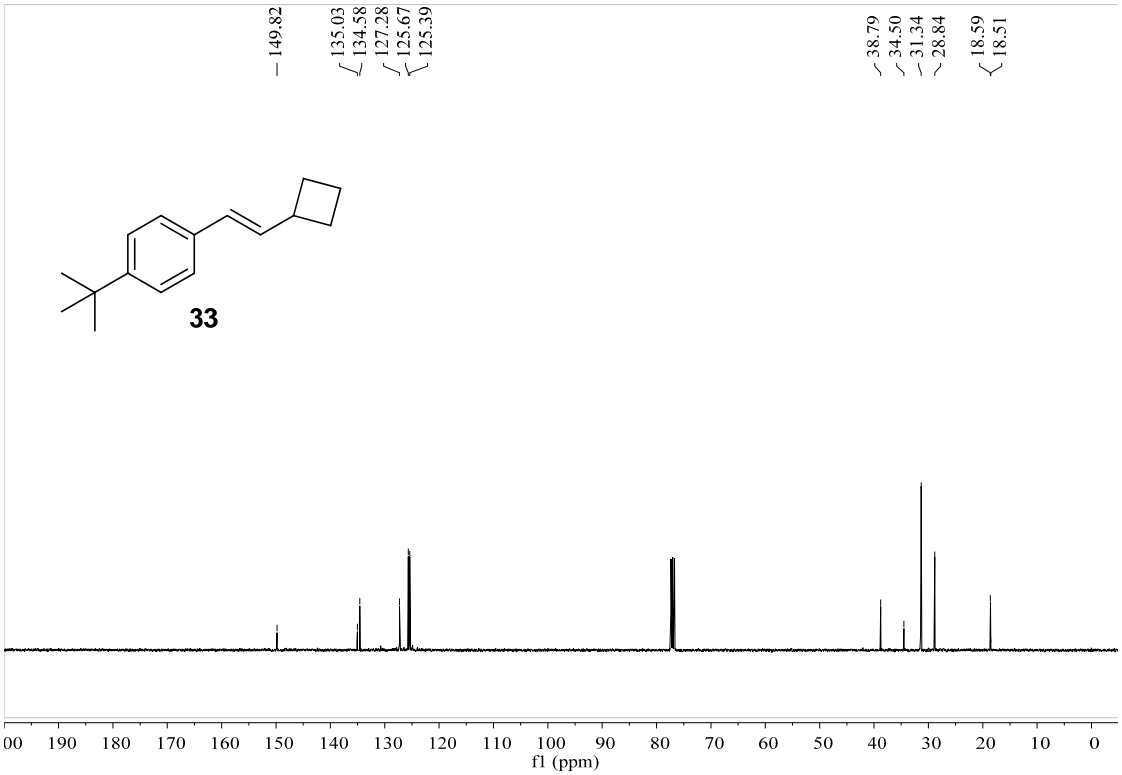



**Figure S106.** $^{13}$C NMR spectrum of compound **33**, related to **Figure 2.**

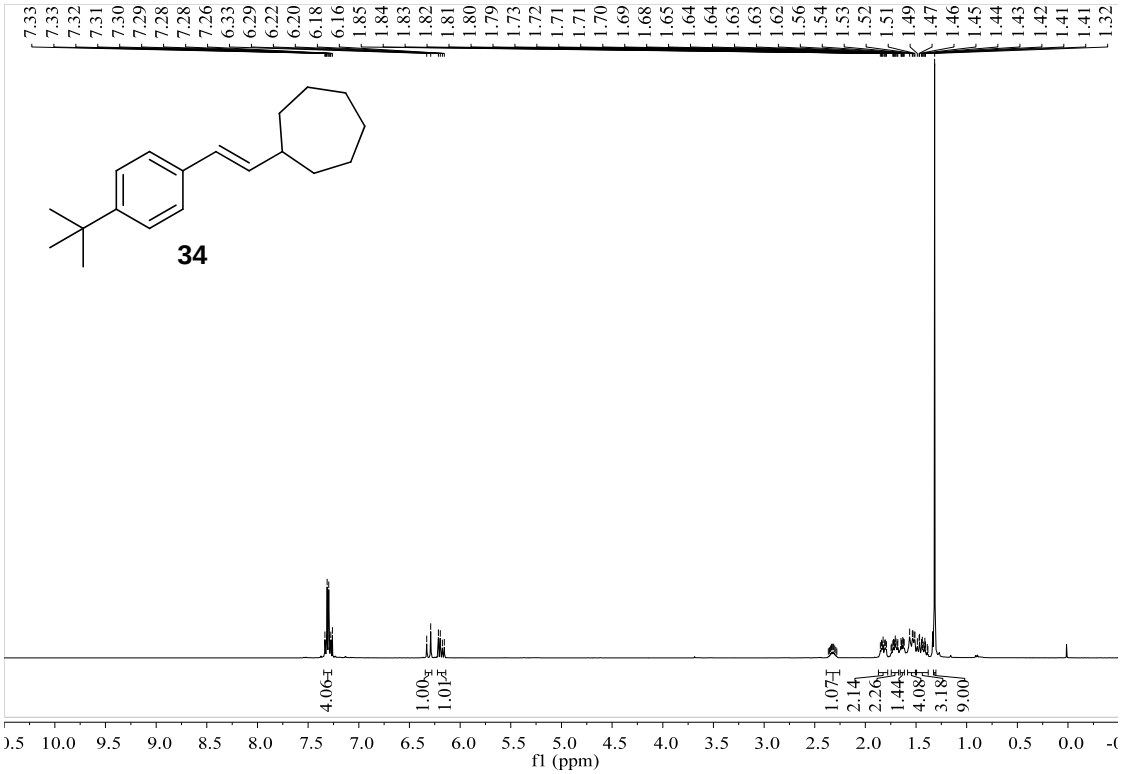



**Figure S107.** $^{1}$H NMR spectrum of compound **34**, related to **Figure 2.**

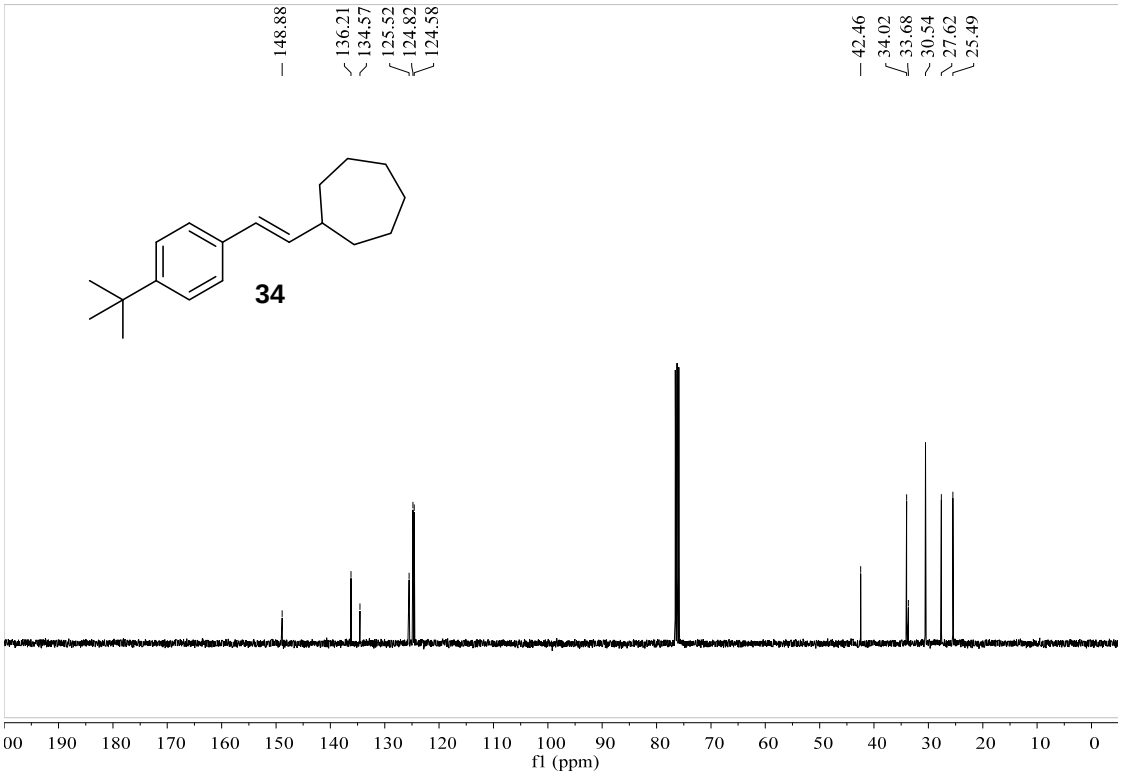



**Figure S108.** $^{13}$C NMR spectrum of compound **34**, related to **Figure 2.**

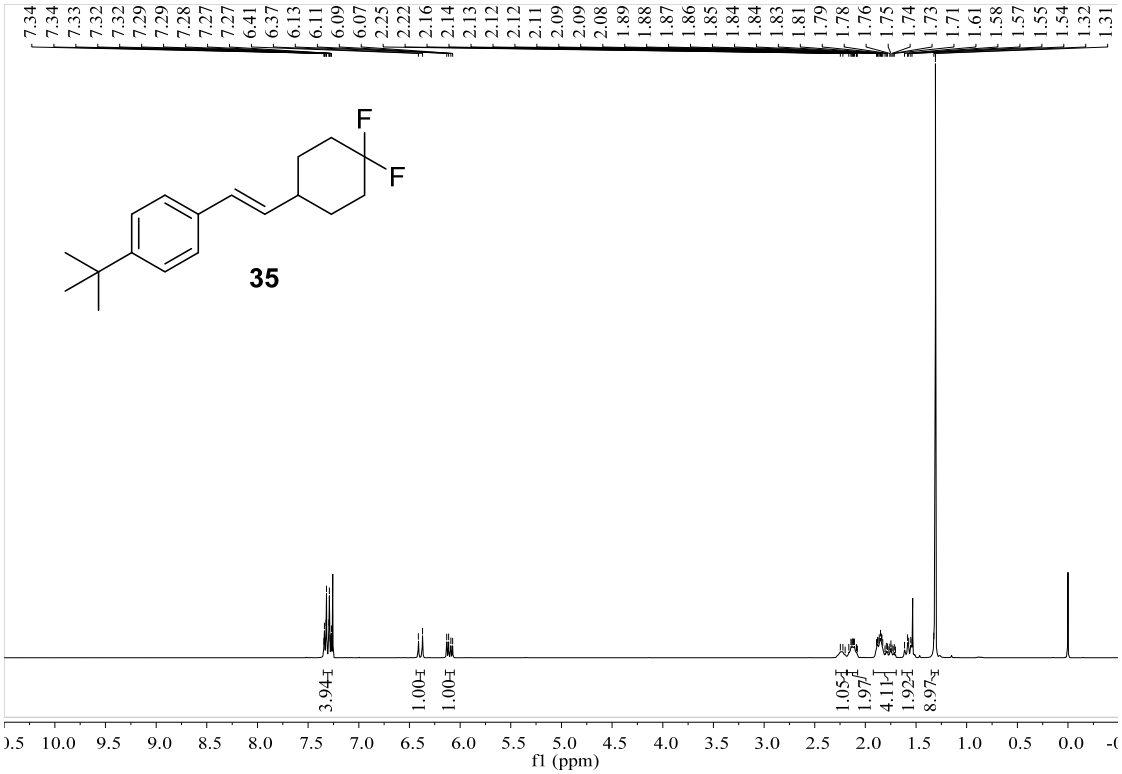



**Figure S109.** $^{1}$H NMR spectrum of compound **35**, related to **Figure 2.**

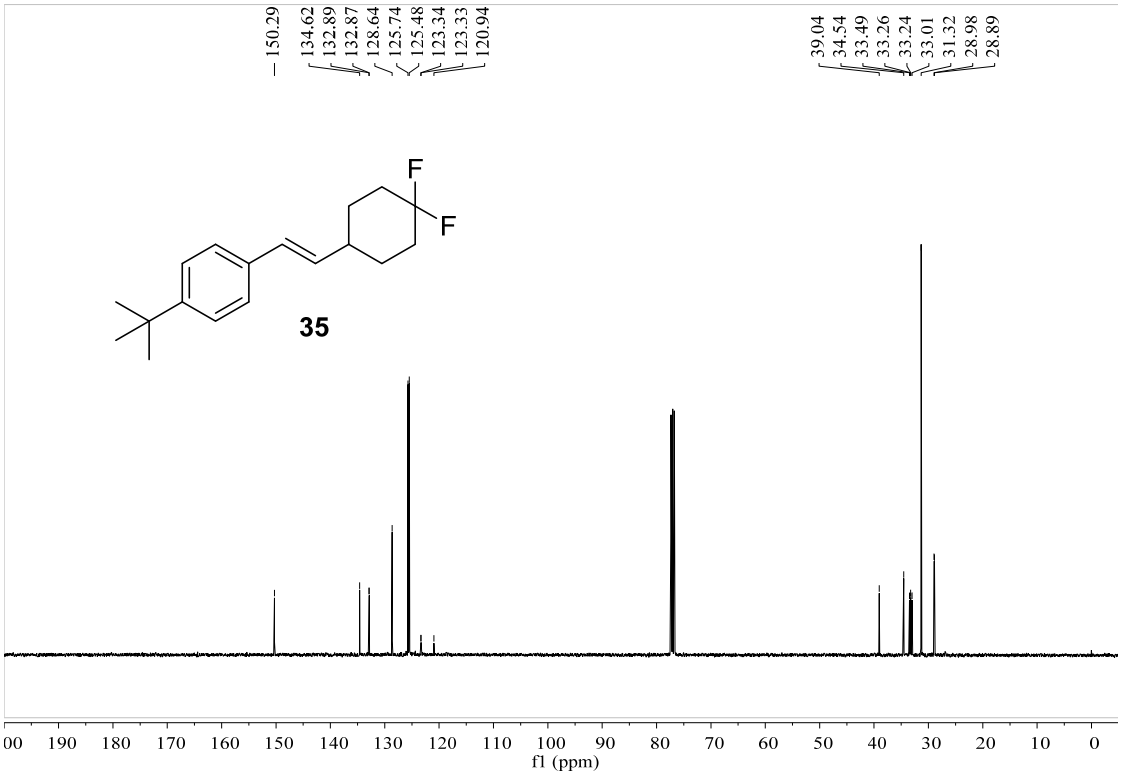



**Figure S110.** $^{13}$C NMR spectrum of compound **35**, related to **Figure 2.**

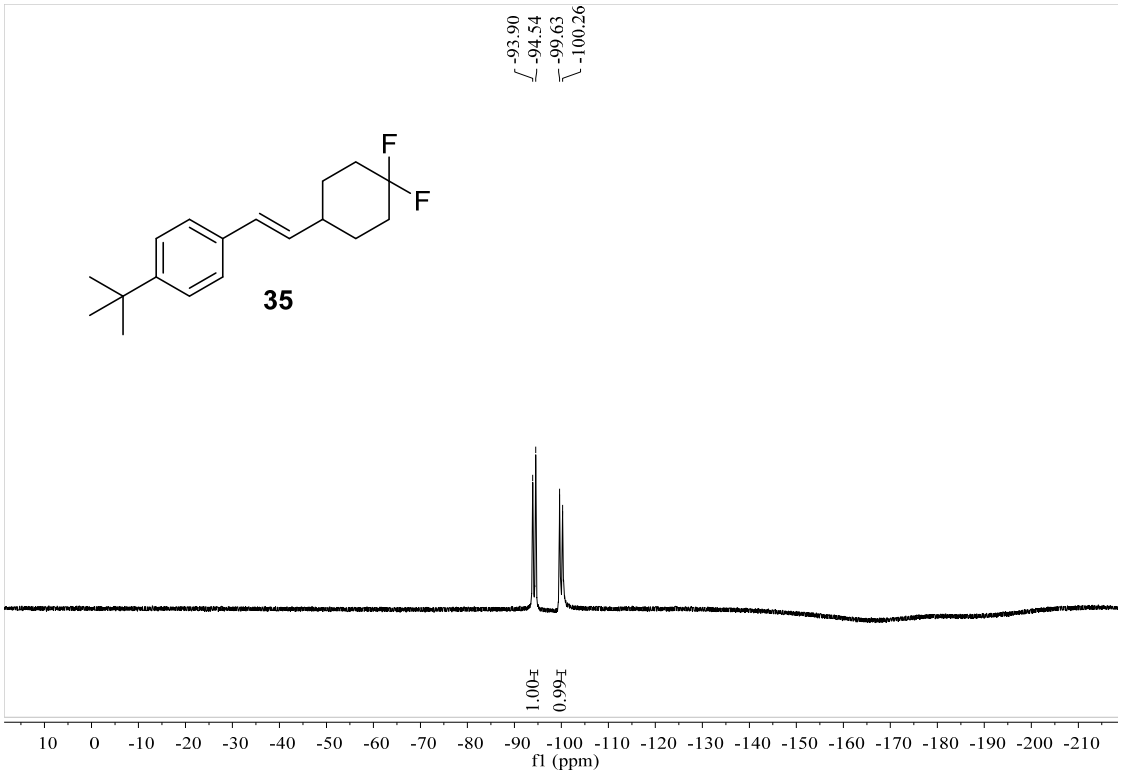



**Figure S111.** $^{19}F$ NMR spectrum of compound **35**, related to **Figure 2.**

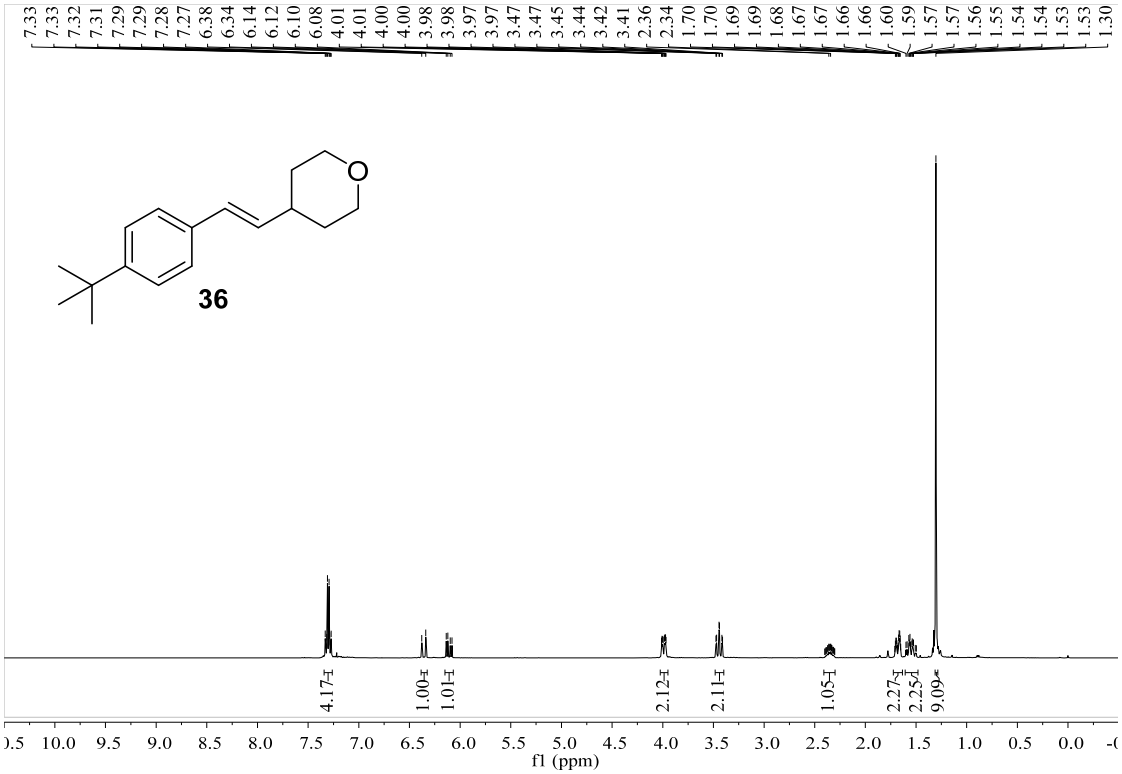



**Figure S112.** [1]H NMR spectrum of compound **36,** related to **Figure 2.**

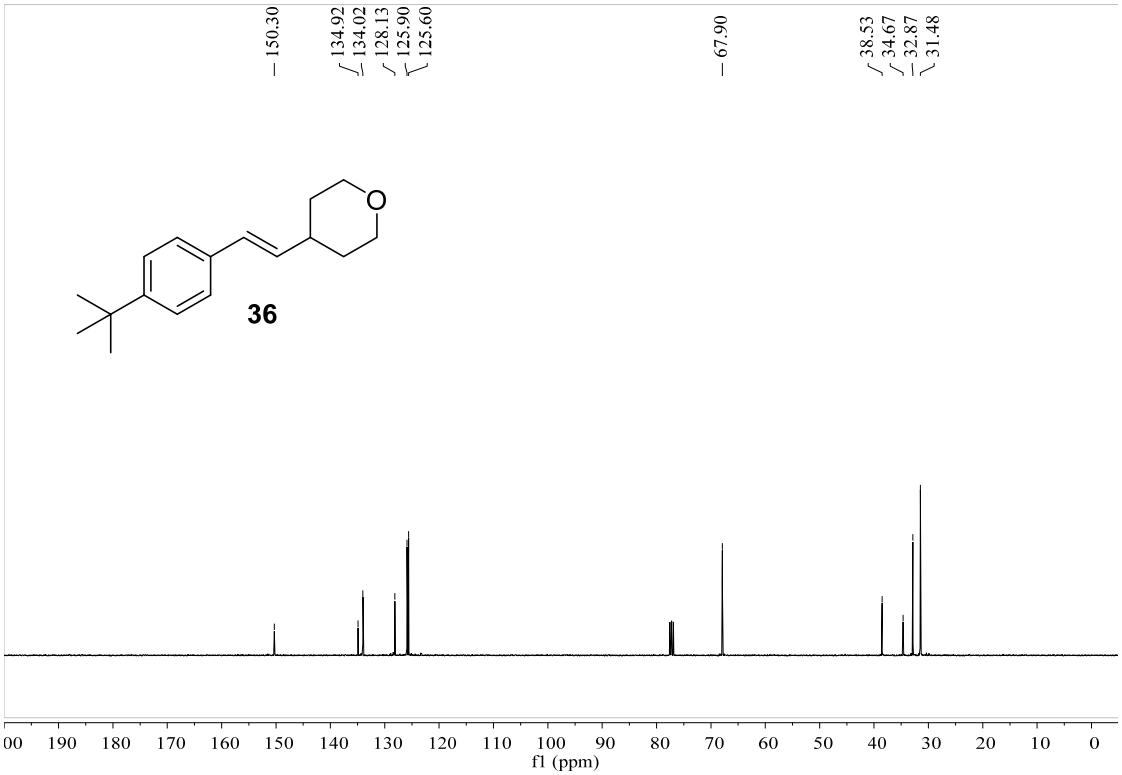



**Figure S113.** [13]C NMR spectrum of compound **36,** related to **Figure 2.**

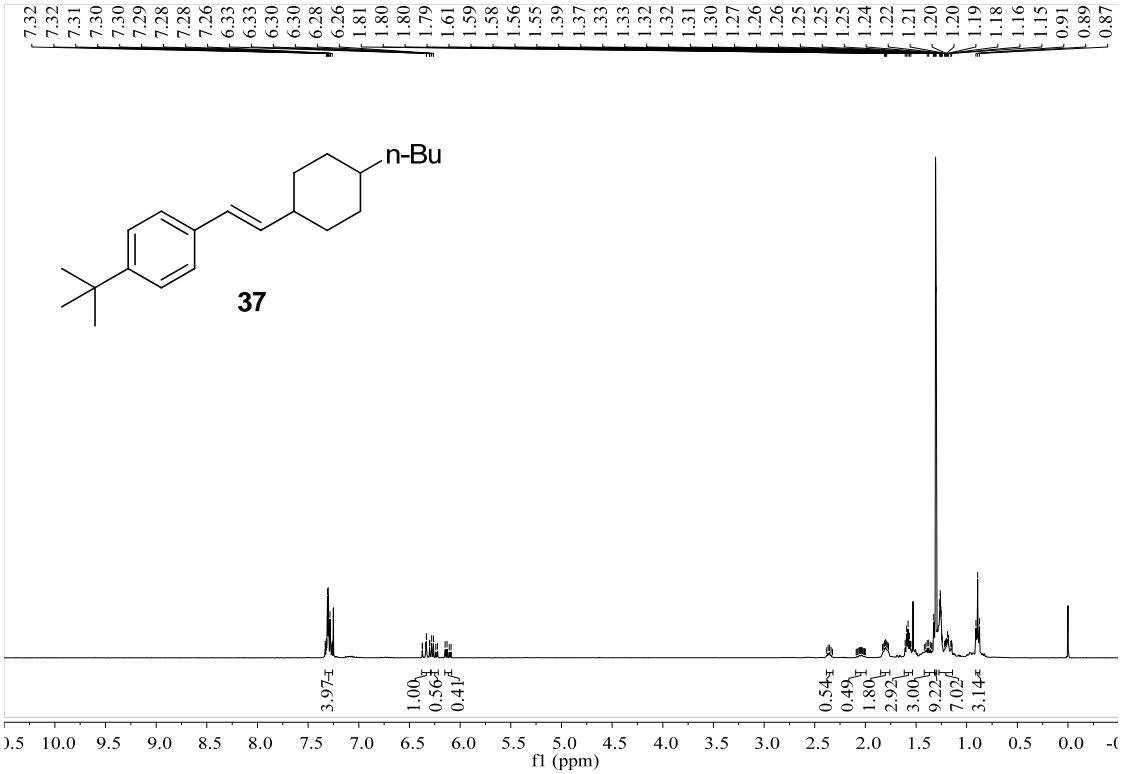



**Figure S114.** [1]H NMR spectrum of compound **37,** related to **Figure 2.**

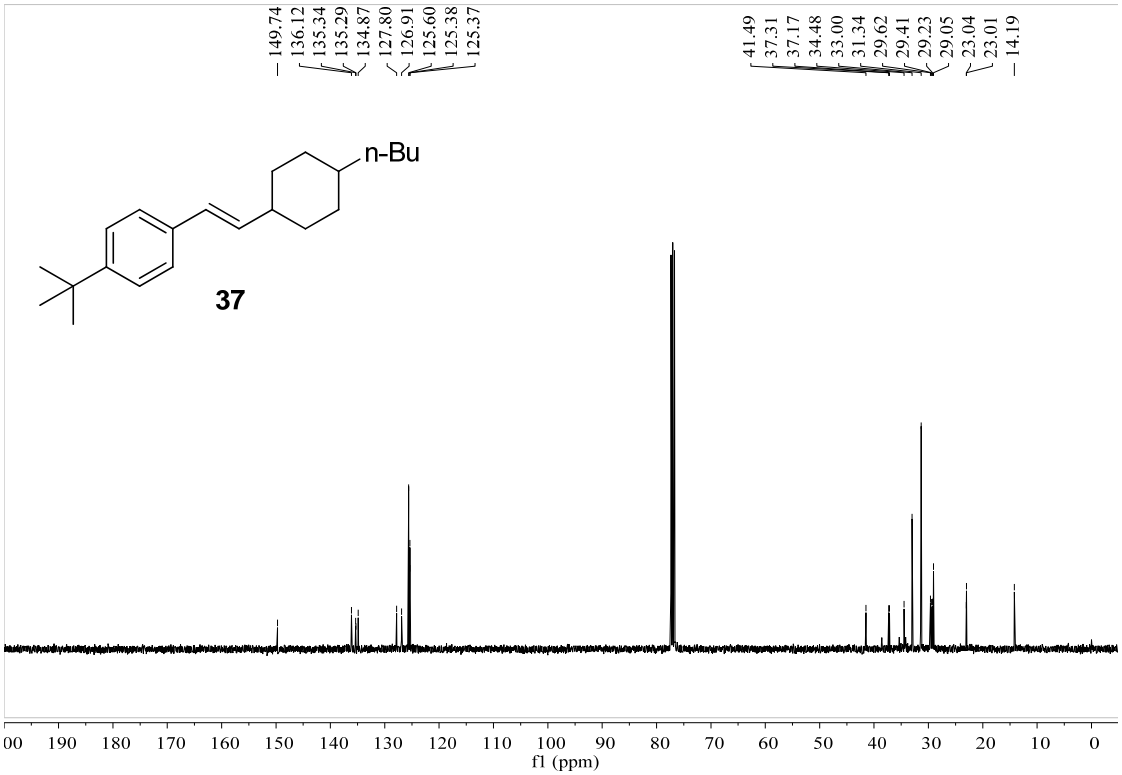



**Figure S115.** [13]C NMR spectrum of compound **37,** related to **Figure 2.**

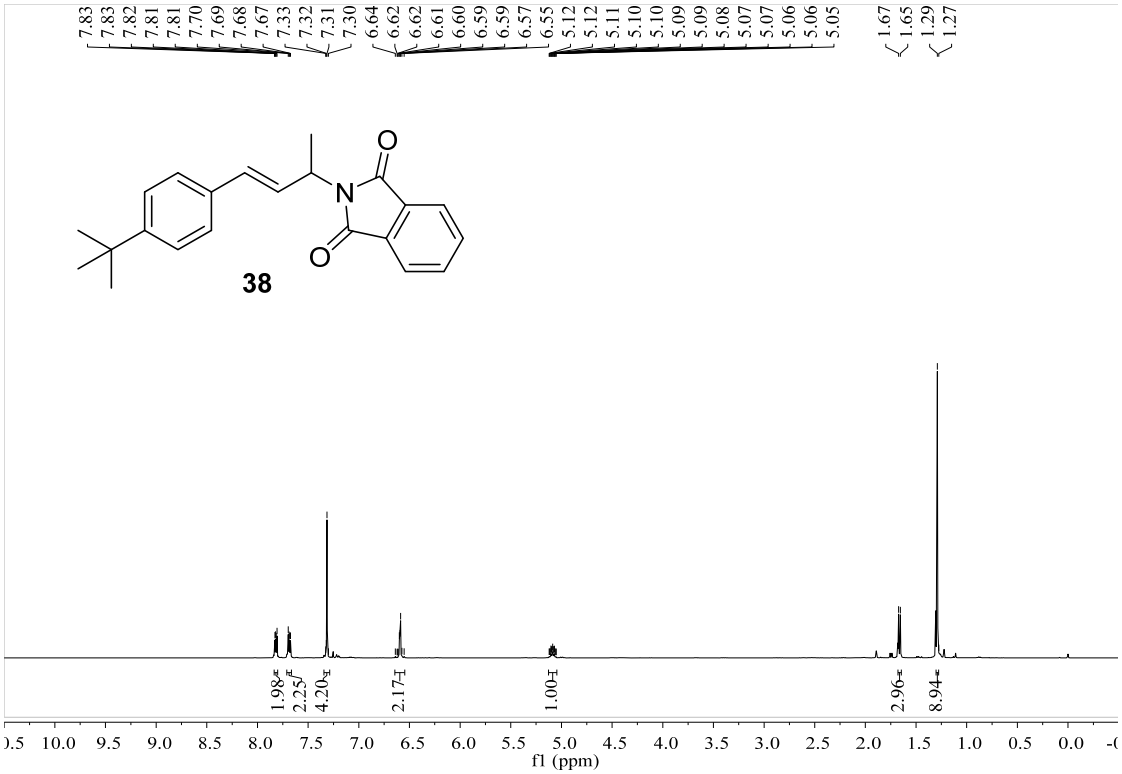



**Figure S116.** [1]H NMR spectrum of compound **38,** related to **Figure 2.**

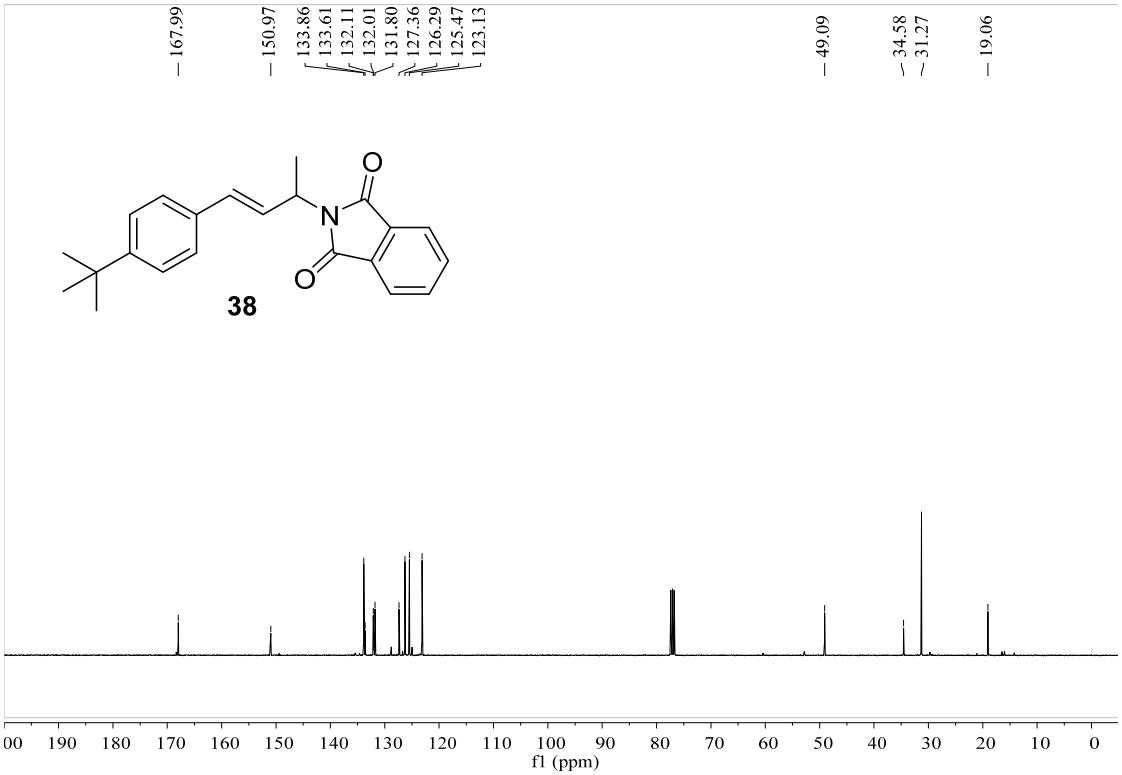



**Figure S117.** [13]C NMR spectrum of compound **38,** related to **Figure 2.**

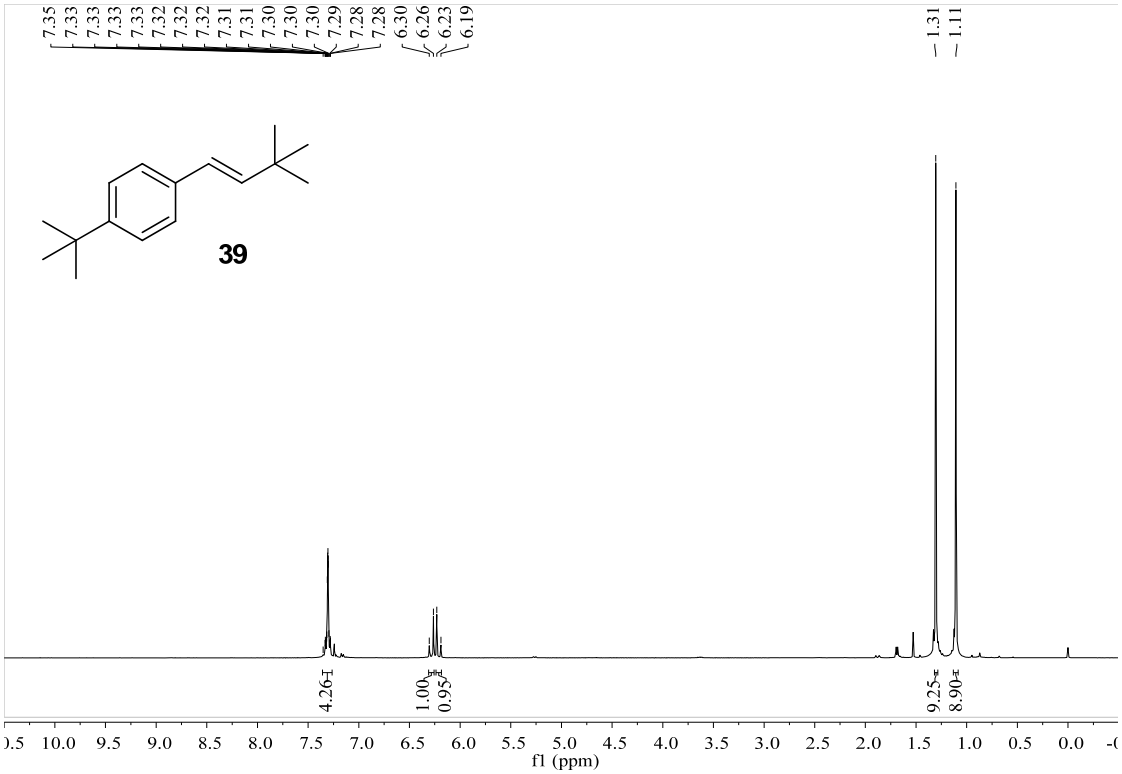



**Figure S118.** [1]H NMR spectrum of compound **39,** related to **Figure 2.**

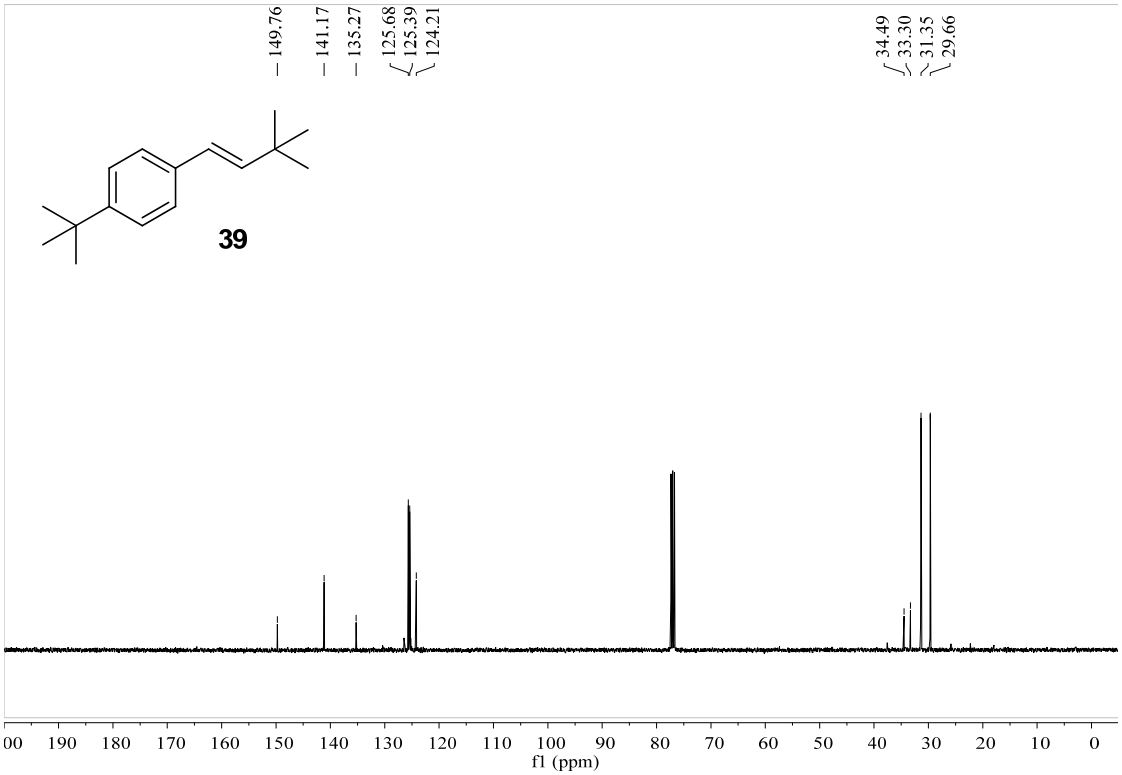



**Figure S119.** [13]C NMR spectrum of compound **39,** related to **Figure 2.**

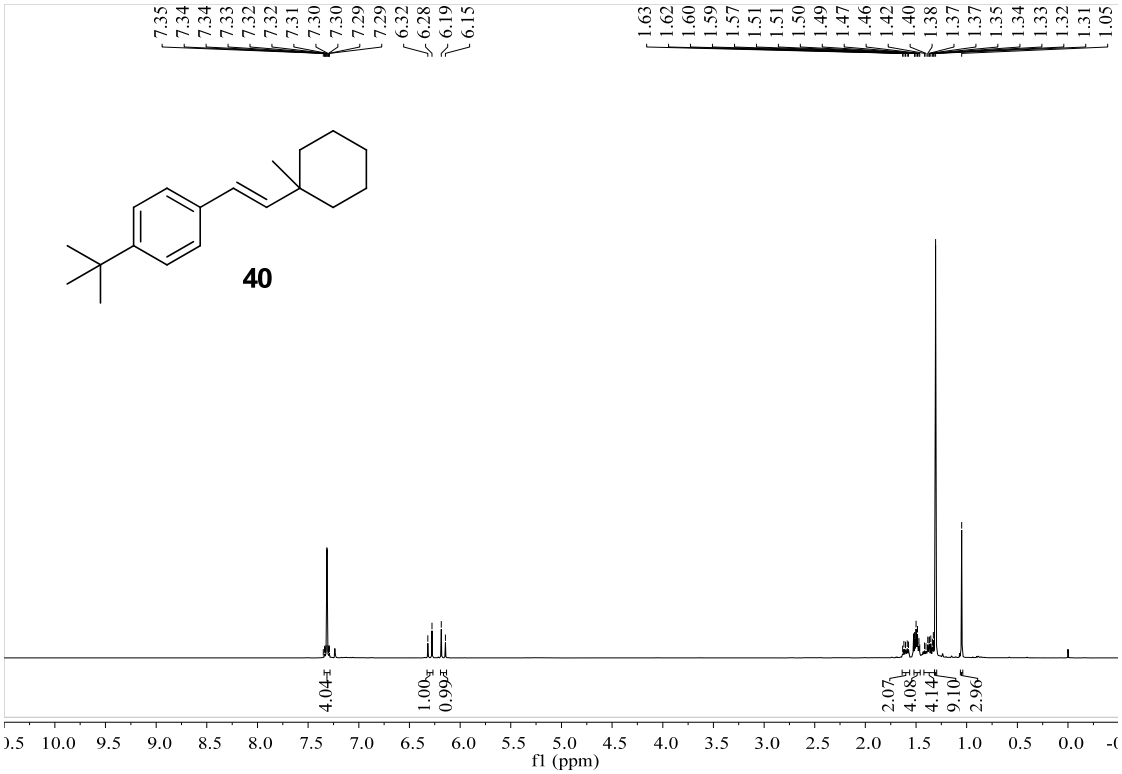



**Figure S120.** $^{1}$H NMR spectrum of compound **40,** related to **Figure 2.**

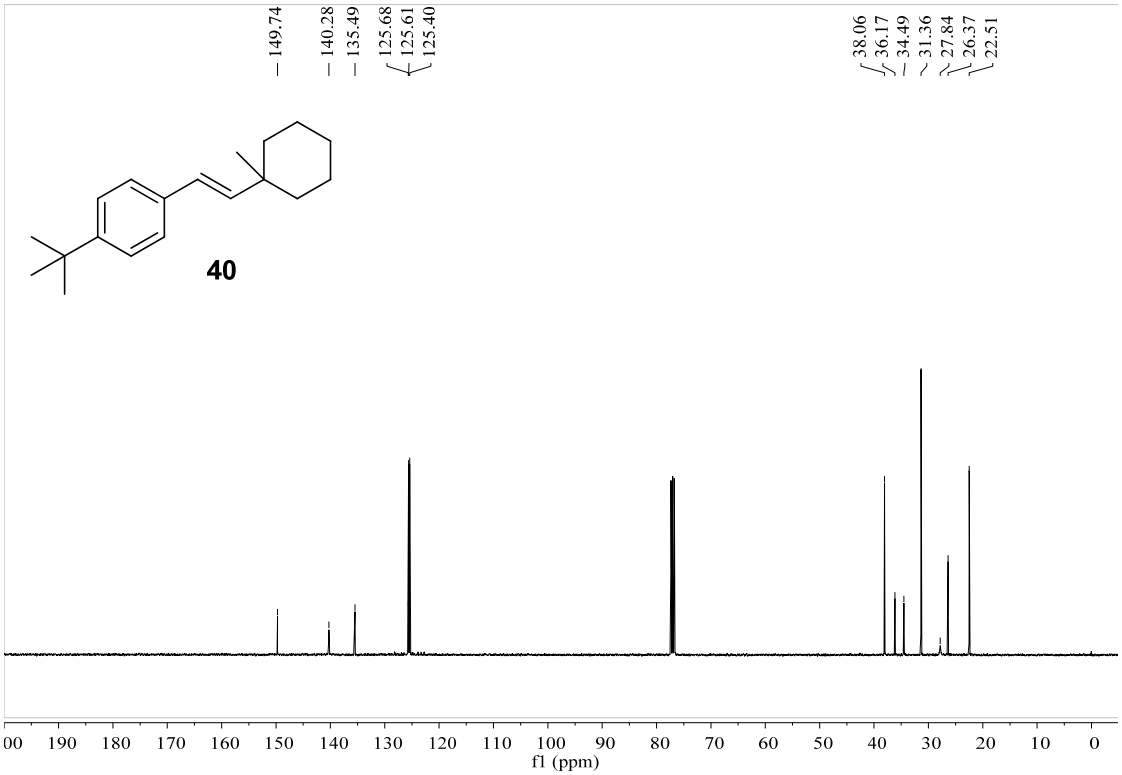



**Figure S121.** $^{13}$C NMR spectrum of compound **40,** related to **Figure 2.**

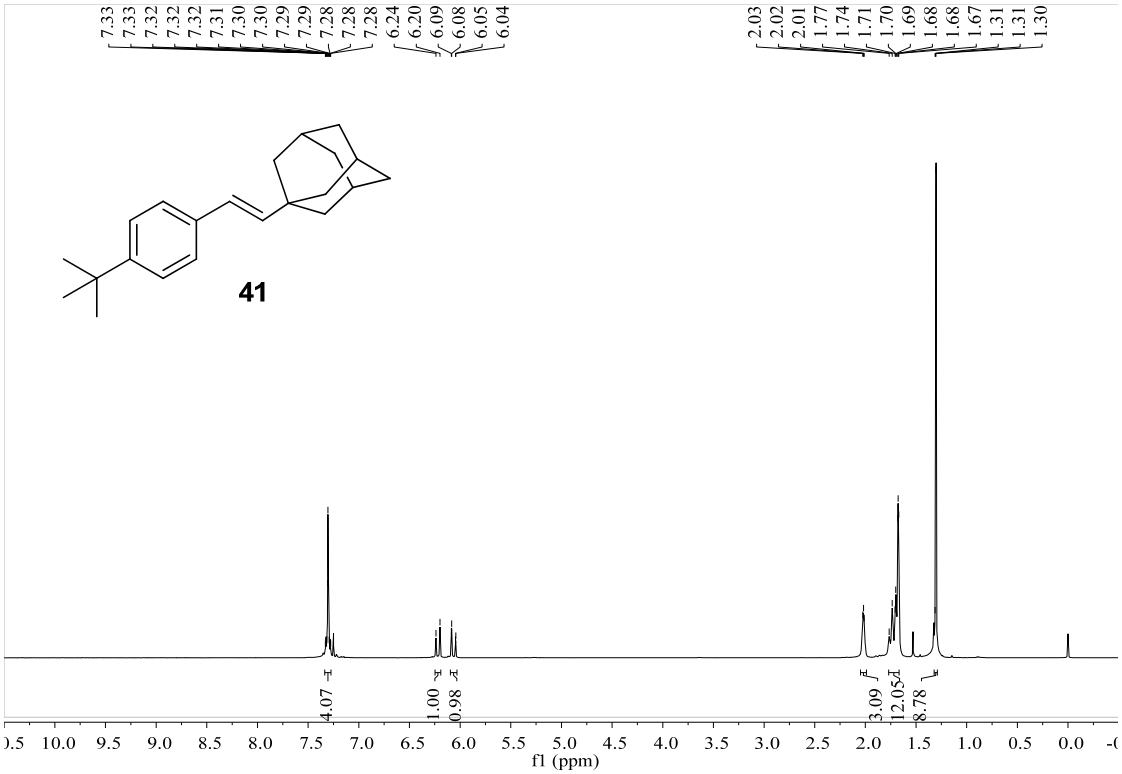



**Figure S122.** [1]H NMR spectrum of compound **41,** related to **Figure 2.**

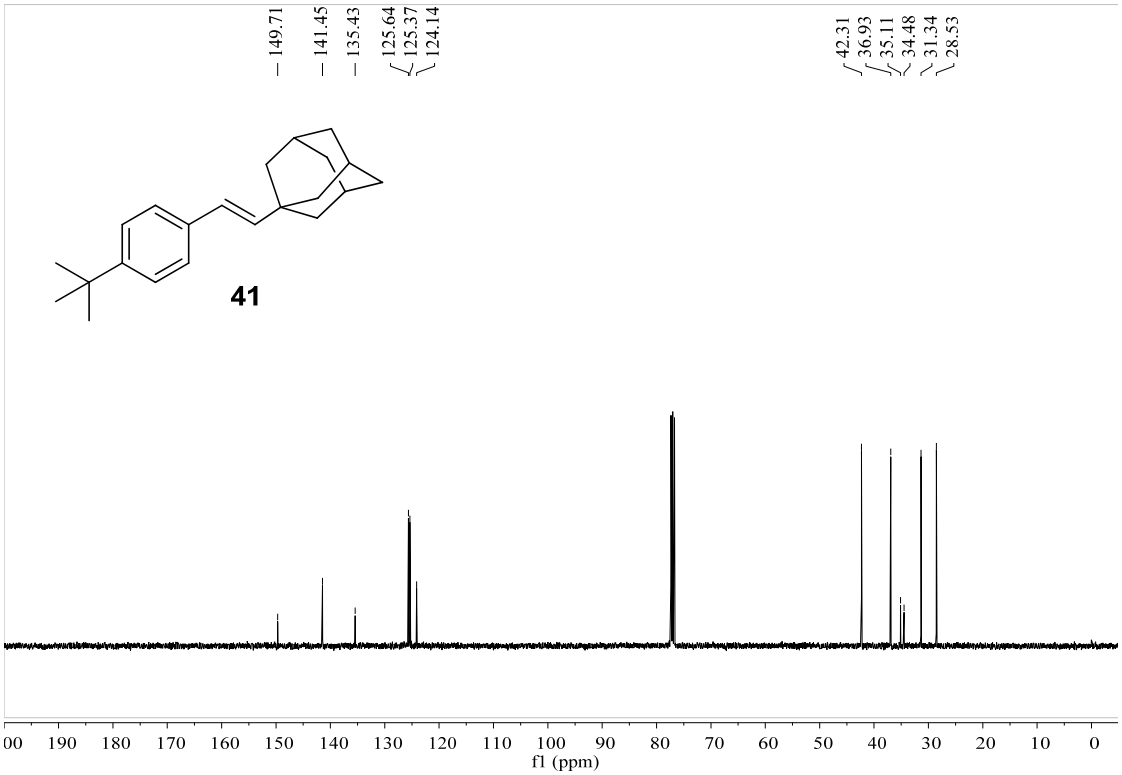



**Figure S123.** [13]C NMR spectrum of compound **41,** related to **Figure 2.**

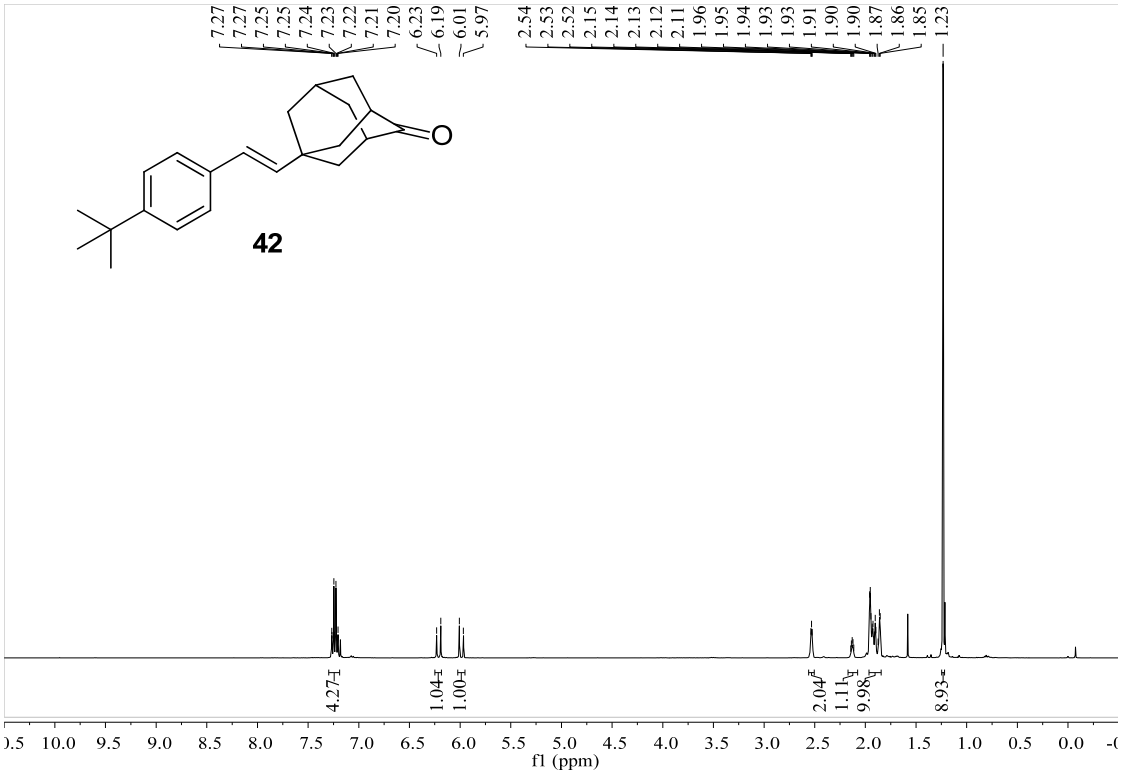



**Figure S124.** $^{1}$H NMR spectrum of compound **42,** related to **Figure 2.**

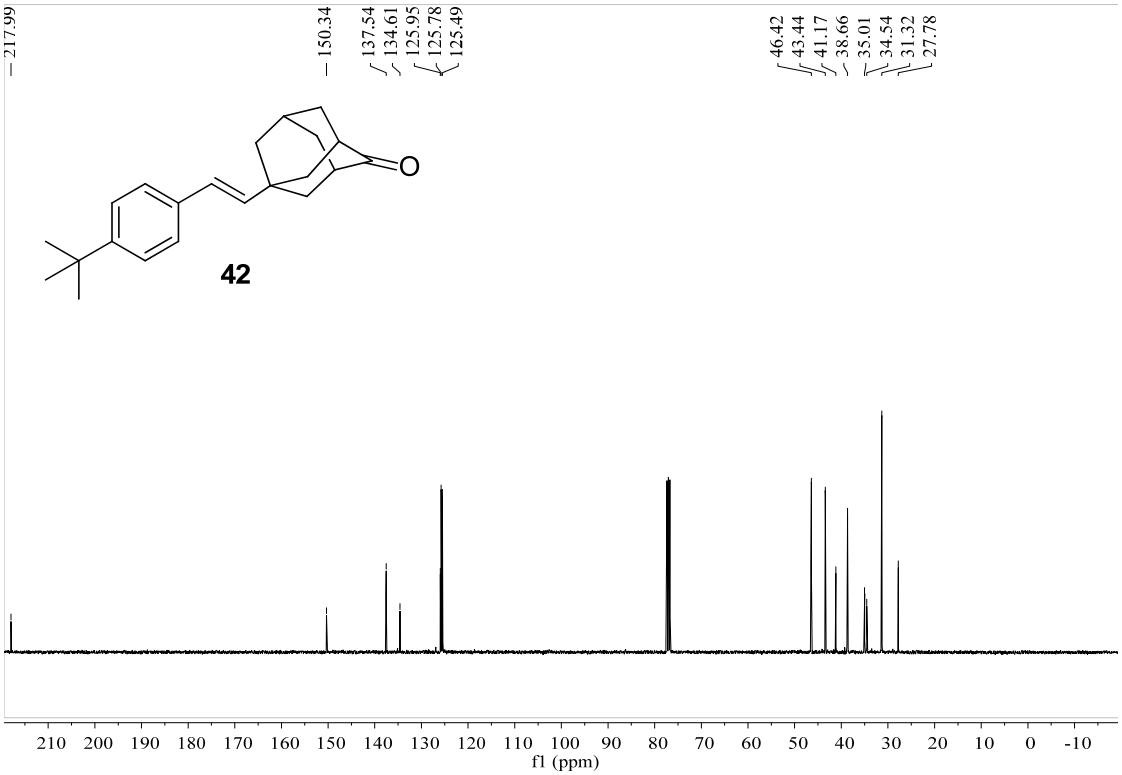



**Figure S125.** $^{13}$C NMR spectrum of compound **42,** related to **Figure 2.**

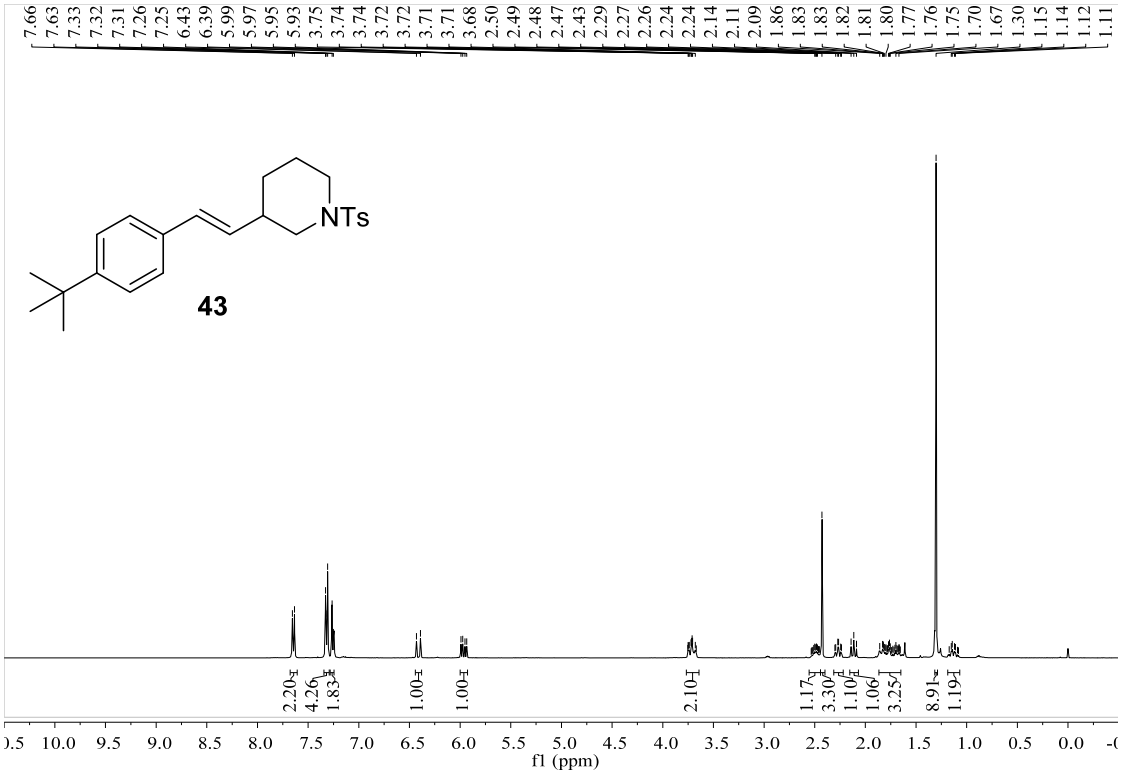



**Figure S126.** $^{1}$H NMR spectrum of compound **43,** related to **Figure 2.**

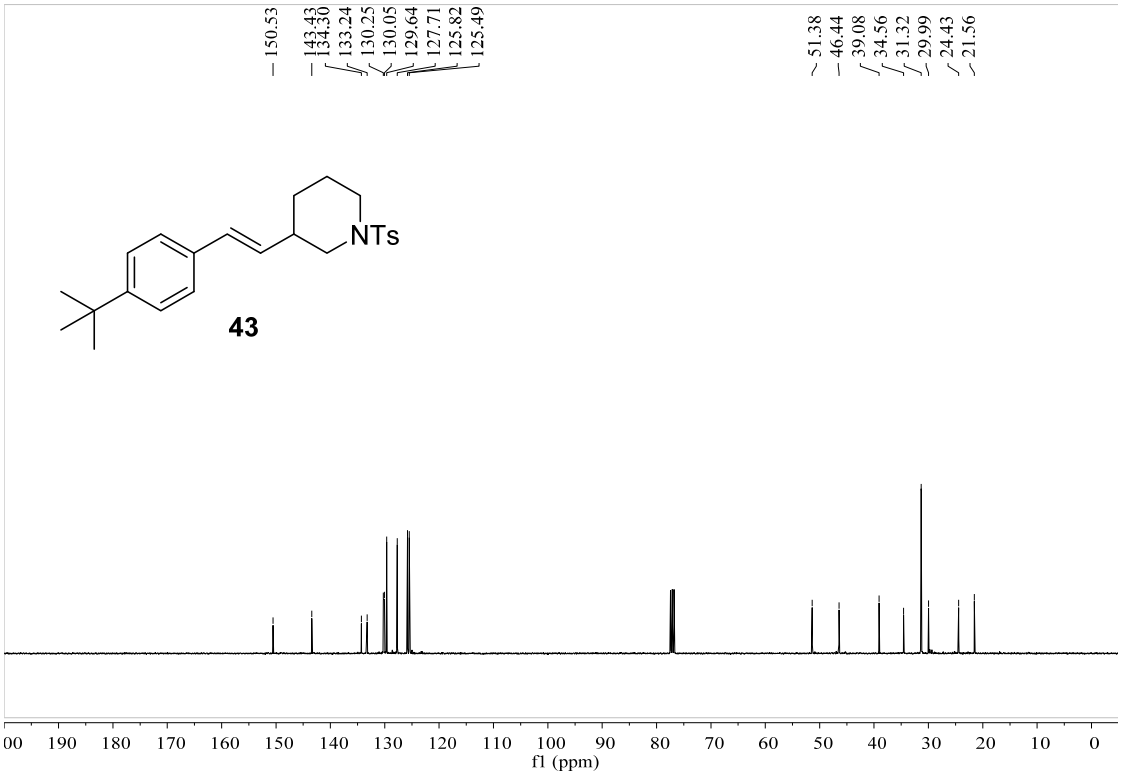



**Figure S127.** $^{13}$C NMR spectrum of compound **43,** related to **Figure 2.**

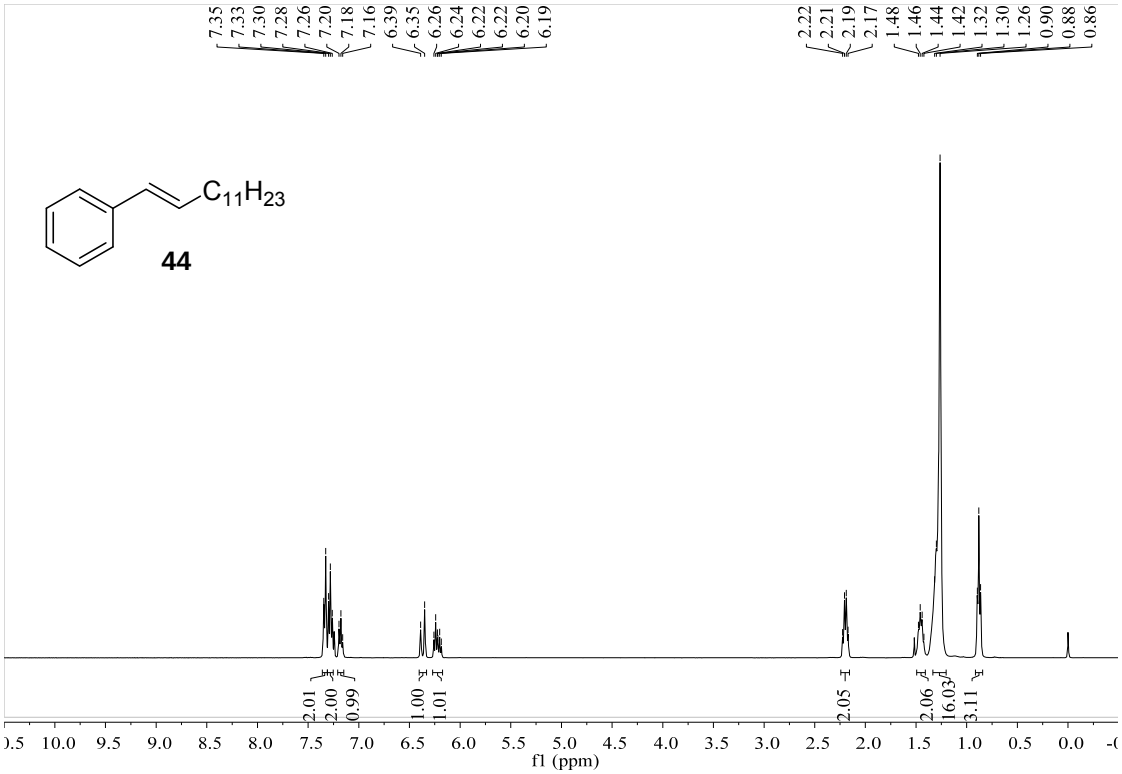



**Figure S128.** $^{1}$H NMR spectrum of compound **44,** related to **Figure 3.**

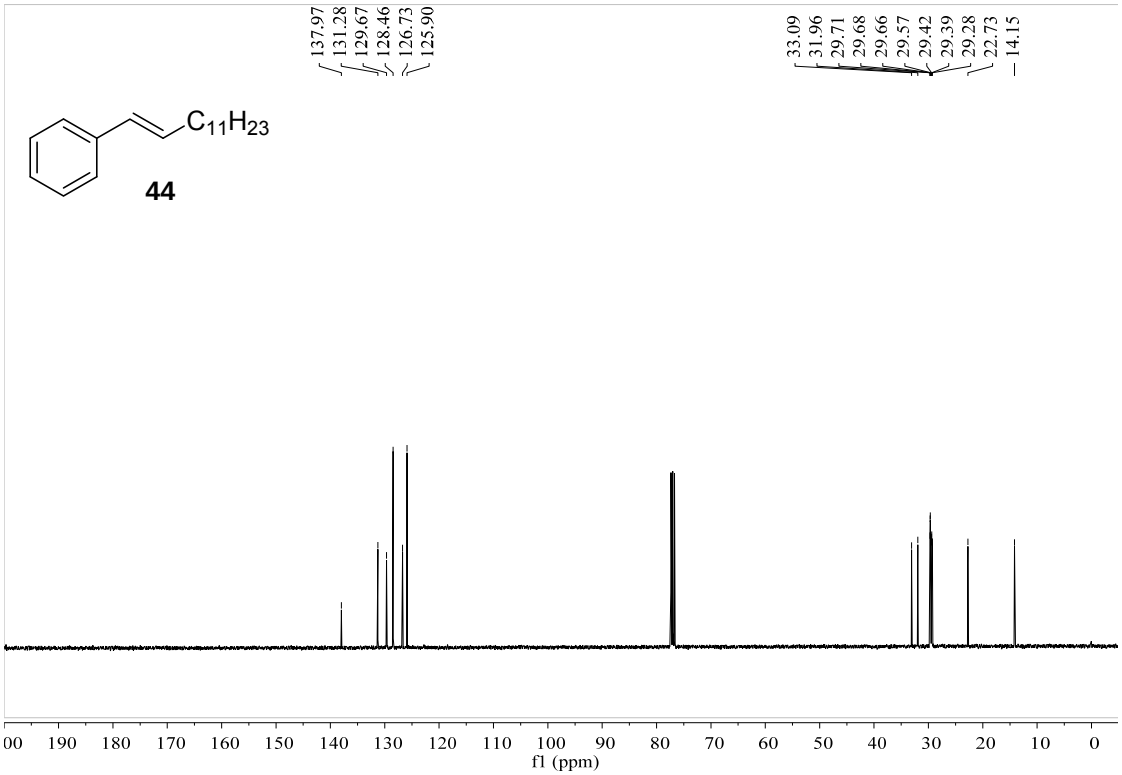



**Figure S129.** $^{13}$C NMR spectrum of compound **44,** related to **Figure 3.**

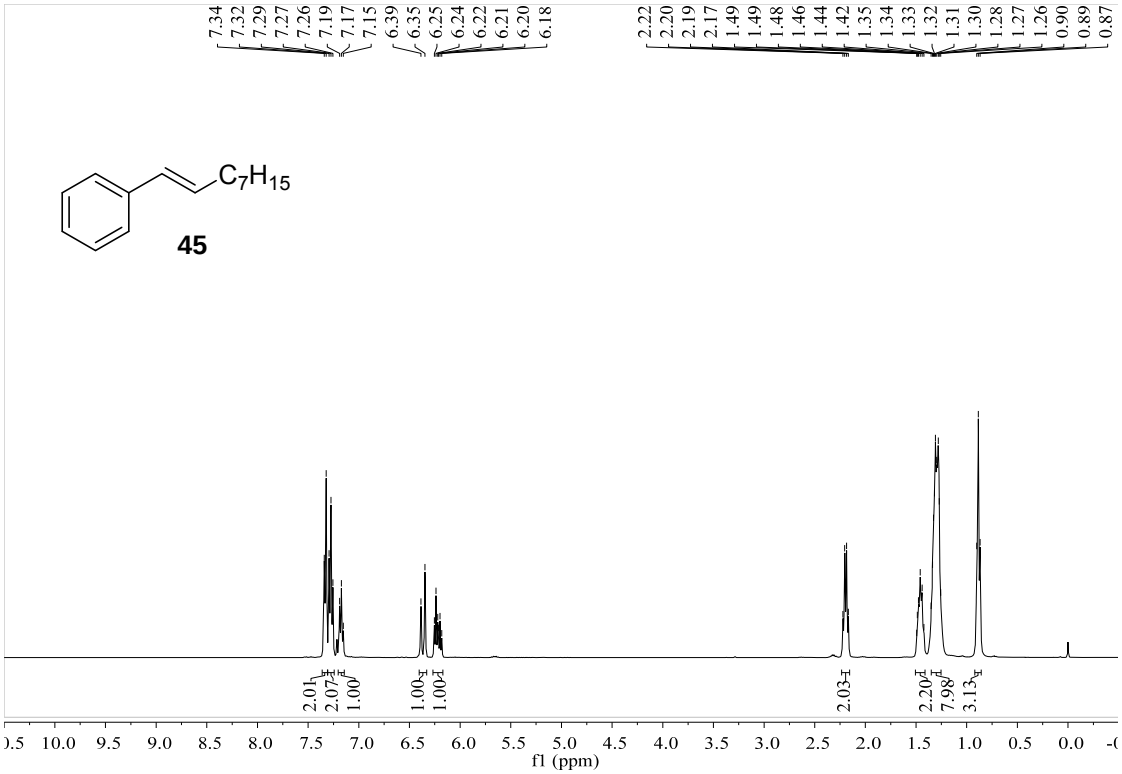



**Figure S130.** $^{1}$H NMR spectrum of compound **45,** related to **Figure 3.**

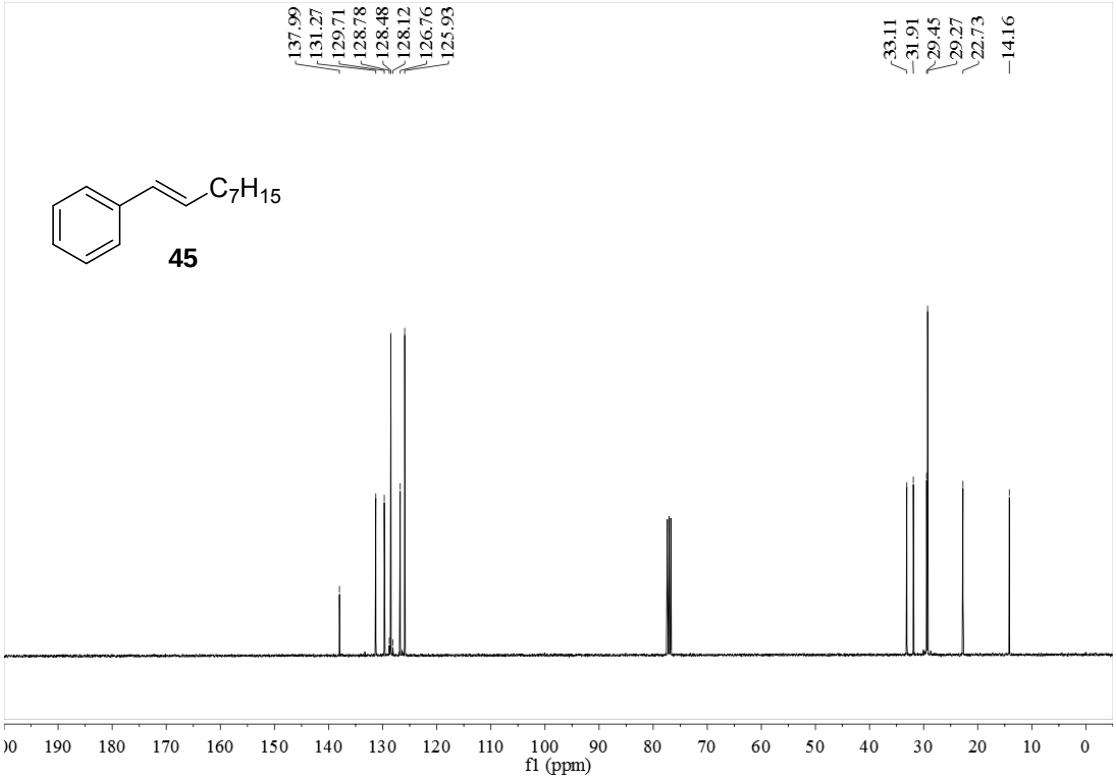



**Figure S131.** $^{13}$C NMR spectrum of compound **45,** related to **Figure 3.**

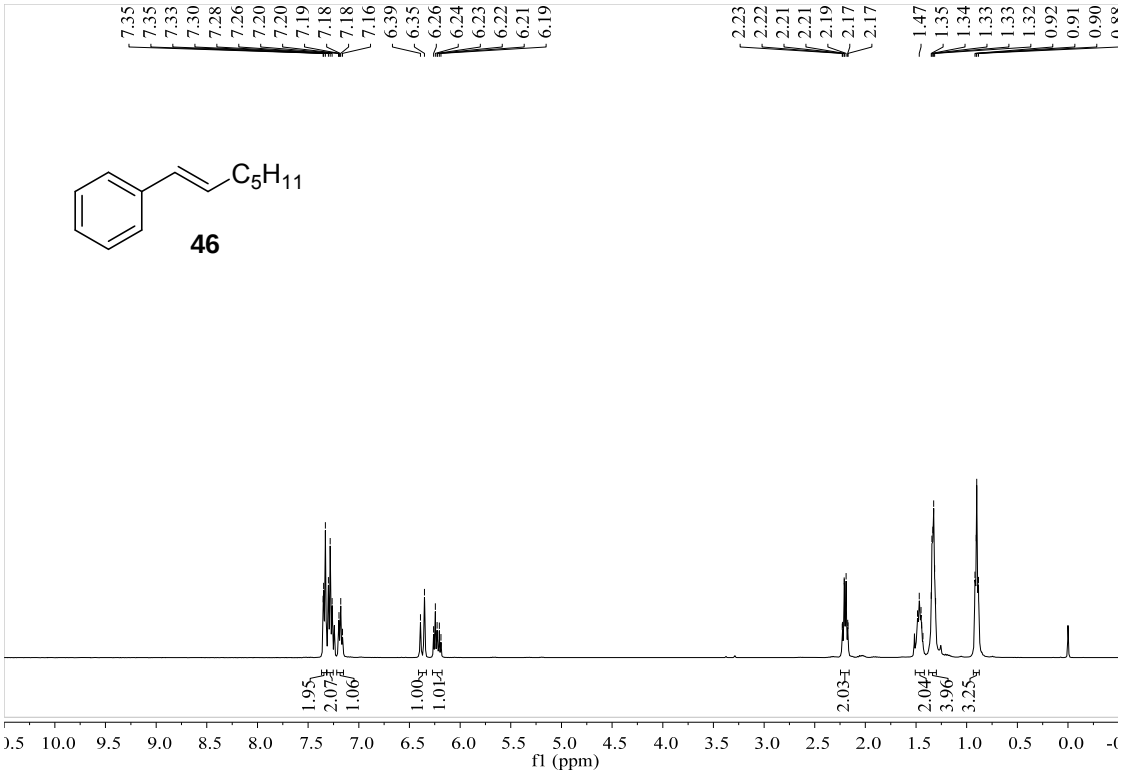



**Figure S132.** $^{1}$H NMR spectrum of compound **46,** related to **Figure 3.**

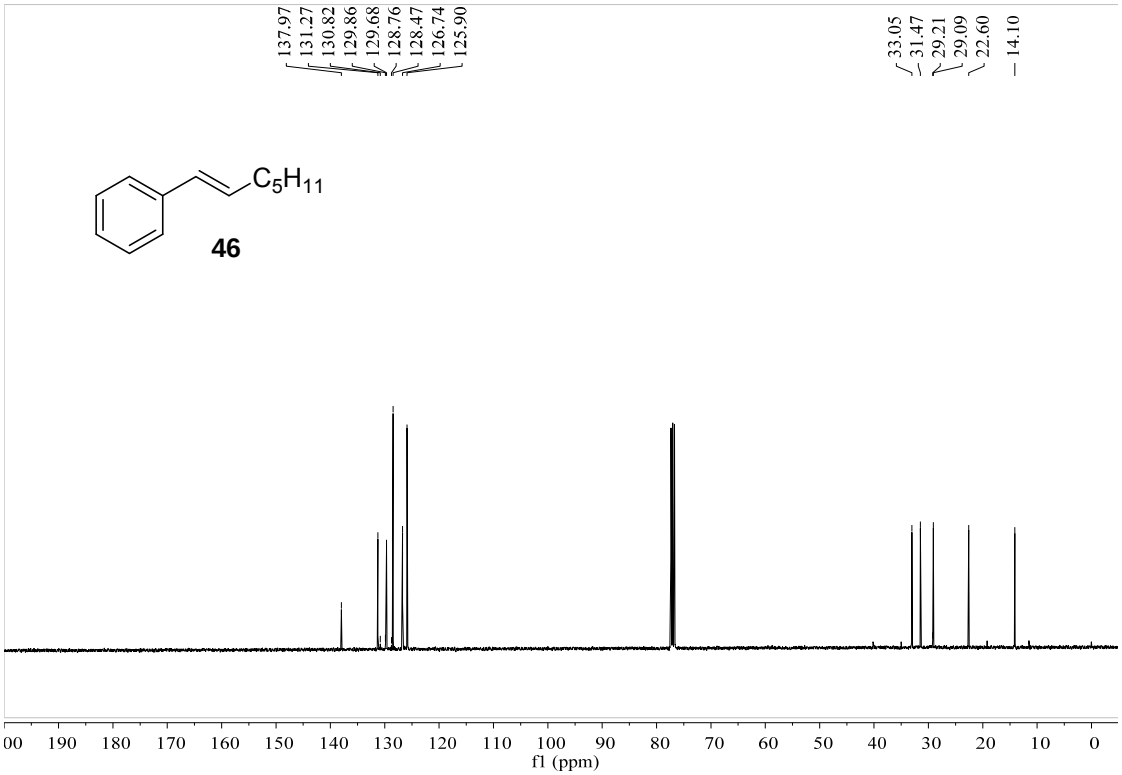



**Figure S133.** $^{13}$C NMR spectrum of compound **46,** related to **Figure 3.**

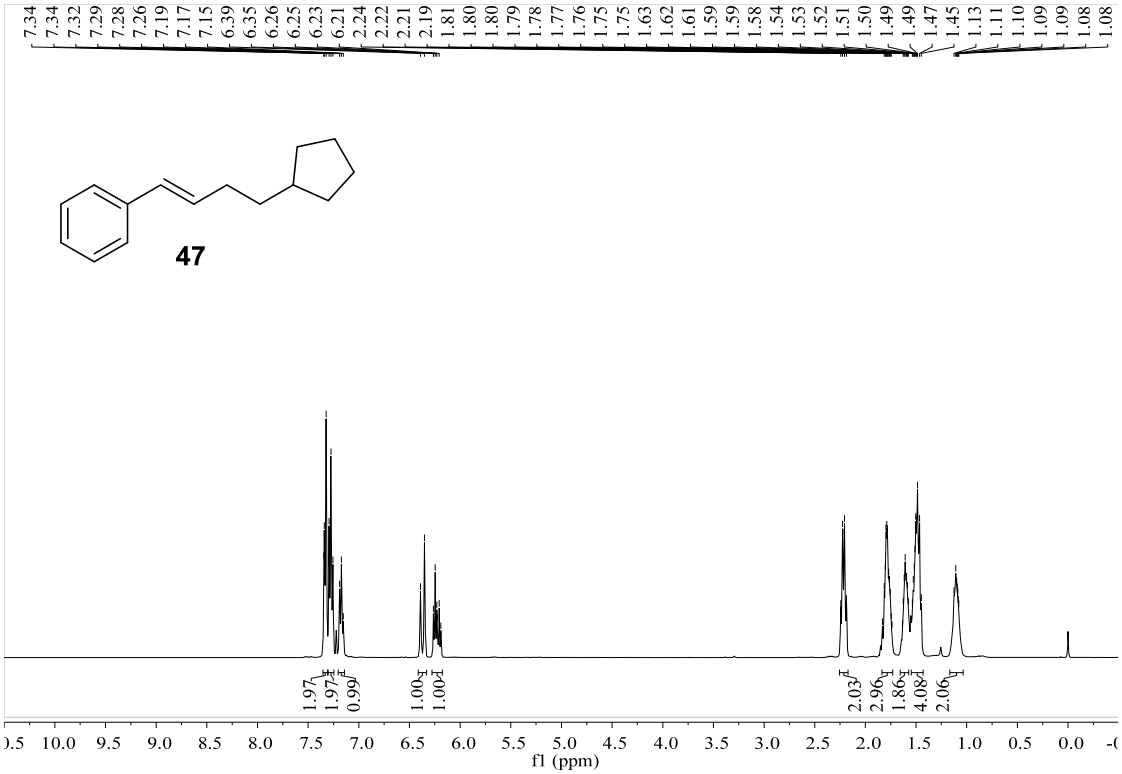



**Figure S134.** $^{1}$H NMR spectrum of compound **47,** related to **Figure 3.**

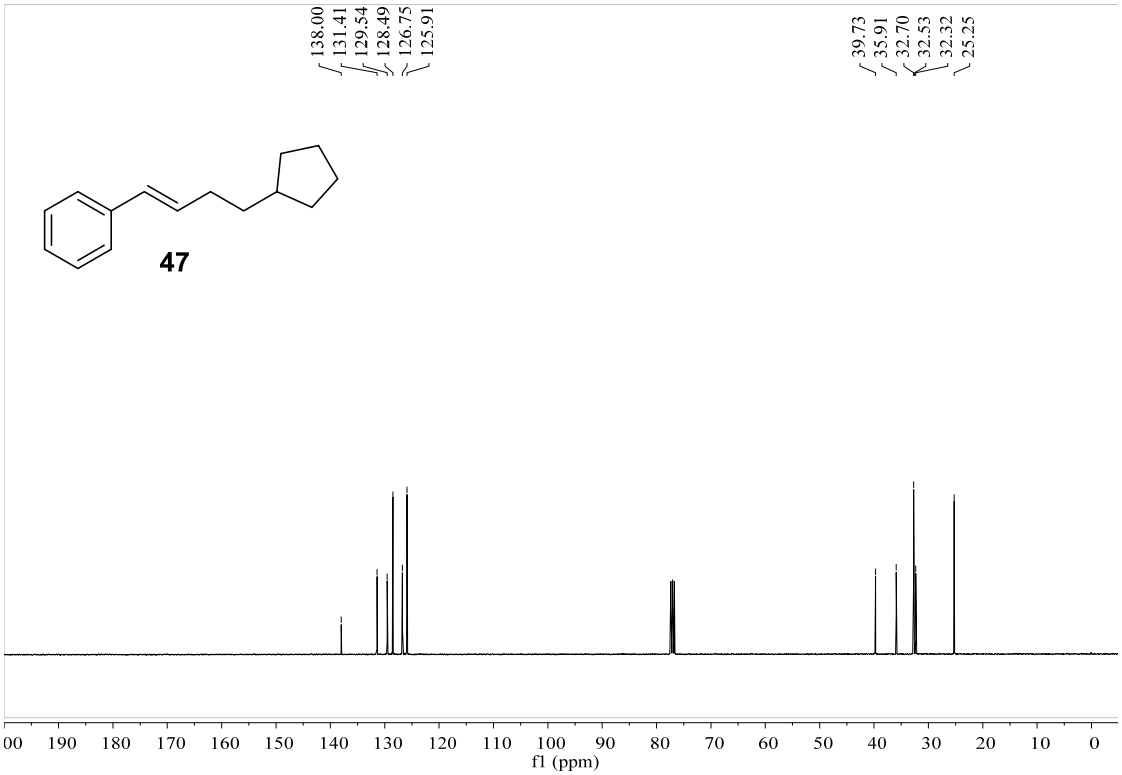



**Figure S135.** $^{13}$C NMR spectrum of compound **47,** related to **Figure 3.**

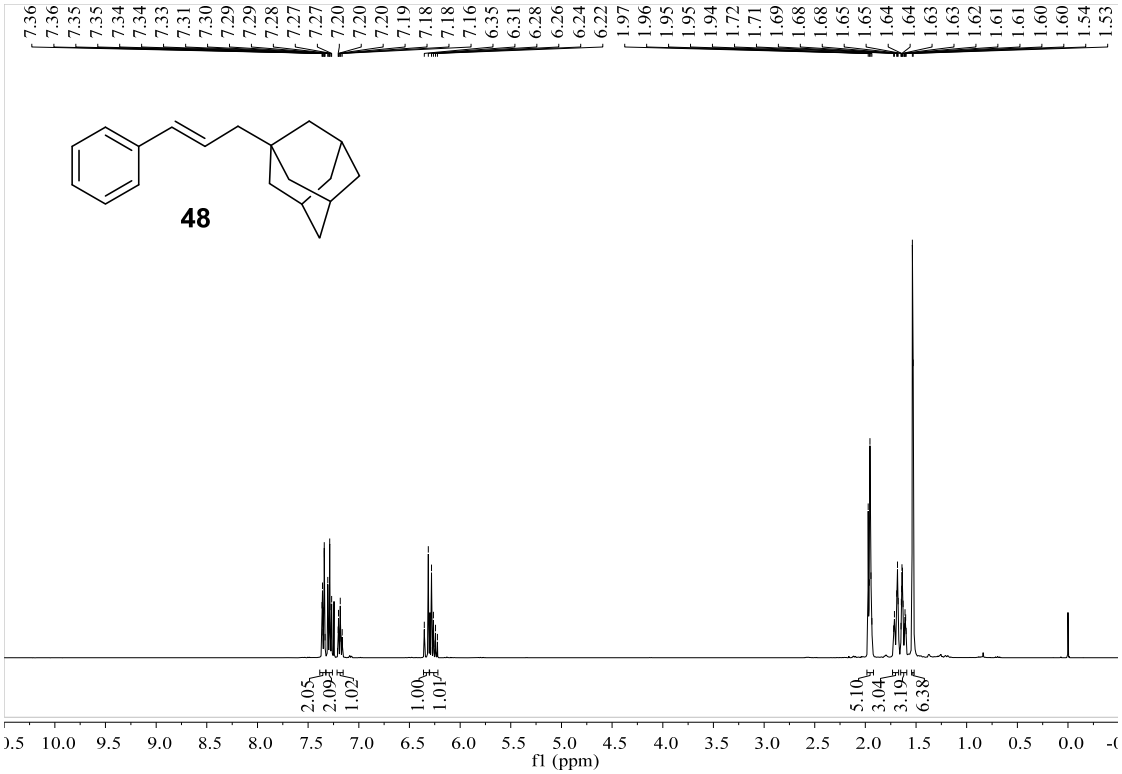



**Figure S136.** [1]H NMR spectrum of compound **48,** related to **Figure 3.**

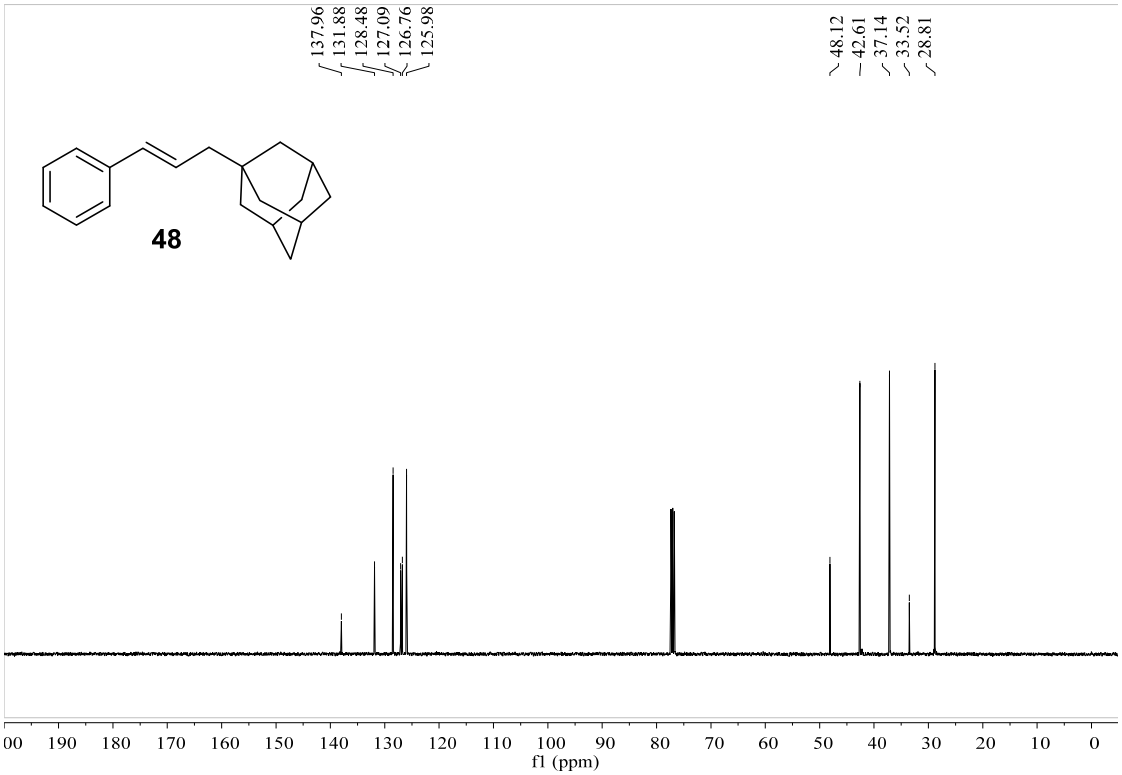



**Figure S137.** [13]C NMR spectrum of compound **48,** related to **Figure 3.**

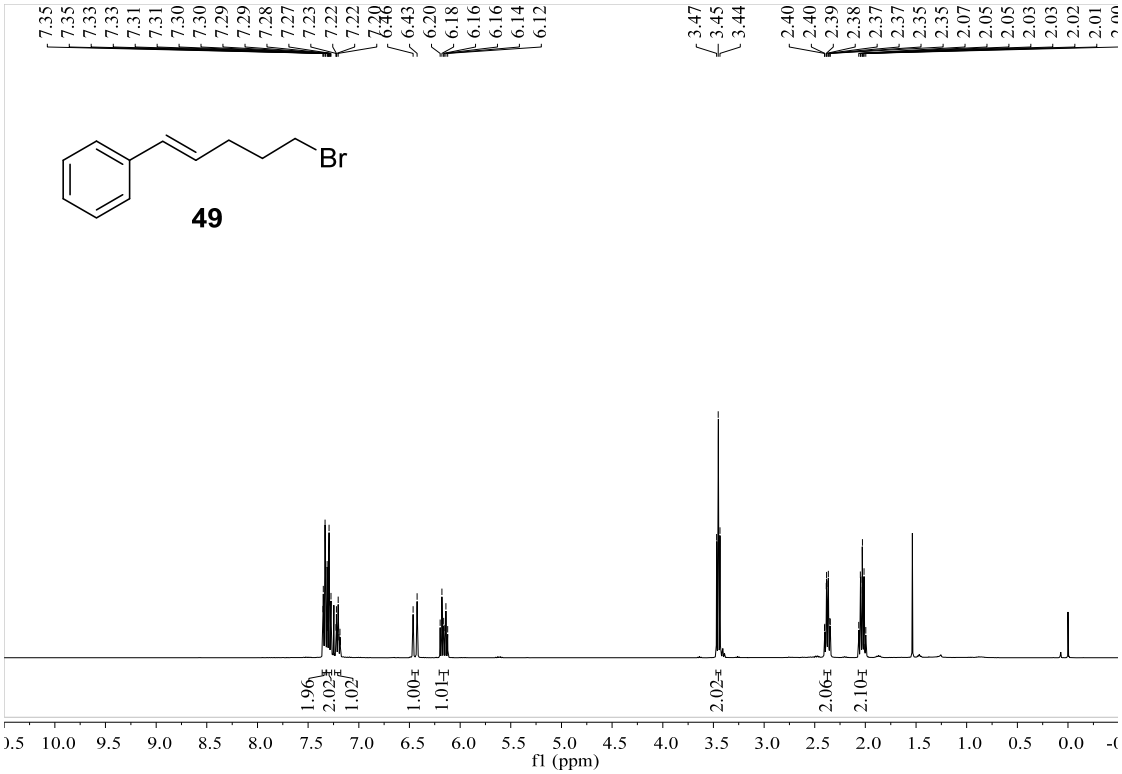



**Figure S138.** $^{1}$H NMR spectrum of compound **49,** related to **Figure 3.**

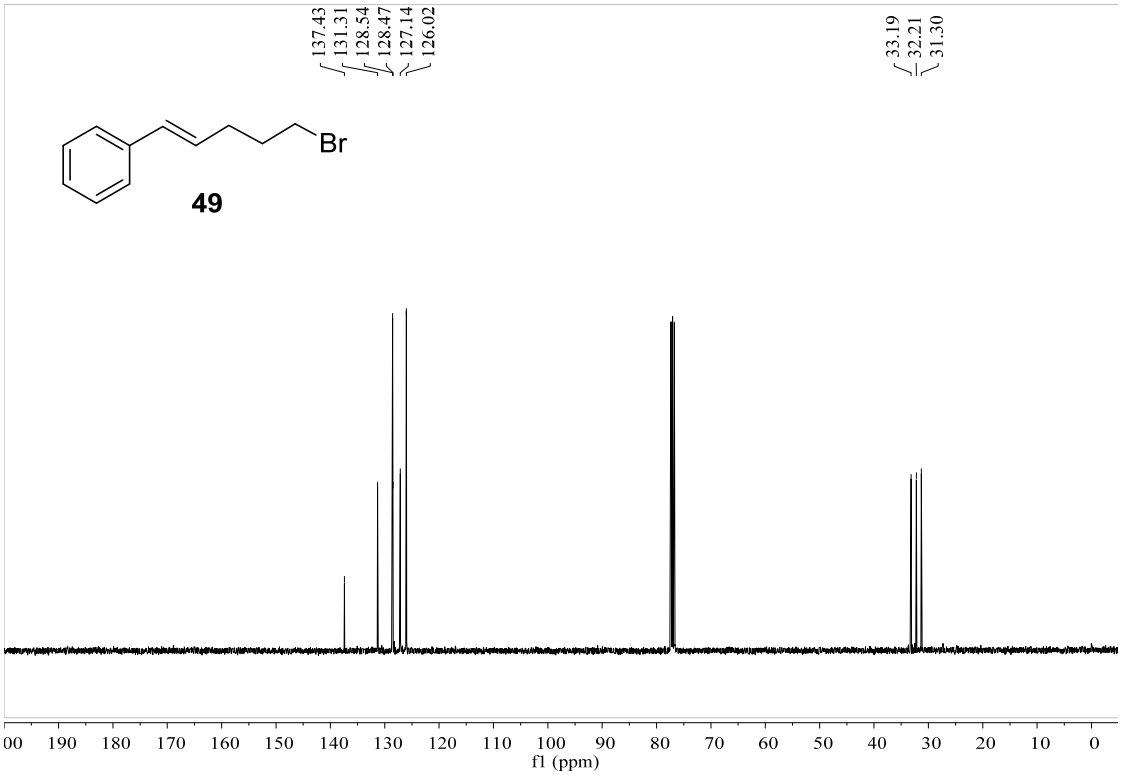



**Figure S139.** $^{13}$C NMR spectrum of compound **49,** related to **Figure 3.**

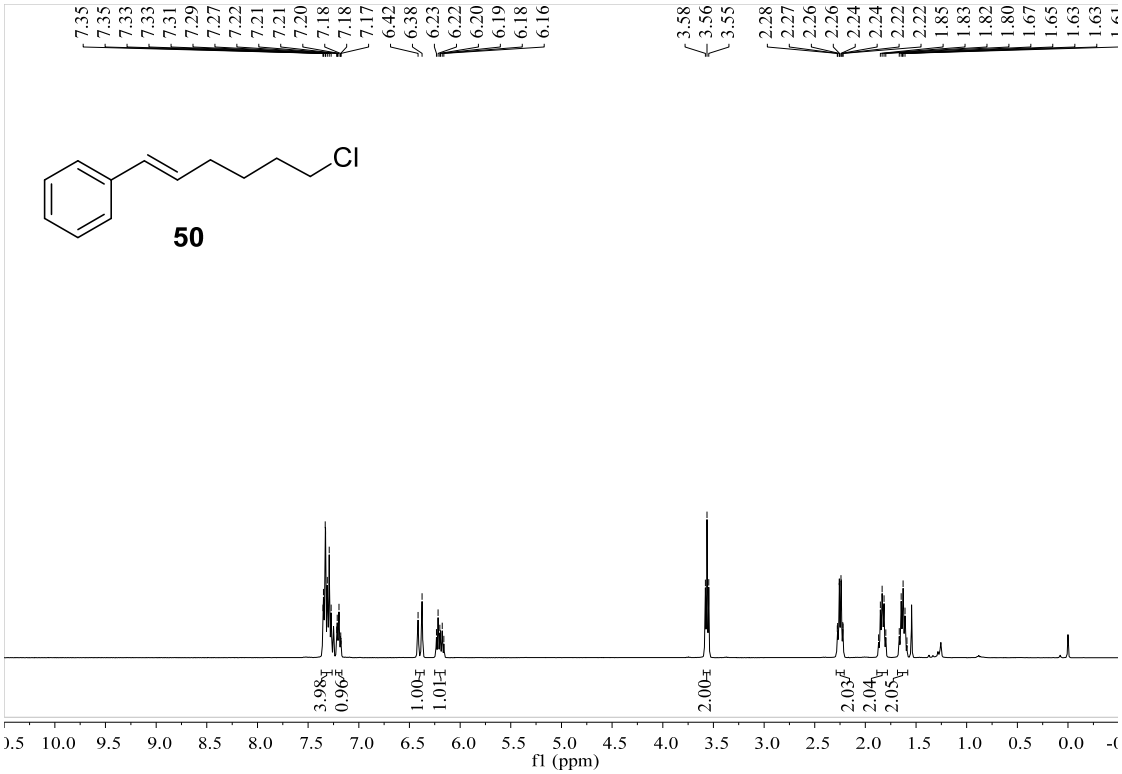



**Figure S140.** [1]H NMR spectrum of compound **50,** related to **Figure 3.**

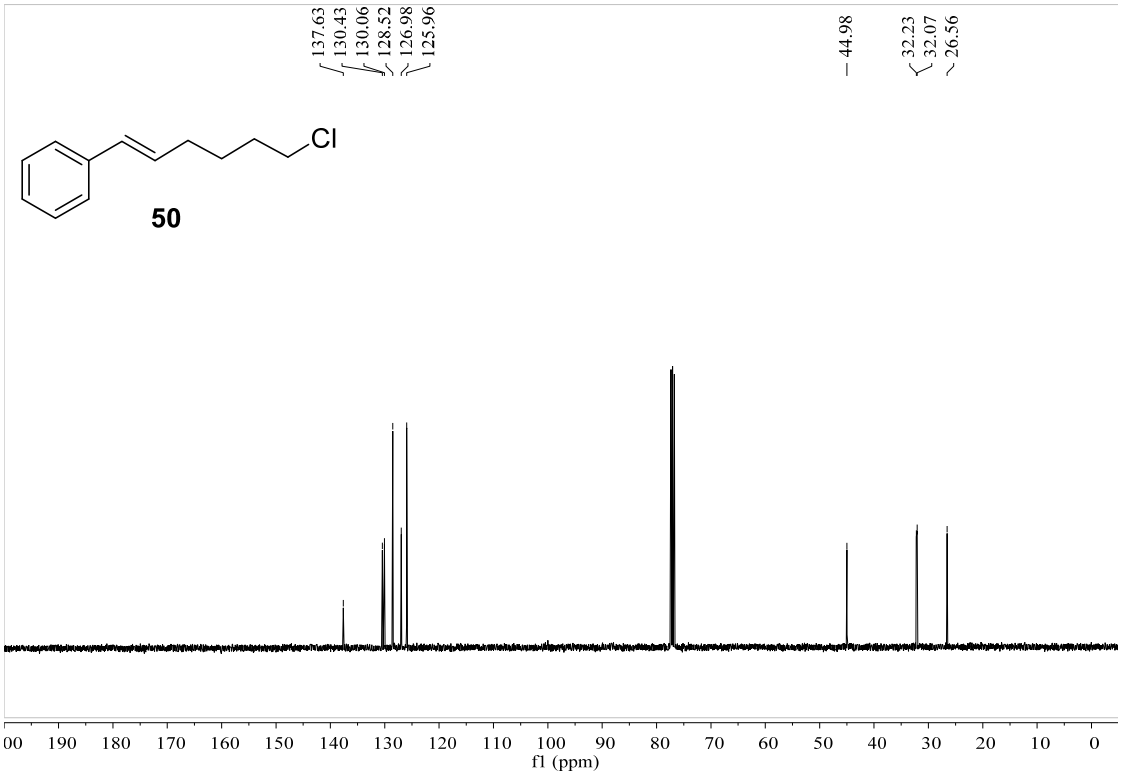



**Figure S141.** [13]C NMR spectrum of compound **50,** related to **Figure 3.**

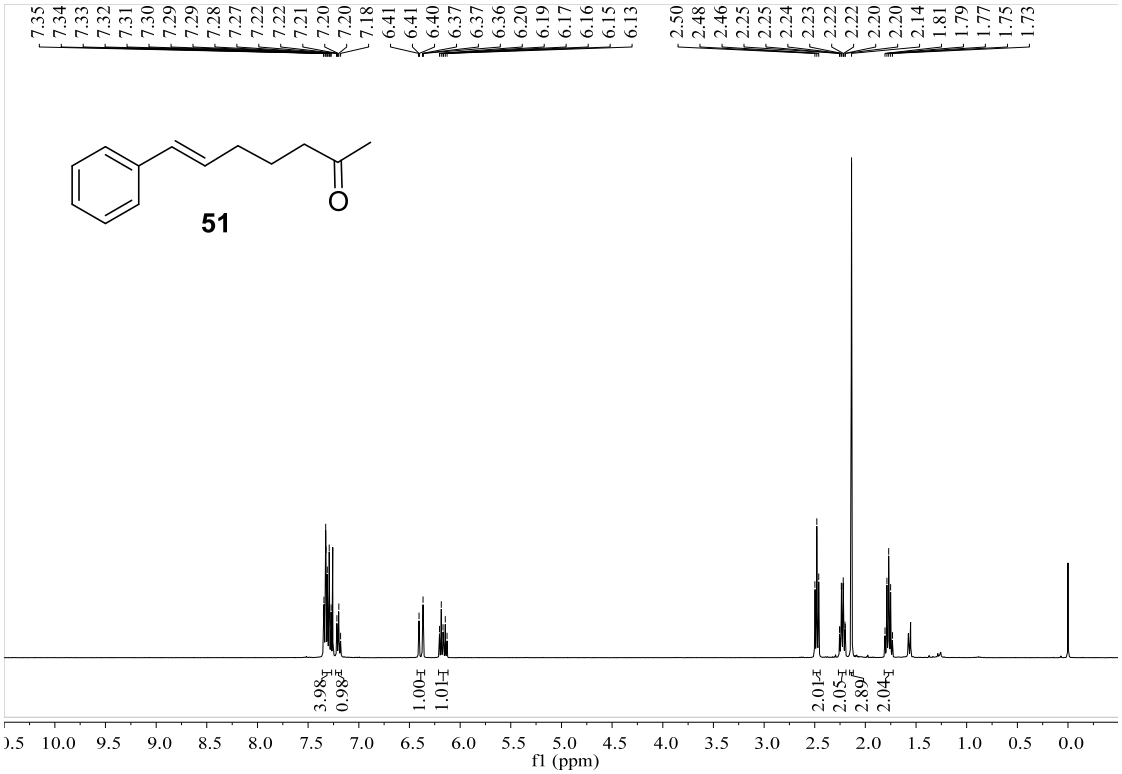



**Figure S142.** $^{1}$H NMR spectrum of compound **51,** related to **Figure 3.**

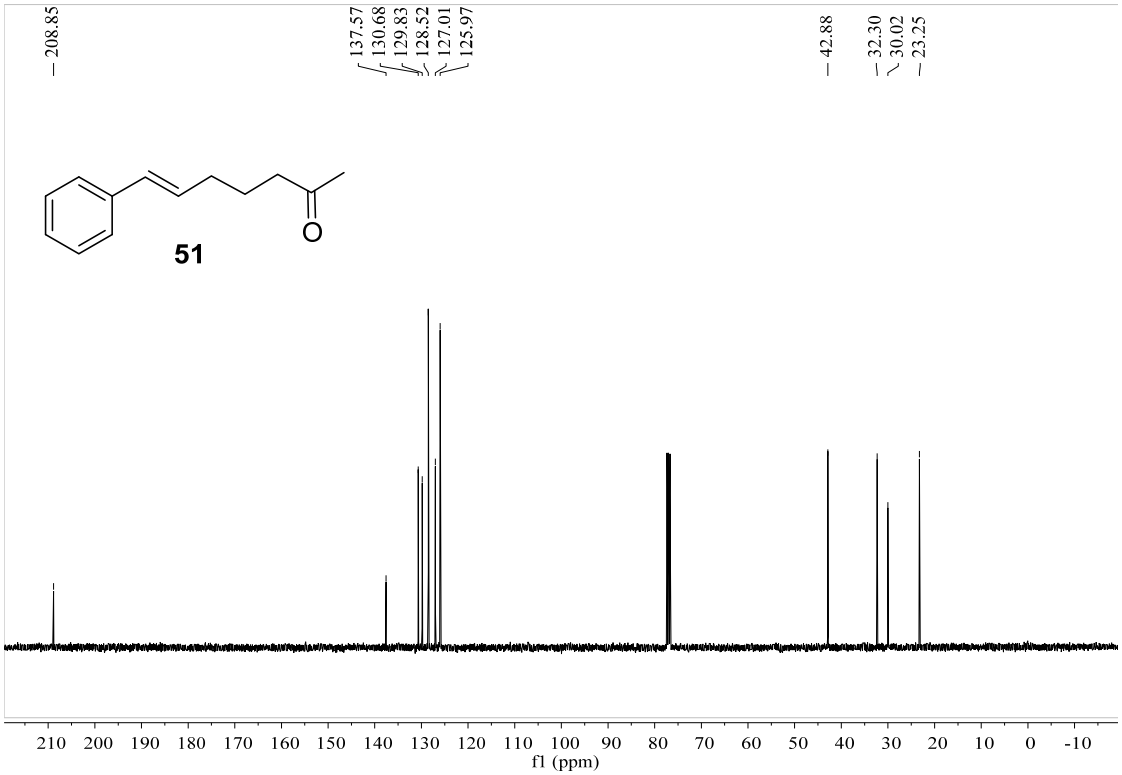



**Figure S143.** $^{13}$C NMR spectrum of compound **51,** related to **Figure 3.**

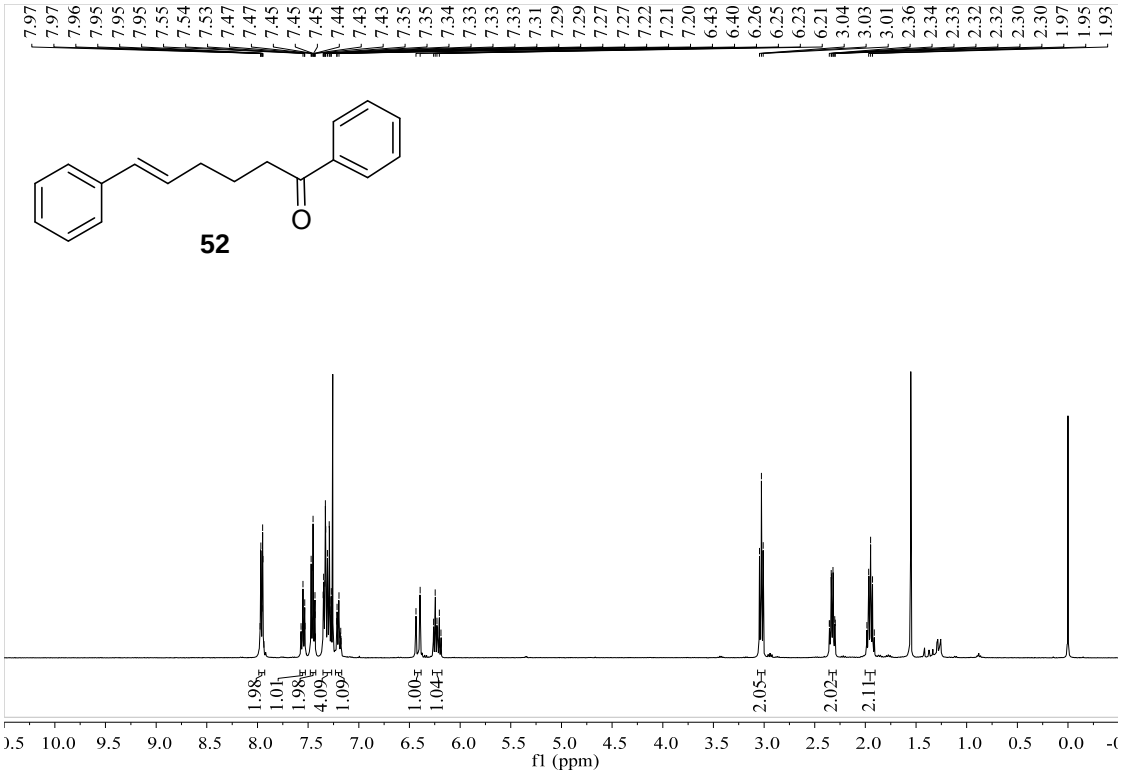



**Figure S144.** $^{1}$H NMR spectrum of compound **52,** related to **Figure 3.**

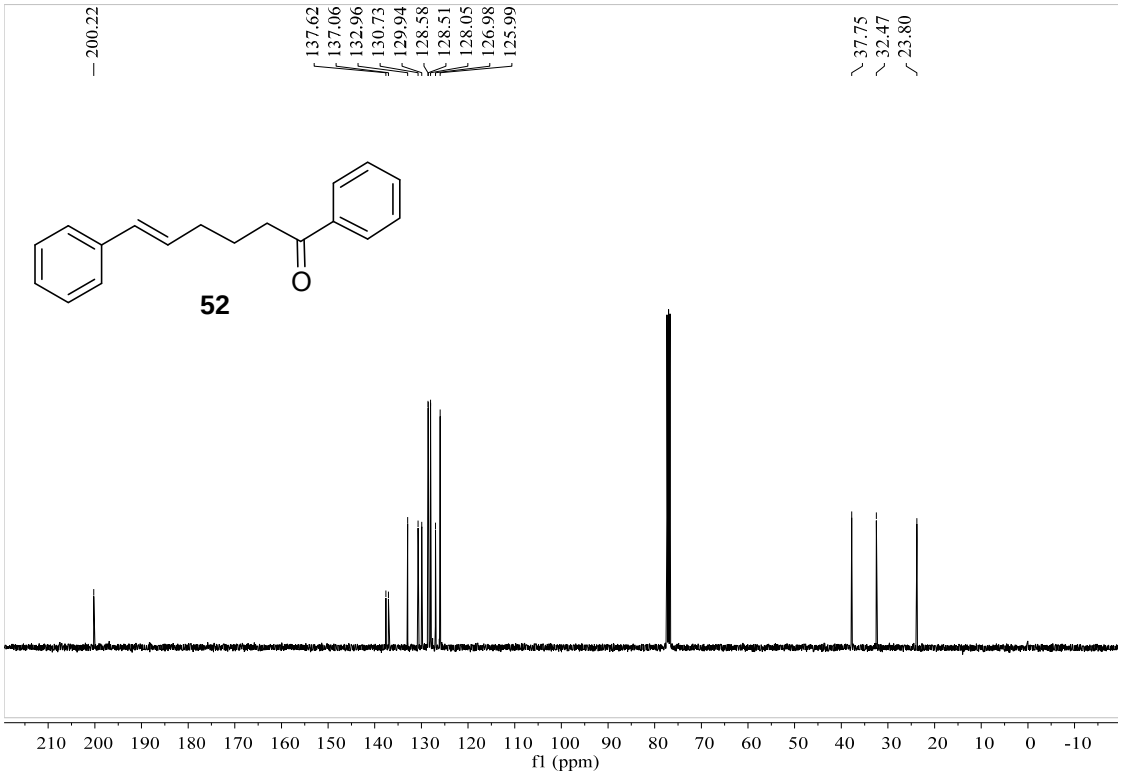



**Figure S145.** $^{13}$C NMR spectrum of compound **52,** related to **Figure 3.**

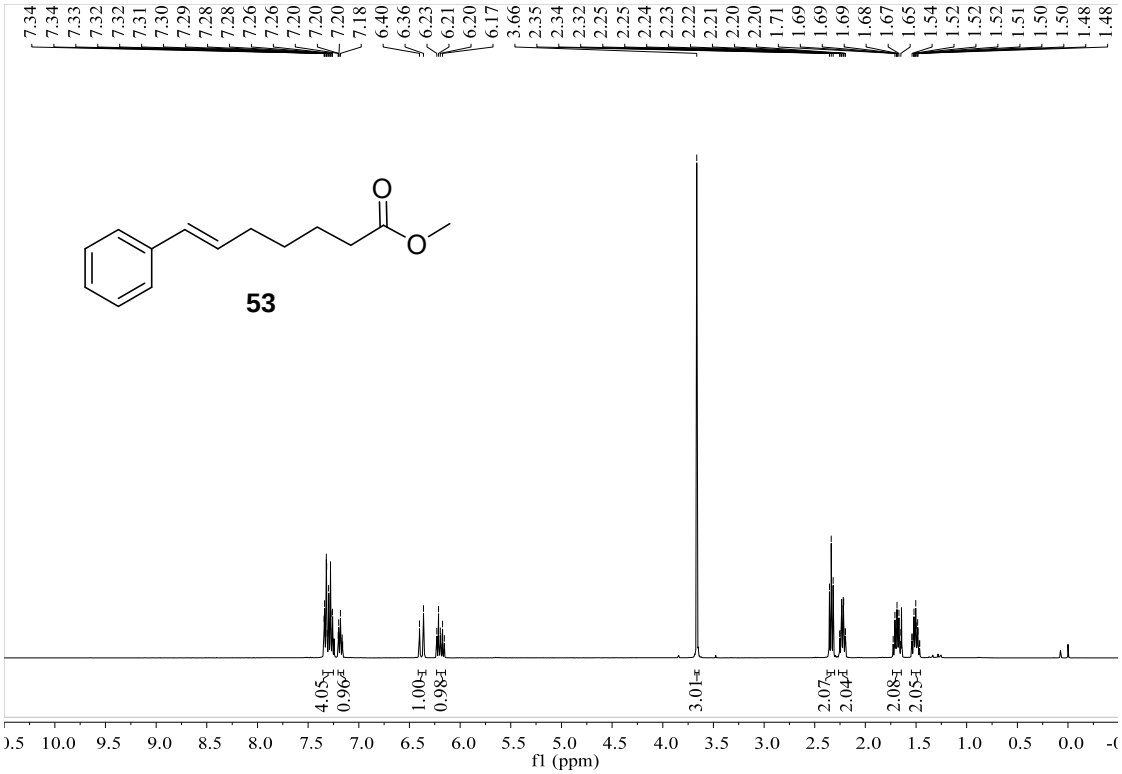



**Figure S146.** [1]H NMR spectrum of compound **53,** related to **Figure 3.**

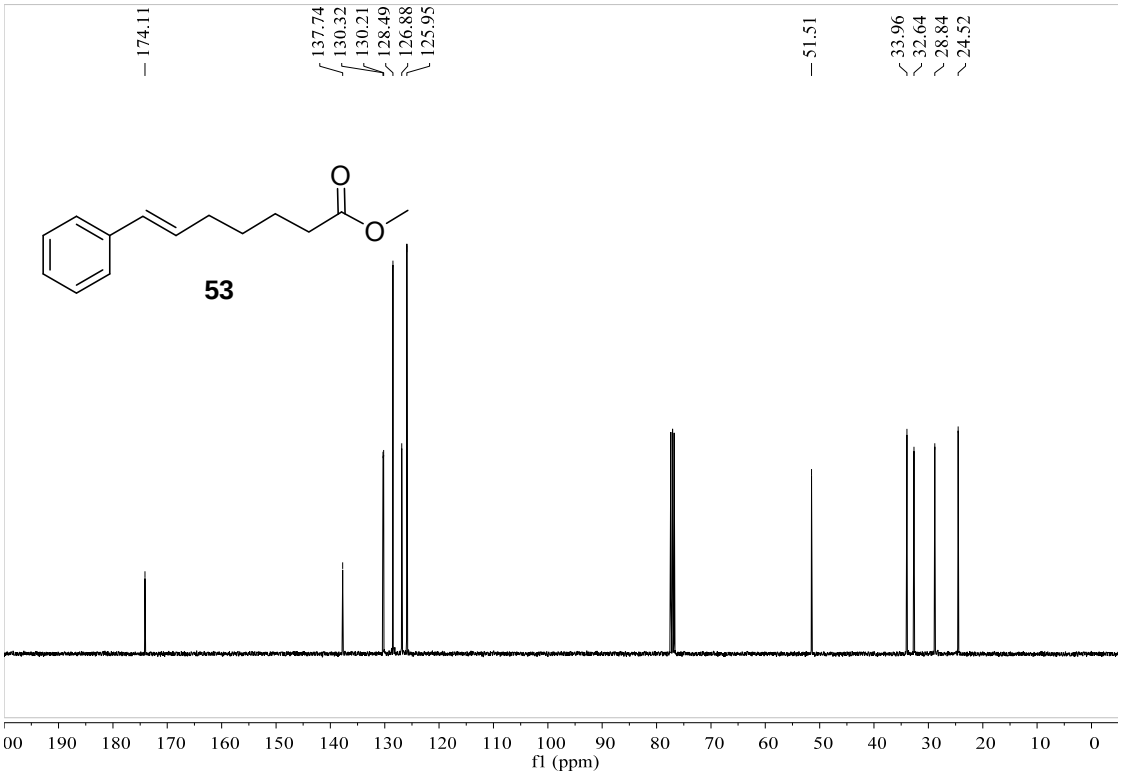



**Figure S147.** [13]C NMR spectrum of compound **53,** related to **Figure 3.**

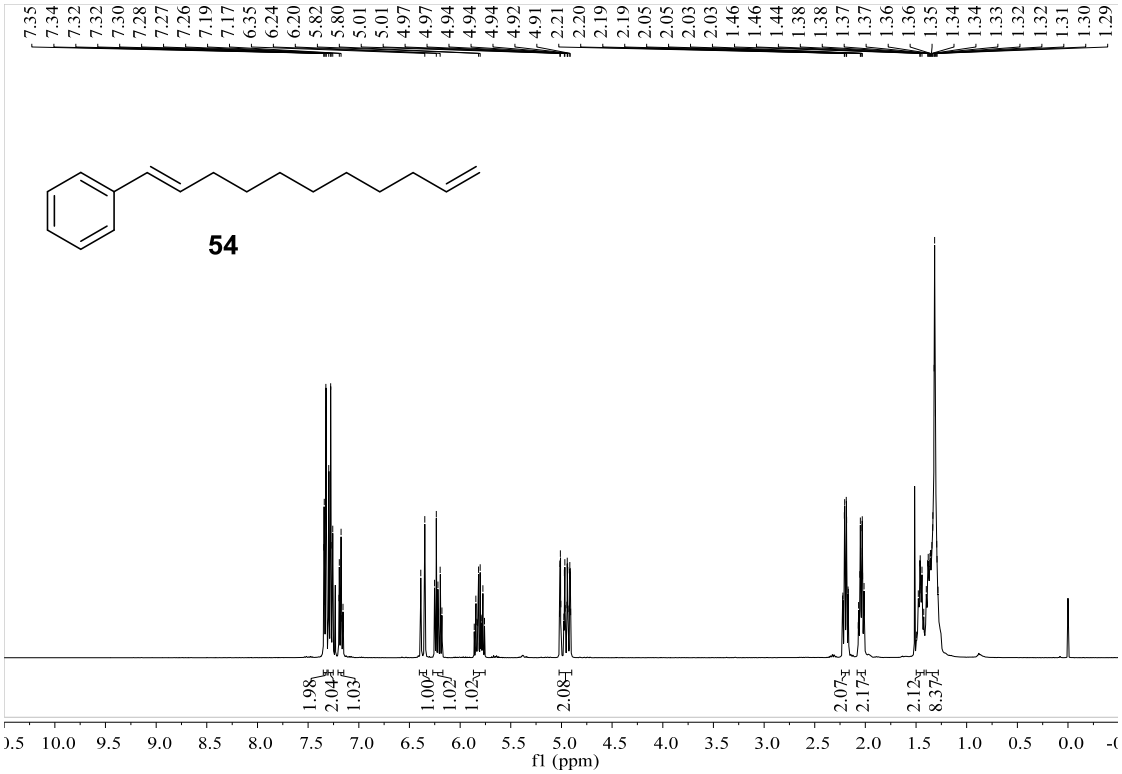



**Figure S148.** $^{1}$H NMR spectrum of compound **54,** related to **Figure 3.**

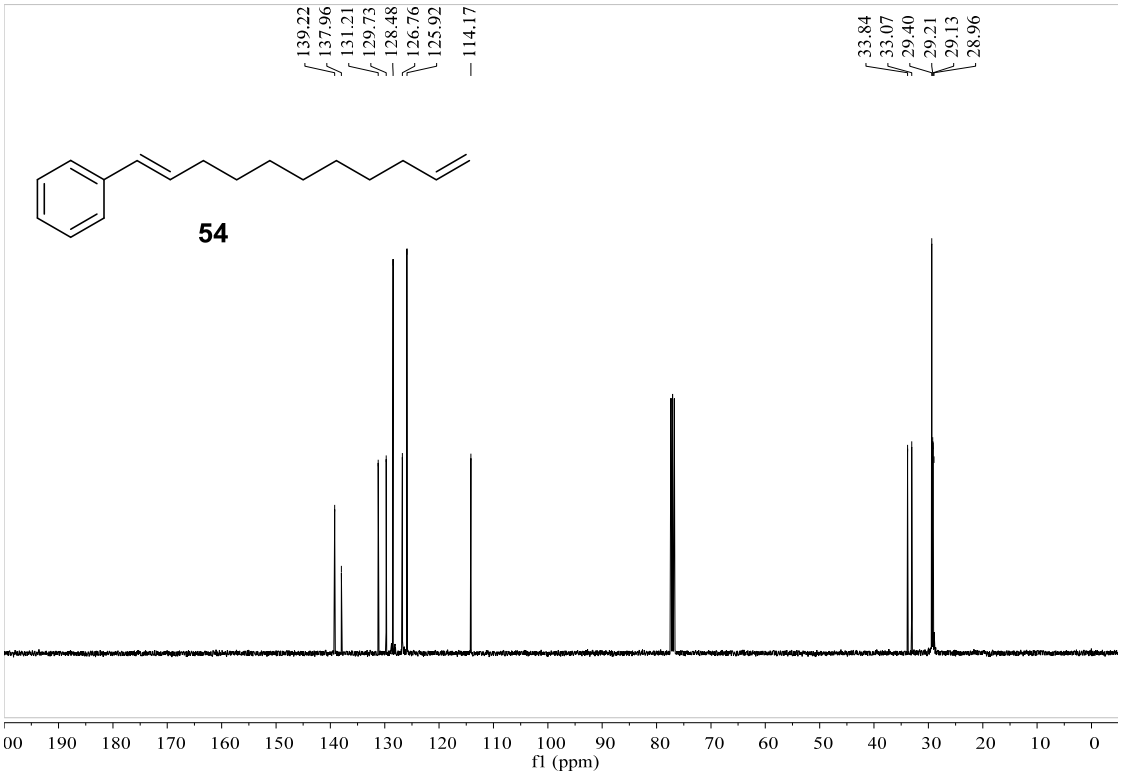



**Figure S149.** $^{13}$C NMR spectrum of compound **54,** related to **Figure 3.**

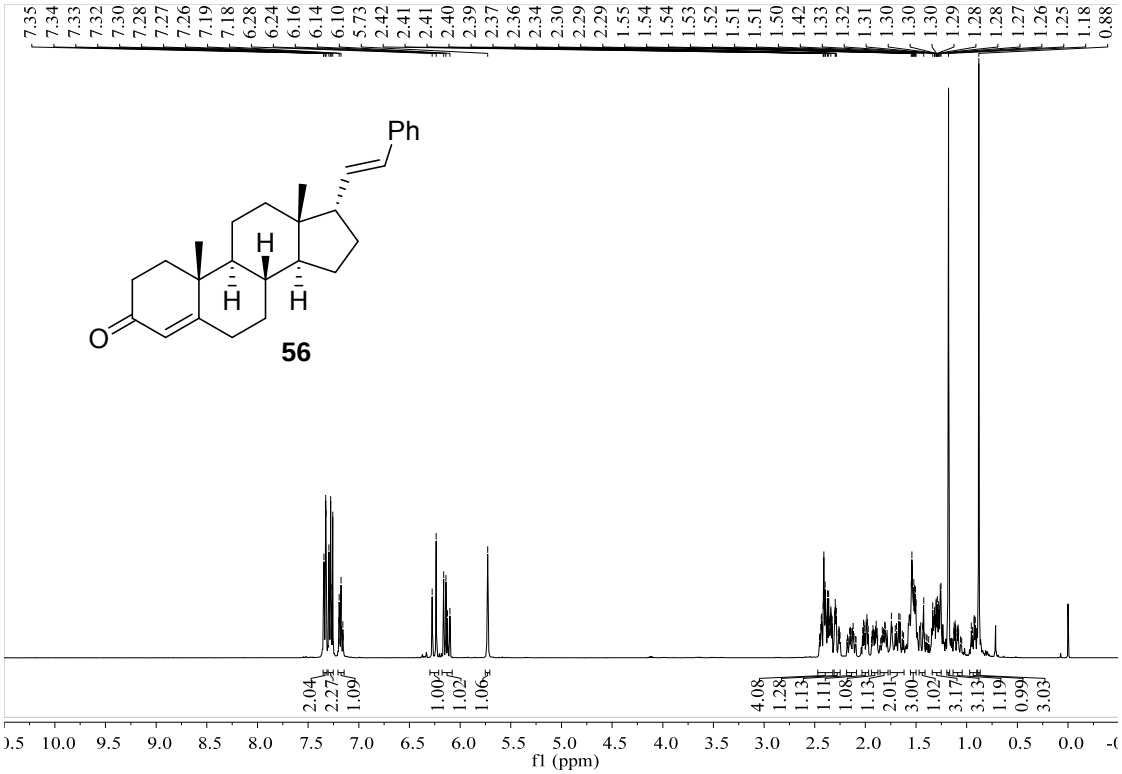



**Figure S150.** $^{1}$H NMR spectrum of compound **56,** related to **Scheme 2.**

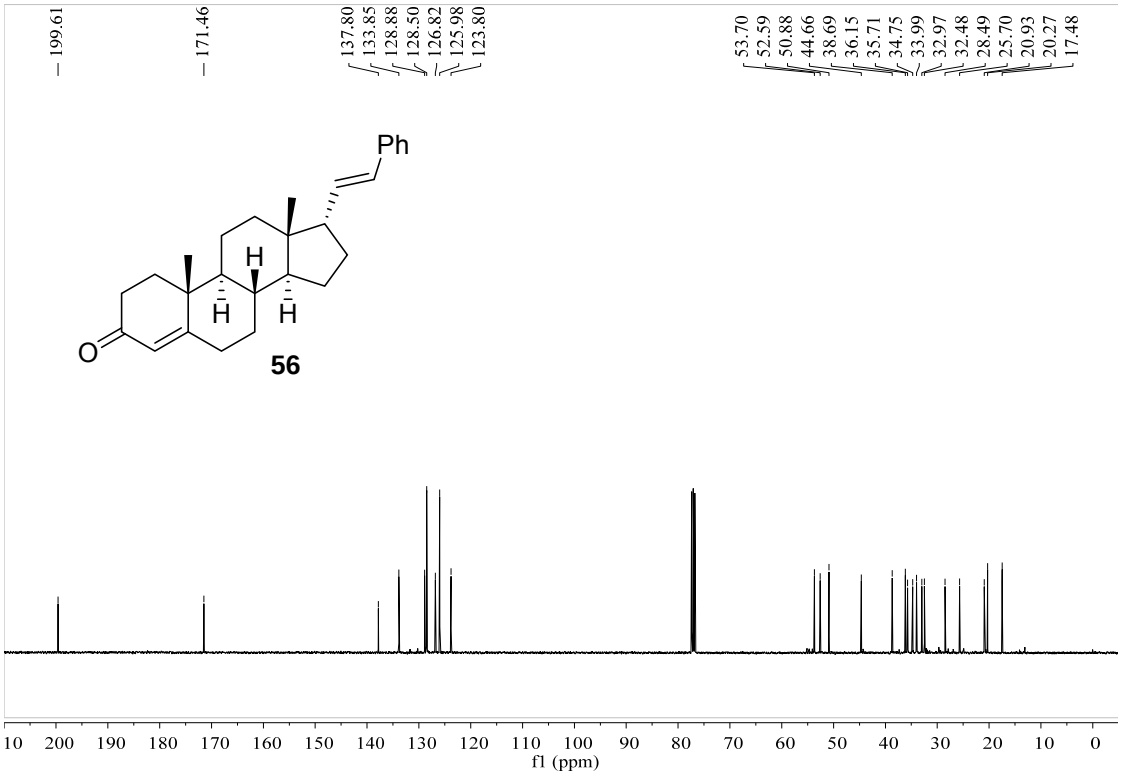



**Figure S151.** $^{13}$C NMR spectrum of compound **56,** related to **Scheme 2.**

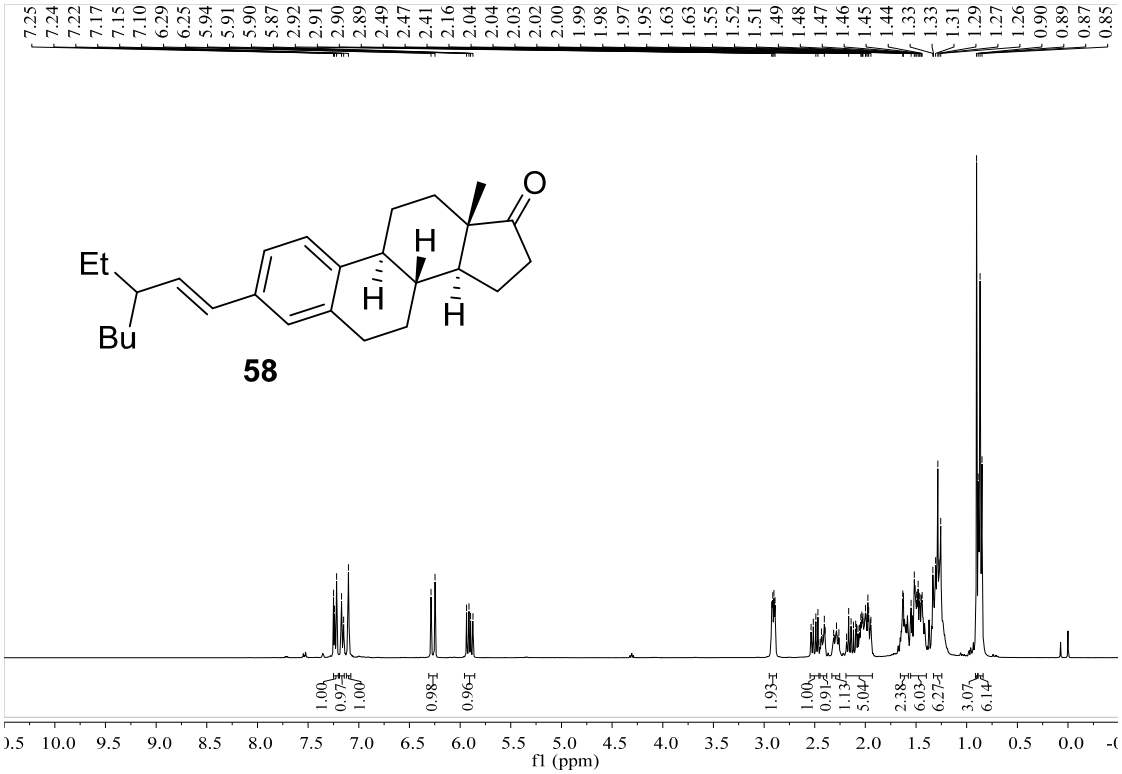



**Figure S152.** $^{1}$H NMR spectrum of compound **58,** related to **Scheme 2.**

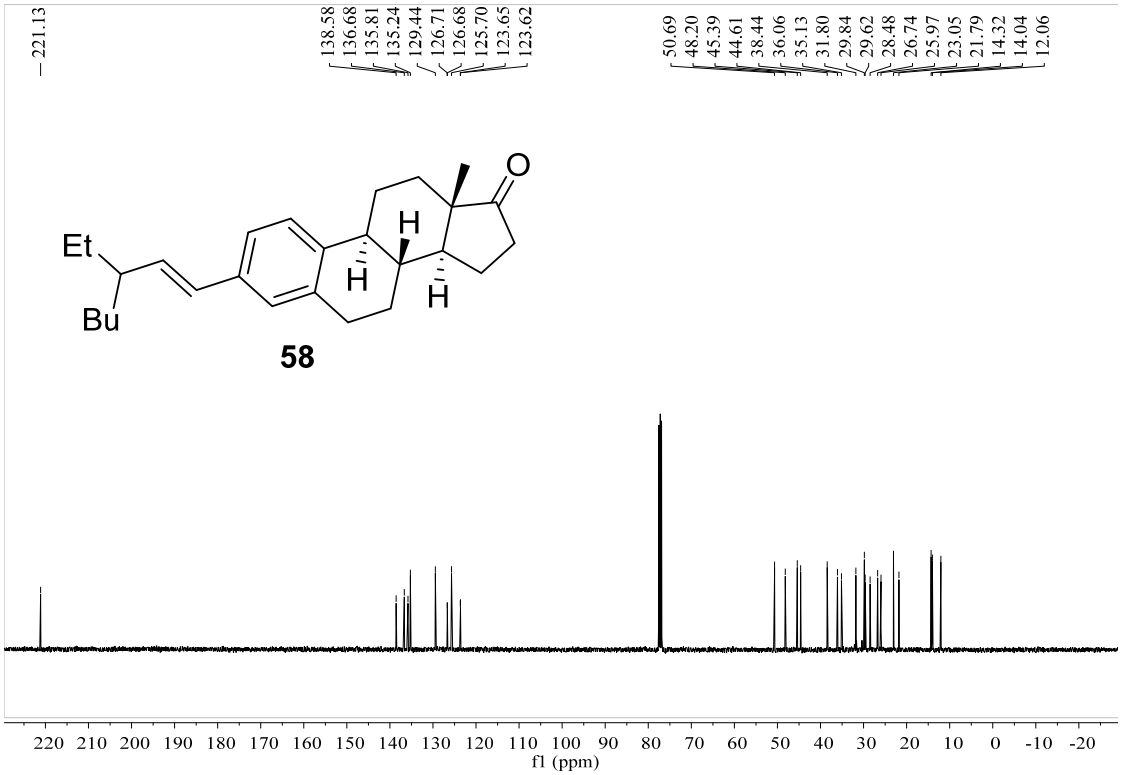



**Figure S153.** $^{13}$C NMR spectrum of compound **58,** related to **Scheme 2.**

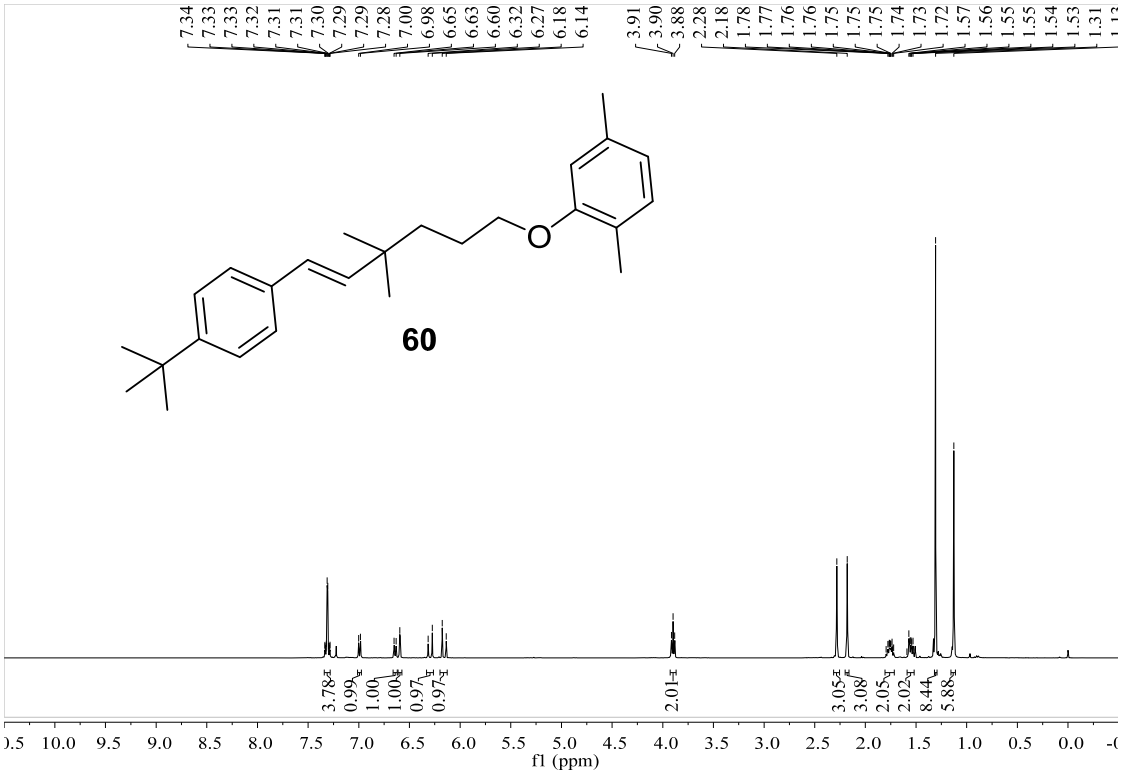



**Figure S154.** $^{1}$H NMR spectrum of compound **60,** related to **Scheme 2.**

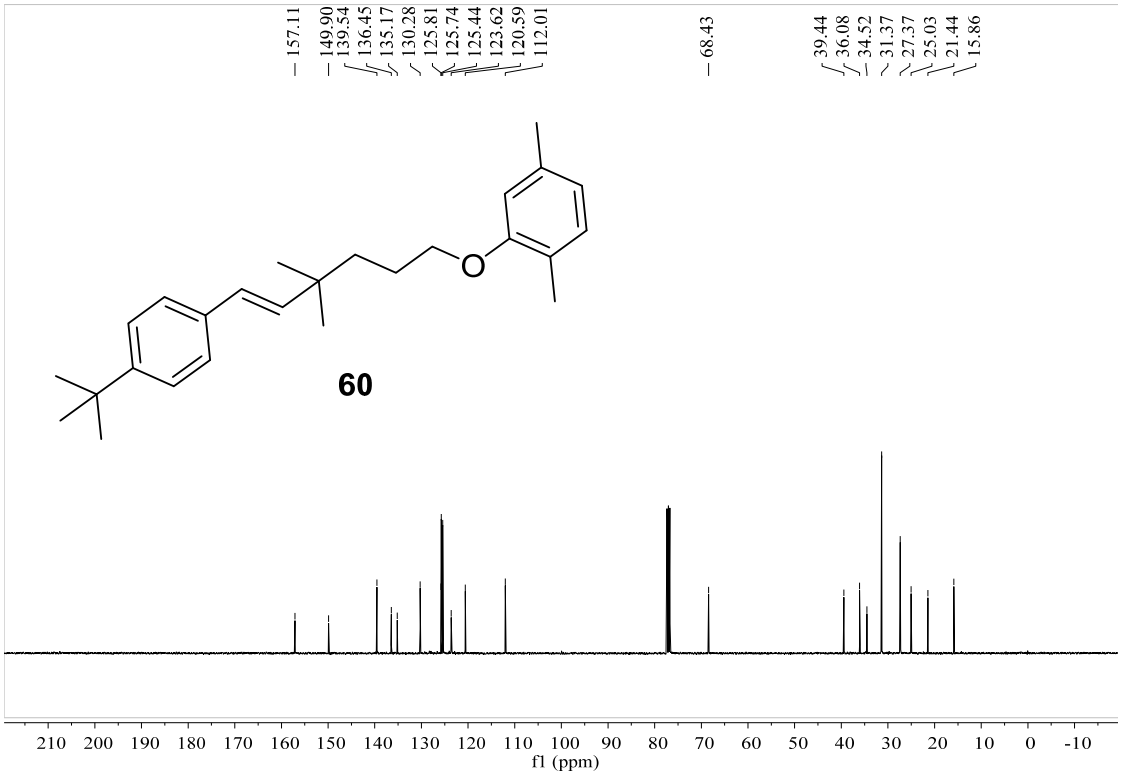



**Figure S155.** $^{13}$C NMR spectrum of compound **60,** related to **Scheme 2.**

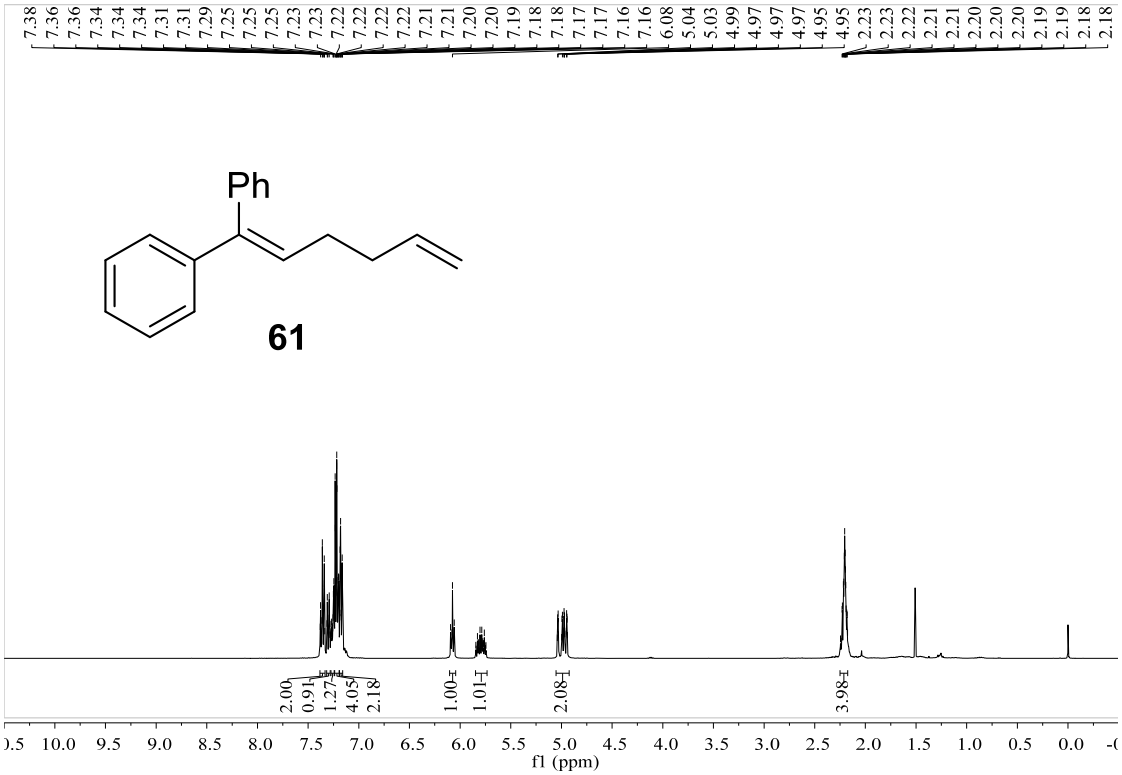



**Figure S156.** $^{1}$H NMR spectrum of compound **61,** related to **Scheme 3A.**

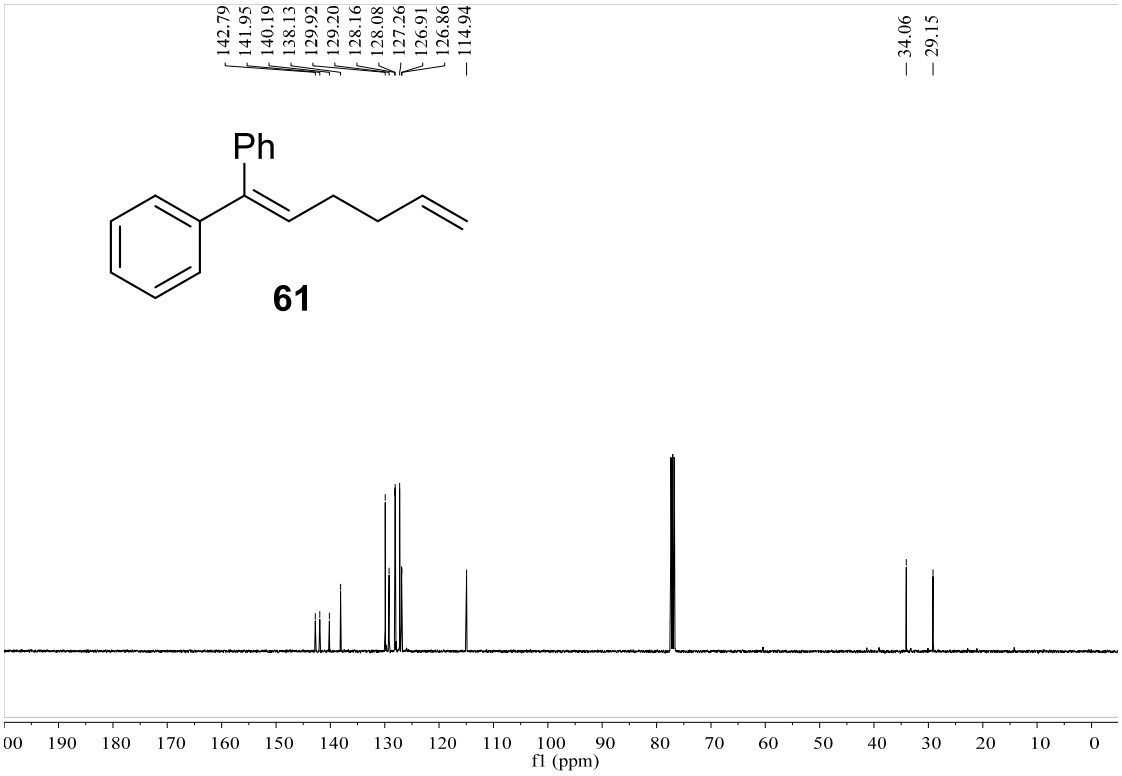



**Figure S157.** $^{13}$C NMR spectrum of compound **61,** related to **Scheme 3A.**

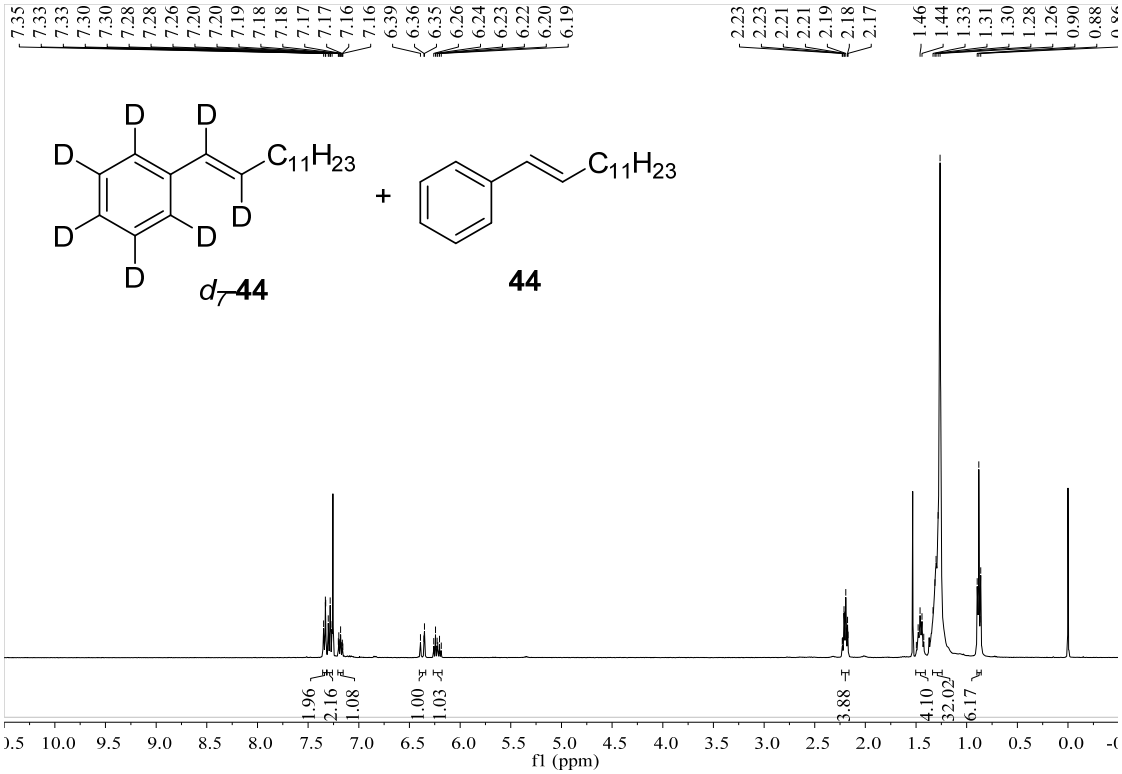



**Figure S158.** $^1$H NMR spectrum of compounds $d_7$**-44 and 44,** related to **Scheme 3B.**

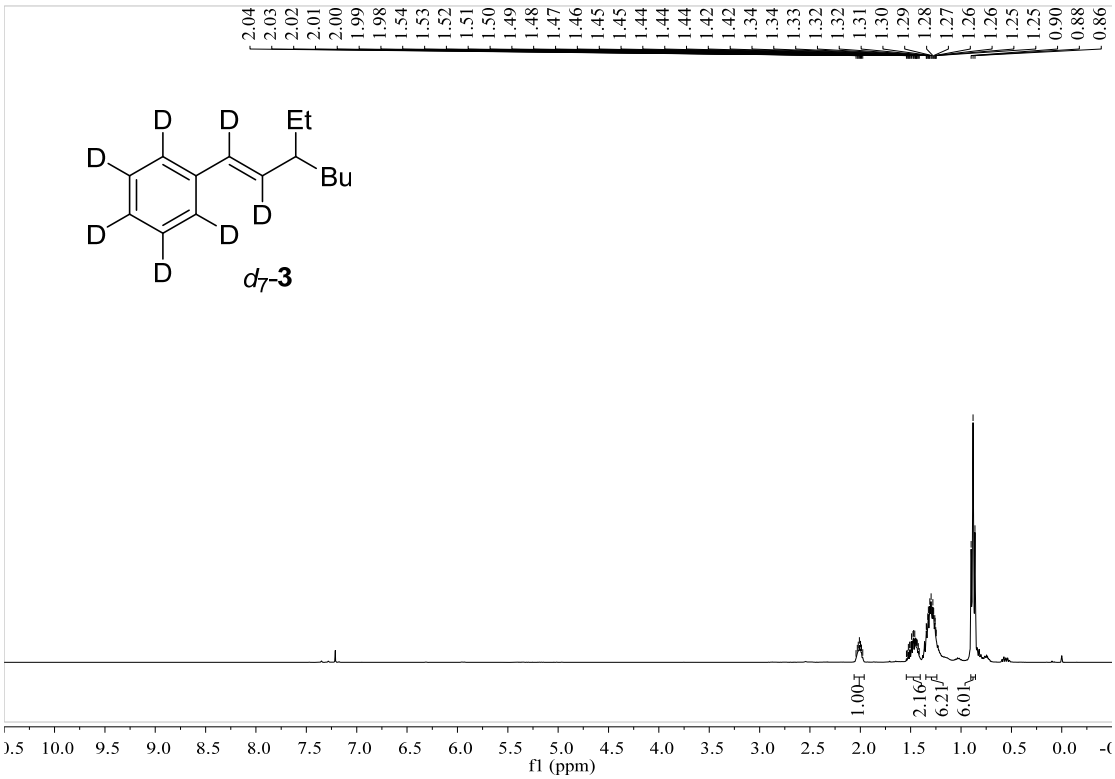



**Figure S159.** $^1$H NMR spectrum of compound $d_7$**-3,** related to **Scheme 3B.**

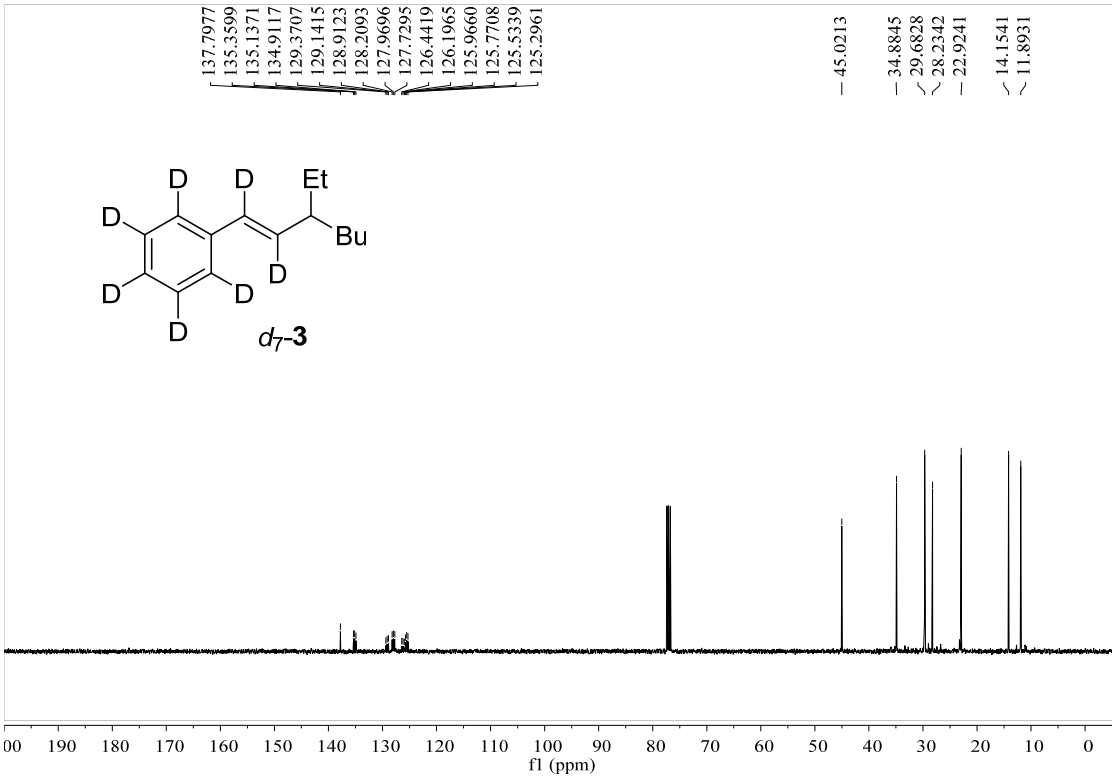



**Figure S160.** $^{13}$C NMR spectrum of compound $d_7$**-3,** related to **Scheme 3B.**

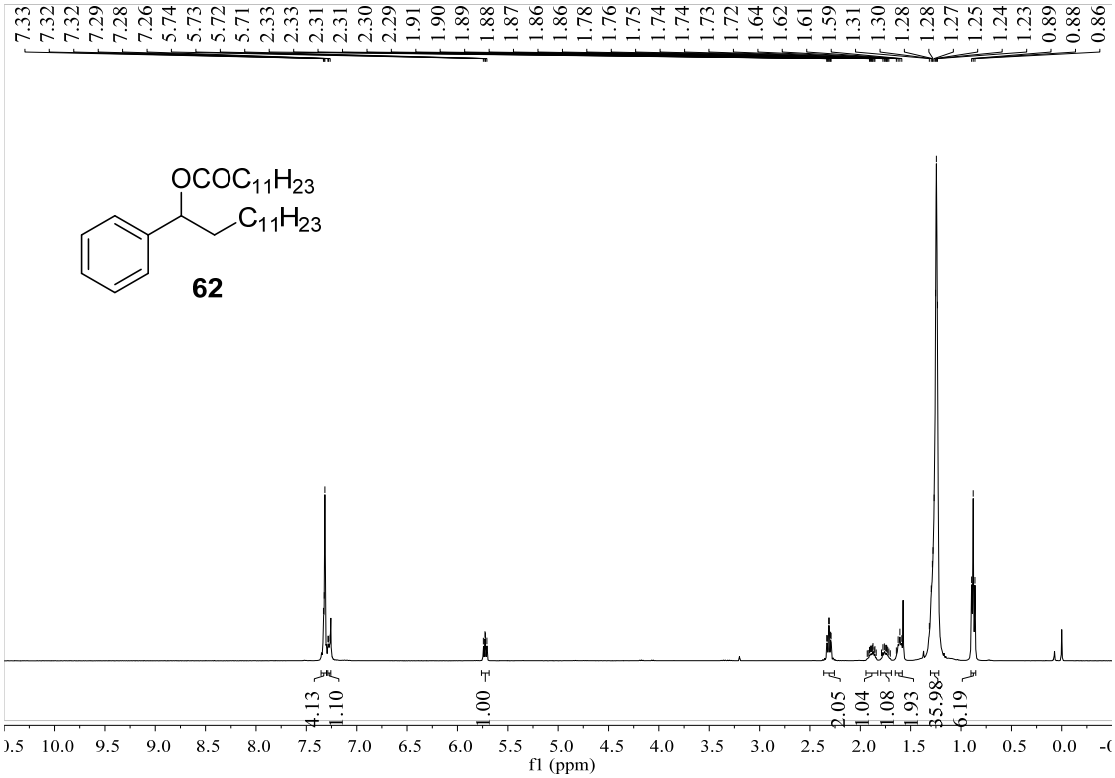



**Figure S161.** $^{1}$H NMR spectrum of compound **62,** related to **Scheme 3C.**

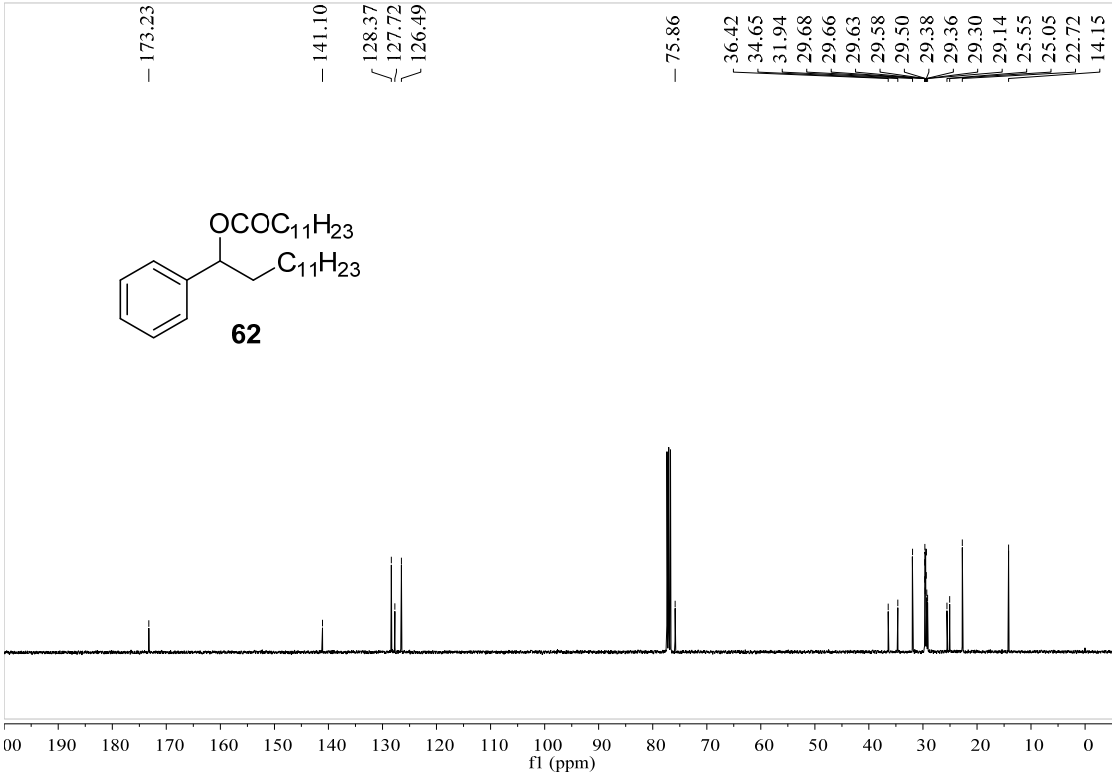



**Figure S162.** $^{13}$C NMR spectrum of compound **62,** related to **Scheme 3C.**

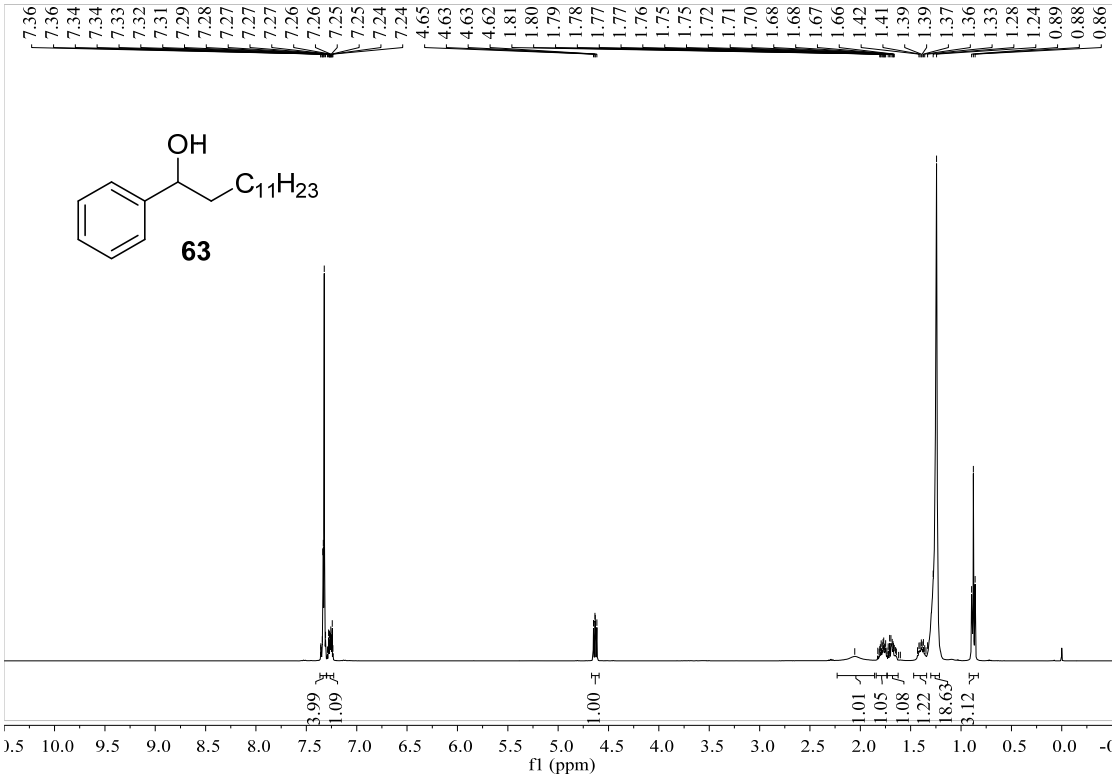



**Figure S163.** $^{1}$H NMR spectrum of compound **63,** related to **Scheme 3C.**

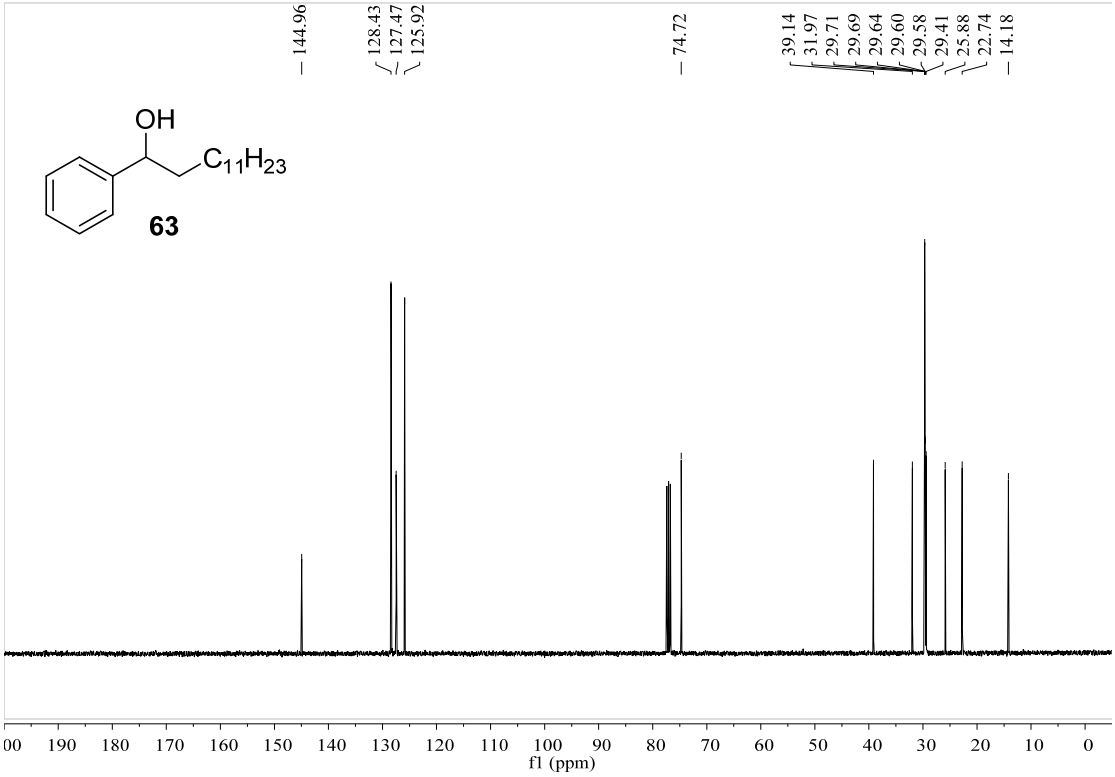
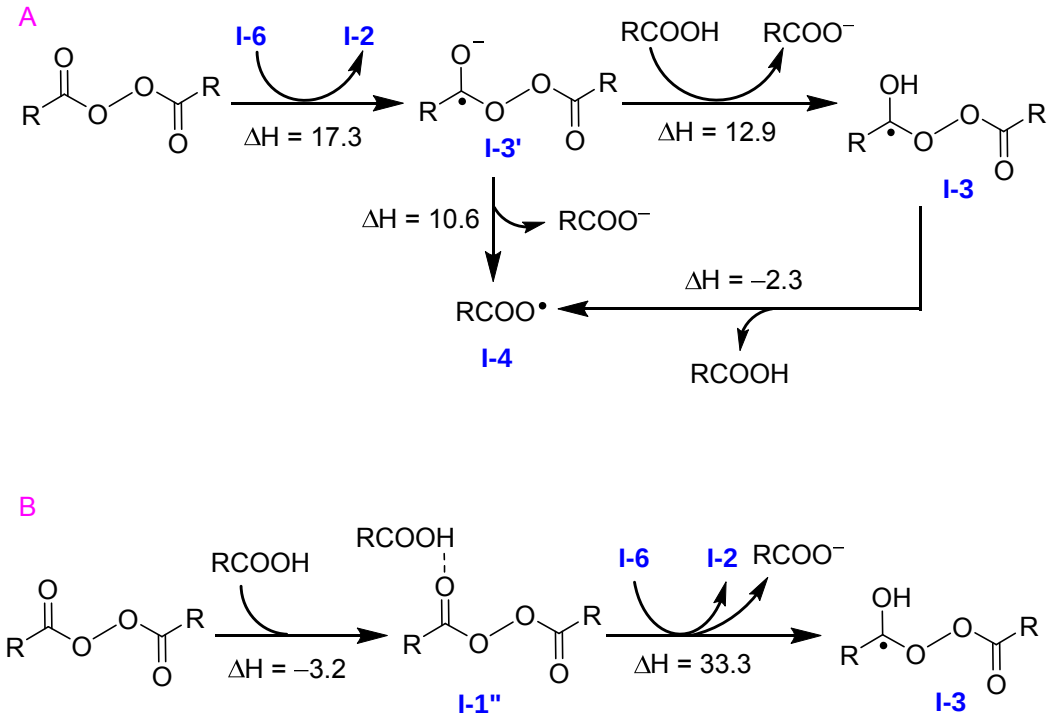



**Figure S164.** $^{13}$C NMR spectrum of compound **63,** related to **Scheme 3C.**

## Supplemental Schemes

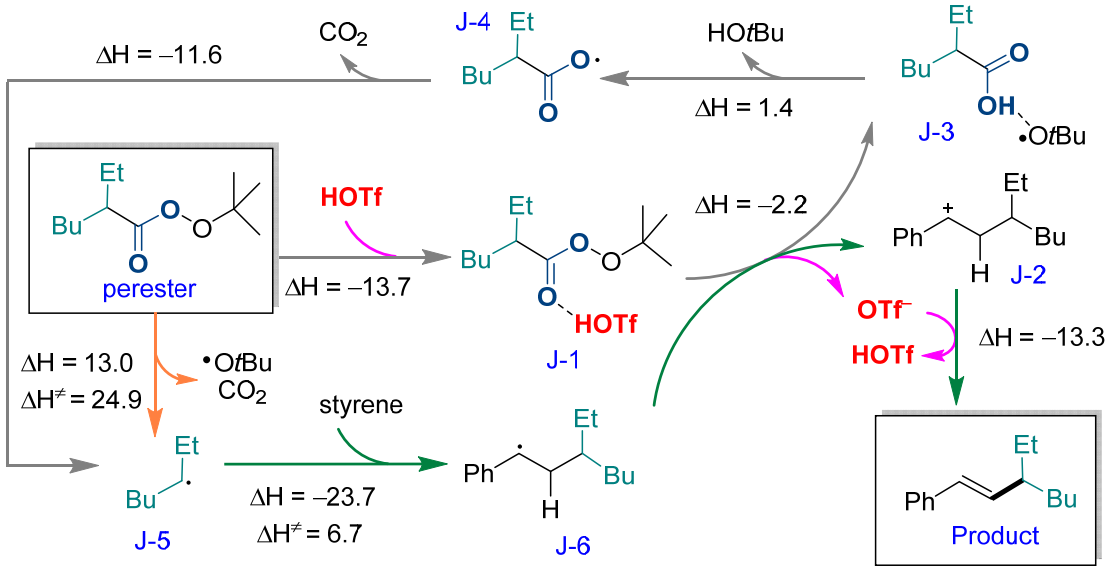
Note: R = *n*-$C_5H_{11}$ was used for the calculation




**Scheme S1**. The reaction profiles without HOTf. Related to **Scheme 4.**

(A) Direct electron transfer from **I6** to peroxide requires a high energy of 17.3 kcal/mol. Protonation of **I-2** by RCOOH to form **I-3** is endothermic of 12.9 kcal/mol. Without acid direct O-O cleavage to form **I-4** is also endothermic of 10.6 kcal/mol. Combined with previous energy requirement of electron transfer the overall reaction energies are more than 27 kcal/mol.

(B) Binding a carboxylic acid RCOOH to peroxide forms a weak hydrogen bond of 3.2 kcal/mol. However, electron transfer process requires high energy of 33.3 kcal/mol. As such, both paths are disfavored compared to the HOTf involved reactions.




**Scheme S2**. The reaction profile of perester, Related to **Scheme 4.**

The perester species has a similar mechanism catalyzed by HOTf. Before the catalytic cycle the R• radical **J-5** can be formed by homolytic dissociation of the alkyl diacyl peroxide (perester), which is a very slow step with a high barrier of 24.9 kcal/mol. However, this is considered as the *trigger* to invoke the following catalytic cycle. Attack on the styrene substrate by the active species R• radical **J-5** to form a benzyl radical (**J-6**) leads to energies lower by 23.7 kcal/mol with a small barrier of 6.7 kcal/mol, indicating that such reaction is both thermodynamically and kinetically favourable. In the beginning of the catalytic cycle, LPO binding a molecule of HOTf forms a complex I-1 with a strong hydrogen bonding of 13.7 kcal/mol. This complex oxidizes benzyl radical (**J-6**) to yield a benzyl cation species (**J-2**), a radical (**J-3**) and an OTf- anion, which is exothermic by 2.2 kcal/mol. Meanwhile, the generated $OTf^-$ deprotonates **J-1** to yield the product and regenerate acid HOTf with reaction energy of -13.3 kcal/mol. Thus, from the reactions of LPO and **J-6** to the product and **J-3** stepwise electron and proton transfers are promoted by HOTf, which serves as the driving force and proton source for the reaction. Thereby hydrogen transfer of **J-3** leads to RCOO• radical (**J-4**) and tBuOH, which is nearly thermal neutral of 1.4 kcal/mol without any barrier. Subsequently, C-C cleavage of **J-4** is exothermic by 11.6 kcal/mol in energy which releases the active species R• radical (**J-5**) and $CO_2$ to close the catalytic cycle.

## Supplemental Tables

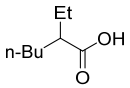
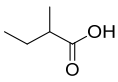
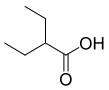
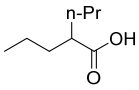
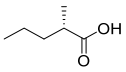
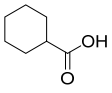
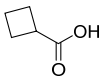
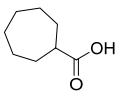
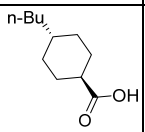
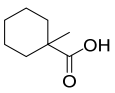
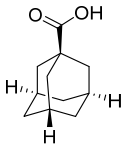
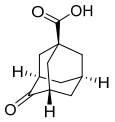
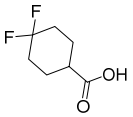
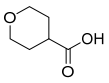
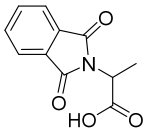
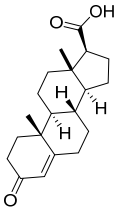
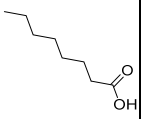
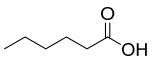
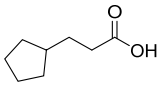
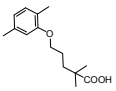
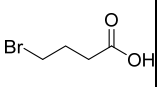
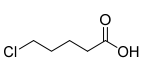
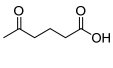
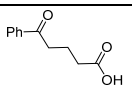
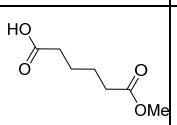
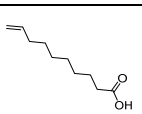
| Acids | Company | Acids | Company | Acids | Company |
|---|---|---|---|---|---|
|  | Energy-chemical |  | Energy-chemical |  | Energy-chemical |
|  | Energy-chemical |  | Energy-chemical |  | Adamas-beta |
|  | Energy-chemical |  | Energy-chemical |  | Adamas-beta |
|  | Energy-chemical |  | TCI-chemicals |  | Energy-chemical |
|  | Bide-pharmatech |  | Bide-pharmatech |  | Bide-pharmatech |
|  | Aladdin |  | Heowns |  | Energy-chemical |
|  | Energy-chemical |  | Energy-chemical |  | Energy-chemical |
|  | Inno-chem |  | Bide-pharmatech |  | Adamas-beta |
|  | Bide-pharmatech |  | Energy-chemical |  | Energy-chemical |

**Table S1**. Sources of acids, related to Figure 2 and Figure 3.

| Alkenes | Company | Alkenes | Company | Alkenes | Company |
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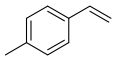
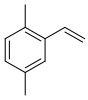
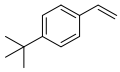
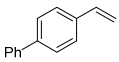
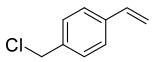
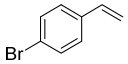
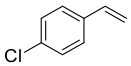
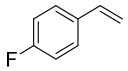
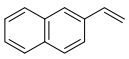
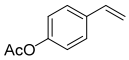
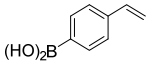
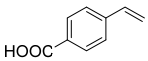
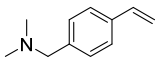
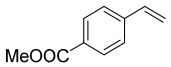
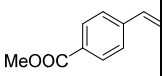
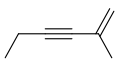
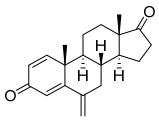
|  | Energy-chemical |  | Energy-chemical |  | Adamas-beta |
|  | Adamas-beta |  | Alfa Aesar |  | Energy-chemical |
|  | Energy-chemical |  | Meryer |  | Energy-chemical |
|  | Energy-chemical |  | Energy-chemical |  | Adamas |
|  | Meryer |  | Energy-chemical |  | Energy-chemical |
|  | Energy-chemical |  | Jkchemical |  | Energy-chemical |
|  | Energy-chemical |  | Energy-chemical |  | Energy-chemical |
|  | Sigma- aldrich |  | Energy-chemical | | |

**Table S2**. Sources of alkenes, related to Figure 1, Figure 2 and Figure 3.

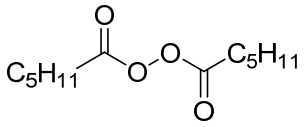
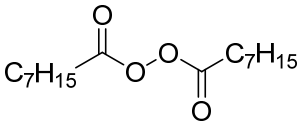
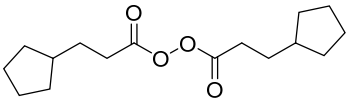
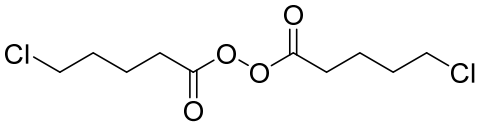
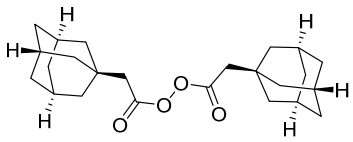
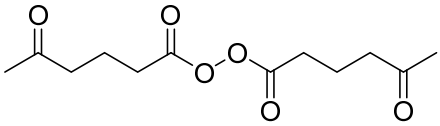
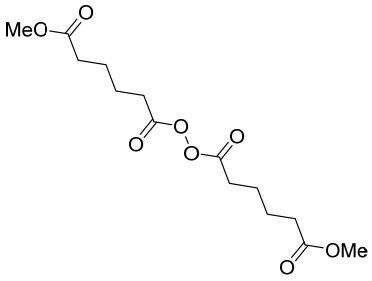
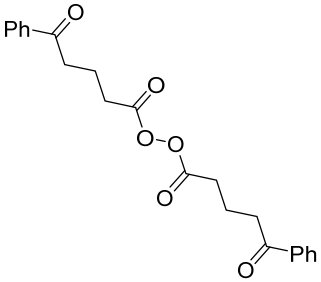
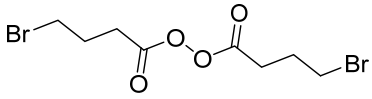
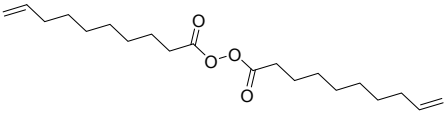
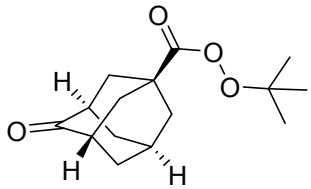
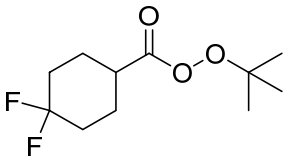
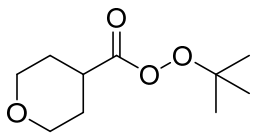
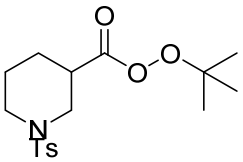
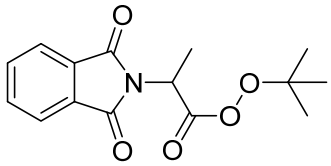
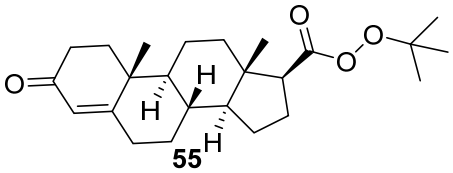
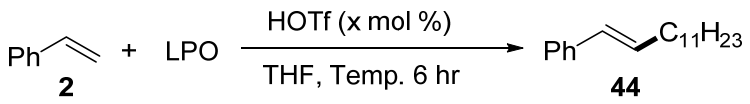
| structure | yield | structure | yield |
|---|---|---|---|
|  | 90% |  | 85% |
|  | 84% |  | 65% |
|  | 84% |  | 73% |
|  | 71% |  | 76% |
|  | 55% |  | 76% |
|  | 75% |  | 70% |
|  | 78% |  | 70% |
|  | 64% |  | 80% |

**Table S3.** The synthesis of peroxides, related to Figure 3.




| Entry | HOTf ( x mol %) | THF (y mL) | Temp. | Yield (%)[b] |
|---|---|---|---|---|
| 1 | 5 mol % | 2 mL | 90°C | 5% |
| 2 | 10 mol % | 2 mL | 90°C | 10% |
| 3 | 15 mol % | 2 mL | 90°C | 36% |
| 4 | 20 mol % | 2 mL | 90°C | 65% |
| 5 | 40 mol % | 2 mL | 90°C | 60% |
| 6 | 50 mol % | 2 mL | 90°C | 76%[c] |
| 7 | 20 mol % | 2 mL | 100°C | 62% |
| 8[d] | 20 mol % | 2 mL | 80°C | 43% |
| 9[d] | 20 mol % | 2 mL | 70°C | 6% |
| 10 | 20 mol % | 1 mL | 90°C | 76% (73%[c]) |
| 11[e] | 20 mol % | 1 mL | 90°C | 67% |
| 12[f] | 20 mol % | 1 mL | 90°C | 54% |
| 13[g] | 20 mol % | 1 mL | 90°C | 70% |
| 14[h] | 20 mol % | 1 mL | 90°C | 40% |

**Table S4.** Optimizations of reaction conditions with primary aliphatic acid, Related to **Figure 3**.[a]

[a]**2** (0.5 mmol), LPO (1.0 mmol).

[b]Yield detected by GC.

[c]Isolated product.

[d]Reaction with 8 hr.

[e]**2** (0.5 mmol), LPO (0.75 mmol).

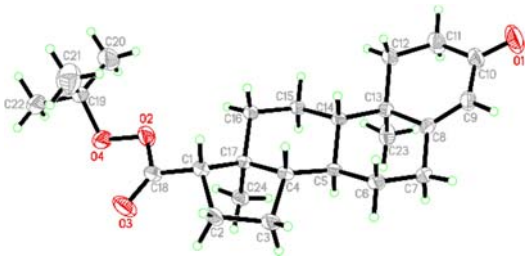
[f]**2** (0.5 mmol), LPO (0.5 mmol).

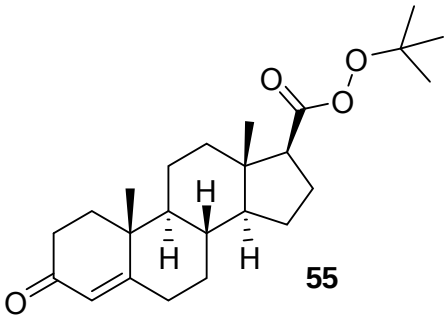
[g]**2** (0.6 mmol), LPO (0.5 mmol).

[h]**2** (0.75 mmol), LPO (0.5 mmol).

**Single Crystal Data of 55 and 56**

Single crystal of **55** and **56** suitable for X-ray diffraction was mounted in Paratone oil onto a glass fiber and frozen under a nitrogen cold stream. The data was collected at 220.0(1) K using a Agilent SuperNova, Dual, Cu at zero, Atlas fitted with Cu Kα radiation (λ = 1.54184 Å). Data collection and unit cell refinement were executed by using CrysAlisPro software. Data processing and absorption correction, giving minimum and maximum transmission factors, were accomplished with CrysAlisPro. The structure was solved with the SHELXT-2014 and refined with the SHELXL-2014 using Least Squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atom positions were determined by geometry and refined by a riding model. CCDC 1477011 and CCDC 1476738 for **55** and **56** contain the supplementary crystallographic data. Crystal data and structure refinements of **55** and **56** are listed in Table S5 and Table S6. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

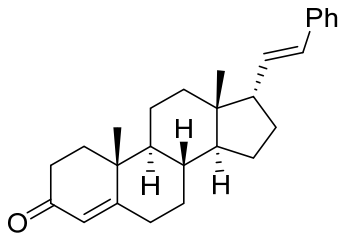




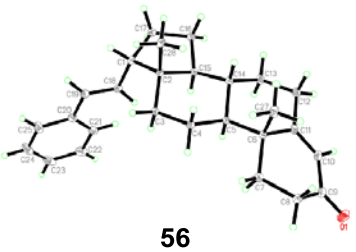

**55**

| | |
|---|---|
| Identification code | **55** |
| Empirical formula | $C_{24}$ $H_{36}$ $O_4$ |
| Formula weight | 388.53 |
| Temperature | 220.0(1) K |
| Wavelength | 1.54184 Å |
| Crystal system | Orthorhombic |
| Space group | P 21 21 21 |
| Unit cell dimensions | a = 6.16790(10) Å |
| | b = 12.5681(3) Å |
| | c = 29.0822(7) Å |
| Volume | 2254.42(8) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.145 $Mg/m^3$ |
| Absorption coefficient | 0.603 $mm^{-1}$ |
| F(000) | 848 |
| Crystal size | 0.220 x 0.200 x 0.170 $mm^3$ |
| Theta range for data collection | 3.831 to 73.663°. |
| Index ranges | -5<=h<=7, -9<=k<=15, -23<=l<=35 |
| Reflections collected | 7382 |
| Independent reflections | 3937 [R(int) = 0.0387] |
| Completeness to theta = 67.684° | 99.3 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.60854 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3937 / 6 / 258 |
| Goodness-of-fit on $F^2$ | 1.023 |
| Final R indices [I>2sigma(I)] | R1 = 0.0531, wR2 = 0.1363 |
| R indices (all data) | R1 = 0.0649, wR2 = 0.1499 |
| Absolute structure parameter | 0.0(3) |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.276 and -0.212 $e.Å^{-3}$ |

**Table S5**. Crystal data and structure refinement for **55**, Related to **Scheme 2**.




**56**



**56**

| | |
|---|---|
| Identification code | **56** |
| Empirical formula | $C_{27}$ $H_{34}$ O |
| Formula weight | 374.54 |
| Temperature | 100.0(2) K |
| Wavelength | 1.54184 Å |
| Crystal system | Orthorhombic |
| Space group | P 21 21 21 |
| Unit cell dimensions | a = 6.23490(10) Å |
| | b = 28.7978(4) Å |
| | c = 11.7959(2) Å |
| Volume | 2117.97(6) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.175 $Mg/m^3$ |
| Absorption coefficient | 0.520 $mm^{-1}$ |
| F(000) | 816 |
| Crystal size | 0.200 x 0.180 x 0.150 $mm^3$ |
| Theta range for data collection | 4.050 to 73.331°. |
| Index ranges | -7<=h<=2, -31<=k<=35, -14<=l<=7 |
| Reflections collected | 5630 |
| Independent reflections | 3761 [R(int) = 0.0141] |
| Completeness to theta = 67.684° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.88083 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3761 / 0 / 256 |
| Goodness-of-fit on $F^2$ | 1.025 |
| Final R indices [I>2sigma(I)] | R1 = 0.0291, wR2 = 0.0733 |
| R indices (all data) | R1 = 0.0302, wR2 = 0.0742 |
| Absolute structure parameter | -0.29(15) |
| Extinction coefficient | 0.0041(3) |
| Largest diff. peak and hole | 0.252 and -0.140 $e.Å^{-3}$ |

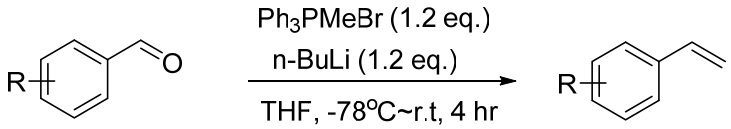
**Table S6**. Crystal data and structure refinement for **56**, Related to **Scheme 2**.

# Transparent Methods

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by Innovative Technology Solvent Purification System. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography. GC-MS data were recorded on Thermo ISQ QD. $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded on Bruker-BioSpin AVANCE III HD. Data for $^{1}H$ NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and integration. Data for $^{13}C$ NMR spectra are reported relative to chloroform as an internal standard (77.23 ppm) and are reported in terms of chemical shift (ppm). HRMS data were recorded on Waters Micromass GCT Premier or Thermo Fisher Scientific LTQ FTICR-MS.

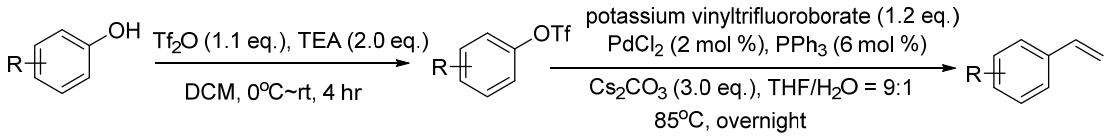
### Experimental procedures for synthesis of materials

#### Procedure A for the synthesis of alkenes




General procedure (Haubenreisser et al., 2016): The reaction vessel was charged with phosphonium salt (1.2 equiv) in dry THF. To the stirred mixture, *n*-butyl lithium (1.2 equiv) was added under $N_2$ atmosphere at -78°C. The mixture was stirred at 0°C for 5 mins and then substituted aldehyde (1.0 equiv.) in dry THF was added dropwise in over 15 min. After stirring at rt for 4 hr, the mixture was quenched with saturated $NH_4Cl$, then extracted three times with dichloromethane and water. The combined organic layers were dried over anhydrous sodium sulfate, concentrated and purified by flash column chromatography afford the desired product.

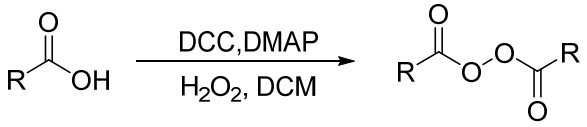
#### Procedure B for the synthesis of alkenes




General procedure (Huang and Doyle, 2012): A flask was flame dried and charged with phenol (1.0 equiv), dichloromethane, and $Et_3N$ (2.0 equiv). The mixture was cooled in a 0°C ice-water bath, and $Tf_2O$ (1.1 equiv) was added dropwise. The mixture was allowed to warm up to room temperature and stirred at room temperature under argon for 5 hr. The resulting brown mixture was diluted with dichloromethane, washed with sat. $NH_4Cl$, and the aqueous layer was

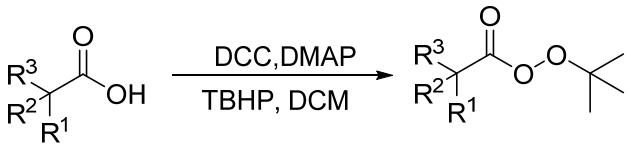
extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$, and the filtrate was concentrated. The crude was purified with column chromatography to afford triflate. A threaded tube was charged with triflate (1.0 equiv), potassium vinyltrifluoroborate (1.2 equiv), $PdCl_2$ (2 mol %), $PPh_3$ (6 mol %), $Cs_2CO_3$ (3.0 equiv) were added, then THF and water were added under $N_2$ atmosphere. The mixture was stirred at 85°C for overnight. The resulting dark brown mixture was allowed to cool to room temperature, diluted with dichloromethane, and washed with water. The aqueous layer was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$, and the filtrate was concentrated. The crude was purified with column chromatography to afford the desired product.

**Procedure C for the synthesis of diacyl peroxides**




General procedure (Jian et al., 2017): A solution of DMAP (10 mol %), 30% hydrogen peroxide (1.2 equiv), and acid in $CH_2Cl_2$ was cooled to -5°C for about 10 min. Then DCC (1.2 equiv) was added. Then the mixture was stirred at -5°C to room temperature for 1.5 ~4 hr. The solution was concentrated on a rotary evaporator under vacuum at 10~15°C and the residue was chromatographed on silica gel to give the diacyl peroxide.

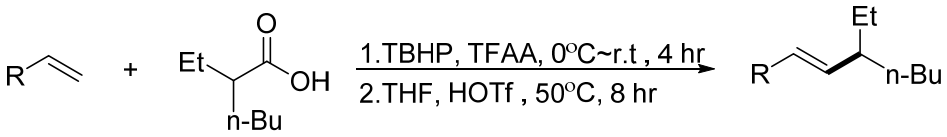
**Procedure D for the synthesis of peresters**




General procedure (Zhu et al., 2017): A solution of DMAP (10 mol %), TBHP (aqueous solution, 1.2 equiv), and acid in $CH_2Cl_2$ was cooled to -5°C for about 10 min. Then DCC (1.2 equiv) was added. Then the mixture was stirred at -5°C to room temperature for 4 hr. The solution was concentrated on a rotary evaporator under vacuum at 20~25°C and the residue was chromatographed on silica gel to give the perester.

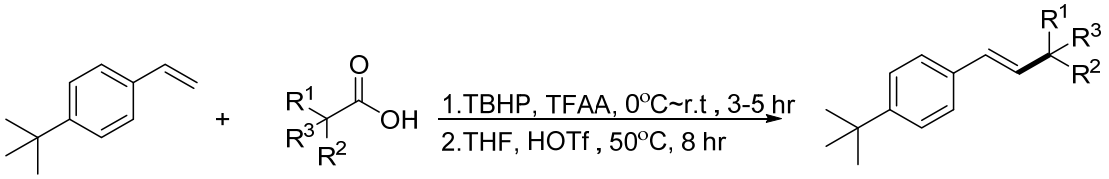
**General procedure for the alkyl-Heck-type reaction**

**Procedure E for the alkyl-Heck-type reaction of alkenes**




To a flame-dried Schlenk tube were added 2-ethylhexanoic acid (1.5 mmol, 3.0 equiv), TBHP (1.5 mmol, 3.0 equiv, in decane) and TFAA (2.0 mmol, 4.0 equiv) at 0°C under the atmosphere of nitrogen. The mixture was then stirred at rt for 4 hours. After completion, THF (2 mL), alkene (0.5 mmol, 1.0 equiv) and HOTf (0.05 mmol, 10 mol %) were added into the Schlenk tube under the atmosphere of nitrogen. The mixture was then stirred at 50°C for 8 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product.

**Procedure F for the alkyl-Heck-type reaction of secondary and tertiary aliphatic acids**




General procedure: To a flame-dried Schlenk tube were added acid (1.5 mmol, 3.0 equiv), TBHP (1.5 mmol, 3.0 equiv, in decane) and TFAA (2.0 mmol, 4.0 equiv) at 0°C under the atmosphere of nitrogen. The mixture was then stirred at rt for 3-5 hours. After completion, THF (2 mL), 4-*tert*-butylstyrene (0.5 mmol, 1.0 equiv) and HOTf (0.05 mmol, 10 mol %) were added into the Schlenk tube under the atmosphere of nitrogen. The mixture was then stirred at 50°C for 8 hours. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product.

**Procedure G for the alkyl-Heck-type reaction with peresters**

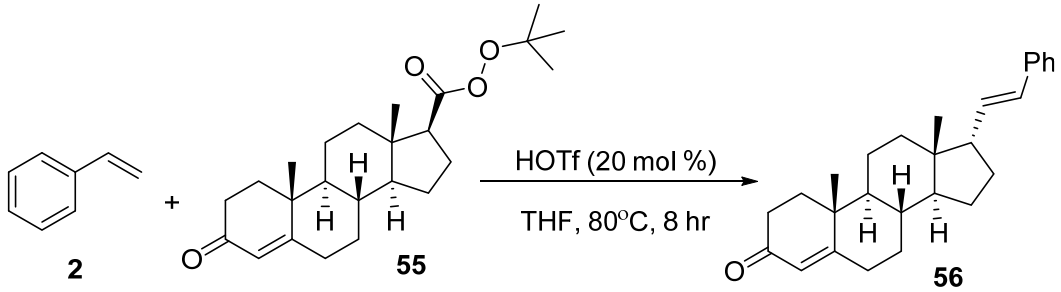

To a flame-dried Schlenk tube were added THF (2 mL), 4-*tert*-butylstyrene (0.5 mmol, 1.0 equiv), perester (1.25 mmol, 2.5 equiv) and HOTf (0.1 mmol, 20 mol %) under the atmosphere of nitrogen. The mixture was then stirred at 80°C for 6 hours. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product.

**Procedure H for the alkyl-Heck-type reaction with diacyl peroxides**

To a flame-dried Schlenk tube were added THF (1 mL), styrene (0.5 mmol, 1.0 equiv) diacyl peroxides (1.0 mmol, 2.0 equiv) and HOTf (0.1 mmol, 20 mol %) under the atmosphere of nitrogen. The mixture was then stirred at 90$^{o}$C for 6 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product.

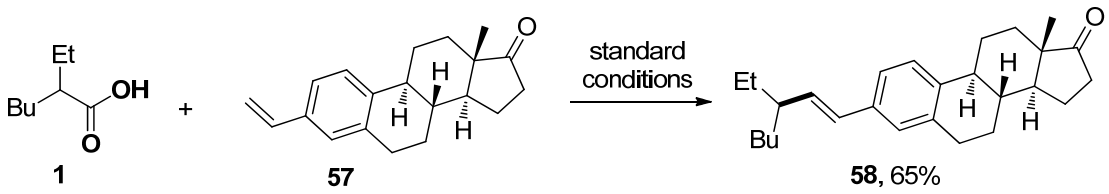
**Experimental procedures for synthetic applications**

(i)



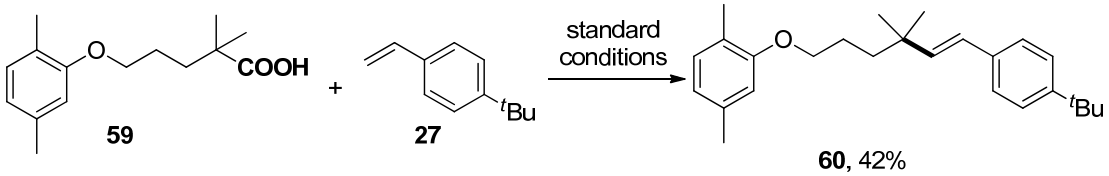

To a flame-dried Schlenk tube were added THF (2 mL), styrene **2** (0.5 mmol, 1.0 equiv) perester **55** (1.25 mmol, 2.5 equiv) and HOTf (0.1 mmol, 20 mol %) under the atmosphere of nitrogen. The mixture was then stirred at 80°C for 8 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product **56**.

(ii)




To a flame-dried Schlenk tube were added acid **1** (1.5 mmol, 3.0 equiv), TBHP (1.5 mmol, 3.0 equiv) and TFAA (2.0 mmol, 4.0 equiv) at 0°C under the atmosphere of nitrogen. The mixture was then stirred at rt for 5 hr. After completion, THF (2 mL), alkene **57** (0.5 mmol, 1.0 equiv) and HOTf (0.05 mmol, 10 mol %) were added into the Schlenk tube under the atmosphere of nitrogen. The mixture was then stirred at 50°C for 8 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product **58**.

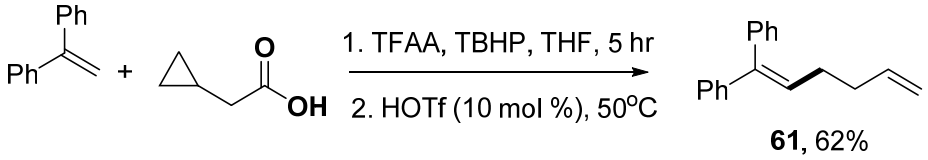
(iii)




To a flame-dried Schlenk tube were added acid **59** (1.5 mmol, 3.0 equiv), TBHP (1.5 mmol, 3.0 equiv) and TFAA (2.0 mmol, 4.0 equiv) at 0°C under the atmosphere of nitrogen. The mixture was then stirred at rt for 5 hr. After completion THF (2 mL), 4-*tert*-butylstyrene **27** (0.5 mmol, 1.0 equiv) and HOTf (0.05 mmol, 10 mol %) were added into the Schlenk tube under the atmosphere of nitrogen. The mixture was then stirred at 50°C for 8 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product **60**.

## Experimental procedures for preliminary mechanistic studies

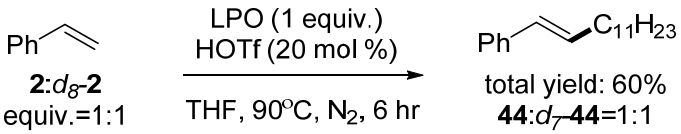
### Radical clock experiment



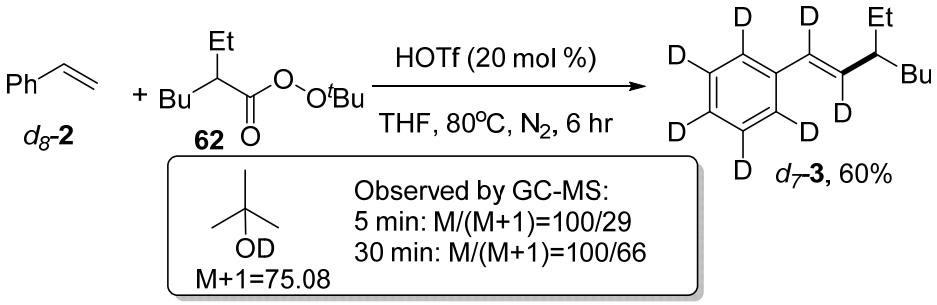

**61**, 62%

To a flame-dried Schlenk tube were added acid (1.5 mmol, 3.0 equiv), TBHP (1.5 mmol, 3.0 equiv) and TFAA (2.0 mmol, 4.0 equiv) at 0°C under the atmosphere of nitrogen. The mixture was then stirred at rt for 5 hr. After completion, THF (2 mL), styrene (0.5 mmol, 1.0 equiv) and HOTf (0.05 mmol, 10 mol %) were added into the Schlenk tube under the atmosphere of nitrogen. The mixture was then stirred at 50°C for 8 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product **61**.

### Deuterium labeling experiment

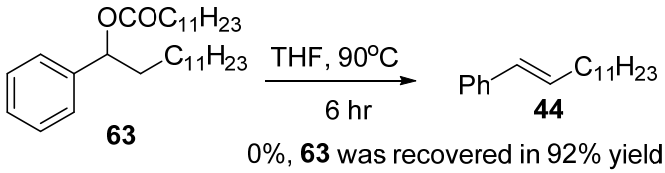



To a flame-dried Schlenk tube were added THF (1 mL), 2 (1.0 mmol, 1.0 equiv), $d_8$-**2** (1.0 mmol, 1.0 equiv), LPO (0.5 mmol, 0.5 equiv) and HOTf (0.1 mmol, 20 mol %) under the atmosphere of nitrogen. The mixture was then stirred at 90°C for 6 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product **44** and $d_7$-**44**.




To a flame-dried Schlenk tube were added THF (2 mL), $d_8$-**2** (0.50 mmol, 1.0 equiv), **62** (1.25 mmol, 2.5 equiv) and HOTf (0.1 mmol, 20 mol %) under the atmosphere of nitrogen. The mixture was then stirred at 80°C. The reaction mixture was tested by GC-MS after 5 minutes and 30 minutes. The deuterated side-products *d*(OD)-butanol was detected by GC-MS. The mixture was then stirred at 80°C for 6 hr. After the reaction mixture was cooled to ambient temperature. The solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired $d_7$-**3**.

**Exclusion of possible intermediates**

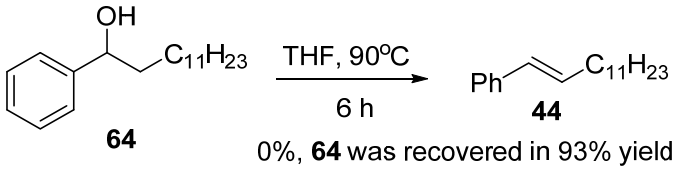



0%, **63** was recovered in 92% yield
0%, $C_{11}H_{23}COOH$ (1 equiv), **63** was recovered in 93% yield
91%, HOTf (20 mol %).

Ester **63** (Ge et al., 2017): (0.2 mmol) was charged in anhydrous THF (0.5 mL) at 90°C and then stirred for 6 hr. No reaction was observed and the ester **63** was recovered in 92% yield.

Ester **63** (0.2 mmol) and $C_{11}H_{23}COOH$ (1 equiv) were charged in anhydrous THF (0.5 mL) at 90°C and then stirred for 6 hr. No reaction was observed and the ester **63** was recovered in 93% yield.

Ester **63** (0.2 mmol) and HOTf (20 mol %) were charged in anhydrous THF (0.5 mL) at 90°C and then stirred for 6hr. The reaction mixture was diluted with DCM (30 mL) and washed with saturated aq. $NaHCO_3$. The organic layer was dried (anhydrous $Na_2SO_4$), filtered, and concentrated in vacuo. The residue was chromatographed on silica gel affording product **44** in 91% yield.



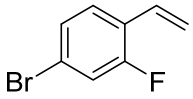

0%, **64** was recovered in 93% yield
0%, $C_{11}H_{23}COOH$ (1 equiv), **64** was recovered in 93% yield
87%, HOTf(20 mol %, 6 hr)

Benzyl alcohol **64** (Jian et al., 2017) (0.2 mmol) was charged in anhydrous THF (0.5 mL) at 90°C and then stirred for 6 hr. No reaction was observed and the alcohol **64** was recovered in 93% yield.

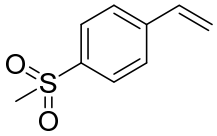
Benzyl alcohol **64** (0.2 mmol) and $C_{11}H_{23}COOH$ (1 equiv) were charged in anhydrous THF (0.5 mL) at 90°C and then stirred for 6hr. No reaction was observed and the alcohol **64** was recovered in 93% yield.

Benzyl alcohol **64** (0.2 mmol) and HOTf (20 mol %) were charged in anhydrous THF (0.5 mL) at 90°C and then stirred for 6hr. The reaction mixture was diluted with DCM (30 mL) and washed with saturated aq. $NaHCO_3$. The organic layer was dried (anhydrous $Na_2SO_4$), filtered, and concentrated in vacuo. The residue was chromatographed on silica gel affording product **44** in 87% yield.

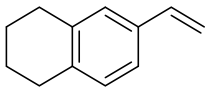
**Characterization of all compounds**



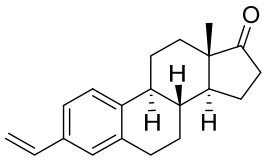

Following procedure A for the synthesis of alkenes, 4-bromo-2-fluoro-1-vinylbenzene (related to **Figure 1**) was obtained as a clear liquid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 8.3 Hz, 1H), 7.26 – 7.19 (m, 2H), 6.79 (dd, *J* = 17.7, 11.2 Hz, 1H), 5.81 (d, *J* = 17.7 Hz, 1H), 5.40 (d, *J* = 11.2 Hz, 1H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 159.92 (d, *J* = 254.0 Hz), 128.45 (d, *J* = 3.6 Hz), 128.11 (d, *J* = 4.4 Hz) 127.43 (d, *J* = 3.7 Hz), 124.49 (d, *J* = 12.4 Hz), 121.34 (d, *J* = 9.7 Hz), 119.34 (d, *J* = 25.5 Hz), 117.10 (d, *J* = 4.7 Hz). $^{19}$F NMR (376 MHz, Chloroform-*d*) δ -115.94.




Following procedure A for synthesis of alkenes, 1-(methylsulfonyl)-4-vinylbenzene (related to **Figure 1**) was obtained as a white solid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 6.77 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.91 (d, *J* = 17.6 Hz, 1H), 5.47 (d, *J* = 10.9 Hz, 1H), 3.05 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 142.88, 139.34, 135.21, 127.74, 126.95, 118.02, 44.57.

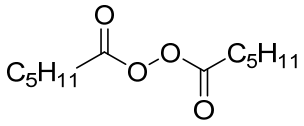


Following procedure B for synthesis of alkenes, 6-vinyl-1,2,3,4-tetrahydronaphthalene (related to **Figure 1**) was obtained as a clear liquid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 7.8 Hz, 1H), 7.09 (s, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.67 (d, *J* = 17.6 Hz, 1H), 5.15 (d, *J* = 10.9 Hz, 1H), 2.79 – 2.70 (m, 4H), 1.84 – 1.74 (m, 4H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 137.19, 137.03, 136.91, 134.91, 129.32, 127.05, 123.27, 112.64, 29.46, 29.28, 23.26.

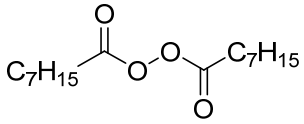



Following procedure B for synthesis of alkenes, (8*R*,9S,13S,14S)-13-Methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (compound **57,** related to **scheme 2**) was obtained as a white solid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.20 (m, 2H), 7.14 (s, 1H), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.70 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.19 (dd, *J* = 10.9, 0.9 Hz, 1H), 2.91 (dd, *J* = 9.0, 4.2 Hz, 2H), 2.50 (dd, *J* = 18.8, 8.7 Hz, 1H), 2.45 – 2.39 (m, 1H), 2.34 – 2.25 (m, 1H), 2.19 – 1.93 (m, 4H), 1.66 – 1.41 (m, 6H), 0.91 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 220.89, 139.55, 136.59, 135.22, 126.89, 125.56, 123.62, 113.20, 50.52, 48.00, 44.46, 38.18, 35.88, 31.61, 29.40, 26.52, 25.74, 21.61, 13.87. The spectrum data matches previously reported values

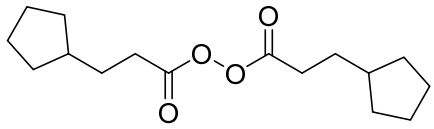
(Huang and Doyle, 2012)



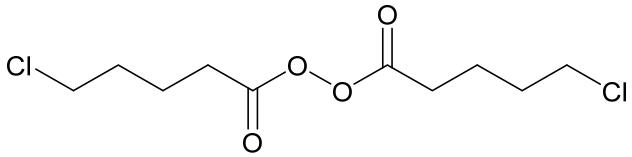
Following procedure C for synthesis of diacyl peroxides, hexanoic peroxyanhydride (related to **Figure 3**) was obtained as a clear liquid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 2.42 (t, *J* = 7.5 Hz, 4H), 1.78 – 1.66 (m, 4H), 1.41 – 1.29 (m, 8H), 0.91 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 169.25, 31.03, 29.95, 24.49, 22.15, 13.78.



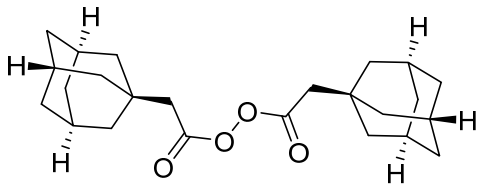
Following procedure C for synthesis of diacyl peroxides, octanoic peroxyanhydride (related to **Figure 3**) was obtained as a clear liquid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 2.42 (t, *J* = 7.5 Hz, 4H), 1.71 (p, *J* = 7.4 Hz, 4H), 1.42 – 1.22 (m, 16H), 0.87 (t, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 169.25, 31.54, 30.00, 28.87, 28.75, 24.81, 22.55, 14.00.



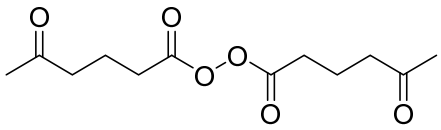
Following procedure C for synthesis of diacyl peroxides, 3-cyclopentylpropanoic peroxyanhydride (related to **Figure 3**) was obtained as a clear liquid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 2.44 (t, *J* = 7.8 Hz, 4H), 1.86 – 1.69 (m, 10H), 1.68 – 1.49 (m, 8H), 1.17 – 1.03 (m, 4H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 169.39, 39.46, 32.29, 30.94, 29.35, 25.10.



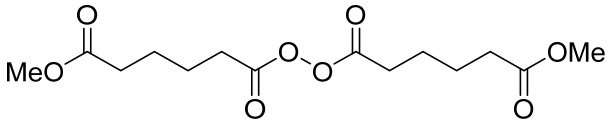
Following procedure C for synthesis of diacyl peroxides, 5-chloropentanoic peroxyanhydride (related to **Figure 3**) was obtained as a clear liquid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 3.61 – 3.54 (m, 4H), 2.53 – 2.45 (m, 4H), 1.97 – 1.82 (m, 8H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 168.70, 44.17, 31.36, 29.14, 22.09.



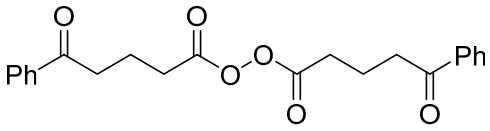
Following procedure C for synthesis of diacyl peroxides, 2-((3*r*,5*r*,7*r*)-adamantan-1-yl)acetic peroxyanhydride (related to **Figure 3**) was obtained as a white solid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 2.19 (s, 4H), 2.00 (s, 6H), 1.74 – 1.62 (m, 24H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 166.72, 44.46, 42.11, 36.53, 32.99, 28.55.



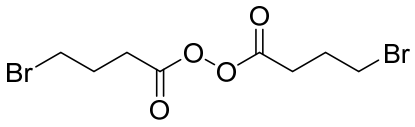
Following procedure C for synthesis of diacyl peroxides, 5-oxohexanoic peroxyanhydride (related to **Figure 3**) was obtained as a white solid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 2.60 (t, *J* = 7.0 Hz, 4H), 2.49 (t, *J* = 7.1 Hz, 4H), 2.16 (s, 6H), 1.97 (p, *J* = 6.9 Hz, 4H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 207.42, 168.74, 41.59, 29.94, 28.88, 18.63.



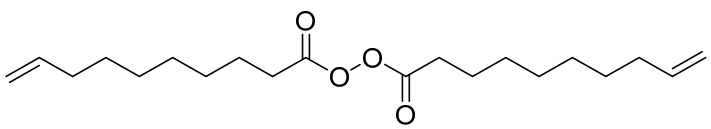
Following procedure C for synthesis of diacyl peroxides, 6-methoxy-6-oxohexanoic peroxyanhydride (related to **Figure 3**) was obtained as a white solid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 3.67 (s, 6H), 2.46 (t, *J* = 7.0 Hz, 4H), 2.35 (t, *J* = 6.9 Hz, 4H), 1.81 – 1.68 (m, 8H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 173.46, 168.75, 51.59, 33.42, 29.65, 24.21, 24.09.



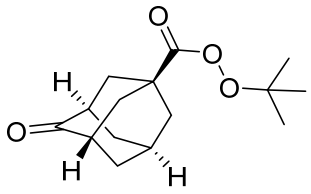
Following procedure C for synthesis of diacyl peroxides, 5-oxo-5-phenylpentanoic peroxyanhydride (related to **Figure 3**) was obtained as a white solid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.93 (m, 4H), 7.63 – 7.54 (m, 2H), 7.53 – 7.42 (m, 4H), 3.14 (t, *J* = 7.0 Hz, 4H), 2.60 (t, *J* = 7.0 Hz, 4H), 2.18 (p, *J* = 7.0 Hz, 4H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 198.85, 168.92, 136.68, 133.21, 128.64, 128.03, 36.85, 29.23, 19.20.



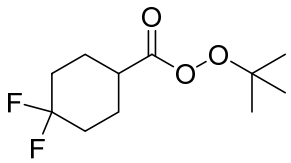
Following procedure C for synthesis of diacyl peroxides, 4-bromobutanoic peroxyanhydride (related to **Figure 3**) was obtained as a clear liquid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 3.55 – 3.40 (m, 4H), 2.69 – 2.56 (m, 4H), 2.31 – 2.14 (m, 4H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 168.19, 31.77, 28.39, 27.60.



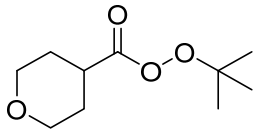
Following procedure C for synthesis of diacyl peroxides, dec-9-enoic peroxyanhydride (related to **Figure 3**) was obtained as a clear liquid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 5.88 – 5.72 (m, 2H), 5.17 – 4.77 (m, 4H), 2.42 (t, *J* = 7.4 Hz, 4H), 2.11 – 1.94 (m, 4H), 1.80 – 1.64 (m, 4H), 1.52 – 1.16 (m, 16H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 169.20, 138.99, 114.23, 33.71, 29.97, 28.92, 28.84, 28.80, 28.78, 24.78.



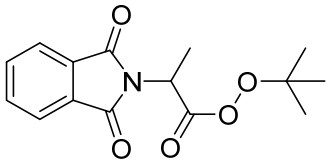
Following procedure D for synthesis of peresters, *tert*-butyl (1*s*,3*r*,5*s*,7*s*)-4-oxoadamantane-1-carboperoxoate (related to **Figure 2**) was obtained as a clear liquid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 2.62 (t, *J* = 3.0 Hz, 2H), 2.27 (d, *J* = 2.9 Hz, 4H), 2.22 (q, *J* = 3.1 Hz, 1H), 2.19 (d, *J* = 3.2 Hz, 2H), 2.11 – 1.99 (m, 4H), 1.32 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 215.64, 172.31, 83.74, 45.66, 40.59, 39.99, 38.12, 37.81, 27.15, 26.07.



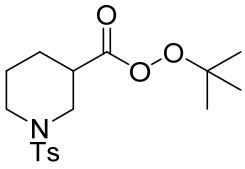
Following procedure D for synthesis of peresters, *tert*-butyl 4,4-difluorocyclohexane-1-carboperoxoate (related to **Figure 2**) was obtained as a white solid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 2.54 – 2.44 (m, 1H), 2.21 – 2.08 (m, 2H), 2.06 – 1.71 (m, 6H), 1.33 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 171.35, 122.25 (t, *J* = 241.2 Hz), 83.65, 38.63, 32.45 (t, *J* = 24.7 Hz), 26.11, 25.22 (dd, *J* = 7.8 Hz, *J* = 2.5 Hz). $^{19}$F NMR (376 MHz, Chloroform-*d*) δ -94.22 (d, *J* = 238.5 Hz), -99.94 (d, *J* = 237.9 Hz).



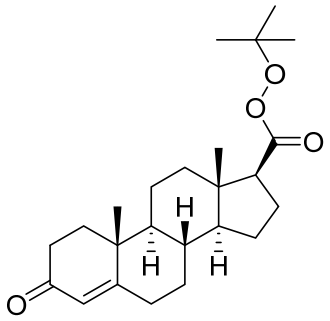
Following procedure D for synthesis of peresters, *tert*-butyl tetrahydro-2*H*-pyran-4-carboperoxoate (related to **Figure 2**) was obtained as a clear liquid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 4.00 (t, *J* = 3.6 Hz, 1H), 3.97 (t, *J* = 3.6 Hz, 1H), 3.48 – 3.41 (m, 2H), 2.68 – 2.59 (m, 1H), 1.93 – 1.82 (m, 4H), 1.33 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 171.51, 83.58, 66.87, 38.30, 28.58, 26.11.



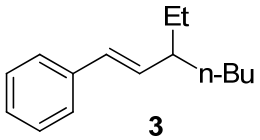
Following procedure D for synthesis of peresters, *tert*-butyl 2-(1,3-dioxoisoindolin-2-yl)propaneperoxoate (related to **Figure 2)** was obtained as a clear liquid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.78 (m, 2H), 7.71 – 7.66 (m, 2H), 5.00 (q, *J* = 7.3 Hz, 1H), 1.68 (d, *J* = 7.3 Hz, 3H), 1.21 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 167.08, 166.96, 134.35, 131.73, 123.59, 84.49, 46.38, 26.04, 15.28.



Following procedure D for synthesis of peresters, *tert*-butyl 1-tosylpiperidine-3-carboperoxoate (related to **Figure 2**) was obtained as a white solid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.80 (dd, *J* = 11.6, 3.7 Hz, 1H), 3.66 – 3.56 (m, 1H), 2.77 – 2.65 (m, 1H), 2.56 (t, *J* = 10.9 Hz, 1H), 2.44 (s, 3H), 2.40 – 2.29 (m, 1H), 2.03 – 1.88 (m, 1H), 1.83 – 1.76 (m, 1H), 1.73 – 1.61 (m, 1H), 1.56 – 1.42 (m, 1H), 1.33 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 170.12, 143.81, 132.89, 129.78, 127.66, 83.94, 47.55, 46.19, 39.23, 26.67, 26.12, 23.84, 21.54.

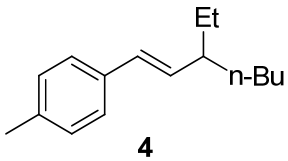


Following procedure D for synthesis of peresters, *tert*-butyl(8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene-17-carboperoxoate (compound **55,** related to **scheme 2**) was obtained as a white solid. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 5.74 (s, 1H), 2.50 – 2.25 (m, 5H), 2.24 – 2.13 (m, 1H), 2.09 – 2.00 (m, 2H), 1.95 – 1.82 (m, 2H), 1.80 – 1.66 (m, 3H), 1.64 – 1.56 (m, 3H), 1.51 – 1.39 (m, 1H), 1.33 (s, 9H), 1.19 (s, 3H), 1.15 – 1.04 (m, 2H), 1.02 – 0.92 (m, 1H), 0.80 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 199.42, 170.94, 170.84, 123.96, 82.94, 55.30, 53.66, 52.67, 44.14, 38.59, 37.89, 35.72, 35.67, 33.95, 32.76, 31.88, 26.32, 24.45, 23.88, 20.90, 17.38, 13.46.



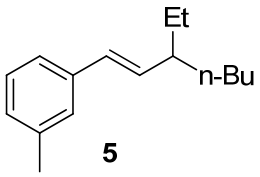

**3**

Following the procedure E, product **3** (related to **Figure 1**) was obtained as a clear liquid (75.8 mg, 75% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.95 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.52 – 1.40 (m, 2H), 1.34 – 1.22 (m, 6H), 0.88 (t, *J* = 7.5 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 138.09, 135.64, 129.78, 128.55, 126.82, 126.08, 45.30, 35.02, 29.78, 28.36, 23.02, 14.24, 11.98. The spectrum data matches previously reported values (Xu et al., 2017).



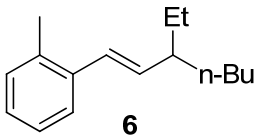

**4**

Following the procedure E, product **4** (related to **Figure 1**) was obtained as a clear liquid (87.5 mg, 81% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 2H), 6.29 (d, *J* = 15.8 Hz, 1H), 5.89 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.32 (s, 3H), 2.03 – 1.94 (m, 1H), 1.52 – 1.39 (m, 2H), 1.37 – 1.20 (m, 6H), 0.87 (t, *J* = 7.2 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 136.41, 135.24, 134.61, 129.44, 129.17, 125.87, 45.19, 34.97, 29.69, 28.31, 22.93, 21.16, 14.17, 11.91. HRMS (EI+) calcd for $[C_{16}H_{24}]^{+}$ ($[M]^{+}$): 216.1878, found: 216.1887.




**5**

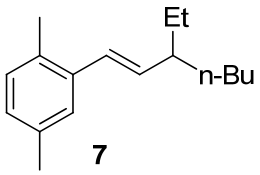
Following the procedure E, product **5** (related to **Figure 1**) was obtained as a clear liquid (78.8 mg, 73% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.13 (m, 3H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.29 (d, *J* = 15.8 Hz, 1H), 5.94 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.33 (s, 3H), 2.05 – 1.95 (m, 1H), 1.52 – 1.41 (m, 2H), 1.35 – 1.24 (m, 6H), 0.88 (t, *J* = 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 138.01, 135.40, 129.81, 128.45, 127.59, 126.74, 123.24, 45.31, 35.03, 29.76, 28.37, 22.99, 21.49, 14.21, 11.96. HRMS (EI+) calcd for $[C_{16}H_{24}]^{+}$ ($[M]^{+}$): 216.1878, found: 216.1880.




**6**

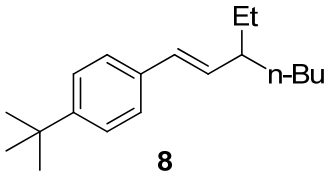
Following the procedure E, product **6** (related to **Figure 1**) was obtained as a clear liquid (79.9 mg, 74% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.0 Hz, 1H), 7.16 – 7.08 (m, 3H), 6.50 (d, *J* = 15.6 Hz, 1H), 5.79 (dd, *J* = 15.6, 9.0 Hz, 1H), 2.33 (s, 3H), 2.07 – 1.98 (m, 1H), 1.52 – 1.45 (m, 2H), 1.36 – 1.27 (m, 6H), 0.90 (t, *J* = 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 137.33, 137.09, 134.90, 130.12, 127.66, 126.72, 126.00, 125.61, 45.45, 34.91,

29.70, 28.29, 22.88, 19.91, 14.17, 11.93. HRMS (EI+) calcd for $[C_{16}H_{24}]^+$ ([M]$^+$): 216.1878, found: 216.1883.



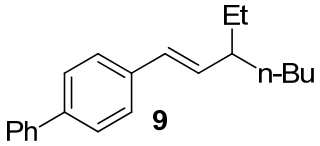

**7**

Following the procedure E, product **7** (related to **Figure 1**) was obtained as a clear liquid (90.7 mg, 79% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.24 (s, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.93 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.48 (d, *J* = 15.6 Hz, 1H), 5.77 (dd, *J* = 15.7, 9.1 Hz, 1H), 2.31 (s, 3H), 2.29 (s, 3H), 2.07 – 1.98 (m, 1H), 1.54 – 1.42 (m, 2H), 1.37 – 1.25 (m, 6H), 0.93 – 0.86 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 137.01, 136.75, 135.32, 131.84, 130.07, 127.70, 127.48, 126.16, 45.48, 34.95, 29.70, 28.32, 22.88, 21.07, 19.43, 14.17, 11.94. HRMS (EI+) calcd for $[C_{17}H_{26}]^+$ ([M]$^+$): 230.2035, found: 230.2028.



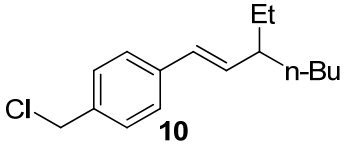

**8**

Following the procedure E, product **8** (related to **Figure 1**) was obtained as a clear liquid (108 mg, 84% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.26 (m, 4H), 6.30 (d, *J* = 15.8 Hz, 1H), 5.91 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.53 – 1.41 (m, 2H), 1.35 – 1.24 (m, 15H), 0.87 (t, *J* = 7.3 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 149.75, 135.25, 134.86, 129.36, 125.68, 125.42, 45.27, 35.02, 34.52, 31.38, 29.71, 28.37, 22.92, 14.18, 11.93. HRMS (EI+) calcd for $[C_{19}H_{30}]^+$ ([M]$^+$): 258.2348, found: 258.2343.




**9**

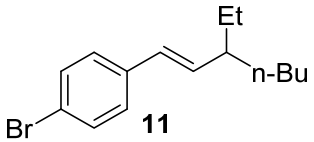
Following the procedure E, product **9** (related to **Figure 1**) was obtained as a white solid (94.5 mg, 68% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.55 (m, 2H), 7.54 – 7.50 (m, 2H), 7.43 – 7.38 (m, 4H), 7.33 – 7.26 (m, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.00 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.08 – 1.97 (m, 1H), 1.55 – 1.44 (m, 2H), 1.37 – 1.24 (m, 6H), 0.92 – 0.85 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 141.01, 139.61, 137.12, 135.90, 129.26, 128.82, 127.26, 127.19, 126.98, 126.45, 45.34, 34.99, 29.76, 28.34, 22.99, 14.23, 11.98. HRMS (EI+) calcd for $[C_{21}H_{26}]^+$ ([M]$^+$): 278.2035, found: 278.2040.




**10**

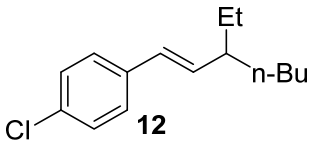
Following the procedure E, product **10** (related to **Figure 1**) was obtained as a clear liquid (87.6 mg, 70% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 4H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.97 (dd, *J* = 15.8, 9.0 Hz, 1H), 4.57 (s, 2H), 2.07 – 1.96 (m, 1H), 1.53 – 1.41 (m, 2H), 1.35 – 1.23 (m, 6H), 0.87 (t, *J* = 7.3 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 138.25,

136.53, 135.80, 128.98, 128.83, 126.27, 46.26, 45.20, 34.81, 29.65, 28.17, 22.87, 14.12, 11.86. HRMS (EI+) calcd for $[C_{16}H_{24}Cl]^+$ ($[M]^+$): 250.1488, found: 250.1485.



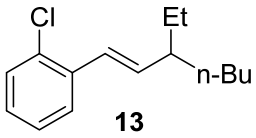

**11**

Following the procedure E product **11** (related to **Figure 1**) was obtained as a clear liquid (105.4 mg, 75% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.26 (d, *J* = 15.8 Hz, 1H), 5.94 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.51 – 1.42 (m, 2H), 1.35 – 1.22 (m, 6H), 0.87 (t, *J* = 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 136.89, 136.53, 131.49, 128.46, 127.51, 120.30, 45.17, 34.74, 29.64, 28.10, 22.87, 14.12, 11.86. HRMS (EI+) calcd for $[C_{15}H_{21}Br]^+$ ($[M]^+$): 280.0827, found: 280.0829.



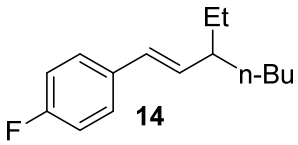

**12**

Following the procedure E, product **12** (related to **Figure 1**) was obtained as a clear liquid (93.9 mg, 80% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.22 (m, 4H), 6.27 (d, *J* = 15.8 Hz, 1H), 5.93 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.54 – 1.41 (m, 2H), 1.35 – 1.24 (m, 6H), 0.87 (t, *J* = 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 136.48, 136.39, 132.25, 128.57, 128.44, 127.17, 45.16, 34.78, 29.65, 28.13, 22.88, 14.12, 11.85. The spectrum data matches previously reported values (Mai et al., 2016)




**13**

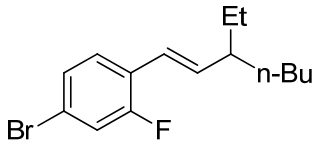
Following the procedure E, product **13** (related to **Figure 1**) was obtained as a clear liquid (81.3 mg, 69% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.15 – 7.09 (m, 1H), 6.70 (d, *J* = 15.8 Hz, 1H), 5.93 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.13 – 2.04 (m, 1H), 1.52 – 1.43 (m, 2H), 1.35 – 1.27 (m, 6H), 0.90 (t, *J* = 7.8 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 138.53, 136.11, 132.55, 129.57, 127.74, 126.68, 125.97, 45.21, 34.70, 29.59, 28.09, 22.86, 14.12, 11.84. HRMS (EI+) calcd for $[C_{15}H_{21}Cl]^+$ ($[M]^+$): 236.1332, found: 236.1329.




**14**

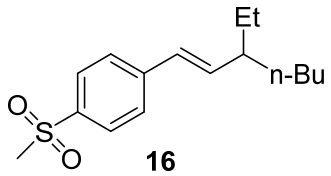
Following the procedure E, product **14** (related to **Figure 1**) was obtained as a clear liquid (76.8 mg, 70% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.30 (dd, *J* = 8.6, 5.4 Hz, 2H), 6.97 (t, *J* = 8.6 Hz, 2H), 6.28 (d, *J* = 15.8 Hz, 1H), 5.86 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.04 – 1.94 (m, 1H), 1.52 – 1.41 (m, 2H), 1.35 – 1.22 (m, 6H), 0.88 (t, *J* = 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 161.85 (d, *J* = 245.4 Hz), 135.34 (d, *J* = 2.2 Hz), 134.13 (d, *J* = 3.3 Hz), 128.43, 127.33 (d, *J* = 7.7 Hz), 115.26 (d, *J* = 21.5 Hz), 45.13, 34.85, 29.66, 28.20, 22.89, 14.12, 11.86. $^{19}$F NMR (376 MHz, Chloroform-*d* ) δ -115.97. HRMS (EI+) calcd for $[C_{15}H_{21}F]^+$ ($[M]^+$):

220.1627, found: 220.1621.



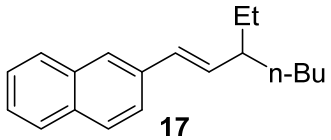

**15**

Following the procedure E, product **15** (related to **Figure 1**) was obtained as a clear liquid (80.5 mg, 54% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.31 (t, *J* = 8.3 Hz, 1H), 7.23 – 7.17 (m, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.03 (dd, *J* = 16.0, 9.0 Hz, 1H), 2.09 – 1.99 (m, 1H), 1.53 – 1.42 (m, 2H), 1.36 – 1.25 (m, 6H), 0.88 (t, *J* = 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 159.57 (d, *J* = 252.6 Hz), 139.09 (d, *J* = 4.3 Hz), 128.01 (d, *J* = 4.8 Hz), 127.26 (d, *J* = 3.6 Hz), 124.87 (d, *J* = 12.5 Hz), 120.99 (d, *J* = 3.3 Hz), 119.90 (d, *J* = 9.7 Hz), 119.19 (d, *J* = 25.7 Hz), 45.57, 34.63, 29.60, 28.00, 22.84, 14.09, 11.81. $^{19}$F NMR (376 MHz, Chloroform-*d* ) δ -116.27. HRMS (EI+) calcd for $[C_{15}H_{20}BrF]^+$ ($[M]^+$): 298.0732, found: 298.0739.



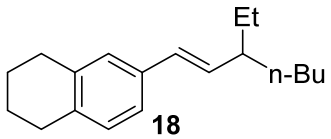

**16**

Following the procedure E, product **16** (related to **Figure 1**) was obtained as a white solid (33.6 mg, 24% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.08 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.96 (s, 3H), 2.05 – 1.93 (m, 1H), 1.50 – 1.36 (m, 2H), 1.29 – 1.18 (m, 6H), 0.81 (t, *J* = 7.5 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 143.44, 140.29, 138.16, 128.11, 127.69, 126.59, 45.32, 44.64, 34.57, 29.62, 27.96, 22.82, 14.08, 11.83. HRMS (EI+) calcd for $[C_{16}H_{24}O_2S]^+$ ($[M]^+$): 280.1497, found: 280.1501.




**17**

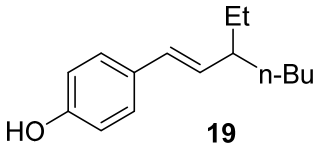
Following the procedure E, product **17** (related to **Figure 2**) was obtained as a clear liquid (91.9 mg, 73% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.84-7.78 (m, 3H), 7.72 (s, 1H), 7.63 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.50 – 7.41 (m, 2H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.13 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.16 – 2.06 (m, 1H), 1.60 – 1.52 (m, 2H), 1.43 – 1.30 (m, 6H), 0.97 – 0.91 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 136.16, 135.44, 133.75, 132.64, 129.72, 128.00, 127.79, 127.62, 126.11, 125.39, 125.27, 123.68, 45.30, 34.91, 29.69, 28.26, 22.91, 14.14, 11.92. HRMS (EI+) calcd for $[C_{19}H_{24}]^+$ ($[M]^+$): 252.1878, found: 252.1873.




**18**

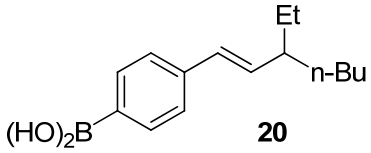
Following the procedure E, product **18** (related to **Figure 1**) was obtained as a clear liquid (79.8 mg, 63% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.10 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.05 (s, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.25 (d, *J* = 15.8 Hz, 1H), 5.87 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.74

(d, *J* = 6.1 Hz, 4H), 2.04 – 1.93 (m, 1H), 1.82 – 1.74 (m, 4H), 1.52 – 1.40 (m, 2H), 1.33 – 1.23 (m, 6H), 0.87 (t, *J* = 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 137.11, 135.86, 135.31, 134.47, 129.59, 129.27, 126.62, 123.16, 45.22, 35.00, 29.69, 29.49, 29.21, 28.35, 23.34, 23.32, 22.91, 14.16, 11.90. HRMS (EI+) calcd for $[C_{19}H_{28}]^+$ ($[M]^+$): 256.2191, found: 256.2197.



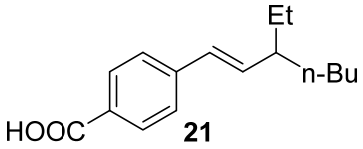

**19**

Following the procedure E, product **19** (related to **Figure 1**) was obtained as a clear liquid (89.3 mg, 82% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 6.25 (d, *J* = 15.8 Hz, 1H), 5.79 (dd, *J* = 15.8, 9.0 Hz, 1H), 4.88 (s, 1H), 2.02 – 1.94 (m, 1H), 1.52 – 1.38 (m, 2H), 1.32 – 1.25 (m, 6H), 0.87 (t, *J* = 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 154.48, 133.55, 131.06, 128.82, 127.21, 115.33, 45.08, 34.94, 29.64, 28.28, 22.89, 14.12, 11.86. HRMS (EI+) calcd for $[C_{15}H_{22}O]^+$ ($[M]^+$): 218.1671, found: 218.1673.



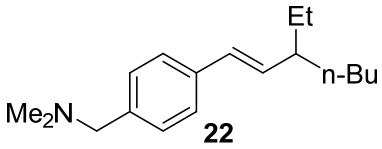

**20**

Following the procedure E, product **20** (related to **Figure 1**) was obtained as a light yellow oil (43.9 mg, 36% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.15 (dd, *J* = 15.8, 8.9 Hz, 1H), 2.10 (m, 1H), 1.61 – 1.47 (m, 2H), 1.44 – 1.30 (m, 6H), 0.96 – 0.90 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) δ 142.23, 137.77, 136.14, 129.90, 125.73, 45.50, 34.99, 29.88, 28.35, 23.11, 14.34, 12.11. HRMS (DART-) calcd for $[C_{15}H_{22}O_2{}^{10}B]^-$ ($[M\text{-}H]^-$): 244.1755, found: 244.1757.




**21**

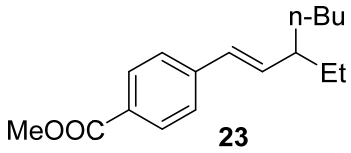
Following the procedure E, product **21** (related to **Figure 1**) was obtained as a clear liquid (64 mg, 52% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.13 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.13 – 2.00 (m, 1H), 1.56 – 1.44 (m, 2H), 1.32 – 1.25 (m, 6H), 0.91 – 0.86 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 171.83, 143.37, 139.21, 130.55, 128.87, 127.33, 125.91, 45.32, 34.67, 29.63, 28.04, 22.85, 14.09, 11.85. HRMS (EI+) calcd for $[C_{16}H_{22}O_2]^+$ ($[M]^+$): 246.1620, found: 246.1621.




**22**

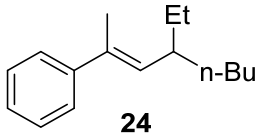
Following the procedure E, product **22** (related to **Figure 1**) was obtained as a clear liquid (65 mg, 50% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.95 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.40 (s, 2H), 2.24 (s, 6H), 2.07 – 1.95 (m, 1H), 1.54 – 1.43 (m, 2H), 1.31 – 1.26 (m, 6H), 0.92 – 0.85 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 137.27, 136.89, 135.33, 129.33, 129.28, 125.84, 64.11, 45.31, 45.16, 34.88, 29.64, 28.23, 22.88, 14.12, 11.87. HRMS (EI+) calcd for $[C_{18}H_{29}N]^+$ ($[M]^+$):

259.2300, found: 259.2305.



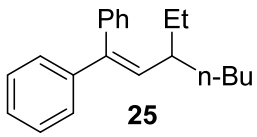

**23**

Following the procedure E, product **23** (related to **Figure 1**) was obtained as a clear liquid (66.3 mg, 51% yield).$^{1}$H NMR (400 MHz, Chloroform-d) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.28 (d, *J* = 15.8 Hz, 1H), 6.02 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.82 (s, 3H), 2.01 – 1.92 (m, 1H), 1.50 – 1.33 (m, 2H), 1.32 – 1.14 (m, 6H), 0.81 (t, J = 7.5 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) δ 167.00, 142.49, 138.63, 129.87, 128.90, 128.19, 125.79, 51.97, 45.29, 34.68, 29.63, 28.05, 22.85, 14.09, 11.84. HRMS (EI+) calcd for $[C_{17}H_{24}O_2]^+$ ($[M]^+$): 260.1776, found: 260.1778.



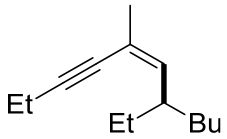

**24**

Following the procedure E, product **24** (related to **Figure 1**) was obtained as a clear liquid (88.5 mg, 82% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.23 – 7.19 (m, 1H), 5.48 (d, *J* = 9.9 Hz, 1H), 2.36 – 2.27 (m, 1H), 2.03 (d, *J* = 1.4 Hz, 3H), 1.54 – 1.44 (m, 2H), 1.33 – 1.22 (m, 6H), 0.88 (t, *J* = 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 144.52, 134.52, 134.42, 128.32, 126.60, 125.90, 40.63, 35.78, 29.98, 29.08, 23.21, 16.57, 14.37, 12.16. HRMS (EI+) calcd for $[C_{16}H_{24}]^+$ ($[M]^+$): 216.1878, found: 216.1875.



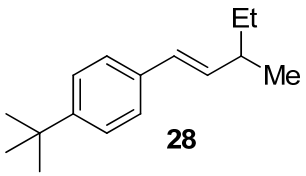

**25**

Following the procedure E, product **25** (related to **Figure 1**) was obtained as a clear liquid (129.7 mg, 93% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 2H), 7.30 – 7.21 (m, 5H), 7.21 – 7.13 (m, 3H), 5.82 (d, *J* = 10.5 Hz, 1H), 2.15 – 2.03 (m, 1H), 1.47 – 1.23 (m, 5H), 1.22 – 1.11 (m, 3H), 0.87 – 0.81 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 142.81, 141.37, 140.77, 135.25, 130.01, 128.08, 128.05, 127.01, 126.72, 126.63, 40.56, 35.47, 29.67, 28.82, 22.97, 14.11, 12.00. HRMS (EI+) calcd for $[C_{21}H_{26}]^+$ ($[M]^+$): 278.2035, found: 278.2038.



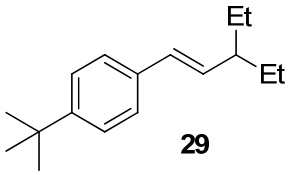

**26**

Following the procedure E, product **26** (related to **Figure 1**) was obtained as a clear liquid (68.2 mg, 71% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 5.27 (dd, *J* = 9.8, 1.6 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.33 (q, *J* = 7.5 Hz, 2H), 1.82 (d, *J* = 1.4 Hz, 2H), 1.43 – 1.21 (m, 8H), 1.20 – 1.14 (m, 4H), 0.90 – 0.83 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 141.60, 117.98, 93.82, 79.91, 41.97, 34.89, 29.49, 28.32, 23.54, 22.90, 14.22, 14.13, 13.17, 11.77. HRMS (EI+) calcd for $[C_{14}H_{24}]^+$ ($[M]^+$): 192.1878, found: 192.1887.



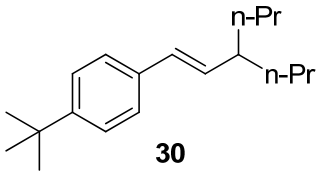

**28**

Following the procedure F, product **28** (related to **Figure 2**) was obtained as a clear liquid (97.2 mg, 90% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 4H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.05 (dd, *J* = 15.8, 7.9 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.45 – 1.35 (m, 2H), 1.31 (s, 9H), 1.06 (d, *J* = 6.7 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 149.76, 136.04, 135.22, 127.83, 125.65, 125.39, 38.96, 34.50, 31.35, 29.88, 20.33, 11.85. HRMS (EI+) calcd for $[C_{16}H_{24}]^{+}$ ($[M]^{+}$): 216.1878, found: 216.1877.



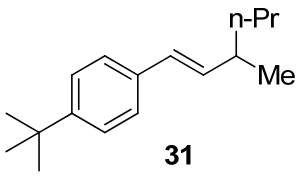

**29**

Following the procedure F, product **29** (related to **Figure 2**) was obtained as a clear liquid (93.4 mg, 81% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 4H), 6.31 (d, *J* = 15.8 Hz, 1H), 5.91 (dd, *J* = 15.8, 8.9 Hz, 1H), 1.97 – 1.87 (m, 1H), 1.52 – 1.44 (m, 2H), 1.33 – 1.28 (m, 11H), 0.87 (t, *J* = 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 149.75, 135.23, 134.52, 129.54, 125.66, 125.38, 46.94, 34.50, 31.35, 27.91, 11.88. HRMS (EI+) calcd for $[C_{17}H_{26}]^{+}$ ($[M]^{+}$): 230.2035, found: 230.2030.



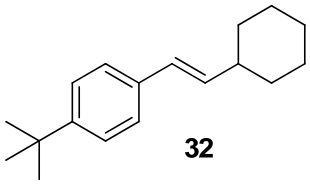

**30**

Following the procedure F, product **30** (related to **Figure 2**) was obtained as a clear liquid (105.8 mg, 82% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 4H), 6.29 (d, *J* = 15.8 Hz, 1H), 5.90 (dd, *J* = 15.8, 9.1 Hz, 1H), 2.18 – 2.08 (m, 1H), 1.37 – 1.25 (m, 17H), 0.87 (t, *J* = 6.9 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 149.72, 135.18, 135.06, 129.06, 125.61, 125.38, 42.91, 37.84, 34.48, 31.33, 20.46, 14.19. HRMS (EI+) calcd for $[C_{19}H_{30}]^{+}$ ($[M]^{+}$): 258.2348, found: 258.2350.



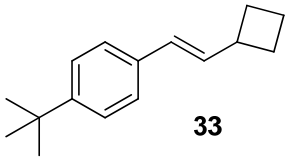

**31**

Following the procedure F, product **31** (related to **Figure 2**) was obtained as a clear liquid (90.9 mg, 79% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 4H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.04 (dd, *J* = 15.8, 8.0 Hz, 1H), 2.33 – 2.23 (m, 1H), 1.36 – 1.31 (m, 4H), 1.30 (s, 9H), 1.05 (d, *J* = 6.7 Hz, 3H), 0.91 – 0.87 (m, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 149.76, 136.32, 135.22, 127.64, 125.65, 125.39, 39.43, 37.05, 34.50, 31.36, 20.79, 20.52, 14.21. HRMS (EI+) calcd for $[C_{17}H_{26}]^{+}$ ($[M]^{+}$): 230.2035, found: 230.2038.



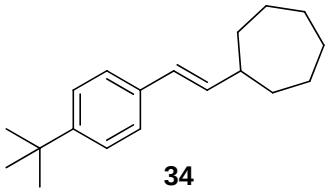
**32**

Following the procedure F, product **32** (related to **Figure 2**) was obtained as a clear liquid (115.0 mg, 95% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.25 (m, 4H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.13 (dd, *J* = 15.9, 7.0 Hz, 1H), 2.17 – 2.06 (m, 1H), 1.91 – 1.62 (m, 6H), 1.30 (s, 9H), 1.27 – 1.13 (m, 4H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 149.74, 136.16, 135.30, 126.89, 125.61, 125.37, 41.18, 34.48, 33.04, 31.34, 26.21, 26.08. The spectrum data matches previously reported values (Zhu and Wei, 2014)



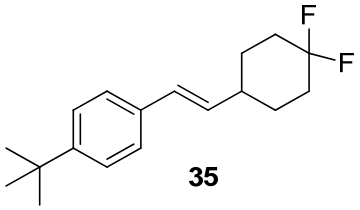
**33**

Following the procedure F, product **33** (related to **Figure 2**) was obtained as a clear liquid (80.1 mg, 75% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 4H), 6.31 – 6.26 (m, 2H), 3.14 – 3.03 (m, 1H), 2.21 – 2.13 (m, 2H), 2.00 – 1.78 (m, 4H), 1.31 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 149.82, 135.03, 134.58, 127.28, 125.67, 125.39, 38.79, 34.50, 31.34, 28.84, 18.59. HRMS (EI+) calcd for $[C_{16}H_{22}]^{+}$ ([M]$^{+}$): 214.1722, found: 214.1725.



**34**

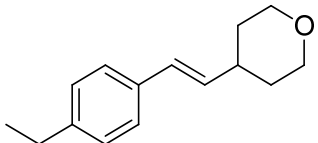
Following the procedure F, product **34** (related to **Figure 2**) was obtained as a clear liquid (117.8 mg, 92% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 4H), 6.31 (d, *J* = 15.9 Hz, 1H), 6.19 (dd, *J* = 15.9, 7.5 Hz, 1H), 2.38 – 2.26 (m, 1H), 1.87 – 1.78 (m, 2H), 1.74 – 1.67 (m, 2H), 1.66 – 1.61 (m, 1H), 1.58 – 1.51 (m, 4H), 1.50 – 1.38 (m, 3H), 1.32 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 148.88, 136.21, 134.57, 125.52, 124.82, 124.58, 42.46, 34.02, 33.68, 30.54, 27.62, 25.49. HRMS (EI+) calcd for $[C_{19}H_{28}]^{+}$ ([M]$^{+}$): 256.2191, found: 256.2190.




**35**

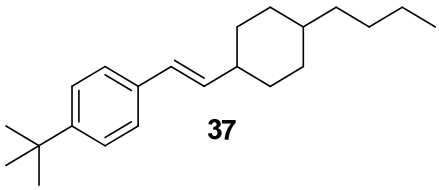
Following the procedure G for the reaction with perester, product **35** (related to **Figure 2**) was obtained as a white solid (73.7 mg, 53% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.26 (m, 4H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.10 (dd, *J* = 16.0, 7.0 Hz, 1H), 2.29 – 2.19 (m, 1H), 2.18 – 2.07 (m, 2H), 1.92 – 1.70 (m, 4H), 1.63 – 1.54 (m, 2H), 1.31 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 150.29, 134.62, 132.88 (d, *J* = 2.5 Hz), 128.64, 125.74, 125.48, 122.14 (d, *J* = 240.2 Hz), 39.04, 34.54, 33.25 (dd, *J* = 25.2, 22.9 Hz), 31.32, 28.93 (d, *J* = 9.2 Hz). $^{19}$F NMR

(376 MHz, Chloroform-*d*) δ -94.22 (d, *J* = 238.6 Hz), -99.94 (d, *J* = 238.3 Hz). HRMS (EI+) calcd for $[C_{18}H_{24}F_2]^+$ ($[M]^+$): 278.1846, found: 278.1848.



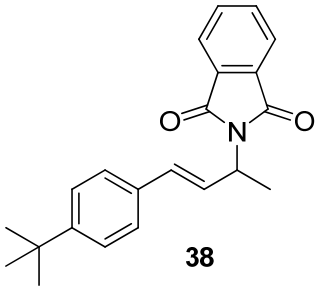
**36**

Following the procedure G for the reaction with perester, product **36** (related to **Figure 2**) was obtained as a white solid (90.3 mg, 74% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 4H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.11 (dd, *J* = 15.9, 6.8 Hz, 1H), 4.02 – 3.96 (m, 2H), 3.48 – 3.37 (m, 2H), 2.40 – 2.30 (m, 1H), 1.71 – 1.65 (m, 2H), 1.61 – 1.49 (m, 2H), 1.30 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 150.30, 134.92, 134.02, 128.13, 125.90, 125.60, 67.90, 38.53, 34.67, 32.87, 31.48. HRMS (EI+) calcd for $[C_{17}H_{24}O]^+$ ($[M]^+$): 244.1827, found: 244.1835.



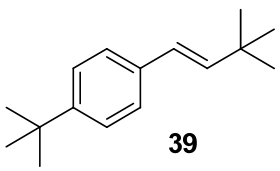
**37**

Following the procedure F, product **37** (related to **Figure 2**) was obtained as a clear liquid (104.5 mg, 70% yield, dr = 1:1). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 4H), 6.38 – 6.29 (m, 1H), 6.25 (dd, *J* = 16.0, 6.4 Hz, 0.56H), 6.12 (dd, *J* = 15.9, 7.0 Hz, 0.41H), 2.39 – 2.32 (m, 0.54H), 2.09 – 1.99 (m, 0.49H), 1.85 – 1.76 (m, 2H), 1.63 – 1.54 (m, 3H), 1.42 – 1.32 (m, 3H), 1.31 – 1.30 (m, 9H), 1.27 – 1.14 (m, 7H), 0.89 (t, *J* = 6.9 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 149.74, 136.12, 135.34, 135.29, 134.87, 127.80, 126.91, 125.60, 125.38, 125.37, 41.49, 37.31, 37.17, 34.48, 33.00, 31.34, 29.62, 29.41, 29.23, 29.05, 23.04, 23.01, 14.19. HRMS (EI+) calcd for $[C_{22}H_{34}]^+$ ($[M]^+$): 298.2661, found: 298.2668.



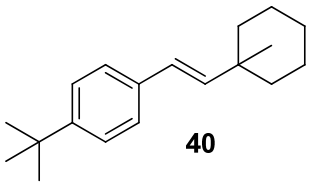
**38**

Following the procedure G for the reaction with perester, product **38** (related to **Figure 2**) was obtained as a clear liquid (95 mg, 57% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.33 – 7.30 (m, 4H), 6.64 – 6.55 (m, 2H), 5.13 – 5.04 (m, 1H), 1.66 (d, *J* = 7.1 Hz, 3H), 1.29 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 167.99, 150.97, 133.86, 133.61, 132.11, 131.80, 127.36, 126.29, 125.47, 123.13, 49.09, 34.58, 31.27, 19.06. HRMS (EI+) calcd for $[C_{22}H_{23}NO_2]^+$ ($[M]^+$): 333.1729, found: 333.1725.



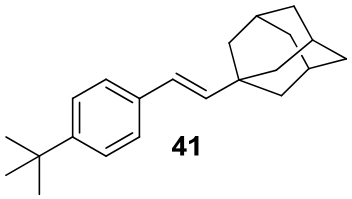
**39**

Following the procedure F, product **39** (related to **Figure 2**) was obtained as clear liquid (82.1 mg, 76 % yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 4H), 6.28 (d, *J* = 16.2 Hz, 1H), 6.21 (d, *J* = 16.2, 1H), 1.31 (s, 9H), 1.11 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 149.76, 141.17, 135.27, 125.68, 125.39, 124.21, 34.49, 33.30, 31.35, 29.66. The spectrum data matches previously reported values (Aydin et al., 2009).



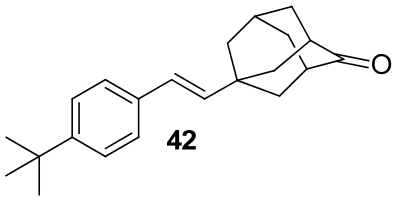
**40**

Following the procedure F, product **40** (related to **Figure 2**) was obtained as a clear liquid (102.4 mg, 80% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 4H), 6.30 (d, *J* = 16.4 Hz, 1H), 6.17 (d, *J* = 16.4 Hz, 1H), 1.64 – 1.56 (m, 2H), 1.52 – 1.46 (m, 4H), 1.42 – 1.32 (m, 4H), 1.31 (s, 9H), 1.05 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 149.74, 140.28, 135.49, 125.68, 125.61, 125.40, 38.06, 36.17, 34.49, 31.36, 27.84, 26.37, 22.51. HRMS (EI+) calcd for $[C_{19}H_{28}]^{+}$ ($[M]^{+}$): 256.2191, found: 256.2189.



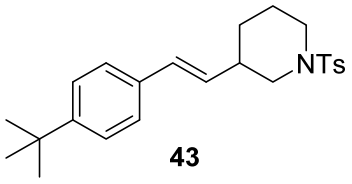
**41**

Following the procedure F, product **41** (related to **Figure 2**) was obtained as a white solid (128 mg, 87% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 4H), 6.22 (d, *J* = 16.2 Hz, 1H), 6.06 (d, *J* = 16.3, 1H), 2.05 – 1.99 (m, 3H), 1.77 – 1.67 (m, 12H), 1.32 – 1.29 (m, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 149.71, 141.45, 135.43, 125.64, 125.37, 124.14, 42.31, 36.93, 35.11, 34.48, 31.34, 28.53. HRMS (EI+) calcd for $[C_{22}H_{30}]^{+}$ ($[M]^{+}$): 294.2348, found: 294.2352.



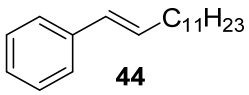

**42**

Following the procedure G for the reaction with perester, product **42** (related to **Figure 2**) was obtained as a white solid (127 mg, 82% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.20 (m, 4H), 6.21 (d, *J* = 16.2 Hz, 1H), 5.99 (d, *J* = 16.3 Hz, 1H), 2.56 – 2.52 (m, 2H), 2.17 – 2.11 (m, 1H), 1.98 – 1.84 (m, 10H), 1.23 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 217.99, 150.34, 137.54, 134.61, 125.95, 125.78, 125.49, 46.42, 43.44, 41.17, 38.66, 35.01, 34.54, 31.32, 27.78. HRMS (EI+) calcd for $[C_{22}H_{28}O]^{+}$ ($[M]^{+}$): 308.2140, found: 308.2134.



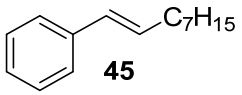

**43**

Following the procedure G for the reaction with perester, product **43** (related to **Figure 2**) was obtained as white solid (79 mg, 40% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.29 (m, 4H), 7.26 (d, *J* = 5.2 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.96 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.79 – 3.57 (m, 2H), 2.54 – 2.46 (m, 1H), 2.43 (s, 3H), 2.30 – 2.23 (m, 1H), 2.11 (t, *J* = 10.9 Hz, 1H), 1.86 – 1.65 (m, 3H), 1.30 (s, 9H), 1.13 (m, 1H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 150.53, 143.43, 134.30, 133.24, 130.25, 130.05, 129.64, 127.71, 125.82, 125.49, 51.38, 46.44, 39.08, 34.56, 31.32, 29.99, 24.43, 21.56. HRMS (EI+) calcd for $[C_{24}H_{31}NO_2S]^+$ ($[M]^+$): 397.2075, found: 397.2079.



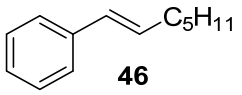

**44**

Following the procedure H for the reaction with diacyl peroxide, product **44** (related to **Figure 3**) was obtained as a clear liquid (94 mg, 73% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.27 – 6.18 (m, 1H), 2.24 – 2.16 (m, 2H), 1.49 – 1.40 (m, 2H), 1.34 – 1.22 (m, 16H), 0.88 (t, *J* = 6.6 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 137.97, 131.28, 129.67, 128.46, 126.73, 125.90, 33.09, 31.96, 29.71, 29.68, 29.66, 29.57, 29.42, 29.39, 29.28, 22.73, 14.15. The spectrum data matches previously reported values (Habrant et al., 2007).



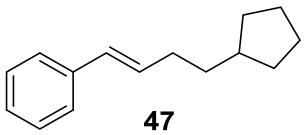

**45**

Following the procedure H for the reaction with diacyl peroxide, product **45** (related to **Figure 3**) was obtained as a clear liquid (61 mg, 60% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.27 – 6.15 (m, 1H), 2.25 – 2.14 (m, 2H), 1.52 – 1.41 (m, 2H), 1.36 – 1.25 (m, 8H), 0.88 (t, *J* = 6.5 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 137.99, 131.27, 129.71, 128.48, 126.76, 125.93, 33.11, 31.91, 29.45, 29.27, 22.73, 14.16. The spectrum data matches previously reported values (Thiot et al., 2007).




**46**

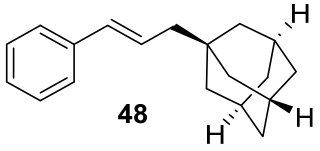
Following the procedure H for the reaction with diacyl peroxide, product **46** (related to **Figure 3**) was obtained as a clear liquid (59 mg, 68% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.1 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.15 (m, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.27 – 6.18 (m, 1H), 2.24 – 2.17 (m, 2H), 1.50 – 1.43 (m, 2H), 1.37 – 1.29 (m, 4H), 0.90 (t, *J* = 6.7 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 137.97, 131.27, 129.68, 128.47, 126.74, 125.90, 33.05, 31.47, 29.09, 22.60, 14.10. The spectrum data matches previously reported values (Denmark and Wehrli, 2000).



**47**

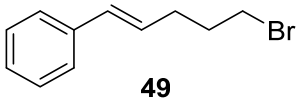
Following the procedure H for the reaction with diacyl peroxide, product **47** (related to **Figure 3**) was obtained as a clear liquid (77 mg, 77% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d,

*J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.27 – 6.18 (m, 1H), 2.25 – 2.18 (m, 2H), 1.84 – 1.73 (m, 3H), 1.66 – 1.57 (m, 2H), 1.54 – 1.44 (m, 4H), 1.17 – 1.04 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 138.00, 131.41, 129.54, 128.49, 126.75, 125.91, 39.73, 35.91, 32.70, 32.32, 25.25. The spectrum data matches previously reported values (Li et al., 2016).



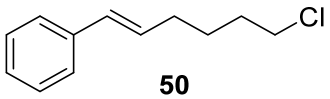

**48**

Following the procedure H for the reaction with diacyl peroxide, product **48** (related to **Figure 3**) was obtained as clear liquid (83 mg, 66% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.21 – 7.15 (m, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 6.29 – 6.22 (m, 1H), 1.98 – 1.93 (m, 5H), 1.73 – 1.67 (m, 3H), 1.66 – 1.59 (m, 3H), 1.55 – 1.52 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ137.96, 131.88, 128.48, 127.09, 126.76, 125.98, 48.12, 42.61, 37.14, 33.52, 28.81. The spectrum data matches previously reported values (Tanaka et al., 1987).



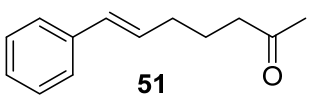

**49**

Following the procedure H for the reaction with diacyl peroxide, product **49** (related to **Figure 3**) was obtained as a clear liquid (62 mg, 55% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.21 – 6.10 (m, 1H), 3.45 (t, *J* = 6.7 Hz, 2H), 2.42 – 2.34 (m, 2H), 2.07 – 1.99 (m, 2H). $^{13}$C NMR (100MHz, Chloroform-*d*) δ 137.43, 131.31, 128.54, 128.47, 127.14, 126.02, 33.19, 32.21, 31.30. The spectrum data matches previously reported values (Matsubara and Jamison, 2010)



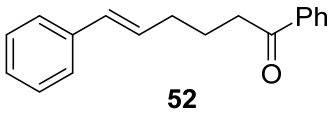

**50**

Following the procedure H for the reaction with diacyl peroxide, product **50** (related to **Figure 3**) was obtained as a clear liquid (53 mg, 55% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 4H), 7.23 – 7.17 (m, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.26 – 6.15 (m, 1H), 3.56 (t, *J* = 6.7 Hz, 2H), 2.29 – 2.22 (m, 2H), 1.90 – 1.77 (m, 2H), 1.69 – 1.57 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 137.63, 130.43, 130.06, 128.52, 126.98, 125.96, 44.98, 32.23, 32.0, 26.56. The spectrum data matches previously reported values (Hu et al., 1999).



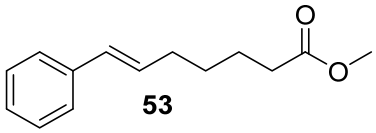

**51**

Following the procedure H for the reaction with diacyl peroxide, product **51** (related to **Figure 3**) was obtained as a white solid (50.7 mg, 54% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 4H), 7.24 – 7.17 (m, 1H), 6.39 (d, *J* = 15.7, 1H), 6.21 – 6.12 (m, 1H), 2.48 (t, *J* = 7.4 Hz, 2H), 2.26 – 2.19 (m, 1H), 2.14 (s, 3H), 1.82 – 1.72 (m, 1H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 208.85, 137.57, 130.68, 129.83, 128.52, 127.01, 125.97, 42.88, 32.30, 30.02, 23.25. The spectrum data matches previously reported values (Musacchio et al., 2014).



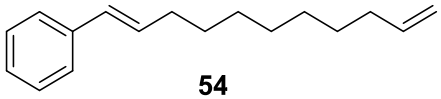

**52**

Following the procedure H for the reaction with diacyl peroxide, product **52** (related to **Figure 3**) was obtained as a white solid (70 mg, 56% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.93 (m, 2H), 7.58 – 7.53 (m, 1H), 7.48 – 7.42 (m, 2H), 7.36 – 7.27 (m, 4H), 7.23 – 7.17 (m, 1H), 6.41 (d, *J* = 15.9 Hz, 1H), 6.27 – 6.18 (m, 1H), 3.03 (t, *J* = 7.3 Hz, 2H), 2.36 – 2.29 (m, 2H), 1.99 – 1.91 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 200.22, 137.62, 137.02, 132.96, 130.73, 129.94, 128.58, 128.51, 128.05, 126.98, 125.99, 37.75, 32.47, 23.80. The spectrum data matches previously reported values (Hilt et al., 2016).



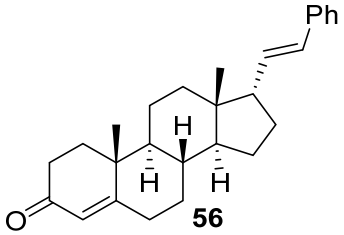

**53**

Following the procedure H for the reaction with diacyl peroxide, product **53** (related to **Figure 3**) was obtained as a white solid (61 mg, 56% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.25 (m, 4H), 7.21 – 7.15 (m, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.23 – 6.15 (m, 1H), 3.66 (s, 3H), 2.34 (t, *J* = 7.5 Hz, 2H), 2.26 – 2.19 (m, 2H), 1.74 – 1.65 (m, 2H), 1.55 – 1.46 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 174.11, 137.74, 130.32, 130.21, 128.49, 126.88, 125.95, 51.51, 33.96, 32.64, 28.84, 24.52. The spectrum data matches previously reported values (Ramón-Azcón et al., 2006).



**54**

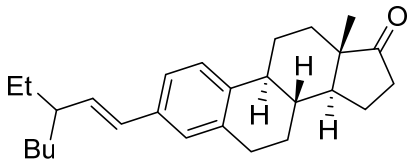
Following the procedure H for the reaction with diacyl peroxide, product **54** (related to **Figure 3**) was obtained as a clear liquid (70 mg, 61% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.32 (m, 2H), 7.30 – 7.25 (m, 2H), 7.21 – 7.15 (m, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.27 – 6.17 (m, 1H), 5.91 – 5.74 (m, 1H), 5.04 – 4.90 (m, 2H), 2.25 – 2.16 (m, 2H), 2.09 – 2.00 (m, 2H), 1.50 – 1.42 (m, 2H), 1.40 – 1.28 (m, 8H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 139.22, 137.96, 131.21, 129.73, 128.48, 126.76, 125.92, 114.17, 33.84, 33.07, 29.40, 29.21, 29.13, 28.96. The spectrum data matches previously reported values (Kulasegaram and Kulawiec, 1997).




**56**

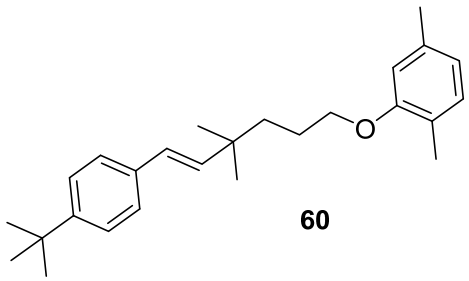
Following the procedure G, product **56** (related to **Scheme 2**) was obtained as a white solid (89.8 mg, 48% yield). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.32 (m, 2H), 7.31 – 7.25 (m, 2H), 7.20 – 7.15 (m, 1H), 6.26 (d, *J* = 15.7 Hz, 1H), 6.13 (dd, *J* = 15.7, 9.3 Hz, 1H), 5.73 (s, 1H), 2.46 – 2.33 (m, 4H), 2.31-2.15 (m, 1H), 2.18 – 2.09 (m, 1H), 2.03 – 1.97 (m, 1H), 1.94 – 1.88 (m, 1H), 1.85 – 1.78 (m, 1H), 1.75 – 1.62 (m, 2H), 1.55 – 1.50 (m, 3H), 1.46 – 1.37 (m, 1H), 1.36 – 1.23 (m, 3H), 1.18 (s, 3H), 1.14 – 1.04 (m, 1H), 0.97 – 0.91 (m, 1H), 0.88 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 199.61, 171.46, 137.80, 133.85, 128.88, 128.50, 126.82,

125.98, 123.80, 53.70, 52.59, 50.88, 44.66, 38.69, 36.15, 35.71, 34.75, 33.99, 32.97, 32.48, 28.49, 25.70, 20.93, 20.27, 17.48. HRMS (EI+) calcd for $[C_{27}H_{34}O]^+$ ($[M]^+$): 374.2610, found: 374.2613.



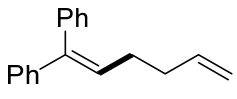

**58**

Following the procedure E, product **58** (related to **Scheme 2**) was obtained as a white solid (123 mg, 65% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.1 Hz, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 7.10 (s, 1H), 6.27 (d, *J* = 15.8 Hz, 1H), 5.90 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.91 (dd, *J* = 8.8, 4.0 Hz, 2H), 2.50 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.45 – 2.39 (m, 1H), 2.33 – 2.26 (m, 1H), 2.19 – 1.93 (m, 5H), 1.65 – 1.58 (m, 2H), 1.55 – 1.39 (m, 6H), 1.33 – 1.24 (m, 6H), 0.90 (s, 3H), 0.87 (t, *J* = 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 221.13, 138.58, 136.68, 135.81, 135.24, 129.44, 126.71, 126.68, 125.70, 123.65, 123.62, 50.69, 48.20, 45.39, 44.61, 38.44, 36.06, 35.13, 31.80, 29.84, 29.62, 28.48, 26.74, 25.97, 23.05, 21.79, 14.32, 14.04, 12.06. HRMS (EI+) calcd for $[C_{27}H_{38}O]^+$ ($[M]^+$): 378.2923, found: 378.2929.



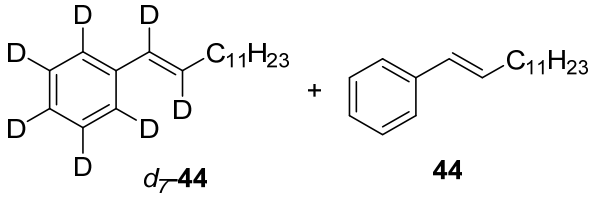

**60**

Following the procedure E, product **60** (related to **Scheme 2**) was obtained as a clear liquid (76 mg, 42% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 4H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 6.60 (s, 1H), 6.29 (d, *J* = 16.2 Hz, 1H), 6.16 (d, *J* = 16.2 Hz, 1H), 3.90 (t, *J* = 6.4 Hz, 2H), 2.28 (s, 3H), 2.18 (s, 3H), 1.80 – 1.71 (m, 2H), 1.59 – 1.52 (m, 2H), 1.31 (s, 9H), 1.13 (s, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 157.11, 149.90, 139.54, 136.45, 135.17, 130.28, 125.81, 125.74, 125.44, 123.62, 120.59, 112.01, 68.43, 39.44, 36.08, 34.52, 31.37, 27.37, 25.03, 21.44, 15.86. HRMS (EI+) calcd for $[C_{26}H_{36}O]^+$ ($[M]^+$): 364.2766, found: 364.2761.



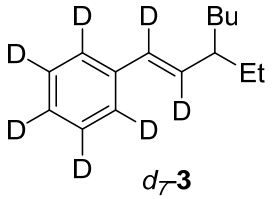

**61**

Following the procedure E, product **61** (related to **Scheme 3A**) was obtained as a clear liquid (72.3 mg, 62%). $^1$H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.33 (m, 2H), 7.32 – 7.28 (m, 1H), 7.27 – 7.24 (m, 1H), 7.24 – 7.19 (m, 4H), 7.19 – 7.16 (m, 2H), 6.10 – 6.05 (m, 1H), 5.86 – 5.73 (m, 1H), 5.08 – 4.80 (m, 2H), 2.25 – 2.17 (m, 4H). $^{13}$C NMR (100 MHz, Chloroform-d) δ 142.79, 141.95, 140.19, 138.13, 129.92, 129.20, 128.16, 128.08, 127.26, 126.91, 126.86, 114.94, 34.06, 29.15. The spectrum data matches previously reported values (Jiménez-Aquino et al., 2011).



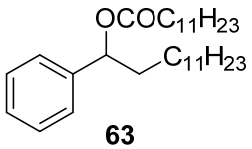

*d*$_7$-**44** **44**

Following the procedure H, product **44** and *d*$_7$-**44** (related to **Scheme 3B**) were obtained as a clear liquid (60% total yield). $^1$H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 2H), 7.21 – 7.15 (m, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.27 – 6.17 (m, 1H), 2.23 – 2.16 (m, 4H), 1.50 – 1.41 (m, 4H), 1.34 – 1.24 (m, 32H), 0.88 (t, *J* = 6.8 Hz, 6H).



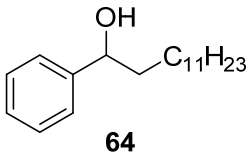

*d*$_7$-**3**

Following the procedure G, product *d*$_7$-**3** (related to **Scheme 3B**) was obtained as a clear liquid (62.2 mg, 60% yield). $^1$H NMR (400 MHz, Chloroform-d) δ 2.05 – 1.97 (m, 1H), 1.54 – 1.41 (m, 2H), 1.35 – 1.24 (m, 6H), 0.88 (t, *J* = 7.5 Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 137.80, 135.14 (t, *J* = 22.4 Hz), 129.14 (t, *J* = 22.9 Hz), 127.97 (t, *J* = 24.00 Hz), 126.20 (t, *J* = 23.8 Hz), 125.54 (t, *J* = 23.7 Hz), 45.02, 34.88, 29.68, 28.23, 22.92, 14.15, 11.89.




**63**

Compound **63** (related to **Scheme 3C**): $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.35-7.30 (m,4H), 7.29-7.26 (m, 1H), 5.72 (dd, *J* = 7.8, 6.1 Hz, 1H), 2.34-2.28 (m, 2H), 1.94-1.83 (m, 1H), 1.80-1.69 (m, 1H), 1.65-1.58 (m, 2H), 1.31-1.21 (m, 36H), 0.88 (t, *J* = 6.7 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 173.23, 141.10, 128.37, 127.72, 126.49, 75.86, 36.42, 34.65, 31.94, 29.68, 29.66, 29.63, 29.58, 29.50, 29.38, 29.36, 29.30, 29.14, 25.55, 25.05, 22.72, 14.15. Synthesized according to reported method (Ge et al., 2017).




**64**

Compound **64** (related to **Scheme 3C**): $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 4H), 7.29 – 7.22 (m, 1H), 4.63 (dd, *J* = 7.5, 5.9 Hz, 1H), 2.06 (s, 1H), 1.83 – 1.73 (m, 1H), 1.72 – 1.62 (m, 1H), 1.45 – 1.35 (m, 1H), 1.31 – 1.18 (m, 19H), 0.88 (t, *J* = 6.9 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 144.96, 128.43, 127.47, 125.92, 74.72, 39.14, 31.97, 29.71, 29.69, 29.64, 29.60, 29.58, 29.41, 25.88, 22.74, 14.18. Synthesized according to reported method (Jian et al., 2017).

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