Supplementary Material (ESI) for Chemical Communications

Thermodynamic- and Kinetic-Controlled Friedel-Crafts Alkenylation of Arenes with Alkynes using an Acidic Fluoroantimonate(V) Ionic Liquid as Catalyst

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PART 1: Experimental Procedures and Spectroscopic Data

General Remarks. All reactions were performed in argon atmosphere using standard Schlenk techniques. Chromatographic purification of products was carried out by flash chromatography using Merck silica gel 60 (230-400 mesh). Thin layer chromatography was carried out on Merck silica gel 60F plates. 1H NMR (300 MHz), 13C NMR (75 MHz) and 19F NMR (282 MHz) were recorded on Varian 300 spectrometers using TMS as an internal standard for 1H and 13C NMR or using CFCl3 as an external standard for 19F NMR. GC-MS analysis was performed using GC/MSD; Varian 4000. Ionic liquid, [bmim][SbF6], was purchased from C-Tri Co., Ltd., Korea, www.c-tri.co.kr and used without further purification. It was nearly chloride-free (<10 ppm) and its water content was <50 ppm (determined by Karl-Fisher titration). Other organic solvents were dried (CaH2 or Na) and distilled under argon atmosphere prior to use. All other chemicals were obtained from commercial sources and used without further purification. The stereochemistry of all adducts were assigned by comparison with literature NMR spectroscopic data.[a) C. Jia, D. Piao, J. Oyamada, W. Lu, T. Kitamura and Y. Fujiwara Science, 2000, 287, 1992-1995; b) C. Jia, W. Lu, J. Oyamada, T. Kitamura, K. Matsuda, M. Irie and Y. Fujiwara, J. Am. Chem. Soc., 2000, 122, 7252-7263; c) C. Jia, T. Kitamura and Y. Fujiwara, Acc. Chem. Res., 2001, 34, 633-639; d) M.T. Reetz and K. Sommer, Eur. J. Org. Chem., 2003, 3485-3496; e) Z. Shi and C. He, J. Org. Chem., 2004, 69, 3669-3671; f) M. S. Viciu, E. D. Stevens, J. L. Petersen and S. P. Nolan, Organometallics, 2004, 23, 3752] In case of new and uncharacterized compounds, E/Z-configuration was established on the basis of 1D differential NOE experiments.

Typical Procedure for the Preparation of 1

The superacidic fluoroantimonate ionic liquid (IL), [bmim][SbF6]11 (1), was prepared by mixing [bmim][SbF6] (16.3 g, 46.3 mmol) and SbF3 (10 g, 46.3 mmol) under an Ar atmosphere. SbF3 was transferred to the dried [bmim][SbF6] under Ar atmosphere over 10 min at 0 °C, affording the pale-yellow liquid. However, the color of 1 changes from pale-yellow to violet with time. Thus, the direct use of freshly prepared 1 is advisable.
Freshly prepared 1

After 3 weeks

The resulting superacidic fluoroantimonate IL 1 was verified by different spectroscopic methods such as \(^1\)H-, \(^{13}\)C- and \(^{19}\)F-NMR and FAB-MS (Note: During NMR experiment, the d\(_8\)-THF solvent used was fast polymerized due to the strong acidity of the catalyst. Therefore, quick NMR experiment was performed (within 10 min)). FAB-MS analysis showed that mainly SbF\(_6^-\) and Sb\(_2\)F\(_{11}^-\) anions exist in the acidic IL 1. The Sb\(_3\)F\(_{16}^-\) anion was observed in a trace of amount.

\(^1\)H NMR (300 MHz, d\(_8\)-THF) \(\delta\) 1.99 1.12 (t, \(J = 6.0\) Hz, 3H), 1.53 (m, \(J = 6.0\) Hz, 2H), 2.03 (m, \(J = 6.0\) Hz, 2H), 4.07 (s, 3H), 4.36 (t, \(J = 6.0\) Hz, 2H), 7.67 (s, 1H), 7.71 (s, 1H), 8.85 (s, 1H); \(^{13}\)C NMR (75 MHz, d\(_8\)-THF) \(\delta\) 14.09, 20.47, 33.06, 36.65, 50.57, 123.46, 124.86, 137.55; \(^{19}\)F NMR (282 MHz, d\(_8\)-THF, CFCl\(_3\) as external standard) \(\delta\) -122.4 ppm (sextet, \(J_{(F-Sb}(I=5/2)\) = 1954 Hz, octet, \(J_{(F-Sb}(I=7/2)\) = 1039 Hz)

FAB-MS (the analysis was proceeded for anionic species without using any external matrix): m/z = 234.8 (100 %) and 236.8 (74 %) for [SbF\(_6^-\)] anion; 428.8 (67 %), 430.7 (100 %) and 432.8 (37 %) for [Sb\(_2\)F\(_6\)O\(^-\)] which might be formed due to the non-anhydrous analysis condition; 450.8 (67 %), 452.8 (100 %) and 454.8 (37 %) for [Sb\(_2\)F\(_{11}^-\)] anion.

**Typical Procedure for Thermodynamically Controlled Hydroarylations of Alkynes (Table 2)**

**Liquid Arenes (entry 5):** Under an Ar atmosphere, 1-phenyl-1-propyne (116 mg, 1 mmol) was added to a mixture of p-xylene (6 mL) and [bmim][Sb\(_2\)F\(_{11}^-\)] (29 mg, 0.05 mmol). The mixture was stirred at 90 °C until the disappearance of alkyne, as monitored by TLC or GC. After cooling to RT, the reaction mixture was poured into a saturated NaCl aqueous solution and extracted with ethyl acetate. The organic layer was washed with saturated NaCl aqueous solution, and dried over anhydrous MgSO\(_4\). The solvent was removed in a vacuum, and the residue was purified by flash column chromatography on silica (hexane) to give 198 mg (89 %) of pure 1-phenyl-1-(p-xylyl)-1-propene in E/Z ratio of 7/93 as a white solid.

**Solid Arenes (entry 13):** Under an Ar atmosphere, 3-butyne-2-one (68 mg, 1 mmol) was added to a mixture of pentamethylbenzene (148 mg, 1 mmol) in dichloroethane (4 mL) and [bmim][Sb\(_2\)F\(_{11}^-\)] (29 mg, 0.05 mmol). The reaction mixture was stirred until the disappearance of alkyne, as monitored by TLC or GC. After cooling to RT, the reaction mixture was poured into a saturated NaCl aqueous solution and extracted with ethyl acetate. The organic layer was washed with saturated NaCl aqueous solution, and dried over anhydrous MgSO\(_4\). The solvent was removed in a vacuum,
and the residue was purified by flash column chromatography on silica (hexane) to give 141 mg (65 %) of pure 4-(pentamethylphenyl)-3-buten-2-one in E/Z ratio of 94/6.

Typical Procedure for Kinetically Controlled Hydroarylations of Alkynes (Table 3)

**Entry 5:** Under an Ar atmosphere, 1,2-diphenylacetylene (178.2 mg, 1 mmol) was added to a mixture of pentamethylbenzene (296 mg, 2 mmol) and [bmim][Sb_{2}F_{11}] (118 mg, 0.2 mmol) in CH_{2}Cl_{2} (2 mL) at -25 °C. The mixture was stirred at -25 °C until the disappearance of alkyne, as monitored by TLC or GC. A mixture of saturated NaCl aqueous solution and pyridine was poured into the reaction mixture and the organic phase was extracted with ethyl acetate. The organic layer was again washed with saturated NaCl aqueous solution, and dried over anhydrous MgSO_{4}. The solvent was removed in a vacuum, and the residue was purified by flash column chromatography on silica (hexane) to give 284 mg (87 %) of pure (E)-1,2-diphenyl-1-pentamethylphenylethane in E/Z ratio of 91/9.

*Detailed experimental conditions in Table 3*

The kinetically controlled hydroarylation reactions for entry 1-3 were carried out with an alkyne (1 mmol), an arene (3.6 mmol), and 1 (20 mol %). 1 mmol and 2 mmol arene was used for entry 4 and 5, respectively. For all the kinetically controlled hydroarylation reactions, CH_{2}Cl_{2} as a cosolvent was used. For example, 2 mL CH_{2}Cl_{2} was used for entries 1, 4 and 5, and 0.2 mL for entry 2 and 0.5 ml for entry 3.

Spectroscopic Data for the Products in Table 1

1-(p-Chlorophenyl)-1-(p-xylyl)ethene (entry 5): ¹H NMR (300 MHz, CDCl_{3}) δ 1.99 (s, 3H), 2.33 (s, 3H), 5.19 (d, J = 1.2 Hz, 1H), 5.71 (d, J = 1.2 Hz, 1H), 7.01 – 7.25 (m, 7H); ¹³C NMR (75 MHz, CDCl_{3}) δ 19.99, 21.31, 115.52, 128.22, 128.83, 128.88, 130.50, 131.02, 133.78, 135.62, 141.35, 148.94.

1-(p-Trifluoromethylphenyl)-1-(p-xylyl)ethane (entry 9): ¹H NMR (300 MHz, CDCl_{3}) δ 1.98 (s, 3H), 2.34 (s, 3H), 5.38 (d, J = 1.1 Hz, 1H), 5.80 (d, J = 1.1 Hz, 1H), 7.02 – 7.58 (m, 7H); ¹³C NMR (75 MHz, CDCl_{3}) δ 20.10, 21.38, 116.82, 124.65 (q, J(C-C-C-F) = 3.8 Hz), 124.67 (q, J(C-F) = 272.4 Hz), 124.67 (q, J(C-C-C-F) = 3.8 Hz), 129.12, 129.28, 130.39, 130.69, 131.16, 131.31 (q, J(C-C-C-F) = 3.8 Hz), 133.26, 135.83, 140.96, 142.05, 149.00.

Spectroscopic Data for the Products in Table 2

1,1-Diphenylethene (entry 1): ¹H NMR (300 MHz, CDCl_{3}) δ 5.45 (s, 2H), 7.29-7.35 (m, 10H); ¹³C NMR (75.5 MHz, CDCl_{3}) δ 114.76, 128.16, 128.61, 128.72, 141.92, 150.48.

1-(p-Chlorophenyl)-1-phenylethene (entry 2): ¹H NMR (300 MHz, CDCl_{3}) δ 5.44 (d, J = 0.9 Hz, 1H), 5.46 (d, J = 0.9 Hz, 1H), 7.20-7.42 (m, 9H); ¹³C NMR (75.5 MHz, CDCl_{3}) δ 114.93, 128.15, 128.41, 128.49, 128.57, 129.78, 133.80, 140.16, 141.23, 149.19.
1-Phenyl-1-(p-Trifluoromethylphenyl)ethene (entry 3): $^1\text{H}$ NMR (300 MHz, CDCl$_3$) $\delta$ 5.51 (d, $J = 0.9$ Hz, 1H), 5.56 (d, $J = 0.9$ Hz, 1H), 7.27-7.64 (m, 9H); $^{13}\text{C}$ NMR (75 MHz, CDCl$_3$) $\delta$ 116.2, 124.4, 125.4 (q, $^3J$(C-C-C-F) = 3.8 Hz), 128.33, 128.61, 128.79, 129.9 (q, $^2J$(C-C-F) = 32.2 Hz), 140.8, 145.3 (q, $^4J$(C-C-C-C-F) = 1.2 Hz), 149.1 (q, $^1J$(C-F) = 271.0 Hz).

1-Phenyl-1-(p-xylyl)ethene (entry 4): $^1\text{H}$ NMR (300 MHz, CDCl$_3$) $\delta$ 1.99 (s, 3H), 2.30 (s, 3H), 5.16 (d, $J = 1.4$ Hz, 1H), 5.73 (d, $J = 1.4$ Hz, 1H), 7.04-7.28 (m, 8H); $^{13}\text{C}$ NMR (75 MHz, CDCl$_3$) $\delta$ 20.12, 21.42, 115.13, 127.00, 128.01, 128.71, 128.81, 128.14, 128.51, 129.76, 130.21, 130.92, 133.57, 136.07, 137.65, 139.76, 141.65, 142.74.

(Z)-1-Phenyl-1-(p-xylyl)-1-propene (entry 5): $^1\text{H}$ NMR (300 MHz, CDCl$_3$) $\delta$ 1.59 (d, $J = 9.0$ Hz, 3H), 2.03 (s, 3H), 2.30 (s, 3H), 6.27 (q, $J = 9.0$ Hz, 1H), 6.82-7.35 (m, 7H); $^{13}\text{C}$ NMR (75 MHz, CDCl$_3$) $\delta$ 15.78, 19.36, 21.32, 123.92, 126.40, 128.14, 128.51, 130.49, 131.17, 133.43, 135.53, 139.41, 141.83.

(Z)-1,2-Diphenyl-1-(p-xylyl)ethene (entry 6): $^1\text{H}$ NMR (300 MHz, CDCl$_3$) $\delta$ 1.99 (s, 3H), 2.27 (s, 3H), 6.94-7.32 (m, 14H); $^{13}\text{C}$ NMR (75 MHz, CDCl$_3$) $\delta$ 19.43, 21.31, 126.91, 127.16, 127.61, 128.28, 128.40, 128.63, 128.68, 129.28, 130.68, 130.77, 133.57, 136.07, 139.76, 141.65, 142.74.

1-Mesityl-1-phenylethene (entry 7): $^1\text{H}$ NMR (300 MHz, CDCl$_3$) $\delta$ 2.11 (s, 6H), 2.31 (s, 3H), 5.09 (d, $J = 1.4$ Hz, 1H), 5.95 (d, $J = 1.4$ Hz, 1H), 6.90 (s, 2H), 6.90 (s, 2H), 7.19 – 7.28 (m, 5H); $^{13}\text{C}$ NMR (75 MHz, CDCl$_3$) $\delta$ 20.1, 21.1, 114.5, 125.8, 127.5, 128.1, 128.4, 133.4, 136.1, 136.4, 138.2, 139.6, 146.9.

1-(p-Chlorophenyl)-1-mesitylethene (entry 8): $^1\text{H}$ NMR (300 MHz, CDCl$_3$) $\delta$ 2.09 (s, 6H), 2.31 (s, 3H), 5.10 (d, $J = 1.2$ Hz, 1H), 5.93 (d, $J = 1.2$ Hz, 1H), 6.90 (s, 2H), 6.90 (s, 2H), 7.17 – 7.24 (m, 4H); $^{13}\text{C}$ NMR (75 MHz, CDCl$_3$) $\delta$ 20.0, 21.0, 115.0, 127.1, 128.2, 128.6, 133.4, 136.0, 136.7, 138.6, 145.8.

1-Mesityl-1-(p-trifluoromethylphenyl)ethene (entry 9): $^1\text{H}$ NMR (300 MHz, CDCl$_3$) $\delta$ 2.09 (s, 6H), 2.31 (s, 3H), 5.21 (d, $J = 1.2$ Hz, 1H), 6.04 (d, $J = 1.2$ Hz, 1H), 6.92 (s, 2H), 7.32 – 7.54 (m, 4H); $^{13}\text{C}$ NMR (75 MHz, CDCl$_3$) $\delta$ 20.39, 21.52, 117.1 (q, $^1J$(C-F) = 271.0 Hz), 124.5 (q, $^3J$(C-C-C-F) = 3.8 Hz), 125.7 (q, $^3J$(C-C-F) = 32.2 Hz), 136.3, 137.2, 137.5, 143.3 (q, $^4J$(C-C-C-C-F) = 1.2 Hz), 146.0.

(E)-4-Mesityl-3-buten-2-one (entry 10): $^1\text{H}$ NMR (300 MHz, CDCl$_3$) $\delta$ 2.29 (s, 3H, CH$_3$), 2.33 (s, 6H, 2CH$_3$), 2.38 (s, 3H, CH$_3$), 6.33 (d, $J = 16.5$ Hz, 1H), 6.90 (s, 2H), 7.67 (d, $J = 16.5$ Hz, 1H); $^{13}\text{C}$ NMR (75MHz, CDCl$_3$) $\delta$ 20.0, 21.31, 21.35, 27.70, 129.49, 131.09, 132.62, 137.04, 138.79, 142.26, 198.80.

(Z)-1-Mesityl -1-phenyl-1-propene (entry 11): $^1\text{H}$ NMR (300 MHz, CDCl$_3$) $\delta$ 1.53 (d, $J = 6.0$ Hz, 3H), 2.04 (s, 6H), 2.32 (s, 3H), 6.36 (q, $J = 6.0$ Hz, 1H), 6.91 (s, 2H), 7.11 – 7.32 (m, 5H); $^{13}\text{C}$ NMR (75 MHz) $\delta$ 15.35, 20.05, 21.44, 123.67, 125.85, 126.91, 128.46, 128.64, 135.90, 136.54, 136.57, 140.16, 140.77.

(Z)-1,2-Diphenyl-1-mesitylethene (entry 12): $^1\text{H}$ NMR (300 MHz, CDCl$_3$) $\delta$ 2.00 (s, 6H), 2.34 (s, 3H), 6.87 – 7.34 (m, 13H); $^{13}\text{C}$ NMR (75MHz, CDCl$_3$) $\delta$ 20.05, 21.45,
126.24, 127.19, 127.51, 128.30, 128.46, 128.66, 128.69, 128.95, 136.13, 136.27, 137.11, 137.71, 140.03, 141.75.

**(E)-4-(Pentamethylphenyl)-3-buten-2-one (entry 13):** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.22-2.23 (s, 12H), 2.26 (s, 3H), 2.39 (s, 3H), 6.15 (d, $J=16.5$ Hz, 1H), 7.73(d, $J=16.5$ Hz, 1H); $^{13}$C NMR (75MHz, CDCl3) $\delta$ 16.43, 16.85, 17.88, 27.33, 131.03, 132.57, 132.79, 133.80, 135.27, 145.05, 198.25.

1-(p-Chlorotoluyl)-1-phenylpropene (entry 14): The reaction gave two sets of total 4 isomers where, the top spot contain the mixture of two inseparable ortho (to methyl group)-Z and $o$-E isomers and the bottom spot contain the mixture of two inseparable meta (to methyl group)-Z and $m$-E isomers. The isomers were identified by NOE experiment and the ratio was determined by $^1$H NMR analysis.

**Top spot:** $E$/Z-mixture of ortho-isomers to the methyl group of p-chlorotoluene (Rf value on TLC in Hexane = 0.35).

![Chemical Structure](image)

**(Z)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene:** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.62 (d, $J=9.0$ Hz, 3H), 2.06 (s, 3H), 6.33 (q, $J=9.0$ Hz, 1H), 7.08-7.30 (m, 8H).

**(E)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene:** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.93 (d, $J=6.0$ Hz, 3H), 1.98 (s, 3H), 5.81(q, $J=6.0$ Hz, 1H), 7.08-7.30 (m, 8H).

$^{13}$C NMR (75 MHz, CDCl$_3$) of the top spot: $\delta$ 15.70, 19.20, 124.74, 126.26, 127.13, 127.42, 128.24, 128.57, 129.63, 130.05, 131.50, 131.62, 135.46, 140.61, 140.93, 141.24.

**Bottom spot:** $E$/Z-mixture of meta-isomers to the methyl group of p-chlorotoluene (Rf value on TLC in Hexane = 0.33).

![Chemical Structure](image)

**(Z)-1-(2-chloro-5-methylphenyl)-1-phenylpropene:** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.63 (d, $J=6.0$ Hz, 3H), 2.31 (s, 3H), 6.32 (q, $J=6.0$ Hz, 1H), 6.98-7.33 (m, 8H).

**(E)-1-(2-chloro-5-methylphenyl)-1-phenylpropene:** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.89 (d, $J=9.0$ Hz, 3H), 2.30 (s, 3H), 5.85 (q, $J=9.0$ Hz, 1H), 6.98-7.33 (m, 8H).

$^{13}$C NMR (75 MHz, CDCl$_3$) of the bottom spot: $\delta$ 15.77, 21.12, 125.62, 126.31, 126.37, 127.04, 128.07, 128.48, 128.60, 129.535, 129.544, 129.72, 131.11, 132.41, 136.82, 138.49, 139.83, 141.10.

1-(Chlorophenyl)-1-phenylpropene (entry 15): The reaction gave two sets of total 4 isomers where, the top spot contain the mixture of two inseparable $p$-Z and $p$-E
isomers and the bottom spot contain the mixture of two inseparable o-Z and o-E isomers. The o- and p-isomers were identified by comparing with standard samples prepared by literature method [Ref. Org. Lett. 2003, Vol.5, No. 20, 3641. J. Org. Chem. 1962, 2377] and their stereoisomer was identified by differential NOE experiments.

**Top spot:** E/Z-mixture of para-isomers (Rf value on TLC in Hexane = 0.3)

(Z)-1-(p-Chlorophenyl)-1-phenylpropene: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.76 ($d$, $J$ = 9.0 Hz, 3H), 6.15 ($q$, $J$ = 9.0 Hz, 1H), 7.1-7.40 (m, 9H).

(E)-1-(p-Chlorophenyl)-1-phenylpropene: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.76 ($d$, $J$ = 9.0 Hz, 3H), 6.18 ($q$, $J$ = 9.0 Hz, 1H), 7.1-7.40 (m, 9H).

$^{13}$C NMR (75 MHz, CDCl$_3$) of the top spot: $\delta$ 15.97, 15.99, 124.94, 124.97, 127.18, 127.29, 127.41, 128.40, 128.42, 128.50, 128.64, 128.70, 130.21, 131.69, 132.74, 132.94, 138.66, 139.74, 141.57, 141.63, 141.68, 142.76.

**Bottom spot:** E/Z-mixture of ortho-isomers (Rf value on TLC in Hexane = 0.27)

(Z)-1-(o-Chlorophenyl)-1-phenylpropene: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.92, ($d$, $J$ = 6.9 Hz, 3H), 6.33 ($q$, $J$ = 6.9 Hz, 1H), 7.1-7.40 (m, 9H).

(E)-1-(o-Chlorophenyl)-1-phenylpropene: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.92, ($d$, $J$ = 7.2 Hz, 3H), 5.87 ($q$, $J$ = 7.2 Hz, 1H), 7.1-7.40 (m, 9H).

Spectroscopic Data for the Products in Table 3

(E)-1,2-Diphenyl-1-(p-xylyl)ethene (entry 1): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.09 (s, 3H), 2.34 (s, 3H), 6.62 (s, 1H), 7.05-7.27 (m, 13H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 20.28, 21.19, 126.95, 127.31, 128.24, 128.36, 128.41, 129.66, 130.13, 130.16, 130.60, 131.10, 133.34, 135.24, 137.68, 140.52, 143.30, 144.07.

(E)-1-Mesityl -1-phenyl-1-propene (entry 2): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.98 (d, $J$ = 9.0 Hz, 3H), 2.15 (s, 6H), 2.27 (s, 3H), 6.63 (s, 1H), 6.86 (s, 2H), 7.14 – 7.30 (m, 5H); $^{13}$C NMR (75 MHz) $\delta$ 15.71, 20.76, 21.30, 126.53, 126.63, 128.09, 128.45, 129.41, 136.30, 136.61, 139.68, 139.74, 141.21.

(E)-1,2-Diphenyl-1-mesitylethene (entry 3): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.24 (s, 6H), 2.30 (s, 3H), 6.51 (s, 1H), 6.90 (s, 2H), 7.10–7.23 (m, 10H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 20.75, 21.36, 127.03, 127.28, 128.27, 128.40, 128.64, 129.56, 129.92, 130.59, 136.56, 136.82, 137.91, 139.51, 141.00, 141.03.
(E)-1-Pentamethylphenyl-1-phenyl-1-propene (entry 4): $^1$H NMR (300 MHz, CDCl$_3$) δ 1.99(d, $J$ = 7.2 Hz, 3H) 2.16 (s, 6H), 2.20 (s, 6H), 2.25 (s, 3H), 5.60 (q, $J$=7.2 Hz, 1H), 7.15-7.31(m, 5H); $^{13}$C NMR (75MHz, CDCl$_3$) δ 15.81, 16.95, 17.10, 18.43, 126.22, 126.53, 128.08, 129.44, 132.11, 132.59, 133.70, 140.12, 141.49, 141.85.

(E)-1,2-Diphenyl-1-pentamethylphenylethene (entry 5): $^1$H NMR (300 MHz, CDCl$_3$) δ 2.23(s, 6H), 2.27(m, 9H), 6.49(s, 1H), 7.10-7.25(m, 10H); $^{13}$C NMR (75MHz, CDCl$_3$) δ 16.90, 17.11, 18.38, 126.90, 127.15, 128.21, 128.36, 129.47, 129.92, 130.26, 131.88, 132.80, 134.14, 138.08, 139.89, 141.60, 142.79.
Part II: NMR and MS Spectra of Compounds and E/Z-Calculation by GC-MS

1. $^1$H, $^{13}$C, and $^{19}$F NMR and FAB-MS spectra of 1

\[ \underset{\text{N}}{\text{N}} \bigg\} \bigg\} \underset{\text{Sb}_2\text{F}_{11}^-}{\text{Sb}_2\text{F}_{11}^-} \]

$^1$H NMR Spectrum of 1 (300 MHz, $d_8$-THF)
During NMR analysis, the d$_8$-THF solvent was very fast polymerized because of very strong acidity of the catalyst [bmim]Sb$_n$F$_{5n+1}$ (n > 2) and we observed two type of THF peaks; a; carbon peaks of d$_8$-THF monomer as a NMR solvent, b; carbon peaks of d$_8$-THF polymerized by the strong acidity of 1.
$^{19}$F NMR Spectrum of 1 (288 MHz, d$_8$-THF)
FAB-MS Spectrum of 1

- $\text{SbF}_5^-$
- $\text{Sb}_2\text{F}_3\text{O}^-$
- $\text{Sb}_2\text{F}_7^-$
- $\text{SbF}_6^-$
- $\text{Sb}_2\text{F}_{11}^-$
2. GC-MS, $^1$H, $^{13}$C NMR and differential NOE spectra for Table 2.

Entry 5 in Table 2

(Z)-1-Phenyl-1-(p-xylyl)propene

**GC-MS Spectrum of 1-phenyl-1-(p-xylyl)propene**

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**MS of Z-Isomer**

**MS of E-Isomer**
$^1$H Spectrum of 1-phenyl-1-(p-xylyl)propene

$^{13}$C Spectrum of 1-phenyl-1-(p-xylyl)propene
Entry 6 in Table 2

(Z)-1,2-Diphenyl-1-(p-xylyl)ethane

GC-MS Spectrum of 1,2-diphenyl-1-(p-xylyl)ethane
$^1$H NMR Spectrum of 1,2-diphenyl-1-(p-xylyl)ethane

$^{13}$C NMR Spectrum of 1,2-diphenyl-1-(p-xylyl)ethane
Entry 10 in Table 2

(E)-4-Mesityl-3-buten-2-one

GC-MS Spectrum of 4-mesityl-3-buten-2-one

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<td>776130</td>
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<td>18.960</td>
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<td>3.967E7</td>
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[Diagram of GC-MS spectrum with peaks labeled Z-isomer and E-isomer]
$^1$H NMR Spectrum of 4-mesityl-3-buten-2-one

$^{13}$C NMR Spectrum of 4-mesityl-3-buten-2-one
Entry 11 in Table 2

(Z)-1-Mesityl -1-phenylpropene

GC-MS Spectrum of 1-mesityl -1-phenylpropene
$^1$H NMR Spectrum of 1-mesityl-1-phenylpropene

$^{13}$C NMR Spectrum of 1-mesityl-1-phenylpropene
Differential NOE spectrum of (Z)-1-Mesityl-1-phenylpropene

b: 0.31% Enhanced

c: 3.87% Enhanced
Entry 12 in table 2

(Z)-1,2-Diphenyl-1-mesitylethene

GC-MS Spectrum of 1,2-diphenyl-1-mesitylethene

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<thead>
<tr>
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<td>40.696</td>
<td>R/C</td>
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<td>97.70</td>
<td>1.109E6</td>
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<tr>
<td>40.849</td>
<td>R/C</td>
<td>106277</td>
<td>2.30</td>
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</table>
$^1$H NMR Spectrum of 1,2-diphenyl-1-mesitylethene

$^{13}$C NMR Spectrum of 1,2-diphenyl-1-mesitylethene
Entry 13 in Table 2

\[ \text{COMe} \]

\((E)-4-(\text{Pentamethylphenyl})-3\text{-buten-2-one}\)

GC-MS Spectrum of 4-(pentamethylphenyl)-3-butene-2-one

<table>
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<tr>
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<td>22.504</td>
<td>RIC</td>
<td>2.18E7</td>
<td>94.02</td>
<td>4.081E5</td>
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$^1$H NMR Spectrum of 4-(pentamethylphenyl)-3-buten-2-one

$^{13}$C NMR Spectrum of 4-(pentamethylphenyl)-3-buten-2-one
Differential NOE spectrum of (E)-4-(Pentamethylphenyl)-3-buten-2-one

![Differential NOE spectrum of (E)-4-(Pentamethylphenyl)-3-buten-2-one](image_url)

- b: 0.34% Enhanced
- c: 0.57% Enhanced
Entry 14 in Table 2
The reaction gave two separable mixtures including ortho- and meta-regioisomers to the methyl group of p-chlorotoluene and the corresponding E/Z isomers. Each isomers were identified by NOE experiment and the ratio was determined by $^1$H NMR analysis.

- The first mixture: Rf value on TLC (Hexane) = 0.35

![Chemical structure of (Z)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene](image)

Exact Mass: 242.1
m/e: 242.1 (100.0%), 244.1 (33.5%), 243.1 (18.0%), 245.1 (5.8%)

(Z)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene

![Chemical structure of (E)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene](image)

Exact Mass: 242.1
m/e: 242.1 (100.0%), 244.1 (33.5%), 243.1 (18.0%), 245.1 (5.8%)

(E)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene
GC-MS Spectrum of 1-(2-methyl-5-chlorophenyl)-1-phenylpropene

From the first mixture
\(^1\)H NMR Spectrum of 1-(2-methyl-5-chlorophenyl)-1-phenylpropene

\(^{13}\)C NMR Spectrum of 1-(2-methyl-5-chlorophenyl)-1-phenylpropene
Differential NOE Spectrum of (Z)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene

- b: 0.54% Enhanced
- c: 4.23% Enhanced
- d: 1.14% Enhanced

- b: 0.62% Enhanced
- c: 3.63% Enhanced
Differential NOE Spectrum of (E)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene

b: 1.12% Enhanced
c: 0.716% Enhanced
d: 8.36% Enhanced

b: 0.27% Enhanced
c: 1.11% Enhanced
d: 1.11% Enhanced
- The second mixture: Rf value on TLC (Hexane) = 0.33

\[ \text{C}_{16}\text{H}_{15}\text{Cl} \]

Exact Mass: 242.1
m/e: 242.1 (100.0%), 244.1 (33.5%), 243.1 (18.0%), 245.1 (5.8%)

(Z)-1-(2-chloro-5-methylphenyl)-1-phenylpropene

\[ \text{C}_{16}\text{H}_{15}\text{Cl} \]

Exact Mass: 242.1
m/e: 242.1 (100.0%), 244.1 (33.5%), 243.1 (18.0%), 245.1 (5.8%)

(E)-1-(2-chloro-5-methylphenyl)-1-phenylpropene

GC-Spectrum of 1-(2-chloro-5-methylphenyl)-1-phenylpropene

From the second mixture
$^1$H NMR Spectrum of 1-(2-chloro-5-methylphenyl)-1-phenylpropene

$^{13}$C NMR Spectrum of 1-(2-chloro-5-methylphenyl)-1-phenylpropene
Differential NOE Spectrum of (Z)-1-(2-chloro-5-methylphenyl)-1-phenylpropene

b: 0.68% Enhanced

b: 4.17% Enhanced

c: 0.62% Enhanced

c: 1.23% Enhanced
Cl

H

Me

Me

b

c

a

b: 0.675% Enhanced
c: 0.675% Enhanced
Entry 15 in Table 2
The reaction gave two separable mixtures including ortho- and para-regioisomers and the corresponding E/Z isomers. The isomers were identified by NOE experiment and the ratio was determined by $^1$H NMR analysis.

- The first mixture: Rf value on TLC (Hexane) = 0.30

\[
\text{C}_{15}\text{H}_{13}\text{Cl} \\
\text{Exact Mass: 228.1} \\
m/e: 228.1 (100.0%), 230.1 (33.3%), 229.1 (16.9%), 231.1 (5.5%)
\]

(Z)-1-(p-Chlorophenyl)-1-phenylpropene

\[
\text{C}_{15}\text{H}_{13}\text{Cl} \\
\text{Exact Mass: 228.1} \\
m/e: 228.1 (100.0%), 230.1 (33.3%), 229.1 (16.9%), 231.1 (5.5%)
\]

(Z)-1-(o-Chlorophenyl)-1-phenylpropene
GC-MS Spectrum of 1-(o-chlorophenyl)-1-phenylpropene

A mixture of two Z-isomers
$^1$H NMR Spectrum of 1-(o-chlorophenyl)-1-phenylpropene

Two quartets from two isomers

Two singlets from two isomers after decoupling experiment
$^{13}$C NMR Spectrum of 1-(o-chlorophenyl)-1-phenylpropene
- The second mixture: Rf value on TLC (Hexane) = 0.27

\[
\text{C}_{15}\text{H}_{13}\text{Cl}
\]

Exact Mass: 228.1
m/e: 228.1 (100.0%), 230.1 (33.3%), 229.1 (16.9%), 231.1 (5.5%)

(E)-1-(p-chlorophenyl)-1-phenylpropene

\[
\text{C}_{15}\text{H}_{13}\text{Cl}
\]

Exact Mass: 228.1
m/e: 228.1 (100.0%), 230.1 (33.3%), 229.1 (16.9%), 231.1 (5.5%)

(E)-1-(o-chlorophenyl)-1-phenylpropene
GC-MS Spectrum of 1-(p-chlorophenyl)-1-phenylpropene

E-isomers
$^{1}H$ NMR Spectrum of 1-(p-chlorophenyl)-1-phenylpropene

$^{13}C$ NMR Spectrum of 1-(p-chlorophenyl)-1-phenylpropene
3. GC-MS, \(^1\)H, \(^{13}\)C NMR and differential NOE spectra for Table 3.

Entry 1 in Table 3

\[
\text{C}_{22}\text{H}_{20}
\]

Exact Mass: 284.2

m/e: 284.2 (100.0\%), 285.2 (24.8\%), 286.2 (2.9\%)

\((E)-1,2\)-Diphenyl-1-(\(p\)-xylyl)ethane

GC-MS Spectrum of \((E)-1,2\)-diphenyl-1-(\(p\)-xylyl)ethane

<table>
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<td>RIC</td>
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<td>2.50E8</td>
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$^1$H NMR Spectrum of (E)-1,2-diphenyl-1-(p-xyllyl)ethane

$^{13}$C NMR Spectrum of (E)-1,2-diphenyl-1-(p-xyllyl)ethane
Differential NOE Spectrum of (E)-1,2-Diphenyl-1-(p-xyl)ethane

b: 2.01% Enhanced
c: 1.73% Enhanced
d: 0.13% Enhanced
Entry 2 in Table 3

\[
\text{C}_{18}\text{H}_{20}
\]

Exact Mass: 236.2

m/e: 236.2 (100.0%), 237.2 (20.3%), 238.2 (2.0%)

\((E)\)-1-Mesityl -1-phenylpropene

GC-MS Spectrum of 1-mesityl -1-phenylpropene

<table>
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<tr>
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<td>1.025E6</td>
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<tr>
<td>19.333</td>
<td>RIC</td>
<td>1.966E7</td>
<td>86.29%</td>
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</tbody>
</table>

\(\text{E-isomer}\)

\(\text{Z-isomer}\)
$^1$H NMR Spectrum of 1-mesityl-1-phenylpropene

$^{13}$C NMR Spectrum of 1-mesityl-1-phenylpropene
Differential NOE Spectrum of (E)-1-Mesityl-1-phenylpropene

b: 0.17% Enhanced
c: 0.73% Enhanced
Entry 3 in Table 3

\[
\text{C}_{23}\text{H}_{22}
\]

Exact Mass: 298.2

m/e: 298.2 (100.0%), 299.2 (25.9%), 300.2 (3.2%)

(\textit{E})-1,2-Diphenyl-1-mesitylene

GC-MS Spectrum of 1,2-diphenyl-1-mesitylene
$^1$H NMR Spectrum of 1,2-diphenyl-1-mesitylethene

$^{13}$C NMR Spectrum of 1,2-diphenyl-1-mesitylethene
Differential NOE Spectrum of (E)-1,2-Diphenyl-1-mesitylethene

b: 0.34% Enhanced
c: 1.42% Enhanced
Entry 4 in Table 3

\[
\text{C}_{20}\text{H}_{24}
\]

Exact Mass: 264.2

m/e: 264.2 (100.0%), 265.2 (22.6%), 266.2 (2.4%)

\textbf{(E)-1-Pentamethylphenyl-1-phenylpropene}

GC-MS Spectrum of 1-pentamethylphenyl-1-phenylpropene
$^1$H NMR Spectrum of 1-pentamethylphenyl-1-phenylpropene

$^{13}$C NMR Spectrum of 1-pentamethylphenyl-1-phenylpropene
Differential NOE Spectrum of (E)-1-Pentamethylphenyl-1-phenylpropene
Entry 5 in Table 3

\[
\begin{align*}
C_{25}H_{26} \\
\text{Exact Mass: 326.2} \\
m/e: 326.2 (100.0\%), 327.2 (28.2\%), 328.2 (3.8\%) \\
(\text{E})-1,2\text{-Diphenyl-1-} (\text{pentamethylphenyl})\text{ethane}
\end{align*}
\]

GC-MS Spectrum of 1,2-diphenyl-1-(pentamethylphenyl)ethane

<table>
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$^1$H NMR Spectrum of 1,2-diphenyl-1-(pentamethylphenyl)ethane

$^{13}$C NMR Spectrum of 1,2-diphenyl-1-(pentamethylphenyl)ethane

E-isomer
Differential NOE Spectrum of \((E)\)-1,2-Diphenyl-1-(pentamethylphenyl)ethane

\[
\begin{array}{c}
\text{b: 0.26\% Enhanced} \\
\text{c: 1.41\% Enhanced}
\end{array}
\]