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Nickel-imidazolium low transition temperature mixtures with Lewis-acidic character

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Supplementary Information

Contents

Sustainability metrics

Equations and general considerations

The sustainability metrics used (E-factor, yield, stoichiometric factor, atom economy, Andraos' reaction mass efficiency, materials recovery parameter) were calculated with equations 1-6:

$$\text{E–factor} = \frac{\sum \text{Mass of components} - \text{Mass of product}}{\text{Mass of product}} \quad \text{(S1)}$$

$$Y = \frac{\text{Mass of product obtained}}{\text{Theoretical mass of product}} \cdot 100 \quad \text{(S2)}$$

$$AE = \frac{MW_{Prod}}{\sum (S_{Reactants} \cdot MW_{Reactants})} \cdot 100 \quad \text{(S3)}$$

$$SF = \frac{\text{Mass of product}}{\text{Mass of stoichiometric reagents}} \cdot 100 \quad \text{(S4)}$$

$$RME_{Andraos} = \frac{\text{Mass of product}}{\sum \text{Mass of components} - \sum \text{Mass recovered}} \cdot 100 \quad \text{(S5)}$$

$$MRP = \frac{1}{(1+(\frac{\text{Mass of product}}{\sum \text{Mass of reagents}} \cdot 100) \cdot E_{Aux})} \cdot 100 \quad \text{(S6)}$$

The Y, AE, SF, $RME_{Andraos}$ and MRP values were combined into a vector magnitude ratio (VMR) using equation 7:

$$VMR = \frac{1}{\sqrt{5}} \sqrt{(Y)^2+(AE)^2+(RME)^2+\left(\frac{1}{SF}\right)^2+(MRP)^2} \quad \text{(S7)}$$

The EcoScale score was obtained using the tool developed by the authors, available at http://ecoscale.cheminfo.org/calculator (last accessed July 24th 2023)

Some additional considerations and standard values applied to the calculations are compiled in Table S1.

Table S1. Standard values for the calculation of sustainability metrics on protocols with missing data.

Parameter	Value
Solvent recovery (reaction, work-up)	80% of the initial mass if not requiring fractional distillation
Water and saturated sodium chloride for work-up	Equal volume to the first fraction of organic solvent used
Work-up reported but not specified	3x10 mL/mmol of ethyl acetate and 10 mL/mmol of saturated sodium chloride
Drying agents	1/5th of the total mass of organic solvent

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Full metrics of the comparison of Table 2

Table S2. Sustainability metrics for the synthesis of 1. Entries correlate with those of Table 2.

Entry	Yield	1/SF	AE	RME	MRP	E-factor	EcoScale
1	0.99	1	0.945	0.201	0.212	3.98	79
2	0.99	1	0.945	0.345	0.369	1.90	89
3	0.88	0.735	0.945	0.054	0.087	17.59	70
4	0.96	0.847	0.945	0.422	0.549	1.37	77
5	0.95	1	0.945	0.01	0.012	94.82	79
6	0.96	1	0.945	0.003	0.003	360.36	69

Purification by chromatography omitted for RME, MRP and E-factor in entries 3 to 6.

Actual Mass of Reagents		0,0817	g	**Parameter**	**Actual**	**Ideal Limit**
Stoichiometric Mass of Reagents		0,08	g	AE	0,945	1
Stoichiometric Factor		1,001097309		Rxn Yield	0,998	1
Materials Recovery Parameter		0,212926766		1/SF	0,999	1
				MRP	0,212926766	1
Raw E-factor profile				RME	0,201	1
E-kernel		0,05987595				
E-excess		0,001163011		VMR	0,771141135	
E-rxn solvent		0		(vector magnitude ratio)		
E-catalyst		0,064935065				
E-work-up		0				
E-purification		12,36363636				
	E-aux	12,43				
E-total		12,48961039				
Corrected E-factor		**3,983**				
Yield		99,8	%			
AE		94,5	%			
PMI		4,983				
RME (global)		20,1	%			

Figure S1. Sustainability metrics for the synthesis of 1 (Table 2, entry 1).

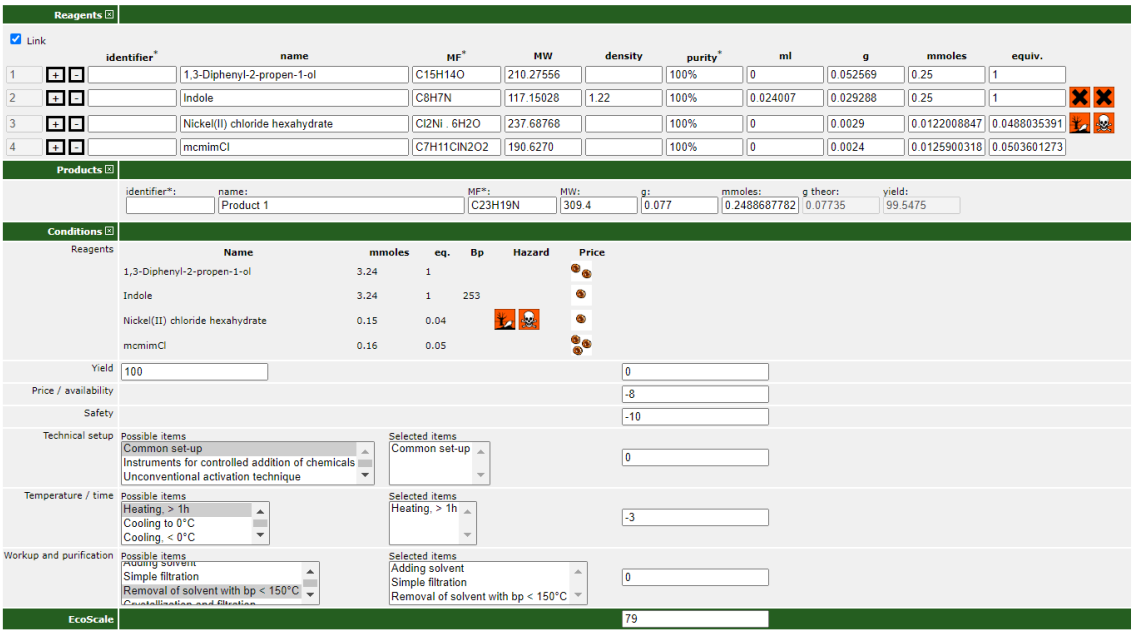

Figure S2. EcoScale for the synthesis of 1 (Table 2, entry 1).

Actual Mass of Reagents		1,65	g	**Parameter**	**Actual**	**Ideal Limit**
Stoichiometric Mass of Reagents		1,65	g	AE	0,945	1
Stoichiometric Factor		1,000619636		Rxn Yield	0,988	1
Materials Recovery Parameter		0,369127517		1/SF	0,999	1
				MRP	0,369127517	1
Raw E-factor profile				RME	0,345	1
E-kernel		0,070765086				
E-excess		0,000663485		VMR	0,790368533	
E-rxn solvent		0		(vector magnitude ratio)		
E-catalyst		0,071428571				
E-work-up		0				
E-purification		6,506493506				
	E-aux	6,58				
E-total		6,649350649				
Corrected E-factor		**1,903**				
Yield		98,8	%			
AE		94,5	%			
PMI		2,903				
RME (global)		34,5	%			

Figure S3. Sustainability metrics for the synthesis of 1 (Table 2, entry 2).

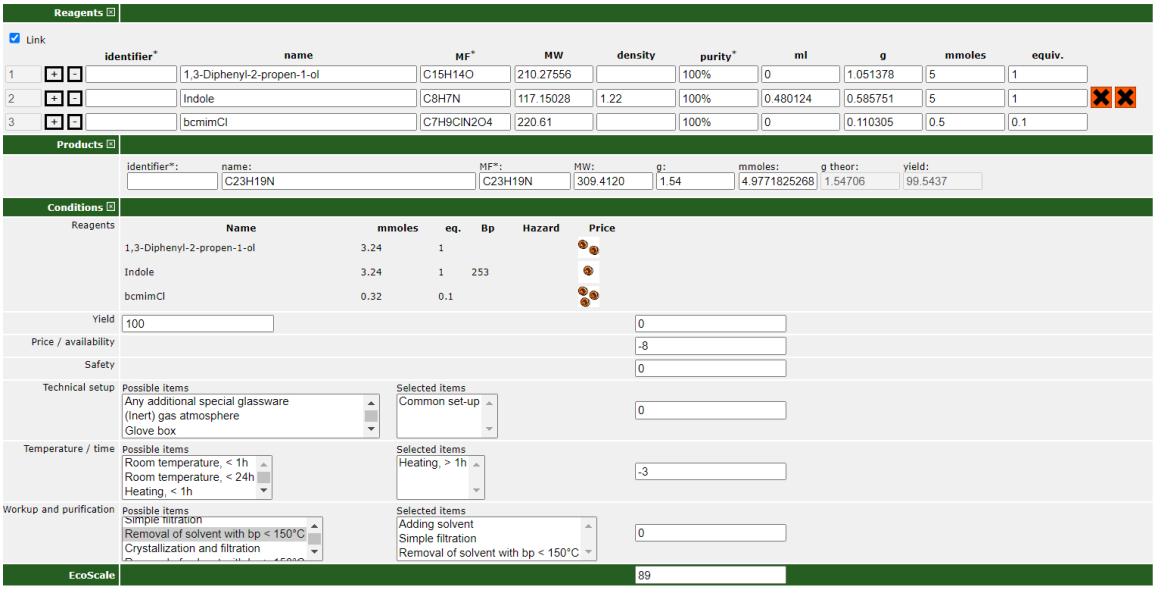

Figure S4. EcoScale for the synthesis of 1 (Table 2, entry 2).

Actual Mass of Reagents		0,222	g	**Parameter**	**Actual**	**Ideal Limit**
Stoichiometric Mass of Reagents		0,16	g	AE	0,945	1
Stoichiometric Factor		1,357799942		Rxn Yield	0,887	1
Materials Recovery Parameter		0,087127159		1/SF	0,736	1
				MRP	0,087127159	1
Raw E-factor profile				RME	0,054	1
E-kernel		0,193429095				
E-excess		0,427008861		VMR	0,668150897	
E-rxn solvent		7,299270073		(vector magnitude ratio)		
E-catalyst		0,102189781				
E-work-up		46,80291971				
E-purification		0				
	E-aux	54,20				
E-total		54,82481752				
Corrected E-factor		**17,599**				
Yield		88,7	%			
AE		94,5	%			
PMI		18,599				
RME (global)		5,4	%			

Figure S5. Sustainability metrics for the synthesis of 1 (Table 2, entry 3).

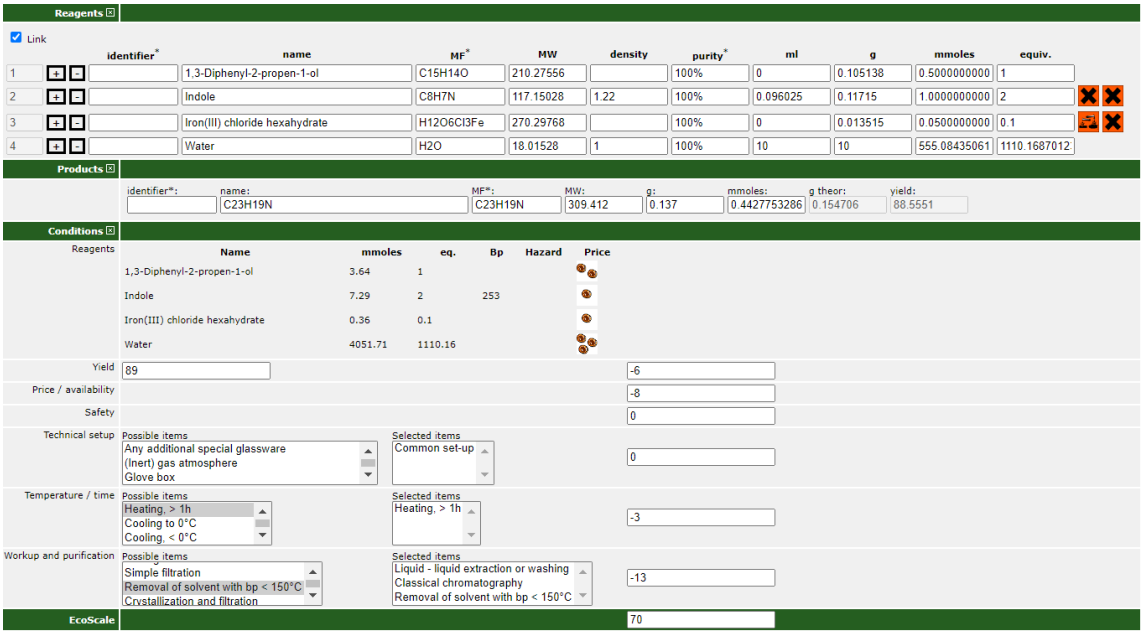

Figure S6. EcoScale for the synthesis of 1 (Table 2, entry 3).

Actual Mass of Reagents		0,193	g	**Parameter**	**Actual**	**Ideal Limit**
Stoichiometric Mass of Reagents		0,16	g	AE	0,945	1
Stoichiometric Factor		1,18042968		Rxn Yield	0,958	1
Materials Recovery Parameter		0,54985755		1/SF	0,847	1
				MRP	0,54985755	1
Raw E-factor profile				RME	0,422	1
E-kernel		0,104728284				
E-excess		0,19932577		VMR	0,77567565	
E-rxn solvent		5,391891892		(vector magnitude ratio)		
E-catalyst		0				
E-work-up		0				
E-purification		0				
	E-aux	5,39				
E-total		5,695945946				
Corrected E-factor		**1,372**				
Yield		95,8	%			
AE		94,5	%			
PMI		2,372				
RME (global)		42,2	%			

Figure S7. Sustainability metrics for the synthesis of 1 (Table 2, entry 4).

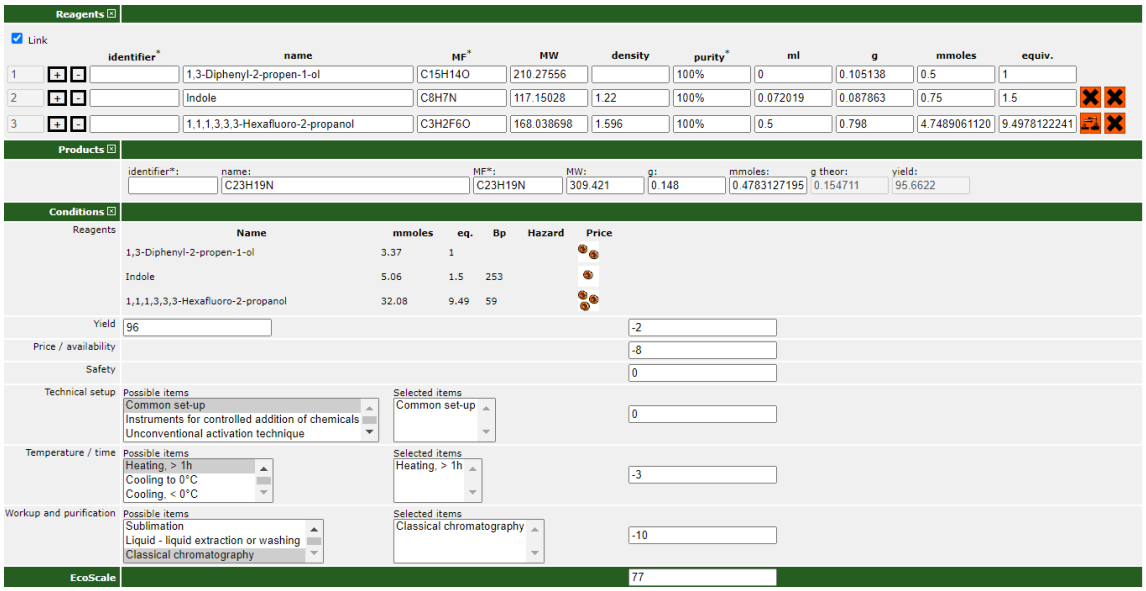

Figure S8. EcoScale for the synthesis of 1 (Table 2, entry 4).

Actual Mass of Reagents	0,327	g	**Parameter**	**Actual**	**Ideal Limit**
Stoichiometric Mass of Reagents	0,33	g	AE	0,945	1
Stoichiometric Factor	1,000001309		Rxn Yield	0,951	1
Materials Recovery Parameter	0,011607476		1/SF	1,000	1
			MRP	0,011607476	1
Raw E-factor profile			RME	0,010	1
E-kernel	0,112243442				
E-excess	1,45585E-06		VMR	0,748124397	
E-rxn solvent	4,523809524		(vector magnitude ratio)		
E-catalyst	0,032312925				
E-work-up	90,15306122				
E-purification	0				
E-aux	94,71				
E-total	94,82142857				
Corrected E-factor	**94,821**				
Yield	95,1	%			
AE	94,5	%			
PMI	95,821				
RME (global)	1,0	%			

Figure S9. Sustainability metrics for the synthesis of 1 (Table 2, entry 5).

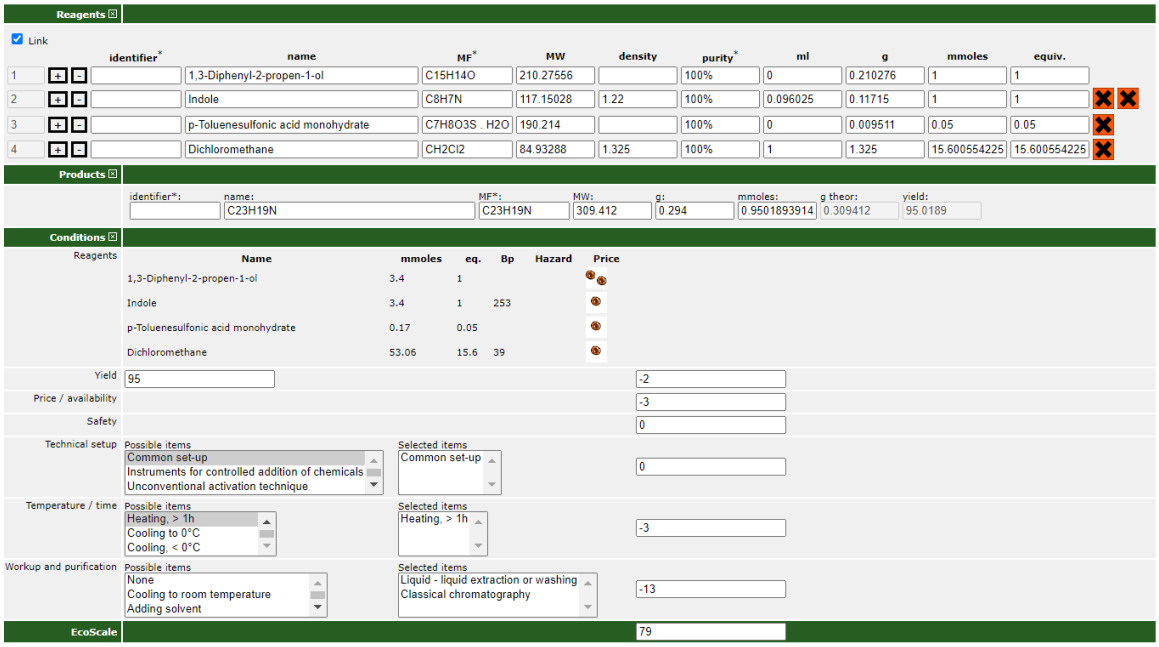

Figure S10. EcoScale for the synthesis of 1 (Table 2, entry 5).

Actual Mass of Reagents		0,0327	g	**Parameter**	**Actual**	**Ideal Limit**
Stoichiometric Mass of Reagents		0,03	g	AE	0,945	1
Stoichiometric Factor		1,000001309		Rxn Yield	0,961	1
Materials Recovery Parameter		0,00304682		1/SF	1,000	1
				MRP	0,00304682	1
Raw E-factor profile				RME	0,003	1
E-kernel		0,10100866				
E-excess		1,44115E-06		VMR	0,750572138	
E-rxn solvent		8,417508418		(vector magnitude ratio)		
E-catalyst		0				
E-work-up		624,3703704				
E-purification		91,11111111				
	E-aux	723,90				
E-total		724				
Corrected E-factor		**360,364**				
Yield		96,1	%			
AE		94,5	%			
PMI		361,364				
RME (global)		0,3	%			

Figure S11. Sustainability metrics for the synthesis of 1 (Table 2, entry 6).

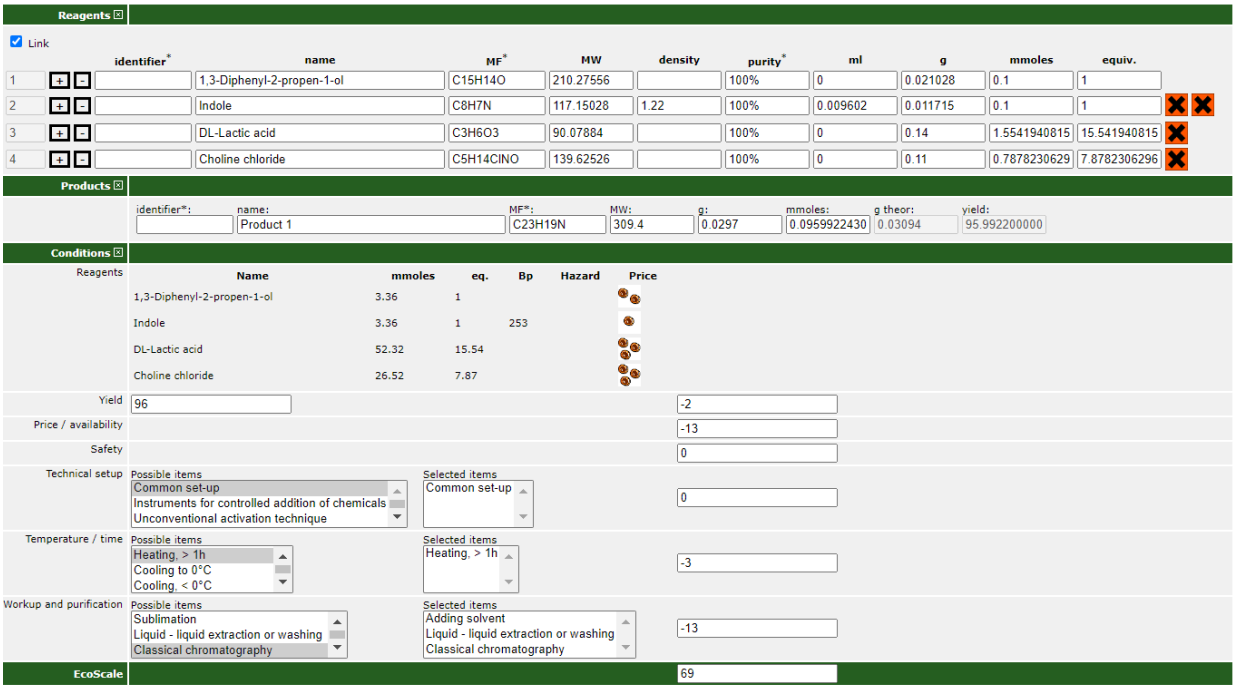

Figure S12. EcoScale for the synthesis of 1 (Table 2, entry 6).

Differential Scanning Calorimetry traces

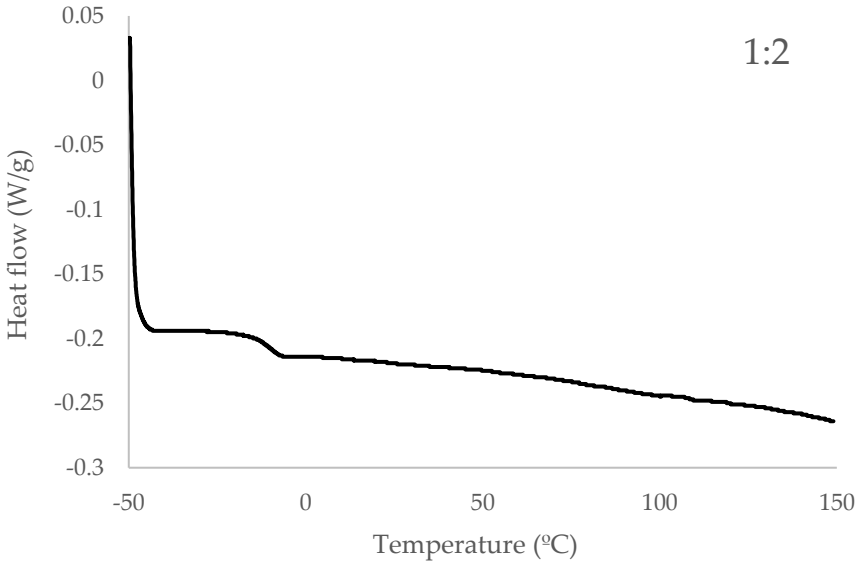

Figure S13. DSC trace of the 1:2 mcmimCl:$NiCl_2$ mixture (scanning rate 5 ºC/min)

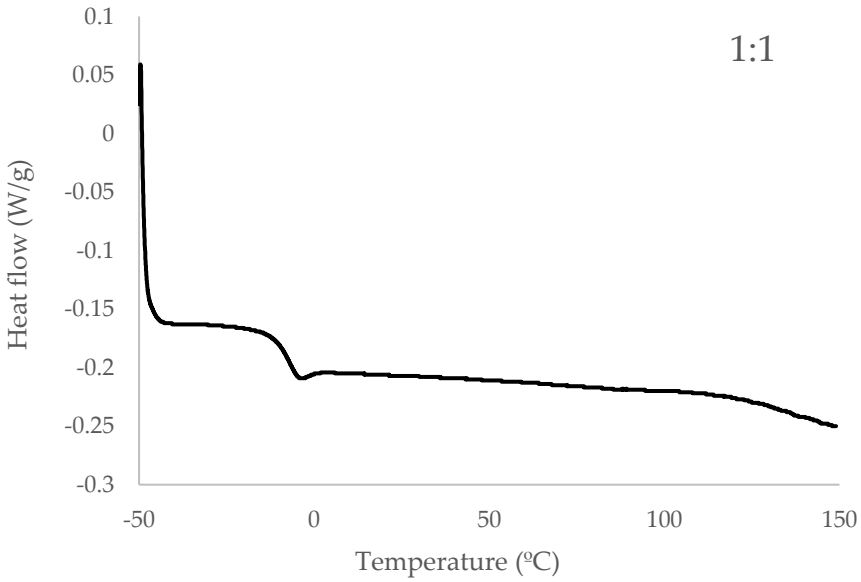

Figure S14. DSC trace of the 1:1 mcmimCl:$NiCl_2$ mixture (scanning rate 5 ºC/min)

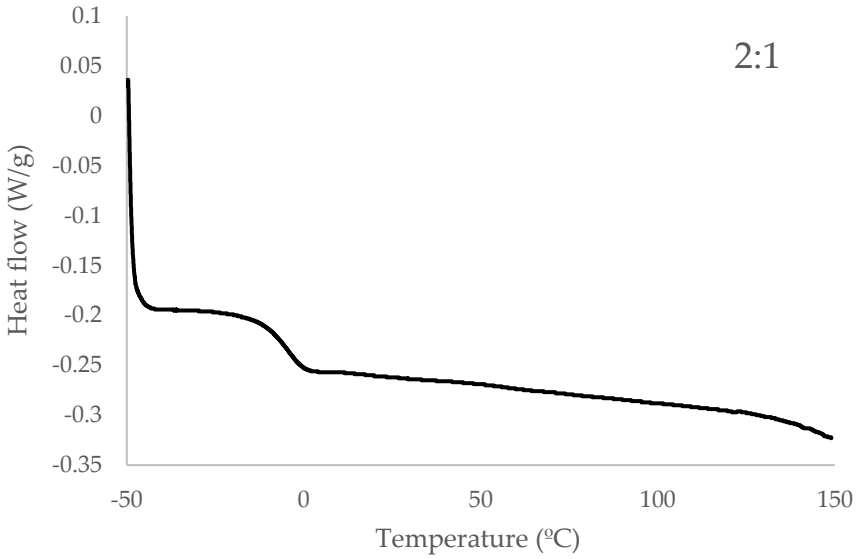

Figure S15. DSC trace of the 2:1 mcmimCl:$NiCl_2$ mixture (scanning rate 5 ºC/min)

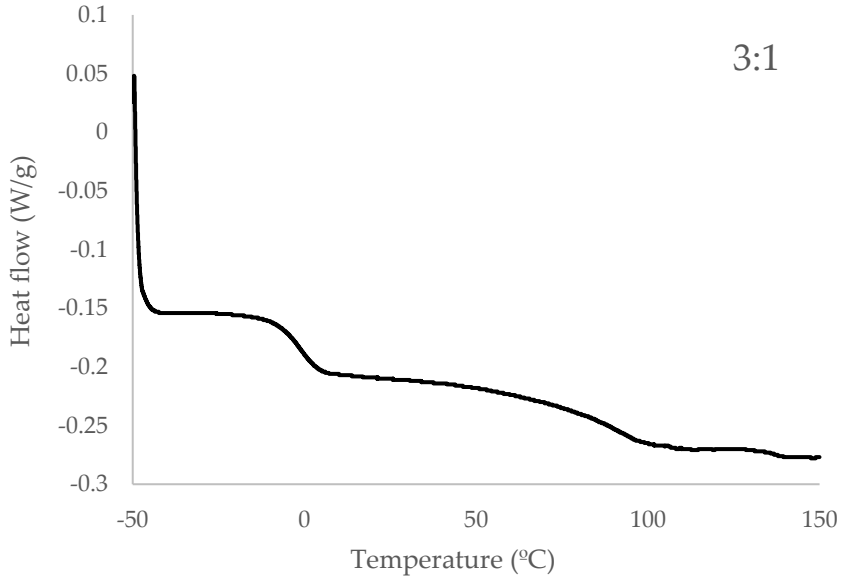

Figure S16. DSC trace of the 3:1 mcmimCl:$NiCl_2$ mixture (scanning rate 5 ºC/min)

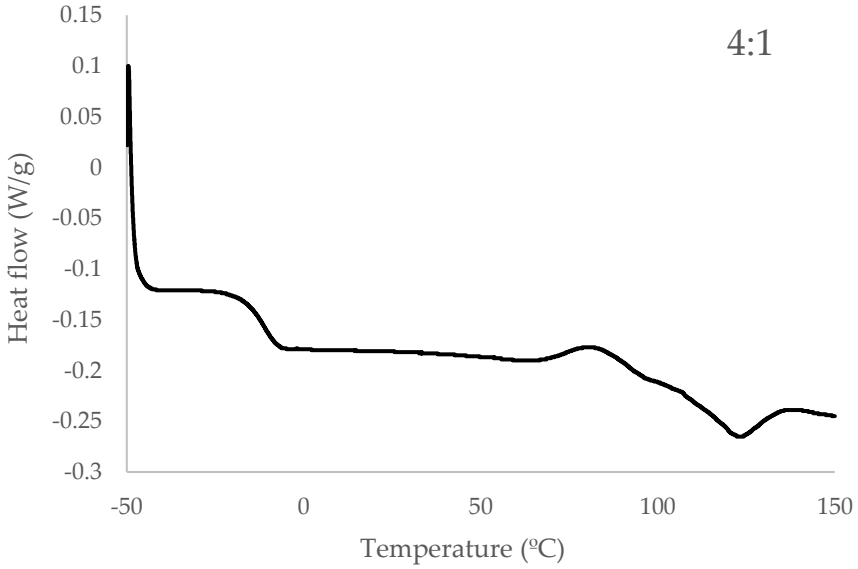

Figure S17. DSC trace of the 4:1 mcmimCl:$NiCl_2$ mixture (scanning rate 5 ºC/min)

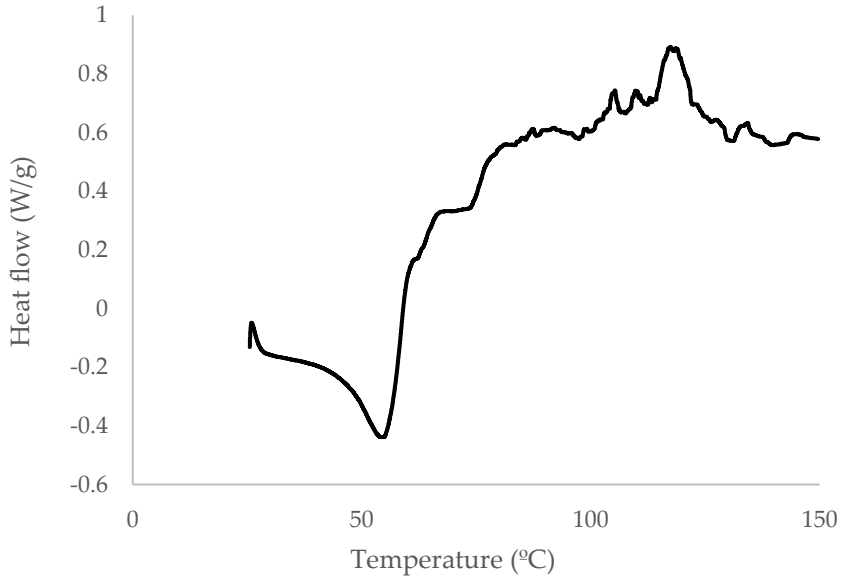

Figure S18. DSC trace of the 1:1 mcmimCl:$NiCl_2 \cdot 6H_2O$ mixture (scanning rate 5 ºC/min)

XPS analyses

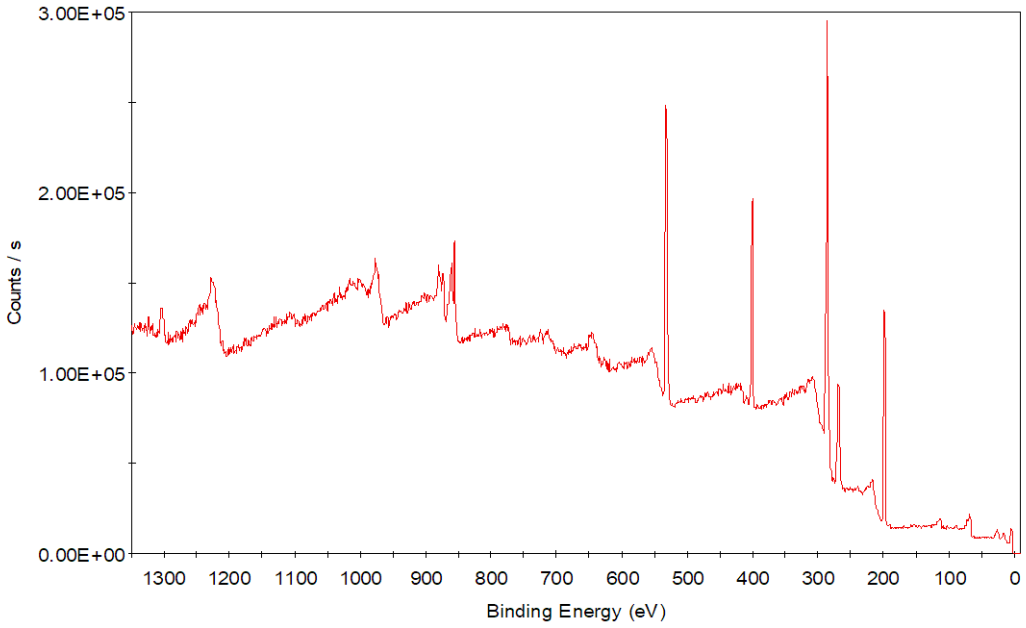

Figure S19. XPS survey of the 2:1 mcmimCl:$NiCl_2$ mixture

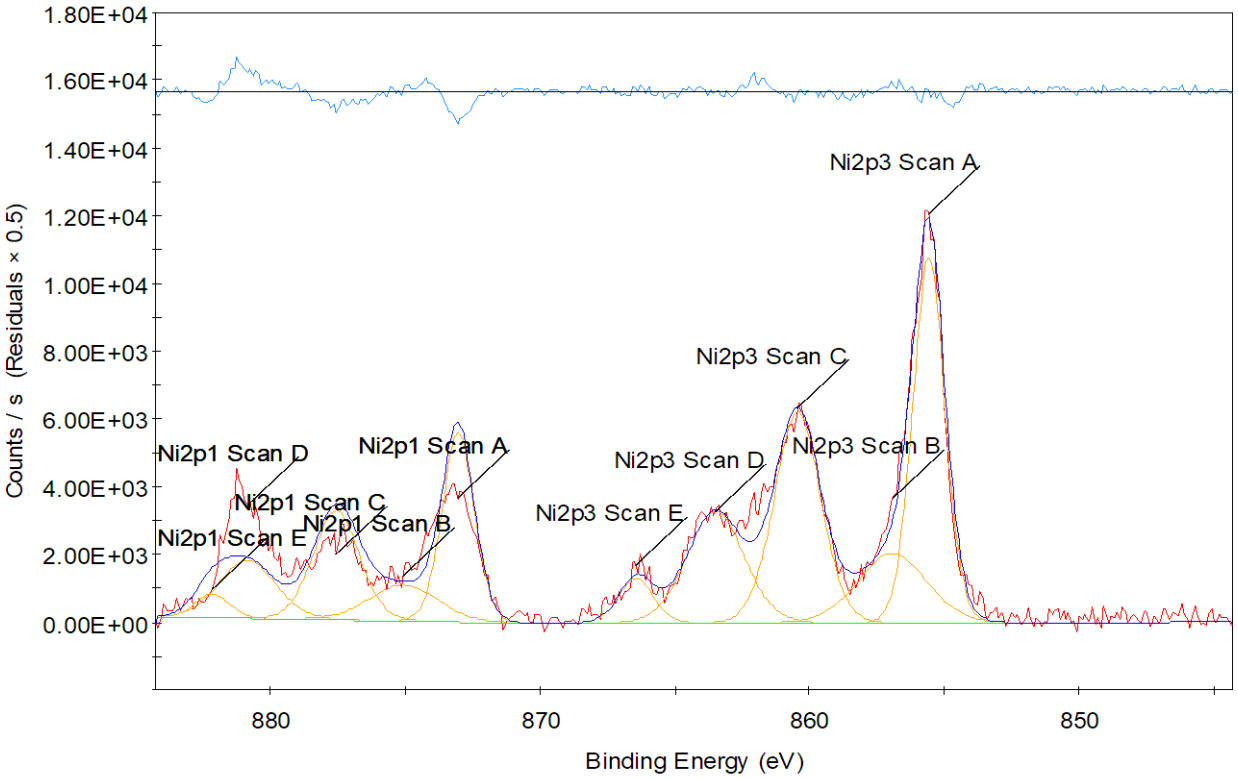

Figure S20. High resolution XPS Ni 2p scan of the 2:1 mcmimCl:$NiCl_2$ mixture

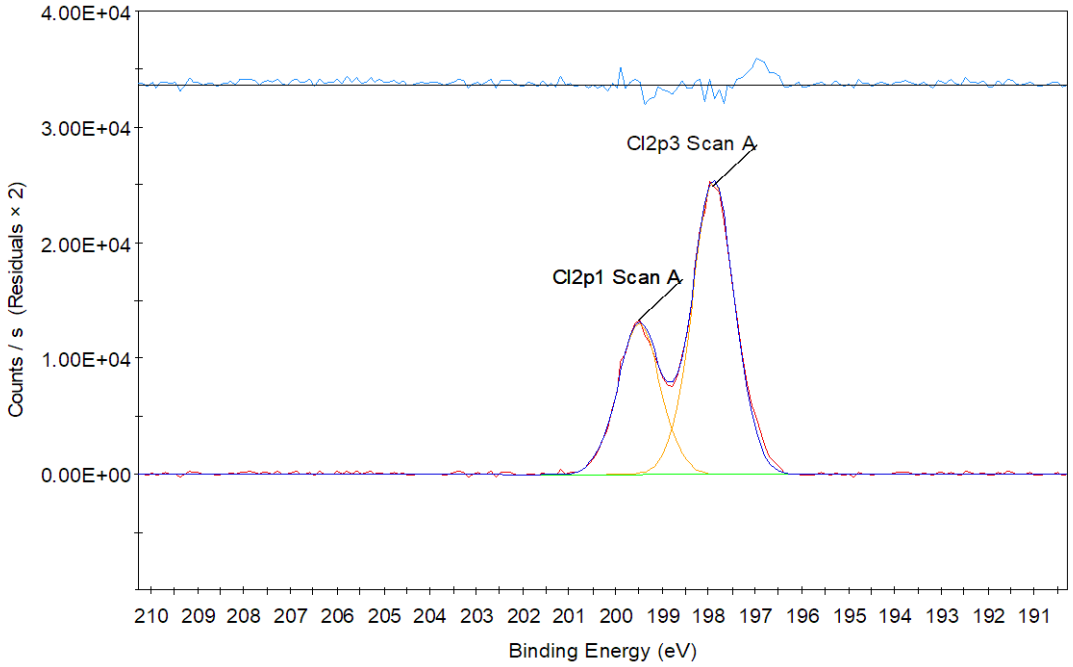

Figure S21. High resolution XPS Cl 2p scan of the 2:1 mcmimCl:$NiCl_2$ mixture

NMR spectra

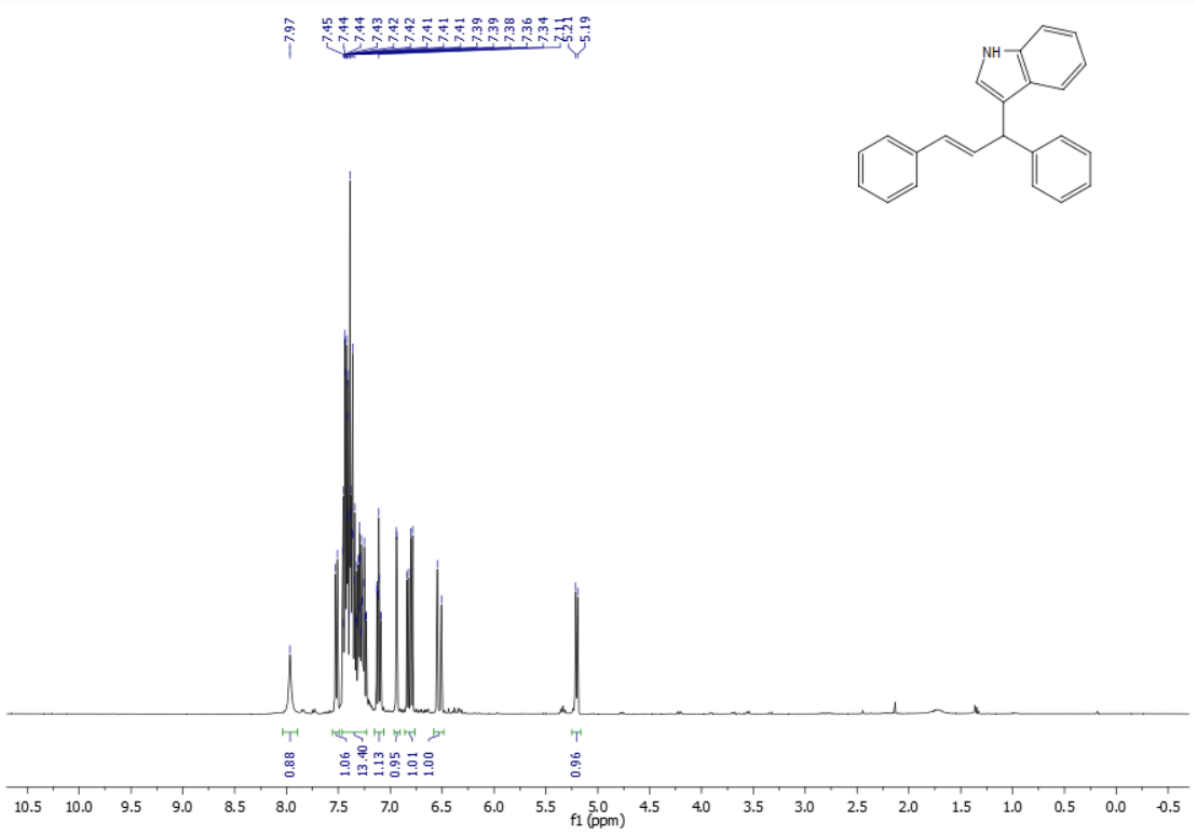

Figure S22. ^{1}H NMR spectrum of *(E)*-3-(1,3-diphenylallyl)-1*H*-indole (1)

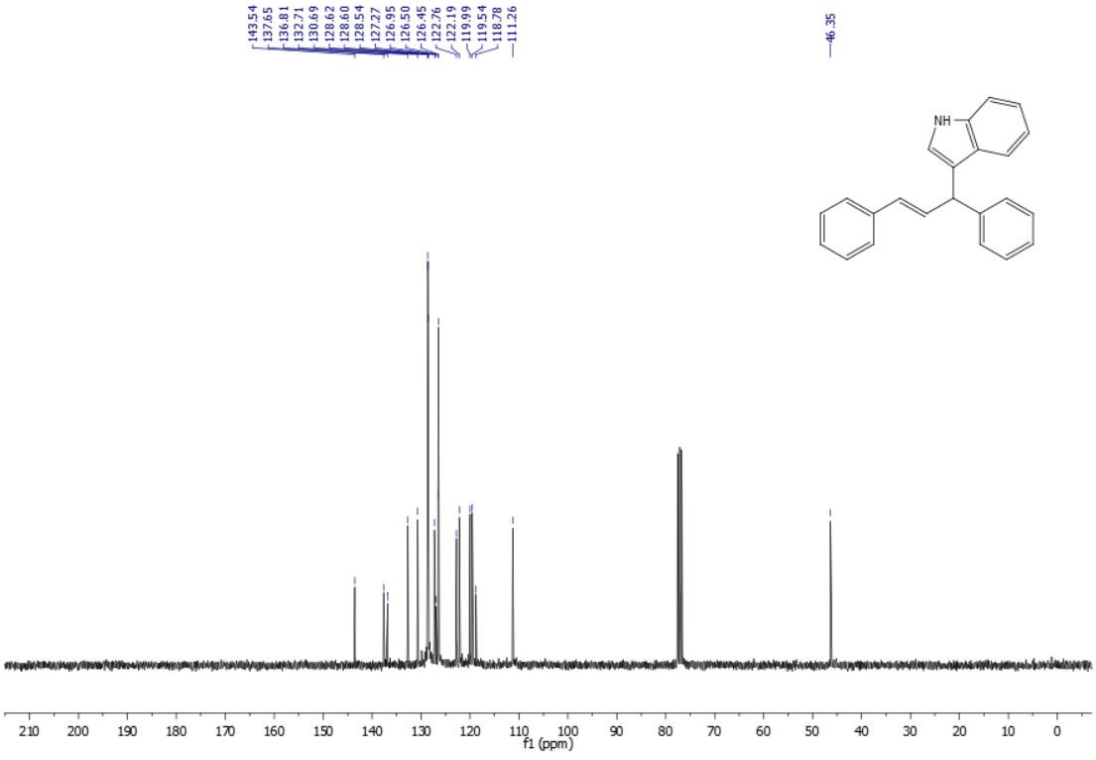

Figure S23. ^{13}C NMR spectrum of *(E)*-3-(1,3-diphenylallyl)-1*H*-indole (1)

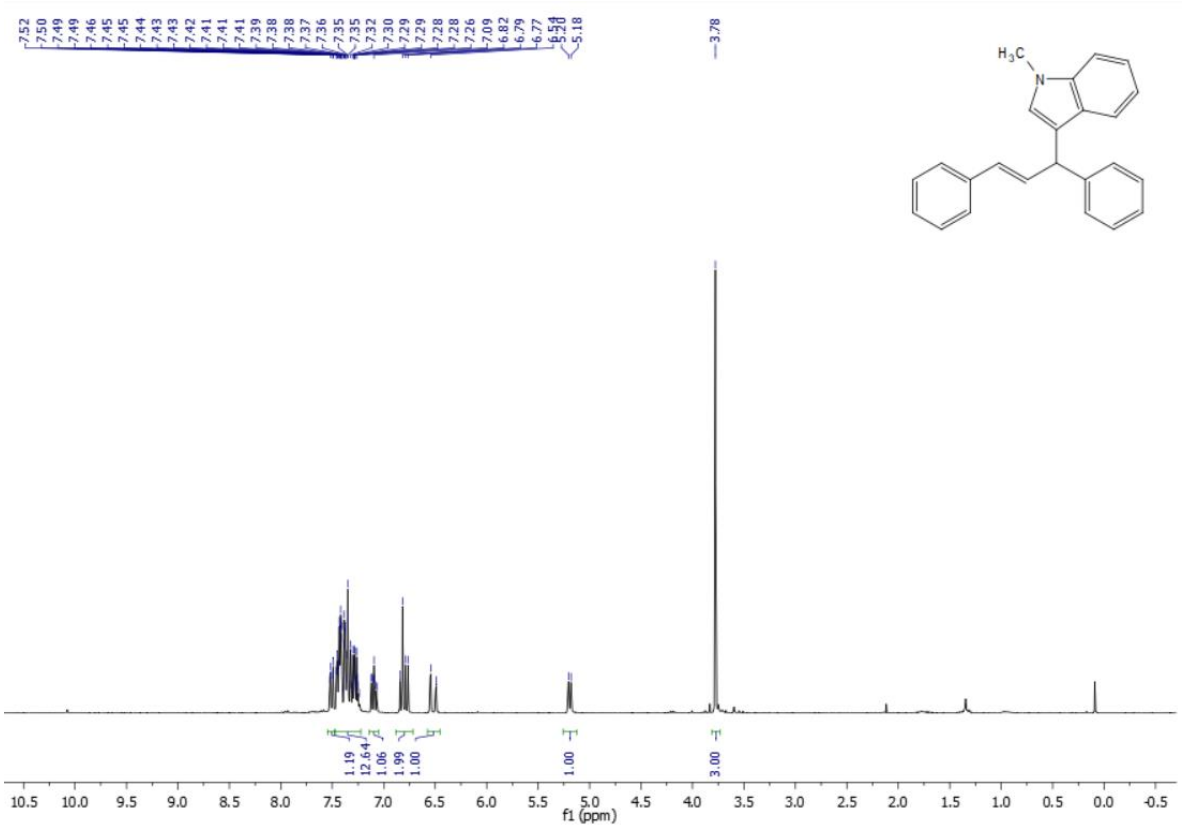

Figure S24. ^{1}H NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-1-methyl-1*H*-indole (2)

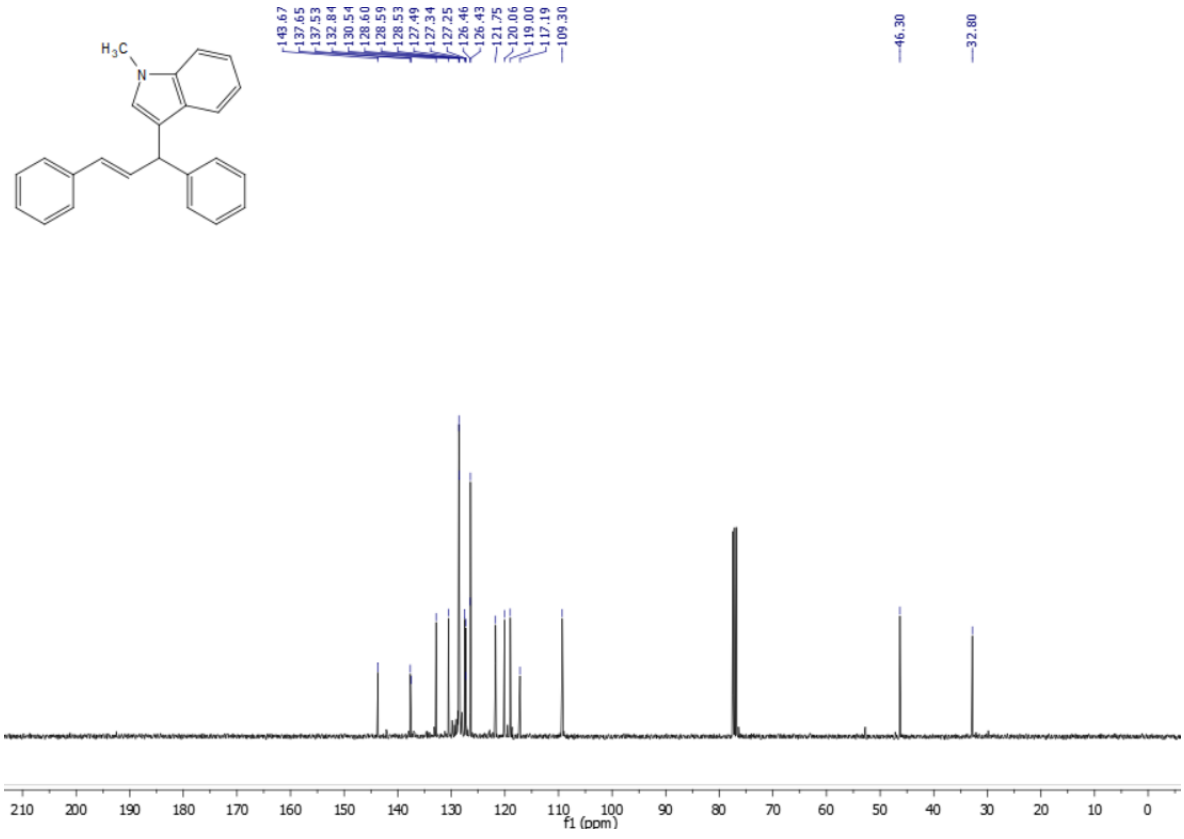

Figure S25. ^{13}C NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-1-methyl-1*H*-indole (2)

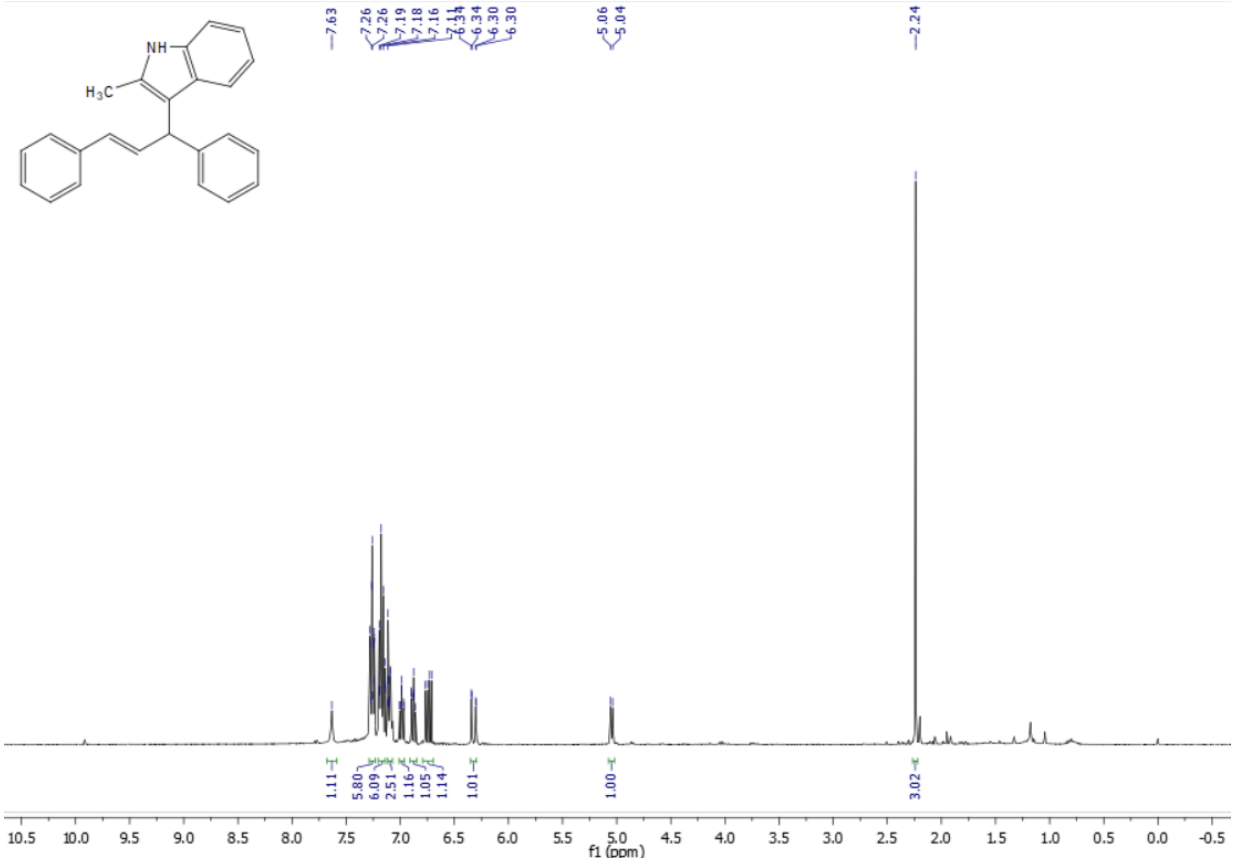

Figure S26. ^{1}H NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-2-methyl-1*H*-indole (3)

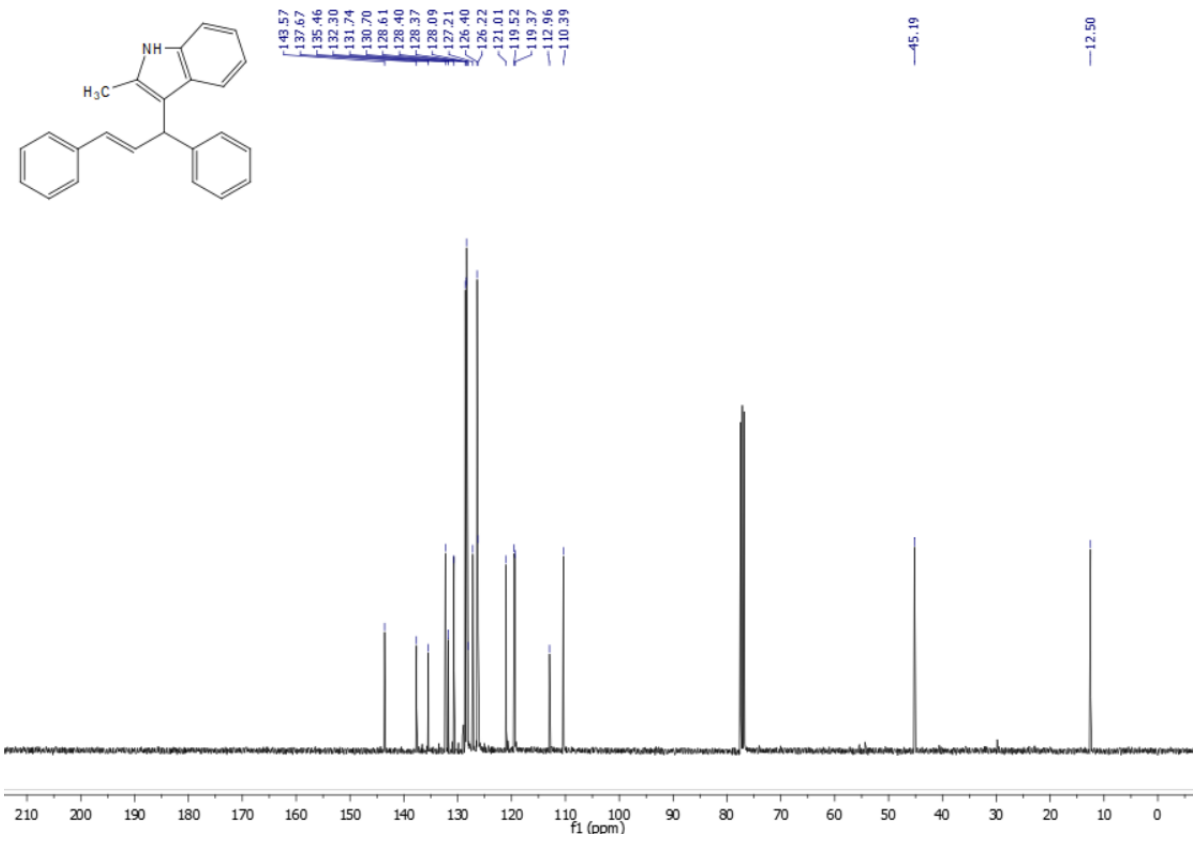

Figure S27. ^{13}C NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-2-methyl-1*H*-indole (3)

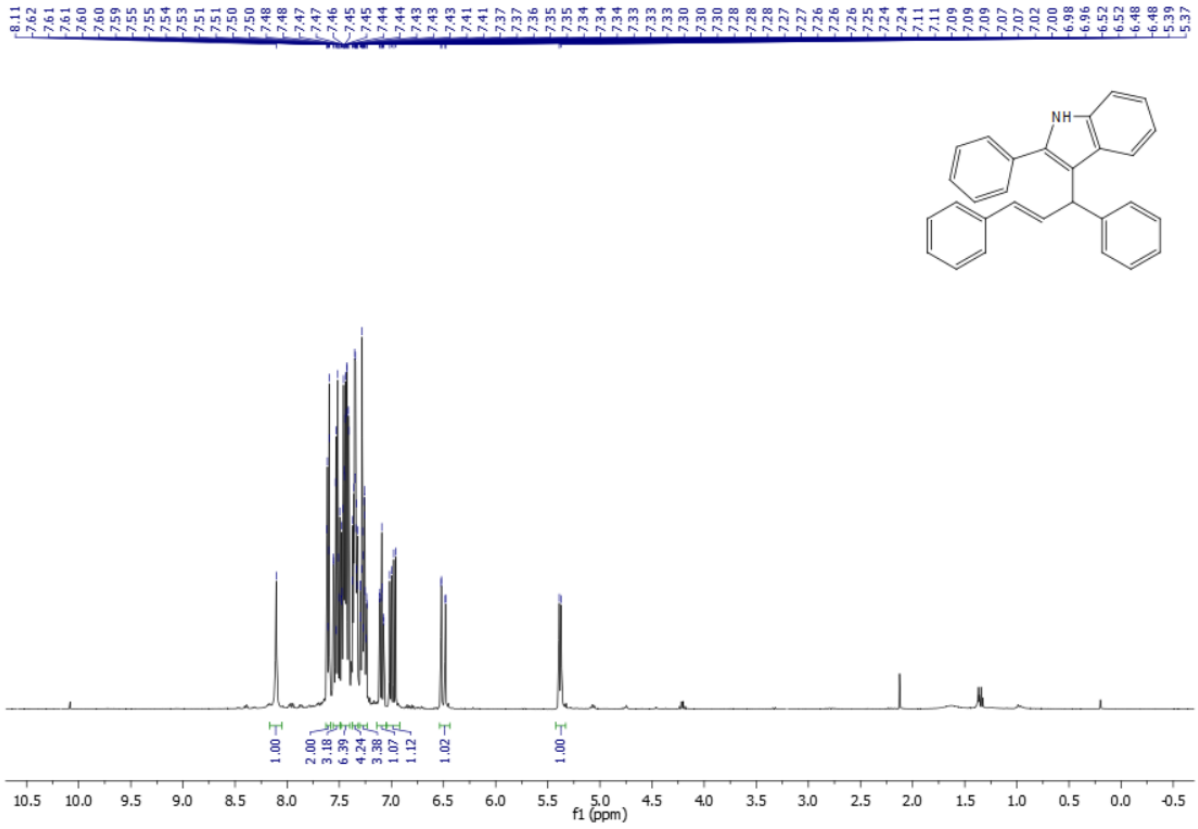

Figure S28. ^{1}H NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-2-phenyl-1*H*-indole (4)

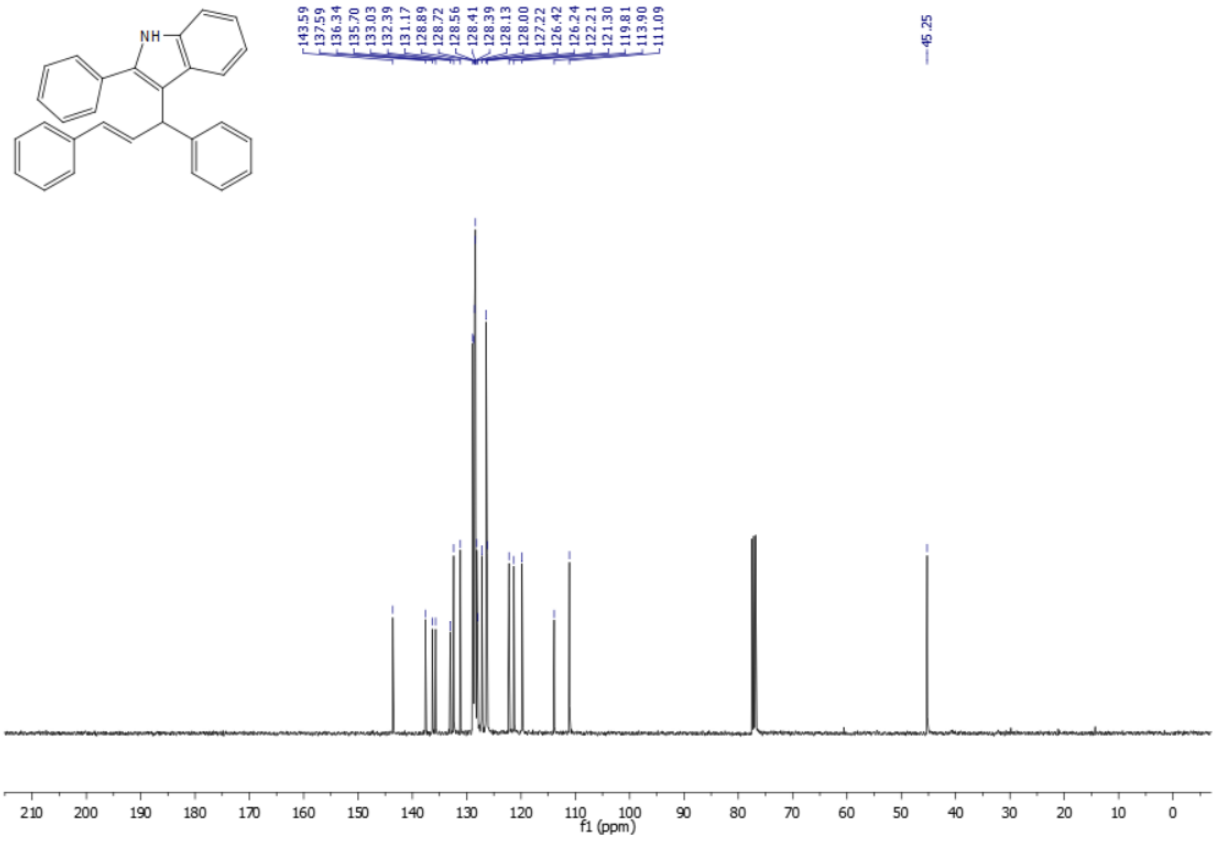

Figure S29. ^{13}C NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-2-phenyl-1*H*-indole (4)

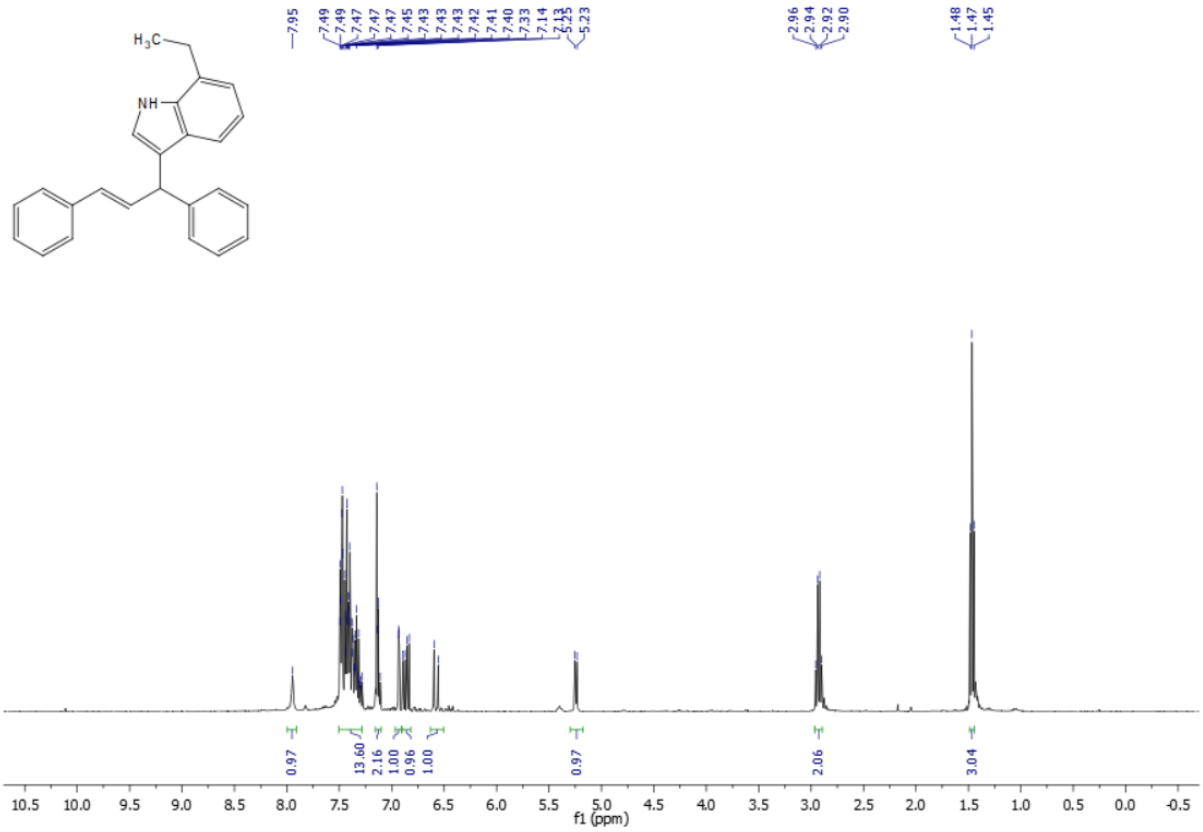

Figure S30. ^{1}H NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-7-ethyl-1*H*-indole (5)

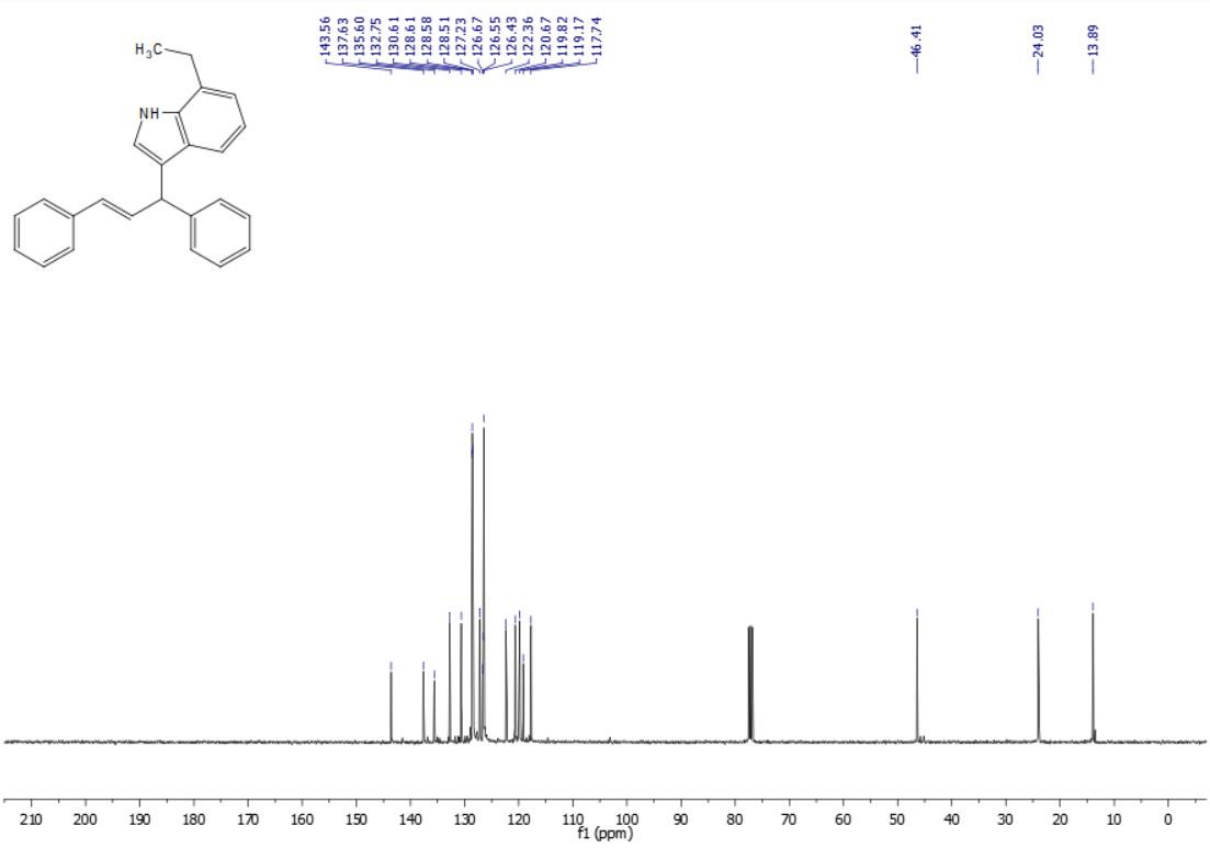

Figure S31. ^{13}C NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-7-ethyl-1*H*-indole (5)

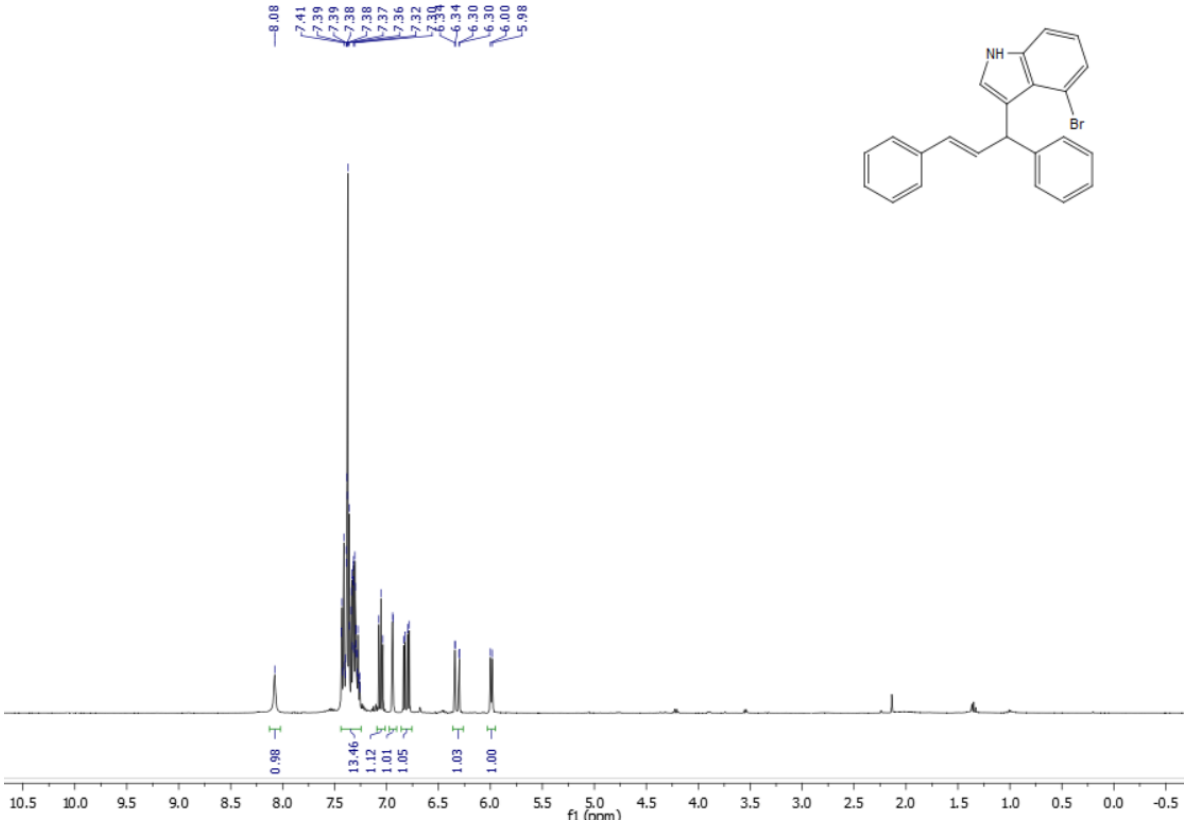

Figure S32. ^{1}H NMR spectrum of (*E*)-4-bromo-3-(1,3-diphenylallyl)-1*H*-indole (6)

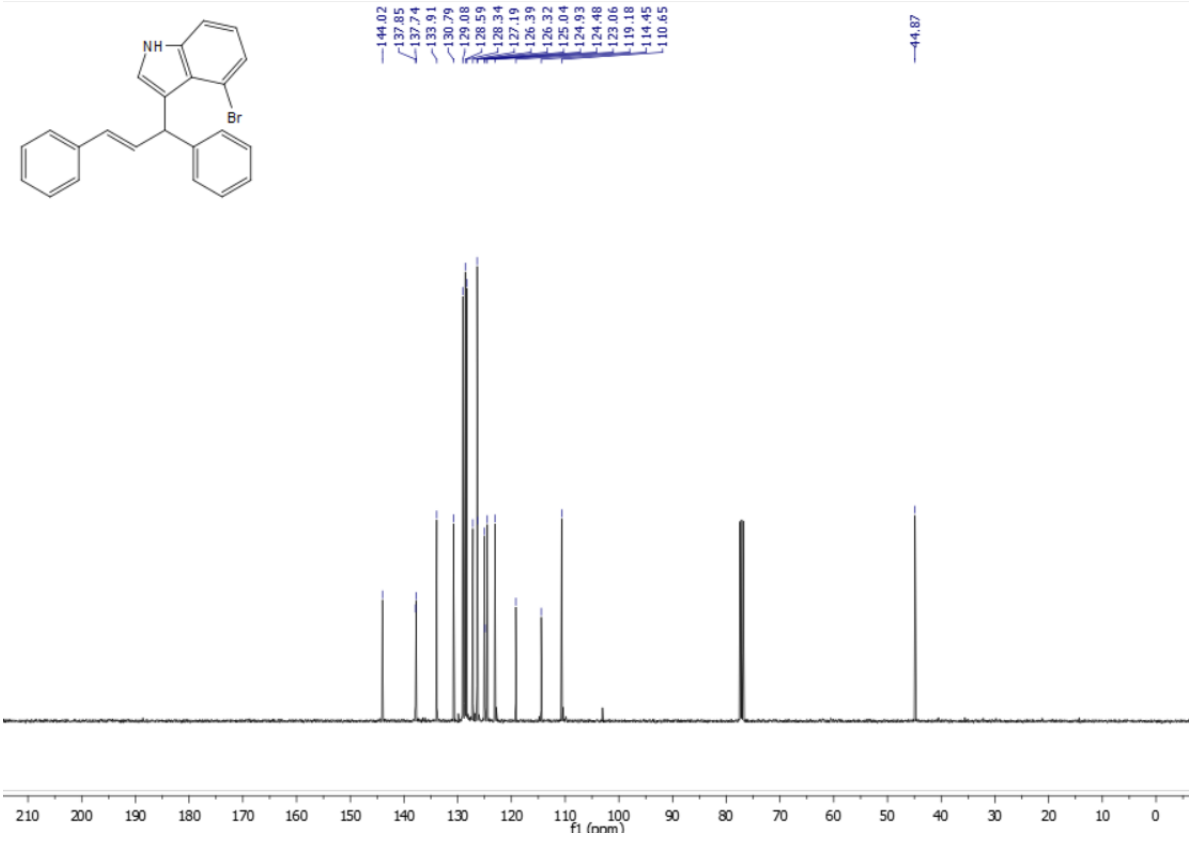

Figure S33. ^{13}C NMR spectrum of (*E*)-4-bromo-3-(1,3-diphenylallyl)-1*H*-indole (6)

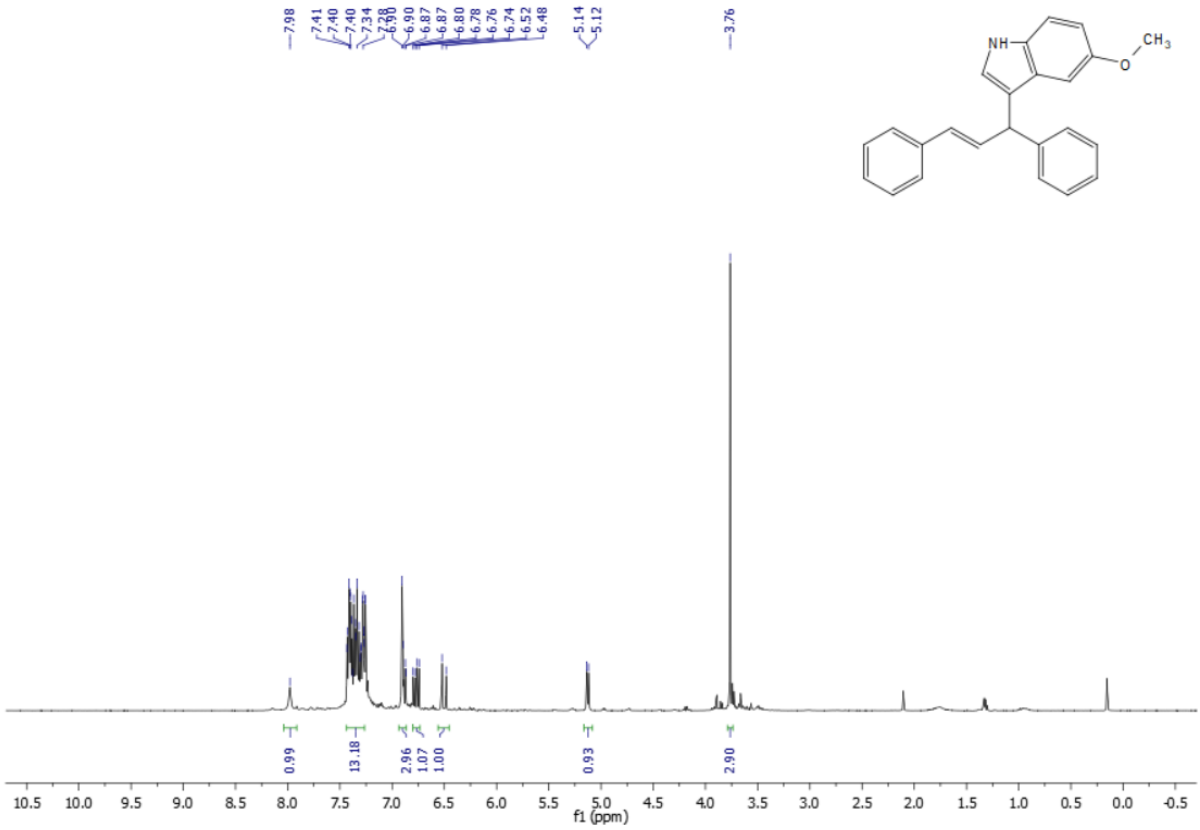

Figure S34. ^{1}H NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-5-methoxy-1*H*-indole (7)

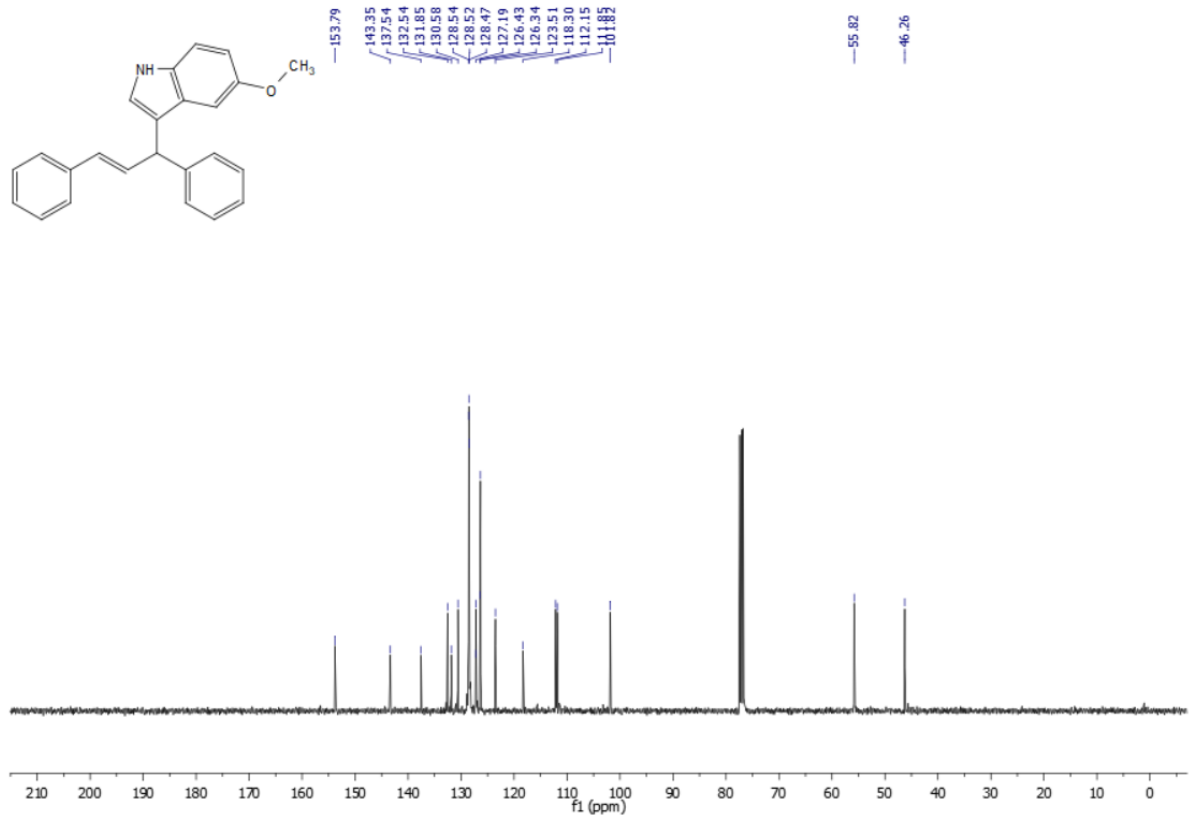

Figure S35. ^{13}C NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-5-methoxy-1*H*-indole (7)

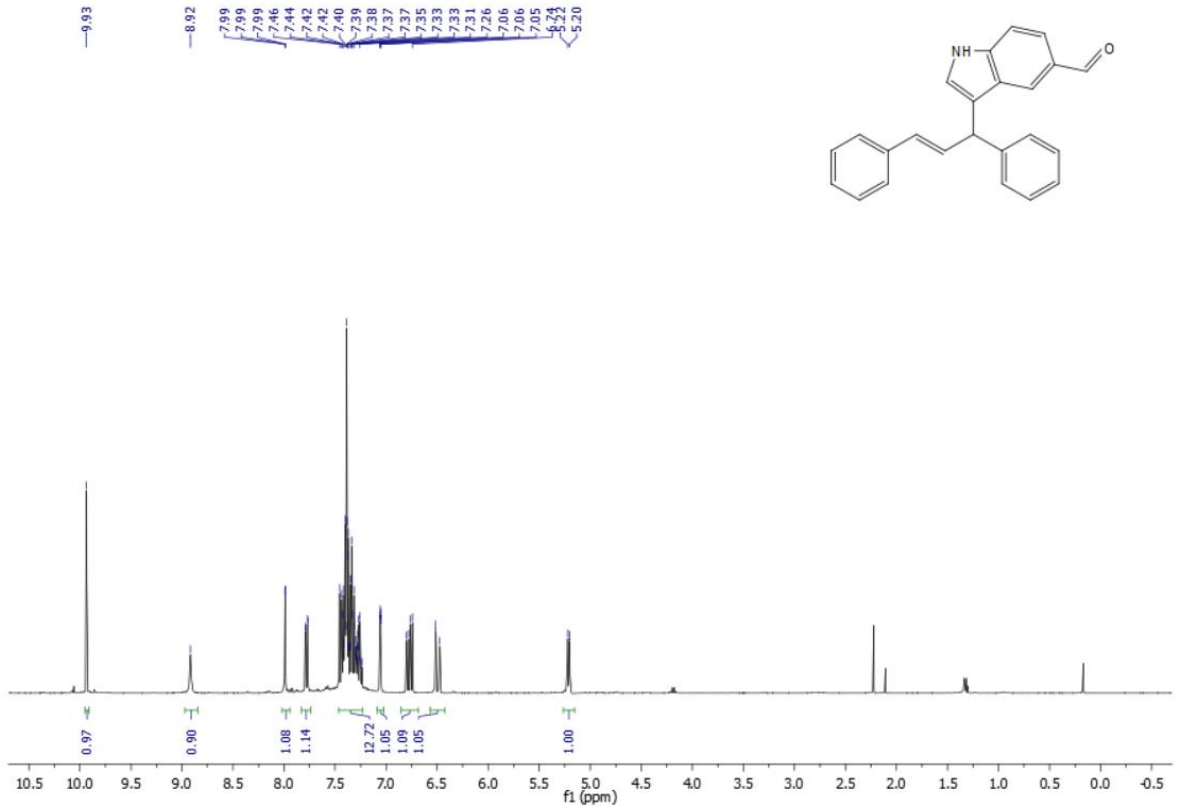

Figure S36. ^{1}H NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-5-formyl-1*H*-indole (8)

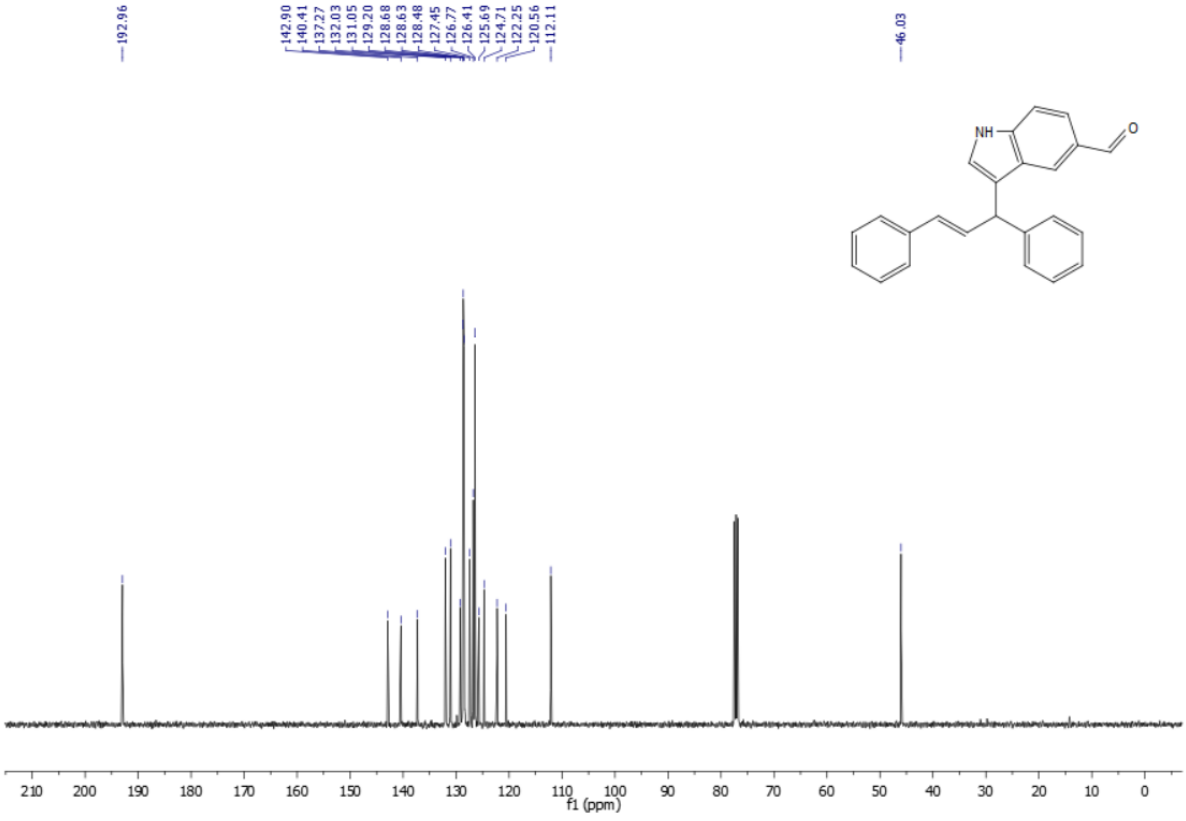

Figure S37. ^{13}C NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-5-formyl-1*H*-indole (8)

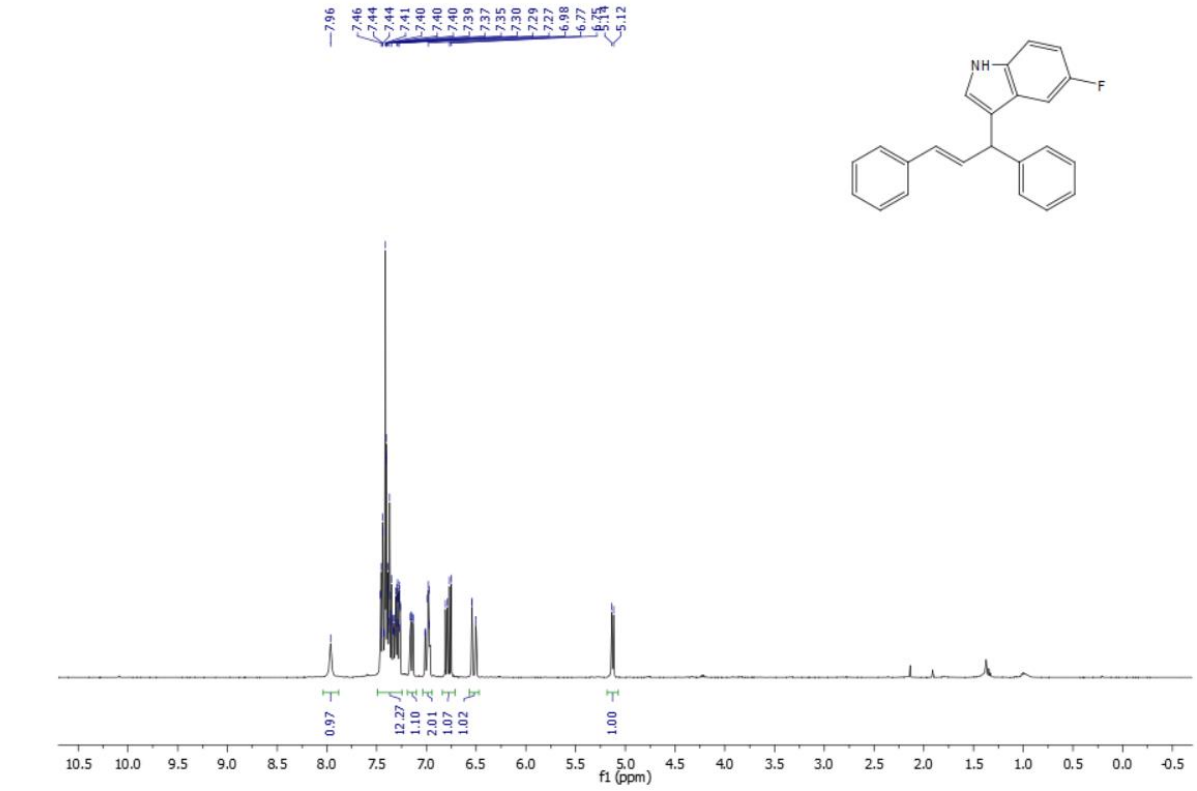

Figure S38. ^{1}H NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-5-fluoro-1*H*-indole (9)

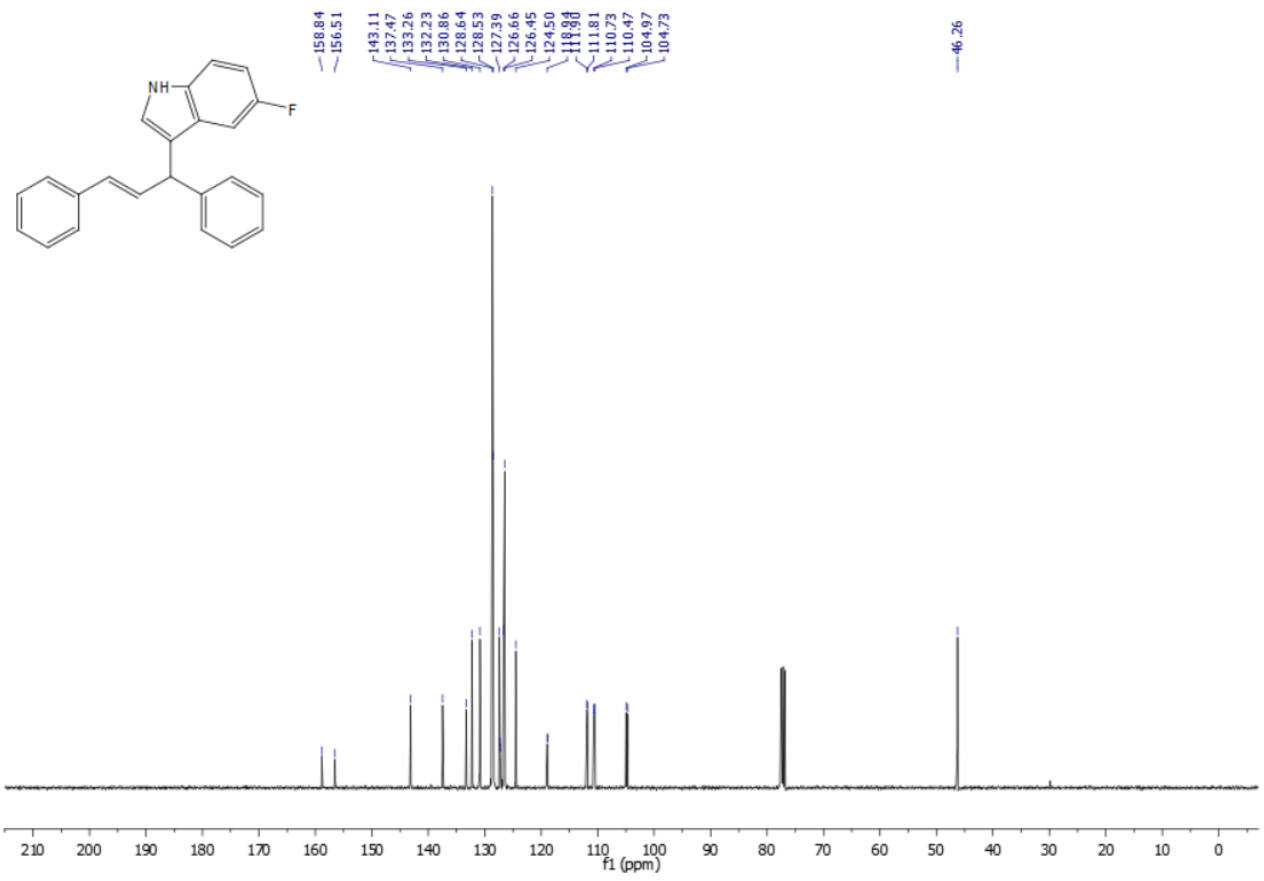

Figure S39. ^{13}C NMR spectrum of (*E*)-3-(1,3-diphenylallyl)-5-fluoro-1*H*-indole (9)

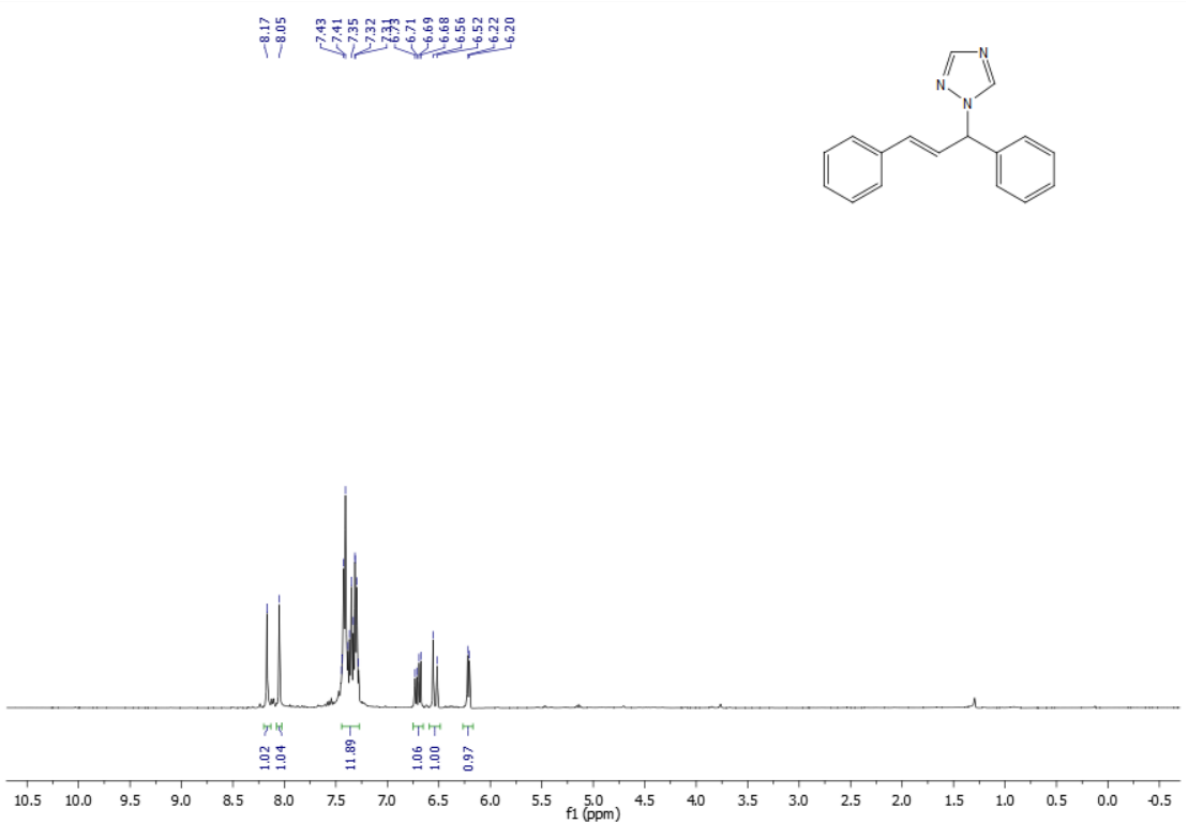

Figure S40. ^{1}H NMR spectrum of (*E*)-1-(1,3-diphenylallyl)-1,2,4-triazole (10)

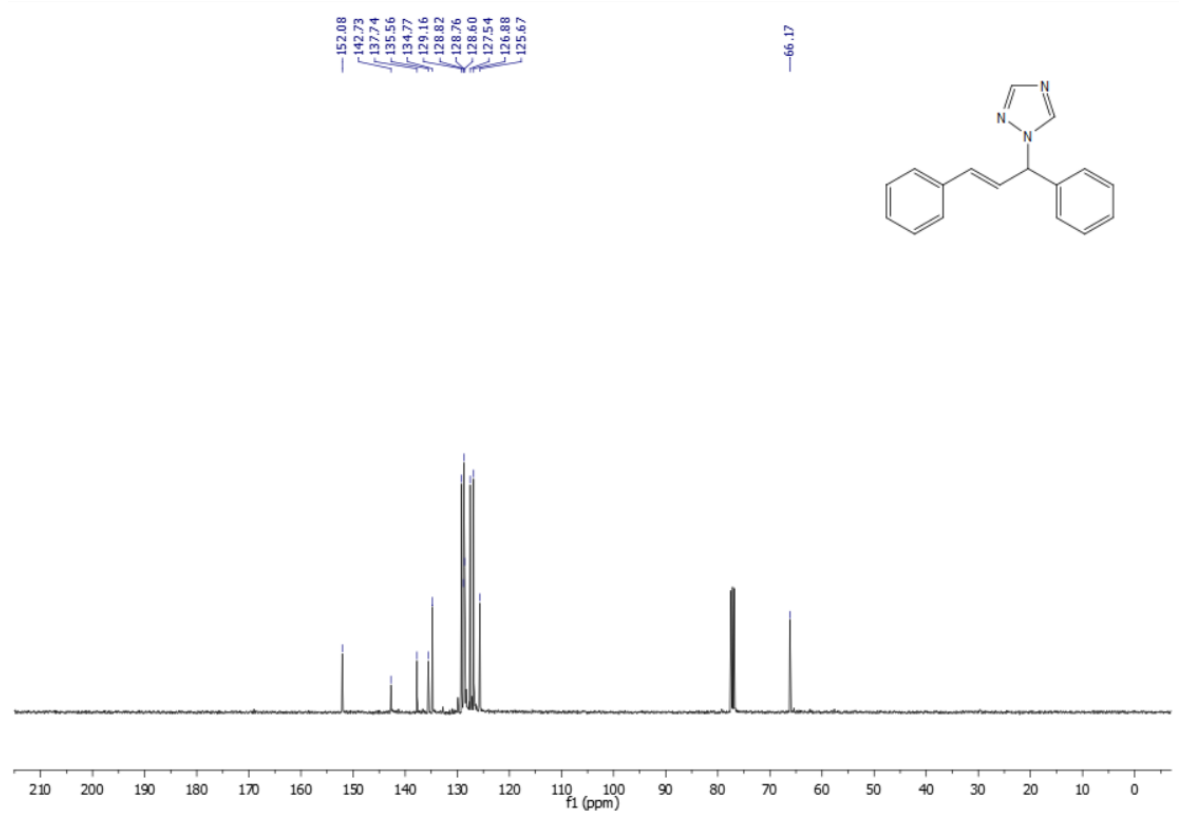

Figure S41. ^{13}C NMR spectrum of (*E*)-1-(1,3-diphenylallyl)-1,2,4-triazole (10)

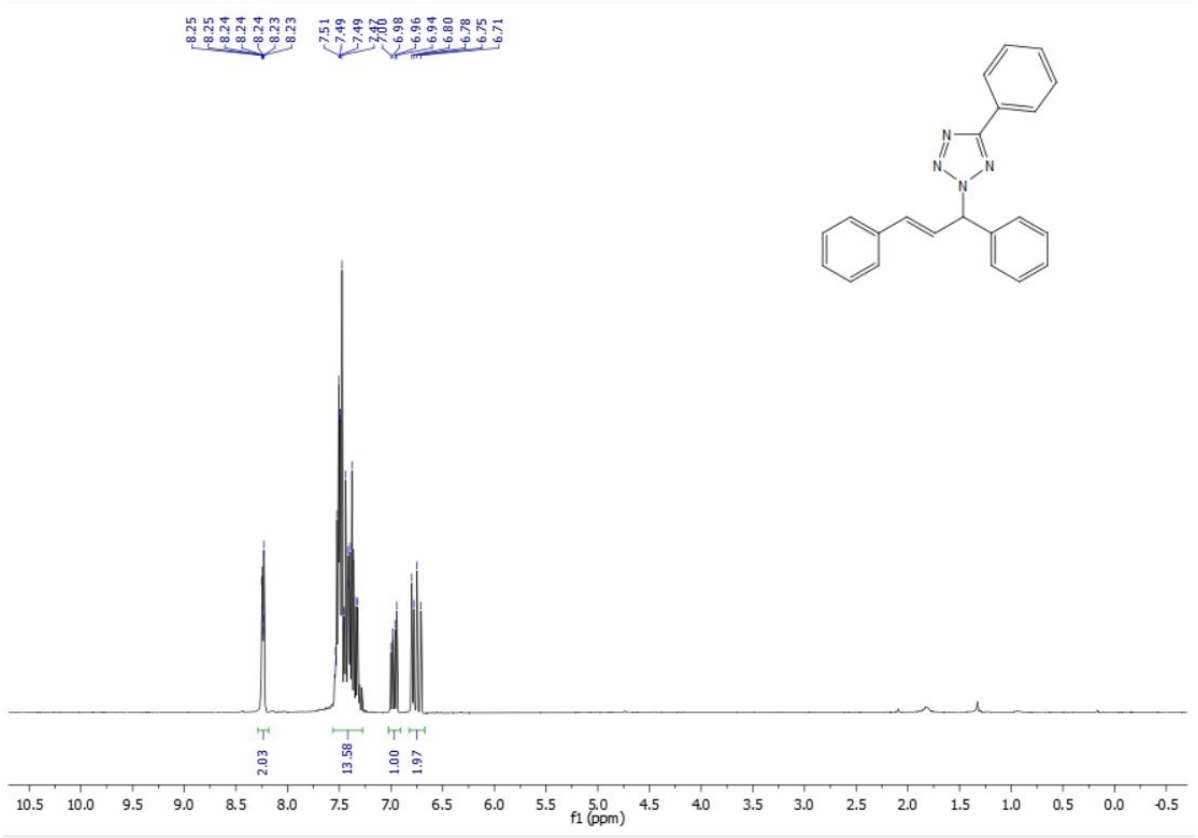

Figure S42. ^{1}H NMR spectrum of (*E*)-2-(1,3-diphenylallyl)-5-phenyl-2*H*-tetrazole (11)

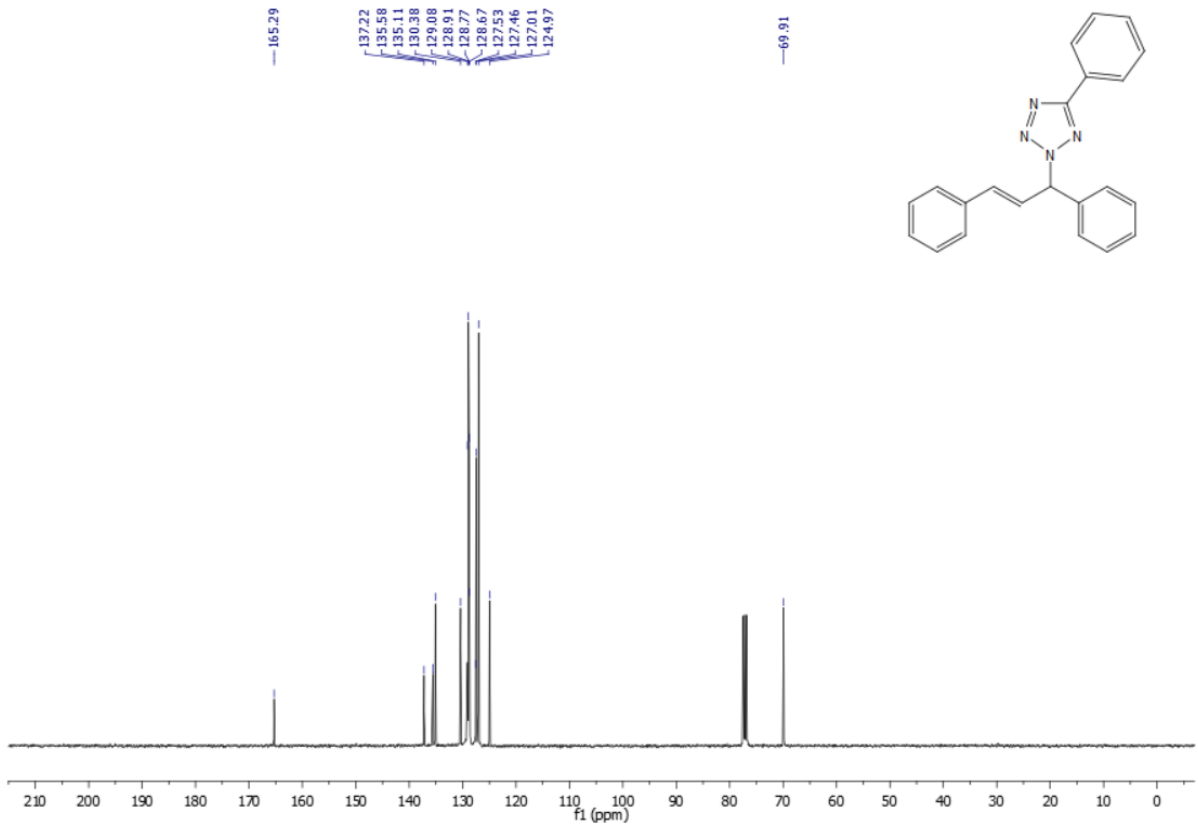

Figure S43. ^{13}C NMR spectrum of (*E*)-2-(1,3-diphenylallyl)-5-phenyl-2*H*-tetrazole (11)

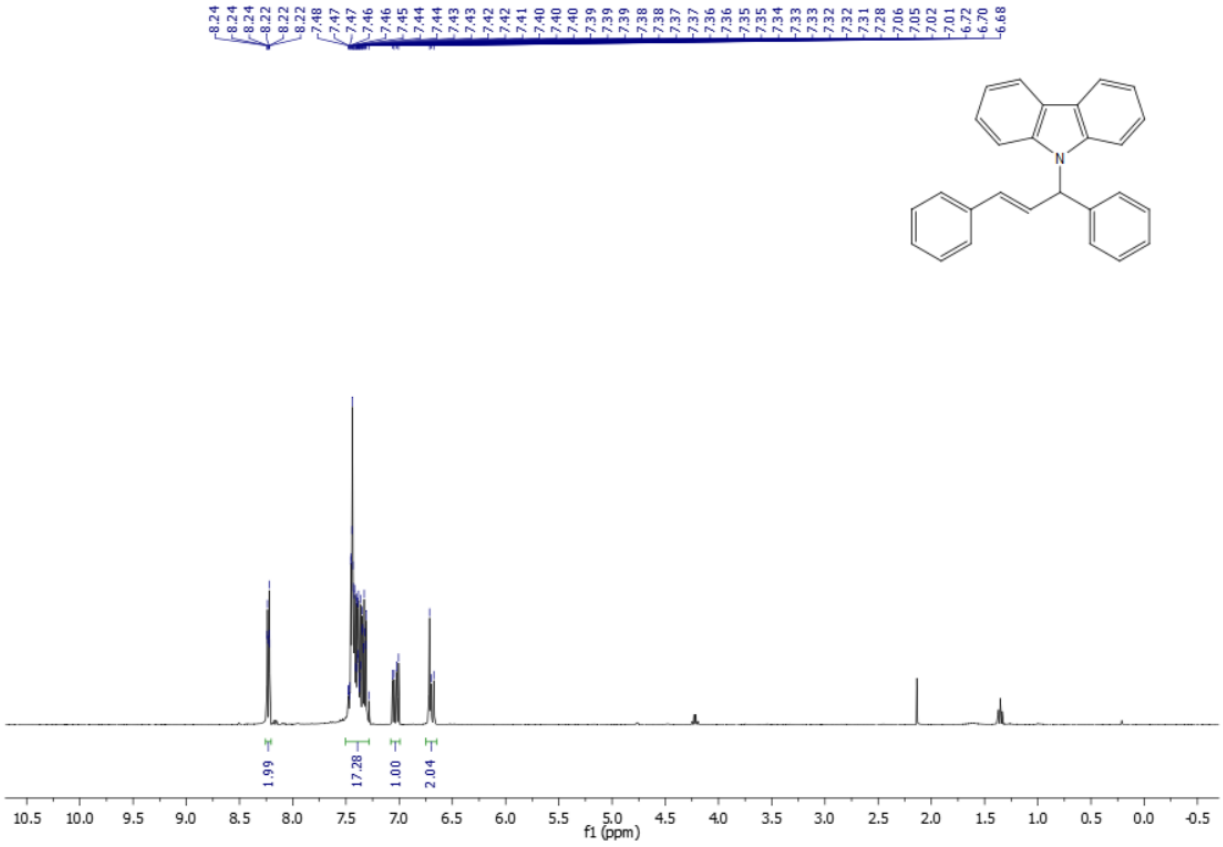

Figure S44. ^{1}H NMR spectrum of (*E*)-9-(1,3-diphenylallyl)-9*H*-carbazole (12)

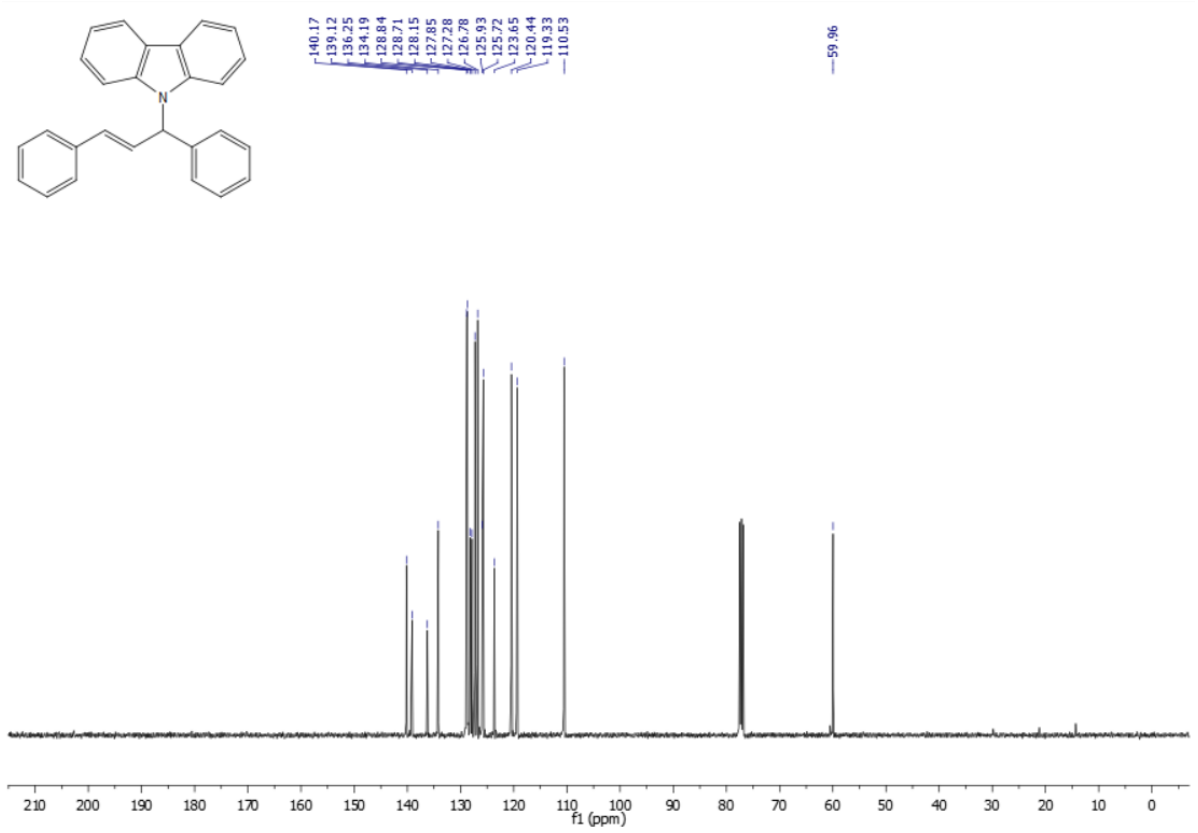

Figure S45. ^{13}C NMR spectrum of (*E*)-9-(1,3-diphenylallyl)-9*H*-carbazole (12)

Miscellaneous images

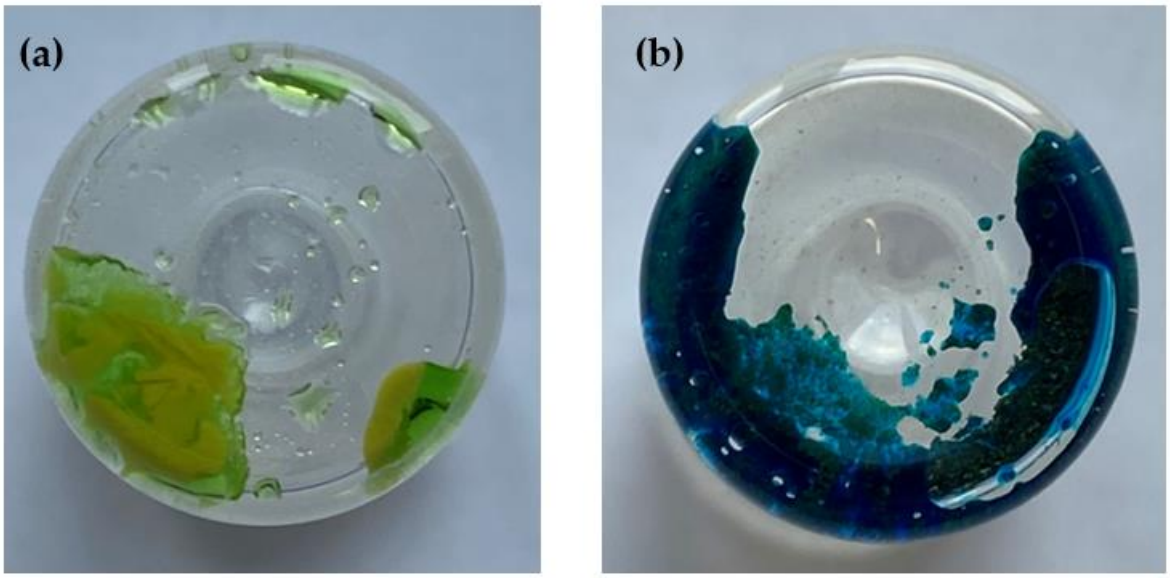

Figure S46. 1:1 mcmimCl:$NiCl_2 \cdot 6H_2O$ mixture (a) cooled down for 5 minutes after preparation (b) heated up again until development of condensation