

# ***Alkylation of amines with allylic alcohols and deep eutectic solvents as metal-free and green promoters***

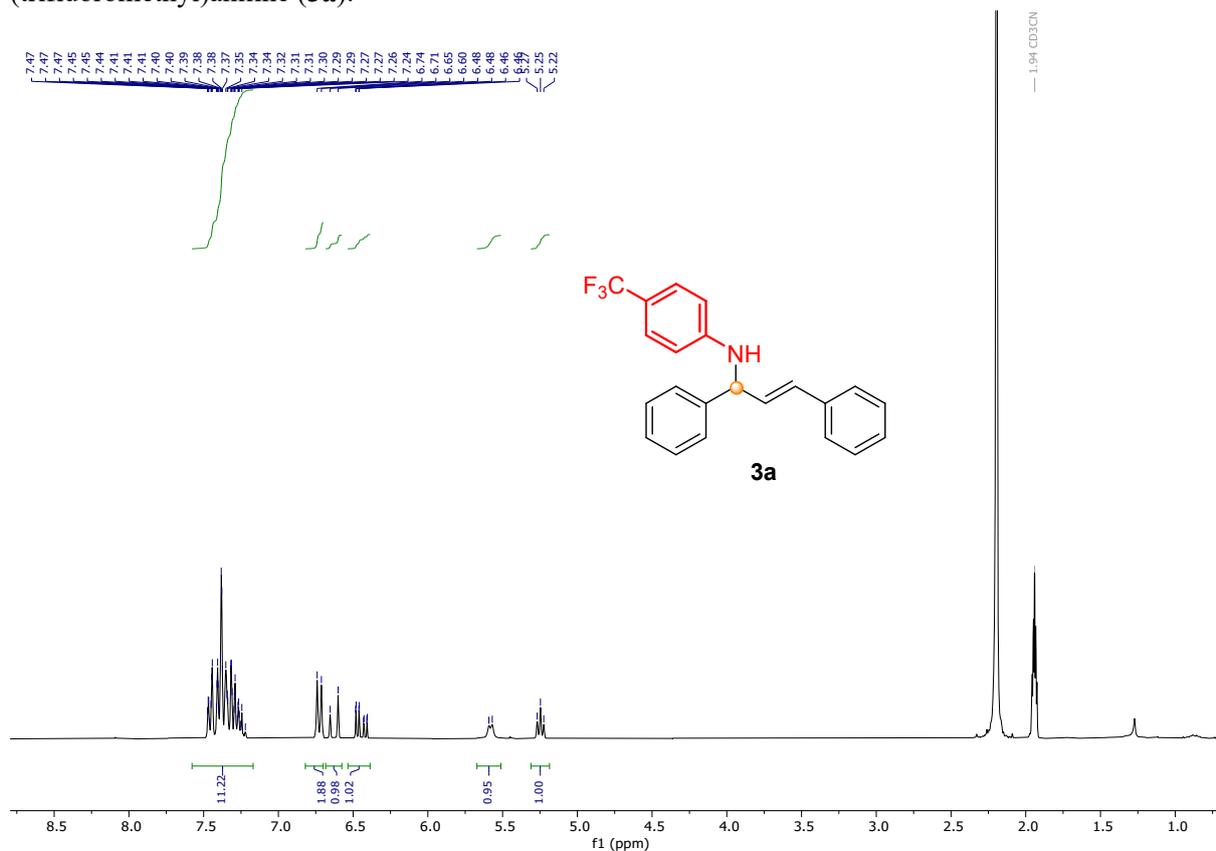
Sthephany Zárate-Roldán,<sup>a,b</sup> M. Concepción Gimeno<sup>\*b</sup> and Raquel P. Herrera<sup>\*a</sup>

<sup>a</sup> *Laboratorio de Organocatálisis Asimétrica, Departamento de Química Orgánica. Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza. C/ Pedro Cerbuna 12, E-50009 Zaragoza, Spain. [raquelph@unizar.es](mailto:raquelph@unizar.es)*

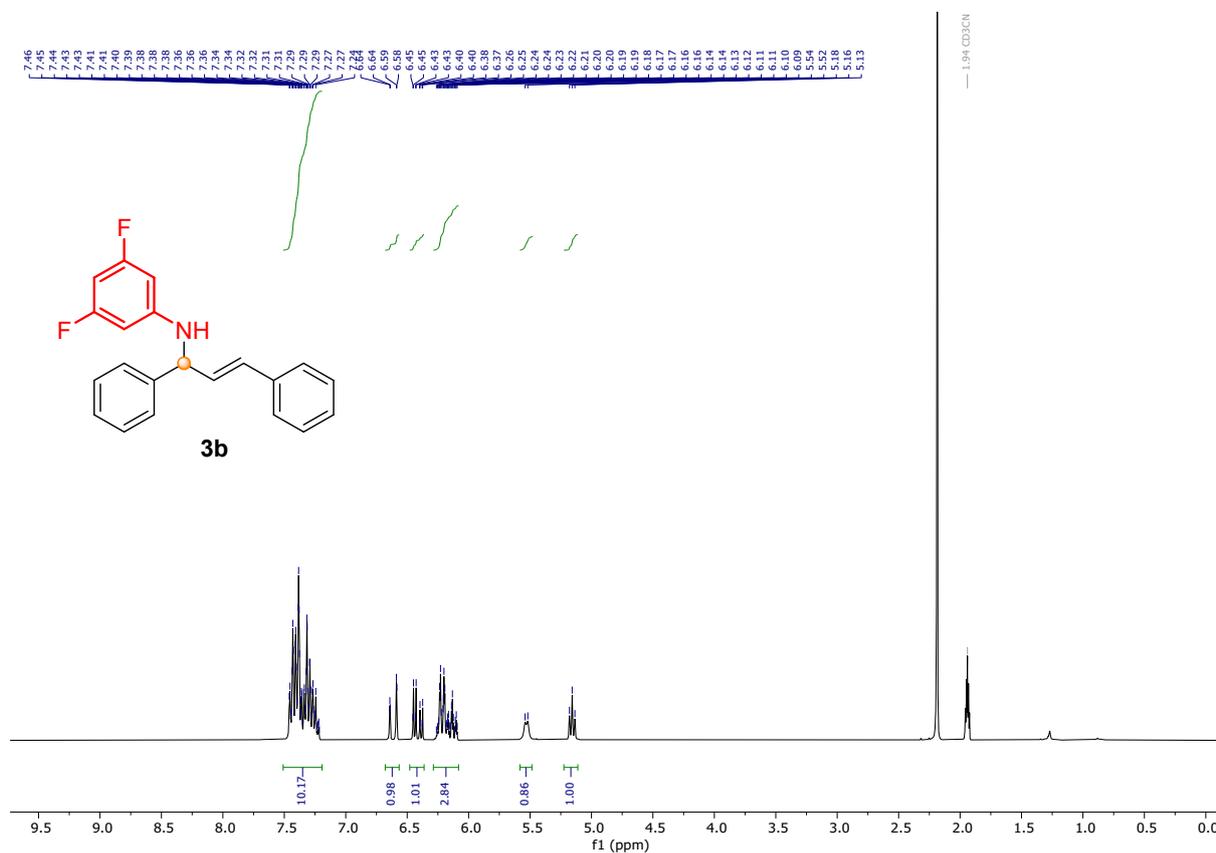
<sup>b</sup> *Departamento de Química Inorgánica. Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza. C/ Pedro Cerbuna 12, E-50009 Zaragoza, Spain. [gimeno@unizar.es](mailto:gimeno@unizar.es)*

## 1. Characterisation of final products

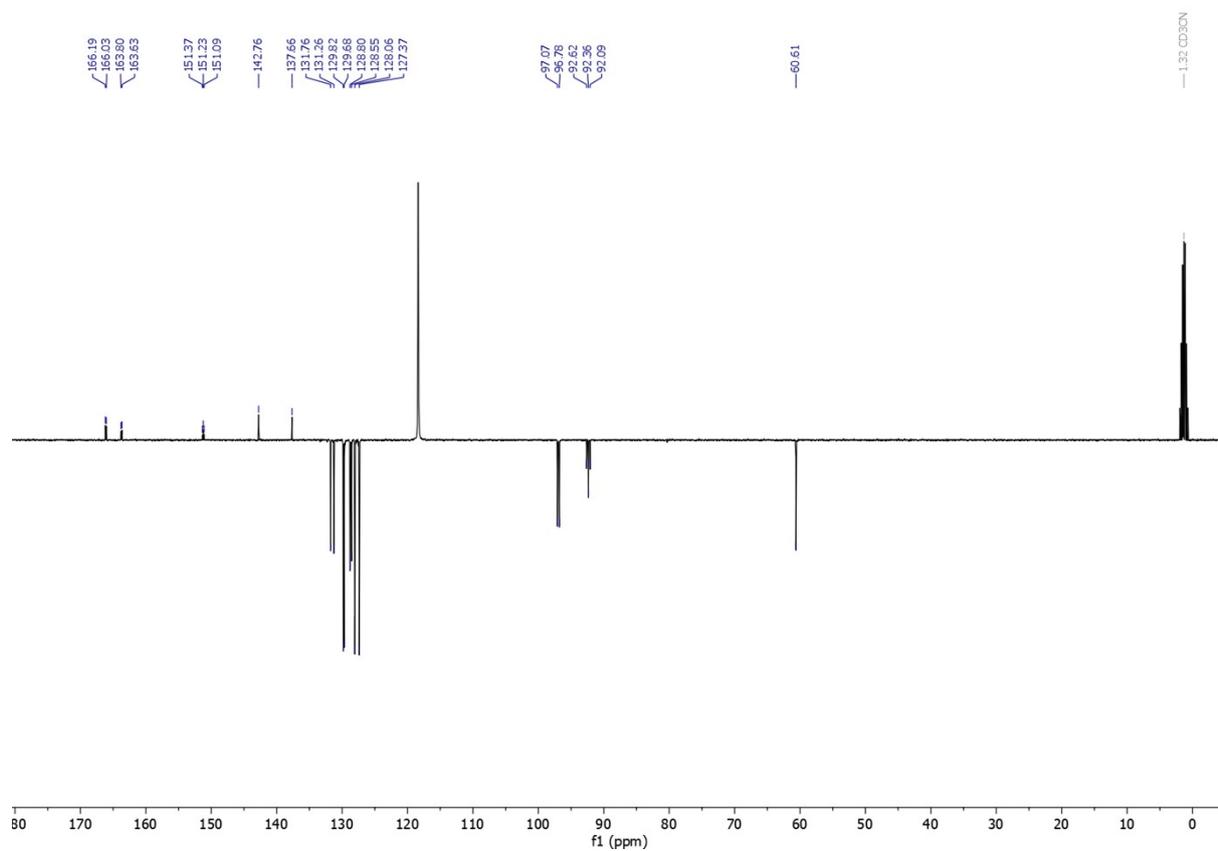
**Figure S1.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-diphenylallyl)-4-(trifluoromethyl)aniline (**3a**).



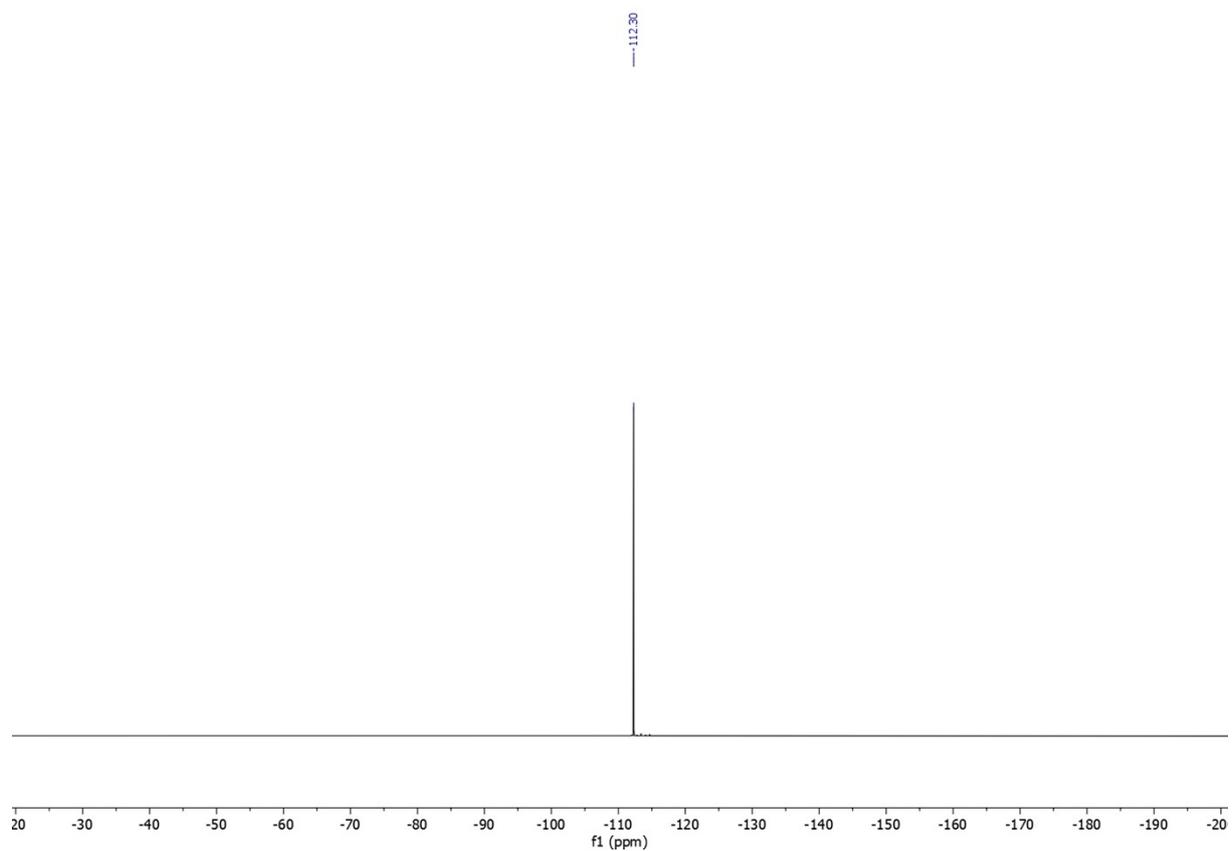
**Figure S2.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-diphenylallyl)-3,5-difluoroaniline (**3b**).



**Figure S3.**  $^{13}\text{C}\{^1\text{H}\}$  APT NMR (75 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-diphenylallyl)-3,5-difluoroaniline (**3b**).

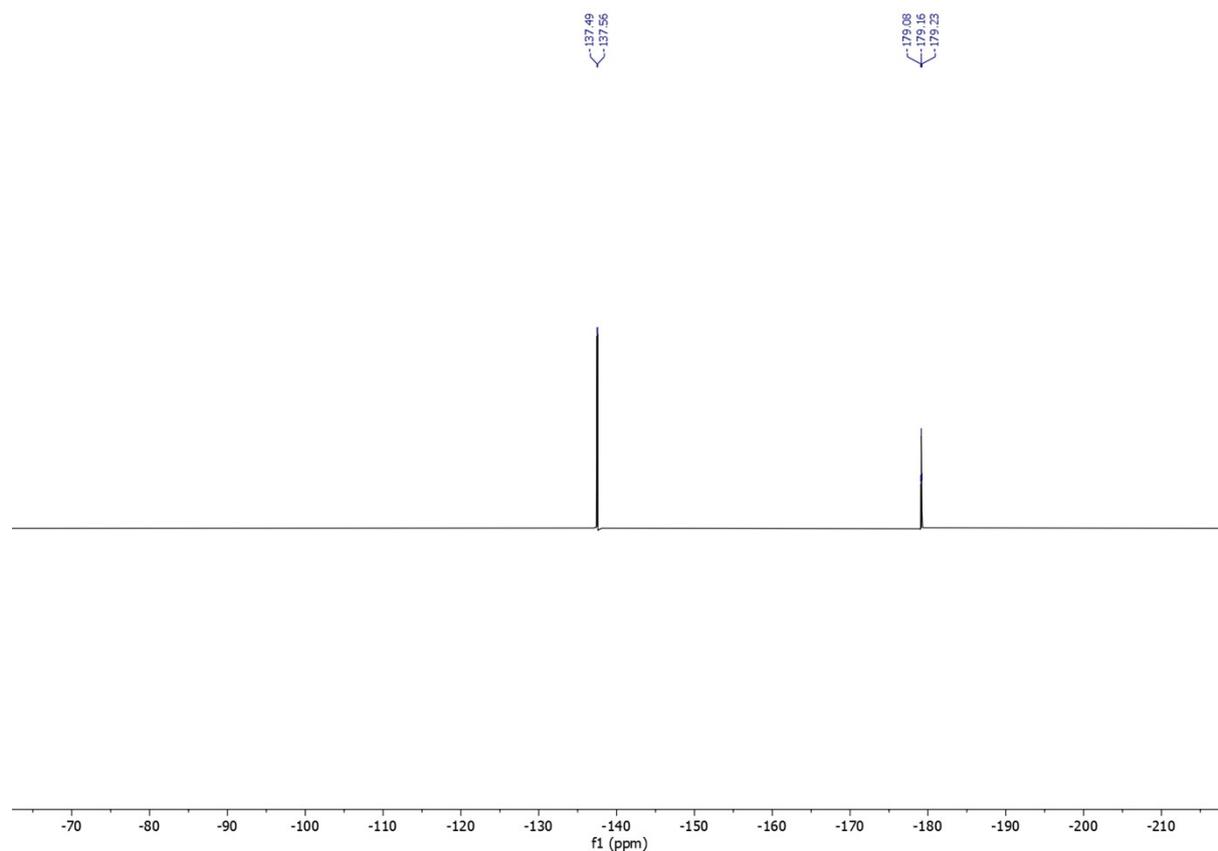


**Figure S4.**  $^{19}\text{F}\{^1\text{H}\}$  NMR (282.4 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-diphenylallyl)-3,5-difluoroaniline (**3b**).

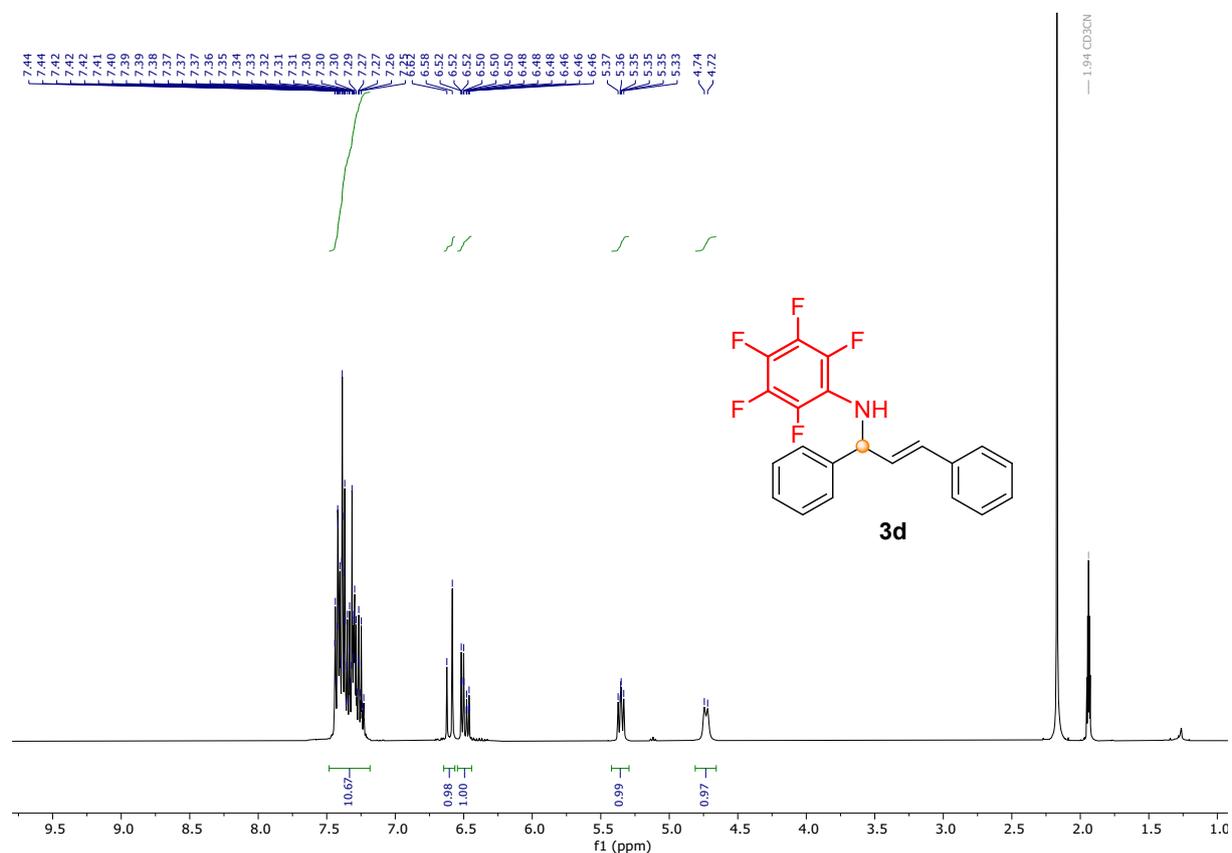




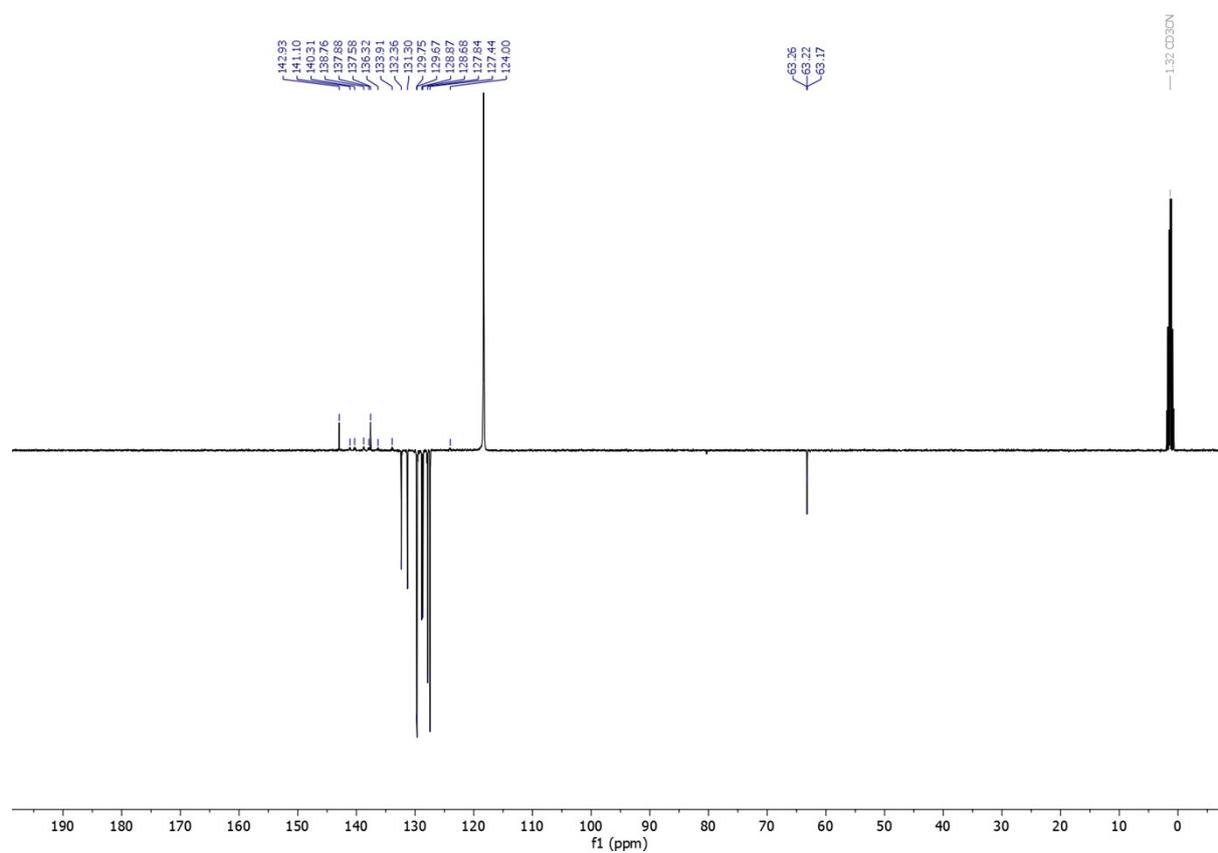
**Figure S7.**  $^{19}\text{F}\{^1\text{H}\}$  NMR (282.4 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-diphenylallyl)-3,4,5-trifluoroaniline (**3c**).



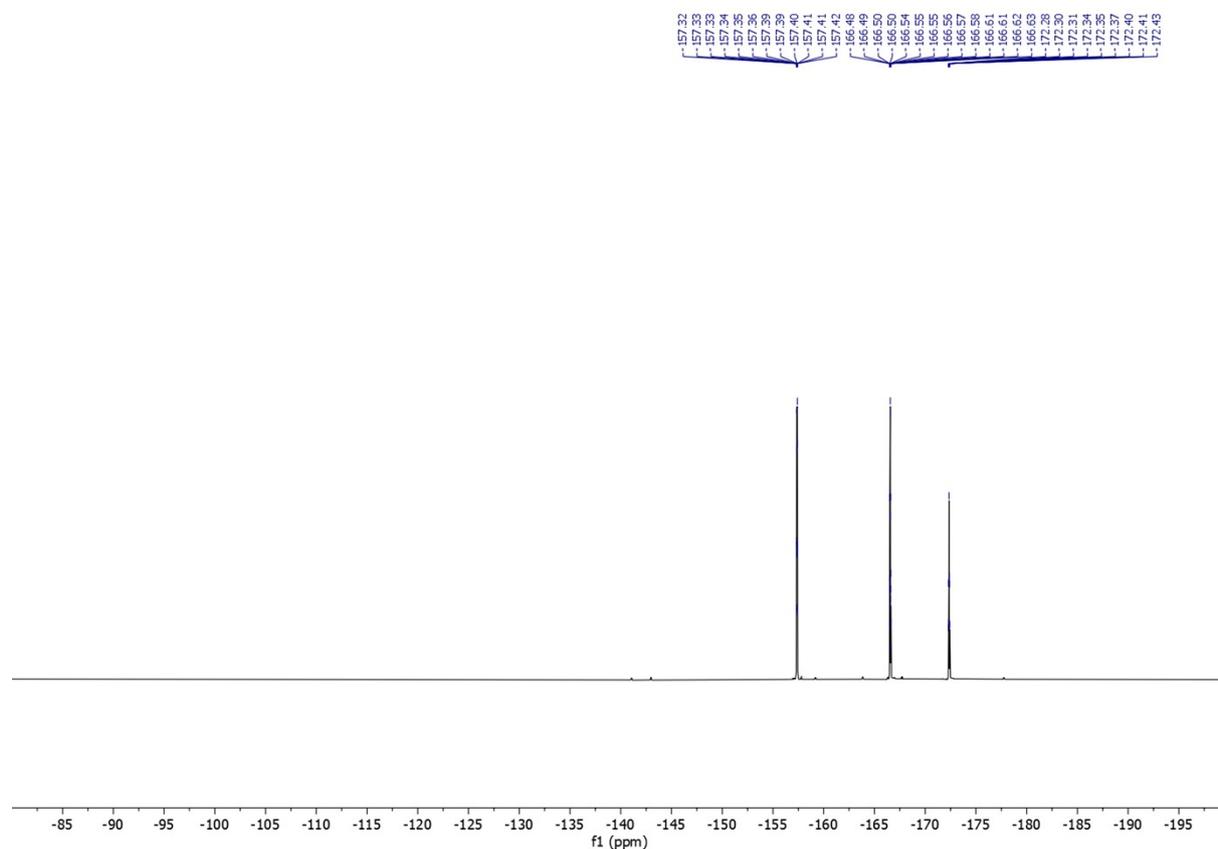
**Figure S8.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-diphenylallyl)-2,3,4,5,6-pentafluoroaniline (**3d**).



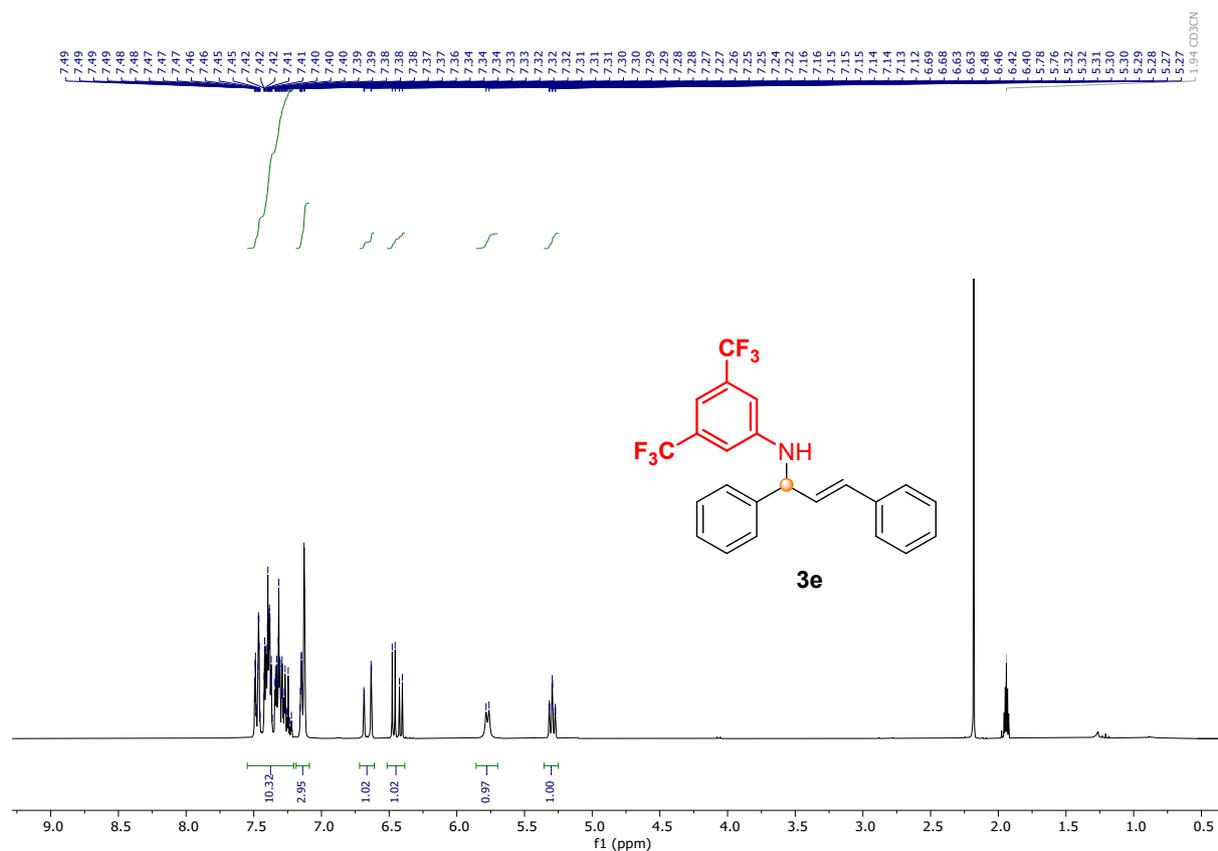
**Figure S9.**  $^{13}\text{C}\{^1\text{H}\}$  APT NMR (75 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-diphenylallyl)-2,3,4,5,6-pentafluoroaniline (**3d**).



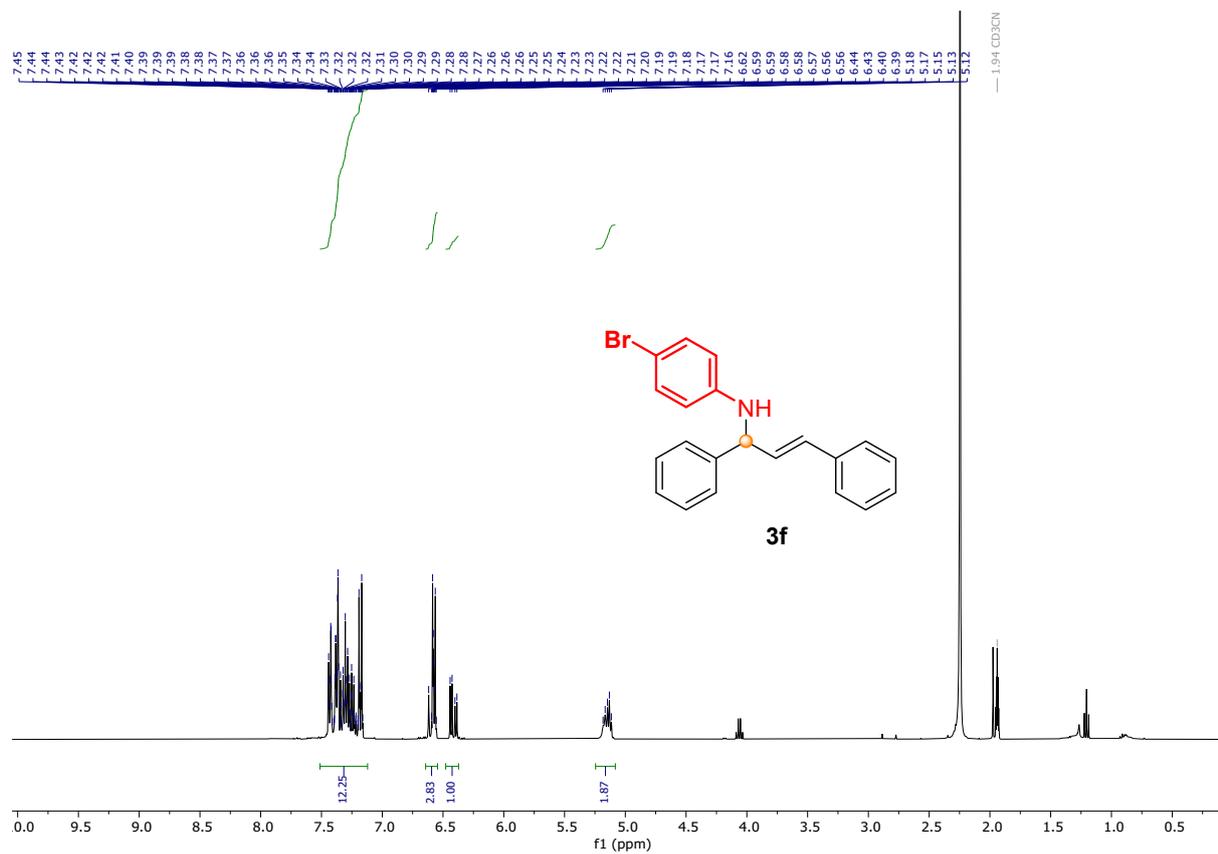
**Figure S10.**  $^{19}\text{F}\{^1\text{H}\}$  NMR (282.4 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-diphenylallyl)-2,3,4,5,6-pentafluoroaniline (**3d**).



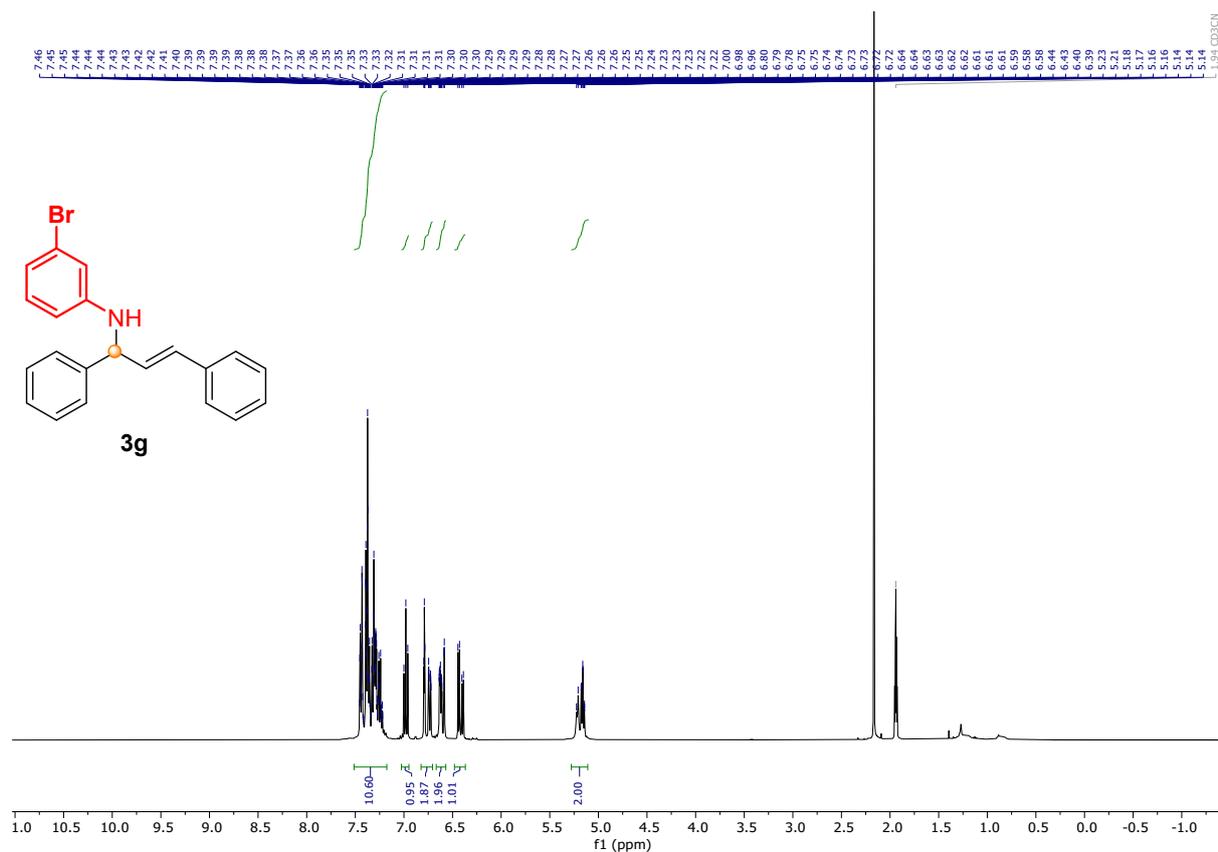
**Figure S11.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-diphenylallyl)-3,5-bis(trifluoromethyl)aniline (**3e**).



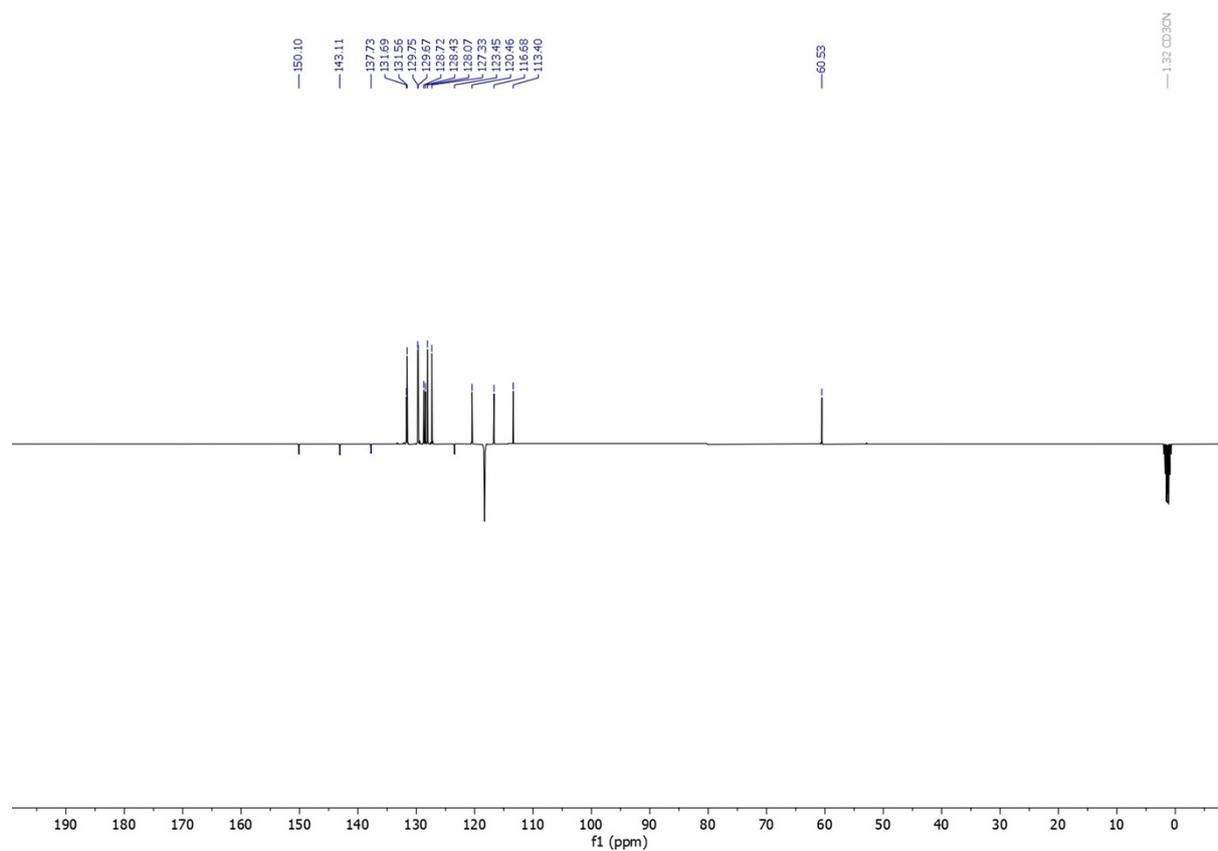
**Figure S12.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-4-bromo-*N*-(1,3-diphenylallyl)aniline (**3f**).



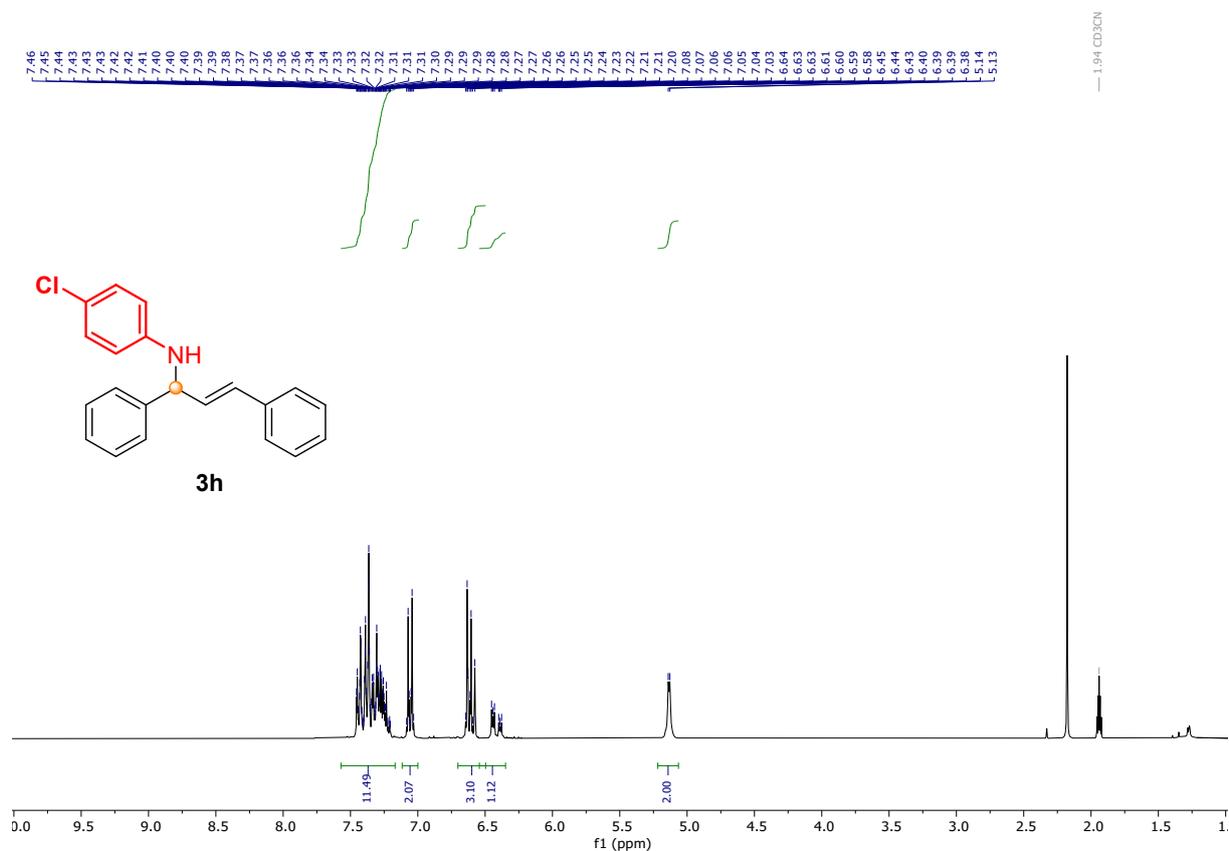
**Figure S13.**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-3-bromo-*N*-(1,3-diphenylallyl)aniline (**3g**).



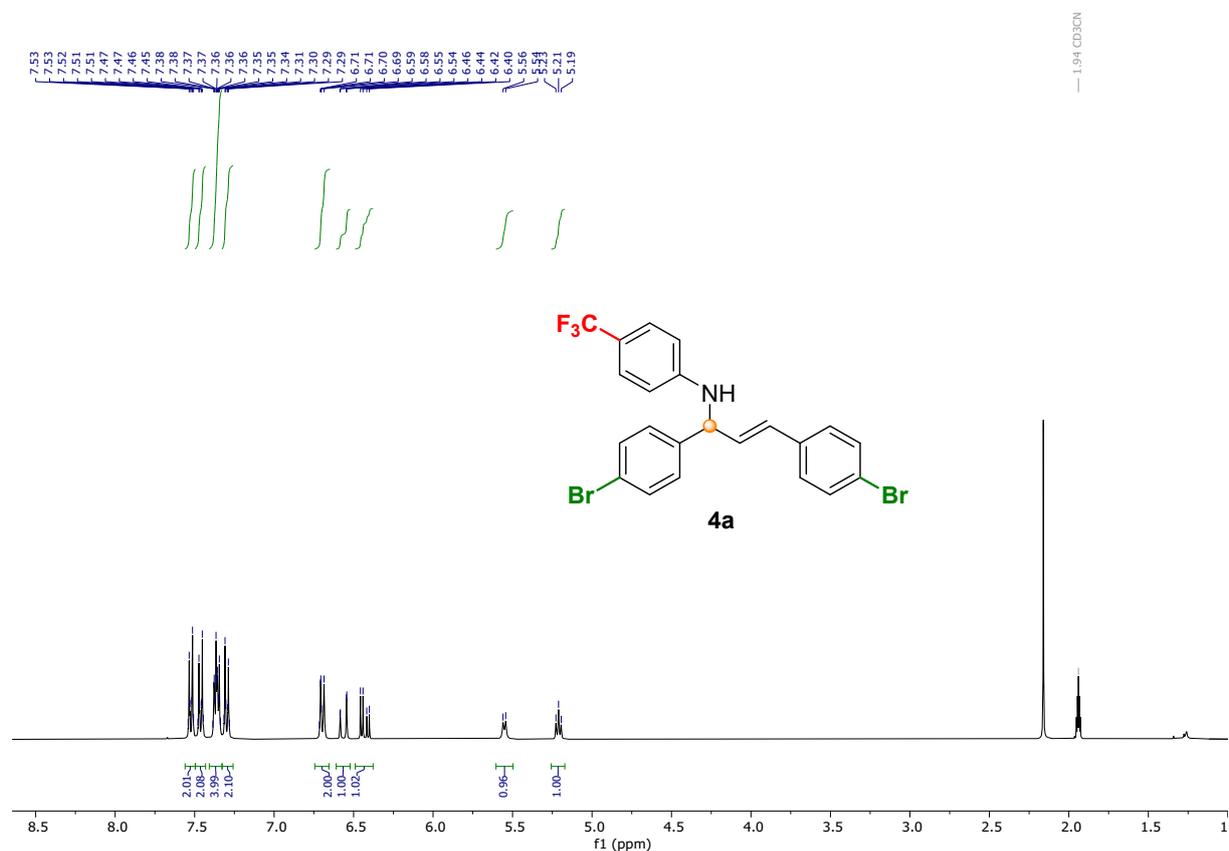
**Figure S14.**  $^{13}\text{C}\{^1\text{H}\}$  APT NMR (101 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-bis(3-bromophenyl)allyl)-4-(trifluoromethyl)aniline (**3g**).



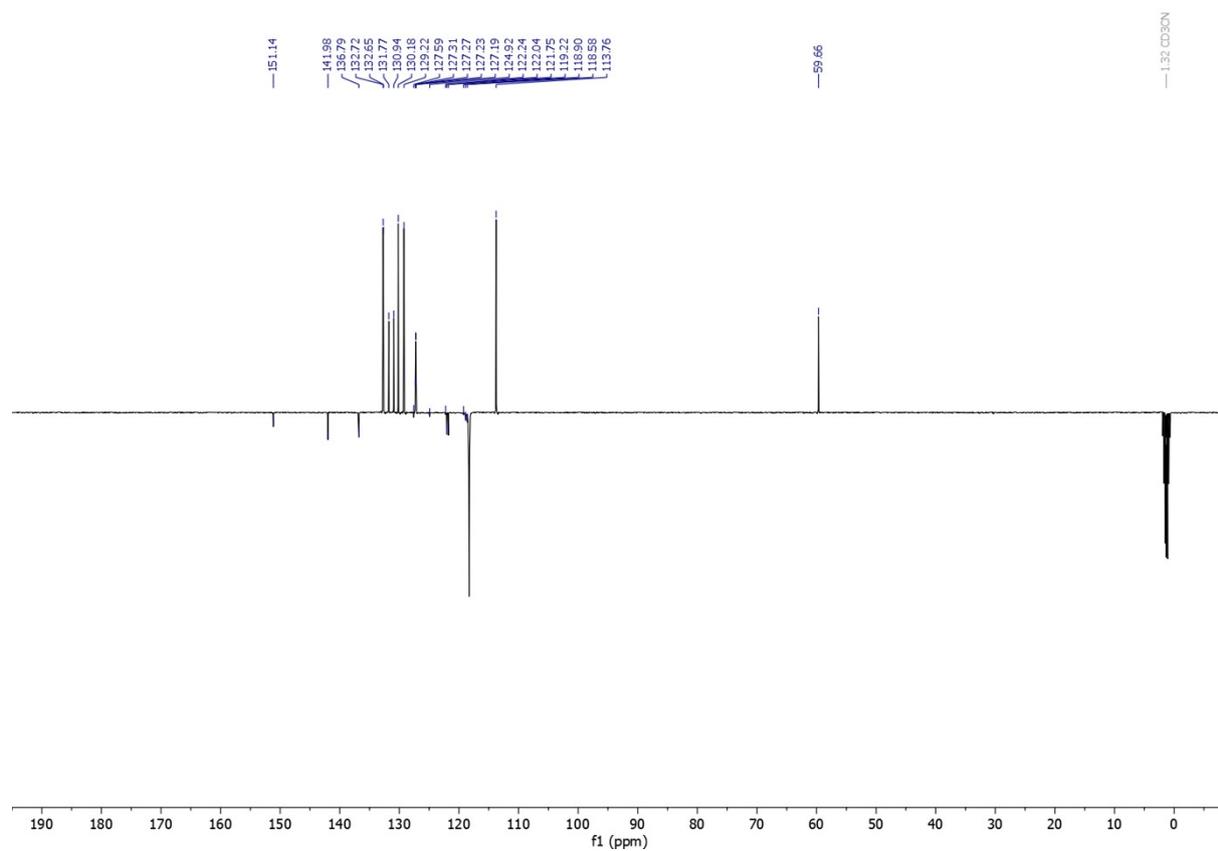
**Figure S15.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-4-chloro-*N*-(1,3-diphenylallyl)aniline (**3h**).



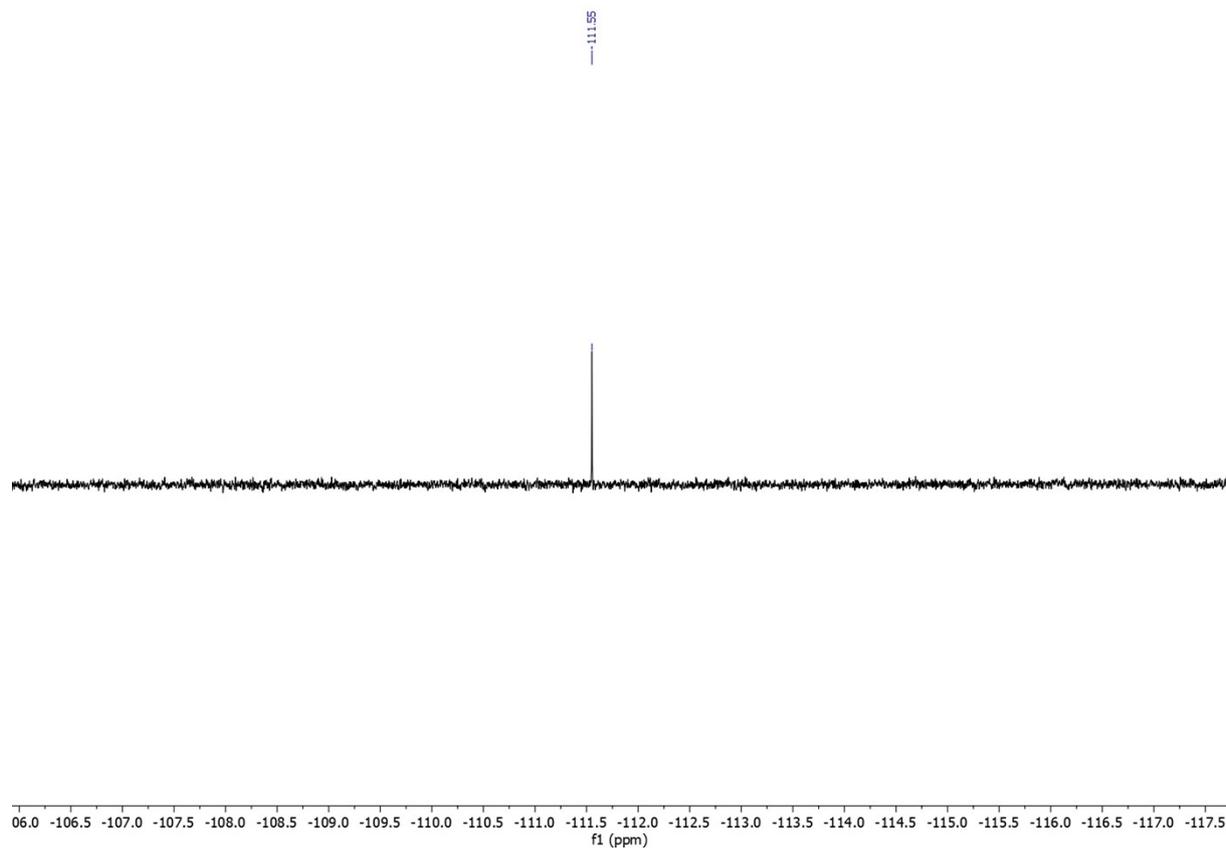
**Figure S16.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-bis(4-bromophenyl)allyl)-4-(trifluoromethyl)aniline (**4a**).



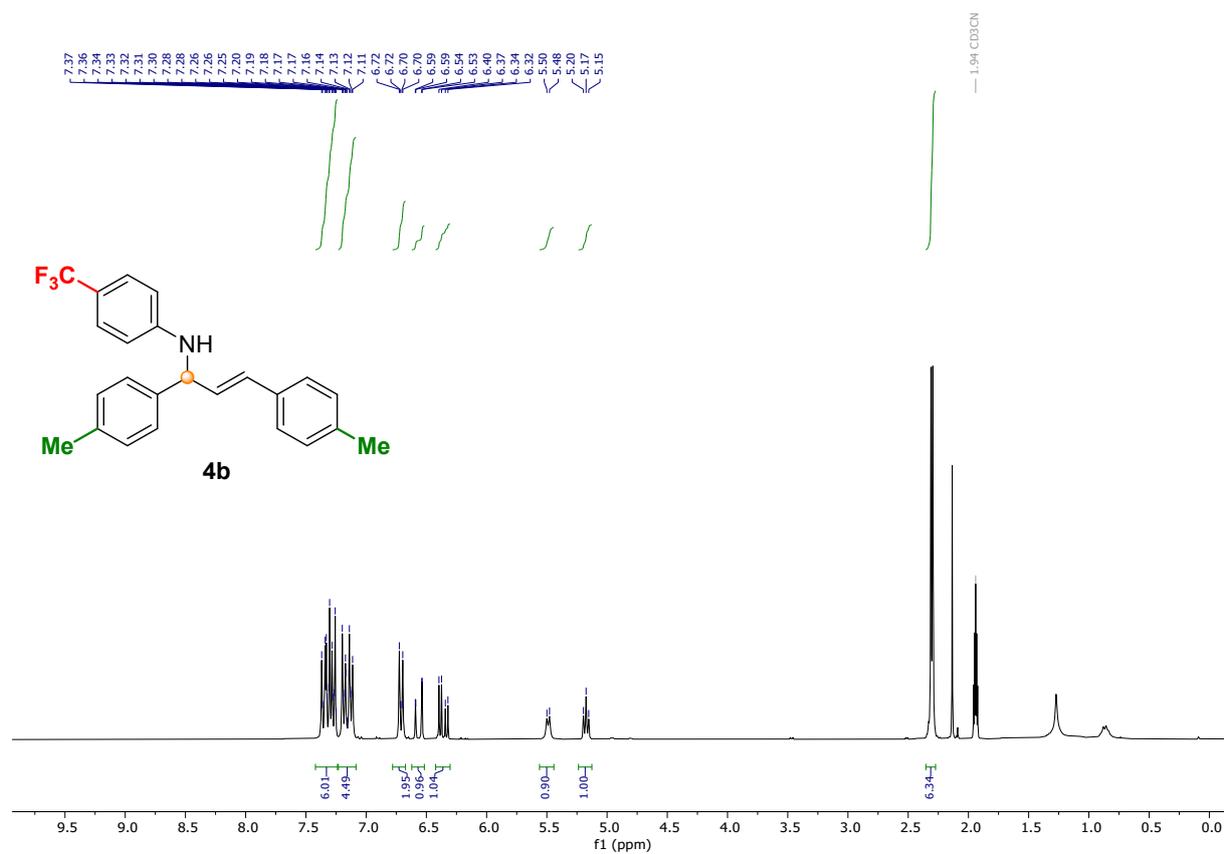
**Figure S17.**  $^{13}\text{C}\{^1\text{H}\}$  APT NMR (75 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-bis(4-bromophenyl)allyl)-4-(trifluoromethyl)aniline (**4a**).



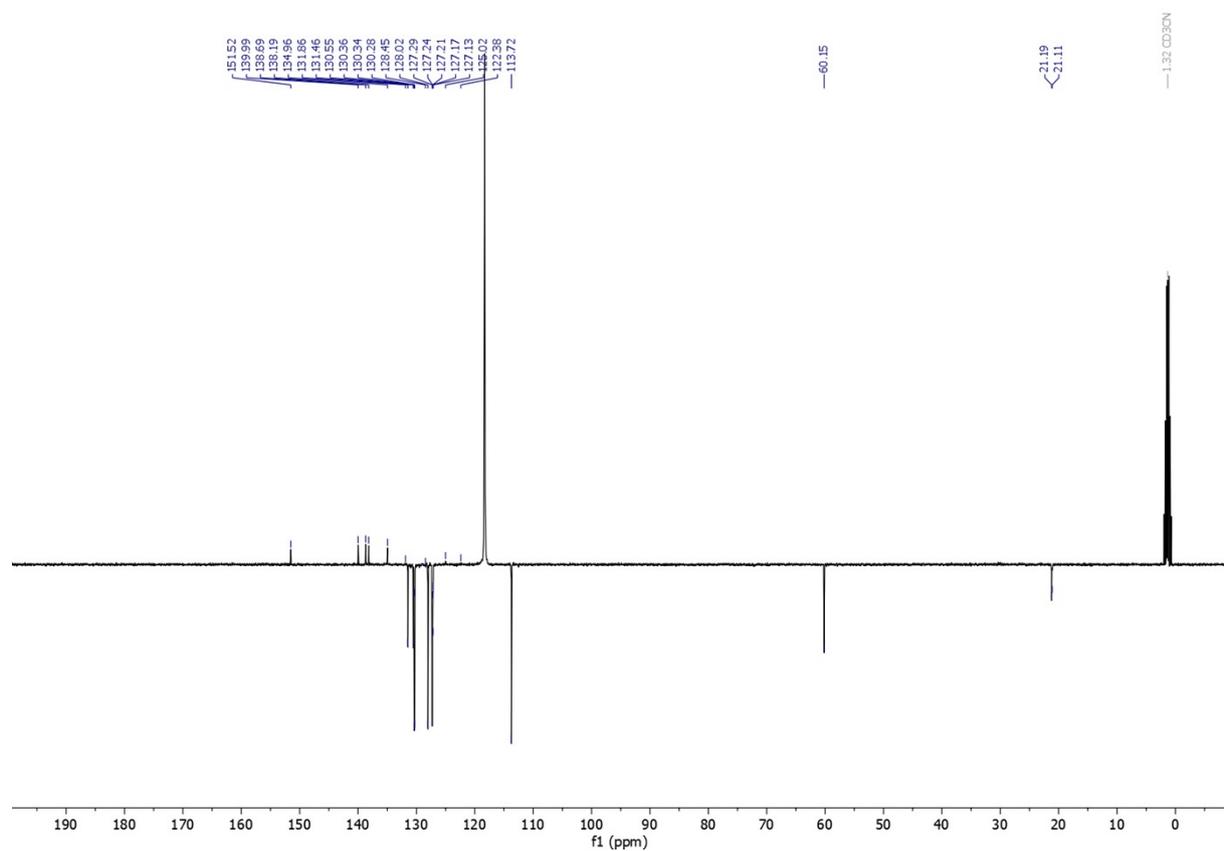
**Figure S18.**  $^{19}\text{F}\{^1\text{H}\}$  NMR (282.4 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-bis(4-bromophenyl)allyl)-4-(trifluoromethyl)aniline (**4a**).



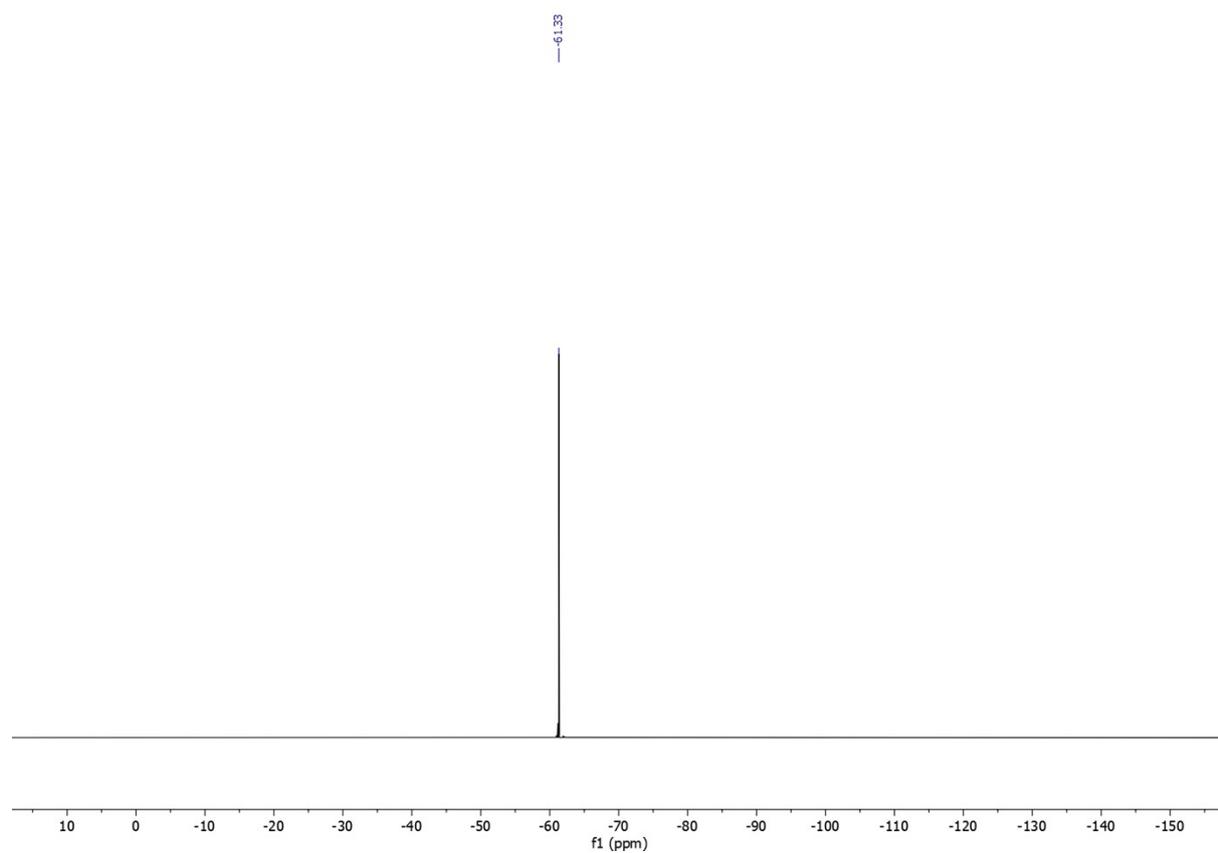
**Figure S19.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-di-*p*-tolylallyl)-4-(trifluoromethyl)aniline (**4b**).



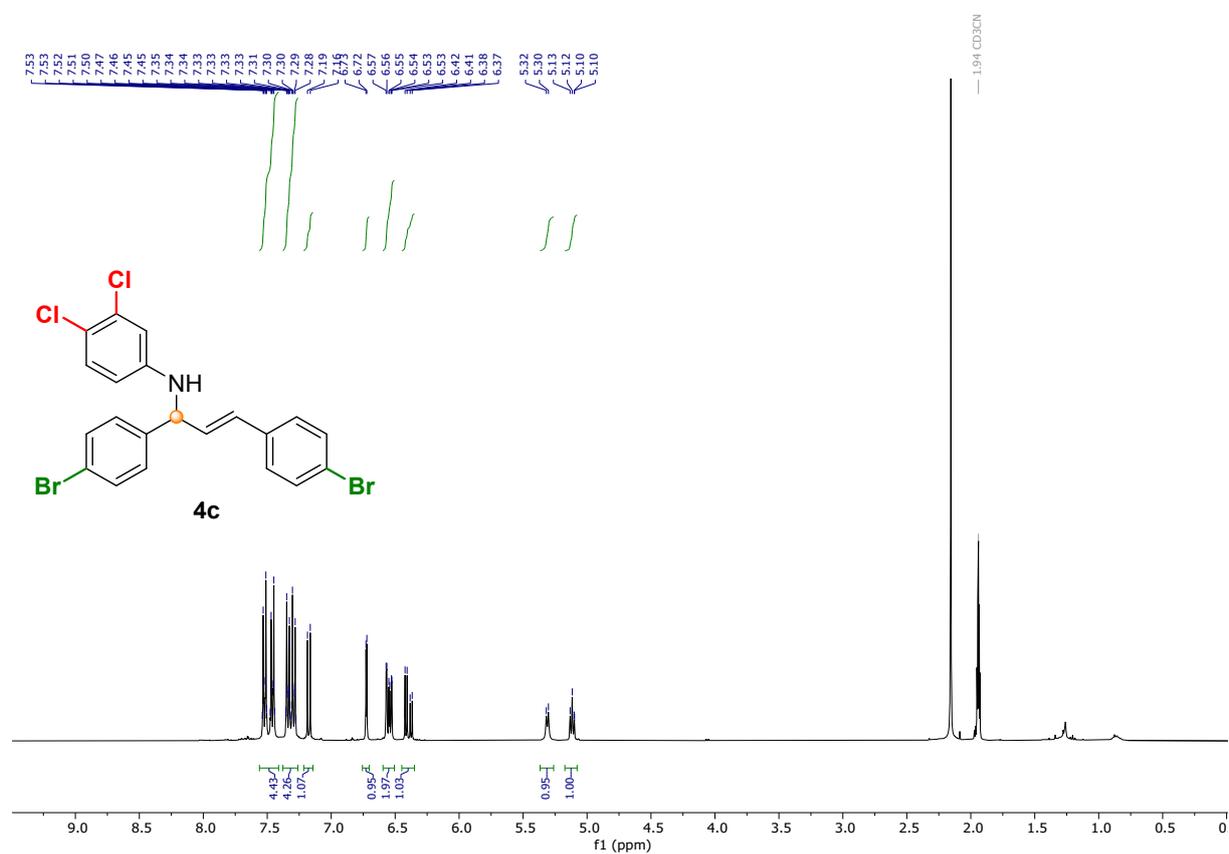
**Figure S20.**  $^{13}\text{C}\{^1\text{H}\}$  APT NMR (75 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-di-*p*-tolylallyl)-4-(trifluoromethyl)aniline (**4b**).



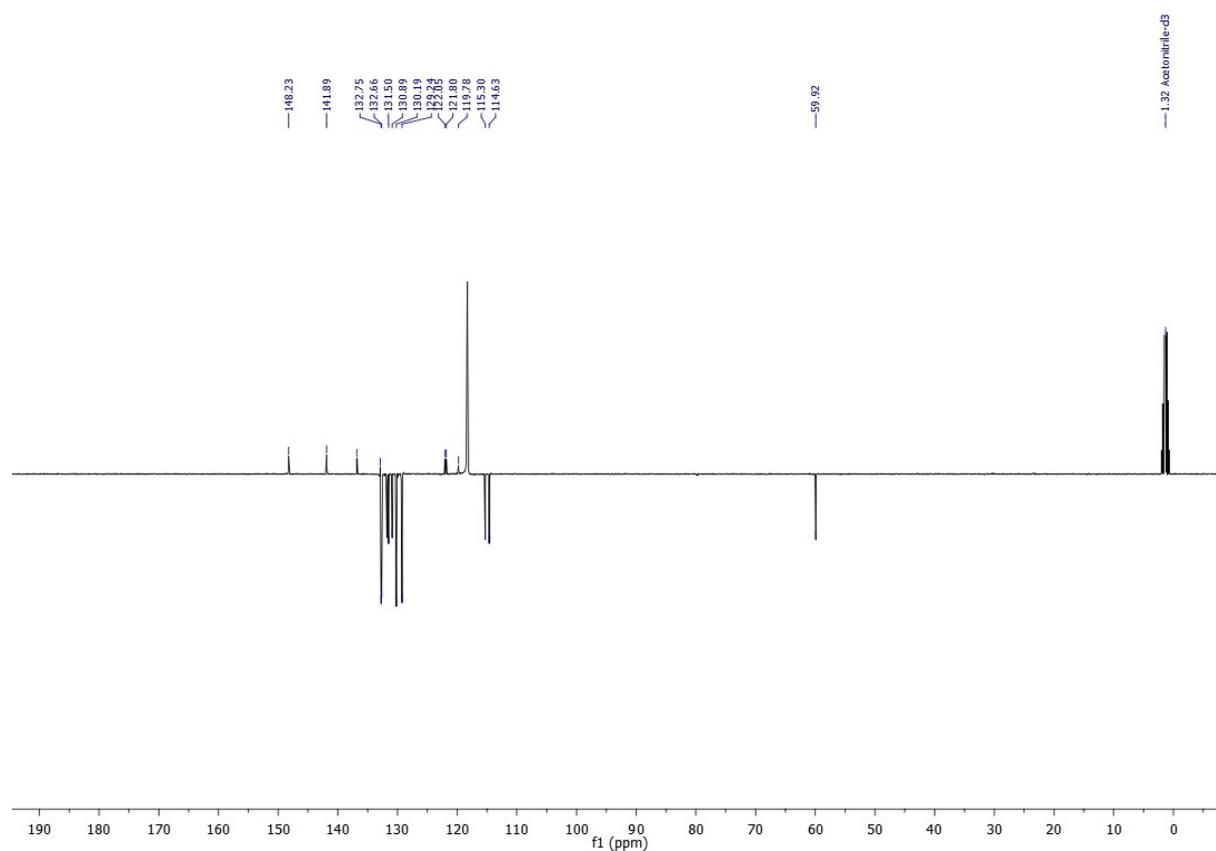
**Figure S21.**  $^{19}\text{F}\{^1\text{H}\}$  NMR (282.4 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-di-*p*-tolylallyl)-4-(trifluoromethyl)aniline (**4b**).



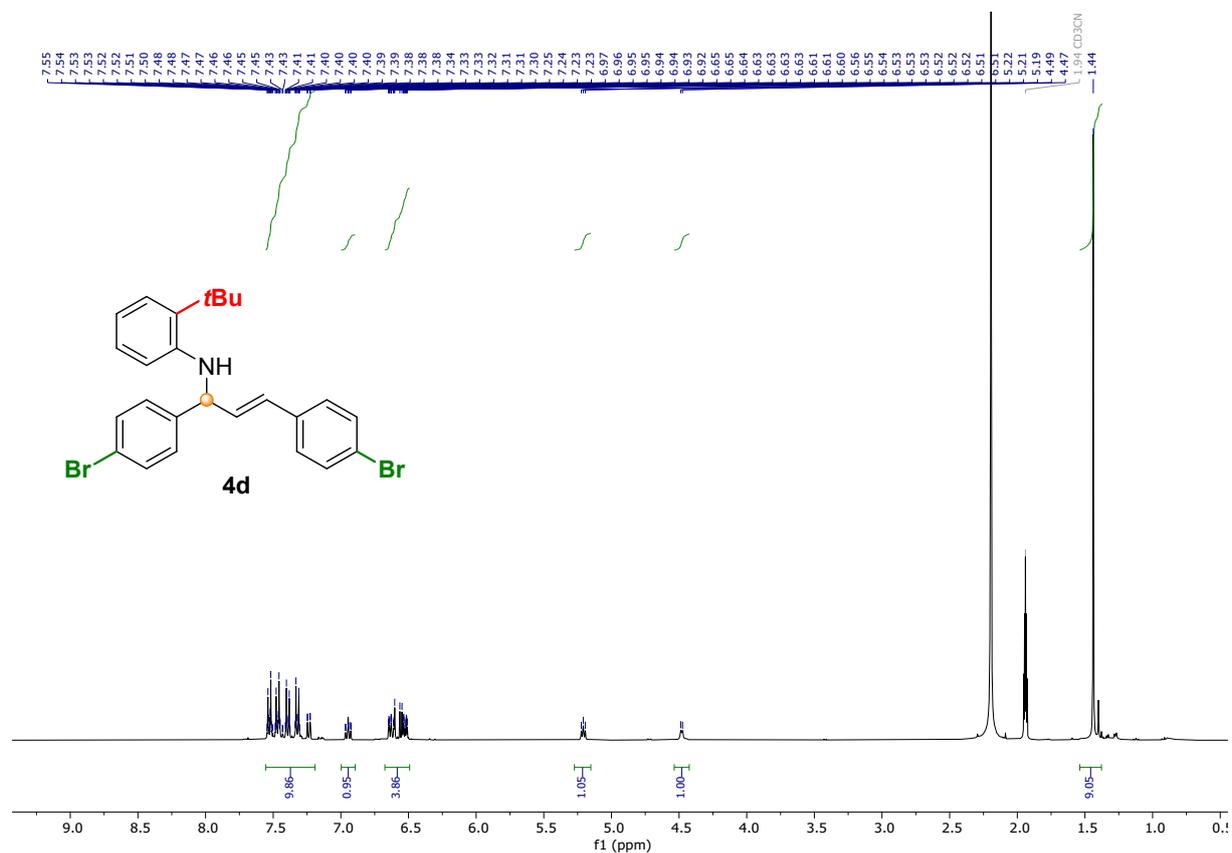
**Figure S22.**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-bis(4-bromophenyl)allyl)-3,4-dichloroaniline (**4c**).



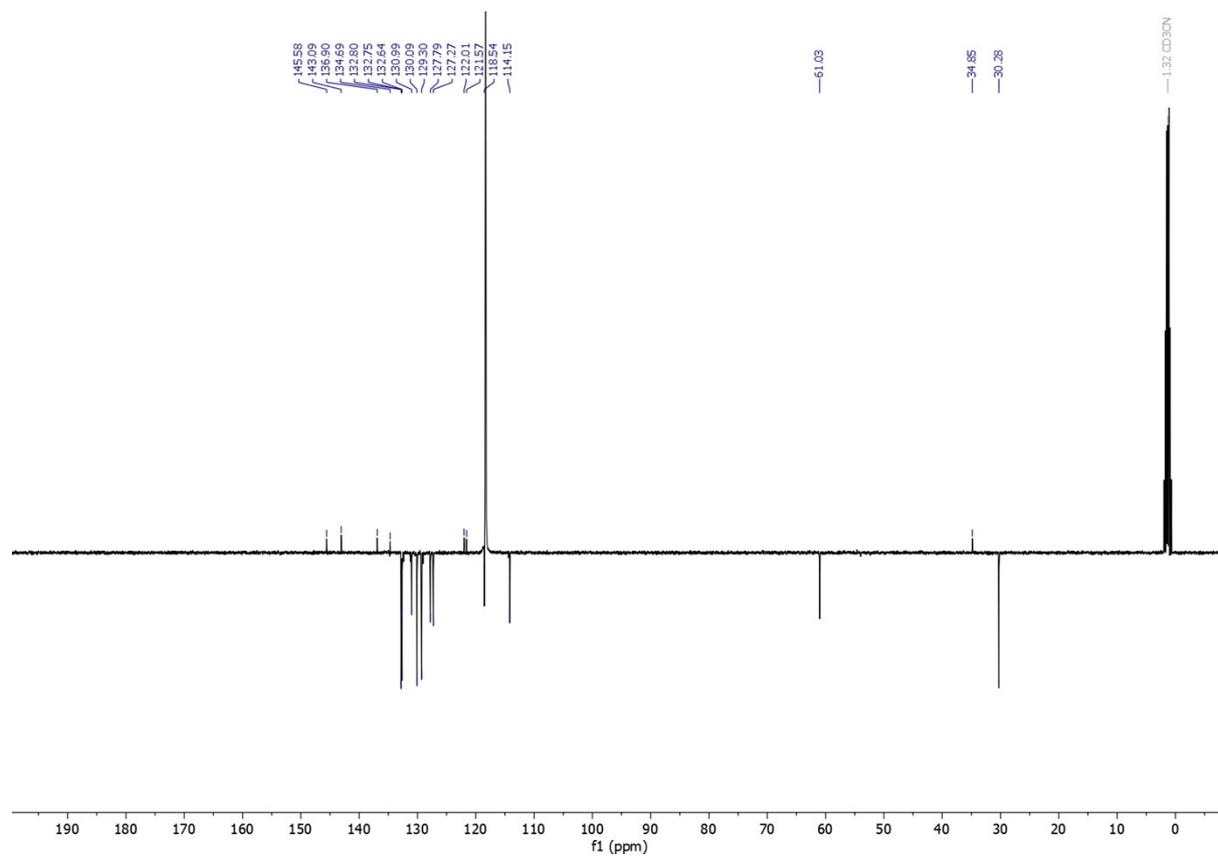
**Figure S23.**  $^{13}\text{C}\{^1\text{H}\}$  APT NMR (101 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-bis(4-bromophenyl)allyl)-3,4-dichloroaniline (**4c**).



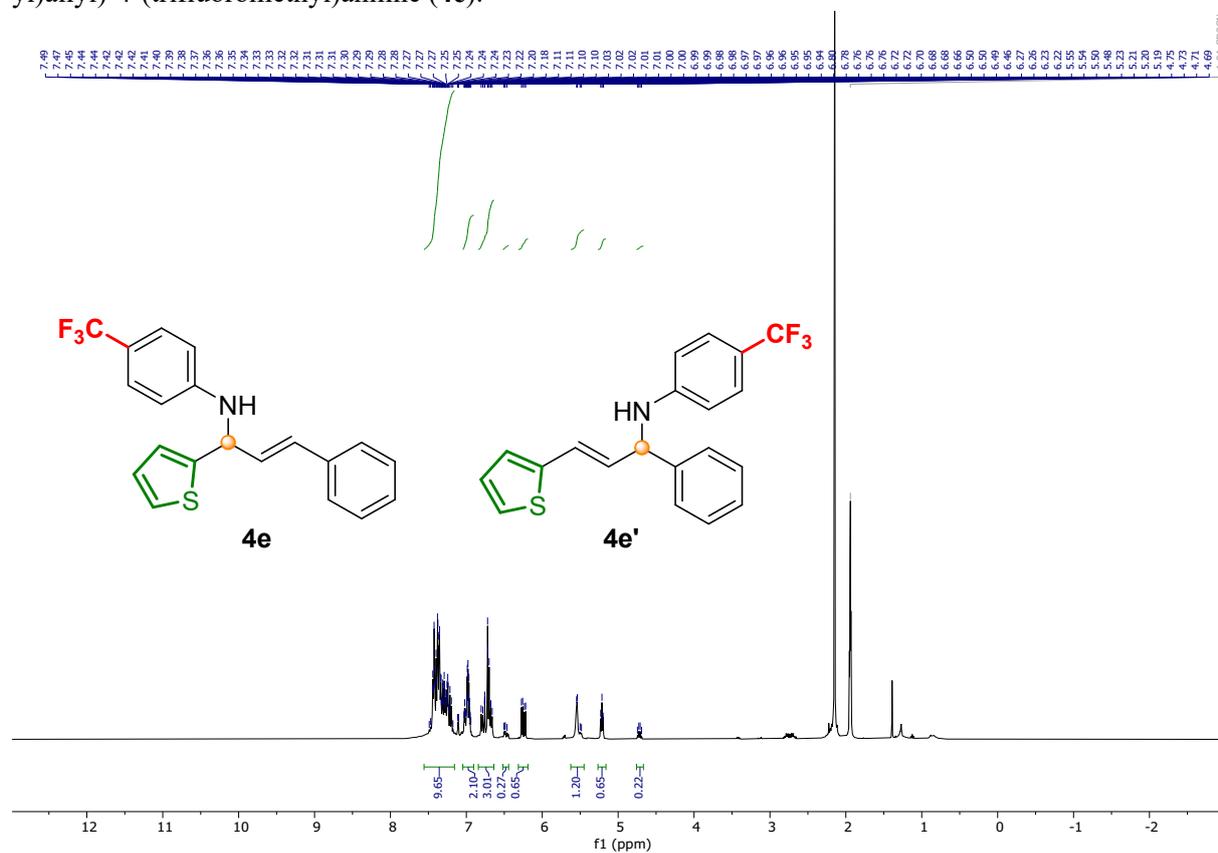
**Figure S24.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-bis(4-bromophenyl)allyl)-2-(*tert*-butyl)aniline (**4d**).



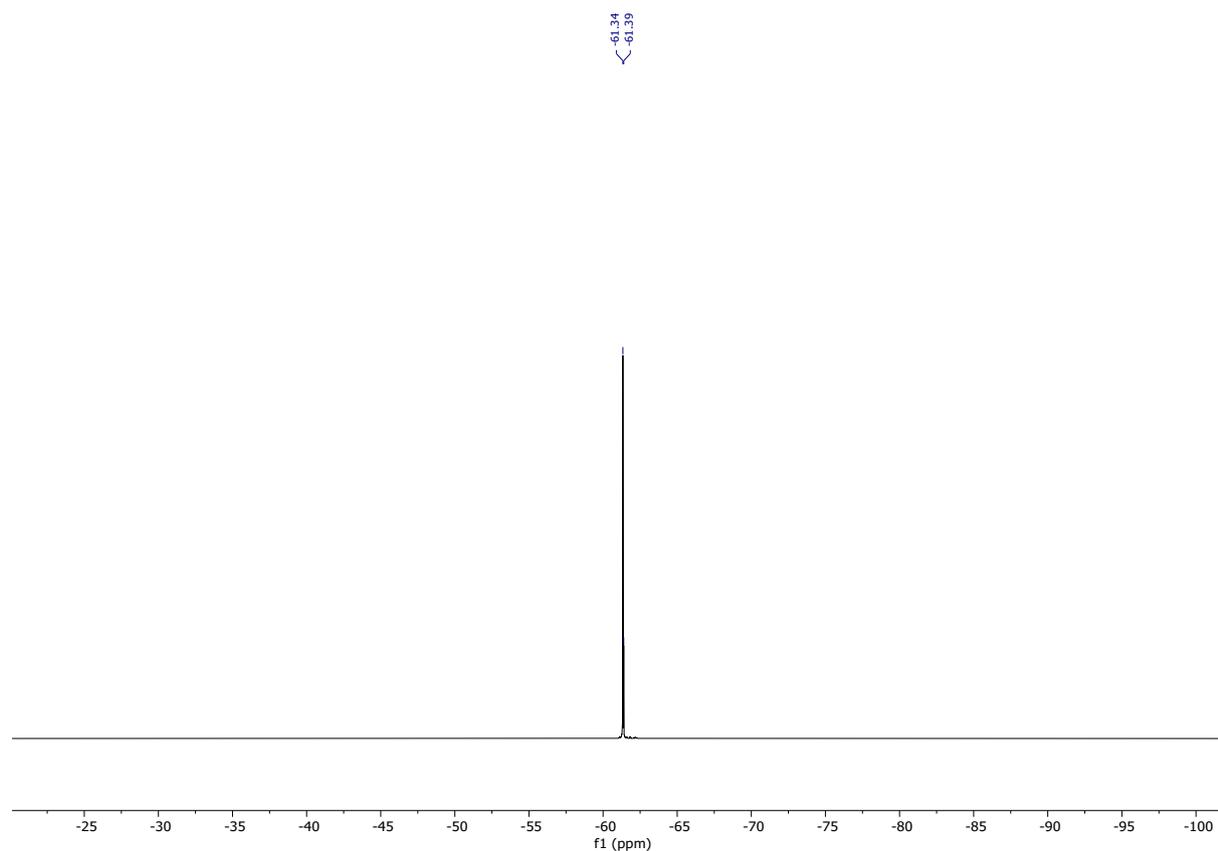
**Figure S25.**  $^{13}\text{C}\{^1\text{H}\}$  APT NMR (75 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(1,3-bis(4-chlorophenyl)allyl)-3-(*tert*-butyl)aniline (**4d**).



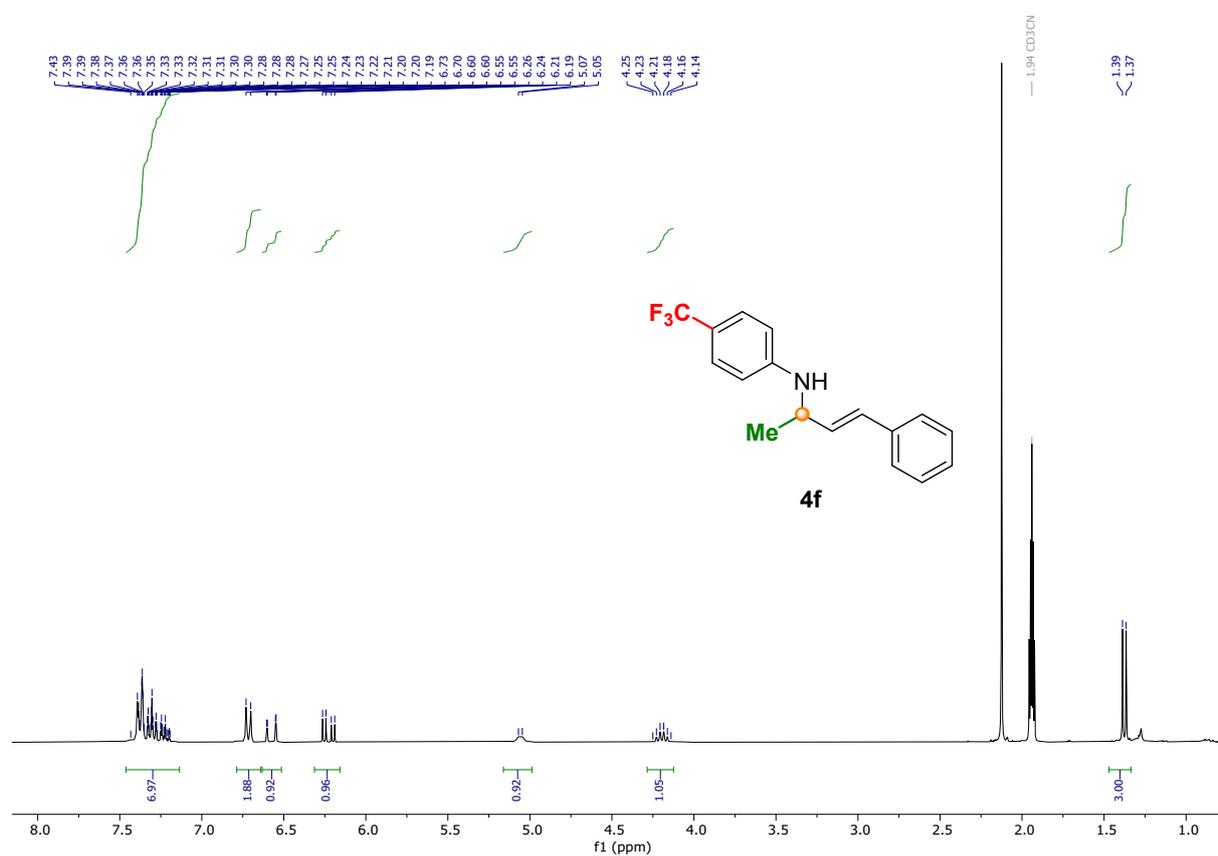
**Figure S26.**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(3-phenyl-1-(thiophen-2-yl)allyl)-4-(trifluoromethyl)aniline (**4e**).



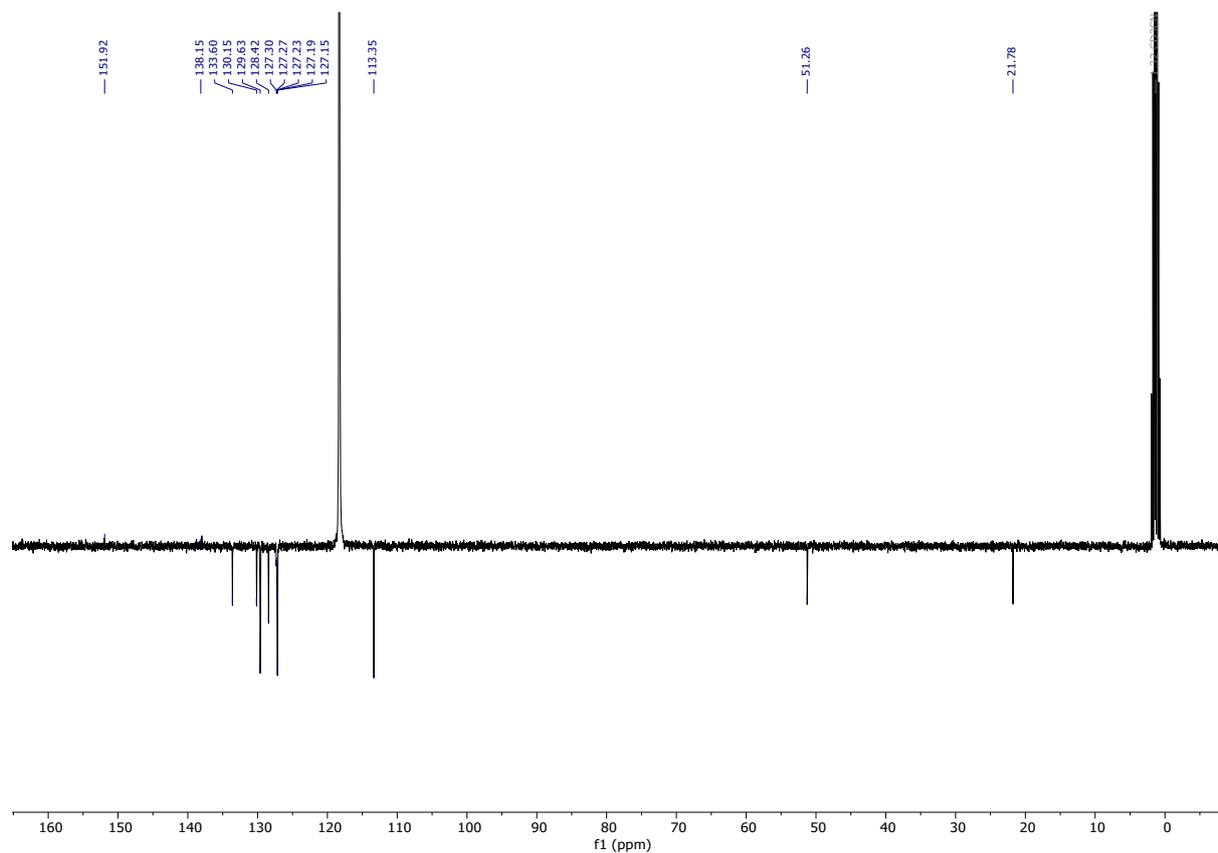
**Figure S27.**  $^{19}\text{F}\{^1\text{H}\}$  NMR (376.5 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(3-phenyl-1-(thiophen-2-yl)allyl)-4-(trifluoromethyl)aniline (**4e**).



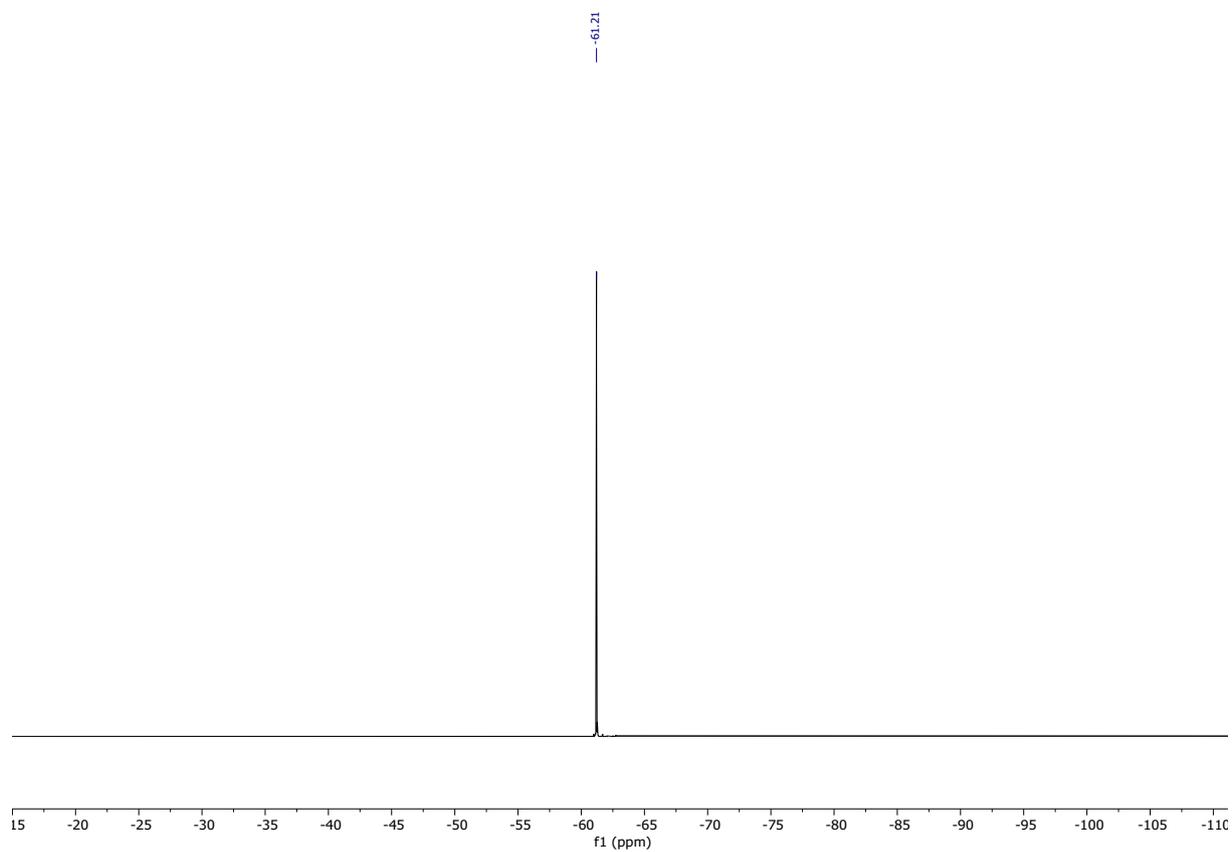
**Figure S28.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{COCD}_3$ ) spectrum of compound (*E*)-*N*-(4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)aniline (**4f**).



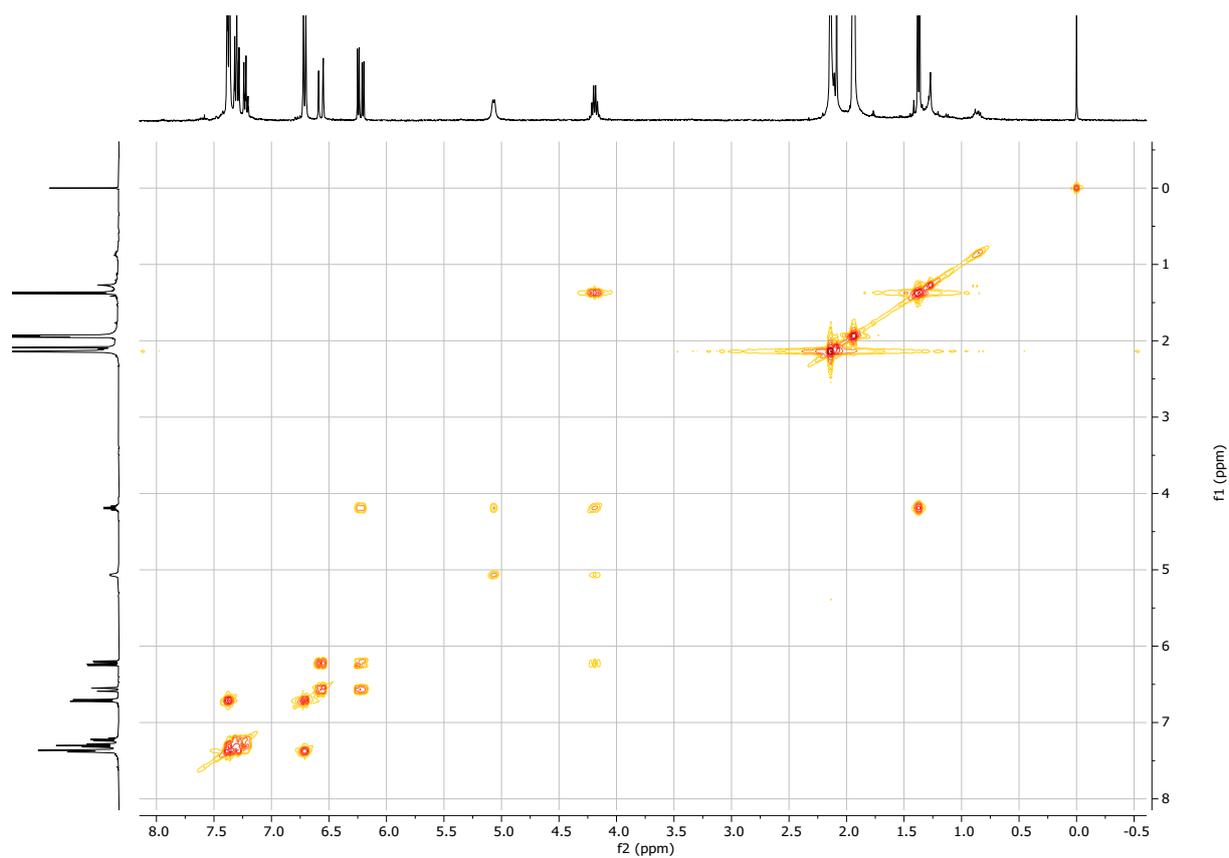
**Figure S29.**  $^{13}\text{C}\{^1\text{H}\}$  APT NMR (101 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N*-(4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)aniline (**4f**).



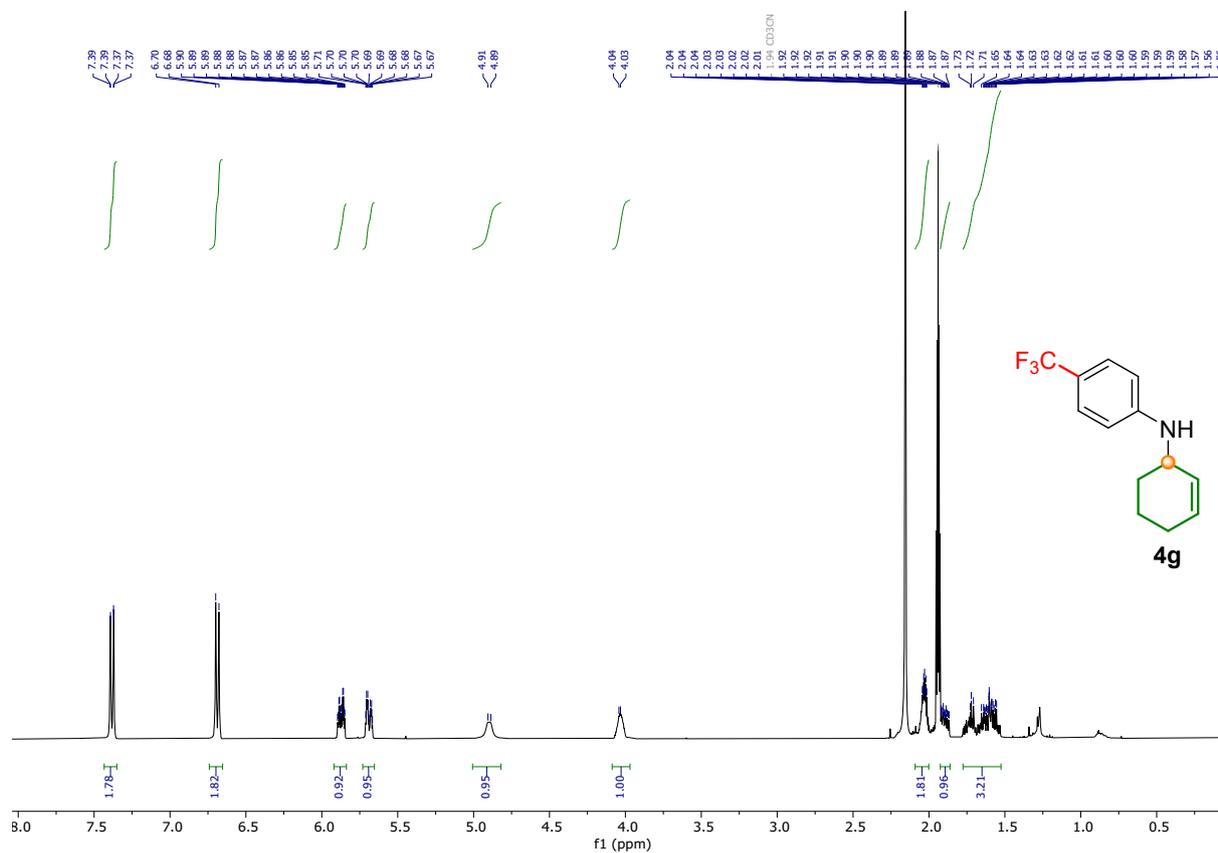
**Figure S30.**  $^{19}\text{F}\{^1\text{H}\}$  NMR (282.4 MHz,  $\text{CD}_3\text{COCD}_3$ ) spectrum of compound (*E*)-*N*-(4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)aniline (**4f**).



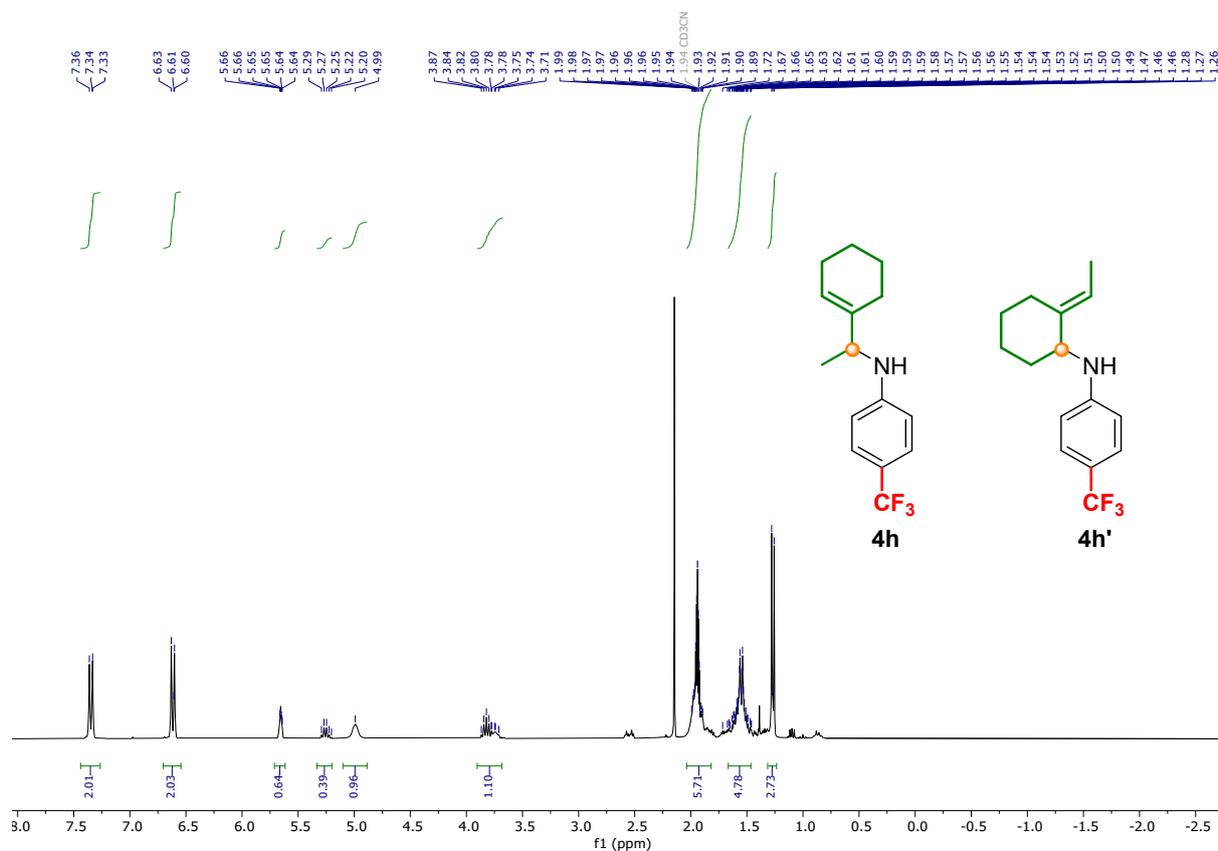
**Figure S31.** COSY (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>) spectrum of compound (*E*)-*N*-(4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)aniline (**4f**).



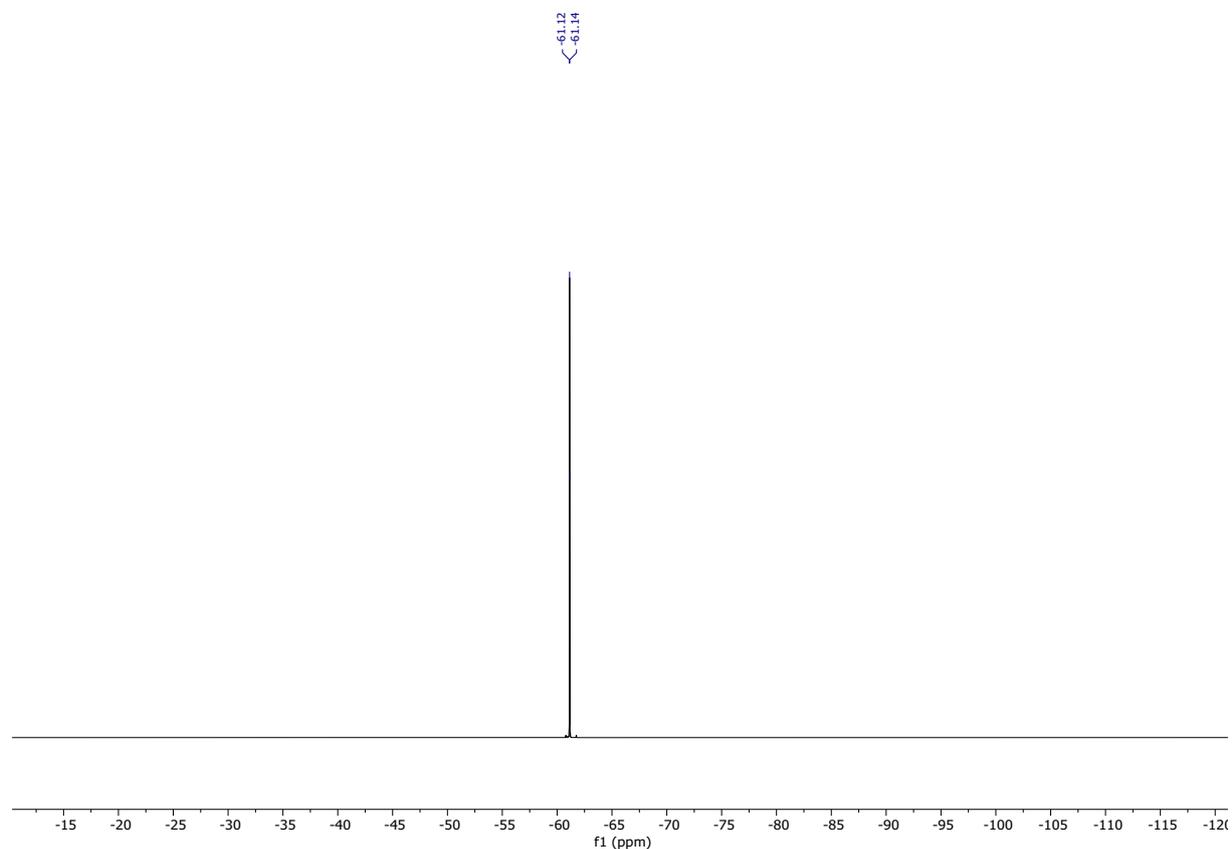
**Figure S32.** <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN) spectrum of compound *N*-(cyclohex-2-en-1-yl)-4-(trifluoromethyl)aniline (**4g**).



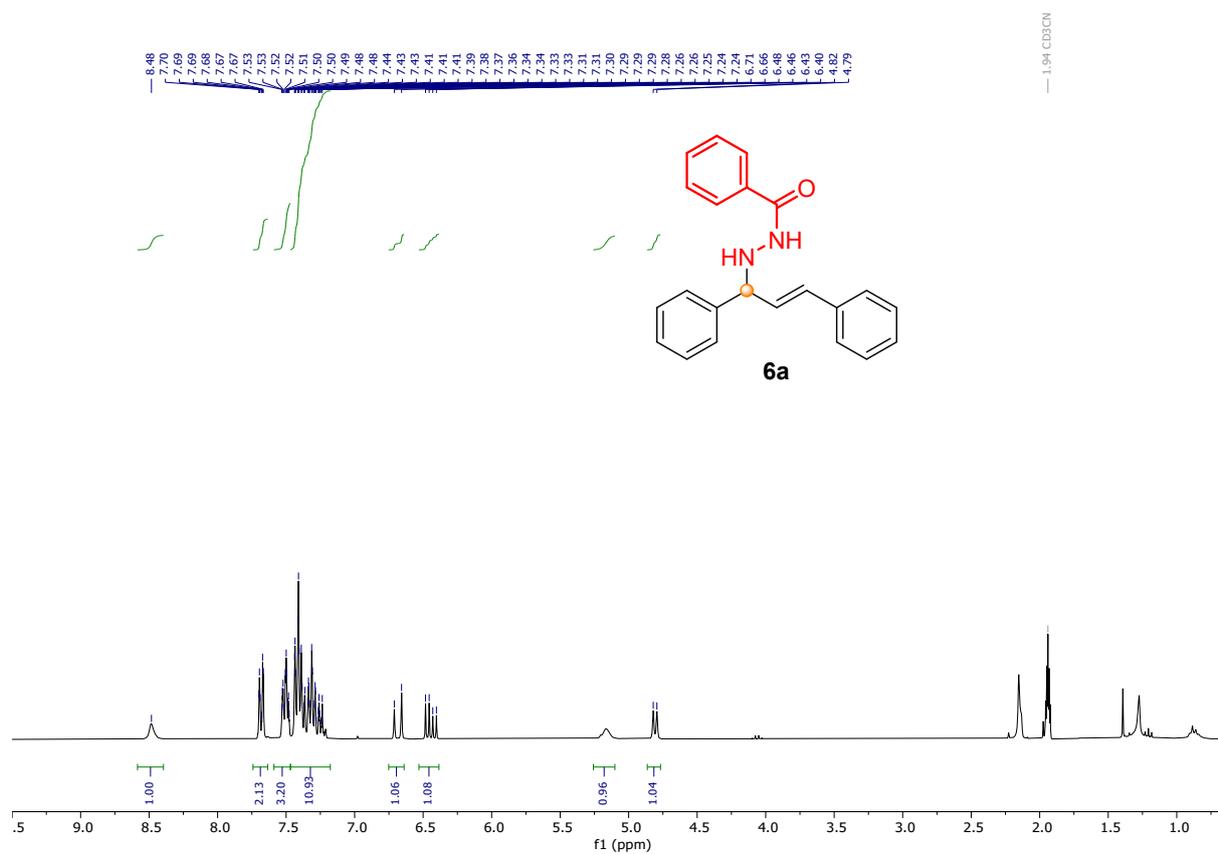
**Figure S33.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound *N*-(2-ethylidenecyclohexyl)-4-(trifluoromethyl)aniline (**4h**).



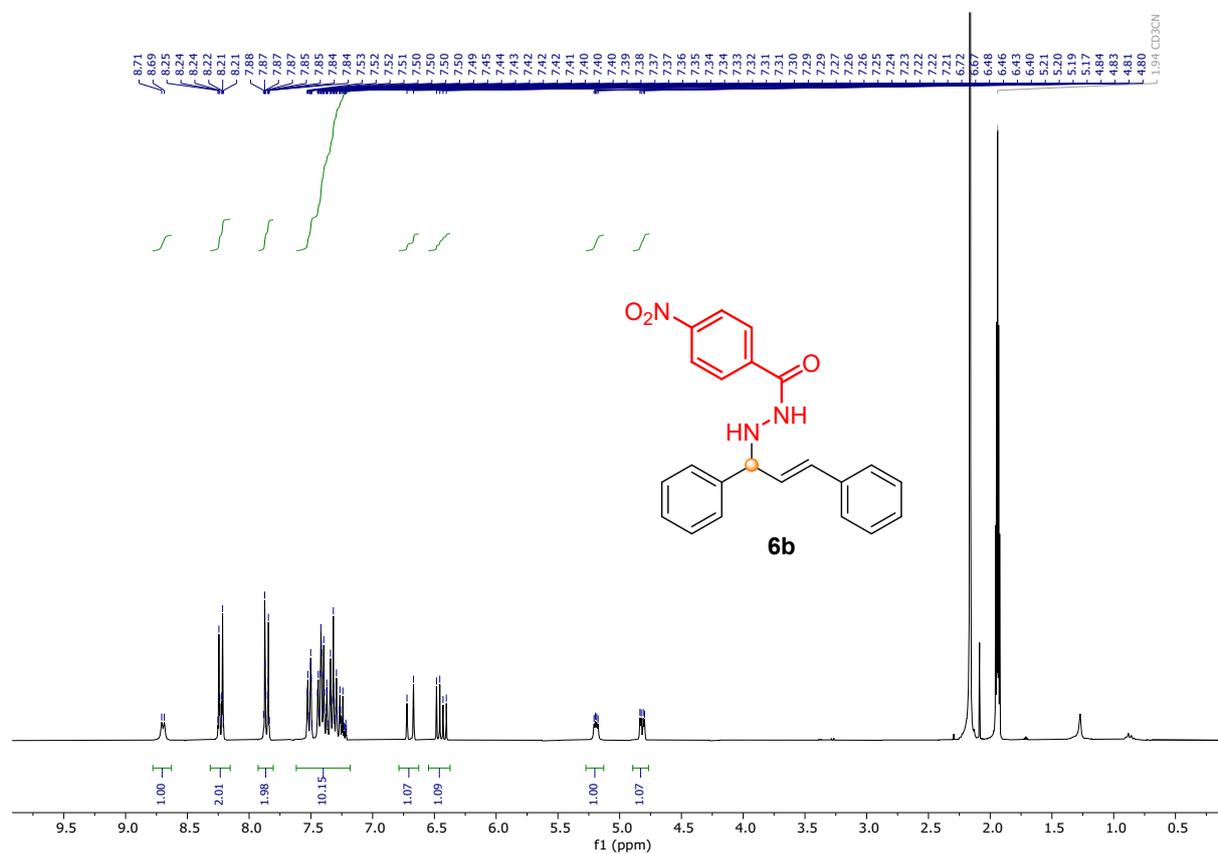
**Figure S34.**  $^{19}\text{F}\{^1\text{H}\}$  NMR (282.4 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound *N*-(2-ethylidenecyclohexyl)-4-(trifluoromethyl)aniline (**4h**).



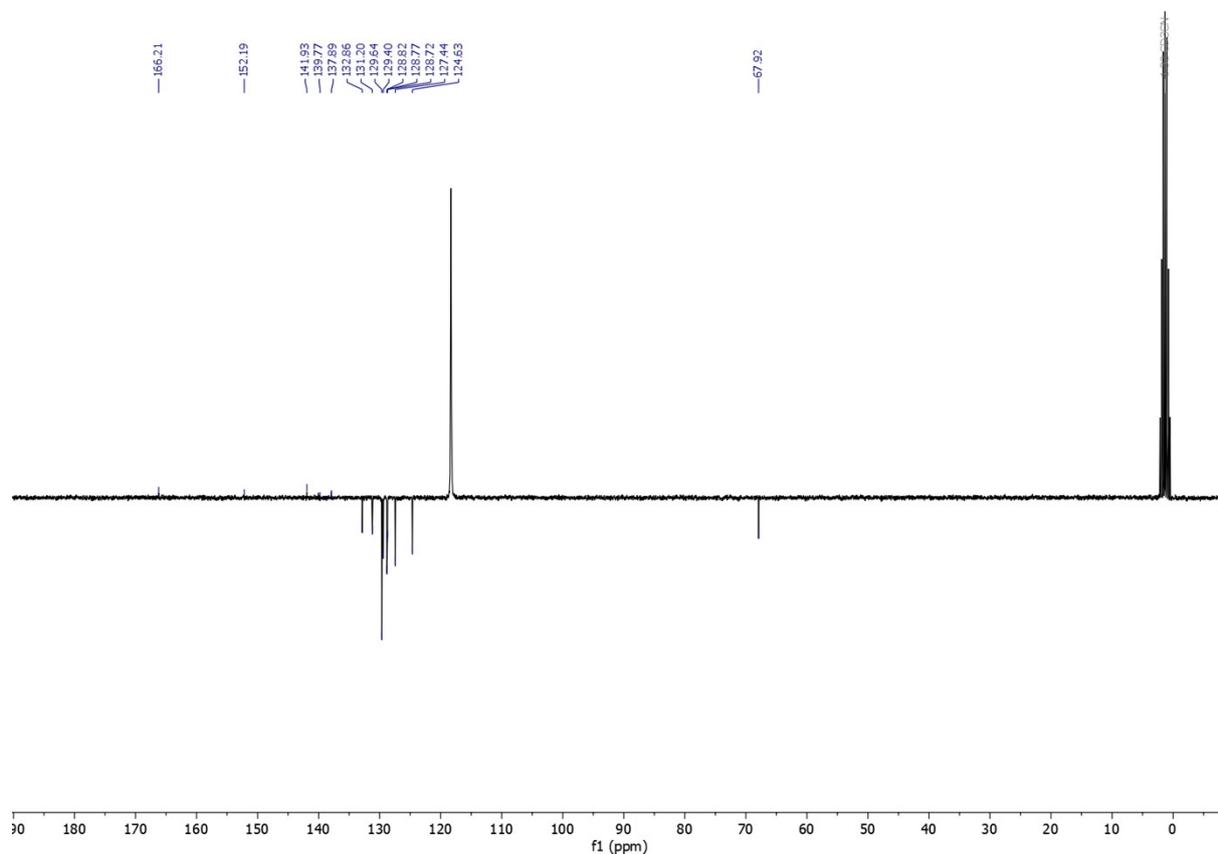
**Figure S35.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N'*-(1,3-diphenylallyl)benzohydrazide (**6a**).



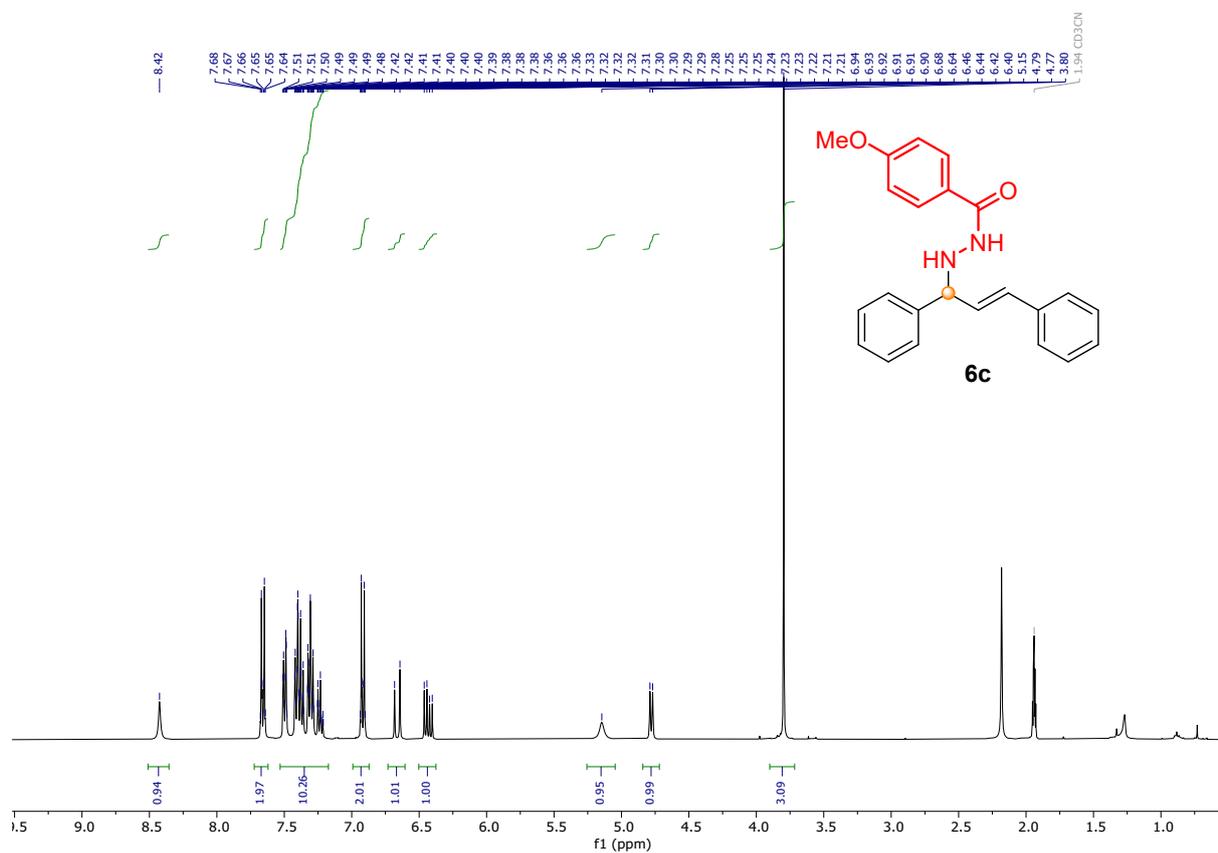
**Figure S36.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N'*-(1,3-diphenylallyl)-4-nitrobenzohydrazide (**6b**).



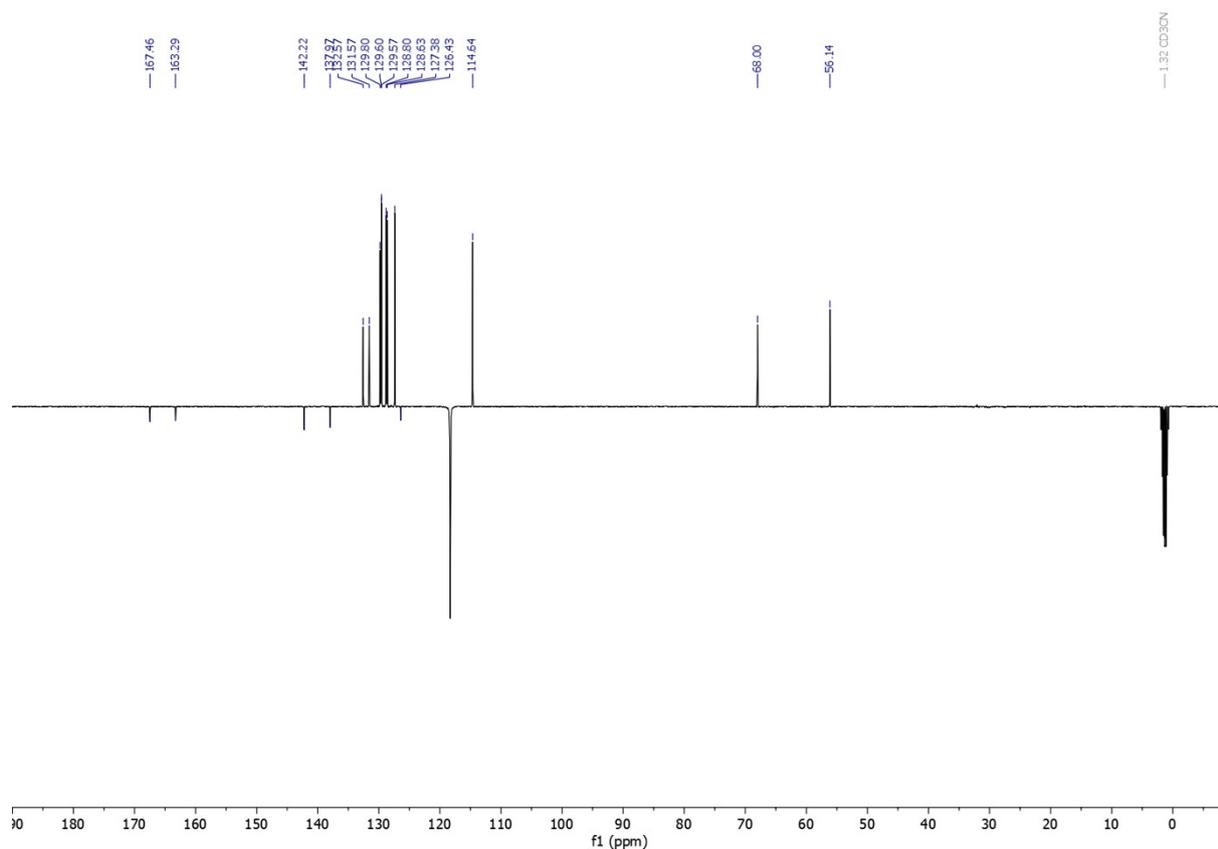
**Figure S37.**  $^{13}\text{C}\{^1\text{H}\}$  APT NMR (75 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N'*-(1,3-diphenylallyl)-4-nitrobenzohydrazide (**6b**).



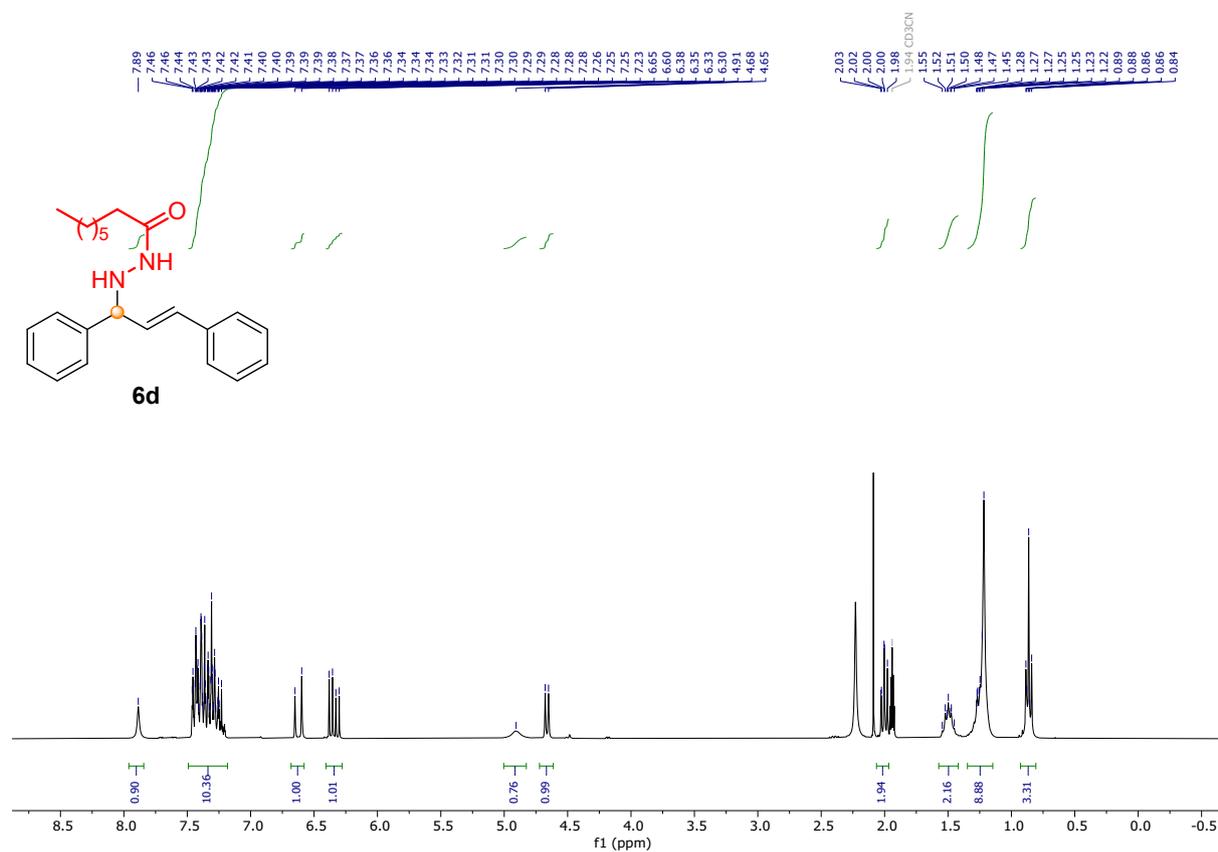
**Figure S38.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N'*-(1,3-diphenylallyl)-4-methoxybenzohydrazide (**6c**).



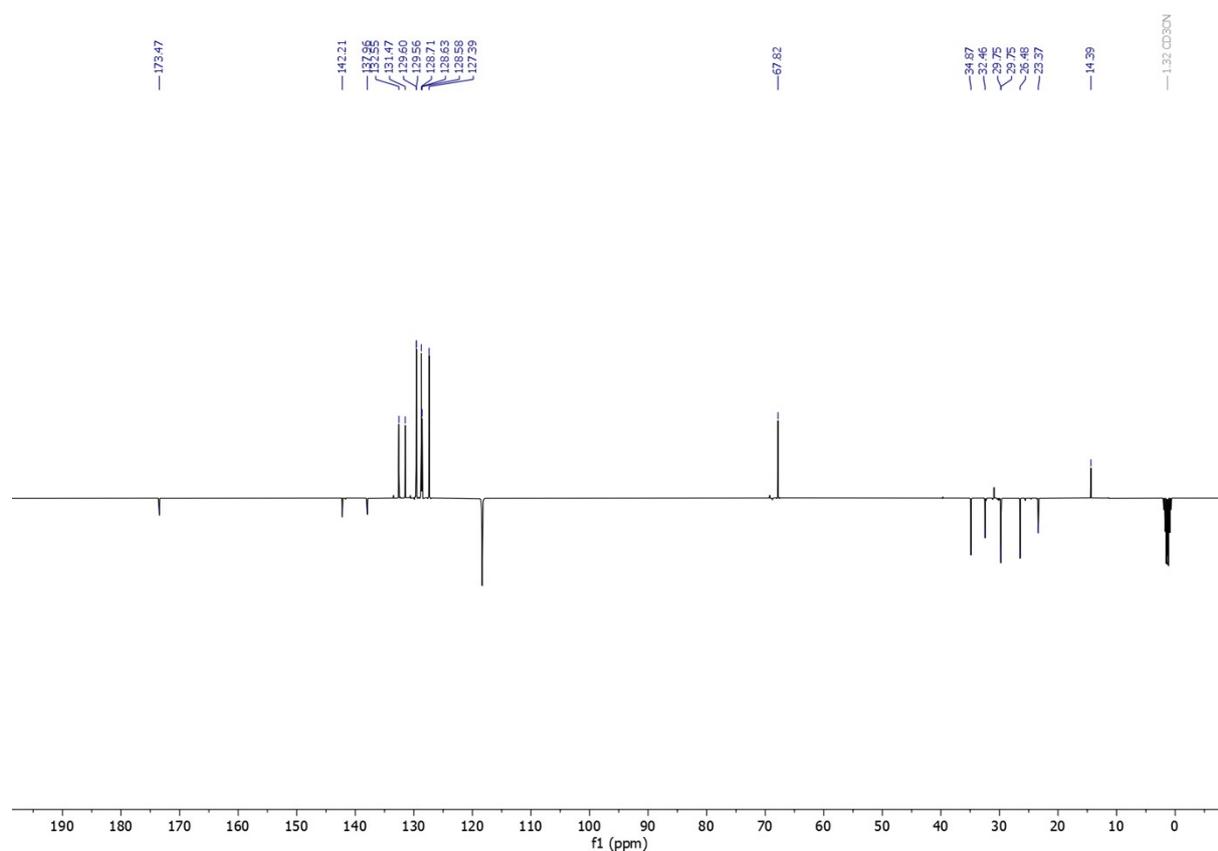
**Figure S39.**  $^{13}\text{C}\{^1\text{H}\}$  APT NMR (75 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N'*-(1,3-diphenylallyl)-4-methoxybenzohydrazide (**6c**).



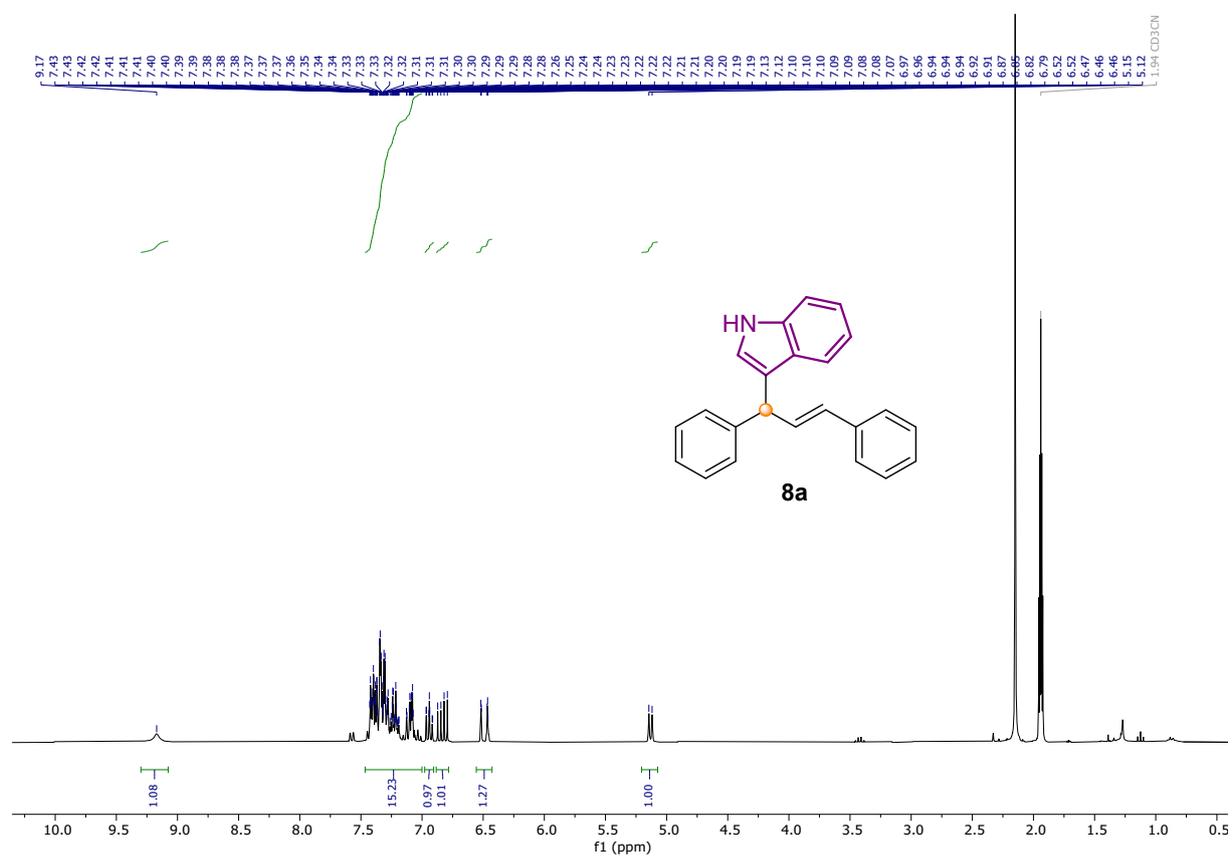
**Figure S40.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N'*-(1,3-diphenylallyl)octanehydrazide (**6d**).



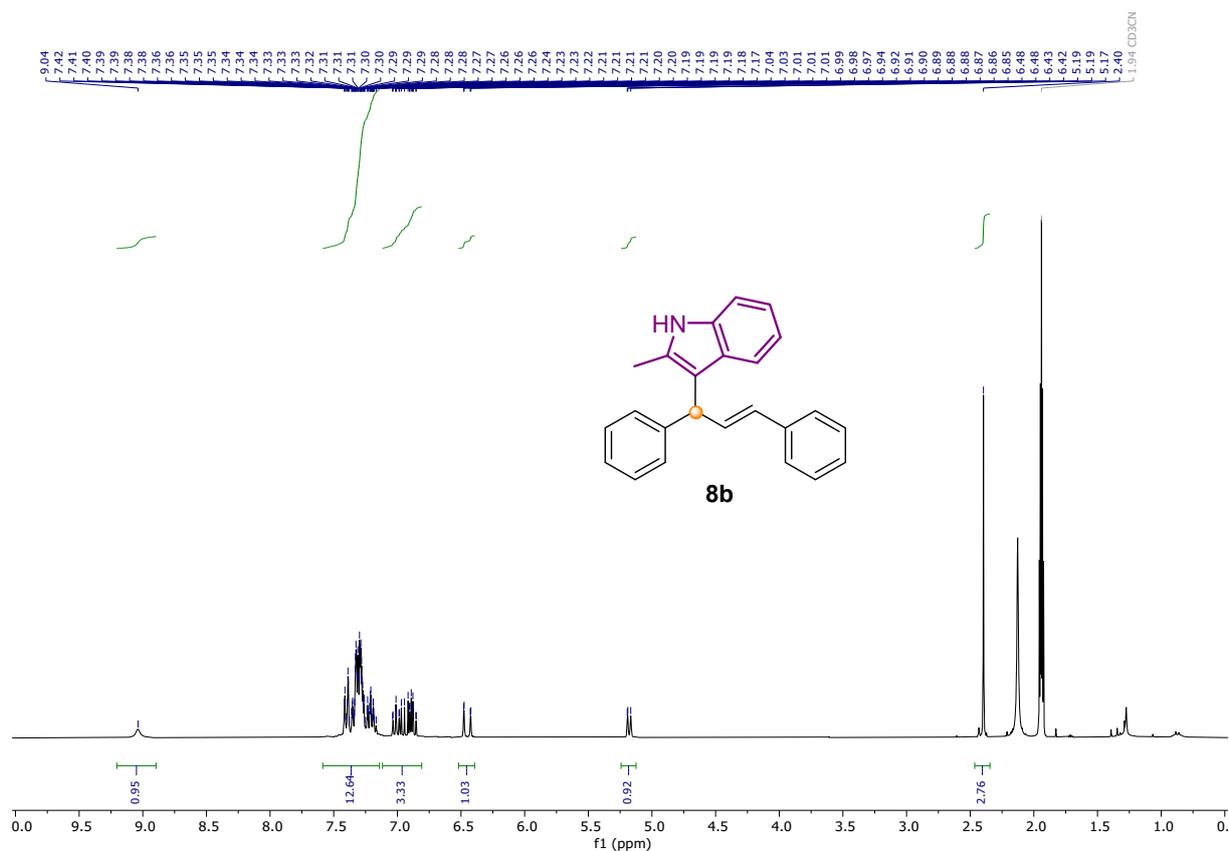
**Figure S41.**  $^{13}\text{C}\{^1\text{H}\}$  APT NMR (75 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-*N'*-(1,3-diphenylallyl)octanehydrazide (**6d**).



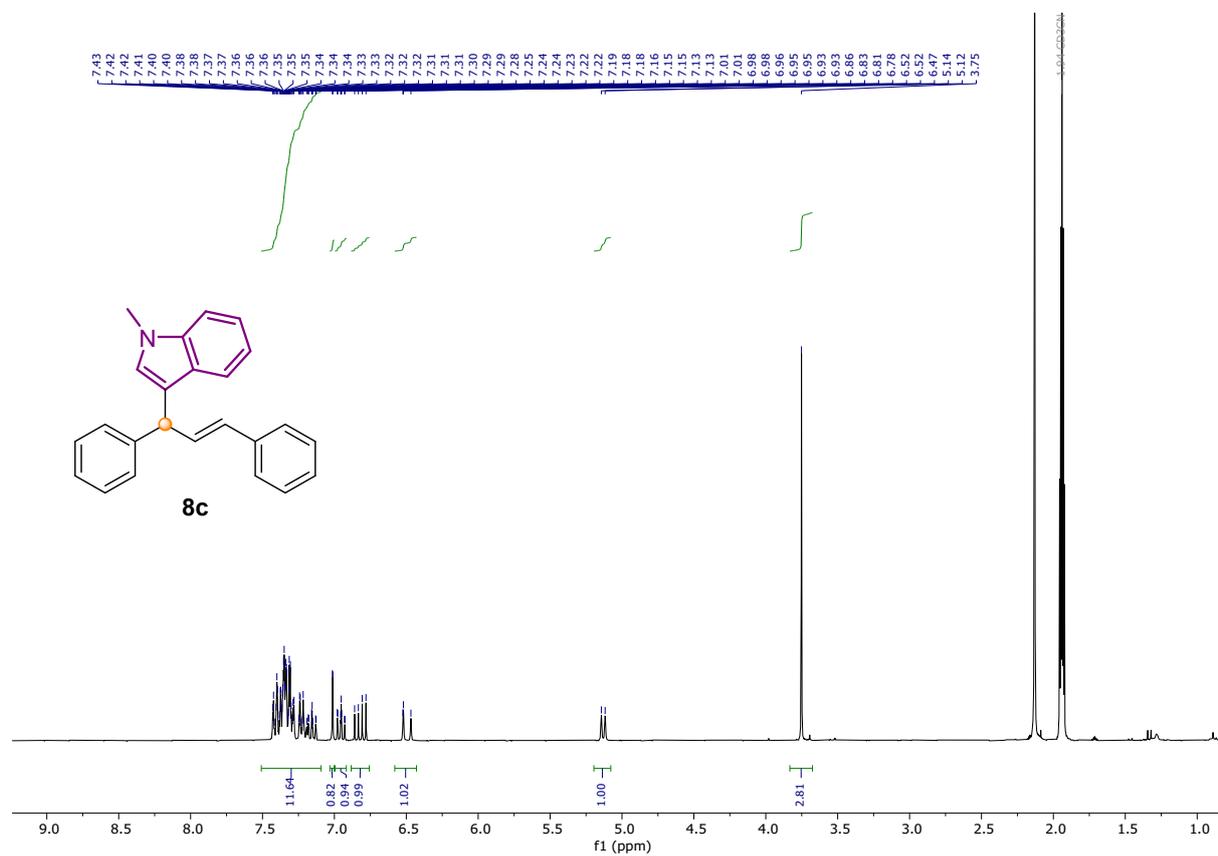
**Figure S42.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-3-(1,3-diphenylallyl)-1*H*-indole (**8a**).



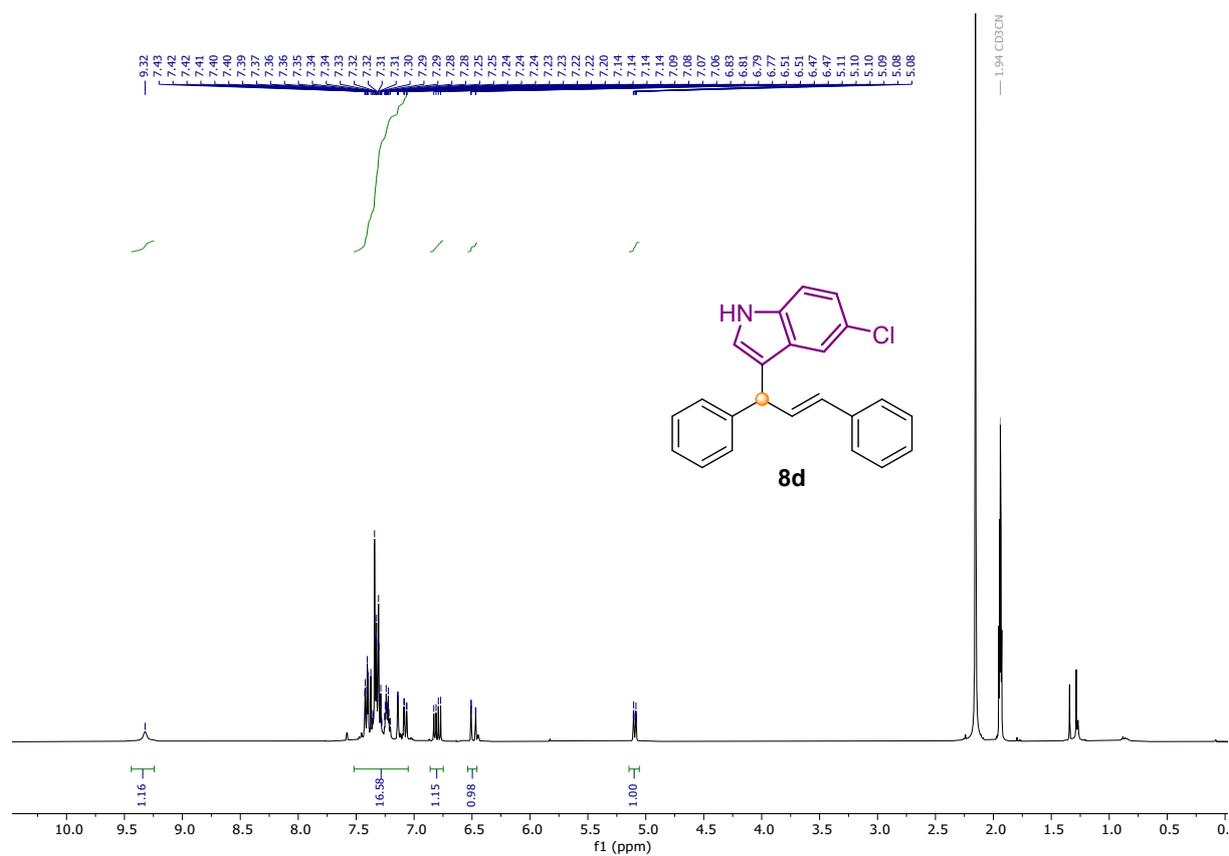
**Figure S43.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-3-(1,3-diphenylallyl)-2-methyl-1*H*-indole (**8b**).



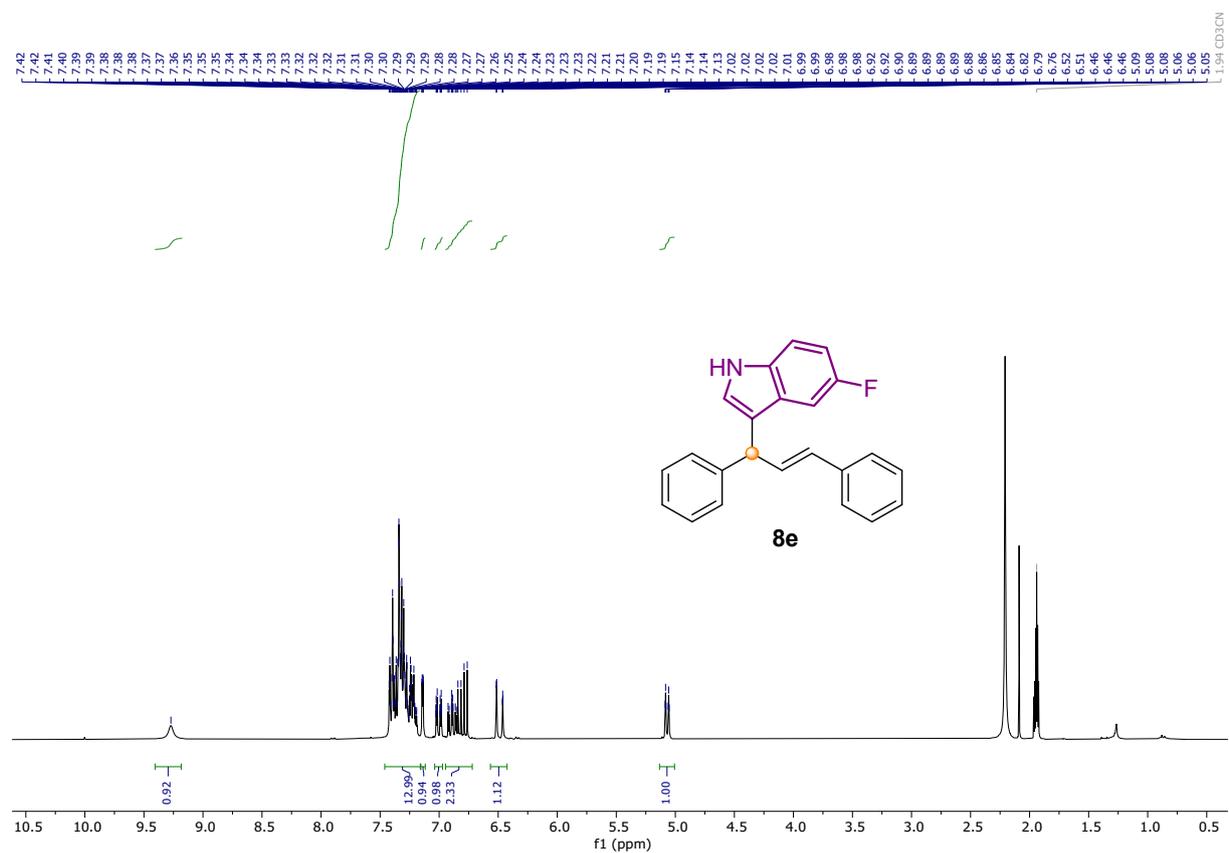
**Figure S44.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-3-(1,3-diphenylallyl)-1-methyl-1*H*-indole (**8c**).



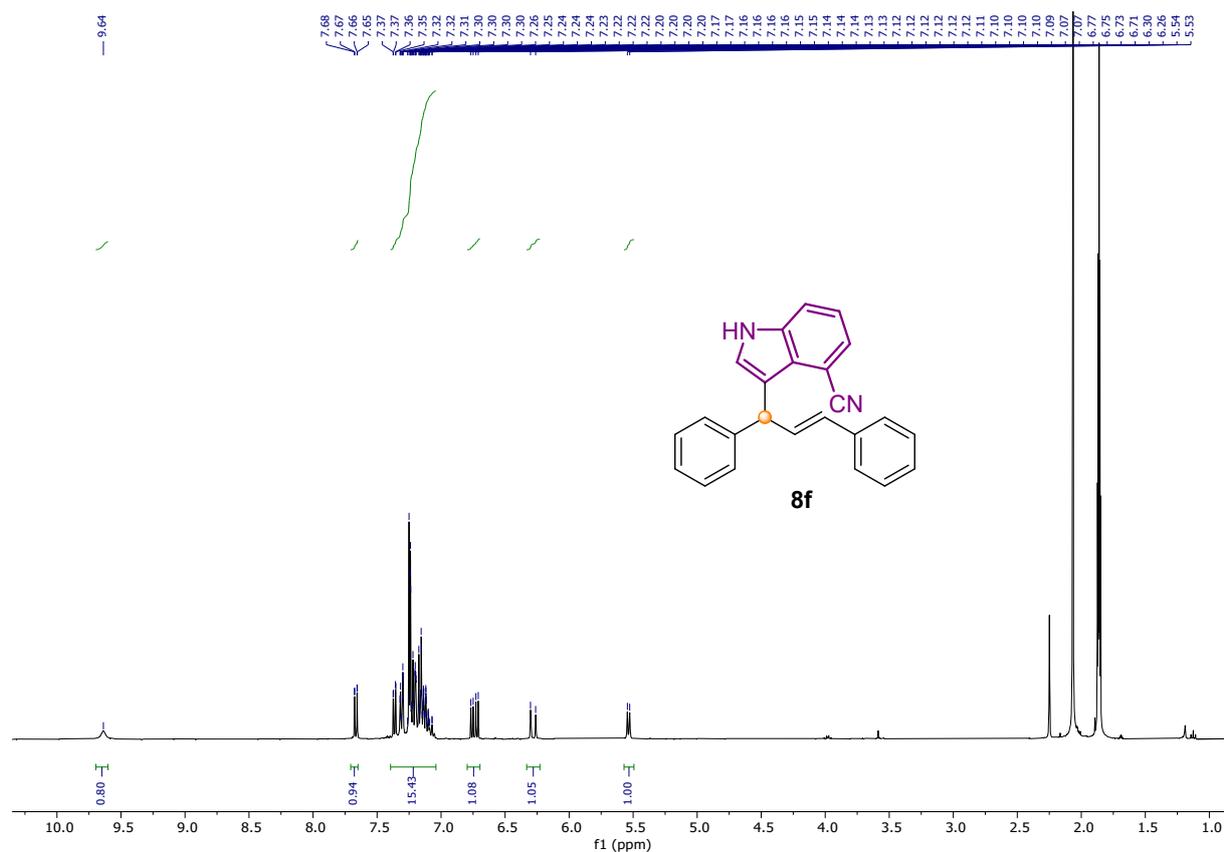
**Figure S45.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-5-chloro-3-(1,3-diphenylallyl)-1*H*-indole (**8d**).



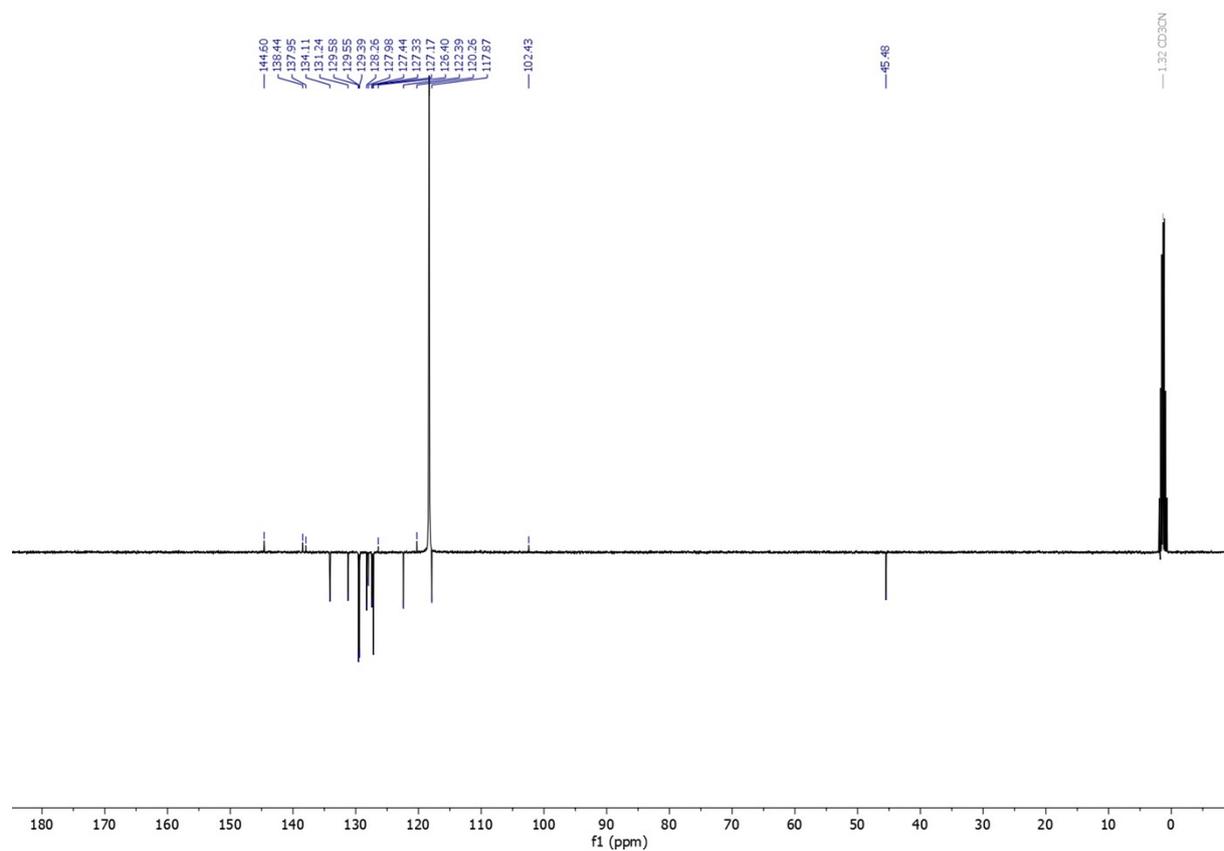
**Figure S46.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-3-(1,3-diphenylallyl)-5-fluoro-1*H*-indole (**8e**).



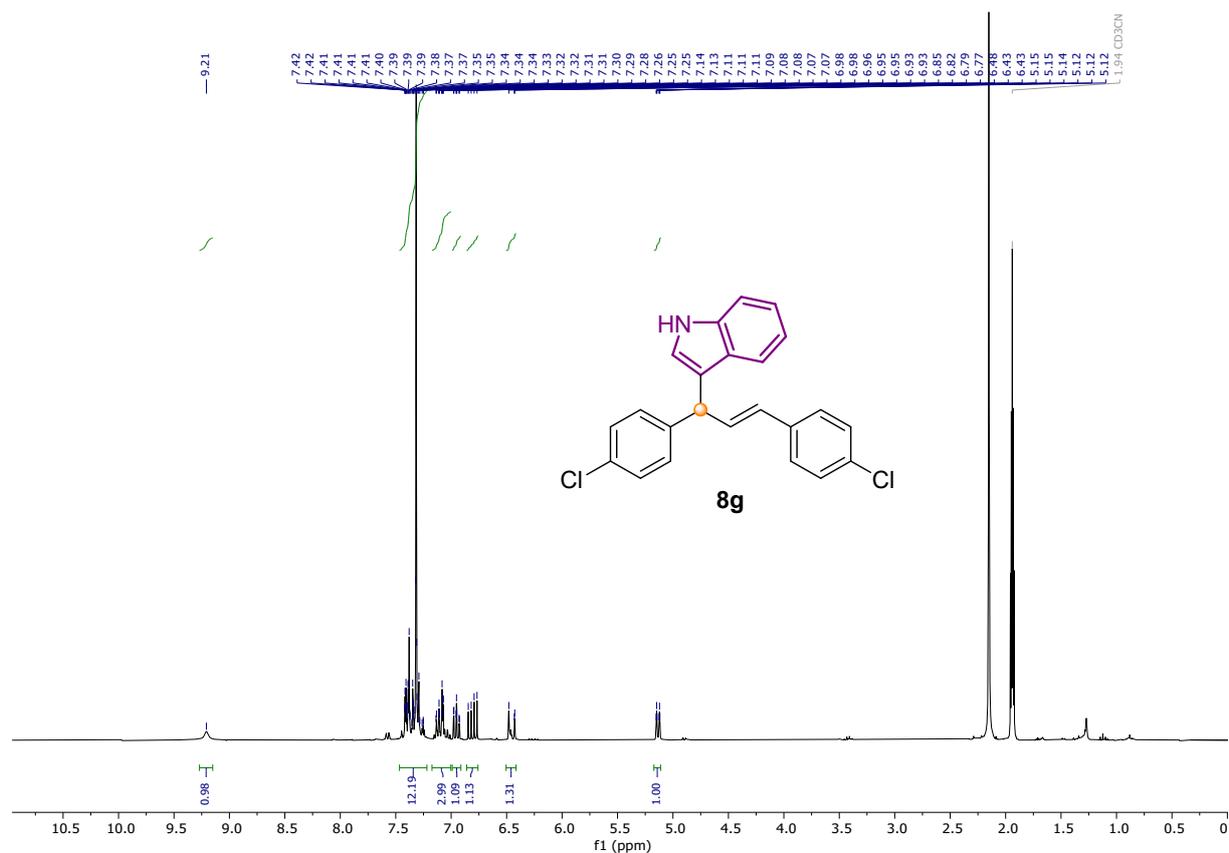
**Figure S47.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-3-(1,3-diphenylallyl)-1*H*-indole-4-carbonitrile (**8f**).



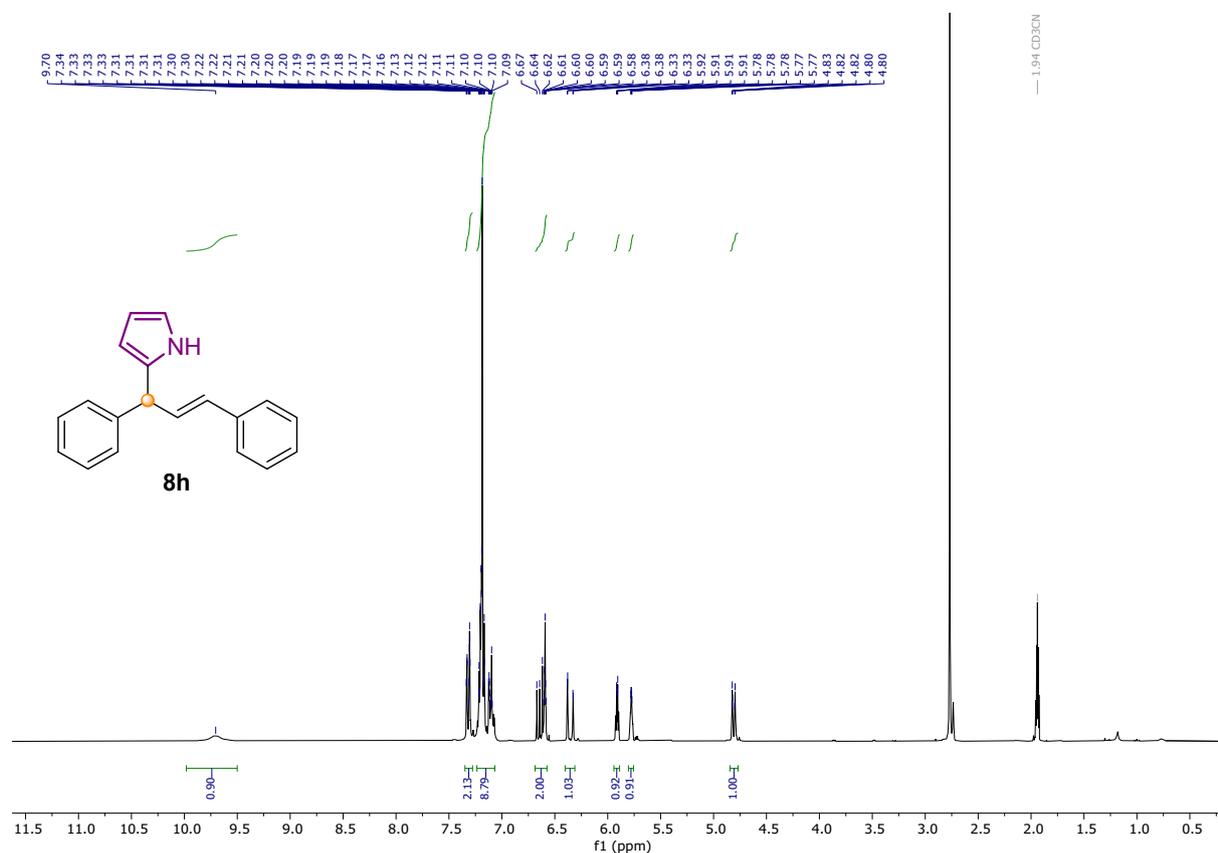
**Figure S48.**  $^{13}\text{C}\{^1\text{H}\}$  APT NMR (75 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-3-(1,3-diphenylallyl)-1*H*-indole-4-carbonitrile (**8f**).



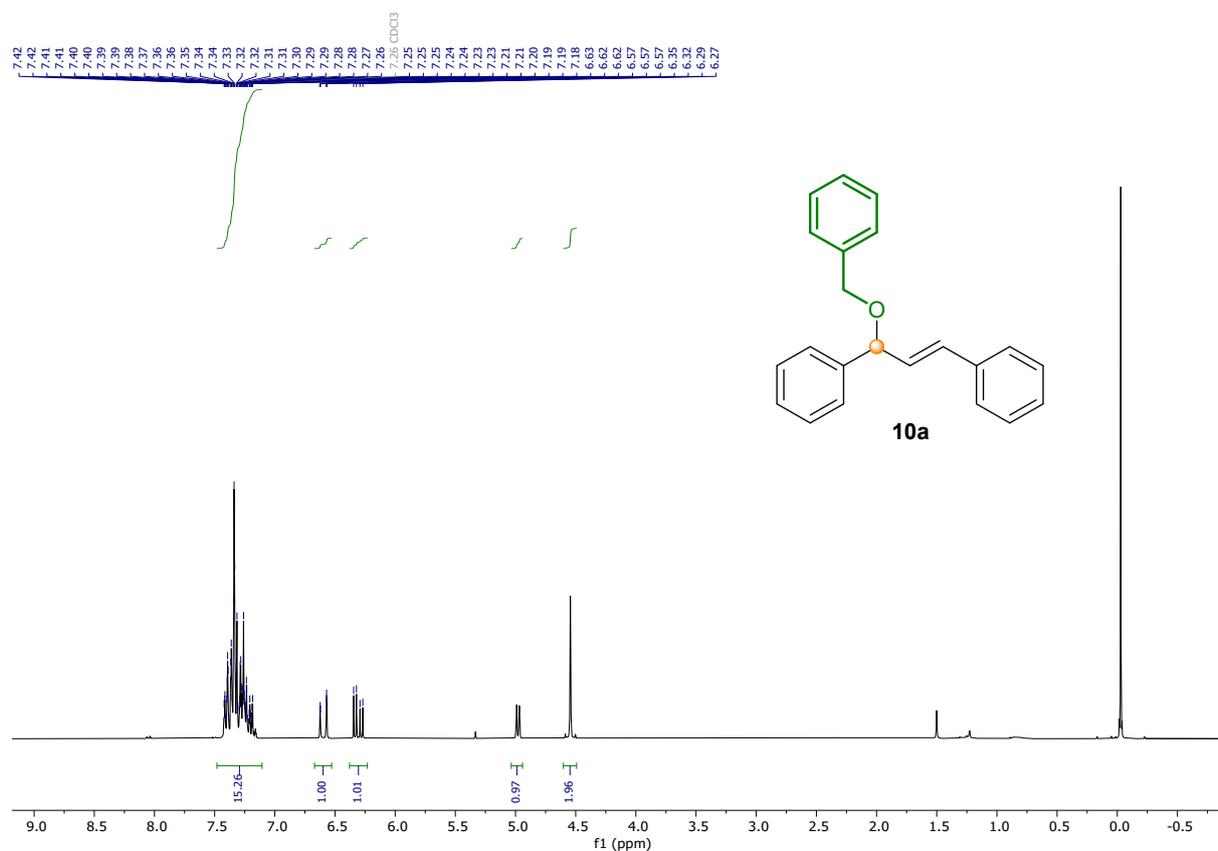
**Figure S49.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-3-(1,3-bis(4-chlorophenyl)allyl)-1*H*-indole (**8g**).



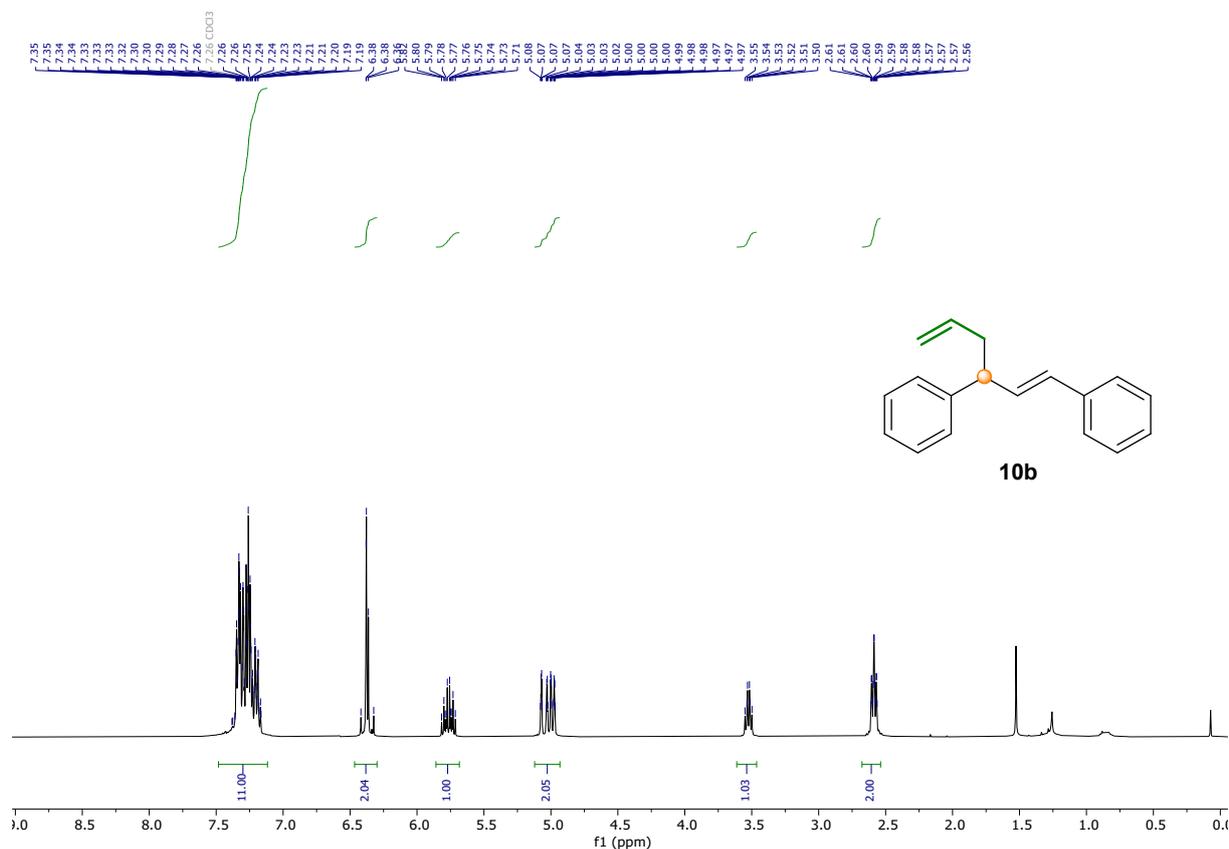
**Figure S50.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound (*E*)-3-(1,3-bis(4-chlorophenyl)allyl)-1*H*-indole (**8h**).



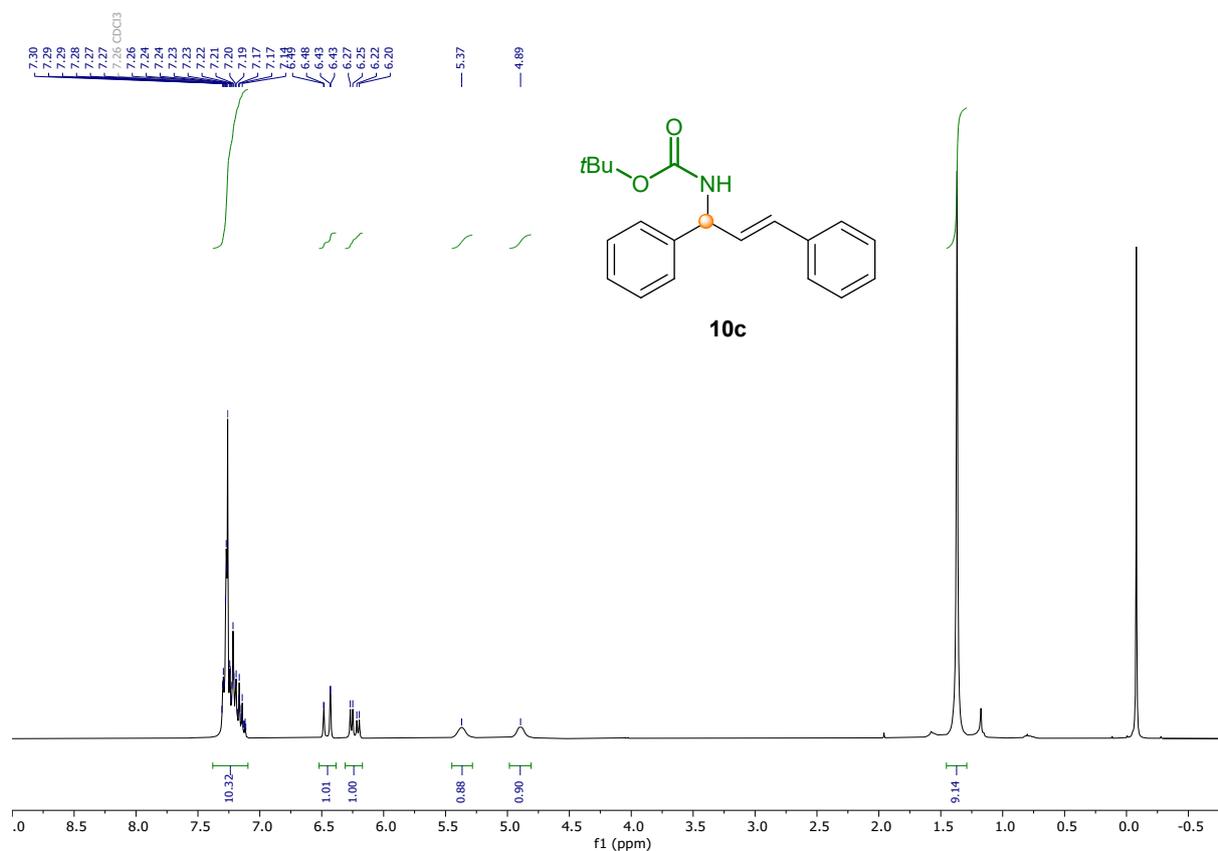
**Figure S51.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum of compound (*E*)-(3-(benzyloxy)prop-1-ene-1,3-diyl)dibenzene (**10a**).



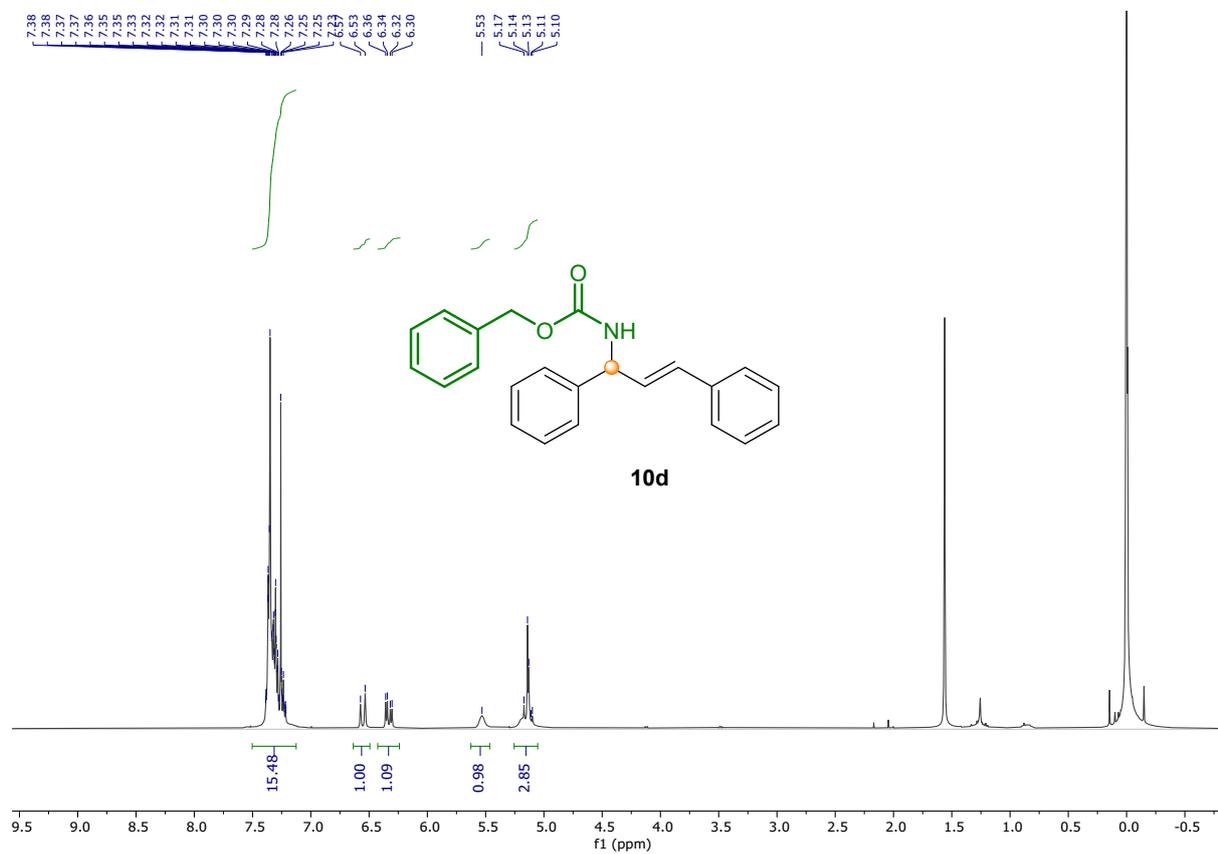
**Figure S52.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound (*E*)-hexa-1,5-diene-1,3-diyl)dibenzene (**10b**).



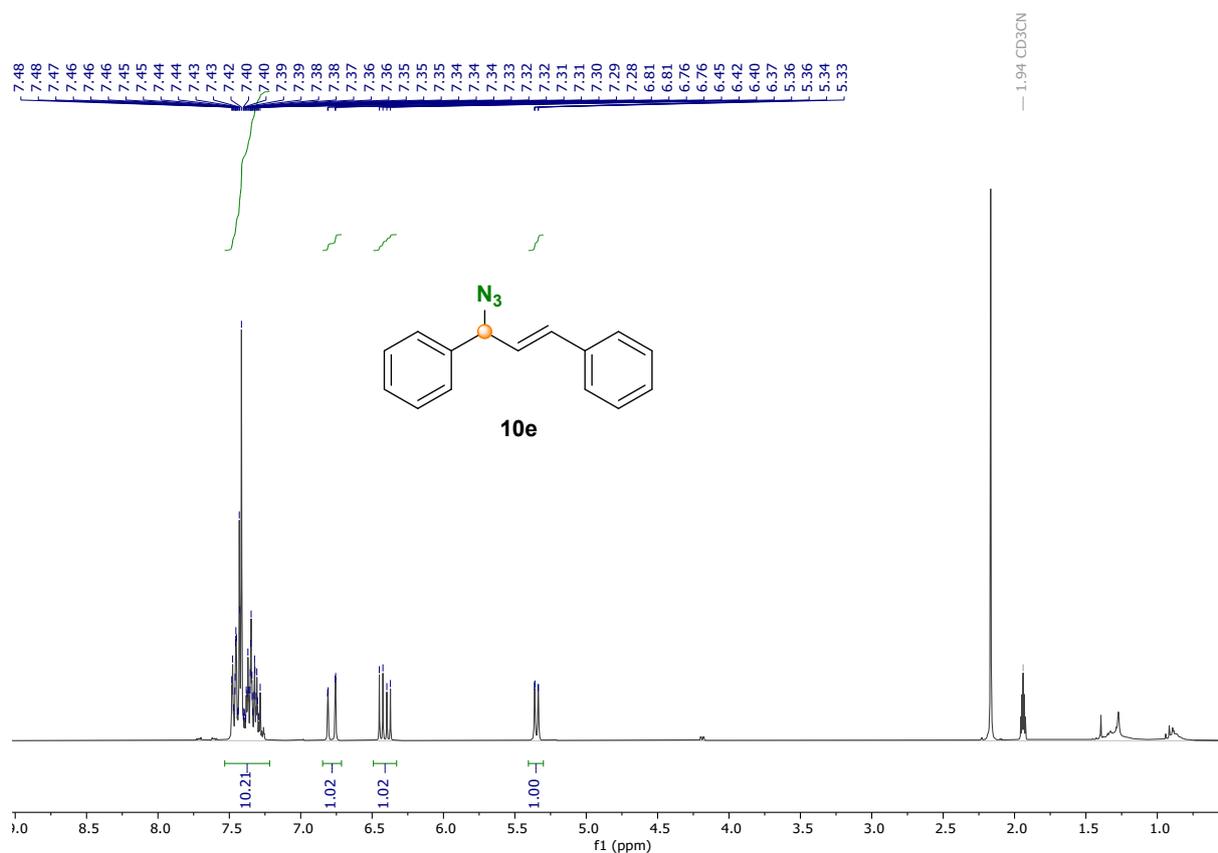
**Figure S53.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum of compound *tert*-butyl (*E*)-(1,3-diphenylallyl)carbamate (**10c**).



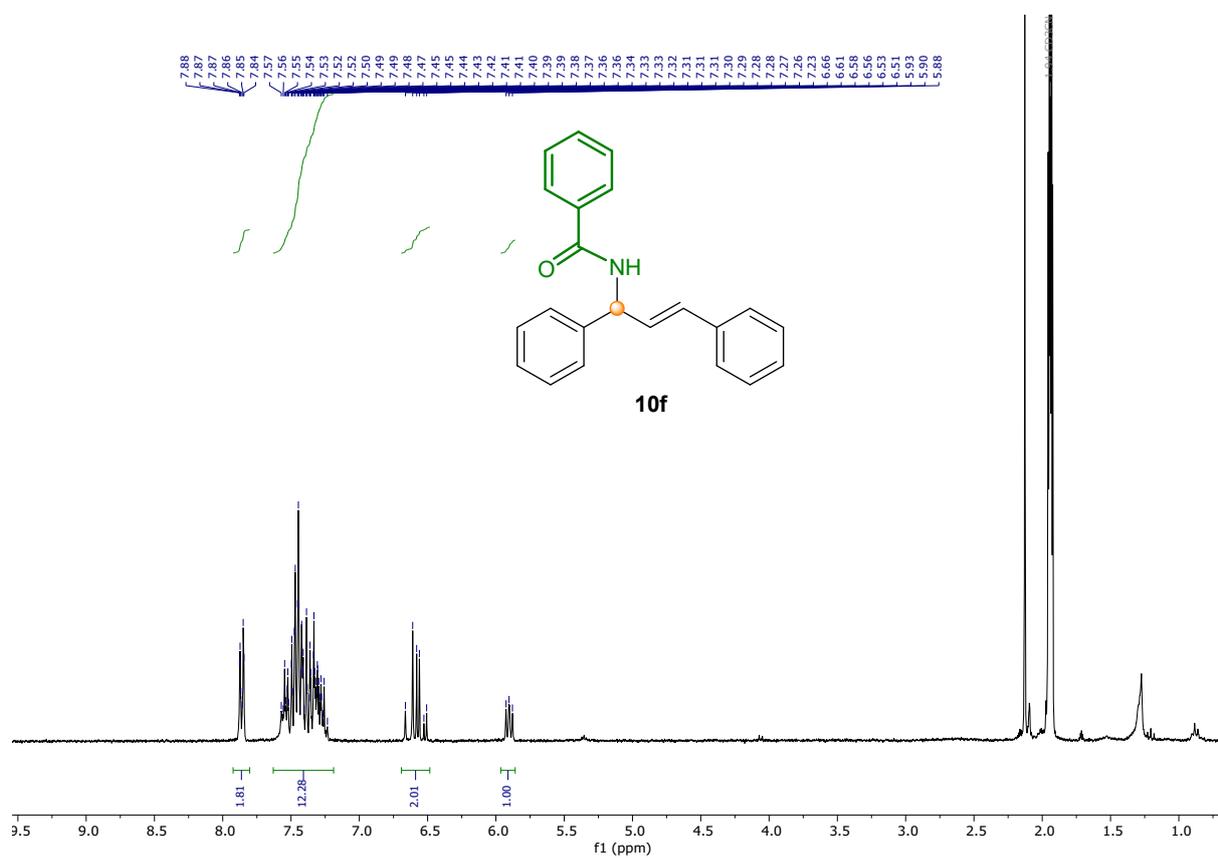
**Figure S54.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound benzyl (*E*)-(1,3-diphenylallyl)carbamate (**10d**).



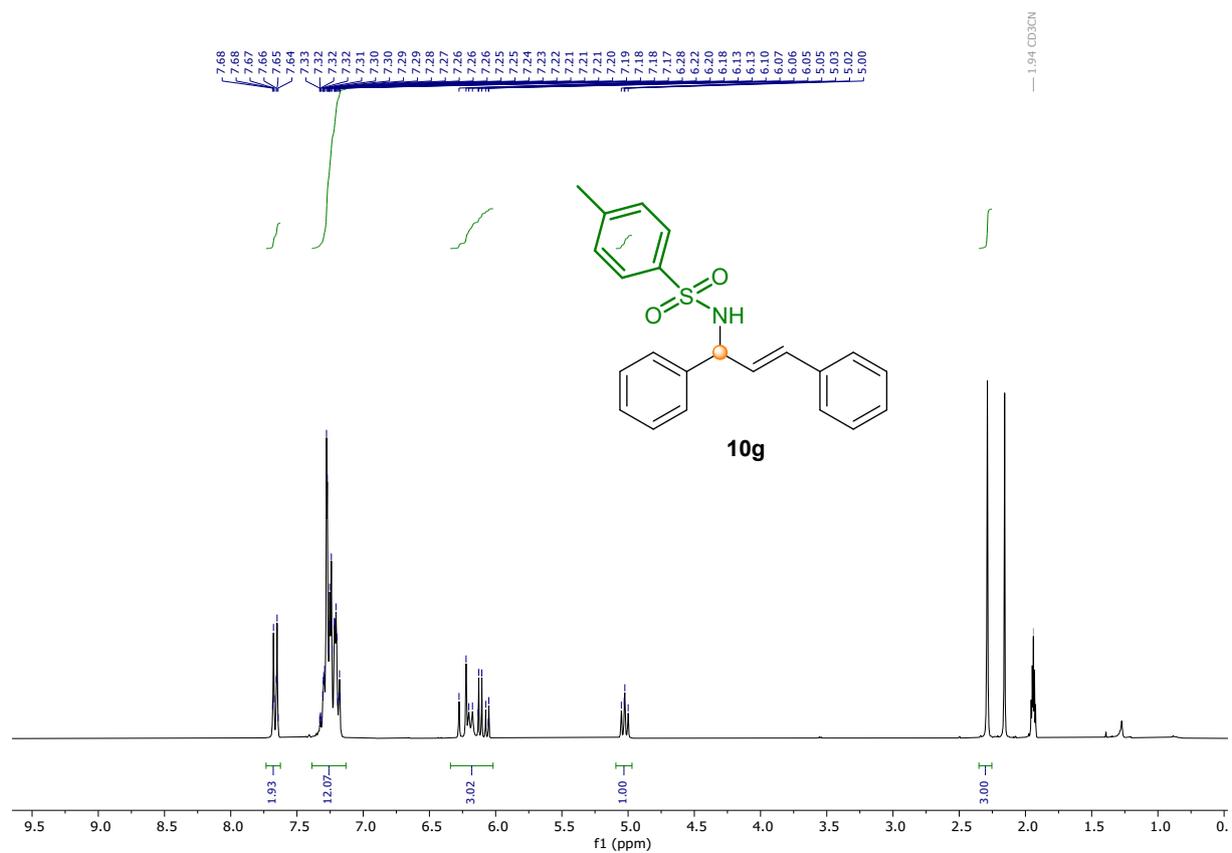
**Figure S55.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum of compound (*E*)-(3-azidoprop-1-ene-1,3-diyl)dibenzene (**10e**).



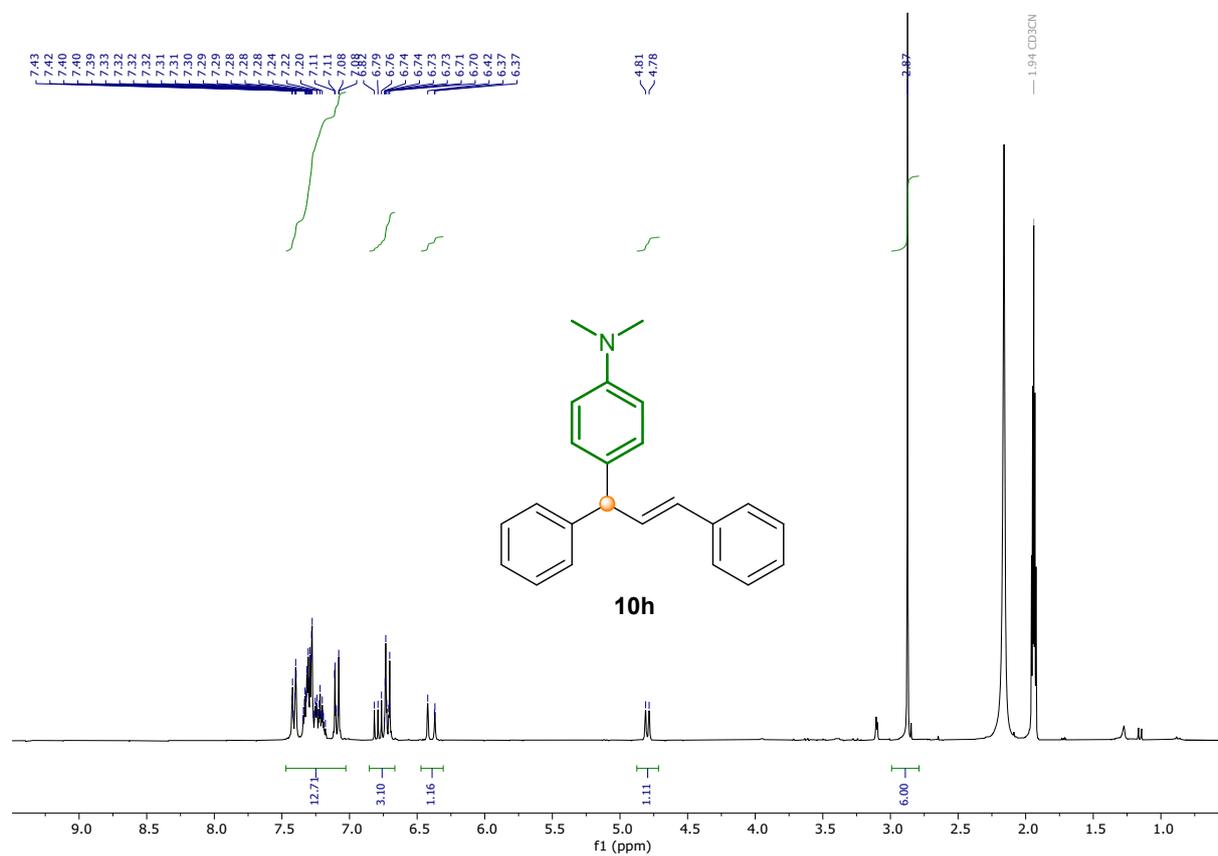
**Figure S56.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum of compound (*E*)-*N*-(1,3-diphenylallyl)benzamide (**10f**).



**Figure S57.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum of compound (*E*)-*N*-(1,3-diphenylallyl)-4-methylbenzenesulfonamide (**10g**).



**Figure S58.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum of compound (*E*)-4-(1,3-diphenylallyl)-*N,N*-dimethylaniline (**10h**).



## 2. Mechanistic assays

Figure S59. Reaction starting from alcohol **1j**.

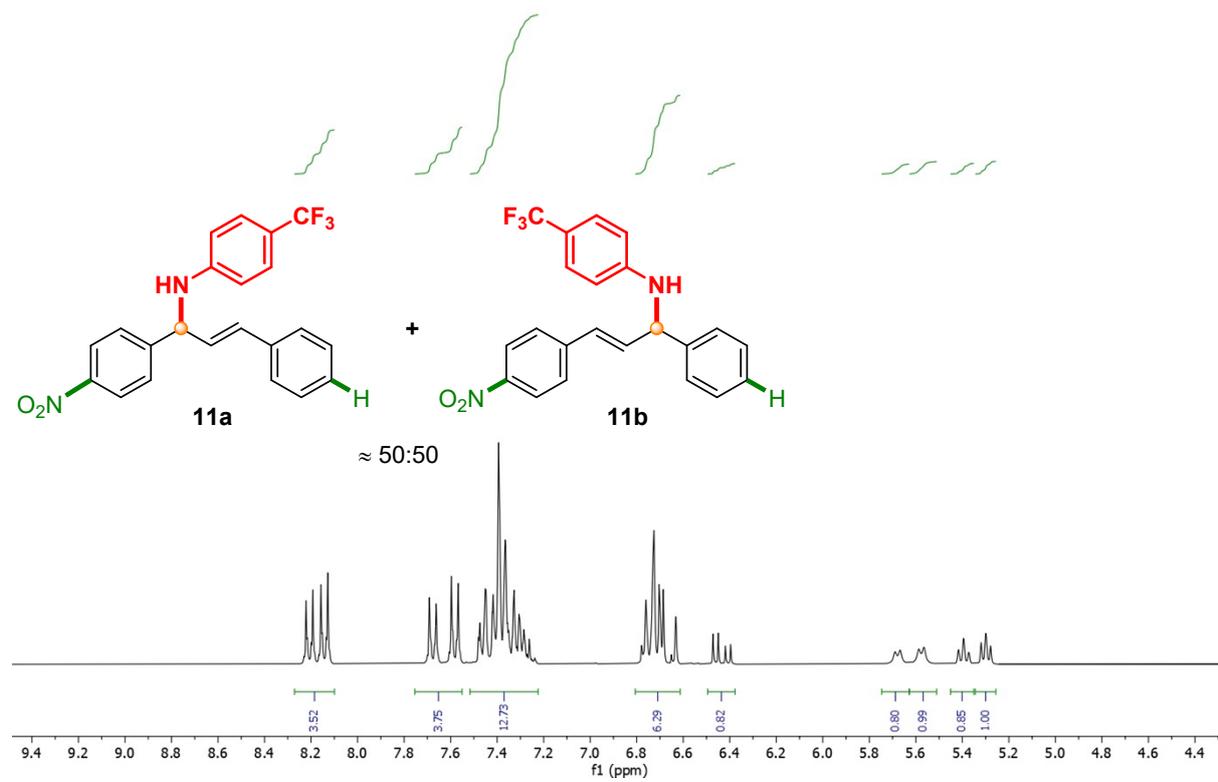


Figure S60. Reaction starting from alcohol **1k**.

