Supporting Information

Chemo- and regioselective head-to-tail heterodimerization of vinylarenes with 1,1-diphenylethene over heterogeneous catalyst (Snβ zeolite)

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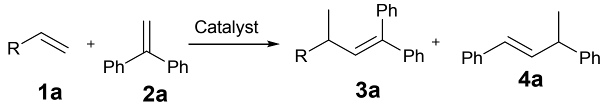
1. Optimization study for the head-to-tail heterodimerization of styrene with 1,1-diphenylethene

i) Solvent variation

The influence of solvent was studied under similar reaction conditions and the results are described in Table S1. Several solvents have been investigated and results revealed that the reaction was proceeded in chlorinated solvents and toluene (Table S1). The best results were obtained when 1,2-dichloroethane (DCE) was used as a solvent among others in terms of reaction yield (Table S1, entry 5).

Table S1 The head-to-tail heterodimerization of styrene with 1,1-diphenylethene over Snβ zeolite-effect of solvent[a,b]



Entry	Solvent	Temperature (° C)	Conversion of **1a**	**3a** Yield (%)	**4a**Yield (%)
1	Toluene	110	60	49	10
2	CCl_4	80	55	45	9
3	$CHCl_3$	80	40	30	8
4	CH_2Cl_2	40	16	10	3
5	DCE	80	99	90	9
6	DMF	100	00	-	-
7	DMA	100	00	-	-
8	DMSO	100	00	-	-
9	DME	100	00	-	-
10	ACN	70	00	-	-
11	1,4 Dioxane	100	00	-	-
12	THF	60	00	-	-
13	MeOH	60	00	-	-
14	EtOH	80	00	-	-
15	H_2O	100	15	10	3

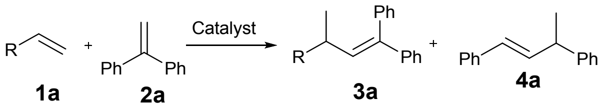
a Reaction conditions: **1a** (2 mmol), **2a** (2.5 mmol), 10% Snβ (100 mg), solvent (1 mL), 100 °C, 15 h, sealed vial. [b] Conversion of **1a** was based on GC. [c] Isolated yields.

ii) Catalyst amount variation

Once 10% Snβ catalyst was found as the best catalyst for the head-to-tail heterodimerization of styrene with 1,1-diphenylethene, the influence of a catalyst amount was also studied. By varying the catalyst amount from 25 to 100 mg, a gradual improvement in yield (53 to 90%) was observed and any further increase of amount did not have accountable effect on the yield (Table

S2, entries 1-6) and it was found that 100 mg of catalyst has shown the best results (Table S2, entry 4).

Table S2. The head-to-tail heterodimerization of styrene with 1,1-diphenylethene over Snβ zeolite-effect of amount of catalyst [a,b]



Entry	10% Snβ (mg)	Conversion **1a** (%)	**3a** Yield (%)	**4a** Yield (%)
1	25	70	53	15
2	50	86	73	13
3	75	90	78	14
4	100	99	90	9
5	150	99	91	8
6	200	99	90	7

a Reaction conditions: **1a** (2 mmol), **2a** (2.5 mmol), 1,2-dichloroethane (DCE) (1 mL), 100 °C, 15 h, sealed vial. [b] Conversion of **1a** was based on GC. [c] Isolated yields.

2. 1. Surface area and pore size distributions of catalysts

The surface properties of catalyst samples were measured by N_2 adsorption at -196 °C, in an Autosorb 3000 physical adsorption apparatus. The specific surface areas were calculated by applying the BET method.

Catalyst samples were characterized for surface area and pore size distribution and the results are given in Table S3. However, there is no direct correlation between pore size and /or pore volume against catalytic activity.

Table S3. Surface area and pore size distributions of the catalysts.

Entry	Catalyst	S_{BET} ($m^2 g^{-1}$)	Pore size (nm)	Pore volume (cc/g)
1	NaY	606	0.32	0.32
2	HY	486	2.75	0.35
3	HMCM-41	1282	3.68	1.82
4	HZSM-5 (40)	339	3.87	0.32
5	Montmorillonite K10	177	5.43	0.24
6	H-Mordenite	333	3.33	0.21
7	Hβ	587	2.28	0.33
8	Snβ	488	2.20	031

2.2. XPS Study

The XPS pattern was recorded using a Kratos Axis Ultra Imaging X-ray photoelectron spectrometer, equipped with Mg anode and a multichannel detector. Charge referencing was done against adventitious carbon (C 1s, 284.8 eV). A Shirley-type background was subtracted from the signals. The recorded spectra were fitted using Gauss–Lorentz curves to determine the binding energies of the different elements.

XPS is also adopted to determine the oxidation states of Sn. As observed in Fig. S1, the Sn 3d shows the regular doublet with peaks at 486.9 and 495.3 eV. The XPS study suggest that Sn^{4+} species are present on the catalyst, which is in good agreement with literature data.[3]

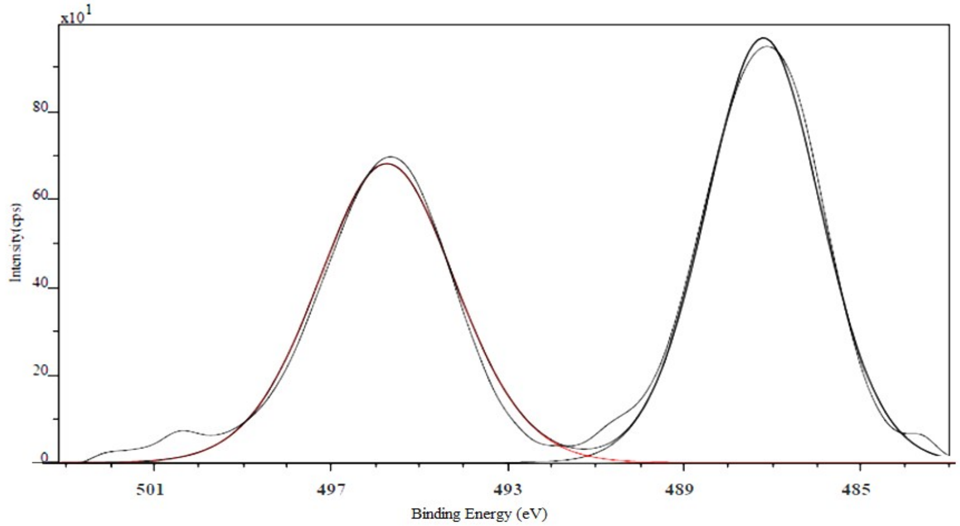


Fig. S1. XPS spectra of SnO_2.

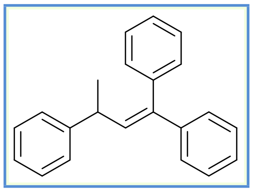
Table S4. Desorption of ammonia of Hβ and modified beta zeolites at different acidic regions[a,b,c]

Catalyst	Acidity[a]	Acidic sites $_{\text{distribution}}$[b]		
	(mmol/g)	LT-peak[c]	MT-peak[c]	HT-peak[c]
Hβ	0.47	25.4	74.6	-
10% Crβ	1.04	55.4	41.5	3.1
10% Coβ	1.73	10.0	32.9	57.1
10% Crβ	1.31	14.5	45.8	39.7
10%Feβ	1.59	12.5	51.5	36.0
10%Moβ	1.40	38.5	27.8	33.7
10%Niβ	1.66	20.9	64.9	14.2
10%Wβ	1.40	8.5	65.1	26.4

[a] Total acidity amount determined by NH_3-TPD. [b] The NH_3-TPD (%) distribution of acidic sites. [c] LT-peak represents weak acid sites (150-250 °C), MT-peak represents medium acid sites (250-550 °C) and HT-peak represents strong acid sites (550- 650 °C).

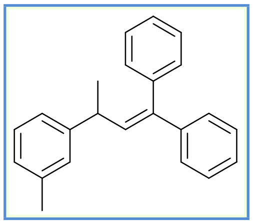
Spectroscopic data

1,1,3-Triphenyl-1-butene (3a)[1]



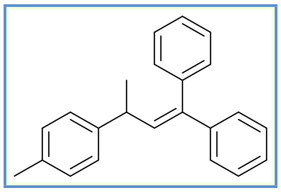
^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 7.34–7.18 (m, 15H), 6.23-6.20 (m, 1H), 3.62-3.58 (m, 1H), 1.39 (d, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) = 146.2, 142.4, 140.1, 134.2, 129.9, 128.5, 128.3, 128.1, 127.3, 127.1, 127.0, 126.9, 126.0, 39.3, 22.4.

1,1-Diphenyl-3-(3-tolyl)-1-butene (3c)



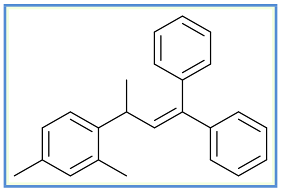
^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 7.40-7.32 (m, 3 H), 7.24-7.15 (m, 8 H), 6.99-7.01 (m, 3 H), 6.22 (d, J = 10.38 Hz, 1 H), 3.60-3.50 (m, 1 H), 2.33 (s, 3 H), 1.37 (d, J = 6.79 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) = 146.1, 142.3, 140.0, 139.9, 137.9, 134.2, 129.8, 128.3, 128.2, 128.0, 127.6, 127.2, 127.0, 126.9, 126.7, 123.9, 39.2, 22.4, 21.5. HRMS (EI): *m/z* calculated for $C_{23}H_{22}$ $[M]^+$ 298.17215, found: 298.172110.

3-(4-Tolyl)-1,1-diphenyl-1-butene (3d) [1]



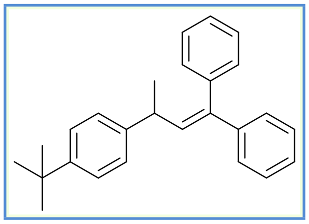
^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 7.40-7.36 (m, 2 H), 7.33-7.30 (m, 1 H), 7.23-7.19 (m, 7 H), 7.11-7.10 (m, 4 H), 6.21-6.18 (m, 1 H), 3.59-3.53 (m, 1 H), 2.31 (s, 3 H), 1.36 (d, J = 6.86 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) = 143.1, 142.4, 140.1, 139.9, 135.4, 134.3, 129.8, 129.1, 128.2, 128.0, 127.2, 127.0, 126.9, 126.7, 38.8, 22.4, 21.0.

3-(2,4-Dimethylphenyl)-1,1-diphenyl-1-butene (3e)



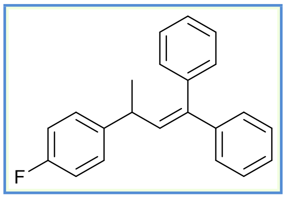
^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 7.37-7.29 (m, 3 H), 7.24-7.19 (m, 6 H), 7.15-7.13 (m, 2 H), 7.01 (d, 7.78 Hz, 1 H), 6.90 (s, 1 H), 6.22 (d, J = 10.07 Hz, 1 H), 3.74-3.68 (m, 1 H), 2.28 (s, 3 H), 2.28 (s, 3 H), 1.93 (s, 3 H), 1.35 (d, J = 6.86 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) = 142.5, 141.9, 140.2, 140.1, 135.1, 134.3, 131.1, 129.7, 128.0, 127.3, 126.9, 125.8, 35.0, 22.7, 20.9, 19.1. HRMS (EI): *m/z* calculated for $C_{24}H_{24}$ [M]$^+$ 312.18780, found: 312.18750.

3-(4-*tert*-Butylphenyl)-1,1-diphenyl-1-butene (3f)



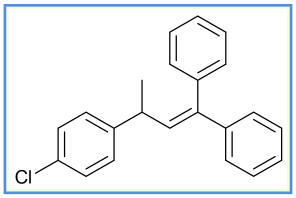
^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 7.40-7.37 (m, 2 H), 7.34-7.30 (m, 3 H), 7.25-7.18 (m, 7 H), 7.15 (d, J = 8.24 Hz, 2 H), 6.20 (d, J = 10.37 Hz, 1 H), 3.60-3.54 (m, 1 H), 1.37 (d, J = 6.86 Hz, 3 H), 1.30 (s, 9 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) = 148.7, 142.9, 142.4, 140.1, 139.8, 134.4, 129.8, 128.2, 128.0, 127.2, 127.0, 126.9, 126.5, 125.3, 38.7, 34.3, 31.4, 22.1. HRMS (EI): *m/z* calculated for $C_{26}H_{28}$ [M]$^+$ 340.21910, found: 340.21890.

3-(4-Fluorophenyl)-1,1-diphenyl-1-butene (3g)



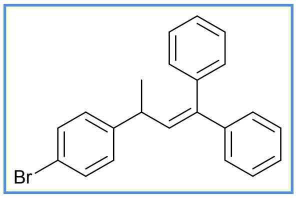
^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 7.39-7.30 (m, 3 H), 7.25-7.19 (m, 5 H), 7.12-7.17 (m, 4 H), 6.97-6.94 (m, 2 H), 6.16 (d, J = 10.37 Hz, 1 H), 3.60-3.54 (m, 1 H), 1.36 (d, J = 7.01 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) = 161.4, 142.2, 141.9, 140.4, 140.0, 133.8, 129.7, 128.3, 128.2, 128.1, 127.2, 127.1, 127.0, 115.3, 115.0, 38.6, 22.4. HRMS (EI): *m/z* calculated for $C_{22}H_{19}F$ [M]$^+$ 302.14708, found: 302.14690.

3-(4-Chlorophenyl)-1,1-diphenyl-1-butene (3h)[1]



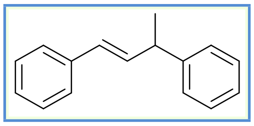
^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) = 7.38 -7.10 (m, 14 H), 6.14 (d, *J* = 10.22 Hz, 1 H), 3.61-3.53 (m, 1 H), 1.36 (d, *J* = 6.86 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) = 144.7, 142.1, 140.6, 139.9, 133.4, 129.7, 128.5, 128.3, 128.2, 128.1, 127.2, 127.1, 127.1, 38.7, 22.3.

3-(4-Bromophenyl)-1,1-diphenyl-1-butene (3i)[1]



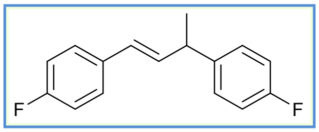
^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) = 7.42-7.31 (m, 5 H), 7.26-7.19 (m, 5 H), 7.16-7.14 (m, 2 H), 7.07-7.04 (m, 2 H), 6.14 (d, *J* = 10.37 Hz, 1 H), 3.58-3.51 (m, 1 H), 1.36 (d, *J* = 6.84 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) = 145.2, 142.1, 140.7, 139.9, 133.3, 131.5, 129.6, 128.7, 128.3, 128.1, 127.2, 127.1, 127.1, 38.8, 22.3.

1,3-Diphenylbut-1-ene (4a)[2]



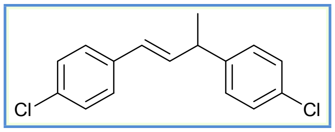
^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) = 7.37-7.34 (m, 2 H), 7.36-7.26 (m, 6 H), 7.22-7.17 (m, 2 H), 6.40-6.38 (m, 2 H), 3.66-3.61 (m, 1 H), 1.47 (d, *J* = 7.01 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) = 145.6, 137.5, 135.2, 128.5, 127.3, 127.0, 126.2, 126.1, 42.6, 21.2.

1,3-Di(4-fluorophenyl)but-1-ene (4d)[2]



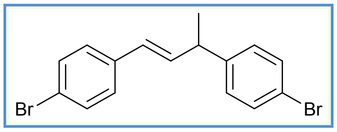
^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) = 7.31-7.28 (m, 2 H), 7.22-7.18 (m, 2 H), 7.02-6.94 (m, 4 H), 6.36-6.21 (m, 2 H), 3.64-3.57 (m, 1 H), 1.43 (d, *J* = 7.01 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) = 163.3, 162.6, 160.8, 160.2, 141.1, 134.7, 133.5, 128.6, 128.7, 127.6, 127.5, 115.4, 115.3, 115.2, 115.1, 41.8, 21.3.

1,3-Di(4-chlorophenyl)but-1-ene (4e)[2]



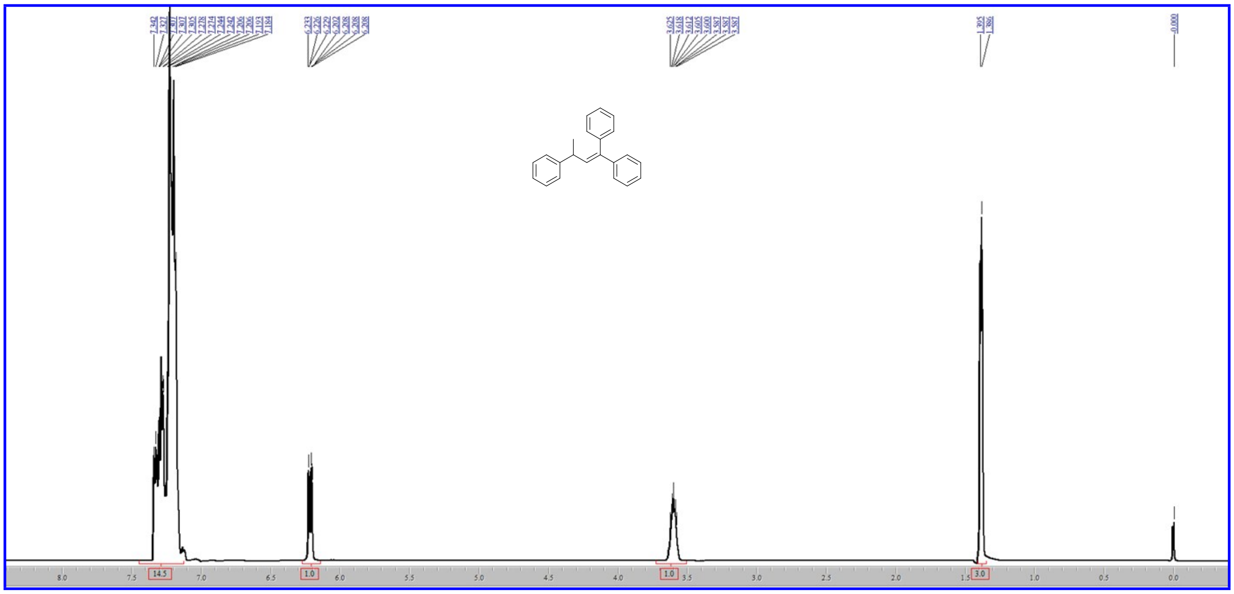
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.29-7.25 (m, 6 H), 7.18 (d, J = 8.39 Hz, 2 H), 6.35-6.26 (m, 2 H), 3.62-3.58 (m, 1 H), 1.43 (d, J = 7.01 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 143.7, 135.8, 135.3, 132.7, 132.0, 128.6, 127.7, 127.3, 41.9, 21.0.

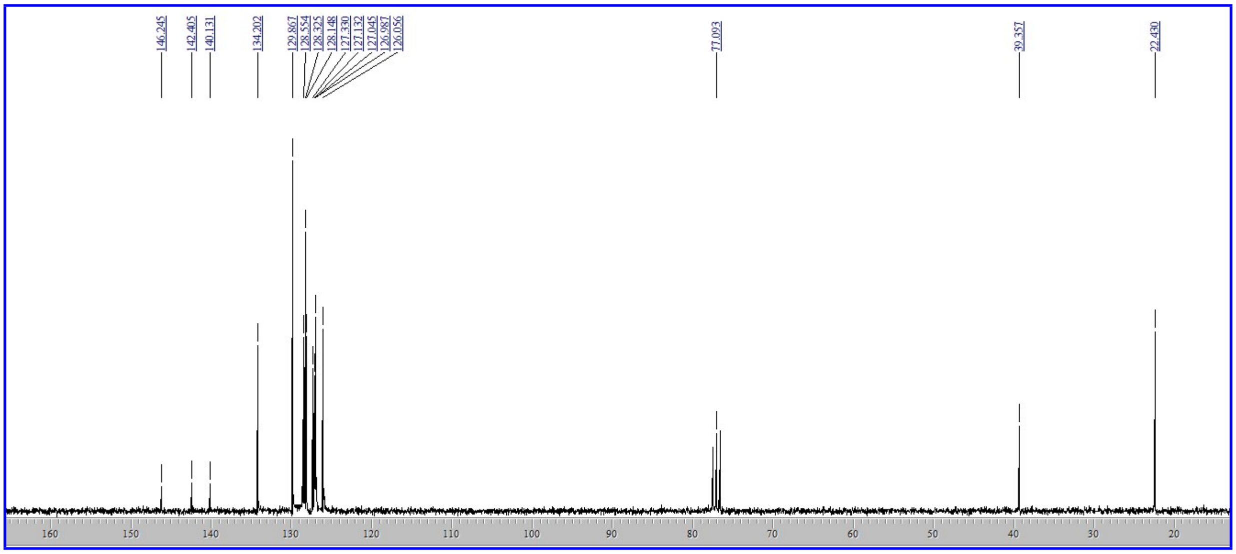
1,3-Di(4-bromophenyl)but-1-ene (4f)[2]



^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.43 (d, J = 8.39 Hz, 2 H), 7.40 (d, J = 8.54 Hz, 2 H), 7.20 (d, J = 8.54 Hz, 2 H), 7.13 (d, J = 8.39 Hz, 2 H), 6.31 (d, J = 2.89 Hz, 2 H), 3.61-3.56 (m, 1 H), 1.43 (d, J = 7.01 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 144.2, 136.2, 135.3, 131.6, 129.0, 127.8, 127.7, 120.9, 120.0, 42.0, 21.0.

<u>Copies of ^{1}H and ^{13}C NMR spectra:</u>

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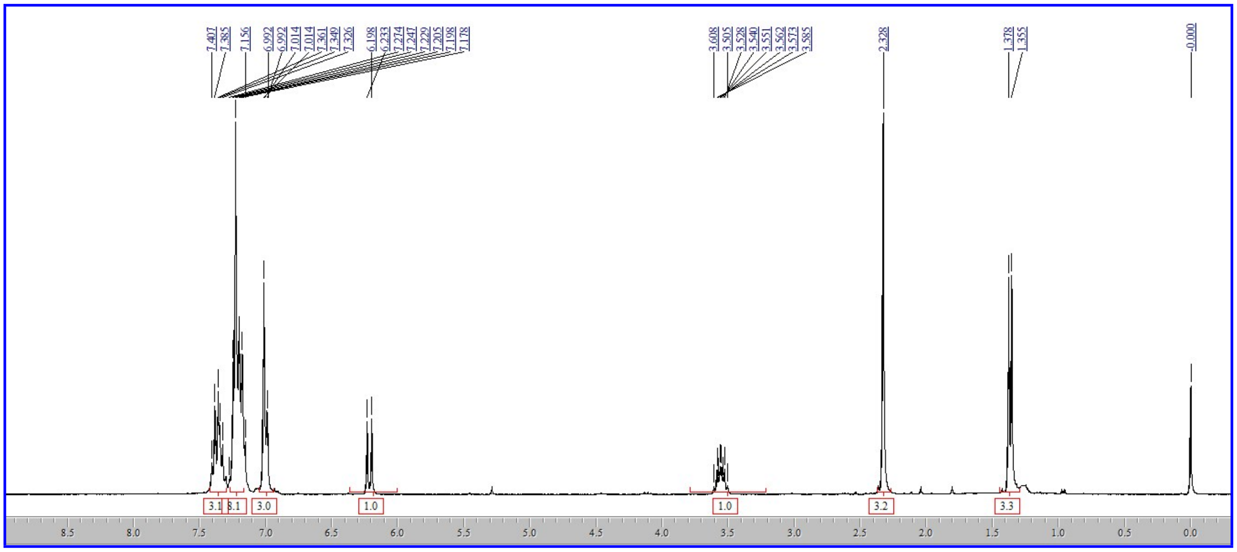
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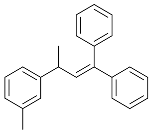

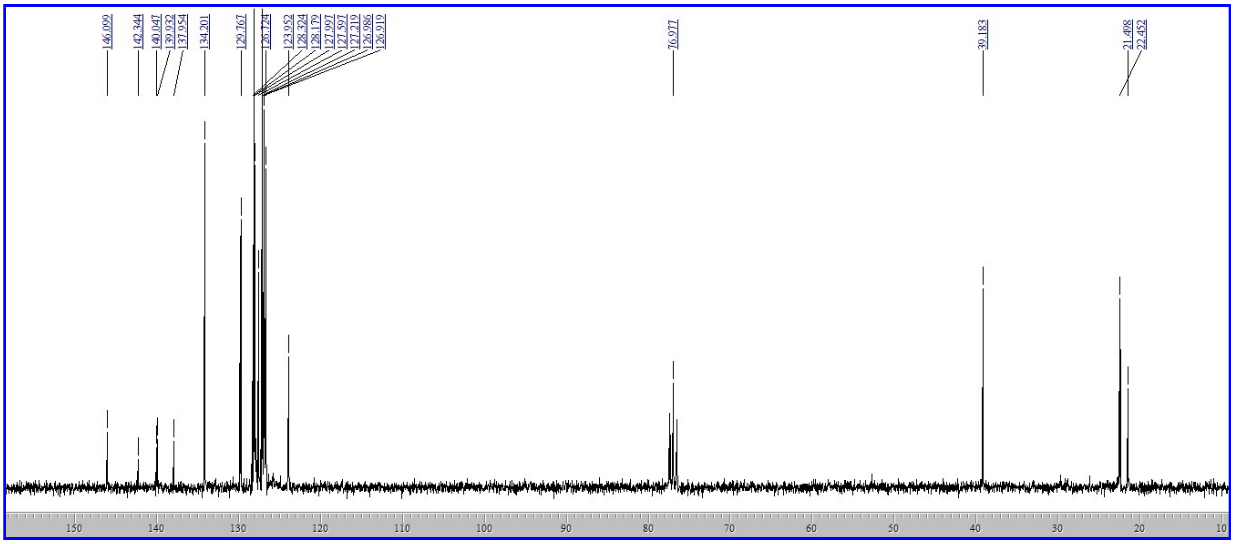
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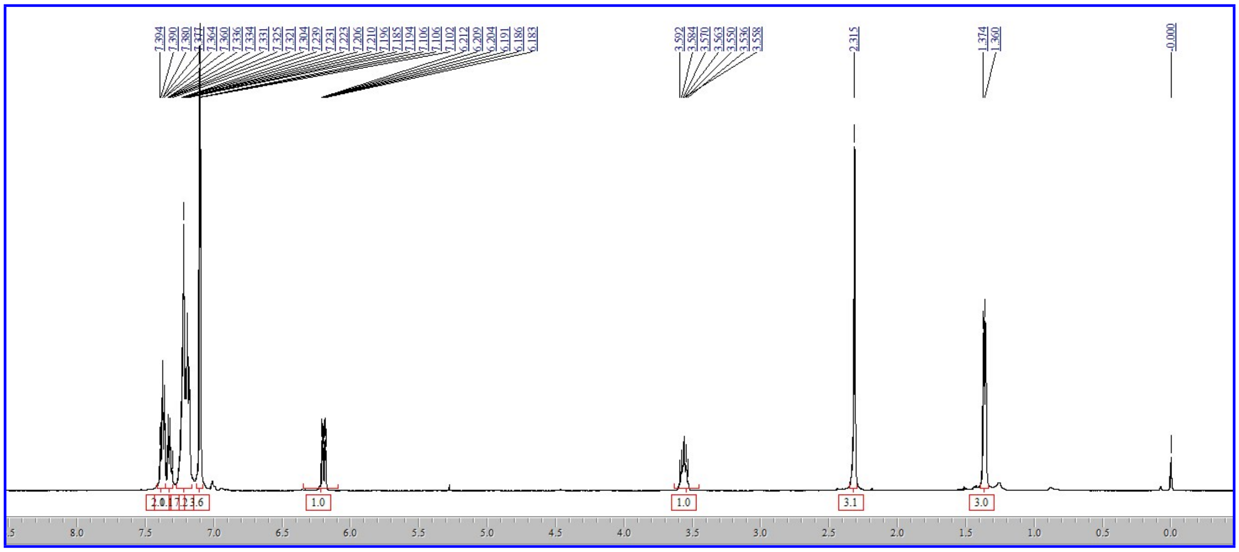
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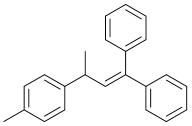

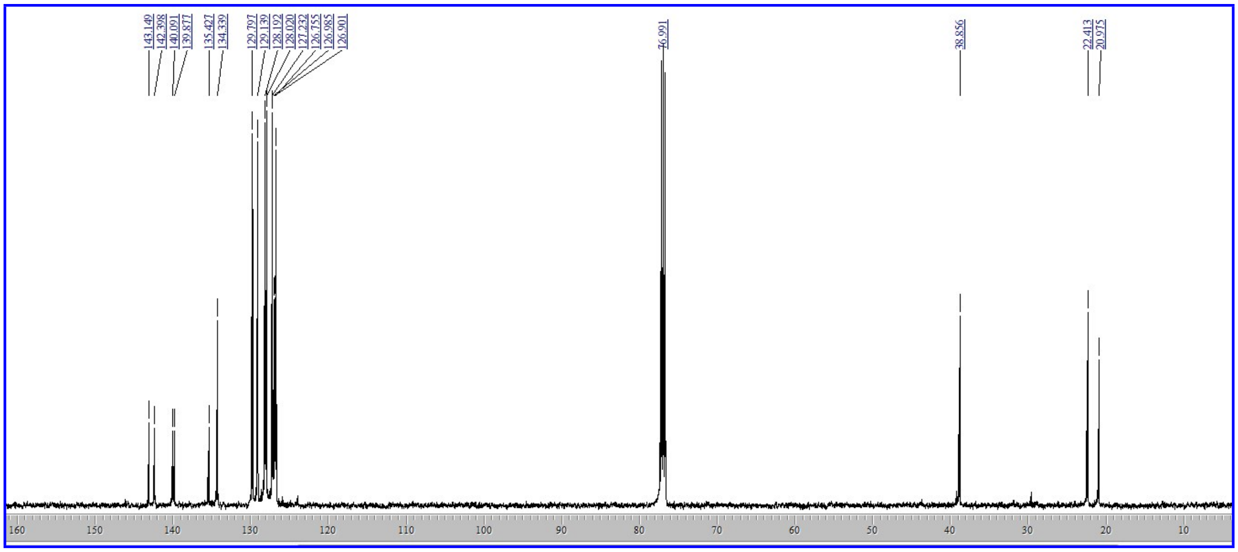
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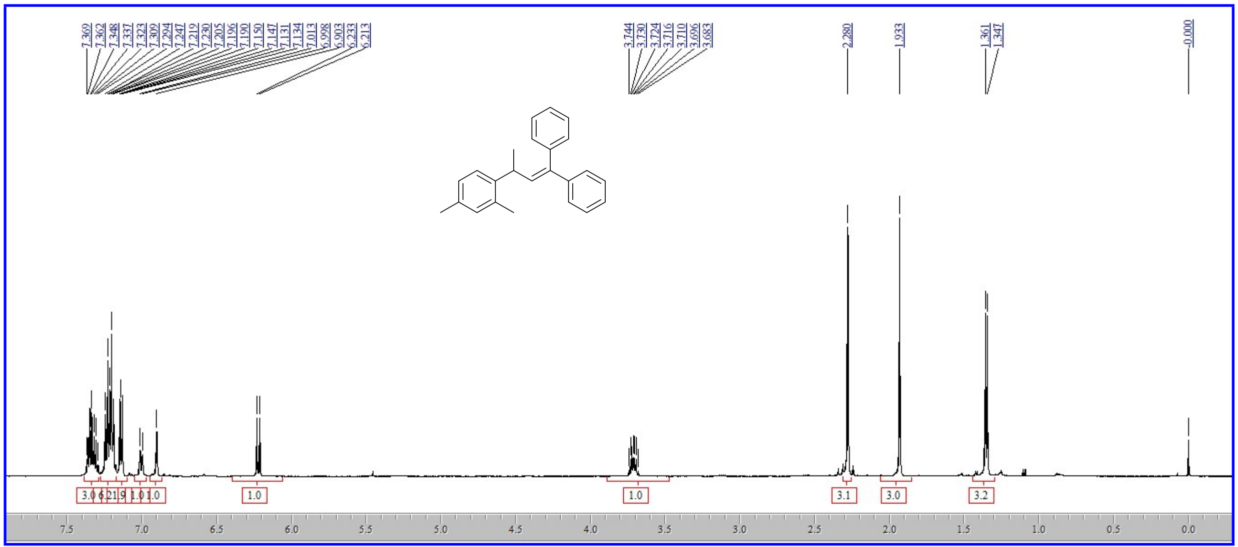
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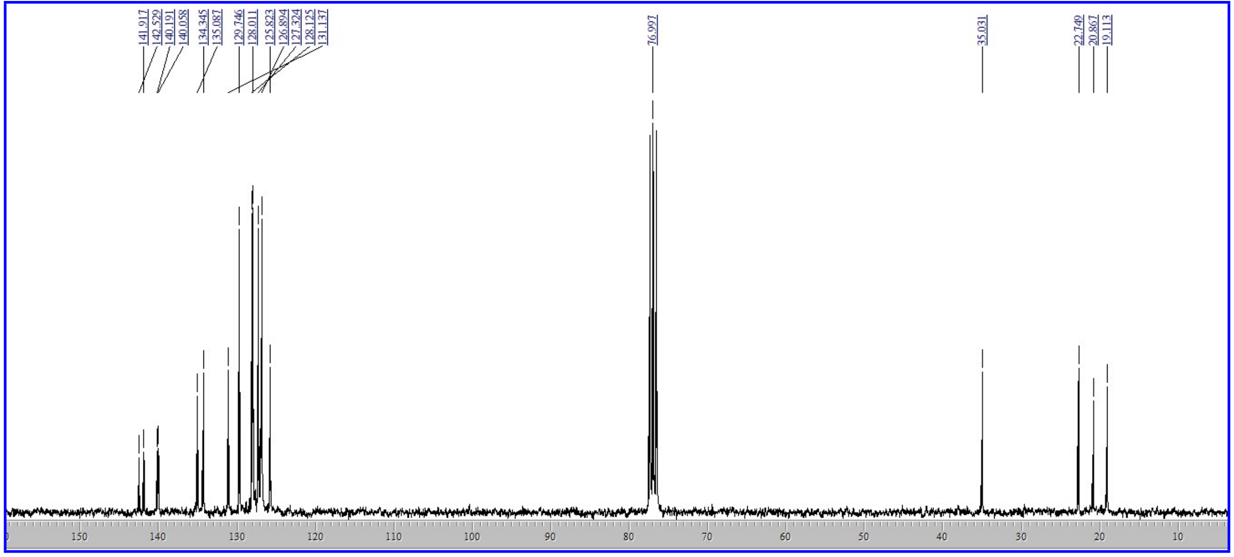
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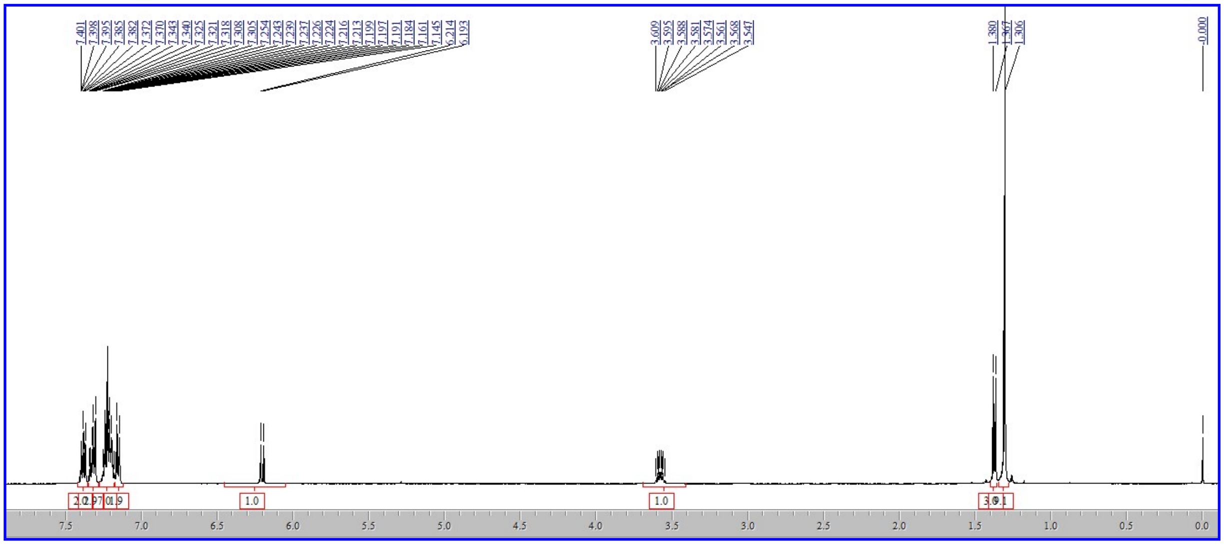
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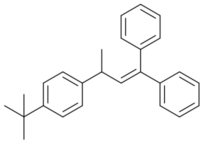

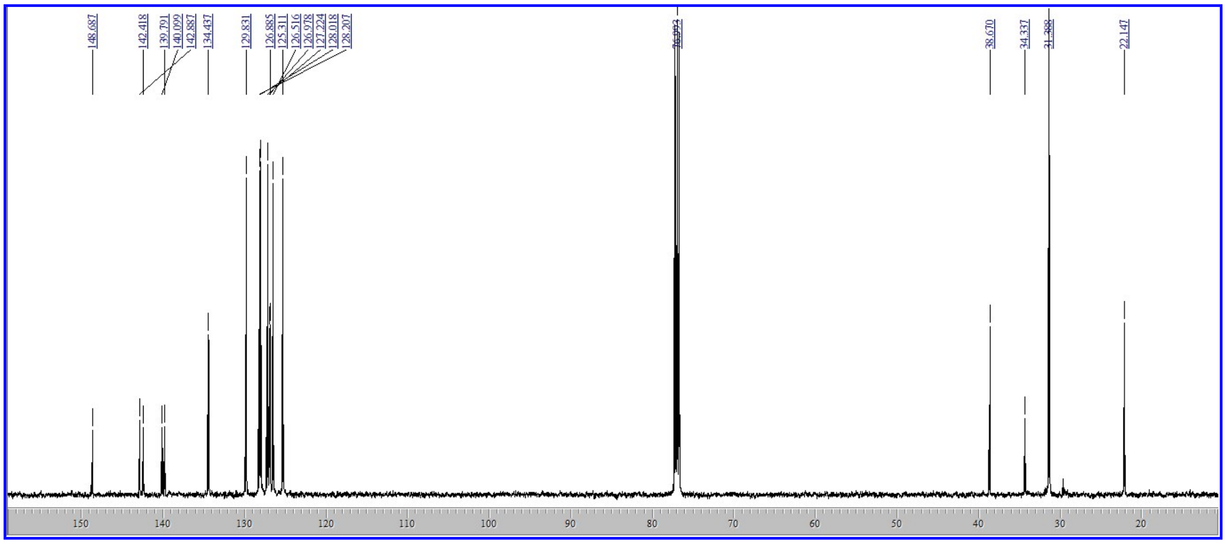
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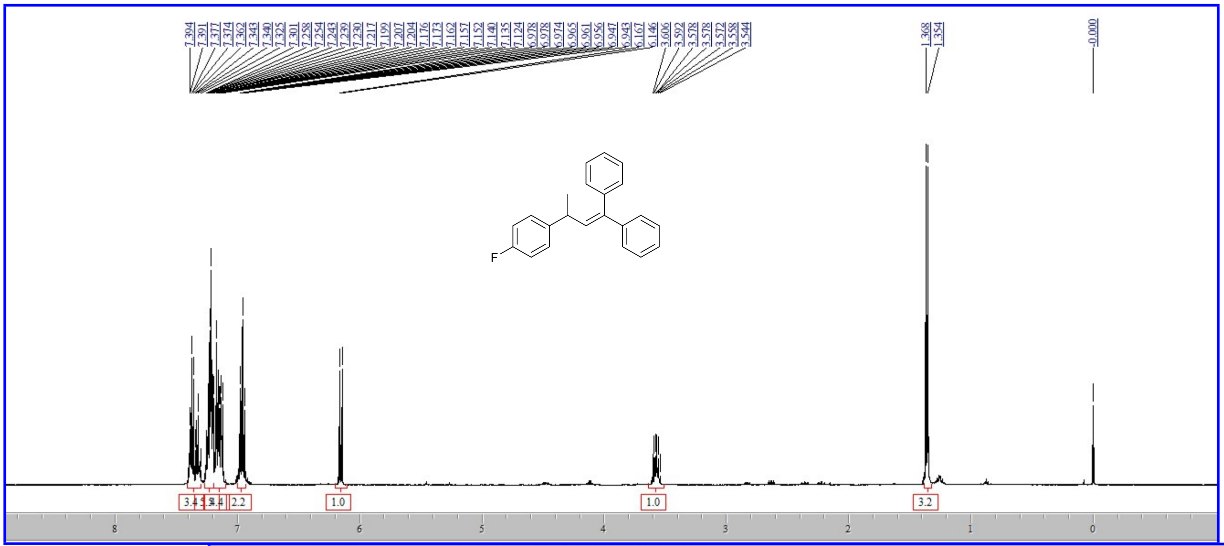
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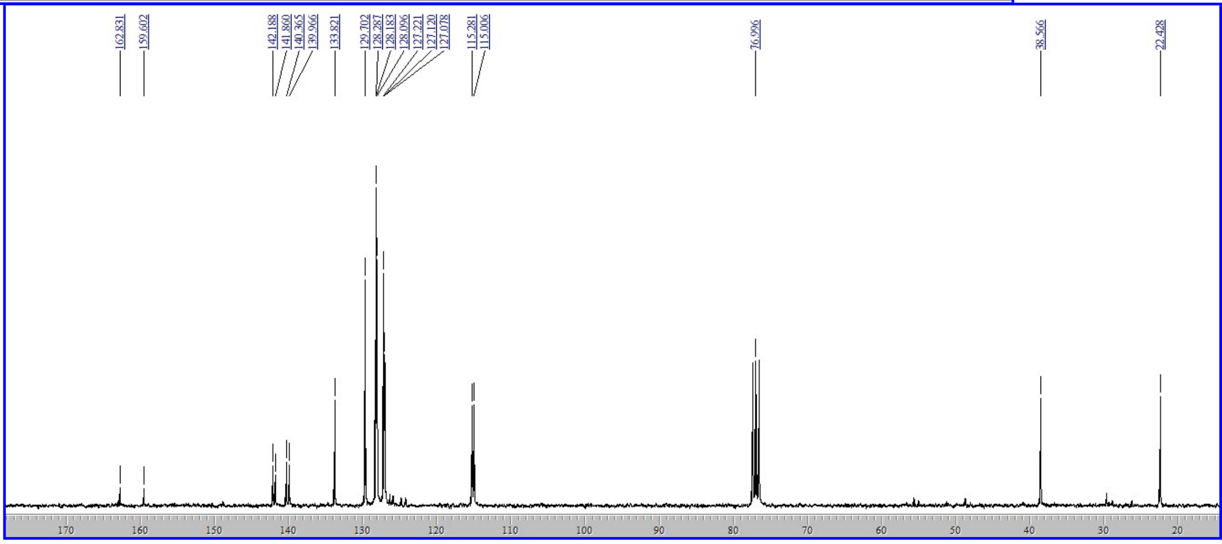
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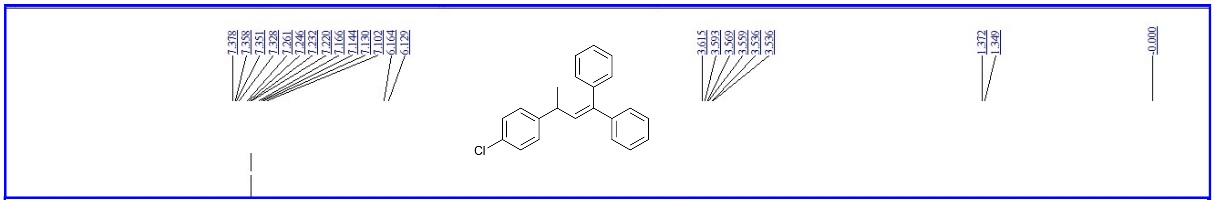
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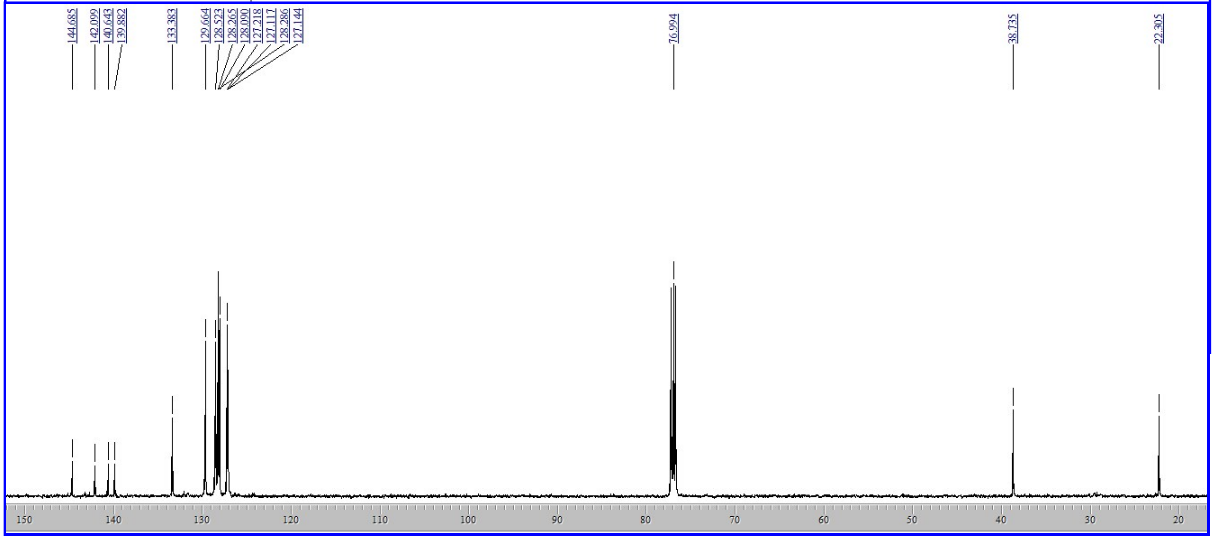
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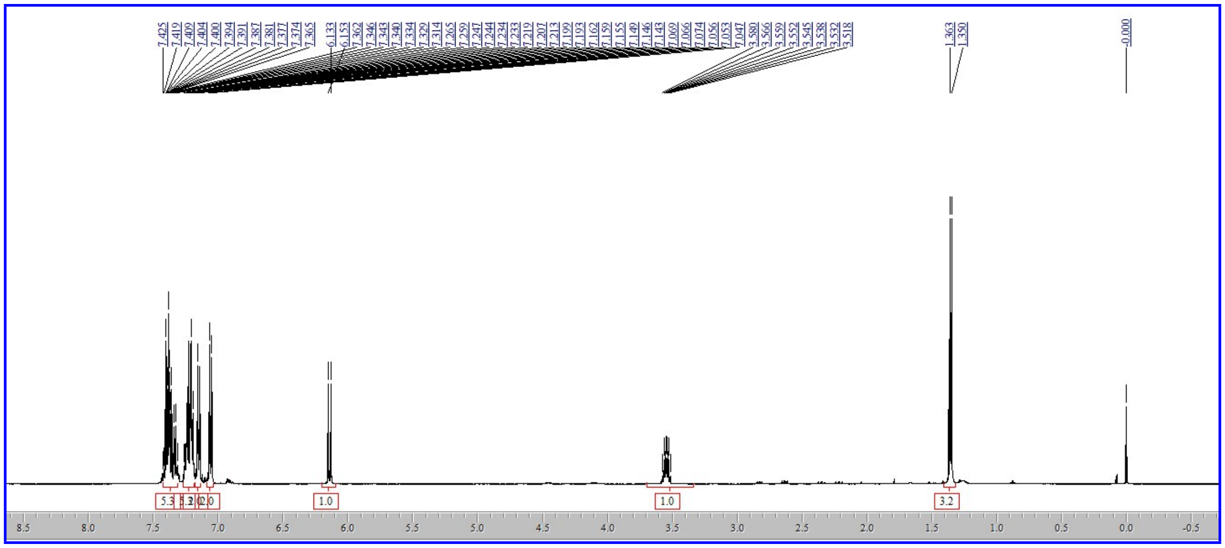

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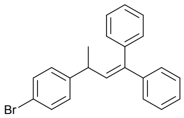
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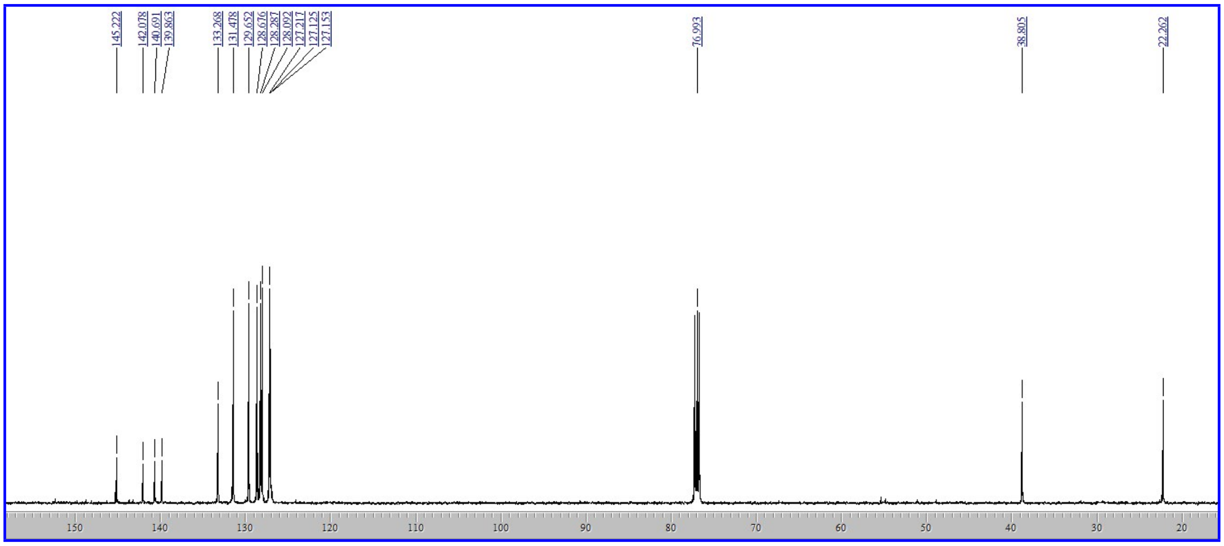
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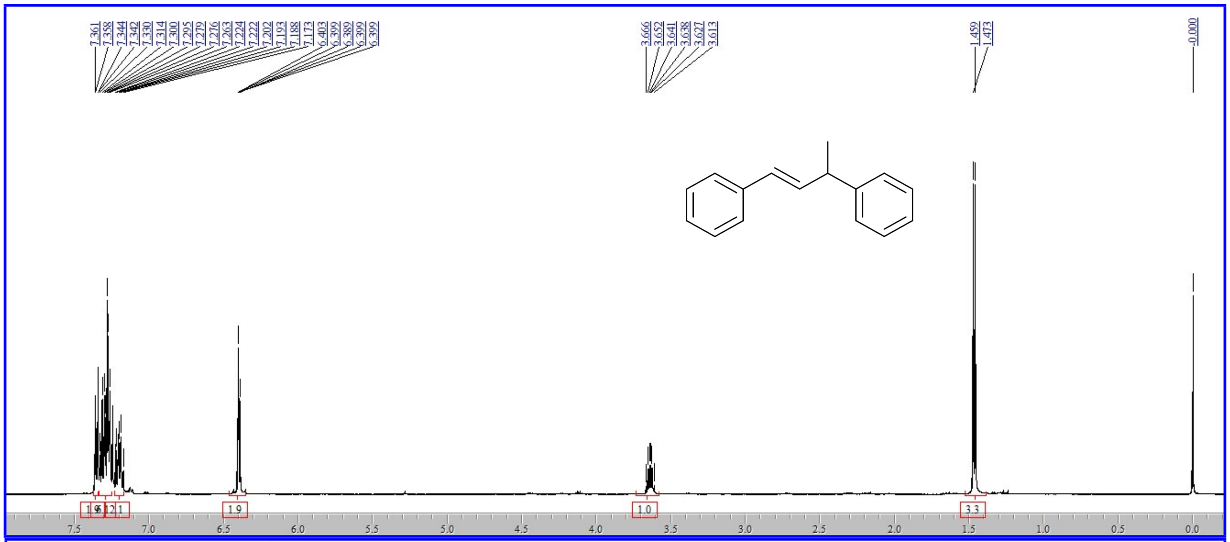
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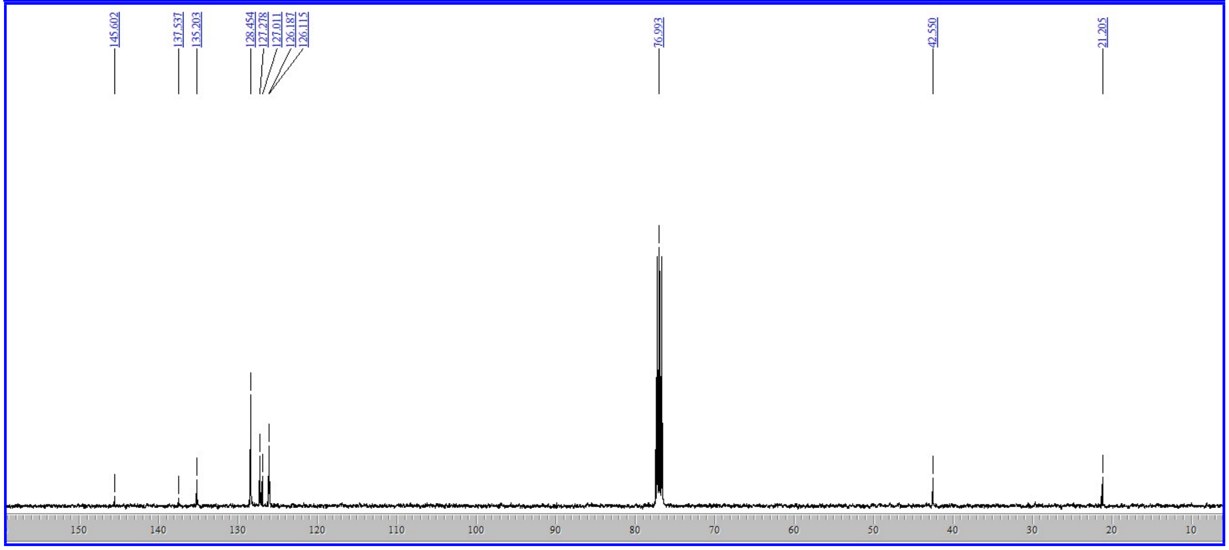
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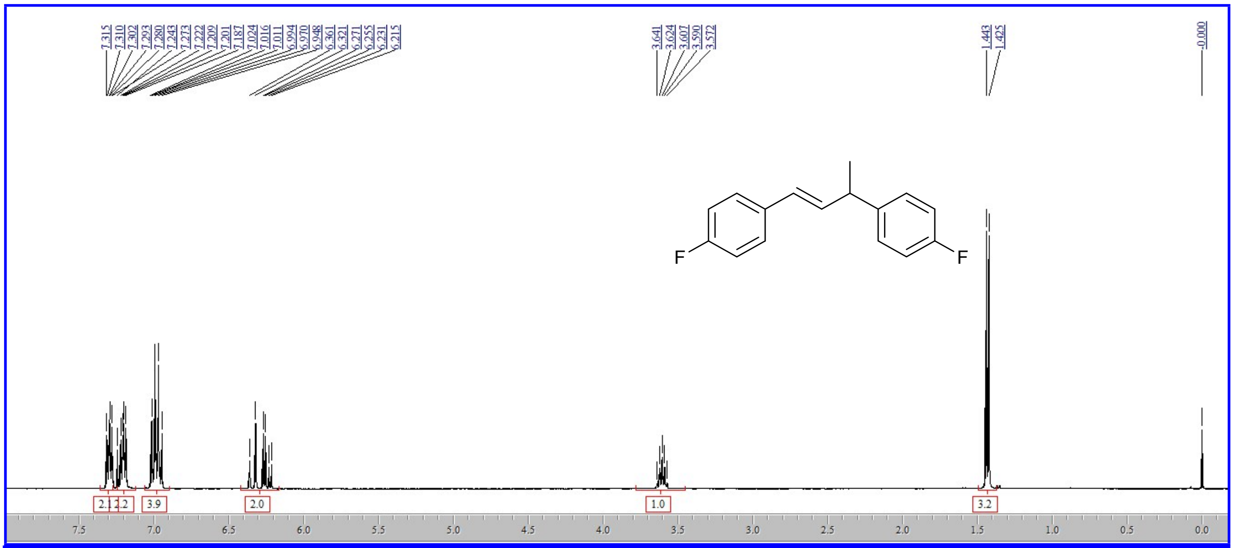
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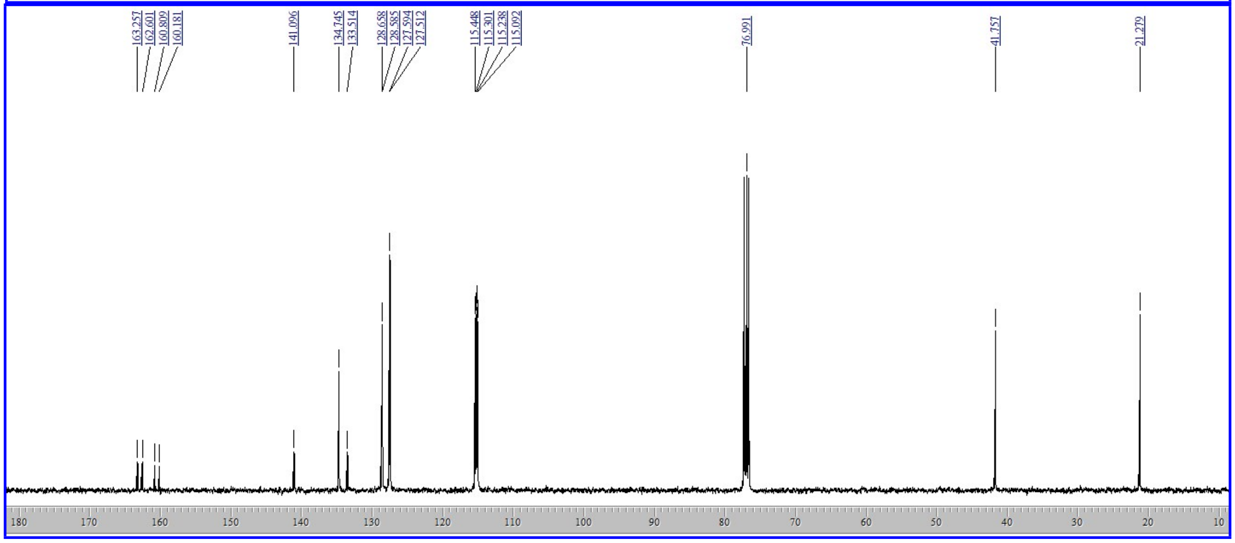
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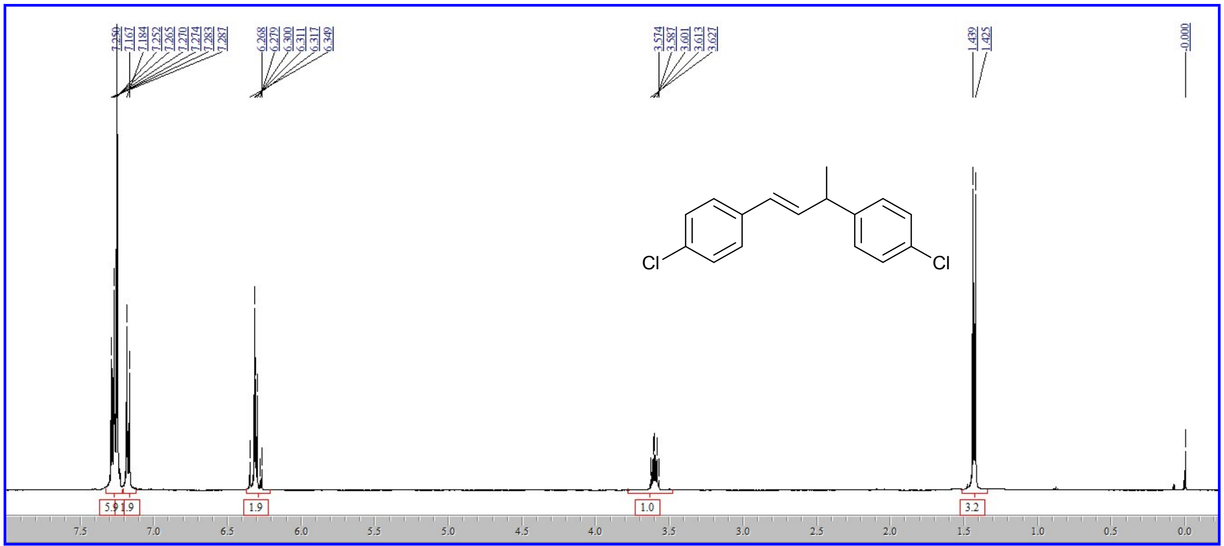
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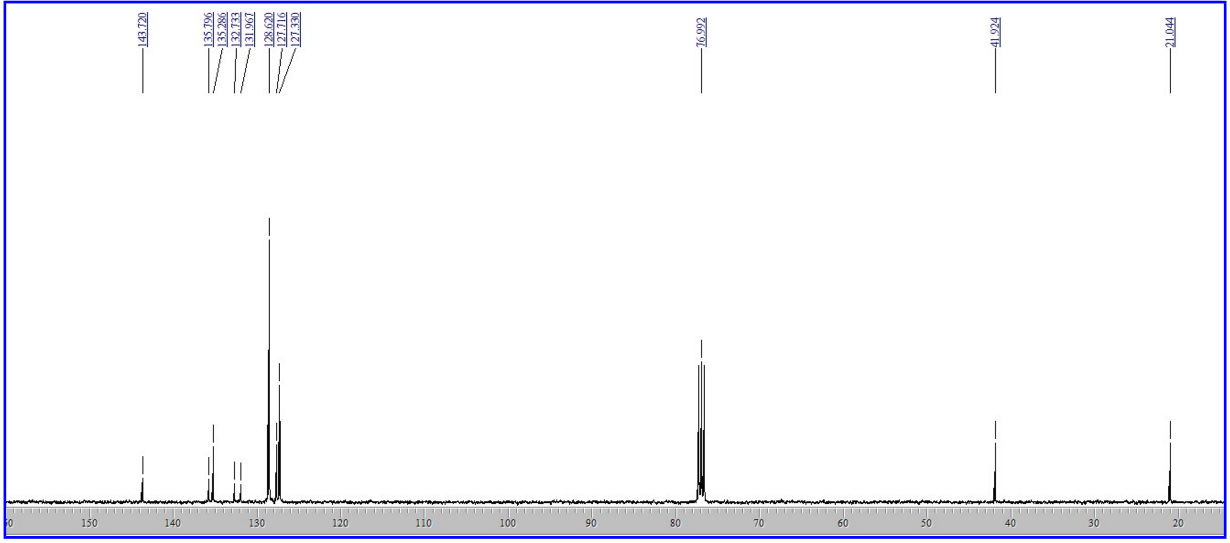
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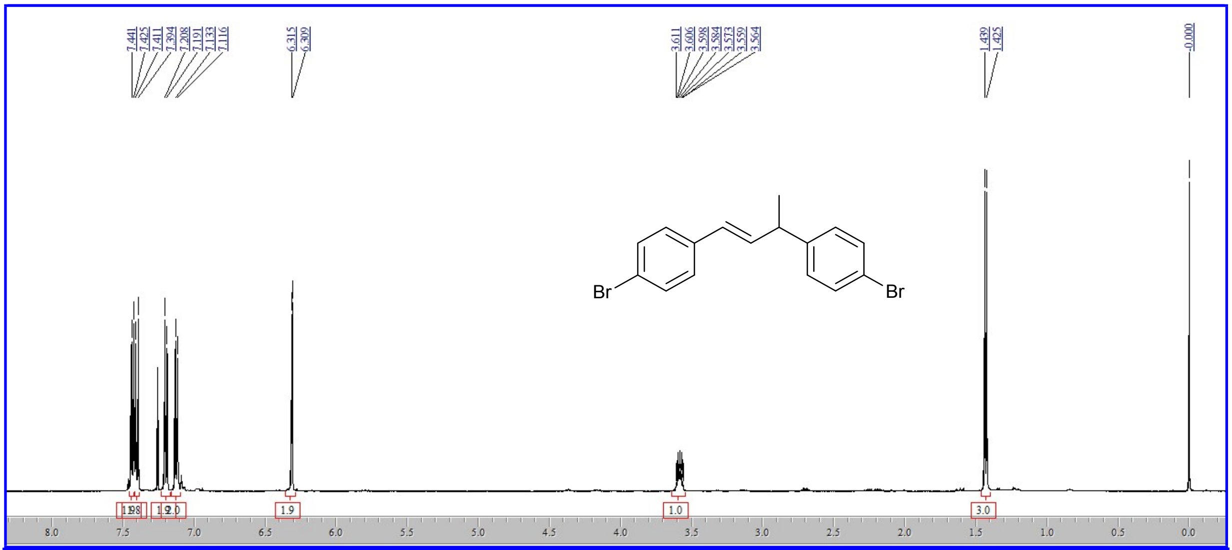

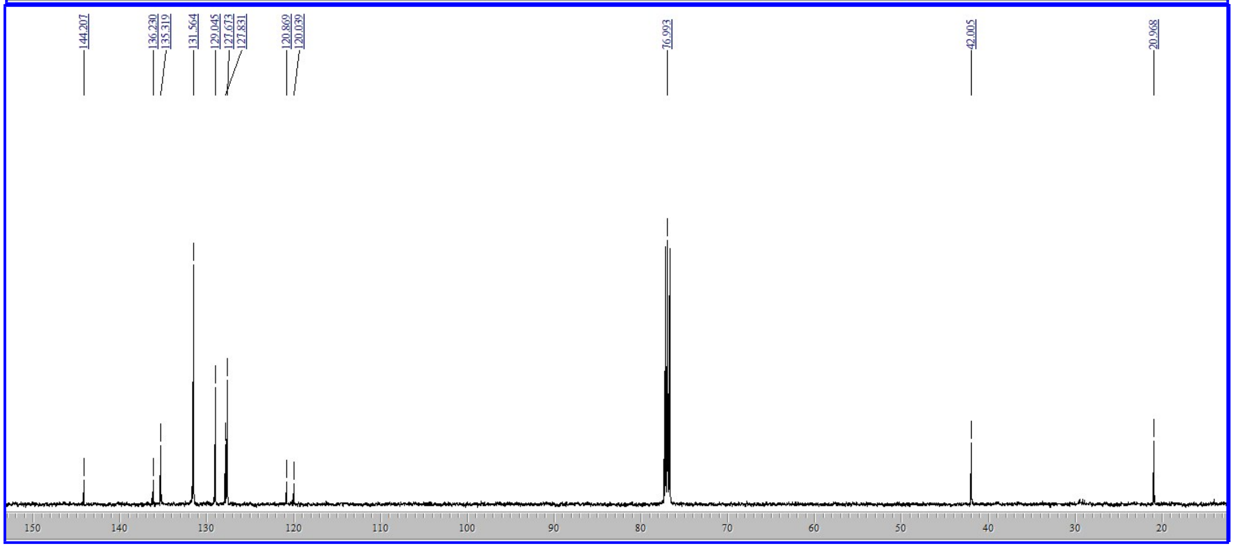

Notes and references

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2. J. H. Choi, J. K. Kwon, T. V. Rajanbabu and H. J. Lim, *Adv. Synth. Catal.,* 2013, **355**, 3633.
3. H. J. Ahn, H. C. Choi, K. W. Park, S. B. Kim and Y. E. Sung, J. Phys. Chem. B, 2004, **108**, 9815.