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Submitted date: 12/11/2020 • Posted date: 16/11/2020

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Citation information: Jiang, Yi; Pan, Jiaoting; Yang, Tao; Lim, Joel Jun Han; Zhao, Yu; Koh, Ming Joo (2020):

Nickel-Catalyzed Site- and Stereoselective Reductive Alkylalkynylation of Alkynes. ChemRxiv. Preprint.

<https://doi.org/10.26434/chemrxiv.13182590.v2>

Development of a catalytic multicomponent reaction by orthogonal activation of readily available substrates for the streamlined difunctionalization of alkynes is a compelling objective in organic chemistry. Alkyne carboalkynylation, in particular, offers a direct entry to valuable 1,3-enynes with different substitution patterns. Here, we show that the synthesis of stereodefined 1,3-enynes featuring a trisubstituted olefin is achieved by merging alkynes, alkynyl bromides and redox-active N-(acyloxy)phthalimides through nickel-catalyzed reductive alkylalkynylation. Products are generated in up to 89% yield as single regio- and E isomers. Transformations are tolerant of diverse functional groups and the resulting 1,3-enynes are amenable to further elaboration to synthetically useful building blocks. With olefin-tethered N-(acyloxy)phthalimides, a cascade radical addition/cyclization/alkynylation process can be implemented to obtain 1,5-enynes. The present study underscores the crucial role of redox-active esters as superior alkyl group donors compared to haloalkanes in reductive alkyne dicarbofunctionalizations.

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Nickel-Catalyzed Site- and Stereoselective Reductive Alkylalkynylation of Alkynes

Yi Jiang¹, Jiaoting Pan^{1,2}, Tao Yang¹, Joel Jun Han Lim¹, Yu Zhao^{1,2*} & Ming Joo Koh^{1*}

Development of a catalytic multicomponent reaction by orthogonal activation of readily available substrates for the streamlined difunctionalization of alkynes is a compelling objective in organic chemistry. Alkyne carboalkynylation, in particular, offers a direct entry to valuable 1,3-enynes with different substitution patterns. Here, we show that the synthesis of stereodefined 1,3-enynes featuring a trisubstituted olefin is achieved by merging alkynes, alkynyl bromides and redox-active *N*-(acyloxy)phthalimides through nickel-catalyzed reductive alkylalkynylation. Products are generated in up to 89% yield as single regio- and *E* isomers. Transformations are tolerant of diverse functional groups and the resulting 1,3-enynes are amenable to further elaboration to synthetically useful building blocks. With olefin-tethered *N*-(acyloxy)phthalimides, a cascade radical addition/cyclization/alkynylation process can be implemented to obtain 1,5-enynes. The present study underscores the crucial role of redox-active esters as superior alkyl group donors compared to haloalkanes in reductive alkyne dicarbofunctionalizations.

Aliphatic carboxylic acids are abundant feedstock chemicals that have found extensive utility in chemical synthesis.¹⁻² With recent advances in cross-coupling chemistry, these readily available organic molecules which were once regarded as non-traditional cross-partners, have emerged as convenient alkyl donors in catalytic decarboxylative C–C bond forming transformations, either via the innate carboxyl groups³⁻¹⁰ or their activated ester derivatives.¹¹⁻²³ These developments are further driven by the much wider commercial availability of alkyl carboxylic acids as compared to conventional alkyl halides or alkylmetal reagents.^{12,22,24} A related class of reactions that utilize *N*-(acyloxy)phthalimides (or NHPI esters) involve decarboxylative alkyl additions to alkynes²⁵ or alkenes.²⁶⁻³⁷ Intrigued by previous studies, we speculated if alkyl NHPI esters could be exploited in three-component processes by merging with an alkyne and an alkynyl halide to deliver synthetically valuable acyclic 1,3-enyne motifs, conjugated entities commonly embedded within natural products, pharmaceuticals, agrochemicals and materials.³⁸⁻⁴²

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Various routes to architecturally analogous 1,3-enynes that contain a trisubstituted alkene moiety⁴³⁻⁵⁴ have been developed, but the majority focused on two-component systems involving coupling reactions of elaborated alkynes/alkenes as starting materials.^{43,47-48,51-54} Three-component catalytic regimes^{44-46,49} starting from simpler, more readily accessible substrates offer a more practical approach to expeditiously assemble the desired products. However, these methods suffer from a number of shortcomings. Activated α -functionalized alkyl halides are frequently employed to generate a stabilized alkyl radical species for alkyne addition,⁴⁴ and a second catalyst is sometimes required to promote C(sp)–C(sp²) bond formation^{44-45,49} which limit broad utility.

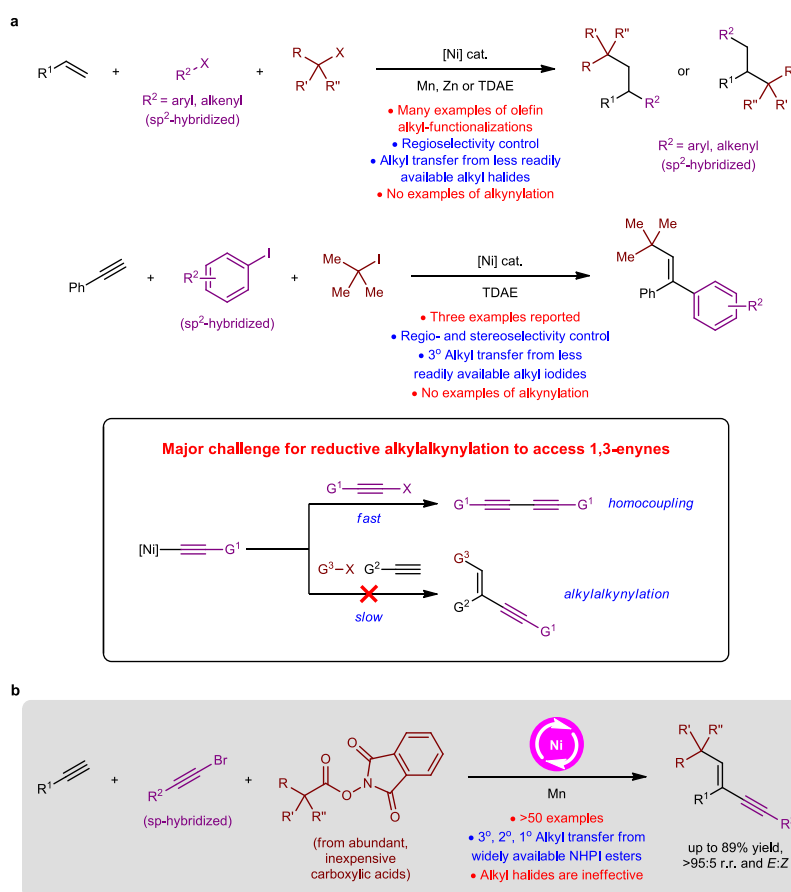


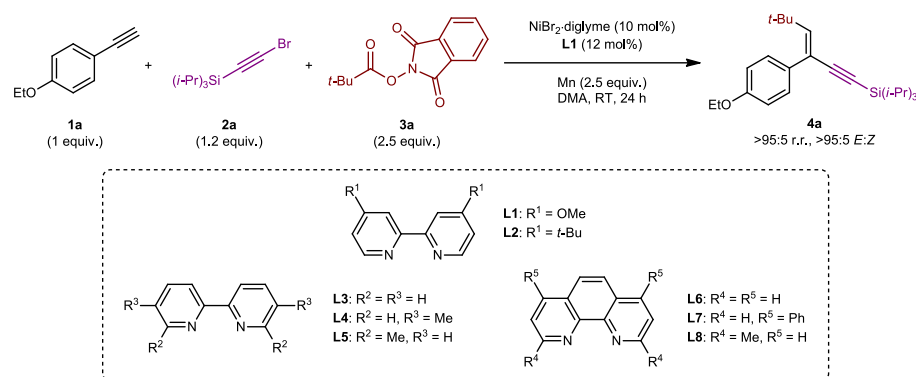
Fig. 1 | The significance of developing site- and stereoselective reductive alkyne alkylalkynylation. a, State-of-the-art advances in multicomponent reductive alkyfunctionalizations of unsaturated C–C bonds. Examples of reductive additions to alkynes with sp-hybridized electrophiles are yet to be reported, presumably due to the difficulties of overcoming rapid homocoupling of the reactive alkynyl halide. **b,** Ni-catalyzed reductive alkylalkynylation of alkynes using NHPI esters and haloalkynes offers a convenient strategy to assemble stereodefined 1,3-enynes in one step by exploiting widely available redox-active esters as efficient alkyl group donors. R, functional group; X, halide; cat., catalyst; NHPI, *N*-hydroxyphthalimide; TDAE, tetrakis(dimethylamino)ethylene.

A growing class of three-component dicarbofunctionalization reactions pertain to the regioselective addition of carbogenic groups, derived from stable electrophilic organohalides (vs. the more sensitive organometallic reagents⁵⁵⁻⁵⁶), across C–C π bonds in the presence of a mild reducing agent.⁵⁷⁻⁶² To date, most reductive alkyl-functionalization processes involve alkyl-aryl or alkyl-alkenyl additions to olefins using iodo- or bromoalkanes as the alkyl group donor (Fig. 1a). In contrast, the corresponding transformations with alkynes are severely under-developed and restricted to alkyl-arylations using organoiodide reagents.⁵⁷ One longstanding challenge that arises from three-component reductive alkynylation processes is the high propensity of the haloalkyne electrophile to undergo facile homocoupling in the presence of a Ni-based complex, inadvertently suppressing the desired alkylalkynylation pathway (Fig. 1a, inset; see Fig. 4 for further discussion). Notwithstanding these limitations, we reasoned that the union of an alkyne, an alkynyl halide and a redox-active NHPI ester can be achieved using a Ni-based catalyst under appropriate reductive conditions to give diverse 1,3-enynes with simultaneous control of site and stereoselectivity (Fig. 1b).

Our motivation to pursue this approach is twofold: (1) The greater variety of *N*-(acyloxy)phthalimides accessible from aliphatic carboxylic acids (vs. alkyl halides) means that diverse aliphatic units (tertiary, secondary, primary) can be incorporated; (2) The ability of NHPI esters to promote challenging alkylalkynylations in which alkyl halides fail to deliver, by minimizing rampant undesired pathways arising from homocoupling⁶³⁻⁶⁴ and cross-coupling^{14,16} of the alkynyl halide and NHPI ester reactants, as well as alkyne cyclotrimerization⁶⁵ (see Fig. 4 for further discussion). Herein, we disclose the first reductive protocol that accomplishes selective alkyne alkylalkynylation using NHPI esters as efficient aliphatic group donors.

Results

Table 1 | Evaluation of reaction conditions for reductive alkylalkynylation



Entry	Deviation from standard conditions	Conversion (%) [*]	Yield (%) [*]
1	none	78	67
2	Zn instead of Mn	>95	16
3	TDAE instead of Mn	36	<5
4	$\text{Ni}(\text{cod})_2$, $\text{NiCl}_2 \cdot \text{glyme}$ or NiI_2 instead of $\text{NiBr}_2 \cdot \text{glyme}$	74–81	39–57
5	L2–L8 instead of L1	31–82	<5–55
6	MeCN, DMF or DMSO instead of DMA	25–82	<5–41
7	TMSCl (0.5 equiv.) added	77	25
8	ZnCl_2 (0.5 equiv.) added	50	15
9	MgBr_2 (0.5 equiv.) added	68	36
10	LiBr (0.5 equiv.) added	85	76 (73)

Reactions were performed on 0.1 mmol scale. ^{*}Conversions (based on consumption of **1a**) and yields determined by GC analysis. Value in parentheses denotes isolated yield. DMA, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; cod, 1,5-cyclooctadiene; TDAE, tetrakis(dimethylamino)ethylene; TMSCl, trimethylsilyl chloride; RT, room temperature.

Reaction optimization. Examination of conditions for the reaction of **1a** (1 equiv.), **2a** (1.2 equiv.) and **3a** (2.5 equiv.) showed that the desired 1,3-enyne product **4a** could be obtained in 67% GC yield (>95% regio- and *E* selectivity) in the presence of 10 mol % of the Ni-based complex derived from $\text{NiBr}_2 \cdot \text{diglyme}$ and **L1**, Mn (2.5 equiv.) and DMA as solvent under ambient conditions (Table 1, entry 1). Switching the reducing agent to Zn or tetrakis(dimethylamino)ethylene (TDAE) led to poor yields of **4a** with excessive by-product formation from **1a** cyclotrimerization⁶⁵ and **2a** homocoupling^{63–64} (Table 1, entries 2 and 3). Other Ni-based complexes were less effective in promoting alkylalkynylation (Table 1, entry 4), while less electron-rich bipyridine and phenanthroline ligands **L2–L8** afforded **4a** in unsatisfactory yields (Table 1, entry 5). Changing DMA to other polar solvents also did not improve results (Table 1, entry 6).

In order to enhance the catalytic efficiency and/or suppress the undesired formation of diyne by-products,^{63–64} various additives were experimented as detailed in Table 1, entries 7–10. Addition of TMSCl (known to activate the Mn(0) surface⁶⁶) to the reaction system was somewhat detrimental (Table 1, entry 7), whereas ZnCl_2 or MgBr_2 additives⁶⁷ also reduced the yield of **4a** (Table 1, entries 8 and 9). Considering the previously reported role of lithium salts in minimizing

diyne formation,¹⁴ we found that the use of LiBr (0.5 equiv.) indeed improved results, affording **4a** in 76% yield (73% isolated; Table 1, entry 10).

Substrate scope. To examine the generality of the established conditions, we tested a range of electronically and sterically diverse aryl- and heteroaryl-substituted alkynes, and the desired products **4b–aa** were isolated in 40–81% yield as single regio- and *E* isomers (Fig. 2). Both electron-rich and electron-deficient arenes are tolerated, including those that contain a Lewis basic aniline (**4g**), Brønsted acidic NHBoc (**4h**) and electrophilic aldehyde (**4k**). Synthesis of **4j** (<5% hydrodebromination side products) that is functionalized with a bromoaryl substituent highlights the transformation's remarkable chemoselectivity. As demonstrated by the preparation of **4b**, the transformations may be performed on larger scale (3 mmol) without appreciable diminution in efficiency.

Products that bear heterocyclic units (**4q** and **4r**), as well as those derived from complex bioactive compounds (**4u–w**) could be generated. By using a D-substituted alkyne, tetrasubstituted deuterium-labelled olefins such as **4x**, which otherwise might be difficult to prepare by other means, could be secured through the present protocol. However, internal alkynes were resistant to alkylalkynylation (cf. 5; <5% conv. to product). Aliphatic alkynes were also found to be ineffective substrates under the standard conditions. Besides silyl-substituted bromoalkynes, aryl- and alkyl-functionalized alkynyl bromides also underwent efficient reaction to deliver the expected 1,3-enynes **4y–aa** in 46–53% yield and 94–95% *E* selectivity.

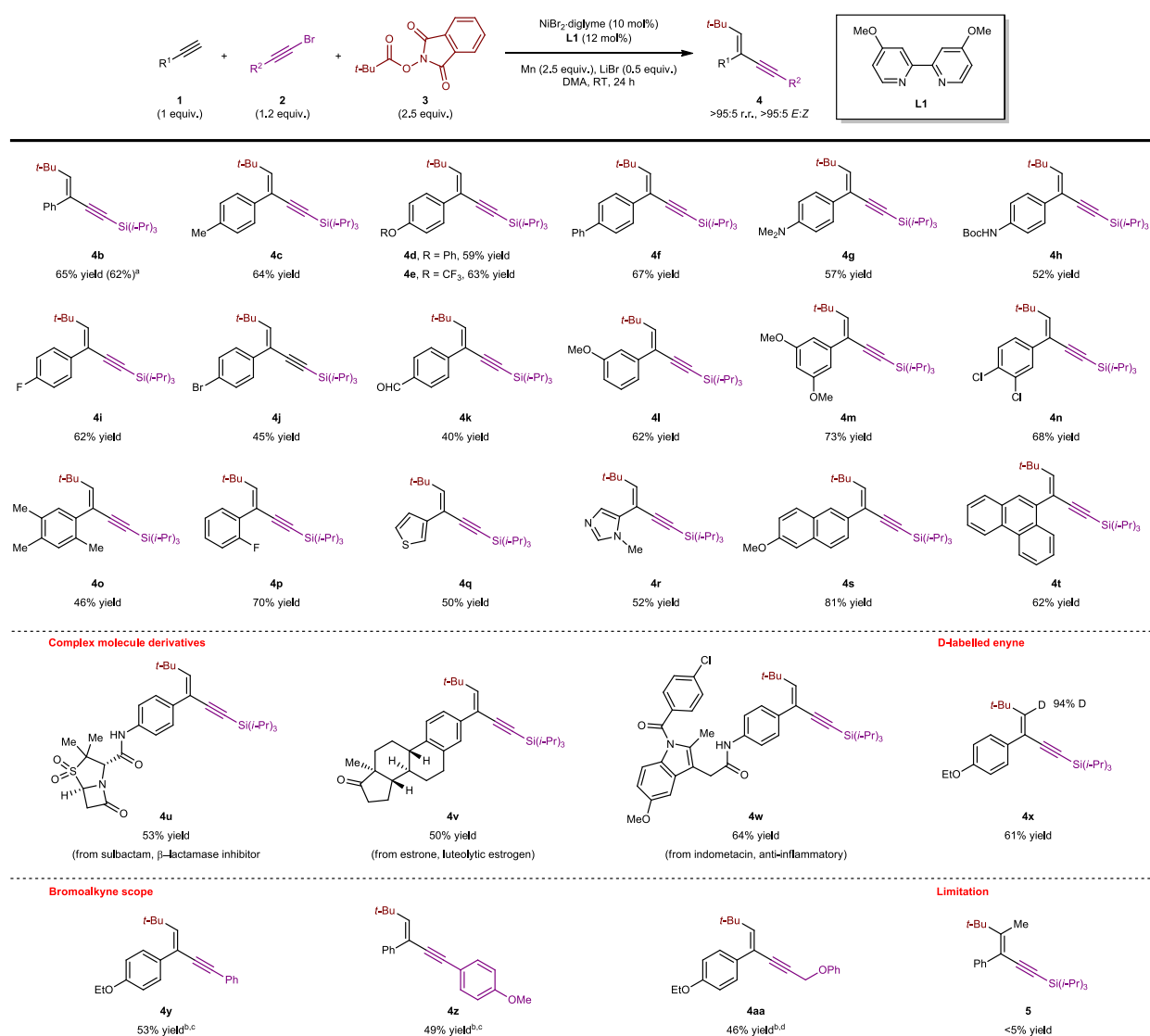


Fig. 2 | The scope of alkynes and alkynyl bromides. Regioisomeric ratios (r.r.) and *E*:*Z* ratios were determined by GC and ¹H NMR analysis. Yields are for isolated and purified products. ^aThe reaction was conducted on 3 mmol scale. ^bThe reactions were conducted with LiBr (1 equiv.) and DMSO as solvent. ^cThe products were generated in 95:5 *E*:*Z* ratio. ^dThe product was generated in 94:6 *E*:*Z* ratio. R, functional group; DMA, *N,N*-dimethylacetamide; RT, room temperature; Boc, *tert*-butoxycarbonyl.

A wide assortment of aliphatic NHPI esters served as effective reagents for alkylalkynylation (Fig. 3). These include tertiary alkyl *N*-(acyloxy)phthalimides (affording **4ab–ar** with quaternary carbon centers), secondary alkyl *N*-(acyloxy)phthalimides (affording **4au** and **4av** with tertiary carbon centers) as well as primary alkyl *N*-(acyloxy)phthalimides (**4aw** and **4ax**). To facilitate secondary and primary alkyl additions, an additional 10 mol % of CuTC was added as co-catalyst to improve yields, possibly by stabilization of the corresponding alkyl radicals generated.⁶⁸ The diversity of aliphatic groups which can be installed (such as oxetane **4af**, pyrans **4ak** and **4al**,

piperidine **4an** and acid-labile acetal **4am**) compares favorably with previous methods that employed less readily available haloalkanes.^{57,60,69}

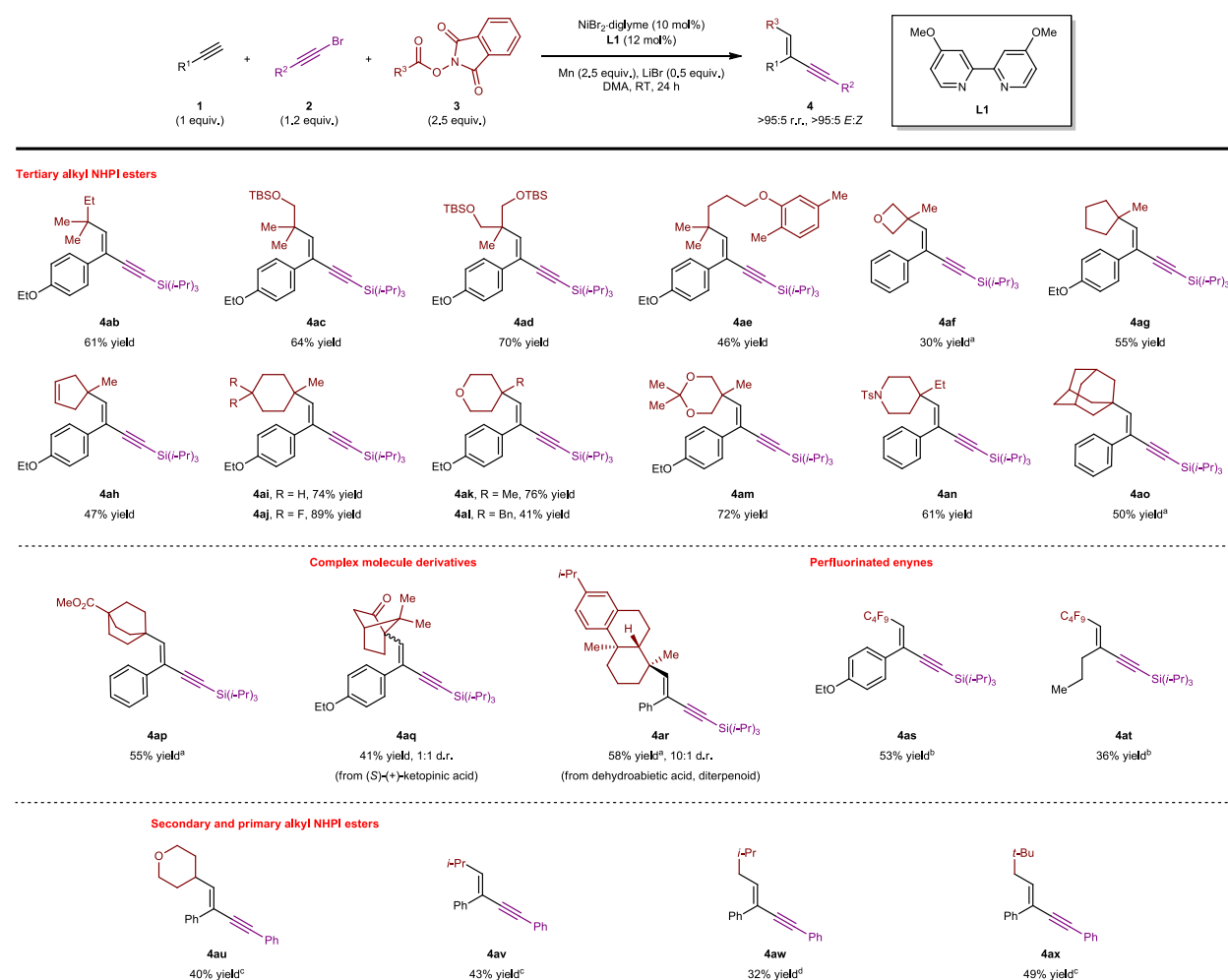


Fig. 3 | The scope of redox-active esters. Regioisomeric ratios (r.r.), diastereomeric ratios (d.r.) and *E:Z* ratios were determined by GC and ¹H NMR analysis. Yields are for isolated and purified products. ^aThe reactions were conducted with **1** (3 equiv.) and **2** (1 equiv.). ^bThe reactions were conducted with **1** (1 equiv.), **2** (1.5 equiv.) and C₄F₉I (1.7–2 equiv.). ^cThe reactions were conducted with **1** (3 equiv.), **2** (1 equiv.) and LiBr (1 equiv.) with **L4** (12 mol %) as ligand and CuTC (10 mol %) as co-catalyst. ^dThe reactions were conducted with **1** (3 equiv.), **2** (1 equiv.) and LiBr (1 equiv.) with **L1** (12 mol%) as ligand and CuTC (10 mol %) as co-catalyst. R, functional group; DMA, *N,N*-dimethylacetamide; RT, room temperature; TBS, *tert*-butyldimethylsilyl; Ts, *p*-toluenesulfonyl; TC, thiophene-2-carboxylate.

Structurally sophisticated alkyl additions could be implemented as exemplified by the products **4aq** (from ketopinonic acid) and **4ar** (from dehydroabiatic acid). To incorporate fluoroalkyl units, due to the difficulty of fluoroalkyl NHPI esters to generate the requisite fluorinated radical species,⁷⁰ we turned to perfluoroalkyl iodide to deliver alkylalkynylation of both aryl- and alkyl-substituted alkynes. In the event, the F-containing 1,3-enynes **4as** and **4at** were successfully isolated in 53% and 36% yields, respectively.

Mechanistic studies. As shown in Fig. 4, studies were carried out to elucidate the mechanism of the reductive alkyne alkylalkynylation process.

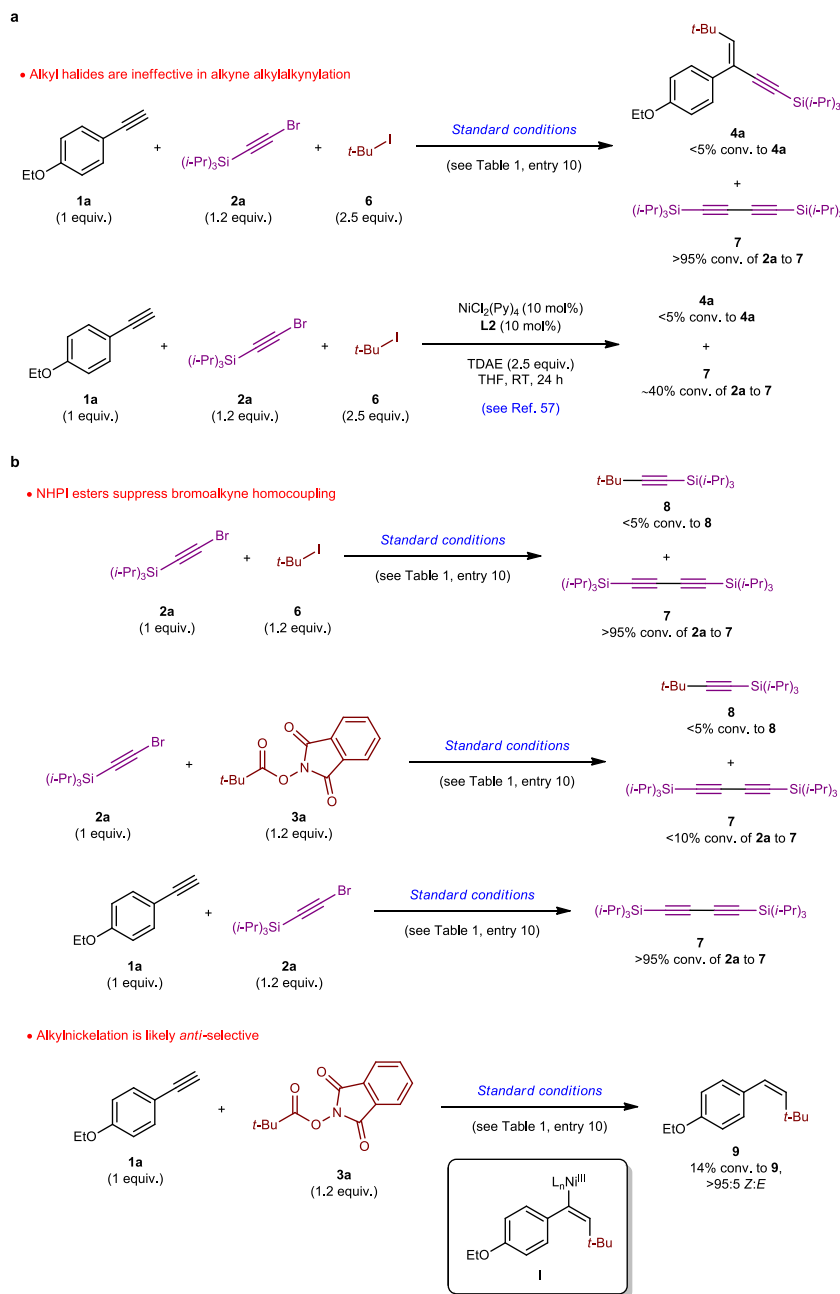


Fig. 4 | Mechanistic investigations. **a**, Unsuccessful alkyne alkylalkynylation attempts using iodoalkane as alkyl group donor. **b**, Two-component control experiments. R, functional group; L, ligand; THF, tetrahydrofuran; Py, pyridine; TDAE, tetrakis(dimethylamino)ethylene; RT, room temperature.

Remarkably, control experiments showed that when NHPI ester **3a** was replaced by the corresponding 2-iodo-2-methylpropane **6**, there was <5% conv. to the 1,3-enyne product **4a**. Instead, the alkyne **1a** was fully consumed in cyclotrimerization⁶⁵ to form arene side products,

and homocoupling of bromoalkyne **2a** to give diyne **7** was detected (Fig. 4a). Repeating the reaction under previously established reductive dicarbofunctionalization conditions⁵⁷ also did not yield **4a** (<5% conv. of **1a**, ~40% conv. of **2a** to **7**). These observations not only highlight the importance of the redox-active ester component as an effective alkyl donor in these multicomponent reactions, but also provide hints that the alkynyl bromide was probably much more reactive (vs. the alkyl iodide), inadvertently suppressing the desired alkylalkynylation pathway and causing homocoupling of the bromoalkyne to predominate.

Additional control experiments shed further light on the reaction (Fig. 4b). Under standard conditions, the reaction between bromoalkyne **2a** and **6** led to full conversion of **2a** to diyne **7** (<5% cross-coupling to **8** detected). When alkyne **1a** was treated with **2a** under the same conditions, >95% conv. to **7** was also detected and **1a** underwent undesired cyclotrimerization. In contrast, replacing the iodoalkane **6** with NHPI ester **3a** only afforded trace amounts of **7** (<5% cross-coupling to **8**) and **3a** was fully consumed (presumably by decomposition under the reductive conditions⁷¹). These observations imply that the presence of **3a** somehow inhibited **2a** homocoupling by preferentially engaging with an in situ-generated organonickel species, albeit no productive reaction could occur if alkyne **1a** was absent to trap the *t*-Bu radical formed (see Fig. 5). Notably, subjecting **1a** to **3a** under the established conditions selectively furnished *Z* alkene **9** in 14% GC yield, leading us to deduce that the C–C(*t*-Bu) bond and the adjacent C–Ni bond are generated in an *anti* configuration (presumably to minimize steric repulsions) within the alkenylnickel intermediate **I** (see Fig. 5). In the absence of the alkynyl bromide, **9** might be formed by adventitious protodemetalation of **I** with residual moisture.

Based on our investigations and related studies,^{14,60,64} a tentative mechanism is proposed in Fig. 5. Starting from an in situ-generated Ni(0) species **i** (e.g. from reduction of the Ni(II) pre-catalyst^{14,64}, oxidative addition with bromoalkyne **2** followed by single-electron reduction in the presence of Mn gives rise to an alkynylnickel(I) species **iii**. At this stage, a second molecule of **2** could potentially react with **iii** to give dialkynylnickel(III) **vii** that subsequently reductively eliminates to afford the undesired diyne side product **7**. However, if a NHPI ester **3** is present in the system, the reaction trajectory could be altered as **3** chemoselectively engages with **iii**, through a single-electron transfer (SET) decarboxylative pathway,¹⁴ to furnish alkynylnickel(II) complex **iv** with concomitant ejection of CO₂, phthalimide anion and an alkyl radical species. Facile capture of the alkyl radical by alkyne **1** generates an alkenyl radical that recombines with **iv** to form *E*-alkenylnickel(III) complex **v**. The ensuing reductive elimination then generates Ni(I)

phthalimide **vi** and releases the desired 1,3-enyne **4**. Following another single-electron reduction by Mn, **i** is regenerated to turn over the catalytic cycle. On the other hand, a less reactive alkyl halide (vs. alkyl NHPI ester) is not capable of efficiently intercepting alkynylnickel(I) complex **iii**, consequently allowing other side reactions such as homocoupling **2** to become competitive in the system.

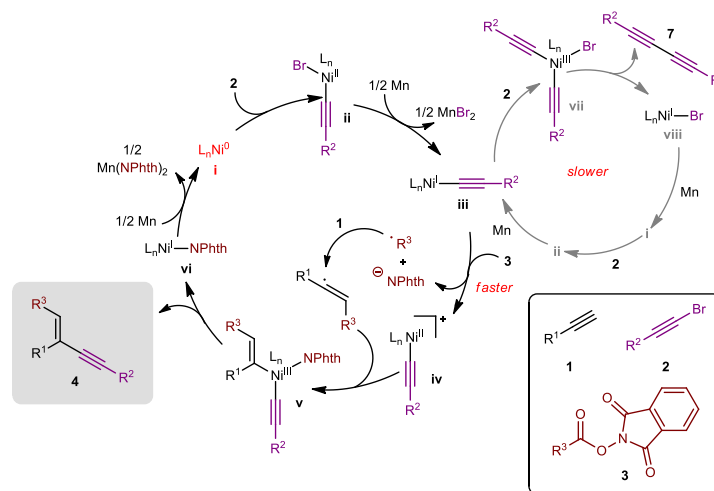


Fig. 5 | Proposed catalytic mechanism for reductive alkylalkynylation. Unlike a haloalkane, NHPI ester **3** is capable of intercepting the putative alkynylnickel intermediate **iii** to promote alkylalkynylation and suppress adventitious homocoupling of **2** to diyne **7**. R, functional group; L, ligand; Phth, phthaloyl.

Synthetic transformations. Using redox-active esters **10** tethered to a terminal olefin, we postulated that a cascade pathway⁷² commencing from alkyl radical addition to the alkyne followed by an intramolecular 5-*exo-trig* cyclization with the C=C bond to give a second alkyl radical species **III** before reassociation with the Ni complex for subsequent alkynylation could occur (Fig. 6a). This would give rise to complex 1,5-enynes **11** bearing a trisubstituted cyclopentene nucleus and an alkyne appendage. Gratifyingly, the Ni-catalyzed cascade processes proceeded smoothly to generate the desired products **11a–e** in up to 85% yield, further demonstrating the versatility of the alkylalkynylation regime by taking advantage of radical-based reactivity modes to construct complex molecules.

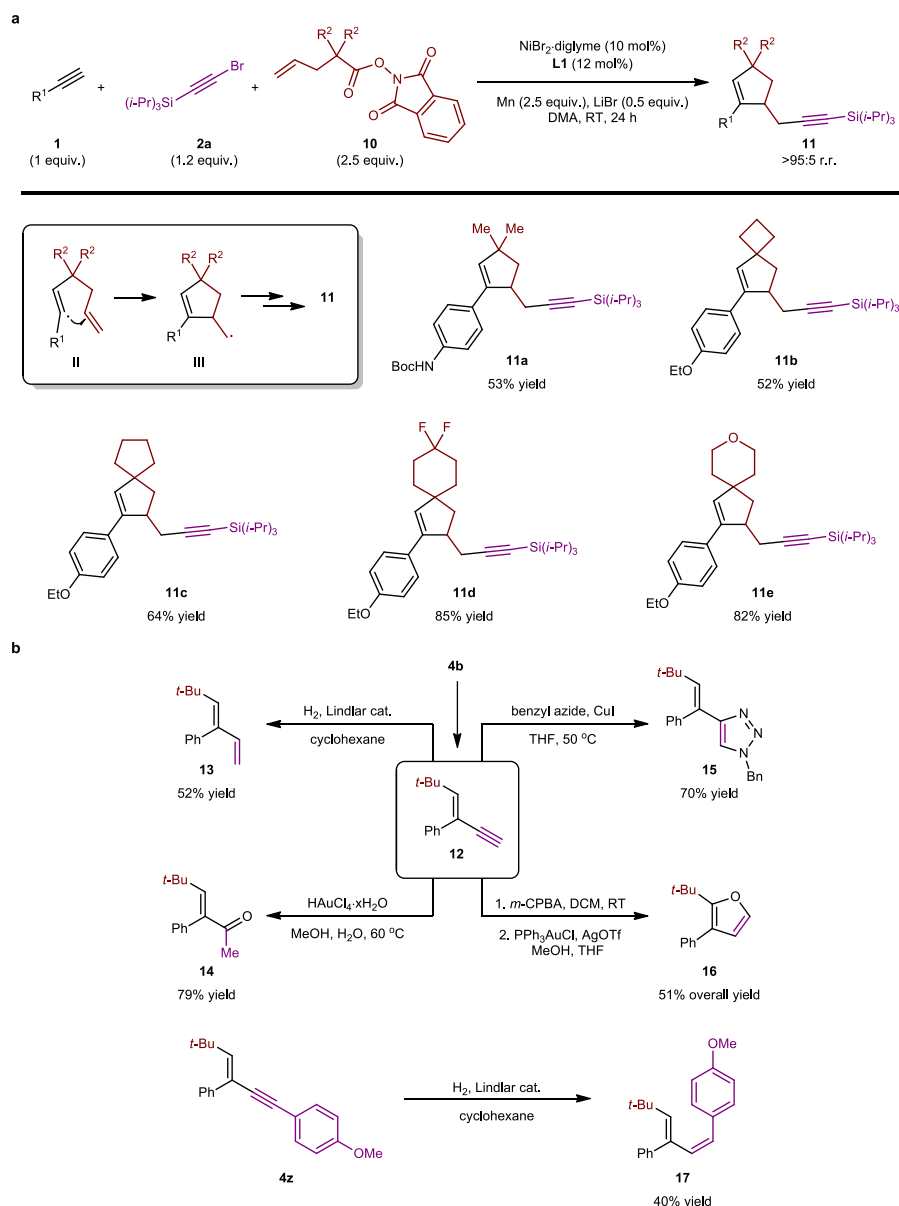


Fig. 6 | Application to cascade processes and further derivatization. a, Cascade radical addition/cyclization/alkynylation to furnish 1,5-enynes. **b,** Chemical transformations of stereodefined 1,3-enynes to synthetically valuable building blocks. R, functional group; DMA, *N,N*-dimethylacetamide; DCM, dichloromethane; THF, tetrahydrofuran; RT, room temperature; cat., catalyst; Bn, benzyl; Boc, *tert*-butoxycarbonyl; Tf, trifluoromethanesulfonyl; *m*-CPBA, *meta*-chloroperoxybenzoic acid.

Utility of the 1,3-enyne products is showcased through a series of synthetic manipulations involving both the olefin and alkyne motifs towards the preparation of diverse molecular structures (Fig. 6b). Using the desilylated derivative **12** from **4b**,⁷³ facile transformation of the terminal alkyne moiety to a spectrum of different products can be effected by partial hydrogenation to the 1,3-diene **13** in 52% yield,⁷⁴ Au-catalyzed hydration to ketone **14** in 79% yield,⁷⁵ and Cu-catalyzed azide-alkyne cycloaddition to 1,2,3-triazole **15** in 70% yield.⁷⁶ In another

instance, chemoselective epoxidation of the trisubstituted olefin followed by Au-catalyzed cycloisomerization⁷⁷ afforded the disubstituted furan derivative **16** in 51% overall yield. On the other hand, partial *cis*-selective hydrogenation of the internal alkyne in **4z** generated sterically congested 1,3-diene **17** in 40% yield as a single *Z* isomer.

To conclude, we have demonstrated that a single Ni-based catalyst is capable of mediating regio- and stereoselective alkyl-alkynyl additions to alkynes to deliver valuable 1,3-enyne products. Access to 1,5-enynes was achieved through a radical-based cascade transformation, and our investigations shed light on the superior performance of redox-active esters in overcoming undesired haloalkyne homocoupling by competitively intercepting a putative alkynylnickel intermediate. In situations where two electrophilic halides proved to be ineffective, the synergistic combination of a redox-active ester and an organohalide may provide viable solutions to address other longstanding challenges in dicarbofunctionalizations that employ multiple electrophiles.

Data availability

All data are available from the corresponding authors upon reasonable request.

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Acknowledgements

This research was supported by the Ministry of Education of Singapore Academic Research Funds Tier 1: R-143-000-B57-114 (M.J.K.) and Tier 2: R-143-000-A94-112 (Y.Z.).

Author contributions

Y.J., J.P. and J.J.H.L. developed the catalytic method. M.J.K. and Y.Z. directed the investigations. M.J.K. wrote the manuscript with revisions provided by the other authors.

Competing interests

The authors declare no competing financial interests.

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Supplementary Information

Nickel-Catalyzed Site- and Stereoselective Reductive

Alkylalkynylation of Alkynes

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1. General information

All commercial reagents were used without additional purification, unless otherwise stated. Anhydrous solvent was purchased from commercial sources and transferred under an argon atmosphere. NMR spectra were recorded on Bruker 400 MHz and Bruker DPX 500 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuterium incorporation as the internal standard (CDCl_3 : δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, dt = doublet of triplet, dd = double doublet, ddd = doublet of a double doublet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on Bruker 400 MHz and Bruker DPX 500 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 77.20 ppm). ^{19}F NMR spectra were recorded on Bruker 400 MHz spectrometer with complete proton decoupling or proton coupling. High-resolution mass spectrometric data (HRMS) were obtained using Agilent 7200 Q-TOF and Bruker MicroTOF-QII (APCI, or Electrospray ionization, ESI). GC-MS analysis was performed on Shimadzu GCMS-QP2020 gas chromatography coupled to a Shimadzu QP2010 mass selective detector. Values for regioisomeric ratio and *E/Z* of products were determined by GC (GC-QP2030) and NMR analysis.

Solvents

Solvents (acetonitrile, CH_2Cl_2 , diethyl ether, tetrahydrofuran and toluene) were purified under a positive pressure of dry nitrogen gas by a modified Innovative Technologies purification system. *N,N*-Dimethylacetamide (anhydrous), *N,N*-dimethylformamide (anhydrous), dimethyl sulfoxide (anhydrous), dimethoxyethane (anhydrous) and 1,4-dioxane (anhydrous) were used as received. All purification procedures of products were carried out with reagent grade solvents.

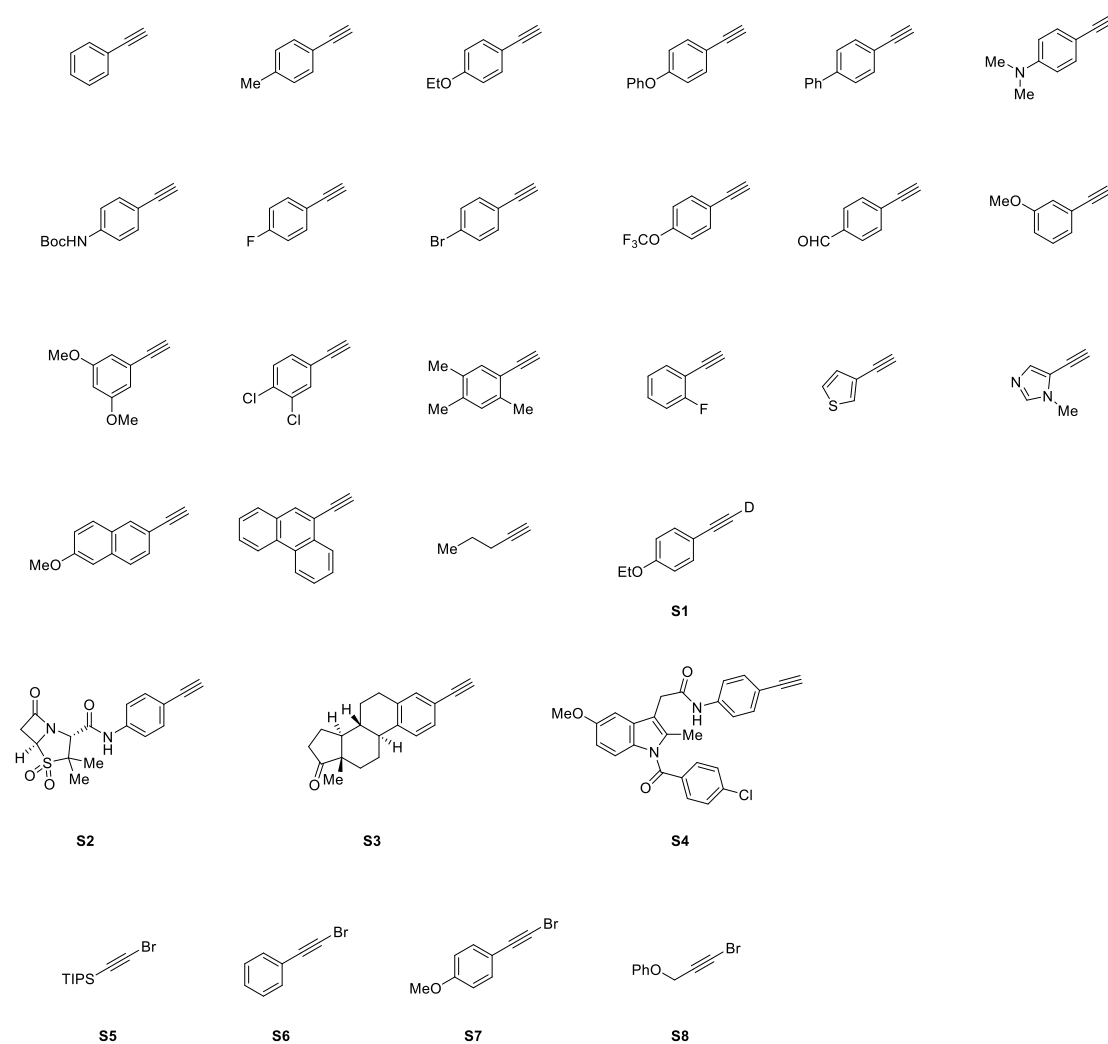
Materials

Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa

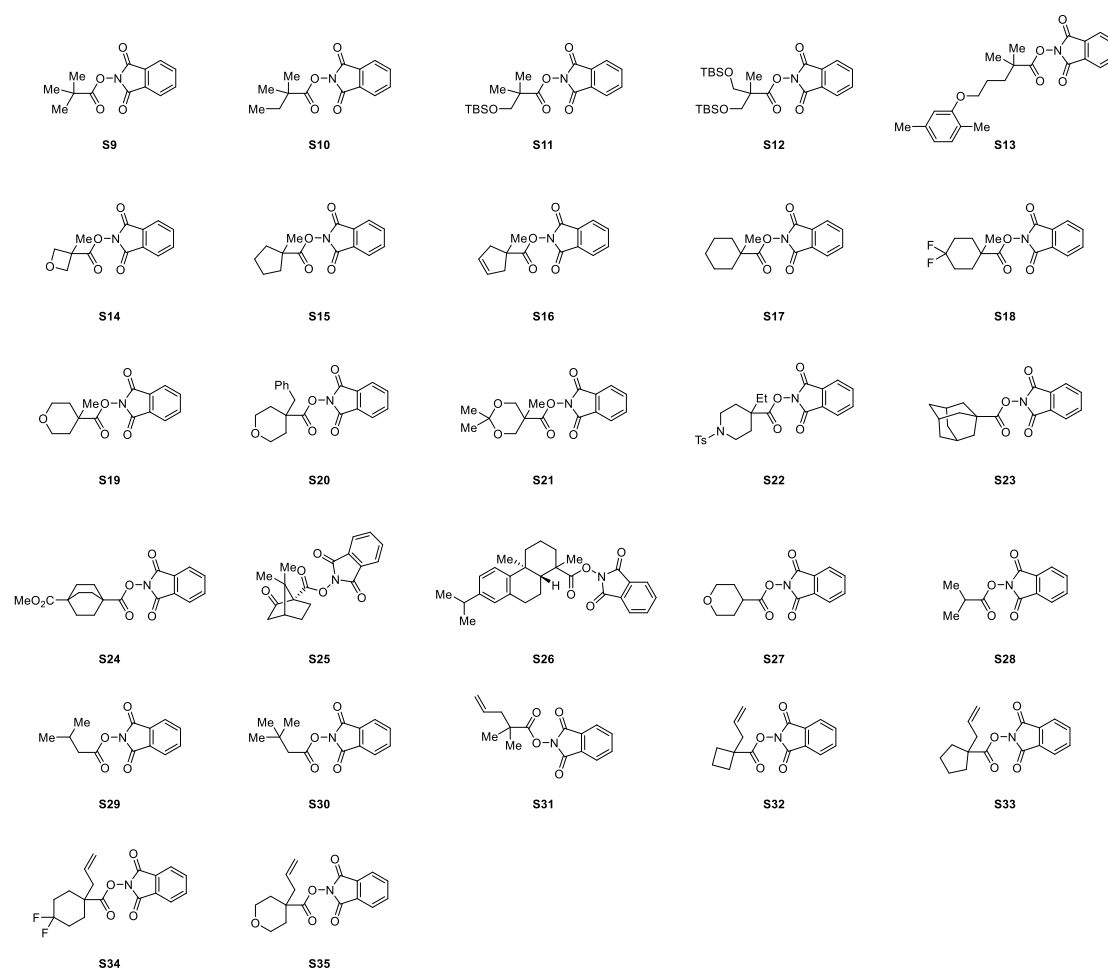
Aesar, or other commercial suppliers and were used as received. Anhydrous NiI_2 (99.5% (metals basis)) were purchased from Alfa Aesar. Anhydrous $\text{NiBr}_2(\text{diglyme})$, $\text{NiCl}_2(\text{glyme})$, and $\text{Ni}(\text{cod})_2$ were purchased from Sigma Aldrich. Mn (powder, $\geq 99.9\%$ trace metals basis) was purchased from Sigma Aldrich. Anhydrous LiBr , anhydrous MgBr_2 , anhydrous ZnCl_2 and TMSCl were purchased from Sigma Aldrich, Alfa Aesar or TCI (Tokyo Chemical Industry).

2. Preparation of Substrates

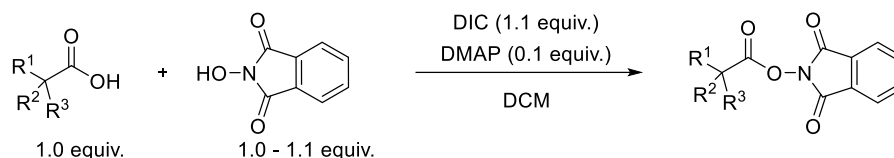
Scheme S1. Substrate scope of alkynes and alkynyl bromides



Scheme S2. Substrate scope of NHPI esters



2.1 General procedure A for preparation of redox-active NHPI esters

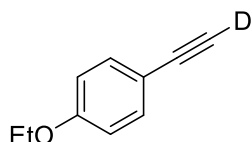


NHPI esters were prepared according to a previously reported procedure^[1]. A round-bottom flask was charged with (if solid) carboxylic acid (1.0 equiv.), *N*-hydroxyphthalimide (1.0 – 1.1 equiv.) and DMAP (0.1 equiv.). Dichloromethane was added (0.2– 0.4 M), and the mixture was stirred vigorously. Carboxylic acid (1.0 equiv.) was added via syringe (if liquid). DIC (1.1 equiv.) was then added dropwise via syringe, and the mixture was allowed to stir until the acid was consumed (determined by TLC). Typical reaction times were between 0.5 to 3 h. The mixture was filtered through a fritted funnel and rinsed with additional CH₂Cl₂/Et₂O. The solvent was removed under reduced pressure, and purification by column

chromatography afforded the corresponding activated esters, which were used without further purification unless otherwise noted. *Note: Some esters are prone to hydrolysis on silica gel during column chromatography and should be purified as quickly as possible to avoid decomposition.*

3. Analytical data of substrates

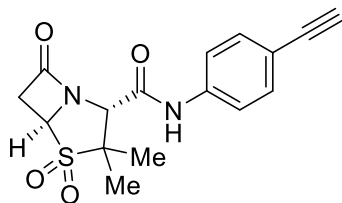
1-Ethoxy-4-(ethynyl-*d*)benzene (S1, 96%D)



The title compound was prepared according to a reported procedure.^[2]

¹H NMR (400 MHz, CDCl₃): δ 7.43 – 7.40 (m, 2H), 6.84 – 6.81 (m, 2H), 4.03 (q, 2H, *J* = 7.0 Hz), 2.99 (s, 0.04H), 1.41 (t, 3H, *J* = 7.0 Hz); HRMS (EI) *m/z* calcd for C₁₀H₉DO [M]⁺: 147.0789, found: 147.0783.

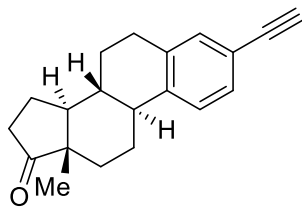
(2*R*,5*S*)-*N*-(4-Ethynylphenyl)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxamide 4,4-dioxide (S2)



The title compound was prepared according to a reported procedure.^[3]

¹H NMR (400 MHz, CDCl₃): δ 8.23 (br, 1H), 7.52 – 7.47 (m, 4H), 4.70 (s, 1H), 4.32 (s, 1H), 3.60 (s, 2H), 3.08 (s, 1H), 1.73 (s, 3H), 1.51 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 172.6, 164.6, 136.7, 133.3, 120.0, 119.3, 83.1, 77.7, 64.7, 64.0, 60.8, 38.7, 19.7, 18.5; HRMS (ESI) *m/z* calcd for C₁₆H₁₆N₂NaO₄S [(M+Na)⁺]: 355.0723, found: 355.0725.

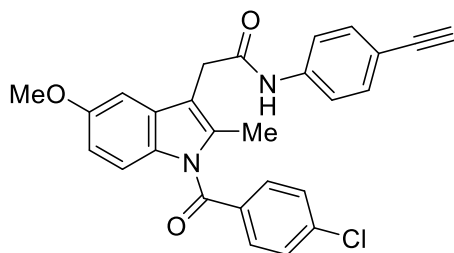
(8*R*,9*S*,13*S*,14*S*)-3-Ethynyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (S3)



The title compound was prepared according to a reported procedure.^[4]

¹H NMR (400 MHz, CDCl₃): δ 7.29 – 7.26 (m, 1H), 7.25 – 7.23 (m, 2H), 3.02 (s, 1H), 2.90 – 2.87 (m, 2H), 2.54 – 2.47 (m, 1H), 2.44 – 2.39 (m, 1H), 2.30 (td, 1H, *J* = 10.6, 4.5 Hz), 2.19 – 2.10 (m, 1H), 2.09 – 1.95 (m, 3H), 1.66 – 1.58 (m, 2H), 1.56 – 1.41 (m, 4H), 0.91 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 220.9, 141.0, 136.8, 132.8, 129.6, 125.5, 119.6, 83.9, 76.6, 50.7, 48.1, 44.6, 38.1, 36.0, 31.7, 29.2, 26.5, 25.7, 21.7, 14.0; HRMS (EI) *m/z* calcd for C₂₀H₂₂O [M]⁺: 278.1665, found: 278.1663.

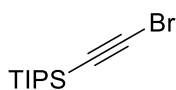
2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)-*N*-(4-ethynylphenyl)acetamide (S4)



The title compound was prepared according to a reported procedure.^[3]

¹H NMR (400 MHz, CDCl₃): δ 7.64 – 7.60 (m, 3H), 7.48 – 7.44 (m, 2H), 7.37 (s, 4H), 6.94 (d, 1H, *J* = 2.5 Hz), 6.86 (d, 1H, *J* = 9.0 Hz), 6.70 (dd, 1H, *J* = 9.0, 2.5 Hz), 3.79 (s, 3H), 3.77 (s, 2H), 3.03 (s, 1H), 2.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 168.50, 168.46, 156.5, 139.8, 138.0, 136.8, 133.6, 133.0, 131.3, 131.1, 130.3, 129.4, 119.8, 118.1, 115.4, 112.5, 112.3, 101.0, 83.4, 77.1, 55.9, 33.5, 13.5; HRMS (ESI) *m/z* calcd for C₂₇H₂₂ClN₂O₃ [(M+H)⁺]: 457.1313, found: 457.1316.

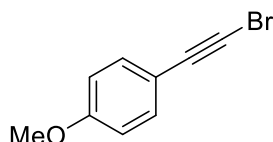
(Bromoethynyl)triisopropylsilane (S5)



The title compound was prepared according to a reported procedure.^[5]

^1H NMR (400 MHz, CDCl_3): δ 1.08 (s, 21H); ^{13}C NMR (101 MHz, CDCl_3): δ 83.7, 61.9, 18.7, 11.5; HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{21}\text{BrSi}$ $[\text{M}]^+$: 260.0590, found: 260.0585.

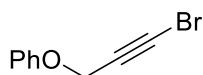
1-(Bromoethynyl)-4-methoxybenzene (S7)



The title compound was prepared according to a reported procedure.^[5]

^1H NMR (400 MHz, CDCl_3): δ 7.40 – 7.37 (m, 2H), 6.85 – 6.81 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 160.1, 133.6, 115.0, 114.1, 80.1, 55.5, 48.0; HRMS (EI) m/z calcd for $\text{C}_9\text{H}_7\text{BrO}$ $[\text{M}]^+$: 209.9675, found: 209.9672.

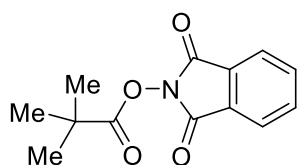
((3-Bromoprop-2-yn-1-yl)oxy)benzene (S8)



The title compound was prepared according to a reported procedure.^[5]

^1H NMR (400 MHz, CDCl_3): δ 7.34 – 7.30 (m, 2H), 7.04 – 6.96 (m, 3H), 4.72 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ 157.7, 129.7, 121.8, 115.0, 75.3, 56.8, 47.7; HRMS (EI) m/z calcd for $\text{C}_9\text{H}_7\text{BrO}$ $[\text{M}]^+$: 209.9675, found: 209.9670.

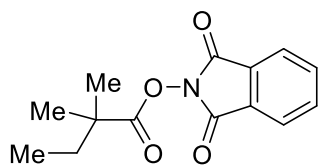
1,3-Dioxoisindolin-2-yl pivalate (S9)



Following the **General procedure A** with pivalic acid (1.02 g, 10.0 mmol) and *N*-hydroxyphthalimide (1.79 g, 11.0 mmol) in CH_2Cl_2 (20.0 mL) at rt for 0.5 h afforded 1.98 g (80%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

^1H NMR (400 MHz, CDCl_3): δ 7.89 – 7.85 (m, 2H), 7.80 – 7.77 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 174.5, 162.2, 134.8, 129.2, 124.0, 38.6, 27.2.

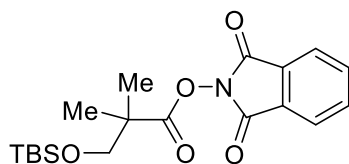
1,3-Dioxoisindolin-2-yl 2,2-dimethylbutanoate (S10)



Following the **General procedure A** with 2,2-dimethylbutanoic acid (232 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 407 mg (78%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.88 – 7.85 (m, 2H), 7.80 – 7.76 (m, 2H), 1.78 (q, 2H, *J* = 7.5 Hz), 1.38 (s, 6H), 1.04 (t, 3H, *J* = 7.5 Hz); ¹³C NMR (101 MHz, CDCl₃): δ 174.1, 162.3, 134.8, 129.3, 124.0, 42.7, 33.7, 24.8, 9.3; HRMS (ESI) *m/z* calcd for C₁₄H₁₅NNaO₄ [(M+Na)⁺]: 284.0893, found: 284.0900.

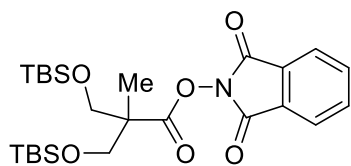
1,3-Dioxoisindolin-2-yl 3-((*tert*-butyldimethylsilyl)oxy)-2,2-dimethylpropanoate (S11)



Following the **General procedure A** with 3-((*tert*-butyldimethylsilyl)oxy)-2,2-dimethylpropanoic acid (464 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 603 mg (80%) of the title compound after purification by column chromatography (eluent, 5:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.75 – 7.72 (m, 2H), 7.68 – 7.64 (m, 2H), 3.66 (s, 2H), 1.29 (s, 6H), 0.82 (s, 9H), 0.00 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 172.8, 161.9, 134.7, 129.1, 123.9, 69.3, 44.9, 25.9, 22.0, 18.3, -5.6; HRMS (ESI) *m/z* calcd for C₁₉H₂₇NNaO₅Si [(M+Na)⁺]: 400.1551, found: 400.1557.

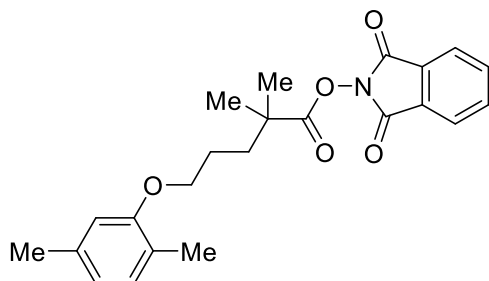
1,3-Dioxoisindolin-2-yl 3-((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-2-methylpropanoate (S12)



Following the **General procedure A** with 3-(((*tert*-butyldimethylsilyl)oxy)methyl)-2-methylpropanoic acid (724 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 790 mg (78%) of the title compound after purification by column chromatography (eluent, 5:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.89 – 7.84 (m, 2H), 7.78 – 7.74 (m, 2H), 3.93 (d, 2H, *J* = 9.4 Hz), 3.81 (d, 2H, *J* = 9.5 Hz), 1.36 (s, 3H), 0.91 (s, 18H), 0.09 (s, 6H), 0.08 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 171.3, 161.9, 134.7, 129.3, 124.0, 63.8, 50.6, 26.0, 18.4, 17.3, -5.4, -5.5; HRMS (ESI) *m/z* calcd for C₂₅H₄₁NNaO₆Si₂ [(M+Na)⁺]: 530.2365, found: 530.2378.

1,3-Dioxoisindolin-2-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (S13)

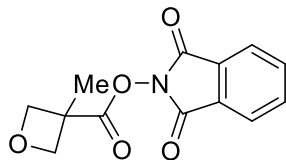


Following the **General procedure A** with 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid (500 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 1 h afforded 561 mg (71%) of the title compound after purification by column chromatography (eluent, 5:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.90 – 7.86 (m, 2H), 7.81 – 7.78 (m, 2H), 7.00 (d, 1H, *J* = 7.8 Hz), 6.67 – 6.65 (m, 2H), 4.01 (t, 2H, *J* = 5.0 Hz), 2.32 (s, 3H), 2.19 (s, 3H), 1.98 – 1.94 (m, 4H), 1.45 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 173.9, 162.3, 157.1, 136.7, 134.9, 130.4, 129.2, 124.0, 123.8, 120.9, 112.2, 67.9, 42.1, 37.6, 25.3, 25.2,

21.6, 15.9; HRMS (ESI) m/z calcd for $C_{23}H_{25}NNaO_5$ $[(M+Na)^+]$: 418.1625, found: 418.1620.

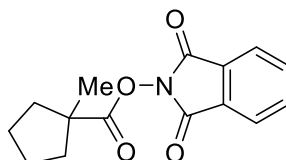
1,3-Dioxoisindolin-2-yl 3-methyloxetane-3-carboxylate (S14)



Following the **General procedure A** with 3-methyloxetane-3-carboxylic acid (232 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH_2Cl_2 (10.0 mL) at rt for 0.5 h afforded 360 mg (69%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

1H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.88 (m, 2H), 7.83 – 7.79 (m, 2H), 5.17 (d, 2H, J = 6.2 Hz), 4.54 (d, 2H, J = 6.2 Hz), 1.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 161.9, 135.0, 129.1, 124.2, 79.2, 43.5, 21.6; HRMS (ESI) m/z calcd for $C_{13}H_{11}NNaO_5$ $[(M+Na)^+]$: 284.0529, found: 284.0523.

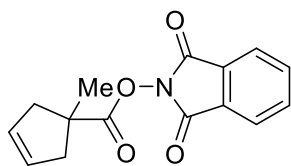
1,3-Dioxoisindolin-2-yl 1-methylcyclopentane-1-carboxylate (S15)



Following the **General procedure A** with 1-methylcyclopentane-1-carboxylic acid (256 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH_2Cl_2 (10.0 mL) at rt for 0.5 h afforded 447 mg (82%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

1H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.85 (m, 2H), 7.80 – 7.75 (m, 2H), 2.40 – 2.33 (m, 2H), 1.85 – 1.73 (m, 4H), 1.70 – 1.63 (m, 2H), 1.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.8, 162.4, 134.8, 129.3, 124.0, 48.5, 38.4, 25.4, 24.8; HRMS (ESI) m/z calcd for $C_{15}H_{15}NNaO_4$ $[(M+Na)^+]$: 296.0893, found: 296.0887.

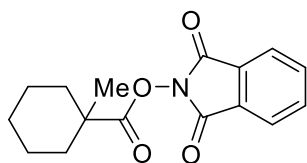
1,3-Dioxoisindolin-2-yl 1-methylcyclopent-3-ene-1-carboxylate (S16)



Following the **General procedure A** with 1-methylcyclopent-3-ene-1-carboxylic acid (252 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 439 mg (81%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.89 – 7.86 (m, 2H), 7.80 – 7.77 (m, 2H), 5.67 (s, 2H), 3.19 (d, 2H, *J* = 14.6 Hz), 2.43 (d, 2H, *J* = 15.0 Hz), 1.52 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 174.3, 162.3, 134.9, 129.2, 128.1, 124.1, 46.6, 45.0, 25.9; HRMS (ESI) *m/z* calcd for C₁₅H₁₃NNaO₄ [(M+Na)⁺]: 294.0737, found: 294.0727.

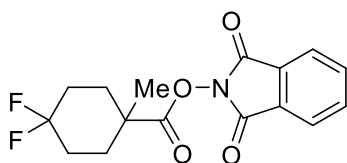
1,3-Dioxoisindolin-2-yl 1-methylcyclohexane-1-carboxylate (S17)



Following the **General procedure A** with 1-methylcyclohexane-1-carboxylic acid (284 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 453 mg (79%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.90 – 7.86 (m, 2H), 7.80 – 7.75 (m, 2H), 2.27 – 2.21 (m, 2H), 1.70 – 1.60 (m, 4H), 1.43 (s, 3H), 1.42 – 1.27 (m, 4H); ¹³C NMR (101 MHz, CDCl₃): δ 173.9, 162.4, 134.8, 129.3, 124.0, 43.4, 35.9, 26.8, 25.7, 23.2; HRMS (ESI) *m/z* calcd for C₁₆H₁₇NNaO₄ [(M+Na)⁺]: 310.1050, found: 310.1060.

1,3-Dioxoisindolin-2-yl 4,4-difluoro-1-methylcyclohexane-1-carboxylate (S18)

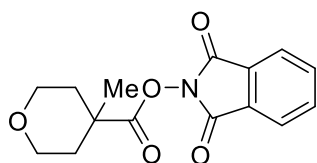


Following the **General procedure A** with

4,4-difluoro-1-methylcyclohexane-1-carboxylic acid (356 mg, 2.0 mmol) and *N*-hydroxyphthalimide (356 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 530 mg (82%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.90 – 7.86 (m, 2H), 7.82 – 7.77 (m, 2H), 2.39 – 2.34 (m, 2H), 2.11 – 2.02 (m, 4H), 1.74 – 1.66 (m, 2H), 1.50 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 172.7, 162.2, 135.0, 129.1, 125.3, 124.2, 122.9, 120.5, 76.9, 42.2, 32.4, 32.3, 31.5, 31.2, 31.0, 26.1.

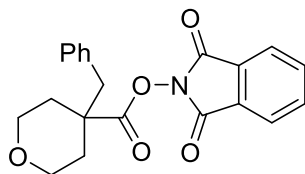
1,3-Dioxoisindolin-2-yl 4-methyltetrahydro-2*H*-pyran-4-carboxylate (S19)



Following the **General procedure A** with 4-methyltetrahydro-2*H*-pyran-4-carboxylic acid (288 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 491 mg (85%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.91 – 7.87 (m, 2H), 7.82 – 7.77 (m, 2H), 3.89 (dt, 2H, *J* = 12.3, 3.9 Hz), 3.67 (ddd, 2H, *J* = 12.1, 10.8, 2.3 Hz), 2.28 – 2.22 (m, 2H), 1.67 (ddd, 2H, *J* = 14.0, 10.9, 4.3 Hz), 1.51 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 173.1, 162.2, 135.0, 129.2, 124.1, 65.2, 41.2, 35.6, 26.7; HRMS (ESI) *m/z* calcd for C₁₅H₁₅NNaO₅ [(*M*+Na)⁺]: 312.0842, found: 312.0833.

1,3-Dioxoisindolin-2-yl 4-benzyltetrahydro-2*H*-pyran-4-carboxylate (S20)

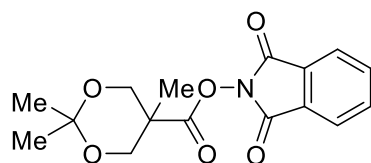


Following the **General procedure A** with 4-benzyltetrahydro-2*H*-pyran-4-carboxylic acid (440 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂

(10.0 mL) at rt for 1 h afforded 533 mg (73%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

^1H NMR (400 MHz, CDCl_3): δ 7.93 – 7.89 (m, 2H), 7.82 – 7.78 (m, 2H), 7.33 – 7.31 (m, 4H), 7.29 – 7.24 (m, 1H), 3.93 (ddd, 2H, J = 12.1, 4.0, 2.1 Hz), 3.68 (td, 2H, J = 12.1, 1.9 Hz), 3.12 (s, 2H), 2.17 (dd, 2H, J = 13.8, 2.0 Hz), 1.76 (ddd, 2H, J = 13.8, 12.0, 4.6 Hz); ^{13}C NMR (101 MHz, CDCl_3): δ 171.7, 162.2, 135.0, 134.9, 130.7, 129.1, 128.5, 127.3, 124.1, 65.2, 46.6, 46.5, 34.5; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{NNaO}_5$ $[(\text{M}+\text{Na})^+]$: 388.1155, found: 388.1164.

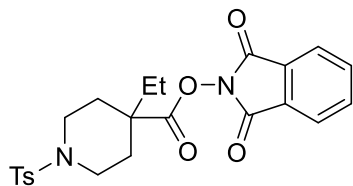
1,3-Dioxoisindolin-2-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (S21)



Following the **General procedure A** with 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (348 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH_2Cl_2 (10.0 mL) at rt for 0.5 h afforded 516 mg (81%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

^1H NMR (400 MHz, CDCl_3): δ 7.88 (dd, 2H, J = 5.5, 3.1 Hz), 7.78 (dd, 2H, J = 5.5, 3.1 Hz), 4.34 (d, 2H, J = 11.9 Hz), 3.79 (d, 2H, J = 11.8 Hz), 1.48 (s, 3H), 1.46 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.8, 161.9, 134.9, 129.1, 124.1, 98.8, 65.8, 42.1, 24.5, 23.0, 18.5; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{17}\text{NNaO}_6$ $[(\text{M}+\text{Na})^+]$: 342.0948, found: 342.0954.

1,3-Dioxoisindolin-2-yl 4-ethyl-1-tosylpiperidine-4-carboxylate (S22)

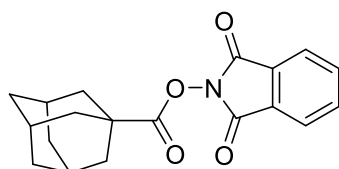


Following the **General procedure A** with 4-ethyl-1-tosylpiperidine-4-carboxylic acid (622 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH_2Cl_2 (10.0

mL) at rt for 1 h afforded 693 mg (76%) of the title compound after purification by column chromatography (eluent, 5:1:1 hexane: EtOAc:DCM). Physical State: white solid.

^1H NMR (400 MHz, CDCl_3): δ 7.84 – 7.80 (m, 2H), 7.79 – 7.76 (m, 2H), 7.67 – 7.64 (m, 2H), 7.34 (d, 2H, J = 8.0 Hz), 3.72 (dt, 2H, J = 12.4, 3.7 Hz), 2.63 (td, 2H, J = 12.3, 2.5 Hz), 2.45 (s, 3H), 2.35 (d, 2H, J = 13.2 Hz), 1.77 (q, 2H, J = 7.5 Hz), 1.67 (ddd, 2H, J = 14.0, 12.1, 4.2 Hz), 1.02 (t, 3H, J = 7.6 Hz); ^{13}C NMR (101 MHz, CDCl_3): δ 171.6, 161.9, 143.7, 134.9, 133.5, 129.9, 129.1, 127.7, 124.1, 45.8, 43.8, 33.6, 33.1, 21.7, 8.3; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}_6\text{S}$ $[(\text{M}+\text{H})^+]$: 457.1428, found: 457.1439.

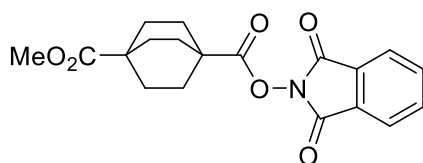
1,3-Dioxoisindolin-2-yl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (S23)



Following the **General procedure A** with (3*r*,5*r*,7*r*)-adamantane-1-carboxylic acid (360 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH_2Cl_2 (10.0 mL) at rt for 0.5 h afforded 468 mg (72%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

^1H NMR (400 MHz, CDCl_3): δ 7.87 (dd, 2H, J = 5.5, 3.1 Hz), 7.77 (dd, 2H, J = 5.5, 3.1 Hz), 2.14 (d, 6H, J = 2.6 Hz), 2.11 – 2.09 (m, 3H), 1.79 – 1.77 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 173.4, 162.3, 134.8, 129.3, 124.0, 40.7, 38.6, 36.4, 27.8; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{19}\text{NNaO}_4$ $[(\text{M}+\text{Na})^+]$: 348.1206, found: 348.1207.

1-(1,3-Dioxoisindolin-2-yl) 4-methyl bicyclo[2.2.2]octane-1,4-dicarboxylate (S24)



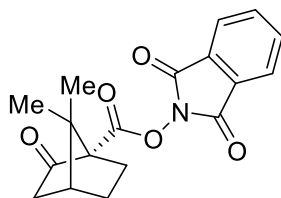
Following the **General procedure A** with

4-(methoxycarbonyl)bicyclo[2.2.2]octane-1-carboxylic acid (424 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 521 mg (73%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.86 (dd, 2H, *J* = 5.5, 3.1 Hz), 7.76 (dd, 2H, *J* = 5.5, 3.1 Hz), 3.66 (s, 3H), 2.07 – 2.03 (m, 6H), 1.90 – 1.86 (m, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 177.5, 173.4, 162.1, 134.8, 129.1, 124.0, 52.0, 38.6, 38.5, 27.8, 27.6; HRMS (ESI) *m/z* calcd for C₁₉H₁₉NNaO₆ [(M+Na)⁺]: 380.1105, found: 380.1119.

1,3-dioxisoindolin-2-yl

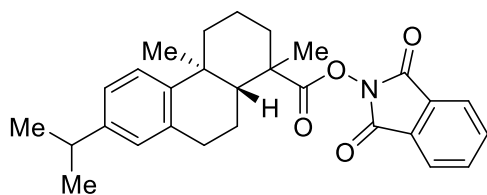
(1*S*,4*S*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-carboxylate (S25)



Following the **General procedure A** with (1*S*,4*S*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-carboxylic acid (364 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 451 mg (69%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.88 – 7.84 (m, 2H), 7.77 (dd, 2H, *J* = 5.5, 3.1 Hz), 2.66 – 2.54 (m, 2H), 2.21 (t, 1H, *J* = 4.5 Hz), 2.19 – 2.13 (m, 1H), 2.05 (d, 1H, *J* = 18.5 Hz), 2.00 – 1.95 (m, 1H), 1.51 (ddd, 1H, *J* = 13.0, 9.3, 4.0 Hz), 1.26 (s, 3H), 1.23 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 207.9, 166.3, 161.8, 134.9, 129.0, 124.1, 67.0, 51.2, 44.5, 44.0, 26.8, 26.4, 21.1, 19.7; HRMS (ESI) *m/z* calcd for C₁₈H₁₇NNaO₅ [(M+Na)⁺]: 350.0999, found: 350.1007.

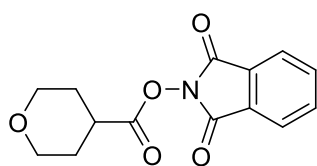
1,3-Dioxisoindolin-2-yl (4*aS*,10*aR*)-7-isopropyl-1,4*a*-dimethyl-1,2,3,4,4*a*,9,10,10*a*-octahydrophenanthrene-1-carboxylate (S26)



Following the **General procedure A** with (4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid (600 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 534 mg (60%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.89 – 7.87 (m, 2H), 7.79 – 7.77 (m, 2H), 7.20 (d, 1H, *J* = 8.2 Hz), 7.03 (d, 1H, *J* = 8.1 Hz), 6.94 (s, 1H), 3.16 – 3.07 (m, 1H), 2.98 (dd, 1H, *J* = 17.3, 6.5 Hz), 2.85 (p, 1H, *J* = 6.9 Hz), 2.45 (d, 1H, *J* = 11.6 Hz), 2.38 (d, 1H, *J* = 12.8 Hz), 2.17 – 2.09 (m, 1H), 1.98 – 1.91 (m, 2H), 1.89 -1.80 (m, 3H), 1.63 – 1.55 (m, 1H), 1.47 (s, 3H), 1.28 (s, 3H), 1.24 (d, 6H, *J* = 6.8 Hz); ¹³C NMR (101 MHz, CDCl₃): δ 174.7, 162.3, 146.5, 146.0, 134.9, 134.8, 129.2, 127.2, 124.3, 124.1, 124.0, 47.9, 45.2, 37.9, 37.2, 36.4, 33.6, 30.1, 25.4, 24.1, 24.1, 21.9, 18.5, 16.7; HRMS (ESI) *m/z* calcd for C₂₈H₃₁NNaO₄ [(M+Na)⁺]: 468.2145, found: 468.2134.

1,3-Dioxoisindolin-2-yl tetrahydro-2*H*-pyran-4-carboxylate (S27)

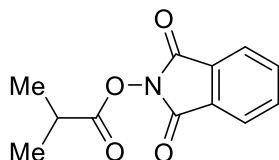


Following the **General procedure A** with tetrahydro-2*H*-pyran-4-carboxylic acid (1.30 g, 10.0 mmol) and *N*-hydroxyphthalimide (1.79 g, 11 mmol) in CH₂Cl₂ (25.0 mL) at rt for 0.5 h afforded 2.15 g (78%) of the title compound after purification by column chromatography (eluent, 6:1:1 hexanes:EtOAc:DCM). Physical State: white solid.

¹H NMR(400 MHz, CDCl₃): δ 7.88 (dd, 2H, *J* = 5.5, 3.1 Hz), 7.78 (dd, 2H, *J* = 5.5, 3.1 Hz), 4.01 (dt, 2H, *J* = 11.8, 3.8 Hz), 3.52 (ddd, 2H, *J* = 11.8, 9.9, 3.3 Hz), 3.03 –

2.95 (m, 1H), 2.06 – 1.92 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.7, 162.1, 134.9, 129.1, 124.1, 66.7, 37.8, 28.5; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{13}\text{NNaO}_5$ $[(\text{M}+\text{Na})^+]$: 298.0686, found: 298.0681.

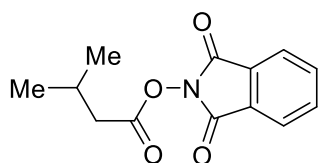
1,3-Dioxoisindolin-2-yl isobutyrate (S28)



Following the **General procedure A** with isobutyric acid (176 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH_2Cl_2 (10.0 mL) at rt for 0.5 h afforded 391 mg (84%) of the title compound after purification by column chromatography (eluent, 5:1 hexane: EtOAc). Physical State: white solid.

^1H NMR (400 MHz, CDCl_3): δ 7.87 (dd, 2H, $J = 5.5, 3.1$ Hz), 7.77 (dd, 2H, $J = 5.5, 3.1$ Hz), 2.95 (hept, 1H, $J = 7.0$ Hz), 1.37 (d, 6H, $J = 7.0$ Hz); ^{13}C NMR (101 MHz, CDCl_3): δ 173.2, 162.2, 134.9, 129.2, 124.1, 31.9, 19.0; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{NNaO}_4$ $[(\text{M}+\text{Na})^+]$: 256.0580, found: 256.0581.

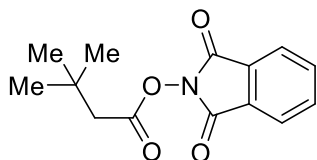
1,3-Dioxoisindolin-2-yl 3-methylbutanoate (S29)



Following the **General procedure A** with 3-methylbutanoic acid (204 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH_2Cl_2 (10.0 mL) at rt for 0.5 h afforded 400 mg (81%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

^1H NMR (400 MHz, CDCl_3): δ 7.89 – 7.85 (m, 2H), 7.80 – 7.76 (m, 2H), 2.54 (d, 2H, $J = 7.1$ Hz), 2.32 – 2.19 (m, 1H), 1.09 (d, 6H, $J = 6.7$ Hz); ^{13}C NMR (101 MHz, CDCl_3): δ 169.0, 162.2, 134.9, 129.2, 124.1, 40.0, 26.2, 22.4.

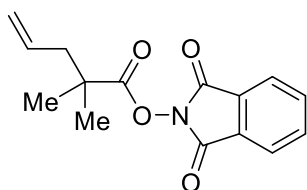
1,3-Dioxoisindolin-2-yl 3,3-dimethylbutanoate (S30)



Following the **General procedure A** with 3,3-dimethylbutanoic acid (232 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 438 mg (84%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.89 – 7.86 (m, 2H), 7.79 – 7.76 (m, 2H), 2.52 (s, 2H), 1.16 (s, 9H); ¹³C NMR (101 MHz, CDCl₃): δ 168.0, 162.2, 134.9, 129.2, 124.1, 44.8, 31.4, 29.6; HRMS (ESI) *m/z* calcd for C₁₄H₁₅NNaO₄ [(M+Na)⁺]: 284.0893, found: 284.0900.

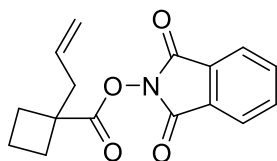
1,3-Dioxoisindolin-2-yl 2,2-dimethylpent-4-enoate (S31)



Following the **General procedure A** with 2,2-dimethylpent-4-enoic acid (256 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 464 mg (85%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.89 – 7.86 (m, 2H), 7.79 – 7.76 (m, 2H), 5.96 – 5.85 (m, 1H), 5.21 – 5.16 (m, 2H), 2.48 (s, 2H), 1.39 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 173.7, 162.2, 134.8, 133.1, 129.2, 124.0, 119.4, 44.7, 42.1, 24.9; HRMS (ESI) *m/z* calcd for C₁₅H₁₅NNaO₄ [(M+Na)⁺]: 296.0893, found: 296.0891.

1,3-Dioxoisindolin-2-yl 1-allylcyclobutane-1-carboxylate (S32)

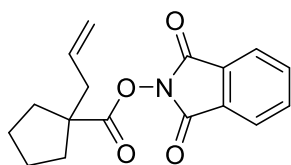


Following the **General procedure A** with 1-allylcyclobutane-1-carboxylic acid (280

mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 444 mg (78%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.87 (dd, 2H, *J* = 5.5, 3.1 Hz), 7.78 (dd, 2H, *J* = 5.5, 3.1 Hz), 5.89 (ddt, 1H, *J* = 17.2, 10.2, 7.2 Hz), 5.36 – 5.17 (m, 2H), 2.72 – 2.64 (m, 4H), 2.16 – 2.09 (m, 2H), 2.07 – 1.99 (m, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 172.7, 162.3, 134.8, 132.7, 129.2, 124.0, 119.1, 46.0, 41.6, 29.8, 15.8; HRMS (ESI) *m/z* calcd for C₁₆H₁₅NNaO₄ [(M+Na)⁺]: 308.0893, found: 308.0890.

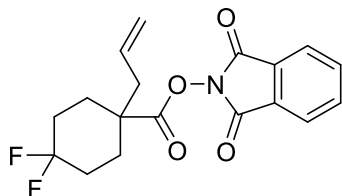
1,3-Dioxoisindolin-2-yl 1-allylcyclopentane-1-carboxylate (S33)



Following the **General procedure A** with 1-allylcyclopentane-1-carboxylic acid (308 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h afforded 460 mg (77%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.87 (dd, 2H, *J* = 5.5, 3.1 Hz), 7.78 (dd, 2H, *J* = 5.5, 3.1 Hz), 5.91 (ddt, 1H, *J* = 17.3, 10.1, 7.2 Hz), 5.22 – 5.14 (m, 2H), 2.56 (dt, 2H, *J* = 7.3, 1.2 Hz), 2.36 – 2.28 (m, 2H), 1.81 – 1.70 (m, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 173.7, 162.3, 134.8, 133.8, 129.3, 124.0, 119.0, 53.0, 42.8, 36.1, 25.2; HRMS (ESI) *m/z* calcd for C₁₇H₁₇NNaO₄ [(M+Na)⁺]: 322.1050, found: 322.1045.

1,3-Dioxoisindolin-2-yl 1-allyl-4,4-difluorocyclohexane-1-carboxylate (S34)

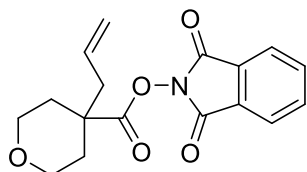


Following the **General procedure A** with 1-allyl-4,4-difluorocyclohexane-1-carboxylic acid (408 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 0.5 h

afforded 530 mg (76%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

^1H NMR(400 MHz, CDCl_3): δ 7.89 (dd, 2H, J = 5.5, 3.1 Hz), 7.80 (dd, 2H, J = 5.5, 3.1 Hz), 5.88 (ddt, 1H, J = 16.7, 10.1, 7.5 Hz), 5.26 – 5.20 (m, 2H), 2.52 (d, 2H, J = 7.5 Hz), 2.40 – 2.33 (m, 2H), 2.13 – 2.02 (m, 4H), 1.72 - 1.62 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ 171.5, 162.2, 135.0, 131.6, 129.1, 124.2, 123.0 (t, J = 243.3 Hz), 120.3, 46.1 (d, J = 1.5 Hz), 44.1 (d, J = 2.1 Hz), 31.1 (t, J = 24.4 Hz), 30.6 (d, J = 9.3 Hz); HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{F}_2\text{NNaO}_4$ $[(\text{M}+\text{Na})^+]$: 372.1018, found: 372.1020.

1,3-Dioxoisindolin-2-yl 4-allyltetrahydro-2H-pyran-4-carboxylate (S35)



Following the **General procedure A** with 4-allyltetrahydro-2H-pyran-4-carboxylic acid (340 mg, 2.0 mmol) and *N*-hydroxyphthalimide (358 mg, 2.2 mmol) in CH_2Cl_2 (10.0 mL) at rt for 0.5 h afforded 479 mg (76%) of the title compound after purification by column chromatography (eluent, 4:1 hexane: EtOAc). Physical State: white solid.

^1H NMR (400 MHz, CDCl_3): δ 7.82 (dd, 2H, J = 5.5, 3.1 Hz), 7.73 (dd, 2H, J = 5.5, 3.0 Hz), 5.82 (ddt, 1H, J = 16.8, 10.1, 7.5 Hz), 5.19 – 5.13 (m, 2H), 3.85 (ddd, 2H, J = 12.2, 4.3, 2.7 Hz), 3.60 (td, 2H, J = 11.9, 2.1 Hz), 2.46 (d, 2H, J = 7.5 Hz), 2.16 (dd, 2H, J = 14.0, 2.4 Hz), 1.62 (ddd, 2H, J = 13.9, 11.5, 4.5 Hz); ^{13}C NMR (101 MHz, CDCl_3): δ 171.8, 162.2, 135.0, 131.4, 129.2, 124.1, 120.2, 65.2, 45.2, 44.9, 34.1; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{17}\text{NNaO}_5$ $[(\text{M}+\text{Na})^+]$: 338.0999, found: 338.0997.

4. Optimization studies and experimental procedures

Table S1. Optimization of reaction conditions

1a (1.0 equiv.)	2a (1.2 equiv.)	3a (2.5 equiv.)					
						> 95:5 r.r., > 95:5 E:Z	
Entry	Catalyst	Ligand	Reductant	Additive	Solvent	Conversion rate (%)	Yield ^a (%)
1	NiBr ₂ ·diglyme	L1	TDAE	/	DMA	36	< 5
2	NiBr ₂ ·diglyme	L1	Zn	/	DMA	>95	16
3	NiBr ₂ ·diglyme	L1	Mn	/	DMA	78	67
4	NiBr ₂ ·diglyme	L2	Mn	/	DMA	78	55
5	NiBr ₂ ·diglyme	L3	Mn	/	DMA	62	39
6	NiBr ₂ ·diglyme	L4	Mn	/	DMA	65	38
7	NiBr ₂ ·diglyme	L5	Mn	/	DMA	82	49
8	NiBr ₂ ·diglyme	L6	Mn	/	DMA	55	46
9	NiBr ₂ ·diglyme	L7	Mn	/	DMA	34	< 5
10	NiBr ₂ ·diglyme	L8	Mn	/	DMA	31	< 5
11	Ni(cod) ₂	L1	Mn	/	DMA	74	39
12	NiCl ₂ ·glyme	L1	Mn	/	DMA	80	57
13	NiI ₂	L1	Mn	/	DMA	81	56
14	NiBr ₂ ·diglyme	L1	Mn	/	MeCN	25	< 5
15	NiBr ₂ ·diglyme	L1	Mn	/	DMF	82	41
16	NiBr ₂ ·diglyme	L1	Mn	/	DMSO	66	34
17	NiBr₂·diglyme	L1	Mn	LiBr	DMA	85	76 (73)
18	NiBr ₂ ·diglyme	L1	Mn	ZnCl ₂	DMA	50	15
19	NiBr ₂ ·diglyme	L1	Mn	MgBr ₂	DMA	68	36
20	NiBr ₂ ·diglyme	L1	Mn	TMSCl	DMA	77	25

L1: R ¹ = OMe	L2: R ¹ = <i>t</i> -Bu	L3: R ² = R ³ = H	L4: R ² = H; R ³ = Me	L5: R ² = Me; R ³ = H	L6: R ⁴ = R ⁵ = H	L7: R ⁴ = H; R ⁵ = Ph	L8: R ⁴ = Me; R ⁵ = H

^aOtherwise noted: **1a** (1.0 equiv., 0.1 mmol), **2** (1.2 equiv., 0.12 mmol), **3** (2.5 equiv., 0.25 mmol), Ni catalyst (10 mol%), Ligand (12 mol%), Mn (2.5 equiv.), additive (0.5 equiv.), Solvent (0.3 mL), RT, 24 h. Conversion rate and yield were determined by GC analysis. ^bIsolated yield in the parenthesis. RT = room temperature (around 20 °C)

4.1 General procedures for Ni-catalyzed alkylalkynylation of alkynes

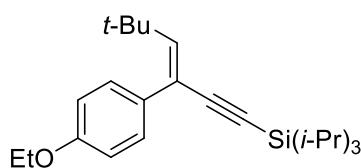
For tertiary alkyl NHPI ester substrates (General procedure B): In a N₂-filled glovebox, to an oven-dried 5 mL vial equipped with a magnetic stir bar was added alkyne substrate (1.0 equiv., 0.1 mmol), alkynyl bromide (1.2 equiv., 0.12 mmol), NHPI ester (2.5 equiv., 0.25 mmol), NiBr₂·diglyme (10 mmol%), Ligand 1 (12 mol%),

Mn powder (2.5 equiv., 0.25 mmol) and LiBr (0.5 equiv., 0.05 mmol) (unless otherwise noted). The mixture was then dissolved in 0.3 mL dry DMA (unless otherwise noted). The vial was tightly capped and removed from the glovebox. The mixture was allowed to vigorously stir at room temperature for 24 h. After the reaction was complete, the mixture was directly subjected to flash silica gel column chromatography to afford the pure product. (**Note: for alkynyl bromide scope, 1.0 equiv. of LiBr and DMSO were used instead for the preparation of 4y, 4z, 4aa; for preparation of 4af, 4ao, 4ap, 4ar, 3.0 equiv. of alkyne and 1.0 equiv. of alkynyl bromide were used; for preparation of 4as, 1.5 equiv. of alkynyl bromide and 1.7 equiv. of C₄F₉I were used; for preparation of 4at, 1.5 equiv. of alkynyl bromide and 2.0 equiv. of C₄F₉I were used*)

For secondary & primary alkyl NHPI ester substrates (General procedure C): In a N₂-filled glovebox, to an oven-dried 5 mL vial equipped with a magnetic stir bar was added alkyne substrate (3.0 equiv., 0.3 mmol), alkynyl bromide (1.0 equiv., 0.1 mmol), NHPI ester (2.5 equiv., 0.25 mmol), NiBr₂·diglyme (10 mmol%), CuTc (10 mmol%), Ligand 4 (12 mol%) (unless otherwise noted), Mn powder (2.5 equiv., 0.25 mmol) and LiBr (1.0 equiv., 0.1 mmol). The mixture was then dissolved in 0.3 mL dry DMA. The vial was tightly capped and removed from the glovebox. The mixture was allowed to vigorously stir at room temperature for 24 h. After the reaction was complete, the mixture was directly subjected to flash silica gel column chromatography to afford the pure product. (**Note: ligand 1 was used instead for preparation of 4aw*)

5. Analytical data of products

(E)-(3-(4-Ethoxyphenyl)-5,5-dimethylhex-3-en-1-yn-1-yl)triisopropylsilane (4a):

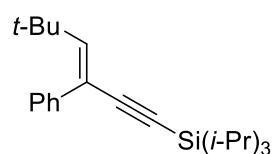


The title compound was prepared from the **General procedure B**. Purification using

flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (28.0 mg, 73% yield).

^1H NMR (500 MHz, CDCl_3): δ 7.18 – 7.15 (m, 2H), 6.83 – 6.80 (m, 2H), 6.16 (s, 1H), 4.03 (q, 2H, $J = 7.0$ Hz), 1.41 (t, 3H, $J = 7.0$ Hz), 1.03 – 1.02 (m, 21H), 0.94 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.2, 149.8, 131.4, 130.3, 122.5, 113.8, 111.2, 87.3, 63.5, 34.6, 31.2, 18.8, 15.1, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{25}\text{H}_{41}\text{OSi}$ [(M+H) $^+$]: 385.2921, found: 385.2918.

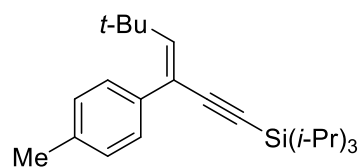
(E)-(5,5-Dimethyl-3-phenylhex-3-en-1-yn-1-yl)triisopropylsilane (4b):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: hexane) gave the pure product as a colorless oil (22.0 mg, 65% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.24 – 7.15 (m, 5H), 6.12 (s, 1H), 0.95 (s, 21H), 0.86 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 149.8, 139.3, 129.2, 127.9, 127.2, 122.8, 110.8, 88.0, 34.6, 31.1, 18.8, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{23}\text{H}_{37}\text{Si}$ [(M+H) $^+$]: 341.2659, found: 341.2658.

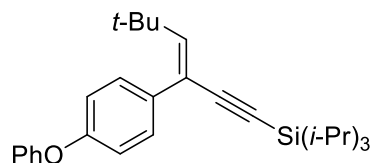
(E)-(5,5-Dimethyl-3-(p-tolyl)hex-3-en-1-yn-1-yl)triisopropylsilane (4c):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: hexane) gave the pure product as a colorless oil (22.6 mg, 64% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.15 (d, 2H, $J = 8.1$ Hz), 7.10 – 7.08 (m, 2H), 6.18 (s, 1H), 2.34 (s, 3H), 1.03 (s, 21H), 0.93 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 149.8, 136.8, 136.2, 129.1, 128.5, 122.8, 111.0, 87.4, 34.6, 31.2, 21.4, 18.84, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{24}\text{H}_{39}\text{Si}$ [(M+H) $^+$]: 355.2816, found: 355.2812.

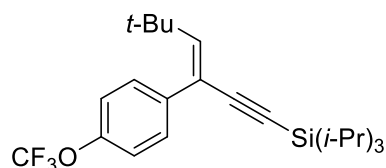
(E)-(5,5-Dimethyl-3-(4-phenoxyphenyl)hex-3-en-1-yn-1-yl)triisopropylsilane (4d):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (25.5 mg, 59% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.37 – 7.31 (m, 2H), 7.25 – 7.21 (m, 2H), 7.12 – 7.08 (m, 1H), 7.03 – 7.00 (m, 2H), 6.96 – 5.92 (m, 2H), 6.19 (s, 1H), 1.04 (s, 21H), 0.96 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 157.4, 156.4, 150.0, 134.3, 130.6, 129.9, 123.4, 122.2, 119.0, 118.3, 110.8, 88.0, 34.7, 31.2, 18.8, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{29}\text{H}_{41}\text{OSi}$ $[(\text{M}+\text{H})^+]$: 433.2921, found: 433.2925.

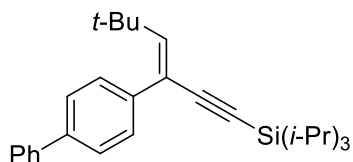
(E)-(5,5-Dimethyl-3-(4-(trifluoromethoxy)phenyl)hex-3-en-1-yn-1-yl)triisopropylsilane (4e):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (26.7 mg, 63% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.30 – 7.27 (m, 2H), 7.16 – 7.13 (m, 2H), 6.21 (s, 1H), 1.02 (s, 21H), 0.93 (s, 9H); ^{19}F NMR (377 MHz, CDCl_3): δ -57.9; ^{13}C NMR (101 MHz, CDCl_3): δ 150.5, 148.52 (q, J = 1.6 Hz), 138.0, 130.6, 121.4, 120.7 (q, J = 256.9 Hz), 120.4, 110.1, 88.8, 34.7, 31.1, 18.8, 11.5; HRMS (APCI) m/z calcd for $\text{C}_{24}\text{H}_{36}\text{F}_3\text{OSi}$ $[(\text{M}+\text{H})^+]$: 425.2482, found: 425.2479.

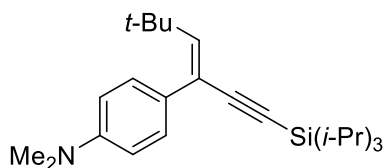
(E)-(3-([1,1'-Biphenyl]-4-yl)-5,5-dimethylhex-3-en-1-yn-1-yl)triisopropylsilane (4f):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (27.9 mg, 67% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.65 – 7.62 (m, 2H), 7.56 – 7.53 (m, 2H), 7.46 – 7.42 (m, 2H), 7.36 – 7.32 (m, 3H), 6.23 (s, 1H), 1.05 (s, 21H), 0.98 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 150.2, 141.0, 139.9, 138.3, 129.7, 128.9, 127.4, 127.2, 126.5, 122.5, 110.7, 88.0, 34.7, 31.2, 18.9, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{29}\text{H}_{41}\text{Si}$ $[(\text{M}+\text{H})^+]$: 417.2972, found: 417.2982.

(E)-4-(5,5-Dimethyl-1-(triisopropylsilyl)hex-3-en-1-yn-3-yl)-N,N-dimethylaniline (4g):

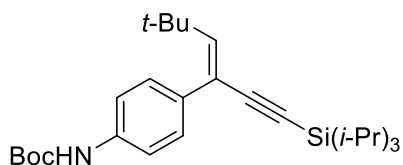


The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 10:1 hexane:EtOAc) gave the pure product as a colorless oil (21.8 mg, 57% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.16 – 7.12 (m, 2H), 6.68 (d, 2H, $J = 8.2$ Hz), 6.14 (s, 1H), 2.96 (s, 6H), 1.04 – 1.02 (m, 21H), 0.96 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3): δ 149.4, 130.1, 127.0, 122.9, 111.9, 111.9, 111., 86.5, 40.9, 31.2, 30.2, 18.9, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{25}\text{H}_{42}\text{NSi}$ $[(\text{M}+\text{H})^+]$: 384.3081, found: 384.3071.

tert-Butyl

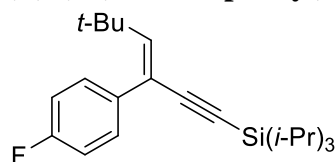
(E)-4-(5,5-dimethyl-1-(triisopropylsilyl)hex-3-en-1-yn-3-yl)phenylcarbamate (4h):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 5:1 hexane:EtOAc) gave the pure product as a colorless oil (23.7 mg, 52% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.29 (d, 2H, $J = 8.6$ Hz), 7.20 – 7.17 (m, 2H), 6.49 (br, 1H), 6.17 (s, 1H), 1.51 (s, 9H), 1.02 (s, 21H), 0.93 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 152.9, 150.0, 137.5, 133.9, 129.9, 122.3, 117.8, 110.8, 87.6, 80.7, 34.6, 31.2, 28.5, 18.8, 11.5; HRMS (APCI) m/z calcd for $\text{C}_{28}\text{H}_{46}\text{NO}_2\text{Si}$ $[(\text{M}+\text{H})^+]$: 456.3292, found: 456.3279.

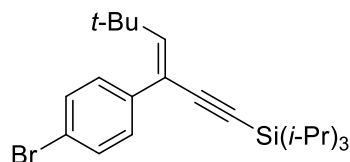
(E)-(3-(4-Fluorophenyl)-5,5-dimethylhex-3-en-1-yn-1-yl)triisopropylsilane (4i):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: hexane) gave the pure product as a colorless oil (22.2 mg, 62% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.24 – 7.20 (m, 2H), 7.01 – 6.95 (m, 2H), 6.19 (s, 1H), 1.02 (s, 21H), 0.93 (s, 9H) ppm; ^{19}F NMR (377 MHz, CDCl_3): δ -115.4; ^{13}C NMR (101 MHz, CDCl_3): δ 162.2 (d, $J = 245.6$ Hz), 150.2, 135.2 (d, $J = 3.6$ Hz), 130.8 (d, $J = 8.0$ Hz), 121.8, 114.9 (d, $J = 21.3$ Hz), 110.5, 88.3, 34.7, 31.1, 18.8, 11.5; HRMS (APCI) m/z calcd for $\text{C}_{23}\text{H}_{36}\text{FSi}$ $[(\text{M}+\text{H})^+]$: 359.2565, found: 359.2570.

(E)-(3-(4-Bromophenyl)-5,5-dimethylhex-3-en-1-yn-1-yl)triisopropylsilane (4j):

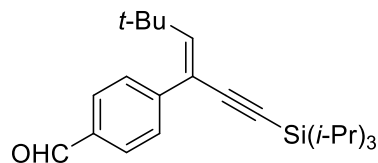


The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: hexane) gave the pure product as a colorless oil (18.8 mg, 45% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.44 – 7.41 (m, 2H), 7.16 – 7.12 (m, 2H), 6.20 (s, 1H), 1.02 (s, 21H), 0.93 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 150.4, 138.3, 131.1, 130.9,

121.6, 121.3, 110.0, 88.6, 34.7, 31.1, 18.8, 11.5; HRMS (APCI) m/z calcd for $C_{23}H_{36}BrSi$ $[(M+H)^+]$: 419.1764, found: 419.1750.

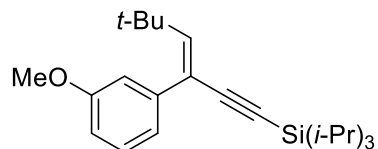
(E)-4-(5,5-Dimethyl-1-(triisopropylsilyl)hex-3-en-1-yn-3-yl)benzaldehyde (4k):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 20:1 hexane:EtOAc) gave the pure product as a colorless oil (14.7 mg, 40% yield).

1H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.83 (d, 2H, $J = 8.3$ Hz), 7.45 (d, 2H, $J = 8.1$ Hz), 6.25 (s, 1H), 1.01 (s, 21H), 0.93 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.1, 150.7, 146.1, 135.4, 130.0, 129.5, 121.6, 109.4, 89.6, 34.8, 31.1, 18.8, 11.5; HRMS (APCI) m/z calcd for $C_{24}H_{37}OSi$ $[(M+H)^+]$: 369.2608, found: 369.2602.

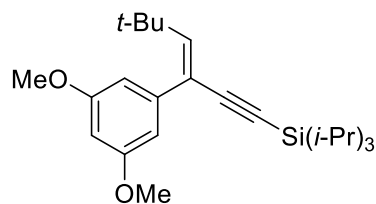
(E)-Triisopropyl(3-(3-methoxyphenyl)-5,5-dimethylhex-3-en-1-yn-1-yl)silane (4l):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (22.9 mg, 62% yield).

1H NMR (400 MHz, $CDCl_3$): δ 7.22 – 7.17 (m, 1H), 6.87 – 6.78 (m, 3H), 6.18 (s, 1H), 3.80 (s, 3H), 1.03 (s, 21H), 0.95 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.17, 149.87, 140.56, 128.82, 122.62, 121.91, 114.64, 113.09, 110.59, 87.95, 55.37, 34.65, 31.06, 18.83, 11.55; HRMS (APCI) m/z calcd for $C_{24}H_{39}OSi$ $[(M+H)^+]$: 371.2765, found: 371.2763.

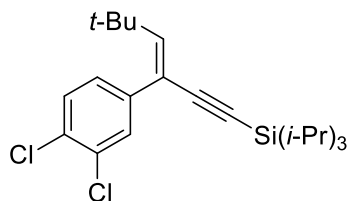
(E)-(3-(3,5-Dimethoxyphenyl)-5,5-dimethylhex-3-en-1-yn-1-yl)triisopropylsilane (4m):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 50:1 hexane:EtOAc) gave the pure product as a colorless oil (29.2 mg, 73% yield).

^1H NMR (400 MHz, CDCl_3): δ 6.44 (d, 2H, $J = 2.3$ Hz), 6.37 (t, 1H, $J = 2.3$ Hz), 6.15 (s, 1H), 3.78 (s, 6H), 1.04 (s, 21H), 0.97 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 160.3, 149.8, 141.1, 122.6, 110.4, 107.5, 99.7, 87.9, 55.5, 34.7, 31.0, 18.8, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{25}\text{H}_{41}\text{O}_2\text{Si}$ $[(\text{M}+\text{H})^+]$: 401.2870, found: 401.2861.

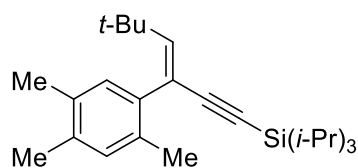
(E)-(3-(3,4-Dichlorophenyl)-5,5-dimethylhex-3-en-1-yn-1-yl)triisopropylsilane (4n):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: hexane) gave the pure product as a colorless oil (27.7 mg, 68% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.37 (dd, 2H, $J = 5.1, 3.1$ Hz), 7.11 (dd, 1H, $J = 8.3, 2.0$ Hz), 6.21 (s, 1H), 1.03 (s, 21H), 0.95 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 151.0, 139.3, 132.0, 131.4, 131.2, 130.0, 128.7, 120.4, 109.5, 89.2, 34.8, 31.1, 18.8, 11.5; HRMS (APCI) m/z calcd for $\text{C}_{23}\text{H}_{35}\text{Cl}_2\text{Si}$ $[(\text{M}+\text{H})^+]$: 409.1880, found: 409.1882.

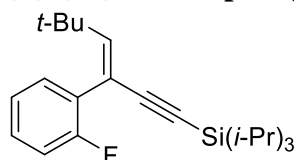
(E)-(5,5-Dimethyl-3-(2,4,5-trimethylphenyl)hex-3-en-1-yn-1-yl)triisopropylsilane (4o):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: hexane) gave the pure product as a colorless oil (17.6 mg, 46% yield).

^1H NMR (400 MHz, CDCl_3): δ 6.88 (d, 2H, $J = 9.0$ Hz), 6.16 (s, 1H), 2.26 (s, 3H), 2.21 (s, 3H), 2.20 (s, 3H), 1.02 (s, 21H), 0.88 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 149.9, 135.6, 135.4, 133.1, 133.0, 131.1, 130.9, 122.1, 110.1, 86.8, 34.6, 30.6, 19.6, 19.4, 19.3, 18.8, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{43}\text{Si}$ $[(\text{M}+\text{H})^+]$: 383.3129, found: 383.3135.

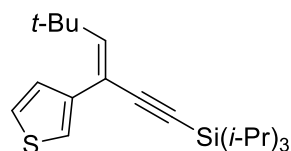
(E)-(3-(2-Fluorophenyl)-5,5-dimethylhex-3-en-1-yn-1-yl)triisopropylsilane (4p):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: hexane) gave the pure product as a colorless oil (25.1 mg, 70% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.29 – 7.22 (m, 2H), 7.11 – 7.01 (m, 2H), 6.30 (s, 1H), 1.03 (s, 21H), 0.94 (s, 9H); ^{19}F NMR (377 MHz, CDCl_3): δ -113.8; ^{13}C NMR (101 MHz, CDCl_3): δ 159.6 (d, $J=245.8$ Hz), 151.8, 131.4 (d, $J = 3.5$ Hz), 129.3 (d, $J = 8.0$ Hz), 126.8 (d, $J = 17.3$ Hz), 123.7 (d, $J = 3.5$ Hz), 115.7, 115.5 (d, $J = 22.1$ Hz), 109.4, 88.0, 34.7, 30.3, 18.8, 11.5; HRMS (APCI) m/z calcd for $\text{C}_{23}\text{H}_{36}\text{FSi}$ $[(\text{M}+\text{H})^+]$: 359.2565, found: 359.2559.

(Z)-(5,5-Dimethyl-3-(thiophen-3-yl)hex-3-en-1-yn-1-yl)triisopropylsilane (4q):

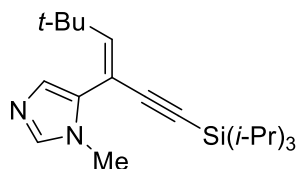


The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: hexane) gave the pure product as a colorless oil (17.3 mg, 50% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.23 (dd, 1H, $J = 4.9, 3.0$ Hz), 7.11 (dd, 1H, $J = 3.0, 1.3$ Hz), 7.02 (dd, 1H, $J = 4.9, 1.3$ Hz), 6.22 (s, 1H), 1.04 (s, 21H), 0.98 (s, 9H); ^{13}C

NMR (101 MHz, CDCl₃): δ 151.2, 138.6, 129.2, 124.6, 123.3, 117.7, 110.2, 87.3, 34.4, 30.9, 18.8, 11.5; HRMS (EI) m/z calcd for C₂₁H₃₄SSi [M]⁺: 346.2145, found: 346.2146.

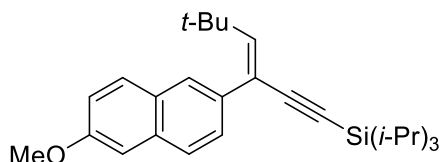
(Z)-5-(5,5-Dimethyl-1-(triisopropylsilyl)hex-3-en-1-yn-3-yl)-1-methyl-1H-imidazole (4r):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 5:1 hexane:EtOAc) gave the pure product as a colorless oil (17.9 mg, 52% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.43 (s, 1H), 6.87 (s, 1H), 6.44 (s, 1H), 3.59 (s, 3H), 1.02 (s, 21H), 0.95 (s, 9H); ¹³C NMR (101 MHz, CDCl₃): δ 156.8, 137.7, 128.8, 127.8, 110.6, 107.6, 88.3, 34.6, 31.7, 30.6, 18.8, 11.4; HRMS (APCI) m/z calcd for C₂₁H₃₇N₂Si [(M+H)⁺]: 345.2721, found: 345.2724.

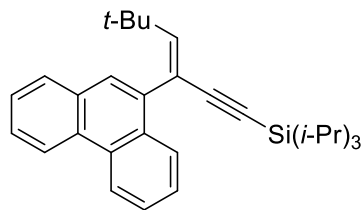
(E)-Triisopropyl(3-(6-methoxynaphthalen-2-yl)-5,5-dimethylhex-3-en-1-yn-1-yl)silane (4s):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (34.0 mg, 81% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.72 – 7.65 (m, 3H), 7.39 (dd, 1H, J = 8.4, 1.7 Hz), 7.16 – 7.14 (m, 2H), 6.27 (s, 1H), 3.92 (s, 3H), 1.03 (s, 21H), 0.95 (s, 9H); ¹³C NMR (101 MHz, CDCl₃): δ 157.9, 150.2, 134.5, 133.8, 129.7, 128.6, 128.2, 127.8, 126.3, 122.8, 119.0, 110.8, 105.8, 88.0, 55.5, 34.7, 31.2, 18.8, 11.5; HRMS (APCI) m/z calcd for C₂₈H₄₁OSi [(M+H)⁺]: 421.2921, found: 421.2918.

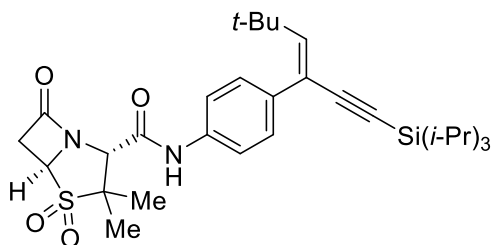
(E)-(5,5-Dimethyl-3-(phenanthren-9-yl)hex-3-en-1-yn-1-yl)triisopropylsilane (4t):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (27.3 mg, 62% yield).

^1H NMR (400 MHz, CDCl_3): δ 8.72 – 8.68 (m, 2H), 8.20 – 8.18 (m, 1H), 7.88 (dd, 1H, $J = 7.7, 1.6$ Hz), 7.68 – 7.58 (m, 5H), 6.50 (s, 1H), 0.97 – 0.94 (m, 21H), 0.90 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 152.0, 135.3, 131.6, 131.1, 130.5, 130.4, 128.8, 127.5, 127.4, 126.8, 126.7, 126.63, 126.60, 122.8, 122.7, 120.8, 110.1, 88.5, 35.0, 30.6, 18.77, 18.75, 11.5; HRMS (APCI) m/z calcd for $\text{C}_{31}\text{H}_{41}\text{Si}$ $[(\text{M}+\text{H})^+]$: 441.2972, found: 441.2974.

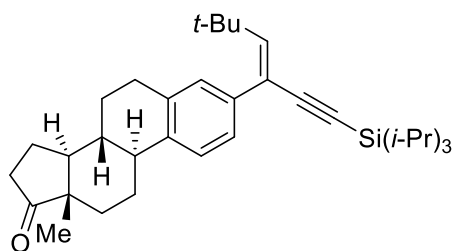
(2R,5S)-N-(4-((E)-5,5-Dimethyl-1-(triisopropylsilyl)hex-3-en-1-yn-3-yl)phenyl)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxamide 4,4-dioxide (4u):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 5:1 hexane:EtOAc) gave the pure product as a colorless oil (30.2 mg, 53% yield).

^1H NMR (400 MHz, CDCl_3): δ 8.20 (s, 1H), 7.47 (d, 2H, $J = 8.6$ Hz), 7.26 (d, 2H, $J = 8.5$ Hz), 6.19 (s, 1H), 4.69 (t, 1H, $J = 3.5$ Hz), 4.33 (s, 1H), 3.59 (d, 2H, $J = 3.4$ Hz), 1.74 (s, 3H), 1.53 (s, 3H), 1.02 (s, 21H), 0.93 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 172.5, 164.4, 150.4, 136.6, 135.3, 130.0, 121.8, 119.6, 110.3, 88.2, 64.7, 64.1, 60.7, 38.6, 34.7, 31.1, 19.8, 18.8, 18.6, 11.5; HRMS (APCI) m/z calcd for $\text{C}_{31}\text{H}_{47}\text{N}_2\text{O}_4\text{SSi}$ $[(\text{M}+\text{H})^+]$: 571.3020, found: 571.3023.

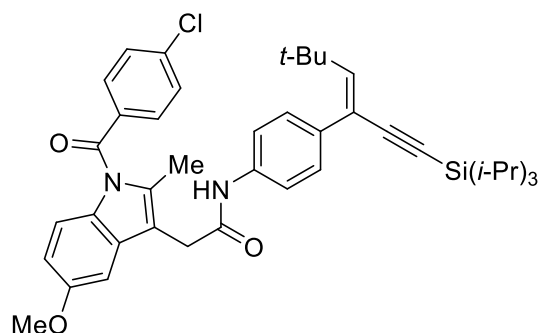
(8*R*,9*S*,13*S*,14*S*)-3-((*E*)-5,5-Dimethyl-1-(triisopropylsilyl)hex-3-en-1-yn-3-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (4v):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 10:1 hexane:EtOAc) gave the pure product as a colorless oil (25.8 mg, 50% yield).

¹H NMR (500 MHz, CDCl₃): δ 7.18 (d, 1H, *J* = 8.0 Hz), 7.04 (dd, 1H, *J* = 8.0, 1.9 Hz), 7.00 (s, 1H), 6.17 (s, 1H), 2.90 – 2.87 (m, 2H), 2.51 (dd, 1H, *J* = 19.0, 8.6 Hz), 2.44 – 2.40 (m, 1H), 2.31 (td, 1H, *J* = 10.8, 4.2 Hz), 2.18 – 2.09 (m, 1H), 2.08 – 1.95 (m, 3H), 1.67 – 1.61 (m, 2H), 1.58 – 1.42 (m, 4H), 1.04 (s, 21H), 0.95 (s, 9H), 0.93 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 221.2, 149.8, 138.6, 136.4, 135.7, 129.8, 126.7, 124.6, 122.8, 111.1, 87.1, 50.8, 48.2, 44.5, 38.3, 36.1, 34.6, 31.8, 31.2, 29.5, 26.8, 25.8, 21.8, 18.9, 14.1, 11.6; HRMS (APCI) *m/z* calcd for C₃₅H₅₃OSi [(M+H)⁺]: 517.3860, found: 517.3856.

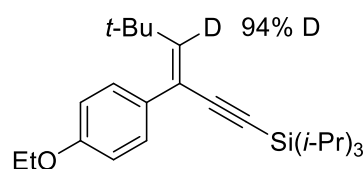
(*E*)-2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)-*N*-(4-(5,5-dimethyl-1-(triisopropylsilyl)hex-3-en-1-yn-3-yl)phenyl)acetamide (4w):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 5:1 hexane:EtOAc) gave the pure product as a colorless oil (44.4 mg, 64% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.70 – 7.67 (m, 2H), 7.51 – 7.48 (m, 2H), 7.34 – 7.32 (m, 2H), 7.31 (br, 1H), 7.18 (d, 2H, $J = 8.6$ Hz), 6.96 (d, 1H, $J = 2.5$ Hz), 6.87 (d, 1H, $J = 9.3$ Hz), 6.72 (dd, 1H, $J = 9.1, 2.5$ Hz), 6.17 (s, 1H), 3.81 (s, 3H), 3.80 (s, 2H), 2.46 (s, 3H), 1.01 (s, 21H), 0.91 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 168.5, 168.2, 156.6, 150.2, 139.9, 136.9, 136.5, 135.6, 133.7, 131.4, 131.2, 130.3, 129.8, 129.5, 122.1, 119.4, 115.4, 112.7, 112.5, 110.5, 100.9, 87.8, 56.0, 34.6, 33.6, 31.1, 18.8, 13.5, 11.5; HRMS (APCI) m/z calcd for $\text{C}_{42}\text{H}_{52}\text{ClN}_2\text{O}_3\text{Si}$ $[(\text{M}+\text{H})^+]$: 695.3430, found: 695.3433.

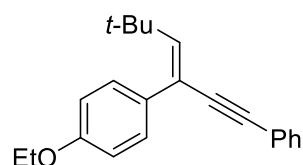
(*E*)-(3-(4-Ethoxyphenyl)-5,5-dimethylhex-3-en-1-yn-1-yl-4-d)triisopropylsilane (4x):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (23.5 mg, 61% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.18 – 7.15 (m, 2H), 6.83 – 6.79 (m, 2H), 6.16 (s, 0.06H), 4.03 (q, 2H, $J = 7.0$ Hz), 1.41 (t, 3H, $J = 7.0$ Hz), 1.03 (s, 21H), 0.94 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.2, 149.8, 131.4, 130.3, 122.4, 113.8, 111.1, 87.3, 63.5, 34.5, 31.1, 18.8, 15.1, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{25}\text{H}_{40}\text{DOSi}$ $[(\text{M}+\text{H})^+]$: 386.2984, found: 386.2983.

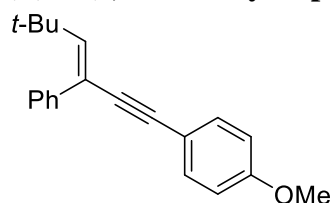
(*E*)-1-(5,5-Dimethyl-1-phenylhex-3-en-1-yn-3-yl)-4-ethoxybenzene (4y):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (16.1 mg, 53% yield, *E*:*Z* 95:5).

^1H NMR (400 MHz, CDCl_3): δ 7.29 – 7.25 (m, 2H), 7.18 – 7.10 (m, 5H), 6.78 – 6.74 (m, 2H), 6.15 (s, 1H), 3.94 (q, 2H, $J = 7.0$ Hz), 1.32 (t, 3H, $J = 7.0$ Hz), 0.87 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.4, 150.1, 131.6, 131.1, 130.4, 128.3, 127.9, 123.9, 122.0, 114.0, 93.2, 87.0, 63.6, 34.8, 31.2, 15.1; HRMS (APCI) m/z calcd for $\text{C}_{22}\text{H}_{25}\text{O}$ $[(\text{M}+\text{H})^+]$: 305.1900, found: 305.1904.

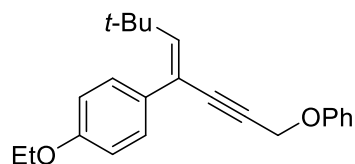
(*E*)-1-(5,5-Dimethyl-3-phenylhex-3-en-1-yn-1-yl)-4-methoxybenzene (4z):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (14.2 mg, 49% yield, *E*:*Z* 95:5).

^1H NMR (400 MHz, CDCl_3): δ 7.33 – 7.29 (m, 7H), 6.81 – 6.77 (m, 2H), 6.24 (s, 1H), 3.79 (s, 3H), 0.95 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3): δ 159.4, 149.4, 139.3, 133.0, 129.3, 128.1, 127.4, 122.5, 116.0, 114.0, 91.5, 87.4, 55.4, 34.7, 31.2; HRMS (EI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{O}$ $[\text{M}]^+$: 290.1665, found: 290.1663.

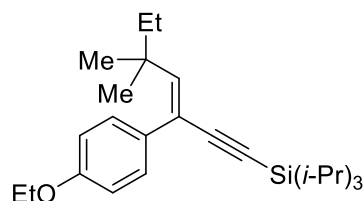
(*E*)-1-(6,6-Dimethyl-1-phenoxyhept-4-en-2-yn-4-yl)-4-ethoxybenzene (4aa):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 50:1 hexane:EtOAc) gave the pure product as a colorless oil (15.4 mg, 46% yield, *E*:*Z* 94:6).

^1H NMR (400 MHz, CDCl_3): δ 7.31 – 7.25 (m, 2H), 7.15 – 7.11 (m, 2H), 6.99 – 6.94 (m, 3H), 6.85 – 6.81 (m, 2H), 6.17 (s, 1H), 4.75 (s, 2H), 4.03 (q, 2H, $J = 7.0$ Hz), 1.42 (t, 3H, $J = 7.0$ Hz), 0.92 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.4, 158.1, 151.0, 130.7, 130.3, 129.6, 121.4, 121.1, 115.2, 114.0, 90.7, 81.4, 63.6, 57.0, 34.7, 31.0, 15.0; HRMS (APCI) m/z calcd for $\text{C}_{23}\text{H}_{27}\text{O}_2$ $[(\text{M}+\text{H})^+]$: 335.2006, found: 335.2004.

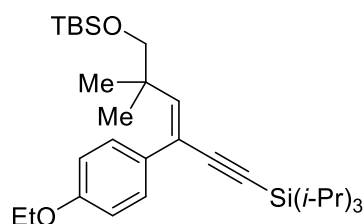
(E)-(3-(4-Ethoxyphenyl)-5,5-dimethylhept-3-en-1-yn-1-yl)triisopropylsilane (4ab):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (24.3 mg, 61% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.18 – 7.14 (m, 2H), 6.82 – 6.79 (m, 2H), 6.07 (s, 1H), 4.03 (q, 2H, $J = 7.0$ Hz), 1.41 (t, 3H, $J = 7.0$ Hz), 1.29 (q, 2H, $J = 7.5$ Hz), 1.03 (s, 21H), 0.85 (s, 6H), 0.81 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (101 MHz, CDCl_3): δ 158.1, 148.9, 131.5, 130.2, 123.2, 113.7, 111.3, 87.1, 63.5, 37.9, 36.9, 28.3, 18.8, 15.1, 11.6, 9.4; HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{43}\text{OSi}$ $[(\text{M}+\text{H})^+]$: 399.3078, found: 399.3079.

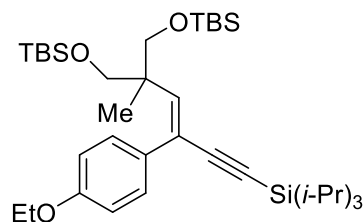
(E)-tert-Butyl((4-(4-ethoxyphenyl)-2,2-dimethyl-6-(triisopropylsilyl)hex-3-en-5-yn-1-yl)oxy)dimethylsilane (4ac):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (32.9 mg, 64% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.20 – 7.16 (m, 2H), 6.83 – 6.79 (m, 2H), 6.19 (s, 1H), 4.03 (q, 2H, $J = 7.0$ Hz), 3.26 (s, 2H), 1.41 (t, 3H, $J = 7.0$ Hz), 1.03 (s, 21H), 0.89 (s, 9H), 0.84 (s, 6H), 0.02 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.2, 146.7, 131.5, 130.3, 123.7, 113.7, 111.1, 87.2, 72.7, 63.5, 40.0, 26.1, 25.2, 18.8, 18.5, 15.1, 11.5, -5.3; HRMS (APCI) m/z calcd for $\text{C}_{31}\text{H}_{55}\text{O}_2\text{Si}_2$ $[(\text{M}+\text{H})^+]$: 515.3735, found: 515.3730.

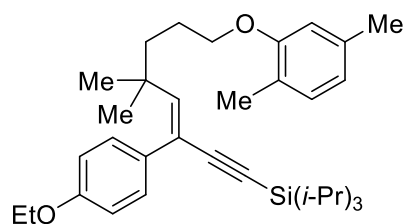
(E)-6-(2-(4-Ethoxyphenyl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)-2,2,3,3,6,9,9,10,10-nonamethyl-4,8-dioxa-3,9-disilaundecane (4ad):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (45.0 mg, 70% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.20 – 7.16 (m, 2H), 6.82 – 6.79 (m, 2H), 6.22 (s, 1H), 4.03 (q, 2H, $J = 7.0$ Hz), 3.36 (d, 4H, $J = 1.6$ Hz), 1.41 (t, 3H, $J = 7.0$ Hz), 1.02 (s, 21H), 0.87 (s, 18H), 0.67 (s, 3H), -0.00 (s, 6H), -0.01 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.3, 143.9, 131.6, 130.3, 124.9, 113.8, 111.1, 87.3, 66.9, 63.6, 45.2, 26.1, 19.3, 18.8, 18.5, 15.1, 11.5, -5.30, -5.31; HRMS (APCI) m/z calcd for $\text{C}_{37}\text{H}_{69}\text{O}_3\text{Si}_3$ $[(\text{M}+\text{H})^+]$: 645.4549, found: 645.4544.

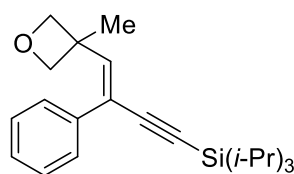
(E)-8-(2,5-Dimethylphenoxy)-3-(4-ethoxyphenyl)-5,5-dimethyloct-3-en-1-yn-1-yl triisopropylsilane (4ae):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (24.5 mg, 46% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.20 – 7.16 (m, 2H), 7.01 (d, 1H, $J = 7.5$ Hz), 6.83 – 6.80 (m, 2H), 6.66 (dd, 1H, $J = 7.5, 1.6$ Hz), 6.67 – 6.64 (m, 1H), 6.12 (s, 1H), 4.02 (q, 2H, $J = 7.0$ Hz), 3.81 (t, 2H, $J = 6.4$ Hz), 2.32 (s, 3H), 2.19 (s, 3H), 1.79 – 1.72 (m, 2H), 1.45 – 1.40 (m, 5H), 1.04 (s, 21H), 0.94 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.2, 157.3, 148.4, 136.6, 131.4, 130.4, 130.2, 123.8, 123.5, 120.8, 113.8, 112.2, 111.1, 87.5, 68.5, 63.5, 40.6, 37.5, 29.0, 25.3, 21.6, 18.8, 16.0, 15.0, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{35}\text{H}_{53}\text{O}_2\text{Si}$ $[(\text{M}+\text{H})^+]$: 533.3809, found: 533.3805.

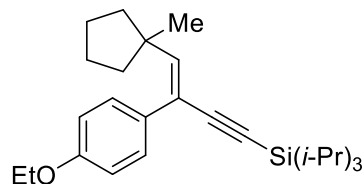
(E)-Triisopropyl(4-(3-methyloxetan-3-yl)-3-phenylbut-3-en-1-yn-1-yl)silane (4af):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 50:1 hexane:EtOAc) gave the pure product as a colorless oil (10.6 mg, 30% yield).

^1H NMR (400 MHz, CDCl_3): δ = 7.34 – 7.27 (m, 3H), 7.26 – 7.23 (m, 2H), 6.16 (s, 1H), 4.38 (d, 2H, J = 5.6 Hz), 4.04 (d, 2H, J = 5.9 Hz), 1.66 (s, 3H), 1.08 (s, 21H); ^{13}C NMR (101 MHz, CDCl_3): δ 142.0, 137.6, 128.4, 128.2, 128.1, 123.8, 108.8, 89.4, 81.8, 41.8, 26.8, 18.9, 11.5; HRMS (APCI) m/z calcd for $\text{C}_{23}\text{H}_{35}\text{OSi}$ $[(\text{M}+\text{H})^+]$: 355.2452, found: 355.2451.

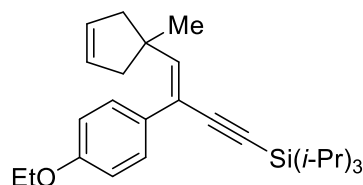
(E)-(3-(4-Ethoxyphenyl)-4-(1-methylcyclopentyl)but-3-en-1-yn-1-yl)triisopropylsilane (4ag):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (22.5 mg, 55% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.23 – 7.19 (m, 2H), 6.83 – 6.80 (m, 2H), 6.30 (s, 1H), 4.03 (q, 2H, J = 7.0 Hz), 1.57 – 1.55 (m, 2H), 1.54 – 1.51 (m, 4H), 1.42 (t, 3H, J = 7.0 Hz), 1.34 – 1.31 (m, 2H), 1.04 (s, 21H), 0.98 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.2, 149.4, 131.5, 130.3, 122.5, 113.7, 111.2, 87.0, 63.5, 45.5, 40.9, 26.9, 23.9, 18.9, 15.1, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{43}\text{OSi}$ $[(\text{M}+\text{H})^+]$: 411.3078, found: 411.3081.

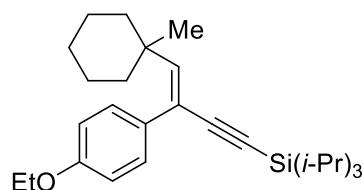
(E)-(3-(4-Ethoxyphenyl)-4-(1-methylcyclopent-3-en-1-yl)but-3-en-1-yn-1-yl)triisopropylsilane (4ah):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (19.2 mg, 47% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.23 – 7.19 (m, 2H), 6.84 – 6.80 (m, 2H), 6.38 (s, 1H), 5.49 (s, 2H), 4.04 (q, 2H, $J = 7.0$ Hz), 2.42 – 2.36 (m, 2H), 2.04 – 1.98 (m, 2H), 1.42 (t, 3H, $J = 7.0$ Hz), 1.11 (s, 3H), 1.05 (s, 21H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.3, 148.5, 131.2, 130.4, 128.7, 122.4, 113.8, 111.0, 87.2, 63.5, 47.7, 44.1, 29.7, 18.9, 15.1, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{41}\text{OSi}$ $[(\text{M}+\text{H})^+]$: 409.2921, found: 409.2923.

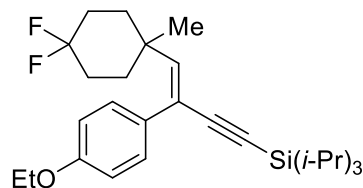
(E)-3-(4-Ethoxyphenyl)-4-(1-methylcyclohexyl)but-3-en-1-yn-1-yltriisopropylsilane (4ai):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (31.4 mg, 74% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.19 – 7.16 (m, 2H), 6.82 – 6.80 (m, 2H), 6.09 (s, 1H), 4.03 (q, 2H, $J = 7.0$ Hz), 1.45 – 1.39 (m, 6H), 1.37 – 1.31 (m, 4H), 1.26 – 1.08 (m, 3H), 1.03 (s, 21H), 0.97 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.2, 149.0, 131.7, 130.1, 123.6, 113.8, 111.5, 86.8, 63.5, 39.2, 38.0, 28.9, 26.2, 22.9, 18.8, 15.1, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{28}\text{H}_{45}\text{OSi}$ $[(\text{M}+\text{H})^+]$: 425.3234, found: 425.3241.

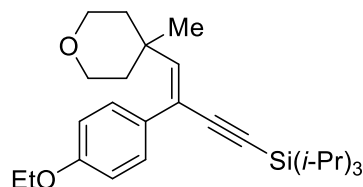
(E)-4-(4,4-Difluoro-1-methylcyclohexyl)-3-(4-ethoxyphenyl)but-3-en-1-yn-1-yltriisopropylsilane (4aj):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (40.9 mg, 89% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.20 – 7.16 (m, 2H), 6.85 – 6.81 (m, 2H), 6.03 (s, 1H), 4.04 (q, 2H, $J = 7.0$ Hz), 1.80 – 1.69 (m, 4H), 1.60 – 1.53 (m, 2H), 1.42 (t, 3H, $J = 7.0$ Hz), 1.35 – 1.26 (m, 2H), 1.10 (s, 3H), 1.04 (s, 21H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.5, 145.2, 130.7, 129.8, 125.7, 11.5, 123.7 (t, $J = 240.7$ Hz), 114.1, 110.5, 88.3, 63.6, 37.1, 34.9 (d, $J = 9.1$ Hz), 31.0 (t, $J = 23.9$ Hz), 28.6, 18.8, 15.0; HRMS (APCI) m/z calcd for $\text{C}_{28}\text{H}_{43}\text{F}_2\text{OSi}$ $[(\text{M}+\text{H})^+]$: 461.3046, found: 461.3036.

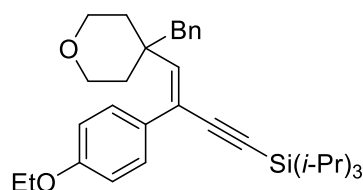
(*E*)-(3-(4-Ethoxyphenyl)-4-(4-methyltetrahydro-2*H*-pyran-4-yl)but-3-en-1-yn-1-yl)triisopropylsilane (4ak):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 50:1 hexane:EtOAc) gave the pure product as a colorless oil (32.4 mg, 76% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.17 – 7.13 (m, 2H), 6.83 – 6.80 (m, 2H), 6.07 (s, 1H), 4.02 (q, 2H, $J = 7.0$ Hz), 3.58 – 3.46 (m, 4H), 1.52 – 1.46 (m, 2H), 1.41 (t, 3H, $J = 7.0$ Hz), 1.28 (ddd, 2H, $J = 13.4, 9.1, 3.9$ Hz), 1.09 (s, 3H), 1.03 (s, 21H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.4, 146.8, 131.2, 129.9, 124.8, 114.0, 110.7, 87.9, 64.7, 63.5, 38.9, 35.8, 28.5, 18.8, 15.0, 11.5; HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{43}\text{O}_2\text{Si}$ $[(\text{M}+\text{H})^+]$: 427.3027, found: 427.3022.

(*E*)-(4-(4-Benzyltetrahydro-2*H*-pyran-4-yl)-3-(4-ethoxyphenyl)but-3-en-1-yn-1-yl)triisopropylsilane (4al):

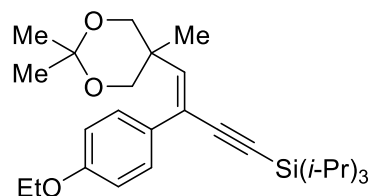


The title compound was prepared from the **General procedure B**. Purification using

flash silica gel column chromatography without workup (eluent: 50:1 hexane:EtOAc) gave the pure product as a colorless oil (20.6 mg, 41% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.32 – 7.27 (m, 3H), 7.19 – 7.17 (m, 2H), 6.86 – 6.83 (m, 2H), 6.75 – 6.71 (m, 2H), 5.86 (s, 1H), 4.01 (q, 2H, $J = 7.0$ Hz), 3.57 (dt, 2H, $J = 11.8, 3.7$ Hz), 3.40 (ddd, 2H, $J = 11.7, 9.3, 3.9$ Hz), 2.76 (s, 2H), 1.42 – 1.38 (m, 7H), 1.04 (s, 21H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.4, 144.9, 137.3, 131.0, 130.9, 129.6, 128.1, 126.6, 125.8, 113.9, 110.8, 88.0, 64.8, 63.5, 49.4, 41.2, 36.7, 18.8, 15.0, 11.5; HRMS (APCI) m/z calcd for $\text{C}_{33}\text{H}_{47}\text{O}_2\text{Si}$ $[(\text{M}+\text{H})^+]$: 503.3340, found: 503.3330.

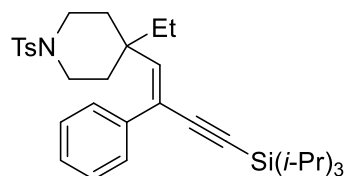
(*E*)-(3-(4-Ethoxyphenyl)-4-(2,2,5-trimethyl-1,3-dioxan-5-yl)but-3-en-1-yn-1-yl)triisopropylsilane (4am):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 20:1 hexane:EtOAc) gave the pure product as a colorless oil (32.8 mg, 72% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.17 – 7.13 (m, 2H), 6.83 – 6.79 (m, 2H), 5.95 (s, 1H), 4.01 (q, 2H, $J = 7.0$ Hz), 3.68 (d, 2H, $J = 11.5$ Hz), 3.32 (d, 2H, $J = 11.7$ Hz), 1.41 (t, 3H, $J = 7.0$ Hz), 1.34 (s, 6H), 1.10 (s, 3H), 1.03 (s, 21H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.6, 141.5, 131.0, 129.9, 126.4, 114.1, 109.9, 97.9, 89.4, 69.2, 63.5, 36.9, 27.0, 21.5, 20.8, 18.8, 15.0, 11.5; HRMS (APCI) m/z calcd for $\text{C}_{28}\text{H}_{45}\text{O}_3\text{Si}$ $[(\text{M}+\text{H})^+]$: 457.3132, found: 457.3128.

(*E*)-4-Ethyl-4-(2-phenyl-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)-1-tosylpiperidine (4an):

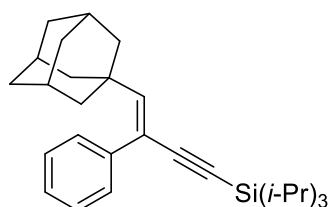


The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 10:1 hexane:EtOAc)

gave the pure product as a colorless oil (33.5 mg, 61% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.63 – 7.61 (m, 2H), 7.35 (d, 2H, $J = 8.0$ Hz), 7.29 – 7.25 (m, 3H), 7.09 – 7.06 (m, 2H), 5.80 (s, 1H), 3.20 (dt, 2H, $J = 11.8, 4.0$ Hz), 2.53 – 2.47 (m, 2H), 2.46 (s, 3H), 1.56 – 1.51 (m, 2H), 1.38 – 1.27 (m, 4H), 0.99 (s, 21H), 0.88 (t, 3H, $J = 7.5$ Hz); ^{13}C NMR (101 MHz, CDCl_3): δ 144.2, 143.5, 138.8, 133.5, 129.7, 128.4, 128.2, 127.9, 127.8, 126.3, 110.1, 88.6, 43.1, 39.6, 35.2, 34.5, 21.7, 18.7, 11.4, 8.5; HRMS (APCI) m/z calcd for $\text{C}_{33}\text{H}_{48}\text{NO}_2\text{SSi}$ $[(\text{M}+\text{H})^+]$: 550.3170, found: 550.3178.

((*E*)-4-((1*s*,3*s*)-Adamantan-1-yl)-3-phenylbut-3-en-1-yn-1-yl)triisopropylsilane (4ao):

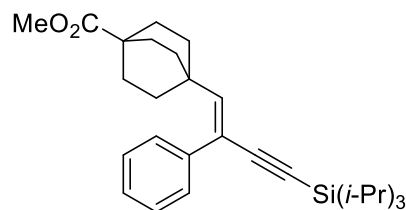


The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 200:1 hexane:EtOAc) gave the pure product as a colorless oil (20.9 mg, 50% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.28 – 7.23 (m, 5H), 5.96 (s, 1H), 1.83 (p, 3H, $J = 3.1$ Hz), 1.61 – 1.57 (m, 3H), 1.54 – 1.50 (m, 9H), 1.02 (s, 21H); ^{13}C NMR (101 MHz, CDCl_3): δ 149.9, 139.4, 129.1, 127.5, 126.9, 122.4, 110.9, 87.8, 42.7, 37.0, 36.6, 28.4, 18.6, 11.4; HRMS (APCI) m/z calcd for $\text{C}_{29}\text{H}_{43}\text{Si}$ $[(\text{M}+\text{H})^+]$: 419.3129, found: 419.3116.

Methyl

(*E*)-4-(2-phenyl-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)bicyclo[2.2.2]octane-1-carboxylate (4ap):

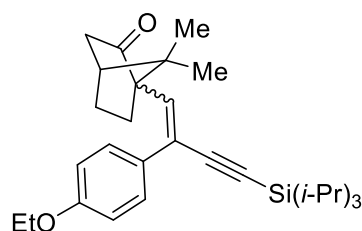


The title compound was prepared from the **General procedure B**. Purification using

flash silica gel column chromatography without workup (eluent: 20:1 hexane:EtOAc) gave the pure product as a colorless oil (24.8 mg, 55% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.31 – 7.25 (m, 3H), 7.23 – 7.21 (m, 2H), 6.02 (s, 1H), 3.58 (s, 3H), 1.67 – 1.63 (m, 6H), 1.48 – 1.44 (m, 6H), 1.01 (s, 21H); ^{13}C NMR (101 MHz, CDCl_3): δ 178.4, 147.6, 139.3, 129.2, 127.9, 127.3, 123.8, 110.6, 88.6, 51.8, 38.7, 34.7, 31.4, 28.4, 18.8, 11.5; HRMS (APCI) m/z calcd for $\text{C}_{29}\text{H}_{43}\text{O}_2\text{Si}$ [(M+H) $^+$]: 451.3027, found: 451.3013.

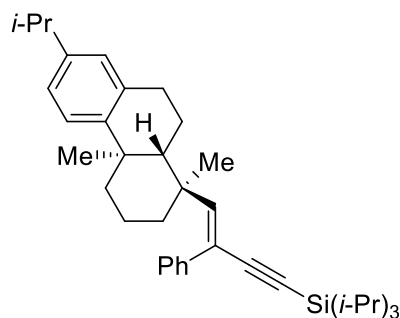
(S)-1-(2-(4-Ethoxyphenyl)-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)-7,7-dimethylbicyclo[2.2.1]heptan-2-one (4aq):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 20:1 hexane:EtOAc) gave the pure product as a colorless oil (19.0 mg, 41% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.37 – 7.33 (m, 2H), 6.79 – 6.75 (m, 2H), 5.91 (s, 1H), 4.01 (q, 2H, $J = 7.0$ Hz), 2.44 (ddd, 1H, $J = 18.3, 4.9, 3.0$ Hz), 2.01 (t, 1H, $J = 4.5$ Hz), 1.83 (d, 1H, $J = 18.3$ Hz), 1.77 – 1.69 (m, 1H), 1.58 (s, 3H), 1.40 (t, 3H, $J = 7.0$ Hz), 1.33 – 1.24 (m, 1H), 1.22 – 1.14 (m, 2H), 1.05 (s, 21H), 0.90 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 216.1, 158.7, 132.3, 131.1, 130.4, 130.3, 113.6, 110.1, 89.4, 65.1 (58.6); 63.5; 49.7 (44.4); 45.6 (44.0); 43.7 (42.4); 23.0 (27.8); 27.1 (27.4); 20.0 (21.9); 20.9 (20.5) 18.8; 15.0; 11.5; HRMS (APCI) m/z calcd for $\text{C}_{30}\text{H}_{45}\text{O}_2\text{Si}$ [(M+H) $^+$]: 465.3183, found: 465.3182.

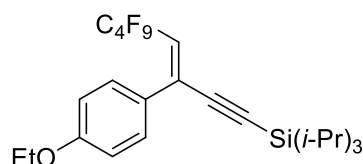
Triisopropyl((E)-4-((1R,4aR,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)-3-phenylbut-3-en-1-yn-1-yl)silane (4ar):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (31.2 mg, 58% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.29 – 7.23 (m, 5H), 7.13 (d, 1H, $J = 8.2$ Hz), 6.98 (dd, 1H, $J = 8.2, 2.1$ Hz), 6.90 (d, 1H, $J = 2.0$ Hz), 6.04 (s, 1H), 2.94 – 2.90 (m, 2H), 2.86 – 2.79 (m, 1H), 2.25 – 2.21 (m, 1H), 1.93 – 1.86 (m, 1H), 1.82 – 1.74 (m, 1H), 1.64 – 1.59 (m, 2H), 1.49 – 1.33 (m, 4H), 1.23 (d, 6H, $J = 6.9$ Hz), 1.13 (s, 3H), 1.02 (s, 21H), 0.74 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 152.3, 147.6, 145.8, 139.5, 135.0, 129.2, 127.9, 127.1, 127.0, 124.2, 124.0, 123.4, 111.3, 88.0, 50.0, 42.6, 40.1, 38.4, 37.4, 33.6, 30.3, 25.3, 24.2, 24.2, 21.1, 19.3, 18.9, 18.8, 11.6; HRMS (APCI) m/z calcd for $\text{C}_{38}\text{H}_{55}\text{Si}$ $[(\text{M}+\text{H})^+]$: 539.4068, found: 539.4064.

(E)-(3-(4-Ethoxyphenyl)-5,5,6,6,7,7,8,8,8-nonafluorooct-3-en-1-yn-1-yl)triisopropylsilane (4as):

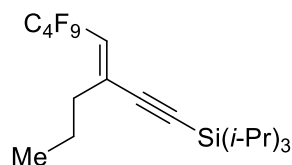


The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (28.9 mg, 53% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.39 (d, 2H, $J = 8.9$ Hz), 6.88 – 6.84 (m, 2H), 6.04 (t, 1H, $J = 15.5$ Hz), 4.05 (q, 2H, $J = 7.0$ Hz), 1.42 (t, 3H, $J = 7.0$ Hz), 1.09 – 1.07 (m, 21H); ^{19}F NMR (377 MHz, CDCl_3): δ -81.03 (t, 3F, $J = 9.5$ Hz), -103.94 – -103.86 (m, 2F), -123.84 – -123.76 (m, 2F), -125.8 – -125.7 (m, 2F); ^{13}C NMR (101 MHz, CDCl_3): δ 159.9, 137.1, 130.2 (t, $J = 3.2$ Hz), 127.8, 118.8 (t, $J = 20.4$ Hz), 114.0, 106.9, 97.5,

63.6, 18.8, 15.0, 11.4; HRMS (APCI) m/z calcd for $C_{25}H_{32}F_9OSi [(M+H)^+]$: 547.2073, found: 547.2071.

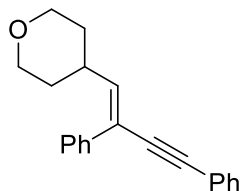
(*E*)-Triisopropyl(5,5,6,6,7,7,8,8,8-nonafluoro-3-propyloct-3-en-1-yn-1-yl)silane (4at):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (16.8 mg, 36% yield).

1H NMR (400 MHz, $CDCl_3$): δ 5.83 (t, 1H, $J = 15.7$ Hz), 2.37 – 2.33 (m, 2H), 1.66 (hept, 2H, $J = 7.4$ Hz), 1.09 (s, 21H), 0.95 (t, 3H, $J = 7.4$ Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -81.0 (t, 3F, $J = 9.6$ Hz), -105.5 - -105.4 (m, 2F), -124.1 - -124.0 (m, 2F), -125.8 – -125.7 (m, 2F); ^{13}C NMR (126 MHz, $CDCl_3$): δ 139.2 (d, $J = 6.7$ Hz), 121.0 (t, $J = 23.3$ Hz), 105.9, 96.3, 34.4, 21.7, 18.7, 13.6, 11.4; HRMS (EI) m/z calcd for $C_{20}H_{29}F_9Si [M]^+$: 468.1889, found: 468.1882.

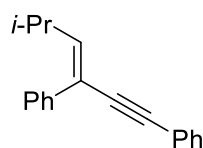
(*E*)-4-(2,4-Diphenylbut-1-en-3-yn-1-yl)tetrahydro-2H-pyran (4au):



The title compound was prepared from the **General procedure C**. Purification using flash silica gel column chromatography without workup (eluent: 50:1 hexane:EtOAc) gave the pure product as a colorless oil (11.5 mg, 40% yield, *E*:*Z* 83:17).

1H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.39 (m, 5H), 7.37 – 7.28 (m, 5H), 6.09 (d, 1H, $J = 10.2$ Hz), 3.94 (dt, 2H, $J = 11.4, 3.4$ Hz), 3.34 (ddd, 2H, $J = 11.6, 7.8, 5.6$ Hz), 2.67 – 2.57 (m, 1H), 1.67 – 1.59 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.6 (137.8), 131.7, 128.7, 128.6, 128.4, 128.2, 127.8, 126.2, 123.6, 123.4, 91.3, 88.2, 67.3 (67.8), 35.5 (37.8), 32.6 (32.2); HRMS (EI) m/z calcd for $C_{21}H_{20}O [M]^+$: 288.1509, found: 288.1503.

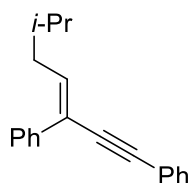
(E)-(5-Methylhex-3-en-1-yne-1,3-diyl)dibenzene (4av):



The title compound was prepared from the **General procedure C**. Purification using flash silica gel column chromatography without workup (eluent: hexane) gave the pure product as a colorless oil (10.5 mg, 43% yield, *E:Z* 95:5).

^1H NMR (400 MHz, CDCl_3): δ 7.45 – 7.37 (m, 6H), 7.33 – 7.28 (m, 4H), 6.10 (d, 1H, $J = 10.5$ Hz), 2.76 – 2.64 (m, 1H), 1.05 (d, 6H, $J = 6.6$ Hz); ^{13}C NMR (101 MHz, CDCl_3): δ 147.5, 138.1, 131.7, 128.8, 128.4, 128.1, 127.6, 123.8, 121.6, 91.6, 87.5, 28.6, 23.0; HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{18}$ $[\text{M}]^+$: 246.1403, found: 246.1402.

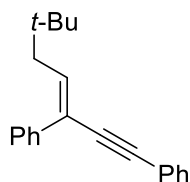
(E)-(6-Methylhept-3-en-1-yne-1,3-diyl)dibenzene (4aw):



The title compound was prepared from the **General procedure C**. Purification using flash silica gel column chromatography without workup (eluent: hexane) gave the pure product as a colorless oil (8.3 mg, 32% yield, *E:Z* 90:10).

^1H NMR (400 MHz, CDCl_3): δ 7.45 – 7.41 (m, 3H), 7.40 – 7.34 (m, 3H), 7.32 – 7.27 (m, 4H), 6.32 (t, 1H, $J = 7.6$ Hz), 2.16 (dd, 2H, $J = 7.6, 6.8$ Hz), 1.78 – 1.68 (m, 1H), 0.92 (d, 6H, $J = 6.6$ Hz); ^{13}C NMR (101 MHz, CDCl_3): δ 139.8, 138.0, 131.7, 129.1, 128.4, 128.3, 128.0, 127.5, 124.2, 123.8, 91.8, 87.4, 38.7, 29.1, 22.6; HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{20}$ $[\text{M}]^+$: 260.1560, found: 260.1561.

(E)-(6,6-Dimethylhept-3-en-1-yne-1,3-diyl)dibenzene (4ax):

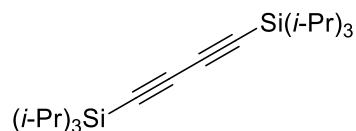


The title compound was prepared from the **General procedure C**. Purification using flash silica gel column chromatography without workup (eluent: hexane) gave the

pure product as a colorless oil (13.4 mg, 49% yield, *E*:*Z* 93:7).

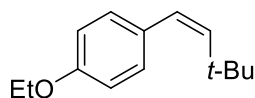
^1H NMR (400 MHz, CDCl_3): δ 7.46 – 7.36 (m, 6H), 7.32 – 7.27 (m, 4H), 6.39 (t, 1H, J = 7.7 Hz), 2.16 (d, 2H, J = 7.8 Hz), 0.92 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 138.1, 138.0, 131.7, 129.1, 128.4, 128.3, 128.0, 127.5, 124.8, 123.8, 91.9, 87.4, 43.3, 31.7, 29.6; HRMS (EI) m/z calcd for $\text{C}_{21}\text{H}_{22}$ $[\text{M}]^+$: 274.1716, found: 274.1716.

1,4-Bis(triisopropylsilyl)buta-1,3-diyne (7):



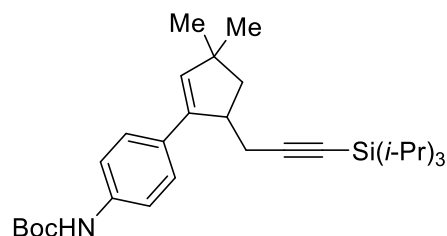
^1H NMR (400 MHz, CDCl_3) δ 1.09 (s, 42H); ^{13}C NMR (101 MHz, CDCl_3) δ 90.4, 81.8, 18.8, 11.5; HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{42}\text{Si}_2$ $[\text{M}]^+$: 362.2820, found: 362.2815.

(*Z*)-1-(3,3-Dimethylbut-1-en-1-yl)-4-ethoxybenzene (9):



^1H NMR (400 MHz, CDCl_3) δ 7.09 – 7.07 (m, 2H), 6.82 – 6.79 (m, 2H), 6.34 (d, J = 12.5 Hz, 1H), 5.55 (d, J = 12.5 Hz, 1H), 4.02 (q, J = 7.0 Hz, 2H), 1.41 (t, J = 7.0 Hz, 3H), 0.98 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 157.6, 142.7, 131.7, 130.2, 127.0, 113.7, 63.5, 31.4, 29.9, 15.1; HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{20}\text{O}$ $[\text{M}]^+$: 204.1509, found: 204.1512.

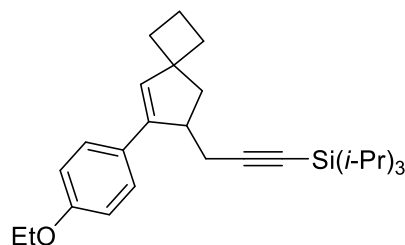
***tert*-Butyl (4-(3,3-dimethyl-5-(3-(triisopropylsilyl)prop-2-yn-1-yl)cyclopent-1-en-1-yl)phenyl)carbamate (11a):**



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 5:1 hexane:EtOAc) gave the pure product as a colorless oil (25.5 mg, 53% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.23 – 7.17 (m, 4H), 6.40 (br, 1H), 5.65 (d, 1H, J = 1.7 Hz), 3.36 – 3.29 (m, 1H), 2.48 (dd, 1H, J = 17.0, 3.6 Hz), 2.14 (dd, 1H, J = 17.0, 9.0 Hz), 2.01 (dd, 1H, J = 13.1, 8.5 Hz), 1.80 (dd, 1H, J = 13.1, 5.6 Hz), 1.45 (s, 9H), 1.11 (s, 3H), 1.03 (s, 3H), 1.01 – 0.95 (m, 21H); ^{13}C NMR (101 MHz, CDCl_3): δ 152.9, 141.8, 138.2, 137.3, 131.4, 127.2, 118.5, 107.8, 81.3, 80.7, 44.9, 44.7, 44.2, 30.0, 29.6, 28.5, 25.5, 18.8, 18.8, 11.5; DEPT 90 (101 MHz, CDCl_3): δ 138.0, 127.0, 118.4, 44.5, 18.7, 11.3; HRMS (APCI) m/z calcd for $\text{C}_{30}\text{H}_{48}\text{NO}_2\text{Si}$ $[(\text{M}+\text{H})^+]$: 482.3449, found: 482.3452.

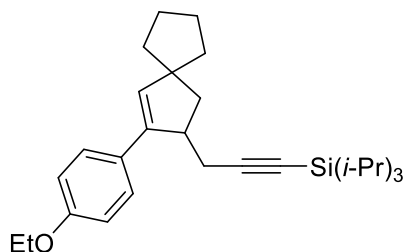
(3-(7-(4-Ethoxyphenyl)spiro[3.4]oct-7-en-6-yl)prop-1-yn-1-yl)triisopropylsilane (11b):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (21.9 mg, 52% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.31 – 7.28 (m, 2H), 6.85 – 6.82 (m, 2H), 6.05 (d, 1H, J = 1.3 Hz), 4.03 (q, 2H, J = 7.0 Hz), 3.28 (dddd, 1H, J = 13.2, 7.8, 3.8, 1.3 Hz), 2.53 (dd, 1H, J = 17.0, 3.6 Hz), 2.32 – 2.21 (m, 2H), 2.15 – 2.05 (m, 4H), 2.05 – 1.97 (m, 1H), 1.93 – 1.84 (m, 2H), 1.41 (t, 3H, J = 7.0 Hz), 1.08 – 1.00 (m, 21H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.3, 143.0, 134.4, 128.5, 127.5, 114.6, 108.2, 81.1, 63.6, 51.5, 44.9, 44.7, 35.9, 35.2, 25.6, 18.9, 18.9, 16.9, 15.0, 11.5; DEPT 90 (101 MHz, CDCl_3): δ 134.2, 127.4, 114.4, 44.7, 18.7, 11.3; HRMS (APCI) m/z calcd for $\text{C}_{28}\text{H}_{43}\text{OSi}$ $[(\text{M}+\text{H})^+]$: 423.3078, found: 423.3069.

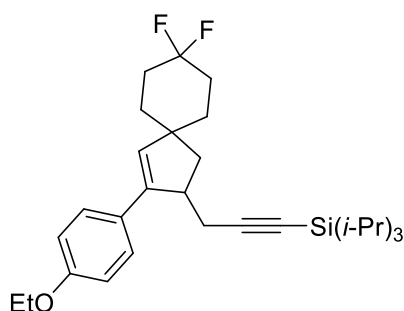
(3-(3-(4-Ethoxyphenyl)spiro[4.4]non-3-en-2-yl)prop-1-yn-1-yl)triisopropylsilane (11c):



The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (27.9 mg, 64% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.30 – 7.26 (m, 2H), 6.85 – 6.82 (m, 2H), 5.79 (d, 1H, $J = 1.4$ Hz), 4.03 (q, 2H, $J = 7.0$ Hz), 3.39 – 3.32 (m, 1H), 2.57 (dd, 1H, $J = 17.0, 3.7$ Hz), 2.23 – 2.12 (m, 2H), 1.97 (dd, 1H, $J = 13.1, 4.6$ Hz), 1.70 – 1.66 (m, 4H), 1.63 – 1.50 (m, 4H), 1.41 (t, 3H, $J = 7.0$ Hz), 1.08 – 1.00 (m, 21H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.2, 142.4, 135.2, 128.9, 127.6, 114.5, 108.2, 81.2, 63.6, 55.4, 44.7, 44.0, 40.5, 40.3, 25.7, 25.0, 24.7, 18.9, 18.8, 15.0, 11.5; DEPT 90 (101 MHz, CDCl_3): δ 135.0, 127.4, 114.4, 44.6, 18.7, 11.3; HRMS (APCI) m/z calcd for $\text{C}_{29}\text{H}_{45}\text{OSi}$ $[(\text{M}+\text{H})^+]$: 437.3234, found: 437.3238.

(3-(3-(4-Ethoxyphenyl)-8,8-difluorospiro[4.5]dec-3-en-2-yl)prop-1-yn-1-yl)triisopropylsilane (11d):

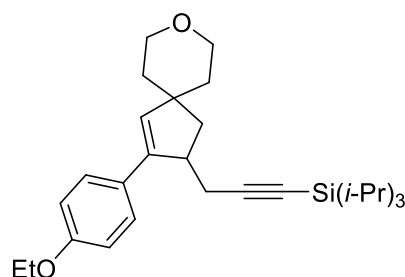


The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (41.3 mg, 85% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.29 – 7.25 (m, 2H), 6.87 – 6.83 (m, 2H), 5.81 (d, 1H, $J = 1.6$ Hz), 4.04 (q, 2H, $J = 7.0$ Hz), 3.46 – 3.39 (m, 1H), 2.59 (dd, 1H, $J = 17.1, 3.7$ Hz), 2.29 – 2.14 (m, 2H), 2.05 – 1.88 (m, 5H), 1.83 – 1.67 (m, 3H), 1.62 (t, 1H, $J = 6.1$ Hz), 1.42 (t, 3H, $J = 7.0$ Hz), 1.08 – 0.99 (m, 21H); ^{13}C NMR (101 MHz, CDCl_3):

δ 158.5, 143.9, 132.9, 128.4, 127.7, 123.64 (t, $J = 240.7$ Hz), 114.6, 107.4, 81.8, 63.6, 47.1, 44.0, 40.5, 35.1 (t, $J = 4.8$ Hz), 34.6 (t, $J = 4.7$ Hz), 31.6 (t, $J = 23.7$ Hz), 31.5 (t, $J = 24.1$ Hz), 25.7, 18.82, 18.80, 15.0, 11.5; DEPT 90 (101 MHz, CDCl_3): δ 132.8, 127.5, 114.4, 43.9, 18.6, 18.6, 11.3; HRMS (APCI) m/z calcd for $\text{C}_{30}\text{H}_{45}\text{F}_2\text{OSi}$ $[(\text{M}+\text{H})^+]$: 487.3202, found: 487.3206.

(3-(3-(4-Ethoxyphenyl)-8-oxaspiro[4.5]dec-3-en-2-yl)prop-1-yn-1-yl)triisopropylsilane (11e):

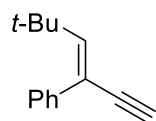


The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography without workup (eluent: 100:1 hexane:EtOAc) gave the pure product as a colorless oil (37.0 mg, 82% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.29 -7.26 (m, 2H), 6.86 – 6.83 (m, 2H), 5.84 (d, 1H, $J = 1.6$ Hz), 4.03 (q, 2H, $J = 7.0$ Hz), 3.87 – 3.77 (m, 2H), 3.64 (ddt, 2H, $J = 12.0, 9.1, 3.2$ Hz), 3.44 – 3.37 (m, 1H), 2.59 (dd, 1H, $J = 17.0, 3.7$ Hz), 2.25 – 2.19 (m, 2H), 1.98 (dd, 1H, $J = 13.4, 5.2$ Hz), 1.80 – 1.73 (m, 1H), 1.71 – 1.65 (m, 1H), 1.61 – 1.56 (m, 1H), 1.49 – 1.45 (m, 1H), 1.41 (t, 3H, $J = 7.0$ Hz), 1.07 – 1.03 (m, 21H); ^{13}C NMR (101 MHz, CDCl_3): δ 158.4, 143.5, 133.9, 128.5, 127.7, 114.6, 107.6, 81.7, 65.6, 65.5, 63.6, 45.9, 44.0, 41.2, 39.0, 38.4, 25.9, 18.8, 18.8, 15.0, 11.5; DEPT 90 (101 MHz, CDCl_3): δ 133.8, 127.5, 114.4, 43.8, 18.7, 18.6, 11.3; HRMS (APCI) m/z calcd for $\text{C}_{29}\text{H}_{45}\text{O}_2\text{Si}$ $[(\text{M}+\text{H})^+]$: 453.3183, found: 453.3172.

6. Chemical transformations of 1,3-enyne products

(Z)-(5,5-Dimethylhex-3-en-1-yn-3-yl)benzene (12):

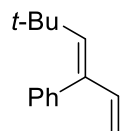


Procedure for synthesis of 12^[6]: To a solution of **4b** (0.2 mmol, 68 mg, 1.0 equiv.) in

dry THF (1 mL) was added TBAF solution (1 mmol, 1M in THF, 1 mL) dropwise under a nitrogen atmosphere. The reaction mixture was allowed to stir for 4 h at room temperature. The reaction was quenched by adding H₂O (5 mL) and the mixture was extracted with Et₂O (3*5 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and evaporated under vacuum. The residue was purified by flash column chromatography through silica gel using hexane as eluent to give **12** (28 mg, 75%) as a colorless oil.

¹H NMR (500 MHz, CDCl₃): δ 7.34 – 7.26 (m, 5H), 6.27 (s, 1H), 2.88 (d, *J* = 0.6 Hz, 1H), 0.94 (s, 9H); ¹³C NMR (126 MHz, CDCl₃): δ 151.3, 138.6, 129.2, 128.2, 127.6, 121.2, 87.1, 75.2, 34.8, 31.0; HRMS (EI) *m/z* calcd for C₁₄H₁₆ [M]⁺: 184.1247, found: 184.1245.

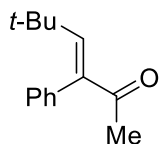
(Z)-(5,5-Dimethylhexa-1,3-dien-3-yl)benzene (13):



Procedure for synthesis of **13^[7]:** To a 4 mL vial was charged with Lindlar catalyst (0.005 mmol, 10.6 mg), **12** (0.1 mmol, 21 μL) and cyclohexane (2 mL). The reaction mixture was stirred at room temperature for 76 min under a H₂ atmosphere using a balloon. Then the volatiles were removed and the residue was purified by flash chromatography on silica gel using hexane as eluent to give **13** (9.6 mg, 52%) as colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.34 – 7.25 (m, 3H), 7.12 – 7.09 (m, 2H), 6.52 (ddd, *J* = 17.2, 10.4, 0.8 Hz, 1H), 5.71 (d, *J* = 0.8 Hz, 1H), 4.93 (ddd, *J* = 10.4, 1.5, 0.7 Hz, 1H), 4.42 (ddd, *J* = 17.2, 1.5, 0.6 Hz, 1H), 0.89 (s, 9H); ¹³C NMR (101 MHz, CDCl₃): δ 144.3, 143.7, 139.2, 138.6, 130.3, 127.8, 126.8, 114.1, 33.9, 31.4; HRMS (EI) *m/z* calcd for C₁₄H₁₈ [M]⁺: 186.1403, found: 186.1405.

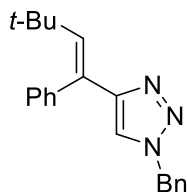
(E)-5,5-Dimethyl-3-phenylhex-3-en-2-one (14):



Procedure for synthesis of **14^[8]:** A 4 mL vial was charged with gold(III) chloride hydrate (0.005 mmol, 1.7 mg), methanol (0.3 mL), **12** (0.1 mmol, 21 μ L, 1.0 equiv.) and H₂O (60 μ L) under a nitrogen atmosphere. The reaction mixture was heated to 60 °C for 5 h. After removing the volatiles, the residue was purified by flash column chromatography (hexane: ethyl acetate 30:1) to give **14** (15.9 mg, 79%) as colorless oil.

¹H NMR (400 MHz, CD₂Cl₂): δ 7.37 – 7.31 (m, 3H), 7.12 – 7.09 (m, 2H), 6.85 (s, 1H), 2.19 (s, 3H), 0.93 (s, 9H); ¹³C NMR (101 MHz, CD₂Cl₂): δ 200.1, 152.6, 140.9, 137.9, 130.7, 128.2, 127.7, 34.7, 30.7, 27.8; HRMS (EI) m/z calcd for C₁₄H₁₈O [M]⁺: 202.1352, found: 202.1349.

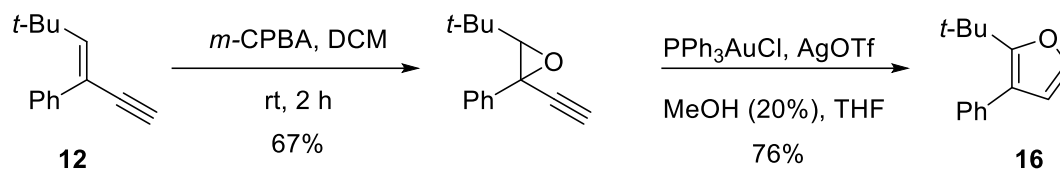
(*E*)-1-Benzyl-4-(3,3-dimethyl-1-phenylbut-1-en-1-yl)-1*H*-1,2,3-triazole (15**):**



Procedure for synthesis of **15^[9]:** To a 4 mL vial was charged with CuI (0.04 mmol, 7.6 mg), THF (0.4 mL), **12** (0.1 mmol, 18.4 mg, 1.0 equiv.) and (azidomethyl)benzene (0.1 mmol, 12.5 μ L) in a glovebox, and the vial was then sealed with a screw cap. The reaction mixture was taken out of the glovebox and heated to 50 °C for 15 h. After removing the volatiles, the residue was purified by flash column chromatography (hexane: ethyl acetate = 10:1) to give **15** (22.1 mg, 70%) as colorless solid.

¹H NMR (500 MHz, CDCl₃): δ 7.34 – 7.29 (m, 6H), 7.21 – 7.16 (m, 4H), 6.88 (s, 1H), 6.67 (s, 1H), 5.39 (s, 2H), 0.96 (s, 9H); ¹³C NMR (126 MHz, CDCl₃): δ 152.0, 139.7, 139.4, 135.1, 129.9, 129.1, 128.6, 128.3, 128.2, 127.8, 127.3, 120.8, 54.0, 34.0, 31.4; HRMS (EI) m/z calcd for C₂₁H₂₃N₃ [M]⁺: 317.1886, found: 317.1890.

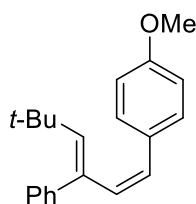
2-(*tert*-Butyl)-3-phenylfuran (16**):**



Procedure for synthesis of 16^[10]: To a solution of **12** (0.15 mmol, 1.0 equiv.) in dry dichloromethane (0.6 mL) was added 3-chloroperbenzoic acid (3.0 mmol, 52 mg). The reaction mixture was stirred at room temperature for 4 hours. After this time, the reaction was quenched with 0.2 mL of aqueous 2 M aqueous sodium hydroxide solution and diluted with 5 mL H₂O. The organic phase was separated and the aqueous phase was extracted with dichloromethane (2*5mL). The combined organic layers were dried over anhydrous sodium sulphate and the volatile components were removed under reduced pressure. The residue was further purified by flash column chromatography (hexane as eluent) to give 3-(*tert*-butyl)-2-ethynyl-2-phenyloxirane (20 mg, 67%) as colorless oil. Methanol (0.02 mmol, 0.8 μ L), chloro(triphenylphosphine)gold(I) (0.005 mmol, 2.5 mg) and silver trifluoromethanesulfonate (0.005 mmol, 1.3 mg) were added to a solution of 3-(*tert*-butyl)-2-ethynyl-2-phenyloxirane (0.1 mmol, 20 mg, 1.0 equiv.) in dry THF (0.4 mL). The resulting mixture was stirred at room temperature for 12 h under an argon atmosphere. After this time, volatile components were carefully removed and the residue was purified by flash chromatography on silica gel using hexane as eluent to give **16** (16 mg, 76%) as colorless oil.

¹H NMR (500 MHz, CDCl₃): δ 7.36 – 7.27 (m, 6H), 6.25 (d, J = 1.8 Hz, 1H), 1.22 (s, 9H); ¹³C NMR (126 MHz, CDCl₃): δ 157.6, 138.7, 136.5, 130.4, 127.9, 126.9, 120.0, 114.4, 34.3, 30.3; HRMS (EI) m/z calcd for C₁₄H₁₆O [M]⁺: 200.1196, found: 200.1195.

1-((1Z,3Z)-5,5-Dimethyl-3-phenylhexa-1,3-dien-1-yl)-4-methoxybenzene (17):



Procedure for synthesis of **17^[7]:** To a 4 mL vial was charged with Lindlar catalyst (0.001 mmol, 2.1 mg), **4z** (0.1 mmol, 29 mg) and cyclohexane (2 mL). The reaction mixture was stirred at room temperature for 13 h under a H₂ atmosphere using a balloon. Then volatile was removed and the residue was purified by flash chromatography (ethyl acetate: hexane = 100:1) to give **17** (11.5 mg, 40%) as colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.43 – 7.41 (m, 2H), 7.26 – 7.20 (m, 5H), 6.78 – 6.75 (m, 2H), 6.22 (d, *J* = 12.0 Hz, 1H), 5.99 (dd, *J* = 12.0, 1.3 Hz, 1H), 5.74 (d, *J* = 1.2 Hz, 1H), 3.80 (s, 3H), 0.84 (s, 9H); ¹³C NMR (101 MHz, CDCl₃): δ 158.4, 141.7, 141.0, 135.3, 134.1, 130.2, 130.1, 129.4, 127.9, 127.1, 126.8, 113.4, 55.4, 34.1, 31.1; HRMS (EI) *m/z* calcd for C₂₁H₂₄O [M]⁺: 292.1822, found: 292.1819.

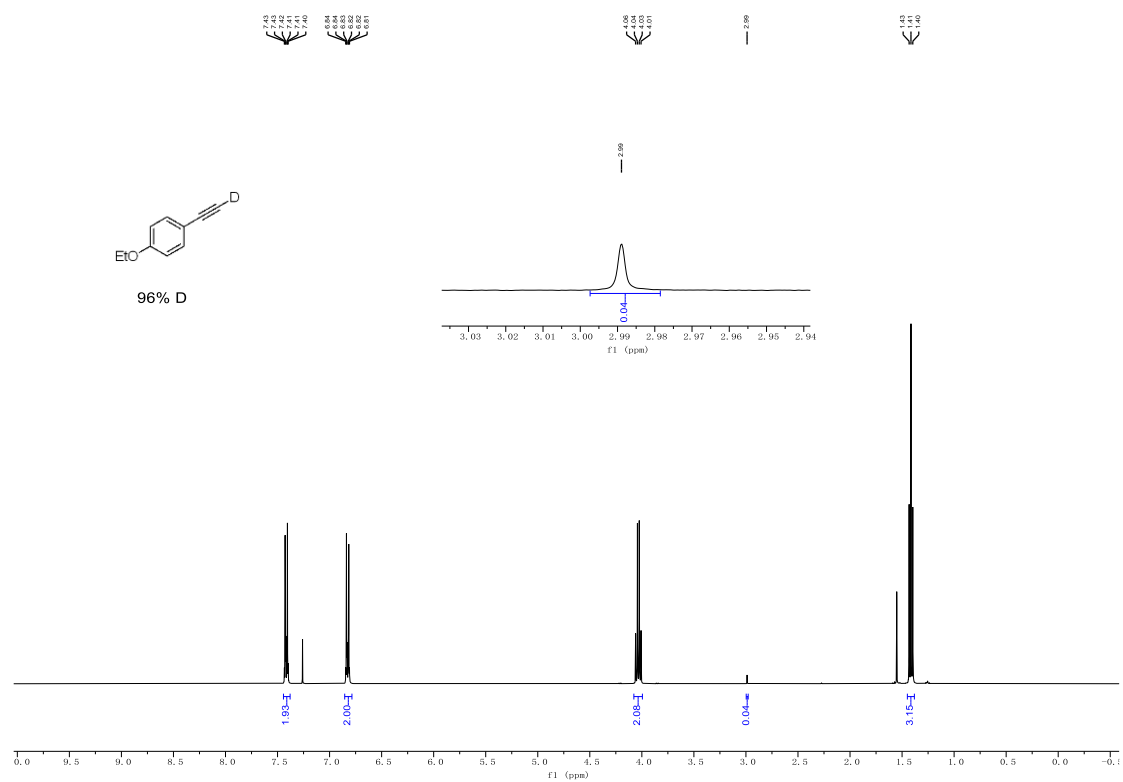
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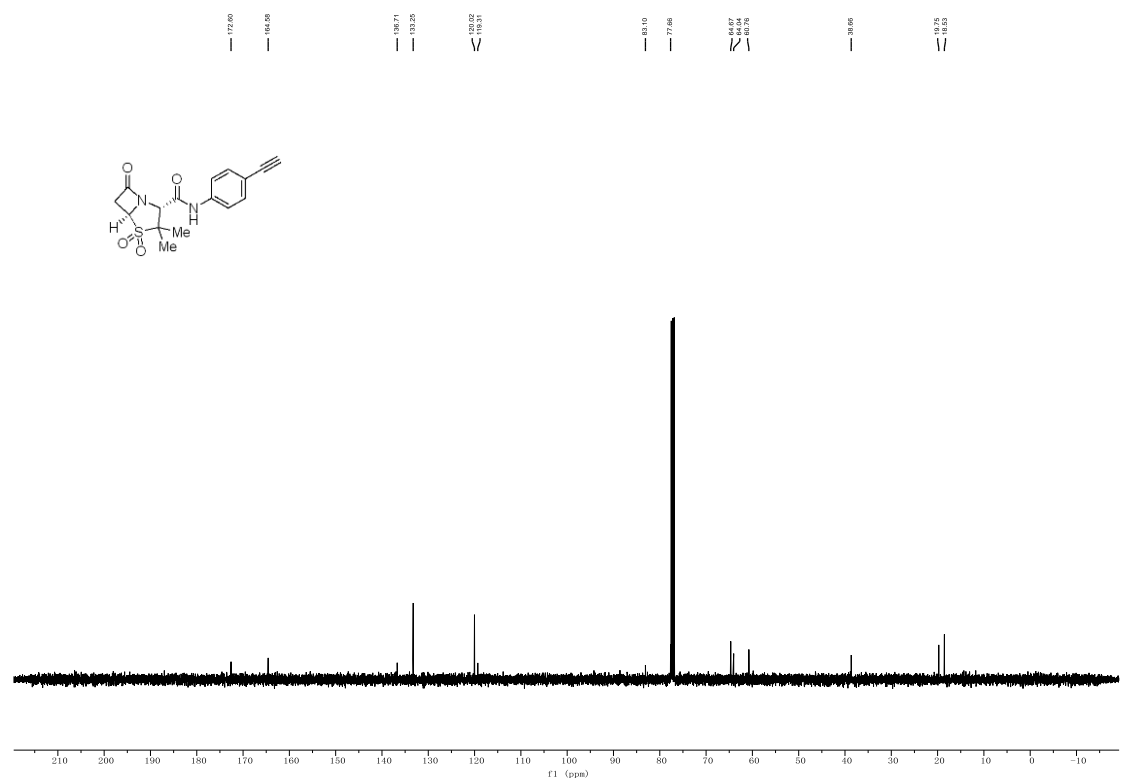
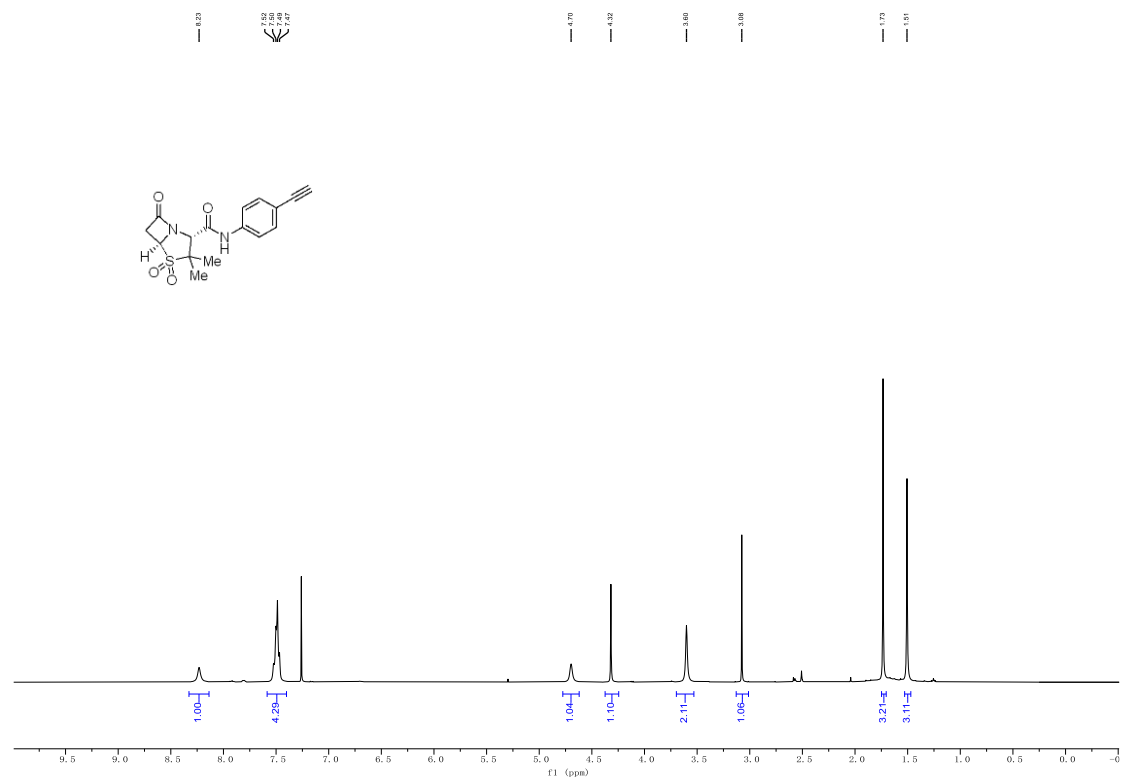
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8 . NMR spectra

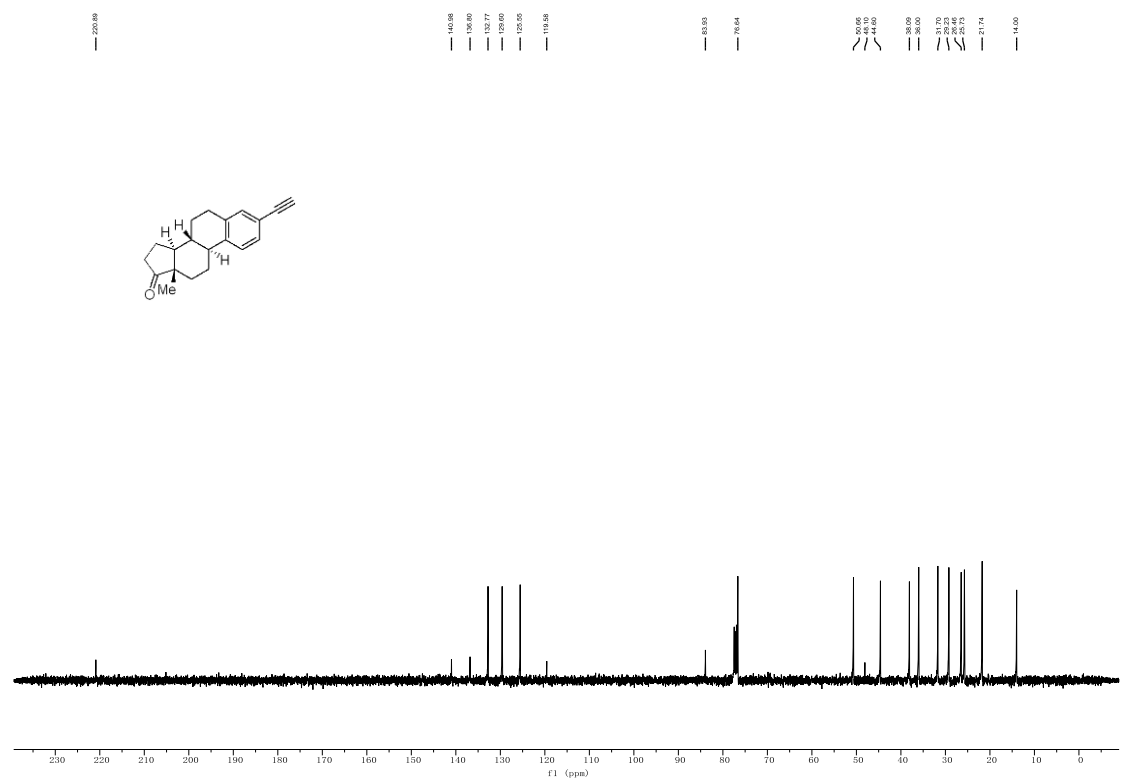
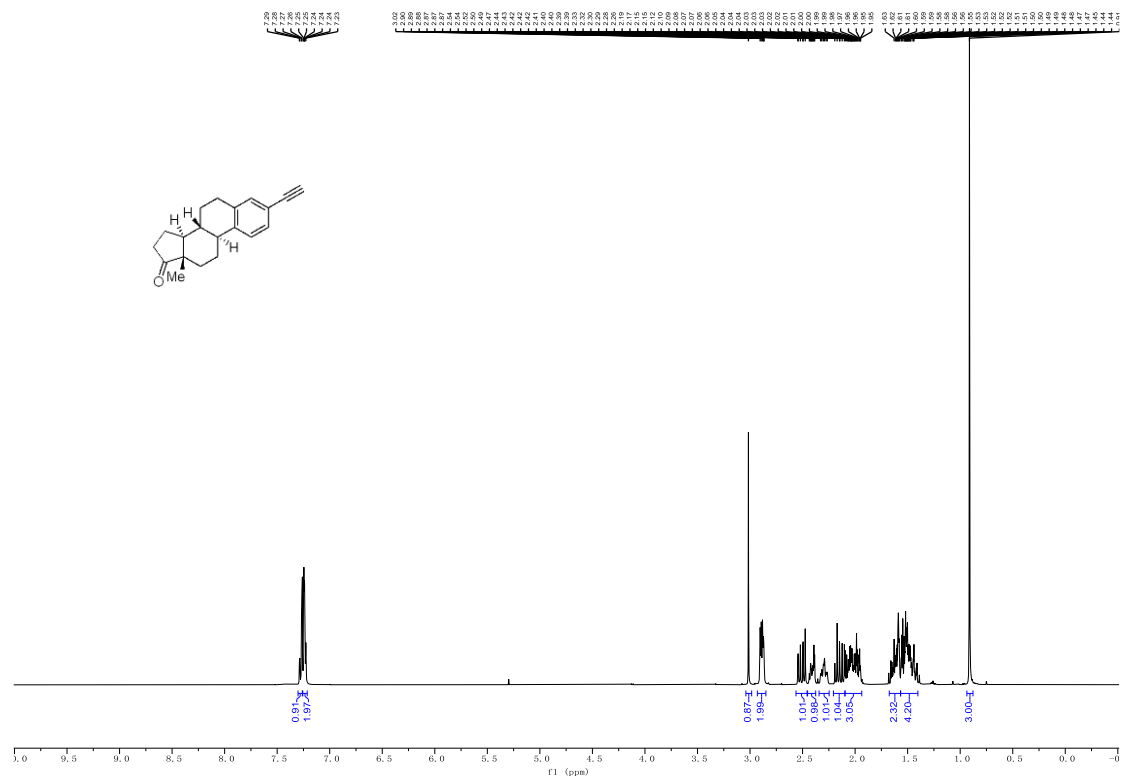
^1H NMR spectra of S1, 96%D



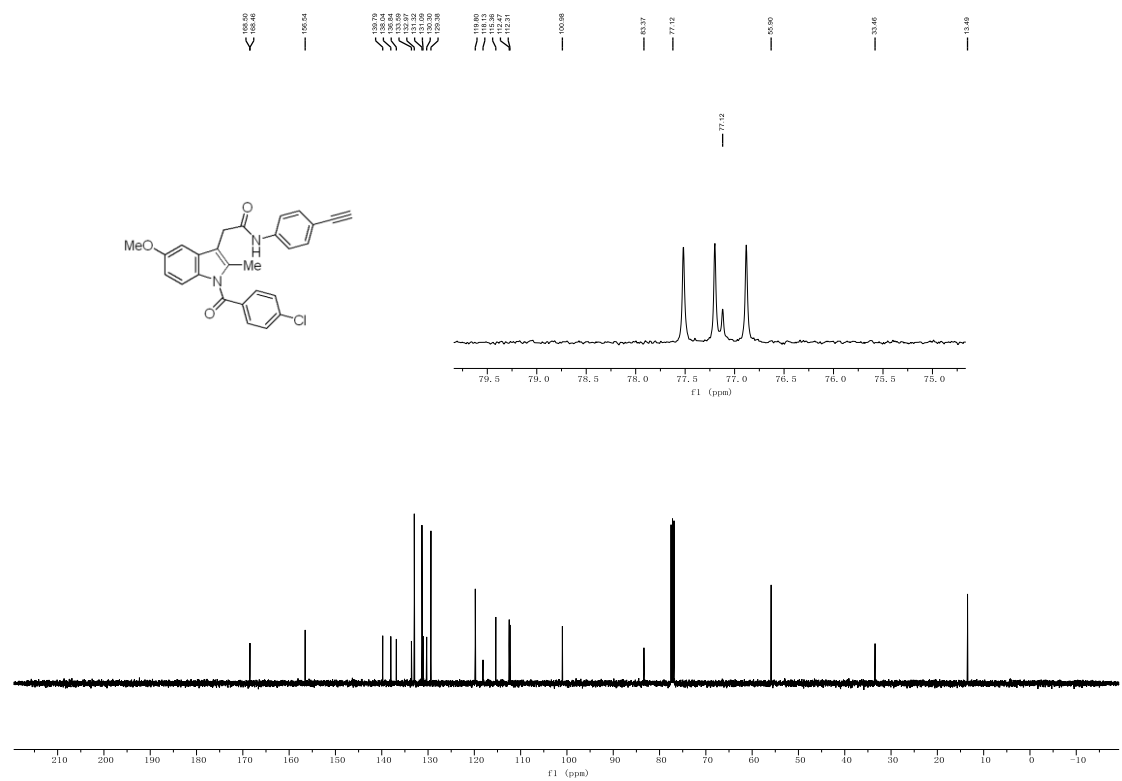
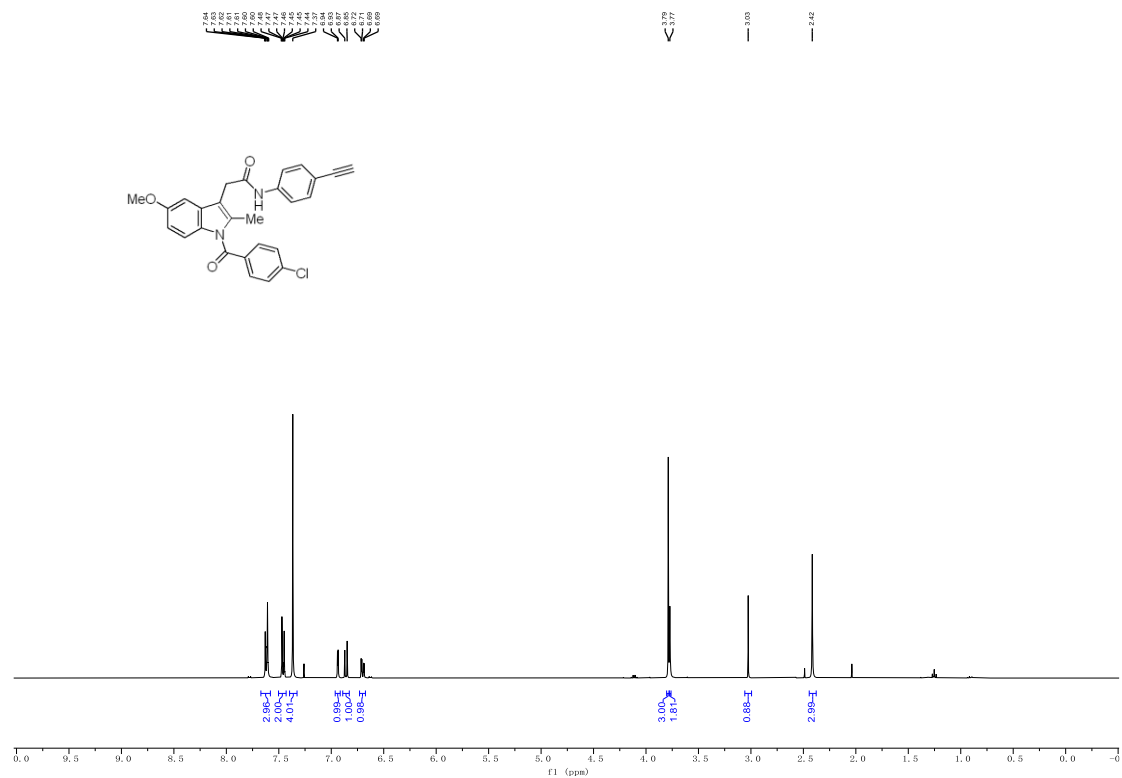
¹H NMR and ¹³C NMR spectra of S2

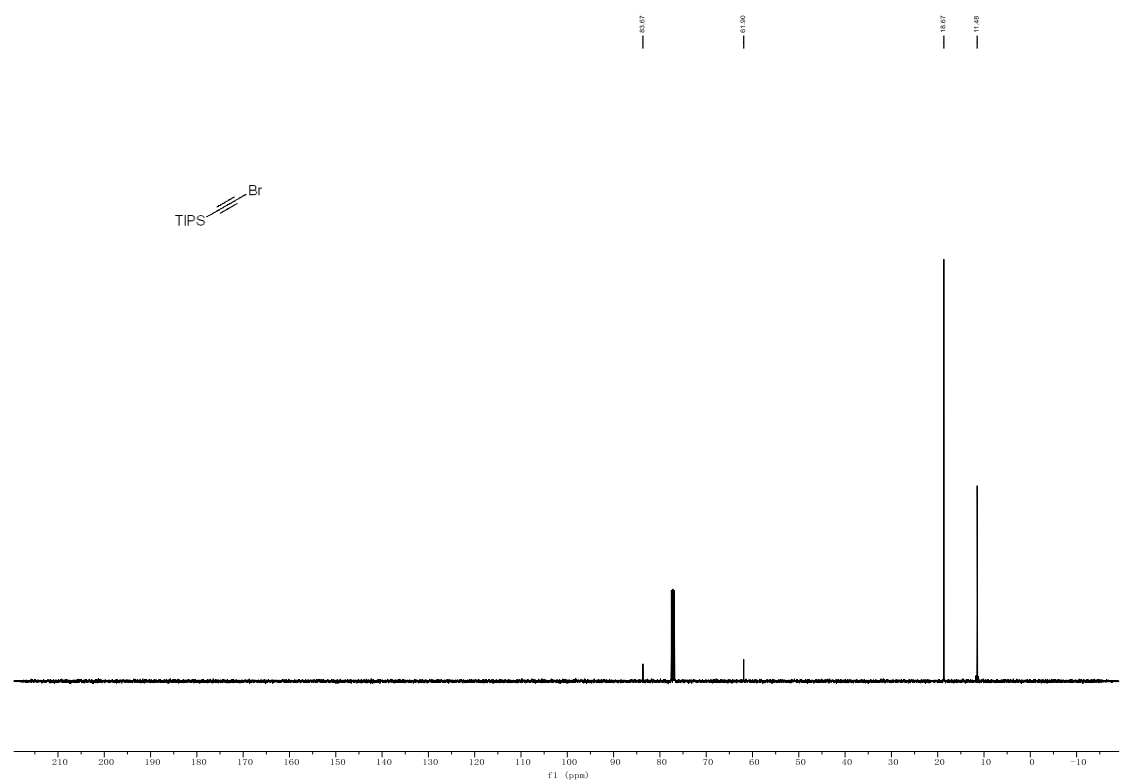


¹H NMR and ¹³C NMR spectra of S3

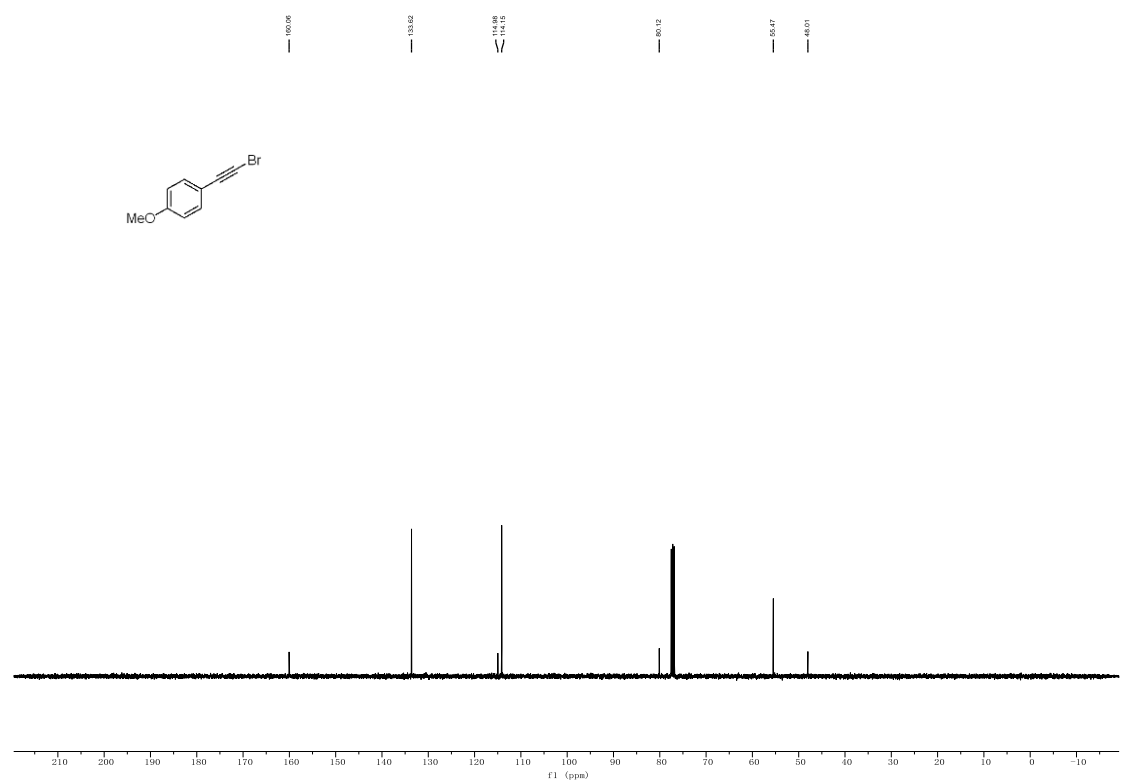
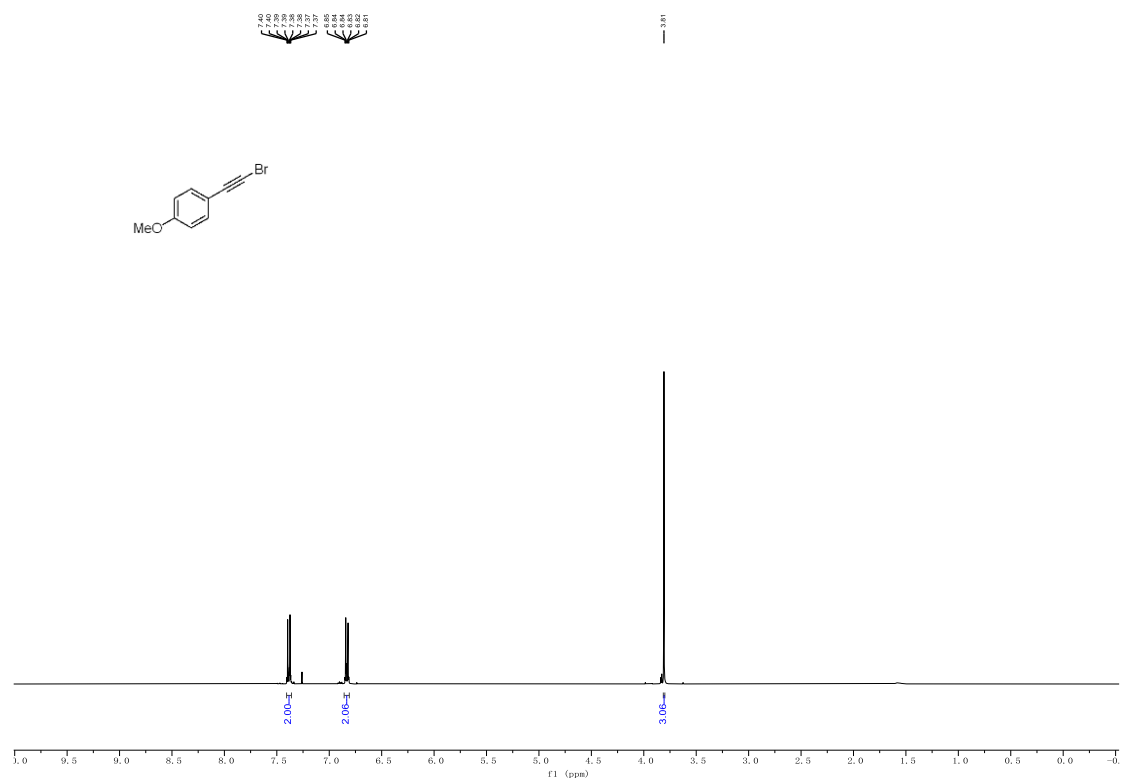


¹H NMR and ¹³C NMR spectra of S4





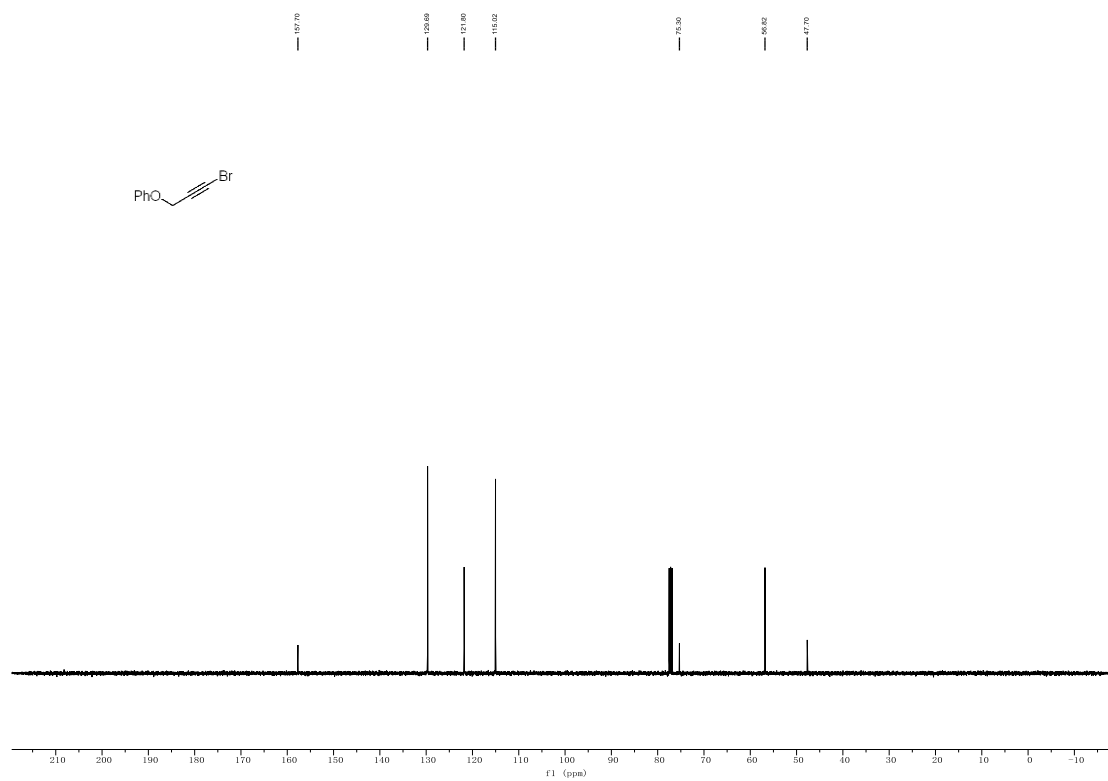
¹H NMR and ¹³C NMR spectra of S7



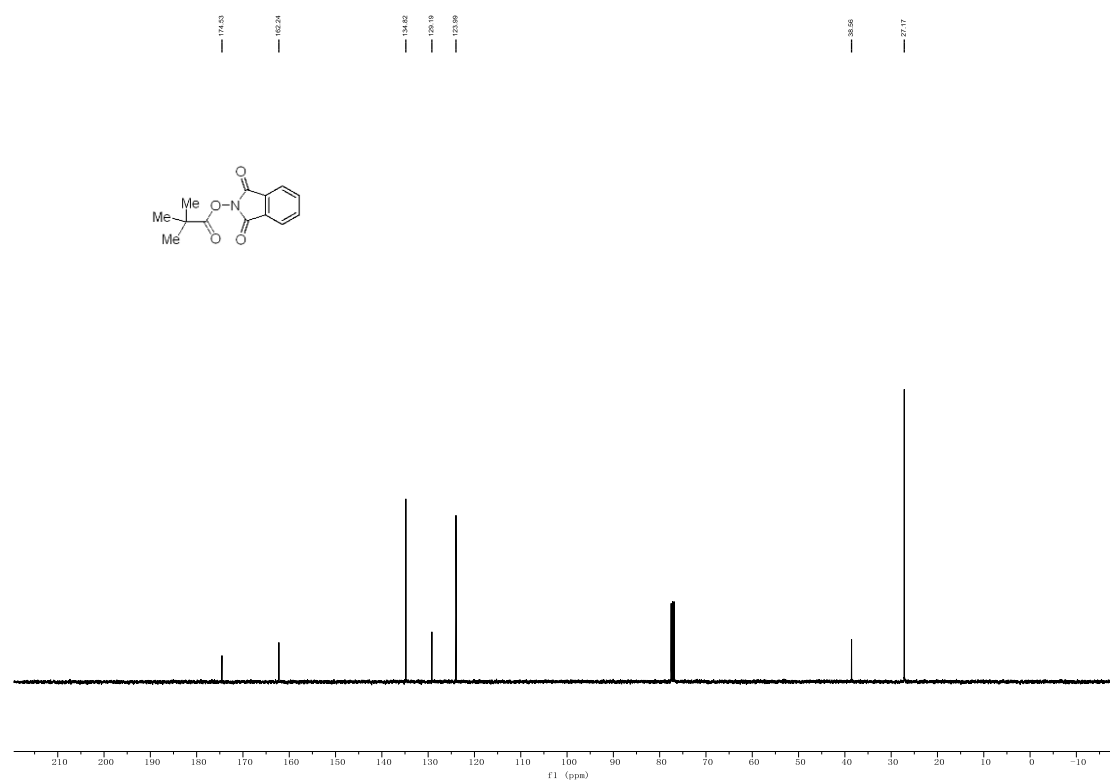
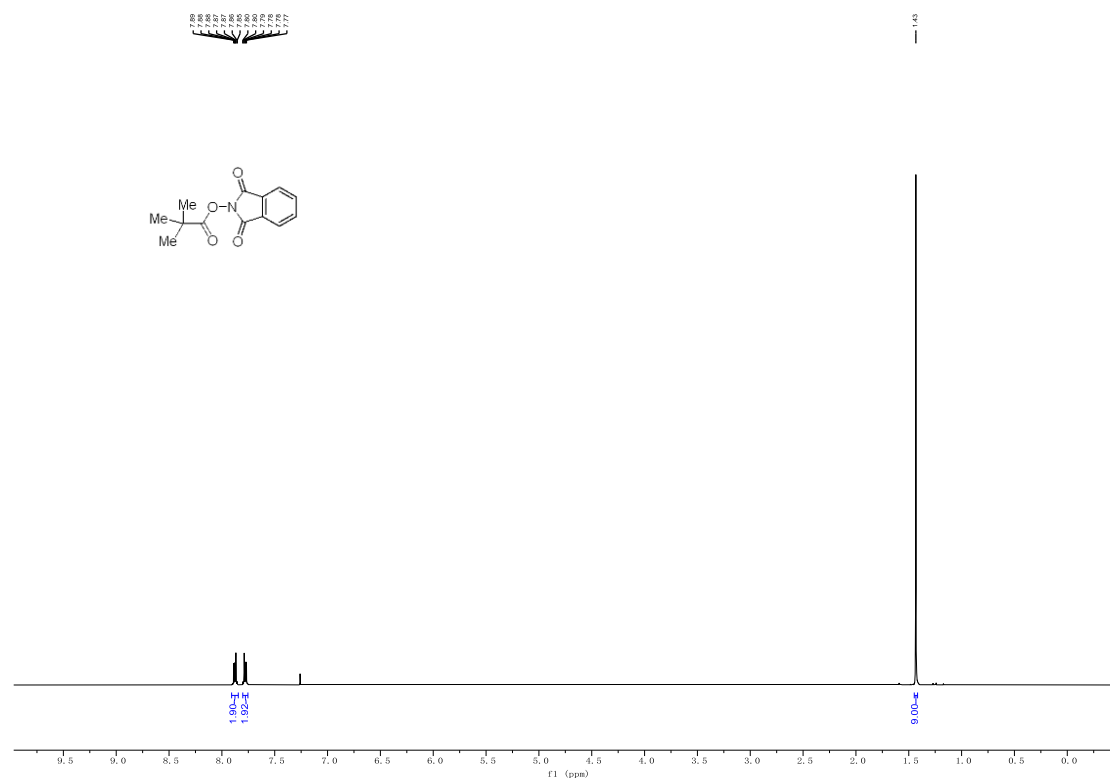
BrC#CCOC1=CC=CC=C1

Chemical structure: 4-bromo-1-ethynylbenzene (Ph-C≡C-Br).

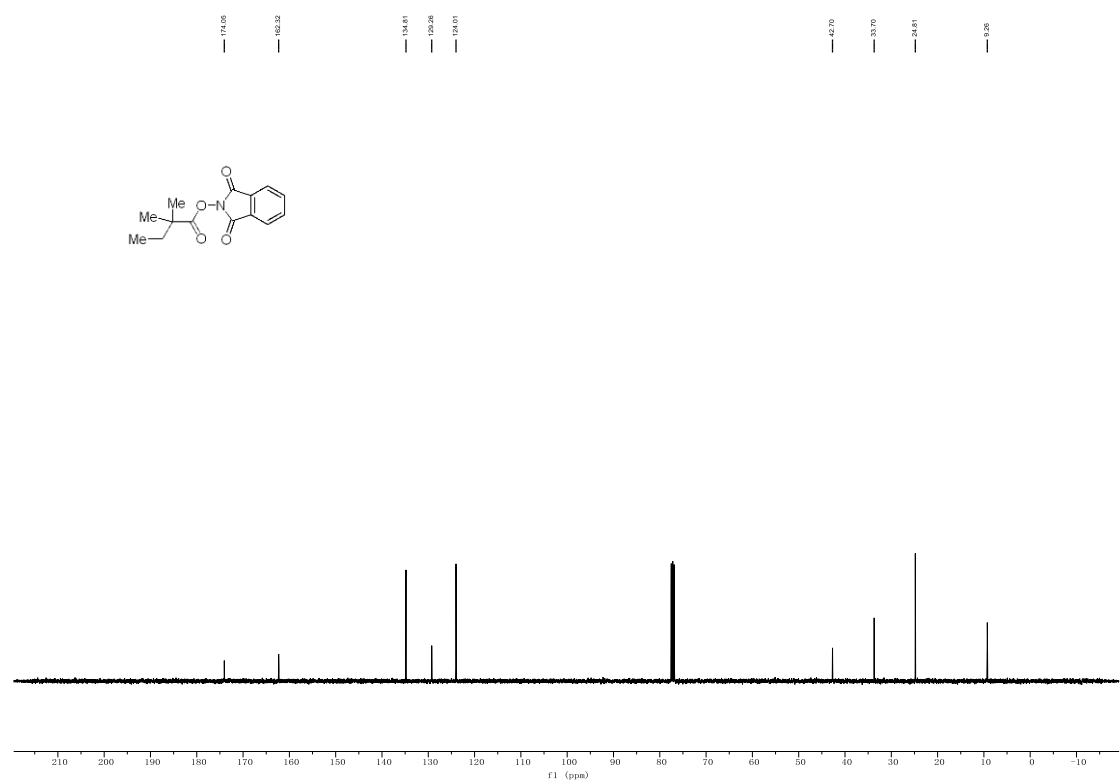
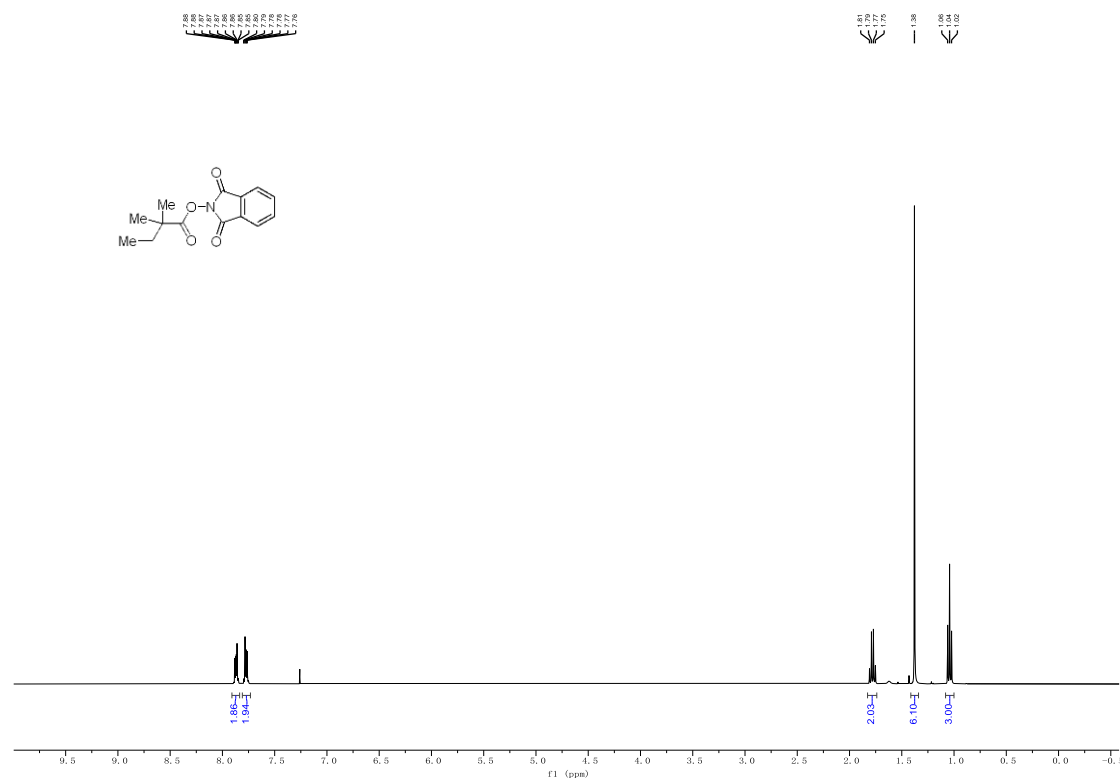
¹H NMR spectrum (CDCl₃) showing peaks at approximately 7.3 ppm (multiplet, integration 2.00), 7.1 ppm (multiplet, integration 3.00), and 4.7 ppm (singlet, integration 2.00). The x-axis is labeled f1 (ppm) and ranges from 0.0 to 10.0.



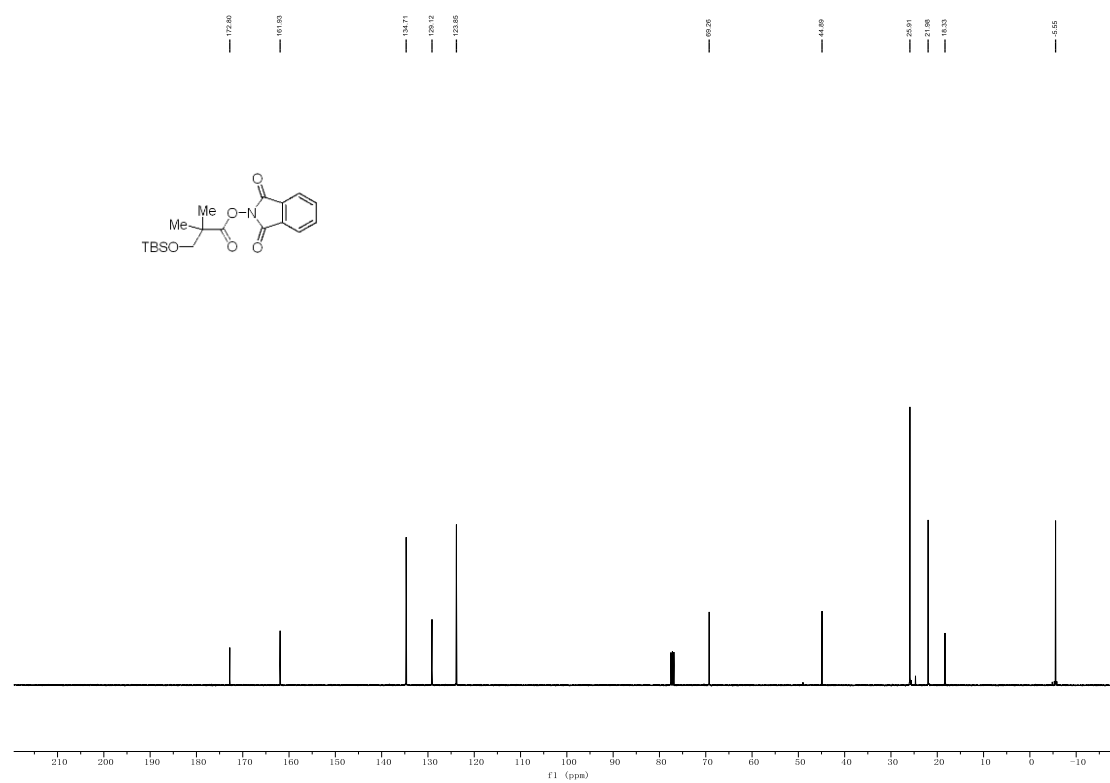
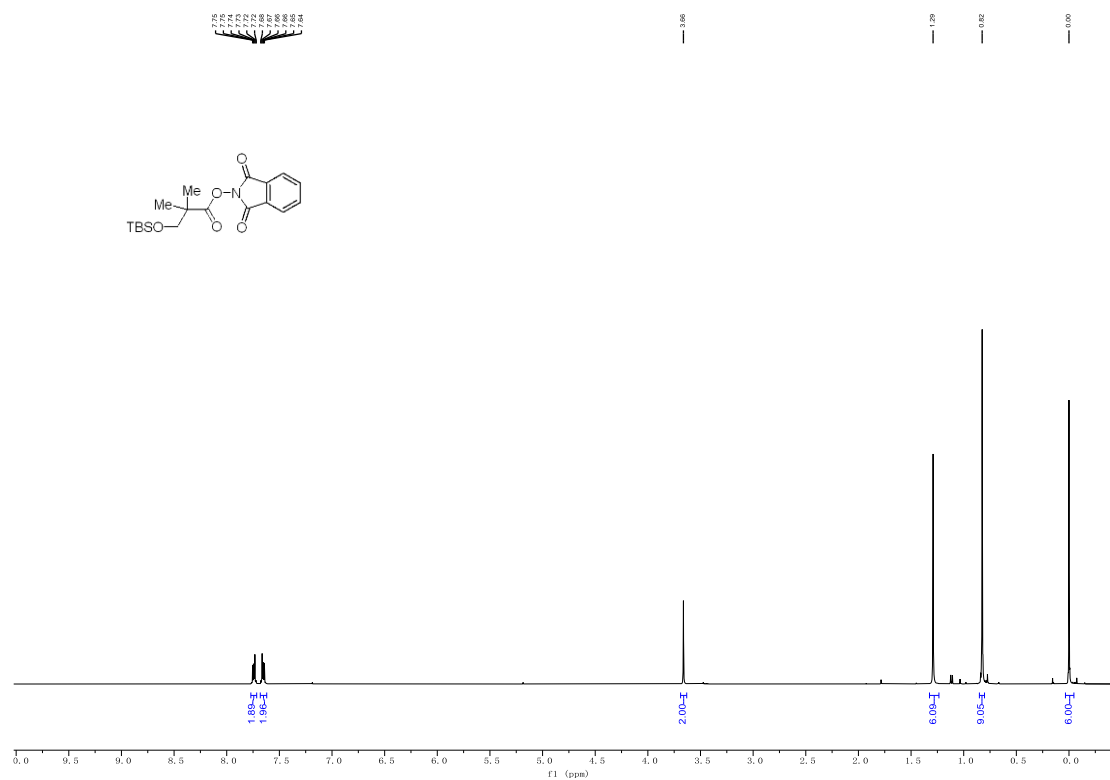
¹H NMR and ¹³C NMR spectra of S9



¹H NMR and ¹³C NMR spectra of S10



¹H NMR and ¹³C NMR spectra of S11

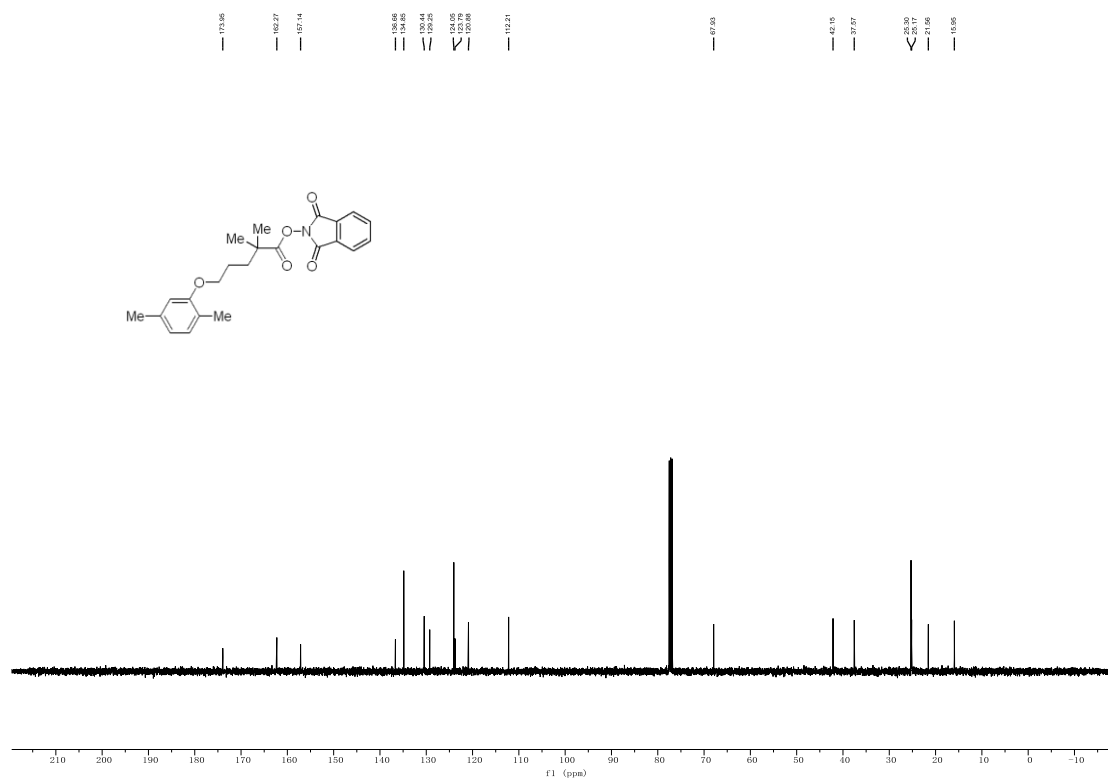


Chemical structure of the compound is shown above the spectrum. The spectrum displays peaks corresponding to the structure, with integration values provided below the baseline.

Integration values (from left to right):

- 1.99
- 2.05
- 2.11
- 2.09
- 3.11
- 18.00
- 6.00
- 5.86

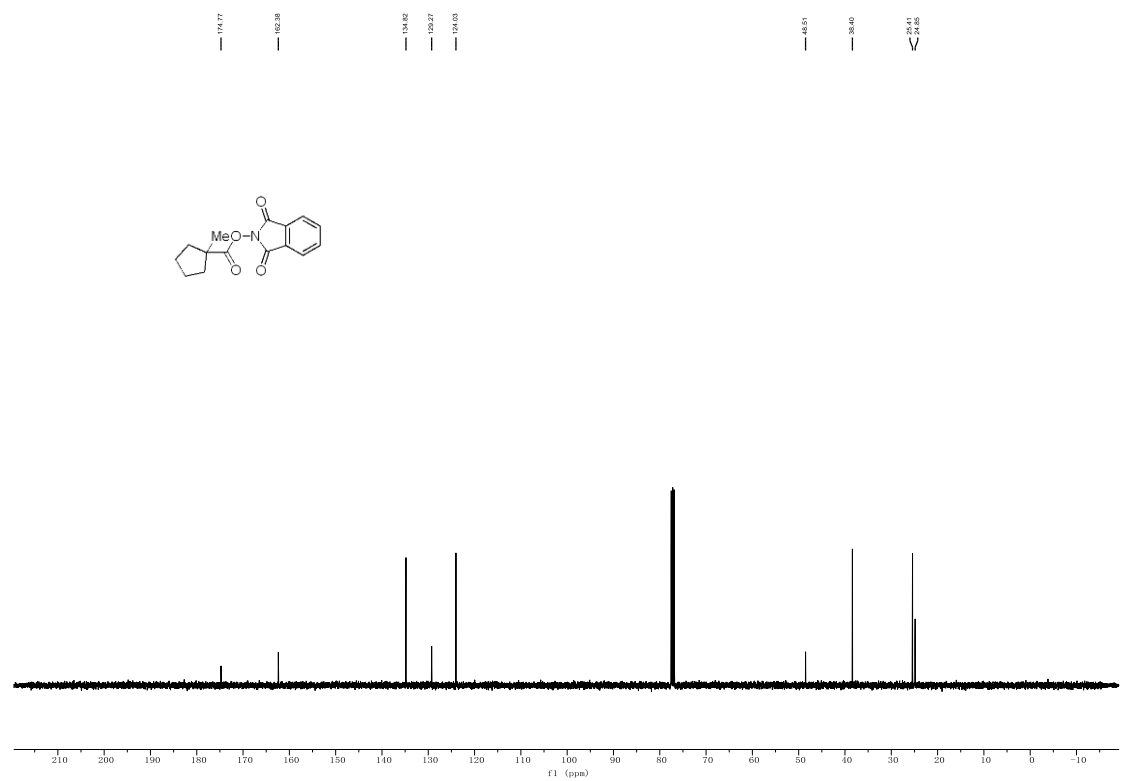
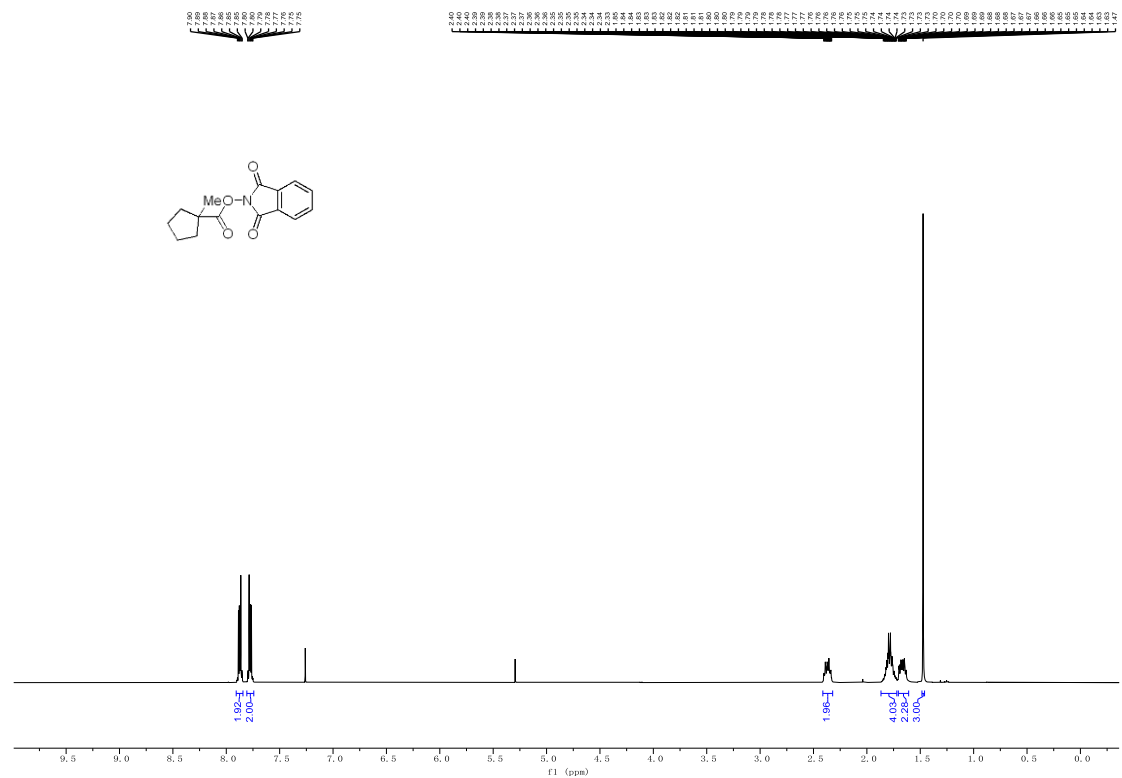


[illegible]

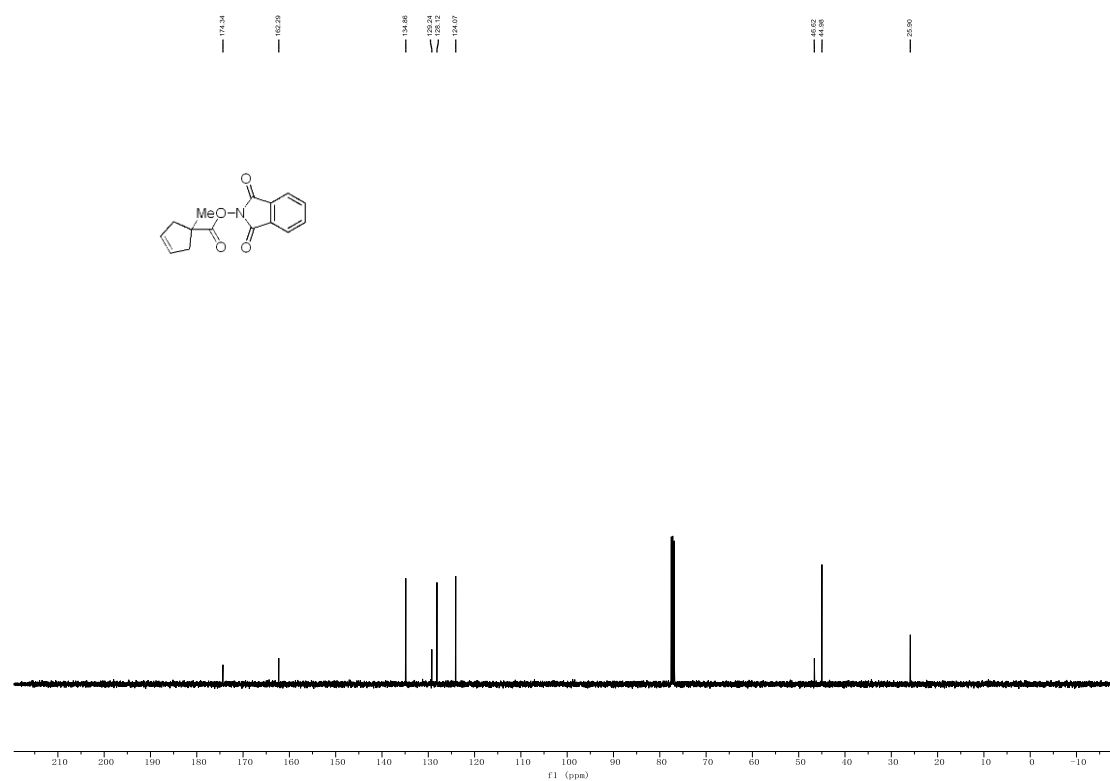
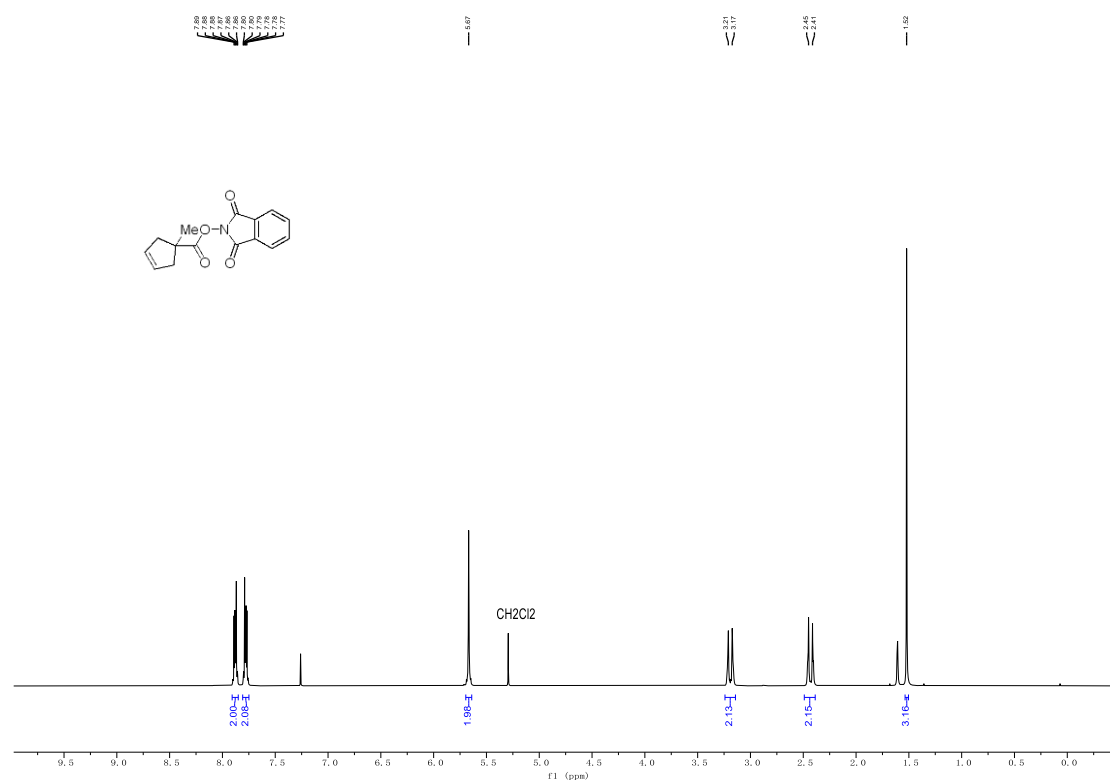
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¹H NMR and ¹³C NMR spectra of S15



¹H NMR and ¹³C NMR spectra of S16



COC(=O)C1(CCCC(CC1)C2=CC=CC=C2)C3=CC(=O)N(C3=O)C4=CC=CC=C4

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (7.2-7.8 ppm), a methoxy singlet (3.8 ppm), and aliphatic signals (1.4-2.5 ppm). Integration values are provided for several peaks.

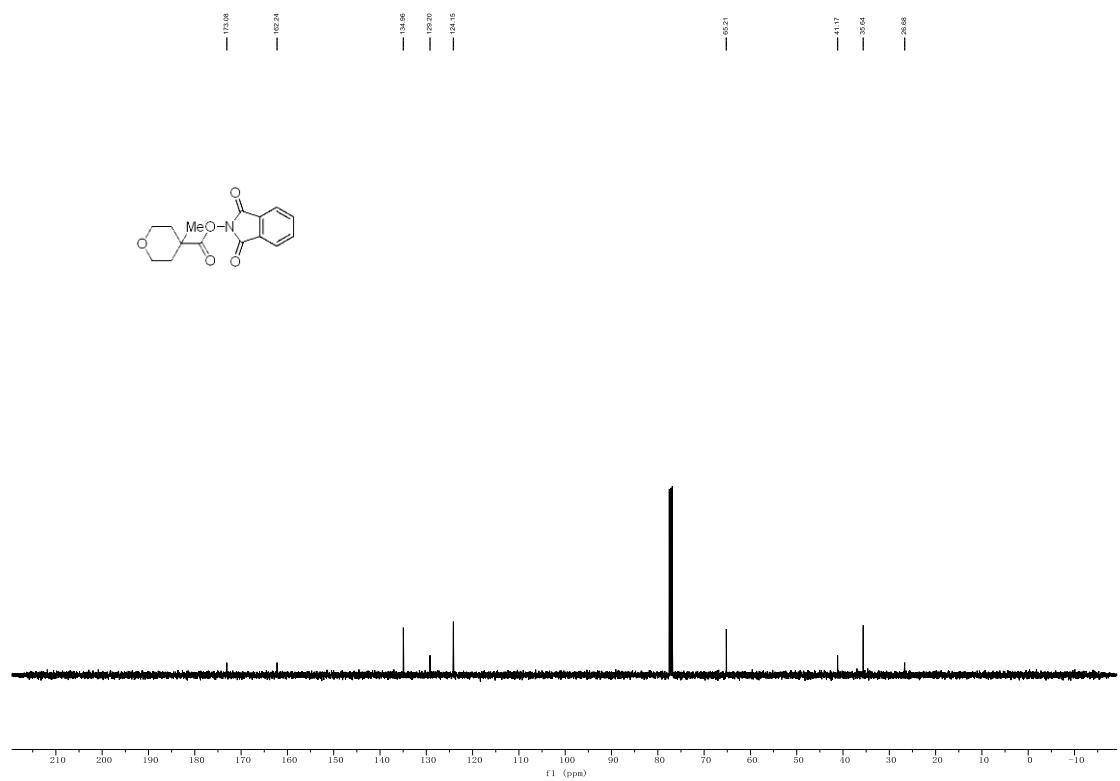


COC(=O)N1C(=O)c2ccccc2C1=O (isoindolin-1-one derivative) + FC1(F)CCCCC1C(=O)N2C(=O)c3ccccc3C2=O (2,2-difluorocyclohexyl derivative)

Chemical structure of the compound: 1-(2,2-difluorocyclohexyl)-3-methoxyisoindolin-1-one.

^1H NMR spectrum (CDCl₃) showing peaks at approximately 7.8-8.0 ppm (aromatic, integration 1.85, 1.95), 5.26 ppm (solvent, CH₂Cl₂), and 1.5-2.6 ppm (aliphatic, integration 2.08, 4.10, 2.15, 3.00).



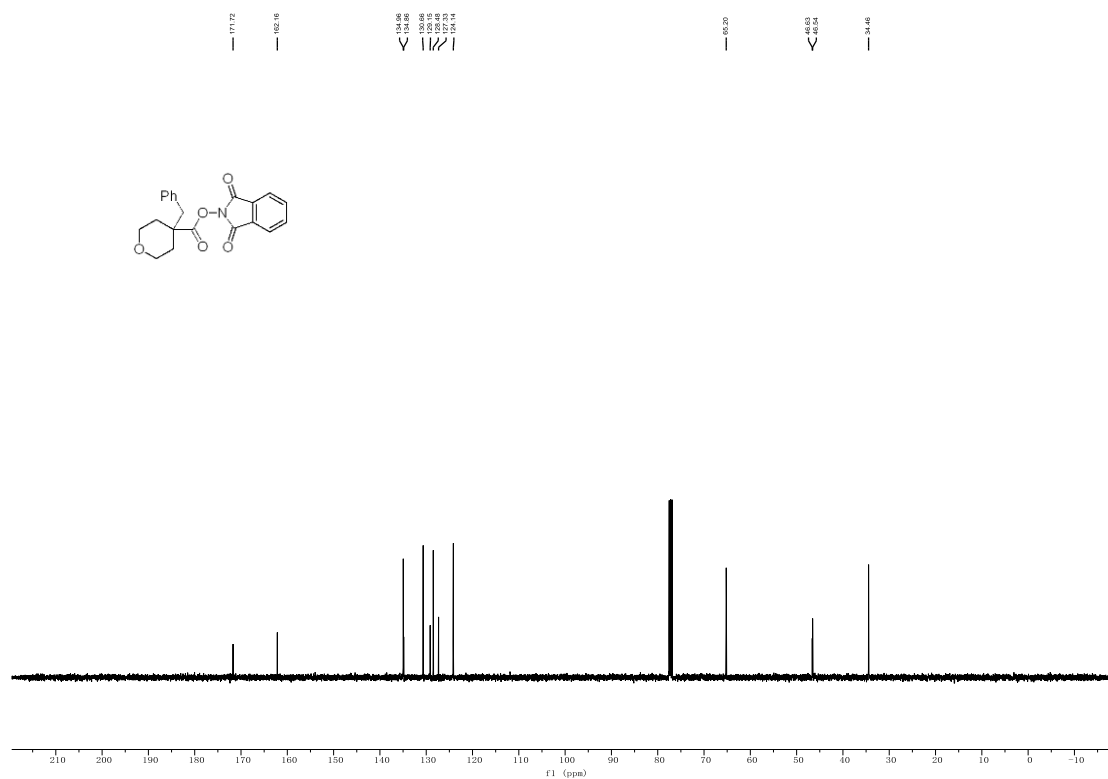


Chemical structure of the compound is shown above the spectrum. The structure is a 1,3-dioxane-2-carboxylic acid derivative, specifically 1,3-dioxane-2-carboxylic acid, which is a six-membered ring containing two oxygen atoms and a carboxylic acid group. The structure is labeled with 'Ph' and 'O'.

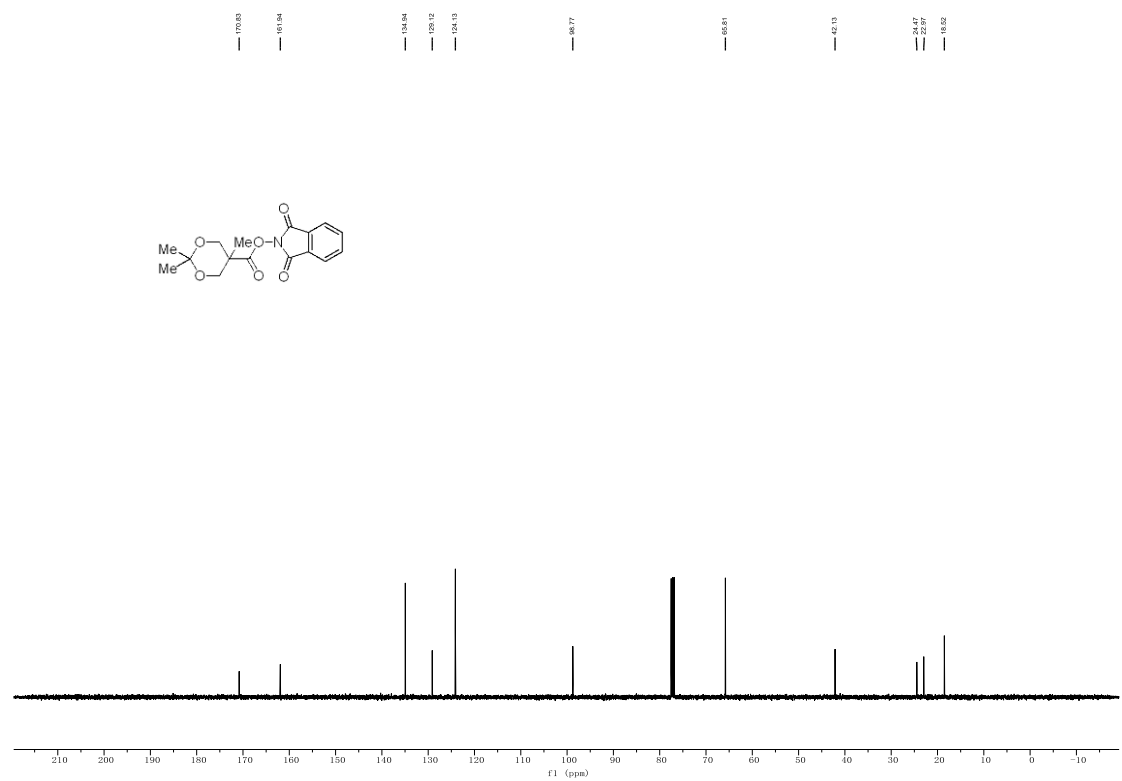
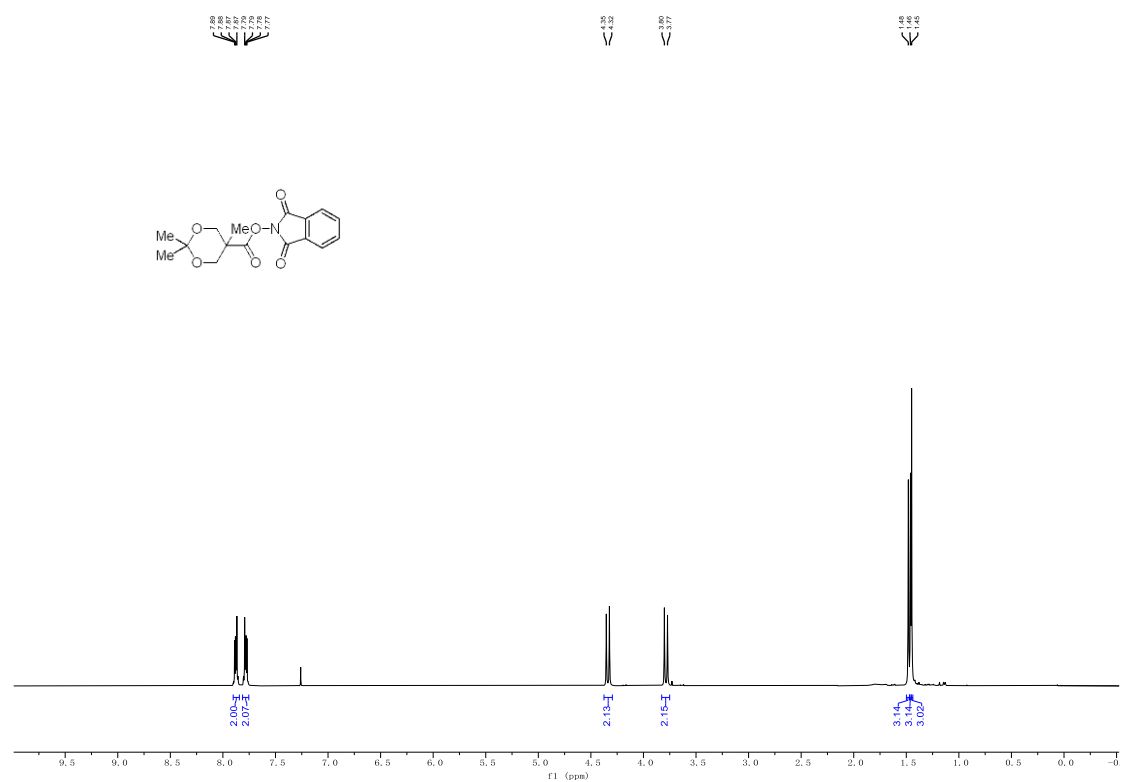
The ¹H NMR spectrum (400 MHz, CDCl₃) shows the following peaks (ppm) and integrations:

- 7.25-7.35 (m, 5H, integration 1.93)
- 7.15-7.25 (m, 5H, integration 2.02)
- 7.05-7.15 (m, 5H, integration 1.95)
- 6.95-7.05 (m, 5H, integration 1.98)
- 3.95-4.05 (m, 2H, integration 2.02)
- 3.75-3.85 (m, 2H, integration 2.01)
- 3.00 (s, 3H, integration 2.00)
- 2.00 (s, 3H, integration 2.01)
- 1.50 (s, 3H, integration 2.09)

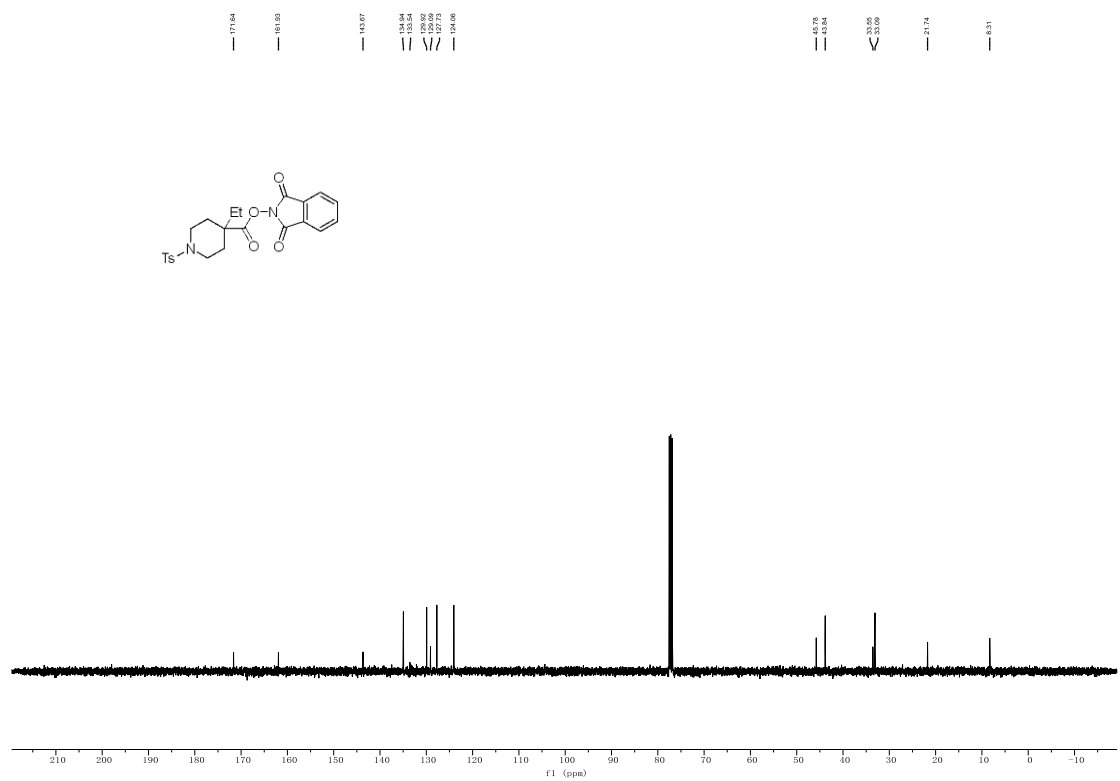
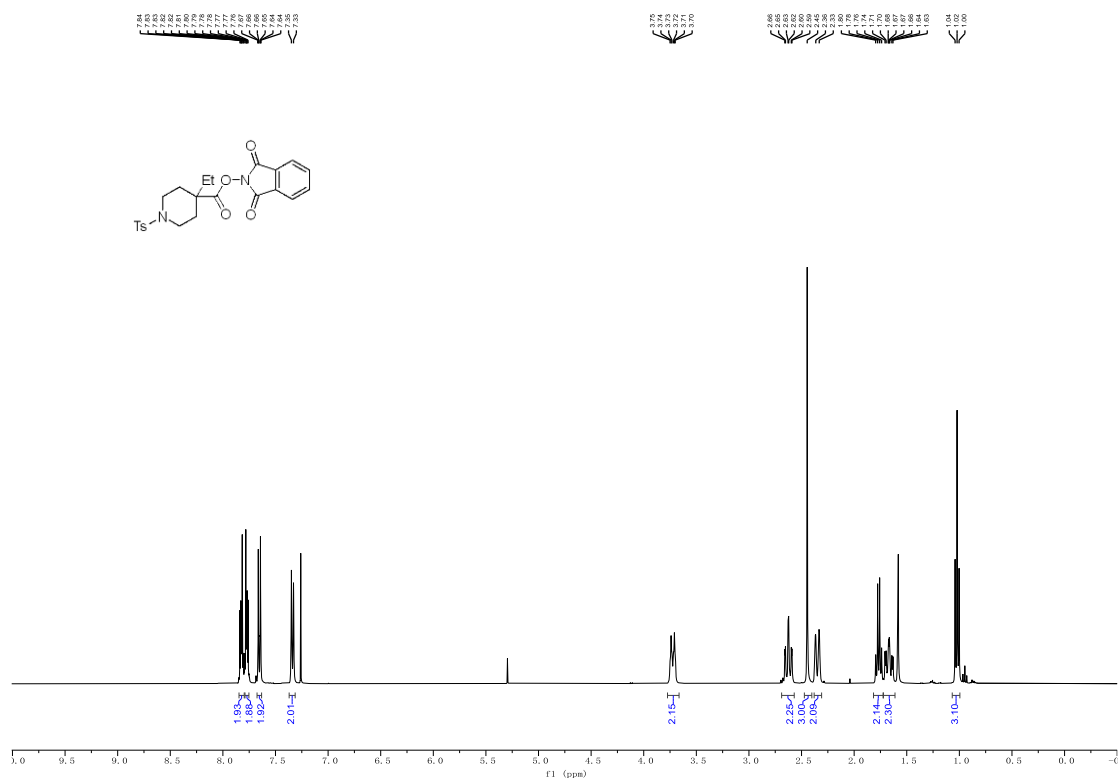
The spectrum is labeled 'F1 (ppm)' on the x-axis, ranging from 0.0 to 10.0 ppm.



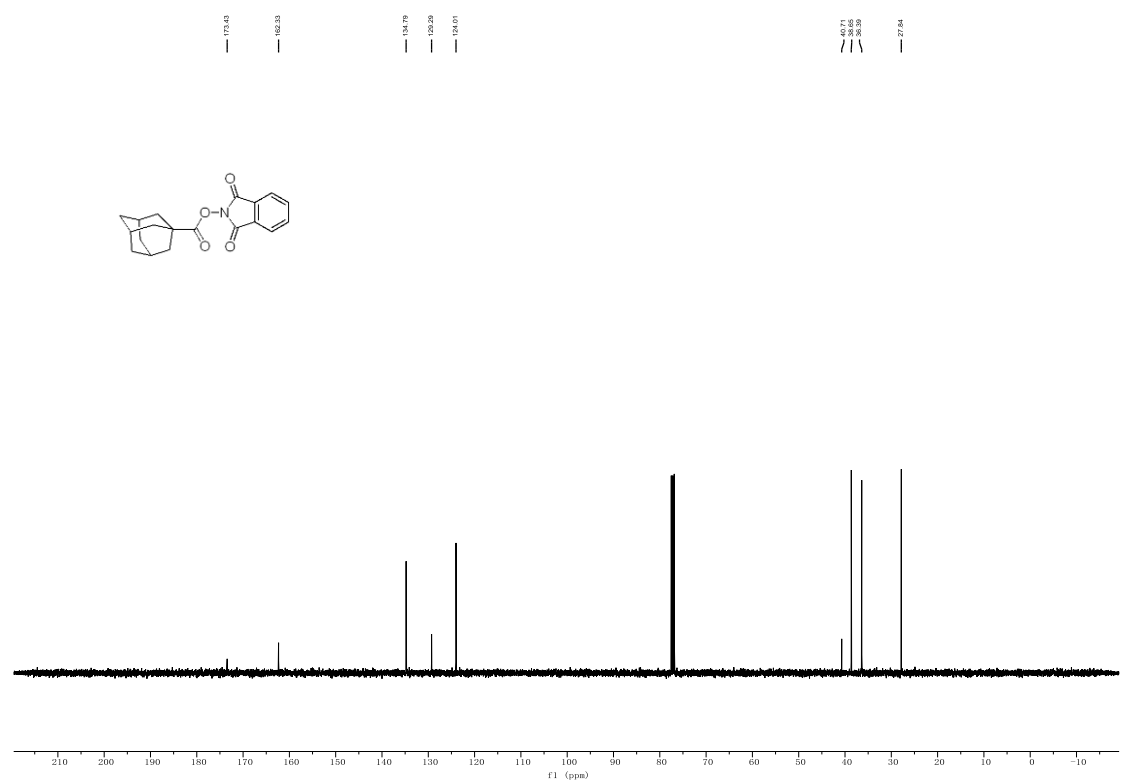
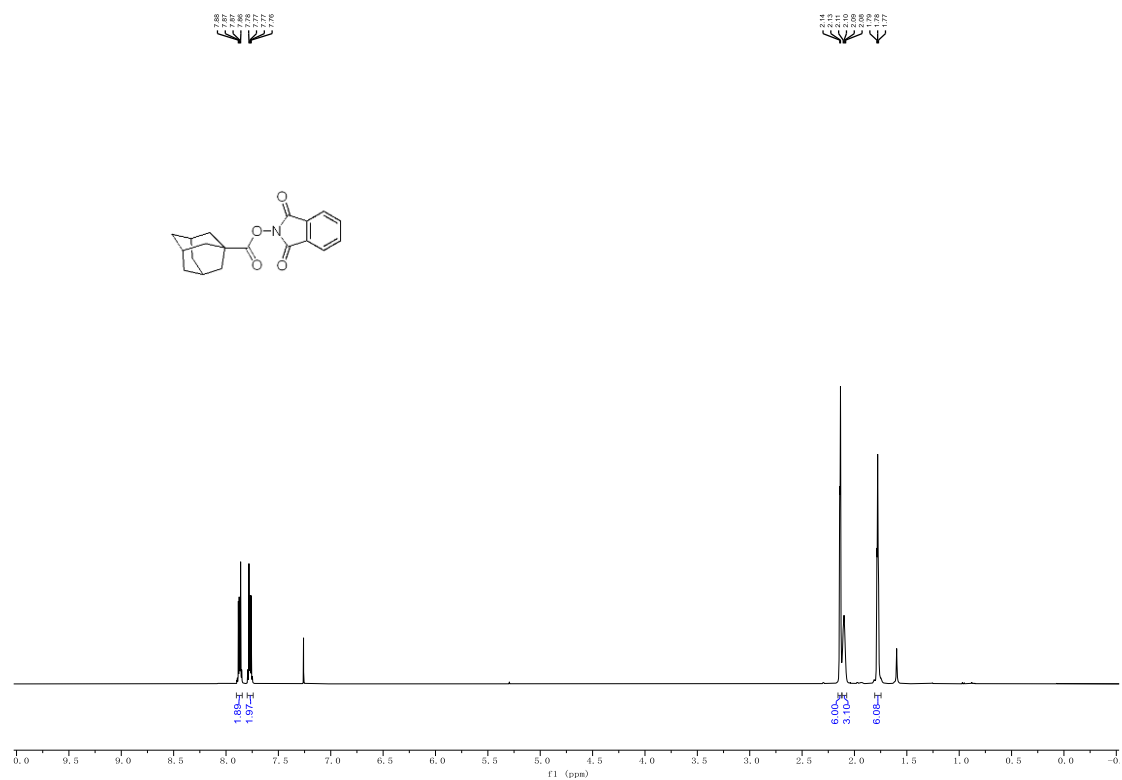
¹H NMR and ¹³C NMR spectra of S21



¹H NMR and ¹³C NMR spectra of S22



¹H NMR and ¹³C NMR spectra of S23

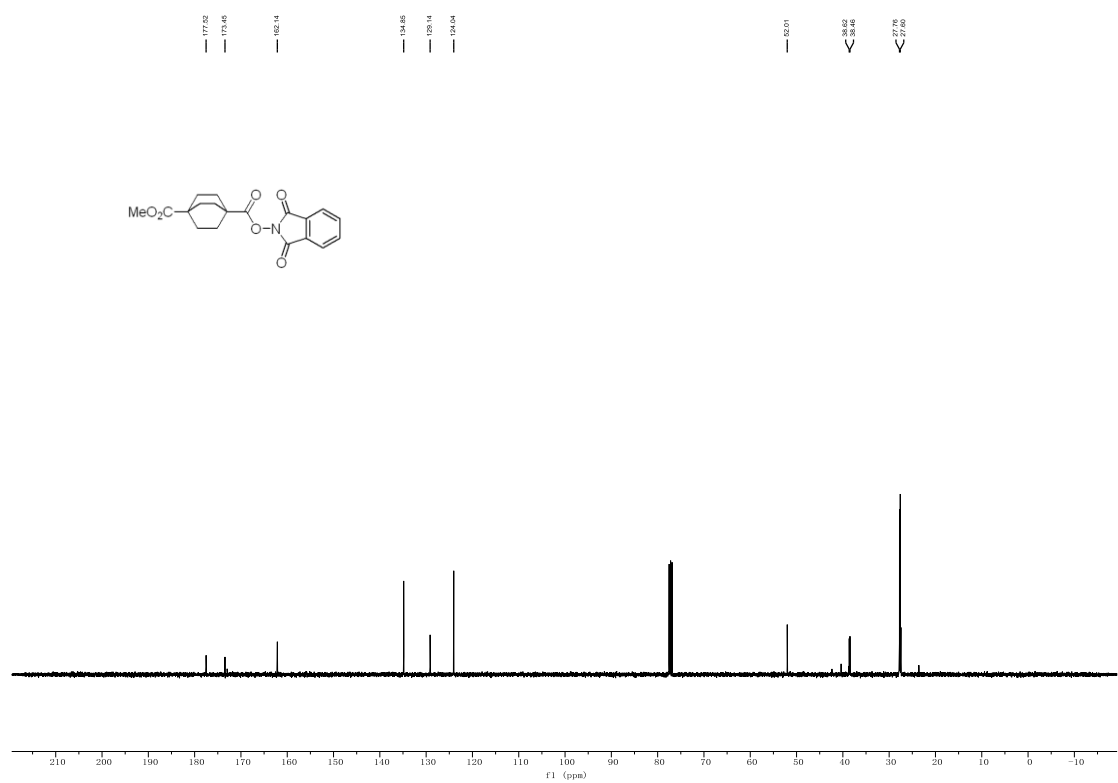


Chemical structure of the compound is shown above the spectrum. The spectrum displays peaks corresponding to the structure, with integration values provided below the baseline.

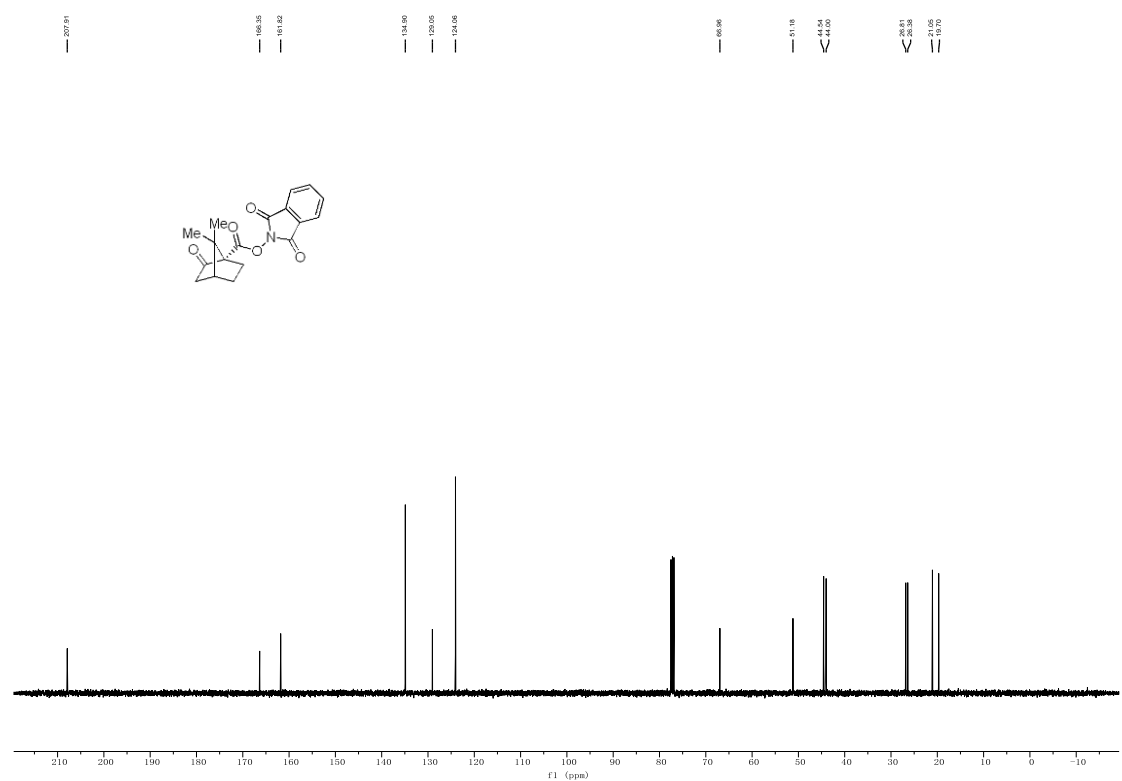
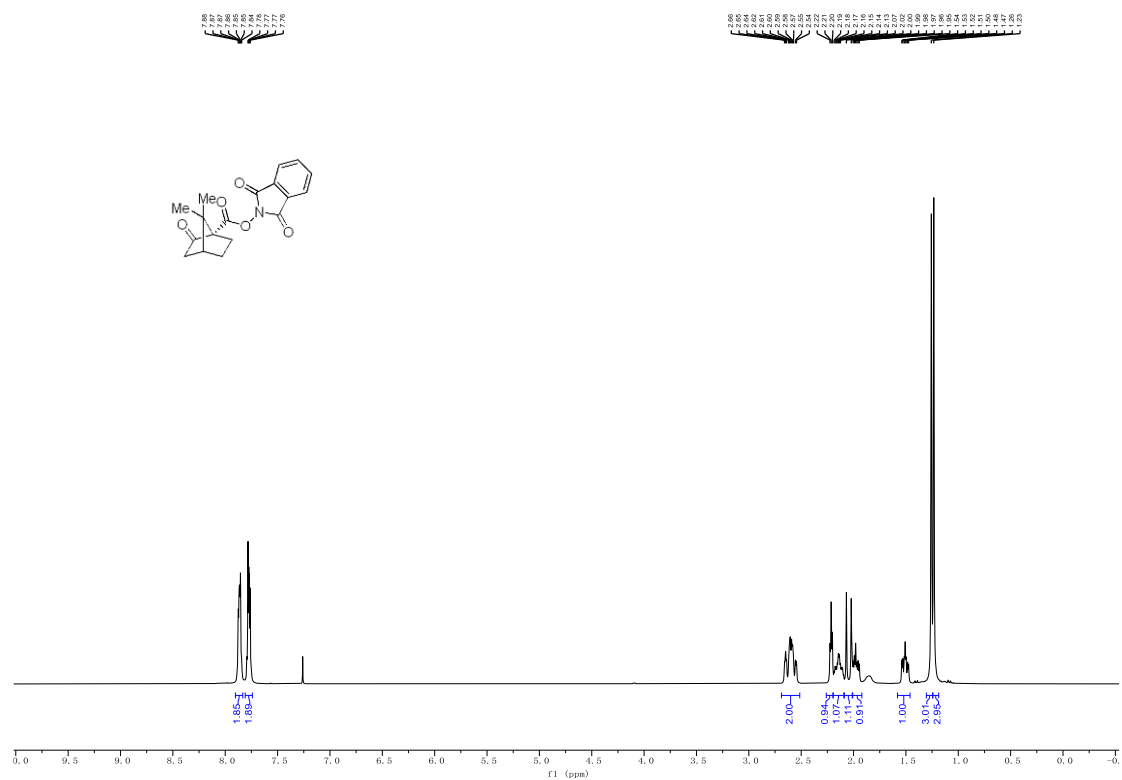
Chemical structure: COC(=O)C1CCC(CC1)C(=O)N2C(=O)c3ccccc3C2=O

Integration values (from left to right): 1.93, 2.00, 2.96, 6.19, 6.39.

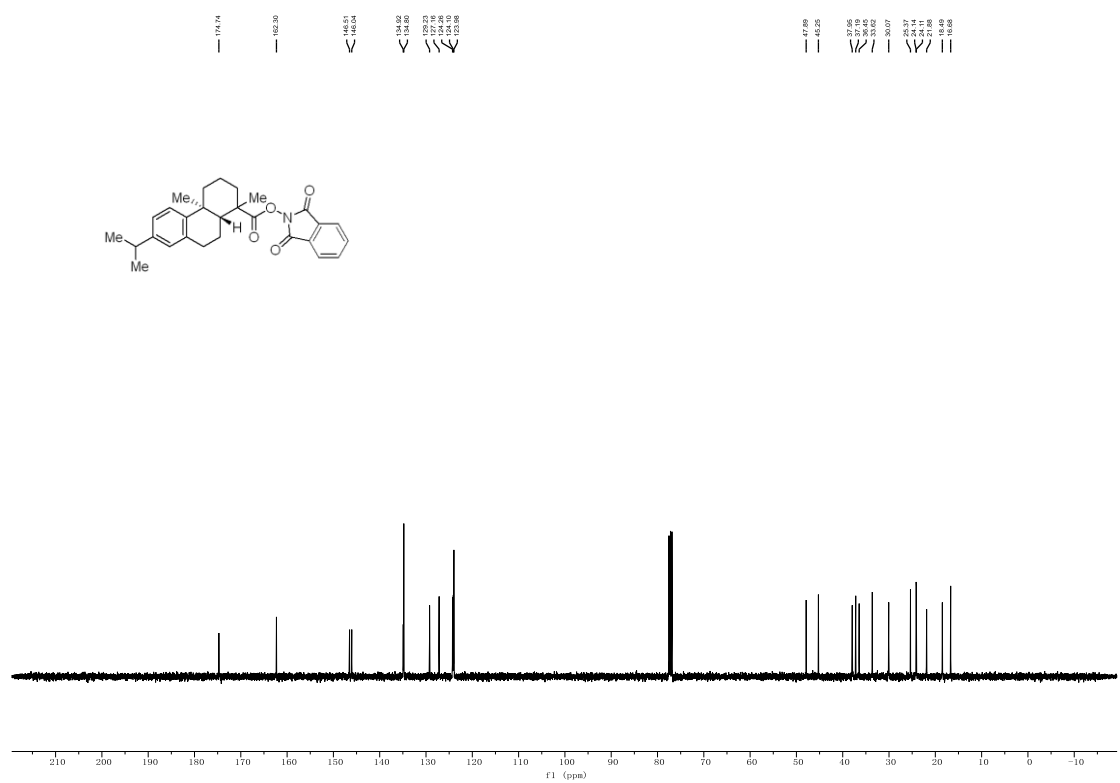
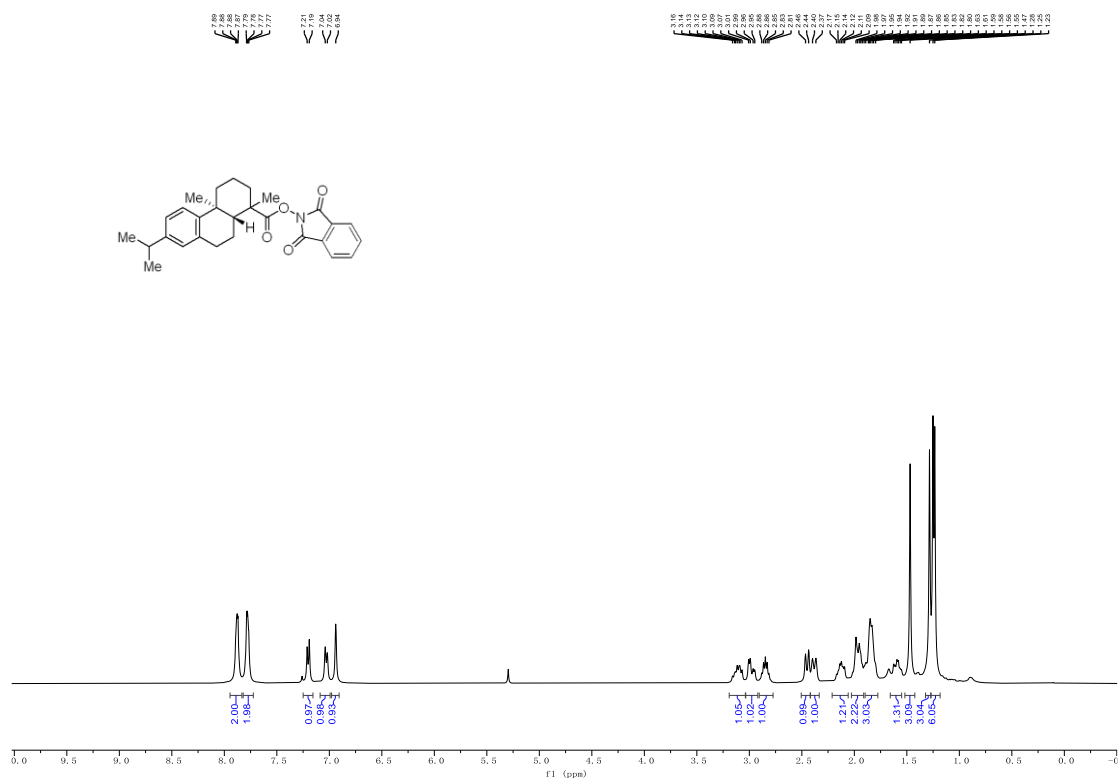
Chemical shift range (ppm): 1.0 to 10.0.



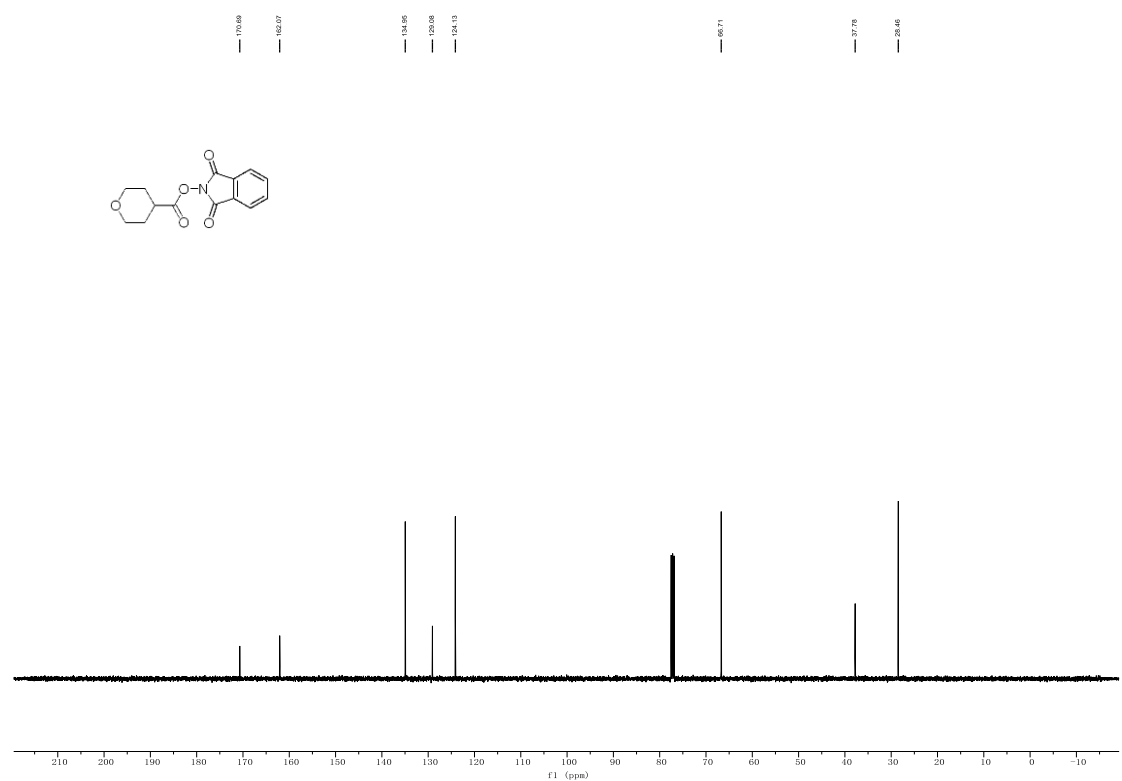
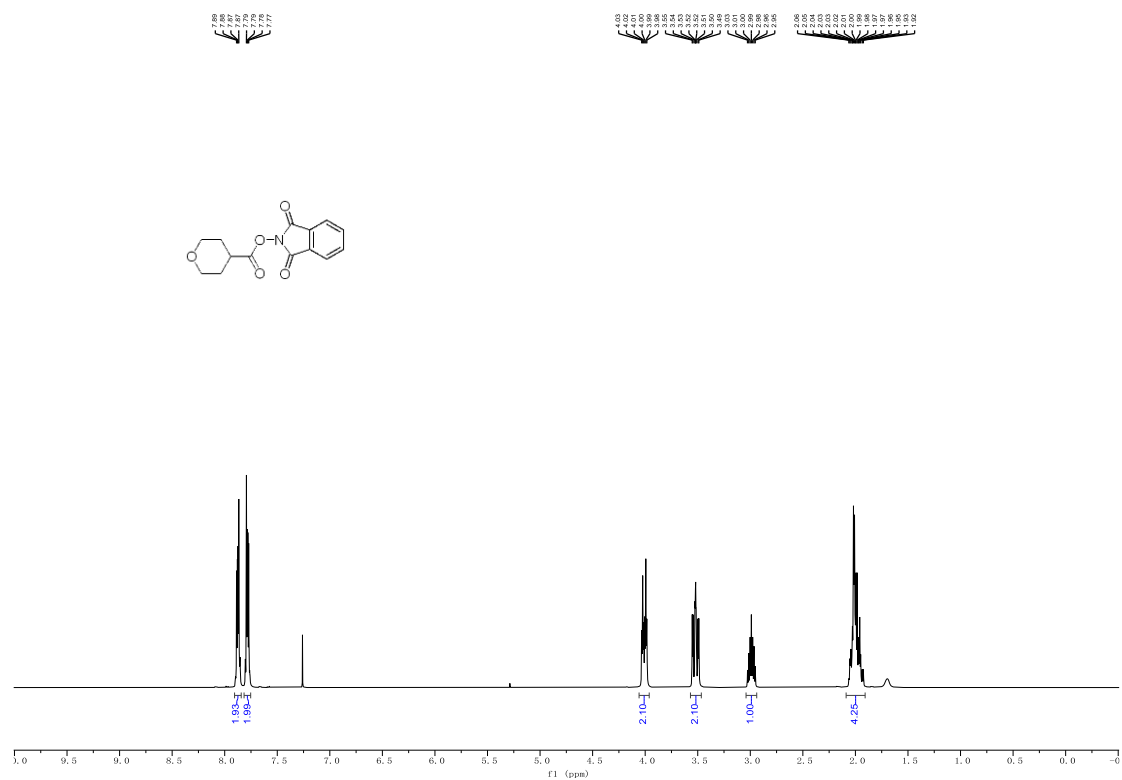
¹H NMR and ¹³C NMR spectra of S25



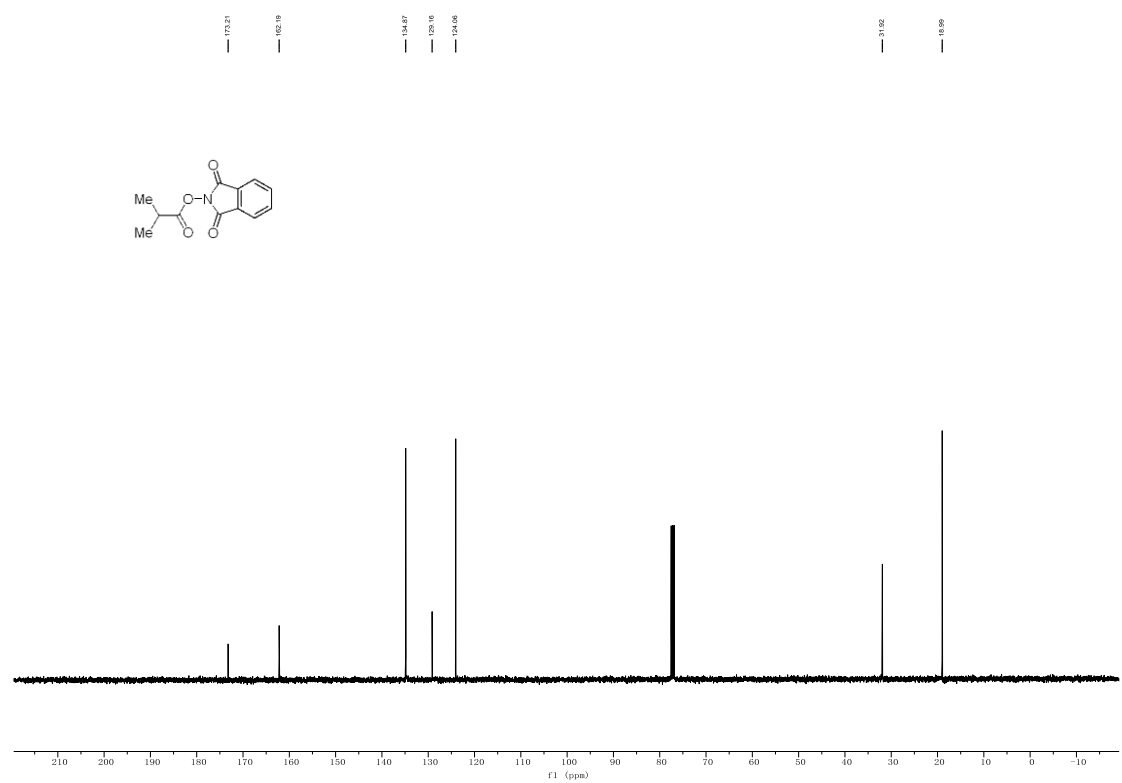
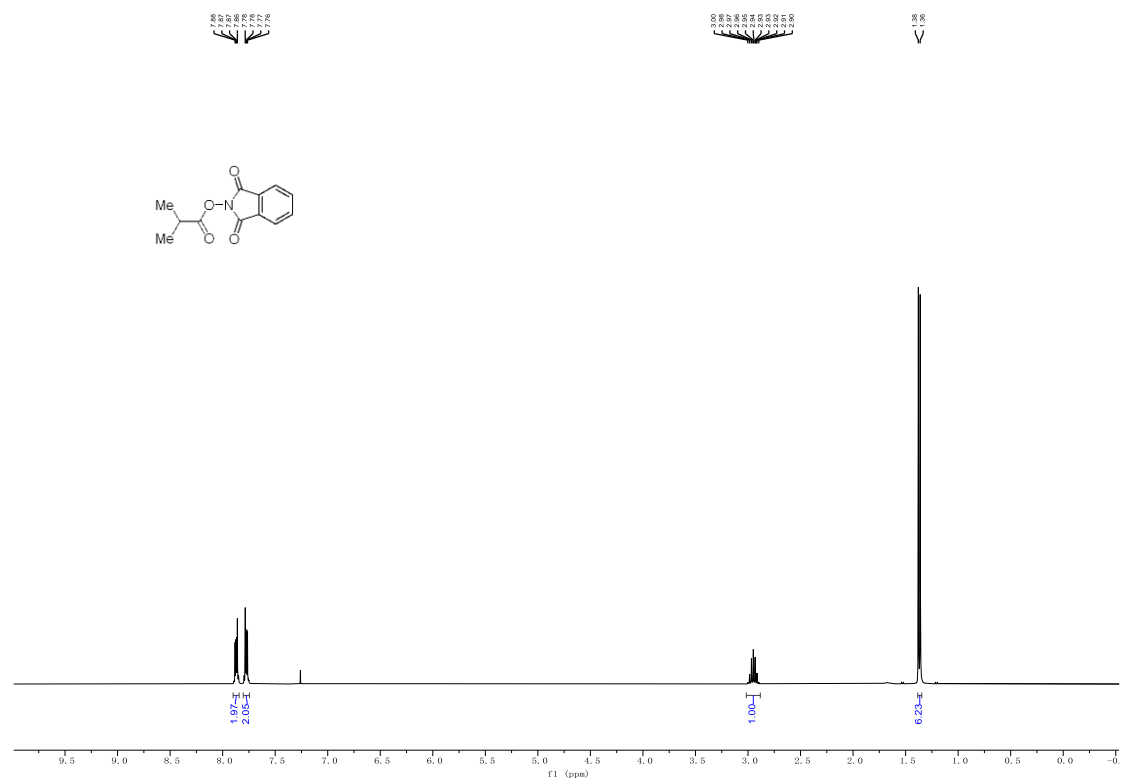
¹H NMR and ¹³C NMR spectra of S26



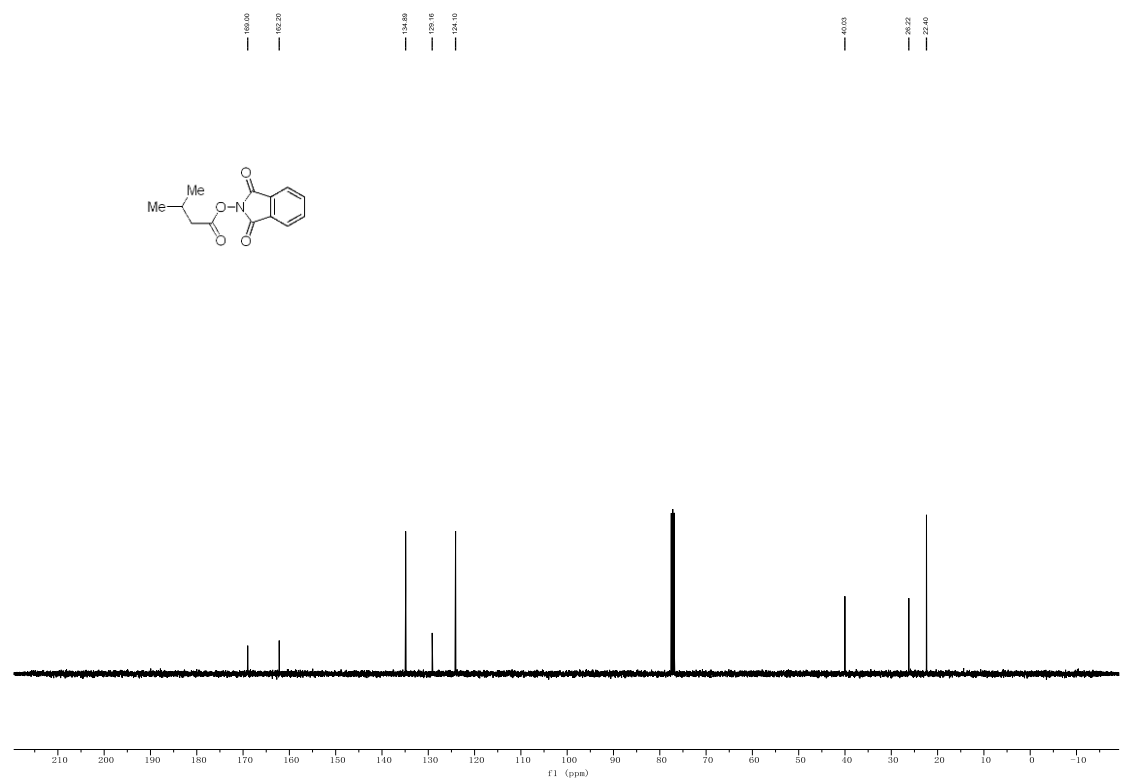
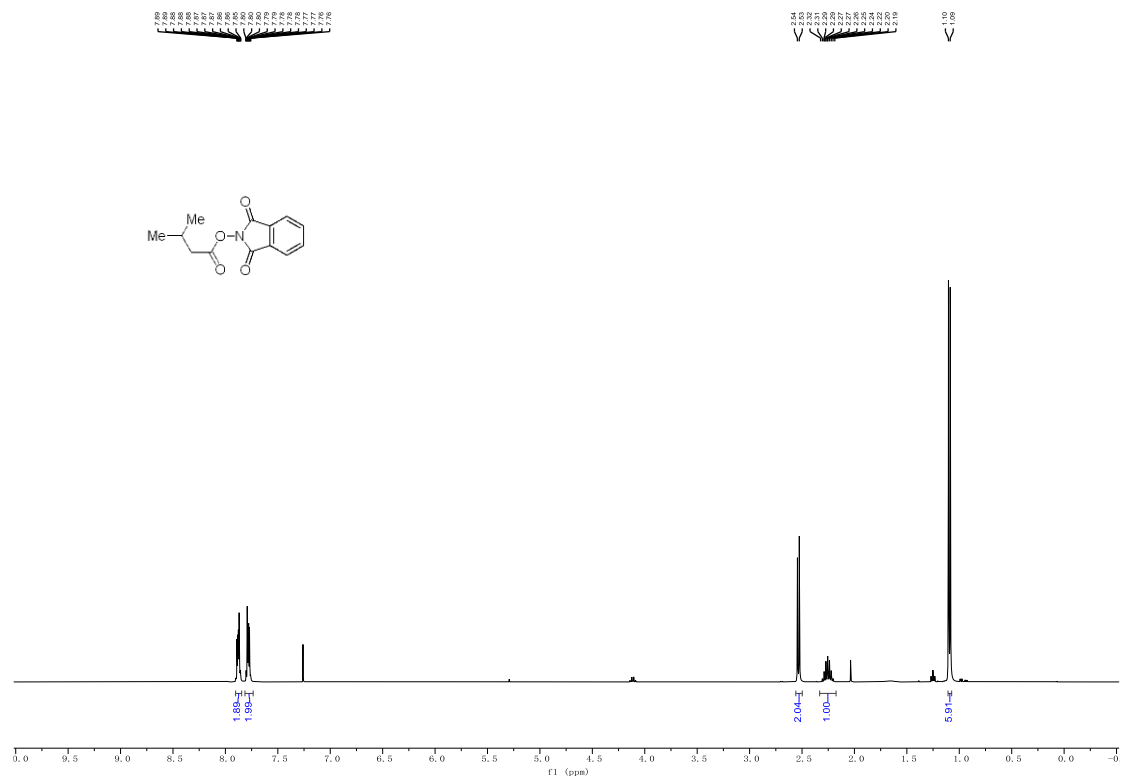
¹H NMR and ¹³C NMR spectra of S27



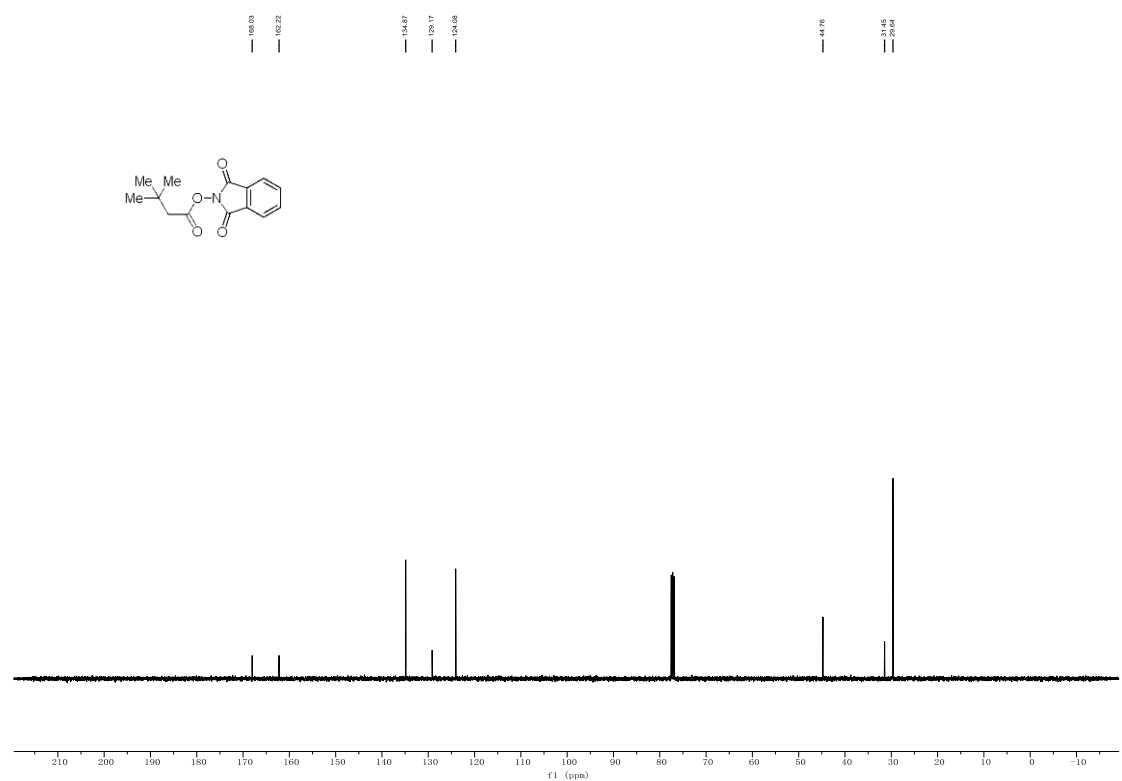
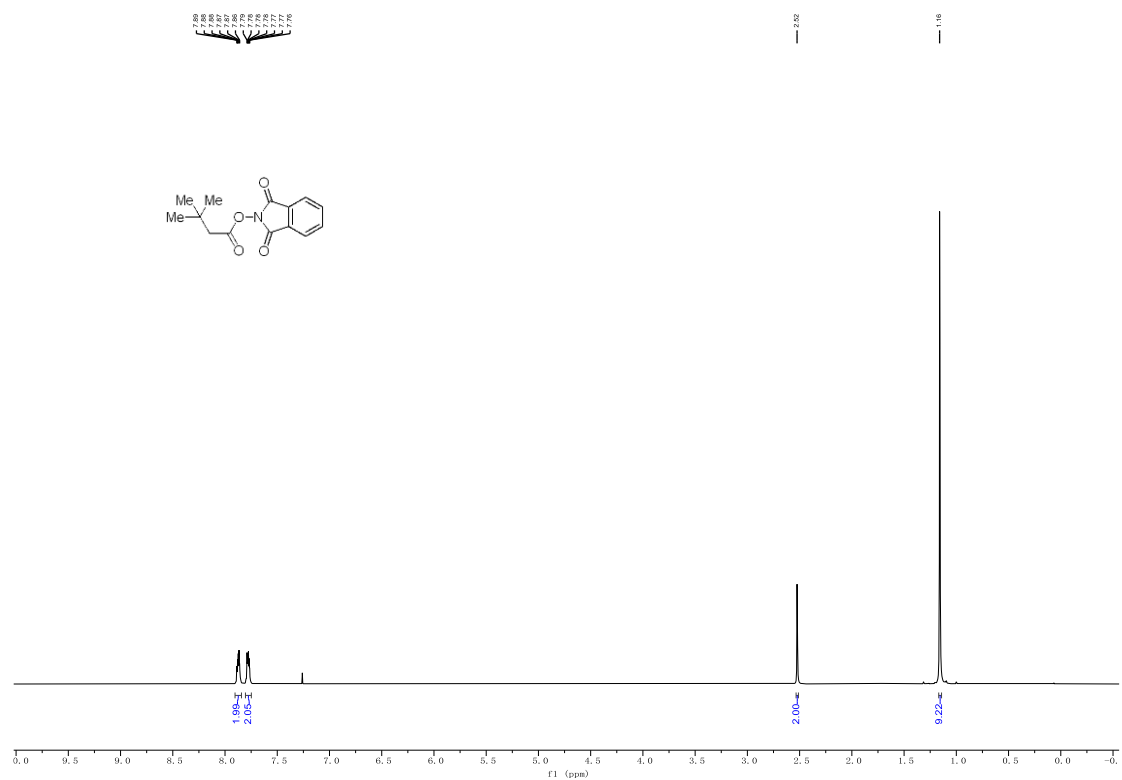
¹H NMR and ¹³C NMR spectra of S28



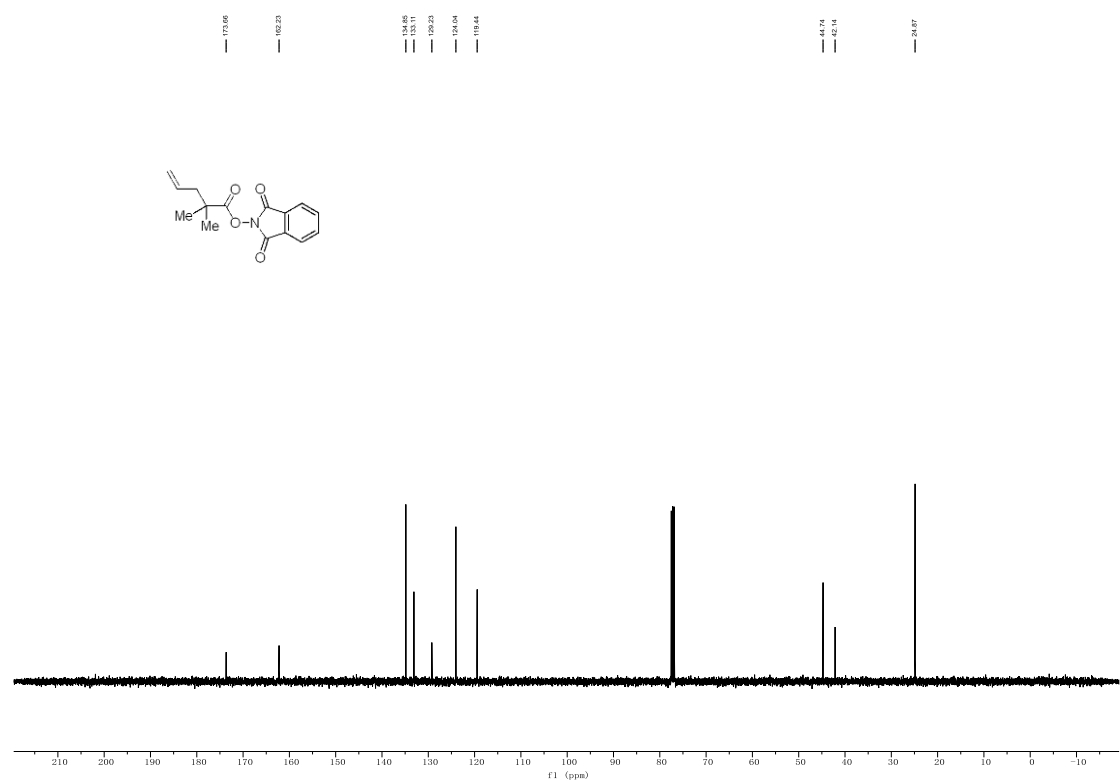
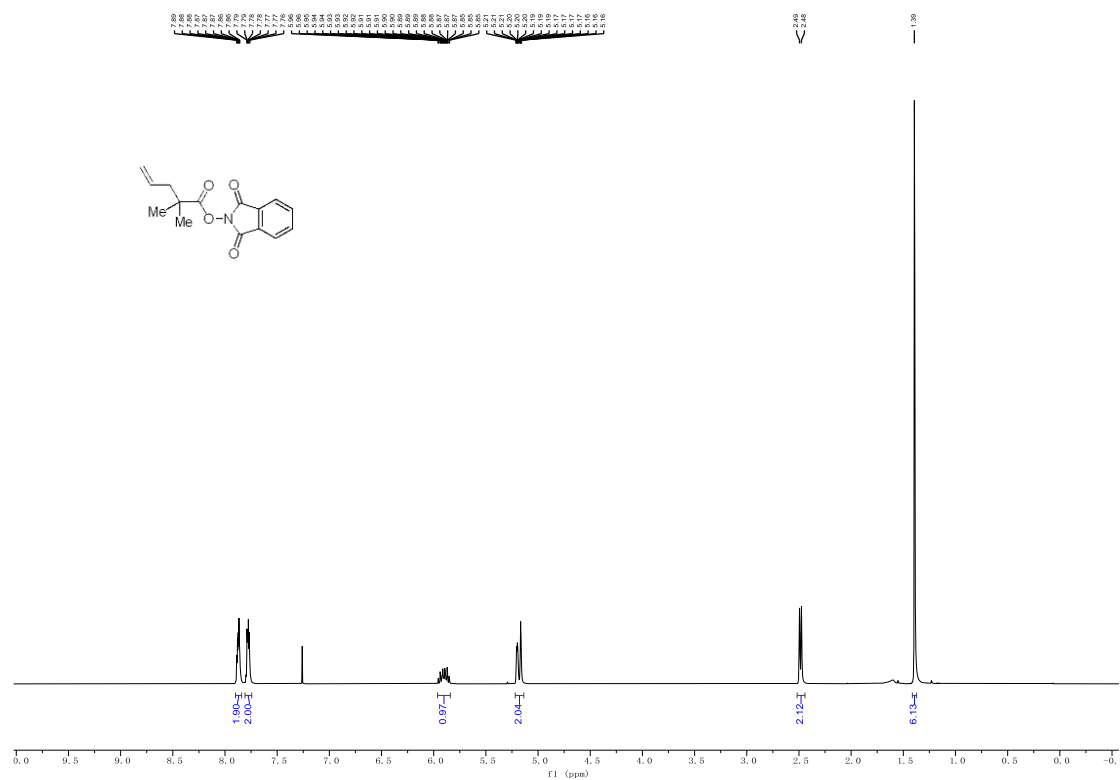
^1H NMR and ^{13}C NMR spectra of S29



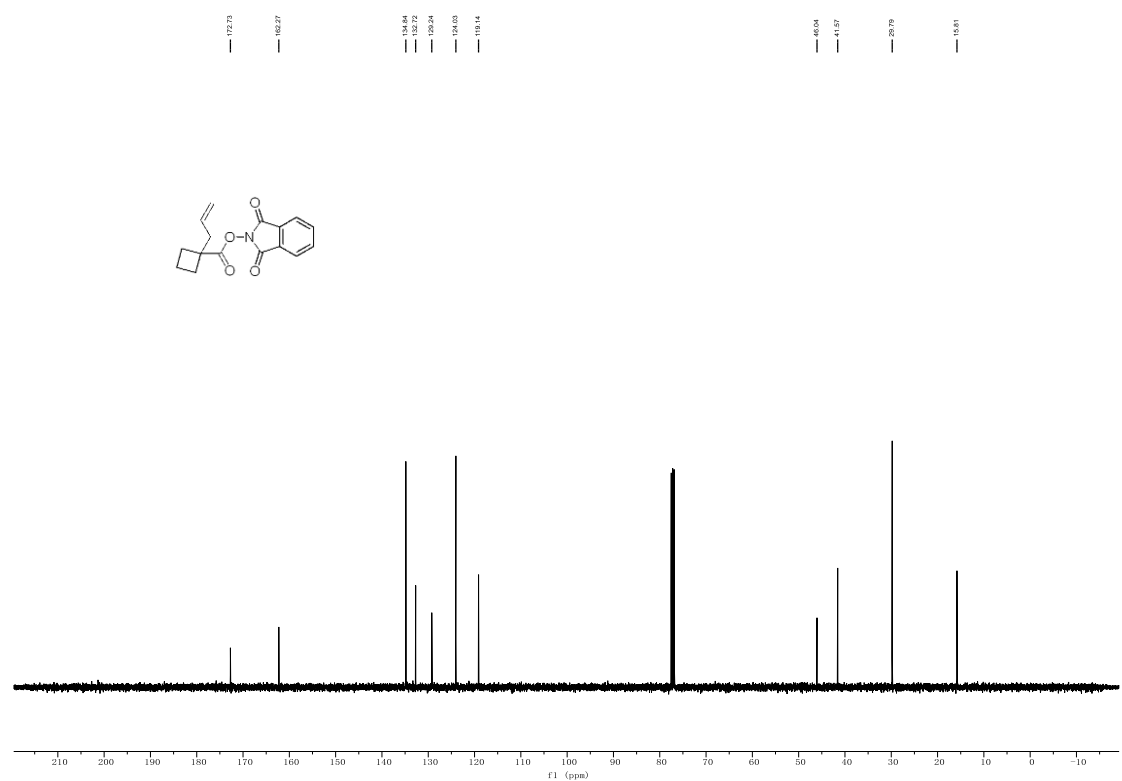
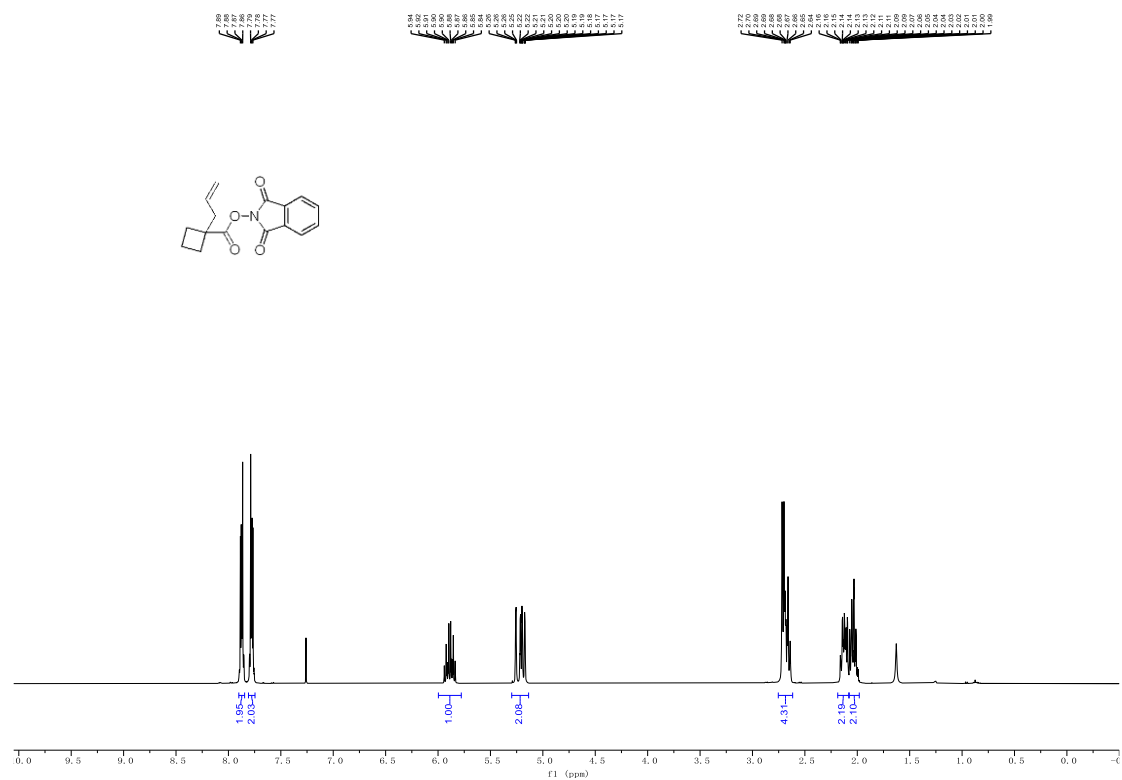
¹H NMR and ¹³C NMR spectra of S30



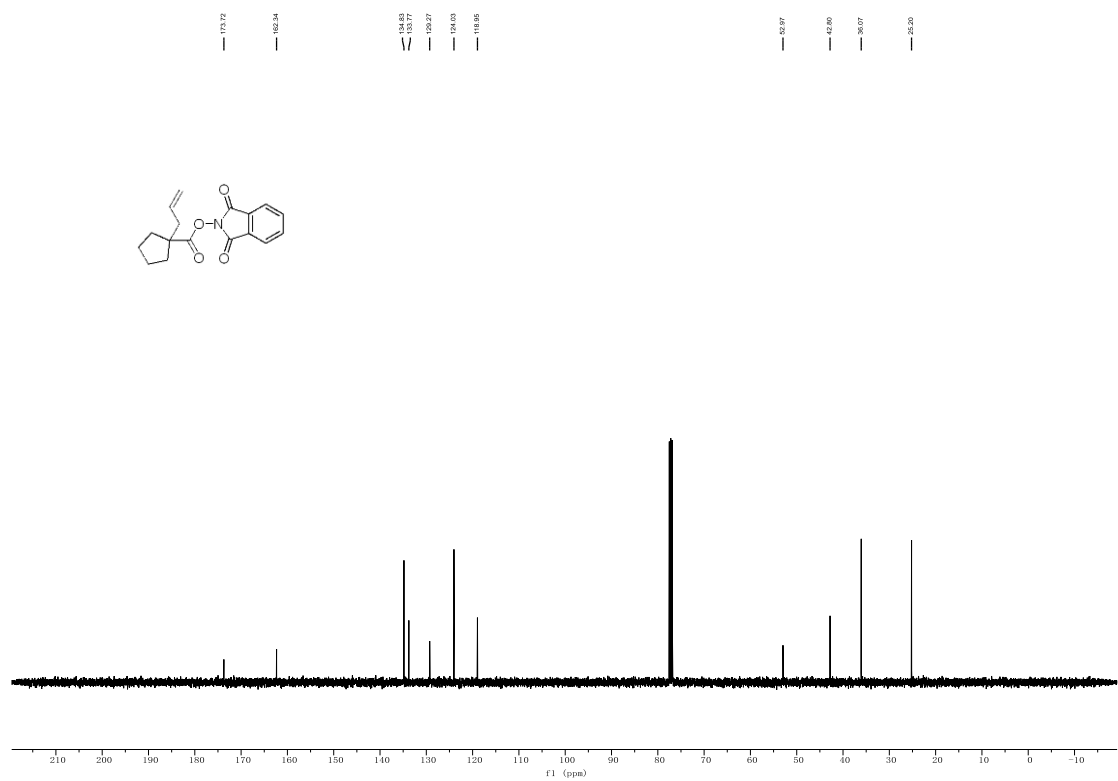
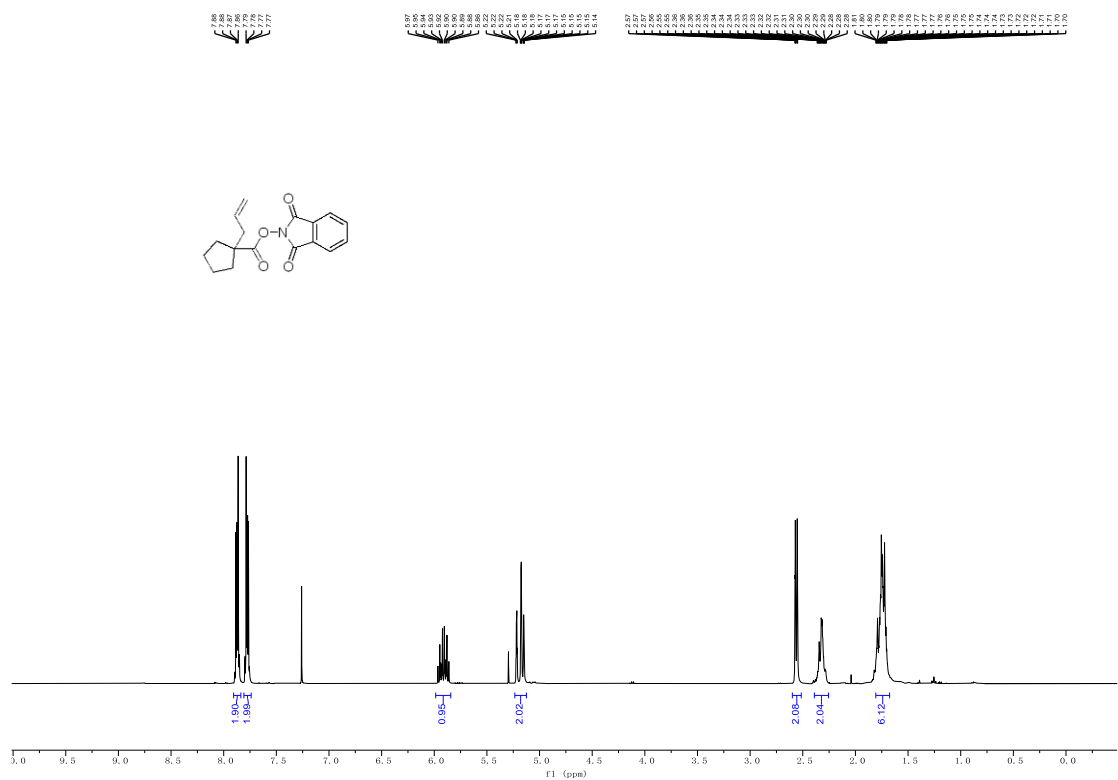
¹H NMR and ¹³C NMR spectra of S31



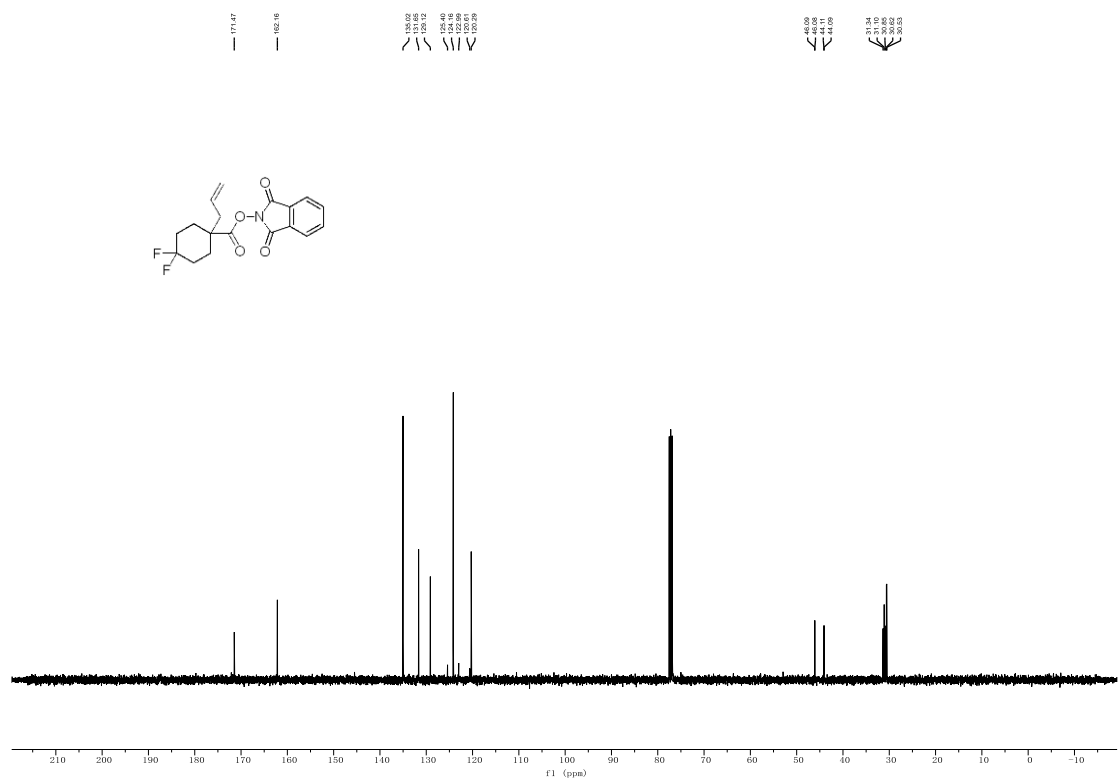
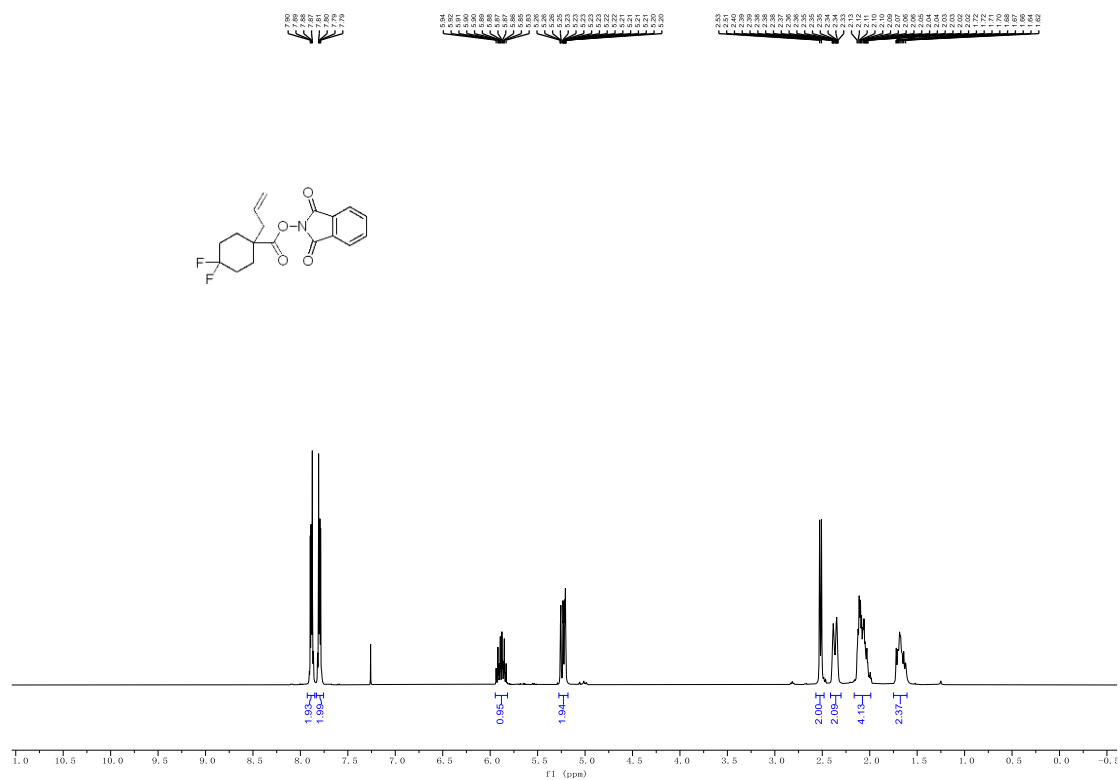
^1H NMR and ^{13}C NMR spectra of S32



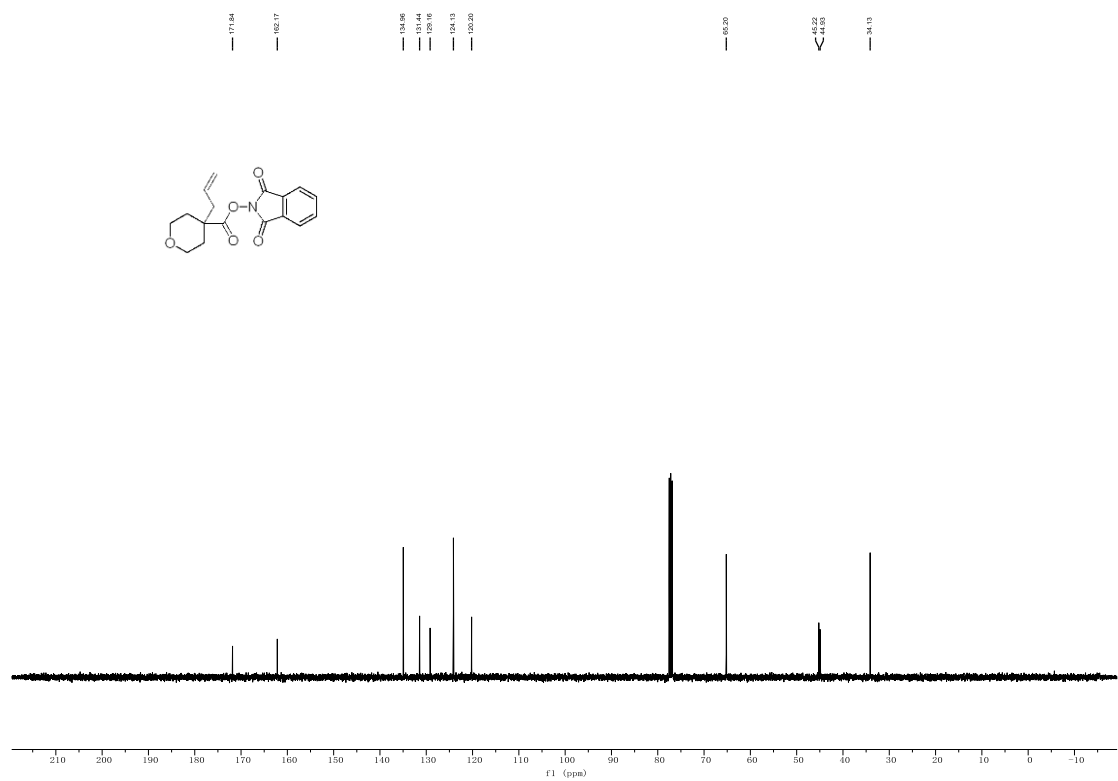
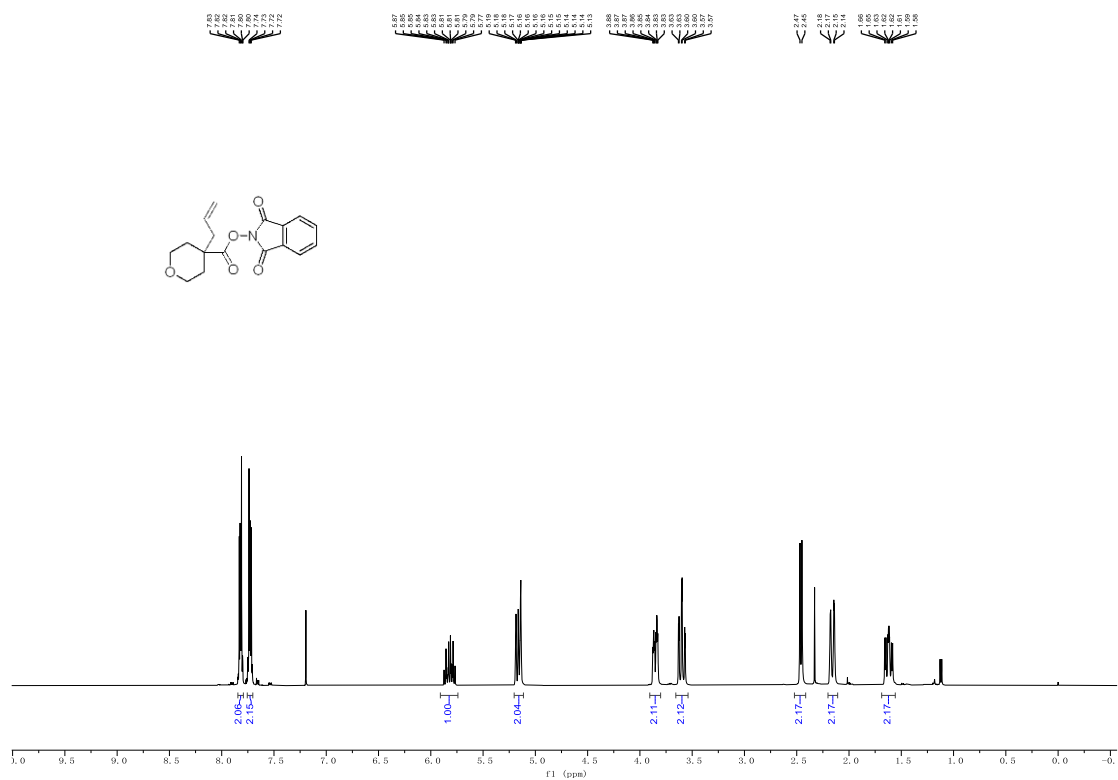
¹H NMR and ¹³C NMR spectra of S33



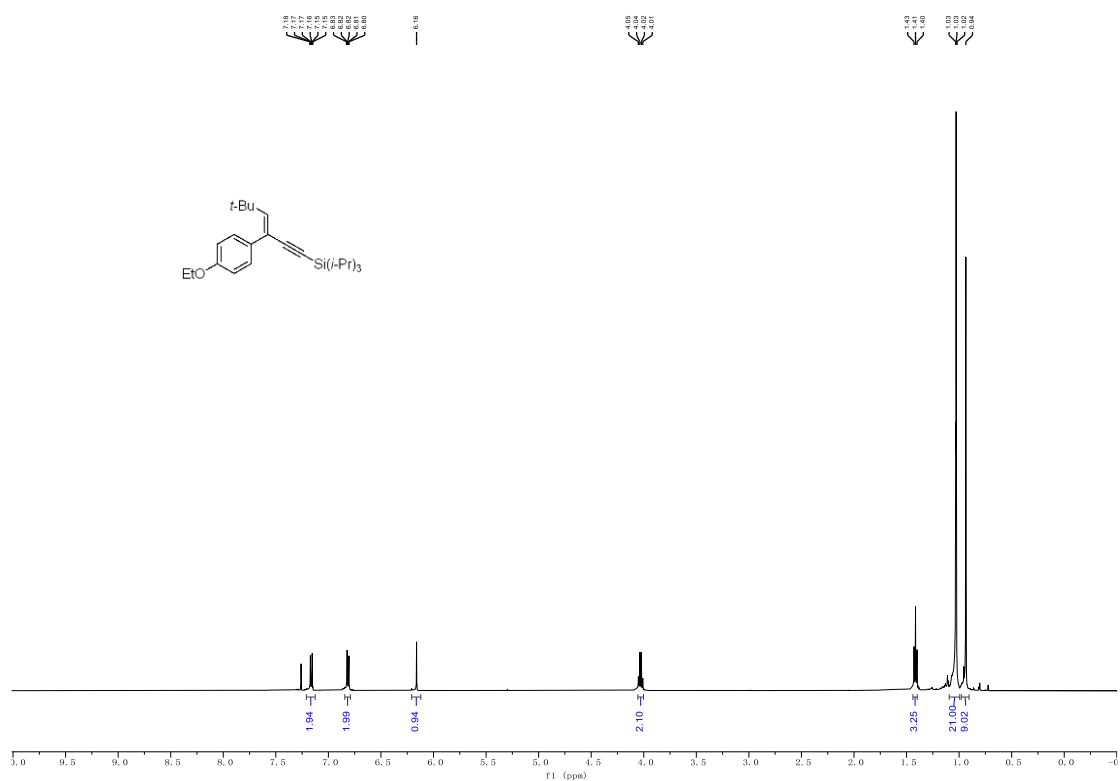
¹H NMR and ¹³C NMR spectra of S34



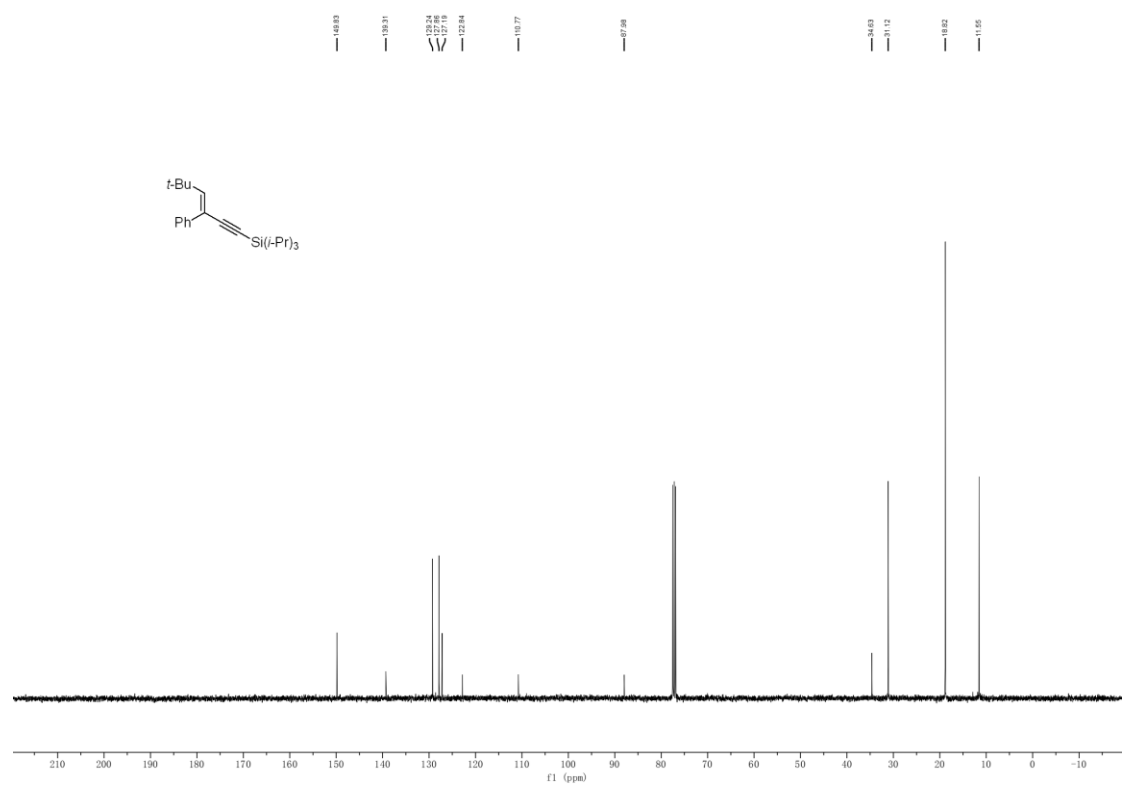
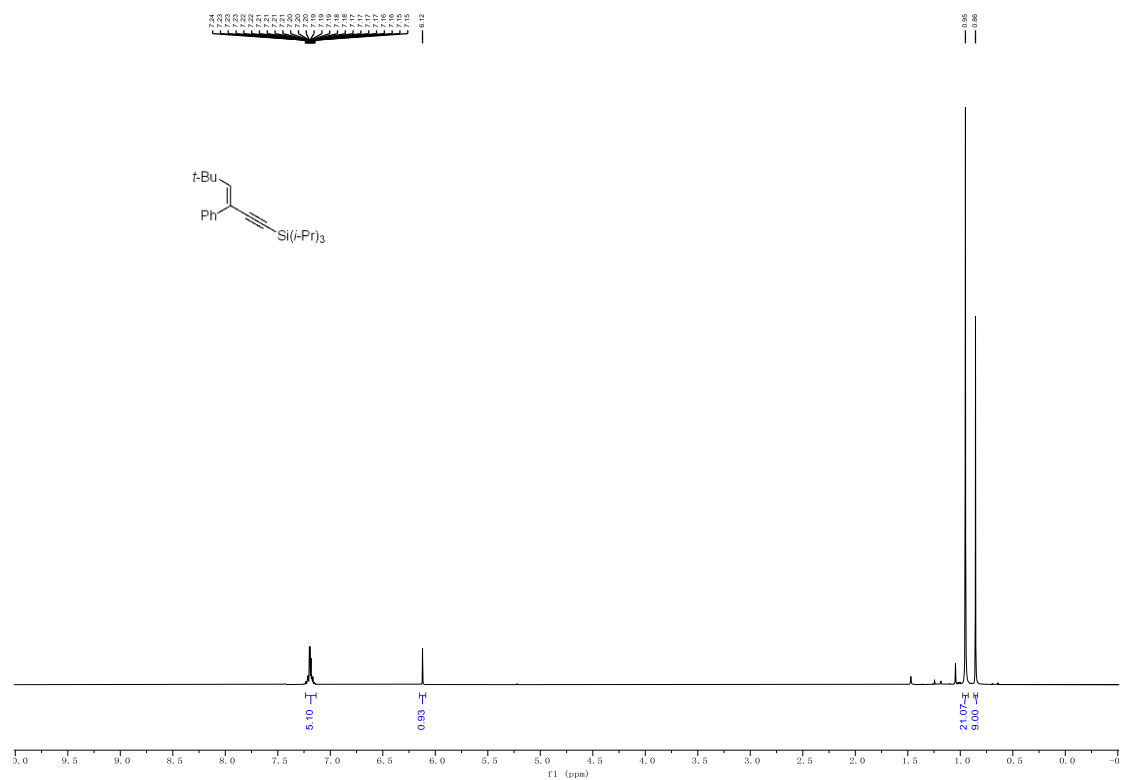
¹H NMR and ¹³C NMR spectra of S35

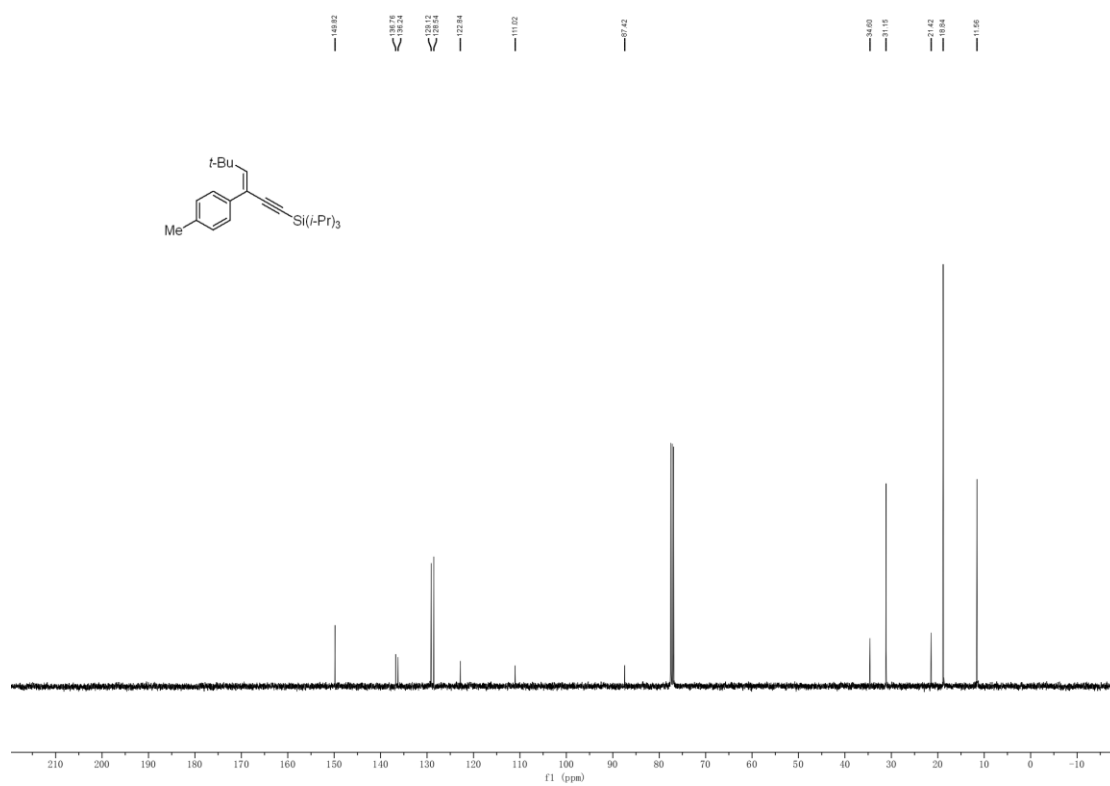


¹H NMR and ¹³C NMR spectra of 4a

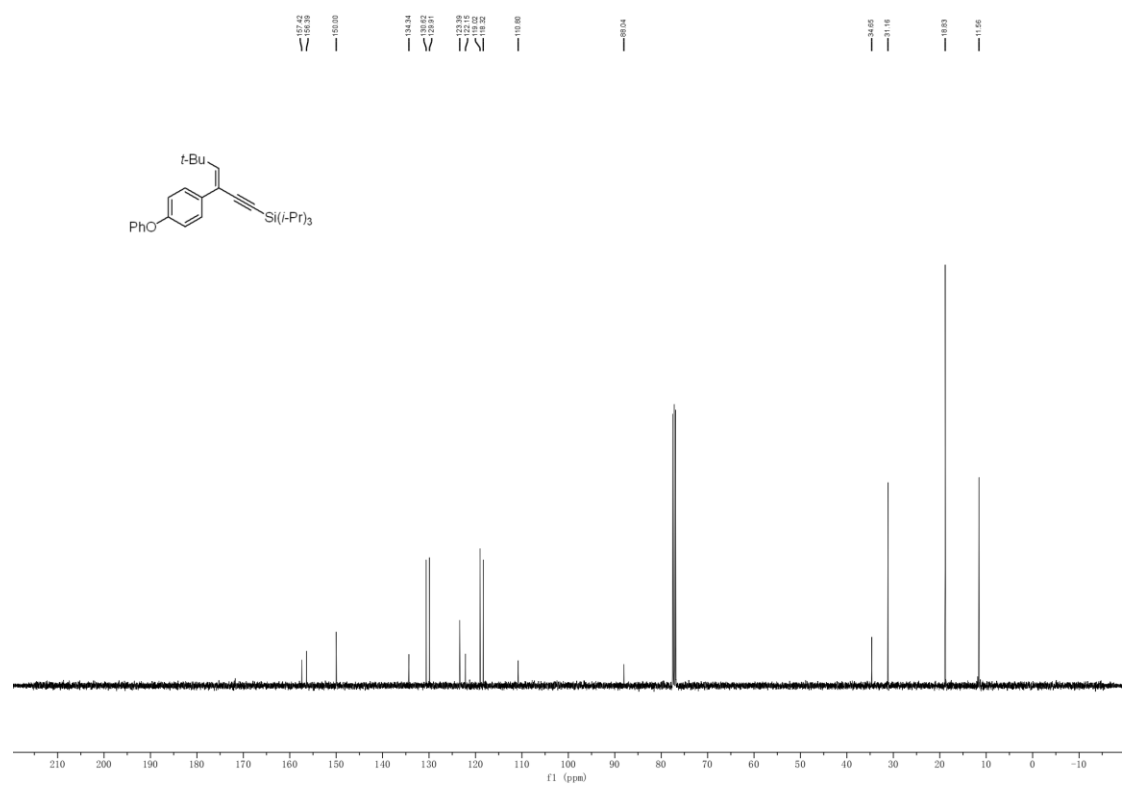
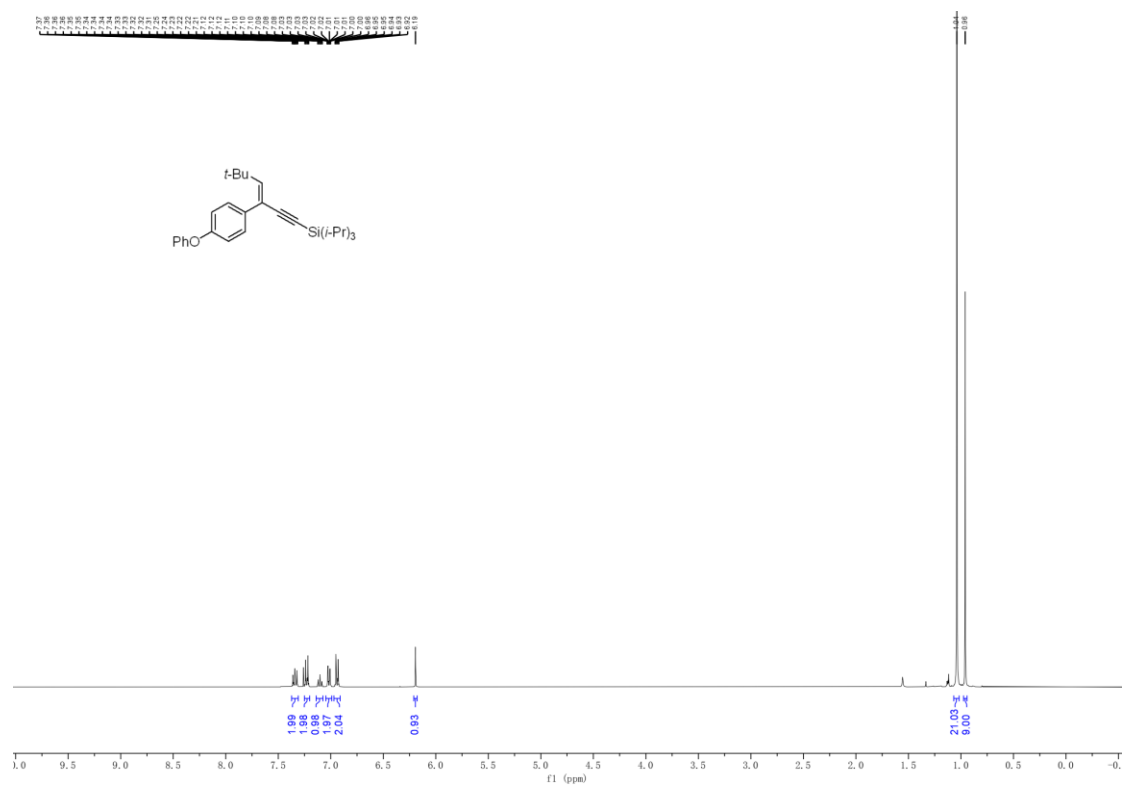


¹H NMR and ¹³C NMR spectra of 4b

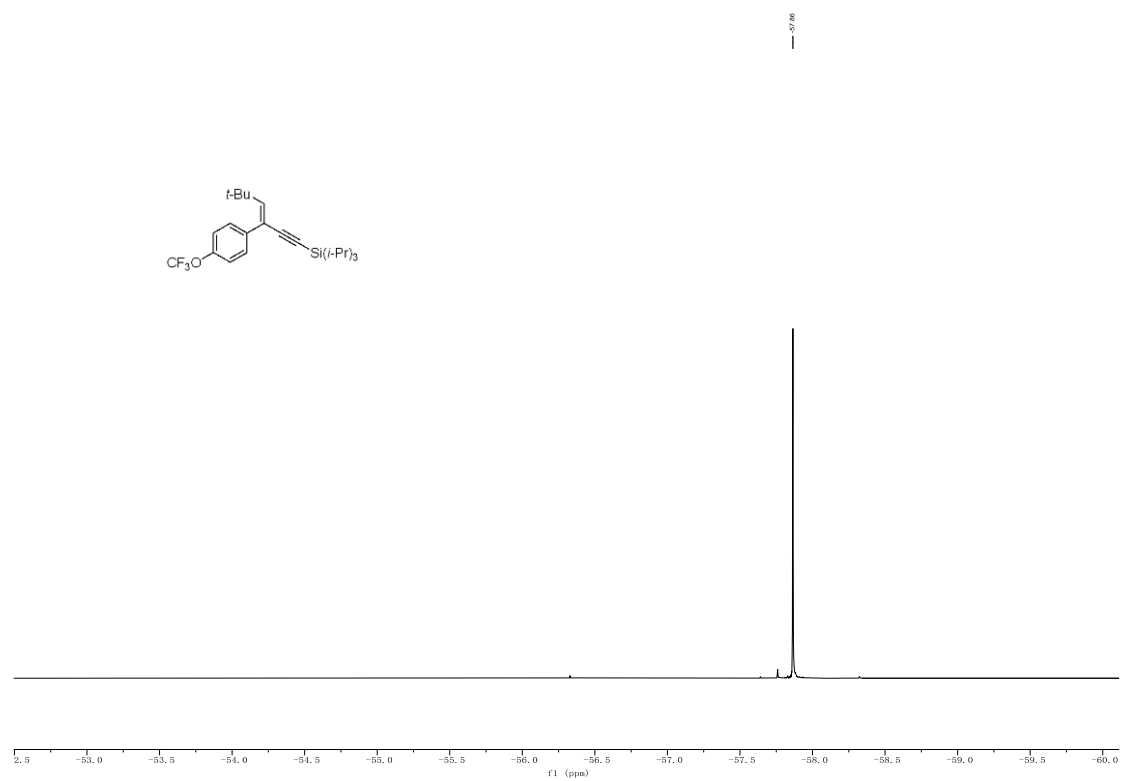
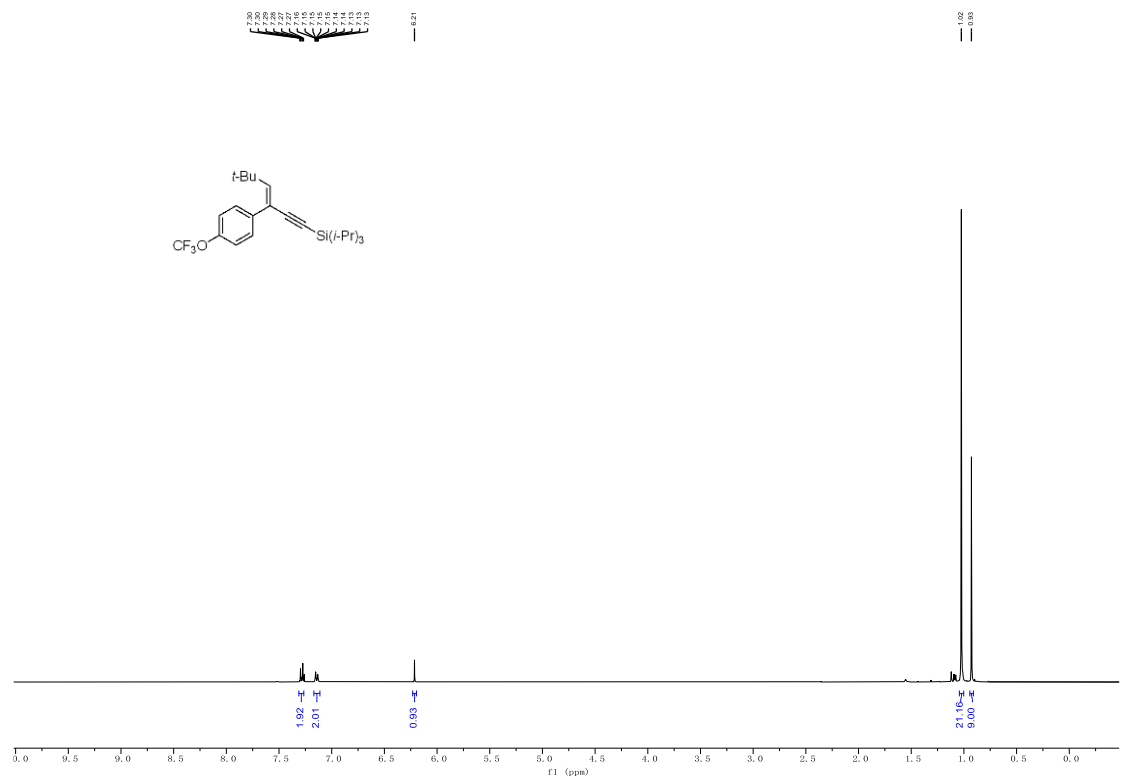


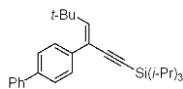
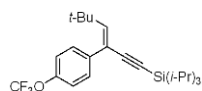
[illegible]

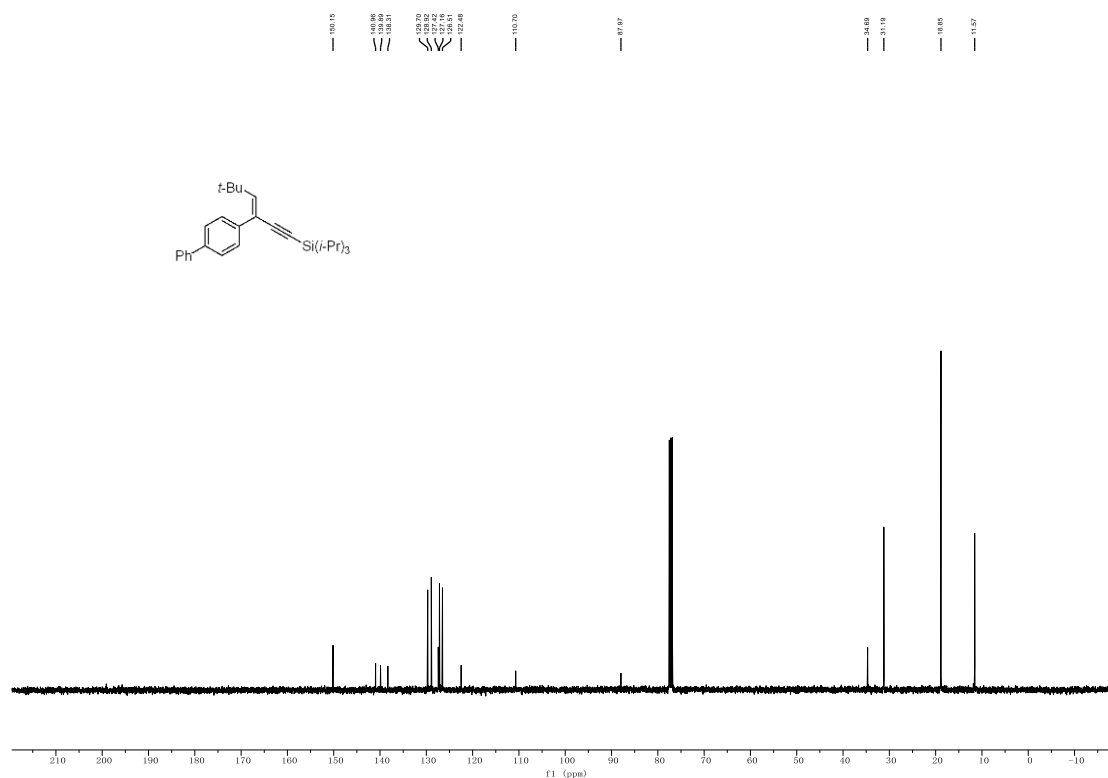
^1H NMR and ^{13}C NMR spectra of 4d



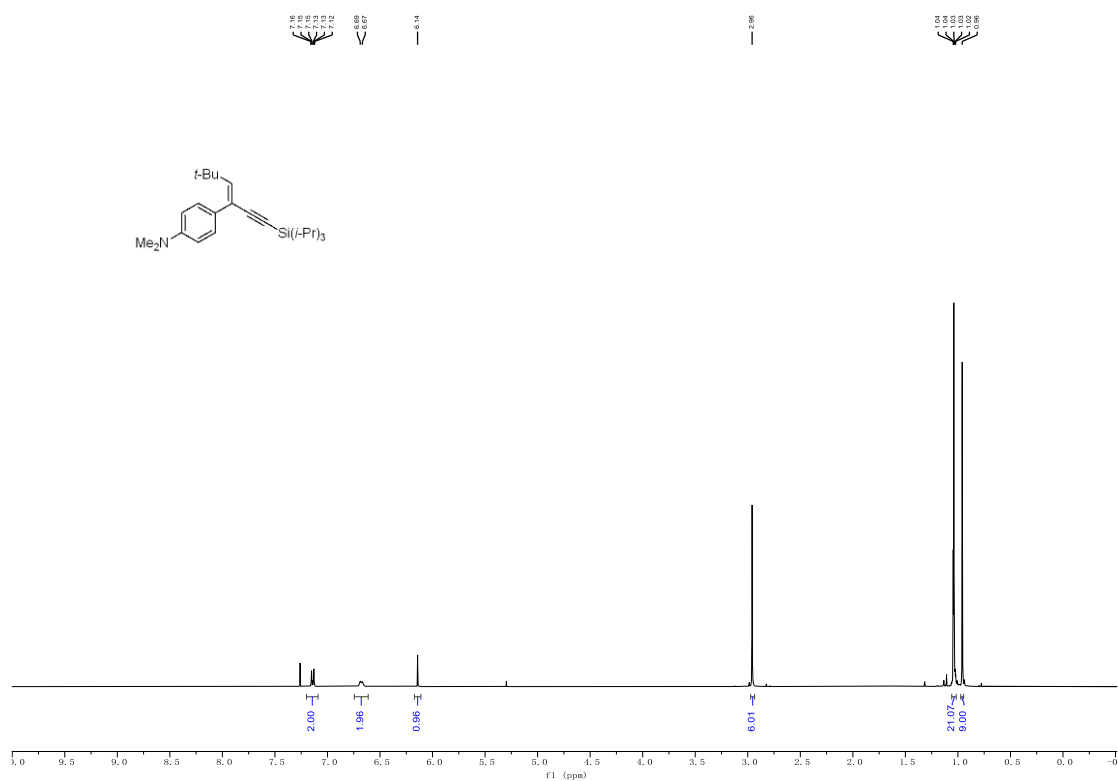
¹H NMR, ¹⁹F NMR and ¹³C NMR spectra of 4e

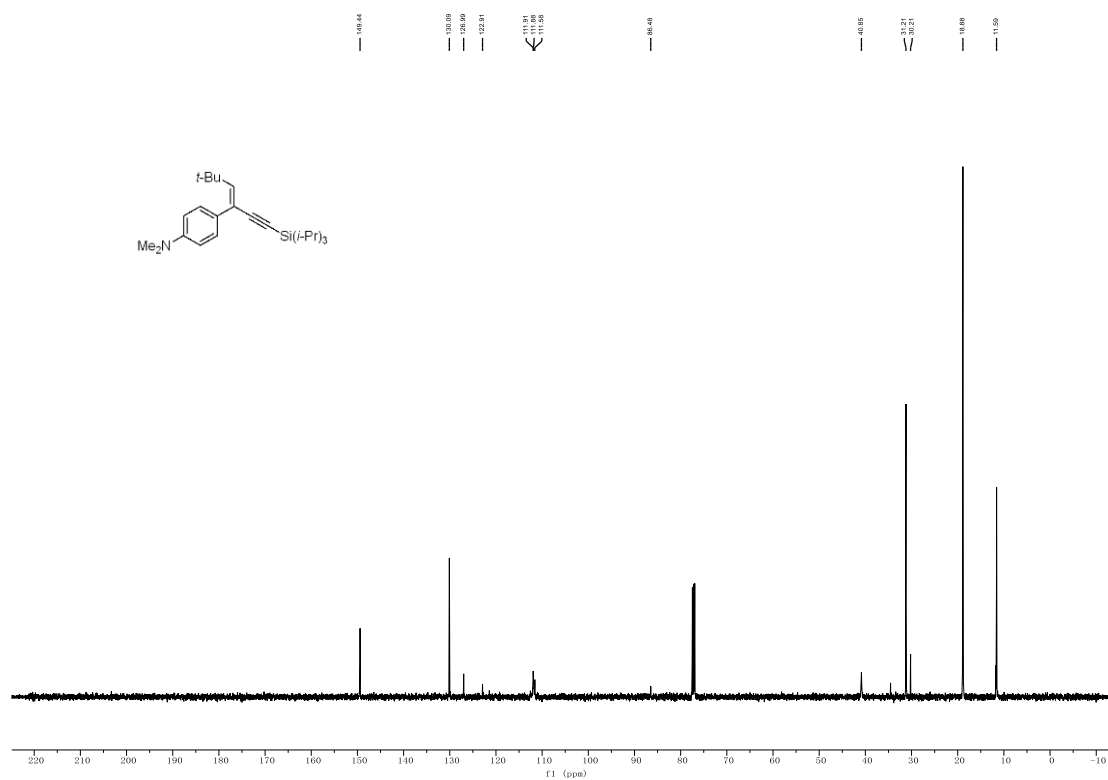




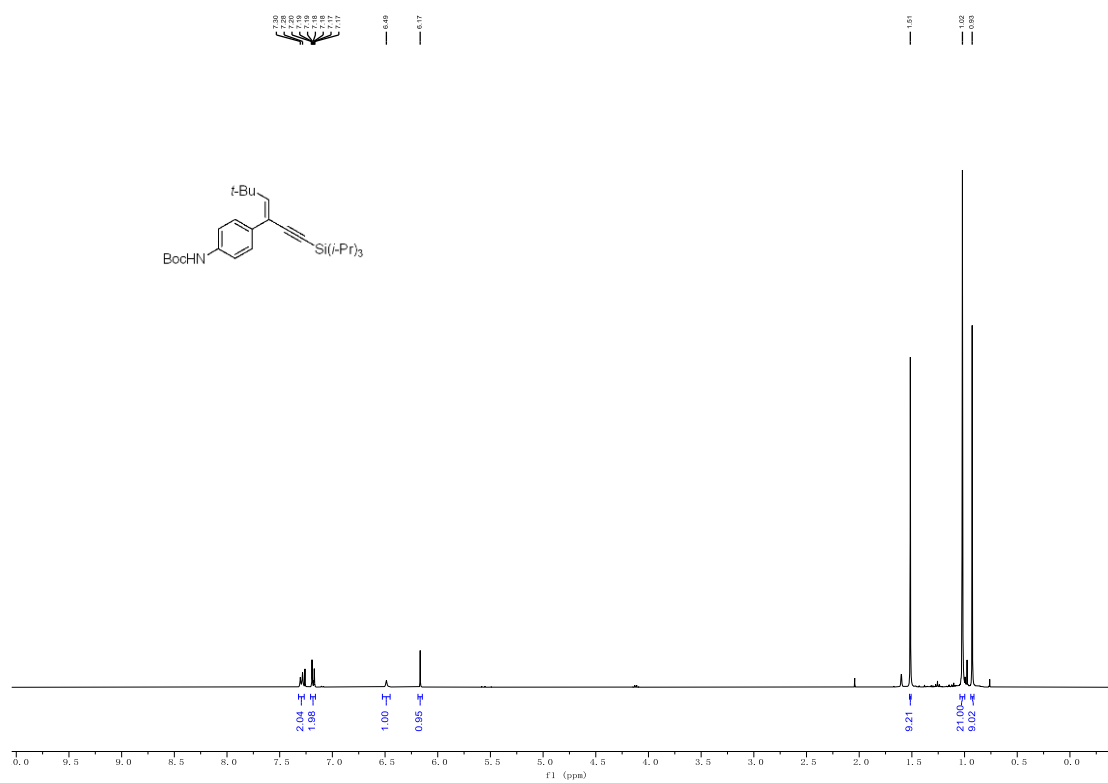


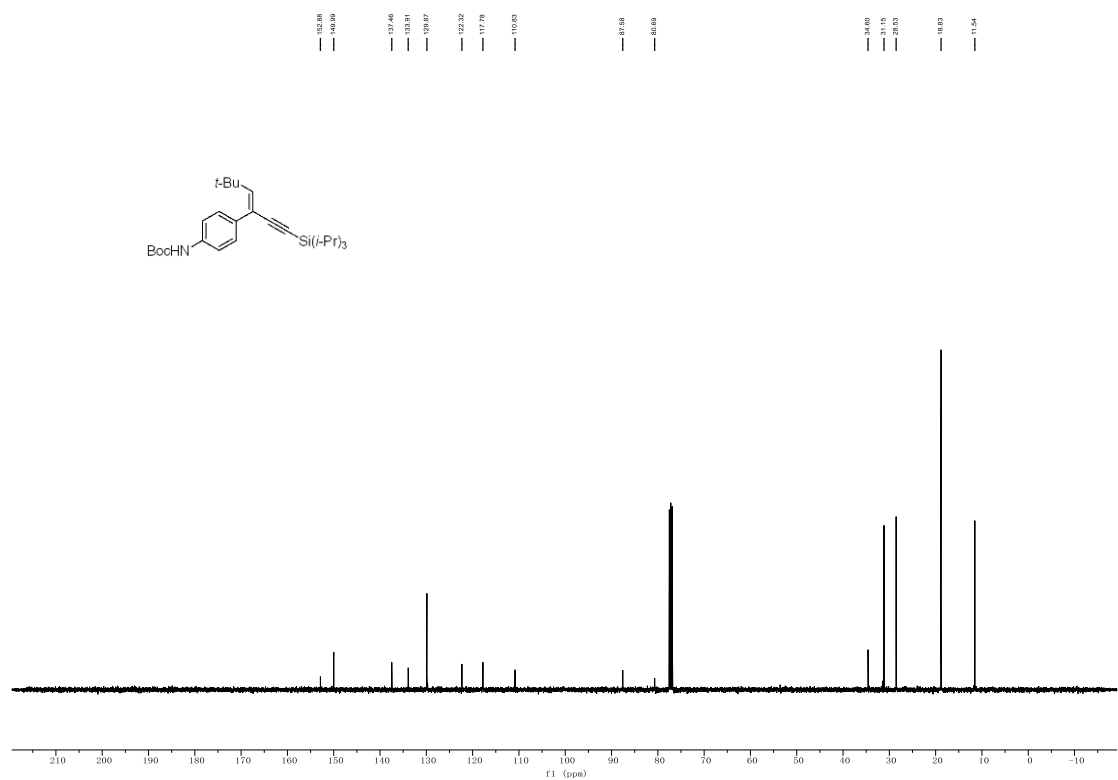
¹H NMR and ¹³C NMR spectra of 4g



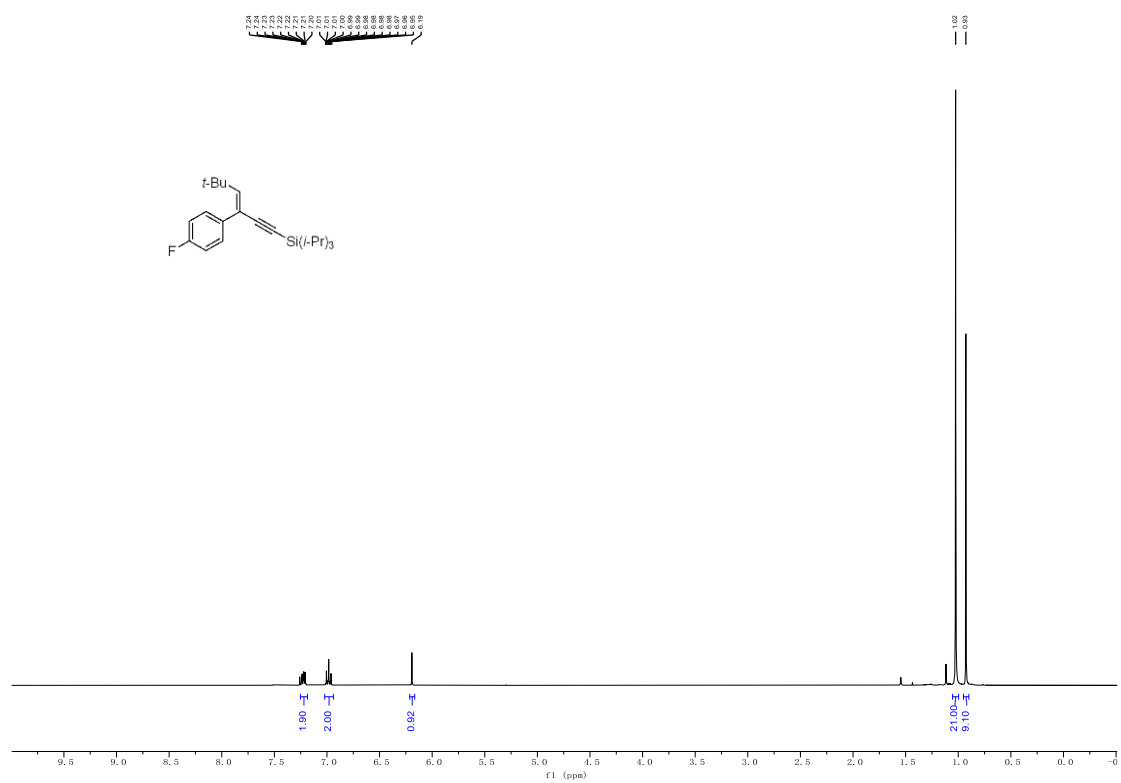


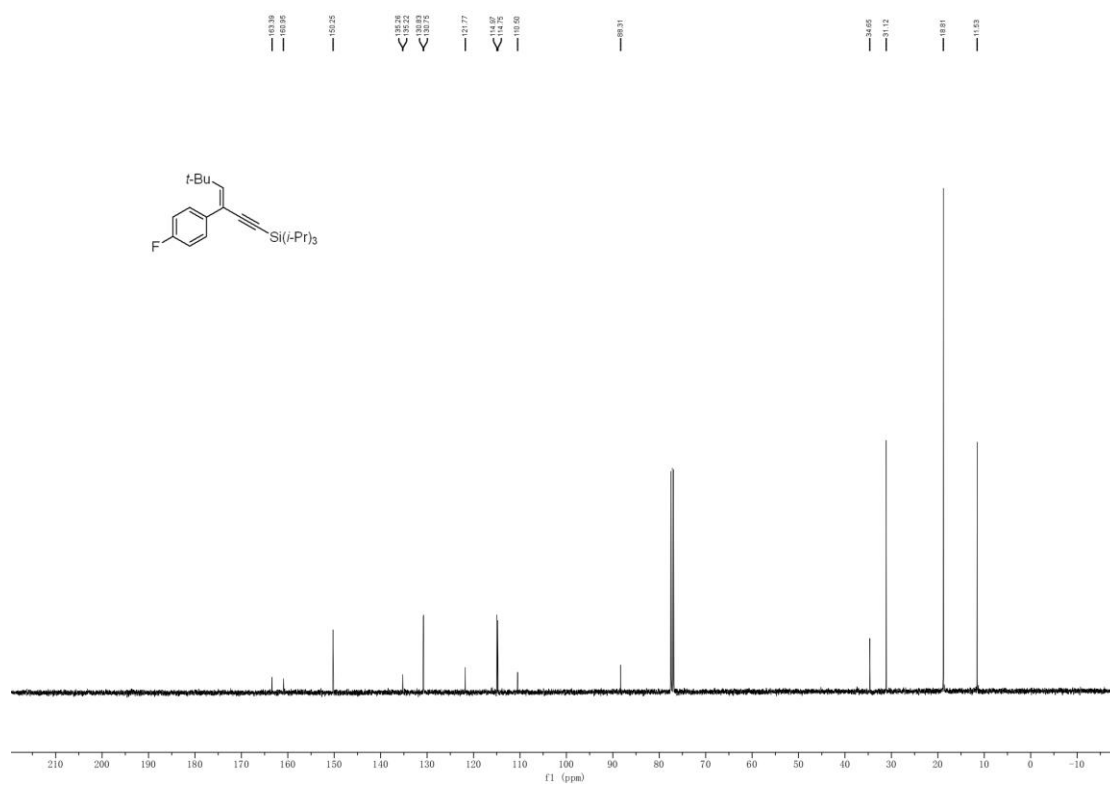
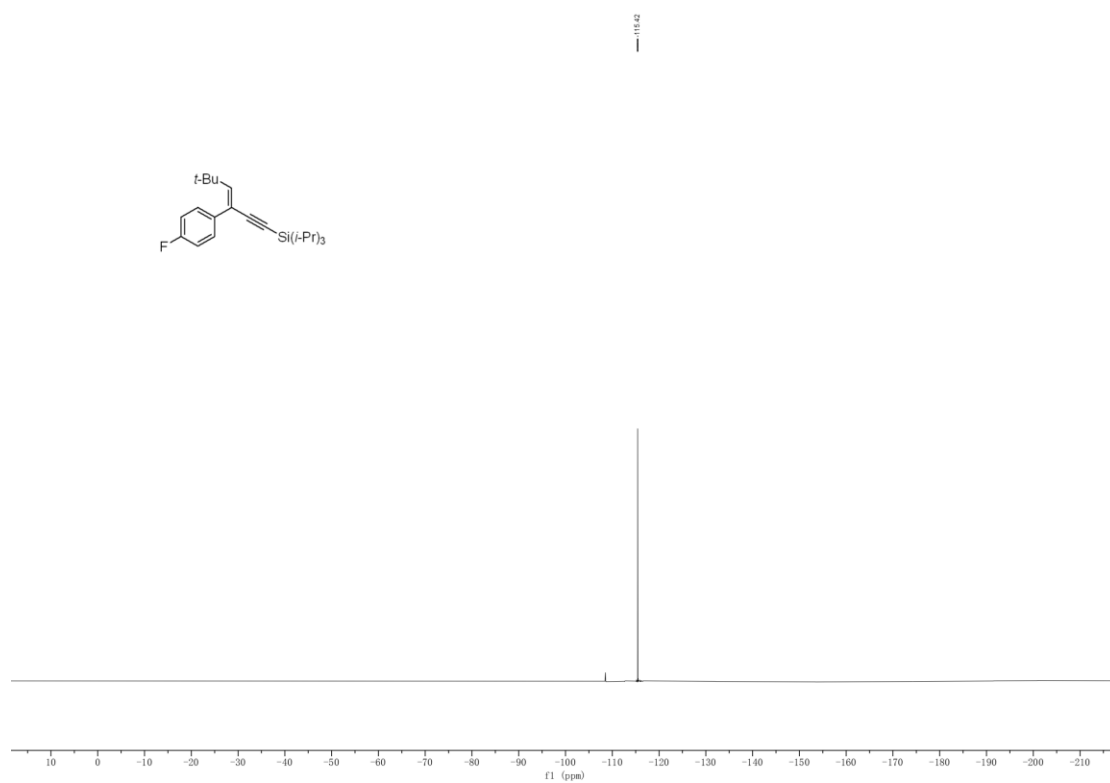
¹H NMR and ¹³C NMR spectra of 4h



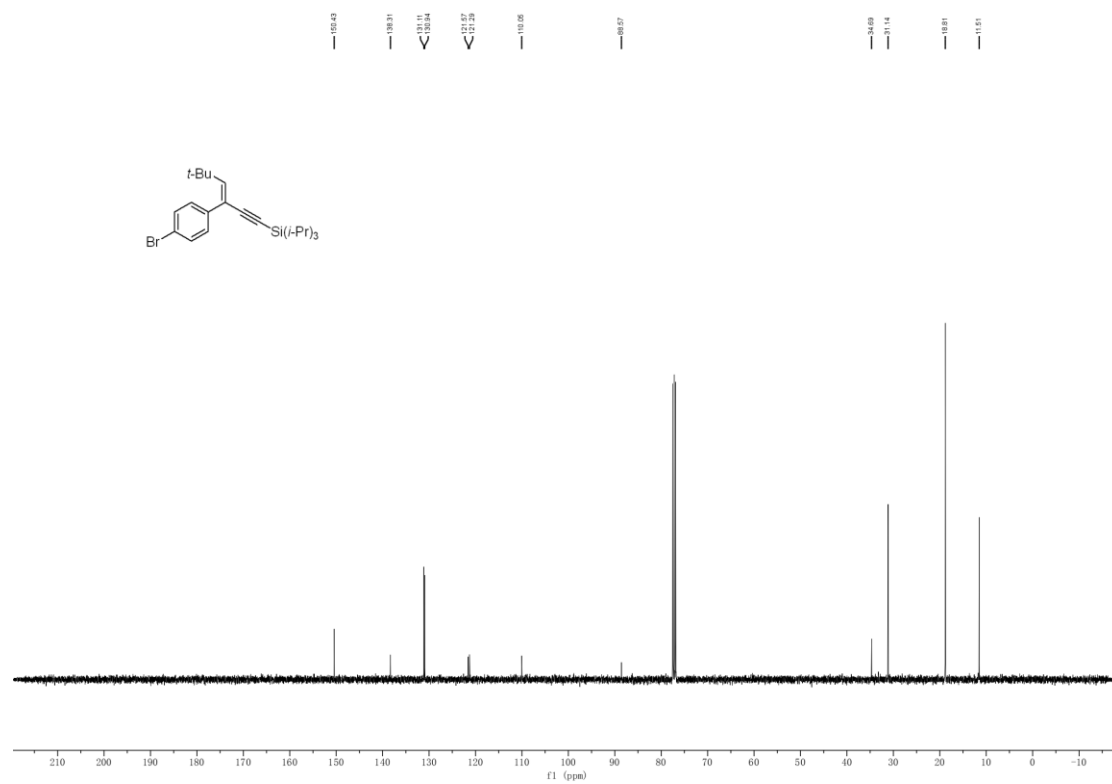
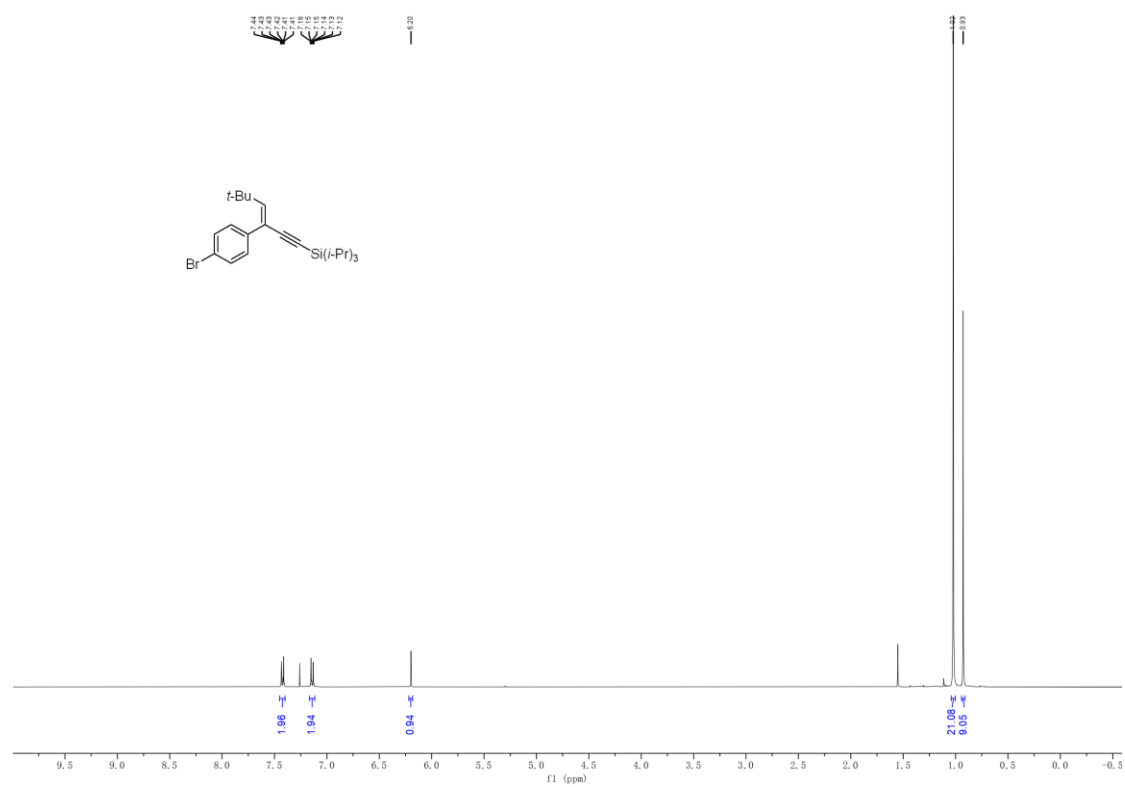


¹H NMR, ¹⁹F NMR and ¹³C NMR spectra of 4i

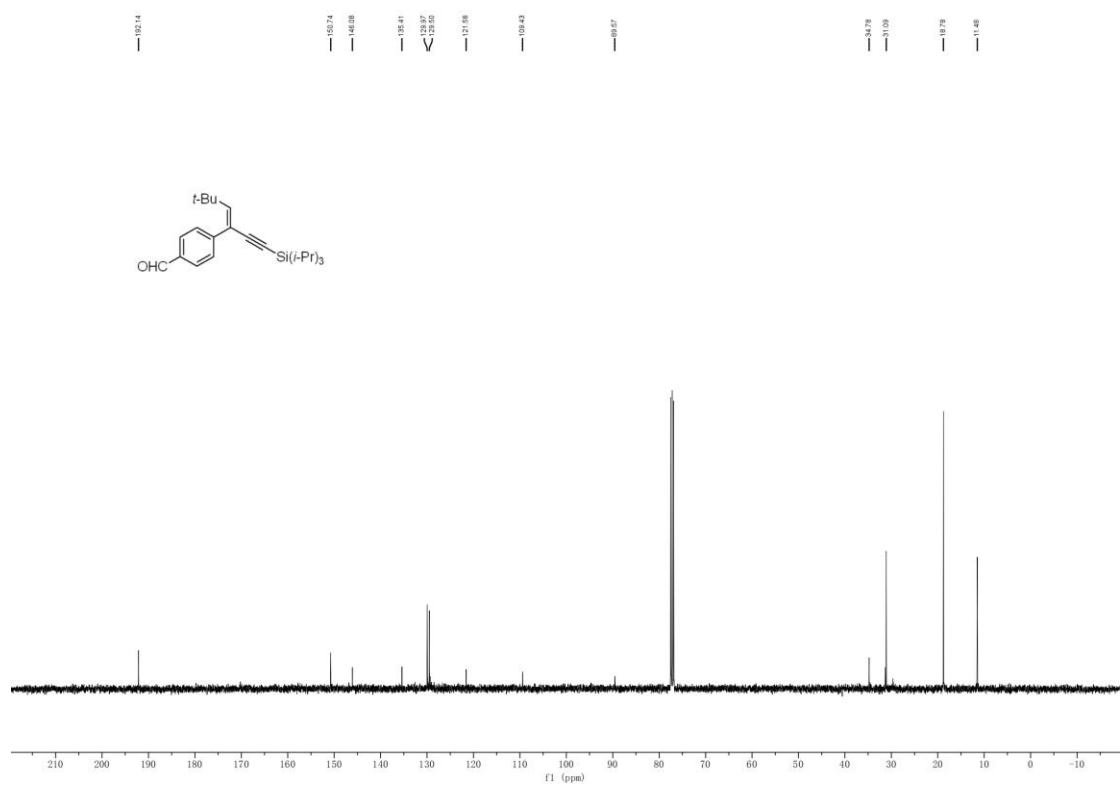
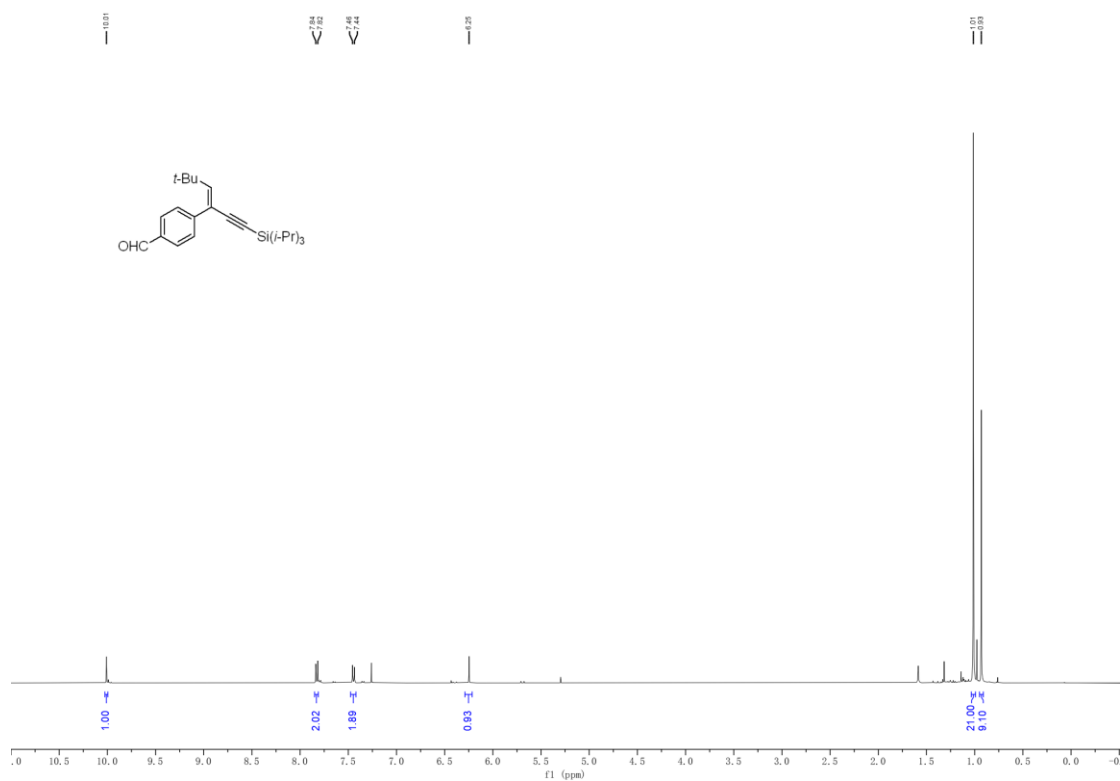




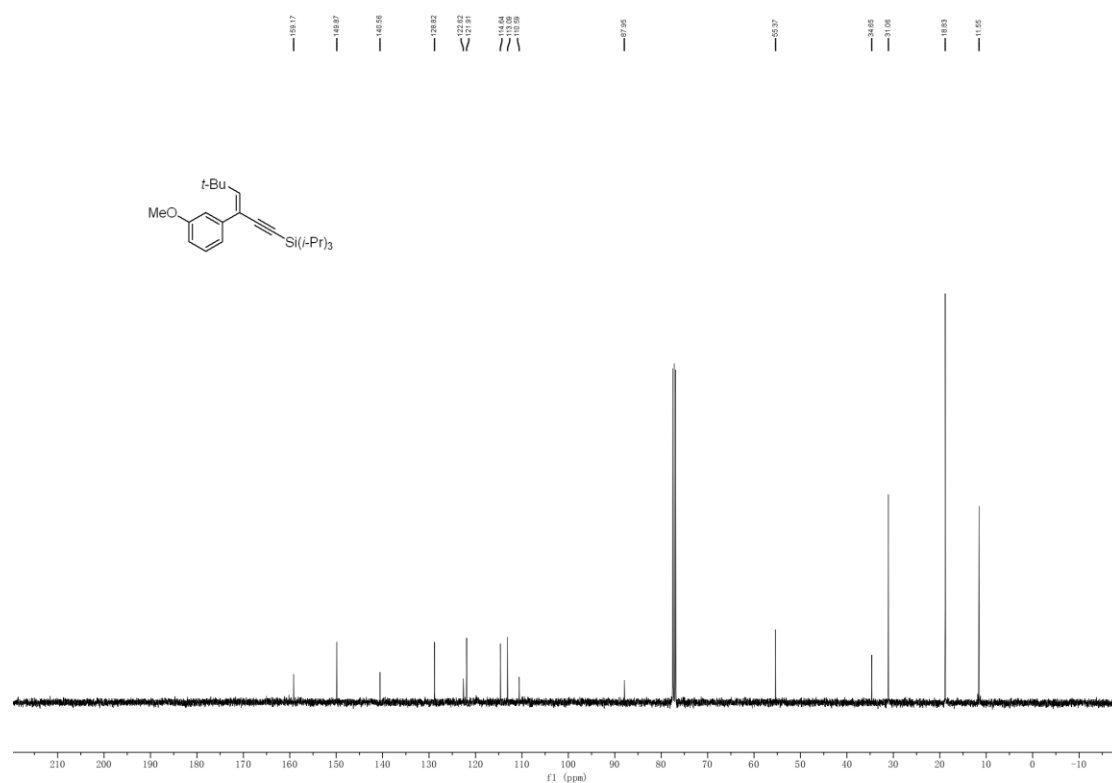
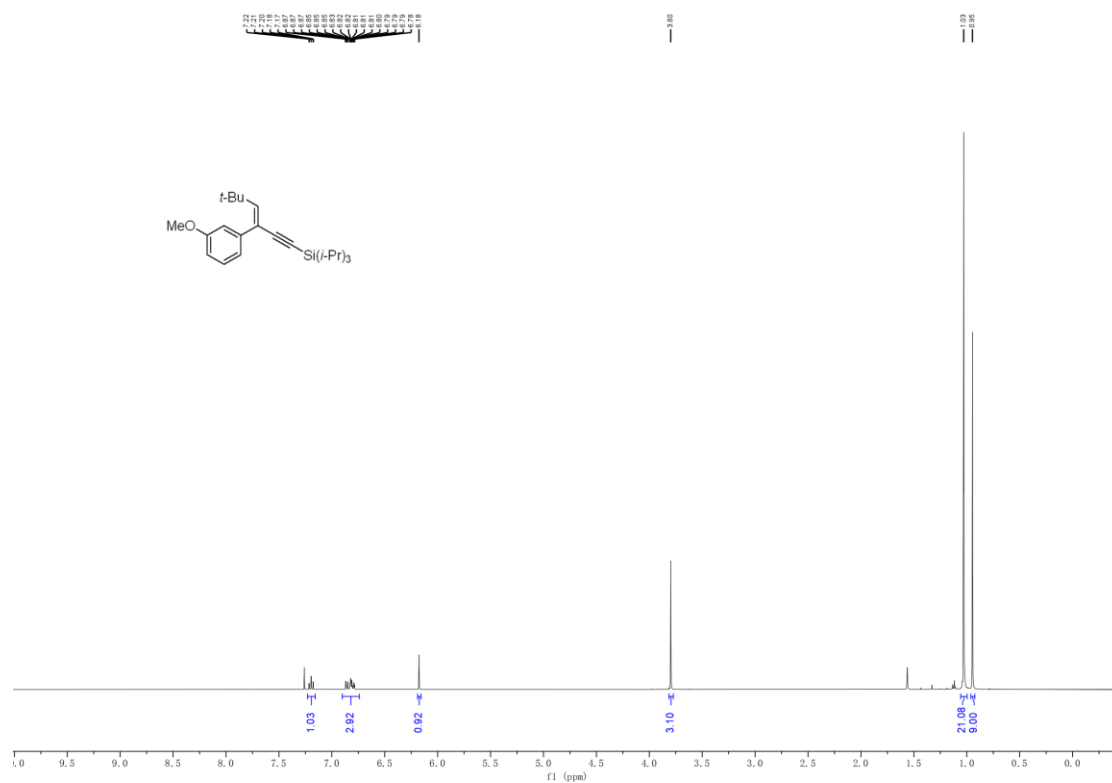
¹H NMR and ¹³C NMR spectra of 4j



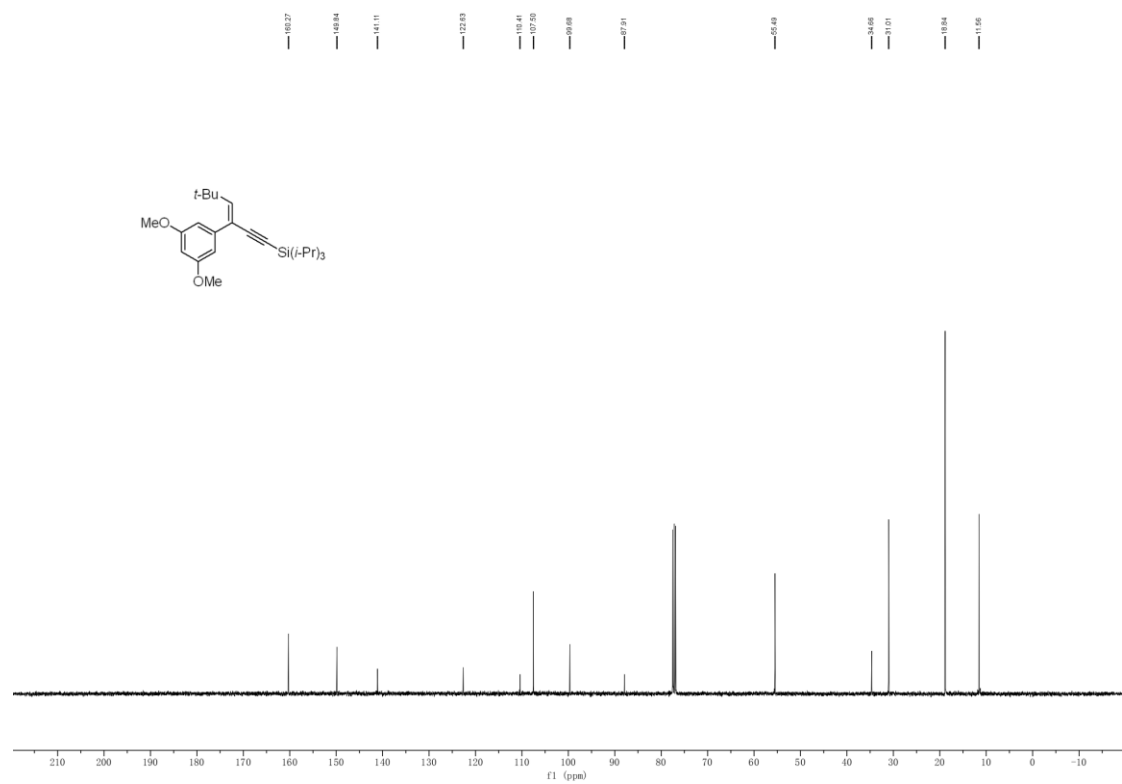
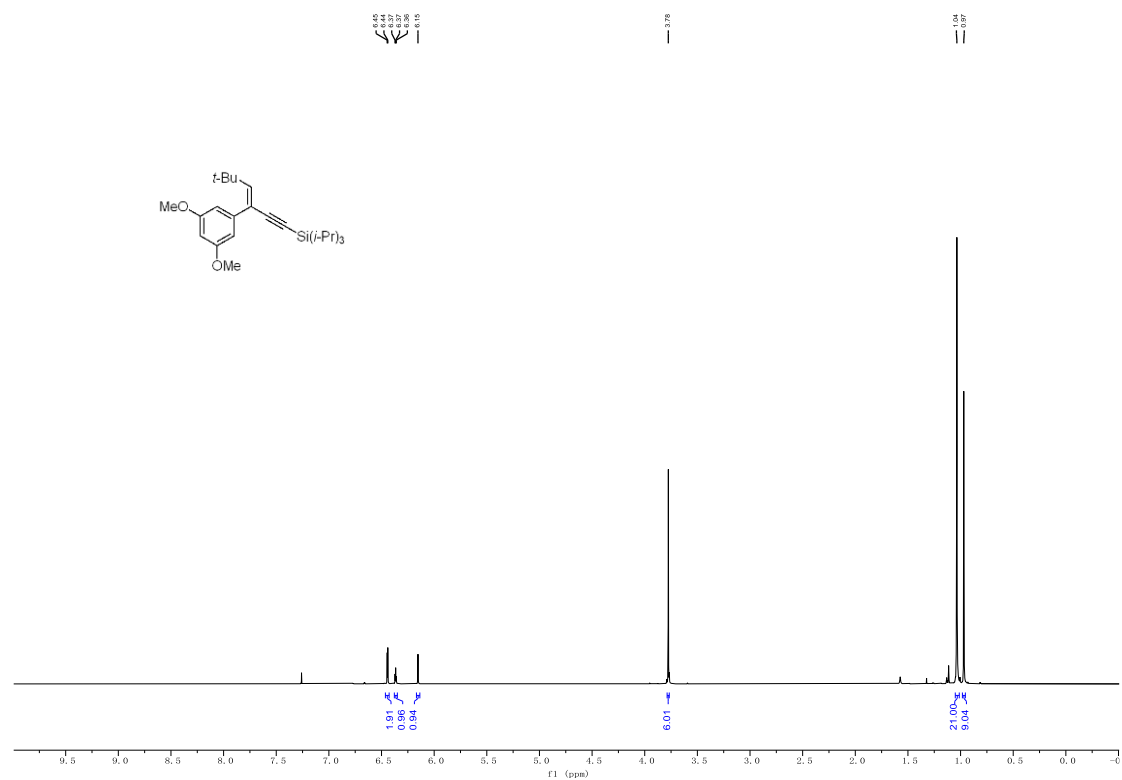
¹H NMR and ¹³C NMR spectra of 4k



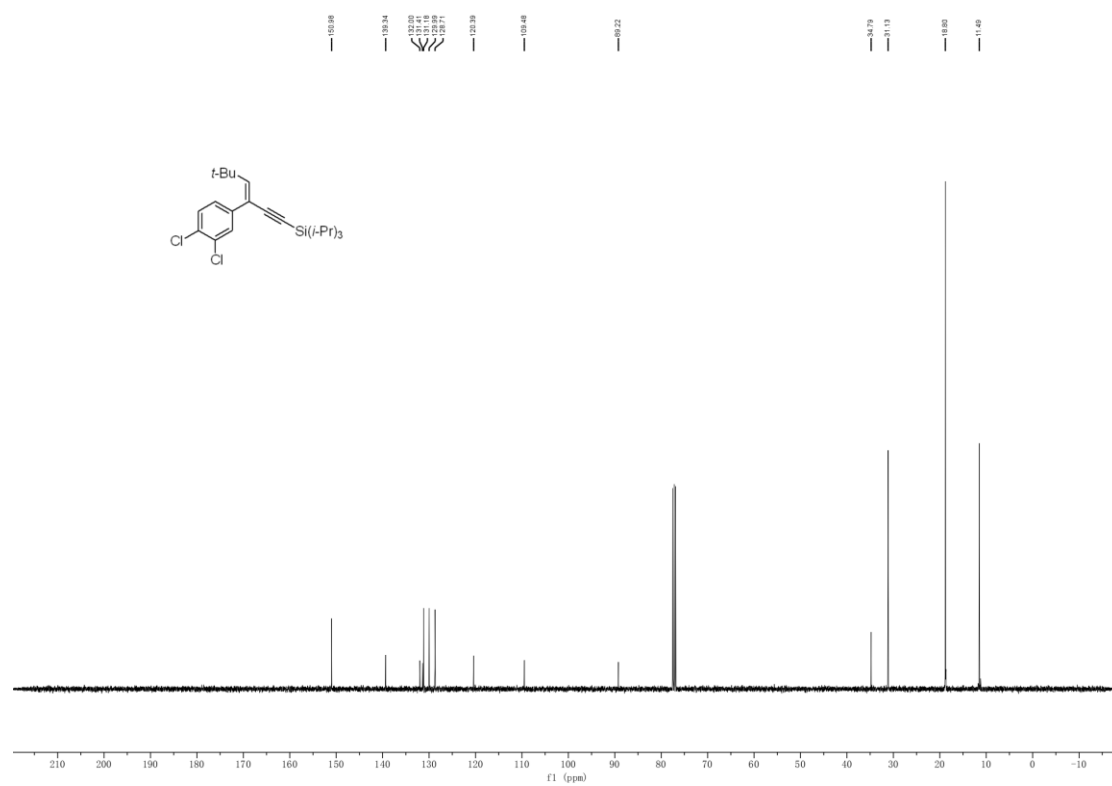
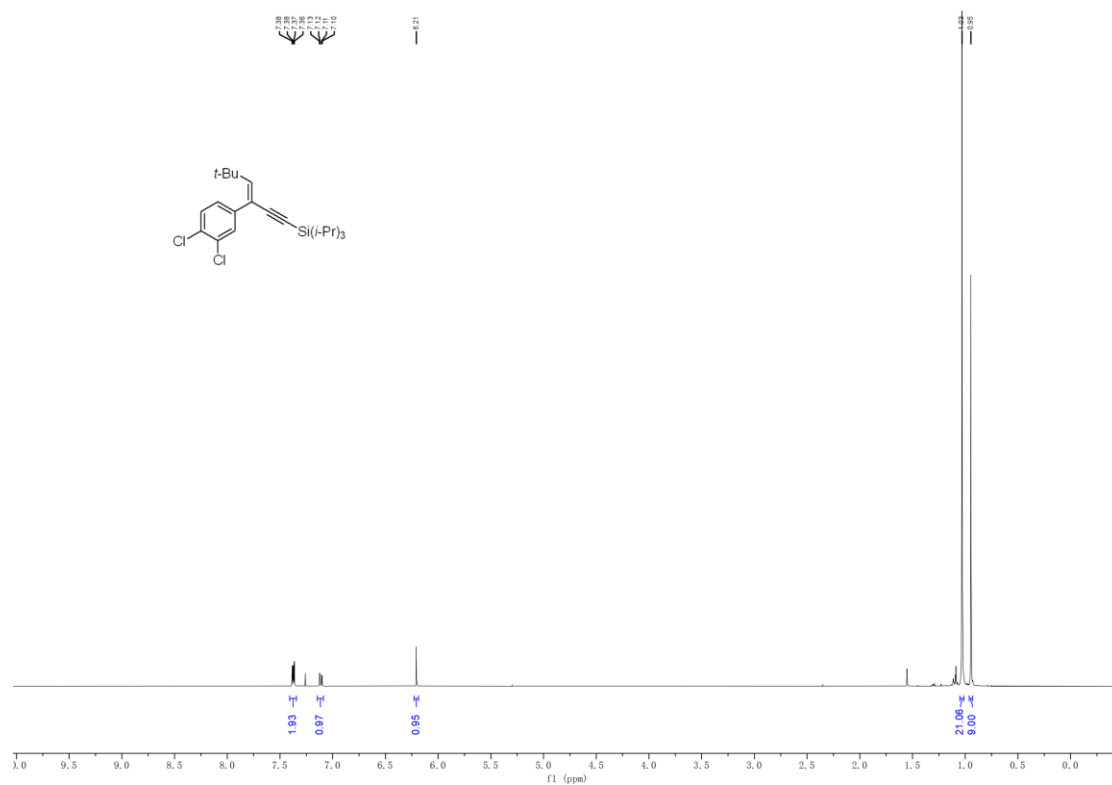
¹H NMR and ¹³C NMR spectra of 4l



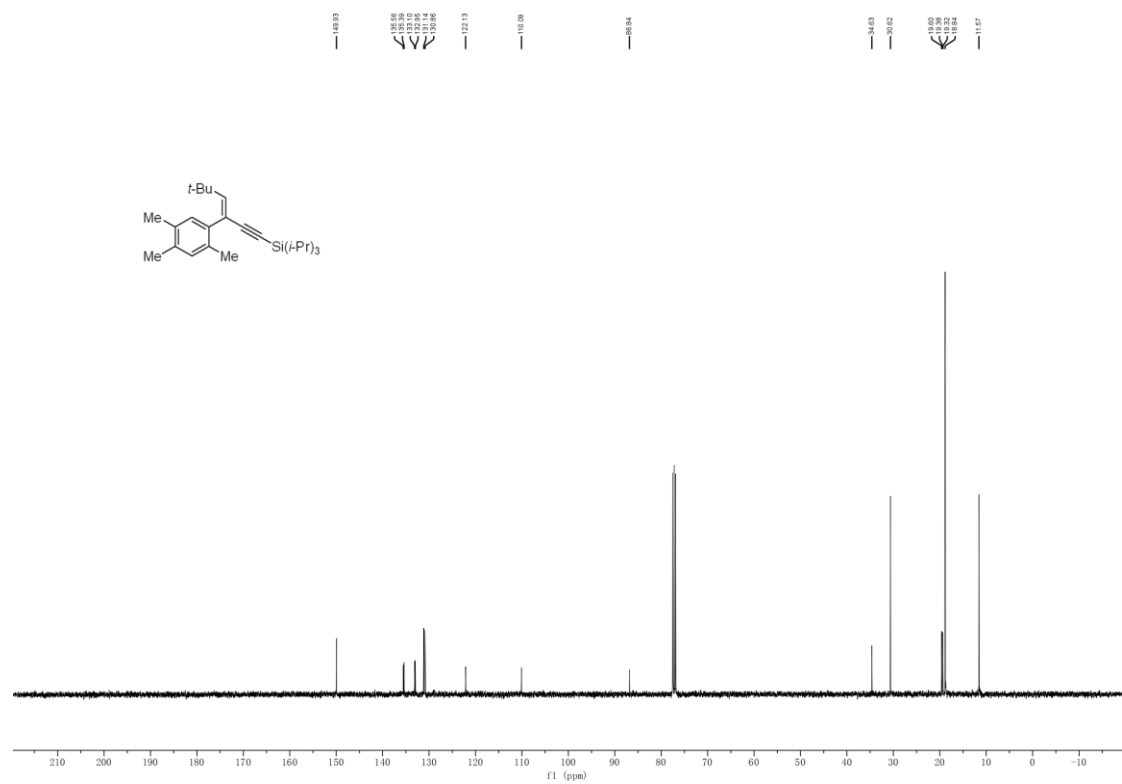
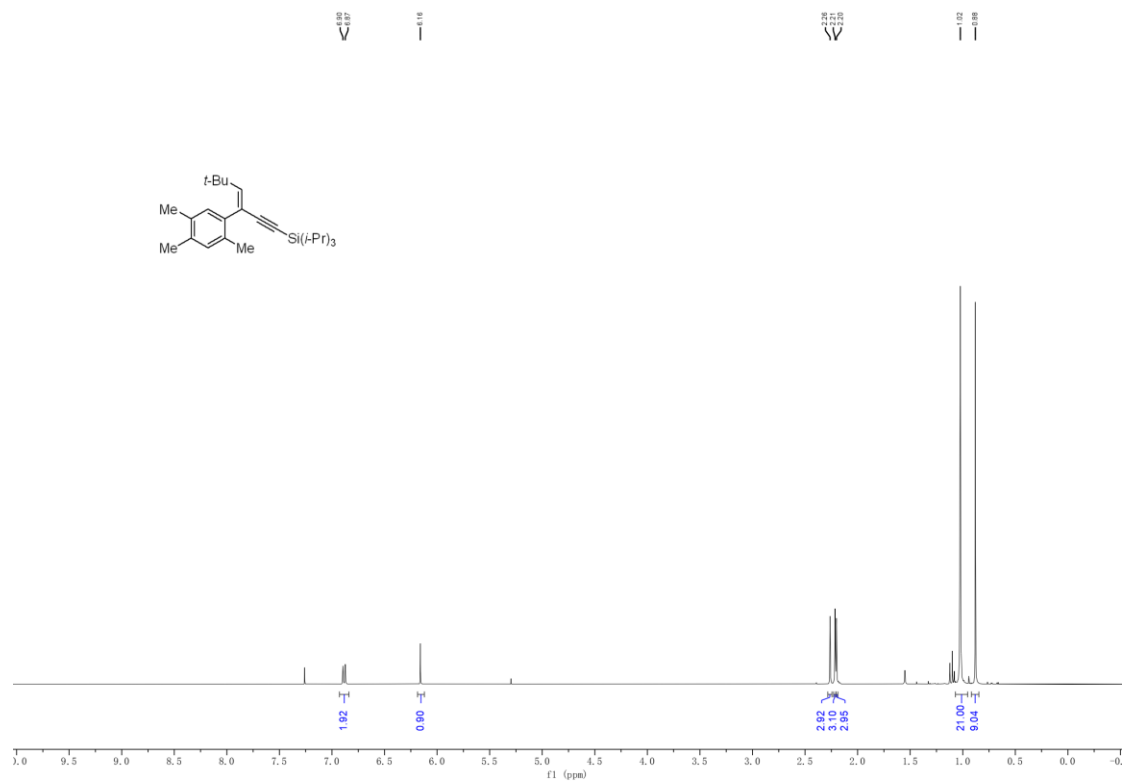
¹H NMR and ¹³C NMR spectra of 4m



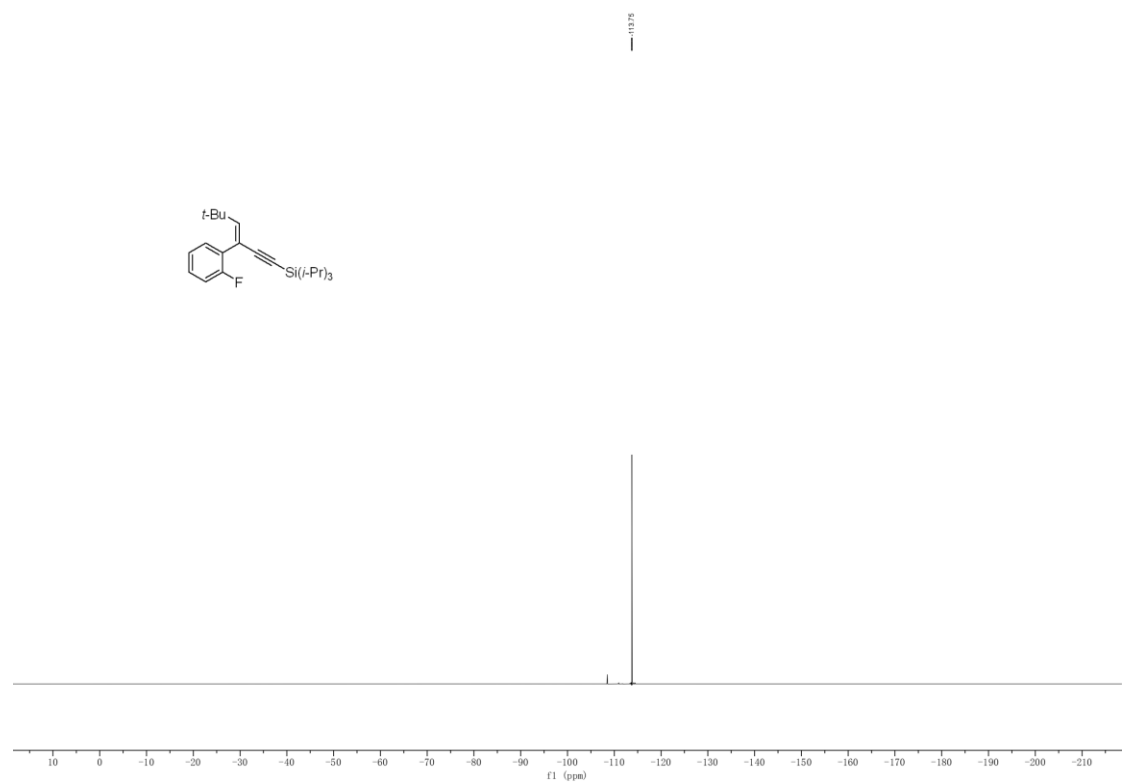
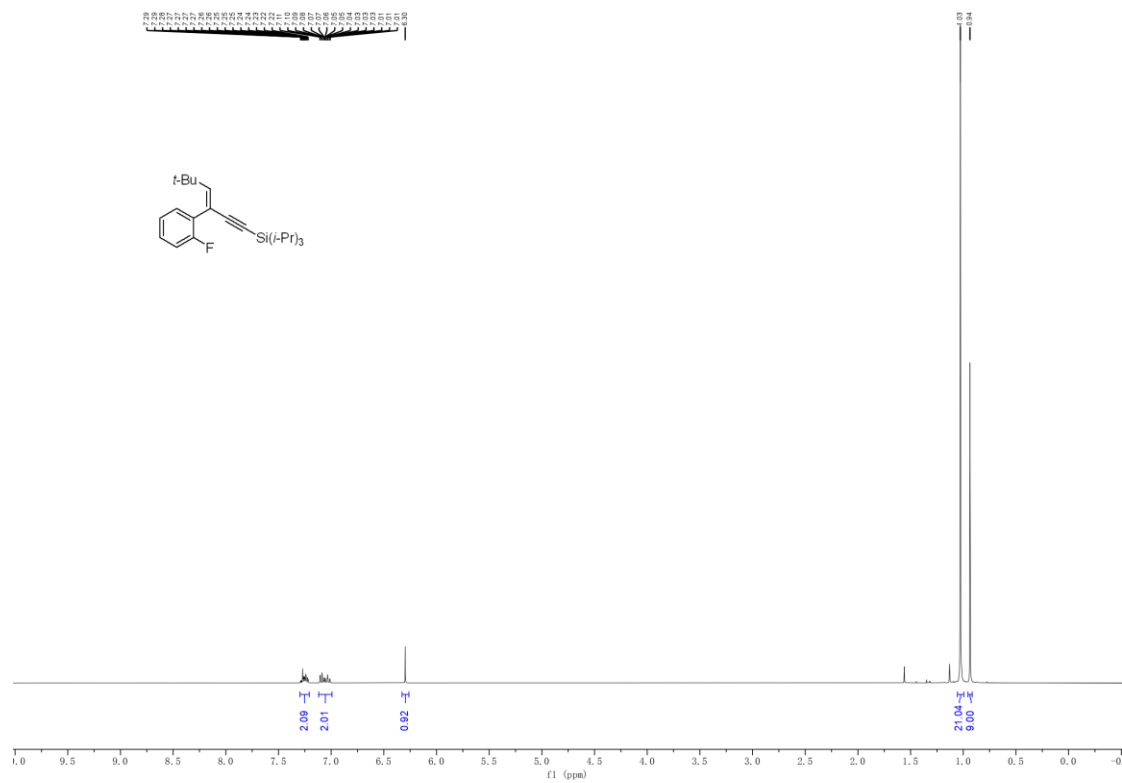
¹H NMR and ¹³C NMR spectra of 4n

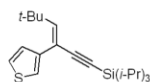
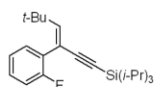


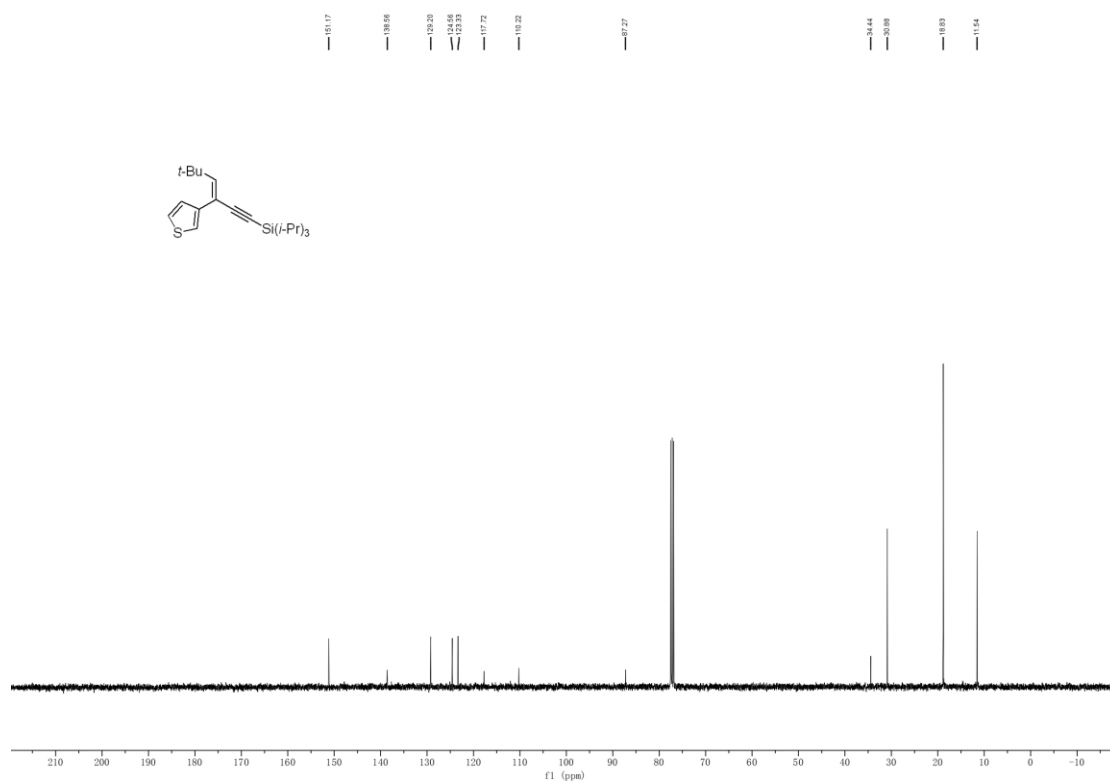
¹H NMR and ¹³C NMR spectra of 4o



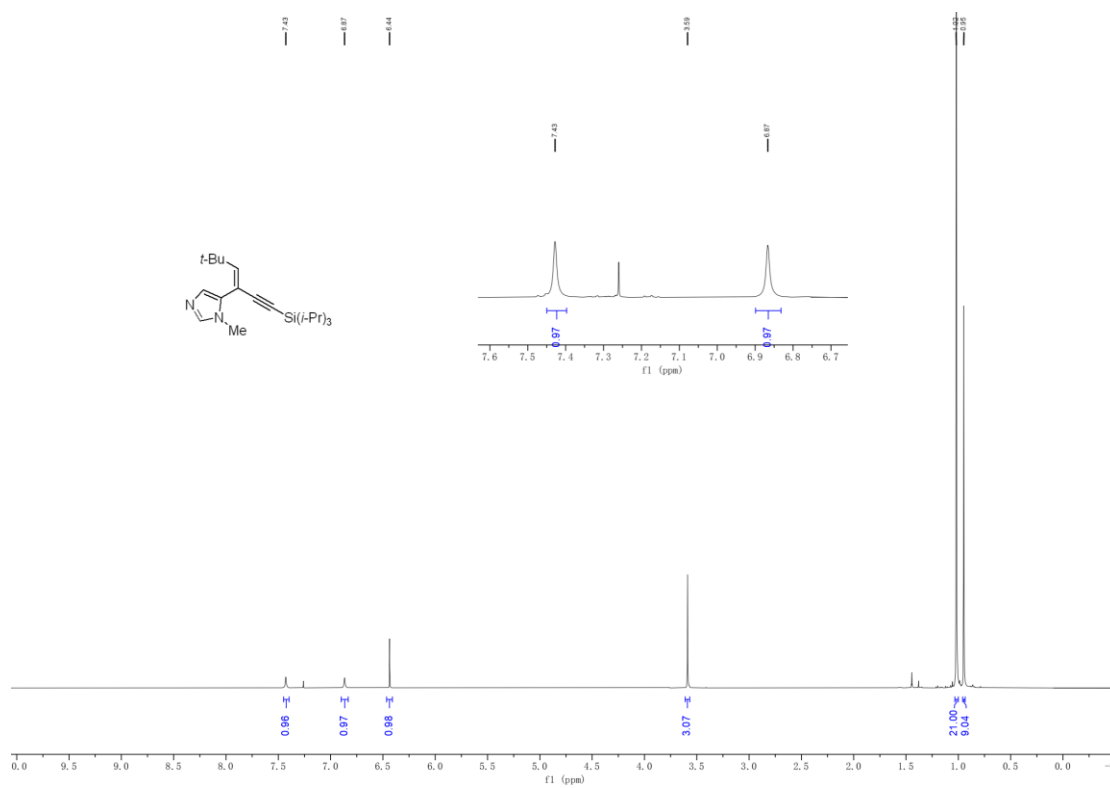
^1H NMR, ^{19}F NMR and ^{13}C NMR spectra of 4p

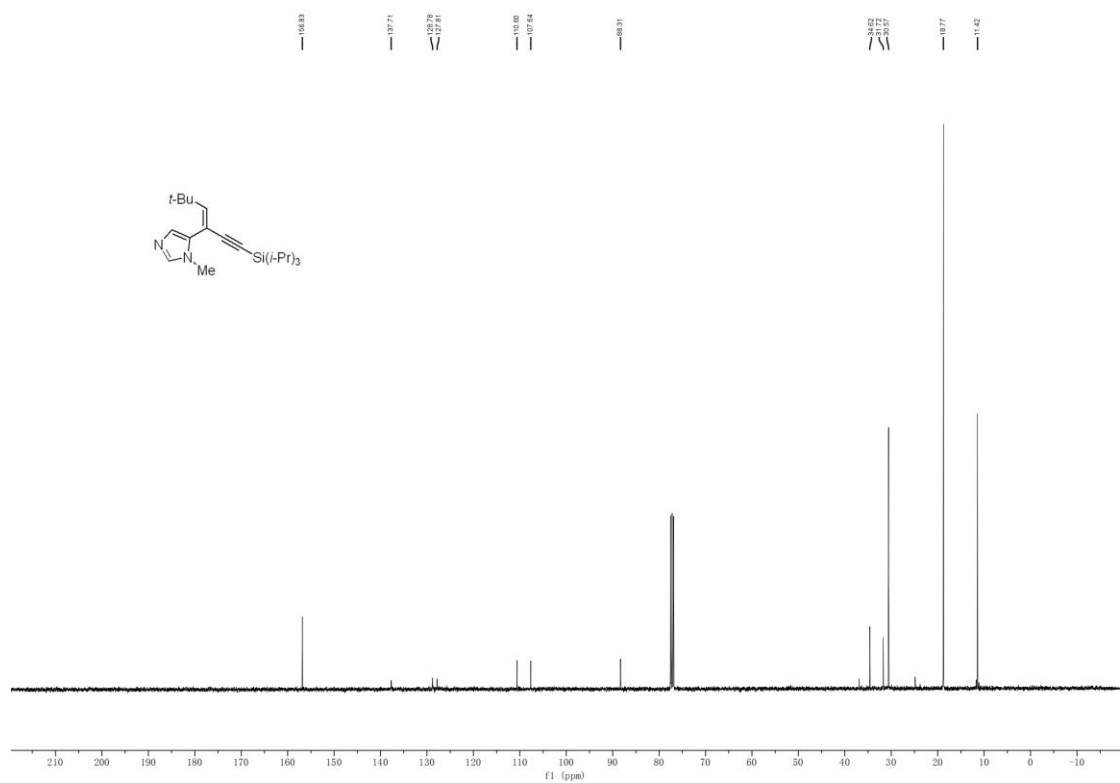




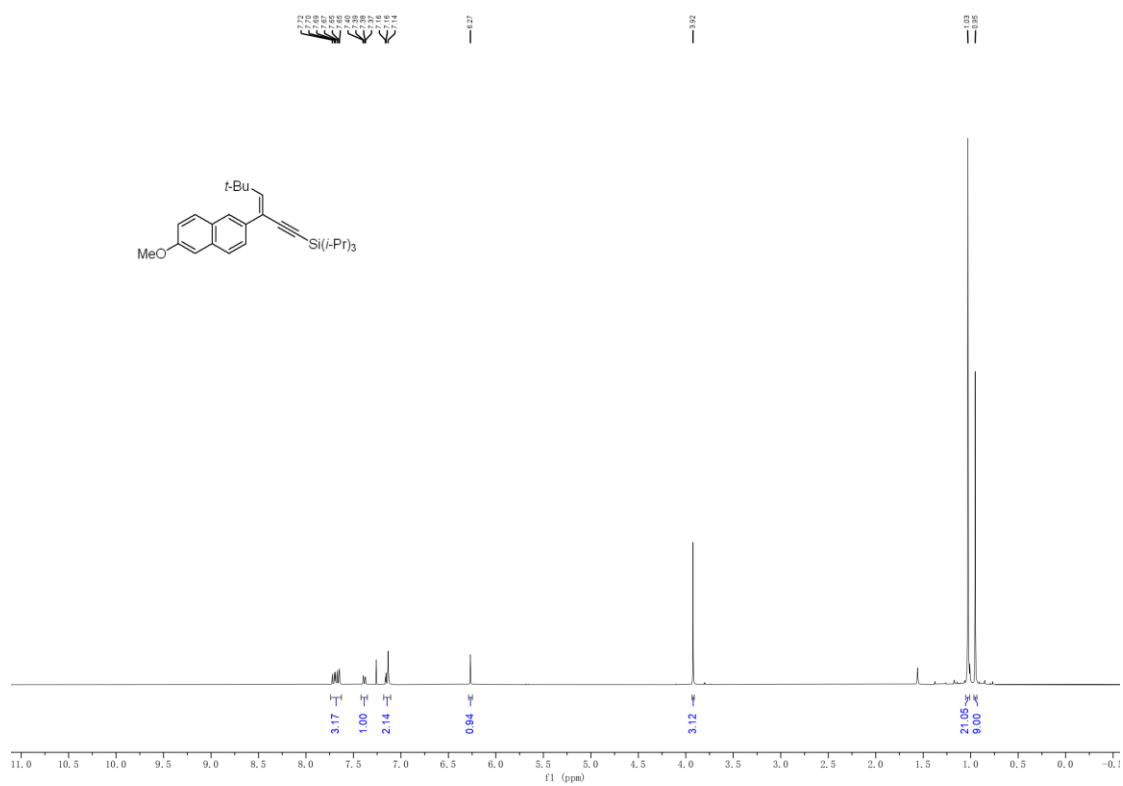


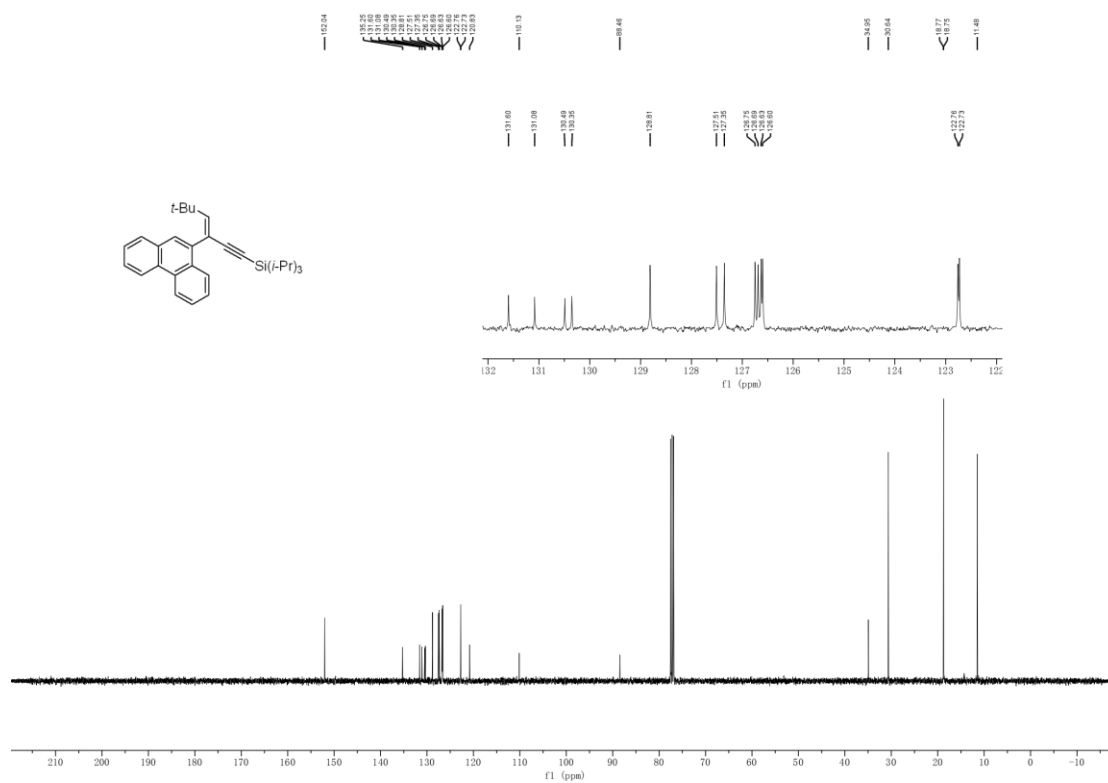
¹H NMR and ¹³C NMR spectra of 4r



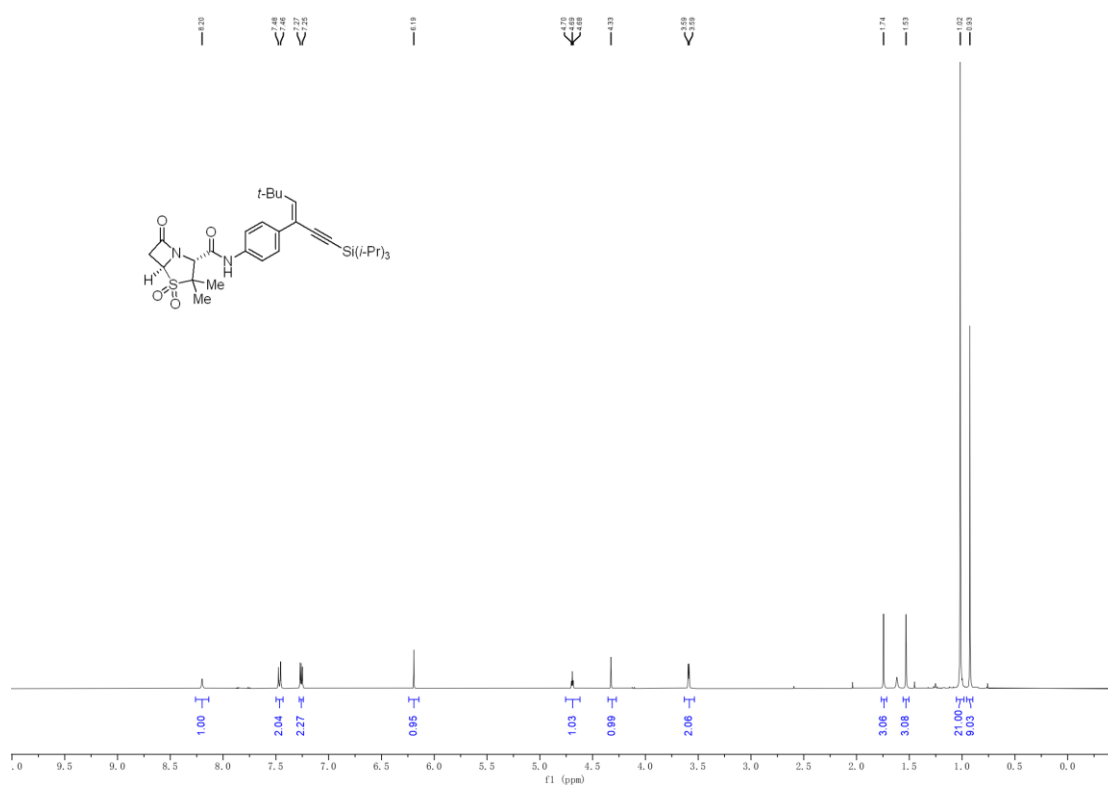


¹H NMR and ¹³C NMR spectra of 4s

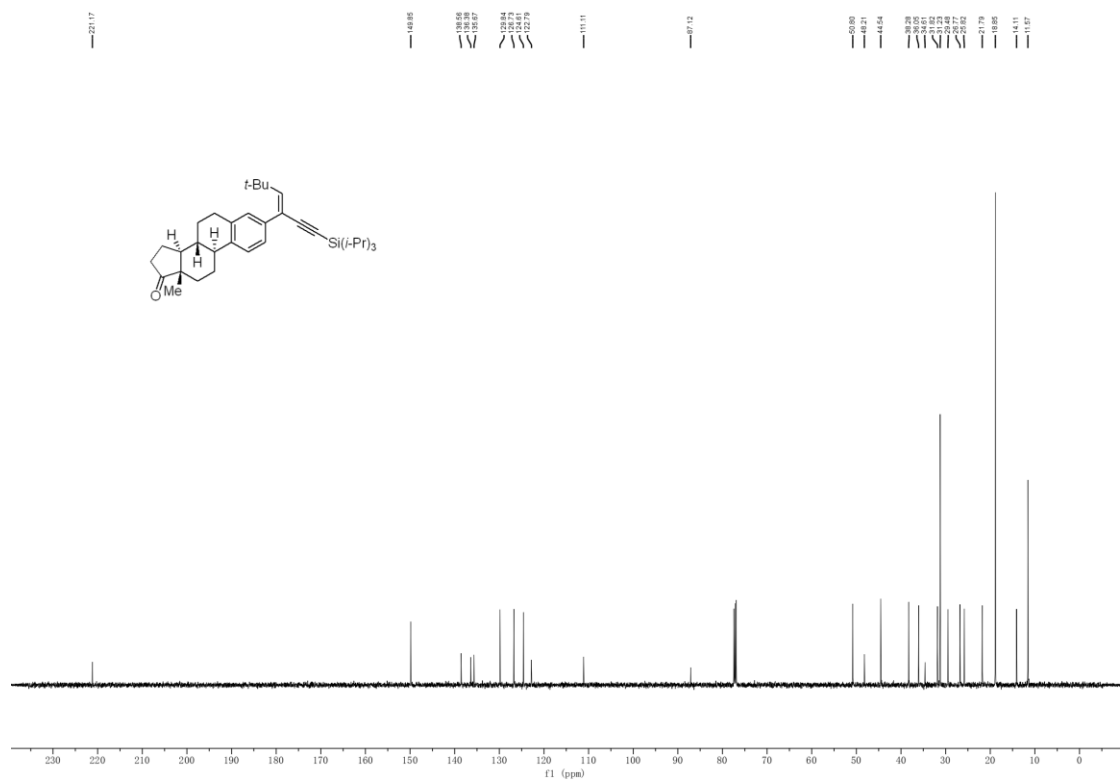




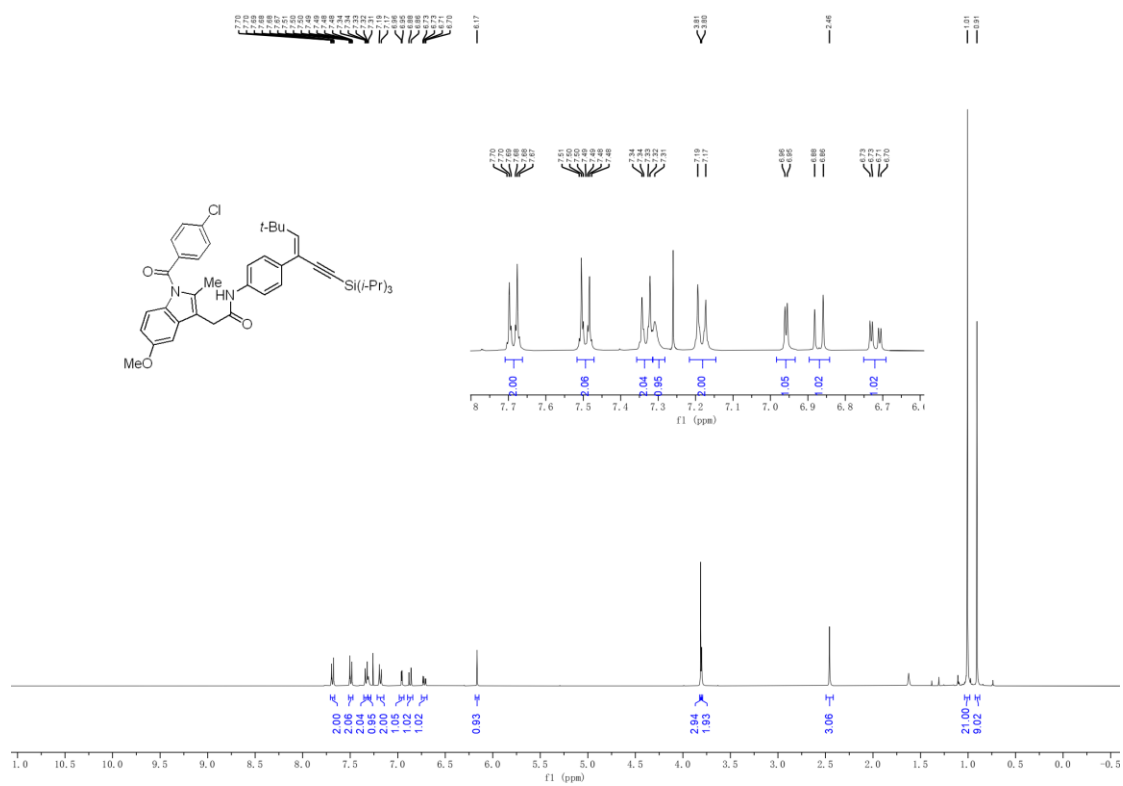
¹H NMR and ¹³C NMR spectra of 4u



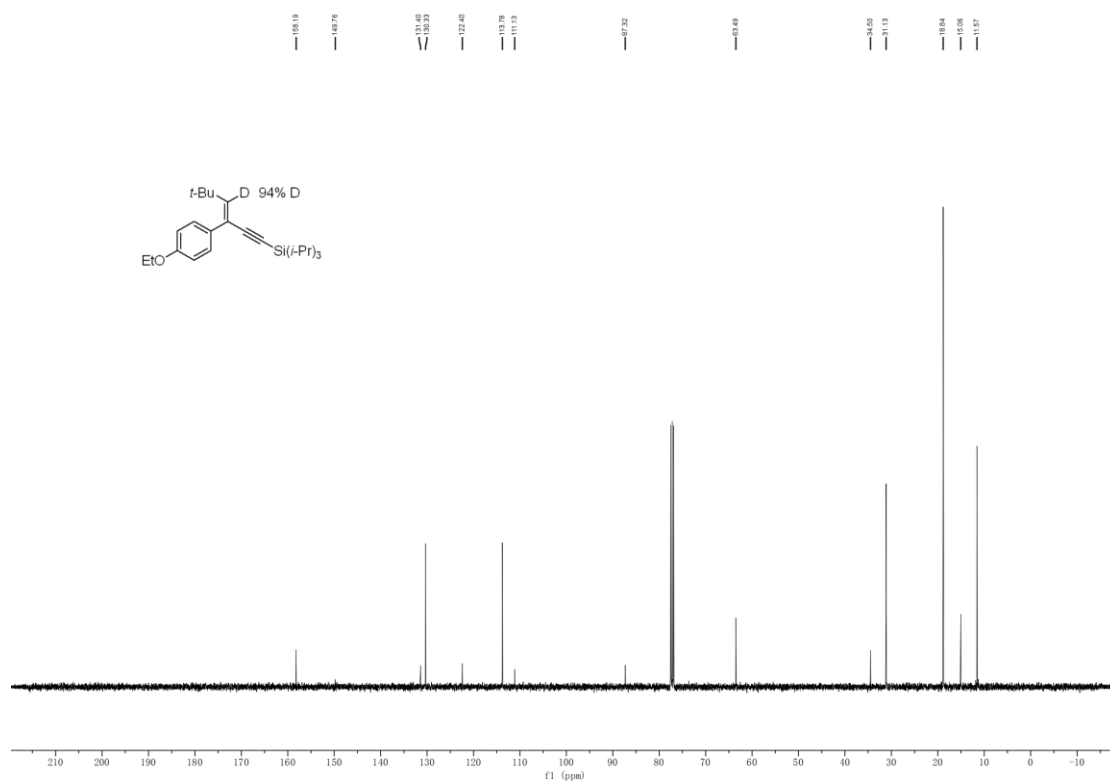




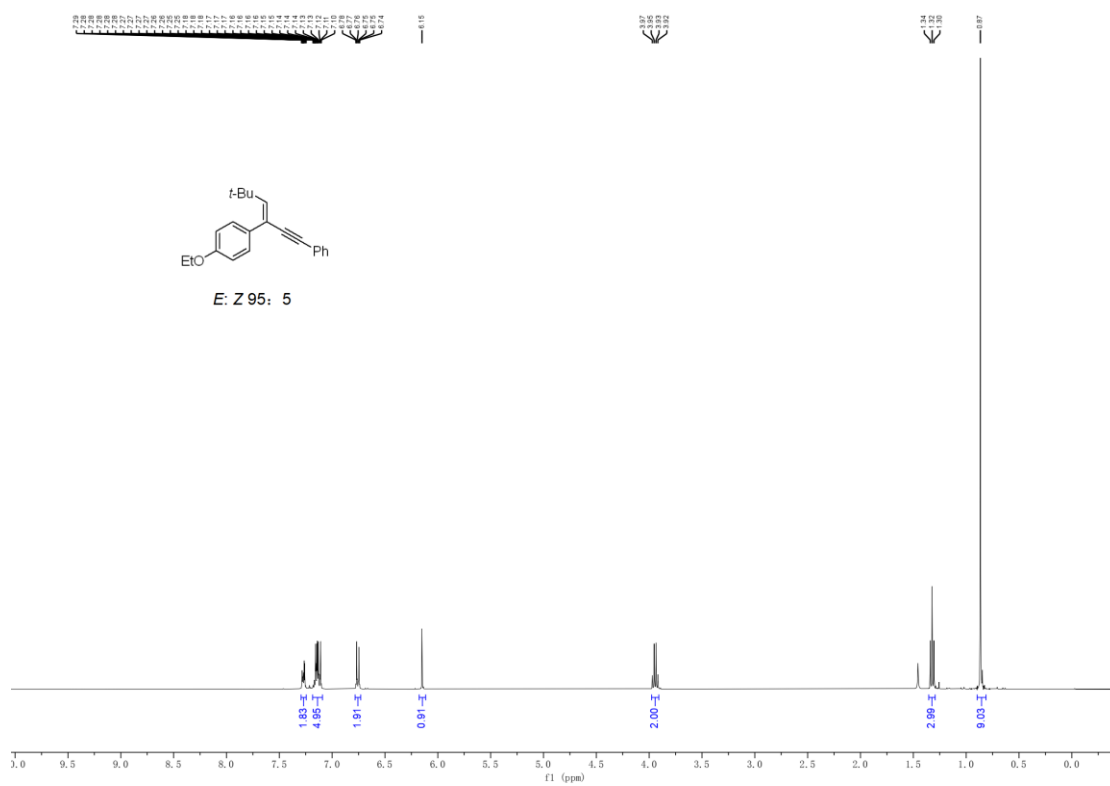
¹H NMR and ¹³C NMR spectra of 4w

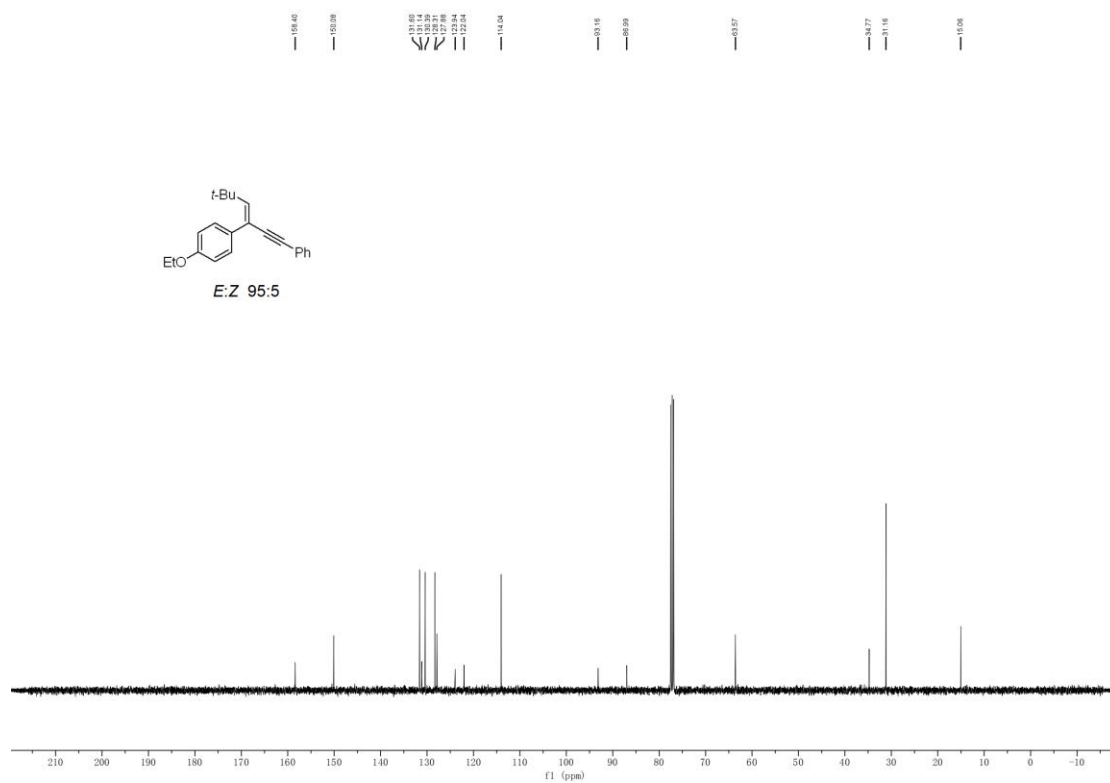




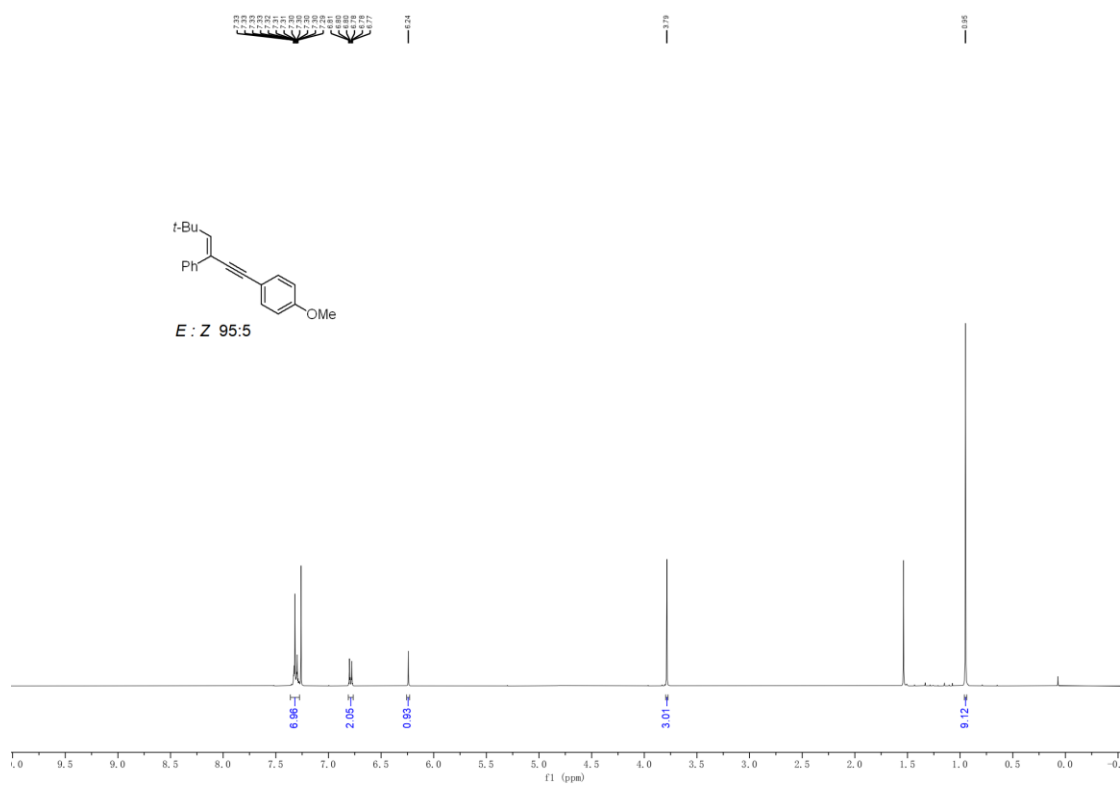


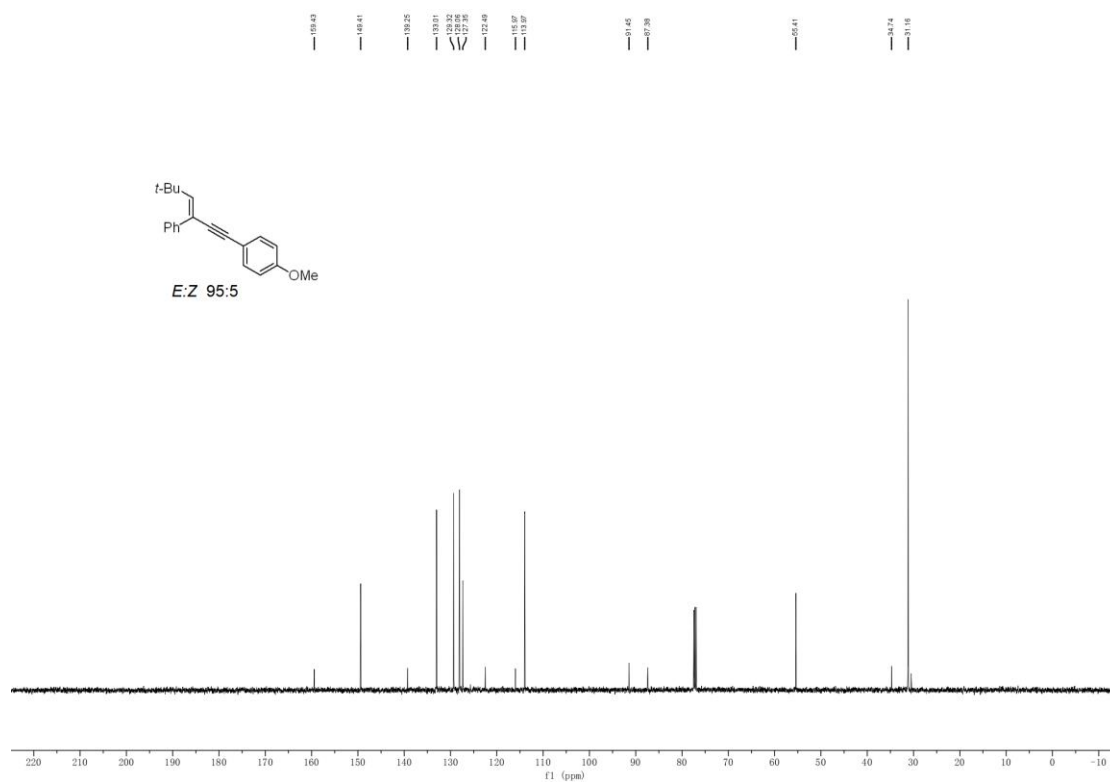
¹H NMR and ¹³C NMR spectra of 4y



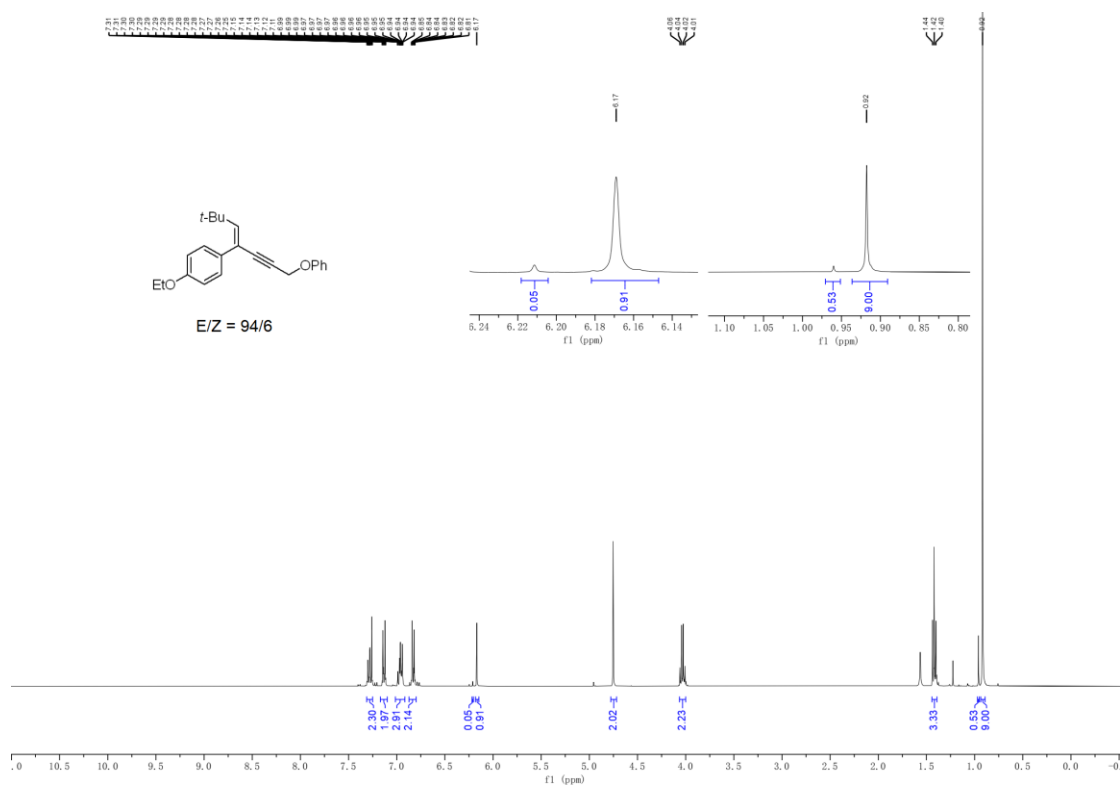


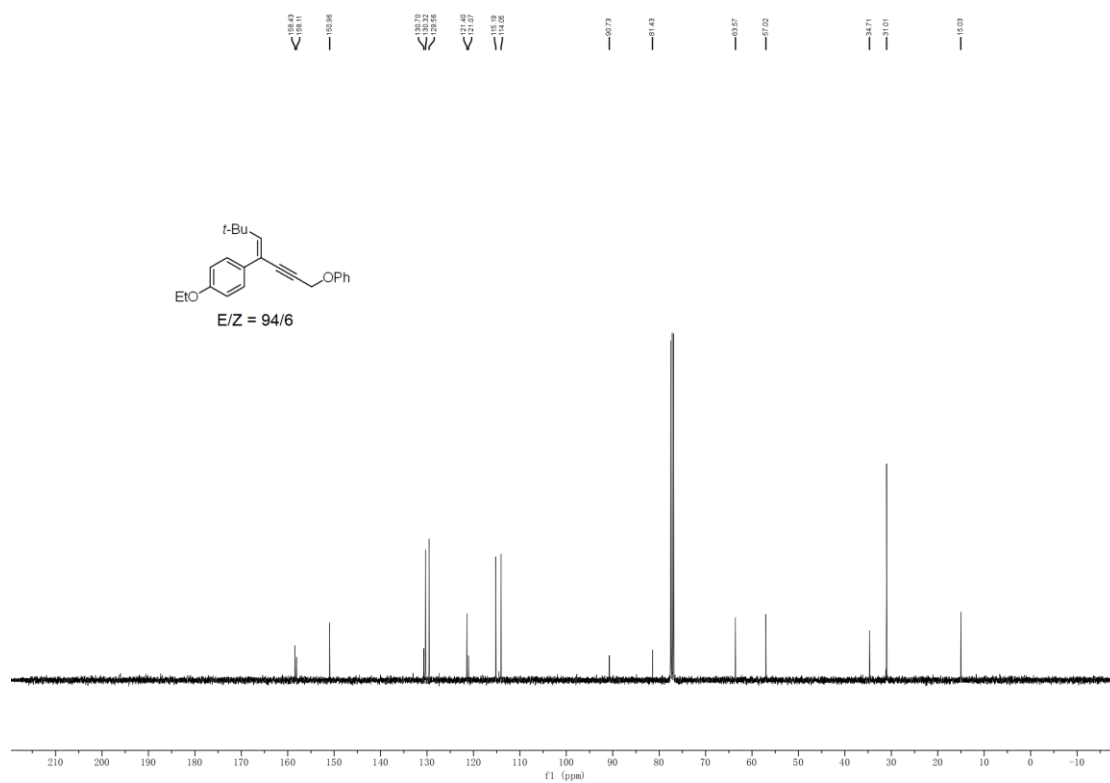
¹H NMR and ¹³C NMR spectra of 4z



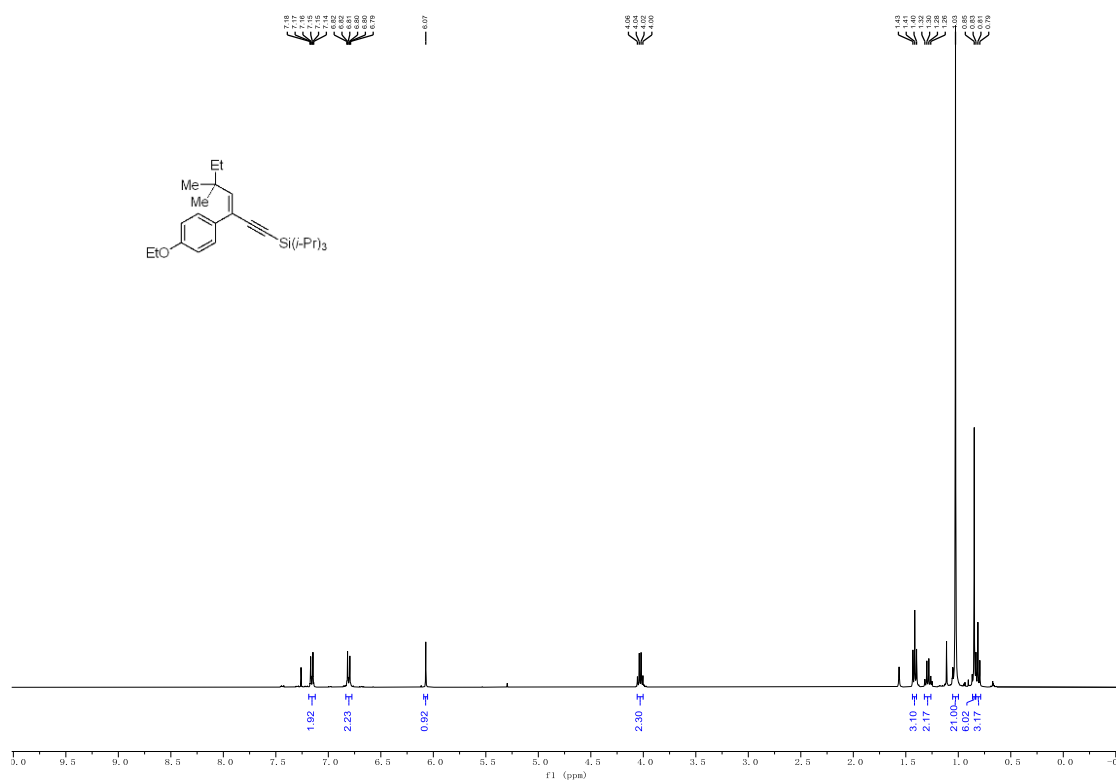


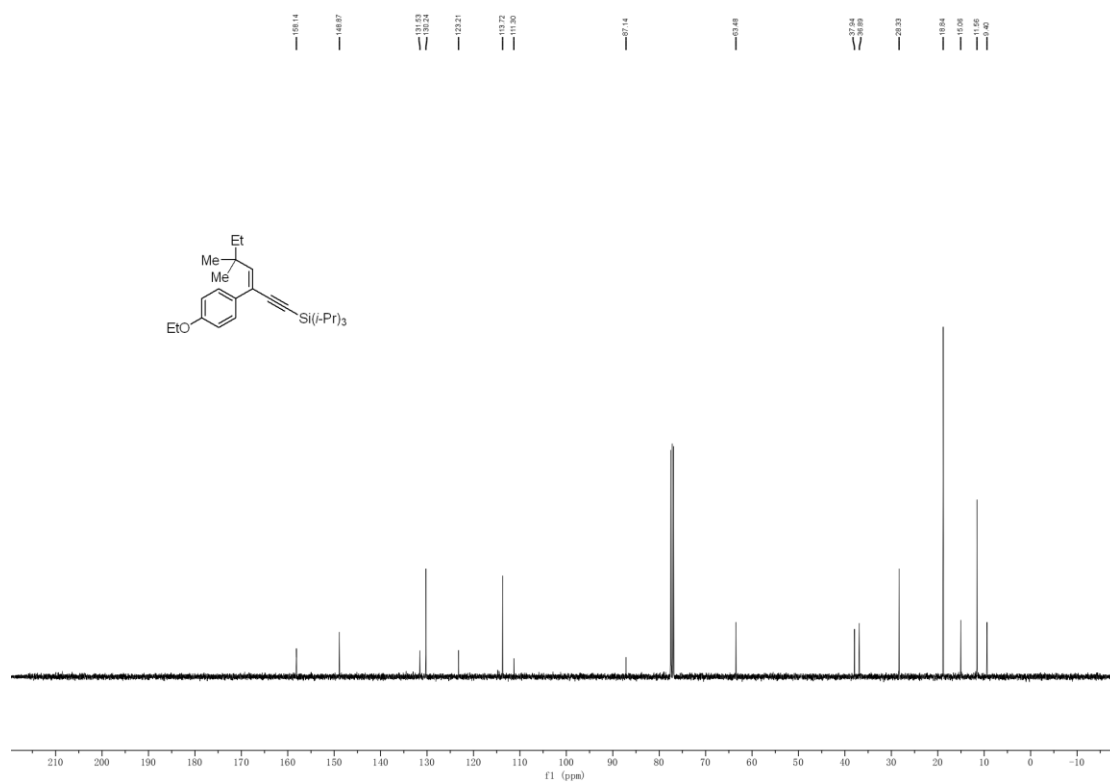
^1H NMR and ^{13}C NMR spectra of 4aa



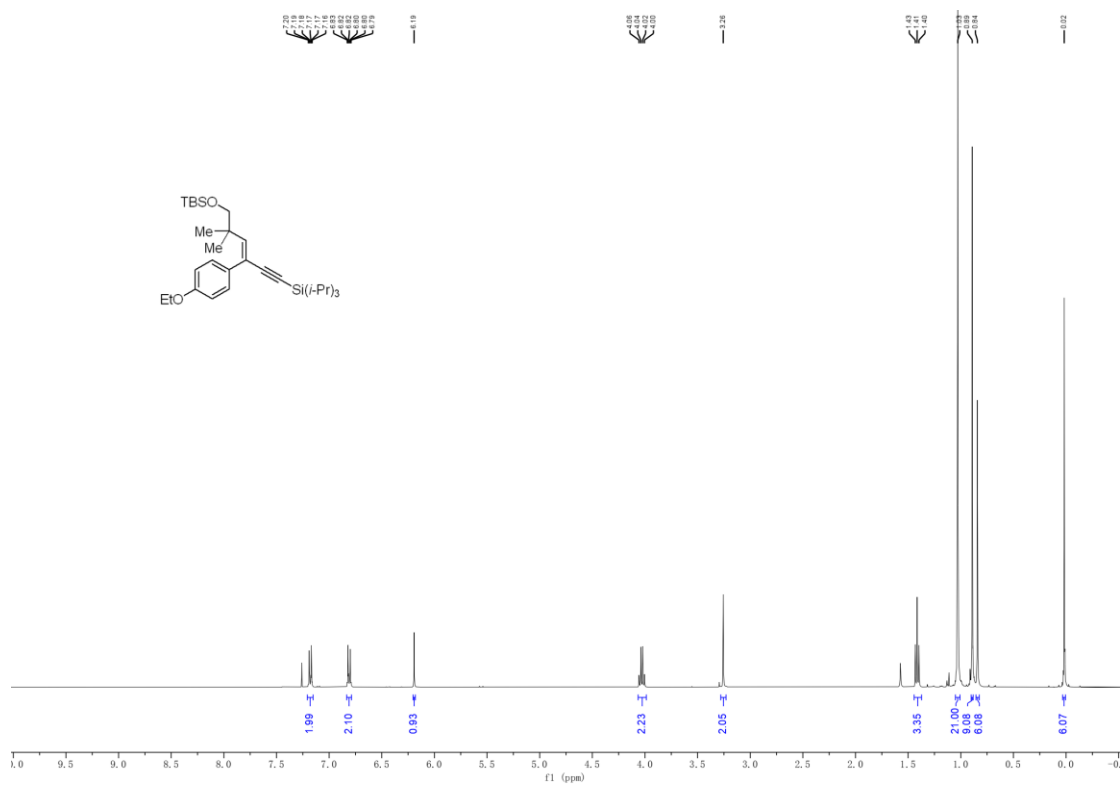


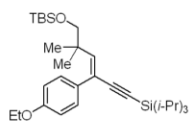
¹H NMR and ¹³C NMR spectra of 4ab





¹H NMR and ¹³C NMR spectra of 4ac



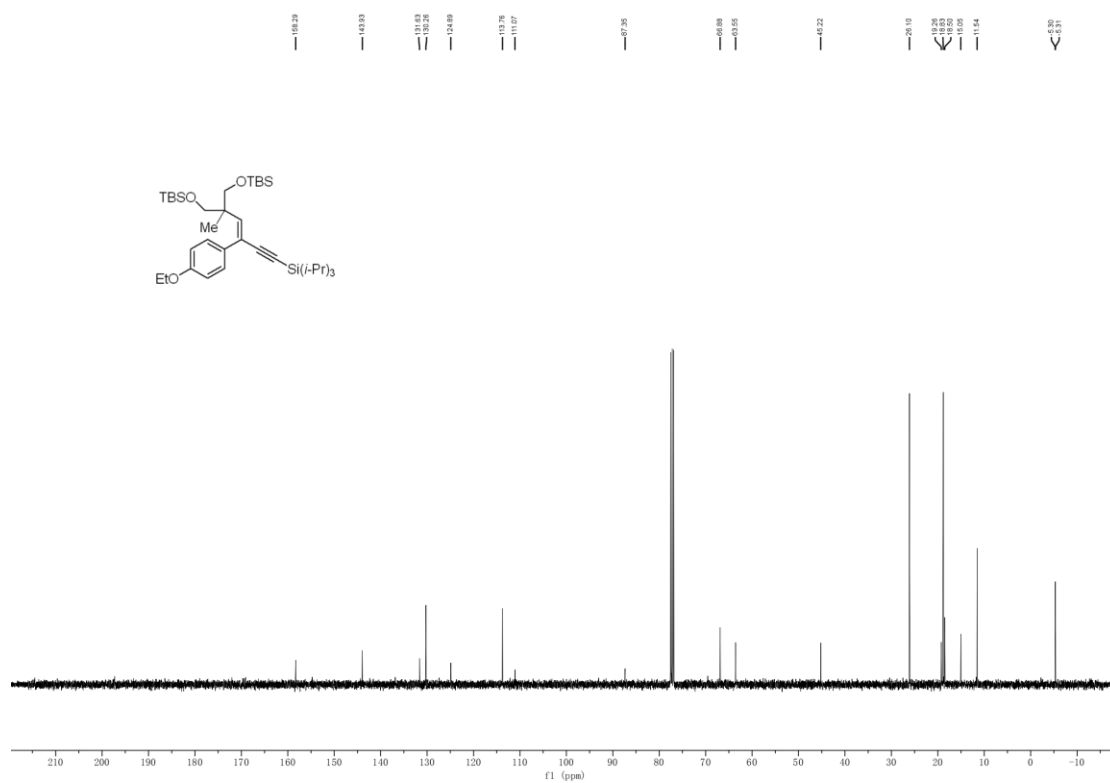


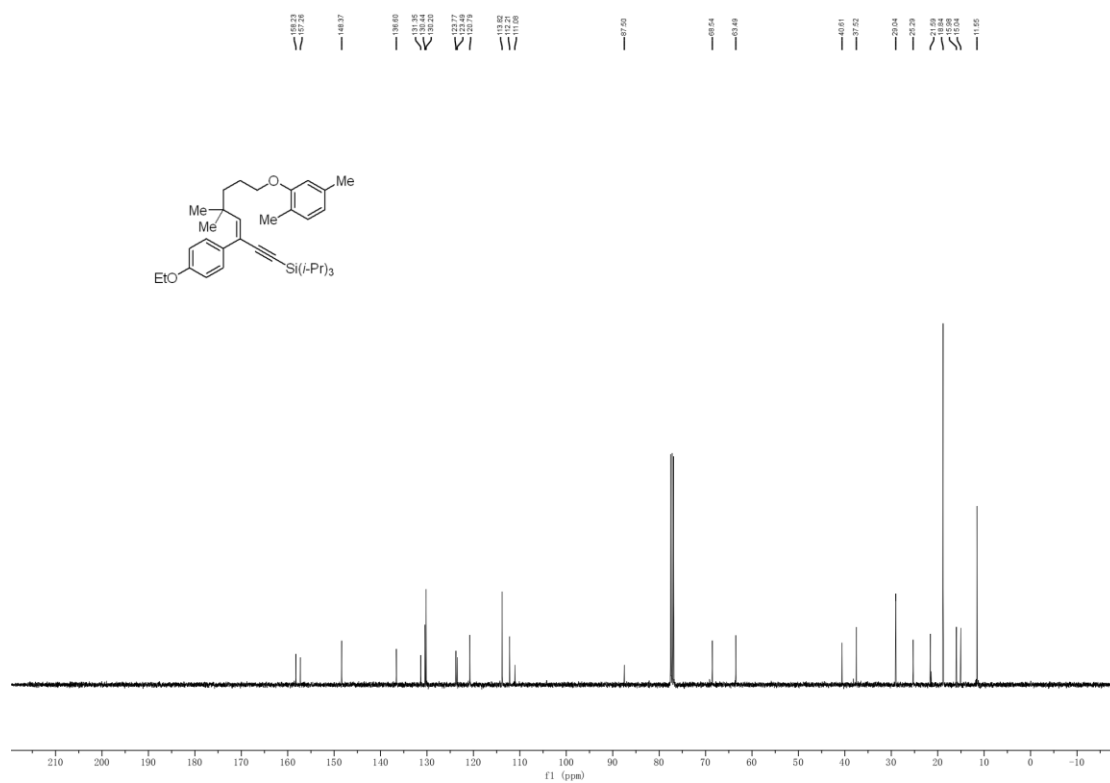
Chemical structure of the compound is shown above the spectrum. The structure is a substituted cyclohexene derivative. It features a cyclohexene ring with a methyl group (Me) at position 1, a tert-butyldimethylsilyloxy (TBSO) group at position 2, and a tert-butyldimethylsilyloxy (OTBS) group at position 3. The ring is also substituted with a 4-ethoxyphenyl group at position 4 and a trimethylsilyl (TMS) group at position 5.

The ¹H NMR spectrum (400 MHz, CDCl₃) shows the following peaks (ppm) and integrations:

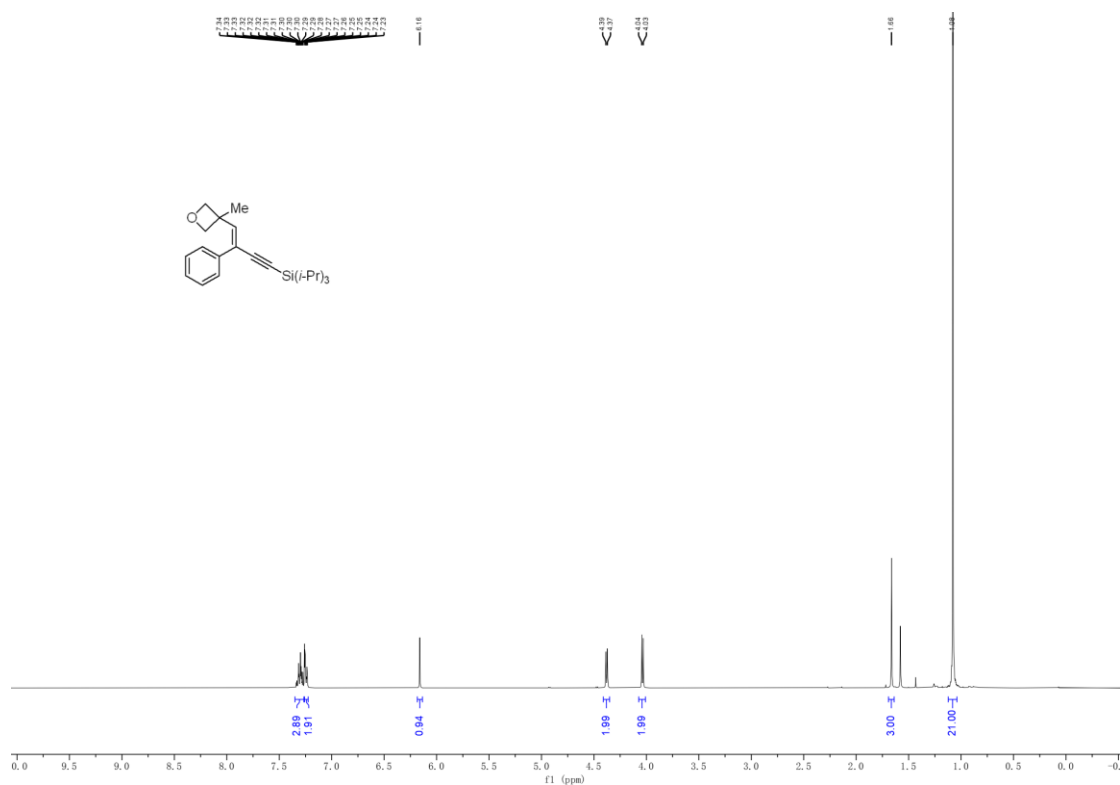
- 7.25 (d, 2H, integration 2.05)
- 7.15 (d, 2H, integration 2.09)
- 6.15 (s, 1H, integration 0.99)
- 4.05 (s, 2H, integration 2.25)
- 3.45 (s, 2H, integration 4.03)
- 1.55 (s, 3H, integration 3.35)
- 1.45 (s, 9H, integration 21.00)
- 1.35 (s, 9H, integration 18.06)
- 1.25 (s, 3H, integration 3.13)
- 0.05 (s, 3H, integration 5.89)
- 0.00 (s, 3H, integration 6.01)

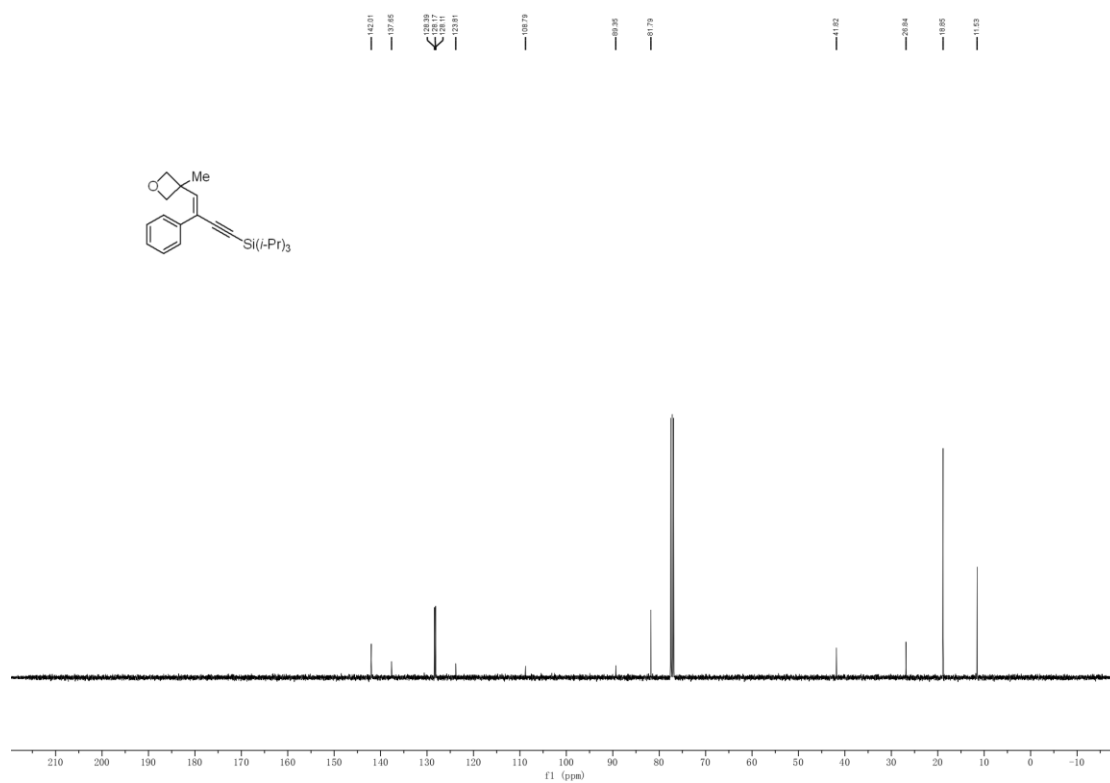
The spectrum is labeled "f1 (ppm)" on the x-axis, ranging from 0.0 to 10.5 ppm.



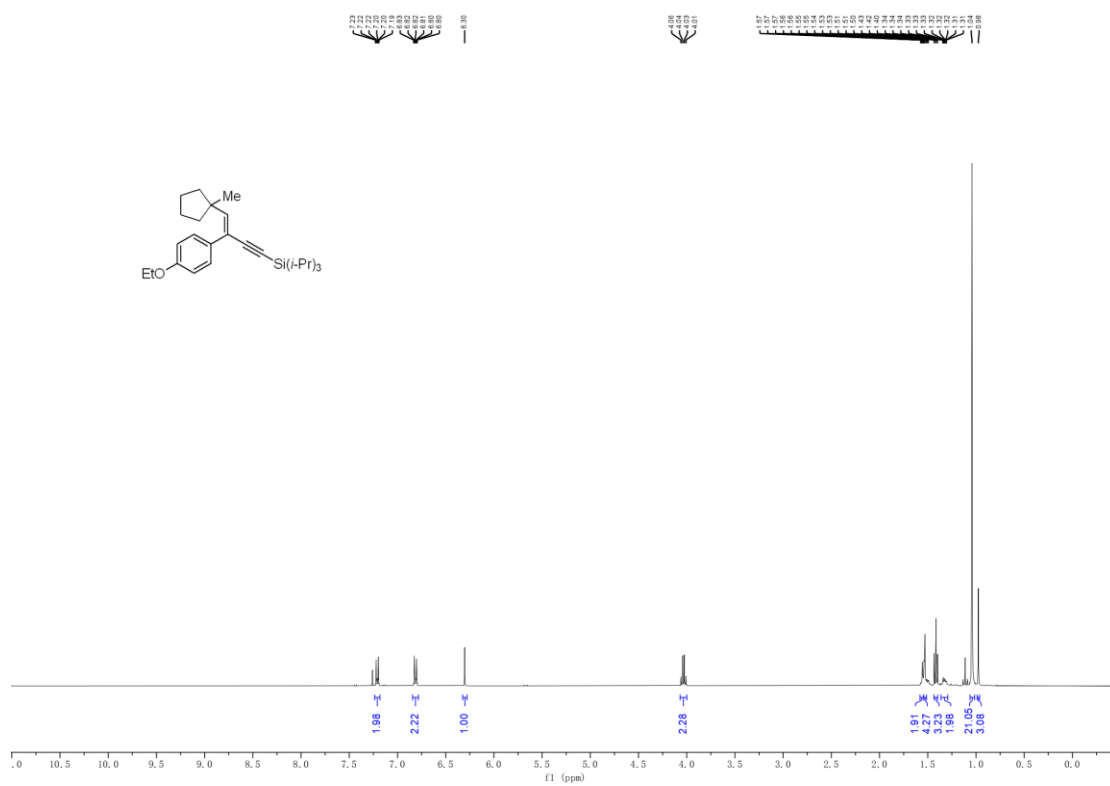


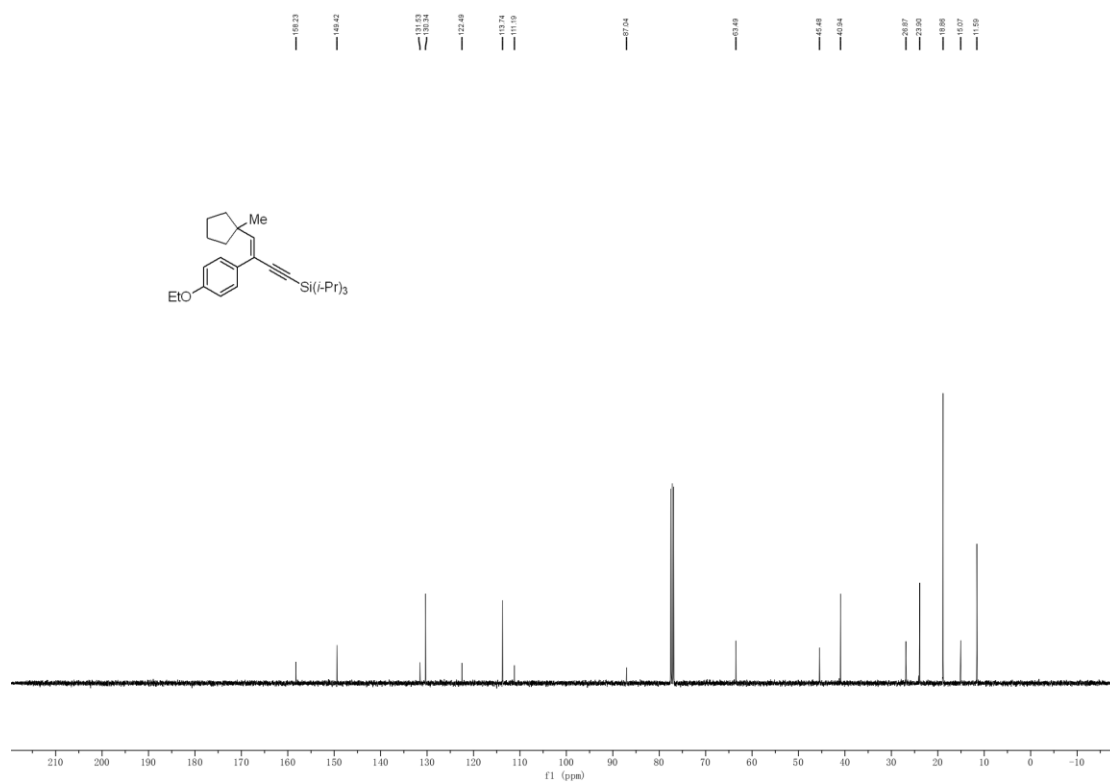
¹H NMR and ¹³C NMR spectra of 4af



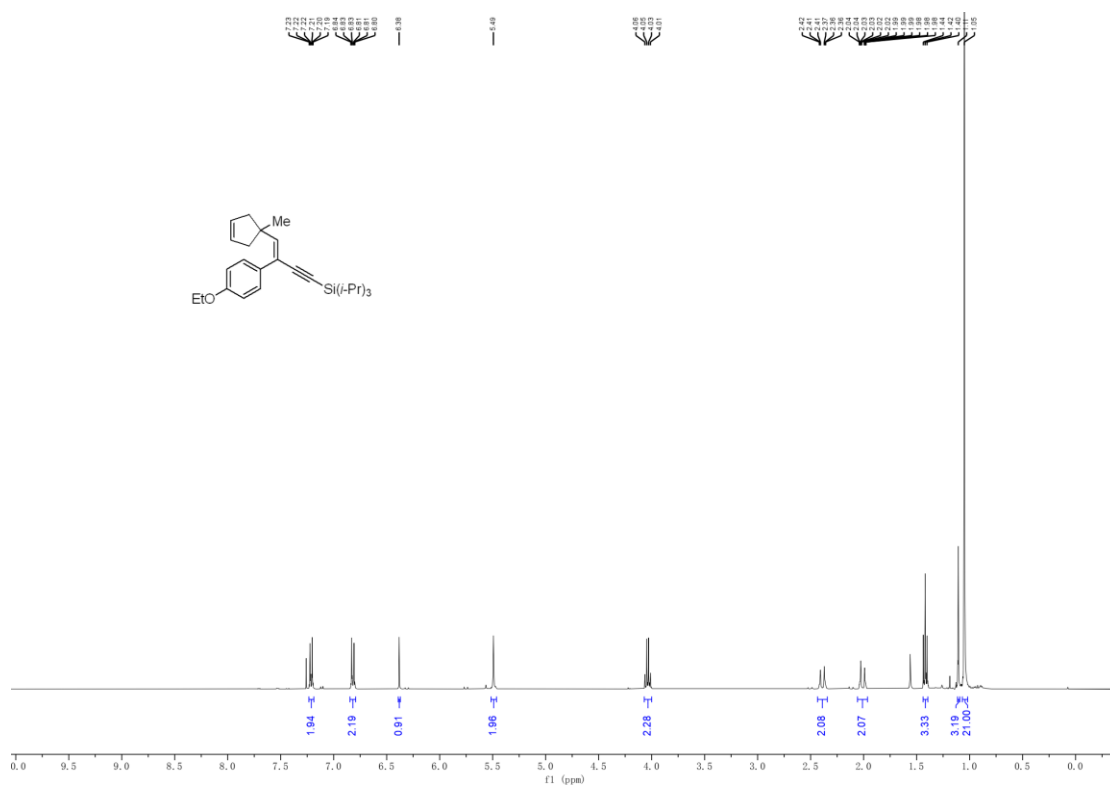


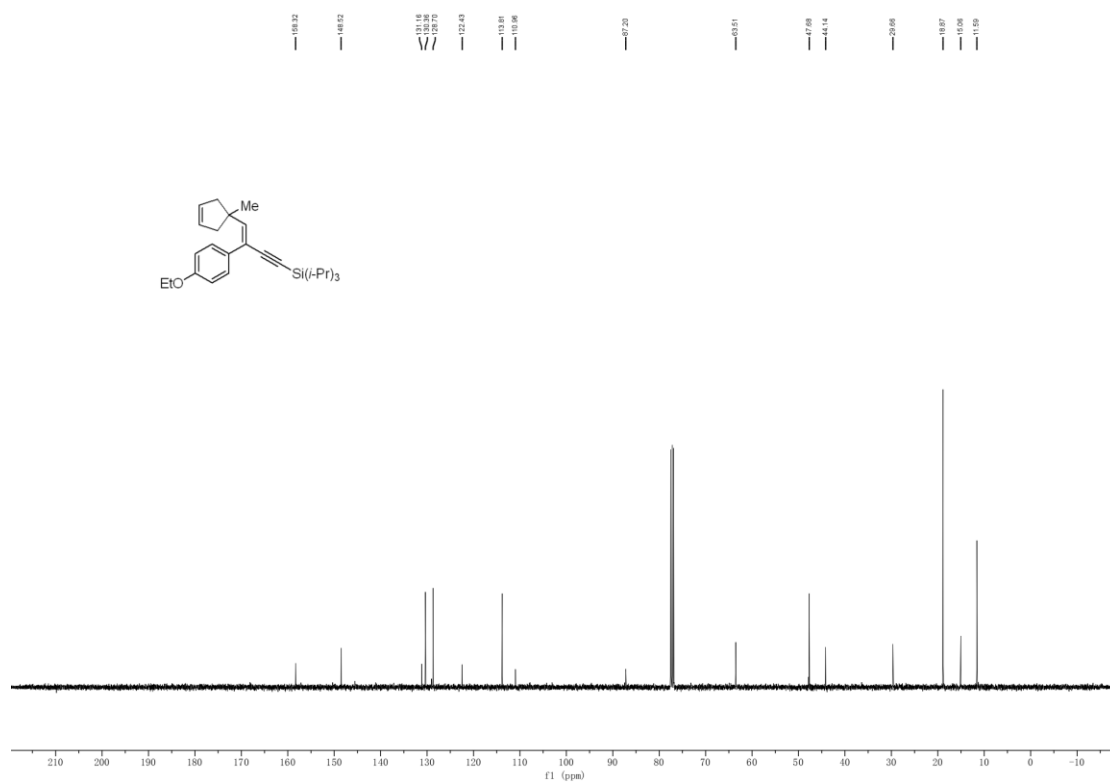
¹H NMR and ¹³C NMR spectra of 4ag



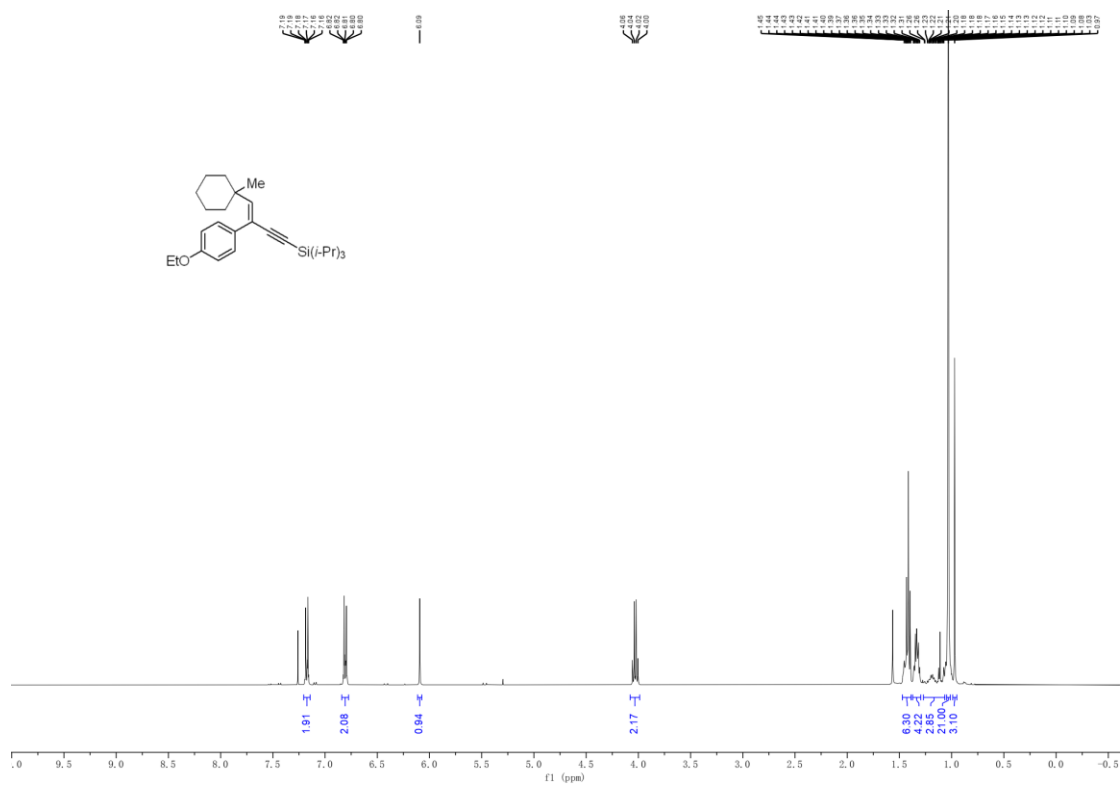


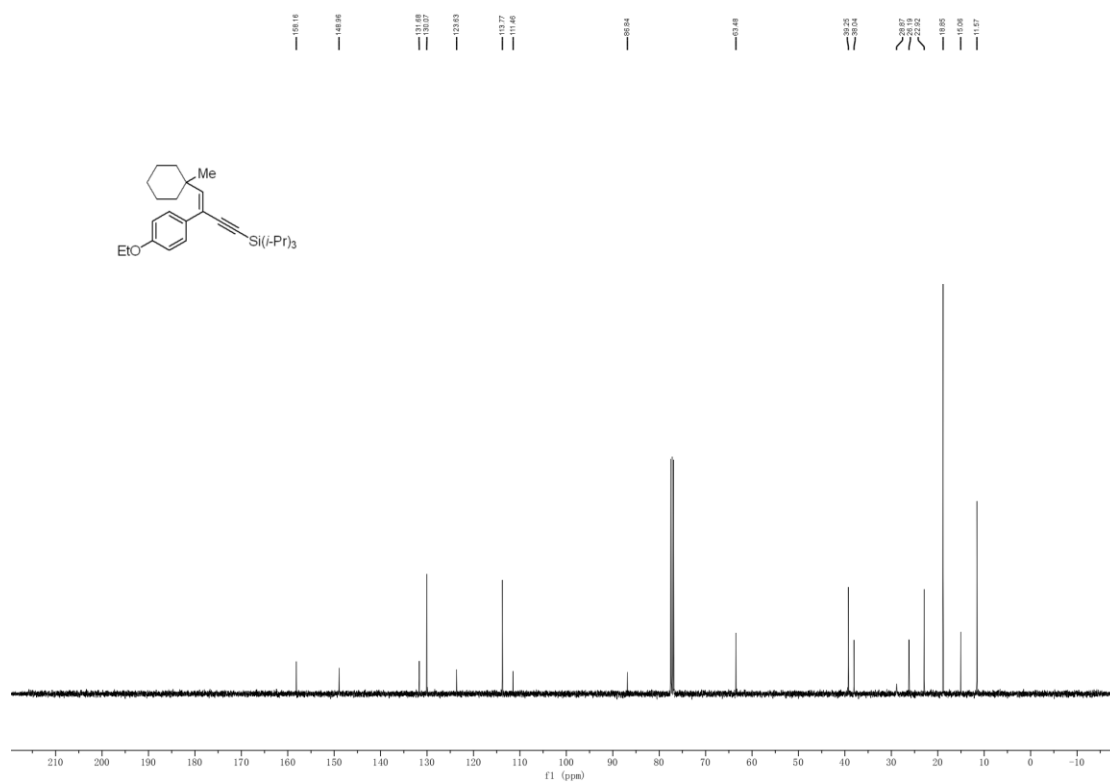
¹H NMR and ¹³C NMR spectra of 4ah



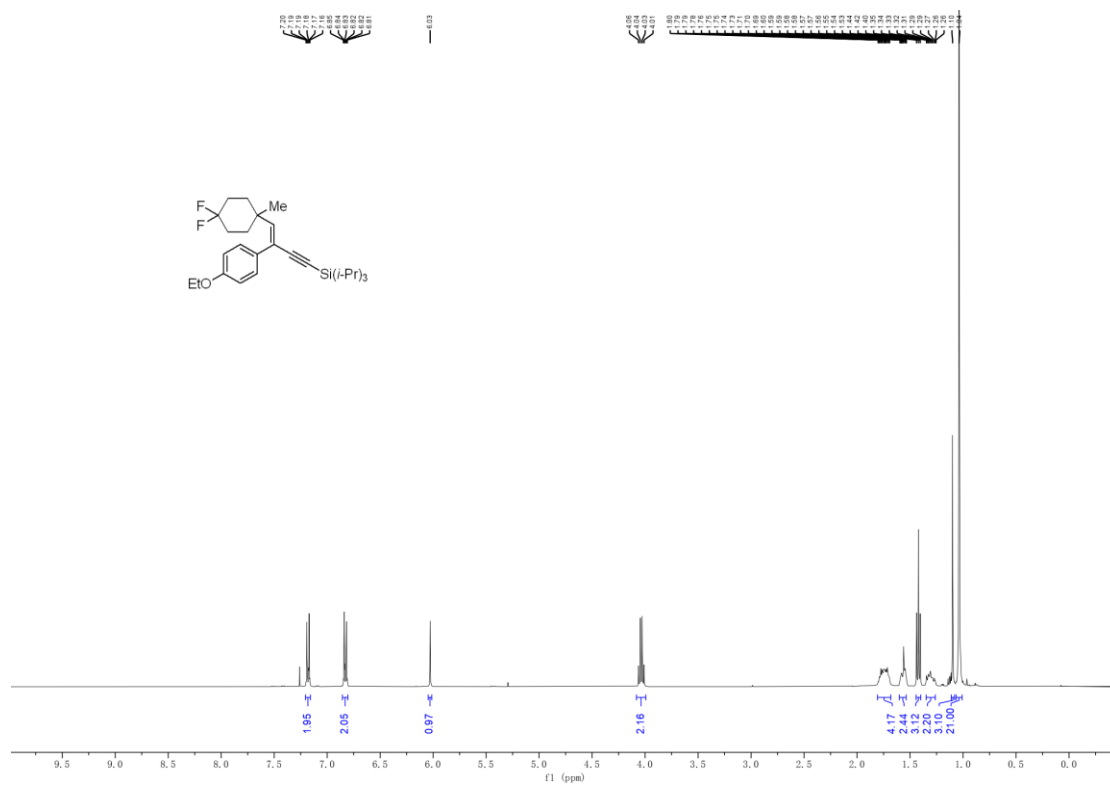


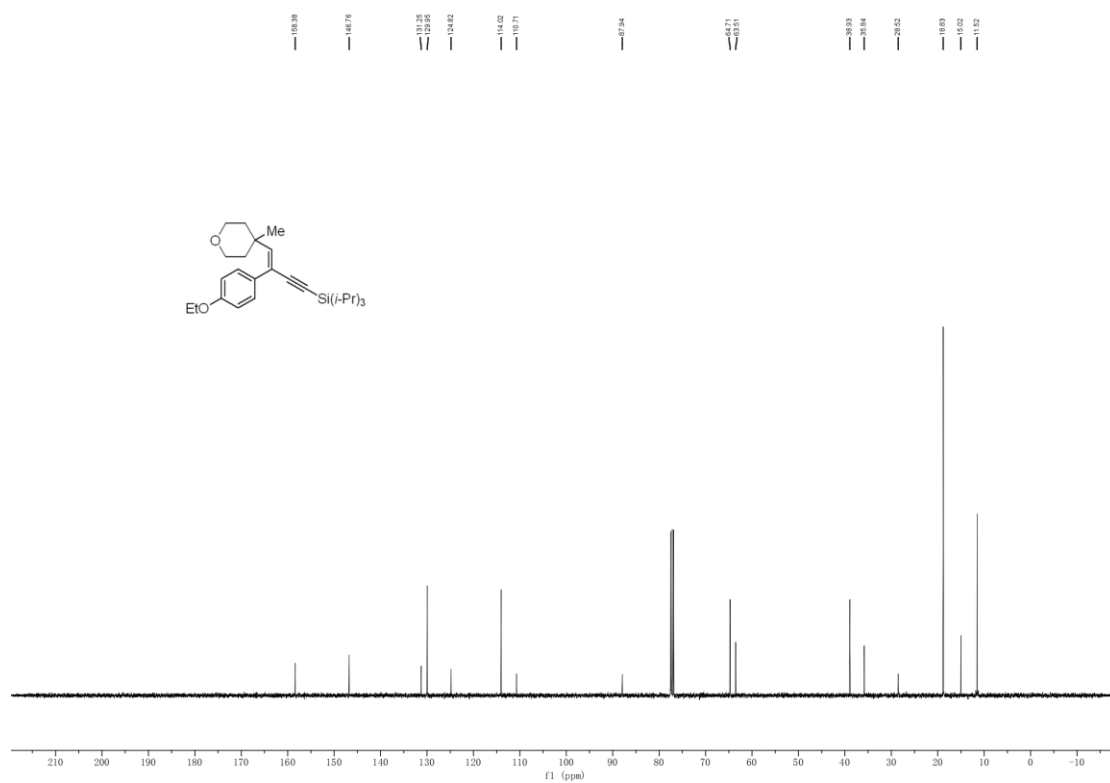
¹H NMR and ¹³C NMR spectra of 4ai



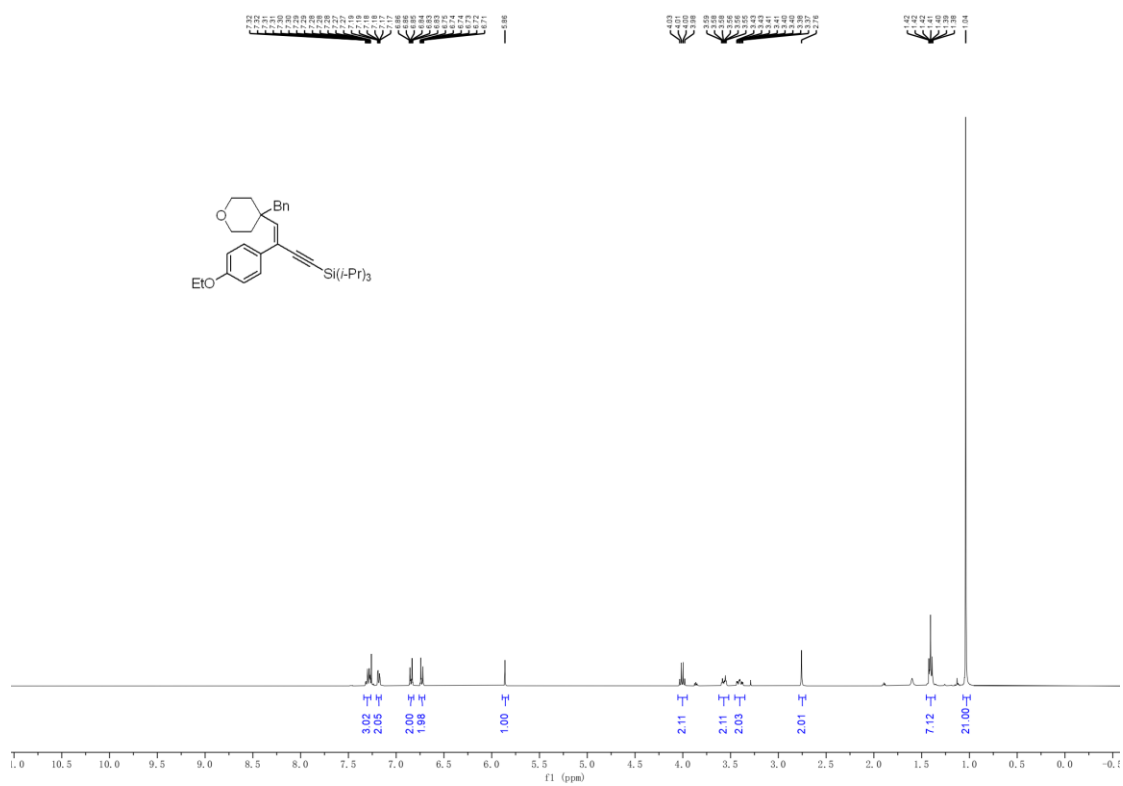


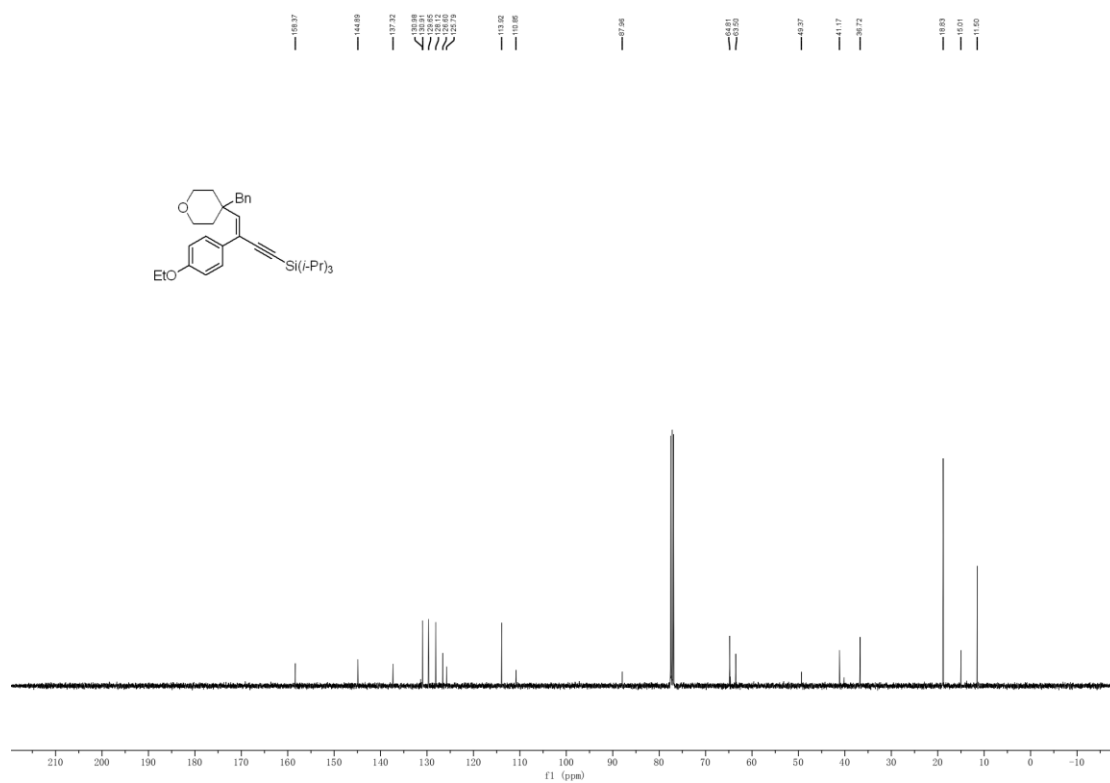
¹H NMR and ¹³C NMR spectra of 4aj



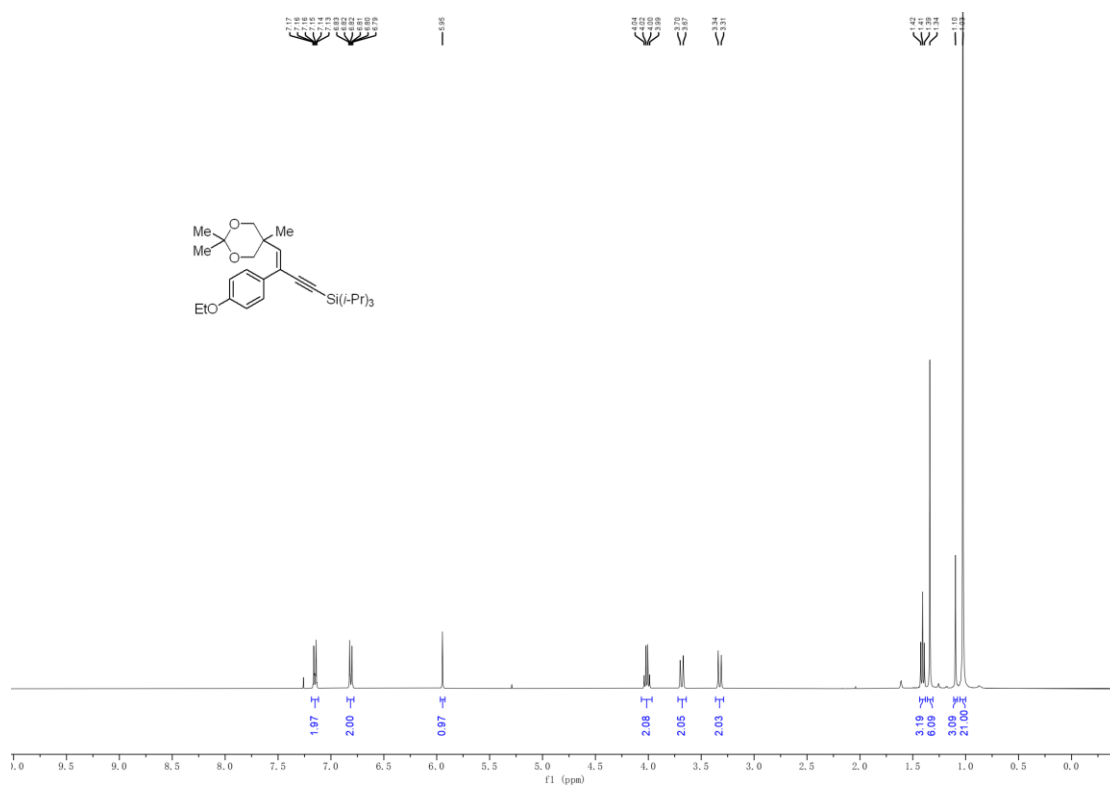


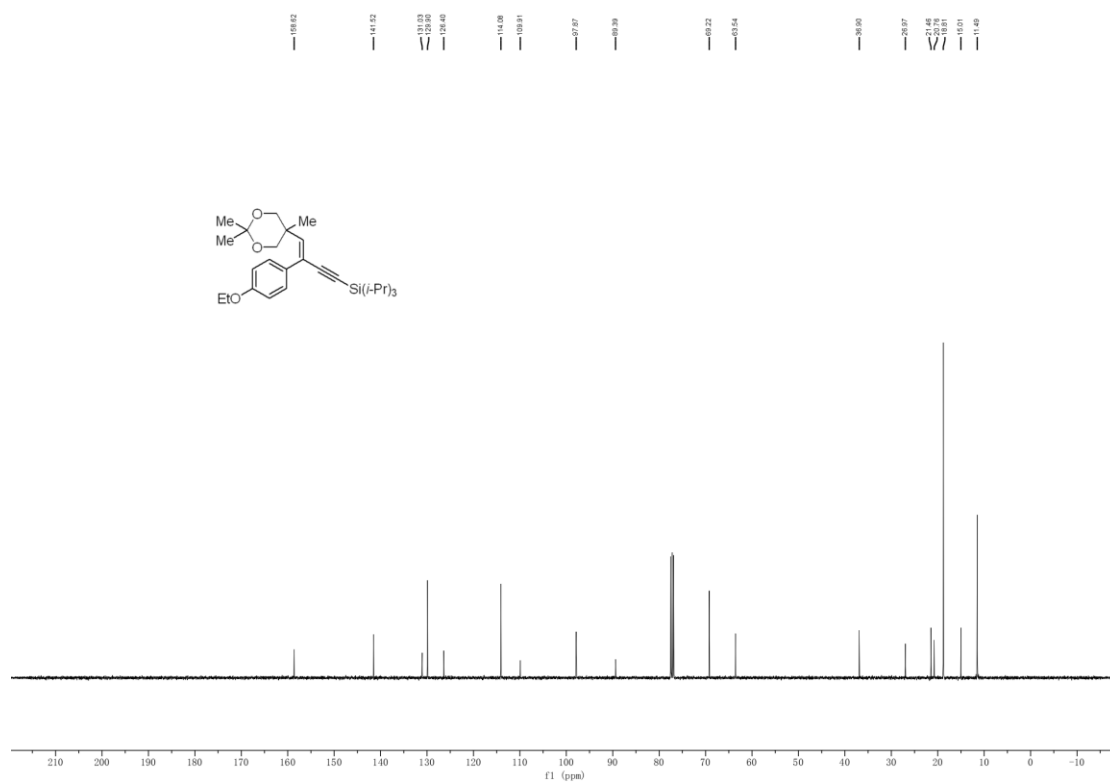
¹H NMR and ¹³C NMR spectra of 4aI



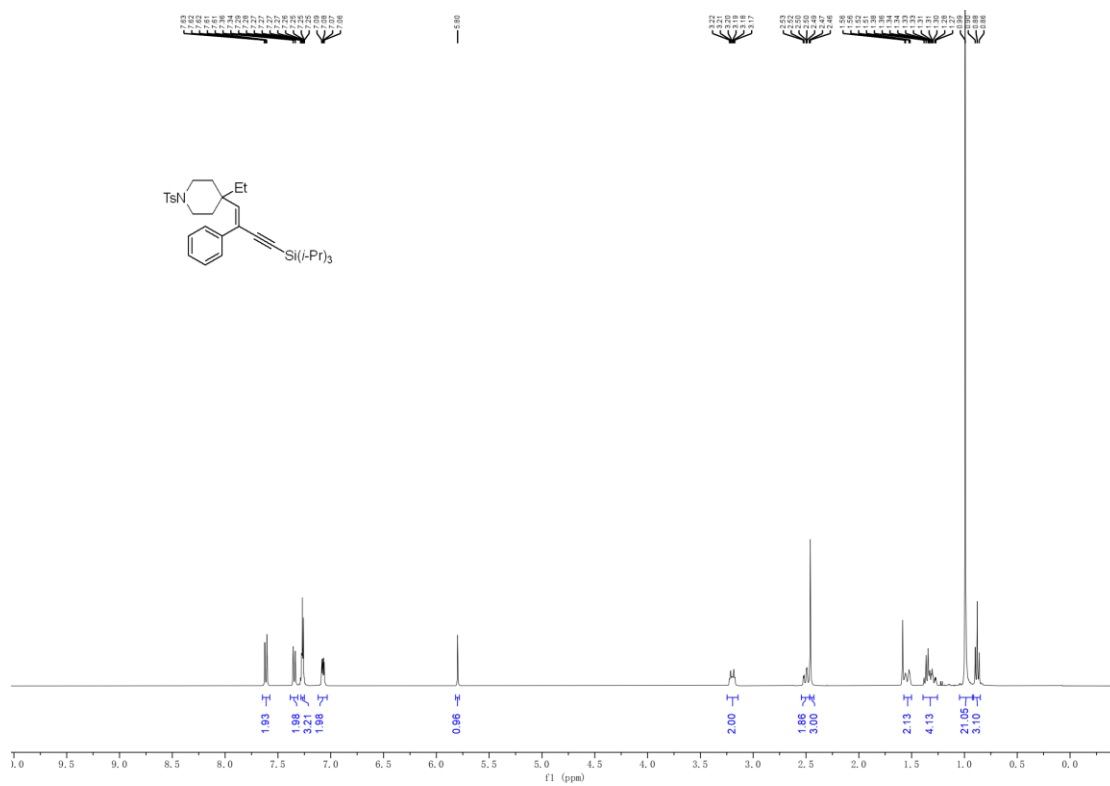


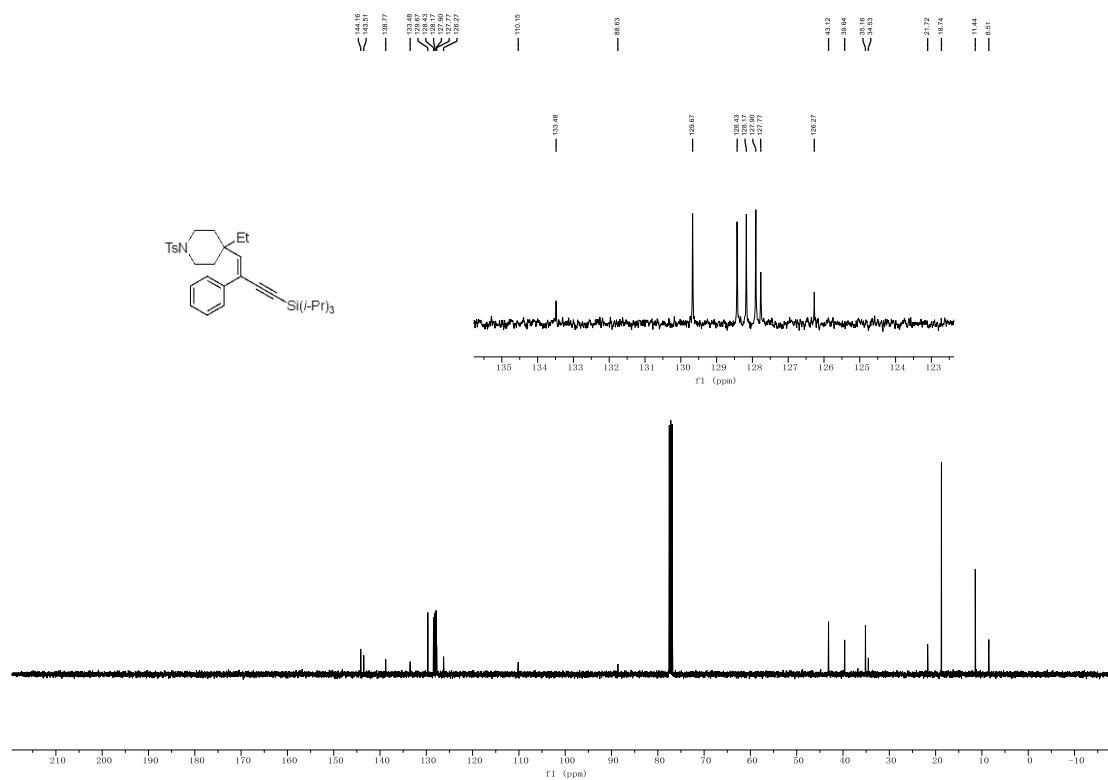
¹H NMR and ¹³C NMR spectra of 4am



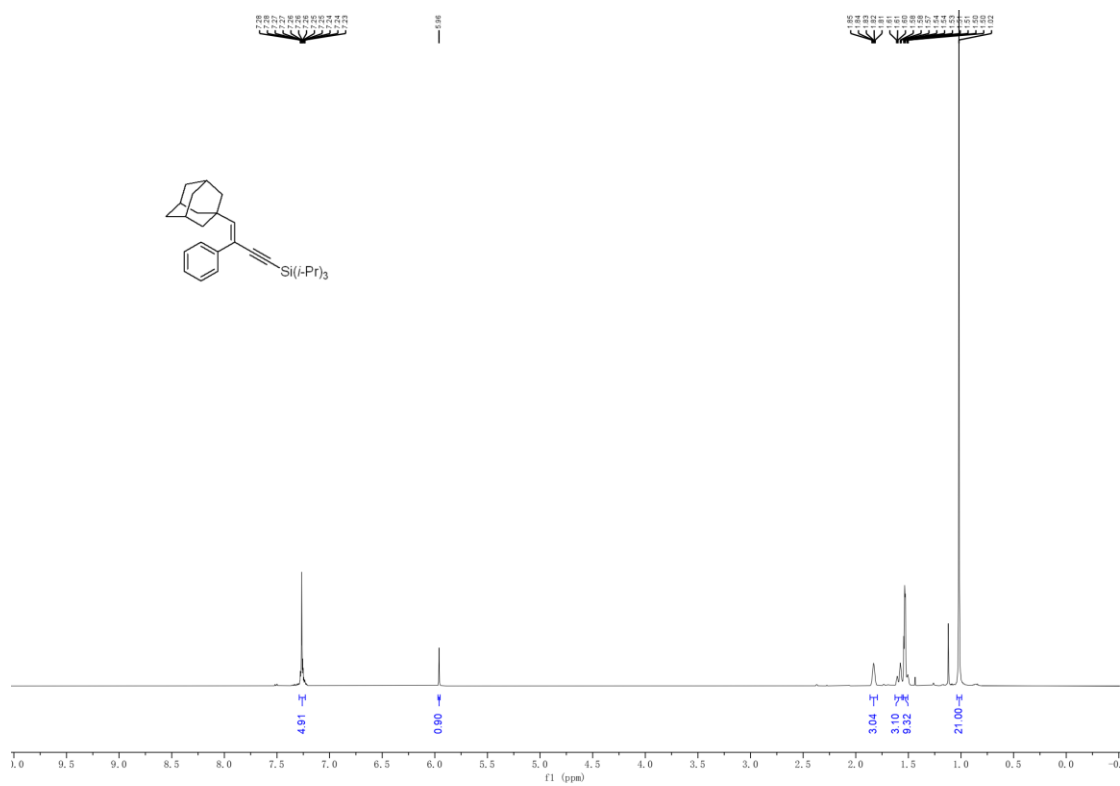


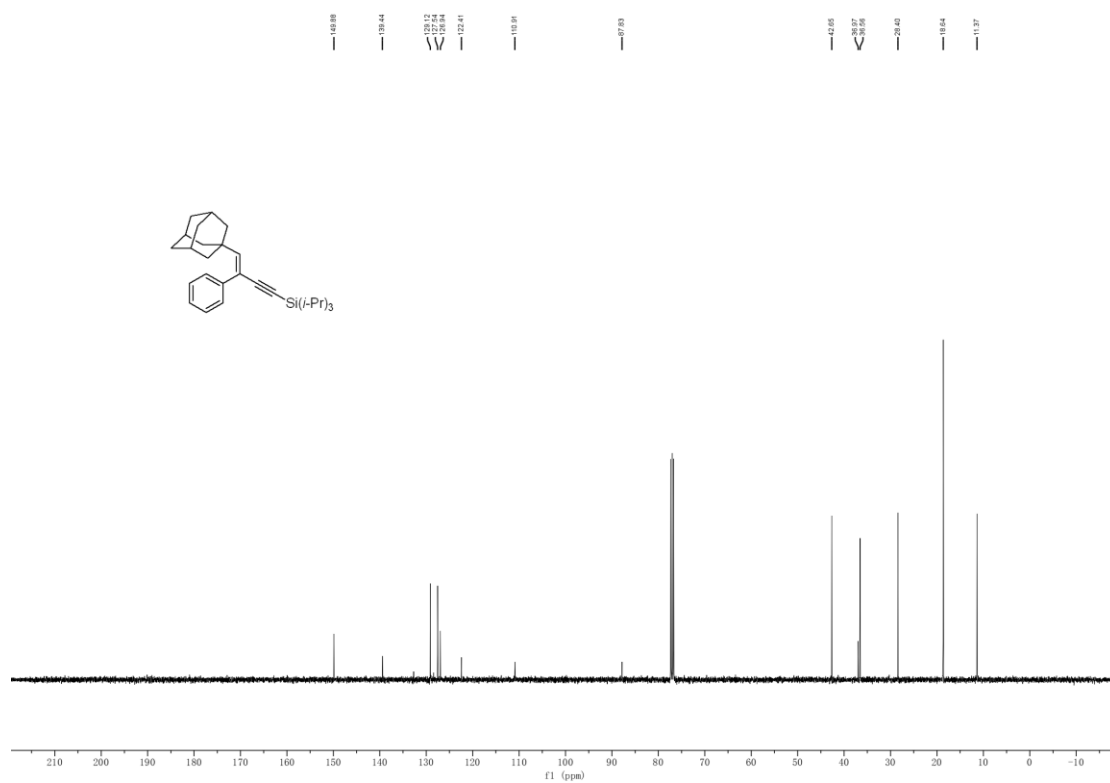
¹H NMR and ¹³C NMR spectra of 4an



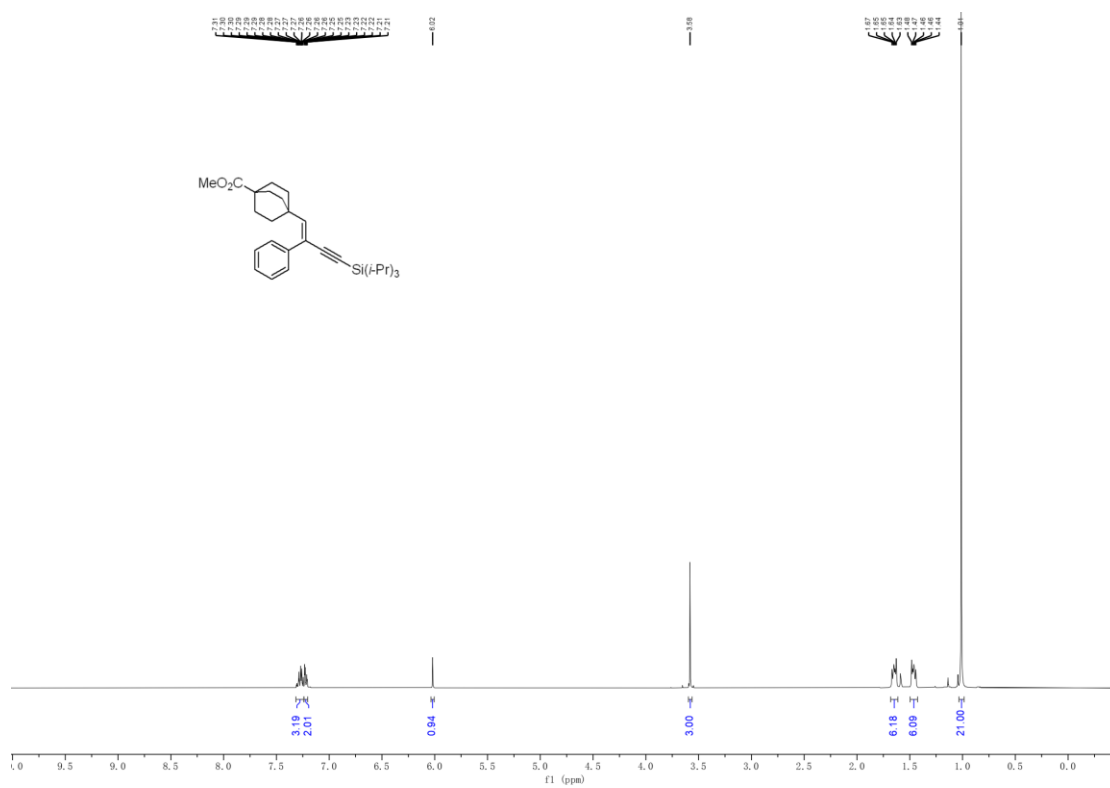


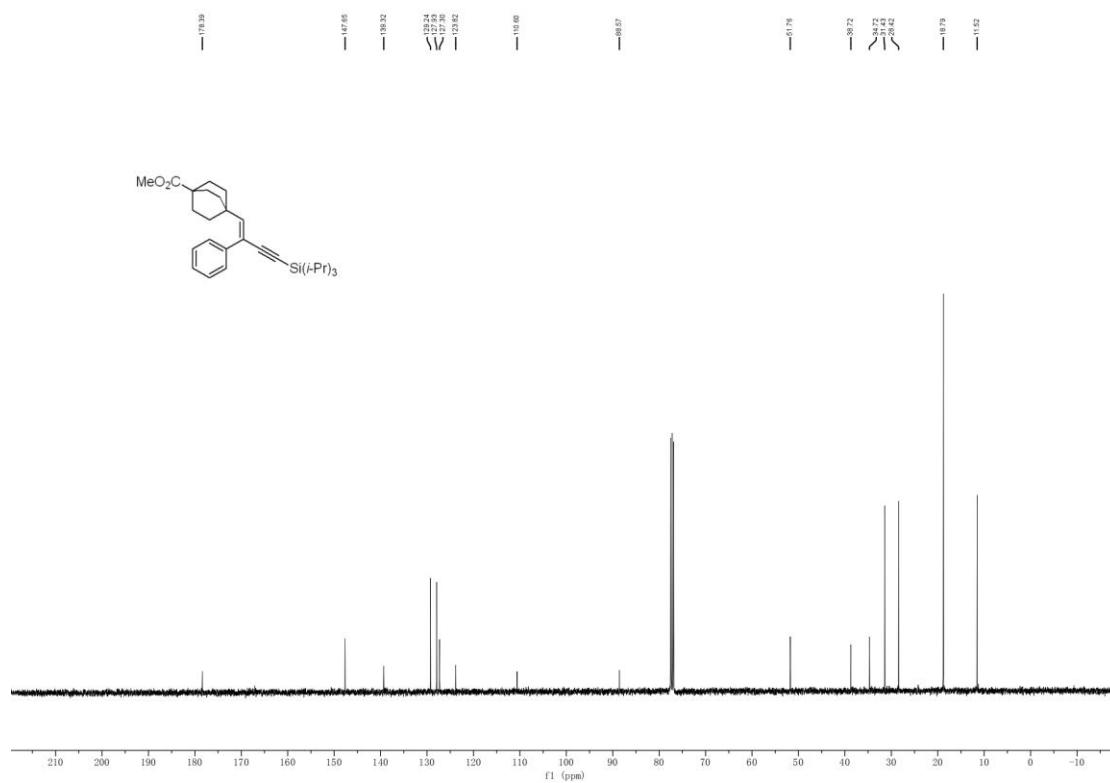
¹H NMR and ¹³C NMR spectra of 4a0



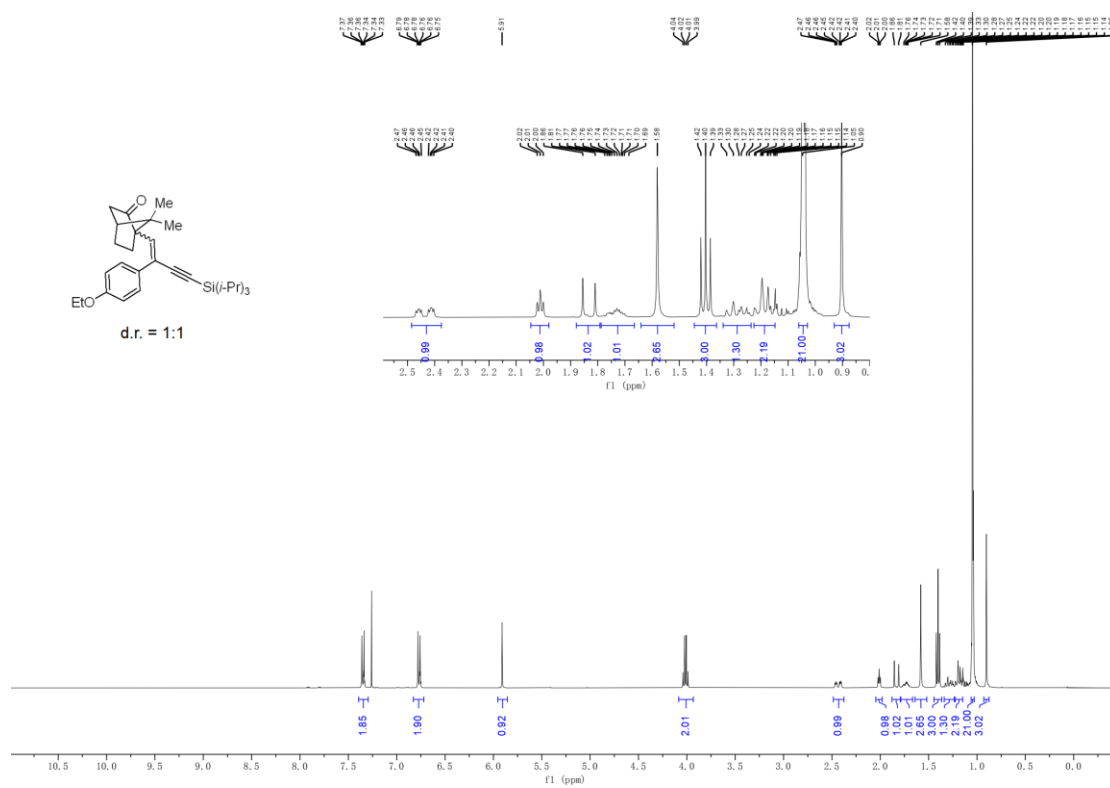


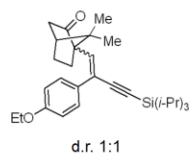
¹H NMR and ¹³C NMR spectra of 4ap





¹H NMR and ¹³C NMR spectra of 4a



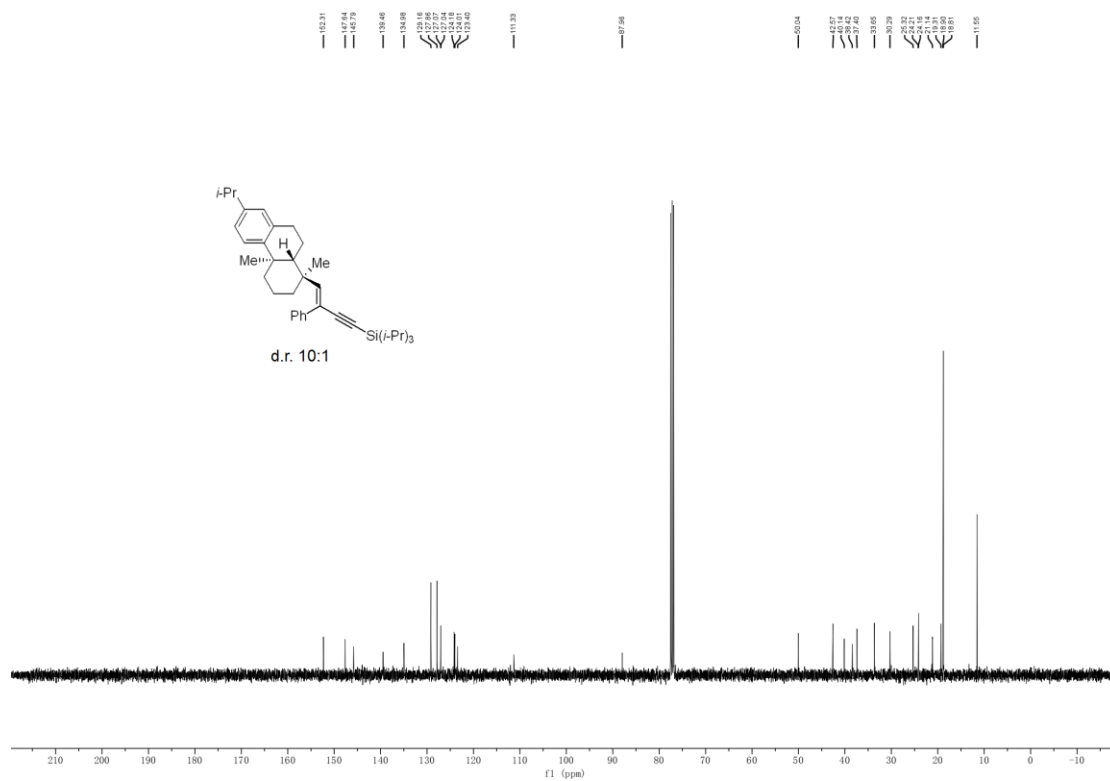


Chemical structure of the compound is shown above the spectrum. The structure is a complex polycyclic molecule featuring a phenyl group, a propargyl group, and a trimethylsilyl group, with stereochemistry indicated by wedges and dashes.

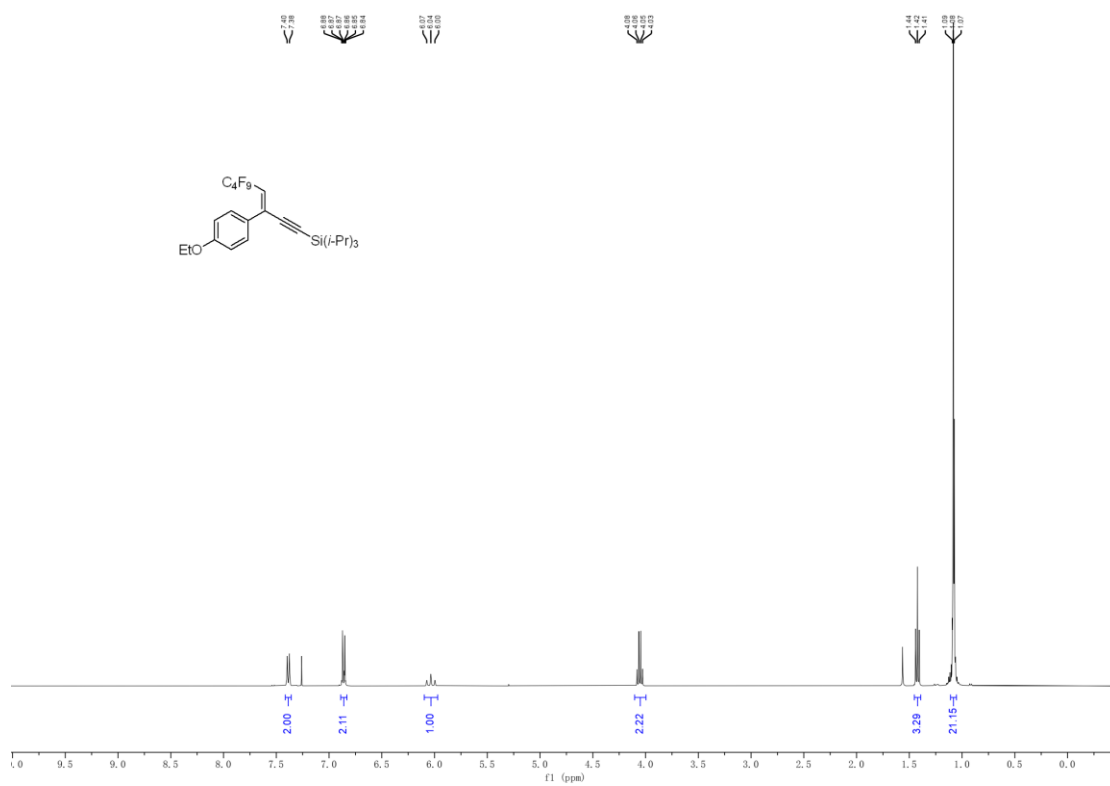
The ¹H NMR spectrum (400 MHz, CDCl₃) displays the following peaks (ppm):

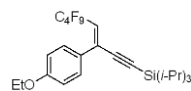
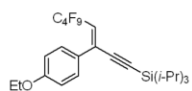
- 7.52 (d, 1H)
- 7.42 (d, 1H)
- 7.39 (d, 1H)
- 7.35 (d, 1H)
- 7.29 (d, 1H)
- 7.25 (d, 1H)
- 7.10 (d, 1H)
- 6.84 (d, 1H)
- 2.97 (d, 1H)
- 2.79 (d, 1H)
- 2.75 (d, 1H)
- 2.71 (d, 1H)
- 2.67 (d, 1H)
- 2.63 (d, 1H)
- 2.59 (d, 1H)
- 2.55 (d, 1H)
- 2.51 (d, 1H)
- 2.47 (d, 1H)
- 2.43 (d, 1H)
- 2.39 (d, 1H)
- 2.35 (d, 1H)
- 2.31 (d, 1H)
- 2.27 (d, 1H)
- 2.23 (d, 1H)
- 2.19 (d, 1H)
- 2.15 (d, 1H)
- 2.11 (d, 1H)
- 2.07 (d, 1H)
- 2.03 (d, 1H)
- 1.99 (d, 1H)
- 1.95 (d, 1H)
- 1.91 (d, 1H)
- 1.87 (d, 1H)
- 1.83 (d, 1H)
- 1.79 (d, 1H)
- 1.75 (d, 1H)
- 1.71 (d, 1H)
- 1.67 (d, 1H)
- 1.63 (d, 1H)
- 1.59 (d, 1H)
- 1.55 (d, 1H)
- 1.51 (d, 1H)
- 1.47 (d, 1H)
- 1.43 (d, 1H)
- 1.39 (d, 1H)
- 1.35 (d, 1H)
- 1.31 (d, 1H)
- 1.27 (d, 1H)
- 1.23 (d, 1H)
- 1.19 (d, 1H)
- 1.15 (d, 1H)
- 1.11 (d, 1H)
- 1.07 (d, 1H)
- 1.03 (d, 1H)
- 0.99 (d, 1H)
- 0.95 (d, 1H)
- 0.91 (d, 1H)
- 0.87 (d, 1H)
- 0.83 (d, 1H)
- 0.79 (d, 1H)
- 0.75 (d, 1H)
- 0.71 (d, 1H)
- 0.67 (d, 1H)
- 0.63 (d, 1H)
- 0.59 (d, 1H)
- 0.55 (d, 1H)
- 0.51 (d, 1H)
- 0.47 (d, 1H)
- 0.43 (d, 1H)
- 0.39 (d, 1H)
- 0.35 (d, 1H)
- 0.31 (d, 1H)
- 0.27 (d, 1H)
- 0.23 (d, 1H)
- 0.19 (d, 1H)
- 0.15 (d, 1H)
- 0.11 (d, 1H)
- 0.07 (d, 1H)
- 0.03 (d, 1H)
- 0.00 (d, 1H)

The spectrum shows a complex pattern of peaks, with a prominent peak at 7.52 ppm and a smaller peak at 6.84 ppm. The x-axis is labeled f1 (ppm) and ranges from 0.0 to 10.0.



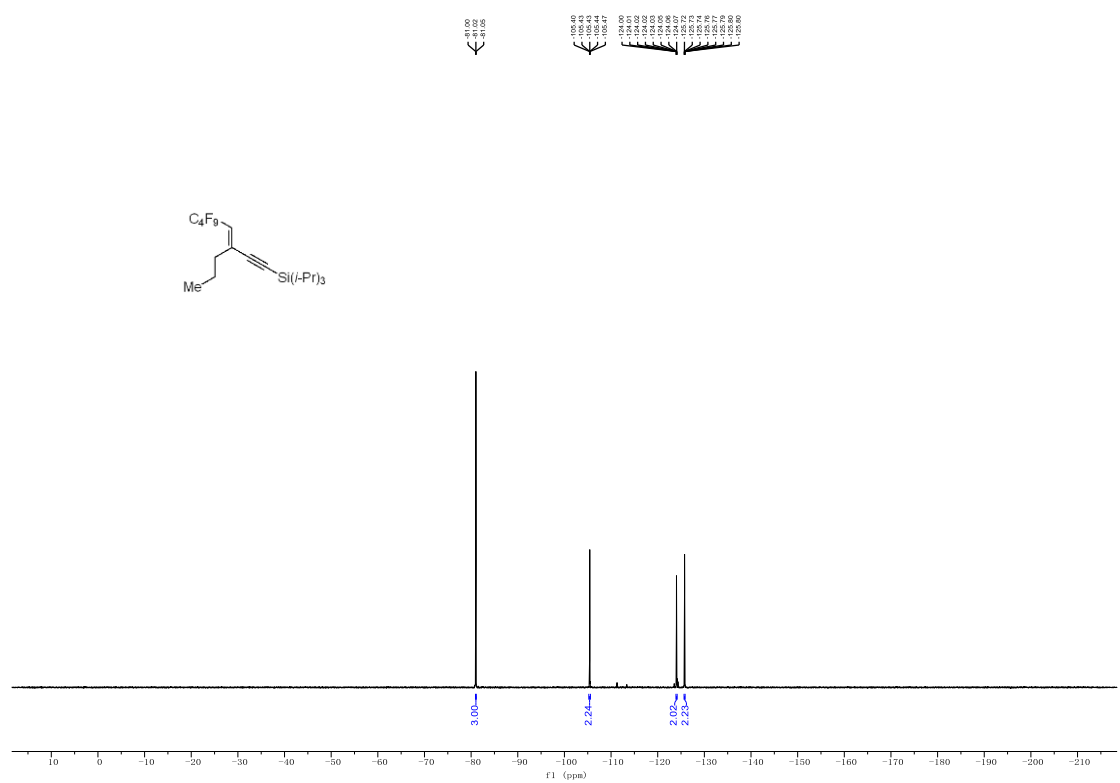
¹H NMR, ¹⁹F NMR and ¹³C NMR spectra of 4as

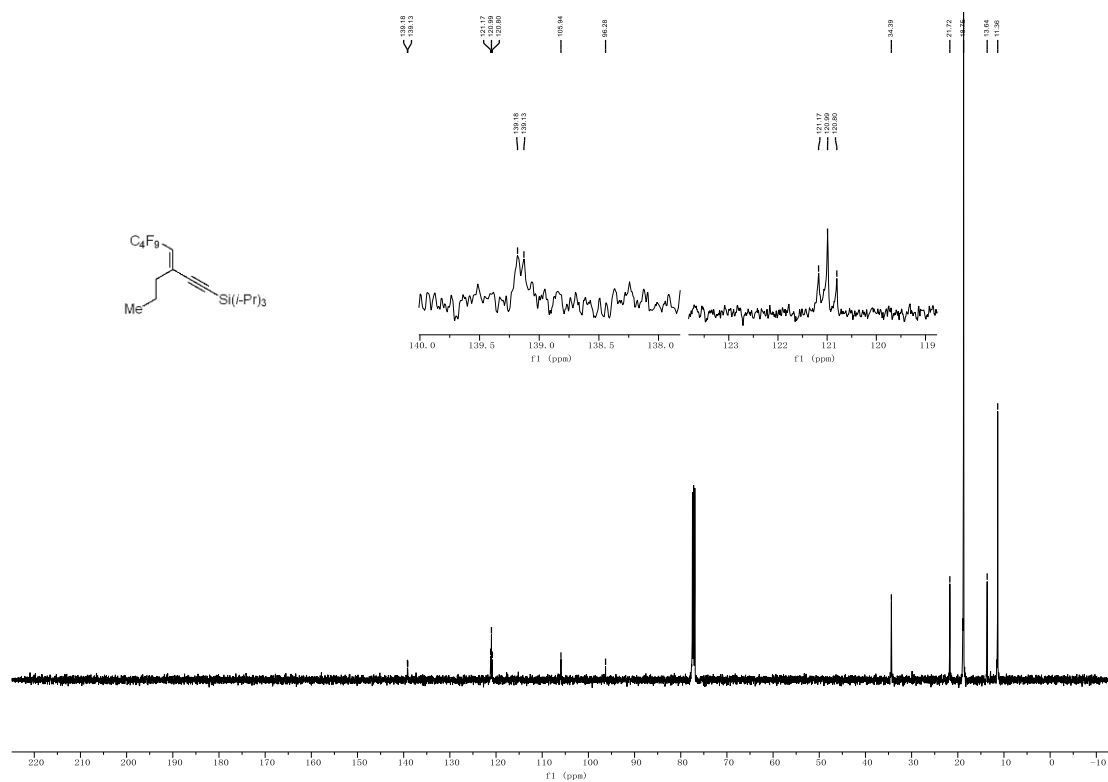




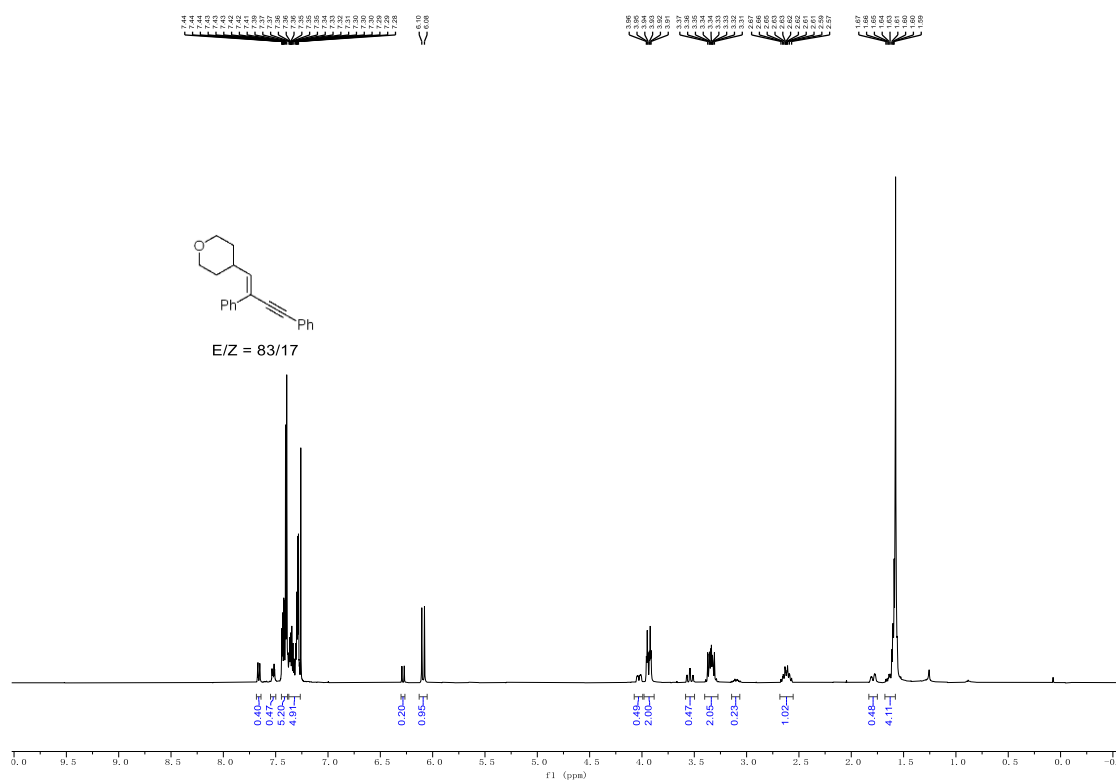
Chemical structure: C[CH2]C=C(C#CC(F)(F)F)C(F)(F)F

¹H NMR spectrum (400 MHz, CDCl₃) showing peaks from 0 to 10 ppm. Integration values are shown below the peaks: 0.91, 1.81, 2.06, 21.00, and 3.02.





¹H NMR and ¹³C NMR spectra of 4au



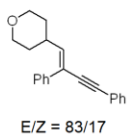
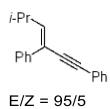
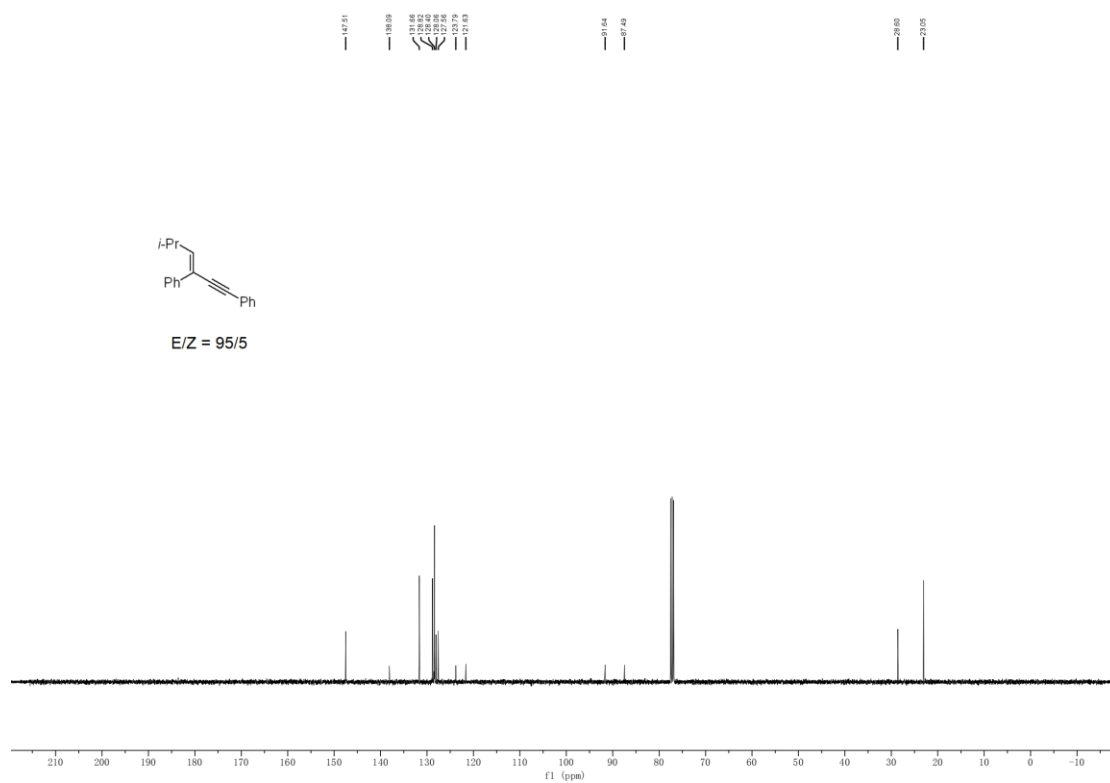
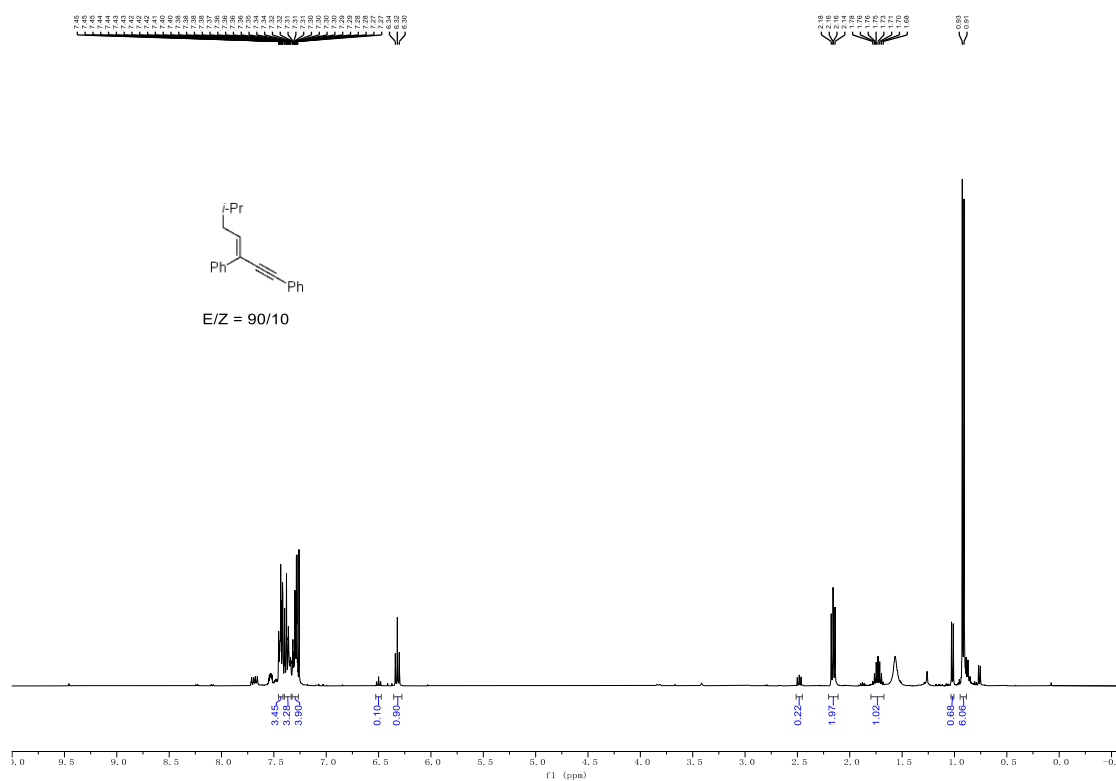


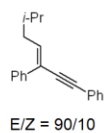
Figure 1: A dendrogram showing the hierarchical clustering of 28 samples. The samples are grouped into two main clusters, each containing a sub-cluster of 14 samples. The dendrogram is rooted at the bottom with a value of 6.11. The sample numbers are listed above the branches: 746, 743, 743, 743, 743, 742, 742, 741, 741, 740, 738, 737, 737, 733, 733, 732, 732, 731, 731, 730, 730, 729, 729, 728, 728. The two main clusters are labeled 6.11 and 6.09.



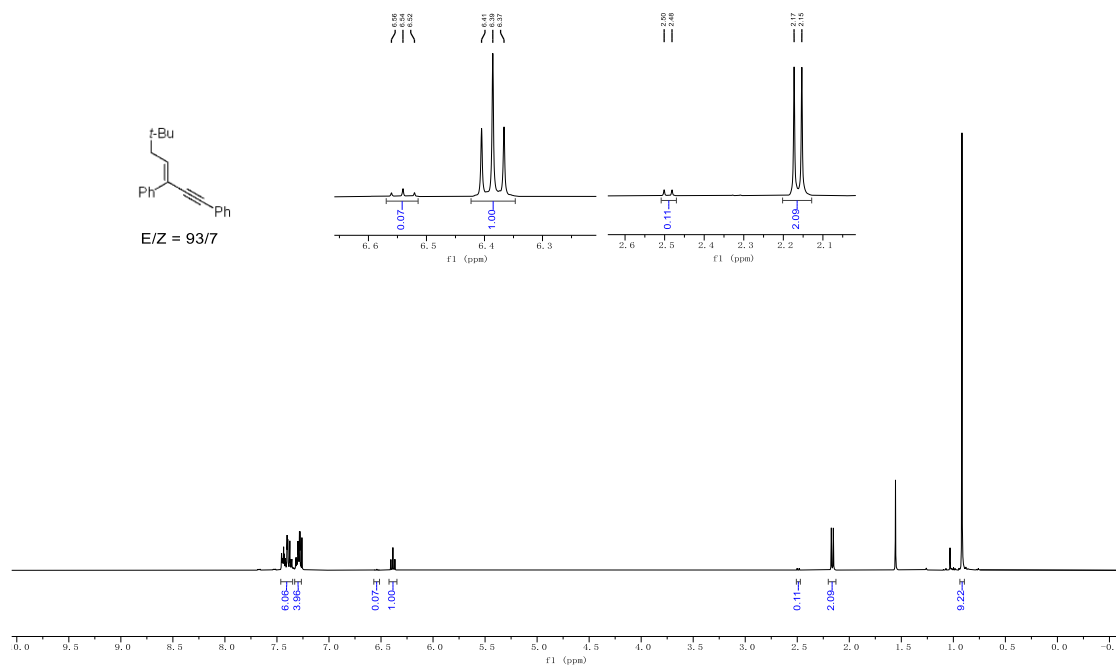


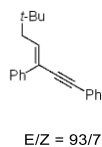
¹H NMR and ¹³C NMR spectra of 4w

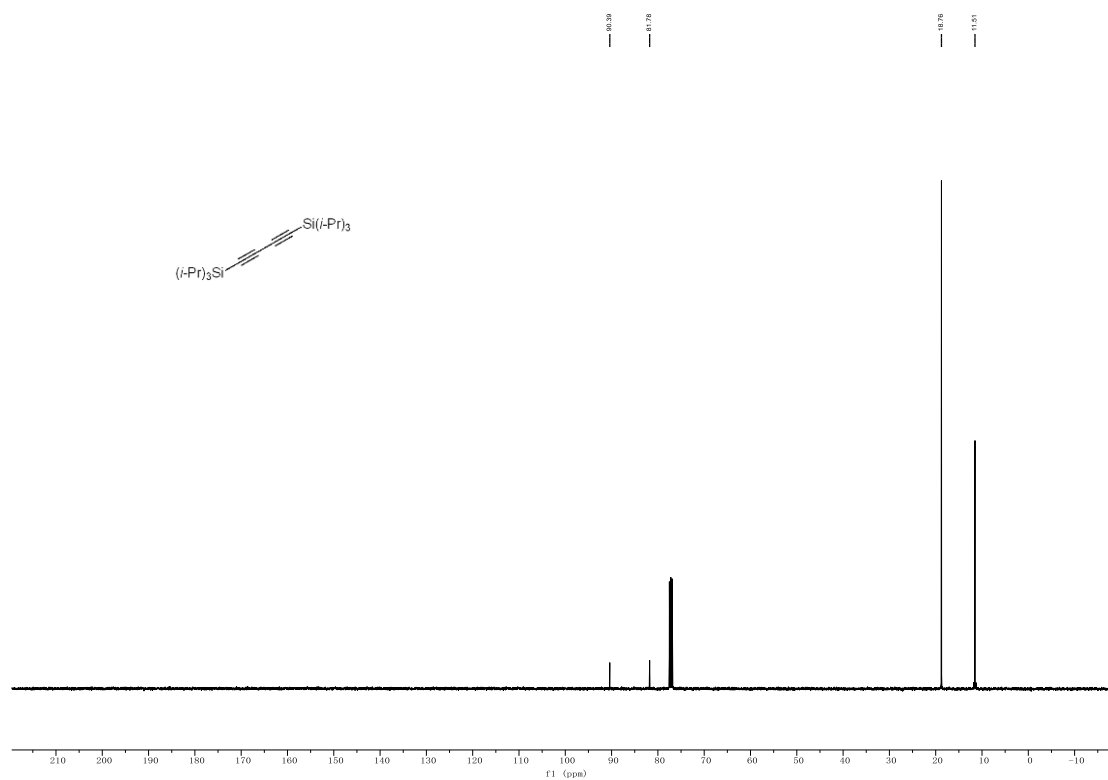




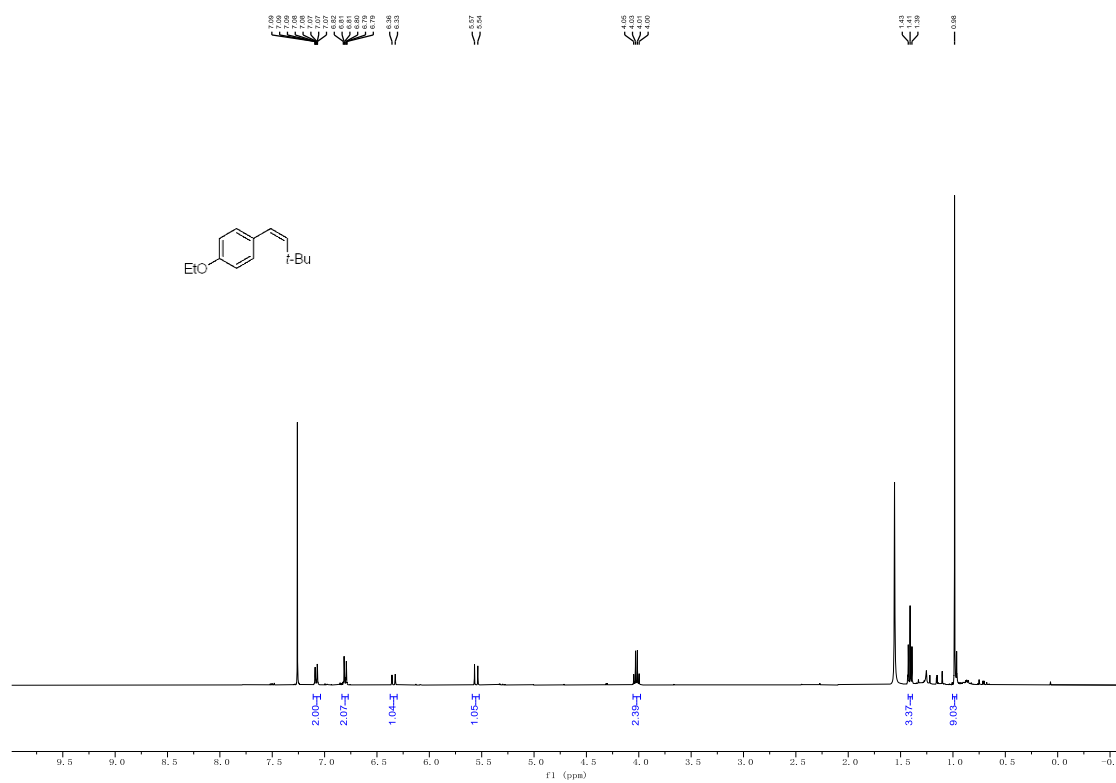
Age Group	Number of People
0-4	746
5-9	745
10-14	745
15-19	744
20-24	744
25-29	744
30-34	743
35-39	743
40-44	742
45-49	742
50-54	741
55-59	741
60-64	740
65+	6,337

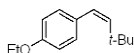


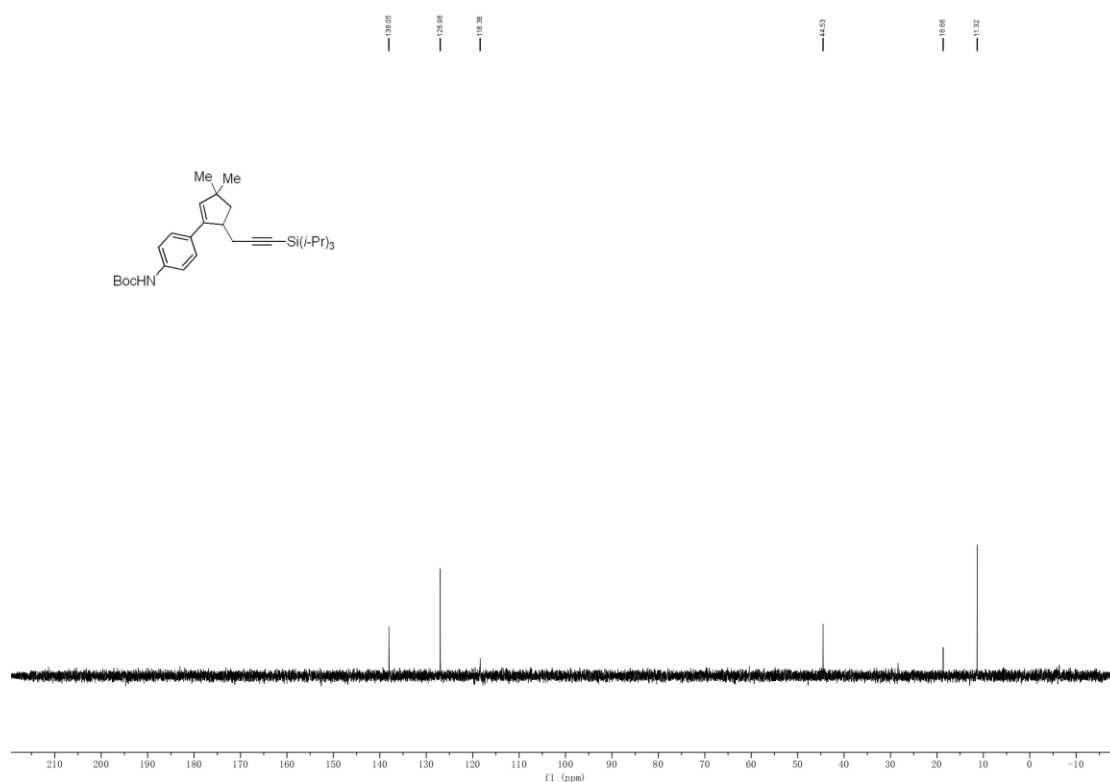
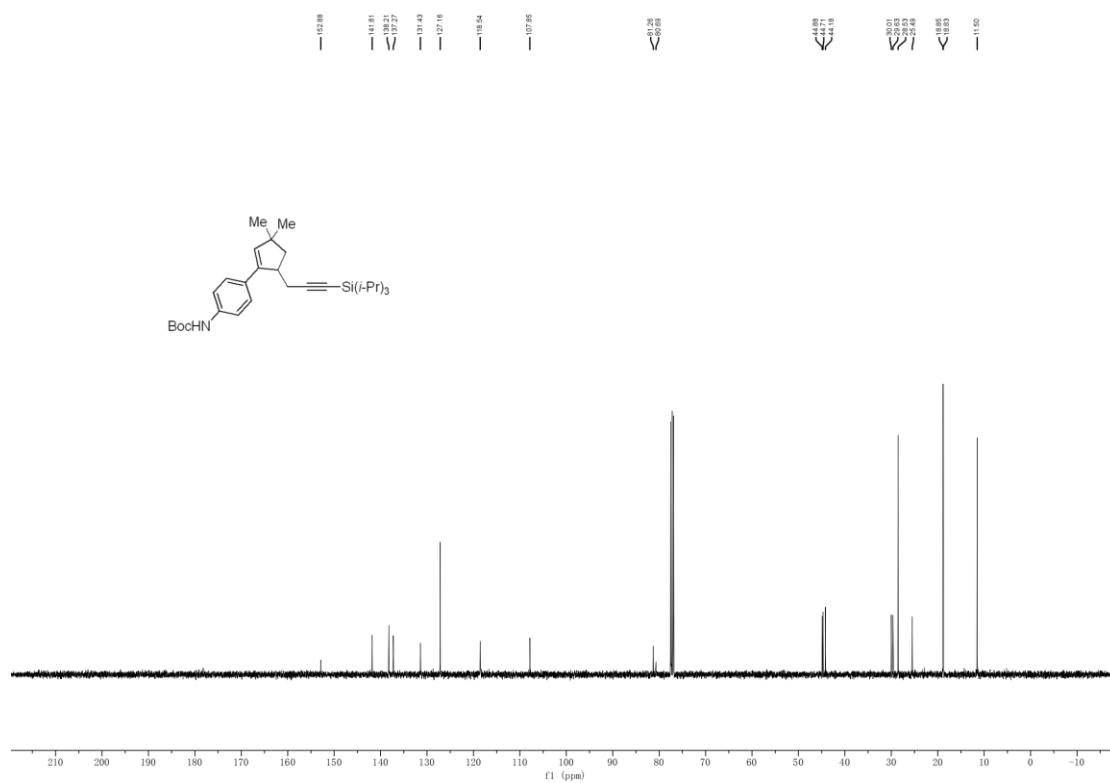




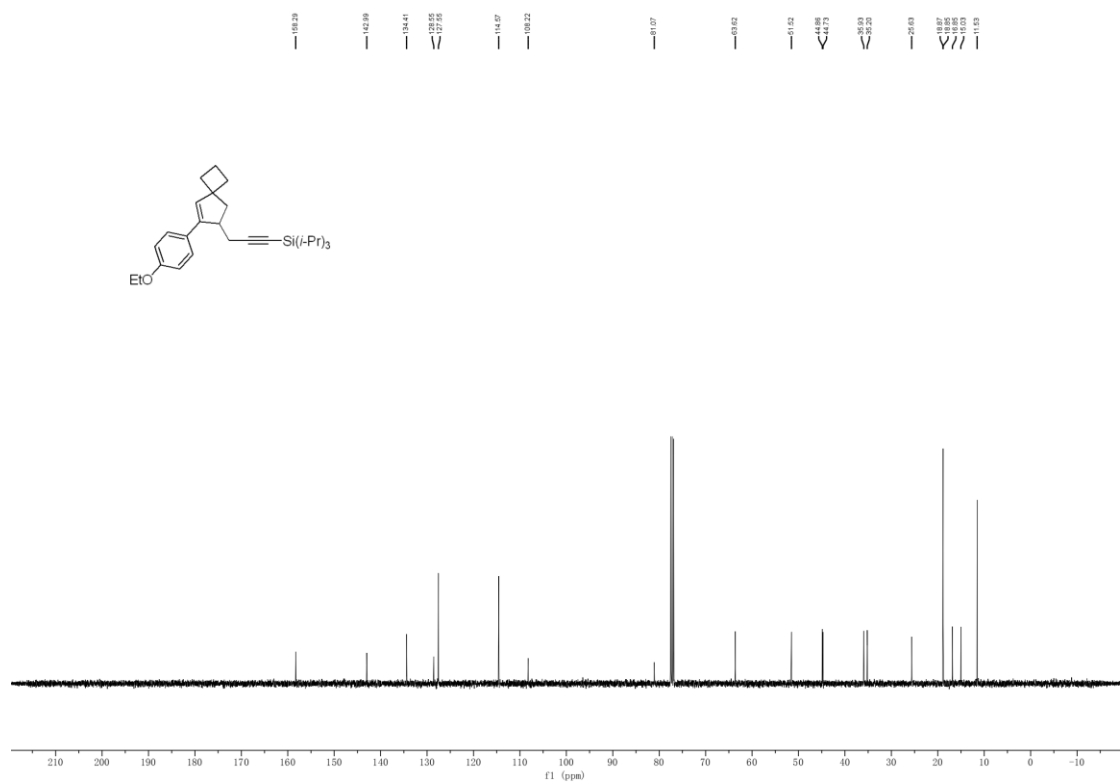
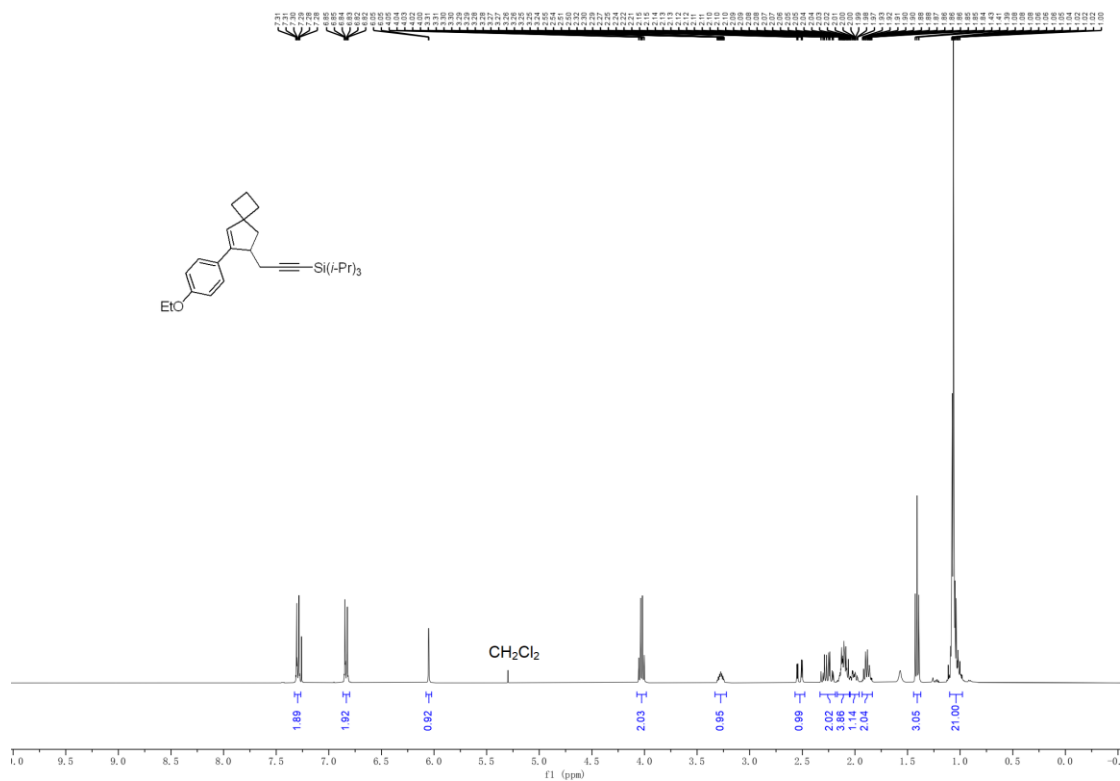
^1H NMR and ^{13}C NMR spectra of 9

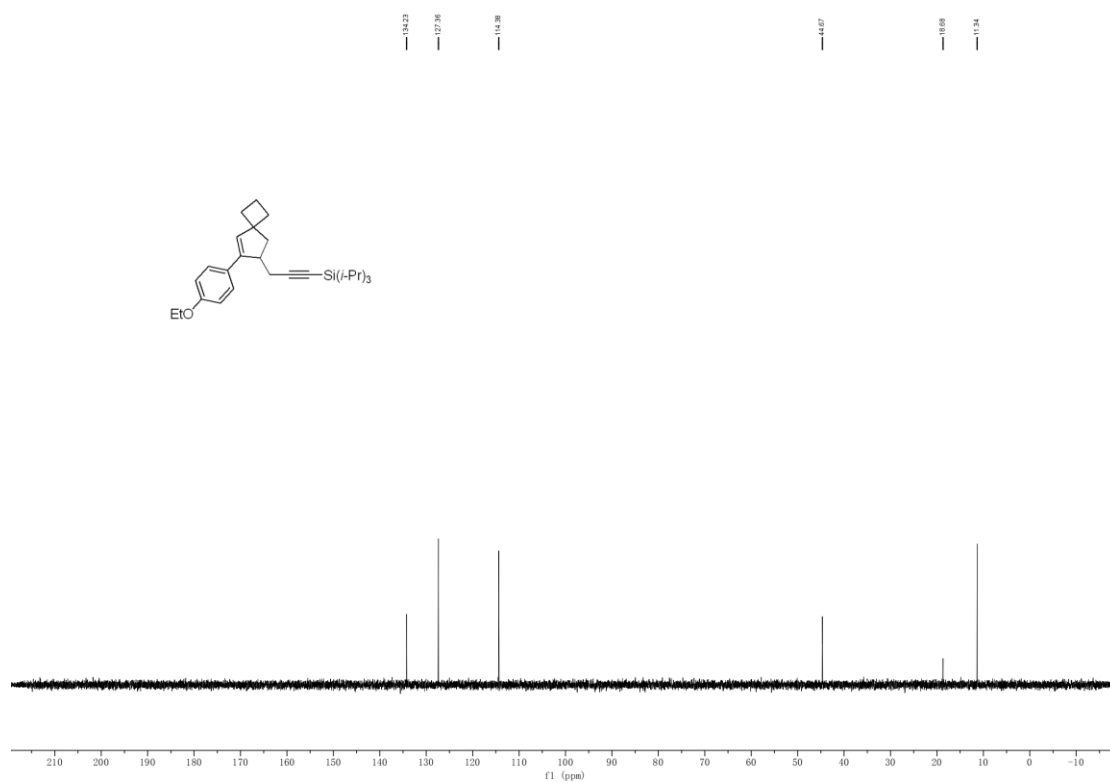




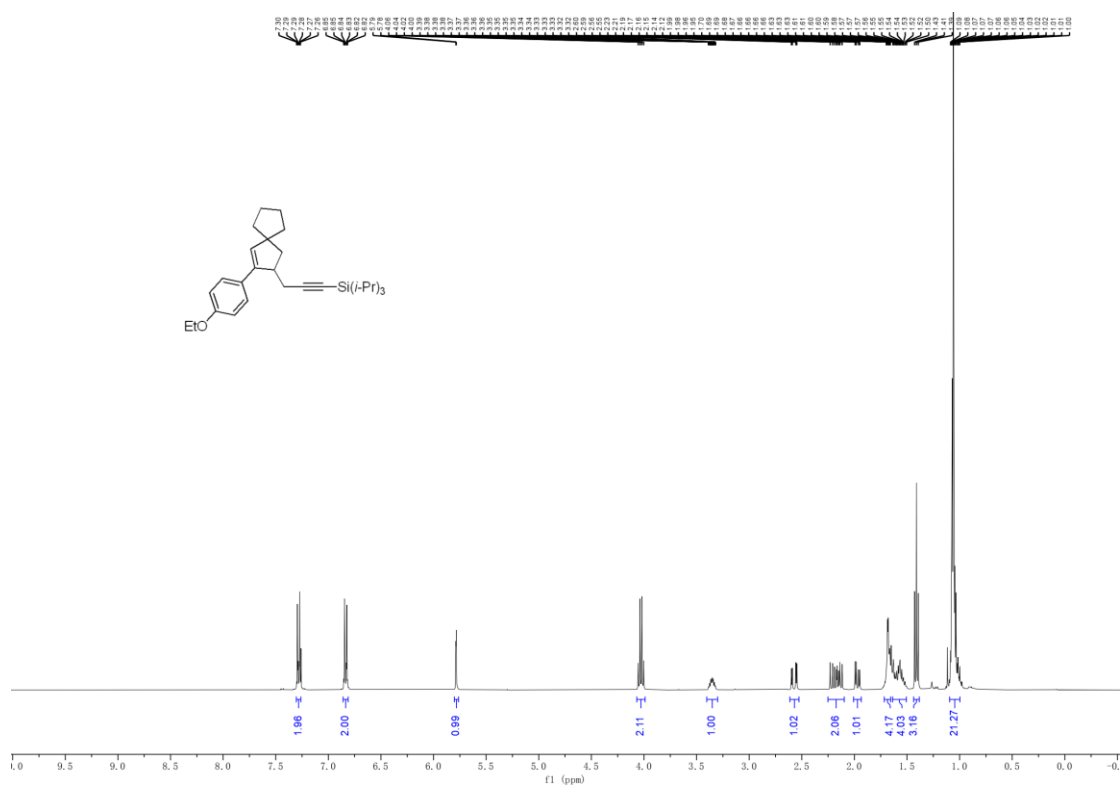


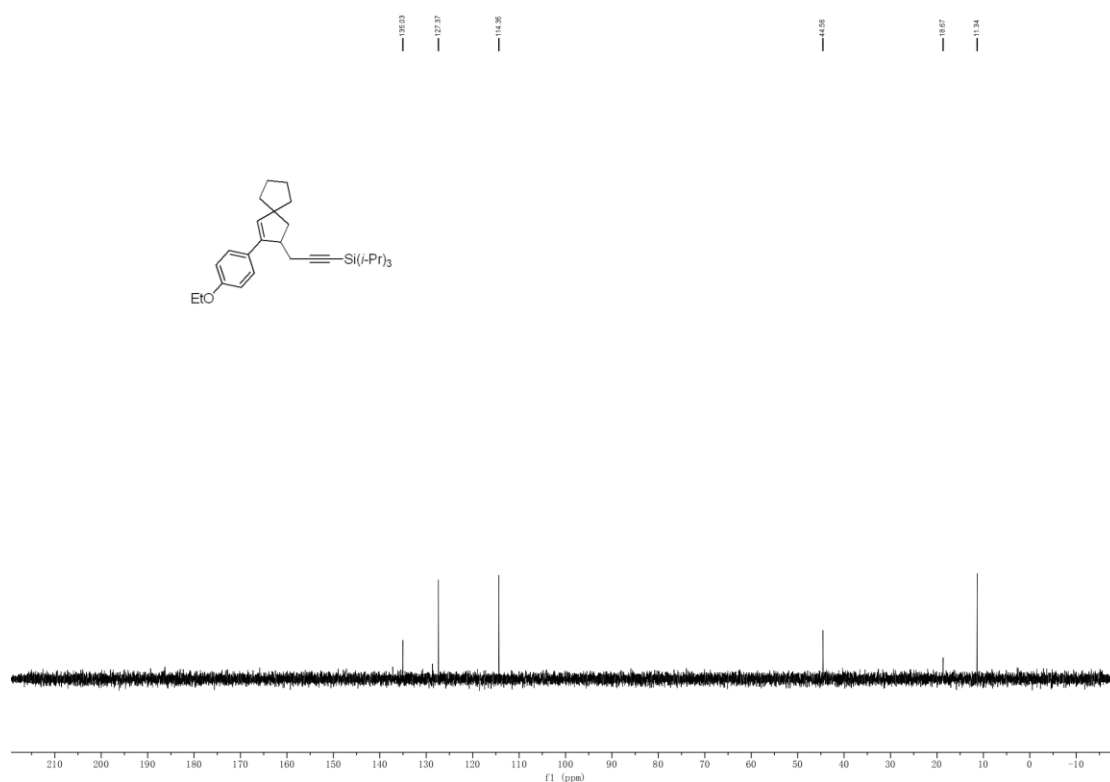
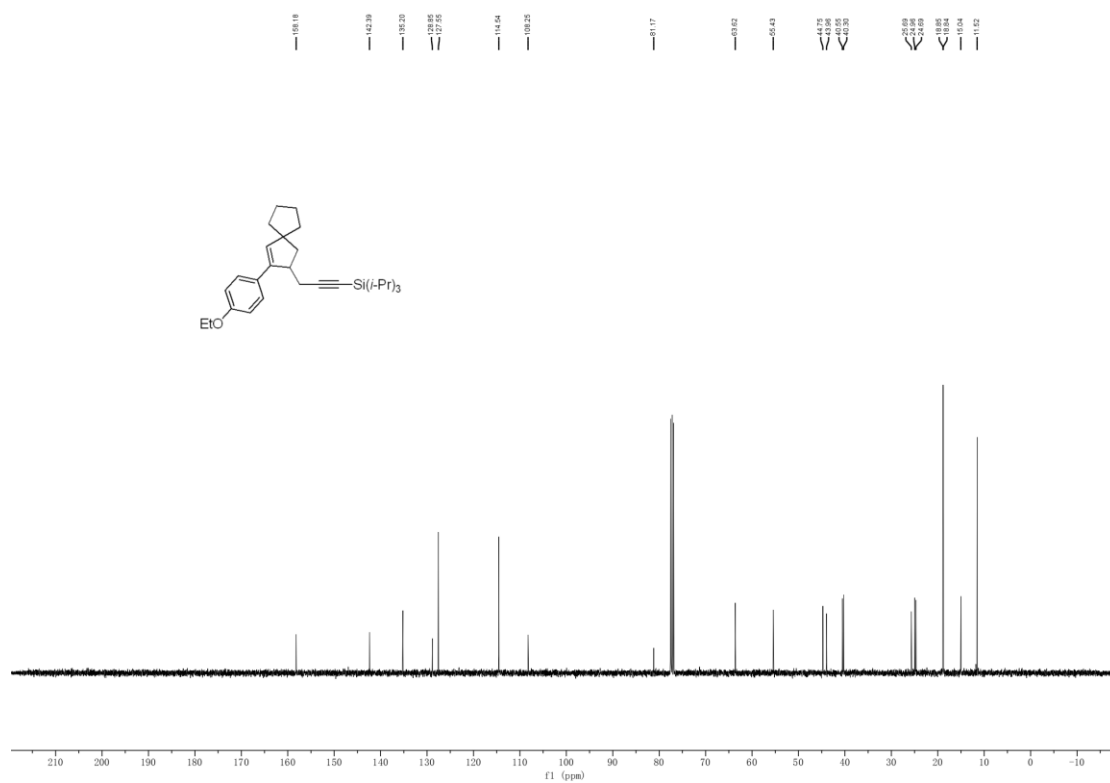
¹H NMR, ¹³C NMR and DPET 90 spectra of 11b



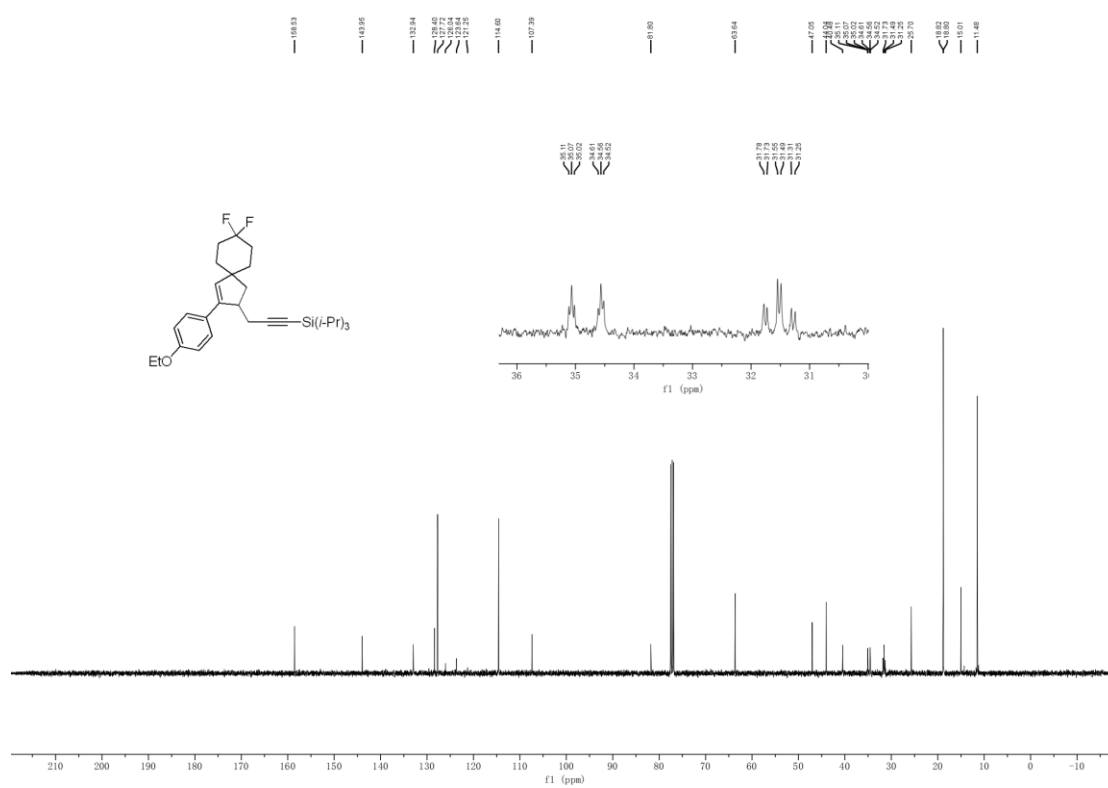
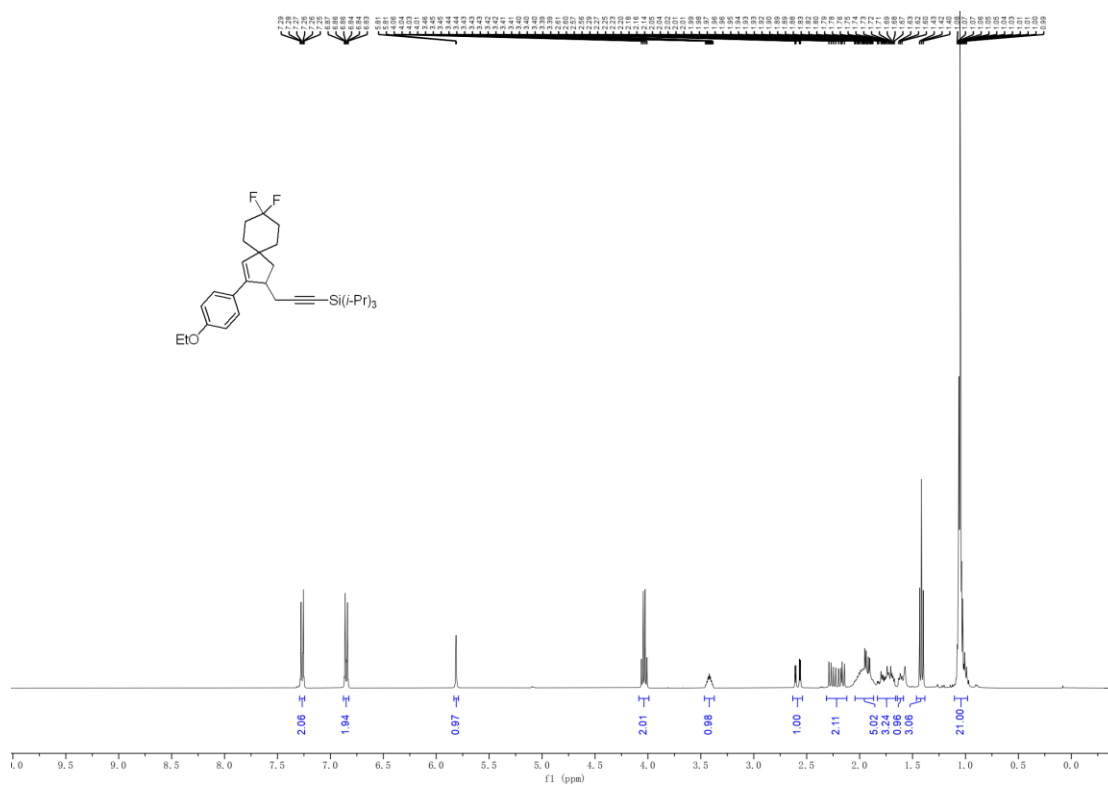


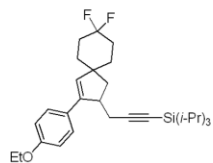
¹H NMR, ¹³C NMR and DPET 90 spectra of 11c



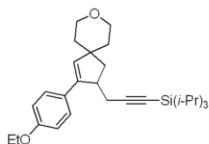


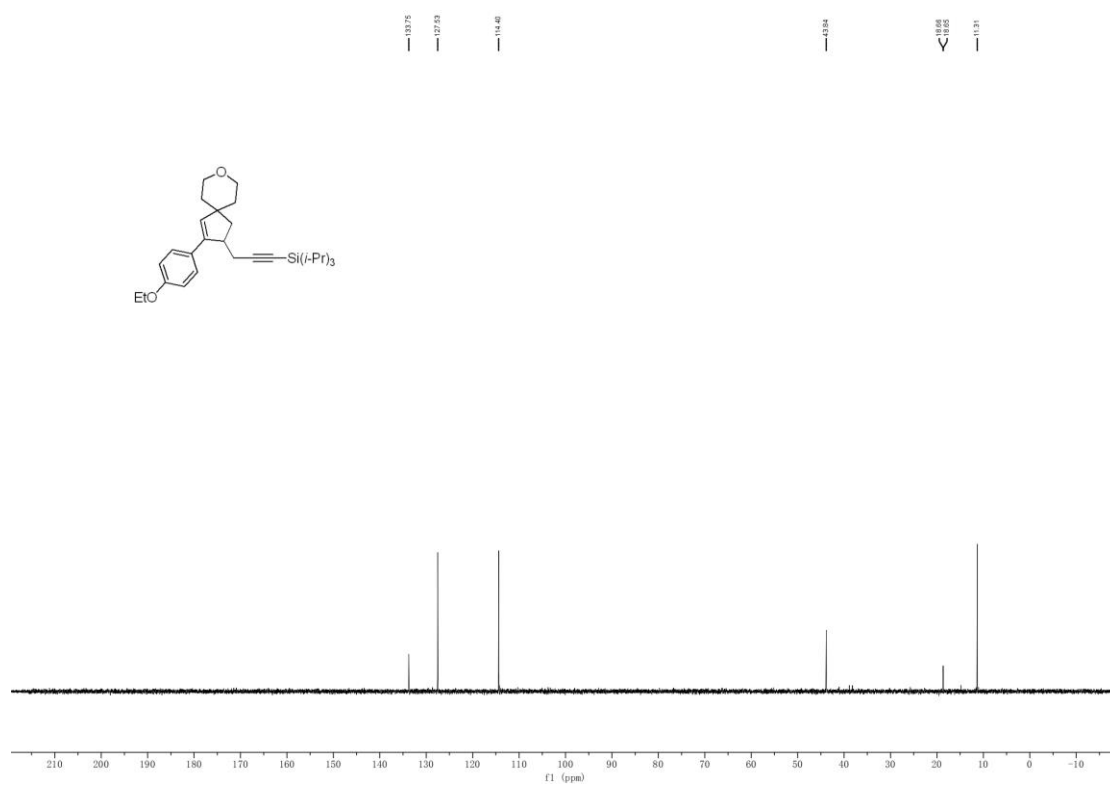
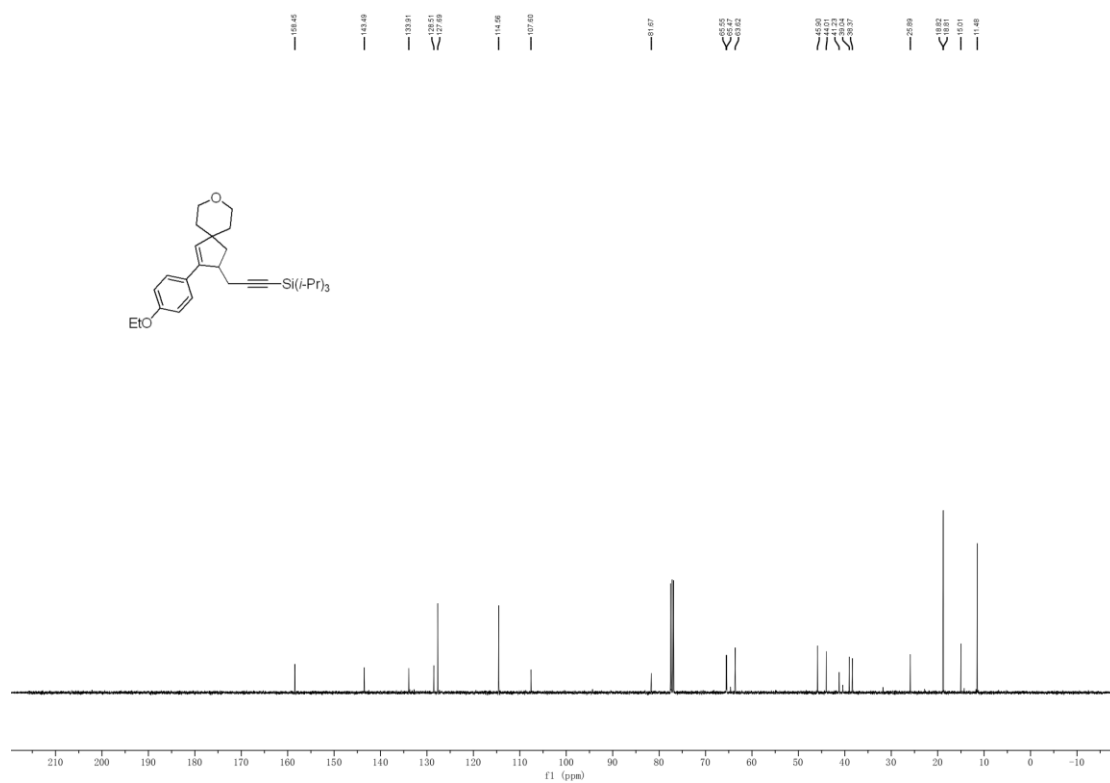
¹H NMR, ¹³C NMR and DPET 90 spectra of 11d



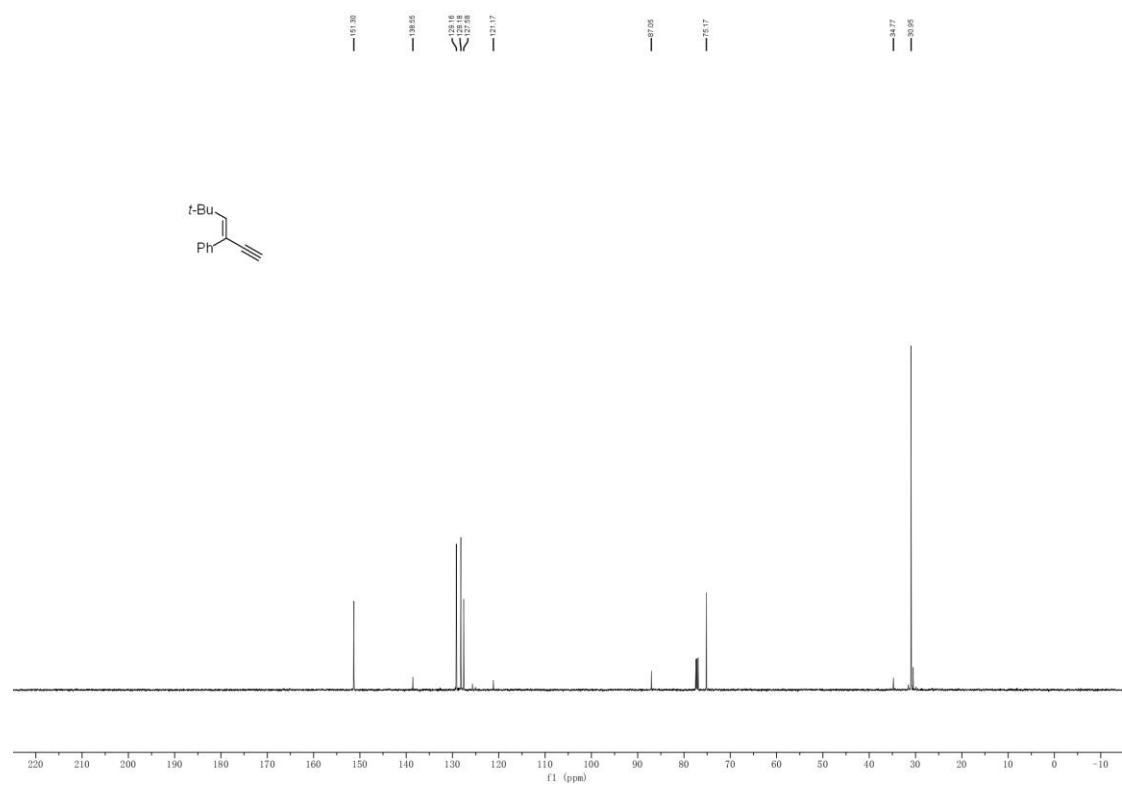
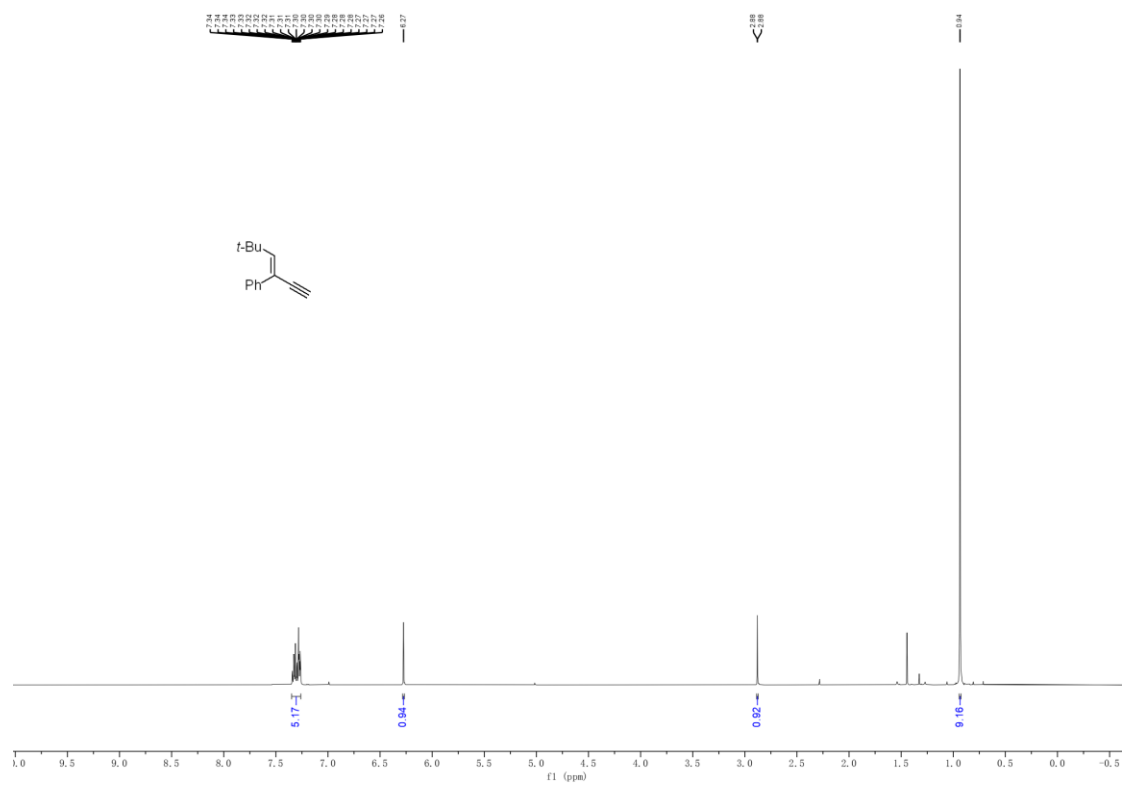


1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

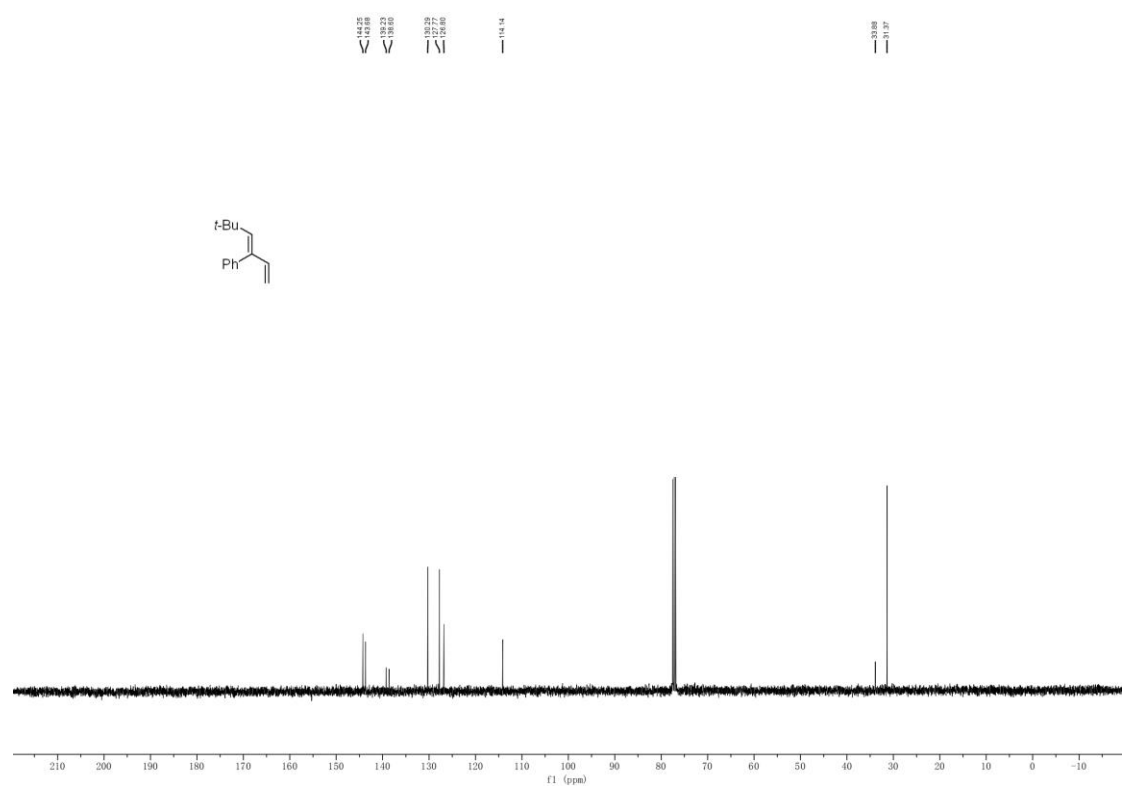
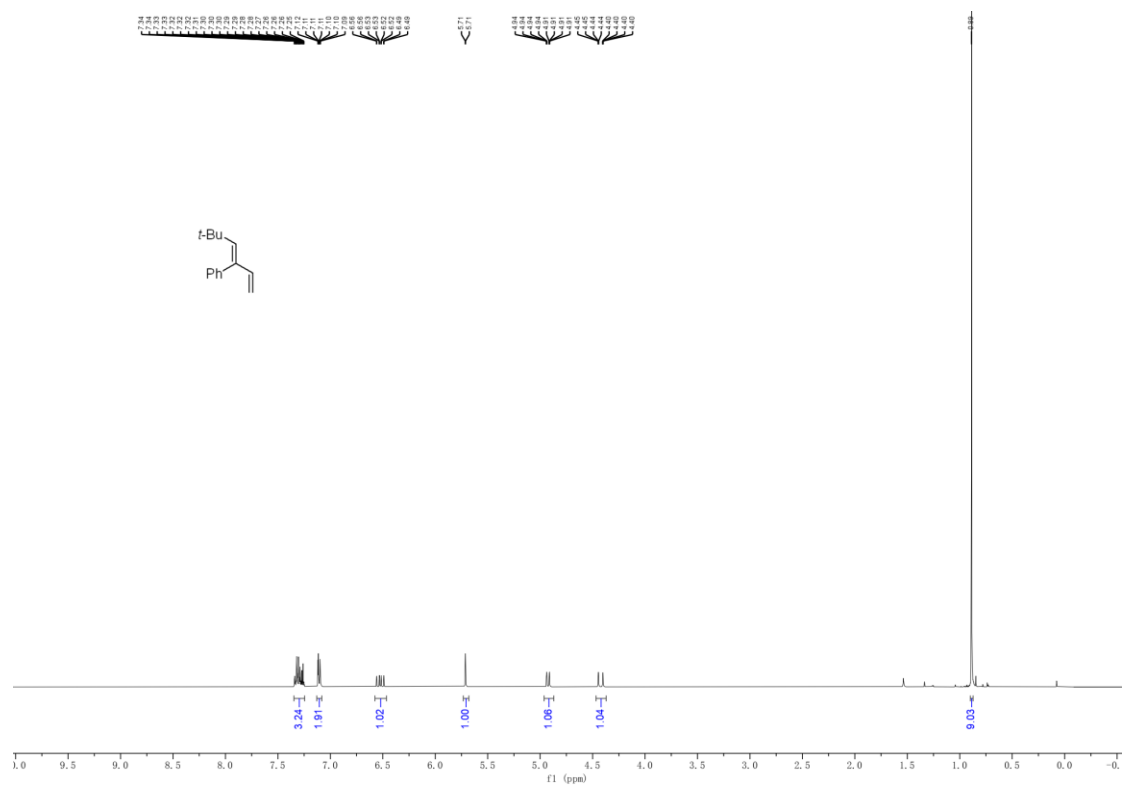




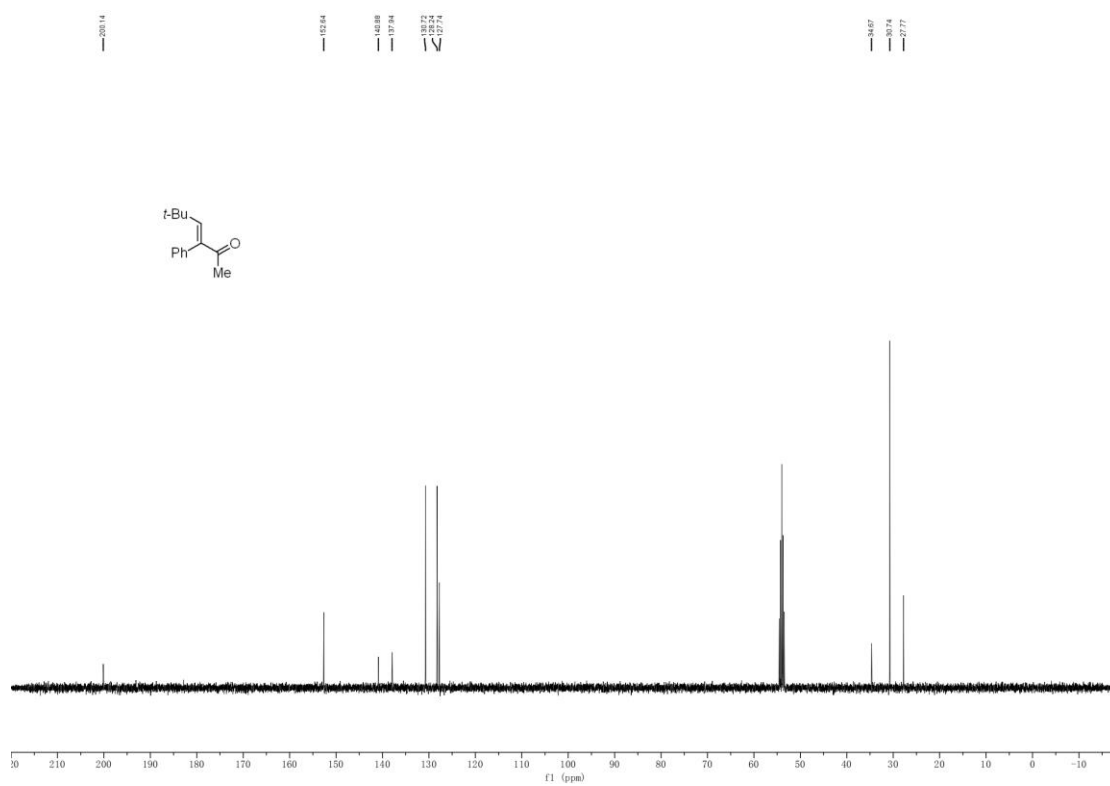
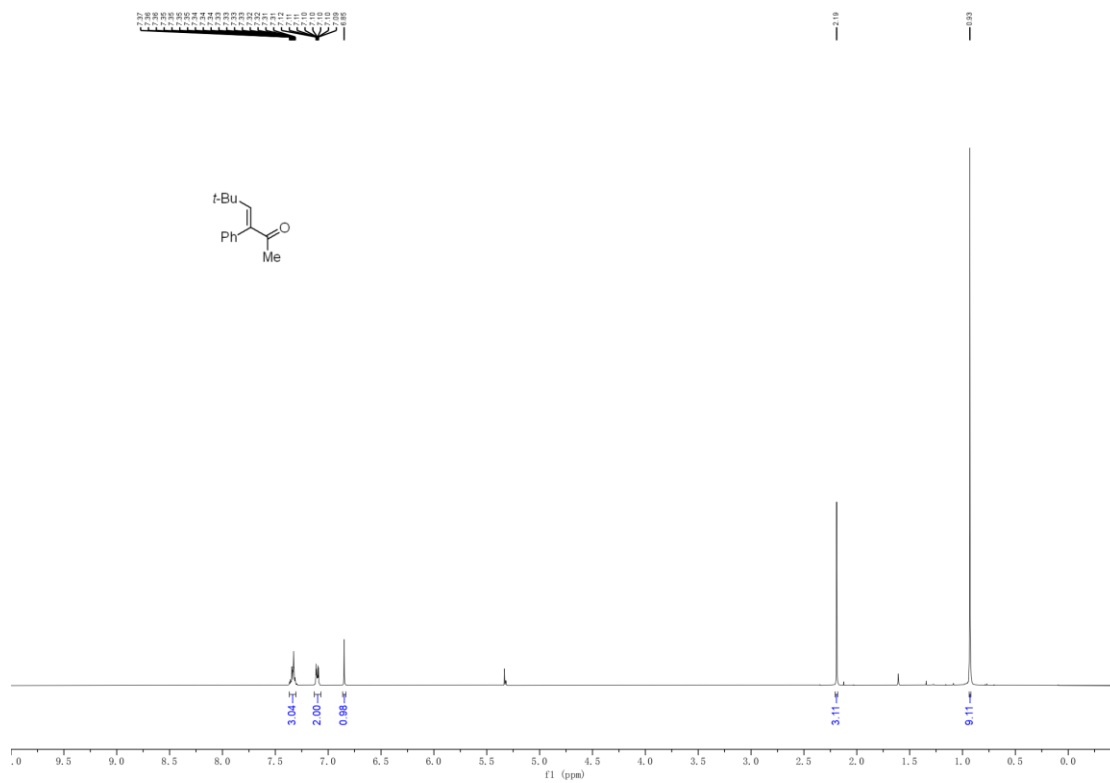
¹H NMR and ¹³C NMR spectra of 12



¹H NMR and ¹³C NMR spectra of 13



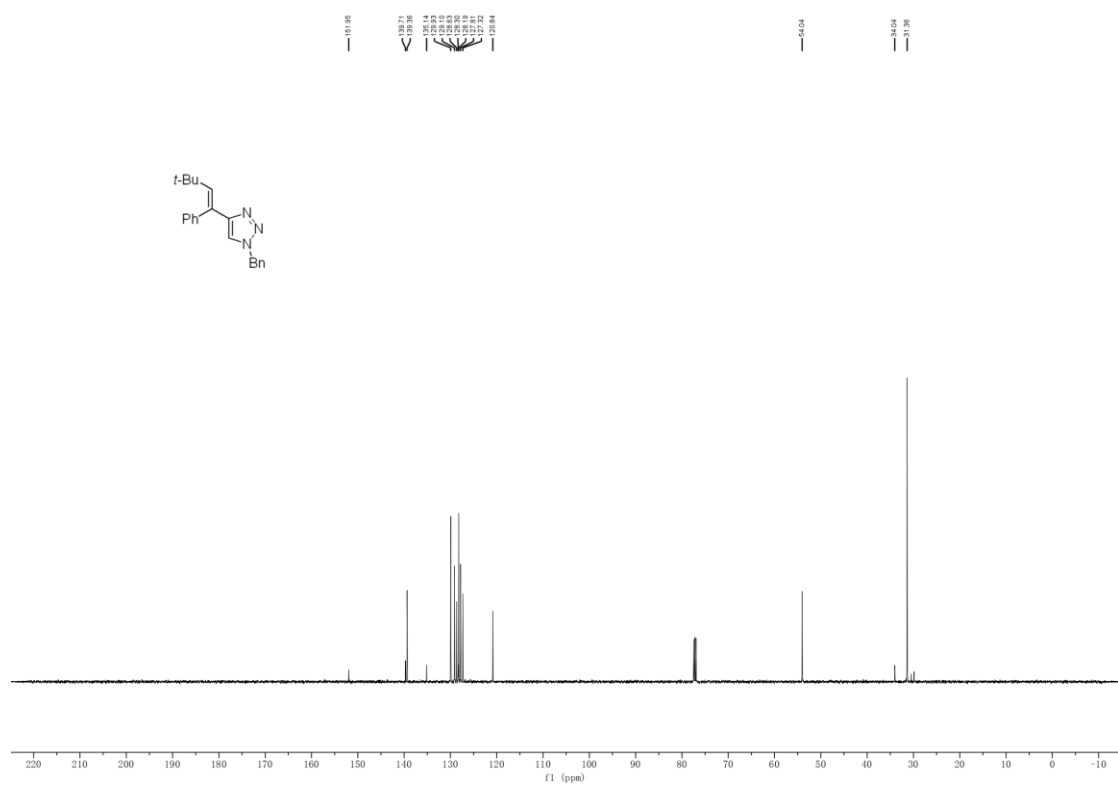
¹H NMR and ¹³C NMR spectra of 14



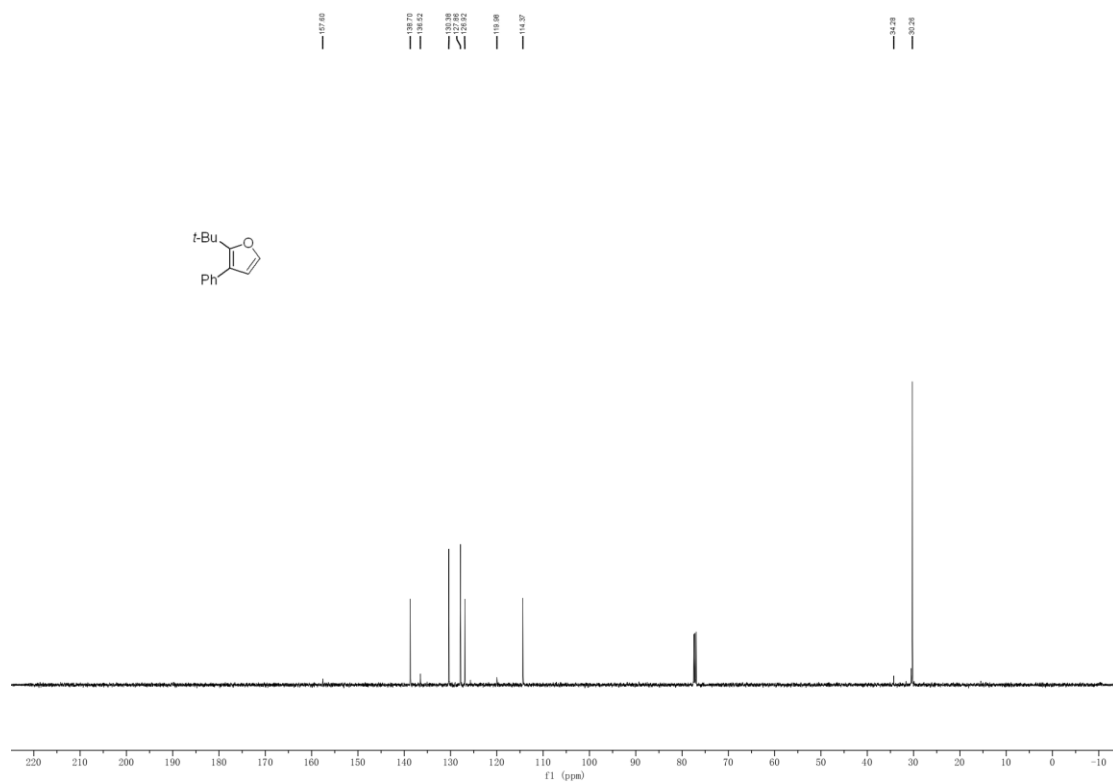
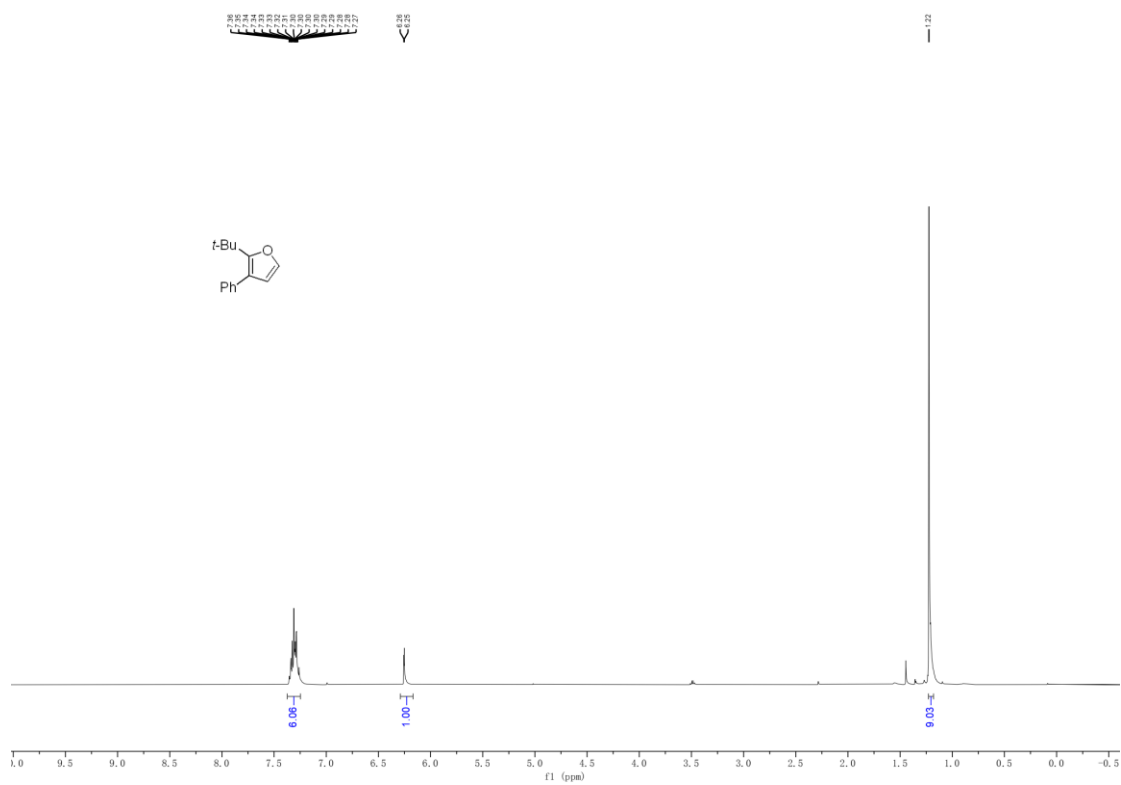
Chemical structure: CC(C)(C)/C=C/c1ccc(cc1)-c2nnn(c2)Cc3ccccc3

¹H NMR spectrum (ppm):

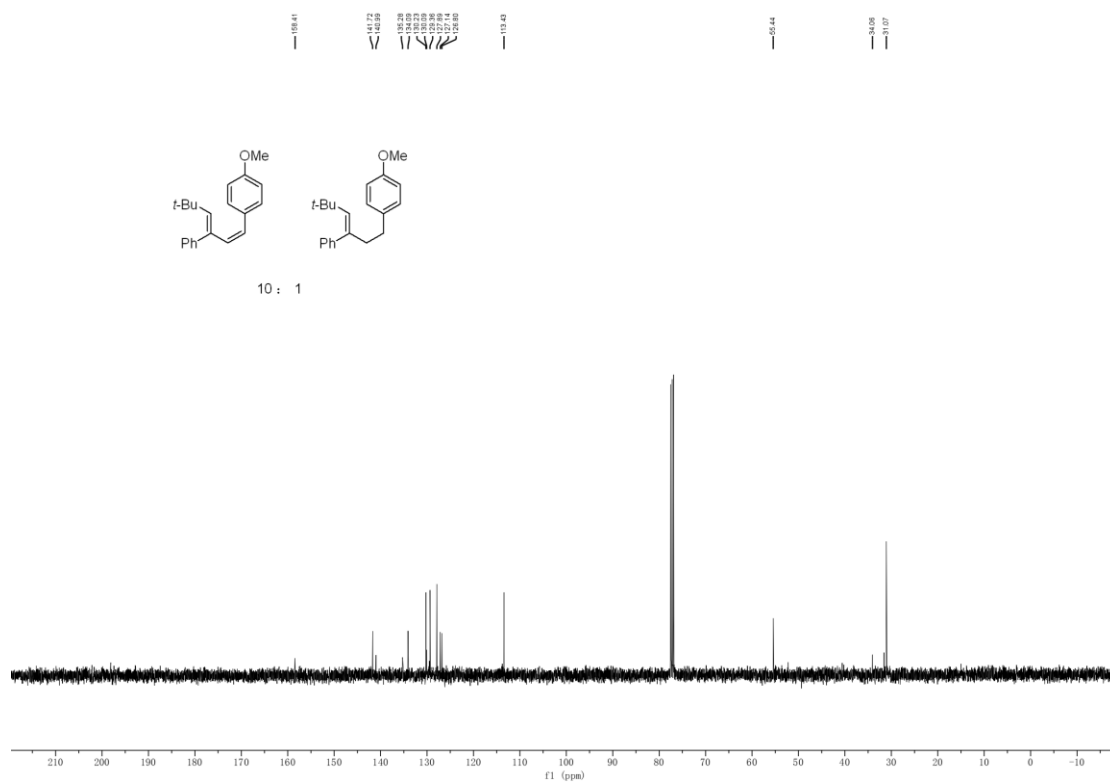
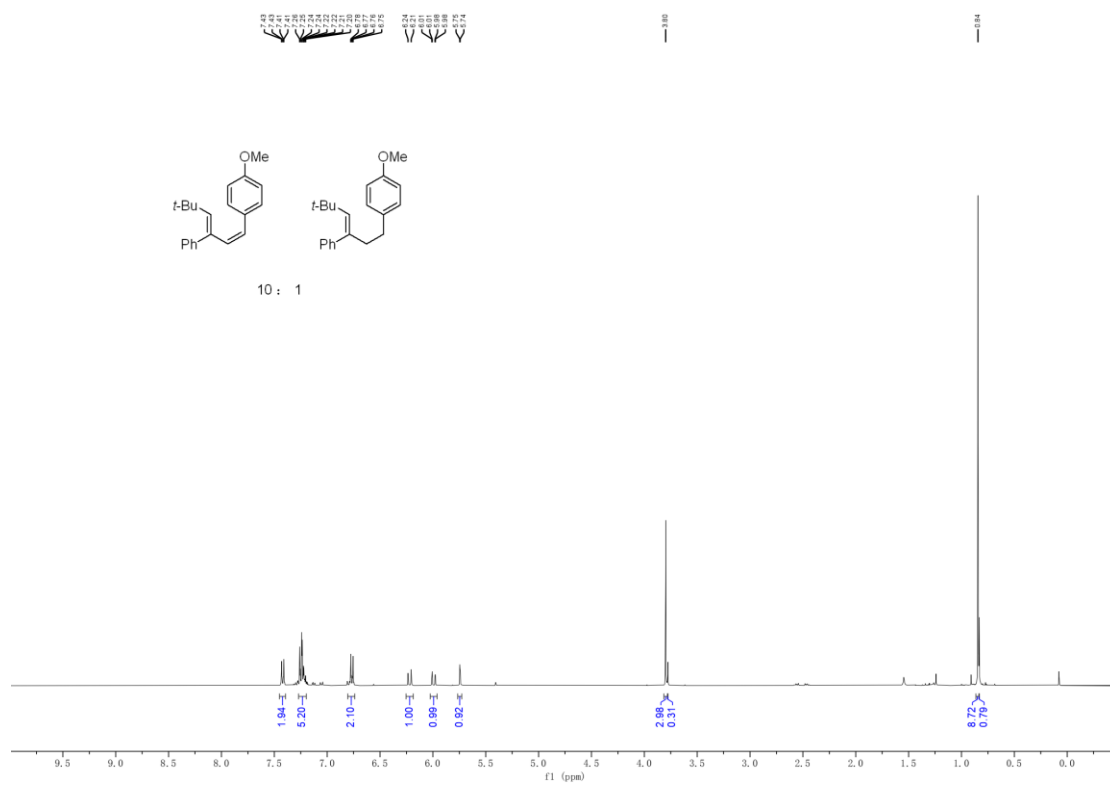
- 7.20 (d, 6.00H)
- 7.00 (d, 4.00H)
- 6.80 (s, 0.96H)
- 6.60 (s, 0.96H)
- 5.50 (s, 2.08H)
- 1.00 (s, 9.20H)



¹H NMR and ¹³C NMR spectra of 16



¹H NMR and ¹³C NMR spectra of 17



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